Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Zinc mediated activation of terminal alkynes; stereoselective synthesis of alkynyl glycosides from acetylenes.

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General information

^{1}H and ^{13}C NMR spectra were recorded on 400 and 500 MHz spectrometers with TMS as the internal standard. Chemical shifts are expressed in parts per million (δ ppm). Silica gel coated aluminium plates were used for TLC. The products were purified by column chromatography on silica gel (60-120/100-200 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. Exact Mass of all products were analysed by using HRMS having QTOF analyser. Reagents used were mostly purchased from Sigma Aldrich.

Genaral procedure for the synthesis of *C*-alkynyl glycosides (1)

Zn (1.5 equiv.) powder was added to a solution of aliphatic alkyne (1.5 equiv.) and bromo ethylacetate (1.0 equiv.) in dichloromethane resulting mixture was stirred at 40 °C for 1h under nitrogen atmosphere. To this refluxing solution glycal (1.0 equiv.) was added and stirring was continued for 6-8 h. The completion of the reaction was monitored through TLC. The reaction mixture was passed through a small celite pad and the organic phase was dried over anhydrous sodium sulphate and concentrated in vacuo. The crude product was purified over a column of silica gel using ethylacetate as elutant to afford the corresponding product.

Genaral procedure for the synthesis of *C*-aryl glycosides (2).

Zn (1.5 equiv.) powder was added to a solution of alkyne (1.3 equiv.) and bromoethylacetate (1 mmol.) in dichloromethane resulting mixture was stirred at 40 ℃ for 1h under nitrogen atmosphere to this refluxing solution glycal (1 equiv.) was added and stirring was continued for 4-5 h. The completion of the reaction was monitored through TLC. The reaction mixture was passed through a small celite pad and the organic phase was dried over anhydrous sodium sulphate and concentrated in vacuo. The crude product was purified over a column of silica gel using ethylacetate as elutant to afford the corresponding product.

Procedure for the synthesis of pseudo disaccharide (3):

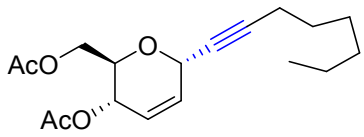
Zn (1.5 equiv.) powder was added to a solution of propargyl glycoside (1.02 equiv.) and bromoethylacetate (1.0 mmol) in dichloromethane. The resulting mixture was stirred at 40 C for 2h under nitrogen atmosphere. To this refluxing solution 3,4,6 Tri-*O*-Acetyl glucal (1.0 equiv.) was added and stirring was continued for 16 h The completion of the reaction was

monitored through TLC. The reaction mixture was passed through a small celite pad and the organic phase was dried over anhydrous sodium sulphate and concentrated in vacuo. The crude product was purified over a column of silica gel using ethylacetate as elutant to afford the corresponding pseudoglycoside.

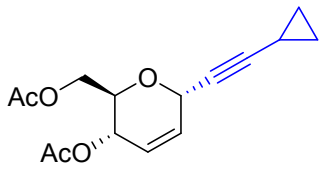
Genaral procedure for the synthesis of *C*-alkynyl glycosides from glycosylacetate (4).

Zn (1.5 equiv.) powder was added to a solution of aliphatic/aromatic alkyne (1.5 equiv.) and bromo ethylacetate(1.0 mmol.) in dichloromethane and the resulting mixture was stirred at 40 ℃ for 1-2 h under nitrogen atmosphere. To this refluxing solution Glycosylacetate (1.0 equiv.) was added and stirring was continued for 24h. The completion of the reaction was monitored through TLC. The reaction mixture was passed through a small celite pad and the organic phase was dried over anhydrous sodium sulphate and concentrated in vacuo. The crude product was purified over a column of silica gel using ethylacetate as elutant to yield the desired product.

Spectral analysis:

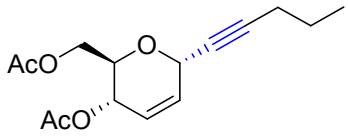


[S1]Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-Octyne (0.75 mmol, 110 µL) to yield **3a** 68% (109 mg). ^{1}H NMR (400 MHz, $CDCl_3CDCl_3$): δ 5.93 – 5.85 (m, 1H), 5.76 – 5.70 (m, 1H), 5.28(dd, *J* =8.8, 1.7 Hz), 4.96 (m, 1H, H-1) 4.23 (d, *J* = 3.2 Hz, 2H), 4.12 (dd, *J* = 8.8, 4.3 Hz, 1H), 2.22 (t, *J* = 7.0 Hz, 2H), 2.10 (s, 3H), 2.09 (s, 3H), 1.51 (dt, *J* = 14.1, 7.0 Hz, 2H), 1.39 (dd, *J* = 14.1, 7.5 Hz, 2H), 1.30 (bs, 4H), 0.89 (t, *J* = 6.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.1, 168.6, 128.3, 123.0, 86.1, 74.0, 67.9, 63.2, 62.5, 61.4, 29.5, 26.73, 26.71, 20.7, 19.2, 19.0, 17.0, 12.2. HRMS (ESI^+) m/z calcd for $C_{18}H_{26}NaO_5$ $(M+Na)^+$ 345.1678, found;345.1682.

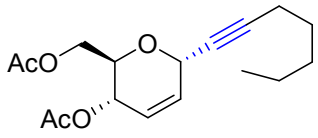


[S1]Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and Cyclopropylacetylene (0.75 mmol, 63 µL) to yield **3b** 72 % (100 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79 (ddd, *J* = 10.2, 3.3, 1.8 Hz, 1H), 5.70 – 5.61 (m,

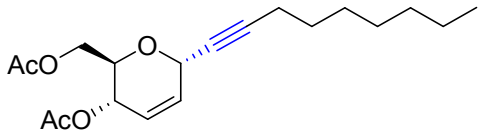
1H), 4.90 – 4.82 (m, 1H, H-1), 4.16 (d, *J* = 3.9 Hz, 2H), 4.03 (dt, *J* = 8.4, 5.4 Hz, 2H), 2.04 (s, 3H), 2.02 (s, 3H), 0.81 (t, *J* = 6.7 Hz, 1H), 0.76 – 0.69 (m, 2H), 0.66 – 0.62 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.4, 170.8, 130.2, 125.2, 91.2, 71.4, 70.1, 65.2, 64.7, 63.5, 30.1, 21.5, 21.4, 8.9. 8.8. HRMS (ESI^+) m/z calcd for $C_{15}H_{19}O_5$ $(M+H)^+$ 279.1232, found;279.1239.



Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-Pentyne (0.75 mmol, 73μL) to yield **3c** 70% (98 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (ddd, *J* = 10.2, 3.4, 1.8 Hz, 1H), 5.74 (dt, *J* = 10.2, 1.8 Hz, 1H), 5.31 – 5.24 (m, 1H), 4.97 (dt, *J* = 3.5, 1.9 Hz, 1H, H-1), 4.26 – 4.21 (m, 2H), 4.15 – 4.08 (m, 1H), 2.21 (t, *J* = 7.0 Hz, 2H), 2.10 (s, 3H), 2.09 (s, 3H), 1.62 – 1.49 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.9, 170.3, 130.0, 124.7, 87.6, 75.9, 69.6, 64.9, 64.2, 63.1, 21.9, 21.0, 20.8, 20.7, 13.4. HRMS (ESI^+) m/z calcd for $C_{15}H_{21}O_5$ $(M+H)^+$ 281.1389, found;281.1391.

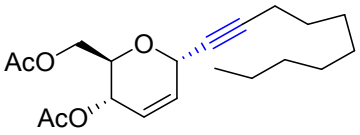


Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-Heptyne (0.75 mmol, 98μL) to yield **3d** 70% (107 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88 (ddd, *J* = 10.2, 3.4, 1.8 Hz, 1H) , 5.74 (dt, *J* = 10.2, 1.8 Hz, 1H), 5.33 – 5.24 (m, 1H), 4.99 – 4.93 (m, 1H, H-1), 4.23 (d, *J* = 4.0 Hz, 2H), 4.11(m, 1H), 2.22 (t, *J* = 7.1), 1.56 – 1.46 (m, 2H), 1.40 – 1.30 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.9, 170.3, 130.1, 124.7, 87.8, 75.7, 69.6, 64.9, 64.2, 63.1, 30.9, 28.1, 22.1, 21.0, 20.8, 18.7, 13.9. HRMS (ESI^+) m/z calcd for $C_{17}H_{25}O_5$ $(M+H)^+$ 309.1702, found;309.1710.

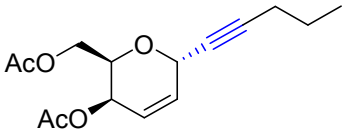


Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-Nonyne (0.75 mmol, 122 μL) to yield **3e** 64% (107 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.81 (ddd, *J*=10.2, 3.4, 1.8, 1H), 5.73 – 5.62 (m, 1H), 5.22 (dd, *J*=8.9, 1.9, 1H), 4.94 – 4.86 (m, 1H, H-1), 4.17 (dd, *J*=6.7, 5.5, 2H), 4.09 – 4.01 (m, 1H), 2.15 (t, *J*=8.0, 2H), 2.02 (s, 3H), 2.01 (s, 3H) 1.51 – 1.40 (m, 2H), 1.33 – 1.25 (m, 2H), 1.22 (bs, 6H), 0.82 (t, *J*=6.9, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 169.0, 168.4,

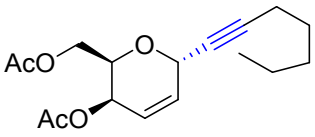
128.1, 122.7, 85.9, 73.8, 67.6, 62.9, 62.3, 61.2, 29.7, 26.8 (2C), 26.5, 20.6, 19.1, 18.9, 16.8, 12.1. HRMS (ESI$^+$) m/z calcd for $C_{19}H_{28}NaO_5$ $(M+Na)^+$ 359.1834, found;359.1834.



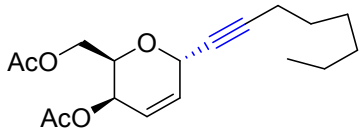
[S2]Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-Decyne (0.75 mmol, 135 µL) to yield **3f** 66% (115 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (d, *J* = 8.5 Hz, 1H), 5.67 (d, *J* = 10.2 Hz, 1H), 5.30 – 5.19 (m, 1H), 4.90 (bs, 1H, H-1), 4.16 (s, 2H), 4.09 – 3.98 (m, 1H), 2.15 (bs, 2H), 2.03 (s, 3H), 2.01 (s, 3H), 1.44 (t, *J* = 6.9 Hz, 2H), 1.21 (s, 10H), 0.81 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.9, 169.3, 129.0, 123.6, 86.8, 74.7, 68.5, 63.8, 63.2, 62.0, 30.7, 28.1, 28.0, 27.7, 27.4, 21.6, 20.0, 19.8, 17.7, 13.0. HRMS (ESI$^+$) m/z calcd for $C_{20}H_{31}O_5$ $(M+H)^+$ 351.2171, found;351.2174.



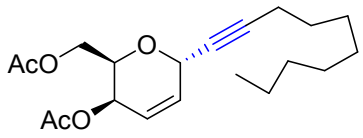
Prepared by the general procedure **1** using of tri-*O*-acetyl-D-Galactal (0.5 mmol, 136 mg) and 1-Pentyne (0.75 mmol, 73 µL) to yield **3g** 69% (96 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.99 (dd, *J* = 10.0, 3.6 Hz, 1H), 5.90 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.00 (dd, *J* = 5.1, 2.0 Hz, 1H), 4.96 (m, 1H, H-1), 4.33 – 4.25 (m, 1H), 4.21 (dd, *J* = 11.5, 5.0 Hz, 1H), 4.11 (dd, *J* = 11.4, 7.4 Hz, 1H), 2.14 (t, *J* = 6.9 Hz, 2H), 1.46 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). HRMS (ESI$^+$) m/z calcd for $C_{15}H_{20}NaO_5$ $(M+Na)^+$ 303.1208, found;303.1211.



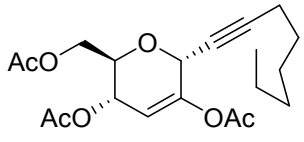
Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-Heptyne (0.75 mmol, 98 µL) to yield **3h** 67% (103 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98 (dd, *J* = 10.0, 3.7 Hz, 1H), 5.90 (ddd, *J* = 10.0, 5.3, 1.6 Hz, 1H), 5.00 (dd, *J* = 5.2, 2.3 Hz, 1H), 4.95 (dd, *J* = 3.3, 1.7 Hz, 1H, H-1), 4.28 (ddd, *J* = 7.3, 5.2, 2.3 Hz, 1H), 4.21 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.11 (dd, *J* = 11.4, 7.3 Hz, 1H), 2.15 (td, *J* = 7.1, 1.9 Hz, 2H), 2.01 (s, 3H), 2.00 (s, 3H), 1.50 – 1.40 (m, 2H), 1.32 – 1.21 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.7, 169.4, 131.8, 120.7, 87.0, 74.1, 68.2, 63.1, 62.4, 61.9, 29.9, 27.1, 21.1, 19.8, 19.7, 17.6, 12.9. HRMS (ESI$^+$) m/z calcd for $C_{17}H_{25}O_5$ $(M+H)^+$ 309.1702, found;309.1711.



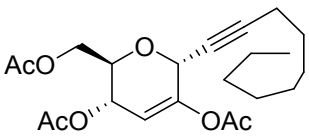
Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-Octyne (0.75 mmol, 110 μL) to yield **3i** 65% (104 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98 (dd, *J* = 10.0, 3.7 Hz, 1H), 5.90 (ddd, *J* = 10.0, 5.3, 1.7 Hz, 1H), 5.00 (dd, *J* = 5.2, 2.3 Hz, 1H), 4.96 (dd, *J* = 3.4, 1.8 Hz, 1H, H-1), 4.28 (ddd, *J* = 7.4, 5.3, 2.3 Hz, 1H), 4.21 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.11 (dd, *J* = 11.4, 7.3 Hz, 1H), 2.15 (t, *J* = 7.0, 2H), 2.02 (s, 3H), 2.01 (s, 3H), 1.47 – 1.40 (m, 2H), 1.30 (m, 2H), 1.25 – 1.21 (m, 3H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.7, 169.4, 131.8, 120.7, 87.0, 74.1, 68.2, 63.1, 62.4, 61.8, 30.2, 27.44, 27.41, 21.4, 19.8, 19.7, 17.7, 13.0. HRMS (ESI$^+$) m/z calcd for $C_{18}H_{27}O_5$ $(M+H)^+$ 323.1858, found;323.1866.



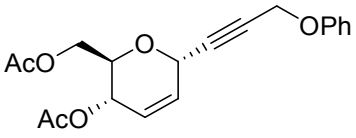
Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-Decyne (0.75 mmol, 135 μL) to yield **3j** 64 % (112 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (dd, *J* = 9.9, 3.6 Hz, 1H), 5.99 (dd, *J* = 8.1, 5.3 Hz, 1H), 5.08 (m, 1H), 5.04 (bs, 1H, H-1), 4.39 – 4.25 (m, 2H), 4.20 (dd, *J* = 11.3, 7.4 Hz, 1H), 2.23 (t, *J* = 6.9 Hz, 2H), 2.10 (s, 3H), 2.09 (s, 3H), 1.51 (m, 2H), 1.38 (bs, 2H), 1.29 (bs, 8H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.7, 169.4, 131.8, 120.6, 87.0, 74.1, 68.2, 63.1, 62.4, 61.9, 30.8, 28.1, 28.0, 27.7, 27.4, 21.6, 19.89, 19.82, 17.7, 13.0. HRMS (ESI$^+$) m/z calcd for $C_{20}H_{31}O_5$ $(M+H)^+$ 351.2171, found;351.2176.



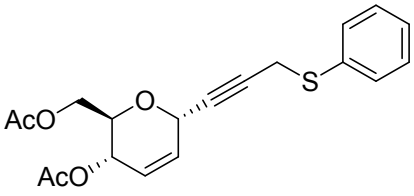
Prepared by the general procedure **1** using of 2-Acetoxy-tri-*O*-acetyl-D-glucal (0.5 mmol, 165 mg) and 1-Octyne (0.75 mmol, 110 μL) to yield **3k** 62% (117 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.63 (s, 1H), 5.42 (d, *J* = 8.8 Hz, 1H), 4.95 (s, 1H, H-1), 4.29 – 4.22 (m, 2H), 4.19 – 4.10 (m, 1H), 2.23 (t, *J* = 7.0 Hz, 2H), 2.18 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 1.51 (dd, *J* = 14.7, 7.1 Hz, 2H), 1.40 – 1.35 (m, 2H), 1.26 (bs, 4H), 0.89 (t, 6.5 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.8, 170.1, 167.9, 147.6, 112.0, 87.9, 74.5, 69.9, 65.0, 63.9, 62.7, 31.2, 29.6, 28.4, 22.5, 20.98, 20.91, 20.7, 18.7, 14.0. HRMS (ESI$^+$) m/z calcd for $C_{20}H_{28}NaO_7$ $(M+Na)^+$ 403.1733, found;403.1737.



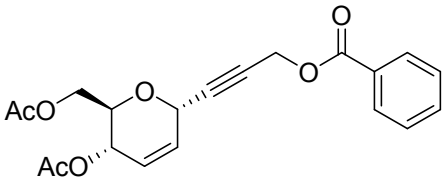
Prepared by the general procedure **1** using of 2-Acetoxy-tri-*O*-acetyl-D-glucal (0.5 mmol, 165 mg) and 1-Decyne (0.75 mmol, 135 μL) to yield **3l** 60% (122 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65 – 5.60 (m, 1H), 5.42 (d, *J* = 8.7 Hz, 1H), 4.96 (s, 1H, H-1), 4.30 – 4.22 (m, 2H), 4.19 – 4.12 (m, 1H), 2.31 (t, *J*= 7.0 Hz, 2H), 2.18 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 1.51 (dd, *J* = 14.7, 7.1 Hz, 2H), 1.43 – 1.33 (m, 2H), 1.28 (bs, 8H) 0.88 (t, *J* = 6.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.8, 170.2, 167.9, 147.6, 112.0, 88.0, 74.5, 69.8, 65.0, 63.9, 62.7 , 31.8, 29.2, 29.0, 28.7, 28.3, 22.6, 21.0, 20.9, 20.8, 18.7, 14.1. HRMS (ESI$^+$) m/z calcd for $C_{22}H_{32}NaO_7$ $(M+Na)^+$ 431.2046, found;431.2052.



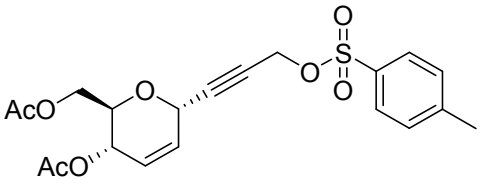
Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-(prop-2-ynyloxy)benzene (0.75 mmol, 99 mg) to yield **3m** 92 % (158 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 14.8, 6.5 Hz, 2H), 6.91 (dd, *J* = 16.3, 8.0 Hz, 3H), 5.79 (ddd, *J* = 10.1, 3.2, 1.7 Hz, 1H), 5.71 (d, *J* = 10.2 Hz, 1H), 5.25 – 5.18 (m, 1H), 4.95 (m, 1H, H-1), 4.67 (m, 2H), 4.13 (m, 2H), 4.02 – 3.89 (m, 1H), 2.01 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$): 169.8, 169.2, 156.5, 128.4 (2C), 127.6, 124.6, 120.5, 113.9 (2C), 82.0, 80.8, 68.9, 63.5, 62.8, 61.8, 54.9, 19.9, 19.7. HRMS (ESI$^+$) m/z calcd for $C_{19}H_{21}O_6$ $(M+H)^+$ 345.1338, found:345.1341.



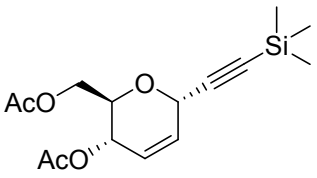
Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and Phenyl(prop-2-ynyl)sulfane (0.75 mmol, 111mg) to yield **3n** 84 % (151 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J*=7.3, 2H), 7.32 (t, *J*=7.4, 2H), 7.26 (d, *J*=7.6, 1H), 5.84 – 5.77 (m, 1H), 5.74 (d, *J*=10.2, 1H), 5.29 – 5.26 (m, 1H), 4.94 (bs, 1H, H-1), 4.20 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.13 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.99 – 3.89 (m, 1H), 3.65 (d, *J*=1.8, 2H), 2.10 (s, 3H), 2.08 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.8, 170.2, 130.6 (2C), 129.1, 129.0, 128.9 (2C), 127.1, 125.3, 82.9, 79.2, 69.7, 64.6, 64.0, 62.9, 23.1, 21.0, 20.8. HRMS (ESI$^+$) m/z calcd for $C_{19}H_{21}O_5S$ $(M+H)^+$ 361.1110, found:361.1115.



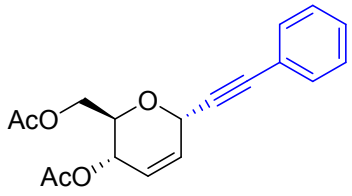
Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and Prop-2-ynyl-benzoate (0.75 mmol, 120 mg) to yield **3o** 88 % (163 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.11 – 8.04 (m, 2H), 7.59 (t, *J*=7.4, 1H), 7.46 (t, *J*=7.7, 2H), 5.90 (ddd, *J*=10.2, 3.4, 1.8, 1H), 5.81 (d, *J*=10.2, 1H), 5.30 (m, 1H), 5.05 (m, 1H, H-1), 4.99 (m, 2H), 4.25 (d, *J*=3.9, 2H), 4.11 (dd, *J*=8.7, 4.0, 1H), 2.10 (s, 3H), 2.09 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.9, 170.3, 165.7, 133.4, 129.8 (2C), 128.6, 128.4 (2C), 125.8, 82.5, 80.9, 70.0, 64.5, 63.8, 62.9, 52.6, 21.0, 20.8. HRMS (ESI$^+$) m/z calcd for HRMS (ESI$^+$) m/z calcd for $C_{20}H_{21}O_7$ $(M+H)^+$ 373.1287, found:373.1291.



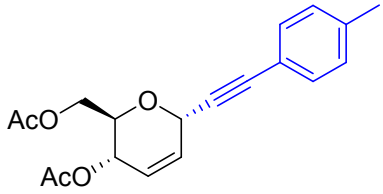
Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and Prop-2-ynyl-4-methylbenzenesulphonate (0.75 mmol, 157mg) to yield **3p** 78 % (164 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.71 (d, *J* = 10.2 Hz, 1H), 5.65 (ddd, *J* = 17.3, 5.9, 4.3 Hz, 1H), 5.20 (dd, *J* = 9.0, 1.7 Hz, 1H), 4.81 (bs, 1H, H-1), 4.68 (d, *J* = 1.6 Hz, 2H), 4.17 – 4.08 (m, 2H), 3.95 – 3.83 (m, 1H), 2.39 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.9, 170.2, 145.2, 132.9, 129.9 (2C), 128.1 (2C), 127.9, 126.1, 84.9, 78.5, 70.0, 64.4, 63.6, 62.7, 57.6, 21.7, 21.0, 20.8. HRMS (ESI$^+$) m/z calcd for HRMS (ESI$^+$) m/z calcd for $C_{20}H_{22}O_8S$ $(M+Na)^+$ 445.0933, found:445.0912.



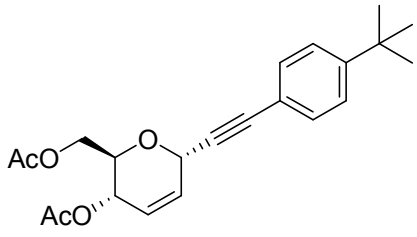
[S2]Prepared by the general procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and TMSactylene (106 μL) to yield **3q** 69 % (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.70 (ddd, *J* = 10.2, 3.4, 1.8 Hz, 1H), 5.6-5.5 (m, 1H), 5.10 (dd, *J* = 8.9, 1.9 Hz, 1H), 4.78 (dd, *J* = 3.2, 1.7 Hz, 1H, H-1), 4.05 (dd, *J* = 9.5, 4.0 Hz, 2H), 3.94 – 3.91 (m, 1H) 1.92 (s, 6H), 0.00 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.0, 170.5, 129.3, 125.6, 101.0, 92.0, 70.1, 65.0, 64.6, 63.2, 21.0, 20.9, 0.03. HRMS (ESI$^+$) m/z calcd for HRMS (ESI$^+$) m/z calcd for $C_{15}H_{23}O_5Si$ $(M+H)^+$ 311.1315, found:311.1357.



[S3]Prepared by the general procedure **2** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and phenyl acetylene (0.65 mmol, 70 µL) to yield **4a** 90% (136 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.2, 2.1 Hz, 2H), 7.37 – 7.29 (m, 3H), 5.98 (ddd, *J* = 10.1, 3.4, 1.8 Hz, 1H), 5.83 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.38 – 5.31 (m, 1H), 5.20 (ddd, *J* = 3.6, 1.7 Hz, 1.7 Hz, 1H, H-1), 4.27 (d, *J* = 3.9 Hz, 2H), 4.21 (dd, *J* = 8.6, 4.1 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.0, 170.4, 131.8 (2C), 129.2, 128.7, 128.3 (2C), 125.4, 122.1, 86.6, 84.6, 70.0, 64.8, 64.4, 63.0, 21.0, 20.8. HRMS (ESI$^+$) m/z calcd for $C_{18}H_{19}O_5$ $(M+H)^+$ 315.1232, found 315.1228.

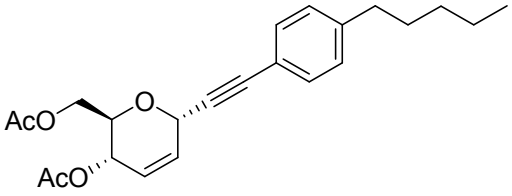


[S3]Prepared by the general procedure **2** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 4-Methylphenyl acetylene (0.65 mmol, 82 µL) to yield **4b** 87% (142 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.98 (ddd, *J* = 10.2, 3.4, 1.8 Hz, 1H), 5.81 (d, *J* = 10.2 Hz, 1H), 5.34 (dd, *J* = 8.8, 1.8 Hz, 1H), 5.19 (bs, 1H, H-1), 4.27 (d, *J* = 3.8 Hz, 1H), 4.20 (dd, *J* = 8.7, 4.0 Hz, 1H), 2.35 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$):170.9, 170.3, 138.9, 131.7, 129.3, 129.0, 125.3, 86.8, 83.9, 69.9, 64.8, 64.5, 63.1, 21.5, 21.0, 20.8. HRMS (ESI$^+$) m/z calcd for $C_{19}H_{20}NaO_5$ $(M+Na)^+$ 351.1208, found. 351.1211.

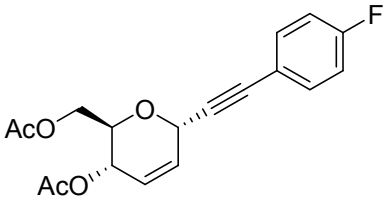


Prepared by the general procedure **2** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 4-tert-Butylphenyl acetylene (0.65 mmol, 116 µL) to yield **4c** 87% (160 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39 (d, *J*=8.6, 2H), 7.34 (d, *J*=8.6, 2H), 5.99 (ddd, *J*=10.1, 3.5, 1.9, 1H), 5.82 (dt, *J*=10.2, 1.9, 1H), 5.34 (ddd, *J*=8.9, 3.9, 1.9, 1H), 5.20 (dt, *J*=3.6, 1.9, 1H, H-1), 4.26 (d, *J*=3.9, 2H), 4.20 (dd, *J*=8.8, 3.9, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 1.31 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.0, 170.4, 152.1, 131.6 (2C), 129.3,

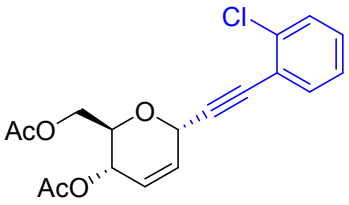
125.36 (2C), 125.34, a 118.8, 86.6, 83.8, 69.4, 64.7, 64.5, 63.3, 34.8, 31.1 (3C), 21.0, 20.8. HRMS (ESI$^+$) m/z calcd for $C_{22}H_{27}O_5$ $(M+H)^+$ 371.1858, found :371.1844.



[S4]Prepared by the general procedure **2** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 4-Pentylphenyl acetylene (0.65 mmol, 126 µL) to yield **4d** 85% (163 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J*=8.1, 2H), 7.13 (d, *J*=8.1, 2H), 5.98 (ddd, *J* = 10.2, 3.5, 1.9 Hz, 1H), 5.82 (dt, *J*=10.2, 1.8, 1H), 5.34 (dd, *J*=8.9, 1.9, 1H), 5.19 (dt, *J* = 3.4, 1.8 Hz, 1H, H-1), 4.26 (d, *J*=3.9, 2H), 4.22 – 4.16 (m, 1H), 2.60 (t, *J* = 7.6 , 2H), 2.11 (s, 1H), 2.10 (s, 1H), 1.60 (m, 2H), 1.36 – 1.25 (m, 4H), 0.88 (t, *J*=6.9, 3H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 171.0, 170.4, 144.0, 131.7 (2C), 129.3, 128.4 (2C), 125.5, 119.2, 86.9, 83.9, 69.9, 64.8, 64.5, 63.1, 35.8, 31.4, 30.9, 22.5, 21.0, 20.8, 14.0. HRMS (ESI$^+$) m/z calcd for $C_{23}H_{29}O_5$ $(M+H)^+$ 385.2015, found : 385.2022.

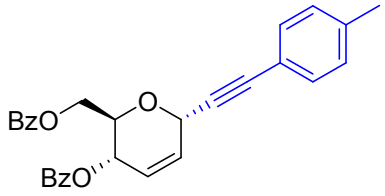


[S4]Prepared by the general procedure **2** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 4-Fluorophenyl acetylene (0.65 mmol, 74 µL) to yield **4e** 86% (142 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.37 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.97 (ddd, *J* = 10.1, 3.3, 1.8 Hz, 1H), 5.83 (d, *J* = 10.2 Hz, 1H), 5.34 (dd, *J* = 8.9, 1.8 Hz, 1H), 5.19 (bs, 1H, H-1), 4.27 (d, *J* = 3.9 Hz, 2H), 4.23 – 4.10 (m, 1H), 2.11 (s, 6H). HRMS (ESI$^+$) m/z calcd for $C_{18}H_{18}FO_5$ $(M+H)^+$ 333.1138, found :333.1145.

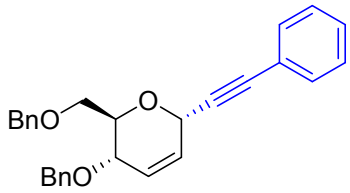


Prepared by the general procedure **2** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 2-Chlorophenyl acetylene (0.65 mmol, 78 µL) to yield **4f** 84% (146 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.31 – 7.15 (m, 2H), 5.15 (br s, 1 H), 6.03 – 5.95 (m, 1H), 5.85 (dd, *J* = 6.9, 5.1 Hz, 1H), 5.35 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.24 (dd, *J* = 3.4, 1.8 Hz, 1H, H-1), 4.26 (dd, *J* = 11.0, 4.6 Hz, 3H), 2.11 (s, 3H), 2.10 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.0, 170.4, 136.0, 133.3,

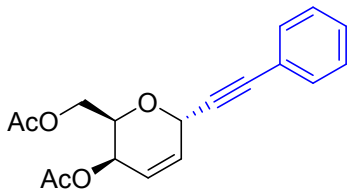
129.7, 129.3, 128.8, 126.4, 125.8, 122.1, 90.0, 83.5, 70.1, 64.8, 64.5, 63.1, 21.0, 20.8. HRMS (ESI$^+$) m/z calcd for $C_{18}H_{18}ClO_5$ $(M+H)^+$ 349.0843, found :349.0850.



Prepared by the general procedure **2** using of tri-*O*-benzoyl-D-glucal (0.5 mmol, 229 mg) and 4-Methylphenyl acetylene (0.65 mmol, 82 µL) to yield **4g** 82% (185 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 11.0, 4.1 Hz, 4H), 7.54 (dt, *J* = 19.4, 7.4 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 12.9, 8.0 Hz, 4H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.05 (ddd, *J* = 10.2, 3.3, 1.7 Hz, 1H), 5.98 (d, *J* = 10.2 Hz, 1H), 5.71 (dd, *J* = 8.8, 1.8 Hz, 1H), 5.26 (dd, *J* = 3.1, 1.7 Hz, 1H, H-1), 4.64 (d, *J* = 9.4 Hz, 1H), 4.56 – 4.45 (m, 2H), 2.36 (s, 3H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): δ 166.4, 165.9, 138.9, 133.3, 133.0, 131.7(2C), 129.8(2C), 129.7(2C), 129.5, 129.0(2C), 128.4(2C), 128.3(2C), 125.7, 119.3, 86.7, 84.1, 70.32, 65.85, 64.7, 63.9, 21.5. HRMS (ESI$^+$) m/z calcd for $C_{29}H_{25}O_5$ $(M+H)^+$ 453.1702, found; 453.1704.

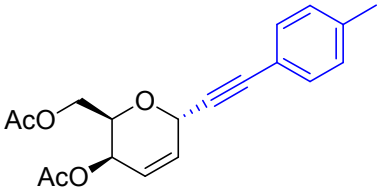


[S4]Prepared by the general procedure **2** using of tri-*O*-benzyl-D-glucal (0.5 mmol, 208 mg) and phenyl acetylene (0.65 mmol, 70 µL) to yield **4h** 60% (123 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.38 (m, 2H), 7.38 – 7.21 (m, 13H), 5.99 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.89 (ddd, *J* = 10.2, 3.4, 1.7 Hz, 1H), 5.18 (dd, *J* = 3.3, 1.8 Hz, 1H, H-1), 4.68 – 4.58 (m, 2H), 4.57 – 4.44 (m, 1H), 4.48 (d, *J* = 11.4 Hz, 1H)), 4.21 (dd, *J* = 8.9, 1.8 Hz, 1H), 4.07 (dt, *J* = 8.8, 3.0 Hz, 1H), 3.77 (d, *J* = 3.1 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 138.1, 138.0, 131.8(2C), 128.5, 128.4 (2C), 128.3 (2C), 128.2(2C), 128.0 (2C), 127.8, 127.6, 127.0, 122.5, 86.1, 85.7, 73.4, 72.3, 71.3, 69.9, 69.0, 64.6. HRMS (ESI$^+$) m/z calcd for $C_{28}H_{26}NaO_3$ $(M+Na)^+$ 433.1780, found; 433.1784.

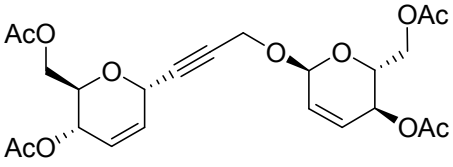


[S4]Prepared by the general procedure **2** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and phenyl acetylene (0.65 mmol, 70 µL) to yield **4i** 88% (138 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.1 Hz, 2H), 7.35 (d, *J* = 6.4 Hz, 3H), 6.17

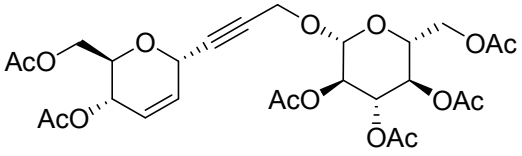
(dd, J = 10.0, 3.6 Hz, 1H), 6.08 (dd, J = 10.0, 5.2 Hz, 1H), 5.29 (s, 1H), 5.14 (d, J = 3.2 Hz, 1H, H-1), 4.46 (d, J = 5.4 Hz, 1H), 4.34 (dd, J = 11.5, 5.2 Hz, 1H), 4.23 (m, 1H), 2.11 (s, 3H), 2.10 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.8, 170.5, 132.0, 131.8(2C), 128.8, 128.3(2C), 122.4, 86.9, 84.0, 69.7, 64.4, 63.3, 62.8, 20.9, 20.8. HRMS (ESI$^+$) m/z calcd for $C_{18}H_{19}O_5$ $(M+H)^+$ 315.1232, found;315.1228.



[S4]Prepared by the general procedure **2** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 4-Methylphenyl acetylene (0.65 mmol, 82 µL) to yield **4j** 84% (137 mg). ^{1}H NMR ($CDCl_3$): δ 7.33 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.15 (dd, J = 10.0, 3.7 Hz, 1H), 6.05 (ddd, J = 10.0, 5.3, 1.7 Hz, 1H), 5.26 (dd, J = 3.3, 1.7 Hz, 1H, H-1), 5.11 (dd, J = 5.3, 2.2 Hz, 1H), 4.44 (ddd, J = 7.3, 5.3, 2.3 Hz, 1H), 4.31 (dd, J = 11.5, 5.2 Hz, 1H), 4.21 (dd, J = 11.5, 7.3 Hz, 1H), 2.35 (s, 2H), 2.10 (s, 3H), 2.07 (s, 3H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): δ 170.8, 170.5, 139.0, 132.1, 131.7 (2C), 129.1 (2C), 122.3, 87.0, 83.3, 69.6, 64.4, 63.4, 62.9, 53.4, 21.5, 20.9, 20.8. HRMS (ESI$^+$) m/z calcd for $C_{19}H_{21}O_5$ $(M+H)^+$ 329.1389, found; 329.1384.

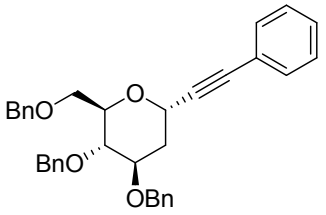


Prepared by the general procedure **3** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and Propargyl glycoside (0.51 mmol, 135 mg) to yield **5a** 73 % (175 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.7-5.9 (m, 4H), 5.38 (m, 2H), 5.25 (bs, 1H), 5.05 (bs, 1H, H-1) 4.38 (bs, 2H), 4.20-4.26 (m, 4H), 4.10 – 4.07 (m, 2H), 2.11 – 2.09(m, 12H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.8, 172.7, 172.2, 172.1, 131.1, 130.2, 128.6, 126.8, 83.7, 83.5, 71.3, 68.5, 66.5, 66.1, 65.2, 64.4, 64.2, 56.5, 22.2, 22.1, 22.0 (2C). HRMS (ESI$^+$) m/z calcd for HRMS (ESI$^+$) m/z calcd for $C_{23}H_{28}NaO_{11}$ $(M+Na)^+$ 503.1529, found:503.1507.

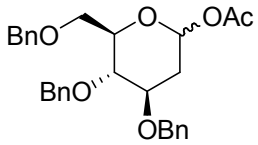


Prepared by the general procedure **3** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and Propargylglycoside (0.51 mmol, 196 mg) to yield **5b** 64 % (191 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.95 – 5.86 (m, 1H), 5.82 (d, J = 10.2 Hz, 1H), 5.32 (dd, J = 8.8, 1.5 Hz, 1H), 5.25 (t, J = 9.5 Hz, 1H), 5.12 (t, J = 9.7 Hz, 1H), 5.03 (m,

1H, H-1), 5.00 (d, *J* = 9.3 Hz, 1H), 4.74 (d, *J* = 7.9 Hz, 1H), 4.44 (d, *J* = 5.9 Hz, 1H), 4.27 (ddd, *J* = 11.5, 9.4, 3.4 Hz, 3H), 4.12 (dd, *J* = 14.3, 7.1 Hz, 4H), 2.13 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H). ^{13}C-NMR (125 MHz, Pyridine-d_5): 172.5, 172.4, 172.25, 172.23, 171.7, 171.5, 131.5, 127.9, 101.1, 85.7, 84.3, 75.4, 74.3, 73.8, 72.5, 70.9, 67.1, 65.9, 65.4, 64.2, 58.5, 22.7, 22.5 (2C), 22.5 (2C), 22.3. HRMS (ESI$^+$) m/z calcd for $C_{27}H_{34}NaO_{15}$ $(M+Na)^+$ 621.1795 found:621.1782.

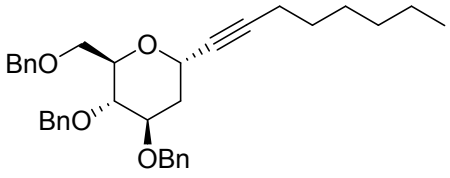


6a



6

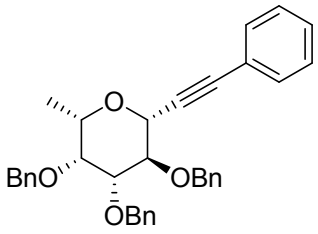
Prepared by the general procedure **4** using of 2-Deoxy glucosylacetate (**6**) (0.5 mmol, 238 mg) and Phenylacetylene (0.75 mmol, 82 µL) to yield **6a** 64 % (165 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 18H), 7.22 – 7.15 (m, 2H), 5.05 (d, *J* = 4.3 Hz, 1H), 4.95 – 4.85 (m, 1H), 4.73 – 4.61 (m, 3H), 4.55 (d, *J* = 4.4 Hz, 1H), 4.52 (d, *J* = 6.0 Hz, 1H), 4.14 – 3.98 (m, 2H), 3.82 (dd, *J* = 10.6, 3.7 Hz, 1H), 3.70 (dd, *J* = 10.6, 1.8 Hz, 1H), 3.64 (t, *J* = 9.3 Hz, 1H), 2.31 (dd, *J* = 12.3, 4.0 Hz, 1H), 2.01 – 1.89 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.5, 138.4, 138.1, 131.8 (2C), 128.5, 128.4 (2C), 128.3 (2C), 128.2 (2C), 128.1 (2C), 128.0 (2C), 127.8 (2C), 127.69 (2C), 127.67 (2C), 122.3, 87.4, 86.1, 78.4, 78.3, 75.2, 74.1, 73.5, 71.8, 68.9, 64.7, 35.9. HRMS (ESI$^+$) m/z calcd for $C_{35}H_{34}O_4$ $(M+H)^+$ 519.2535, found; 519.2518.



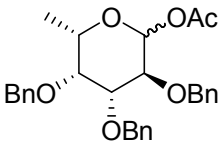
6b

Prepared by the general procedure **4** using of 2-Deoxy glucosylacetate (**6**) (0.5 mmol, 238 mg) and 1-Octyne (0.75 mmol, 110 µL) to yield **6b** 60% (157 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.07 (m, 15H), 4.88 – 4.70 (m, 2H), 4.65 – 4.53 (m, 3H), 4.50 (d, *J* = 5.3 Hz, 1H), 4.46 (d, *J* = 3.4 Hz, 1H), 4.43 (d, *J* = 4.7 Hz, 1H), 3.89 (dd, *J* = 13.8, 6.6 Hz, 1H), 3.76 – 3.67 (m, 1H), 3.59 (dd, *J* = 10.6, 1.7 Hz, 1H), 3.50 (t, *J* = 9.3 Hz, 1H), 2.16 – 1.98 (m, 3H), 1.81-1.74 (m, 1H), 1.46 – 1.35 (m, 2H), 1.32 – 1.22 (m, 1H), 1.21 (bs, 4H), 0.80 (t, *J* = 6.8 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.58, 137.51, 137.1, 127.36 (2C), 127.3 (2C), 127.0 (2C), 126.9 (2C), 126.8, 126.76, 126.7 (2C), 126.6, 16.5 (2C), 87.3, 77.5, 77.4, 74.0, 73.3, 72.6, 72.4, 70.6, 67.9, 63.4, 36.1, 31.3, 28.6, 28.5,

22.5, 18.7, 14.0. HRMS (ESI$^+$) m/z calcd for $C_{35}H_{42}NaO_4$ $(M+Na)^+$ 549.2981 found: 549.2959.

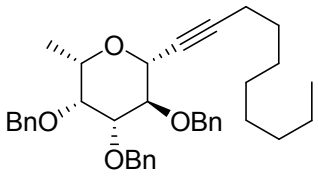


7a



7

Prepared by the general procedure **4** using of L-Fucosylacetate (**7**) (0.5 mmol, 238 mg) and Phenylacetylene (0.75 mmol, 82 μL) to yield **7a** 60 % (155 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.14 (m, 20H), 4.95 (d, *J* = 5.7 Hz, 1H, H-1), 4.91 (d, *J* = 11.5 Hz, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.69 (m, 3H), 4.59 (d, *J* = 11.5 Hz, 1H), 4.09 (dd, *J* = 9.8, 5.7 Hz, 1H), 4.03 (q, *J* = 6.3 Hz, 1H), 3.88 (dd, *J* = 9.8, 2.6 Hz, 1H), 3.59 (s, 1H), 1.08 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.7, 137.5, 130.9 (2C), 127.5 (2C), 127.4, 127.3 (2C), 127.2 (2C), 127.1 (2C), 126.7 (2C), 126.6, 126.58 (2C), 126.53, 126.4, 86.7, 83.7, 79.0, 76.4, 76.2, 76.0, 75.7, HRMS (ESI$^+$) m/z calcd for $C_{35}H_{35}O_4$ $(M+H)^+$ 519.2535, found; 519.2519.



7b

Prepared by the general procedure **4** using L-Fucosylacetate (**7**) (0.5 mmol, 238 mg) and 1-Decyne (0.75 mmol, 135 μL) to yield **7b** 58 % (160 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.12 (m, 15H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.74 (d, *J* = 5.5 Hz, 1H, H-1), 4.68-4.62 (m, 3H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.05 – 3.91 (m, 1H), 3.79 (dd, *J* = 9.8, 2.7 Hz, 1H), 3.56 (bs, 1H), 2.17 (t, *J* = 7.0 Hz, 1H), 1.48 – 1.38 (m, 1H), 1.36 – 1.26 (m, 1H), 1.18 (bs, 1H), 1.05 (d, *J* = 6.4 Hz, 1H), 0.79 (t, *J* = 6.2 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.9, 137.5 (2C), 127.4 (2C), 127.29 (2C), 127.22 (2C), 127.1 (2C), 126.7 (2C), 126.5, 126.48 (2C), 126.41 (2C), 87.6, 79.3, 76.6, 74.5, 74.2, 73.8, 72.2, 71.6, 68.2, 66.2, 30.8, 28.2, 28.0, 27.8, 27.6, 21.6, 17.8, 15.8, 13.0. HRMS (ESI$^+$) m/z calcd for $C_{37}H_{47}O_4$ $(M+H)^+$ 555.3474, found; 555.3459.

References:

S1. Vieira, A. S.; Fiorante, P. F.; Hough, T. L. S.; Ferreira, F. P.; Ludtke, D. S.; Stefani, H. A. *Org. Lett*. **2008**, *10*, 5215.

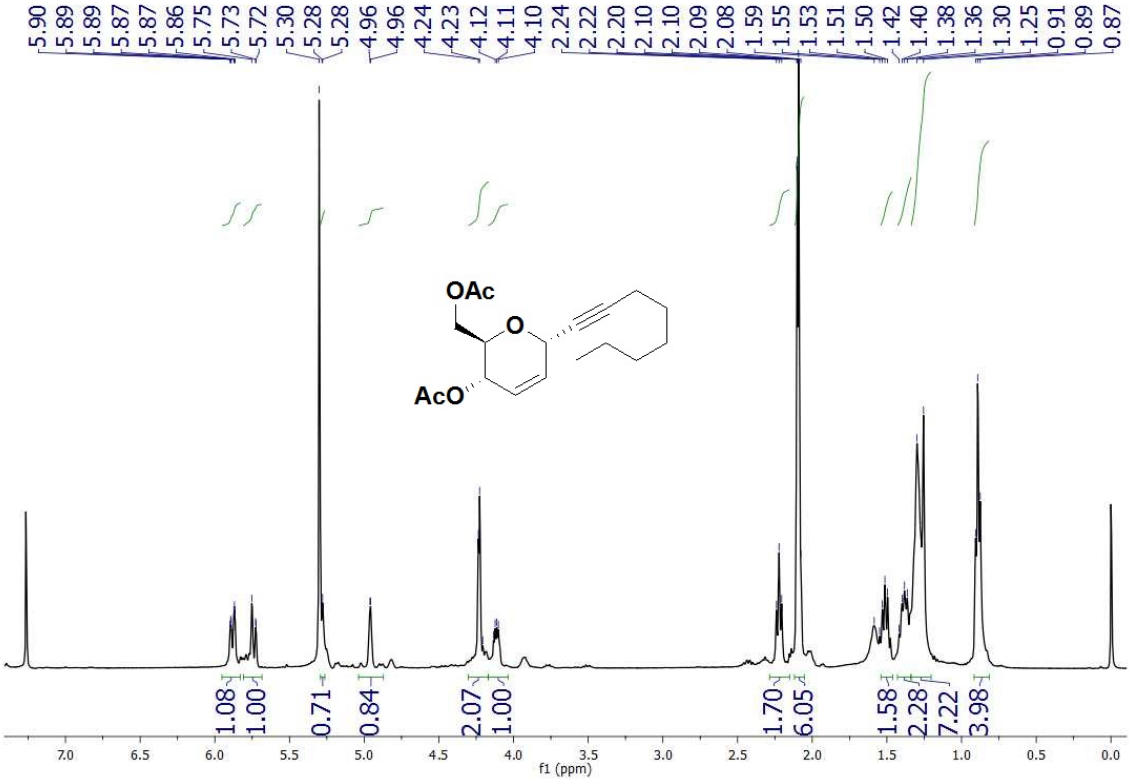
S2. Lubin-Germain, N.; Hallonet, A.; Huguenot, F.; Palmier, S.; Uziel, J.; Auge, J. *Org. Lett*. **2007**, *9*, 3679.

S3. Yadav, J. S.; Reddy, B.V. S.; Rao, C. V.; Sridhar Reddy, M.; *Synthesis* **2003**, 247–250

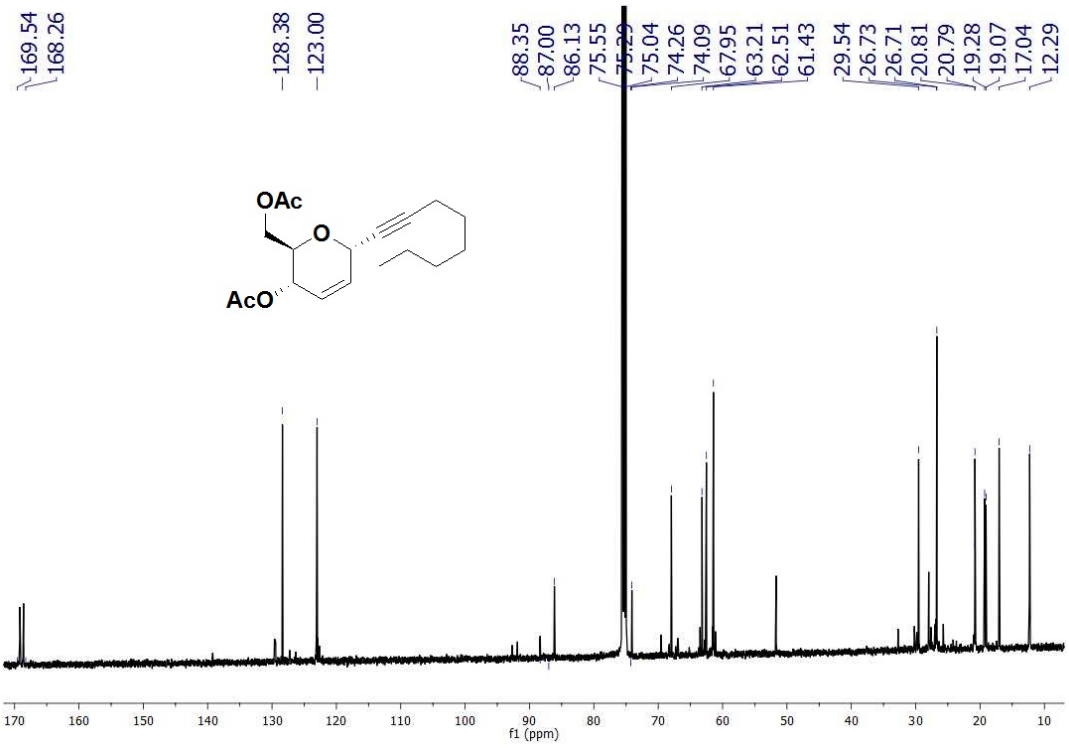
S4. Kusunuru, A. K.; Madhubabu, T.; Yousuf S. K.; Mukherjee, D. *Chem. Commun*. **2013**, *49*, 10154.

Copies of NMR images

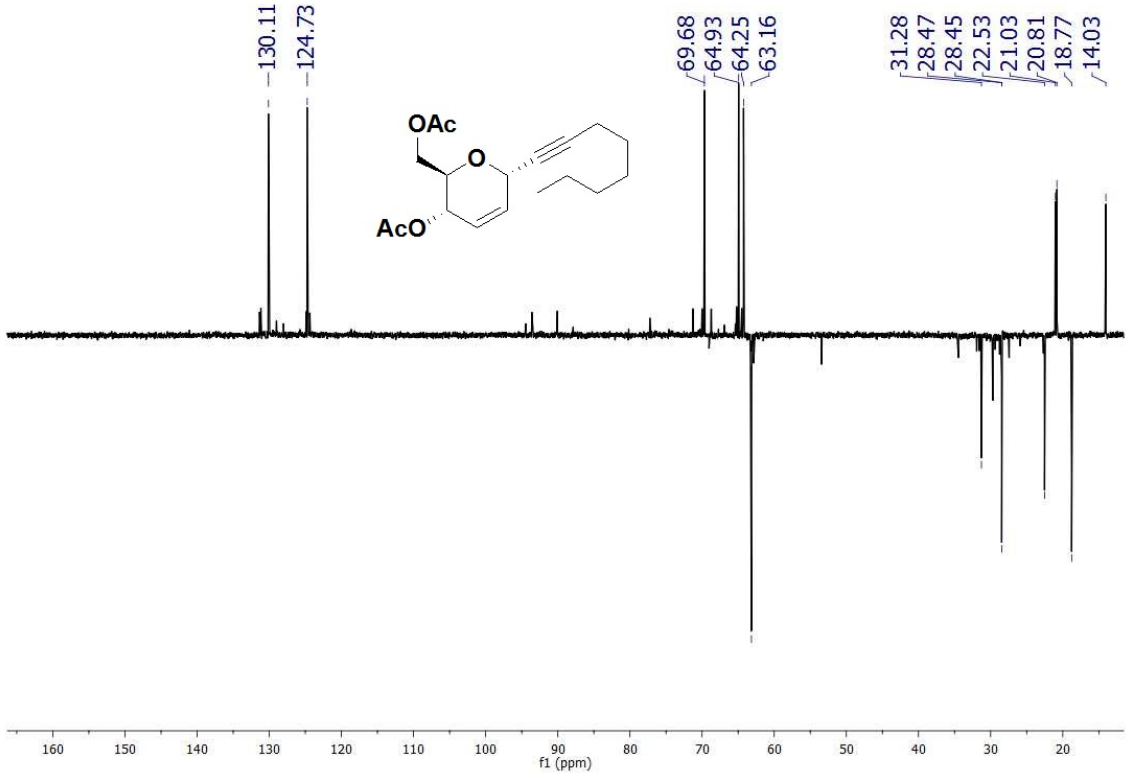
^{1}H NMR of compound **3a**



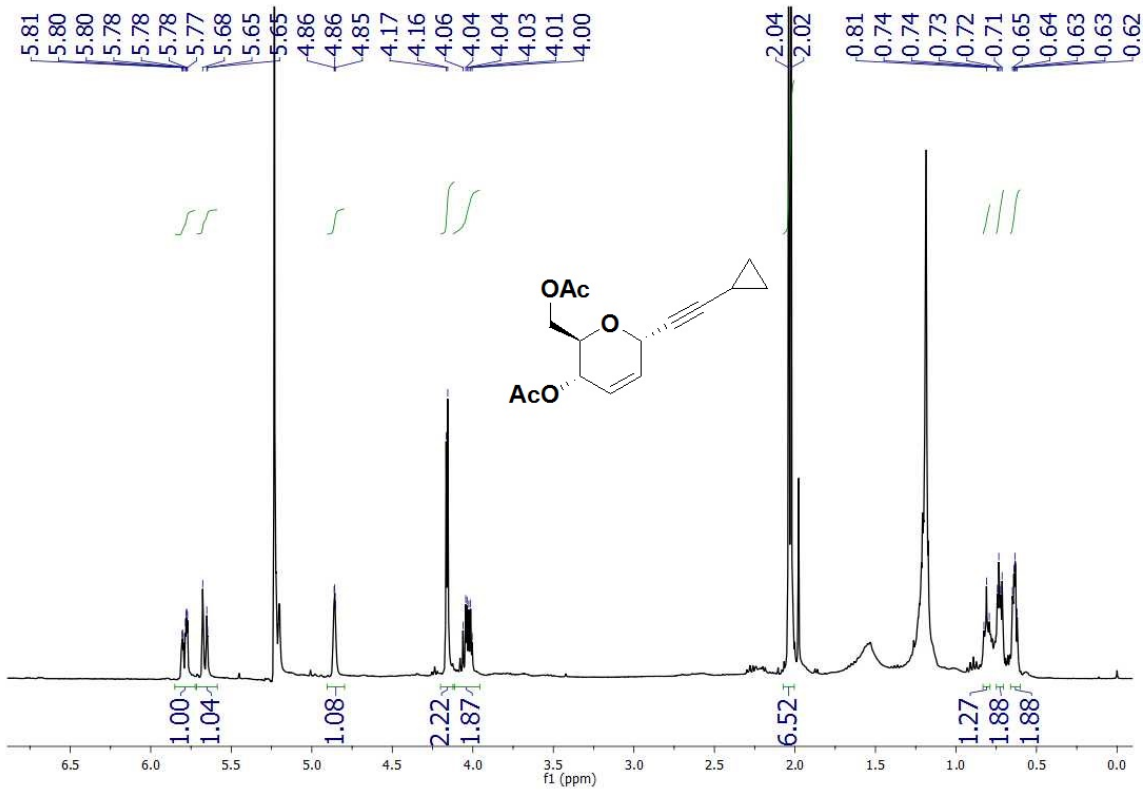
^{13}C NMR of compound **3a**



DEPT of compound **3a**



^{1}H NMR of compound **3b**



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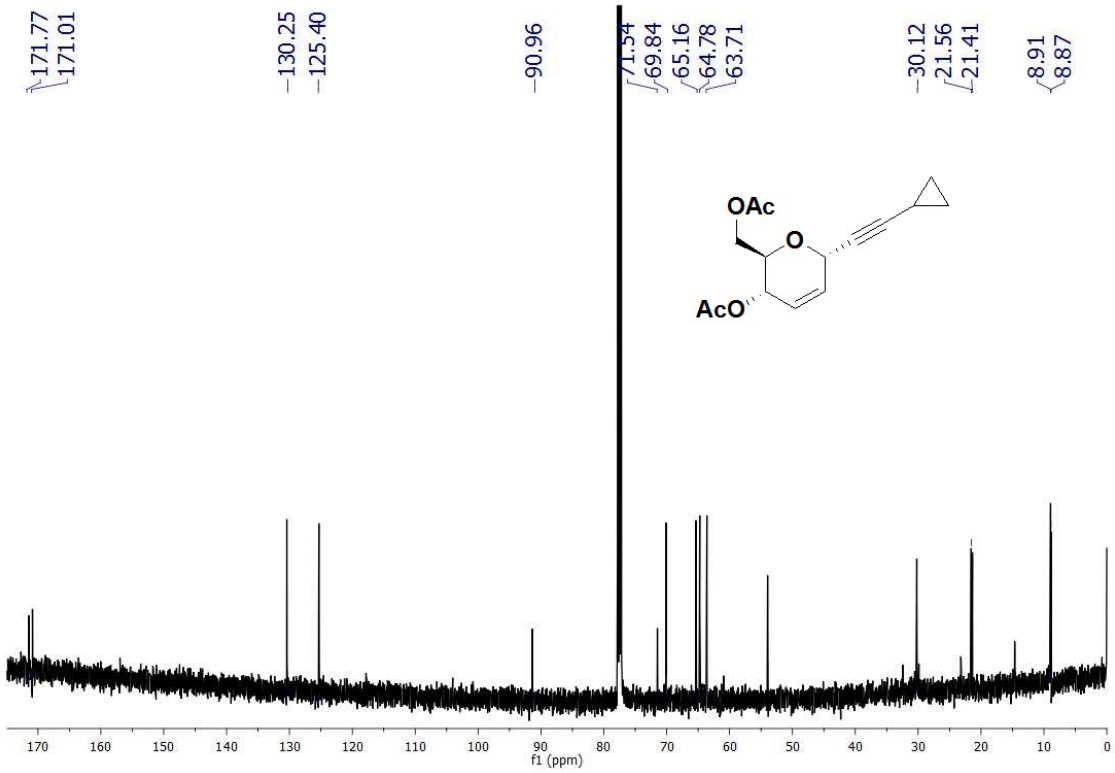

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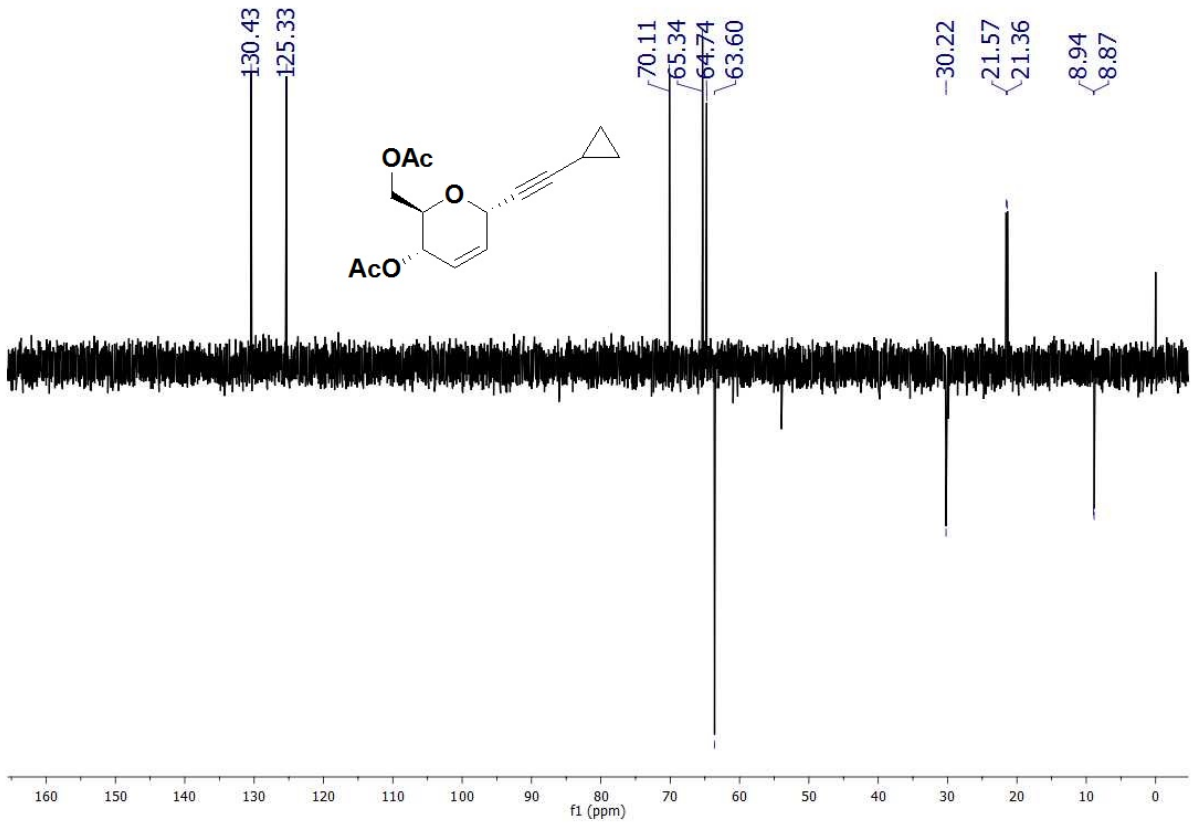

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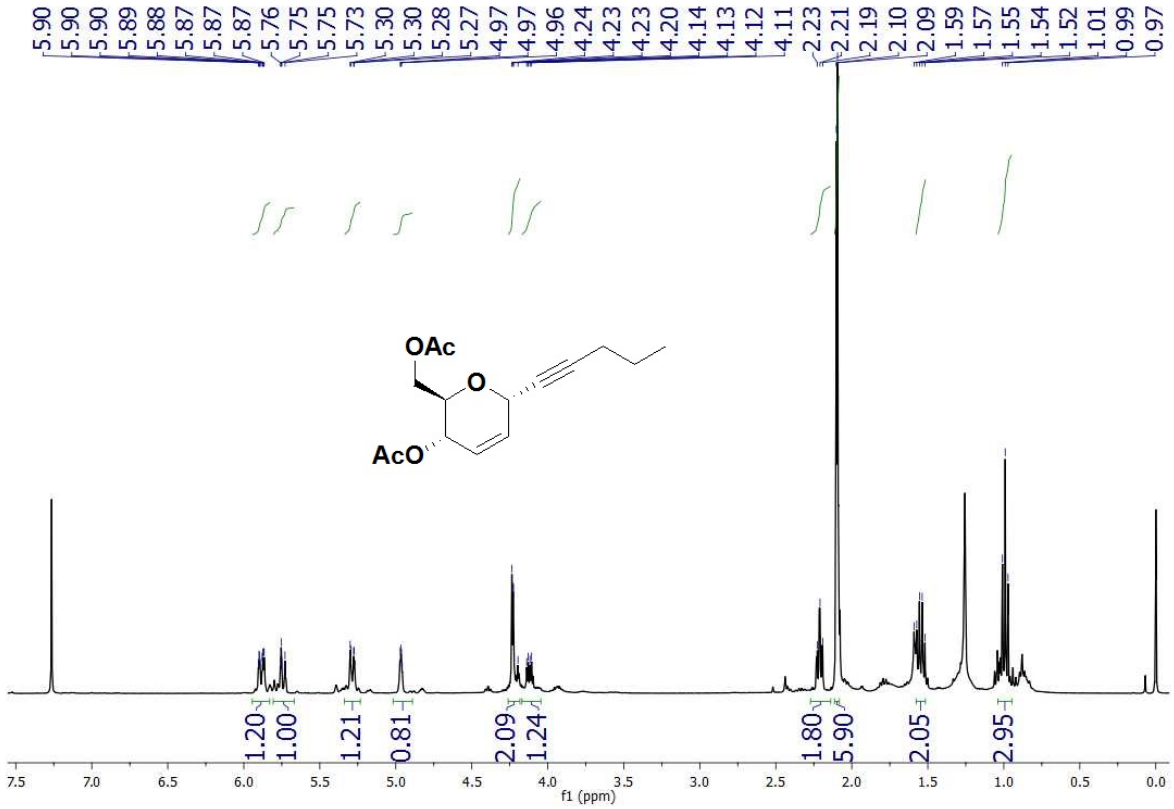

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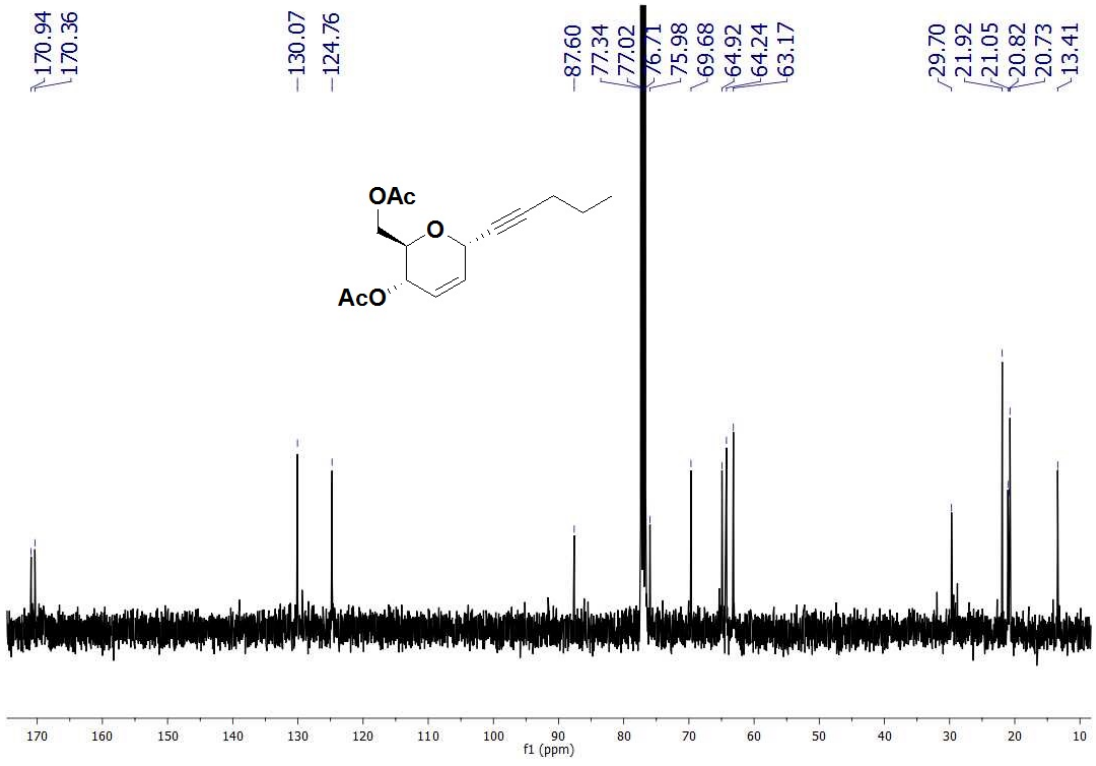

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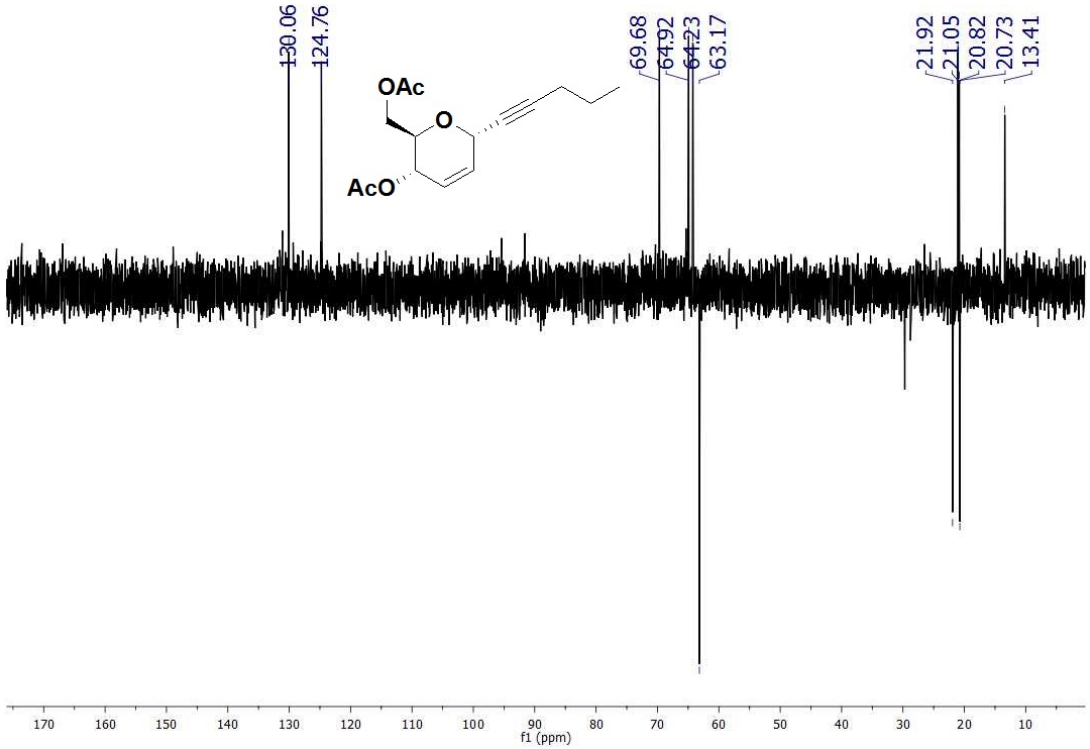
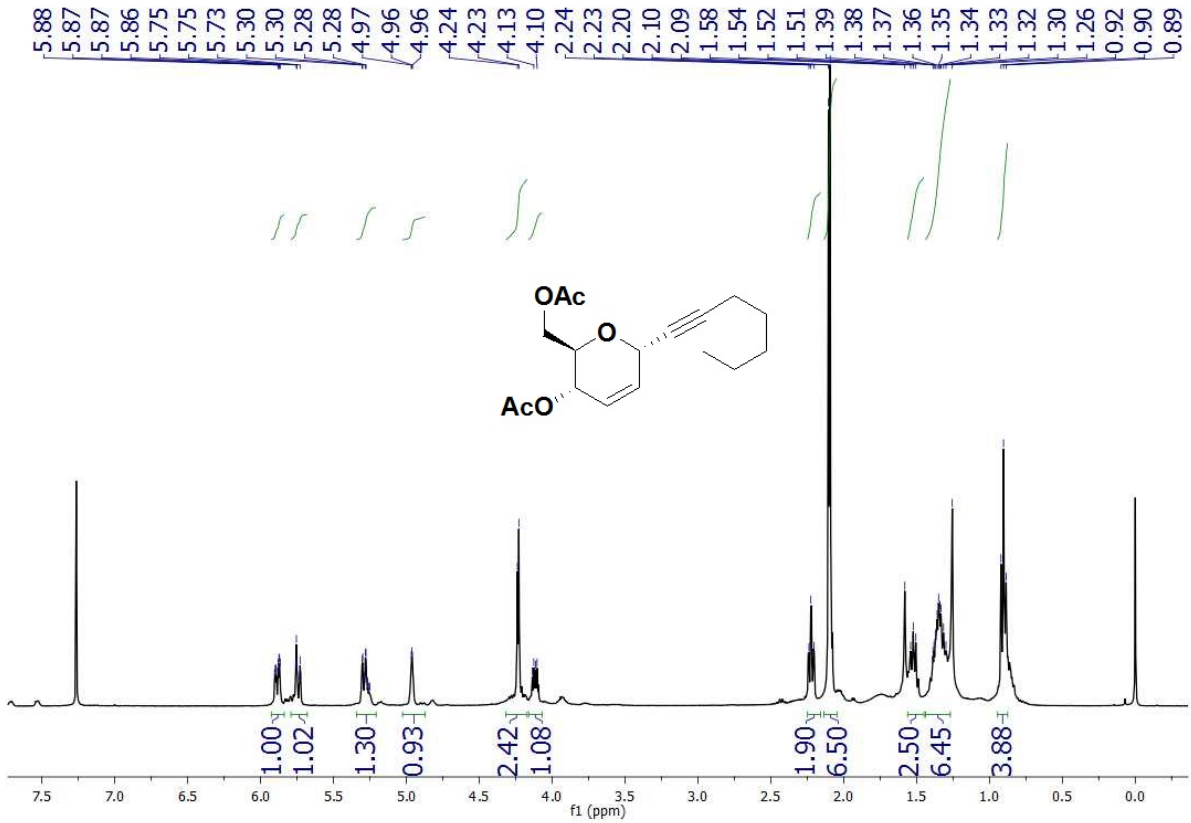
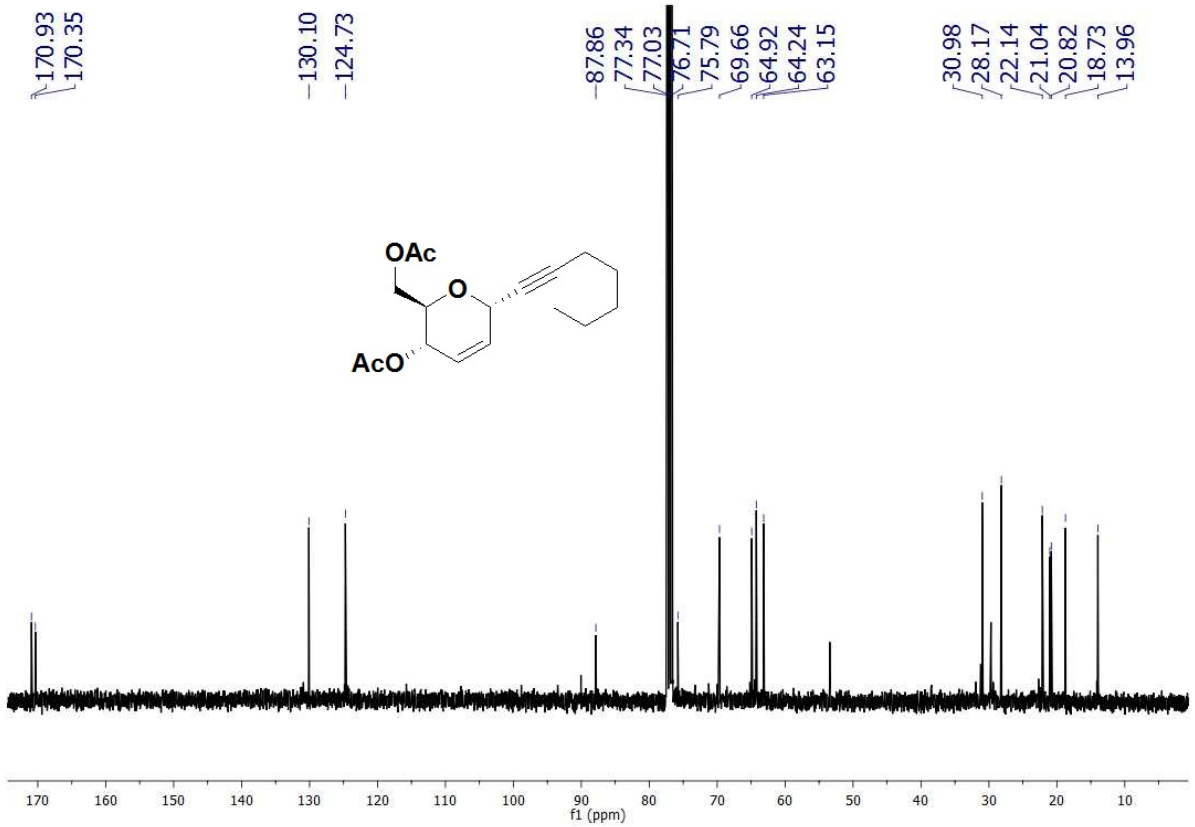


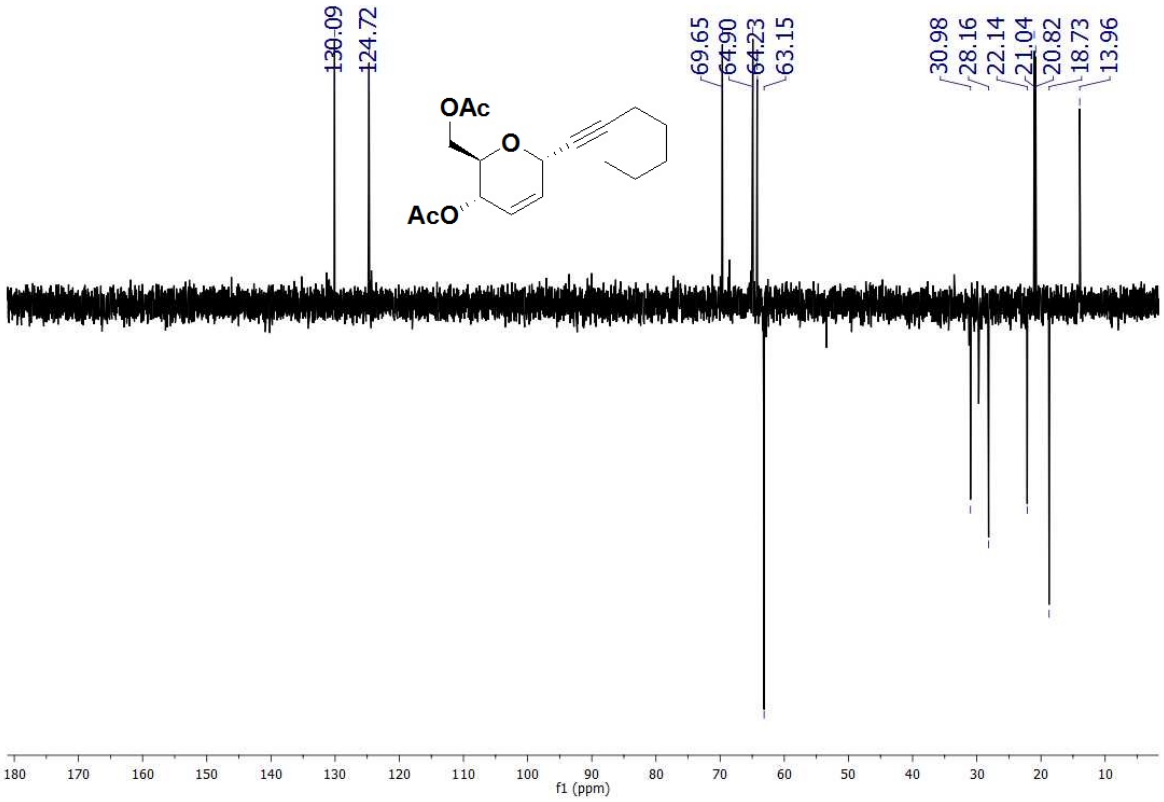
^{1}H NMR of compound **3d**



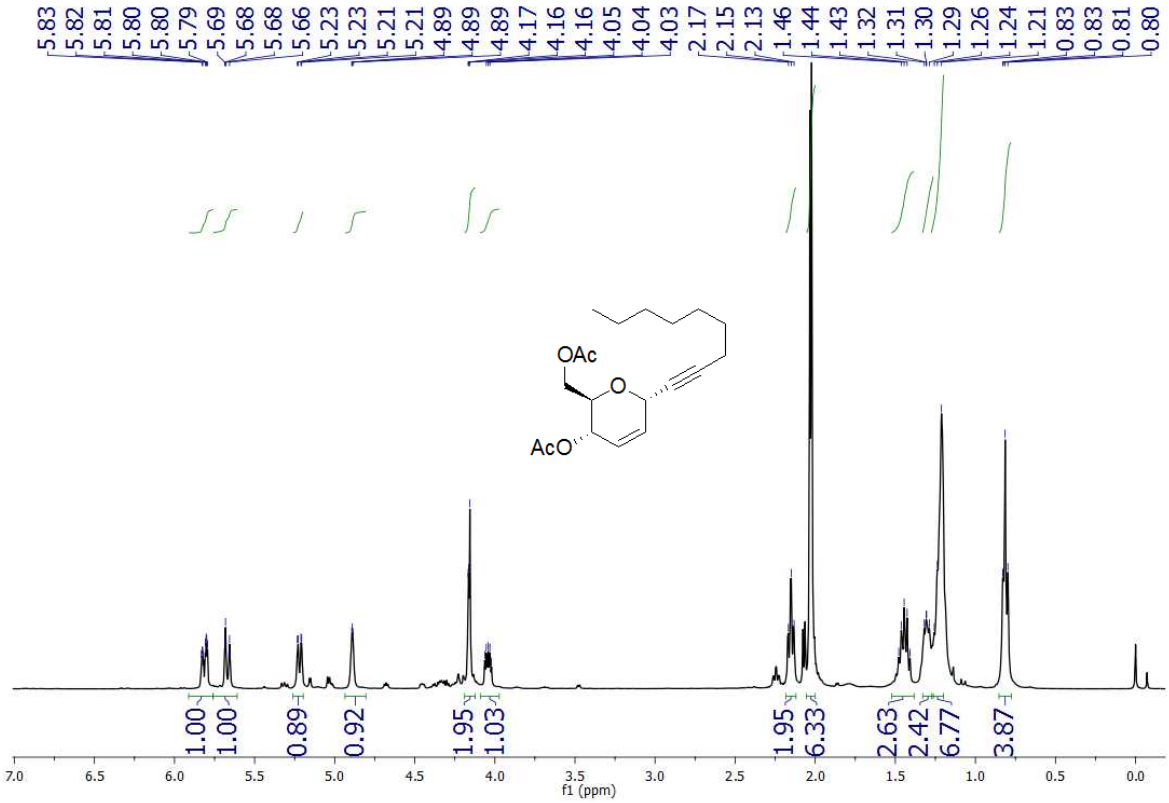
^{13}C NMR of compound **3d**



DEPT of Compound **3d**



^{1}H NMR of compound **3e**



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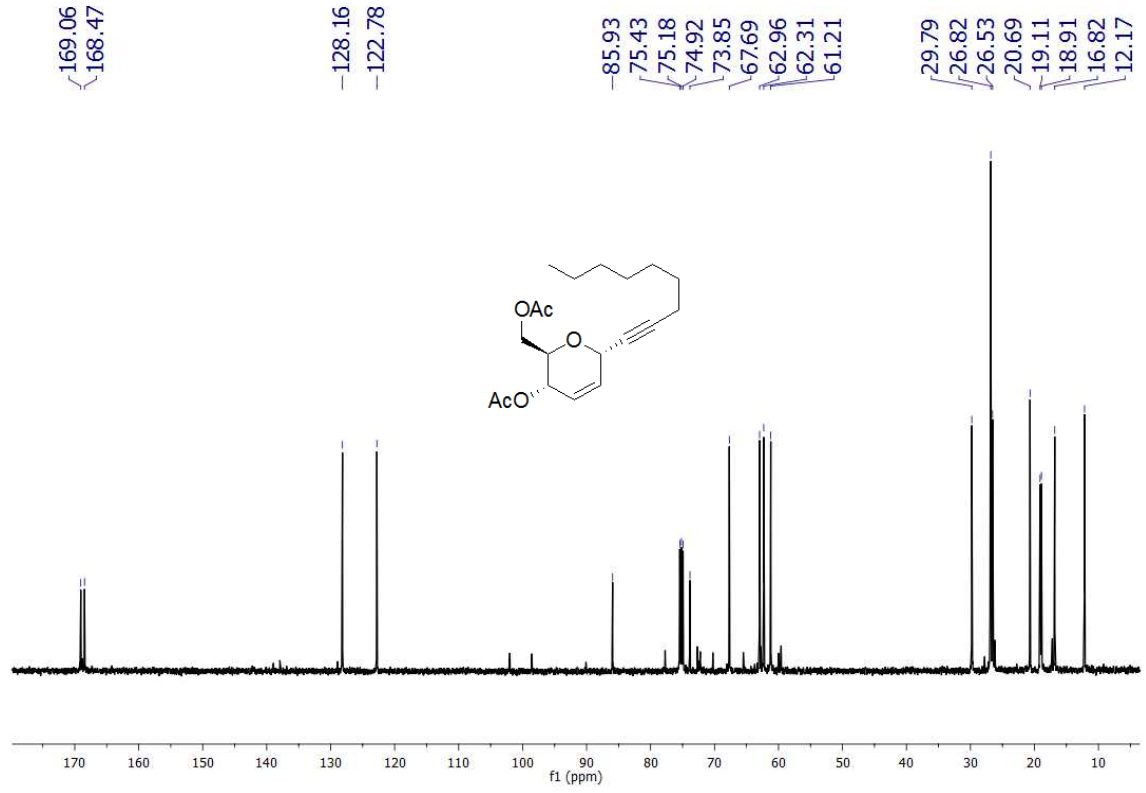

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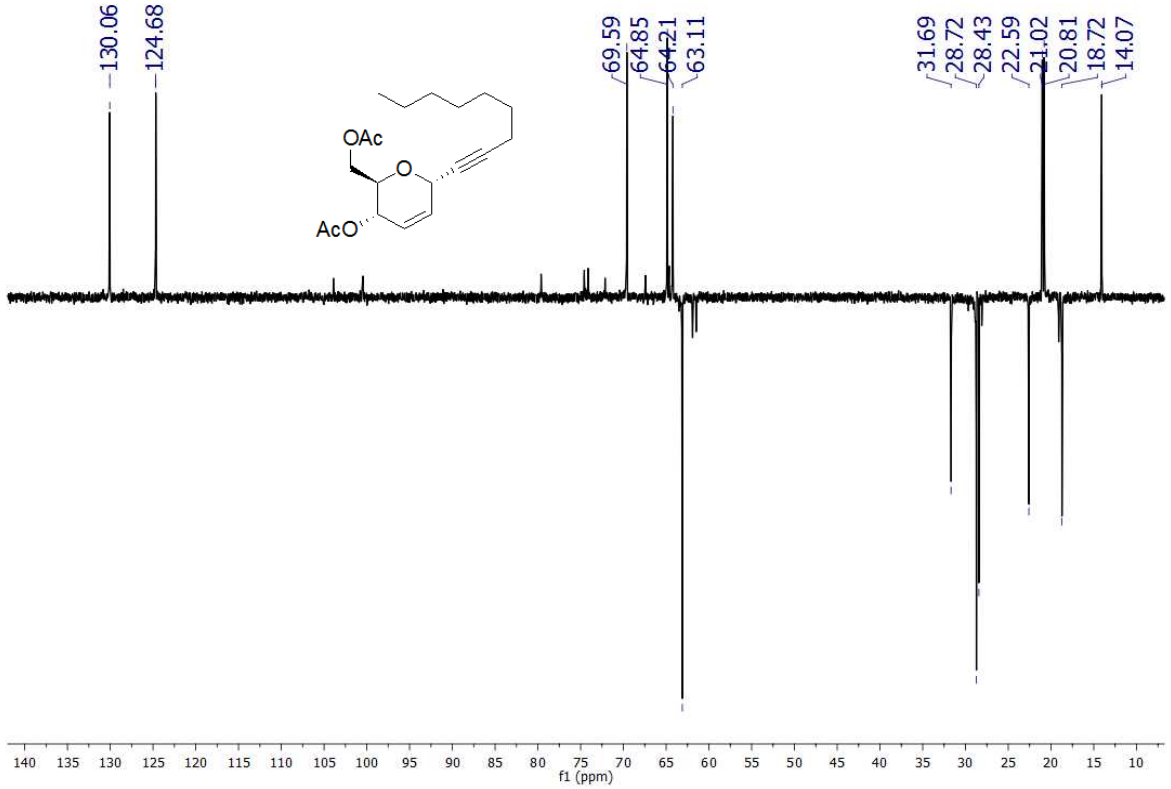
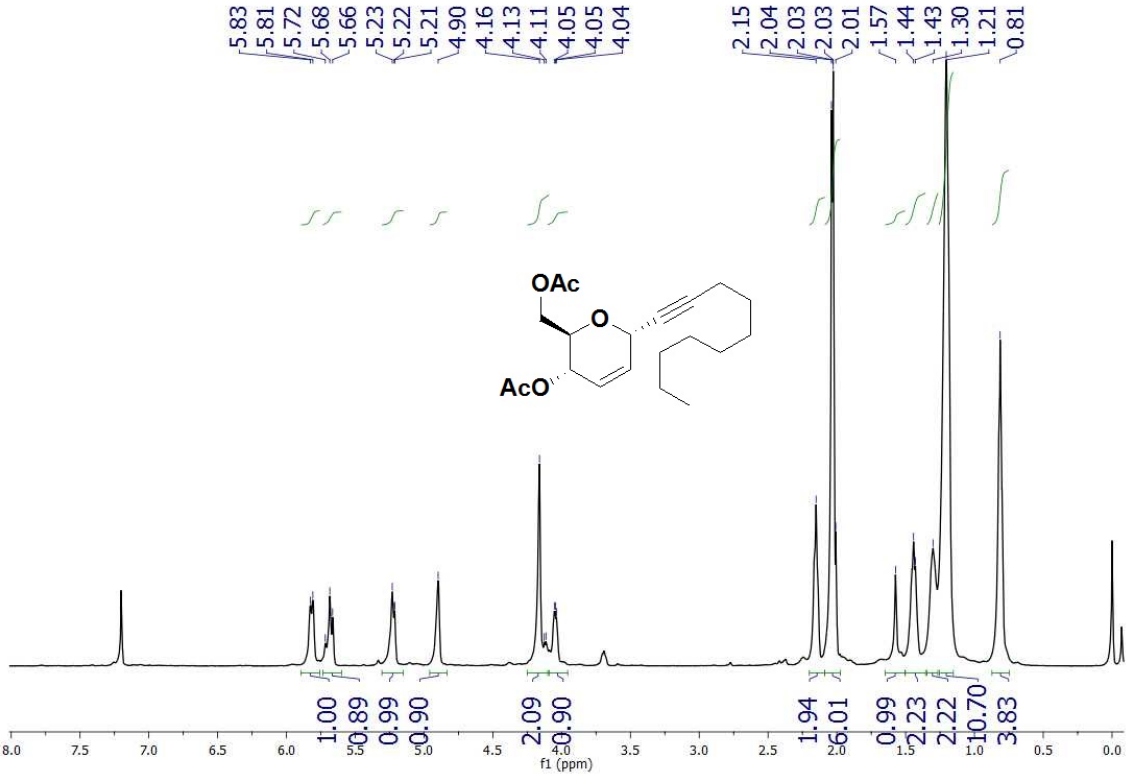
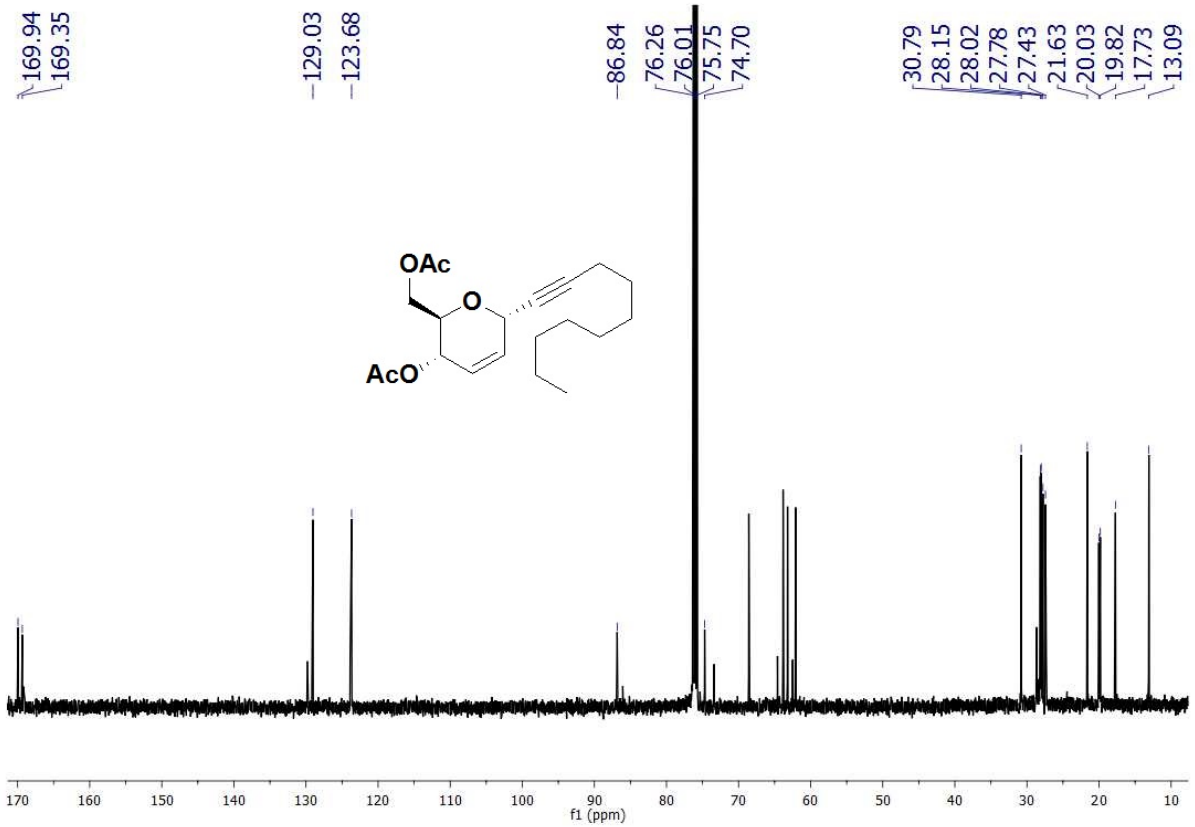


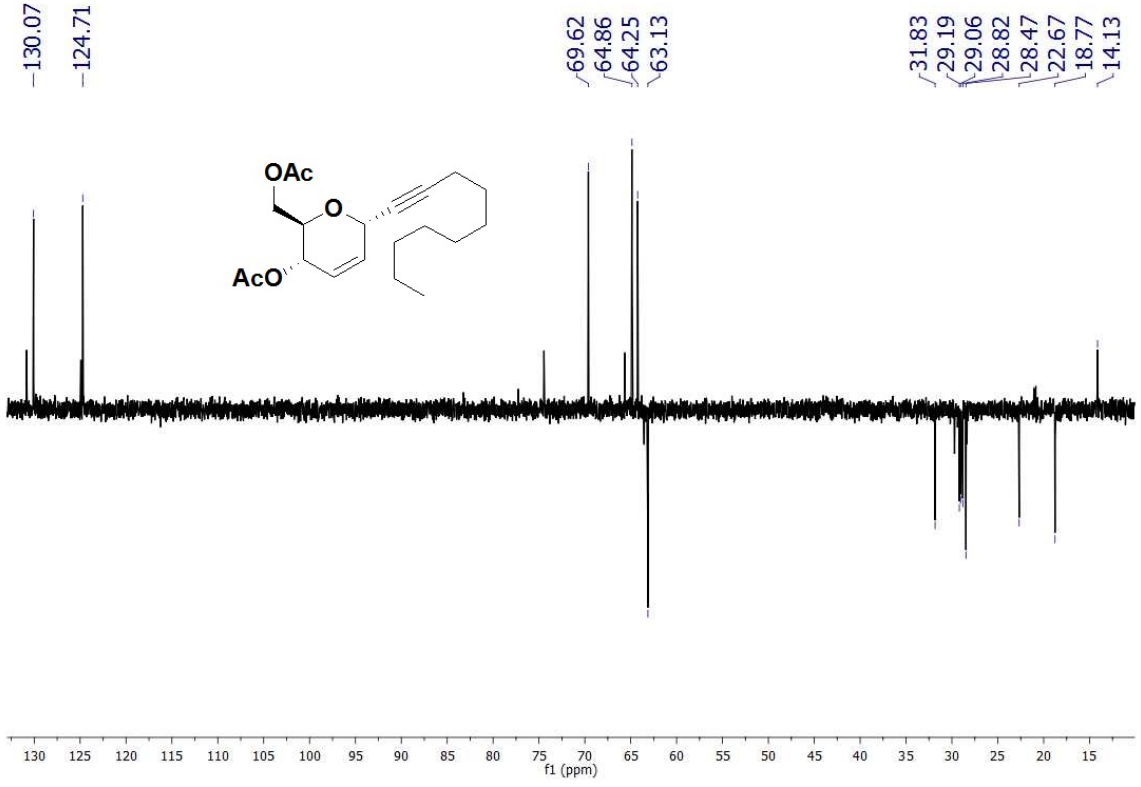
H[1] NMR of compound **3f**



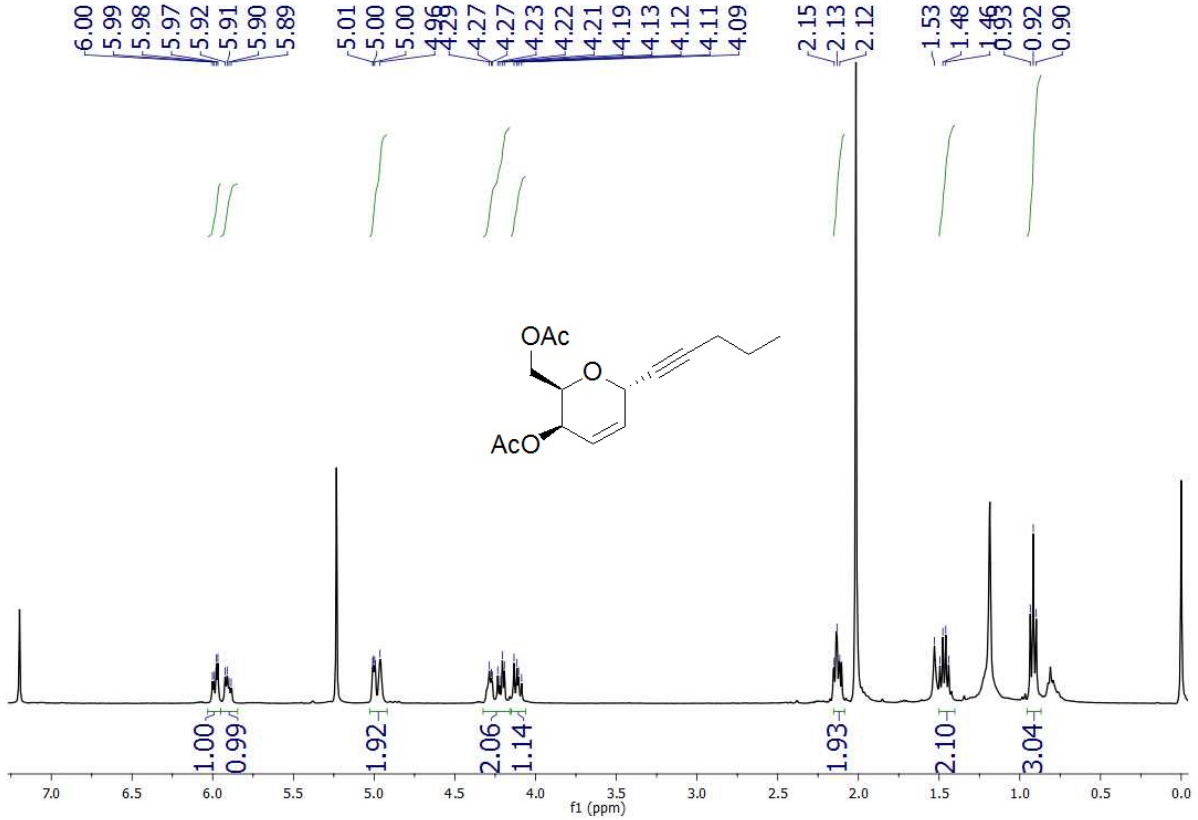
^{13}C NMR of compound **3f**



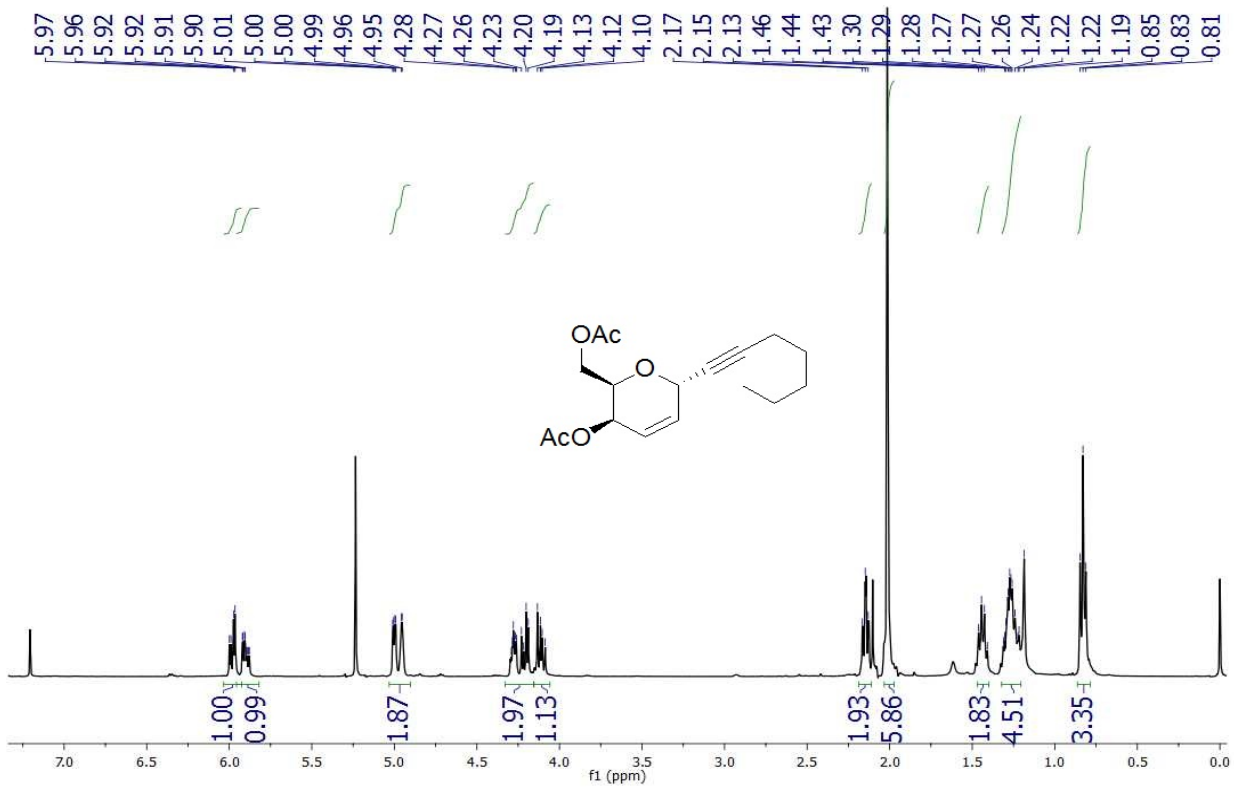
DEPT of Compound **3f**



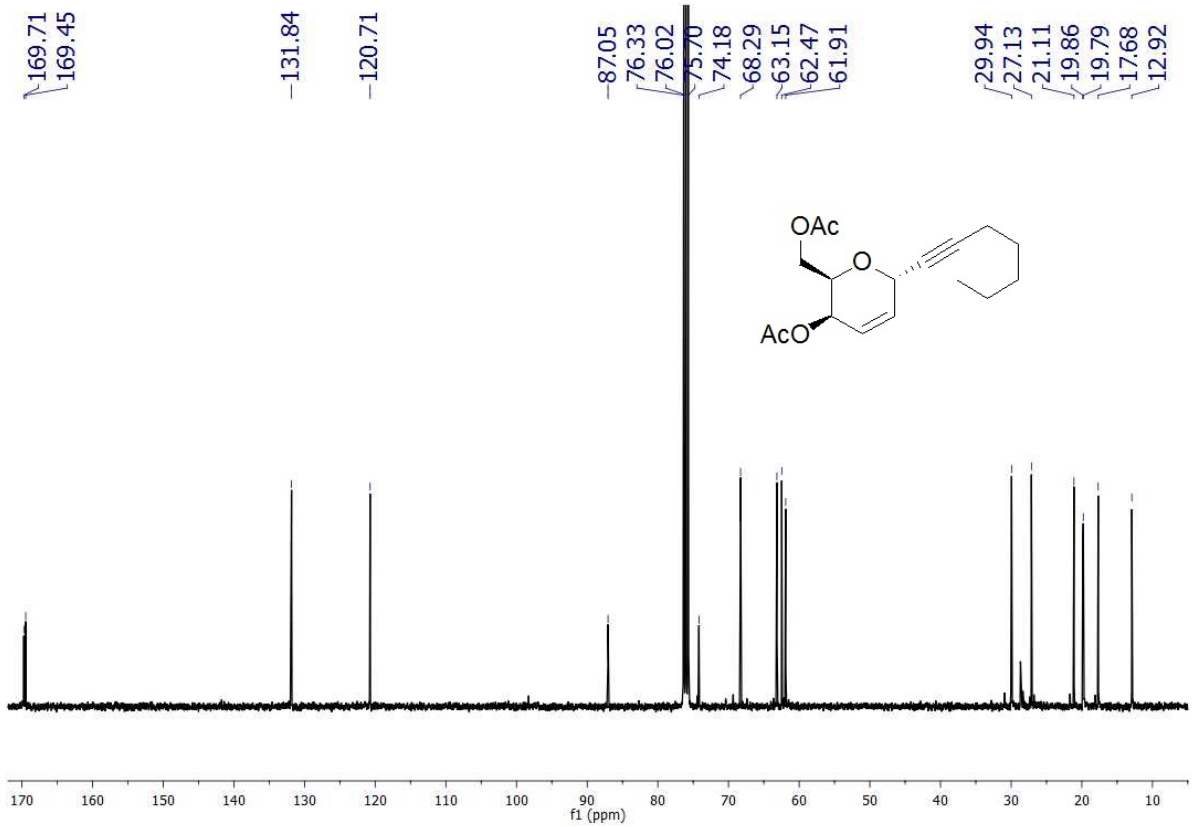
[1]H NMR of compound **3g**



[1]H NMR of compound **3h**



^{13}C NMR of compound **3h**



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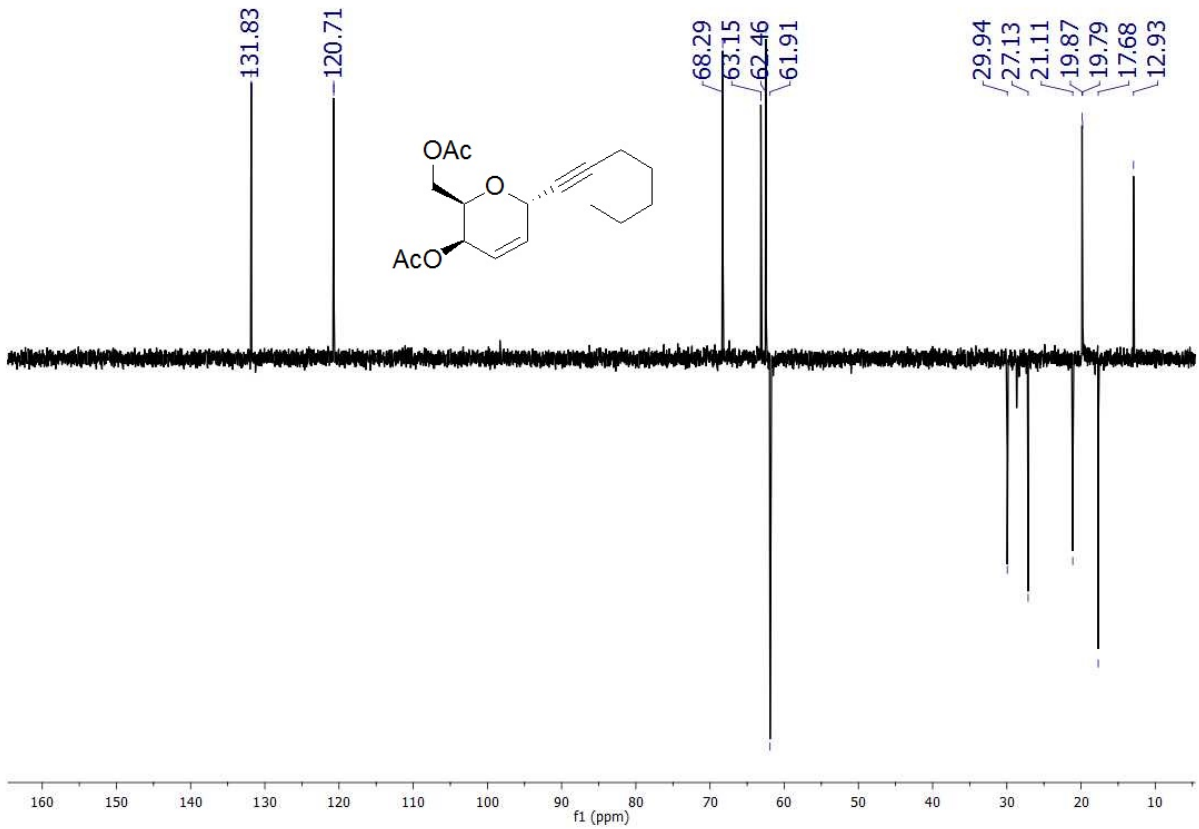
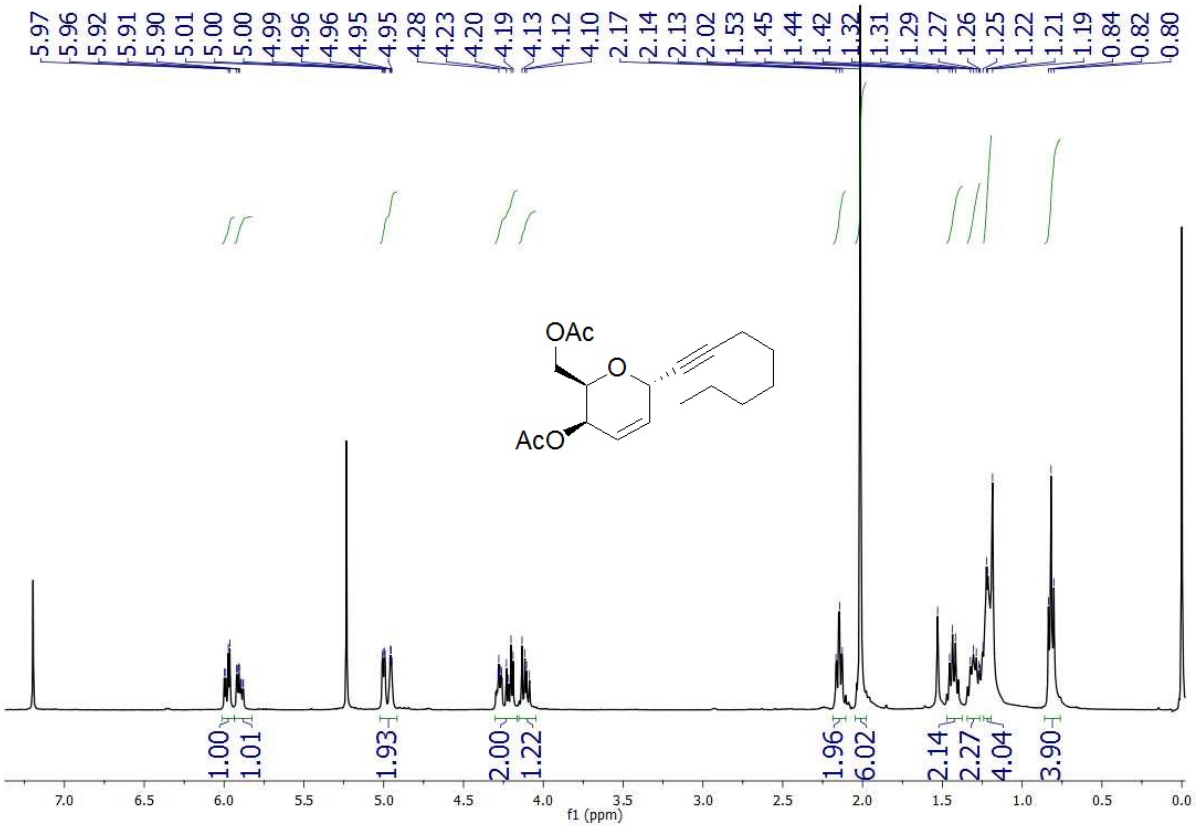


[1]H NMR of compound **3i**



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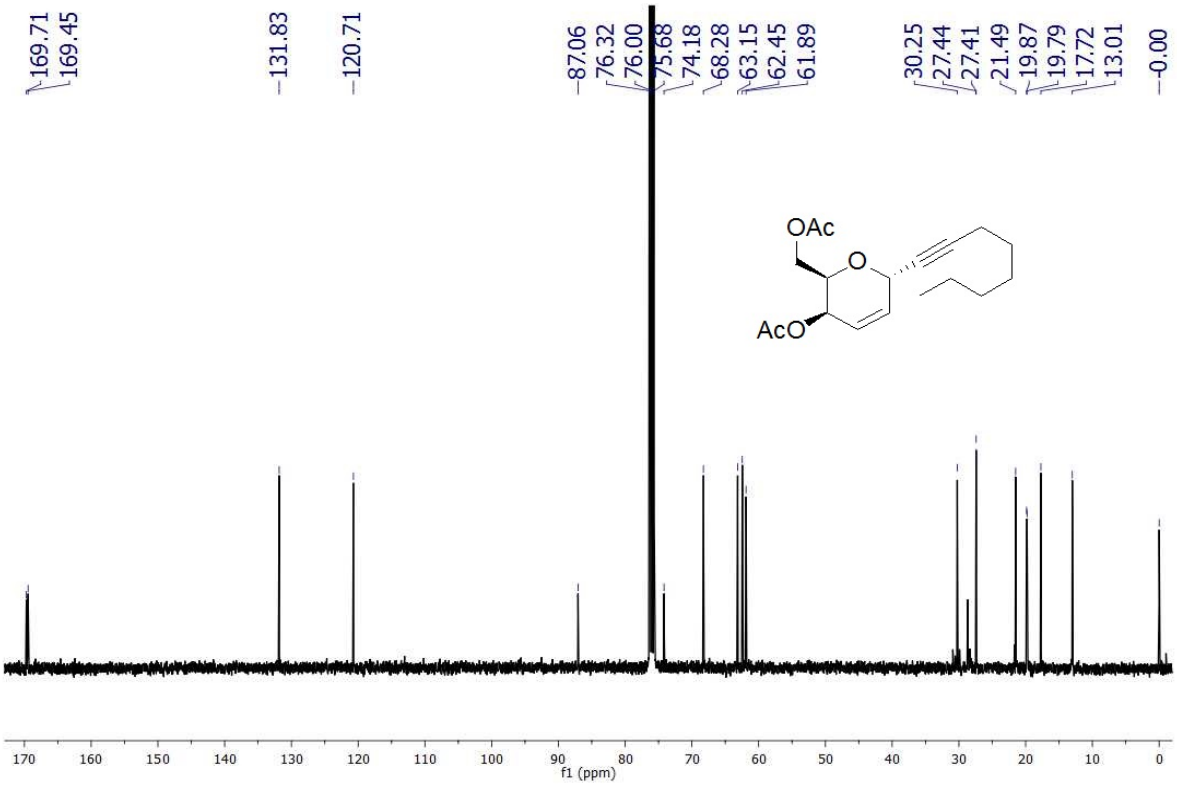

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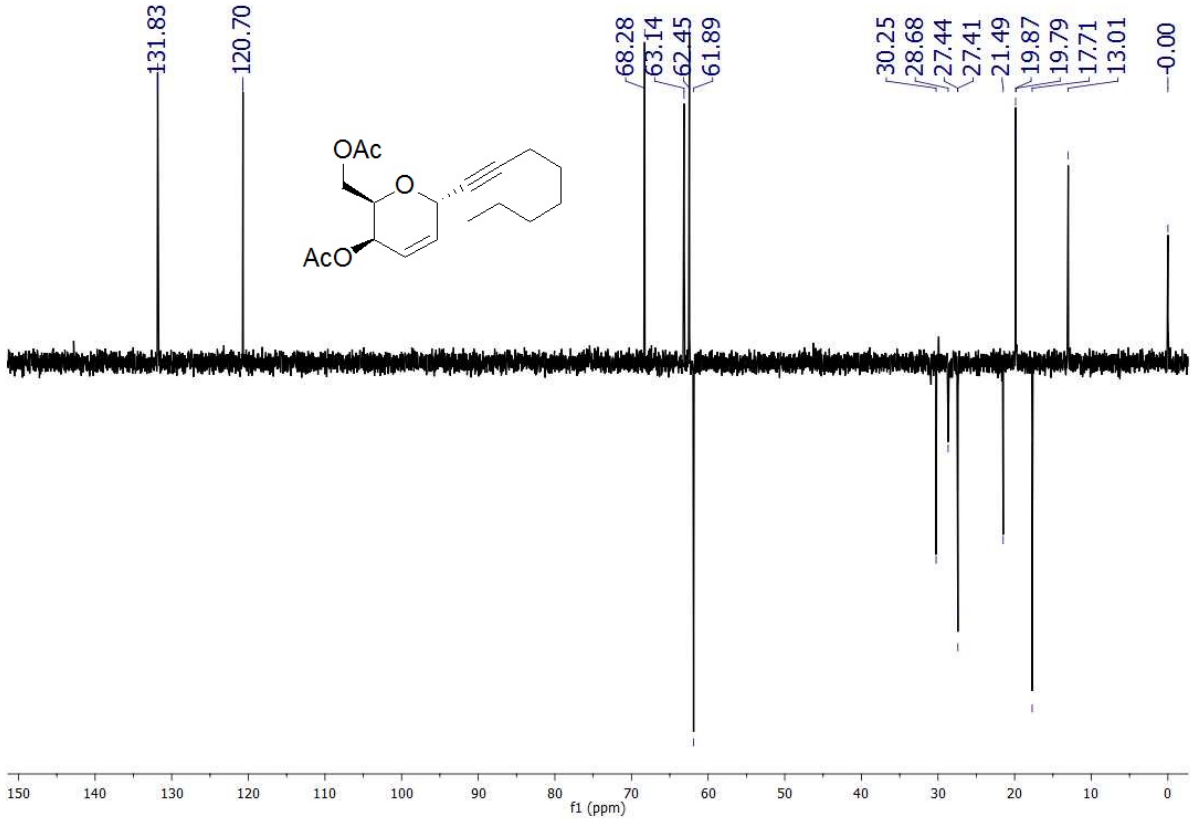
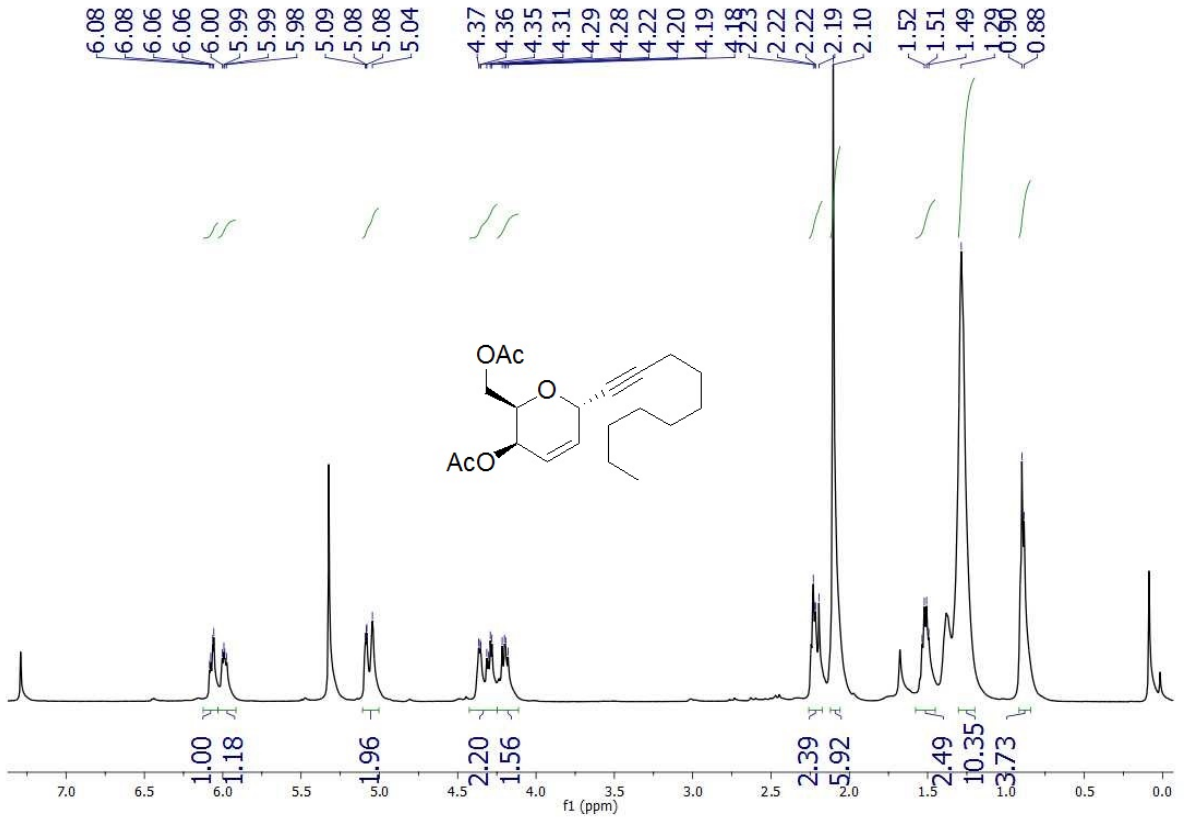
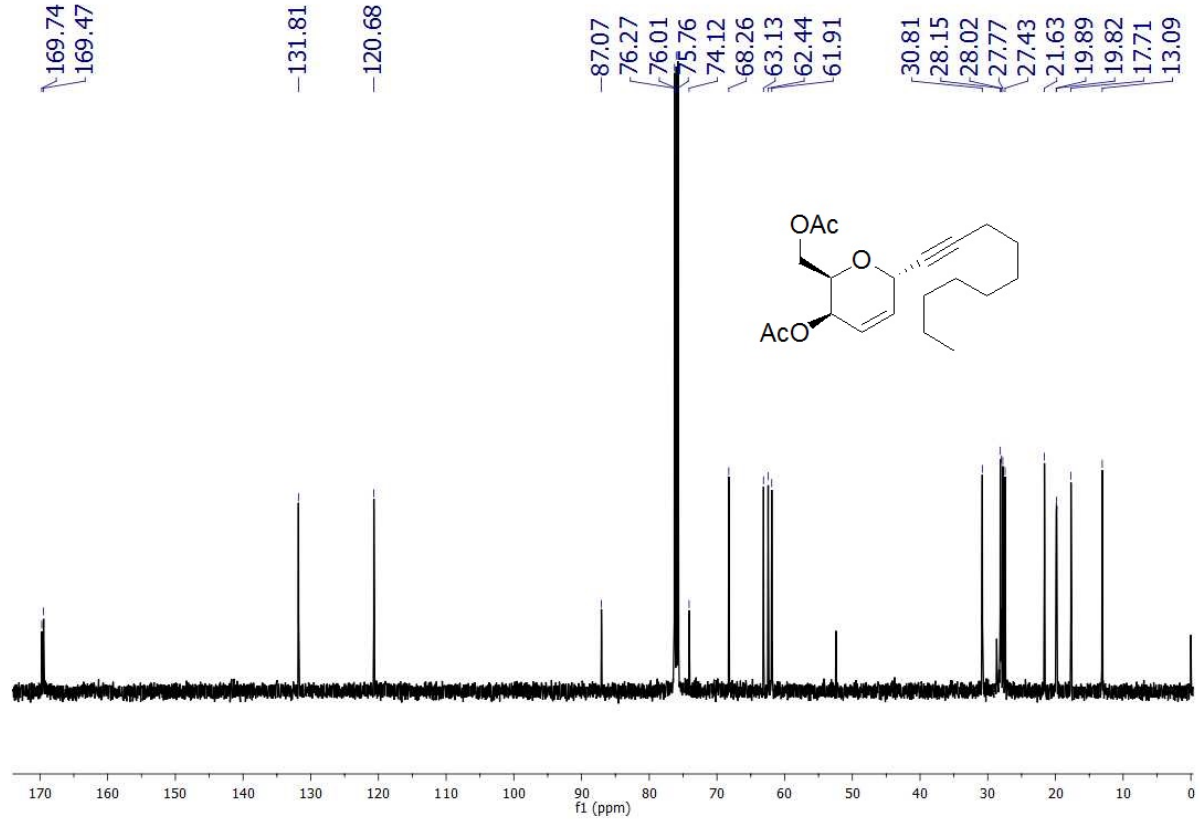


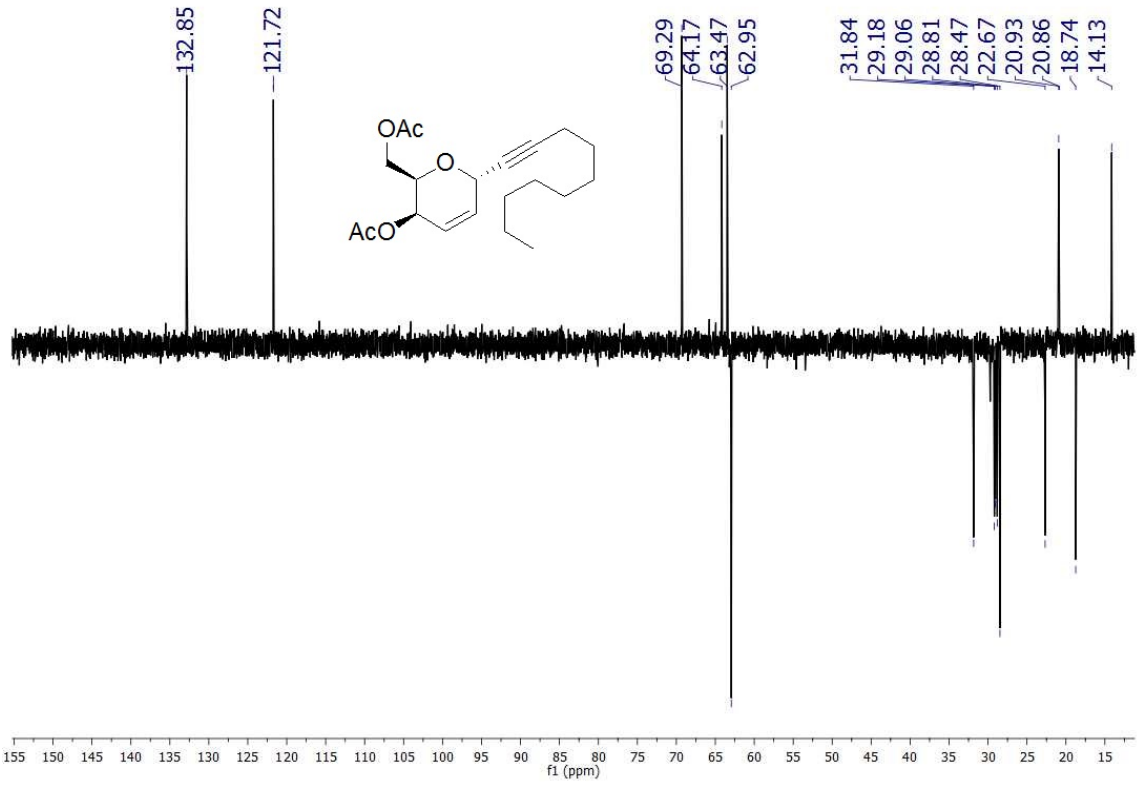
^{1}H NMR of compound **3j**



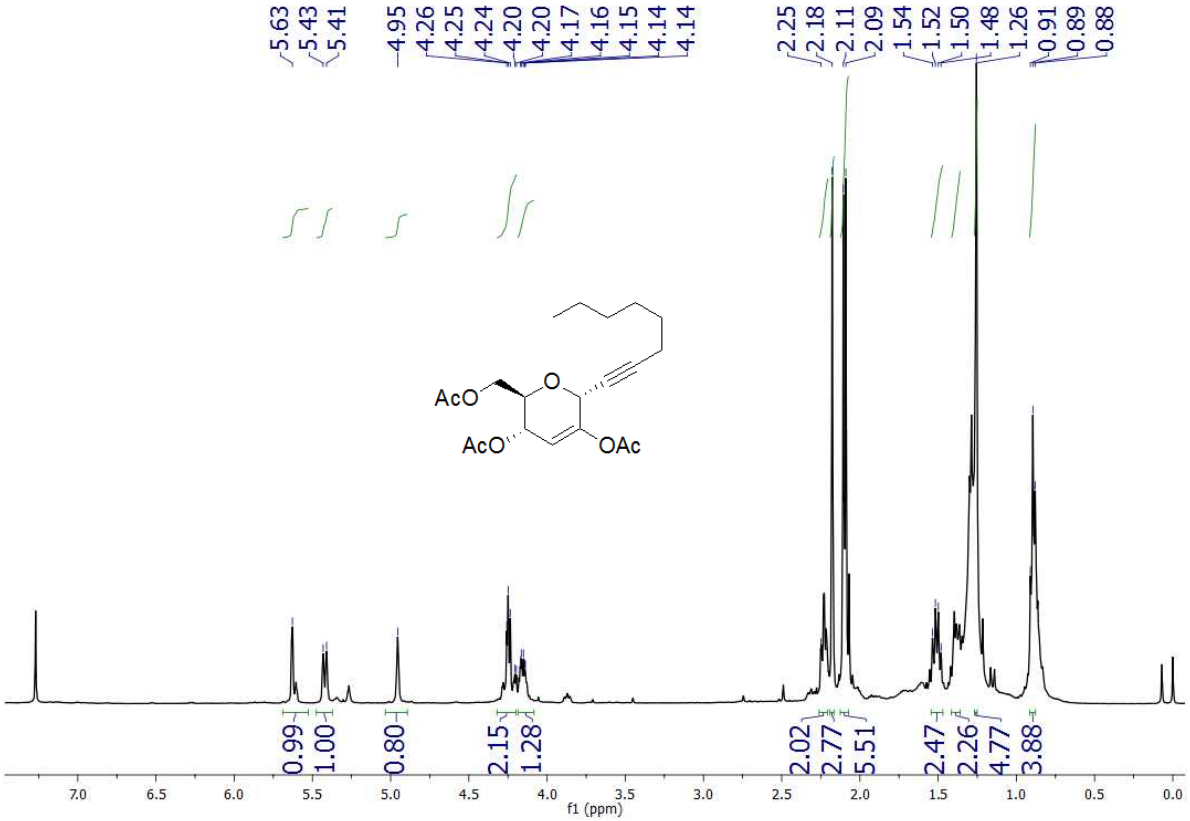
^{13}C NMR of compound **3j**



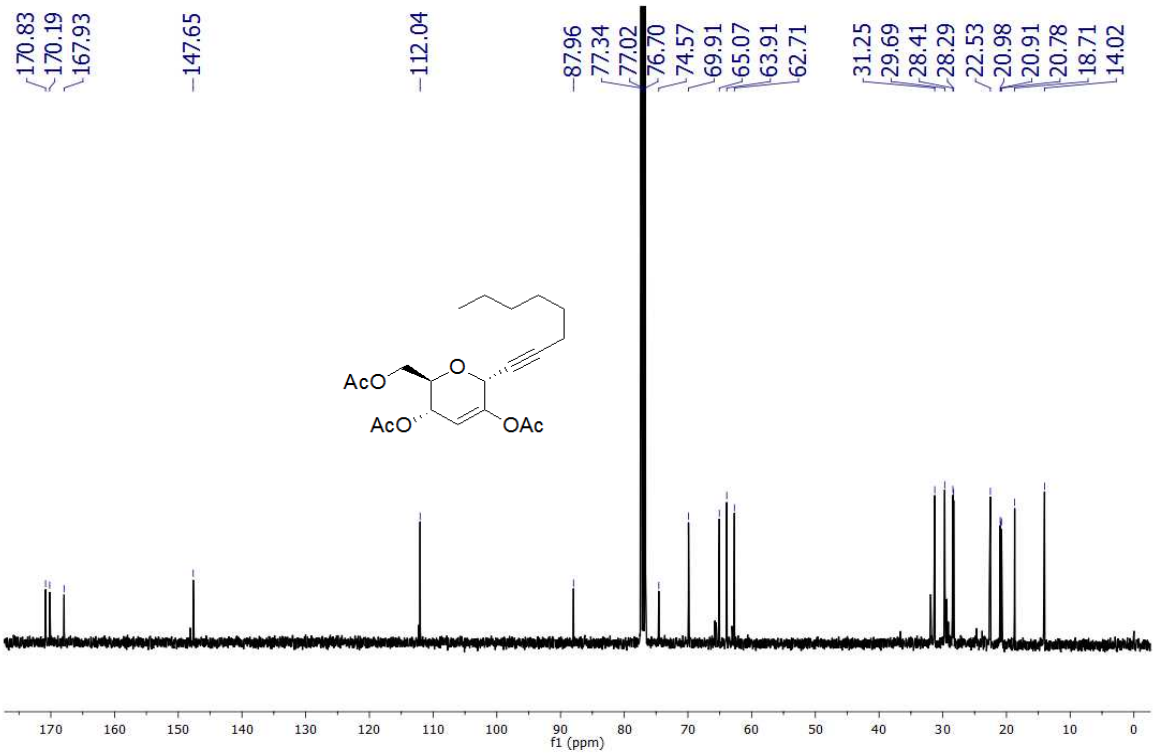
DEPT of Compound **3j**



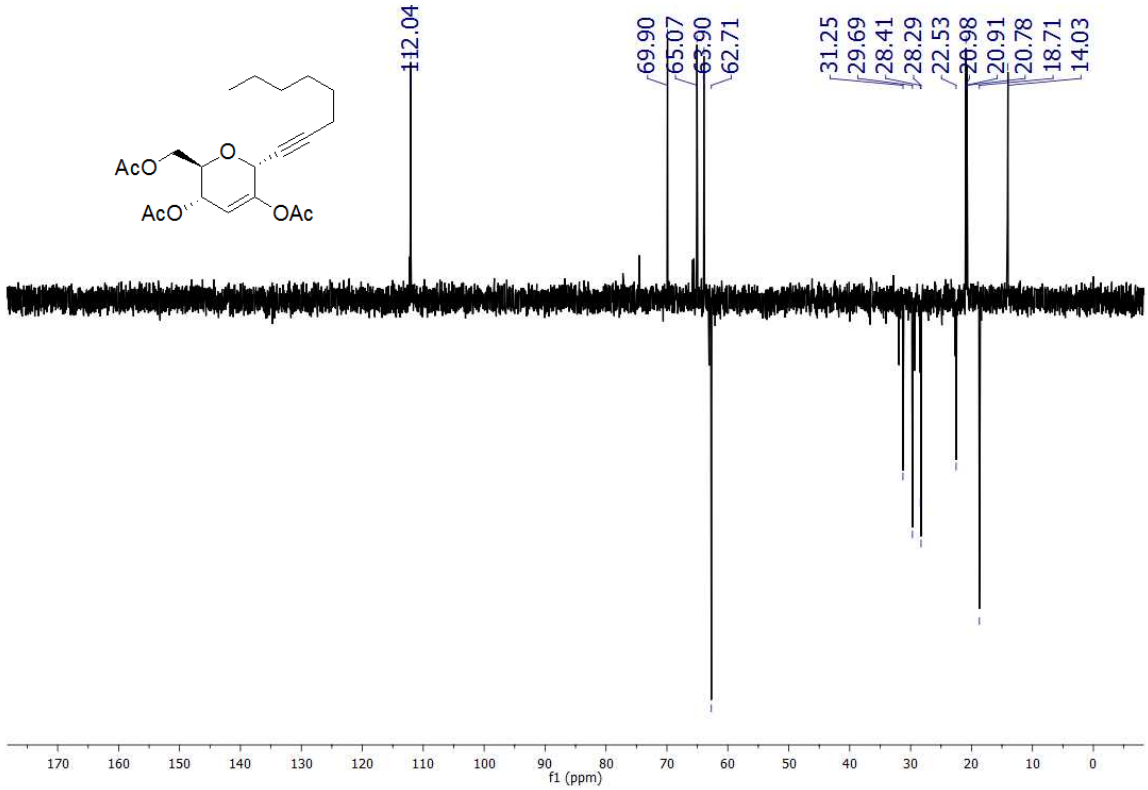
[1]H NMR of compound **3k**



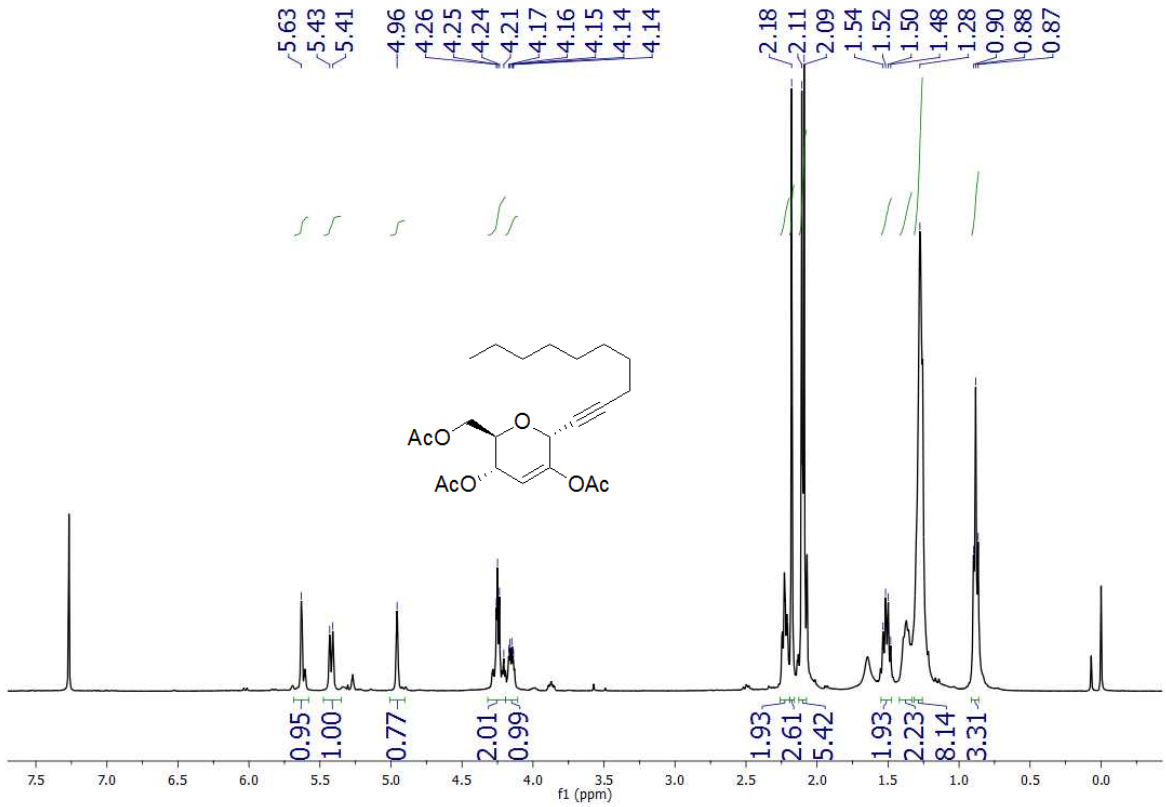
[13]C NMR of compound **3k**



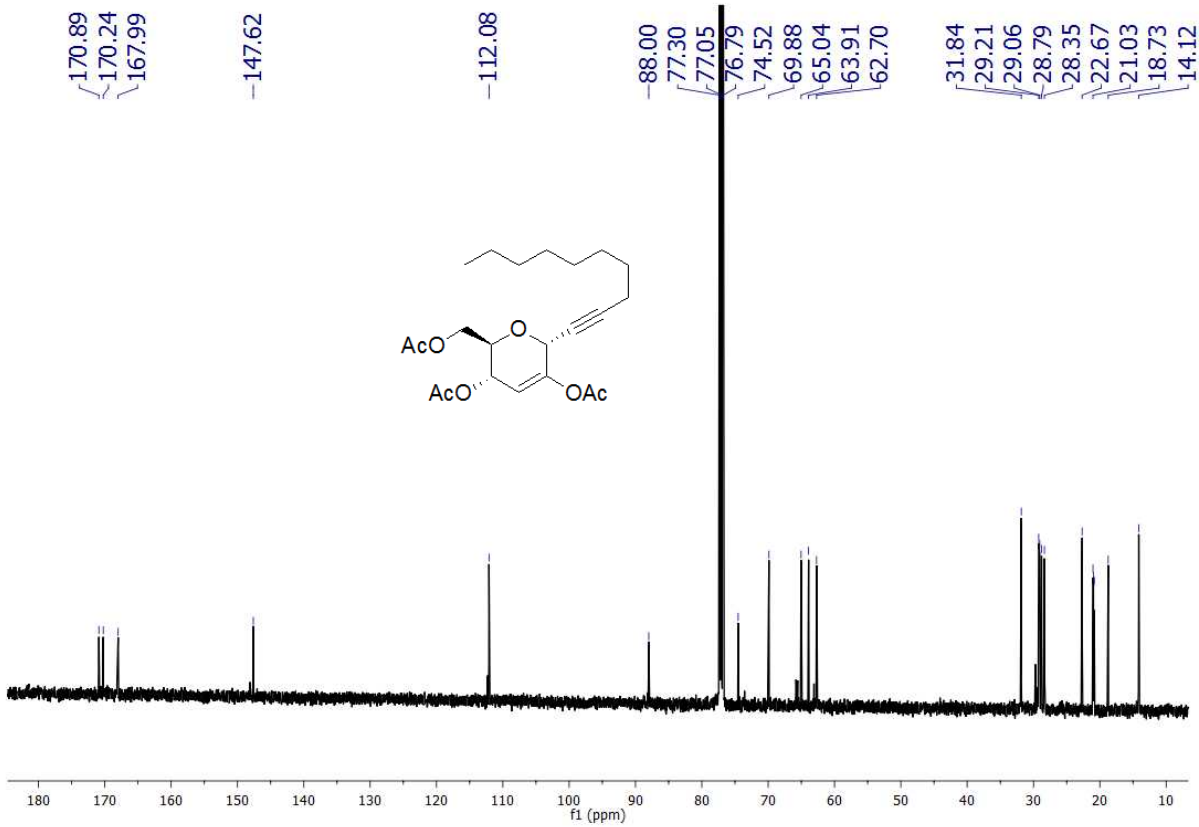
DEPT of Compound **3k**



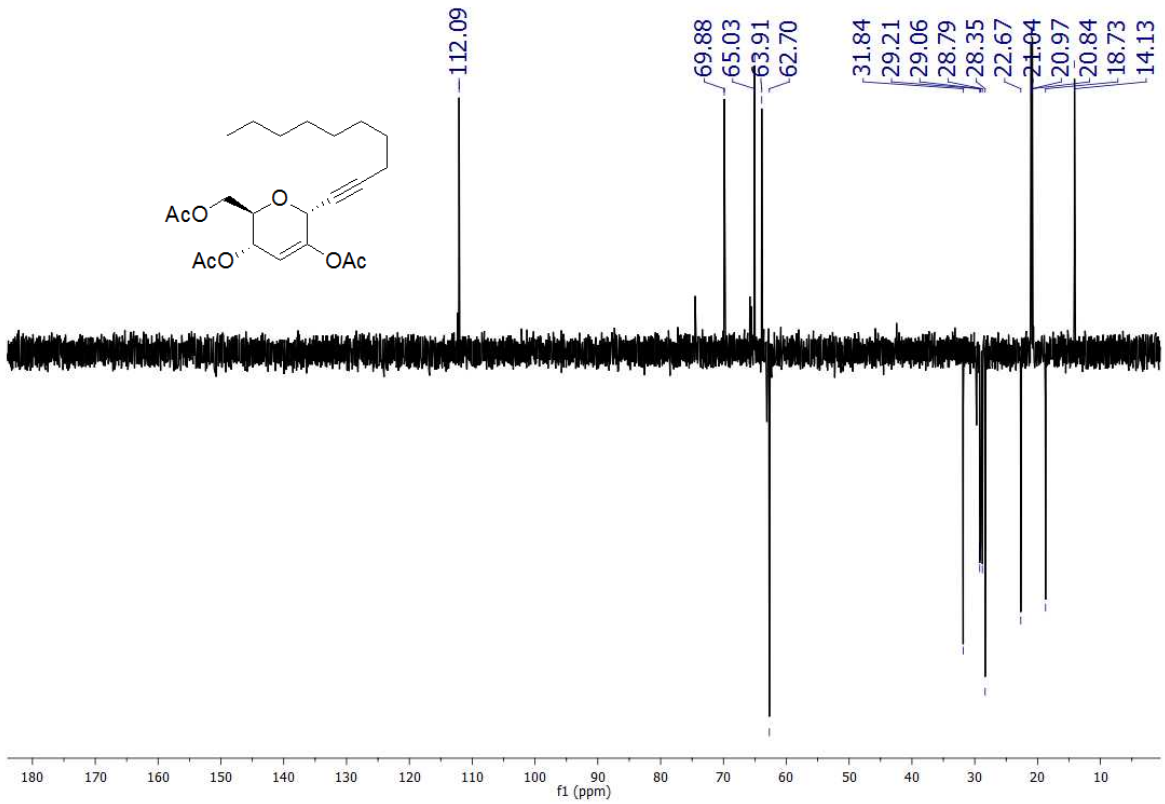
^{1}H NMR of compound **3l**



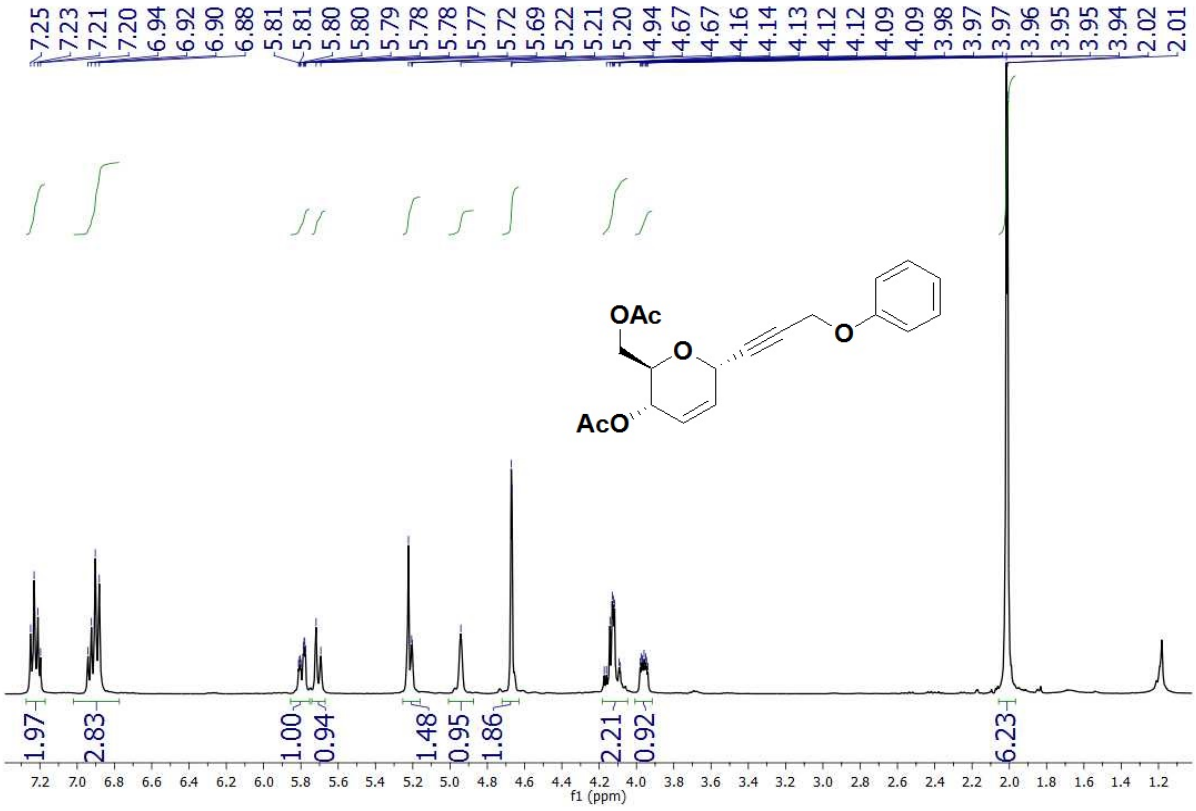
^{13}C NMR of compound **3l**



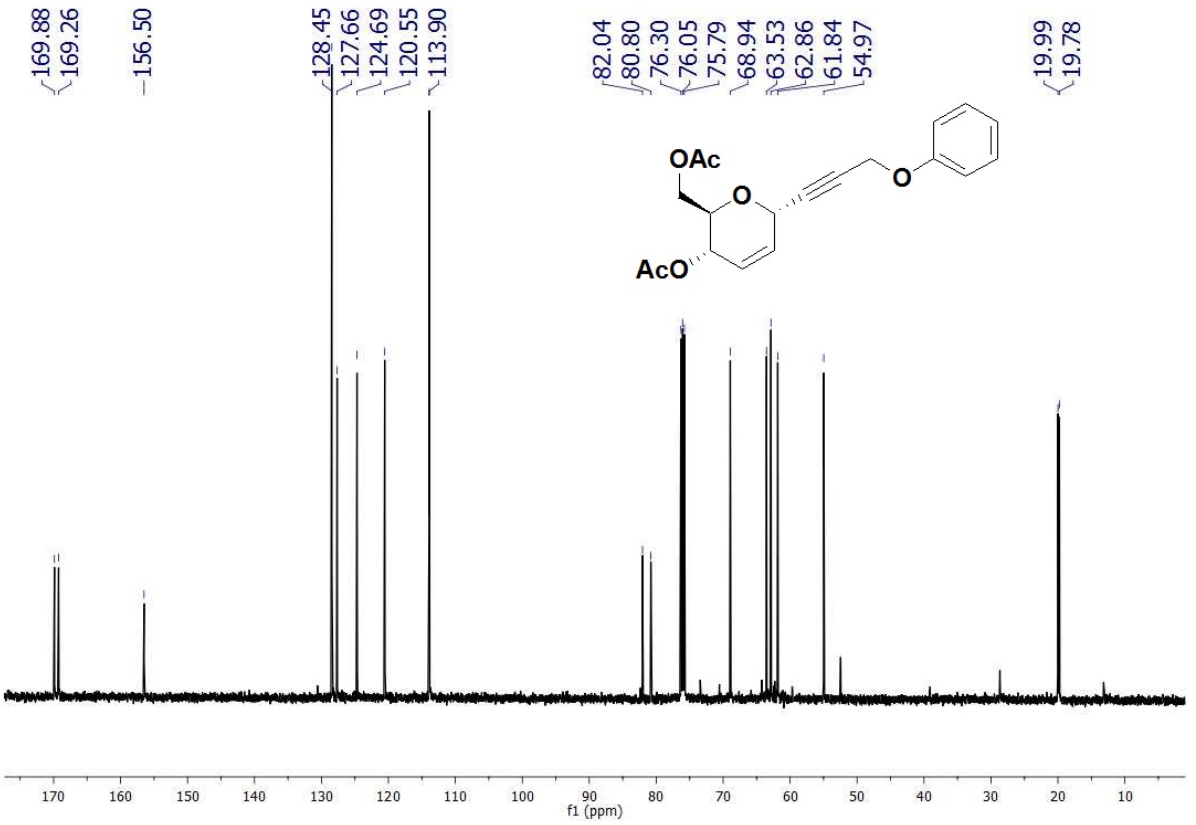
DEPT of Compound **3l**



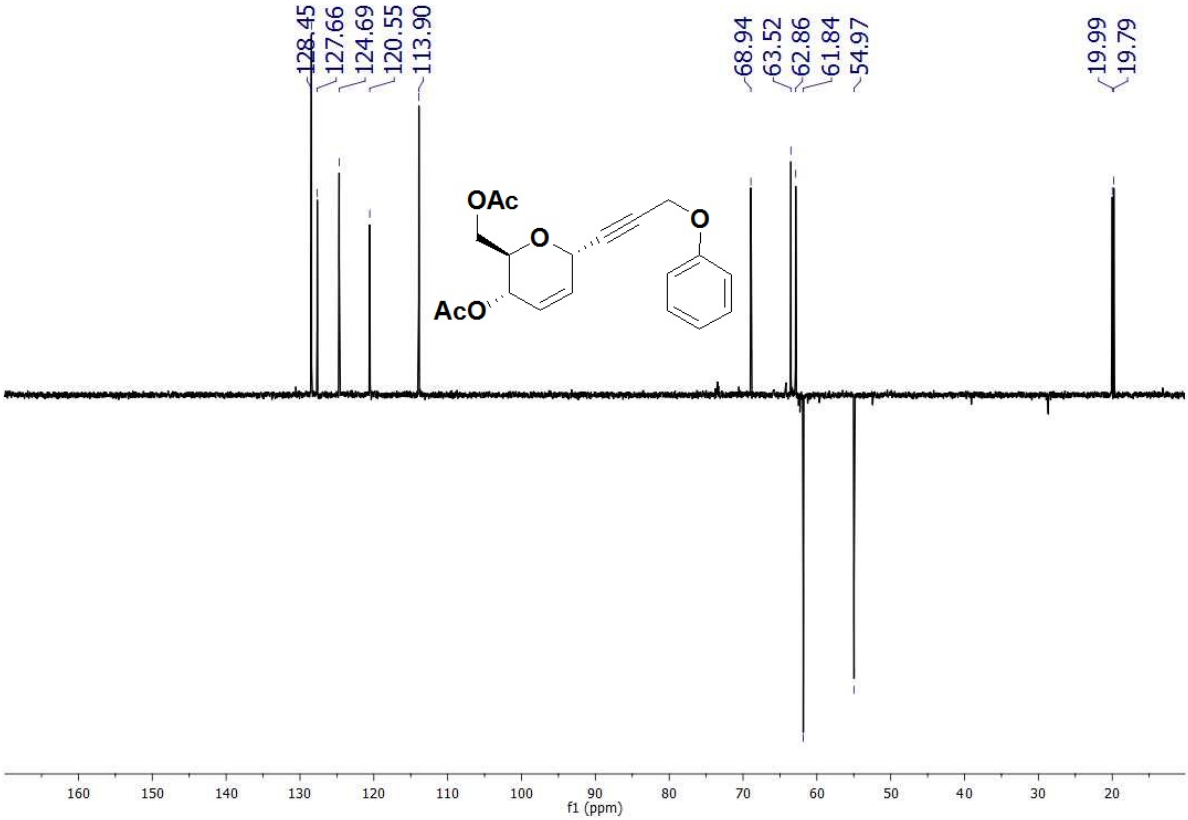
[1]H NMR of compound **3m**



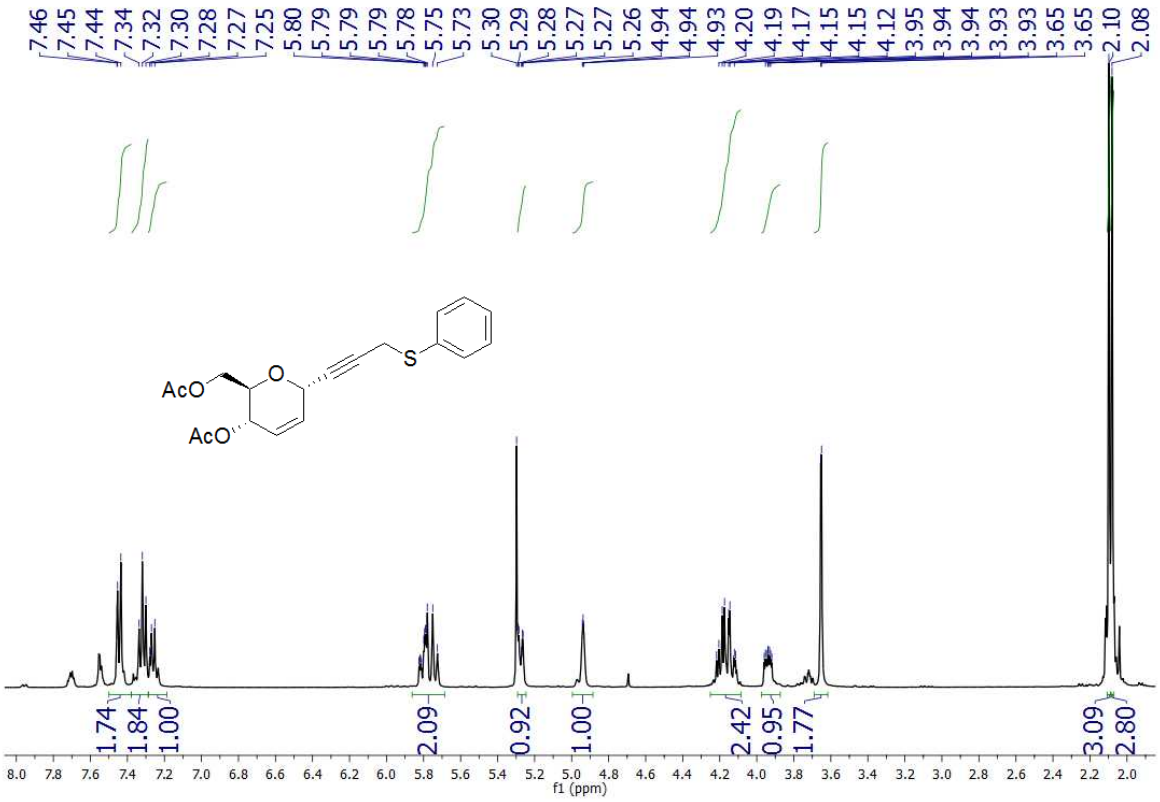
[13]C NMR of compound **3m**



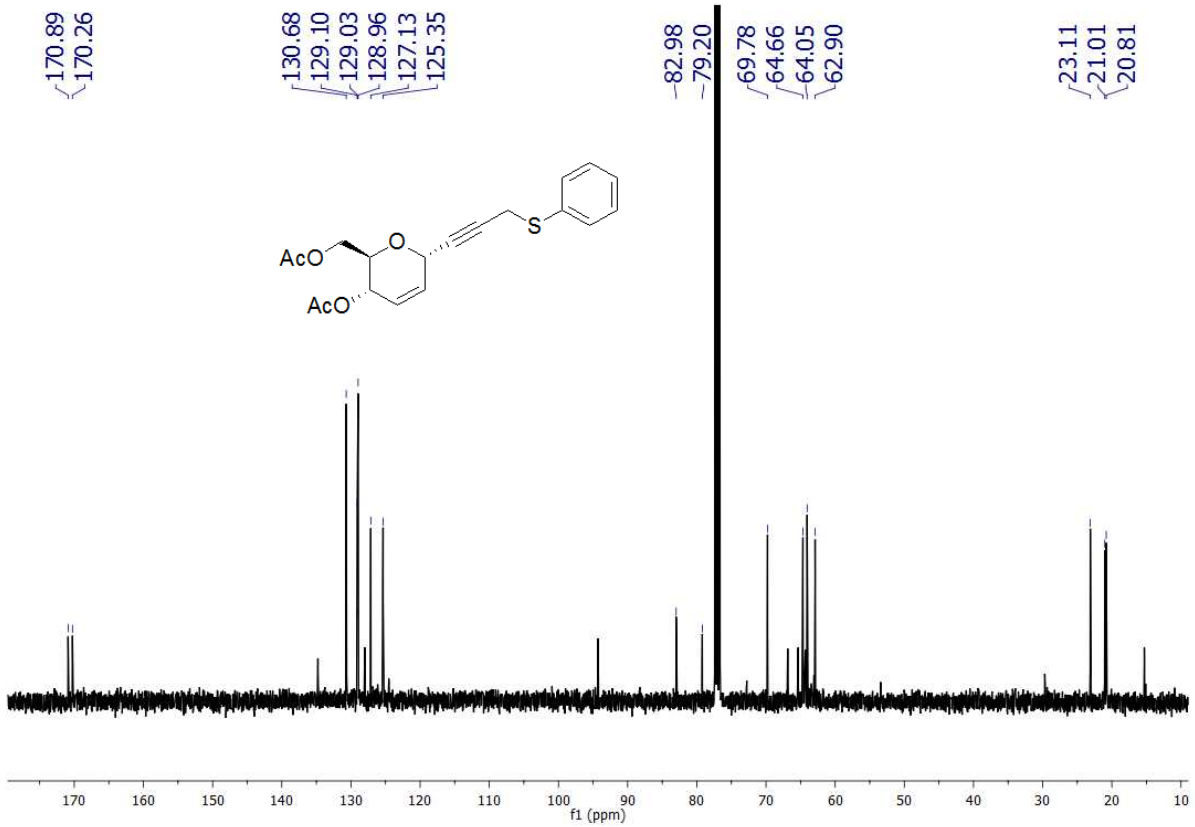
DEPT of Compound **3m**



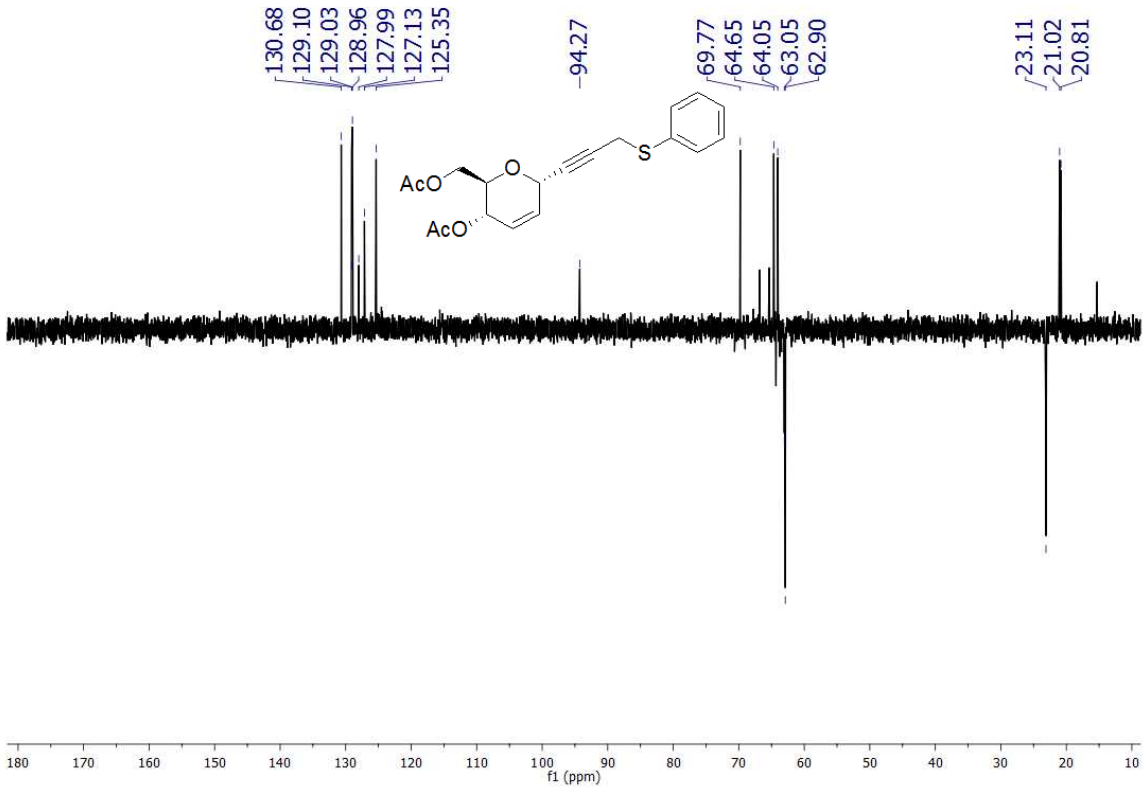
^{1}H NMR of compound **3n**



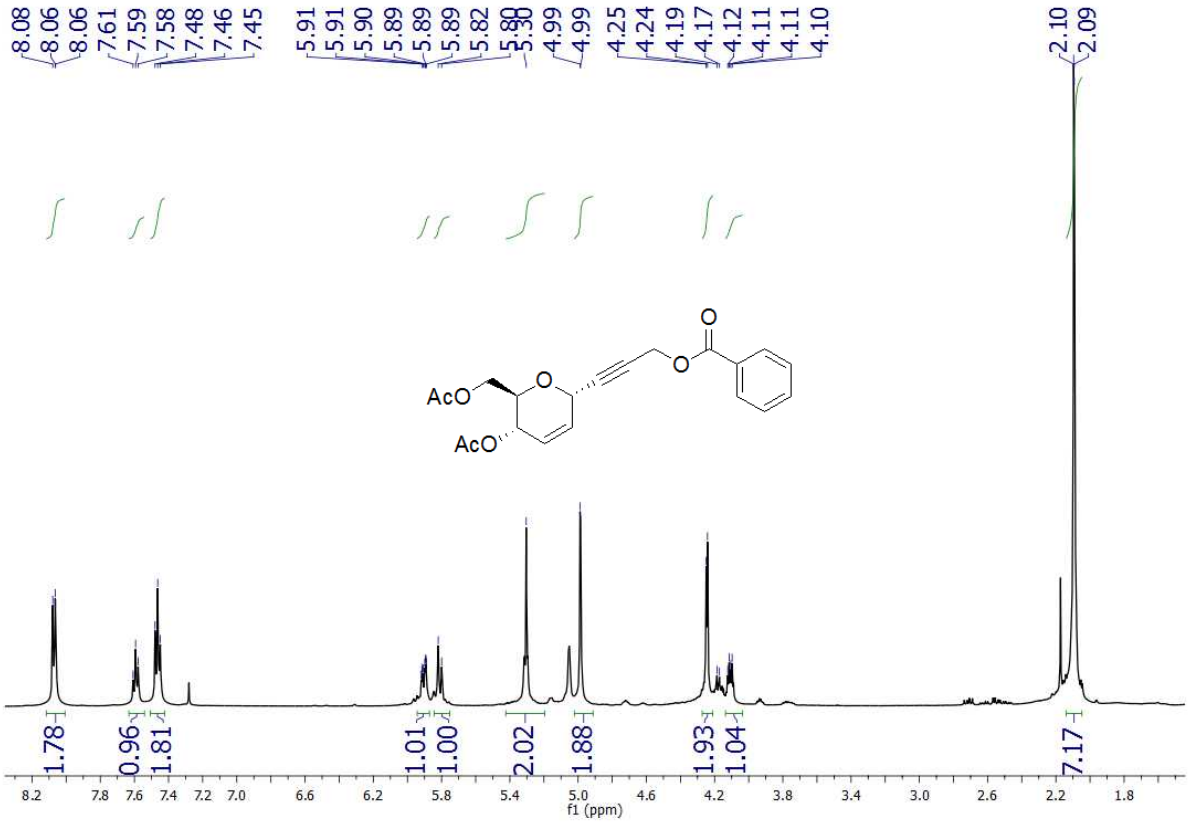
^{13}C NMR of compound **3n**



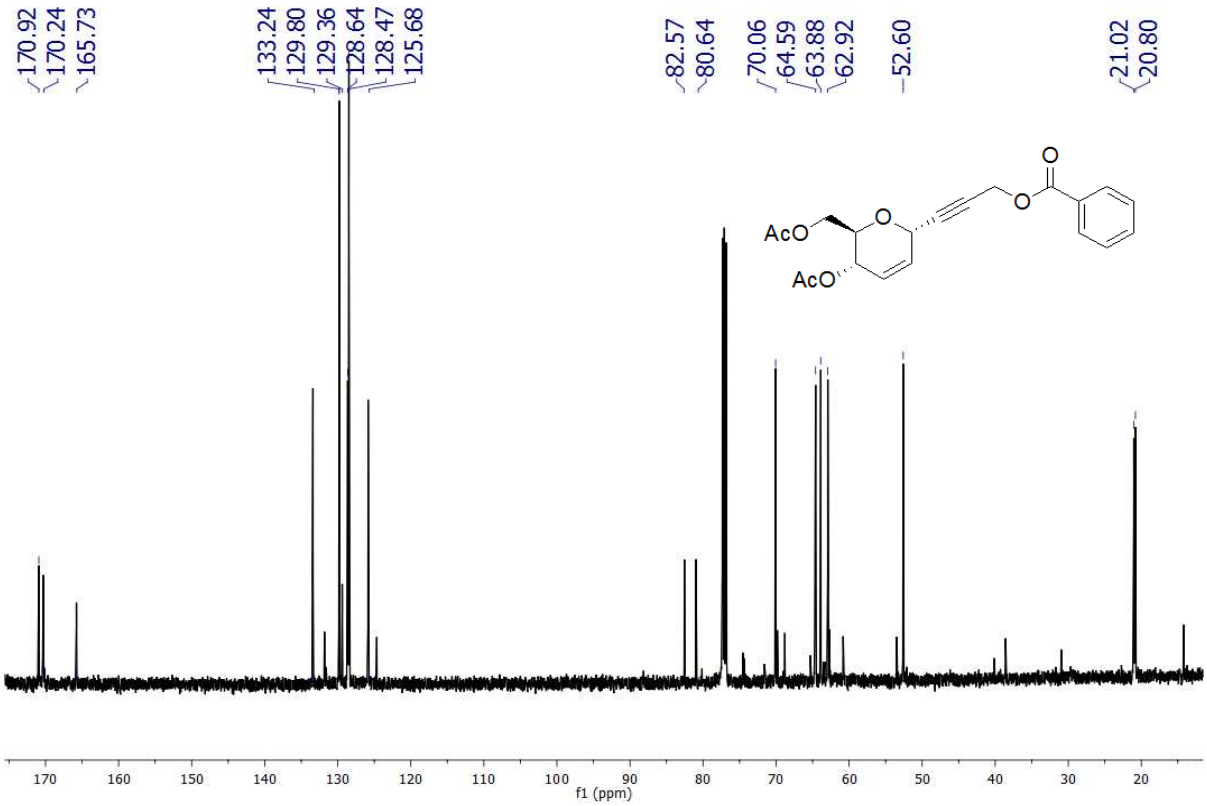
DEPT of Compound **3n**



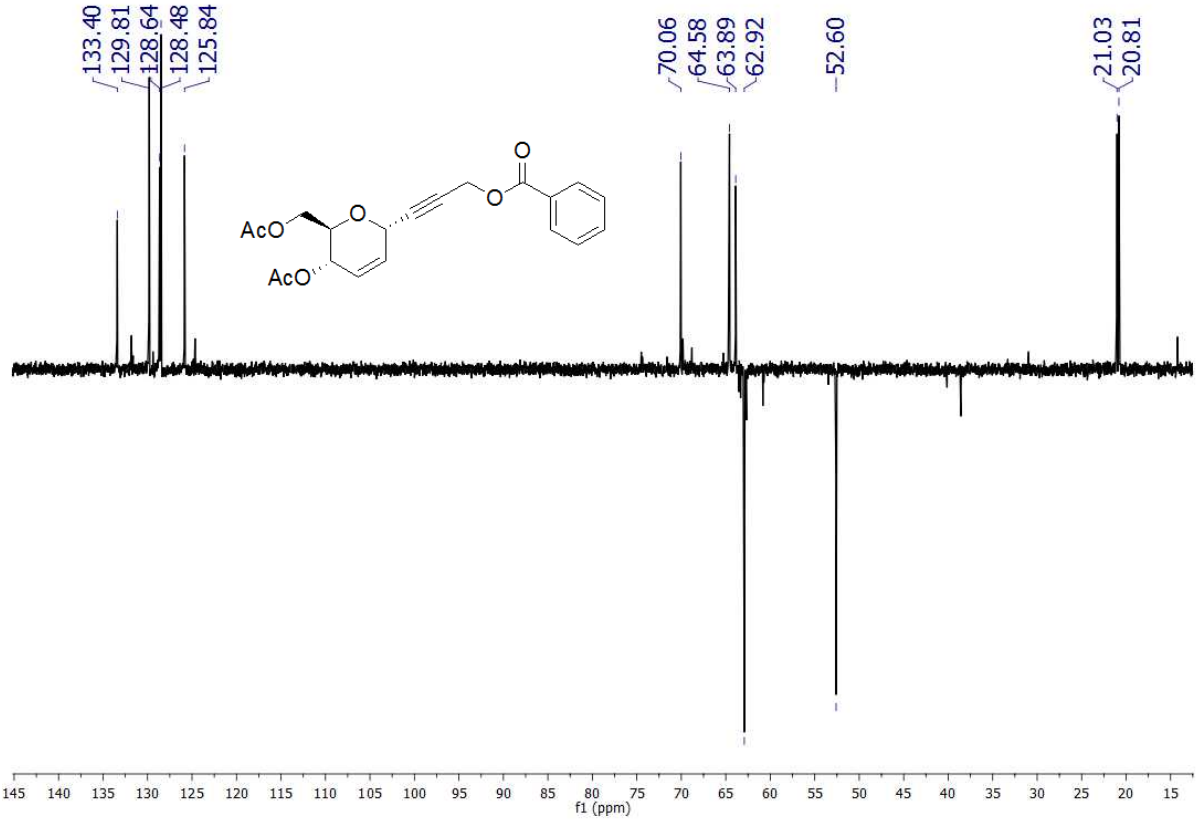
^{1}H NMR of compound **3o**



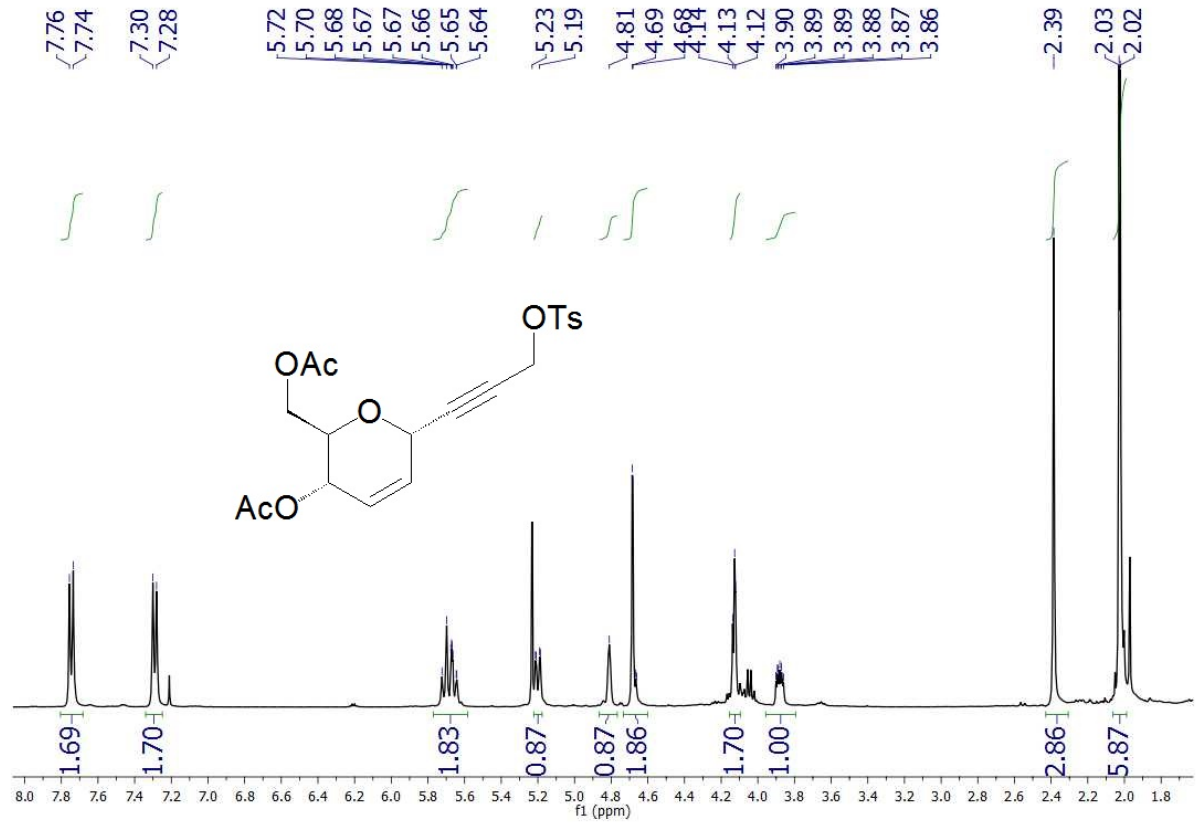
^{13}C NMR of compound **3o**



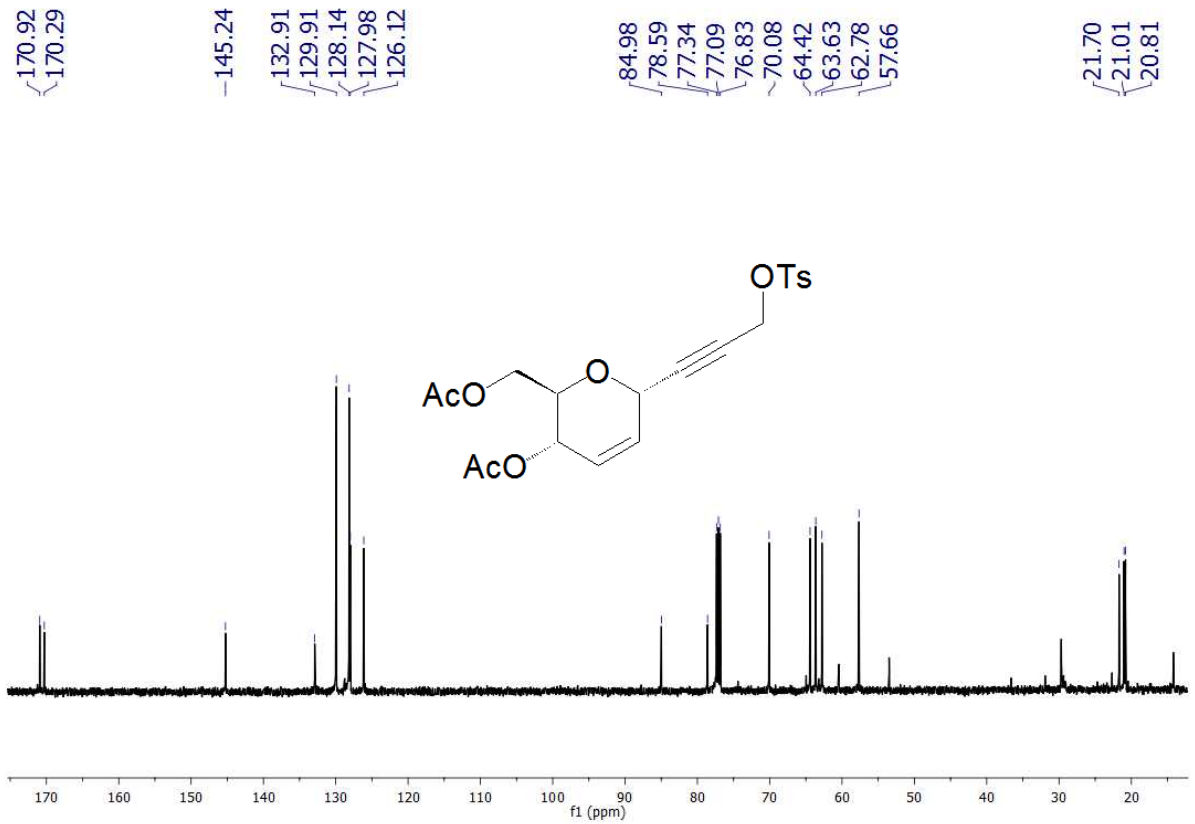
DEPT of Compound **3o**



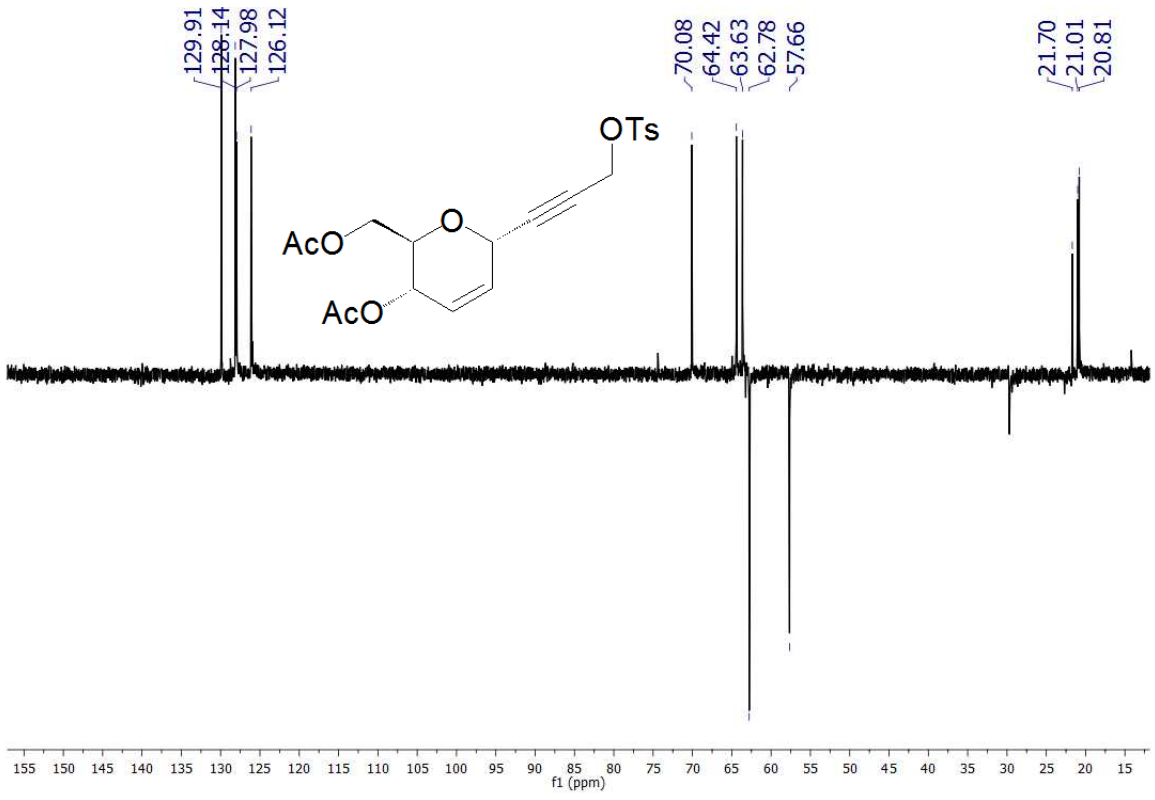
^{1}H NMR of compound **3p**



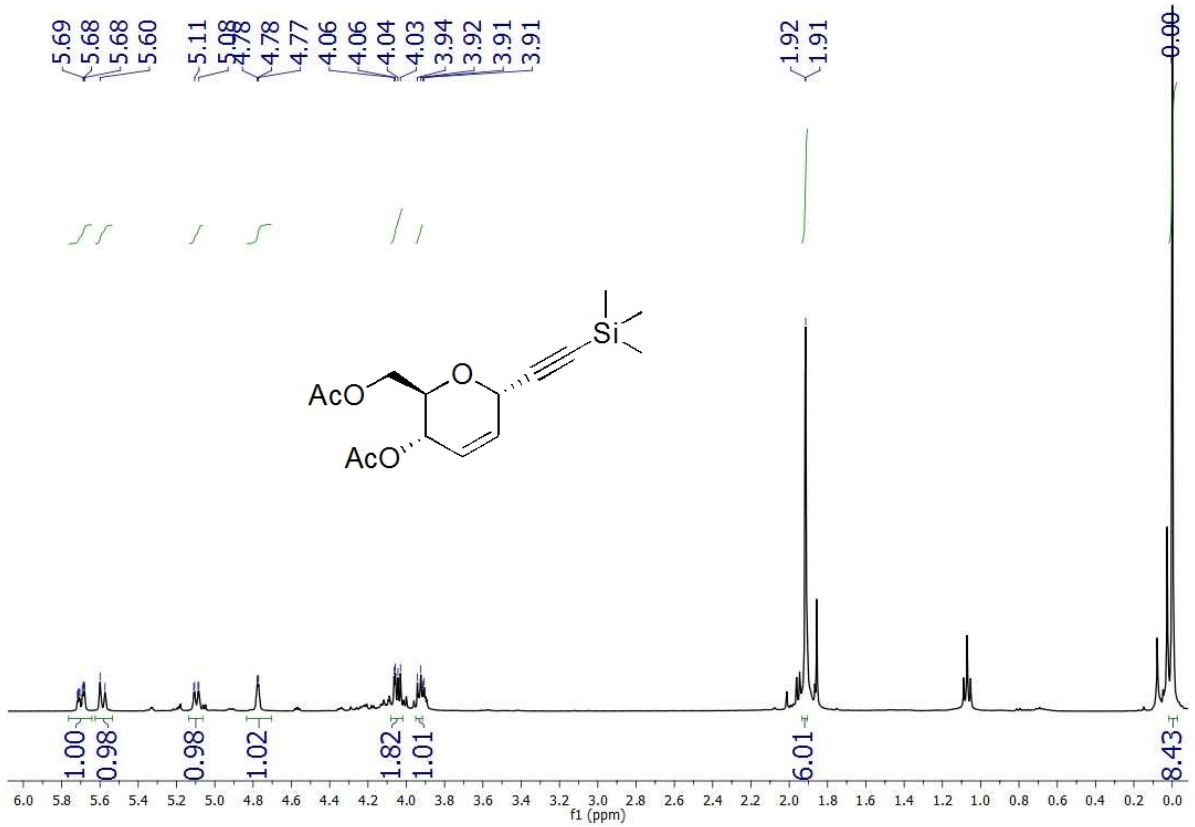
^{13}C NMR of compound **3p**



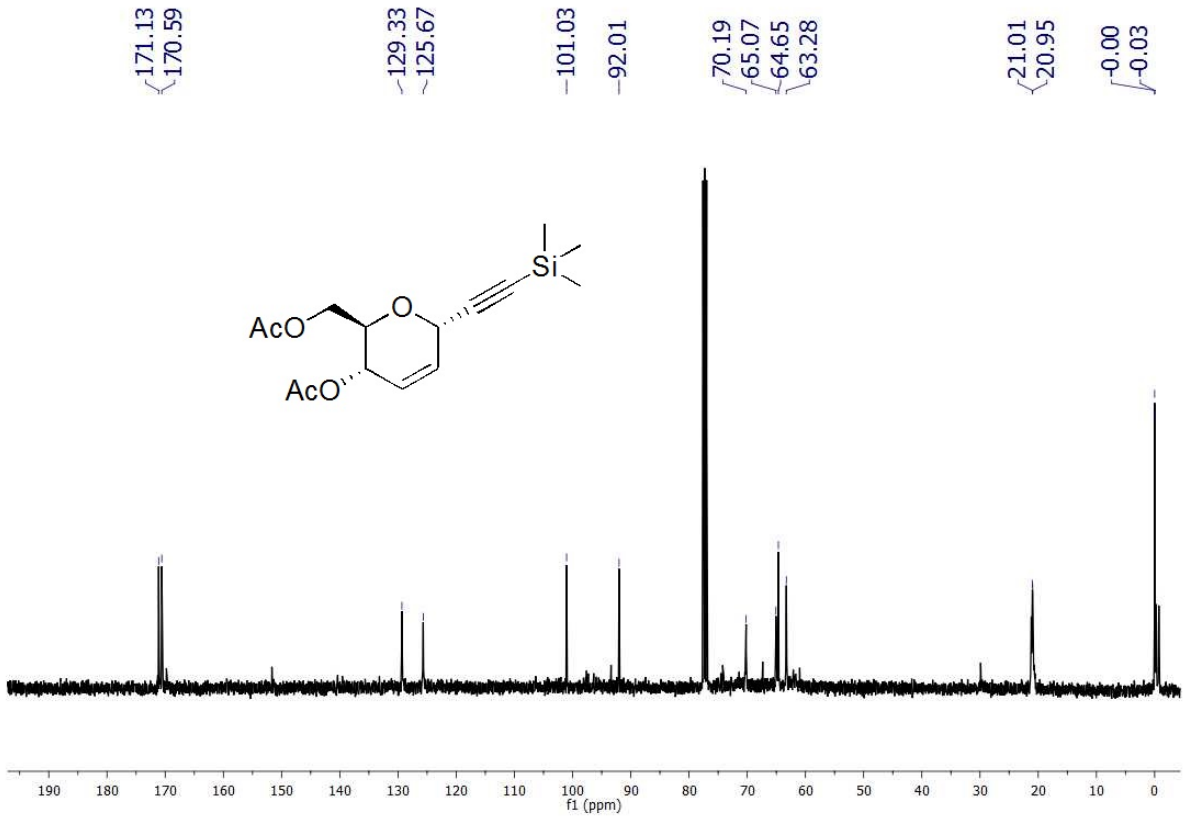
DEPT of compound **3p**



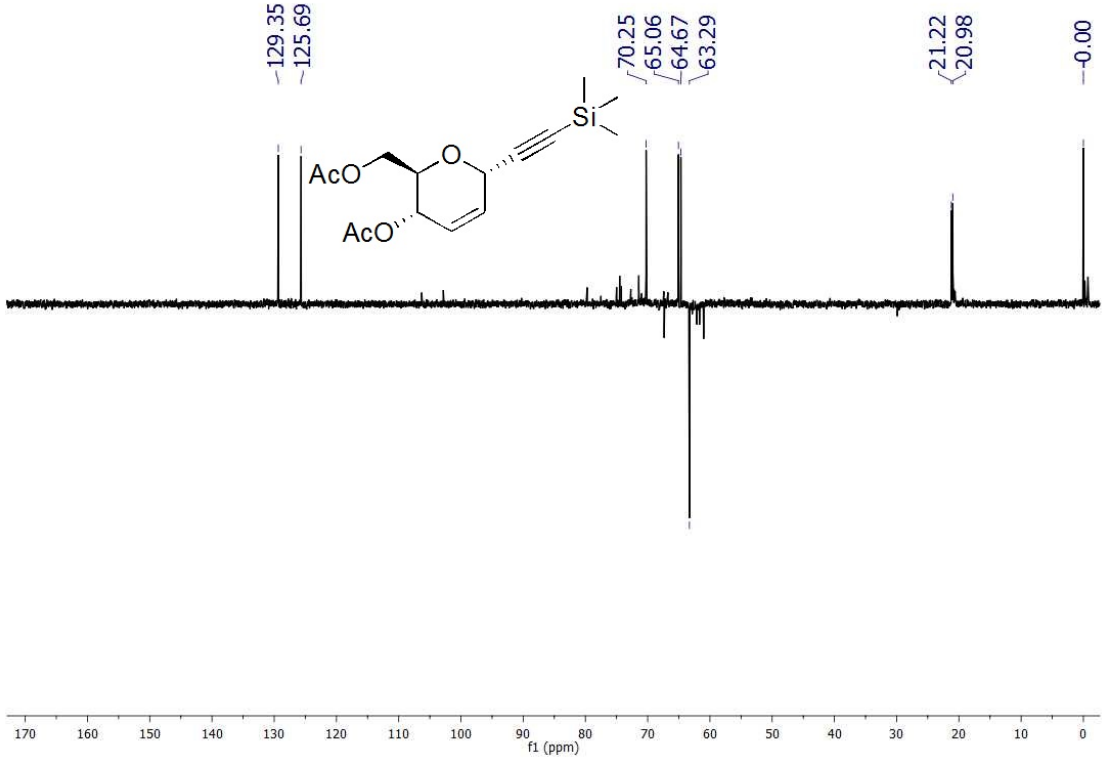
[1]H NMR of compound **3q**



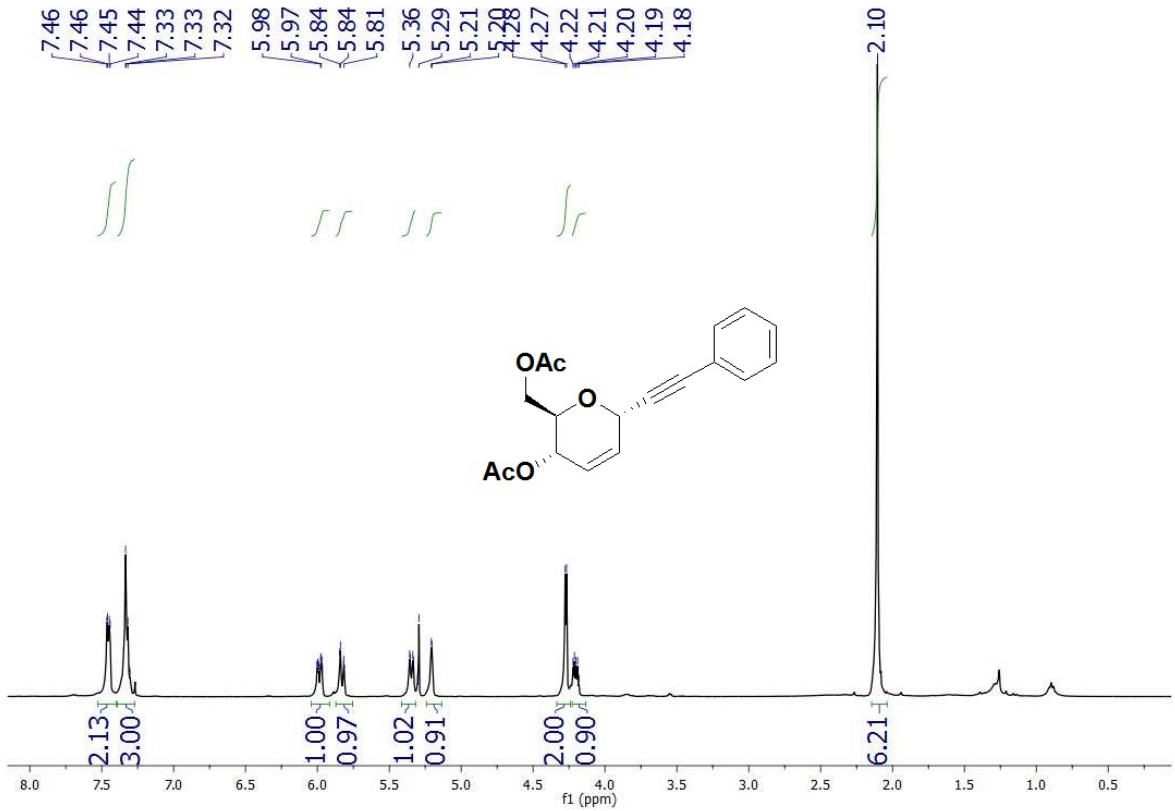
[13]C NMR of compound **3q**



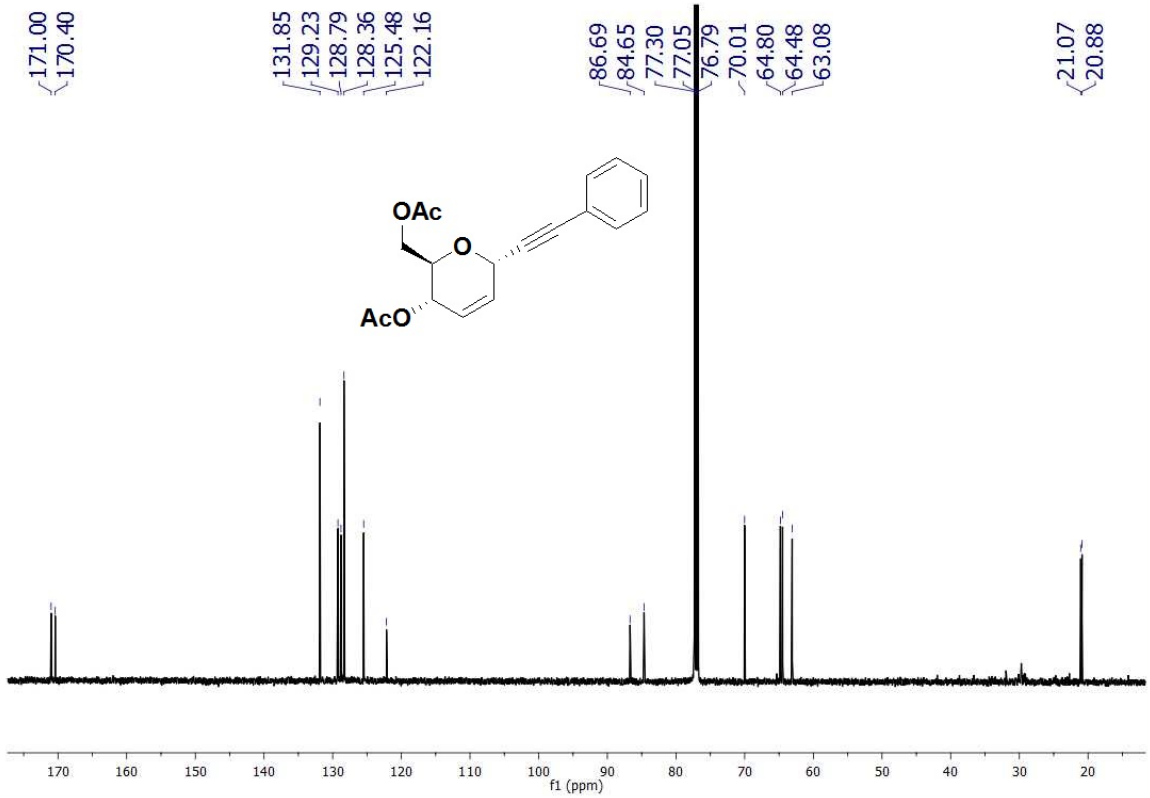
DEPT of Compound **3q**



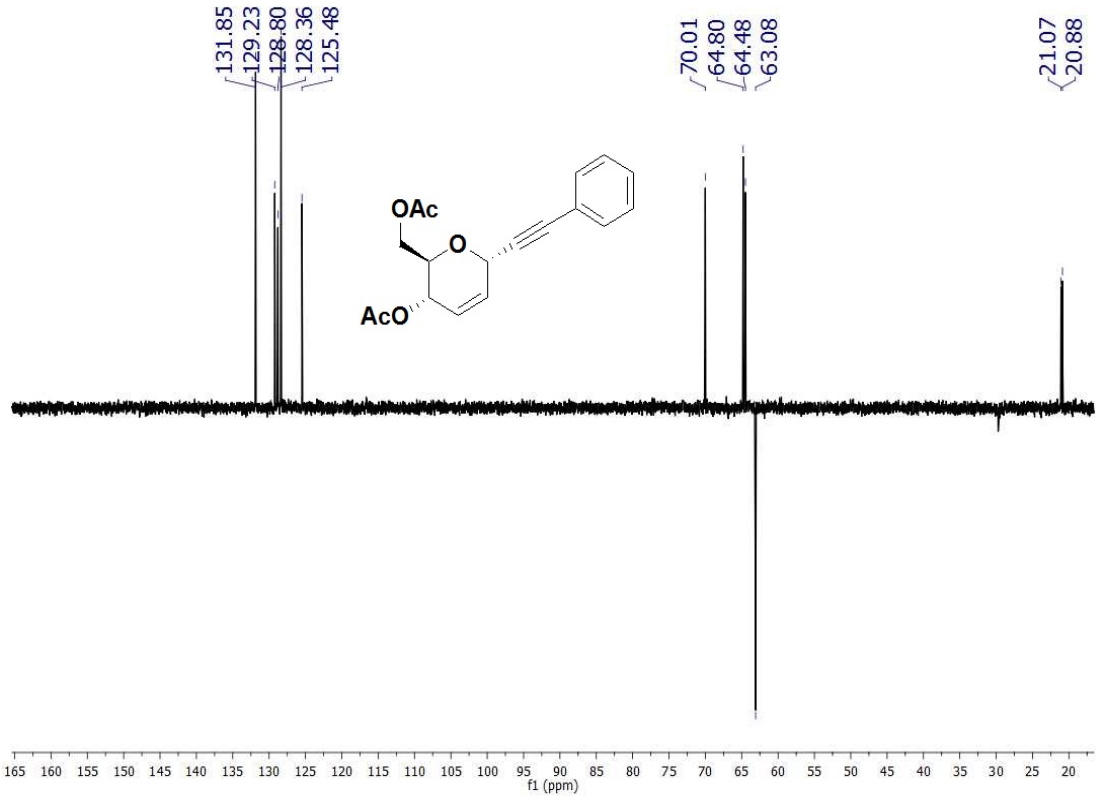
^{1}H NMR of compound **4a**



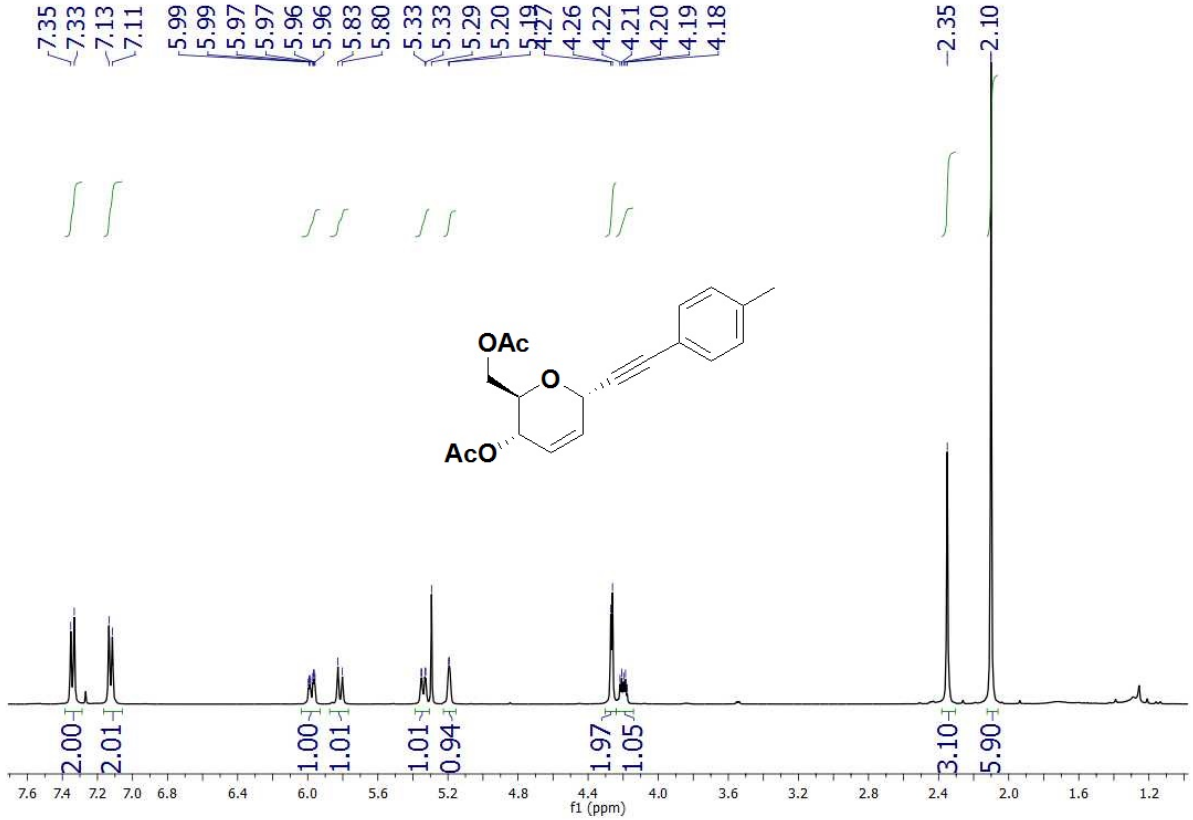
^{13}C NMR of compound **4a**



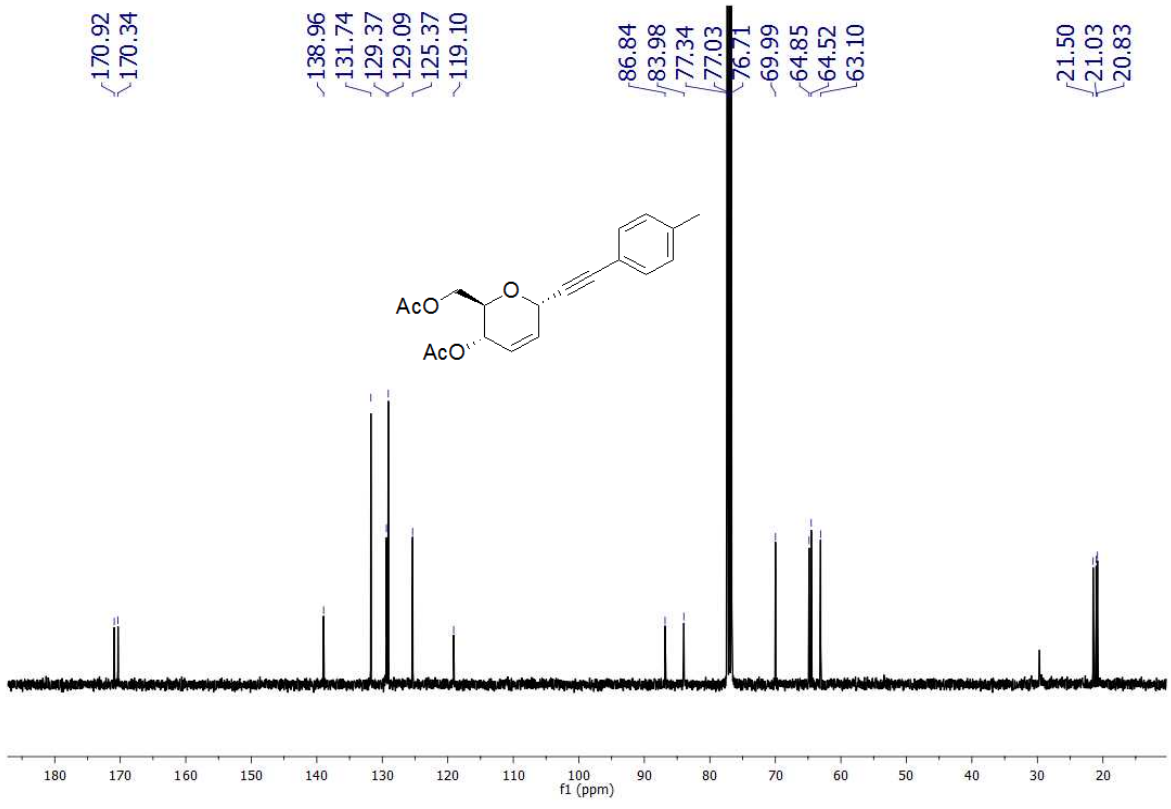
DEPT of Compound **4a**



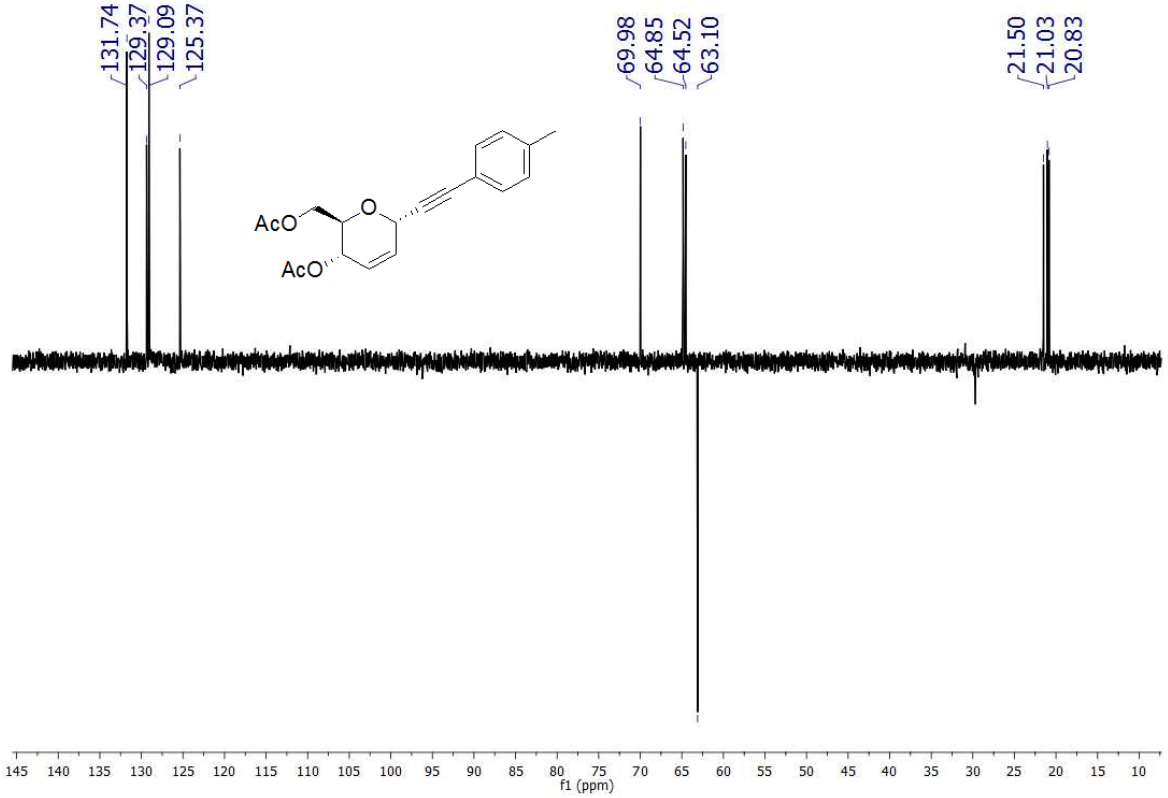
^{1}H NMR of compound **4b**



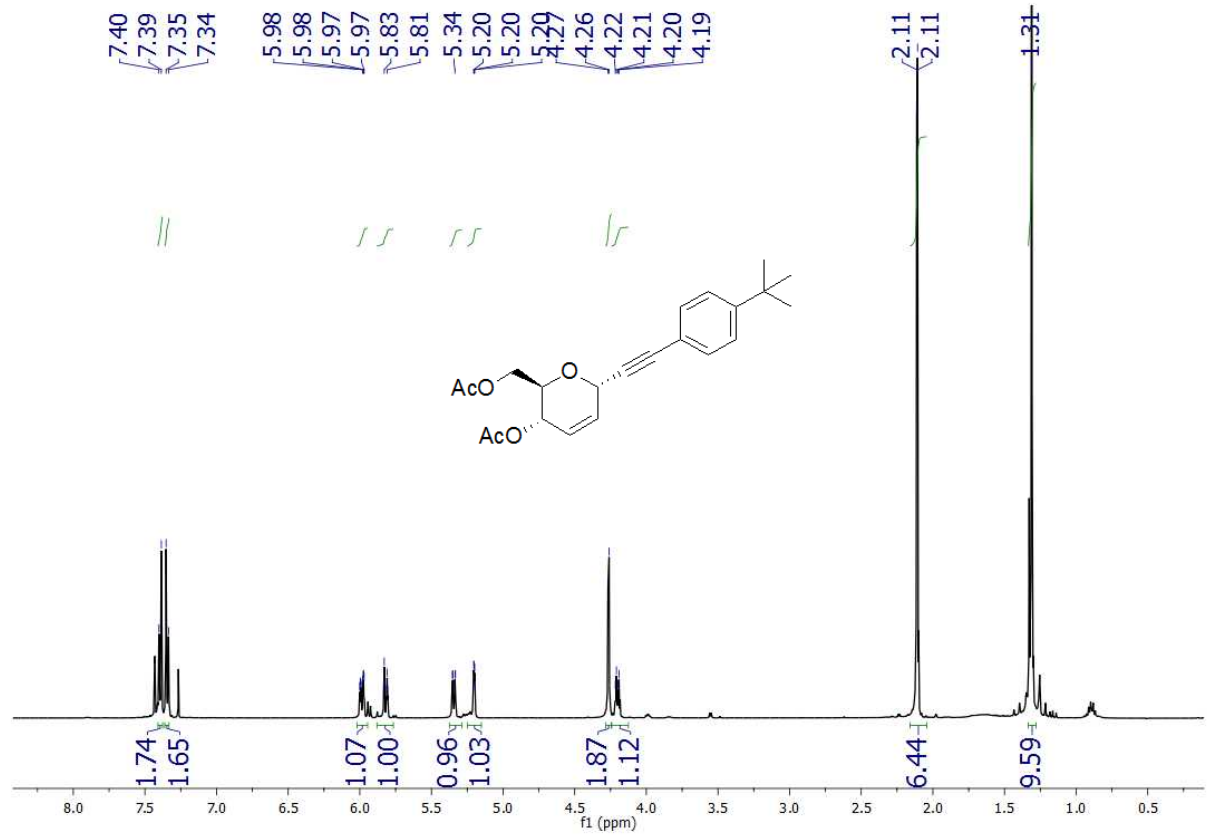
^{13}C NMR of compound **4b**



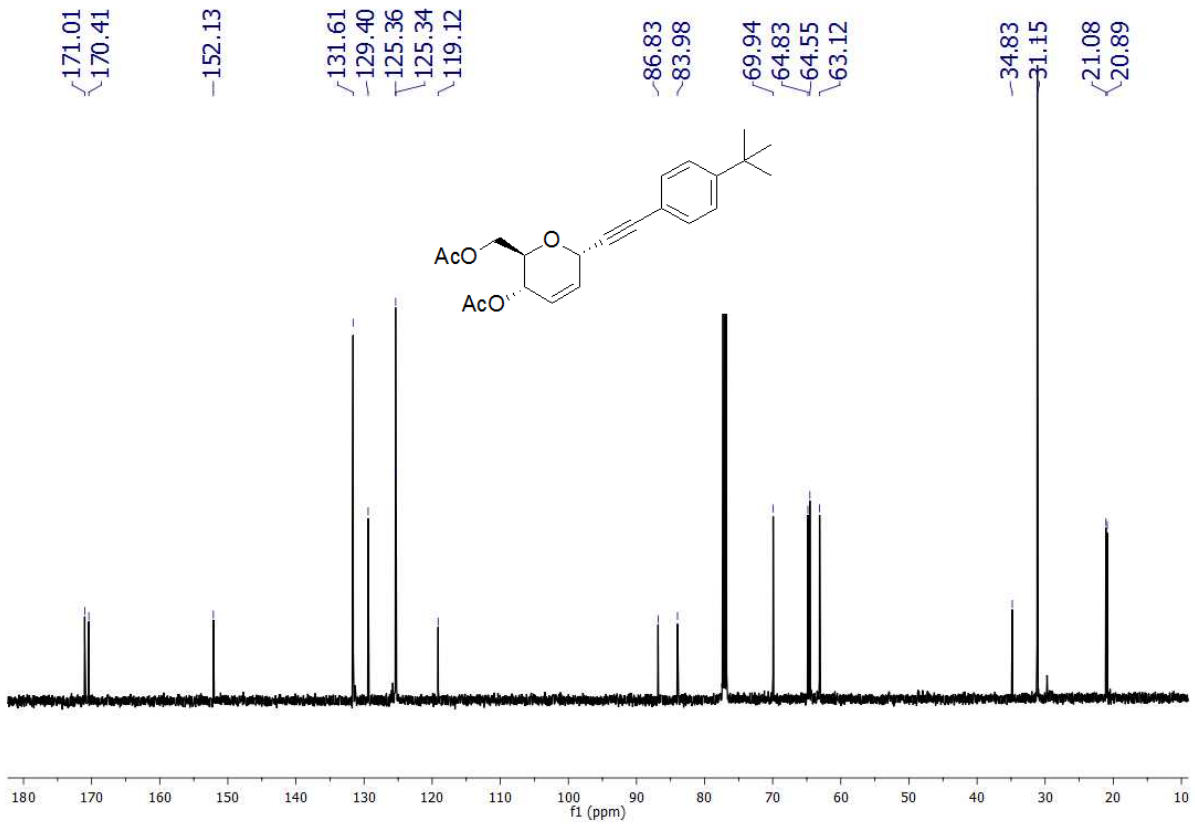
DEPT of Compound **4b**



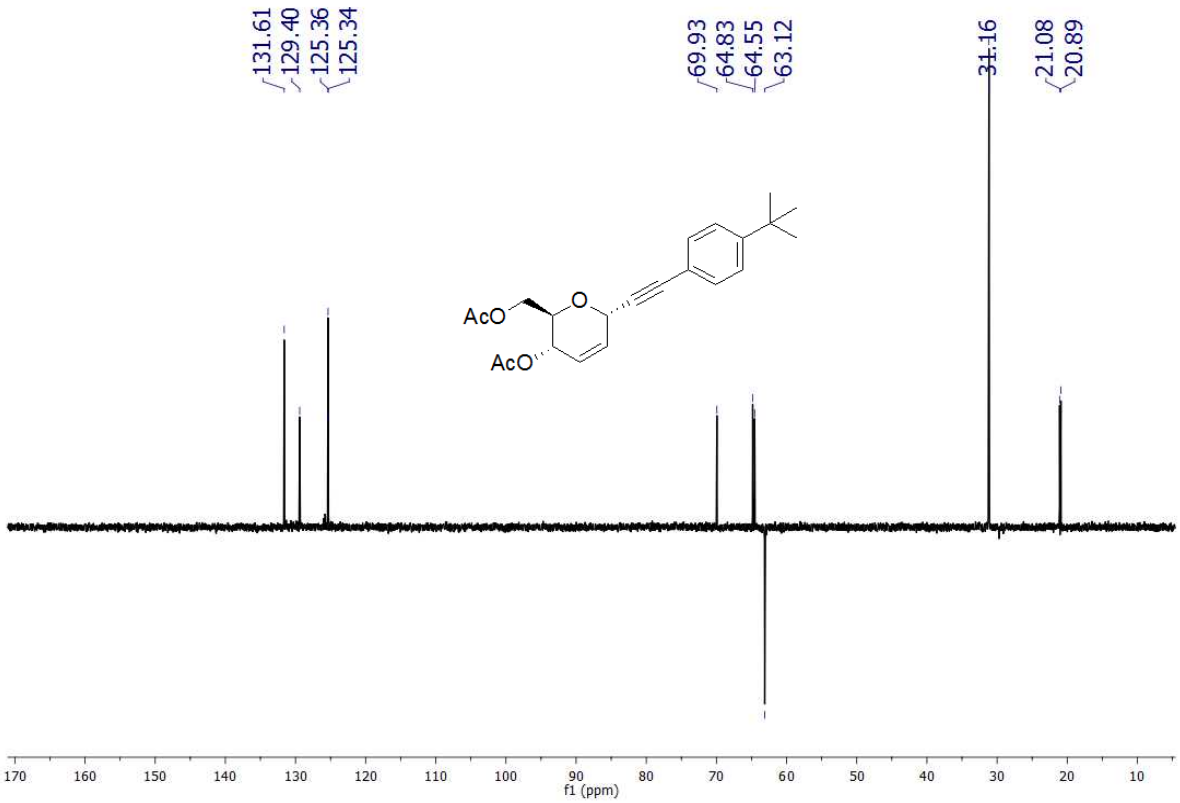
H NMR of compound **4c**



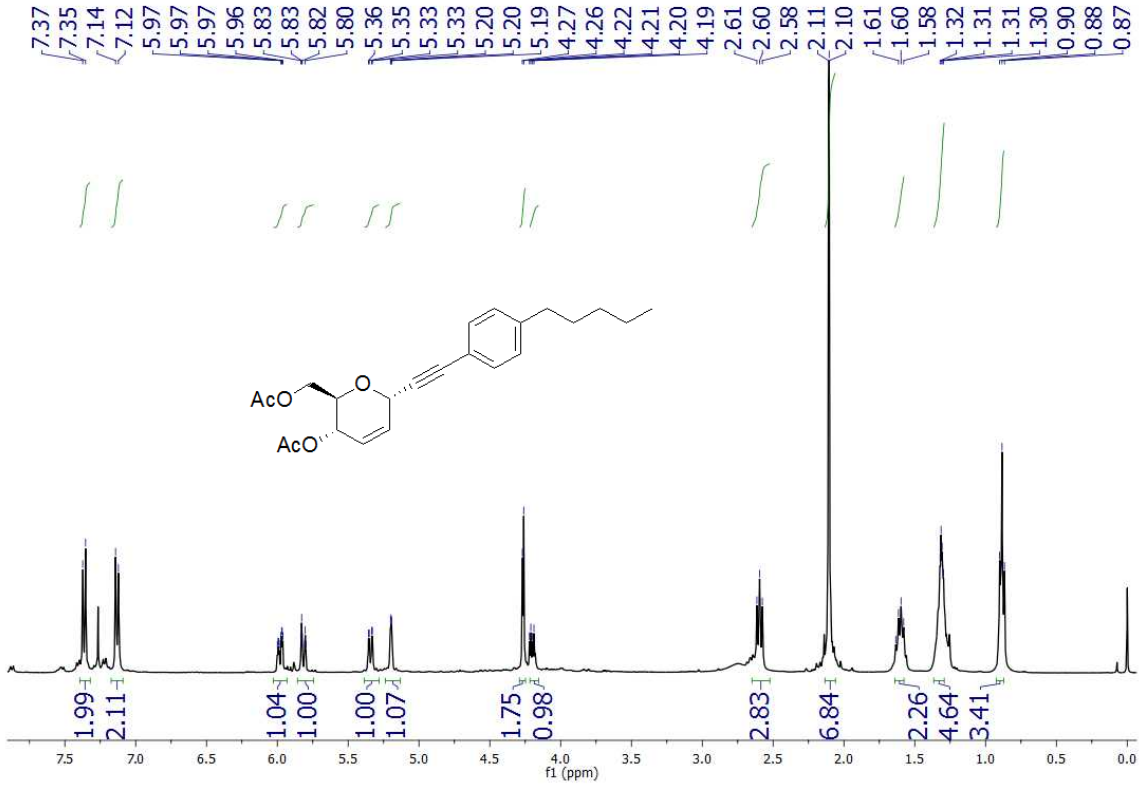
^{13}C NMR of compound **4c**



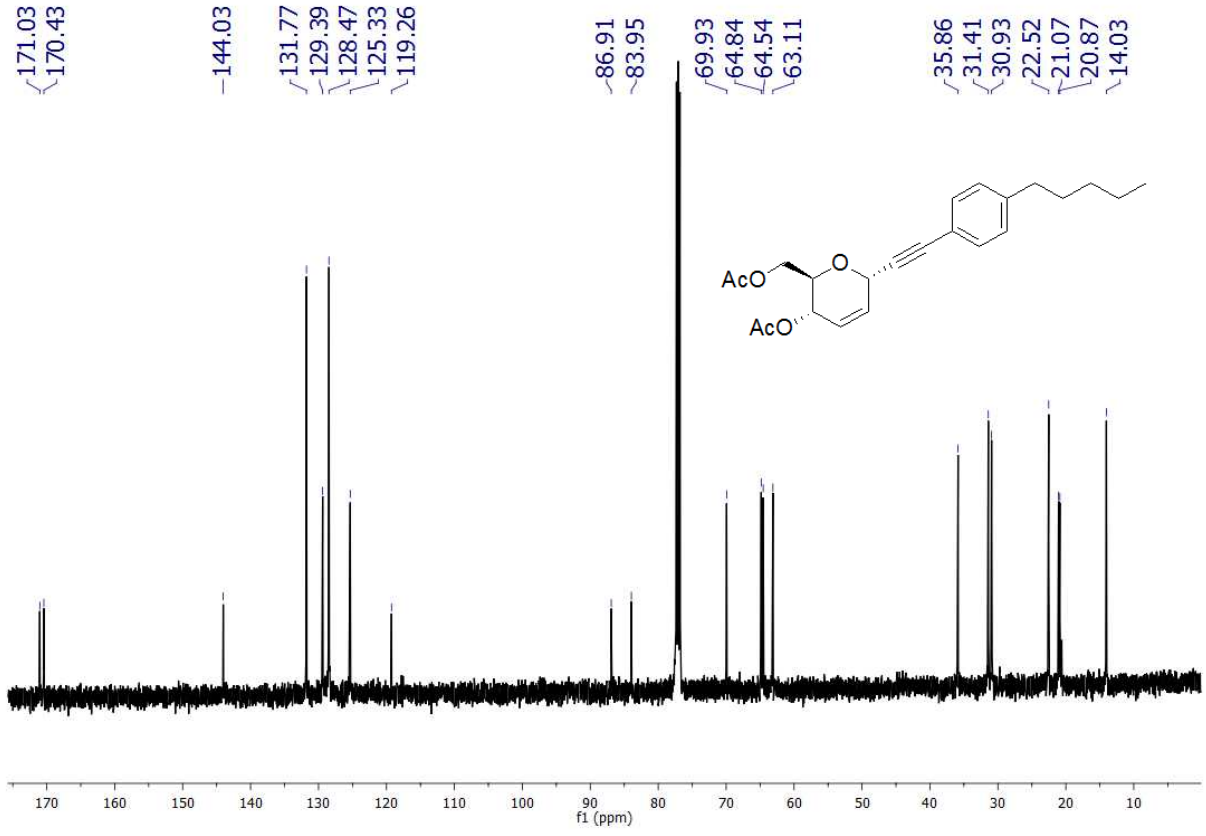
DEPT of Compound **4c**



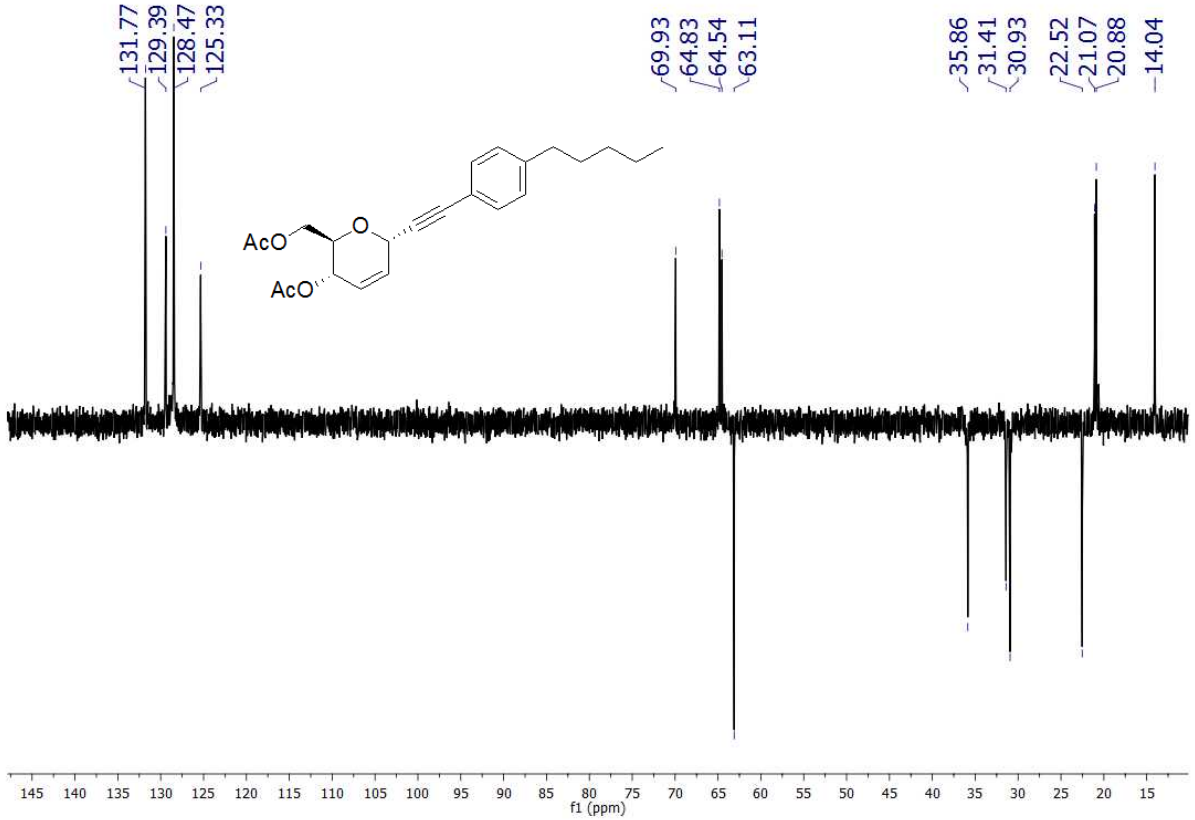
[1]H NMR of compound **4d**



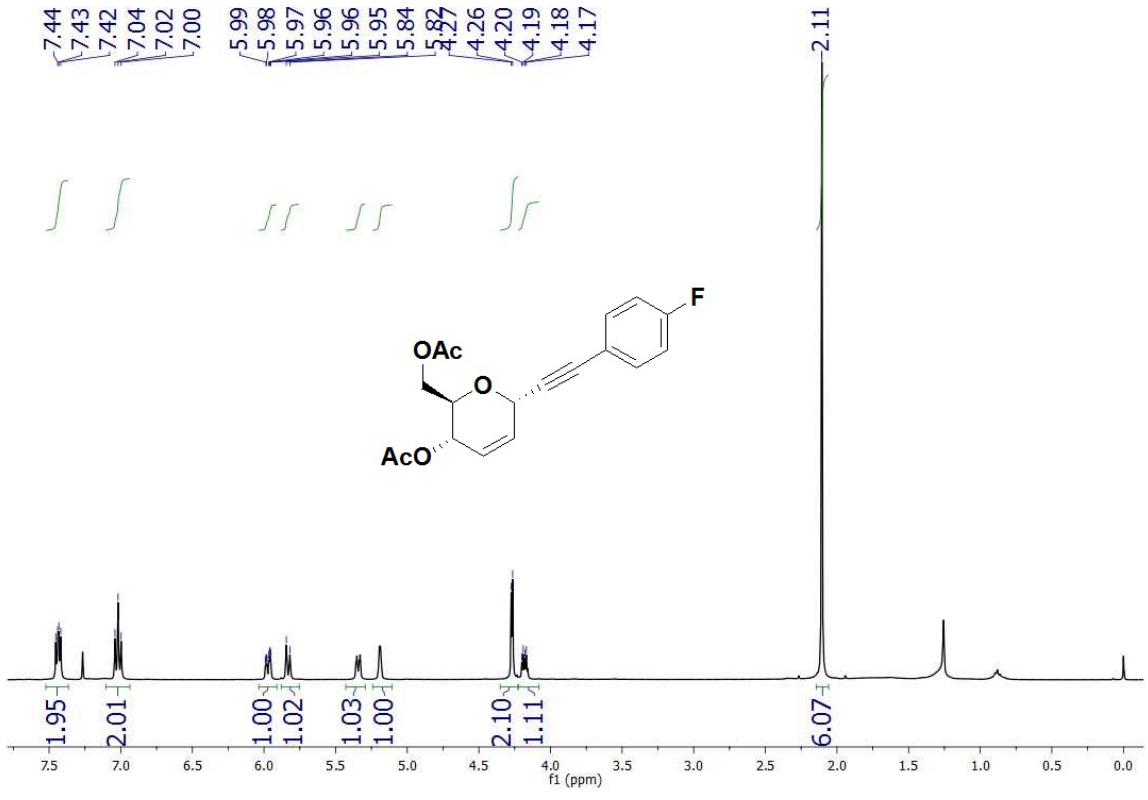
[13]C NMR of compound **4d**



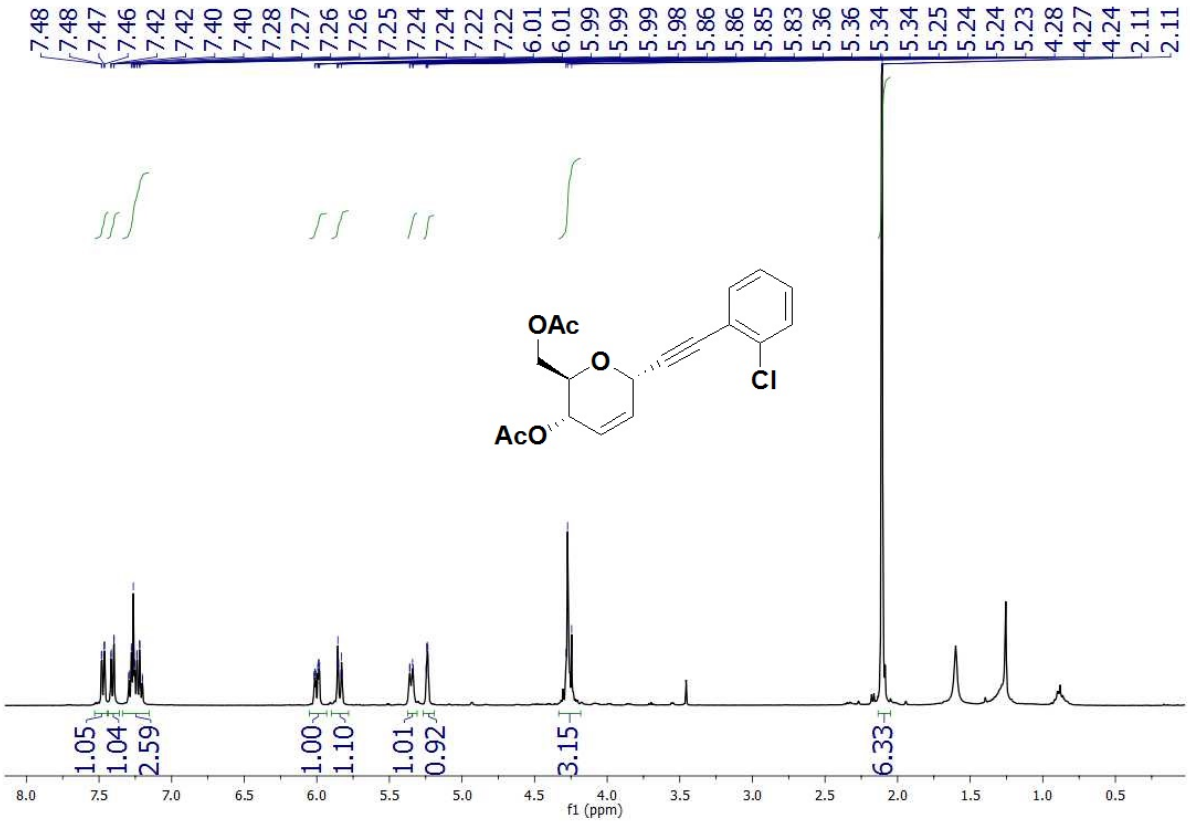
DEPT of Compound **4d**



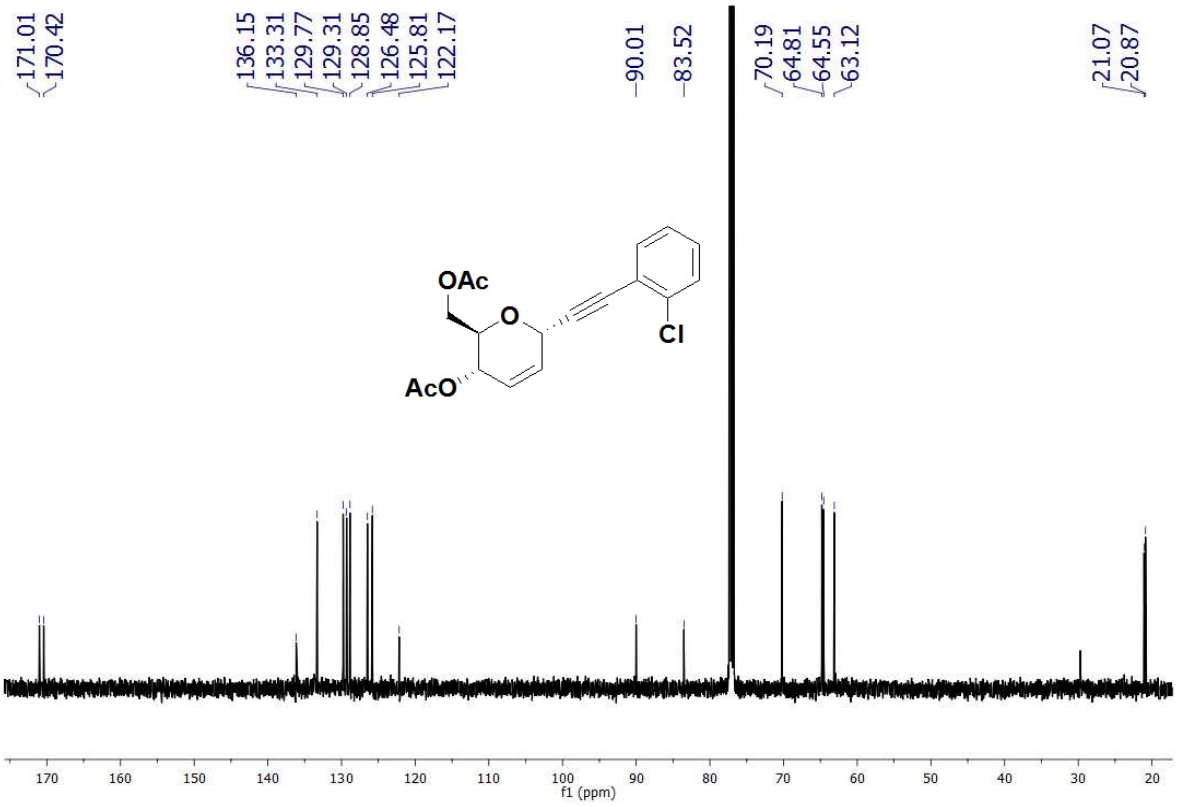
H^1 NMR of compound **4e**



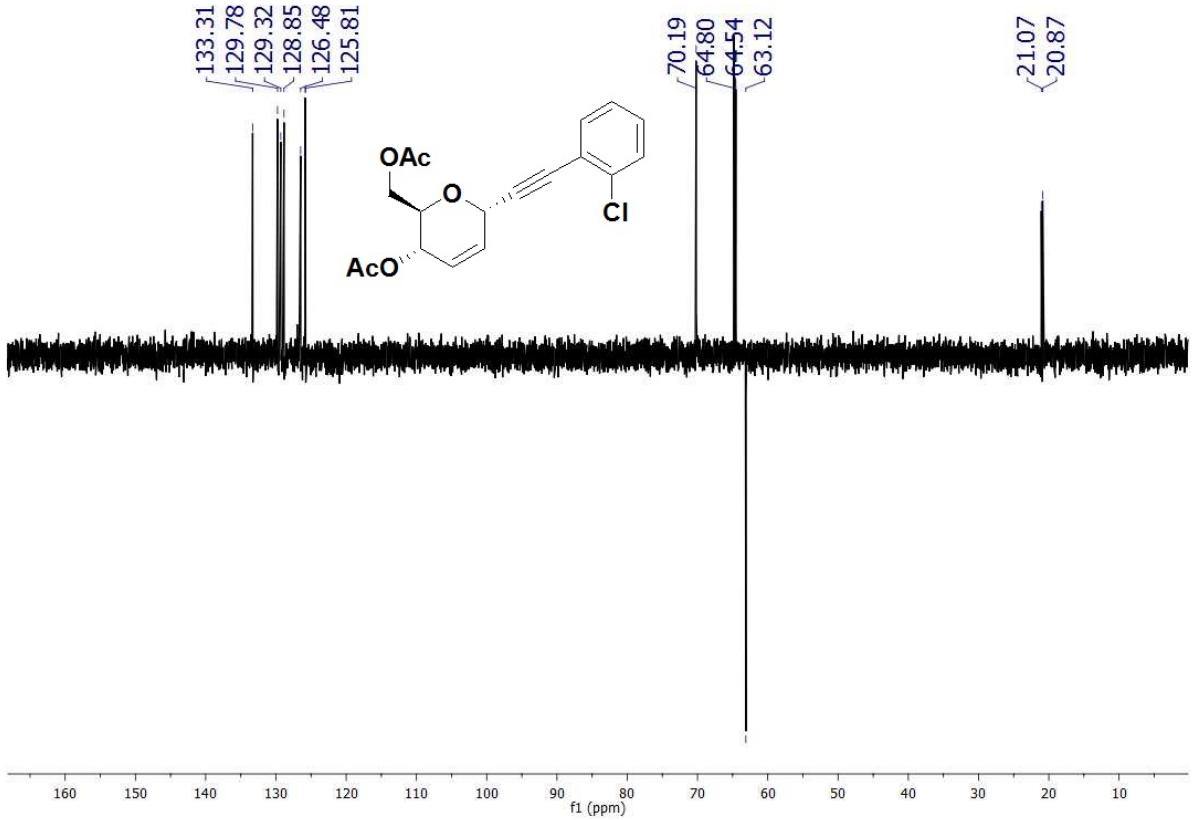
[1]H NMR of compound **4f**



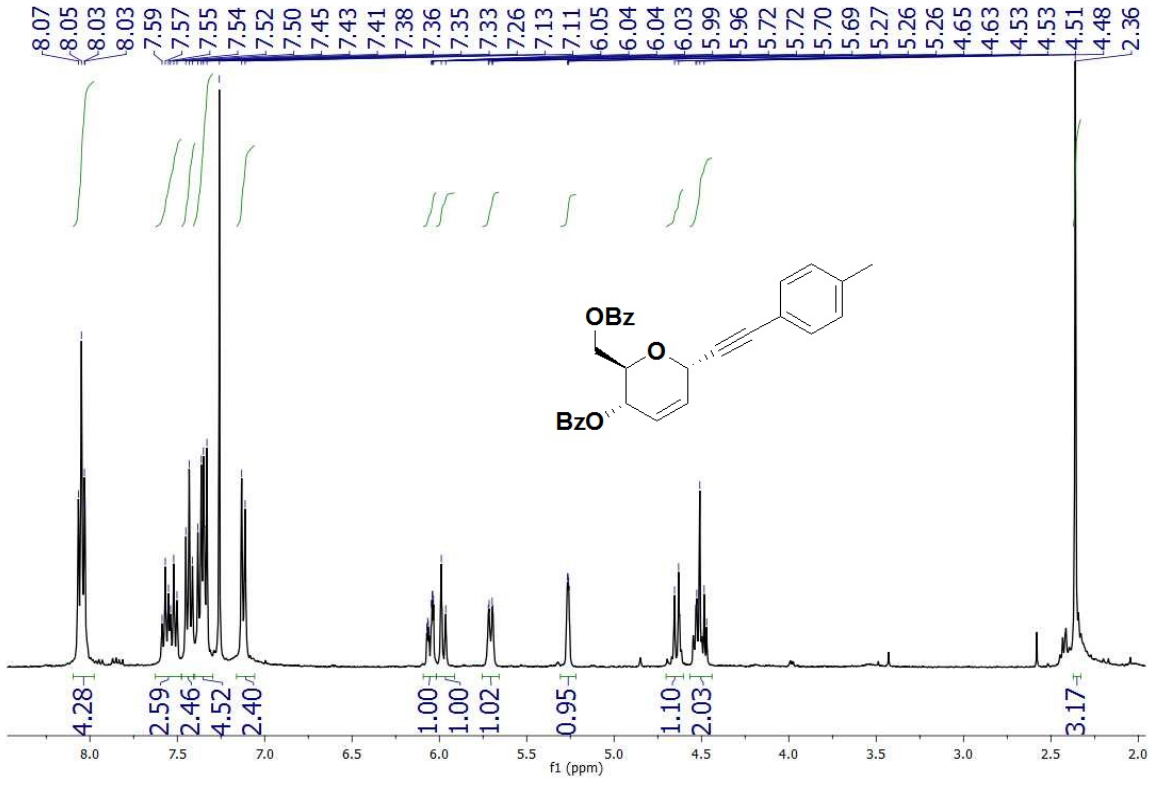
[13]C NMR of compound **4f**



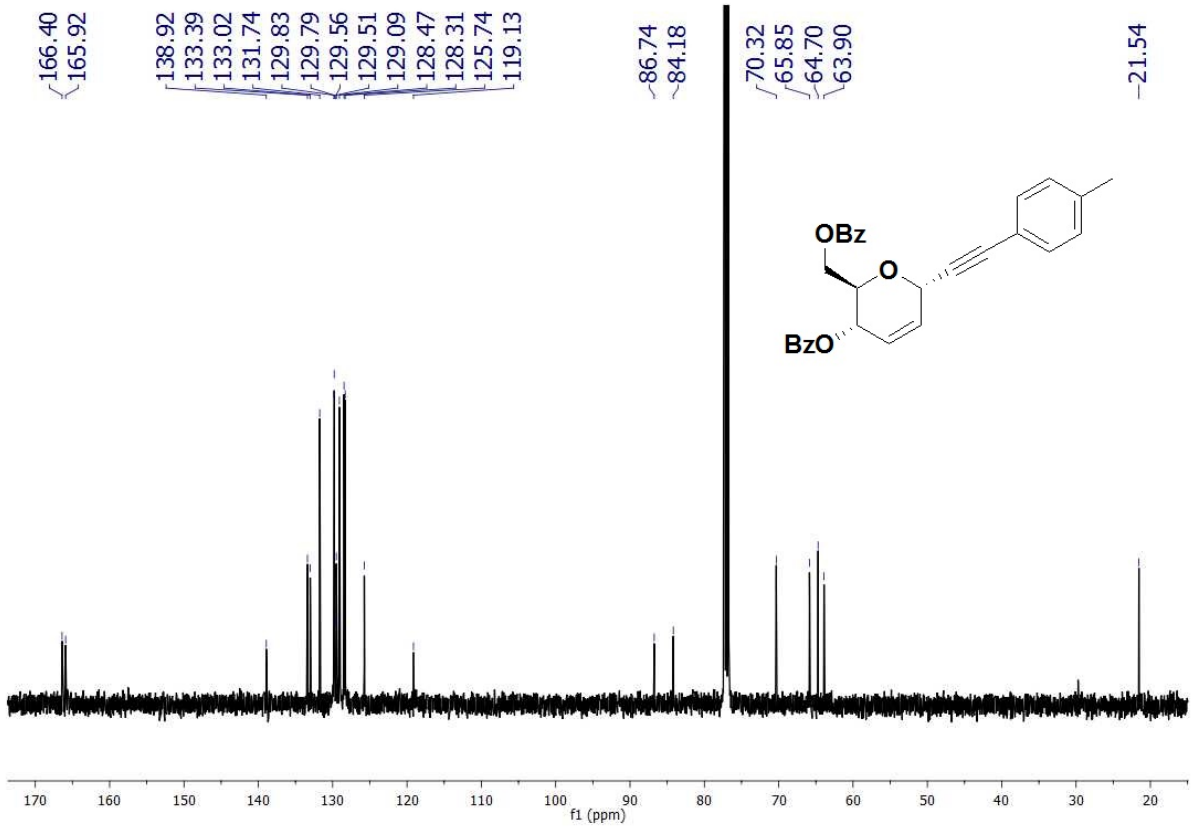
DEPT of Compound **4f**



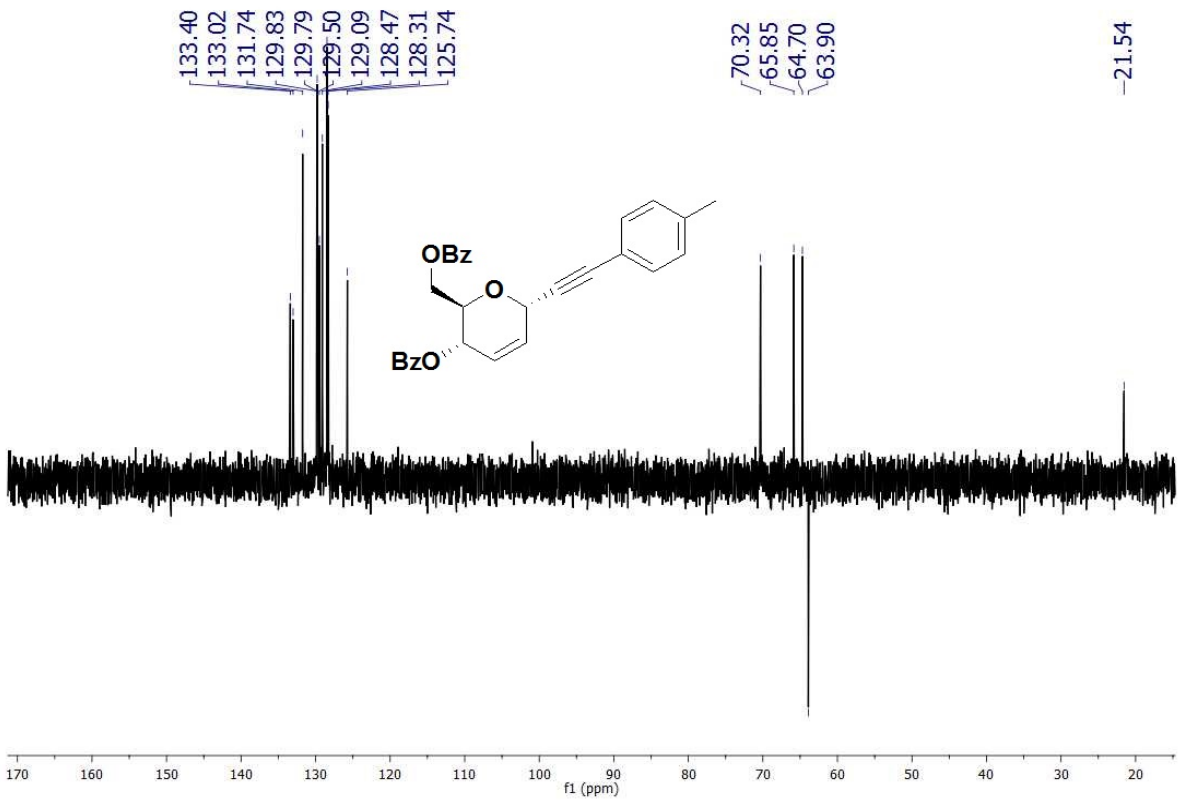
^{1}H NMR of compound **4g**



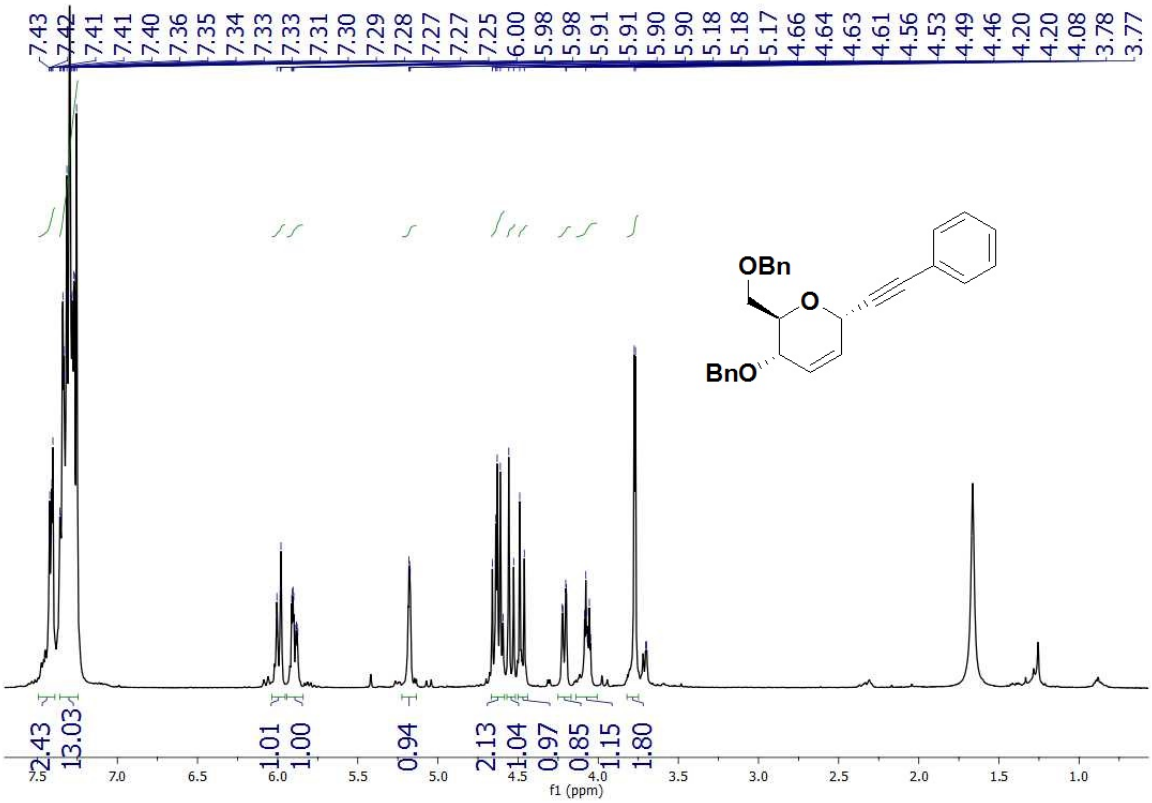
^{13}C NMR of compound **4g**



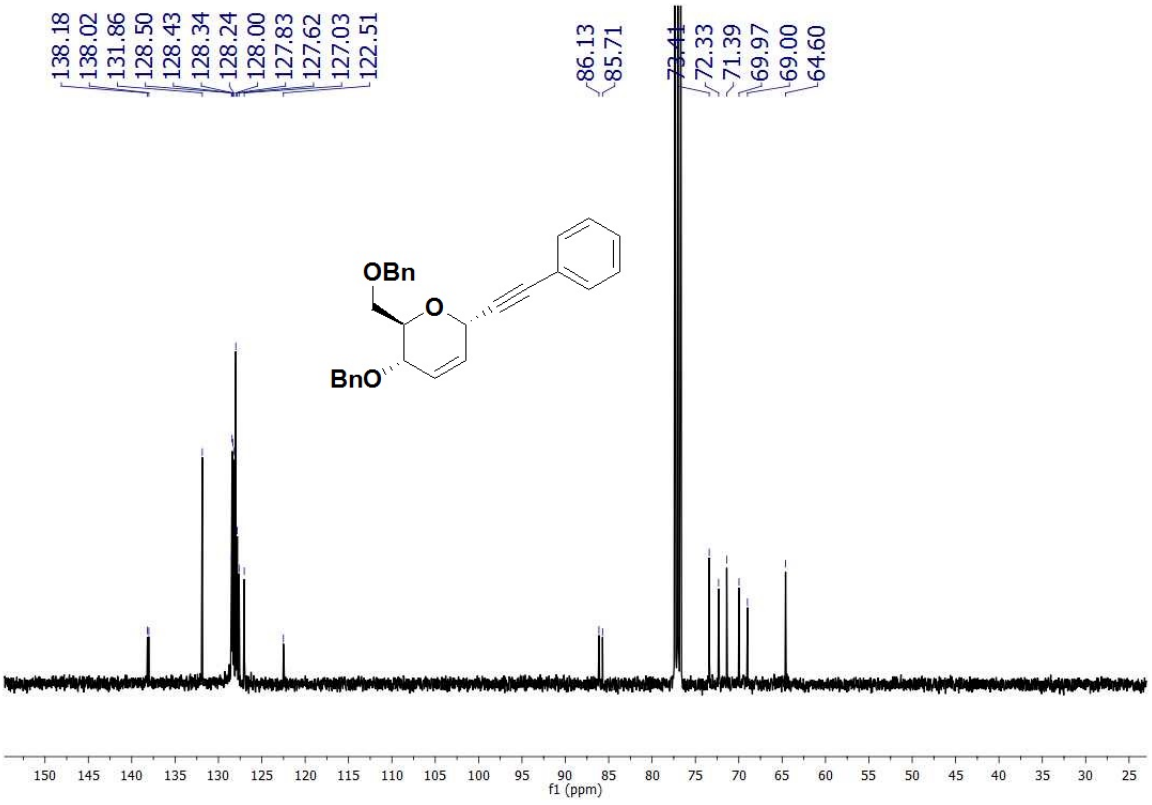
DEPT of Compound **4g**



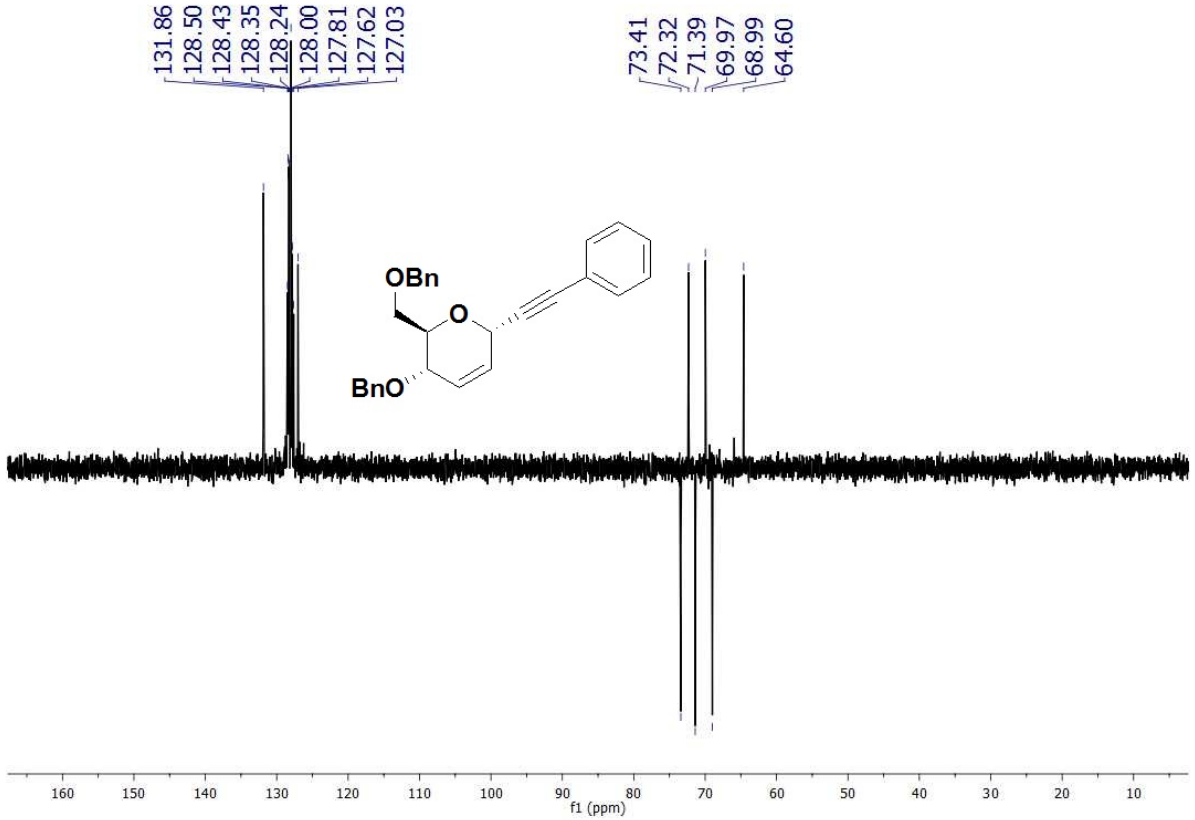
^{1}H NMR of compound **4h**



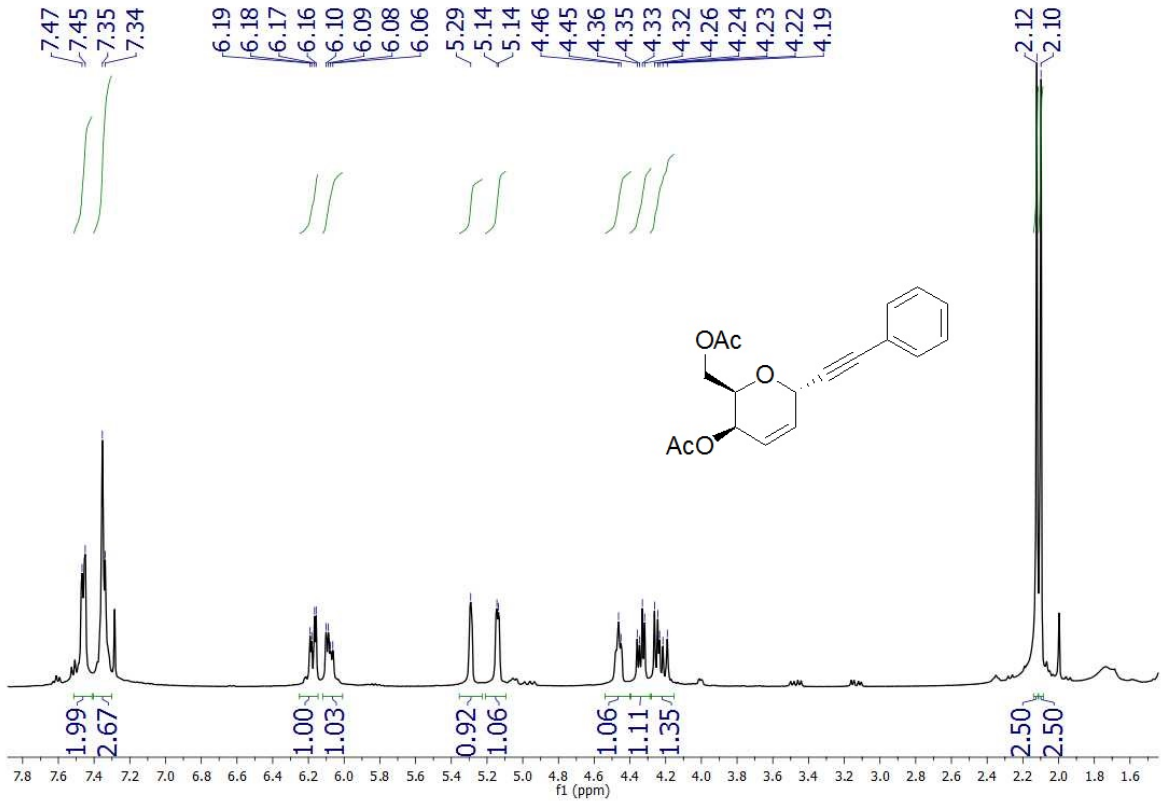
^{13}C NMR of compound **4h**



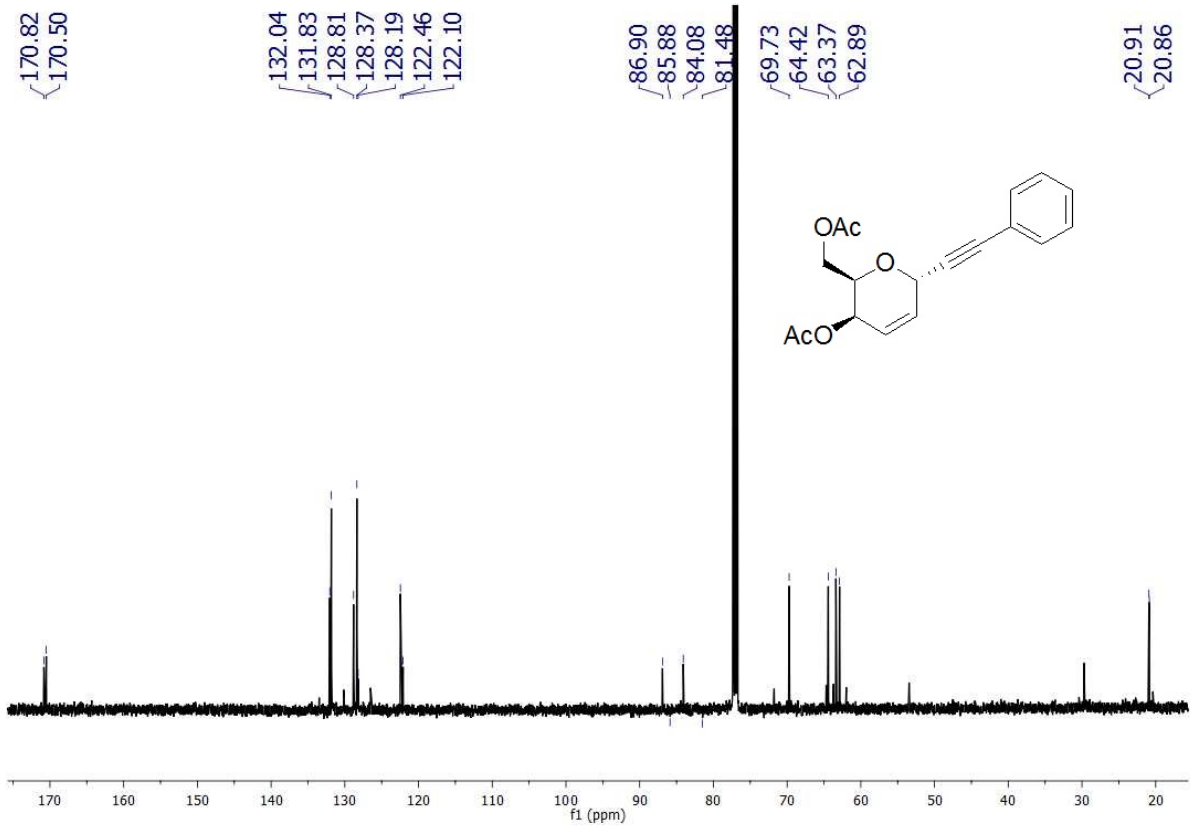
DEPT of Compound **4h**



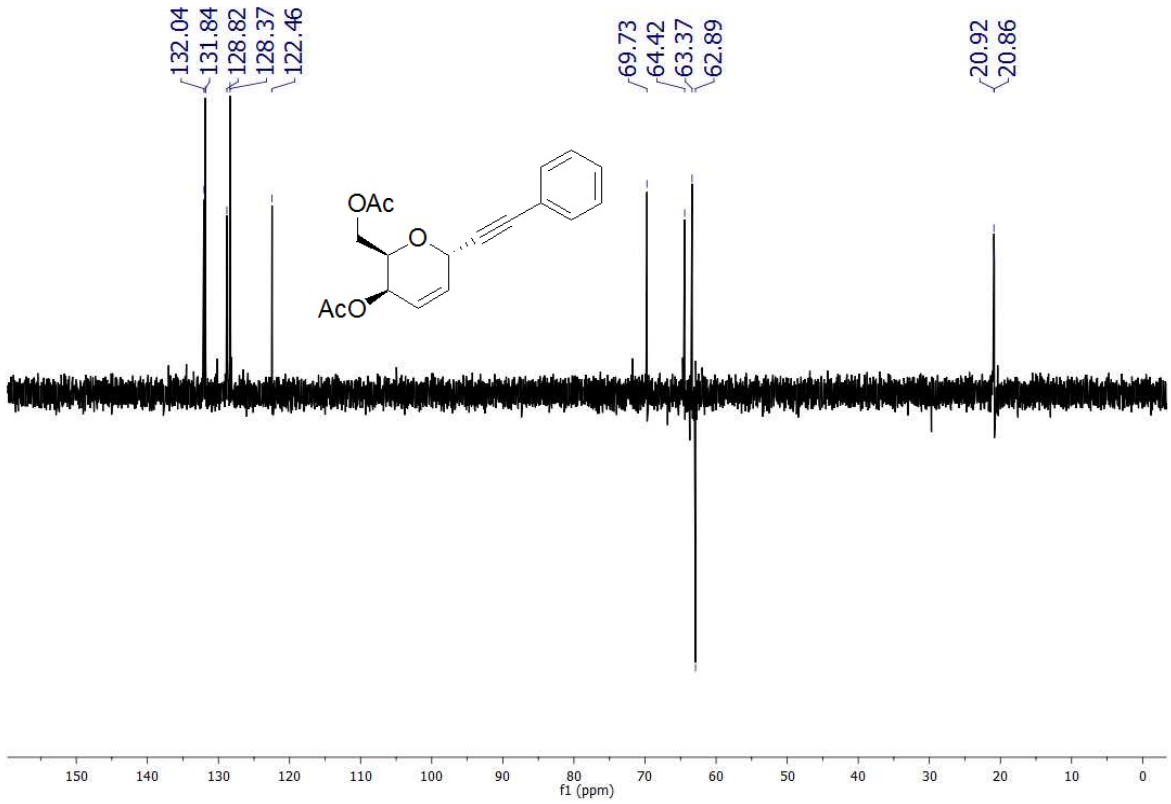
^{1}H NMR of compound **4i**



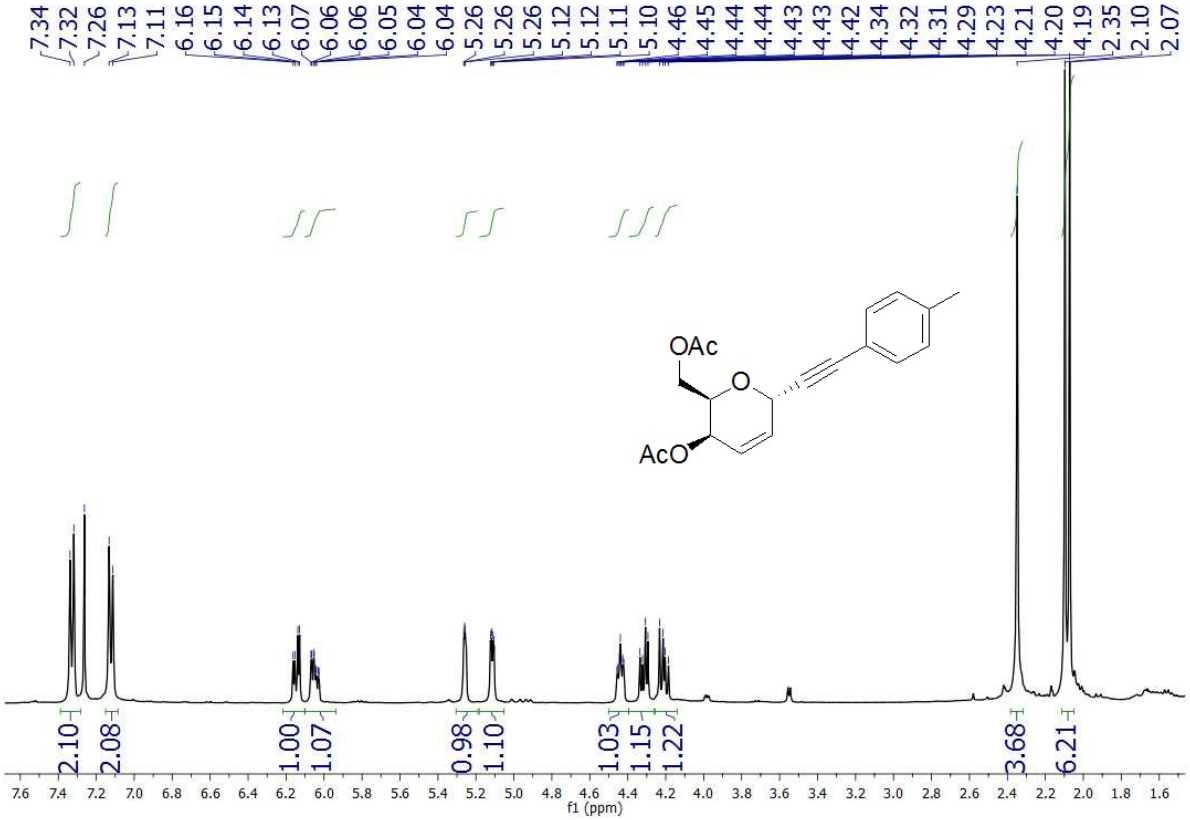
^{13}C NMR of compound **4i**



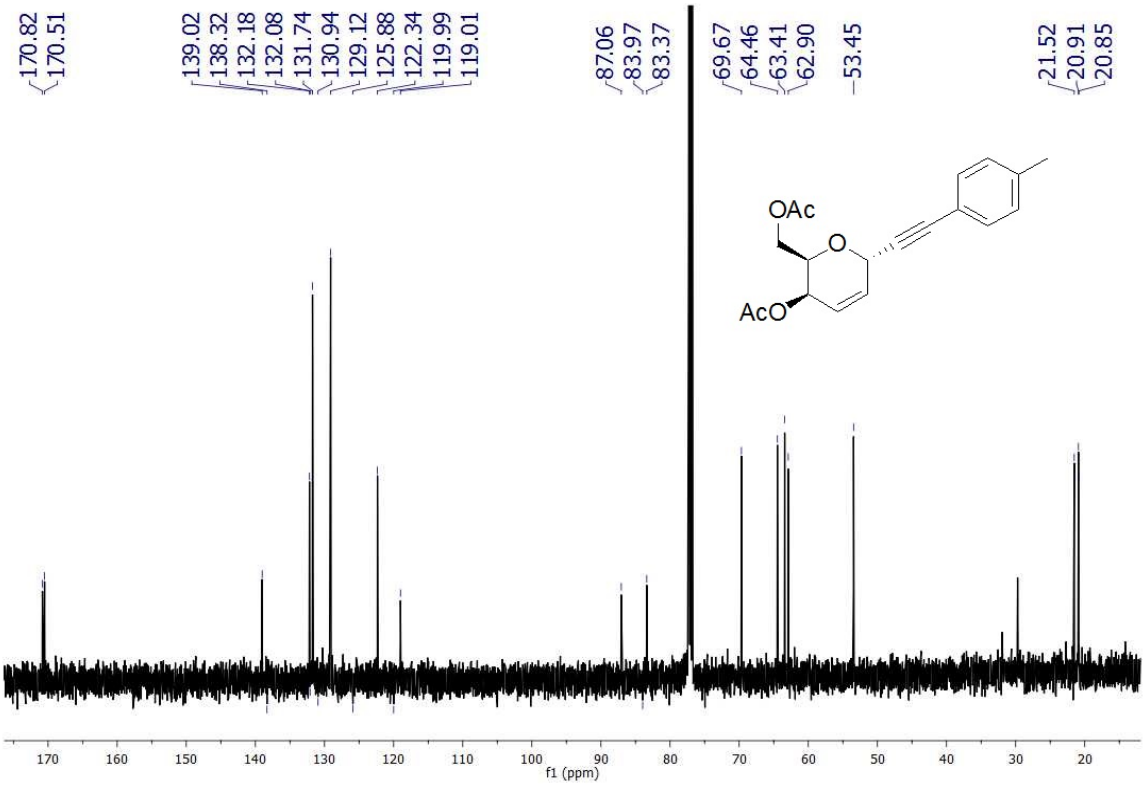
DEPT of Compound **4i**



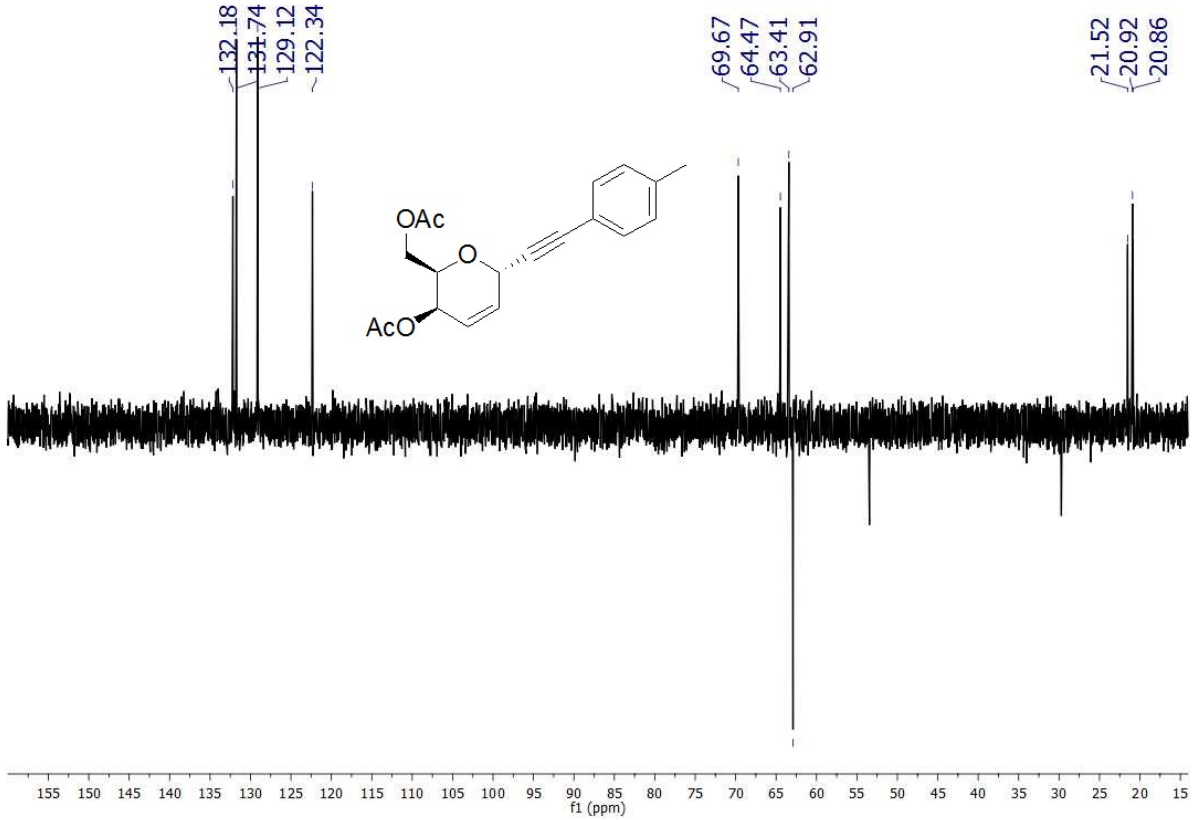
H NMR of compound**4j**



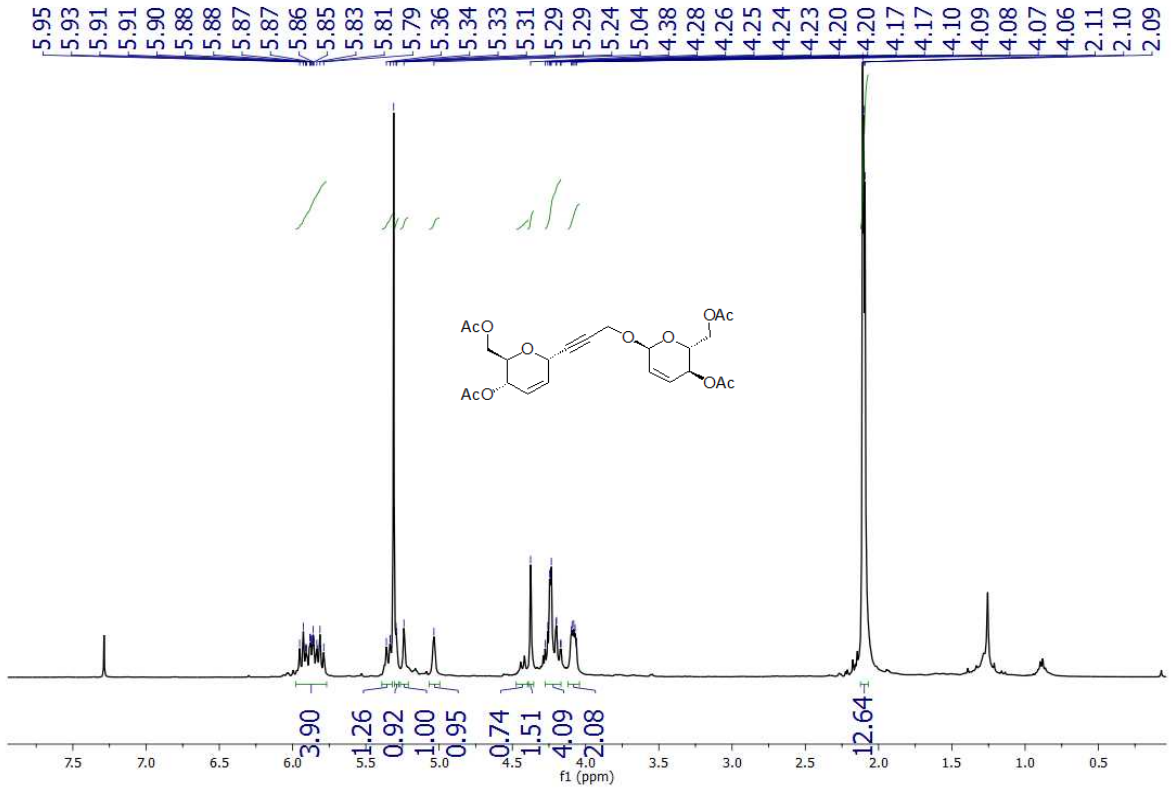
^{13}C NMR of compound **4j**



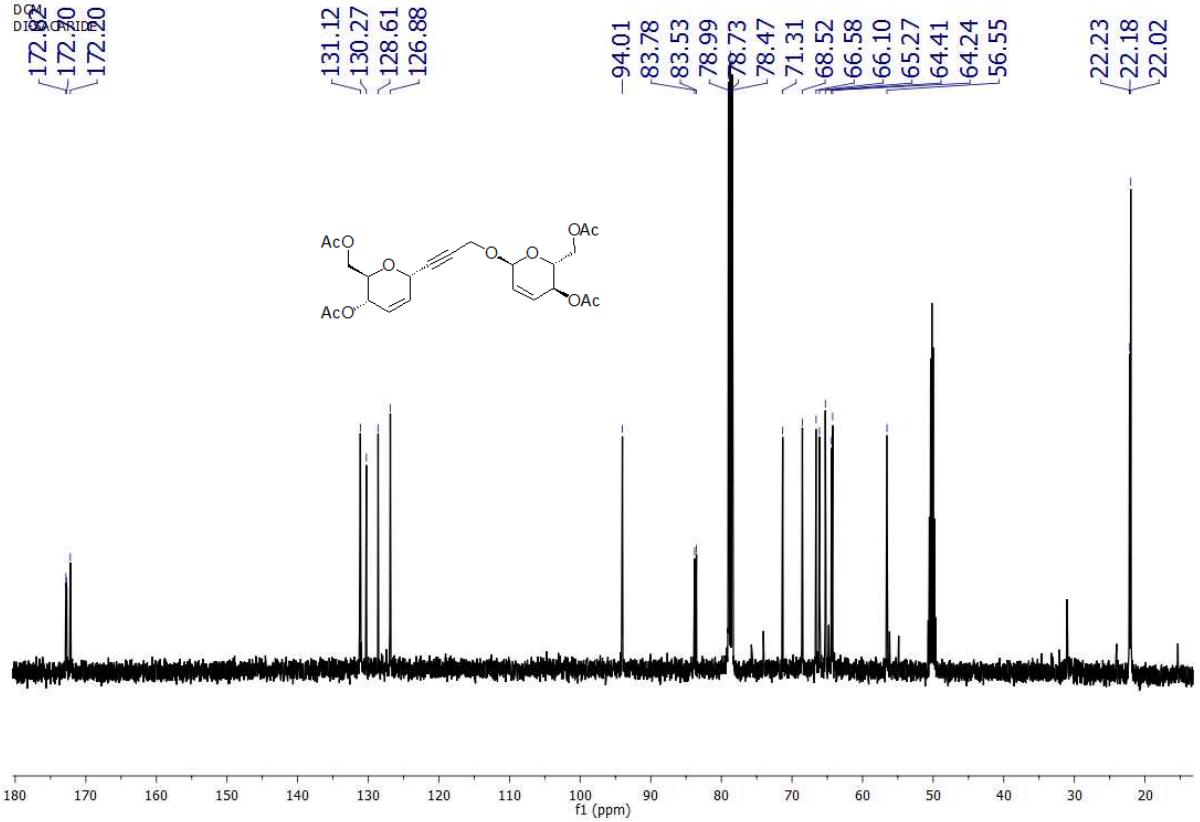
DEPT of Compound **4j**



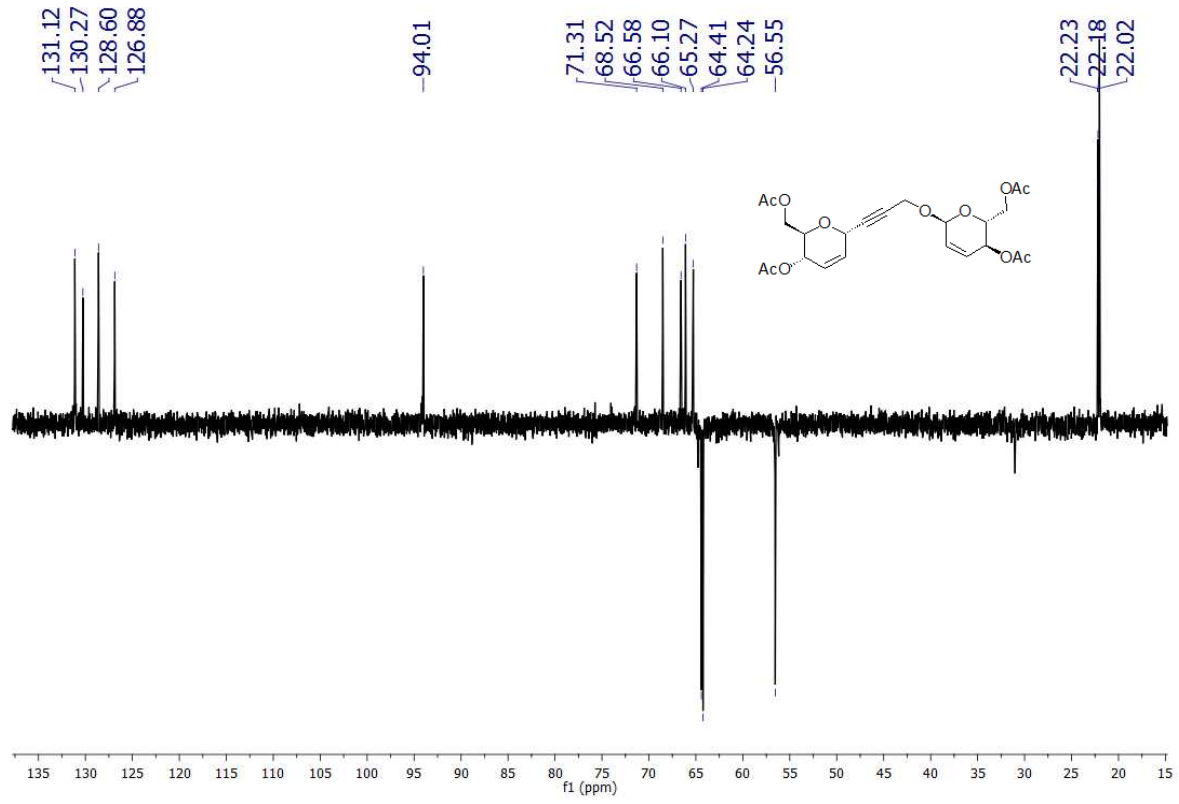
^{1}H NMR of compound **5a**



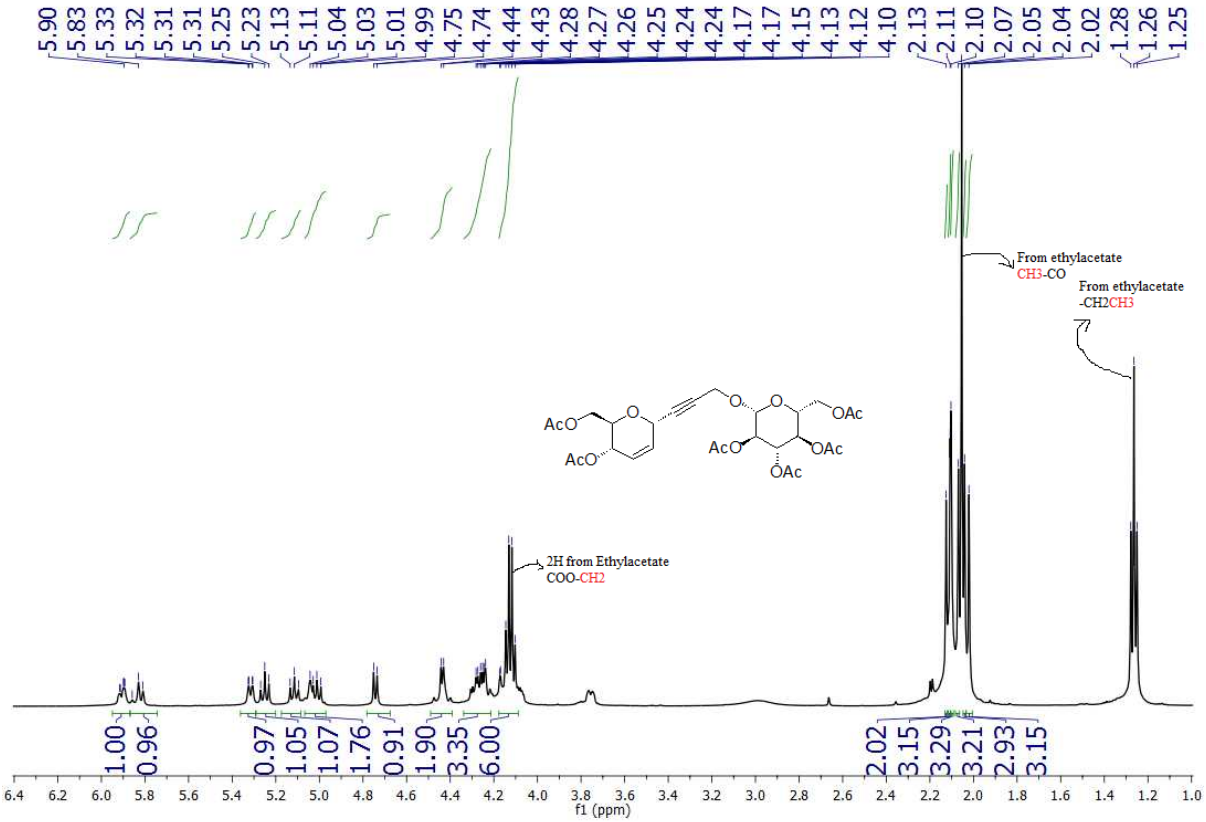
^{13}C NMR of compound **5a**



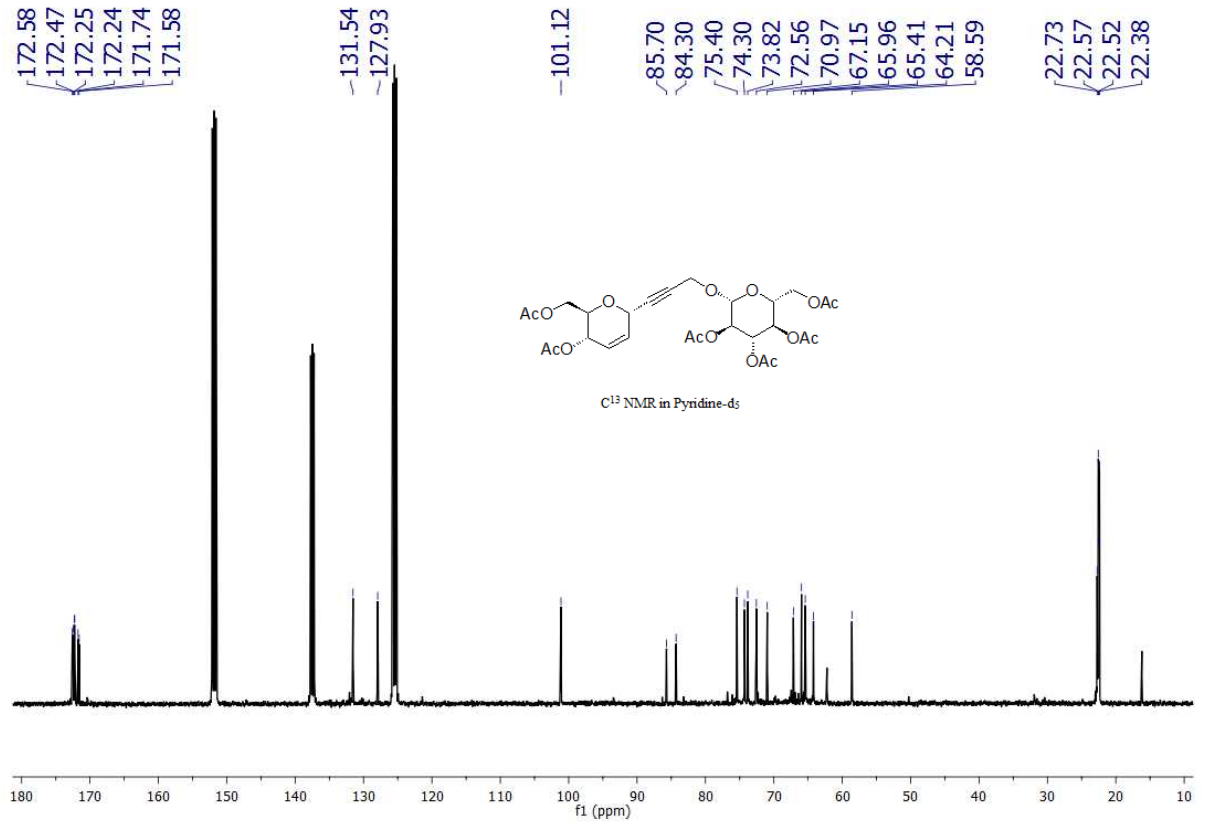
DEPT of Compound **5a**



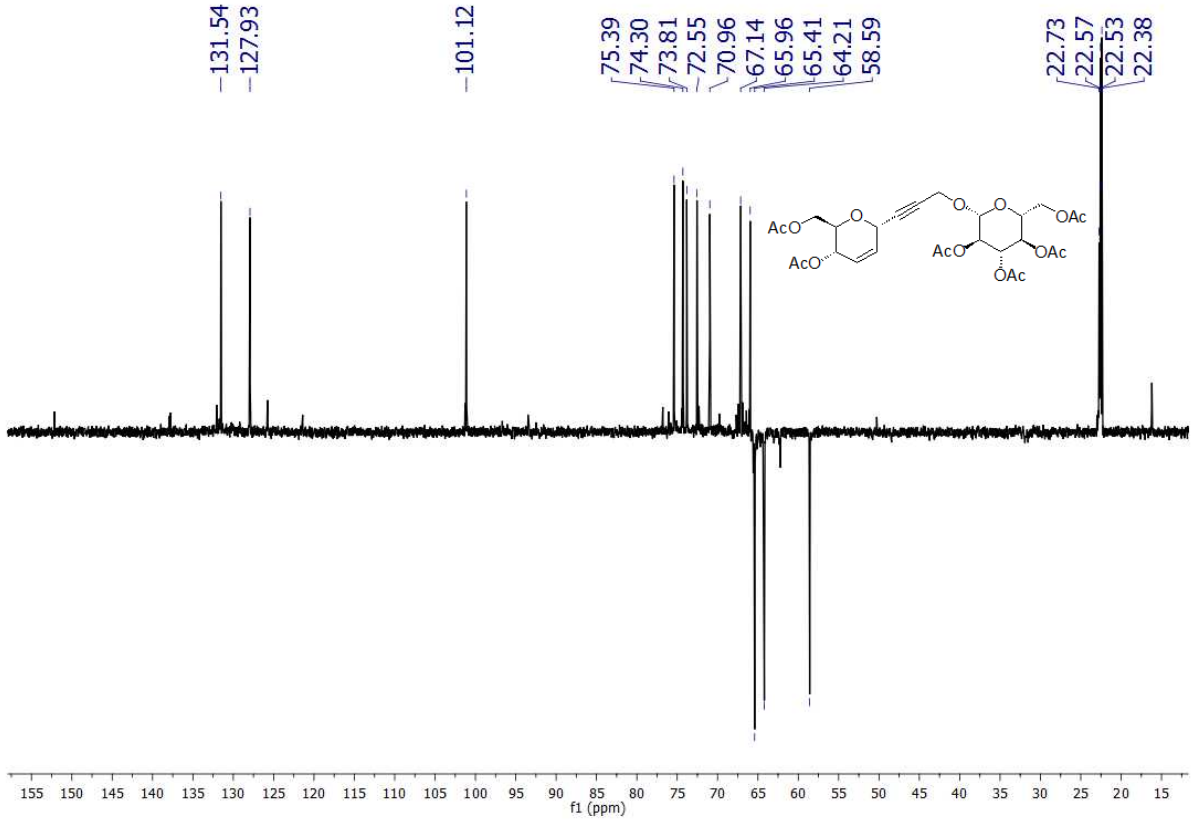
[1]H NMR of compound **5b**



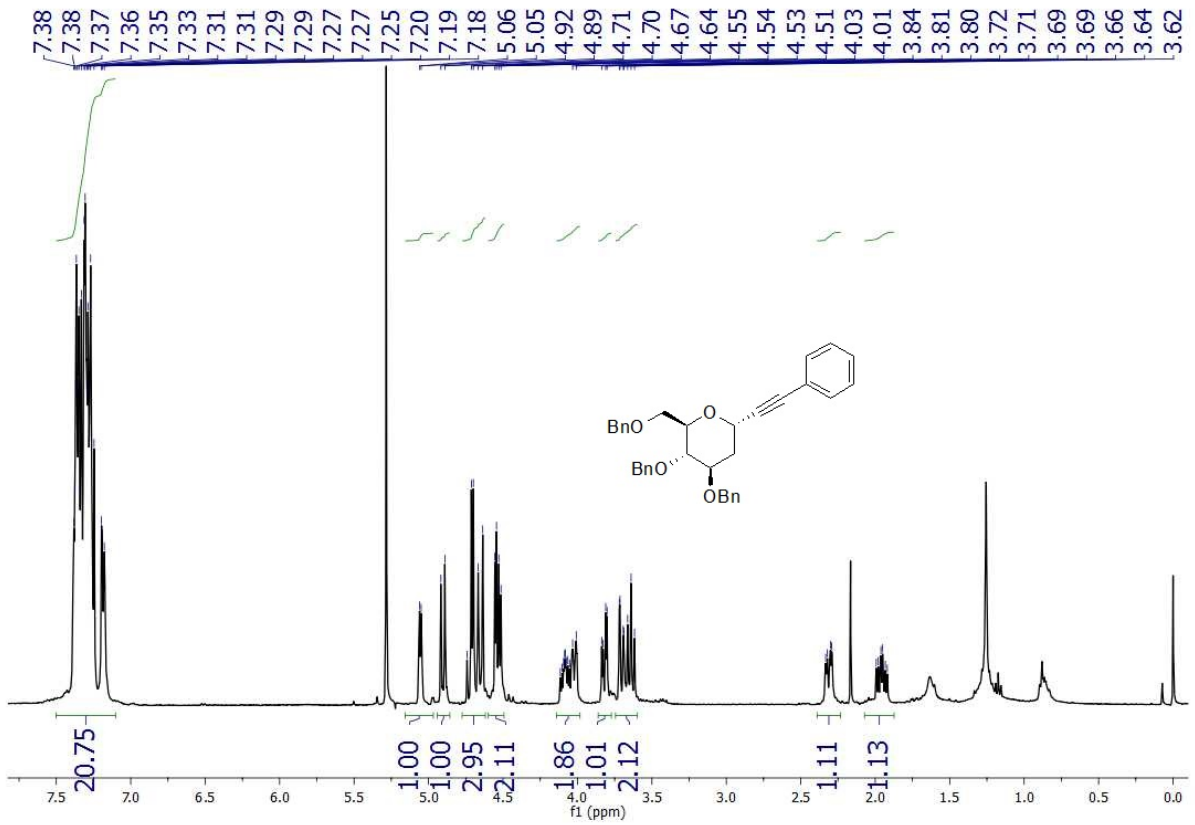
[13]C NMR of compound **5b**



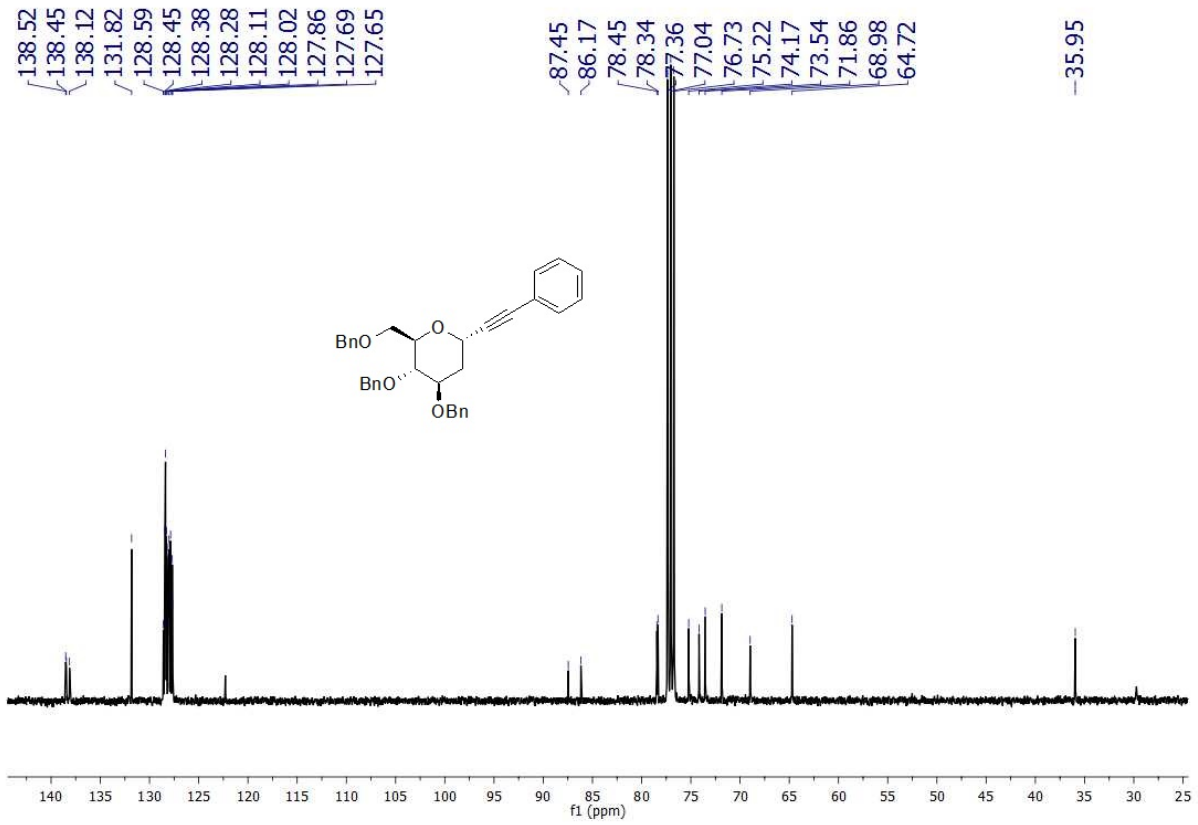
DEPT of Compound **5b**



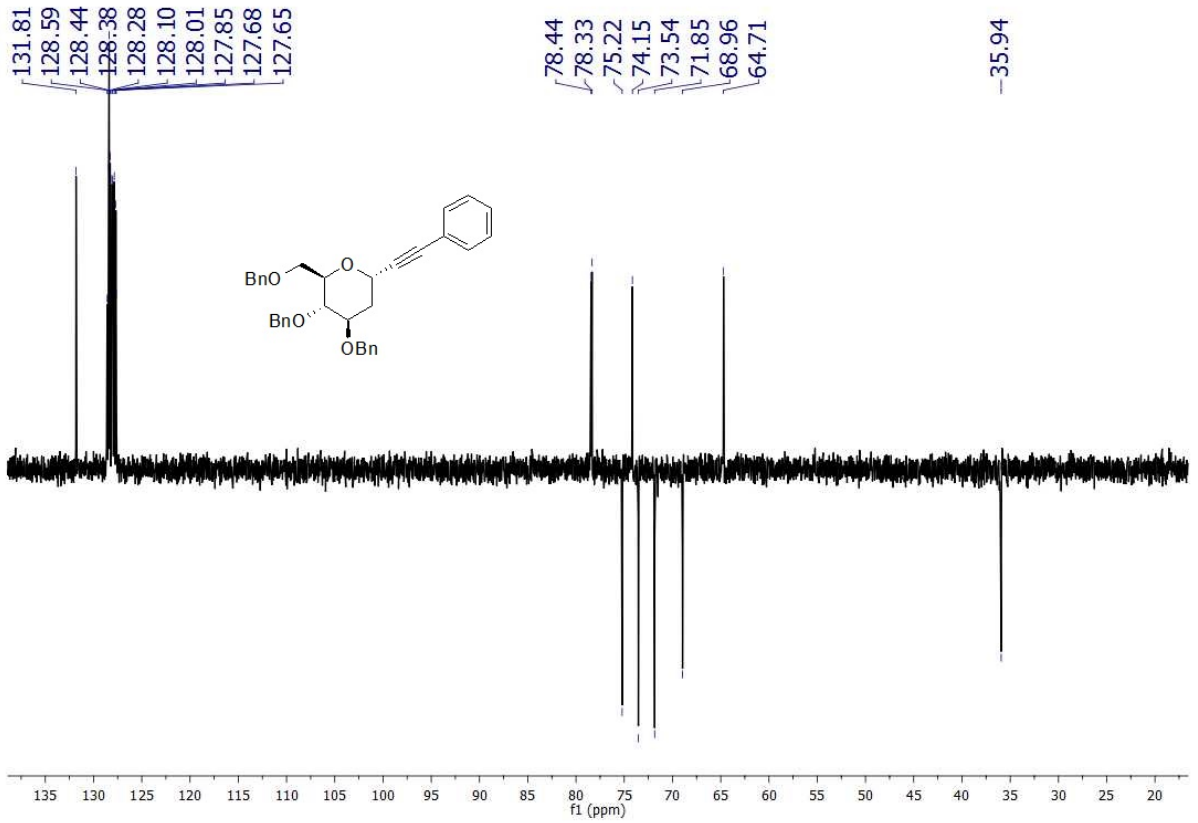
^{1}H NMR of compound **6a**



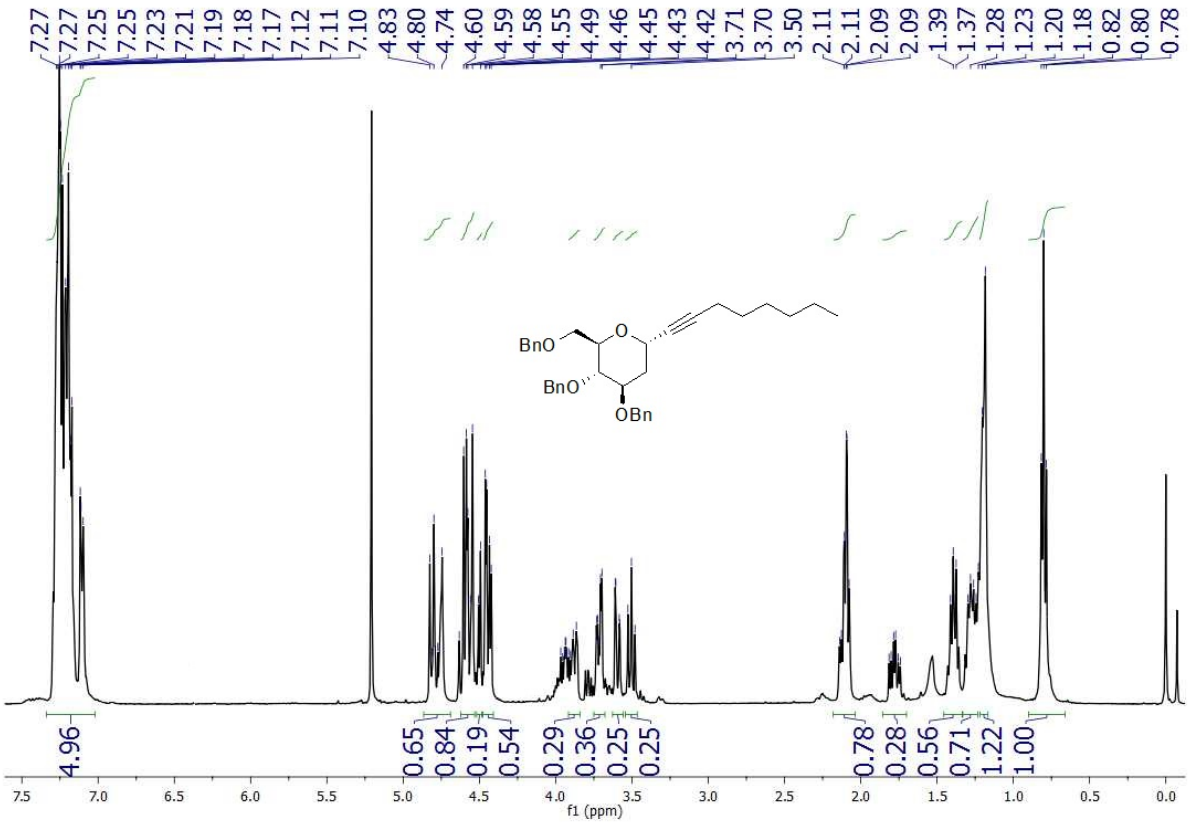
^{13}C NMR of compound **6a**



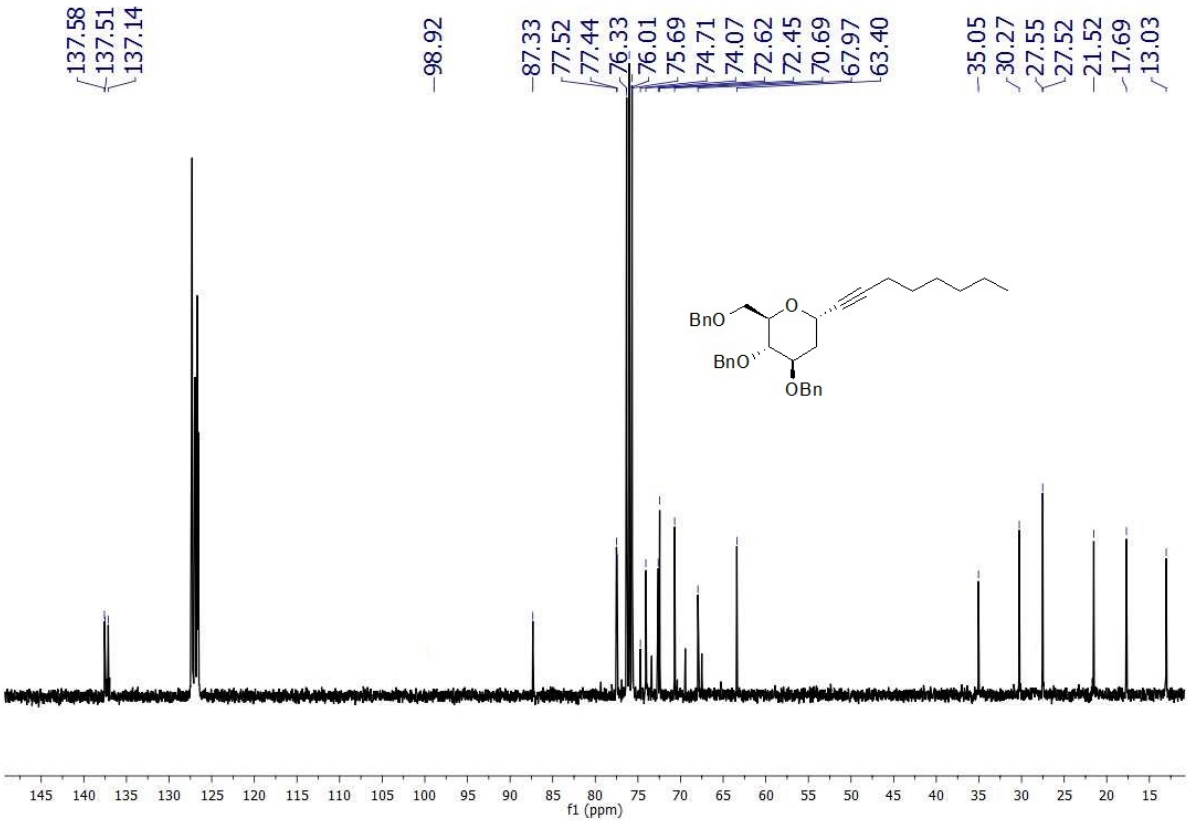
DEPT of compound **6a**



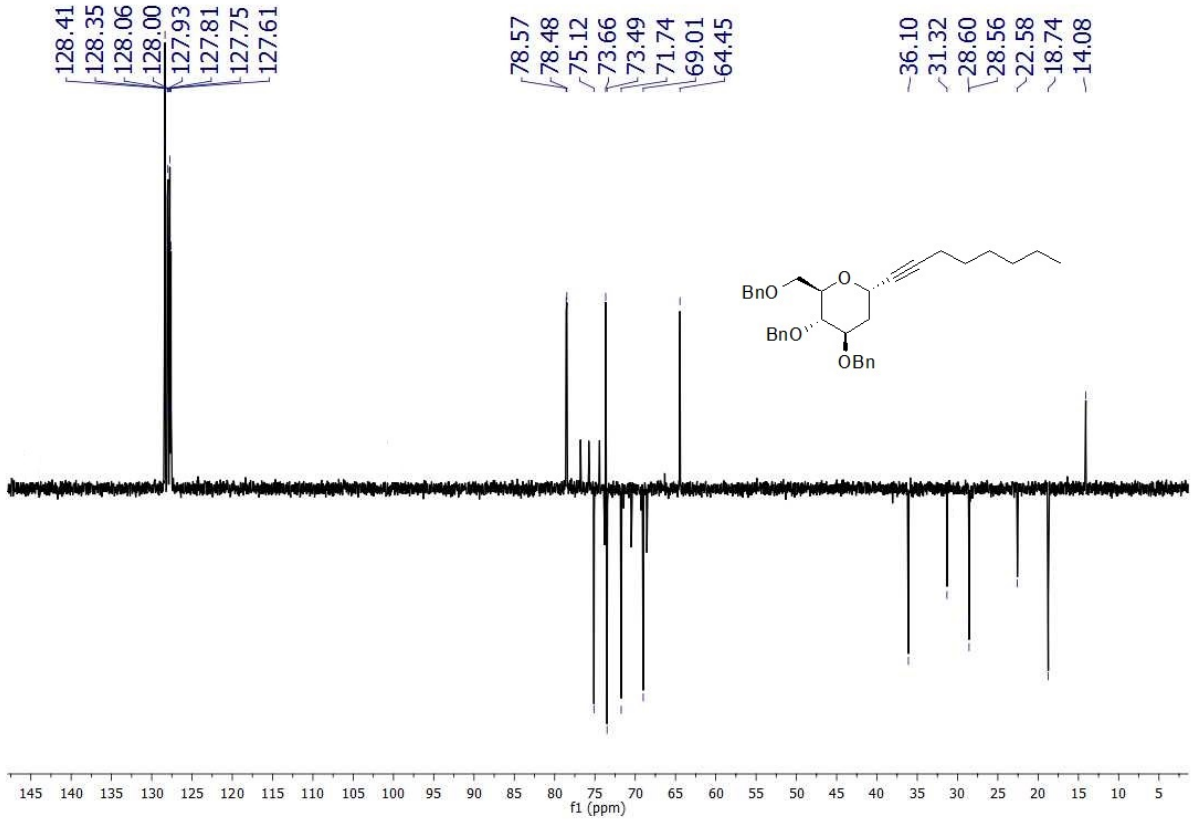
^{1}H NMR of compound **6b**



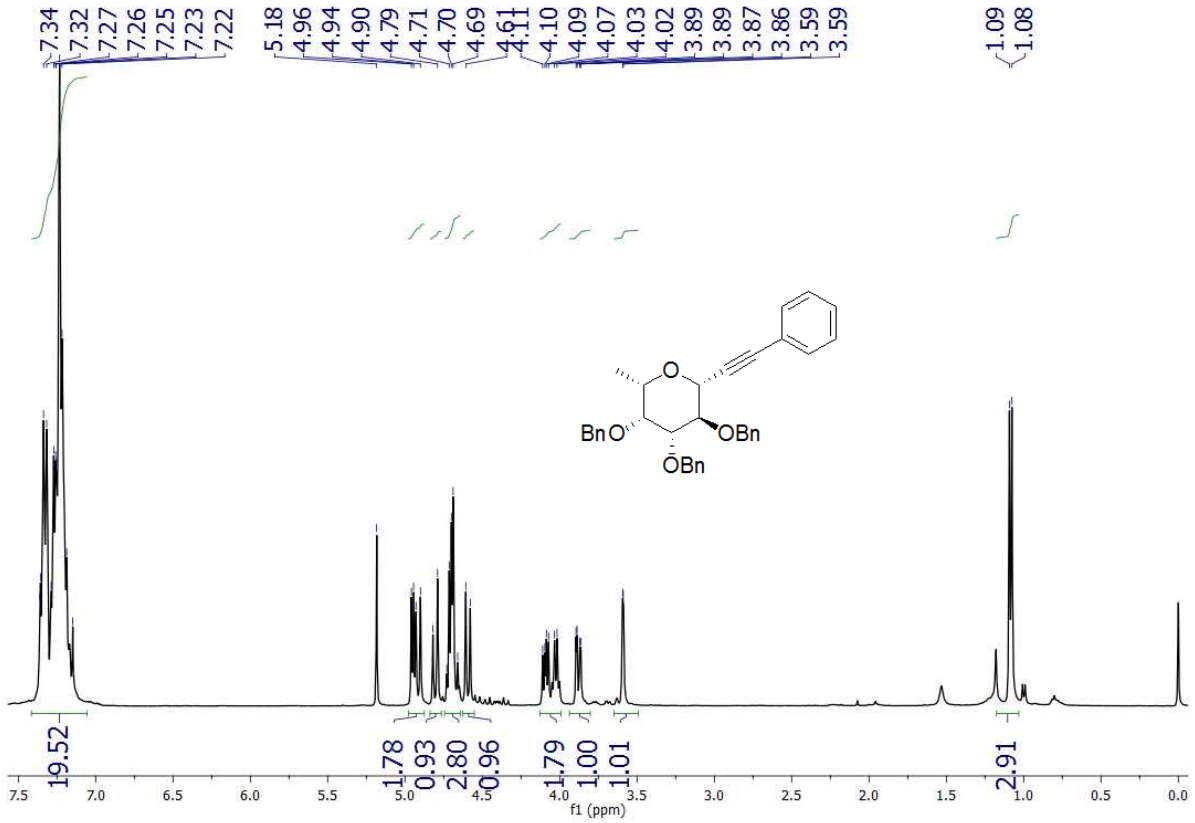
^{13}C NMR of compound **6b**



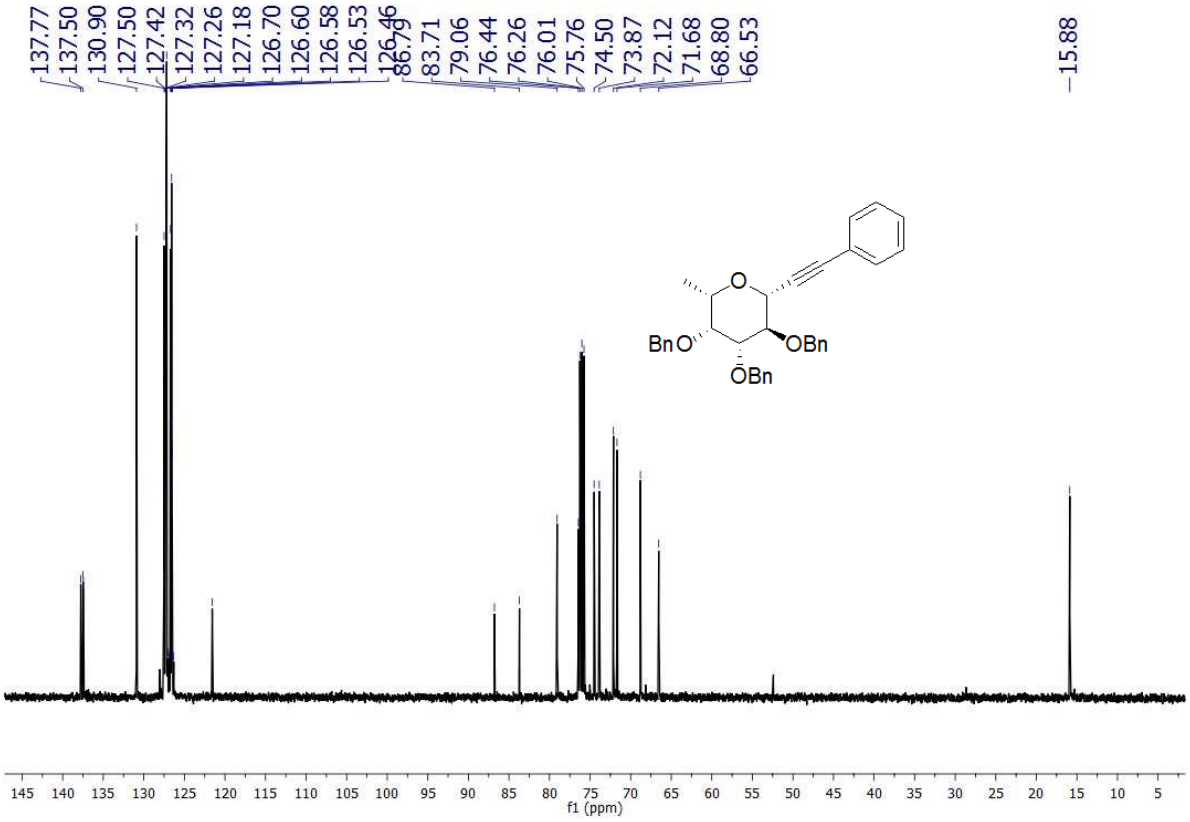
DEPT of compound **6b**



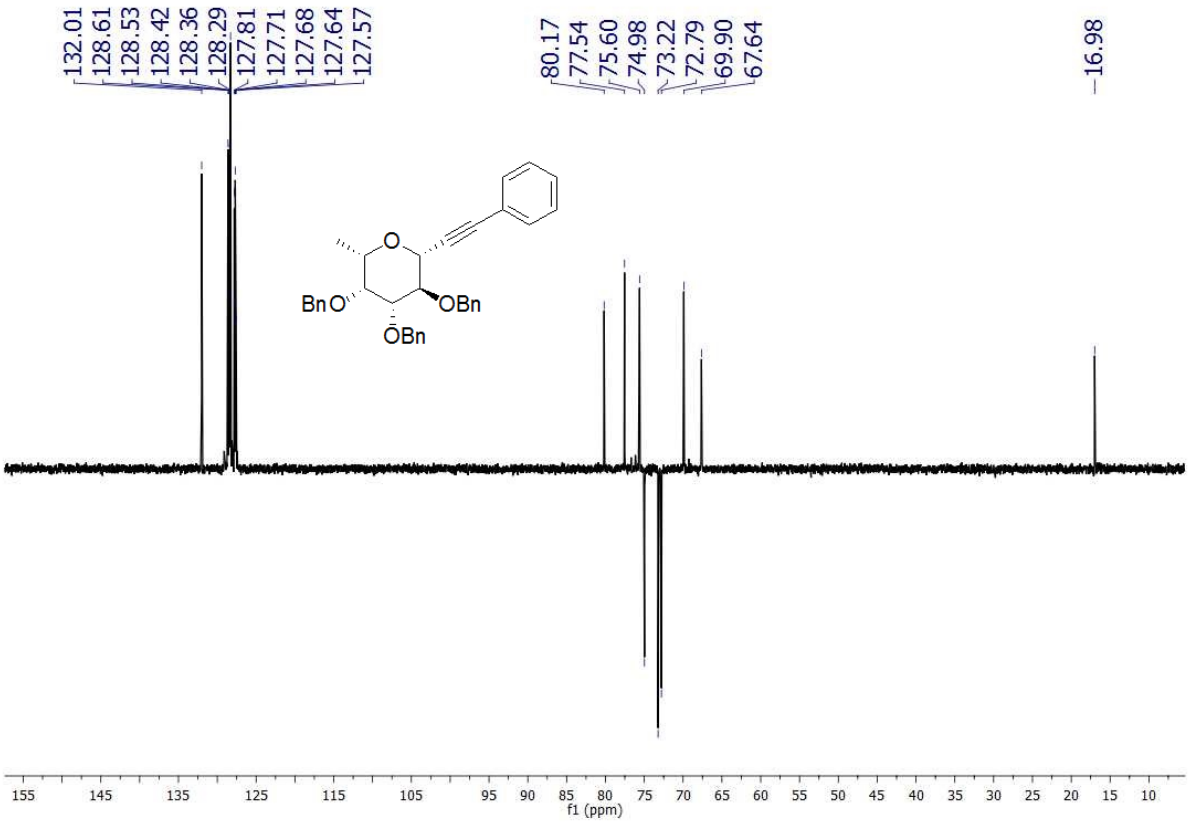
^{1}H NMR of compound of **7a**



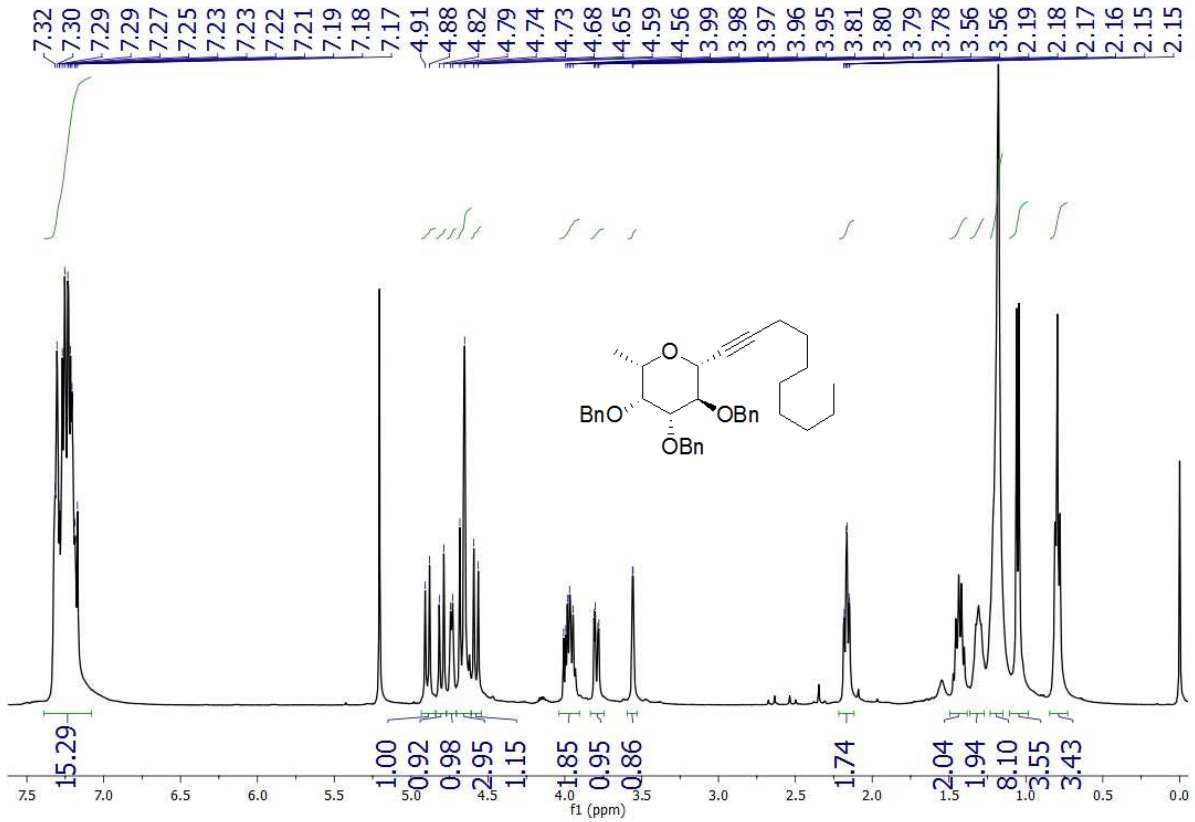
^{13}C NMR of compound **7a**



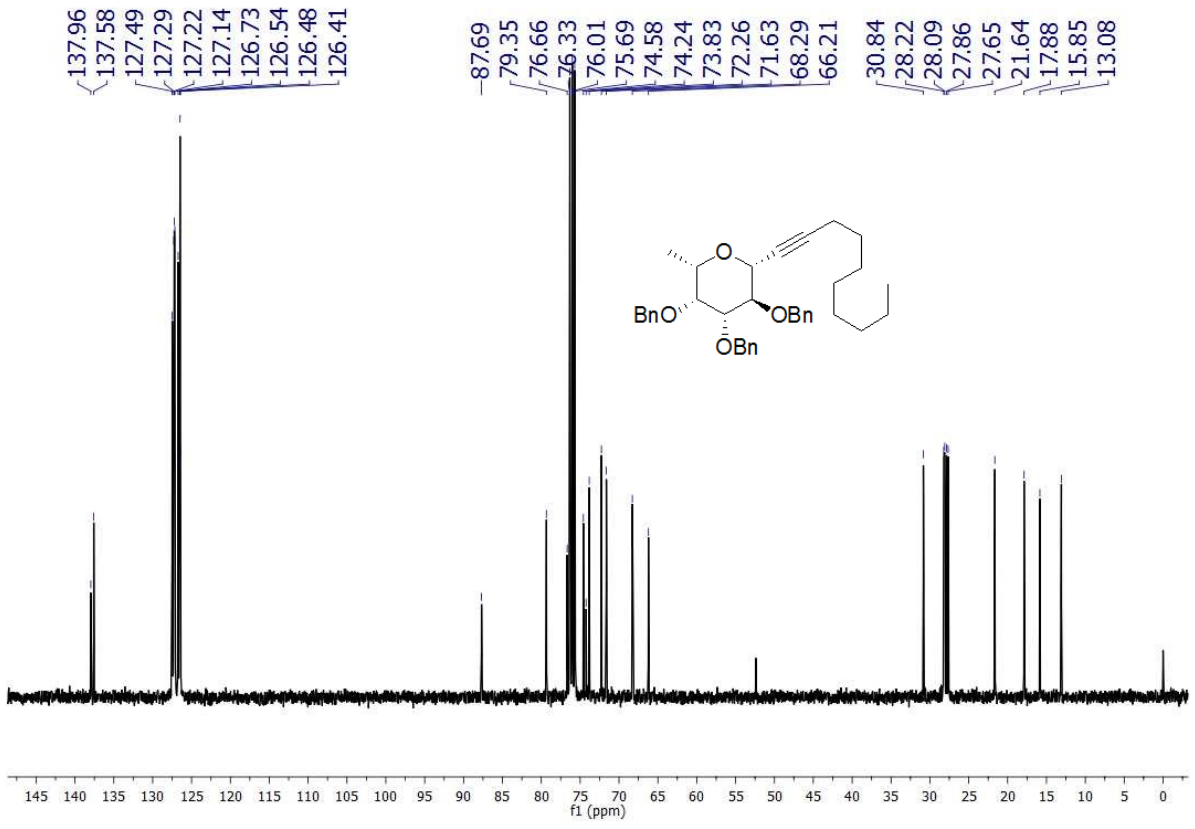
DEPT of compound **7a**



[1]HNMR of compound **7b**



[13]C NMR of compound **7b**



DEPT of compound **7b**