Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information for

Gold Mediated Glycosylations: Selective Activation of Propargyl 1,2-Orthoesters in the Presence of Aglycones Containing Propargyl Moiety

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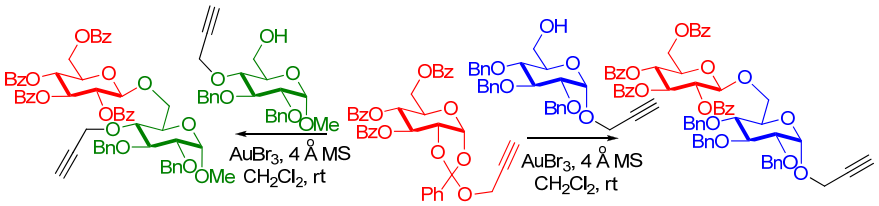
Contents

Abstract



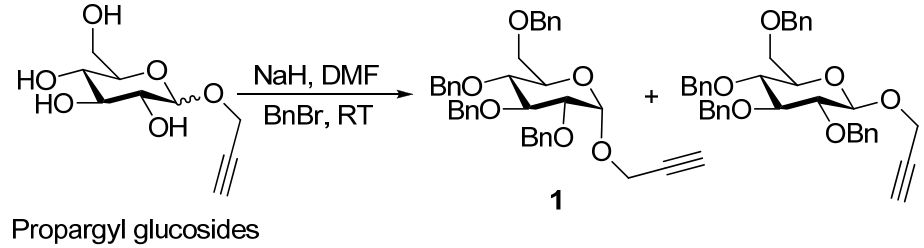
Selective activation of propargyl 1,2-orthoesters in the presence of propargyl glycosides and propargyl ethers was studied. Catalytic amount of $AuBr_3$ activated propargyloxy group of 1,2-orthoester making it glycosyl donor thereby giving disaccharides with propargyl group at the reducing end. Furthermore, propargyl ethers were unaffected under the reaction conditions

General Experimental Techniques and Apparatus

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported all reactions were performed under argon atmosphere. Removal of solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. $AuBr_3$ was purchased from Aldrich. Analytical thin-layer chromatography was performed on pre-coated silica plates (F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. ^1H, ^{13}C NMR spectra were recorded on 200 MHz for ^1H and 50 MHz for ^{13}C NMR or 300 MHz for ^1H and 75 MHz for ^{13}C NMR spectrometers. Chemical shifts (δ_H) are quoted in ppm and are referenced to tetramethylsilane (internal).

Experimental Procedures

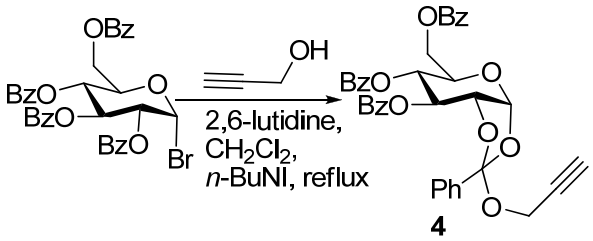
Synthesis of Compound **1**



Propargyl glucosides

To a solution of propargyl-α,β-glucopyranosides[1] (3.0g, 13.8 mmol) in anhydrous DMF (20mL) was added 60% suspension of NaH in paraffin (2.8g, 6.9 mmol) at 0 ^{o}C under argon atmosphere. The resulting solution was stirred for 30min. at room temperature. Benzyl bromide (9.8mL, 82.5mol) was added drop-wise at 0 ^{o}C followed by a catalytic amount of tetra-*n*-butyl ammonium iodide. The resulting reaction mixture was stirred at room temperature under argon for 10h. After completion of reaction (as judged by TLC), excess NaH was quenched with methanol followed by ice water and extracted with ether (3x20ml). Combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase to give propargyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **1** (6.3g, 79%) as a white solid.

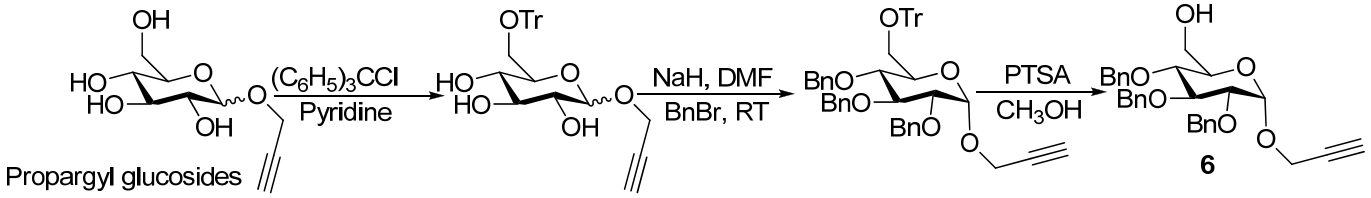
Synthesis of Compounds **4, 14** and **16:**



2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide, 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide and 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide were synthesized from the corresponding D-(+)-Glucose, D-(+)-Galactose, and D-(+)-Mannose by literature procedure.[2] To a solution of 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (20.0g, 30.3 mmol) in anhydrous CH_2Cl_2 (100mL) was added 2,6-lutidine (15mL), propargyl alcohol (9mL, 15.2 mmol) followed by tetra-*n*-butyl ammonium iodide (50mg) under argon atmosphere at room temperature. Then, the reaction mixture was refluxed at 65 °C for 48 h, diluted with water and extracted with CH_2Cl_2 (2x50mL). Combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate and concentrated *in vacuo* to obtain brownish black residue which was purified by silica gel column chromatography to afford propargyl-1,2-orthoester of glucose **4** (16.3g, 85%) as a white solid.

Same procedure was adopted for the preparation of Propargyl-1,2-orthoesters of mannose **(14)** and galactose **(16)**.

Synthesis of Compound **6**:



Propargyl glucosides

To a solution of Propargyl-α,β-glucopyranosides (5.0g, 23mmol) in pyridine (25mL) was added trityl chloride (8.3g, 30mmol), dimethyl amino pyridine (20mg) and stirred at room temperature for 48h. The reaction mixture was concentrated *in vacuo*, redissolved in CH_2Cl_2, washed with water (3x50mL). The organic layer was concentrated *in vacuo* to get a thick syrup which was purified by silica gel column chromatography to obtain pure propargyl 6-*O*-trityl α,β-glucopyranosides (6.3g, 60%).

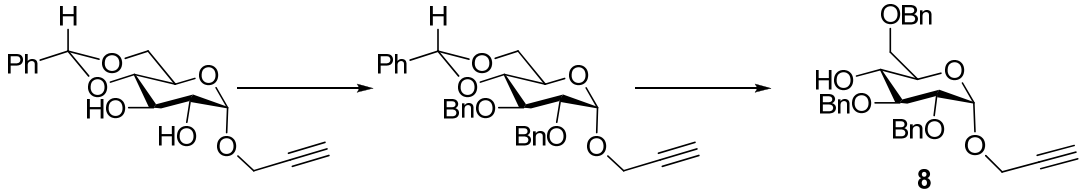
To a solution of tritylated product prepared *vide supra* (4.0g, 8.7mmol) in anhydrous DMF (20mL) was added 60% suspension of NaH in paraffin (1.4g, 34.7 mmol) at 0 ^oC under argon atmosphere. The resulting solution was stirred for 30min. at room temperature. Benzyl bromide (4.1mL, 34.7 mmol) was added drop-wise at 0 ^oC followed by a catalytic amount of tetra-*n*-butyl ammonium iodide (20mg). The resulting reaction mixture was stirred at room temperature under argon for 10h. After completion of the reaction (as judged by TLC), excess NaH was quenched with methanol followed by ice water and extracted with ether (3x50mL). Combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude residue was purified by flash silica gel column chromatography (230-400 mesh) using ethyl acetate-petroleum ether as mobile phase to give propargyl-6-*O*-trityl-2,3,4-tri-*O*-Bn-α-D-glucopyranoside (4.4g, 70%) as a thick syrup.

To a solution of propargyl-6-*O*-trityl-2,3,4-tri-*O*-Bn-α-D-glucopyranoside (in CH_2Cl_2 and methanol was added a catalytic amount (20mg) of PTSA and the reaction mixture was stirred for 5h at room temperature. Quenched with triethylamine and the solvent was removed *in vacuo* to obtain a yellow gummy residue which was purified by silica gel column chromatography in order to get propargyl-2,3,4-tri-*O*-Bn-α-D-glucopyranoside **6** (2.7g, 90%).

The same sequence of reactions were performed to get the compound **2** from commercially available methyl α-D-glucopyranside.

Characterization data for compound **6**: $[\alpha]_D(CHCl_3, c\ 1.0) = +49.4$; ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.45 (1 H, t, *J* 2.4 Hz), 3.56 (2 H, dd, *J* 3.6, 9.6 Hz), 3.69 (3 H, m), 4.02 (1 H, t, *J* 8.8 Hz), 4.26 (2 H, d, *J* 2.4 Hz), 4.60-5.06 (7 H, m), 7.24-7.45 (15 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.4, 61.7, 71.3, 73.0, 74.9, 75.1, 75.8, 77.1, 78.8, 79.4, 81.7, 95.1, 127.5-128.5, 137.9, 138.0, 138.7; Mol. Wt. calculated for $C_{30}H_{32}O_6$: 488.57, Found: 511.02 (M^++23 for Na).

Synthesis of Compound **8**:



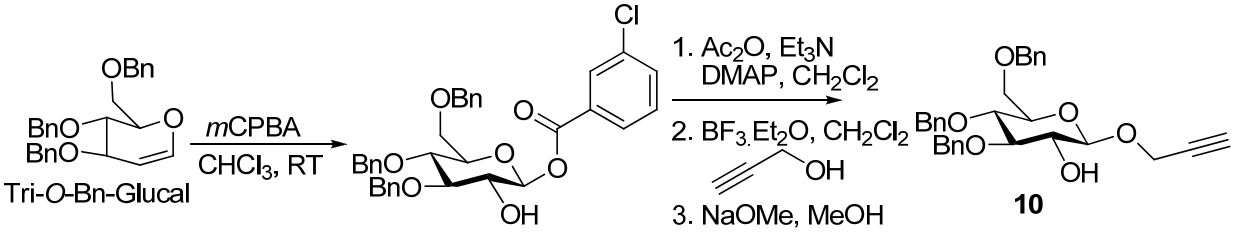
8

To a solution of Propargyl-4,6-*O*-benzylidene-α-D-glucopyranoside[3] (5.0g, 16.3mmol) in anhydrous DMF (20mL) was added 60% suspension of NaH in paraffin (1.6g, 40.8 mmol) at 0 ^oC under argon atmosphere. The resulting solution was stirred for 30min. at room temperature. Benzyl bromide (4.9mL, 40.8 mmol) was added drop-wise at 0 ^oC followed by a catalytic amount of tetra-*n*-butyl ammonium iodide (20mg). The resulting reaction mixture was stirred at room temperature under argon for 4h. After completion of the reaction (as judged by TLC), excess NaH was quenched with methanol followed by ice water and extracted with ether (3x50mL). Combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude residue was purified by flash silica gel column chromatography (230-400 mesh) using ethyl acetate-petroleum ether as mobile phase to give propargyl-4,6-*O*-benzylidene-2,3-di-*O*-Benzyl-α-D-glucopyranoside (7.1g, 90%) as a thick syrup.

The resulting product (2.0g, 4.11 mmol) was dissolved in anhydrous tetrahydrofuan (10mL) and was added sodium cyanoborohydride (2.2g, 34.9 mmol) followed by a saturated solution of HCl gas in diethyl ether at 0 ^{o}C drop-wise till the disappearance of frothing. The reaction mixture was quenched with water and extracted with ethyl acetate, combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give propargyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **8** (1.7g, 82%).

Characterization data for compound **8**: $[\alpha]_D(CHCl_3, c\ 0.8) = +58.0$; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.44 (1 H, t, *J* 2.4 Hz), 3.53-3.51 (6 H, m), 4.28 (2 H, d, *J* 2.4 Hz), 4.55 (2 H, d, *J* 3.7 Hz), 4.71 (2 H, s), 4.86 (2 H, ABq, *J* 3.9 Hz), 5.10 (1 H, d, *J* 3.95 Hz), 7.21-7.43 (15 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.3, 61.2, 70.4, 70.5, 72.6, 73.5, 74.8, 75.4, 78.8, 78.9, 81.2, 95.0, 127.4-128.6, 137.8, 137.9, 138.7; Mol. Wt. calculated for $C_{30}H_{32}O_6$: 488.57, Found: 511.14 (M^++23 for Na).

Synthesis of Compound **10**:



To a solution of tri-O-benzyl glucal (1.0g, 2.41 mmol) in chloroform (5mL) was added a solution of *m*-CPBA (1.0g, 6.0 mmol) in chloroform (10mL) at 0 ^{o}C under argon atmosphere.[4] The reaction mixture was stirred at room temperature for 15 h, diluted with water and extracted with chloroform. Combined organic layers were washed water, aq.$NaHCO_3$, water, brine and dried over anhydrous sodium sulfate, concentrated *in vacuo* followed by silica gel column chromatography to give *m*-Chloroperbenzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (0.6 g, 43%).

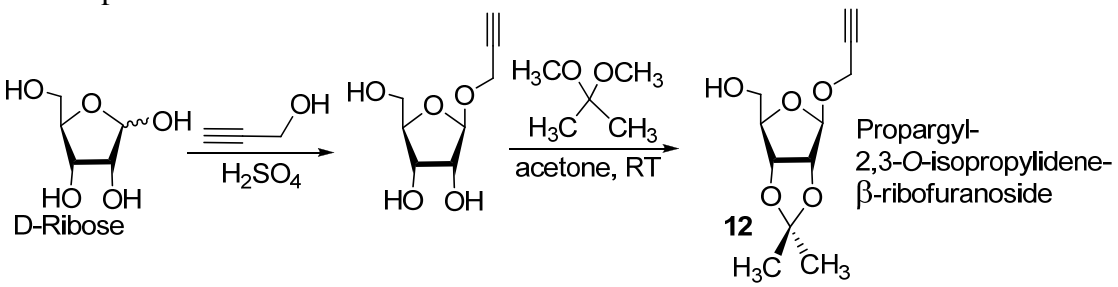
m-Chloroperbenzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (0.8g, 1.43 mmol) prepared *vide supra* was dissolved in anhydrous CH_2Cl_2 and was added dimethyl amino pyridine (10mg), triethylamine (0.6mL, 4.29 mmol) and acetic anhydride (1.32mL, 2.15mmol) at room temperature and stirred. After 2h, the reaction mixture was diluted with CH_2Cl_2, washed with water and CH_2Cl_2 layer was concentrated *in vacuo* to obtain a residue which was purified by column chromatography to yield acetylated product (0.8g, 88%).

The acetylated product (2.0g, 3.16 mmol) was dissolved in dry CH_2Cl_2 (15mL) along with propargyl alcohol (1.0mL, 15.8 mmol). $BF_3.Et_2O$ (1.2mL, 9.50 mmol) was added drop-wise at 0 ^{o}C under argon atmosphere and the reaction mixture was stirred for 2h at room temperature, quenched with $NaHCO_3$ solution and extracted with CH_2Cl_2 (3x25mL). Combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate and concentrated *in vacuo* to obtain a black residue which was purified by silica gel column chromatography using ethyl acetate and petroleum ether as eluent to afford a mixture of propargyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α,β-glucopyranosides (1.3g, 74%).

To a solution of this mixture of propargyl-2-*O*-aceyl-3,4,6-tri-*O*-Bn-α,β-glucopyranosides (1.3g, 2.35 mmol) in anhydrous methanol (15mL) was added a catalytic amount of sodium at room temperature under argon atmosphere. The reaction mixture was stirred for 30 min at room temperature and the excess methanol was removed *in vacuo* and the crude residue was purified by flash silica gel (230-400 mesh) column purification to give propargyl-3,4,6-tri-O-benzyl-β-D-glucopyranoside **10** (0.6 g, 52%).

Characterization data for compound **10**: $[\alpha]_D(CHCl_3, c\ 1.0) = -25.2$; ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.39 (1 H, t, *J* 2.3 Hz), 2.48 (1 H, bs), 3.39-3.67 (6 H, m), 4.33 (2 H, t, *J* 2.8 Hz), 4.41 (1 H, d, *J* 6.1 Hz), 4.49 (2 H, ABq, *J* 12.3 Hz), 4.60 (2 H, ABq, *J* 10.6 Hz), 4.82 (2 H, ABq, *J* 11.2 Hz), 7.04-7.33 (15 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 55.9, 68.6, 73.4, 74.3, 74.9, 75.1, 75.2, 75.3, 77.3, 78.3, 84.4, 100.4, 127.6-128.4, 137.9, 138.0, 138.5; Mol. Wt. calculated for $C_{30}H_{32}O_6$: 488.57, Found: 511.23 (M^++23 for Na).

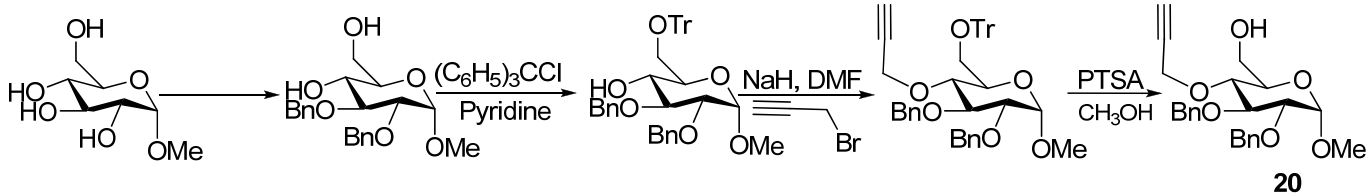
Synthesis of Compound **12**:



To a solution of D-Ribose (2 g, 13.3 mmol) in propargyl alcohol (15 mL) was added a few drops of H_2SO_4 at room temperature under argon atmosphere.[5] The reaction mixture was stirred for 15h at room temperature, neutralized with triethylamine, and the unreacted propargyl alcohol was removed *in vacuo*. The resulting yellow syrup was directed in the next step without further purification. To a solution of propargyl-β-ribofuranoside in acetone (10 mL) was added 2,2'-dimethoxy propane (3 mL) followed by a catalytic amount of PTSA at room temperature under nitrogen atmosphere and stirred for 2h, neutralized with triethyl amine and concentrated *in vacuo* followed by flash silica gel (230-400 mesh) column purification using ethyl acetate-petroleum ether as eluent to afford propargyl-2,3-di-*O*-isopropylidene-β-ribofuranoside **12** (1.3 g, 43% over two steps).

Characterization data for compound **12**: $[\alpha]_D(CHCl_3, c\ 0.8) = -97.3$; ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.33, 1.49 (6 H, 2s), 2.52 (1 H, t, *J* 2.4 Hz), 2.97 (1 H, dd, *J* 4.6, 8.4 Hz), 3.60-3.75(2 H, m), 4.30 (2 H, d, *J* 2.4 Hz), 4.42 (1 H, t, *J* 3.8 Hz), 4.72 (2 H, ABq, *J* 5.9 Hz), 5.27 (1 H, s); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 24.6, 26.2, 55.0, 63.7, 75.3, 78.3, 81.3, 85.7, 88.4, 107.5, 112.2; Mol. Wt. calculated for $C_{11}H_{16}O_5$: 228.24, Found: 251.12 (M^++23 for Na).

Synthesis of Compound **20**:



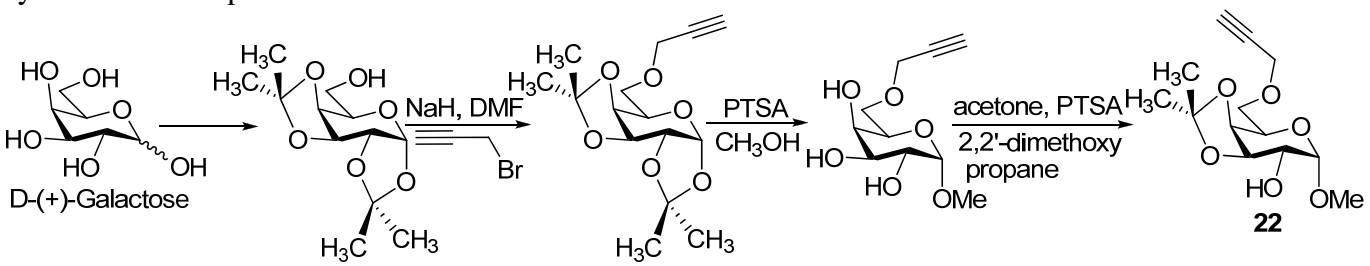
20

Methyl-2,3-di-*O*-benzyl-α-D-glucopyranoside[6] (2.0 g, 53.5 mmol) was tritylated at *C*-6 position selectively under standard conditions $(C_6H_5)_3CCl$/DMAP/Pyridine/50 °C/85%. The resulting trityl ether (2.0 g, 32.4 mmol) was propargylated under NaH/DMF/propargyl bromide/*n*-Bu_4NI/0 °C followed by flash silica gel (230-400 mesh) column chromatography using ethyl acetate-petroleum ether as mobile phase to give methyl-2,3-di-*O*-benzyl-4-*O*-propargyl-6-*O*-trityl-α-D-glucopyranoside (2.0 g, 95%) that was redissolved in CH_2Cl_2 (10 mL) and methanol and was treated with a catalytic amount of PTSA. The reaction mixture was stirred for 5h at room temperature, quenched with triethyl amine, and the solvent was concentrated *in vacuo* to obtain a yellow syrupy residue which was purified by silica gel column

chromatography in order to get methyl-2,3-di-*O*-benzyl-4-*O*-propargyl-α-D-glucopyranoside **20** (1.1 g, 90%).

Characterization data for compound **20**: $[\alpha]_D$($CHCl_3$, *c* 0.9) = +64.4; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.00 (1 H, bs), 2.46 (1 H, t, *J* 2.4 Hz), 3.36 (3 H, s), 3.40-3.52 (2 H, m), 3.59 (1 H, td, *J* 3.3, 10.0 Hz), 3.81 (2 H, dd, *J* 3.2, 6.1 Hz), 3.95 (1 H, t, *J* 9.1 Hz), 4.38 (2 H, d, *J* 2.4 Hz), 4.56 (1 H, d, *J* 12.3 Hz), 4.71 (2 H, ABq, *J* 12.3 Hz), 4.87 (2 H, ABq, *J* 10.7 Hz), 7.21-7.39 (10 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 55.2, 59.8, 61.6, 70.3, 73.3, 74.4, 75.7, 76.6, 79.8, 80.1, 81.7, 98.0, 127.6-128.5, 137.9, 138.4; Mol. Wt. calculated for $C_{11}H_{16}O_5$: 412.47, Found: 435.64 (M^++23 for Na).

Synthesis of Compound **22**:



1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside[7] (3g, 0.1154 mol) was propargylated using NaH/DMF/propargyl bromide/*n*-Bu_4NI/0 °C followed by silica gel column chromatography to give 6-*O*-propargyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (2.9 g, 85%) that was redissolved in anhydrous methanol, added PTSA at room temperature. The reaction mixture was stirred for 10h at 80 °C under argon atmosphere and the reaction mixture was neutralized with triethylamine, and the excess methanol was concentrated *in vacuo*. The resulting crude residue was taken for the next step without further purification. To a solution of mixture of methyl-6-*O*-propargyl-α,β-glucopyranoside in acetone (15 mL) was added 2,2'-dimethoxy propane (5 mL) followed by a catalytic amount of PTSA at room temperature under nitrogen atmosphere and stirred for 5h at room temperature, neutralized with triethyl amine and concentrated *in vacuo*. The resulting crude residue was purified by flash silica gel (230-400 mesh) column chromatography using ethyl acetate-petroleum ether as mobile phase to obtain methyl-3,4-di-O-isopropylidene-6-O-propargyl-α-D-galactopyranoside **22** (0.8 g, 30% over 2 steps).

Characterization data for compound **22**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +94.4; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.35, 1.51 (6 H, 2s), 2.47 (1 H, t, *J* 2.4 Hz), 2.55 (1 H, bs), 3.46 (3 H, s), 3.58-3.89 (3 H, m), 4.12-4.29 (5 H, m), 4.78 (1 H, d, *J* 3.8 Hz); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 25.9, 27.7, 55.5, 58.6, 67.1, 69.3, 69.5, 73.2, 74.7, 76.1, 79.4, 98.4, 109.6; Mol. Wt. calculated for $C_{13}H_{20}O_6$: 272.29, Found: 295.67 (M^++23 for Na).

General experimental procedure for Compounds **5,7,9,11,13,15,17-19,21** and **23-26**:

To a solution of glycosyl donor (0.1 mmol), glycosyl acceptor (0.11 mmol) and 4Å molecular sieves powder (50 mg) in anhydrous CH_2Cl_2 (5 mL) was added $AuBr_3$ (10 mol%) under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature for the specified time and the reaction mixture was filtered and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether as the mobile phase.

Characterization data for compound **7**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +30.5; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.38 (1 H, t, *J* 2.3 Hz), 3.21-3.52 (2 H, m), 3.89 (1 H, t, *J* 9.2 Hz), 3.72-3.92 (2 H, m), 4.10-4.32 (5 H, m), 4.45-5.02 (9 H, m), 5.58 (1 H, dd, *J* 8.0, 9.6 Hz), 5.67 (1 H, t, *J* 9.6 Hz), 5.90 (1 H, t, *J* 9.5 Hz), 7.00-7.57

(27 H, m), 7.78-8.02 (8 H, m); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 54.3, 63.2, 68.1, 69.8, 70.1, 71.8, 72.2, 72.9, 72.9, 74.6, 74.7, 75.5, 77.2, 79.0, 79.3, 81.7, 95.0, 101.3, 127.4-129.7, 133.1, 133.1, 133.2, 133.4, 138.0, 138.2, 138.8, 165.0, 165.1, 165.2, 165.8; Mol. Wt. calculated for $C_{64}H_{58}O_{15}$: 1067.13, Found: 1090.52 (M^++23 for Na).

Characterization data for compound **9**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +17.8; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.27 (1 H, t, *J* 2.2 Hz), 3.41 (1 H, dd, *J* 1.5, 10.8 Hz), 3.50 (1 H, dd, *J* 3.7, 9.3 Hz), 3.56 (1 H, d, *J* 9.8 Hz), 3.62-3.78 (2 H, m), 3.93 (1 H, d, *J* 2.5 Hz), 3.94 (1 H, ABq, *J* 8.8 Hz), 4.15 (2 H, d, *J* 2.2 Hz), 4.21-4.46 (3 H, m), 4.55-5.10 (7 H, m), 5.40-5.68 (3 H, m), 7.12-7.58 (27 H, m), 7.75-8.05 (8 H, m); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 54.7, 63.1, 67.3, 69.8, 70.1, 71.8, 72.2, 73.0, 73.2, 73.6, 74.7, 75.3, 77.1, 78.3, 78.8, 79.7, 95.6, 100.3, 127.1-129.7, 132.9, 133.1, 133.2, 133.3, 137.8, 138.2, 139.2, 164.7, 165.0, 165.7, 166.0; Mol. Wt. calculated for $C_{64}H_{58}O_{15}$: 1067.13, Found: 1090.52 (M^++23 for Na).

Characterization data for compound **11**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +25.6; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.47 (1 H, t, *J* 2.4 Hz), 3.30-3.68 (5 H, m), 3.80 (1 H, t, *J* 8.2 Hz), 4.14-4.85 (12 H, m), 5.35 (1 H, d, *J* 7.8 Hz) 5.59 (1 H, dd, *J* 7.8, 9.2 Hz), 5.72-5.92 (2 H, m), 6.93-7.58 (27 H, m), 7.72-8.10 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 56.2, 63.0, 68.5, 69.4, 72.0, 72.5, 73.4, 73.4, 74.6, 74.8, 75.2, 75.3, 77.3, 78.9, 81.4, 84.1, 100.2, 100.3, 127.1-129.9, 133.0, 133.0, 133.1, 133.3, 137.8, 137.9, 138.3, 165.1, 165.1, 165.1, 165.8, 166.2; Mol. Wt. calculated for $C_{64}H_{58}O_{15}$: 1067.13, Found: 1090.08 (M^++23 for Na).

Characterization data for compound **13**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = -18.8; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.17, 1.38 (6 H, 2s), 2.40 (1 H, t, *J* 2.4 Hz), 3.65 (1 H, dd, *J* 6.6, 10.3 Hz), 3.87 (1 H, dd, *J* 7.6, 10.1 Hz), 4.04 (1 H, q, *J* 2.4 Hz), 4.15 (2 H, m), 4.31 (1 H, t, *J* 7.1 Hz), 4.40-4.72 (4 H, m), 4.91 (1 H, d, *J* 7.9 Hz), 5.17 (1 H, s), 5.56 (1 H, dd, *J* 7.8, 9.6 Hz), 5.68 (1 H, t, *J* 9.8 Hz), 5.91 (1 H, t, *J* 9.6 Hz), 7.21-7.62 (12 H, m), 7.76-8.10 (8 H, m) ; ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 24.6, 26.2, 53.9, 63.0, 69.6, 69.7, 71.6, 72.3, 72.8, 74.7, 78.7, 81.5, 84.9, 85.0 100.7, 106.4, 112.3, 128.20-129.81, 133.1, 133.2, 133.2, 133.4, 165.0, 165.1, 165.8, 166.1; Mol. Wt. calculated for $C_{45}H_{42}O_{14}$: 806.80, Found: 829.26 (M^++23 for Na).

Characterization data for compound **15**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +18.8; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.47 (1 H, t, *J* 2.3 Hz), 3.48-3.69 (2 H, m), 3.75-4.12 (4 H, m), 4.15-4.87 (10 H, m), 4.48-5.16 (3 H, m), 5.69-5.76 (1 H, m), 5.87 (1 H, dd, *J* = 3.2, 10.1 Hz), 6.09 (1 H, t, *J* = 10.1 Hz), 7.10-7.65 (27 H, m), 7.78-8.15 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.6, 62.7, 66.7, 66.8, 68.9, 70.0, 70.2, 70.6, 73.0, 75.0, 75.0, 75.7, 77.6, 78.9, 79.7, 81.9, 95.0, 97.7, 127.4-130.0, 133.0, 133.1, 133.4, 133.4, 138.0, 138.1, 138.7, 165.2, 165.4, 165.4, 166.1; Mol. Wt. calculated for $C_{64}H_{58}O_{15}$: 1067.13, Found: 1090.52 (M^++23 for Na).

Characterization data for compound **17**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +89.8; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.30 (1 H, t, *J* 2.1 Hz), 3.35 (1 H, d, *J* 10.3 Hz), 3.45 (1 H, dd, *J* 3.6, 9.9 Hz), 3.67-3.98 (3 H, m), 4.09-5.03 (14 H, m), 5.61 (1 H, dd, *J* 3.32, 10.4 Hz), 5.84 (1 H, dd, *J* 8.1, 10.4 Hz), 5.97 (1 H, d, *J* 2.5 Hz), 7.05-7.68 (27 H, m), 7.72-8.18 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.3, 61.9, 68.0, 68.3, 69.7, 70.2, 71.3, 71.5, 72.9, 74.7, 74.7, 75.5, 77.2, 78.9, 79.3, 81.7, 94.9, 101.9, 127.4-130.0, 133.1, 133.3, 133.3, 133.6, 137.9, 138.1, 138.7, 165.1, 165.5, 165.6, 166.0; Mol. Wt. calculated for $C_{64}H_{58}O_{15}$: 1067.13, Found: 1090.52 (M^++23 for Na).

Characterization data for compound **18**: $[\alpha]_D$($CHCl_3$, *c* 0.8) = +40.0; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.30 (1 H, t, *J* 2.3 Hz), 3.51 (2 H, ABq, *J* 10.6 Hz), 3.55 (1 H, dd, *J* 3.9, 9.5 Hz), 3.69 (1 H, dd, *J* 2.7, 10.4 Hz), 3.85-4.10 (3 H, m), 4.17 (2 H, d, *J* 2.3 Hz), 4.23-4.48 (3 H, m), 4.61-4.84 (4 H, m), 4.98 (2 H, ABq, *J* 11.2 Hz), 5.01 (1 H, d, *J* 3.6 Hz), 5.30 (1 H, dd, *J* 3.4, 10.4 Hz), 5.69 (1 H, dd, *J* 8.0, 10.4 Hz), 5.85 (1 H, d, *J* 3.0 Hz), 7.12-7.61 (27 H, m), 7.70-8.08 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.7, 61.3, 67.3, 67.7, 70.1, 70.2, 70.9, 71.8, 73.2, 73.6, 74.7, 75.3, 76.5, 78.2, 78.8, 79.6, 95.7, 100.4, 127.1-129.8, 133.1,

133.2, 133.3, 133.4, 137.7, 138.1, 139.3, 164.8, 165.3, 165.3, 165.8; Mol. Wt. calculated for $C_{64}H_{58}O_{15}$: 1067.13, Found: 1090.02 (M^++23 for Na).

Characterization data for compound **19**: $[\alpha]_D$($CHCl_3$, *c* 1.2) = +49.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.19, 1.38 (6 H, 2s), 2.40 (1 H, t, *J* 2.3 Hz), 3.68 (1 H, dd, *J* 6.8, 10.3 Hz), 3.84-4.00 (1 H, m), 4.06 (2 H, dd, *J* 2.4, 5.6 Hz), 4.23-4.48 (3 H, m), 4.51-4.75 (3 H, m), 4.89 (1 H, d, *J* 7.9 Hz), 5.18 (1 H, s), 5.60 (1 H, dd, *J* 3.2, 10.3 Hz), 5.81 (1 H, dd, *J* 7.9, 10.5 Hz), 6.00 (1 H, d, *J* 3.1 Hz), 7.20-7.65 (12 H, m), 7.75-8.13 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 24.7, 26.3, 53.9, 61.9, 68.0, 69.4, 69.9, 71.4, 71.7, 74.7, 78.7, 81.6, 84.9, 85.0, 101.2, 106.4, 112.4, 128.2-130.1, 133.2, 133.3, 133.3, 133.6, 165.1, 165.5, 165.6, 166.0; Mol. Wt. calculated for $C_{45}H_{42}O_{14}$: 806.80, Found: 829.26 (M^++23 for Na).

Characterization data for compound **21**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +62.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.38 (1 H, t, *J* 2.4 Hz), 3.17 (3 H, s), 3.24 (1 H, t, *J* 9.4 Hz), 3.37 (1 H, dd, *J* 9.6 Hz), 3.62-3.89 (3 H, m), 4.06 (2 H, dd, *J* 2.4, 7.7 Hz), 4.13-4.28 (2 H, m), 4.42-5.00 (8 H, m), 5.64 (1 H, t, *J* 9.9 Hz), 5.65 (1 H, dd, *J* 9.7, 19.4 Hz), 5.91 (1 H, t, *J* 9.6 Hz), 7.20-7.57 (22 H, m), 7.78-8.05 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.9, 59.7, 63.2, 68.5, 69.2, 69.7, 71.7, 72.1, 72.8, 73.2, 74.5, 75.4, 76.9, 79.6, 79.8, 81.6, 97.6, 101.3, 127.5-129.8, 133.1, 133.2, 133.2, 133.4, 137.9, 138.5, 164.9, 165.1, 165.8, 166.1; Mol. Wt. calculated for $C_{58}H_{54}O_{15}$: 991.04, Found: 1014.65 (M^++23 for Na).

Characterization data for compound **23**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +65.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.20, 1.36 (6 H, 2s), 2.45 (1 H, t, *J* 2.4 Hz), 3.32 (3 H, s), 3.65-3.86 (3 H, m), 4.04-4.20 (4 H, m), 4.21 (2 H, dd, *J* 2.4, 4.5 Hz), 4.46 (1 H, dd, *J* 5.2, 12.2 Hz), 4.67 (1 H, dd, *J* 3.1, 12.2 Hz), 4.86 (1 H, d, *J* 3.4 Hz), 5.19 (1 H, d, *J* 7.7 Hz), 5.56 (1 H, dd, *J* 7.9, 9.7 Hz), 5.67 (1 J. t, *J* 9.7 Hz), 5.92 (1 H, t, *J* 9.7 Hz), 7.20-7.59 (12 H, m), 7.81-8.05 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 26.3, 28.2, 55.6, 58.6, 63.0, 66.4, 69.2, 69.5, 71.8, 72.3, 72.8, 73.8, 74.7, 75.0, 79.0, 79.5, 98.9, 101.9, 109.0, 128.0-129.9, 132.92, 133.1, 133.2, 133.4, 165.0, 165.1, 165.8, 166.0; Mol. Wt. calculated for $C_{47}H_{46}O_{15}$: 850.85, Found: 873.60 (M^++23 for Na).

Characterization data for compound **24**: $[\alpha]_D$($CHCl_3$, *c* 0.9) = +86.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.39 (1 H, t, *J* 2.3 Hz), 3.17 (3 H, s), 3.24 (1 H, t, *J* 9.3 Hz), 3.34 (1 H, dd, *J* 3.6, 9.6 Hz), 3.65-3.90 (3 H, m), 4.13 (2 H, dd, *J* 2.5, 3.6 Hz), 4.22-4.74 (8 H, m), 4.91 (2 H, t, *J* 9.6 Hz), 5.61 (1 H, dd, *J* 3.4, 10.4 Hz), 5.85 (1 H, dd, *J* 3.2 Hz), 7.10-7.65 (22 H, m), 7.70-8.11 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.9, 59.7, 61.9, 68.1, 68.9, 69.3, 69.7, 71.3, 71.6, 73.2, 74.6, 75.4, 76.9, 79.7, 79.9, 81.7, 97.6, 102.0, 127.5-130.0, 133.1, 133.2, 133.2, 133.5, 138.0, 138.5, 165.1, 165.5, 165.5, 166.0; Mol. Wt. calculated for $C_{47}H_{46}O_{15}$: 850.85, Found: 873.60 (M^++23 for Na).

Characterization data for compound **25**: $[\alpha]_D$($CHCl_3$, *c* 0.9) = +128.9; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.20, 1.36 (6 H, 2s), 2.45 (1 H, t, *J* 2.4 Hz), 3.36 (3 H, s), 3.74-3.80 (2 H, m), 3.84 (1 H, dd, *J* 3.4 Hz), 4.06-4.18 (3 H, m), 4.22 (2H, dd, *J* 2.6, 5.1 Hz), 4.25-4.37 (1 H, m), 4.45 (1 H, dd, *J* 6.2, 11.1 Hz), 4.63 (1 H, dd, *J* 6.7, 11.2 Hz), 4.90 (1 H, d, *J* 3.2 Hz), 5.15 (1 H, d, *J* 7.8 Hz), 5.61 (1 H, dd, *J* 3.3, 10.4 Hz), 5.82 (1 H, dd, *J* 7.8, 10.3 Hz), 5.99 (1 H, d, *J* 3.0 Hz), 7.20-7.68 (12 H, m), 7.70-8.14 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 26.3, 28.2, 55.7, 58.7, 62.2, 66.4, 68.1, 69.2, 69.6, 71.5, 71.8, 73.8, 74.7, 75.0, 79.3, 79.5, 98.9, 102.4, 109.1, 128.0-130.1, 132.9, 133.2, 133.3, 133.5, 165.2, 165.6, 165.6, 166.0; Mol. Wt. calculated for $C_{47}H_{46}O_{15}$: 850.85, Found: 873.31 (M^++23 for Na).

Characterization data for compound **26**: $[\alpha]_D$($CHCl_3$, *c* 1.0) = +6.6; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.56 (1 H, t, *J* 2.3 Hz), 3.46 (3 H, s), 3.53 (2 H, dd, *J* 3.9, 9.7 Hz), 3.71-4.08 (4 H, m), 4.40-5.05 (10 H, m), 5.21 (1 H, d, *J* 1.5 Hz), 5.73 (1 H, dd, *J* 1.8, 3.3 Hz), 5.93 (1 H, dd, *J* 3.3, 10.0 Hz), 6.09 (1 H, t, *J* 10.0 Hz), 7.20-7.65 (22 H, m), 7.80-8.14 (8 H, m); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 55.2, 59.8, 62.8, 66.6,

67.0, 68.8, 69.5, 69.9, 70.3, 73.3, 75.1, 76.3, 75.5, 79.8, 80.1, 82.0, 97.6, 97.7, 127.5-129.9, 133.0, 133.1, 133.3, 133.4, 138.0, 138.5, 165.3, 165.4, 166.1; Mol. Wt. calculated for $C_{47}H_{54}O_{15}$: 991.04, Found: 1014.65 (M^++23 for Na).

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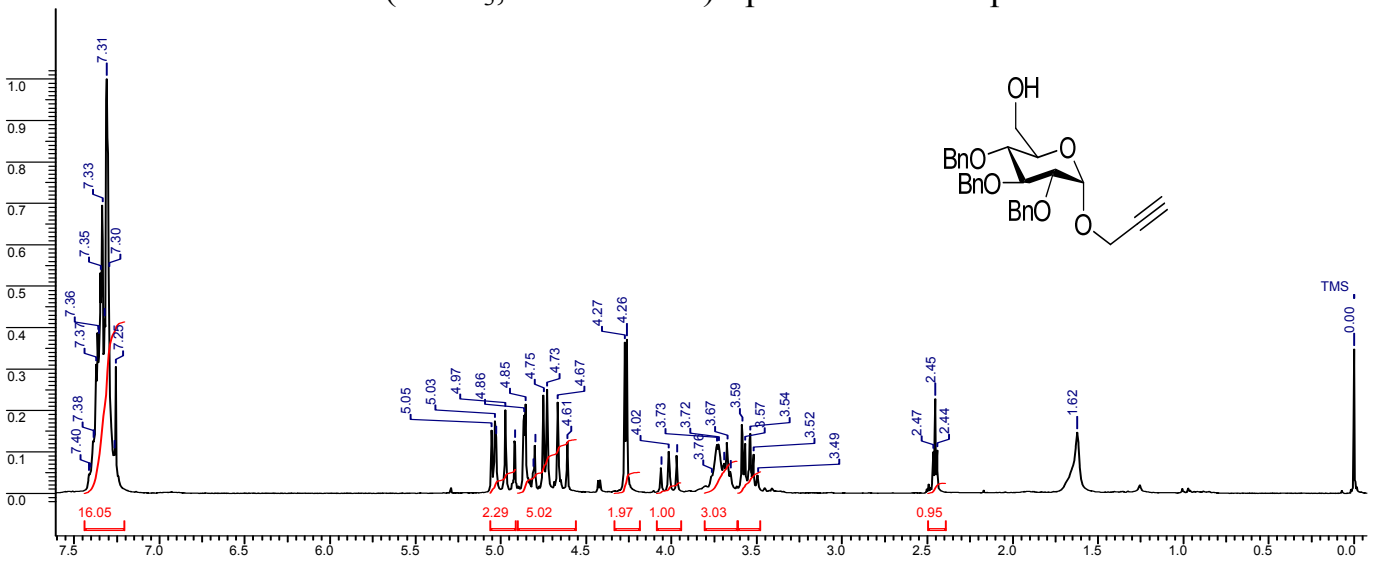
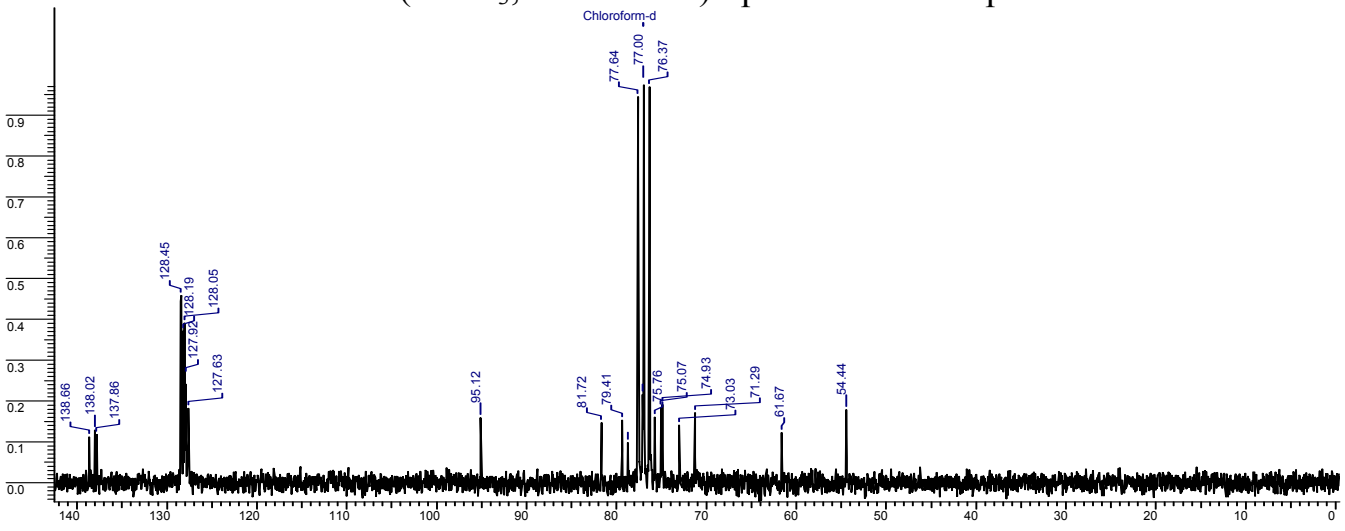
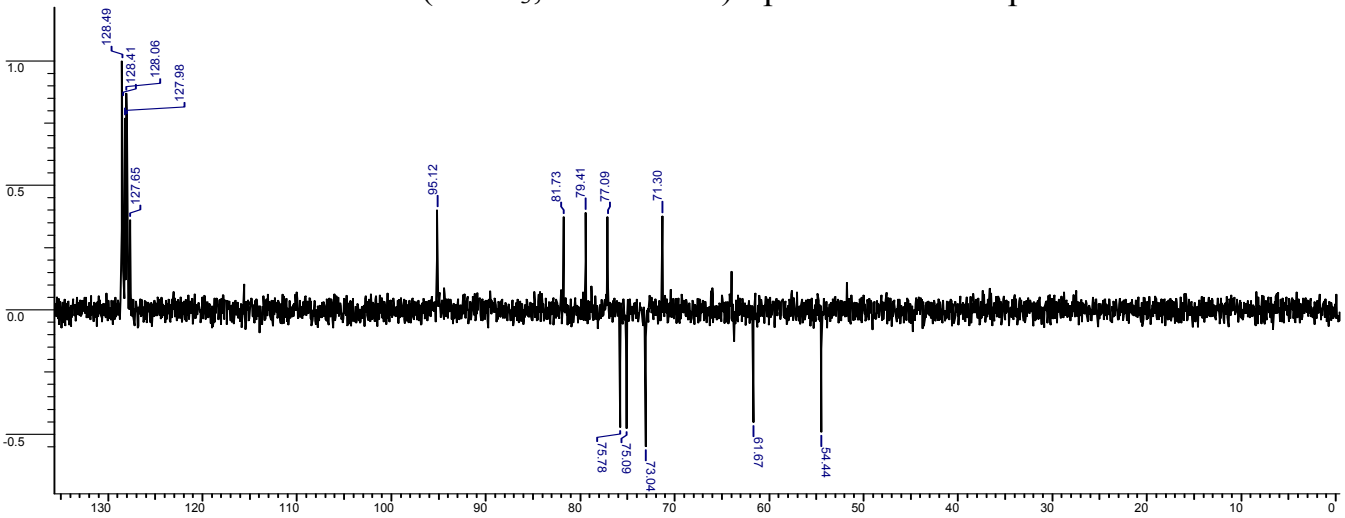
H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **6**



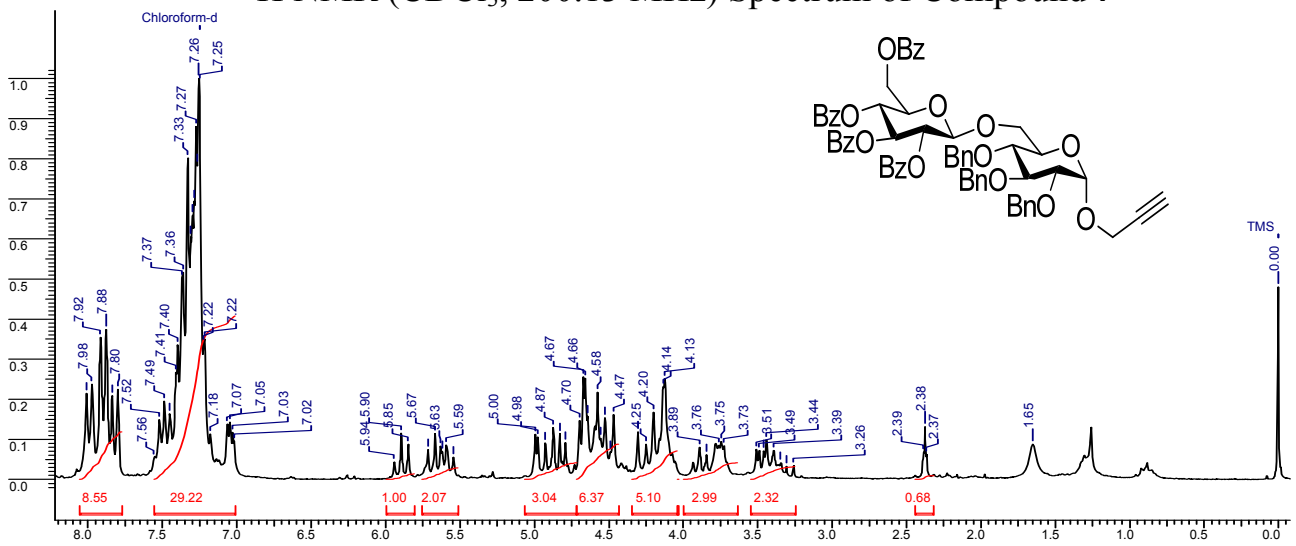
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **6**



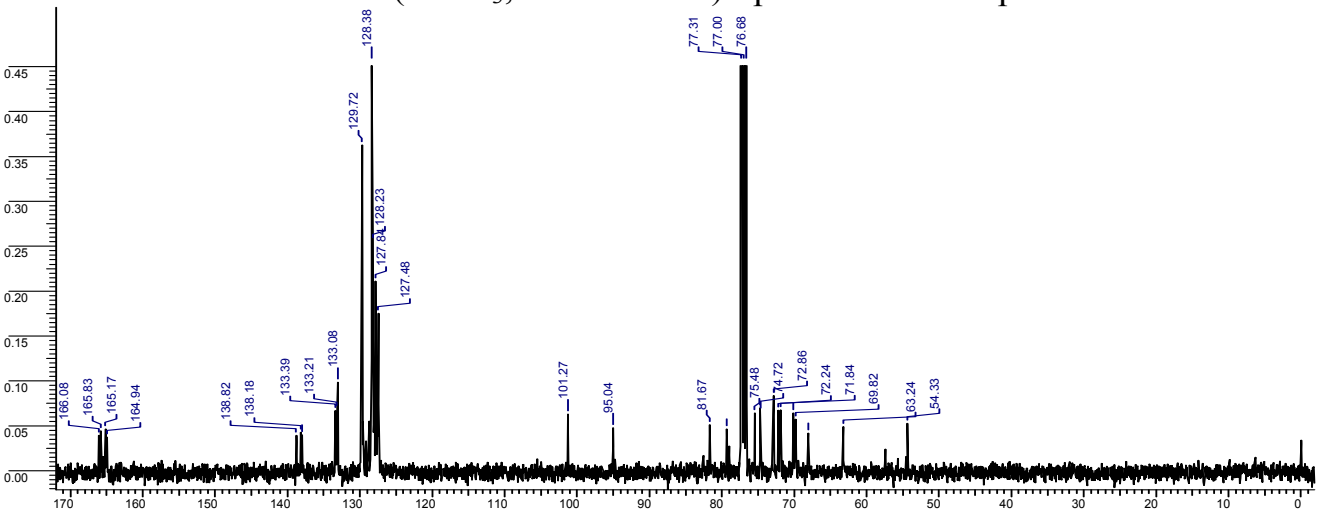
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **6**



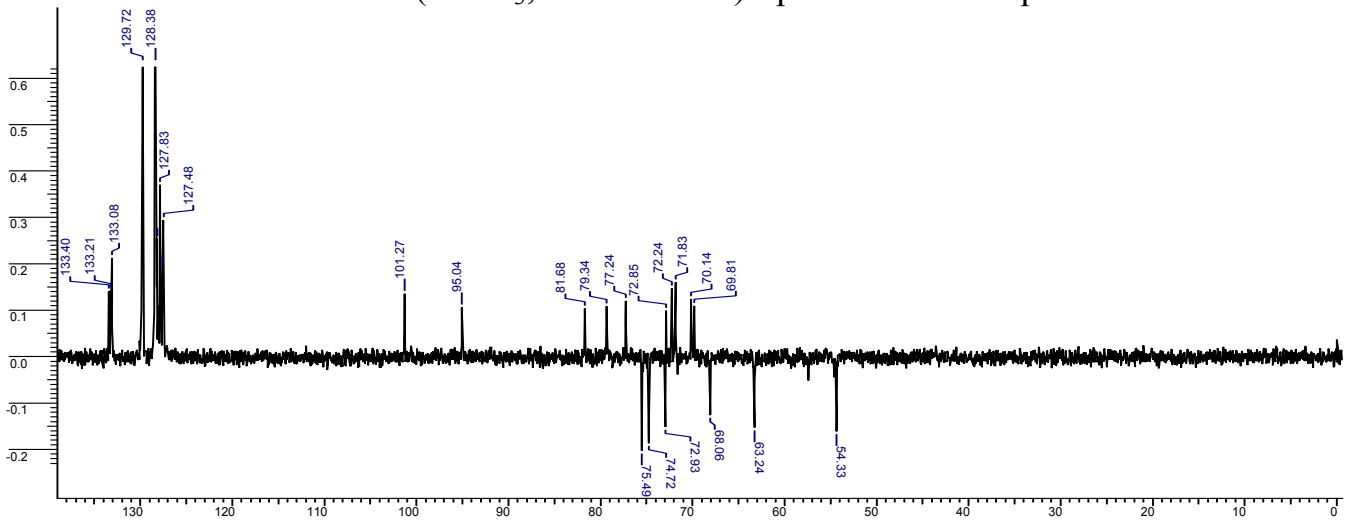
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **7**



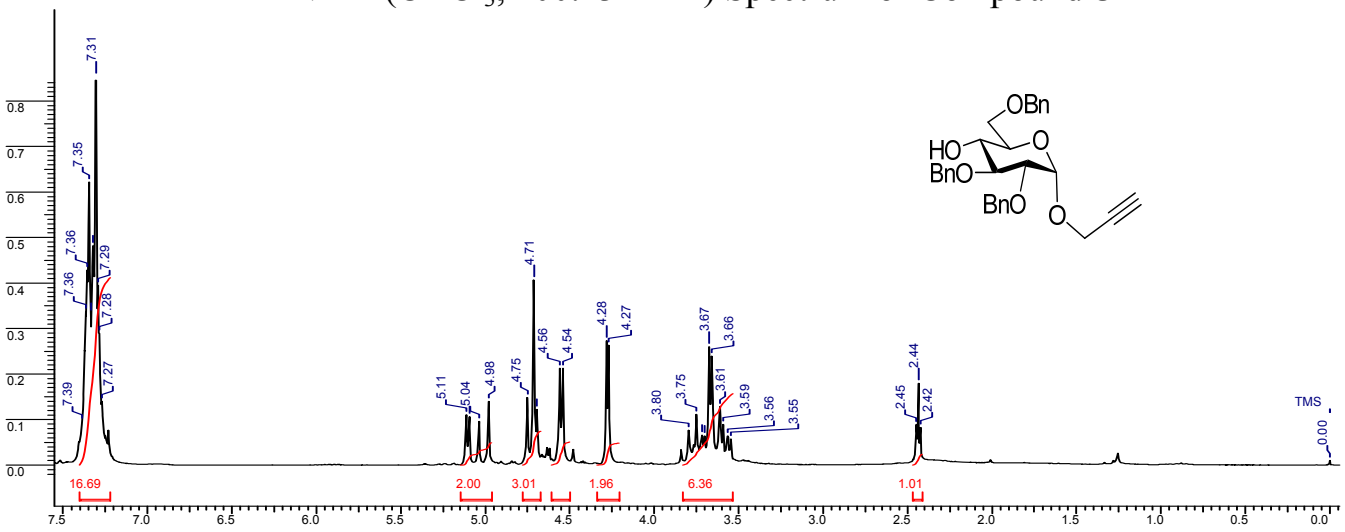
^{13}C NMR ($CDCl_3$, 100.61 MHz) Spectrum of Compound **7**



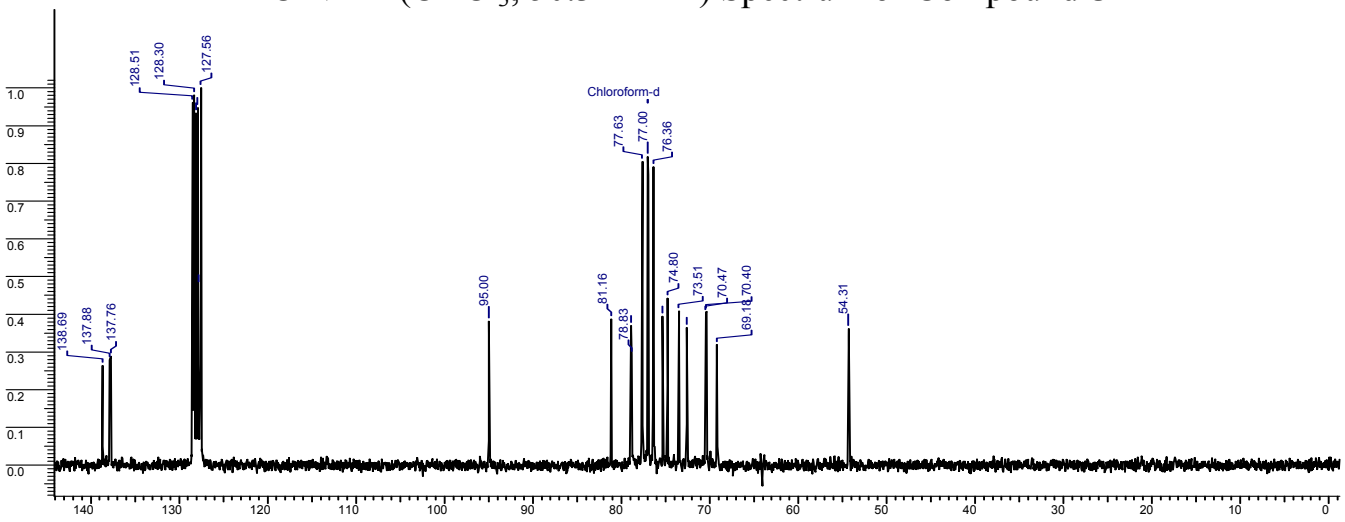
DEPT NMR ($CDCl_3$, 100.61 MHz) Spectrum of Compound **7**



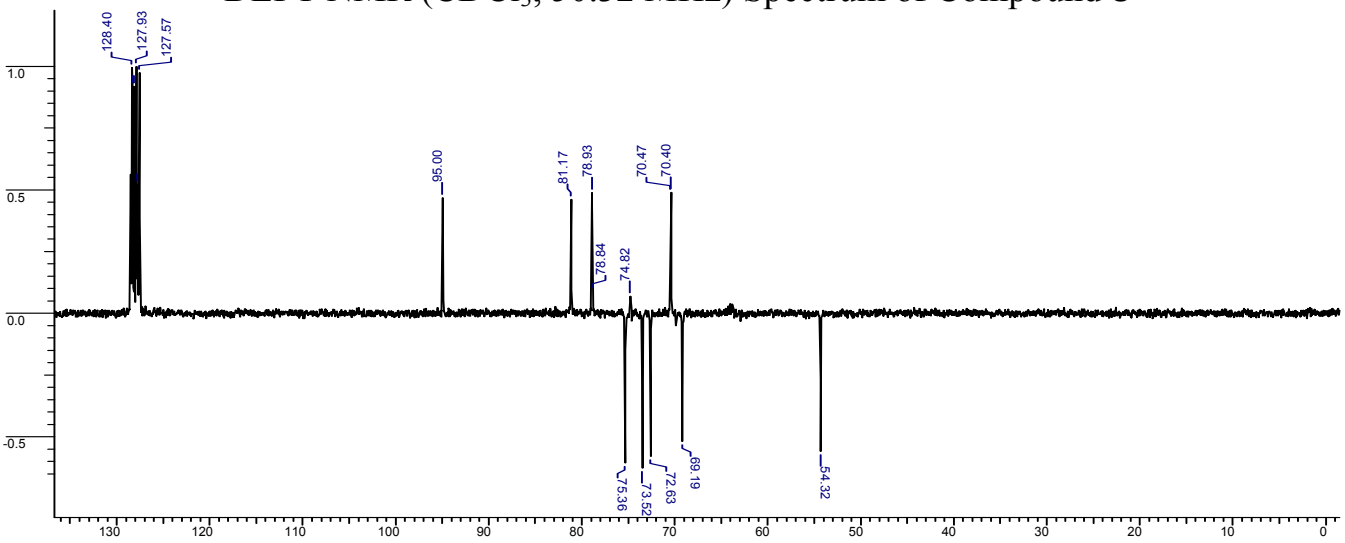
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **8**



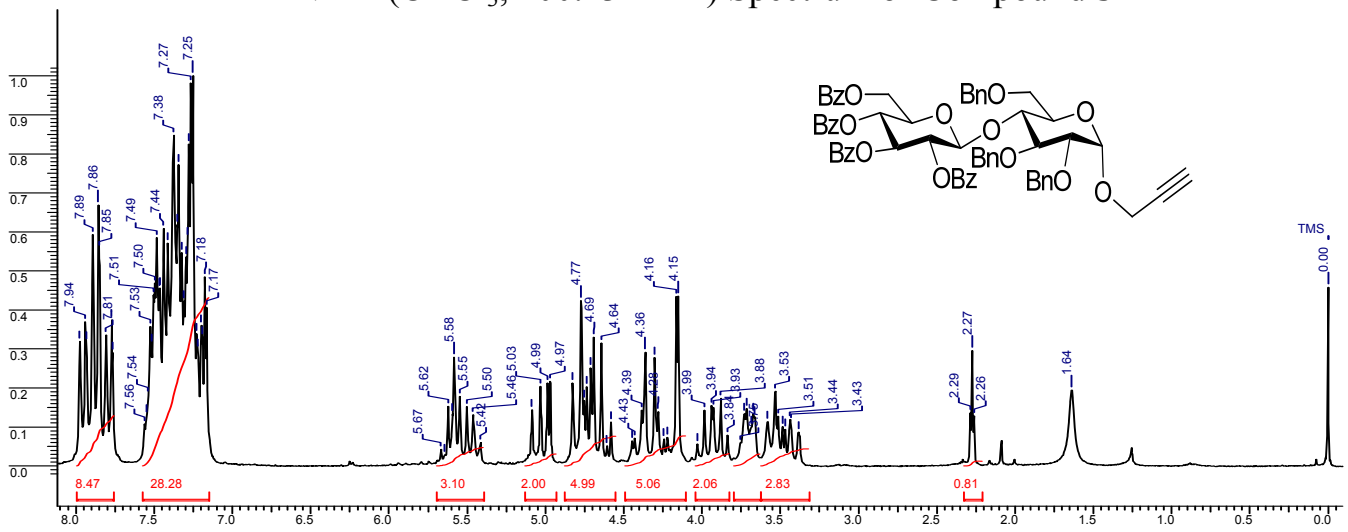
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **8**



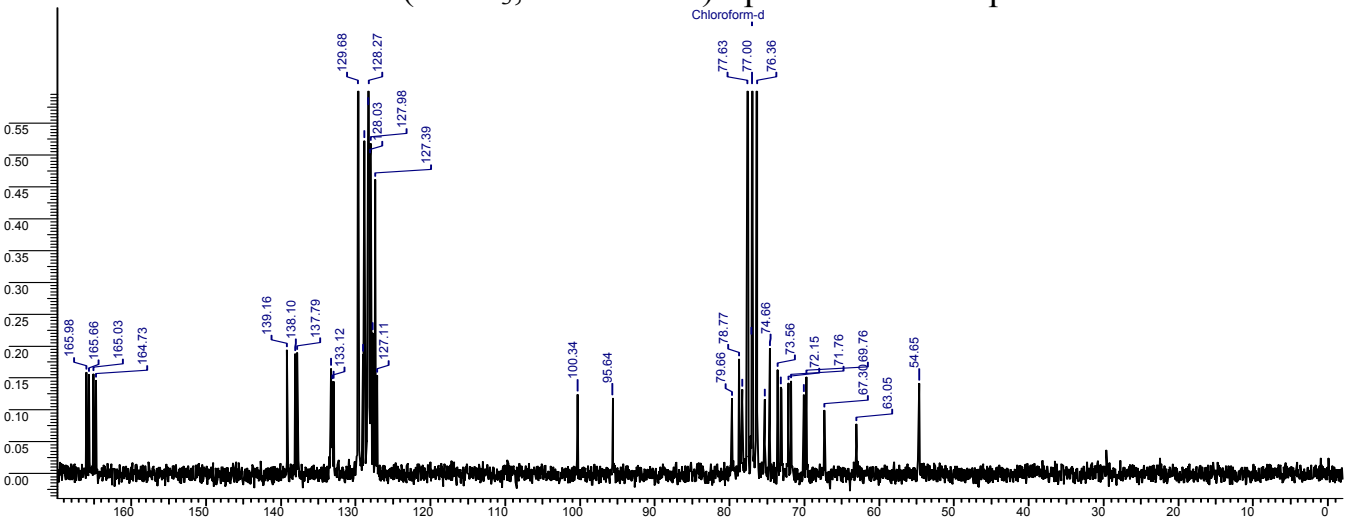
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **8**



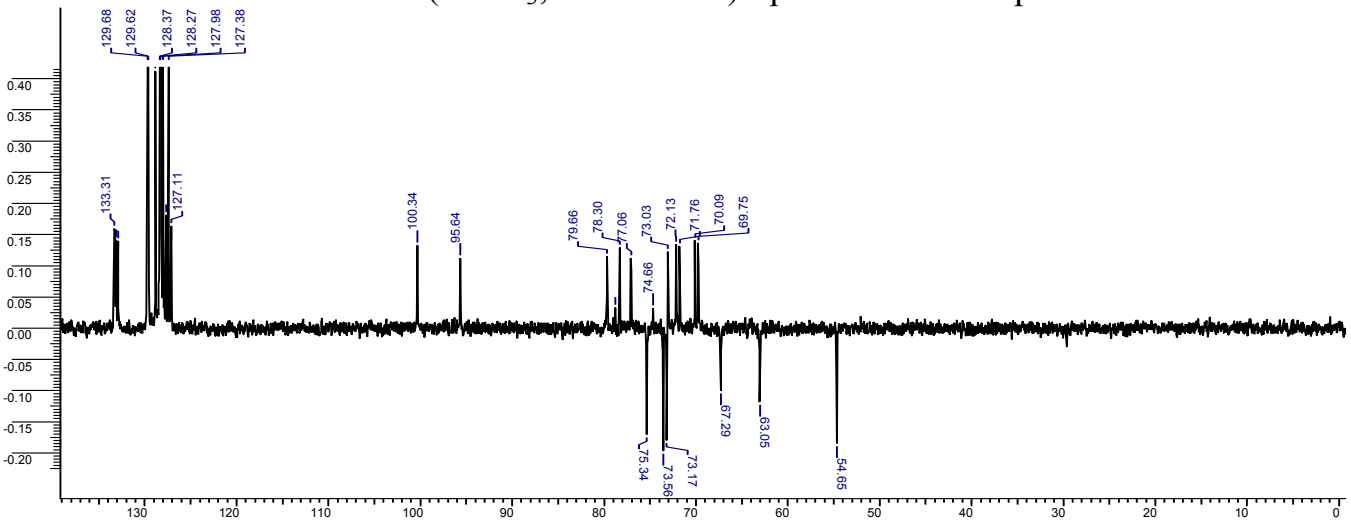
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **9**



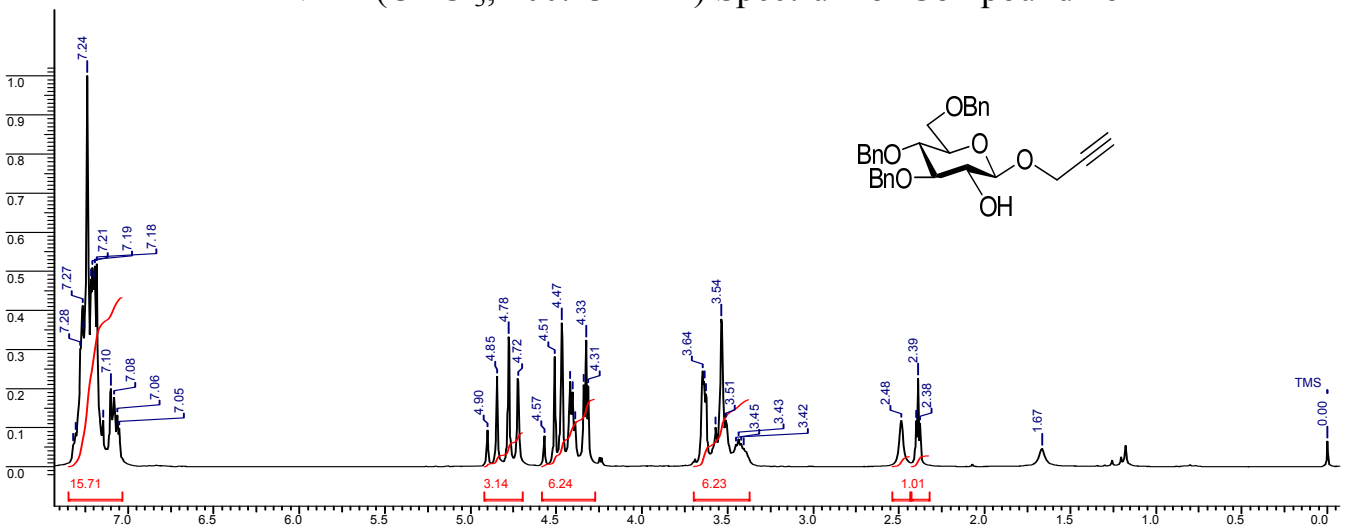
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **9**



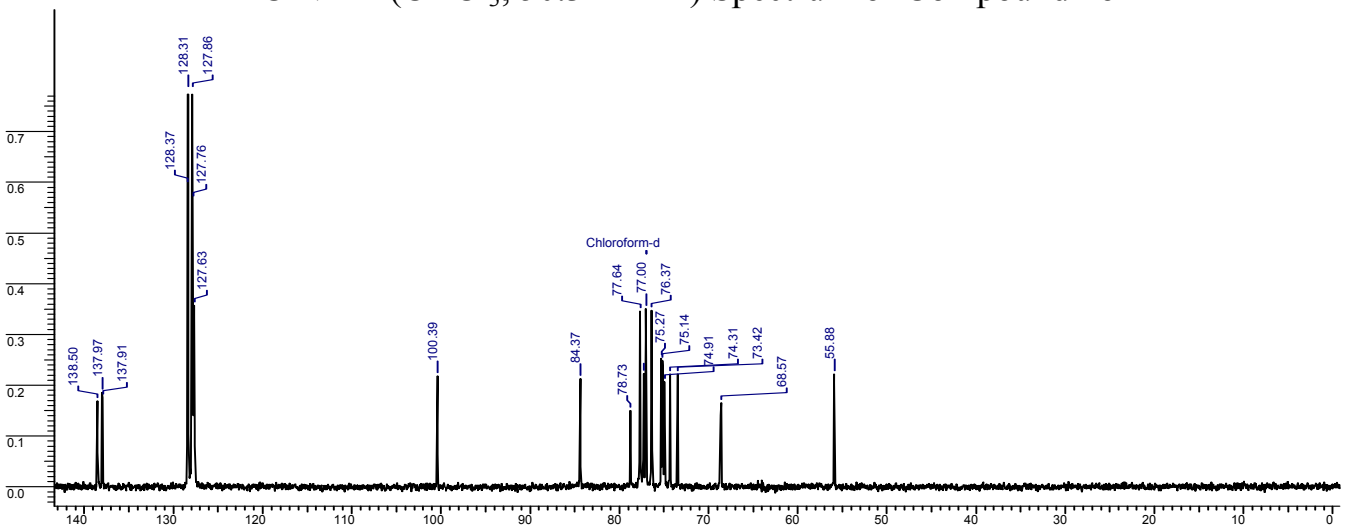
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **9**



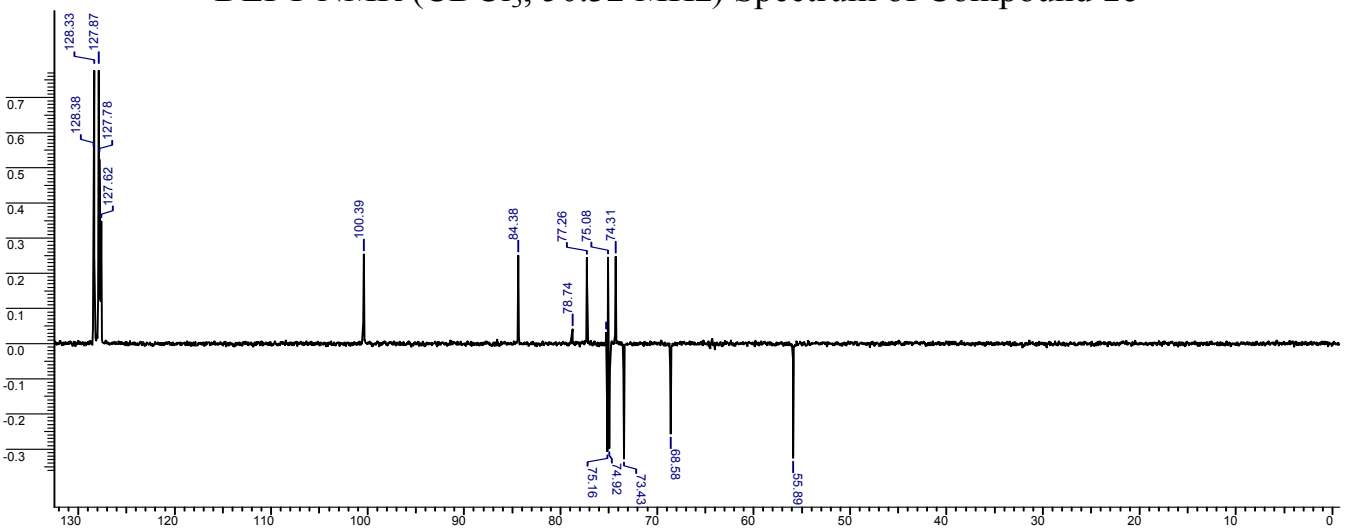
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **10**



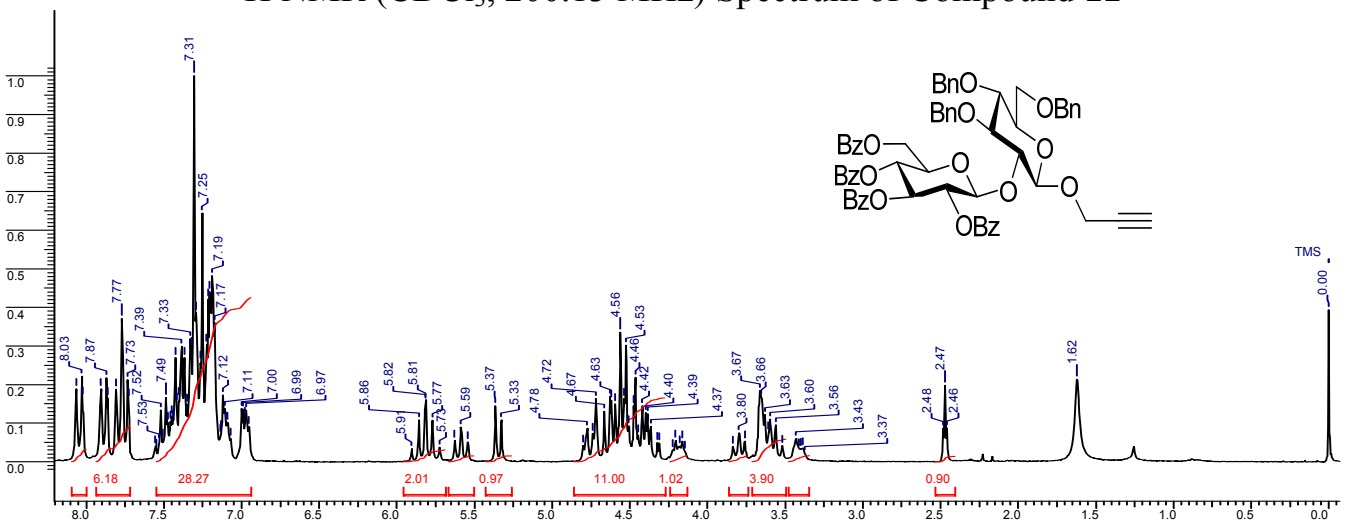
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **10**



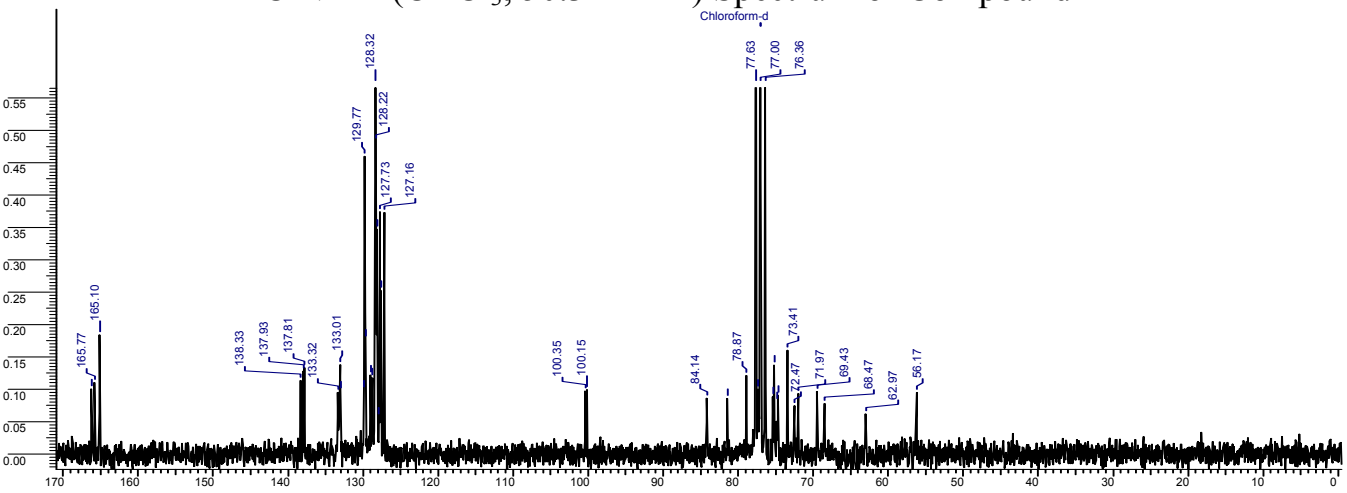
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **10**



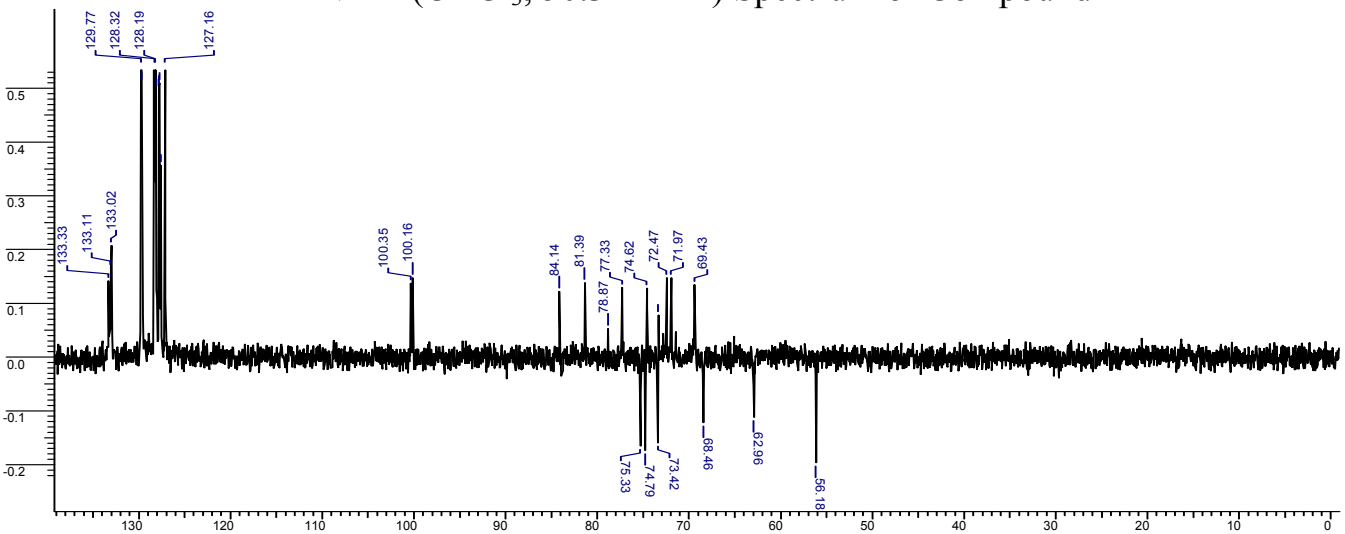
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **11**



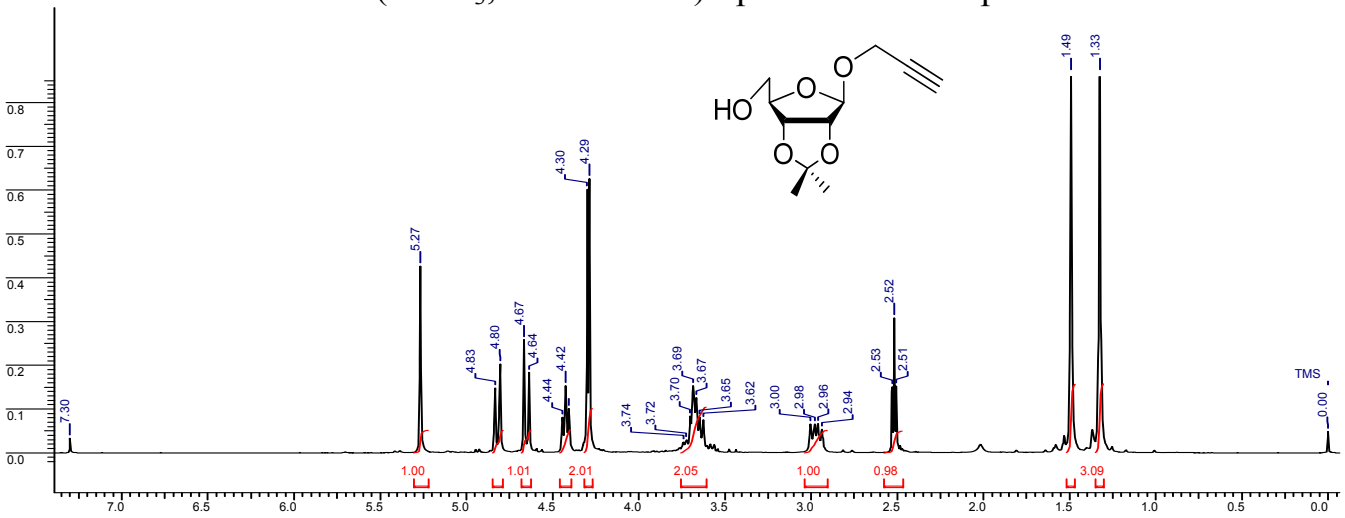
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **11**



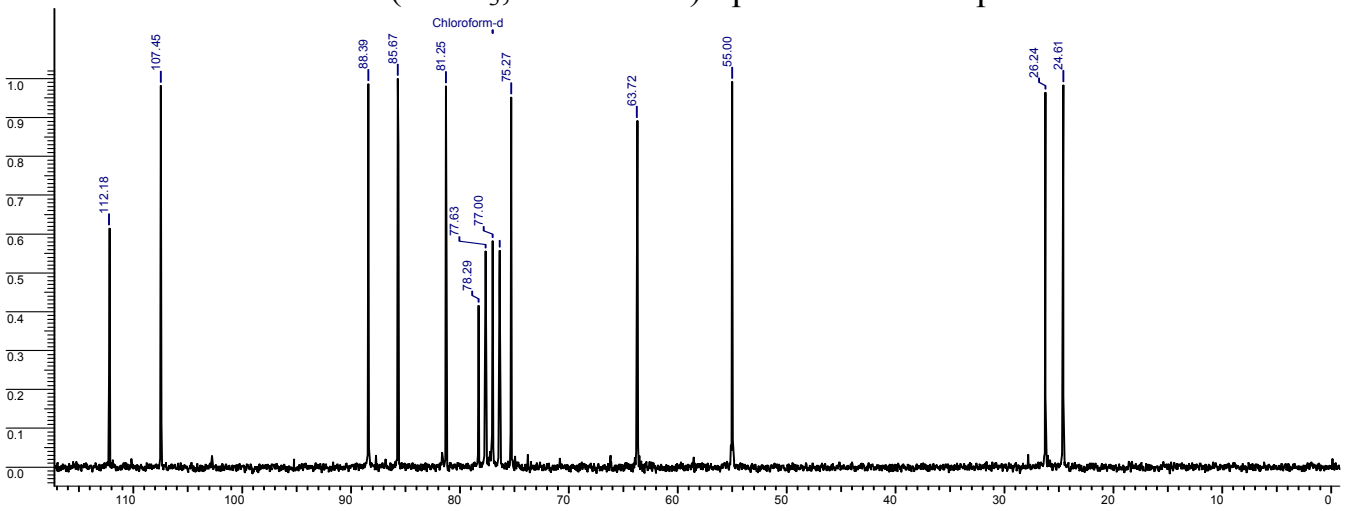
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **11**



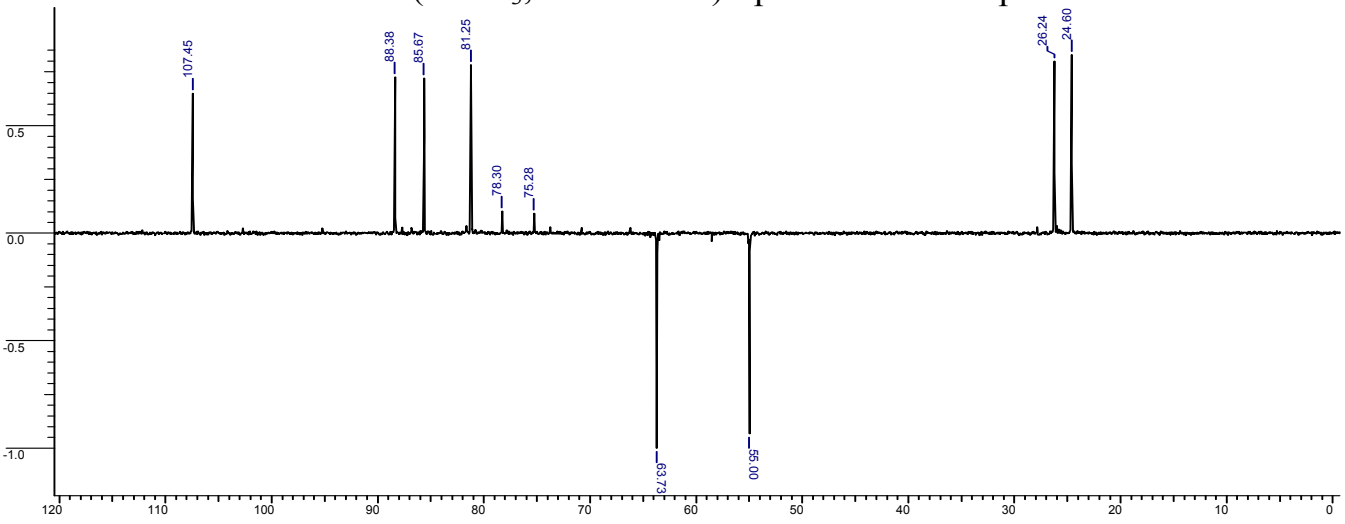
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **12**



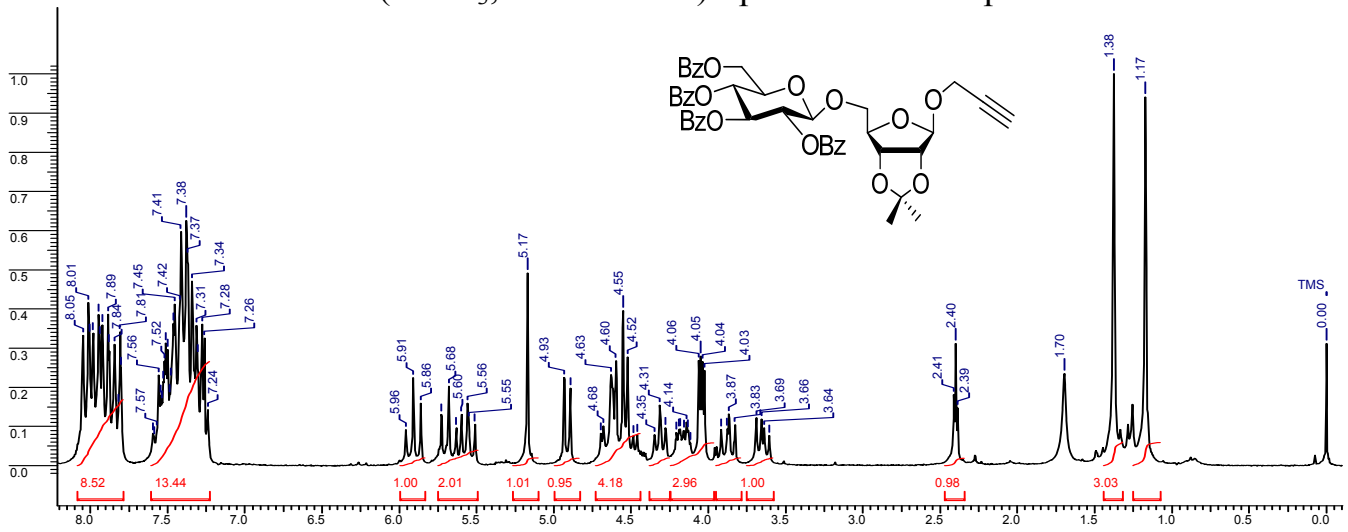
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **12**



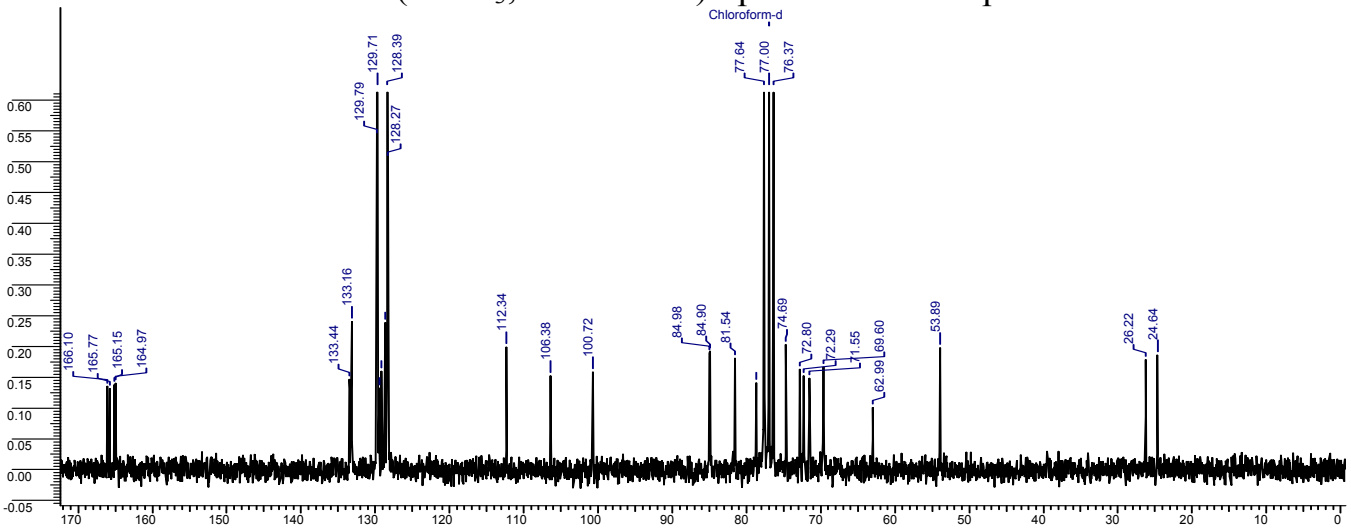
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **12**



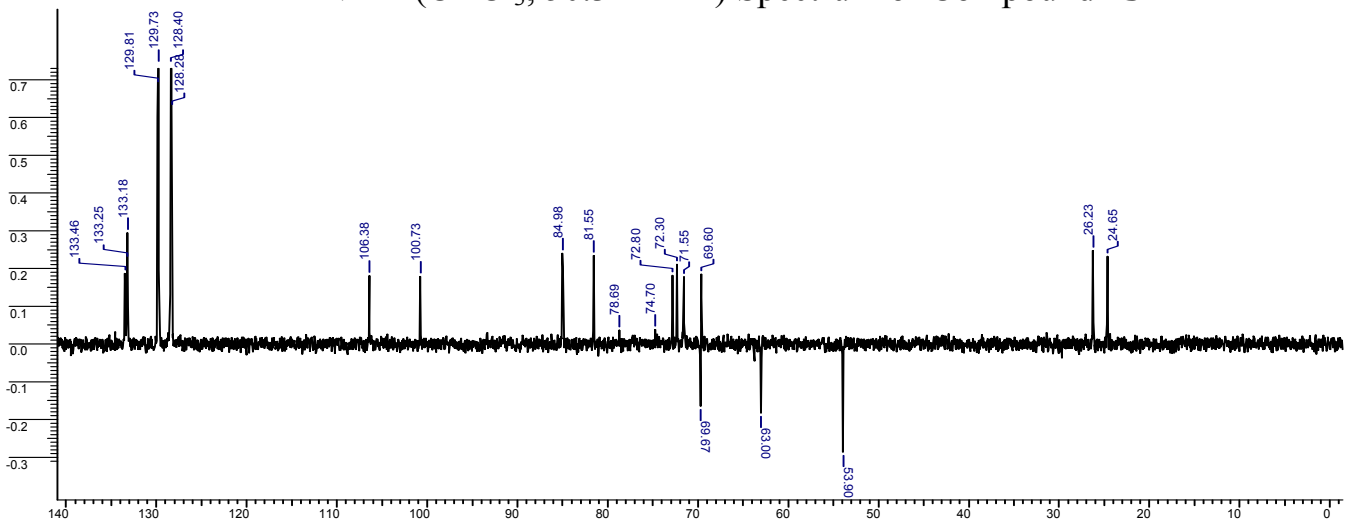
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **13**



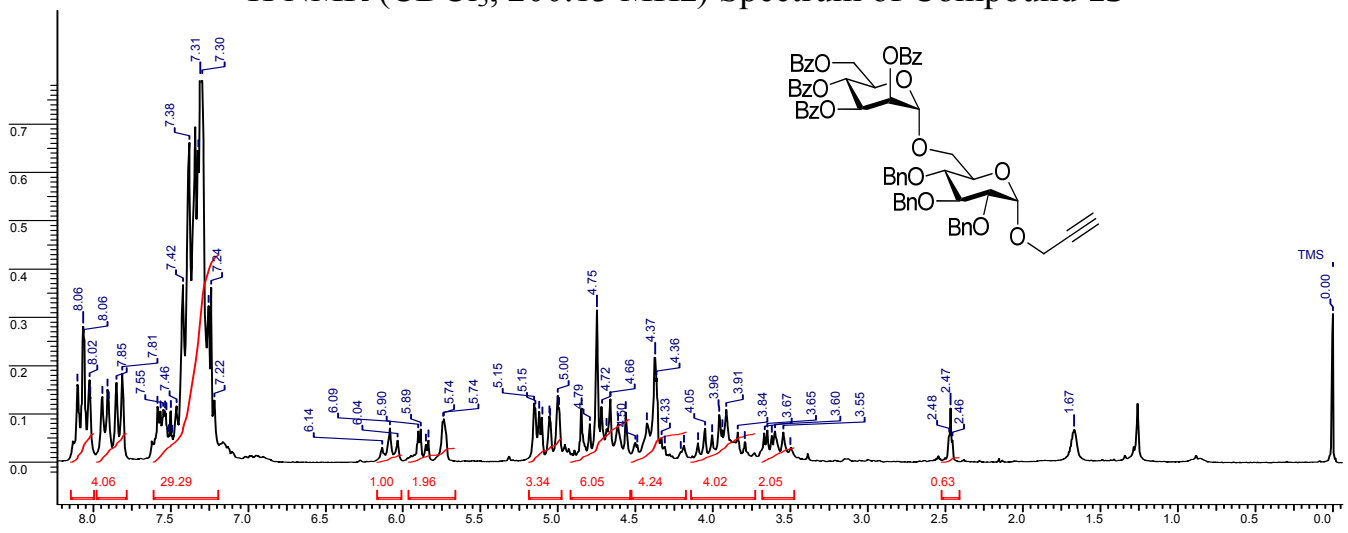
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **13**



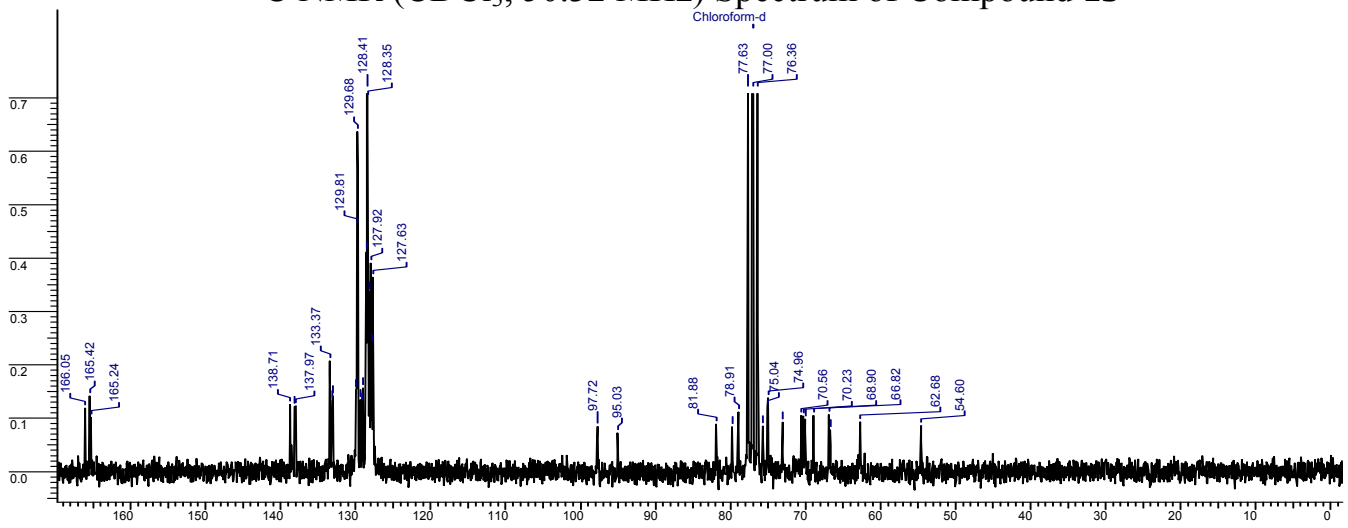
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **13**



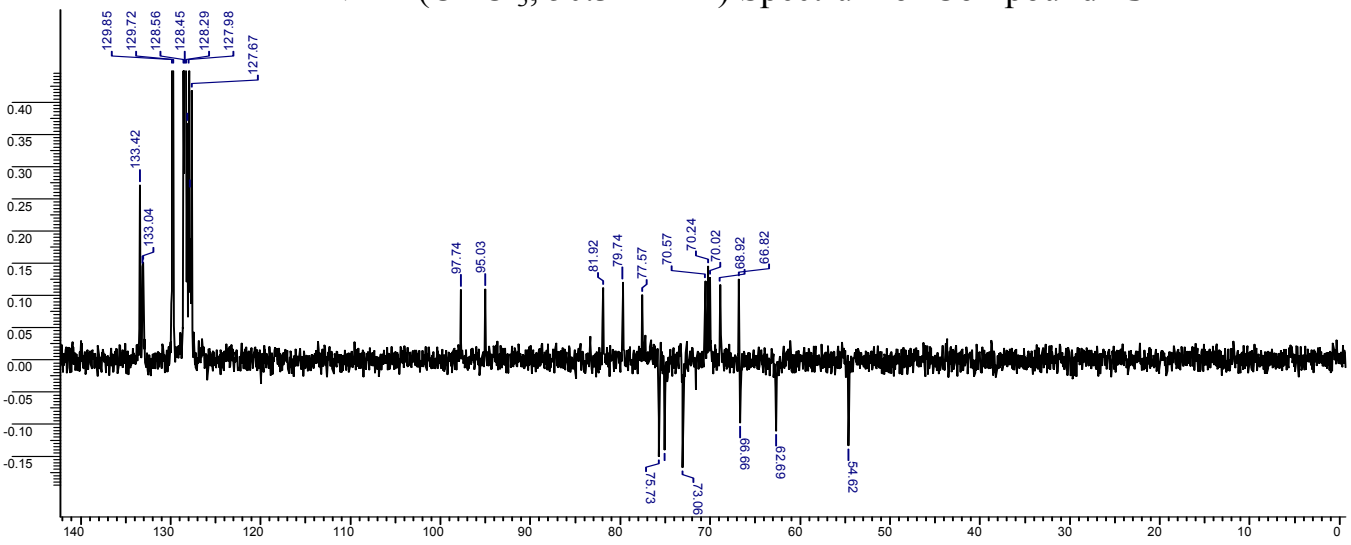
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **15**



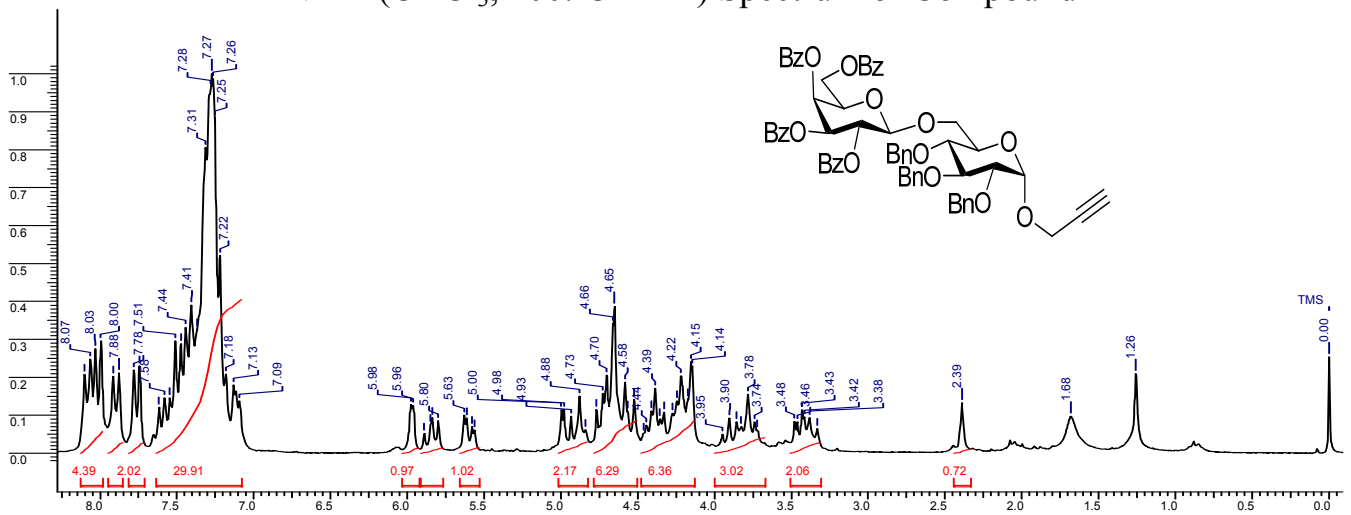
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **15**



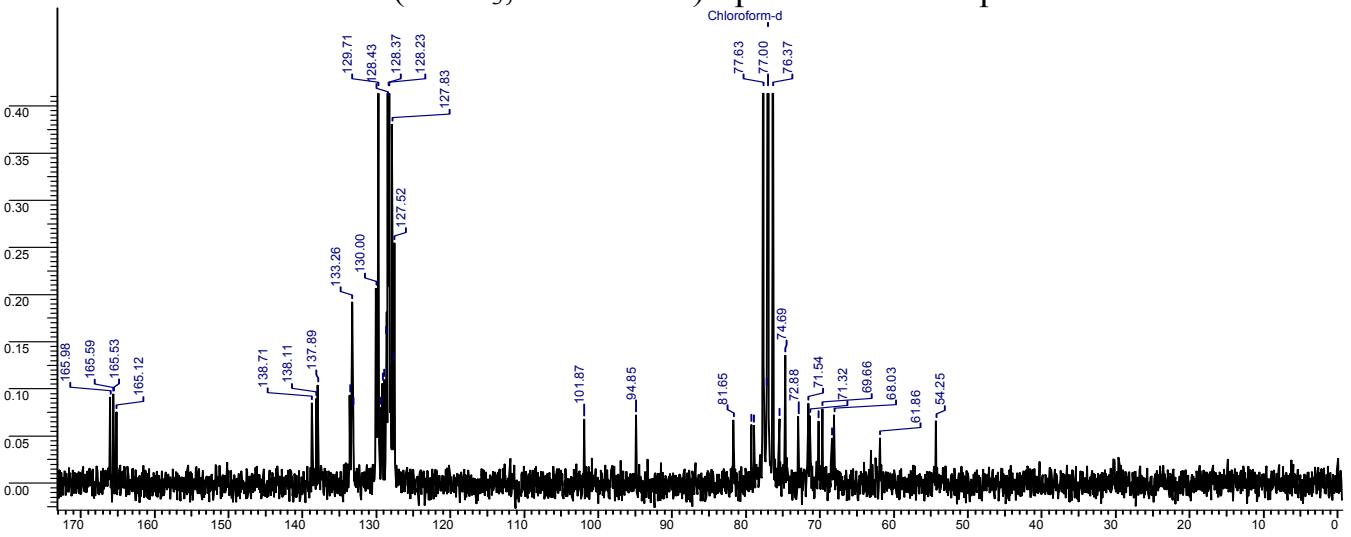
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **15**



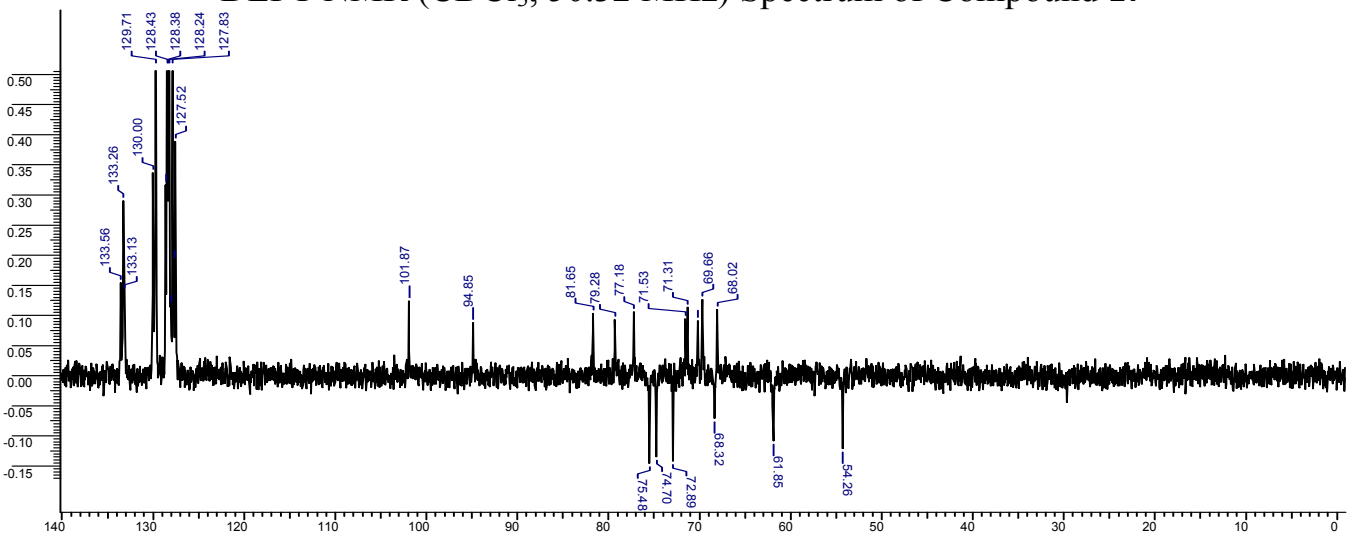
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **17**



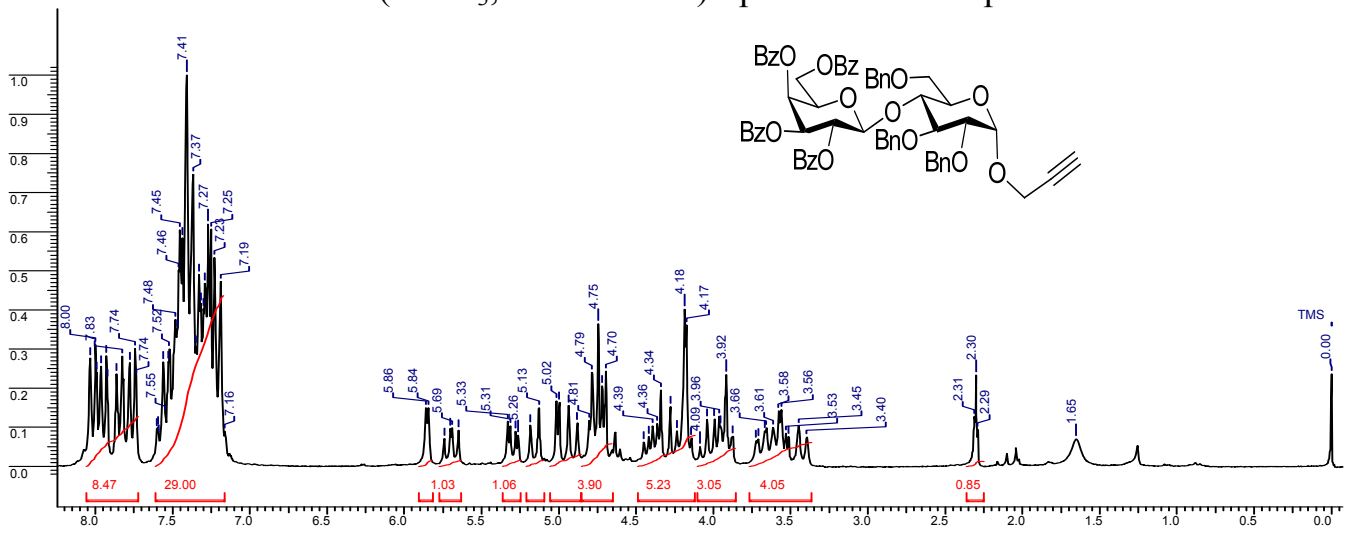
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **17**



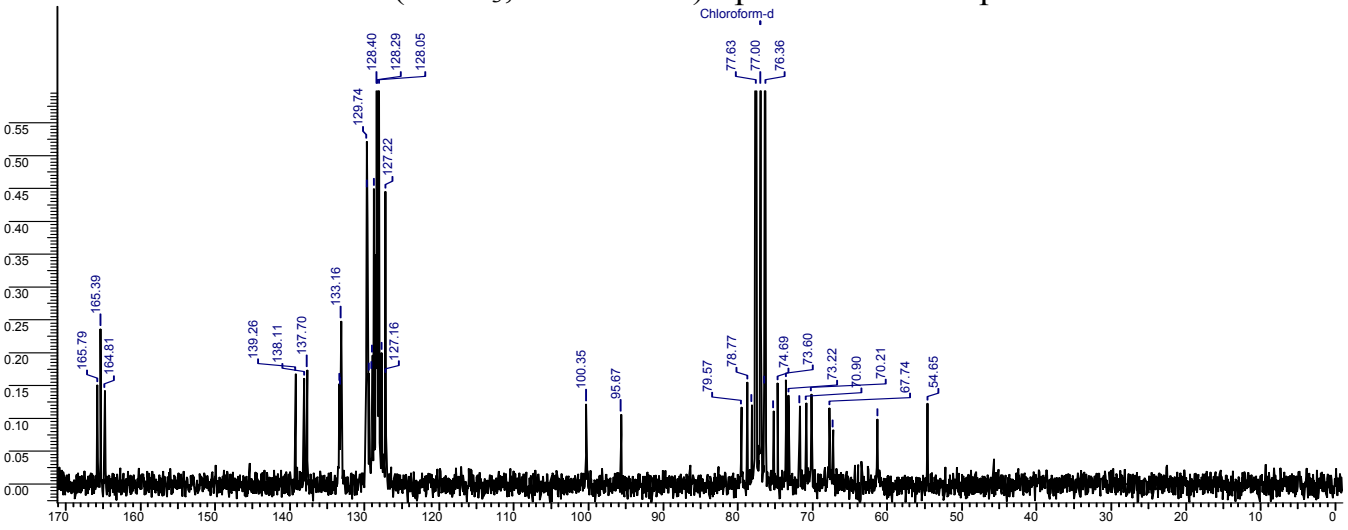
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **17**



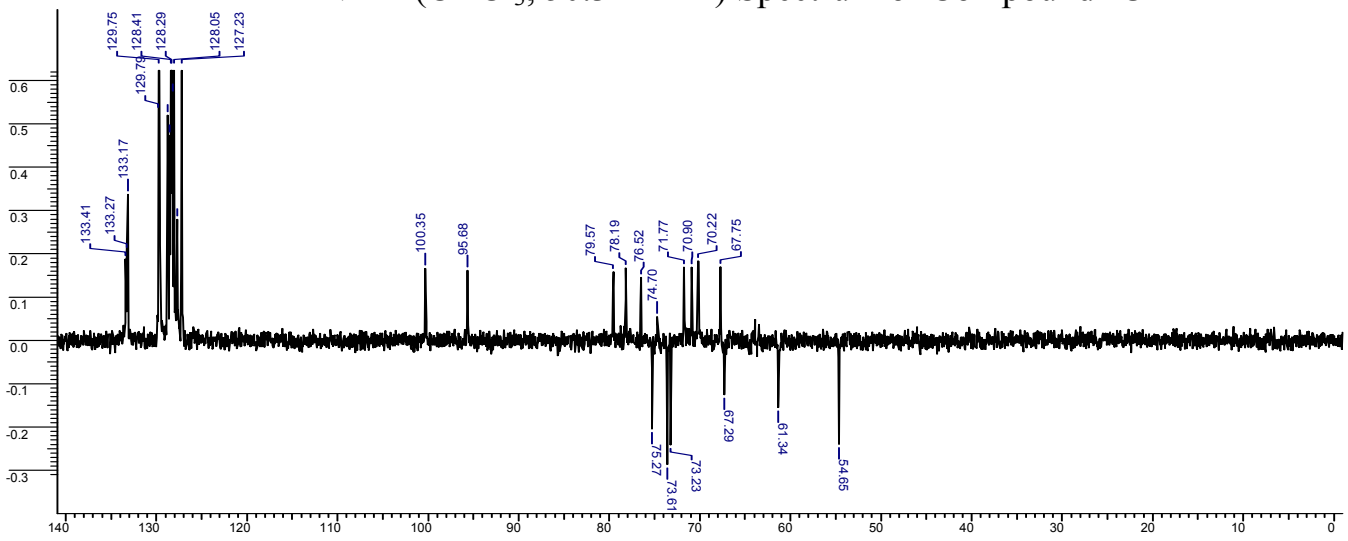
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **18**



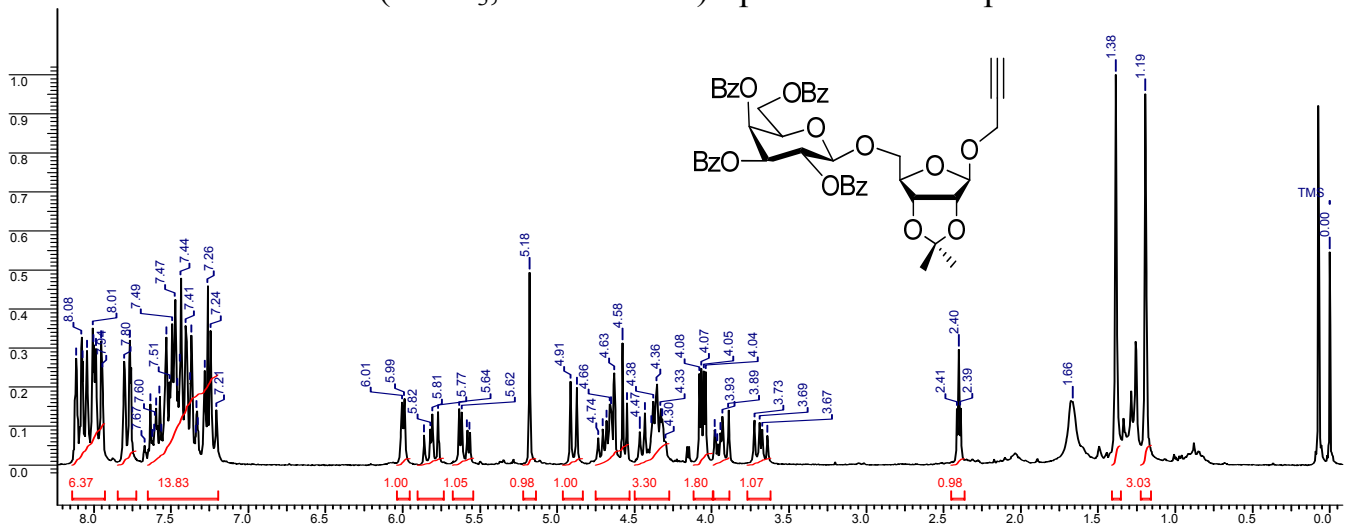
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **18**



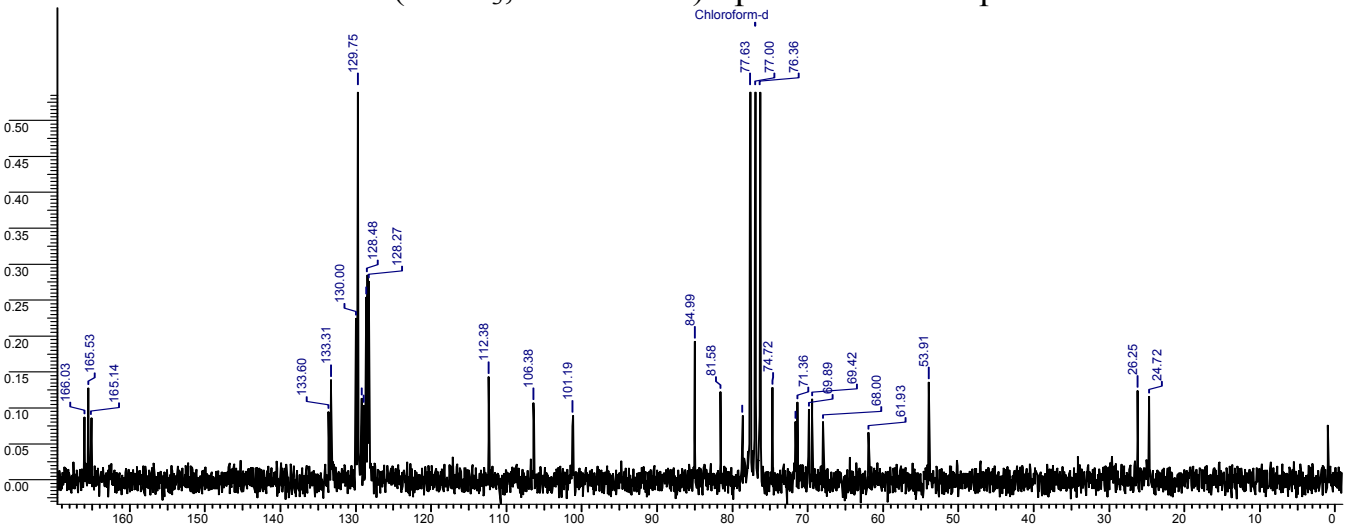
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **18**



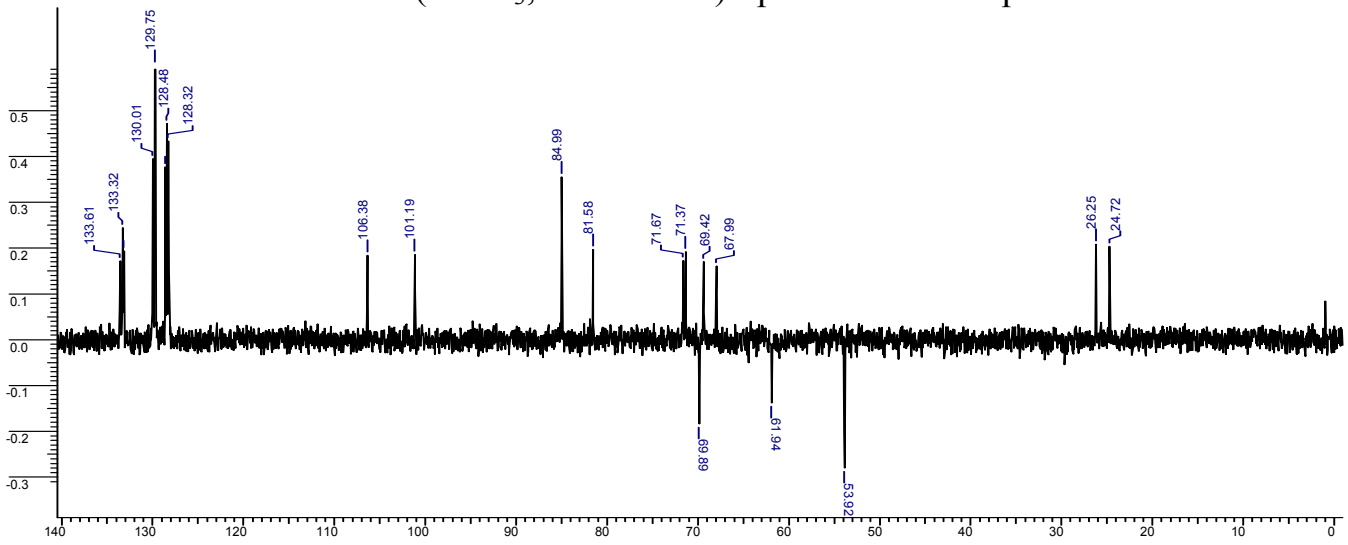
H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **19**



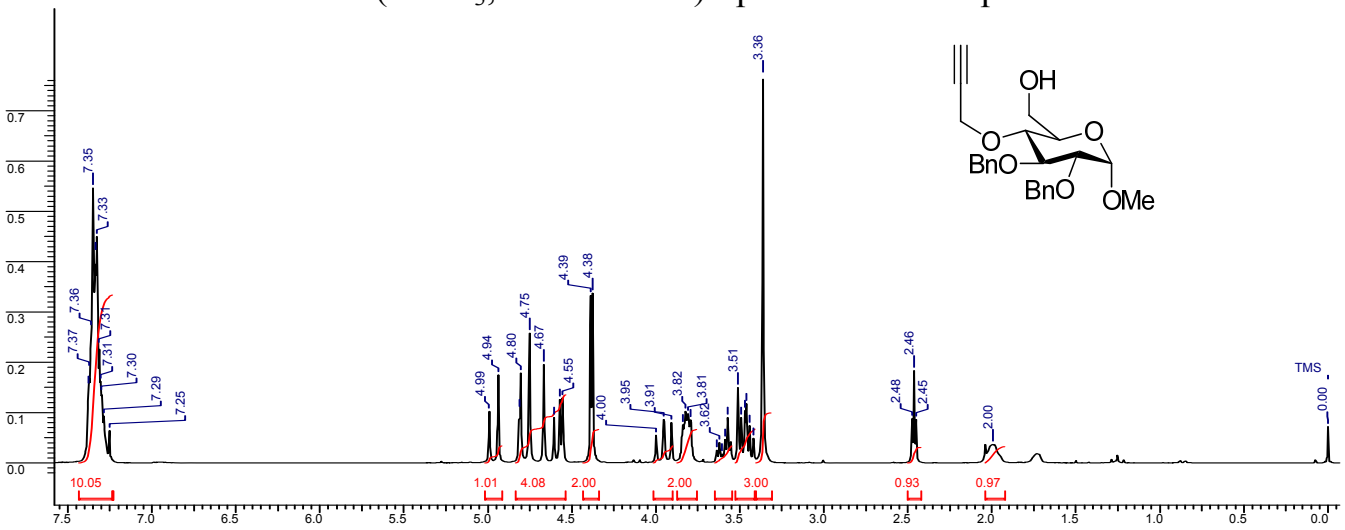
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **19**



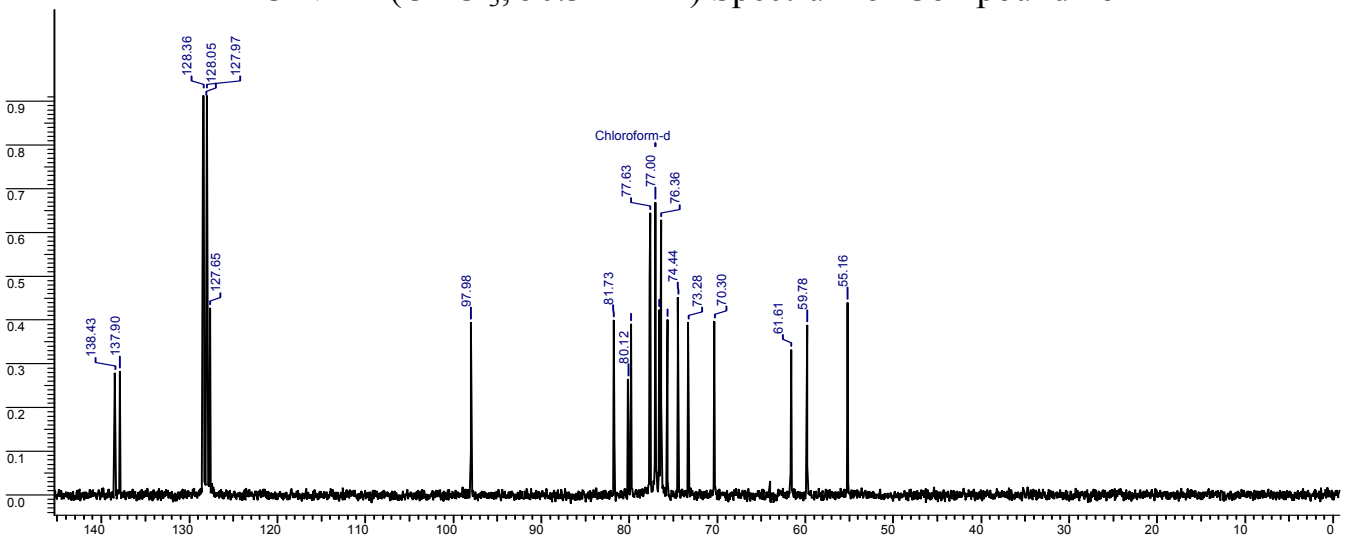
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **19**



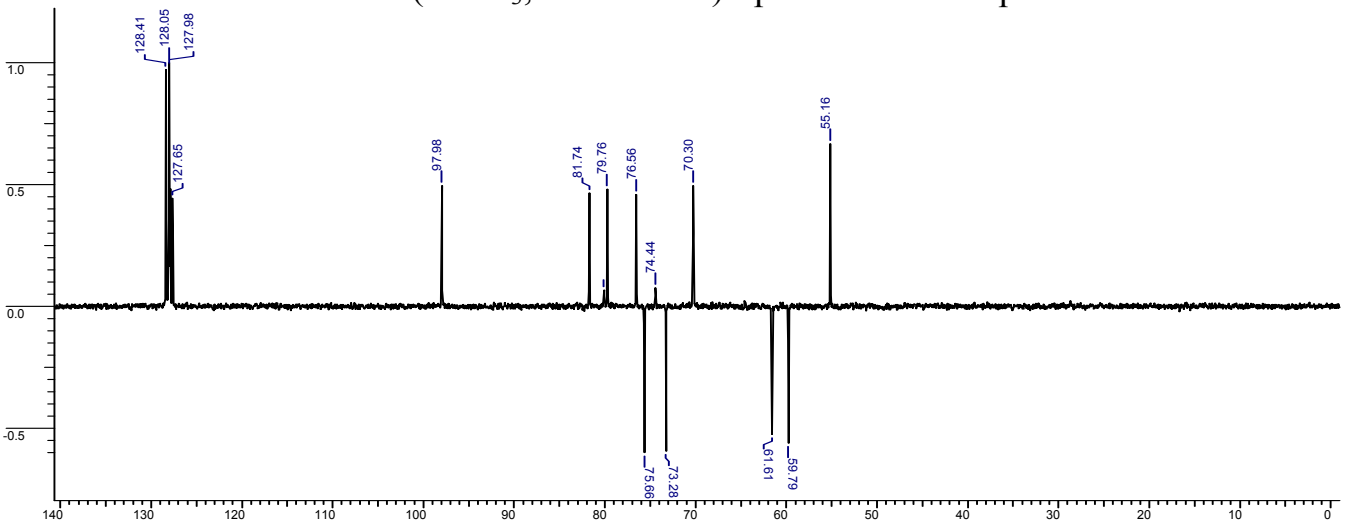
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **20**



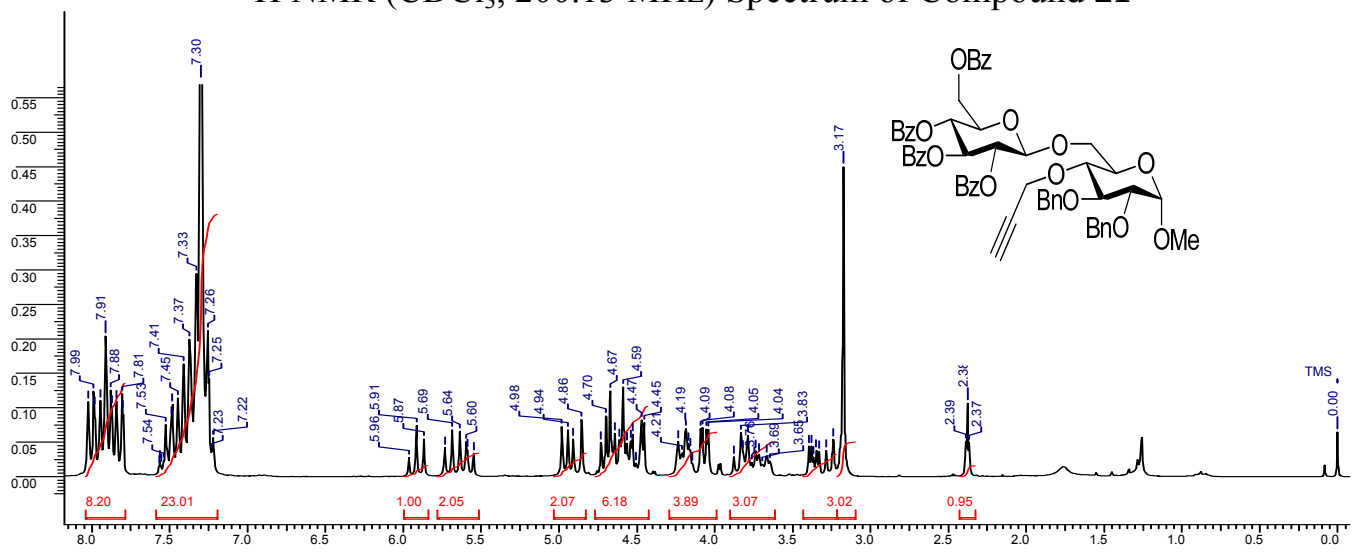
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **20**



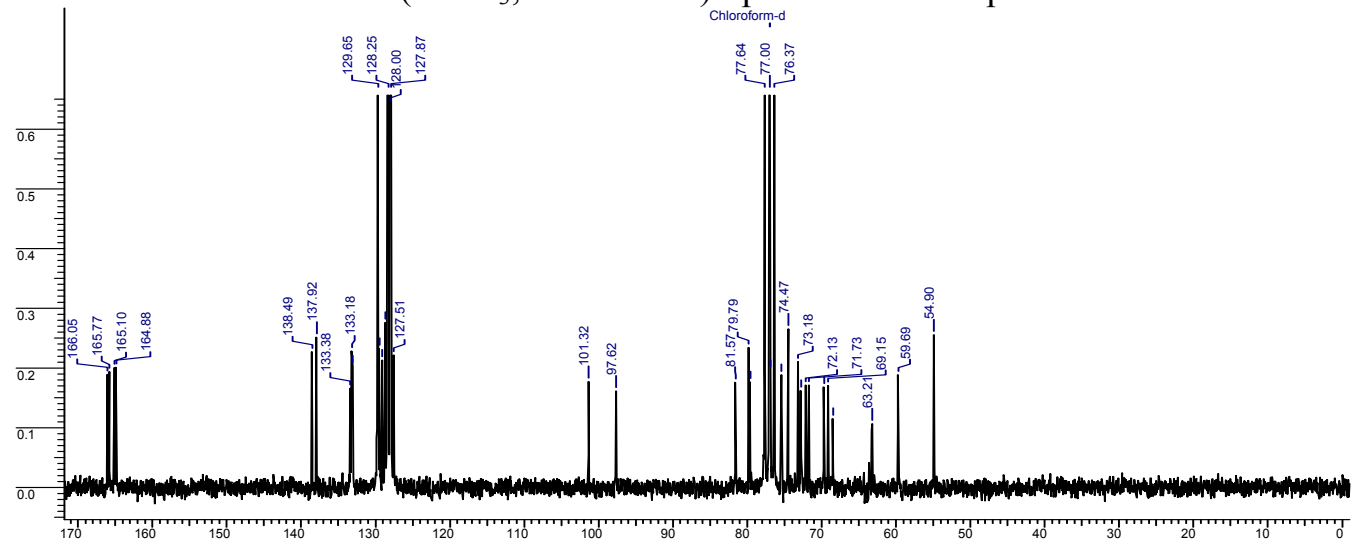
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **20**



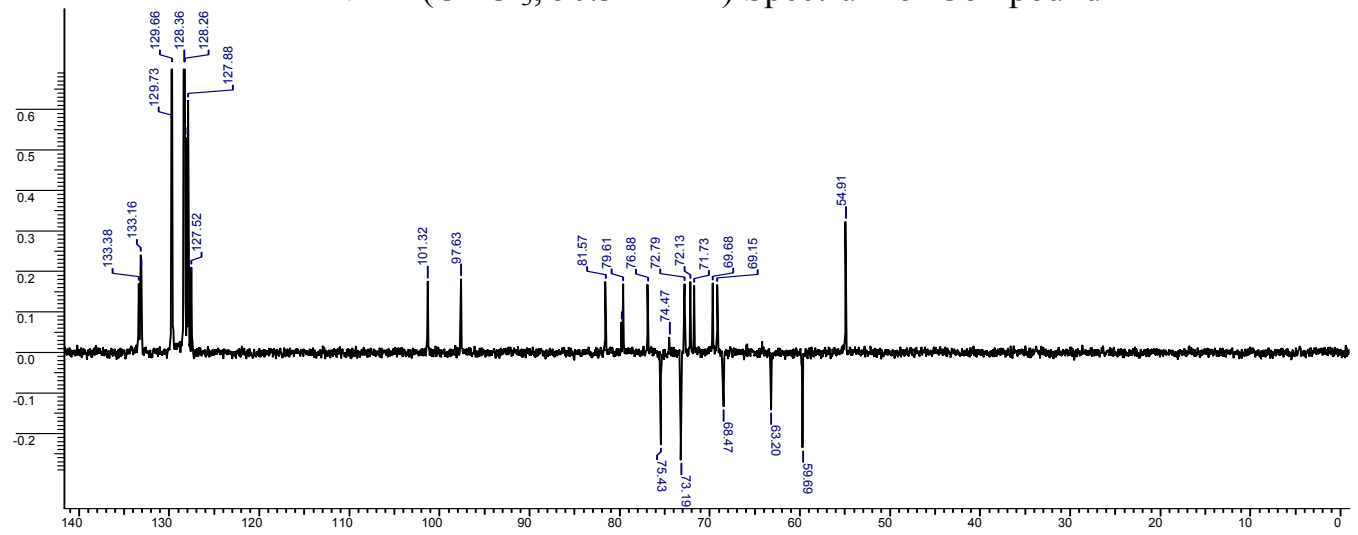
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **21**



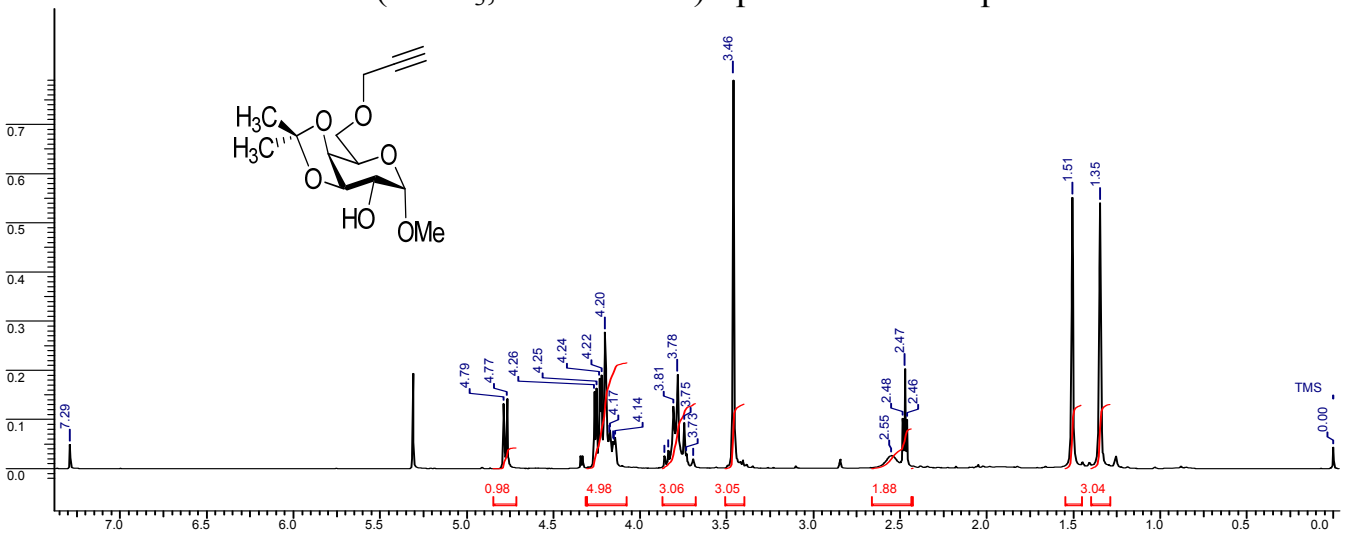
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **21**



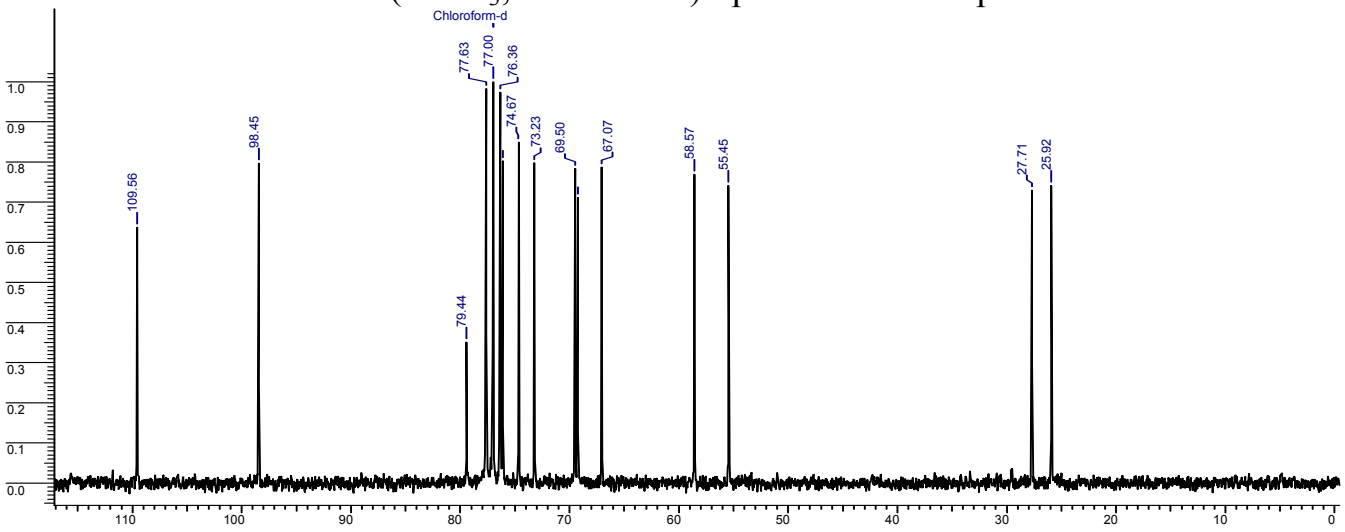
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **21**



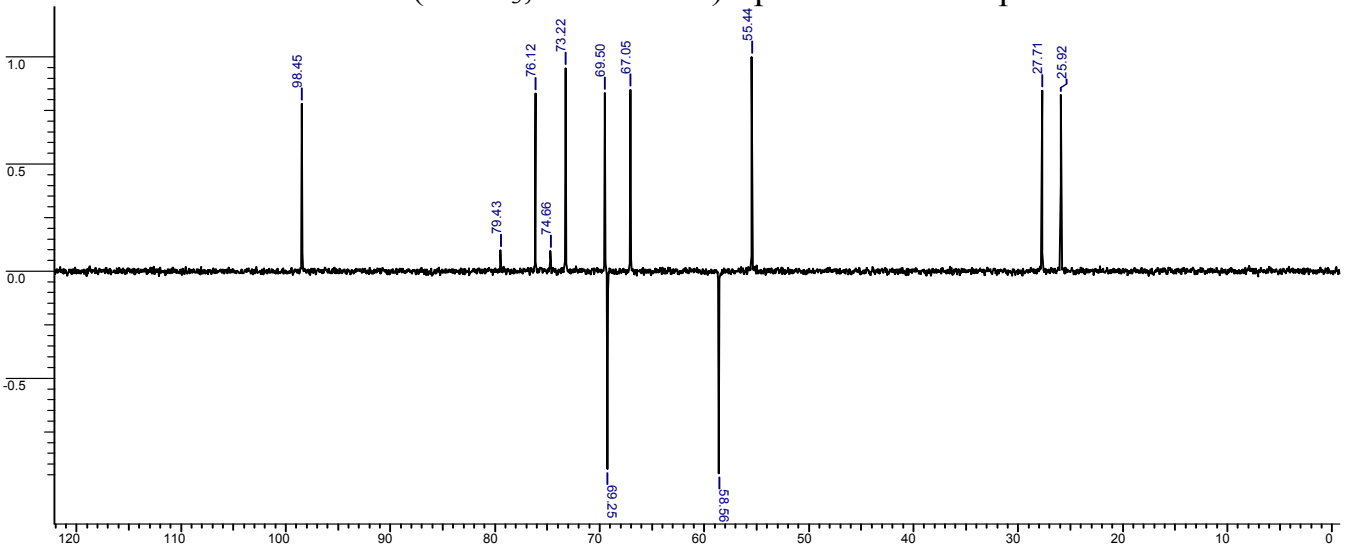
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **22**



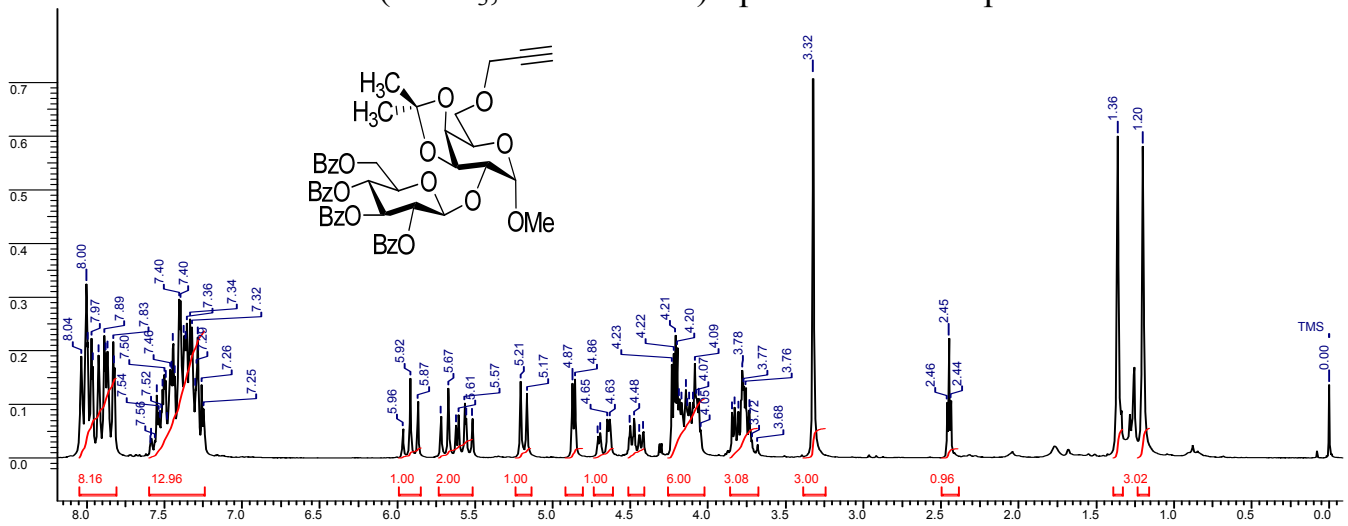
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **22**



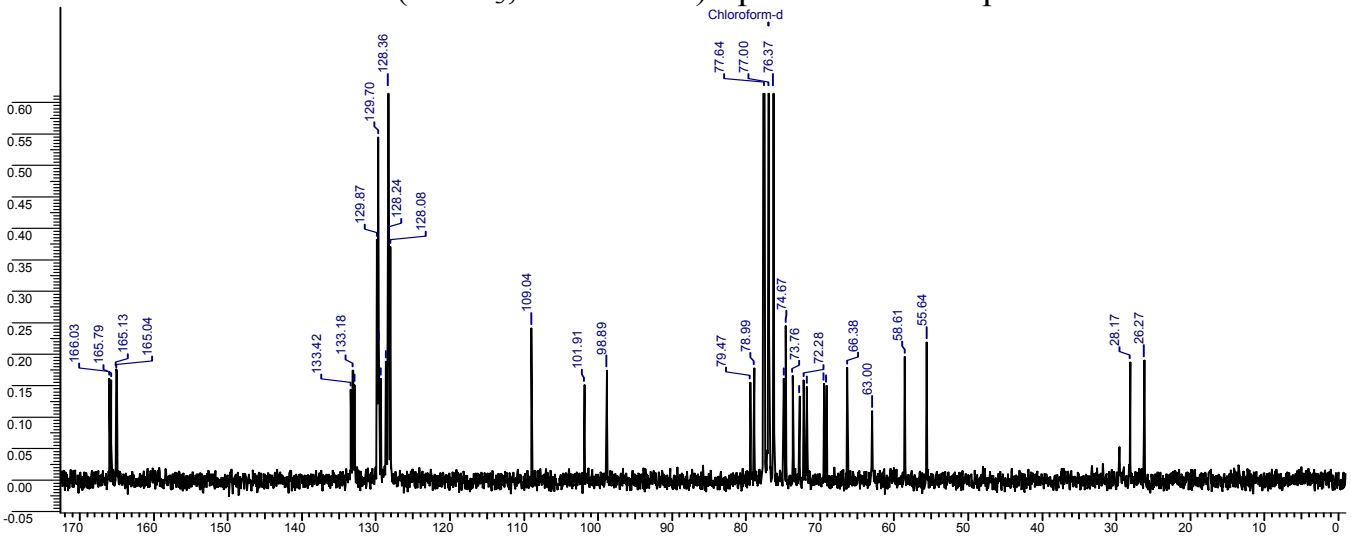
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **22**



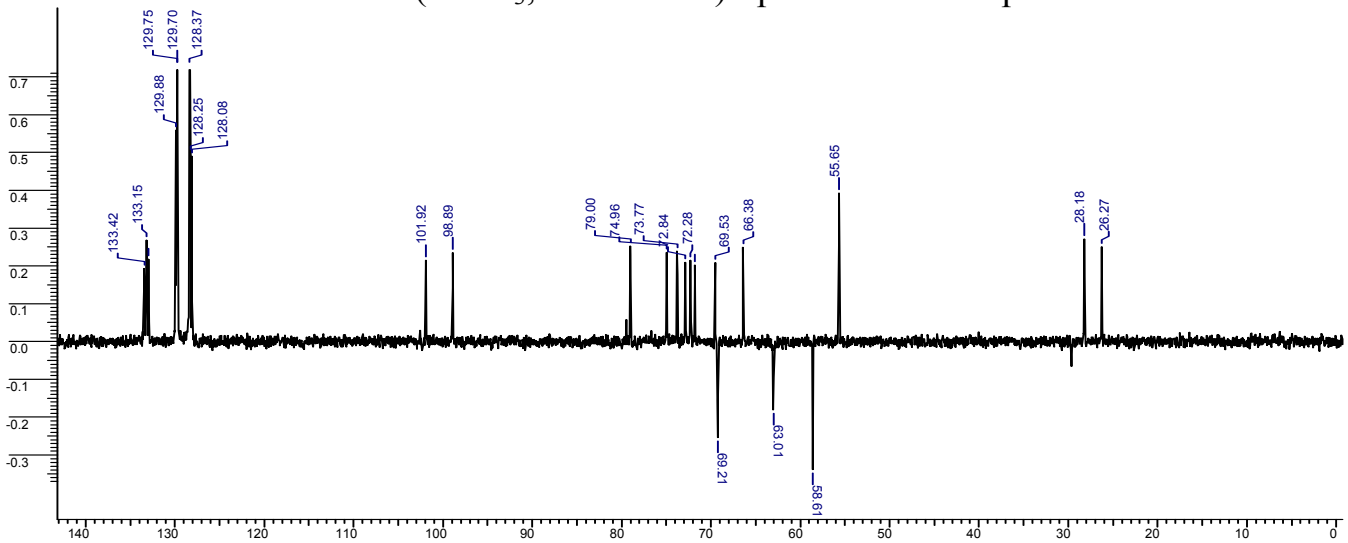
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **23**



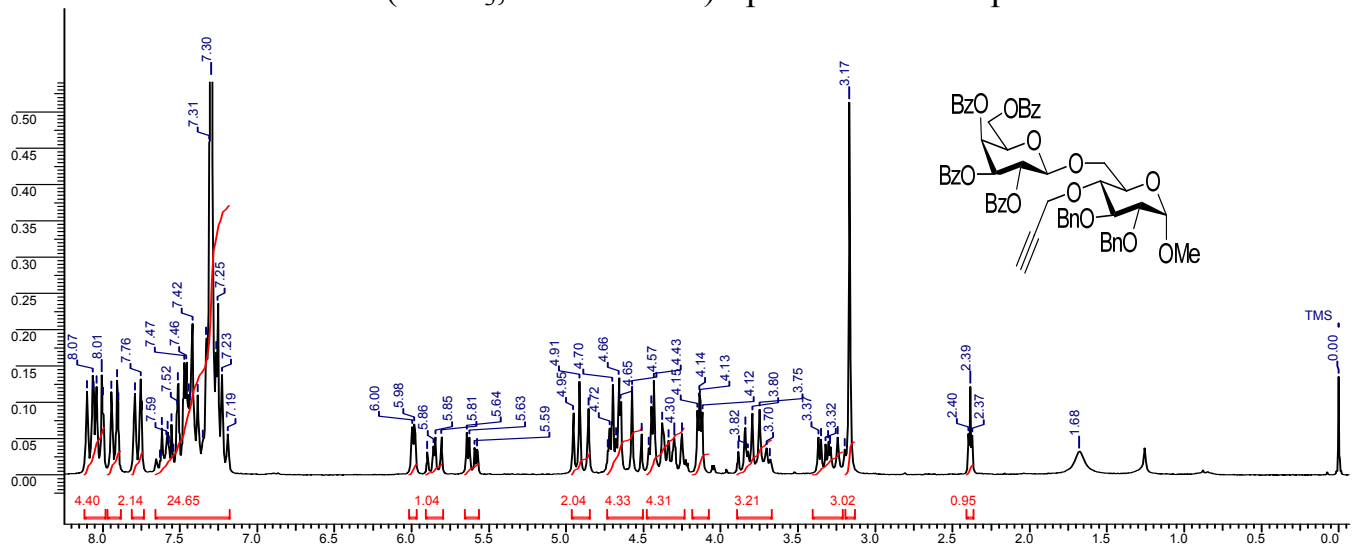
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **23**



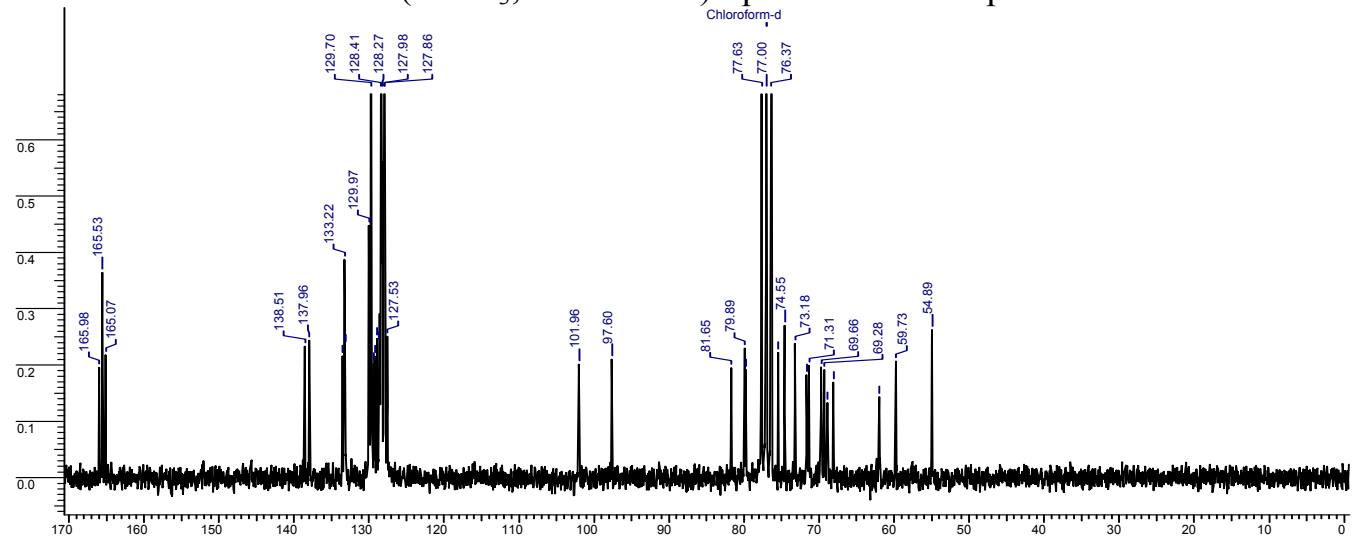
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **23**



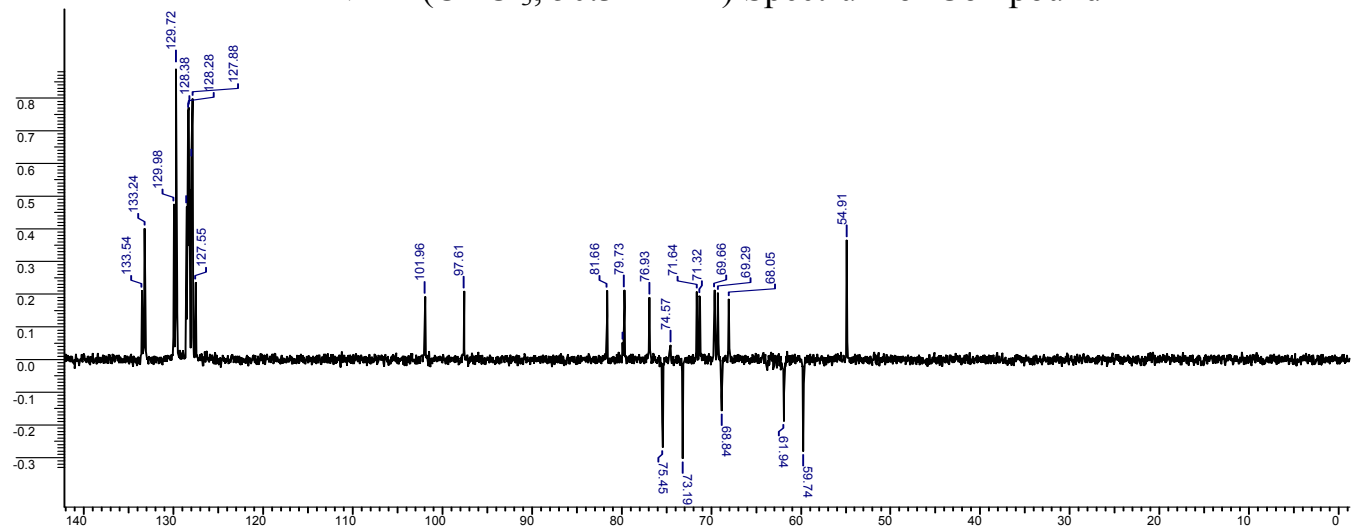
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **24**



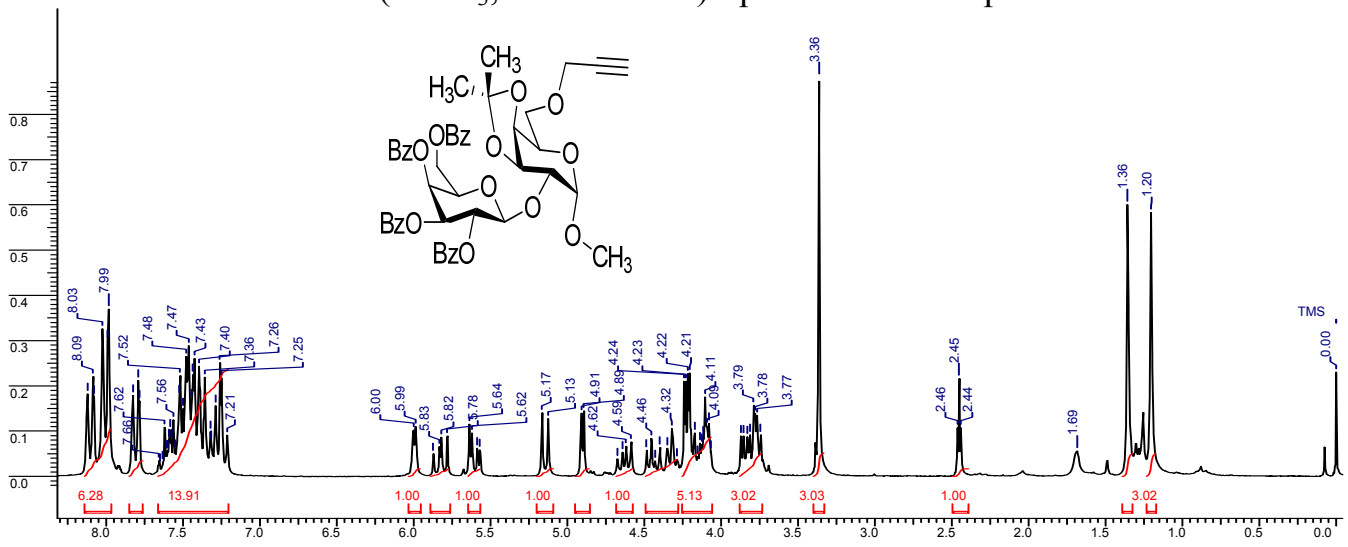
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **24**



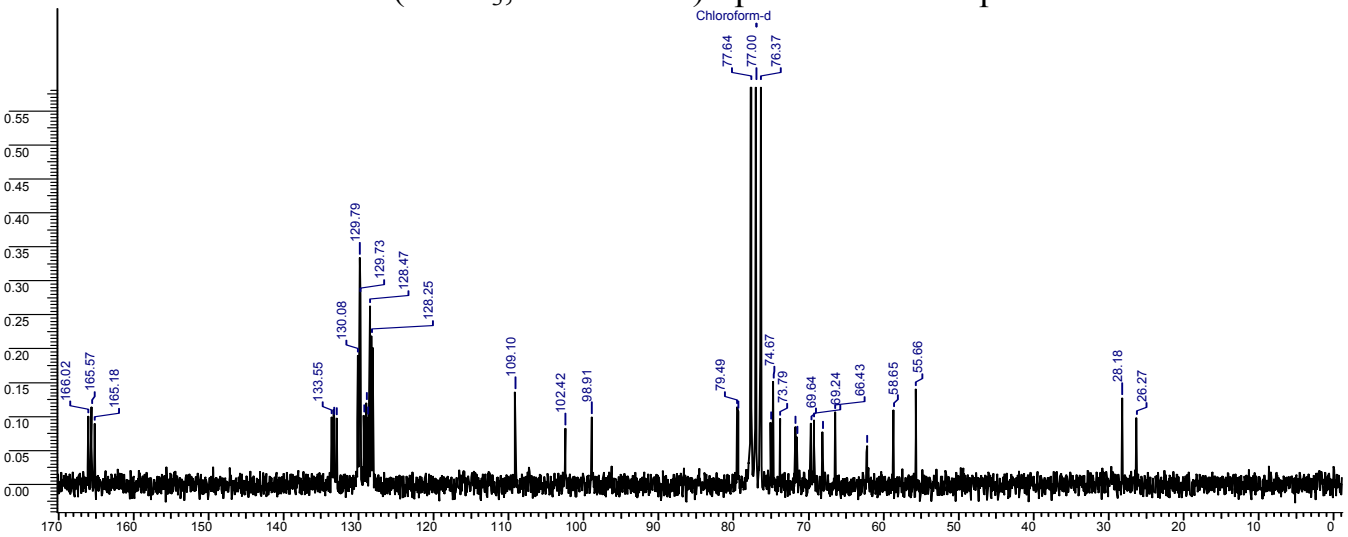
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **24**



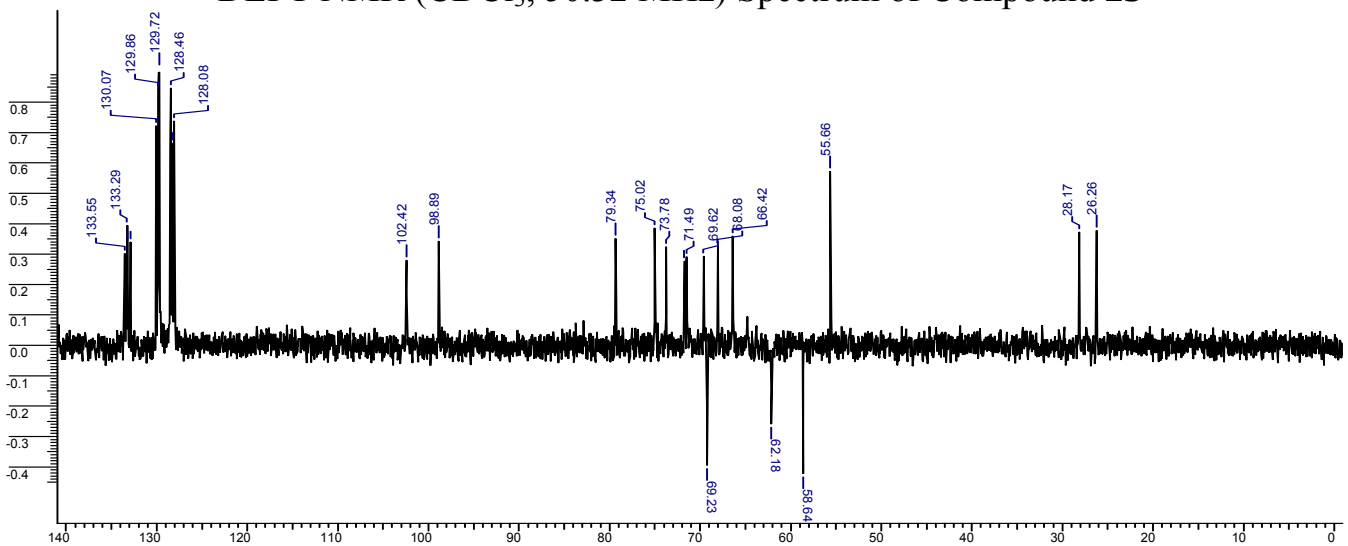
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **25**



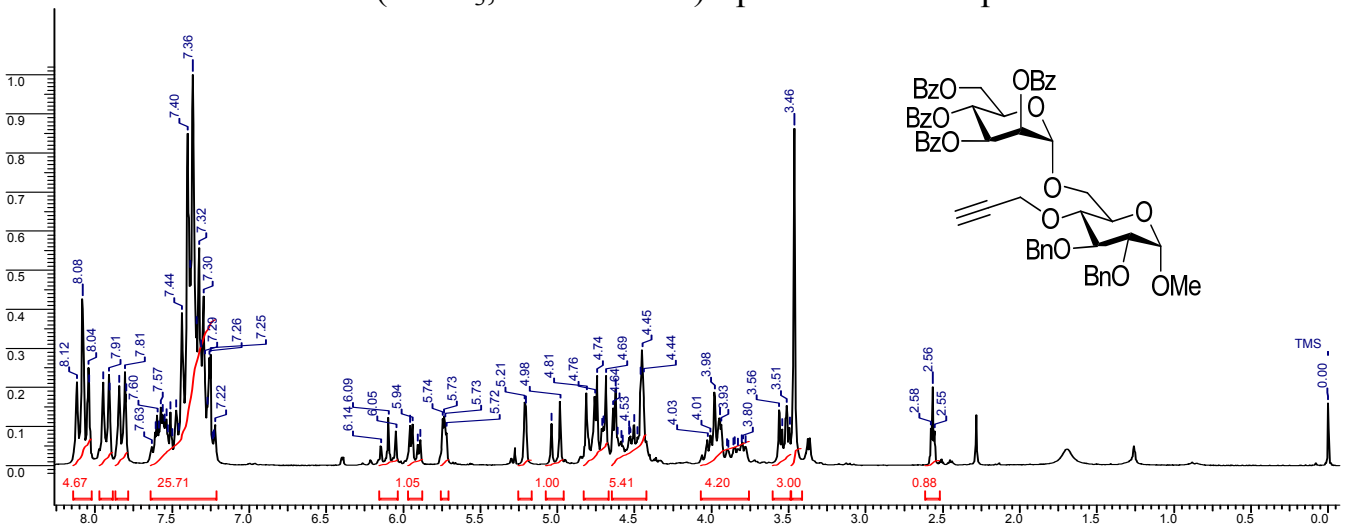
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **25**



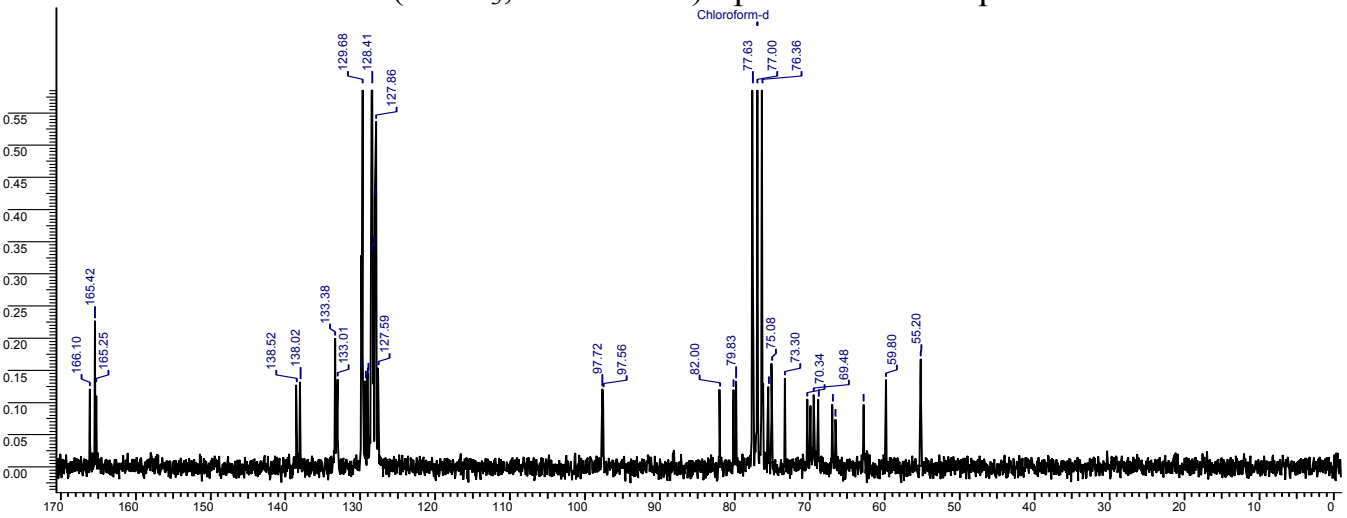
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **25**



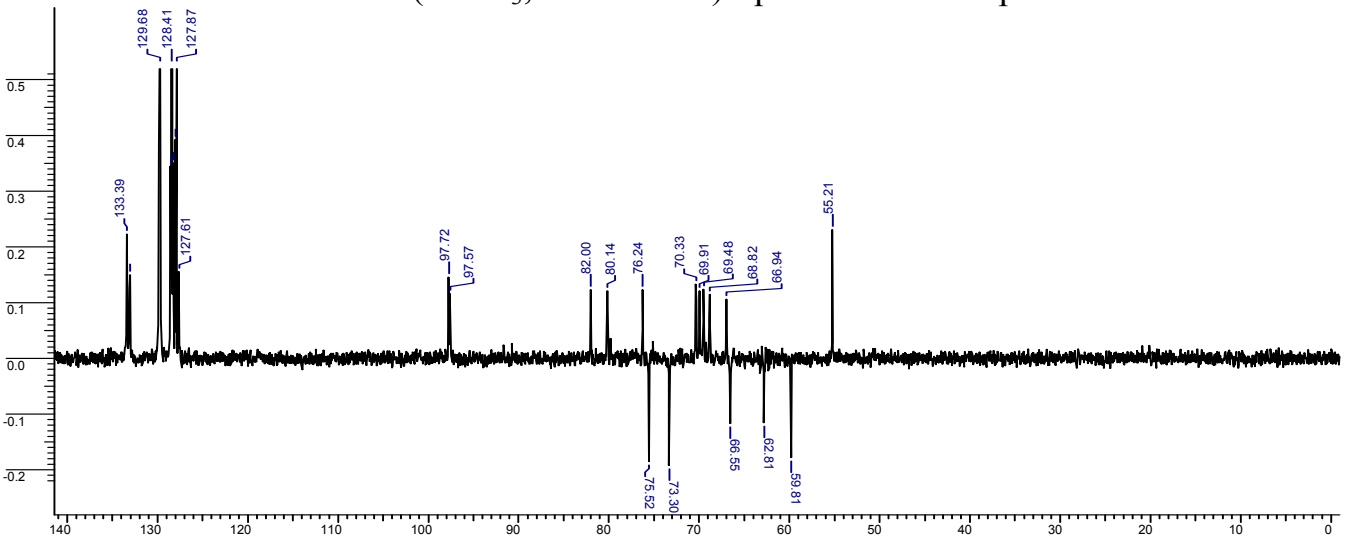
H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **26**



^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **26**



DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **26**



Mass Spectral Data of All New Compounds

Compound No.	Molecular Formula	Calculated Mass M^+	Observed Mass $(M+23 \text{ for } Na)^+$
6	$C_{30}H_{32}O_6$	488.57	511.02
7	$C_{64}H_{58}O_{15}$	1067.13	1090.52
8	$C_{30}H_{32}O_6$	488.57	511.14
9	$C_{64}H_{58}O_{15}$	1067.13	1090.52
10	$C_{30}H_{32}O_6$	488.57	511.23
11	$C_{64}H_{58}O_{15}$	1067.13	1090.08
12	$C_{11}H_{16}O_5$	228.24	251.12
13	$C_{45}H_{42}O_{14}$	806.80	829.56
15	$C_{64}H_{58}O_{15}$	1067.13	1090.52
17	$C_{64}H_{58}O_{15}$	1067.13	1090.52
18	$C_{64}H_{58}O_{15}$	1067.13	1090.02
19	$C_{45}H_{42}O_{14}$	806.80	829.26
20	$C_{24}H_{28}O_6$	412.47	435.64
21	$C_{58}H_{54}O_{15}$	991.04	1014.65
22	$C_{13}H_{20}O_6$	272.29	295.67
23	$C_{47}H_{46}O_{15}$	850.85	873.60
24	$C_{58}H_{54}O_{15}$	991.04	1014.65
25	$C_{47}H_{46}O_{15}$	850.85	873.31
26	$C_{58}H_{54}O_{15}$	991.04	1014.65