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Versatile Gold Catalyzed Transglycosidation at Ambient Temperature

*Abhijeet K. Kayastha and Srinivas Hotha**

Department of Chemistry, Indian Institute of Science Education & Research, Pune – 411 008, India

s.hotha@iiserpune.ac.in

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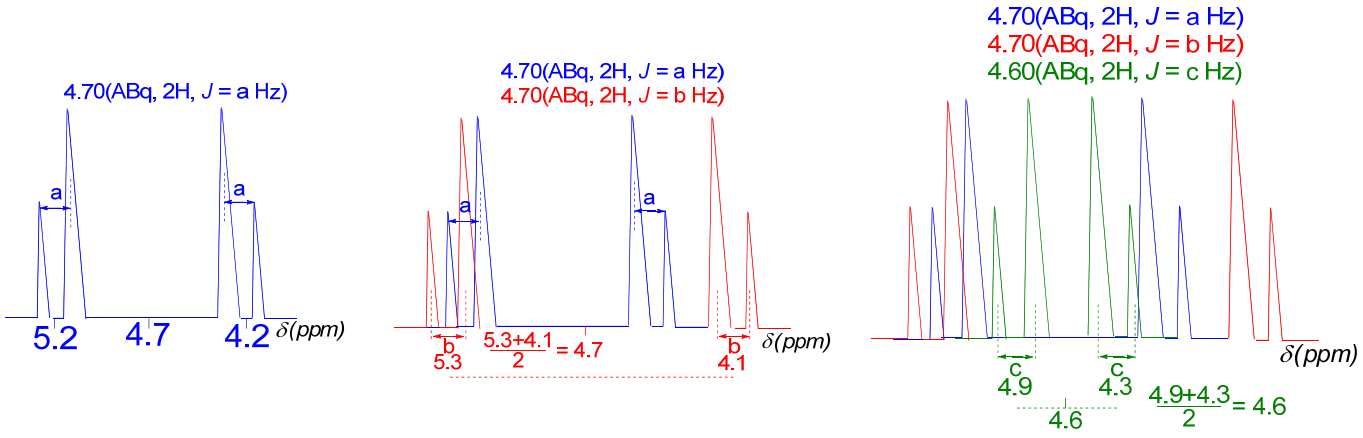
General Experimental Techniques

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 multi-national commercial vendors. Analytical thin-layer chromatography was performed on pre-coated Merck silica plates (F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. Optical rotations were measured on a JASCO P-1020 or Rudolph polarimeter. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. NMR spectra were recorded either on a Bruker AC 200, AV 400, AV 500 or JEOL ECX 400 or Bruker Avance 500 with $CDCl_3$ as the solvent and internal standard. GC Analyses were carried out on an Agilent 7890 instrument equipped with a hydrogen flame ionization detector and HP-5 capillary column (30m x 0.32mm x 0.25 µm, J & W Scientific). Nitrogen was used as the carrier gas at a flow rate of 1mL/min. Initially the column temperature was maintained at 30°C for 15 min followed by a temperature gradient from 30°C to 120°C at 5°C/min and then finally temperature gradient was raised from 120°C to 220°C at 20°C/min. Total time for one GC was 45min. High resolution mass spectroscopy (HRMS) was performed on ABI-MALDI-TOF using TiO_2 as the solid matrix. Low resolution mass spectroscopy (LRMS) was performed on Waters Acquity UPLC-MS (H Class). α- vs β- ratio of anomeric position was determined by relative peak intensities of resonances from the most characteristic protons in the ^{1}H NMR spectrum of the partially purified product. ^{1}H NMR spectral charts given in the supporting information are after purification by silica gel column chromatography.

Calculation of Multiple ABq: Two pairs of peaks (1:2:2:1 ratio) that have the same coupling constant were identified and then the median of the δ value becomes the overall chemical shift value for that ABq. The same is continued in the case of multiple ABq's. Examples are shown below for single ABq, overlapped two ABqs and overlapped three ABqs below.



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Compound Characterization Data

3-Phenylprop-2-yn-1-yl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1D**: $[\alpha]_D^{25}$ = +27.9 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3030, 2918, 2883, 1497, 1454, 1363, 1208, 1059, 1028, 735, 696; ^1H NMR(200.13 MHz, $CDCl_3$): δ 3.73-3.85(m, 3H), 3.87(dt, 1H, *J* = 0.7, 1.9, 2.8 Hz), 3.93(dd, 1H, *J* = 2.8, 8.9 Hz), 3.99(dd, 1H, *J* = 9.0, 17.5 Hz), 4.42(s, 2H), 4.60(ABq, 2H, *J* = 12.2 Hz), 4.61(s, 2H), 4.70(ABq, 2H, *J* = 10.8 Hz), 4.75(s, 2H), 5.19(s, 1H), 7.10-7.48(m, 25H); ^{13}C NMR(50.32 MHz, $CDCl_3$): δ 54.8, 69.1, 72.0, 72.2, 72.6, 73.4, 74.3, 74.8, 75.1, 80.0, 84.2, 86.3, 96.3, 122.4, 127.5-128.5, 138.1, 138.2, 138.4, 138.4; HRMS (MALDI-TOF): calcd. for $C_{43}H_{42}NaO_6$[M^++Na]: 677.2879; found: 677.2856.

1-Phenylprop-2-yn-1-yl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1E**: $[\alpha]_D^{25}$ = +5.9 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3032, 2919, 2883, 2117, 1497, 1454, 1364, 1208, 1060, 1028, 735, 696; ^1H NMR(399.78 MHz, $CDCl_3$): δ 2.54-2.65(m, 2H), 3.51-4.15(m, 12H), 4.29-5.05(m, 18H), 5.32-5.75(m, 2H), 7.10-7.62(m, 50H); ^{13}C NMR(100.53 MHz, $CDCl_3$): δ 67.3, 67.9, 68.3, 68.9, 69.1, 69.4, 71.4, 72.1, 72.2, 72.4, 72.5, 72.5, 73.3, 73.4, 73.9, 74.2, 76.6, 74.8, 75.0, 75.1, 80.1, 80.6, 81.9, 82.4, 95.5, 95.7, 127.3-128.9, 137.3, 137.4, 137.8, 137.9, 138.2, 138.2, 138.4, 138.4, 138.5, 138.6; HRMS (MALDI-TOF): calcd. for $C_{43}H_{42}NaO_6$ [M^++Na]: 677.2879; found: 677.2869.

But-3-yn-2yl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1F**:$[\alpha]_D^{25}$ = +34.1 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3032, 2883, 2117, 1497, 1454, 1364, 1208, 1060, 1028, 735, 696; ^1H NMR(400.13 MHz, $CDCl_3$): δ 1.39(d, 3H, *J* = 6.7 Hz), 2.36(t, 1H, *J* = 2.0 Hz), 3.66-3.82(m, 3H), 3.83(d, 1H, *J* = 2.0 Hz), 3.90(dd, 1H, *J* = 2.8, 9.3 Hz), 4.01(t, 1H, *J* = 9.5 Hz), 4.47(dd, 1H, *J* = 4.9, 6.8 Hz), 4.59(ABq, 2H, *J* = 12.2 Hz), 4.60(s, 2H), 4.71(ABq, 2H, *J* = 12.0 Hz), 4.75(s, 2H), 5.28(s, 1H), 7.10-7.45(m, 20H); ^{13}C NMR(100.61 MHz, $CDCl_3$): δ 21.8, 61.1, 69.2, 71.9, 72.3, 72.5, 73.1, 73.4, 74.5, 74.8, 75.8, 80.0, 82.8, 95.2, 127.3-128.3, 138.2, 138.3, 138.4, 138.5 ; HRMS (MALDI-TOF): calcd. for $C_{38}H_{40}NaO_6$ [M^++Na]: 615.2723; found: 615.2723.

2-Phenylbut-3-yn-2-yl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1G**:$[\alpha]_D^{25}$ = +25.0 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3285, 3035, 2920, 2883, 2121, 1497, 1454, 1364, 1208, 1061, 1028, 735, 700; ^1H NMR(400.13 MHz, $CDCl_3$): δ 1.77(s, 3H), 2.62(s, 1H), 3.64(t, 1H, *J* = 2.2 Hz), 3.76(d, 1H, *J* = 10.8 Hz), 3.86(dd, 1H, *J* = 3.8, 10.8 Hz), 3.98(dd, 1H, *J* = 2.7, 8.6 Hz), 4.03-4.13(m, 2H), 4.57(ABq, 2H, *J* = 12.3 Hz), 4.58 (d, 1H, *J* = 9.3 Hz), 4.59(ABq, 2H, *J* = 12.4 Hz), 4.62(ABq, 2H, *J* = 12.0 Hz), 4.93(d, 1H, *J* = 10.8 Hz), 5.44(s, 1H), 7.14-7.55(m, 25H); ^{13}C NMR(100.61 MHz, $CDCl_3$): δ 32.1, 69.2, 71.9, 71.9, 79.2, 72.4, 73.3, 74.7, 75.0, 75.3, 75.6, 76.0, 77.2, 79.7, 83.8, 94.4, 125.5, 127.3-128.4, 138.2, 138.4, 138.5, 138.5, 142.8; HRMS (MALDI-TOF): calcd. for $C_{44}H_{44}NaO_6$ [M^++Na]: 691.3036; found: 691.3035.

Pent-3-yn-2-yl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1H**:$[\alpha]_D^{25}$ = +37.6 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3288, 3030, 2919, 2883, 1497, 1454, 1363, 1208, 1059, 1030, 735, 698; ^1H NMR(200.13 MHz, $CDCl_3$): δ 1.29-1.30(m, 3H), 1.75-1.84(m, 3H), 3.73-4.00(m, 6H), 4.36-5.30(m, 10H), 7.10-7.45(m, 20H); ^{13}C NMR(125.76 MHz, $CDCl_3$): δ 3.5, 22.2, 61.5, 69.3, 70.0, 72.2, 72.5, 73.4, 74.6, 75.0, 75.2, 78.2, 80.2, 81.3, 95.0, 127.4-128.4, 138.3, 138.4, 138.5, 138.6; HRMS (MALDI-TOF): calcd. for $C_{39}H_{42}NaO_6$ [M^++Na]: 629.2879; found: 629.2894.

2-Methylbut-3-yn-2-yl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1I**:$[\alpha]_D^{25}$ = +37.7 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3285, 3031, 2883, 2119, 1497, 1454, 1362, 1210, 1060, 1028, 735, 700; ^{1}H NMR(200.13 MHz, $CDCl_3$): δ 1.41, 1.53(2s, 6H), 2.37(s, 1H), 3.65-4.10(m, 6H), 4.59(s, 2H), 4.60(ABq, 2H, *J* = 12.1 Hz), 4.68(ABq, 2H, *J* = 10.6 Hz), 4.76(s, 2H), 5.52(d, 1H, *J* = 2.0 Hz), 7.10-7.45(m, 20H); ^{13}C NMR(50.32 MHz, $CDCl_3$): δ 29.1, 30.2, 69.2, 71.7, 71.9, 72.0, 72.2, 72.5, 73.3, 75.0, 75.0, 75.1, 80.0, 84.4, 94.3, 127.3-128.3, 138.4, 138.4, 138.5, 138.5; HRMS (MALDI-TOF): calcd. for $C_{39}H_{42}NaO_6$ [M^++Na]: 629.2879; found: 629.2892.

1-Ethynylcyclopentyl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1J**:$[\alpha]_D^{25}$ = +21.5 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3030, 2918, 2883, 2119, 1497, 1458, 1360, 1210, 1060, 1028, 753, 698; ^{1}H NMR(200.13 MHz, $CDCl_3$): δ 1.60-1.98(m, 8H), 2.38(s, 1H), 3.65-4.10(m, 6H), 4.59(s, 2H), 4.60(ABq, 2H, *J* = 12.2 Hz), 4.70(ABq, 2H, *J* = 10.5 Hz), 4.76(s, 2H), 5.47(d, 1H, *J* = 2.0 Hz), 7.15-7.40(m, 20H); ^{13}C NMR(50.32 MHz, $CDCl_3$): δ 22.8, 23.1, 39.3, 40.9, 69.3, 71.9, 72.2, 72.5, 72.9, 73.3, 74.5, 75.0, 75.2, 80.0, 81.5, 84.8, 94.9, 127.3-128.3, 138.4, 138.5, 138.5, 138.5; HRMS (MALDI-TOF): calcd. for $C_{41}H_{44}NaO_6$ [M^++Na]: 655.3036; found: 655.3045.

1-Ethynylcyclohexyl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1K**: $[\alpha]_D^{25}$ = +28.2 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3030, 2918, 2883, 2119, 1497, 1458, 1360, 1210, 1060, 1028, 753, 698; ^{1}H NMR(200.13 MHz, $CDCl_3$): δ 1.10-2.15(m, 10H), 2.40(s, 1H), 3.65-4.12(m, 6H), 4.59(s, 2H), 4.60(ABq, 2H, *J* = 12.6 Hz), 4.71(ABq, 2H, *J* = 10.6 Hz), 4.76(s, 2H), 5.56(d, 1H, *J* = 1.8 Hz), 7.13-7.42(m, 20H); ^{13}C NMR(50.32 MHz, $CDCl_3$): δ 22.7, 22.7, 25.0, 37.6, 38.2, 69.3, 71.9, 72.1, 72.3, 73.3, 74.1, 75.0, 75.2, 75.2, 75.5, 80.0, 84.6, 94.0, 127.3-128.3, 138.4, 138.5, 138.5, 138.5; HRMS (MALDI-TOF): calcd. for $C_{42}H_{46}NaO_6$ [M^++Na]: 669.3192; found: 669.3173.

1-(Prop-2-yn-1-yl)cyclohexyl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **1L**: $[\alpha]_D^{25}$ = +54.5 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3030, 2919, 2883, 2129, 1500, 1458, 1360, 1210, 1060, 1028, 753, 696; ^{1}H NMR(500.13 MHz, $CDCl_3$): δ 1.05-1.75(m, 10H), 1.90(t, 1H, *J* = 2.8 Hz), 2.36(d, 2H, *J* = 2.6 Hz), 3.62(t, 1H, *J* = 2.5 Hz), 3.70(dd, 1H, *J* = 1.6, 10.7 Hz), 3.81(dd, 1H, *J* = 4.1, 10.7 Hz), 3.95(dd, 1H, *J* = 2.9, 9.1 Hz), 3.99(ddd, 1H, *J* = 1.5, 4.0, 6.1 Hz), 4.04(d, 1H, *J* = 9.8 Hz), 4.60(ABq, 2H, *J* = 11.9 Hz), 4.67-4.72(m, 2H), 4.71(ABq, 2H, *J* = 10.8 Hz), 4.72(ABq, 2H, *J* = 11.5 Hz), 5.05(d, 1H, *J* = 1.5 Hz), 7.18-7.45(m, 20H); ^{13}C NMR(125.76 MHz, $CDCl_3$): δ 21.7, 21.8, 25.3, 29.6, 33.1, 34.9, 69.3, 70.5, 72.1, 72.4, 72.5, 73.3, 75.0, 75.2, 76.0, 76.9, 79.8, 81.0, 92.1, 127.3-128.3, 138.4, 138.5, 138.6, 138.6; HRMS (MALDI-TOF): calcd. for $C_{43}H_{48}NaO_6$ [M^++Na]: 683.3349; found: 683.3361.

2-((1-ethynylcyclohexyl)oxy)tetrahydro-2*H*-pyran **4**:$[\alpha]_D^{25}$ = +5.3 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3030, 2918, 2883, 2119, 1360, 1210, 1060, 1028, 753, 698; ^{1}H NMR(500.13 MHz, $CDCl_3$): δ 1.26(m, 1H), 1.45-2.08(m, 15H), 2.48(s, 1H), 3.51(quintet, 1H, *J* = 5.2 Hz), 3.96(t, 1H, *J* = 10.5 Hz), 5.13(t, 1H, *J* = 4.1 Hz); ^{13}C NMR(125.76 MHz, $CDCl_3$): δ 20.5, 23.0, 23.0, 25.3, 25.4, 32.1, 38.4, 38.7, 63.5, 73.8, 74.8, 85.4, 95.7; HRMS (MALDI-TOF): calcd. for $C_{13}H_{20}NaO_2$ [M^++Na]: 231.1361; found: 231.1364.

2-((4-methylbenzyl)oxy)tetrahydro-2*H*-pyran **6**:$[\alpha]_D^{25}$ = +5.6 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3030, 2918, 2883, 1438, 1362, 1210, 1065, 1028, 753; ^{1}H NMR(500.13 MHz, $CDCl_3$): δ 1.48-1.93(m, 6H), 2.34(s, 3H), 3.54(m, 1H), 3.92(ddd, 1H, *J* = 3.0, 8.6, 11.5 Hz), 4.60(ABq, 2H, *J* = 11.9 Hz), 4.69 (t, 1H, *J* = 3.3 Hz), 7.15(d, 2H, *J* = 7.9 Hz), 7.26(d, 2H, *J* = 7.91 Hz); ^{13}C NMR(125.76 MHz, $CDCl_3$): δ 19.3, 21.1, 25.5, 30.5,

62.0, 68.6, 97.5, 127.9, 127.9, 129.0, 129.0, 135.2, 137.1; HRMS (MALDI-TOF): calcd. for $C_{13}H_{18}NaO_2$ [M^++Na]: 229.1204; found: 229.1225.

1-Ethynylcyclohexyl 2,3,4,6-tetra-*O*-benzyl β-D-glucopyranoside **13**: $[\alpha]_D^{25}$ = +16.0 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3285, 3029, 2918, 2880, 2121, 1497, 1458, 1360, 1210, 1060, 1028, 753, 702; ^{1}H NMR(399.78 MHz, $CDCl_3$): δ 1.15-2.15(m, 10H), 2.55(s, 1H), 3.52(m, 2H), 3.57(t, 1H, *J* = 9.1 Hz), 3.64(dd, 1H, *J* = 5.0, 10.7 Hz), 3.69(m, 2H), 4.55(d, 1H, *J* = 10.3 Hz), 4.56(ABq, 2H, *J* = 12.3 Hz), 4.75(ABq, 2H, *J* = 11.0 Hz), 4.85(ABq, 2H, *J* = 10.7 Hz), 5.02(s, 1H), 5.04(d, 1H, *J* = 2.8 Hz), 7.13-7.43(m, 20H); ^{13}C NMR(100.53 MHz, $CDCl_3$): δ 22.9, 23.0, 25.1, 38.6, 38.8, 69.1, 73.2, 74.4, 74.7, 74.8, 75.3, 75.6, 76.8, 77.8, 82.1, 84.4, 84.9, 99.3, 127.3-128.4, 138.1, 138.2, 138.4, 138.6; HRMS (MALDI-TOF): calcd. for $C_{42}H_{46}NaO_6$ [M^++Na]: 669.3192; found: 669.3207.

1-Ethynylcyclohexyl 2,3,4,6-tetra-*O*-benzyl β-D-galactopyranoside **14**: $[\alpha]_D^{25}$ = +6.6 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3282, 3030, 2919, 2880, 2118, 1497, 1458, 1360, 1210, 1060, 1028, 753, 700; ^{1}H NMR(500.13 MHz, $CDCl_3$): δ 1.05-2.10(m, 10H), 2.51(s, 1H), 3.55(m, 4H), 3.84(dd, 1H, *J* = 7.8, 9.7 Hz), 3.87(d, 1H, *J* = 2.9 Hz), 4.40(ABq, 2H, *J* = 11.4 Hz), 4.70(ABq, 2H, *J* = 11.6 Hz), 4.80(ABq, 2H, *J* = 11.9 Hz), 4.86(ABq, 2H, *J* = 10.8 Hz), 4.97(d, 1H, *J* = 7.8 Hz), 7.20-7.45(m, 20H); ^{13}C NMR(100.53 MHz, $CDCl_3$): δ 23.0, 23.1, 25.1, 38.6, 38.7, 69.2, 73.2, 73.3, 73.4, 73.4, 74.4, 75.1, 75.1, 76.7, 79.5, 82.6, 84.7, 99.6, 127.3-128.5, 138.0, 138.6, 138.7, 138.8; HRMS (MALDI-TOF): calcd. for $C_{42}H_{46}NaO_6$ [M^++Na]: 669.3192; found: 669.3181.

(1*R*,2*R*,5*S*-Menthyl) 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **15**: $[\alpha]_D^{25}$ = +5.2 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3030, 2918, 2880, 1497, 1458, 1360, 1210, 1060, 1028, 753, 698; ^{1}H NMR(200.13 MHz, $CDCl_3$): δ 0.64(d, 3H, *J* = 6.7 Hz), 0.80(d, 3H, *J* = 1.3 Hz), 0.84(d, 3H, *J* = 2.0 Hz), 0.87-1.85(m, 9H), 2.15(m, 1H), 3.23(dt, 1H, *J* = 4.3, 10.5 Hz), 3.67(q, 1H, *J* = 2.0, 4.1 Hz), 3.76(dd, 1H, *J* = 1.6, 4.7 Hz), 3.84-3.98(m, 3H), 4.63(ABq, 2H, *J* = 12.1 Hz), 4.63(d, 1H, *J* = 1.4 Hz), 4.67(ABq, 2H, *J* = 11.5 Hz), 4.68(ABq, 2H, *J* = 12.1 Hz), 4.70(ABq, 2H, *J* = 10.7 Hz), 7.10-7.38(m, 20H); ^{13}C NMR(50.32 MHz, $CDCl_3$): δ 16.2, 21.0, 22.2, 23.2, 25.7, 31.6, 34.2, 42.8, 48.6, 69.4, 71.7, 72.2, 72.4, 73.3, 74.3, 75.2, 75.2, 80.0, 81.0, 99.8, 127.3-128.4, 138.2, 138.4, 138.5, 138.5; HRMS (MALDI-TOF): calcd. for $C_{44}H_{54}NaO_6$ [M^++Na]: 701.3818; found: 701.3821.

4-Methylbenzyl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **16**: $[\alpha]_D^{25}$ = +15.4 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3282, 3029, 2918, 2880, 1497, 1458, 1360, 1210, 1060, 1028, 753, 688; ^{1}H NMR(200.13 MHz, $CDCl_3$): δ 2.34(s, 3H), 3.68-4.08(m, 6H), 4.48 (ABq, 2H, *J* = 11.8 Hz), 4.60(s, 2H), 4.68(ABq, 2H, *J* = 10.6 Hz), 4.69(ABq, 2H, *J* = 10.7 Hz), 4.70(s, 2H), 4.96(d, 1H, *J* = 1.8 Hz), 7.10-7.40(m, 24H); ^{13}C NMR(50.32 MHz, $CDCl_3$): δ 21.2, 68.8, 69.2, 72.0, 72.1, 72.5, 73.3, 74.6, 74.9, 75.1, 80.2, 97.0, 127.3-128.3, 129.0, 129.0, 134.2, 137.4, 138.2, 138.3, 138.4, 138.5; HRMS (MALDI-TOF): calcd. for $C_{42}H_{44}NaO_6$ [M^++Na]: 667.3036; found: 667.3032.

Cholesteryl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **17**: $[\alpha]_D^{25}$ = +19.1 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3031, 2920, 2922, 2880, 1497, 1458, 1360, 1210, 1060, 1029, 755, 696; ^{1}H NMR(400.13 MHz, $CDCl_3$): δ 0.61(s, 3H), 0.86(d, 3H, *J* = 1.6 Hz), 0.87(d, 3H, *J* = 1.6 Hz), 0.89-2.10(m, 31H), 2.16(s, 1H), 2.24(t, 1H, *J* = 12.3 Hz), 2.33(dd, 1H, *J* = 4.7, 12.3 Hz), 3.37(dd, 1H, *J* = 1.8, 14.7 Hz), 3.48(m, 1H), 3.75(s, 1H), 3.81(dd, 1H, *J* = 4.7, 10.7 Hz), 3.87(m, 1H), 3.94(dd, 1H, *J* = 2.7, 9.3 Hz), 3.99(dd, 1H, *J* = 9.1, 18.8 Hz), 4.60(ABq, 2H, *J* = 12.0 Hz), 4.63(s, 2H), 4.70(ABq, 2H, *J* = 10.8 Hz), 4.74(ABq, 2H, *J* = 12.6 Hz), 5.03(d, 1H, *J*

= 1.5 Hz), 5.27(d, 1H, *J* = 5.0 Hz), 7.10-7.40(m, 20H); ^{13}C NMR(100.61 MHz, $CDCl_3$): δ 11.8, 18.7, 19.3, 21.0, 22.5, 22.8, 23.8, 24.3, 27.5, 28.0, 28.2, 31.8, 31.9, 35.8, 36.2, 36.6, 37.0, 39.5, 39.7, 39.8, 42.2, 50.0, 56.1, 56.7, 69.3, 71.7, 72.1, 72.5, 73.3, 75.1, 75.1, 76.5, 77.2, 80.3, 95.7, 121.8, 127.3-128.3, 138.4, 138.4, 138.5, 138.6, 140.6; HRMS (MALDI-TOF): calcd. for $C_{61}H_{80}NaO_6$ [M^++Na]: 931.5853; found: 931.5849.

(1R,4S)-bicyclo[2.2.1]heptan-7yl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **18** *(isomers at the norbornol 2^o-alcohol)*: $[\alpha]_D^{25}$ = +34.8 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3030, 2918, 2880, 1497, 1458, 1360, 1210, 1060, 1028, 753, 698; ^{1}H NMR(400.13 MHz, $CDCl_3$): δ 0.88-1.58(m, 18H), 1.63(s, 2H), 2.25(m, 2H), 3.55-4.05(m, 12H), 4.45-4.98(m, 18H), 7.12-7.40(m, 40H); ^{13}C NMR(100.61 MHz, $CDCl_3$): δ 24.2, 24.5, 28.4, 28.4, 34.6, 35.0, 35.1, 35.1, 39.5, 39.6, 39.6, 41.9, 69.3, 69.4, 71.7, 71.8, 72.1, 72.1, 72.4, 72.5, 73.2, 73.2, 75.1, 75.2, 75.2, 75.2, 75.3, 75.4, 78.5, 80.2, 80.3, 81.1, 96.0, 96.8, 127.3-128.4, 138.4, 138.4, 138.4, 138.4, 138.5, 138.5, 138.6, 138.6; HRMS (MALDI-TOF): calcd. for $C_{41}H_{46}NaO_6$ [M^++Na]: 657.3192; found: 657.3178.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzyl α-D-mannopyranosyl)-L-threoninate **19**: $[\alpha]_D^{25}$ = +16.5 ($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3285, 3030, 2918, 2884, 1726, 1690, 1497, 1458, 1360, 1210, 1060, 1028, 753, 700; ^{1}H NMR(500.13 MHz, $CDCl_3$): δ 1.28(d, 3H, *J* = 6.3 Hz), 3.50(t, 1H, *J* = 2.4 Hz), 3.58-3.85(m, 4H), 3.93(t, 1H, *J* = 9.2 Hz), 4.34(ddd, 1H, *J* = 2.1, 6.7, 8.7 Hz), 4.38(dd, 1H, *J* = 1.8, 10.1 Hz), 4.46(d, 1H, *J* = 10.6 Hz), 4.54(s, 2H), 4.54(ABq, 2H, *J* = 12.5 Hz), 4.57(ABq, 2H, *J* = 12.5 Hz), 4.83(dd, 2H, *J* = 5.0, 6.3 Hz), 5.02(ABq, 2H, *J* = 12.2 Hz), 5.12(ABq, 2H, *J* = 12.3 Hz), 5.29(d, 1H, *J* = 9.8 Hz), 7.13-7.41(m, 30H); ^{13}C NMR(125.76 MHz, $CDCl_3$): δ 18.5, 58.8, 67.2, 67.3, 69.1, 72.0, 72.3, 72.4, 73.3, 74.7, 74.7, 75.1, 76.4, 79.3, 99.6, 127.6-128.7, 135.0, 136.0, 138.2, 138.2, 138.3, 138.3, 156.6, 170.4; HRMS (MALDI-TOF): calcd. for $C_{53}H_{55}NNaO_{10}$ [M^++Na]: 888.3724; found: 888.3728.

Prop-2-yn-1-yl 2,3,4-tri-*O*-benzoyl-6-*O*-[2,3,4,6-tetra-*O*-benzyl α-D-mannopyranosyl] α-D-mannopyranoside **20**: $[\alpha]_D^{25}$ = -23.3($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3298, 3030, 2924, 2854, 2121, 1732, 1601, 1497, 1452, 1360, 1278, 1261, 1107, 1095, 1068, 1028, 752, 711, 698; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.50(t, 1H, *J* = 2.4 Hz), 3.53-3.78(m, 4H), 3.84(dd, 1H, *J* = 3.3, 9.2 Hz), 3.88-4.05(m, 2H), 4.22(m, 1H), 4.31(d, 2H, *J* = 2.4 Hz), 4.37(d, 2H, *J* = 4.5 Hz), 4.43(s, 2H), 4.49(ABq, 2H, *J* = 12.3 Hz), 4.63(s, 2H), 4.86(d, 1H, *J* = 10.9 Hz), 4.96(d, 1H, *J* = 1.8 Hz), 5.26(d, 1H, *J* = 1.8 Hz), 5.68(dd, 1H, *J* = 1.8, 2.9 Hz), 5.89(m, 2H), 7.10-7.56(m, 29H), 7.75-8.11(m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 55.1, 66.6, 67.1, 69.0, 69.7, 69.8, 70.4, 71.8, 71.9, 72.5, 73.2, 74.7, 74.8, 74.9, 75.7, 78.1, 80.1, 96.2, 98.2, 127.3-128.9, 133.1, 133.3, 133.5, 138.3, 138.4, 138.5, 138.6, 165.3, 165.4, 165.4; HRMS(MALDI-TOF) calcd for $C_{64}H_{60}NaO_{14}$[M^++Na]: 1075.3881; found: 1075.3889.

Prop-2-yn-1-yl 3,4,6-tri-O-benzyl-2-*O*-[2,3,4,6-tetra-*O*-benzyl α-D-mannopyranosyl] α-D-mannopyranoside **21**: $[\alpha]_D^{25}$ = -22.6($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3028, 2924, 2854, 2117, 1504, 1454, 1361, 1273, 1097, 1028, 734, 696, 667; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.35(t, 1H, *J* = 2.4 Hz), 3.42(ddd, 1H, *J* = 1.7, 4.7, 6.5 Hz), 3.58(dd, 1H, *J* = 2.3, 9.2 Hz), 3.73(m, 4H), 3.80-3.88(m, 2H), 3.94(ddd, 1H, *J* = 1.5, 3.1, 4.7 Hz), 4.04(dd, 1H, *J* = 1.4, 10.3 Hz), 4.26(dd, 2H, *J* = 1.8, 18.4 Hz), 4.32(m, 2H), 4.35-4.63(m, 9H), 4.66(ABq, 2H, *J* = 12.0 Hz), 4.68(ABq, 2H, *J* = 11.0 Hz), 4.84(d, 1H, *J* = 1.9 Hz), 4.87(d, 1H, *J* = 1.7 Hz), 5.28(m, 1H), 7.13-7.41(m, 35H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.4, 69.2, 69.3, 71.4, 71.8, 72.1, 72.6, 72.7, 73.2, 73.5, 74.7, 74.9, 74.9, 75.0, 75.1, 75.7, 77.2, 78.9, 79.8, 82.7, 97.1, 98.4, 127.2-128.6, 137.7,

138.2, 138.3, 138.5, 138.7, 138.8, 138.8; HRMS(MALDI-TOF) calcd for $C_{64}H_{66}NaO_{11}[M^+Na]$: 1033.4503; found: 1075.4517.

Prop-2-yn-1-yl 2,3,6-tri-*O*-benzoyl 4-*O*-[2,3,4,6-tetra-*O*-benzyl α-D-mannopyranosyl] β-D-glucopyranoside **22**: $[\alpha]_D^{25}$ = +16.4($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3299, 3031, 2922, 2854, 2122, 1729, 1599, 1497, 1452, 1360, 1280, 1264, 1107, 1095, 1068, 1028, 752, 712, 700; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.36(t, 1H, *J* = 2.4 Hz), 3.55(dd, 1H, *J* = 1.6, 7.7 Hz), 3.57(d, 1H, *J* = 1.8 Hz), 3.70(dd, 1H, *J* = 3.7, 10.4 Hz), 3.79(m, 1H), 3.87(d, 1H, *J* = 11.6 Hz), 3.89(ddd, 1H, *J* = 2.0, 4.5, 7.1 Hz), 3.97(t, 1H, *J* = 9.3 Hz), 4.12(d, 1H, *J* = 10.8 Hz), 4.19(t, 1H, *J* = 9.1 Hz), 4.36(ABq, 2H, *J* = 12.5 Hz), 4.36(ABq, 2H, *J* = 11.1 Hz), 4.39 (ABq, 2H, *J* = 12.1 Hz), 4.39-4.56(m, 3H), 4.74(d, 1H, *J* = 10.8 Hz), 4.81(dd, 1H, *J* = 2.1, 12.1 Hz), 5.03(d, 1H, *J* = 7.7 Hz), 5.14(d, 1H, *J* = 2.1 Hz), 5.40(dd, 1H, *J* = 8.0, 9.8 Hz), 5.78(t, 1H, *J* = 9.6 Hz), 6.90-7.60(m, 29H), 7.90-8.15(m, 6H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 55.9, 63.3, 68.7, 71.6, 71.8, 72.6, 73.2, 73.3, 73.4, 74.3, 74.9, 75.3, 75.5, 76.1, 76.3, 78.1, 79.4, 98.1, 100.7, 127.0-129.9, 133.1, 133.2, 133.7, 138.1, 138.3, 138.3, 138.5, 165.3, 165.6, 166.1; HRMS(MALDI-TOF) calcd for $C_{64}H_{60}NaO_{14}[M^+Na]$: 1075.3881; found: 1075.3891.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4,6-tetra-*O*-benzyl α-D-mannopyranosyl] α-D-glucopyranoside **23**: $[\alpha]_D^{25}$ = +41.8($CHCl_3$, *c* 1.00); IR(cm^{-1}): 3284, 3028, 2924, 2854, 1504, 1454, 1361, 1273, 1097, 1028, 734, 696, 676; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 3.3(s, 3H), 3.39(t, 1H, *J* = 9.3 Hz), 3.45(dd, 1H, *J* = 3.5, 9.3 Hz), 3.60(dt, 2H, *J* = 1.3, 8.8 Hz), 3.69(m, 3H), 3.78(t, 1H, *J* = 2.3 Hz), 3.83(dd, 1H, *J* = 3.8, 10.5 Hz), 3.86(dd, 1H, *J* = 3.0, 7.0 Hz), 3.98(q, 2H, *J* = 9.2 Hz), 4.48(d, 1H, *J* = 1.5 Hz), 4.50 (d, 1H, *J* = 1.7 Hz), 4.61(ABq, 2H, *J* = 11.7 Hz), 4.61(s, 2H), 4.66(m, 2H), 4.67(ABq, 2H, *J* = 11.1 Hz), 4.70(ABq, 2H, *J* = 12.6 Hz), 4.73(ABq, 2H, *J* = 12.1 Hz), 4.84(ABq, 2H, *J* = 10.6 Hz), 7.11-7.42(m, 35H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 55.0, 65.7, 69.0, 69.7, 71.8, 71.9, 72.4, 73.2, 73.2, 74.6, 74.8, 74.9, 75.0, 75.7, 77.6, 79.5, 79.9, 82.1, 97.8, 98.2, 127.3-128.5, 138.1, 138.1, 138.3, 138.3, 138.4, 138.6, 138.6; HRMS(MALDI-TOF) calcd for $C_{62}H_{66}NaO_{11}[M^+Na]$: 1009.4503; found: 1009.4508.

Cholesteryl 2,3,4,6-tetra-*O*-benzyl α/β-D-glucopyranosides **24** *(1:8.9 α:β)*: IR(cm^{-1}): 3290, 3030, 2918, 2922, 2880, 1497, 1458, 1360, 1210, 1060, 1029, 755, 700; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.68(s, 3H), 0.86(d, 3H, *J* = 1.8 Hz), 0.88(d, 3H, *J* = 1.8 Hz), 0.89-2.48(m, 34H), 3.44(m, 2H), 3.54(t, 1H, *J* = 9.3 Hz), 3.63(m, 3H), 3.73(dd, 1H, *J* = 1.7, 10.7 Hz), 4.50(d, 1H, *J* = 7.7 Hz), 4.57(ABq, 2H, *J* = 12.3 Hz), 4.68(ABq, 2H, *J* = 10.9 Hz), 4.82(ABq, 2H, *J* = 10.9 Hz), 4.88(ABq, 2H, *J* = 10.8 Hz), 5.35(d, 1H, *J* = 4.7 Hz), 7.10-7.38(m, 20H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 11.8, 18.7, 19.4, 21.1, 21.6, 22.8, 23.8, 24.3, 28.0, 28.2, 30.0, 31.9, 31.9, 35.8, 36.2, 36.7, 37.3, 39.1, 39.5, 39.8, 42.3, 50.2, 56.1, 56.7, 69.1, 73.4, 74.8, 74.9, 75.0, 75.7, 78.0, 79.7, 82.3, 84.8, 102.2, 121.9, 127.4-128.4, 138.1, 138.3, 138.5, 138.6, 140.6; HRMS(MALDI-TOF) calcd for $C_{61}H_{80}NaO_6[M^+Na]$: 931.5853; found: 931.5850.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzyl α/β-D-glucopyranosyl)-L-threoninate **25** *(1:1.3 α:β)*: IR(cm^{-1}): 3285, 3030, 2918, 2884, 1726, 1690, 1497, 1458, 1360, 1210, 1060, 1028, 753, 696; ^{1}H NMR(500.13 MHz, $CDCl_3$): δ 1.27, 1.30(2d, 6H, *J* = 7.0 Hz), 3.25(td, 1H, *J* = 2.4, 5.6 Hz), 3.33(t, 1H, *J* = 8.2 Hz), 3.45(dd, 1H, *J* = 3.6, 9.7 Hz), 3.50-3.65(m, 6H), 3.71(dd, 1H, *J* = 3.2, 10.5 Hz), 3.79(td, 1H, *J* = 2.9, 5.0 Hz), 3.88(t, 1H, *J* = 9.3 Hz), 4.30-5.20(m, 30H), 5.80, 5.91(2d, 2H, *J* = 8.4 Hz), 7.10-7.51(m, 60H); ^{13}C NMR(100.61 MHz, $CDCl_3$): δ 17.7, 19.1, 58.9, 59.1, 67.1, 67.1, 67.1, 67.2, 68.3, 68.8, 70.9, 73.1, 73.4, 73.5, 74.7, 74.7, 74.9, 75.0, 75.2, 75.5, 75.5, 75.6, 77.2, 77.2, 77.6, 79.6, 81.6, 81.8, 98.0, 101.4, 127.5-

128.5, 135.2, 135.4, 136.3, 136.3, 137.8, 137.9, 138.1, 138.1, 138.1, 138.2, 138.6, 138.6, 156.8, 156.8, 170.2, 170.5; HRMS (MALDI-TOF): calcd. for $C_{53}H_{55}NNaO_{10}$ [M^++Na]: 888.3724; found: 888.3721.

Prop-2-yn-1-yl 2,3,4-tri-*O*-benzoyl-6-*O*-[2,3,4,6-tetra-*O*-benzyl α/β-D-glucopyranosyl] α-D-mannopyranoside **26** *(1:3.1 α:β)*: IR(cm^{-1}): 3300, 3030, 2925, 2850, 2121, 1722, 1599, 1497, 1452, 1360, 1278, 1261, 1107, 1095, 1068, 1028, 752, 711, 696; ^{1}H NMR(399.78 MHz, $CDCl_3$): δ 2.39, 2.46(2t, 2H, *J* = 2.4 Hz), 3.35-4.30(m, 16H), 4.16-4.98(m, 22H), 5.00(d, 1H, *J* = 10.3 Hz), 5.09(d, 1H, *J* = 10.7 Hz), 5.27(d, 1H, *J* = 1.7 Hz), 5.31(d, 1H, *J* = 1.7 Hz), 5.67-5.93(m, 6H), 7.10-7.61(m, 58H), 7.75-8.15(m, 12H); ^{13}C NMR(100.53 MHz, $CDCl_3$): δ 54.5, 54.9, 67.2, 67.3, 67.4, 68.2, 68.7, 69.1, 69.9, 70.0, 70.2, 70.2, 70.3, 70.4, 70.5, 73.1, 73.3, 73.4, 73.5, 74.8, 74.8, 74.9, 75.0, 75.6, 75.7, 75.7, 75.8, 77.5, 77.6, 77.9, 78.0, 81.7, 81.8, 82.4, 95.4, 95.9, 97.4, 104.1, 127.3-130.5, 131.1, 131.1, 133.2, 133.2, 133.4, 133.4, 138.0, 138.0, 138.1, 138.1, 138.3, 138.4, 138.5, 138.8, 165.2, 165.2, 165.3, 165.4, 165.4, 165.6; HRMS (MALDI-TOF): calcd. for $C_{64}H_{60}NaO_{14}$ [M^++Na]: 1075.3881; found: 1075.3871.

Prop-2-yn-1-yl 2,3,6-tri-*O*-benzoyl 4-*O*-[2,3,4,6-tetra-*O*-benzyl α/β-D-glucopyranosyl] β-D-glucopyranoside **27** *(1:3.2 α:β)*: IR(cm^{-1}): 3299, 3031, 2922, 2854, 2122, 1729, 1599, 1497, 1452, 1360, 1280, 1264, 1107, 1095, 1068, 1028, 752, 712, 700; ^{1}H NMR(500.13 MHz, $CDCl_3$): δ 2.37, 2.48(2t, 2H, *J* = 2.4 Hz), 2.98-3.98(m, 16H), 4.10-4.90(m, 24H), 5.03(m, 2H), 5.49(m, 2H), 5.87(m, 2H), 5.75(m, 2H), 7.00-7.65(m, 58H), 7.95-8.15(m, 12H); ^{13}C NMR(125.76 MHz, $CDCl_3$): δ 55.2, 55.8, 62.5, 63.2, 66.9, 68.2, 68.3, 68.8, 71.2, 71.6, 71.7, 71.8, 72.8, 73.0, 73.2, 73.4, 73.7, 74.1, 74.3, 74.7, 74.8, 74.9, 75.0, 75.1, 75.4, 75.5, 75.5, 75.6, 78.1, 78.2, 78.7, 78.9, 81.4, 81.7, 98.1, 99.8, 102.2, 104.8, 127.3-130.2, 132.8, 133.0, 133.1, 133.2, 133.5, 133.7, 137.9, 138.1, 138.2, 138.3, 138.4, 138.5, 138.6, 138.6, 165.4, 165.5, 165.8, 165.9, 165.9, 166.0; HRMS (MALDI-TOF): calcd. for $C_{64}H_{60}NaO_{14}$ [M^++Na]: 1075.3881; found: 1075.3888.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4,6-tetra-*O*-benzyl α/β-D-glucopyranosyl] α-D-glucopyranoside **28** *(1:2.8 α:β)*: IR(cm^{-1}): 3286, 3038, 2920, 2854, 1504, 1454, 1361, 1273, 1097, 1028, 734, 699; ^{1}H NMR(400.13 MHz, $CDCl_3$): δ 3.32, 3.35(2s, 6H), 3.39-4.25(m, 24H), 4.32-5.00(m, 32H), 7.10-7.39(m, 70H); ^{13}C NMR(100.61 MHz, $CDCl_3$): δ 55.1, 55.2, 68.4, 68.5, 69.0, 69.8, 70.2, 70.3, 72.3, 72.3, 73.3, 74.3, 74.9, 74.9, 74.9, 75.0, 75.0, 75.5, 75.6, 75.7, 75.7, 77.6, 77.7, 77.8, 77.9, 79.7, 79.9, 80.1, 81.6, 81.9, 82.0, 82.1, 84.7, 97.2, 97.9, 98.0, 103.8, 127.3-128.5, 137.9, 138.0, 138.0, 138.1, 138.1, 138.2, 138.3, 138.3, 138.4, 138.4, 138.4, 138.5, 138.8, 138.8; HRMS (MALDI-TOF): calcd. for $C_{62}H_{66}NaO_{11}$ [M^++Na]: 1009.4503; found: 1009.4512.

Cholesteryl 2,3,4,6-tetra-*O*-benzyl α/β-D-galactopyranosides **29***(1:2.7 α:β)*: IR(cm^{-1}): 3295, 3030, 2918, 2922, 2880, 1497, 1458, 1360, 1210, 1060, 1029, 755, 695, 676; ^{1}H NMR (500.20 MHz, $CDCl_3$): δ 0.60-2.51(m, 86H), 3.54(m, 7H), 3.93-4.08(m, 7H), 4.36-5.02(m, 18H), 5.26(d, 1H, *J* = 4.8 Hz), 5.32(d, 1H, *J* = 4.8 Hz), 7.10-7.38(m, 40H); ^{13}C NMR (125.78 MHz, $CDCl_3$): δ 11.8, 11.8, 18.7, 18.8, 19.4, 19.4, 21.0, 21.0, 22.6, 22.5, 22.8, 22.8, 23.8, 23.8, 24.3, 24.4, 27.6, 27.6, 28.0, 28.1, 28.2, 28.2, 29.7, 29.8, 31.9, 31.9, 35.6, 35.6, 36.2, 36.3, 36.8, 36.8, 37.1, 37.3, 39.0, 39.1, 39.5, 39.5, 39.8, 39.9, 42.3, 42.4, 50.1, 50.2, 56.1, 56.2, 56.7, 56.8, 67.5, 69.0, 69.1, 73.1, 73.2, 73.4, 74.4, 74.4, 74.7, 74.9, 75.2, 75.2, 75.3, 75.4, 76.5, 76.5, 79.2, 79.2, 79.4, 79.7, 95.4, 102.4, 121.6, 121.7, 127.3-128.6, 137.3, 138.0, 138.0, 138.6, 138.7, 138.7, 138.8, 138.9, 140.8, 140.9; HRMS(MALDI-TOF) calcd for $C_{61}H_{80}NaO_6$[M^++Na]: 931.5853; found: 931.5862.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzyl α/β-D-galactopyranosyl)-L-threoninate **30** *(1:8.1 α:β)*: IR(cm^{-1}): 3285, 3030, 2918, 2884, 1726, 1690, 1497, 1458, 1360, 1210, 1060, 1028, 753, 696; ^{1}H NMR(500.13 MHz, $CDCl_3$): δ 1.13(d, 3H, *J* = 6.3 Hz), 3.53(m, 2H), 3.88(dd, 1H, *J* = 2.3, 10.3 Hz), 3.97(m, 3H), 4.35(dd, 1H, *J* = 2.3, 8.6 Hz), 4.40(m, 1H), 4.44-4.57(m, 2H), 4.56(d, 1H, *J* = 11.5 Hz), 4.61(ABq, 2H, *J* = 11.7 Hz), 4.68(s, 2H), 4.90(d, 1H, *J* = 3.6 Hz), 4.94(d, 1H *J* = 11.4 Hz), 5.06(s, 2H), 5.15(s, 2H), 6.05(d, 1H, *J* = 8.6 Hz), 7.20-7.51(m, 30H); ^{13}C NMR(125.76 MHz, $CDCl_3$): δ 19.1, 59.1, 67.0, 67.2, 68.8, 69.9, 72.8, 73.5, 73.5, 74.7, 74.8, 74.8, 76.0, 78.8, 98.3, 127.4-128.6, 133.3, 136.3, 137.9, 138.3, 138.6, 138.6, 156.9, 170.6; HRMS (MALDI-TOF): calcd. for $C_{53}H_{55}NNaO_{10}$ [M^++Na]: 888.3724; found: 888.3834.

Prop-2-yn-1-yl 2,3,4-tri-*O*-benzoyl-6-*O*-[2,3,4,6-tetra-*O*-benzyl α/β-D-galactopyranosyl] α-D-mannopyranoside **31** *(1:8.2 α:β)*: IR(cm^{-1}): 3294, 3033, 2925, 2850, 2121, 1722, 1599, 1497, 1452, 1360, 1278, 1261, 1100, 1095, 1072, 1028, 752, 711, 700; ^{1}H NMR(200.13 MHz, $CDCl_3$): δ 2.46(t, 1H, *J* = 2.4 Hz), 3.40(d, 1H, *J* = 6.5 Hz), 3.58(dt, 1H, *J* = 2.1, 11.2 Hz), 3.85-4.13(m, 5H), 4.20-5.10(m, 13H), 5.25(d, 1H, *J* = 1.4 Hz), 5.72(t, 1H, *J* = 2.4 Hz), 5.87(d, 1H, *J* = 1.4 Hz), 5.89(dd, 1H, *J* = 10.1, 12.1Hz), 7.10-7.56(m, 29H), 7.72-8.15(m, 6H); ^{13}C NMR(100.53 MHz, $CDCl_3$): δ 54.7, 66.9, 67.2, 68.6, 69.1, 70.1, 70.1, 70.2, 72.9, 73.1, 73.2, 74.7, 75.0, 75.8, 76.4, 78.1, 78.7, 95.8, 98.0, 127.3-130.0, 133.1, 134.0, 134.0, 138.0, 138.6, 138.7, 138.8, 165.4, 165.5, 165.5 ; HRMS (MALDI-TOF): calcd. for $C_{64}H_{60}NaO_{14}$ [M^++Na]: 1075.3881; found: 1075.3868.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4,6-tetra-*O*-benzyl α/β-D-galactopyranosyl] α-D-glucopyranoside **32** *(1:7.9 α:β)*: IR(cm^{-1}): 3300, 3035, 2918, 2854, 1504, 1454, 1361, 1273, 1097, 1028, 734, 700; ^{1}H NMR(200.13 MHz, $CDCl_3$): δ 3.29(s, 3H), 3.29(m, 1H), 3.41(dd, 1H, *J* = 3.4, 9.5 Hz), 3.50(m, 2H), 3.58(t, 1H, *J* = 9.2 Hz), 3.68-3.82(m, 2H), 3.91(dd, 1H, *J* = 3.3, 12.8 Hz), 3.92(s, 1H), 3.96(m, 2H), 4.03(dd, 1H, *J* = 3.3, 9.2 Hz), 4.39(ABq, 2H, *J* = 12.2 Hz), 4.52(d, 1H, *J* = 3.5 Hz), 4.55 (d, 1H, *J* = 5.1 Hz), 4.58-4.98(m, 11H), 5.00(d, 1H, *J* = 3.7 Hz), 7.10-7.48(m, 35H); ^{13}C NMR(125.76 MHz, $CDCl_3$): δ 55.0, 66.4, 68.9, 69.3, 70.3, 72.5, 72.8, 73.3, 73.3, 74.7, 75.0, 75.1, 75.7, 76.5, 78.0, 78.2, 80.1, 82.0, 97.8, 97.9, 127.3-128.4, 138.0, 138.2, 138.4, 138.7, 138.7, 138.8, 138.8 ; HRMS (MALDI-TOF): calcd. for $C_{62}H_{66}NaO_{11}$ [M^++Na]: 1009.4503; found: 1009.4508.

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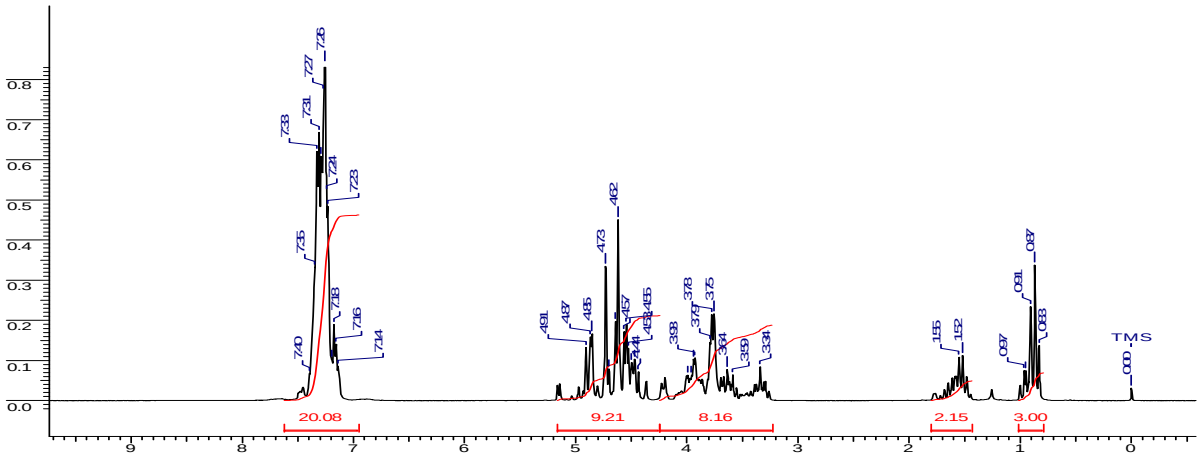
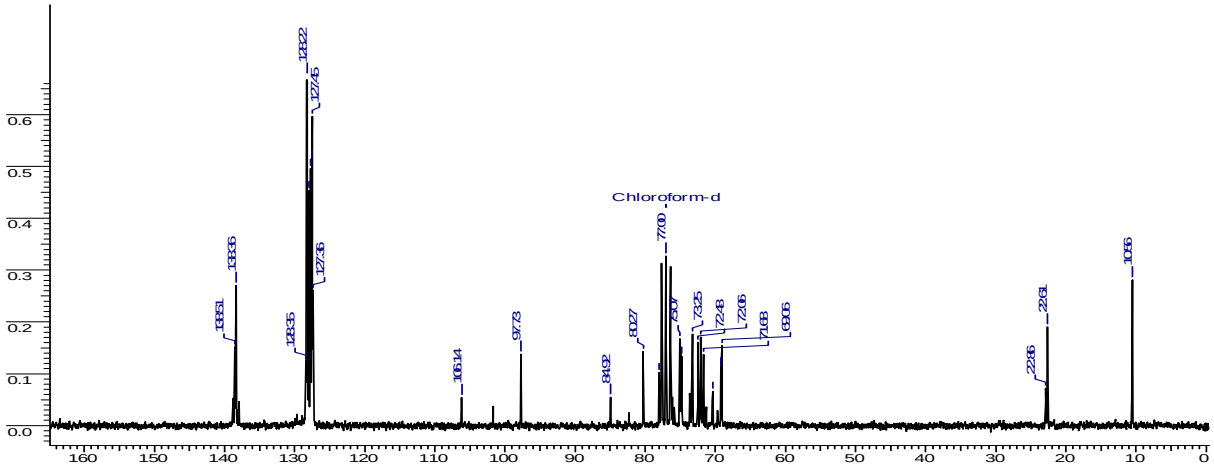
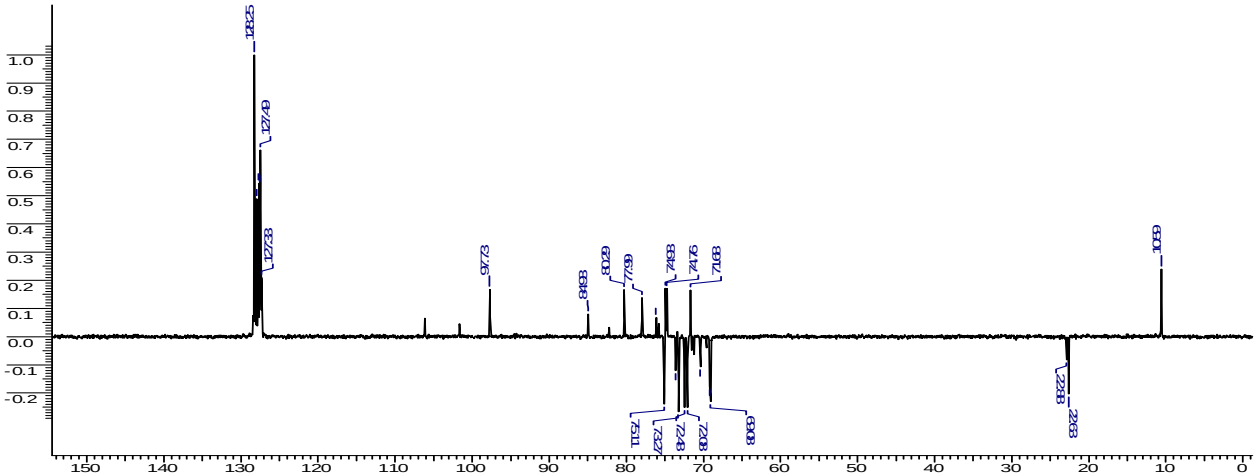
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1A**



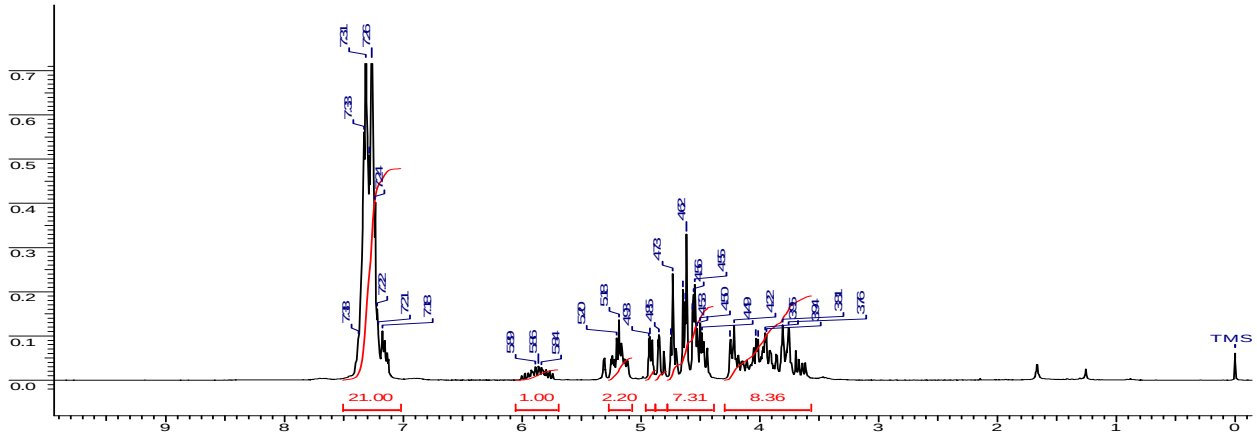
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1A**



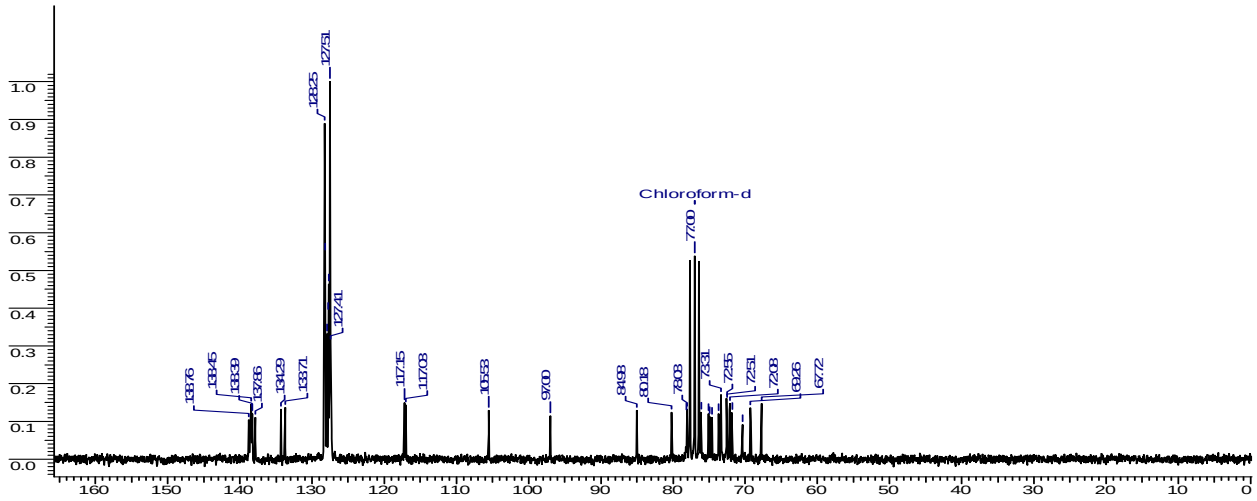
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1A**



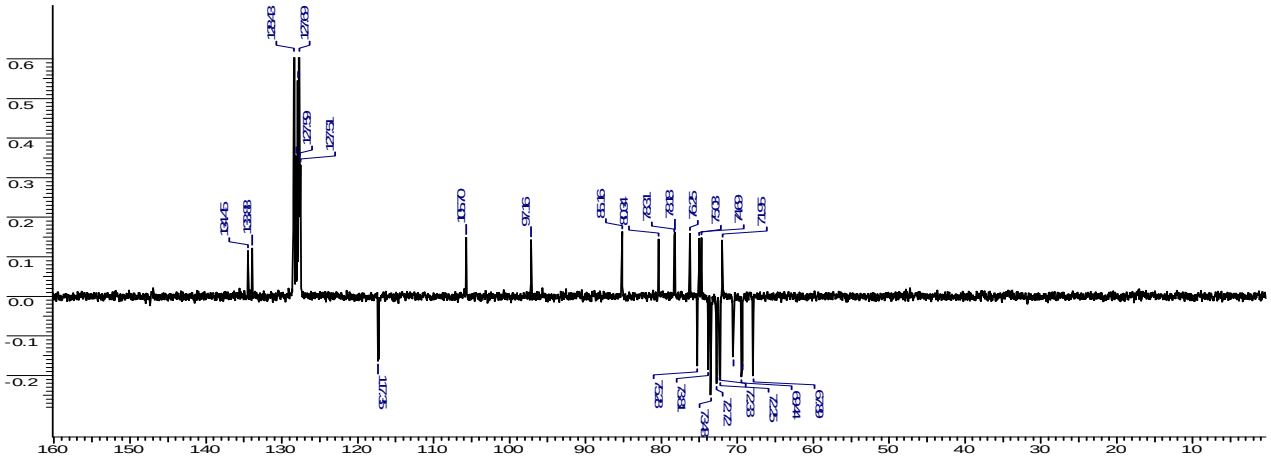
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1B**



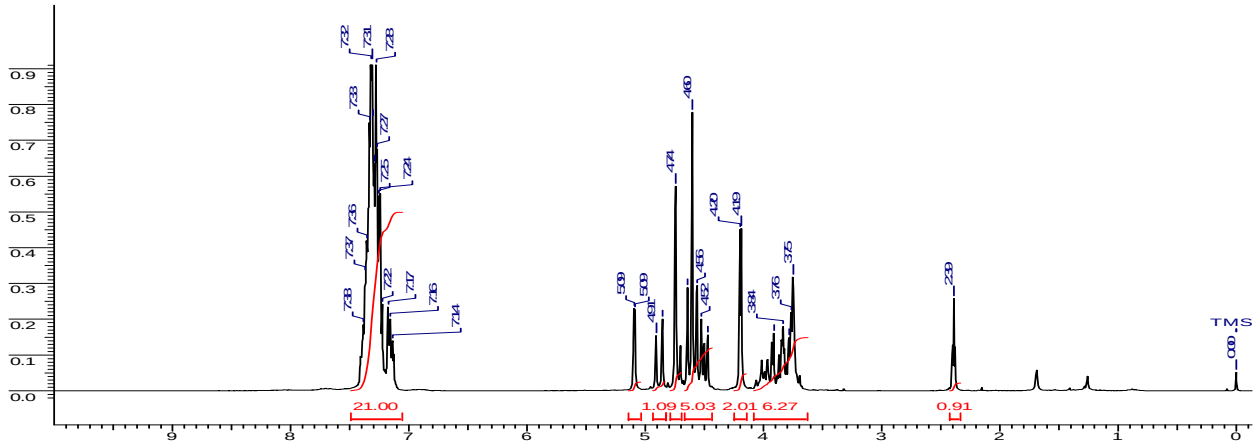
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1B**



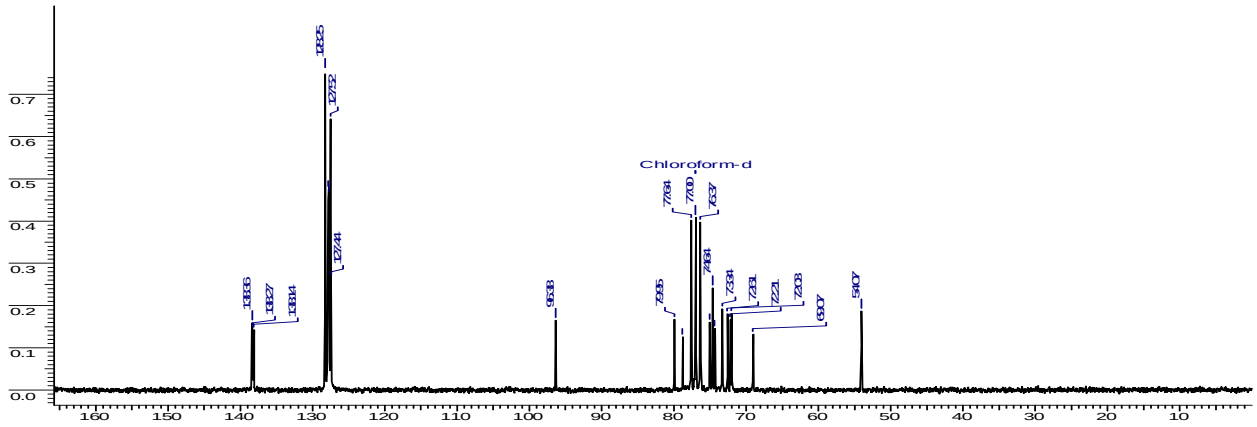
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1B**



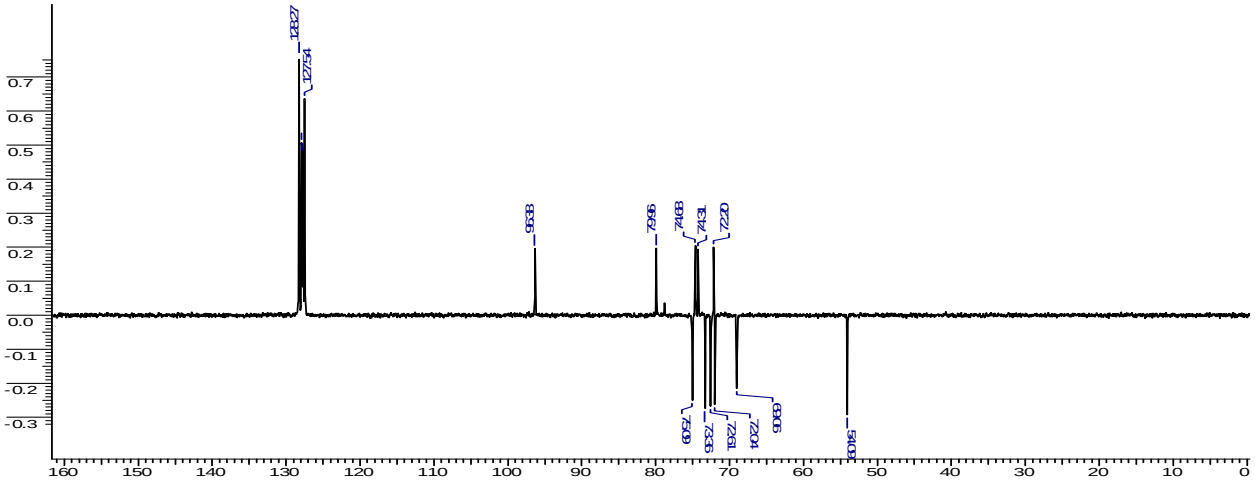
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1C**



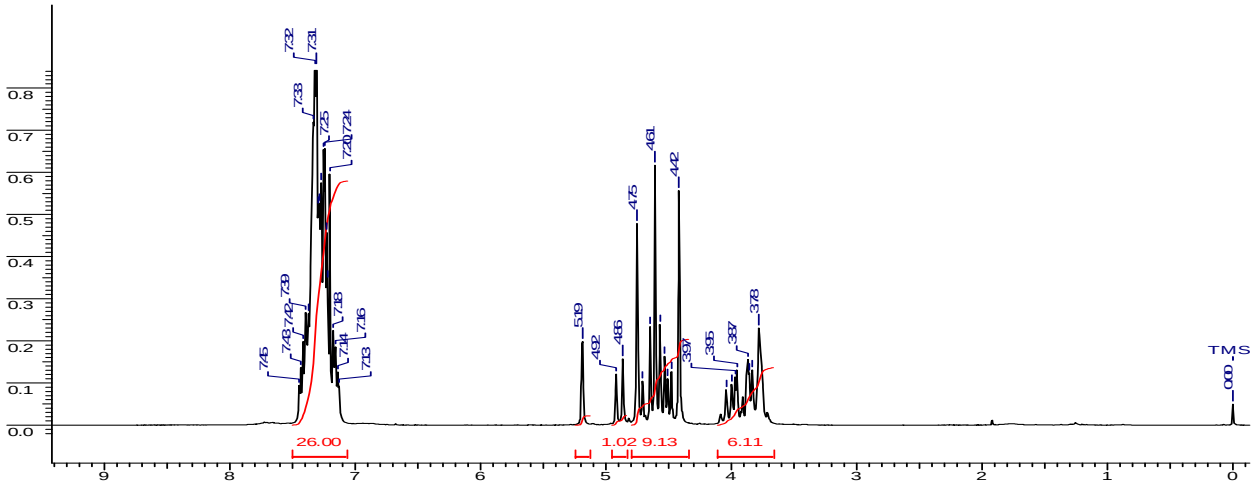
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1C**



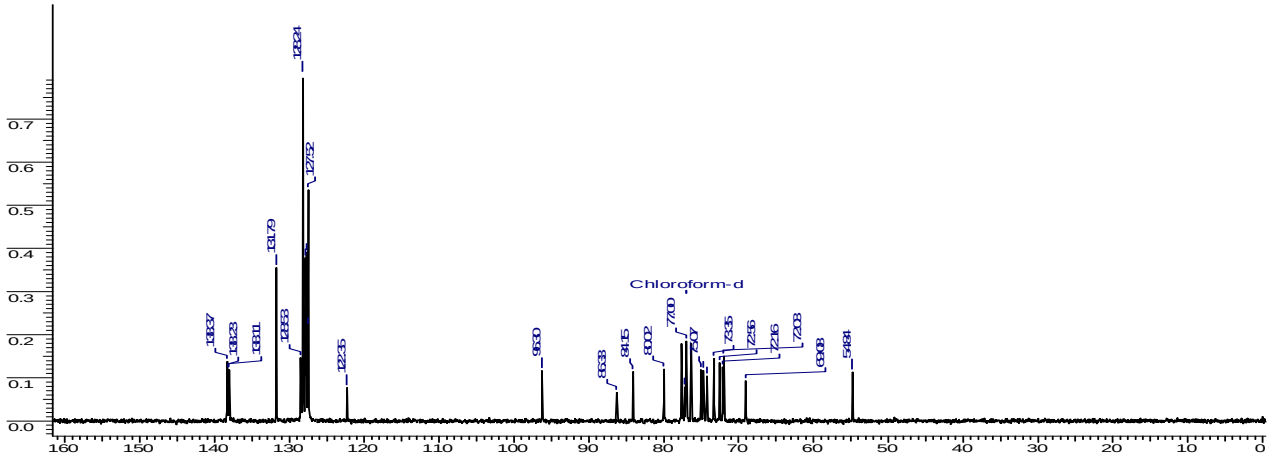
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1C**



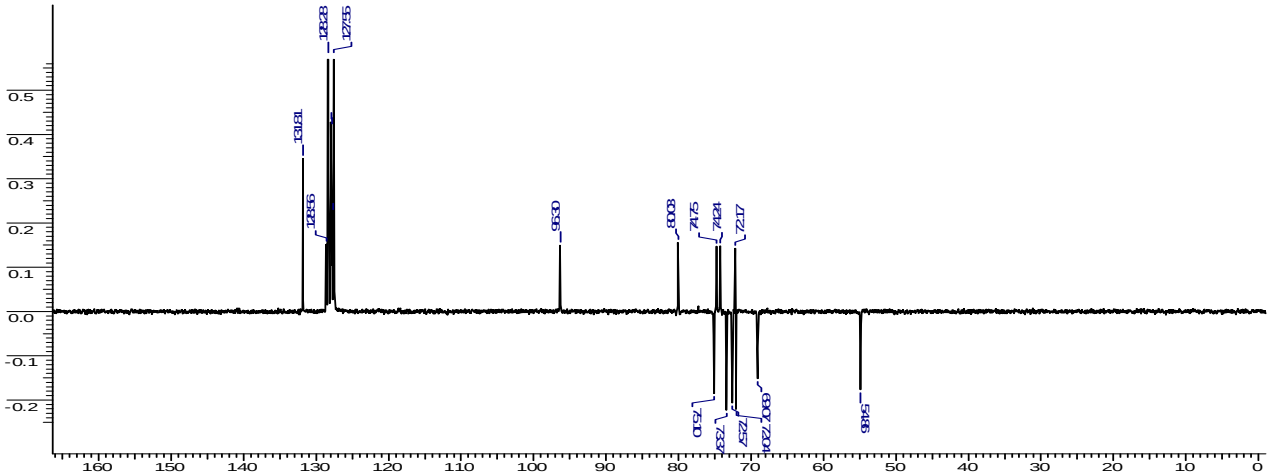
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1D**



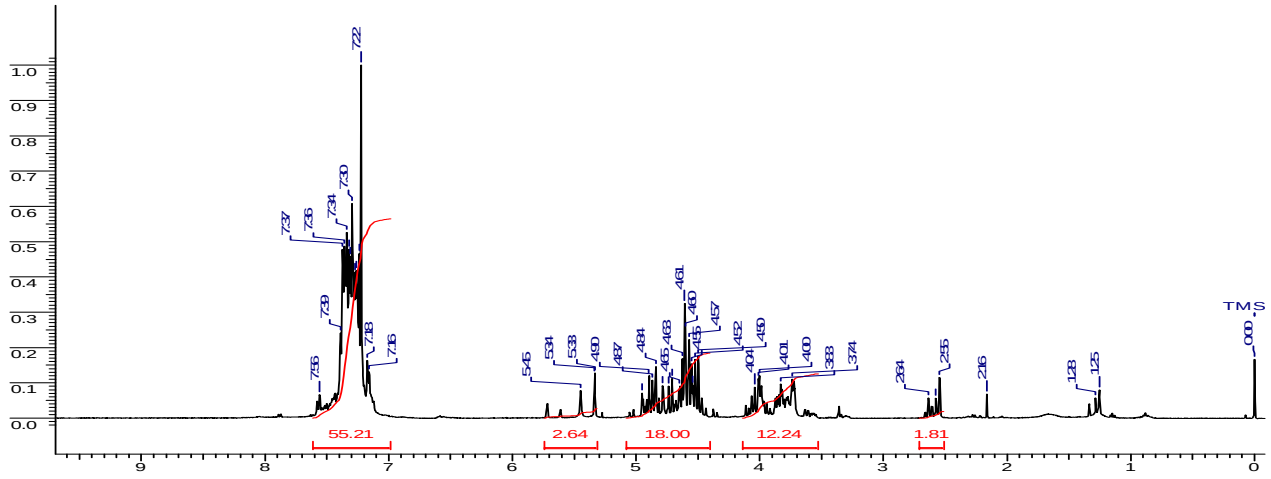
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **1D**



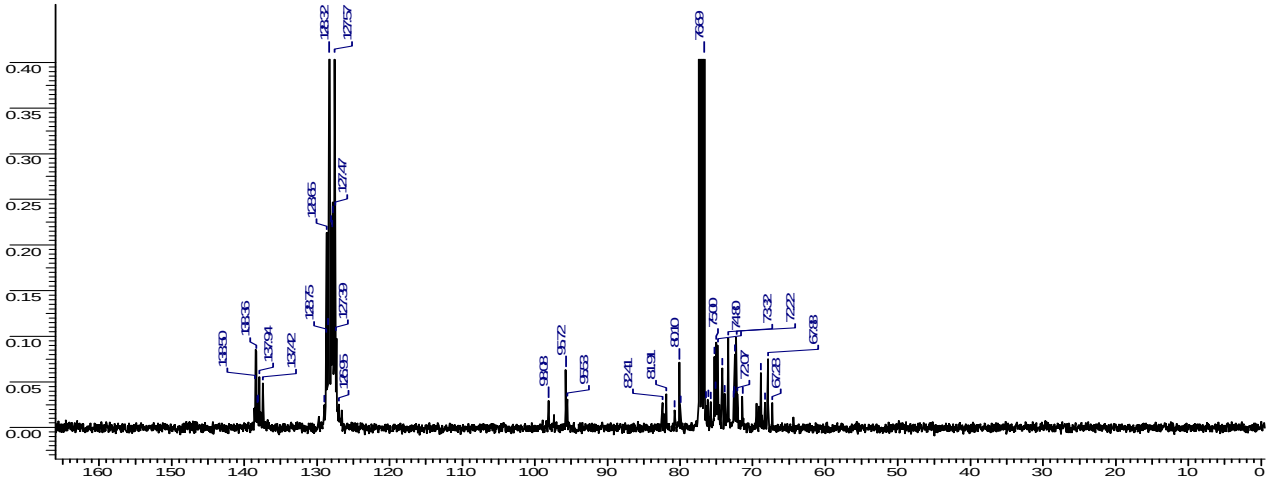
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **1D**



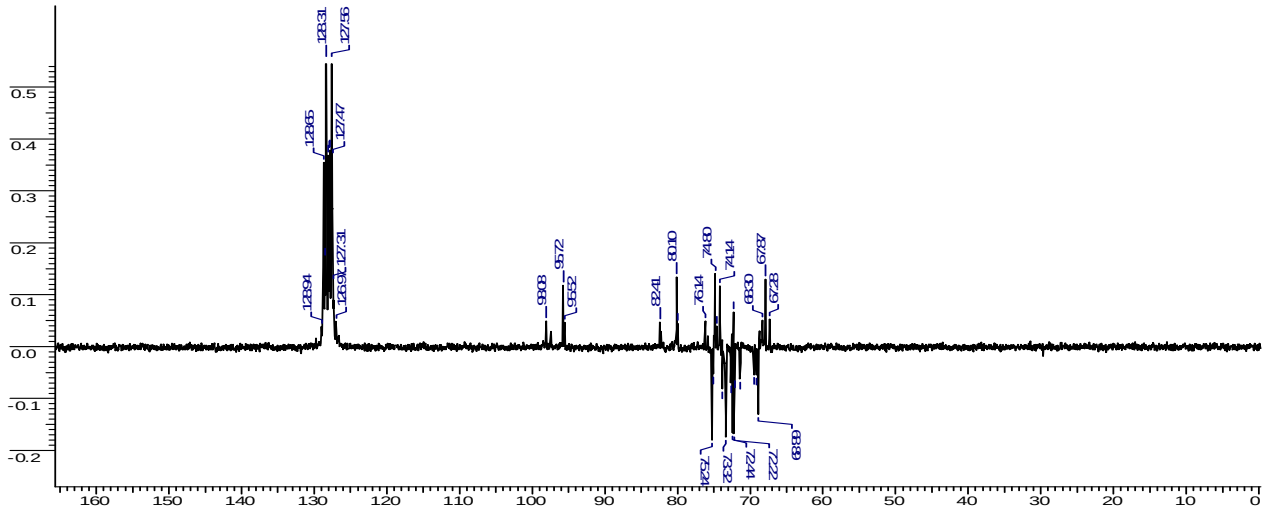
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **1E**



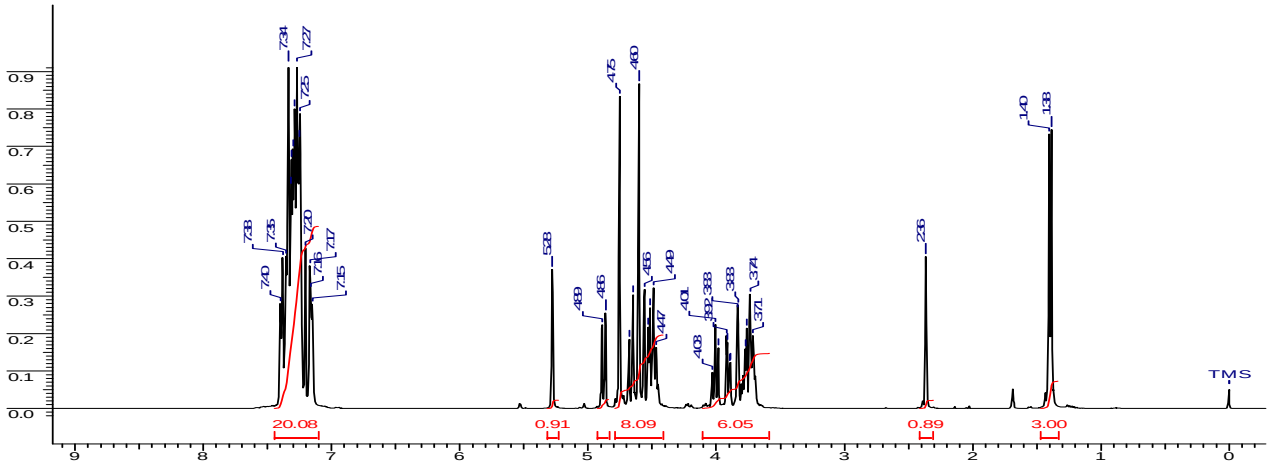
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **1E**



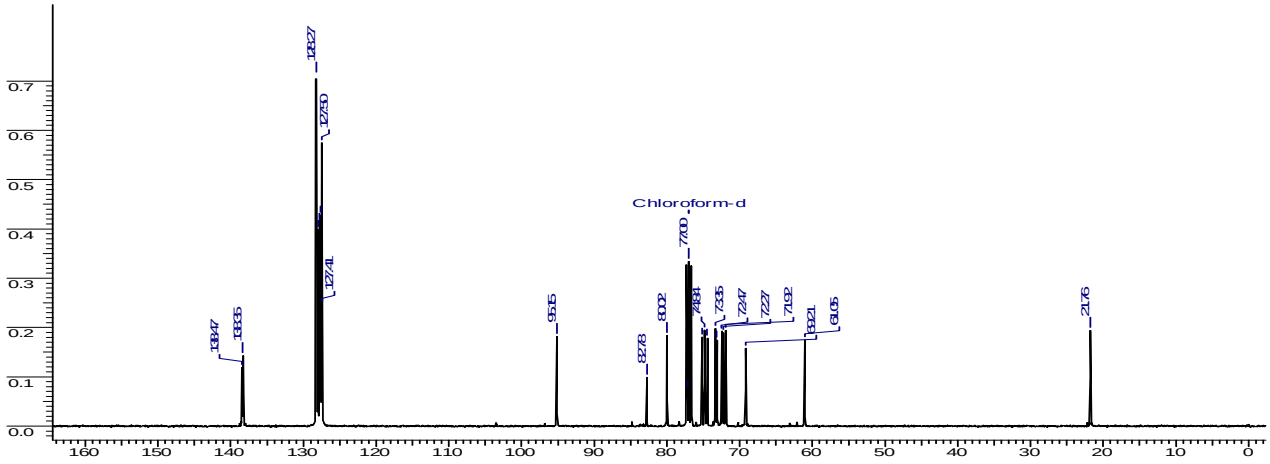
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **1E**



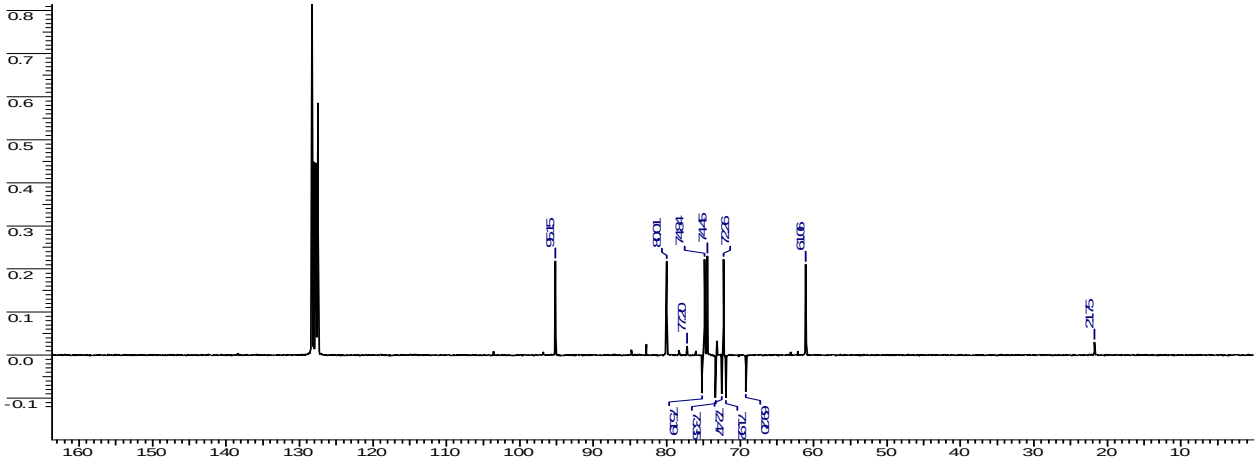
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **1F**



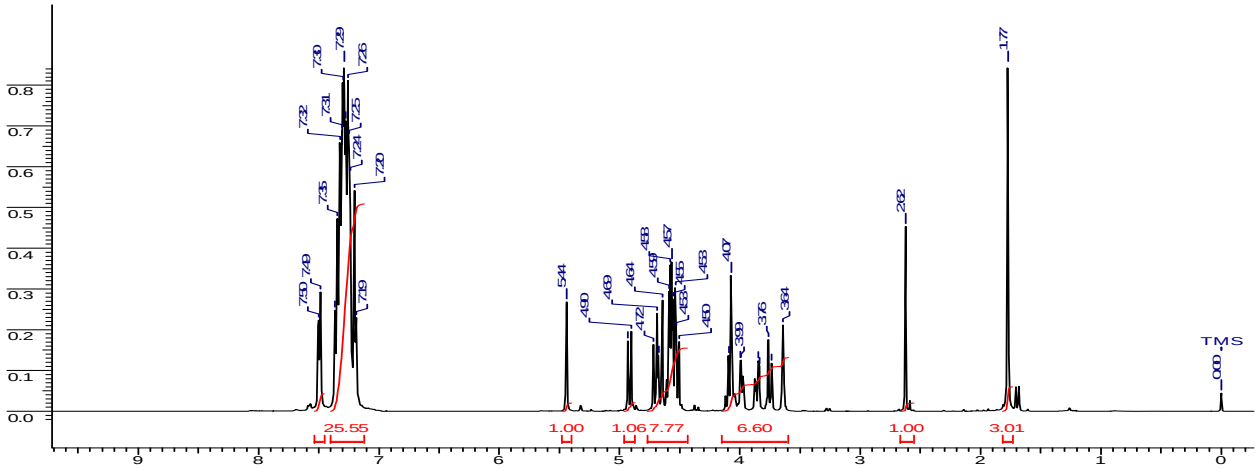
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **1F**



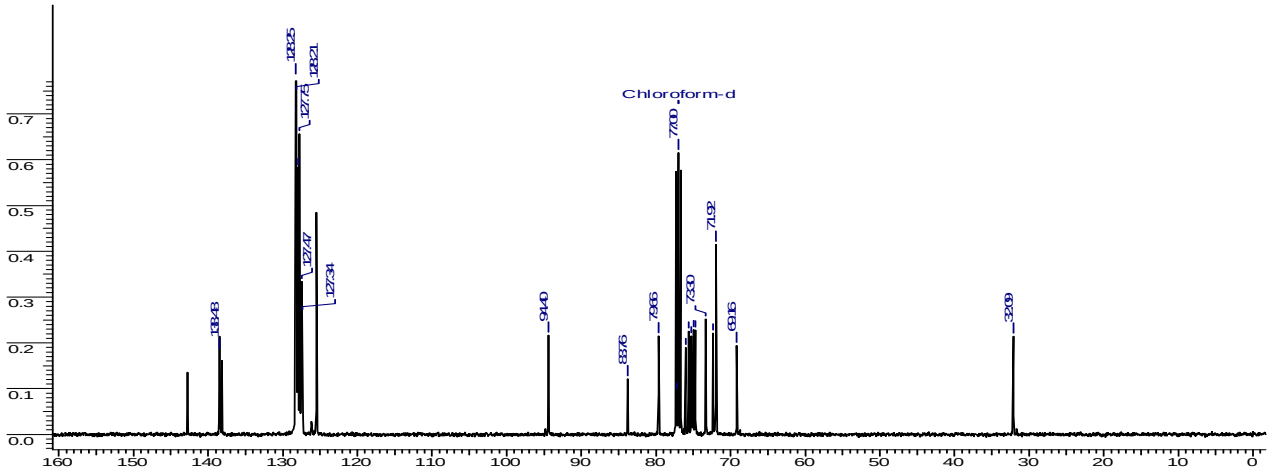
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **1F**



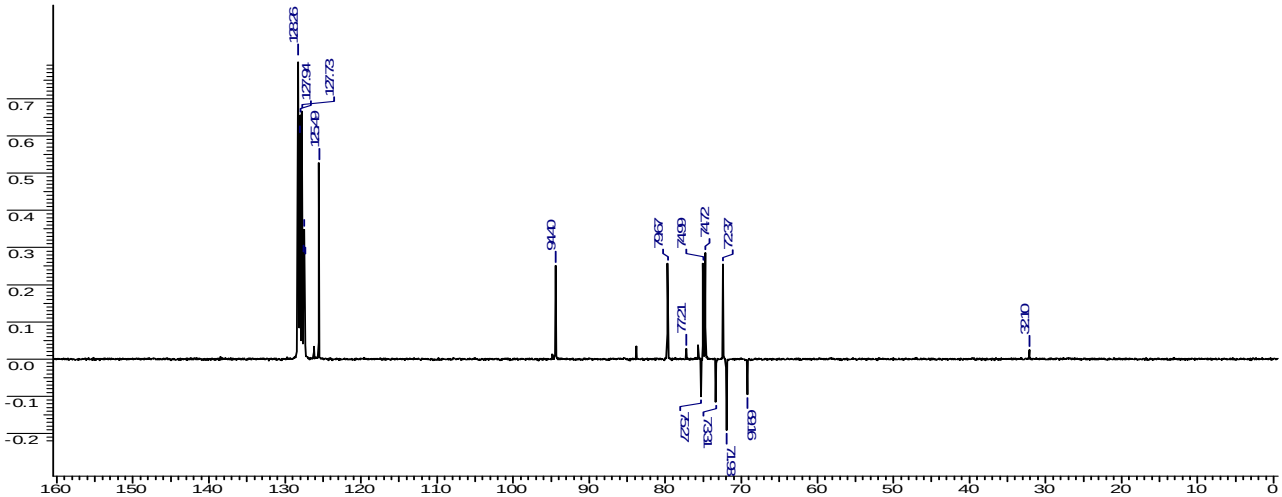
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **1G**



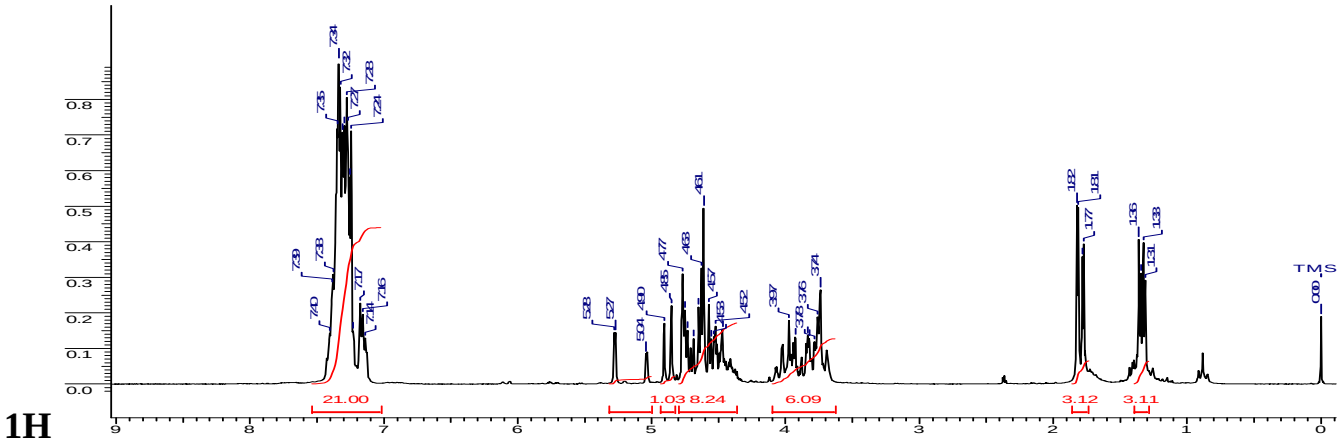
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **1G**



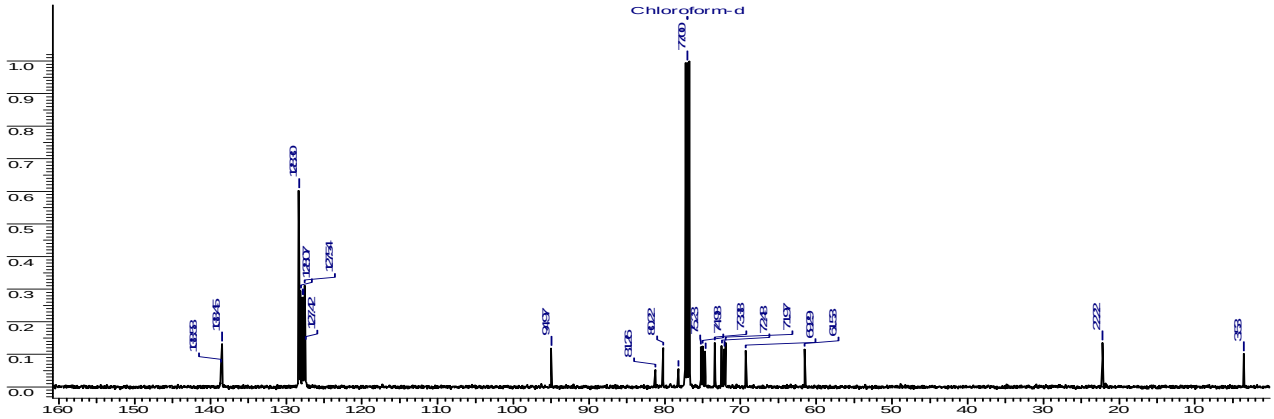
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **1G**



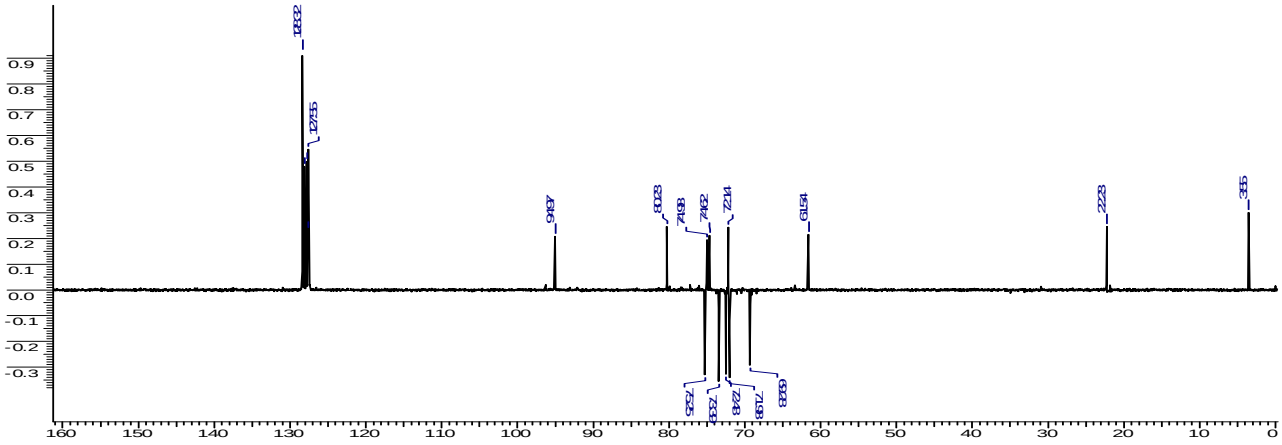
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound



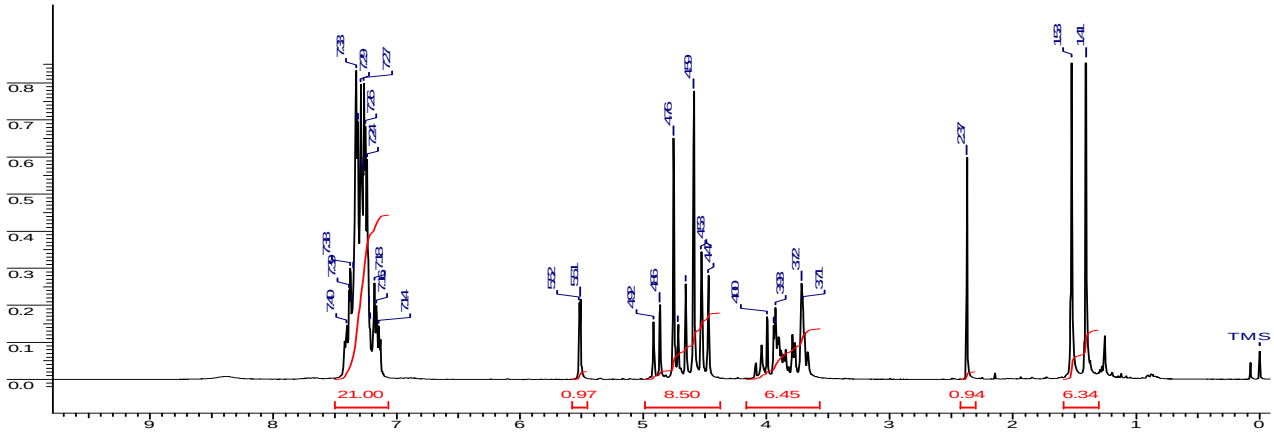
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **1H**



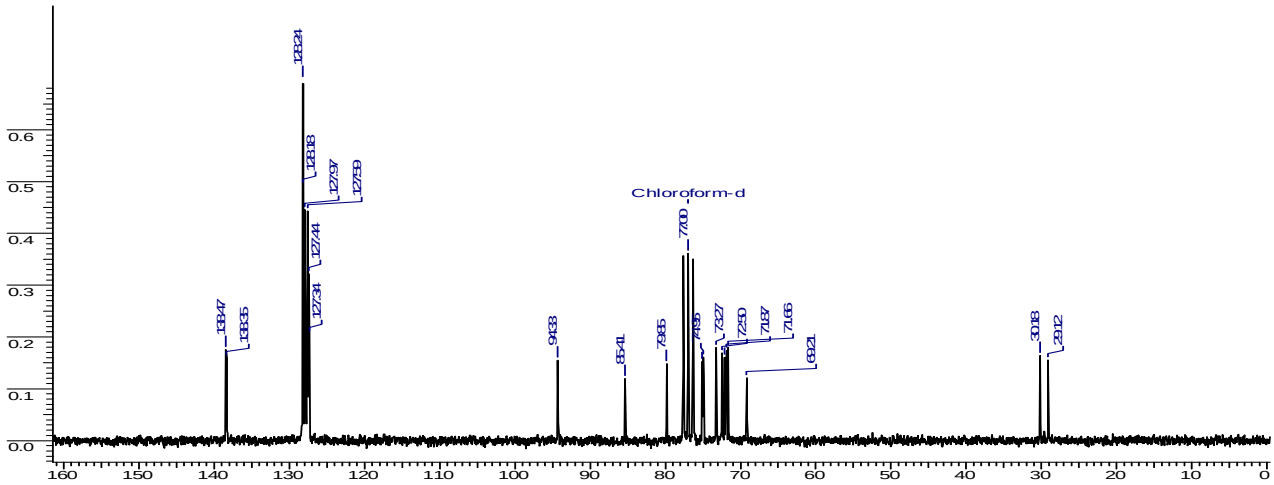
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **1H**



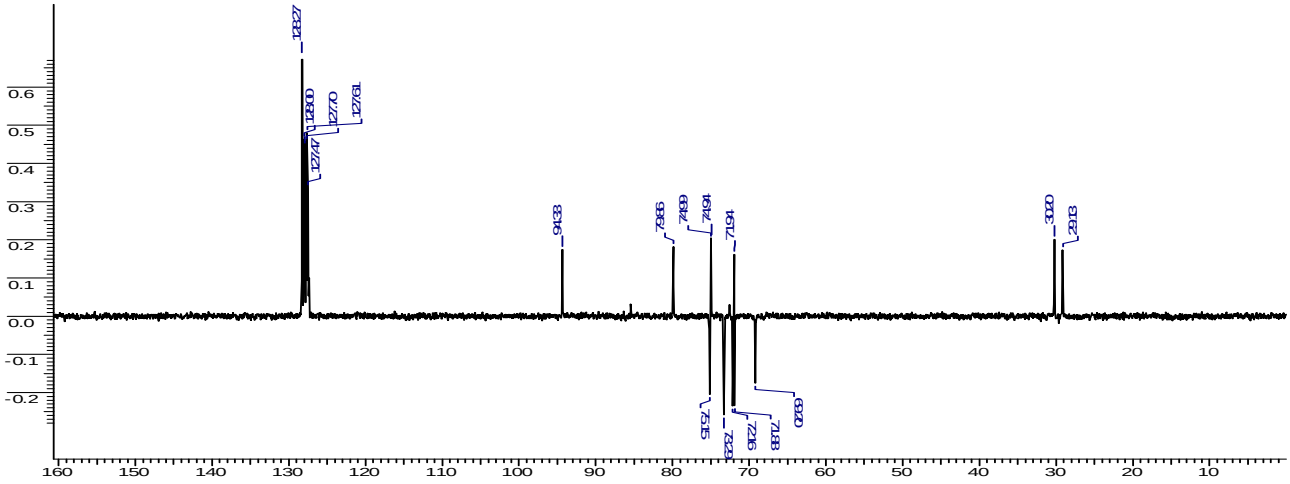
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1I**



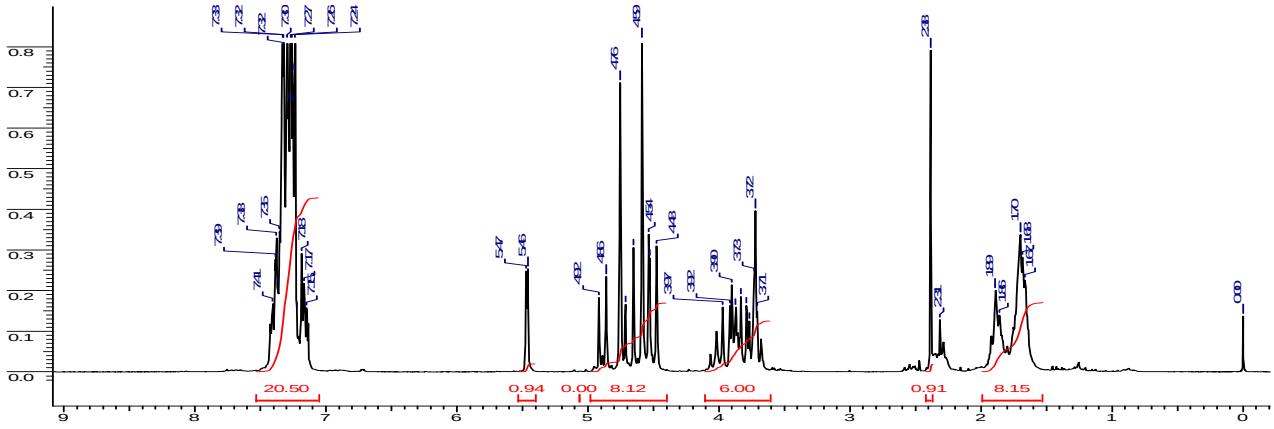
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **1I**



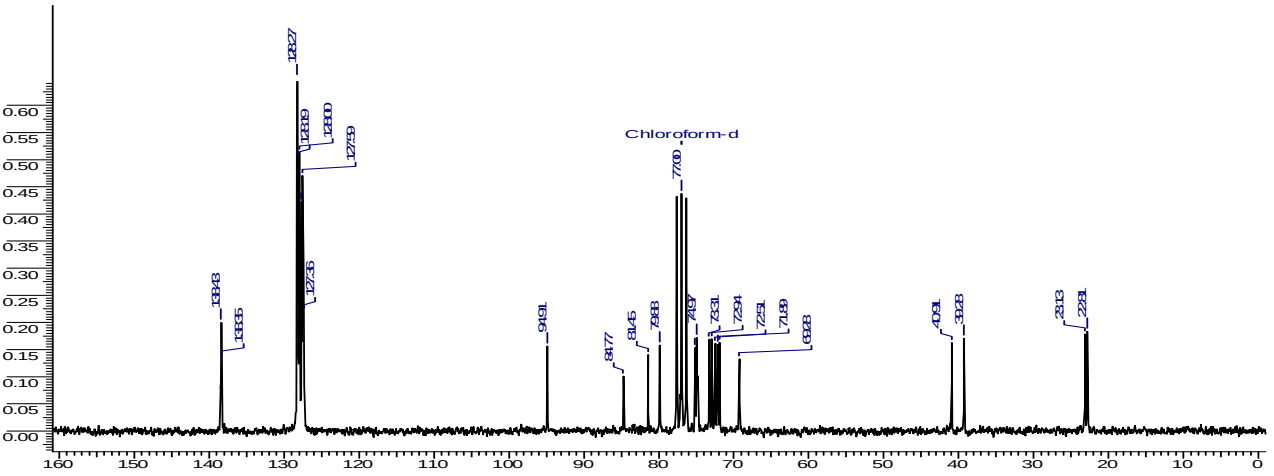
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **1I**



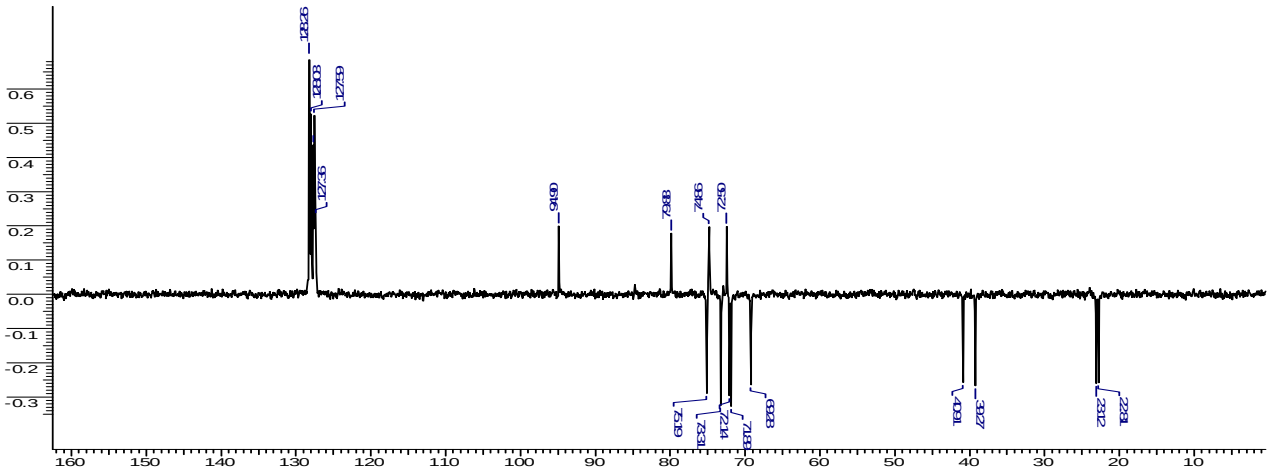
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1J**



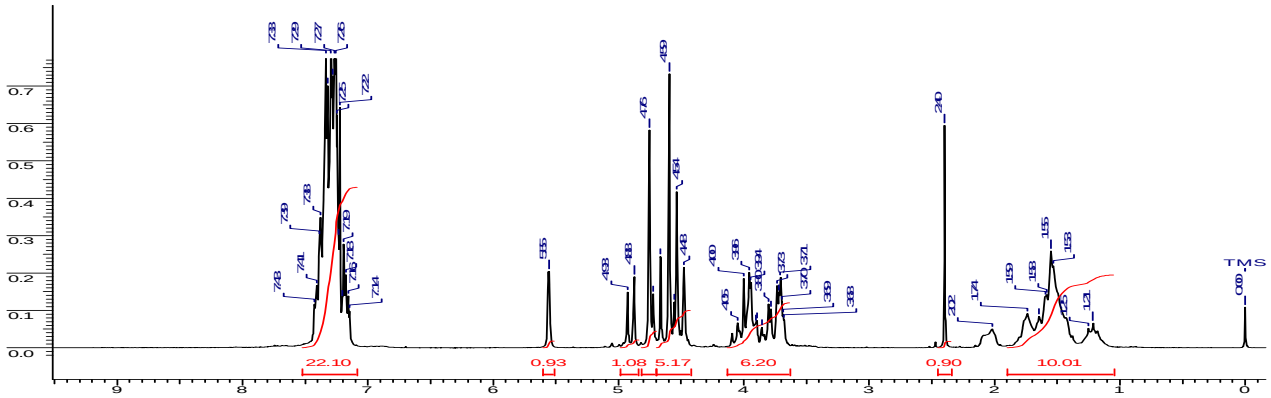
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **1J**



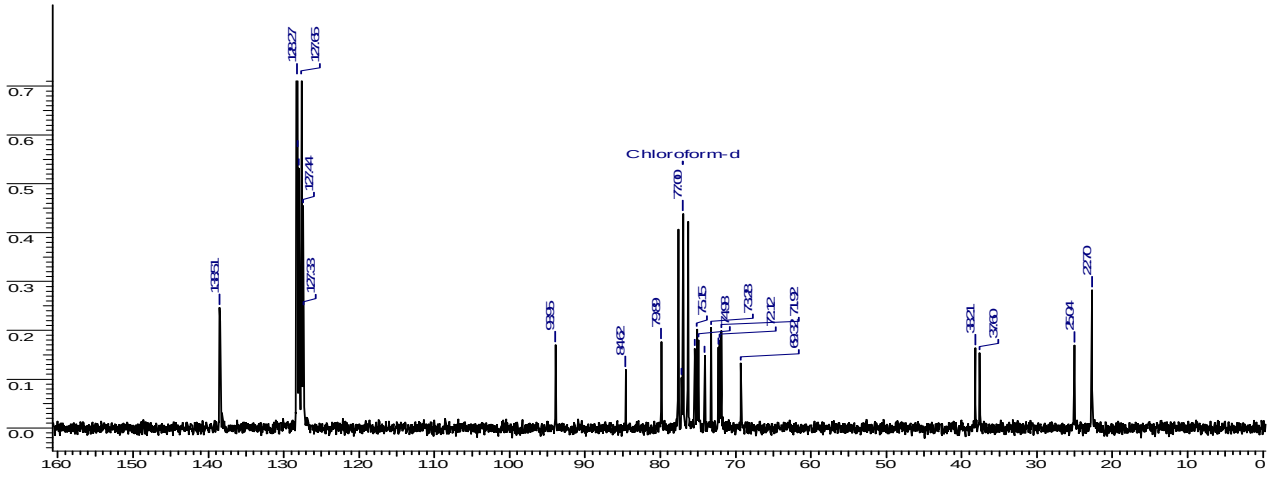
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **1J**



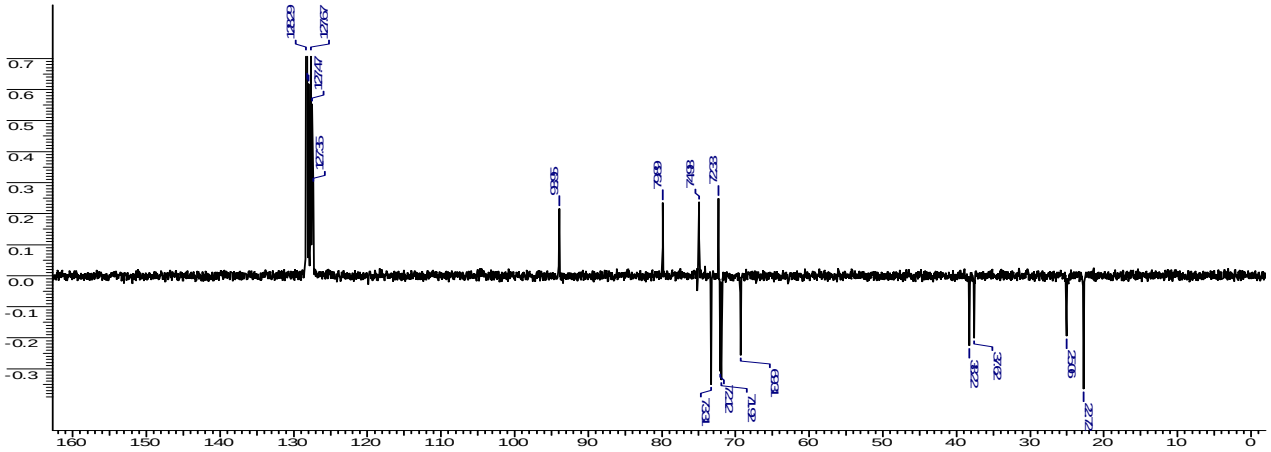
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1K**



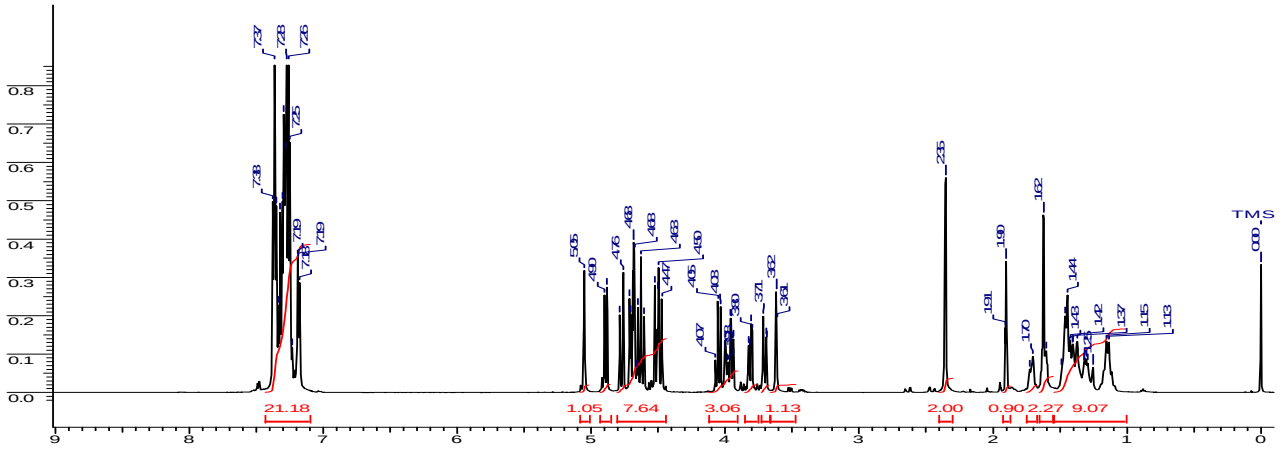
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **1K**



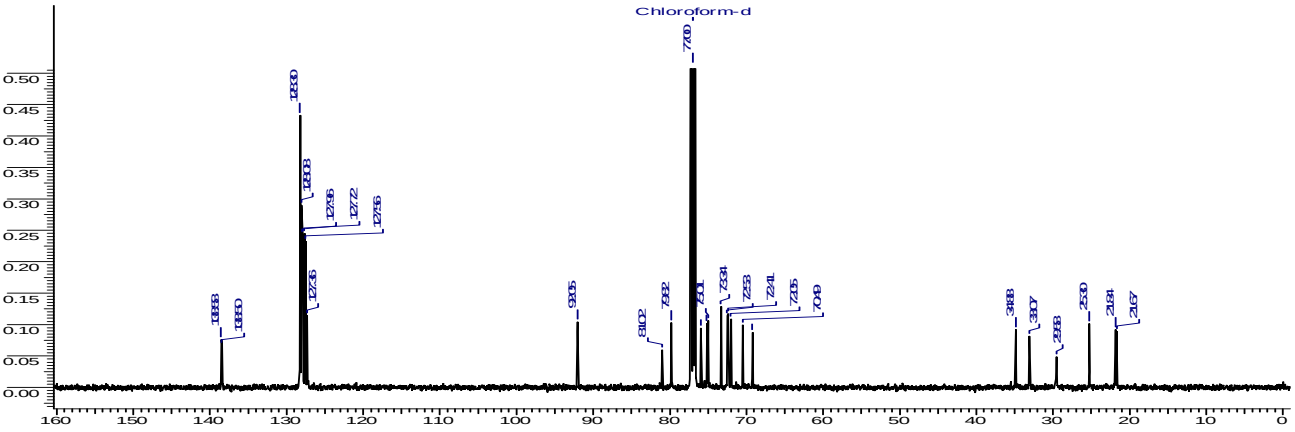
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **1K**



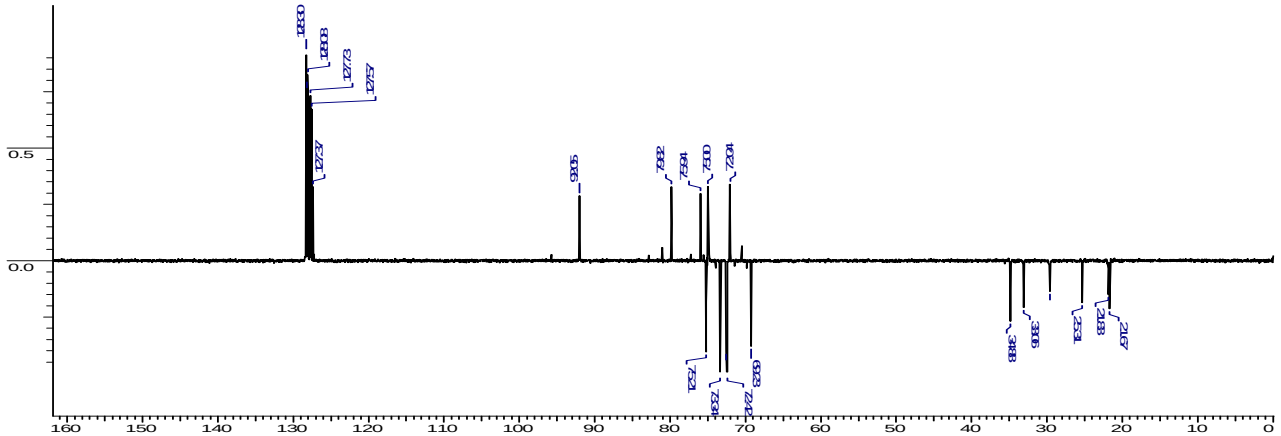
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **1L**



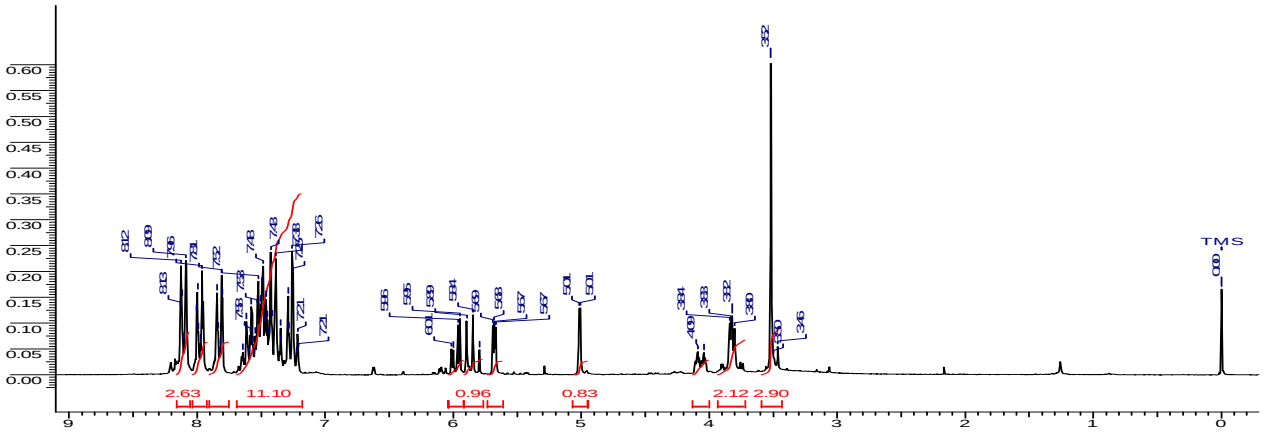
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **1L**



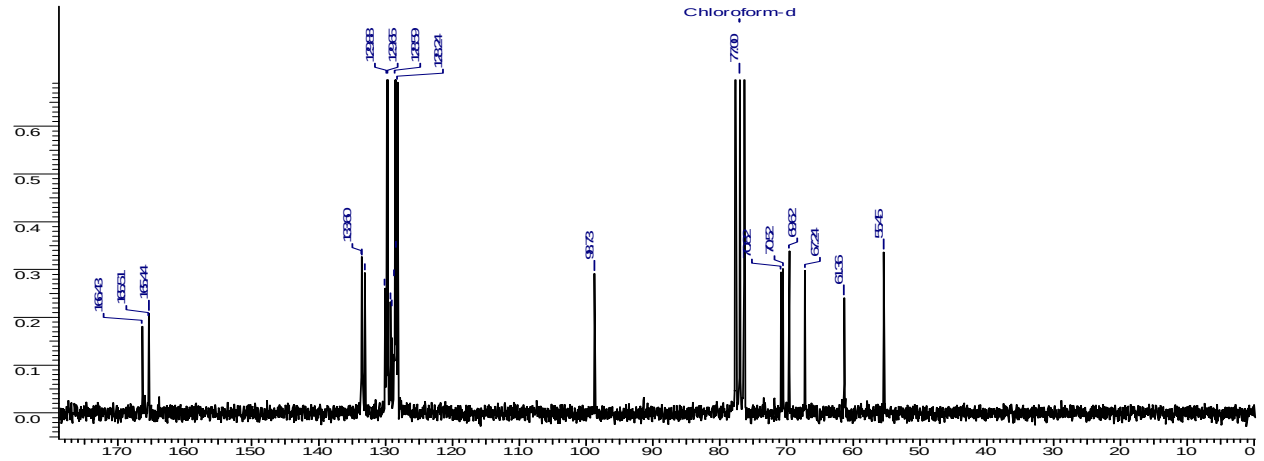
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **1L**



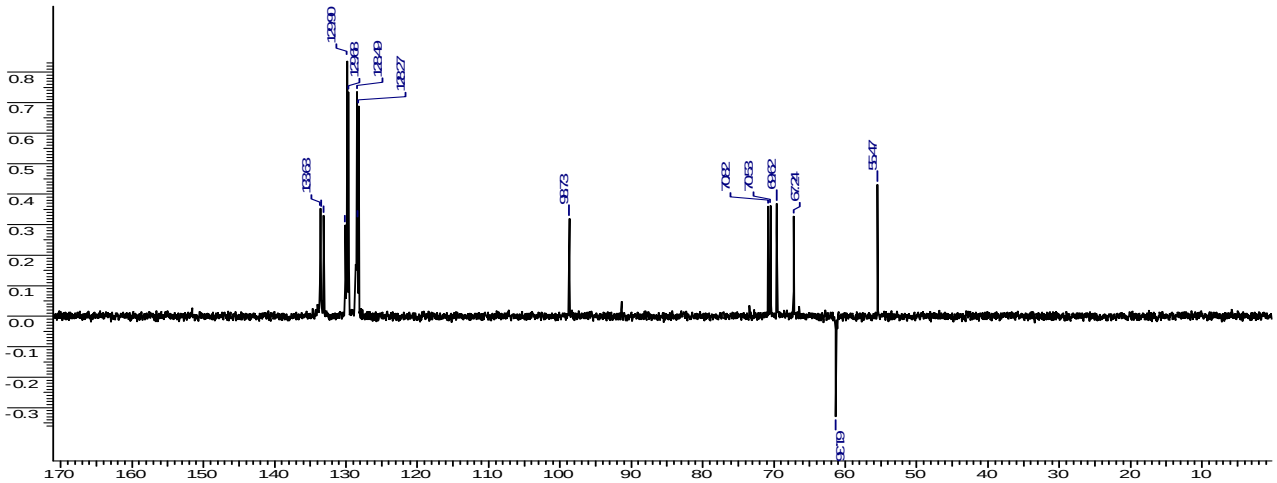
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **2a**



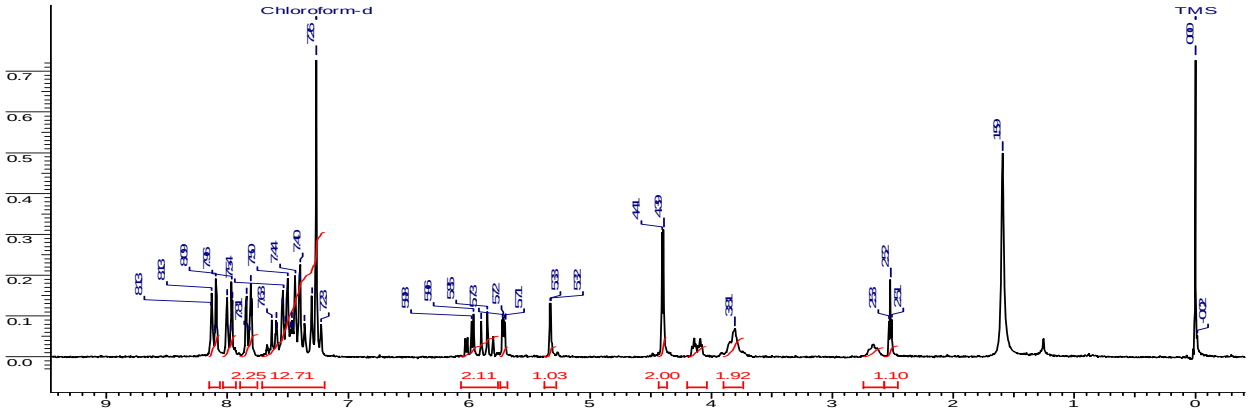
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2a**



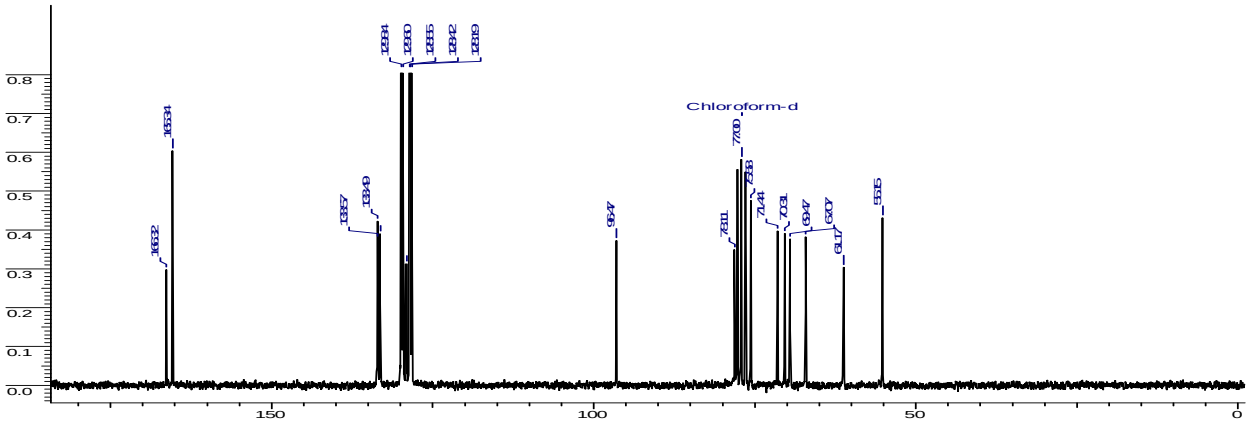
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2a**



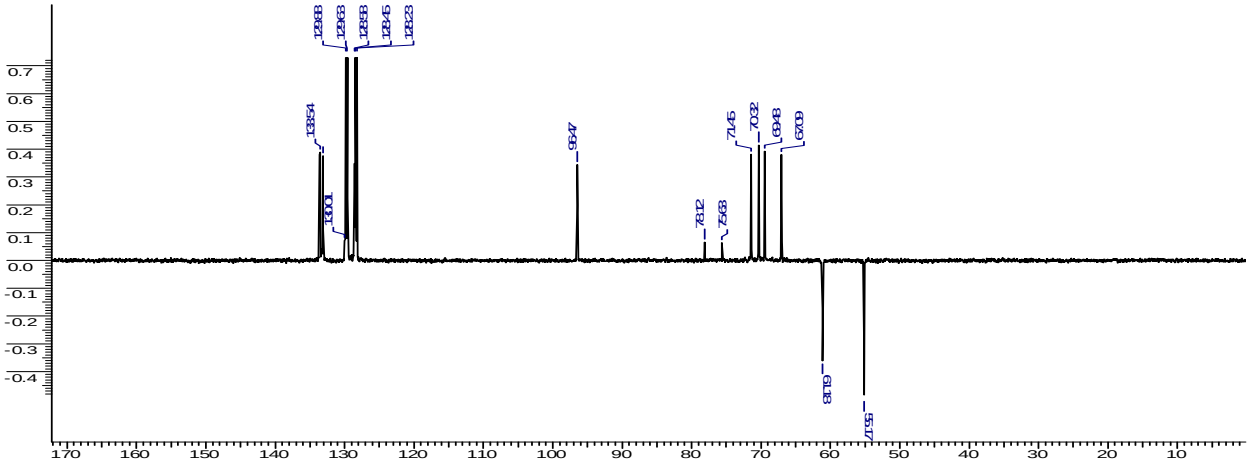
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **2g**



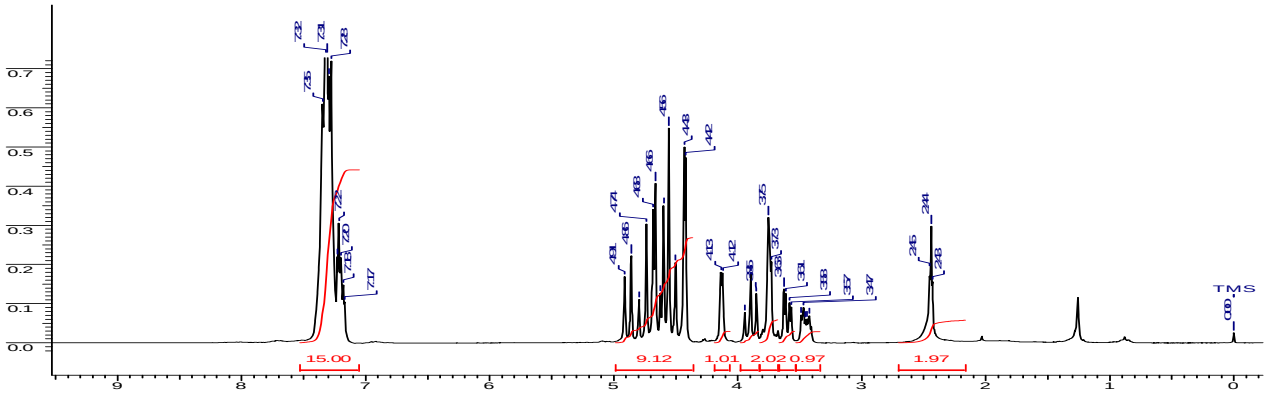
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2g**



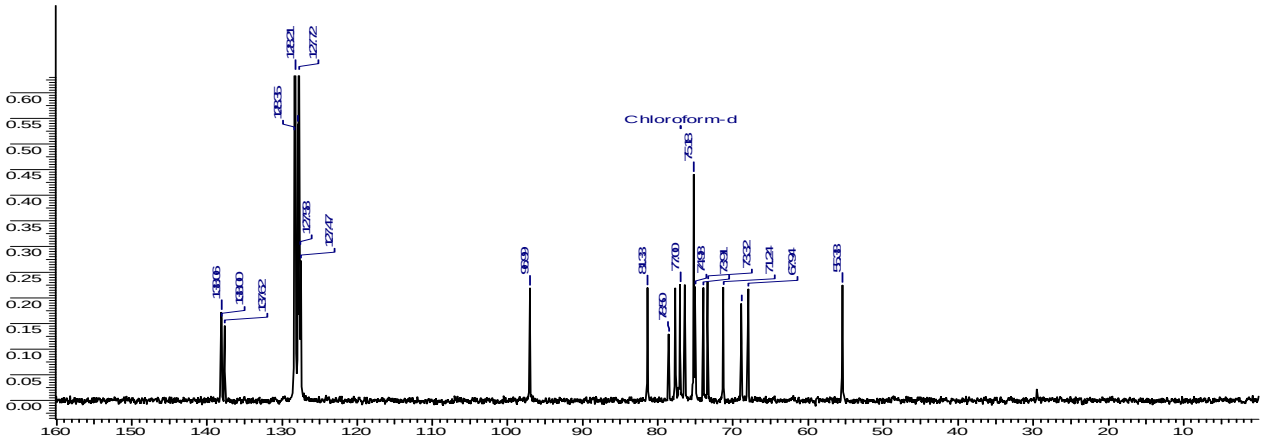
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2g**



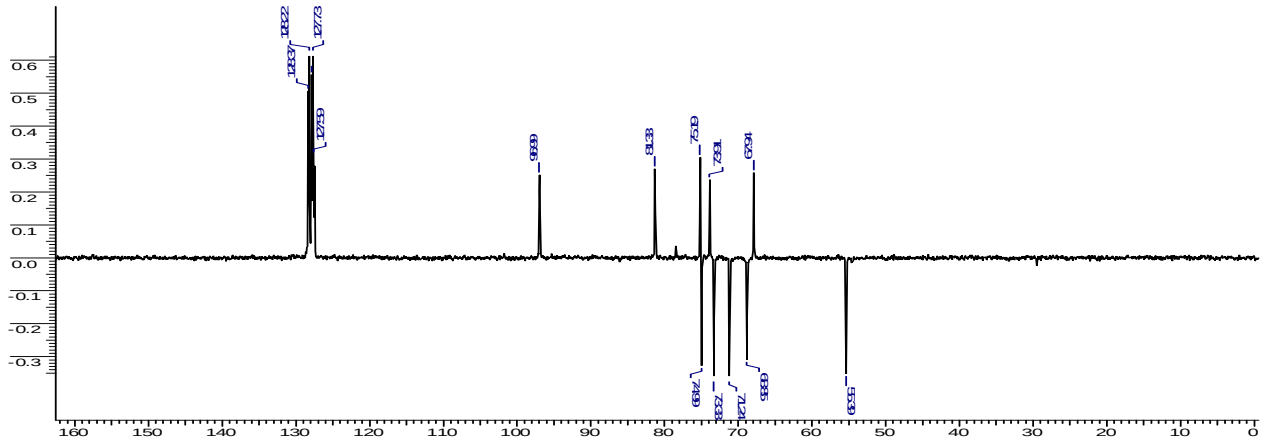
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **2h**



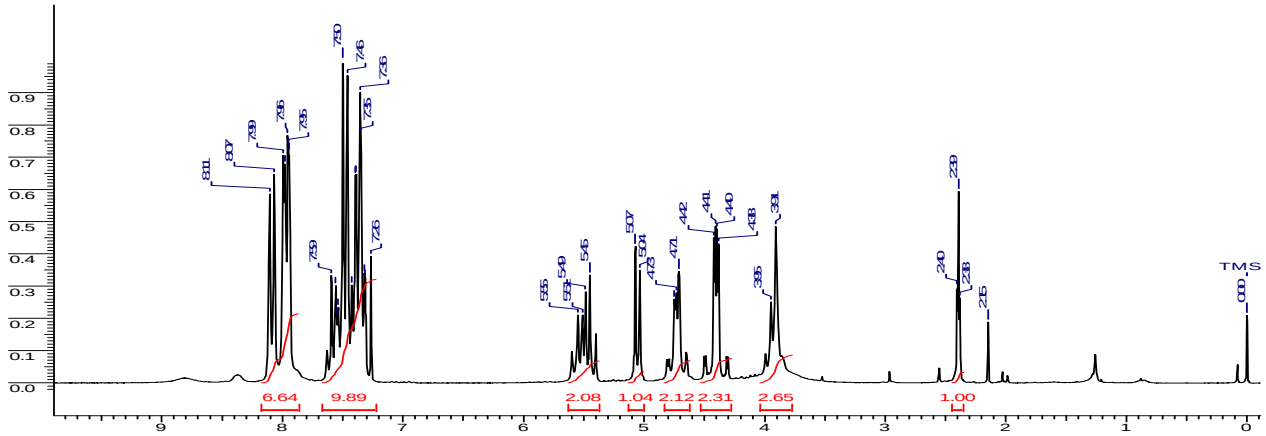
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2h**



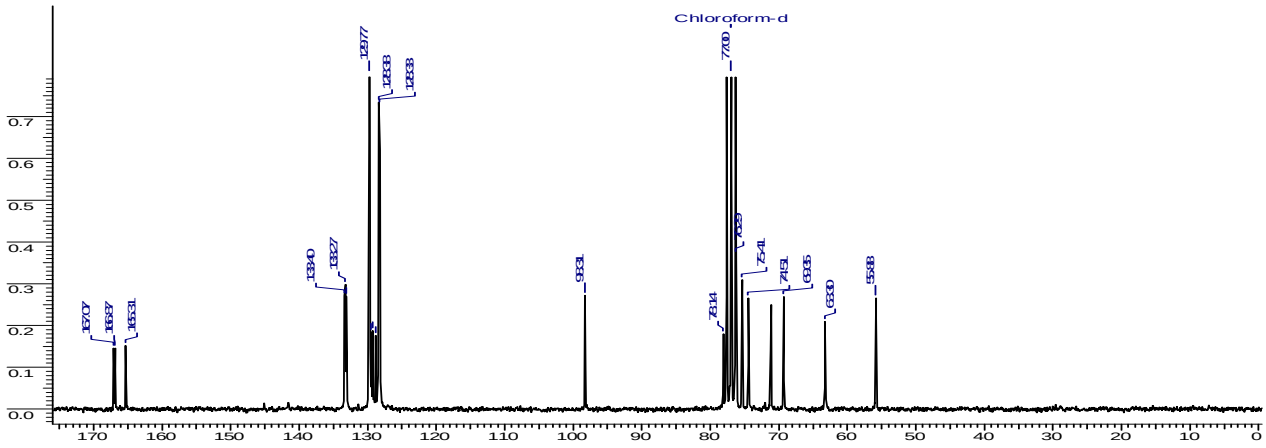
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2h**



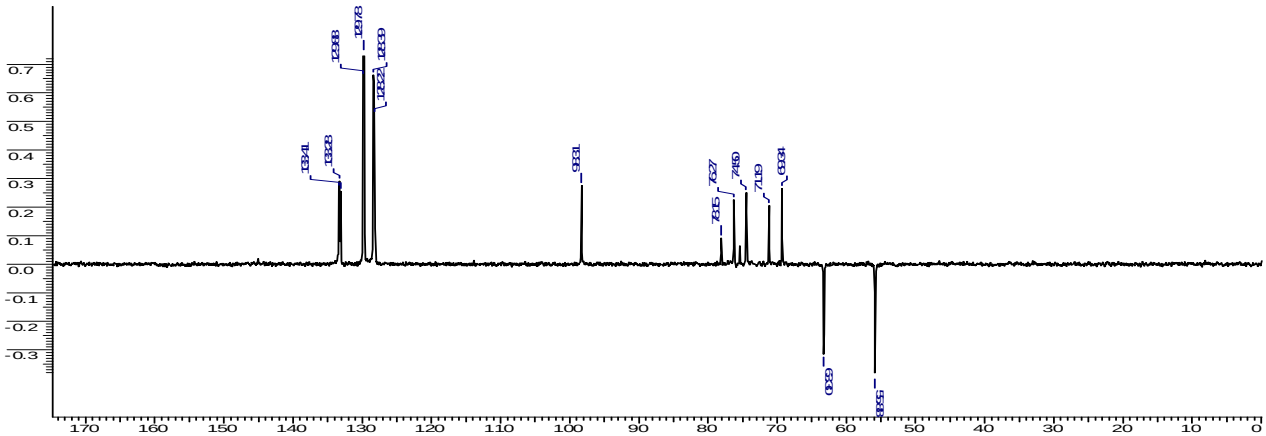
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **2i**



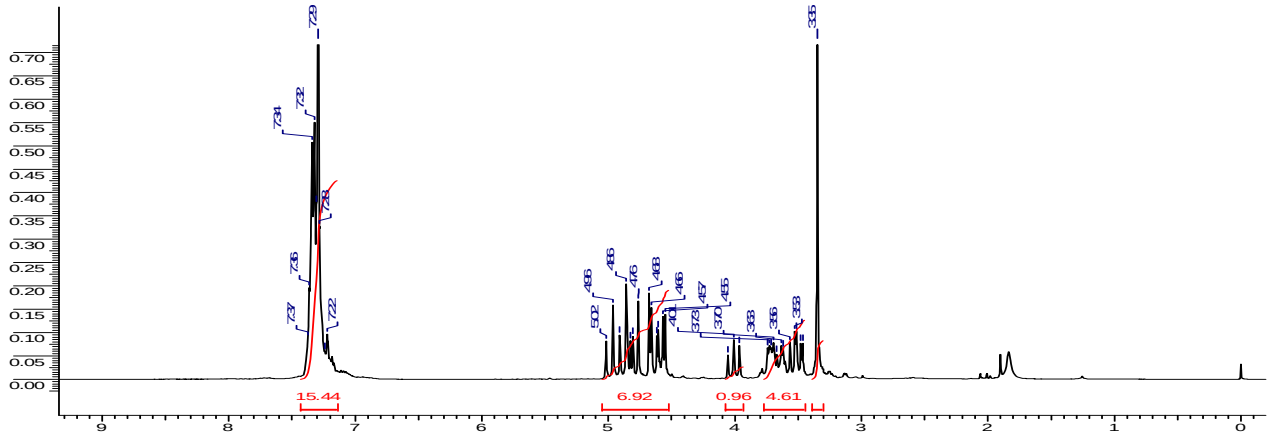
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2i**



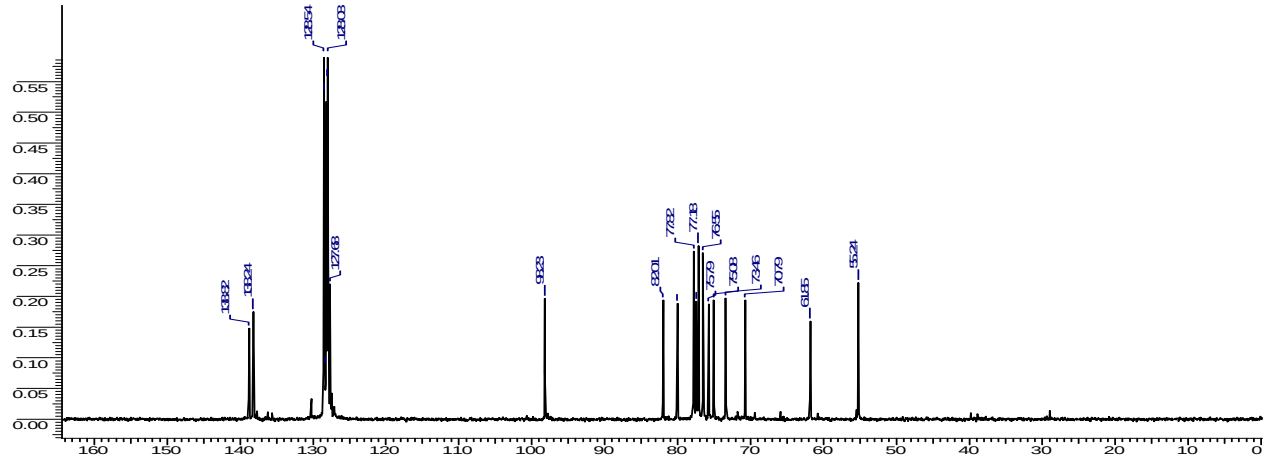
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2i**



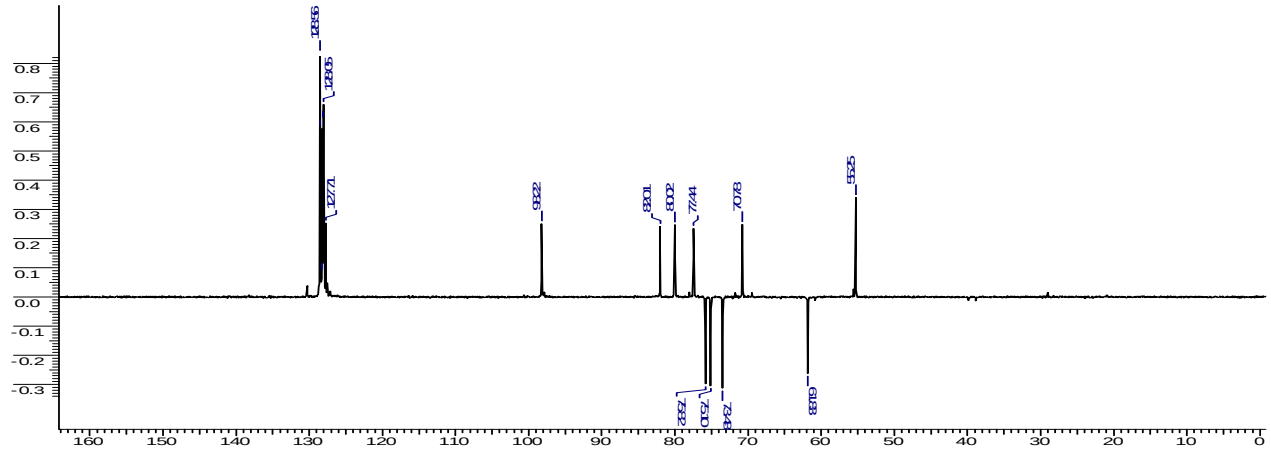
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **2j**



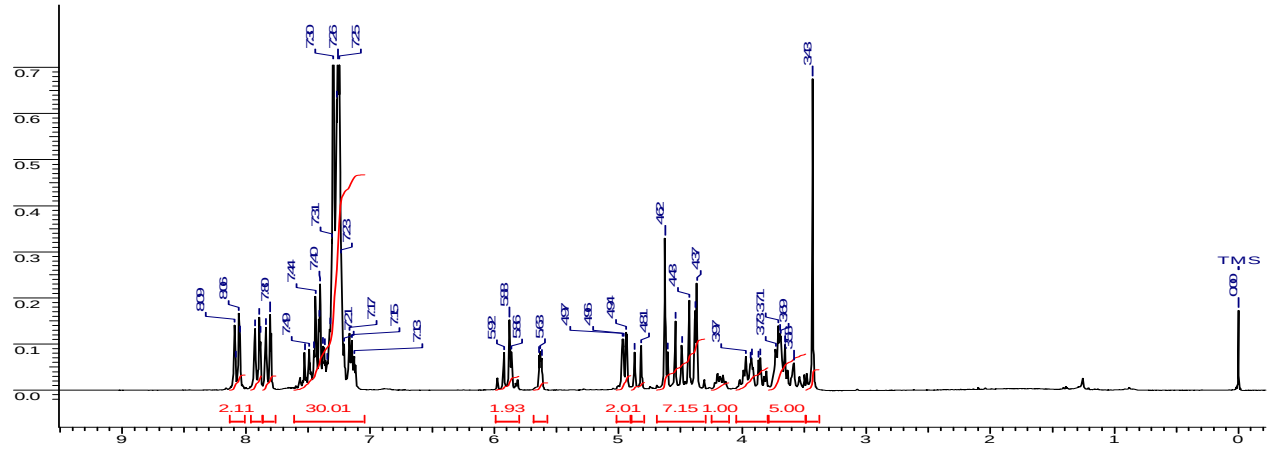
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2j**



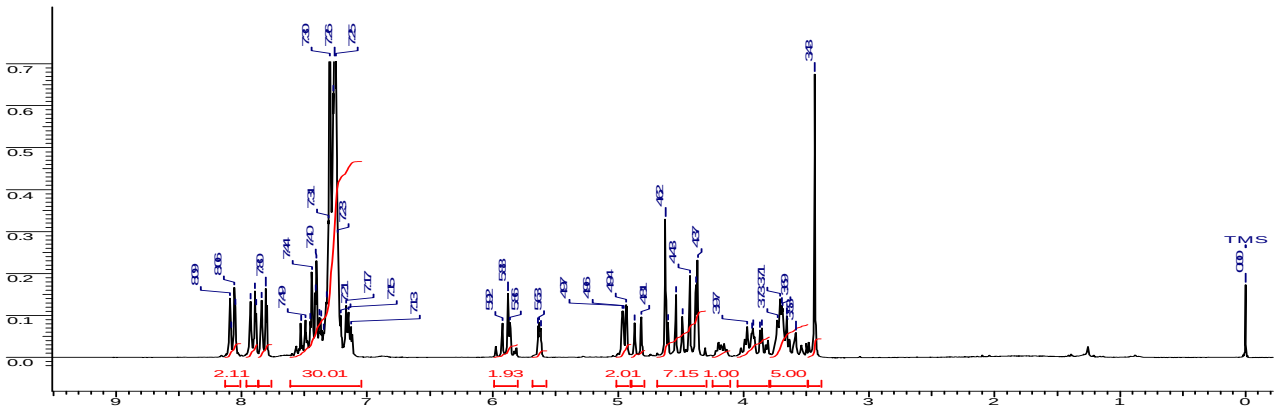
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **2j**



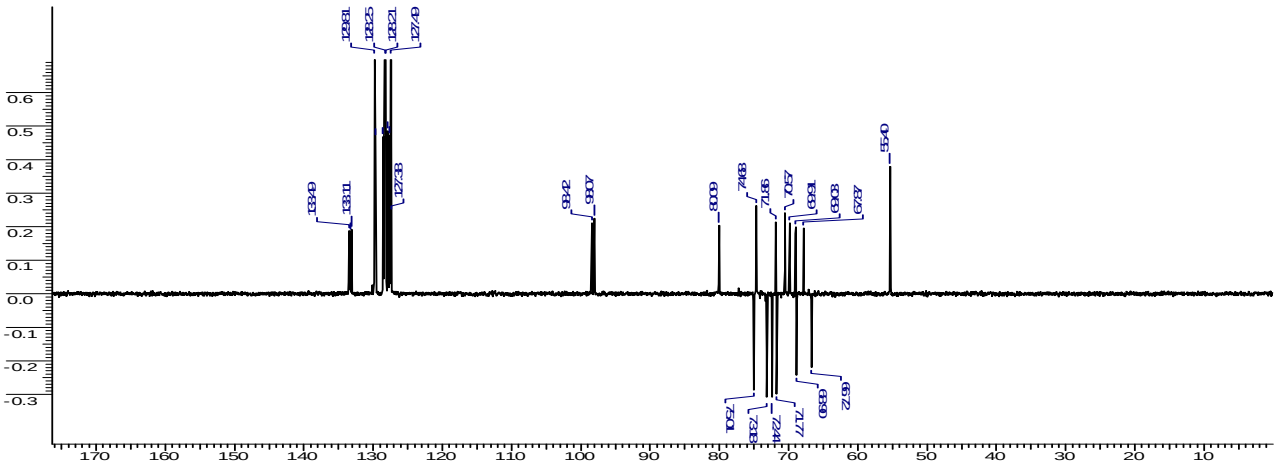
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **3**



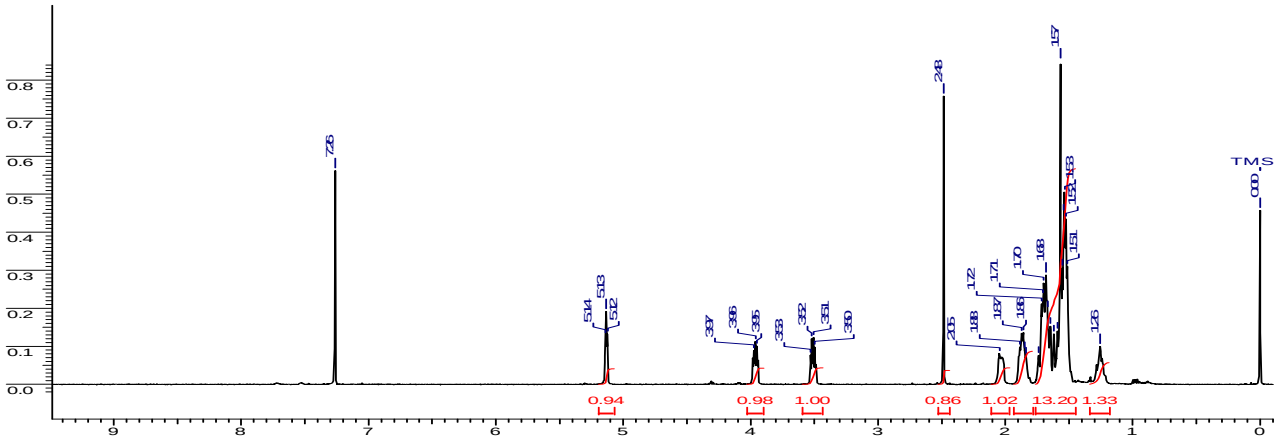
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **3**



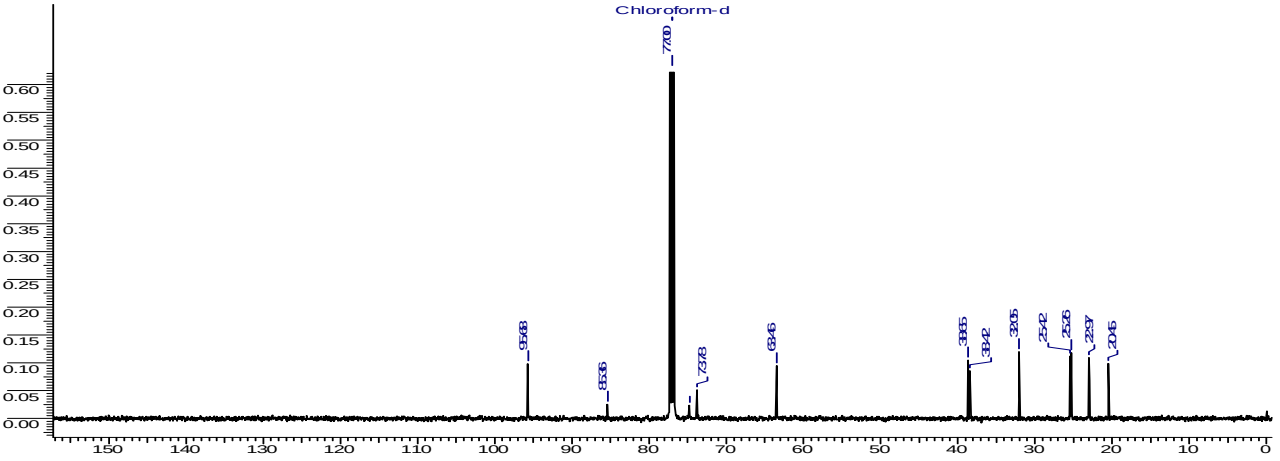
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **3**



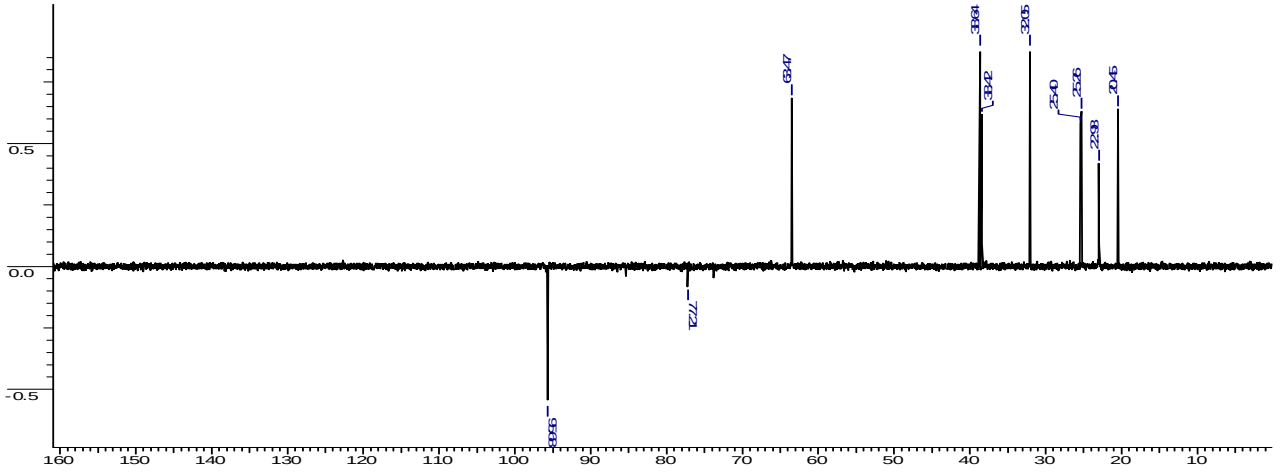
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **4**



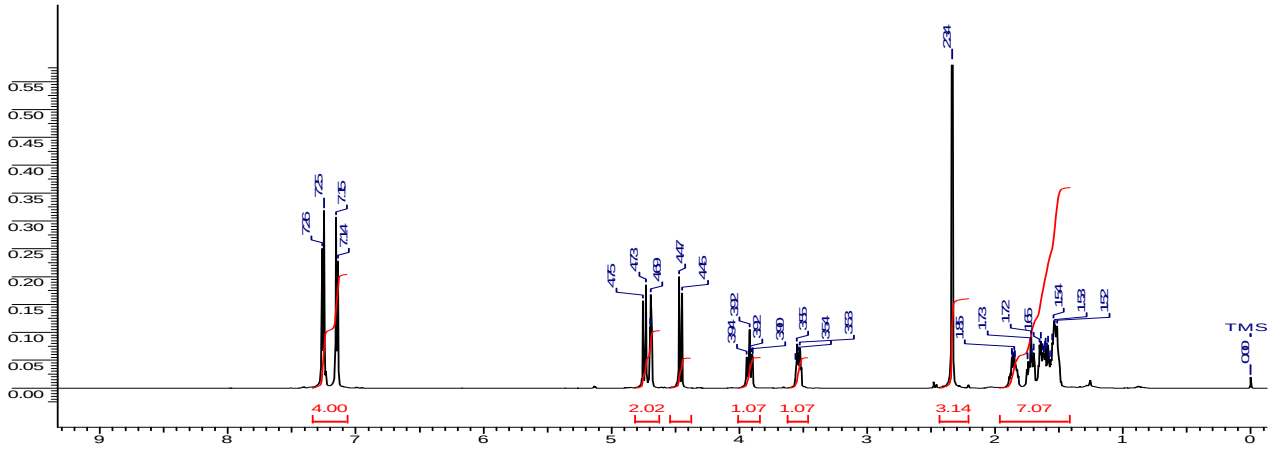
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **4**



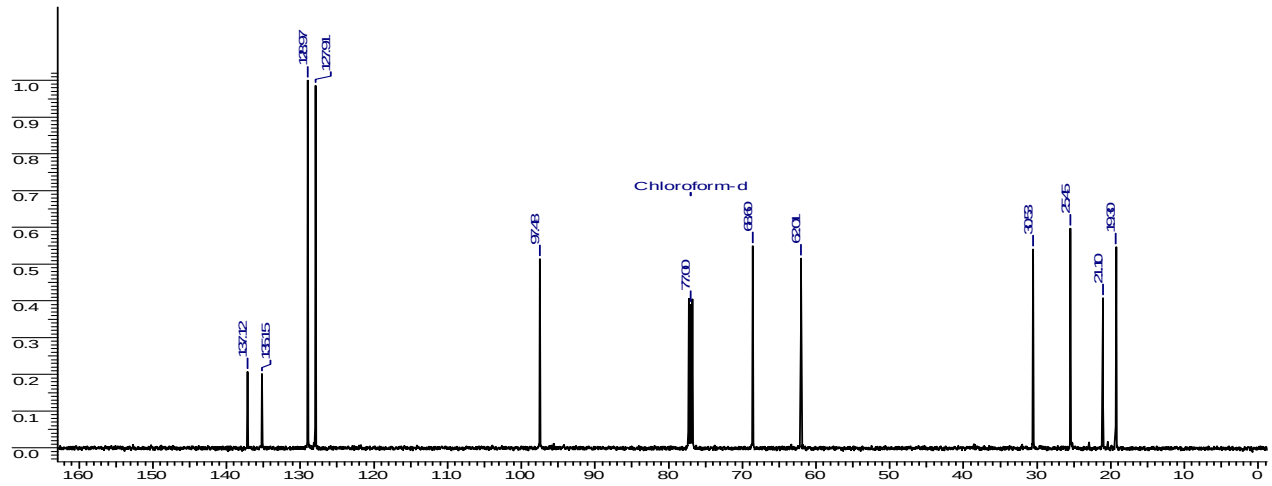
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **4**



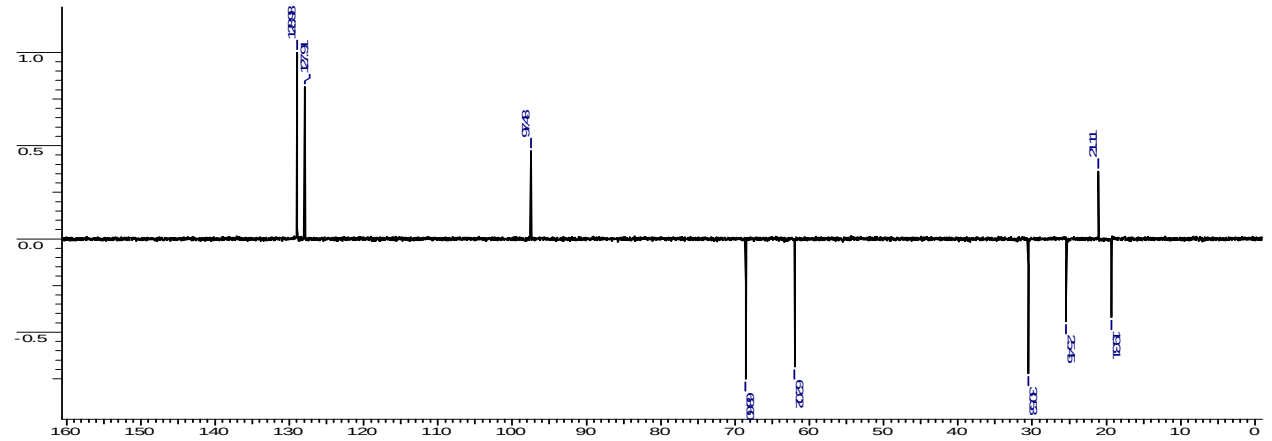
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **6**



^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **6**



DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **6**



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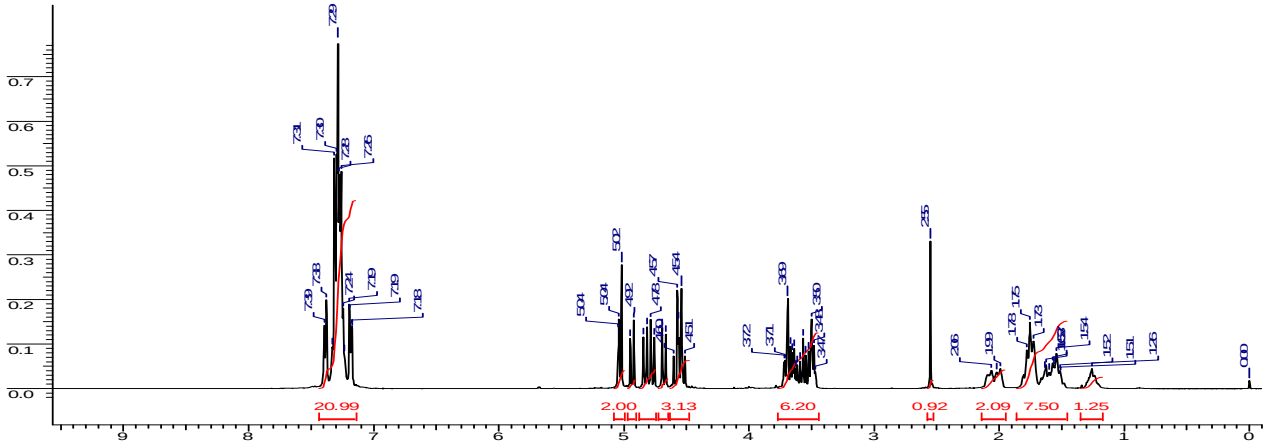
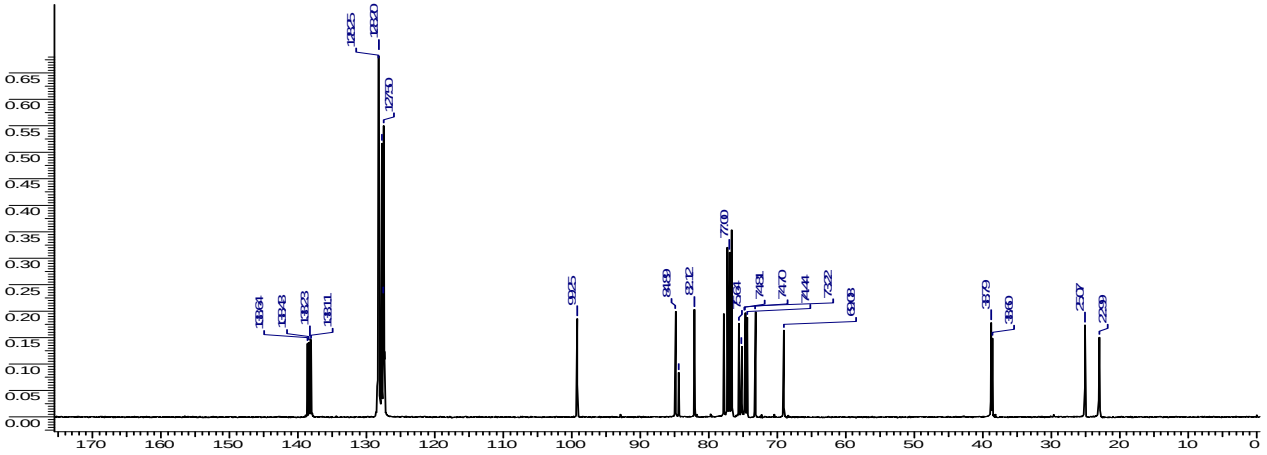
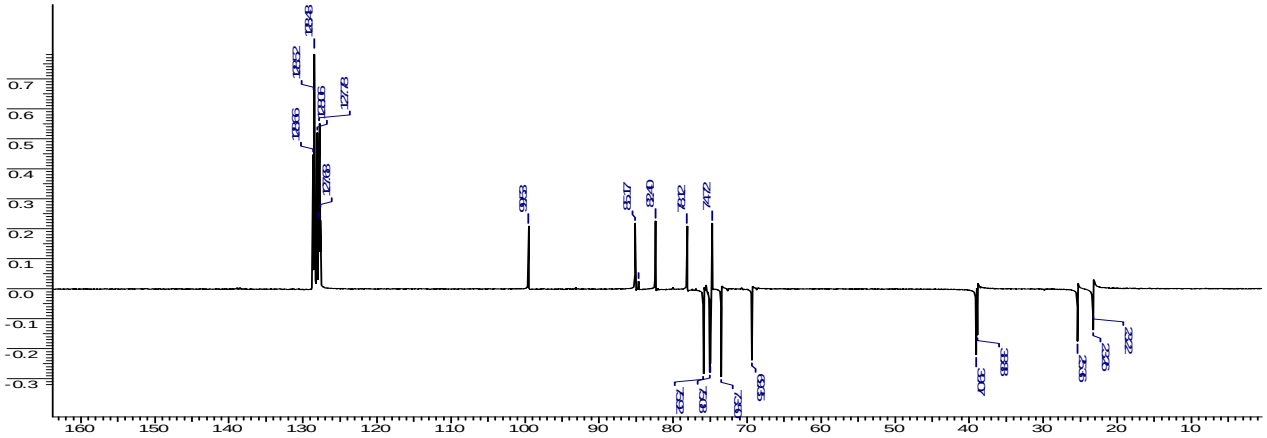
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **13**



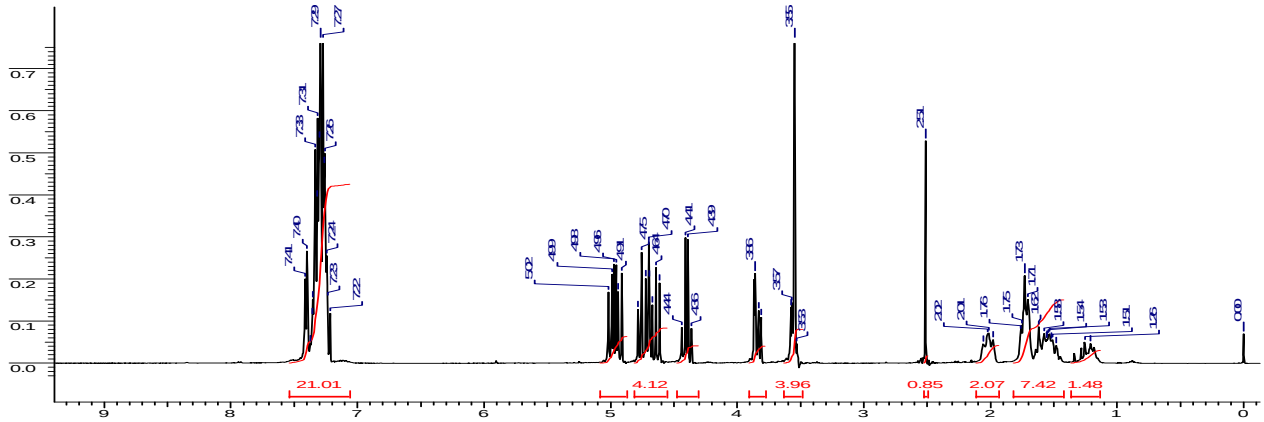
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **13**



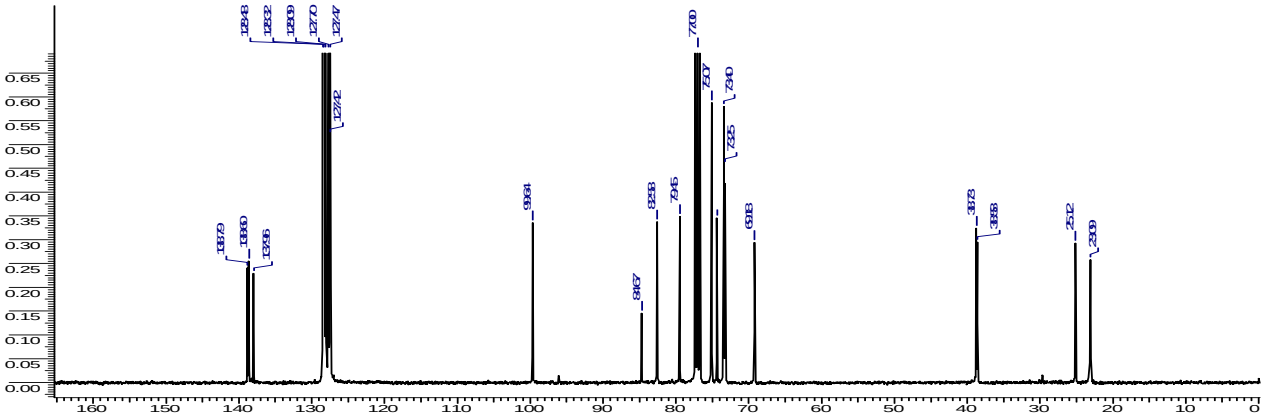
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **13**



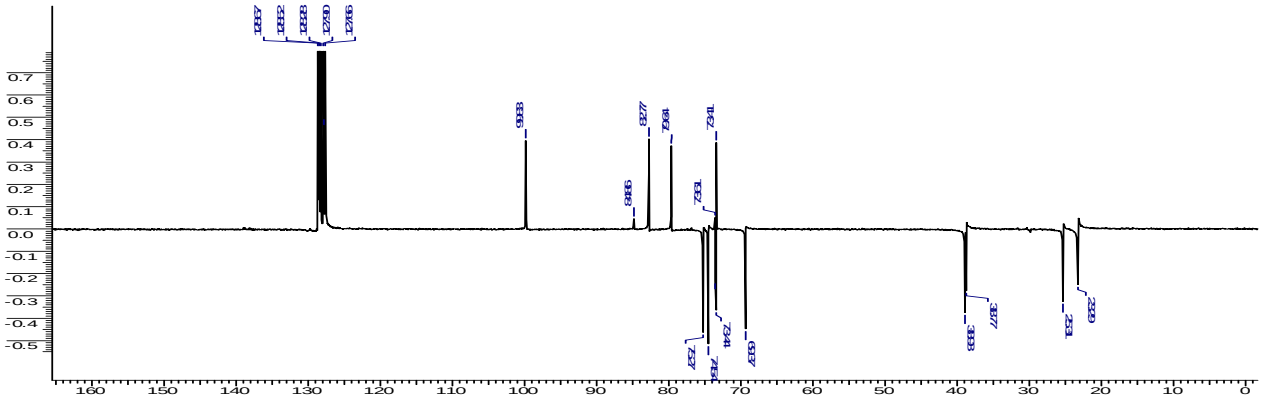
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **14**



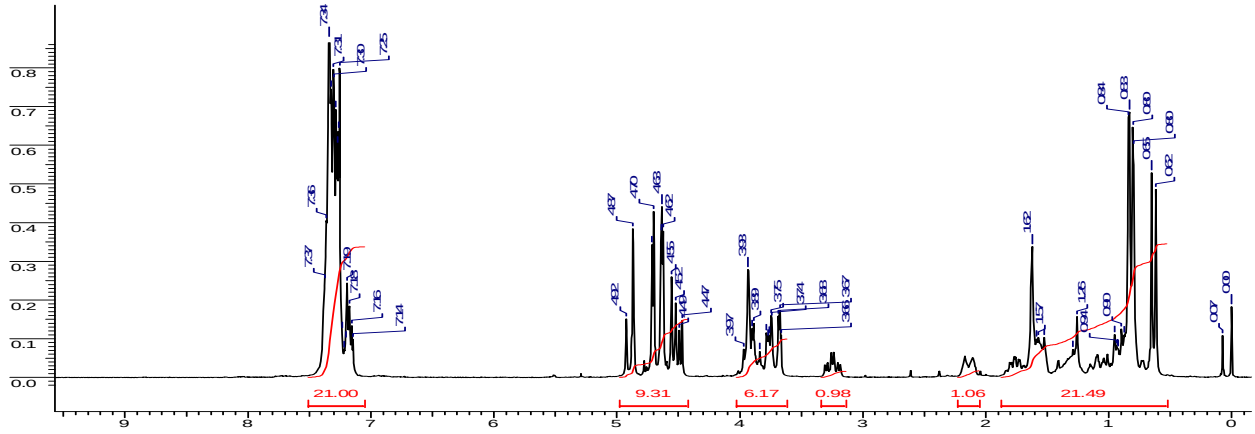
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **14**



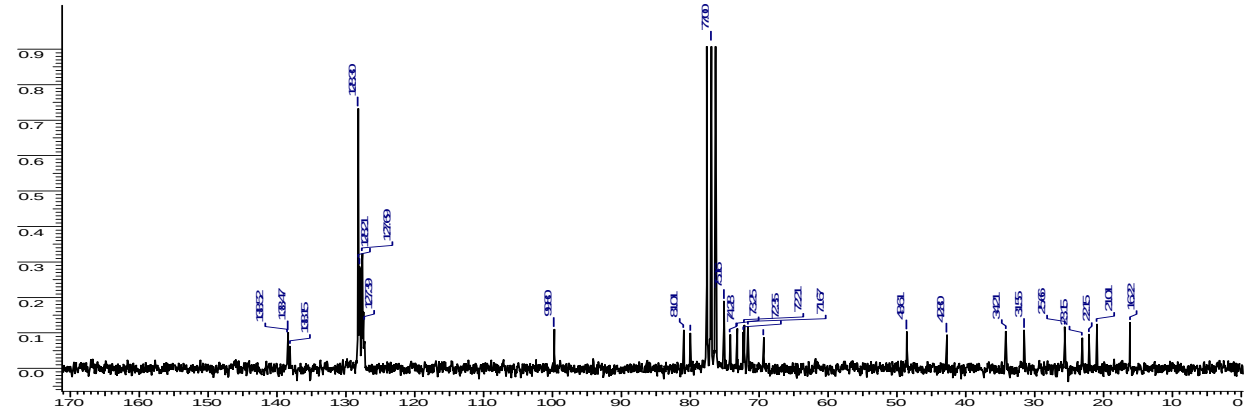
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **14**



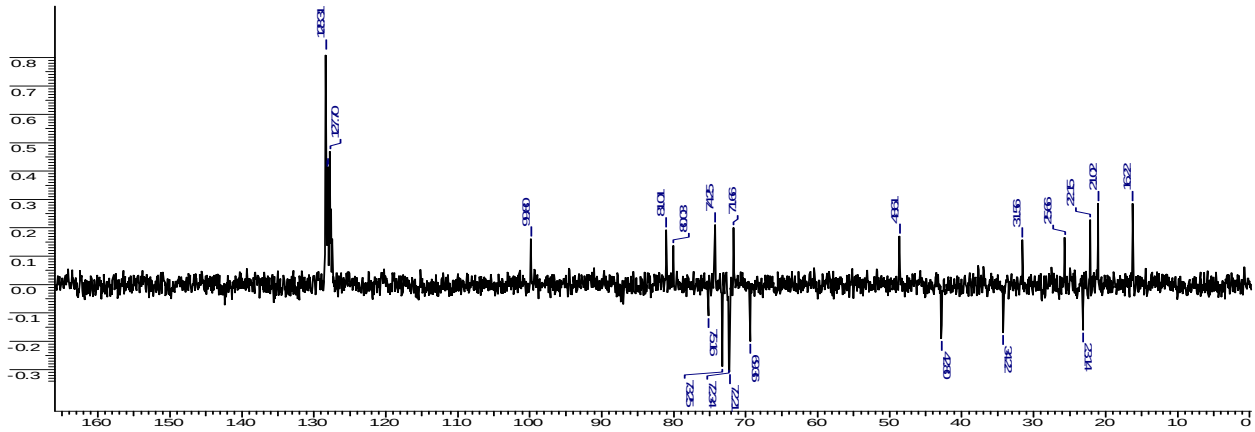
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **15**



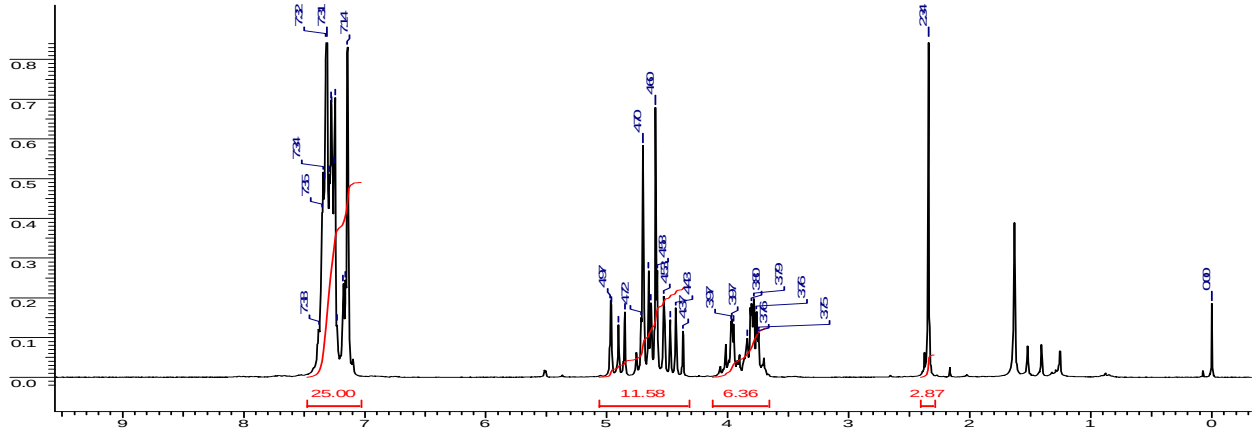
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **15**



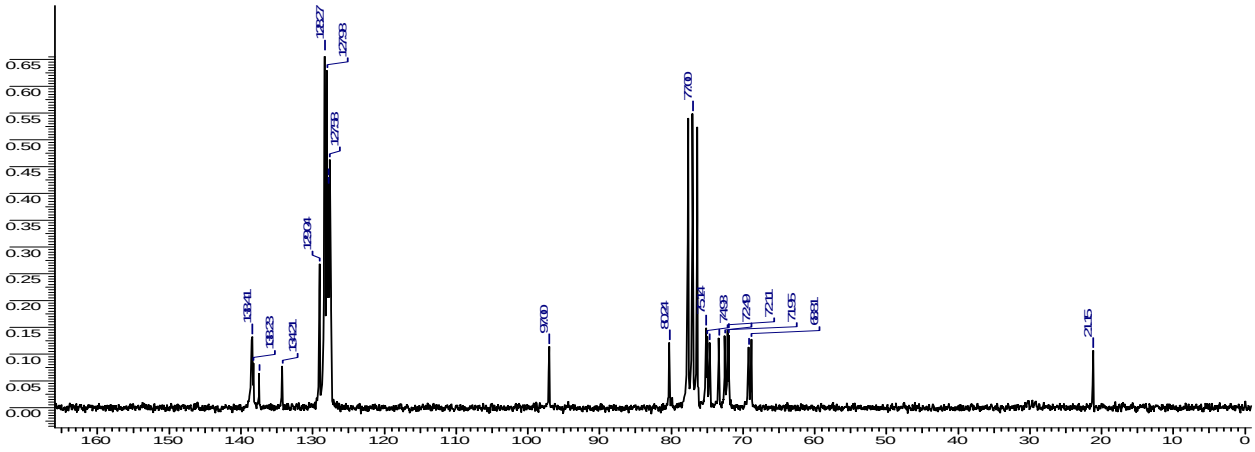
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **15**



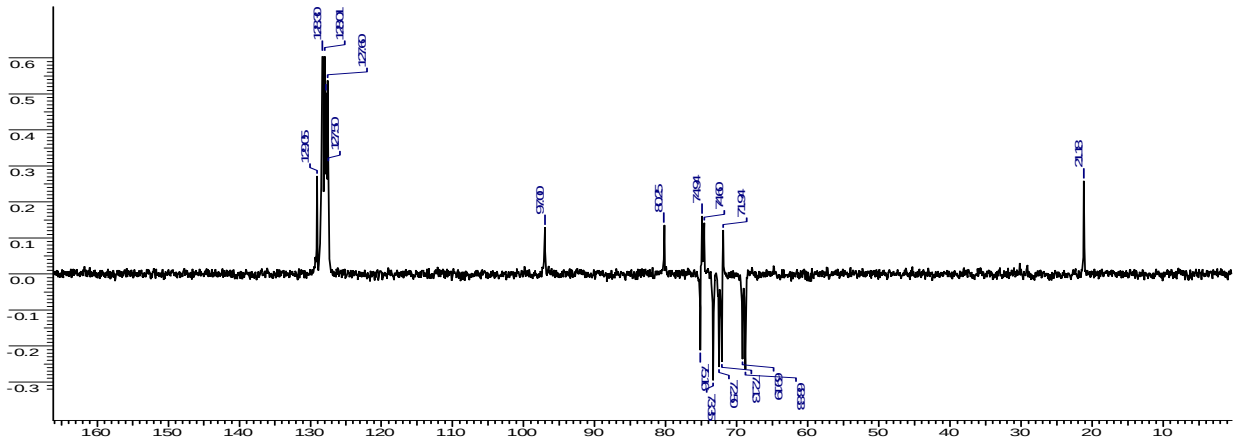
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **16**



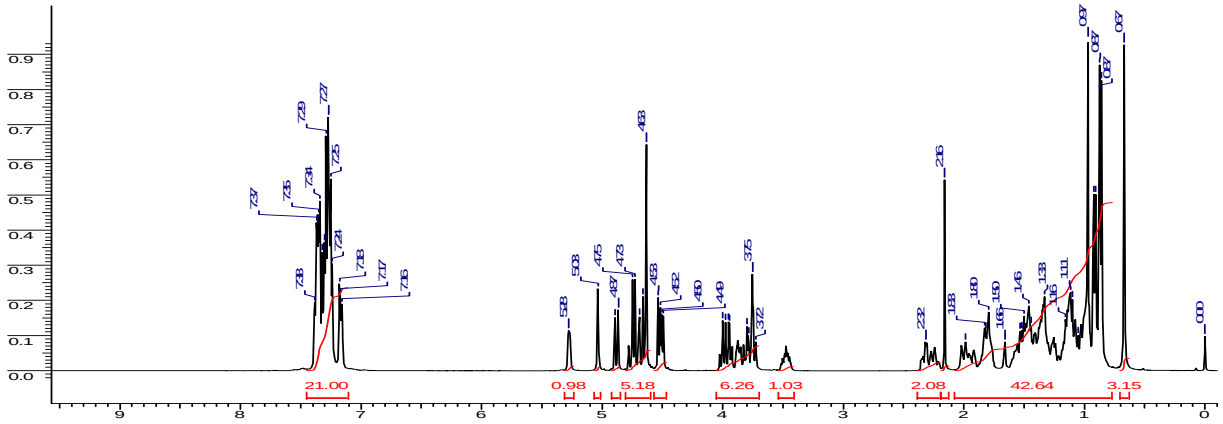
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **16**



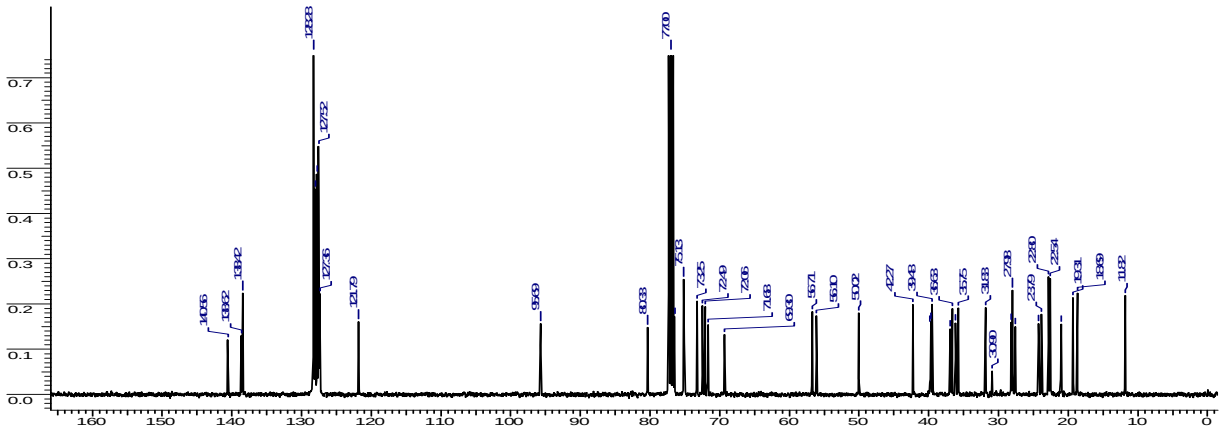
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **16**



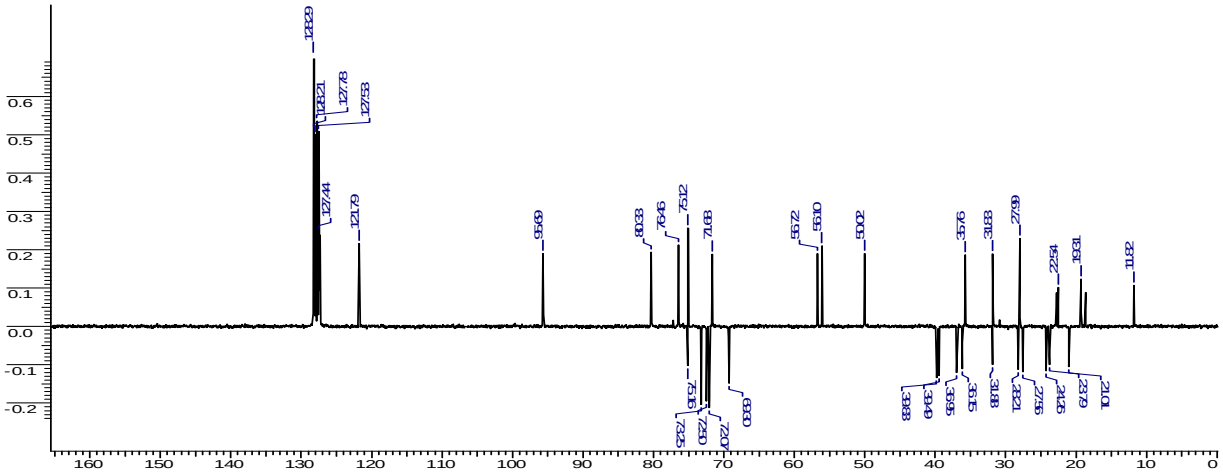
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **17**



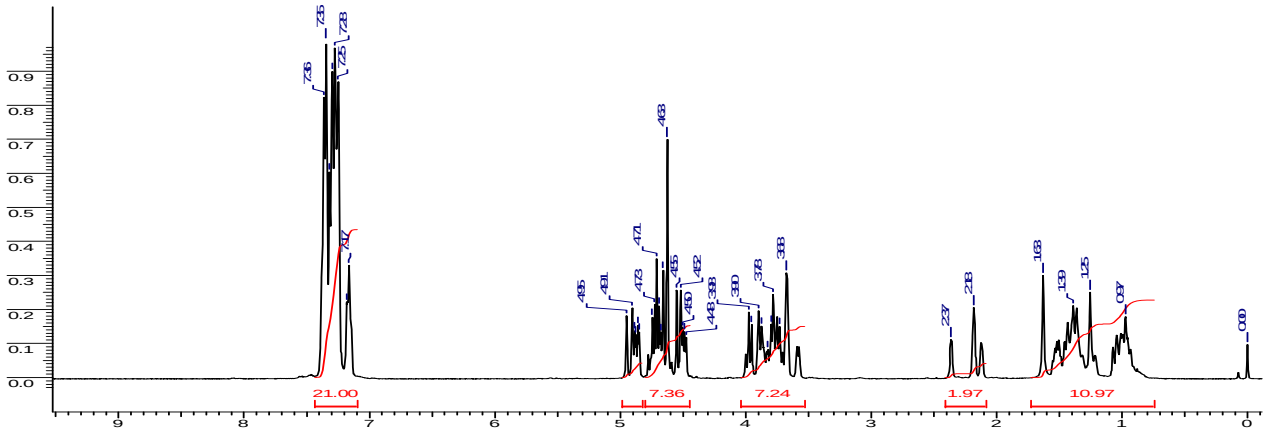
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **17**



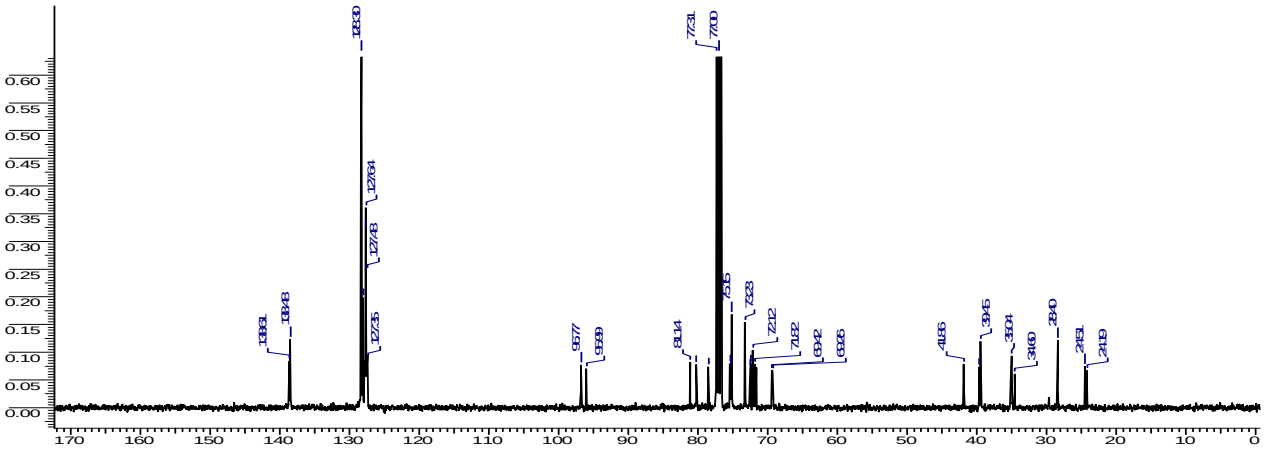
DEPT NMR Spectrum (100.6 MHz, $CDCl_3$) of Compound **17**



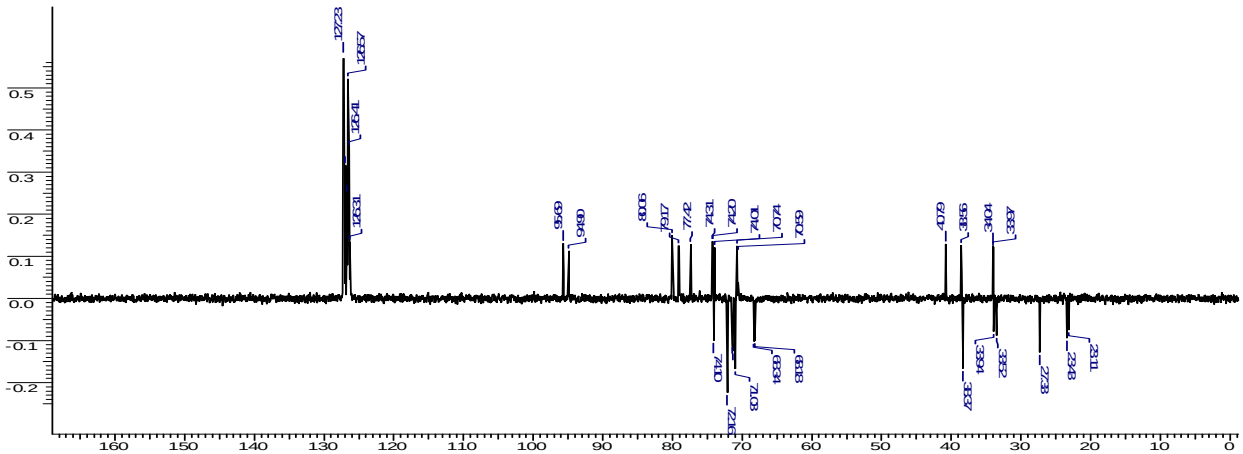
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **18**



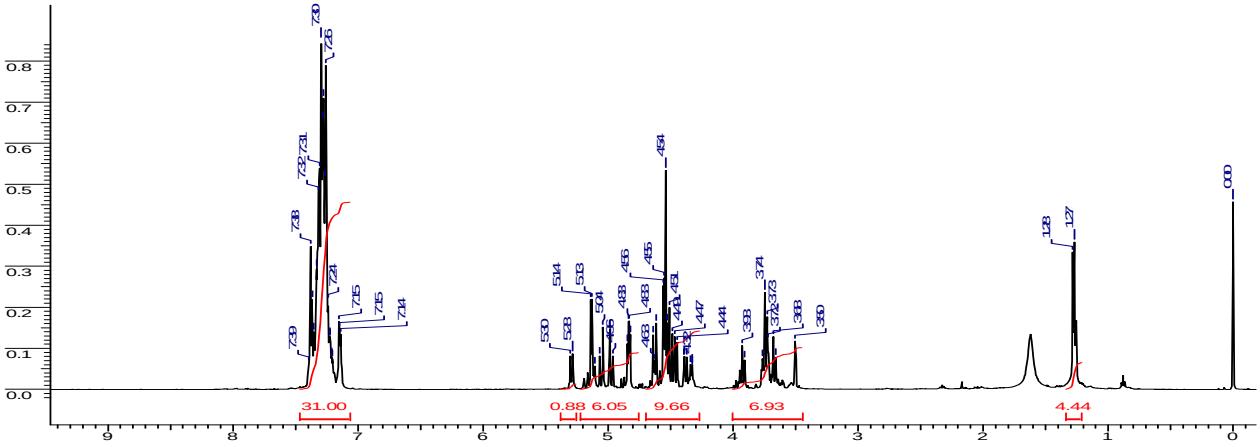
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **18**



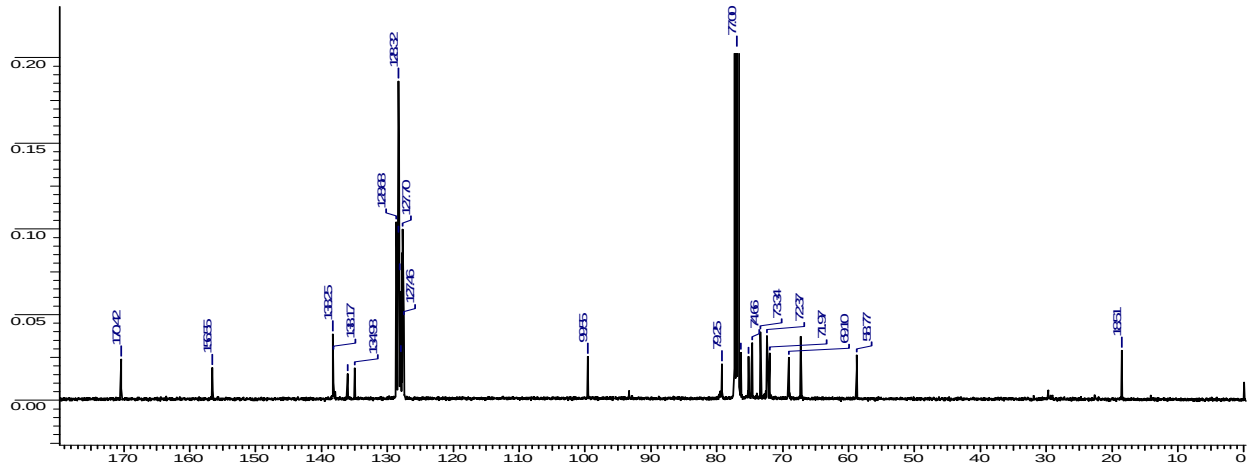
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **18**



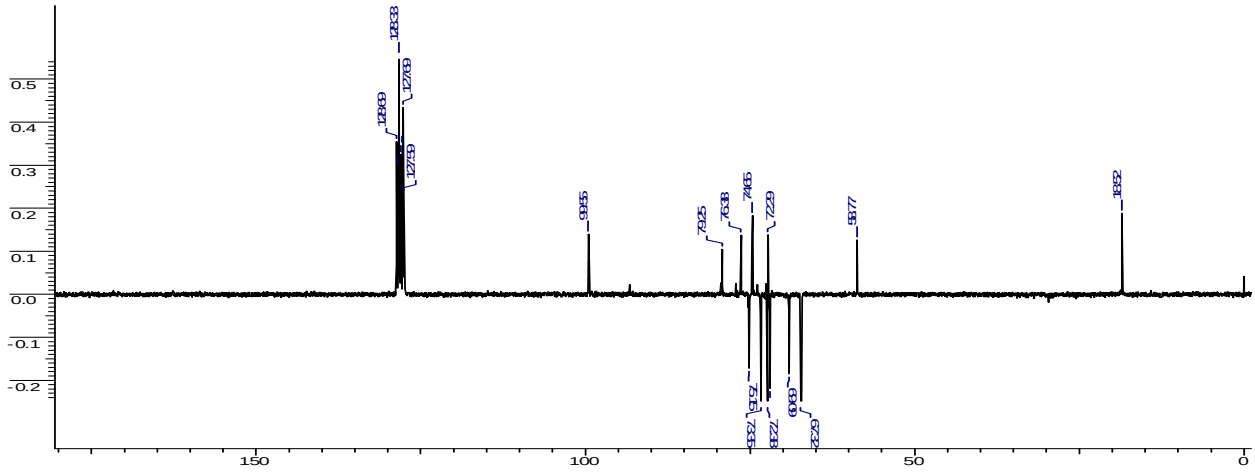
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **19**



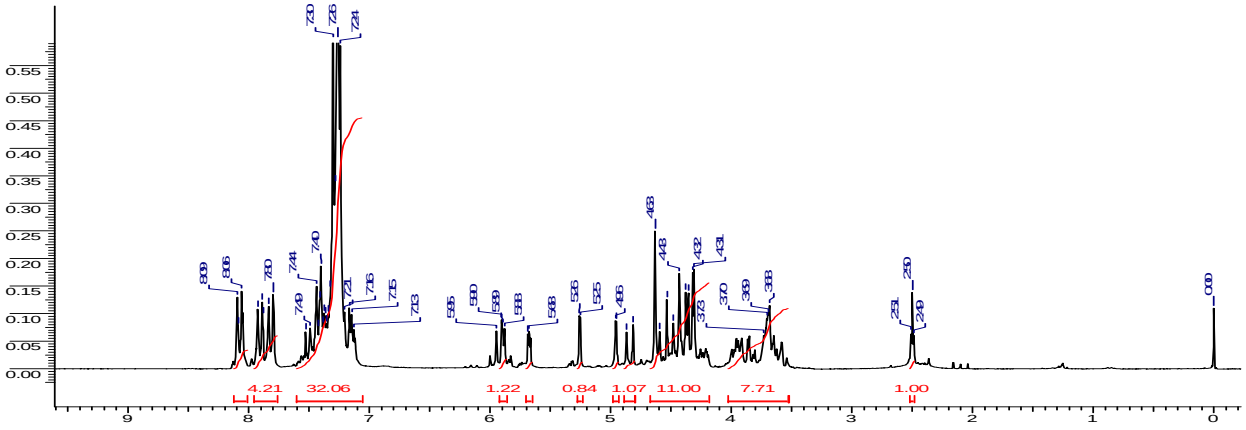
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **19**



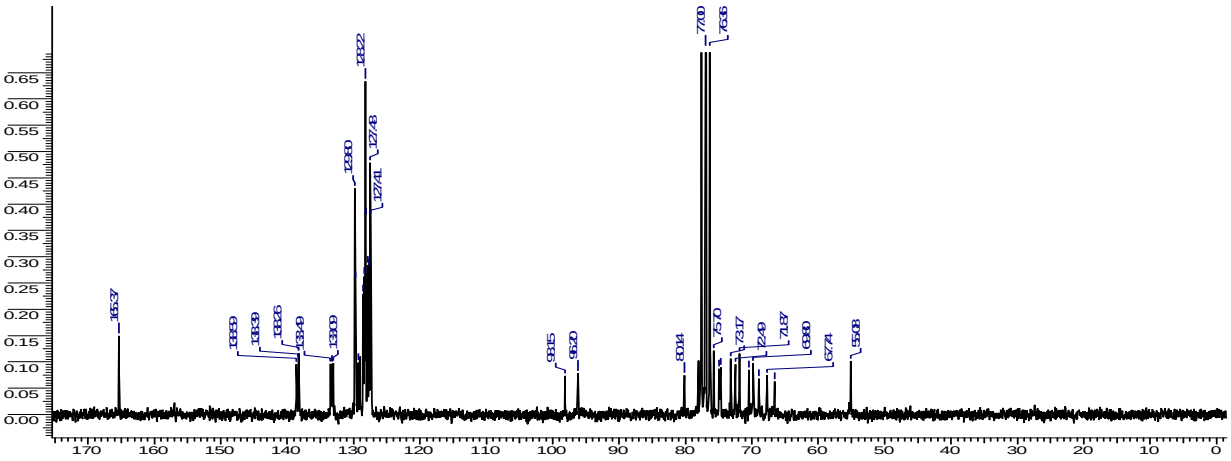
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **19**



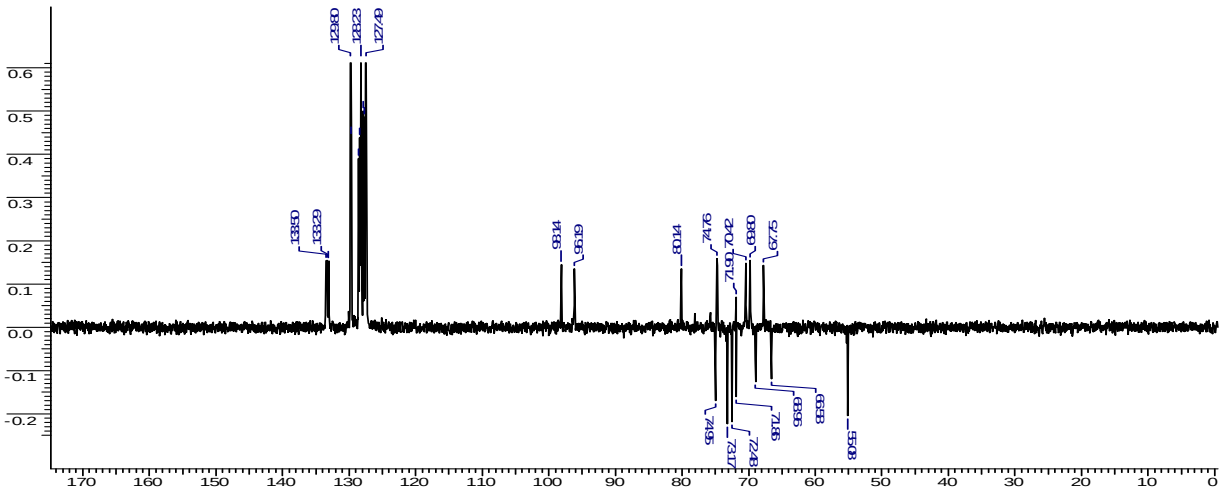
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **20**



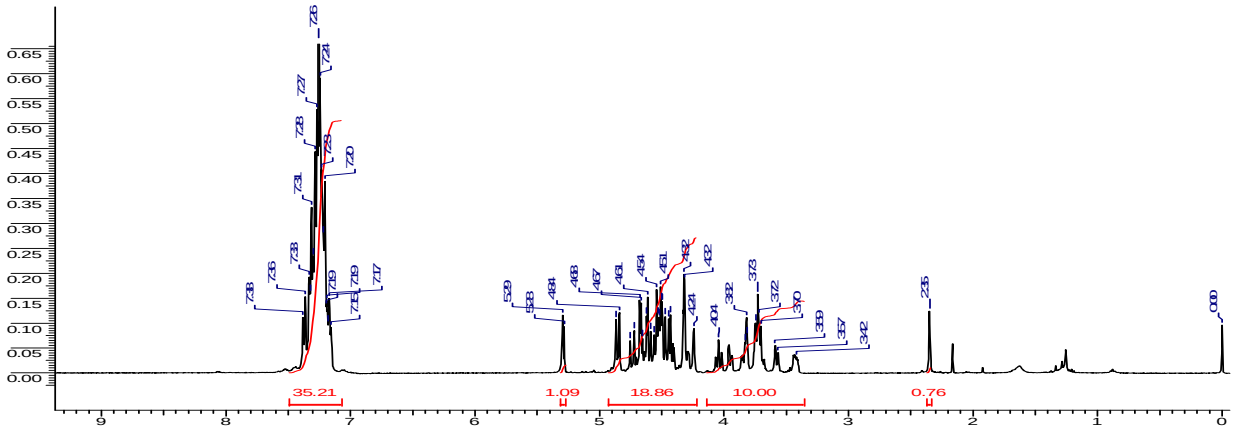
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **20**



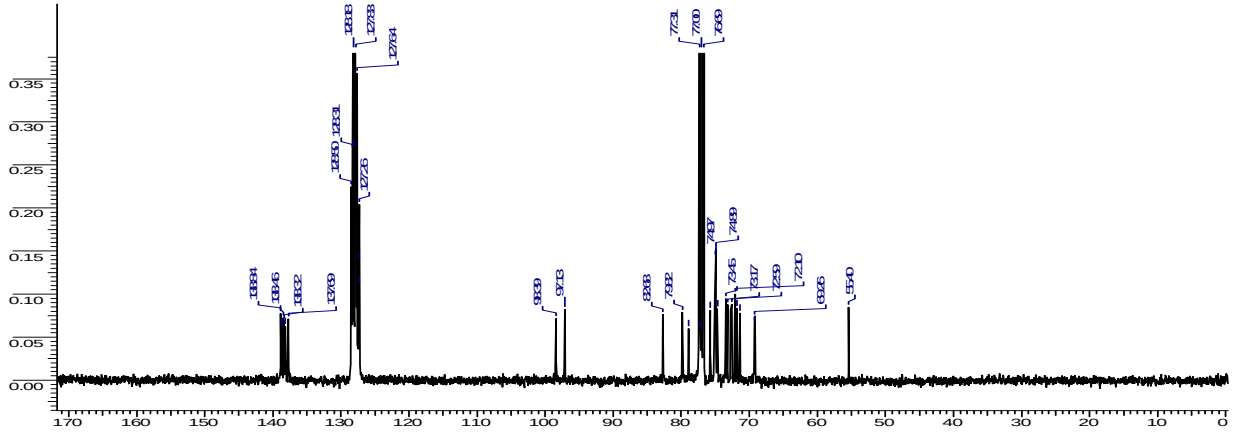
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **20**



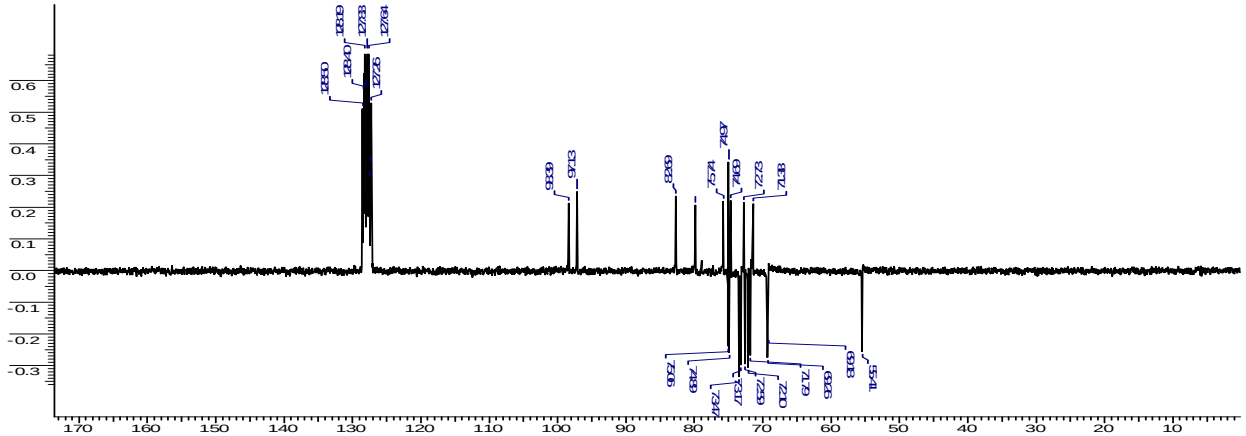
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **21**



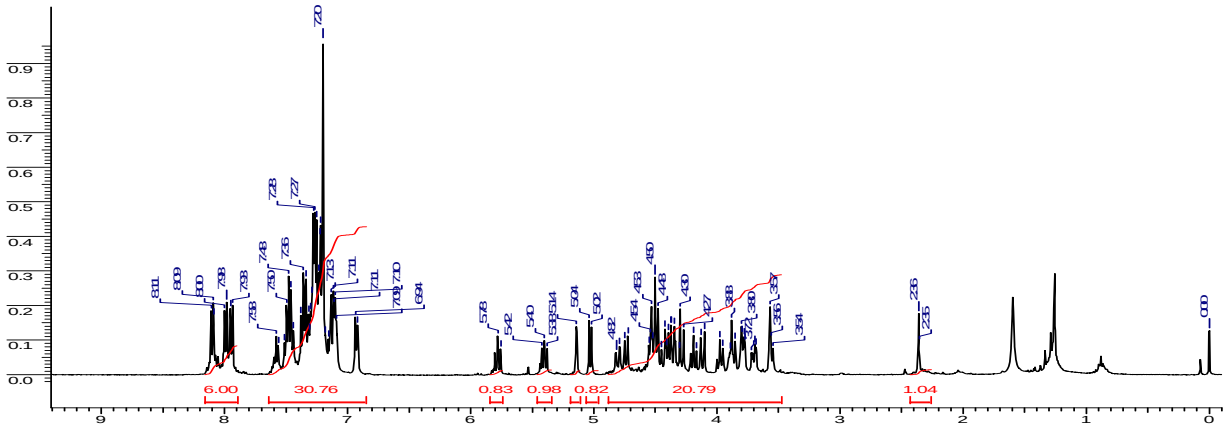
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **21**



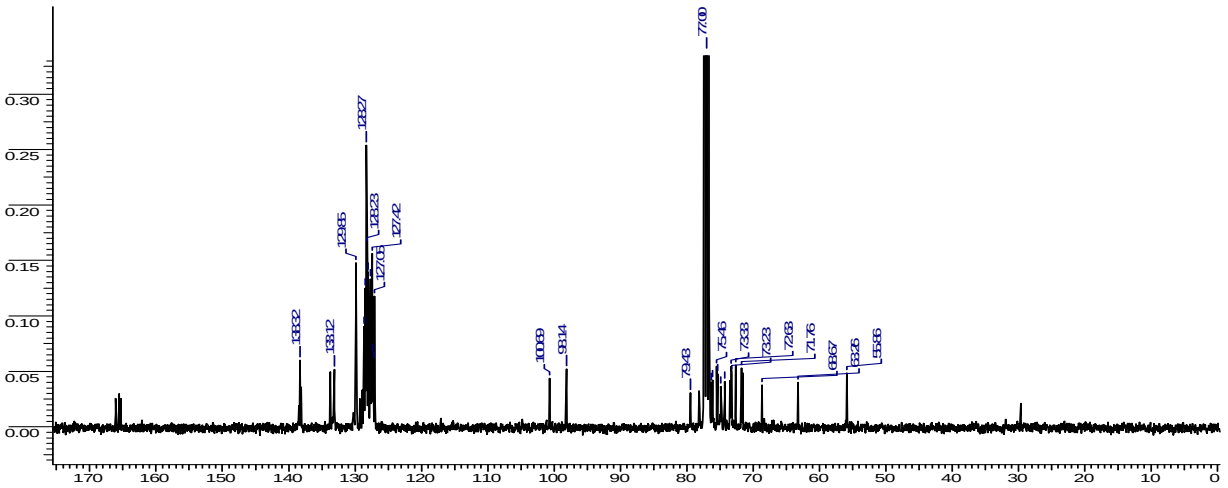
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **21**



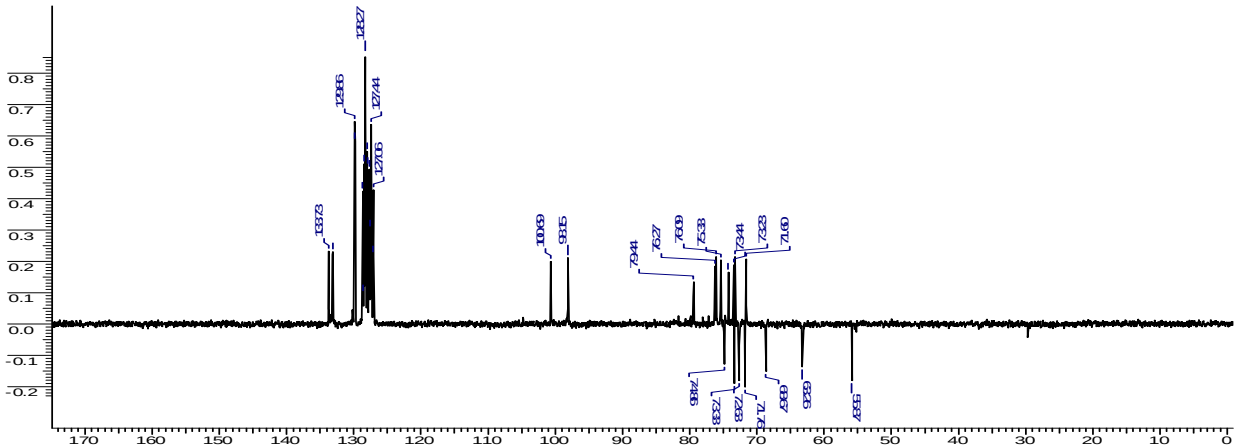
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **22**



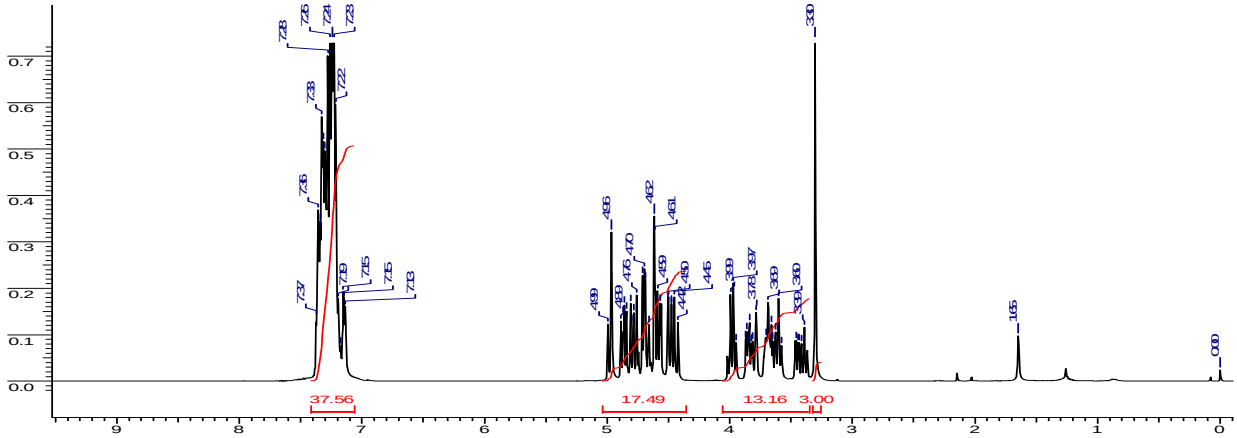
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of C10ompound **22**



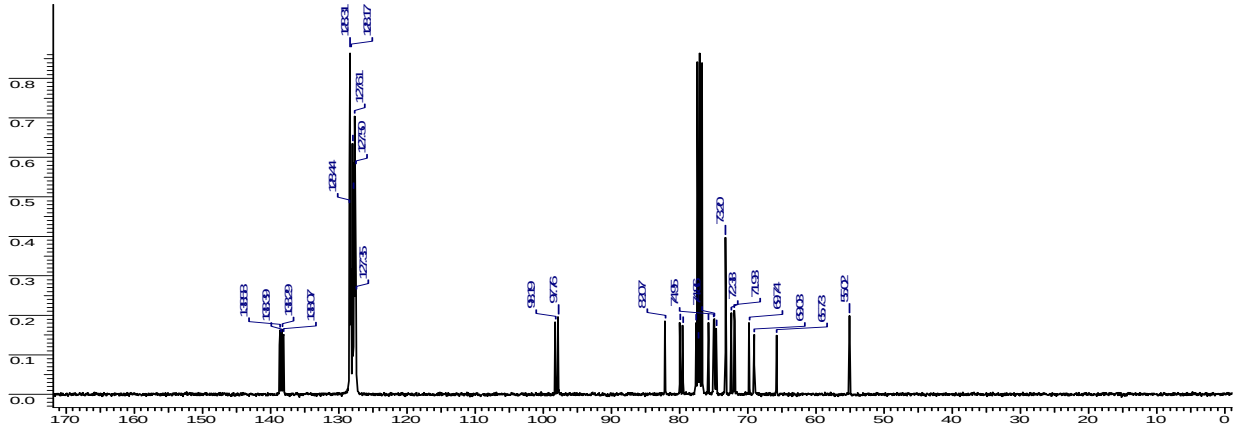
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **22**



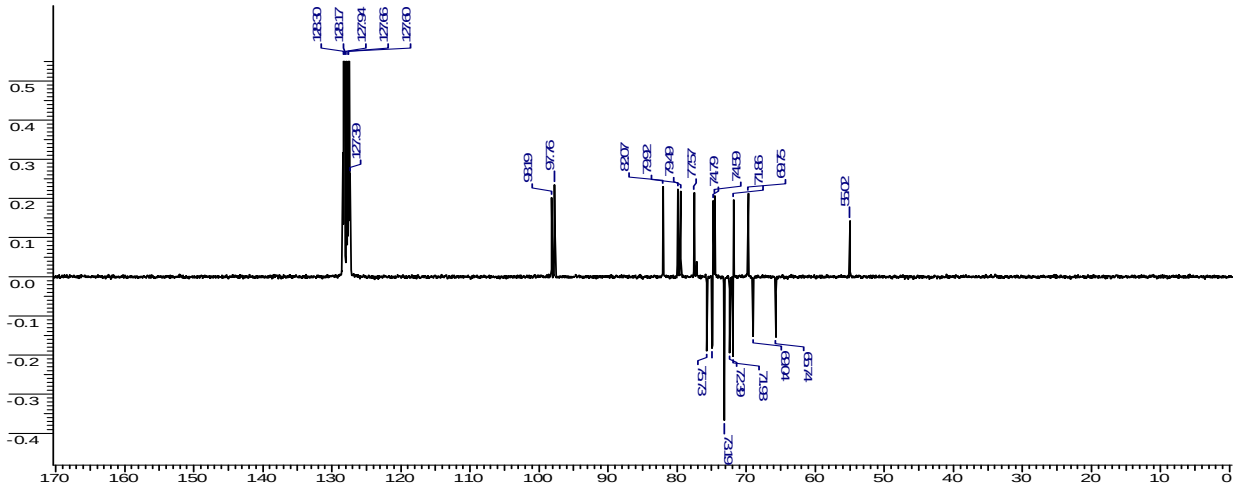
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **23**



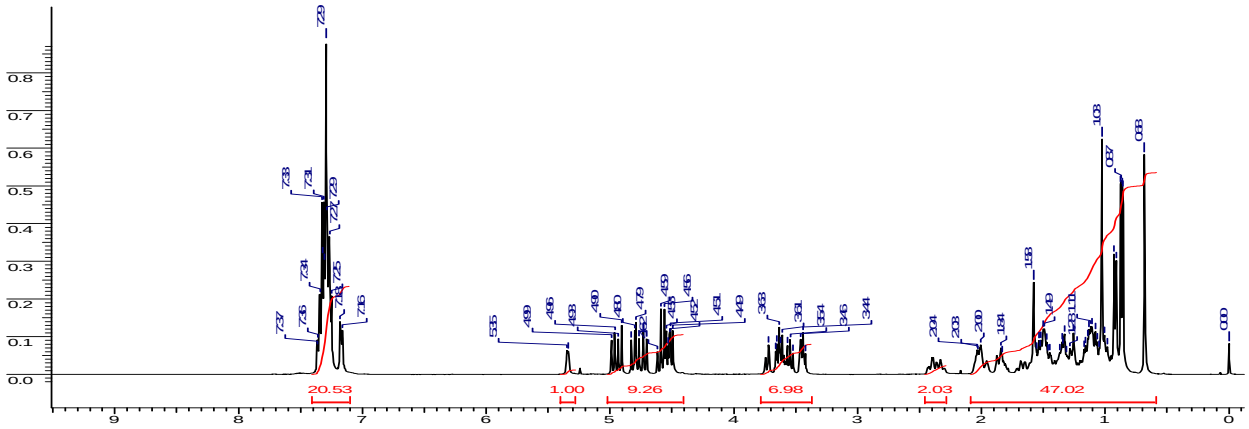
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **23**



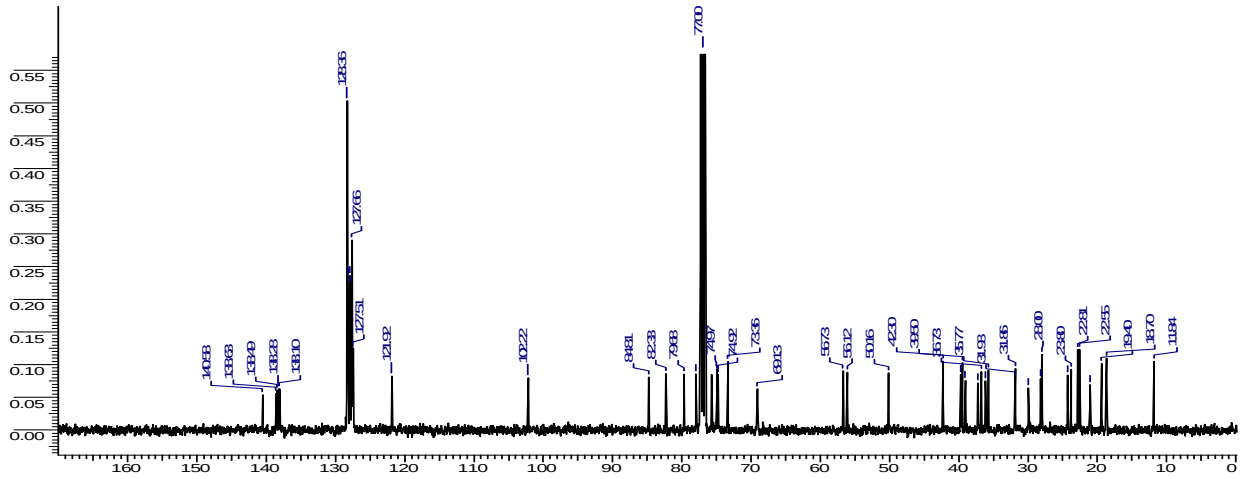
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **23**



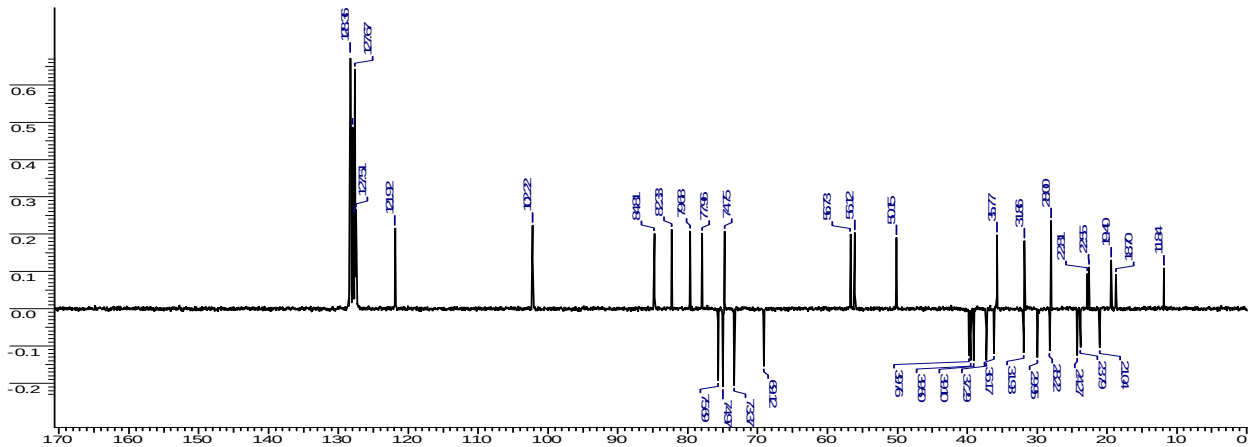
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **24**



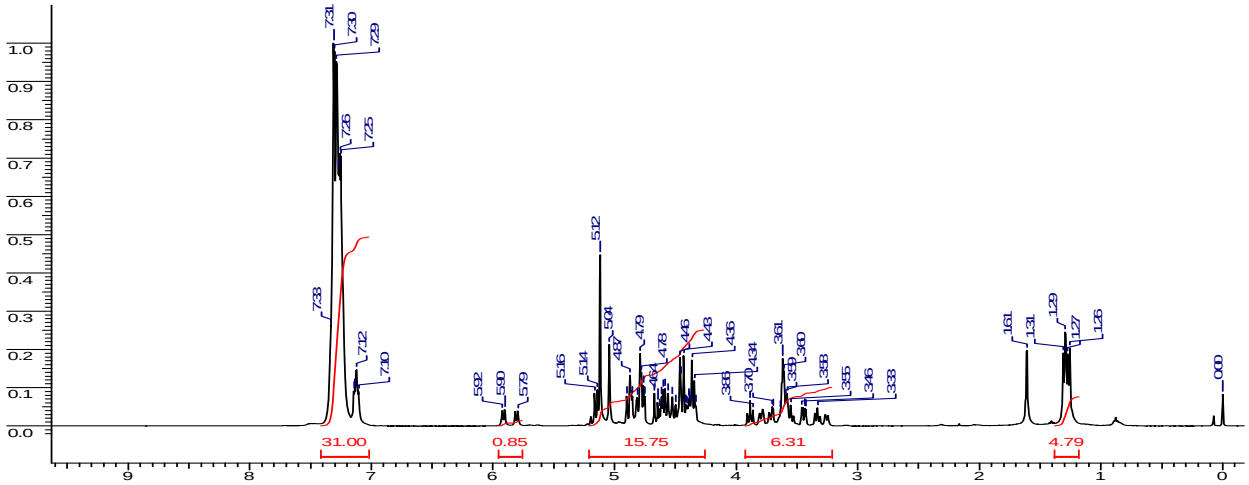
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **24**



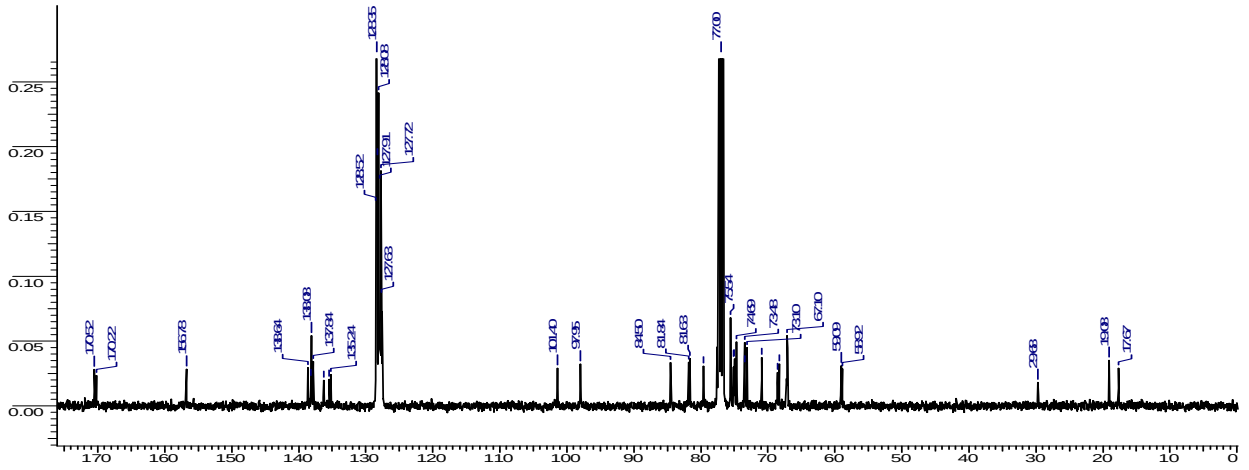
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **24**



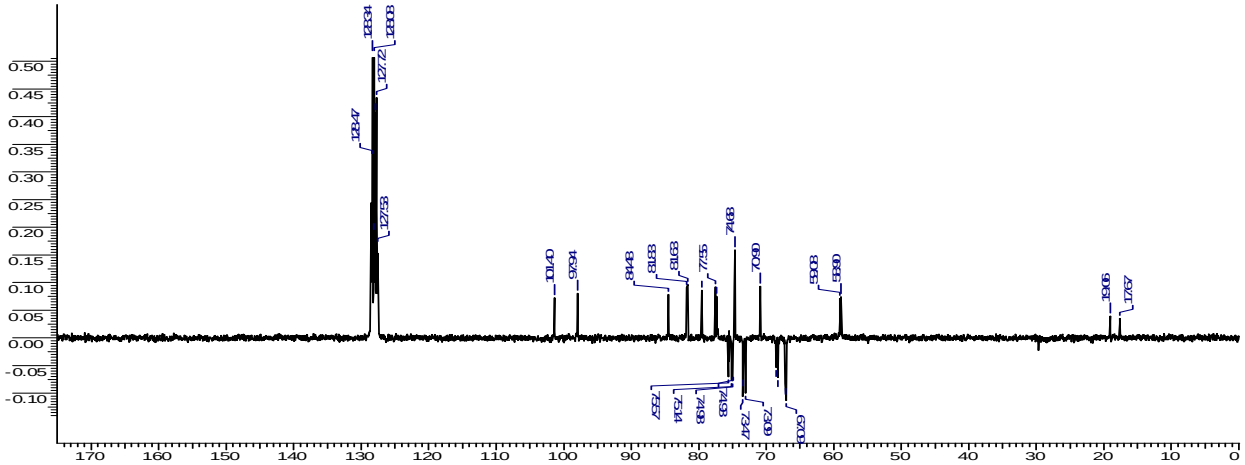
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **25**



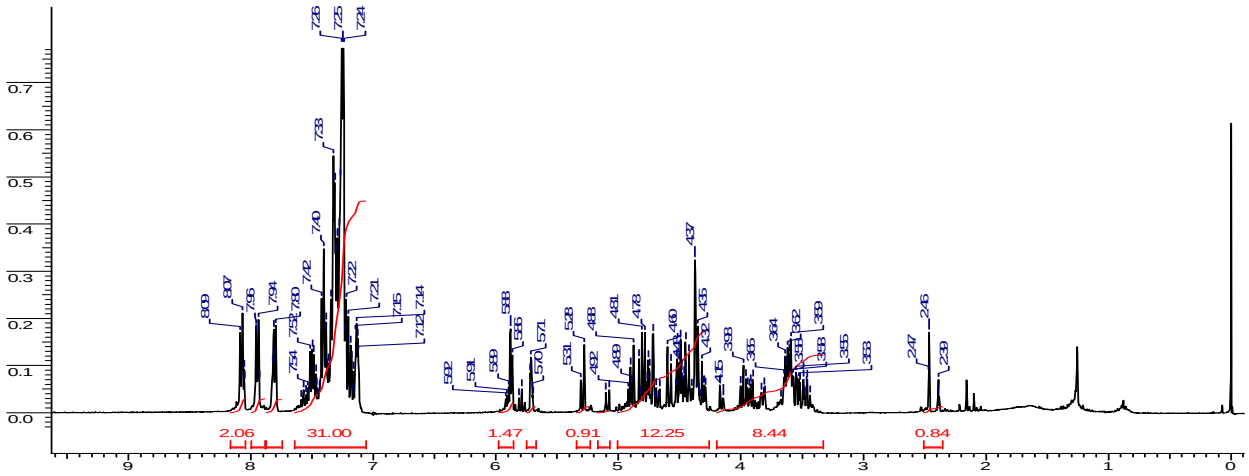
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **25**



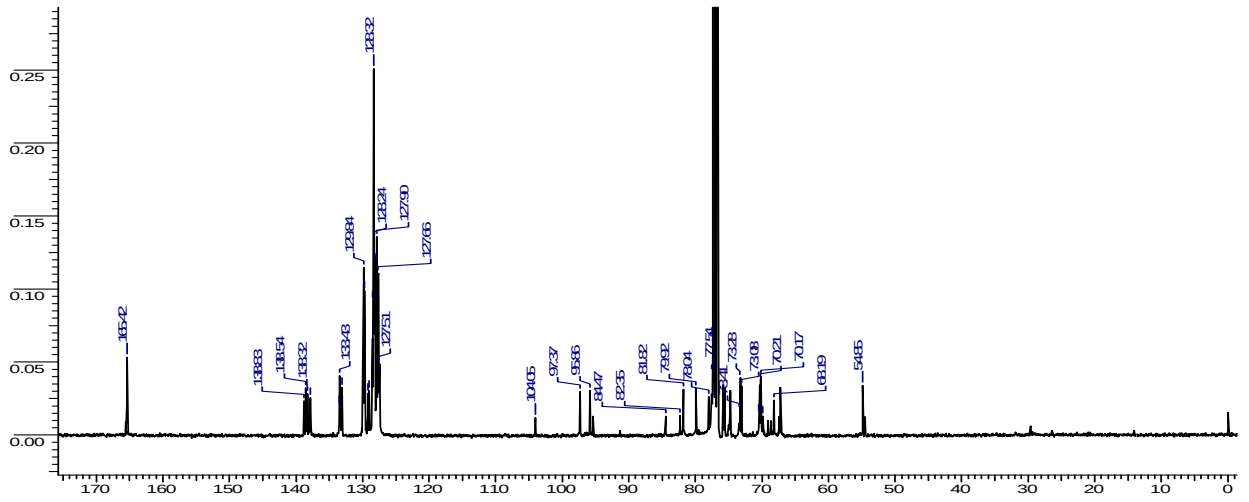
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **25**



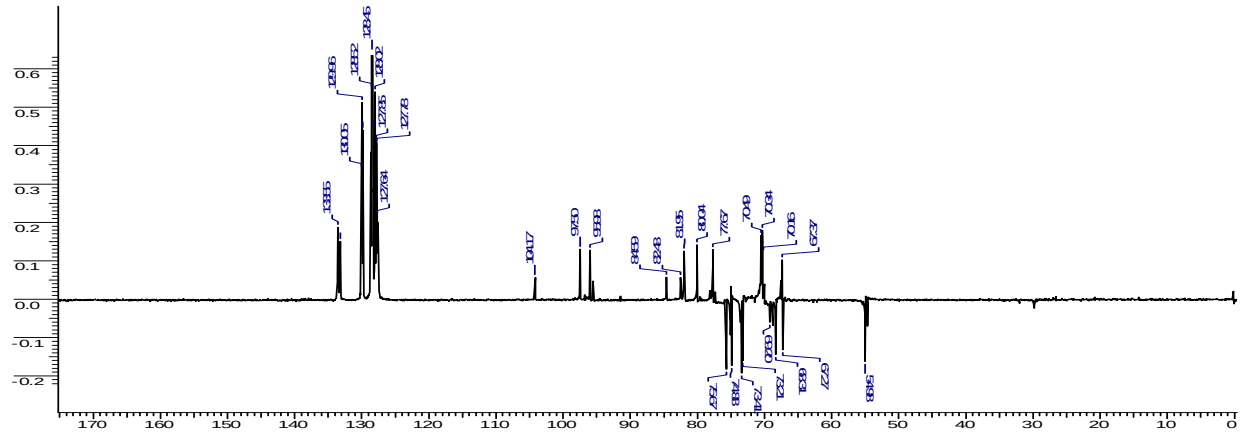
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **26**



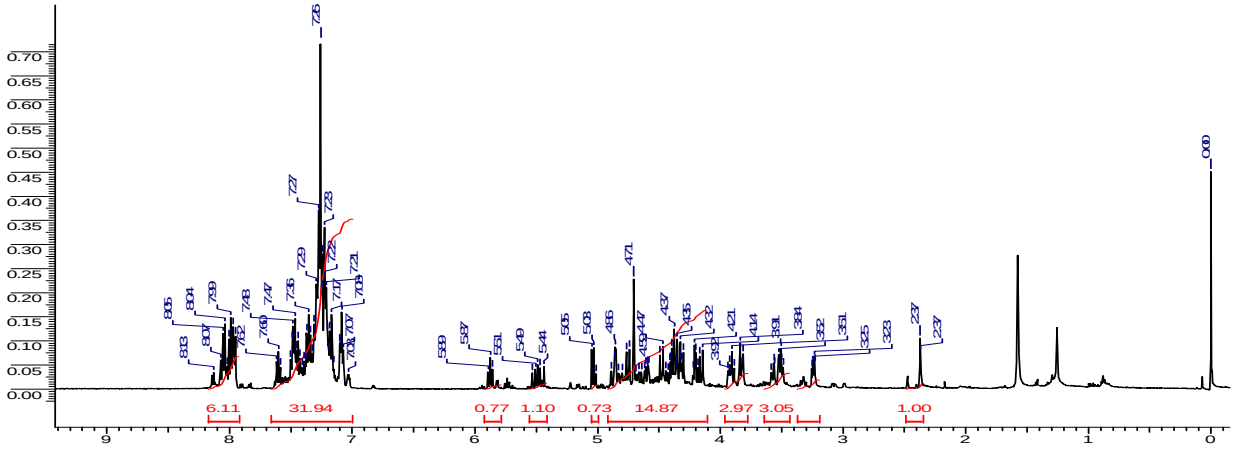
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **26**



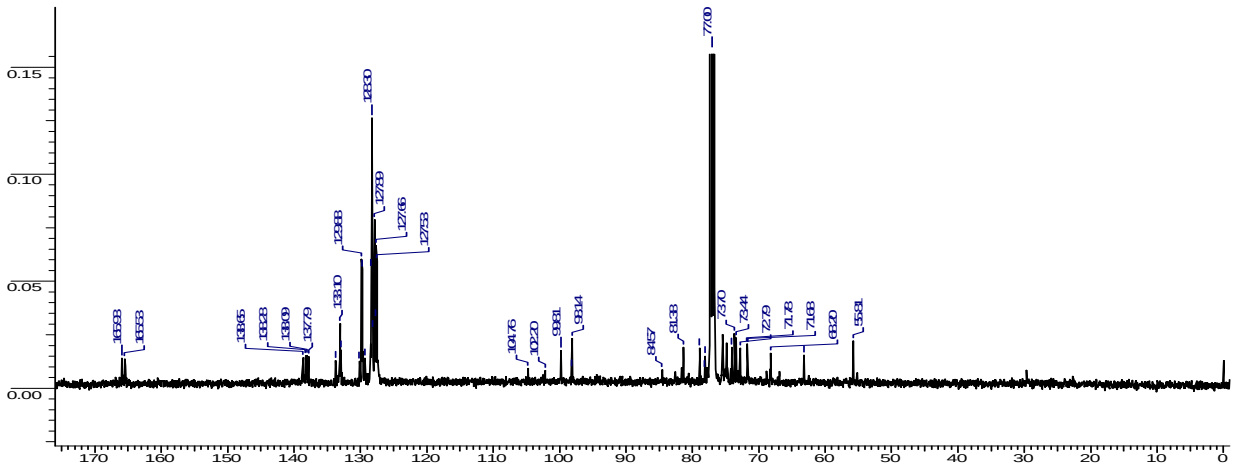
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **26**



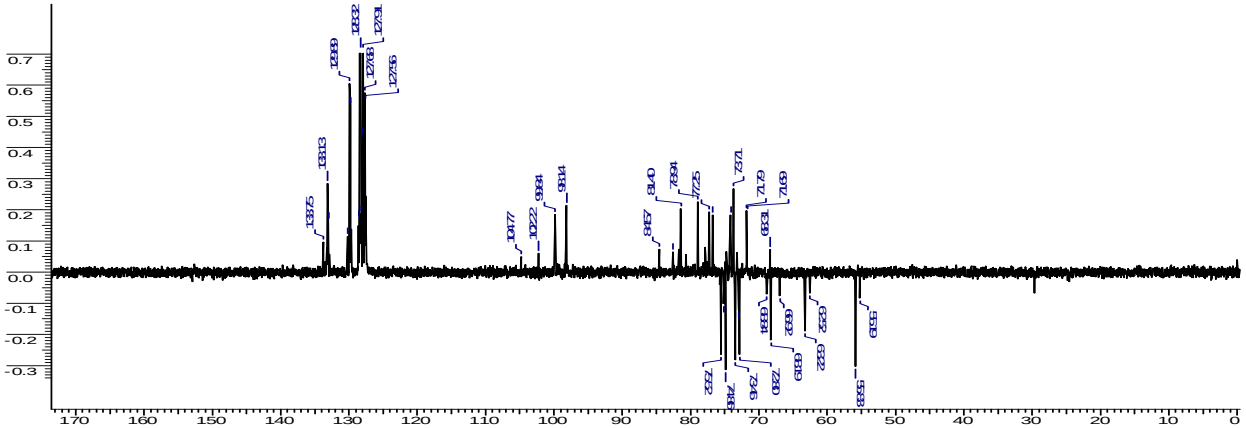
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **27**



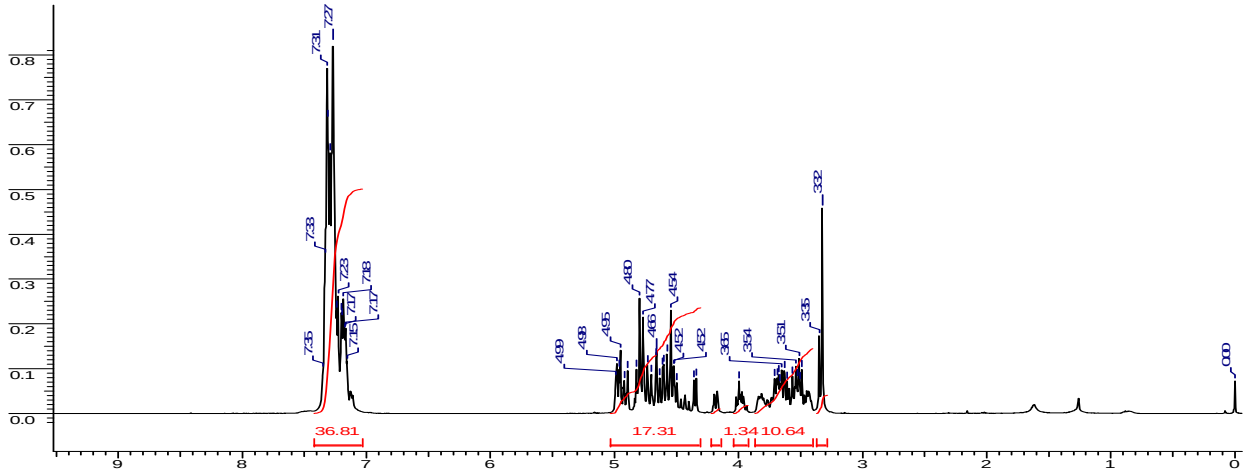
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **27**



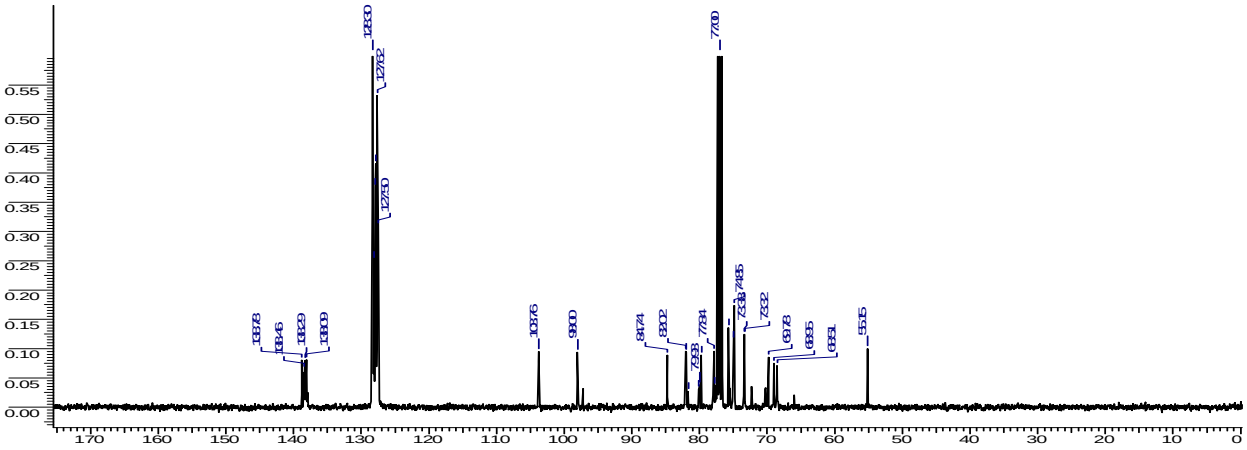
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **27**



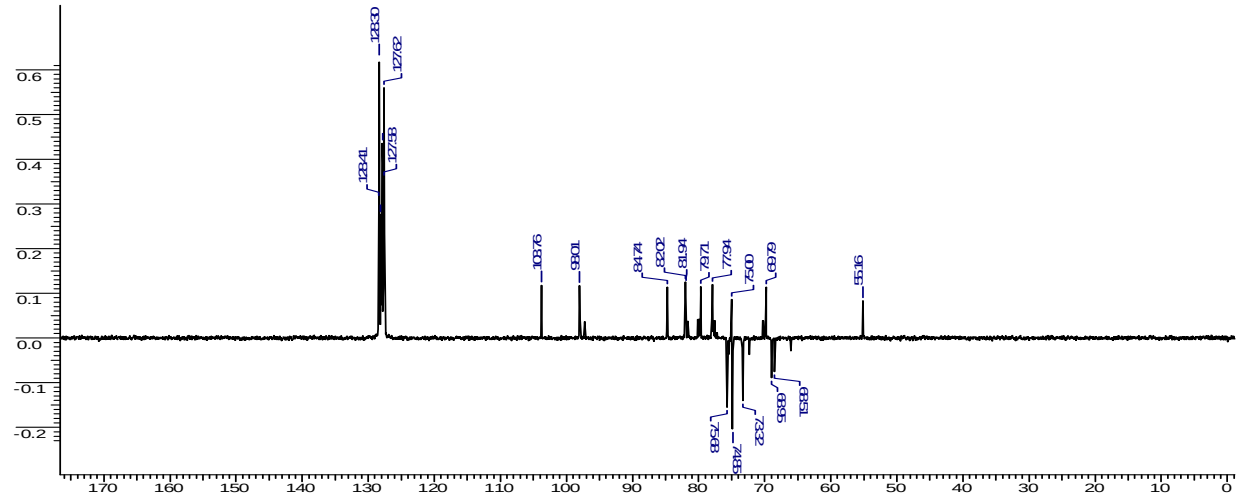
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **28**



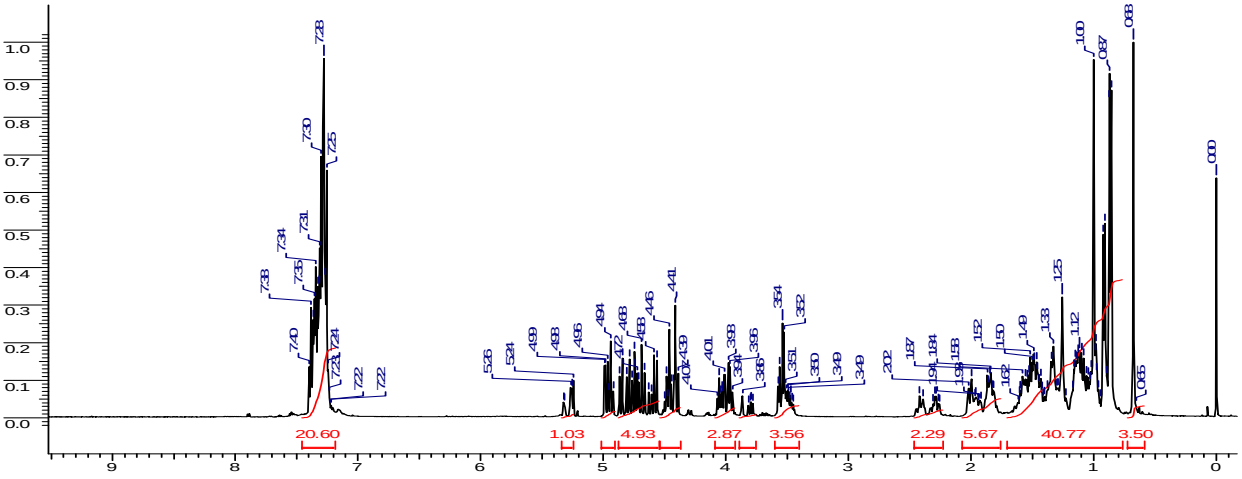
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **28**



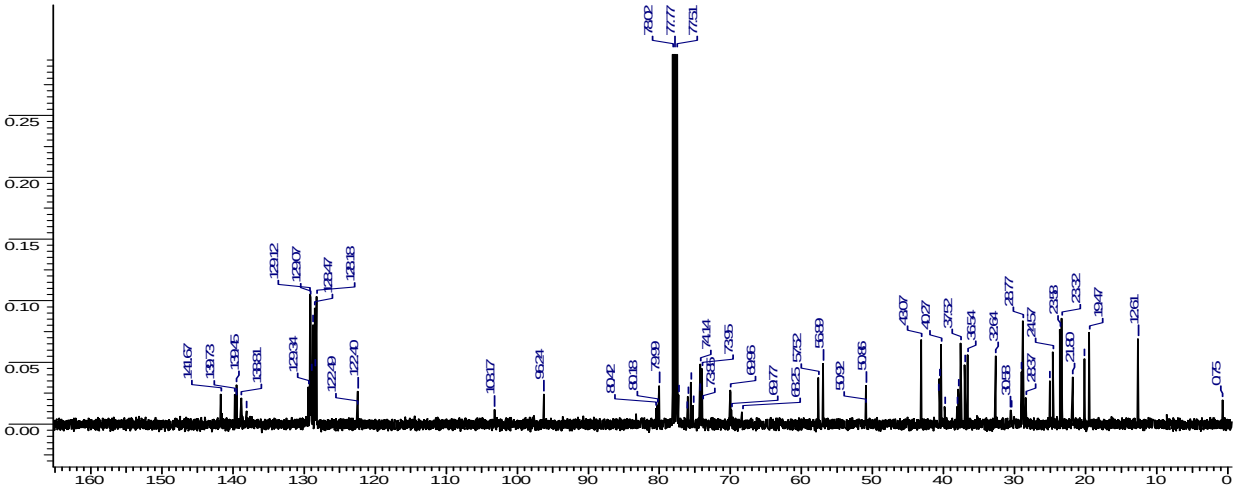
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **28**



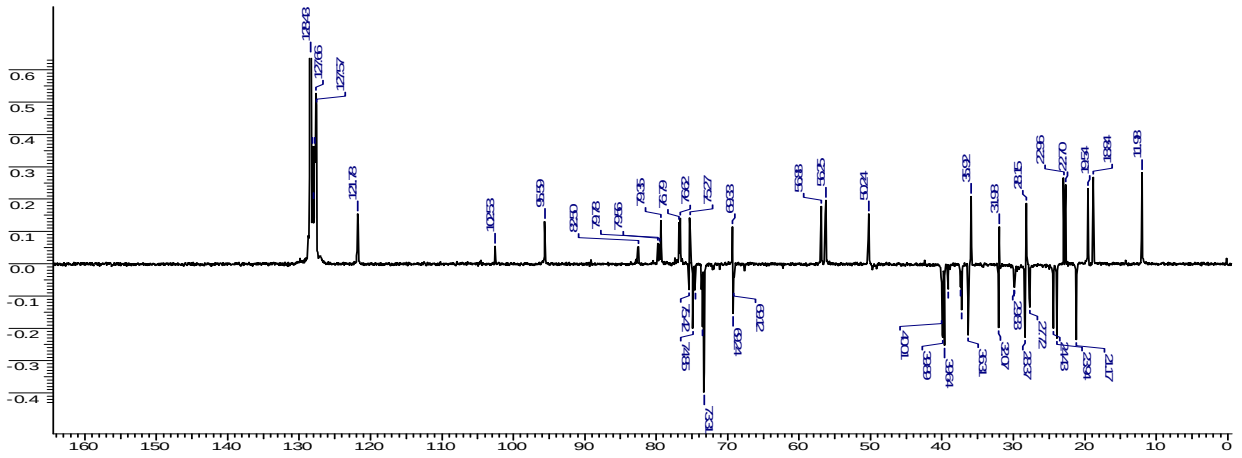
^{1}H NMR Spectrum (500.20 MHz, $CDCl_3$) of Compound **29**



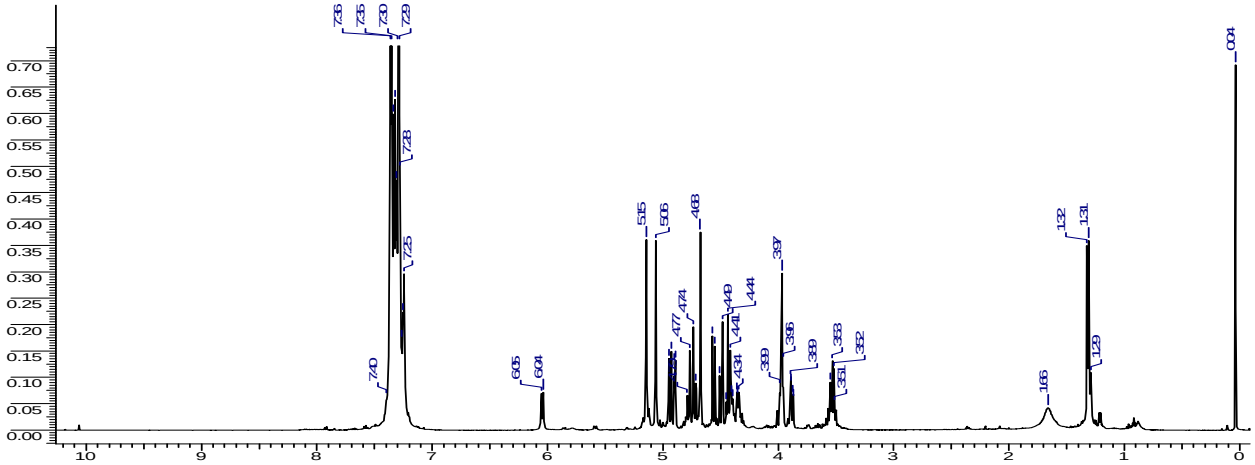
^{13}C NMR Spectrum 100.53 MHz, $CDCl_3$) of Compound **29**



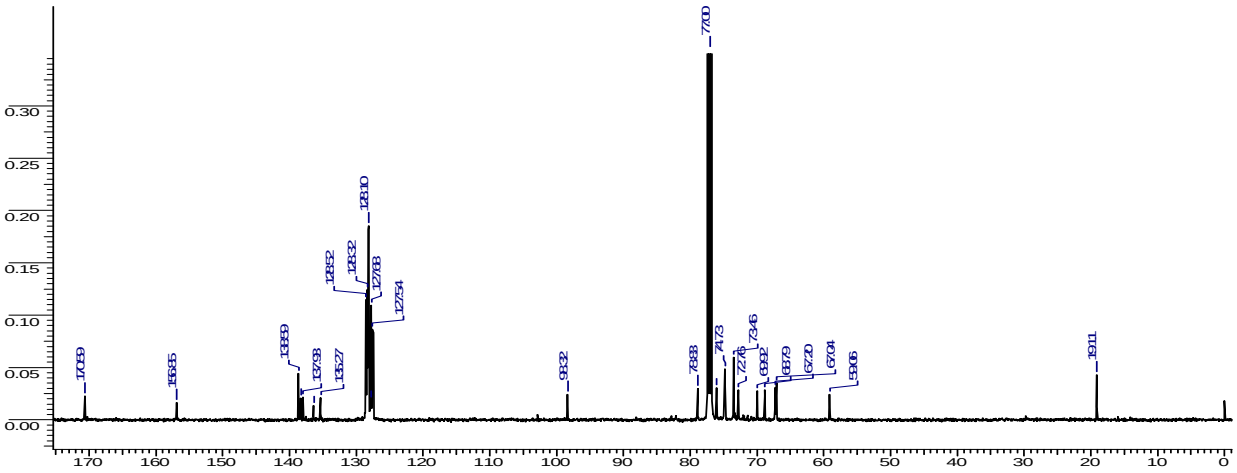
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **29**



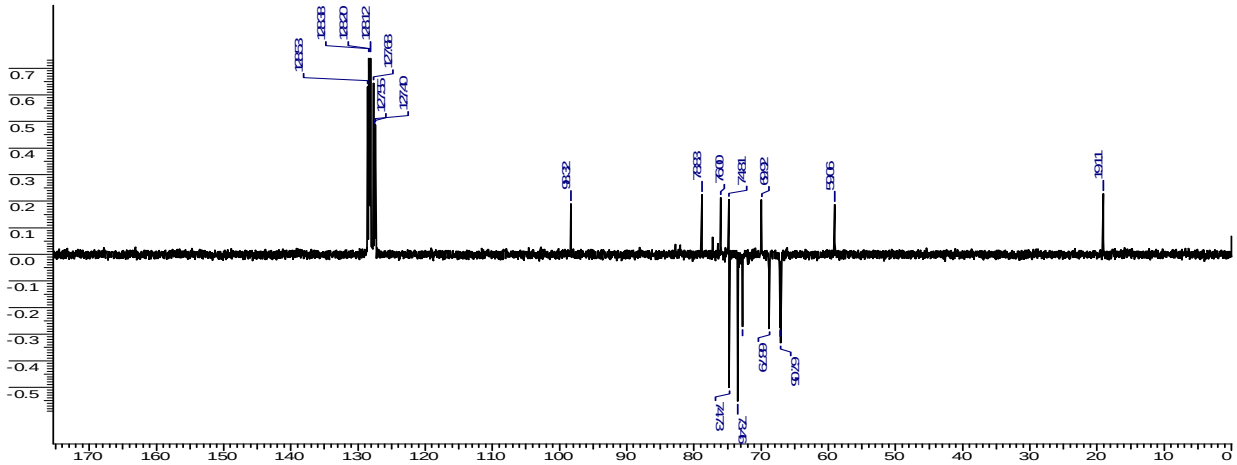
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **30**



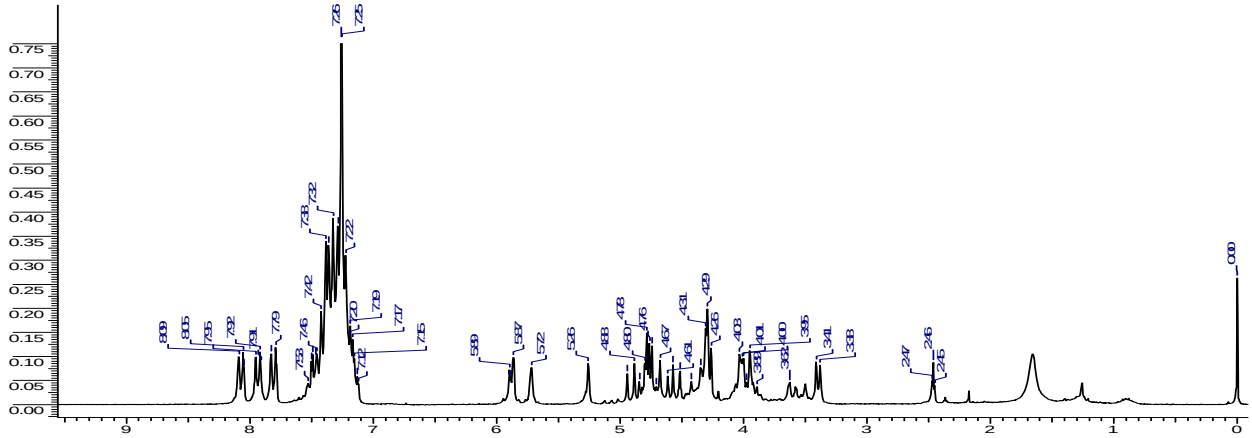
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **30**



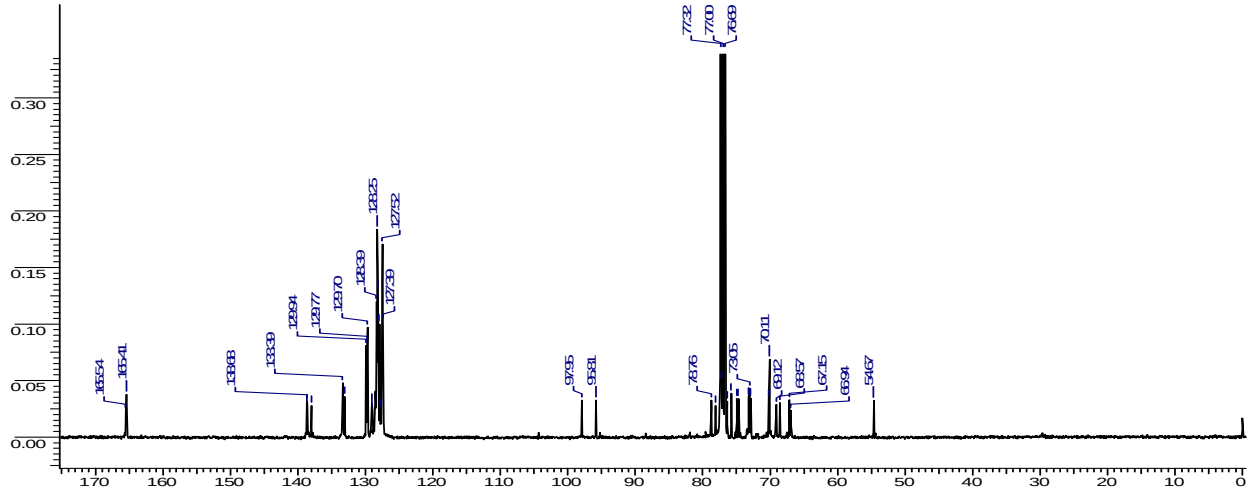
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **30**



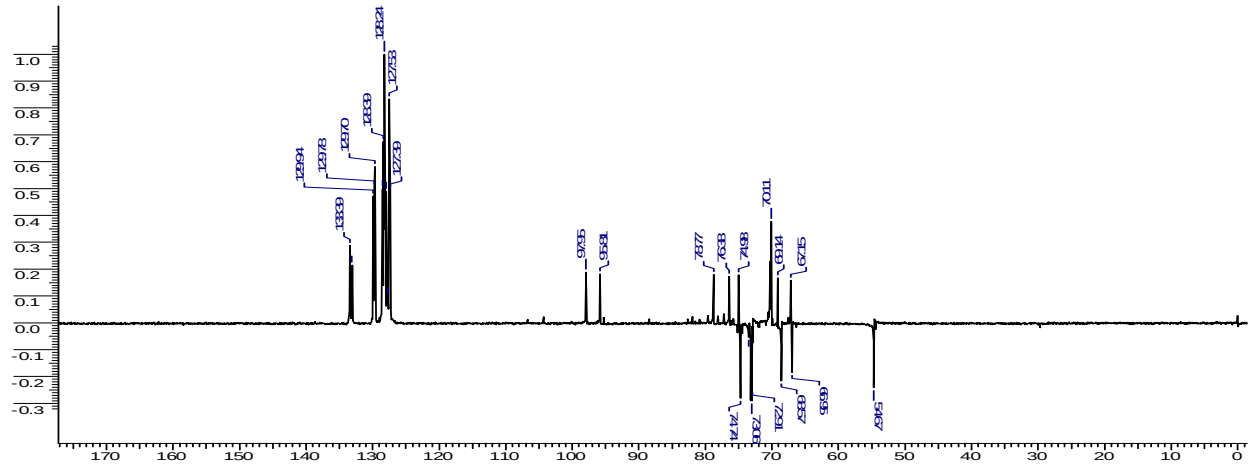
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **31**



^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **31**



DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **31**



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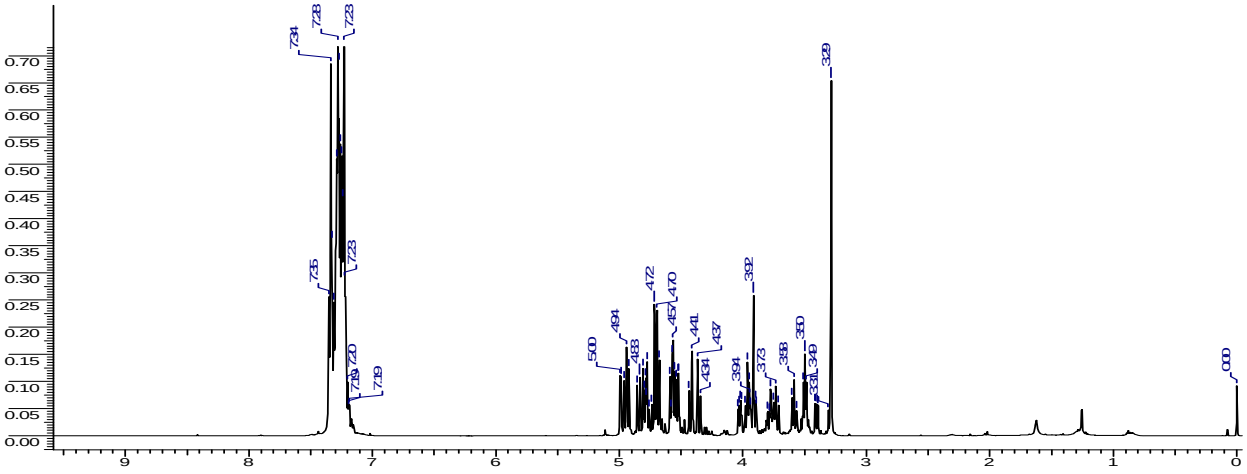
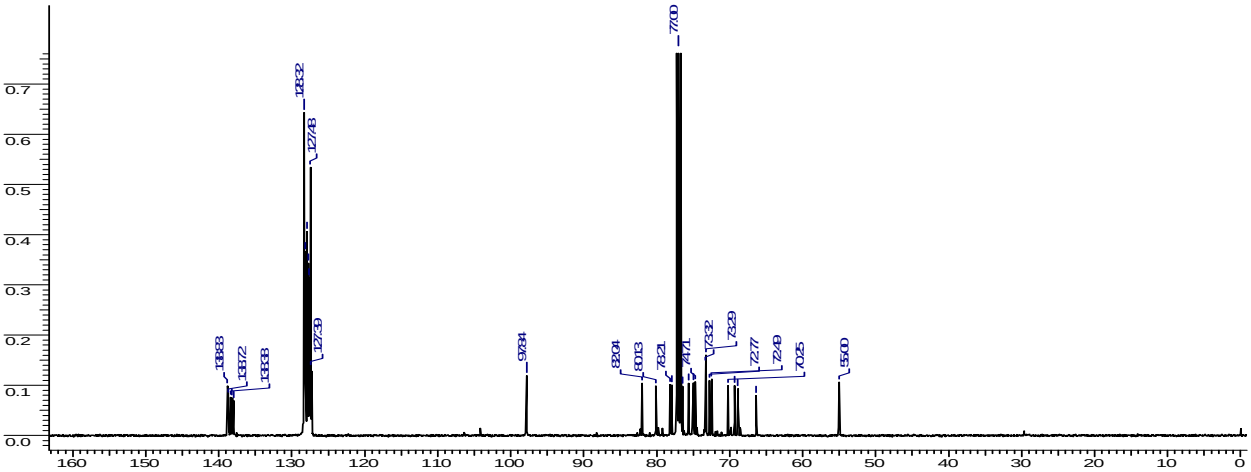
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **32**



^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **32**



DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **32**