Supporting Information

for

Propargyl/Methyl Furanosides as Potential Glycosyl Donors

Srinivasa Rao Vidadala,[a] Gaddamannugu Gayatri[b], G. Narahari Sastry*[b] and Srinivas Hotha*[c]

gnsastry@gmail.com, s.hotha@iiserpune.ac.in

Contents

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 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 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 or AV 500 with $CDCl_3$ as the solvent and internal standard. Elemental analyses were performed on an ELEMENTAR vario EL analysator. High resolution mass spectroscopy (HRMS) was performed on MALDI-TOF using 2,5-dihydroxybenzoic acid as the solid matrix. Low resolution mass spectroscopy (LRMS) was performed on Waters Acquity UPLC-MS.

General Experimental Procedures

General Procedure for $AuBr_3$-mediated transfuranosylations using ***propargyl*** *furanosides as glycosyl donors:* To a solution of glycosyl donor (0.2 mmol) and aglycone (0.22 mmol) in anhydrous acetonitrile (5 mL) was added 8 mol% of $AuBr_3$ and AgOTf under argon atmosphere at room temperature. The resulting mixture was stirred at room temperature until TLC showed complete conversion. The reaction mixture was concentrated *in vacuo* to obtain a crude residue which was purified by silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase.

General Procedure for $AuBr_3$-mediated transfuranosylations using ***methyl*** *furanosides as glycosyl donors:* To a solution of glycosyl donor (0.2 mmol) and aglycone (0.22 mmol) in anhydrous acetonitrile (5 mL) was added 8 mol% of $AuBr_3$ and AgOTf under argon atmosphere at room temperature. The resulting mixture was stirred at 65°C until TLC showed complete conversion. The reaction mixture was concentrated *in vacuo* to obtain a crude residue which was purified by silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase.

Compound Characterization Data

Compound 1a:

$[\alpha]_D$($CHCl_3$, *c* 1.6) = -37.6; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.37(t, 1H, J = 2.4Hz), 3.48(dd, 1H, J = 5.4, 10.6Hz), 3.62(dd(1H, J = 3.3, 10.6Hz), 3.90(d, 1H, J = 4.9Hz), 4.07(dd, 1H, J = 4.6, 7.4Hz), 4.15(d, 2H, J = 2.3Hz), 4.31-4.71(m, 5H), 4.54(ABq, 2H, J = 11.8Hz), 5.21(s, 1H), 7.16-7.40(m, 15H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 53.9, 70.6, 72.2, 72.3, 72.9, 74.5, 78.0, 79.0, 79.4, 80.5, 103.0, 127.4-128.3, 137.6, 137.6, 138.1; Mol. Wt. calculated for $C_{29}H_{30}O_5Na$: 481.535, Found: 481.512.

Compound 1b:

$[\alpha]_D$($CHCl_3$, *c* 1.3) = +52.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.41(t, 1H, J = 2.4Hz), 3.70(dd, 1H, J = 7.2, 10.2Hz), 3.77(dd, 1H, J = 4.8, 10.1Hz), 4.06(s, 1H), 4.08(dd, 1H J = 2.8, 8.3Hz), 4.27(dd, 2H, J = 1.4, 2.3Hz), 4.42-4.61(m, 6H), 4.45(dd, 1H, J = 3.3, 5.1Hz), 5.27(s, 1H), 7.22-7.38(m, 15H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 54.5, 69.6, 71.9, 72.1, 73.4, 74.5, 79.2, 80.4, 81.6, 86.6, 104.8, 127.5-128.4, 137.4, 137.7, 138.2; Mol. Wt. calculated for $C_{29}H_{30}O_5Na$: 481.535, Found: 481.449.

Compound 1c:

$[\alpha]_D$($CHCl_3$, *c* 1.6) = -20.4; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.41(t, 1H, J = 2.4Hz), 3.60(d, 1H, J = 2.4 Hz), 3.62(d, 1H, J = 1.0Hz), 3.92(dd, 1H, J = 3.0, 6.6Hz), 4.05(dd, 1H J = 0.9, 3.0Hz), 4.22(m, 1H), 4.28(d, 2H, J = 2.2Hz), 4.51(ABq, 2H, J = 12.0), 4.53(ABq, 2H, J = 12.0Hz), 4.56(s, 2H), 5.32(s, 1H), 7.22-7.32(m, 15H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 54.0, 69.6, 71.9, 72.1, 73.4, 74.4, 79.2, 81.1, 83.4, 88.0, 104.2, 127.6-128.4, 137.4, 137.7, 138.0; Mol. Wt. calculated for $C_{29}H_{30}O_5Na$: 481.535, Found: 481.510.

Compound 1d:

$[\alpha]_D$($CHCl_3$, *c* 1.5) = +29.4; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.40(t, 1H, J = 2.4Hz), 3.77(d, 2H, J = 5.9Hz), 3.94(dd, 1H, J = 2.0, 4.6Hz), 4.23(dd, 2H, J = 2.4, 5.0Hz), 4.34(t, 1H, J = 5.9Hz), 4.46(d,1H, J = 0.7Hz), 4.52(s, 2H), 4.60(dd, 2H, J = 7.4, 12.0Hz), 4.68(dd, 2H, J = 4.5, 12.1Hz), 5.31(d, 1H, J = 2.0Hz), 7.22-7.34(m, 15H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 54.7, 69.6, 72.4, 73.1, 73.3, 74.4, 77.8, 78.5, 79.2, 82.1, 103.5, 127.5-128.3, 137.7, 137.9, 138.1; Mol. Wt. calculated for $C_{29}H_{30}O_5Na$: 481.535, Found: 481.510.

Compound 3a:

$[\alpha]_D$($CHCl_3$, *c* 1.2) = +42.9; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.38(s, 3H), 3.46-3.65(m, 1H), 3.51(dd, 1H, J = 5.7, 10.5Hz), 3.62(dd, 1H, J = 4.1, 10.5Hz), 3.91(dd, 1H, J = 2.2, 11.5Hz), 3.95(d, 1H, J = 4.9Hz), 4.02(dd, 1H, J = 4.7, 7.3Hz), 4.14(qd, 1H, J = 2.5, 9.9Hz), 4.31(dd, 1H, J

= 3.5, 6.1Hz), 4.45(ABq, 2H, J = 11.9Hz), 4.51(s, 2H), 4.66(d, 2H, J =4.4Hz), 5.00(s, 1H), 5.16(dd, 1H J = 3.6, 8.4Hz), 5.23(dd, 1H, J = 3.6, 14.9Hz), 5.58(t, 1H, J = 9.9Hz), 6.12(t, 1H, 9.9Hz), 7.21-7.55(m, 24H), 7.85-8.00(m, 6H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.4, 66.1, 68.6, 69.3, 70.6, 71.4, 72.1, 72.3, 73.1, 77.2, 78.2, 79.3, 80.6, 96.9, 106.0, 127.5-129.9, 13.1, 133.3, 133.4, 137.8, 137.9, 138.3, 165.2, 165.8, 165.8; Mol. Wt. calculated for $C_{54}H_{52}O_{13}Na$: 931.973, Found: 931.909.

Compound 3b:

$[\alpha]_D$($CHCl_3$, *c* 1.8) = +11.8; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.68(m, 2H), 2.11(m, 2H), 3.25-3.60(m, 4H), 3.92(dd, 1H, J = 3.1, 6.8Hz), 4.03(dd, 1H, J = 1.2, 3.3Hz), 4.05-4.25(m, 2H), 4.44-4.67(m, 6H), 4.96(dq, 1H, J = 1.0, 8.8Hz), 5.04(s, 1H), 5.80(m, 1H), 7.22-7.36(m, 15H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 28.6, 30.2, 67.2, 71.4, 72.2, 72.3, 73.1, 78.5, 79.7, 80.3, 105.2, 114.7, 127.4-128.3, 129.6, 137.8, 138.1, 138.2; Mol. Wt. calculated for $C_{31}H_{36}O_5Na$: 511.604, Found: 511.551.

Compound 3c:

$[\alpha]_D$($CHCl_3$, *c* 1.0) = -20.8; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.70(d, 3H, J = 7.0Hz), 0.81, 0.84, 0.88, 0.91(4s, 6H), 1.28(m, 3H), 1.61(m, 4H), 2.03(m, 2H), 3.40(dd, 1H, J = 4.0, 10.5Hz), 3.49(dd, 1H, J = 6.6, 10.4Hz), 3.61(dd, 1H, J = 4.0, 10.4Hz), 3.80(dd, 1H, J = 1.2, 4.7Hz), 3.91(m, 1H), 4.36(dt, 1H, J = 4.1, 7.0Hz), 4.52(dd, 2H, J = 11.7, 18.7Hz), 4.55(d, 2H, J = 1.8Hz), 4.64(s, 2H), 5.21(d, 1H, J = 0.7Hz), 7.25-7.39(m, 15H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 15.9, 21.1, 22.3, 23.0, 25.1, 29.7, 31.3, 34.4, 39.8, 47.9, 72.0, 72.3, 73.1, 75.3, 78.8, 79.7, 80.4, 101.6, 127.5-128.4, 137.8, 138.0, 138.3; Mol. Wt. calculated for $C_{36}H_{46}O_5Na$: 581.737, Found: 581.235.

Compound 3d:

$[\alpha]_D$($CHCl_3$, *c* 1.5) = +5.3; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.29(s, 3H), 3.31-3.65(m, 5H), 3.72(dd, 1H, J = 4.0, 9.7Hz), 3.89(dt, 1H, J = 0.9, 4.7Hz), 3.90-4.05(m, 3H), 4.33(dd, 1H, J = 5.7, 10.8Hz), 4.41-4.65(m, 8H), 4.72(ABq, 2H, J = 12.2Hz), 4.82(t, 1H, J = 10.9Hz), 4.88(ABq, 2H, J = 10.8Hz), 5.06(d, 1H, J = 0.8Hz), 7.22-7.33(m, 30H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.0, 66.5, 69.9, 71.3, 72.2, 72.3, 73.1, 73.3, 74.9, 75.7, 77.9, 78.3, 79.7, 78.8, 80.5, 82.0, 97.8, 105.7, 127.4-128.4, 137.7, 137.7, 138.1, 138.1, 138.2, 138.6 ; Mol. Wt. calculated for $C_{54}H_{58}O_{10}Na$: 890.022, Found: 889.903.

Compound 3e:

$[\alpha]_D$($CHCl_3$, *c* 1.3) = +48.1; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.44-3.52(m, 2H), 3.60(dd, 1H, J = 3.5, 10.6Hz), 3.70(dd, 1H J = 1.2, 4.6Hz), 3.73-3.83(m, 2H), 4.00(dd, 1H, J = 4.8, 6.6Hz), 4.16(dd, 1H, J = 2.0, 11.6Hz), 4.27(ABq, 2H, J = 11.9Hz), 4.30(dd, 1H , J = 3.0, 7.9Hz), 4.47(d,

1H, J = 1.4Hz), 4.50(ABq, 2H, J = 11.6Hz), 4.56(s, 2H), 4.80(s, 2H), 4.95(d, 1H, J = 1.1Hz), 5.11(s, 2H), 5.36(d, 1H, J = 8.1Hz), 5.91(d, 1H, J = 1.0Hz), 7.14-7.38(m, 30H), 7.51(d, 1H, J = 1.7Hz), 7.58(d, 2H, J = 8.1Hz) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 43.9, 65.5, 70.0, 71.3, 72.0, 72.4, 73.3, 74.0, 77.4, 78.1, 79.7, 80.8, 80.9, 89.2, 100.9, 105.8, 127.5-128.7, 129.3, 136.7, 137.2, 137.2, 137.4, 137.4, 137.5, 137.8, 150.6, 162.4 ; Mol. Wt. calculated for $C_{56}H_{56}N_2O_{10}Na$: 940.0410, Found: 939.899.

Compound 3f:

$[\alpha]_D$($CHCl_3$, *c* 2.1) = +61.3; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.34(t, 1H, J = 2.3Hz), 3.42-3.67(m, 3H), 3.85-4.00(m, 2H), 4.04(dd, 1H, J = 4.6, 7.2Hz), 4.15-4.55(m, 8H), 4.66(d, 2H, J = 3.6Hz), 4.99(s, 1H), 5.31(dd, 1H J = 3.7Hz), 5.50(dd, 1H, J = 3.5Hz), 5.61(t, 1H, J = 9.9Hz), 6.13(t, 1H, J = 10.0Hz), 7.24-7.56(m, 24H), 7.85-8.01(m, 6H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.2, 66.0, 69.1, 69.2, 70.4, 71.3, 71.6, 72.1, 72.3, 73.1, 75.3, 78.2, 78.3, 79.3, 80.6, 94.7, 106.0, 127.5-129.9, 133.1, 133.3, 133.4, 137.8, 137.9, 138.2, 165.2, 165.7, 165.8 ; Mol. Wt. calculated for $C_{56}H_{52}O_{13}Na$: 955.994, Found: 955.545.

Compound 4a(α/β):

^{1}H NMR (500.13 MHz, $CDCl_3$): δ 3.35(s, 3H), 3.46-3.54(m, 2H), 3.43(s, 3H), 3.60-3.79(m, 6H), 3.94-4.10(m, 6H), 4.20-4.25(m, 2H), 4.35-4.68(m, 12H), 5.04(s, 1H), 5.08(s, 1H), 5.19-5.27(m, 4H), 5.59(t, 1H. J = 9.8Hz), 5.69(t, 1H, J = 9.8Hz), 6.10-6.16(m, 2H), 7.23-7.52(m, 48H), 7.86-7.99(m, 12H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 55.3, 55.5, 65.7, 66.5, 68.7, 68.8, 69.1, 69.3, 69.3, 69.7, 70.6, 70.7, 71.8, 71.9, 72.0, 72.2, 72.3, 72.7, 73.2, 73.3, 79.8, 80.2, 81.5, 81.9, 86.6, 86.7, 96.8, 96.9, 101.7, 107.5, 127.5-129.9, 133.0, 133.0, 133.2, 133.3, 133.3, 133.3, 137.5, 137.7, 137.8, 137.9, 138.3, 138.3, 165.1, 165.2, 165.8, 165.8, 165.8, 165.9 ; Mol. Wt. calculated for $C_{54}H_{52}O_{15}Na$: 931.973, Found: 931.769.

Compound 4b(α/β):

^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.68(m, 4H), 2.13(m, 4H), 3.25-3.80, 8H), 3.92(dd, 1H, J = 3.3, 6.8Hz), 4.03(dd, 1H, J = 1.2, 3.2Hz), 4.05-4.12(m, 2H), 4.16-4.24(m, 2H), 4.44-4.68(m, 12H), 4.85-5.10(m, 6H), 5.68-5.93(m, 2H), 7.20-7.45(m, 30H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 28.6, 28.7, 29.6, 30.2, 66.8, 67.2, 69.7, 71.9, 72.0, 72.2, 72.4, 72.6, 73.3, 73.3, 80.1, 80.4, 83.4, 83.5, 84.2, 88.3, 100.5, 106.1, 114.8, 114.8, 127.5-128.4, 137.5, 137.7, 137.9, 138.0, 138.1, 138.1, 138.2, 138.2 ; Mol. Wt. calculated for $C_{31}H_{36}O_5Na$: 511.604, Found: 511.550.

Compound 4c(α/β):

^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.69-0.92(m, 22H), 0.95-1.49(m, 6H), 1.54-1.70(m, 4H), 2.05-2.40(m, 4H), 3.30-3.58(m, 2H), 3.60-3.85(m, 4H), 3.96-4.05(m, 4H), 4.30-4.70(m, 14H), 5.17(d, 1H, J = 4.3Hz), 5.25(s, 1H), 7.18-7.40(m, 30H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ

15.8, 15.9, 21.1, 21.1, 22.2, 22.4, 22.8, 23.0, 24.8, 25.1, 31.3, 31.7, 34.3, 34.5, 39.6, 43.2, 48.0, 48.0, 48.4, 69.5, 71.8, 71.9, 72.5, 72.6, 73.3, 73.3, 74.8, 75.5, 80.0, 80.2, 81.4, 81.7, 84.4, 86.3, 100.8, 102.8, 127.4-128.4, 137.8, 138.1, 138.2, 138.3, 138.3, 138.4; Mol. Wt. calculated for $C_{36}H_{46}O_5Na$: 581.737, Found: 581.236.

Compound 4d(α/β):

^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.28(s, 3H), 3.34(s, 3H), 3.35(dd, 1H, J = 9.4, 16.8Hz), 3.43(dd, 1H, J = 3.7, 9.5Hz), 3.49(ABq, 2H, J = 9.4Hz), 3.57(dd, 2H, J = 6.7, 10.7Hz), 3.63-3.80(m, 8H), 3.96-4.13(m, 8H), 4.28(dd, 1H, J = 5.8, 7.0Hz), 4.37(m, 1H), 4.42-4.88(m, 22H), 4.93-4.98(m, 2H), 5.07(d, 1H, J = 1.5Hz), 5.13(d, 1H, J = 4.3Hz), 7.20-7.38(m, 60H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.0, 55.1, 66.5, 66.9, 69.3, 69.6, 70.0, 70.2, 71.9, 72.1, 72.1, 72.4, 73.3, 73.3, 73.4, 73.4, 75.0, 75.1, 75.6, 75.7, 76.2, 77.8, 78.1, 80.0, 80.0, 80.0, 81.6, 81.8, 82.0, 82.0, 83.6, 86.7, 97.9, 98.1, 100.5, 107.3, 127.5-128.4, 137.5, 137.8, 138.0, 138.1, 138.2, 138.2, 138.2, 138.2, 138.3, 138.3, 138.7, 138.9 ; Mol. Wt. calculated for $C_{54}H_{58}O_{10}Na$: 890.022, Found: 890.811.

Compound 5a:

$[\alpha]_D$($CHCl_3$, *c* 1.3) = +0.8; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.38(s, 3H), 3.44-3.68(m, 3H), 3.75-4.20(m, 4H), 4.27-4.80(m, 3H), 4.46(ABq, 2H, J = 11.8Hz), 4.66(ABq, 2H, J = 11.8Hz), 5.01(s, 1H), 5.22(dd, 1H, J = 3.5, 9.4Hz), 5.25(dd, 1H, J = 3.5, 19.5Hz), 5.59(t, 1H, J = 9.8Hz), 6.13(t, 1H, J = 9.8Hz), 7.24-7.50(m, 24H), 7.86-8.00(m, 6H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.4, 66.1, 68.6, 69.2, 70.5, 71.3, 72.0, 72.0, 72.2, 73.0, 78.2, 79.2, 80.5, 96.8, 105.9, 127.4-129.8, 133.0, 133.3, 133.3, 137.8, 137.8, 138.2, 165.2, 165.7, 165.8 ; Mol. Wt. calculated for $C_{54}H_{52}O_{13}Na$: 931.973, Found: 931.916.

Compound 5b(α/β):

^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.57(m, 4H), 2.03(m, 4H), 3.20-3.78(m, 8H), 3.86(dd, 1H, J = 0.8, 4.5Hz), 4.01(dd, 1H, J = 4.7, 7.0Hz), 4.10-4.40(m, 4H), 4.42-4.72(m, 12H), 4.90-5.15(m, 6H), 5.59-5.90(m, 2H), 7.21-7.60(m, 30H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 28.5, 28.6, 29.6, 30.2, 66.8, 67.2, 69.6, 69.7, 71.9, 72.0, 72.2, 72.3, 72.6, 73.3, 80.1, 80.3, 83.4, 84.1, 88.2, 88.3, 100.5, 106.0, 114.8, 114.8, 127.5-128.4, 137.5, 137.6, 137.8, 137.9, 138.0, 138.0, 138.0, 138.1 ; Mol. Wt. calculated for $C_{31}H_{36}O_5Na$: 511.604, Found: 511.551.

Compound 5c:

$[\alpha]_D$($CHCl_3$, *c* 1.2) = +14.4; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.79(d, 3H, J = 6.9Hz), 0.87, 0.90, 0.90, 0.94(4s, 6H), 1.01(m, 2H), 1.25(m, 3H), 1.63(m, 2H), 2.16(m, 2H), 3.36(dt, 1H, J = 4.3, 10.4Hz), 3.63(t, 1H, J = 10.9Hz), 3.63(dd, 1H, J = 10.9, 19.8Hz), 3.90(dd, 1H, J = 3.3, 7.1Hz), 4.03(dd, 1H, J = 1.2, 3.4Hz), 4.25(m, 1H), 4.51(ABq, 2H, J = 11.9Hz), 4.52(ABq, 2H, J

= 11.8Hz), 4.56(d, 2H, J = 1.5Hz), 5.16(s, 1H), 7.26-7.32(m, 15H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 16.1, 21.2, 22.2, 23.0, 25.6, 31.6, 34.3, 43.3, 48.4, 69.7, 71.9, 72.0, 73.2, 79.7, 80.0, 83.7, 88.6, 107.6, 127.5-128.4, 137.6, 138.0, 138.2; Mol. Wt. calculated for $C_{36}H_{46}O_5Na$: 581.737, Found: 581.423.

Compound 5d:

$[\alpha]_D$($CHCl_3$, *c* 2.3) = +24.4; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.36(s, 3H), 3.47-3.78(m, 5H), 3.97(dd, 2H, J = 8.8, 17.2Hz), 4.04-4.15(m, 2H), 4.20(dd, 1H, J = 4.9, 9.5Hz), 4.40-4.65(m, 8H), 4.74(ABq, 2H, J = 3.7Hz), 4.76(t, 2H, J = 8.6Hz), 4.89(ABq, 2H, J = 11.0Hz), 5.18(s, 1H), 7.23-7.33(m, 30H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.1, 65.7, 69.6, 69.9, 71.7, 72.0, 73.2, 73.3, 75.0, 75.9, 77.6, 79.8, 81.1, 82.0, 83.2, 87.8, 98.1, 106.7, 127.5-128.4, 137.4, 137.7, 138.0, 138.1, 138.3, 138.8 ; Mol. Wt. calculated for $C_{54}H_{58}O_{10}Na$: 890.022, Found: 889.839.

Compound 6a:

$[\alpha]_D$($CHCl_3$, *c* 1.8) = +54.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.44(s, 3H), 3.56-3.74(m, 3H), 3.92-4.03(m, 2H), 4.15-4.35(m, 3H), 4.40-4.60(m, 2H), 4.53(ABq, 2H, J = 11.8Hz), 4.59(ABq, 2H, J = 11.9Hz), 5.12(d, 1H, J = 1.3Hz), 5.23-5.31(m, 1H), 5.24(s, 1H), 5.68(t, 1H, J = 9.8Hz), 6.12(t, 1H, J = 9.5Hz), 7.20-7.55(m, 24H), 7.86-8.01(m, 6H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.6, 65.3, 68.3, 68.8, 69.8, 70.7, 72.1, 72.4, 73.0, 73.2, 77.9, 78.1, 81.7, 97.1, 104.6, 127.3-129.9, 133.0, 133.2, 133.3, 137.9, 138.1, 138.3, 165.0, 165.8, 165.8 ; Mol. Wt. calculated for $C_{54}H_{52}O_{13}Na$: 931.973, Found: 931.904.

Compound 6b:

$[\alpha]_D$($CHCl_3$, *c* 1.3) = +27.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.64(m, 2H), 2.18(m, 2H), 3.41(dd, 1H, J = 6.6, 16.1Hz), 3.66-3.80(m, 3H), 3.90(dd, 1H, J = 2.6, 4.6Hz), 4.10(t, 1H, J = 4.9Hz), 4.35(m, 1H), 4.55(ABq, 2H, J = 12.0Hz), 4.61(ABq, 2H, J = 12.0Hz), 4.62(d, 2H, J = 2.5Hz), 4.91-5.06(m, 2H), 5.10(d, 1H, J = 2.5Hz), 5.80(m, 1H), 7.22-7.40(m, 15H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 28.7, 30.2, 67.6, 70.0, 72.4, 73.2, 73.4, 77.9, 78.1, 82.5, 105.2, 114.8, 127.5-128.3, 137.8, 138.1, 138.1, 138.2; Mol. Wt. calculated for $C_{31}H_{36}O_5Na$: 511.604, Found: 511.550.

Compound 6c:

$[\alpha]_D$($CHCl_3$, *c* 1.3) = +1.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.76(d, 3H, J = 6.9Hz), 0.86, 0.87, 0.89, 0.90(4s, 6H), 0.80-1.00(m, 2H), 1.10-1.35(m, 3H), 1.51-1.70(m, 2H), 2.00-2.20(m, 2H), 3.31(dt, 1H, J = 4.27, 10.5Hz), 3.76(dd, 1H, J = 6.8, 10.0Hz), 3.79(dd, 1H, J = 5.2, 10.1Hz), 3.89(dd, 1H, J = 2.7, 4.5Hz), 4.19(t, 1H, J = 5.0Hz), 4.38(dd, 1H J = 5.3, 12.0Hz), 4.56(ABq, 2H, 11.9Hz), 4.60(ABq, 2H, J = 11.9Hz), 4.60(s, 2H), 5.18(d, 1H, J = 2.5Hz), 7.22-7.40(m, 15H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 16.2, 21.1, 21.2, 23.1, 25.5, 31.5, 34.3, 43.1, 48.5, 69.6, 72.5,

73.2, 73.3, 77.6, 77.9, 79.8, 82.6, 106.5, 127.5-128.3, 137.8, 138.1, 138.3; Mol. Wt. calculated for $C_{36}H_{46}O_5Na$: 581.737, Found: 581.426.

Compound 6d:

$[\alpha]_D$($CHCl_3$, *c* 1.2) = +28.1; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.34(s, 3H), 3.41-3.75(m, 6H), 3.96(dd, 1H, J = 2.4, 4.5Hz), 4.07(dd, 1H, J = 3.2, 10.8Hz), 4.21(dd, 1H, J = 4.5, 5.8Hz), 4.33(dd, 1H, J = 5.8, 11.5Hz), 4.46-4.86(m, 12H), 4.9(ABq, 2H, J = 10.9Hz), 5.21(d, 1H, J = 1.9Hz), 7.24-7.38(m, 30H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.1, 66.3, 69.7, 69.9, 72.3, 73.2, 73.2, 73.3, 75.1, 75.8, 77.2, 77.8, 77.9, 78.2, 79.8, 82.0, 98.0, 105.4, 127.4-128.4, 137.9, 137.9, 138.1, 138.1, 138.2, 138.7 ; Mol. Wt. calculated for $C_{54}H_{58}O_{10}Na$: 890.022, Found: 889.905.

Compound 6e:

$[\alpha]_D$($CHCl_3$, *c* 1.3) = +48.1; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.70-3.85(m, 4H), 3.93(dd, 1H, J = 2.1, 11.6Hz), 4.05(dd, 1H, J = 5.1, 9.9Hz), 4.18-4.37(m, 4H), 4.46(dd, 2H, J = 2.4, 11.8Hz), 4.54-4.63(m, 4H), 4.79(s, 2H), 5.12(s, 2H), 5.14(d, 1H, J = 2.4Hz), 5.34(d, 1H, J = 8.1Hz), 6.00(d, 1H, J = 1.4Hz), 7.16-7.38(m, 30H), 7.50-7.55(m, 2H), 7.64(d, 1H, J = 8.3Hz); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 44.0, 65.7, 69.3, 71.2, 72.2, 72.5, 73.3, 73.4, 74.4, 78.2, 78.6, 81.0, 82.2, 89.1, 101.1, 105.1, 127.56-128.67, 129.2, 136.7, 137.1, 137.1, 137.1, 137.2, 137.6, 137.9, 150.6, 162.4 ; Mol. Wt. calculated for $C_{56}H_{56}N_2O_{10}Na$: 940.041, Found: 939.896.

Compound 7:

$[\alpha]_D$($CHCl_3$, *c* 1.7) = +13.7; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.28(s, 3H), 3.49(dd, 1H, J = 5.6, 10.6Hz), 3.60(dd, 1H, J = 3.7, 10.5Hz), 3.83(d, 1H, J = 4.5Hz), 4.02(d, 1H, J = 4.8Hz), 4.35(dd, 1H, J = 3.9, 5.9Hz), 4.46(ABq, 2H, J = 11.9Hz), 4.53(d, 2H, J = 1.7Hz), 4.60(dd, 2H, J = 12.0, 16.8Hz), 4.92(s, 1H), 7.15-7.38(m, 15H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 54.7, 71.0, 72.0, 72.1, 72.8, 78.1, 79.4, 80.2, 106.1, 127.2-128.1, 137.6, 137.6, 138.1; Mol. Wt. calculated for $C_{27}H_{30}O_5Na$: 457.514, Found: 457.426.

Compound 8:

$[\alpha]_D$($CHCl_3$, *c* 1.6) = -17.7; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.39(s, 3H), 3.71(dd, 1H, J = 6.9, 10.2Hz), 3.79(dd, 1H, J = 5.0, 10.2Hz), 3.97(dd, 1H, J = 1.4, 2.5Hz), 4.05(dd, 1H, J = 2.5, 5.8Hz), 4.42(m, 1H), 4.49(d, 2H, J = 2.5Hz), 4.52(ABq, 2H J = 10.7Hz), 4.55(dd, 2H, J = 6.6, 12.3Hz), 4.92(d, 1H, J = 1.4Hz), 7.21-7.38(m, 15H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.6, 69.6, 71.8, 72.1, 73.3, 80.0, 81.4, 86.7, 108.0, 127.5-128.4, 137.4, 137.7, 138.2; Mol. Wt. calculated for $C_{27}H_{30}O_5Na$: 457.514, Found: 457.495.

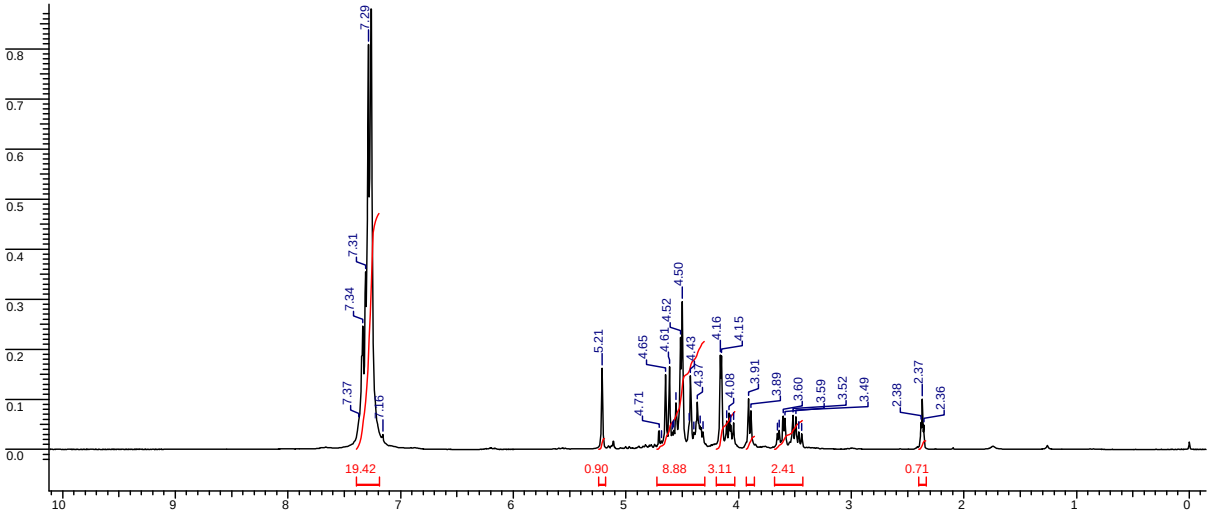
Compound 9:

$[\alpha]_D$($CHCl_3$, *c* 1.3) = +53.3; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.39(s, 3H), 3.60(d, 1H, J = 0.6Hz), 3.61(s, 1H), 3.90(dd, 1H, J = 2.6, 6.2Hz), 3.99(d, 1H, J = 1.9Hz), 4.22(dd, 1H, J = 4.9, 10.6Hz), 4.50(ABq, 2H, J = 11.9Hz), 4.53(Abq, 2H, J = 12.7Hz), 4.53(d, 2H, J = 10.6Hz), 4.96(s, 1H), 7.16-7.41(m, 15H) ; ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 54.9, 69.8, 71.8, 72.0, 73.3, 80.8, 83.4, 88.0, 107.2, 127.5-128.3, 137.5, 17.8, 138.0; Mol. Wt. calculated for $C_{27}H_{30}O_5Na$: 457.514, Found: 457.426.

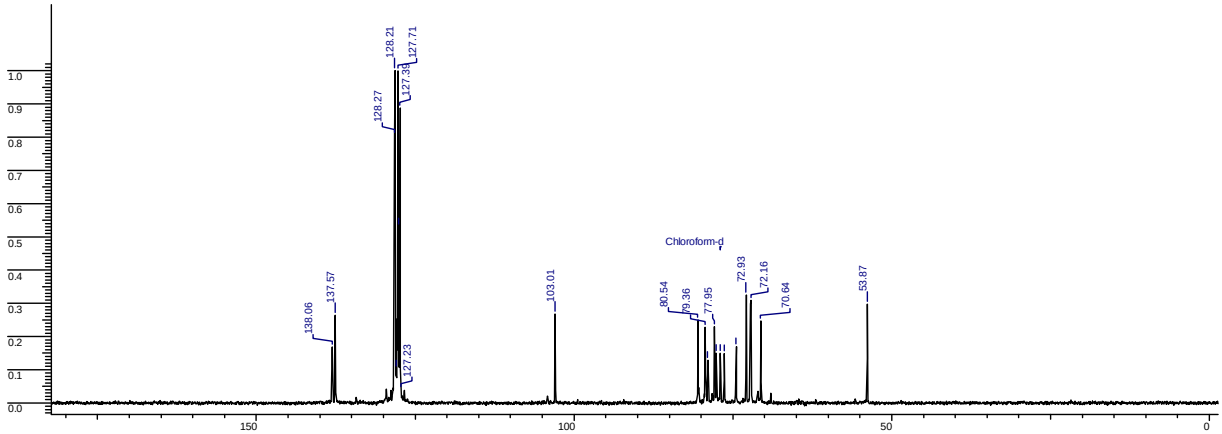
Compound 10:

$[\alpha]_D$($CHCl_3$, *c* 1.2) = +16.9; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.37(s, 3H), 3.75(d, 1H, J = 0.6Hz), 3.78(s, 1H), 3.89(dd, 1H, J = 2.4, 4.5Hz), 4.19(m, 1H), 4.36(dd, 1H, J = 5.5, 11.9Hz), 4.58(ABq, 2H, J = 12.1Hz), 4.59(ABq, 2H, J = 12.0Hz), 4.60(s, 2H), 5.02(d, 1H, J = 1.5Hz), 7.20-7.38(m, 15H); ^{13}C NMR (55.32 MHz, $CDCl_3$): δ 55.5, 69.6, 72.5, 73.2, 73.4, 77.8, 78.2, 82.4, 106.3, 127.5-128.3, 137.8, 138.0, 138.2; Mol. Wt. calculated for $C_{27}H_{30}O_5Na$: 457.51, Found: 457.495.

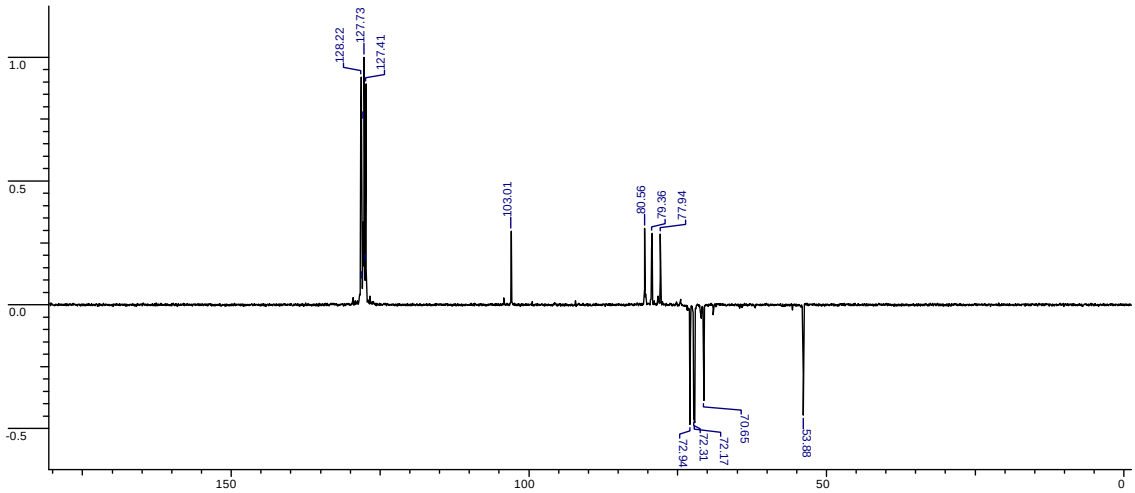
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1a**



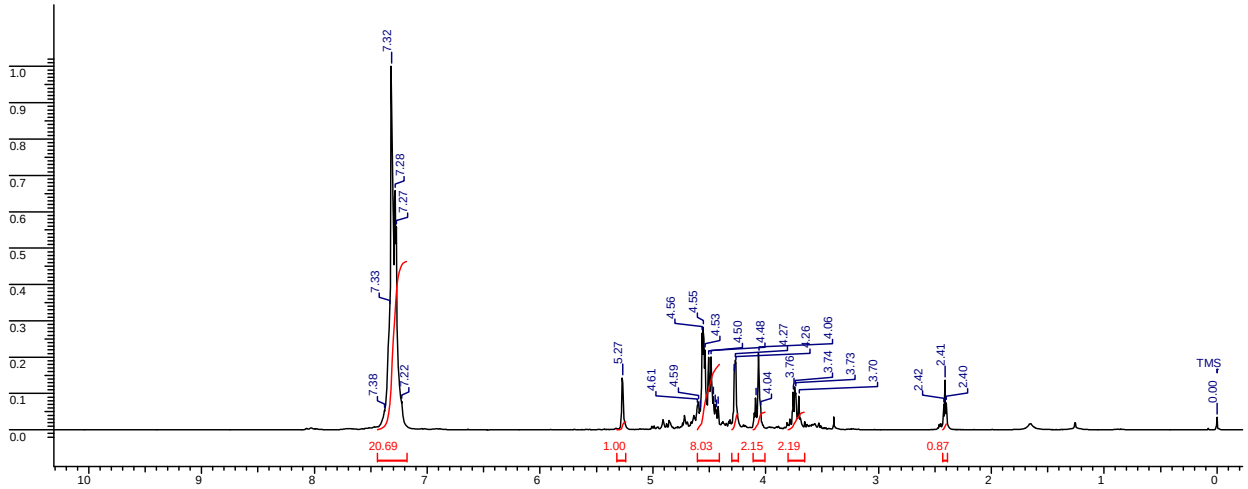
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1a**



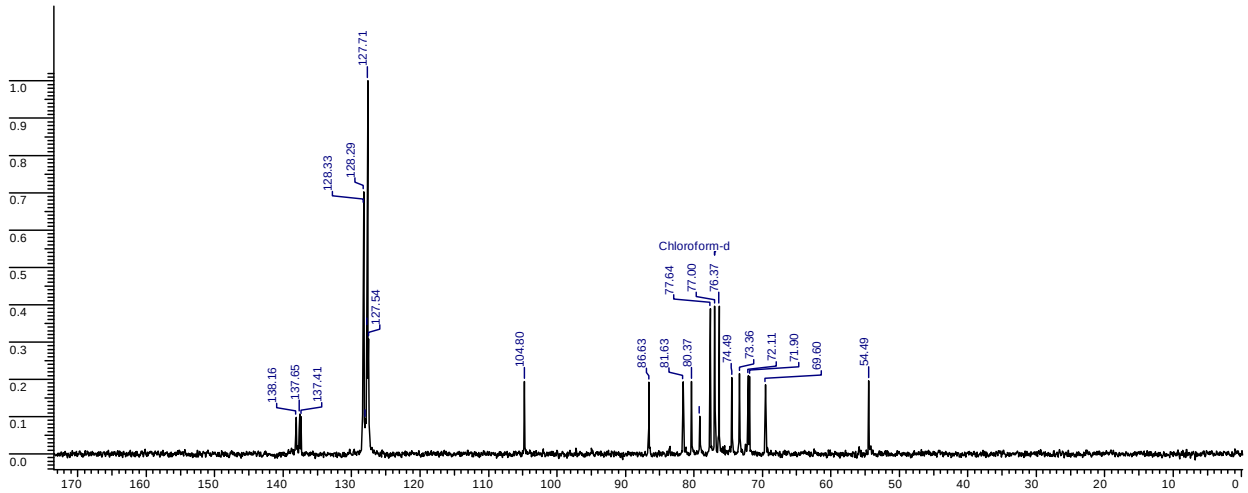
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound**1a**



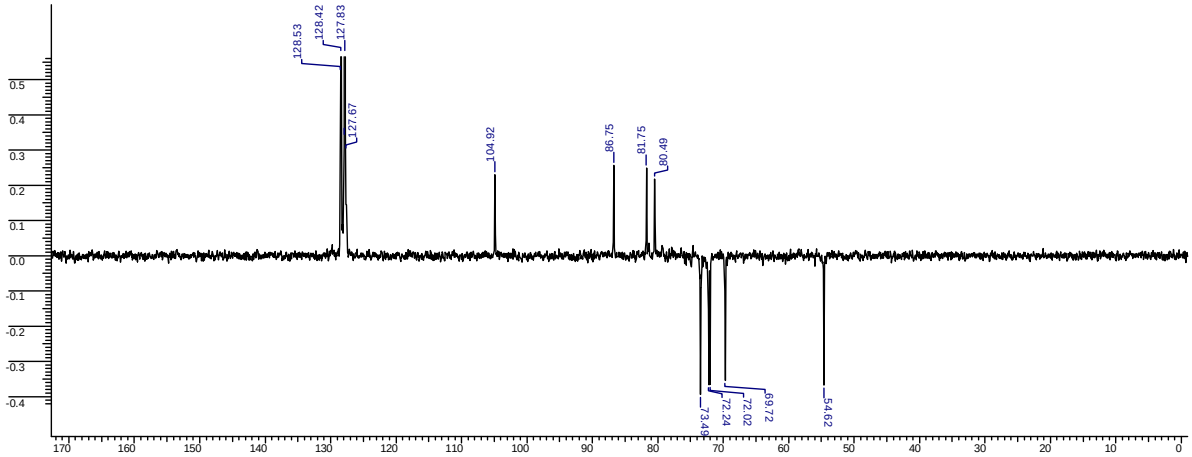
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1b**



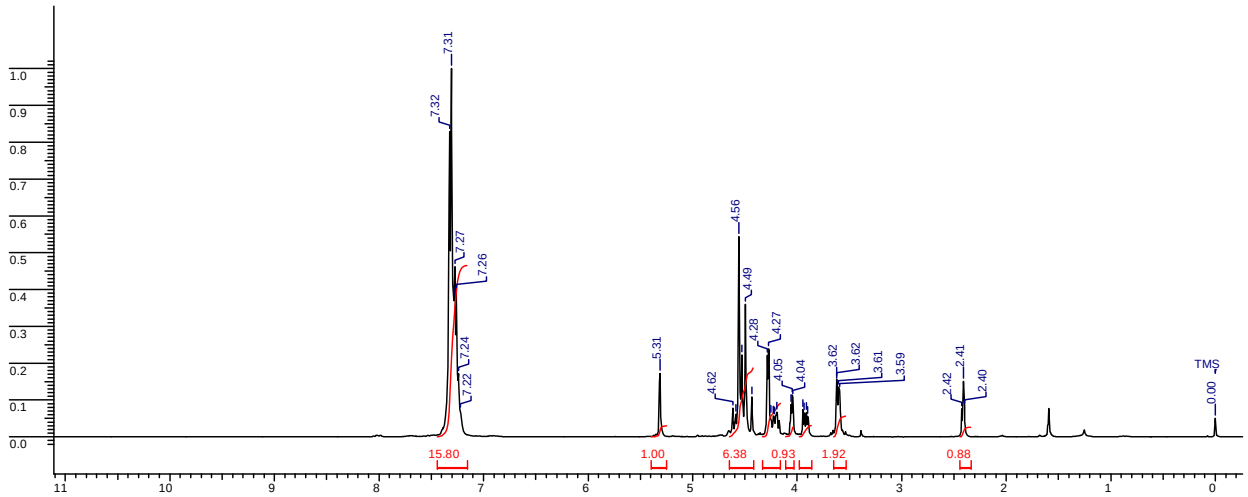
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1b**



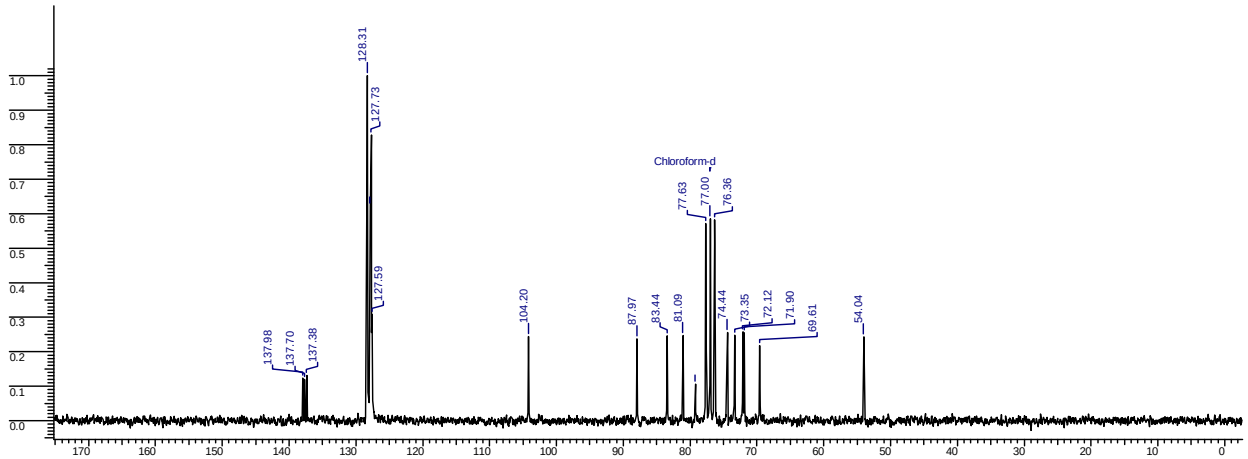
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1b**



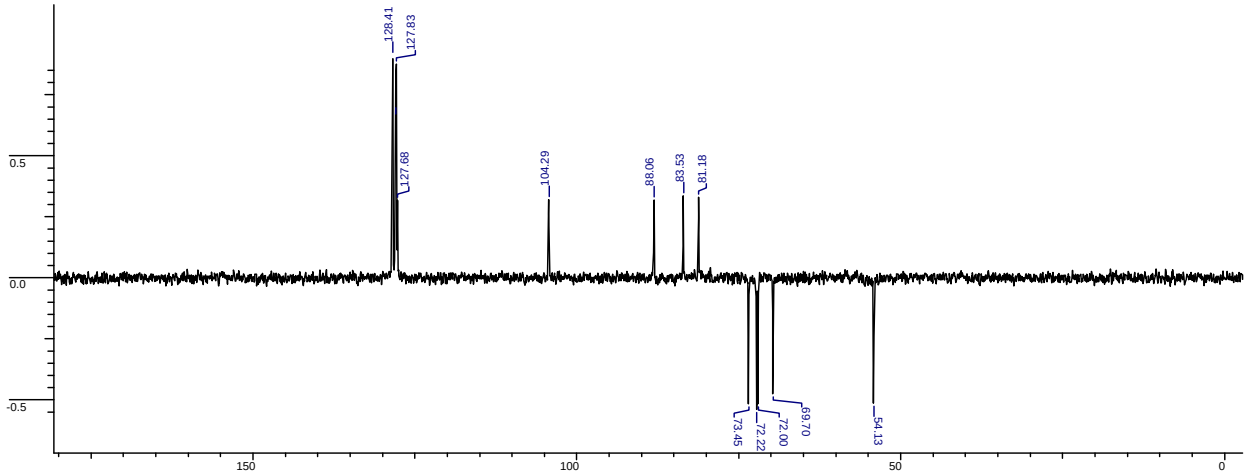
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1c**



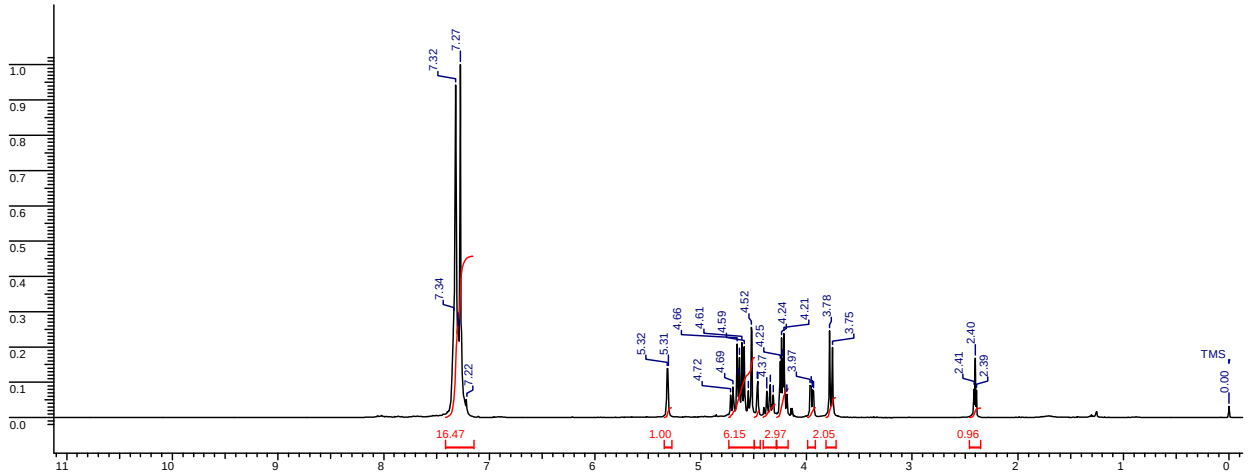
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1c**



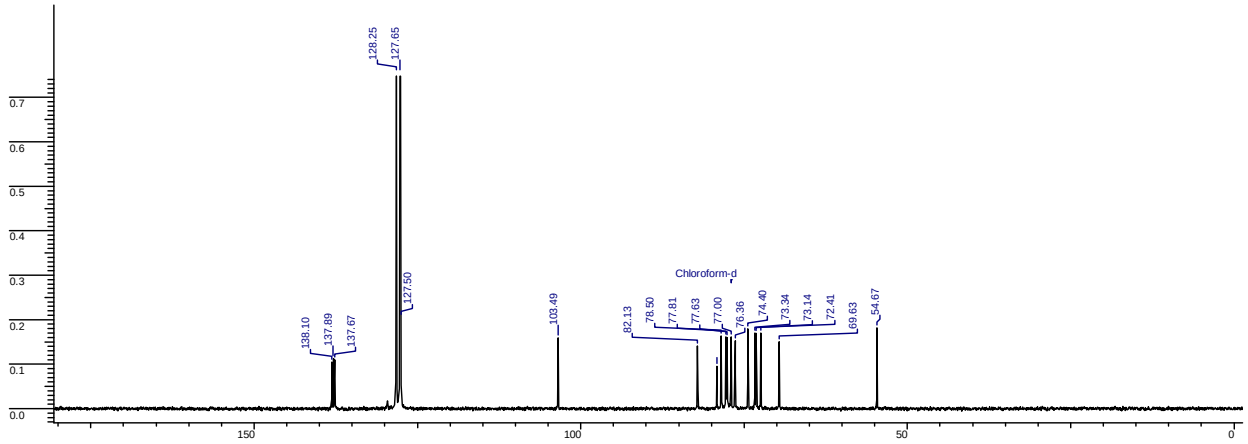
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1c**



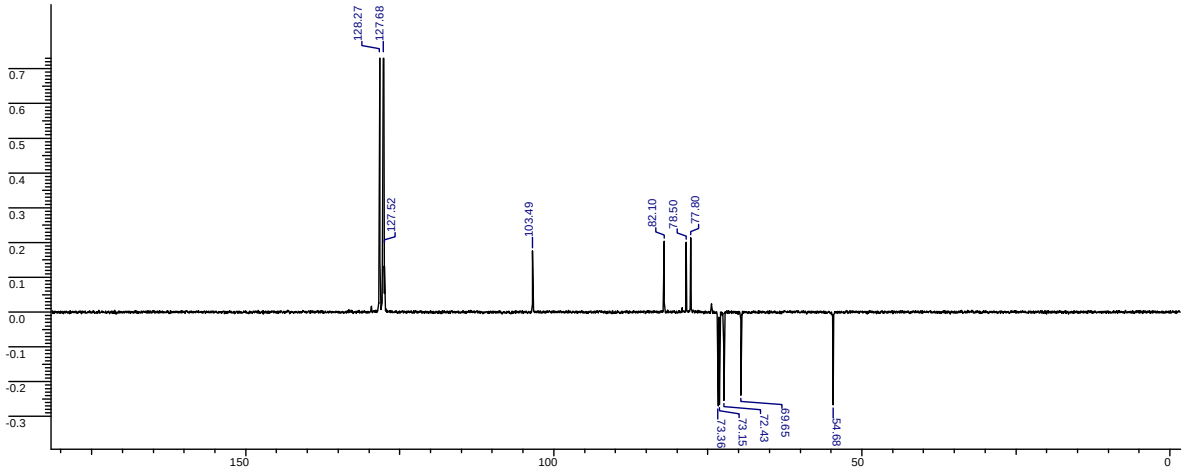
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **1d**



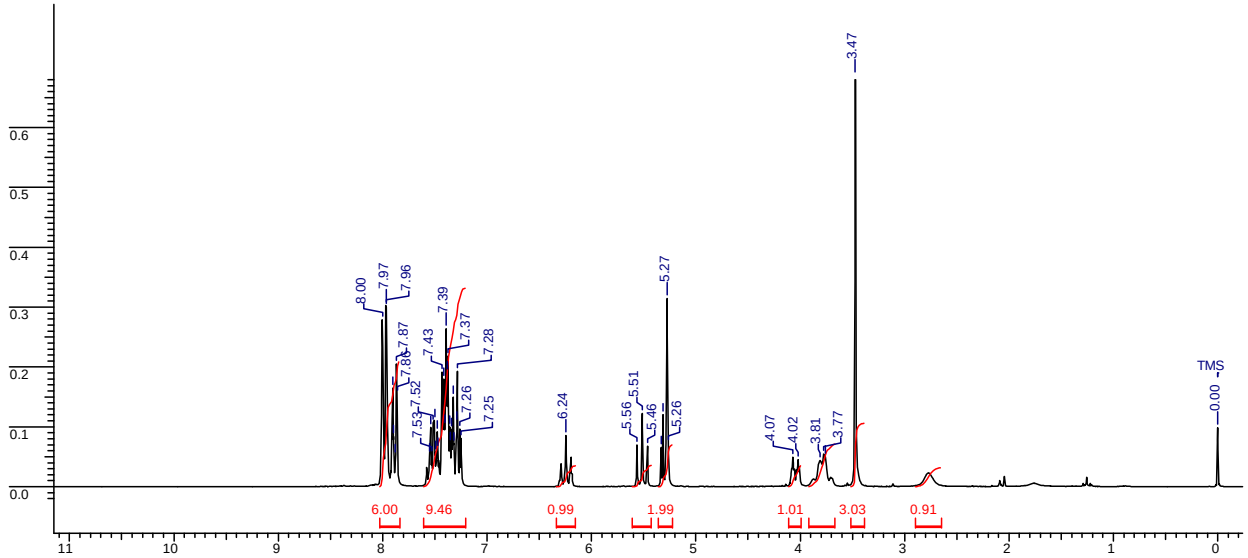
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1d**



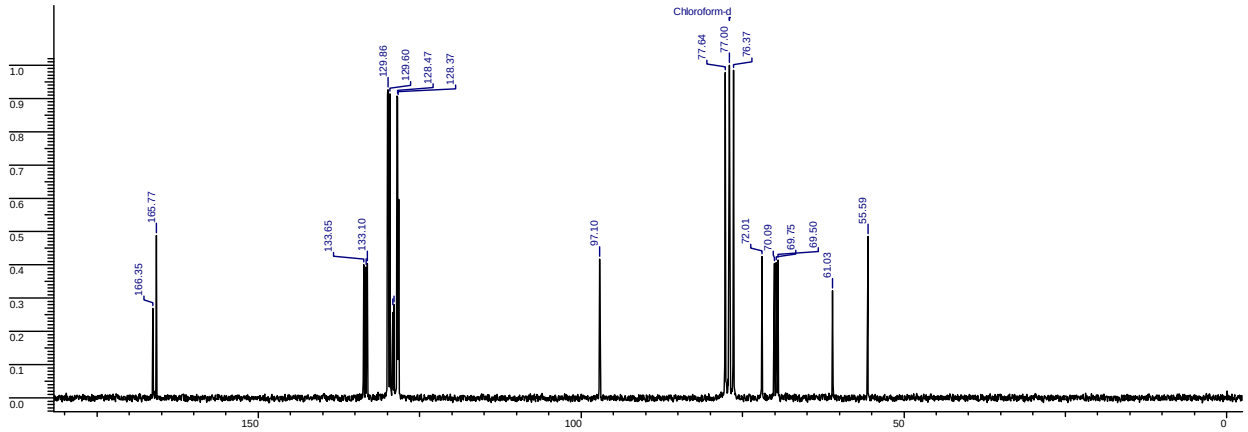
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **1d**



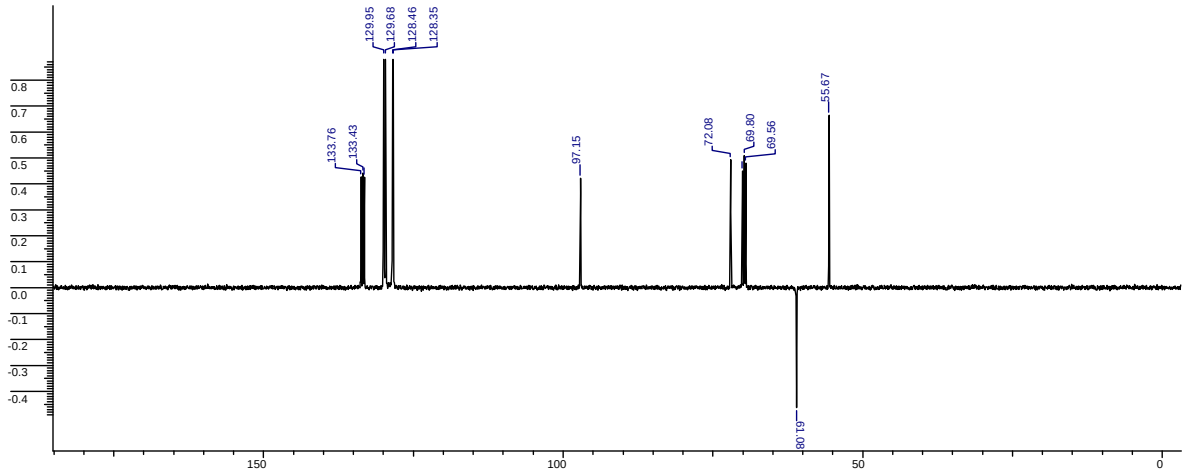
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **2a**



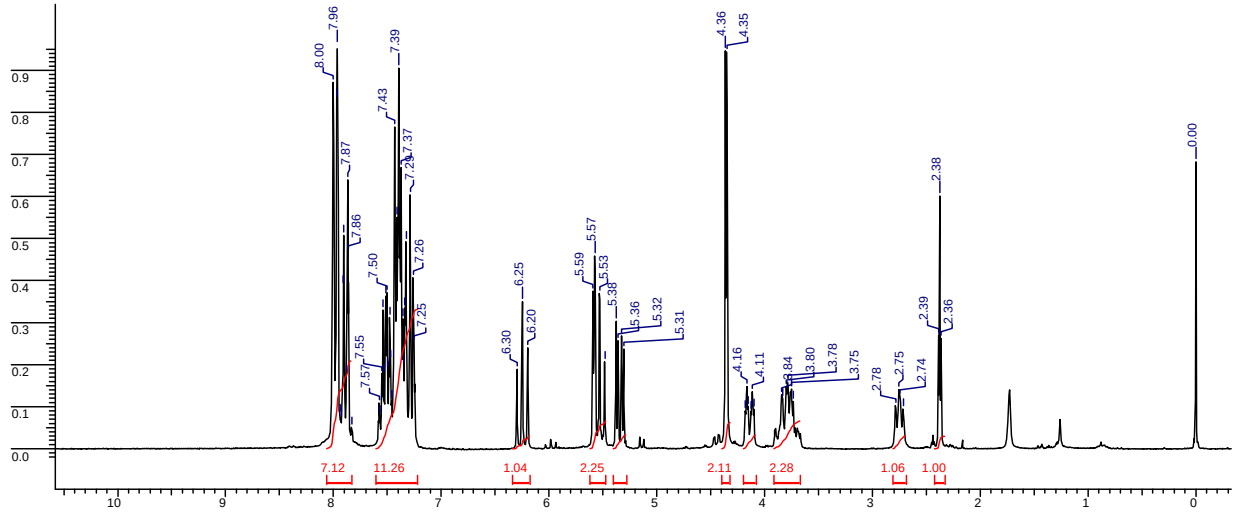
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **2a**



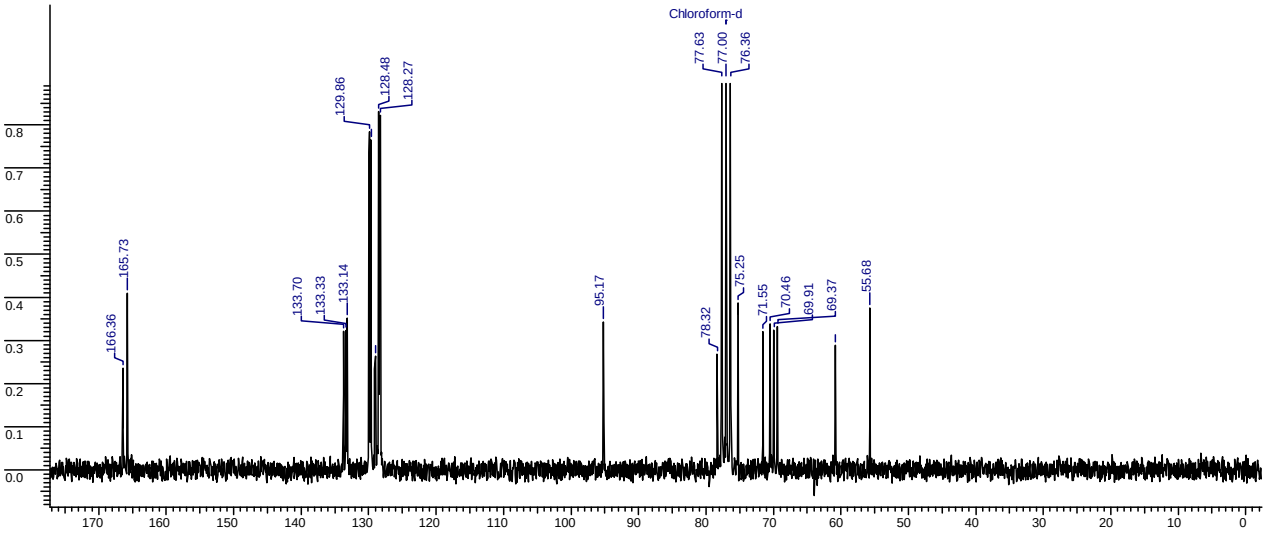
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **2a**



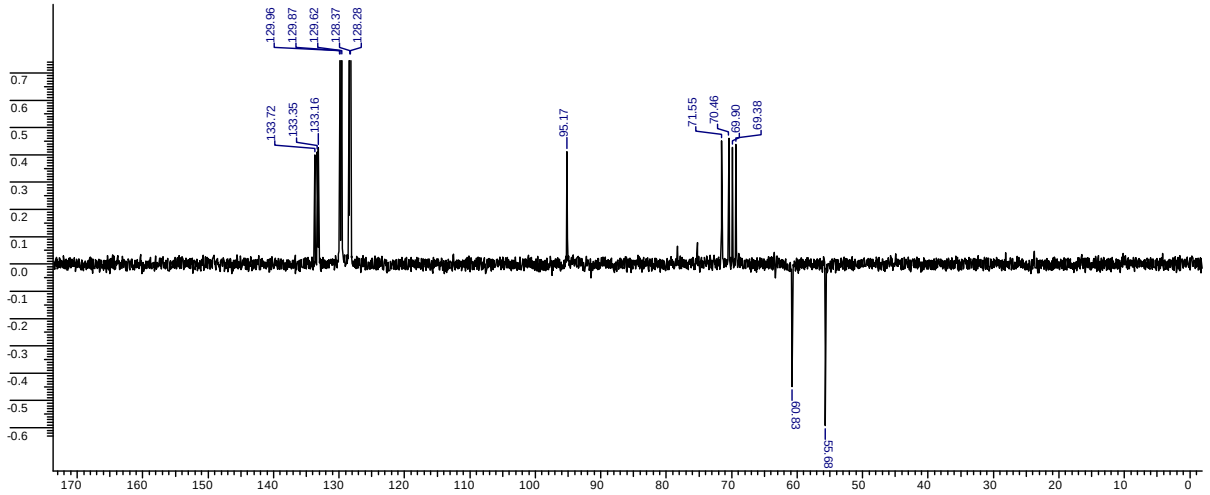
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **2f**



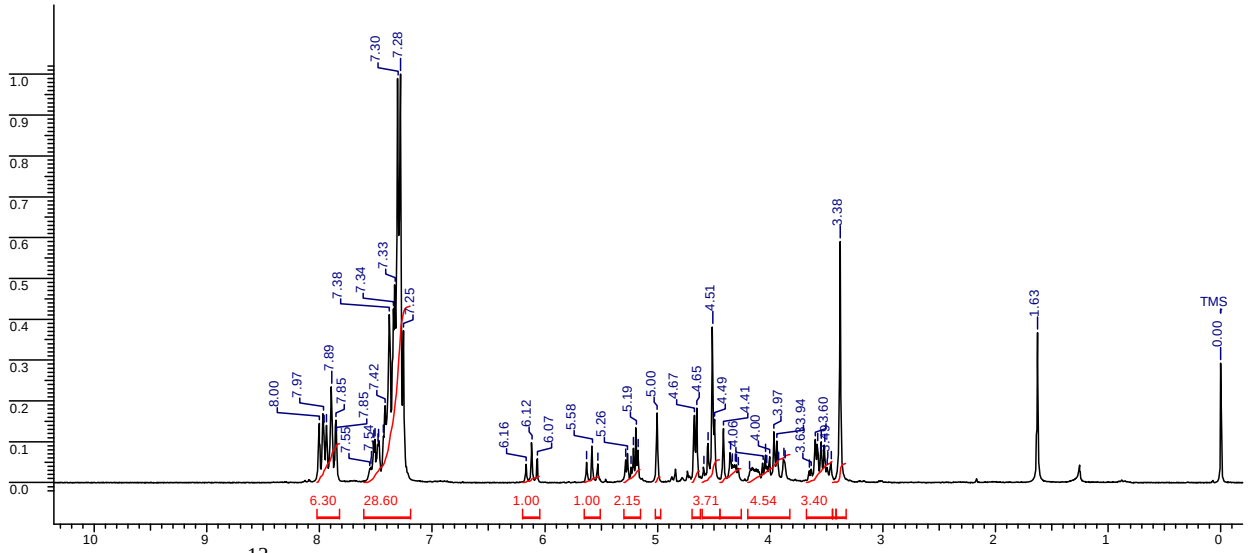
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **2f**



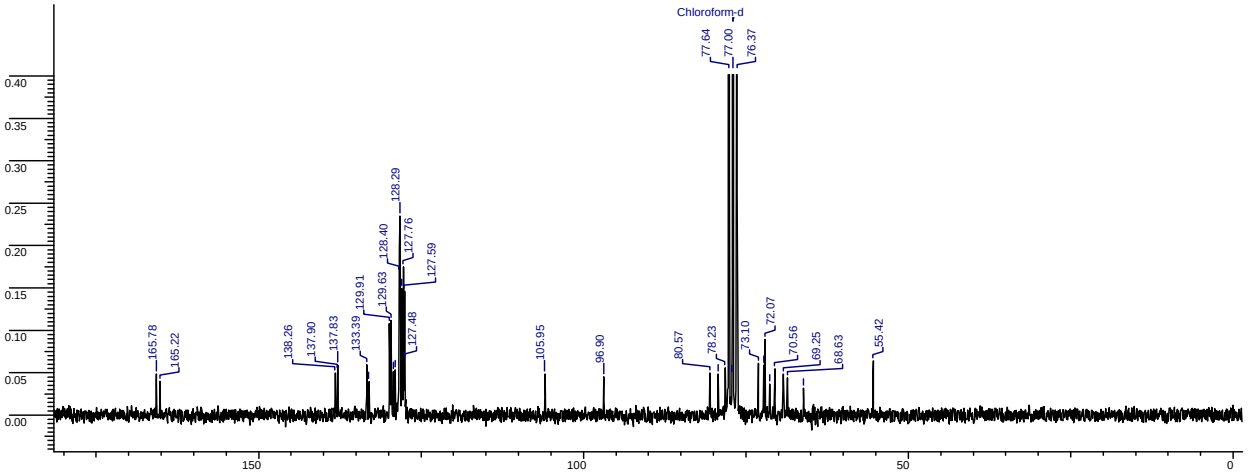
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **2f**



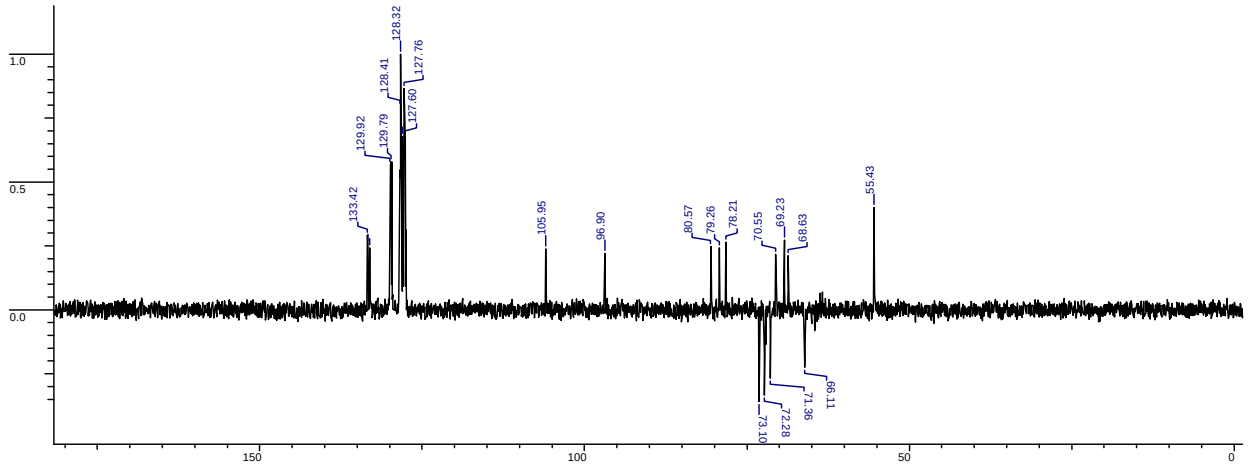
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **3a**



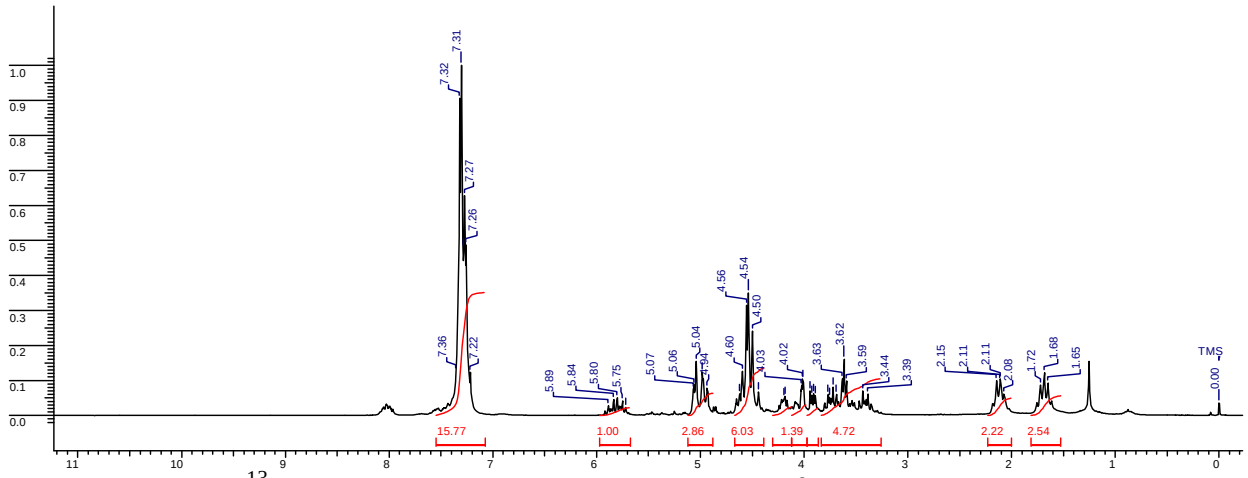
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3a**



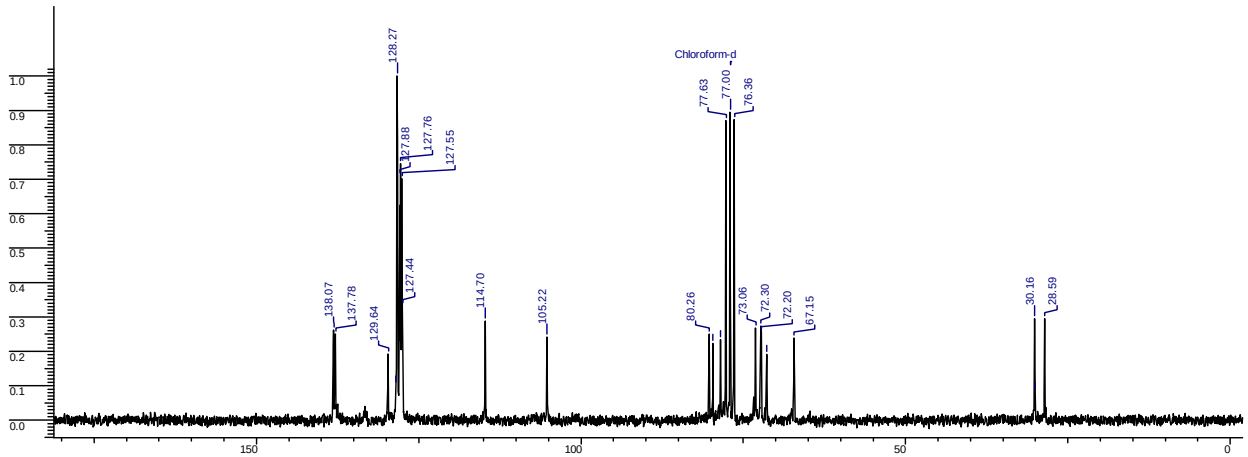
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3a**



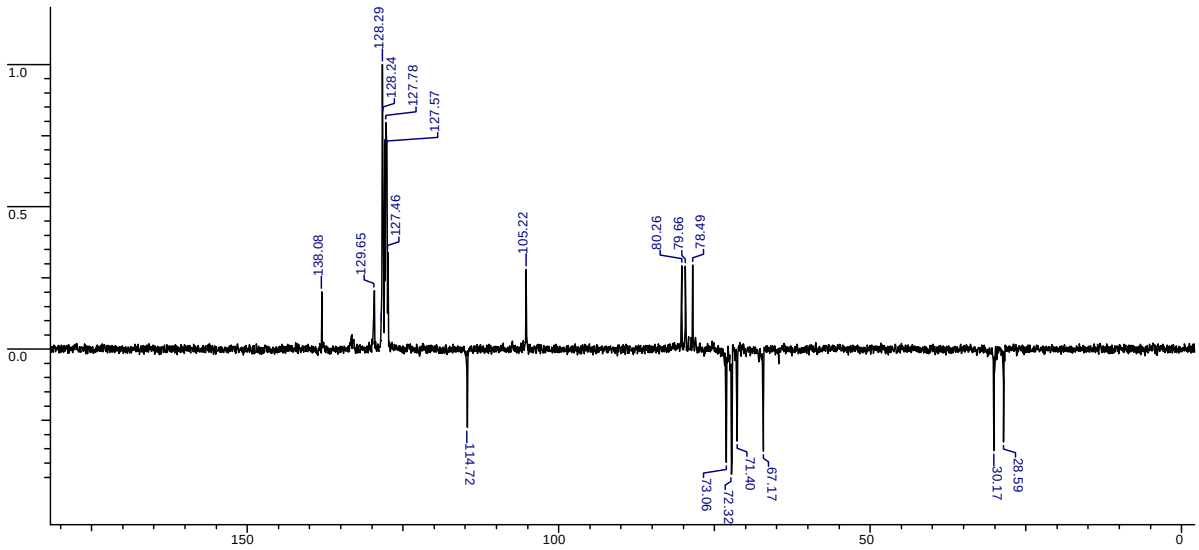
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **3b**



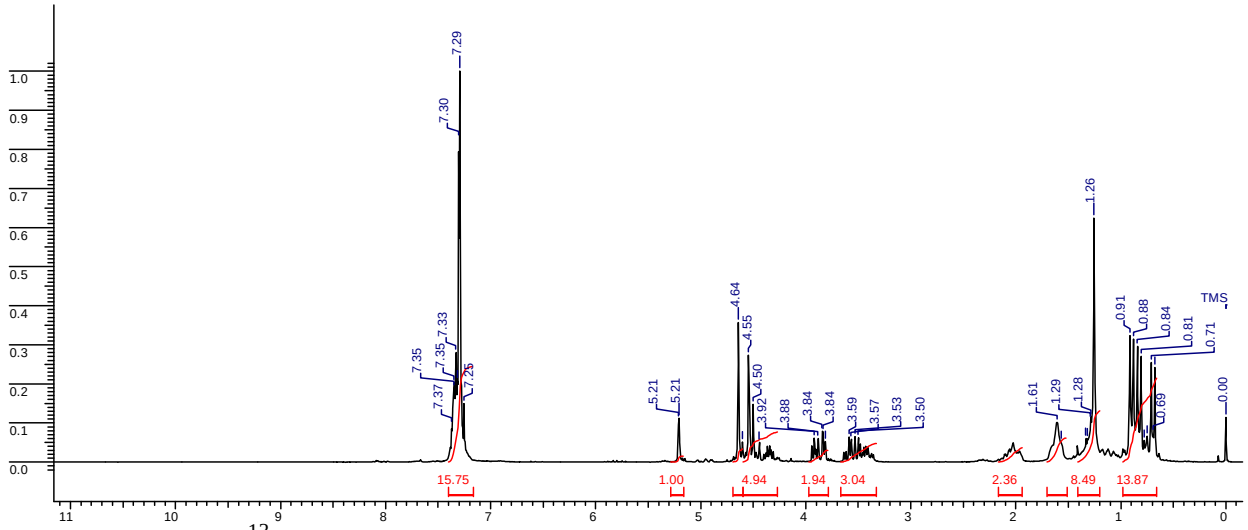
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3b**



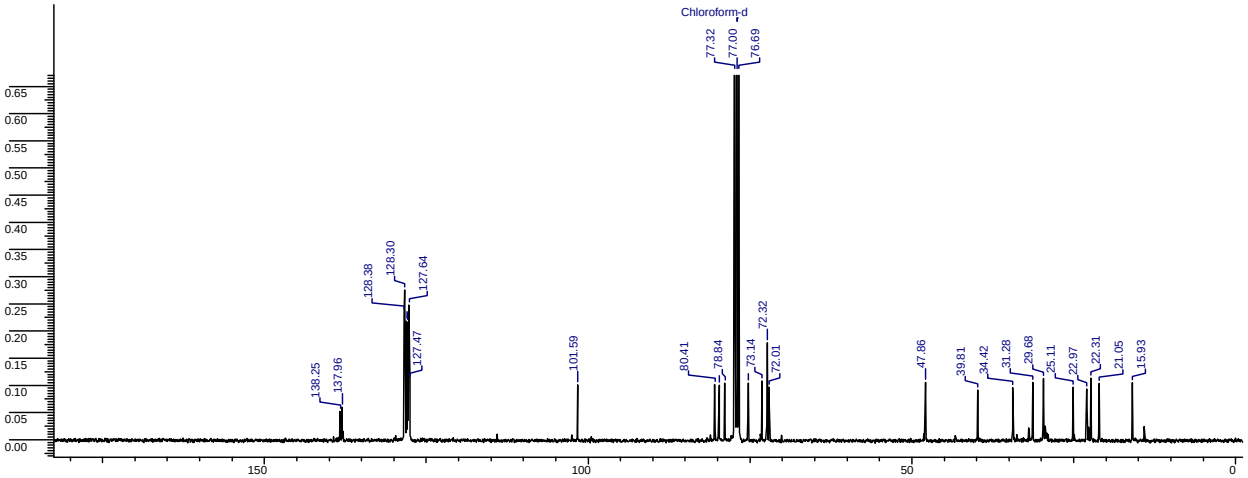
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3b**



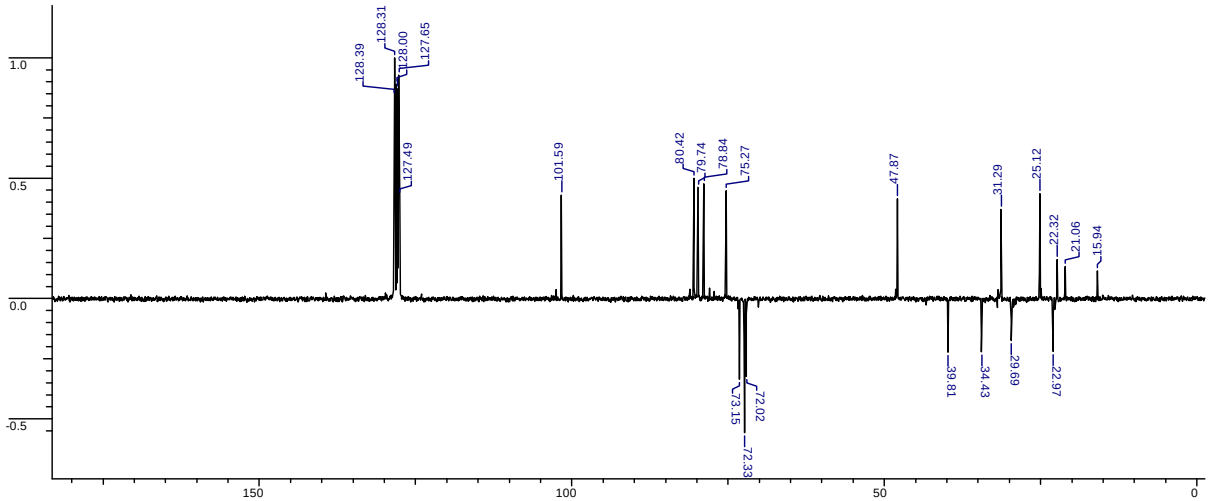
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **3c**



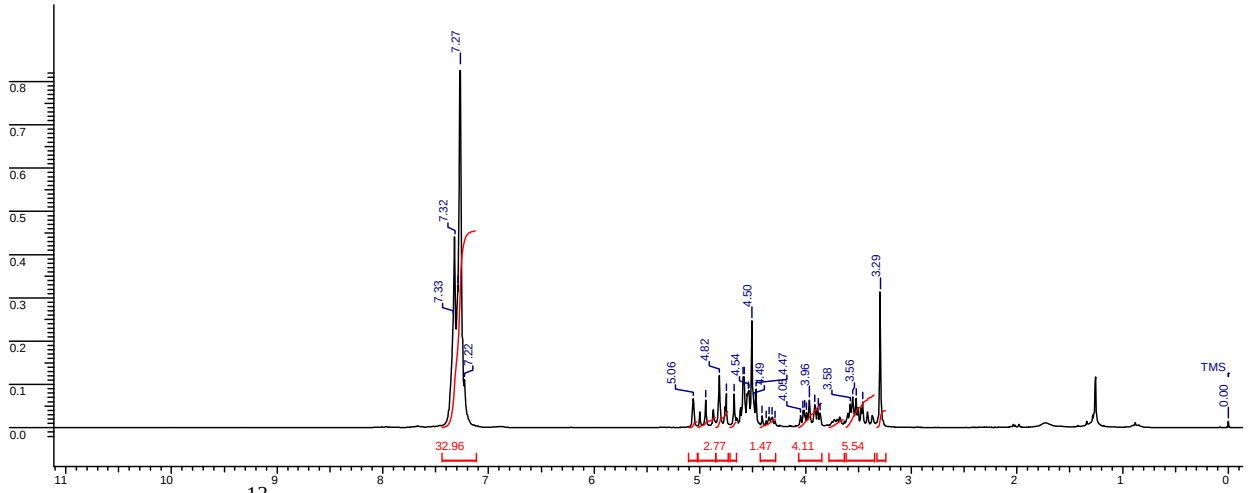
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3c**



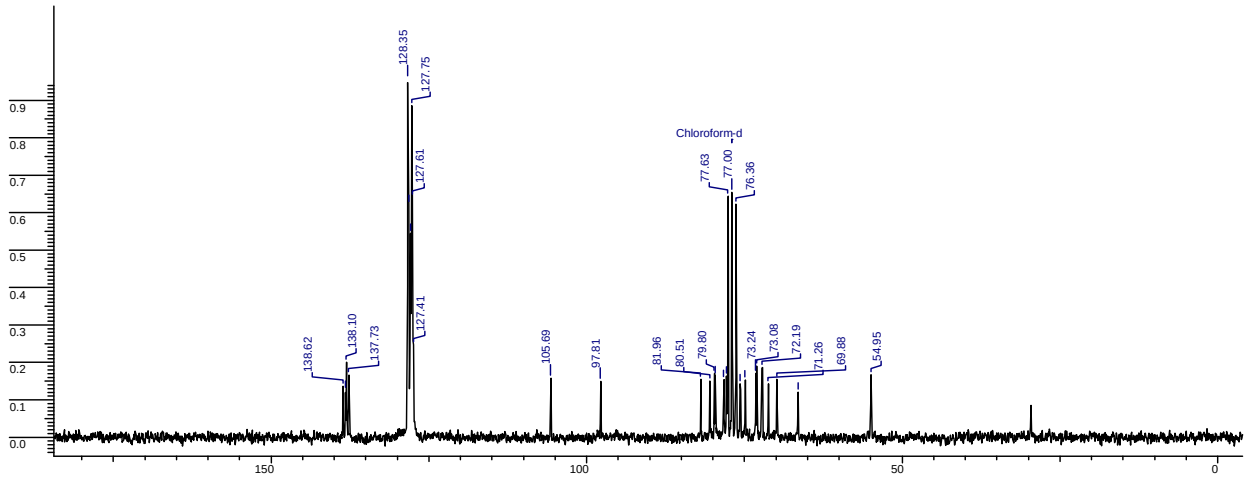
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3c**



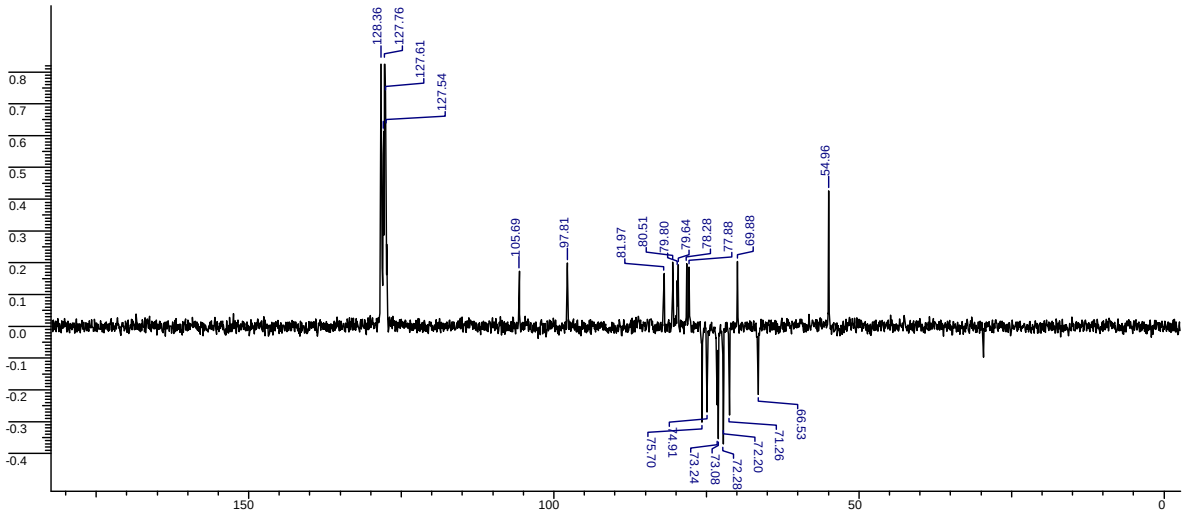
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **3d**



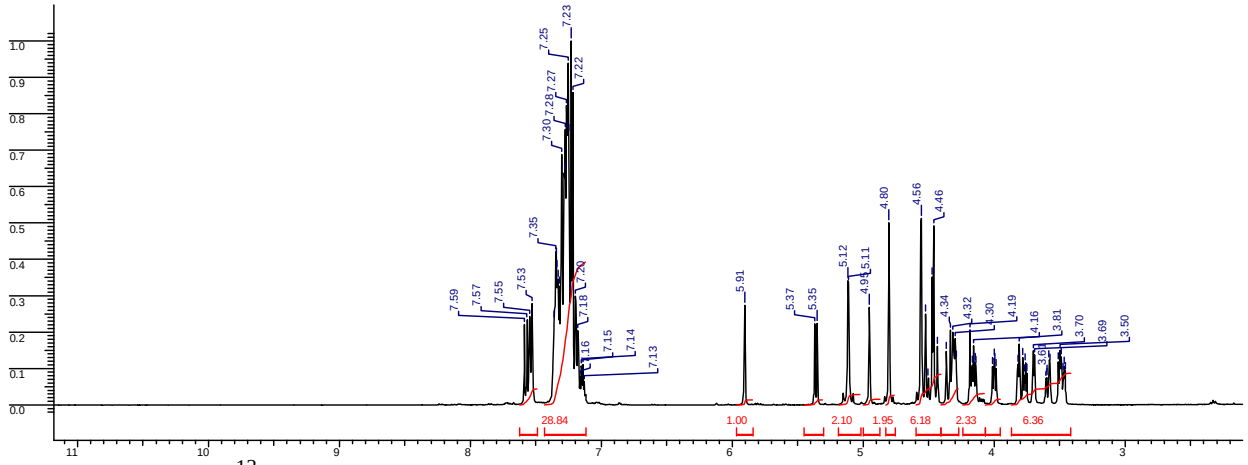
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3d**



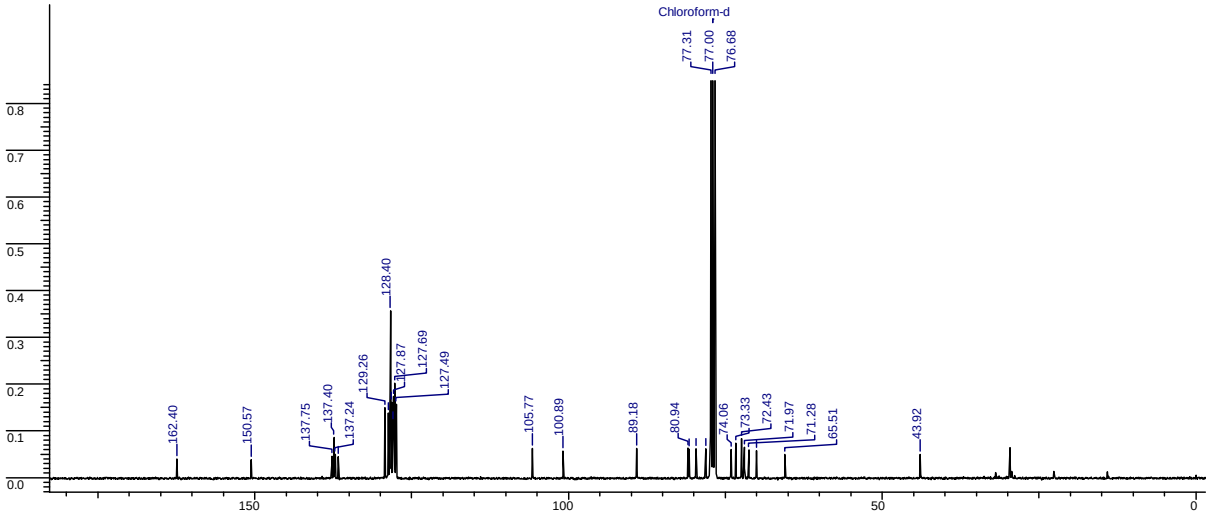
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3d**



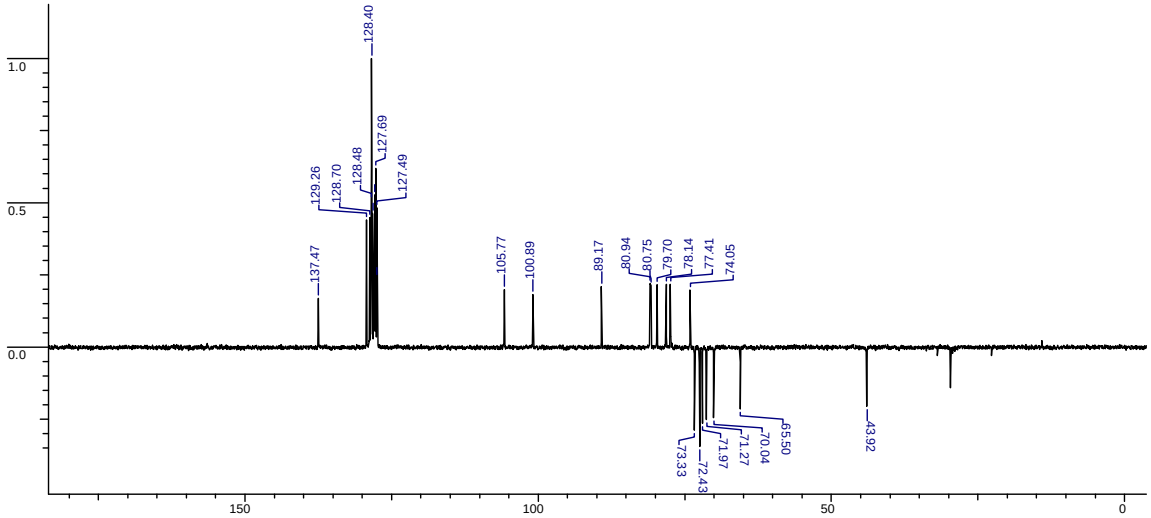
^{1}H NMR Spectrum (400.13 MHz, $CDCl_3$) of Compound **3e**



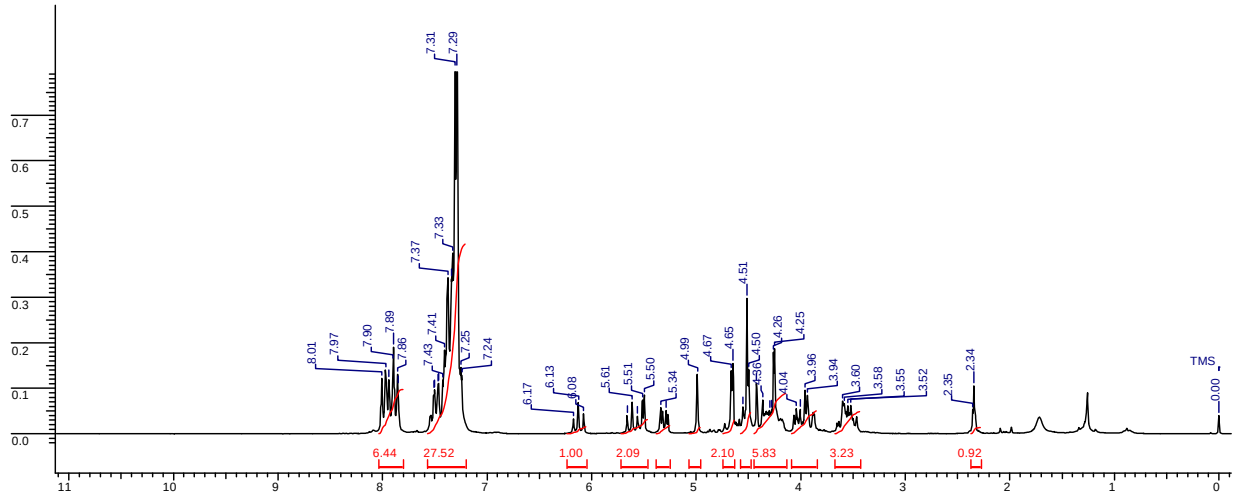
^{13}C NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **3e**



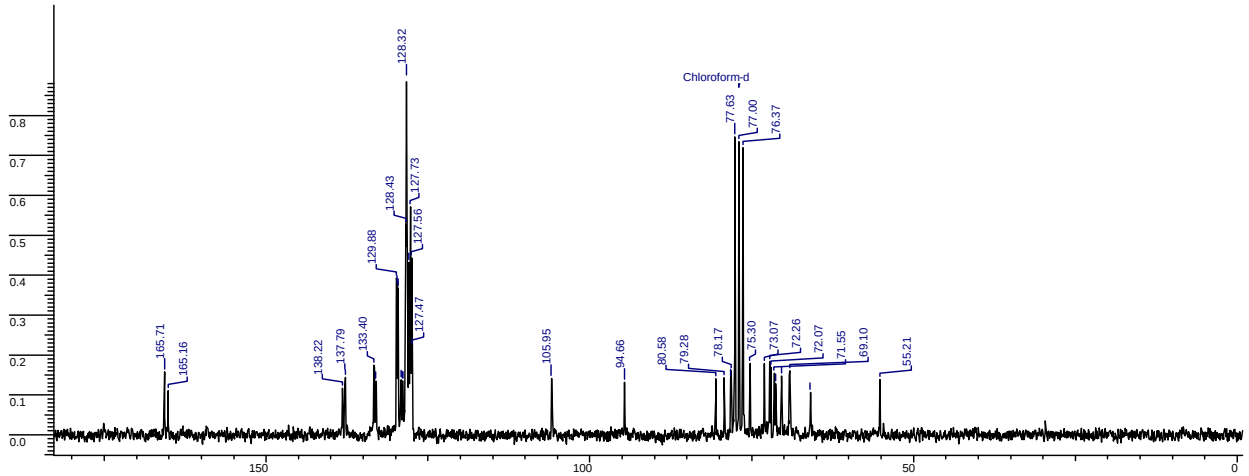
DEPT NMR Spectrum (100.61 MHz, $CDCl_3$) of Compound **3e**



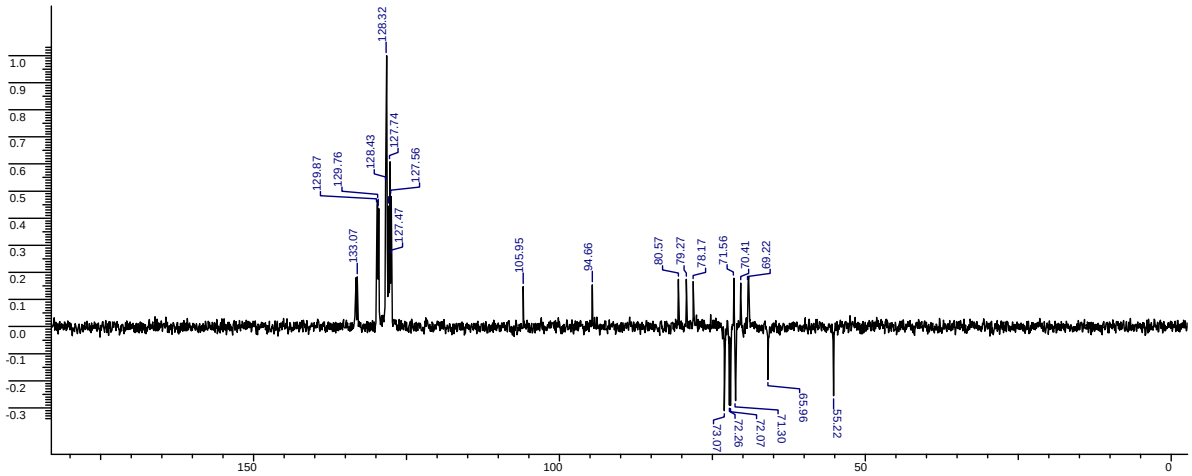
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **3f**



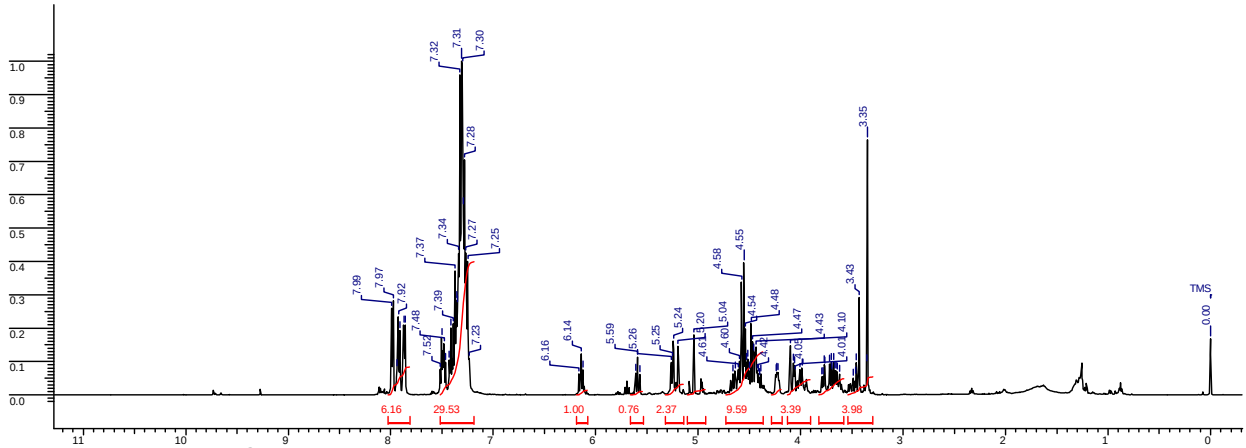
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3f**



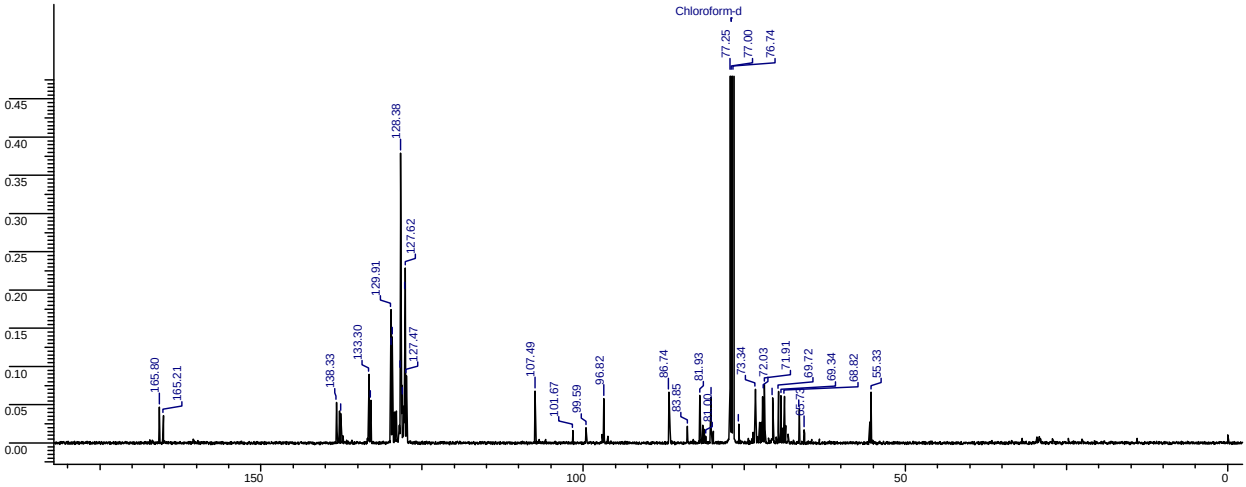
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **3f**



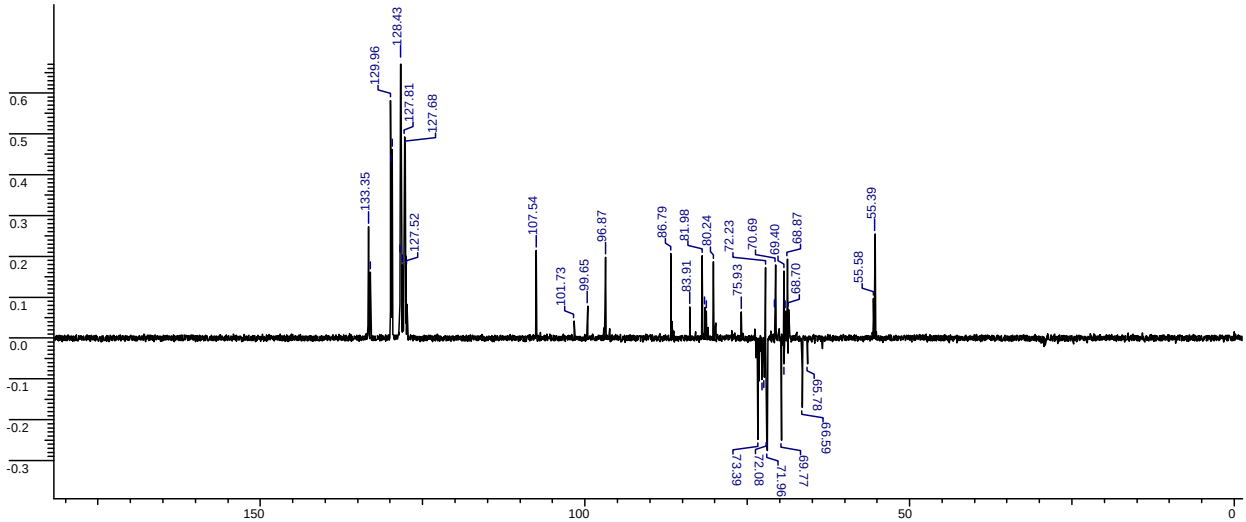
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **4a**



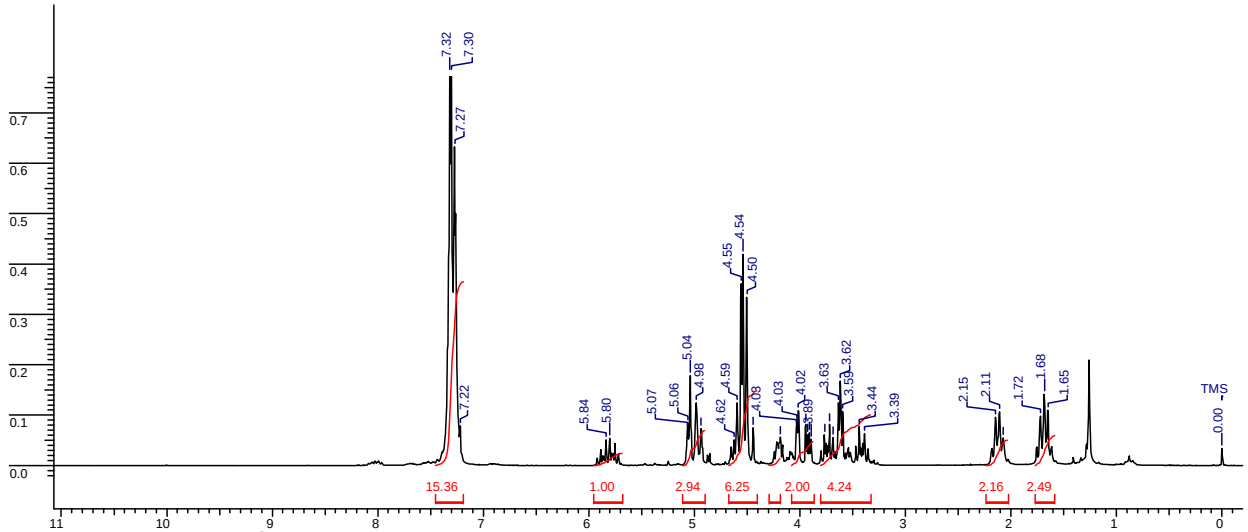
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **4a**



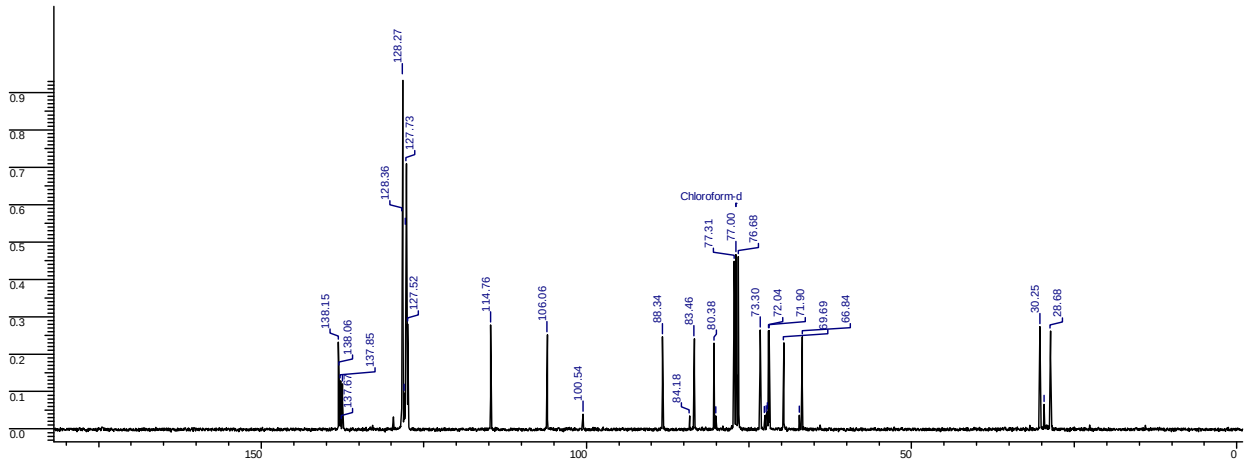
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **4a**



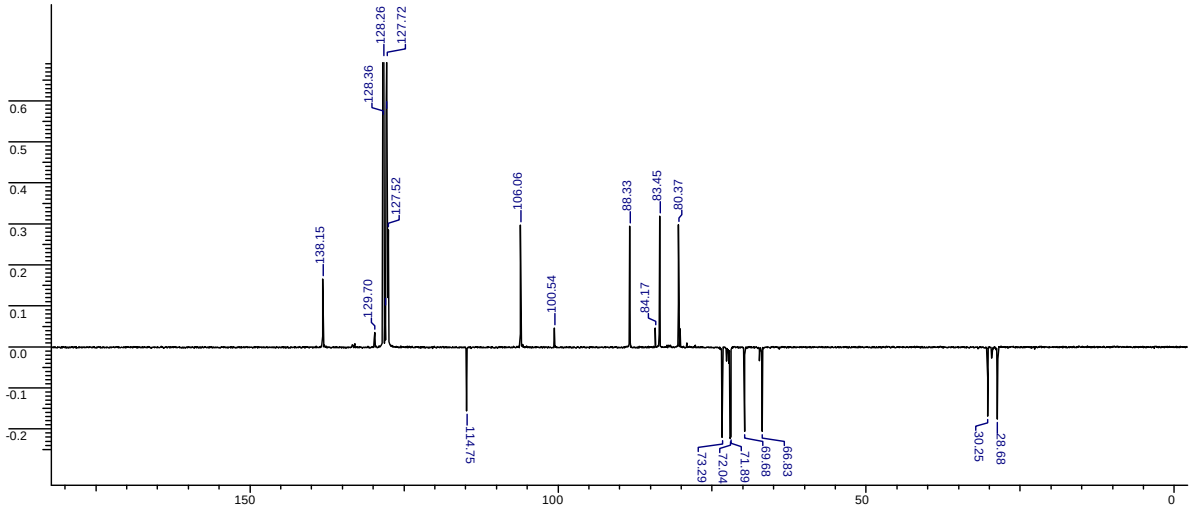
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **4b**



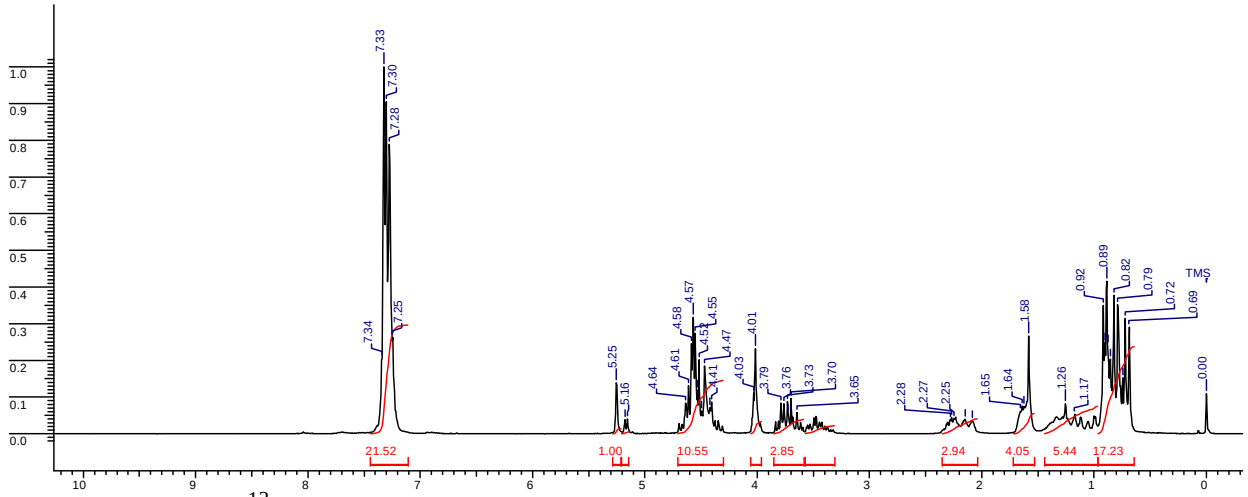
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **4b**



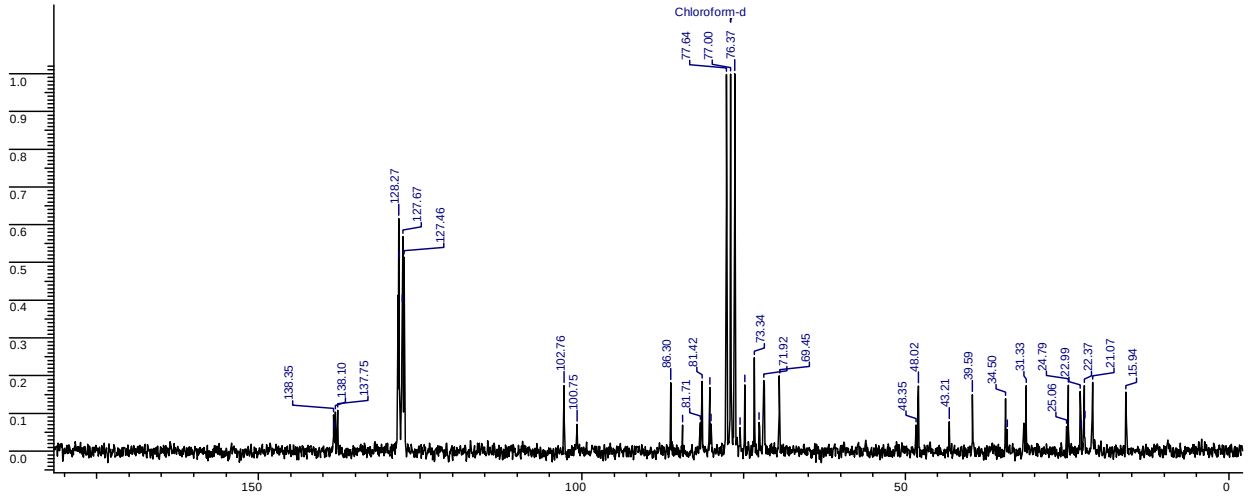
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **4b**



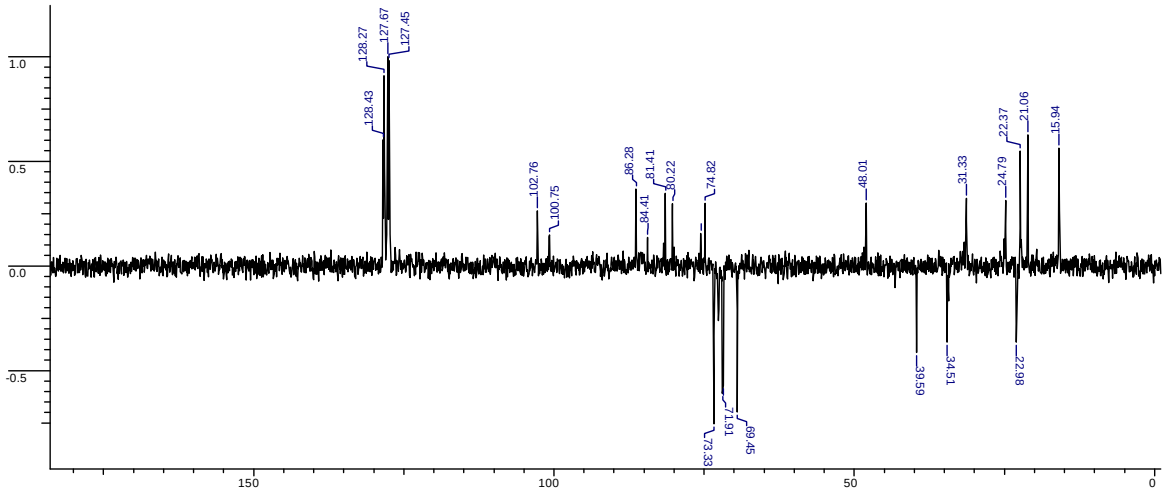
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **4c**



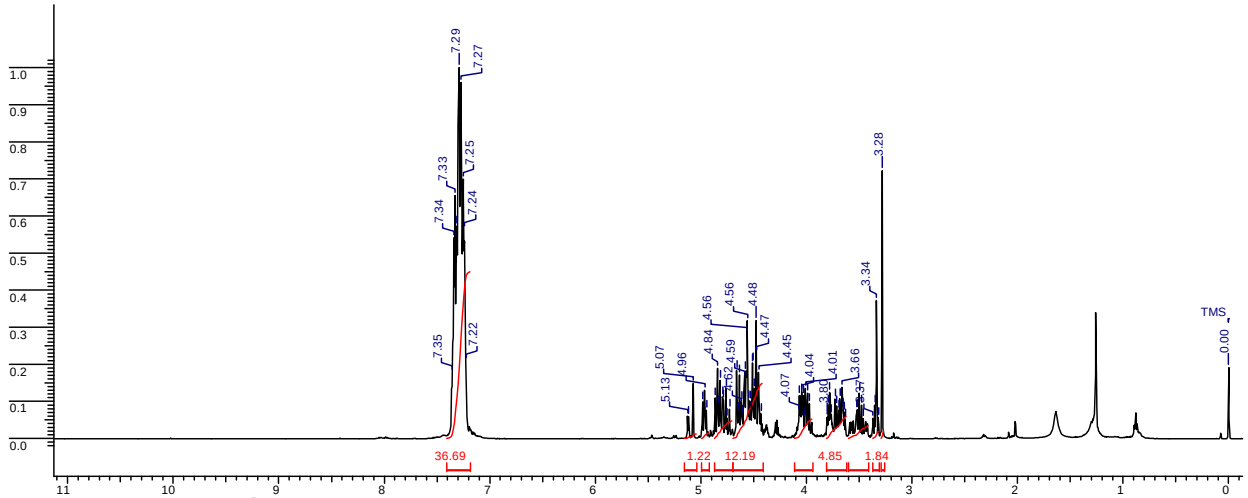
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **4c**



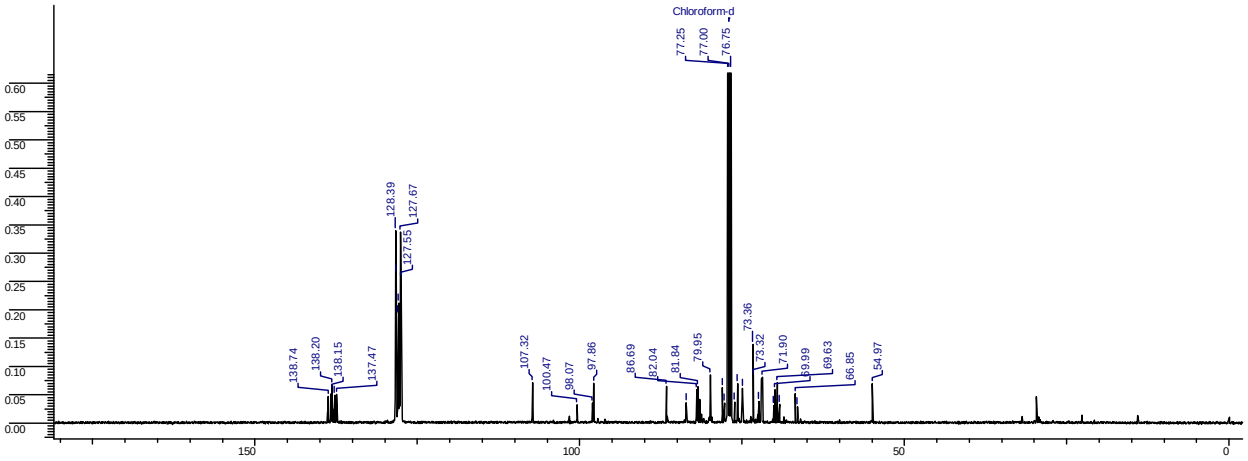
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **4c**



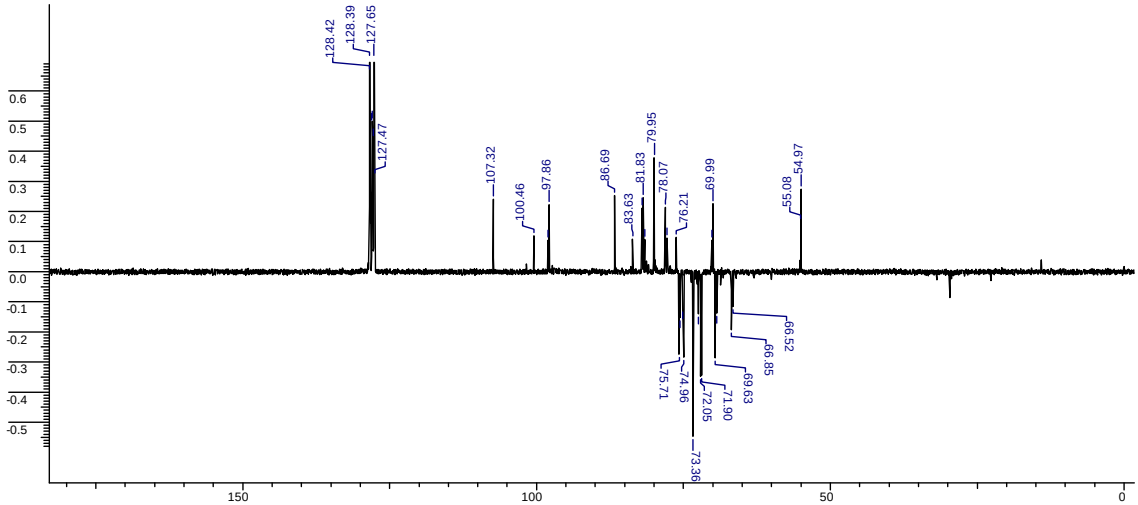
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **4d**



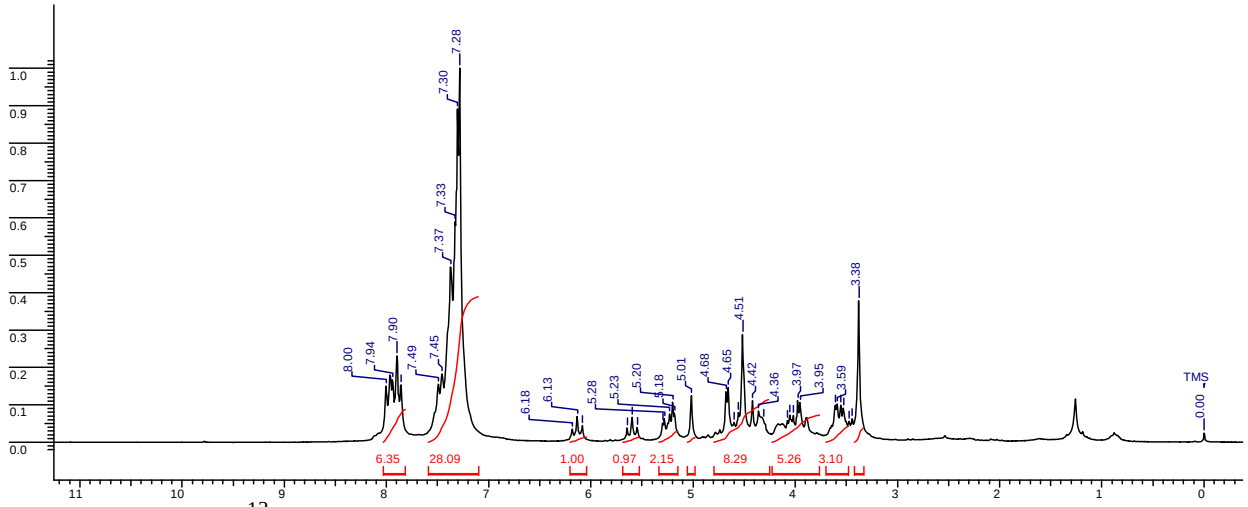
^{13}C NMR Spectrum (125.76MHz, $CDCl_3$) of Compound **4d**



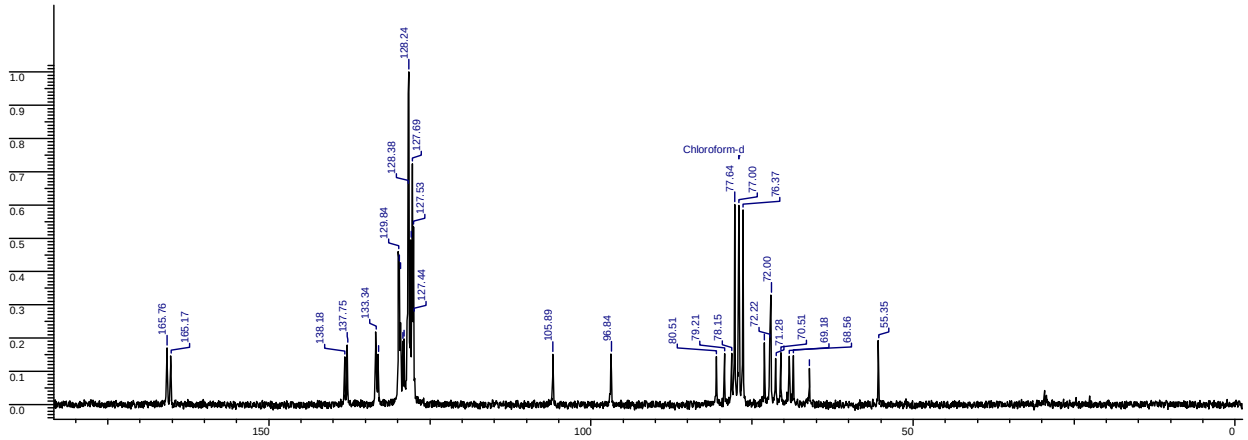
DEPT NMR Spectrum (125.76MHz, $CDCl_3$) of Compound **4d**



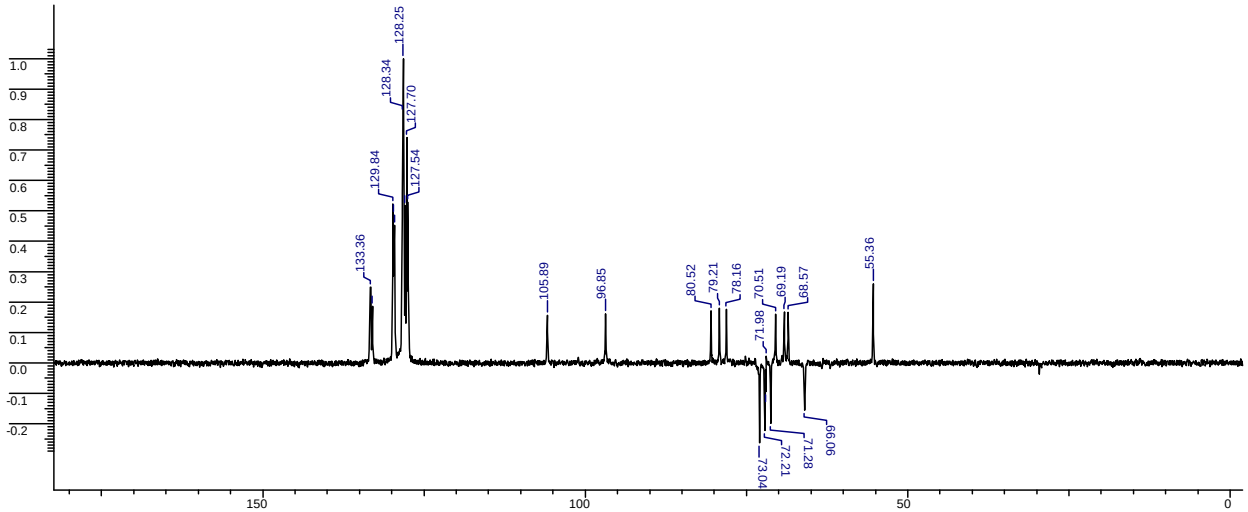
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **5a**



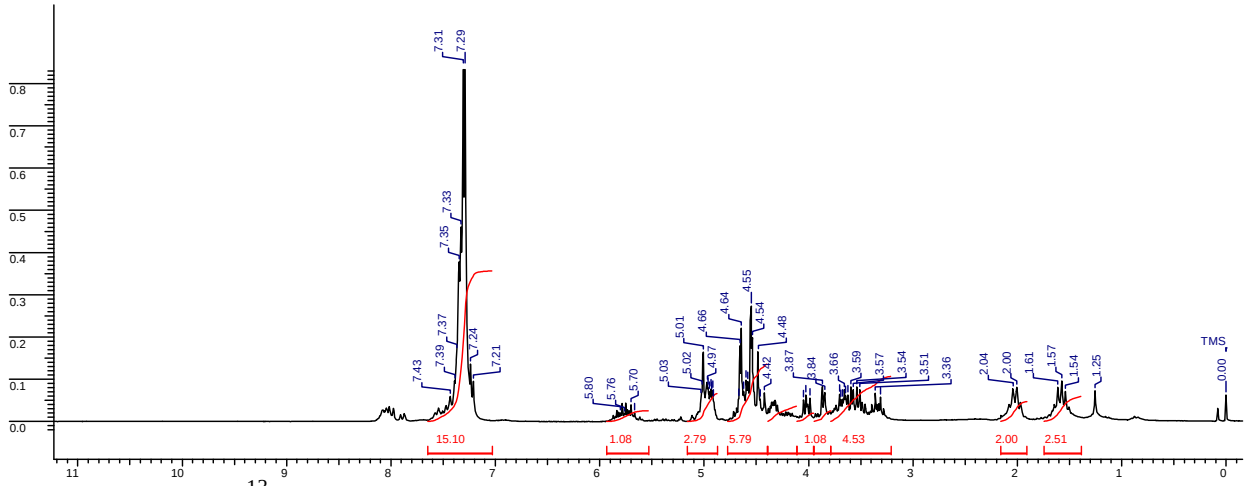
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **5a**



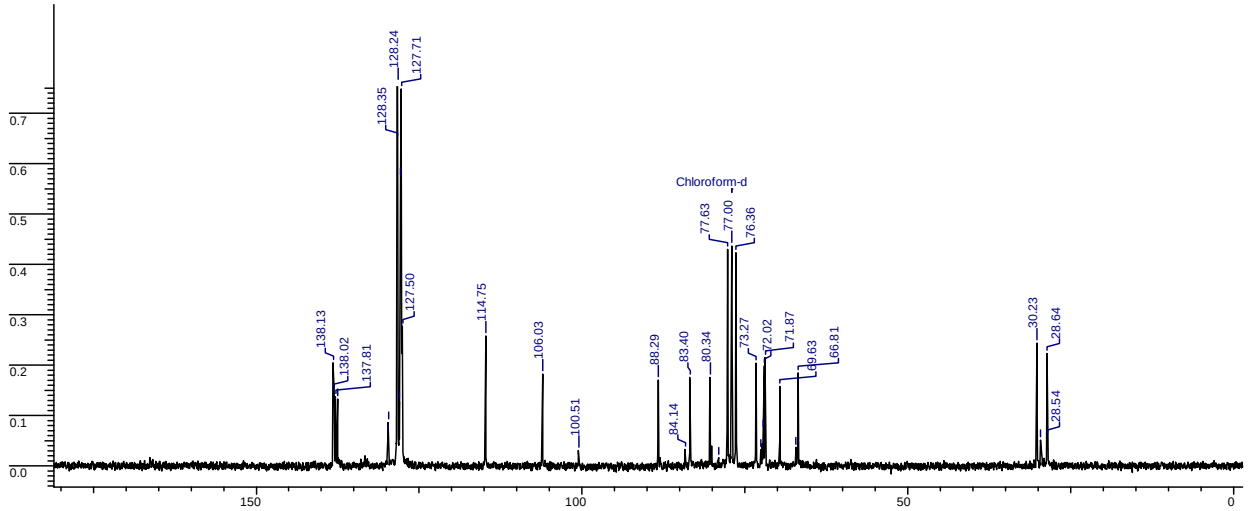
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **5a**



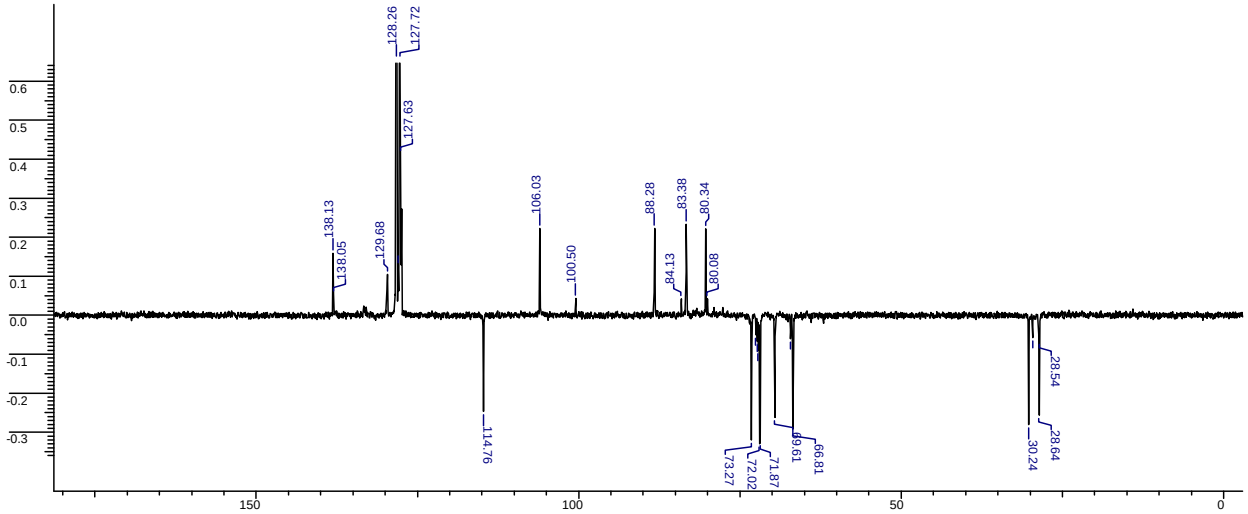
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **5b**



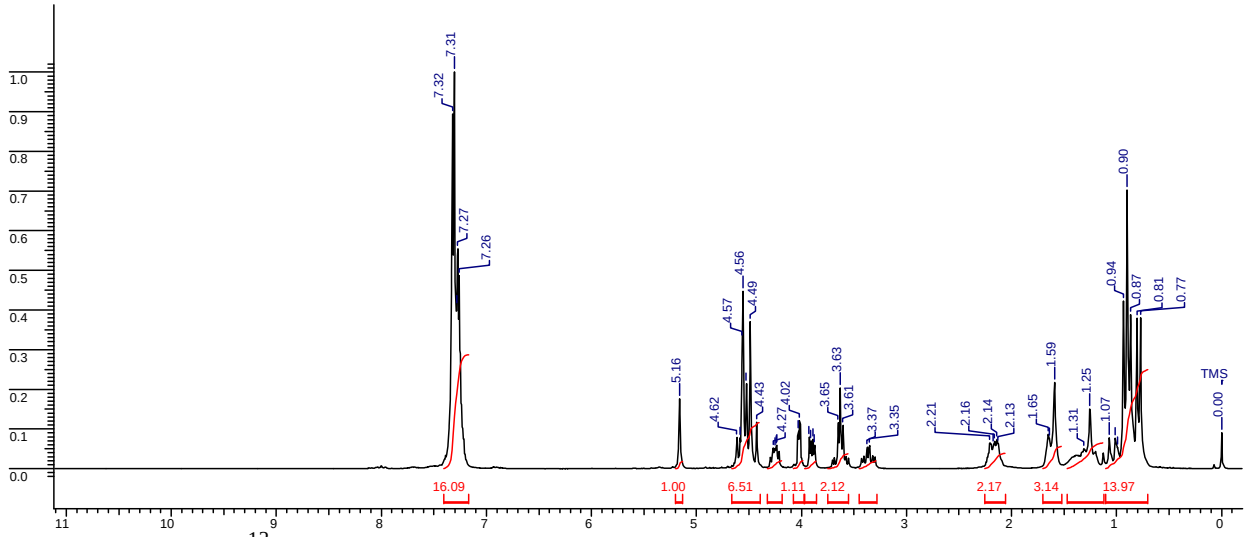
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **5b**



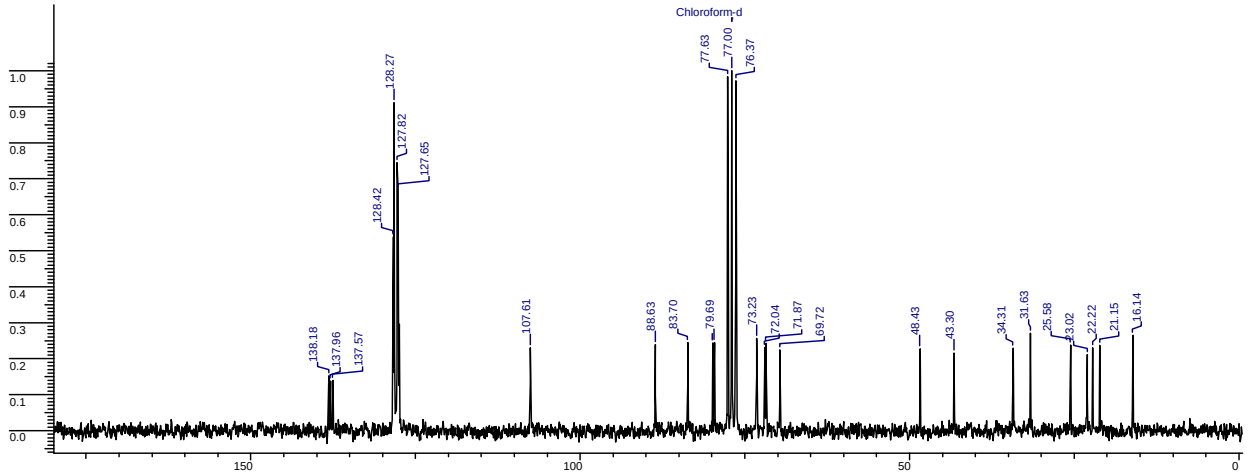
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **5b**



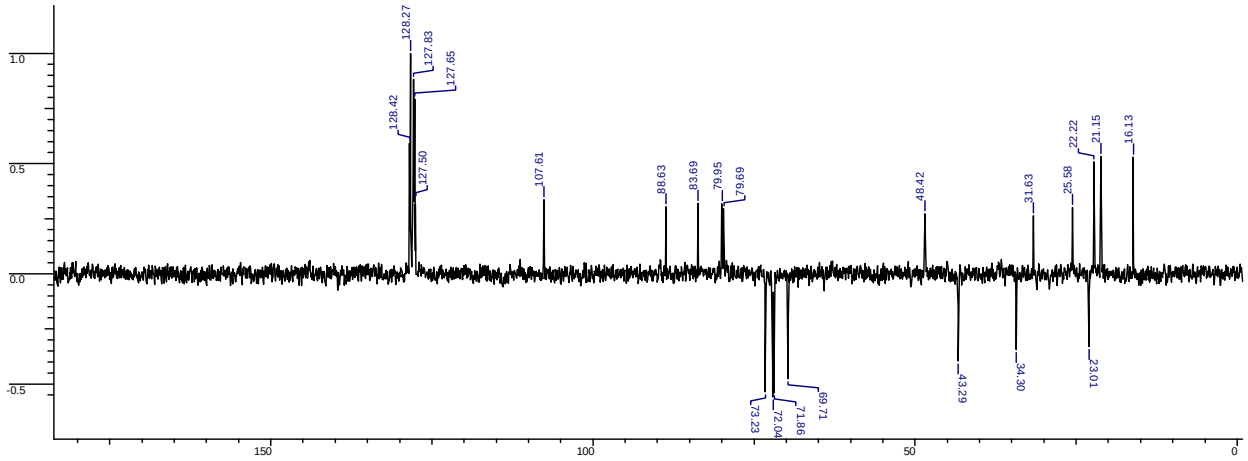
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **5c**



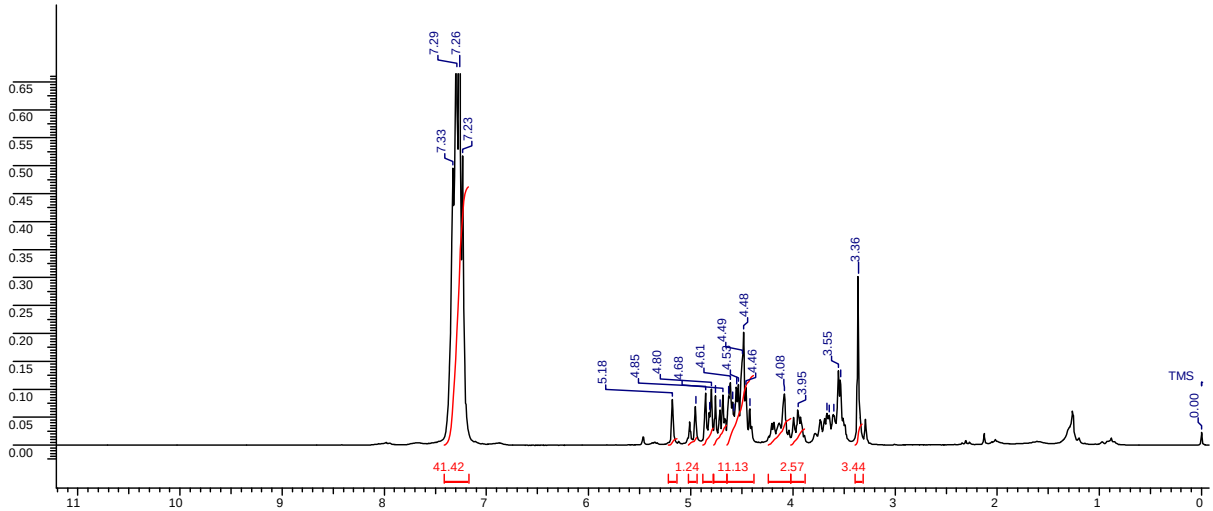
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **5c**



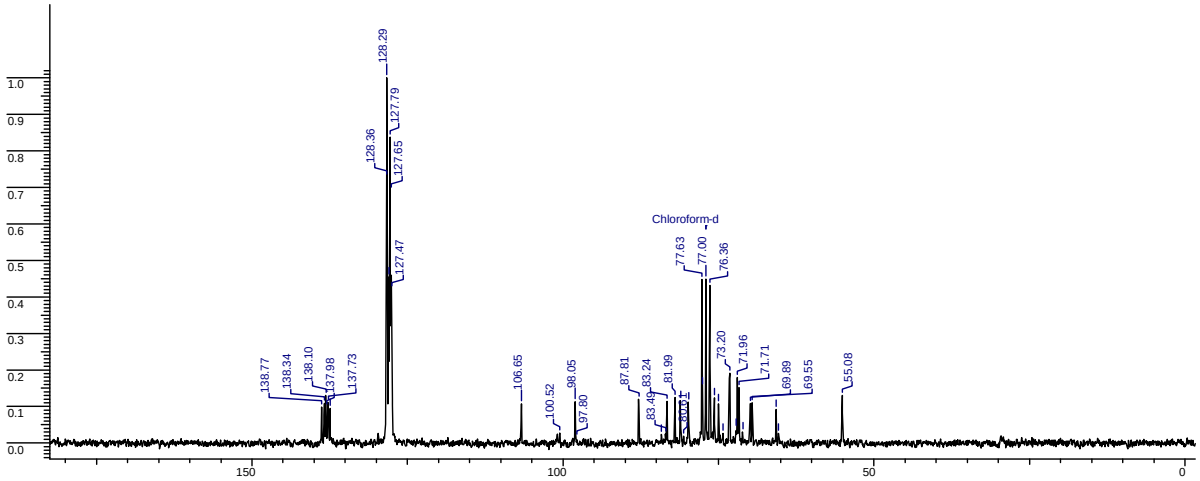
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **5c**



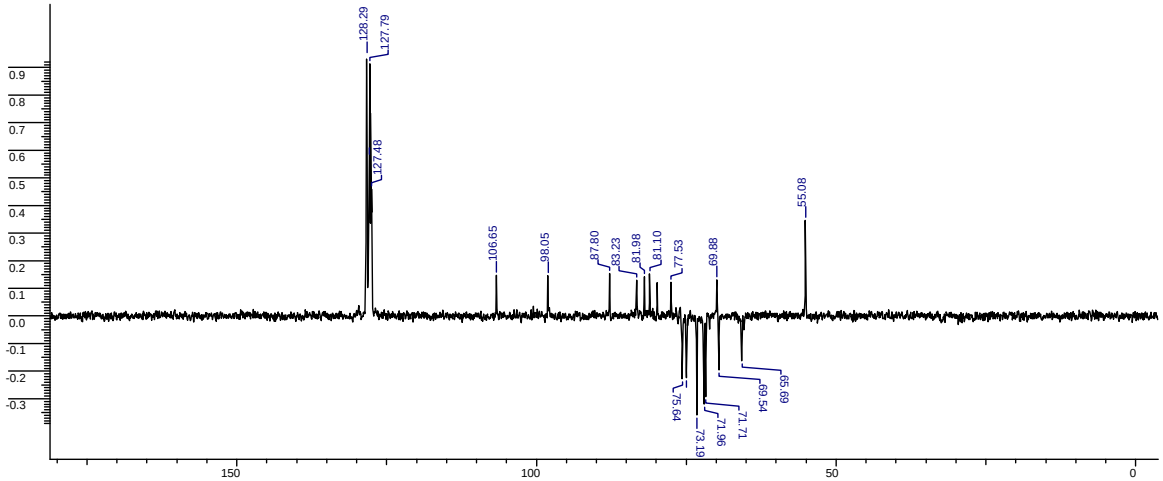
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **5d**



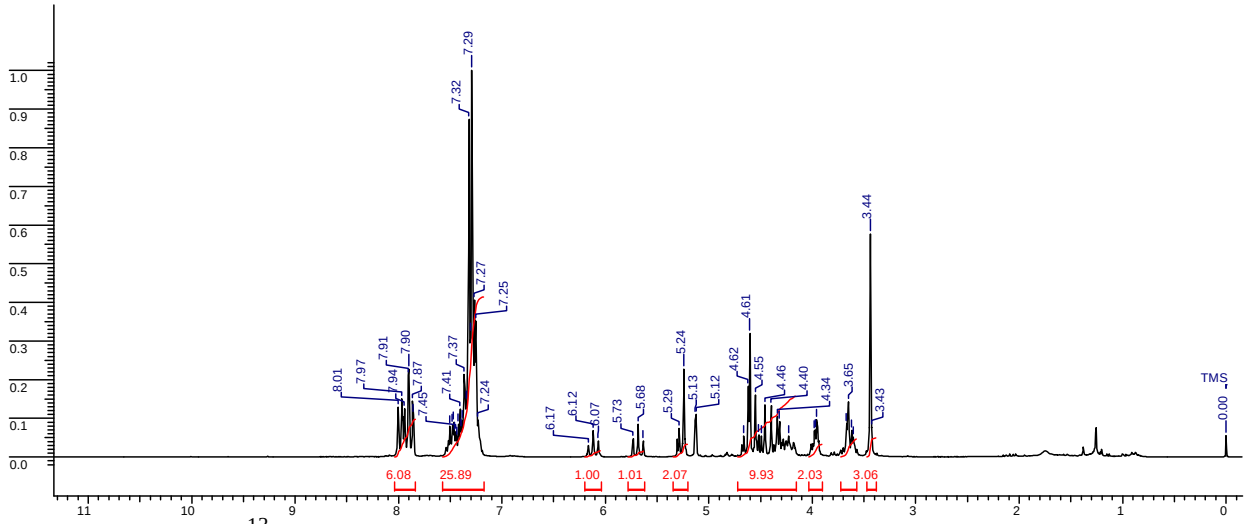
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **5d**



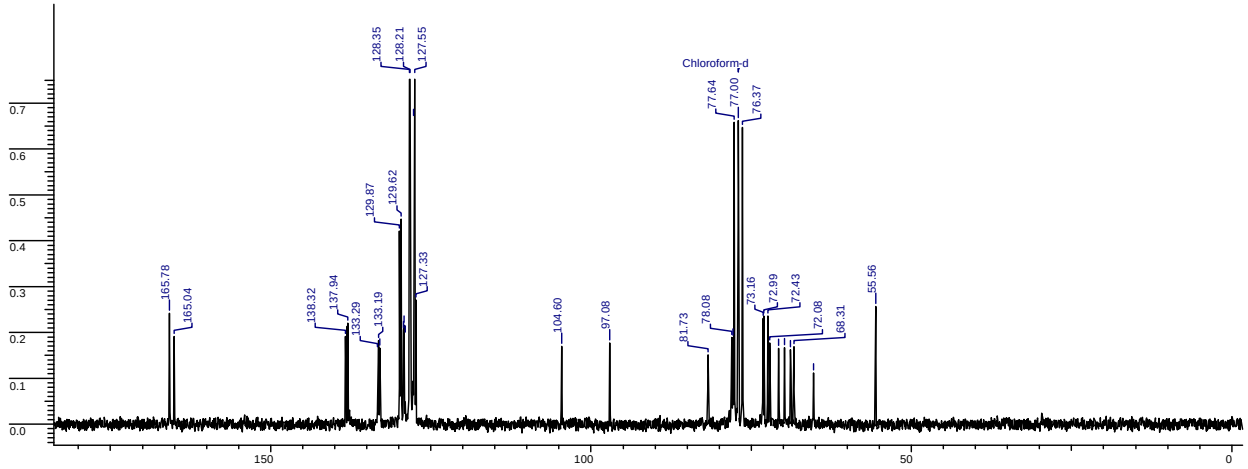
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **5d**



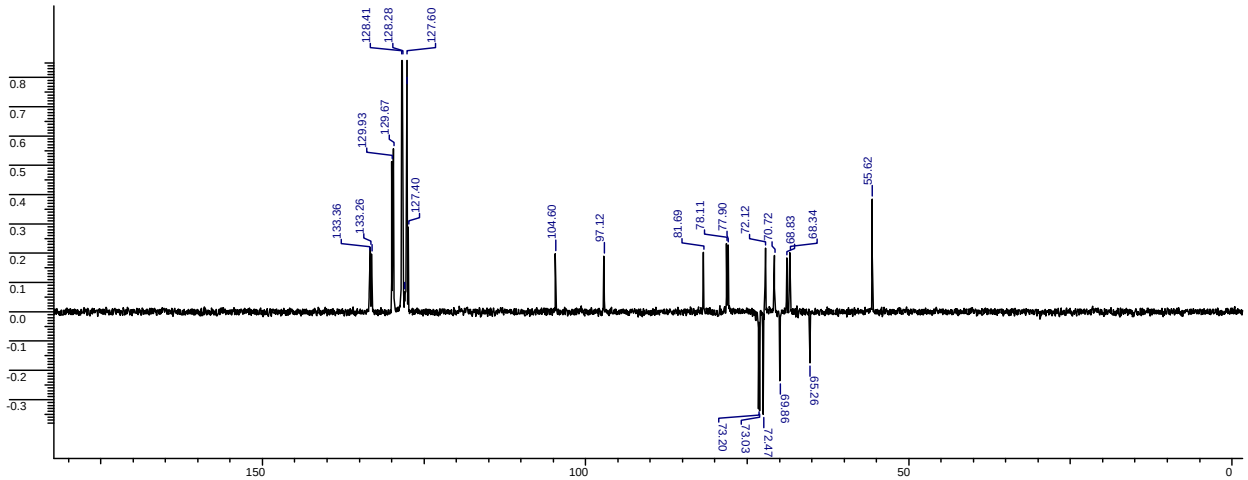
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **6a**



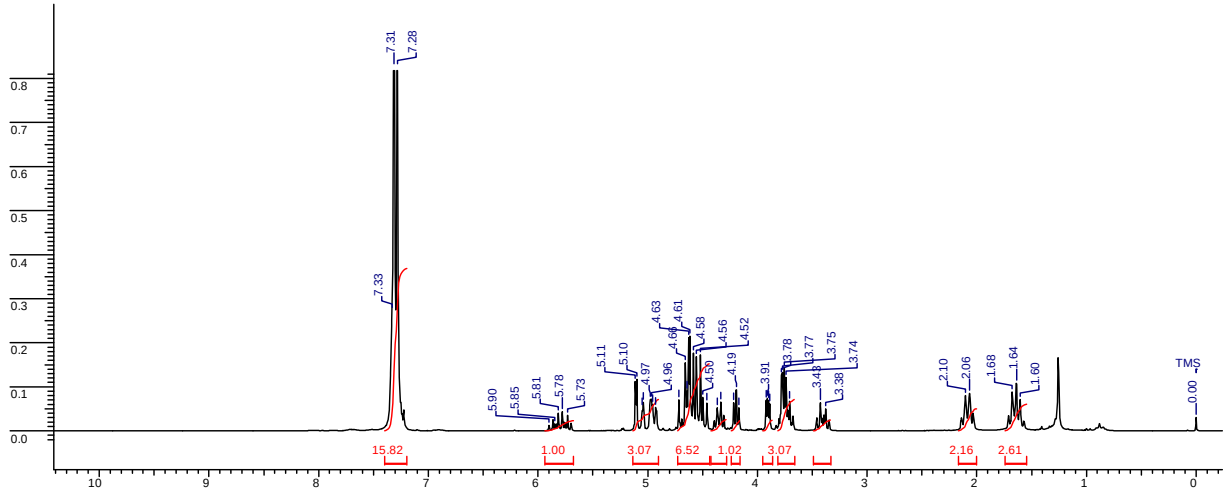
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6a**



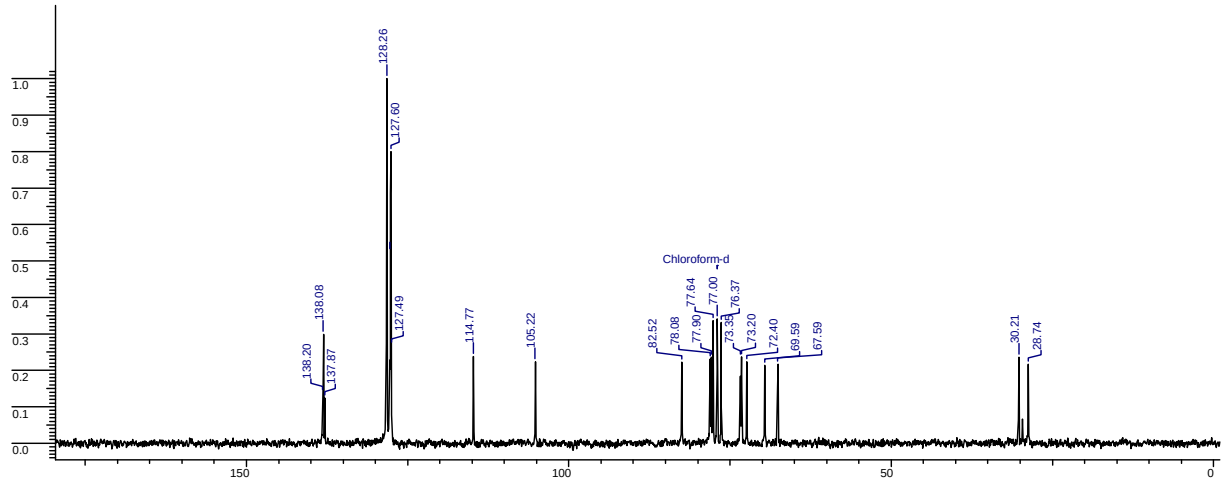
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6a**



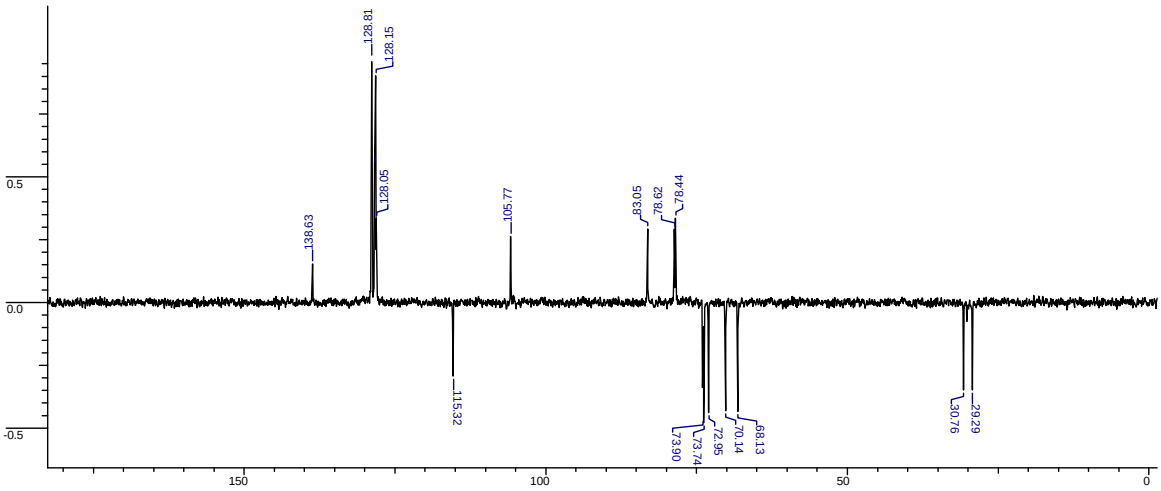
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **6b**



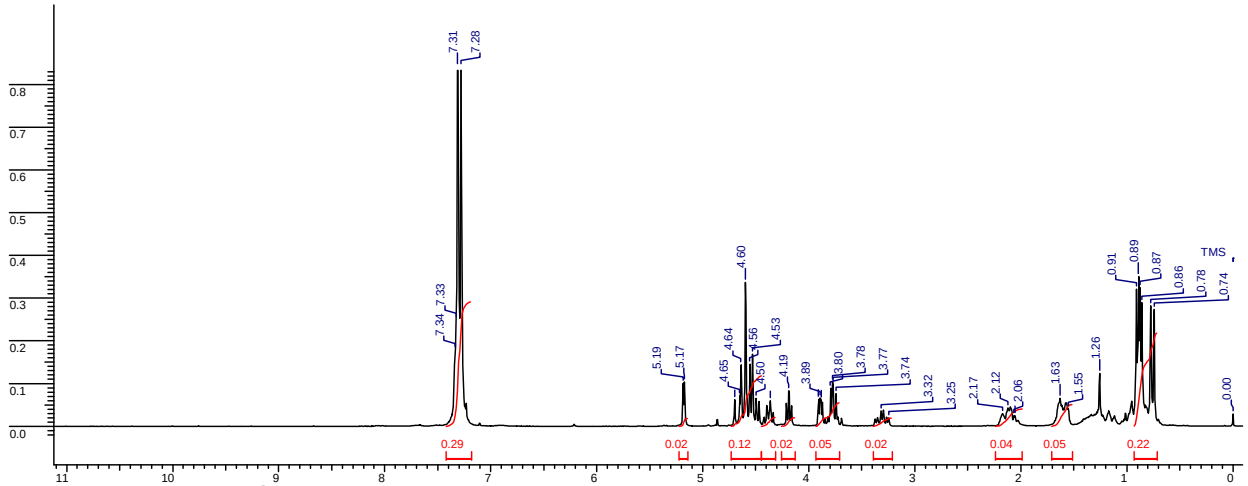
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6b**



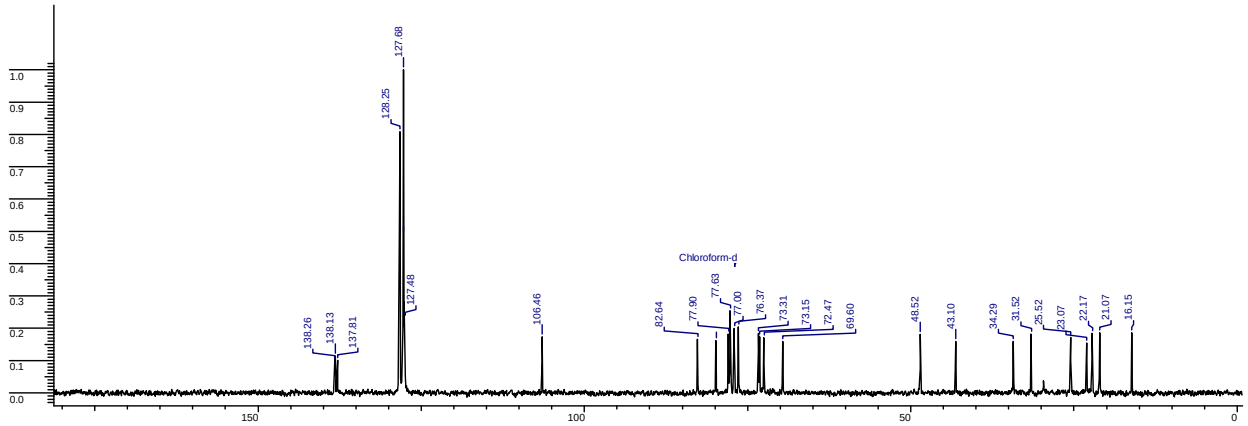
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6b**



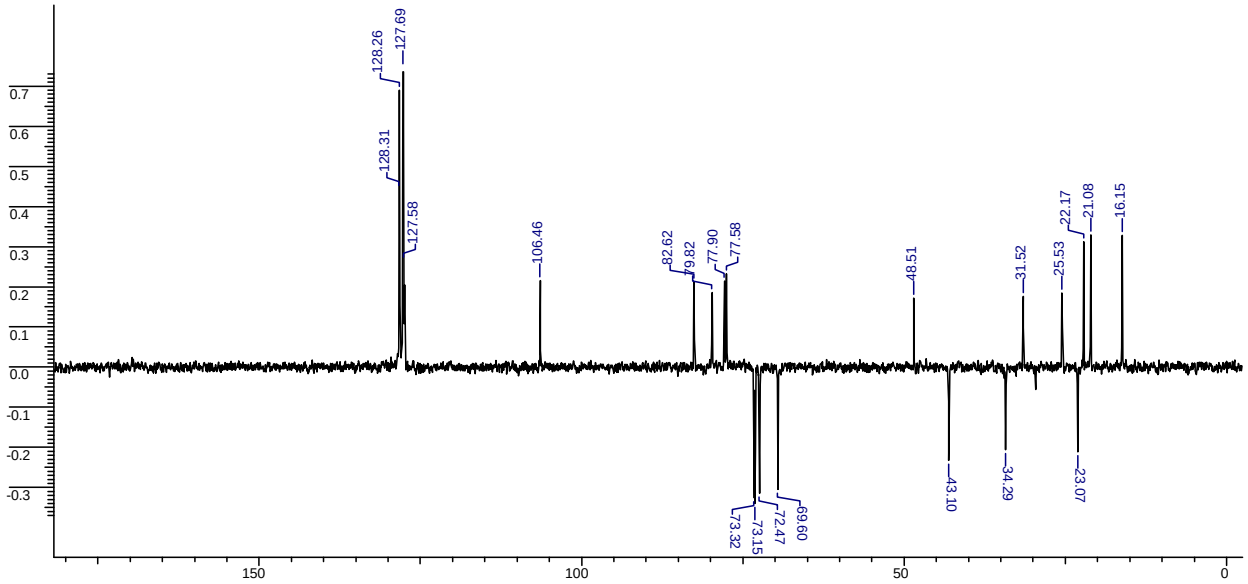
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **6c**



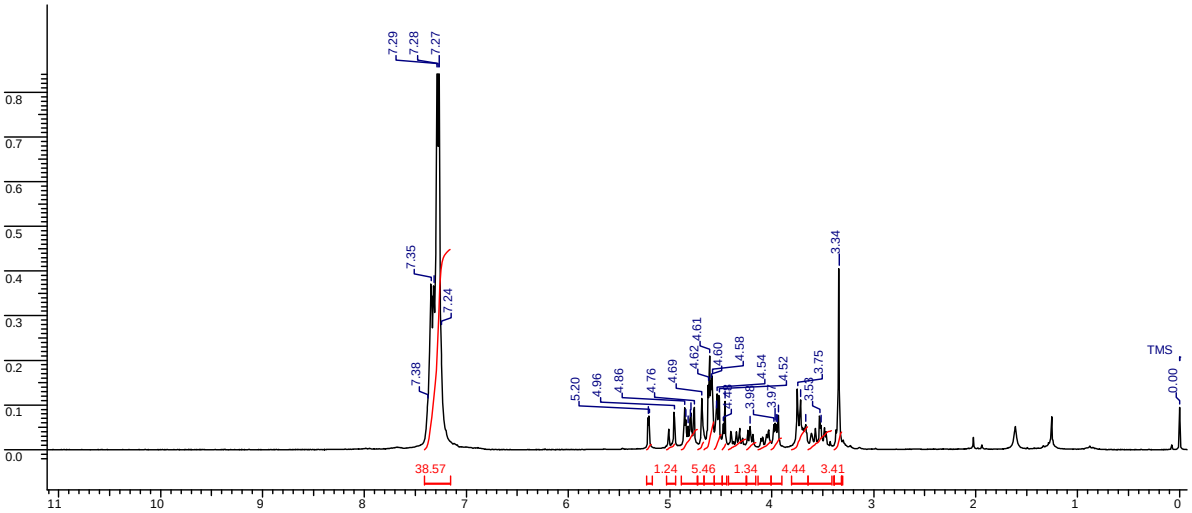
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6c**



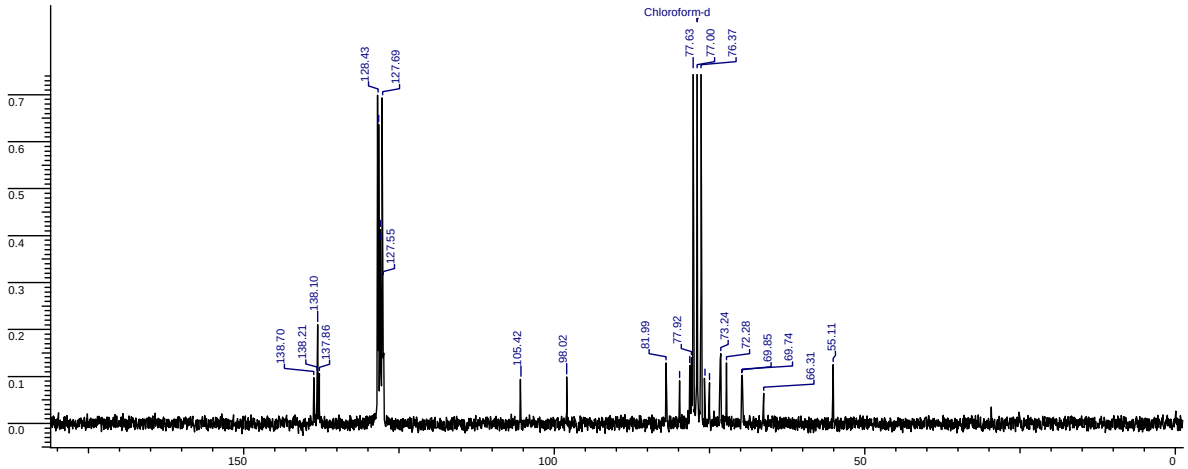
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6c**



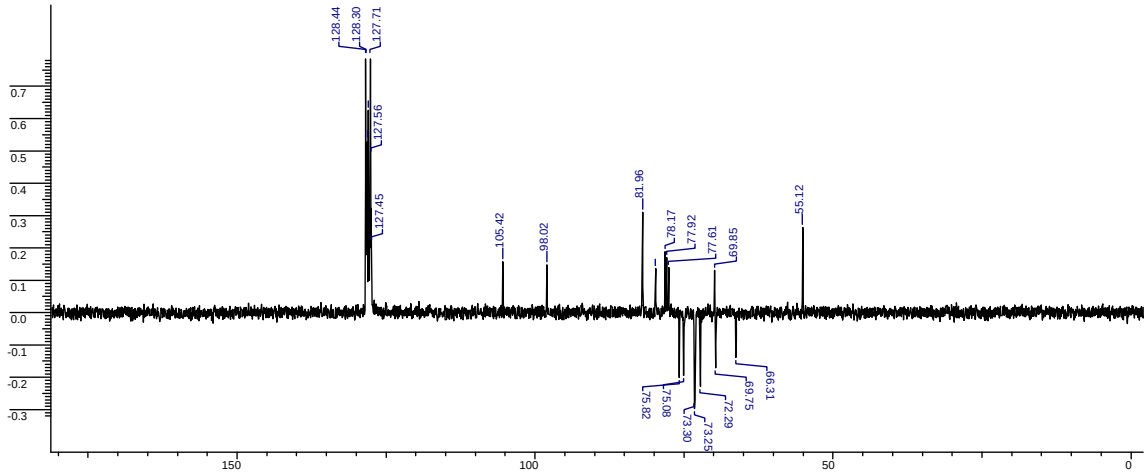
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **6d**



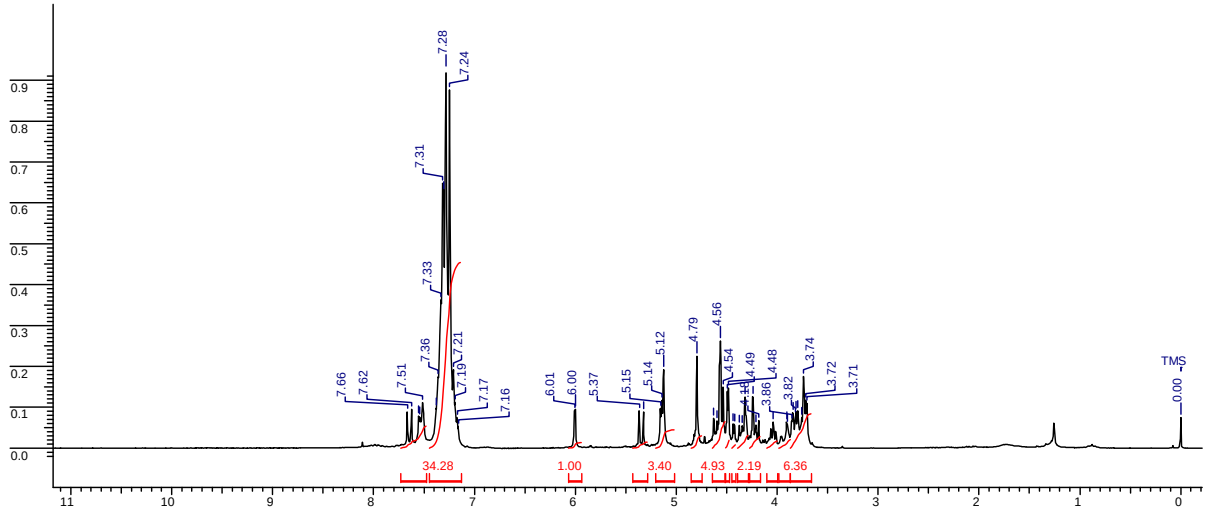
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6d**



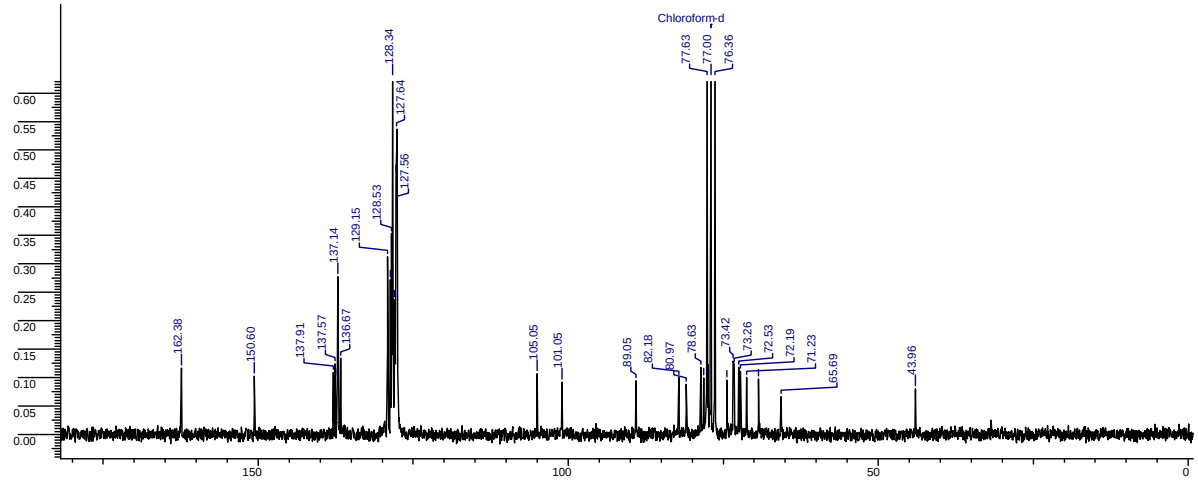
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6d**



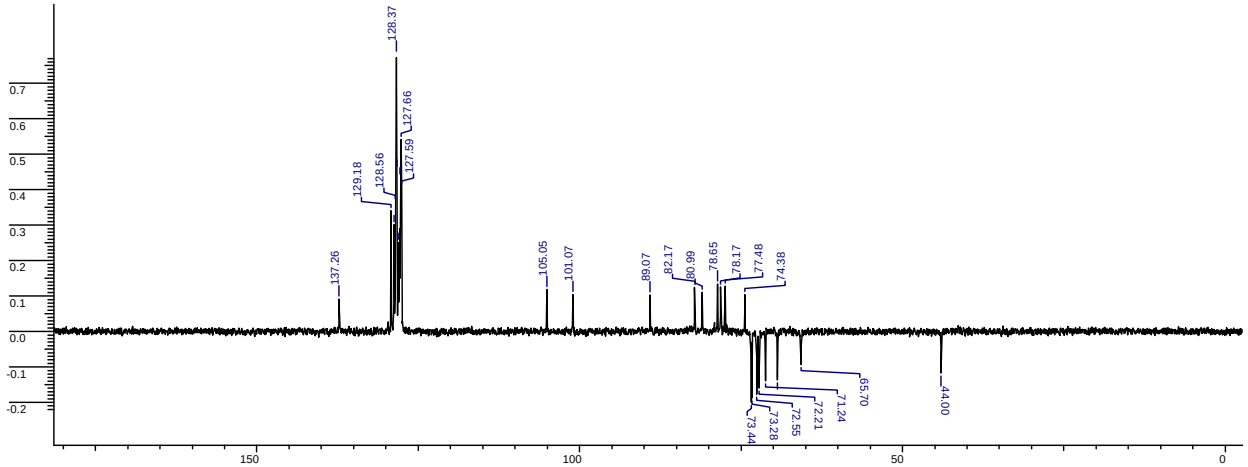
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **6e**



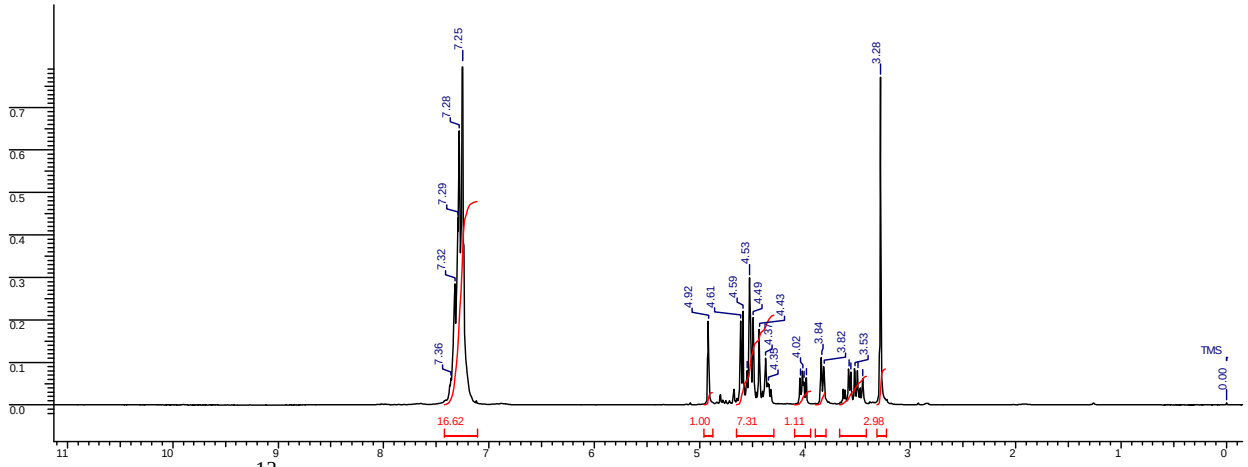
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6e**



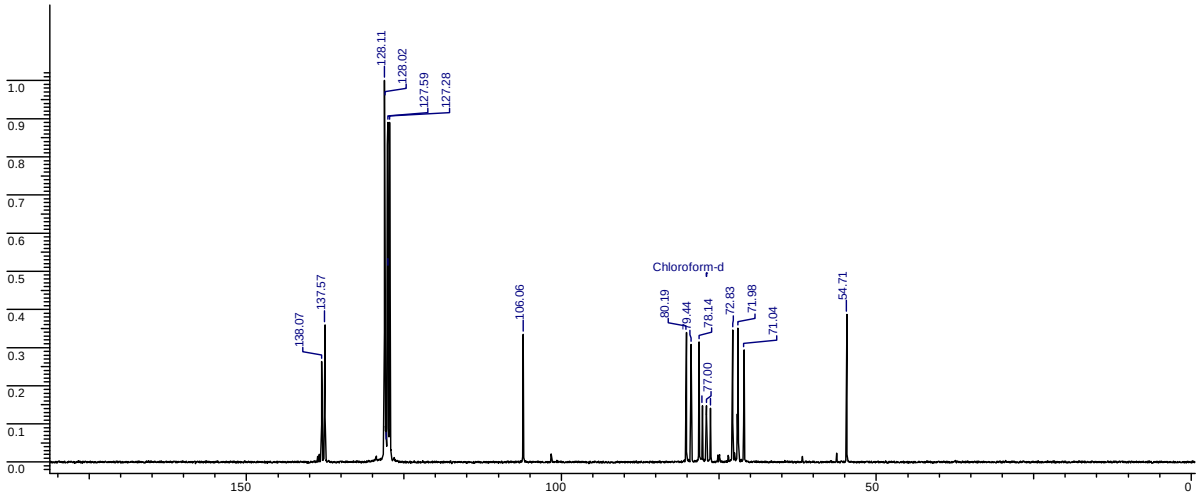
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **6e**



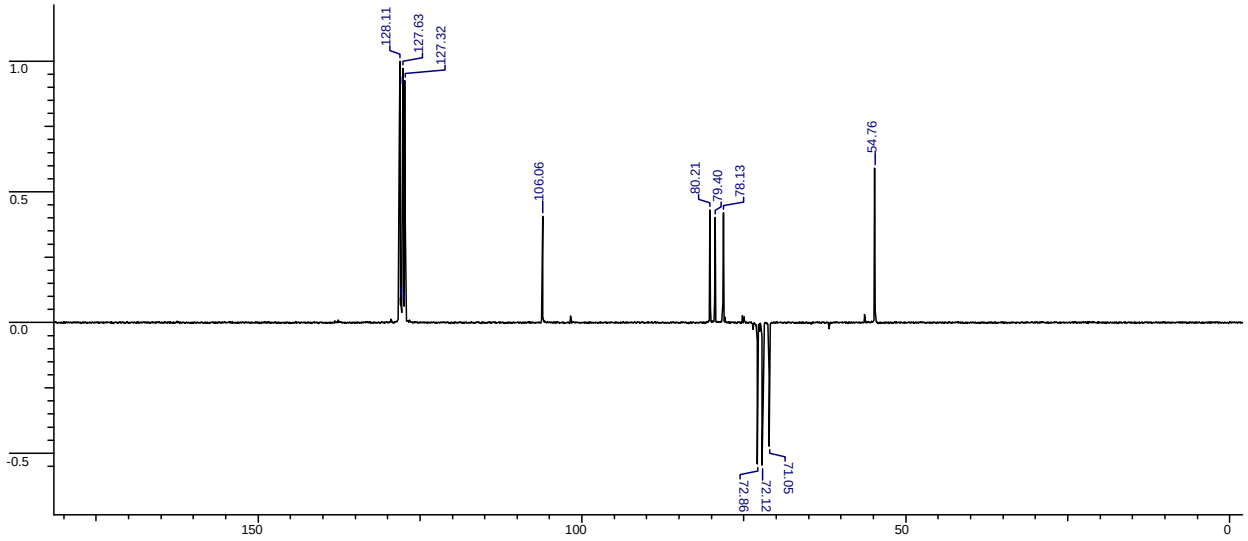
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **7**



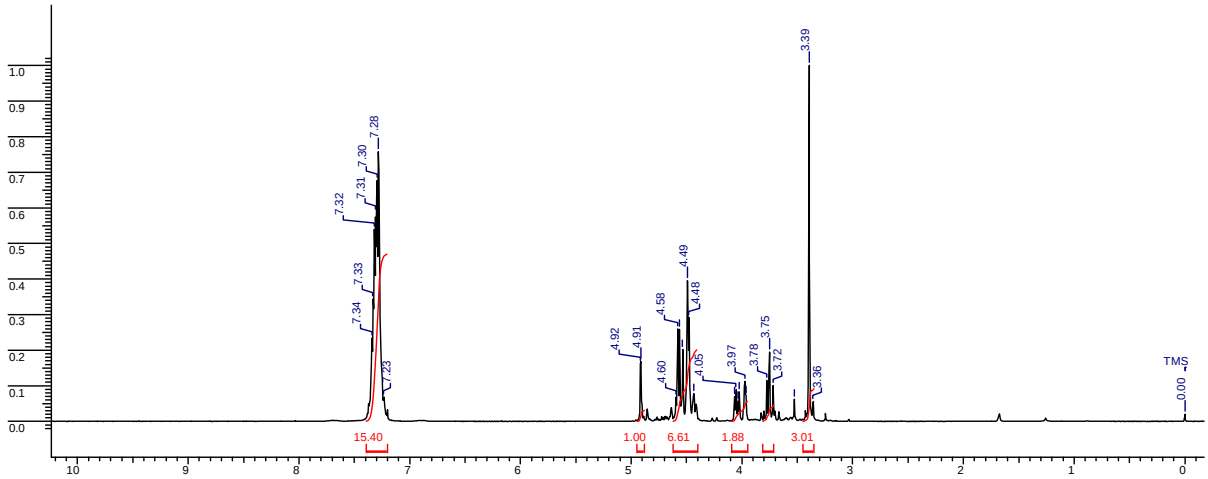
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **7**



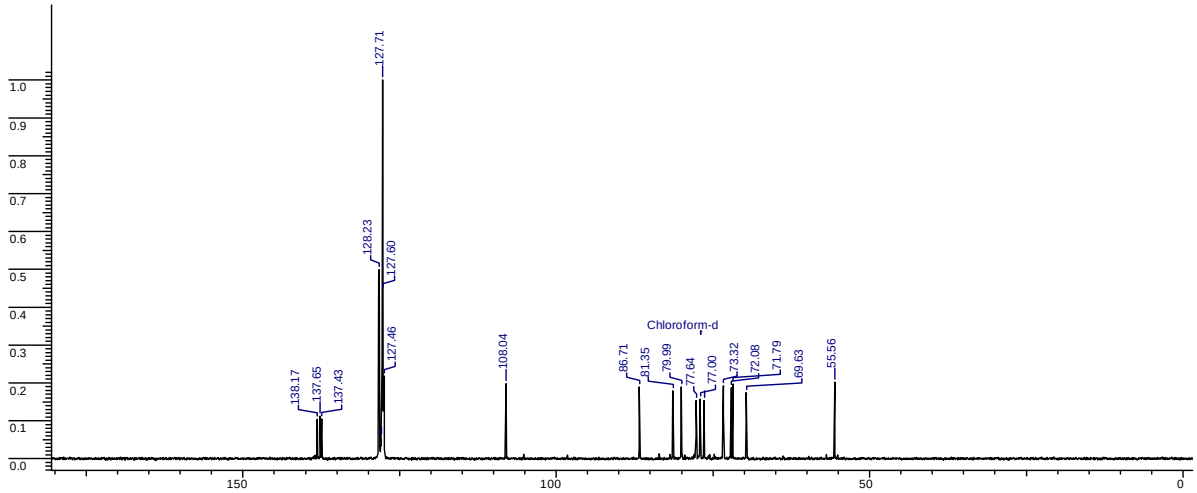
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **7**



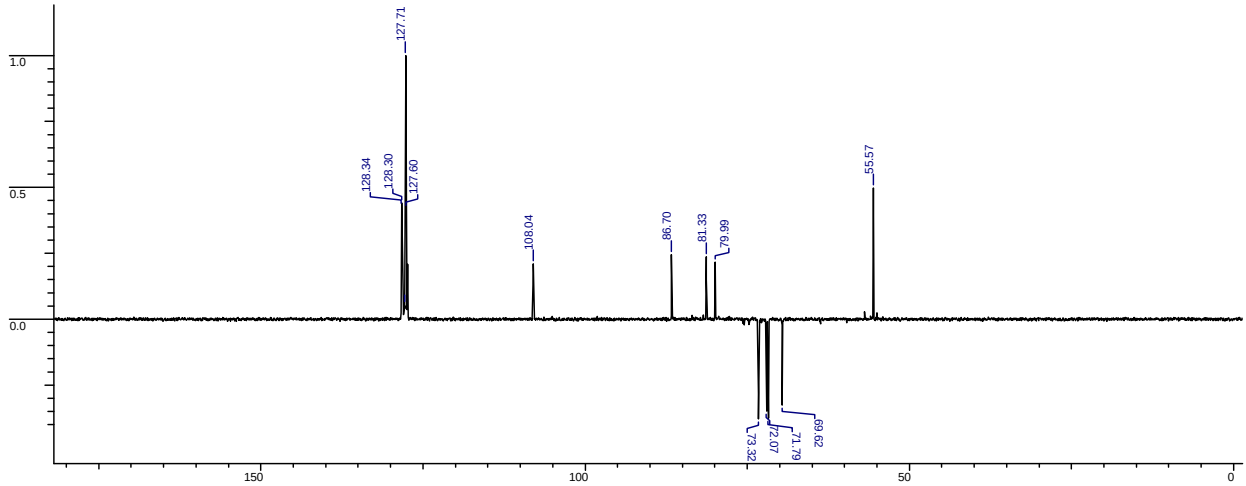
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **8**



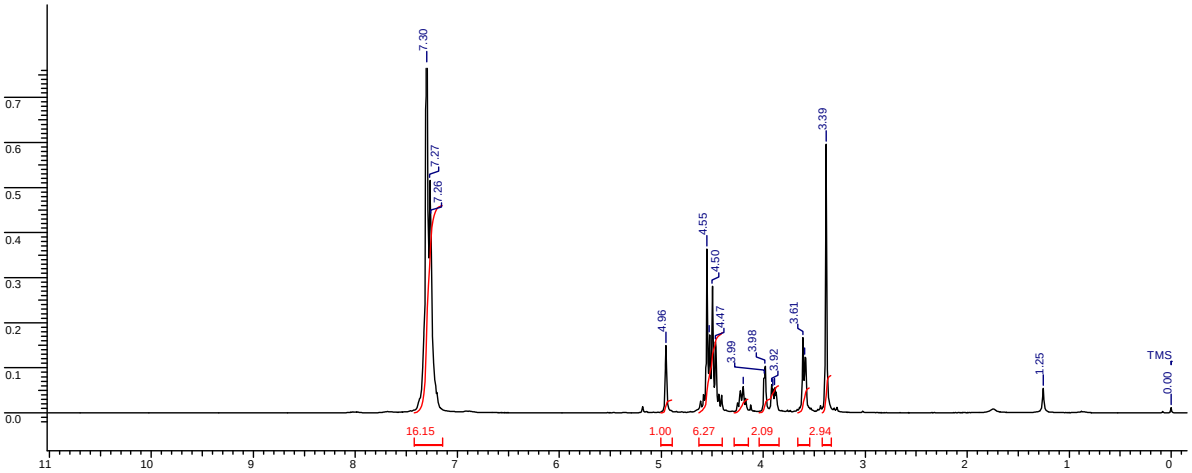
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **8**



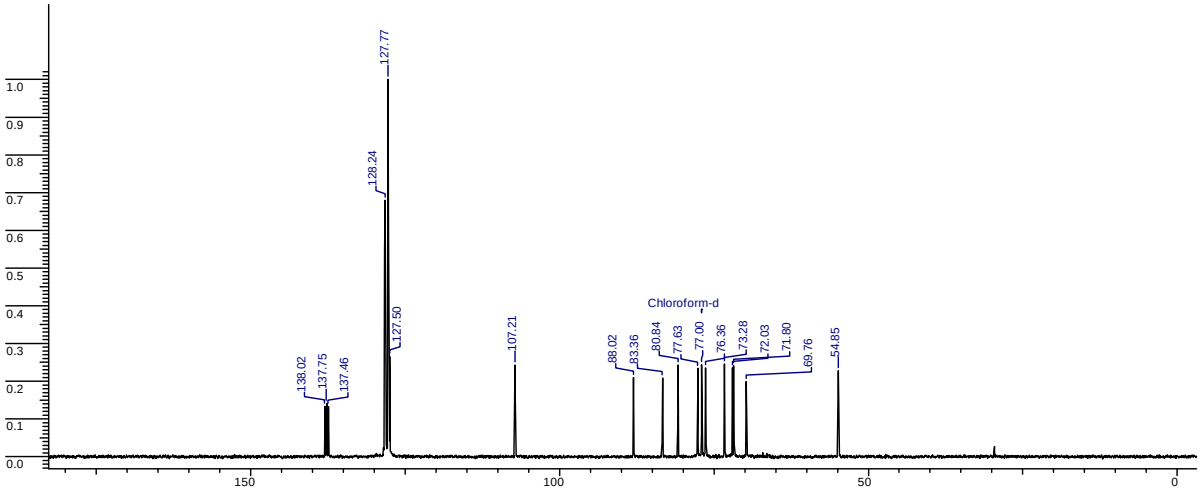
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **8**



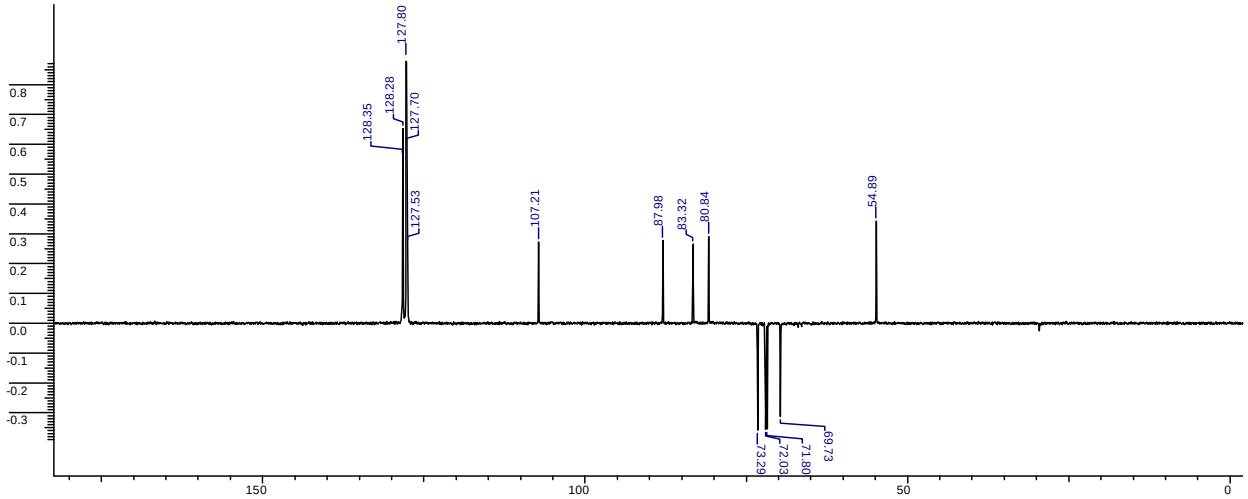
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **9**



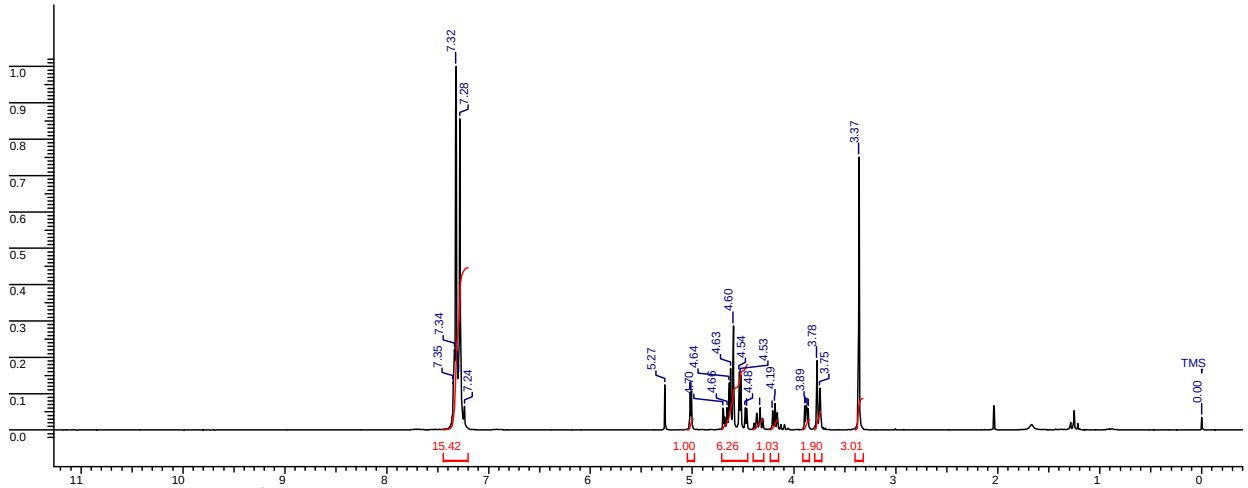
^{13}C NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **9**



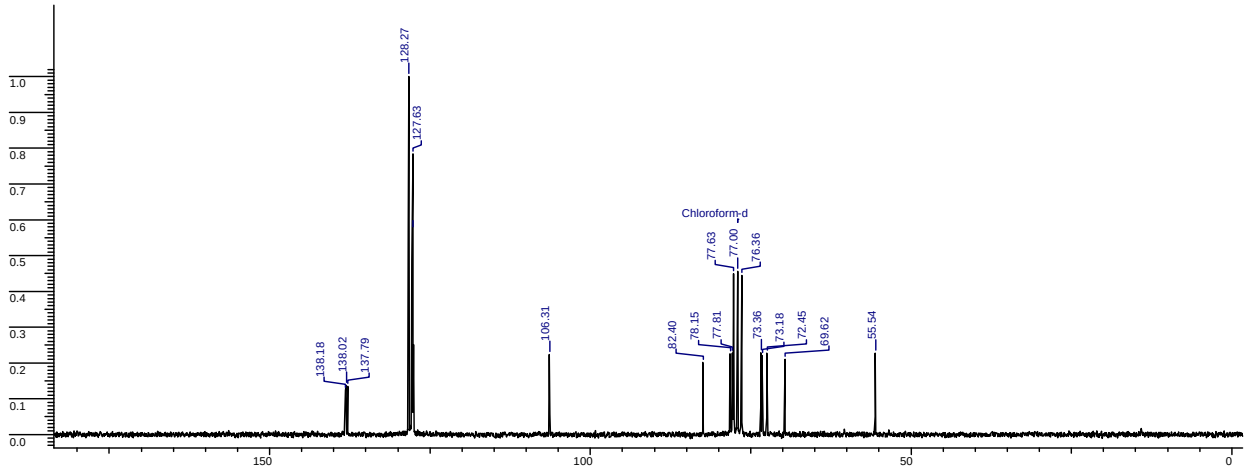
DEPT NMR Spectrum (50.32MHz, $CDCl_3$) of Compound **9**



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



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



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

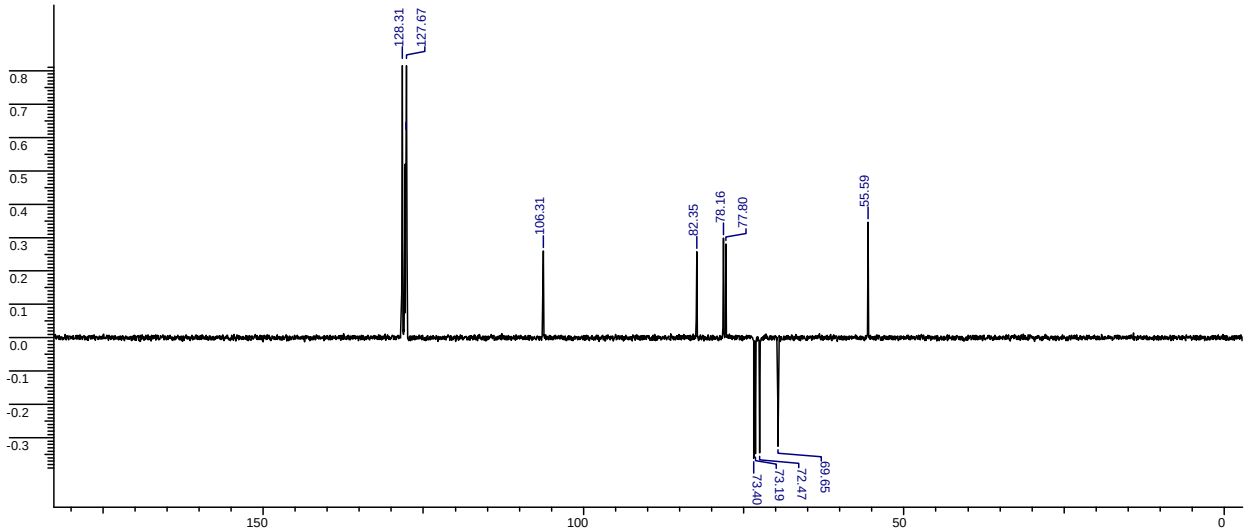
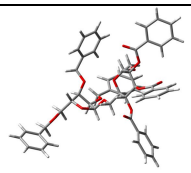
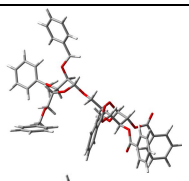
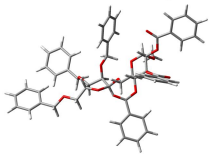
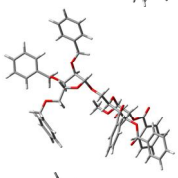
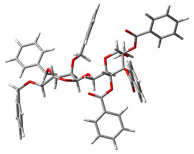
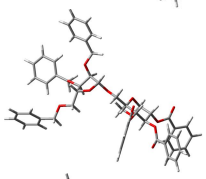
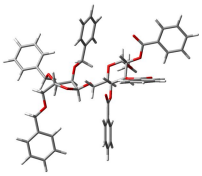
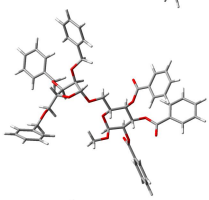
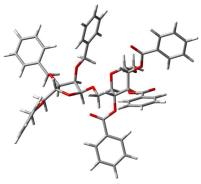
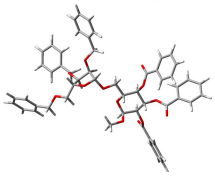
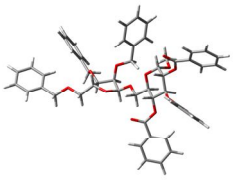
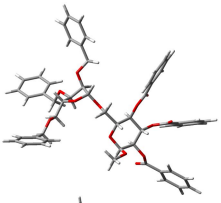
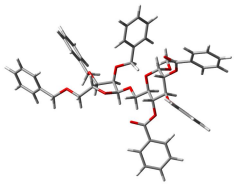
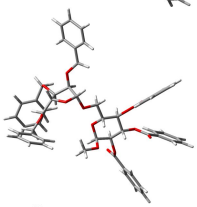
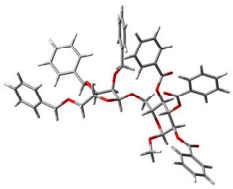
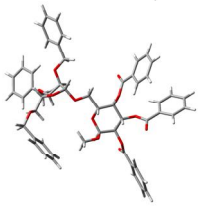
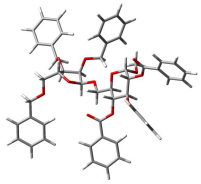
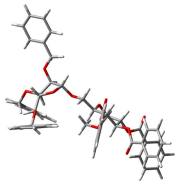
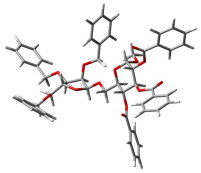
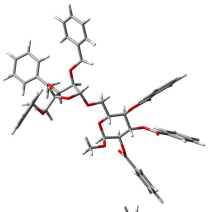
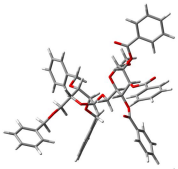
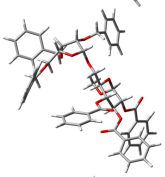
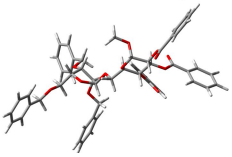
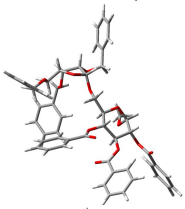
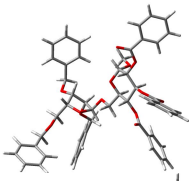
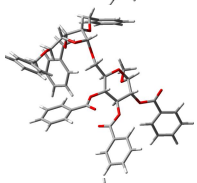
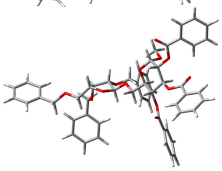
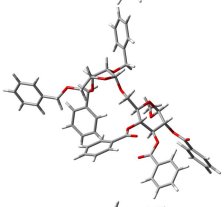
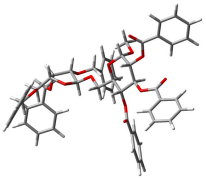
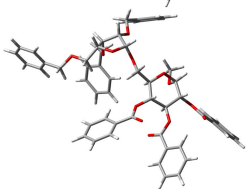
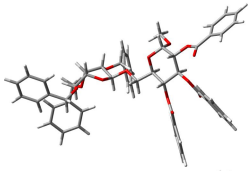
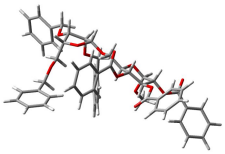
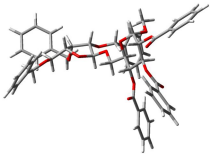
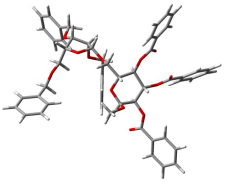
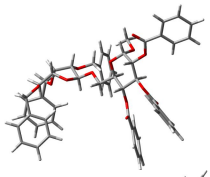
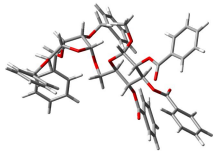
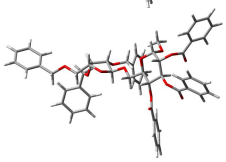
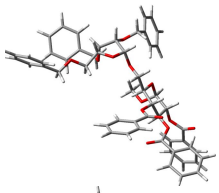
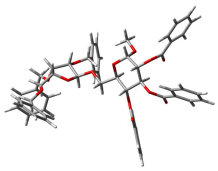
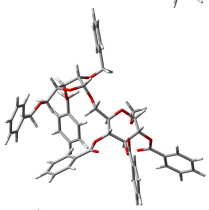
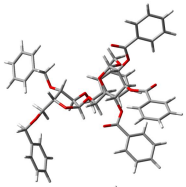
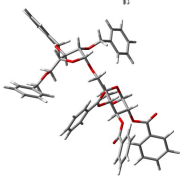
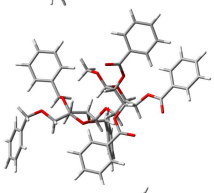
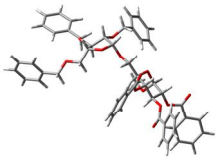
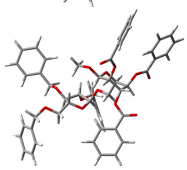
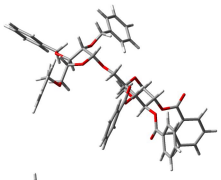
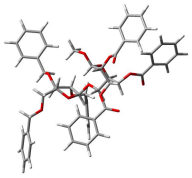
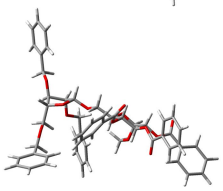
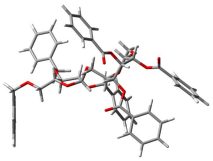
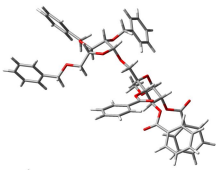
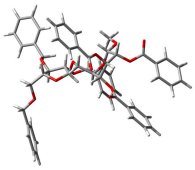
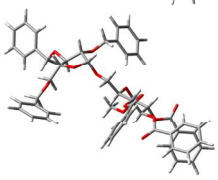
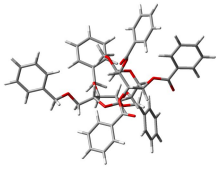
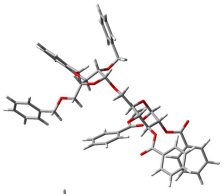
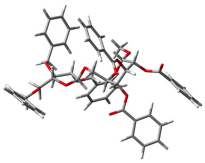
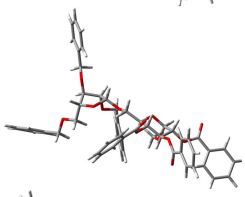
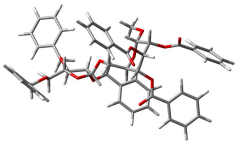
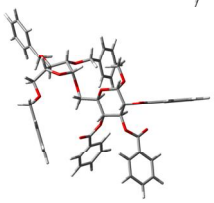
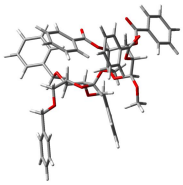
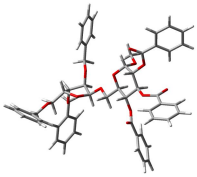
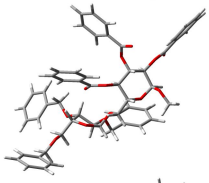
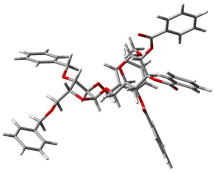
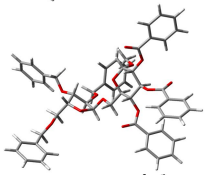
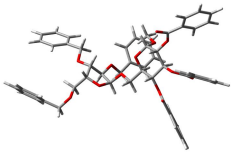
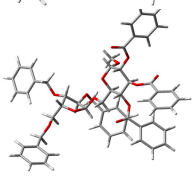
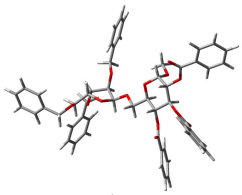
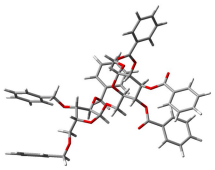
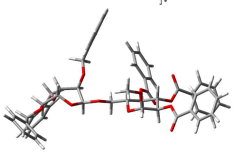
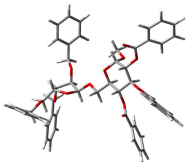


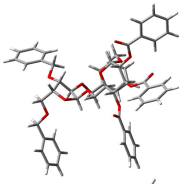
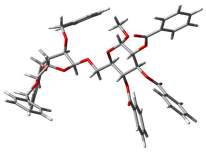
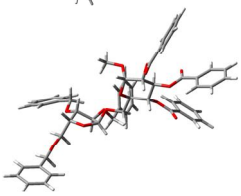
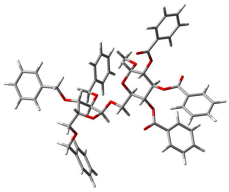
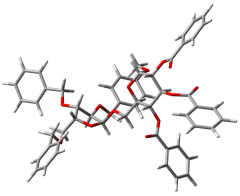
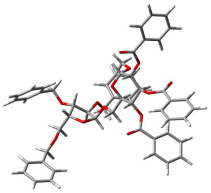
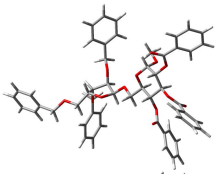
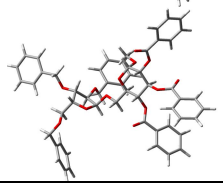
Table 1: Structures of the various conformations generated using OPLS_2005 force field along with the relative energies, in kcal/mol, at AM1 level for the α and β isomers of the products.

	α		β	
	Structure	RE	Structure	RE
rib*f*-1		1.8		2.3
rib*f*-2		0.2		0.0
rib*f*-3		1.1		2.5
rib*f*-4		0.0		5.9
rib*f*-5		4.1		7.0
rib*f*-6		3.2		3.9
rib*f*-7		4.1		6.3
rib*f*-8		12.6		7.1

rib*f*-9		2.1		2.8
rib*f*-10		5.7		8.6
lyx*f*-1		0.0		1.1
lyx*f*-2		3.2		1.4
lyx*f*-3		1.3		5.9
lyx*f*-4		0.1		1.2
lyx*f*-5		0.7		6.0
lyx*f*-6		2.7		8.3
lyx*f*-7		2.3		5.8

lyx*f*-8		2.8		8.4
lyx*f*-9		9.4		2.4
lyx*f*-10		11.1		0.0
ara*f*-1		10.0		0.7
ara*f*-2		7.4		2.2
ara*f*-3		4.0		1.4
ara*f*-4		4.0		3.4
ara*f*-5		0.0		4.5
ara*f*-6		5.1		5.6

ara*f*-7		3.7		2.8
ara*f*-8		0.6		1.6
ara*f*-9		1.8		0.0
ara*f*-10		4.1		3.7
xyl*f*-1		3.3		2.8
xyl*f*-2		2.1		1.7
xyl*f*-3		0.0		0.0
xyl*f*-4		4.1		0.0
xyl*f*-5		11.7		6.0

xyl*f*-6		1.4		3.3
xyl*f*-7		5.9		2.0
xyl*f*-8		5.8		2.5
xyl*f*-9	-	-		5.7
xyl*f*-10	-	-		0.0