Supporting Information

for

Gold-catalyzed glycosidation for the synthesis of trisaccharides by applying the armed–disarmed strategy

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Detailed experimental data

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General experimental procedure

To a solution of glycosyl donor (1 equiv) and aglycon (1.1 equiv) in 3 mL CH_3CN/CH_2Cl_2 (1:1) was added a solution of $AuCl_3$ (5 mol %) and $AgSbF_6$ (5 mol %) in 3 mL of CH_3CN/CH_2Cl_2 (1:1) and the mixture was stirred at 25 °C for 4 h under argon atmosphere. After completion of the reaction (judged by TLC), the dark brown reaction mixture was concentrated in vacuo and the crude residue was purified through silica gel column chromatography using ethyl acetate/petroleum ether (1:5) to give the corresponding transglycosides.

Compound characterization data

Characterization data for compound **3** [1]:

$[\alpha]_D^{25}$ = -23.3 ($CHCl_3$, *c* 1.0); ^{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 $C_{64}H_{60}NaO_{14}[M^+ +Na]$: 1075.388; found: 1075.3889.

Characterization data for compound **4** [1]

$[\alpha]_D^{25}$ = +31.4 ($CHCl_3$, *c* 1.0); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.37 (t, 1H, *J* = 2.4 Hz), 3.58–4.07 (m, 12H), 4.10 (dd, 2H, *J* = 0.7, 2.4 Hz), 4.42–4.71 (m, 8H), 4.61 (s, 2H), 4.68 (s, 2H), 4.87 (d, 2H, *J* = 10.8 Hz), 4.99 (d, 1H, *J* = 1.6 Hz), 5.11 (d, 1H, *J* = 1.6 Hz), 7.10–7.45 (m, 35H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 54.1, 65.9, 69.1, 71.5, 71.8, 72.0, 72.1, 72.4, 72.9, 73.2, 74.4, 74.6, 74.7, 74.7, 74.9, 74.9, 75.0, 78.8, 79.3, 80.0, 96.5, 98.1, 127.3–128.4, 138.1, 138.4,138.4,138.4,138.4, 138.6, 138.7; HRMS (MALDI-TOF): calcd. for $C_{64}H_{66}NaO_{11}[M^+ +Na]$: 1033.4503; found: 1033.4510.

Characterization data for compound **5** [1]

$[\alpha]_D^{25}$ = -16.6 ($CHCl_3$, *c* 1.0); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.47 (t, 1H, *J* = 1.8 Hz), 3.58 (dd, 1H, *J* = 1.8, 5.4 Hz), 3.73 (dd, 1H, *J* = 6.0, 7.1 Hz), 3.81 (qd, 1H, *J* = 1.6, 3.1, 5.0 Hz), 4.25 (dd, 1H, *J* = 0.9, 7.1 Hz), 4.43–4.57 (m, 5H), 4.52 (ABq, 2H, *J* = 12.4 Hz), 5.46 (s,

1H), 7.20–7.38 (m, 15H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 65.0, 71.3, 71.4, 73.4, 74.1, 74.4, 74.5, 76.5, 100.1, 127.7–128.5, 137.6, 137.9, 137.9; Mol. Wt. Calculated for $C_{27}H_{28}NaO_5[M^+ +Na]$: 455.1825; found: 455.1830.

Characterization data for compound **6**

$[\alpha]_D^{25}$ = -38.5 ($CHCl_3$, *c* 1.0);^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.45–3.51 (m, 2H), 3.79–3.96 (m, 4H), 4.67 (ABq, 2H, *J* = 3.0 Hz), 4.69 (ABq, 2H, *J* = 5.2 Hz), 4.56-4.70 (m, 4H), 4.92 (m, 2H), 5.05 (m, 1H), 7.17-7.47 (m, 25H); ^{13}C NMR (50.32 MHz, $CDCl_3$): 69.6, 70.7, 71.4, 73.4, 73.8, 73.8, 74.8, 75.0, 75.9, 82.3, 100.2, 127.2-128.3, 137.4, 138.0, 138.3, 138.4, 138.7; HRMS (MALDI-TOF): calcd. for $C_{41}H_{42}NaO_6[M^+ +Na]$: 653.2879; found: 653.2875.

Characterization data for compound **7**

$[\alpha]_D^{25}$ = +9.5 ($CHCl_3$, *c* 1.0);^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.42–4.08 (m, 7H), 4.53 (m, 1H), 4.60 (s, 2H), 4.72 (d, 2H, *J* = 1.9 Hz), 4.72 (ABq, 2H, *J* = 11.3 Hz), 4.85 (t, 1H, *J* = 5.5 Hz), 5.24 (d, 1H, *J* = 1.2 Hz); ^{13}C NMR (50.32 MHz, $CDCl_3$): 69.6, 71.5, 72.1, 72.6, 73.2, 74.8, 75.0, 75.2, 79.7, 92.7, 127.6-128.5, 138.0, 138.1, 138.3, 138.5; HRMS (MALDI-TOF): calcd. for $C_{34}H_{36}NaO_6[M^+ +Na]$: 563.2410; found: 563.2416.

Characterization data for compound **8**

$[\alpha]_D^{25}$= +34.7 ($CHCl_3$, *c* 1.0);^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.38 (t, 1H, *J* = 2.4 Hz), 3.68-3.77 (m, 3H), 3.83 (dd, 1H, *J* = 1.9, 1.2 Hz), 3.88 (dd, 1H, *J* = 3.2, 9.2 Hz), 3.99 (t, 1H, *J* = 9.5 Hz), 4.10 (d, 2H, *J* = 2.2 Hz), 4.58 (ABq, 2H, *J* = 11.9 Hz), 4.59 (s, 2H), 4.65 (ABq, 2H, *J* = 11.0 Hz), 4.73 (q, 2H, *J* = 2.8, 15.2 Hz), 5.08 (d, 1H, *J* = 1.8 Hz), 7.09-7.39 (m, 19H); ^{13}C NMR (100.53 MHz, $CDCl_3$): 21.2, 54.0, 68.7, 72.0, 72.2, 72.6, 73.2, 74.3, 74.6, 74.7, 75.0, 78.8, 79.9, 96.4, 127.4-128.9, 135.1, 137.1, 138.1, 138.3, 138.4; Mol. Wt. Calculated for $C_{38}H_{40}NaO_6$ $[M^+ +Na]$: 615.2723; found: 615.2731.

Characterization data for compound **12**

$[\alpha]_D^{25}$= N/R (racemic);^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.56–3.65 (m, 4H), 3.80 (s, 4H), 4.46 (s, 2H), 4.53 (s, 2H), 4.69 (s, 2H), 6.86 (d, 2H *J* = 8.2 Hz), 7.22-7.34 (m, 12H); ^{13}C NMR (100.53 MHz, $CDCl_3$): 55.2, 69.9, 70.3, 72.1, 73.0, 73.3, 77.2, 113.7, 127.4-130.3, 138.2, 138.6, 159.1; HRMS (MALDI-TOF): calcd. for $C_{25}H_{28}NaO_4$[M^+ +Na]: 415.1885; found: 415.1889.

Characterization data for compound **13**

$[\alpha]_D^{25}$= N/R (racemic);^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.15 (bs, 1H), 3.59-3.73 (m, 5H), 4.54 (s, 2H), 4.65 (dd, 2H, *J* = 10.1, 12.0 Hz), 7.24-7.36 (m, 10H); ^{13}C NMR (50.32 MHz, $CDCl_3$): 62.8, 70.1, 72.1, 73.5, 78.0, 127.6-128.4, 137.9, 138.2; HRMS (MALDI-TOF): calcd. for $C_{17}H_{20}NaO_3$[M^+ Na]: 295.1310; found: 295.1318.

Characterization data for compound **14**

$[\alpha]_D^{25}$ = N/R (racemic);^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.50-3.57 (m, 3H), 3.65-3.87 (m, 7H), 4.00 (m, 1H), 4.46-4.52 (m, 4H), 4.59-4.70 (m,7H), 4.86-4.90 (m, 2H), 7.15-7.36 (m, 30H); ^{13}C NMR (100.53 MHz, $CDCl_3$): 67.2, 69.0, 69.8, 71.7, 72.1, 72.2, 72.4, 73.2, 73.3, 74.6, 74.8, 75.0, 76.7, 79.9, 98.0, 127.4-128.3, 138.1, 138.3, 138.3, 138.3, 138.5, 138.6; HRMS (MALDI-TOF): calcd. for $C_{51}H_{54}NaO_8$ [M^+ +Na]: 817.3716; found: 817.3723.

Characterization data for compound **15j** [2]

$[\alpha]_D^{25}$ = +28.2 ($CHCl_3$, *c* 1.00); ^{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.

Characterization data for compound **15k**

$[\alpha]_D^{25}$ = -11.9 ($CHCl_3$, *c* 1.00); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.07-1.90 (m, 10H), 3.50 (t, 1H, *J* = 2.0 Hz), 3.68 (dd, 1H, *J* = 0.8, 10.3 Hz), 3.82 (dd, 1H, *J* = 3.7, 10.3 Hz), 3.92 (m, 3H), 4.59 (ABq, 2H, *J* = 12.1 Hz), 4.63 (ABq, 2H, *J* = 11.8 Hz), 4.68 (s, 2H), 4.71 (ABq, 2H, *J* = 10.6 Hz), 4.97 (d, 1H, *J* = 1.8 Hz), 5.03 (dd, 1H, *J* = 1.2, 7.2 Hz), 5.01 (s, 1H), 5.65 (m, 1H), 7.15-7.37 (m, 20H); ^{13}C NMR (50.32 MHz, $CDCl_3$):δ 21.9, 21.9, 25.5, 33.9, 35.4, 69.3, 72.0, 72.1, 72.2, 73.3, 75.1, 75.2, 75.6, 77.9, 79.8, 92.6, 115.1, 127.3-128.3, 138.3, 138.5, 138.5, 138.5, 142.7; HRMS (MALDI-TOF): calcd. for $C_{42}H_{48}NaO_6$ [M^++Na]: 671.3349; found: 671.3360.

Characterization data for compound **15l**

$[\alpha]_D^{25}$ = +48.2 ($CHCl_3$, *c* 1.00); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.68 (t, 3H, *J* = 7.9 Hz), 1.08-1.65 (m, 12H), 3.53 (t, 1H, *J* = 2.2 Hz), 3.68 (dd, 1H, *J* = 1.2, 9.5 Hz), 3.83 (dd, 1H, *J* = 3.3, 10.4 Hz), 3.98 (m, 3H), 4.60 (ABq, 2H, *J* = 12.0 Hz), 4.68 (ABq, 2H, *J* = 11.8 Hz), 4.68 (ABq, 2H, *J* = 10.3 Hz), 4.72 (ABq, 2H, *J* = 12.1 Hz), 4.98 (d, 1H, *J* = 1.9 Hz), 7.20-7.39 (m, 20H);^{13}C NMR (50.32 MHz, $CDCl_3$):δ 7.5, 21.9, 22.1, 25.7, 30.3, 33.6, 34.4, 69.3, 71.8, 72.4, 72.4, 73.3, 75.1, 75.2, 75.9, 78.4, 79.8, 91.4, 127.3-128.3, 138.4, 138.5, 138.6, 138.6; HRMS (MALDI-TOF): calcd. for $C_{42}H_{50}NaO_6$ [M^++Na]: 673.3505; found: 673.3507.

Characterization data for compound **17** [2]

$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) = -43.8; ^{1}H NMR (200.13 MHz, $CDCl_3$):δ 3.43 (s, 3H), 3.54–3.75 (m, 5H), 3.81-4.01(m 3H), 4.18 (m, 1H), 4.37 (d, 2H, *J* = 2.5 Hz), 4.49 (t, 2H, *J* = 10.3 Hz), 4.49 (ABq, 2H, *J* = 12.3 Hz), 4.68 (s, 2H), 4.95 (dd, 2H, *J* = 1.7, 5.6 Hz), 5.62 (dd, 1H, *J* = 1.8, 2.9

Hz), 5.89 (m, 2H),7.13–7.53 (m, 29H), 7.78–8.10 (m, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 55.4,66.7, 67.8, 68.9, 69.0, 69.9, 70.6, 71.7, 71.8, 72.4, 73.2, 74.6, 74.7, 75.0, 80.1, 98.1, 98.4, 127.3–129.8, 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 $C_{28}H_{26}NaO_9$[M^++Na]: $C_{62}H_{60}NaO_{14}$, 1051.3881; found, 1051.3889.

Characterization data for compound **20** [2]

$[\alpha]_D^{25}$ = +5.2 ($CHCl_3$, *c* 1.00); ^{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.

Characterization data for compound **24**

$[\alpha]_D^{25}$ = +26.5 ($CHCl_3$, *c* 1.00); ^{1}H NMR (200.13 MHz): δ 1.26-1.73 (m, 10H), 2.41 (s, 1H), 3.61-4.01 (m, 12H), 4.43-4.69 (m, 12H), 4.87 (dd, 2H, *J* = 3.1, 10.8 Hz), 5.11 (d, 1H, *J* = 1.3 Hz), 5.46 (d, 1H, J = 1.8 Hz), 7.11-7.41 (m, 35H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 22.6, 22.6, 25.0, 37.6, 38.1, 66.3, 69.0, 71.4, 71.6, 71.9, 72.1, 72.3, 72.3 73.1, 74.2, 74.5, 74.6, 74.8, 74.9, 75.0, 75.3, 75.3, 79.4, 79.9, 84.4, 93.9, 98.1, 127.2-128.4, 138.2, 138.3, 138.3, 138.4, 138.4, 138.4, 138.6; HRMS (MALDI-TOF): calcd. for $C_{69}H_{74}NaO_{11}$ [M^++Na]: 1101.5129; found: 1101.5134.

Characterizationdataforcompound**25**

$[\alpha]_D^{25}$ = -10.6 ($CHCl_3$, *c* 1.00); ^{1}H NMR (500.13 MHz, $CDCl_3$):δ 3.42 (s, 3H), 3.51-3.69 (m, 8H), 3.80 (dd, 1H, *J* = 3.9, 11.6 Hz), 3.84-3.88 (m, 4H), 3.95 (dt, 2H, *J* = 9.4, 25.7 Hz), 4.14 (dt, 1H, *J* = 4.2, 9.6 Hz), 4.35-4.4.62 (m, 8H), 4.41 (ABq, 2H, *J* = 11.0 Hz), 4.61 (s, 2H), 4.84 (ABq, 2H, *J* = 11.0 Hz), 4.88 (d, 1H, *J* = 1.5 Hz), 4.90 (d, 1H, *J* = 1.5 Hz), 5.03 (t, 1H, *J* = 10.0 Hz), 5.06 (d, 1H, *J* = 1.3 Hz), 5.84 (dd, 1H, *J* = 3.3, 10.2 Hz), 7.11-7.51 (m, 44H), 7.81-8.08 (m, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 55.4, 65.6, 66.6, 69.0, 69.1, 69.8, 70.6, 71.3, 71.7, 71.7, 71.7, 71.7, 72.2, 72.7, 73.2, 74.2, 74.6, 74.8, 74.9, 74.9, 75.0, 79.2, 80.2, 98.1, 98.2, 98.4, 127.2-129.8, 133.1, 133.3, 133.5, 138.3, 138.3, 138.4, 138.4, 138.6, 138.6, 138.7, 165.3, 165.4, 165.5; HRMS (MALDI-TOF): calcd. for $C_{89}H_{88}NaO_{19}$ [M^++Na]: 1483.5818; found: 1483.5837.

Characterization data for compound **26**

$[\alpha]_D^{25}$ = +20.3 ($CHCl_3$, *c* 1.00); ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.42-1.75 (m, 10H), 2.34 (s, 1H), 3.43 (ddd, 1H, *J* = 1.8, 4.3, 9.0 Hz), 3.49-3.76 (m, 7H), 3.97 (m, 2H), 4.08 (t, 1H, *J* = 9.6 Hz), 4.23 (dd, 1H, *J* = 1.4, 3.5, Hz), 4.48-4.83 (m, 8H), 4.54 (ABq, 2H, *J* = 7.8 Hz), 4.58 (s, 2H), 4.80 (d, 1H, *J* = 2.9 Hz), 5.02 (ABq, 2H, *J* = 11.1 Hz), 5.57 (d, 1H, *J* = 1.7 Hz), 7.16-7.40 (m, 35H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 22.7, 22.7, 24.9, 37.5, 38.2, 68.8, 69.0, 71.7, 71.9, 72.2, 73.3, 74.1, 74.8, 74.8, 74.9, 74.9, 75.0, 75.2, 75.5, 75.6, 77.9, 79.8, 82.1, 84.5, 84.7, 94.0, 104.0, 127.3-129.5, 138.1. 138.2, 138.4, 138.5, 138.6, 138.6, 138.7; HRMS (MALDI-TOF): calcd. for $C_{69}H_{74}NaO_{11}$ [M^++Na]: 1101.5129; found: 1101.5138.

Characterization data for compound **27**

$[\alpha]_D^{25}$ = +19.3 ($CHCl_3$, *c* 1.00); ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.58 (d, 2H *J* = 6.7 Hz), 0.73 (m, 2H), 0.81 (t, 6H, *J* = 7.4Hz), 0.93 (t, 1H, *J* = 12.0 Hz), 1.06 (t, 1H, *J* = 10.7 Hz), 1.23 (t, 1H, *J* = 7.0 Hz), 1.51 (m, 2H), 1.59 (s, 2H), 1.73 (m, 1H), 2.08 (d, 1H, *J* = 12.4 Hz),

3.16 (dt, 1H, *J* = 4.4, 14.8, Hz), 3.42-4.04 (m, 11H), 4.27-5.11 (m, 11H), 4.64 (ABq, 2H, *J* = 11.1 Hz), 4.87 (d, 1H, *J* = 1.4 Hz), 5.02 (ABq, 2H, *J* = 10.8 Hz), 7.15-7.42 (m, 35H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 16.1, 21.0, 22.2, 23.0, 25.5, 31.5, 34.1, 42.8, 48.7, 69.0, 69.2, 71.1, 72.0, 72.4, 73.4, 74.1, 74.9, 74.9, 75.0, 75.0, 75.1, 75.7, 77.8, 80.1, 80.6, 82.2, 84.6, 99.8, 104.2, 127.4-128.5, 138.1, 138.1, 138.2, 138.5, 138.6, 138.6, 138.6; HRMS (MALDI-TOF): calcd. for $C_{71}H_{82}NaO_{11}$ [M^++Na]: 1133.5755; found: 1133.5763.

Characterizationdataforcompound**29**

$[\alpha]_D^{25}$ = +18.4 ($CHCl_3$, *c* 1.00); ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.54 (t, 2H, *J* = 7.2 Hz), 1.59 (s, 2H), 1.99 (m, 2H), 3.26-3.98 (m, 12H), 4.25-5.06 (m, 18H), 5.73 (m, 1H), 7.15-7.37 (m, 35H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.4, 30.2, 66.8, 68.9, 69.0, 71.3, 72.0, 72.6, 73.4, 74.7, 74.7, 74.9, 74.9, 74.9, 75.0, 75.7, 77.8, 80.2, 82.0, 84.6, 97.7, 104.0, 114.8, 126.9-128.5, 137.9, 138.1, 138.2, 138.3, 138.5, 138.5, 138.6 ; HRMS (MALDI-TOF): calcd. for $C_{66}H_{72}NaO_{11}$ [M^++Na]: 1063.4972; found: 1063.4994.

Characterization data for compound **31**

$[\alpha]_D^{25}$ = +23.1 ($CHCl_3$, *c* 1.00); ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.17 (s, 3H), 3.25-3.94 (m, 17H), 4.11 (dd, 1H, *J* = 1.8, 9.1 Hz), 4.24-4.96 (m, 23H), 7.04-7.32 (m, 50H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.0, 65.6, 68.7, 69.0, 69.8, 71.3, 71.8, 72.5, 73.2, 73.4, 73.4, 74.5, 74.6, 74.7, 74.8, 74.9, 74.9, 74.9, 74.9, 77.5, 77.8,79.5, 79.9, 82.0, 82.0, 84.6, 97.6, 98.1, 104.0, 127.3-128.4, 138.1, 138.1, 138.1, 138.2, 138.3, 138.3, 138.5, 138.6, 138.6, 138.7; HRMS (MALDI-TOF): calcd. for $C_{89}H_{94}NaO_{16}$ [M^++Na]: 1441.6440; found: 1441.6457.

Characterization data for compound **32**

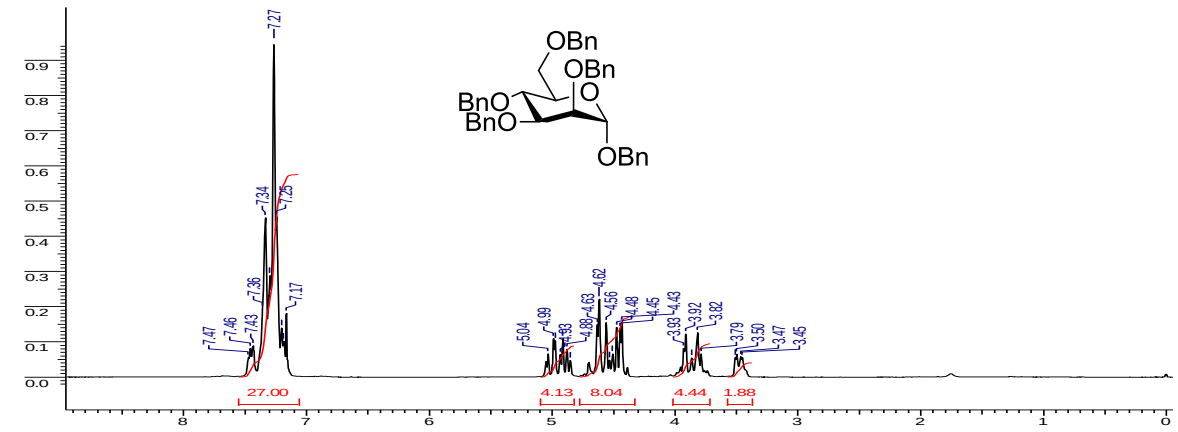
$[\alpha]_D^{25}$ = +11.5 ($CHCl_3$, *c* 1.00); ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.25-1.72 (m, 10H), 1.99-2.03 (4s, 12H), 2.42 (s, 1H), 3.58 (dq, 1H, *J* = 2.5, 9.6 Hz), 3.71 (m, 2H), 3.80 (m, 1H), 3.92

(dd, 2H, *J* = 2.7, 9.1 Hz), 4.12 (m, 2H), 4.22 (dd, 1H, *J* = 4.6, 12.6 Hz), 4.53 (ABq, 2H, *J* = 7.8 Hz), 4.57 (s, 2H), 4.71 (ABq, 2H, *J* = 12.8 Hz), 4.95-5.16 (m, 4H), 5.48 (d, 1H, *J* = 1.6 Hz), 7.26-7.38 (m, 15H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 20.5, 20.5, 20.6, 20.6, 22.6, 22.7, 25.0, 37.5, 38.2, 61.9, 68.3, 69.0, 71.1, 71.6, 71.7, 72.0, 72.2, 73.0, 74.3, 74.7, 74.9, 75.0, 75.7, 79.7, 84.4, 93.8, 100.7, 125.5-128.4, 138.2, 138.3, 138.4, 169.1, 169.3, 170.3, 170.7; HRMS (MALDI-TOF): calcd. for $C_{49}H_{58}NaO_{15}$ [M^++Na]: 909.3673; found: 909.3678.

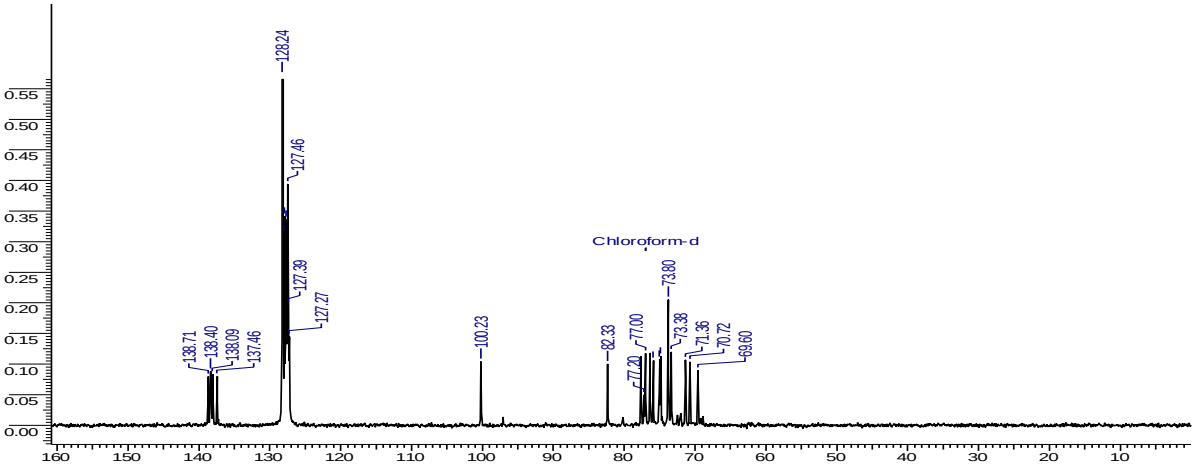
Characterization data for compound **33**

$[\alpha]_D^{25}$ = -63.8 ($CHCl_3$, *c* 1.00); ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.95 (s, 3H), 1.99 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 3.50-4.21 (m, 13H), 4.33-4.37 (m, 3H), 4.52 (d, 1H, *J* = 11.4 Hz), 4.58 (s, 2H), 4.90-4.96 (m, 3H), 5.01 (t, 1H, *J* = 9.8 Hz), 5.03 (t, 1H, *J* = 10.1Hz), 5.13 (t, 1H, *J* = 9.4 Hz), 5.63 (dd, 1H, *J* = 1.8, 3.2 Hz), 5.84 (dd, 1H, *J* = 3.2, 9.8 Hz), 7.23-7.54 (m, 24H), 7.81-8.11 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 20.5, 20.5, 20.6, 20.6, 55.4, 61.8, 66.6, 67.8, 68.3, 68.7, 69.1, 69.9, 70.5, 71.0, 71.1, 71.5, 71.5, 72.5, 72.8, 74.4, 74.6, 74.8, 80.1, 98.0, 98.4, 100.9, 127.4-129.8, 133.0, 133.3, 133.4, 138.2, 138.3, 138.5, 165.3, 165.4, 165.5, 169.0, 169.4, 170.3, 170.6 ; HRMS (MALDI-TOF): calcd. for $C_{69}H_{72}NaO_{23}$ [M^++Na]: 1291.4362; found: 1291.4377.

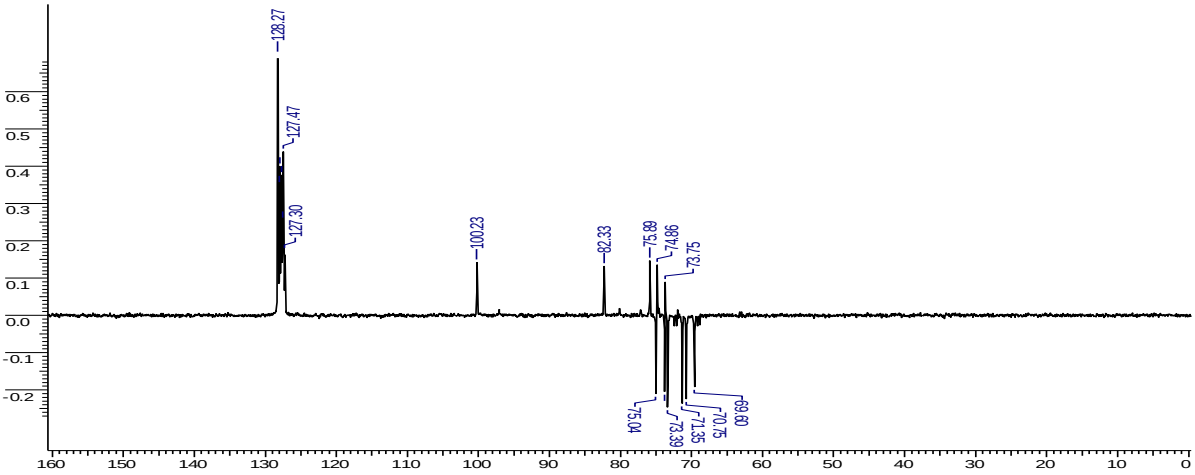
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **6**



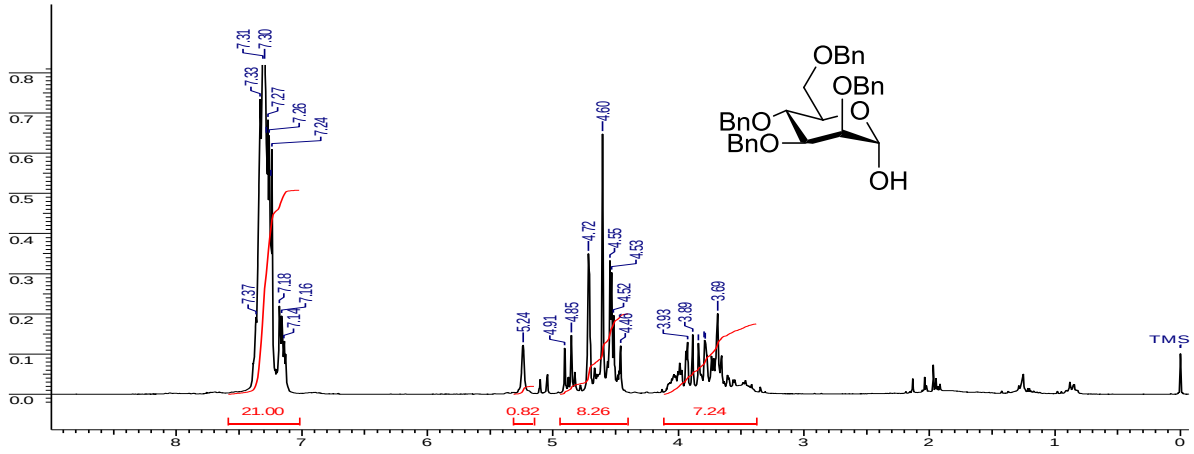
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **6**



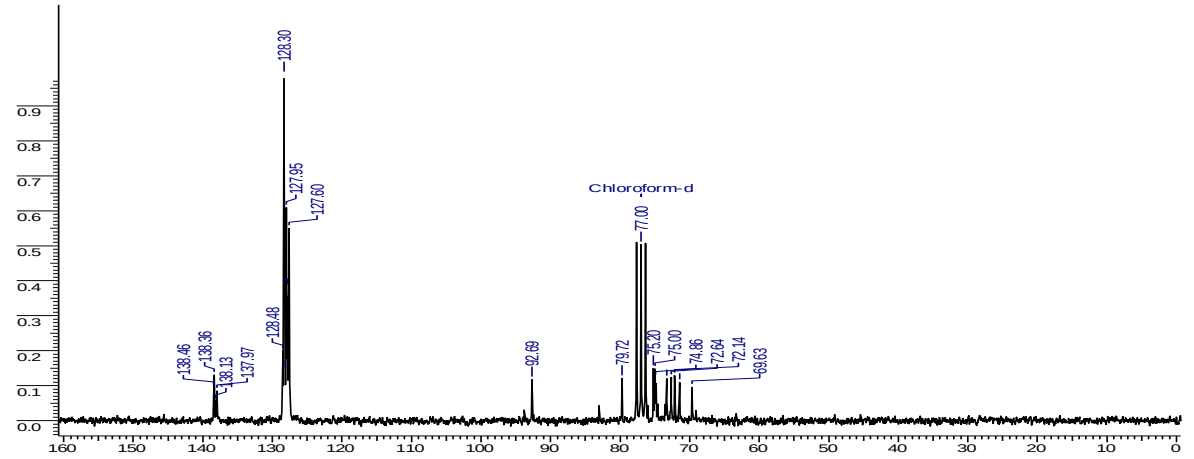
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **6**



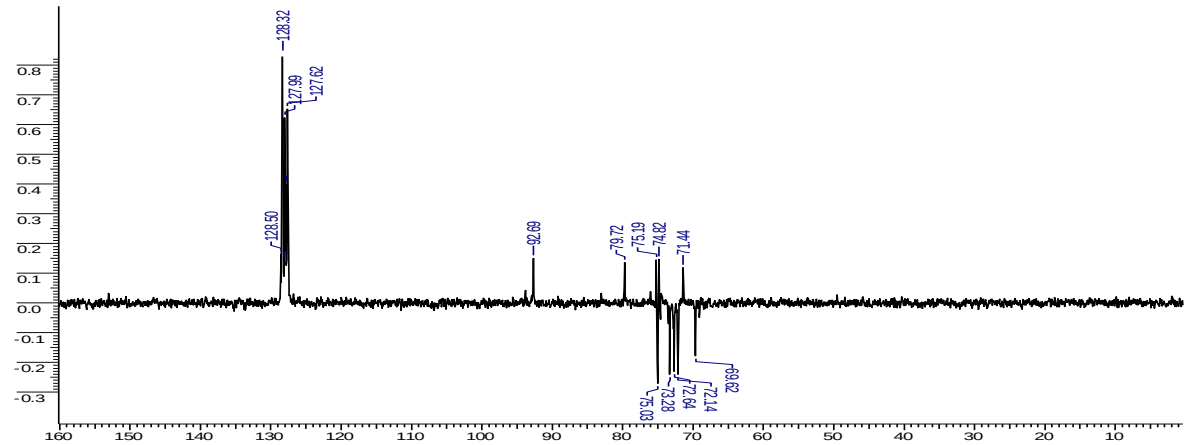
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **7**



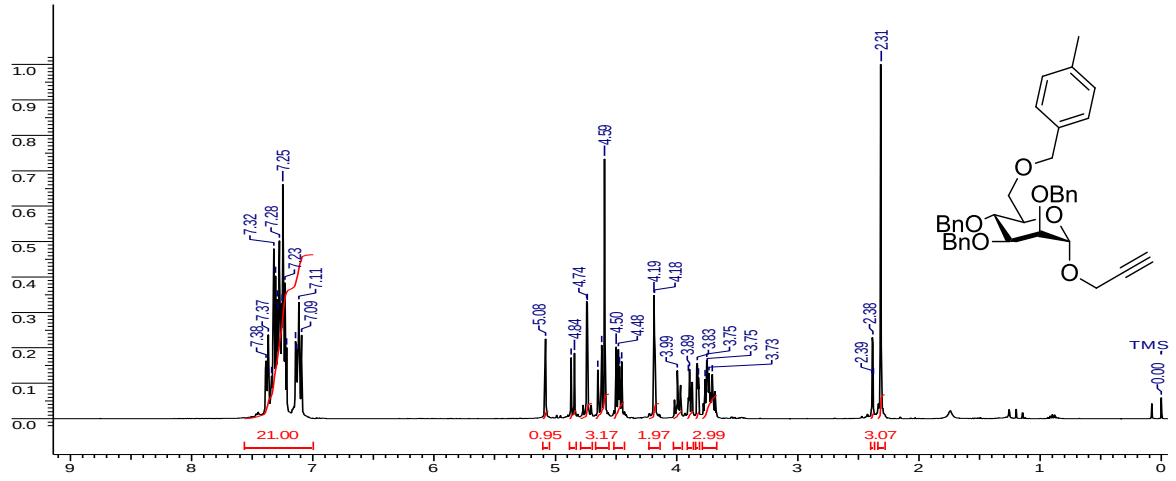
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **7**



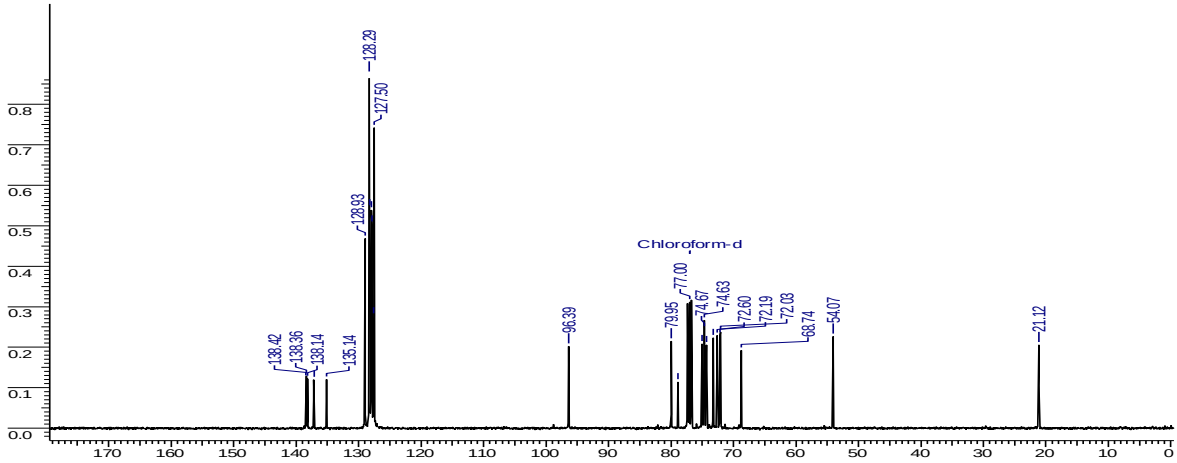
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **7**



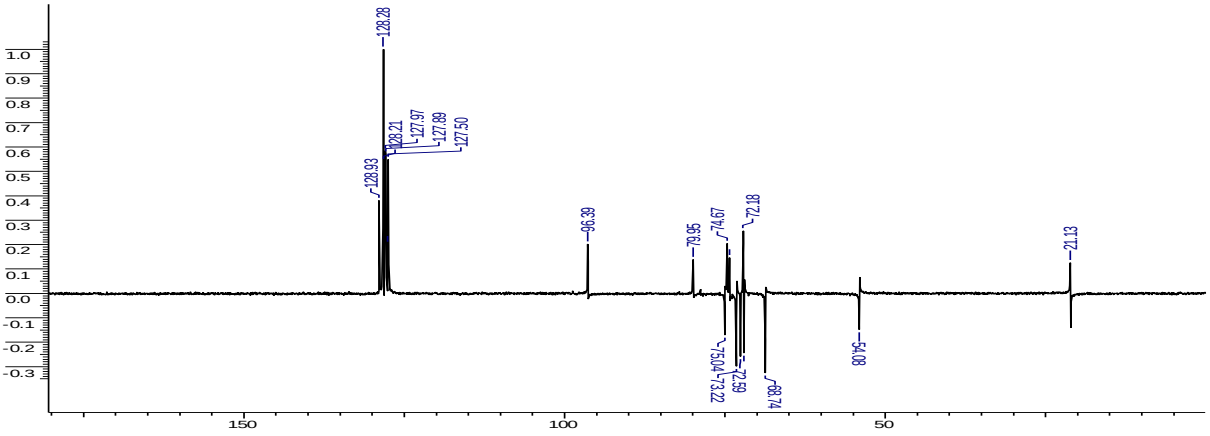
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **8**



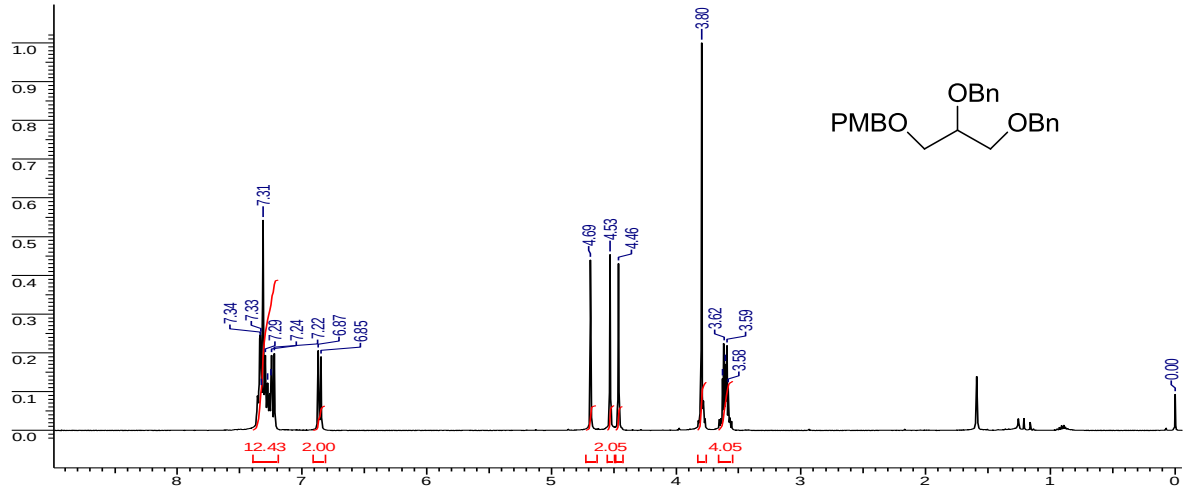
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **8**



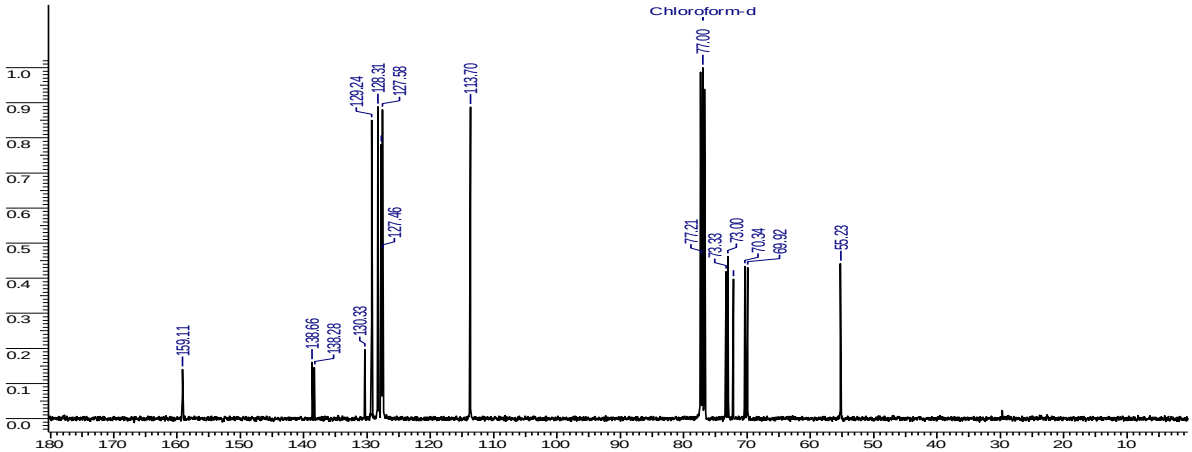
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **8**



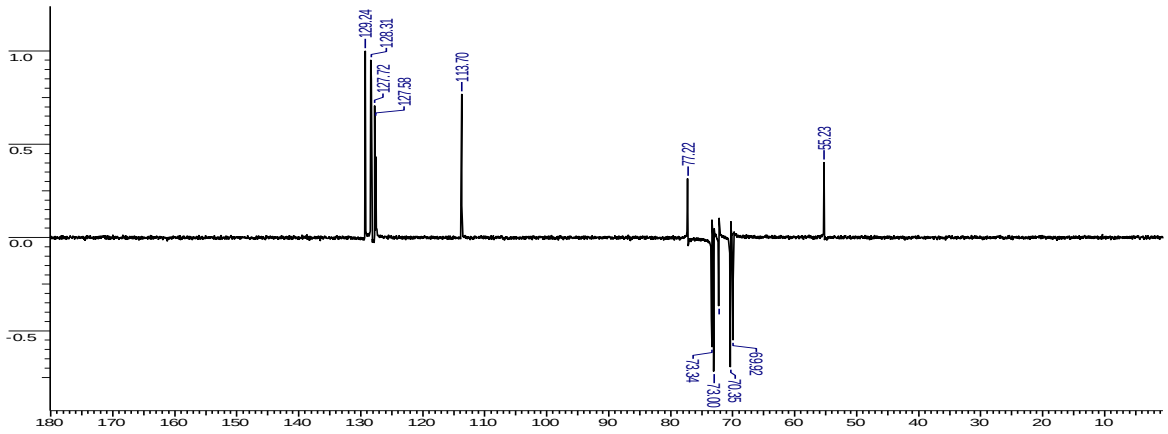
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **12**



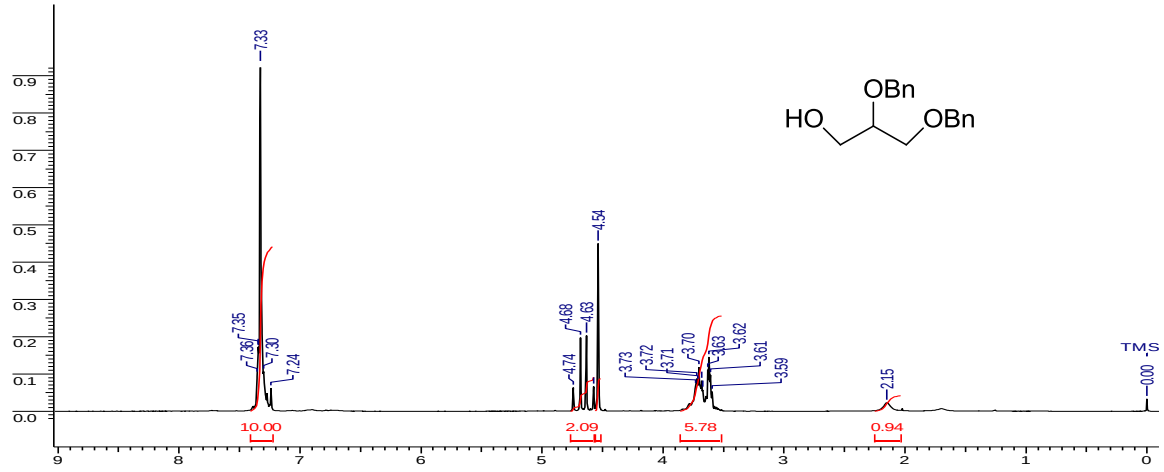
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **12**



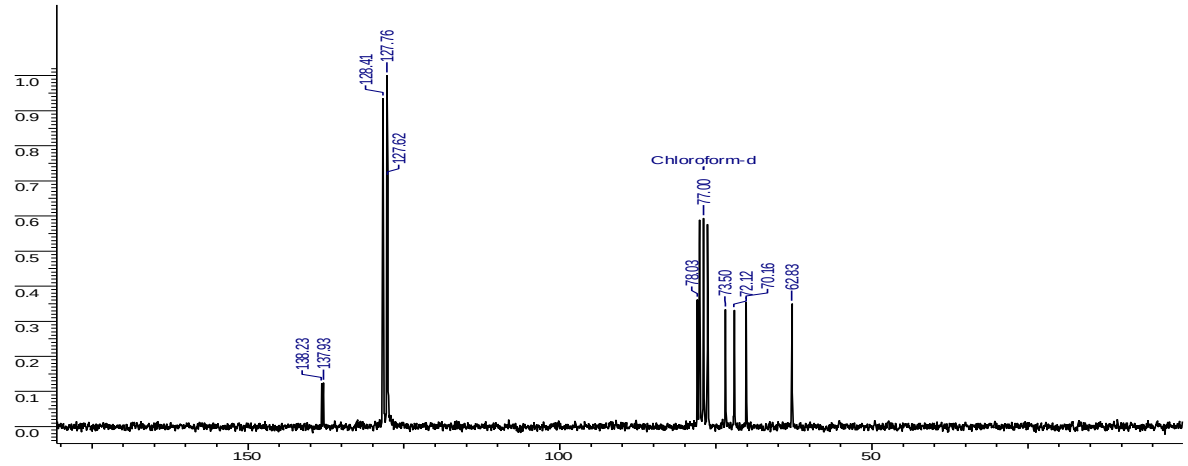
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **12**



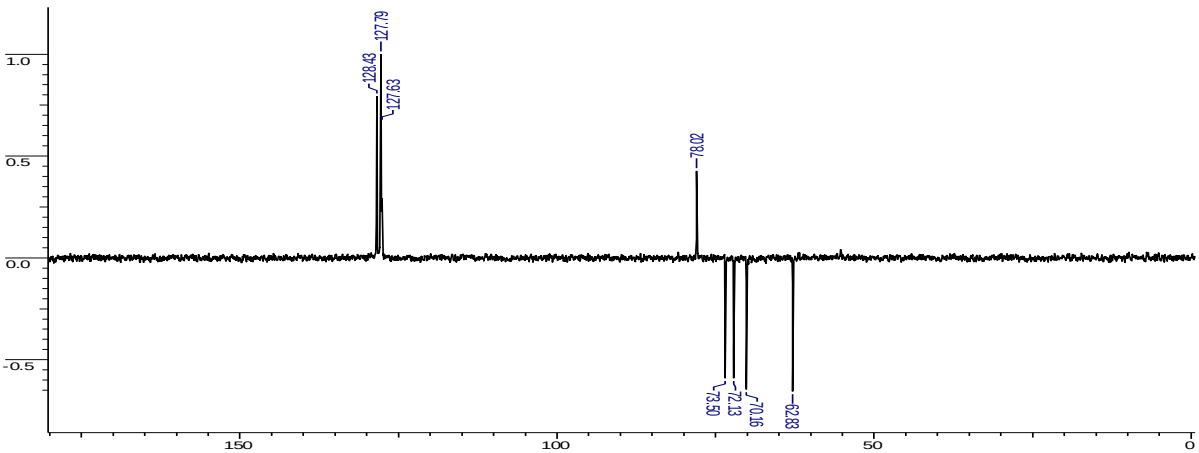
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **13**



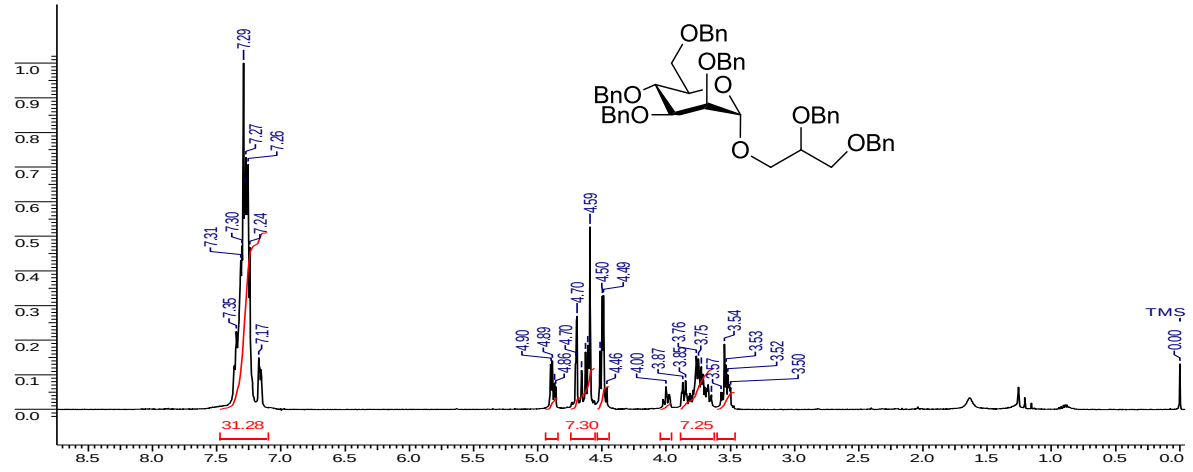
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **13**



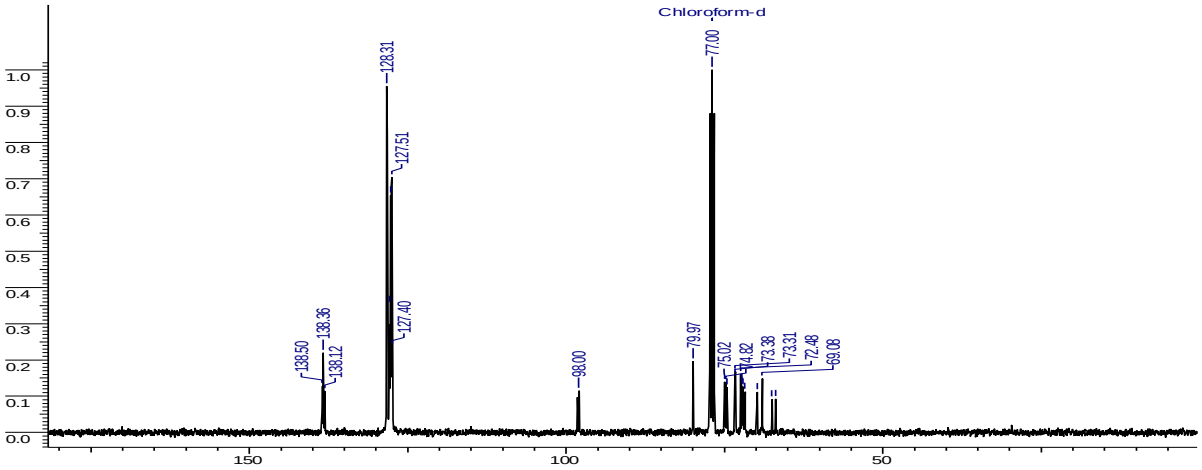
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **13**



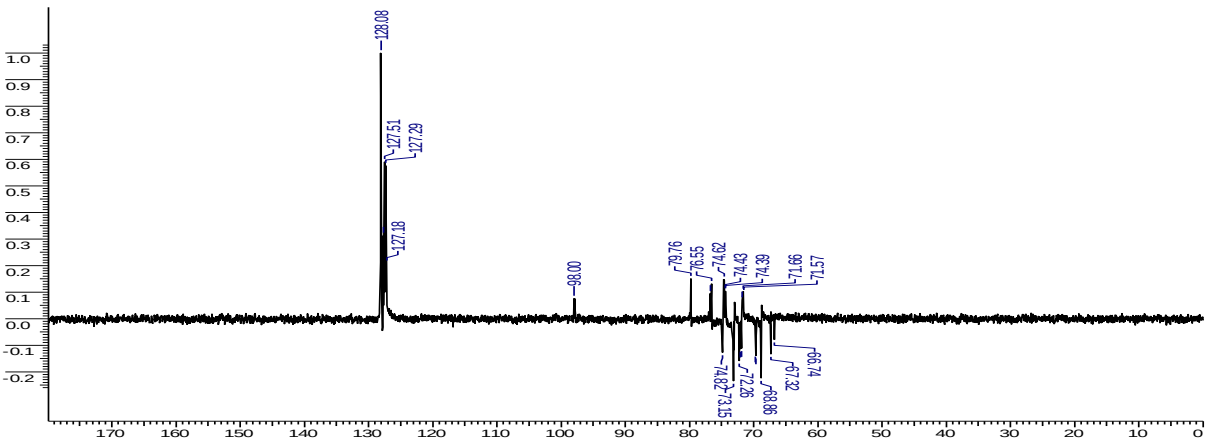
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **14**



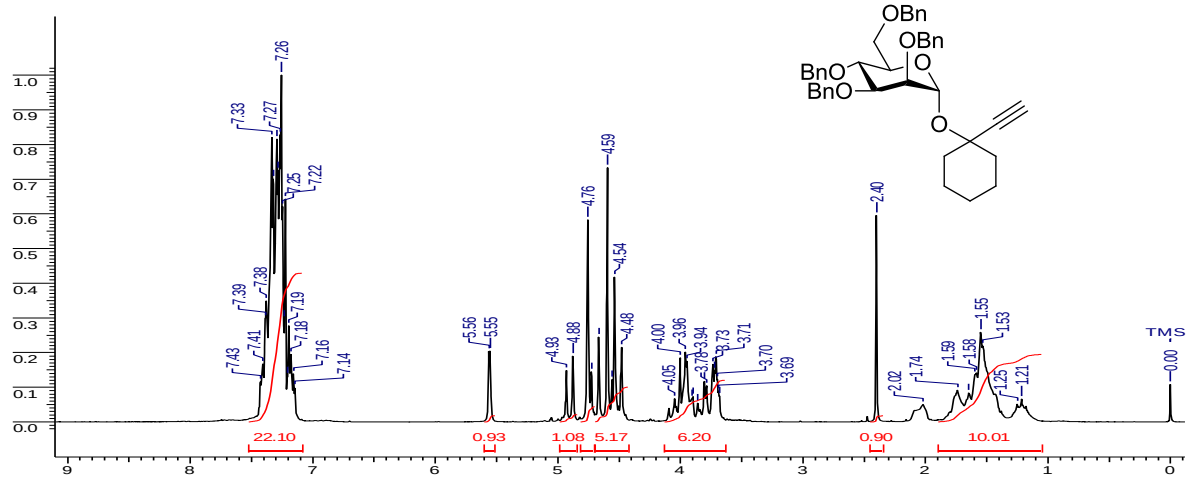
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **14**



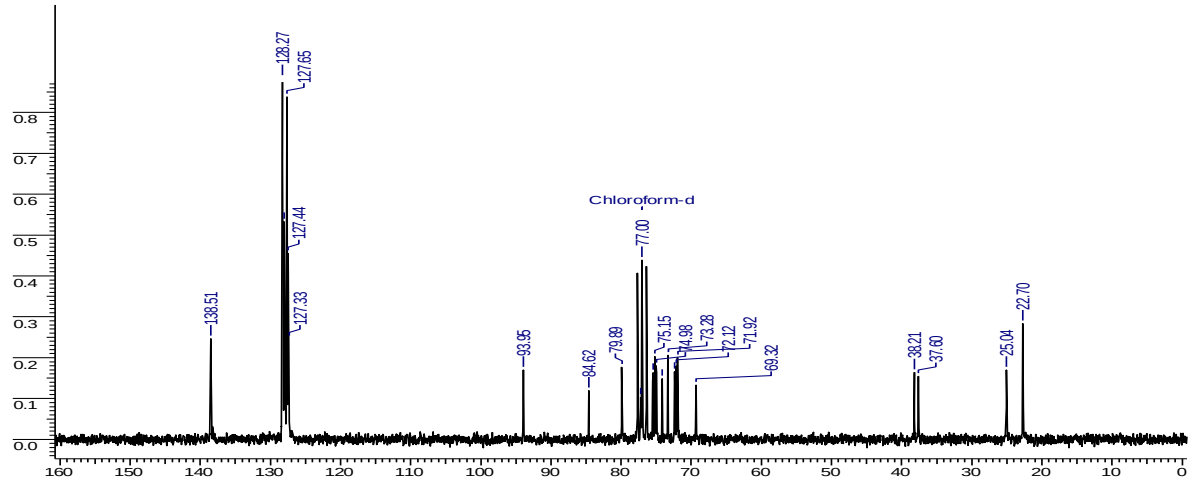
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **14**



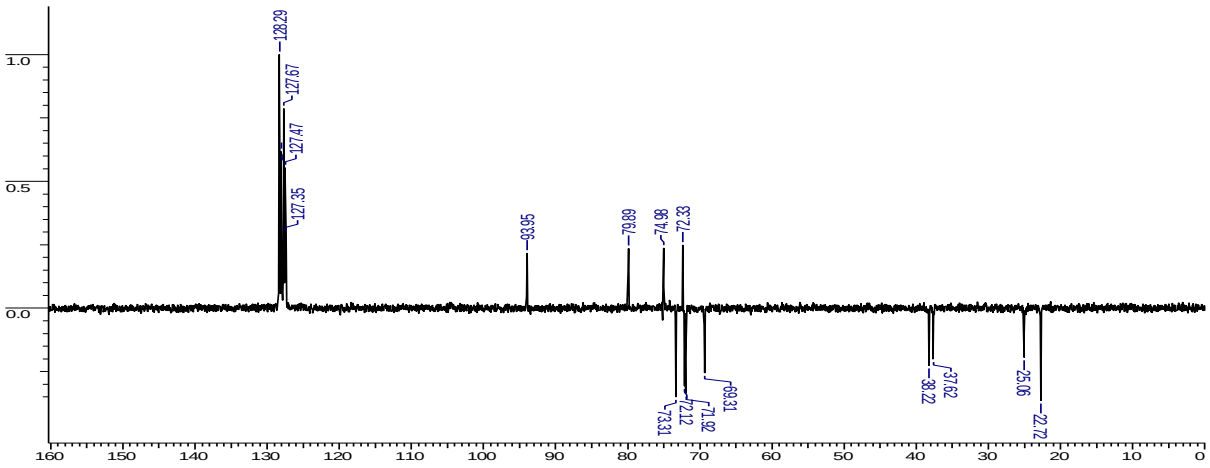
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **15j**



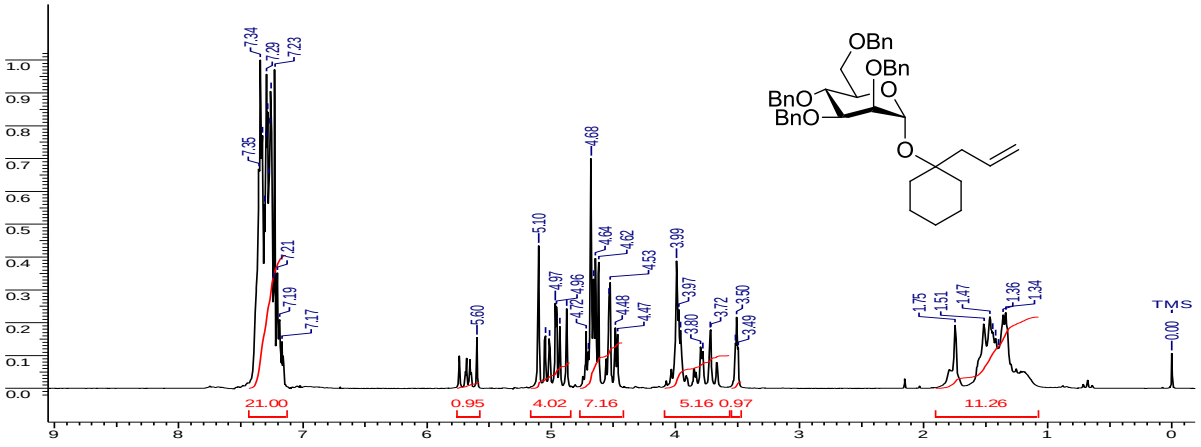
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **15j**



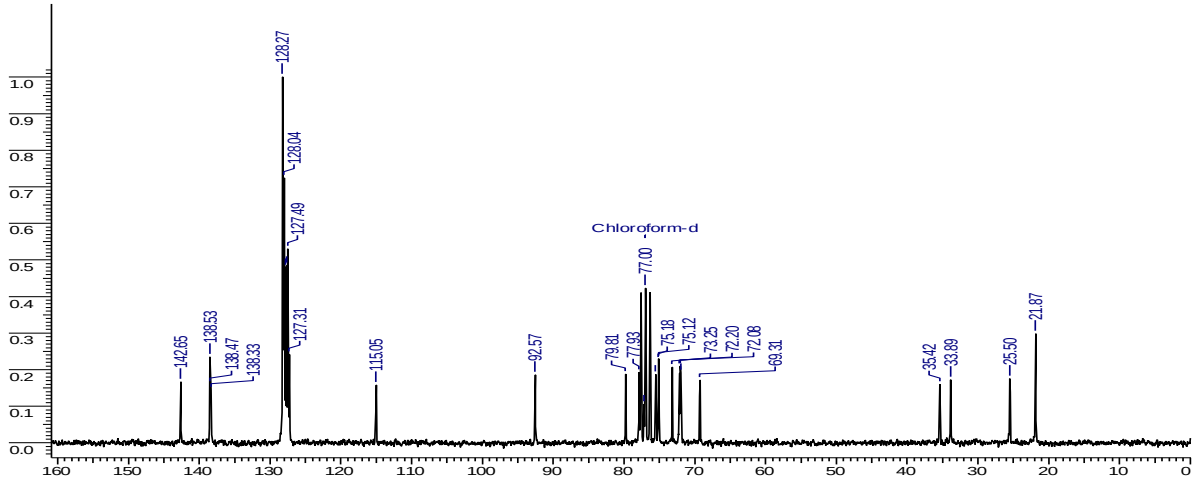
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **15j**



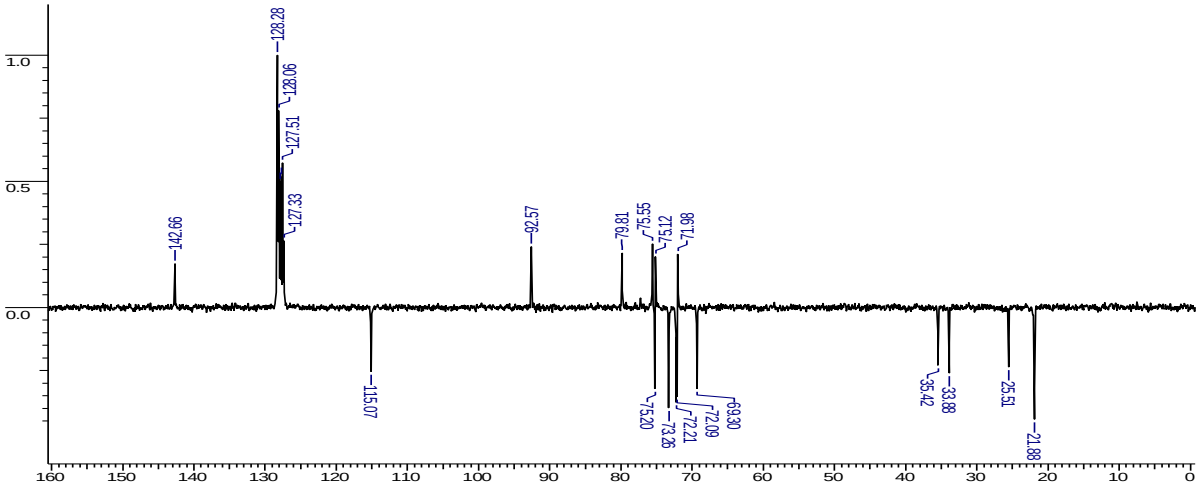
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **15k**



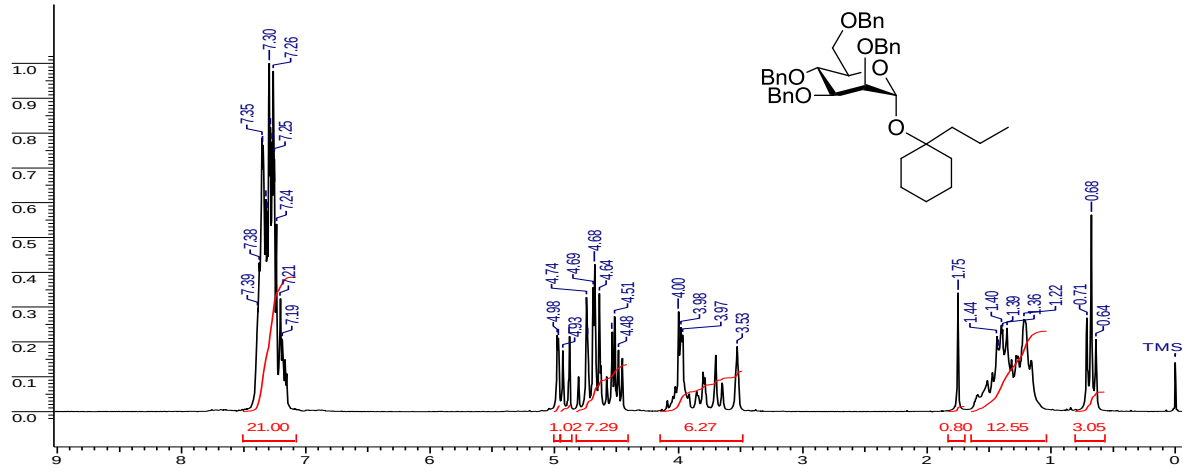
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **15k**



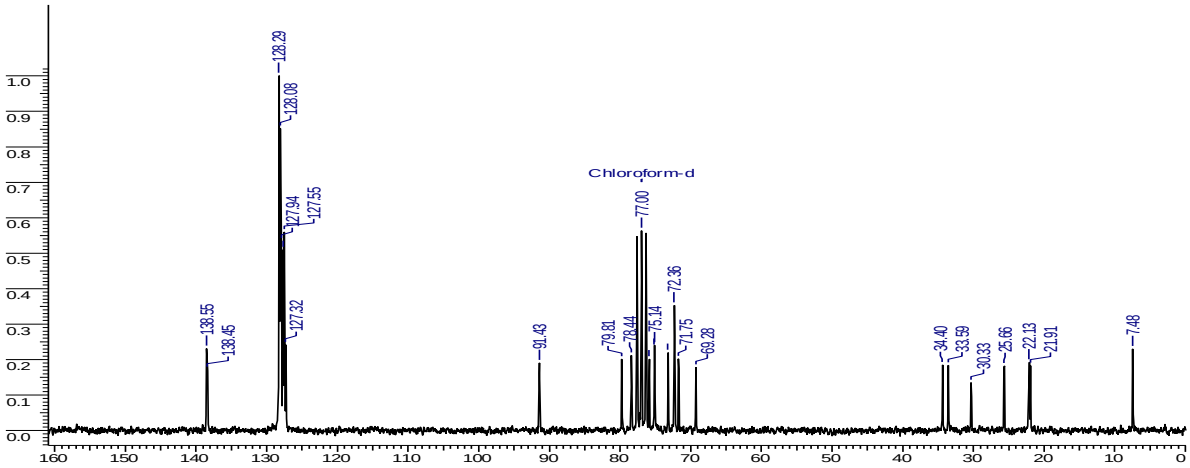
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **15k**



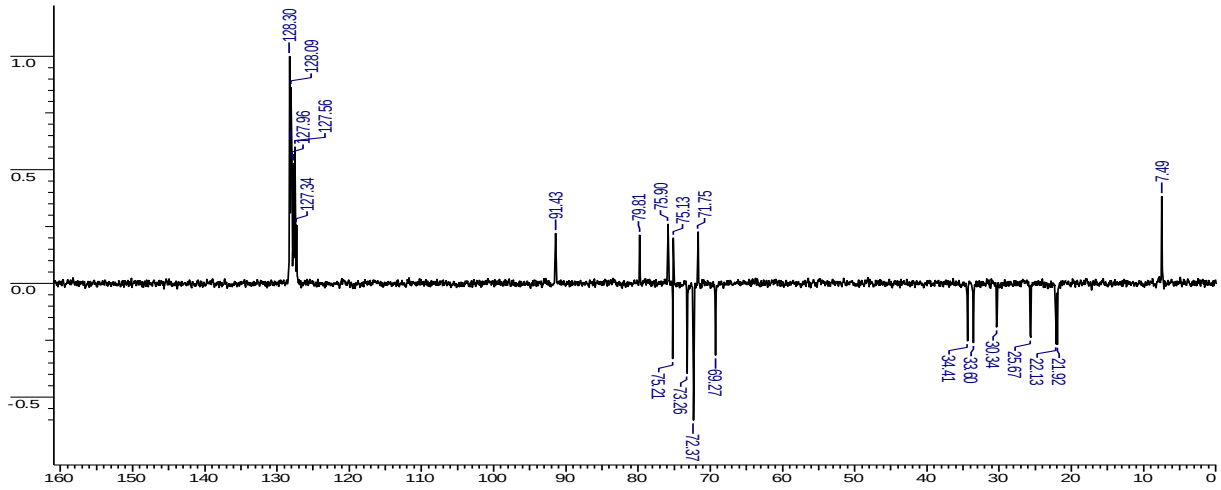
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **15l**



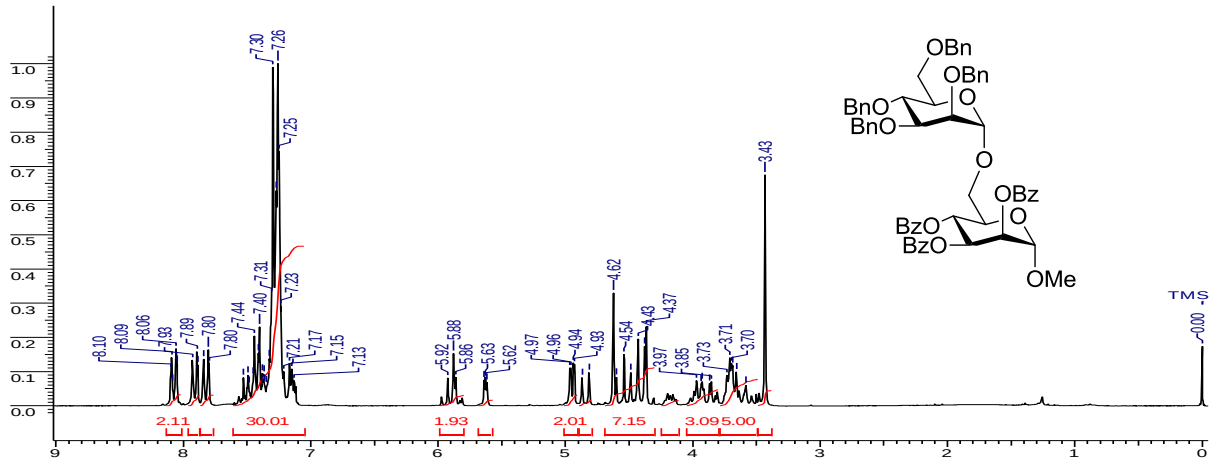
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **15l**



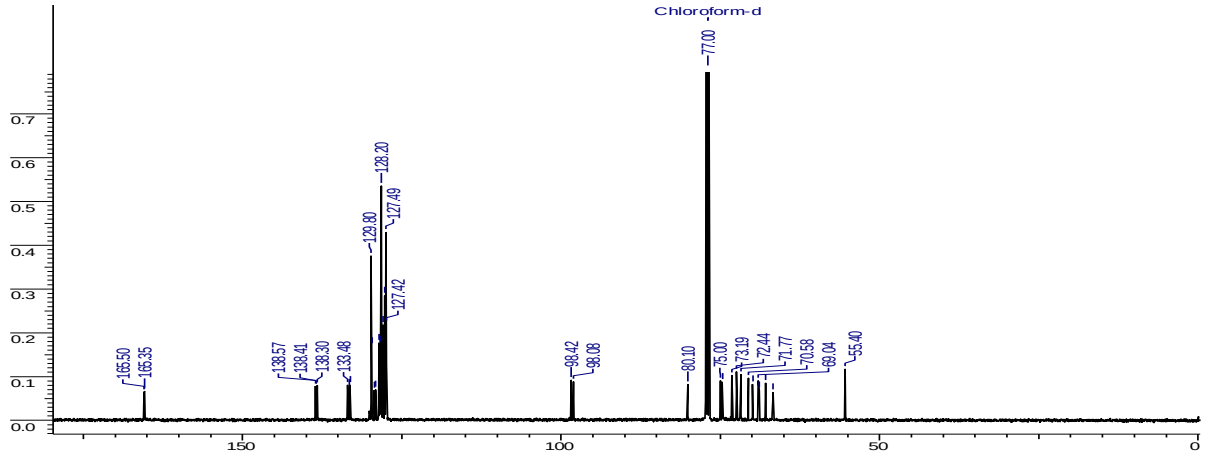
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **15l**



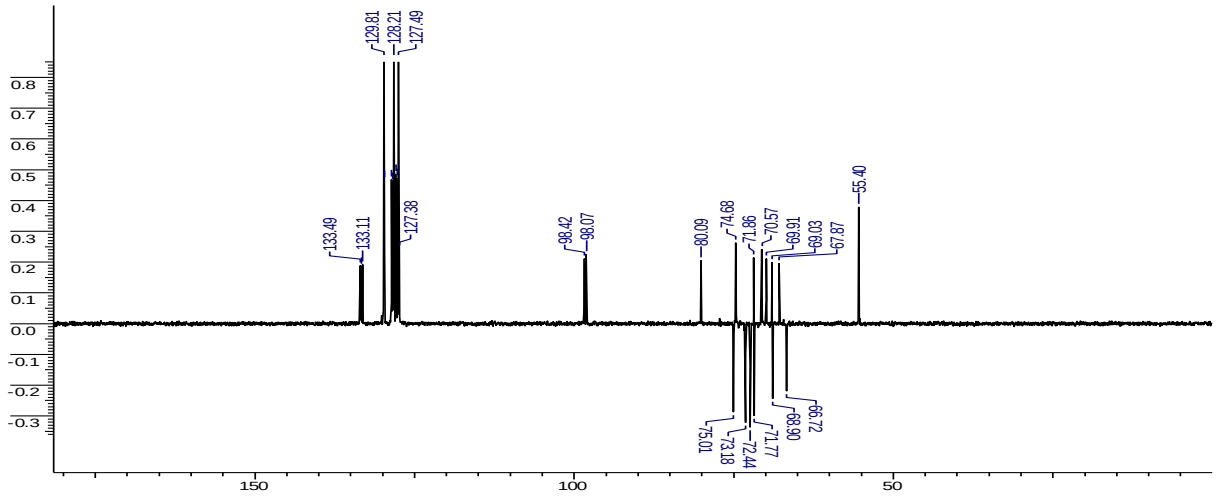
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **17**



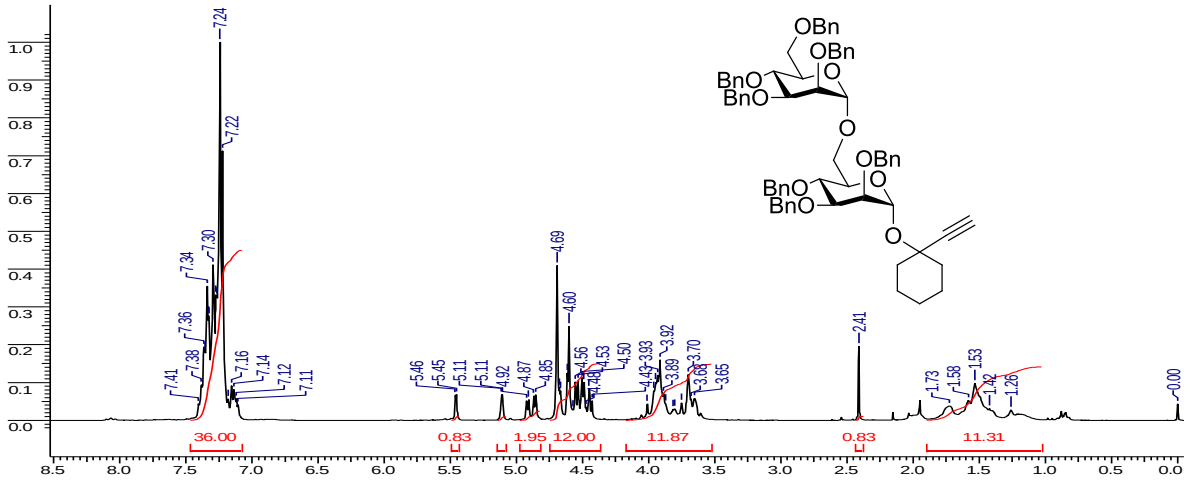
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **17**



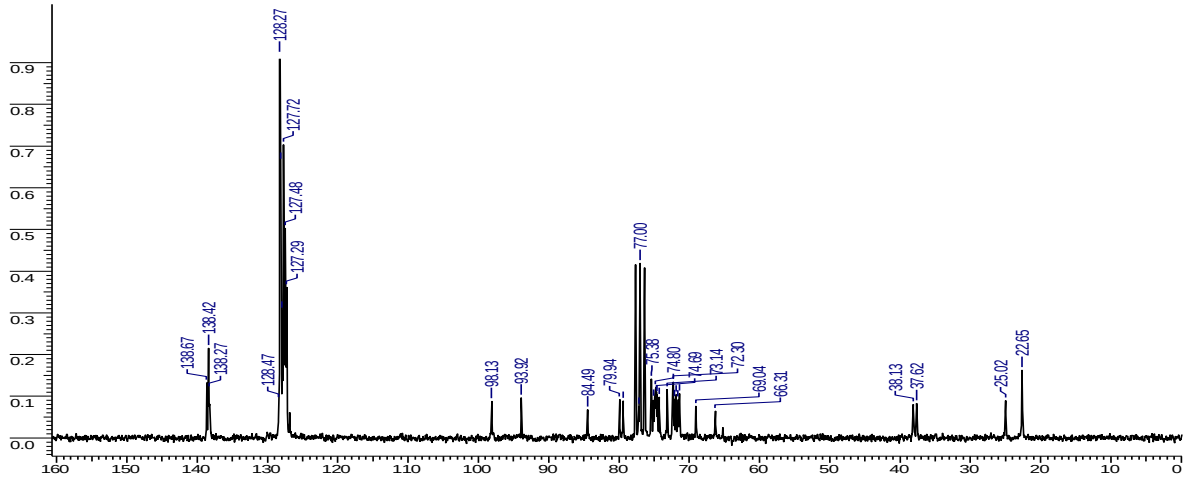
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **17**



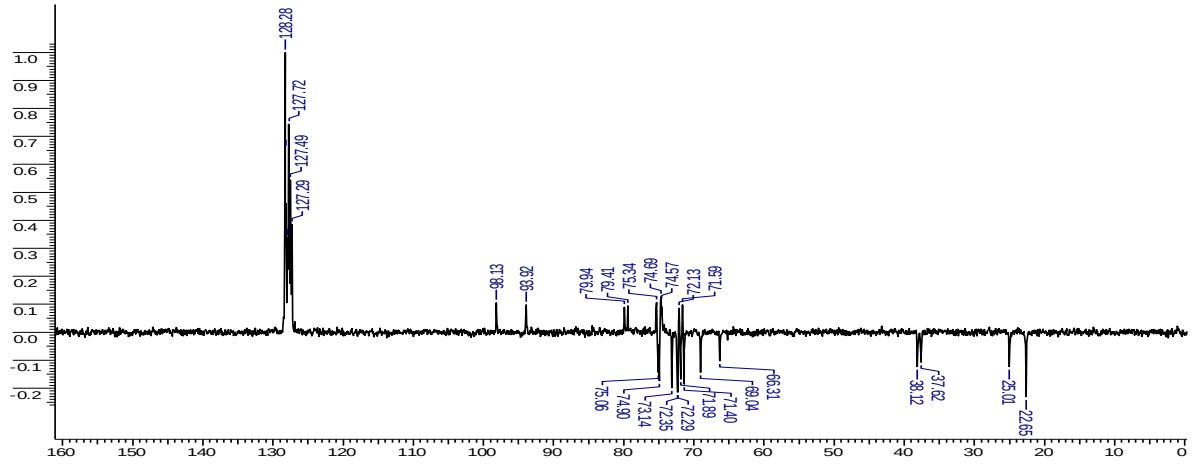
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **24**



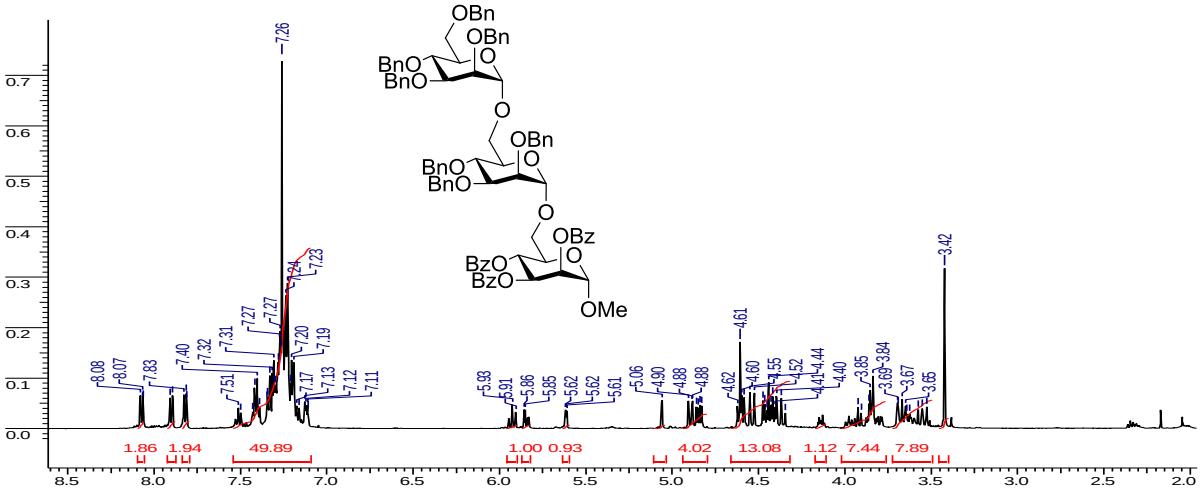
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **24**



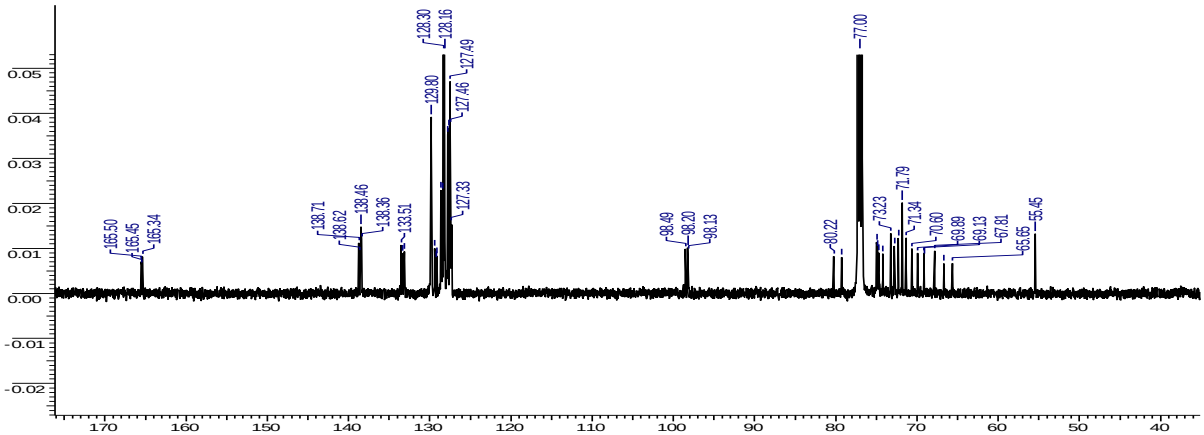
DEPT NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **24**



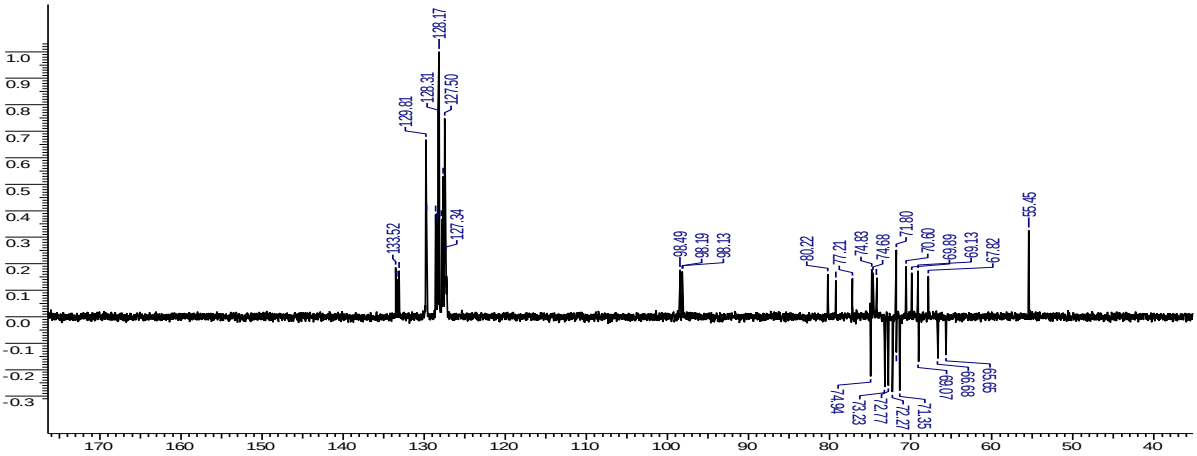
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **25**



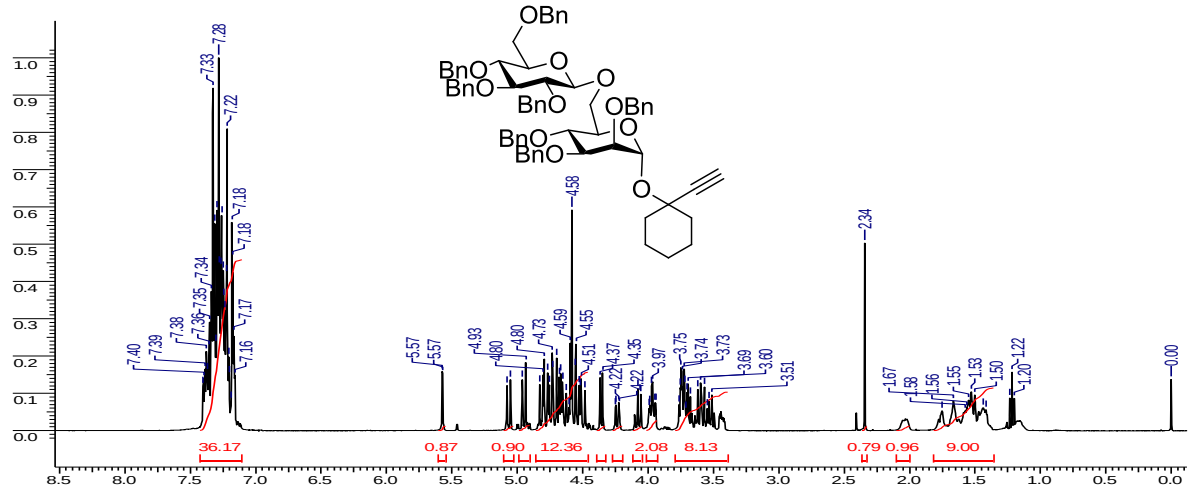
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **25**



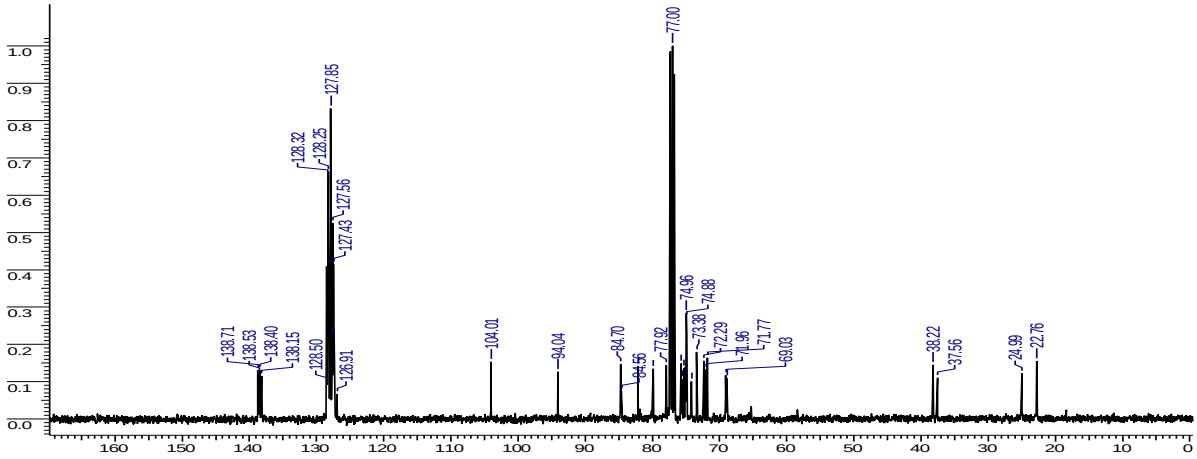
DEPT NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **25**



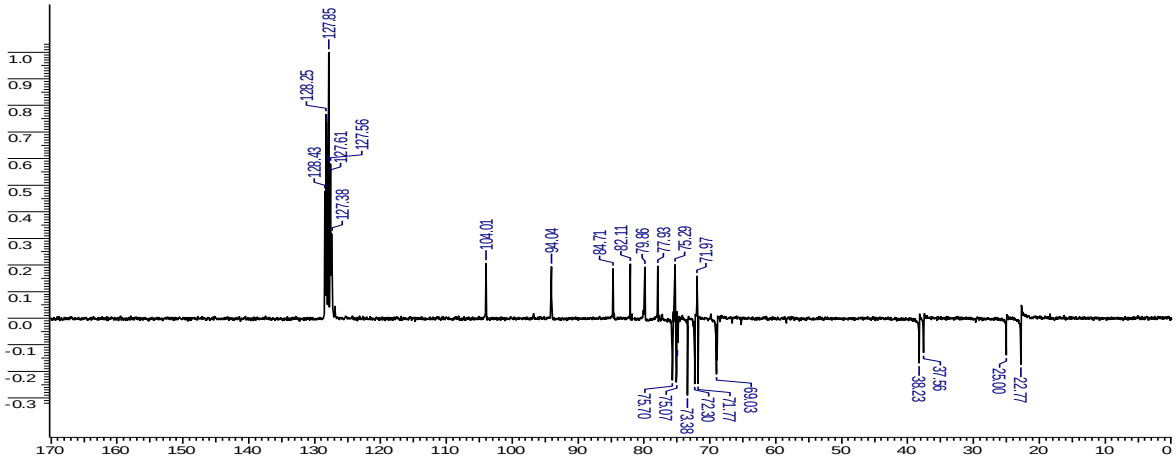
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **26**



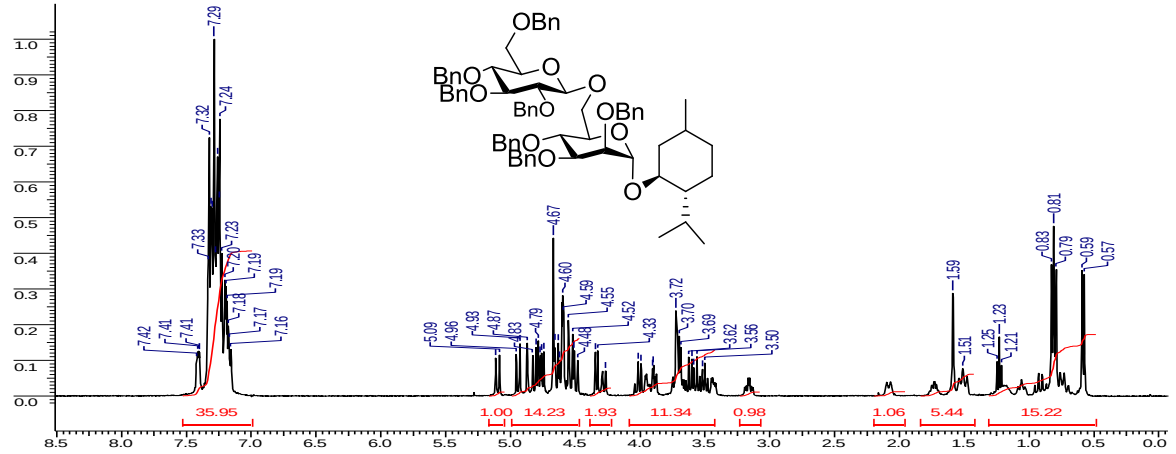
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **26**



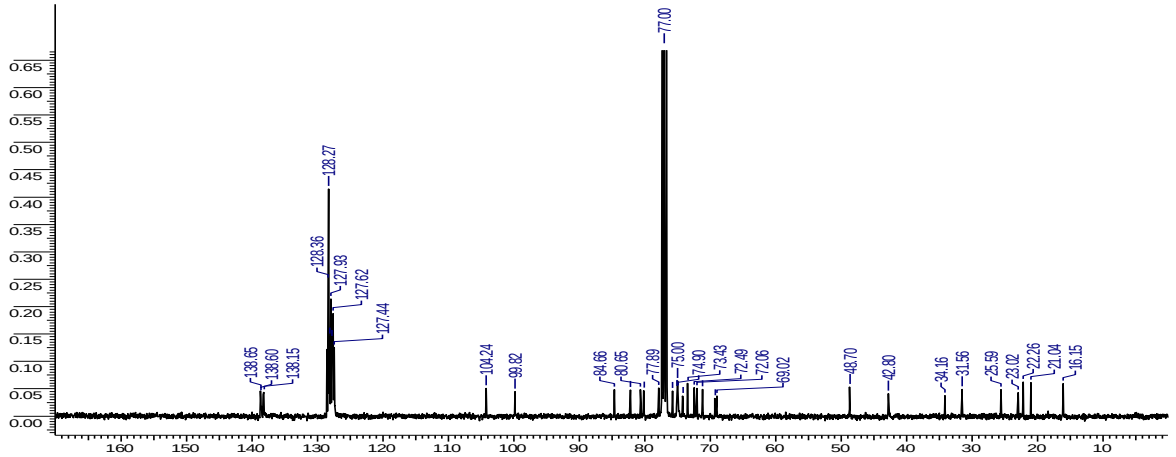
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **26**



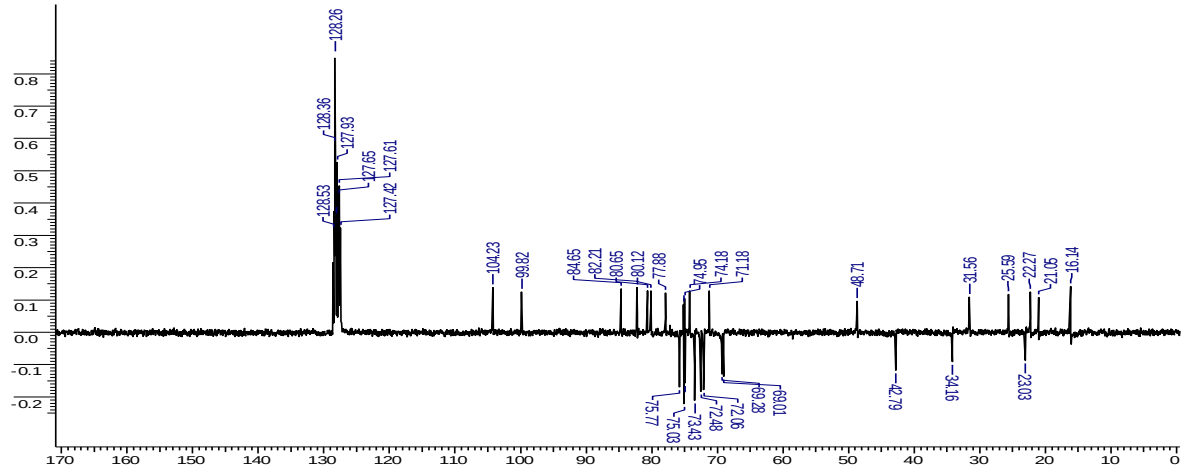
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **27**



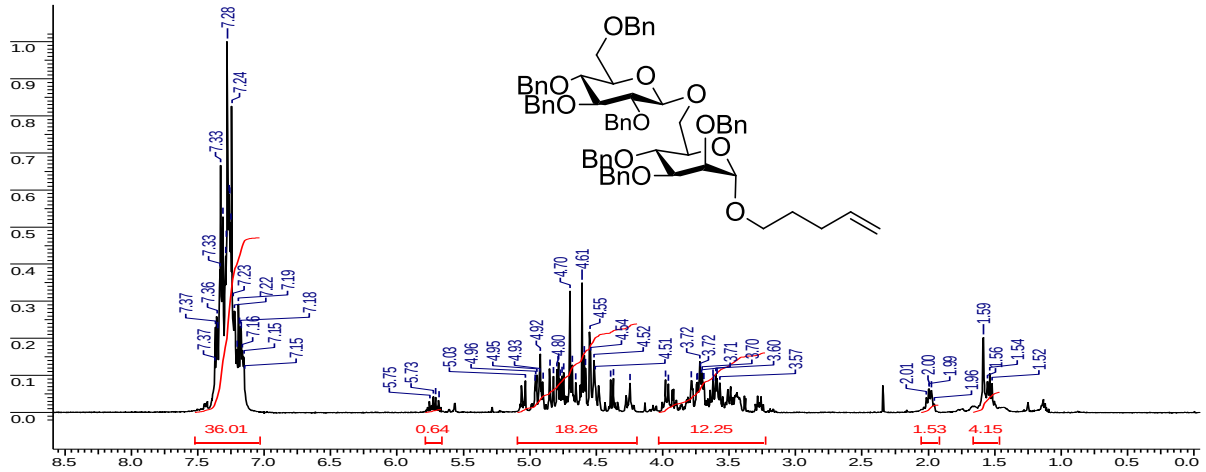
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **27**



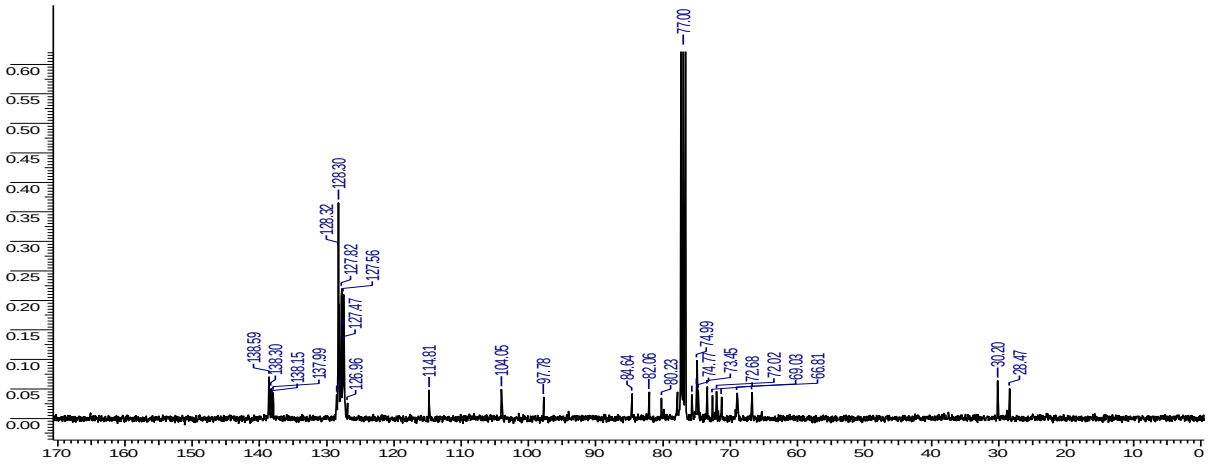
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **27**



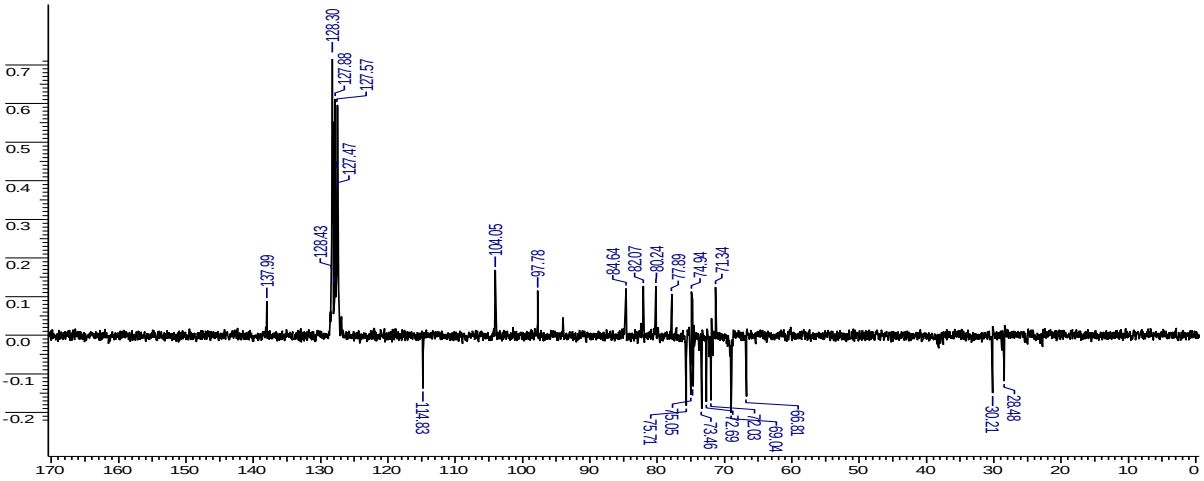
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **29**



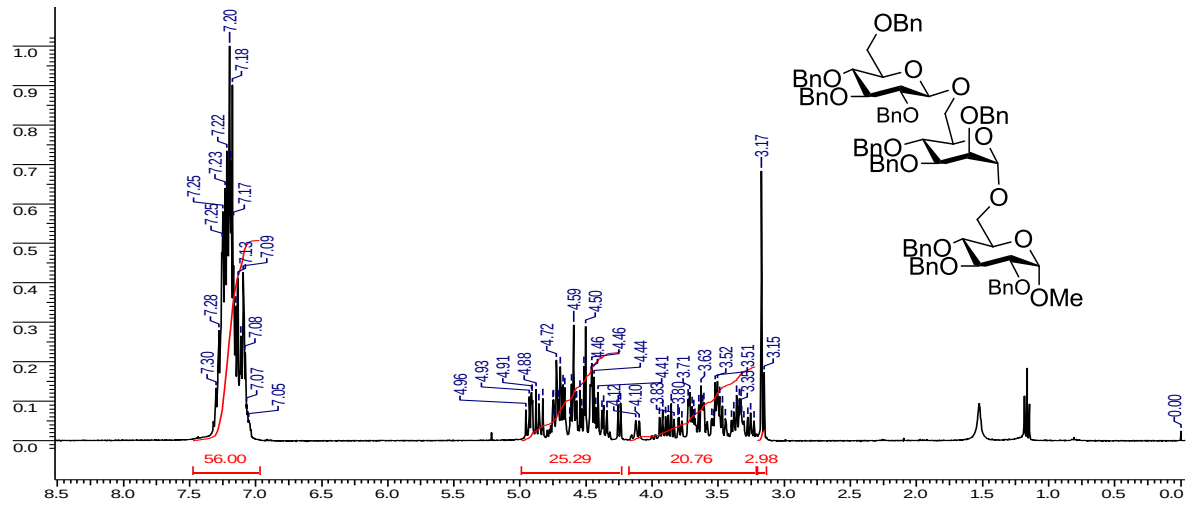
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **29**



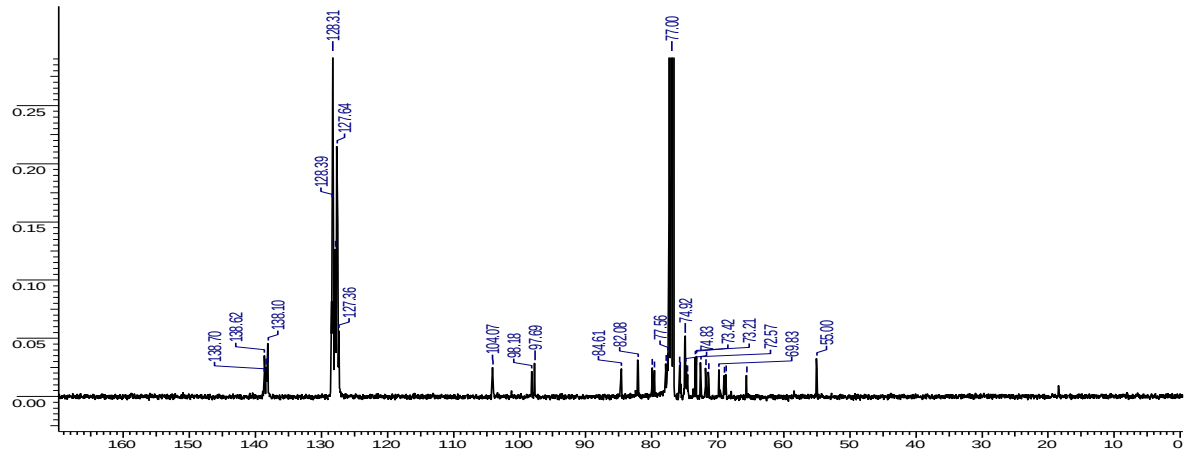
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **29**



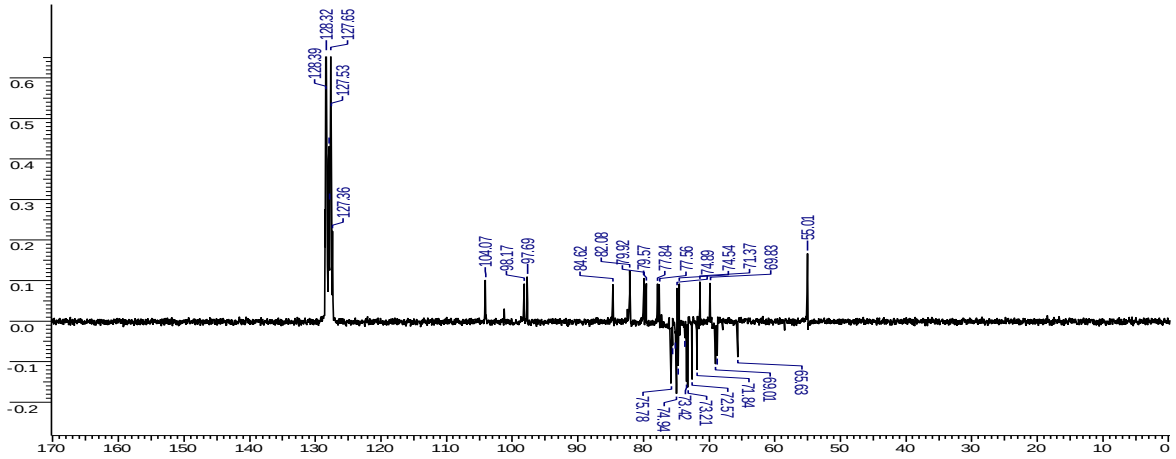
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **31**



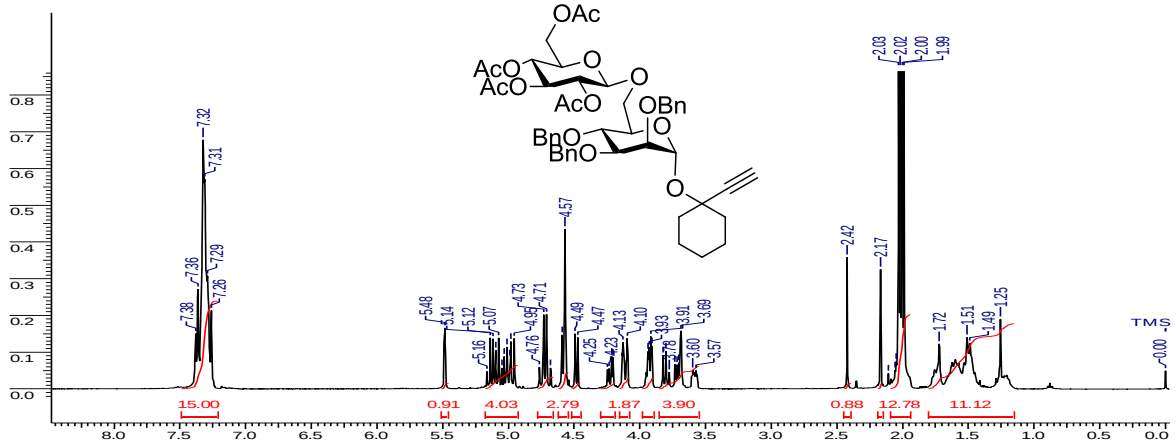
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **31**



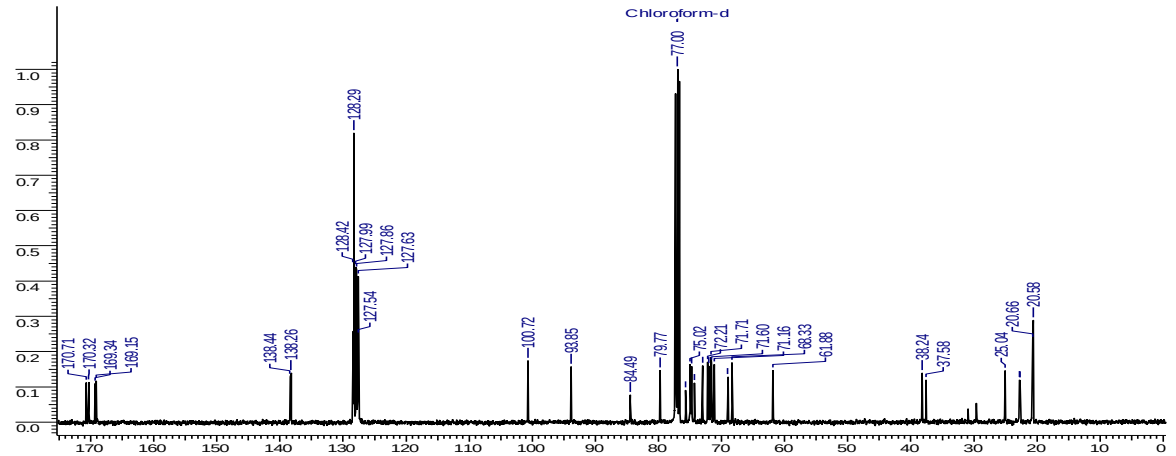
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **31**



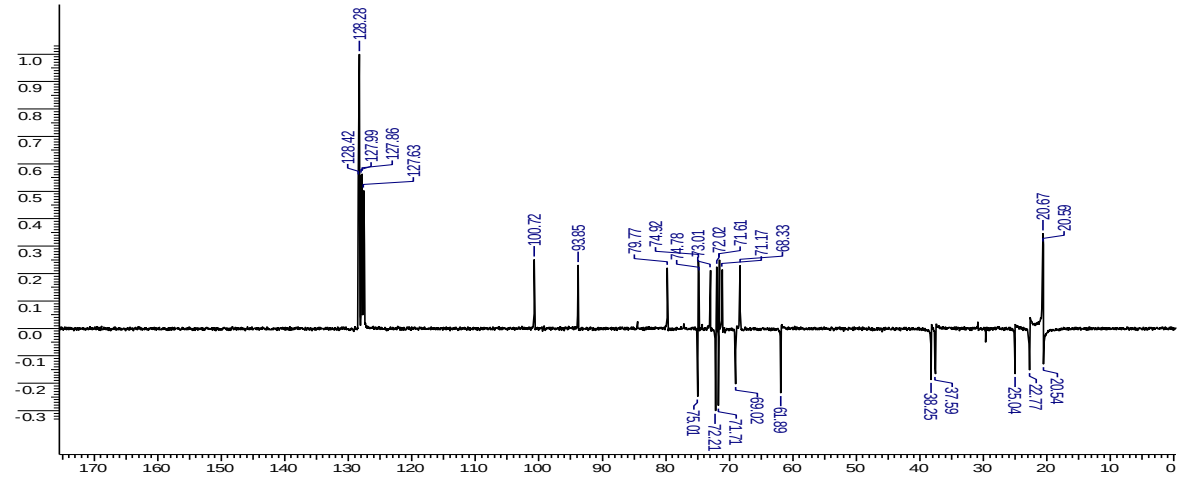
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **32**



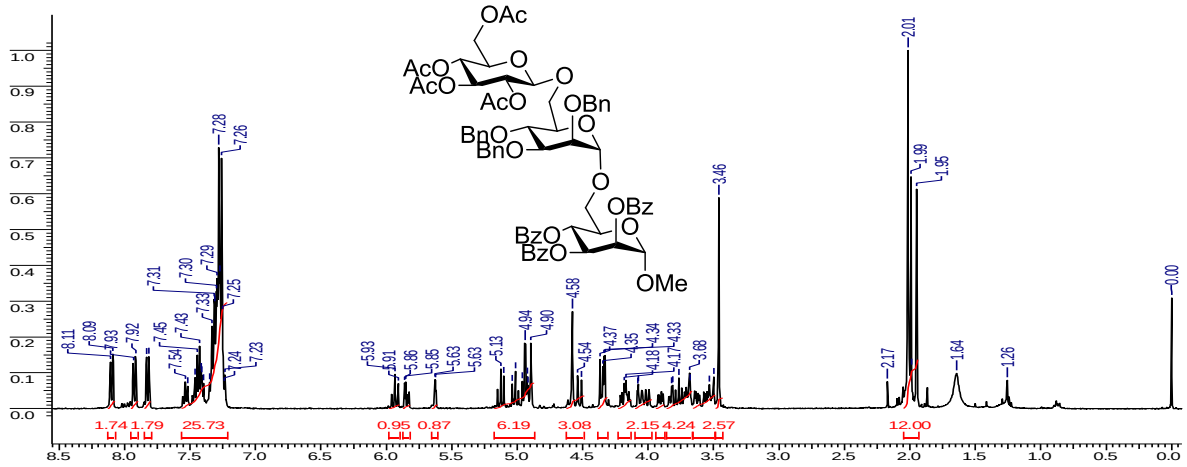
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **32**



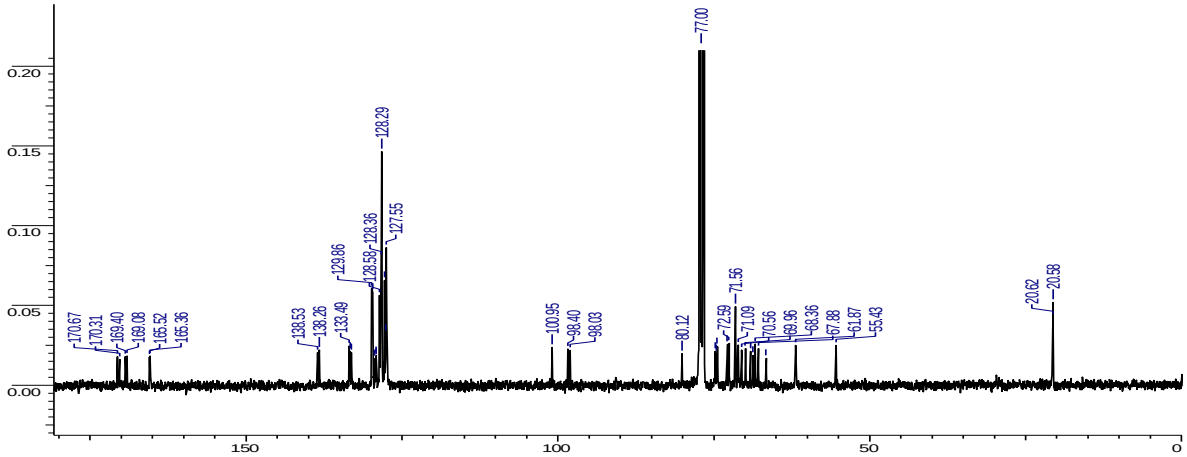
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **32**



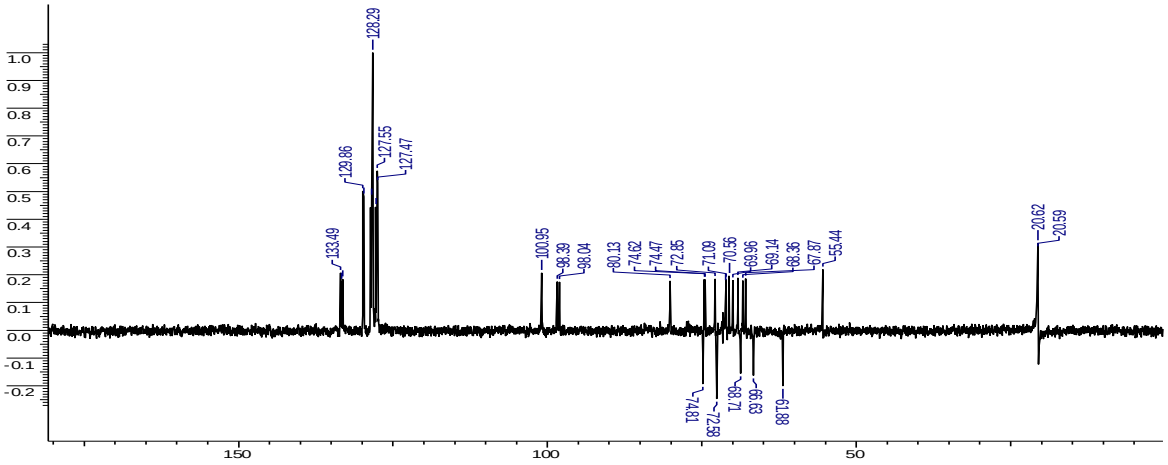
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **33**



^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **33**



DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **33**



References

1. Kayastha, A.K.; Hotha, S. *Tetrahedron Lett.* **2010,** *51,* 5269–5272.

2. Kayastha, A. K.; Hotha, S. *Chem. Commun.* **2012,** *48,* 7161–7163.