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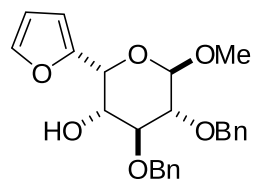
Syn Addition to 4α-Epoxypyranosides: Synthesis of L-Idopyranosides
Supporting Information

General Methods. All starting materials and reagents were obtained from commercial sources and used as received unless otherwise noted. All solvents used were freshly distilled prior to use. Optical rotations were measured at room temperature with a Rudolph Research AUTOPOL® III polarimeter. ^{1}H and ^{13}C spectra were recorded on a Varian Unity Inova NMR spectrometer operating at 300 MHz and 75 MHz, respectively, or a Bruker DRX 400 operating at 400 MHz and 100 MHz, respectively, and referenced to the solvent used (7.27 and 77.00 ppm for $CDCl_3$, 7.16 and 128.00 ppm for C_6D_6, 3.31 and 49.15 ppm for CD_3OD) unless otherwise stated. Mass spectra were acquired using either a Hewlett-Packard 5989B or a Finnigan 4000 mass spectrometer. Silica gel chromatography was performed with ICN SiliTech 32-63 D. Preparative TLC separation was performed with Silica G Prep TLC (Sorbent Tech, 500 μm).

General procedure for $ZnBr_2$-mediated organozinc addition to 4α-epoxypyranoside (4-EP). A solution of sublimed $ZnBr_2$ (232 mg, 1.02 mmol) in dry THF (2 mL) was treated at –78 °C with an organolithium or Grignard reagent (0.294 mmol), then stirred at 0 °C for 30 min before cooling again to –78 °C. A solution of 4-EP (**6**) (50 mg, 0.147 mmol) in dry CH_2Cl_2 (1 mL) was cannulated dropwise to the reaction mixture, stirred for 15 min at –78 °C, then stirred to 0 °C in an ice bath and slowly allowed to warm up to rt over 2 h. The reaction was quenched with saturated NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 × 25 mL), washed with brine (5 mL), dried over anhydrous Na_2SO_4, then concentrated under reduced pressure. Purification by silica gel chromatography yielded the corresponding L-idopyranoside in good yields (see Tables 1 and 2 in main text).

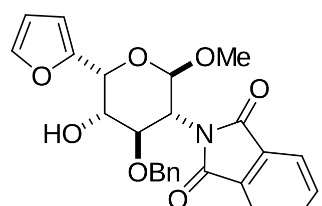
***General procedure for ozonolysis*:** In the instance provided, a solution of **11e** (20 mg, 0.066 mmol) in a 1:1 mixture of MeOH and CH_2Cl_2 (8 mL) was cooled to –78 °C and treated with a stream of electrically generated ozone at a flow rate of 2 L/min. The flow was stopped after 10 min and the reaction mixture was stirred at –78 °C for another 30 min, then treated with Me_2S and warmed to rt over 2 h. The solvent was removed under reduced pressure to afford the intermediate aldehyde as a pale yellow oil, which was used without further purification.

***General procedure for catalytic dihydroxylation*:** In the instance provided, a solution of olefin **9m** (20 mg, 0.051 mmol) in a 1:8 mixture of water:acetone (4.5 mL) was treated at rt with *N*-methylmorpholine (13 mg, 0.11 mmol) and a 2.5% (w/v) solution of OsO_4 in *t*-BuOH (40 µL, 5 mol%). The reaction mixture was stirred at rt for 12 h, quenched with a saturated $Na_2S_2O_3$ solution (3 mL) and stirred for 10 min, then extracted with EtOAc (3 × 15 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Purification by preparative TLC yielded the diol as colorless oil (18 mg, 83%).



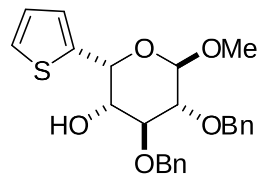
9a

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.29 (m, 11H), 6.56 (d, 1H, J = 3.6 Hz), 6.39 (dd, 1H, J = 1.8, 3.0 Hz), 5.23 (s, 1H), 4.86 (s, 1H), 4.70 (d, 1H, J = 12.3 Hz), 4.64 (d, 1H, J = 12.9 Hz), 3.94 (bs, 1H), 3.88 (t, 1H, J = 3.0 Hz), 3.59 (bs, 1H), 3.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1, 142.1, 137.7, 136.9, 128.5, , 128.1, 127.9, 127.7, 110.3, 108.7, 100.4, 74.1, 74.0, 72.6, 72.0, 68.1, 63.9, 55.8; IR (thin film): 3467, 3064, 3034, 2920, 1452, 1259, 1101 cm^{-1}; $[\alpha]^{20}_D$ = –21.4 (*c* 0.8, CH_2Cl_2); ESI-MS: *m/z* calcd for $C_{24}H_{26}O_6Na$ $[M+Na]^+$ 433; found: 433.12.



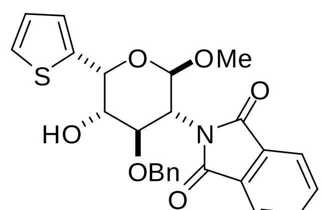
10a

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79–7.70 (m, 4H), 7.56 (s, 1H), 7.11–7.01 (m, 5H), 6.66 (d, 1H, J = 3.6 Hz), 6.49 (bs, 1H), 5.30 (d, 1H, J = 5.7 Hz), 5.20 (d, 1H, J = 8.4 Hz), 4.79 (d, 1H, J = 11.7 Hz), 4.71 (dd, 1H, J = 9.0, 9.9 Hz), 4.58 (d, 1H, J = 12.3 Hz), 4.31–4.20 (m, 2H), 3.30 (s, 3H), 2.4 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 149.9, 14.0, 137.9, 133.9 131.7, 128.3, 127.8, 127.6, 123.4, 111.1, 110.6, 96.5, 74.11, 73.1, 69.7, 56.3, 55.0; IR (thin film): 3467, 3059, 3028, 2925, 2853, 1775, 1711, 1468, 1390, 1091, 1044, 1013, 910; $[\alpha]^{20}_{D}$ = +11.7 (*c* 1.67, $CHCl_3$); ESI-MS: *m/z* calcd for $C_{25}H_{23}NO_7Na$ $[M+Na]^+$ 472; found: 472.08.



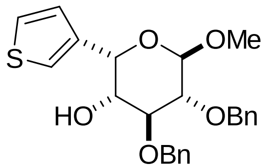
9b

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.20 (m, 11H), 7.05 (d, 1H, J = 3.3 Hz), 6.99 (dd, 1H, J = 3.6, 4.2 Hz), 5.26 (s, 1H), 4.79 (s, 1H), 4.60–4.42 (m, 4H), 3.80-3.71 (m, 2H), 3.44 (s, 1H), 3.39 (s, 3H), 3.37 (d, 1H, J = 11.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.0, 137.7, 136.7, 128.5, 128.2, 127.9, 127.8, 126.1, 125.8, 125.7, 100.5, 73.7, 73.3, 72.4, 71.9, 69.2, 65.5, 55.8; IR (thin film): 3510, 3065, 3028, 2920, 1493, 1452, 1204, 1192, 1096, 1026 cm^{-1}; $[\alpha]^{20}_{D}$ = –51.4 (*c* 1.33 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{24}H_{26}O_5SNa$ $[M+Na]^+$ 449; found: 448.95.



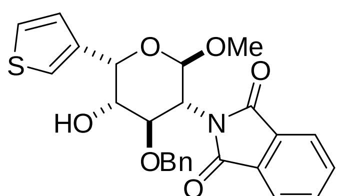
10b

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70–7.58 (m, 4H), 7.28 (d, 1H, J = 5.1 Hz), 7.20 (d, 1H, J = 3.6 Hz), 7.08–6.90 (m, 6H), 5.42 (d, 1H, J = 5.4 Hz), 5.19 (d, 1H, J = 8.1 Hz), 4.70 (d, 1H, J = 12.3 Hz), 4.51 (d, 1H, J = 11.7 Hz), 4.42 (dd, 1H, J = 3.6, 10.5 Hz), 4.34 (dd, 1H, J = 8.1, 10.5 Hz), 4.17 (dd, 1H, J = 5.1, 5.4 Hz), 3.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 138.9, 137.8, 134.0, 131.6, 128.2, 127.8, 127,6, 126.9, 126.6, 126.0, 123.4, 96.9, 74.2, 73.5, 70.9, 56.0, 54.3; IR (thin film): 3467, 3064, 3023, 2930, 1772, 1713, 1468, 1452, 1388, 1093, 1070, 1037 cm^{-1}; $[\alpha]^{20}_{D}$ = +27.2 (*c* 1.33 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{25}H_{23}NO_6SNa$ $[M+Na]^+$ 488; found: 487.98.



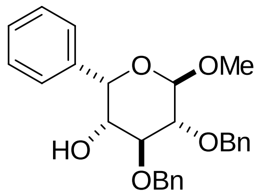
9c

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.10 (m, 12H), 7.04 (d, 1H, J = 3.6 Hz), 5.13 (bs, 1H), 4.75 (bs, 1H), 4.59 (d, 1H, J = 12.3 Hz), 4.46 (d, 1H, J = 12.9 Hz), 4.44 (bs, 2H), 3.75–3.68 (m, 2H), 3.47 (m, 1H), 3.43 (s, 3H), 3.12 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.6, 137.8, 128.5, 128.1, 127.9, 126.8, 125.3, 122.4, 100.4, 74.0, 73.6, 72.5, 72.0, 69.2, 65.7, 55.8; IR (thin film): 3519, 3059, 3018, 2920, 1493, 1452, 1192, 1145, 1099, 1026 cm^{-1}; $[\alpha]^{20}_{D}$ = –14.7 (*c* 0.67 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{24}H_{26}O_5SNa$ $[M+Na]^+$ 449; found: 448.94.



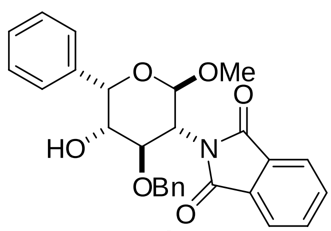
10c

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81–7.70 (m, 5H), 7.53 (m, 1H), 7.42 (dd, 1H, J = 2.7, 3.0 Hz), 7.23 (dd, 1H, J = 1.2, 5.4 Hz), 7.12–7.05 (m, 5H), 5.40 (d, 1H, J = 4.2 Hz), 5.22 (d, 1H, J = 6.9 Hz), 4.78 (d 1H, J = 12.3 Hz), 4.59 (d, 1H, J = 12.3 Hz), 4.44 (m, 2H), 4.21 (m, 1H), 3.37 (s, 3H), 2.38 (d, 1H, J = 5.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 137,8, 137.1, 134.0, 131.6, 128.2, 127.7, 127.5, 126.7, 126.2, 123.4, 123.2, 97.2, 77.2, 74.6, 73.1, 70.9, 55.8, 54.1; IR (thin film): 3472, 3059, 3023, 2925, 1775, 1713, 1468, 1450, 1390, 1067, 1041, 972 cm^{-1}; $[\alpha]^{20}_{D}$ = +33.9 (*c* 1.33 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{25}H_{23}NO_6SNa$ $[M+Na]^+$ 488; found: 487.98.



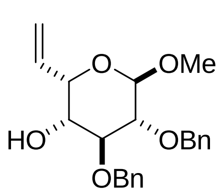
9d

^{1}H NMR (300 MHz, C_6D_6): δ 7.57 (bs, 1H), 7.54 (bs, 1H), 7.31–7.07 (m, 13H), 5.45 (bs, 1H), 4.95 (bs, 1H), 4.48 (d, 1H, J = 12.3 Hz), 4.37 (d, 1H, J = 12.3 Hz), 4.30 (d, 1H, J = 11.7 Hz), 4.24 (d, 1H, J = 11.7 Hz), 4.01–3.93 (m, 2H), 3.64 (m, 1H), 3.35 (d, 1H, J = 11.1 Hz), 3.15 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ 139.8, 138.8, 137.7, 128.7, 128.6, 128.2, 128.1, 127.4, 101.0, 75.4, 74.0, 72,4, 71.9, 70.8, 69.2, 55.0; IR (thin film): 3525, 3059, 3023, 2904, 1599, 1496, 1452, 1204, 1194, 1142, 1098, 1023 cm^{-1}; $[\alpha]^{20}_{D}$ = –52.8 (*c* 1.67 $CHCl_3$); ESI-MS *m/z* calcd for $C_{26}H_{28}O_5Na$ $[M+Na]^+$ 443; found: 443.09.

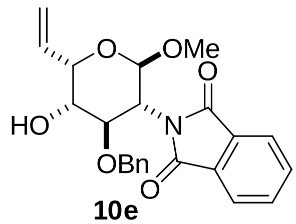


10d

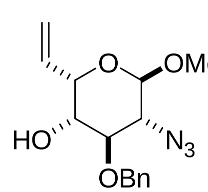
^{1}H NMR (300 MHz, C_6D_6): δ 7.58–7.44 (m, 4H), 7.38–7.20 (m, 5H), 7.09–6.92 (m, 5H), 5.79 (d, 1H, J = 6.6 Hz), 5.35 (d, 1H, J = 3.3 Hz), 5.17 (dd, 1H, J = 6.6, 6.9 Hz), 4.94, (d, 1H, J = 11.7 Hz), 4.84, (dd, 1H, J = 4.5, 4.8 Hz), 4.73 (d, 1H, J = 12.3 Hz), 4.07 (dd, 1H, J = 3.3, 4.8 Hz), 3.21 (s, 3H), 1.89 (d, 1H, J = 4.2 Hz); ^{13}C NMR (75 MHz, C_6D_6): δ 167.9, 138.5, 136.7, 133.3, 131.8, 128.2, 127.5, 127,1, 126.9, 122.9, 98.7, 78.4, 75.8, 73.0, 72.3, 54.7, 53.6; IR (thin film): 3473, 3059, 3028, 2930, 1772, 1713, 1496, 1467, 1452, 1388, 1119, 1070, 1039 cm^{-1}; $[\alpha]^{20}_{D}$ = +14.7 (*c* 1.67 $CHCl_3$); ESI-MS *m/z* calcd for $C_{27}H_{25}NO_6Na$ $[M+Na]^+$ 482; found: 482.04.



9e



10e



11e

Compound **9e**:

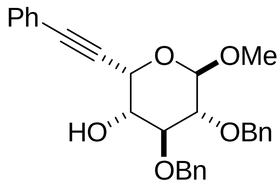
^{1}H NMR (300 MHz, C_6D_6): δ 7.26–7.05 (m, 10H), 6.28–6.17 (m, 1H), 5.47 (d, 1H, J = 11.1 Hz), 5.21 (d, 1H, J = 10.5 Hz), 4.83–4.78 (m, 2H), 4.46 (d, 1H, J = 12.3 Hz), 4.34 (d, 1H, J = 12.3 Hz), 4.26 (bs, 2H), 3.82 (m, 2H), 3.55 (bs, 1H), 3.25–3.20 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6): δ 138.9, 137.9, 136.1, 128.7, 128.6, 127.9, 127.8, 116.7, 100.4, 100.3, 75.6, 74.7, 72.6, 72.1, 70.1, 69.3, 55.0; IR (thin film): 3519, 3059, 3023, 2910, 1493, 1452, 1142, 1099, 1059, 1026 cm^{-1}; $[\alpha]^{20}_D$ = –42.0 (*c* 0.67 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{22}H_{26}O_5Na$ $[M+Na]^+$ 393; found: 393.09.

Compound **10e**:

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78–7.68 (m, 4H), 7.08–6.98 (m, 5H), 6.26–6.14 (m, 1H), 5.60–5.48 (m, 2H), 5.32 (d, 1H, J = 7.2 Hz), 4.76 (d, 1H, J = 11.7 Hz), 4.69 (dd, 1H, J = 5.1, 6.0 Hz), 4.53 (d, 1H , J = 12.3 Hz), 4.32–4.22 (m, 2H), 4.06–4.00 (m, 1H), 3.35 (s, 3H), 2.64 (d, 1H, J = 5.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 137.9, 133.9, 131.9, 131.5, 128.1, 127.6, 127.4, 123.3, 120.1, 96.0, 77.1, 73.8, 73.6, 55.9, 54.9; IR (thin film): 3467, 2935, 1775, 1711, 1467, 1452, 1388, 1199, 1088 cm^{-1}; $[\alpha]^{20}_D$ = –8.8 (*c* 0.67 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{23}H_{23}NO_6Na$ $[M+Na]^+$ 432; found: 432.08.

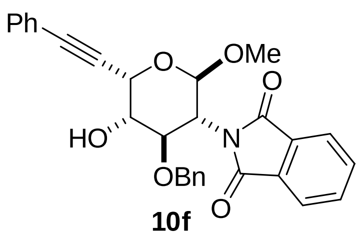
Compound **11e**:

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (m, 10H), 6.07–5.88 (m, 1H), 5.53–5.34 (m, 2H), 4.85 (d, 1H, J = 12.3 Hz), 4.74 (d, 1H, J = 12.3 Hz), 4.62 (m, 2H), 3.76 (m, 1H), 3.58 (m, 2H), 3.43 (s, 3H), 2.40 (d, 1H, J = 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.5, 132.6, 128.5, 128.0, 127.9, 118.6, 99.5, 78.0, 77.4, 70.4, 62.0, 56.0; IR (thin film): 3462, 3053, 3023, 2914, 2847, 2109, 1635, 1450, 1357, 1259, 1091, 1052 cm^{-1}; $[\alpha]^{20}_D$ = –101.8 (*c* 1.0 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{15}H_{20}N_3O_4$ $[M+H]^+$ 306; found: 306.21.



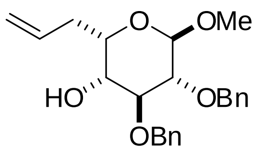
9f

[1]H NMR (300 MHz, C_6D_6): δ 7.43 (m, 2H), 7.32 (m, 3H), 7.20 (m, 7H), 6.93 (m, 3H), 5.12 (m, 2H), 4.97 (d, 1H, J = 12.0 Hz), 4.92 (d, 1H, J = 11.7 Hz), 4.77 (d, 1H, J = 11.7 Hz), 4.70 (d, 1H, J = 12.0 Hz), 4.27 (dd, 1H, J = 5.7, 9.3 Hz); [13]C NMR (75 MHz, C_6D_6): δ 138.9, 138.6, 132.0, 128.5, 128.3, 127.4, 122.6, 101.8, 88.7, 84.8, 80.1, 79.8, 74.2, 74.1, 71.0, 65.2, 56.2; IR (thin film): 3452, 3065, 3028, 2910, 2847, 1597, 1491, 1449, 1351, 1212, 1191, 1098, 1053 1026, 962 cm^{-1}; $[\alpha]^{20}_D$ = –45.2 (*c* 1.0 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{28}H_{28}O_5Na$ $[M+Na]^+$ 467; found: 466.94.



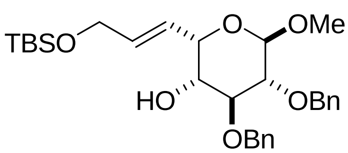
10f

[1]H NMR (300 MHz, C_6D_6): δ 7.83 (dd, 2H, J = 1.8, 8.1 Hz), 7.41 (dd, 2H, J = 5.1, 6.0 Hz), 7.08–6.78 (m, 10H), 6.15 (d, 1H, J = 8.7 Hz), 4.97–4.90 (m, 2H), 4.80 (d, 1H, J = 12.3 Hz), 4.75 (dd, 1H, J = 8.7, 10.5 Hz), 4.56 (d, 1H, J = 12.3 Hz), 3.88 (m, 1H), 3.23 (s 3H), 2.09 (m, 1H); [13]C NMR (75 MHz, C_6D_6): δ 167.9, 138.6, 133.2, 132.3, 132.0, 128.7, 128.4, 127.1, 122.9, 122.6, 96.9, 90.5, 83.8, 76.8, 74.1, 73.4, 67.1, 56.0, 55.8; IR (thin film): 3473, 3065, 3028, 2935, 1775, 1711, 1497, 1388, 1091, 1044, 972 cm^{-1}; $[\alpha]^{20}_D$ = +23.2 (*c* 2.0 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{29}H_{25}NO_6Na$ $[M+Na]^+$ 506; found: 505.96.



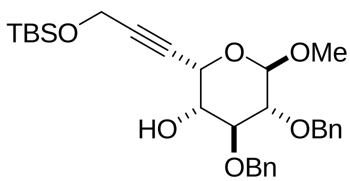
9g

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–7.16 (m, 10H), 5.82 (m, 1H), 5.07–4.96 (m, 2H), 4.89 (dd, 2H, J = 11.1, 12.0 Hz), 4.62 (dd, 2H, J = 11.7, 12.3 Hz), 4.20 (m, 1H), 3.47 (s, 3H), 3.32–3.12 (m, 4H), 2.50 (m, 1H), 2.18 (m, 1H), 2.06 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5, 138.4, 134.1, 128.6, 128.4, 128.1, 128.0, 127.7, 117.2, 104.7, 83.9, 82.1, 75.2, 74.5, 74.3, 73.0, 56.9, 35.8; IR (thin film): 3354, 3065, 3023, 2905, 2848, 1641, 1493, 1449, 1390, 1359, 1316, 1269 1210, 1108, 1088, 1073, 1049, 995, 980 cm^{-1}; $[\alpha]^{20}_D$ = –54.7 (*c* 0.53 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{23}H_{28}O_5Na$ $[M+Na]^+$ 407; found: 407.01.



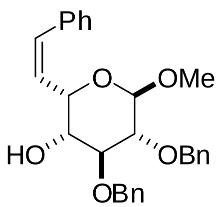
9h

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48–7.24 (m, 10H), 6.05–5.91 (m, 2H), 4.86 (bs, 1H), 4.73–4.61 (m, 5H), 4.30–4.29 (m, 2H), 3.82 (m, 1H), 3.68 (m, 1H), 3.59 (m, 1H), 3.50 (s, 3H), 3.13 (d, 1H, J = 10.8 Hz), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.8, 137.0, 132.8, 128.5, 128.4, 128.0, 127.9, 127.7, 126.6, 100.0, 74.0, 73.7, 72.4, 72.0, 69.1, 67.6, 63.4, 55.6, 25.9, 18.4, –5.20; IR (thin film): 3364, 3064, 3034, 2925, 2858, 1493, 1455, 1388, 1359, 1315, 1253, 1194, 1096, 1065, 967 cm^{-1}; $[\alpha]^{20}_D$ = –57.5 (*c* 0.80 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{29}H_{42}O_6SiNa$ $[M+Na]^+$ 537; found: 537.17.



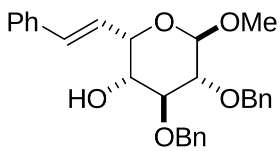
9i

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39–7.26 (m, 10H), 4.90 (m, 1H), 4.85–4.78 (m, 3H), 4.70 (dd, 2H, J = 11.4, 11.7 Hz), 4.41 (d, 2H, J = 1.8 Hz), 3.76 (m, 2H), 3.53 (s, 3H), 3.44 (m, 1H), 2.58 (m, 1H), 0.90 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.1, 137.9, 128.5, 128.4, 128.0, 127.9, 101.3, 87.4, 79.4, 78.9, 74.3, 73.9, 70.2, 63.7, 56.8, 51.7, 25.8, 18.3, –5.1; IR (thin film): 3411, 3059, 3023, 2915, 1496, 1452, 1357, 1272, 1094, 1055, 1026 cm^{-1}; $[\alpha]^{20}_{D}$ = –44.4 (*c* 1.0 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{29}H_{40}O_6SiNa$ $[M+Na]^+$ 535; found: 534.91.



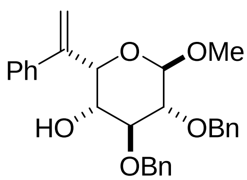
9j

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.26 (m, 15H), 6.75 (d, 1H, J = 12.0 Hz), 6.03 (dd, 1H, J = 9.0, 12.0 Hz), 5.20 (d, 1H, J = 9.0 Hz), 4.76 (d, 1H, J = 1.8 Hz), 4.70–4.57 (m, 4H), 3.81–3.77 (m, 2H), 3.54 (m, 1H), 3.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.0, 137.1, 136.5, 133.1, 128.8, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.5, 127.3, 100.2, 75.0, 74.8, 72.8, 72.2, 69.3, 64.7, 55.9; IR (thin film): 3514, 3059, 3028, 2920, 1493, 1450, 1393, 1352, 1194, 1142, 1096, 1052, 1026 cm^{-1}; $[\alpha]^{20}_{D}$ = –5.2 (*c* 0.53 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{28}H_{30}O_5Na$ $[M+Na]^+$ 469; found: 469.11.



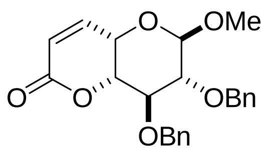
9k

^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.44–7.21 (m, 15H), 6.76 (d, 1H, J = 15.9 Hz), 6.46 (dd, 1H, J = 6.6, 15.9 Hz), 4.85 (bs, 1H), 4.75 (bs, 1H), 4.73 (bs, 1H), 4.69 (d, 1H, J = 12.3 Hz), 4.61 (d, 1H, J = 12.3 Hz), 4.56 (bs, 2H), 3.81 (m, 1H), 3.72 (m, 1H), 3.56 (m, 2H), 3.47 (s, 3H), 3.20 (d, 1H, J = 10.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.8, 136.9, 136.7, 132.6, 128.5, 128.1, 127.9, 127.8, 127.6, 126.6, 126.1, 100.1, 74.0, 73.6, 72.5, 72.0, 69.3, 68.3, 55.7; IR (thin film):3504, 3054, 3023, 2915, 1496, 1450, 1362, 1315, 1269, 1194, 1145, 1096, 1026, 967 cm^{-1}; $[\alpha]^{20}_{D}$ = –5.5 (*c* 0.8 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{28}H_{30}O_5Na$ $[M+Na]^+$ 469; found: 469.11.



9l

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.22 (m, 15H), 5.61 (t, 1H, J = 1.8 Hz), 5.49 (bs, 1H), 4.92 (bs, 1H), 4.62–4.50 (m, 4H), 3.80 (m, 1H), 3.65 (m, 1H), 3.58 (m, 1H), 3.47 (s, 3H), 3.01 (d 1H, J = 11.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.3, 139.5, 137.8, 137.0, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 126.9, 114.1, 100.9. 74.1, 73.9, 72.4, 71.9, 67.1, 66.5, 55.8; IR (thin film):3467, 3064, 3028, 2920, 1497, 1450, 1393, 1352, 1194, 1142, 1093, 1052, 1026 cm^{-1}; $[\alpha]^{20}_{D}$ = –72 (*c* 1.0 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{28}H_{30}O_5Na$ $[M+Na]^+$ 469; found: 469.07.

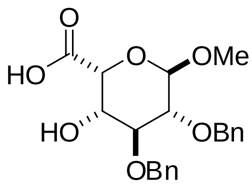


9m

A solution of **9i** (51 mg, 0.1 mmol) in hexanes (6 mL) was treated with Lindlar catalyst (14 mg) and quinoline (13 mg) at rt and stirred for 2h, then exposed to a positive hydrogen atmosphere for 3h at rt with stirring. The reaction mixture was filtered, washed with 1 M HCl, saturated $NaHCO_3$, and brine, dried over anhydrous Na_2SO_4, and concentrated to afford *cis*-alkene **18** as light yellow oil in quantitative yield. Alkene **18** was dissolved in THF (2 mL) and treated with TBAF in THF (1 M, 0.12 mL) at room temperature for 5 min. The reaction mixture was then concentrated and the resulting oil was dissolved in EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated to a yellow oil. The crude allylic alcohol was dissolved in CH_2Cl_2 (3 mL), followed by addition of *bis*-acetoxyiodobenzene (96 mg, 0.3 mmol) and 2,2,6,6,-tetramethylpiperidine-*N*-oxide (3 mg, 20 mol%) at room temperature. After stirring for 3 h, the reaction mixture was quenched with a saturated solution of $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with saturated $NaHCO_3$, NH_4Cl, and brine, dried over anhydrous Na_2SO_4, then filtered and concentrated. The residue was purified by silica gel chromatography (16.7% EtOAc in hexanes) to afford unsaturated lactone **9m** as a white solid (37 mg, 93% over three steps).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.28 (m, 10H), 6.83 (dd 1H, J = 4.8, 9.9 Hz), 6.23 (d, 1H, J = 9.9 Hz), 4.85–4.66 (m, 5H), 4.59-4.52 (m, 2H), 3.96 (dd, 1H, J = 4.5, 8.1 Hz), 3.57 (dd, 1H, J = 4.8, 8.1 Hz), 3.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5, 140.8, 137.8, 137.6, 128.4, 128.3, 128.0, 127.8, 127.8, 124.4, 102.7, 79.0, 78.1, 77.8, 73.7, 59.2, 56.0; IR (thin film): 3467, 3025, 2924,1731, 1606, 1493, 1452, 1401, 1256, 1105, 1071, 1046 cm^{-1}; $[\alpha]^{20}_{D}$ = –45.0 (*c* 0.67 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{23}H_{24}O_6Na$ [M+Na]$^+$ 419; found: 419.02.

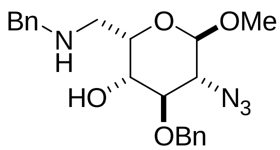
Methyl 2,3-*O*-dibenzyl-α-L-iduronic acid (**12**)



12

A solution of **9a** (80 mg, 0.195 mmol) in a 1:1 mixture of MeOH and CH_2Cl_2 (10 mL) was cooled to –78 °C and treated with a stream of electrically generated ozone at a flow rate of 2 L/min. The flow was stopped after 10 min and the reaction mixture was stirred at –78 °C for another 30 min, then treated with Me_2S and warmed to rt over 2 h. The mixture was concentrated and purified by silica gel chromatography (20% MeOH in $CHCl_3$) to yield L-iduronic acid **12** as a white solid (55 mg, 73%). ^{1}H NMR (300 MHz, CD_3OD): δ 7.30 (m, 10H), 5.02 (bs, 1H), 4.64 (d, 1H, J = 11.7 Hz), 4.60 (bs, 2H), 4.57 (d, 1H, J = 11.7 Hz), 4.51 (bs, 1H), 4.04 (bs, 1H), 3.71 (t, 1H, J = 4.2 Hz), 3.48 (m, 1H), 3.42 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD): δ 178.0, 140.4, 139.9, 130.3, 130.2, 129.8, 129.6, 103.1, 78.3, 77.3, 74.8, 74.3, 72.3, 71.3, 57.2; IR (thin film): 3416, 3059, 3028, 2920, 1721, 1605, 1496, 1452, 1148, 1106, 1026, 949 cm^{-1}; $[\alpha]^{20}_D$ = –4.3 (*c* 1.0 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{21}H_{24}O_7Na$ $[M+Na]^+$ 411; found: 410.89.

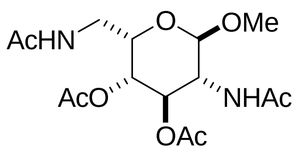
Methyl 6-(*N*-benzyl)amino-2-azido-3-*O*-benzyl-2,6-dideoxy-α-L-idopyranoside (**13**)



13

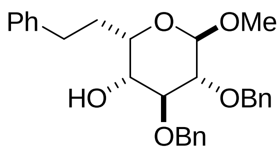
Ozonolysis of C5 vinyl adduct **11e** (20 mg, 0.066 mmol) produced the corresponding aldehyde, which was dissolved in 1,2-dichloroethane (2 mL), treated with benzylamine (6.5 μL, 0.079 mmol), and stirred at rt for 3 h. The reaction mixture was then treated with a solution of $NaCNBH_3$ (41 mg, 0.66 mmol) in anhydrous MeOH (2 mL). The mixture was stirred for overnight at rt, then concentrated and redispersed in brine (5 mL), extracted with EtOAc (3 × 15 mL), dried over Na_2SO_4, and concentrated to a yellow oil. Purification with silica gel chromatography (1% MeOH in $CHCl_3$) yielded methyl 6-(*N*-benzyl) amino-2-azido-3-*O*-benzyl-2,6-dideoxy-α-L-idopyranoside **13** as a pale yellow oil (17 mg, 66% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.29 (m, 10H), 4.80 (d, 1H, J = 11.7 Hz), 4.74 (d, 1H, J = 11.7 Hz), 4.63 (d, 1H, J = 3.3 Hz), 4.17 (m , 1H), 3.97 (dd, 1H, J = 3.0, 3.3 Hz), 3.87 (d, 1H, J = 12.9 Hz), 3.81 (d, 1H, J = 12.9 Hz), 3.61 (dd, 1H, J = 3.6, 6.6 Hz), 3.50 (dd, 1H, J = 4.2, 6.6 Hz), 3.42 (s, 3H), 3.21 (dd, 1H, J = 4.2, 12.3 Hz), 2.97 (dd, 1H, J = 2.7, 12.3 Hz); ^{13}C NMR (75 MHz, C_6D_6): δ 138.8, 137.8, 128.6, 128.4, 128.2, 127.8, 127.4, 100.7, 79.4, 73.0, 72.6, 66.4, 60.4, 55.7, 53.9, 50.4; IR (thin film): 3328, 3023, 2920, 2853, 2103, 1644, 1494, 1452, 1357, 1266, 1109, 1075, 1049, 967 cm^{-1}; $[\alpha]^{20}_D$ = –55.8 (*c* 0.67 $CHCl_3$); HRESI-MS: *m/z* calcd for $C_{21}H_{24}N_4O_4Na$ $[M+H]^+$ 399; found: 398.96.

Neosamine B methyl glycoside peracetate **(15)**



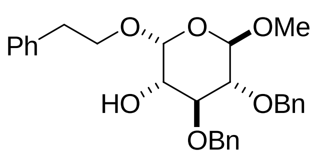
15

The synthesis of **15** has been previously described (see Ref. 19 in the main text). Compound **13** (15 mg, 0.038 mmol) was treated with 20% $Pd(OH)_2$ on carbon (52 mg) in 80% AcOH (6 mL), and stirred at 60 ^{o}C under a positive hydrogen atmosphere for 12 h. The mixture was passed through Celite, which was washed thoroughly with H_2O (3 × 10 mL) and MeOH (3 × 20 mL). The combined filtrates were concentrated and azeotroped with toluene (3 × 10 mL) to yield neosamine B methyl glycoside **14** as a red-brown oil. The crude product was dissolved in 70% aqueous AcOH (5 mL) and stirred at 70 °C for 2 h, then concentrated and azeotroped with toluene (3 × 10 mL). The crude 2,6-*N,N*'-diacetate was further acetylated by treatment with Ac_2O (2 mL) in pyridine (4 mL) at rt for 12 h. The mixture was concentrated, azeotroped with toluene (3 × 10 mL), and purified by preparative TLC (10% MeOH in $CHCl_3$) to afford peracetate **15** as a white solid (7 mg, 52% over three steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.09 (d, 1H, J = 9.9 Hz), 5.87 (m, 1H), 4.94 (bs, 1H), 4.79 (m, 1H), 4.59 (bs 1H), 4.25 (m, 2H), 3.38 (s, 3H), 3.48 (dd, 1H, J = 6.9, 14.1 Hz), 3.30 (dt, 1H, J = 14.1, 6.6 Hz), 2.21 (s, 3H), 2.11 (s, 3H), 2.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 169.4, 169.3, 168.8, 100.6, 67.8, 67.4, 64.0, 55.6, 46.8, 38.9, 23.4, 23.3, 20.9, 20.8; IR (thin film): 3287, 3091, 2925, 1739, 1659, 1556, 1434, 1370, 1246, 1034 cm^{-1}; $[\alpha]^{20}_{D} = -15.8$ (*c* 0.47 $CHCl_3$); ESI-HRMS *m/z* calcd for $C_{15}H_{25}N_2O_8$ $[M+H]^+$ 361.1611; found: 361.1613.



16

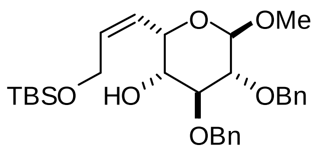
C5 phenethyl adduct **16** was prepared according to the general procedure described for $ZnBr_2$-mediated organozinc addition to 4-EPs, and isolated as a colorless oil in 43% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38–7.18 (m, 15H), 4.78 (bs, 1H), 4.65 (d, 1H, J = 12.3 Hz), 4.57 (d, 1H, 12.3 Hz), 4.54 (bs, 2H), 4.13 (dd, 1H, J = 4.2, 9.6 Hz), 3.76 (m, 1H), 3.55 (m, 2H), 3.45 (s, 3H), 3.02 (d, 1H, J = 11.1 Hz), 2.92 (m, 1H), 2.71 (m, 1H), 2.17 (m, 1H), 1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 137.9, 137.0, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 125.8, 100.0, 73.9, 73.8, 72.4, 71.9, 68.6, 66.9, 55.6, 33.1, 32.1; IR (thin film): 3519, 3064, 3023, 2910, 2853, 1602, 1496, 1452, 1148, 1104, 1073, 1029 cm^{-1}; $[\alpha]^{20}_D = -5.2$ (*c* 0.53 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{28}H_{32}O_5Na$ $[M+Na]^+$ 471; found:471.20.



17

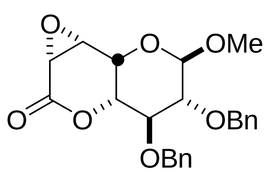
C5 phenethoxy adduct **17** was isolated as a byproduct of the reaction above, as a colorless oil in 24% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.14 (m, 15H), 4.83 (d, 1H, J = 11.4 Hz), 4.82 (d, 1H, 11.1 Hz), 4.75 (d, 1H, J = 11.1 Hz), 4.66 (d, 1H, J = 11.1 Hz), 4.35 (m, 2H), 4.12 (m, 1H), 3.73 (m, 1H), 3.56–3.38 (m, 6H), 2.95 (t, 2H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5, 138.3, 128.9, 128.4, 128.3, 128.0, 127.9, 127.7, 126.4, 101.6, 99.6, 81.8, 81.4, 75.0, 74.6, 73.9, 70.5, 56.8, 36.2.

Higher-order monosaccharides with L-ido configuration:



18

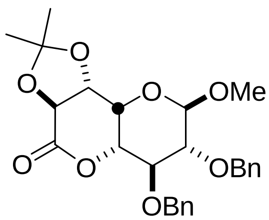
A solution of **9i** (51 mg, 0.1 mmol) in hexanes (6 mL) was treated with Lindlar catalyst (14 mg) and quinoline (13 mg) at rt and stirred for 2h, then exposed to a positive hydrogen atmosphere for 3h at rt with stirring. The reaction mixture was filtered, washed with 1 M HCl, saturated $NaHCO_3$, and brine, dried over anhydrous Na_2SO_4, and concentrated to afford *cis*-alkene **18** as a light yellow oil in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.22 (m, 10H), 5.85–5.72 (m, 2H), 4.89 (dd, 1H, J = 1.8, 6.3 Hz), 4.75 (bs, 1H), 4.68 (d, 1H, J = 12.3 Hz), 4.61 (d, 1H, J = 12.3 Hz), 4.56 (s, 2H), 4.34 (m, 2H), 3.76 (m, 1H), 3.58 (m, 2H), 3.46 (s, 3H), 3.16 (d, 1H, J = 10.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 137.0, 134.0, 128.5, 128.4, 128.1, 127.9, 127.7, 126.4, 100.1, 74.1, 72.6, 69.4, 64.1, 59.7, 56.0, 25.9, 18.3, –5.2.



19

Unsaturated lactone **9m** (20 mg, 0.051 mmol) was dissolved in pyridine (2 mL) and treated with commercial bleach (5% NaOCl, 0.2 mL) at 0 °C. The resulting yellowish solution was warmed to rt and stirred for 4 h, then quenched with saturated $Na_2S_2O_3$ (3 mL), extracted with EtOAc (3 × 15 mL), washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by preparative TLC (25% EtOAc in hexanes) yielded 6,7-epoxide **19** as a single stereoisomer and a white solid (16 mg, 78%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.30 (m, 10H), 4.72 (m, 1H), 4.68 (m, 1H), 4.60 (d, 1H, J = 11.7 Hz), 4.57 (bs, 2H), 4.51 (d, 1H, J = 11.7 Hz), 4.43 (t, 1H, J = 2.4 Hz), 3.78 (t, 1H, J = 3.3 Hz), 3.74 (t, 1H, J = 3.6 Hz), 3.61 (d, 1H, 3.6 Hz), 3.51 (m, 1H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 165.4, 137.4, 137.0, 128.5, 128.3, 128.1, 127.9, 127.7, 101.3, 74.0, 73.8, 73.2, 72.4, 72.3, 60.0, 55.9, 52.7, 48.4; IR (thin film): 3028, 2915, 1749, 1496, 1452, 1365, 1323, 1261, 1117, 1104 cm^{-1}; $[\alpha]^{20}_{D} = -101$ (*c* 1.0 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{23}H_{24}O_7Na$ $[M+Na]^+$ 435; found: 434.95.

Methyl 2,3-di-*O*-benzyl-6,7-isopropylidene-D-*threo*-α-L-*ido*-octono-4,8-lactone (**20**)

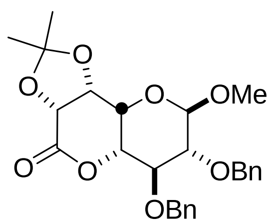


20

A solution of *trans*-alkene **9h** (50 mg, 0.097 mmol) in THF (2 mL) was treated with TBAF in THF (1 M, 100 μL) at rt. After stirring for 5 min, the reaction mixture was concentrated and redissolved in a 2:1 mixture of Ac_2O and pyridine (6 mL) and stirred for 12 h at rt. The mixture was concentrated and azeotroped with toluene (3 × 10 mL) and passed through a silica gel plug to afford the intermediate 4,8-diacetate as a colorless oil. This intermediate was subjected to the catalytic osmylation conditions previously described to yield the intermediate 6,7-diol as a 5:1 mixture of diastereoisomers, the major product having a D-*threo*-L-*ido* configuration. The crude diol was then dissolved in THF (3 mL) and treated with 2-methoxypropene (120 μL, 0.1 mmol) and *d*-CSA (4 mg, 0.017 mmol) at 0 °C. The mixture was warmed to rt and stirred for 4 h, then quenched with Et_3N at 0 °C and concentrated to give the crude acetonide as a yellow oil. This was redissolved in MeOH (3 mL), treated with K_2CO_3 (25 mg), and stirred for 1 h at rt. The resulting white suspension was filtered and washed with EtOAc (3 × 25 mL). The combined organic washings were concentrated and the residue was dried *in vacuo* for 2 h, then dissolved in CH_2Cl_2 (3 mL) and treated with *bis*-acetoxyiodobenzene (96 mg, 0.3 mmol) and TEMPO (3 mg, 20 mol%) at rt. The reaction mixture was stirred for 3 h, then quenched with saturated $Na_2S_2O_3$, extracted with CH_2Cl_2 (3 × 15 mL), followed by a standard aqueous workup. The residue was purified by silica gel chromatography (33.3% EtOAc in hexanes) to afford D-*threo*-L-idooctopyranoside derivative **20** as a colorless oil (17 mg, 37% over six steps). The relative stereochemistry was confirmed by NOE difference spectroscopy (see spectra below). ^1H NMR (300 MHz, C_6D_6): δ 7.43 (d, 2H, J

= 7.5 Hz), 7.35 (d, 2H, J = 7.5 Hz), 7.22 (m, 6H), 4.83 (d, 1H, J = 11.7 Hz), 4.75 (d, 1H, J = 11.7 Hz), 4.70 (d, 1H, J = 11.7 Hz), 4.63 (d, 1H, J = 11.7 Hz), 4.54 (d, 1H, J = 4.8 Hz), 4.50 (d, 1H, J = 11.1 Hz), 4.04 (dd, 1H, J = 1.2, 4.2 Hz), 3.94 (dd, 1H, J = 1.2, 6.0 Hz), 3.57 (dd, 1H, J = 3.6, 9.9 Hz), 3.43 (dd, 1H, J = 3.3, 11.1 Hz), 3.37 (dd, 1H, J = 4.8, 9.9 Hz), 3.10 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 165.3, 138.2, 130.5, 127.4, 112.7, 103.2, 83.9, 79.6, 79.2, 74.0, 73.7, 73.4, 70.0, 64.1, 54.4, 26.4, 26.2; IR (thin film): 2925, 1780, 1496, 1452, 1372, 1227, 1163, 1111, 1062, 1037, 1024 cm^{-1}; $[\alpha]^{20}_{D}$ = –52.5 (*c* 0.67 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{26}H_{30}O_8Na$ $[M+Na]^+$ 493; found:493.06.

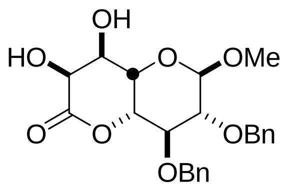
Methyl 2,3-di-*O*-benzyl-6,7-isopropylidene-L-*erythro*-α-L-*ido*-octono-4,8-lactone (**21**)



21

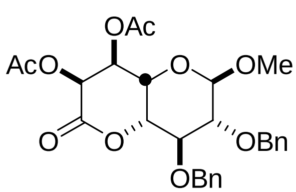
Compound **21** was obtained from *cis*-alkene **18** using the same synthetic sequence described above, and isolated as colorless oil (15 mg, 34% over six steps). The relative stereochemistry was confirmed by NOE difference spectroscopy (see spectra below). ^{1}H NMR (300 MHz, C_6D_6): δ 7.39 (d, 2H, J = 7.5 Hz), 7.27 (d, 2H, J = 6.9 Hz), 7.21 (m, 6 H), 4.78 (d, 1H, J = 2.7 Hz), 4.46 (m, 4H), 4.20 (m, 1H), 4.08 (d, 1H, J = 8.7 Hz), 3.94 (t, 1H, J = 3.9 Hz), 3.84 (m, 1H), 3.81 (dd, 1H, J = 3.9, 8.7 Hz), 3.53 (dd, 1H, J = 3.0, 3.6 Hz), 3.20 (s, 3H), 1.52 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ 167.6, 137.7, 137.2, 128.6, 128.4, 128.2, 128.0, 127.8, 111.6, 100.7, 74.2, 73.9, 73.6, 72.5, 72.3, 71.5, 60.0, 55.5, 25.8, 25.4; IR (thin film): 2930, 1755, 1496, 1452, 1372, 1204, 1111, 1094, 1037, 962 cm^{-1}; $[\alpha]^{20}_{D}$ = –78.3 (*c* 0.67 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{26}H_{30}O_8Na$ $[M+Na]^+$ 493; found:493.06.

Methyl 2,3-di-*O*-benzyl-D-*erythro*-α-L-*ido*-octono-4,8-lactone



Unsaturated lactone **9m** (27 mg) was subjected to the catalytic osmylation previously described to yield the corresponding 6,7-diol as a single diastereomer and a colorless oil (26 mg, 87% yield). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.41–7.24 (m, 10H), 4.79–4.63 (m, 5H), 4.55 (d, 1H, J = 12.3 Hz), 4.54 (d, 1H, J = 3.0 Hz), 4.41 (dd, 1H, J = 3.6, 4.2 Hz), 4.35 (dd, 1H, J = 3.0, 3.9 Hz), 3.85 (dd, 1H, J = 4.2, 6.3 Hz), 3.61 (bs, 1H), 3.54 (dd, 1H, J = 3.6, 6.3 Hz), 3.43 (s, 3H), 3.22 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 137.6, 137.4, 128.4, 128.3, 128.0, 127.8, 102.0, 78.9, 76.4, 76.1, 73.1, 73.0, 68.8, 67.9, 64.7, 55.7; IR (thin film): 3432, 3059, 3028, 2915, 1744, 1496, 1452, 1364, 1197, 1114, 1042, 946 cm^{-1}; $[\alpha]^{20}_{D}$ = –82.2 (*c* 0.67 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{23}H_{26}O_8Na$ $[M+Na]^+$ 453; found:452.90.

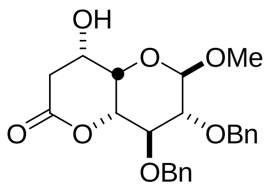
Methyl 6,7-di-*O*-acetyl-2,3-di-*O*-benzyl-D-*erythro*-α-L-*ido*-octono-4,8-lactone (**22**)



22

Compound **22** was prepared from the diol above (4 mg, 91% yield), and its relative stereochemistry was confirmed by NOE difference spectroscopy (see spectra below). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.38–7.24 (m, 10H), 5.88 (d, 1H, J = 3.3 Hz), 5.54 (dd, 1H, J = 2.7, 3.6 Hz), 4.77 (d, 1H, J = 3.6 Hz), 4.72 (s, 2H), 4.66 (d, 1H, J = 11.7 Hz), 4.59 (dd, 1H, J = 3.3, 3.6 Hz), 4.57 (d, 1H, J = 11.7 Hz), 4.34 (dd, 1H, J = 3.3, 4.2 Hz), 3.87 (dd, 1H, J = 4.2, 6.6 Hz), 3.53 (dd, 1H, J = 3.6, 6.6 Hz), 3.44 (s, 3H); ESI-MS: *m/z* calcd for $C_{26}H_{30}O_8Na$ $[M+Na]^+$ 537; found:537.03.

Methyl 2,3-di-*O*-benzyl-7-deoxy-L-*glycero*-α-L-*ido*-octono-4,8-lactone (**23**)



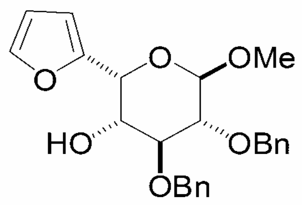
23

A solution of $(PhSe)_2$ (60 mg, 0.19 mmol) in EtOH (1 mL) was treated with $NaBH_4$ (14.5 mg, 0.38 mmol) under Ar at rt and stirred for 5 min before being cooled to 0 °C. The reaction mixture was then treated with the dropwise addition of AcOH (14 µL, 0.38 mmol), then stirred for 5 min at rt to generate the unstable phenylselenol. This was immediately treated with a solution of epoxide **19** (10 mg, 0.024 mmol) in EtOH (0.5 mL) and stirred for 15 min at rt, then diluted with EtOAc (3 mL). The reaction was quenched with NaCl solution (2 mL), extracted with EtOAc (2 × 15 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification with preparative TLC (50% EtOAc in hexanes) yielded C6 alcohol **23** as a colorless oil (9 mg, 90%). ^{1}H NMR (300 MHz, C_6D_6:CD_3OD = 5:1): δ 7.31–7.03 (m, 10H), 4.70 (t, 1H, J = 3.6 Hz), 4.69 (d, 1H, J = 11.7 Hz), 4.62 (d, 1H, J = 3.6 Hz), 4.59 (d, 1H, J = 11.7 Hz), 4.56 (d, 1H, J = 11.7 Hz), 4.47 (d, 1H, J = 11.7 Hz), 4.18 (dd, 1H, J = 3.6, 4.2 Hz), 4.09 (dd, 1H, J = 4.2, 8.4 Hz), 3.84 (dd, 1H, J = 3.0, 7.5 Hz), 3.52 (dd, 1H, J = 3.6, 7.8 Hz), 3.16 (s, 3H), 2.85 (dd, 1H, J = 4.2, 17.1 Hz), 2.61 (dd, 1H, J = 4.5, 17.1 Hz); ^{13}C NMR (75 MHz, 5:1 C_6D_6:CD_3OD): δ 170.3, 138.5, 138.4, 102.6, 78.3, 77.4, 77.3, 73.3, 73.2, 65.8, 65.3, 55.0, 35.2; IR (thin film): 3432, 3065, 3028, 2920, 1731, 1496, 1452, 1365, 1235, 1114, 1070, 1042 cm^{-1}; $[\alpha]^{20}_D$ = –2.2 (*c* 0.67 $CHCl_3$); ESI-MS: *m/z* calcd for $C_{23}H_{26}O_7Na$ $[M+Na]^+$ 426; found: 426.24.

Table S1. Chemical Shifts and Coupling Constants of Select C4 acetates.

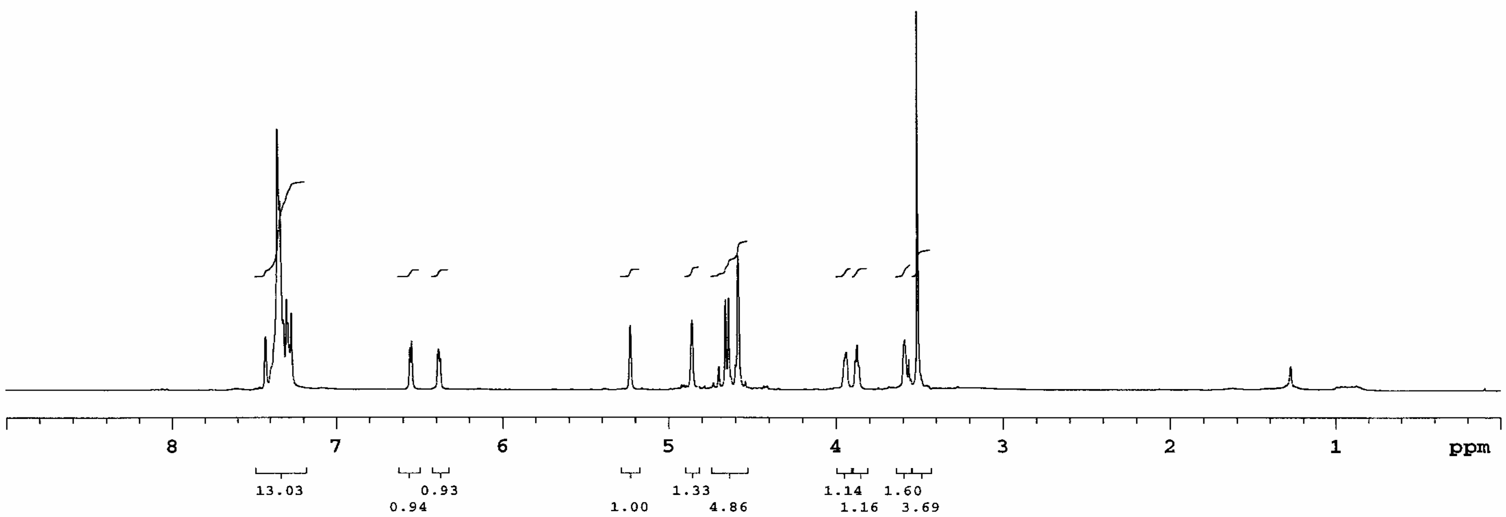
compd (C4 acetate)	δ (^{1}H NMR, 300 MHz)	$J_{4,5}$ (Hz)
9a [a]	5.16	4.2
10a [a]	5.32	6.6
9b[a]	5.11	2.4
10b[a]	5.43	5.4
9c[a]	5.16	2.7
10c[a]	5.75	5.1
9d[b]	5.09	2.7
10d[b]	5.66	3.6
9e[a]	4.92	3.6
10e[a]	5.25	5.1
9f[b]	5.32	5.4
10f[b]	5.08	4.2
9h[a]	4.95	3.6
9k[a]	5.02	1.2
9l[a]	4.91	3.0

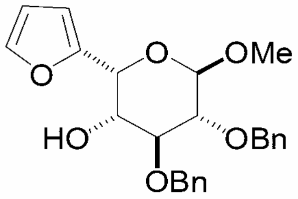
[a] $CDCl_3$. [b]benzene-d_6.



9a

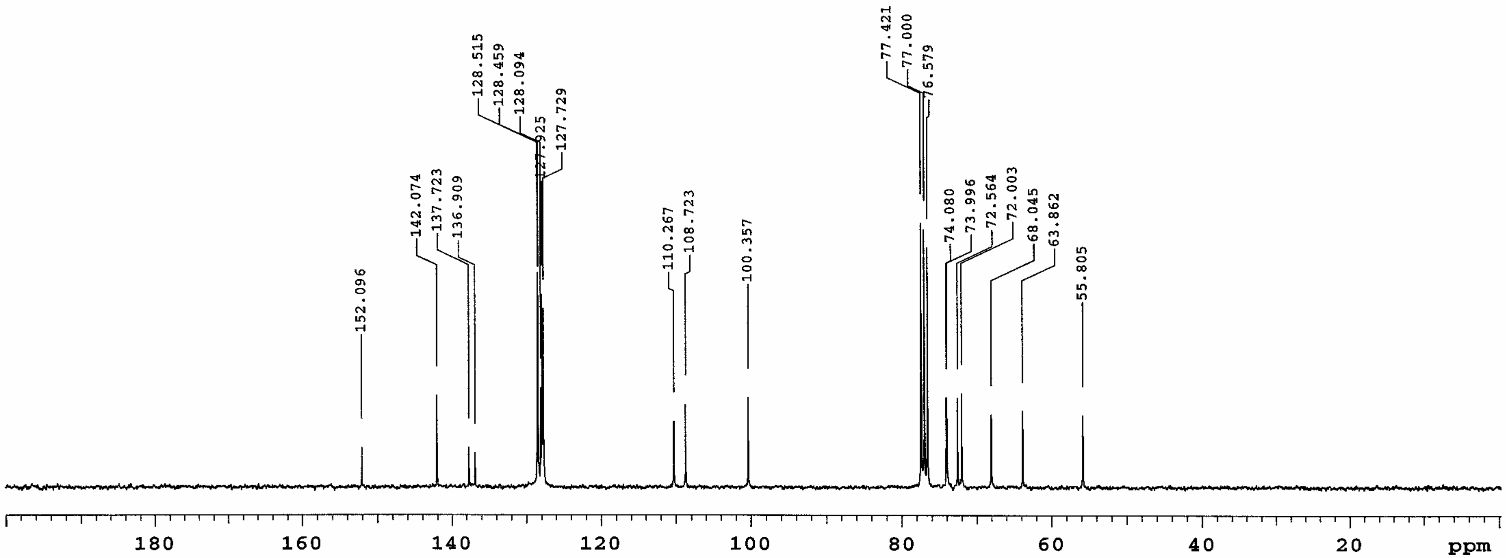
[1] H NMR, 300MHz, $CDCl_3$

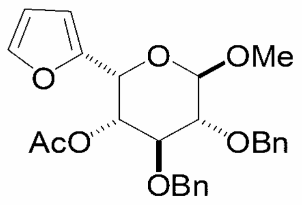




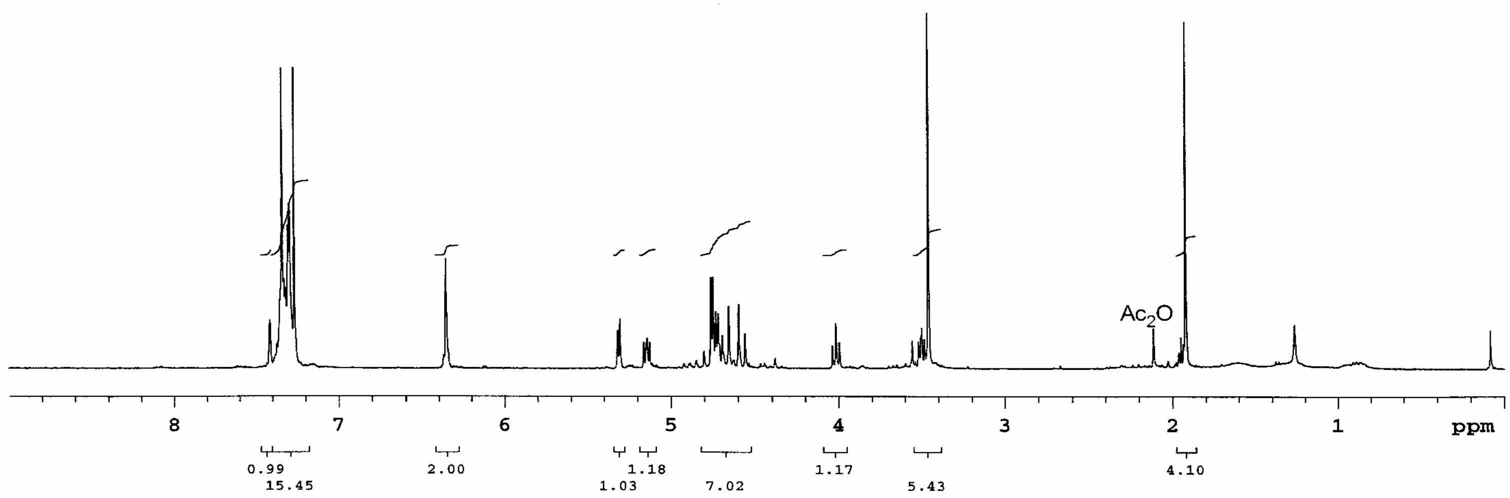
9a

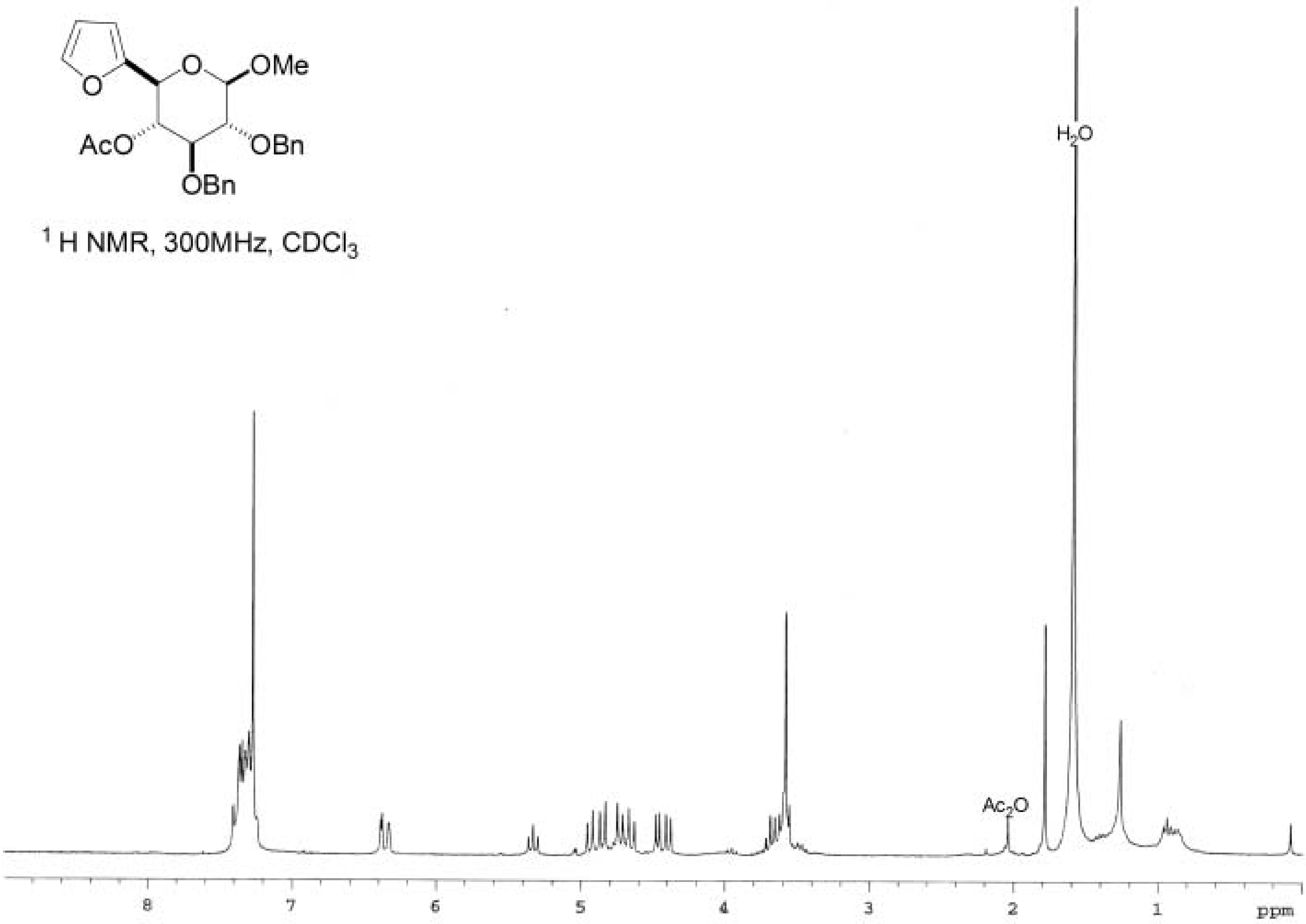
^{13}C NMR,75MHz, $CDCl_3$

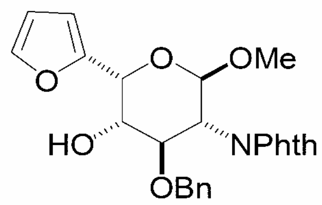




^{1}H NMR, 300MHz, $CDCl_3$

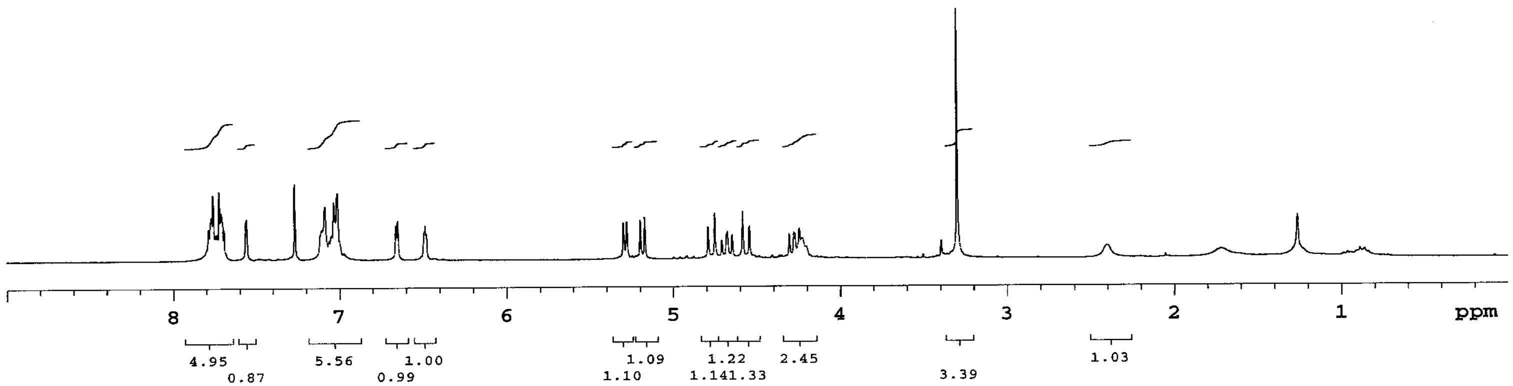


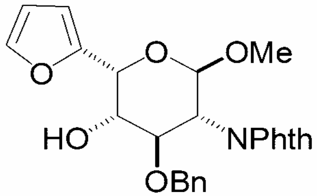

OMe
AcO
OBn
OBn
O
O
¹H NMR, 300MHz, CDCl₃
H₂O
Ac₂O
8
7
6
5
4
3
2
1
ppm



10a

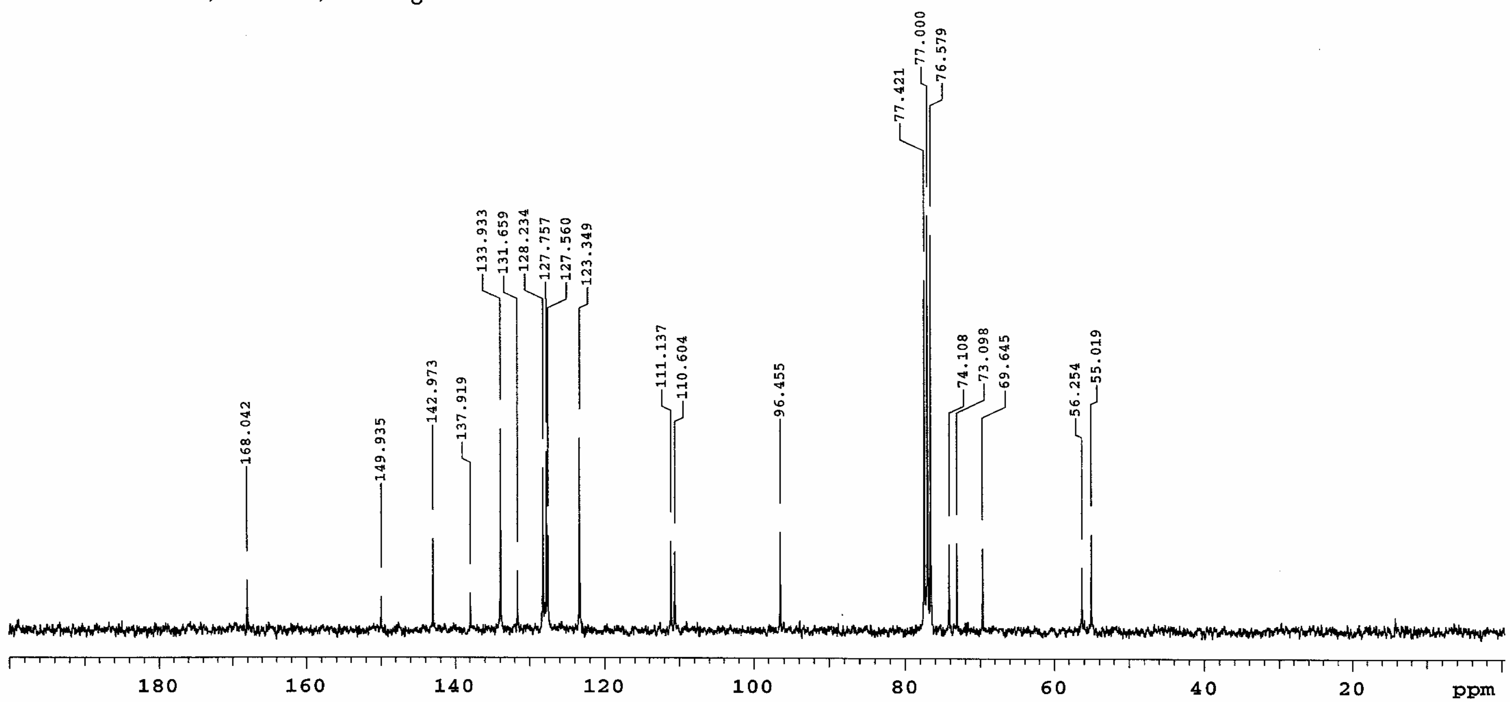
^1H NMR, 300MHz, $CDCl_3$

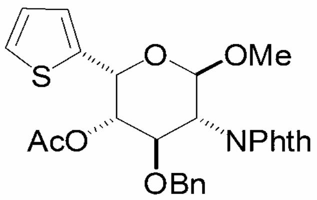




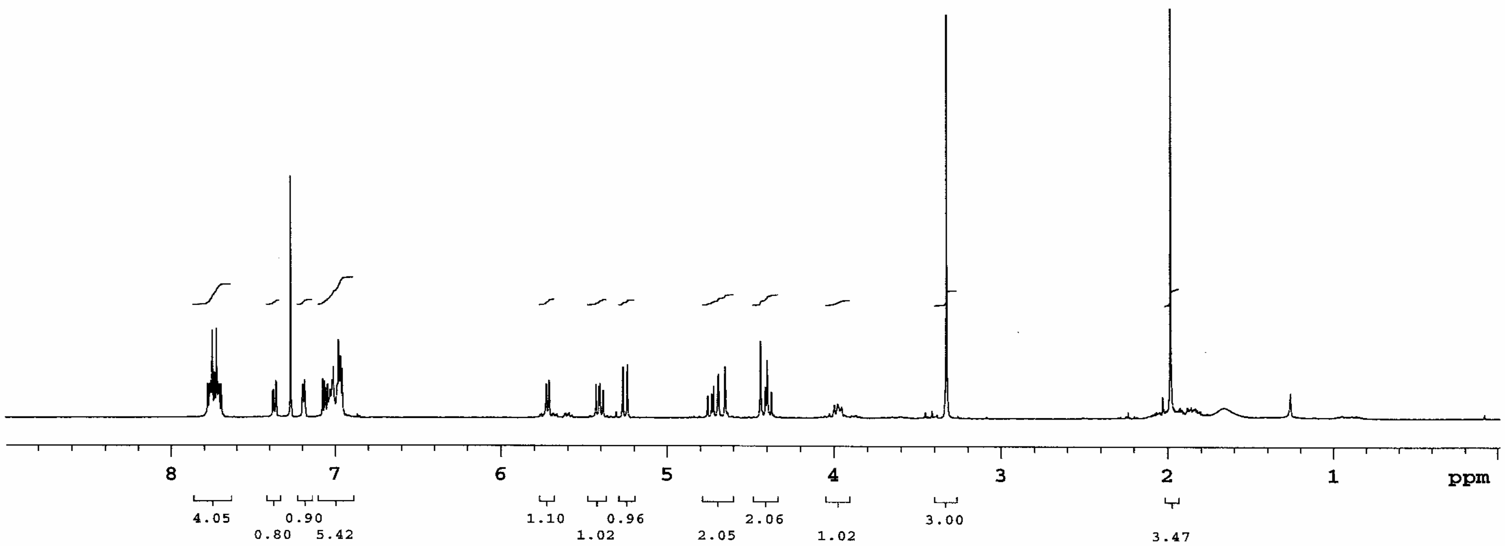
10a

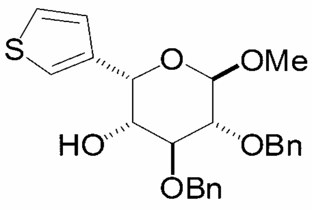
^{13}C NMR,75MHz, $CDCl_3$





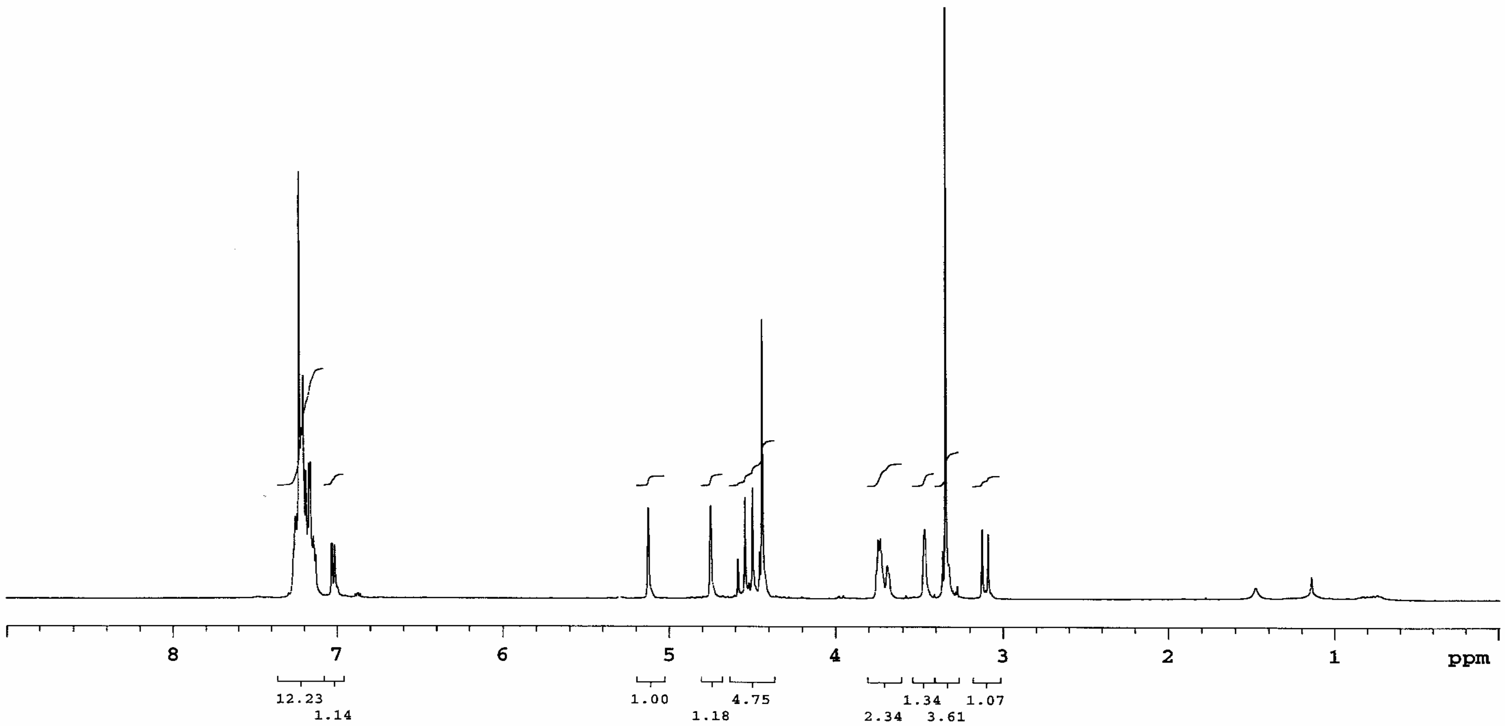
^{1}H NMR, 300MHz, $CDCl_3$

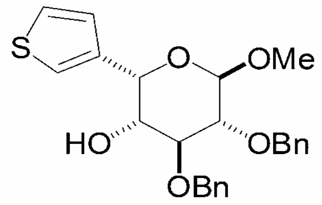




9c

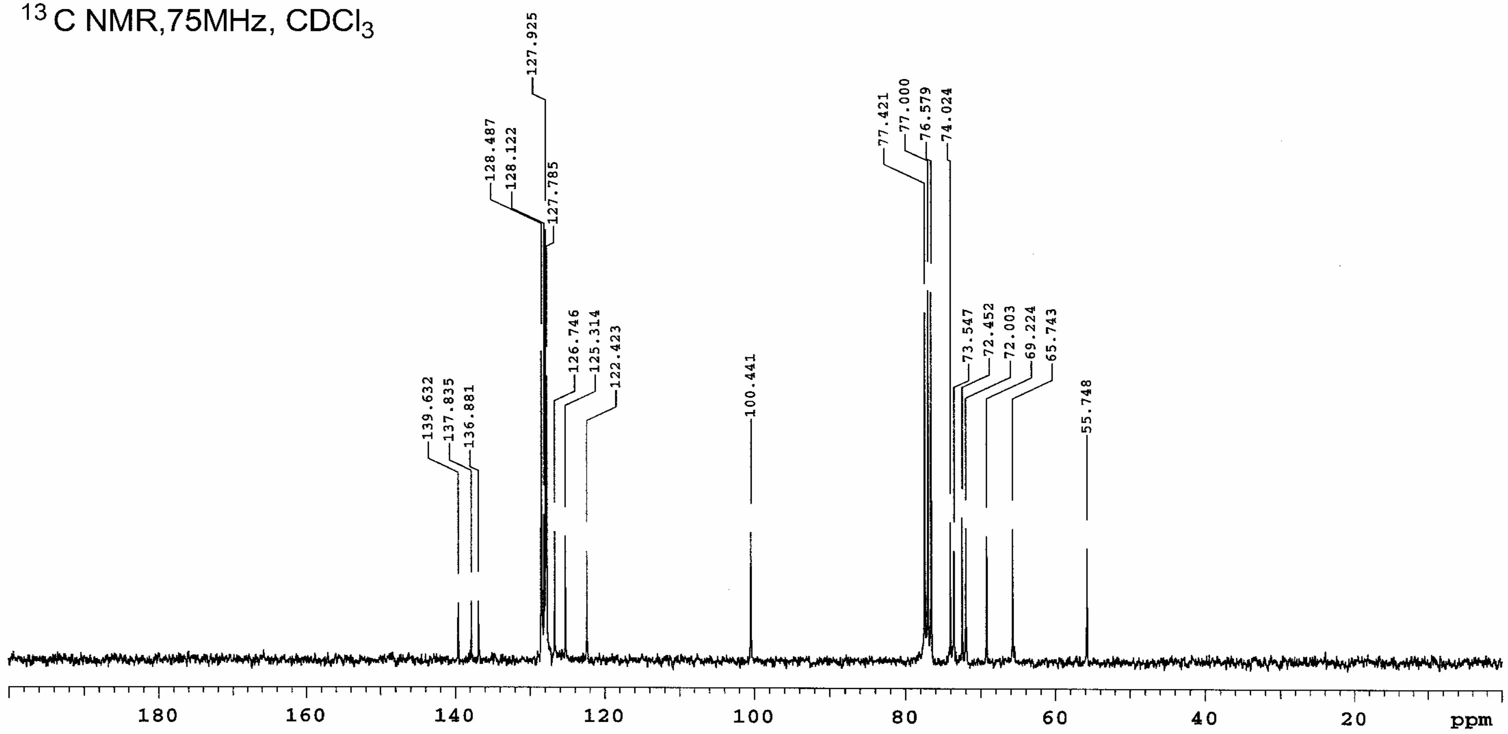
^{1}H NMR, 300MHz, $CDCl_3$

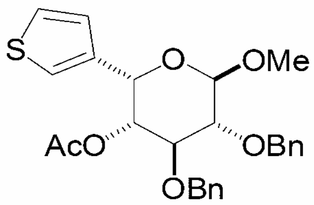




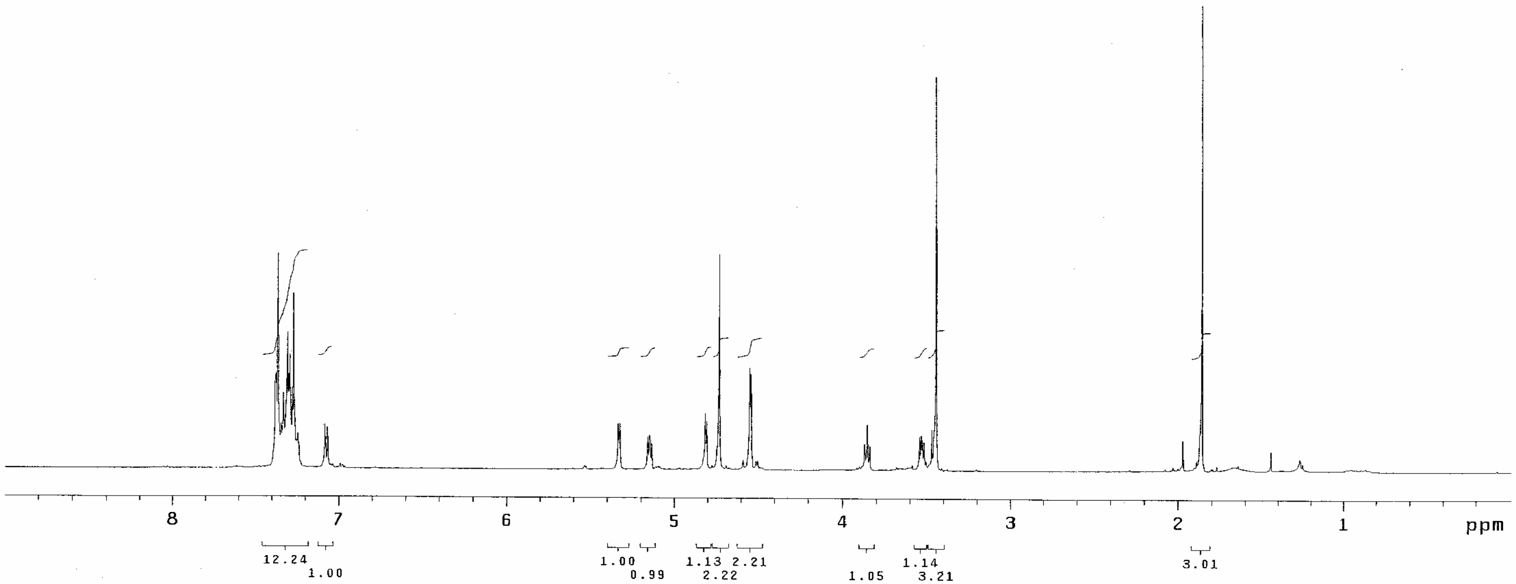
9c

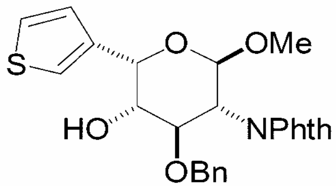
^{13}C NMR,75MHz, $CDCl_3$





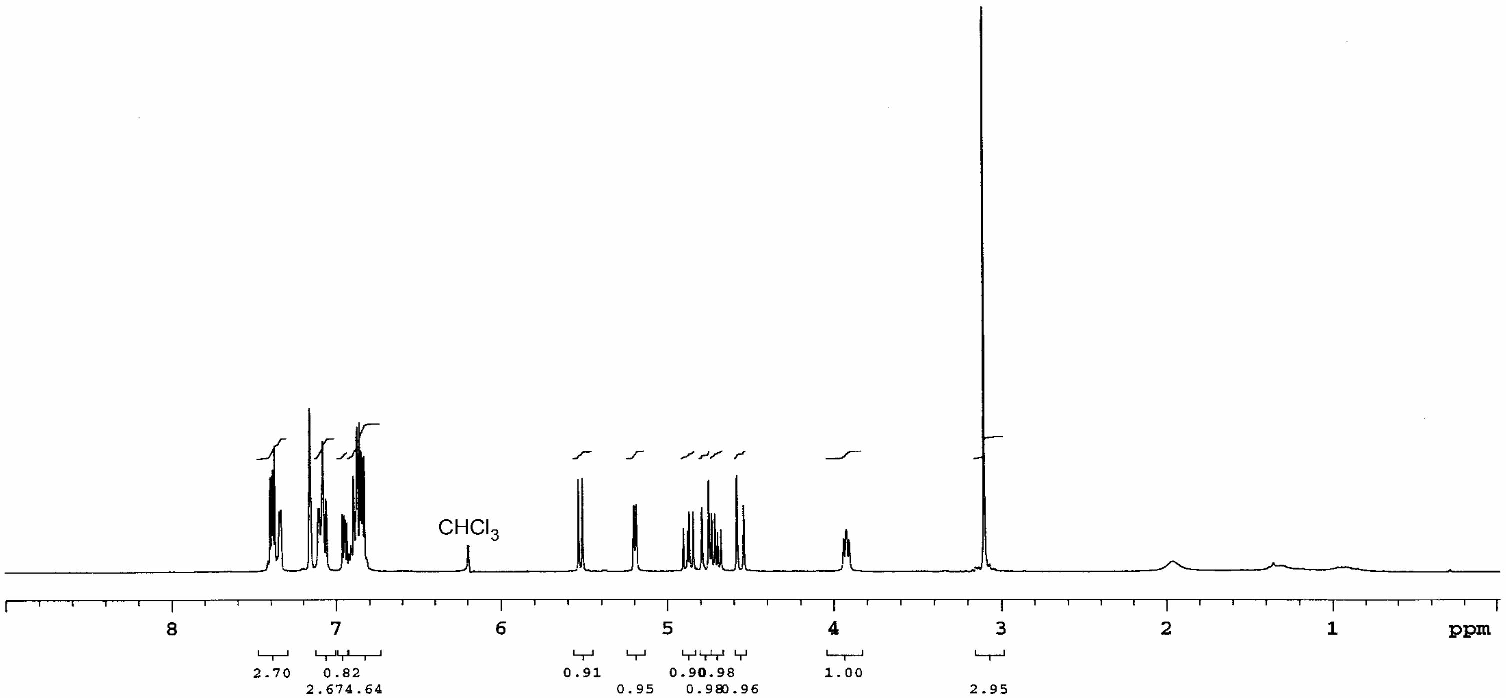
^{1}H NMR, 300MHz, $CDCl_3$

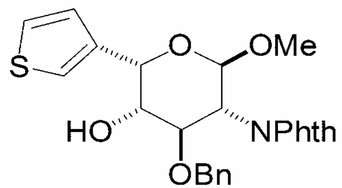




10c

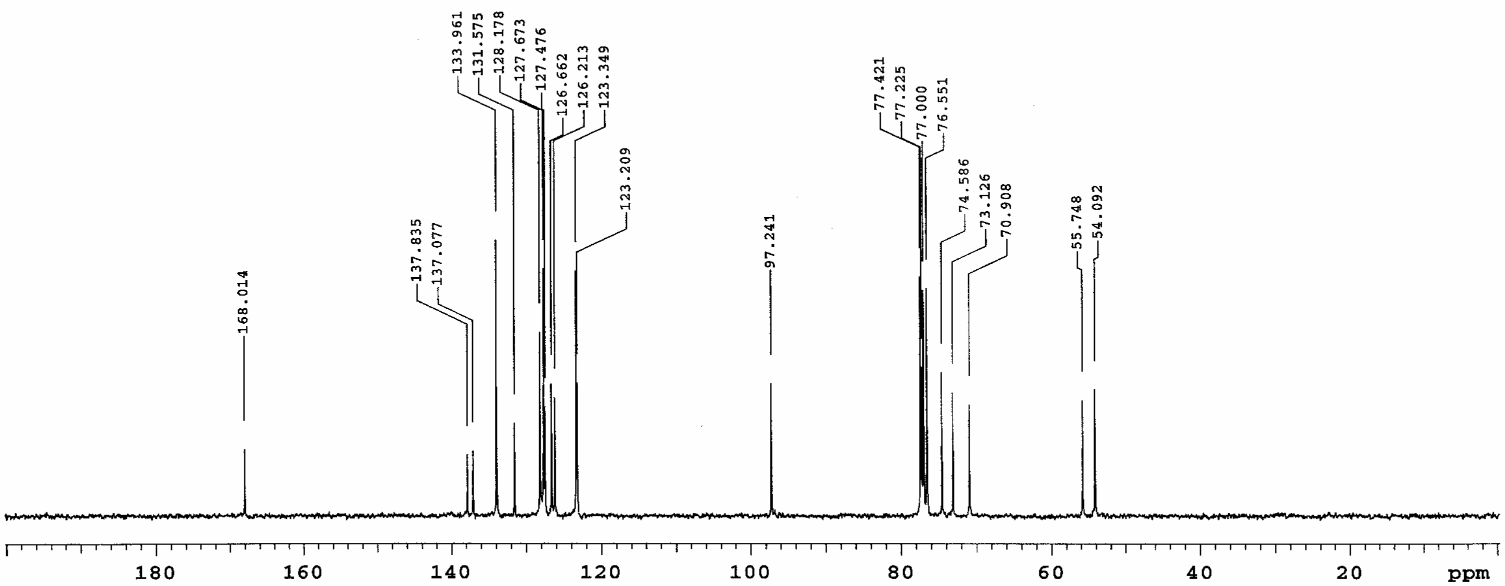
^{1}H NMR, 300MHz, C_6D_6

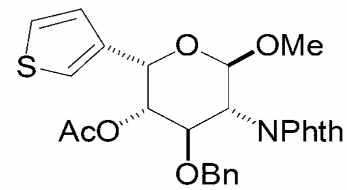




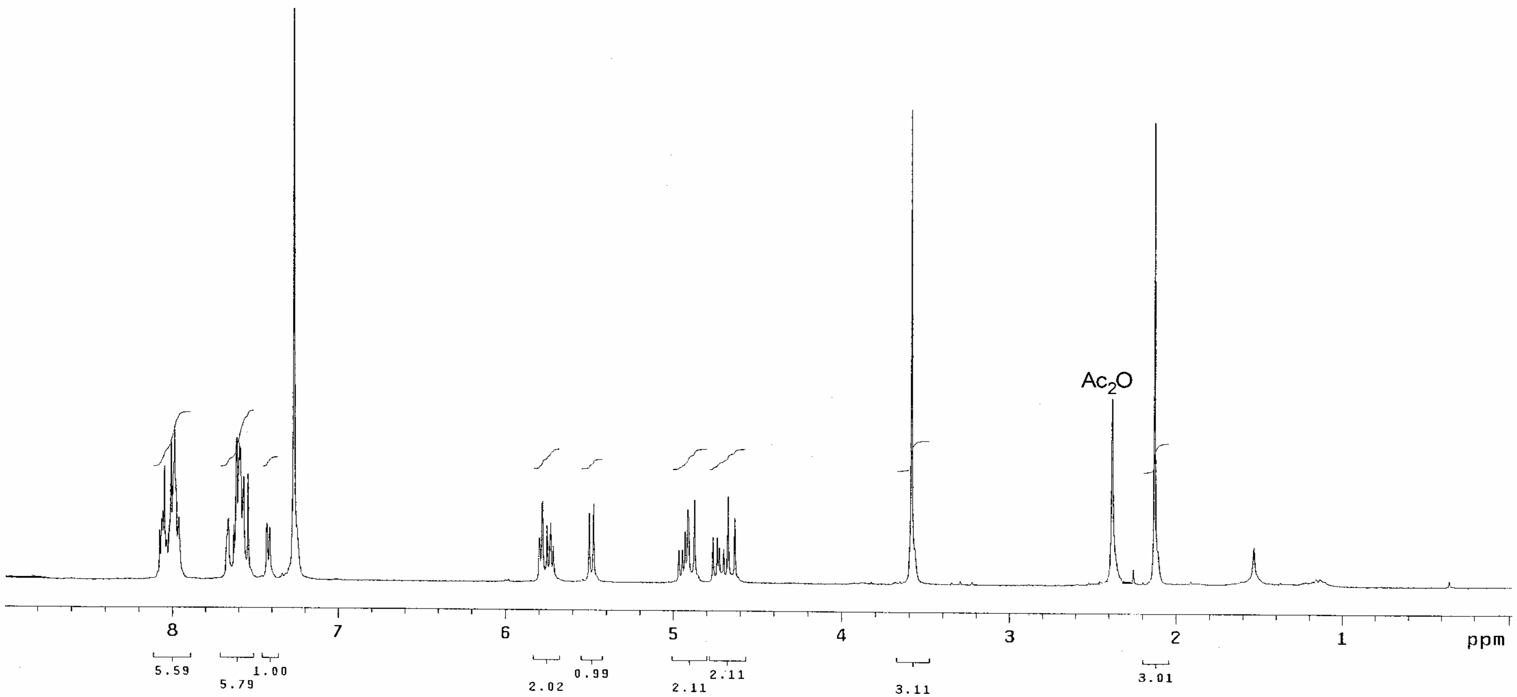
10c

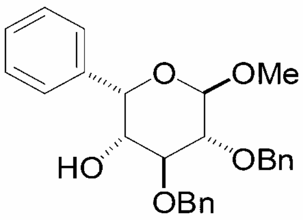
^{13}C NMR,75MHz, $CDCl_3$





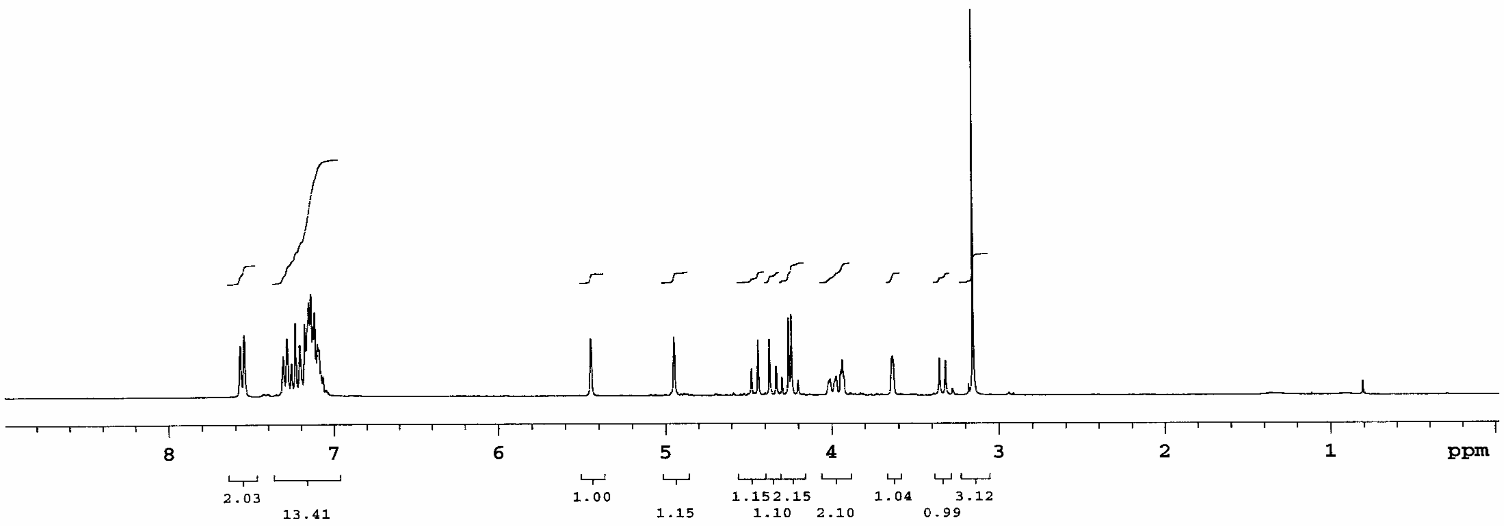
^{1}H NMR, 300MHz, $CDCl_3$

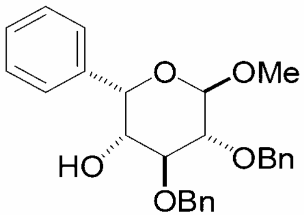




9d

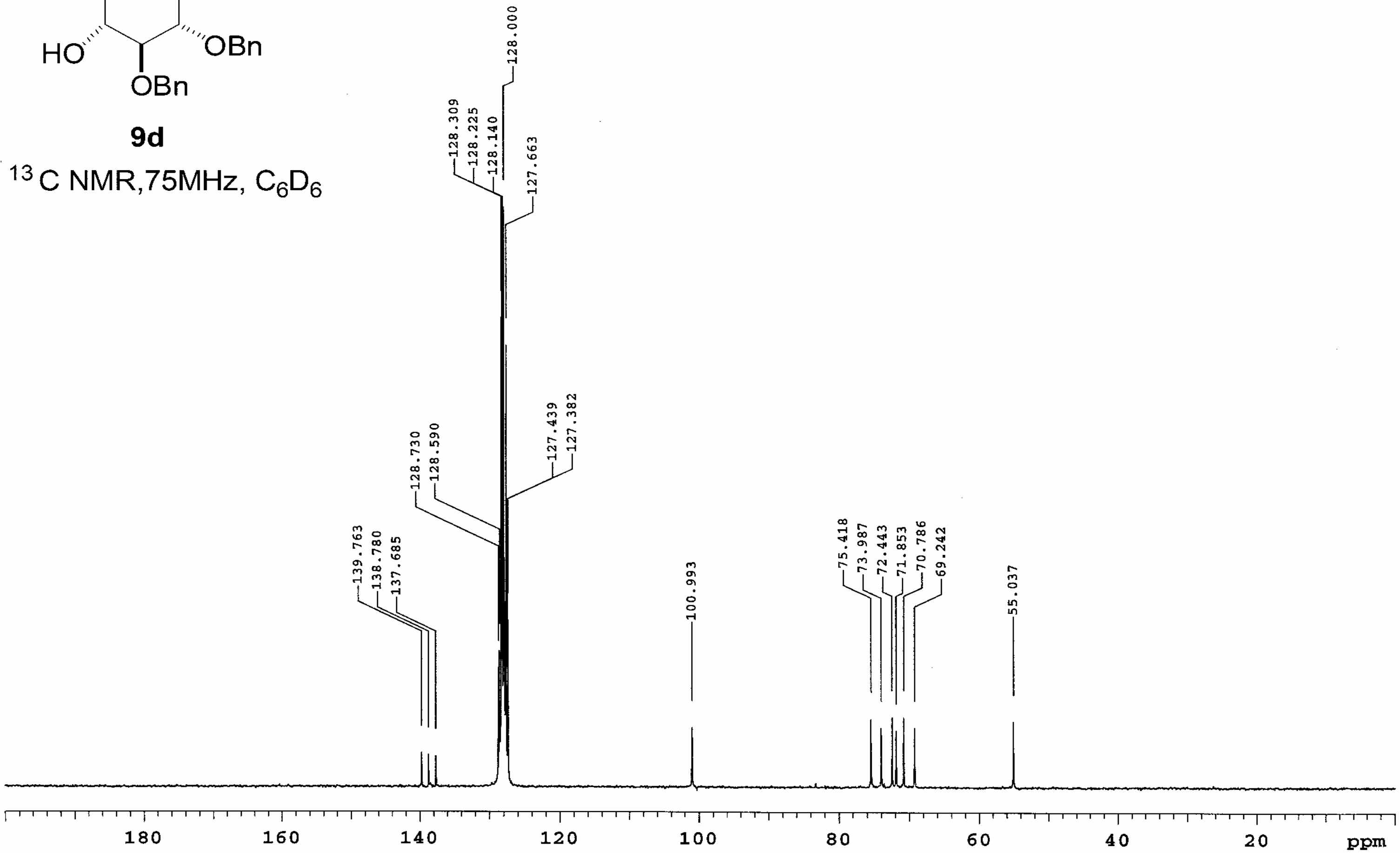
^{1}H NMR, 300MHz, C_6D_6

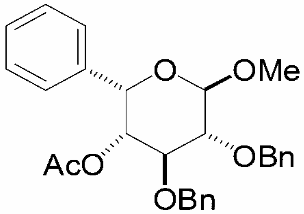




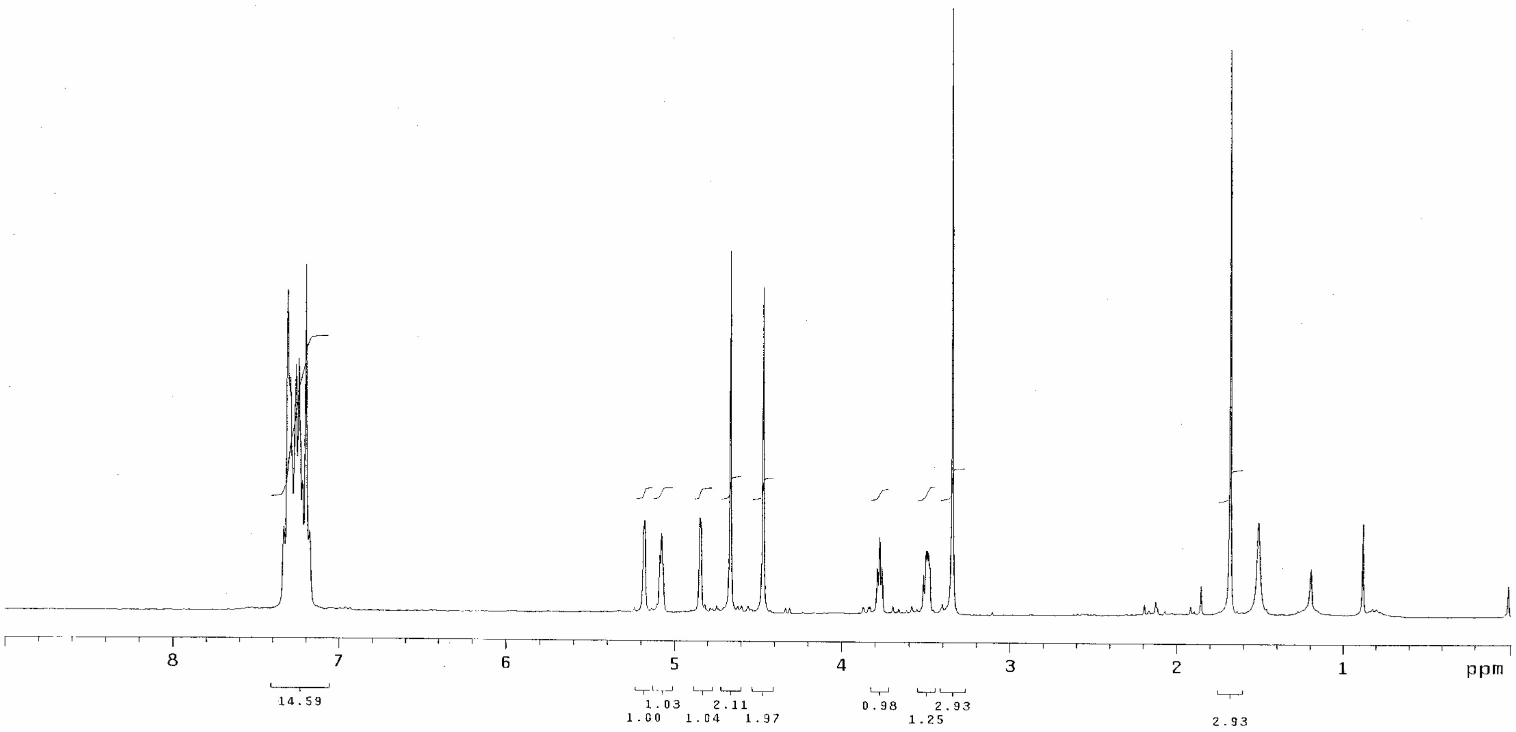
9d

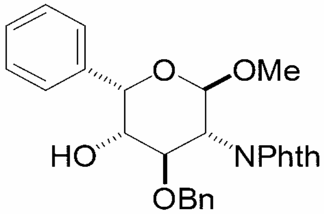
^{13}C NMR,75MHz, C_6D_6





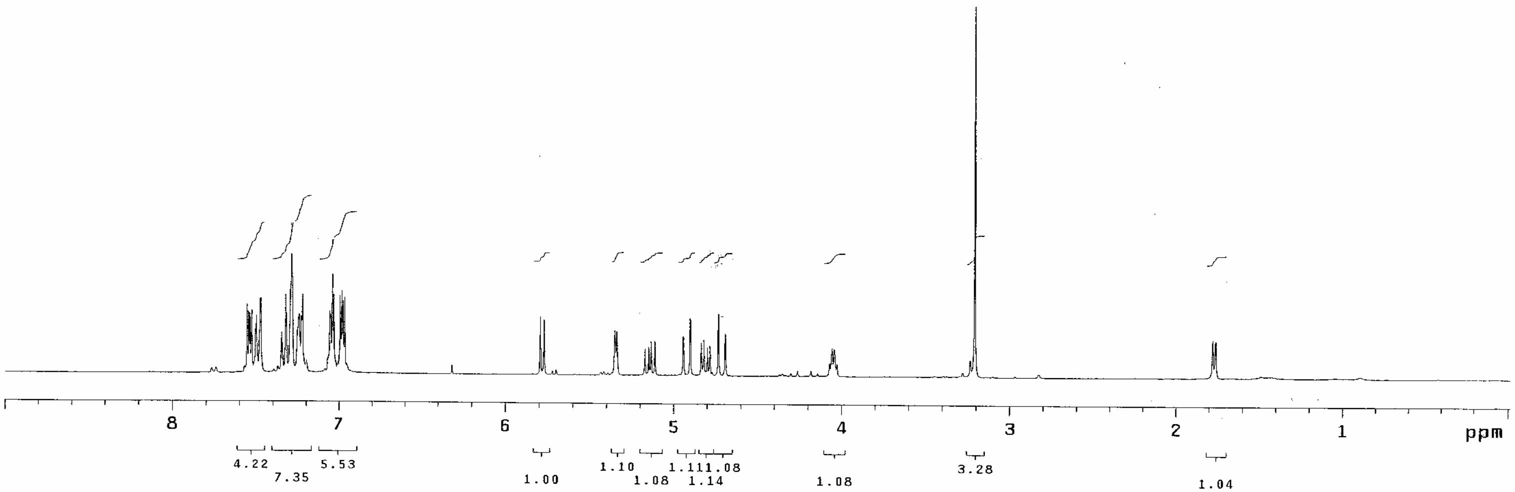
^1H NMR, 300MHz, C_6D_6

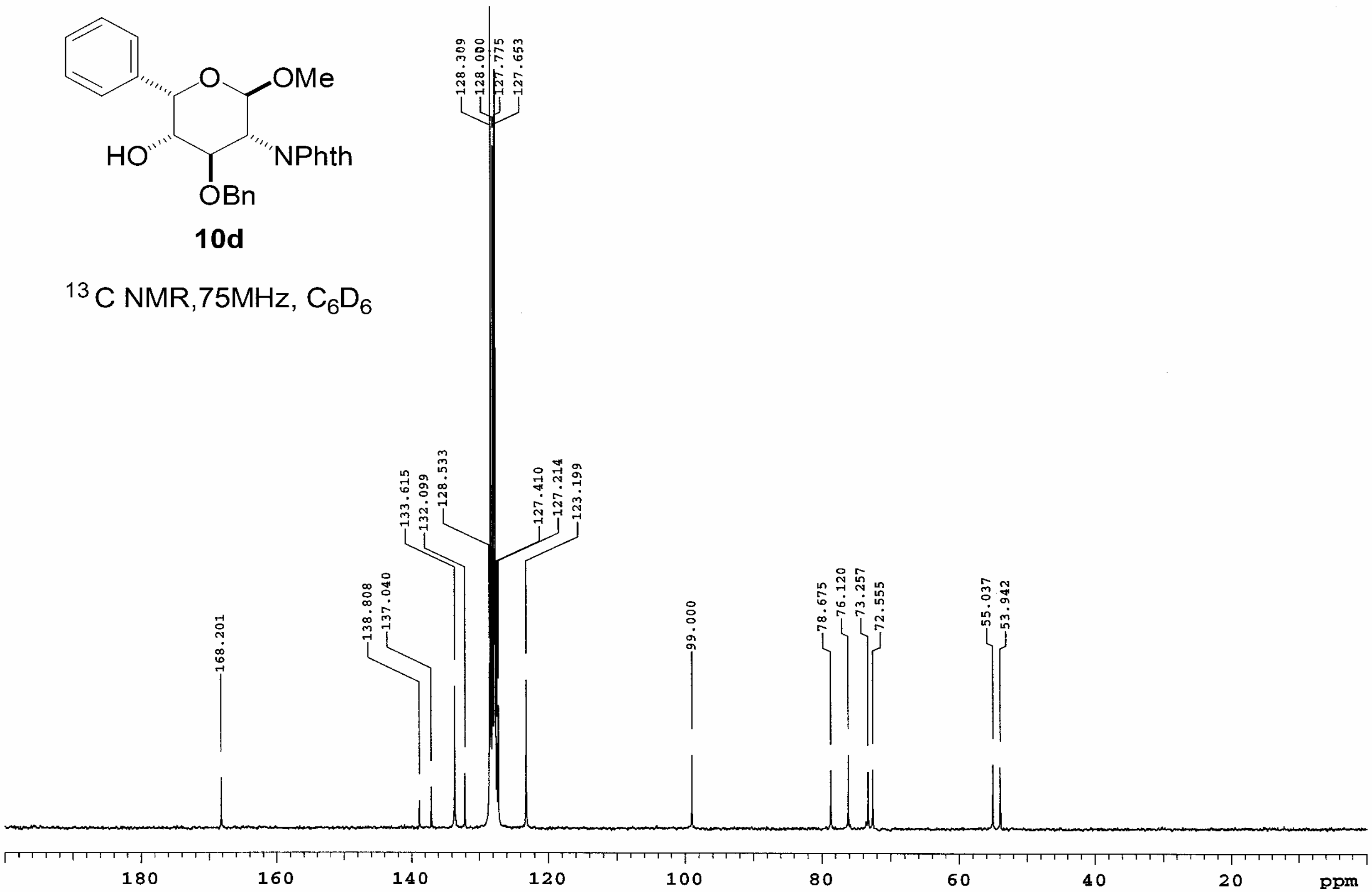




10d

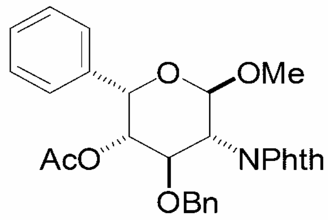
^{1}H NMR, 300MHz, C_6D_6



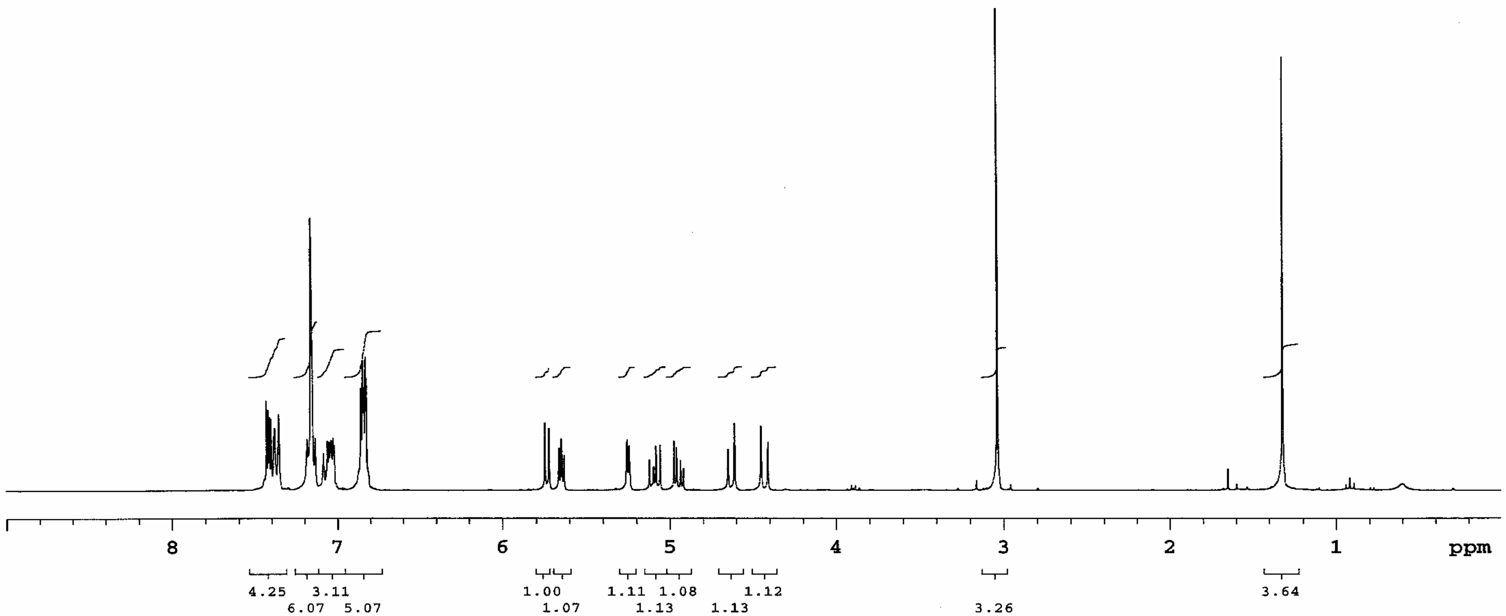


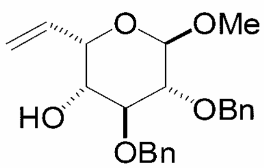
10d

^{13}C NMR, 75MHz, C_6D_6



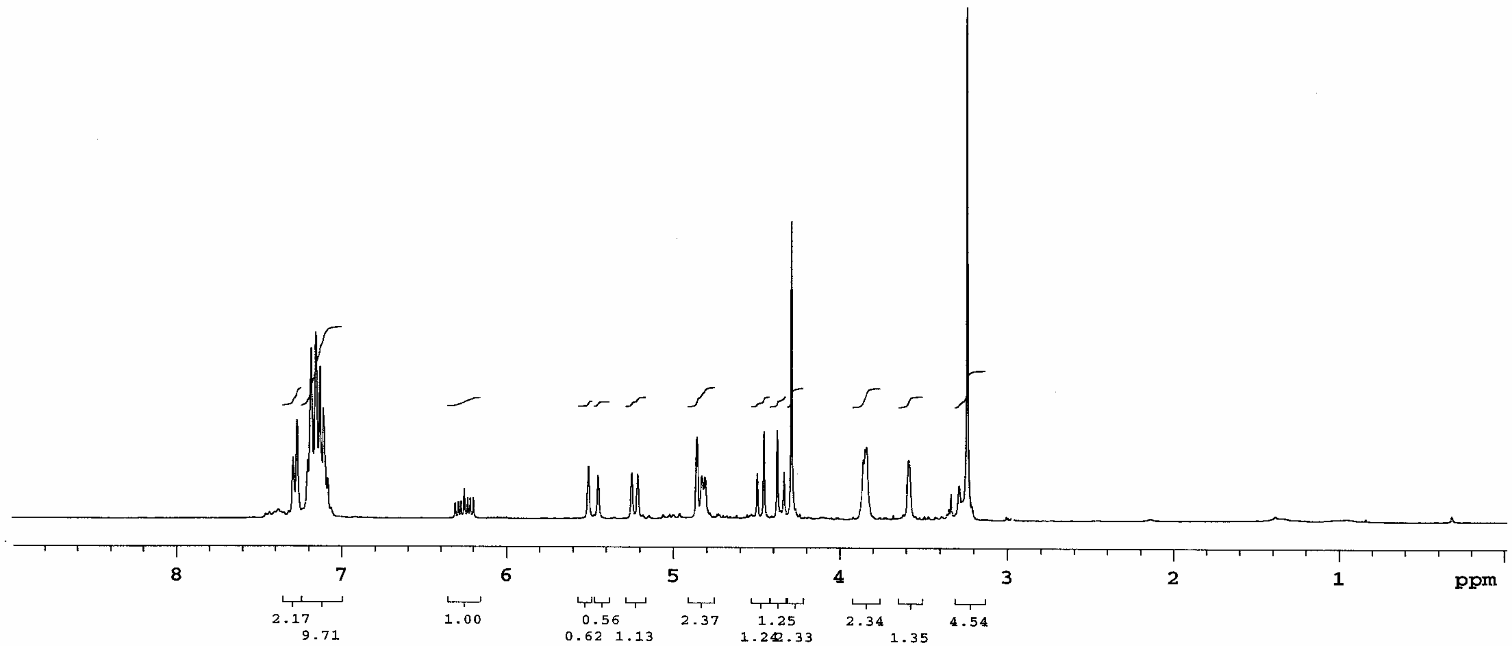
^{1}H NMR, 300MHz, C_6D_6

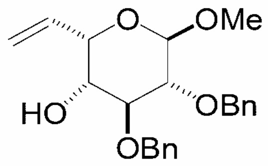




9e

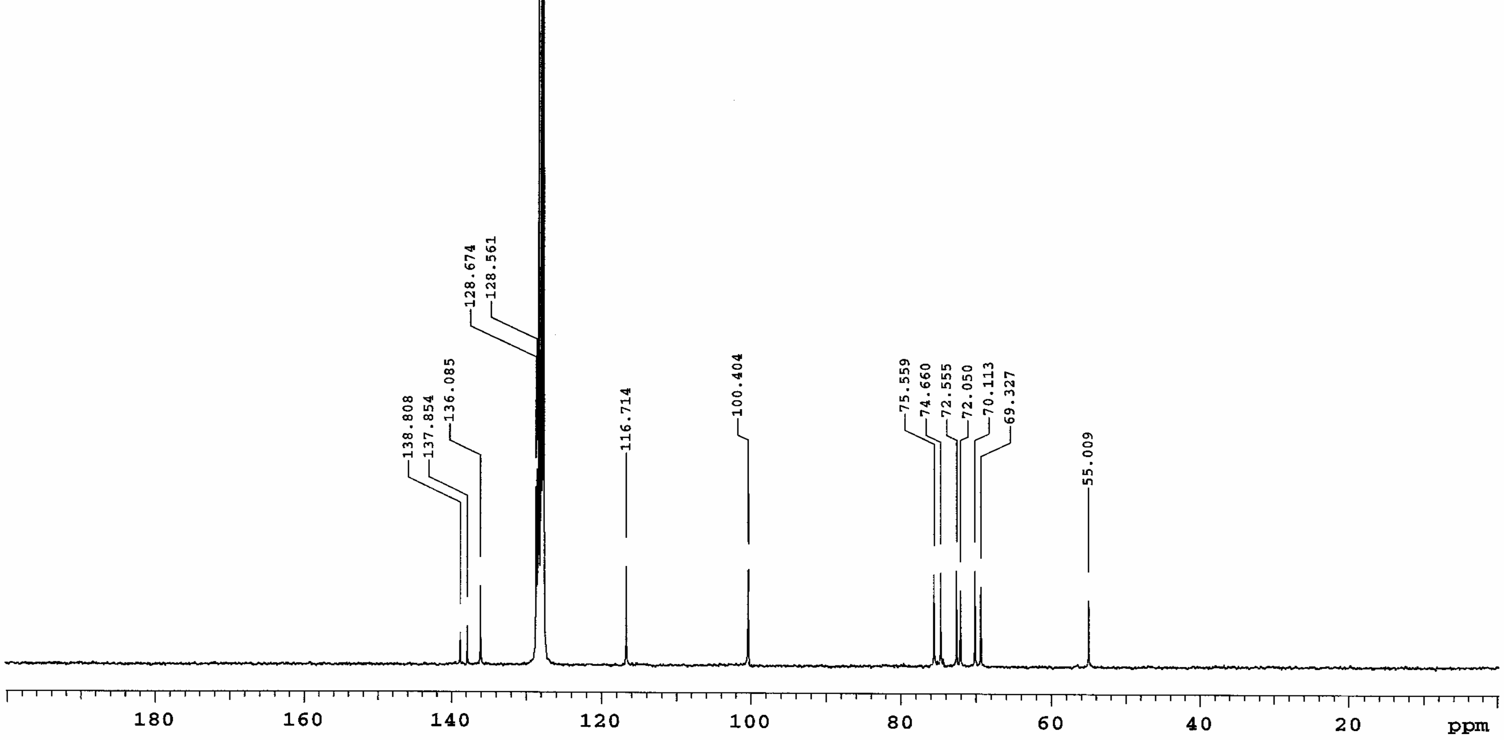
^{1}H NMR, 300MHz, $CDCl_3$

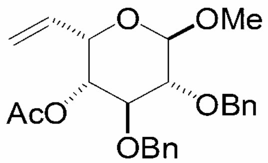




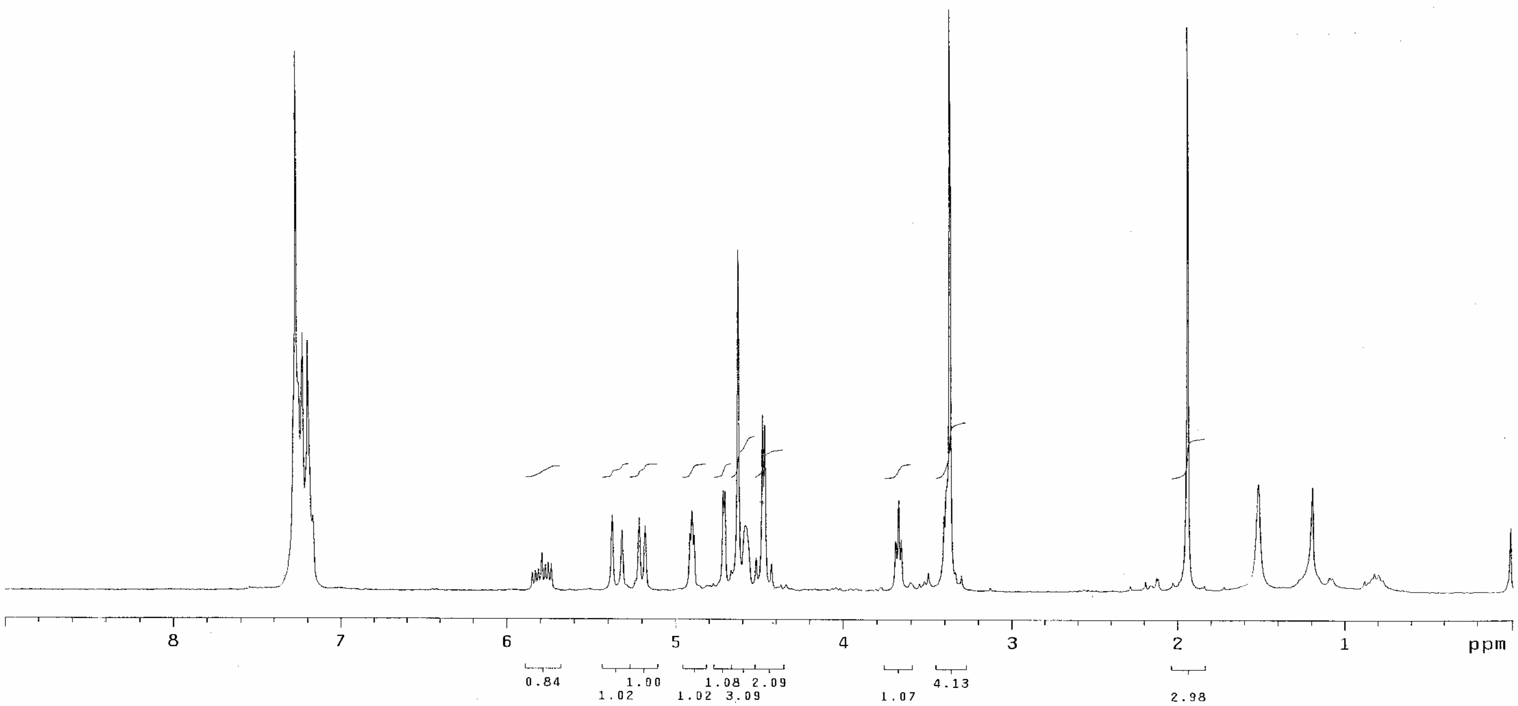
9e

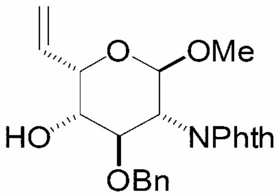
^{13}C NMR,75MHz, C_6D_6





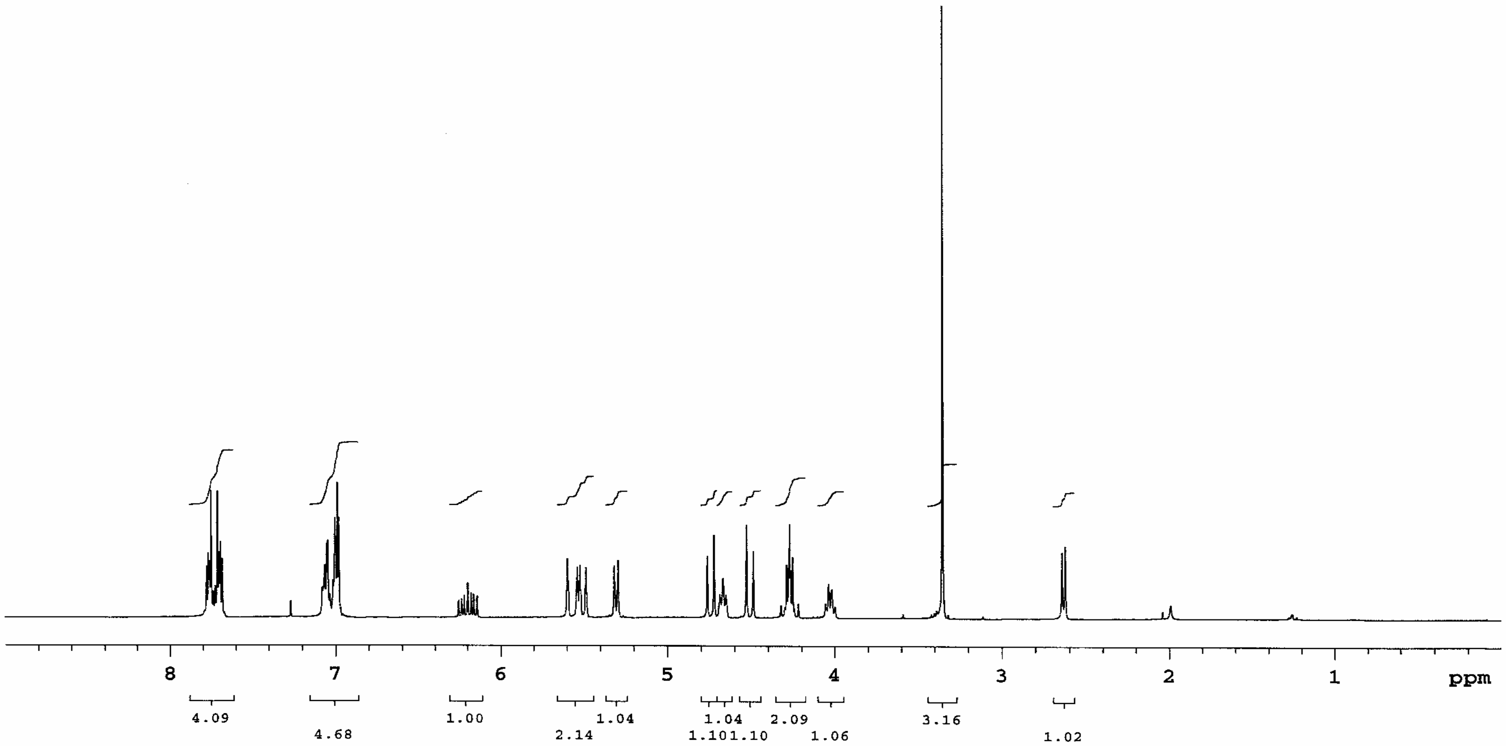
^{1}H NMR, 300MHz, $CDCl_3$

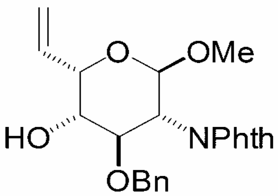




10e

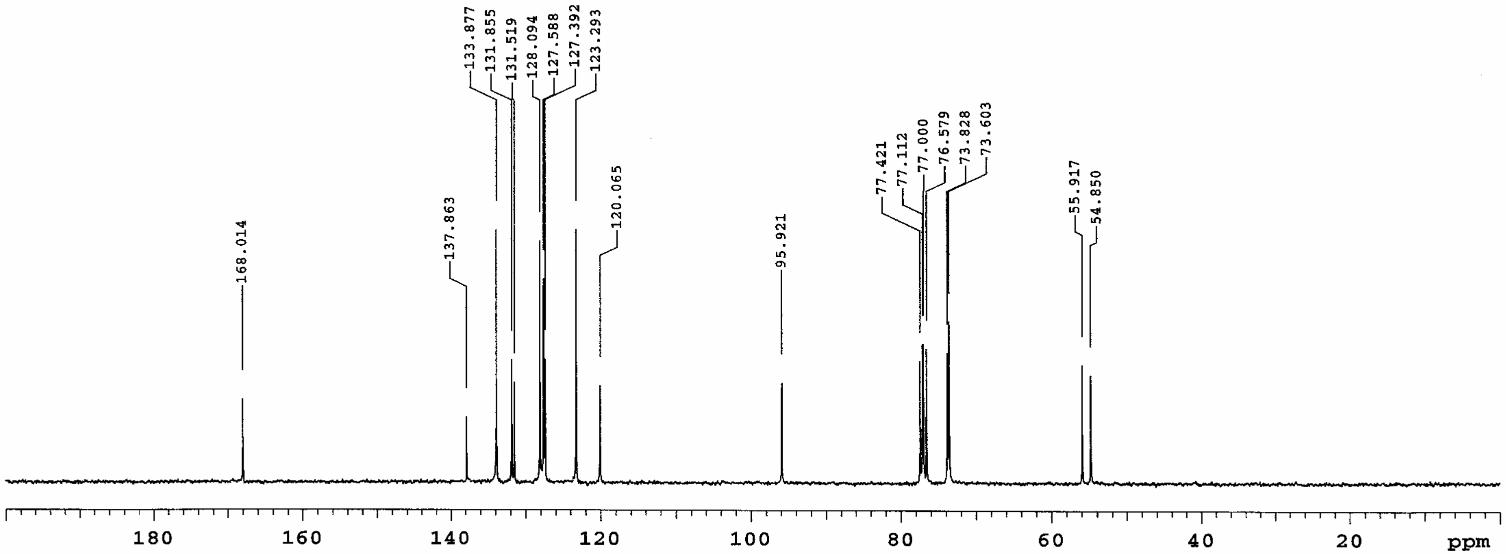
^{1}H NMR, 300MHz, $CDCl_3$

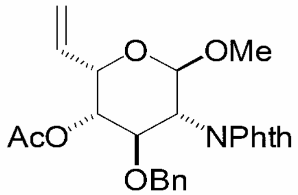




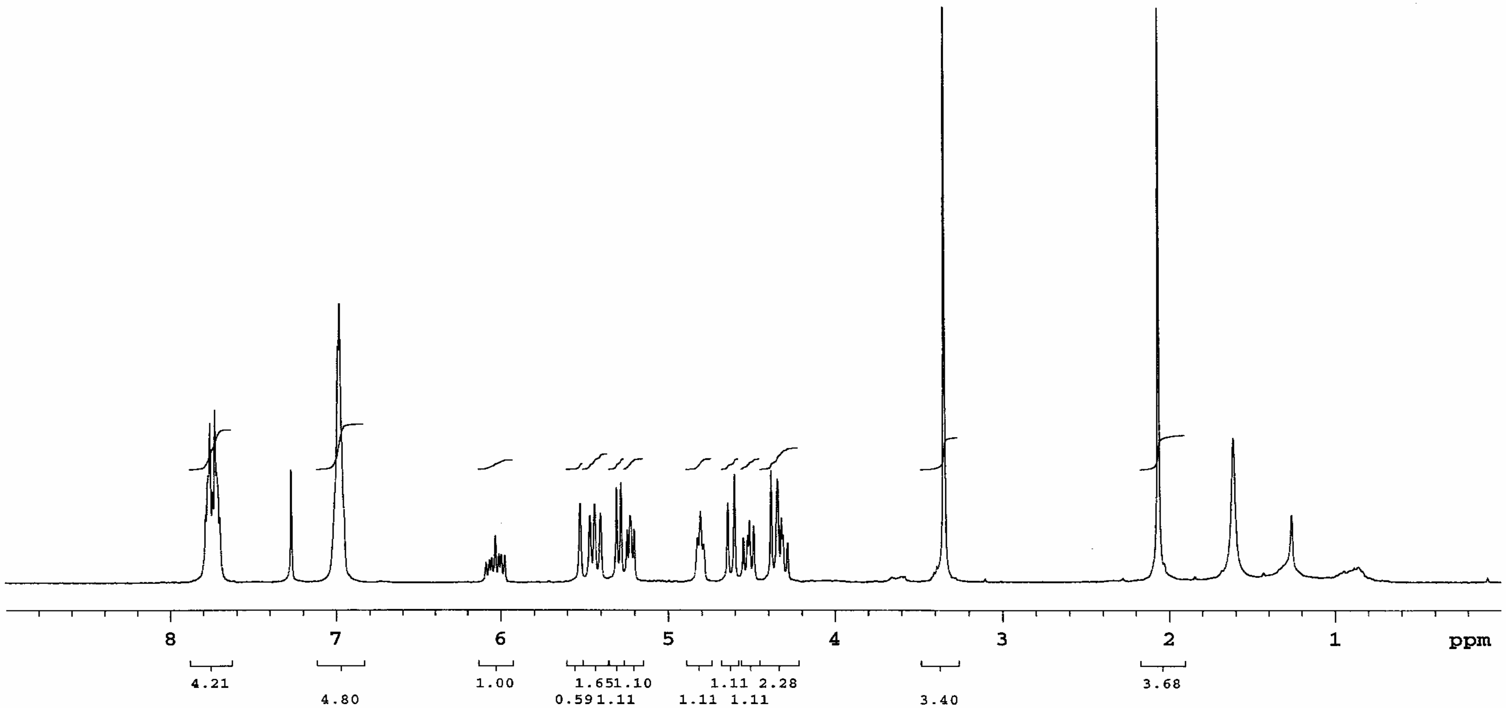
10e

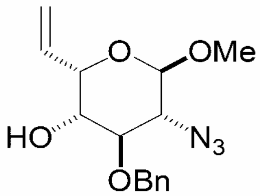
^{13}C NMR,75MHz, $CDCl_3$





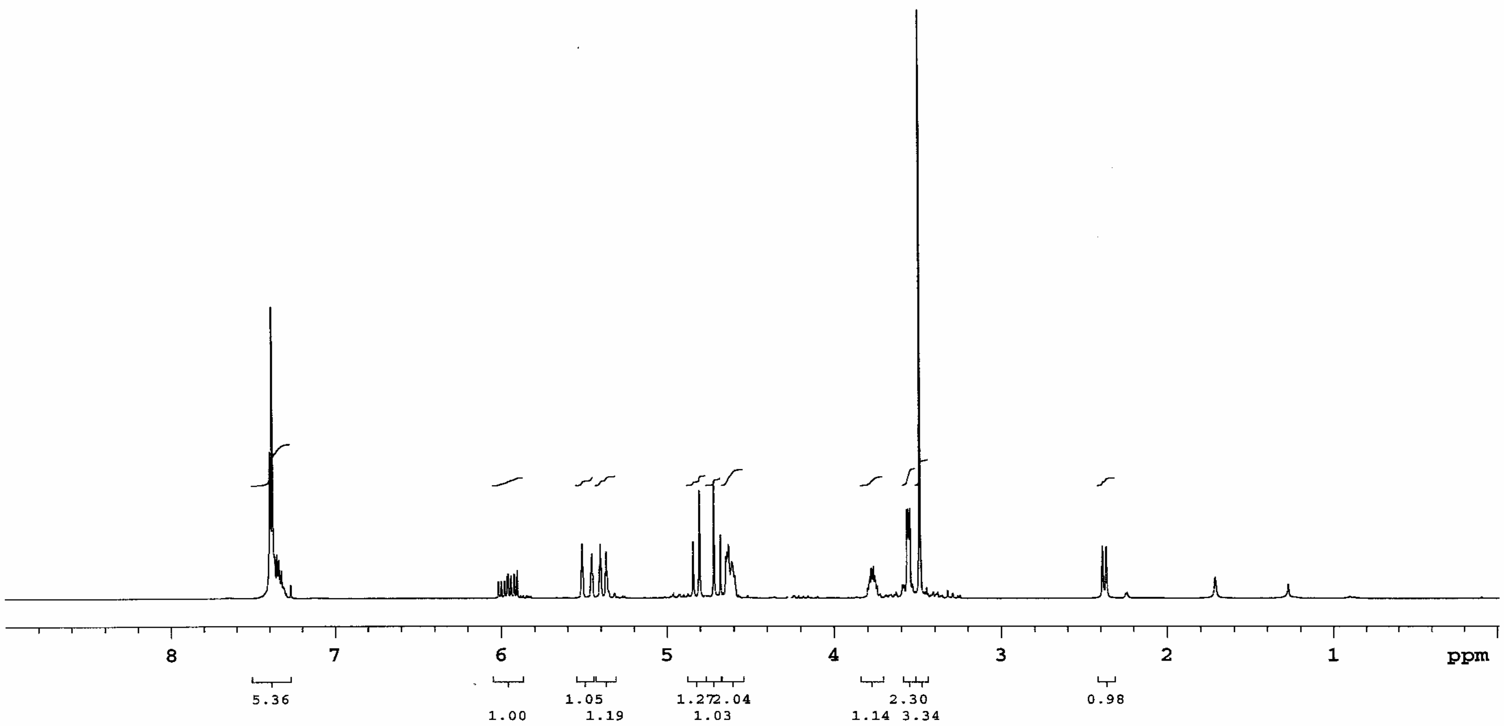
^1H NMR, 300MHz, $CDCl_3$

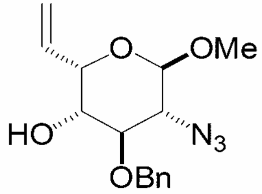




11e

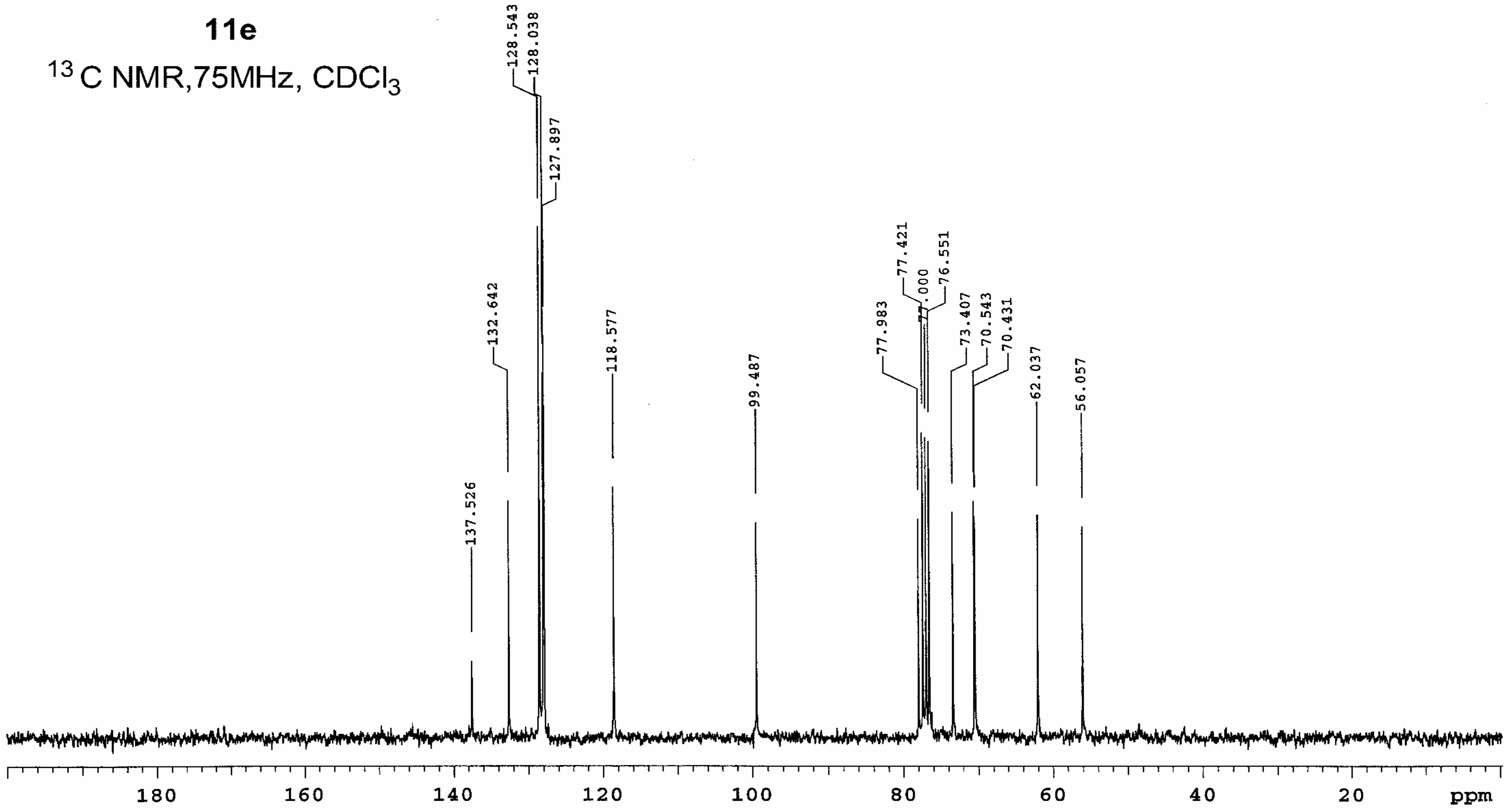
^1H NMR, 300MHz, $CDCl_3$

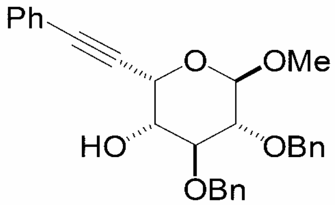




11e

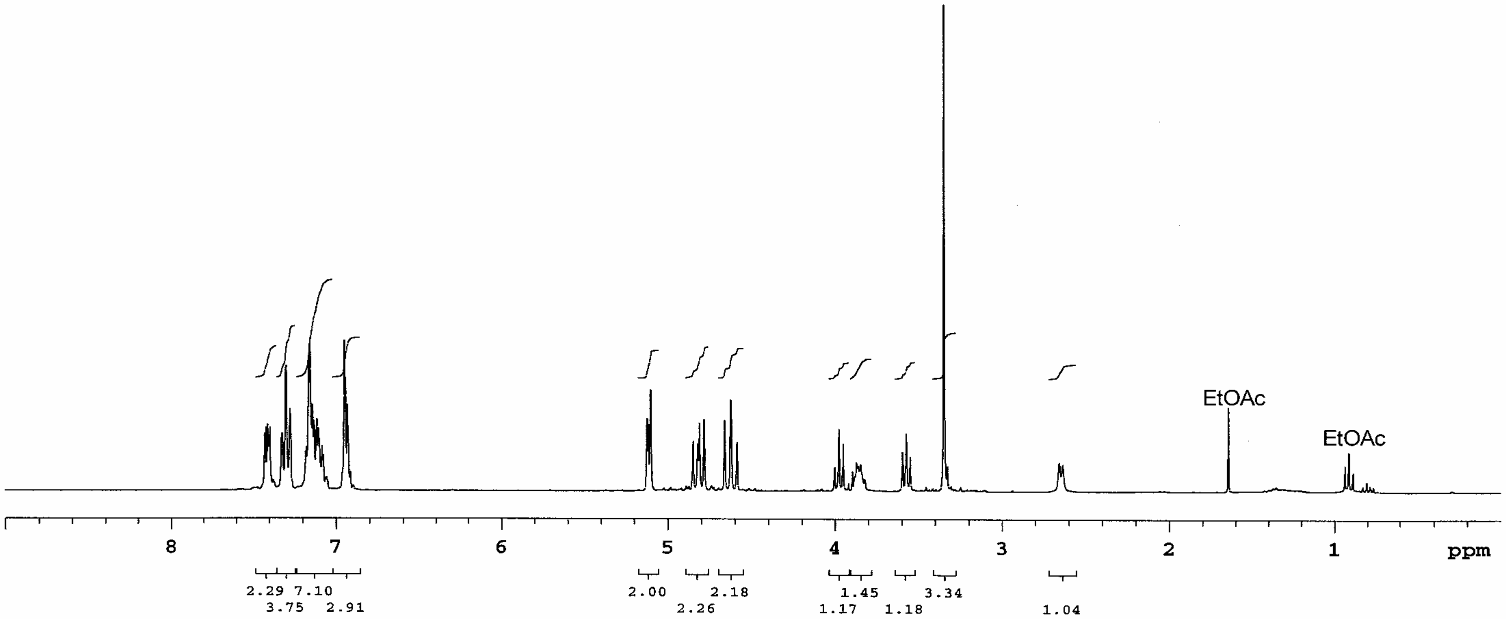
^{13}C NMR,75MHz, $CDCl_3$

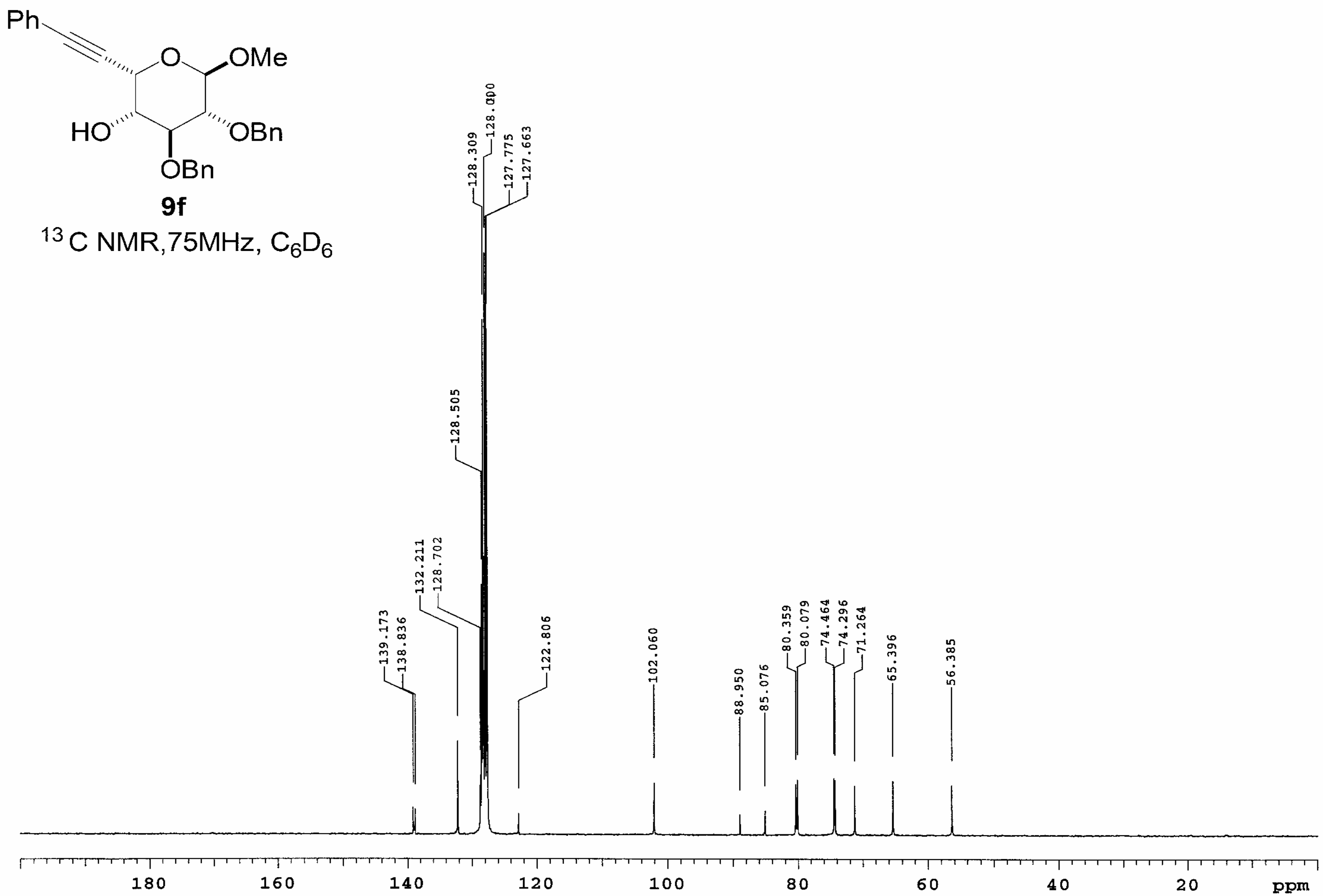




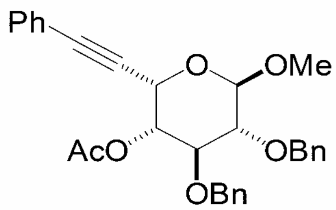
9f

^1H NMR, 300MHz, C_6D_6

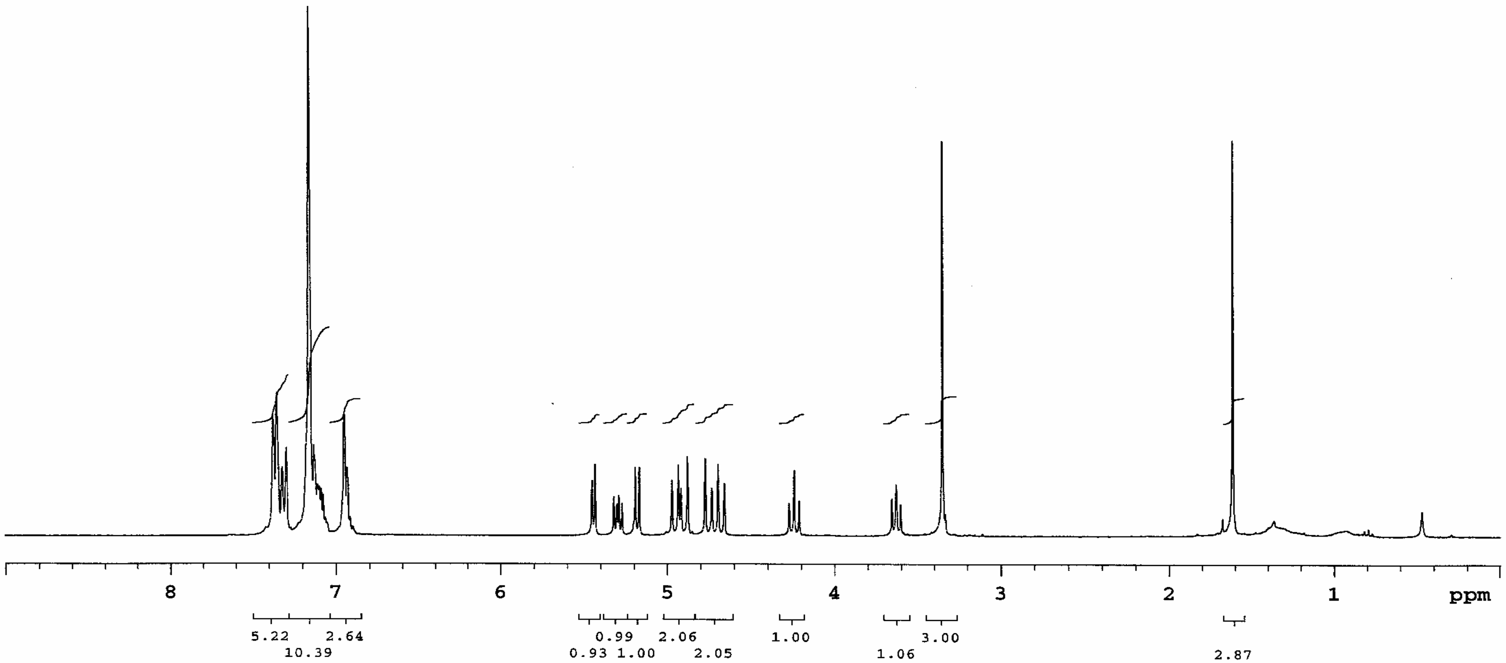


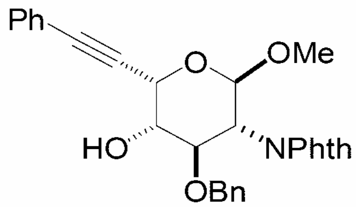


Ph
O
OMe
HO
OBn
OBn
9f
13C NMR,75MHz, C6D6
128.309
128.000
127.775
127.663
128.505
132.211
128.702
139.173
138.836
122.806
102.060
88.950
85.076
80.359
80.079
74.464
74.296
71.264
65.396
56.385
180
160
140
120
100
80
60
40
20
ppm



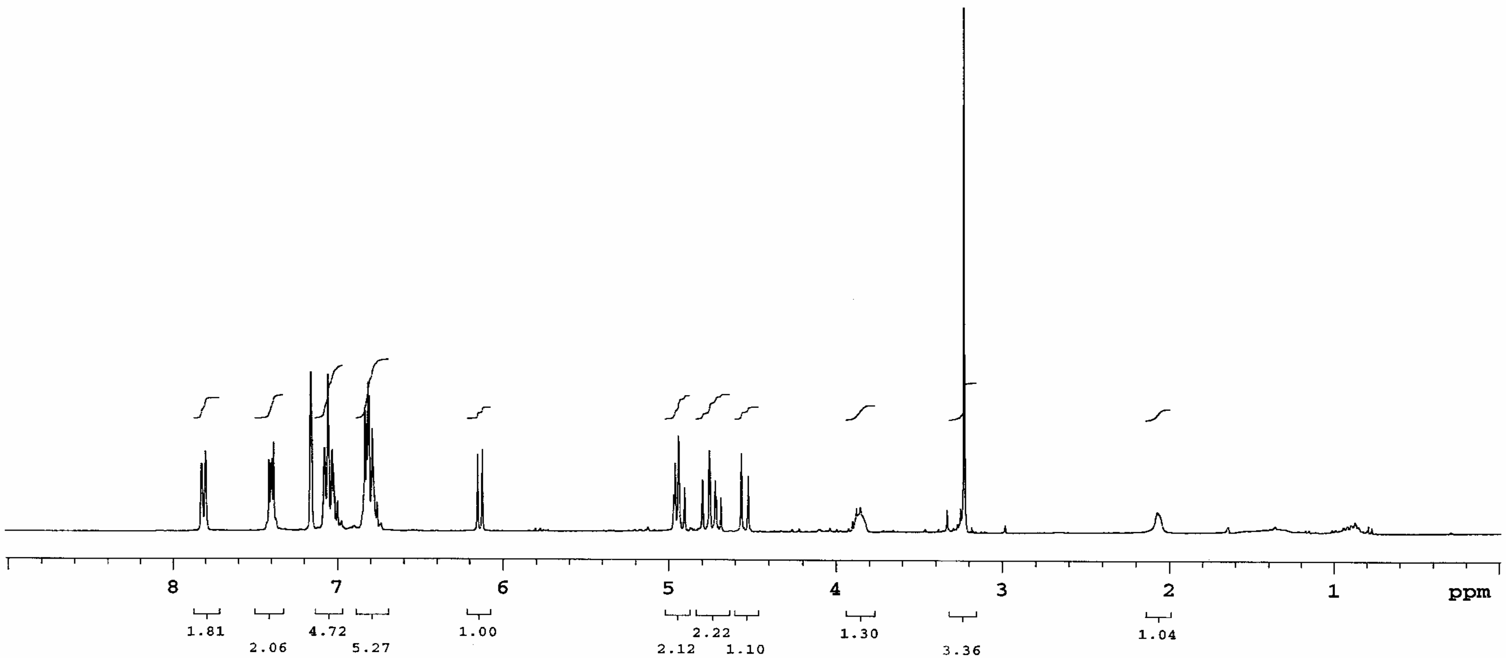
^{1}H NMR, 300MHz, C_6D_6

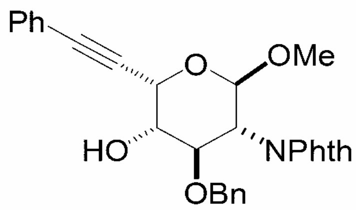




10f

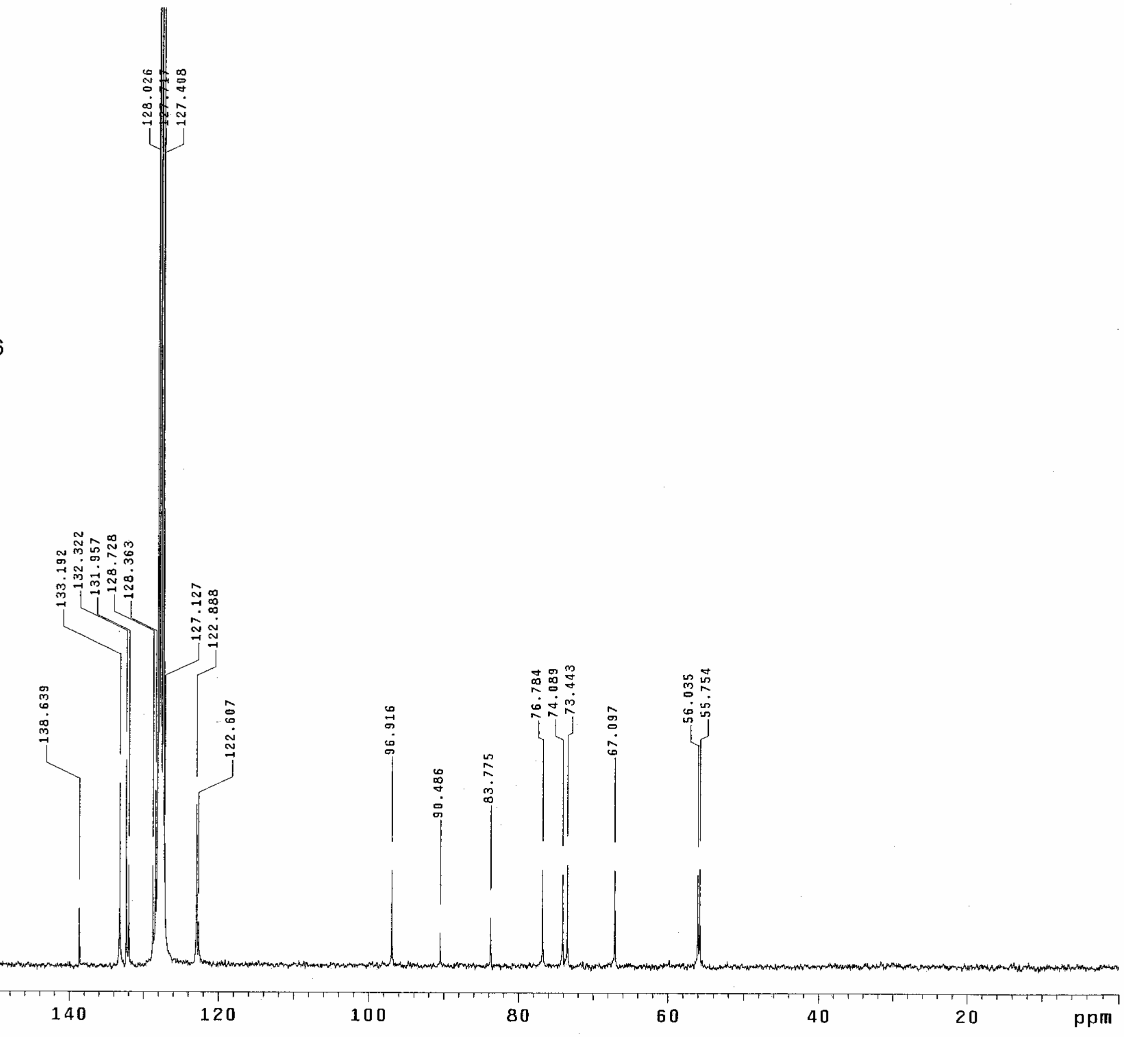
[1] H NMR, 300MHz, C_6D_6

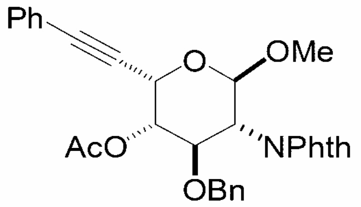




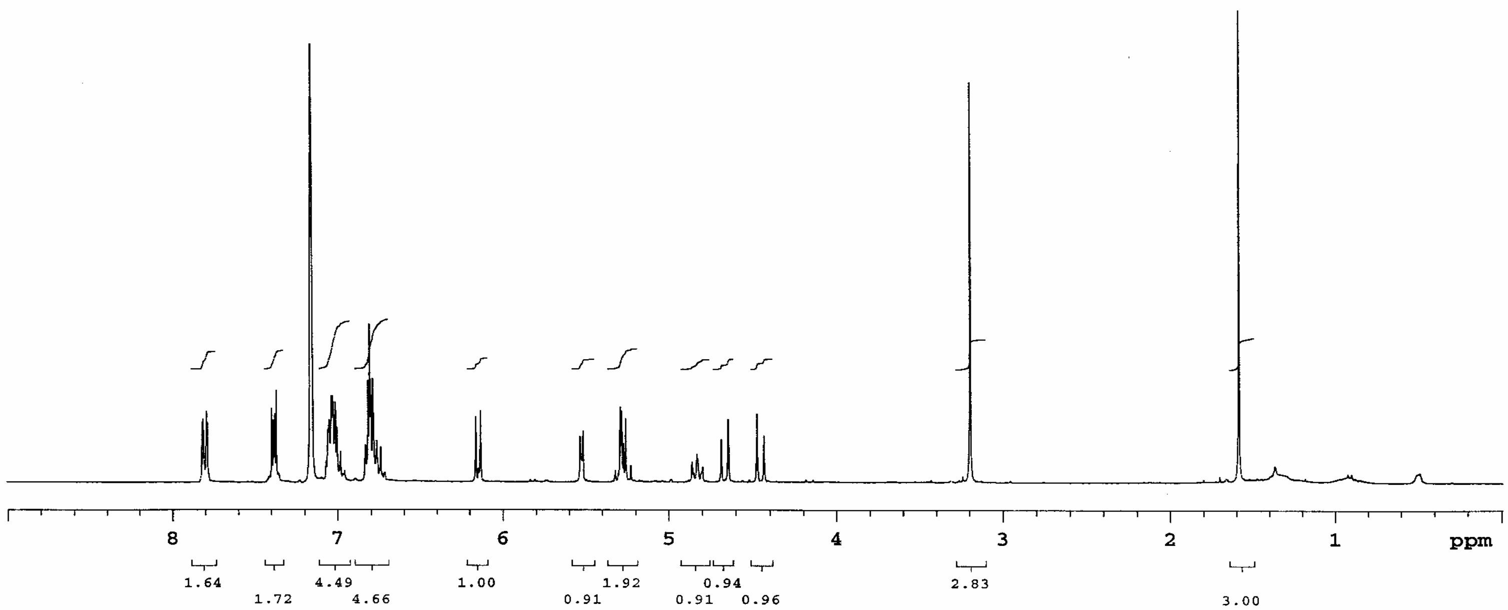
10f

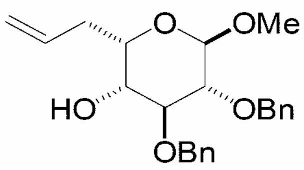
^{13}C NMR,75MHz, C_6D_6





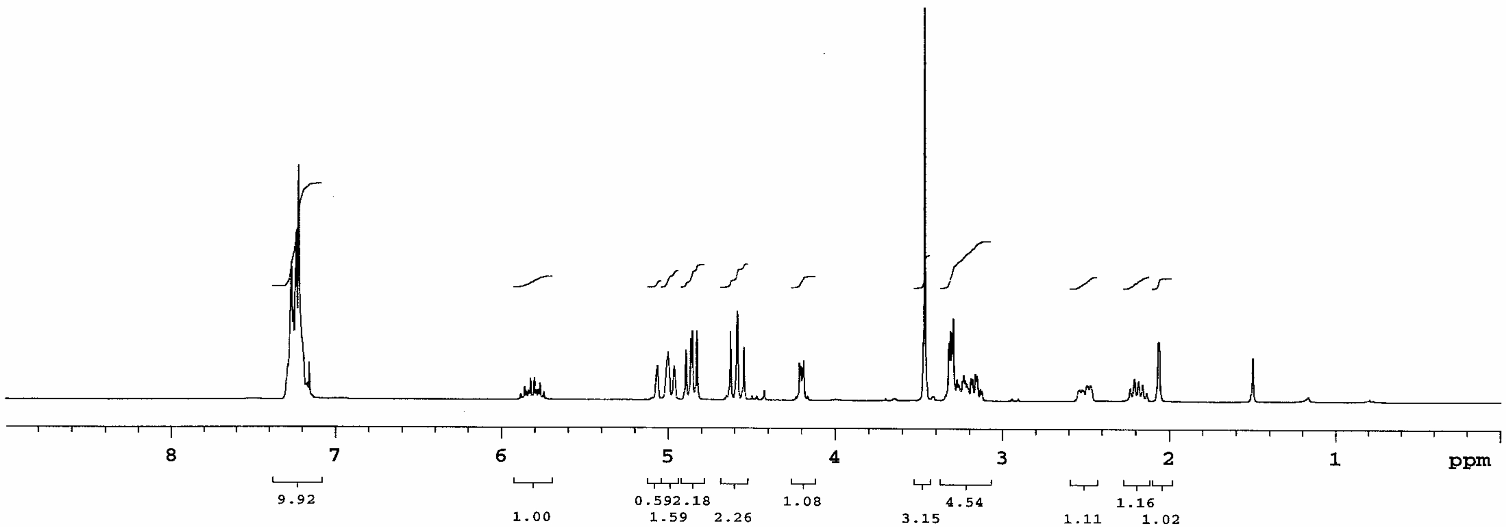
^{1}H NMR, 300MHz, C_6D_6

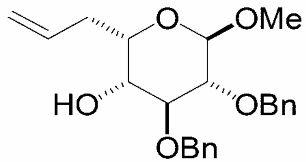




9g

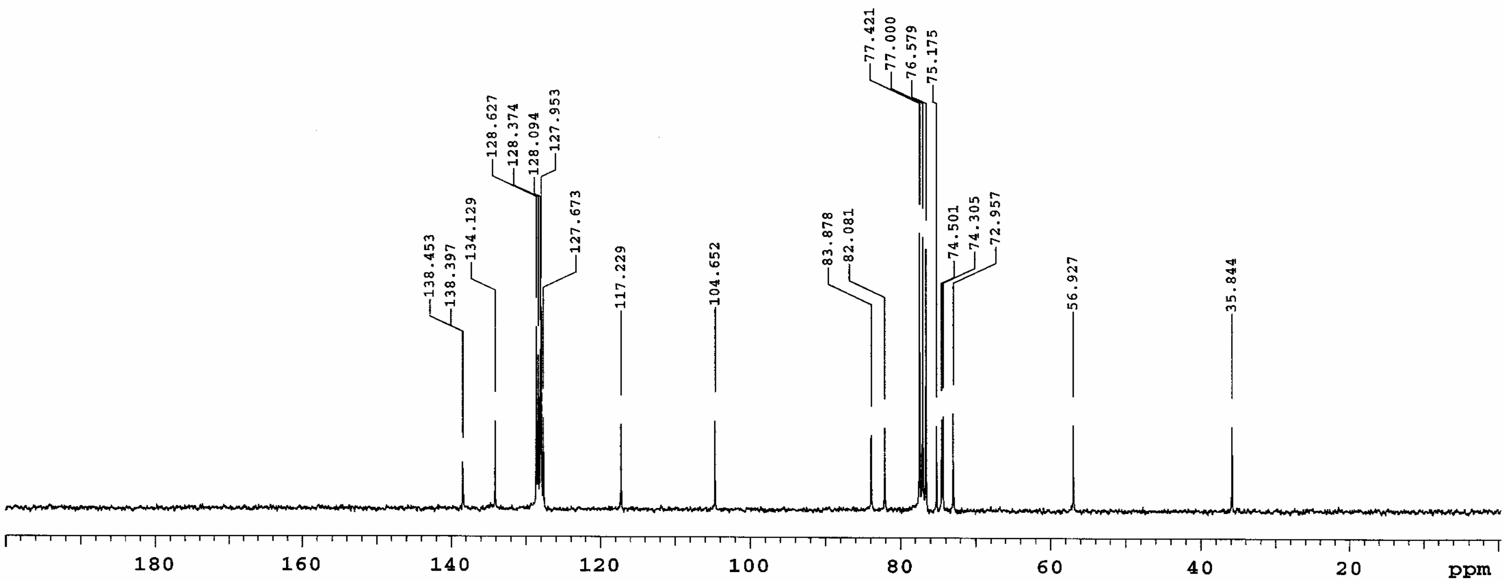
^{1}H NMR, 300MHz, $CDCl_3$

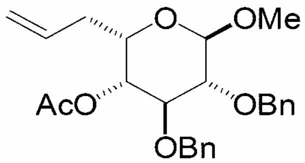




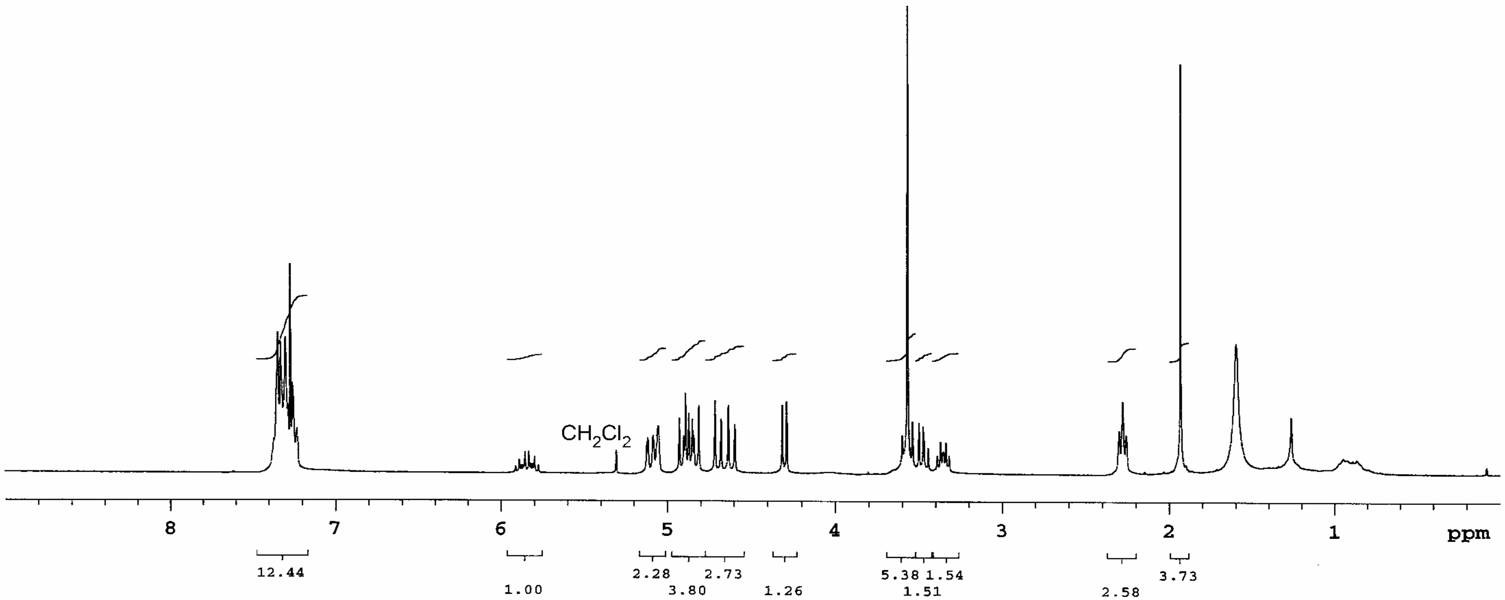
9g

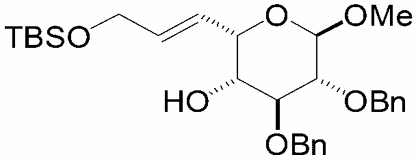
^{13}C NMR,75MHz, $CDCl_3$





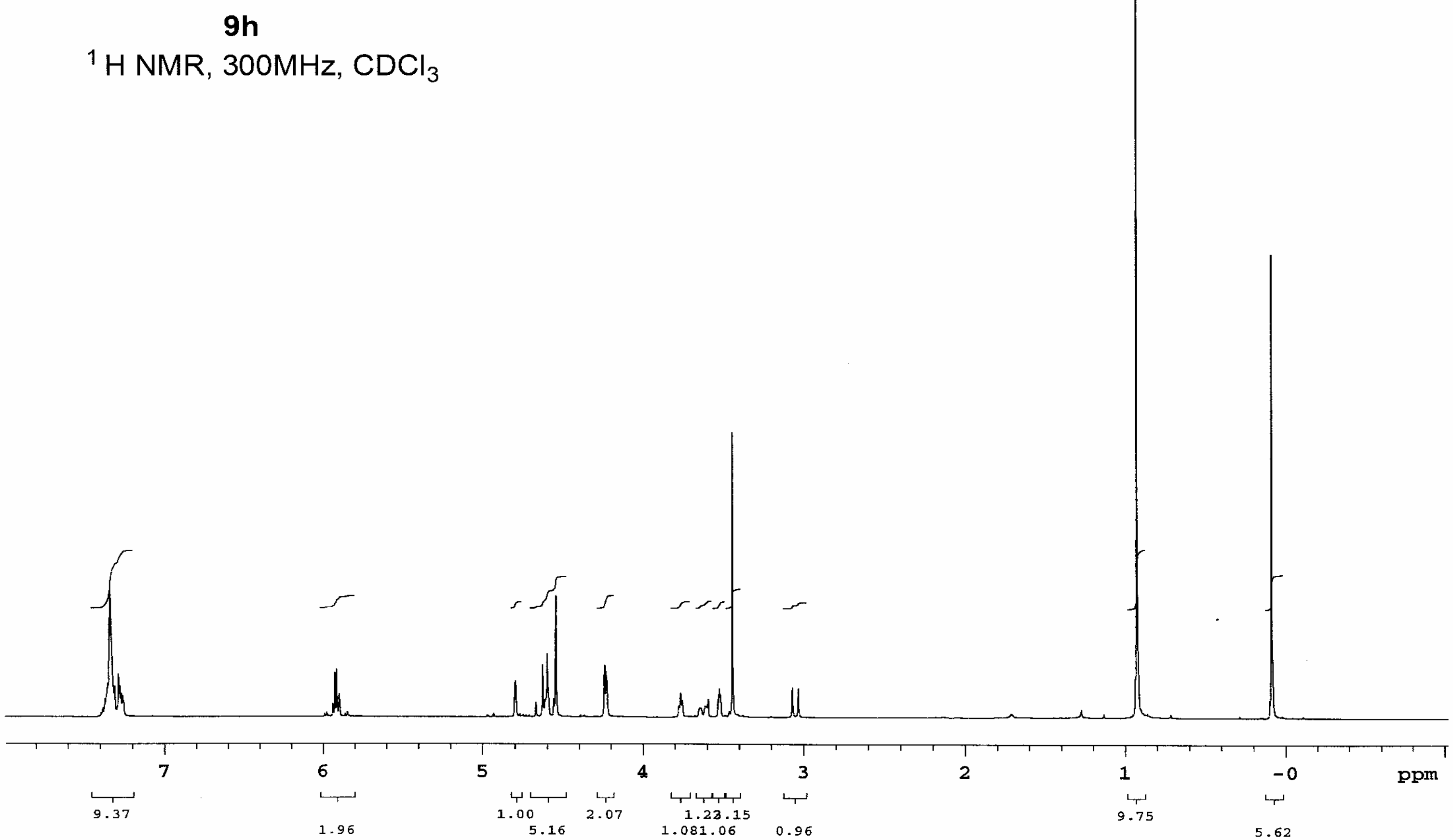
^1H NMR, 300MHz, $CDCl_3$

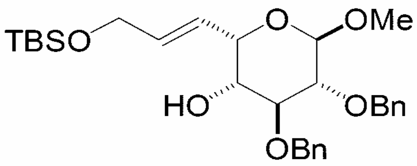




9h

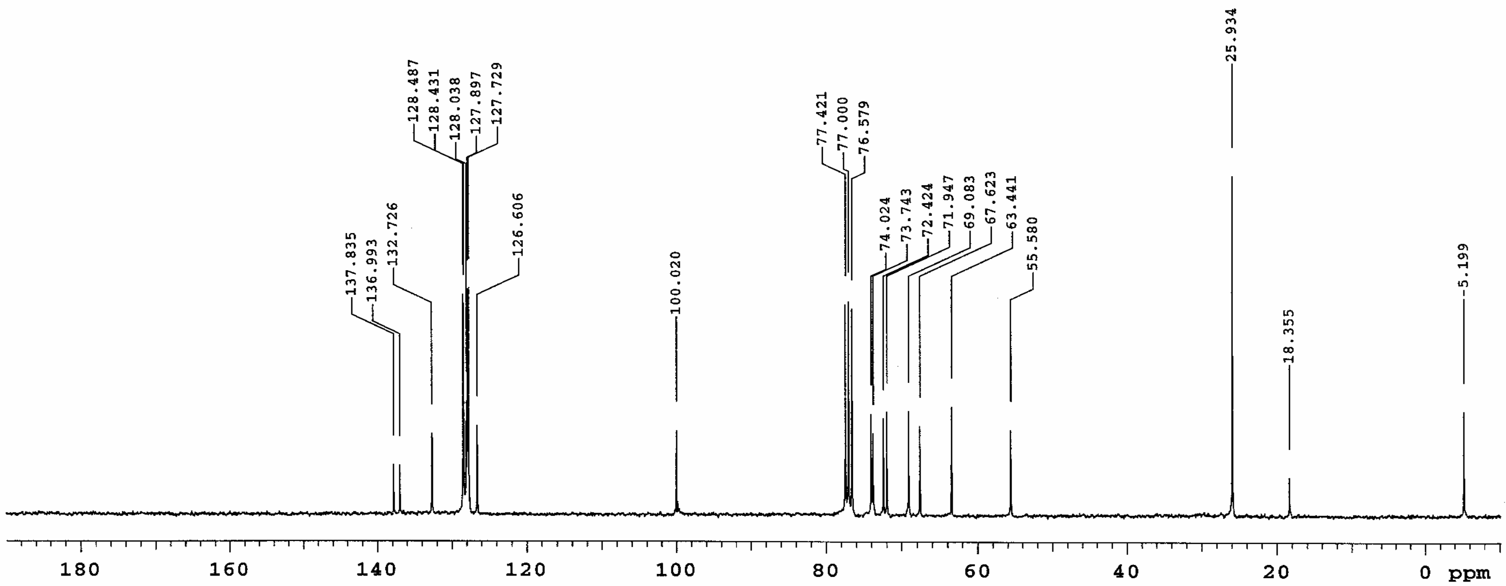
^{1}H NMR, 300MHz, $CDCl_3$

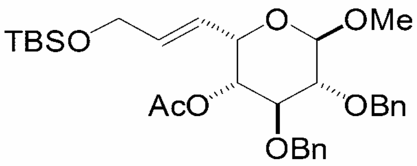




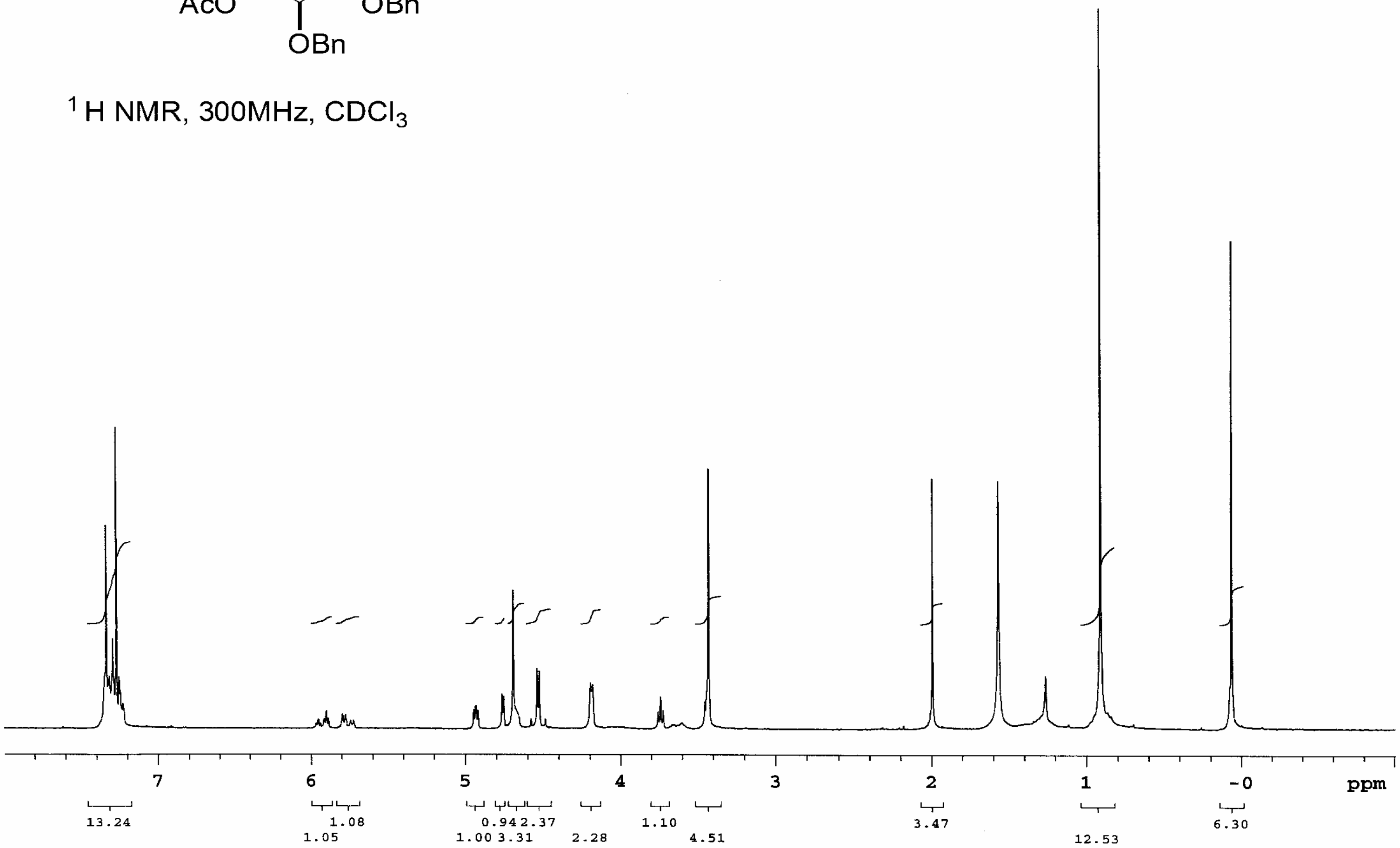
9h

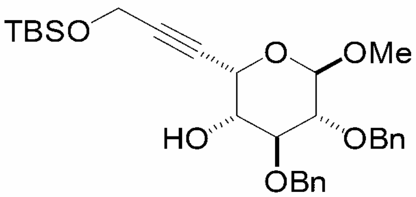
^{13}C NMR,75MHz, $CDCl_3$





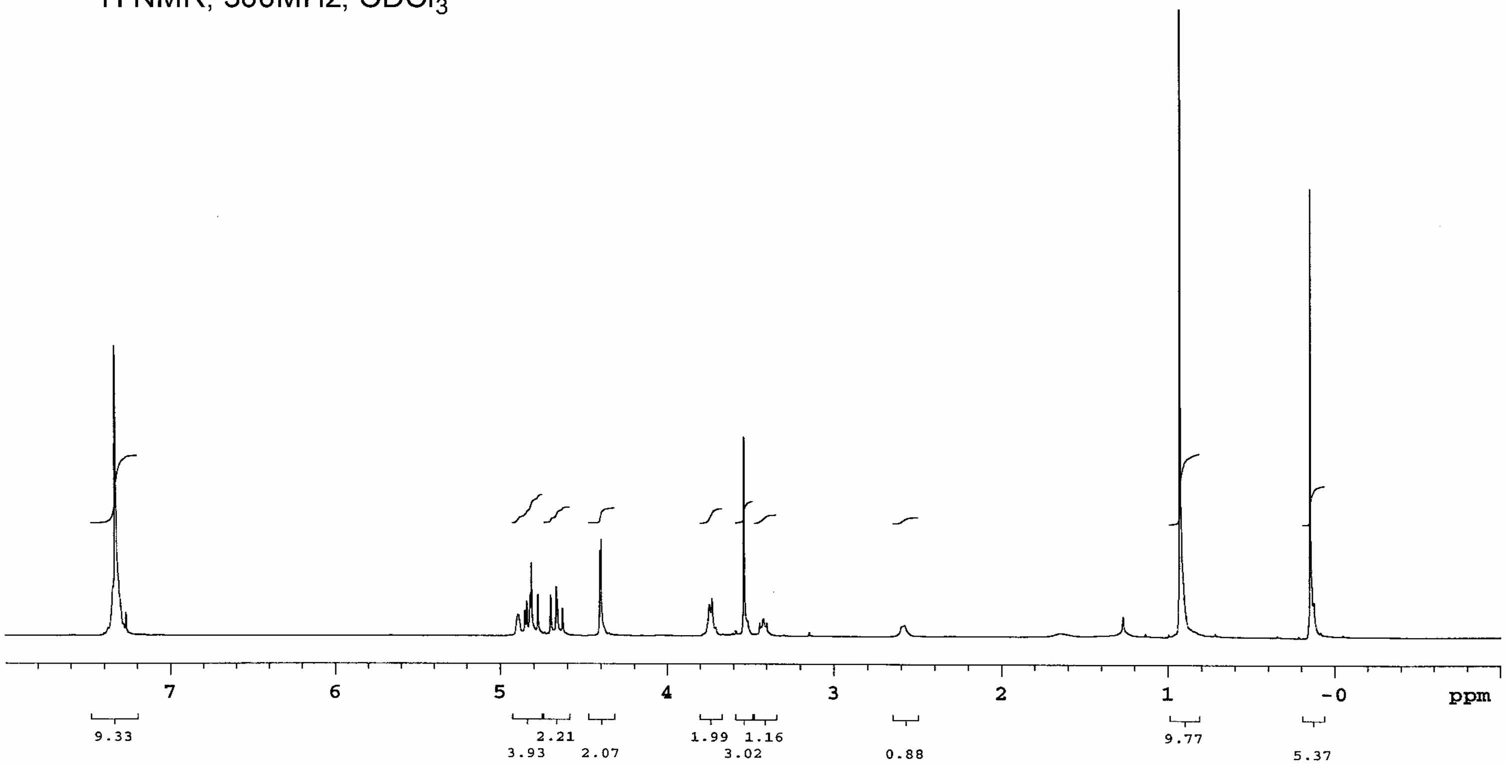
^{1}H NMR, 300MHz, $CDCl_3$

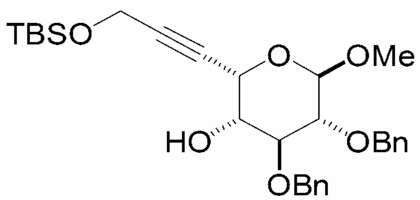




9i

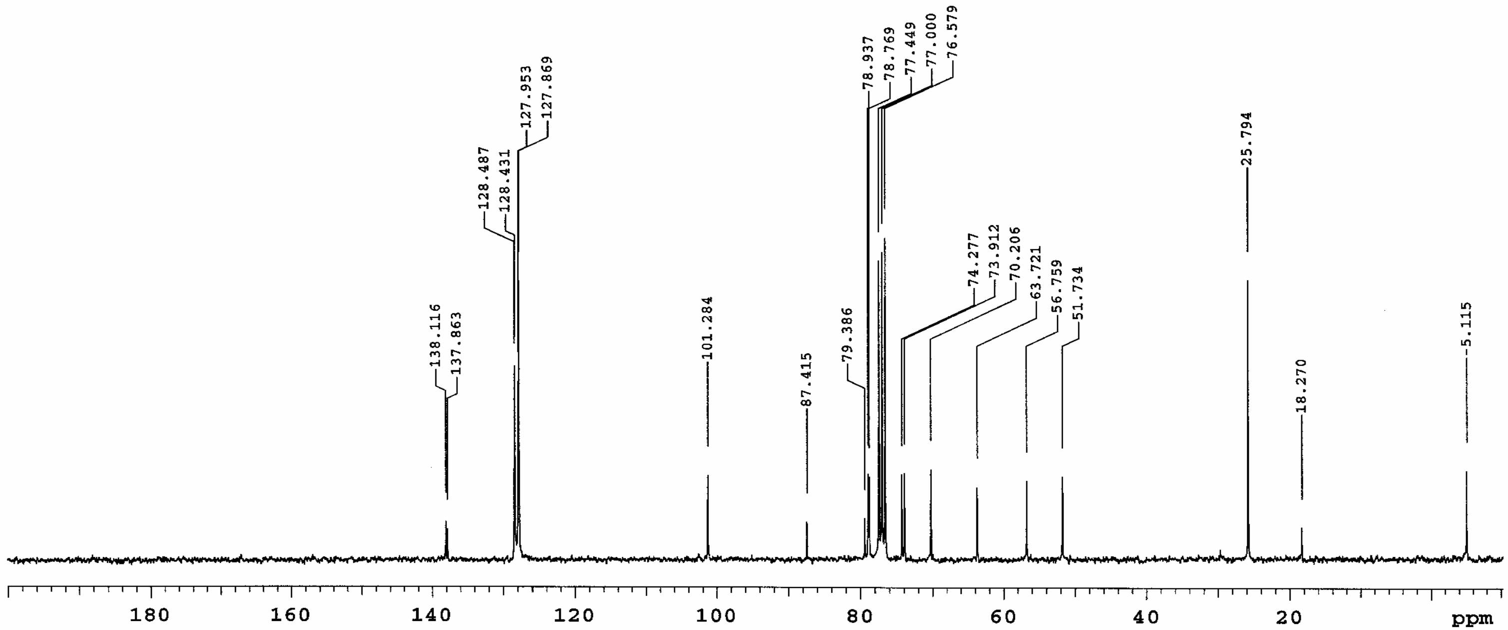
^{1}H NMR, 300MHz, $CDCl_3$

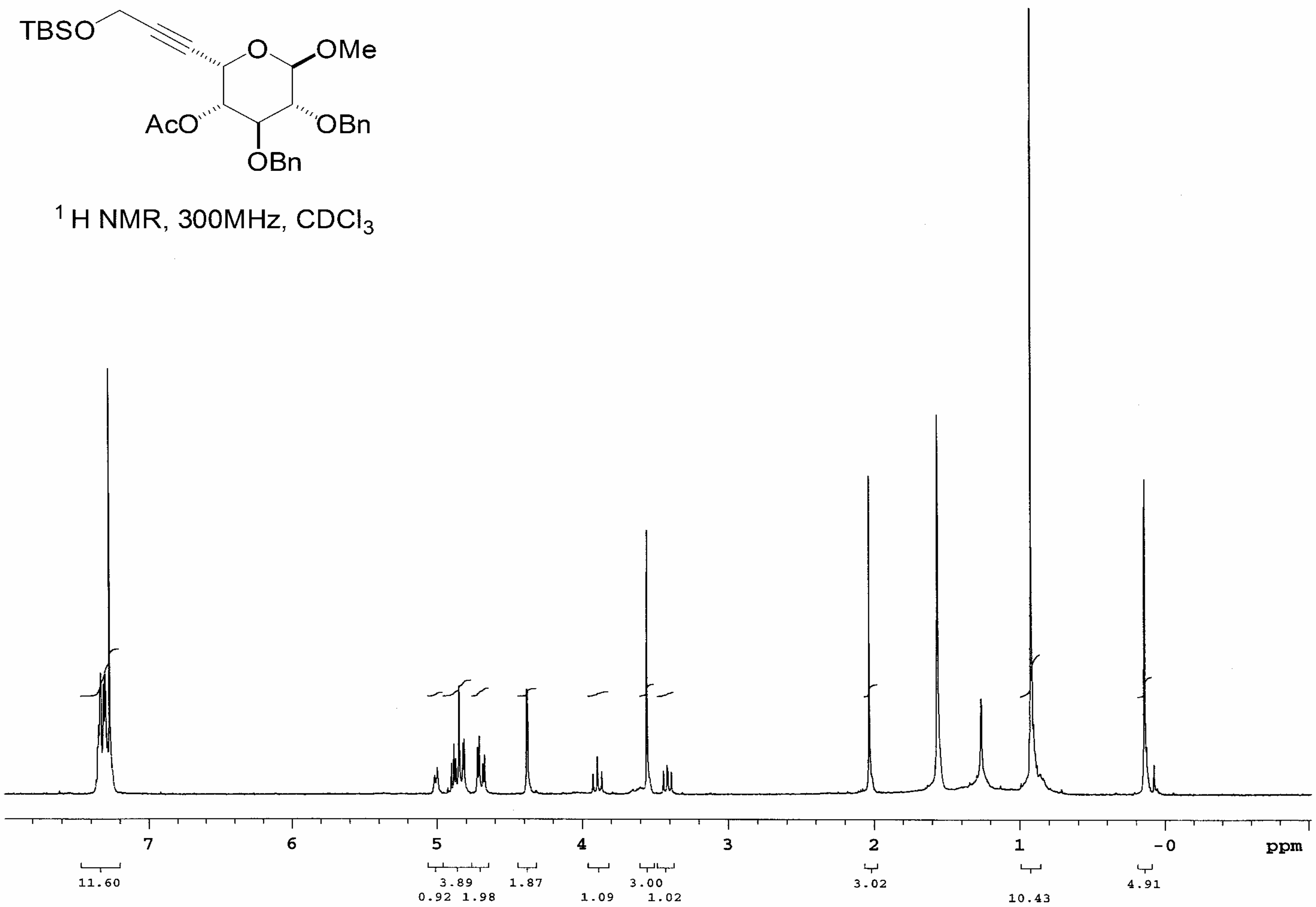




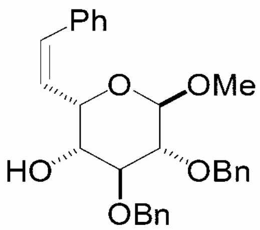
9i

^{13}C NMR,75MHz, $CDCl_3$



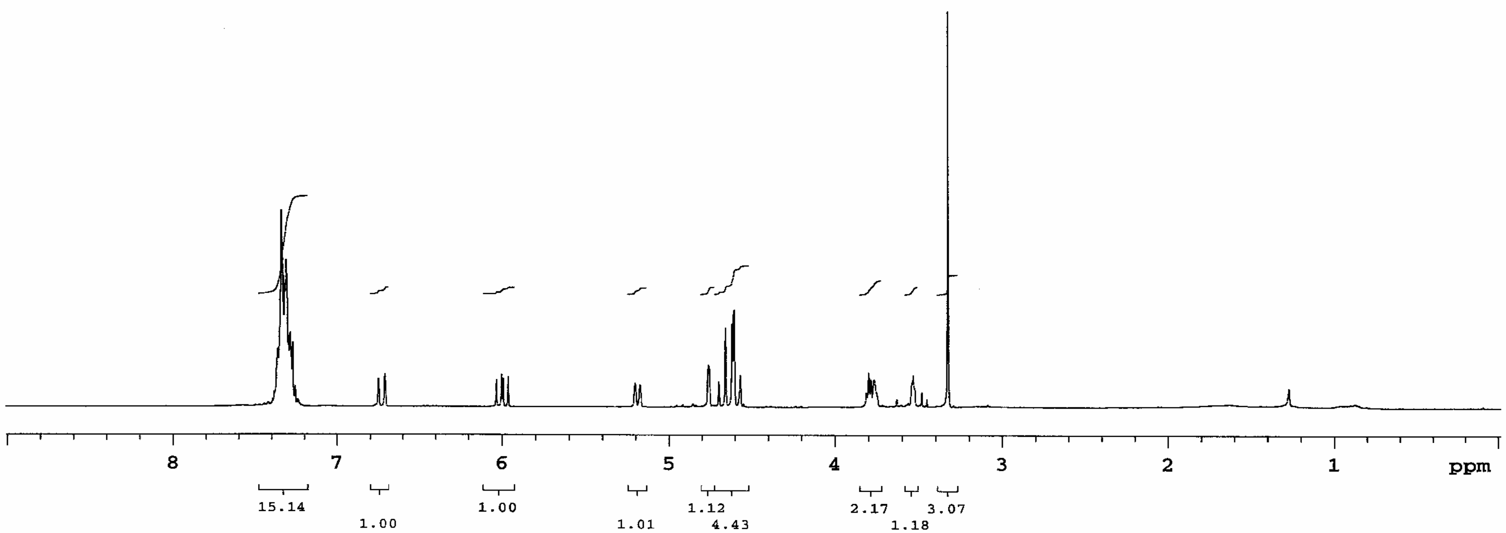


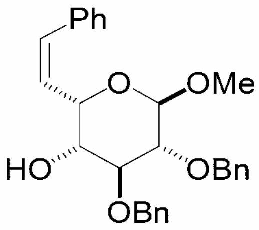
TBSO
OMe
AcO
OBn
OBn
O
^{1}H NMR, 300MHz, $CDCl_3$
7
6
5
4
3
2
1
-0
ppm
11.60
3.89
0.92
1.98
1.87
1.09
3.00
1.02
3.02
10.43
4.91



9j

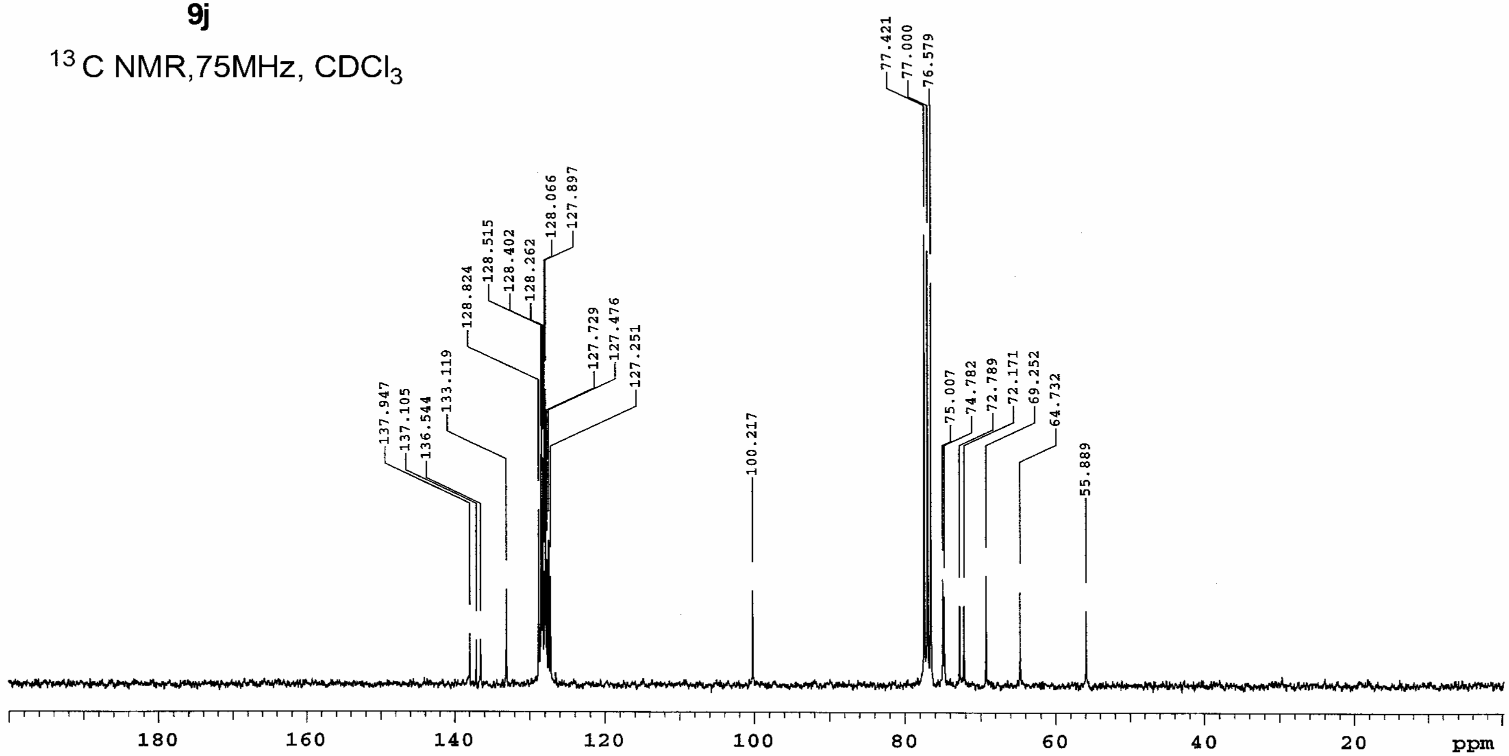
^{1}H NMR, 300MHz, $CDCl_3$

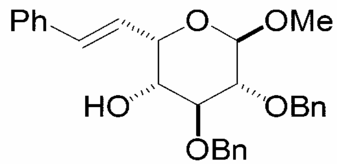




9j

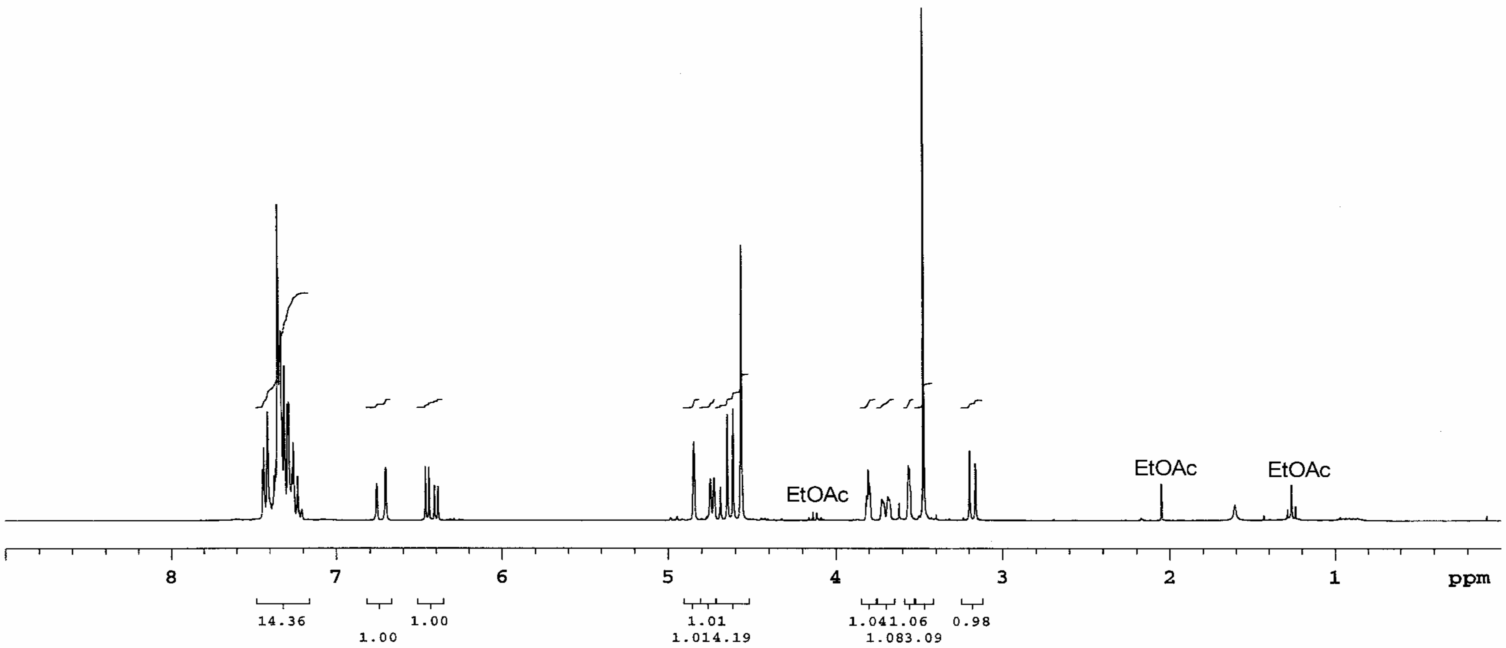
^{13}C NMR,75MHz, $CDCl_3$

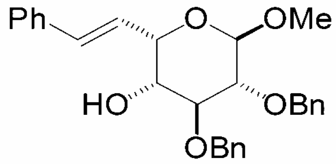




9k

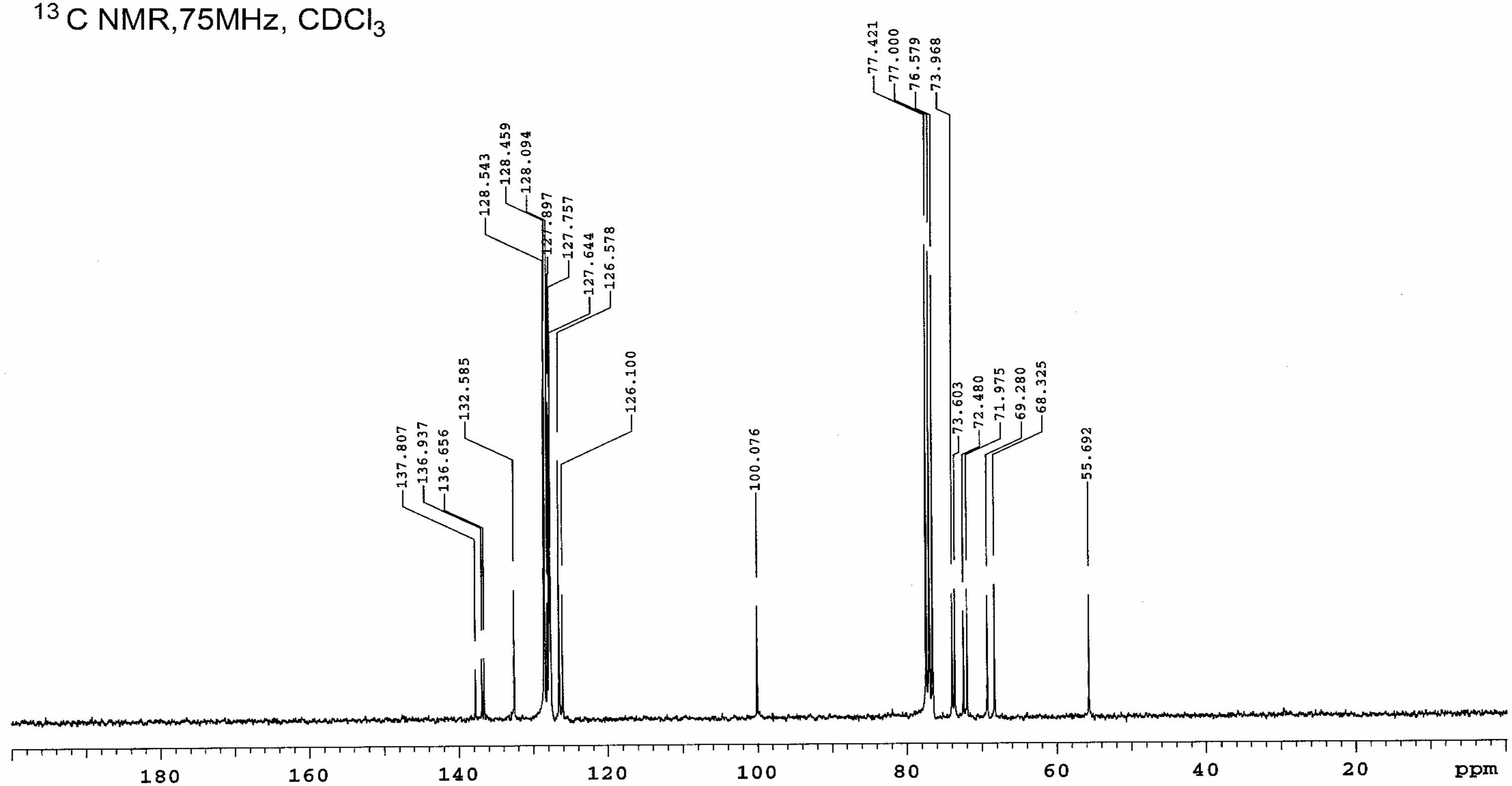
^{1}H NMR, 300MHz, $CDCl_3$

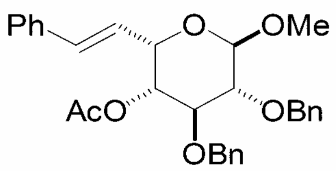




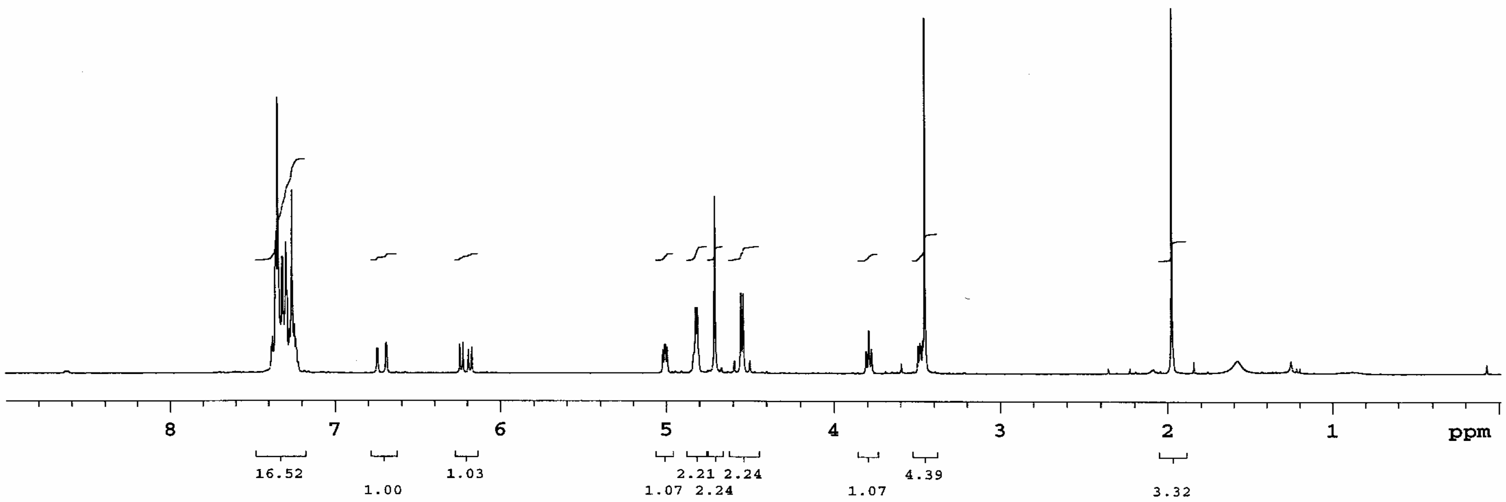
9k

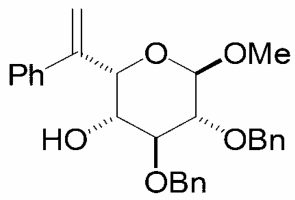
^{13}C NMR,75MHz, $CDCl_3$





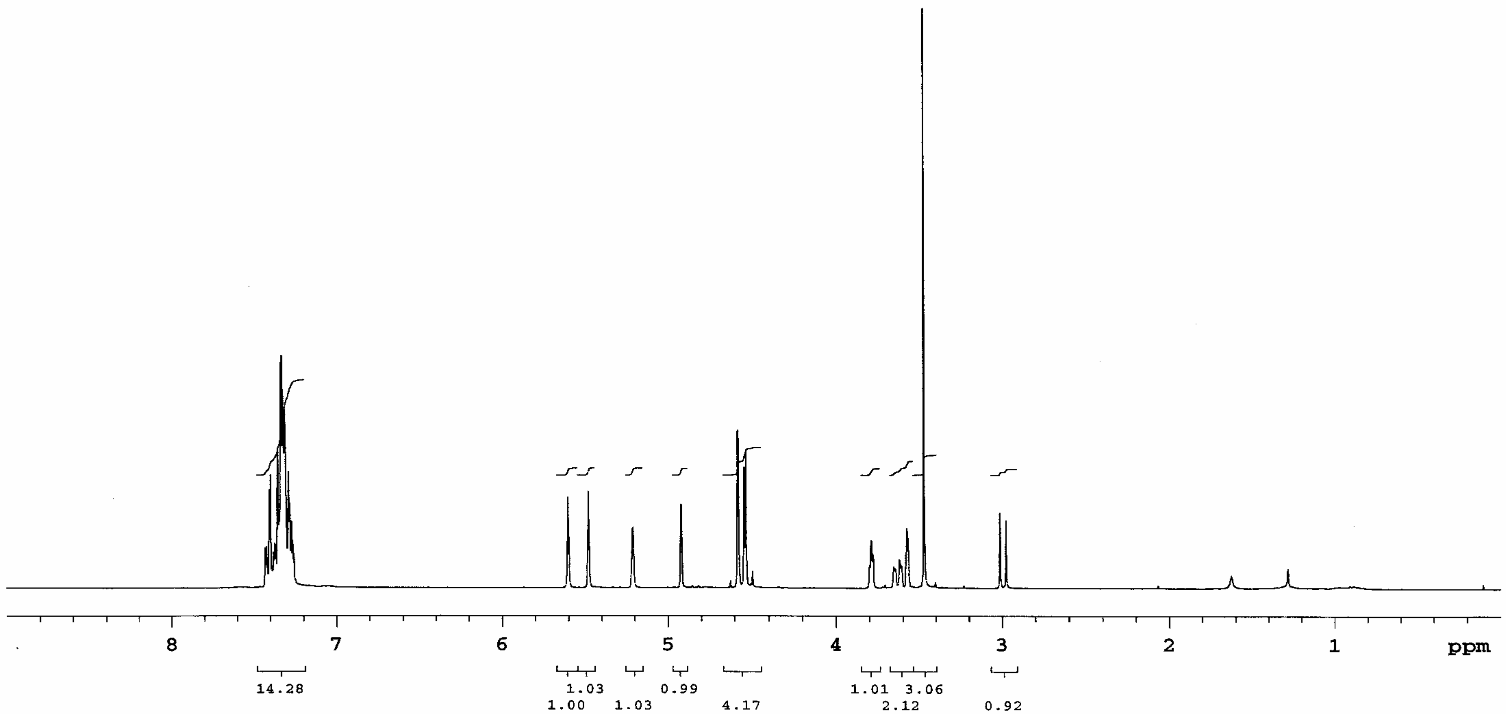
^1H NMR, 300MHz, $CDCl_3$

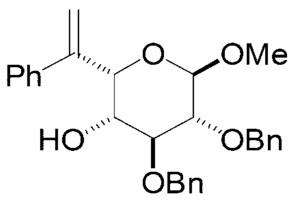




9l

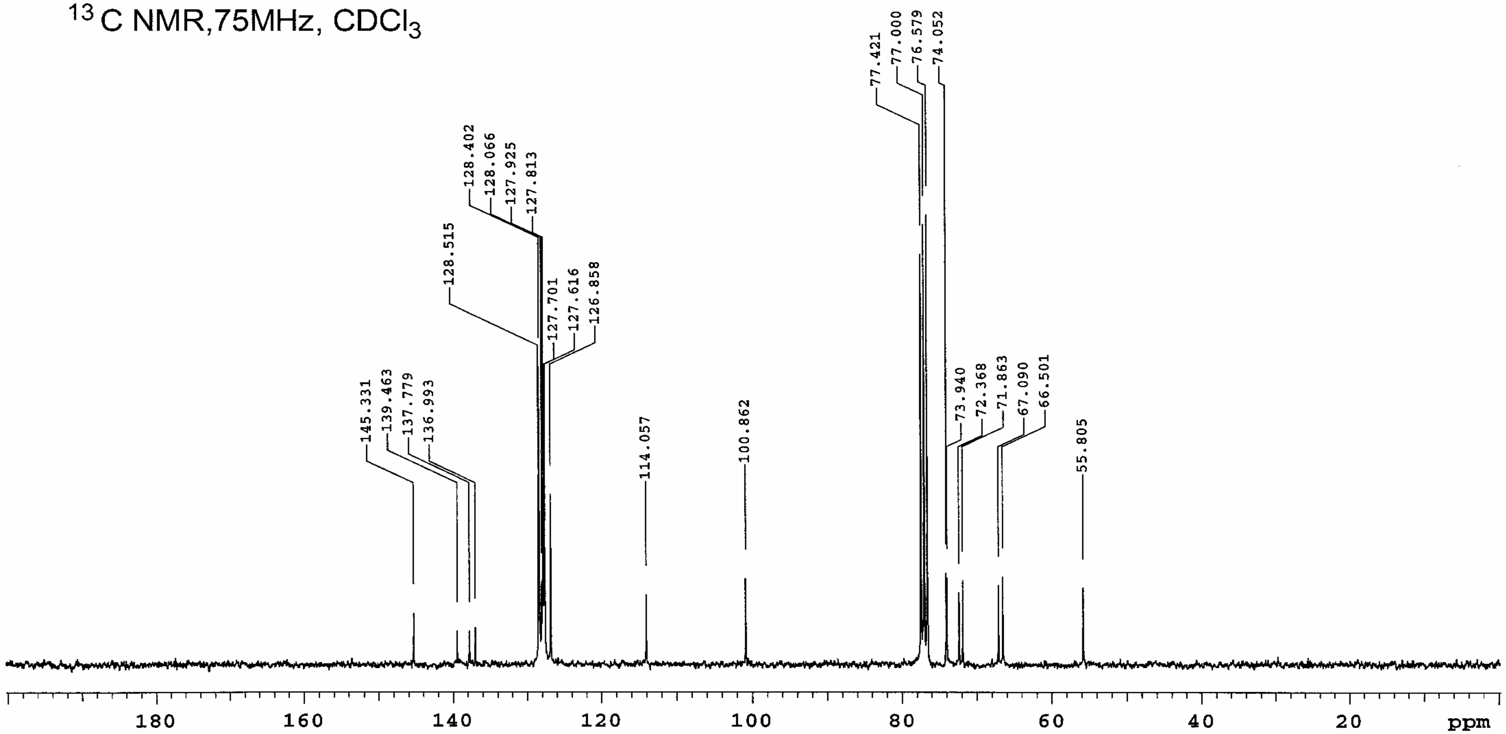
^{1}H NMR, 300MHz, $CDCl_3$

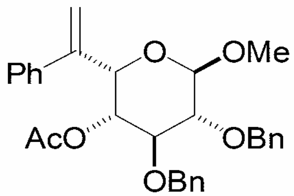




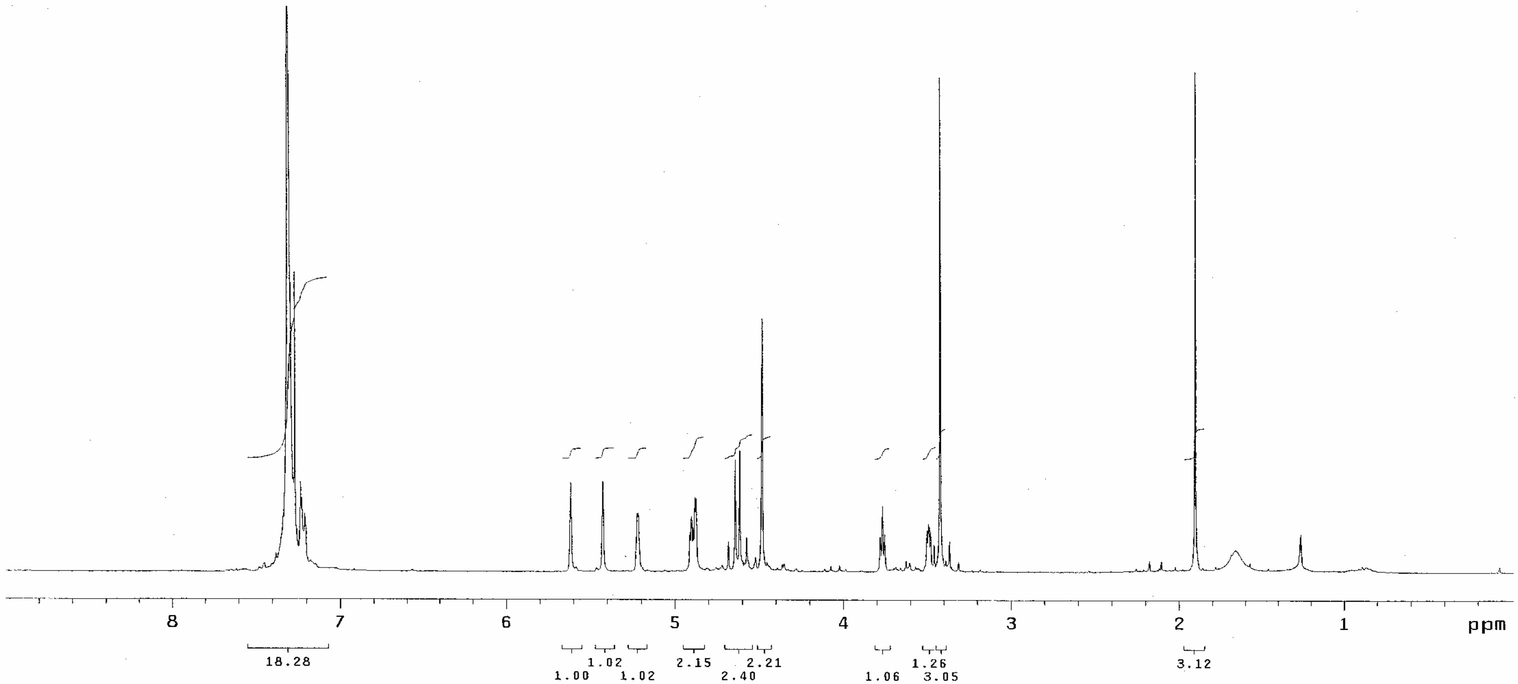
9l

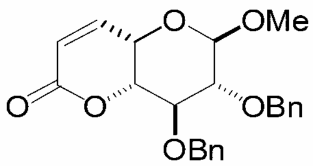
^{13}C NMR,75MHz, $CDCl_3$





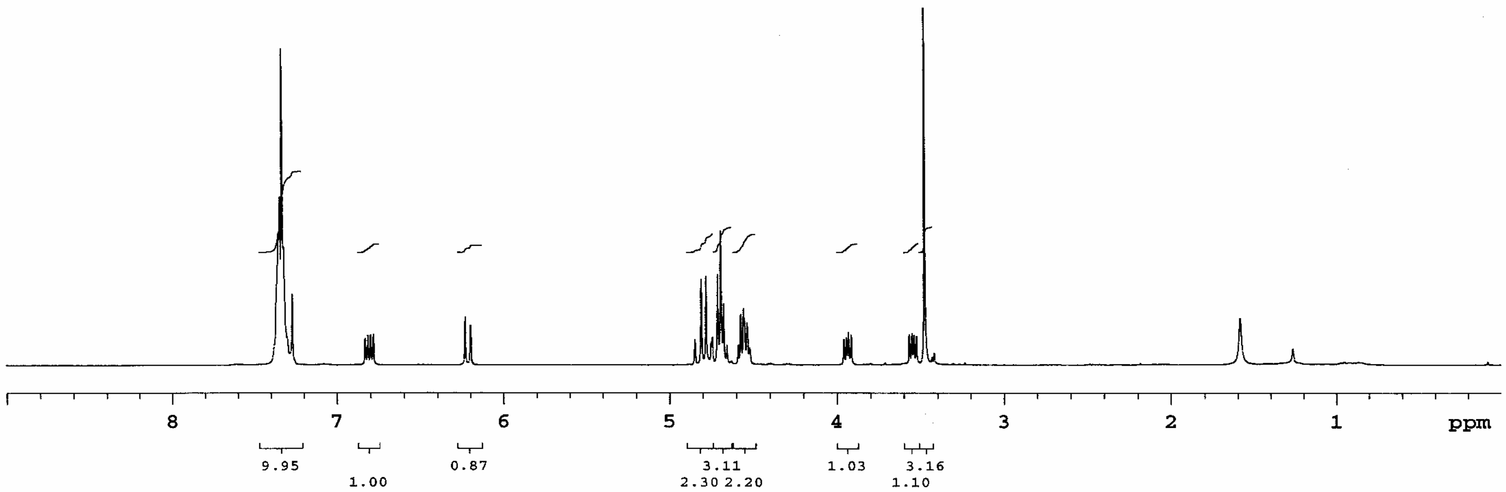
^1H NMR, 300MHz, $CDCl_3$

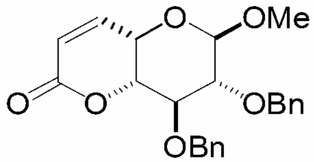




9m

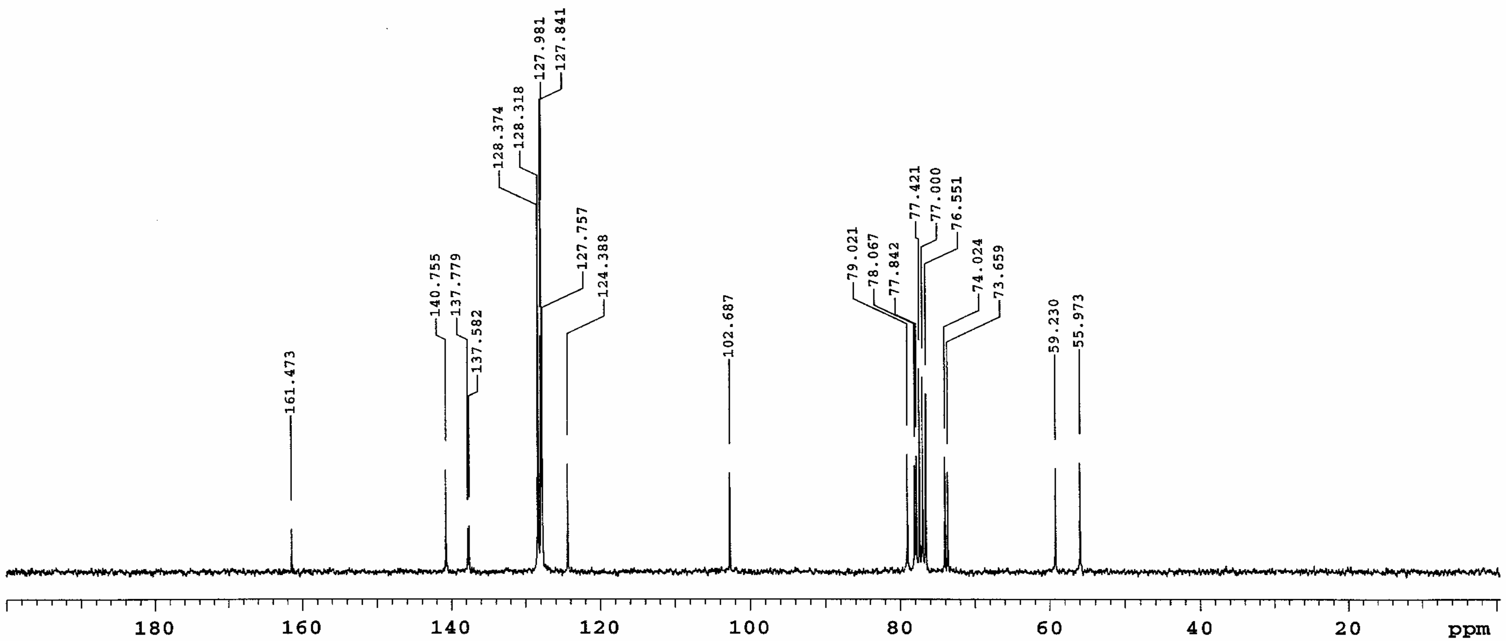
^{1}H NMR, 300MHz, $CDCl_3$

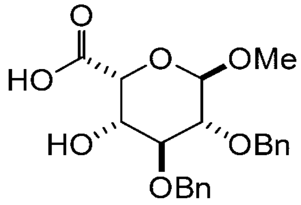




9m

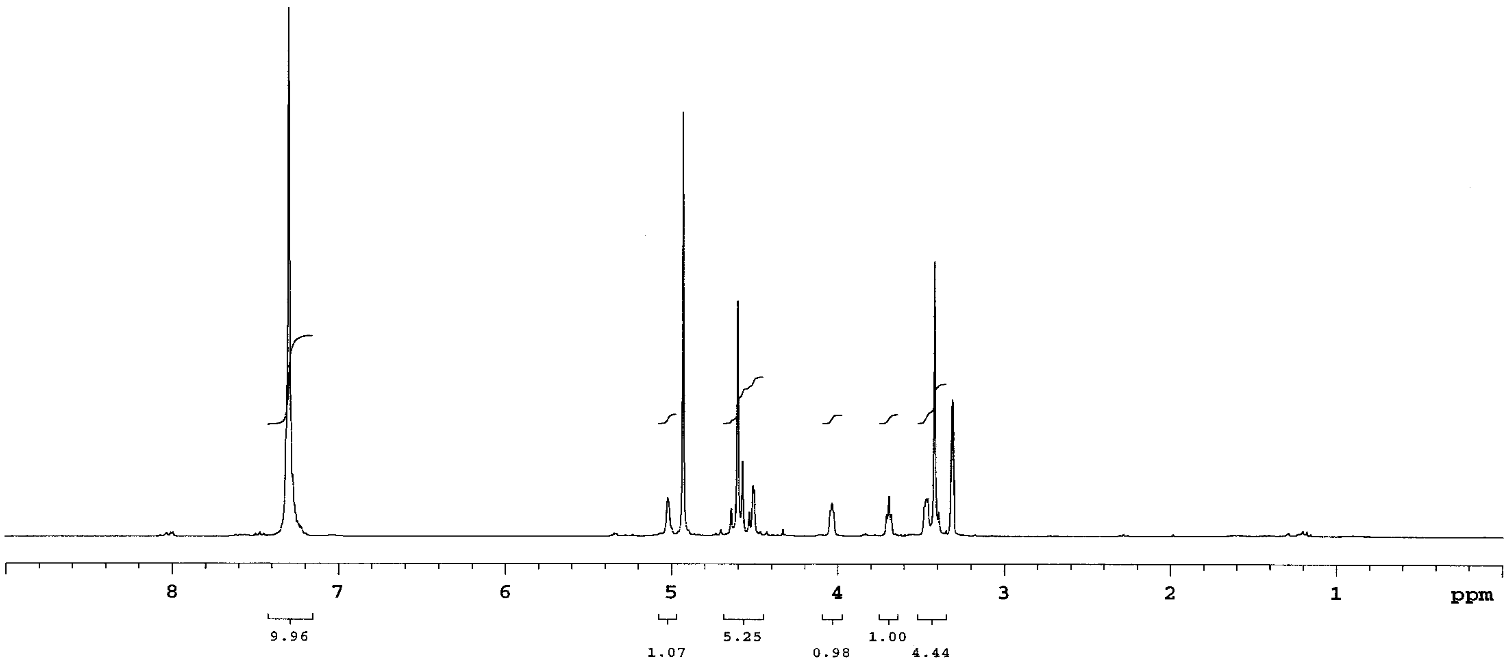
^{13}C NMR,75MHz, $CDCl_3$

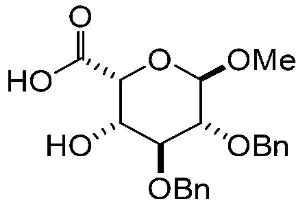




12

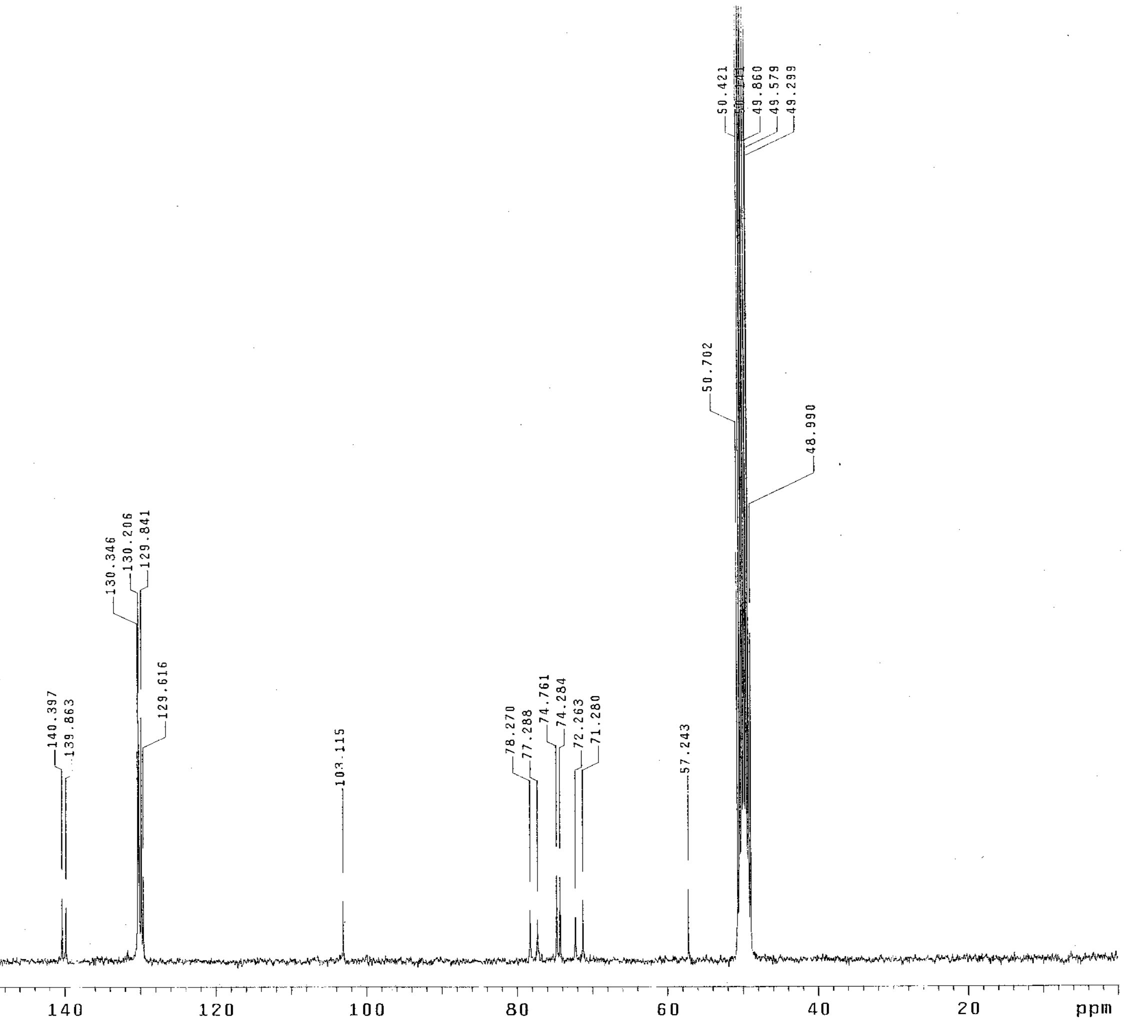
^{1}H NMR, 300MHz, CD_3OD

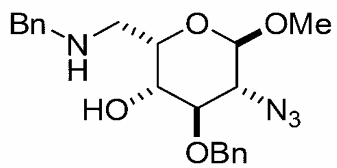




12

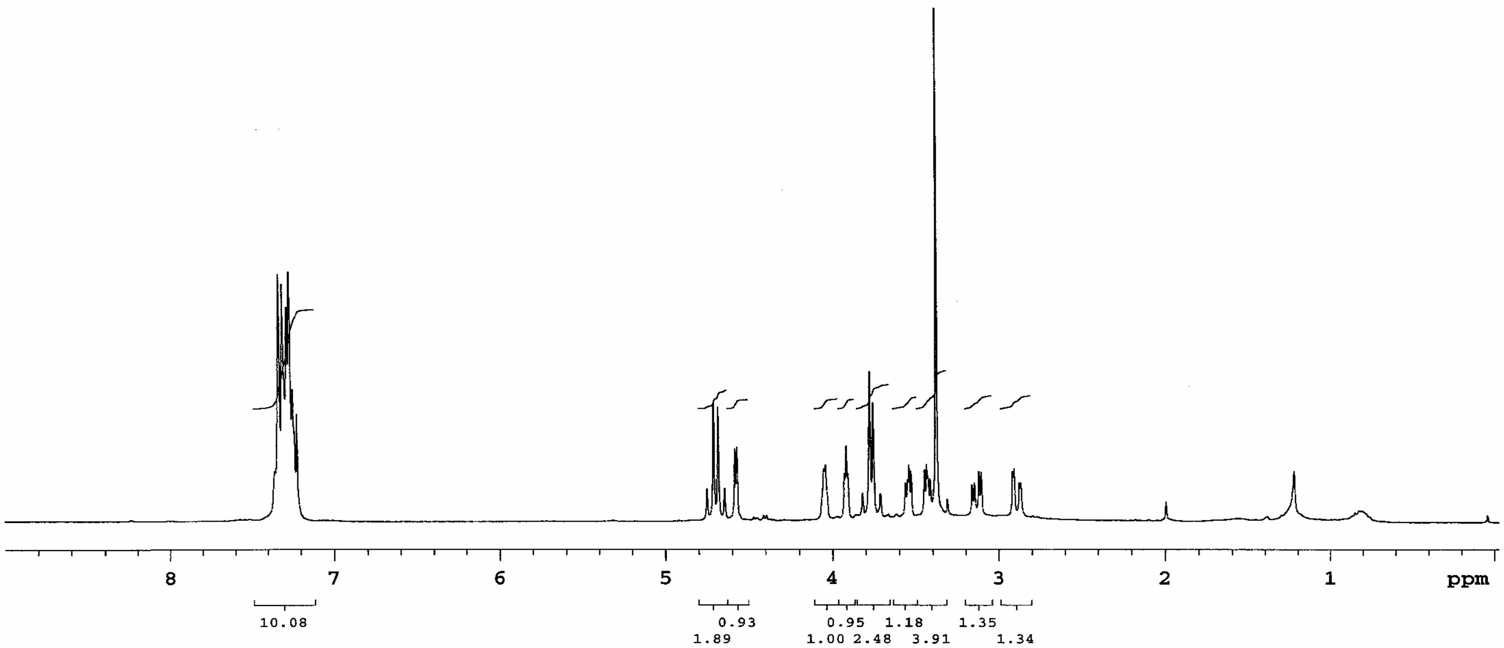
^{13}C NMR, 75MHz, CD_3OD

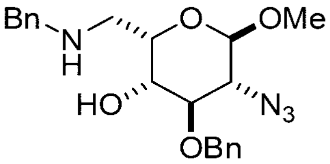




13

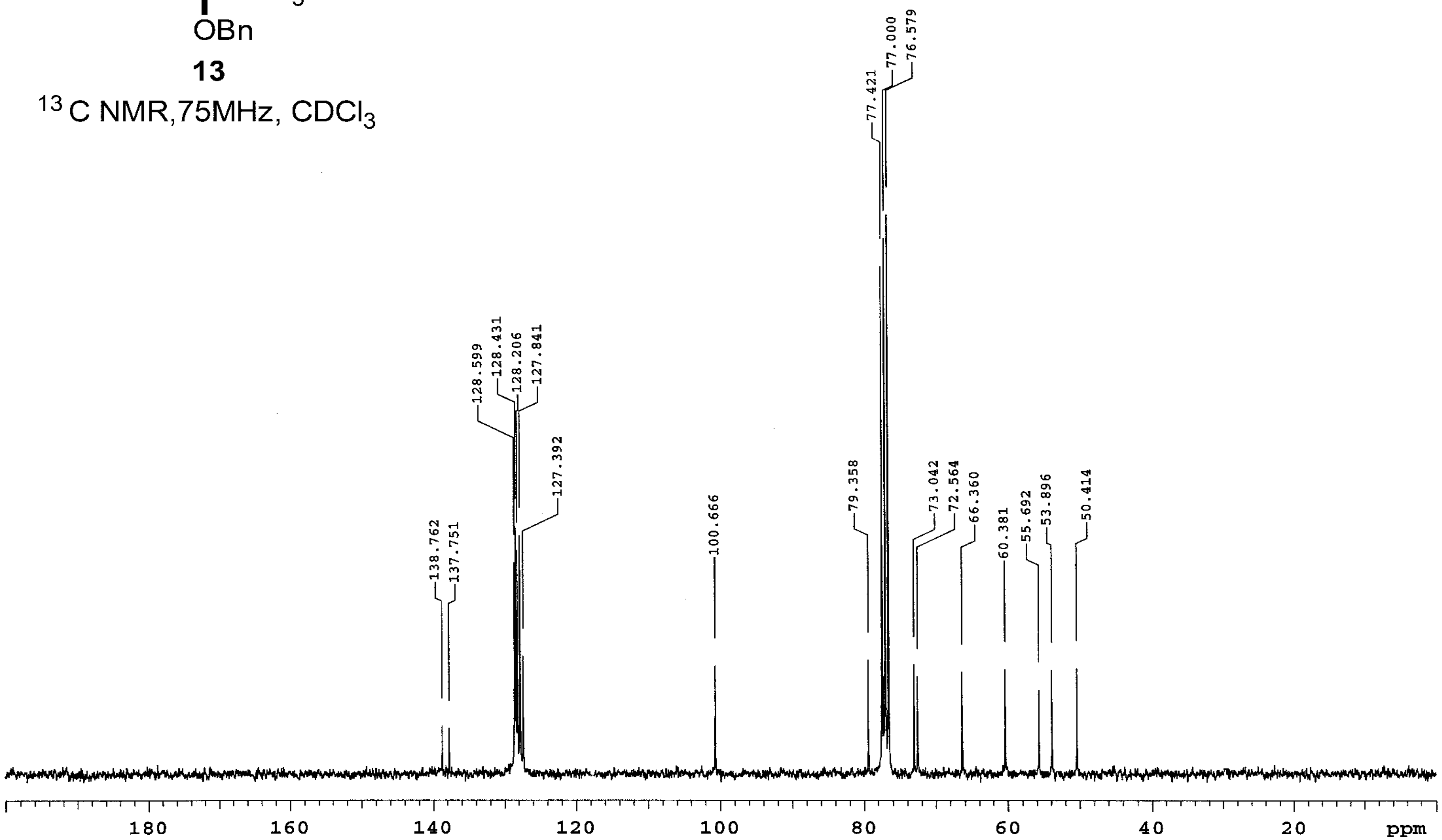
^{1}H NMR, 300MHz, $CDCl_3$

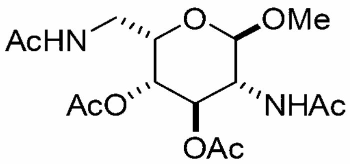




13

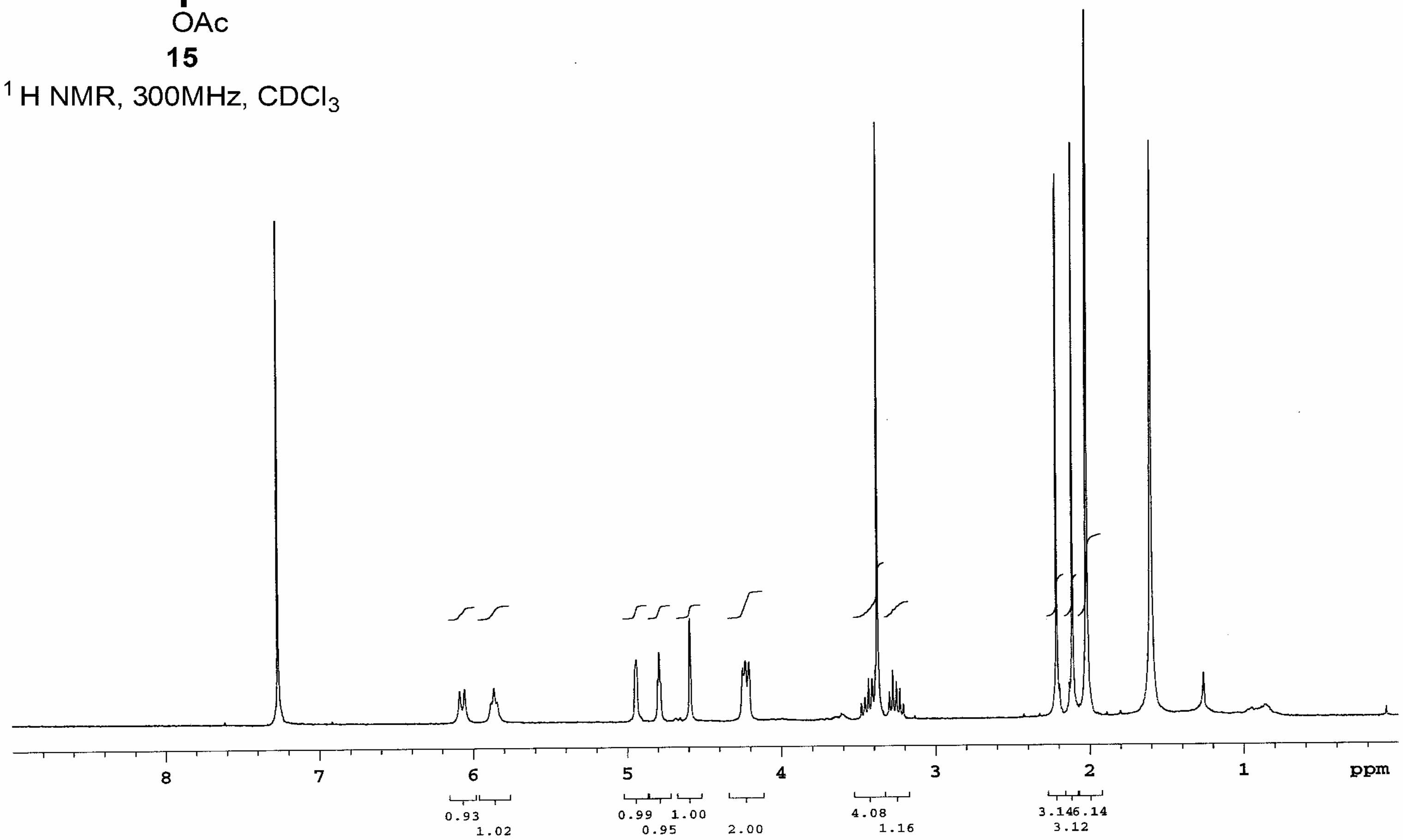
^{13}C NMR,75MHz, $CDCl_3$

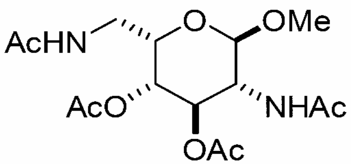




15

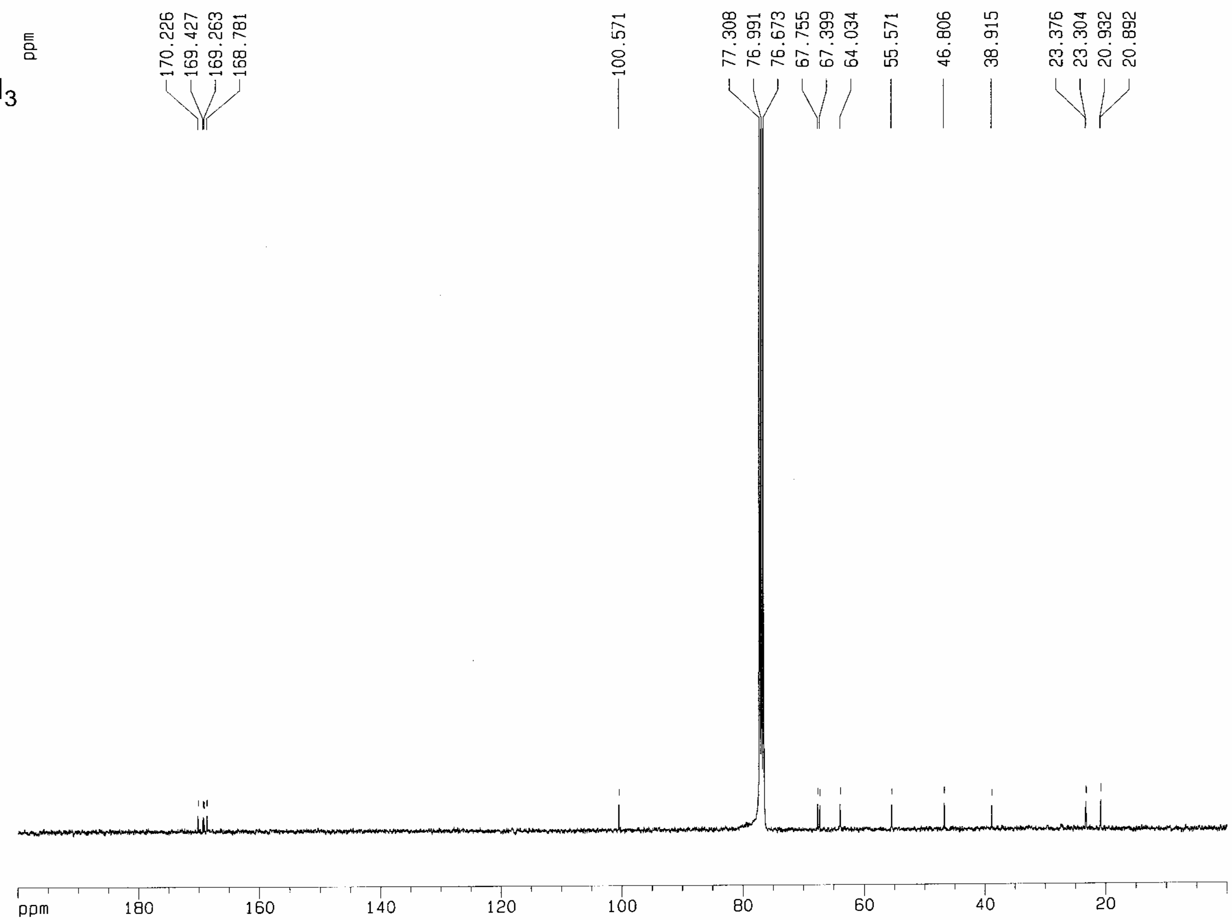
^{1}H NMR, 300MHz, $CDCl_3$

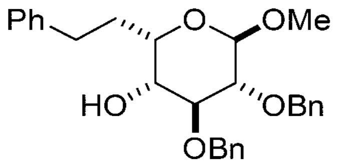




15

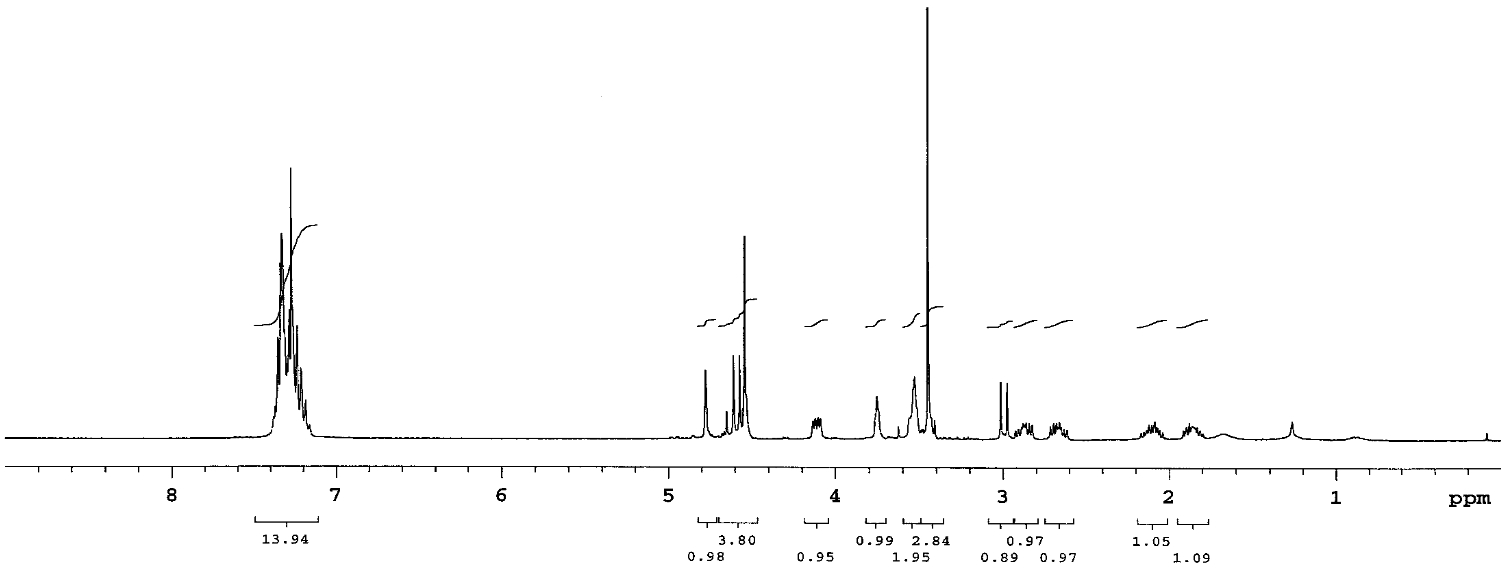
^{13}C NMR, 100MHz, $CDCl_3$

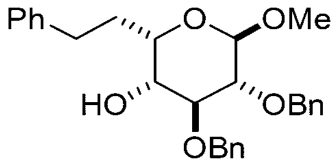




16

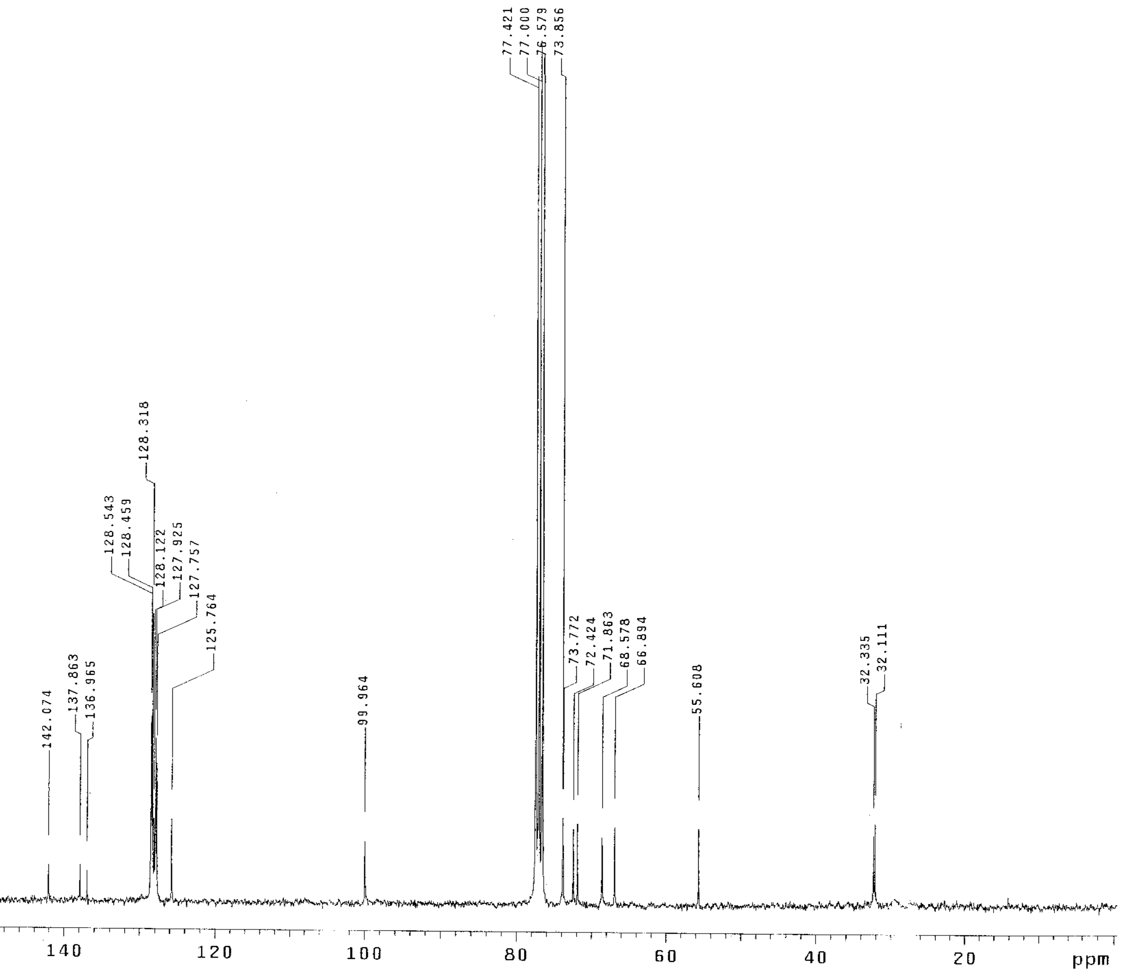
[1]H NMR, 300MHz, $CDCl_3$

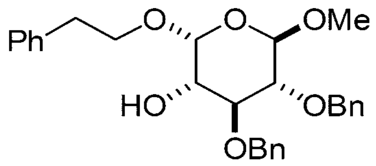




16

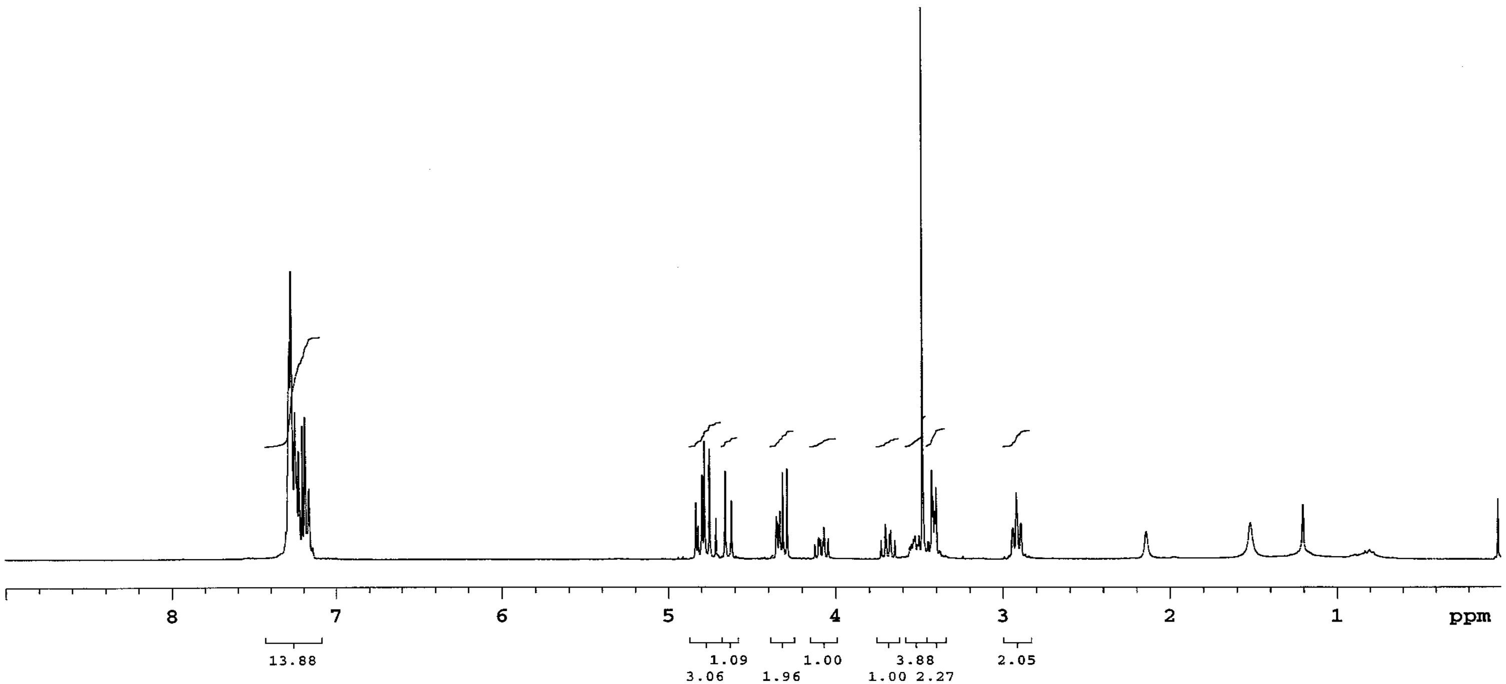
^{13}C NMR,75MHz, $CDCl_3$

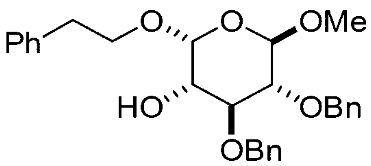




17

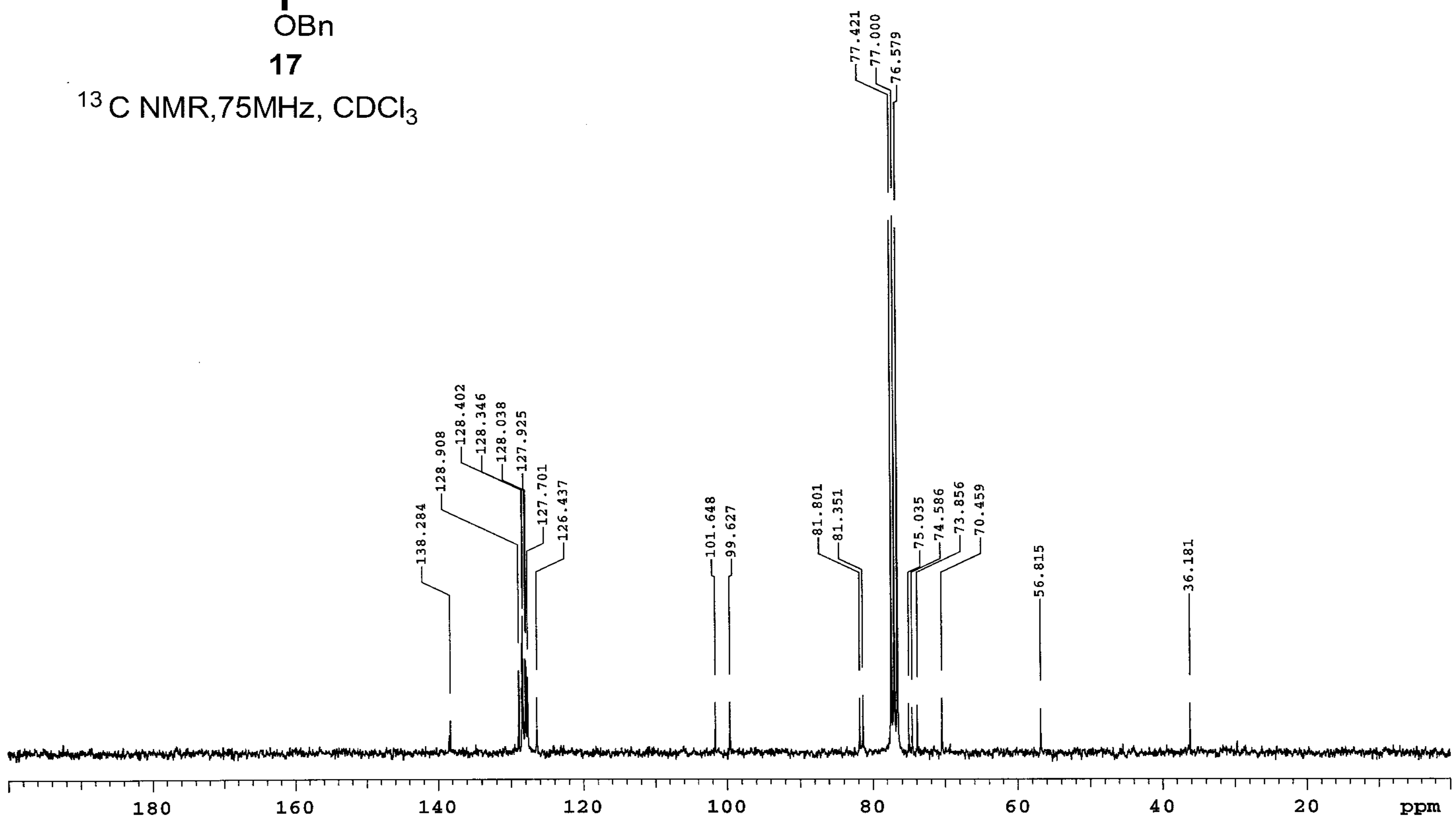
^{1}H NMR, 300MHz, $CDCl_3$

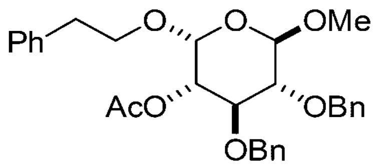




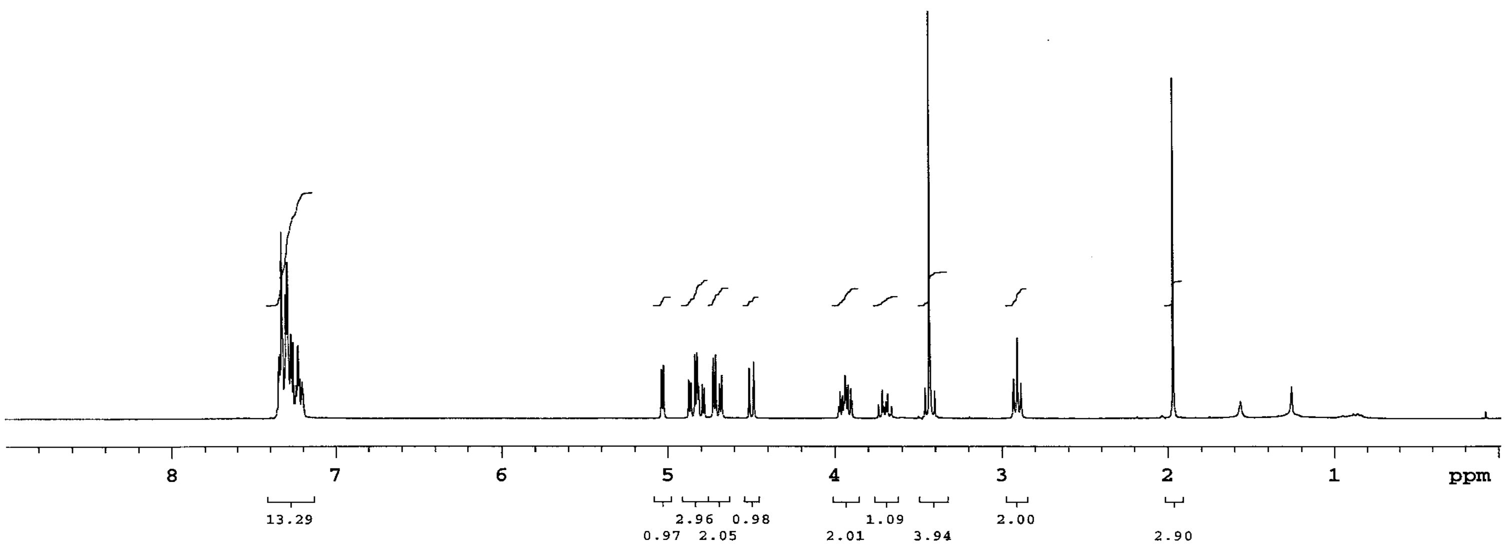
17

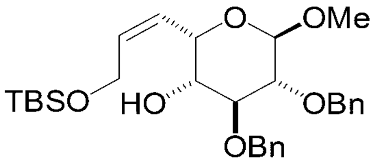
^{13}C NMR,75MHz, $CDCl_3$





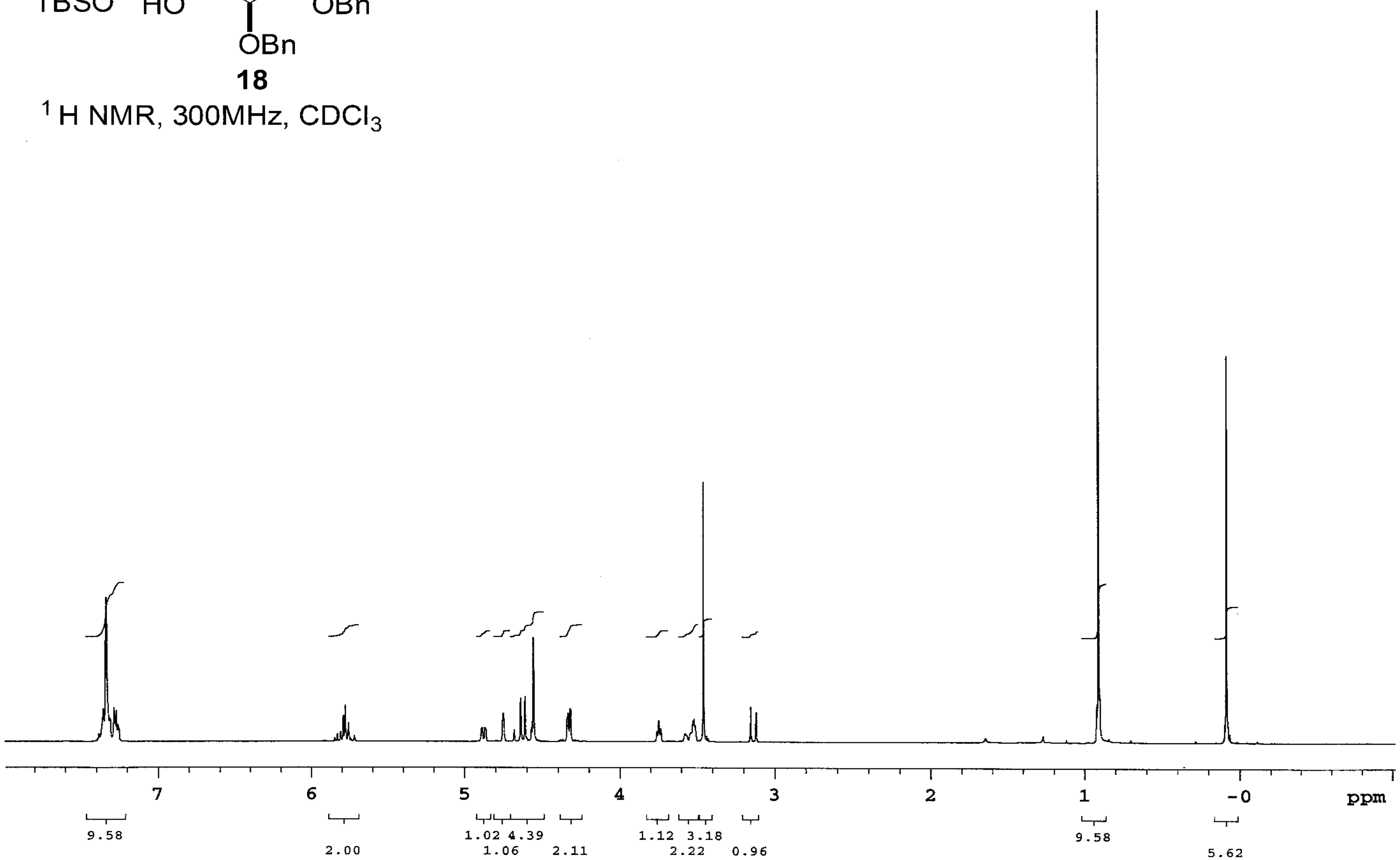
[1] H NMR, 300MHz, $CDCl_3$

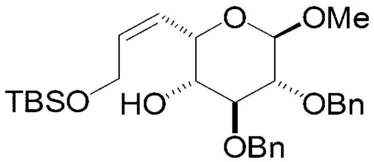




18

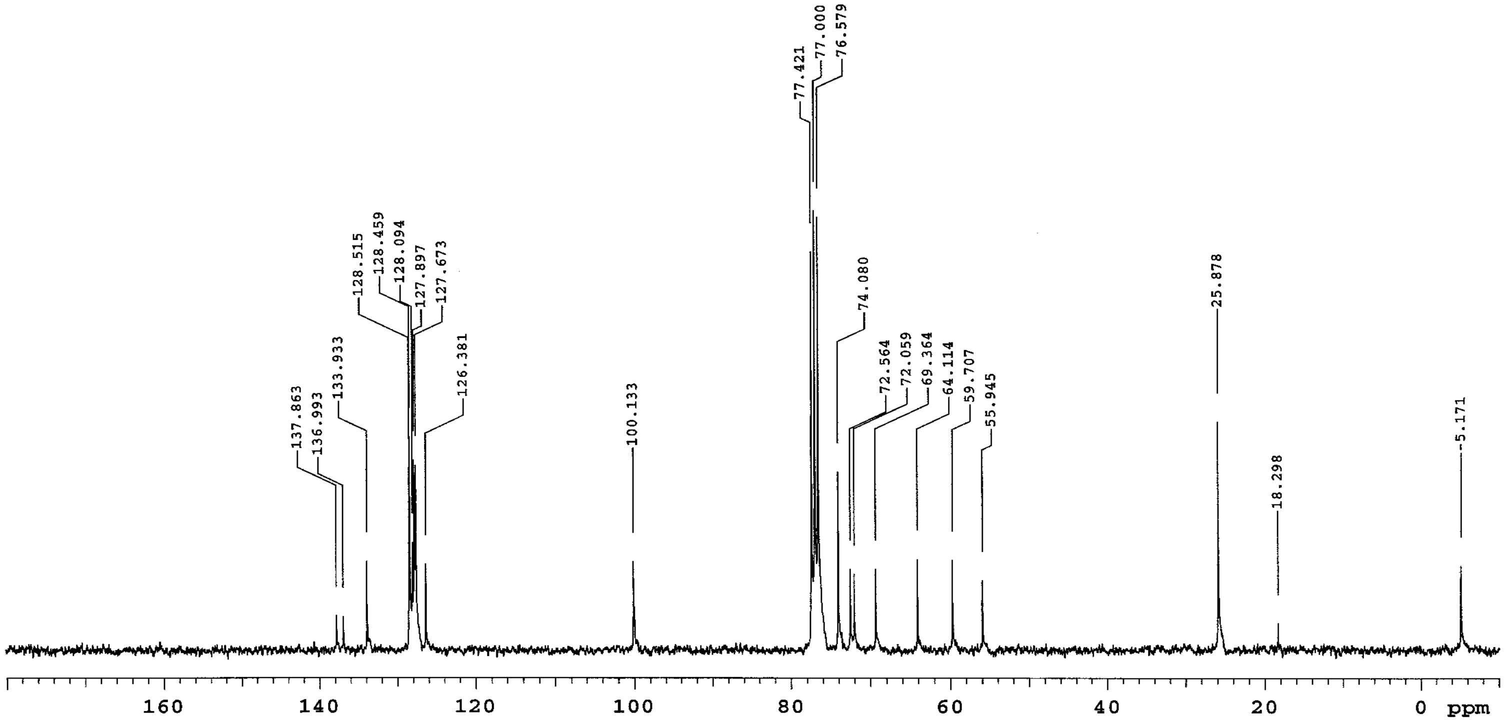
^{1}H NMR, 300MHz, $CDCl_3$

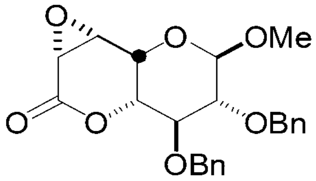




18

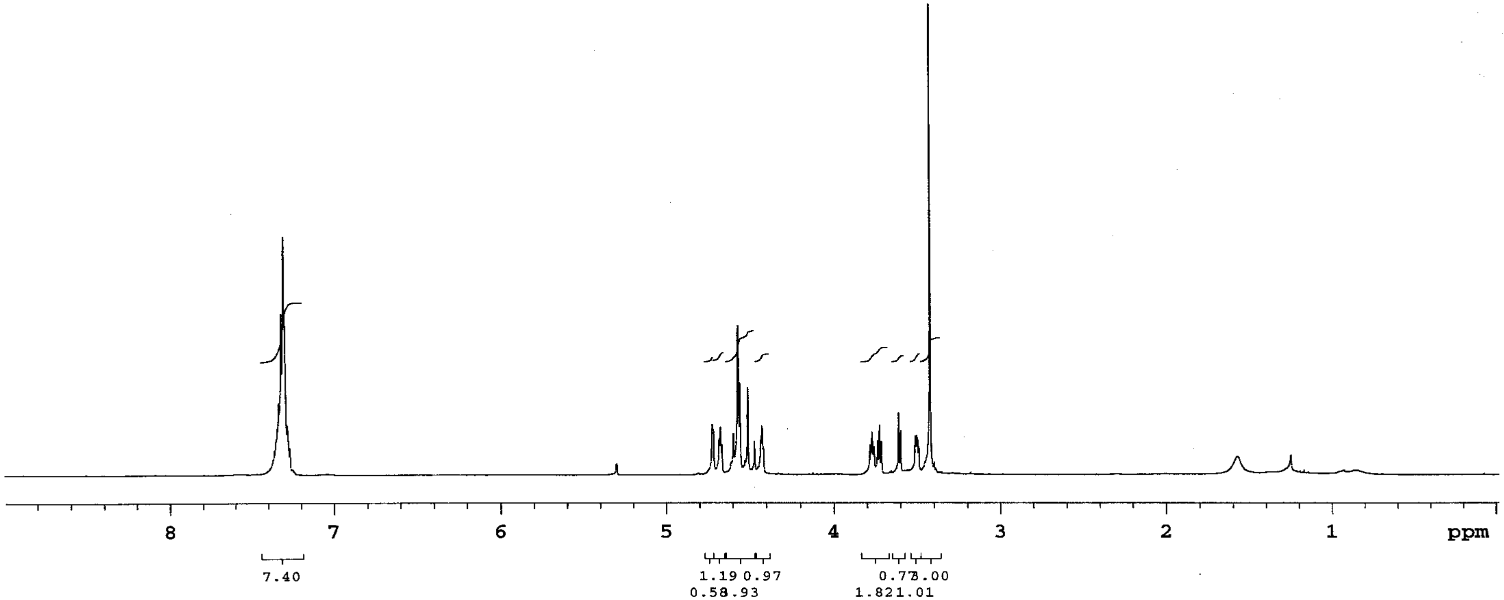
^{13}C NMR,75MHz, $CDCl_3$

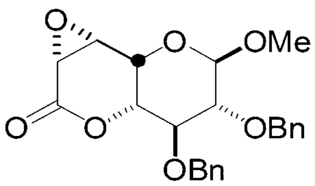




19

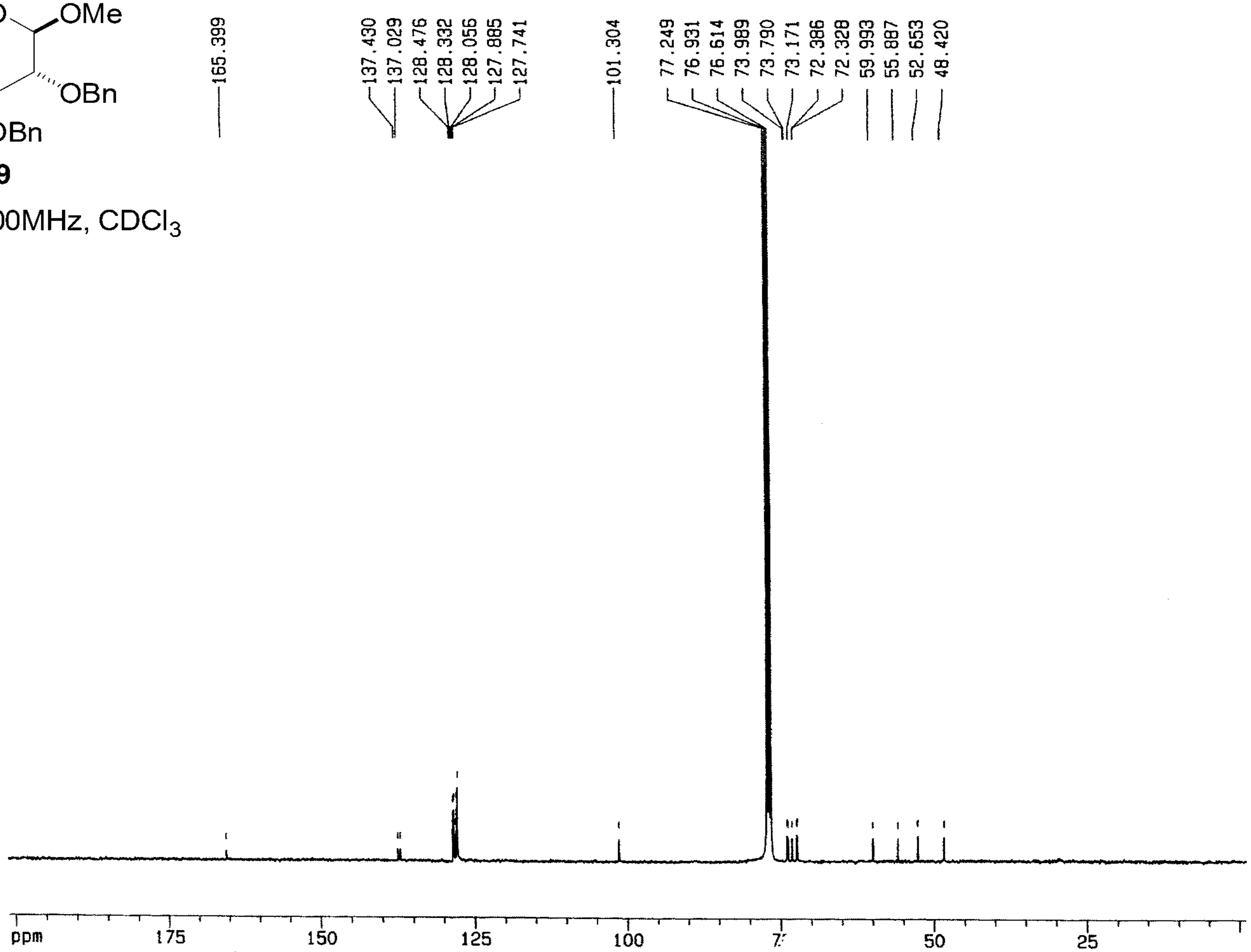
^{1}H NMR, 300MHz, CD_2Cl_2

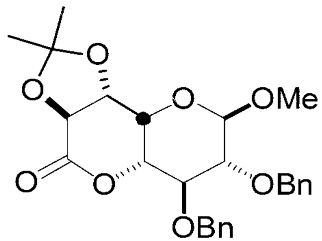




19

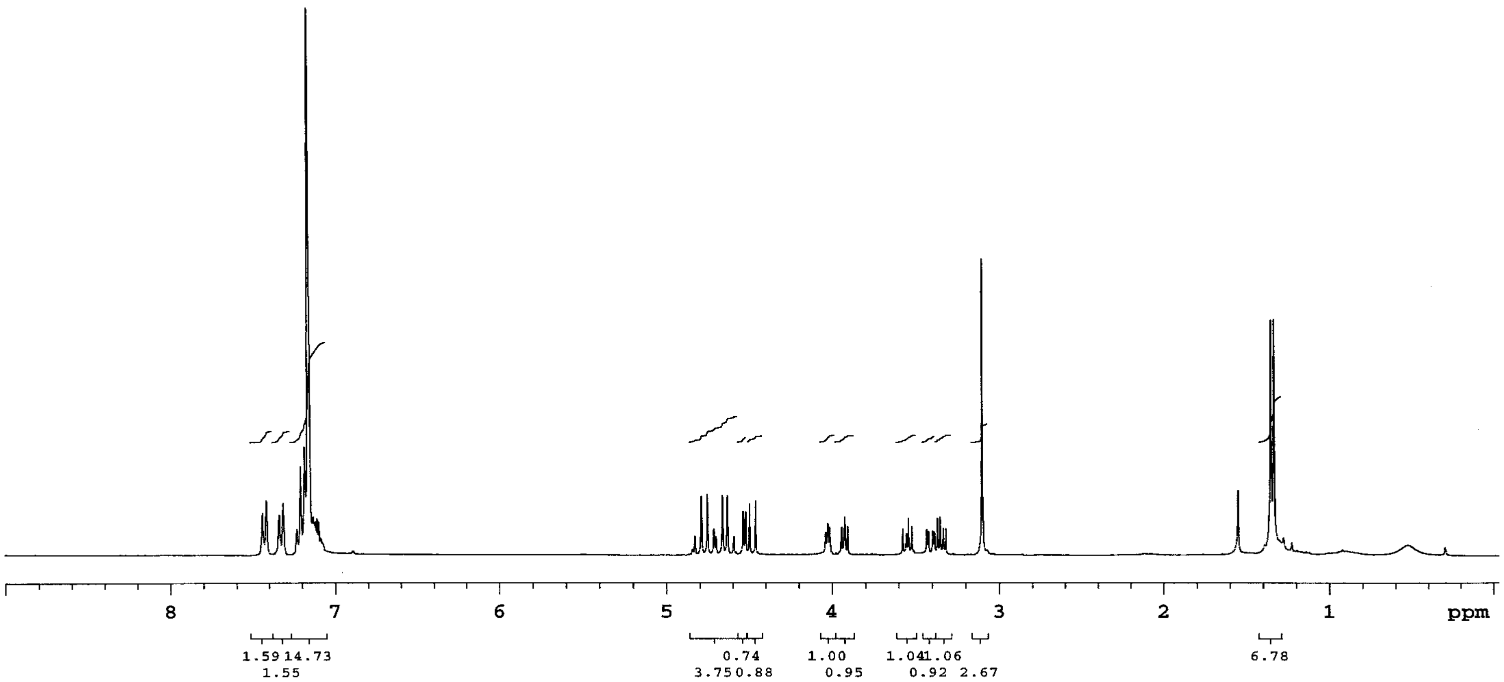
^{13}C NMR, 100MHz, $CDCl_3$

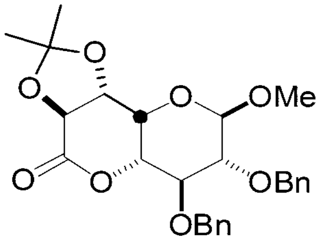




20

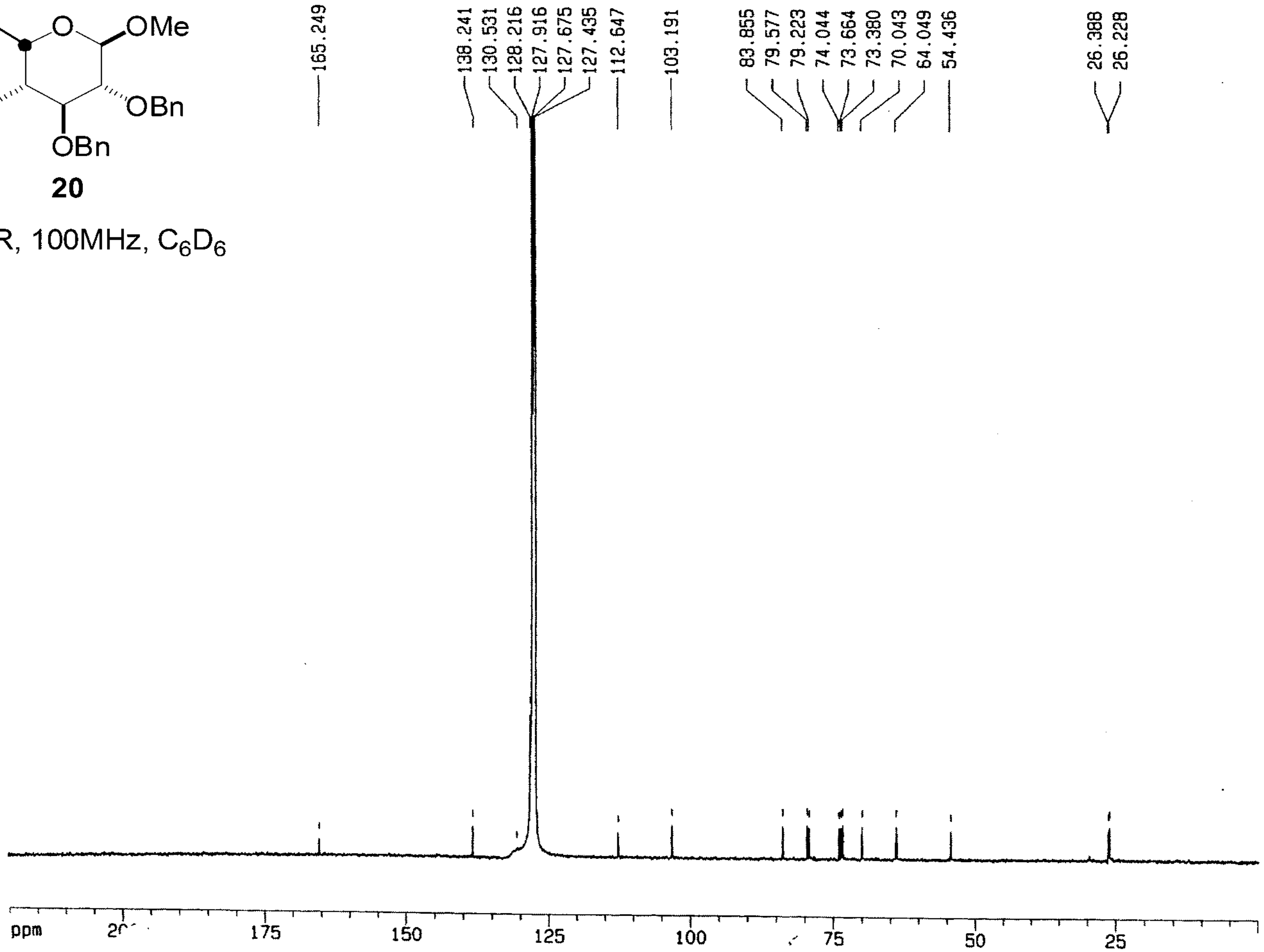
^{1}H NMR, 300MHz, C_6D_6

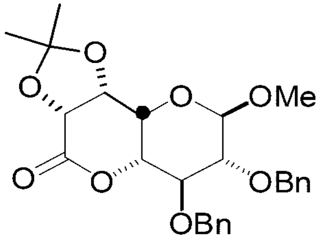




20

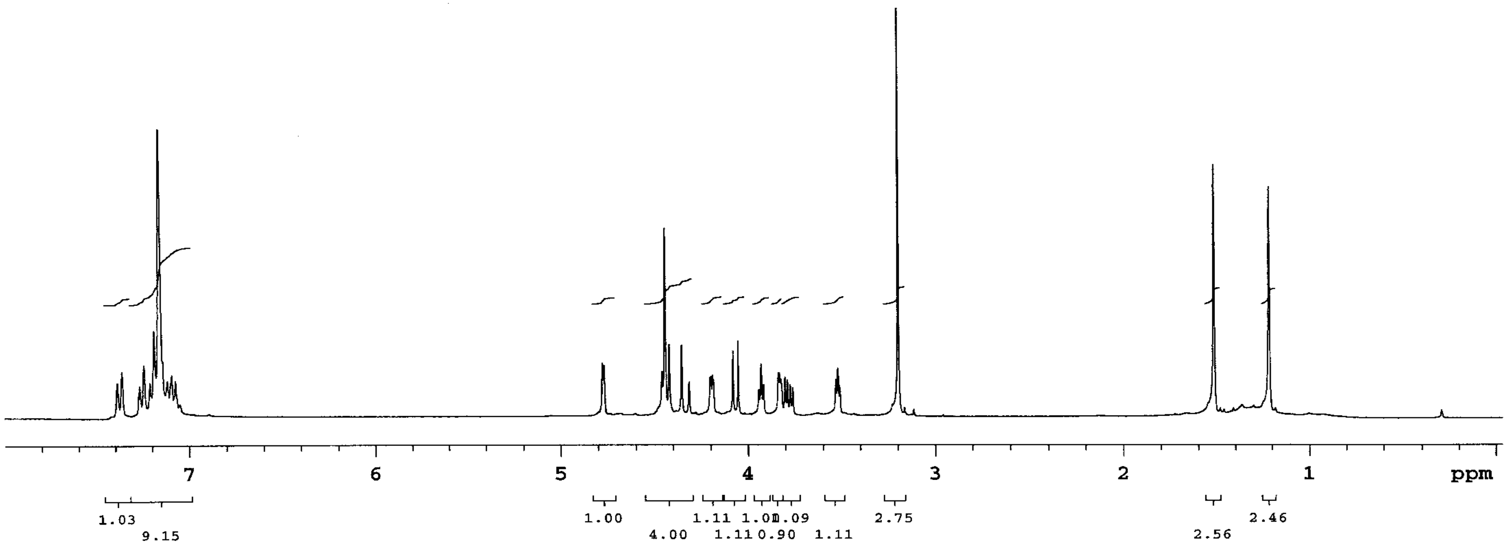
^{13}C NMR, 100MHz, C_6D_6

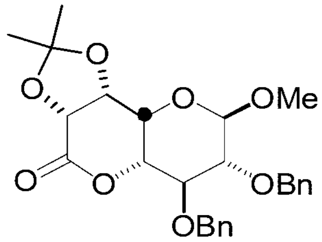




21

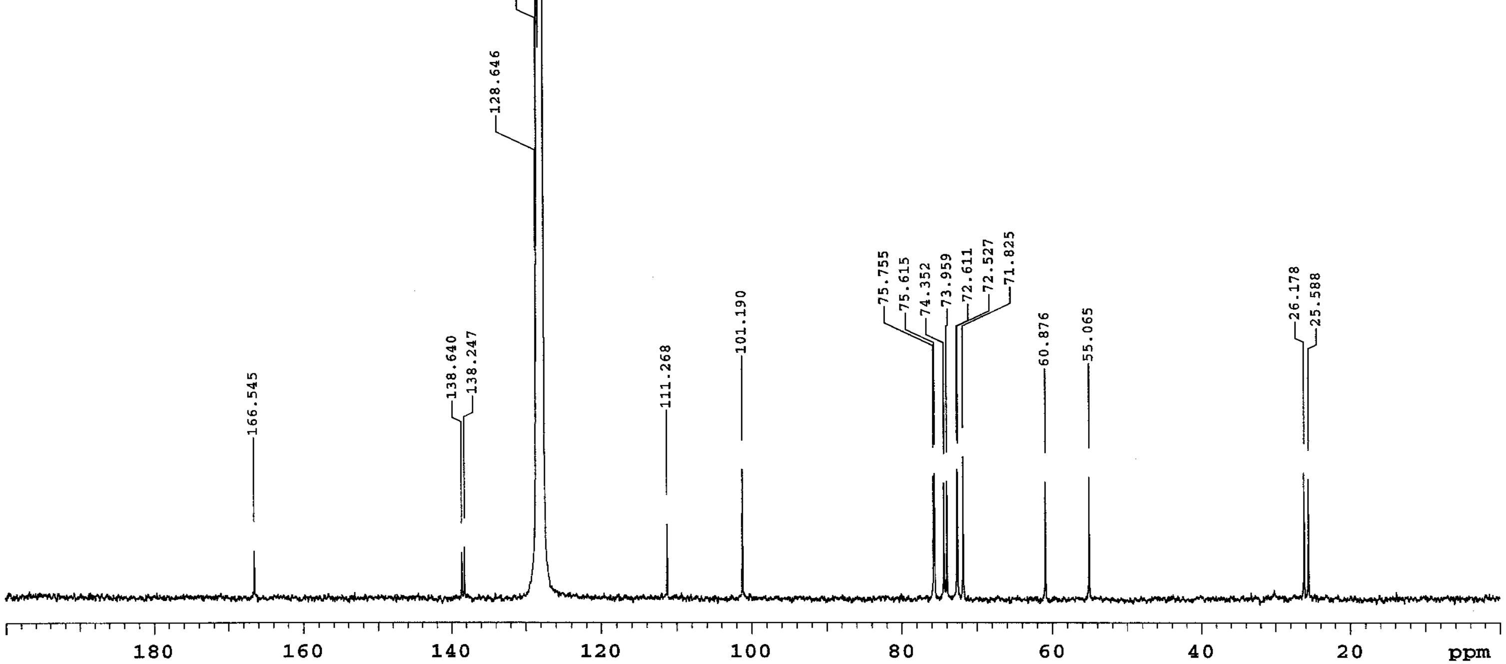
^1H NMR, 300MHz, C_6D_6

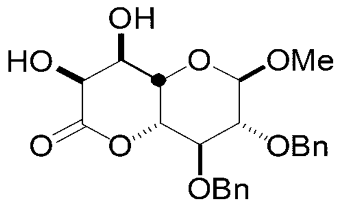




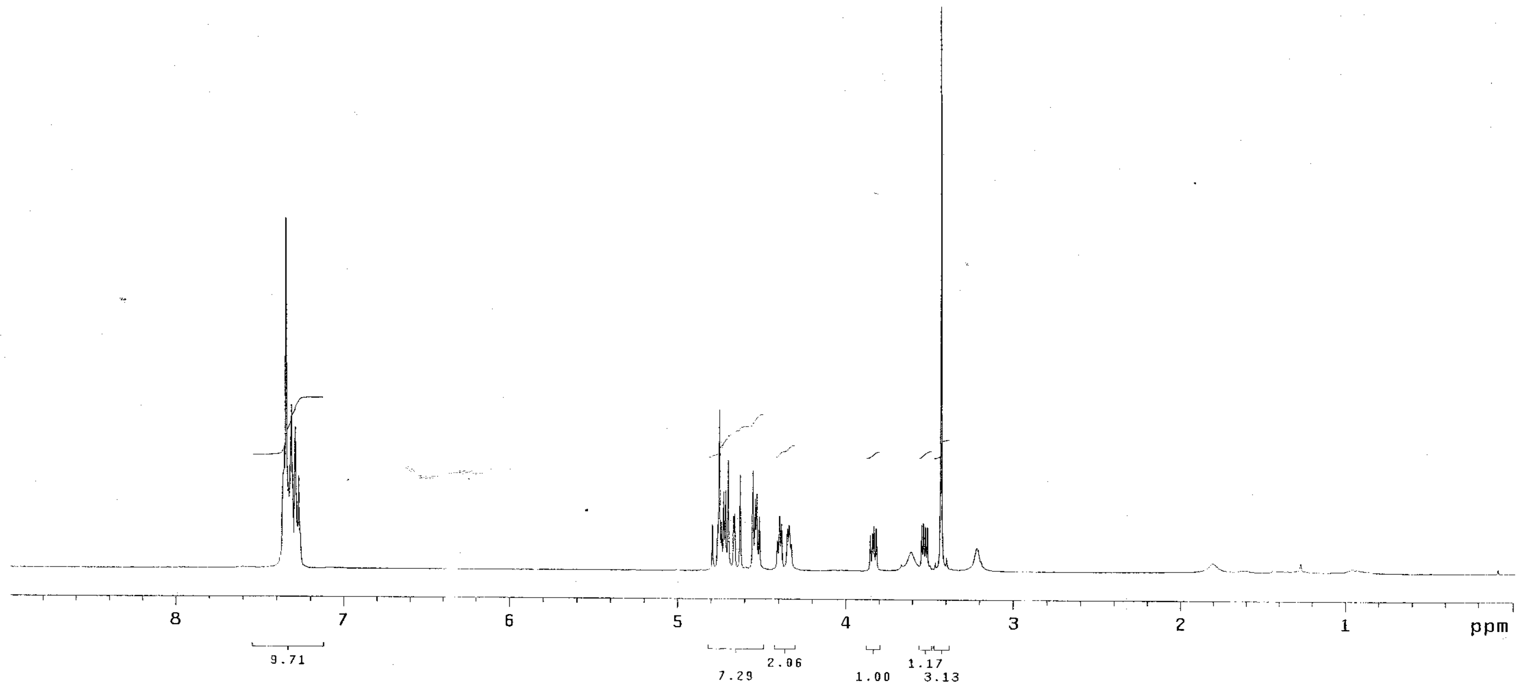
21

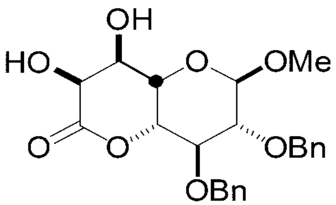
^{13}C NMR,75MHz, C_6D_6



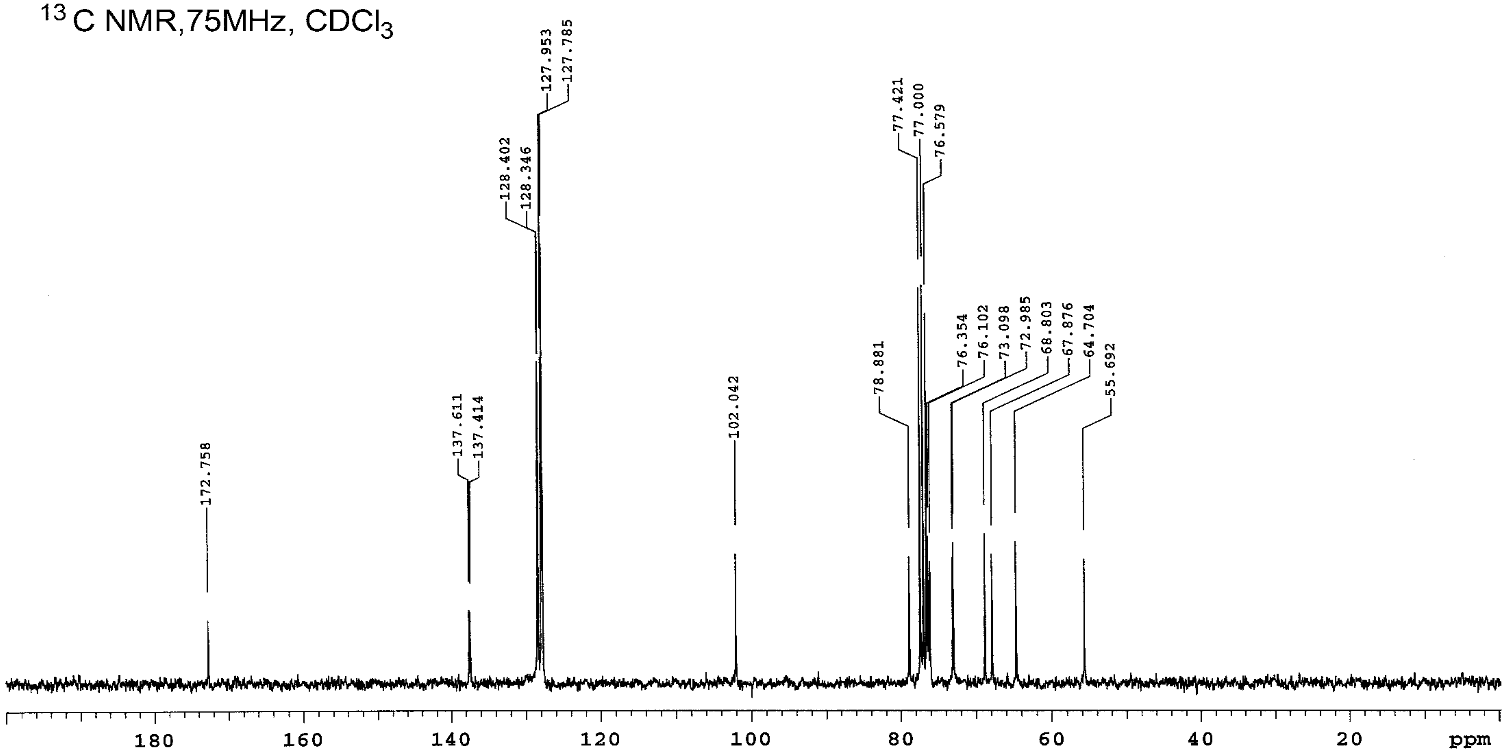


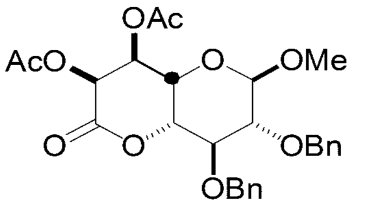
^1H NMR, 300MHz, $CDCl_3$





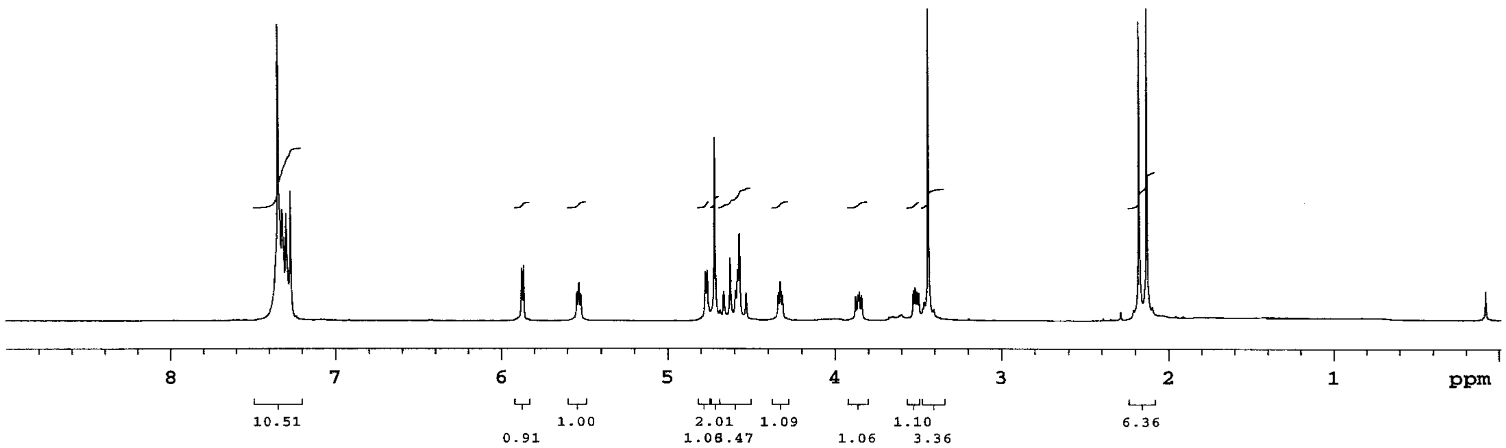
^{13}C NMR,75MHz, $CDCl_3$

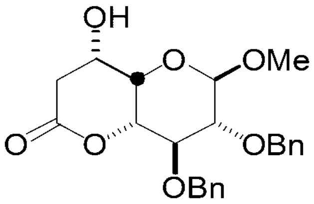




22

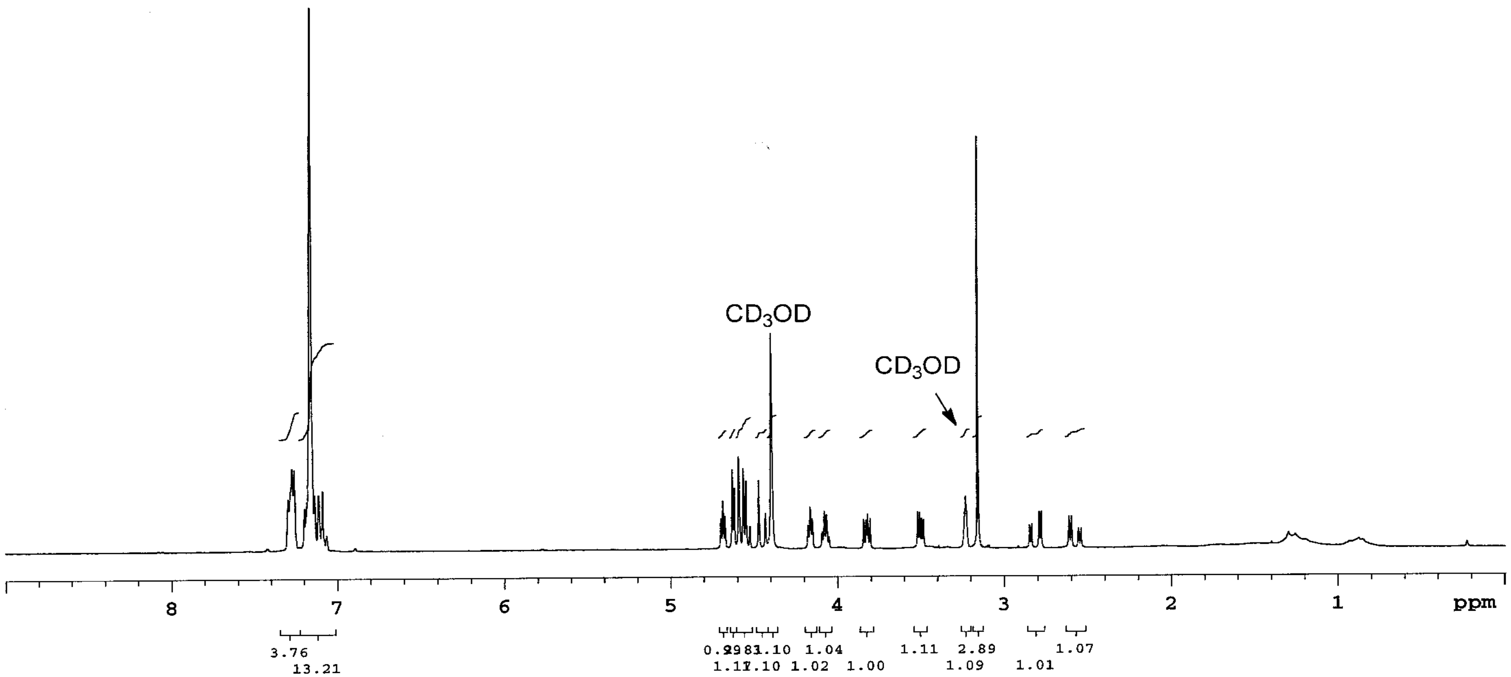
^1H NMR, 300MHz, $CDCl_3$

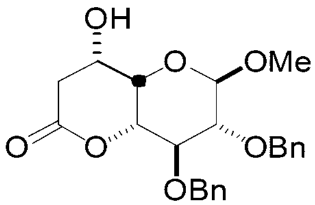




23

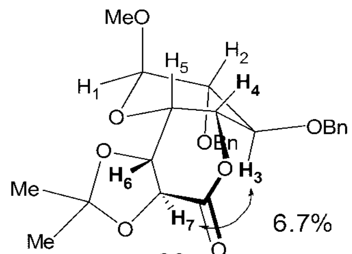
[1] H NMR, 300MHz, C_6D_6:CD_3OD = 5:1





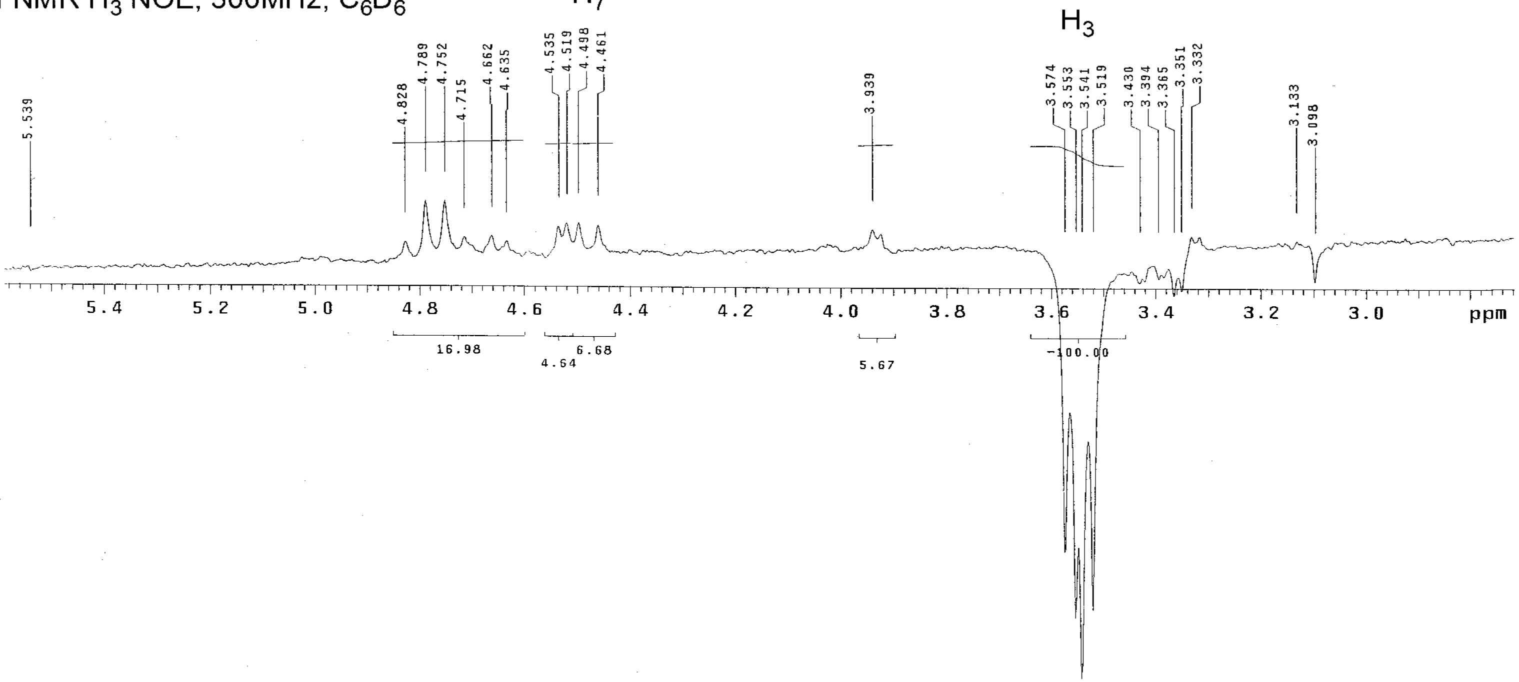
23

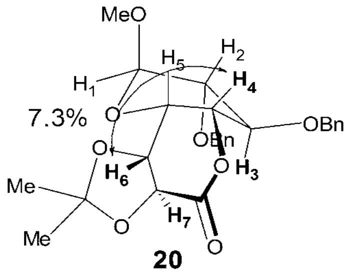
^{13}C NMR, 75MHz, C_6D_6:CD_3OD = 5:1



20

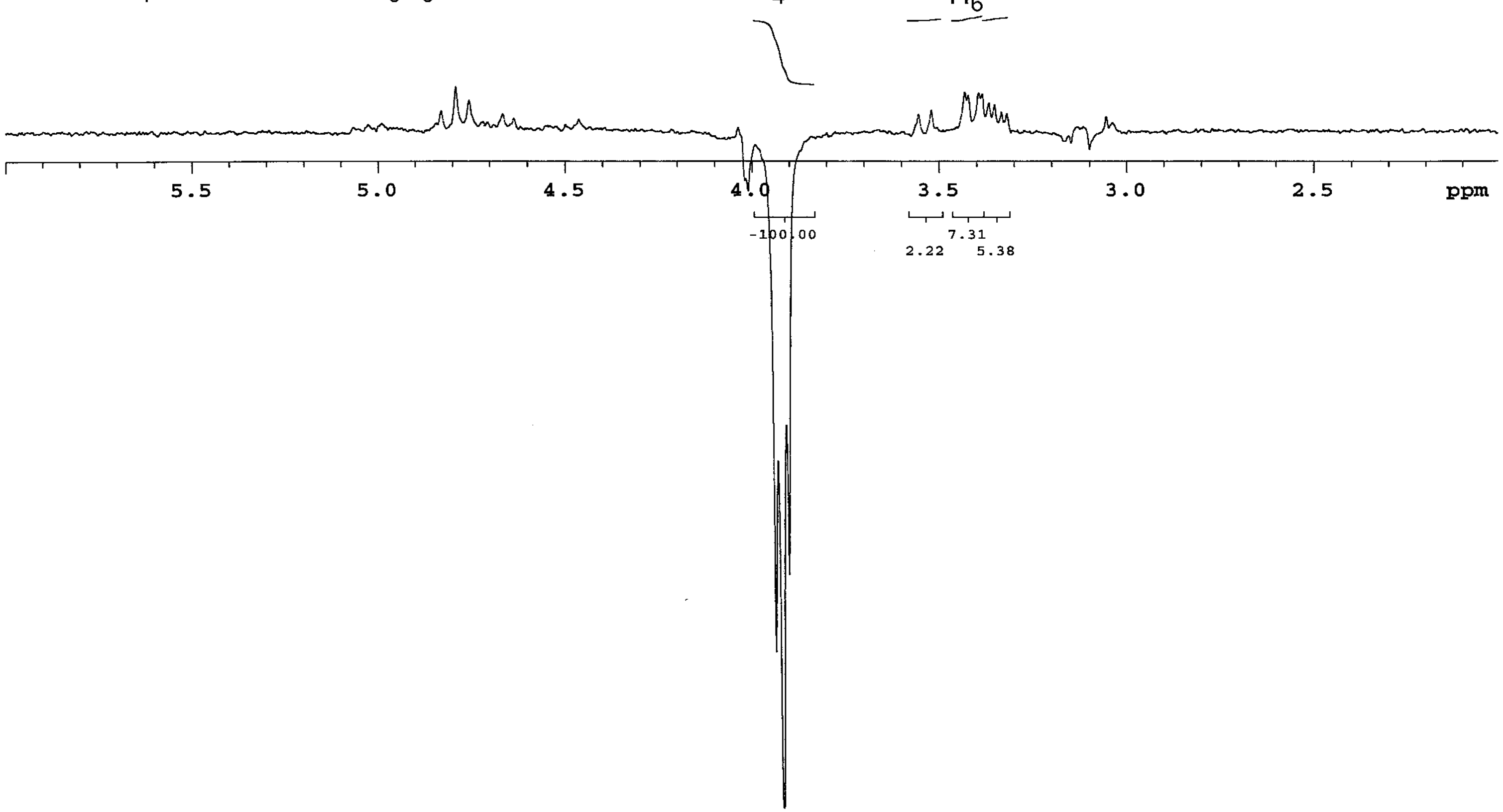
^{1}H NMR H_3 NOE, 300MHz, C_6D_6

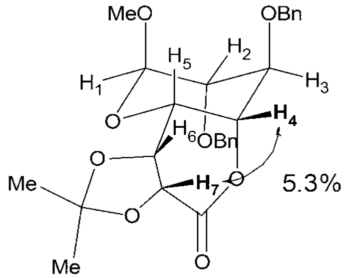




20

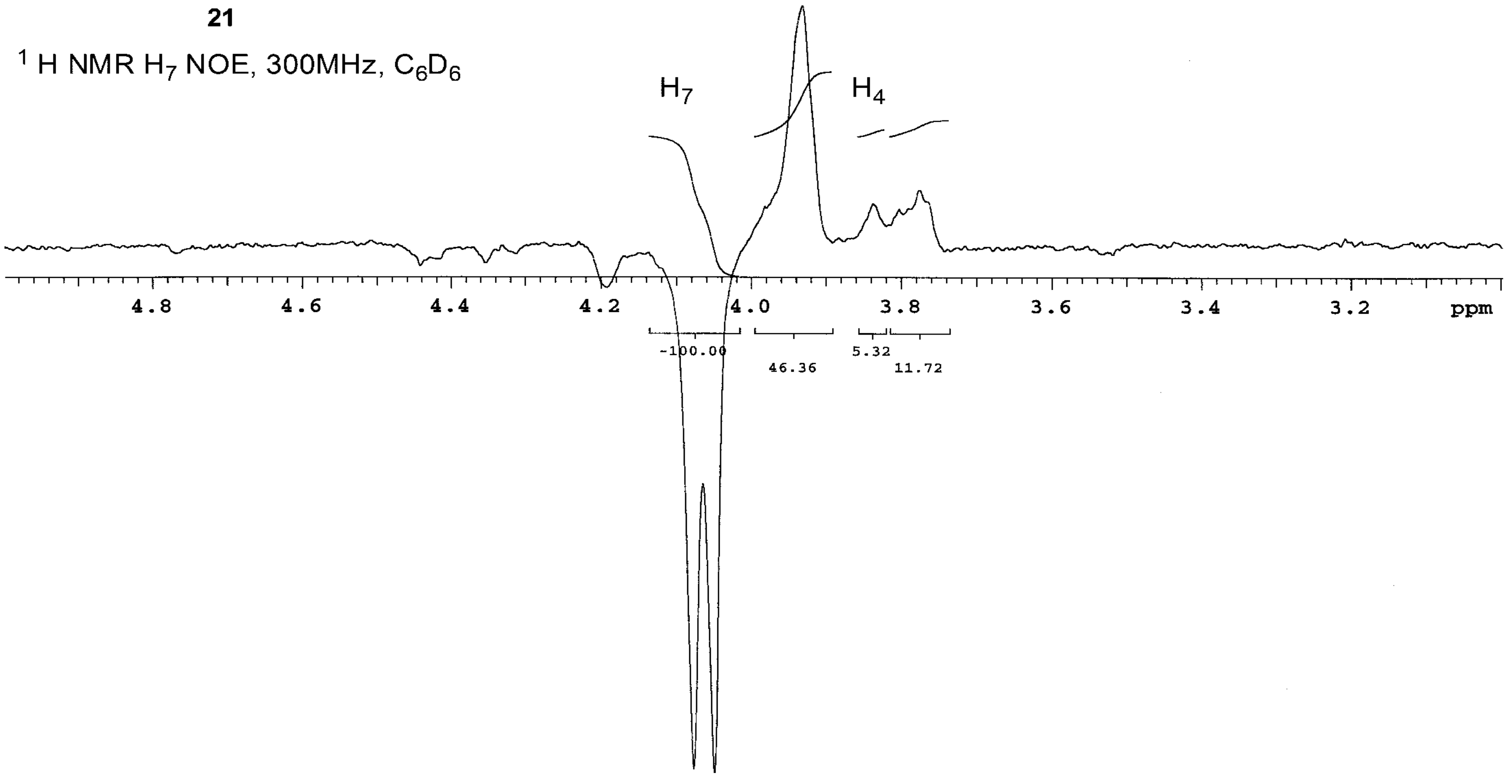
[1] H NMR H_4 NOE, 300MHz, C_6D_6

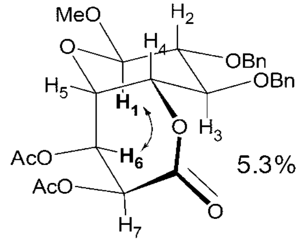




21

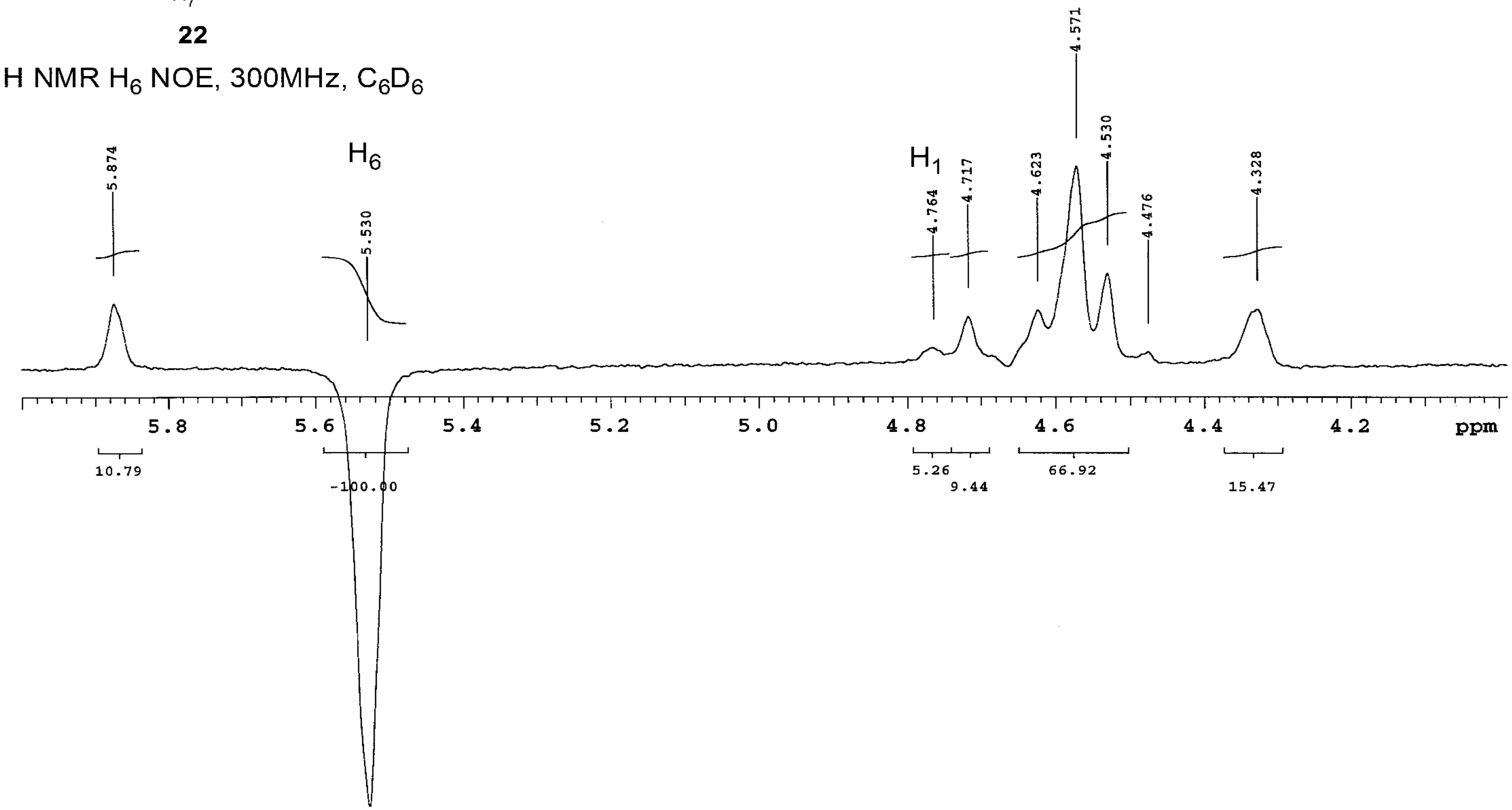
[1] H NMR H_7 NOE, 300MHz, C_6D_6

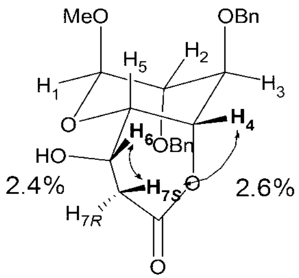




22

^{1}H NMR H_6 NOE, 300MHz, C_6D_6





23

[1] H NMR, 300MHz, C_6D_6:CD_3OD = 5:1