Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Facile *O*-Glycosylation of Glycals Using Glu-Fe_3O_4-SO_3H, a Magnetic Solid Acid Catalyst

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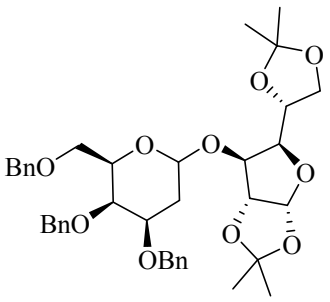


Table 2, Entry 3, 10a: Clear oil (97%, α:β = 83:17); R_f = 0.3 (20% EtOAc/ Pet ether); IR ($CHCl_3$) 2931, 2873, 1594, 1448, 1374, 1216, 1029, 846, 763, 669 cm $^{-1}$; Data for major α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 15H), 5.82 (d, *J* = 3.6 Hz, 1H), 5.25 (d, *J* = 3.6 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 3.6 Hz, 1H), 4.62- 4.56 (m, 3H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.22 (d, *J* = 2.8 Hz, 1H), 4.19-4.14 (m, 1H), 4.09-4.06 (m, 2H), 3.99-3.84 (m, 4H), 3.66-3.60 (m, 1H), 3.55-3.52 (m, 1H), 2.23 (dt, *J* = 13.7 and 3.6 Hz, 1H), 2.00 (dd, *J* = 12.8 and 3.6 Hz, 1H), 1.47 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.3, 138.0, 128.4, 128.3, 128.2, 128.1, 127.7 127.6, 127.6, 127.5, 127.3, 111.8, 109.1, 105.2, 99.4, 83.5, 81.2, 80.8, 74.3, 74.2, 73.6, 73.0, 72.5, 70.9, 70.4, 70.0, 67.6, 31.0, 26.8, 26.7, 26.1, 25.3; HRMS (ESI): calcd. for $C_{39}H_{48}O_{10}Na$ 699.3140, found 699.3138. (NMR data are consistent with the literature)[4].

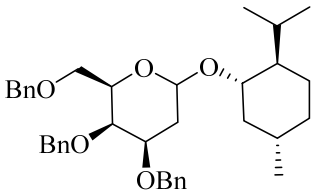


Table 3, Entry 1, 10b, Colourless syrup (82%, only α); R_f = 0.2 (10% EtOAc/ Pet ether); IR ($CHCl_3$) 3017, 2925, 2869, 1454, 1362, 1217, 1093, 1029, 768, 668 cm^{-1}; Data for major α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 15H), 5.03 (bs, 1H), 4.94 (dd, *J* = 11.9 and 4.5 Hz, 1H), 4.63 (d, *J* = 4.6 Hz, 1H), 4.61 (bd, *J* = 3.2 Hz, 2H), 4.52-4.41 (q, 2H), 4.09-4.05 (q, 1H), 3.95-3.92 (m, 2H), 3.59-3.56 (m, 2H), 3.33-2.26 (m, 1H), 2.23-2.13 (m, 1H), 2.11-1.98 (m, 3H), 1.65-1.58 (m, 3H), 1.19-1.34 (bs, 1H), 1.20-1.15 (m, 1H), 1.0-0.92 (m, 2H), 0.91 (dd, *J* = 7.3 and 4.5 Hz, 3H), 0.82 (m, 3H), 0.75 (dd, *J* = 6.9 and 4.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.5,

138.1, 128.3, 128.2, 128.1, 127.5, 127.4, 127.2, 99.7, 79.9, 74.9, 74.1, 73.3, 73.1, 70.3, 69.8, 69.6, 48.8, 42.8, 34.3, 31.6, 31.6, 25.7, 23.2, 22.2, 21.1, 16.3; HRMS (ESI): calcd. for $C_{37}H_{48}O_5Na$ 595.3394, found 595.3383.

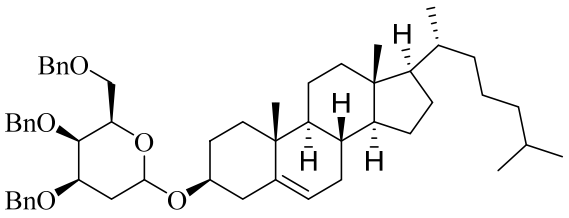


Table 3, Entry 2, 10c, White solid (89%, α), mp. 135 ºC; R_f = 0.3 (10% EtOAc/ Pet ether); IR ($CHCl_3$) 2953, 2856, 1593, 1471, 1371, 1218, 1085, 1031, 768, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.22 (m, 15H), 5.25 (d, *J* = 4.6 Hz, 1H), 5.14 (d, *J* = 3.2 Hz, 1H), 4.93 (d, *J* = 11.9 Hz, 1H), 4.63 (s, 1H), 4.60 (bs, 2H), 4.52-4.41 (q, 2H), 4.02-3.93 (m, 3H), 3.63-3.55 (m, 2H), 3.48-3.41 (m, 1H), 2.29-2.16 (m, 3H), 2.02-1.91 (m, 3H), 1.88-1.78 (m, 3H), 1.60-1.40 (m, 9H), 1.38-1.30 (m, 4H), 1.27-1.21 (m, 1H), 1.18-1.07 (m, 5H),1.05-1.00 (m, 2H), 0.99 (s, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 1.3 Hz, 3H), 0.85 (d, *J* = 1.8 Hz, 3H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.9, 138.6, 138.1, 128.3, 128.3, 128.1, 127.7, 127.5, 127.4, 127.3, 121.6, 95.6, 76.1, 75.0, 74.2, 73.4, 73.1, 70.4, 69.8, 69.6, 56.7, 56.1, 50.0, 42.3, 40.0, 39.7, 39.5, 37.0, 36.7, 36.1, 35.7, 31.9, 31.8, 31.6, 28.2, 28.0, 27.8, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8; HRMS (ESI): calcd. for $C_{54}H_{74}O_5Na$ 825.5434, found 825.5438.

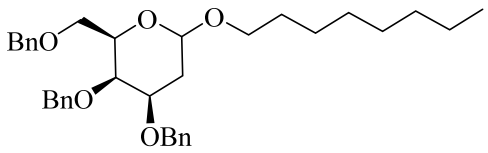


Table 3, Entry 3, 10d, Liquid (91%, only α), R_f = 0.2 (10% EtOAc/ Pet ether); IR ($CHCl_3$) 3018, 2928, 2864, 1457, 1363, 1216, 1161, 1098, 1061, 797, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.22 (m, 15H), 4.96 (bd, *J* = 3.1 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.60 (m, 2H), 4.49-4.41 (q, *J* = 11.9 Hz, 2H), 3.95-3.82 (m, 3H), 3.67-3.51 (m, 3H), 3.48-3.32 (m, 1H), 2.25-1.96 (m, 2H), 1.60-1.51 (m, 2H), 1.27 (bs, 10H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 138.9, 138.5, 138.3, 128.4, 127.2, 97.7, 74.9, 74.2, 73.5, 73.0, 70.4, 69.7, 69.5, 31.8, 31.2, 29.5, 29.4, 29.2, 29.2, 26.2, 22.6, 14.1; HRMS (ESI): calcd. for $C_{35}H_{46}O_5Na$ 569.3237, found 569.3235.

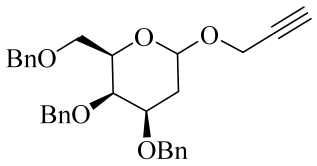


Table 3, Entry 4, 10e, liquid (96%, α:β = 71:29); R_f = 0.2 (20% EtOAc/ Pet ether); IR ($CHCl_3$) 3305, 3020, 2919, 2871, 2404, 1492, 1361, 1217, 1097, 1037, 768, 671 cm^{-1}; Data for major α isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 15H), 5.15 (d, *J* = 3.2 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.67-4.57 (m, 3H), 4.51-4.41 (q, 2H), 4.18 (t, *J* = 2.7 Hz, 2H), 3.95-3.88 (m, 3H), 3.62-3.54 (m, 2H), 2.38 (t, *J* = 2.7 Hz, 1H), 2.30-2.23 (dt, *J* = 12.8 and 3.7 Hz, 1H), 2.06-2.01 (dd, *J* = 12.8 and 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.5, 138.0, 128.3, 128.2, 127.8, 127.7, 127.5, 127.2, 96.6, 79.3, 74.5, 73.4, 72.8, 70.3, 70.2, , 69.3, 54.1, 30.8; HRMS (ESI): calcd. for $C_{30}H_{32}O_5Na$ 495.2142, found 495.2142. (NMR data are consistent with the literature) [5]

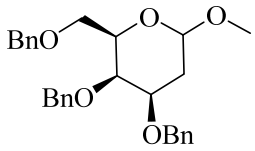


Table 3, Entry 5, 10f, Liquid (94%, only α); R_f = 0.3 (20% EtOAc/ Pet ether); IR ($CHCl_3$) 2922, 2858, 1454, 1357, 1128, 1091, 1053, 1028, 943, 881, 754, 736 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.15 (m, 15H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.87 (d, *J* = 2.7 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.59 (s, 2H), 4.51 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 3.93-3.85 (m, 3H), 3.62-3.55 (m, 2H), 3.32 (s, 3H), 2.22 (dt, *J* = 12.4 and 3.4 Hz, 1H), 1.99 (dd, *J* = 8.5 and 4.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.5, 138.1, 128.4, 128.3, 128.2, 128.2, 127.7, 127.6, 127.5, 127.2, 98.9, 77.3, 76.7, 74.7, 74.2, 73.4, 72.9, 70.4, 69.7, 69.6, 54.8, 31.1; HRMS (ESI): calcd. for $C_{28}H_{32}O_5Na$ 471.2142, found 471.2140.

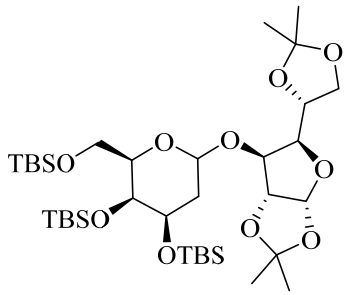


Table 3, Entry 6, 10g, Colorless oil (88%, α:β = 91:9); R_f = 0.6 (20% EtOAc/ Pet ether); IR ($CHCl_3$) 2953, 2929, 2856, 1471, 1371, 1251, 1085, 1074, 1022, 833, 775 cm^{-1}; Data for major α isomer: ^1H NMR (400 MHz, $CDCl_3$) 5.84 (d, *J* = 3.4 Hz, 1H), 5.1 (d, *J* = 3.0 Hz, 1H), 4.64 (d, *J* = 3.5 Hz, 1H), 4.22-4.18 (m, 2H), 4.13-4.08 (m, 2H), 4.00-3.96 (m, 2H), 3.83 (s, 1H), 3.75-3.63 (m, 3H), 2.1 (dt, *J* = 12.2 and 3.7 Hz, 1H), 1.65 (dd, *J* = 12.2 and 4.4 Hz, 1H), 1.49 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H) 0.91 (s, 27H), 0.11 (s, 3H), 0.09 (s, 3H), 0.09 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.7, 109.0, 105.3, 100.0, 83.7, 81.5, 81.2, 73.6, 72.6, 70.3, 68.0, 67.6, 63.1, 33.6, 27.0, 26.7, 26.3, 26.1, 26.0, 25.9, 25.3, 18.5, 18.4, 18.3, -3.8, -4.3, -4.6, -4.9, -5.3, -5.3; HRMS (ESI): calcd. for $C_{36}H_{72}O_{10}Si_3Na$ 771.4325, found 771.4322. (NMR data are consistent with the literature)[4].

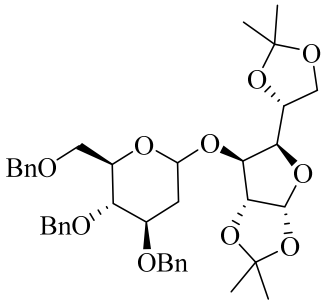


Table 3, Entry 8, 10h, Clear oil (84%, α:β = 77:23); R_f = 0.3 (20% EtOAc/ Pet ether); IR ($CHCl_3$) 2985, 2935, 2873, 1452, 1371, 1213, 1089, 1061, 1026, 846, 734, 696 cm^{-1}; Data for major α isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.16 (m, 15H), 5.82 (d, *J* = 3.6 Hz, 1H), 5.25 (d, *J* = 3.6 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.68-4.60 (m, 4H), 4.54-4.48 (m, 2H), 4.24 (d, *J* = 2.8 Hz, 1H), 4.15-4.05 (m, 2H), 3.99-3.91 (m, 2H), 3.80-3.75 (m, 2H), 3.73-3.69 (m, 1H), 3.67-3.58 (m, 2H), 2.28 (dt, *J* = 13.7 and 3.6 Hz, 1H), 1.72 (dd, *J* = 12.8 and 3.6 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 3H),

1.32 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.2, 138.0, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 111.8, 109.4, 105.2, 98.6, 83.7, 81.3, 80.2, 78.1, 75.1, 73.4, 73.3, 72.4, 71.8, 71.4, 68.9, 67.7, 35.1, 29.7, 26.8, 26.1, 25.4; HRMS (ESI): calcd. for $C_{39}H_{48}O_{10}Na$ 699.3140, found 699.3138.

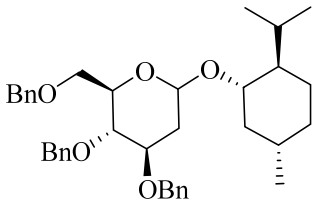


Table 3, Entry 9, 10i, Colorless syrup (80%, α:β=83:17); R_f = 0.2 (10% EtOAc/ Pet ether); IR ($CHCl_3$) 3017, 2925, 2869, 1454, 1362, 1217, 1093, 1029, 768, 668 cm^{-1}; Data for major α isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.26 (m, 15H), 5.01 (d, *J* = 3.1 Hz, 1H), 4.89 (d, *J* = 10.7 Hz, 1H), 4.66-4.63 (m, 3H), 4.50-4.48 (m, 2H), 4.01-3.92 (m, 2H), 3.79 (dd, *J* = 10.3 and 3.9 Hz, 1H), 3.67-3.65 (dd, *J* = 8.2 and 3.6 Hz, 1H), 3.59 (t, *J* = 9.4 Hz, 1H), 3.32-3.27 (ddd, *J* = 10.6 and 4.2 Hz, 1H), 2.28-2.24 (m, 1H), 2.11-2.09 (m, 1H), 2.04-1.98 (m, 1H), 1.71-1.64 (m, 1H), 1.63-1.59 (m, 3H), 1.35-1.32 (m, 1H), 1.23-1.13 (m, 1H), 0.99-0.93 (m, 2H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.5, 138.2, 128.3, 128.3, 127.9, 127.9, 127.7, 127.5, 99.5, 80.5, 78.4, 77.7, 77.3, 76.7, 74.9, 73.4, 71.7, 70.8, 69.0, 48.7, 43.0, 36.0, 34.3, 31.6, 25.7, 23.3, 22.3, 21.1, 16.3; HRMS (ESI): calcd. for $C_{37}H_{48}O_5Na$ 595.3394, found 595.3389.

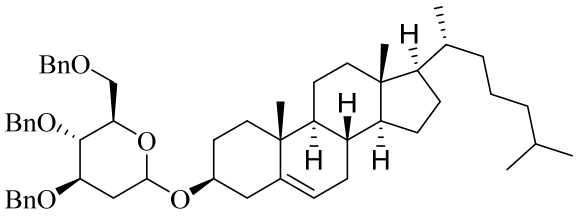


Table 3, Entry 10, 10j, White solid (83%, α:β =77:23); mp 133 ºC, R_f = 0.2 (10% EtOAc/ Pet ether); IR ($CHCl_3$) 2953, 2856, 1593, 1471, 1371, 1218, 1085 cm^{-1}; Data for major α isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.18 (m, 15H), 5.27 (d, *J* = 4.9 Hz, 1H), 5.14 (d, *J* = 2.5 Hz, 1H), 4.89 (bd, *J* = 10.8 Hz, 1H) 4.13 (d, *J* = 2.5 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.70-4.56 (m, 4H),

4.54-4.42 (m, 2H), 4.04-3.99 (m, 1H), 3.87-3.55 (m, 4H), 3.50-3.39 (m, 1H), 2.34-2.23 (m, 3H), 2.02-1.91 (m, 2H), 1.89-1.78 (m, 4H), 1.53-1.22 (m, 12H), 1.19-1.04 (m, 6H), 0.99 (s, 3H), 0.91 (d, J = 6.4 Hz, 3H), 0.87 (d, J = 1Hz, 3H), 0.85 (d, J = 1Hz, 3H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.8, 138.5, 138.1, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 127.4, 121.6, 95.0, 75.8, 75.0, 74.9, 73.4, 73.3, 70.6, 69.4, 69.9, 56.7, 56.1, 50.0, 42.3, 39.9, 39.7, 39.5, 37.0, 36.7, 36.1, 35.7, 31.9, 31.8, 28.2, 28.0, 27.6, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8; HRMS (ESI): calcd. for $C_{54}H_{74}O_5Na$ 825.5434, found 825.5438.

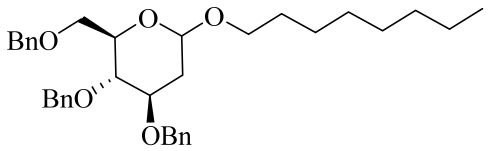


Table 3, Entry 11, 10k, liquid (80%); (91: 9[a], 50:50[b], 90:10[c]); a = α:β ratio of 2-deoxy-*O*-glycoside, b = Ratio of the Ferrier product and 2-deoxy-*O*-glycoside, c = α:β ratio of the Ferrier product.

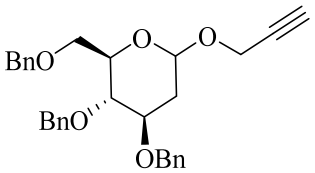


Table 3, Entry 12, 10l, liquid (93%); (90: 10[a], 50:50[b], 83:27[c]); a = α:β ratio of 2-deoxy-*O*-glycoside, b = Ratio of the Ferrier product and 2-deoxy-*O*-glycoside, c = α:β ratio of the Ferrier product. This compound is previously reported.

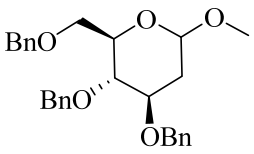


Table 3, Entry 13, 10m, Clear oil (94%); (69: 31[a], 38:62[b], 91:9[c]); a = α:β ratio of 2-deoxy-*O*-glycoside, b = Ratio of the Ferrier product and 2-deoxy-*O*-glycoside, c = α:β ratio of the Ferrier product. This compound is previously reported[3].

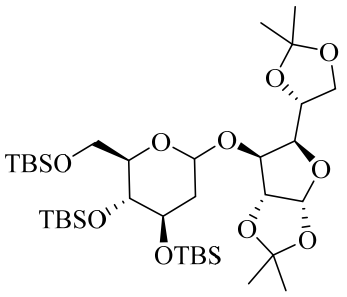
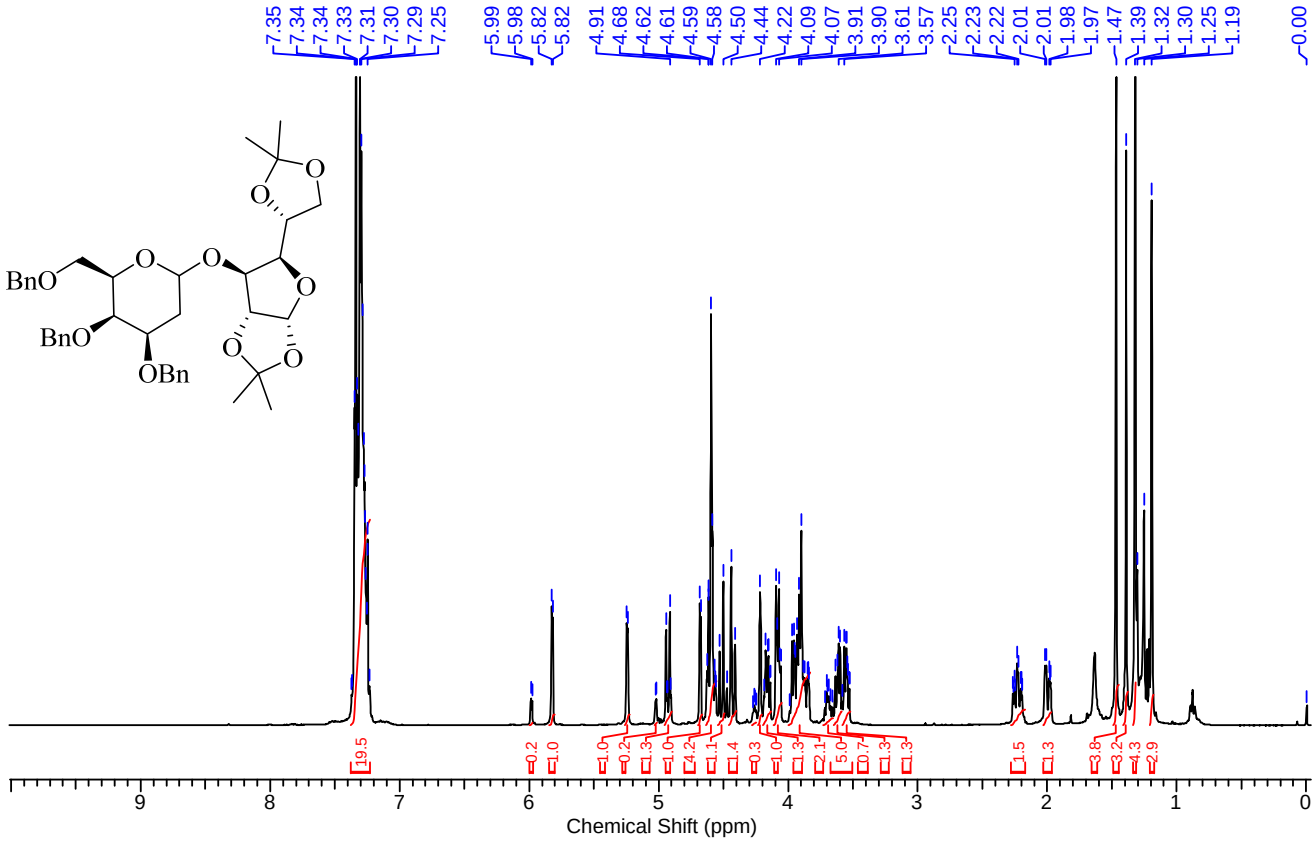
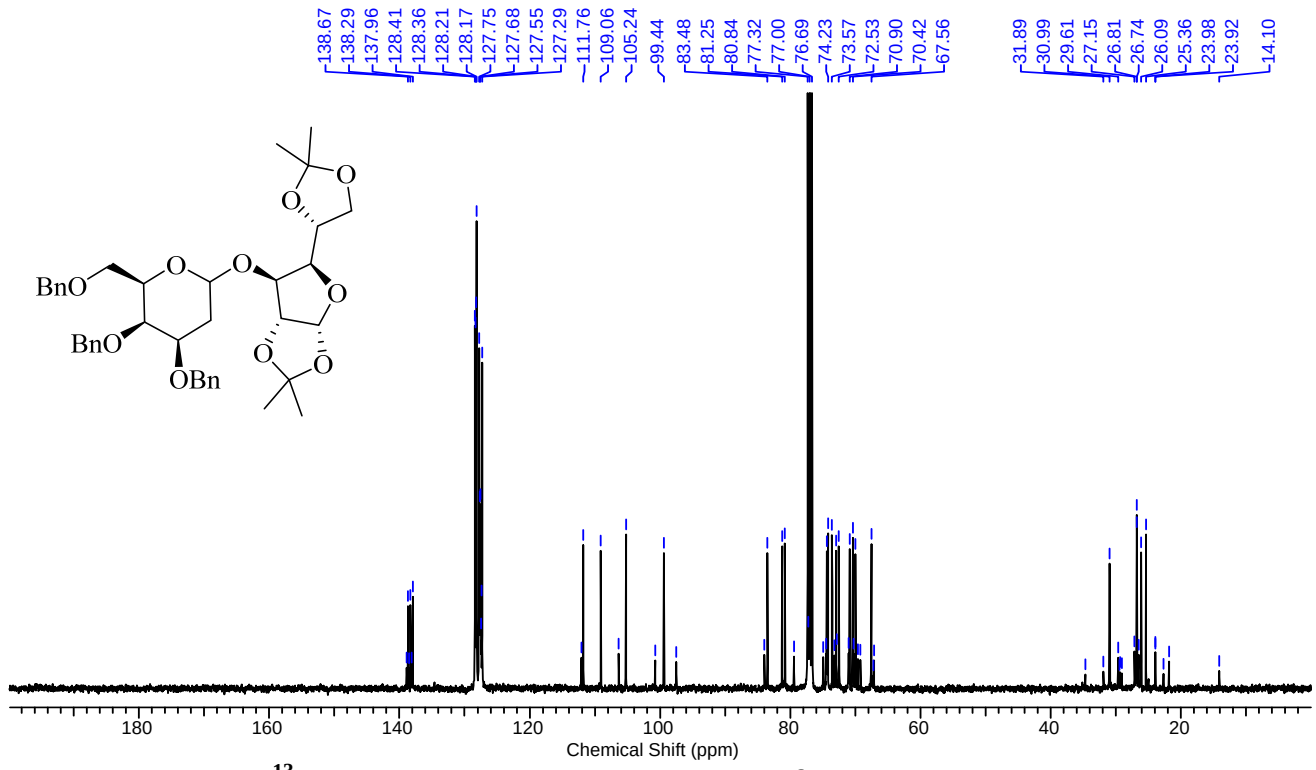


Table 3, Entry 14, 10n, Colorless oil (81%, α:β =91:9); R_f = 0.3 (10% EtOAc/ Pet ether); IR ($CHCl_3$) 2953, 2929, 2856, 1471, 1371, 1251, 1085, 1074, 1022, 833, 775 cm^{-1}; Data for major α isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (d, *J* = 3.5 Hz, 1H), 5.2 (s, 1H), 4.72 (d, *J* = 3.5 Hz, 1H), 4.34-4.30 (m, 1H), 4.24-4.19 (m, 1H), 4.14-4.10 (m, 2H), 4.01-3.96 (m, 1H), 3.93-3.87 (m, 1H), 3.78-3.66 (m, 2H), 2.16-2.02 (m, 1H), 2.71 (m, 1H), 1.50 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H) 0.93 (s, 6H), 0.90 (s, 18H), 0.10 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.8, 109.1, 105.4, 98.9, 83.7, 81.5, 81.4, 77.3, 76.7, 75.0, 73.0, 72.5, 70.7, 67.7, 63.3, 29.7, 27.0, 26.8, 26.5, 26.3, 26.2, 26.1, 26.0, 25.9, 25.6, 25.3, 18.5, 18.3, 18.1, -3.1, -4.3, -4.6, -5.0, -5.3; HRMS (ESI): calcd. for $C_{36}H_{72}O_{10}Si_3Na$ 771.4326, found 771.4325.

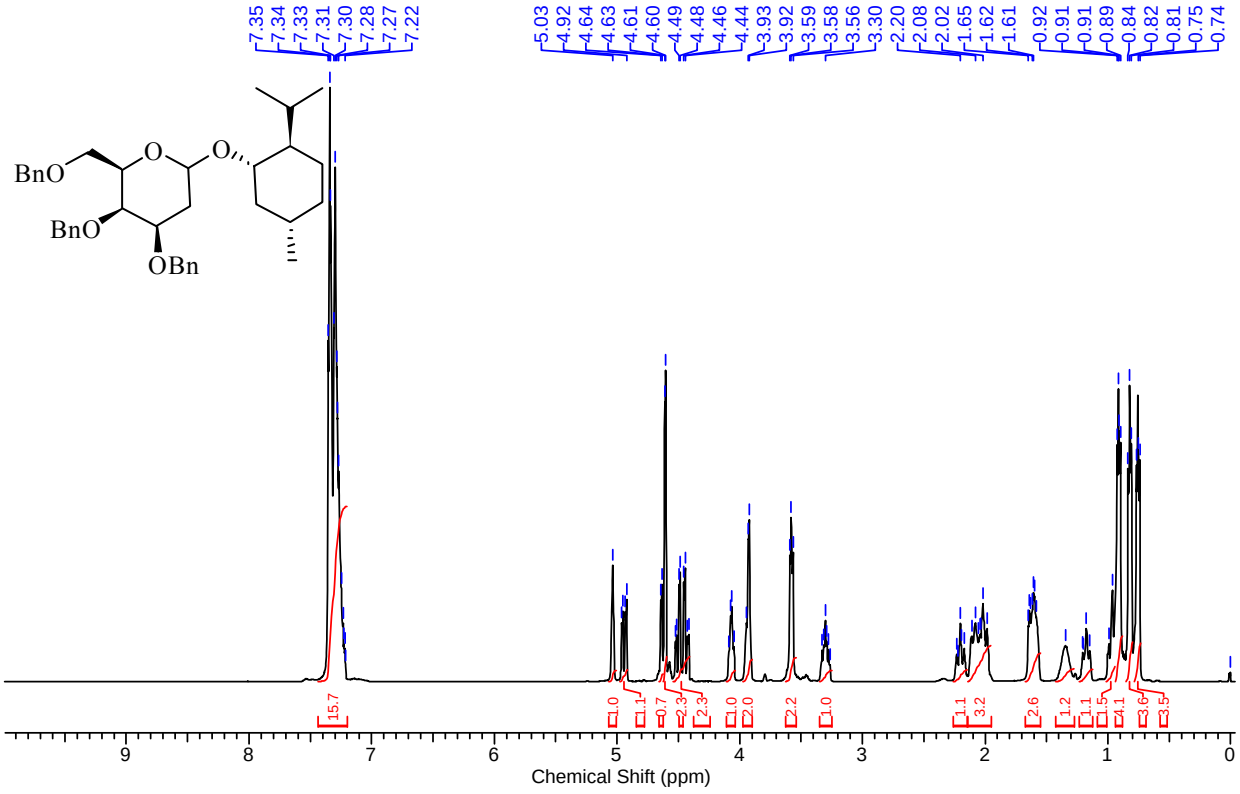
^{1}H and ^{13}C NMR spectra



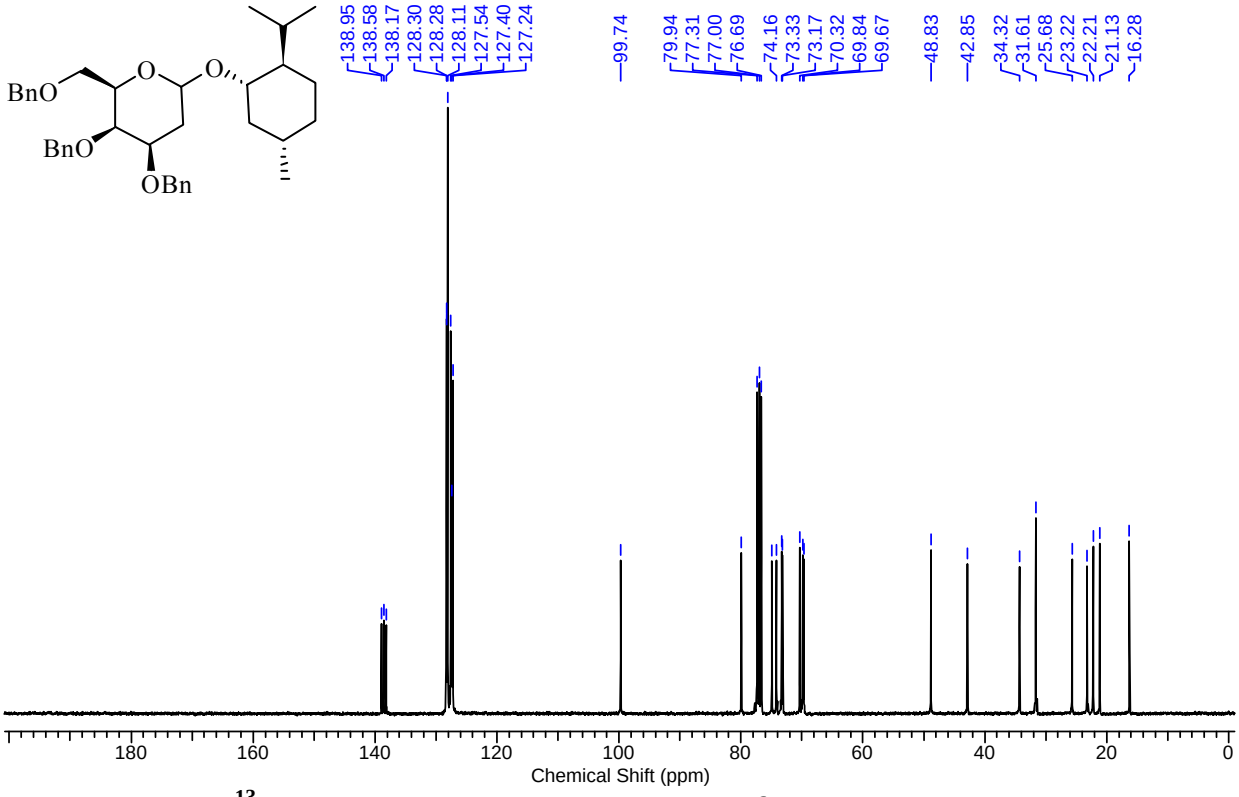
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10a



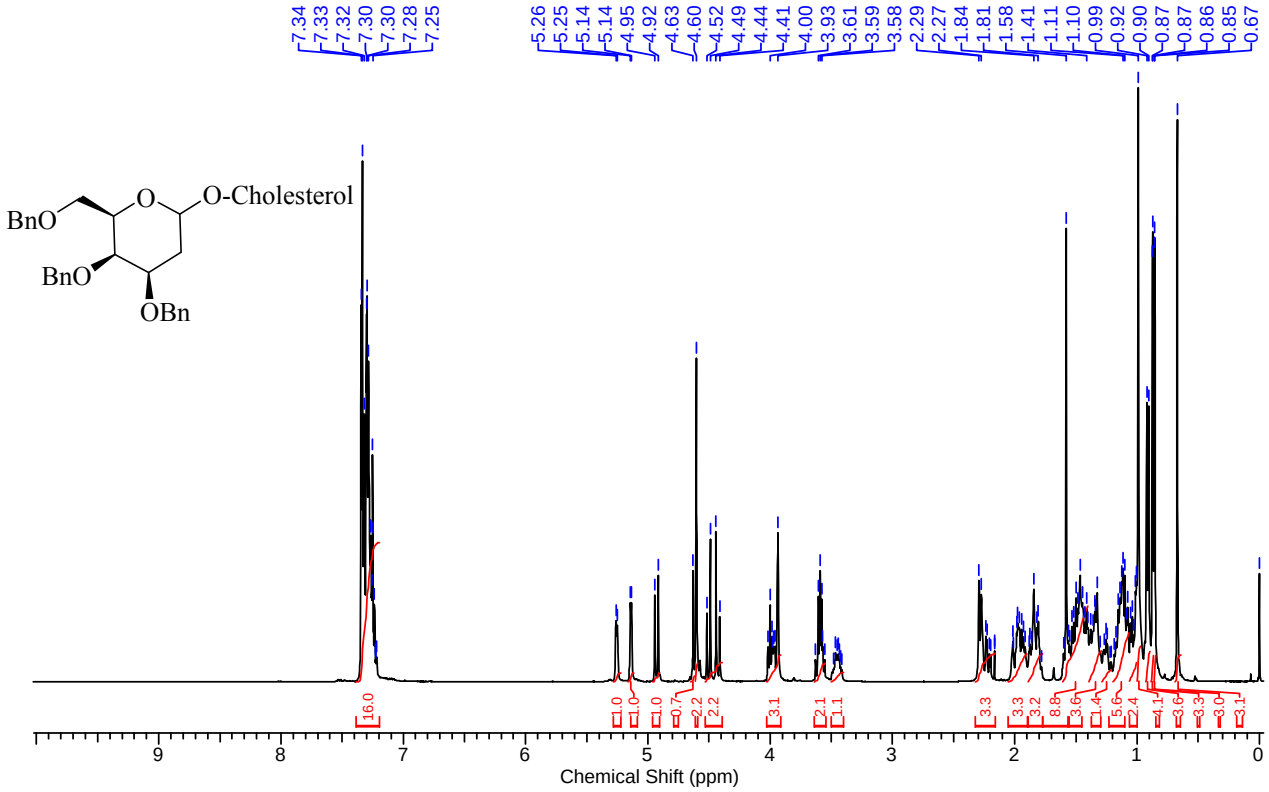
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10a



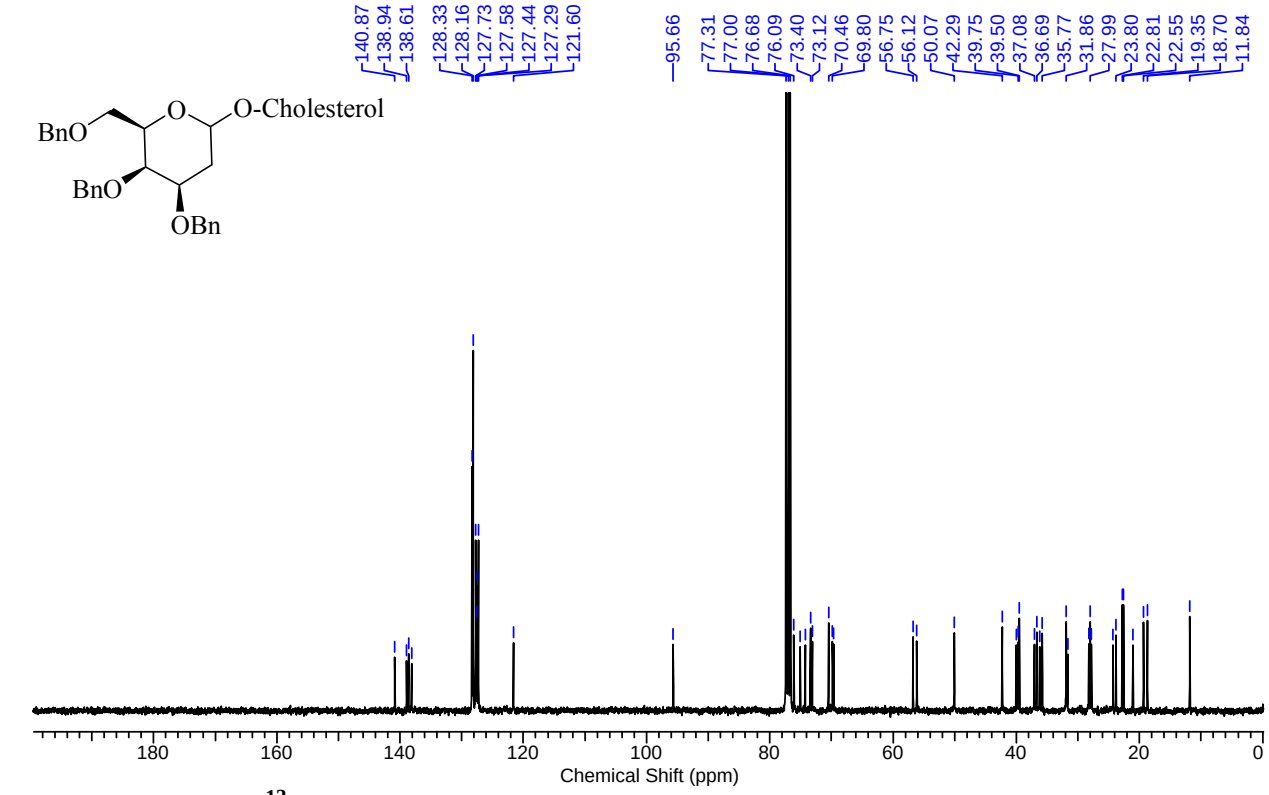
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10b



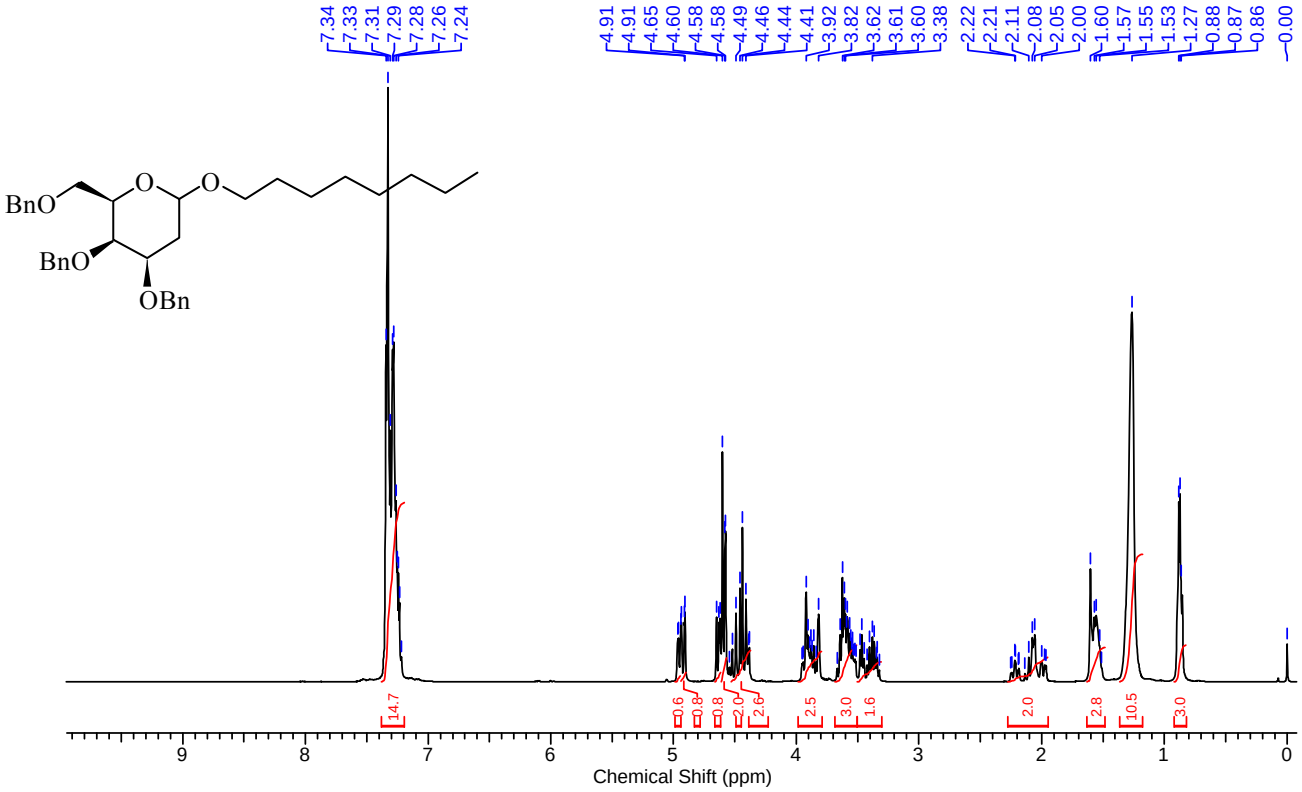
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10b



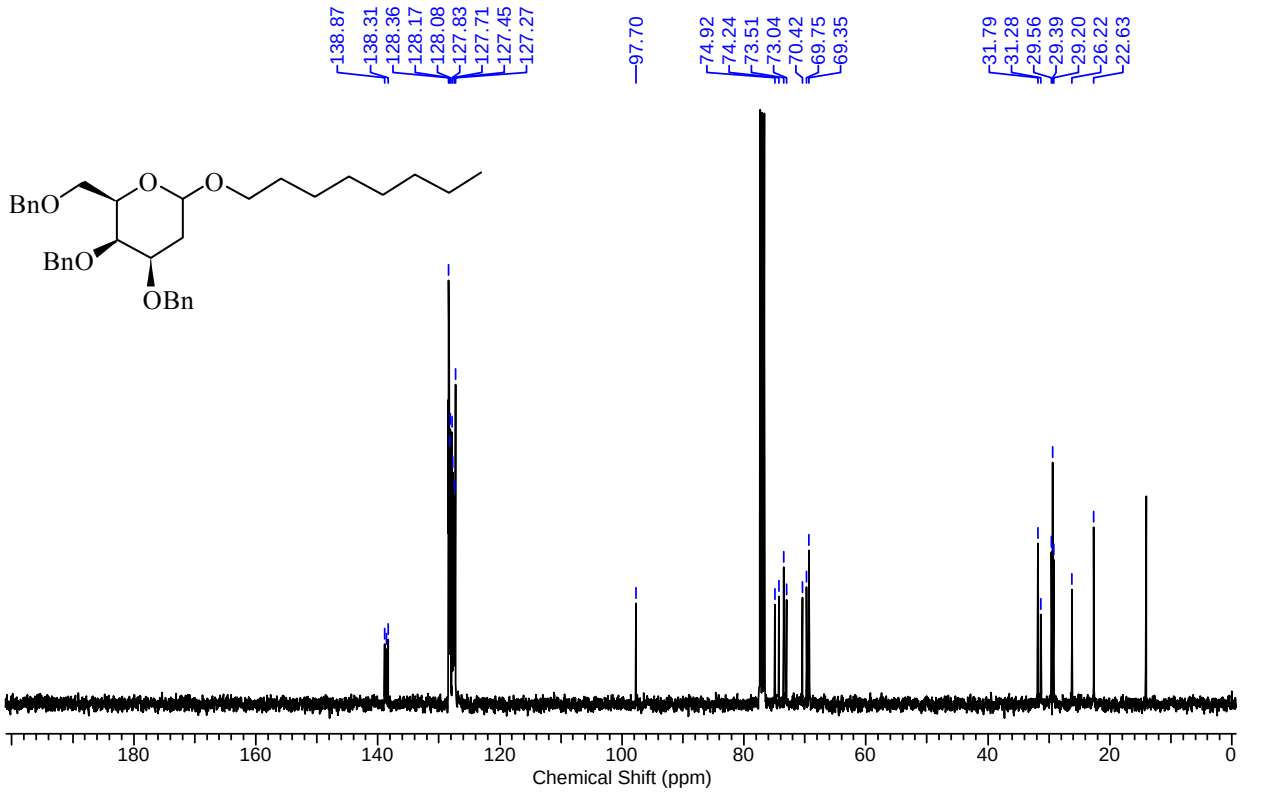
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10c



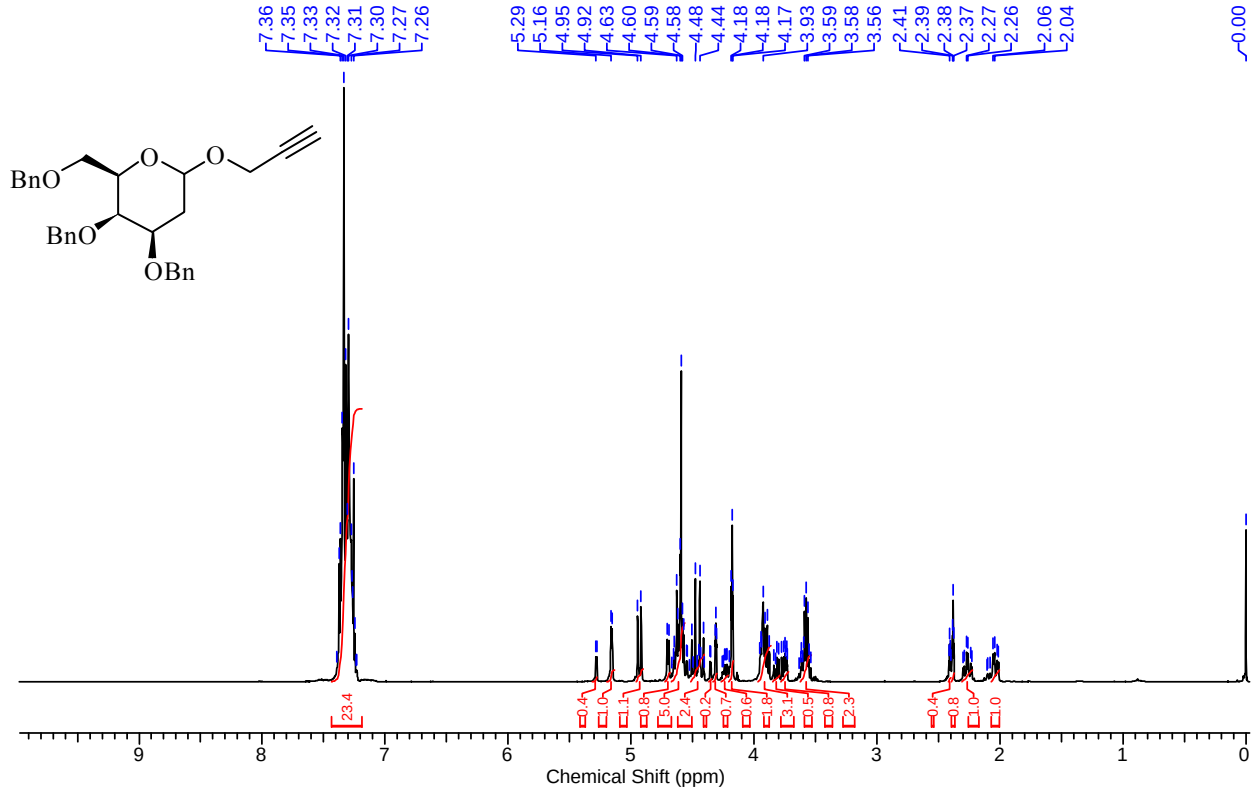
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10c



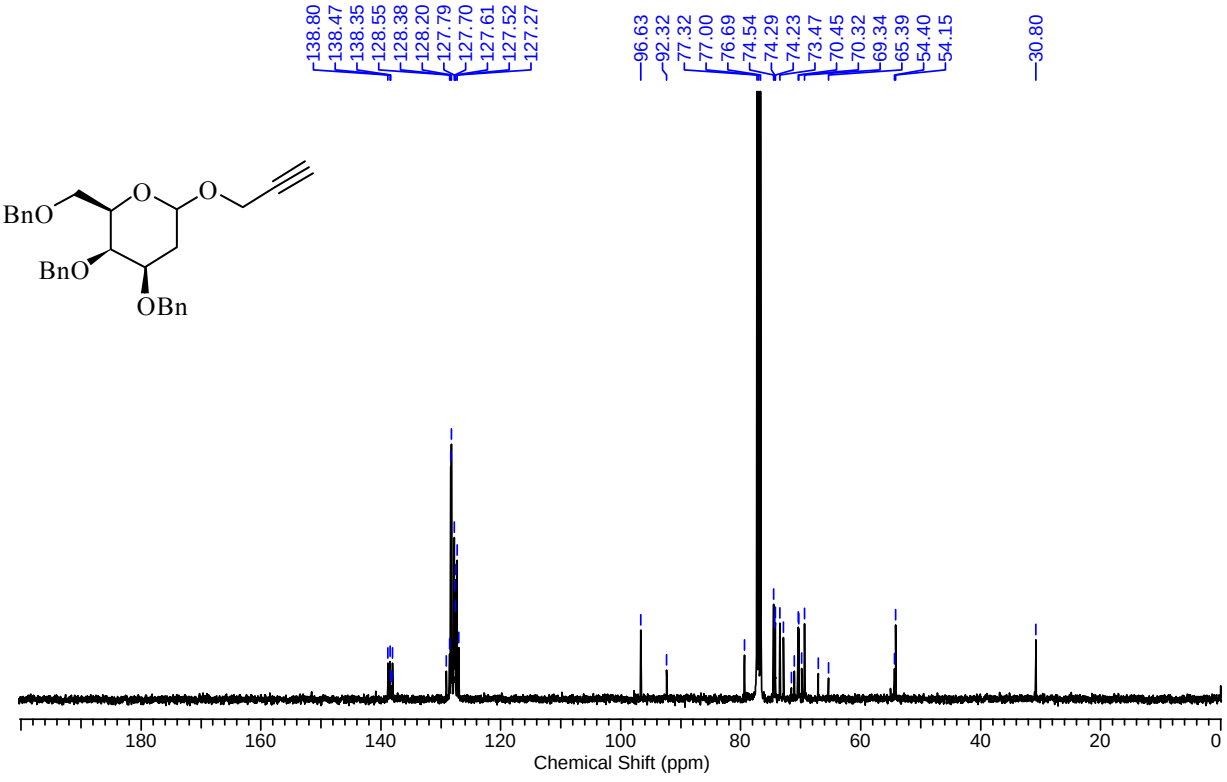
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10d



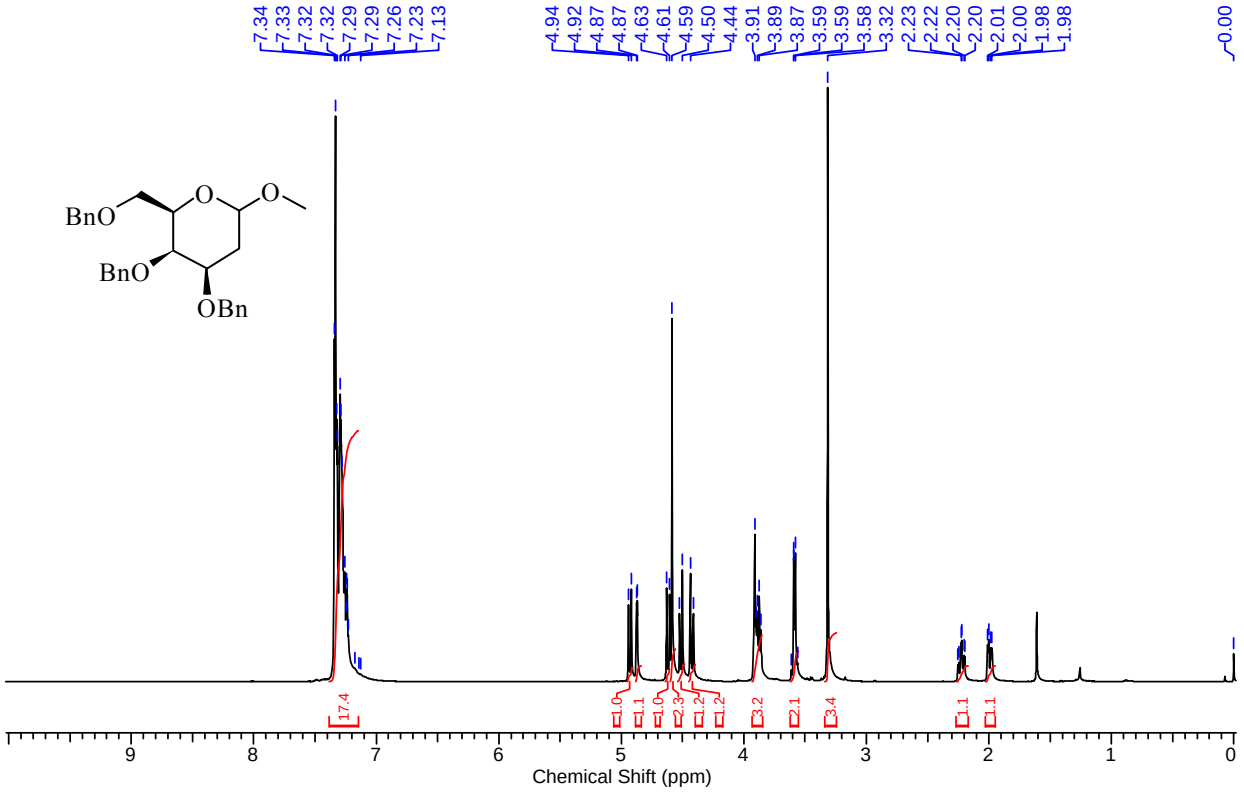
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10d



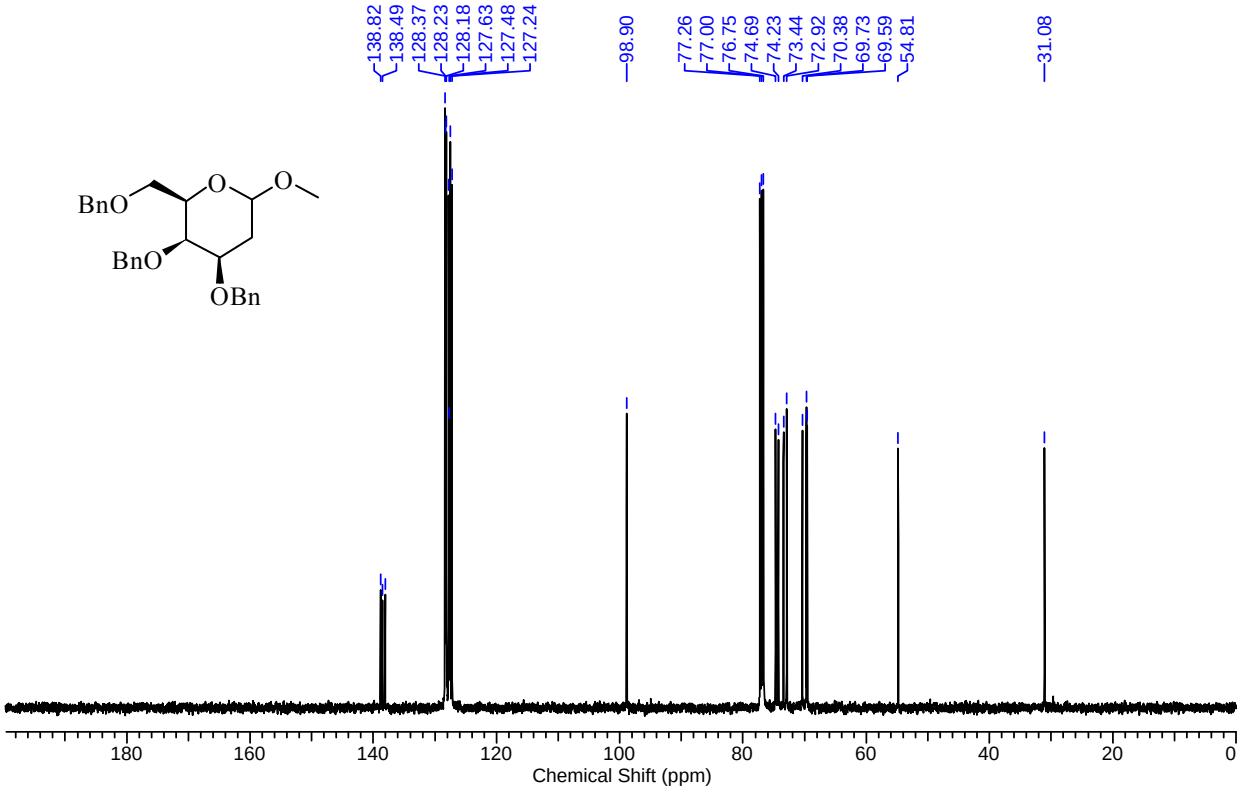
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10e



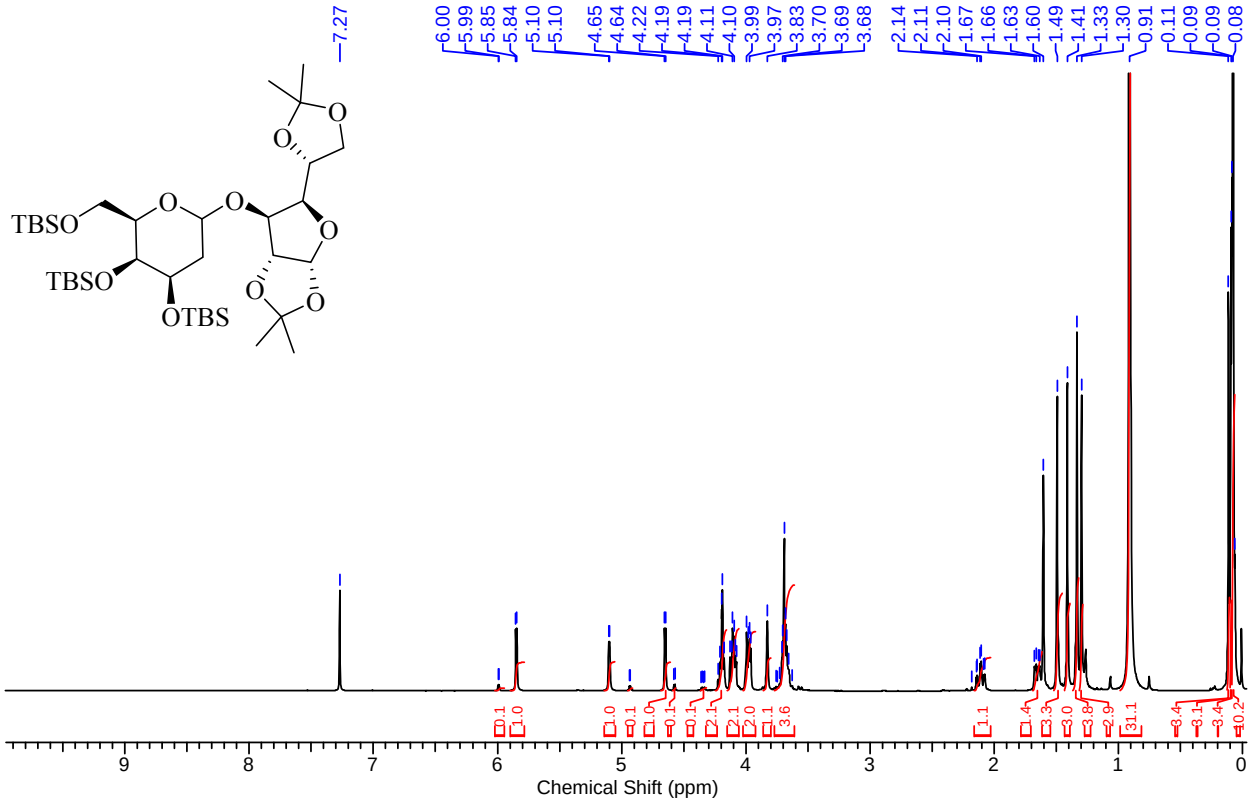
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10e



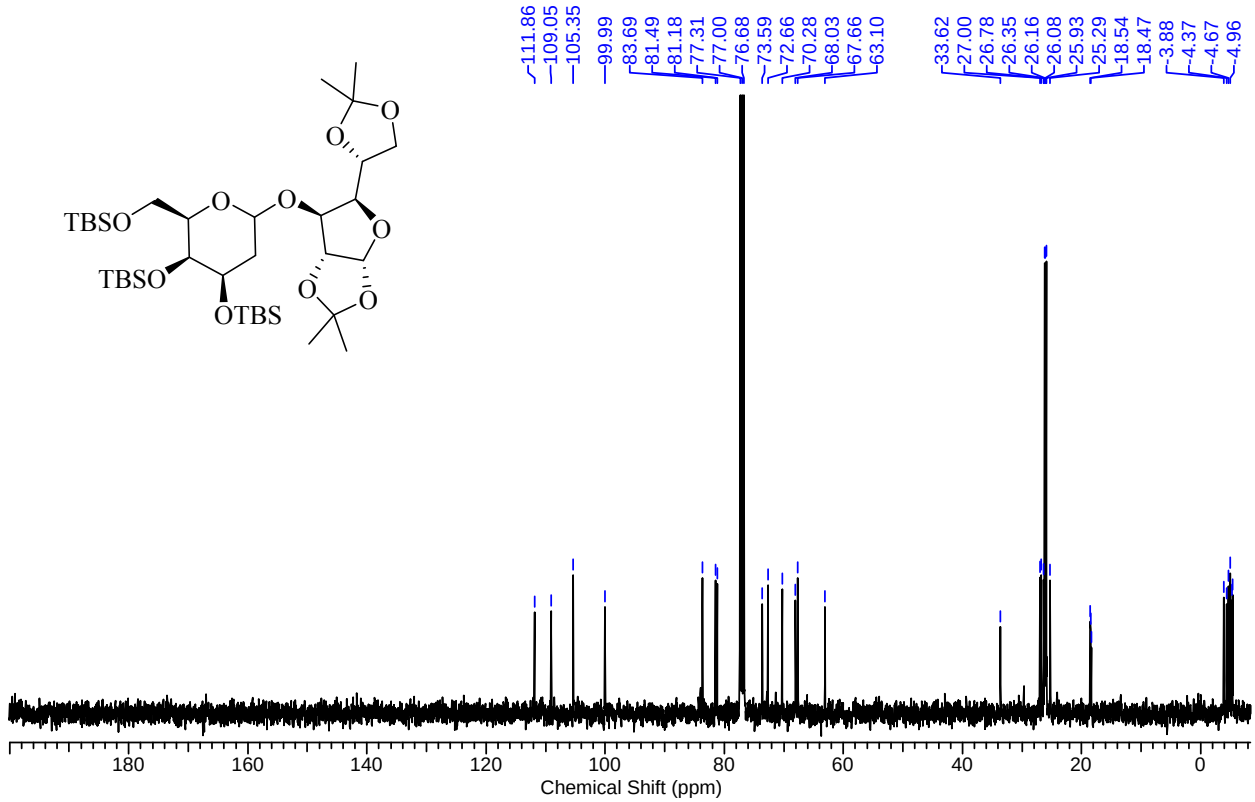
^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 10f



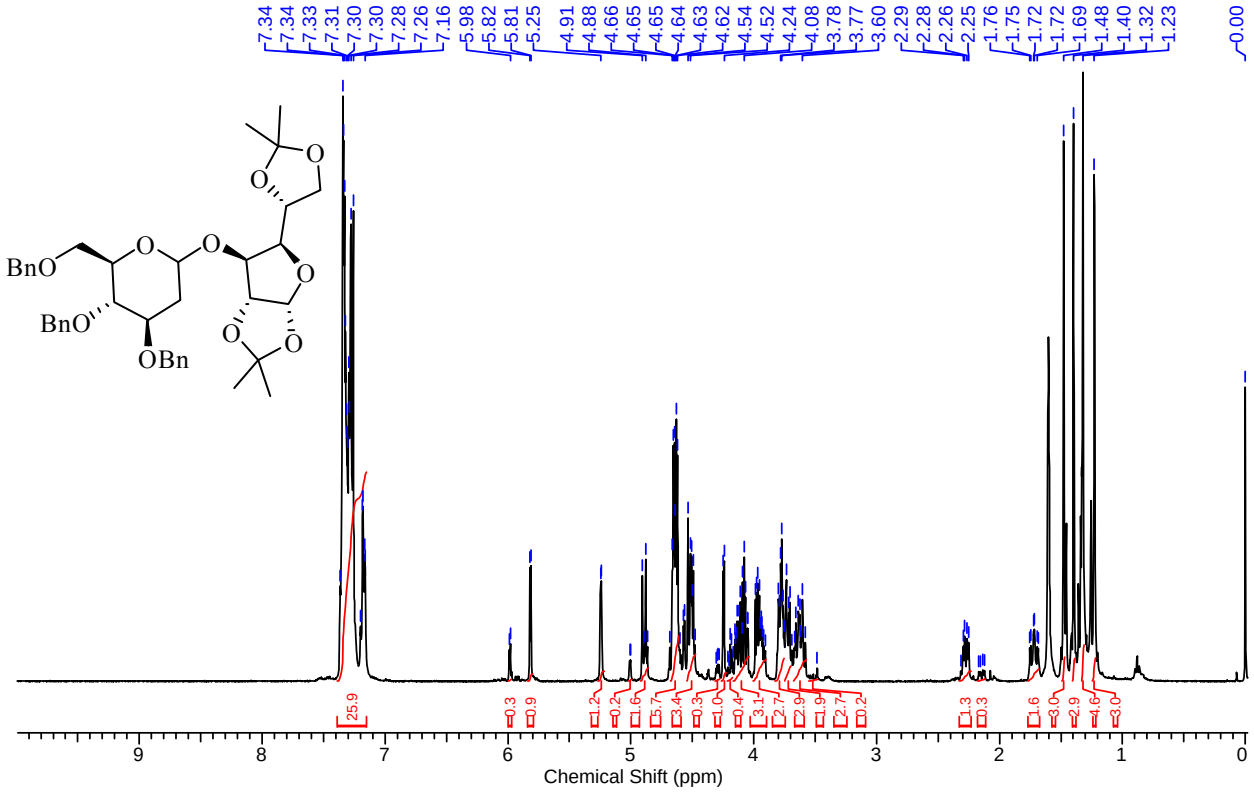
^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound 10f



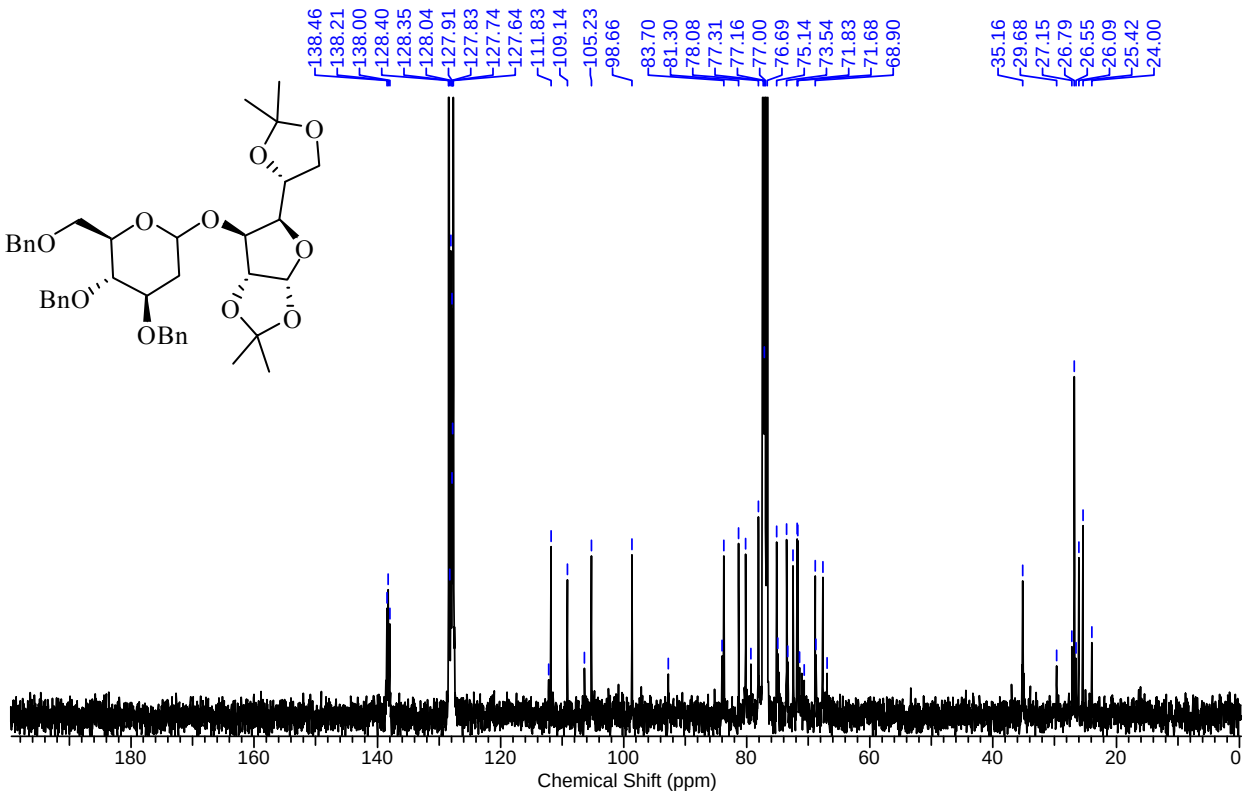
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10g



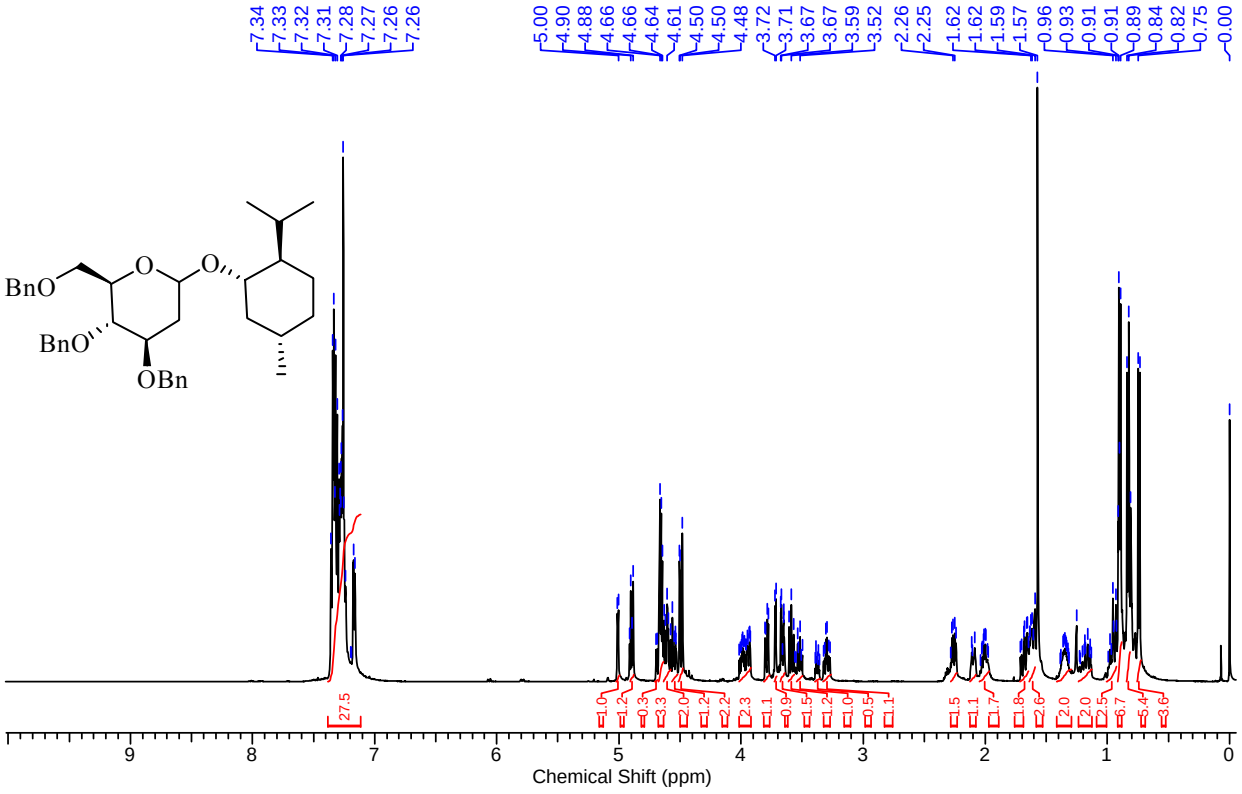
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10g



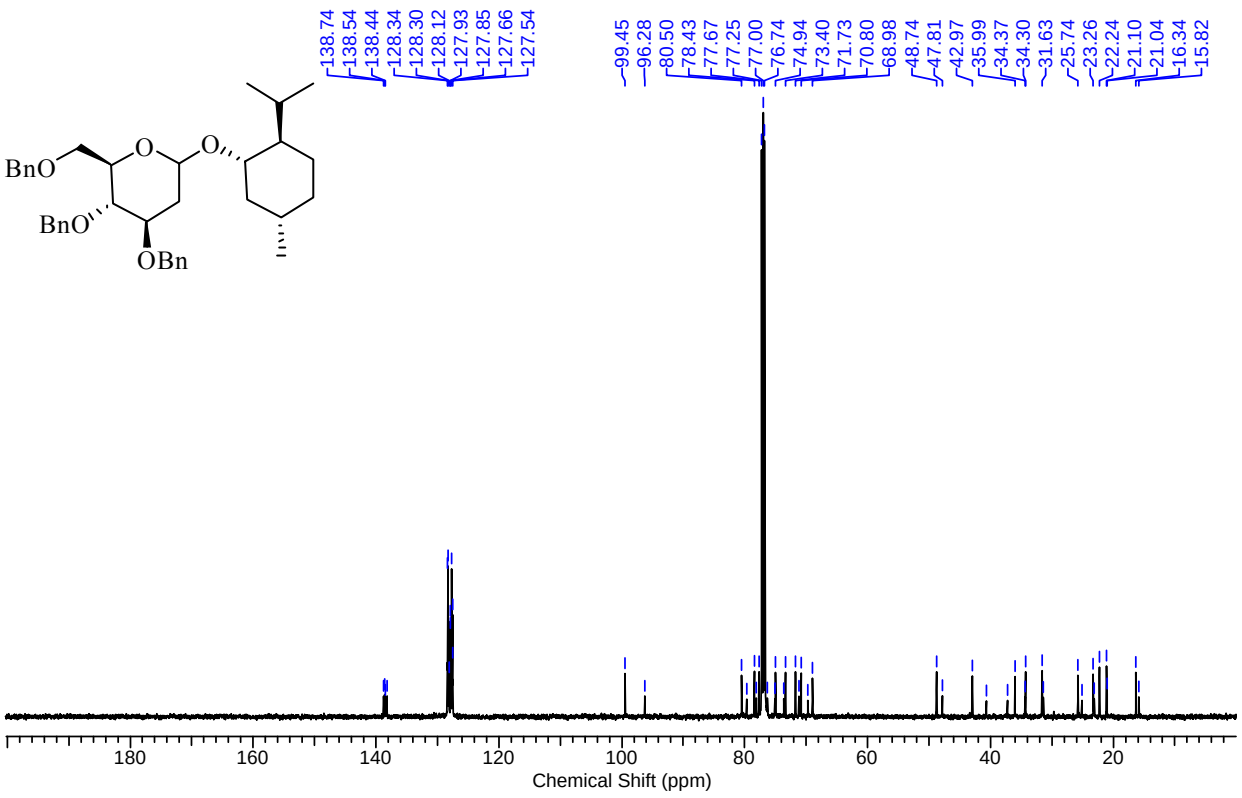
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10h



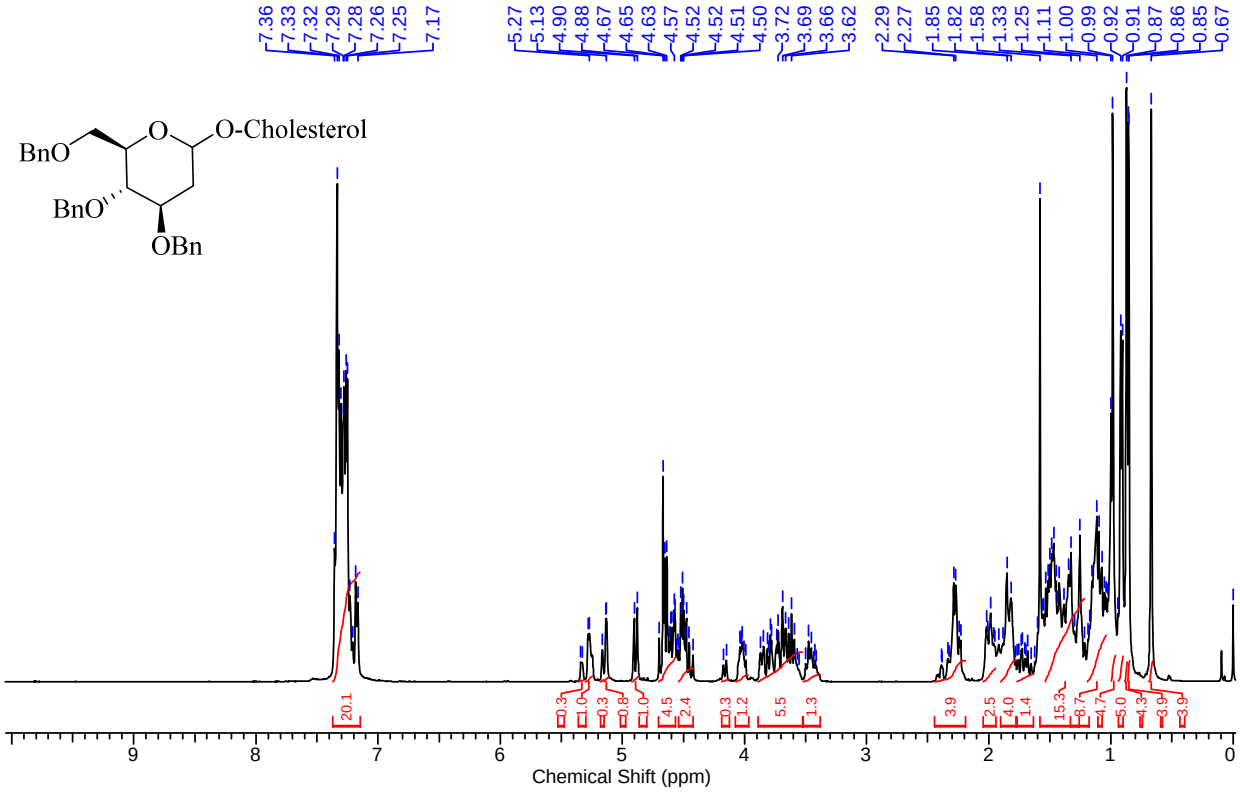
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10h



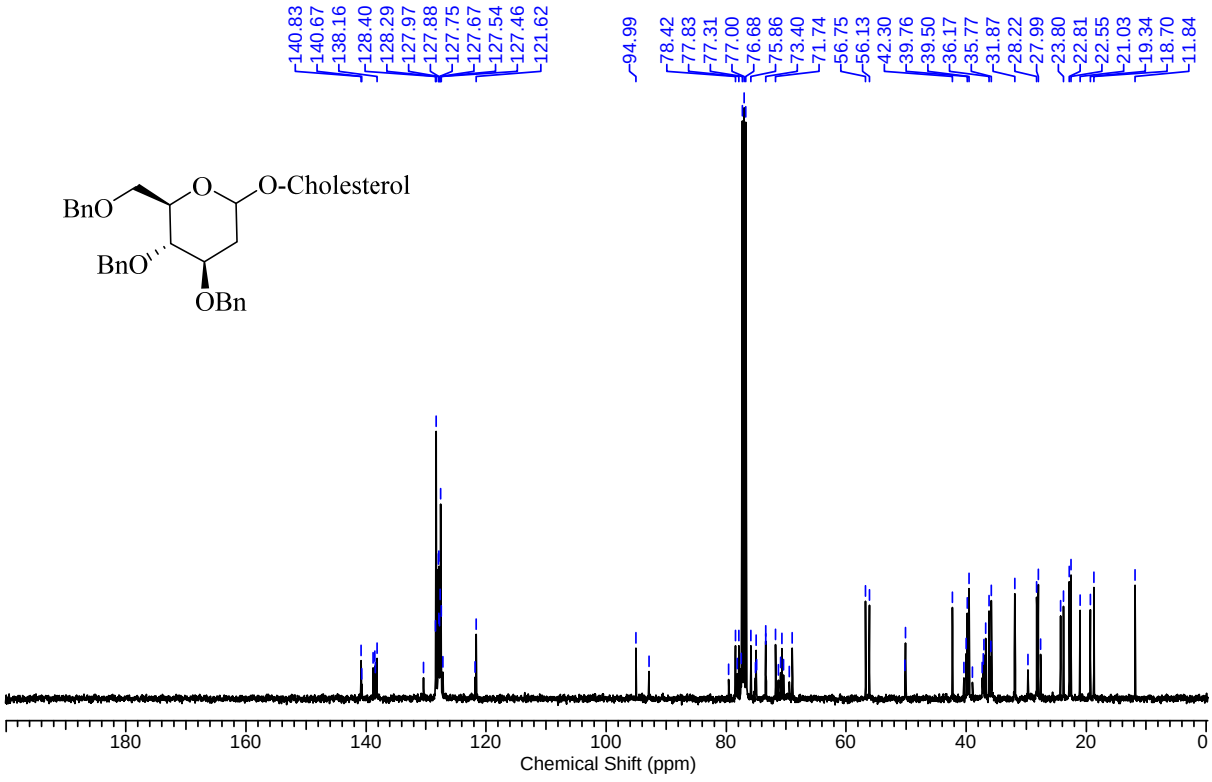
^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 10i



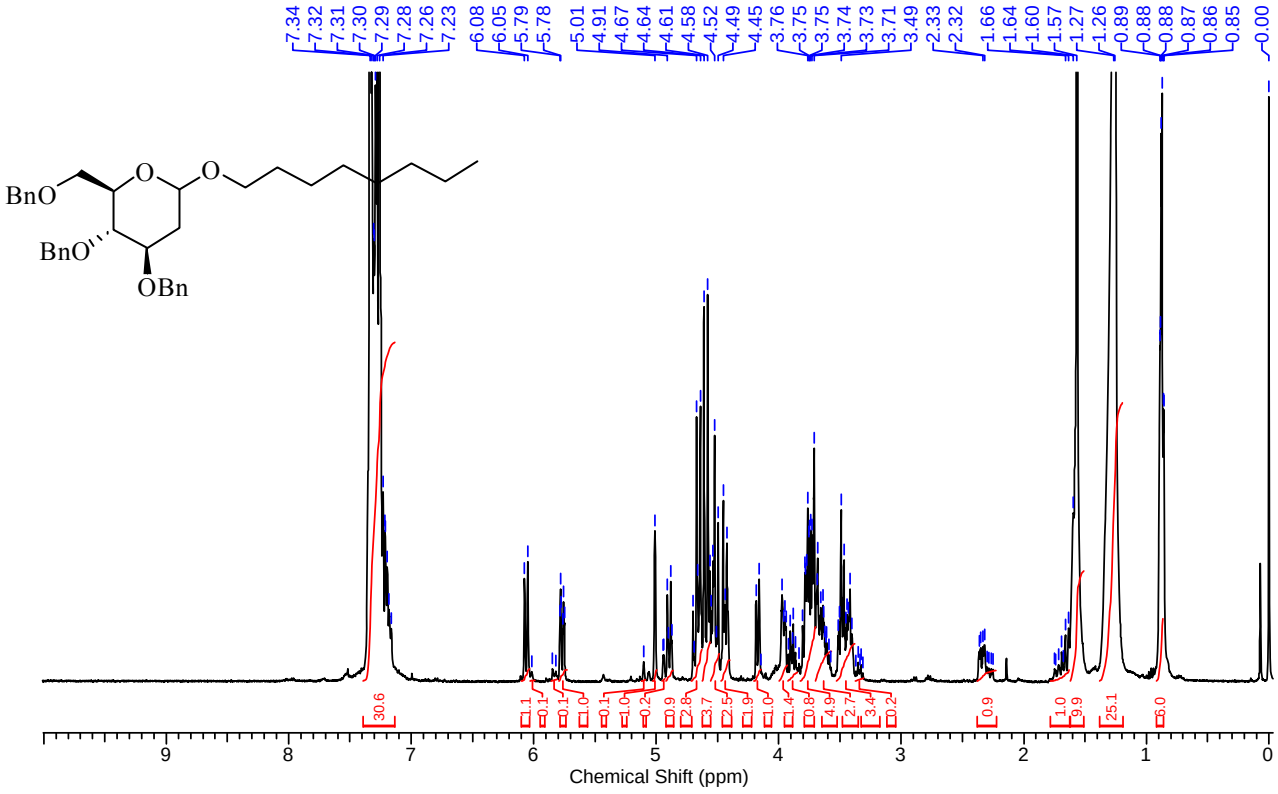
^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound 10i



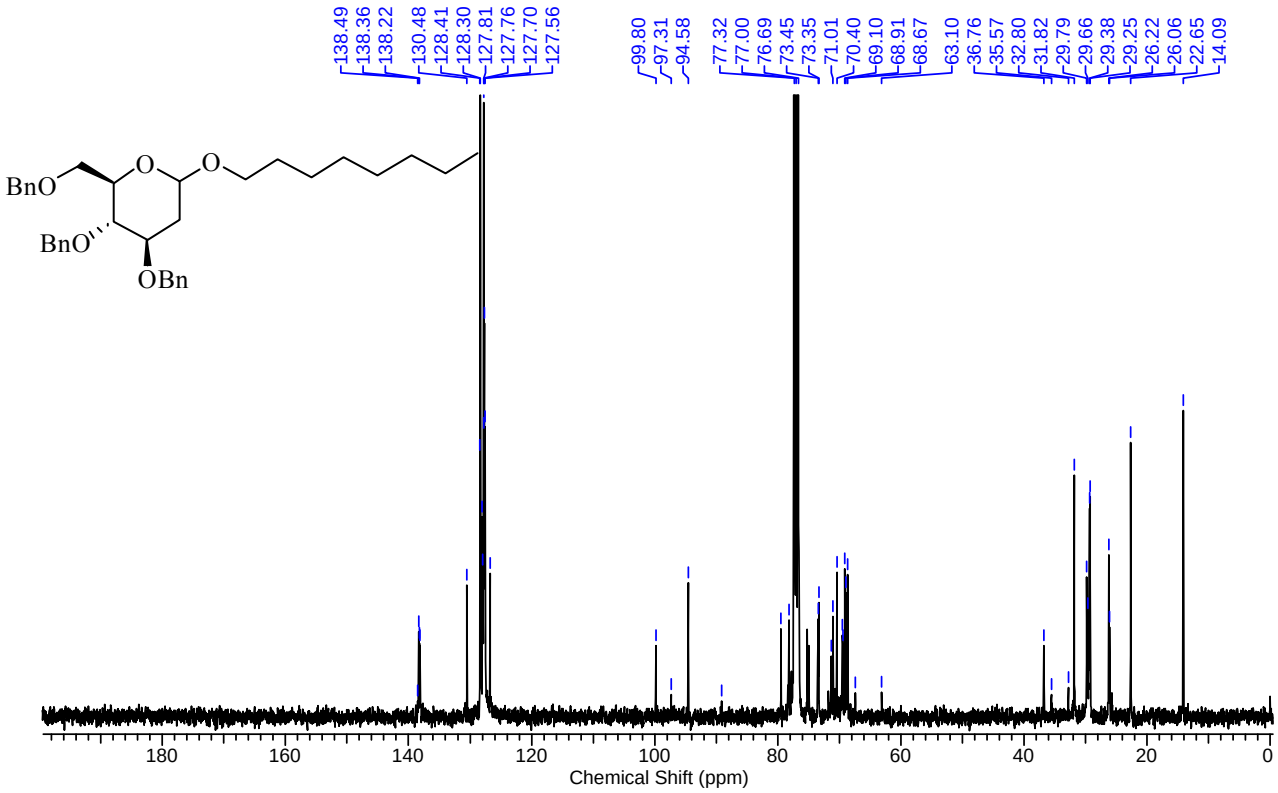
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10j



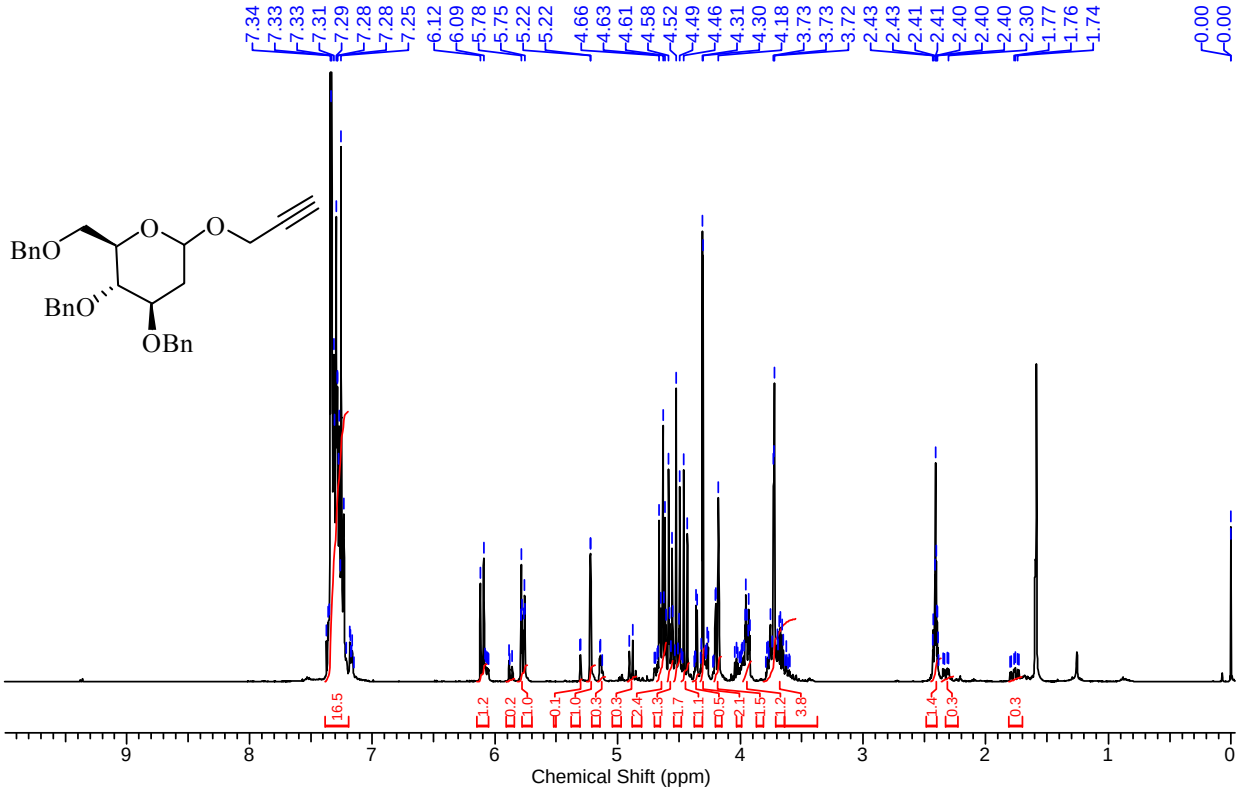
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10j



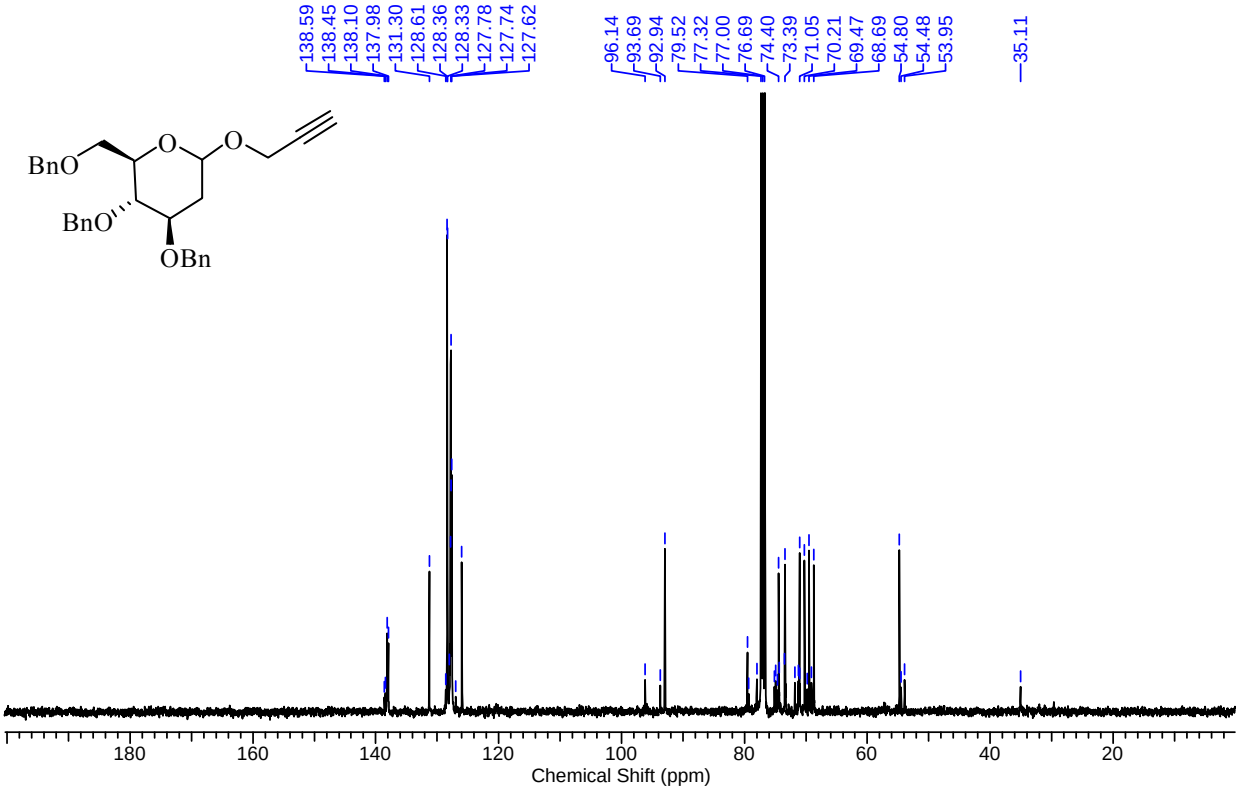
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10k



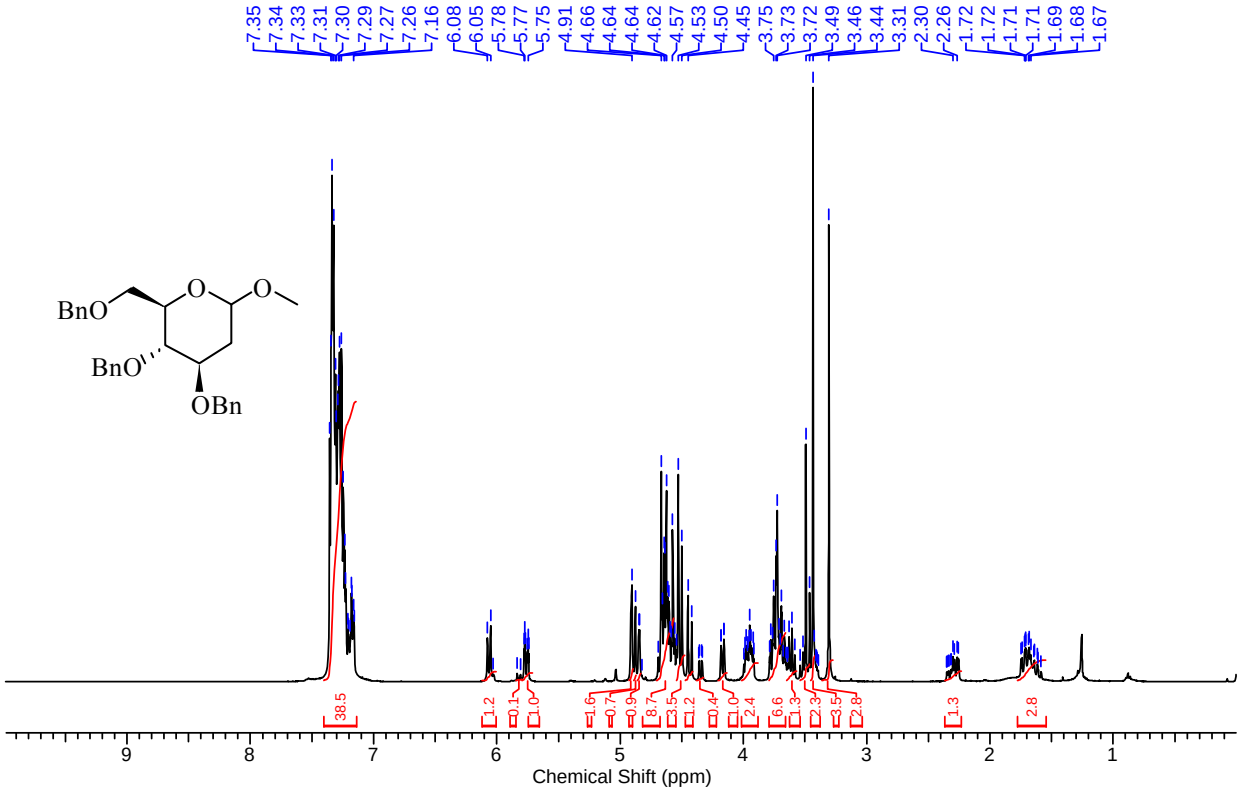
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10k



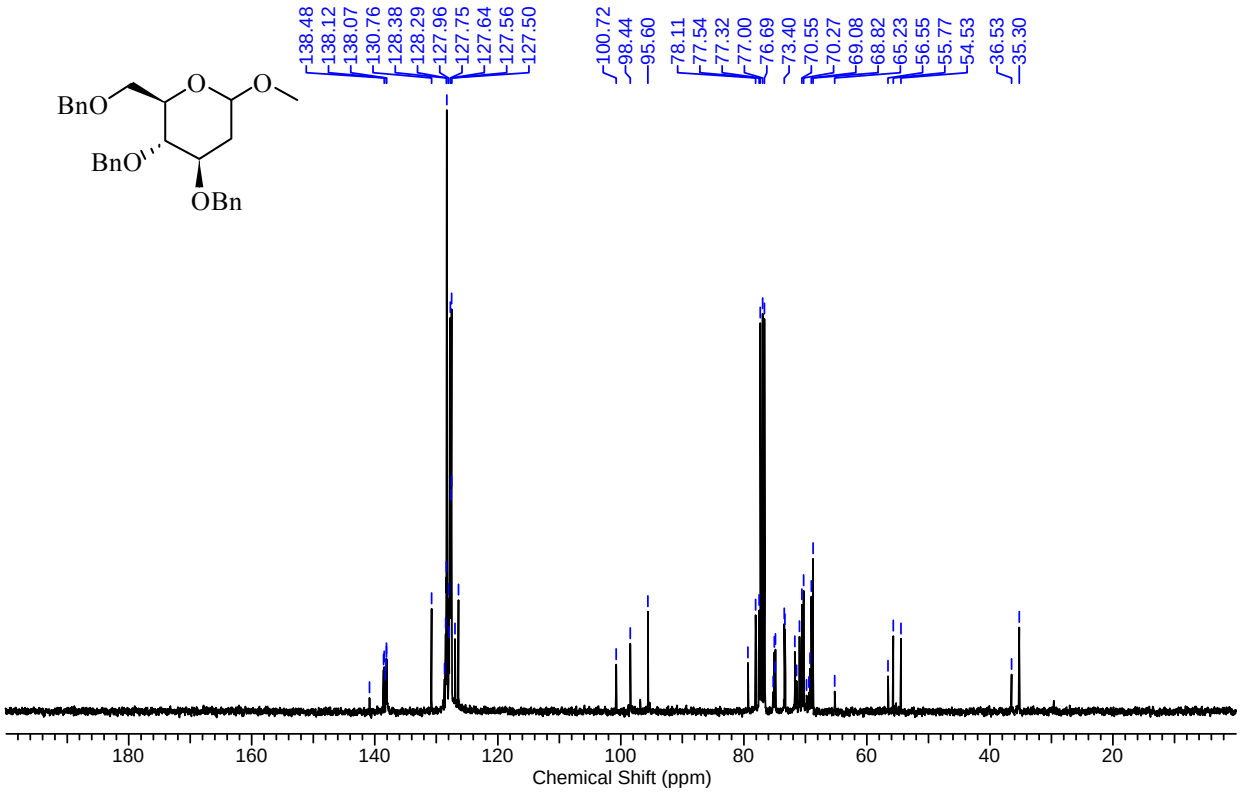
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10l



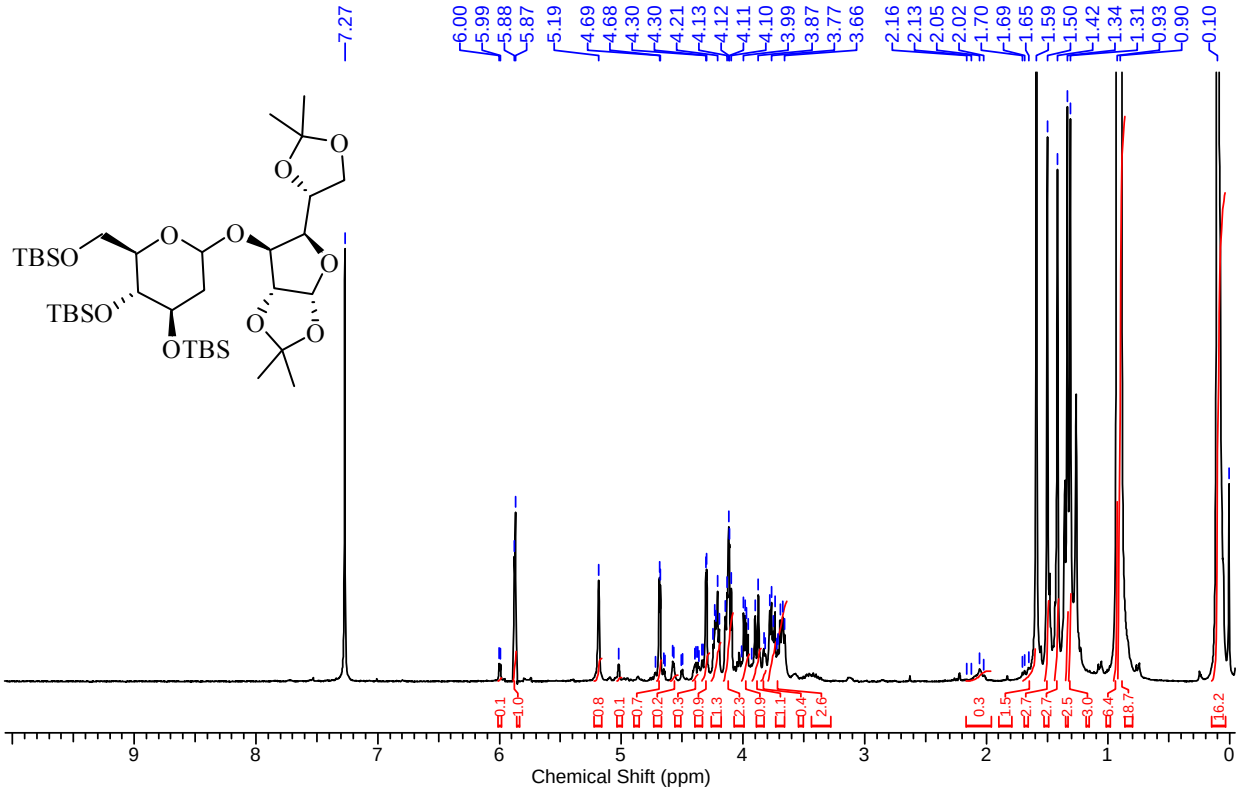
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10l



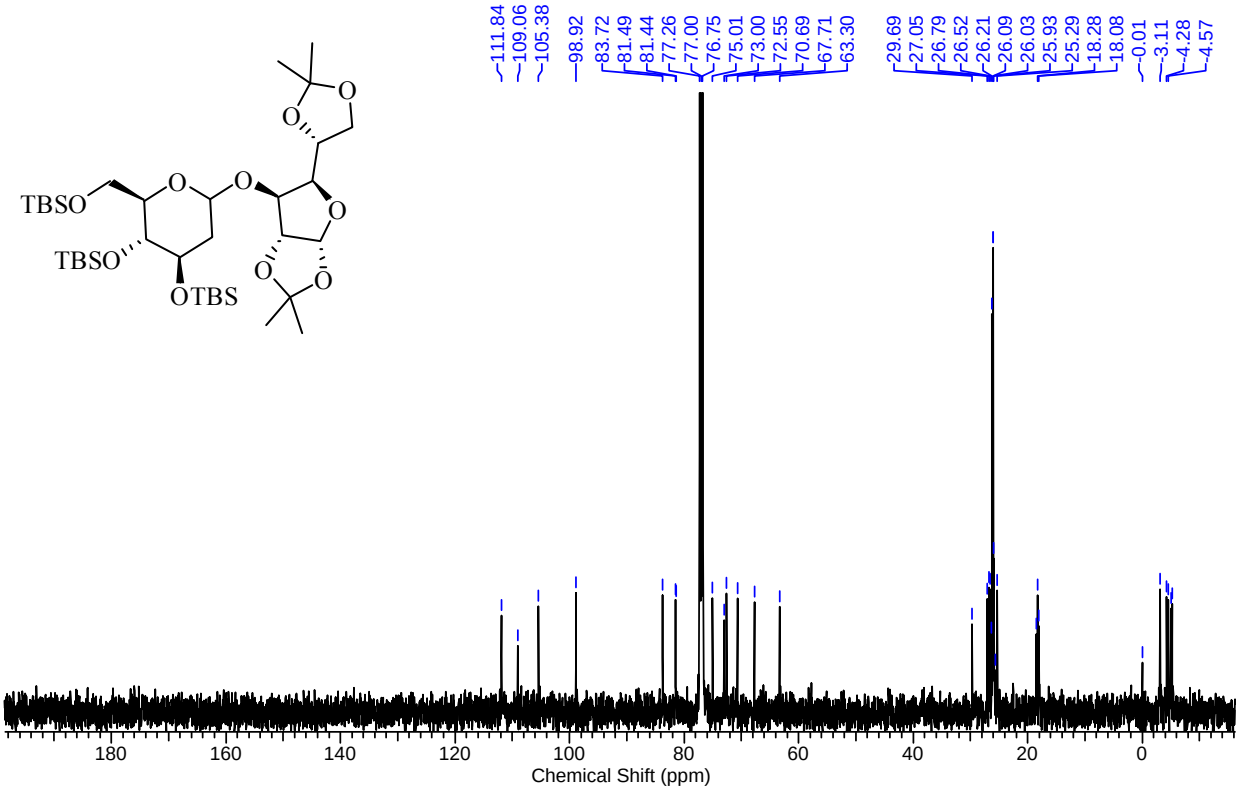
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 10m



^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 10m



^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 10n



^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound 10n