

N-Halosuccinimide/AgNO₃–Efficient Reagent Systems for One Step Synthesis of 2-Haloglycals from Glycals: Application in the Synthesis of 2C-Branched Sugars via Heck Coupling Reactions

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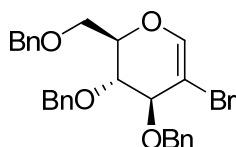
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General Experimental Methods. IR spectra were recorded with FT-IR as a thin film or using KBr pellets and are expressed in cm^{-1} . ^1H (500 MHz or 400 MHz) and ^{13}C (125 MHz or 100 MHz) NMR spectra were recorded using CDCl_3 as a solvent. Chemical shifts are reported in ppm downfield to tetramethylsilane. Coupling constants are reported and expressed in Hz; splitting patterns are designated as br (broad), s (singlet), d (doublet), dd (double doublet), m (multiplet), td (triplet of doublet), dt (doublet of triplet). Optical rotations were measured using a polarimeter (AUTOPOL II) at 28 °C. All reactions were carried out using freshly distilled and dry solvents. The visualization of spots on TLC plates was effected by exposure to iodine or spraying with 10% H_2SO_4 and charring. Column chromatography was performed over silica gel (100–200 Mesh) using hexane and ethyl acetate as eluents. Mass spectra were obtained from high resolution ESI mass spectrometer using Q–TOF analyser.

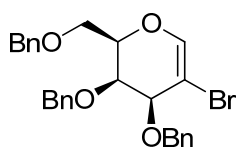
(2*R*,3*R*,4*S*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-5-bromo-3,4-dihydro-2*H*-pyran (2*b*)



To a stirred solution of **1** (100 mg, 0.24 mmol) in dry CH_3CN (2 mL) at 80 °C under N_2 atmosphere were added NBS (51 mg, 0.28 mmol) and AgNO_3 (8.1 mg, 0.048 mmol) successively and stirred for 2 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (5–10% of EtOAc/hexane) to obtain **2b** (74 mg, 63%) as a colorless oil. R_f 0.10 (hexane:ethyl acetate, 4:1); $[\alpha]_D^{28} = +8.3$ (c 0.60, CH_2Cl_2); IR (neat) ν_{max} 2968, 2880, 1690, 1615, 1381, 1194, 1069 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35–7.25 (m, 15H), 6.70 (s, 1H), 4.70 (d, $J = 11.5$ Hz, 1H), 4.67 (d,

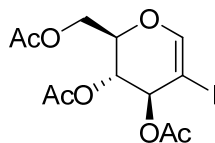
$J = 11.5$ Hz, 1H), 4.61 (d, $J = 8.5$ Hz, 1H), 4.59 (d, $J = 8.5$ Hz, 1H), 4.52 (s, 2H), 4.30 (dd, $J = 5.7, 10.0$ Hz, 1H), 4.12 (d, $J = 4.3$ Hz, 1H), 3.97 (dd, $J = 4.6, 6.0$ Hz, 1H), 3.79 (dd, $J = 6.0, 10.6$ Hz, 1H), 3.70 (dd, $J = 4.0, 10.6$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.2, 137.8–127.8 (ArC), 98.7, 76.4, 74.0, 73.5, 72.9, 72.4, 67.8; HRMS calcd for $\text{C}_{27}\text{H}_{31}\text{BrNO}_4$ $[\text{M} + \text{NH}_4]^+$ 512.1436, found 512.1439.

(2*R*,3*S*,4*S*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-5-bromo-3,4-dihydro-2*H*-pyran (4b)



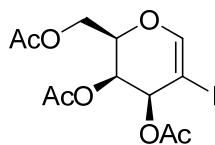
To a stirred solution of **4** (100 mg, 0.24 mmol) in dry CH_3CN (2 mL) at 80°C under N_2 atmosphere were added NBS (51 mg, 0.28 mmol) and AgNO_3 (8.1 mg, 0.048 mmol) successively and stirred for 1 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (5–10% of EtOAc/hexane) to obtain **4b** (77 mg, 65%) as a colorless oil. R_f 0.10 (hexane:ethyl acetate, 4:1); $[\alpha]_D^{28} = -2.0$ (c 0.50, CH_2Cl_2); IR (neat) ν_{max} 3063, 2921, 2867, 1637, 1453, 1363, 1181, 1095, 1027 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.37–7.25 (m, 15H), 6.57 (s, 1H), 4.81–4.79 (m, 2H), 4.76 (d, $J = 11.9$ Hz, 1H), 4.59 (d, $J = 11.6$ Hz, 1H), 4.52 (d, $J = 11.6$ Hz, 1H), 4.41 (d, $J = 11.9$ Hz, 1H), 4.35–4.32 (m, 1H), 4.12 (d, $J = 4.0$ Hz, 1H), 4.01 (t, $J = 3.9$ Hz, 1H), 3.85 (dd, $J = 7.9, 10.7$ Hz, 1H), 3.73 (dd, $J = 3.6, 10.6$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.4, 138.2–127.8 (ArC), 98.5, 75.8, 74.5, 74.1, 73.5, 73.0, 67.8; HRMS calcd for $\text{C}_{27}\text{H}_{27}\text{BrNaO}_4$ $[\text{M} + \text{Na}]^+$ 517.0990, found 517.0990.

(2*R*,3*R*,4*S*)-2-(acetoxymethyl)-5-iodo-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (5a**)**



To a stirred solution of **5** (1 g, 3.67 mmol) in dry CH₃CN (10 mL) at 80 °C under N₂ atmosphere were added NIS (991 mg, 4.4 mmol) and AgNO₃ (124 mg, 0.73 mmol) successively and stirred for 4 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (20–30% of EtOAc/hexane) to obtain **5a** (1.28 g, 88%) as a colorless oil. *R_f* 0.40 (hexane:ethyl acetate, 2:1); $[\alpha]_D^{28} = +30.0$ (*c* 1.00, CH₂Cl₂); IR (neat) ν_{\max} 2924, 2853, 1746, 1626, 1370, 1223, 1167, 1053, 1029 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.78 (s, 1H), 5.49 (d, *J* = 5.1 Hz, 1H), 5.22 (dd, *J* = 5.1, 7.0 Hz, 1H), 4.41–4.36 (m, 2H), 4.18 (dd, *J* = 5.5, 14.3 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.5, 170.3, 169.4, 149.4, 74.0, 70.6, 67.6, 66.3, 61.0, 20.9, 20.8, 20.7; HRMS calcd for C₁₂H₁₅INaO₇ [*M* + Na]⁺ 420.9760, found 420.9763.

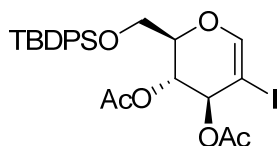
(2*R*,3*S*,4*S*)-2-(acetoxymethyl)-5-iodo-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (6a**)**



To a stirred solution of **6** (1 g, 3.67 mmol) in dry CH₃CN (2 mL) at 80 °C under N₂ atmosphere were added NIS (991 mg, 4.4 mmol) and AgNO₃ (124 mg, 0.73 mmol) successively and stirred for 3 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered

through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (20–30% of EtOAc/hexane) to obtain **6a** (1.2 g, 82%) as a white powder. mp 106–108 °C; R_f 0.40 (hexane:ethyl acetate, 2:1); $[\alpha]_D^{28} = +36.2$ (c 1.60, CH₂Cl₂); IR (neat) ν_{\max} 2965, 2928, 1744, 1660, 1627, 1433, 1409, 1267, 1226, 1134 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.76 (s, 1H), 5.57 (d, J = 4.6 Hz, 1H), 5.48 (dd, J = 2.1, 4.6 Hz, 1H), 4.41 (t, J = 5.8 Hz, 1H), 4.24 (dd, J = 7.6, 11.6 Hz, 1H), 4.17 (dd, J = 5.5, 11.6 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.9, 169.9, 149.3, 73.2, 67.2, 67.0, 64.5, 61.5, 20.8, 20.7, 20.6; HRMS calcd for C₁₂H₁₅INaO₇ [M + Na]⁺ 420.9760, found 420.9760.

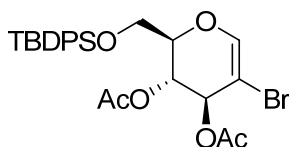
(2*R*,3*R*,4*S*)-2-((tert-butyldiphenylsilyloxy)methyl)-5-iodo-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (7a**)**



To a stirred solution of **7** (100 mg, 0.21 mmol) in dry CH₃CN (2 mL) at 80 °C under N₂ atmosphere were added NIS (57.6 mg, 0.25 mmol) and AgNO₃ (7.2 mg, 0.042 mmol) successively and stirred for 2 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (15–20% of EtOAc/hexane) to obtain **7a** (96 mg, 76%) as a colorless oil. R_f 0.40 (hexane:ethyl acetate, 2:1); $[\alpha]_D^{28} = +50.0$ (c 0.40, CH₂Cl₂); IR (neat) ν_{\max} 2930, 2857, 1758, 1626, 1427, 1370, 1232, 1170, 1113, 1053, 1029 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.65–7.62 (m, 4H), 7.43–7.36 (m, 6H),

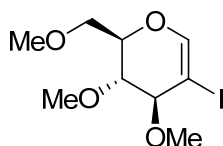
6.72 (s, 1H), 5.52–5.40 (m, 2H), 4.25 (t, $J = 5.7$ Hz, 1H), 3.84 (dd, $J = 4.6, 11.4$ Hz, 1H), 3.79 (dd, $J = 5.1, 11.4$ Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.1, 169.2, 149.9, 135.6, 133.0, 129.9, 127.8, 127.8, 76.4, 70.9, 67.9, 65.5, 61.2, 26.7, 20.9, 20.8, 19.2; HRMS calcd for $\text{C}_{26}\text{H}_{35}\text{INO}_6\text{Si}$ $[\text{M} + \text{NH}_4]^+$ 612.1278, found 612.1279.

(2*R*,3*R*,4*S*)-5-bromo-2-((*tert*-butyldiphenylsilyloxy)methyl)-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (7b**)**



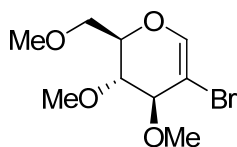
To a stirred solution of **7** (100 mg, 0.21 mmol) in dry CH_3CN (2 mL) at 80 °C under N_2 atmosphere were added NBS (45.5 mg, 0.25 mmol) and AgNO_3 (7.2 mg, 0.042 mmol) successively and stirred for 5 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (15–20% of EtOAc/hexane) to obtain **7b** (79 mg, 68%) as a colorless oil. R_f 0.40 (hexane:ethyl acetate, 2:1); $[\alpha]_D^{28} = +30.6$ (c 0.75, CH_2Cl_2); IR (neat) ν_{max} 2930, 2857, 1760, 1747, 1642, 1427, 1369, 1232, 1176, 1113, 1053, 1033 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.65–7.62 (m, 4H), 7.43–7.36 (m, 6H), 6.67 (s, 1H), 5.45 (d, $J = 4.2$ Hz, 1H), 5.41 (dd, $J = 4.2, 5.5$ Hz, 1H), 4.26–4.23 (m, 1H), 3.86–3.78 (m, 2H), 2.04 (s, 3H), 2.02 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.1, 169.3, 145.6, 135.7, 135.6, 133.0, 132.9, 130.0, 129.9, 127.8, 95.0, 76.3, 69.2, 68.0, 61.0, 26.7, 20.9, 20.8, 19.2; HRMS calcd for $\text{C}_{26}\text{H}_{35}\text{BrNO}_6\text{Si}$ $[\text{M} + \text{NH}_4]^+$ 564.1417, found 564.1412.

(2*R*,3*R*,4*S*)-5-iodo-3,4-dimethoxy-2-(methoxymethyl)-3,4-dihydro-2*H*-pyran (8a**)**



To a stirred solution of **8** (100 mg, 0.53 mmol) in dry CH₃CN (2 mL) at 80 °C under N₂ atmosphere were added NIS (143.0 mg, 0.63 mmol) and AgNO₃ (18.0 mg, 0.10 mmol) successively and stirred for 15 min. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (10–20% of EtOAc/hexane) to obtain **8a** (105 mg, 63%) as a colorless oil. *R_f* 0.30 (hexane:ethyl acetate, 2:1); $[\alpha]_D^{28} = +74.5$ (*c* 0.55, CH₂Cl₂); IR (neat) ν_{\max} 2928, 2828, 1626, 1455, 1164, 1104, 1054 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.67 (s, 1H), 4.18–4.15 (m, 1H), 3.77 (d, *J* = 4.9 Hz, 1H), 3.66 (dd, *J* = 6.1, 11.0 Hz, 1H), 3.63–3.62 (m, 1H), 3.57 (dd, *J* = 2.9, 10.3 Hz, 1H), 3.56 (s, 3H), 3.49 (s, 3H), 3.38 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.3, 80.6, 76.2, 75.5, 70.5, 70.2, 59.2, 58.9, 57.4; HRMS calcd for C₉H₁₉INO₄ [M + NH₄]⁺ 332.0359, found 332.0357.

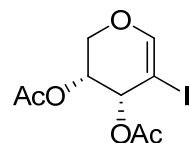
(2*R*,3*R*,4*S*)-5-bromo-3,4-dimethoxy-2-(methoxymethyl)-3,4-dihydro-2*H*-pyran (8b**)**



To a stirred solution of **8** (100 mg, 0.53 mmol) in dry CH₃CN (2 mL) at 80 °C under N₂ atmosphere were added NBS (113.0 mg, 0.63 mmol) and AgNO₃ (18.0 mg, 0.10 mmol) successively and stirred for 0.5 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (10–20% of

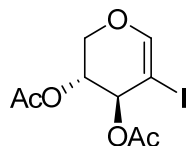
EtOAc/hexane) to obtain **8b** (82 mg, 58%) as a colorless oil. R_f 0.30 (hexane:ethyl acetate, 2:1); $[\alpha]_D^{28} = +71.1$ (c 0.45, CH_2Cl_2); IR (neat) ν_{max} 2928, 2831, 1651, 1455, 1173, 1381, 1173, 1110, 1054 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.64 (s, 1H), 4.20–4.16 (m, 1H), 3.83 (d, $J = 4.9$ Hz, 1H), 3.67–3.62 (m, 2H), 3.58–3.53 (m, 1H), 3.51 (s, 6H), 3.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.1, 98.6, 78.9, 76.8, 76.0, 70.1, 59.2, 58.7, 57.5; HRMS calcd for $\text{C}_9\text{H}_{16}\text{BrO}_4$ $[\text{M}+\text{H}]^+$ 267.0232, found 267.0232.

(3*R*,4*R*)-5-iodo-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (9a)



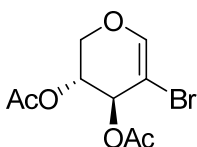
To a stirred solution of **9** (100 mg, 0.49 mmol) in dry CH_3CN (2 mL) at 80 °C under N_2 atmosphere were added NIS (134.8 mg, 0.59 mmol) and AgNO_3 (16.8 mg, 0.10 mmol) successively and stirred for 1 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (10–15% of EtOAc/hexane) to obtain **9a** (139 mg, 86%) as a colorless oil. R_f 0.40 (hexane:ethyl acetate, 3:1); $[\alpha]_D^{28} = +169.2$ (c 0.65, CH_2Cl_2); IR (neat) ν_{max} 2992, 2889, 1742, 1624, 1458, 1429, 1371, 1245, 1219, 1085, 1052, 1027 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.78 (d, $J = 2.3$ Hz, 1H), 5.61 (s, 1H), 5.30 (dd, $J = 4.0, 9.7$ Hz, 1H), 4.08 (d, $J = 10.8$ Hz, 1H), 3.98 (td, $J = 2.9, 10.3$ Hz, 1H), 2.13 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.2, 169.5, 151.0, 68.6, 66.0, 63.3, 62.6, 20.8, 20.6; HRMS calcd for $\text{C}_9\text{H}_{15}\text{INO}_5$ $[\text{M} + \text{NH}_4]^+$ 343.9995, found 343.9997.

(3*R*,4*S*)-5-iodo-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (10a)



To a stirred solution of **10** (100 mg, 0.49 mmol) in dry CH₃CN (2 mL) at 80 °C under N₂ atmosphere were added NIS (134.8 mg, 0.59 mmol) and AgNO₃ (16.8 mg, 0.10 mmol) successively and stirred for 1 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (10–15% of EtOAc/hexane) to obtain **10a** (136 mg, 84%) as a colorless oil. *R_f* 0.40 (hexane:ethyl acetate, 3:1); $[\alpha]_D^{28} = -150.0$ (*c* 0.55, CH₂Cl₂); IR (neat) ν_{\max} 2923, 2852, 1742, 1623, 1458, 1449, 1367, 1215, 1176, 1081, 1023 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.91 (s, 1H), 5.24 (s, 1H), 4.95 (d, *J* = 1.7 Hz, 1H), 4.28 (dt, *J* = 2.9, 11.4 Hz, 1H), 3.95 (d, *J* = 12.0 Hz, 1H), 2.12 (s, 3H), 2.10 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.7, 169.5, 151.4, 69.1, 68.2, 63.7, 63.0 20.9; HRMS calcd for C₉H₁₅INO₅ [M + NH₄]⁺ 343.9995, found 343.9998.

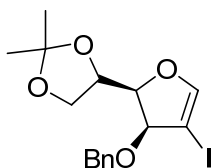
(3R,4S)-5-bromo-3,4-dihydro-2H-pyran-3,4-diyl diacetate (10b)



To a stirred solution of **10** (100 mg, 0.49 mmol) in dry CH₃CN (2 mL) at 80 °C under N₂ atmosphere were added NBS (106.6 mg, 0.59 mmol) and AgNO₃ (16.8 mg, 0.10 mmol) successively and stirred for 3 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (10–15% of

EtOAc/hexane) to obtain **10b** (102 mg, 73%) as a colorless oil. R_f 0.40 (hexane:ethyl acetate, 3:1); $[\alpha]_D^{28} = -196.0$ (c 0.35, CH_2Cl_2); IR (neat) ν_{max} 2924, 1741, 1638, 1368, 1215, 1180, 1081, 1023 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.81 (s, 1H), 5.24 (s, 1H), 4.90 (br s, 1H), 4.20 (d, $J = 12.0$ Hz, 1H), 3.84 (d, $J = 10.5$ Hz, 1H), 2.07 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.7, 169.4, 147.3, 94.6, 68.1, 67.5, 63.3, 20.9; HRMS calcd for $\text{C}_9\text{H}_{11}\text{BrNaO}_5$ $[\text{M} + \text{Na}]^+$ 300.9688, found 300.9689.

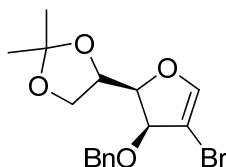
(S)-4-((2R,3S)-3-(benzyloxy)-4-iodo-2,3-dihydrofuran-2-yl)-2,2-dimethyl-1,3-dioxolane (11a)



To a stirred solution of **11** (50 mg, 0.18 mmol) in dry CH_3CN (2 mL) at 80 $^\circ\text{C}$ under N_2 atmosphere were added NIS (48.8 mg, 0.21 mmol) and AgNO_3 (6.1 mg, 0.036 mmol) successively and stirred for 10 min. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (1–5% of EtOAc/hexane) to obtain **11a** (41 mg, 57%) as a colorless oil. R_f 0.50 (hexane:ethyl acetate, 4:1); $[\alpha]_D^{28} = -26.6$ (c 0.30, CH_2Cl_2); IR (neat) ν_{max} 2925, 2854, 1638, 1604, 1455, 1370, 1118, 1065 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.39–7.29 (m, 5H), 6.57 (s, 1H), 4.76 (d, $J = 11.0$ Hz, 1H), 4.73 (d, $J = 11.0$ Hz, 1H), 4.56 (d, $J = 7.3$ Hz, 1H), 4.48–4.40 (m, 2H), 4.08 (dd, $J = 6.7, 8.5$ Hz, 1H), 3.96 (dd, $J = 5.5, 8.5$ Hz, 1H), 1.44 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ

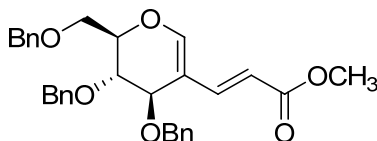
153.2, 137.8, 128.4, 128.3, 128.0, 109.2, 84.6, 83.9, 74.1, 72.5, 66.2, 61.7, 26.7, 25.3; HRMS calcd for $C_{16}H_{23}INO_4$ $[M + NH_4]^+$ 420.0672, found 420.0674.

(S)-4-((2R,3S)-3-(benzyloxy)-4-bromo-2,3-dihydrofuran-2-yl)-2,2-dimethyl-1,3-dioxolane (11b)



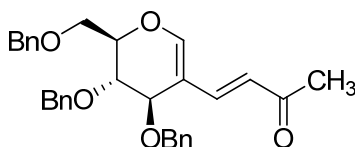
To a stirred solution of **11** (50 mg, 0.18 mmol) in dry CH_3CN (2 mL) at 80 °C under N_2 atmosphere were added NBS (38.6 mg, 0.21 mmol) and $AgNO_3$ (6.1 mg, 0.036 mmol) successively and stirred for 30 min. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (1–5% of EtOAc/hexane) to obtain **11b** (23 mg, 35%) as a colorless oil. R_f 0.20 (hexane:ethyl acetate, 4:1); IR (neat) ν_{max} 2924, 2853, 1619, 1454, 1370, 1253, 1213, 1066 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.25 (m, 5H), 6.60 (s, 1H), 4.77 (d, J = 11.6 Hz, 1H), 4.73 (d, J = 11.6 Hz, 1H), 4.58 (d, J = 6.7 Hz, 1H), 4.49–4.43 (m, 2H), 4.09 (dd, J = 6.1, 9.1 Hz, 1H), 3.97 (dd, J = 5.5, 9.1 Hz, 1H), 1.44 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.6, 128.2, 128.0, 127.8, 100.2, 108.1, 84.6, 82.4, 73.1, 72.7, 47.0, 26.7, 25.4 (the product was not very stable).

(E)-methyl 3-((2R,3S,4R)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2H-pyran-5-yl)acrylate (12)



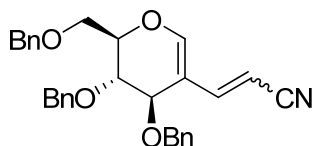
To a stirred solution of **2a** (50 mg, 0.092 mmol) in DMF (1.0 mL), were added Pd(OAc)₂ (2.0 mg, 0.009 mmol), PPh₃ (4.8 mg, 0.018 mmol), methyl acrylate (0.016 mL, 0.184 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 3 h at 90 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (10–15% of EtOAc/hexane) to obtain **12** (39 mg, 85%) as a colorless oil. *R*_f 0.40 (hexane:ethyl acetate, 3:1); [α]_D²⁸ = +37.7 (*c* 0.45, CH₂Cl₂); IR (neat) ν_{max} 3031, 2925, 2855, 1714, 1622, 1496, 1435, 1311, 1284, 1164, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.37–7.18 (m, 16H), 6.92 (s, 1H), 5.66 (d, *J* = 15.9 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.53 (br s, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.44–4.41 (m, 3H), 4.15 (s, 1H), 3.99 (t, *J* = 3.0 Hz, 1H), 3.76 (dd, *J* = 6.7, 10.4 Hz, 1H), 3.71 (s, 3H), 3.63 (dd, *J* = 4.9, 10.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 167.9, 152.2, 143.2, 137.8–127.7 (ArC), 112.7, 111.1, 76.5, 73.4, 71.9, 70.7, 70.1, 70.0, 68.0, 51.4; HRMS calcd for C₃₁H₃₃O₆ [M + H]⁺ 501.2277, found 501.2279.

(E)-4-((2R,3S,4R)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2H-pyran-5-yl)but-3-en-2-one (13)



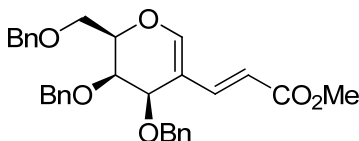
To a stirred solution of **2a** (50 mg, 0.092 mmol) in DMF (1.0 mL), were added Pd(OAc)₂ (2.0 mg, 0.009 mmol), PPh₃ (4.8 mg, 0.018 mmol), methyl vinyl ketone (0.015 mL, 0.184 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 3 h at 90 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (20–25% of EtOAc/hexane) to obtain **13** (34 mg, 76%) as a colorless oil. *R*_f 0.30 (hexane:ethyl acetate, 3:1); [α]_D²⁸ = +43.4 (*c* 0.35, CH₂Cl₂); IR (neat) ν_{max} 2924, 2854, 1714, 1662, 1588, 1454, 1360, 1255, 1173, 1069, 1027 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.17 (m, 15H), 7.08 (d, *J* = 16.0 Hz, 1H), 6.96 (s, 1H), 5.90 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 12.3 Hz, 1H), 4.61 (d, *J* = 12.3 Hz, 1H), 4.58–4.56 (m, 1H), 4.49–4.39 (m, 4H), 4.13 (br s, 1H), 4.00 (t, *J* = 2.7 Hz, 1H), 3.76 (dd, *J* = 7.0, 10.5 Hz, 1H), 3.63 (dd, *J* = 5.2, 10.5 Hz, 1H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.0, 152.9, 142.1, 137.7–127.8 (ArC), 122.6, 111.1, 76.6, 73.5, 71.9, 70.9, 69.8, 69.5, 68.0, 27.5; HRMS calcd for C₃₁H₃₃O₅ [M + H]⁺ 485.2328, found 485.2322.

3-((2*R*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)acrylonitrile (14**)**



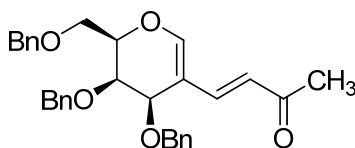
To a stirred solution of **2a** (50 mg, 0.092 mmol) in DMF (1.0 mL), were added Pd(OAc)₂ (2.0 mg, 0.009 mmol), PPh₃ (4.8 mg, 0.018 mmol), acrylonitrile (0.012 mL, 0.184 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 3 h at 90 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (20–25% of EtOAc/hexane) to obtain **14** (30 mg, 71%) as a colorless oil. *R*_f 0.40 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2923, 2853, 2210, 1621, 1496, 1454, 1376, 1293, 1180, 1069, 1027 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, E:Z; 4:1 mixture of diastereomer) δ 7.39–7.14 (m, 15H, both isomers), 6.98 (s, 1H, minor isomer), 6.87 (s, 1H, major isomer), 6.84 (d, *J* = 16.4 Hz, 1H, major isomer), 6.45 (d, *J* = 12.3 Hz, 1H, minor isomer), 4.99 (d, *J* = 12.3 Hz, 1H, minor isomer), 4.84 (br s, 1H, minor isomer), 4.79 (m, *J* = 16.4 Hz, 1H, major isomer), 4.73 (t, *J* = 2.2 Hz, 1H, minor isomer), 4.70–4.67 (m, 2H, major isomer), 4.62 (br s, 1H, major isomer), 4.59 (br s, 1H, minor isomer), 4.57–4.52 (m, 1H, both isomers), 4.49 (br s, 1H, major isomer), 4.46–4.41 (m, 5H, 2H major isomer, 3H minor isomer), 4.38 (br s, 1H, minor isomer), 4.07–4.03 (m, 1H, both isomers), 3.77–3.72 (m 1H, both isomers), 3.65 (dd, *J* = 5.5, 10.5 Hz, 1H, major isomer), 3.56 (dd, *J* = 5.0, 10.5 Hz, 1H, minor isomer); ¹³C NMR (100 MHz, CDCl₃, 4:1 mixture of diastereomer) δ 152.6, 152.0, 147.6, 145.5, 137.8–127.6 (ArC), 119.2, 112.7, 112.6, 90.6, 89.0, 77.3, 76.8, 73.7, 73.6, 72.9, 72.8, 72.4, 68.6, 68.2, 67.9; HRMS calcd for C₃₀H₃₃N₂O₄ [M + NH₄]⁺ 485.2440, found 485.2440.

(*E*)-methyl 3-((2*R*,3*R*,4*R*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)acrylate (15)



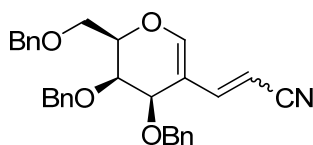
To a stirred solution of **4a** (50 mg, 0.092 mmol) in DMF (1.0 mL), were added Pd(OAc)₂ (2.0 mg, 0.009 mmol), PPh₃ (4.8 mg, 0.018 mmol), methyl acrylate (0.016 mL, 0.184 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 2 h at 90 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (10–15% of EtOAc/hexane) to obtain **15** (42 mg, 90%) as a colorless oil. *R_f* 0.30 (hexane:ethyl acetate, 3:1); [α]_D²⁸ = +25.4 (*c* 0.55, CH₂Cl₂); IR (neat) ν_{max} 2920, 1724, 1638, 1453, 1272, 1206, 1107, 1027 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.27 (m, 15H), 7.25 (d, *J* = 16.0 Hz, 1H), 7.17 (s, 1H), 5.68 (d, *J* = 16.0 Hz, 1H), 4.92 (d, *J* = 11.0 Hz, 1H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.66 (d, *J* = 10.5 Hz, 1H), 4.64 (d, *J* = 10.5 Hz, 1H), 4.57–4.54 (m, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.32–4.31 (m, 1H), 4.01–3.93 (m, 2H), 3.89–3.86 (m, 1H), 3.70 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.0, 154.4, 145.5, 140.8, 140.3, 131.4–130.5 (ArC), 115.4, 115.3, 79.4, 77.1, 77.0, 76.0, 75.3, 71.6, 70.9, 54.2; HRMS calcd for C₃₁H₃₃O₆ [*M* + H]⁺ 501.2277, found 501.2274.

(*E*)-4-((2*R*,3*R*,4*R*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2H-pyran-5-yl)but-3-en-2-one (16)



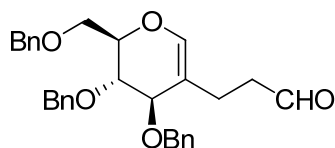
To a stirred solution of **4a** (50 mg, 0.092 mmol) in DMF (1.0 mL), were added Pd(OAc)₂ (2.0 mg, 0.009 mmol), PPh₃ (4.8 mg, 0.018 mmol), methyl vinyl ketone (0.015 mL, 0.184 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 3 h at 90 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (20–25% of EtOAc/hexane) to obtain **16** (37 mg, 83%) as a colorless oil. *R_f* 0.20 (hexane:ethyl acetate, 2:1); [α]_D²⁸ = +79.2 (*c* 0.55, CH₂Cl₂); IR (neat) ν_{max} 2923, 2857, 1722, 1676, 1587, 1453, 1360, 1255, 1171, 1102, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.37–7.23 (m, 15H), 7.04 (d, *J* = 16.0 Hz, 1H), 6.81 (s, 1H), 5.97 (d, *J* = 16.0 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.70–4.65 (m, 2H), 4.66 (d, *J* = 10.9 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 12.0, 1H), 4.34 (d, *J* = 2.2 Hz, 1H), 4.03–3.99 (m, 3H), 2.18 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.9, 152.2, 142.4, 138.0–122.7 (ArC), 122.6, 112.7, 74.4, 74.2, 73.5, 72.6, 68.8, 68.1, 27.5; HRMS calcd for C₃₁H₃₃O₅ [M + H]⁺ 485.2328, found 485.2322.

3-((2*R*,3*R*,4*R*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)acrylonitrile (17**)**



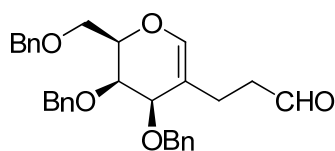
To a stirred solution of **4a** (50 mg, 0.092 mmol) in DMF (1.0 mL), were added Pd(OAc)₂ (2.0 mg, 0.009 mmol), PPh₃ (4.8 mg, 0.018 mmol), acrylonitrile (0.012 mL, 0.184 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 1.5 h at 90 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (25–20% of EtOAc/hexane) to obtain **17** (34 mg, 79%) as a colorless oil. *R*_f 0.30 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2922, 2856, 2209, 1618, 1453, 1370, 1263, 1175, 1096, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, E:Z; 4:1 mixture of diastereomer) δ 7.30–7.20 (m, 15H, both isomers), 6.84 (s, 1H, minor isomer), 6.73 (d, *J* = 16.4 Hz, 1H, major isomer), 6.66 (s, 1H, major isomer), 6.41 (d, *J* = 12.3 Hz, 1H, minor isomer), 4.95 (d, *J* = 12.3 Hz, 1H, minor isomer), 4.90 (br s, 1H, minor isomer), 4.86–4.82 (m, 3H, 2H major isomer, 1H minor isomer), 4.76 (d, *J* = 12.0 Hz, 1H, minor isomer), 4.69 (d, *J* = 12.0 Hz, 1H, major isomer), 4.64–4.61 (m, 1H, both isomers), 4.53 (d, *J* = 12.0 Hz, 1H, major isomer), 4.52–4.47 (m, 5H, 2H major isomer, 3H minor isomer), 4.41–4.38 (m, 1H, both isomers), 4.21 (t, *J* = 3.3 Hz, 1H, major isomer), 4.02 (t, *J* = 3.4 Hz, 1H, minor isomer), 3.97 (t, *J* = 4.0 Hz, 1H, major isomer), 3.89–3.84 (m, 3H, 1H major isomer, 2H minor isomer), 3.81 (dd, *J* = 2.9, 10.9 Hz, 1H, major isomer); ¹³C NMR (125 MHz, CDCl₃, 4:1 mixture of diastereomer) δ 152.6, 152.0, 147.6, 145.5, 137.8–127.6 (ArC), 112.7, 112.6, 90.6, 89.0, 76.9, 76.8, 73.6, 72.8, 68.6, 68.2, 67.9; HRMS calcd for C₃₀H₃₃N₂O₄ [M + NH₄]⁺ 485.2440, found 485.2443.

3-((2*R*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)propanal
(18)



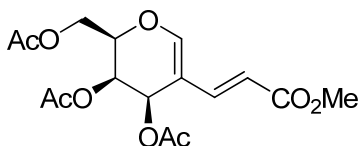
To a stirred solution of **2a** (50 mg, 0.092 mmol) in DMF (2.0 mL), were added Pd(OAc)₂ (2.0 mg, 0.009 mmol), PPh₃ (4.8 mg, 0.018 mmol), allyl alcohol (0.018 mL, 0.276 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 8 h at 100 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration *in vacuo* gave a crude residue which was purified by silica gel column chromatography (10–15% of EtOAc/hexane) to obtain **18** (27 mg, 61%) as a colorless oil. *R_f* 0.40 (hexane:ethyl acetate, 3:1); $[\alpha]_D^{28} = +28.8$ (*c* 0.45, CH₂Cl₂); IR (neat) ν_{max} 2861, 1722, 1666, 1496, 1454, 1363, 1157, 1069, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.64 (s, 1H), 7.32–7.23 (m, 15H), 6.27 (s, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.0 Hz, 1H), 4.53 (br s, 2H), 4.43 (d, *J* = 11.6 Hz, 1H), 4.15 (dd, *J* = 5.5, 9.8 Hz, 1H), 3.95–3.91 (m, 2H), 3.77 (dd, *J* = 6.1, 10.3 Hz, 1H), 3.69–3.66 (m, 1H), 2.40–2.08 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 202.2, 141.1, 138.1–127.7 (ArC), 110.3, 75.9, 75.2, 73.6, 72.9, 71.5, 68.1, 42.7, 21.8; HRMS calcd for C₃₀H₃₆NO₅ [M + NH₄]⁺ 490.2593, found 490.2594.

3-((2R,3R,4R)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-3,4-dihydro-2H-pyran-5-yl)propanal
(**19**)



To a stirred solution of **4a** (50 mg, 0.092 mmol) in DMF (2.0 mL), were added Pd(OAc)₂ (2.0 mg, 0.009 mmol), PPh₃ (4.8 mg, 0.018 mmol), allyl alcohol (0.018 mL, 0.276 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 5 h at 100 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (10–15% of EtOAc/hexane) to obtain **19** (23 mg, 53%) as a colorless oil. *R*_f 0.40 (hexane:ethyl acetate, 3:1); [α]_D²⁸ = +20.0 (*c* 0.50, CH₂Cl₂); IR (neat) ν_{max} 2921, 2855, 1721, 1663, 1496, 1453, 1347, 1206, 1142, 1094, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.62 (s, 1H), 7.34–7.25 (m, 15H), 6.16 (s, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.43 (d, *J* = 11.6 Hz, 1H), 4.19 (br s, 1H), 4.07 (br s, 1H), 4.01–4.00 (m, 1H), 3.76 (dd, *J* = 7.3, 10.3 Hz, 1H), 3.68 (dd, *J* = 4.8, 10.3 Hz, 1H), 2.39–2.23 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 202.4, 140.0, 138.2–127.8 (ArC), 110.7, 75.3, 73.5, 73.4, 72.9, 72.8, 68.2, 42.9, 21.9; HRMS calcd for C₃₀H₃₆NO₅ [M + NH₄]⁺ 490.2593, found 490.2594.

(2*R*,3*R*,4*R*)-2-(acetoxymethyl)-5-((*E*)-3-methoxy-3-oxoprop-1-enyl)-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (20**)**



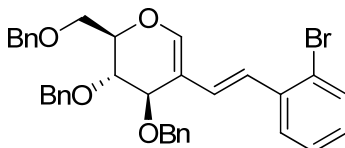
To a stirred solution of **6a** (100 mg, 0.251 mmol) in DMF (3.0 mL), were added Pd(OAc)₂ (5.6 mg, 0.025 mmol), PPh₃ (13.1 mg, 0.050 mmol), methyl acrylate (0.045 mL, 0.502 mmol) followed by Et₃N (0.070 mL, 0.502 mmol) under N₂ atmosphere. The reaction mixture was stirred for 1 h at 90 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (2 × 20 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (25–30% of EtOAc/hexane) to obtain **20** (84 mg, 94%) as a colorless oil. *R_f* 0.30 (hexane:ethyl acetate, 2:1); $[\alpha]_D^{28} = +43.9$ (*c* 0.30, CH₂Cl₂); IR (neat) ν_{\max} 2923, 2852, 1746, 1626, 1435, 1371, 1228, 1165, 1044, 1020 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, *J* = 16.0 Hz, 1H), 6.90 (s, 1H), 5.85 (d, *J* = 4.1 Hz, 1H), 5.59 (d, *J* = 16.0 Hz, 1H), 5.43 (t, *J* = 4.1 Hz, 1H), 4.43–4.37 (m, 2H), 4.26 (d, *J* = 9.1 Hz, 1H), 3.70 (s, 3H), 2.08 (s, 6H), 2.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 170.3, 169.6, 167.5, 152.1, 140.3, 114.2, 110.3, 73.7, 64.7, 61.7, 61.5, 51.6, 20.8, 20.6; HRMS calcd for C₁₆H₂₀NaO₉ [M + Na]⁺ 379.1005, found 379.1000.

Preparation of 21 and 22

To a stirred solution of **2a** (100 mg, 0.184 mmol) in DMF (3.0 mL), were added Pd(OAc)₂ (4.1 mg, 0.018 mmol), PPh₃ (9.6 mg, 0.036 mmol), 2-bromostyrene (37.0 mg, 0.202 mmol) followed by K₂CO₃ (25.4 mg, 0.184 mmol) under N₂ atmosphere. The reaction mixture was stirred for 2 h at 100 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (3 × 10 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration

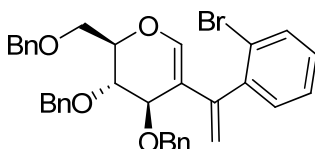
in *vacuo* gave a crude residue which was separated by silica gel column chromatography (5–10% of EtOAc/hexane) to afford **21** (61 mg, 56%) and **22** (21 mg, 19%) as a colorless oils.

(2*R*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-5-(2-bromostyryl)-3,4-dihydro-2*H*-pyran (21)



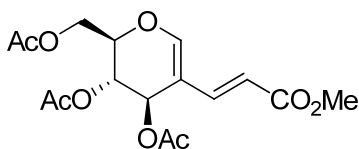
R_f 0.40 (hexane:ethyl acetate, 4:1); $[\alpha]_D^{28} = +37.3$ (c 0.75, CH_2Cl_2); IR (neat) ν_{max} 2923, 2855, 1632, 1465, 1453, 1362, 1267, 1165, 1026 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.53–7.51 (m, 2H, *ArH*), 7.36–7.01 (m, 17H, *ArH*), 6.83 (d, $J = 16.0$ Hz, 1H), 6.80(s, 1H), 6.60 (d, $J = 16.0$ Hz, 1H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.65 (br s, 1H), 4.64 (d, $J = 10.8$ Hz, 1H), 4.54 (d, $J = 10.8$ Hz, 1H), 4.53–4.52 (m, 1H), 4.51 (d, $J = 12.0$ Hz, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 4.53 (br s, 1H), 3.99 (t, $J = 2.8$ Hz, 1H), 3.80 (dd, $J = 6.9, 10.3$ Hz, 1H), 3.66 (dd, $J = 5.1, 10.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 147.1, 137.9–122.5 (*ArC*), 76.0, 73.4, 71.9, 71.3, 71.1, 70.8, 68.2; HRMS calcd for $\text{C}_{35}\text{H}_{37}\text{BrNO}_4$ $[\text{M} + \text{NH}_4]^+$ 614.1906, found 614.1908.

(2*R*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-5-(1-(2-bromophenyl)vinyl)-3,4-dihydro-2*H*-pyran (22)



R_f 0.60 (hexane:ethyl acetate, 4:1); $[\alpha]_D^{28} = +9.0$ (c 0.55, CH_2Cl_2); IR (neat) ν_{max} 2922, 2854, 1453, 1360, 1269, 1094, 1026 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.56–7.12 (m, 19H, ArH), 6.20 (s, 1H), 5.35 (s, 1H), 4.85 (s, 1H), 4.70 (d, $J = 11.9$ Hz, 1H), 4.66 (d, $J = 11.9$ Hz, 1H), 4.55 (d, $J = 11.9$ Hz, 1H), 4.52–4.43 (m, 4H), 4.32 (br s, 1H), 4.01 (t, $J = 3.6$ Hz, 1H), 3.80 (dd, $J = 6.4, 10.0$ Hz, 1H), 3.68 (dd, $J = 5.0, 10.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.3, 145.5, 141.9, 138.0–123.4 (ArC), 112.9, 112.0, 75.8, 73.4, 71.9, 71.8, 71.2, 70.1, 68.3; HRMS calcd for $\text{C}_{35}\text{H}_{33}\text{BrNaO}_4$ $[\text{M} + \text{Na}]^+$ 619.1460, found 619.1460.

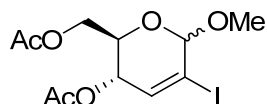
(2R,3S,4R)-2-(acetoxymethyl)-5-((E)-3-methoxy-3-oxoprop-1-enyl)-3,4-dihydro-2H-pyran-3,4-diyl diacetate (23)



To a stirred solution of **5a** (100 mg, 0.251 mmol) in DMF (3.0 mL), were added $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.050 mmol), methyl acrylate (0.045 mL, 0.502 mmol) followed by Et_3N (0.070 mL, 0.502 mmol) under N_2 atmosphere. The reaction mixture was stirred for 1 h at 90 $^\circ\text{C}$. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (2×20 mL), and the combined organic extracts were washed with water (1×10 mL), brine (1×10 mL), and then dried over Na_2SO_4 . Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (25–30% of EtOAc/hexane) to obtain **23** (79 mg, 89%) as a colorless oil. R_f 0.30 (hexane:ethyl acetate, 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 16.0$ Hz, 1H), 6.96 (s, 1H), 5.60 (d, $J = 16.0$ Hz, 1H), 5.57 (d, $J = 2.3$ Hz, 1H), 5.13 (t, $J = 3.6$ Hz, 1H), 4.49–4.40

(m, 2H), 4.16 (d, $J = 3.6, 11.4$ Hz, 1H), 3.70 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.4, 169.9, 169.4, 167.5, 152.3, 141.1, 113.8, 109.4, 74.4, 66.4, 62.7, 61.1, 51.6, 20.8, 20.6.

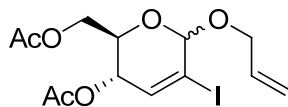
((2*R*,3*R*)-3-acetoxy-5-iodo-6-methoxy-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (24**)**



To a stirred solution of an acetylated 2-iodoglucal **5a** (100 mg, 0.251 mmol) and CH_3OH (0.013 mL, 0.301 mmol) in dry CH_2Cl_2 (2 mL) at room temperature under N_2 atmosphere was added $\text{BF}_3\cdot\text{OEt}_2$ (0.053 mL, 0.502 mmol) and the reaction mixture was stirred for 2 h. After the consumption of starting material (TLC monitoring), the reaction mixture was quenched with NaHCO_3 (5.0 mL) solution and extracted with CH_2Cl_2 (2×10 mL) and the combined organic extracts were washed with water (1×10 mL), brine (1×10 mL), and then dried over Na_2SO_4 . Evaporation of solvents under vacuum gave a crude residue which was purified by silica gel column chromatography (5–10% of EtOAc/hexane) to obtain **24** (85 mg, 92%) as a colorless oil. R_f 0.50 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2917, 1742, 1637, 1438, 1369, 1228, 1108, 1050 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 5:1 mixture of anomers) δ 6.60 (d, $J = 4.0$ Hz, 1H, minor isomer), 6.46 (d, $J = 2.3$ Hz, 1H, major isomer), 5.28 (d, $J = 9.7$ Hz, 1H, major isomer), 5.10 (t, $J = 4.0$ Hz, 1H, minor isomer), 4.96 (s, 1H, minor isomer), 4.89 (s, 1H, major isomer), 4.77–4.74 (m, 1H, minor isomer), 4.23–4.11 (m, 3H, major isomer), 4.01–3.98 (m, 1H, minor isomer), 3.60 (dd, $J = 1.8, 8.0$ Hz, 1H, minor isomer), 3.47 (s, 3H, minor isomer), 3.45 (s, 3H, major isomer), 2.11 (s, 3H, minor isomer), 2.08 (s, 3H, minor isomer), 2.07 (s, 6H, major isomer); ^{13}C NMR (100 MHz, CDCl_3 , 5:1 mixture of anomers) δ 170.8, 170.1, 137.8, 136.2, 130.1, 100.6,

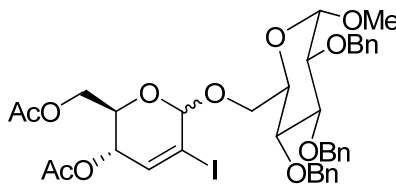
96.7, 73.2, 69.9, 67.2, 66.2, 63.6, 63.0, 56.7, 55.4, 20.9, 20.8; HRMS calcd for $C_{11}H_{15}INaO_6$ [$M + Na$] $^+$ 392.9811, found 392.9816.

((2*R*,3*S*)-3-acetoxy-6-(allyloxy)-5-iodo-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (25**)**



To a stirred solution of an acetylated 2-iodoglucal **5a** (100 mg, 0.251 mmol) and allyl alcohol (0.034 mL, 0.502 mmol) in dry CH_2Cl_2 (2 mL) at room temperature under N_2 atmosphere was added $BF_3 \cdot OEt_2$ (0.053 mL, 0.502 mmol) and the reaction mixture was stirred for 2 h. After the consumption of starting material (TLC monitoring), the reaction mixture was quenched with $NaHCO_3$ (5.0 mL) solution and extracted with CH_2Cl_2 (2×10 mL) and the combined organic extracts were washed with water (1×10 mL), brine (1×10 mL), and then dried over Na_2SO_4 . Evaporation of solvents under vacuum gave a crude residue which was purified by silica gel column chromatography (5–10% of EtOAc/hexane) to obtain **25** (86 mg, 87%) as a colorless oil. R_f 0.60 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2923, 1744, 1637, 1427, 1370, 1224, 1105, 1042 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$, 10:1 mixture of anomers) δ 6.60 (d, $J = 4.0$ Hz, 1H, minor isomer), 6.46 (d, $J = 2.3$ Hz, 1H, major isomer), 5.98–5.90 (m, 1H, both isomers), 5.37 (d, $J = 1.7$ Hz, 1H, major isomer), 5.34 (d, $J = 1.7$ Hz, 1H, major isomer), 5.29–5.23 (m, 1H, both isomers), 5.08–5.07 (m, 2H, minor isomer), 5.03 (s, 1H, both isomers), 4.26–4.23 (m, 1H, both isomers), 4.21–4.14 (m, 3H, both isomers), 4.12–4.08 (m, 1H, both isomers), 2.08 (s, 3H, both isomers), 2.07 (s, 3H, both isomers); ^{13}C NMR (125 MHz, $CDCl_3$, 10:1 mixture of anomers) δ 170.7, 170.1, 137.8, 133.5, 118.2, 98.6, 97.0, 69.9, 67.3, 66.4, 62.7, 20.9, 20.8; HRMS calcd for $C_{13}H_{17}INaO_6$ [$M + Na$] $^+$ 418.9968, found 418.9963.

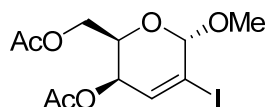
((2*R*,3*S*)-3-acetoxy-5-iodo-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methoxy)-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (26**)**



To a stirred solution of an acetylated 2-iodoglucal **5a** (50 mg, 0.125 mmol) and XOH (58.3 mg, 0.125 mmol) in dry CH₂Cl₂ (3 mL) at room temperature under N₂ atmosphere was added BF₃·OEt₂ (0.026 mL, 0.251 mmol) and the reaction mixture was stirred for 2 h. After the consumption of starting material (TLC monitoring), the reaction mixture was quenched with NaHCO₃ (5.0 mL) solution and extracted with CH₂Cl₂ (2 × 10 mL) and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Evaporation of solvents under vacuum gave a crude residue which was purified by silica gel column chromatography (20–25% of EtOAc/hexane) to obtain **26** (66 mg, 66%) as a colorless oil. *R*_f 0.30 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2927, 1745, 1637, 1453, 1369, 1229, 1029 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 10:2 mixture of anomers) δ 7.36–7.24 (m, 15H, both isomers), 6.56 (d, *J* = 2.0 Hz, 1H, minor isomer), 6.43 (d, *J* = 2.0 Hz, 1H, major isomer), 5.35–5.34 (m, 1H, minor isomer), 5.28–5.26 (m, 1H, major isomer), 5.16 (s, 1H, major isomer), 5.10 (t, *J* = 5.0 Hz, 1H, minor isomer), 5.04 (s, 1H, minor isomer), 4.97 (d, *J* = 10.9 Hz, 1H, major isomer), 4.92 (d, *J* = 10.9 Hz, 1H, major isomer), 4.83–4.77 (m, 2H, both isomer), 4.68 (d, *J* = 9.4 Hz, 1H, major isomer), 4.66–4.57 (m, 3H, minor isomer), 4.58 (d, *J* = 3.4 Hz, 1H, major isomer), 4.28–4.25 (m, 2H, minor isomers), 4.20–4.15 (m, 1H, both isomers), 4.13–4.09 (m, 2H, both isomers), 4.03–3.97 (m, 1H, both isomers), 3.86 (d, *J* = 3.2 Hz, 1H, minor isomer), 3.83 (d, *J* =

3.4 Hz, 1H, major isomer), 3.82–3.81 (m, 1H, both isomers), 3.78–3.69 (m, 2H, both isomer), 3.78–3.57 (m, 2H, major isomers), 3.39 (s, 3H, minor isomer), 3.37 (s, 3H, major isomer), 2.07 (s, 3H, both isomer), 2.03 (s, 3H, major isomer), 2.02 (s, 3H, minor isomer); ^{13}C NMR (100 MHz, CDCl_3 , 10:2 mixture of anomers) δ 170.7, 170.5, 170.0, 138.8–127.7 (ArC), 99.6, 98.3, 98.1, 96.9, 82.1, 82.0, 80.6, 79.6, 76.8, 75.8, 75.1, 73.4, 72.7, 71.0, 69.6, 67.3, 67.0, 66.8, 66.6, 63.2, 62.6, 55.4, 55.3, 20.9, 20.8; HRMS calcd for $\text{C}_{38}\text{H}_{47}\text{INO}_{11}$ $[\text{M} + \text{NH}_4]^+$ 820.2194, found 820.2191.

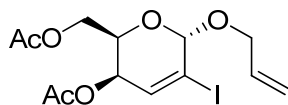
((2*R*,3*R*,6*S*)-3-acetoxy-5-iodo-6-methoxy-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (27**)**



To a stirred solution of an acetylated 2-iodogalactal **6a** (100 mg, 0.251 mmol) and CH_3OH (0.013 mL, 0.301 mmol) in dry CH_2Cl_2 (2 mL) at room temperature under N_2 atmosphere was added $\text{BF}_3\cdot\text{OEt}_2$ (0.053 mL, 0.502 mmol) and the reaction mixture was stirred for 2 h. After the consumption of starting material (TLC monitoring), the reaction mixture was quenched with NaHCO_3 (5.0 mL) solution and extracted with CH_2Cl_2 (2×10 mL) and the combined organic extracts were washed with water (1×10 mL), brine (1×10 mL), and then dried over Na_2SO_4 . Evaporation of solvents under vacuum gave a crude residue which was purified by silica gel column chromatography (5–10% of EtOAc/hexane) to obtain **27** (79 mg, 85%) as a colorless oil. R_f 0.60 (hexane:ethyl acetate, 3:1); $[\alpha]_D^{28} = -128$ (c 0.70, CH_2Cl_2); IR (neat) ν_{max} 2928, 2832, 1745, 1635, 1370, 1228, 1191, 1055 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.67 (d, $J = 5.5$ Hz, 1H), 4.94 (s, 1H), 4.91 (d, $J = 4.8$ Hz, 1H), 4.33 (br s, 1H), 4.20–4.19 (m, 2H), 3.46 (s, 3H), 2.08

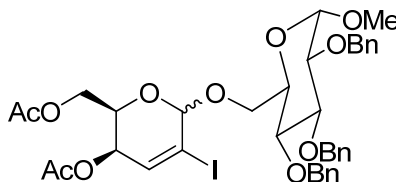
(s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 170.2, 134.4, 102.1, 100.5, 65.8, 65.3, 62.5, 56.3, 20.8; HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{INaO}_6$ $[\text{M} + \text{Na}]^+$ 392.9811, found 392.9813.

((2*R*,3*R*,6*S*)-3-acetoxy-6-(allyloxy)-5-iodo-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (28**)**



To a stirred solution of an acetylated 2-iodogalactal **6a** (100 mg, 0.251 mmol) and allyl alcohol (0.034 mL, 0.502 mmol) in dry CH_2Cl_2 (2 mL) at room temperature under N_2 atmosphere was added $\text{BF}_3\cdot\text{OEt}_2$ (0.053 mL, 0.502 mmol) and the reaction mixture was stirred for 4 h. After the consumption of starting material (TLC monitoring), the reaction mixture was quenched with NaHCO_3 (5.0 mL) solution and extracted with CH_2Cl_2 (2×10 mL) and the combined organic extracts were washed with water (1×10 mL), brine (1×10 mL), and then dried over Na_2SO_4 . Evaporation of solvents under vacuum gave a crude residue which was purified by silica gel column chromatography (5–10% of EtOAc/hexane) to obtain **28** (88 mg, 89%) as a colorless oil. R_f 0.70 (hexane:ethyl acetate, 3:1); $[\alpha]_D^{28} = -124.0$ (c 0.48, CH_2Cl_2); IR (neat) ν_{max} 2923, 2854, 1744, 1634, 1370, 1225, 1101, 1055, 1025 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.68 (d, $J = 5.4$ Hz, 1H), 5.98–5.89 (m, 1H), 5.34 (dd, $J = 1.4, 17.4$ Hz, 1H), 5.23 (dd, $J = 1.4, 10.5$ Hz, 1H), 5.08 (s, 1H), 4.37 (td, $J = 2.2, 6.4$ Hz, 1H), 4.25–4.21 (m, 1H), 4.18–4.17 (m, 2H), 4.12–4.07 (m, 1H), 2.06 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 170.2, 134.4, 133.5, 118.4, 102.1, 98.4, 69.5, 65.9, 65.4, 62.5, 20.8, 20.7; HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{INaO}_6$ $[\text{M} + \text{Na}]^+$ 418.9968, found 418.9966.

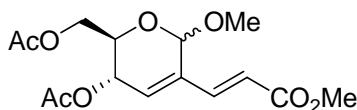
((2*R*,3*R*)-3-acetoxy-5-iodo-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methoxy)-3,6-dihydro-2*H*-pyran-2-yl)methyl acetate (29**)**



To a stirred solution of an acetylated 2-iodogalactal **6a** (50 mg, 0.125 mmol) and XOH (58.3 mg, 0.125 mmol) in dry CH₂Cl₂ (3 mL) at room temperature under N₂ atmosphere was added BF₃·OEt₂ (0.026 mL, 0.251 mmol) and the reaction mixture was stirred for 2 h. After the consumption of starting material (TLC monitoring), the reaction mixture was quenched with NaHCO₃ (5.0 mL) solution and extracted with CH₂Cl₂ (2 × 10 mL) and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Evaporation of solvents under vacuum gave a crude residue which was purified by silica gel column chromatography (20–25% of EtOAc/hexane) to obtain **29** (53 mg, 53%) as a colorless oil. *R*_f 0.30 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2923, 1744, 1637, 1454, 1370, 1227, 1104, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 2:1 mixture of anomers) δ 7.36–7.27 (m, 15H, both isomers), 6.77 (d, *J* = 5.6 Hz, 1H, major isomer), 6.65 (d, *J* = 5.5 Hz, 1H, minor isomer), 5.46 (s, 1H, major isomer), 5.22 (s, 1H, minor isomer), 5.01 (d, *J* = 2.4 Hz, 1H, minor isomer), 5.00–4.98 (m, 2H, minor isomer), 4.96 (d, *J* = 3.5 Hz, minor isomer), 4.95–4.83 (m, 2H, both isomers), 4.82–4.78 (m, 1H, both isomers), 4.68 (d, *J* = 4.9 Hz, 1H, minor isomer), 4.64 (d, *J* = 4.3 Hz, 1H, major isomer), 4.64–4.59 (m, 2H, both isomers), 4.57–4.55 (m, 1H, major isomer), 4.34–4.30 (m, 2H, minor isomer), 4.27–4.22 (m, 2H, both isomers), 4.19–4.17 (m, 1H, both isomers), 4.03–3.98 (m, 1H, major isomer), 3.87–3.81 (m, 1H, both isomers), 3.78–3.74 (m, 1H,

major isomer), 3.70–3.63 (m, 2H, minor isomers), 3.58–3.48 (m, 3H, 2H major isomer, 1H minor isomer), 3.37 (s, 3H, major isomer), 3.35 (s, 3H, minor isomer), 2.10 (s, 3H, major isomer), 2.08 (s, 3H, major isomer), 2.07 (s, 3H, minor isomer), 1.98 (s, 3H, minor isomer); ^{13}C NMR (125 MHz, CDCl_3 , 2:1 mixture of anomers) δ 170.7, 170.6, 170.2, 138.7–127.7 (ArC), 102.4, 101.1, 99.5, 98.2, 98.1, 94.9, 84.5, 82.4, 82.0, 79.9, 79.5, 76.8, 75.8, 75.2, 75.1, 75.0, 73.5, 73.4, 70.9, 70.7, 66.6, 66.3, 65.8, 65.7, 65.2, 62.5, 62.4, 62.2, 57.4, 21.1, 20.8; HRMS calcd for $\text{C}_{38}\text{H}_{47}\text{INO}_{11}$ $[\text{M} + \text{NH}_4]^+$ 820.2194, found 820.2193.

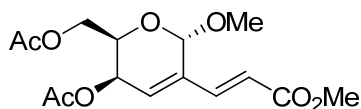
(*E*)-methyl 3-((5*S*,6*R*)-5-acetoxy-6-(acetoxymethyl)-2-methoxy-5,6-dihydro-2*H*-pyran-3-yl)acrylate (30**)**



To a stirred solution of **24** (50 mg, 0.135 mmol) in DMF (2.0 mL), were added $\text{Pd}(\text{OAc})_2$ (3.0 mg, 0.013 mmol), PPh_3 (5.4 mg, 0.027 mmol), methyl acrylate (0.024 mL, 0.270 mmol) followed by K_2CO_3 (37.2 mg, 0.270 mmol) under N_2 atmosphere. The reaction mixture was stirred for 0.5 h at 80 $^\circ\text{C}$. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (2×10 mL), and the combined organic extracts were washed with water (1×10 mL), brine (1×10 mL), and then dried over Na_2SO_4 . Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (10–15% of EtOAc/hexane) to obtain **30** (34 mg, 79%) as a colorless oil. R_f 0.20 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2953, 1745, 1647, 1623, 1436, 1371, 1288, 1234, 1178, 1078 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 4:1 mixture of anomers) δ 7.15–7.12 (m, 1H, both anomers), 6.21 (d, $J = 4.3$ Hz, 1H, minor anomer), 6.11 (d, $J = 1.8$ Hz, 1H, major anomer), 6.05

(d, $J = 16.5$ Hz, 1H, minor anomer), 5.91 (d, $J = 16.4$ Hz, 1H, major isomer), 5.42 (d, $J = 7.9$ Hz, 1H, major anomer), 5.25 (t, $J = 4.2$ Hz, 1H, minor anomer), 5.18 (s, 1H, minor anomer), 5.05 (s, 1H, major anomer), 4.26–4.19 (m, 3H, major anomer) 4.14–4.11 (m, 3H, minor anomer), 3.74 (s, 3H, both anomers), 3.50 (s, 3H, major anomer), 3.47 (s, 3H, minor anomer), 2.08 (s, 6H, major anomer), 2.07 (s, 6H, minor anomer); ^{13}C NMR (125 MHz, CDCl_3 , 4:1 mixture of anomers) δ 170.7, 170.2, 166.9, 140.9, 136.6, 136.0, 134.1, 130.9, 121.0, 120.0, 95.6, 72.6, 66.9, 65.6, 64.6, 63.2, 62.7, 55.9, 55.0, 51.8, 20.9, 20.8; HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_8$ $[\text{M} + \text{Na}]^+$ 351.1056, found 351.1052.

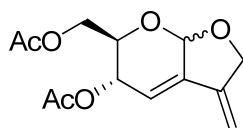
(*E*)-methyl 3-((2*S*,5*R*,6*R*)-5-acetoxy-6-(acetoxymethyl)-2-methoxy-5,6-dihydro-2*H*-pyran-3-yl)acrylate (31**)**



To a stirred solution of **27** (50 mg, 0.135 mmol) in DMF (2.0 mL), were added $\text{Pd}(\text{OAc})_2$ (3.0 mg, 0.013 mmol), PPh_3 (5.4 mg, 0.027 mmol), methyl acrylate (0.024 mL, 0.270 mmol) followed by K_2CO_3 (37.2 mg, 0.270 mmol) under N_2 atmosphere. The reaction mixture was stirred for 0.5 h at 80 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (2×10 mL), and the combined organic extracts were washed with water (1×10 mL), brine (1×10 mL), and then dried over Na_2SO_4 . Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (10–15% of EtOAc/hexane) to obtain **31** (36 mg, 81%) as a colorless oil. R_f 0.40 (hexane:ethyl acetate, 3:1); $[\alpha]_D^{28} = -150.0$ (c 0.55, CH_2Cl_2); IR (neat) ν_{max} 2953, 2832, 1741, 1647, 1621, 1436, 1370, 1227, 1173, 1043 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.18 (d, J

= 15.9 Hz, 1H), 6.28 (d, J = 5.5 Hz, 1H), 5.98 (d, J = 15.9 Hz, 1H), 5.16 (d, J = 5.4 Hz, 1H), 5.10 (s, 1H), 4.34–4.24 (m, 3H), 3.76 (s, 3H), 3.50 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.6, 170.3, 166.8, 141.2, 137.6, 129.8, 120.6, 95.2, 66.4, 63.4, 62.6, 55.6, 51.9, 20.8; HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_8$ $[\text{M} + \text{Na}]^+$ 351.1056, found 351.1050.

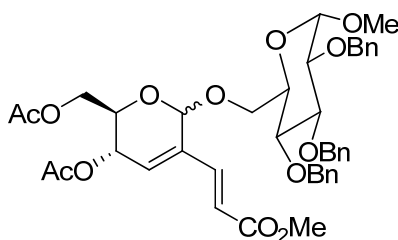
((5*S*,6*R*)-5-acetoxy-3-methylene-3,5,6,7a-tetrahydro-2*H*-furo[2,3-*b*]pyran-6-yl)methyl acetate (32**)**



To a stirred solution of **25** (50 mg, 0.126 mmol) in DMF (2.0 mL), were added $\text{Pd}(\text{OAc})_2$ (2.8 mg, 0.012 mmol), PPh_3 (6.6 mg, 0.025 mmol) followed by K_2CO_3 (34.8 mg, 0.252 mmol) under N_2 atmosphere. The reaction mixture was stirred for 2 h at 80 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (2×10 mL), and the combined organic extracts were washed with water (1×10 mL), brine (1×10 mL), and then dried over Na_2SO_4 . Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (5–10% of EtOAc/hexane) to obtain **32** (26 mg, 78%) as a colorless oil. R_f 0.30 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2920, 2852, 1740, 1371, 1230, 1153, 1034 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 5:1 mixture of diastereomers) δ 6.11 (d, J = 4.0 Hz, 1H, minor isomer), 6.03 (s, 1H, major isomer), 5.47–5.42 (m, 2H, both isomers), 5.05 (s, 1H, minor isomer), 4.99 (s, 1H, major isomer), 4.64–4.58 (m, 1H, both isomers), 4.47–4.35 (m, 1H, both isomers), 4.34 (dd, J = 5.7, 12.0 Hz, 1H, major isomer), 4.27–4.21 (m, 3H, 1H major isomer, 2H minor isomer), 4.03–4.00 (m, 1H, minor isomer), 3.96–3.93 (m, 1H, major isomer), 2.11 (s, 3H, major isomer), 2.08 (m, 9H, 3H major isomer, 6H minor isomer); ^{13}C

NMR (125 MHz, CDCl₃, 5:1 mixture of diastereomers) δ 170.8, 170.3, 140.0, 138.3, 120.1, 106.5, 105.4, 100.5, 97.8, 72.0, 70.6, 69.7, 66.4, 65.8, 63.5, 62.4, 21.0, 20.9; HRMS calcd for C₁₃H₁₆NaO₆ [M + Na]⁺ 291.0845, found 291.0841.

(E)-methyl 3-((5S,6R)-5-acetoxy-6-(acetoxymethyl)-2-(((2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methoxy)-5,6-dihydro-2H-pyran-3-yl)acrylate (33)



To a stirred solution of **26** (100 mg, 0.124 mmol) in DMF (3.0 mL), were added Pd(OAc)₂ (2.7 mg, 0.012 mmol), PPh₃ (6.5 mg, 0.024 mmol), methyl acrylate (0.022 mL, 0.249 mmol) followed by K₂CO₃ (34.3 mg, 0.249 mmol) under N₂ atmosphere. The reaction mixture was stirred for 1 h at 80 °C. After confirmation of the completion of the reaction by TLC, the mixture diluted with water and extracted from diethyl ether (2 × 20 mL), and the combined organic extracts were washed with water (1 × 10 mL), brine (1 × 10 mL), and then dried over Na₂SO₄. Concentration in *vacuo* gave a crude residue which was purified by silica gel column chromatography (20–25% of EtOAc/hexane) to obtain **33** (84 mg, 89%) as a colorless oil. *R_f* 0.20 (hexane:ethyl acetate, 3:1); IR (neat) ν_{max} 2923, 2853, 1744, 1646, 1454, 1369, 1230, 1072, 1028 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 10:2 mixture of anomers) δ 7.38–7.24 (m, 15H, both isomers), 7.14–7.13 (m, 1H, minor isomer), 7.13 (d, *J* = 16.0 Hz, 1H, major isomer), 6.36 (d, *J* = 16.0 Hz, 1H, major isomer), 6.27 (d, *J* = 16.0 Hz, 1H, minor isomer), 6.20 (d, *J* = 4.12 Hz, 1H,

minor isomer), 6.03 (m, 1H, major isomer), 5.42 (d, $J = 7.2$ Hz, 1H, major isomer), 5.24 (s, 1H, both isomers), 4.99–4.98 (m, 1H, minor isomer), 4.94 (d, $J = 11.0$ Hz, 1H, major isomer), 4.88 (d, $J = 11.4$ Hz, 1H, minor isomer), 4.87 (d, $J = 11.0$ Hz, 1H, major isomer), 4.84–4.76 (m, 4H, both isomers), 4.70 (d, $J = 11.4$ Hz, 1H, major isomer), 4.67–4.64 (m, 1H, minor isomer), 4.61 (d, $J = 11.4$ Hz, 1H, major isomer), 4.58–4.56 (m, 1H, minor isomer), 4.22 (d, $J = 5.4$ Hz, 1H, minor isomer), 4.19 (d, $J = 5.0$ Hz, 1H, major isomer), 4.15 (d, $J = 2.2$ Hz, 1H, major isomer), 4.13 (d, $J = 2.2$ Hz, 1H, minor isomer), 4.09–3.95 (m, 3H, both isomers), 3.81–3.78 (m, 1H, both isomers), 3.75–3.73 (m, 1H, both isomers), 3.68 (s, 3H, major isomer), 3.64 (s, 3H, minor isomer), 3.62–3.51 (m, 2H, both isomers), 3.39 (s, 3H, major isomer), 3.36–3.35 (m, 1H, both isomers), 3.31 (s, 3H, minor isomer), 2.10 (s, 3H, major isomer), 2.08 (s, 3H, minor isomer), 2.02 (s, 3H, major isomer), 1.99 (s, 3H, minor isomer), ^{13}C NMR (100 MHz, CDCl_3 , 10:2 mixture of anomers) δ 170.7, 170.2, 167.1, 141.0–120.9 (ArC), 98.0, 97.7, 95.5, 95.1, 82.1, 81.9, 80.8, 80.1, 80.0, 78.1, 75.8, 75.2, 74.9, 73.4, 73.3, 72.6, 70.7, 70.2, 69.6, 68.0, 67.0, 66.9, 65.6, 64.7, 63.3, 62.7, 56.3, 56.2, 51.7, 21.0, 20.8; HRMS calcd for $\text{C}_{42}\text{H}_{52}\text{NO}_{13}$ $[\text{M} + \text{NH}_4]^+$ 778.3439, found 778.3439.

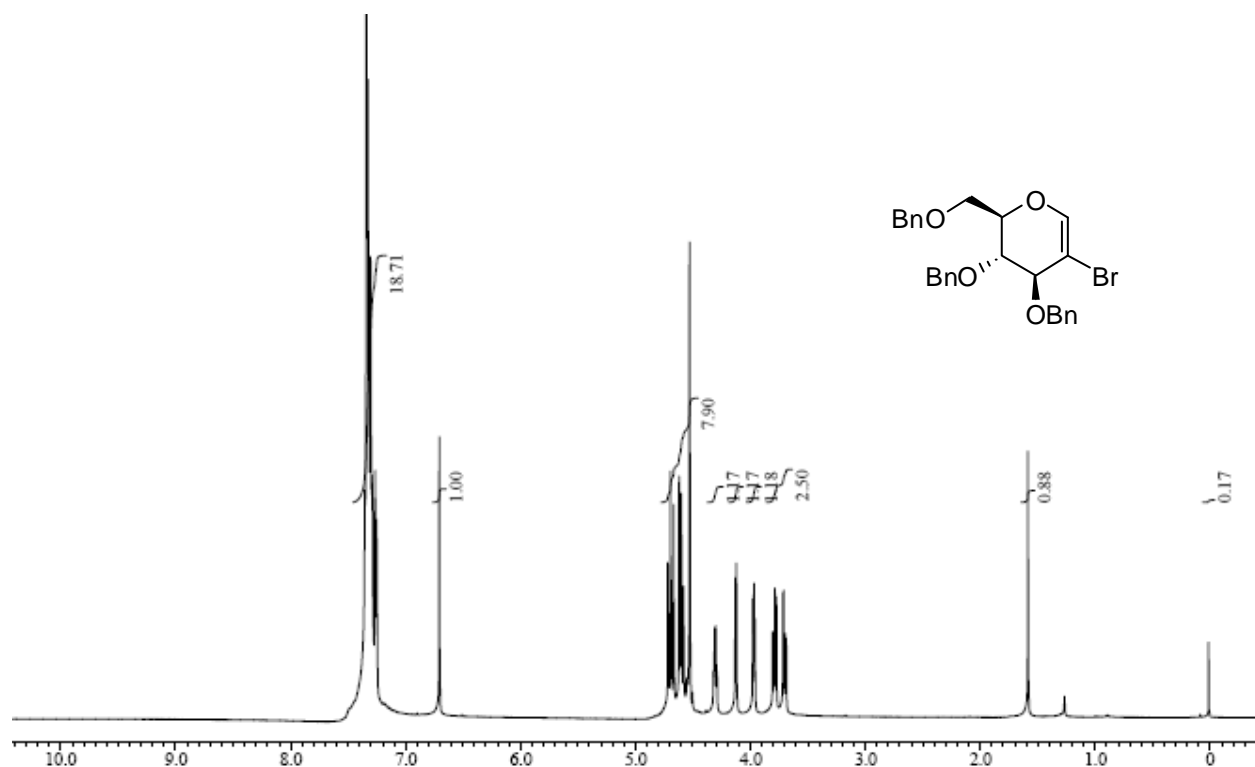


Figure 1.1: ^1H NMR (500 MHz, CDCl_3) Spectrum of Compound **2b**

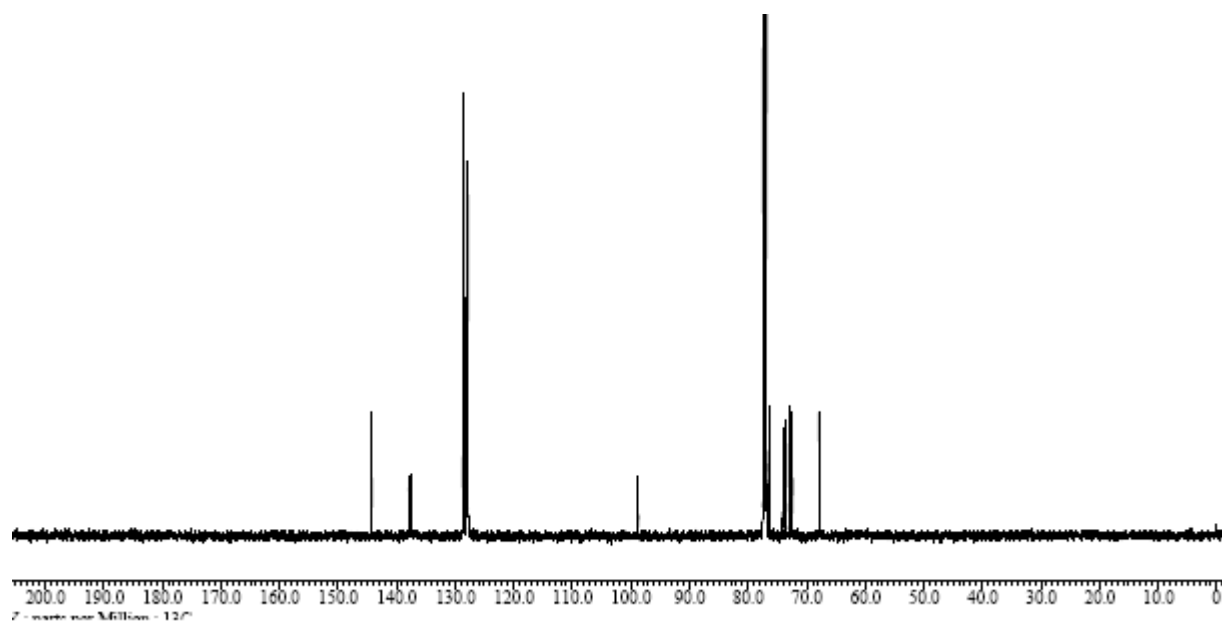


Figure 1.2: ^{13}C NMR (125 MHz, CDCl_3) Spectrum of Compound **2b**

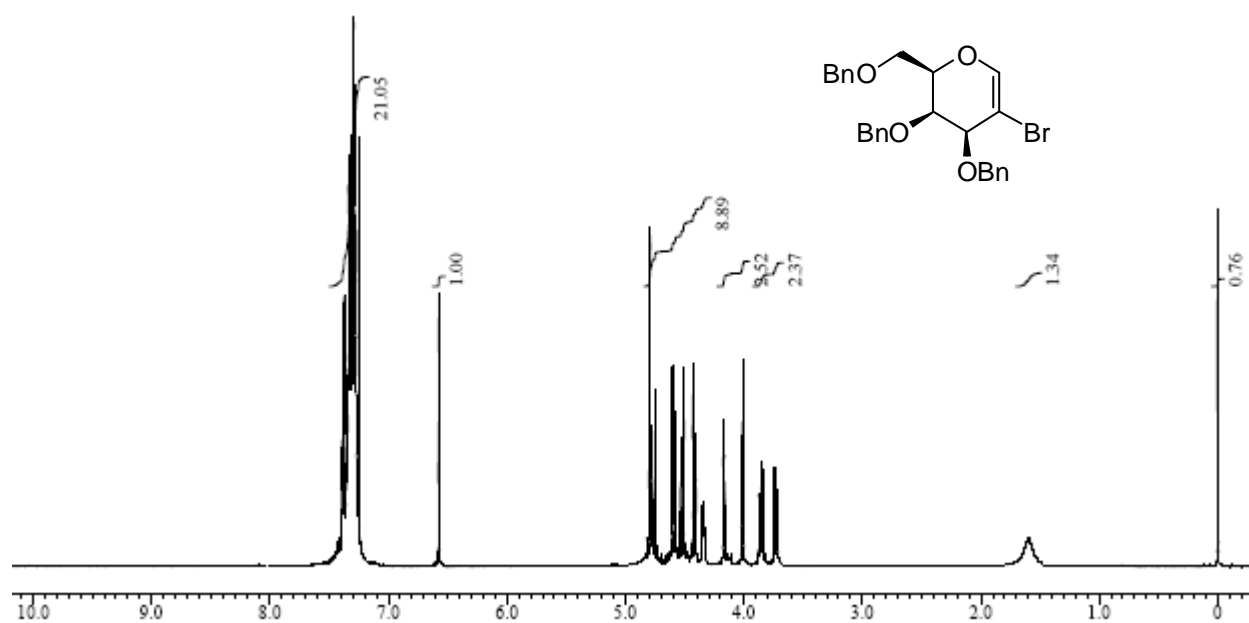


Figure 2.1: ^1H NMR (500 MHz, CDCl_3) Spectrum of Compound **4b**

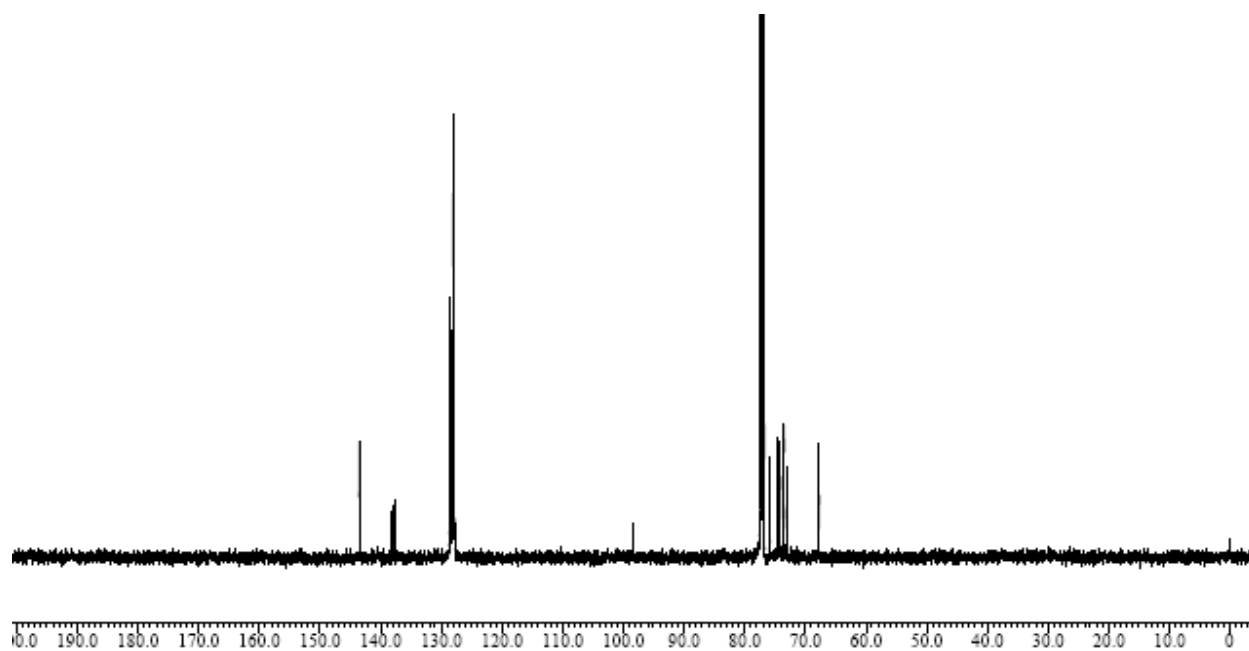


Figure 2.2: ^{13}C NMR (125 MHz, CDCl_3) Spectrum of Compound **4b**

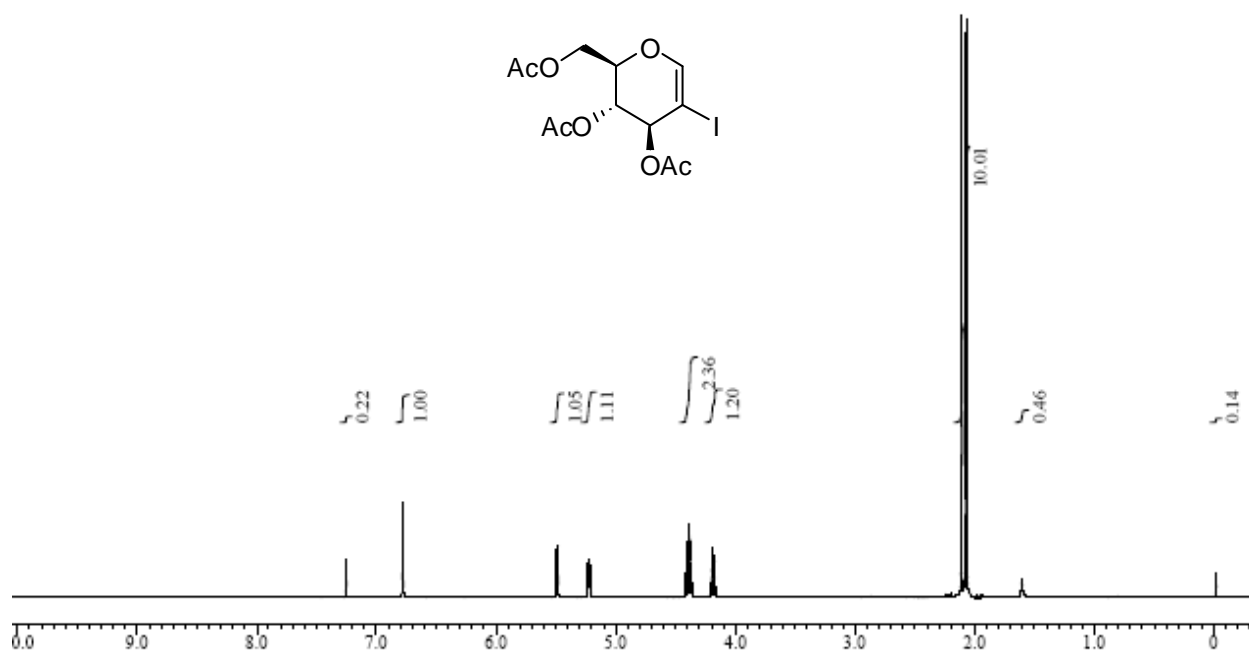


Figure 3.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound **5a**

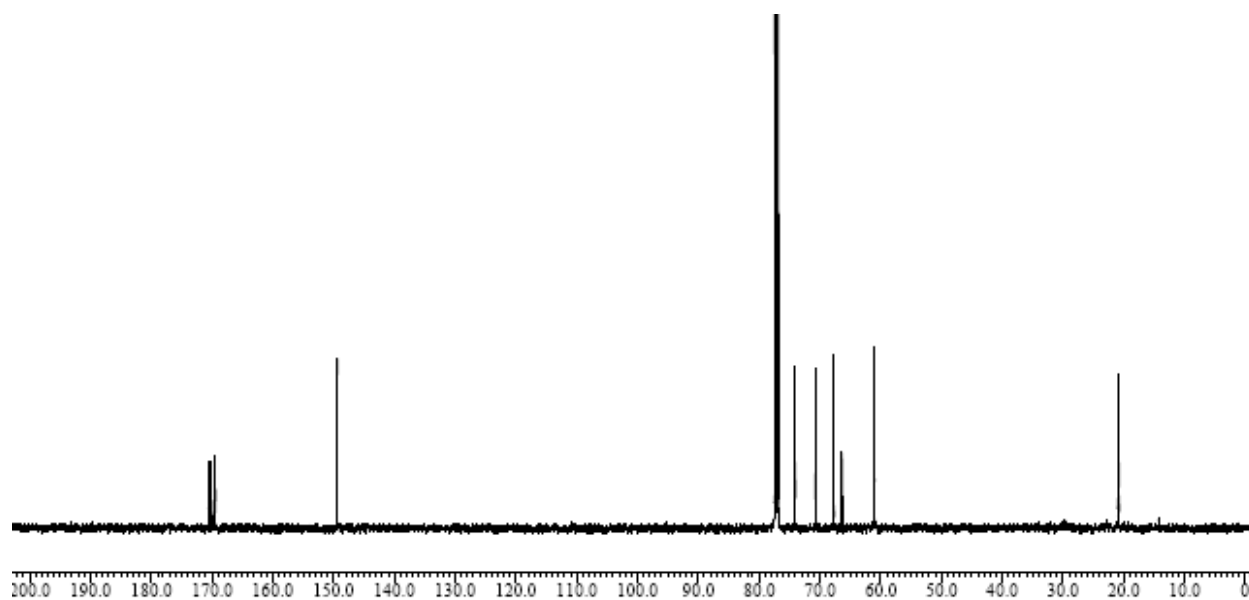


Figure 3.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound **5a**

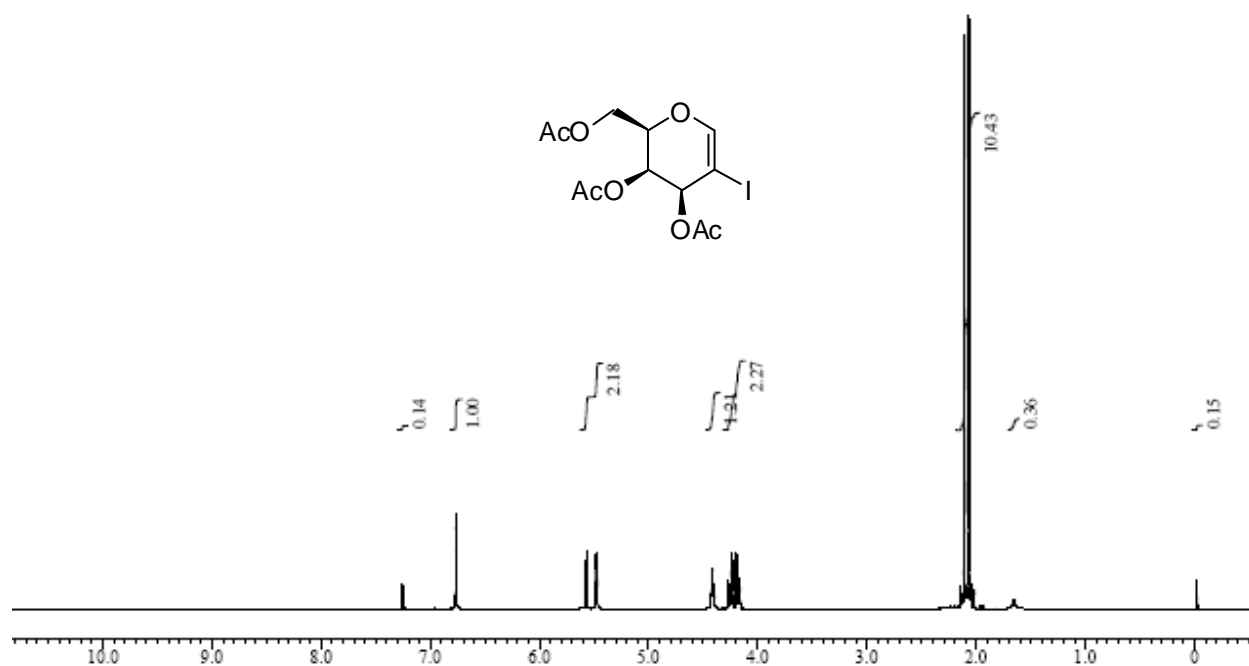


Figure 4.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 6a

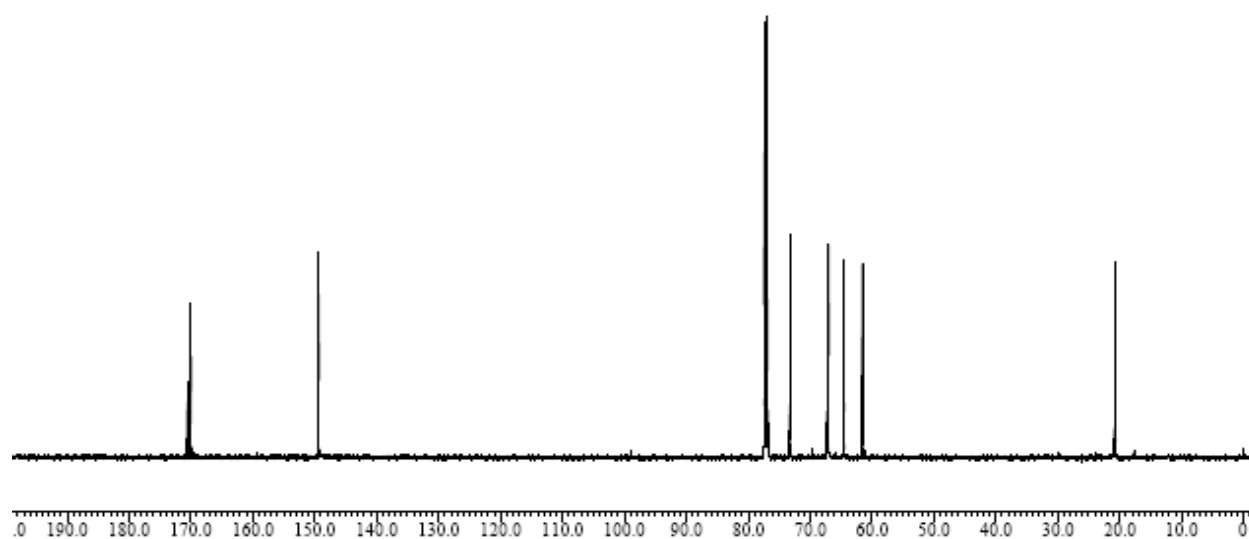


Figure 4.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 6a

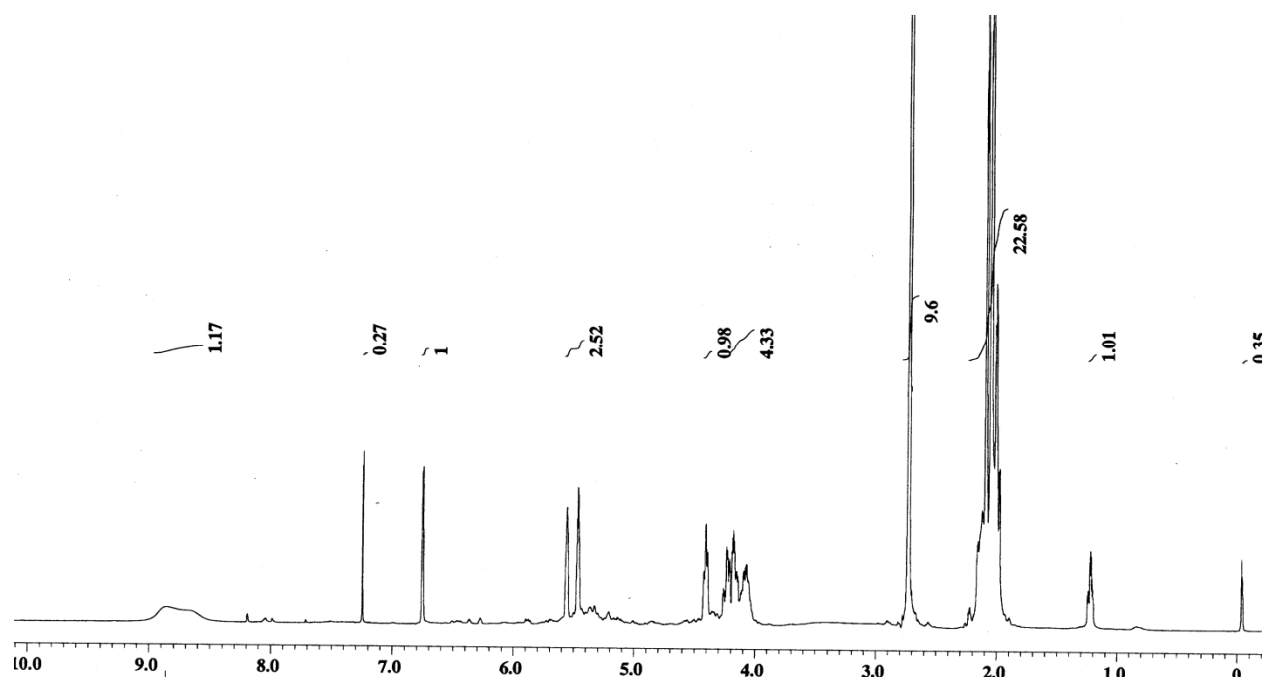


Figure 4.3: Crude ^1H NMR (400 MHz, CDCl_3) Spectrum of Compound 6a

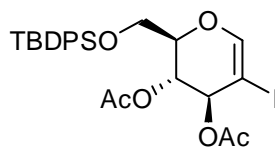


Figure 5.2: ^{13}C NMR (125 MHz, CDCl_3) Spectrum of Compound **7a**

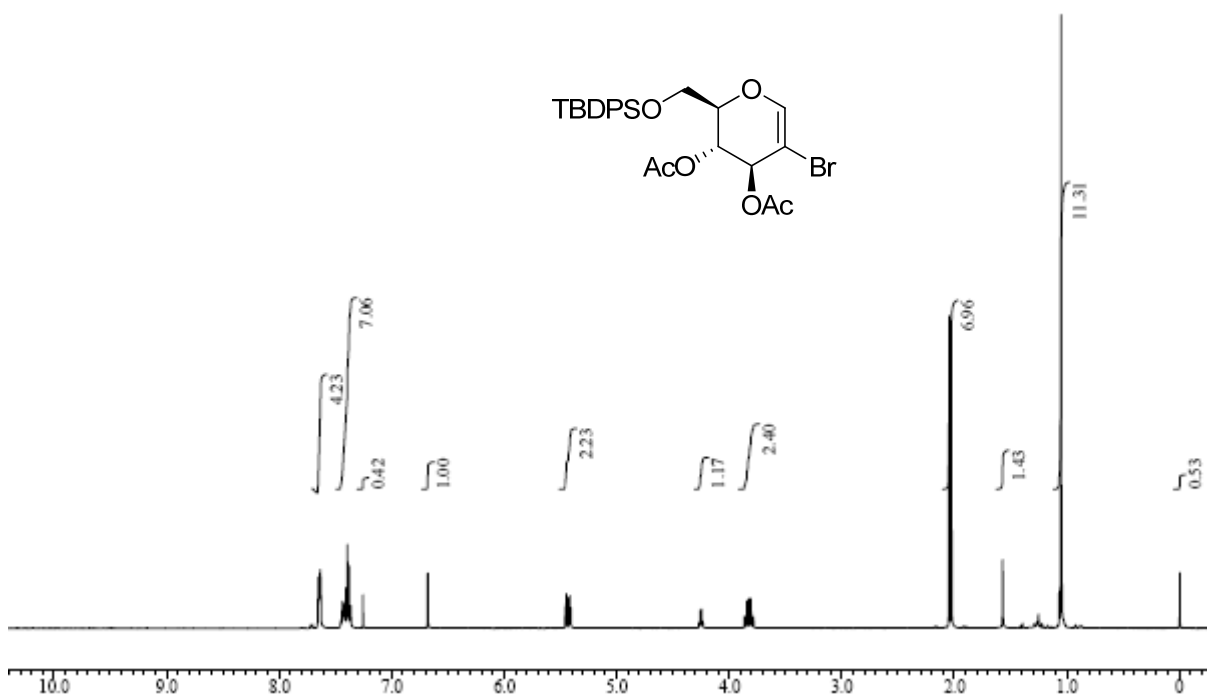


Figure 6.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound **7b**

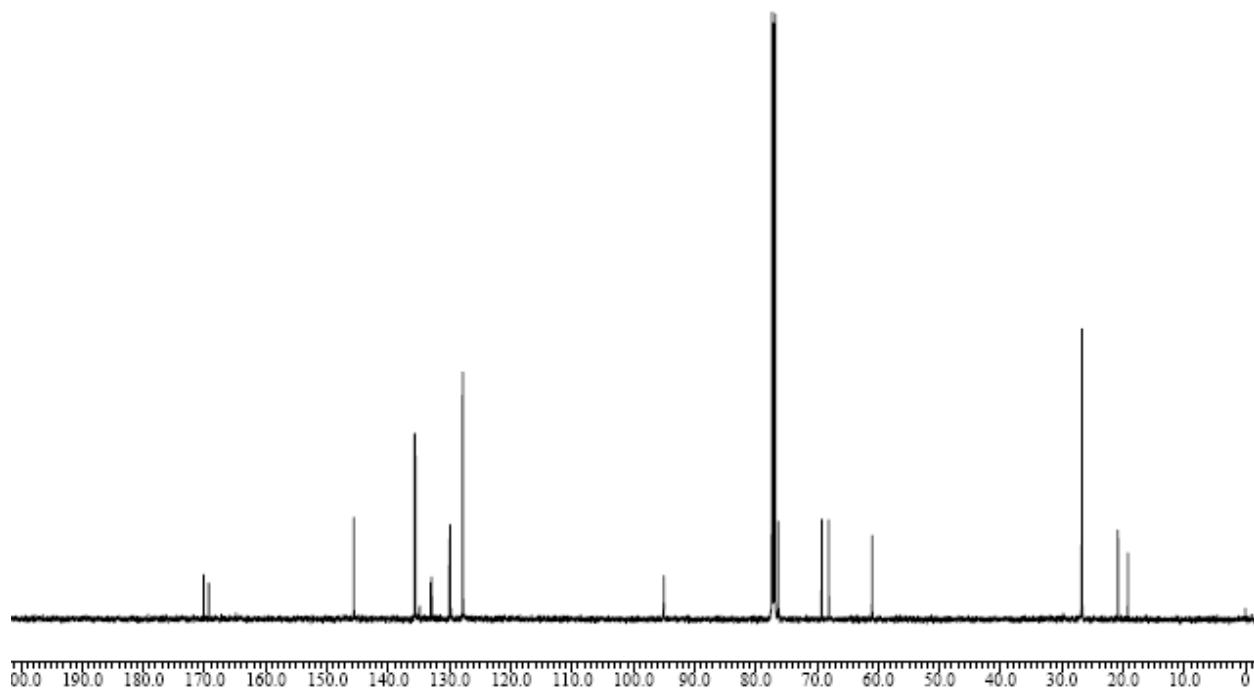


Figure 6.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound **7b**

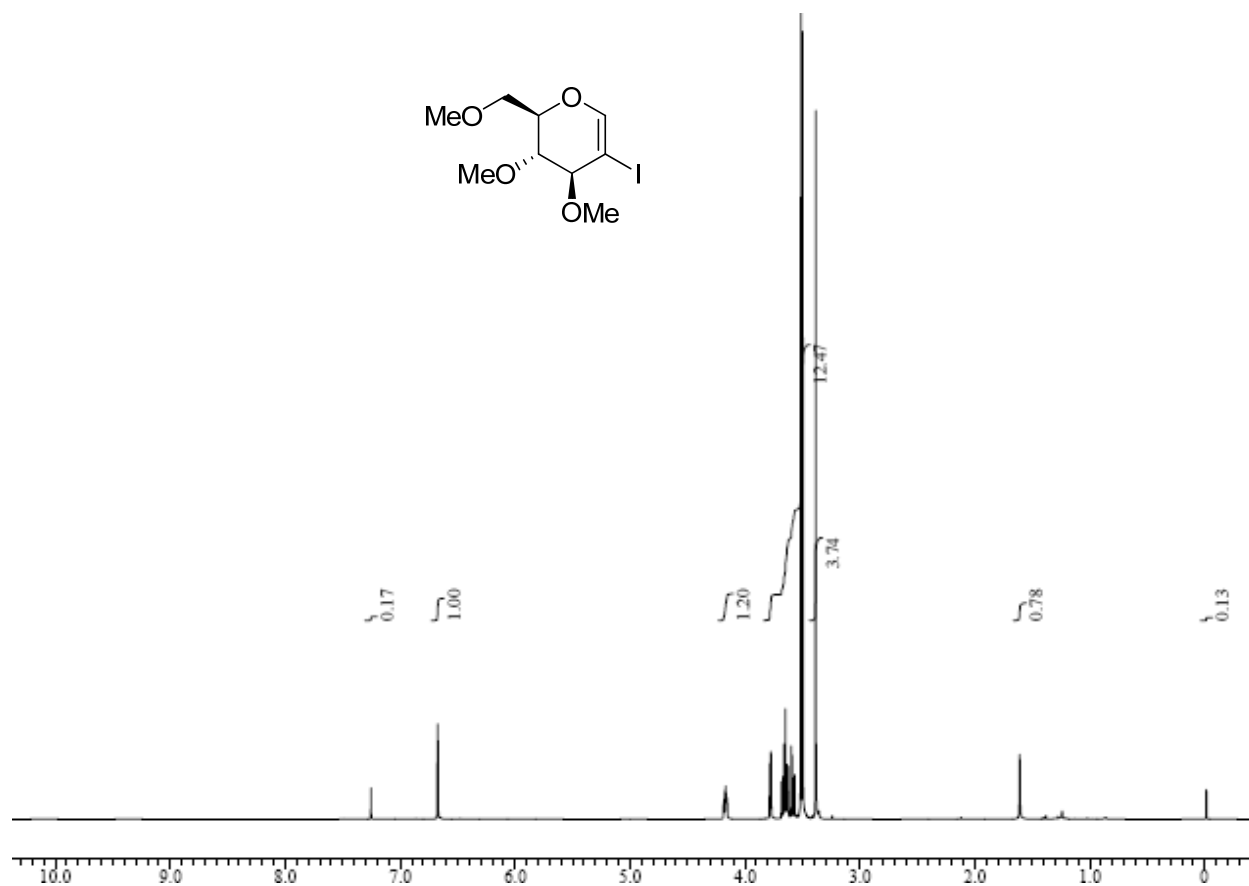


Figure 7.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 8a

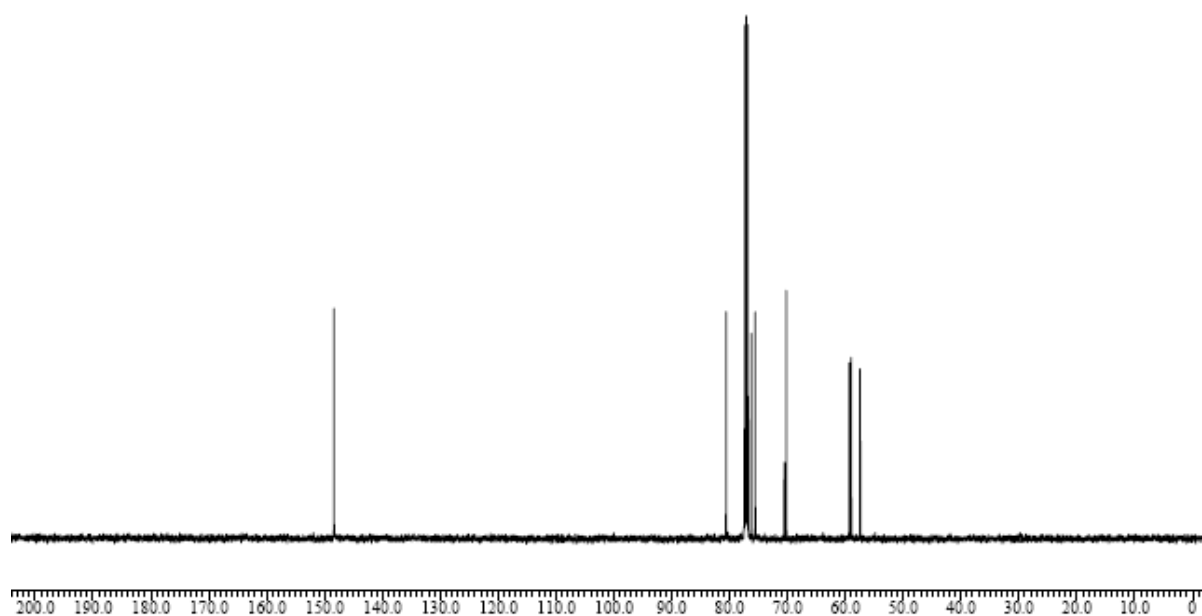


Figure 7.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 8a

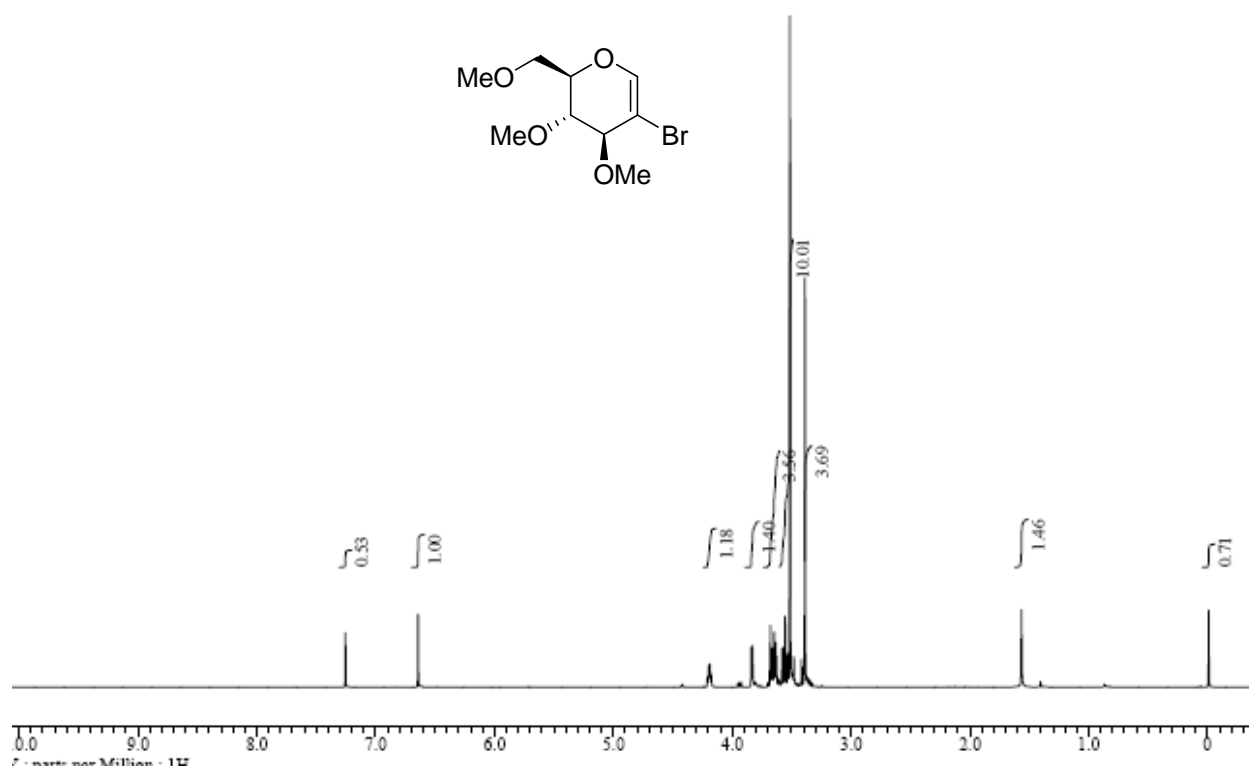


Figure 8.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 8b

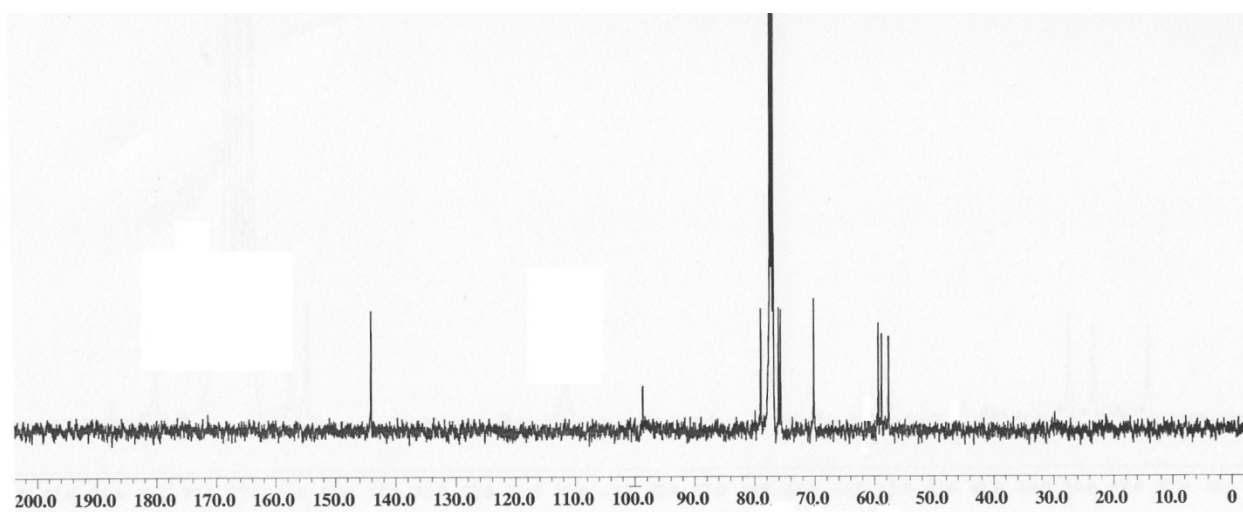


Figure 8.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 8b

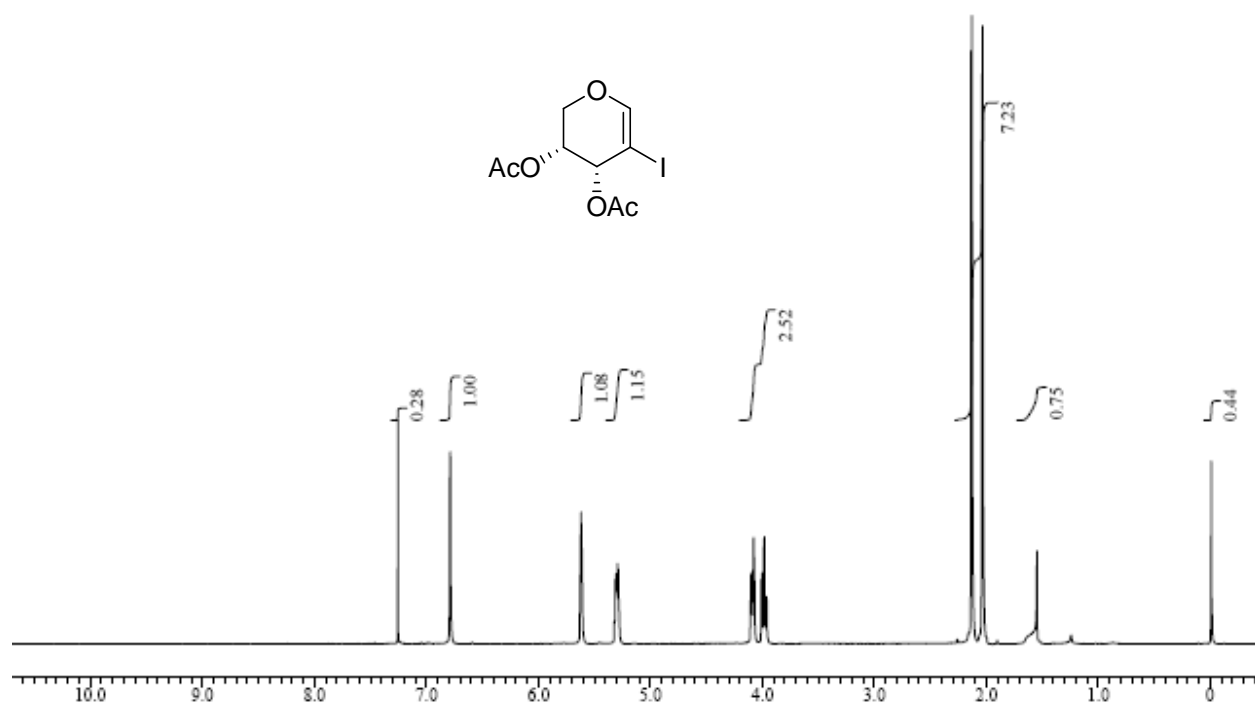


Figure 9.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 9a

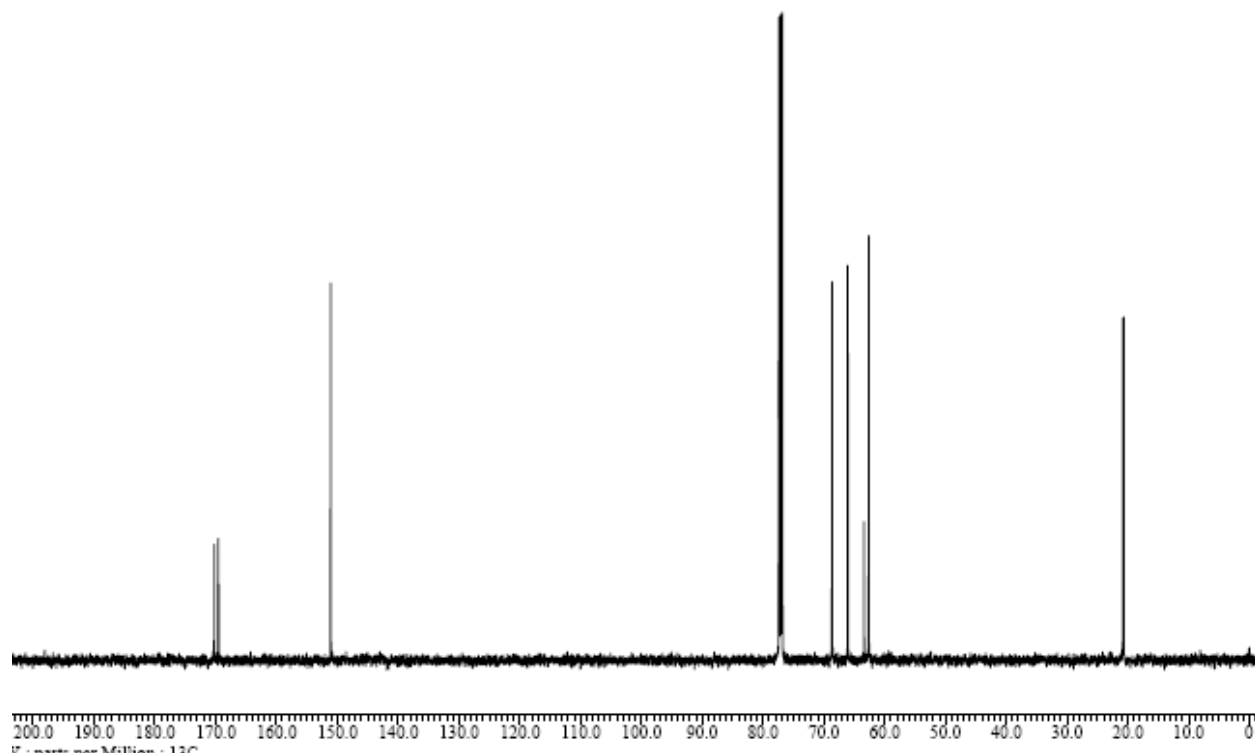


Figure 9.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 9a

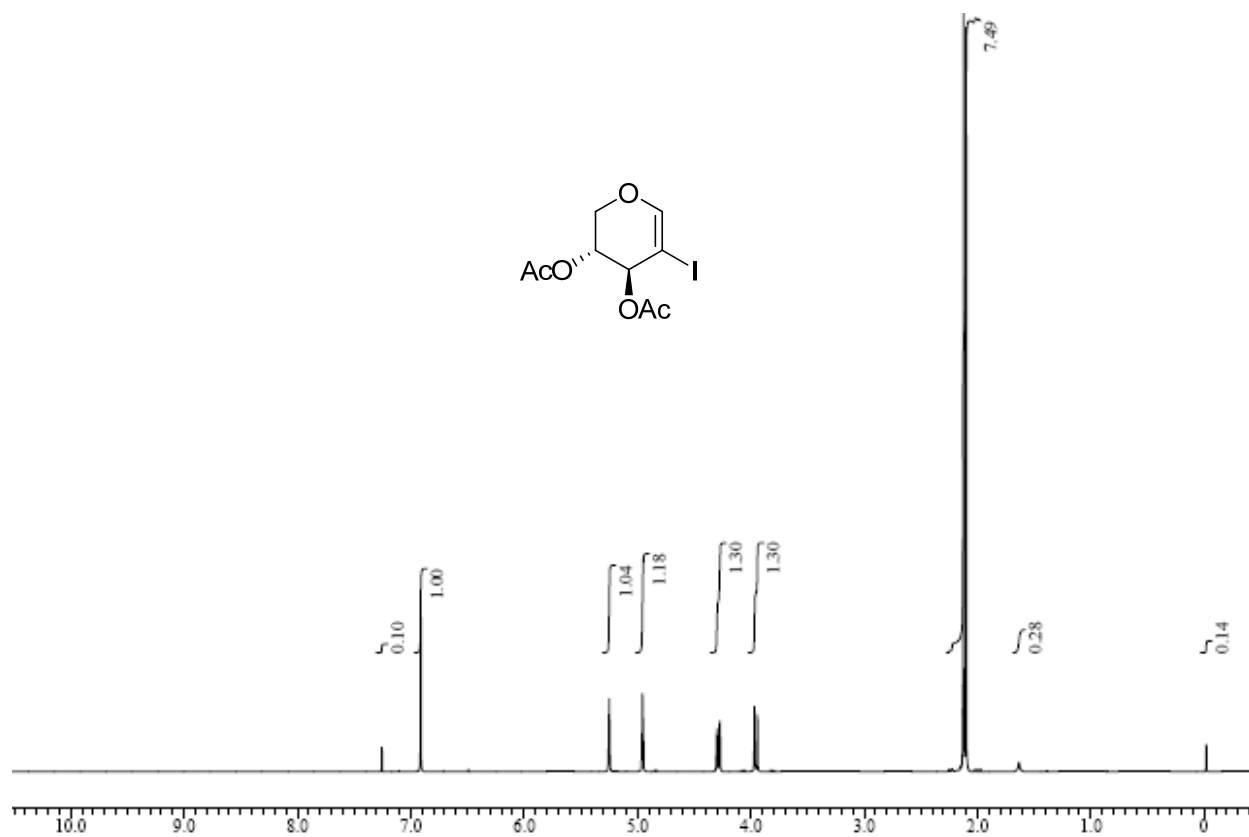


Figure 10.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 10a

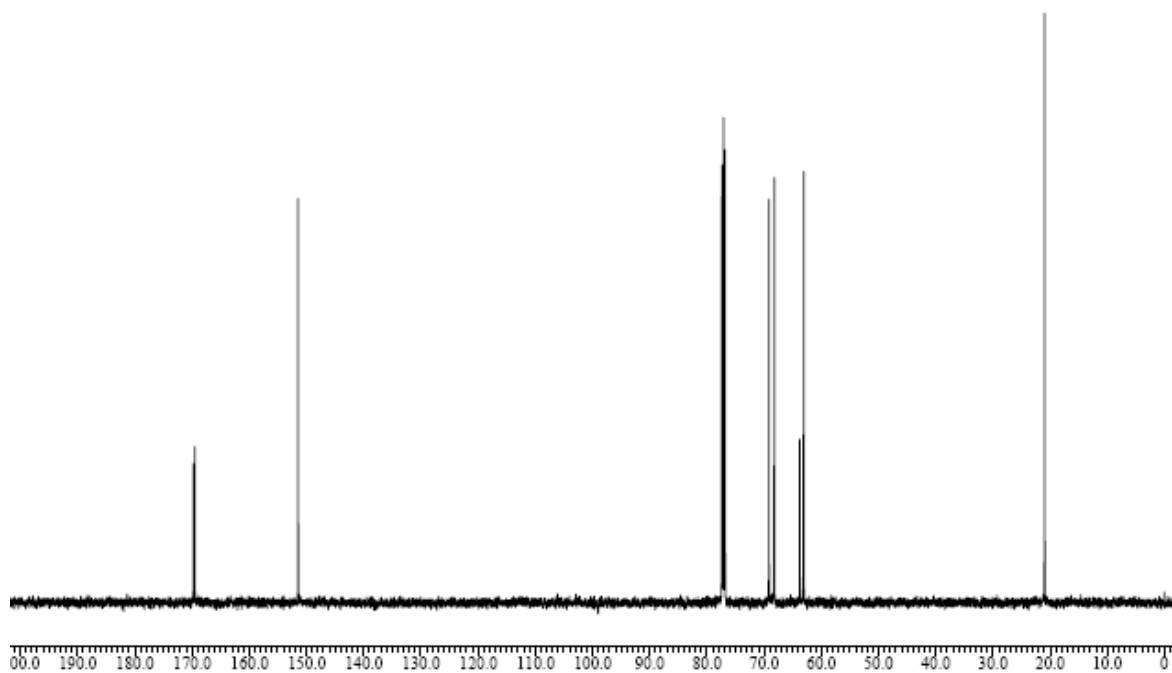


Figure 10.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 10a

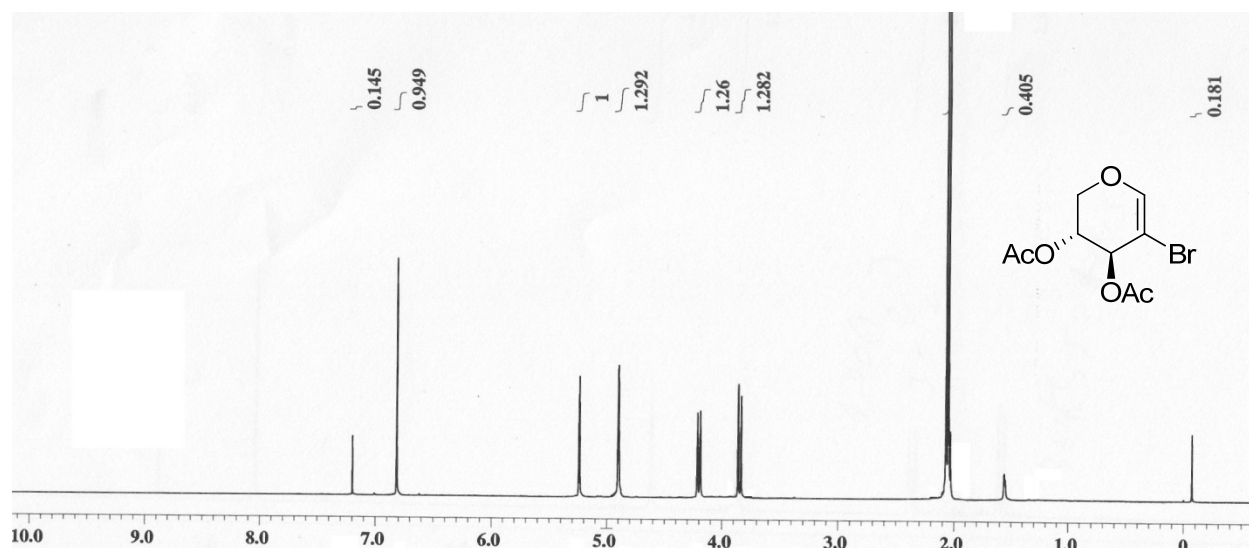


Figure 11.1: ^1H NMR (500 MHz) , CDCl_3 Spectrum of Compound **10b**

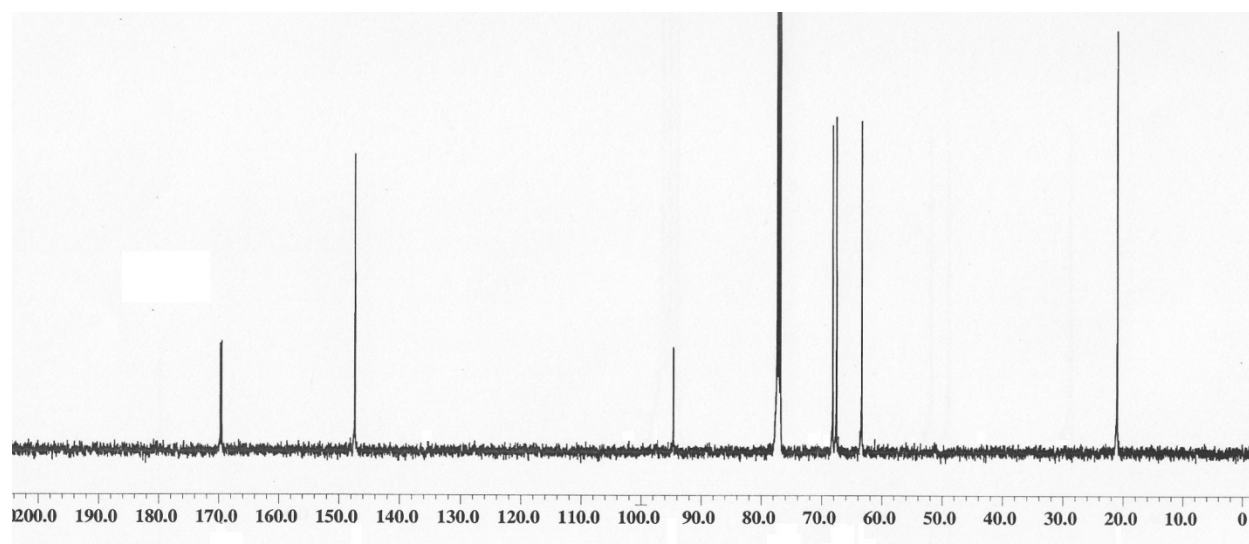


Figure 11.2: ^{13}C NMR (125 MHz, CDCl_3) Spectrum of Compound **10b**

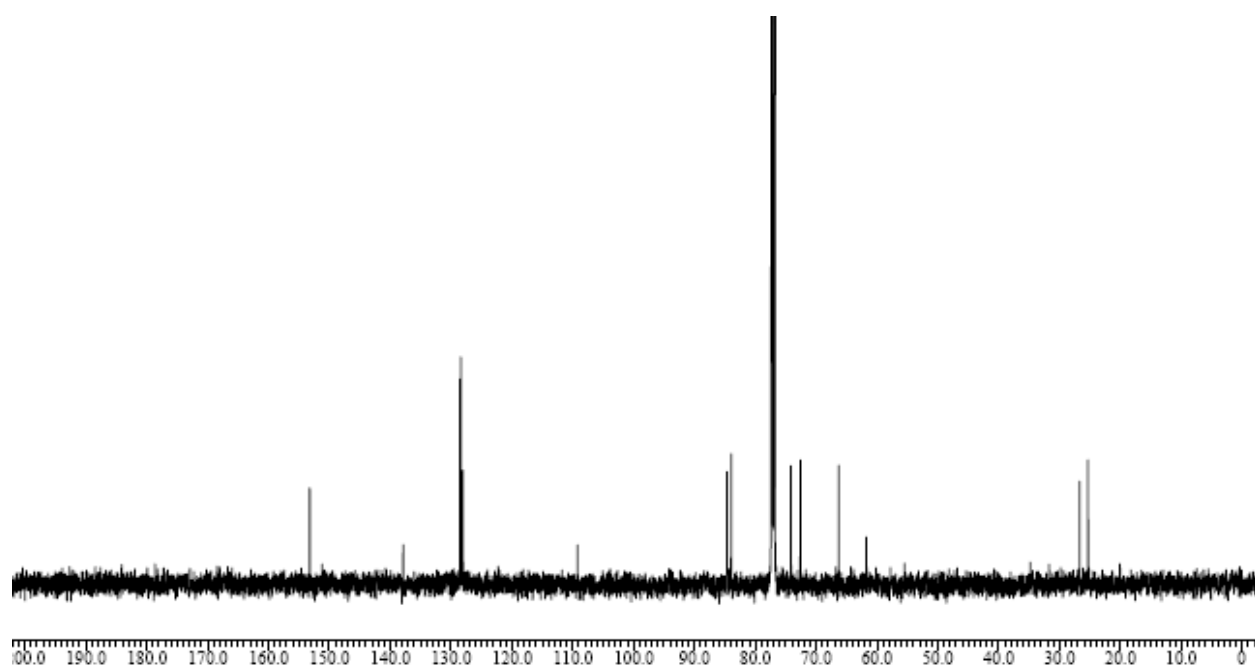
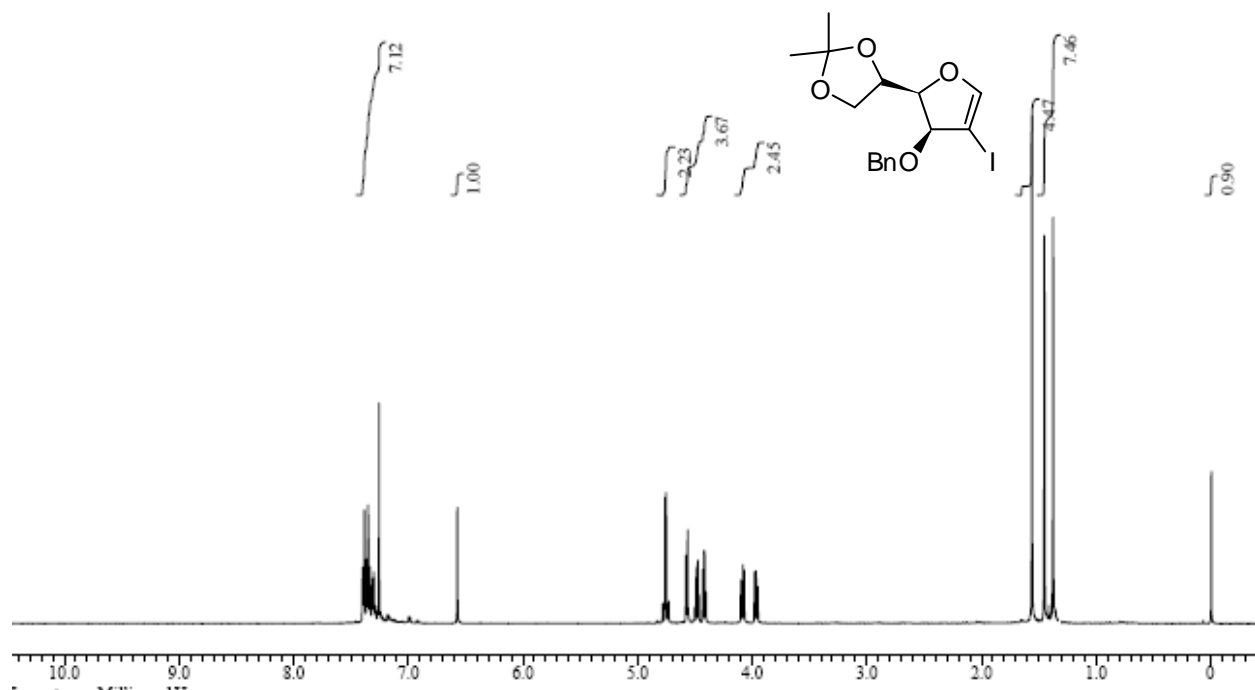
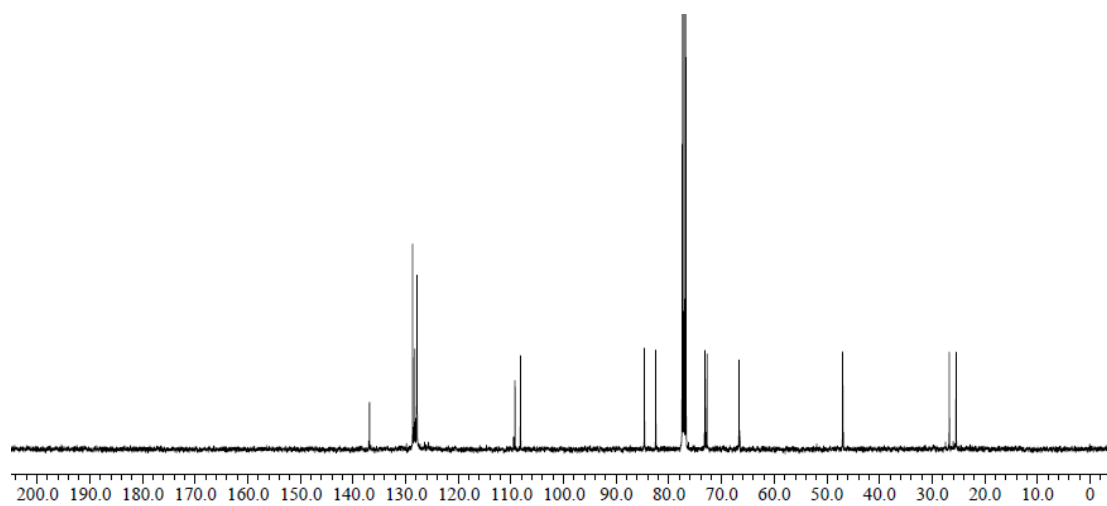
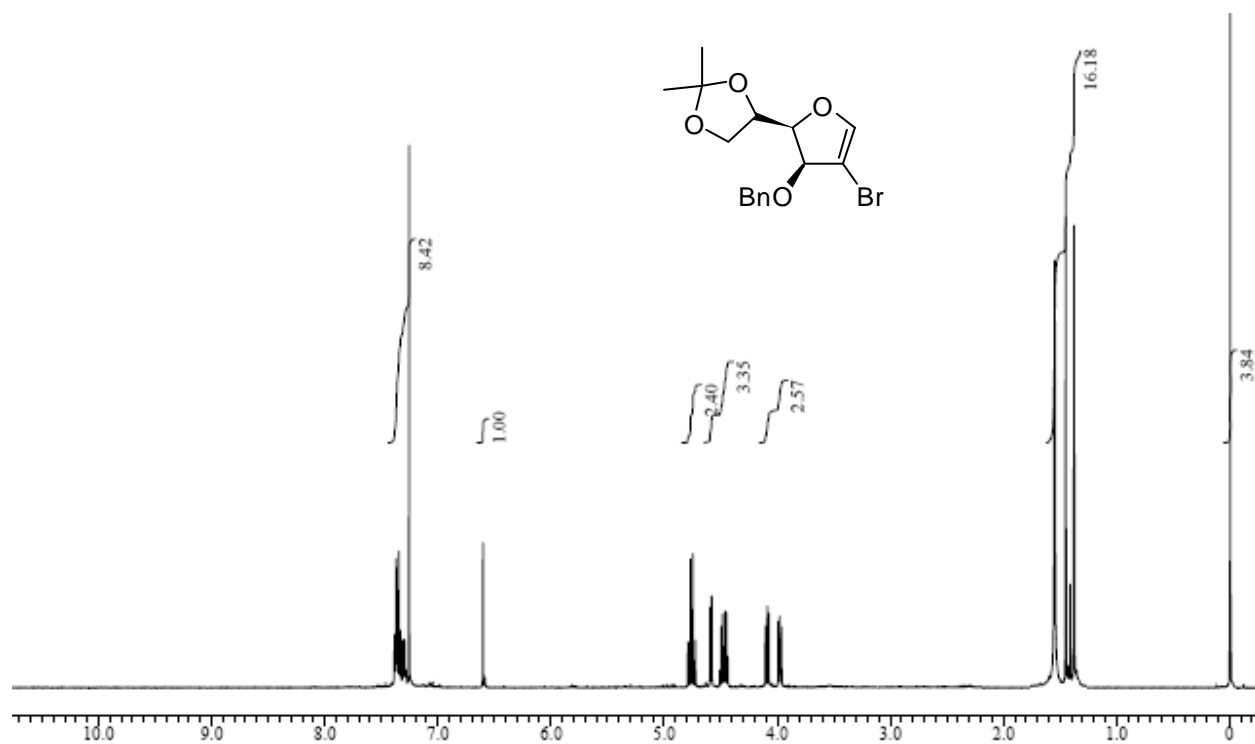


Figure 12.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 11a



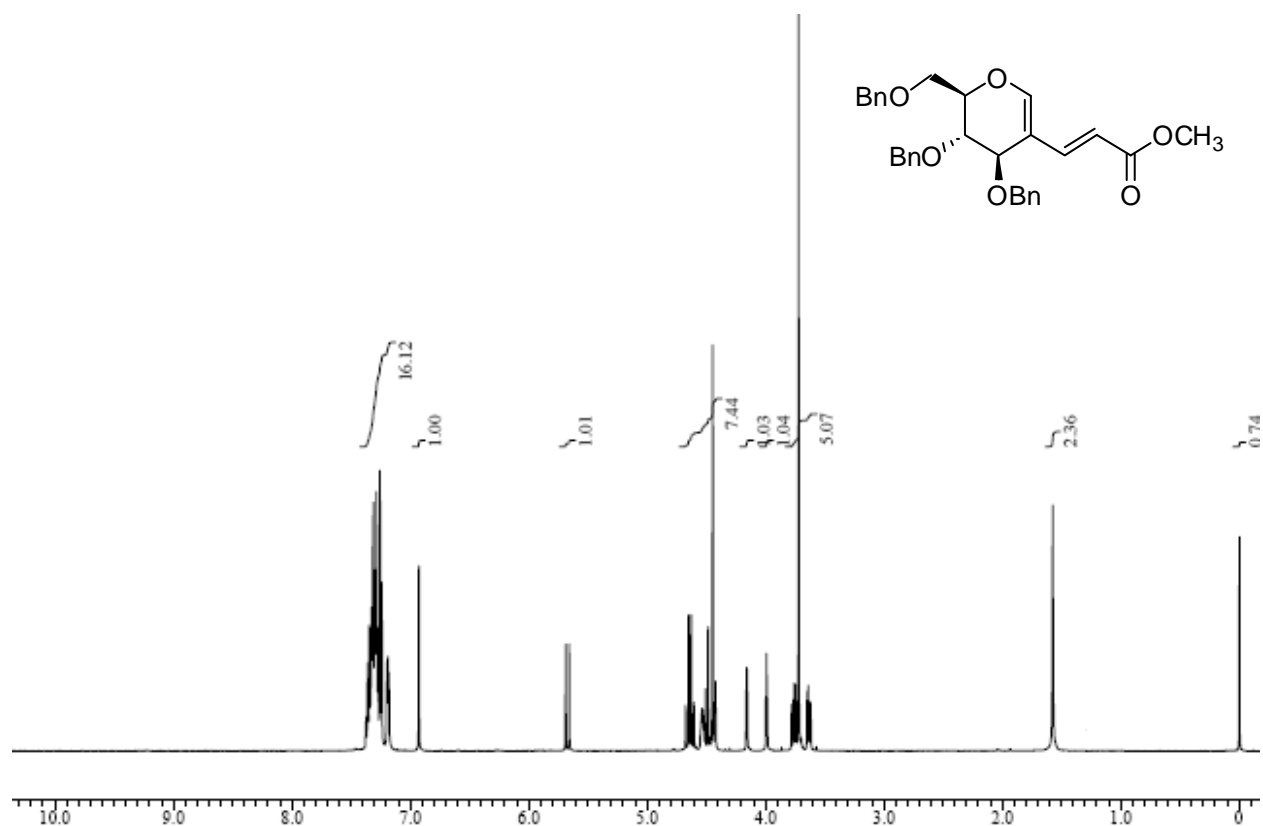


Figure 14.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 12

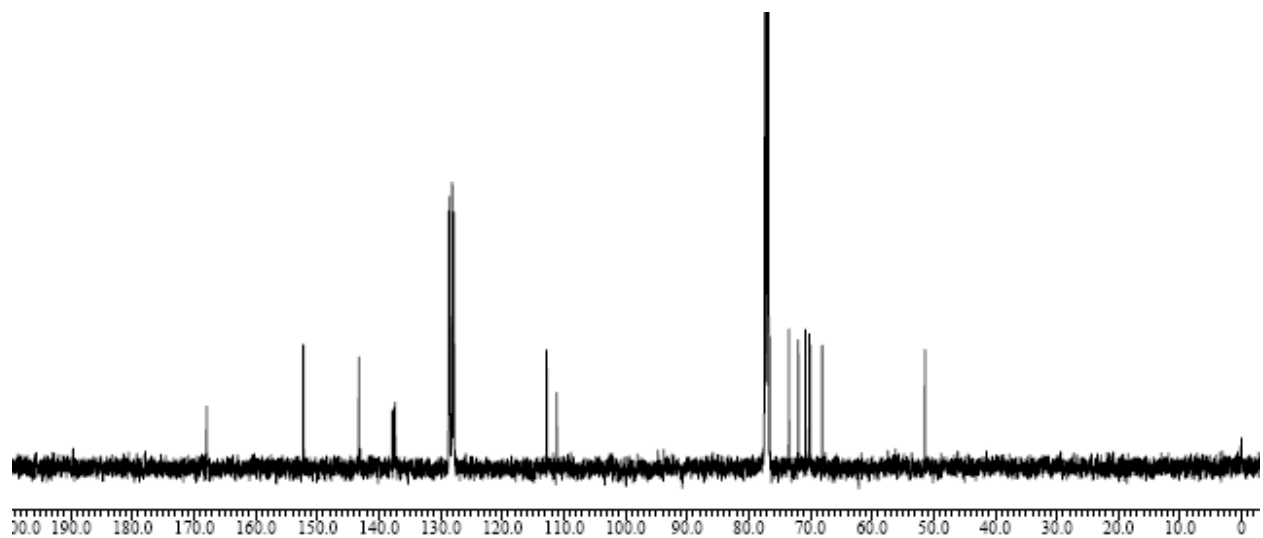


Figure 14.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 12

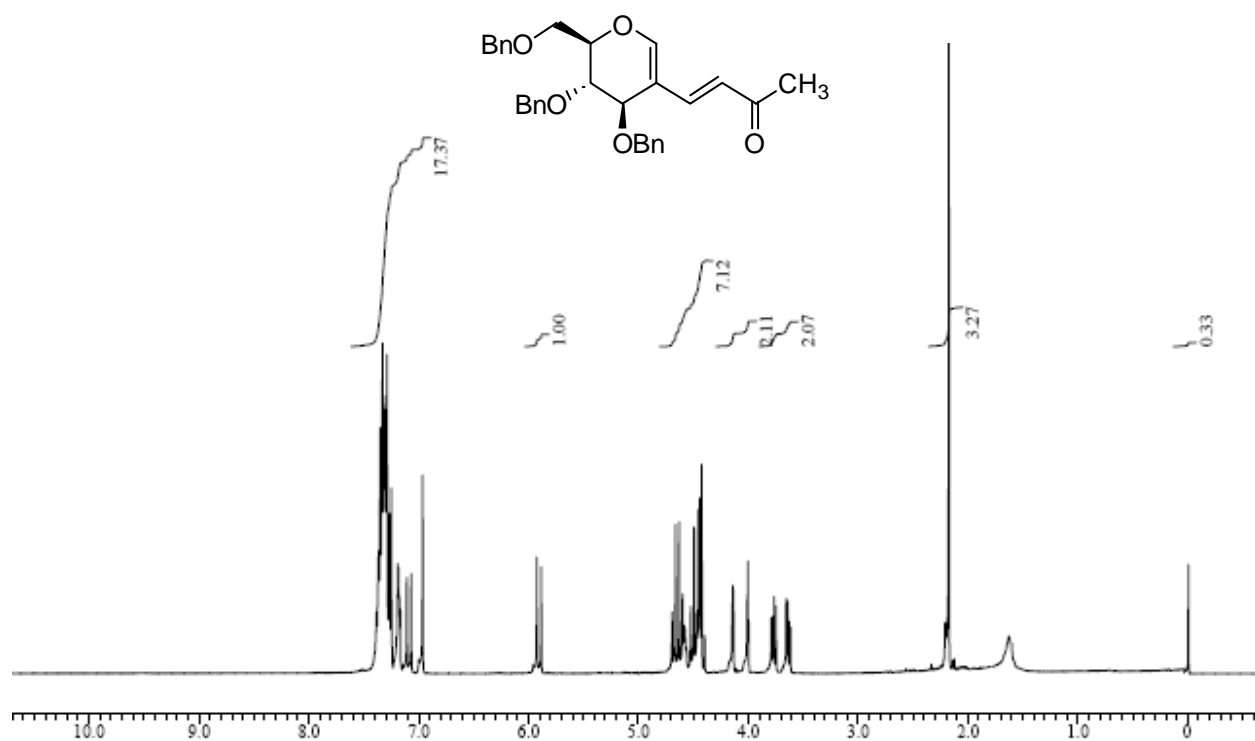


Figure 15.1: ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound 13

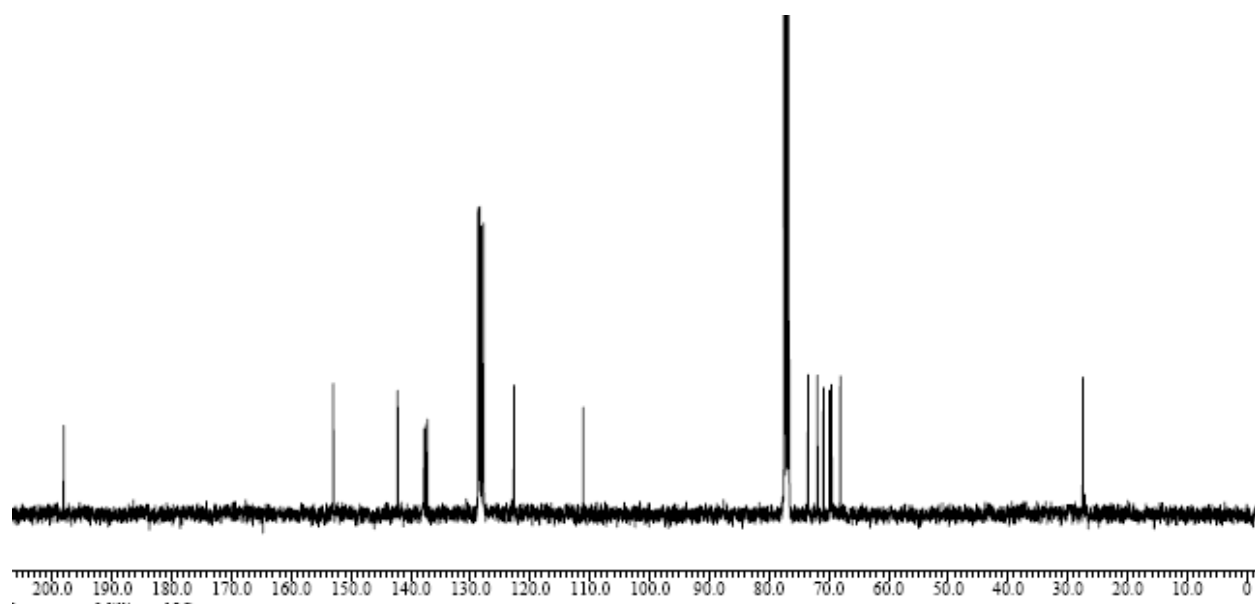


Figure 15.2: ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 13

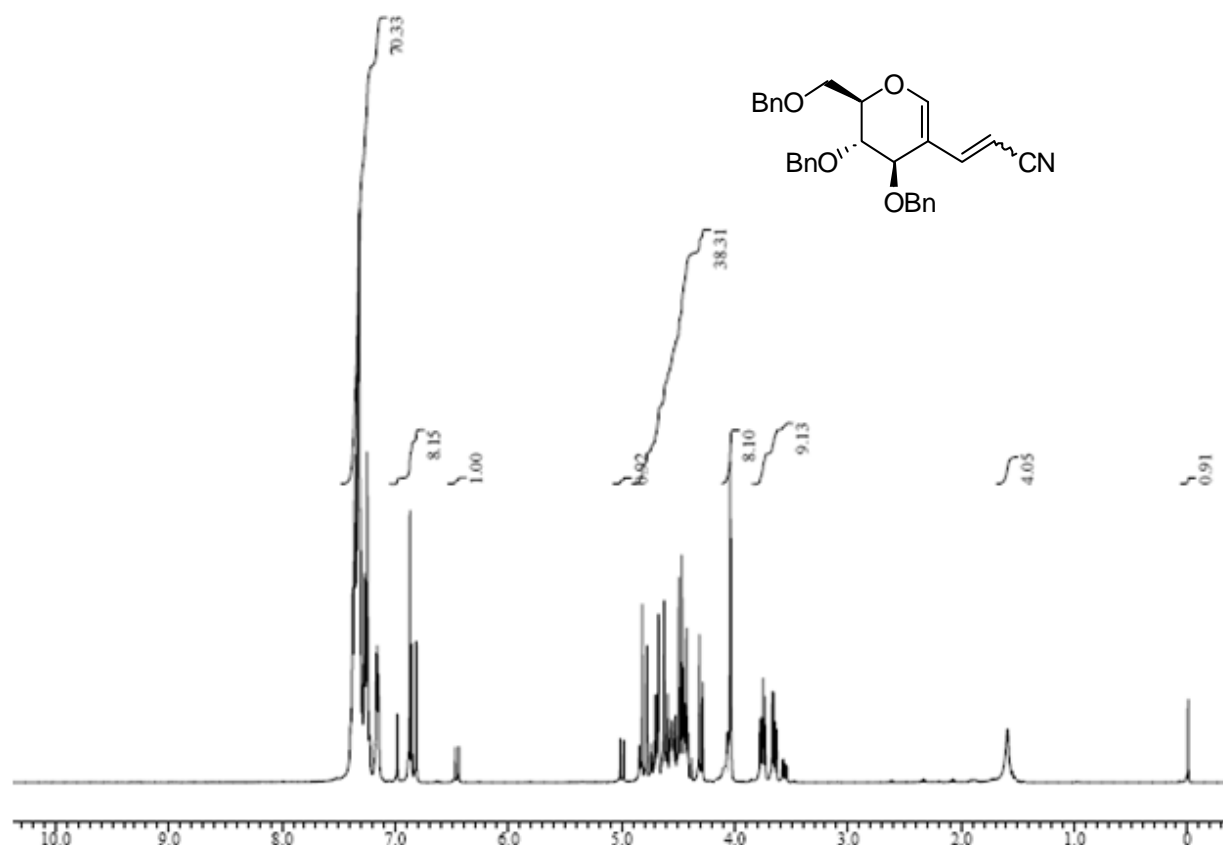


Figure 16.1: ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound 14

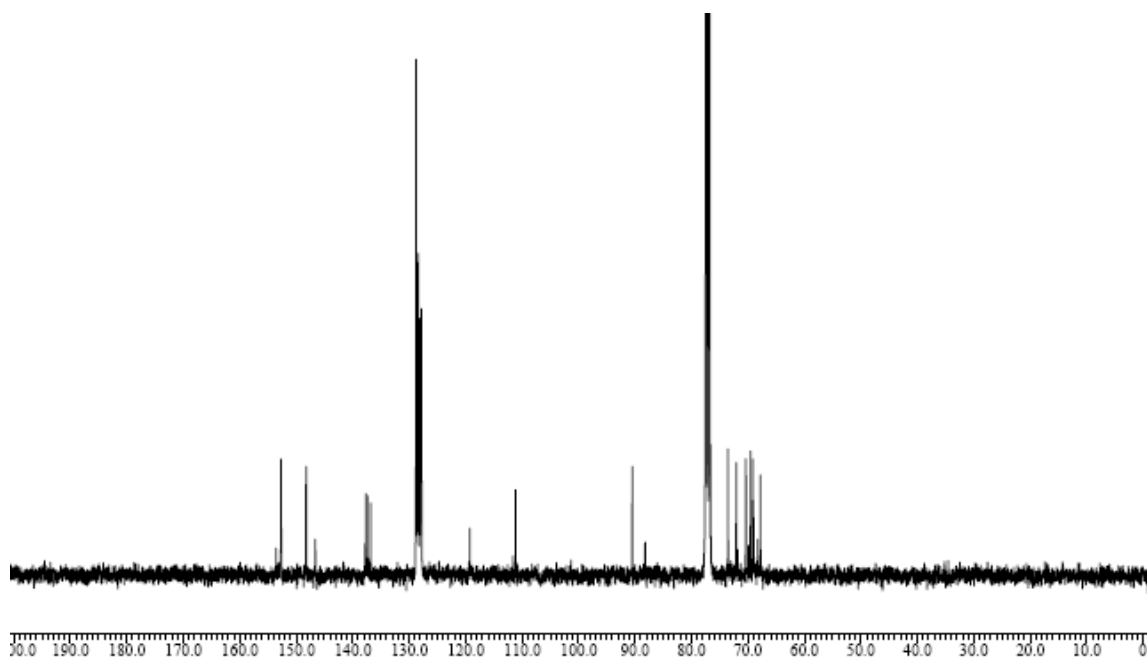


Figure 16.2: ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 14

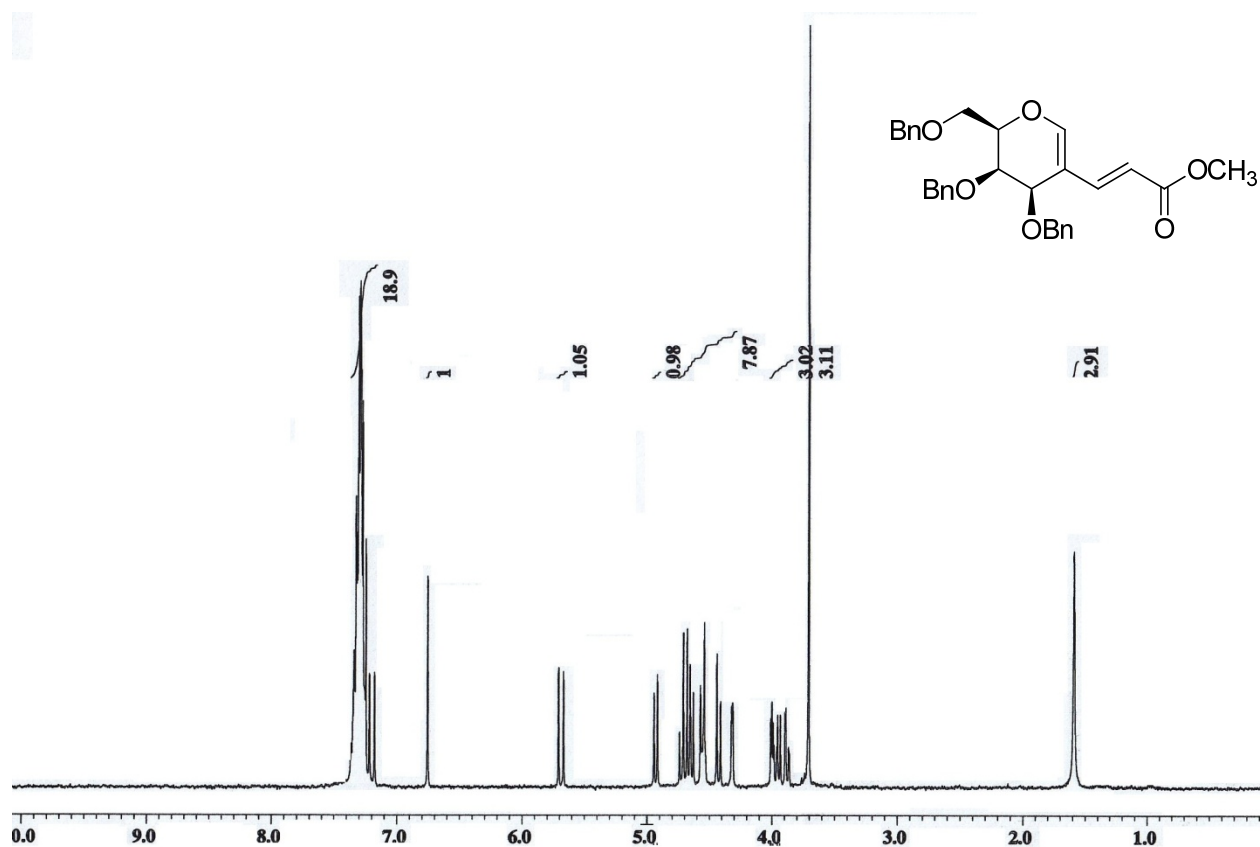


Figure 17.1: ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound 15

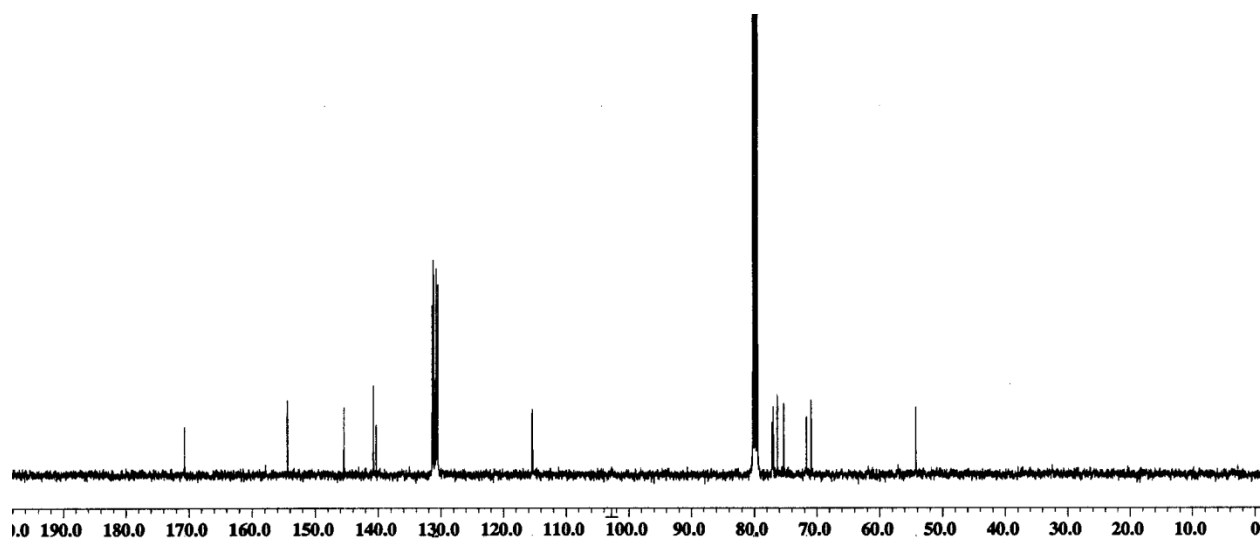


Figure 17.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 15

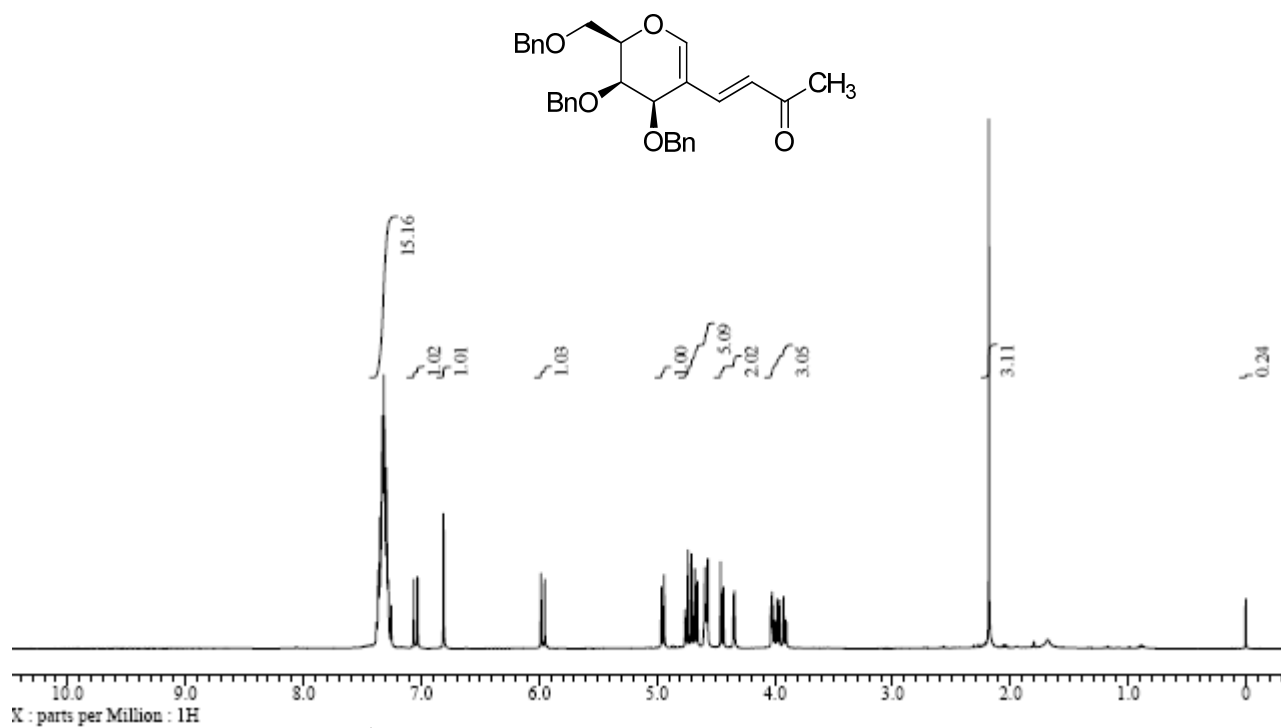


Figure 18.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 16

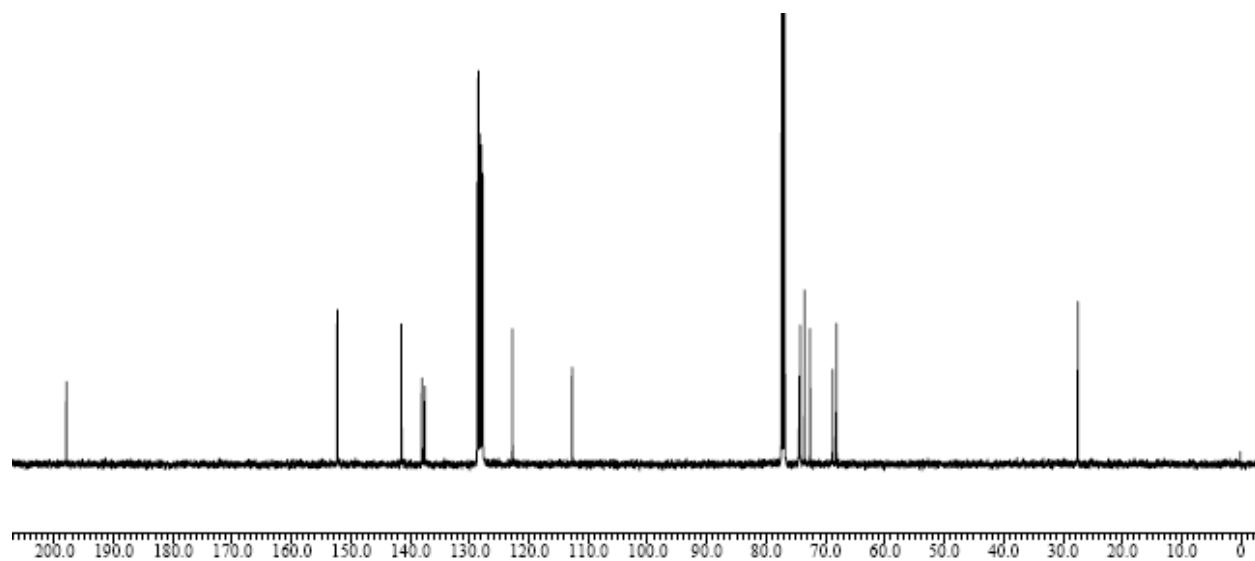


Figure 18.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 16

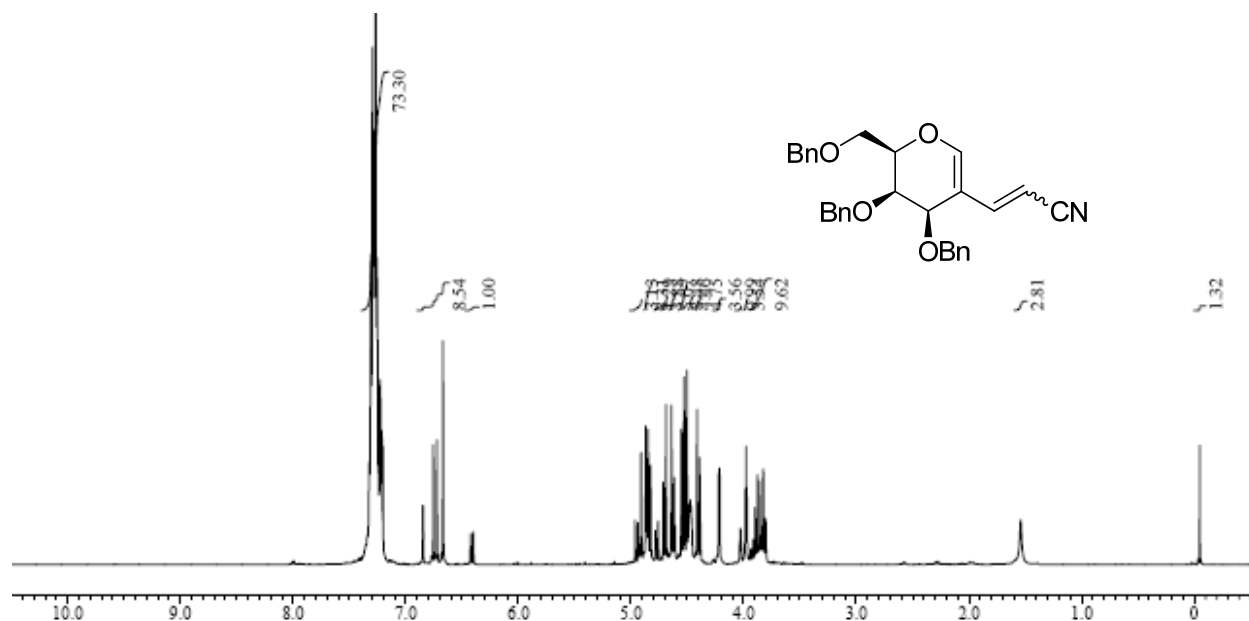


Figure 19.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 17

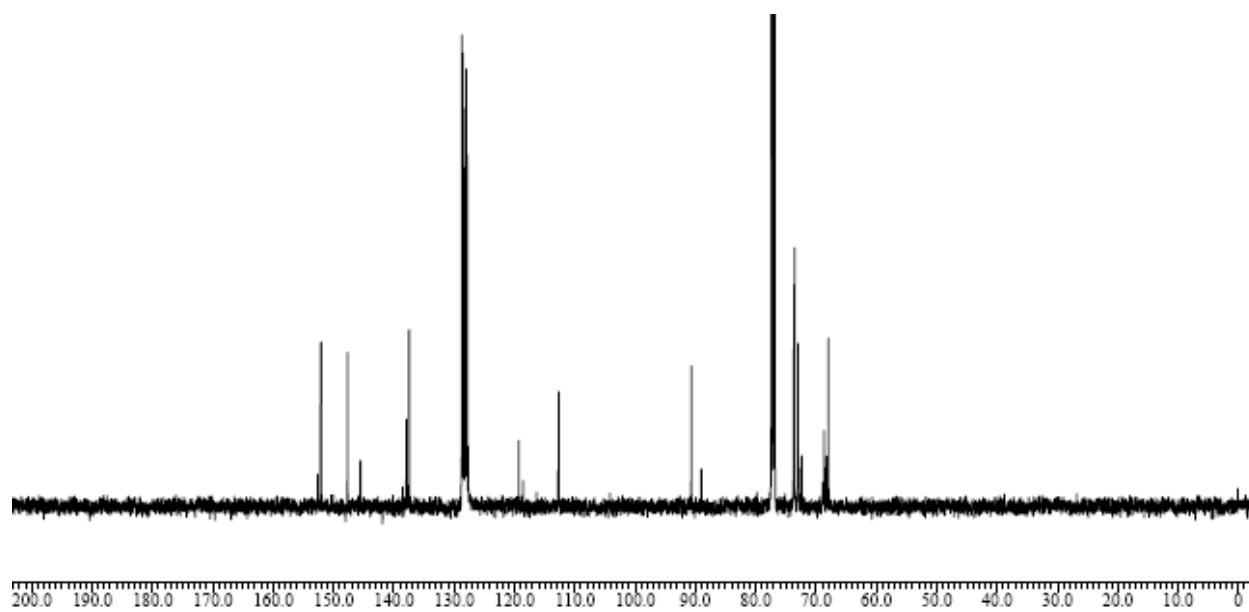


Figure 19.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 17

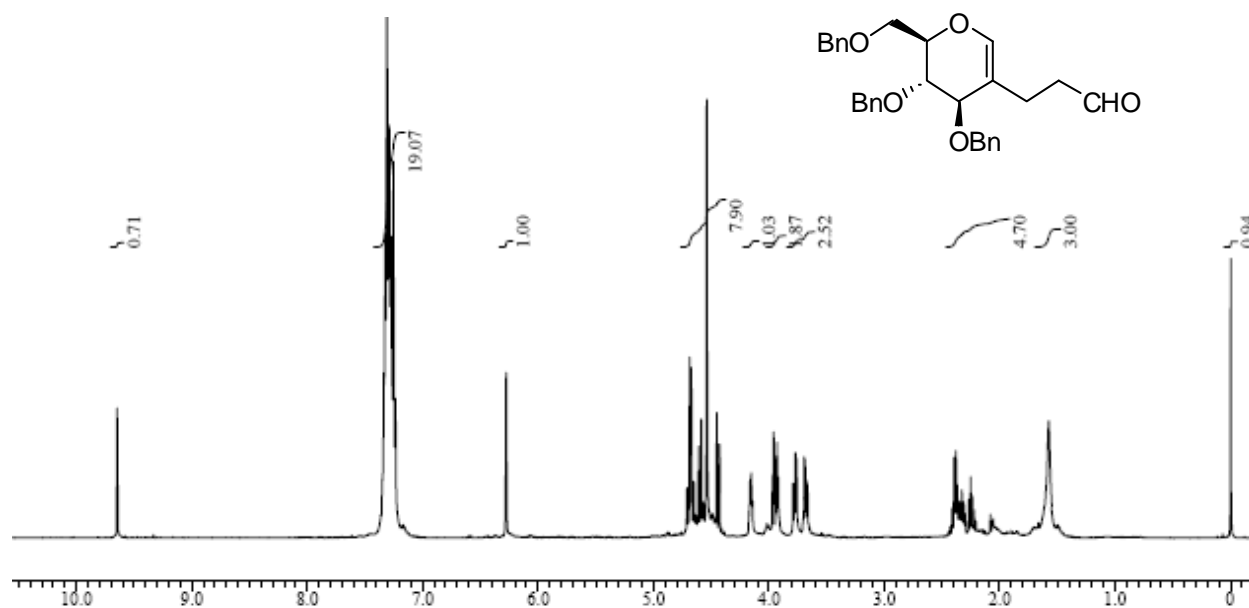


Figure 20.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 18

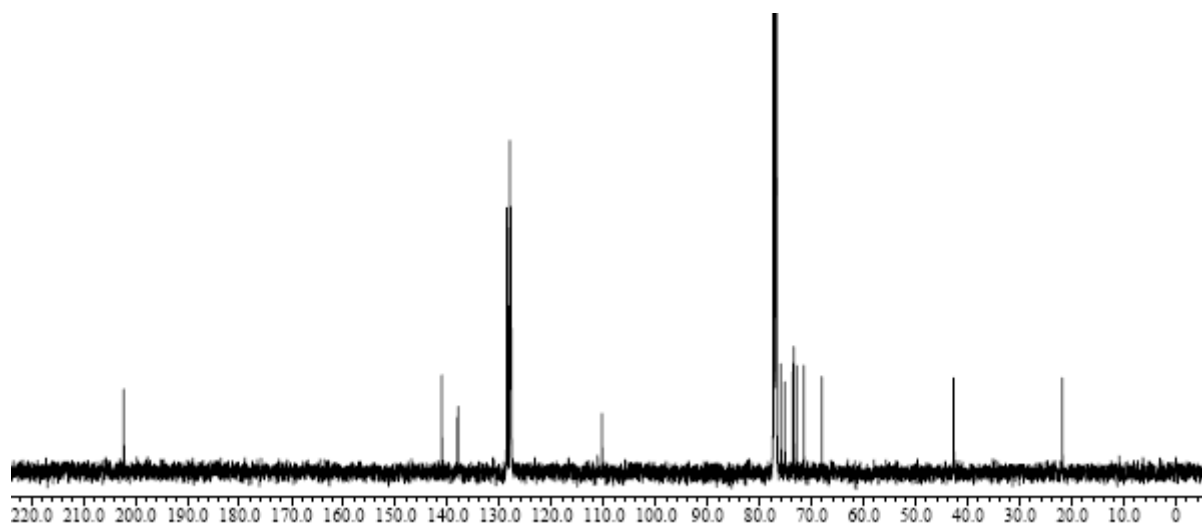


Figure 20.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 18

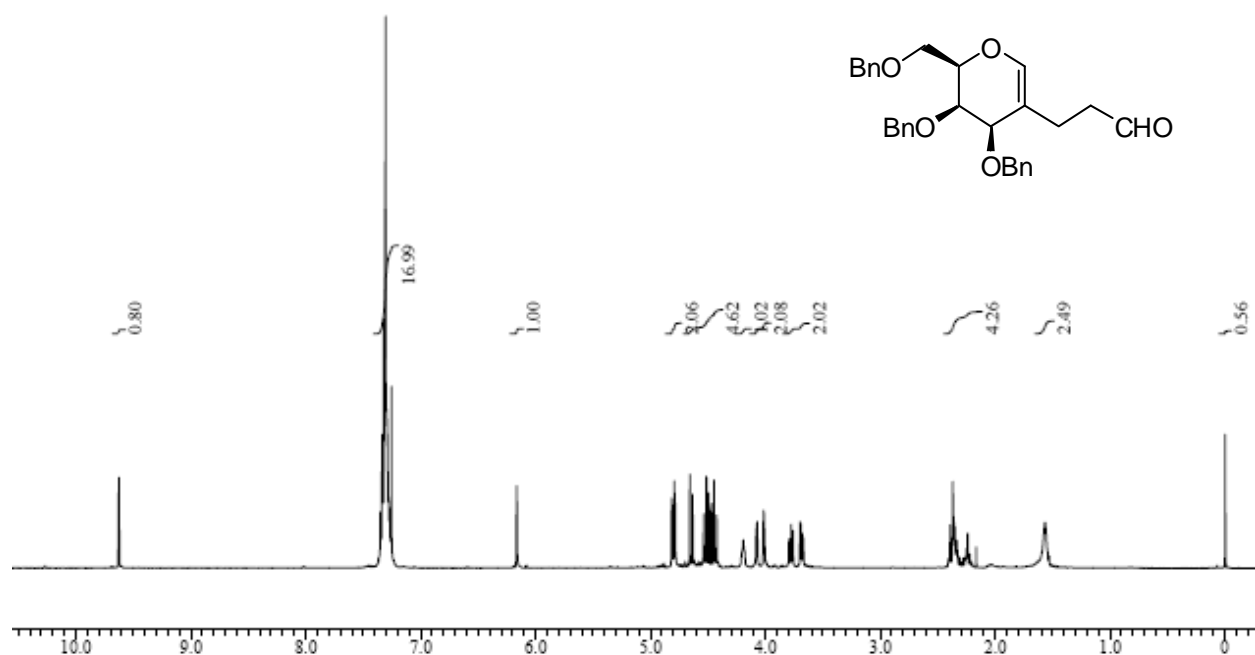


Figure 21.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 19

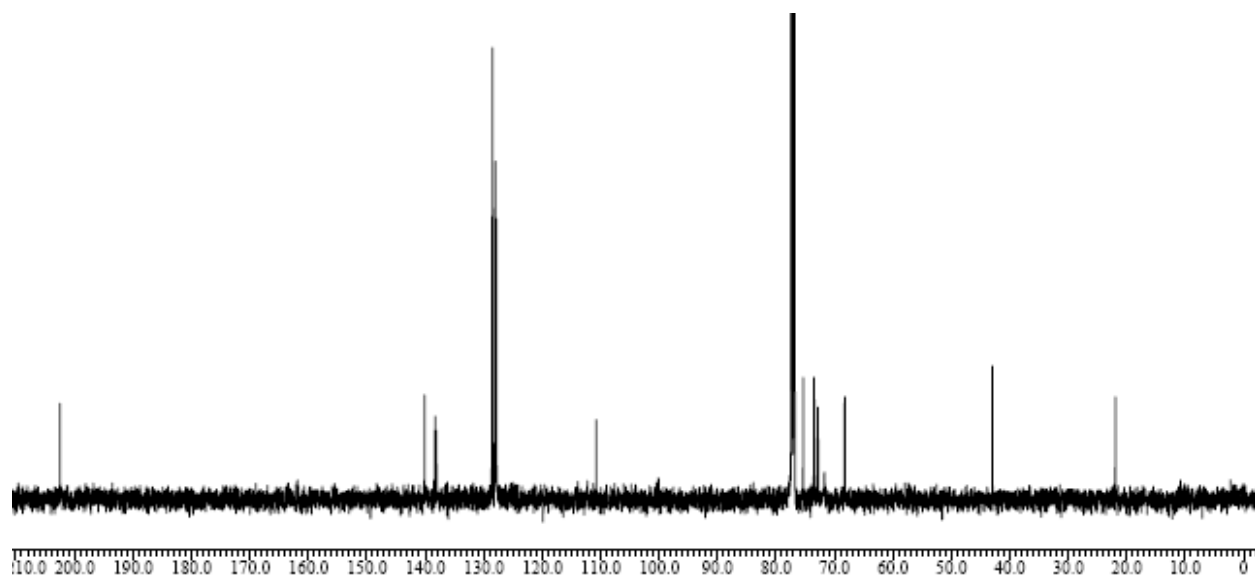


Figure 21.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 19

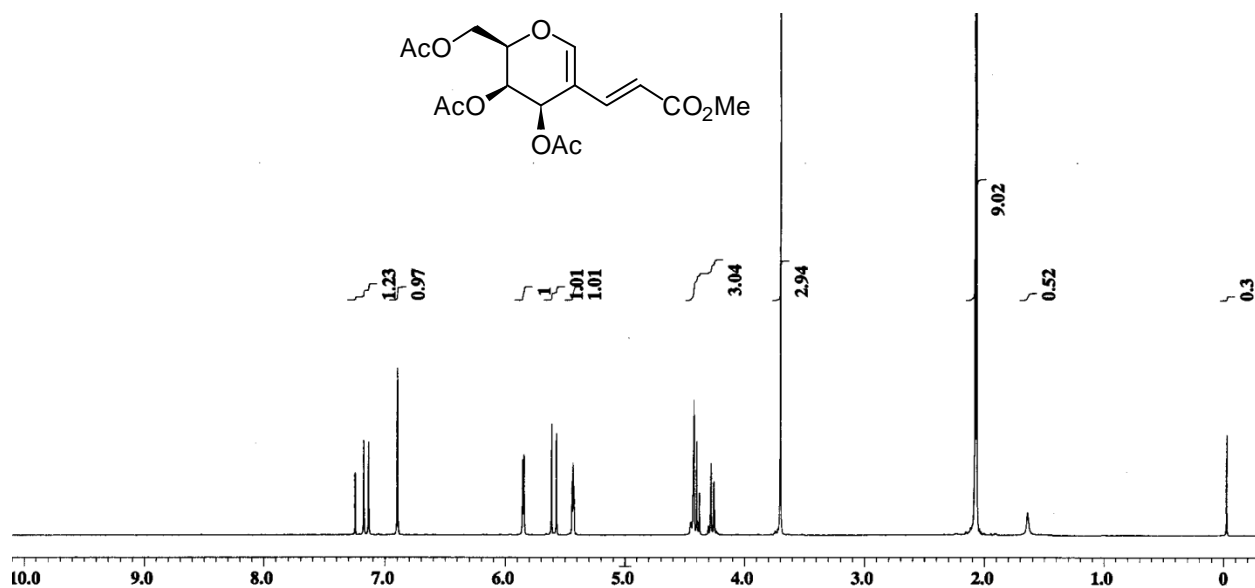


Figure 22.1: ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound 20

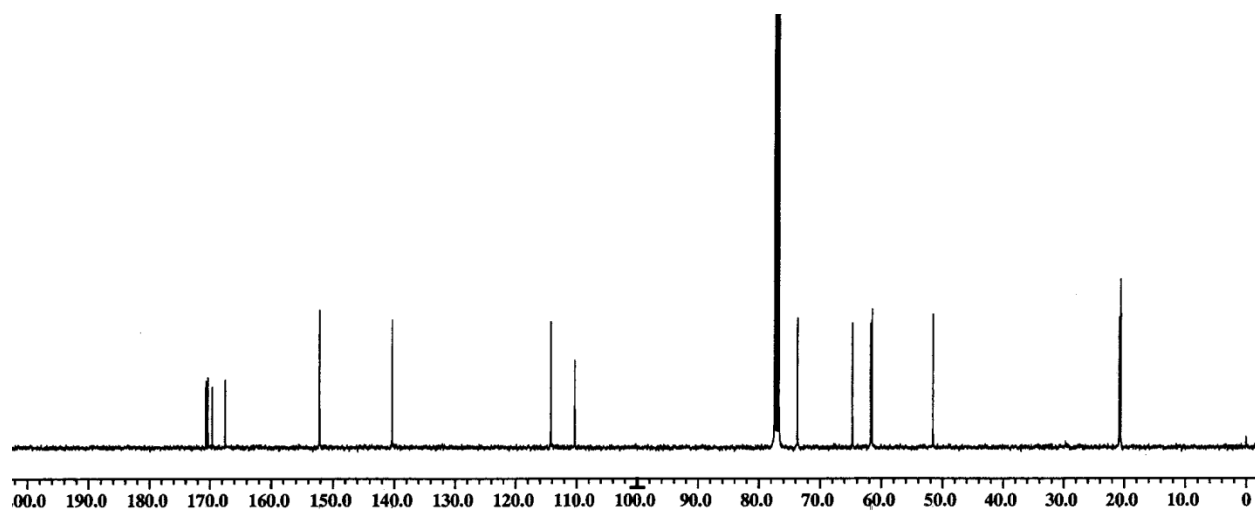


Figure 22.2: ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 20

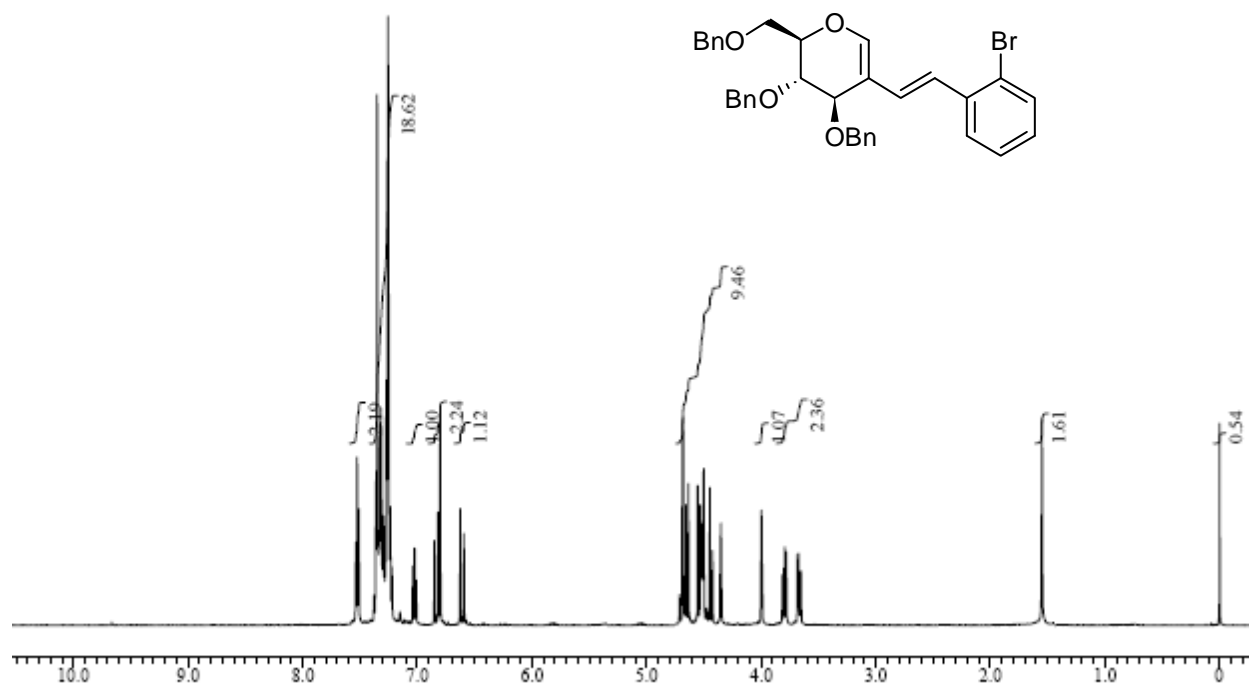


Figure 23.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 21

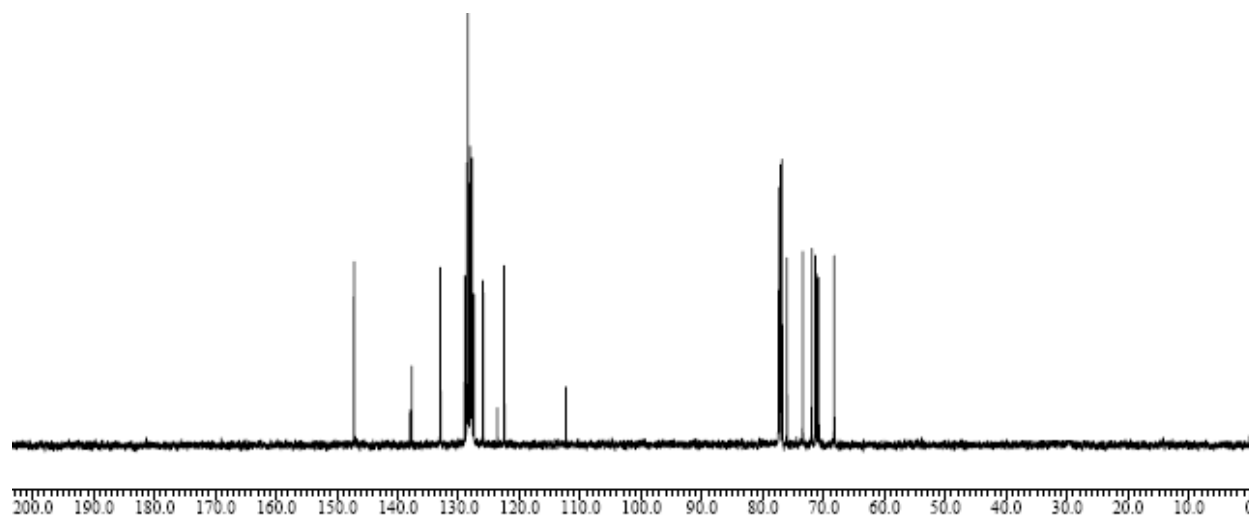


Figure 23.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 21

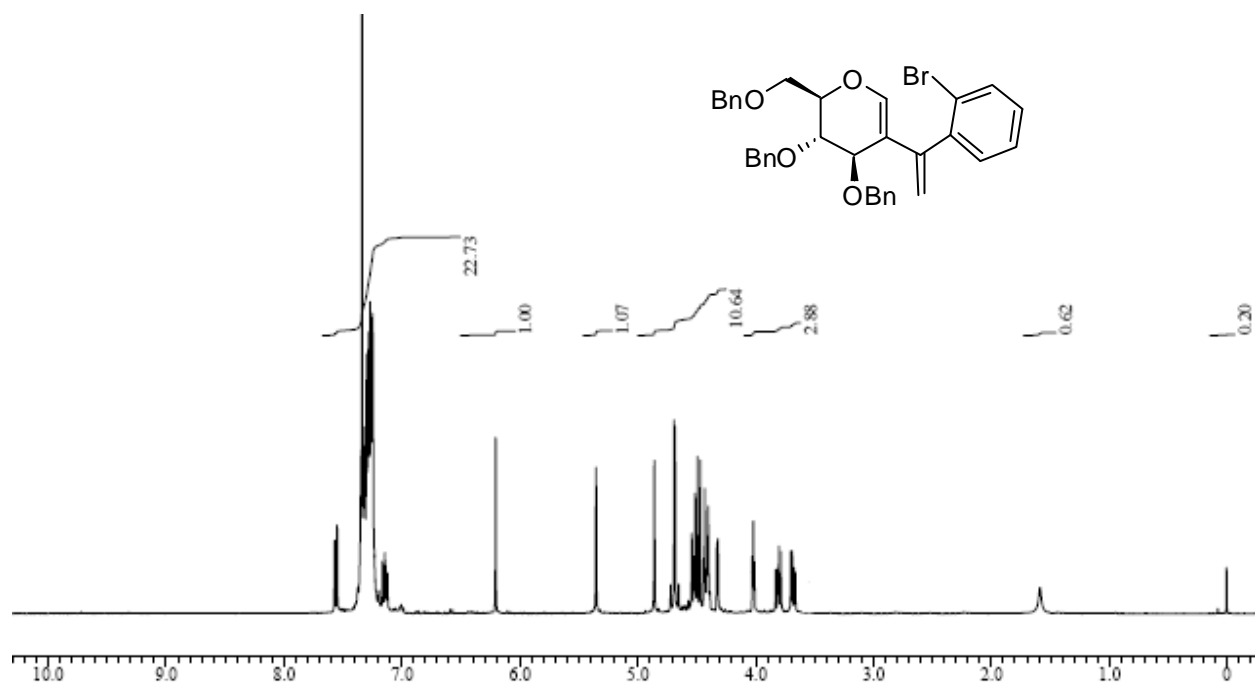


Figure 24.1: ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound 22

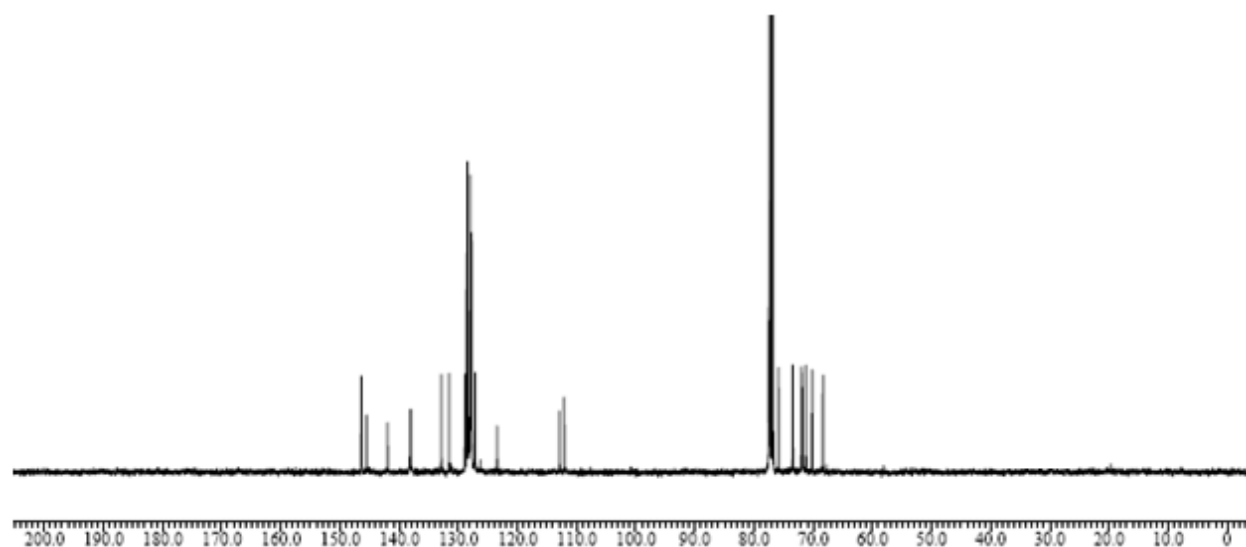


Figure 24.2: ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 22

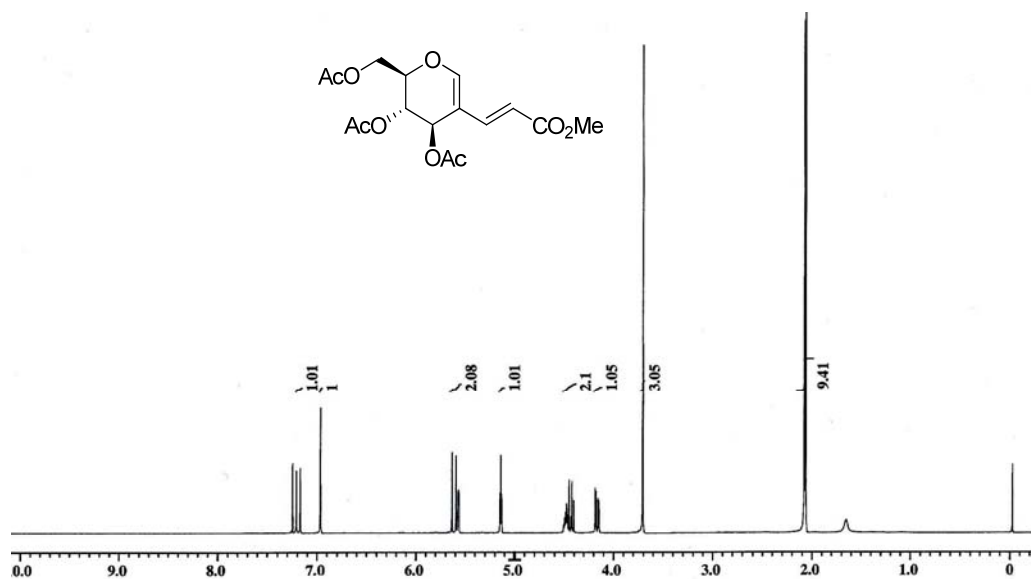


Figure 25.1: ^1H NMR (400 MHz, CDCl_3) Spectrum of Compound 23

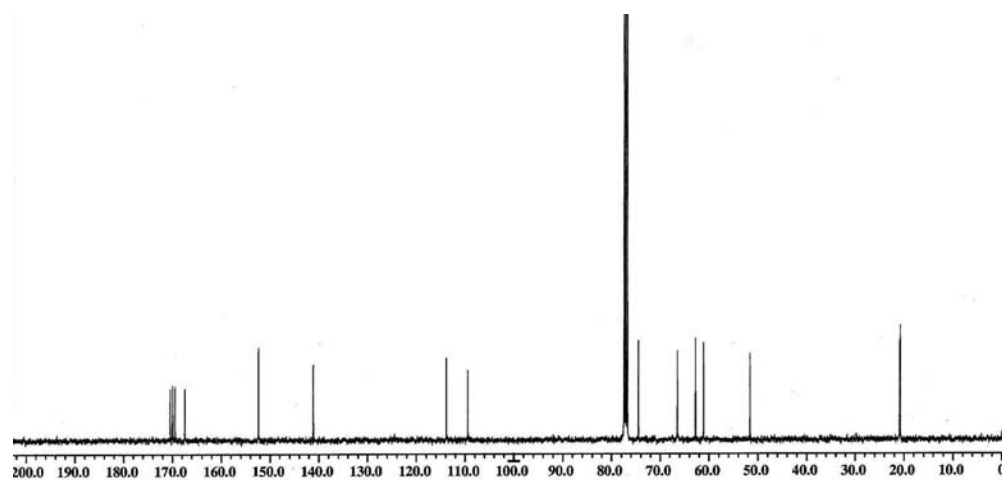


Figure 25.2: ^{13}C NMR (100 MHz, CDCl_3) Spectrum of Compound 23

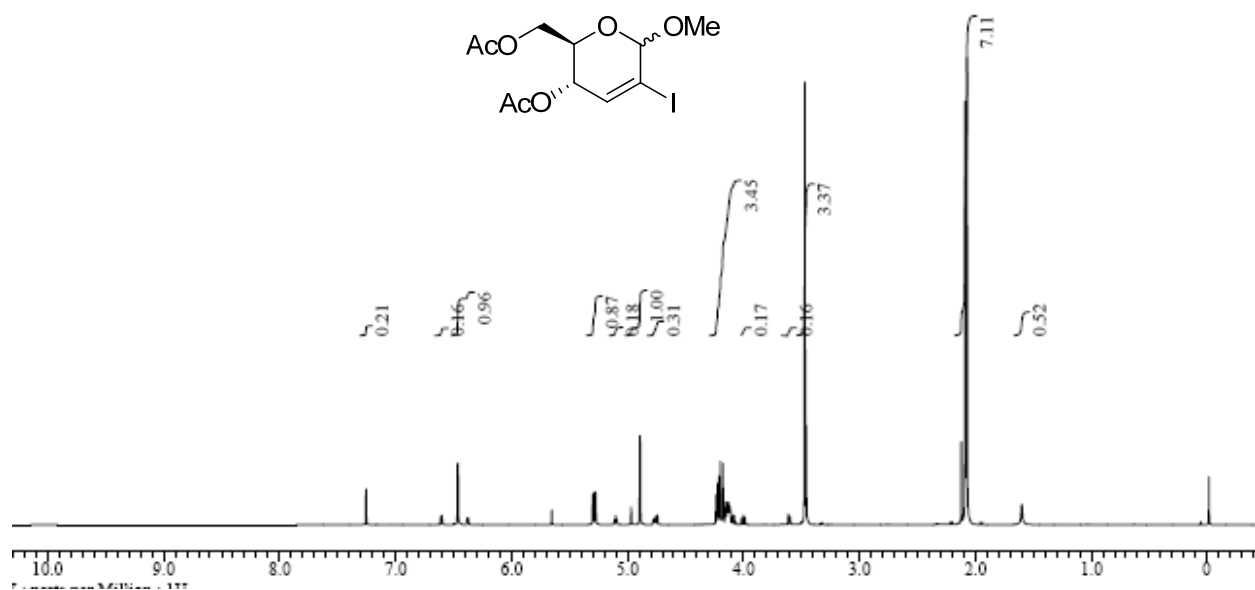


Figure 26.1: ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound 24

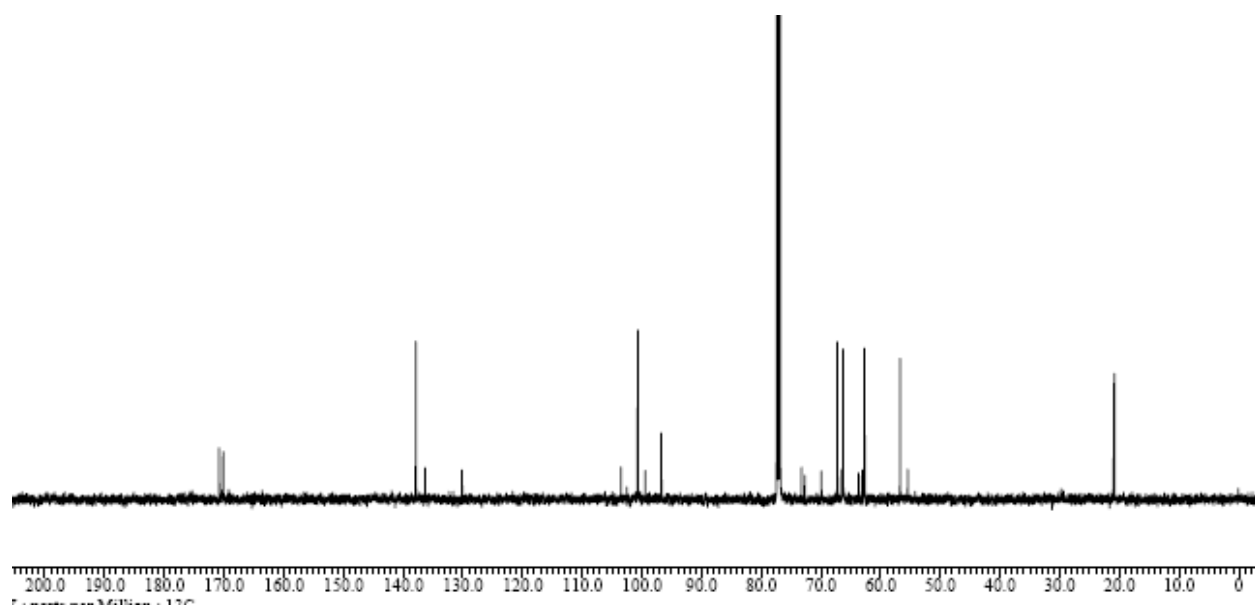


Figure 26.2: ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 24

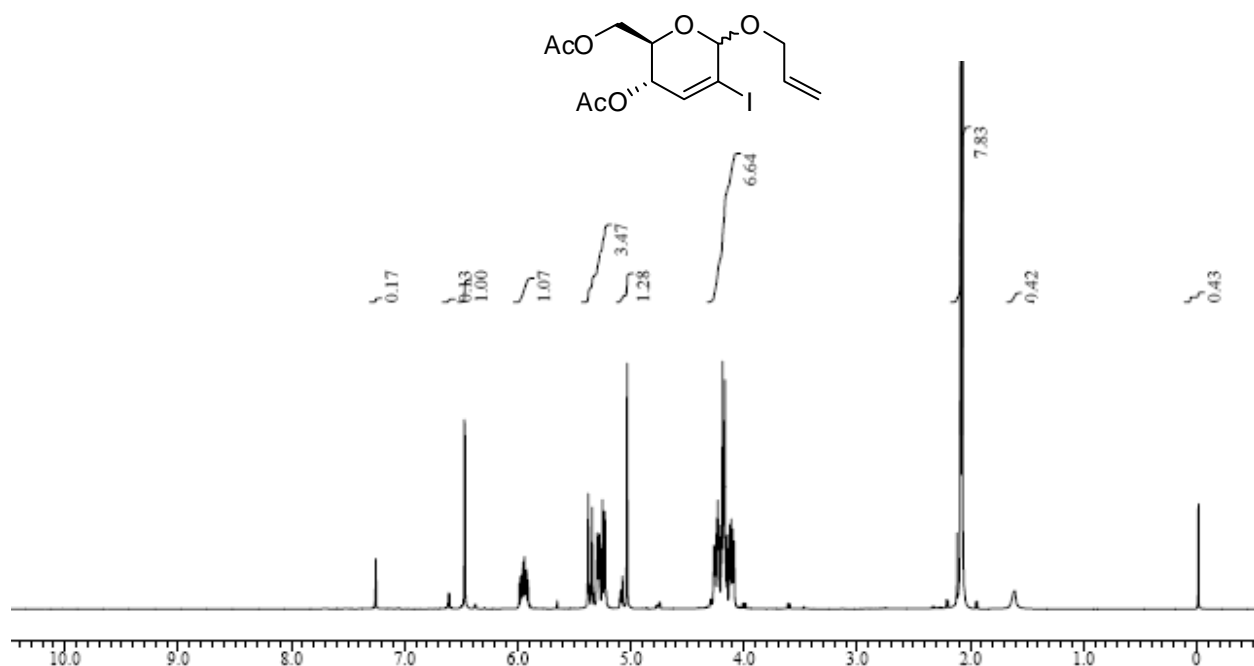


Figure 27.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 25

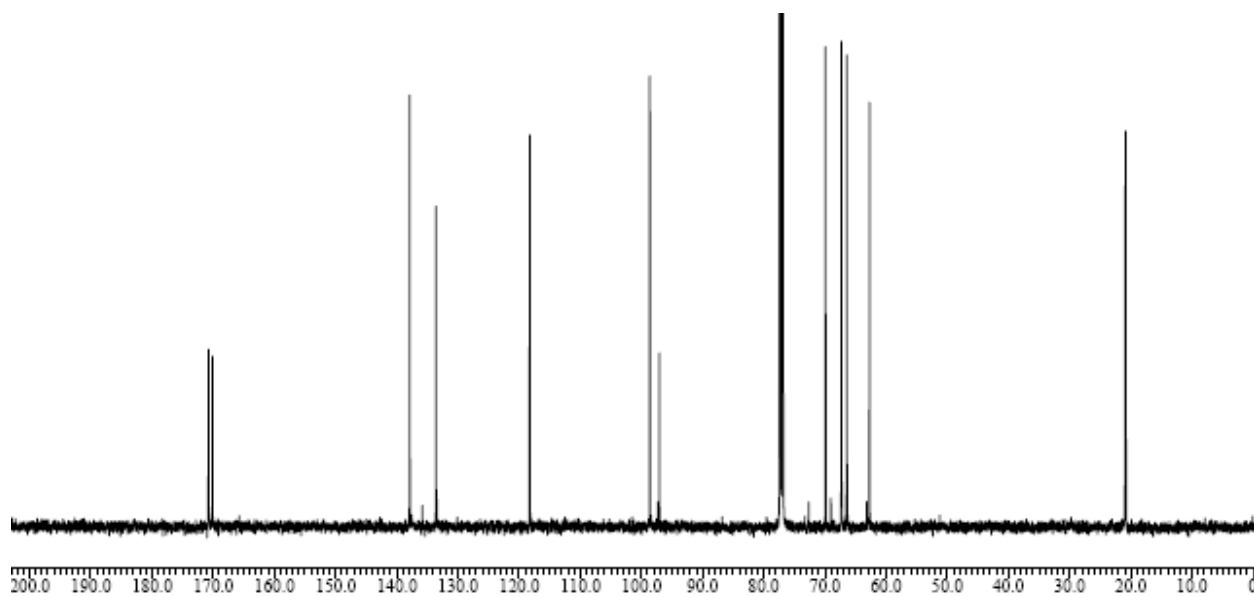


Figure 27.2: ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 25

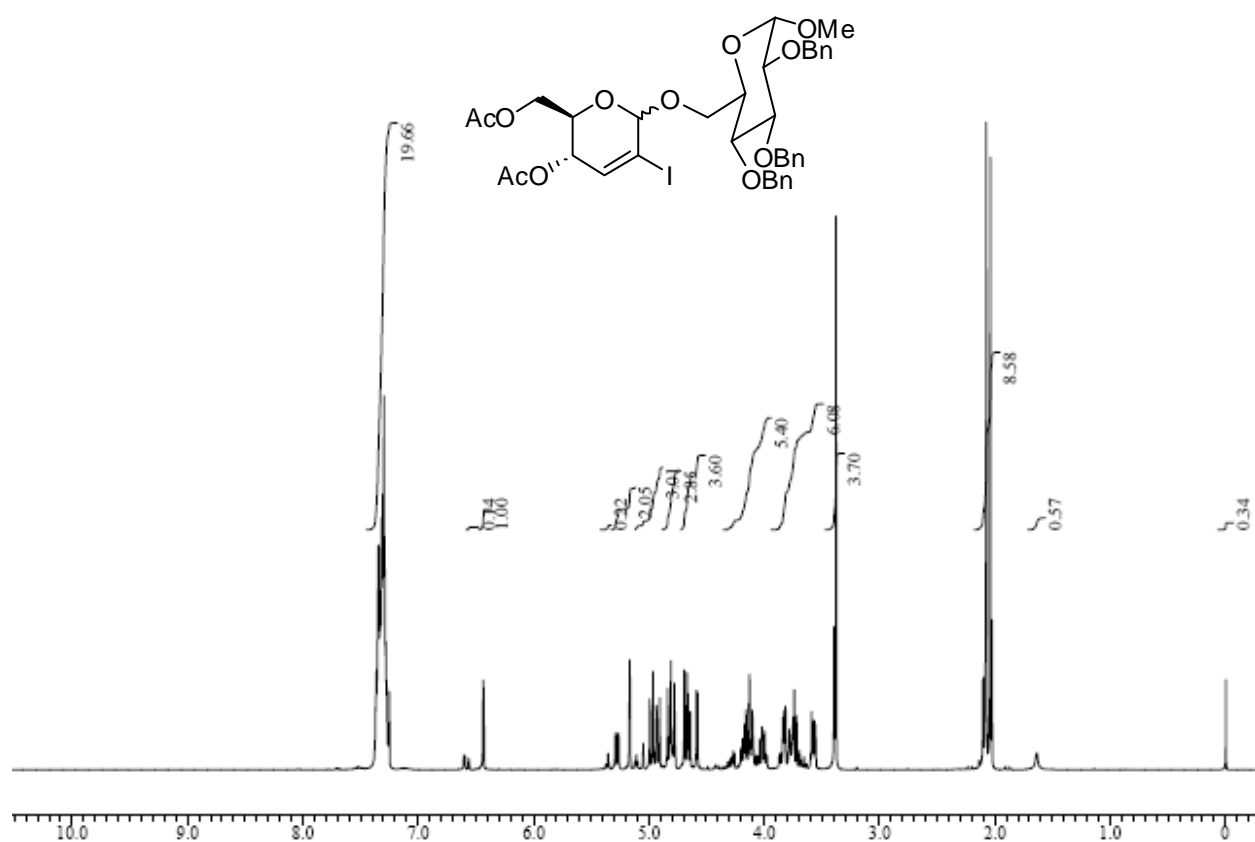


Figure 28.1: ^1H NMR (400 MHz, CDCl_3) Spectrum of Compound 26

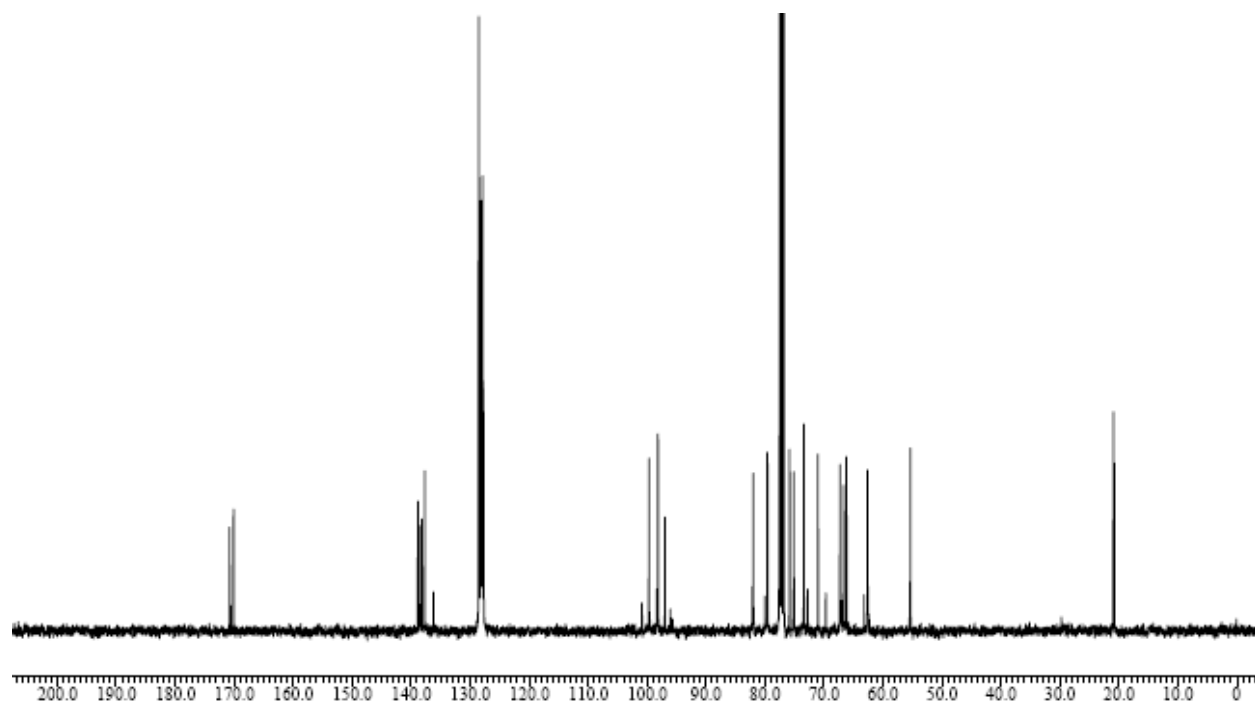


Figure 28.2: ^{13}C NMR (100 MHz, CDCl_3) Spectrum of Compound 26

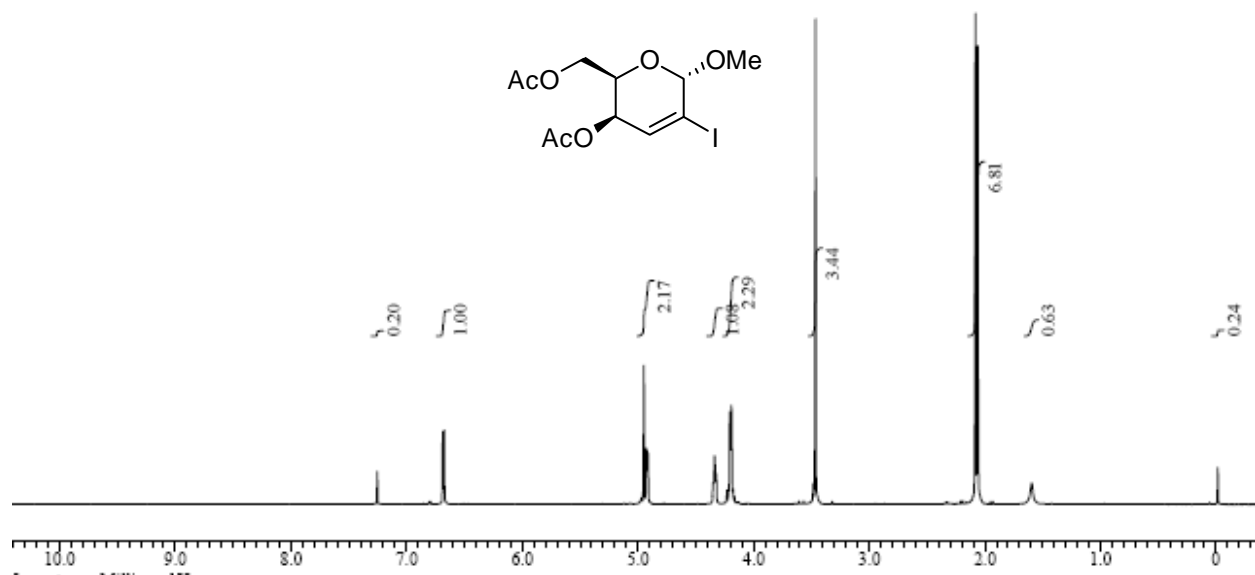


Figure 29.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 27

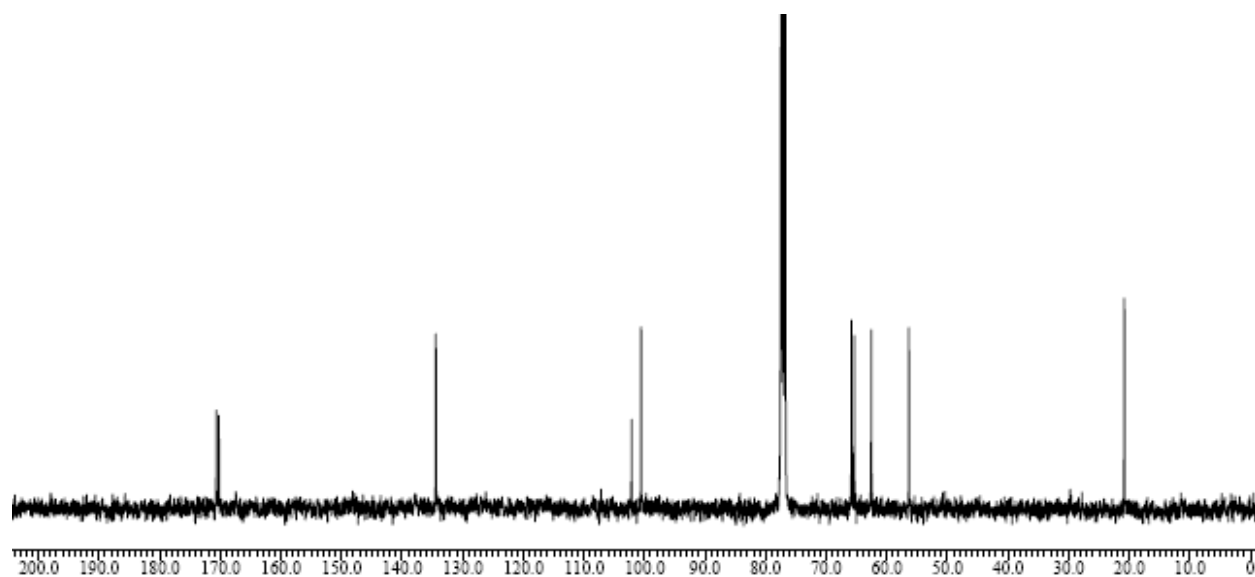


Figure 29.2: ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 27

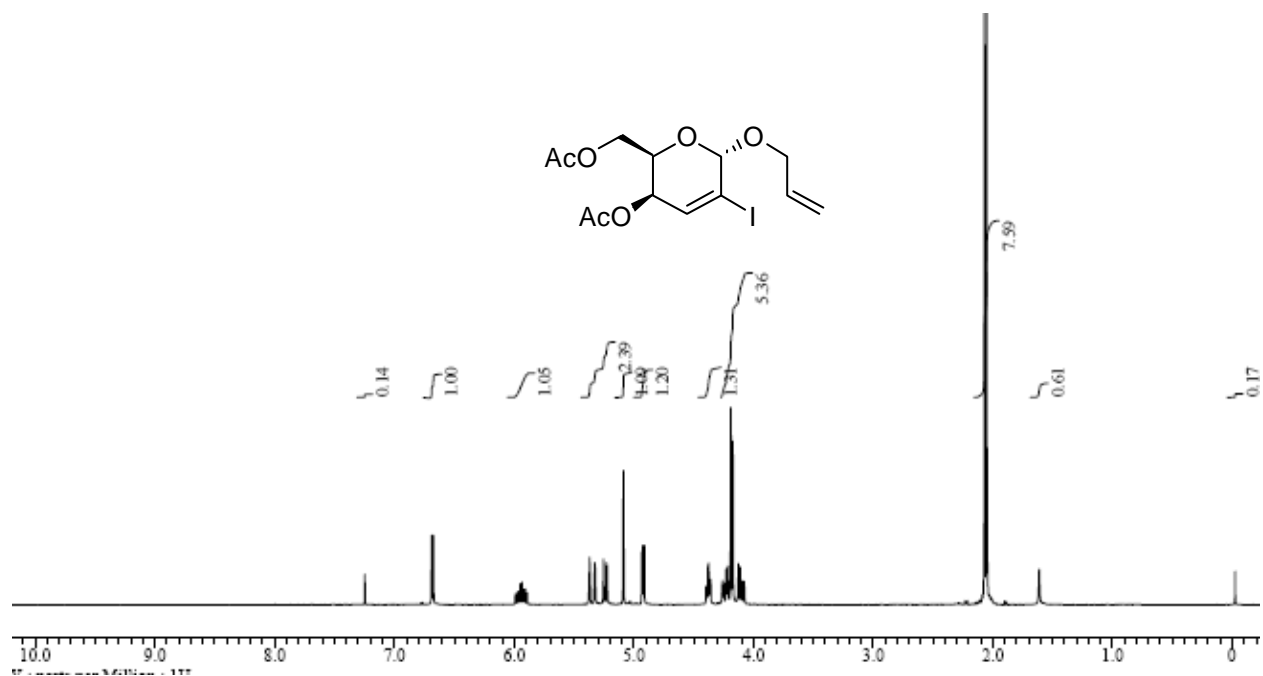


Figure 30.1: ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound 28

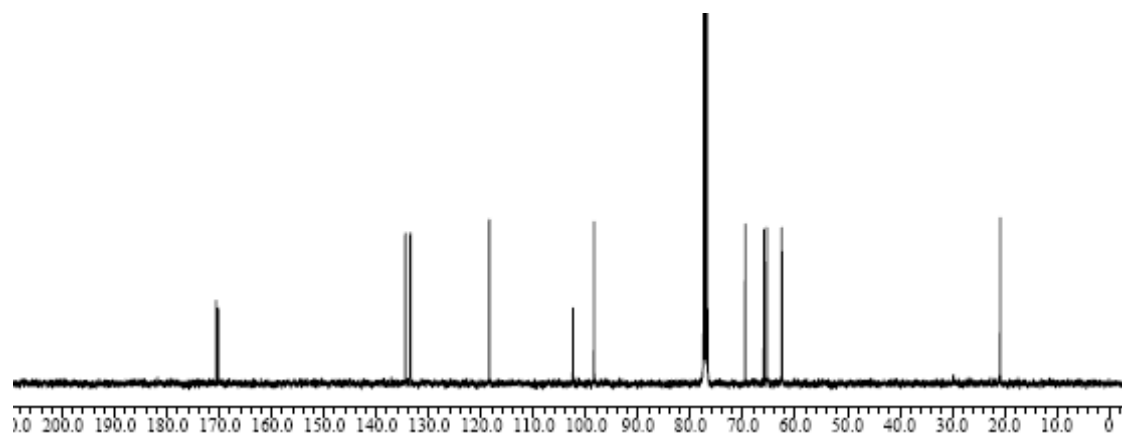


Figure 30.2: ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 28

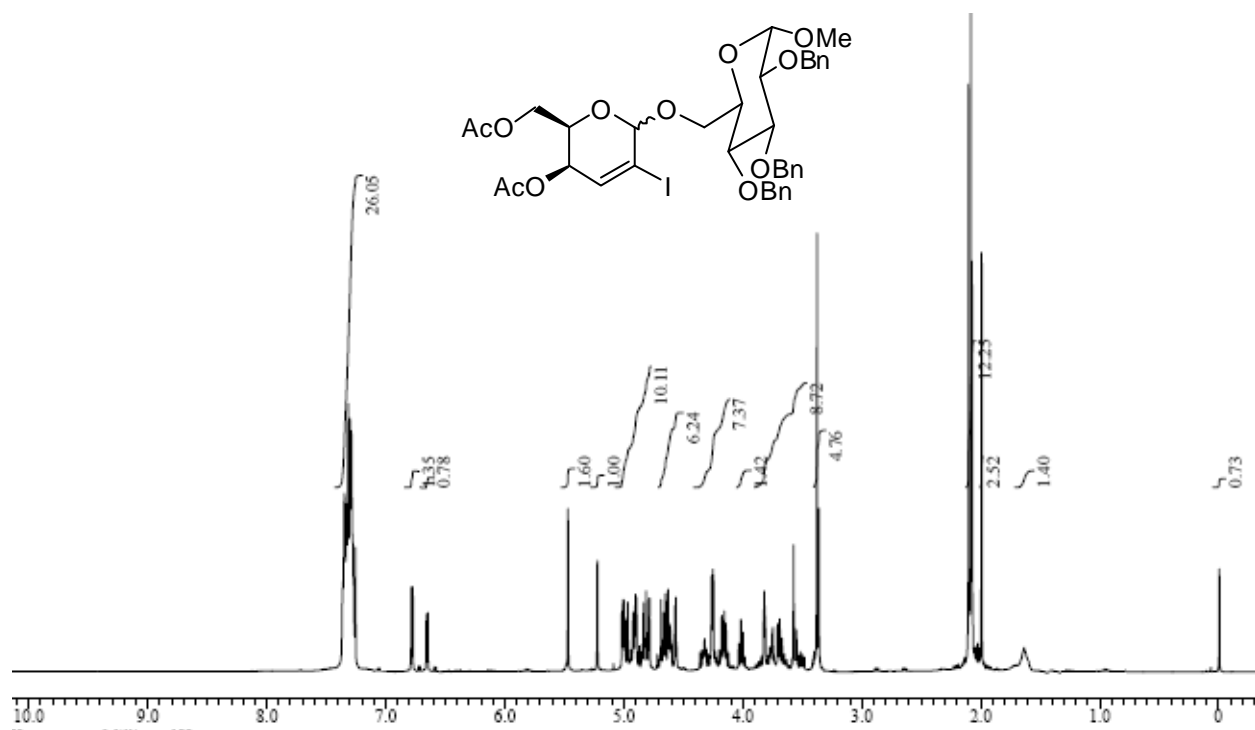


Figure 31.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 29

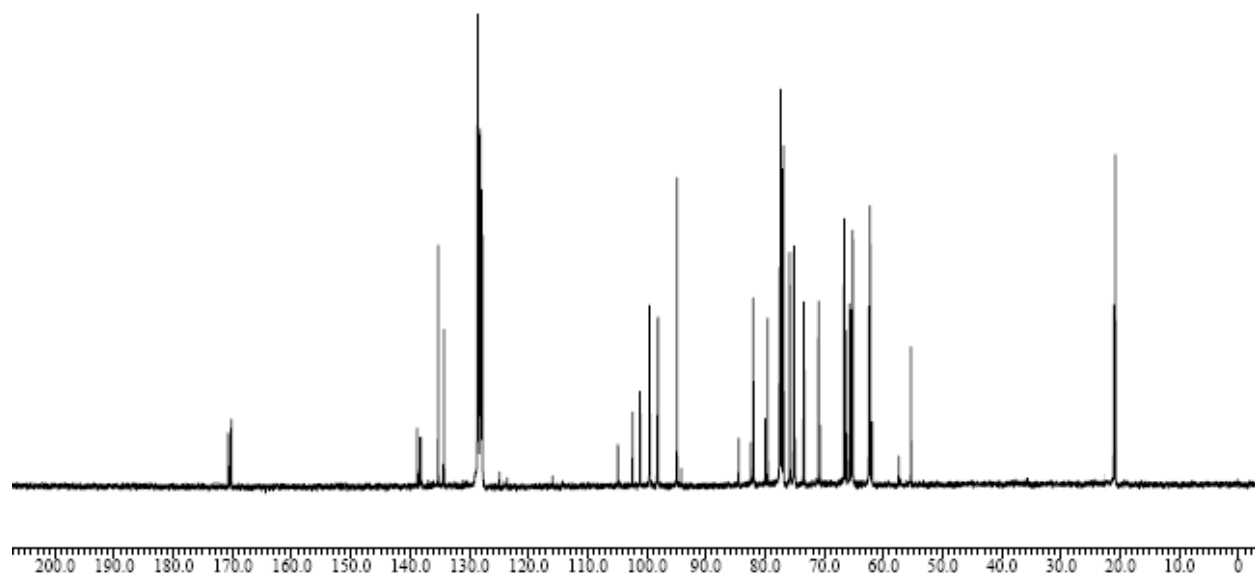


Figure 31.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 29

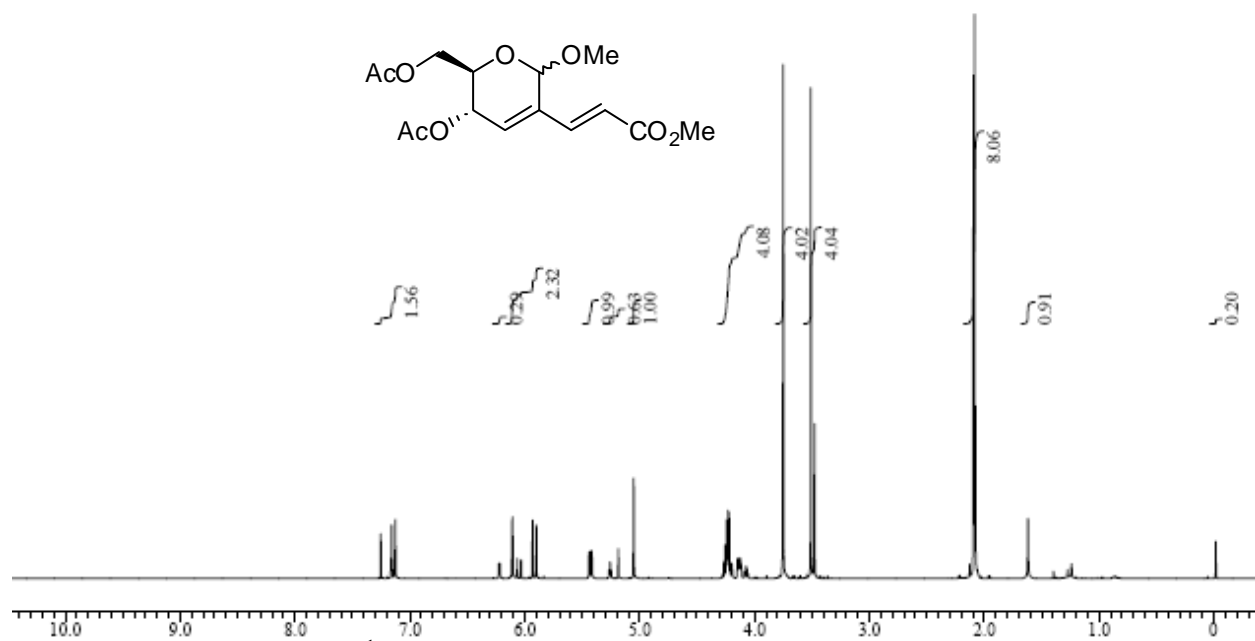


Figure 32.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 30

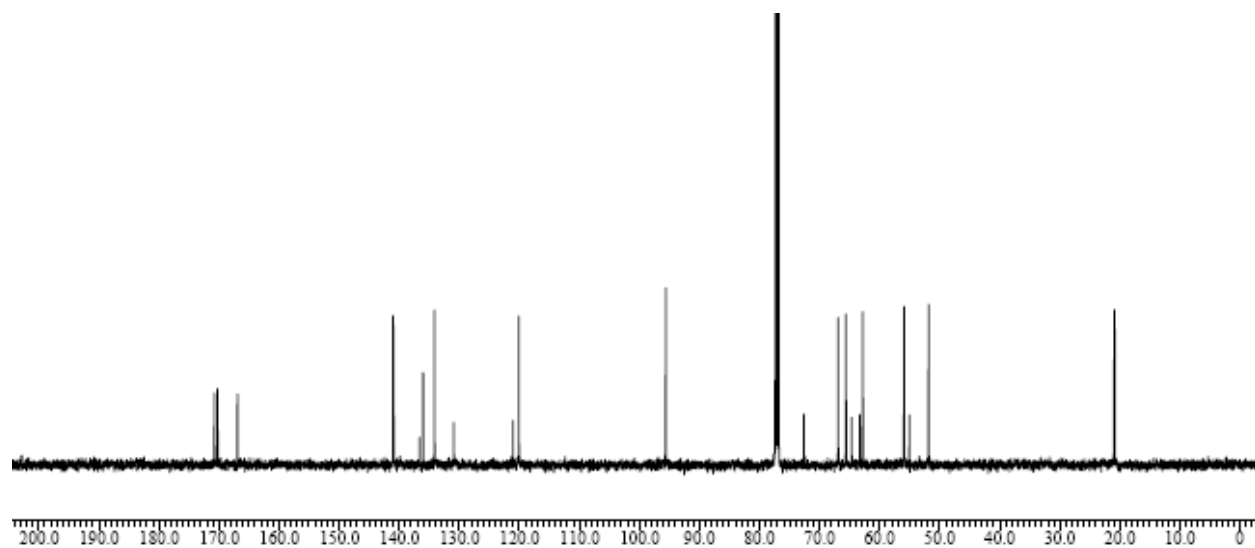


Figure 32.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 30

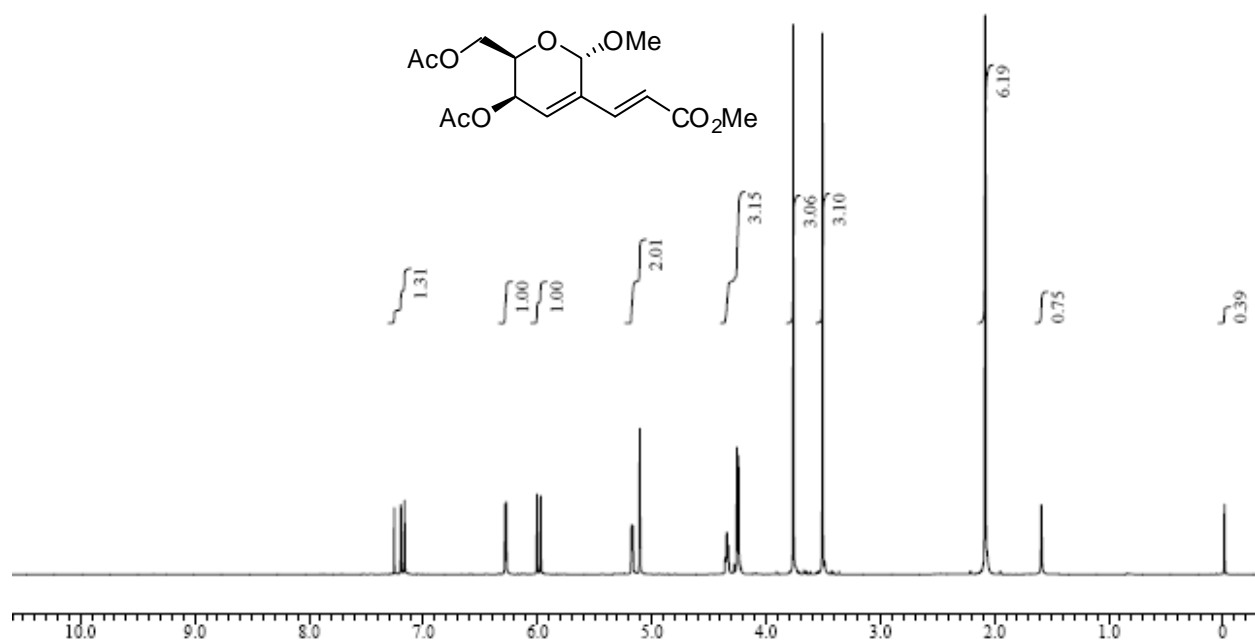


Figure 33.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 31

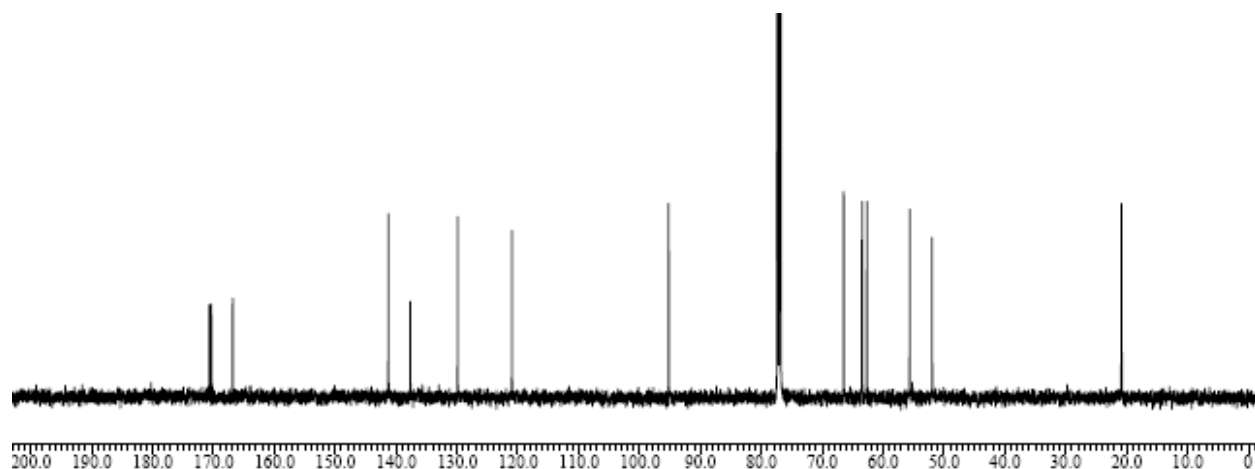


Figure 33.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 31

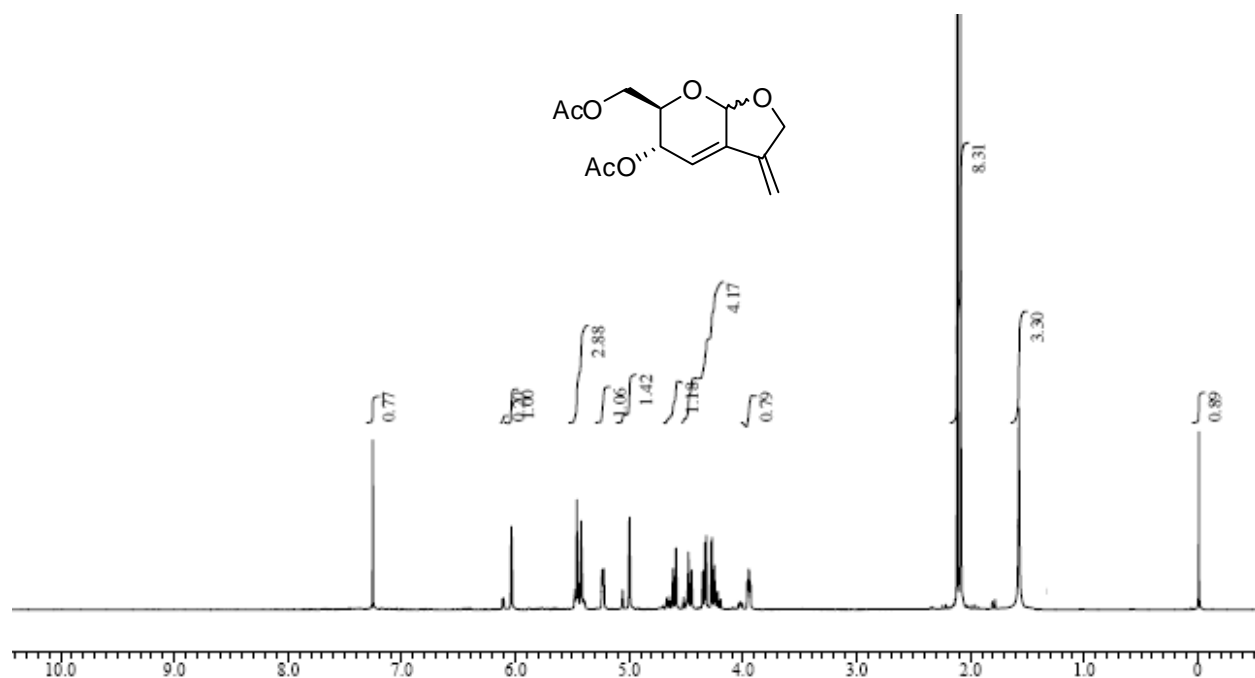


Figure 34.1: ¹H NMR (500 MHz, CDCl₃) Spectrum of Compound 32

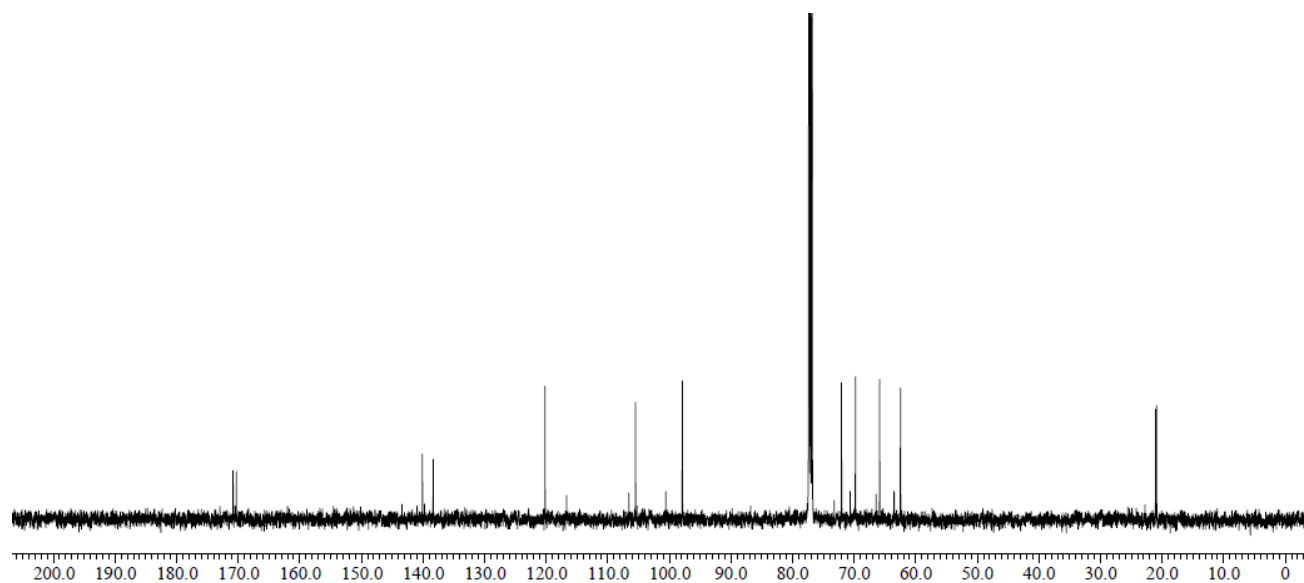


Figure 34.2: ¹³C NMR (125 MHz, CDCl₃) Spectrum of Compound 32

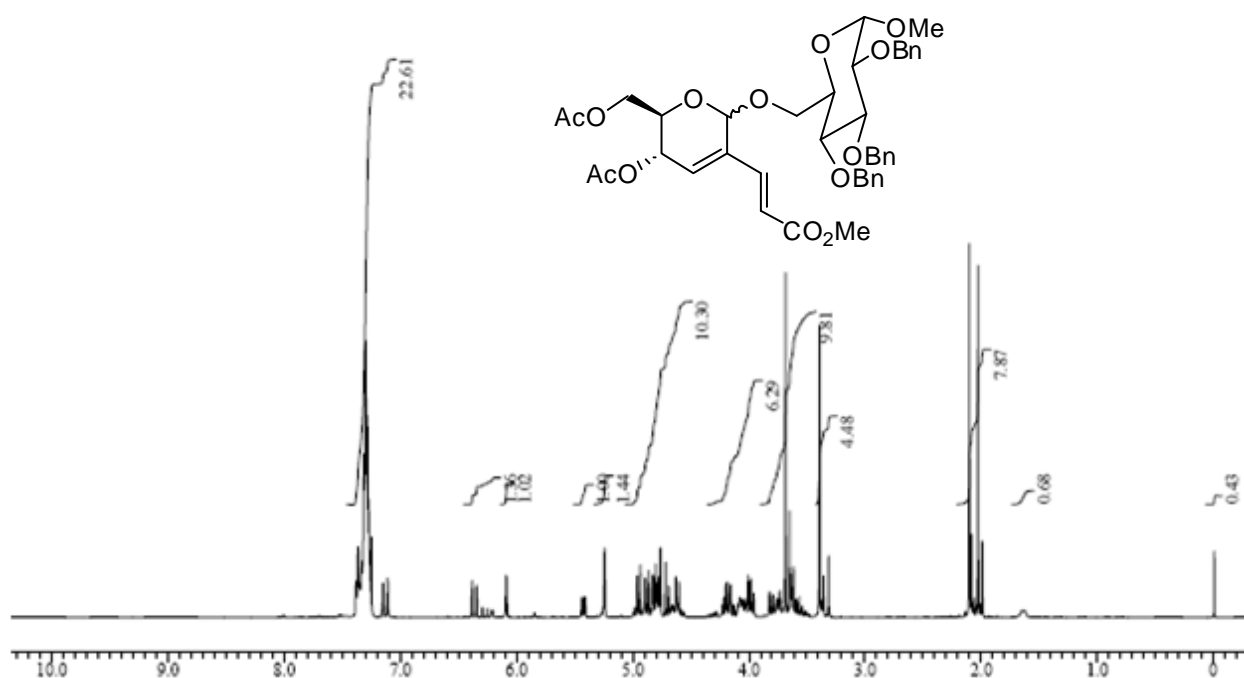


Figure 35.1: ^1H NMR (400 MHz, CDCl_3) Spectrum of Compound **33**

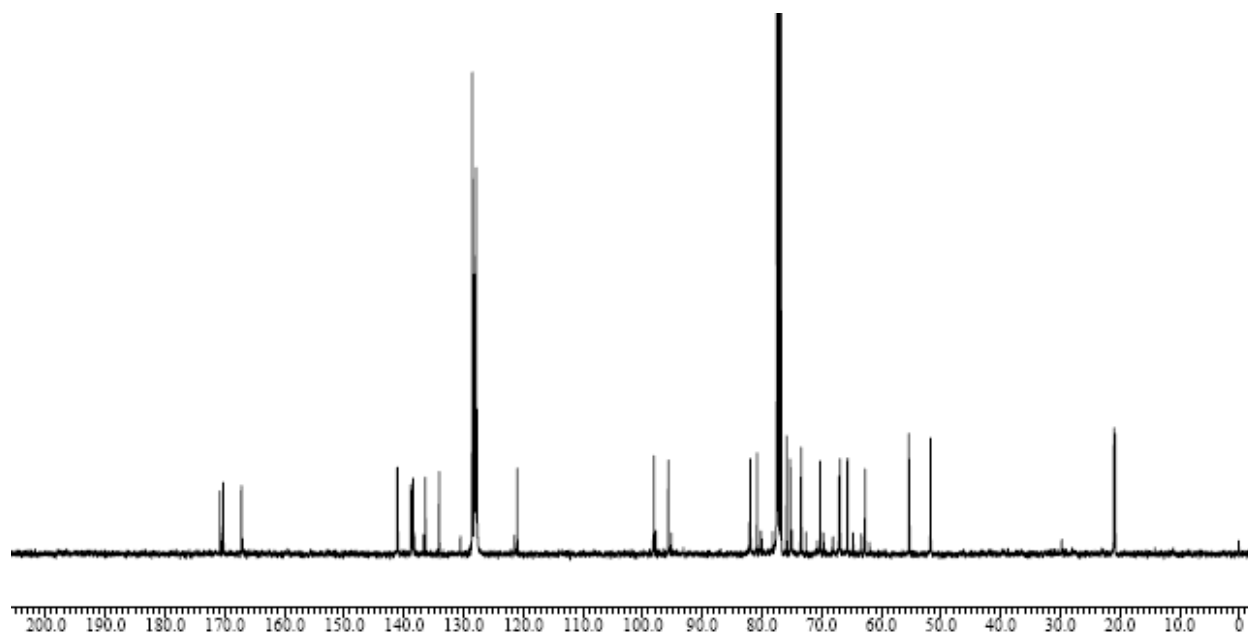


Figure 35.2: ^{13}C NMR (100 MHz, CDCl_3) Spectrum of Compound **33**

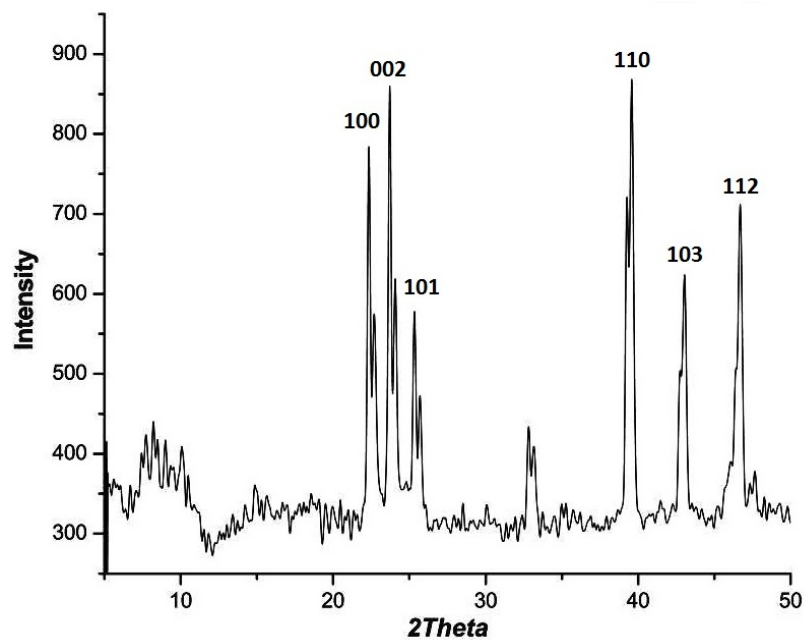


Figure 36.1: Powder XRD patterns of AgI

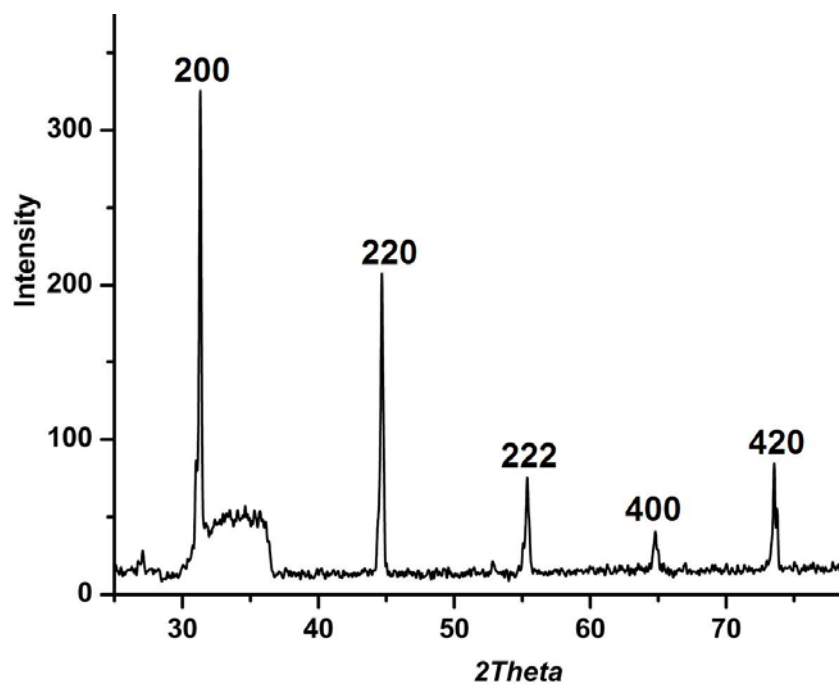


Figure 36.2: Powder XRD patterns of AgBr