Supporting Information

Hydroxamate-Directed Access to β-Kdo Glycosides

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1. General Materials and Methods

Organic reactions were performed under an atmosphere of argon using anhydrous solvents unless otherwise noted. Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} coated aluminium sheets. TLC plates were detected with UV-absorption (254nm), and sprayed with 10% sulfuric acid in ethanol (1:9, v/v), followed by heating for visualization. Flash column chromatography was performed on silica gel (200-300 mesh). Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a BrukerAvance III 400 spectrometer (at 400MHz). Multiplicities were given as singlet (s), broad signal (br), doublet (d), doublet of doublets (dd), triplet (t), quartet (q) or multiplet (m). Carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a BrukerAvance III 400 Spectrometer (at 100 MHz). Non-decoupling ^{13}C NMR spectra were recorded on a BrukerAvance III 400 Spectrometer (at 100 MHz). The ^{1}H and ^{13}C NMR spectra were calibrated against the proton and carbon signals of the solvents as internal references ($CDCl_3$: $^{\delta}$H = 7.26 ppm and $^{\delta}$C = 77.2 ppm). The stereochemistry of the desired C-glycosides was assigned by the heteronuclear coupling constant between ^{13}C carbon at the C1 and the axial proton at C3 ($^{3}J_{C1, H3ax}$) in the non-decoupling ^{13}C NMR spectra.

2. List of glycosyl acceptors (alcohols/thiol/hydroperoxide) used in the study

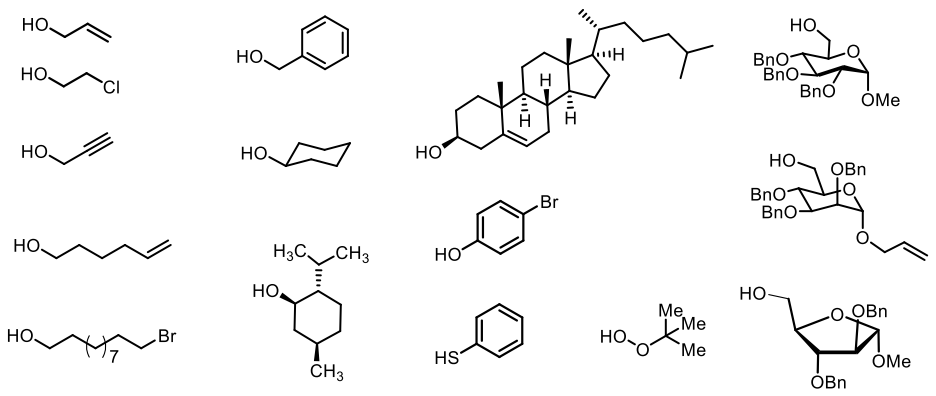
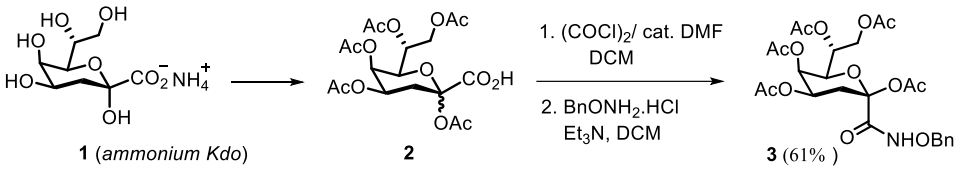


Figure S1

3. **Preparation of Glycosyl Donors**

*Kdo-glycosyl acetate:**3***



Scheme 2 (*from main text*).

Transformation of compound **1** to **2** was carried out following the literature procedure.[1] To a solution of compound **2** (0.5 g, 1.1 mmol, 1 equiv.) in dry CH_2Cl_2 (10.0 mL) and catalytic amount of DMF was added. The reaction mixture was cooled to 0° C and stirred for five minutes. Then, $(COCl)_2$ (0.2 mL, 1.5 equiv) was added dropwise to the reaction mixture and stirred at room temperature for 2h. To this solution was added *O*-benzylhydroxylamine hydrochloride (0.27 g, 1.7 mmol, 1.5 equiv) and Et_3N (0.4 mL, 3.0 equiv) in dry CH_2Cl_2 (10.0 mL) maintaining 0° C and resulting mixture was stirred at room temperature for 2h. Upon completion of the reaction (TLC monitored), it was quenched with water. Organic layer was separated, and aqueous layer was extracted two times with CH_2Cl_2 (5 mL x 2). The combined organic layer was again washed with saturated aqueous $NaHCO_3$ solution (5 mL), collected, dried over anhydrous Na_2SO_4 and finally concentrated in *vacuo*. The crude was purified by silica gel column chromatography (40% ethyl acetate in hexane as eluent) to afford the final product **3** (0.376 g, 61% yield);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.51 (d, *J* = 6.9 Hz, 2H), 7.42 - 7.39 (m, 3H), 5.35 - 5.29 (m, 2H), 5.03 - 4.97 (m, 2H), 4.86 (d, *J* = 11.3 Hz, 1H), 4.34 (dd, *J* = 12.4, 1.5 Hz, 1H), 4.10 (d, *J* = 9.9 Hz, 1H), 3.93 - 3.88 (m, 1H), 2.33 (dd, *J* = 13.3, 4.7 Hz, 1H), 2.15 (s, 3H), 2.05 (d, *J* = 2.8 Hz, 6H), 1.99 (s, 6H), 1.95 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.4, 170.3, 170.1, 169.7, 167.9, 164.3, 134.8, 130.1, 129.2, 128.8, 97.8, 78.5, 69.8, 67.1, 65.8, 63.9, 62.5, 32.0, 20.9(2), 20.8, 20.7(2); $^3J_{C1,H3ax}$:12 Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{31}NNaO_{13}$ calcd. 576.1693, found, 576.1681.

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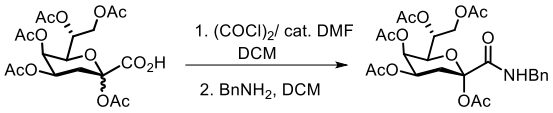
1. M. Mazur, B. Barycza, H. Andriamboavonjy, S. Lavoie, M. T. Kenfack, A. Laroussarie, Y. Bleriot and C. Gauthier, *J. Org. Chem.,* 2016,**81**,10585 - 10599.

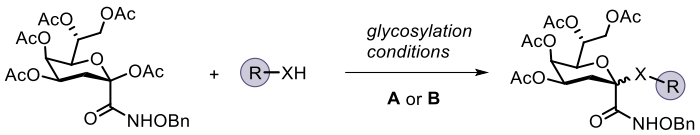
Preparation of Kdo-glycosyl acetate **24**



To a solution of compound **2** (0.060 g, 0.13 mmol, 1.0 equiv) in dry CH_2Cl_2 (3.0 mL) and catalytic amount of DMF was added. The reaction mixture was cooled to 0^o C and stirred for five minutes. Then, $(COCl)_2$ (20 µL, 1.5 equiv) was added dropwise to the reaction mixture and stirred at room temperature for 2h. To this solution was added benzylamine (0.022 g, 0.20 mmol, 1.5 equiv) in dry CH_2Cl_2 (3.0 mL) maintaining 0^o C and resulting mixture was stirred at room temperature for 2h. Upon completion of the reaction (TLC monitored), it was quenched with water. Organic layer was separated, and aqueous layer was extracted two times with CH_2Cl_2 (5 mL x 2). The combined organic layer was again washed with saturated aqueous $NaHCO_3$ solution (5 mL), collected, dried over anhydrous Na_2SO_4 and finally concentrated in *vacuo*. The crude was purified by silica gel column chromatography (30% ethyl acetate in hexane as eluent) to afford the final product **24** (0.040 g, 56% yield); The $^3J_{C1,H3ax}$: 6Hz indicated that α-anomer was formed predominantly in the transformation.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.29 (m, 5H), 6.85 (t, *J* = 5.6 Hz, 1H), 5.40 - 5.35 (m, 2H), 5.14 (d, *J* = 10.8 Hz, 1H), 4.62-4.56 (m, 1H), 4.48-4.43 (m, 2H), 4.15 (d, *J* = 9.9 Hz, 1H), 3.99 (dd, *J* = 12.4, 4.0 Hz, 1H), 2.37 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.00 (s, 6H), 1.97 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.4, 170.2, 170.0, 169.7, 167.8, 167.1, 137.6, 128.8, 127.6, 127.4, 97.6, 69.8, 67.1, 66.0, 64.0, 62.3, 43.3, 32.0, 20.8, 20.7(2), 20.6; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{31}NNaO_{12}$ calcd. 560.1744, found, 560.1757.

4. General procedure for glycosylation

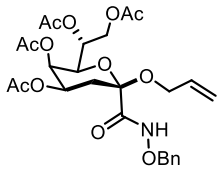


Conditions A: Kdo donor (1.0 equiv), acceptor (2.0 equiv) and freshly activated 4Å MS were taken in dry CH_2Cl_2 (0.1 M) and stirred under argon at room temperature for 30 min. The reaction mixture was then cooled to 0° C followed by addition of TMSOTf (1.0 equiv). Stirring was continued at room temperature until consumption of starting materials were observed (*ca*. 12h). The crude was then filtered through a pad of celite. The filtrate was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give Kdo glycoside.

Conditions B: Kdo donor (1.0 equiv), acceptor (2.0 equiv) and freshly activated 4Å MS were taken in dry CH_2Cl_2 (0.1 M) and stirred under argon at room temperature for 30 min. The reaction mixture was then cooled to 0° C followed by addition of $BF_3.OEt_2$ (1.0 equiv). Stirring was continued at room temperature until consumption of starting materials were observed (*ca*. 12h). The crude was then filtered through a pad of celite. The filtrate was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give Kdo glycoside.

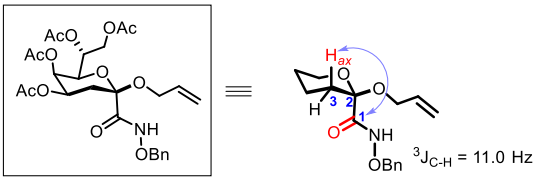
5. Experimental details and characterization of glycosides

*Synthesis of glycoside **5***

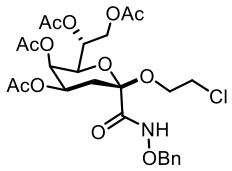


Title compound was prepared according to the general procedure **A/B**. For procedure B, Kdo donor **3** (0.027 g, 0.05 mmol, 1.0 equiv), allyl alcohol (0.006 g, 0.10 mmol, 2.0 equiv) were used in presence of TMSOTf (8.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 64% (0.017 g) yield and isolated as mixture of anomer (*β*:*α* 9:1); R_f 0.4 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -56.6 (*c* =0.120, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55(s,0.1H), 8.94 (s, 0.91H), 7.43 -7.39 (m, 5H), 5.89 - 5.80 (m, 1H), 5.33 - 5.25 (m, 3H), 5.19 (d, *J* = 10.4 Hz, 1H), 5.05 (d, *J* = 10.1 Hz, 1H), 4.98 - 4.94 (m, 2H), 4.45 (dd, *J* = 12.3, 1.4 Hz, 1H), 4.08 (d, *J* = 9.8 Hz, 1H), 3.92 - 3.86 (m, 2H), 3.76 (dd, *J* = 12.0, 5.7 Hz, 1H), 2.28 (dd, *J* = 12.9, 4.7 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.90 (t, *J* = 12.5 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.7, 170.3, 170.1, 169.9, 164.4, 134.7, 133.1, 129.7, 129.3, 128.8, 117.7, 99.9, 78.5, 68.7, 67.6, 66.2, 64.8, 64.5, 62.4, 32.3, 20.9(2), 20.8, 20.7; $^3J_{C1,H3ax}$ = 11Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{33}NNaO_{12}$ calcd. 574.1900, found, 574.1909; [The β:α ratio was determined by the NH protons at 9.55 -8.94 ppm].

Note: The anomeric configuration of glycosides was determined by the measurement of coupling constant $^3J_{C1,H3ax}$ of proton decoupled ^{13}C NMR experiment (see the figure below).

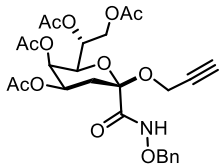


*Synthesis of glycoside**7***



Preparation of the title compound via general procedure **A** is provided here. It was prepared from Kdo donor **3** (0.025 g, 0.05 mmol, 1.0 equiv), 2-chloroethanol (0.008 g, 0.09 mmol, 2.0 equiv) in presence of $BF_3.OEt_2$ (5 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 50% (0.013 g) yield (*β*:*α*> 20:1); R_f 0.4 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -5.0(*c* =0.14, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ9.00 (s, 1H), 7.42 - 7.39 (m, 5H), 5.35 (s, 1H), 5.32 - 5.27 (m, 1H), 5.05 (dd, *J* = 10.1, 3.1 Hz, 1H), 4.98 (s, 2H), 4.48 (dd, *J* = 12.2, 1.3 Hz, 1H), 4.24 (d, *J* = 9.9 Hz, 1H), 3.89 (dd, *J* = 12.4, 4.5 Hz, 1H), 3.69 - 3.56 (m, 3H), 3.45 - 3.38 (m, 1H), 2.26 (dd, *J* = 13.1, 4.8 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.89 (t, *J* = 12.7 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.9, 170.3, 170.0, 164.0, 134.6, 129.7, 129.3, 128.9, 99.6, 78.6, 68.8, 67.7, 66.0, 64.4, 63.9, 62.6, 42.5, 32.2, 21.0, 20.9, 20.8(2); $^3J_{C1,H3ax}$ = 11Hz; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{32}ClNNaO_{12}$ calcd. 596.1511, found, 596.1525. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

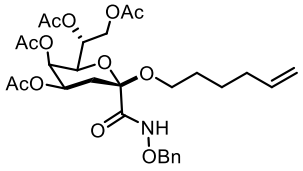
*Synthesis of glycoside **8***



Preparation of the title compound via general procedure **A** is provided here. It was prepared from Kdo donor **3** (0.025 g, 0.05 mmol, 1.0 equiv), propargyl alcohol (0.005 mg, 0.09 mmol, 2.0 equiv) in presence of $BF_3.OEt_2$ (5 µL) as promoter. Crude was purified by flash silica gel column chromatography (6:4 Hexane/EtOAc) to give the desired products as a colourless oil in 52% (0.013 g) yield (*β*:*α*> 20:1); R_f 0.4 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -77.0(*c* =0.1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.43 - 7.39 (m, 5H), 5.35 - 5.28 (m, 2H), 5.08 (dd, *J* = 9.3, 4.8 Hz, 1H), 4.98 (s, 2H), 4.50 (d, *J* = 12.3 Hz, 1H), 4.20 (d, *J* = 9.8 Hz, 1H), 4.07 (dd, *J* = 14.9, 1.7 Hz, 1H), 3.92 - 3.84 (m, 2H), 2.48 (s, 1H), 2.26 (dd, *J* = 13.0, 4.7

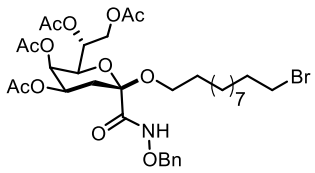
Hz, 1H), 2.11 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.89 (t, *J* = 12.6 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ170.9, 170.3, 170.0(2), 163.7, 134.6, 129.7, 129.3, 128.9, 100.2, 78.8, 78.6, 75.4, 69.2, 67.8, 66.0, 64.4, 62.9, 52.2, 32.2, 20.9(2), 20.8(2); $^{3}J_{C1,H3ax}$ = 12Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{31}NNaO_{12}$ calcd. 572.1744, found, 572.1761. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

*Synthesis of glycoside **9***



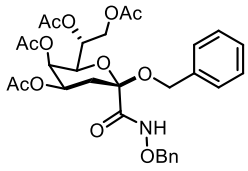
Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.025 g, 0.05 mmol, 1.0 equiv), 5-hexene-1-ol (0.01 g, 0.09 mmol, 2.0equiv) in presence of TMSOTf (8.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as colourless oil in 49% (0.013 g) yield (*β*:*α*> 20:1); R_f 0.25 (EtOAc : Hexane 2:8); $[\alpha]_D^{25}$= -33.12 (*c* =0.16, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.41 - 7.37 (m, 5H), 5.84 - 5.73 (m, 1H), 5.35-5.33 (m, 1H), 5.28 - 5.24 (m, 1H), 5.05 - 4.95 (m, 5H), 4.46 (dd, *J* = 12.3, 1.3 Hz, 1H), 4.03 (d, *J* = 9.9 Hz, 1H), 3.88 (dd, *J* = 12.4, 4.1 Hz, 1H), 3.33 - 3.20 (m, 2H), 2.24 (dd, *J* = 12.9, 4.7 Hz, 1H), 2.07 (s, 3H), 2.04-2.02 (m, 4H), 1.99 (s, 3H), 1.97 (s, 3H), 1.91 - 1.82 (m, 2H), 1.55 (dd, *J* = 13.8, 6.8 Hz, 2H), 1.43 (dd, *J* = 14.5, 7.3 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.3, 170.1, 169.9, 164.6, 138.4, 134.7, 129.6, 129.3, 128.8, 115.1, 99.9, 78.5, 68.5, 67.7, 66.3, 64.5, 63.9, 62.4, 33.6, 32.3, 29.0, 25.6, 20.9(2), 20.8(2); $^{3}J_{C1,H3ax}$ = 11Hz; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{29}H_{39}NNaO_{12}$ calcd. 616.2370, found, 616.2379. [The β:α ratio was determined by the NH protons at ~ 8.9 ppm].

*Synthesis of glycoside **10***



Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.030 g, 0.05 mmol, 1.0 equiv), 11-bromo-1-undecanol (0.026g, 0.11 mmol, 2.0equiv) in presence of TMSOTf (10.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 57% (0.023 g) yield (*β*:*α*> 20:1); R_f 0.4 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -21.1(*c* =0.26, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.44 - 7.37 (m, 5H), 5.33 (s, 1H), 5.30 - 5.25 (m, 1H), 5.04 (ddd, *J* = 9.8, 4.1, 2.2 Hz, 1H), 5.00 - 4.94 (m, 2H), 4.45 (dd, *J* = 12.3, 2.0 Hz, 1H), 4.03 (dd, *J* = 9.8, 0.7 Hz, 1H), 3.89 (dd, *J* = 12.4, 4.2 Hz, 1H), 3.40 (t, *J* = 6.9 Hz, 2H), 3.33 - 3.27 (m, 1H), 3.25 - 3.19 (m, 1H), 2.24 (dd, *J* = 12.8, 4.6 Hz, 1H), 2.05 (d, *J* = 10.2 Hz, 6H), 1.98 (d, *J* = 11.3 Hz, 6H), 1.89 - 1.83 (m, 3H), 1.57 - 1.54 (m, 2H), 1.43-1.38 (dd, *J*= 12.9, 3.6 Hz, 2H), 1.28 (s, 12H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.3, 170.1, 169.9, 164.6, 134.8, 129.6, 129.2, 128.8, 99.9, 78.5, 68.5, 67.7, 66.3, 64.5, 64.1, 62.5, 34.2, 33.0, 32.3, 29.6, 29.5, 28.9, 28.3, 26.3, 20.9(2), 20.8, 20.7; $^3J_{C1,H3ax}$ = 12Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{34}H_{50}BrNNaO_{12}$ calcd. 766.2414, found, 766.2437. [The β:α ratio was determined by the NH protons at ~ 8.9 ppm].

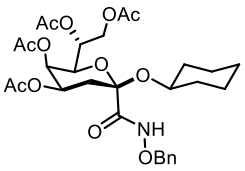
*Synthesis of glycoside **11***



Preparation of the title compound via general procedure **B** is provided here. It was prepared using Kdo donor **3** (0.030 g, 0.05 mmol, 1.0 equiv), benzyl alcohol (0.012g, 0.11 mmol, 2.0equiv) in presence of TMSOTf (10.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 52% (0.017 g) yield (*β*:*α*> 20:1); R_f 0.35 (EtOAc : Hexane 3:7); $[\alpha]_D^{25}$ = -16.2(*c* =0.4, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.46 - 7.44 (m, 2H), 7.40 - 7.37 (m, 3H), 7.34 (d, *J* = 6.5 Hz, 2H), 7.31 - 7.29 (m, 3H), 5.35 (s, 1H), 5.33 - 5.28 (m, 1H),

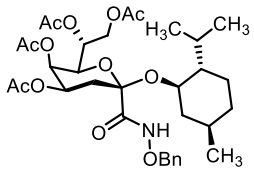
5.06 (d, *J* = 9.7 Hz, 1H), 5.01 (s, 2H), 4.46 - 4.39 (m, 2H), 4.25 (m, 1H), 4.12 (d, *J* = 9.9 Hz, 1H), 3.87 (dd, *J* = 12.4, 4.0 Hz, 1H), 2.34 (dd, *J* = 13.0, 4.8 Hz, 1H), 2.09 (t, *J* = 9.3 Hz, 1H), 2.05 (s, 3H), 1.97 (d, *J* = 9.5 Hz, 6H), 1.91 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.3, 170.1, 169.9, 164.4 136.4, 134.7, 129.7, 129.3, 128.8, 128.7, 128.2, 127.6, 100.1, 78.5, 68.6, 67.6, 66.2, 65.9, 64.4, 62.3, 32.3, 20.9, 20.8, 20.7(2); $^{3}J_{C1,H3ax}$ = 10Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{30}H_{35}NNaO_{12}$ calcd. 624.2057, found, 624.2047. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

*Synthesis of glycoside **12***



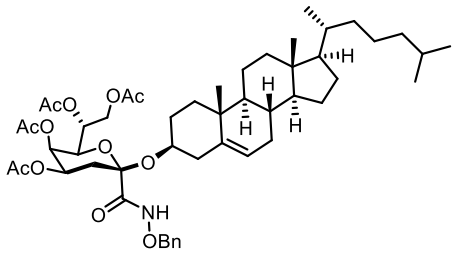
Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.025 g, 0.05 mmol, 1.0 equiv), cyclohexanol (0.009 g, 0.09 mmol, 2.0 equiv) in presence of TMSOTf (8.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 53% (0.014 g) yield as mixture of anomer (*β*:*α* 10:1); R_f 0.5 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -27.8 (*c*=0.140, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50(s,0.09H), 9.03 (s, 0.91H), 7.45 - 7.38 (m, 5H), 5.33 (s, 1H), 5.29 - 5.24 (m, 1H), 5.04 - 5.01 (m, 1H), 4.99 - 4.93 (m, 2H), 4.45 (dd, *J* = 12.2, 1.7 Hz, 1H), 4.17 (d, *J* = 9.7 Hz, 1H), 3.85 (dd, *J* = 12.3, 4.3 Hz, 1H), 3.51 - 3.45 (m, 1H), 2.29 (dd, *J* = 12.8, 4.7 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.87 (t, *J* = 12.6 Hz, 2H), 1.72 -1.70 (m, 3H), 1.50 -1.49 (m, 1H), 1.36 - 1.31 (m, 2H), 1.25 - 1.17 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.7, 170.3, 170.2, 169.9, 165.4, 134.8, 129.5, 129.2, 128.8, 100.3, 78.5, 74.4, 68.9, 68.1, 66.4, 64.7, 62.3, 34.0, 33.3, 32.9, 25.4, 24.5, 24.3, 20.9(2), 20.8(2); $^{3}J_{C1,H3ax}$ = 11Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{29}H_{39}NNaO_{12}$ calcd. 616.2370, found, 616.2397; [The β:α ratio was determined by the NH protons at ~ 9.5-9.0 ppm].

*Synthesis of glycoside **13***



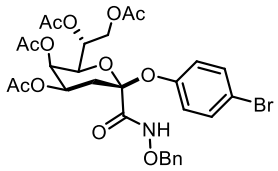
Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.025 g, 0.05 mmol, 1.0 equiv), (−)-menthol (0.015 g, 0.09 mmol, 2.0equiv) in presence of TMSOTf (9.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 48% (0.014 g) yield (*β*:*α*> 20:1); R_f 0.4 (EtOAc : Hexane 3:7); $[\alpha]_D^{25}$ = -21.1(*c*=0.18, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.44 - 7.37 (m, 5H), 5.33 - 5.27 (m, 2H), 5.07 - 4.94 (m, 3H), 4.54 (dd, *J* = 12.1, 2.1 Hz, 1H), 4.23 (d, *J* = 9.6 Hz, 1H), 3.72 (dd, *J* = 12.1, 5.7 Hz, 1H), 3.55 (td, *J* = 10.5, 4.3 Hz, 1H), 2.26 (dd, *J* = 12.5, 4.5 Hz, 1H), 2.21 - 2.14 (m, 1H), 2.05 (d, *J* = 5.3 Hz, 6H), 1.97 (d, *J* = 2.2 Hz, 6H), 1.88 (t, *J* = 12.5 Hz, 1H), 1.60 (s, 4H), 1.27 (m, 2H), 1.19 -1.14 (m, 1H), 0.97 - 0.93 (m, 1H), 0.88 (d, *J* = 7.1 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ170.7, 170.4, 170.3, 169.9, 164.4, 134.9, 129.4, 129.2, 128.9, 101.0, 78.5, 69.1, 68.3, 66.4, 64.8, 62.8, 48.6, 43.0, 34.3, 33.7, 31.4, 25.8, 23.2, 22.4, 21.2, 21.0, 20.8, 16.4; $^3J_{C1,H3ax}$ = 11Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{33}H_{47}NNaO_{12}$ calcd. 672.2996, found, 672.2992. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

*Synthesis of glycoside **14***



Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.020 g, 0.04 mmol, 1.0 equiv), cholesterol (0.028 g, 0.07 mmol, 2.0 equiv) in presence of TMSOTf (6.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (8:2 Hexane/EtOAc) to give the desired products as a colourless oil in 32% (0.01 g) yield (*β*:*α*> 20:1); R_f 0.4 (EtOAc : Hexane 2:8); $[\alpha]_D^{25}$ = -66.1(*c* =0.18, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.41 - 7.38 (m, 5H), 5.34 (s, 1H), 5.29 - 5.27 (m, 2H), 5.06 - 5.03 (m, 1H), 4.96 (dd, *J* = 24.0, 11.1 Hz, 2H), 4.52 (dd, *J* = 12.2, 1.7 Hz, 1H), 4.17 (d, *J* = 9.8 Hz, 1H), 3.84 (dd, *J* = 12.6, 5.0 Hz, 1H), 3.43 - 3.35 (m, 1H), 2.64 - 2.60 (m, 1H), 2.43 - 2.33 (m, 2H), 2.27 (dd, *J* = 13.2, 5.0 Hz, 1H), 2.16 - 2.11 (m, 2H), 2.04 (d, *J* = 7.3 Hz, 6H), 1.97 (d, *J* = 7.3 Hz, 6H), 1.88 (d, *J* = 12.8 Hz, 2H), 1.83-1.79 (m, 3H), 1.43-1.42 (m, 3H), 1.33 (d, *J* = 4.3 Hz, 2H), 1.28 -1.25 (m, 4H), 1.15 -1.09 (m, 6H), 0.98 (s, 3H), 0.91 (d, *J* = 6.3 Hz, 4H), 0.86 (d, *J* = 6.5 Hz, 9H), 0.67 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.4, 170.2, 169.9, 165.3, 140.6, 134.8, 129.6, 129.2, 128.9, 122.3, 100.5, 78.5, 76.3, 69.2, 68.2, 66.4, 64.7, 62.6, 56.9, 56.3, 50.3, 42.5, 40.6, 39.9, 39.7, 37.4, 36.7,36.3, 35.9, 32.1, 32.0, 29.3, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.0, 20.9, 20.8(2), 19.4, 18.9, 12.0; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{50}H_{73}NNaO_{12}$ calcd. 902.5030, found, 902.5030. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

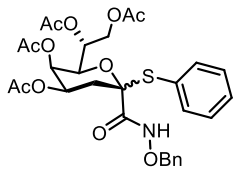
*Synthesis of glycoside **15***



Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.020 g, 0.04 mmol, 1.0 equiv), 4-bromophenol (0.013 g, 0.07 mmol, 2.0 equiv) in presence of TMSOTf (7.0 µL) as promoter. Crude was purified by flash silica gel column

chromatography (6:4 Hexane/EtOAc) to give the desired products as a colourless oil in 63% (0.015 g) yield (*β*:*α*> 20:1); R_f 0.35 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -5.41(*c* =0.2, $CHCl_3$);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.41 - 7.39 (m, 3H), 7.35-7.32 (m, 4H), 6.84 (d, *J* = 8.9 Hz, 2H), 5.47 - 5.42 (m, 1H), 5.40 (s, 1H), 5.07 (ddd, *J* = 9.8, 3.4, 2.2 Hz, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.82 (d, *J* = 11.3 Hz, 1H), 4.27 - 4.20 (m, 2H), 3.79 (dd, *J* = 12.5, 3.7 Hz, 1H), 2.45 (dd, *J* = 13.0, 4.6 Hz, 1H), 2.07 (s, 3H), 2.03 (m, 1H), 2.00 (s, 3H), 1.98 (s, 3H), 1.78 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.2, 170.1, 169.8, 163.6, 152.7, 134.6, 132.6, 129.4, 129.3, 128.9, 120.0, 116.4, 100.4, 78.6, 69.5, 67.3, 65.9, 64.3, 62.1, 33.3, 20.9, 20.7, 20.5; $^3J_{C1,H3ax}$ =12Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{29}H_{32}BrNNaO_{12}$ calcd. 688.1006, found, 681.1024. [The β:α ratio was determined by the NH protons at ~ 8.9 ppm].

*Synthesis of glycoside **16***



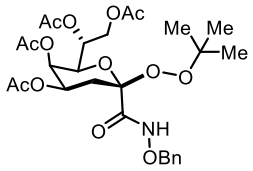
Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.022 g, 0.04 mmol, 1.0 equiv), thiophenol (0.009 g, 0.08 mmol, 2.0equiv) in presence of TMSOTf (7.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to obtain α- andβ-anomer separately. *α-anomer*: The α-anomer was obtained as a colourless oil in 55% (0.013 g) yield; R_f 0.4 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$= -17.2(*c* =0.18, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.43 - 7.39 (m, 2H), 7.36 (s, 1H), 7.34 - 7.33 (m, 3H), 7.21 - 7.19 (m, 2H), 5.41 - 5.37 (m, 2H), 5.05 - 5.03 (m, 1H), 4.78 (d, *J* = 10.9 Hz, 1H), 4.67 (d, *J* = 9.4 Hz, 1H), 4.45 (d, *J* = 11.0 Hz, 1H), 4.24 (dd, *J* = 12.5, 1.1 Hz, 1H), 3.74 (dd, *J* = 12.5, 5.0 Hz, 1H), 2.44 (dd, *J* = 13.8, 4.7 Hz, 1H), 2.24 (t, *J* = 13.0 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.3, 170.0, 169.8, 165.5, 136.6, 134.7, 130.2, 129.5, 129.3, 129.1, 129.0, 128.7, 91.1, 78.5, 70.0, 67.9, 66.7, 64.5, 62.8, 32.2, 21.0, 20.9, 20.8, 20.7.

β-anomer: It was obtained as a colourless oil in 17% (0.004 g) yield; R_f 0.35 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -67.9(*c* =0.24, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.56 (d, *J* =

6.9 Hz, 2H), 7.40 (d, *J* = 7.1 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.34 - 7.31 (m, 3H), 7.18 - 7.16 (m, 2H), 5.32 (dd, *J* = 6.6, 3.0 Hz, 1H), 5.08 (td, *J* = 6.2, 2.5 Hz, 1H), 4.85 - 4.80 (m, 1H), 4.68 (d, *J* = 11.0 Hz, 1H), 4.51 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.29 (dd, *J* = 12.5, 2.6 Hz, 1H), 4.24 (d, *J* = 11.0 Hz, 1H), 3.97 (dd, *J* = 12.5, 5.8 Hz, 1H), 2.98 (dd, *J* = 14.8, 7.9 Hz, 1H), 2.32 (dd, *J* = 14.8, 5.0 Hz, 1H), 2.10 (s, 6H), 2.06 - 2.01 (s, 3H), 1.95 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ170.6, 170.3, 170.1, 169.6, 165.7, 136.6, 134.9, 130.4, 129.9, 129.4, 129.0, 128.6, 127.7, 95.0, 82.1, 78.4, 72.0, 69.9, 69.6, 61.9, 42.8, 21.1, 20.9(2), 20.6; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{29}H_{33}NNaO_{11}$Scalcd. 626.1672, found, 626.1689.

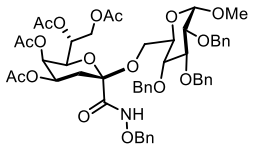
Note: Experiment performed to determine the heteronuclear coupling constant between the carbonyl carbon at C1 and axial proton at C3 for one anomer did not give any splitting of the target carbonyl, which we characterized as the α-anomer. The other one provided $^{3}J_{C1,H3ax}$=12 Hz and characterized as β-anomer.

*Synthesis of glycoside **17***



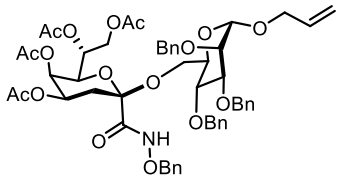
Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.027 g, 0.05 mmol, 1.0 equiv), *tert*-butyl hydroperoxide (0.010 g, 0.10 mmol, 2.0equiv) in presence of TMSOTf (8.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 49% (0.014 g) yield (*β*:*α*> 20:1); R_f 0.35 (EtOAc : Hexane 3:7); $[\alpha]_D^{25}$= -25.6 (*c* =0.18, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.45 - 7.44 (m, 2H), 7.41 - 7.36 (m, 3H), 5.34 (d, *J* = 2.0 Hz, 1H), 5.17 - 5.06 (m, 2H), 4.99 (d, *J* = 11.1 Hz, 1H), 4.90 (d, *J* = 11.1 Hz, 1H), 4.41 (dd, *J* = 12.2, 1.6 Hz, 1H), 4.19 (d, *J* = 10.0 Hz, 1H), 4.02 (dd, *J* = 12.3, 4.7 Hz, 1H), 2.33 (dd, *J* = 13.7, 5.1 Hz, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00 - 1.93 (m, 4H), 1.24 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.7, 170.5, 170.1, 169.9, 163.7, 134.9, 129.7, 129.1, 128.8, 101.6, 81.6, 78.5, 68.7, 67.9, 66.3, 64.3, 63.0, 29.7, 26.6, 21.0, 20.9, 20.8, 20.7; $^{3}J_{C1,H3ax}$ =12Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{37}NNaO_{13}$calcd. 606.2163, found, 606.2174. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

*Synthesis of glycoside **18***



Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.050 g, 0.09 mmol, 1.0 equiv), 3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl) methanol (0.084 g, 0.18 mmol, 2.0equiv) in presence of TMSOTf (17.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 60% (0.052 g) yield (*β*:*α*> 20:1); R_f 0.35 (EtOAc : Hexane 3:7); $[\alpha]_D^{25}$ = -4.17 (*c*=0.12, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.34 - 7.32 (m, 9H), 7.30 - 7.29 (m, 6H), 7.26 - 7.24 (m, 5H), 5.25 (s, 1H), 5.23 - 5.19 (m, 1H), 5.06 - 5.01 (m, 1H), 4.97-4.88 (m, 3H), 4.82 - 4.74 (m, 3H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.51 (dd, *J* = 16.0, 7.3 Hz, 2H), 4.34 (d, *J* = 11.8 Hz, 1H), 3.96 (t, *J* = 10.1 Hz, 2H), 3.79 (dd, *J* = 12.3, 4.4 Hz, 2H), 3.62 (d, *J* = 9.9 Hz, 1H), 3.43 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.36 - 3.30 (m, 5H), 2.12 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.03 (s, 3H), 1.99 (brs, 1H), 1.97 (s, 3H), 1.95 (s, 3H), 1.82 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.4, 170.0, 169.8, 164.4, 138.6, 138.1(2), 134.9, 129.5, 129.1, 128.7, 128.6(2), 128.5, 128.2, 128.1(2), 127.9, 127.8, 99.7, 97.9, 82.1, 80.0, 78.4, 77.8, 75.9, 75.0, 73.4, 69.3, 68.9, 67.7, 66.2, 64.4, 63.3, 62.6, 55.4, 32.3, 20.9, 20.8, 20.7(2); $^3J_{C1,H3ax}$ = 11Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{51}H_{59}NNaO_{17}$ calcd. 980.3681, found, 980.3678. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

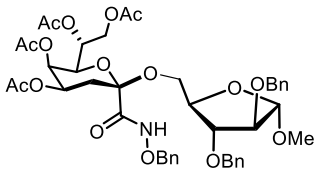
*Synthesis of glycoside **19***



Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.038 g, 0.07 mmol, 2.0 equiv), 6-(allyloxy)-3,4,5-tris(benzyloxy)tetrahydro-2H-pyran-2-yl) methanol (0.017 g, 0.03 mmol, 1.0equiv) in presence of TMSOTf (7.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 35% (0.012 g) yield which was isolated as mixture of anomer (*β*:*α*> 20:1); R_f 0.3 (EtOAc : Hexane

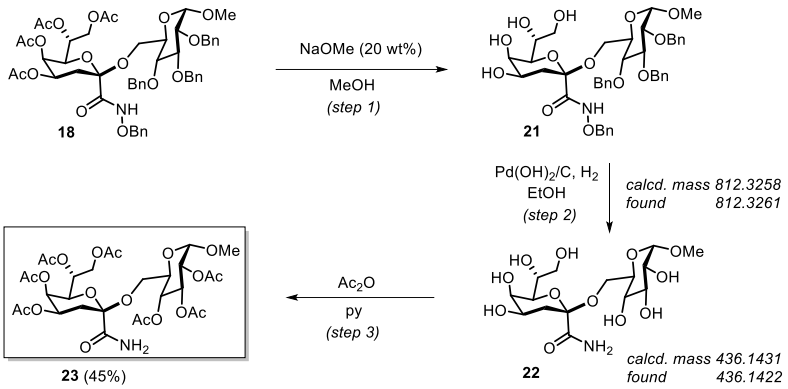
3:7); $[\alpha]_D^{25}$ = -49.28 (*c*=0.140, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.47- 7.44 (3H), 7.44 - 7.37 (m, 6H), 7.35 (s, 2H), 7.34 (s, 2H), 7.32 - 7.31 (m, 4H), 7.29 - 7.28 (m, 3H), 5.91 - 5.78 (m, 1H), 5.35 - 5.28 (m, 4H), 5.24 - 5.18 (m, 1H), 5.06 (ddd, *J* = 9.9, 3.9, 2.1 Hz, 2H), 5.02 (s, 2H), 4.98 - 4.81 (m, 2H), 4.74 - 4.66 (m, 1H), 4.62 - 4.51 (m, 2H), 4.46 - 4.40 (m, 3H), 4.26 (d, *J* = 11.0 Hz, 1H), 4.19 - 4.10 (m, 2H), 3.95 - 3.73(m, 5H), 2.35 (dd, *J* = 12.8, 4.7 Hz, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H), 1.87 (s, 1H);**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.7, 170.3, 170.0, 169.9, 164.4, 138.4, 136.5, 134.8, 133.6, 129.7, 129.5, 129.3, 128.9, 128.7, 128.6, 128.5(2), 128.2, 128.0(2), 127.8, 127.7, 117.7, 100.2, 99.7, 78.6, 78.5, 75.1, 75.0, 73.1, 72.3, 71.0, 68.8, 68.0, 67.7, 66.3, 66.0, 64.6, 64.5, 62.4, 32.3, 20.9, 20.8(2), 20.7; $^3J_{C1,H3ax}$ = 10 Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{53}H_{61}NNaO_{17}$ calcd. 1006.3837, found, 1006.3829. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

*Synthesis of glycoside **20***



Title compound was prepared according to the general procedure **B**, using Kdo donor **3** (0.058 g, 0.10 mmol, 1.2equiv), 3,4-bis(benzyloxy)-5-methoxytetrahydrofuran-2-yl) methanol (0.030 g, 0.09 mmol, 1.0 equiv) in presence of TMSOTf (10.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (6:4 Hexane/EtOAc) to give the desired products as a colourless oil in 42% (0.031 g) yield which was isolated as anomeric mixture (*β*:*α*> 20:1); R_f 0.35 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -19.4(*c*=0.180, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.30 - 7.26 (m, 9H), 7.24 - 7.22(m, 4H), 7.20 (s, 2H), 5.25 (s, 1H), 5.18 - 5.15 (m, 1H), 5.04 - 5.01 (m, 1H), 4.89 - 4.80 (m, 3H), 4.56 - 4.34 (m, 6H), 4.11 (d, *J* = 4.3 Hz, 1H), 4.04 (d, *J* = 9.7 Hz, 1H), 3.90 (brs, 1H), 3.81 - 3.74 (m, 2H), 3.45 (dd, *J* = 9.9, 3.5 Hz, 1H), 3.31 (s, 3H), 2.09 (dd, *J* = 12.9, 4.9 Hz, 1H), 1.99 (s, 3H), 1.94 (d, *J* = 3.8 Hz, 6H), 1.91 (s, 3H), 1.85(m, 1H); **^{13}C{^{1}H} NMR**(100 MHz, $CDCl_3$) δ 170.8, 170.4, 170.0, 169.9, 164.3, 137.8, 137.5, 134.8, 129.6, 129.1, 128.8, 128.6(2), 128.1(2), 128.0, 107.5, 99.8, 87.6, 83.4, 80.5, 78.4, 72.3, 72.0, 68.9, 67.8, 66.2, 64.6, 64.4, 63.1, 55.1, 32.3, 20.9, 20.8(3); $^3J_{C1,H3ax}$ =12Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{43}H_{51}NNaO_{16}$ calcd. 860.3106, found, 860.3102. [The β:α ratio was determined by the NH protons at ~ 9.0 ppm].

6. **Follow-up transformations**

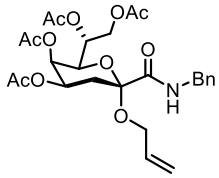


Scheme 3 (*from main text*).

Step-(i): To a solution of **18** (0.030g, 0.03mmol, 1.0equiv) in MeOH (0.05M) was added 20 wt% MeONa in MeOH (freshly prepared). The reaction mixture was stirred for 30min at room temperature and then neutralized with Amberlite® IR-120-H resin and filtered. The filtered was concentrated in *vacuo* to give a crude of product **21** which was used in the next reaction.
Step-(ii): Crude product **21** and $Pd(OH)_2$ (0.2 equiv.) were taken in absolute ethanol (0.05M), purged two times consecutively with N_2 and H_2 and stirring was continued with H_2balloon at room temperature for 12h. Upon completion (TLC monitored) reaction was filtered through celite and concentrated in *vacuo* to obtain crude product **22** and was analysed with LC-MS. The crude was directly used in the next step.
Step-(iii): Crude **22** was taken in a mixture of pyridine (30µL) in acetic anhydride (30µL)and stirred under argon at room temperature for 12h. Solvents were removed in vacuo and the crude was purified by silica gel column chromatography (using 20% EtOAc/ hexane as eluent) to afford compound **23** (0.010g; 45% overall yield); R_f 0.3 (EtOAc : Hexane 2:8 ; $[\alpha]_D^{25}$ = -20.8(*c* =0.12, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.67 (d, *J* = 2.6 Hz, 1H), 5.63 (d, *J* = 2.9 Hz, 1H), 5.47 (t, *J* = 9.7 Hz, 1H), 5.36 - 5.33 (d, *J* = 10.7 Hz, 2H), 5.22 - 5.18 (m, 1H), 4.97 - 4.95 (m, 1H), 4.89 - 4.86 (m, 1H), 4.84 - 4.80 (m, *J* = 10.3, 3.8 Hz, 1H), 4.63 (dd, *J* = 12.2, 2.2 Hz, 1H), 4.24 (d, *J* = 9.2 Hz, 1H), 4.06-4.02 (m, 1H), 4.01 - 3.98 (m, 1H), 3.45 (s, 3H), 3.43-3.41 (m, 2H), 2.23 (dd, *J* = 12.8, 5.4 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 6H), 2.05 (s, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.9, 170.4, 170.1, 170.0(3), 169.3, 99.2, 96.5, 71.1, 70.2, 69.4, 69.3, 68.1(2), 66.2, 64.7,

63.1, 62.8, 55.6, 32.1, 21.0, 20.9, 20.8(2); **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{29}H_{41}NNaO_{19}$ calcd. 730.2170, found, 730.2168

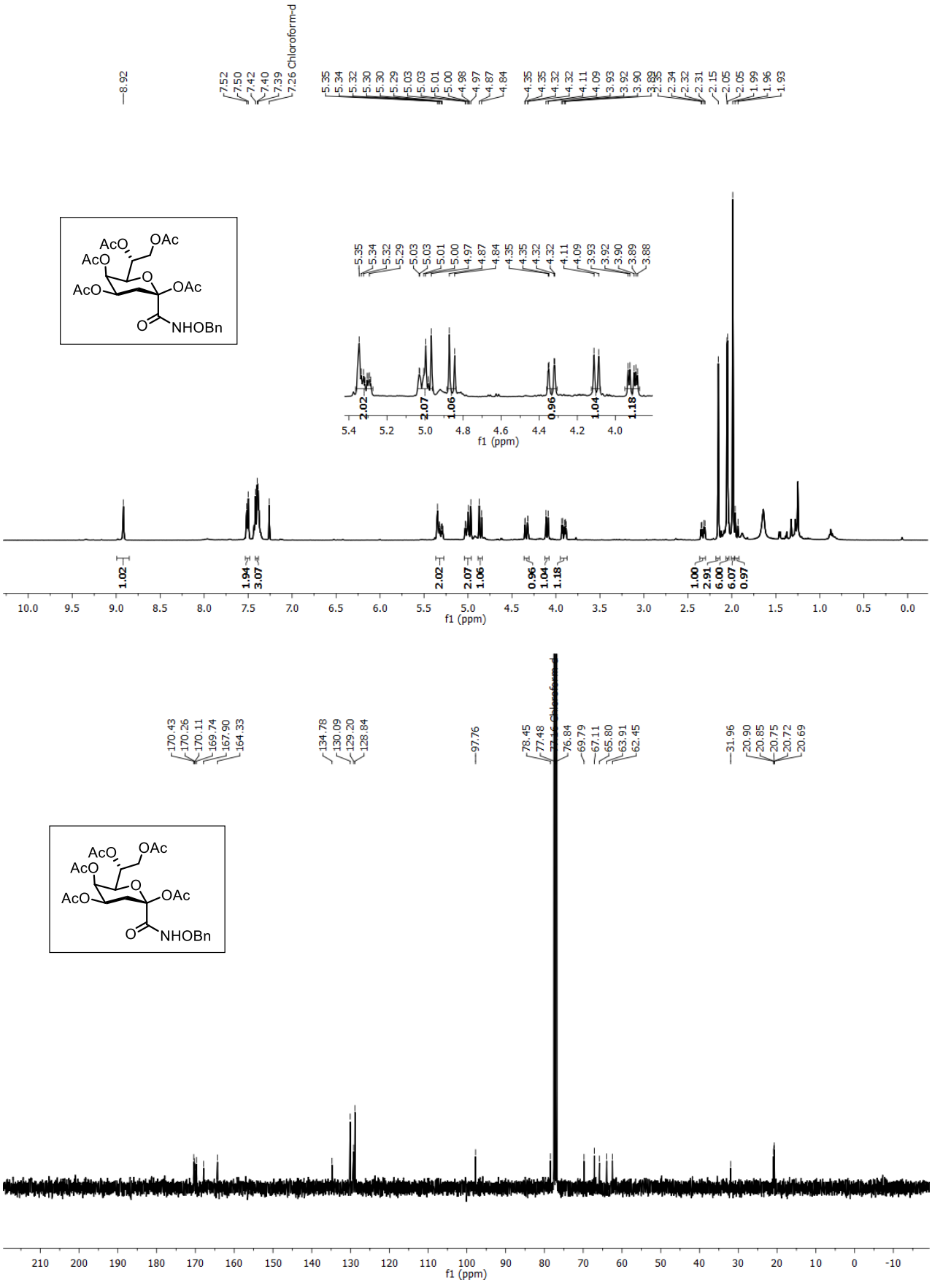
*Synthesis of glycoside **25***



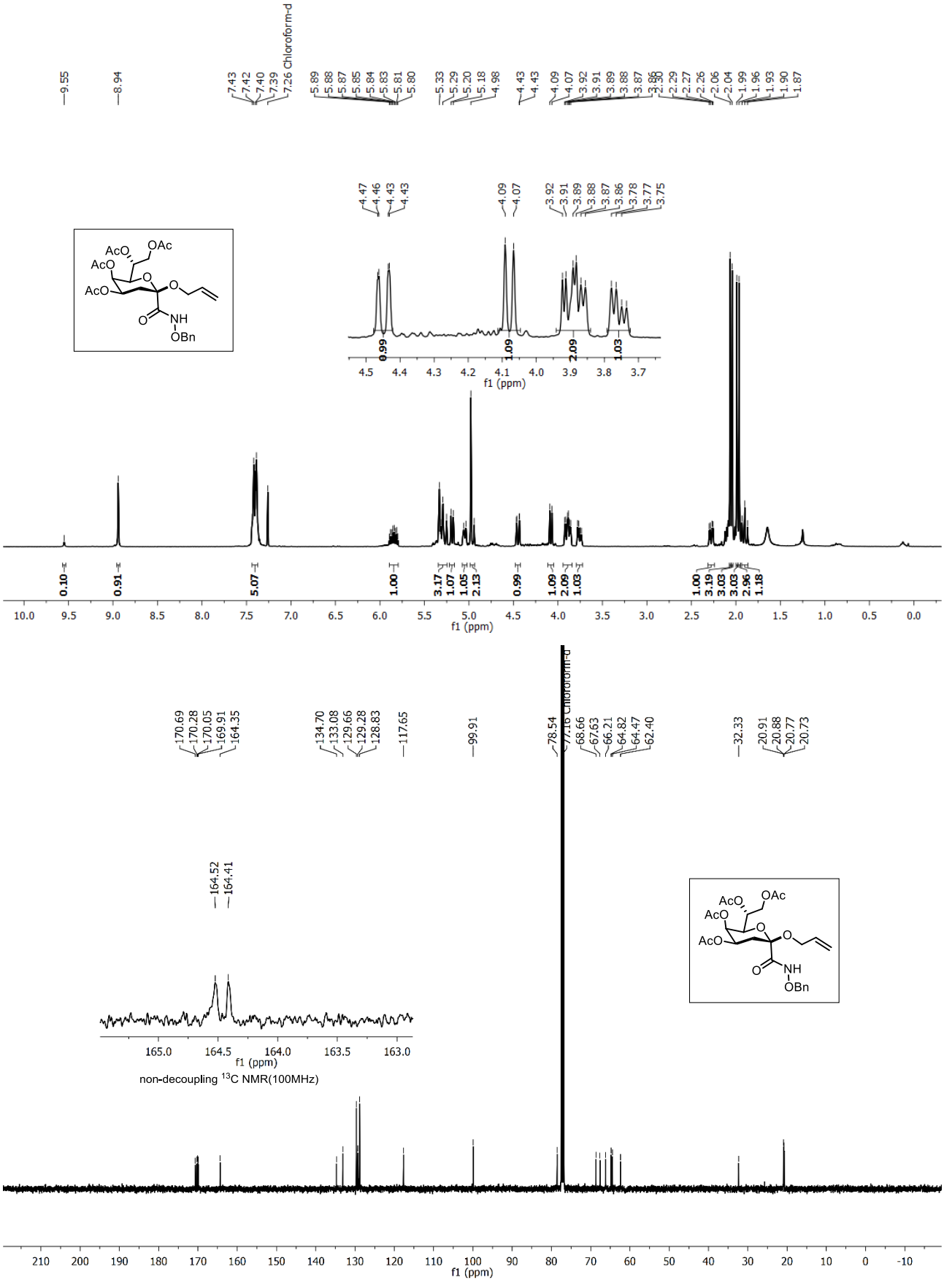
Title compound was prepared according to the general procedure **B**, using Kdo donor **24** (0.05 g, 0.09 mmol, 1.0 equiv), allyl alcohol (0.01 g, 0.19 mmol, 2.0 equiv) in presence of TMSOTf (17.0 µL) as promoter. Crude was purified by flash silica gel column chromatography (7:3 Hexane/EtOAc) to give the desired products as a colourless oil in 22% (0.011 g) yield as single anomer; R_f 0.5 (EtOAc : Hexane 4:6); $[\alpha]_D^{25}$ = -33.5(*c*=0.140, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (m, 1H), 7.35 (t, *J* = 1.7 Hz, 1H), 7.30 (s, 2H), 7.28 (s, 1H), 6.94 (t, *J* = 5.9 Hz, 1H), 5.89 (m, 1H), 5.41- 5.36 (m, 2H), 5.31 - 5.26 (m, 1H), 5.21 - 5.15 (m, 2H), 4.54 - 4.50 (m, 4H), 4.18 (dd, *J* = 9.9, 1.0 Hz, 1H), 4.05 (dd, *J* = 12.4, 4.1 Hz, 1H), 3.95 (ddt, *J* = 12.1, 5.3, 1.4 Hz, 1H), 3.86 (ddt, *J* = 12.1, 5.6, 1.4 Hz, 1H), 2.34 (ddd, *J* = 13.0, 4.5, 1.4 Hz, 1H), 2.06 (s, 6H), 2.00 (s, 3H), 1.97 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.4, 170.1, 170.0, 167.5, 137.8, 133.3, 129.0, 127.9, 127.7, 117.5, 99.7, 68.8, 67.7, 66.5, 64.8, 64.7, 62.5, 43.4, 32.5, 20.9, 20.8; $^3J_{C1,H3ax}$ = 3 Hz; **HRMS(ESI-TOF)** m/z: $[M + Na]^+C_{26}H_{33}NNaO_{11}$ calcd. 558.1951, found, 558.1951.

7. **NMR Spectra of new compounds**

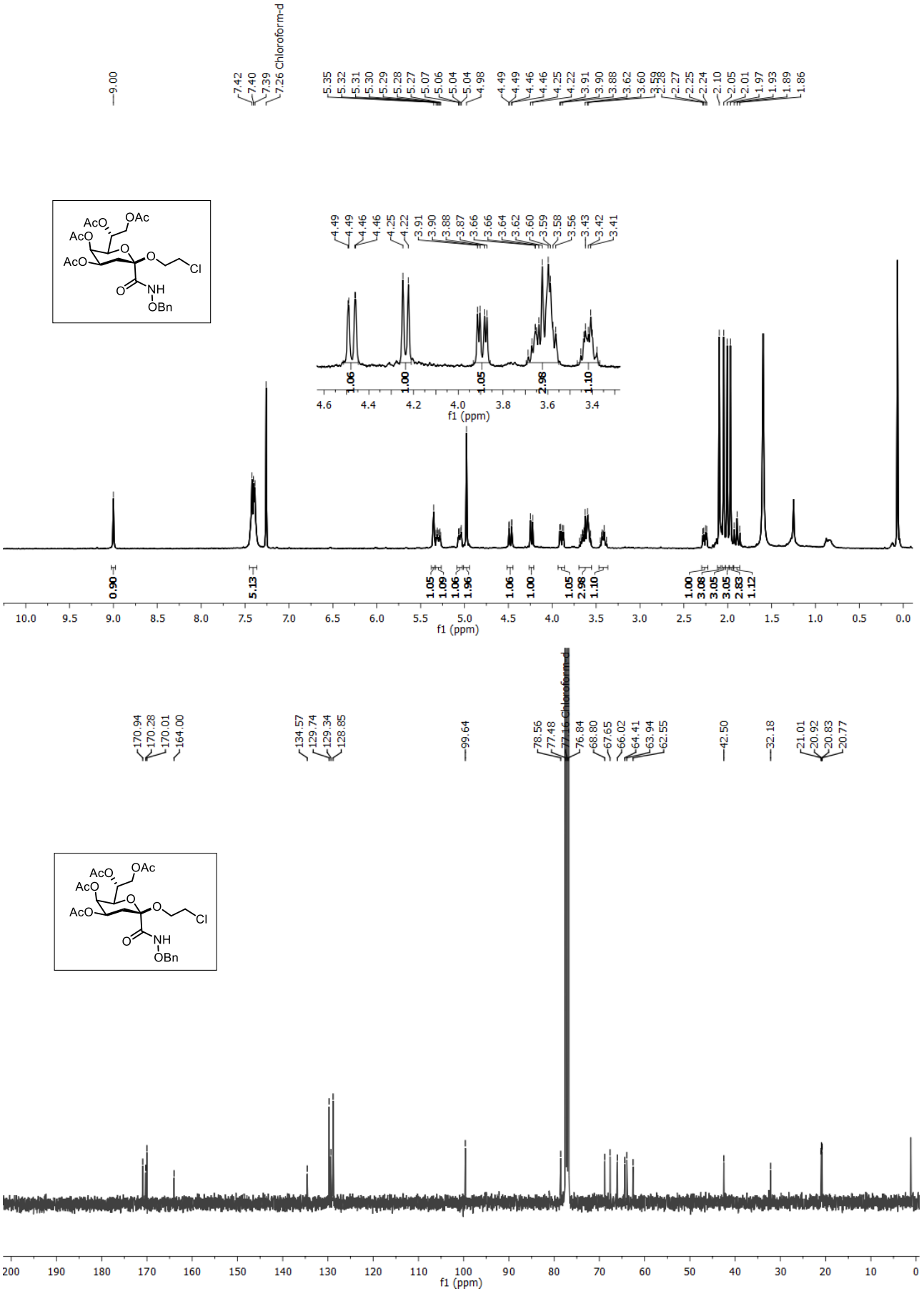
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(3)***



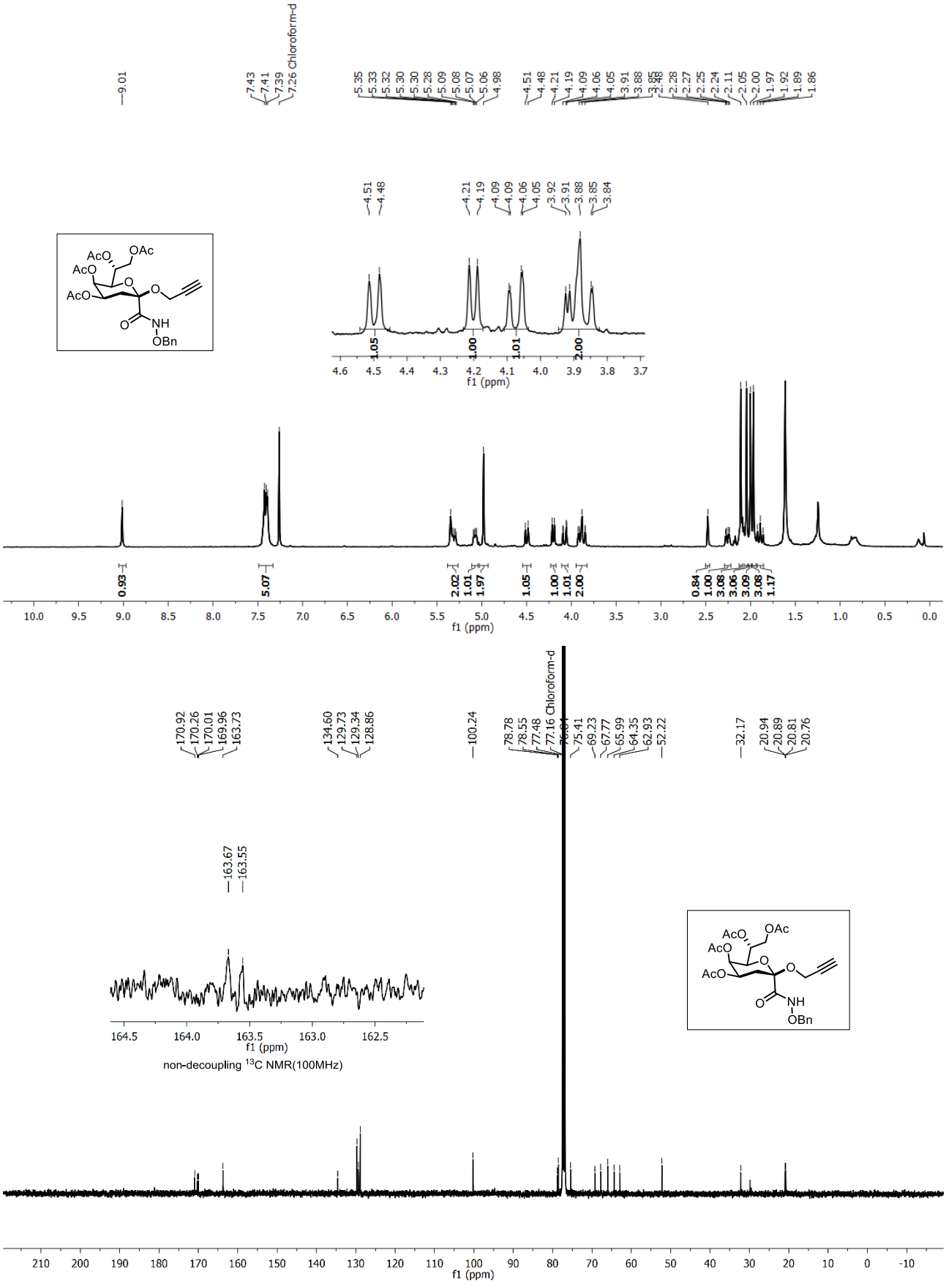
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(5)***



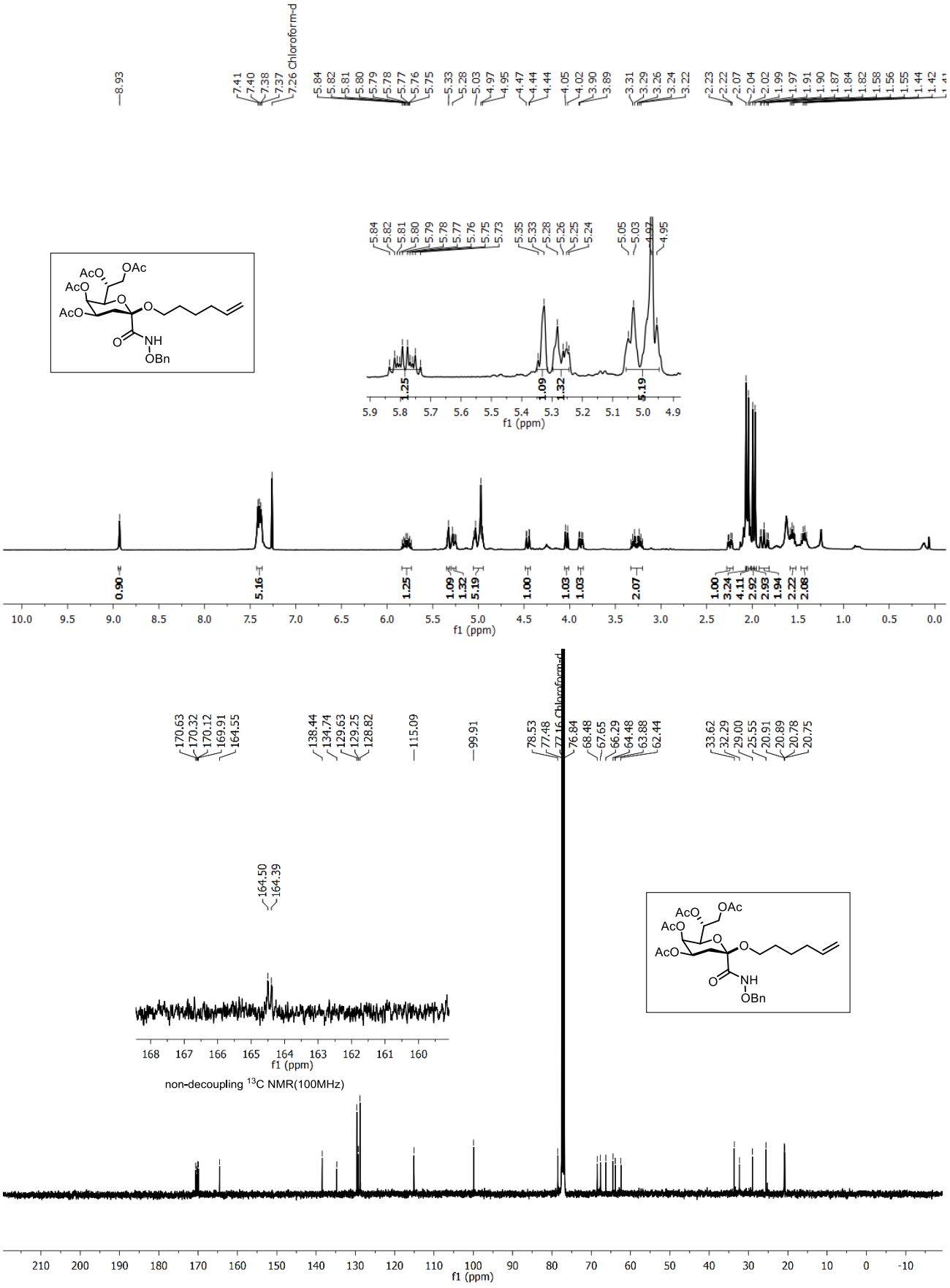
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(7)***



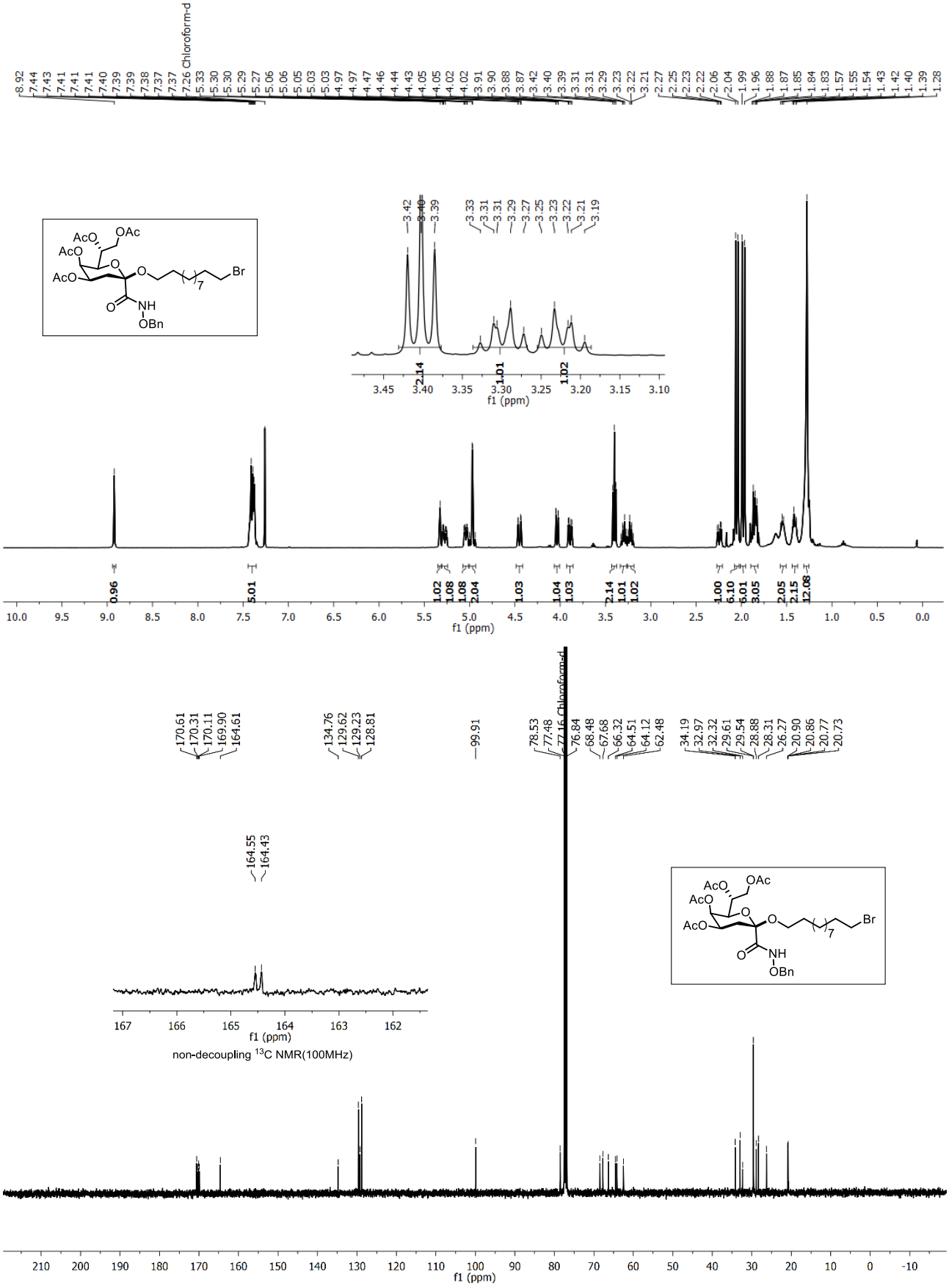
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(8)***



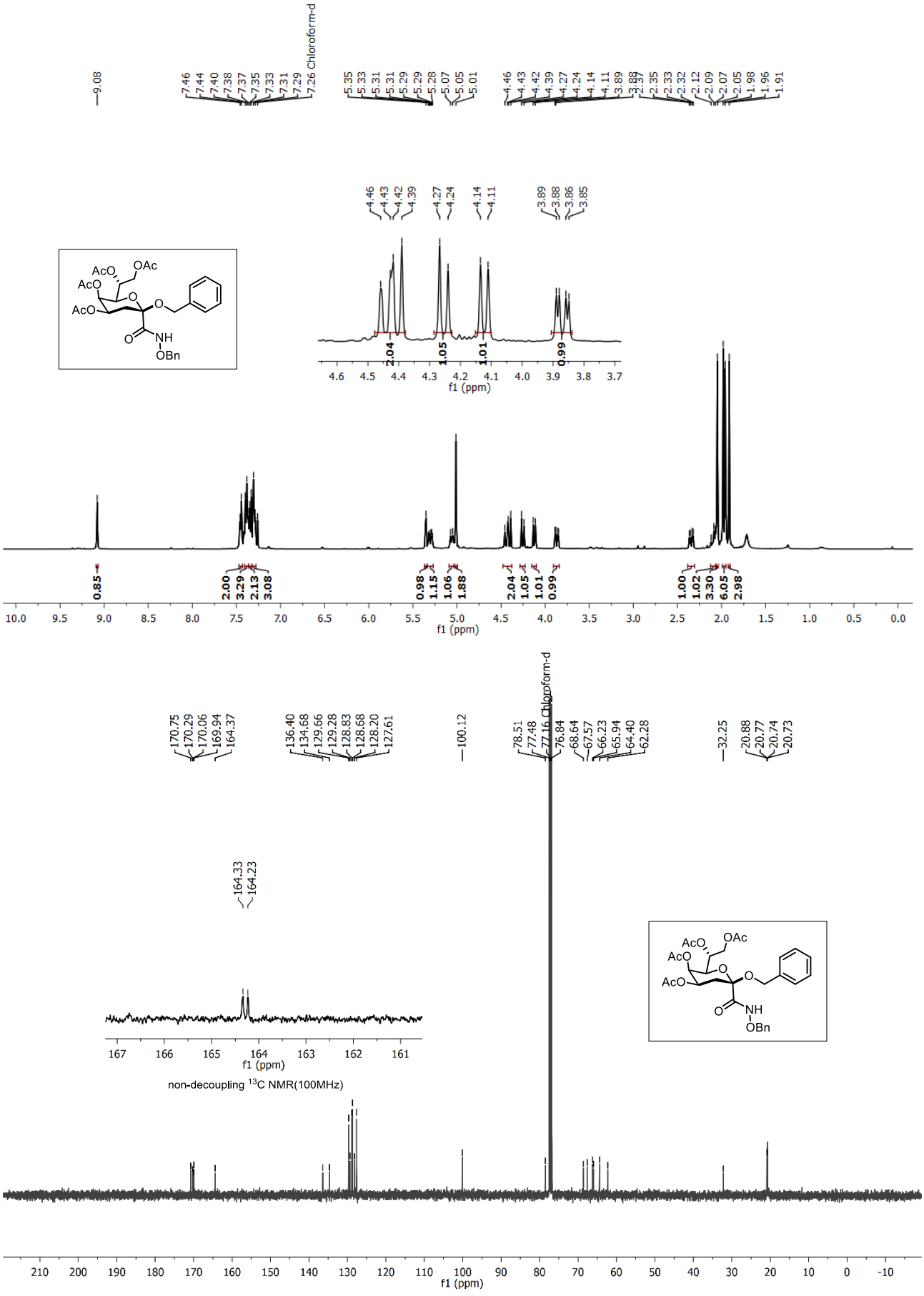
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(9)***



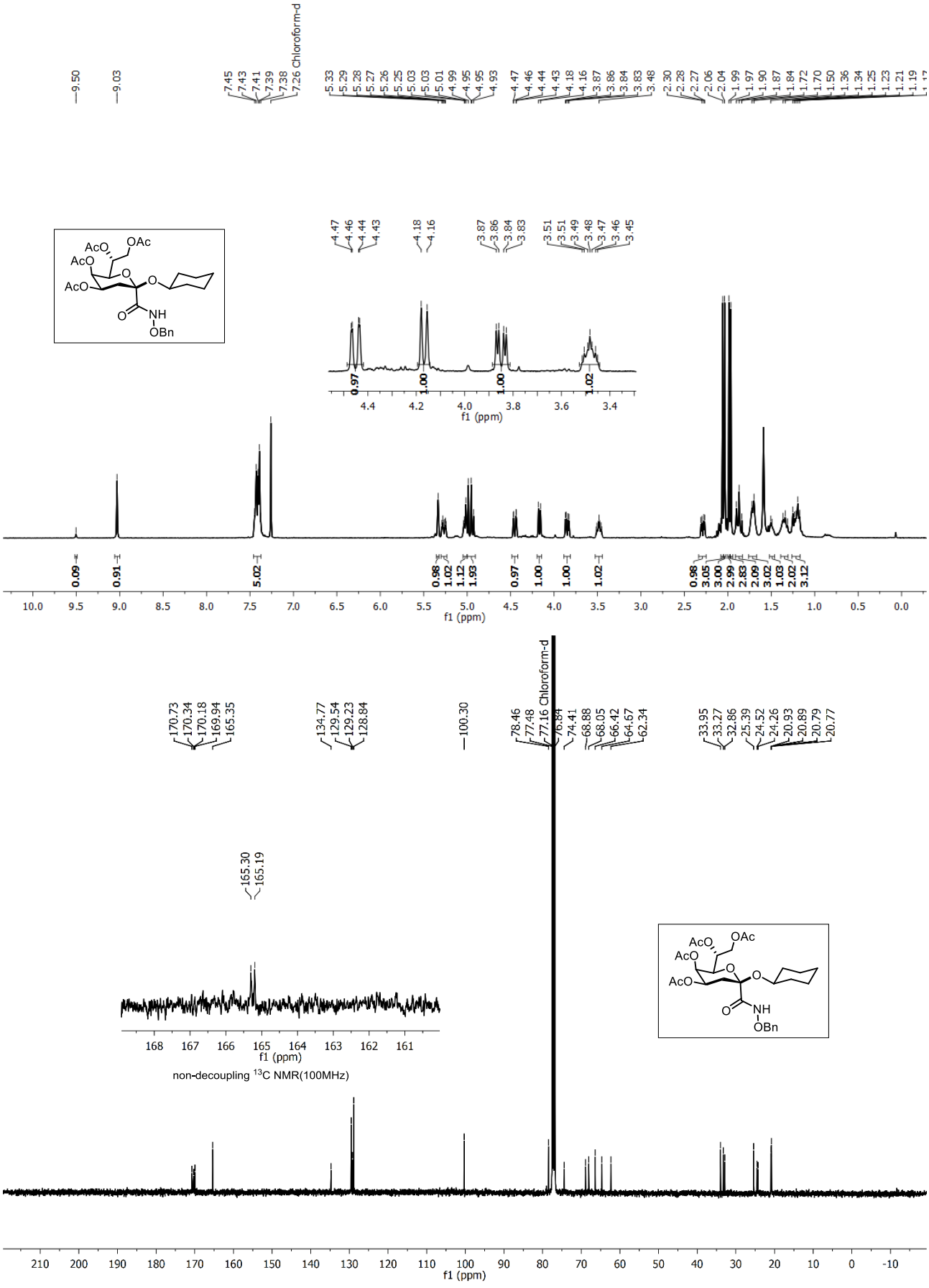
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(10)***



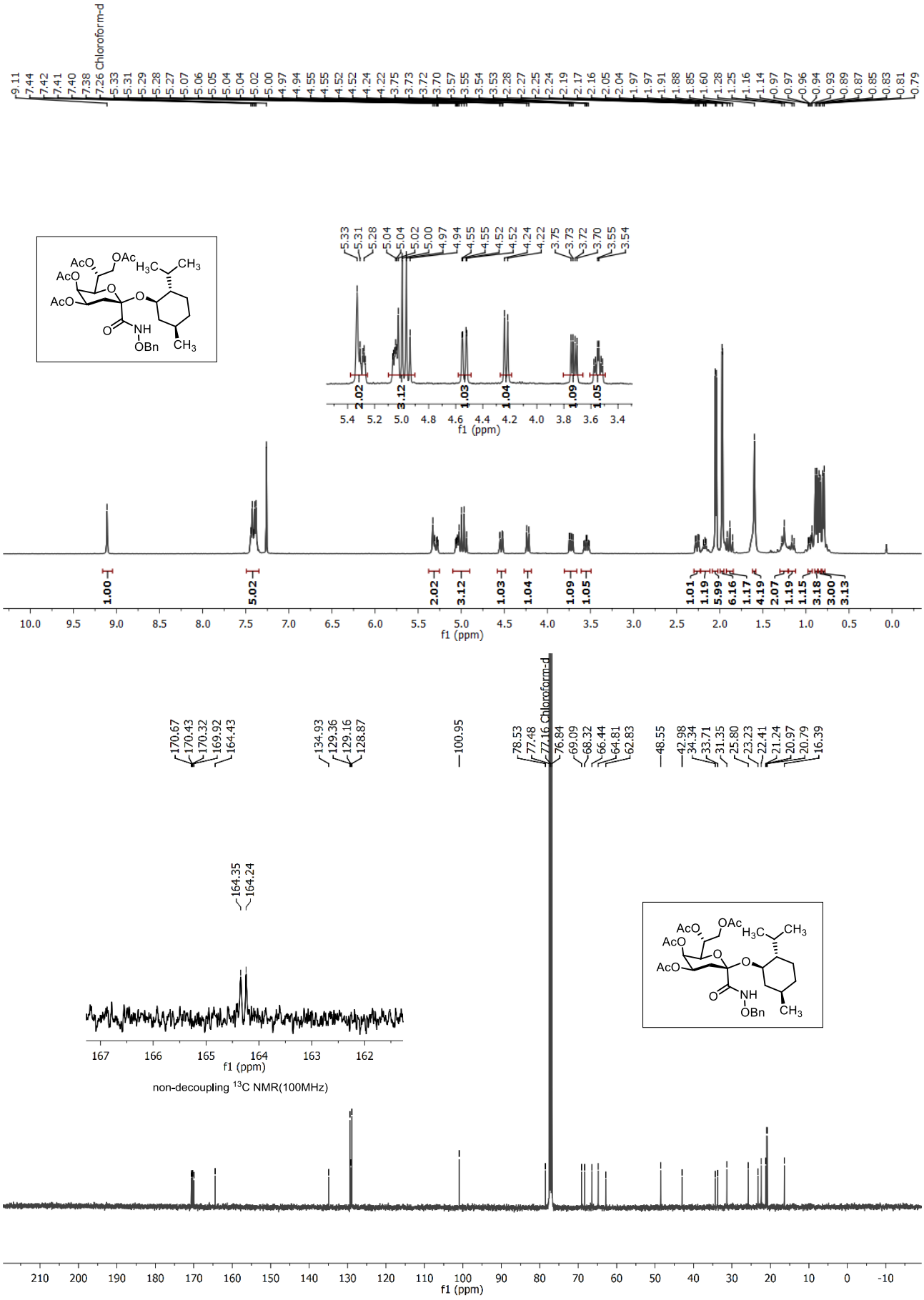
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(11)***



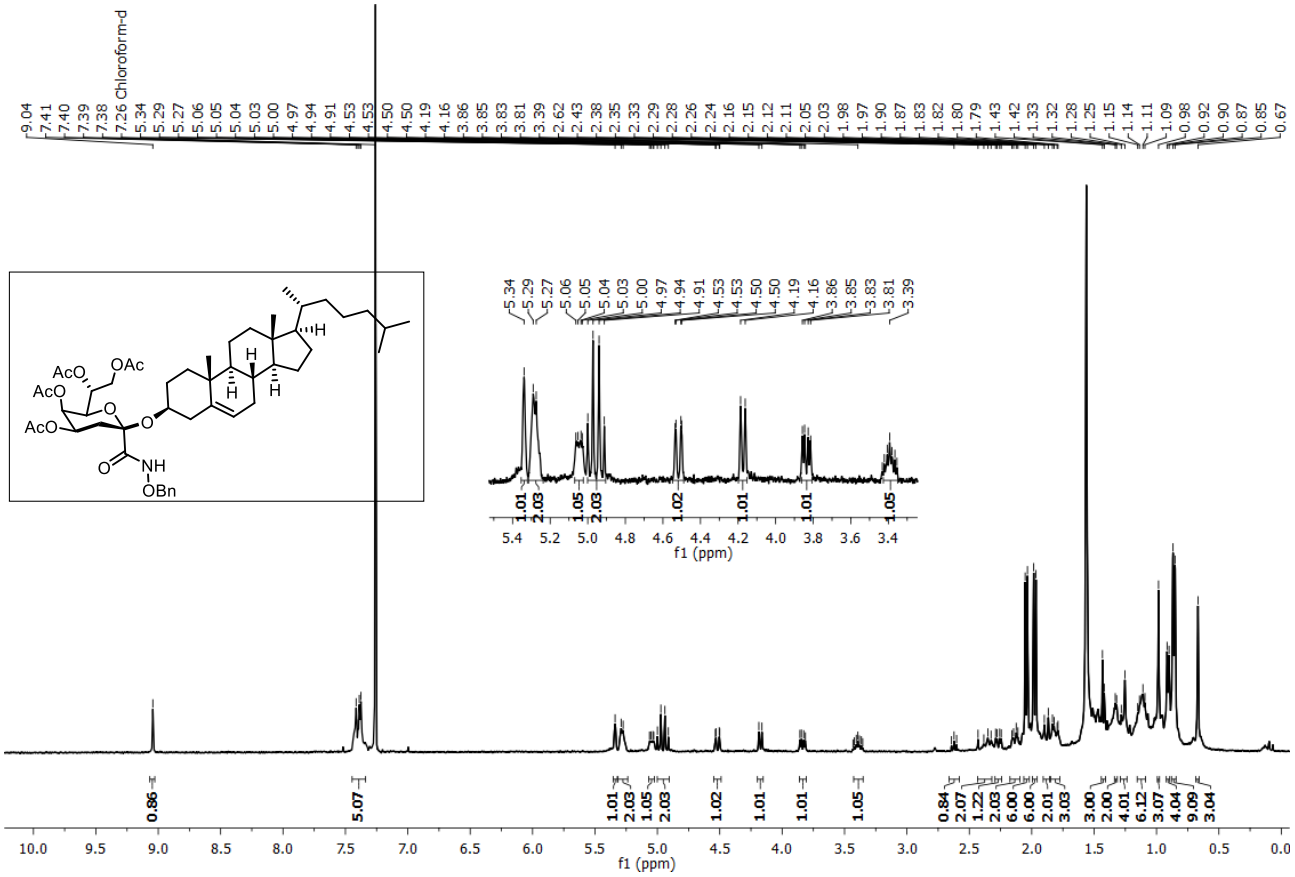
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(12)***

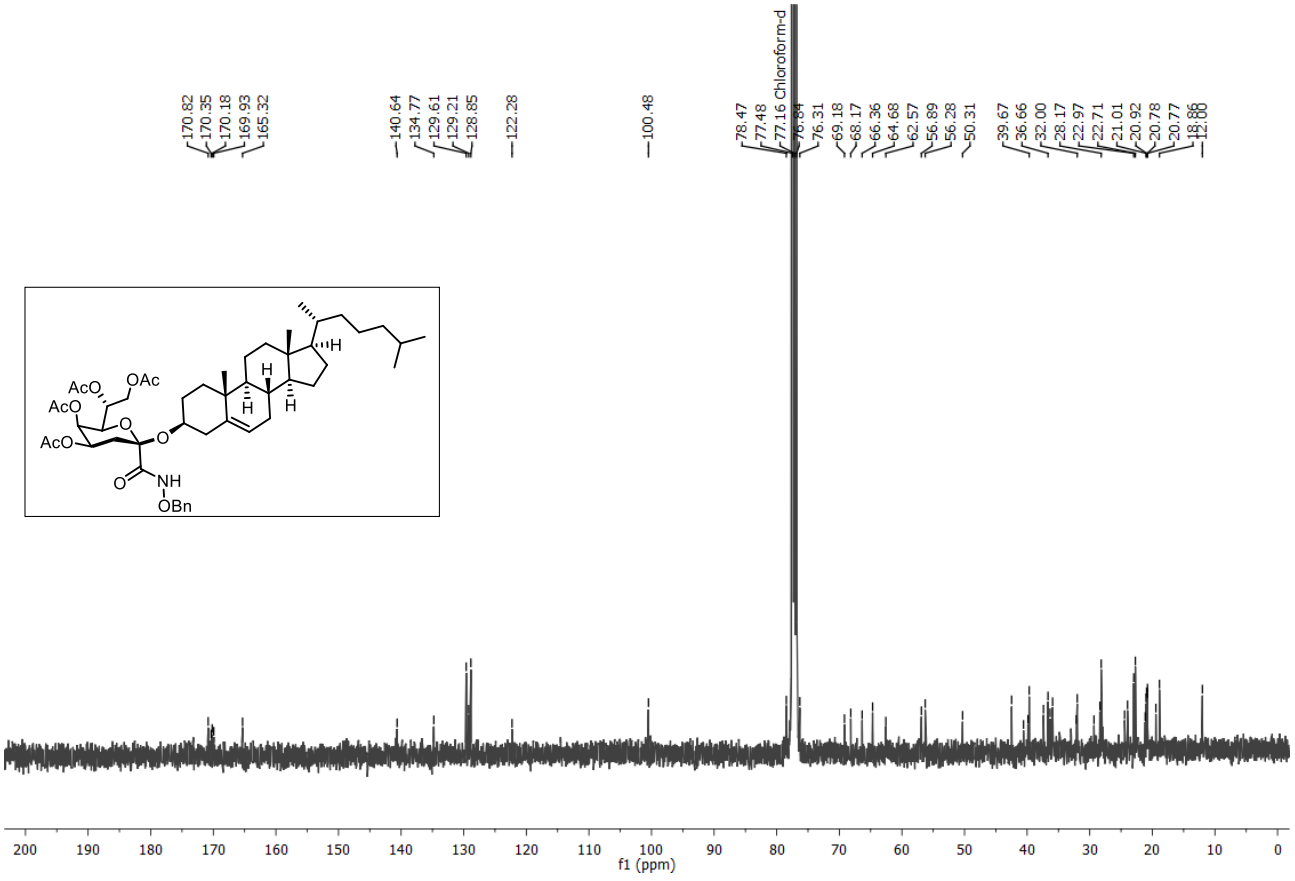


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(13)***

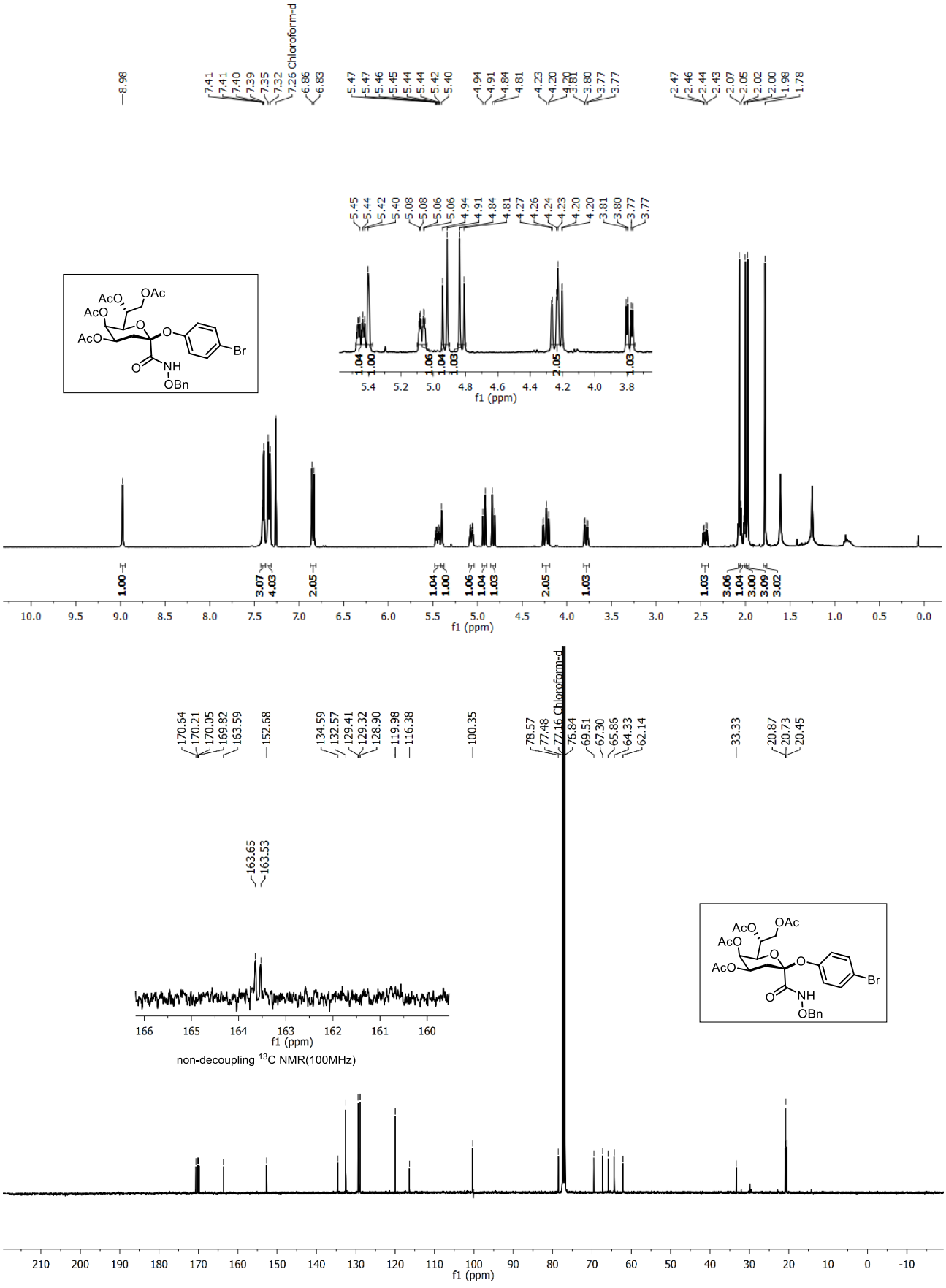


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(14)***

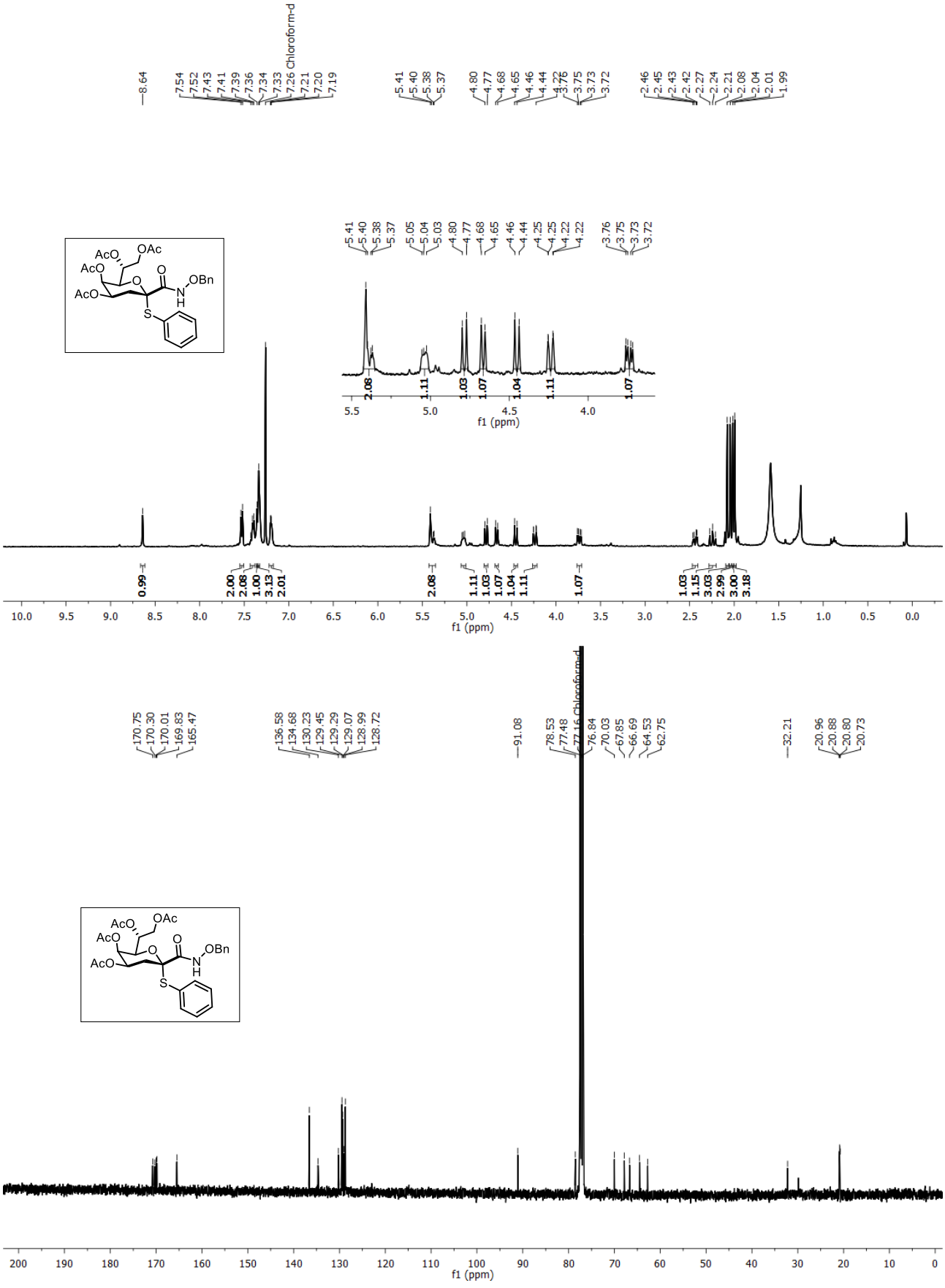




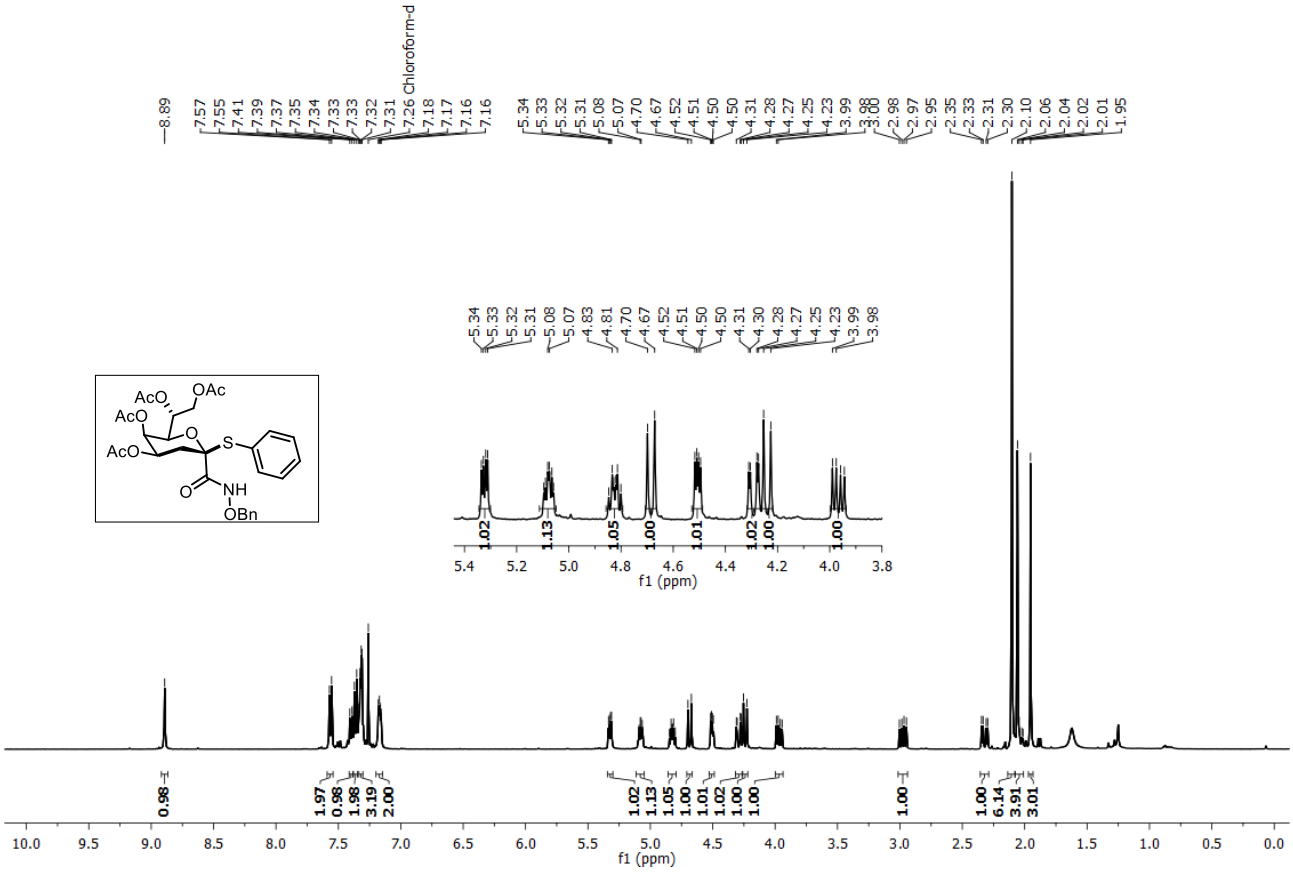
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(15)***

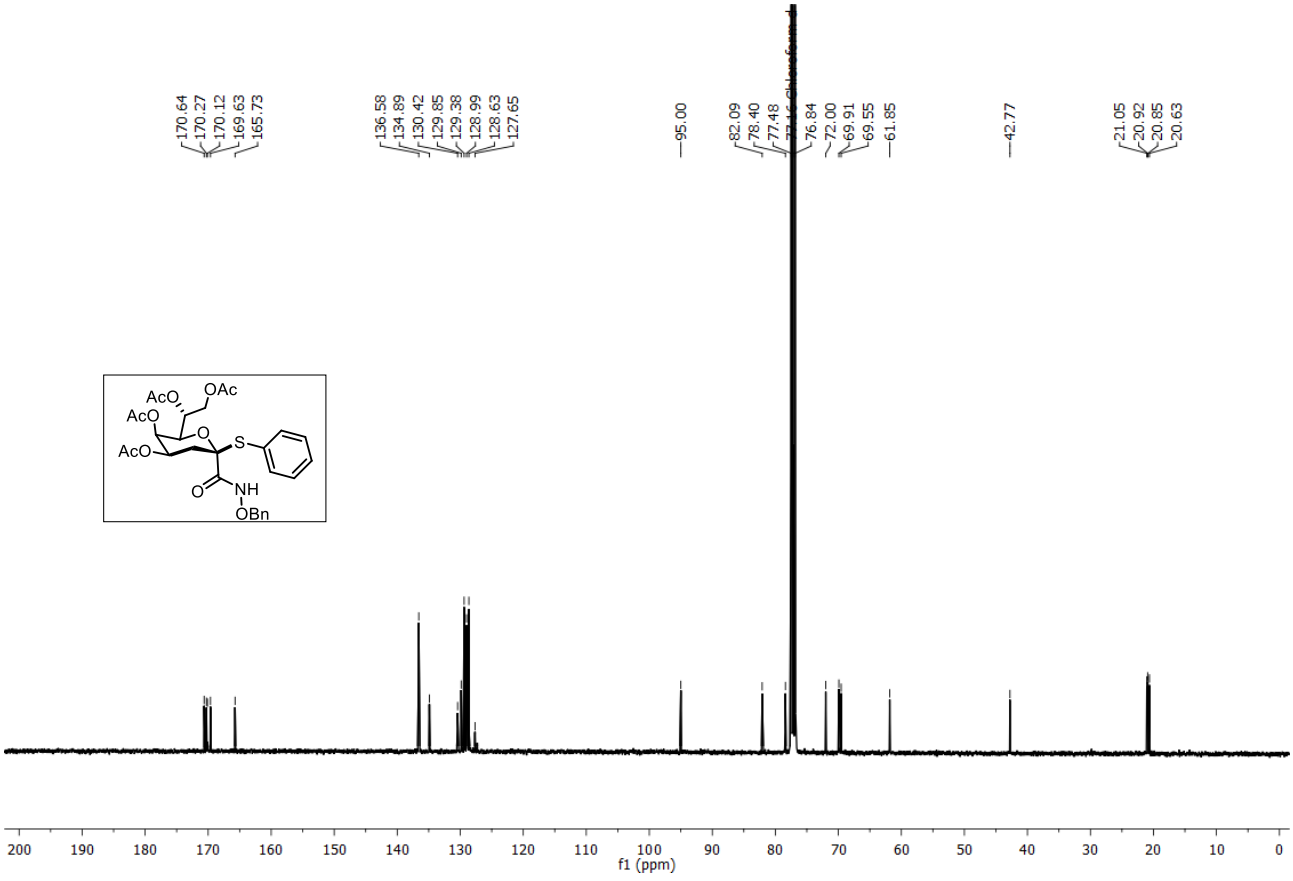


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(16α)***

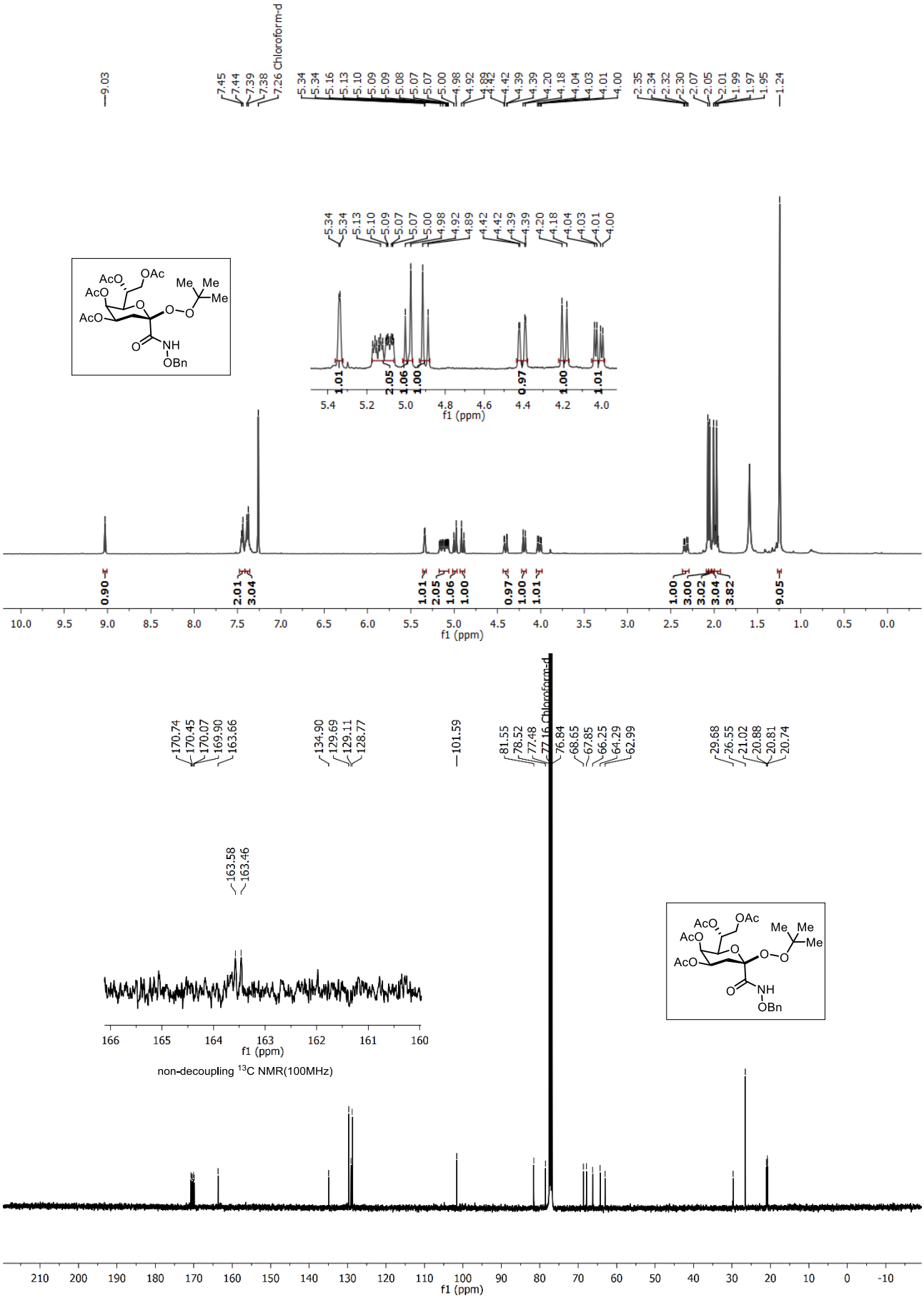


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(16β)***

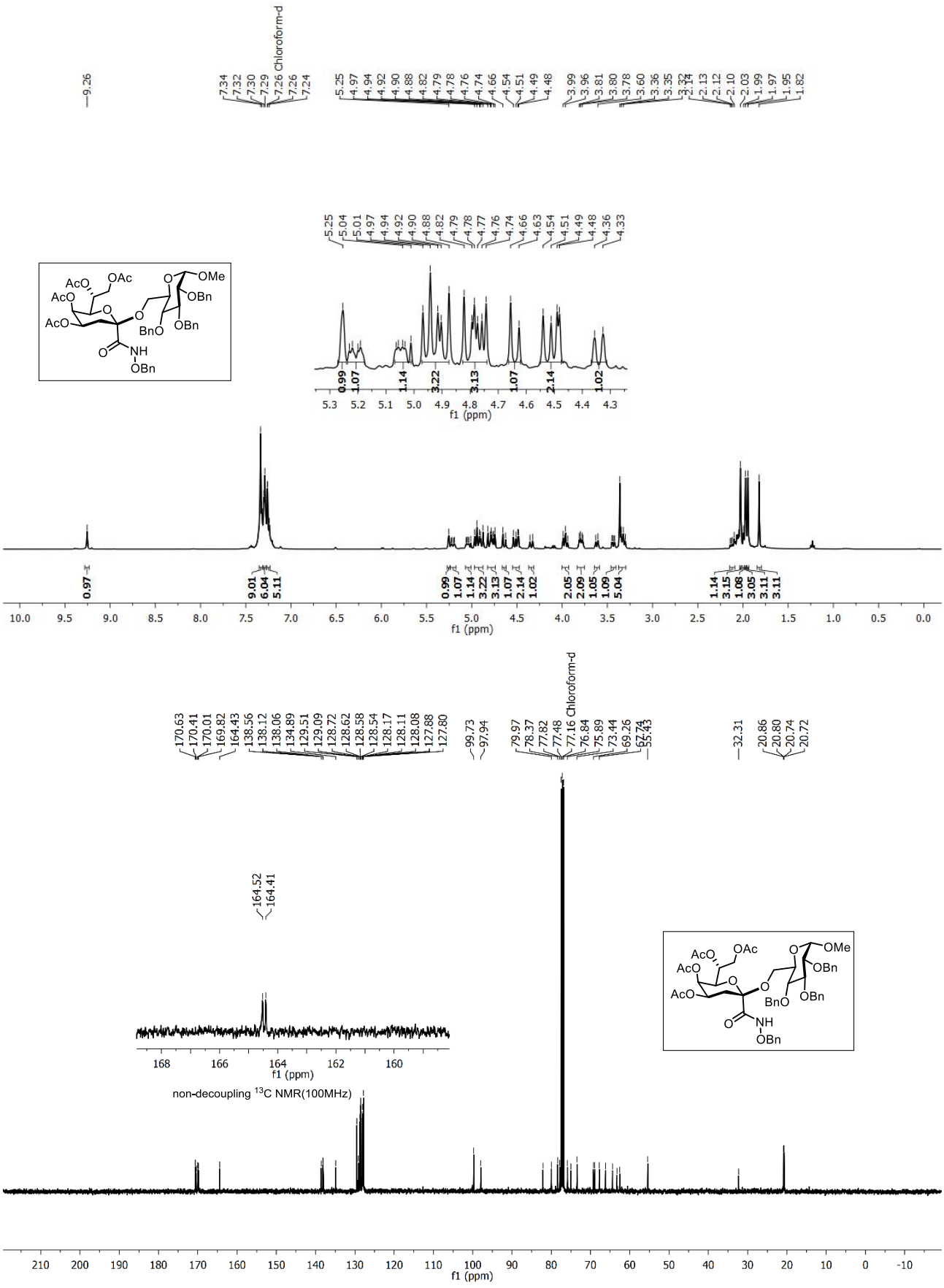




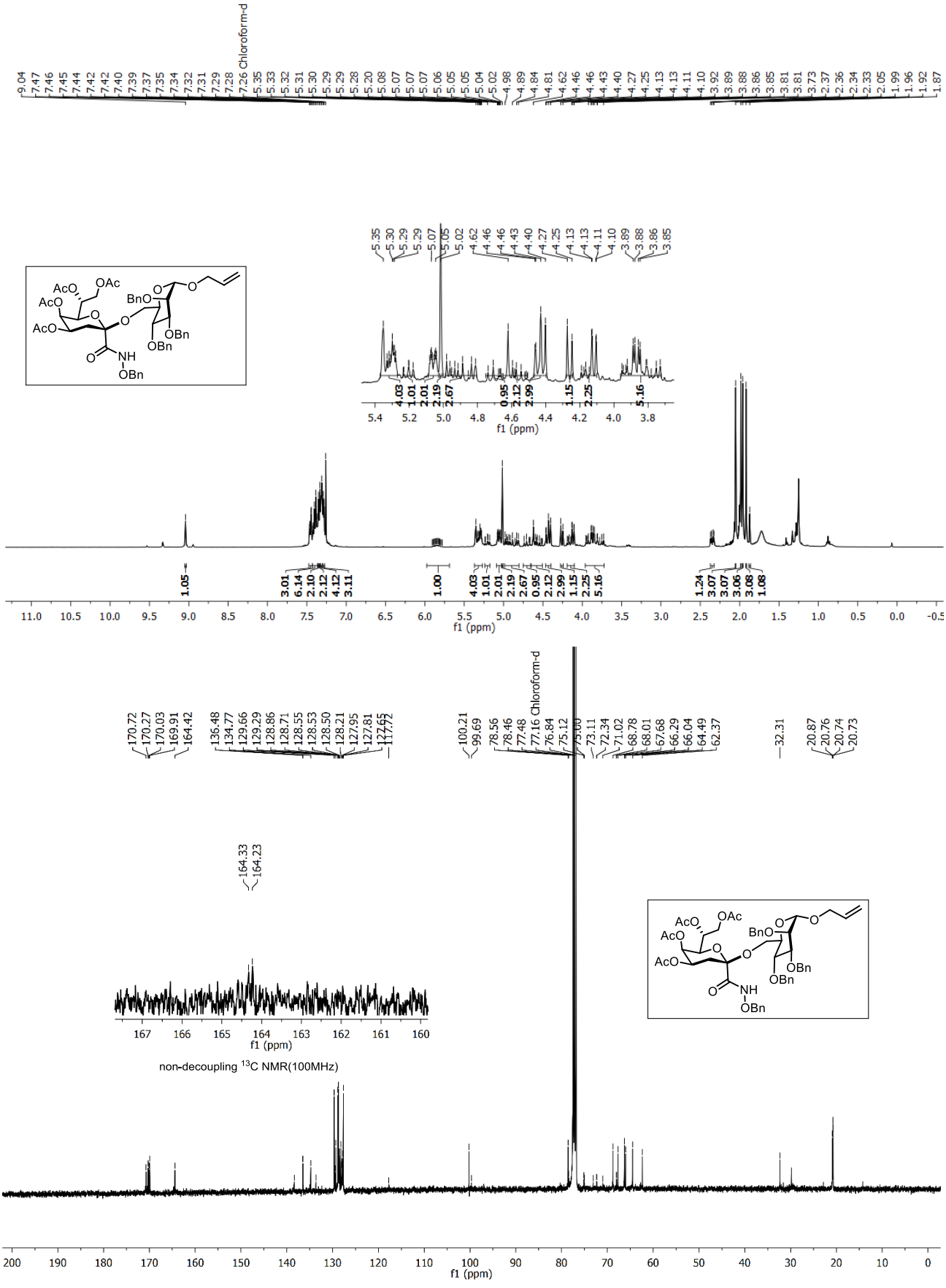
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(17)***



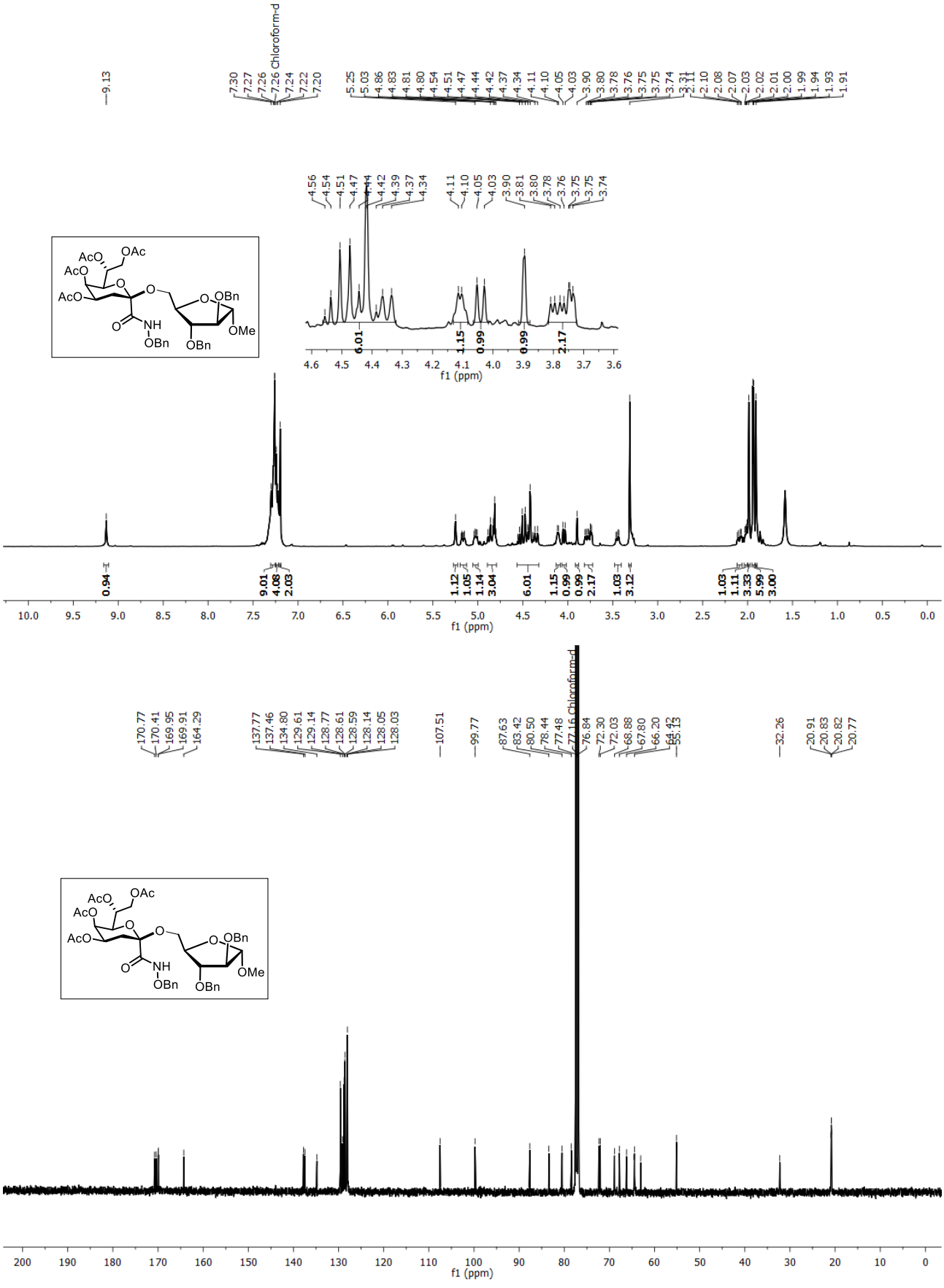
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(18)***



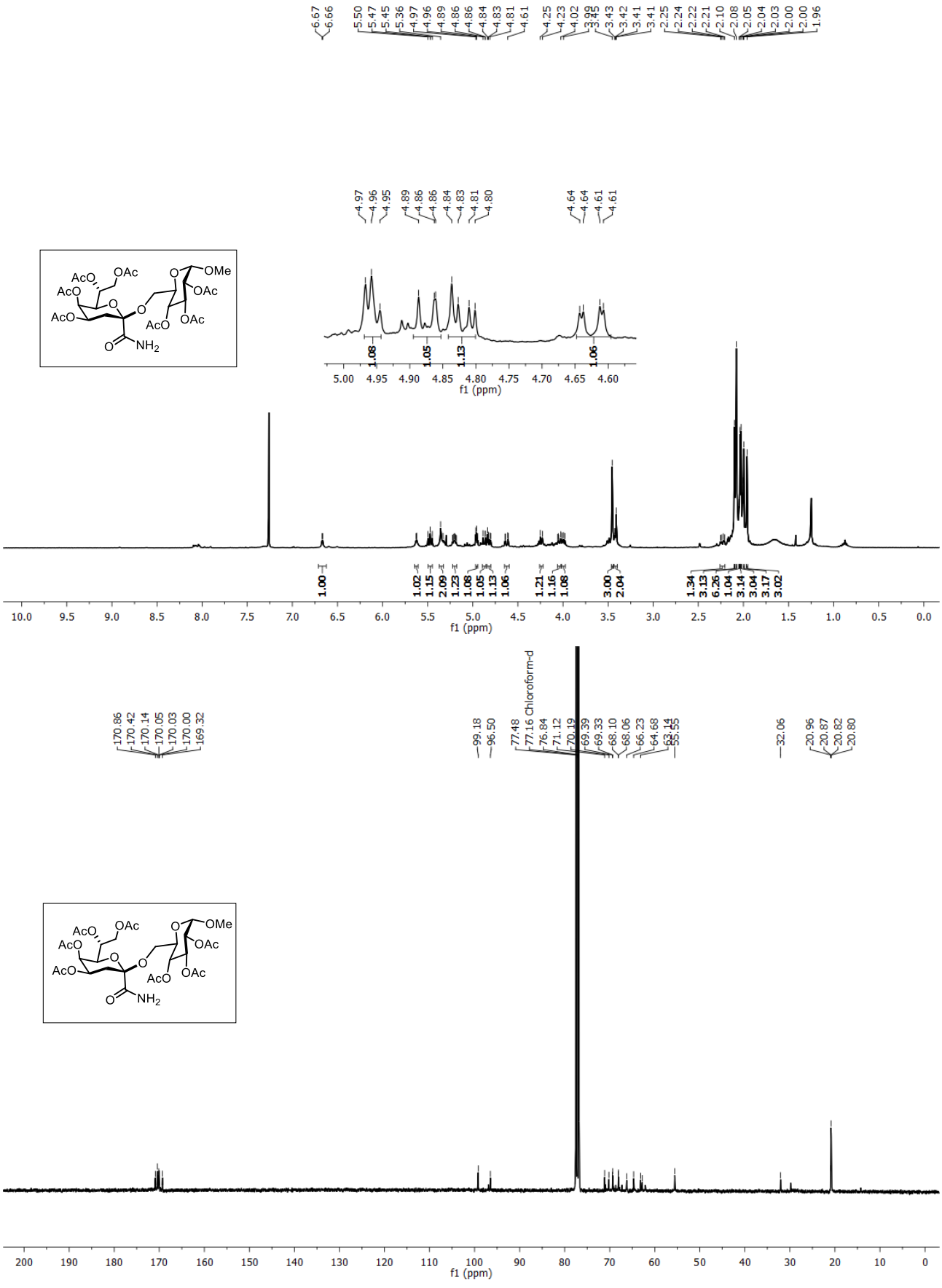
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(19)***



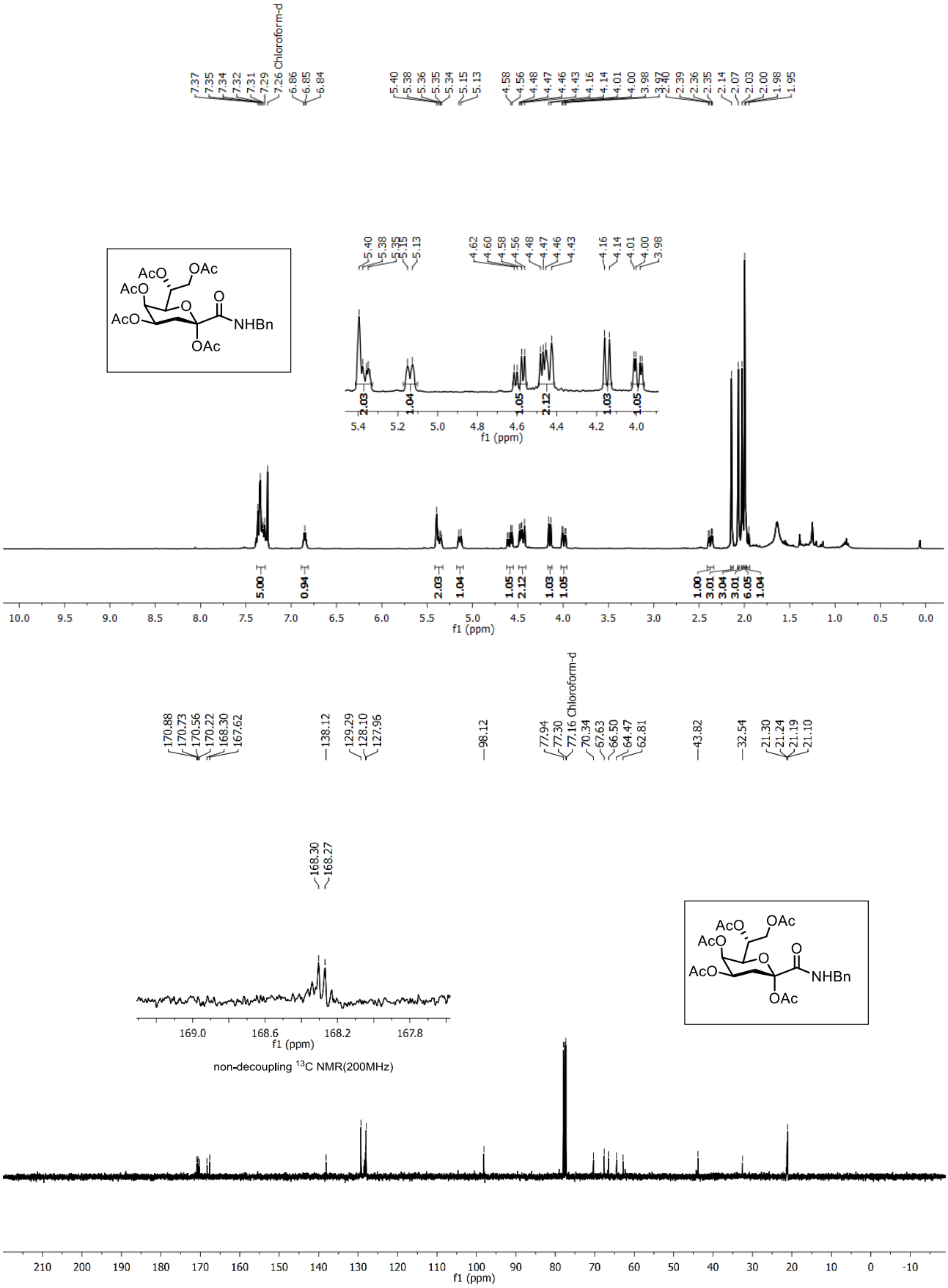
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(20)***



^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(23)***



^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(24)***



^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(25)***