Supporting Information

Zinc Tetrafluoroborate Catalyzed *α*-Stereoselective Synthesis of Pseudoglycals: Efficient Synthesis of digitoxin *α*-L-amicetose

Mrinmoy Manash Bharali[ab], Abhishek Santra *[ab]

[a] Department of Organic Synthesis and Process Chemistry, CSIR-Indian Institute of Chemical Technology, Uppal Road, Hyderabad-500007, India

[b] Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India

*Corresponding author: Email: asantra@iict.res.in

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Experimental procedures

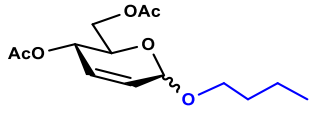
General methods

All reactions were carried out in oven-dried glassware, using dry solvents, in an inert atmosphere (nitrogen). All reagents were obtained from commercial suppliers (Sigma, TCI chemicals and Spectrochem). TLC was performed on aluminium plates that had already been pre-coated with Silica Gel 60 F_{254} (0.25 mm, E. Merck). 10% sulfuric acid in ethanol staining was used in thin-layer chromatography (TLC, Sorbent Technologies) on silica gel plates in order monitor reaction progress. The synthesized compounds were purified using column chromatography with silica gel (230 - 400 and 100 - 200 mesh), and the solvent polarity was chosen based on the TLC mobility. Structural characterization was done with the help of 1D, 2D (COSY, HSQC) NMR-Spectroscopy. All NMR experiments (^{1}H, ^{13}C, COSY and HSQC) were performed on a Bruker Advance III (400/500/600 MHz) spectrometer. Chemical shifts were reported in δ ppm respective to the internal standard of the residual chloroform (^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm). The following information is provided for proton NMR data: chemical shift (ppm), multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, and m: multiplet), coupling constant (*J* in Hz), integration, and the corresponding assigned proton (s). Data from ^{13}C NMR are presented as follows: chemical shift (ppm) and the corresponding carbon. High-resolution mass spectra HRMS were obtained using (ESI - TOF) techniques. Anton Paar analytical was used to collect optical rotation data at 589 nm (Na) and 20°C, and specific rotation was reported in units of (deg mL)/ (g dm). Unless otherwise specified, reaction yields for all processes pertain to chromatographically and spectroscopically pure compounds.

General glycosylation procedure:

To a solution of glycal donor (1.2 eq.) and acceptor (1.0 eq.) in 1.0 mL anhydrous dichloroethane $Zn(BF_4)_2.xH_2O$ (0.2 eq.) was added under N_2 atmosphere and stirred at 50°C until the reaction was determined to be complete by TLC of the crude material. Then the solvent was concentrated in a vacuo. The dry residue was purified by silica gel column chromatography.

***n*-Butyl-4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (3A)**



3A

Following the general glycosylation procedure. Acceptor **2A** (20 µL, 0.22 mmol) and donor **1** (71 mg, 0.26 mmol) to afford after 2 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 3:1), **3A** as a yellow oil (55 mg, 89%, *α*:*β* = 6:1).

Data of the compound (3A)

$[\alpha]_D^{20}$ + 47.2 (*c* 0.9, $CHCl_3$)

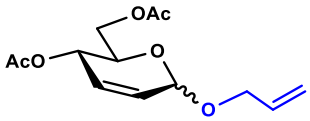
IR ($CHCl_3$) *v* 2920, 2875, 1760, 1621, 1376, 1211, 1040, 769 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 - 5.81 (m, 2H, H-2, H-3), 5.31 (dd, *J* = 9.7, 1.3 Hz, 1H, H-4), 5.03 (brs, 1H, H-1), 4.28 - 4.19 (m, 2H, H-6ab), 4.13 - 4.10 (m, 1H, H-5), 3.81 - 3.75 (m, 1H, -OCH_2), 3.54 - 3.48 (m, 1H, -OCH_2), 2.10 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), 1.61 - 1.58 (m, 2H, -$OCH_2CH_2CH_2$), 1.43 - 1.37 (m, 2H, -$OCH_2CH_2CH_2$), 0.94 (t, *J* = 7.4 Hz each, 3H, -$OCH_2CH_2CH_2CH_3$)

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8 (*C*OCH_3), 170.3 (*C*OCH_3), 128.9, 128.0, 94.4 C-1), 68.6, 66.9, 65.3, 63.1, 31.8, 21.0 (CO*C*H_3), 20.8 (CO*C*H_3), 19.4, 13.8

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. For $C_{14}H_{22}O_6Na$ 309.1309, found 309.1314.

Allyl-4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (3B)



3B

Following the general glycosylation procedure. Acceptor **2B** (20 µL, 0.29 mmol) and donor **1** (96 mg, 0.35 mmol) to afford after 2 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 3:1), **3B** as a yellow oil (75 mg, 95%, *α*:*β* = 6:1).

Data of the compound (3B)

$[\alpha]_D^{20}$ + 135.0 (*c* 1.0, $CHCl_3$)

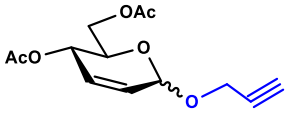
IR ($CHCl_3$) *v* 2930, 2345, 1751, 1367, 1211, 1056 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 - 5.84 (m, 3H, H-2, H-2′, H-3), 5.33 - 5.28 (m, 2H, H-4, H-3′a), 5.23 - 5.19 (m, 1H, H-3′b), 5.08 (br s, 1H, H-1), 4.30 - 4.10 (m, 5H, H-5, H-6ab, H-1′ab), 2.11 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3)

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8 (*C*OCH_3), 170.3 (*C*OCH_3), 134.1, 129.2, 127.7, 117.5, 93.6 (C-1), 69.3, 67.0, 65.3, 63.0, 21.0 (CO*C*H_3), 20.8 (CO*C*H_3)

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. For $C_{13}H_{18}O_6Na$ 293.0996, found 293.0970.

Propargyl 4,6-Di-*O*-acetyl-2,3-dideoxy-*α*-D-erythro-hex-2-enopyranoside (3C)



3C

Following the general glycosylation procedure. Acceptor **2C** (20 µL, 0.35 mmol) and donor **1** (113 mg, 0.42 mmol) to afford after 1.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 3:1), **3C** as a white solid (92 mg, 99%, *α*:*β* = 6:1).

Data of the compound (3C)

$[\alpha]_D^{20}$ + 39.0 (*c* 1.2, $CHCl_3$)

mp 54 - 55 °C

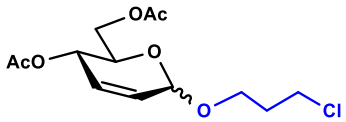
IR ($CHCl_3$) *v* 3260, 1765, 1345, 1267, 1056, 951, 733 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 5.93 (d, *J* = 10.2 Hz, 1H, H-3), 5.85 (dt, *J* = 10.2, 2.3 Hz, 1H, H-2), 5.36 - 5.33 (m, 1H, H-4), 5.25 (br s, 1H, H-1), 4.32 (d, *J* = 2.4 Hz, 2H, OCH_2), 4.26 - 4.19 (m, 2H, H-6ab), 4.10 (ddd, *J* = 9.3, 5.1, 2.4 Hz, 1H, H-5), 2.46 (t, *J* = 2.4 Hz each, 1H, CC*H*), 2.11 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.7 ($COCH_3$), 170.2 ($COCH_3$), 129.7, 127.2, 92.8 (C-1), 74.8, 72.7, 67.2, 65.1, 62.8, 55.0, 20.9 ($COCH_3$), 20.8 ($COCH_3$)

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{13}H_{16}O_6Na$ 291.0839, found 291.0811.

Chloropropyl 4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (3D)



3D

Following the general glycosylation procedure. Acceptor **2D** (18 µL, 0.21 mmol) and donor **1** (69 mg, 0.25 mmol) to afford after 2 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =3:1), **3D** as a colourless gel (63 mg, 95%, *α*:*β* = 7:1).

Data of the compound (3D)

$[\alpha]_D^{20}$ + 54.7 (*c* 1.1, $CHCl_3$)

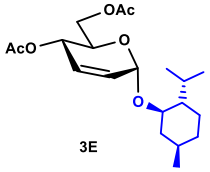
IR ($CHCl_3$) *v* 2960, 2945, 2857, 1757, 1425, 1360, 1221, 1065, 978, 746, 739, 668, 605 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 5.93 - 5.80 (m, 2H, H-2, H-3), 5.32 (dq, *J* = 9.7, 1.6 Hz, 1H, H-4), 5.05 (brs, 1H, H-1), 4.30 - 4.16 (m, 2H, H-6ab), 4.11 - 4.08 (m, 1H, H-5), 4.00 - 3.94 (m, 1H, Linker CH_2), 3.70 - 3.61 (m, 3H, Linker CH_2), 2.11 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.08 - 2.04 (m, 2H, Linker CH_2).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8 ($COCH_3$), 170.2 ($COCH_3$), 129.2, 127.6, 94.4 (C-1), 67.0, 65.2, 65.0, 63.0, 41.7, 32.5, 20.9, 20.8

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{13}H_{19}ClO_6Na$ 329.0762, found 329.0770.

L-Menthyl 4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (3E)



3E

Following the general glycosylation procedure. Acceptor **2E** (20 mg, 0.13 mmol) and donor **1** (42 mg, 0.15 mmol) to afford after 1.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =), **3E** as a colourless gel (40 mg, 85%).

Data of the compound (3E)

$[\alpha]_D^{20}$ + 30.5 (*c* 3.0, $CHCl_3$)

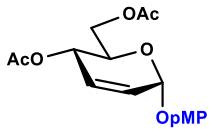
IR ($CHCl_3$) ν 2967, 2910, 2863, 1740, 1446, 1378, 1221,1022, 989, 738, 669, 611 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 5.89 - 5.82 (m, 2H, H-2, H-3), 5.29 (d, *J* = 9.5 Hz, 1H, H-4), 5.09 (s, 1H, H-1), 4.25 - 4.16 (m, 3H, H-5, H-6ab), 3.44 - 3.39 (m, 1H, H-menthol), 2.21 - 2.17 (m, 1H, H-menthol), 2.11 (s, 3H, COCH_3), 2.07 (s, 3H, COCH_3), 1.66 - 1.61 (m, 2H, H-menthol), 1.46 - 1.40 (m, 1H, H-menthol), 1.27 - 1.21 (m, 1H-menthol), 1.09 - 1.02 (m, 1H, H-menthol), 0.99 - 0.96 (m, 1H, H-menthol), 0.92 (d, *J* = 2.5 Hz, 3H, CH_3-menthol), 0.90 (d, *J* = 2.5 Hz, 3H, CH_3-menthol), 0.89- 0.80 (m, 1H, H-menthol), 0.78 (d, *J* = 7.0 Hz, 3H, CH_3-menthol)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.8 (*C*OCH_3), 170.3 (*C*OCH_3), 128.5, 128.0, 96.1 (C-1), 81.0, 66.7, 65.3, 63.3, 48.8, 43.35, 34.29, 31.73, 25.63, 23.18, 22.38, 21.1, 20.9 (CO*C*H_3), 20.8 (CO*C*H_3), 16.2

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{20}H_{32}O_6Na$ 391.2091, found 391.2081.

***p*-Methoxyphenyl-4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (3F)**



3F

Following the general glycosylation procedure. Acceptor **2F** (20 mg, 0.16 mmol) and donor **1** (53 mg, 0.19 mmol) to afford after 1.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 3:1), **3F** as a white solid (38 mg, 70%).

Data of the compound (3F)

$[\alpha]_D^{20}$ + 121.5 (*c* 0.8, $CHCl_3$)

mp 78 - 79 °C

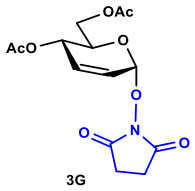
IR ($CHCl_3$) *v* 2935, 1756, 1610, 1501, 1367, 1222, 1022, 978 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 9.1 Hz, 2H, Ar-H), 6.83 (d, *J* = 9.1 Hz, 2H, Ar-H), 6.01 (brs, 2H, H-2, H-3), 5.57 (brs, 1H, H-1), 5.37 (d, *J* = 9.2 Hz, 1H, H-4), 4.31 - 4.24 (m, 2H, H-6ab), 4.16 (dt, *J* = 12.4, 2.9 Hz, 1H, H-5), 3.78 (s, 3H, OCH_3), 2.11 (s, 3H, COCH_3), 2.02 (s, 3H, COCH_3)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.7 (*C*OCH_3), 170.3 (*C*OCH_3), 155.2, 151.1, 129.9, 127.2, 118.6, 114.5, 94.0 (C-1), 67.6, 65.1, 62.8, 55.7, 21.0 (CO*C*H_3), 20.7 (CO*C*H_3)

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{17}H_{20}O_7Na$ 359.1101, found 359.1076.

***N*-Succinimido-4,6-di-acetyl-2,3-dideoxy-*α*-D-*erythro*-2-enopyranoside (3G)**



Following the general glycosylation procedure. Acceptor **2G** (20 mg, 0.17 mmol) and donor **1** (57 mg, 0.21 mmol) to afford after 0.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 1:1), **3G** as a colourless gel (50 mg, 88%).

Data of the compound (3G)

$[\alpha]_D^{20}$ + 109.9 (*c* 3.1, $CHCl_3$)

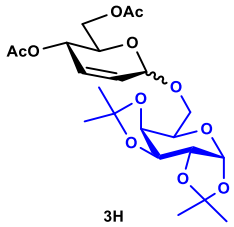
IR ($CHCl_3$) *v* 2934, 2846, 1754, 1430, 1380, 1221, 1211, 1106, 1065, 909, 836, 765, 650, 604 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 6.16 - 6.13 (m, 1H, H-3), 6.00 (ddd, *J* = 10.2, 2.8, 2.0 Hz, 1H, H-2), 5.57 (s, 1H, H-1), 5.45 (dq, *J* = 10.0, 1.8 Hz, 1H, H-4), 4.58 (dt, *J* = 10.0, 2.9 Hz, 1H, H-5), 4.32 (dd, *J* = 12.6, 3.4 Hz, 1H, H-6a), 4.16 (dd, *J* = 12.6, 2.3 Hz, 1H, H-6b), 2.74 (s, 4H, NHS-$2CH_2$), 2.12 (s, 3H, COC*H*$_3$), 2.09 (s, 3H, COC*H*$_3$)

^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 171.1(2*C*O-NHS), 170.7 (*C*OCH_3), 170.2 (*C*OCH_3), 133.5, 123.0, 98.1(C-1), 68.3, 64.3, 61.8, 25.5(2CH_2-NHS), 20.9 (CO*C*H$_3$), 20.8(CO*C*H$_3$)

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{14}H_{17}NO_8Na$ 350.0846, found 350.0821.

4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (3H)



Following the general glycosylation procedure. Acceptor **2H** (20 mg, 0.08 mmol) and donor **1** (25.1 mg, 0.09 mmol) to afford after 1.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 2:1), **3H** as a white solid (32 mg, 88%, *α*:*β* = 7:1).

Data of the compound (3H)

$[\alpha]_D^{20}$ + 6.4 (*c* 2.6, $CHCl_3$)

mp 114 - 115 °C

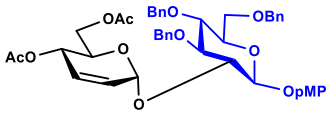
IR ($CHCl_3$) *v* 2990, 2945, 2856, 1761, 1476, 1211, 1165, 1100, 1098, 1008, 945, 899, 766, 600 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 5.90 - 5.83 (m, 2H, H-2′, H-3′), 5.52 (d, *J* = 4.8 Hz, 1H, H-1), 5.32 (dd, *J* = 9.7, 1.2 Hz, 1H, H-4′), 5.09 (s, 1H, H-1′), 4.62 (dd, *J* = 7.9, 2.4 Hz, 1H, H-5′), 4.34 - 4.22 (m, 3H, H-6a′b′, H-2), 4.18 - 4.10 (m, 2H, H-3, H-5), 4.05 - 3.97 (m, 1H, H-4), 3.87 (dd, *J* = 10.2, 6.3 Hz, 1H, H-6a), 3.76 (dd, *J* = 10.2, 7.0 Hz, 1H, H-6b), 2.11 (s, 3H, COC*H*$_3$), 2.08 (s, 3H, COC*H*$_3$), 1.53 (s, 3H, CC*H*$_3$), 1.44 (s, 3H, CC*H*$_3$), 1.34 (d, *J* = 5.2 Hz, 6H, CC*H*$_3$)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.8 (*C*OCH$_3$), 170.3 (*C*OCH$_3$), 129.2 (C-3), 127.7 (C-2), 109.3 ($O_2C(CH_3)_2$), 108.5 ($O_2C(CH_3)_2$), 96.3 (C-1′), 94.6 (C-1), 70.9 (C-2), 70.6 (C-4), 70.5 (C-3), 67.0 (C-5), 66.9 (C-4′), 66.2 (C-5′), 65.2 (C-6), 62.8 (C-6′), 26.1 ($O_2C(CH_3)_2$), 26.0 ($O_2C(CH_3)_2$), 24.9 ($O_2C(CH_3)_2$), 24.5 ($O_2C(CH_3)_2$), 20.9 (CO*C*H$_3$), 20.8 (CO*C*H$_3$)

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{22}H_{32}O_{11}Na$ 495.1837, found 495.1825.

_p_-Methoxyphenyl-4,6-di-_O_-acetyl-2,3-dideoxy-_α_-D-_erythro_-hex-2-enopyranosyl)-(1→2)-3,4,6-tri-_O_-benzyl-_β_-D-glucopyranoside (3I)



3I

Following the general glycosylation procedure. Acceptor **2I** (20 mg, 0.04 mmol) and donor **1** (12 mg, 0.04 mmol) to afford after 7 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 2:1), **3I** as a white solid (17 mg, 60%, *α*:*β* = 99 > 1).

Data of the compound (3I)

$[\alpha]_D^{20}$ + 10.7 (*c* 1.5, $CHCl_3$)

mp 103 - 104 °C

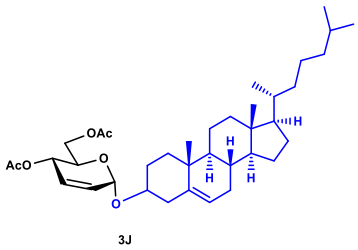
IR ($CHCl_3$) *v* 3021, 2956, 1754, 1498, 1320, 1209, 1086, 998, 752 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.26 (m, 13H, Ar-H), 7.15 (dd, *J* = 6.7, 2.9 Hz, 2H, Ar-H), 6.97 (d, *J* = 9.1 Hz, 2H, Ar-H), 6.80 (d, *J* = 9.1 Hz, 2H, Ar-H), 5.89 - 5.80 (m, 2H, H-2′, H-3′), 5.72 (s, 1H, H-1′), 5.31 (dd, *J* = 9.8, 1.4 Hz, 1H, H-4′), 4.98 (d, *J* = 11.2 Hz, 1H, PhC*H*$_2$), 4.85 (dd, *J* = 11.0, 3.1 Hz, 3H, H-1, PhC*H*$_2$), 4.58 (dt, *J* = 25.5, 7.5 Hz, 3H, PhC*H*$_2$), 4.05 - 3.95 (m, 2H, H-5′, H-2), 3.81 - 3.77 (m, 1H, H-6b′), 3.77 (s, 3H, OC*H*$_3$), 3.74 - 3.71 (m, 3H, H-2, H-3, H-5), 3.66 (dt, *J* = 18.3, 6.7 Hz, 2H, H-4, H-6a), 3.60 - 3.55 (m, 1H, H-6b), 2.02 (d, *J* = 3.4 Hz, 6H, COC*H*$_3$)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.7 (*C*OCH$_3$), 170.1 (*C*OCH$_3$), 155.3 - 137.7 (Ar-C), 129.3 (C-2′), 128.4 - 128.0 (Ar-C), 127.9 (C-3′), 127.7 - 127.4 (Ar-C), 102.6 (C-1), 93.7 (C-1′), 83.5 (C-3), 78.3 (C-4), 76.8 (C-2), 75.7 (Ph*C*H$_2$), 75.3 (Ph*C*H$_2$), 75.1 (C-5), 73.5 (Ph*C*H$_2$), 68.7 (C-6′), 66.6 (C-5′), 64.8 (C-4′), 62.1 (C-6), 55.6 (O*C*H$_3$), 20.9 (CO*C*H$_3$), 20.7 (CO*C*H$_3$)

HRMS (ESI-TOF) m/z $[M + NH_4]^+$ calcd. For $C_{44}H_{52}NO_{12}$ 786.3484, found 786.3450.

Cholesteryl-4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (3J)



3J

Following the general glycosylation procedure. Acceptor **2J** (20 mg, 0.05 mmol) and donor **1** (17 mg, 0.06 mmol) to afford after 2 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 4:1), **3J** as a white solid (26 mg, 84%).

Data of the compound (3J)

$[\alpha]_D^{20}$ + 42.8 (*c* 2.4, $CHCl_3$)

mp 102 - 103 °C

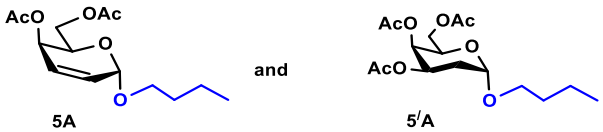
IR ($CHCl_3$) *v* 2935, 2856, 1776, 1445, 1358, 1221, 1035, 999, 756, 657, 600 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 5.91 - 5.85 (m, 1H, H-2), 5.85 - 5.79 (m, 1H, H-3), 5.36 (d, *J* = 5.2 Hz, 1H, H-1), 5.29 (dd, *J* = 9.3, 1.3 Hz, 1H, H-4), 5.17 (s, 1H, CH), 4.24 (dd, *J* = 12.1, 6.0 Hz, 1H, H-5), 4.21 - 4.15 (m, 2H, H-6ab), 3.56 (dt, *J* = 15.9, 5.4 Hz, 1H, Cholesterol), 2.44 - 2.30 (m, 2H, Cholesterol), 2.10 (s, 3H, COC*H*$_3$), 2.08 (s, 3H, COC*H*$_3$), 1.92 - 1.80 (m, 3H, Cholesterol), 1.64 - 1.43 (m, 10H, Cholesterol), 1.41 - 1.30 (m, 4H, Cholesterol), 1.27 - 1.04 (m, 9H, Cholesterol), 1.00 (s, 3H, C*H*$_3$- Cholesterol), 0.91 (d, *J* = 6.5 Hz, 3H, C*H*$_3$- Cholesterol), 0.86 (dd, *J* = 6.6, 1.7 Hz, 6H, C*H*$_3$- Cholesterol), 0.68 (s, 3H, C*H*$_3$- Cholesterol)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.8 (*C*OCH$_3$), 170.3 (*C*OCH$_3$), 140.8, 128.8, 128.4, 121.8, 92.8 (C-1), 78.2, 66.8, 65.4, 63.2, 56.7, 56.1, 50.1, 42.3, 40.4, 39.7, 39.5, 37.1, 36.7, 36.2, 35.8, 31.9, 31.9, 28.2, 28.0, 24.3, 23.8, 22.8, 22.5, 21.1 (CO*C*H$_3$), 21.0 (CO*C*H$_3$), 20.8, 19.3, 18.7, 11.8

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{37}H_{58}O_6Na$ 621.4126, found 621.4132.

***n*-Butyl-4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*threo*-hex-2-enopyranoside (5A) and *n*-Butyl-2-deoxy-3,4,6-tri-*O*-acetyl -*α*-D-*lyxo*-hex-2-enopyranoside (5′A)**



5A 5′A

Following the general glycosylation procedure. Acceptor **2A** (20 µL, 0.22 mmol) and donor **4** (71 mg, 0.26 mmol) to afford after 12 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 3:1), **5A** as a colourless gel (47 mg, 75%) and also 2-deoxyglycoside **5′A** as a colourless gel (11 mg, 15%)

Data of the compound (5A)

$[\alpha]_D^{20}$ - 65.9 (*c* 1.2, $CHCl_3$)

IR ($CHCl_3$) *v* 2930, 2856, 1762, 1620, 1367, 1211, 1050, 701 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 6.11 (dd, *J* = 10.8, 5.3 Hz, 1H, H-3), 6.04 (dd, *J* = 10.1, 3.0 Hz, 1H, H-2), 5.06 (d, *J* = 2.9 Hz, 1H, H-1), 5.02 (dd, *J* = 5.3, 2.5 Hz, 1H, H-4), 4.38 - 4.34 (m, 1H, H-5), 4.25 - 4.20 (m, 2H, $H\text{-}6_{ab}$), 3.82 - 3.76 (m, 1H, -OCH_2), 3.54 - 3.48 (m, 1H, -OCH_2), 2.09 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), 1.62 - 1.58 (m, 2H, -OCH_2CH_2), 1.43 - 1.36 (m, 2H, -$OCH_2CH_2CH_2$), 0.94 (t, J = 7.4 Hz each, 3H, -$OCH_2CH_2CH_2CH_3$)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.6 (*C*OCH_3), 170.4 (*C*OCH_3), 130.8, 125.0, 93.9 (C-1), 68.3, 66.7, 62.9, 62.9, 31.7, 20.9, 20.8, 19.4, 13.8

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{14}H_{22}O_6Na$ 309.1309, found 309.1293.

Data of the compound (5′A)

$[\alpha]_D^{20}$ + 221.5 (*c* 0.2, $CHCl_3$)

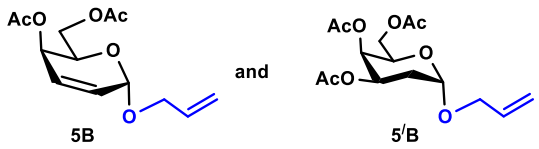
IR ($CHCl_3$) *v* 2945, 2830, 1776, 1367, 1221, 1010, 783 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 5.35 - 5.27 (m, 2H, H-3, H-4), 5.00 (d, *J* = 2.8 Hz, 1H, H-1), 4.18 - 4.12 (m, 1H, H-5), 4.11 - 4.08 (m, 2H, H-6ab), 3.67 - 3.61 (m, 1H, -OCH_2), 3.42 - 3.37 (m, 1H, -OCH_2), 2.13 (s, 3H, COCH_3), 2.09 (dd, *J* = 12.4, 3.6 Hz, 1H, H-2a), 2.05 (s, 3H, COCH_3), 1.98 (s, 3H, COCH_3), 1.87 (dd, *J* = 12.4, 4.3 Hz, 1H, H-2b), 1.58 - 1.54 (m, 2H, -OCH_2CH_2), 1.41 - 1.35 (m, 2H, -$OCH_2CH_2CH_2$), 0.93 (t, *J* = 7.4 Hz each, 3H, -$OCH_2CH_2CH_2CH_3$)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.0, 97.4 (C-1), 67.5, 66.7, 66.6, 66.3, 62.6, 31.5, 30.3, 20.9, 20.7, 19.4, 13.8

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{16}H_{26}O_8Na$ 369.1520, found 369.1503.

Allyl-4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*threo*-hex-2-enopyranoside (5B) and Allyl-2-deoxy-3,4,6-tri-*O*-acetyl-*α*-D-*lyxo*-hex-2-enopyranoside (5′B)



Following the general glycosylation procedure. Acceptor **2B** (20 µL, 0.29 mmol) and donor **4** (96 mg, 0.35 mmol) to afford after 12 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 3:1), **5B** as a yellow oil (56 mg, 70%) and also 2-deoxyglycoside as a yellow oil **5′B** (19 mg, 20%)

Data of the compound (5B)

$[\alpha]_D^{20}$ - 74.2 (*c* 2.0, $CHCl_3$)

IR ($CHCl_3$) *v* 2920, 2356, 1750, 1345, 1210, 1067 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 6.13 (dd, *J* = 9.6, 5.8 Hz, 1H, H-3), 6.04 (dd, *J* = 10.1, 3.0 Hz, 1H, H-2), 6.00 - 5.90 (m, 1H, C*H*CH_2), 5.34 - 5.28 (m, 1H, CHC*H*$_2$), 5.23 - 5.20 (m, 1H, CHC*H*$_2$), 5.12 (d, *J* = 2.9 Hz, 1H, H-1), 5.03 (dd, *J* = 5.4, 2.5 Hz, 1H, H-4), 4.39 - 4.35 (m, 1H, H-5), 4.31 - 4.23 (m, 3H, OC*H*$_2$, H-6a), 4.13 - 4.06 (m, 1H, H-6b), 2.09 (s, 3H, COC*H*$_3$), 2.08 (s, 3H, COC*H*$_3$)

$^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 170.6 (*C*OCH_3), 170.4 (*C*OCH_3), 134.0, 130.6, 125.3, 117.8, 93.0 (C-1), 68.9, 66.8, 62.8, 20.8 (CO*C*H_3), 20.8 (CO*C*H_3)

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{13}H_{18}O_6Na$ 293.0996, found 293.0986.

Data of the compound (5′B)

$[\alpha]_D^{20}$ + 130.0 (*c* 1.0, $CHCl_3$)

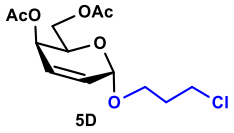
IR ($CHCl_3$) *v* 2960, 2366, 1720, 1223, 1045 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 5.95 - 5.84 (m, 1H, C*H*CH_2), 5.35 - 5.27 (m, 3H, H-3, H-4, CHC*H*$_2$), 5.21 (dd, *J* = 10.4, 1.6 Hz, 1H, CHC*H*$_2$), 5.08 - 5.04 (brd, *J* = 2.8 Hz, 1H, H-1), 4.19 - 4.13 (m, 2H, H-5, OC*H*$_2$), 4.10 - 4.08(m, 2H, OC*H*$_2$, H-6a), 4.00 - 3.95 (m, 1H, H-6b), 2.14 (s, 3H, COC*H*$_3$), 2.12 - 2.08 (m, 1H, H-2a), 2.06 (s, 3H, COC*H*$_3$), 1.99 (s, 3H, COC*H*$_3$), 1.92 - 1.87 (m, 1H, H-2b)

^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.0, 133.7, 117.5, 96.6 (C-1), 68.2, 66.7, 66.7, 66.2, 62.4, 30.1, 20.8, 20.7

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{15}H_{22}O_8Na$ 353.1207, found 353.1190.

Chloropropyl 4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*threo*-hex-2- enopyranoside (5D)



5D

Following the general glycosylation procedure. Acceptor **2D** (18 µL, 0.21 mmol) and donor **4** (69 mg, 0.25 mmol) to afford after 7 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =3:1), **5D** as a colourless gel (54 mg, 82%)

Data of the compound (5D)

$[\alpha]_D^{20}$ - 134.9 (*c* 1.3, $CHCl_3$)

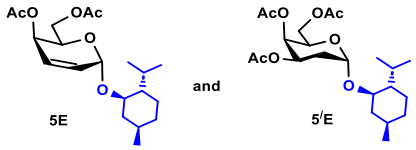
IR ($CHCl_3$) *v* 2993, 2946, 2876, 1764, 1422, 1348, 1221, 1035, 988, 745, 720, 668, 609 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (ddd, *J* = 10.0, 6.4, 1.2 Hz, 1H, H-2), 6.04 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 5.08 (d, *J* = 3.2 Hz, 1H, H-1), 5.02 (dd, *J* = 5.2, 2.4 Hz, 1H, H-4), 4.36 - 4.32 (m, 1H, H-6a), 4.27 - 4.19 (m, 2H, H-6b, Linker C*H*$_2$), 3.99 - 3.93 (m, 1H, H-5), 3.67 - 3.62 (m, 3H, Linker C*H*$_2$), 2.06 (brs, 6H, COC*H*$_3$), 2.10-2.04 (m, 2 H, Linker C*H*$_2$)

^{13}C {^{1}H} NMR (175 MHz, $CDCl_3$) δ 170.7 (*C*OCH_3), 170.4 (*C*OCH_3), 130.4, 125.2, 94.0 (C-1), 66.9, 64.8, 62.9, 62.8, 41.7, 32.5, 20.8

HRMS (ESI-TOF) m/z [M + Na]$^{+}$ calcd. For $C_{13}H_{19}ClO_6Na$ 329.0762, found 329.0751.

L-Menthyl 4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*threo*-hex-2-enopyranoside (5E) and L-Menthyl 2-deoxy-3,4,6-tri-*O*-acetyl -*α*-D-*lyxo*-hex-2-enopyranoside (5′E)



Following the general glycosylation procedure. Acceptor **2E** (20 mg, 0.13 mmol) and donor **4** (41.8 mg, 0.15 mmol) to afford after 12 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc=4:1), **5E** as a white solid (38 mg, 80%) and also 2-deoxyglycoside as a white solid **5′E** (9 mg, 17%)

Data of the compound (5E)

$[\alpha]_D^{20}$ - 121.6 (*c* 2.6, $CHCl_3$)

mp 72 - 74 °C

IR ($CHCl_3$) *v* 2982, 2939, 2851, 1756, 1454, 1376, 1208,1042, 988, 749, 668 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.10 (dd, *J* = 11.5, 5.5 Hz, 1H, H-2), 6.05 (dd, *J* = 10.0, 3.0 Hz, 1H, H-3), 5.14 (d, *J* = 3.0 Hz, 1H, H-1), 5.02 (dd, *J* = 5.0, 2.5 Hz, 1H, H-4), 4.43 - 4.40 (m, 1H, H-5), 4.26 - 4.18 (m, 2H, H-6ab), 3.46 - 3.40 (m, 1H, H-menthol), 2.24 - 2.19 (m, 1H, H-menthol), 2.08 (d, *J* = 4.0 Hz, 6H, 2 COC*H*$_3$), 1.67 - 1.60 (m, 2H, H-menthol), 1.48 - 1.40 (m, 1H, H-menthol), 1.26 - 1.20 (m, 1H, H-menthol), 1.09 - 0.98 (m, 2H, H-menthol), 0.92 (dd, *J* = 6.5, 4.5 Hz, 6H, C*H*$_3$-menthol), 0.88 - 0.82 (m, 1H, H-menthol), 0.79 (d, *J* = 7.0 Hz, 3H, C*H*$_3$-menthol)

^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 170.6 (*C*OCH_3), 170.4 (*C*OCH_3), 130.7, 124.7, 95.6 (C-1), 80.7, 66.6, 63.2, 63.0, 48.9, 43.2, 34.3, 31.7, 25.6, 23.1, 22.4, 21.1, 20.8, 16.2

HRMS (ESI-TOF) m/z [M + Na]$^{+}$ calcd. For $C_{20}H_{32}O_6Na$ 391.2091, found 391.2078.

Data of the compound (5′E)

$[\alpha]_D^{20}$ + 11.8 (*c* 0.9, $CHCl_3$)

mp 78 - 79 °C

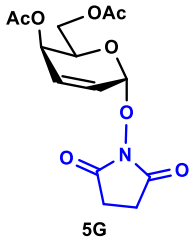
IR ($CHCl_3$) *v* 2977, 2953, 1739, 1486, 1312, 1231,1056, 956, 787, 661 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 5.34 - 5.26 (m, 2H, H-3, H-4), 5.07 (d, *J* = 3.5 Hz, 1H, H-1), 4.34 - 4.30 (m, 1H, H-5), 4.08 (d, *J* = 7.0 Hz, 2H, H-6ab), 3.35 - 3.30 (m, 1H, H-menthol), 2.13 (s, 3H, COC*H*$_3$), 2.12 - 2.07 (m, 1H, H-2a), 2.06 (s, 3H, COC*H*$_3$), 2.04 - 2.20 (m, 1H, H-2b), 1.98 (s, 3H, COC*H*$_3$), 1.88 - 1.84 (m, 1H, H-menthol), 1.66 - 1.59 (m, 2H, H-menthol), 1.44 - 1.36 (m, 1H, H-menthol), 1.24 - 1.17 (m, 1H, H-menthol), 1.06 - 0.94 (m, 2H, H-menthol), 0.91 (t, *J* = 6.0 Hz each, 6H, C*H*$_3$-menthol), 0.86 - 0.79 (m, 1H, H-menthol), 0.76 (d, *J* = 6.5 Hz, 3H, C*H*$_3$-menthol)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.3, 170.1, 99.5 (C-1), 81.2, 67.0, 66.8, 66.4, 63.0, 48.6, 42.8, 34.2, 31.7, 30.7, 25.7, 23.1, 22.3, 21.1, 20.9, 20.7, 16.2

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{22}H_{36}O_8Na$ 451.2302, found 451.2326.

_N_-Succinimido-4,6-di-acetyl-2,3-dideoxy-*α*-D-*threo*-2-enopyranoside (5G)



Following the general glycosylation procedure. Acceptor **2G** (20 mg, 0.17 mmol) and donor **4** (57 mg, 0.21 mmol) to afford after 1 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =1.5:1), **5G** as a colouless gel (51 mg, 89%)

Data of the compound (5G)

$[\alpha]_D^{20}$ - 54.9 (*c* 3.0, $CHCl_3$)

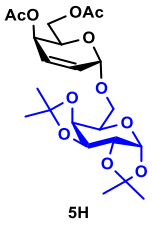
IR ($CHCl_3$) *v* 2922, 2866, 1757, 1434, 1386, 1220, 1201, 1109, 1086, 910, 826, 769, 670, 606 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 6.36 (dd, *J* = 10.0, 5.6 Hz, 1H, H-3), 6.20 (dd, *J* = 10.4, 3.2 Hz, 1H, H-2), 5.64 (d, *J* = 3.2 Hz, 1H, H-1), 5.16 - 5.14 (m, 1H, H-4), 4.83 - 4.79 (m, 1H, H-5), 4.33 (ddd, *J* = 11.6, 6.4, 1.6 Hz, 1H, H-6a), 4.07 (ddd, *J* = 11.2, 6.4, 1.2 Hz, 1H, H-6b), 2.75 (d, *J* = 1.2 Hz, 4H, NHS-2C*H*$_2$), 2.08 (s, 3H, COC*H*$_3$), 2.07 (s, 3H, COC*H*$_3$)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.0, 170.5, 170.1, 128.8, 125.9, 97.5 (C-1), 68.3, 61.9, 61.8, 25.5, 20.8, 20.7

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{14}H_{17}NO_8Na$ 350.0846, found 350.0827.

4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*threo*-hex-2-enopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (5H)



Following the general glycosylation procedure. Acceptor **2H** (20 mg, 0.08 mmol) and donor **4** (25 mg, 0.09 mmol) to afford after 2 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =2:1), **5H** as a white solid (25 mg, 70%)

Data of the compound (5H)

$[\alpha]_D^{20}$ - 9.2 (*c* 1.0, $CHCl_3$)

mp 96 - 97 °C

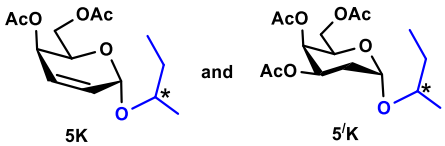
IR ($CHCl_3$) *v* 2998, 2973, 235 4, 1756, 1624, 1598, 1368, 1245, 1069, 1011, 899 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 6.11 (ddd, *J* = 10.0, 5.5, 1.0 Hz, 1H, H-3′), 6.04 (dd, *J* = 10.0, 3.0 Hz, 1H, H-2′), 5.52 (d, *J* = 5.0 Hz, 1H, H-1), 5.13 (d, *J* = 2.0 Hz, 1H, H-1′), 5.02 (dd, *J* = 5.5, 2.5 Hz, 1H, H-4′), 4.63 (dd, *J* = 8.0, 2.5 Hz, 1H, H-3), 4.39 - 4.36 (m, 1H, H-5′), 4.32 (dd, *J* = 5.0, 2.5 Hz, 1H, H-2), 4.27 (dd, *J* = 7.5, 1.5 Hz, 1H, H-4), 4.23 (d, *J* = 6.5 Hz, 2H, H-6ab′), 4.02 - 3.99 (m, 1H, H-5), 3.87 (dd, *J* = 10.5, 6.5 Hz, 1H, H-6a_A), 3.76 (dd, *J* = 10.5, 7.5 Hz, 1H, H-6b_A), 2.08 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), 1.53 (s, 3H, CCH_3), 1.45 (s, 3H, CCH_3), 1.35 (s, 3H, CCH_3), 1.33 (s, 3H, CCH_3)

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 170.7 (*C*OCH_3), 170.3 (*C*OCH_3), 130.5, 125.1, 109.3, 108.5, 96.3 (C-1), 94.1 (C-1′), 70.9, 70.6, 70.6, 66.8, 66.7, 66.1, 62.7, 62.6, 26.1, 26.0, 24.9, 24.5, 20.8 (2CO*C*H_3)

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{22}H_{32}O_{11}Na$ 495.1837, found 495.1838.

Sec-butyl 4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*threo*-hex-2-enopyranoside (5K) Sec-butyl 2-deoxy-3,4,6-tri-*O*-acetyl -*α*-D-*lyxo*-hex-2-enopyranoside (5′K)



Following the general glycosylation procedure. Acceptor **2K** (20 µL, 0.22 mmol) and donor **4** (71 mg, 0.26 mmol) to afford after 24 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =4:1), **5K** as a colourless gel (56 mg, 90%) and also 2-deoxyglycoside as a colourless gel **5′K** (7 mg, 10%)

Data of the compound (5K)

$[\alpha]_D^{20}$ - 79.8 (*c* 2.6, $CHCl_3$)

IR ($CHCl_3$) *v* 3460, 3045, 2967, 2956, 2882, 1745, 1650, 1375, 1220, 1146, 1055, 999, 968 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 6.13 - 6.08 (m, 1H, H-2), 6.04 - 5.97 (m, 1H, H-3), 5.20 - 5.14 (m, 1H, H-4), 5.03 - 5.01 (m, 1H, H-1), 4.42 - 4.38 (m, 1H, H-5), 4.29 - 4.16 (m, 2H, H-6ab), 3.85 - 3.69 (m, 1H, $CH_3CH(O)CH_2CH_3$), 2.08 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 1.66 - 1.41 (m, 2H, $CH_3CH(O)CH_2CH_3$), 1.25 (d, *J* = 6.0 Hz, 1.5 H, $CH_3CH(O)CH_2CH_3$), 1.16 (d, *J* = 6.0 Hz, 1.5 H, $CH_3CH(O)CH_2CH_3$), 0.93 (dt, *J* = 14.8, 7.6 Hz, 3H, $CH_3CH(O)CH_2CH_3$)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.6 ($COCH_3$), 170.3 ($COCH_3$), 131.3, 131.0, 124.8, 93.9 (C-1), 91.5, 74.6, 66.8, 66.6, 63.1, 63.0, 30.0, 29.5, 21.1, 20.8, 20.7, 19.1, 10.2, 9.8

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{14}H_{22}O_6Na$ 309.1309, found 309.1293.

Data of the compound (5′K)

$[\alpha]_D^{20}$ + 72.3 (*c* 0.3, $CHCl_3$)

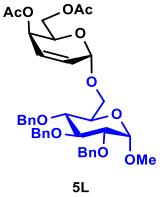
IR ($CHCl_3$) *v* 3460, 3045, 2967, 2956, 2882, 1745, 1650, 1375, 1220, 1146, 1055, 999, 968 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 5.36 - 5.24 (m, 2H, H-1, H-3), 5.16 - 5.09 (m, 1H, H-4), 4.27 - 4.21 (m, 1H, H-5), 4.12 - 4.05 (m, 2H, H-6ab), 3.69 - 3.60 (m, 1H, $CH_3CH(O)CH_2CH_3$), 2.13 (s, 3H, $COCH_3$), 2.12 - 2.06 (m, 1H, H-2a), 2.05 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.87 - 1.78 (m, 1H, H-2b), 1.53 - 1.41 (m, 2H, $CH_3CH(O)CH_2CH_3$), 1.19 (d, *J* = 6.4 Hz, 2H, $CH_3CH(O)CH_2CH_3$), 1.12 (d, *J* = 6.4 Hz, 1H, $CH_3CH(O)CH_2CH_3$), 0.94 - 0.86 (m, 3H, $CH_3CH(O)CH_2CH_3$)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.5, 170.4, 170.1, 97.2 (C-1), 94.6, 76.3, 73.5, 66.9, 66.8, 66.6, 66.4, 62.7, 62.6, 30.7, 29.9, 29.7, 29.0, 20.9, 20.7, 20.7, 20.6, 18.4, 10.3, 9.6

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{16}H_{26}O_8Na$ 369.1520, found 369.1495.

Methyl-4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*threo*-hex-2-enopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (5L)



5L

Following the general glycosylation procedure. Acceptor **2L** (20 mg, 0.04 mmol) and donor **4** (14 mg, 0.05 mmol) to afford after 3 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =2.5:1), **5L** as a colourless gel (19 mg, 66%)

Data of the compound (5L)

$[\alpha]_D^{20}$ - 31.8 (*c* 0.5, $CHCl_3$)

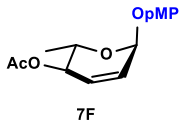
IR ($CHCl_3$) *v* 3033, 2976, 1759, 1468, 1342, 1220, 1011, 996, 790 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 7.39 - 7.23 (m, 15H, Ar-H), 6.09 (dd, *J* = 11.0, 5.5 Hz, 1H, H-3′), 6.03 (dd, *J* = 10.0, 2.5 Hz, 1H, H-2′), 5.14 (d, *J* = 3.5 Hz, 1H, H-1′), 5.03 - 4.95 (m, 2H, H-4′, PhCH_2), 4.91 (d, *J* = 11.5 Hz, 1H, PhCH_2), 4.82 - 4.77 (m, 2H, PhCH_2), 4.67 - 4.61 (m, 2H, PhCH_2), 4.60 (d, *J* = 4.0 Hz, 1H, H-1), 4.30 - 4.27 (m, 1H, H-5′), 4.19 (dd, *J* = 11.5, 6.0 Hz, 1H, H-6a′), 4.11 (dd, *J* = 11.5, 7.0 Hz, 1H, H-6b′), 4.03 - 3.94 (m, 2H, H-3, H-6a), 3.79 - 3.72 (m, 2H, H-4, H-5), 3.59 - 3.48 (m, 2H, H-2, H-6b), 3.37 (s, 3H, OCH_3), 2.07 (s, 3H, COCH_3), 1.92 (s, 3H, , COCH_3)

^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 170.5, 170.3, 138.6 - 125.01 (Ar-C), 98.0 (C-1), 94.2 C-1′), 82.0, 79.9, 77.8, 75.8, 74.9, 73.3, 69.9, 66.7, 62.7, 62.6, 55.2, 20.8, 20.6

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{38}H_{44}O_{11}Na$ 699.2776, found 699.2777.

***p*-Methoxyphenyl-4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranoside (7F)**



7F

Following the general glycosylation procedure. Acceptor **2F** (20 mg, 0.16 mmol) and donor **6** (41.5 mg, 0.19 mmol) to afford after 4 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 2:1), **7F** as a white solid (21 mg, 46%)

Data of the compound (7F)

$[\alpha]_D^{20}$ - 123.4 (*c* 1.1, $CHCl_3$)

mp 75 - 76 °C

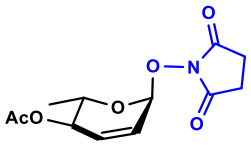
IR ($CHCl_3$) *v* 3020, 2929, 1737, 1504, 1457, 1373, 1216, 1097, 1033, 994, 829, 752, 668 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 9.2 Hz, 2H, Ar-H), 6.84 (d, *J* = 9.2 Hz, 2H, AR-H), 6.02 - 5.92 (m, 2H, H-2, H-3), 5.53 (brs, 1H, H-1), 5.12 (dd, *J* = 9.2, 1.2 Hz, 1H, H-4), 4.15 - 4.07 (m, 1H, H-5), 3.78 (s, 3H, OCH_3), 2.11 (s, 3H, COCH_3), 1.23 (d, *J* = 6.4 Hz, 3H, Rham-CH_3)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.5, 154.9 - 127.1 (Ar-C), 118.3, 114.5, 93.9 (C-1), 70.6, 65.6, 55.6, 21.0, 17.9

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{14}H_{22}O_6Na$ 209.0784, found 209.0776.

***N*-Succinimido-4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranoside (7G)**



7G

Following the general glycosylation procedure. Acceptor **2G** (20 mg, 0.17 mmol) and donor **6** (45 mg, 0.21 mmol) to afford after 0.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 1:1), **7G** as a colourless gel (43 mg, 91%)

Data of the compound (7G)

$[\alpha]_D^{20}$ - 135.1 (*c* 2.8, $CHCl_3$)

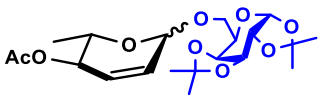
IR ($CHCl_3$) *v* 3022, 2930, 1724, 1372, 1204, 1106, 1043, 995, 902, 812, 747, 661 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 6.09 (d, *J* = 10.0 Hz, 1H, H-3), 5.98 - 5.95 (m, 1H, H-2), 5.49 (brs, 1H, H-1), 5.13 (dd, *J* = 9.6, 2.0 Hz, 1H, H-4), 4.49 - 4.41 (m, 1H, H-5), 2.75 (s, 4H, NHS-2CH_2), 2.11 (s, 3H, COCH_3), 1.19 (d, *J* = 6.0 Hz, 3H, Rham-CH_3)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2 (2C), 170.4, 133.9, 123.1, 98.1 (C-1), 70.1, 66.6, 25.5 (2C), 21.0, 17.3

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{12}H_{15}NO_6Na$ 292.0792, found 292.0798

4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-*α*-D-galactopyranoside (7H)



7H

Following the general glycosylation procedure. Acceptor **2H** (20 mg, 0.08 mmol) and donor **6** (20 mg, 0.09 mmol) to afford after 2 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =2:1), **7H** as a colourless gel (31 mg, 97%, *α*:*β* = 11:1)

Data of the compound (7H)

$[\alpha]_D^{20}$ – 65.7 (*c* 3.1, $CHCl_3$)

IR ($CHCl_3$) *v* 2946, 2922, 1768, 1346, 1260, 1210, 1161, 1126, 1087, 1010, 947, 898, 750, 661 cm^{-1}

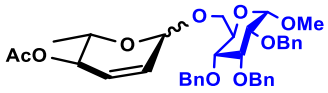
^1H NMR (400 MHz, $CDCl_3$) δ 5.83 (brs, 2H, H-2′, H-3′), 5.54 (d, *J* = 4.8 Hz, 1H, H-1), 5.08 - 5.03 (m, 2H, H-1′, H-4′), 4.60 (dd, *J* = 8.0, 2.4 Hz, 1H, H-3), 4.33 - 4.26 (m, 2H, H-2, H-5′), 4.01 - 3.93 (m, 3H, H-4, H-6ab), 3.72 - 3.65 (m, 1H, H-5), 2.08 (s, 3H, COCH_3), 1.54 (s, 3H,

CCH_3), 1.45 (s, 3H, CCH_3), 1.34 (d, J = 2.4 Hz, 6H, CCH_3), 1.22 (d, J = 6.4 Hz, 3H, Rham-CH_3)

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 129.5, 127.9, 109.2, 108.5, 96.3 (C-1), 94.2 (C-1′), 71.1, 71.0, 70.6, 70.5, 67.1, 66.5, 64.8, 26.0, 26.0, 24.9, 24.4, 21.1, 17.8

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. For $C_{20}H_{30}O_9Na$ 437.1782, found 437.1766.

Methyl 4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (7L)



7L

Following the general glycosylation procedure. Acceptor **2L** (20 mg, 0.04 mmol) and donor **6** (11 mg, 0.05 mmol) to afford after 4 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 4:1), **7L** as a white semisolid (21 mg, 77%, *α*:*β* = 20:1).

Data of the compound (7L)

$[\alpha]_D^{20}$ - 12.7 (*c* 1.3, $CHCl_3$)

mp 76 - 77 °C

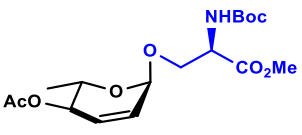
IR ($CHCl_3$) *v* 3031, 2926, 1740, 1453, 1369, 1235, 1157, 1033, 913, 739, 699 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 15H, Ar-H), 5.83 - 5.69 (m, 2H, H-2′, H-3′), 5.01 (dd, J = 11.6, 9.2 Hz, 2H, H-4′, PhCH_2), 4.89 (d, J = 11.2 Hz, 1H, PhCH_2), 4.86 - 4.75 (m, 3H, H-1′, PhCH_2), 4.66 (d, J = 12.4 Hz, 1H, PhCH_2), 4.60 - 4.53 (m, 2H, H-1, PhCH_2), 4.03 - 3.91 (m, 3H, H-5′, H-5, H-6a), 3.78 - 3.73 (m, 1H, H-3), 3.62 (dd, J = 10.8, 4.8 Hz, 1H, H-6b), 3.55 - 3.47 (m, 2H, H-2, H-4), 3.38 (s, 3H, OCH_3), 2.06 (s, 3H, COCH_3), 1.18 (d, J = 6.2 Hz, 3H, Rham-CH_3)

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 138.7 - 127.5 (Ar-C), 98.0 (C-1), 94.8 (C-1′), 82.1, 79.9, 77.7, 75.7, 74.9, 73.3, 70.8, 70.1, 67.2, 64.8, 55.1, 21.0, 17.8

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. For $C_{36}H_{42}O_9Na$ 641.2721, found 641.2679.

***O*-(4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranosyl)-*N*-(Boc)-D-serine methyl ester (7M)**



7M

Following the general glycosylation procedure. Acceptor **2M** (20 mg, 0.09 mmol) and donor **6** (23.5 mg, 0.10 mmol) to afford after 12 h at 50°C and after purification using silica gel column

chromatography (Hexane/EtOAc = 3:1), **7M** as a colourless gel (25 mg, 71%)

Data of the compound (7M)

$[\alpha]_D^{20}$ - 10.5 (*c* 1.7, $CHCl_3$)

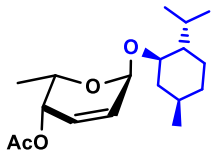
IR ($CHCl_3$) *v* 2977, 2930, 1743, 1717, 1504, 1446, 1369, 1237, 1165, 1037, 756 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 5.84 (d, *J* = 10.5 Hz, 1H, H-2), 5.77 - 5.74 (m, 1H, H-3), 5.35 (d, *J* = 9.0 Hz, 1H, N*H*), 5.04 - 5.01 (m, 1H, H-4), 4.93 (brs, 1H, H-1), 4.51 - 4.48(m, 1H, H-5), 4.19 (dd, *J* = 10.0, 3.5 Hz, 1H, CH_2), 3.77 (s, 3H, COOCH_3), 3.75 - 3.71 (m, 2H, C*H*, CH_2), 2.08 (s, 3H, COCH_3), 1.46 (s, 9H, NH(CH_3)$_3$), 1.21 (d, *J* = 6.5 Hz, 3H, Rham-CH_3)

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 170.9, 170.4, 155.4, 130.0, 127.1, 94.2 (C-1), 80.1, 70.6, 68.1, 65.0, 53.8, 52.4, 43.4, 28.3 (3C), 21.0, 17.7

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{17}H_{27}NO_8Na$ 396.1629, found 396.1628.

L-Menthyl-4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranoside (9E)



9E

Following the general glycosylation procedure. Acceptor **2E** (20 mg, 0.13 mmol) and donor **8** (33 mg, 0.15 mmol) to afford after 4 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =3:1), **9E** as a colourless gel (27 mg, 68%, *α*:*β* = 22:1)

Data of the compound (9E)

$[\alpha]_D^{20}$ + 81.7 (*c* 2.3, $CHCl_3$)

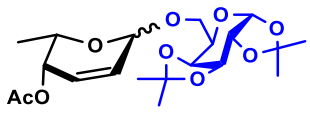
IR ($CHCl_3$) *v* 2953, 2923, 1732, 1454, 1373, 1237, 1158, 1099, 1012, 917, 748, 667 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 6.10 - 6.06 (m, 1H, H-2), 5.95 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3), 5.21 (d, *J* = 3.2 Hz, 1H, H-1), 4.93 (dd, *J* = 5.2, 2.4 Hz, 1H, H-4), 4.28 - 4.22 (m, 1H, H-5), 3.59 - 3.53 (m, 1H, H-6a), 2.26 - 2.17 (m, 1H, H-6b), 2.10 (s, 3H, COCH_3), 2.09 - 2.04 (m, 1H, H-menthol), 1.69 - 1.63 (m, 3H, H-menthol), 1.42 - 1.32 (m, 1H, H-menthol), 1.26 - 1.23 (m, 1H, H-menthol), 1.22 (d, *J* = 6.4 Hz, 3H, Fucal-CH_3), 0.93 - 0.89 (m, 6H, CH_3-menthol), 0.82 (d, *J* = 7.2 Hz, 3H, CH_3-menthol)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.7, 131.2, 125.6, 90.3 (C-1), 75.4, 65.2, 65.0, 47.9, 40.2, 34.4, 31.4, 25.3, 22.8, 22.3, 21.1, 20.8, 16.0, 15.6

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{18}H_{30}O_4Na$ 333.2036, found 333.2048.

4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-*α*-D-galactopyranoside (9H)



9H

Following the general glycosylation procedure. Acceptor **2H** (20 mg, 0.08 mmol) and donor **8** (20 mg, 0.09 mmol) to afford after 1.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =2.5:1), **9H** as a colourless gel (28 mg, 88%, *α*:*β* = 12:1)

Data of the compound (9H)

$[\alpha]_D^{20}$ + 24.4 (*c* 2.7, $CHCl_3$)

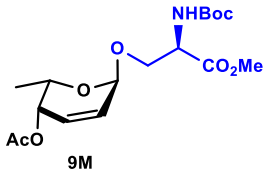
IR ($CHCl_3$) *v* 2986, 2934, 1733, 1376, 1240, 1215, 1168, 1109, 1069, 1006, 920, 894, 752, 668 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 6.07 - 6.03 (m, 2H, H-2′, H-3′), 5.53 (d, *J* = 5.5 Hz, 1H, H-1), 5.10 (d, *J* = 1.5 Hz, 1H, H-1′), 4.92 (dd, *J* = 4.5, 2.5 Hz, 1H, H-4′), 4.60 (dd, *J* = 8.0, 2.5 Hz, 1H, H-3), 4.31 (dd, *J* = 5.0, 2.5 Hz, 1H, H-2), 4.27 - 4.22 (m, 2H, H-4, H-5′), 3.98 - 3.92 (m, 2H, H-5, H-6a), 3.71 - 3.65 (m, 1H, H-6b), 2.10 (s, 3H, COCH_3), 1.53 (s, 3H, CCH_3), 1.45 (s, 3H, CCH_3), 1.33 (s, 6H, CCH_3), 1.22 (d, *J* = 6.5 Hz, 3H, Fucal-CH_3)

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 170.7, 130.4, 125.8, 109.2, 108.5, 96.3 (C-1), 94.0 (C-1′), 71.1, 70.6, 70.5, 67.0, 66.1, 65.1, 64.6, 26.0, 26.0, 24.9, 24.5, 20.8, 15.9

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{20}H_{30}O_9Na$ 437.1782, found 437.1749.

***O*-(4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranosyl)-*N*-(Boc)-D-serine methyl ester (9M)**



9M

Following the general glycosylation procedure. Acceptor **2M** (20 mg, 0.09 mmol) and donor **8** (23.5 mg, 0.10 mmol) to afford after 8 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 3.5:1), **9M** as a colourless gel (24.5 mg, 70%)

Data of the compound (9M)

$[\alpha]_D^{20}$ + 86.6 (*c* 1.8, $CHCl_3$)

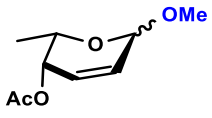
IR ($CHCl_3$) *v* 2952, 2930, 1768, 1711, 1509, 1456, 1328, 1237, 1186, 1037, 788 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 - 6.05 (m, 1H, H-2), 5.98 (dd, *J* = 10.0, 2.8 Hz, 1H, H-3), 5.34 (d, *J* = 8.8 Hz, 1H, N*H*), 5.00 (d, *J* = 3.6 Hz, 1H, H-1), 4.89 (dd, *J* = 5.2, 2.4 Hz, 1H, H-4), 4.55 - 4.45 (m, 1H, H-5), 4.19 (dd, *J* = 10.0, 3.4 Hz, 1H, CH_2), 4.09 - 4.03 (m, 1H, C*H*), 3.76 (s, 3H, COOCH_3), 3.75 - 3.71 (m, 1H, CH_2), 2.10 (s, 3H, COCH_3), 1.46 (s, 9H, NH(CH_3)$_3$), 1.21 (d, *J* = 6.4 Hz, 3H, Fucal-CH_3)

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 155.4, 129.7, 126.2, 94.1 (C-1), 80.1, 67.8, 64.9, 64.8, 53.8, 52.4, 28.3 (3C), 20.8, 15.9

HRMS (ESI-TOF) m/z [M + Na]$^{+}$ calcd. For $C_{17}H_{27}NO_8Na$ 396.1629, found 396.1604.

Methyl-4-*O*-(acetyl)-2,3,6-trideoxy-*α*-L-hex-2-enopyranoside (9N)



9N

Following the general glycosylation procedure. Acceptor **2N** (20 µL, 0.5 mmol) and donor **8** (128 mg, 0.6 mmol) to afford after 2 h at 50°C and after purificaion using silica gel column chromatography (Hexane/EtOAc = 4:1), **9N** as a colourless gel (75 mg, 80%, *α*:*β* = 11:1)

Data of the compound (9N)

$[\alpha]_D^{20}$ - 92.3 (*c* 2.1, $CHCl_3$)

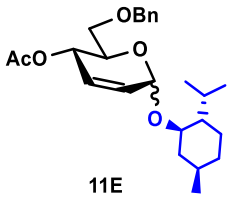
IR ($CHCl_3$) *v* 2953, 2920, 1740, 1231, 1012, 921, 772, 656 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 - 6.06 (m, 1H, H-2), 6.02 (dd, *J* = 9.6, 2.8 Hz, 1H, H-3), 4.93 (q, *J* = 2.8 Hz, 2H, H-1, H-4), 4.25 - 4.19 (m, 1H, H-5), 3.44 (s, 3H, OCH_3), 2.11 (s, 3H, COCH_3), 1.24 (d, *J* = 6.4 Hz, 3H, Fucal-CH_3)

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 130.2, 126.0, 95.2 (C-1), 65.0, 64.5, 55.6, 20.8, 16.0

HRMS (ESI-TOF) m/z [M + Na]$^{+}$ calcd. For $C_9H_{14}O_4Na$ 209.0784, found 209.0789.

L-Menthyl-6-*O*-benzyl-4-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (11E)



11E

Following the general glycosylation procedure. Acceptor **2E** (20 mg, 0.13 mmol) and donor **10** (49 mg, 0.15 mmol) to afford after 12 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =3:1), **11E** as a colourless gel (41.5 mg, 78%, α:β = 8:1)

Data of the compound (11E)

$[\alpha]_D^{20}$ + 41.3 (*c* 2.0, $CHCl_3$)

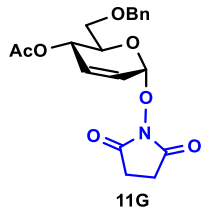
IR ($CHCl_3$) *v* 2953, 2923, 2867, 1740, 1371, 1234, 1102, 1032, 751, 668 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.28 (m, 5H, Ar-H), 5.90 - 5.82 (m, 2H, H-2, H-3), 5.41 (dd, *J* = 9.6, 1.2 Hz, 1H, H-4), 5.12 (brs, 1H, H-1), 4.67 (d, *J* = 12.0 Hz, 1H, PhCH_2), 4.50 (d, *J* = 12.0 Hz, 1H, PhCH_2), 4.14 - 4.08 (m, 1H, H-5), 3.60 - 3.55 (m, 2H, H-6ab), 3.46 - 3.40 (m, 1H, H-menthol), 2.25 - 2.19 (m, 1H, H-menthol), 2.12 - 2.05 (m, 1H, H-menthol), 1.95 (s, 3H, COCH_3), 1.66 - 1.59 (m, 3H, H-menthol), 1.44 - 1.35 (m, 1H, H-menthol), 1.30 - 1.19 (m, 2H, H-menthol), 0.92 - 0.87 (m, 4H, H-menthol, CH_3-menthol), 0.82 (d, *J* = 6.4 Hz, 3H, CH_3-menthol), 0.77 (d, *J* = 6.8 Hz, 3H, CH_3-menthol)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.3, 138.0, 129.0, 128.3, 127.9, 127.8, 127.6, 96.1 (C-1), 80.7, 73.3, 68.7, 67.7, 65.6, 48.9, 43.4 (2C), 43.3, 34.3, 31.7, 25.6, 23.2, 22.2, 21.2, 21.0, 16.2

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{25}H_{36}O_5Na$ 439.2455, found 439.2455.

***N*-Succinimido-6-*O*-benzyl-4-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (11G)**



11G

Following the general glycosylation procedure. Acceptor **2G** (20 mg, 0.17 mmol) and donor **10** (67 mg, 0.21 mmol) to afford after 1.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 1:1), **11G** as a colourless gel (52 mg, 80%).

Data of the compound (11G)

$[\alpha]_D^{20}$ + 233.7 (*c* 0.7, $CHCl_3$)

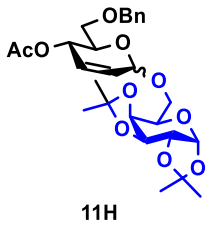
IR ($CHCl_3$) *v* 3022, 2924, 2860, 1724, 1368, 1204, 1115, 1043, 964, 750, 655 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 7.35 - 7.27 (m, 5H, Ar-H), 6.16 (d, *J* = 10.0 Hz, 1H, H-3), 5.98 - 5.95 (m, 1H, H-2), 5.65 - 5.62 (m, 1H, H-4), 5.61 (brs, 1H, H-1), 4.67 (d, *J* = 12.0 Hz, 1H, PhCH_2), 4.48 - 4.45 (m, 1H, H-5), 4.38 (d, *J* = 12.0 Hz, 1H, PhCH_2), 3.60 - 3.53 (m, 2H, H-6ab), 2.70 (s, 4H, NHS-2CH_2), 1.96 (s, 3H, COCH_3)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 171.2 (2C), 170.0, 137.7, 134.0, 128.3, 128.0, 127.7, 122.8, 98.2 (C-1), 73.3, 69.2, 66.9, 64.6, 25.5 (2C), 20.9

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{19}H_{21}NO_7Na$ 398.1210, found 398.1201.

6-*O*-benzyl-4-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-*α*-D-galactopyranoside (11H)



11H

Following the general glycosylation procedure. Acceptor **2H** (20 mg, 0.08 mmol) and donor **10** (30 mg, 0.09 mmol) to afford after 12 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =2.5:1), **11H** as a colourless gel (27 mg, 68%, α:β = 6:1)

Data of the compound (11H)

$[\alpha]_D^{20}$ + 29.4 (*c* 1.2, $CHCl_3$)

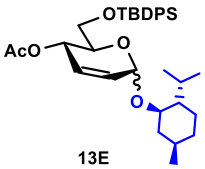
IR ($CHCl_3$) *v* 2987, 2927, 1738, 1454, 1375, 1214, 1170, 1068, 1040, 1002, 893, 803, 746, 667 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.38 (m, 2H, Ar-H), 7.34 - 7.32 (m, 3H, Ar-H), 5.91 - 5.81 (m, 2H, H-2′, H-3′), 5.52 (d, *J* = 5.2 Hz, 1H, H-1), 5.46 (dd, *J* = 9.6, 1.6 Hz, 1H, H-4′), 5.12 (brs, 1H, H-1′), 5.01 (brs, 1H, H-5′), 4.66 (d, *J* = 12.4 Hz, 1H, PhCH_2), 4.59 (dd, *J* = 8.0, 2.4 Hz, 1H, H-3), 4.48 (d, *J* = 12.4 Hz, 1H, PhCH_2), 4.31 (dd, *J* = 4.8, 2.0 Hz, 1H, H-2), 4.26 (dd, *J* = 8.0, 2.0 Hz, 1H, H-4), 4.05 - 3.99 (m, 2H, H-5, H-6b), 3.89 (dd, *J* = 10.0, 6.0 Hz, 1H, H-6a), 3.78 (dd, *J* = 10.4, 7.6 Hz, 1H, H-6a′), 3.59 - 3.56 (m, 1H, H-6b′), 1.95 (s, 3H, COCH_3), 1.53 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.33 (d, *J* = 5.0 Hz, 6H, CH_3)

^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.2, 138.0 - 127.6 (Ar-C), 109.3, 108.5, 96.3 (C-1), 94.7 (C-1′), 79.2, 73.3, 70.8, 70.6 (2C), 68.3, 68.1, 66.9, 66.0, 65.5, 26.1, 26.0, 24.9, 24.5, 20.9

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{27}H_{36}O_{10}Na$ 543.2201, found 543.2193.

L-Menthyl-6-*O*-tert-butyldiphenylsilyl-4-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (13E)



13E

Following the general glycosylation procedure. Acceptor **2E** (20 mg, 0.13 mmol) and donor **12** (72 mg, 0.15 mmol) to afford after 8 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc =4:1), **13E** as a colourless gel (54 mg, 75%, α:β = 6:1)

Data of the compound (13E)

$[\alpha]_D^{20}$ + 68.1 (*c* 1.4, $CHCl_3$)

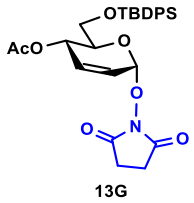
IR ($CHCl_3$) *v* 3340, 2986, 2844, 1757, 1336, 1226, 1158, 1021, 740, 698 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 7.73 - 7.65 (m, 4H, Ar-H), 7.42 - 7.36 (m, 6H, Ar-H), 5.92 - 5.80 (m, 2H, H-2, H-3), 5.43 (dd, *J* = 9.6, 1.6 Hz, 1H, H-4), 5.11 (brs, 1H, H-1), 4.05 - 4.01 (m, 1H, H-5), 3.81 - 3.76 (m, 2H, H-6ab), 3.44 - 3.37 (m, 1H, H-menthol), 2.15 - 2.06 (m, 2H, H-menthol), 1.96 (s, 3H, $COCH_3$), 1.65 - 1.58 (m, 4H, H-menthol), 1.29 - 1.19 (m, 3H, H-menthol), 1.06 (s, 9H, $SiC(CH_3)_3$), 0.91 (d, *J* = 6.8 Hz, 3H, CH_3-menthol), 0.80 (d, *J* = 6.8 Hz, 3H, CH_3-menthol), 0.76 (d, *J* = 6.4 Hz, 3H, CH_3-menthol)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.3, 135.7, 135.6, 133.5, 133.3, 129.6, 129.6, 129.0, 127.9, 127.6, 127.6, 127.5, 96.1 (C-1), 80.8, 69.1, 65.5, 63.3, 48.9, 43.3, 34.3, 31.7, 26.8, 26.7, 25.6, 23.2, 22.2, 21.1, 21.0, 19.3, 16.2

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{34}H_{48}O_5SiNa$ 587.3163, found 587.3152.

_N_-Succinimido-6-_O_-tert-butyldiphenylsilyl-4-_O_-acetyl-2,3-dideoxy-_α_-D-_erythro_-hex-2-enopyranoside (13G)



13G

Following the general glycosylation procedure. Acceptor **2G** (20 mg, 0.17 mmol) and donor **12** (98 mg, 0.21 mmol) to afford after 1 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 1.5:1), **13G** as a colourless gel (79 mg, 86%).

Data of the compound (13G)

$[\alpha]_D^{20}$ + 101.3 (*c* 1.7, $CHCl_3$)

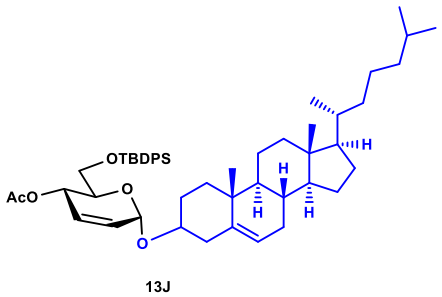
IR ($CHCl_3$) *v* 3236, 2922, 2855, 1712, 1346, 1225, 1108, 1056, 987, 766, 698 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 7.66 - 7.62 (m, 5H, Ar-H), 7.42 - 7.34 (m, 5H, Ar-H), 6.20 (d, *J* = 10.0 Hz, 1H, H-2), 5.98 - 5.94 (m, 1H, H-3), 5.71 (dd, *J* = 10.0, 2.0 Hz, 1H, H-4), 5.59 (brs, 1H, H-1), 4.39 - 4.37 (m, 1H, H-5), 3.86 (dd, *J* = 12.0, 2.8 Hz, 1H, H-6a), 3.74 (dd, *J* = 11.6, 2.0 Hz, 1H, H-6b), 2.69 - 2.55 (m, 4H, NHS-$2CH_2$), 2.01 (s, 3H, $COCH_3$), 1.04 (s, 9H, $SiC(CH_3)_3$)

^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.1 (2C), 170.1, 135.8, 135.7, 133.9, 133.5, 133.4, 129.6, 129.5, 127.6, 127.3, 122.8, 98.1 (C-1), 70.3, 64.5, 61.8, 26.8 (3C), 25.4 (2C), 20.9, 19.3

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{28}H_{33}NO_7SiNa$ 546.1919, found 546.1905.

Cholesteryl-6-*O*-tert-butyldiphenylsilyl-4-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranoside (13J)



13J

Following the general glycosylation procedure. Acceptor **2J** (20 mg, 0.05 mmol) and donor **12** (29 mg, 0.06 mmol) to afford after 1.5 h at 50°C and after purification using silica gel column chromatography (Hexane/EtOAc = 4:1), **13J** as a colourless gel (33 mg, 80%).

Data of the compound (13J)

$[\alpha]_D^{20}$ + 54.2 (*c* 2.0, $CHCl_3$)

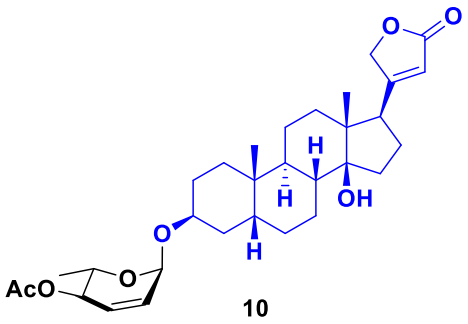
IR ($CHCl_3$) *v* 3036, 2926, 2845, 1771, 1467, 1342, 1220, 1061, 997, 768, 642, 601 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 7.71 - 7.64 (m, 4H, Ar-H), 7.41 - 7.35 (m, 6H, Ar-H), 5.89 - 5.85 (m, 1H, H-2), 5.83 - 5.79 (m, 1H, H-3), 5.33 - 5.30 (m, 1H, H-4), 5.23 - 5.19 (m, 2H, H-1, CH), 4.08 - 4.04 (m, 1H, H-5), 3.76 - 3.74 (m, 2H, H-6ab), 3.64 (dt, *J* = 10.7, 4.8 Hz, 1H, Cholesterol), 2.40 - 2.30 (m, 2H, Cholesterol), 1.95 (s, 3H, $COCH_3$), 1.59 - 1.56 (m, 3H, Cholesterol), 1.54 - 1.35 (m, 10H, Cholesterol), 1.34 - 1.26 (m, 4H, Cholesterol), 1.22 - 1.08 (m, 9H, Cholesterol), 1.05 (s, 9H, $SiC(CH_3)_3$), 0.99 (s, 3H, CH_3- Cholesterol), 0.92 (d, *J* = 6.5 Hz, 3H, CH_3- Cholesterol), 0.86 (dd, *J* = 6.6, 1.7 Hz, 6H, CH_3- Cholesterol), 0.67 (s, 3H, CH_3- Cholesterol)

^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 170.3, 140.4, 135.7 (2C), 135.6 (2C), 133.4, 133.3, 129.6, 129.1, 128.5, 127.7 (2C), 127.6, 121.9, 92.0 (C-1), 69.5, 65.6, 63.5, 56.8, 56.1, 50.1, 42.3, 40.3, 39.8, 39.5, 37.1, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.9, 26.8 (2C), 24.3, 23.8, 22.8, 22.5, 21.1, 21.0, 19.3, 19.2, 18.7, 11.8

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. For $C_{51}H_{74}O_5SiNa$ 817.5198, found 817.5201.

(Digitoxigenin-3-yl)-4-*O*-acetyl-2,3,6-trideoxy-*α*-L-*erythro*-hex-2-enopyranoside (10)



10

Following the general glycosylation procedure. Acceptor **2O** (20 mg, 0.05 mmol) and donor **6** (13.7 mg, 0.06 mmol) to afford after 1h at rt and after purification using silica gel column chromatography (Hexane/EtOAc =2:1), **10** as a colourless gel (18 mg, 64%)

Data of the compound (10)

$[\alpha]_D^{20}$ - 21.0 (*c* 1.3, $CHCl_3$)

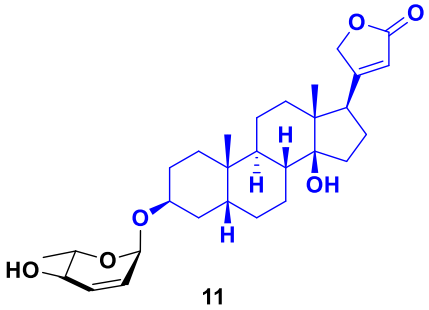
IR ($CHCl_3$) *v* 3422, 2958, 2289, 1776, 1656, 1438, 1321, 1308, 1220, 1145, 1182, 1056, 998, 956, 908, 821, 802 cm^{-1}

^1H NMR (600 MHz, $CDCl_3$) δ 5.90 - 5.87 (m, 1H), 5.85 - 5.82 (m, 1H), 5.79 (ddd, *J* = 10.4, 2.6, 1.9 Hz, 1H), 5.05 - 5.03 (m, 2H), 4.99 (dd, *J* = 18.2, 1.8 Hz, 1H), 4.81 (dd, *J* = 18.0, 1.8 Hz, 1H), 4.02 - 3.97 (m, 2H), 2.78 (dd, *J* = 9.0, 5.4 Hz, 1H), 2.19 - 2.11 (m, 2H), 2.09 (s, 3H), 1.80 - 1.37 (m, 20H), 1.20 (d, *J* = 6.3 Hz, 3H), 0.94 (s, 3H), 0.88 (s, 3H)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.5, 170.5, 129.1, 128.6, 117.7, 93.4, 85.6, 73.8, 73.4, 71.0, 64.8, 50.9, 49.6, 41.8, 40.0, 36.4, 35.7, 35.2, 33.2, 30.7, 30.3, 29.7, 26.9, 26.7, 26.6, 23.7, 21.3, 21.2, 21.1, 17.9, 15.7

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd. For $C_{31}H_{45}O_7$ 529.3160, found 529.3207.

(2S,3R,6R)-3,6-Dihydro-2-methyl-6-(Digitoxigenoxy)-2*H*-pyran-4,5-en-3-ol (11)



11

To a stirred solution of compound **10** (18 mg, 0.03 mmol) in DCM: MeOH (2 mL), MeONa (10 mg) was added, and the reaction mixture was stirred for 2 h at room temperature. After complete consumption of the starting material, the reaction was neutralized with Dowex® H^+ resin filtered and concentrated under reduced pressure to obtain glycoside **11**(16.4 mg, 96%)

as white solid. This intermediate was characterized and used in the next step without further purification.

Data of the compound (11)

$[\alpha]_D^{20}$ - 38.3 (*c* 0.7, $CHCl_3$)

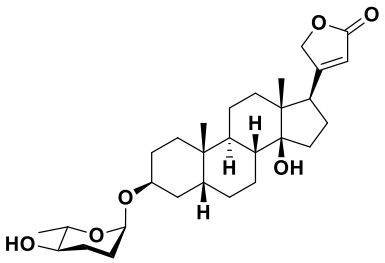
IR ($CHCl_3$) *v* 3462, 2920, 2856, 1778, 1728, 1609, 1457, 1386, 1320, 1141, 1168, 1036, 1012, 1022, 998, 748 cm^{-1}

^1H NMR (600 MHz, $CDCl_3$) δ 5.90 (ddd, *J* = 10.0, 4.6, 1.2 Hz, 1H), 5.86 (m, 1H), 5.72 (d, *J* = 10.2 Hz, 1H), 5.07 - 5.01 (m, 1H), 4.98 (dd, *J* = 18.2, 1.2 Hz, 1H), 4.80 (dd, *J* = 18.0, 1.8 Hz, 1H), 3.98 (s, 1H), 3.82 (dq, *J* = 6.5, 2.4 Hz, 1H), 3.76 - 3.73 (m, 1H), 2.77 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.20 - 2.11 (m, 2H), 1.80 - 1.34 (m, 21H), 1.29 (d, *J* = 6.0 Hz, 3H), 0.93 (s, 3H), 0.87 (s, 3H)

^{13}C {^1H} NMR (150 MHz, $CDCl_3$) δ 174.5, 132.8, 127.6, 117.7, 93.2, 85.6, 73.7, 73.4, 69.8, 68.0, 50.9, 49.6, 41.8, 40.0, 36.4, 35.7, 35.2, 33.1, 30.7, 30.3, 26.8, 26.7 (2C), 26.6, 23.7, 21.3, 21.1, 18.0, 15.7

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd. For $C_{29}H_{43}O_6$ 487.3054, found 487.3041.

(2S,3R,6R)-3,6-dihydro-2-methyl-6-(Digitoxigenoxy)-2*H*-pyran-3-ol (12)



12

To a stirred solution of allylic alcohol **11** (15 mg, 0.03 mmol) in NMM (0.2 mL), was added *O*-nitrobenzenesulfonyl hydrazine (NBSH) (40 mg, 0.18 mmol) and Et_3N (8.6 µL, 0.06 mmol) at 0°C. The resulting mixture was stirred and gradually raised to room temperature for 12 h. After the TLC analysis showed the disappearance of the starting material, the reaction was diluted with 20 mL of EtOAc and quenched by the addition of saturated aqueous $NaHCO_3$. The mixture was extracted with EtOAc (3×30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 1: 1) on silica gel to afford compound **12** (13.3 mg, 88%) as white solid.

Data of the compound (12)

$[\alpha]_D^{20}$ - 11.8 (*c* 0.3, $CHCl_3$)

mp 174 - 175 °C

IR ($CHCl_3$) *v* 3430, 2946, 2231, 1776, 1745, 1621,1456, 1345, 1330, 1221, 1179, 1102, 1029, 998, 938, 900, 837, 812 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (m, 1H), 4.99 (dd, *J* = 18.8, 1.6 Hz, 1H), 4.82 (m, 1H), 4.79 (dd, *J* = 18.8, 1.2 Hz, 1H), 3.92 (s, 1H), 3.67 - 3.60 (m, 1H), 3.29 - 3.24 (m, 1H), 2.78 (dd, *J* = 9.7, 6.0 Hz, 1H), 2.21 - 2.09 (m, 3H), 1.85 - 1.40 (m, 21H), 1.24 - 1.20 (m, 6H), 0.94 (s, 3H), 0.88 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.5, 117.7, 94.1, 85.6, 73.4, 72.4, 70.9, 69.6, 50.9, 49.6, 41.9, 40.0, 36.4, 35.7, 35.2, 33.2, 30.5, 30.2, 29.8, 27.7, 26.9, 26.7 (2C), 26.6, 23.7, 21.4, 21.2, 17.9, 15.7

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd. For $C_{29}H_{45}O_6$ 489.3211, found 489.3238.

NMR studies of the interaction between Donor 1 and $Zn(BF_4)_2.xH_2O$

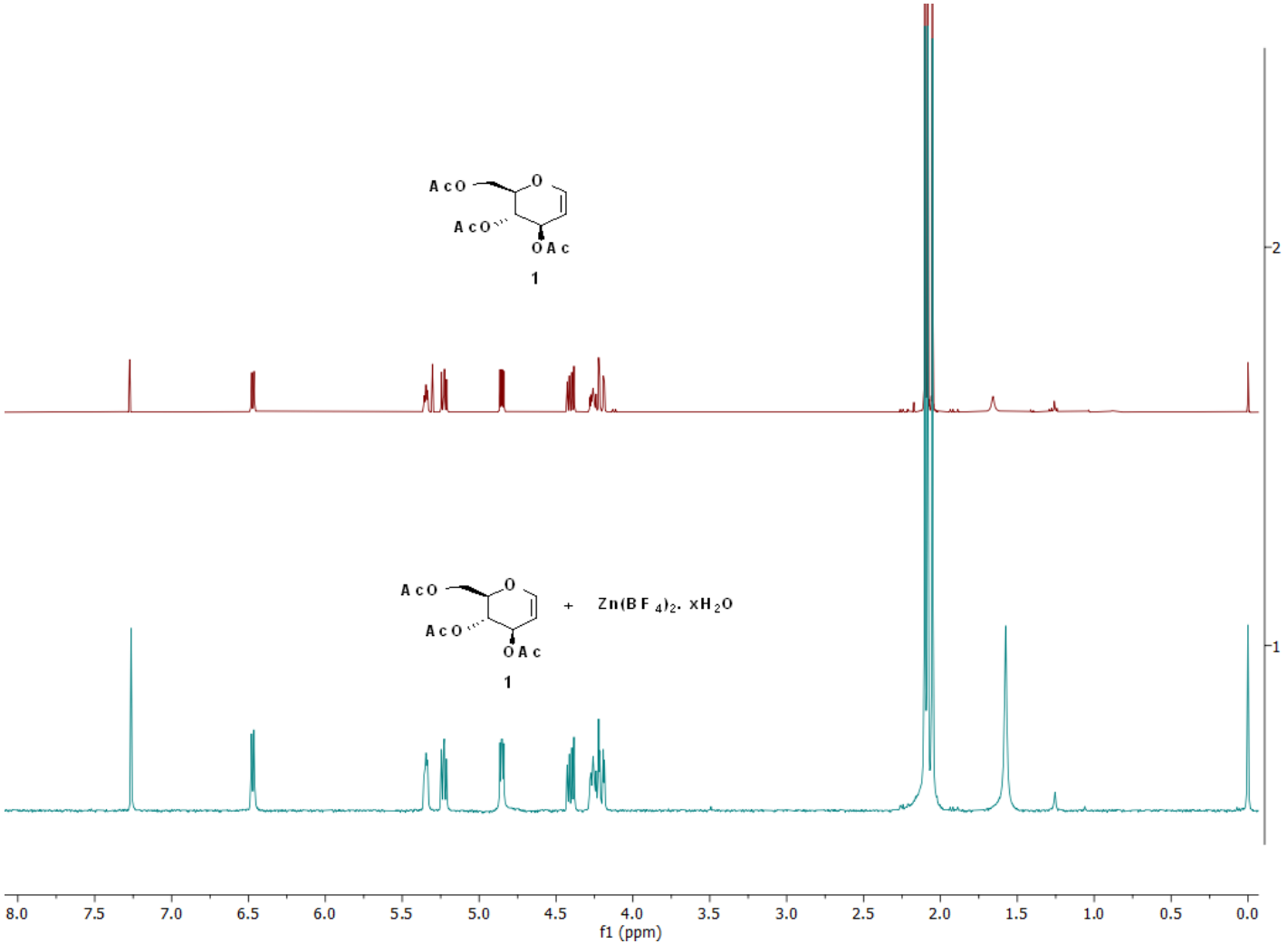
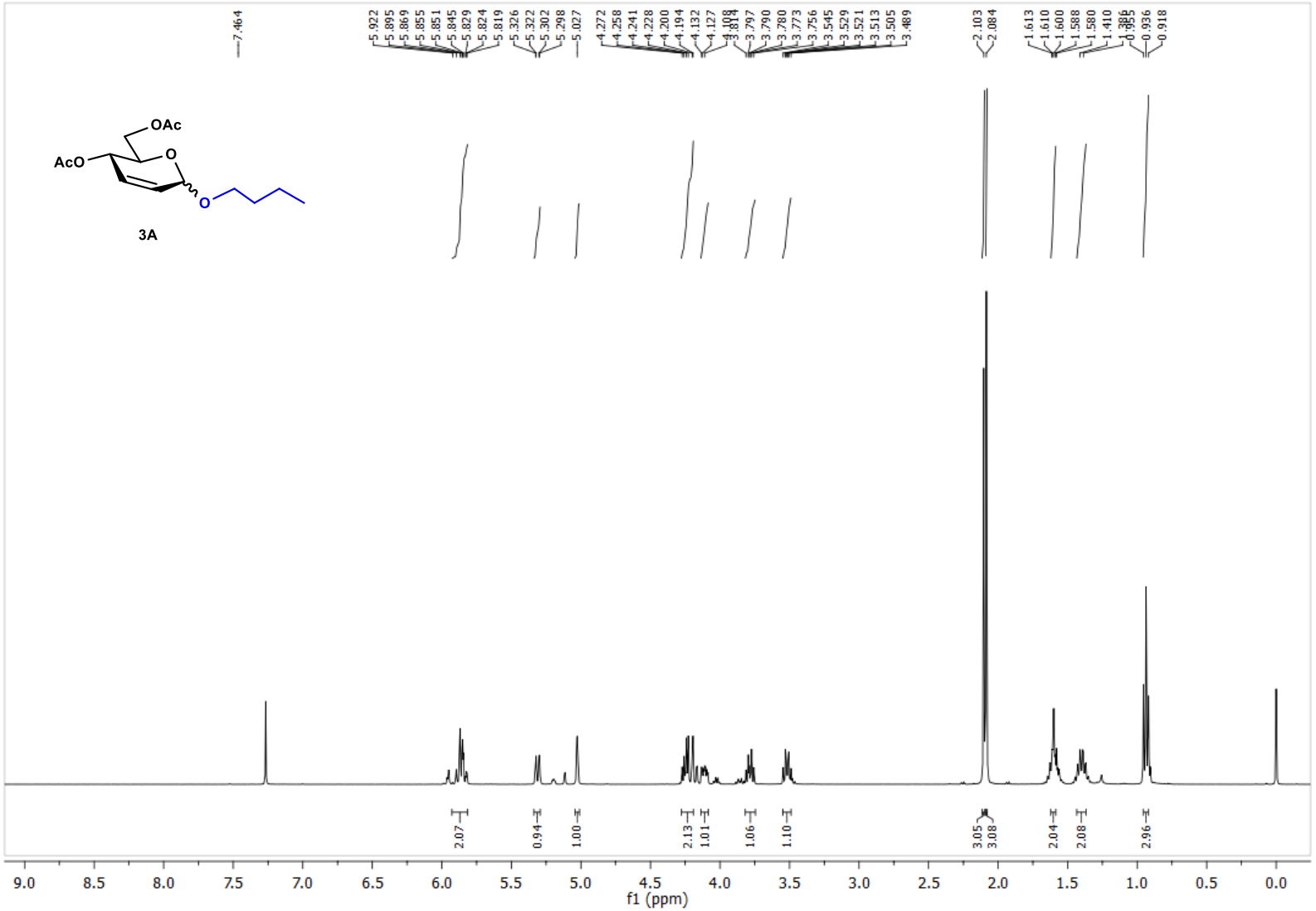
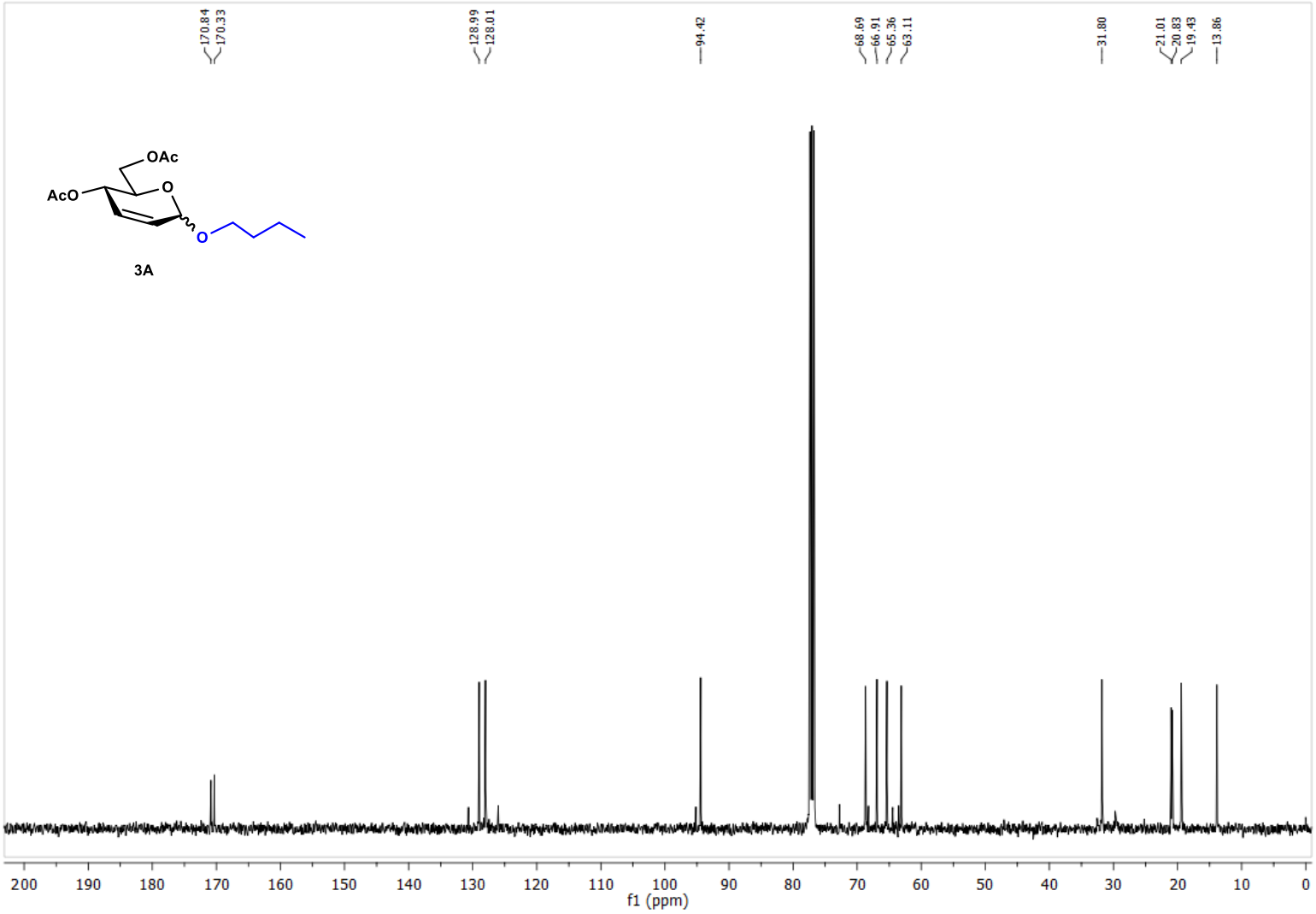


Figure S1. ^{1}H NMR of donor 1 and a mixture of donor 1 and $Zn(BF_4)_2.xH_2O$ (0.2 eq.) in $CDCl_3$

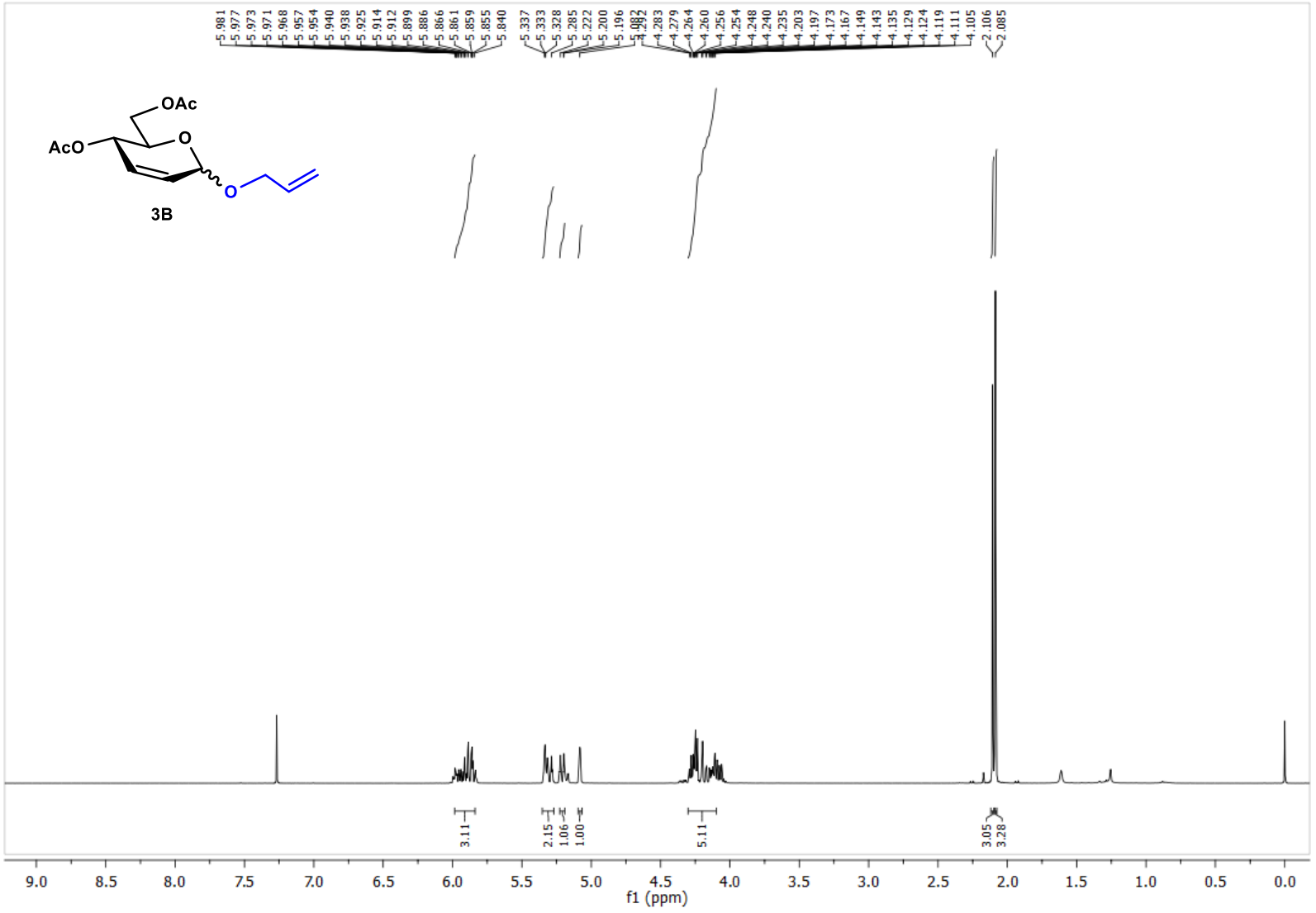
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (3A)



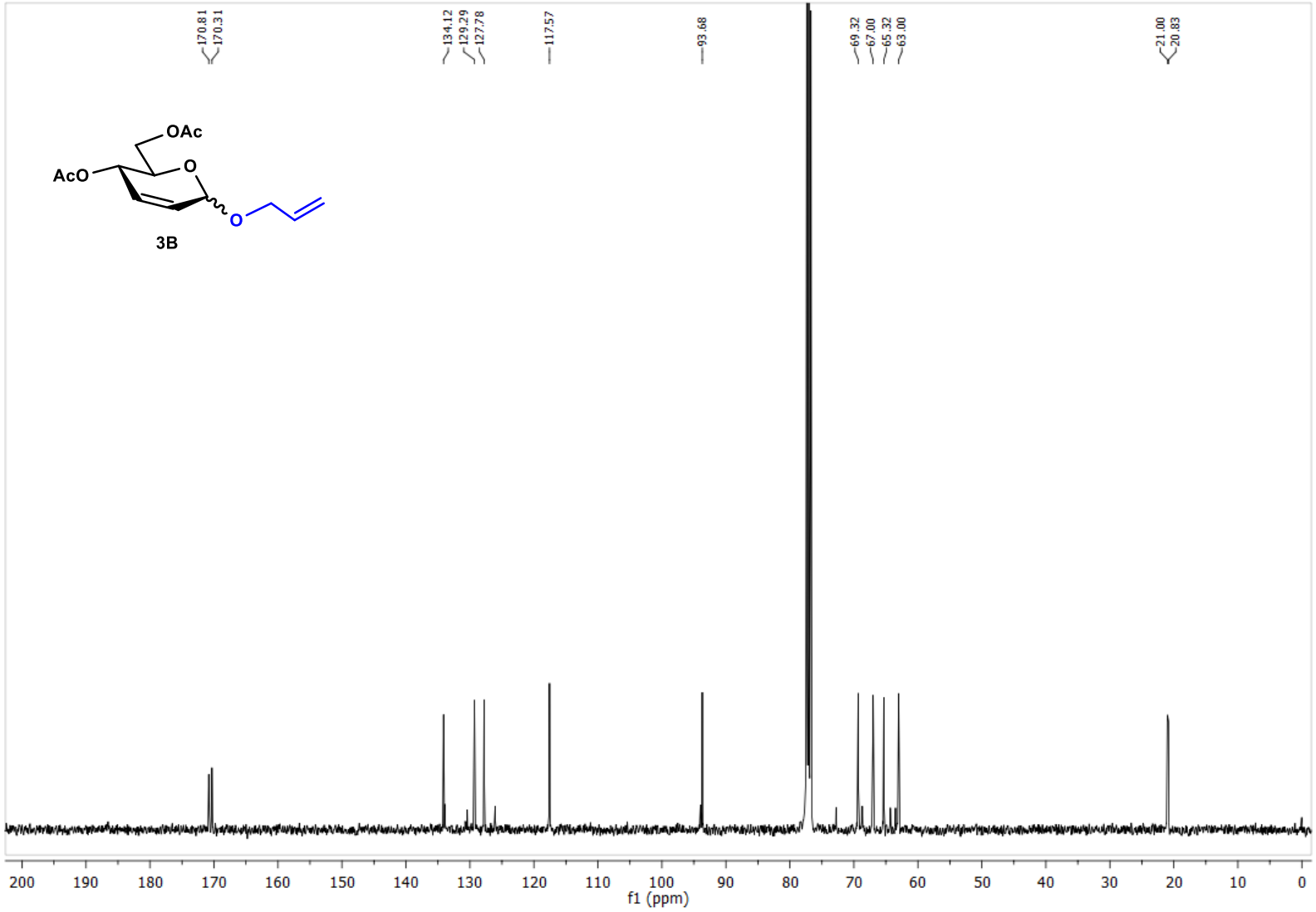
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3A)



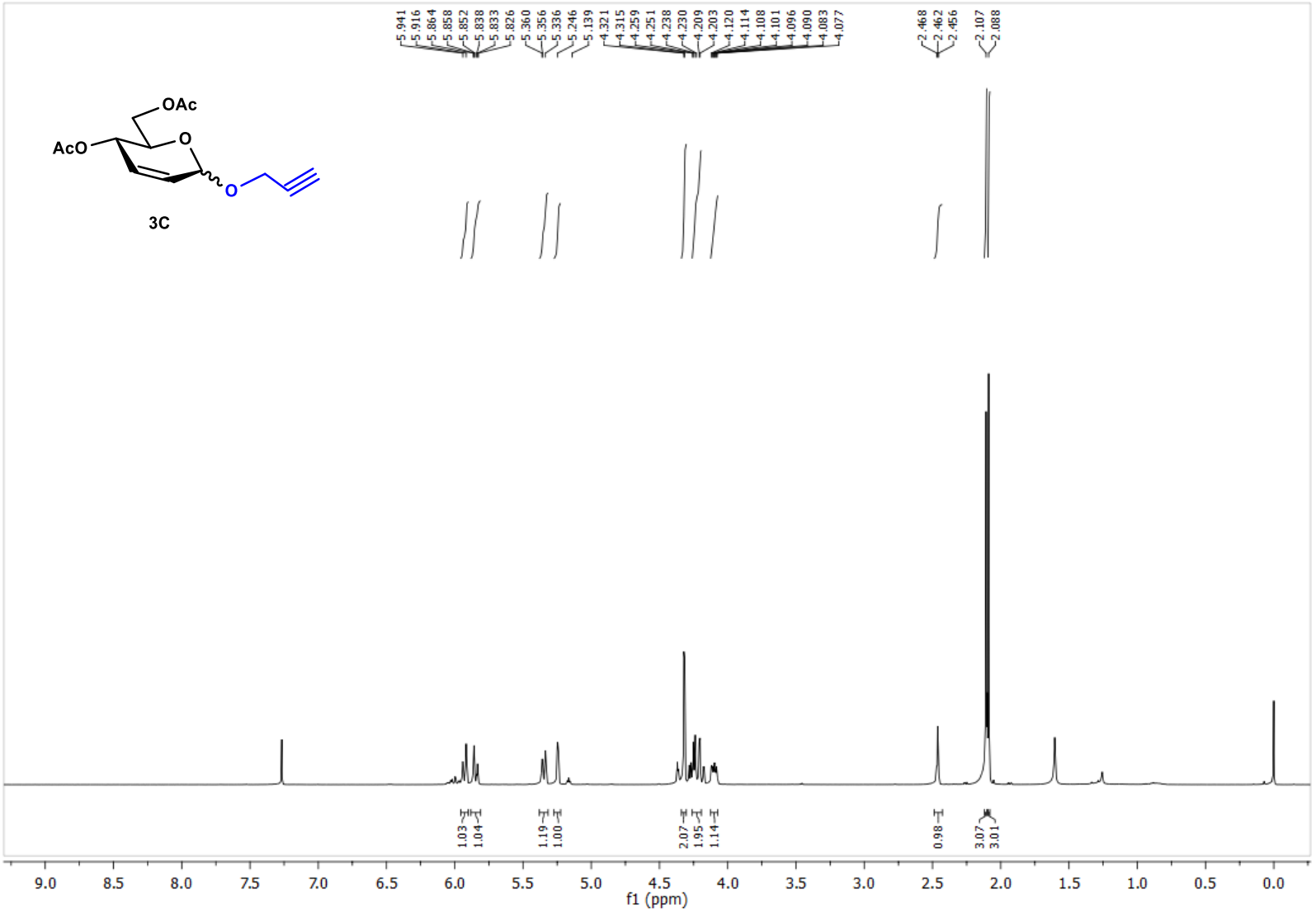
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (3B)



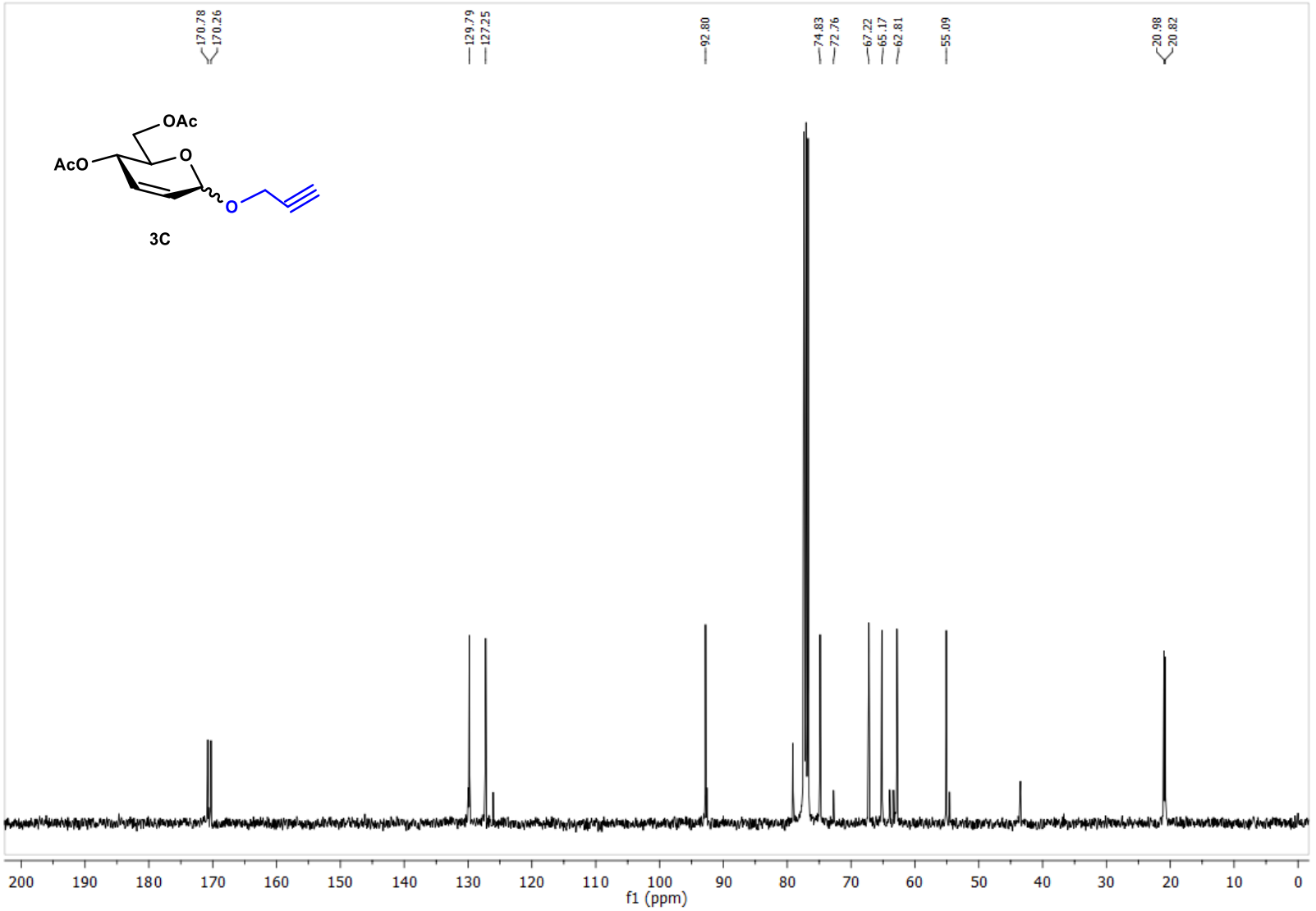
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3B)



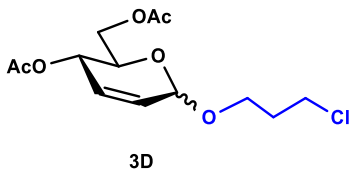
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (3C)



$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3C)

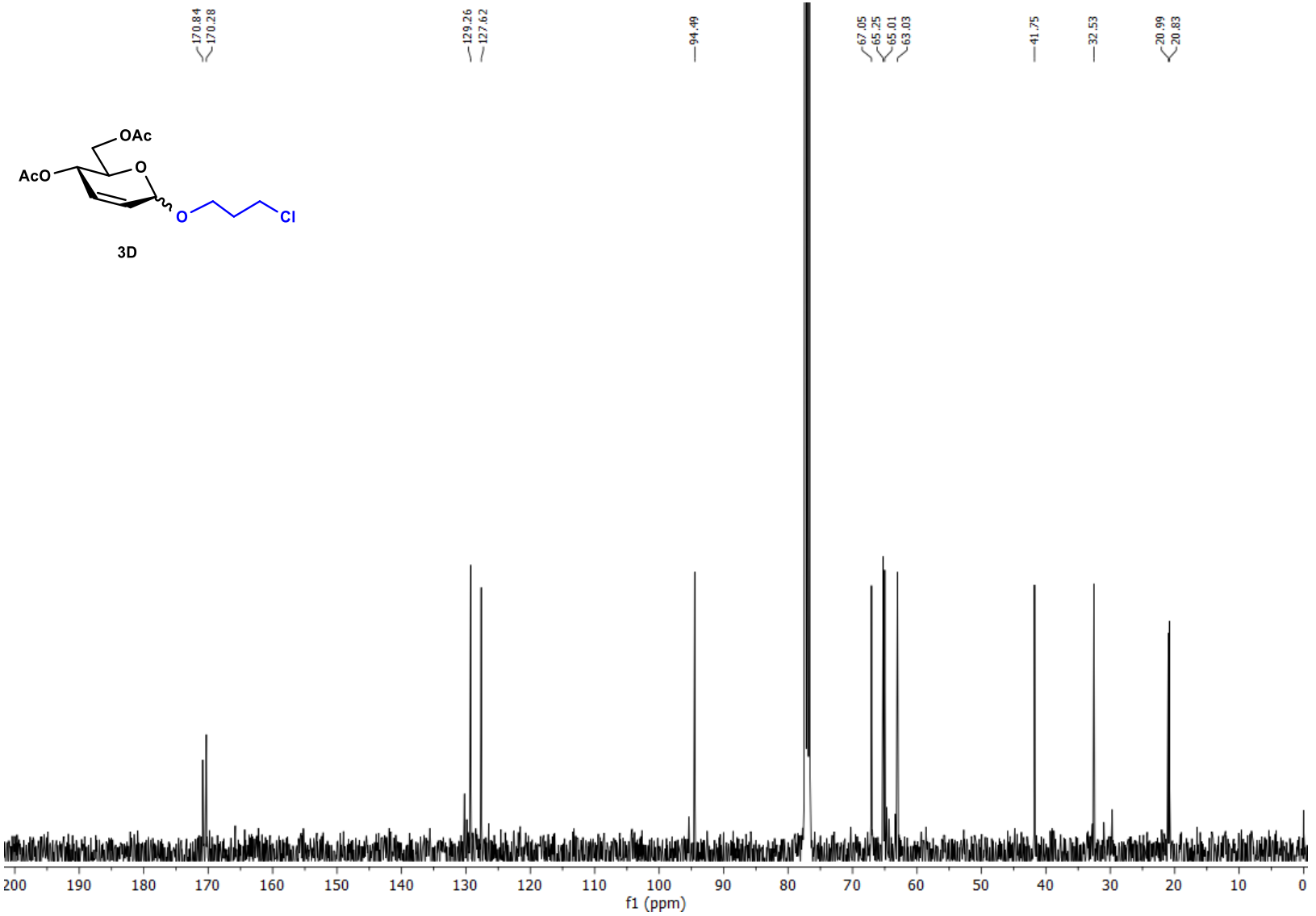


^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (3D)

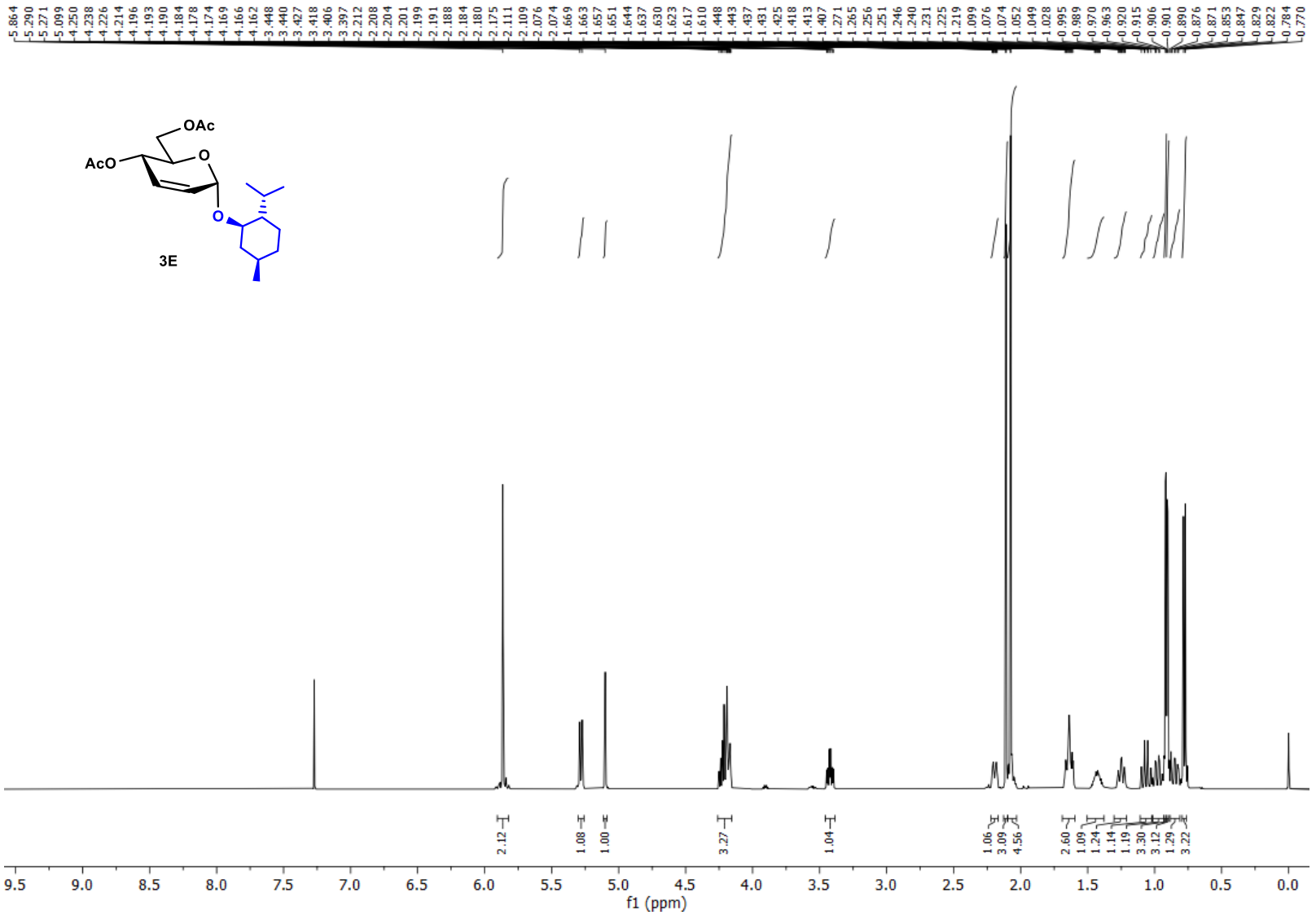


3D

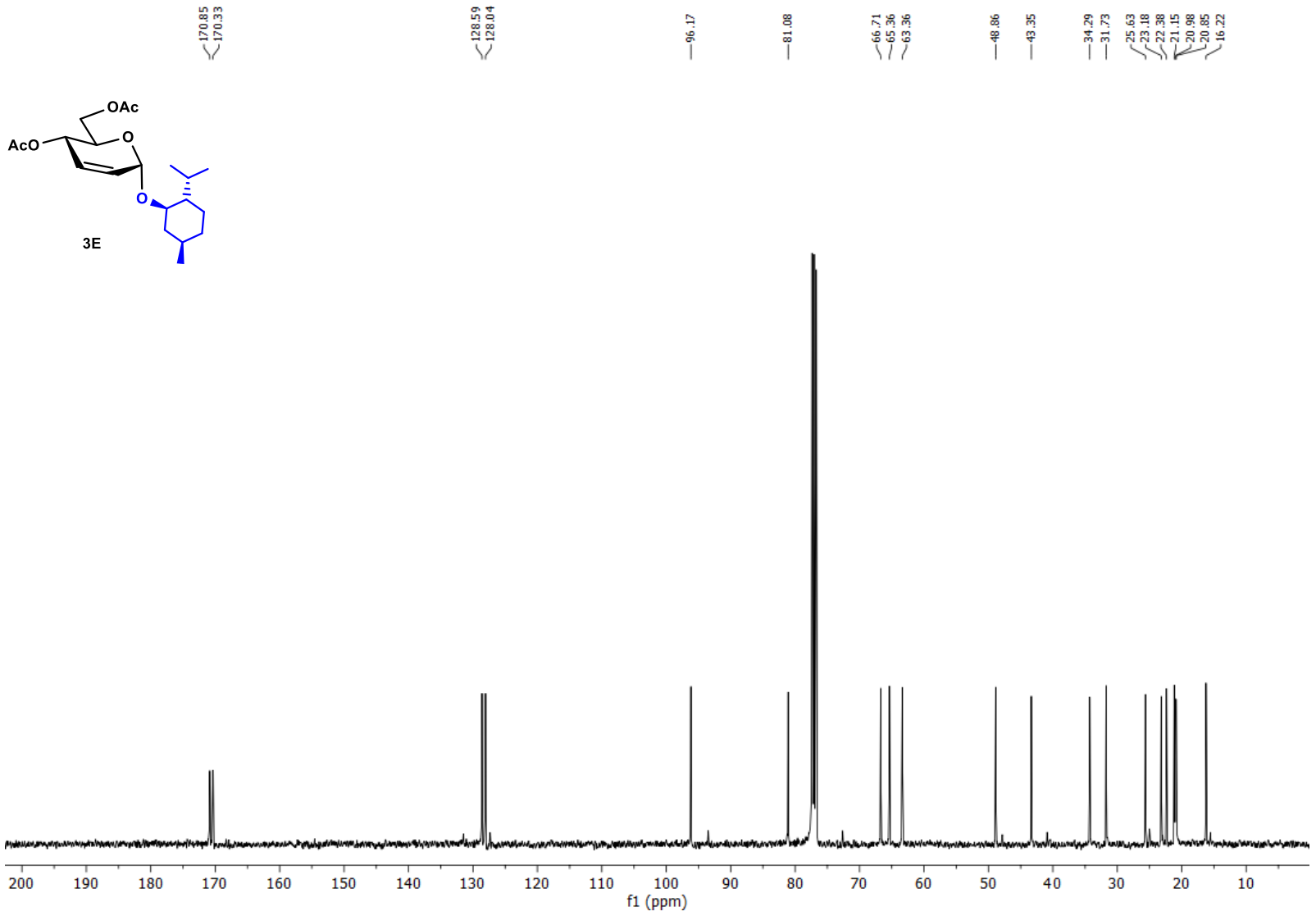
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3D)



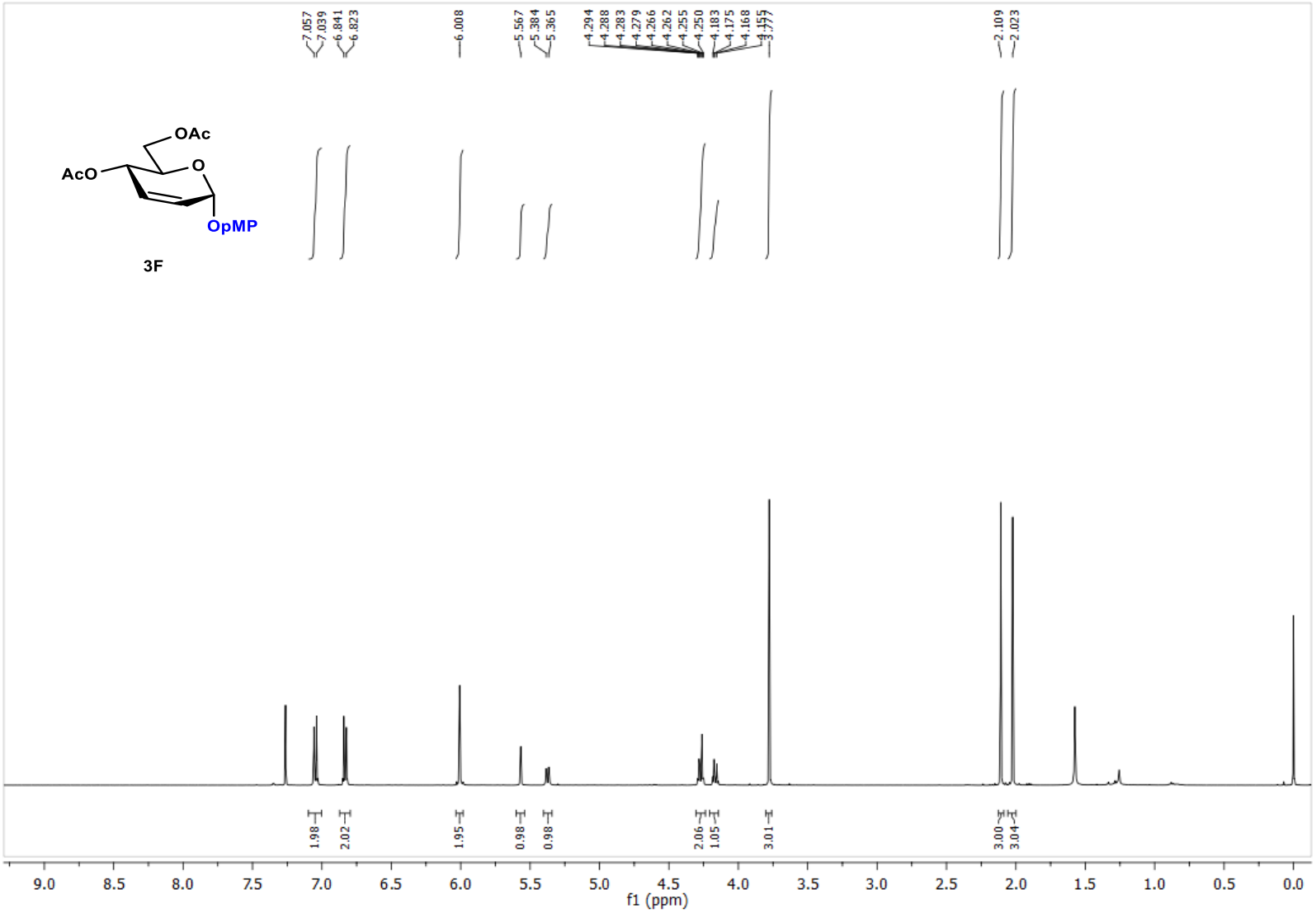
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of compound (3E)



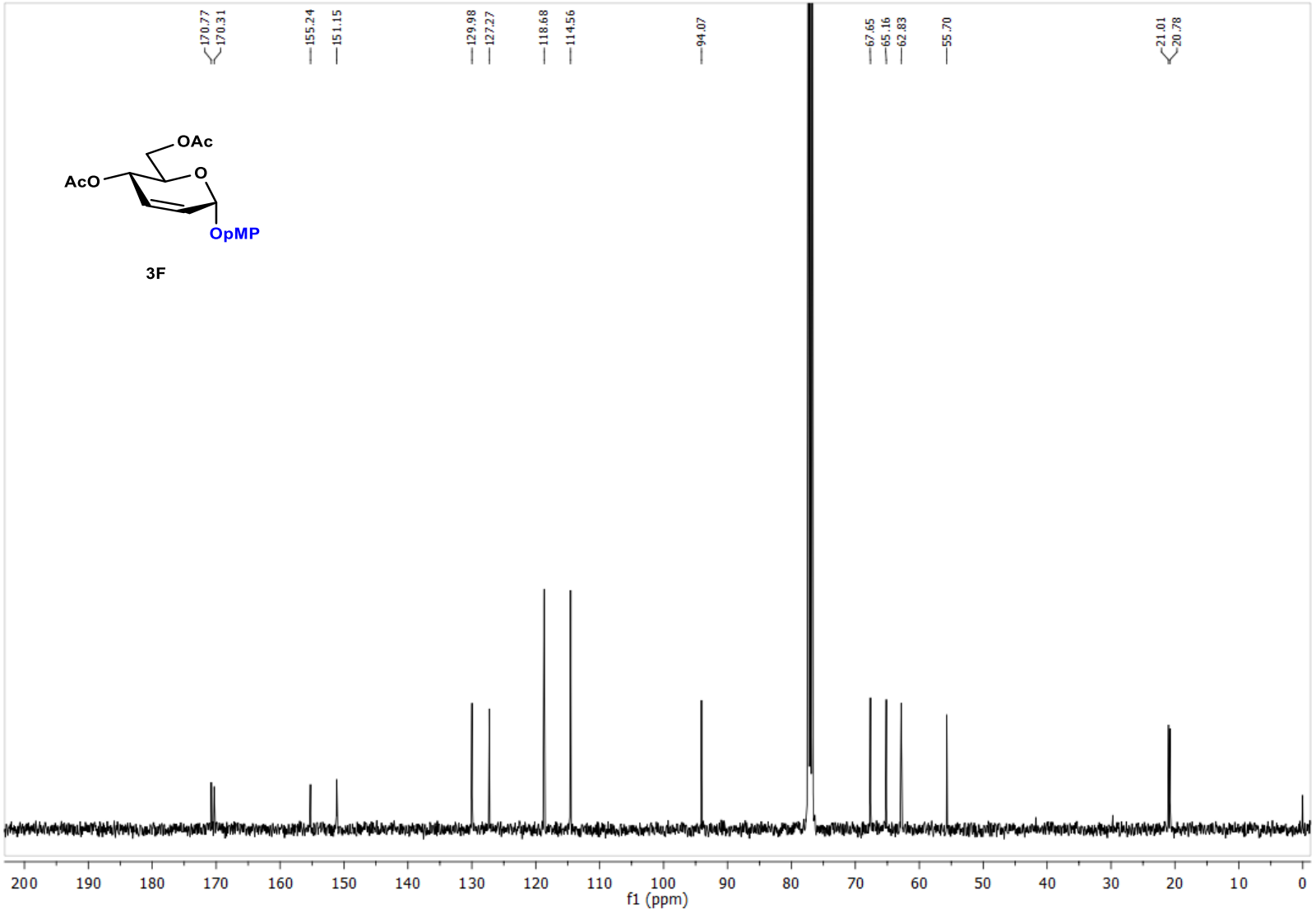
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3E)



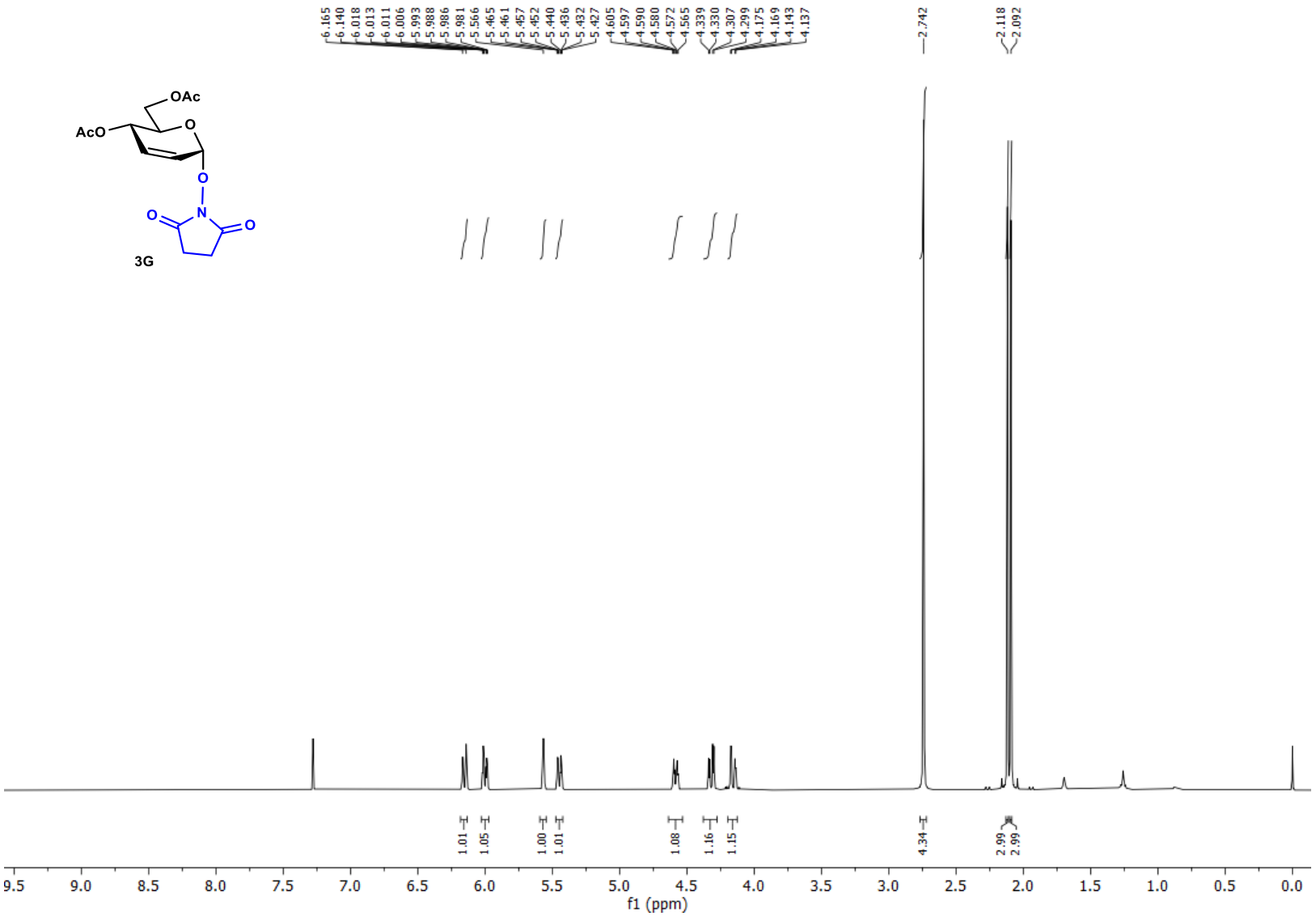
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of compound (3F)



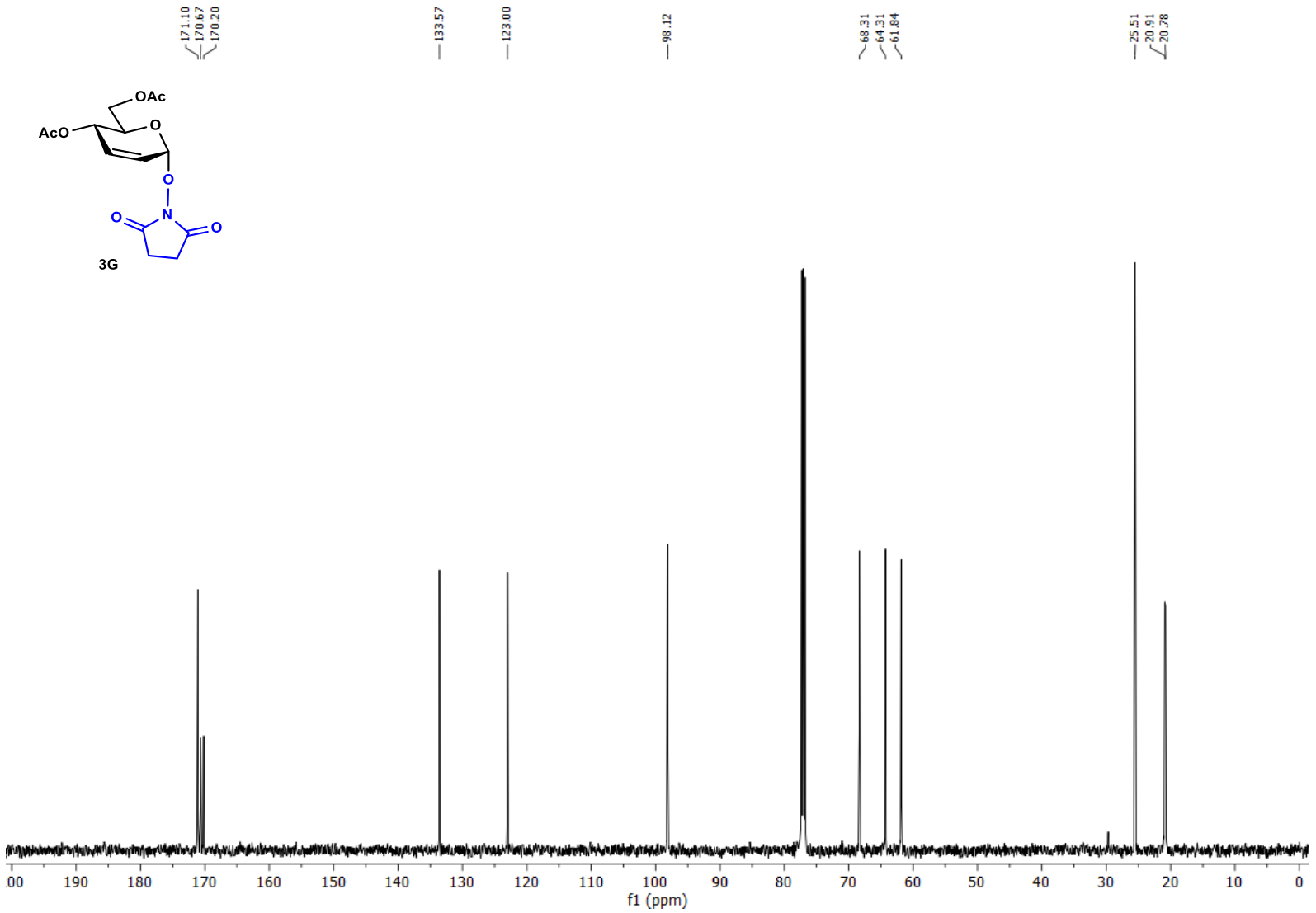
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3F)



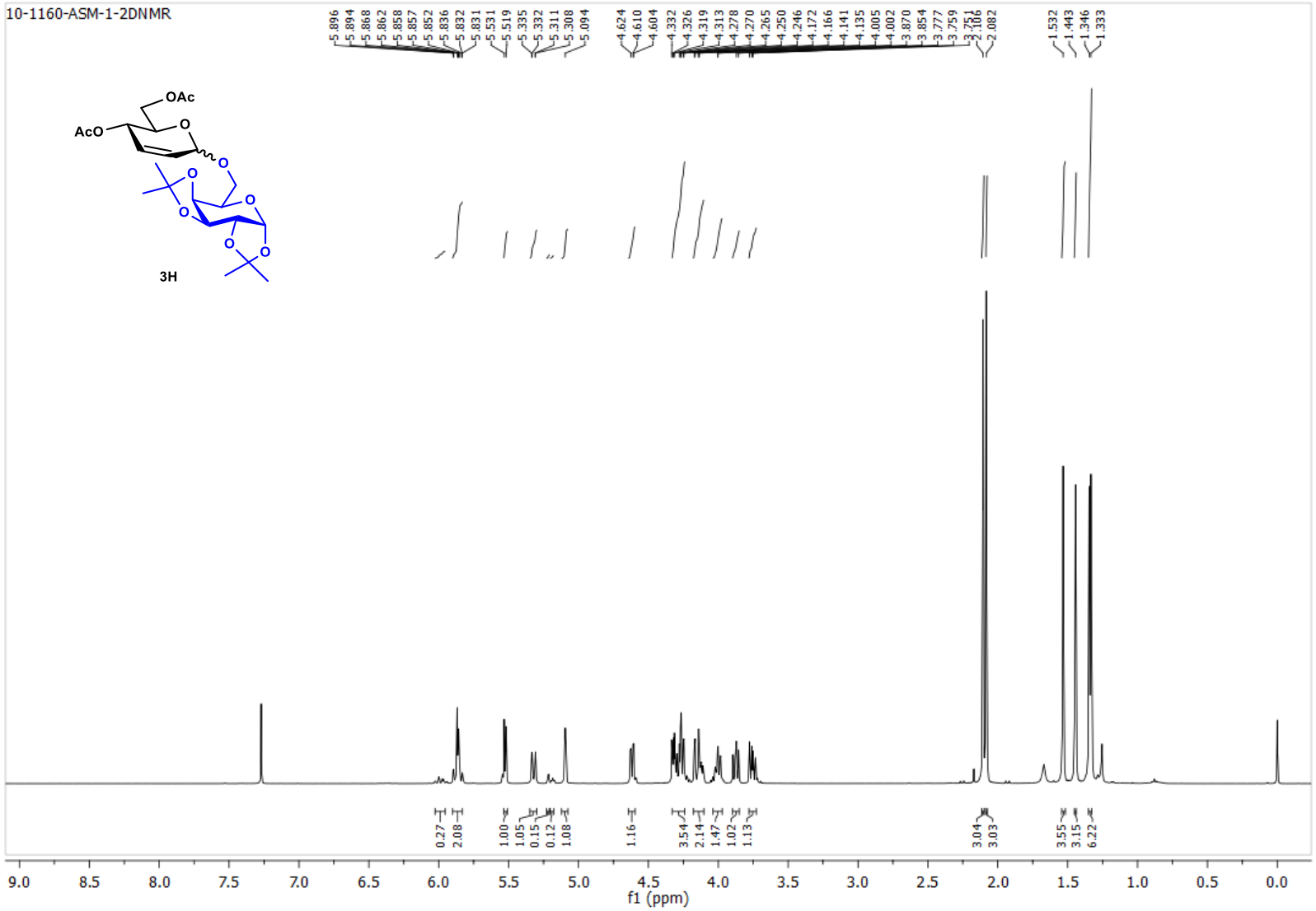
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (3G)



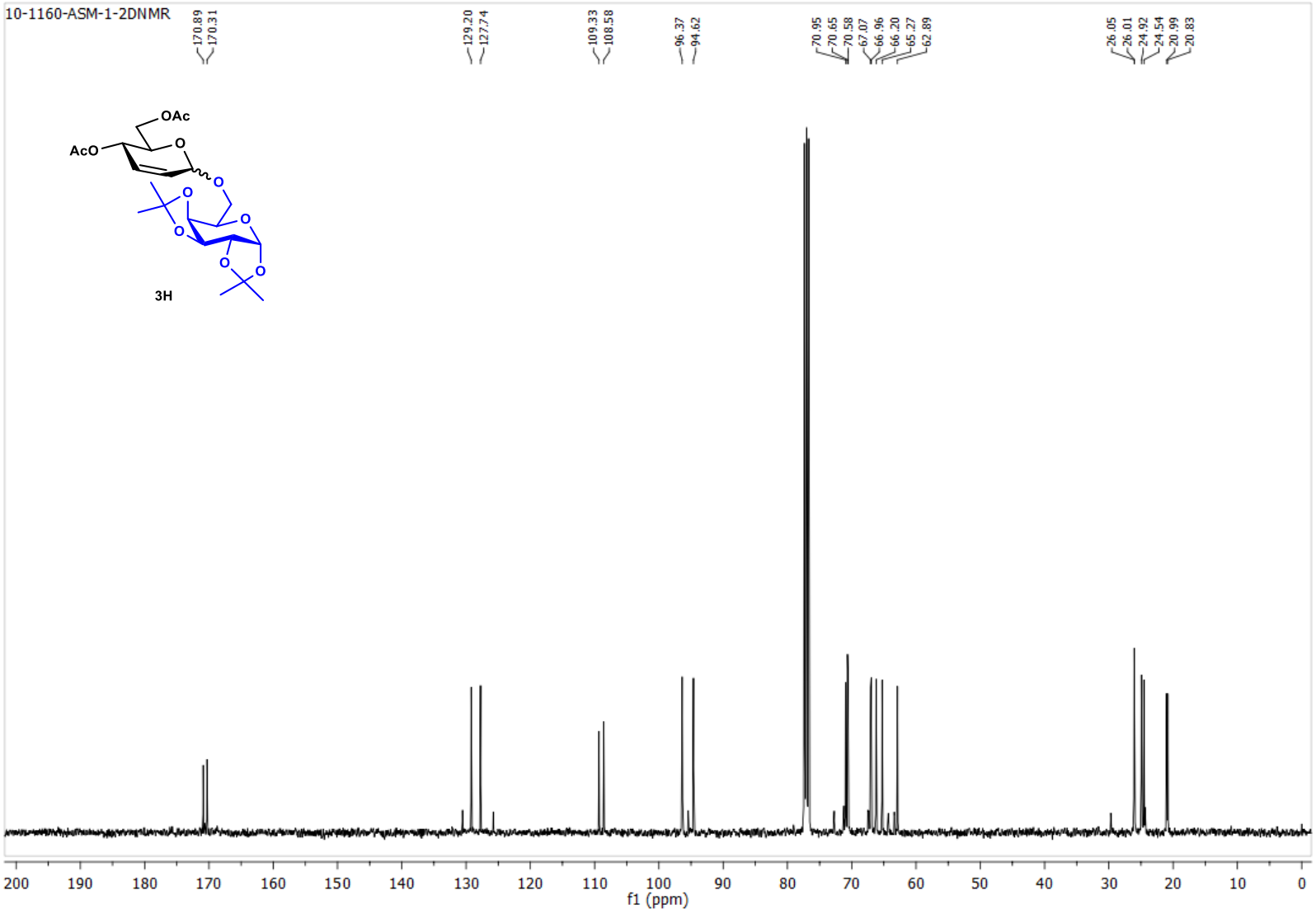
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of compound (3G)



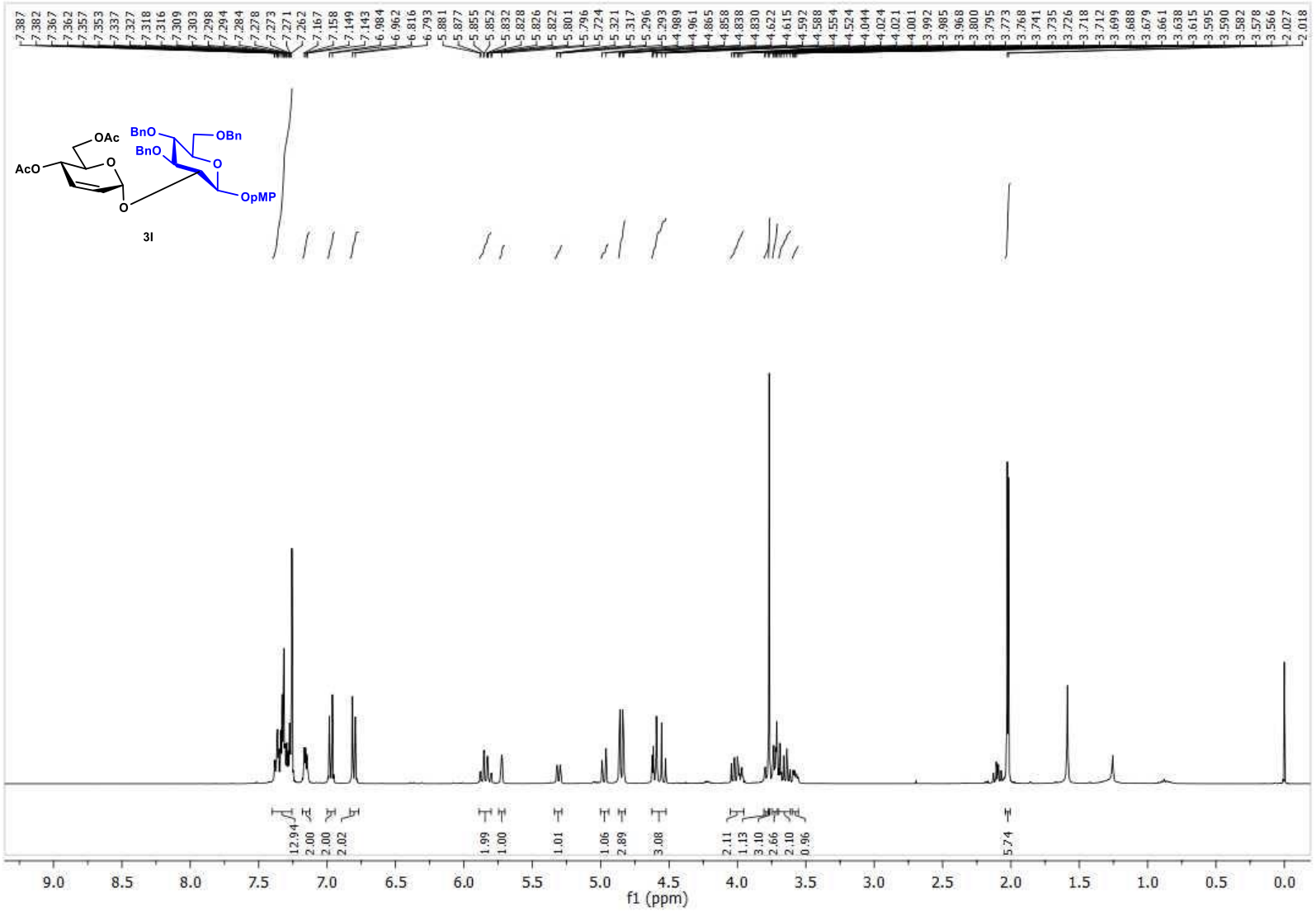
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (3H)



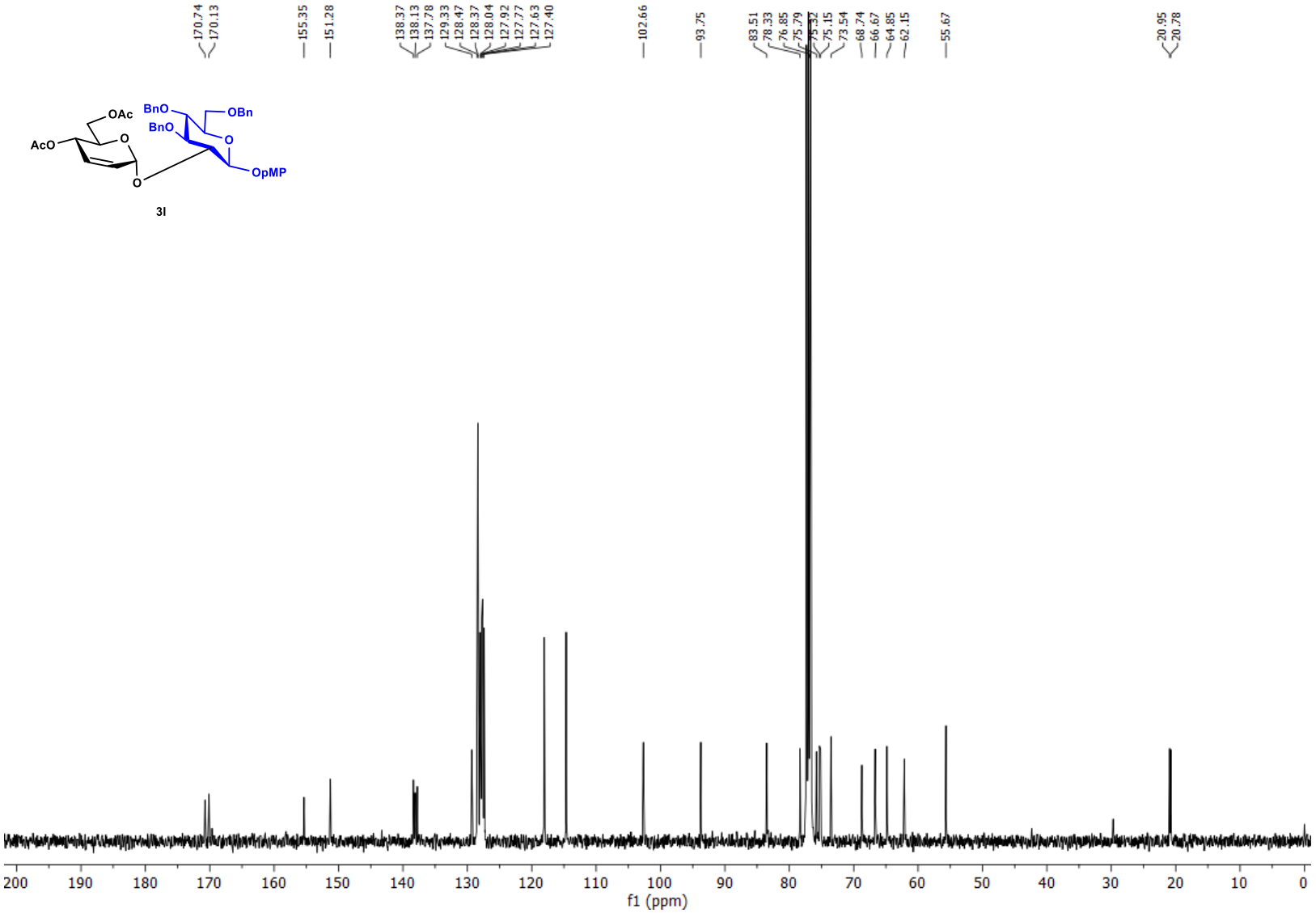
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3H)



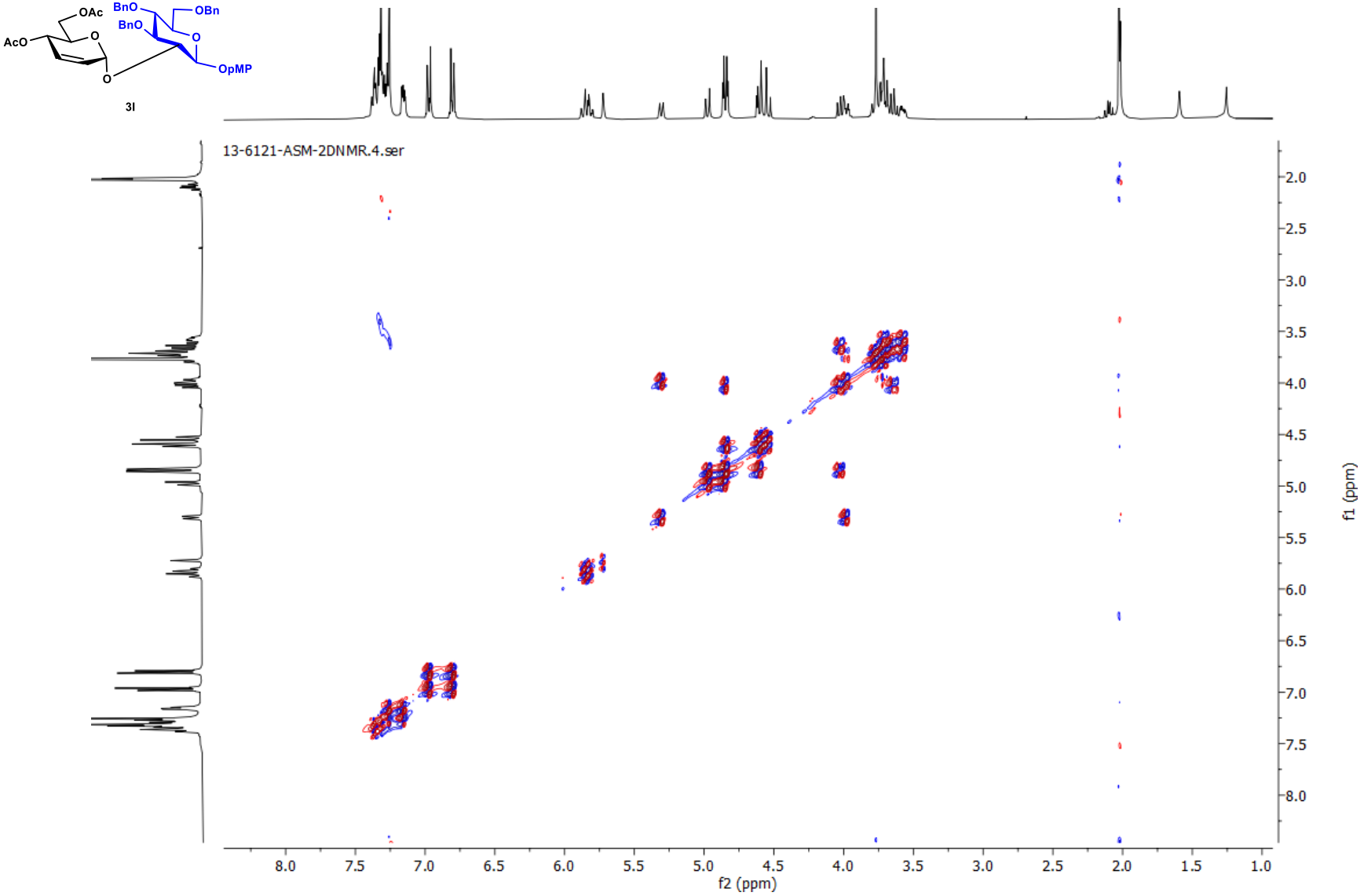
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (3I)



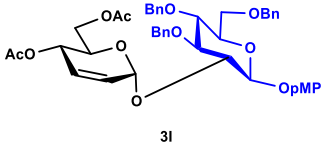
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3I)



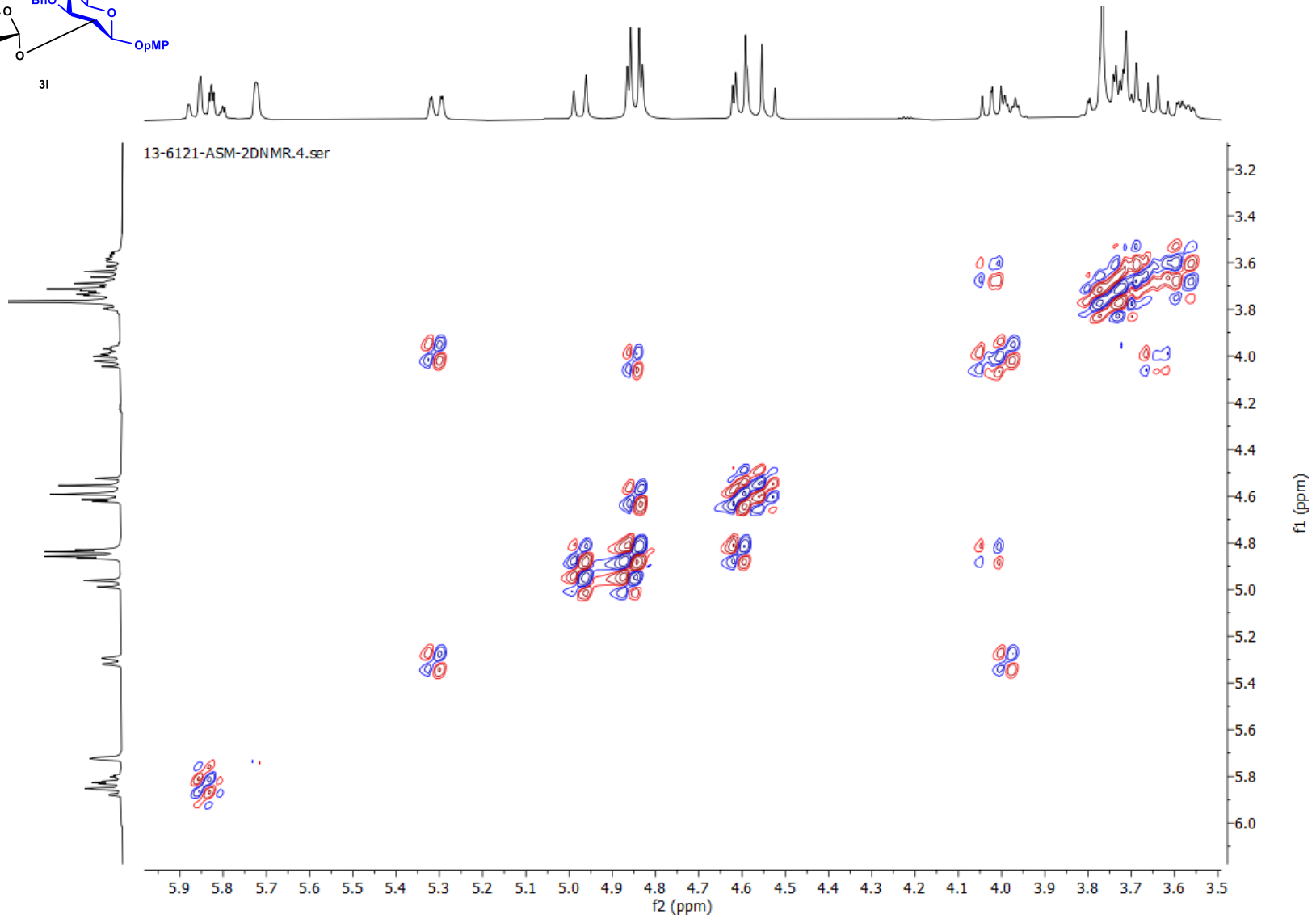
COSY (Full region) (400 MHz, $CDCl_3$) NMR spectrum of compound(3I)



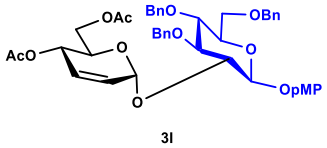
COSY (Expanded region) (400 MHz, $CDCl_3$) NMR spectrum of compound(3I)



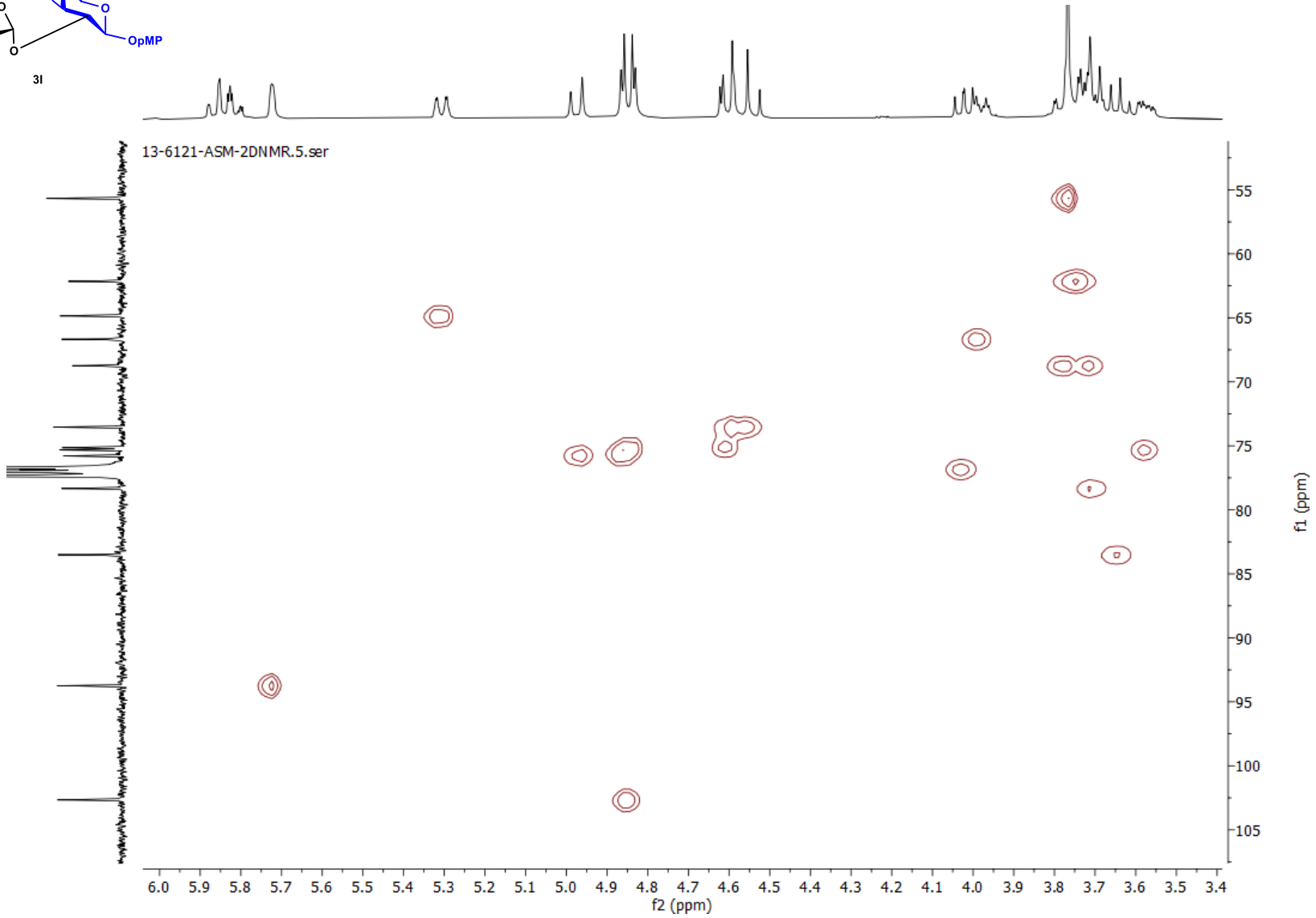
3I



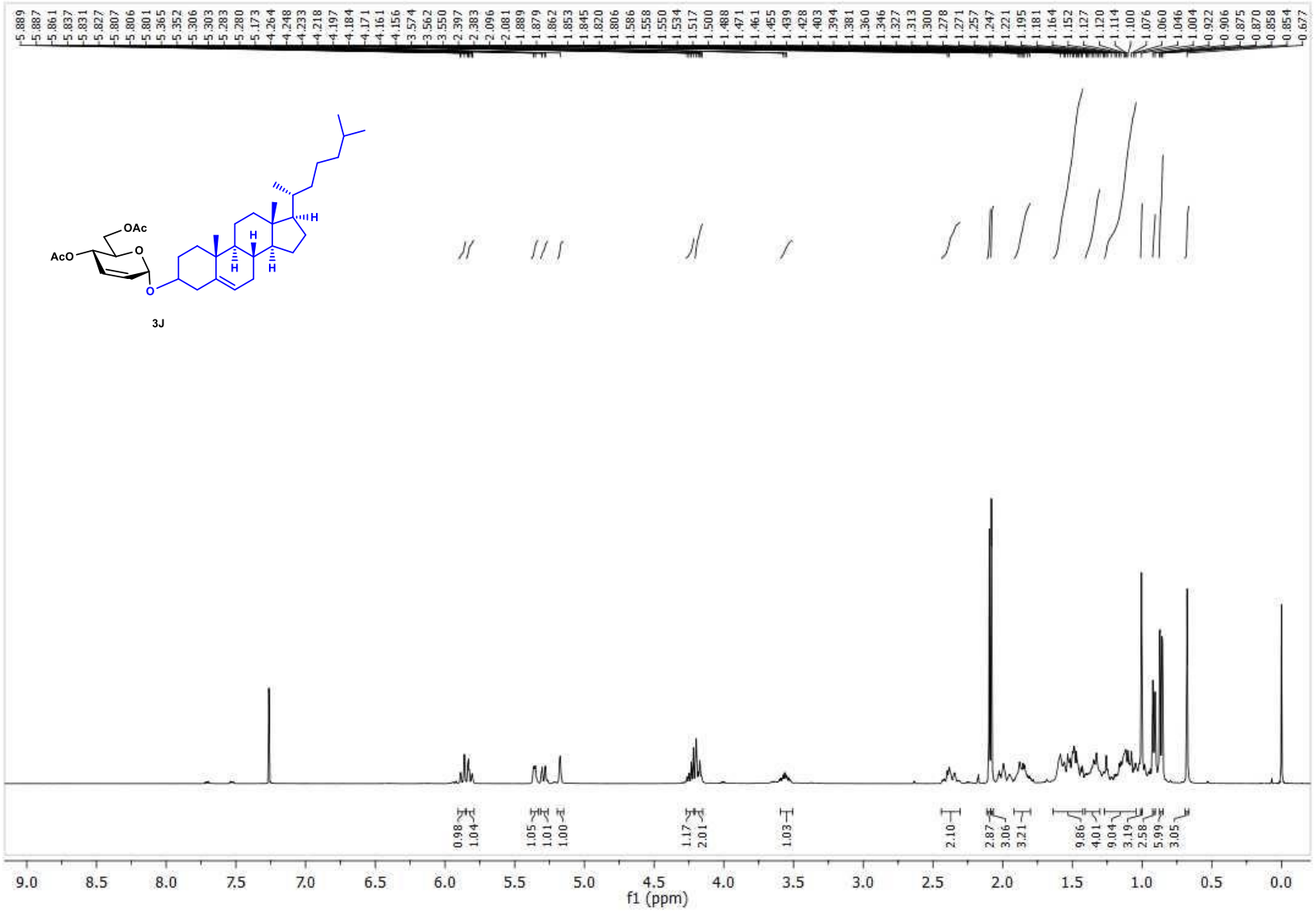
HSQC (Expanded region) (400 MHz, $CDCl_3$) NMR spectrum of compound(3I)



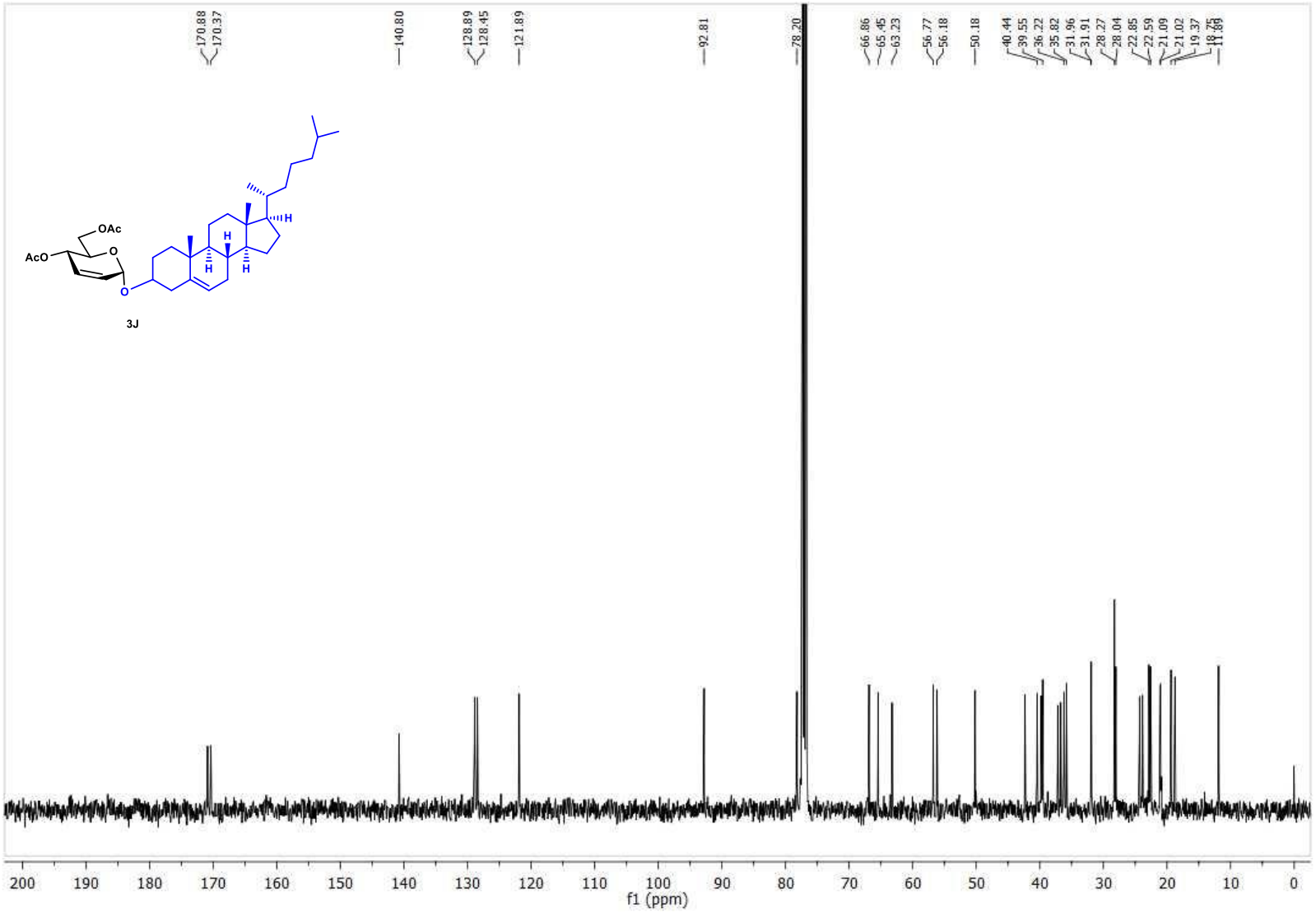
3I



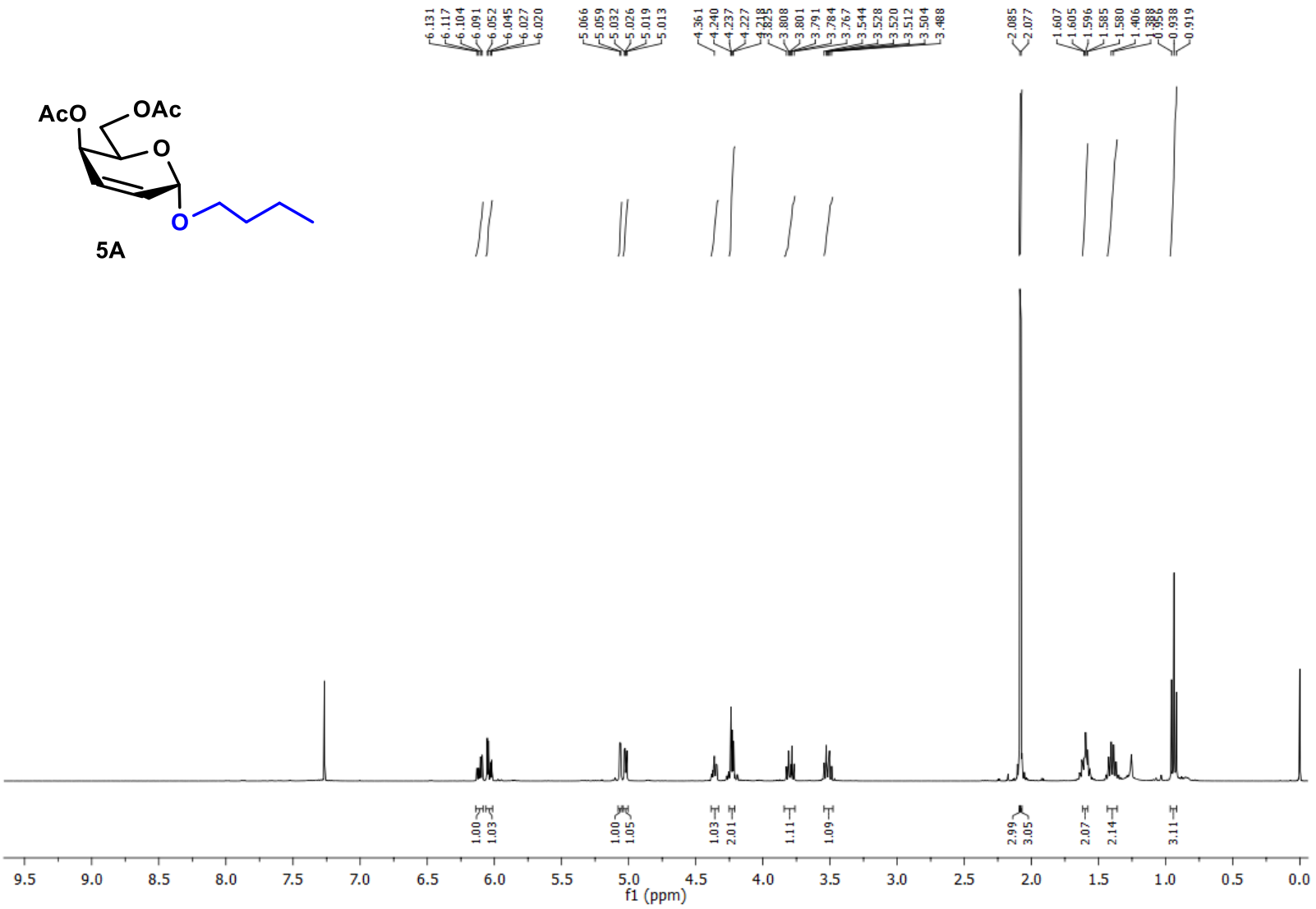
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (3J)



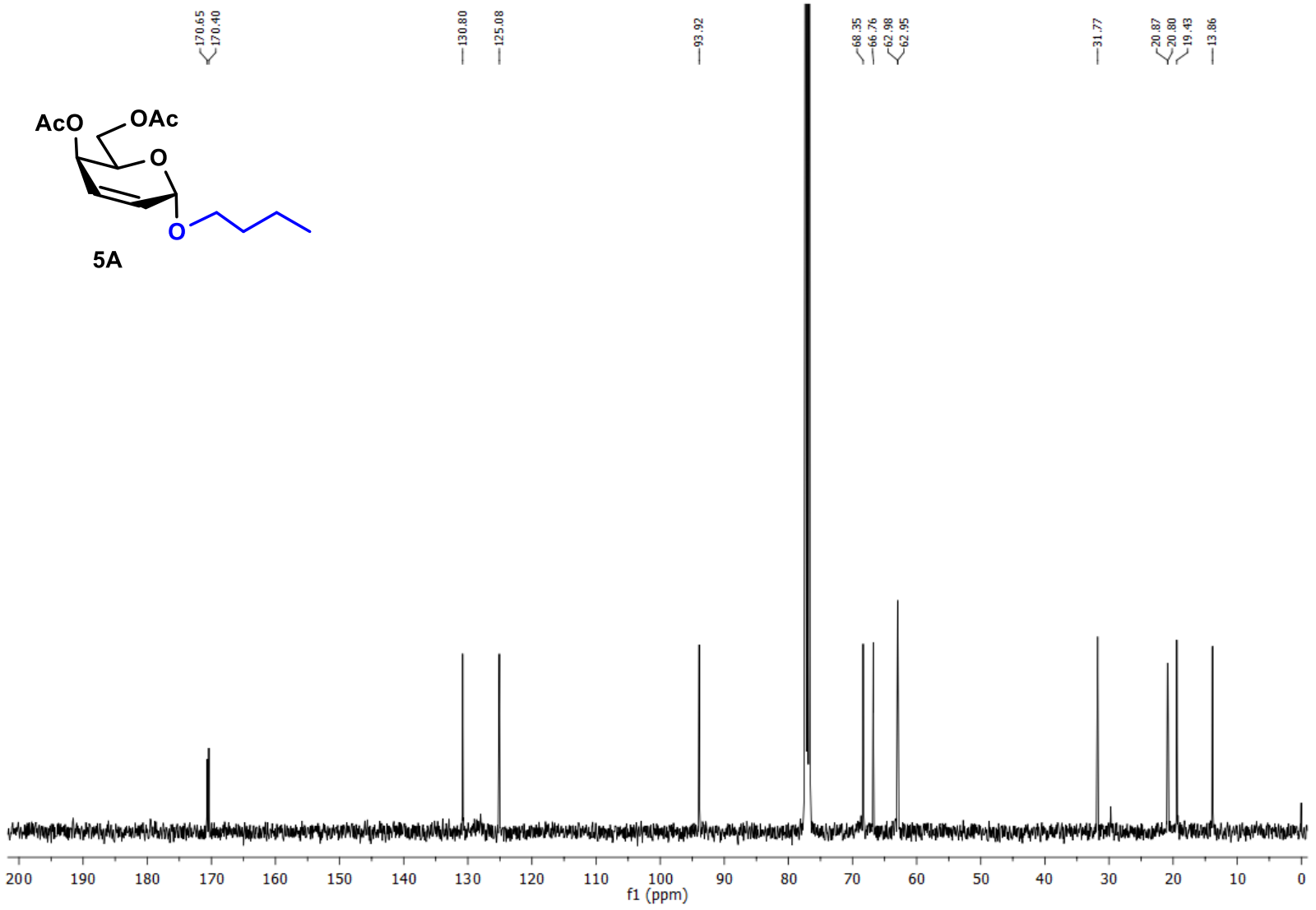
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (3J)



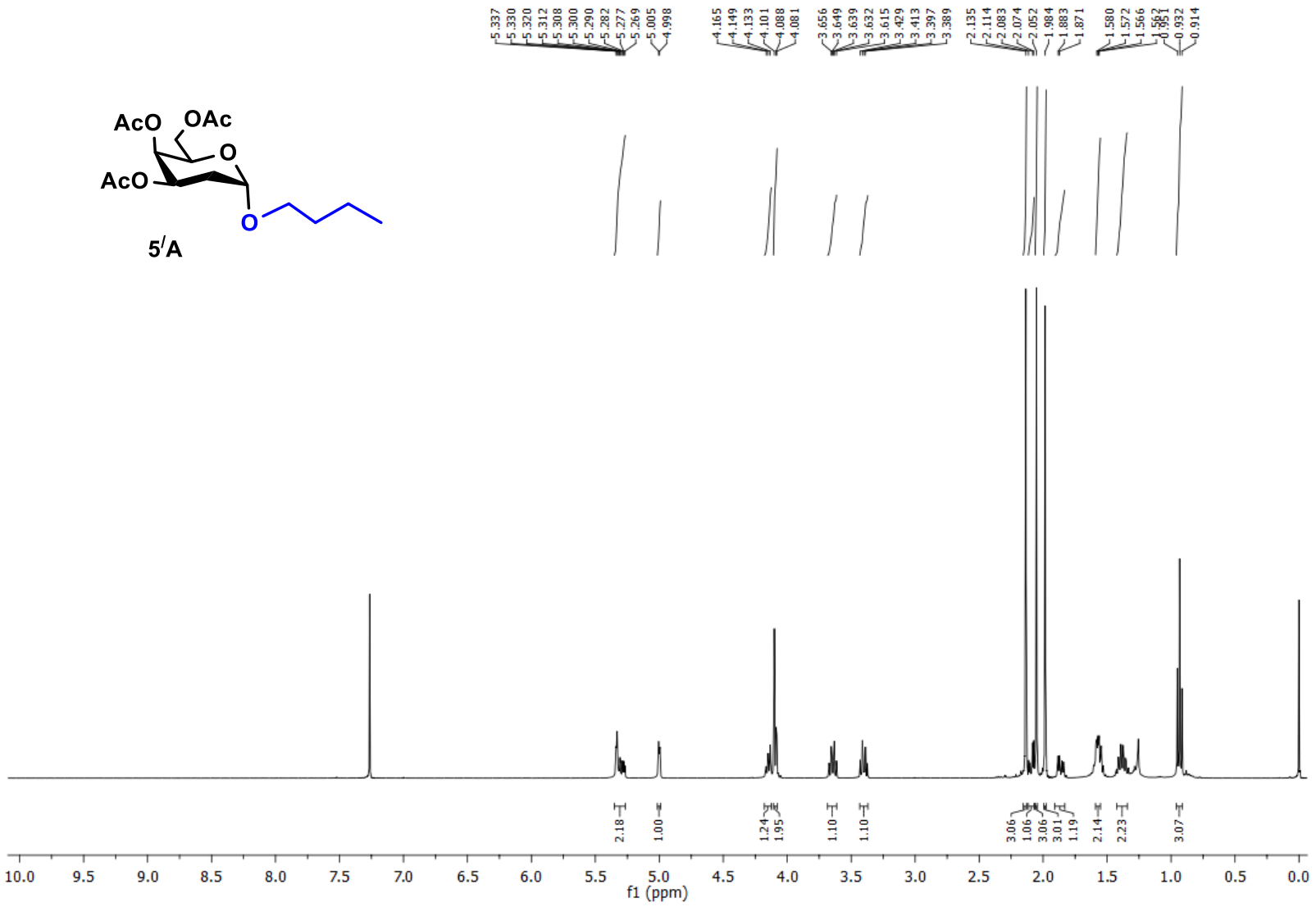
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (5A)



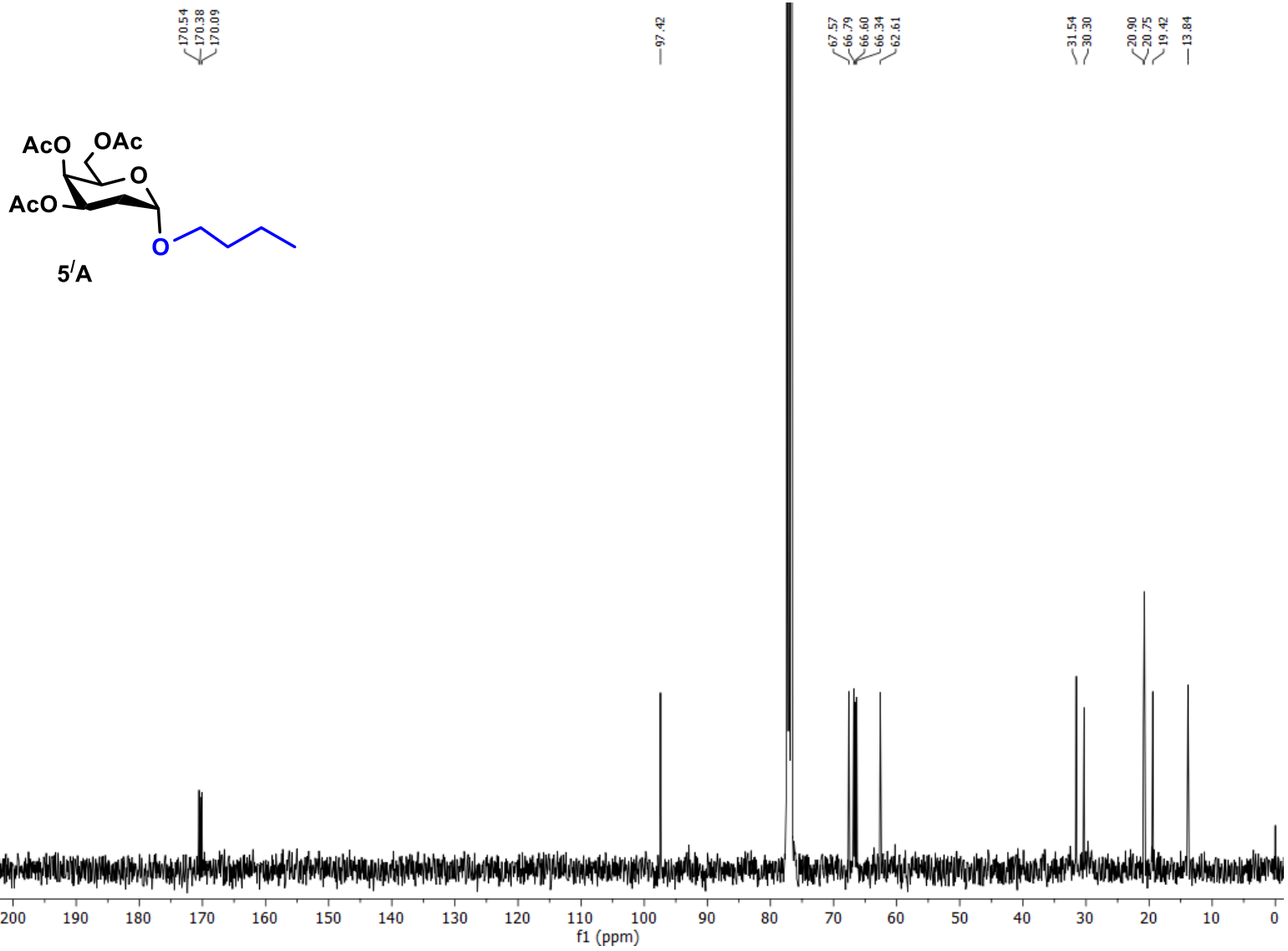
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (5A)



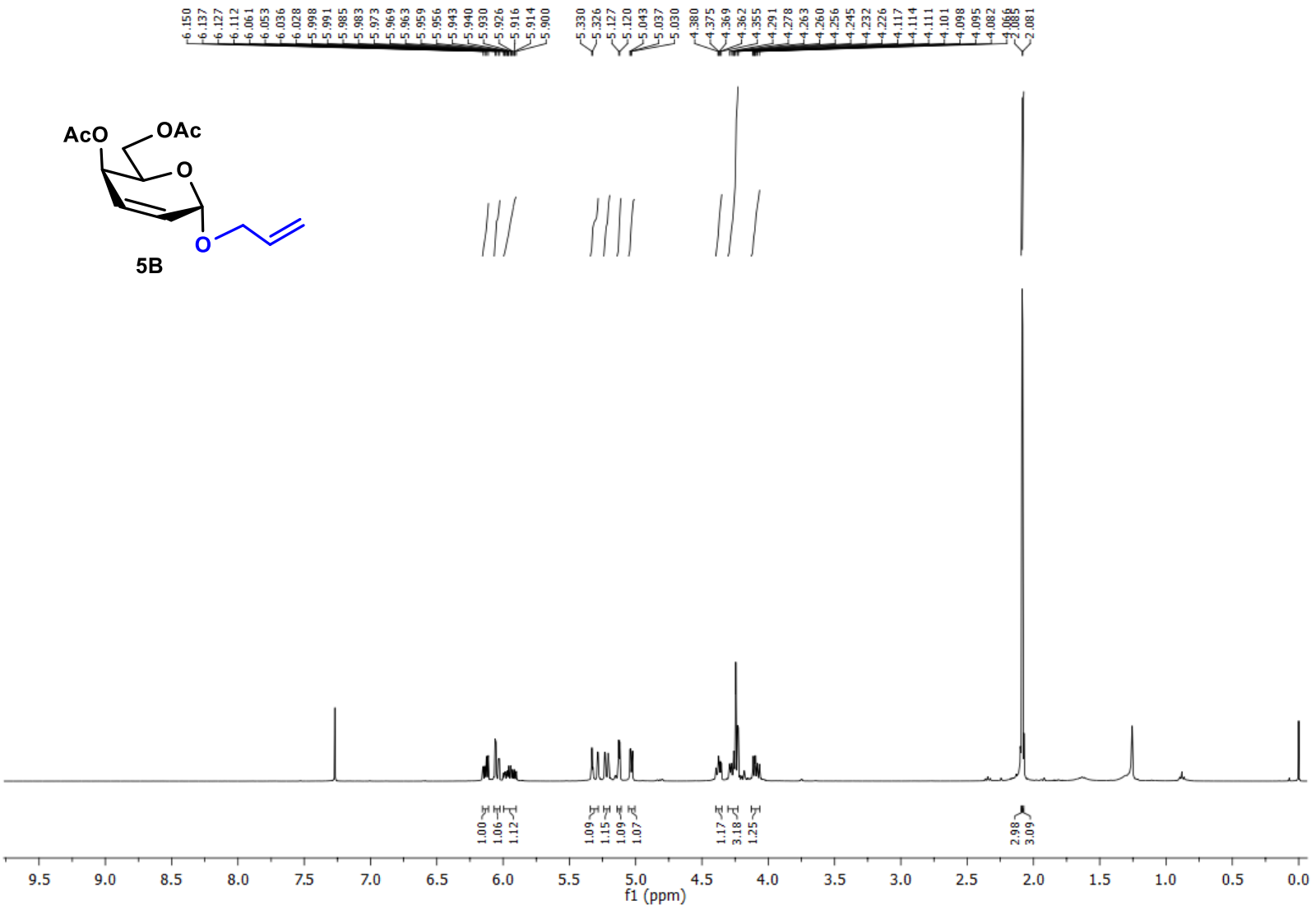
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (5′A)



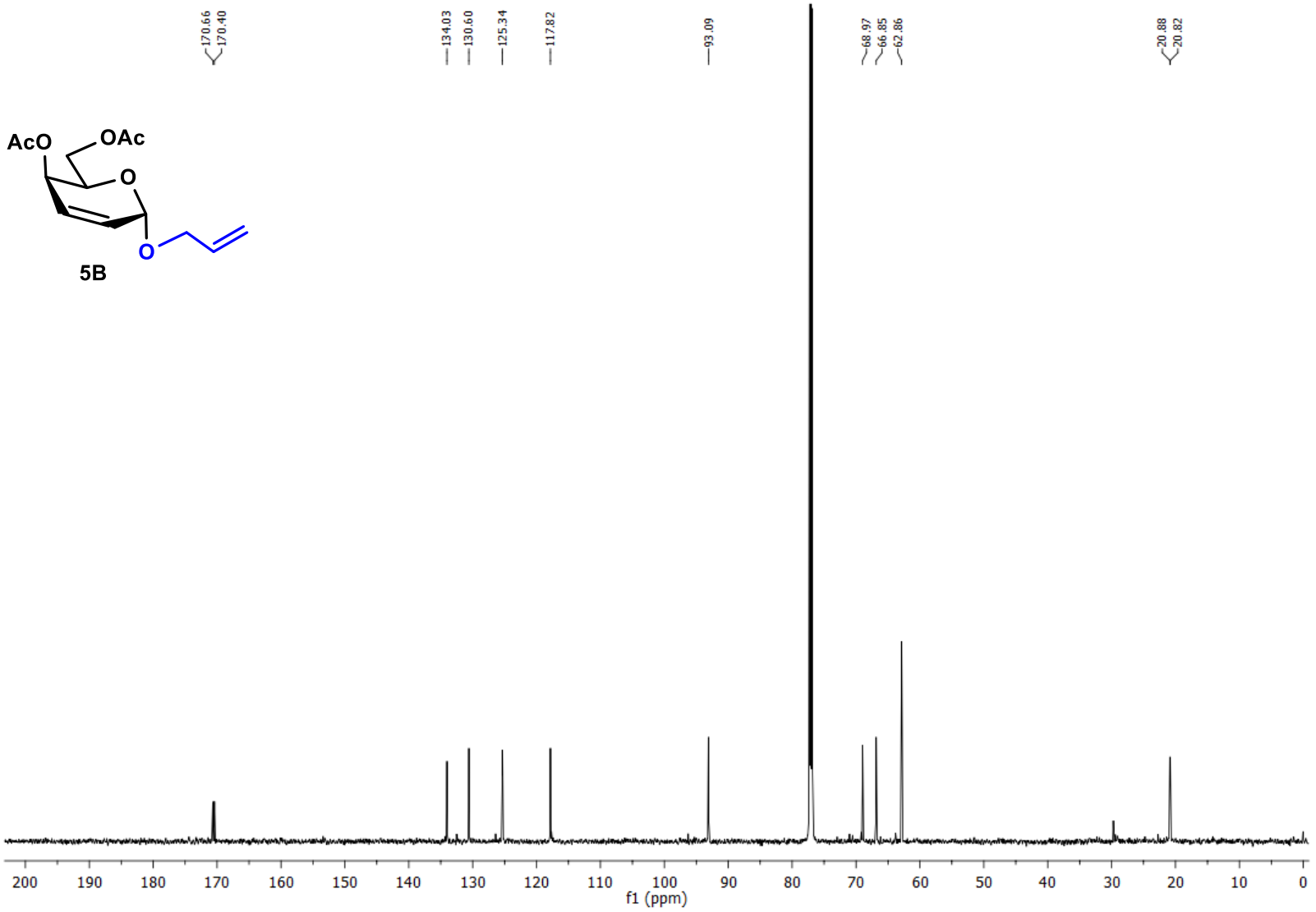
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (5′A)



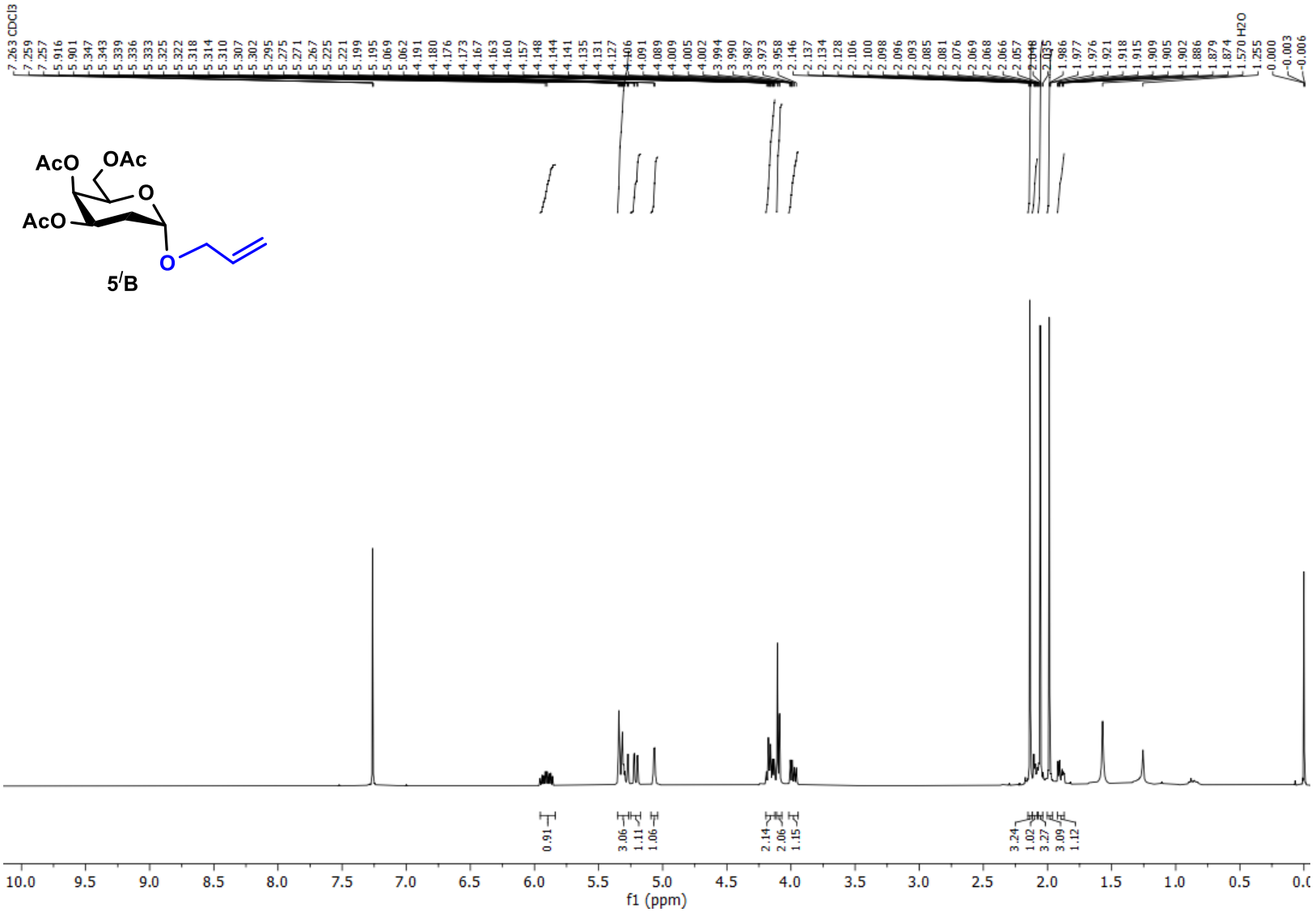
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (5B)



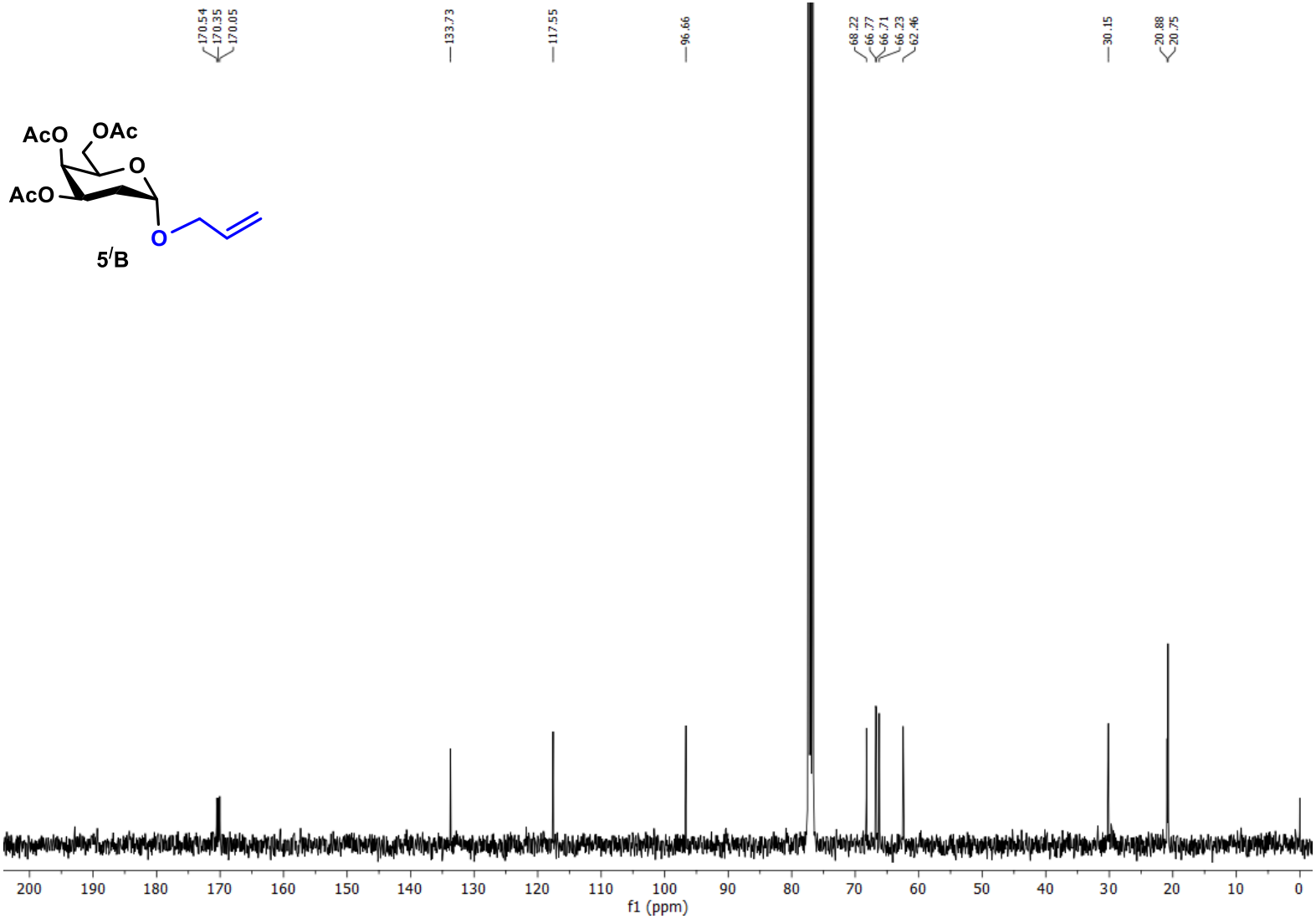
$^{13}C\{^{1}H\}$ (175 MHz, $CDCl_3$) NMR spectrum of compound (5B)



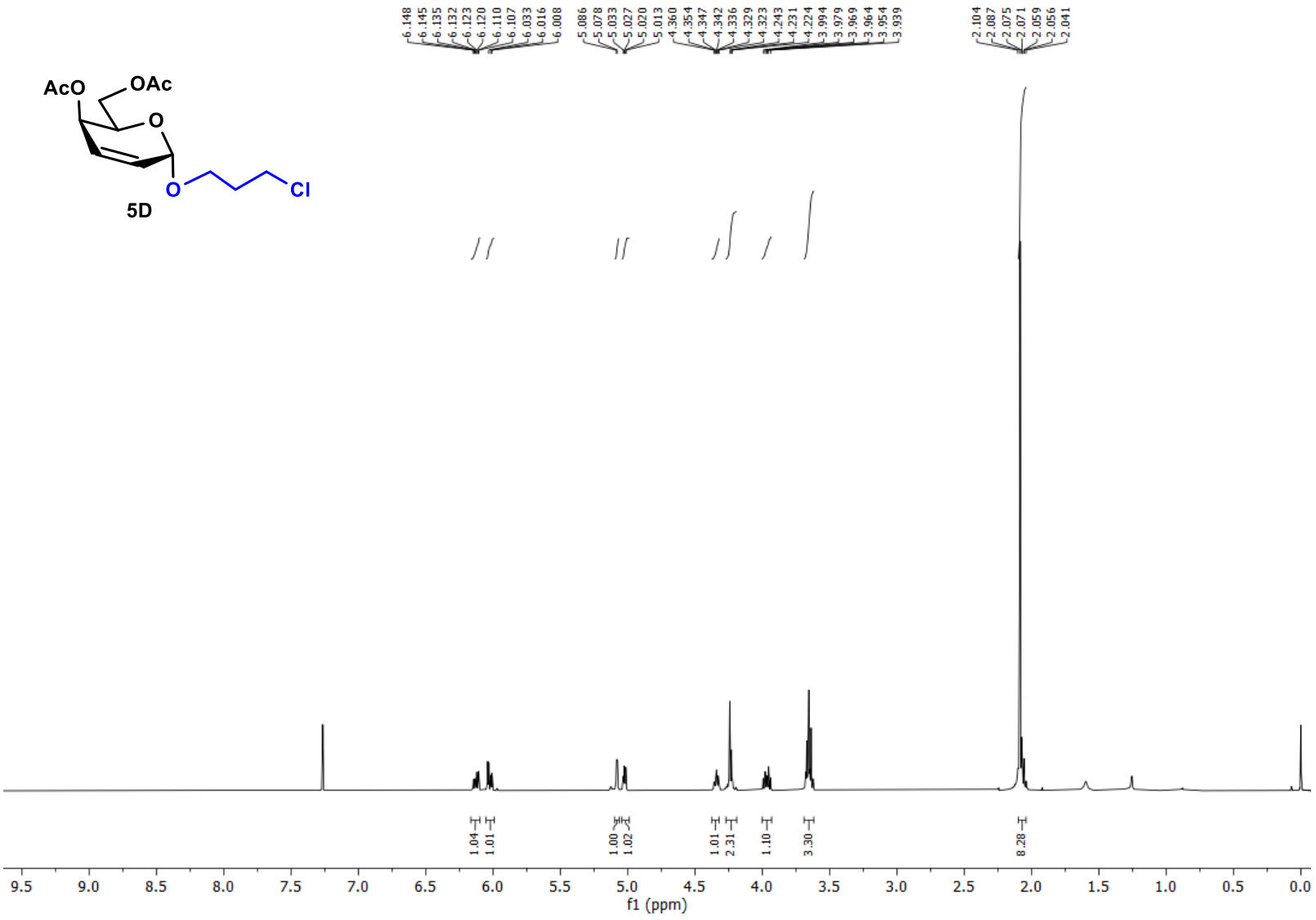
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (5′B)



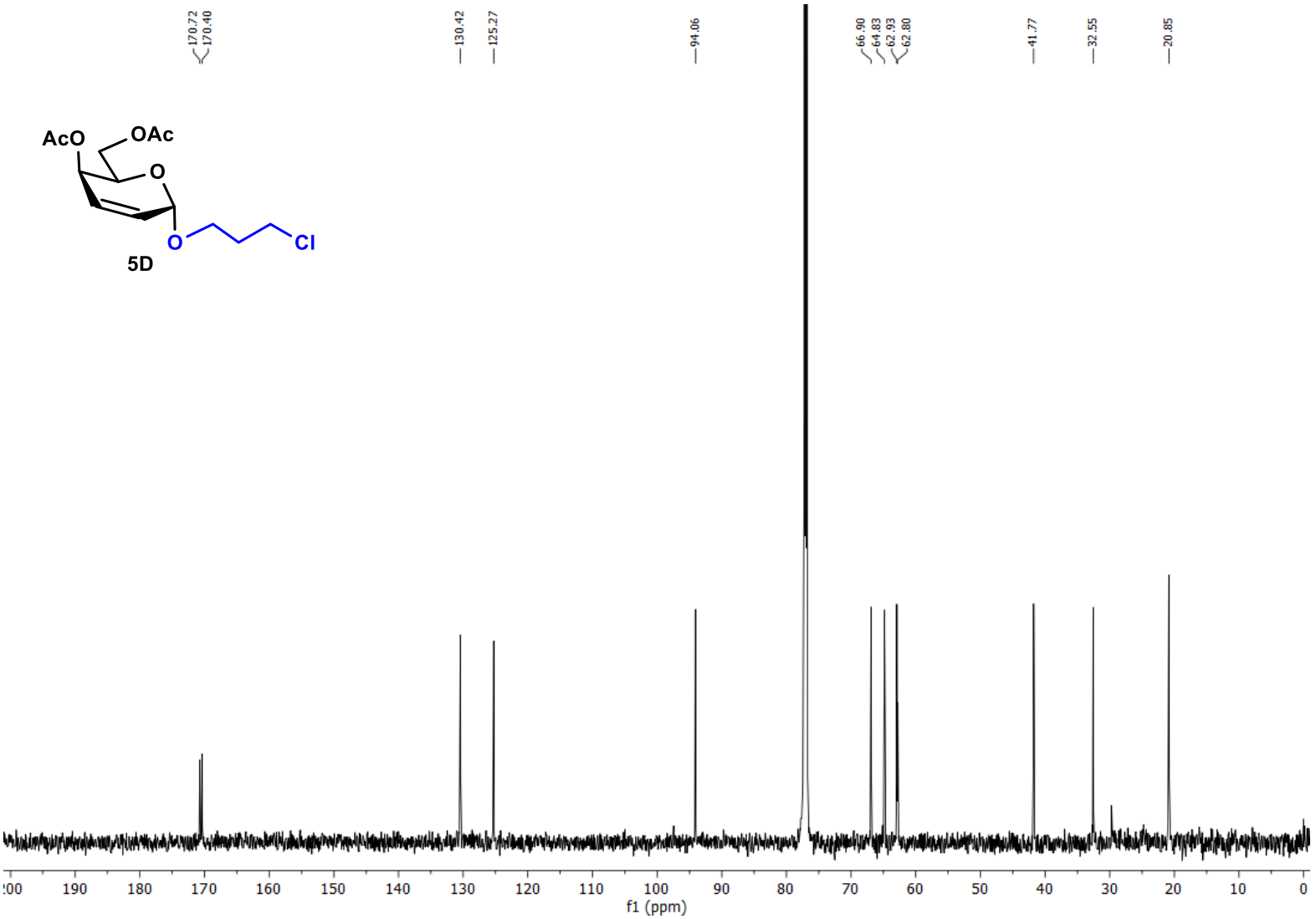
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (5′B)



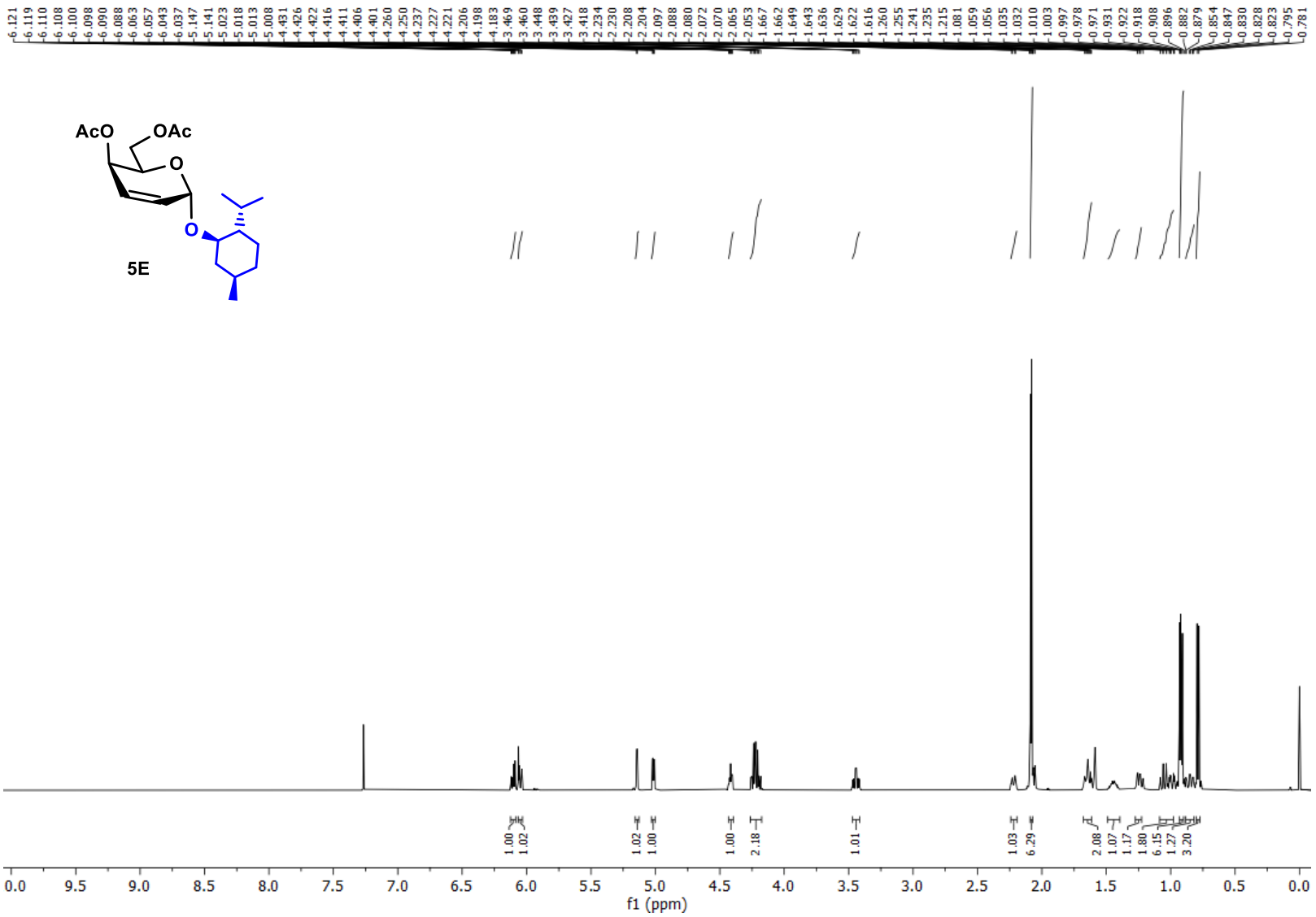
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (5D)



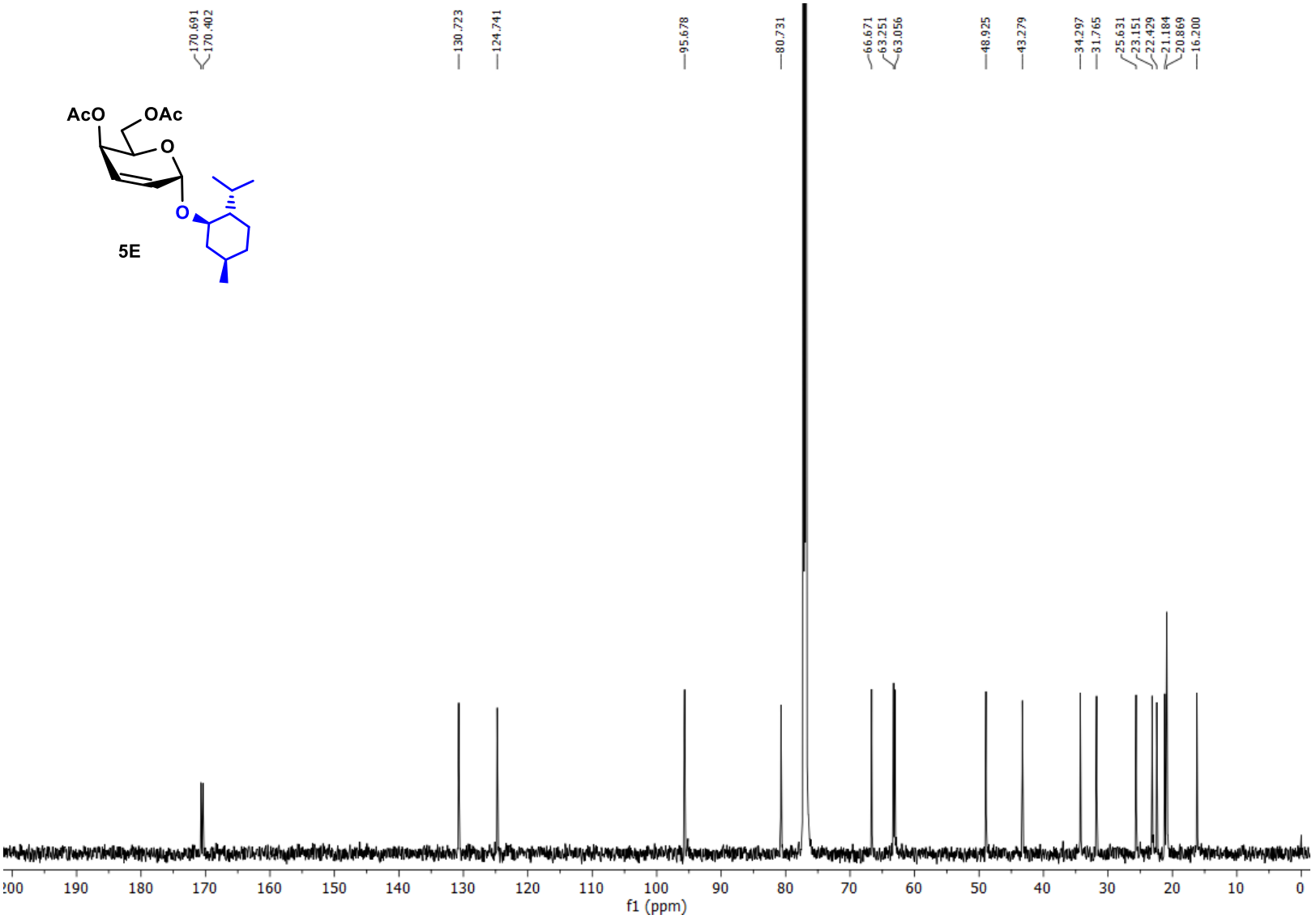
$^{13}C\{^{1}H\}$ (175 MHz, $CDCl_3$) NMR spectrum of compound (5D)



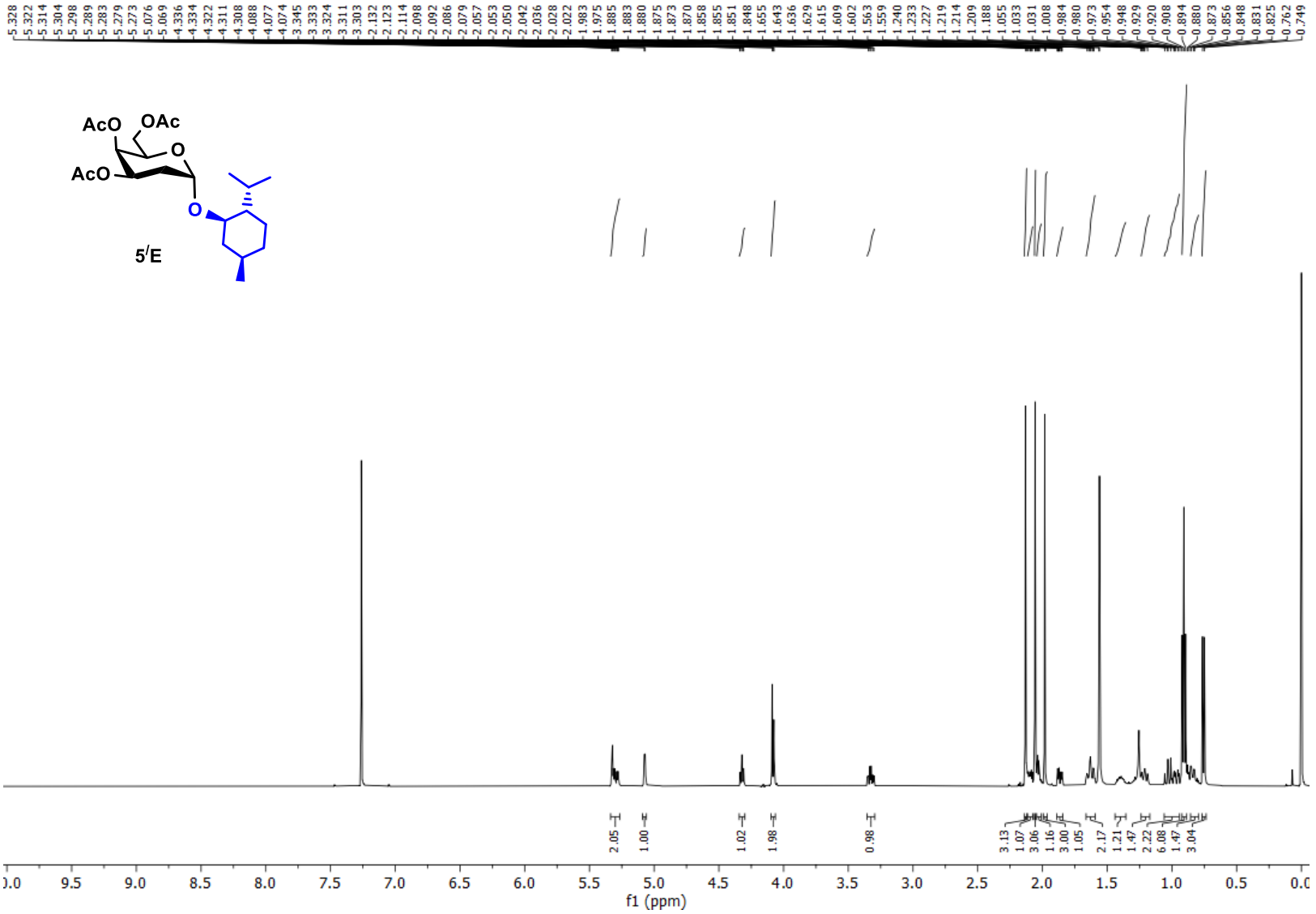
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of compound (5E)



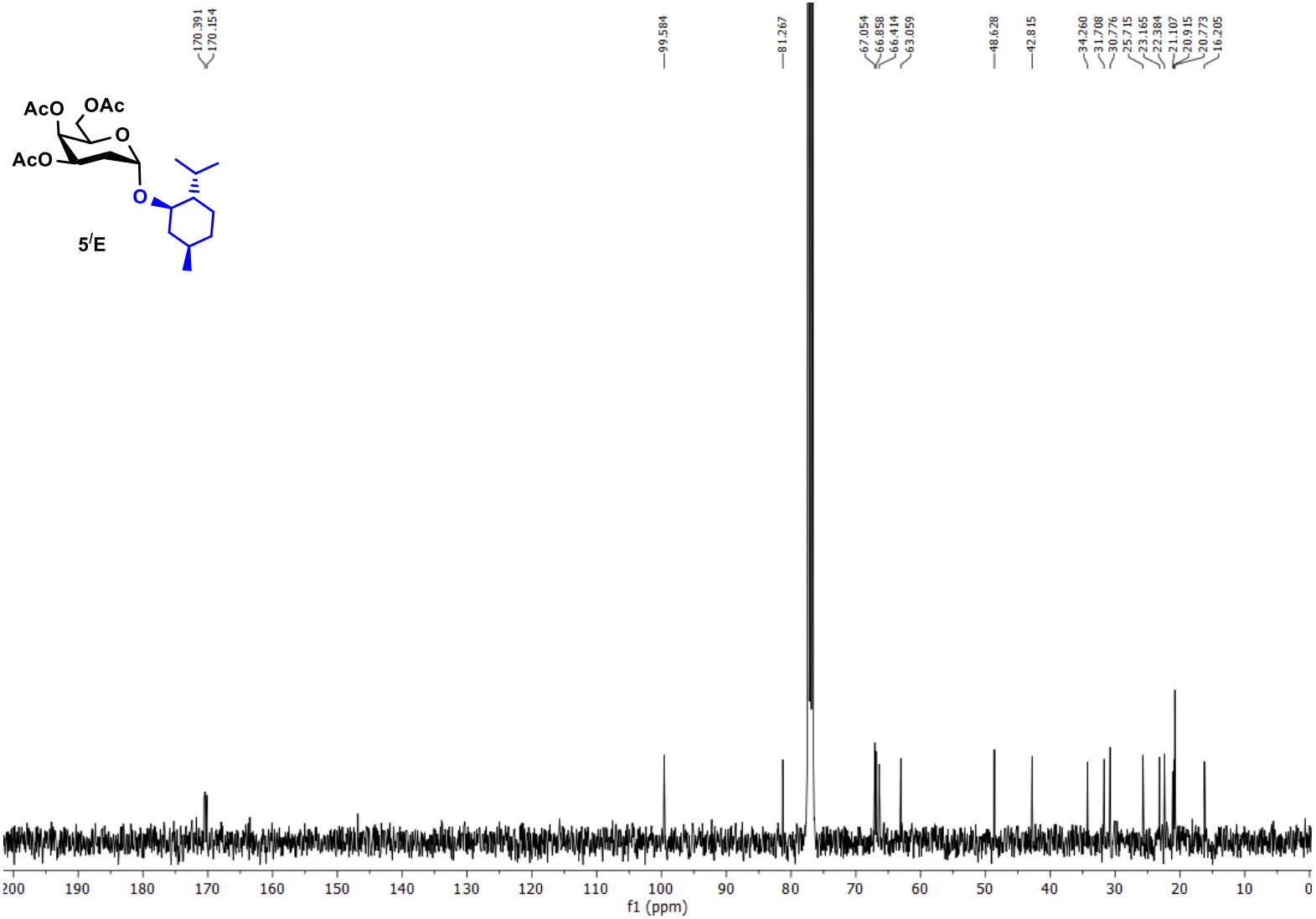
$^{13}C\{^{1}H\}$ (175 MHz, $CDCl_3$) NMR spectrum of compound (5E)



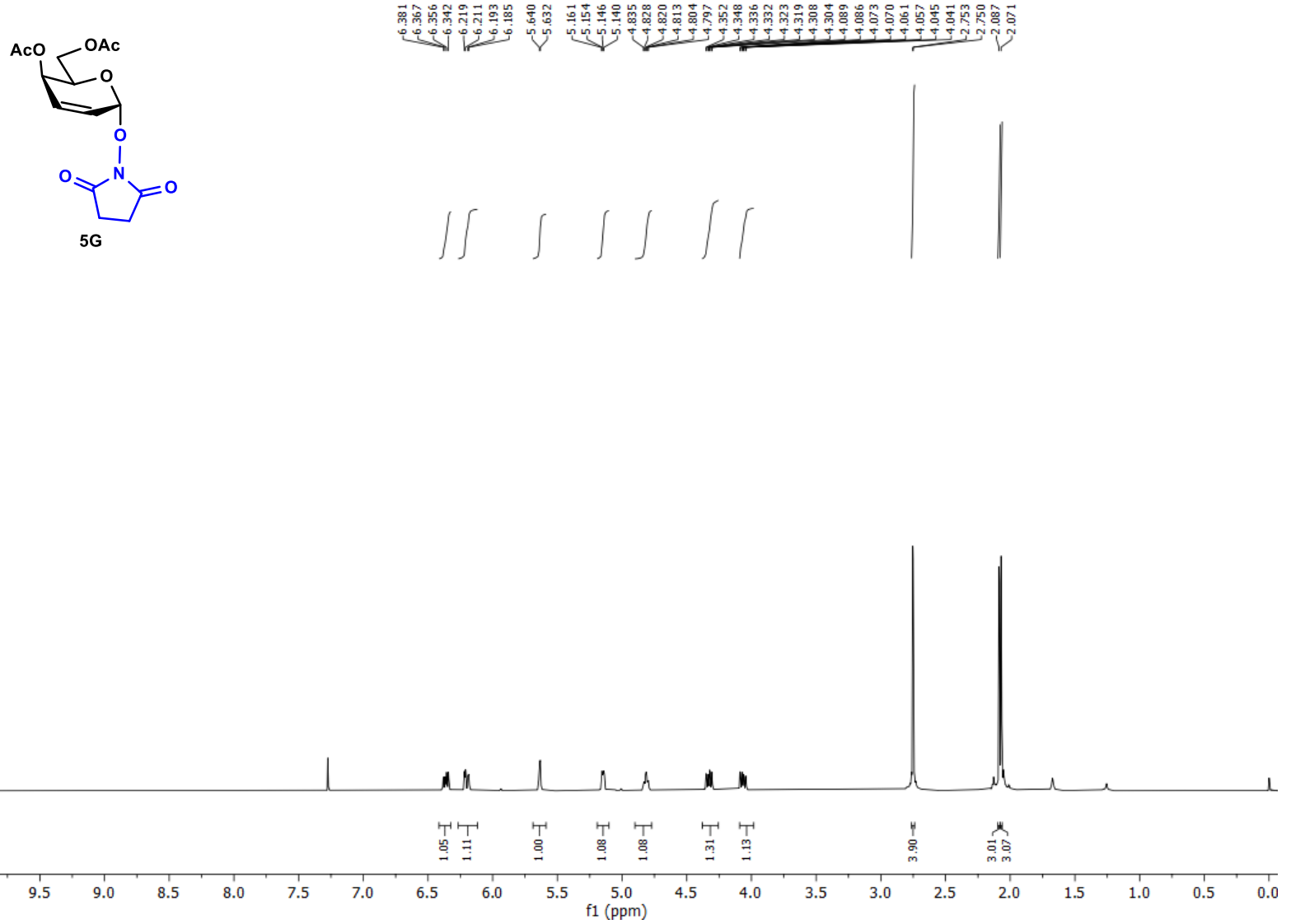
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of compound (5′E)



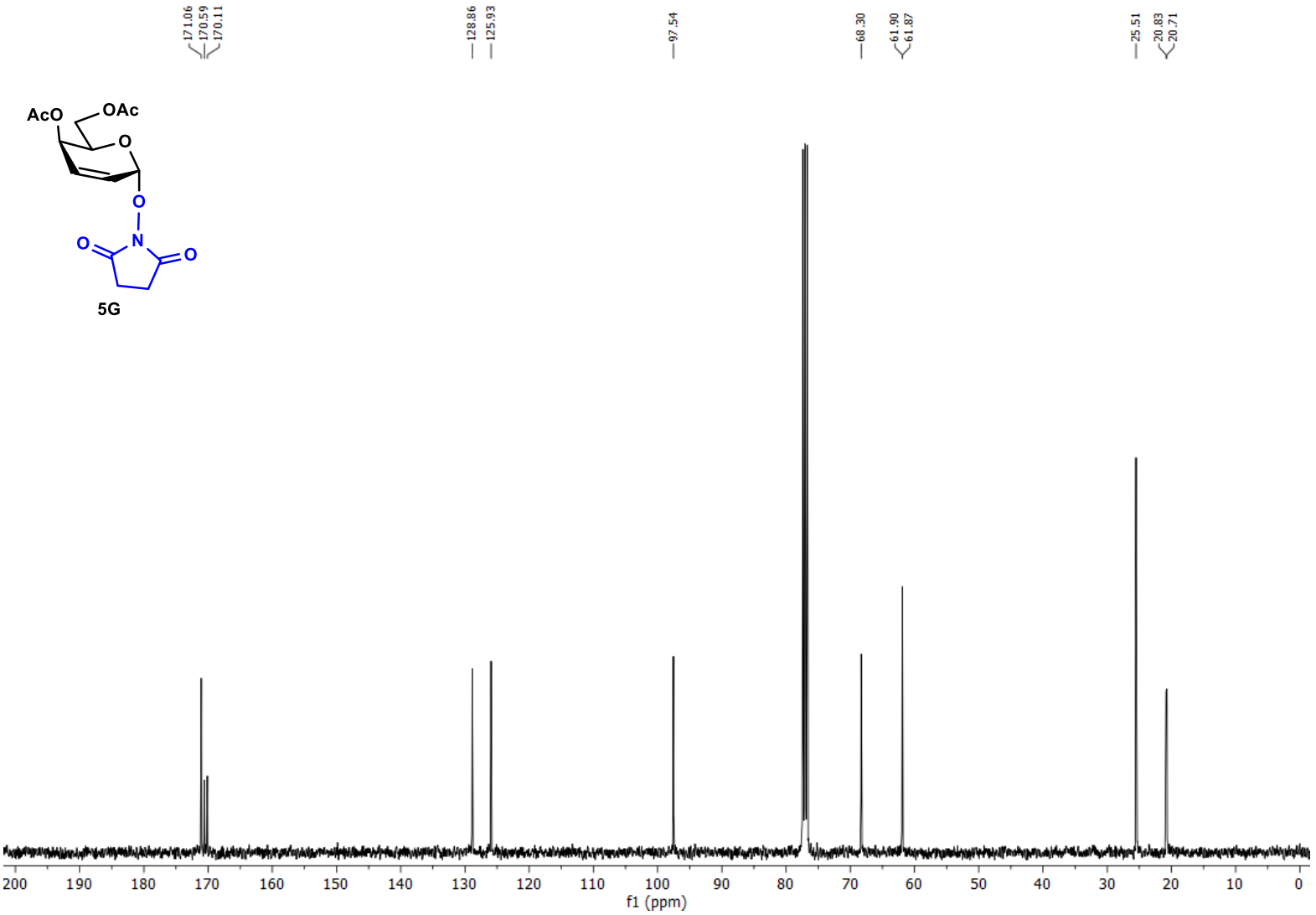
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (5′E)



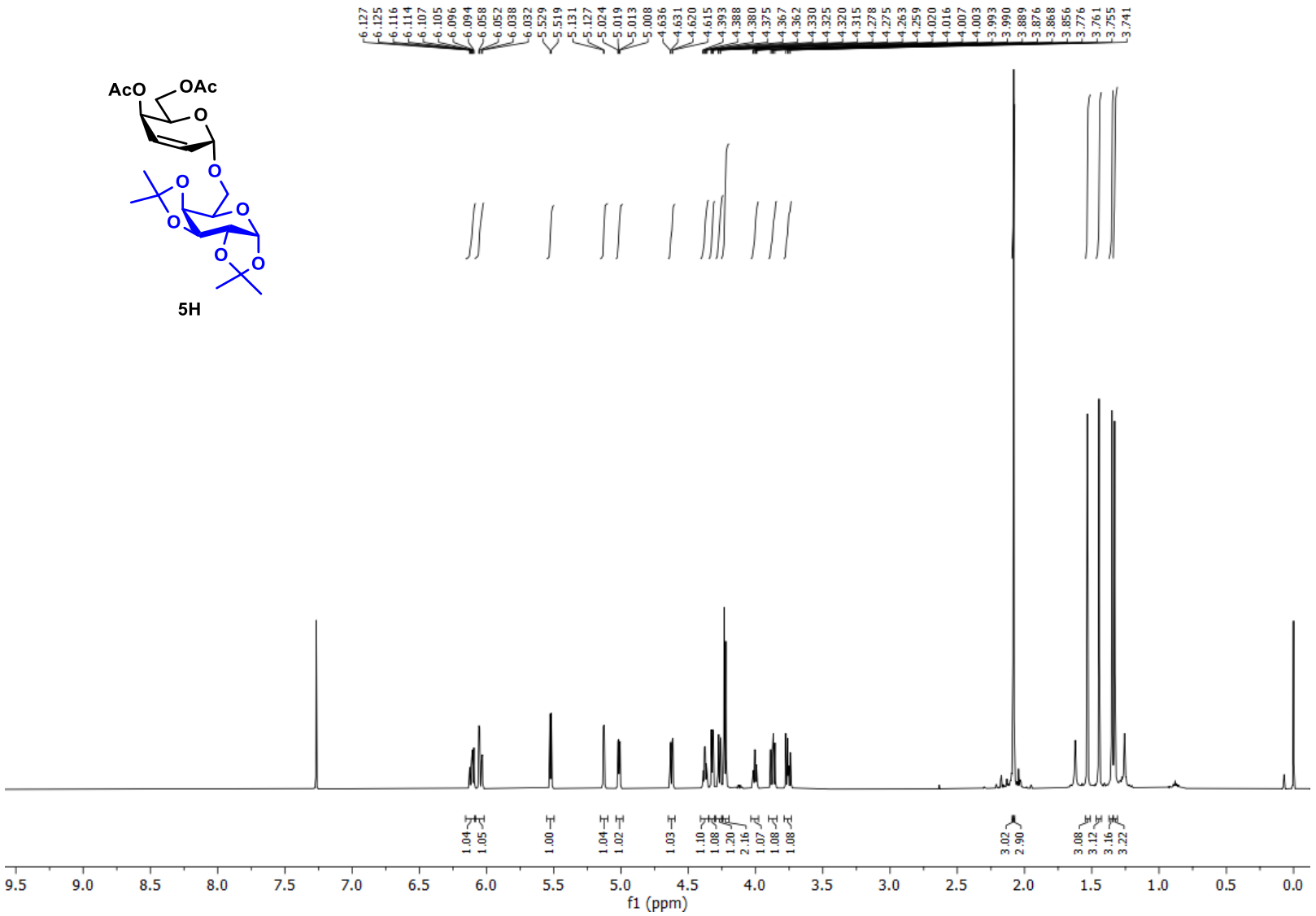
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (5G)



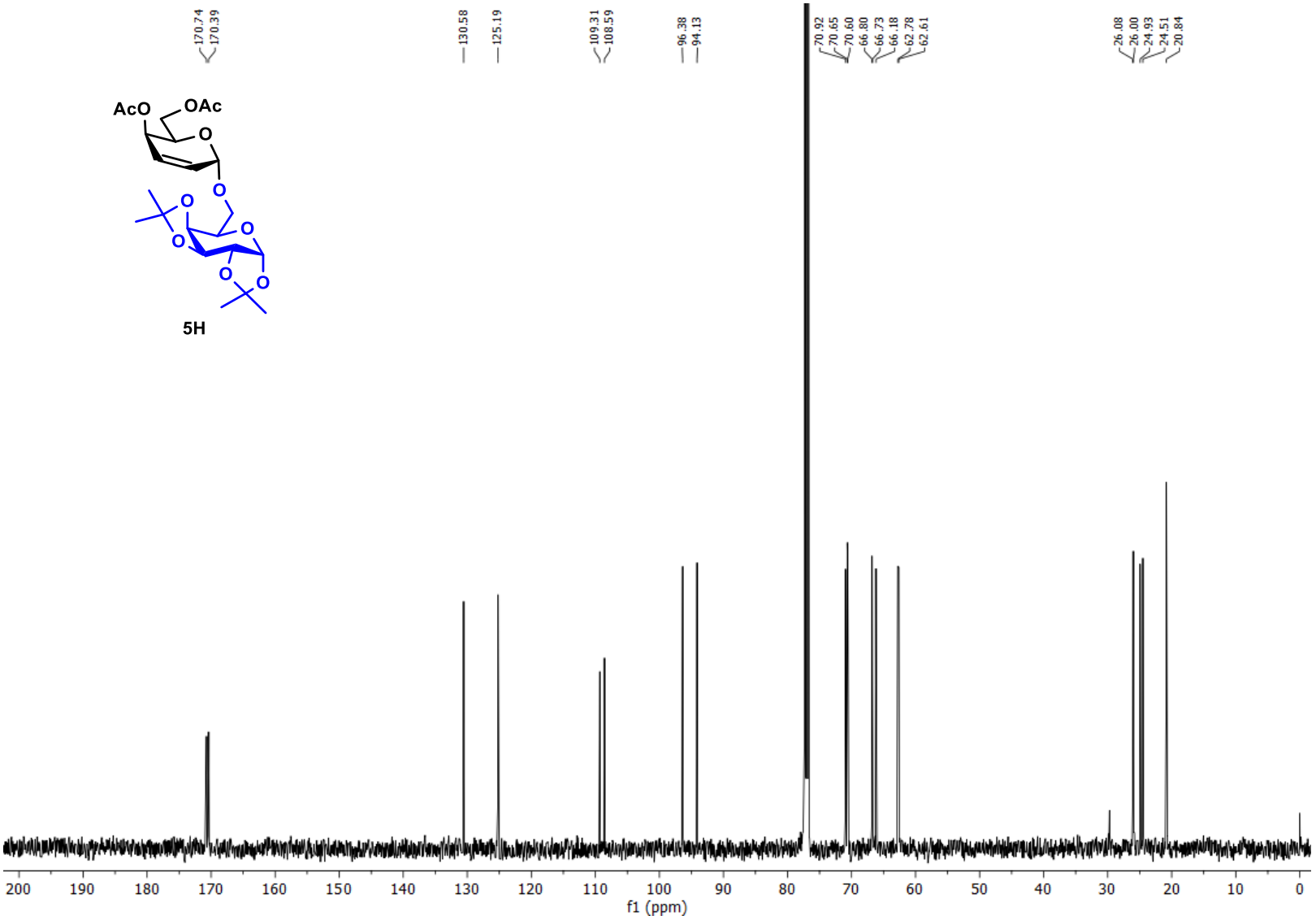
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (5G)



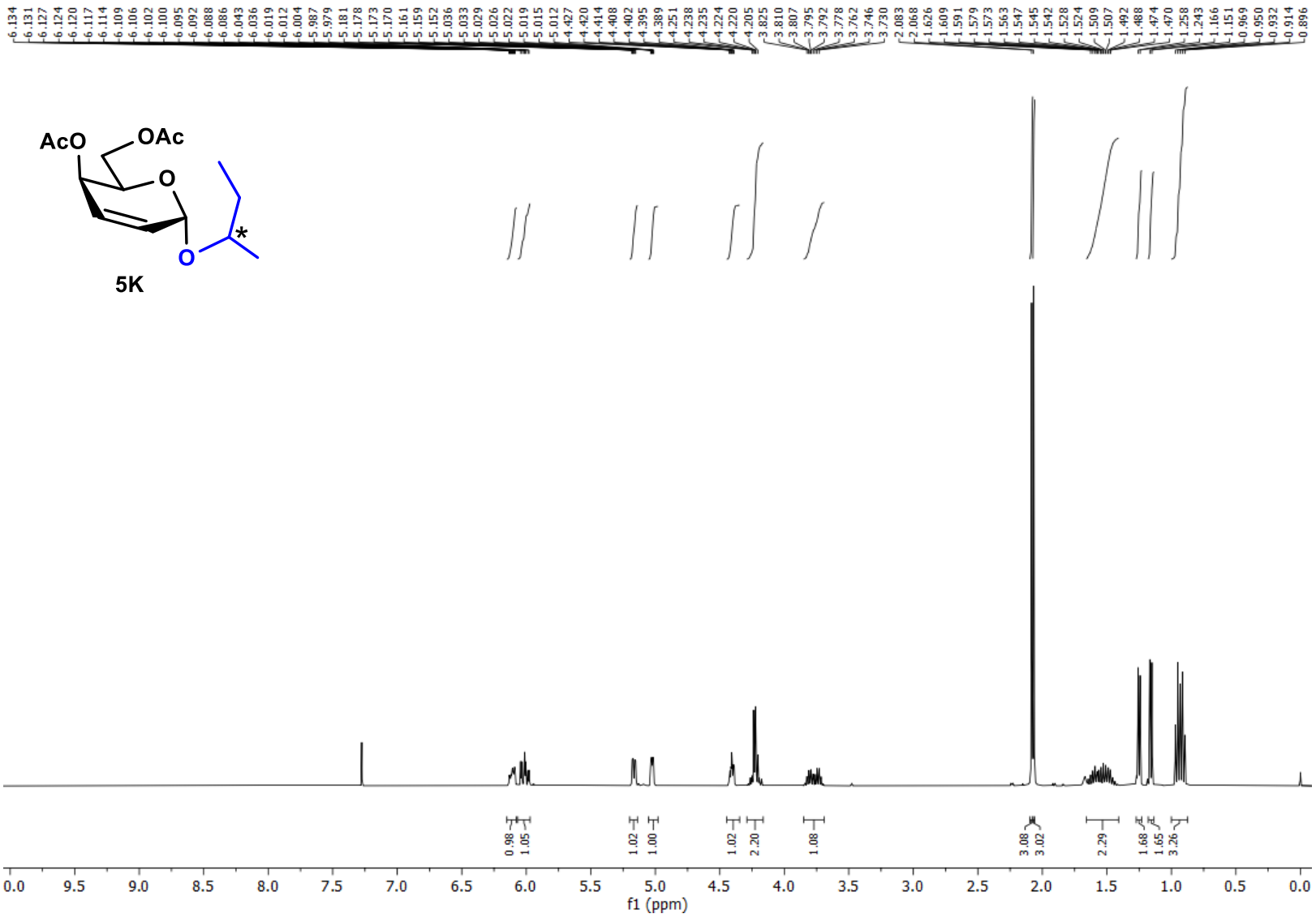
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of compound (5H)



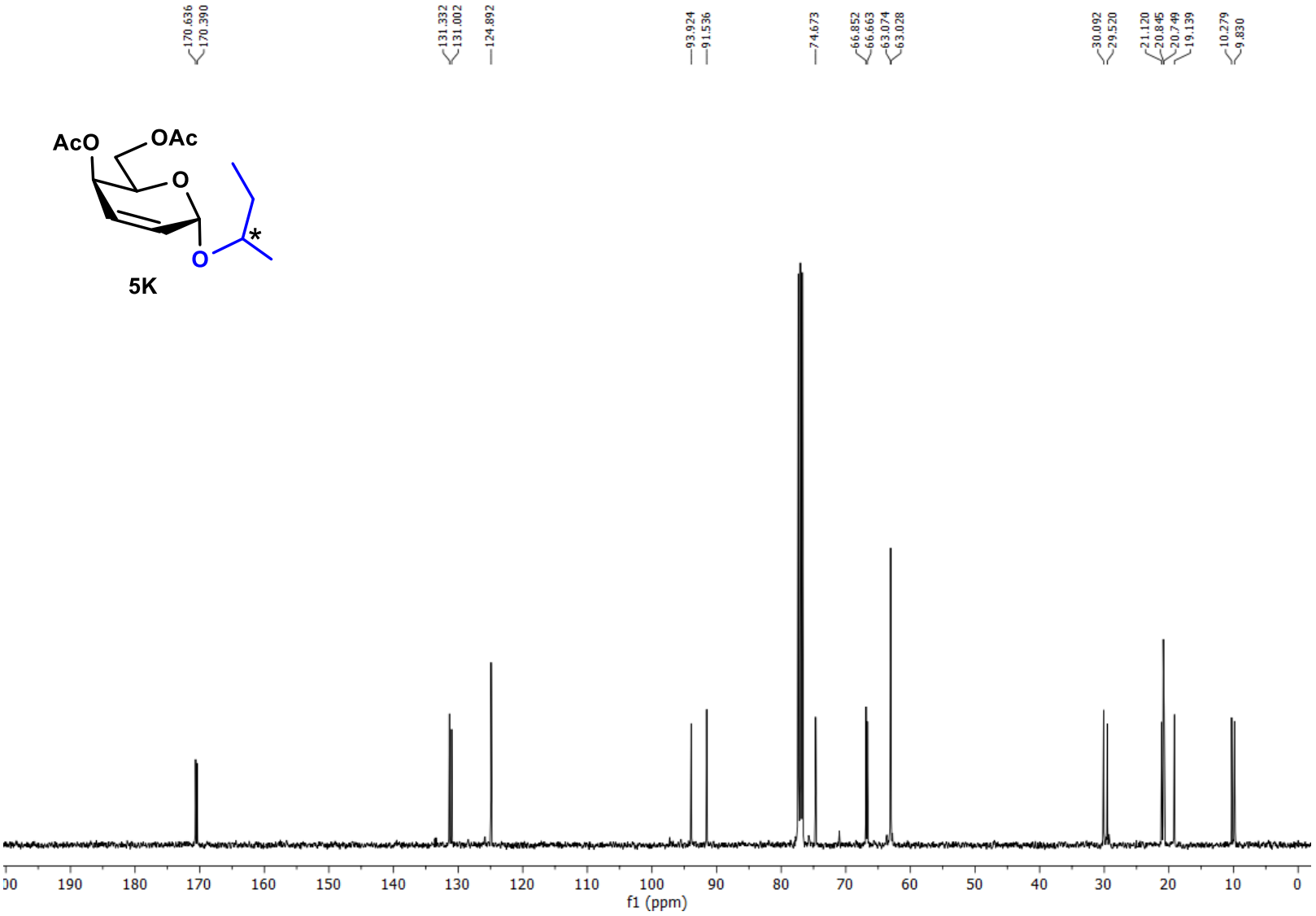
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of compound (5H)



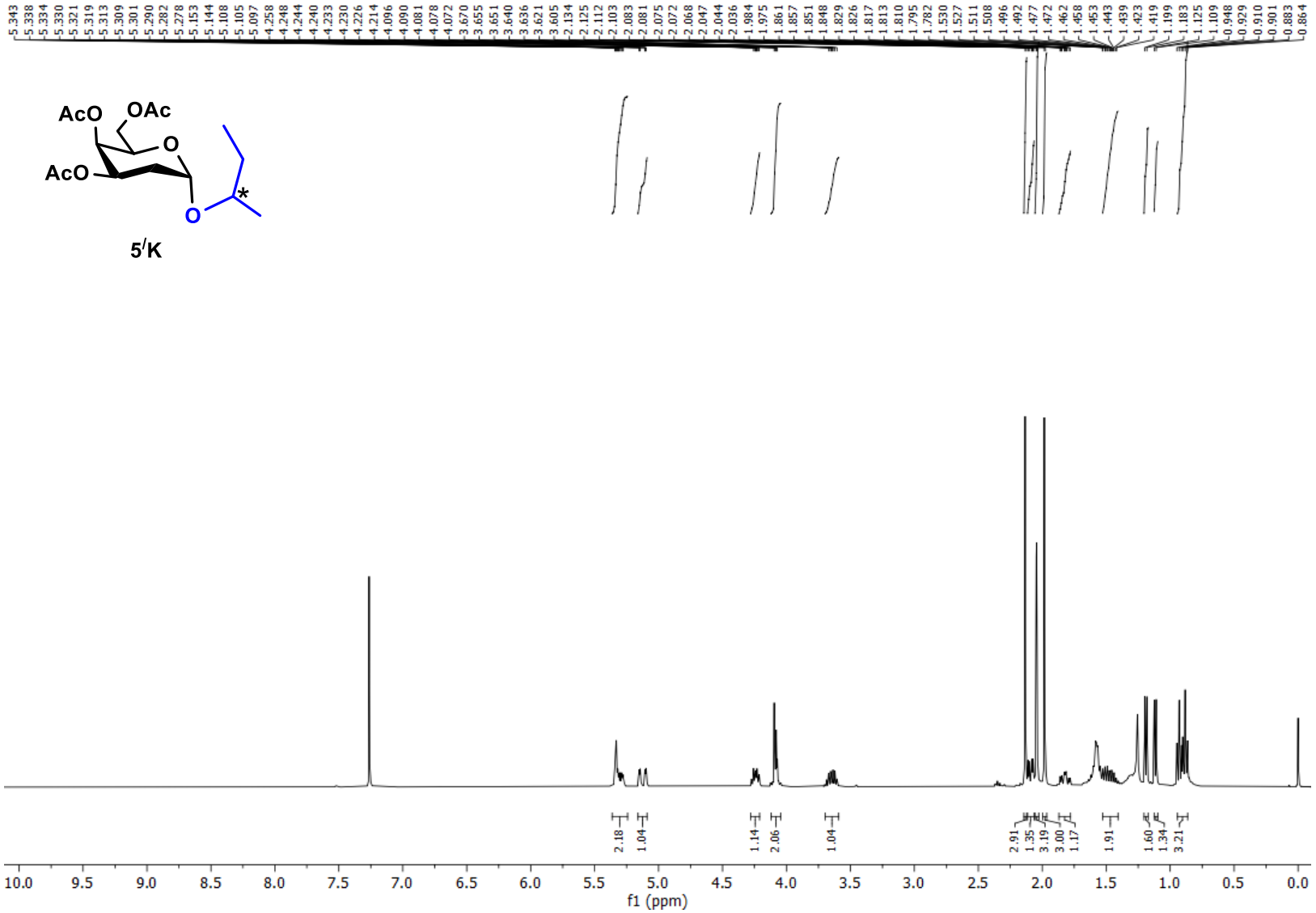
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (5K)



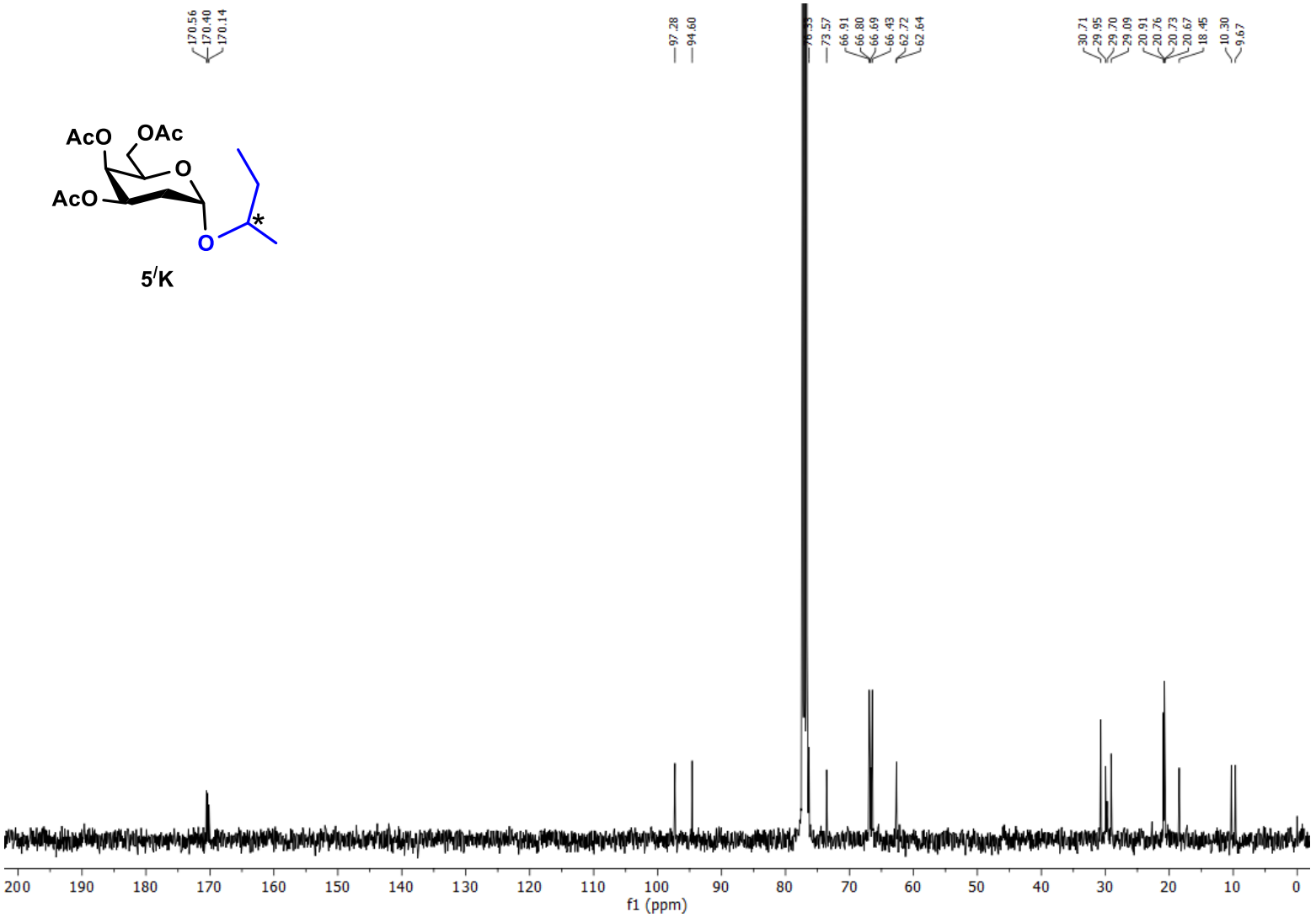
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (5K)



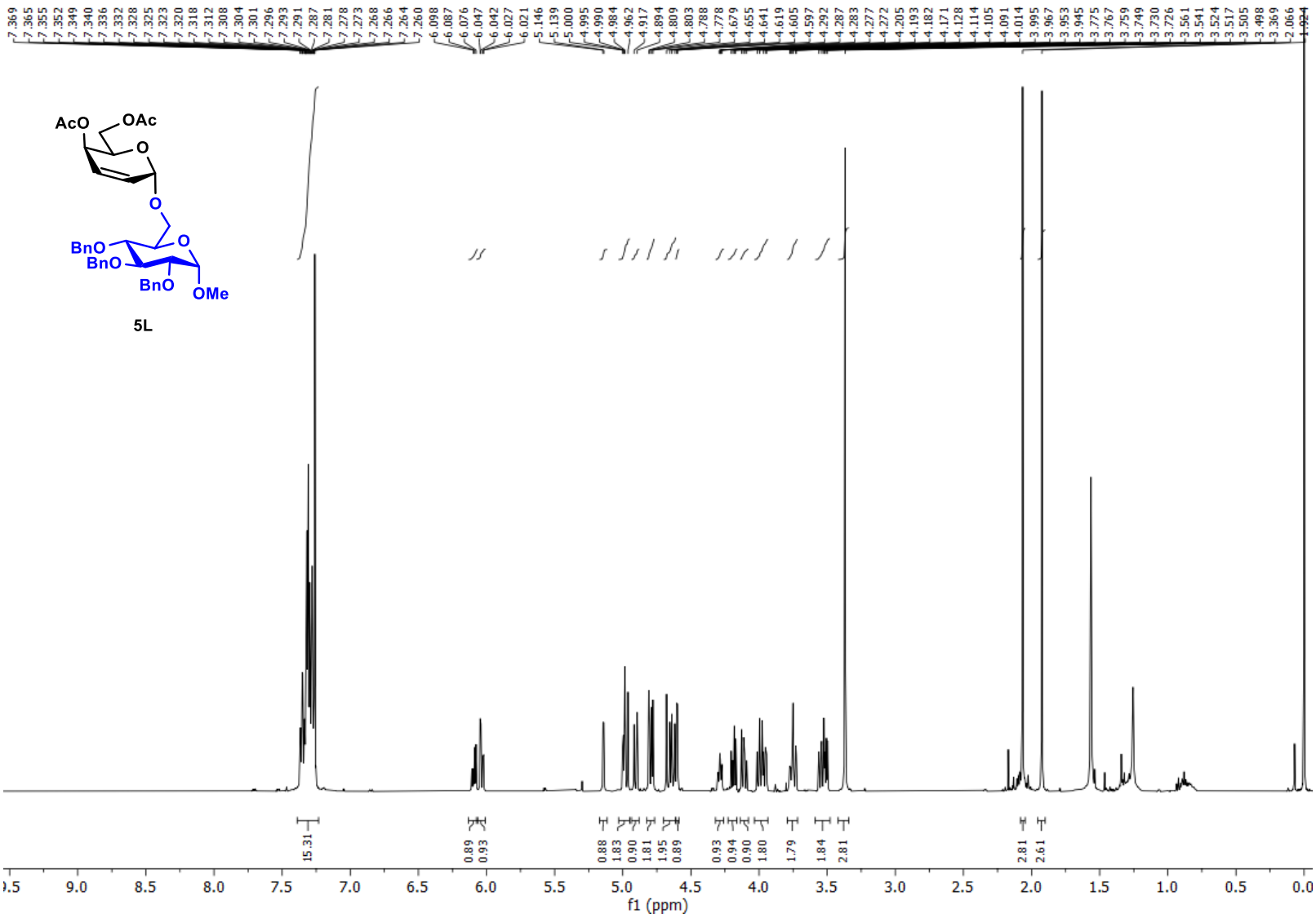
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (5′K)



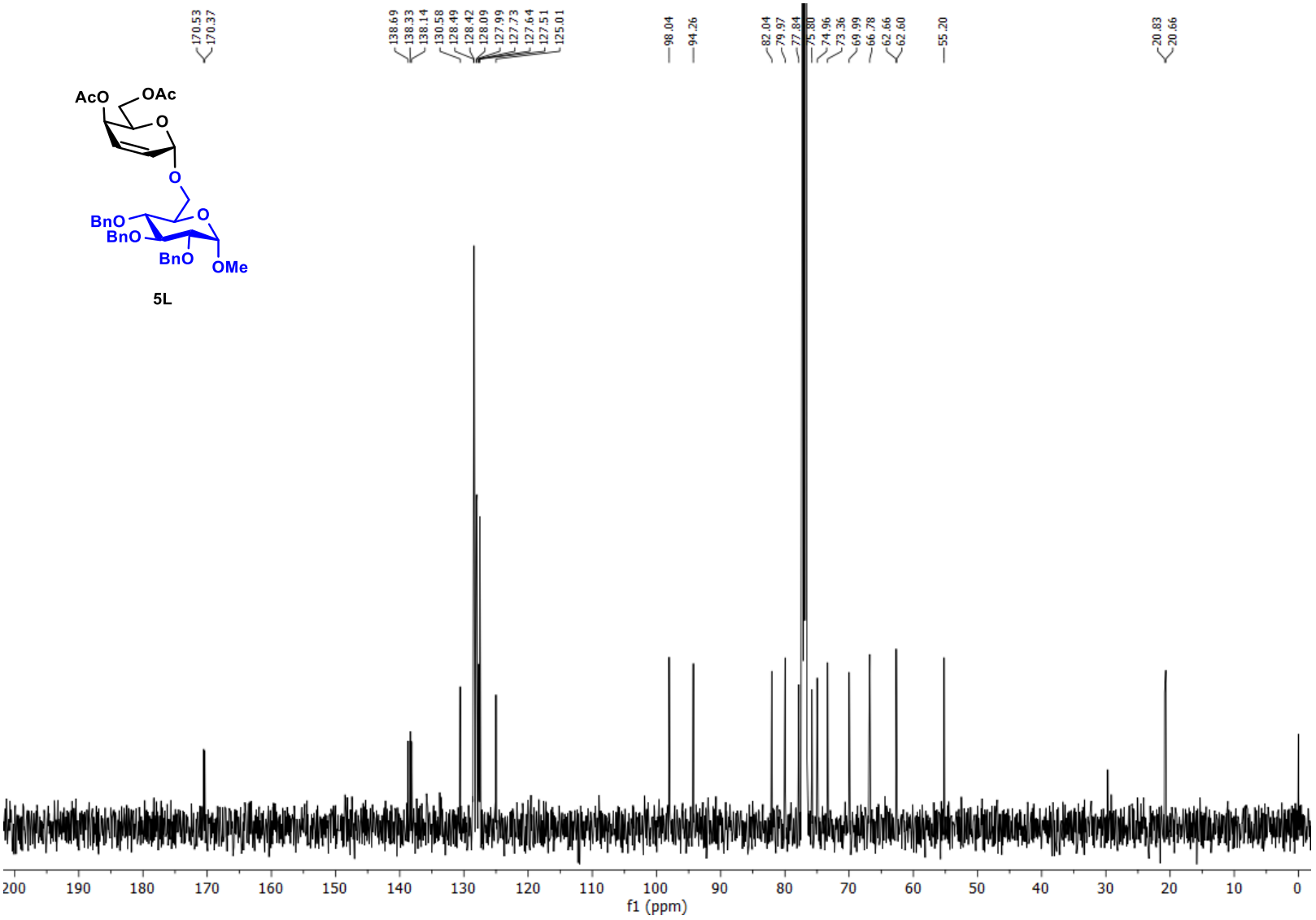
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (5′K)



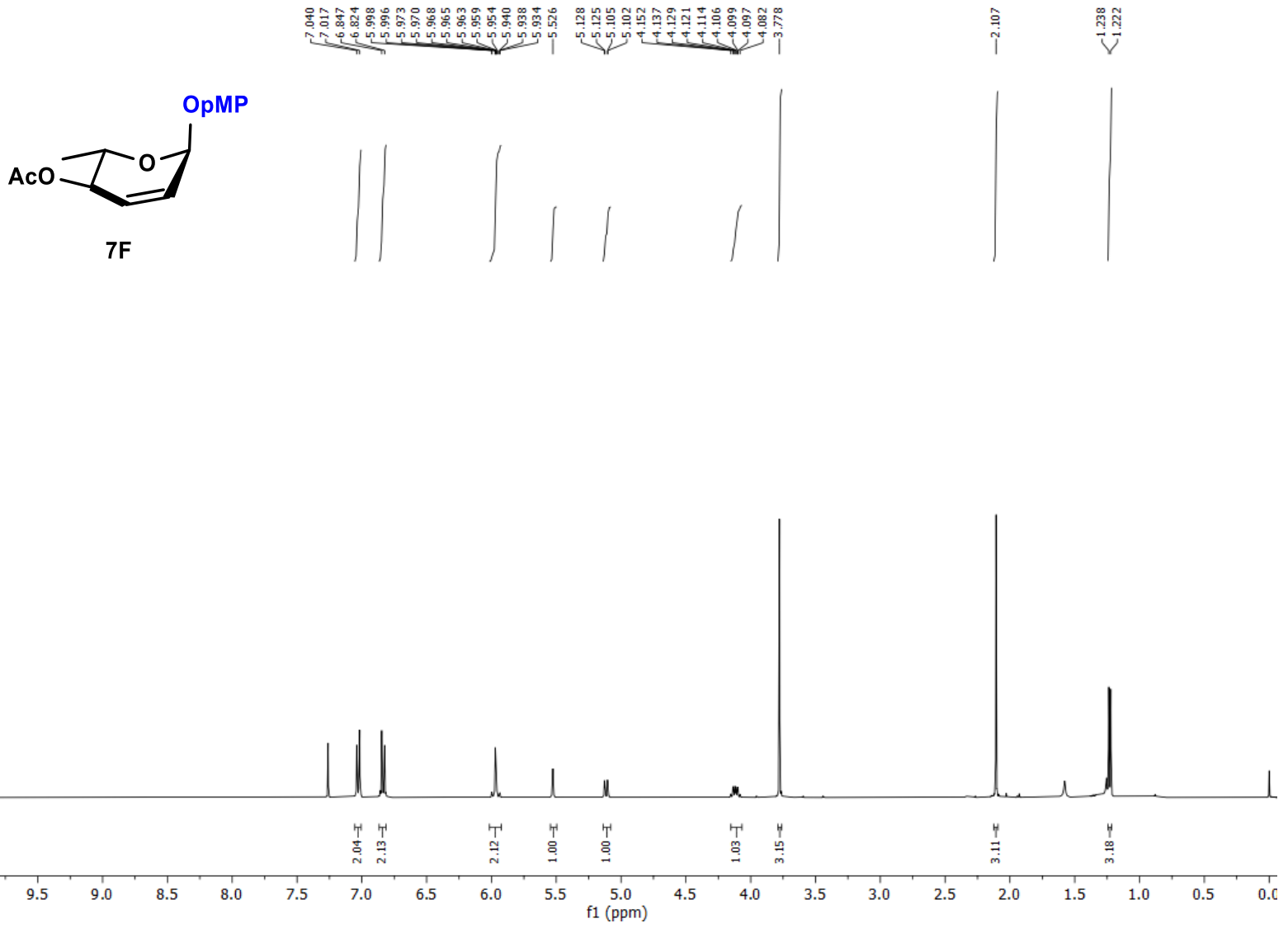
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of compound (5L)



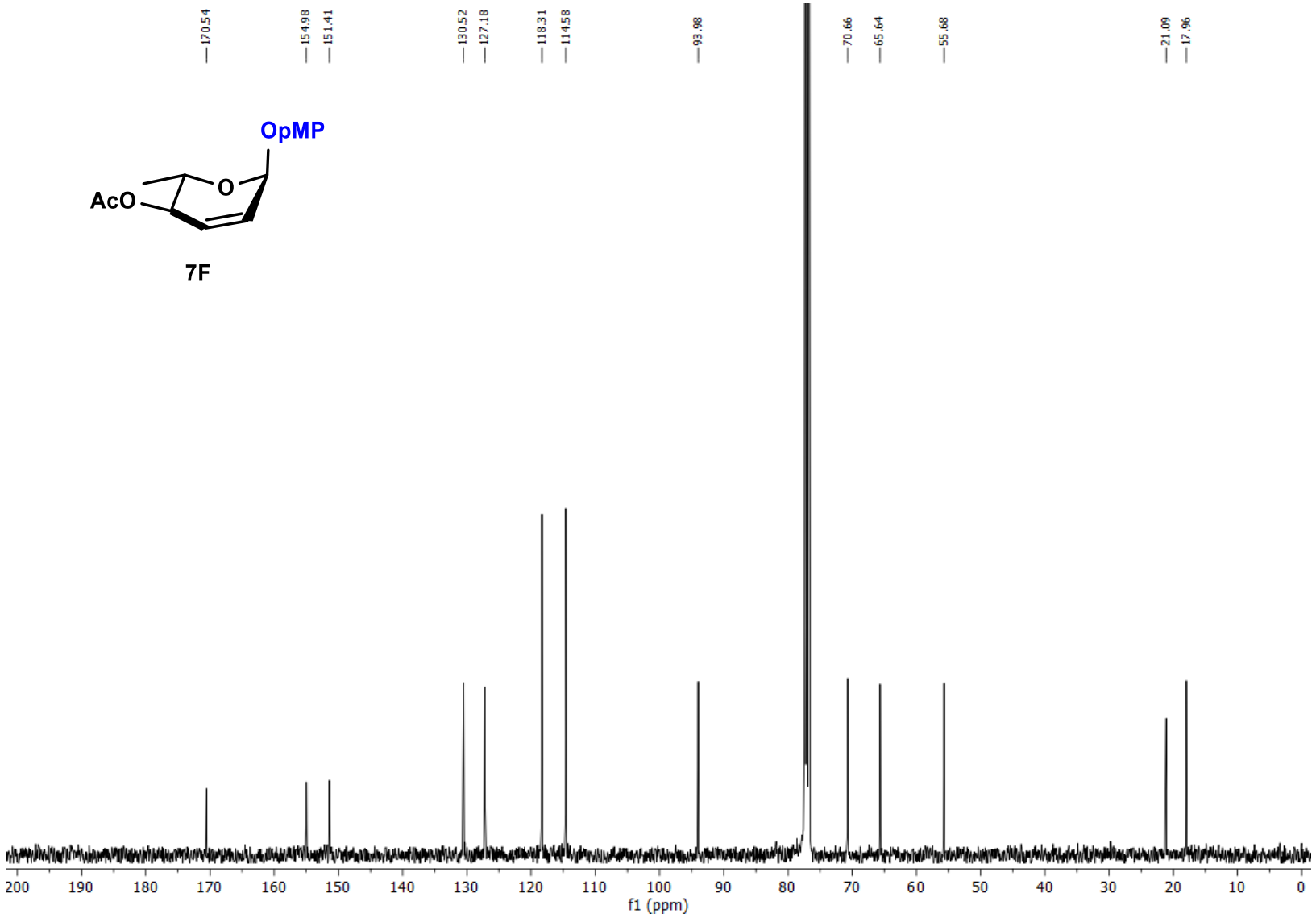
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of compound (5L)



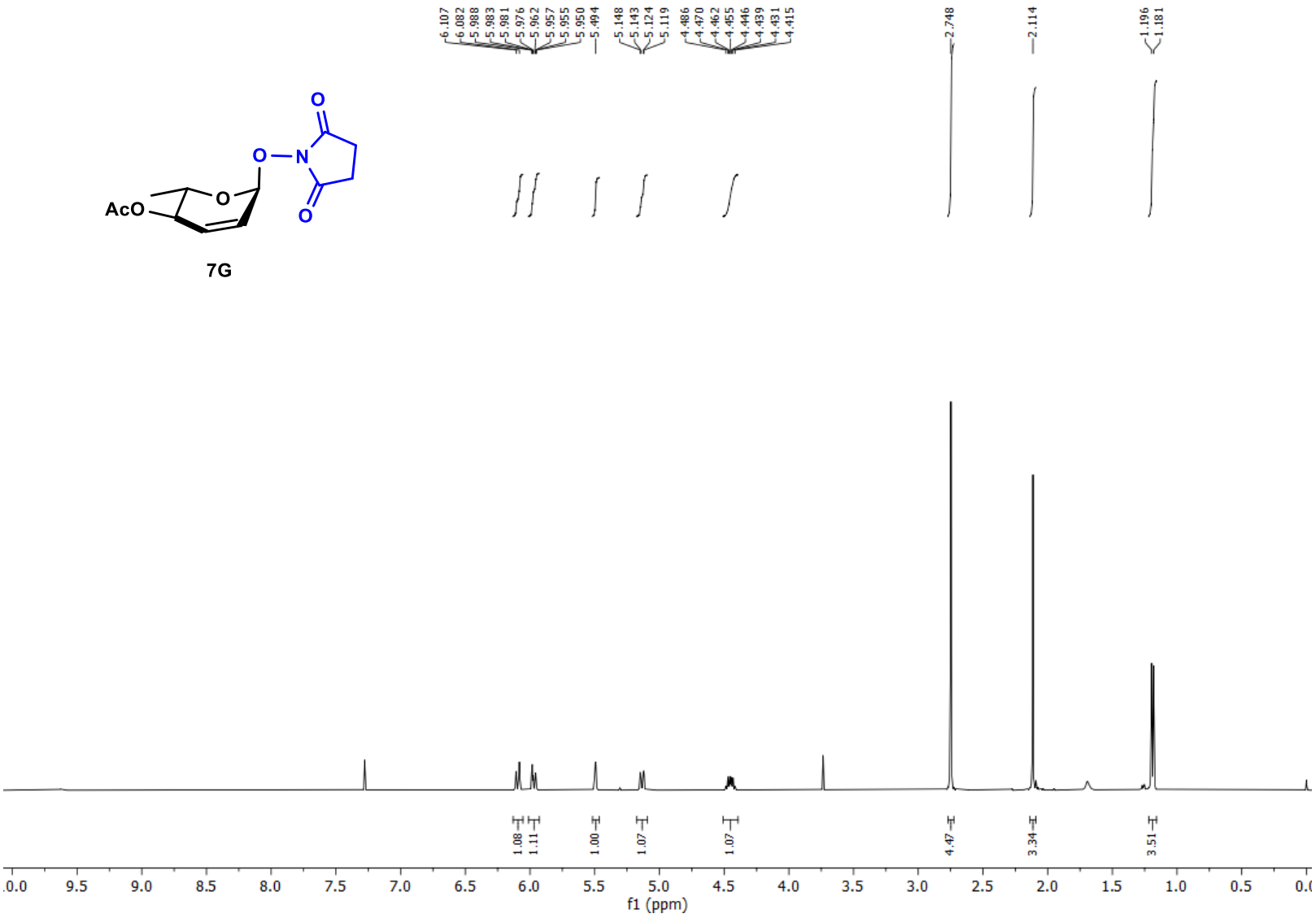
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (7F)



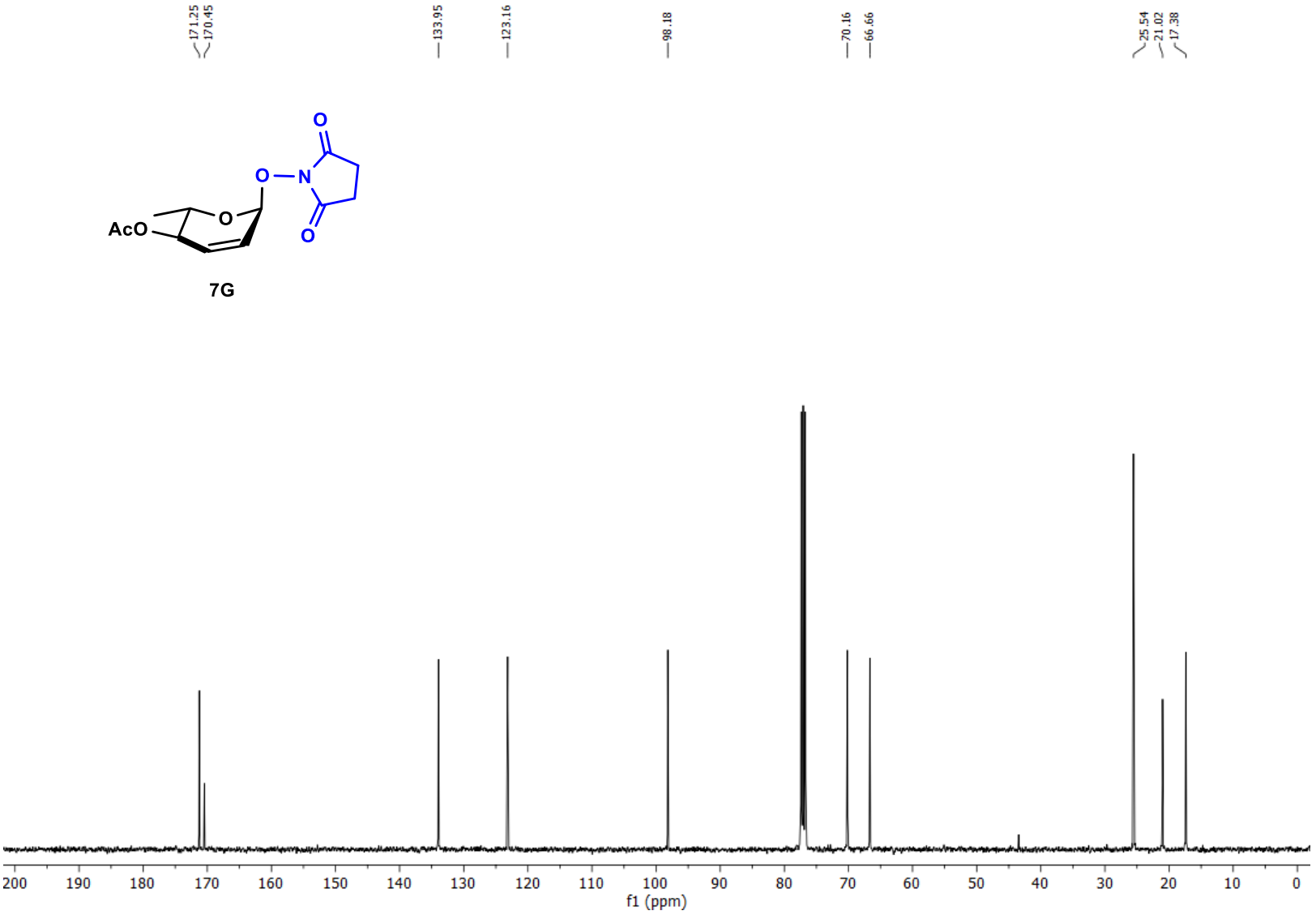
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (7F)



^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (7G)

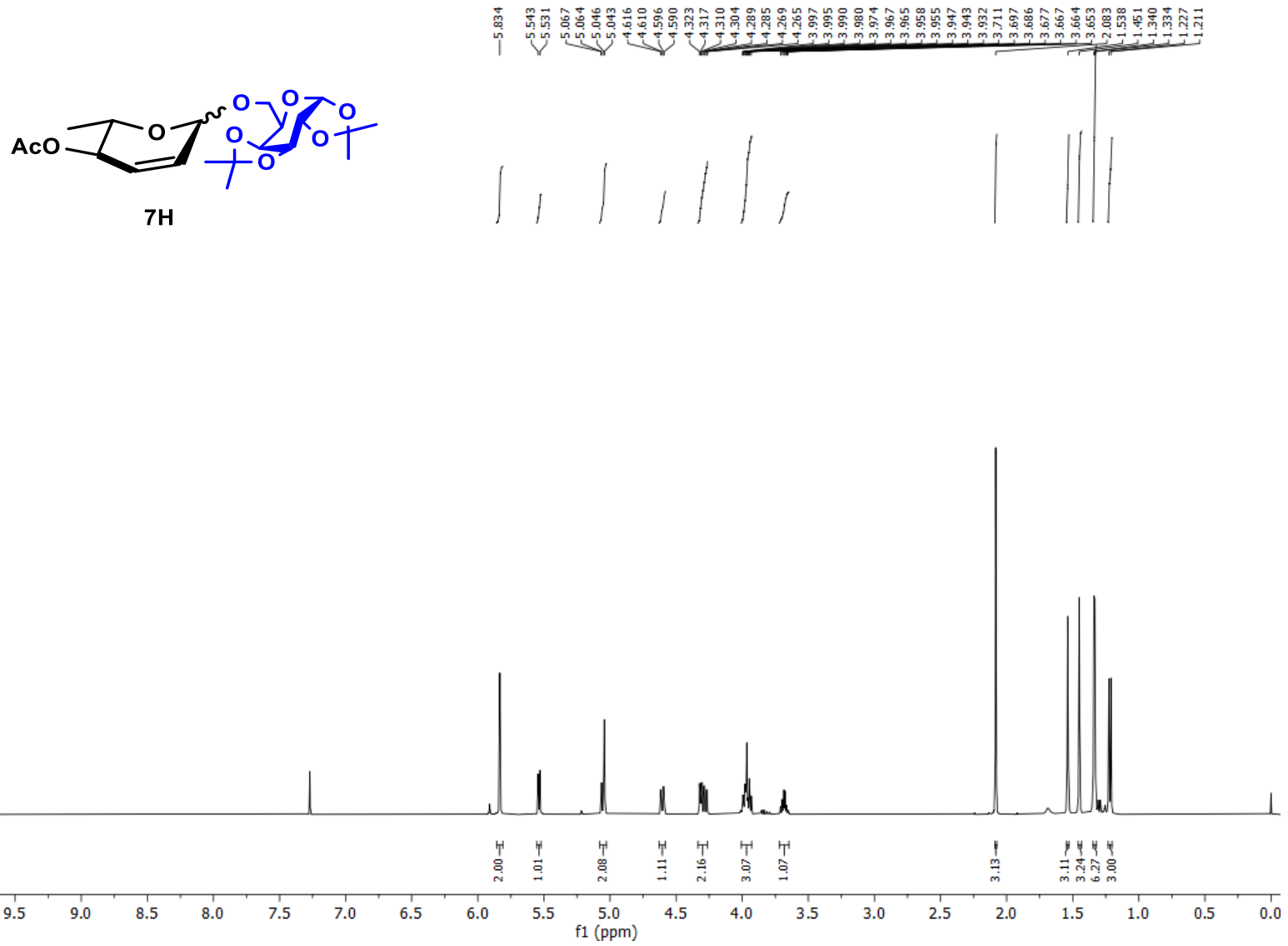


$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (7G)

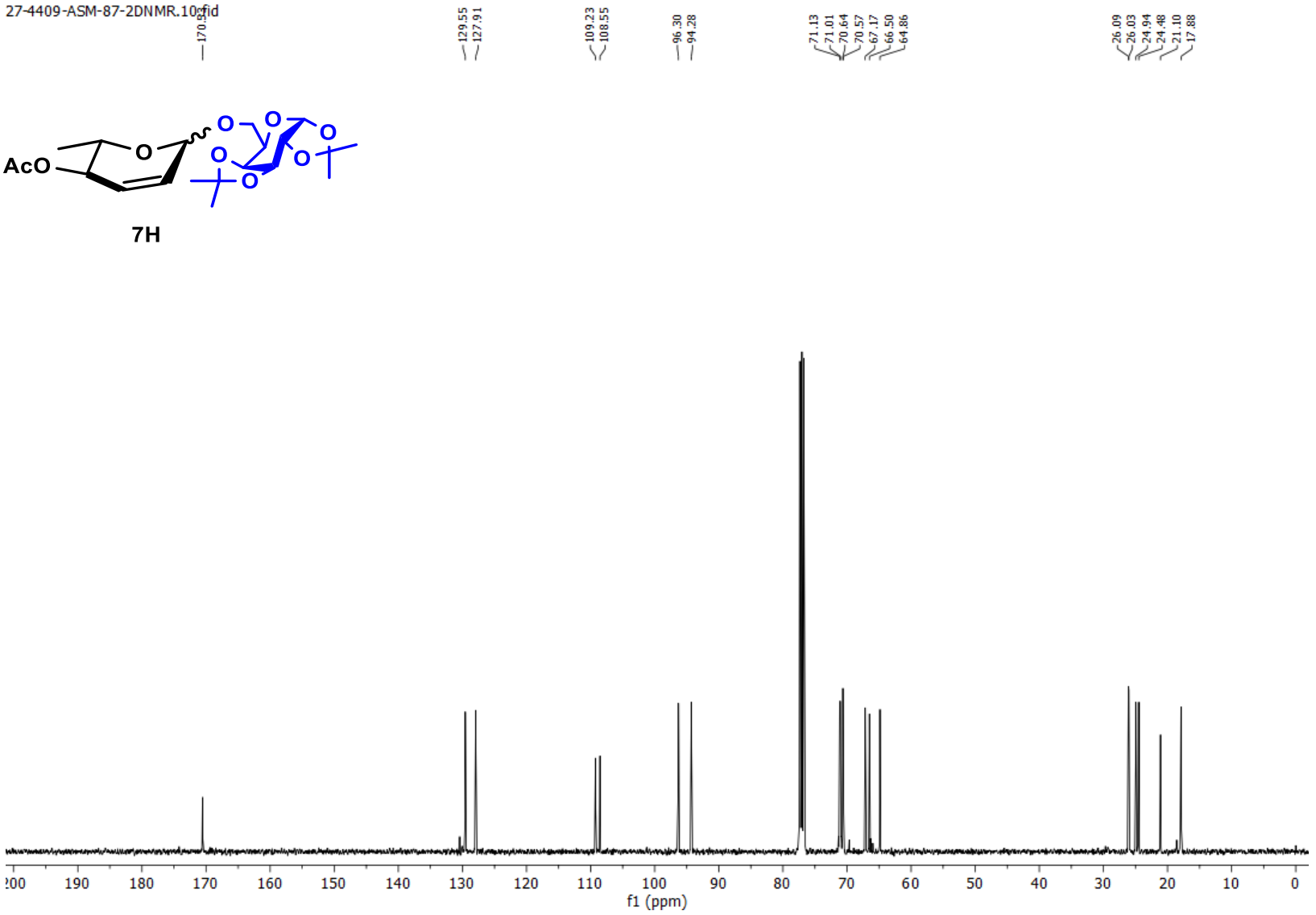


7G

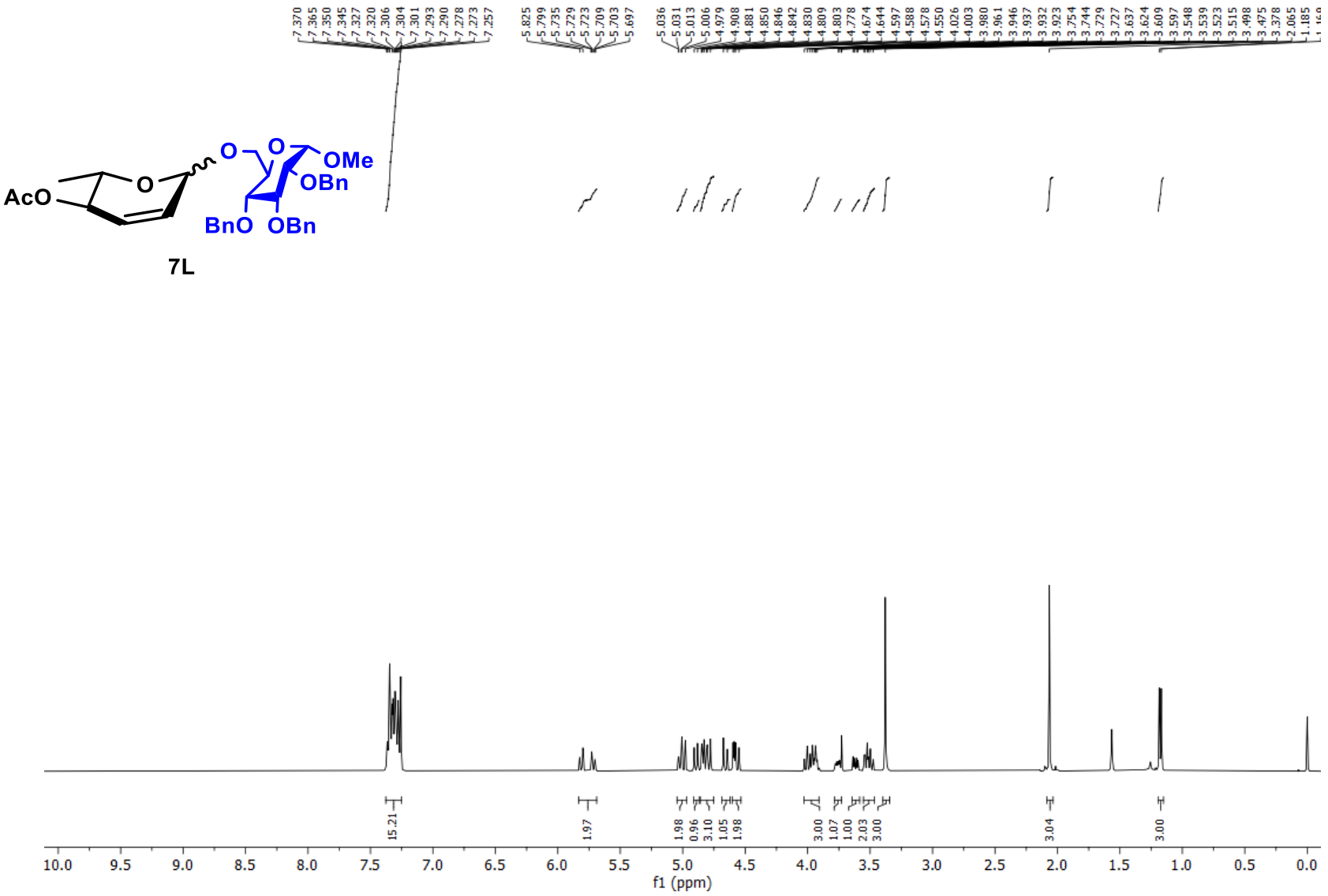
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (7H)



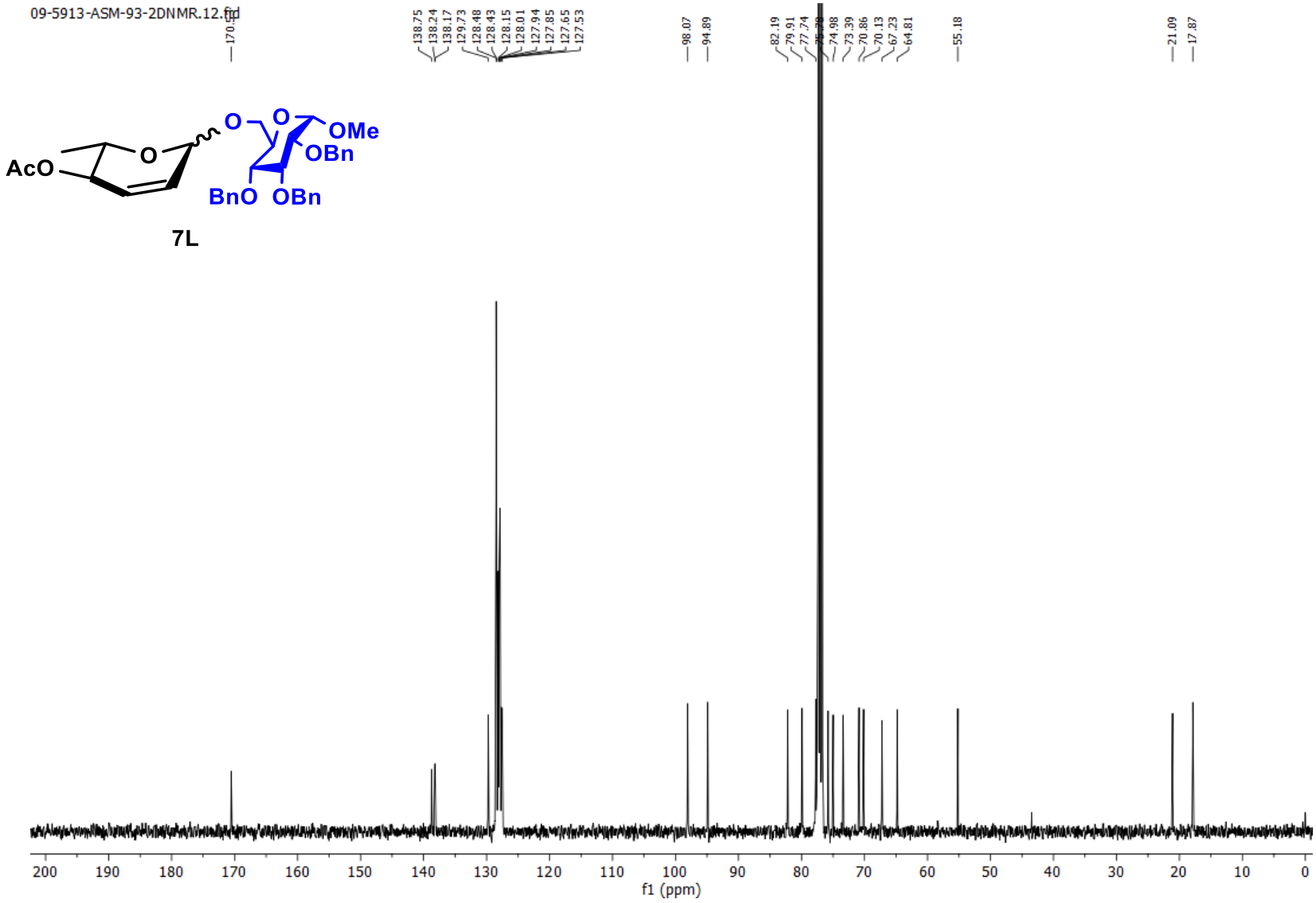
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (7H)

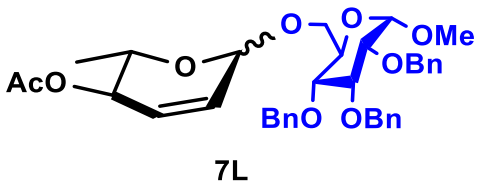


^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (7L)



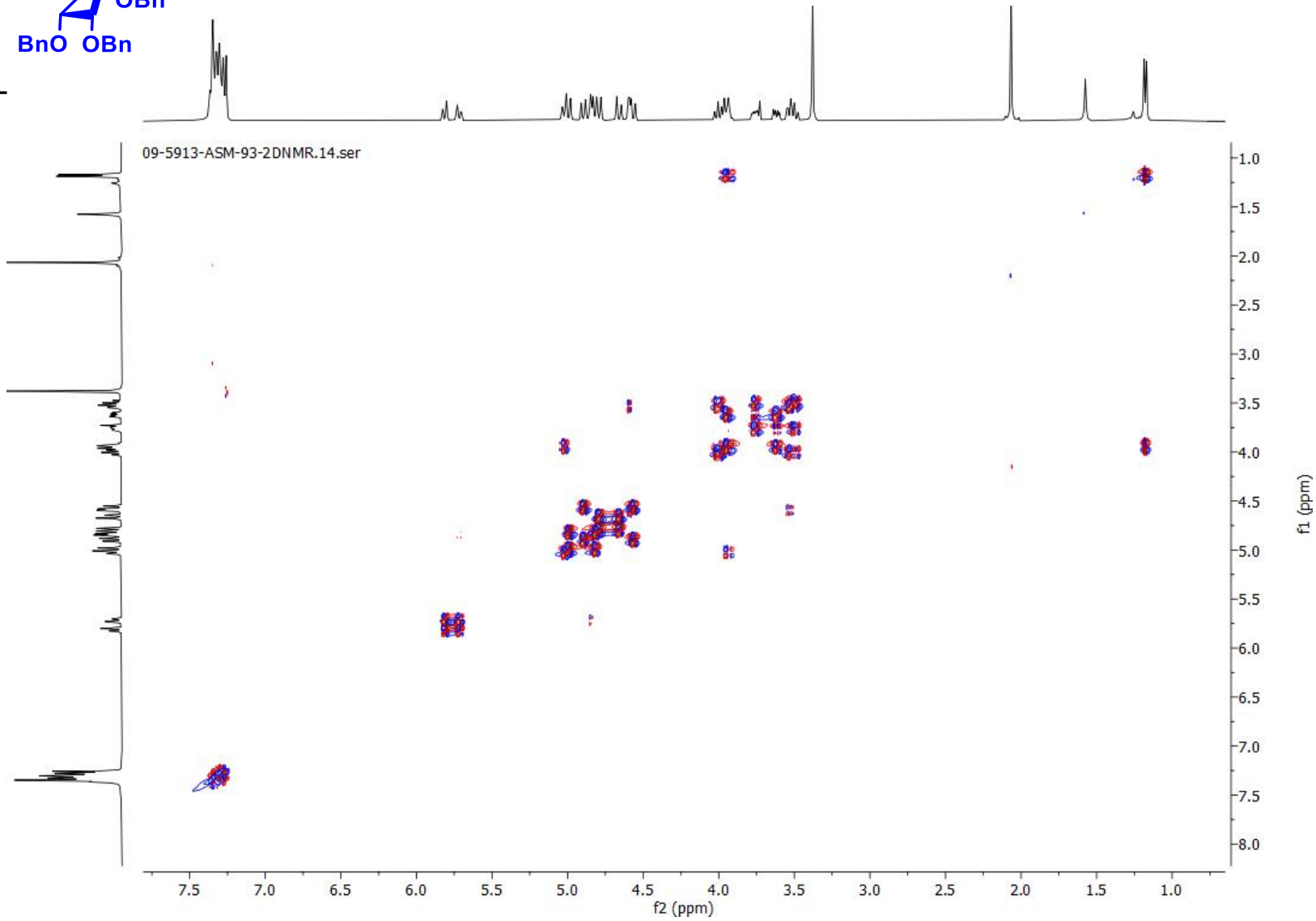
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (7L)



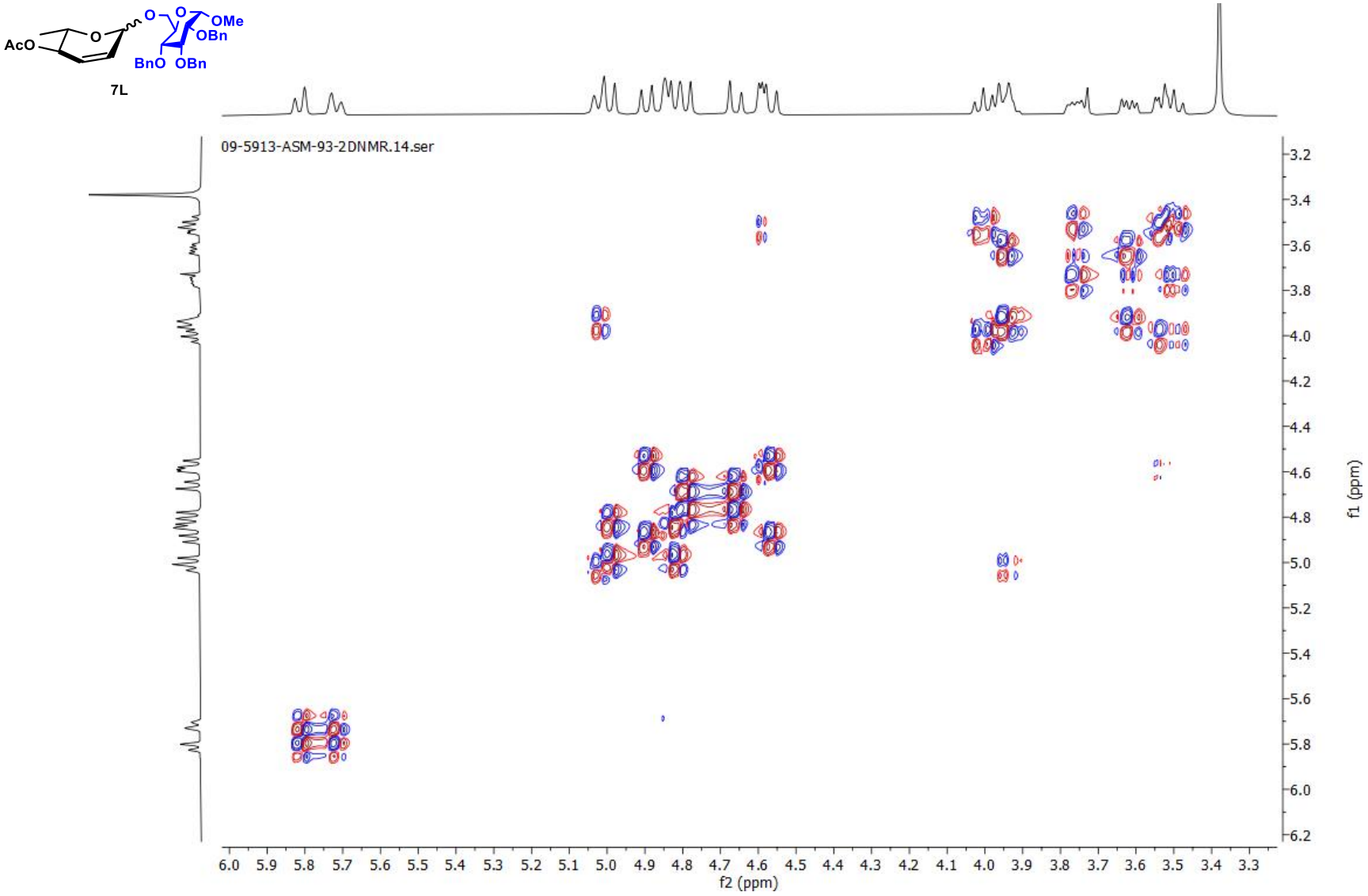


7L

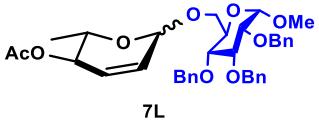
COSY (Full region) (400 MHz, $CDCl_3$) NMR spectrum of compound (7L)



COSY (Expanded region) (400 MHz, $CDCl_3$) NMR spectrum of compound (7L)

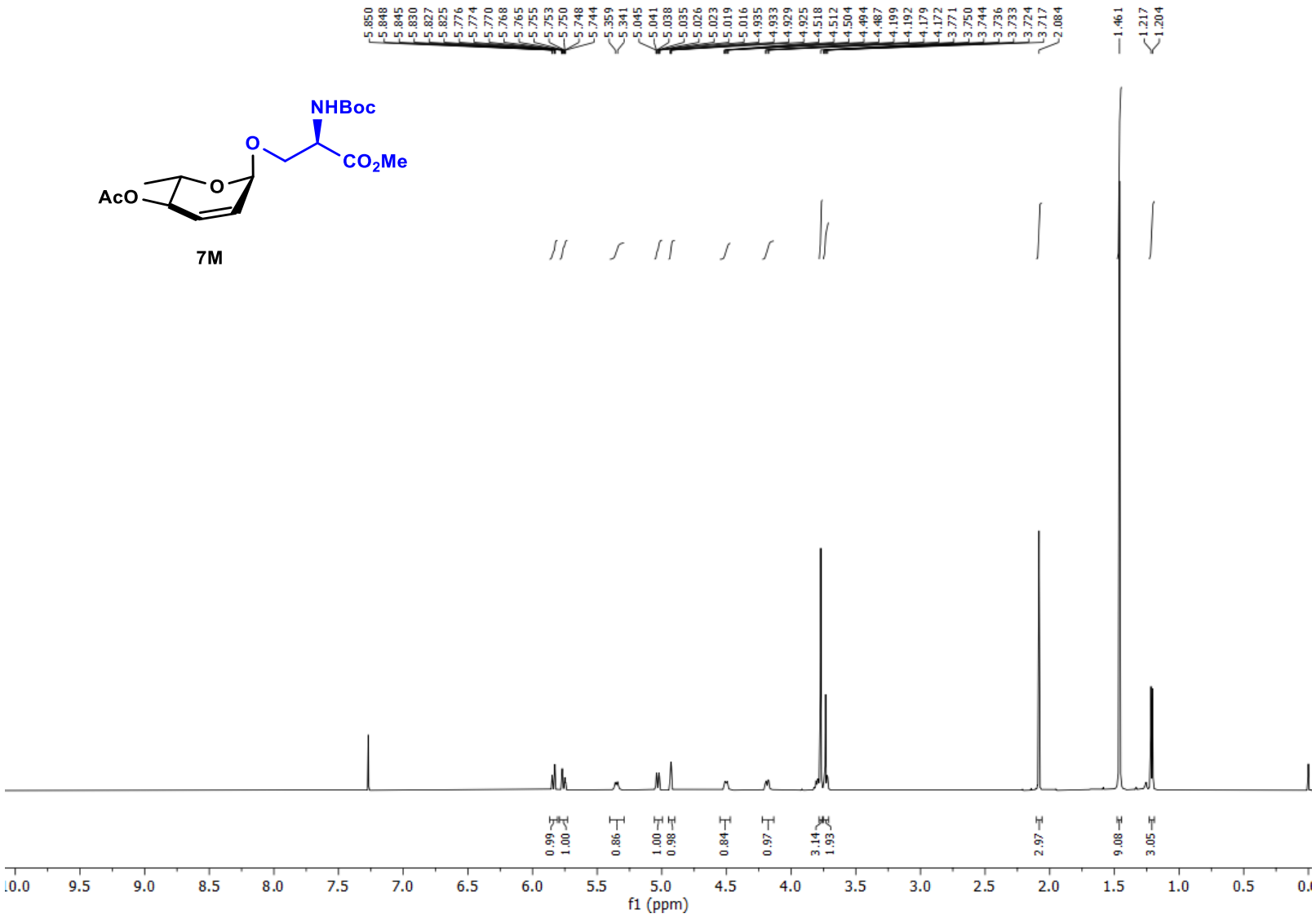


HSQC (Expanded region) (400 MHz, $CDCl_3$) NMR spectrum of compound(7L)

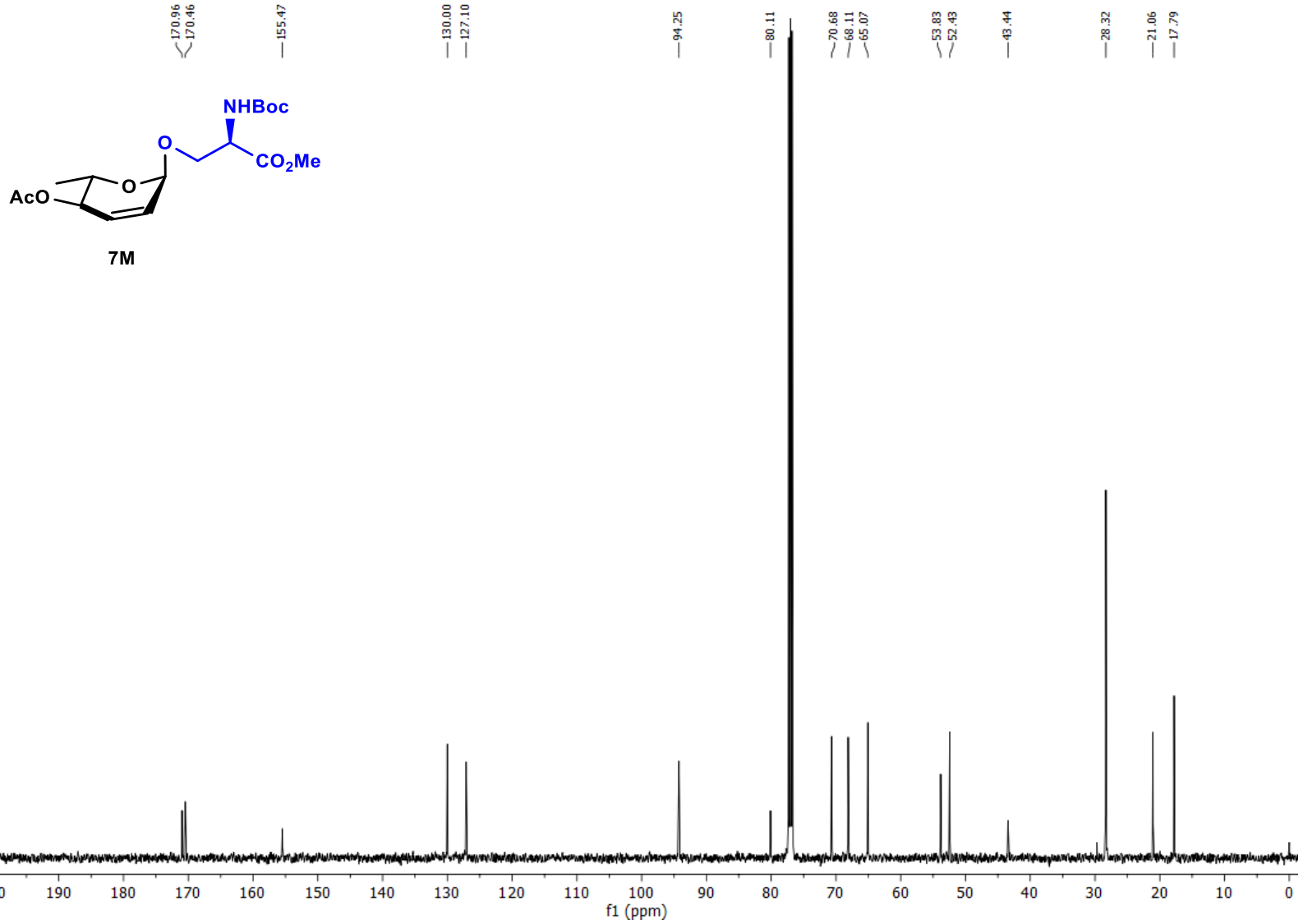


7L

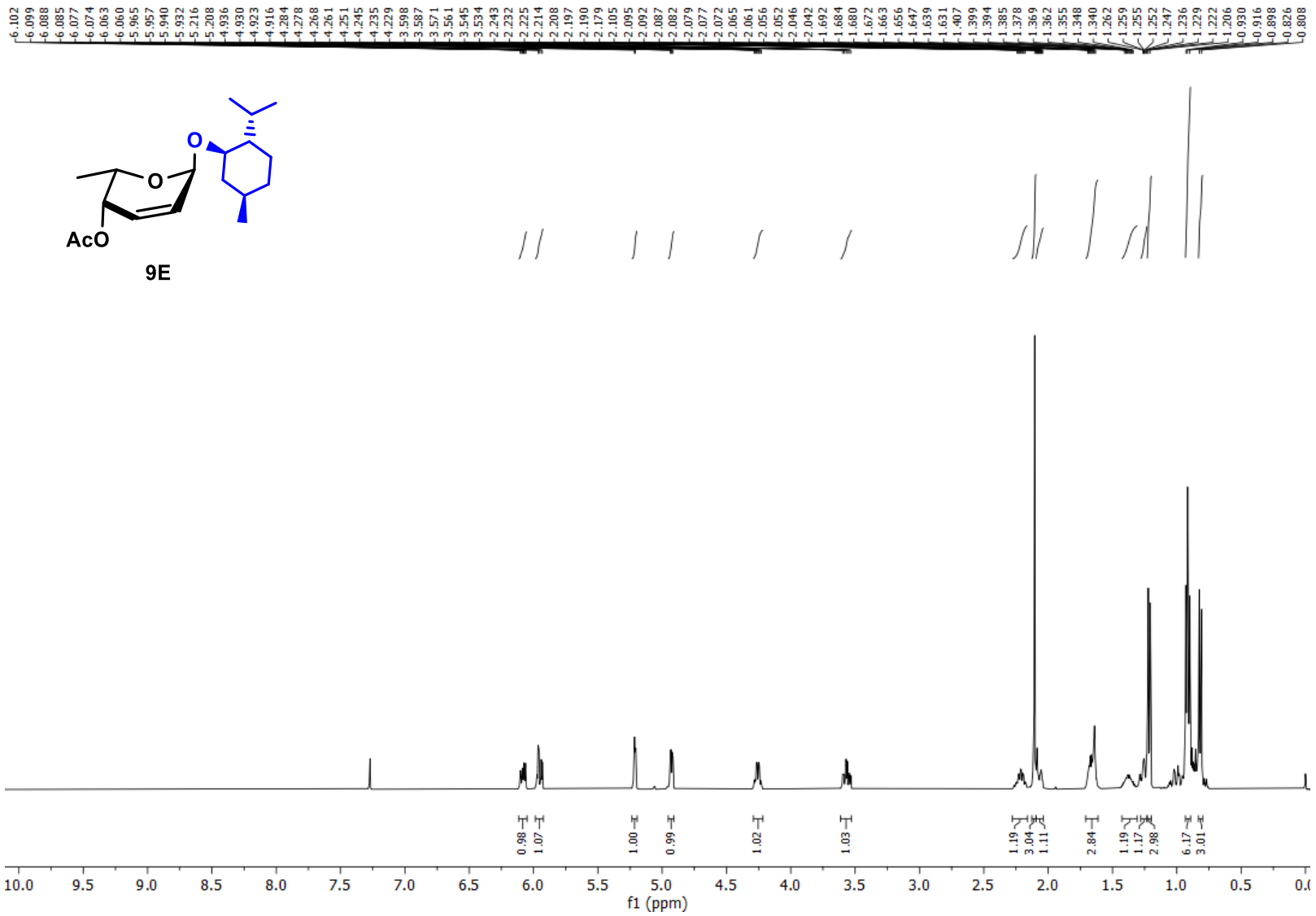
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of compound (7M)



$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of compound (7M)

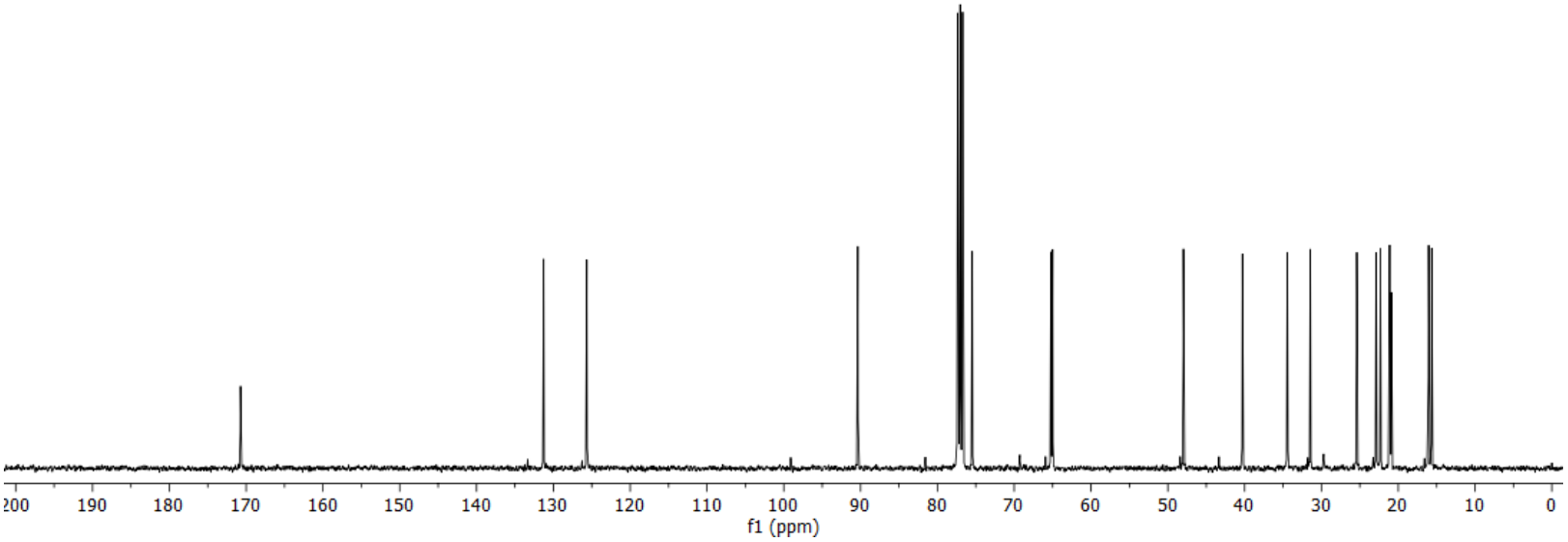


^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (9E)

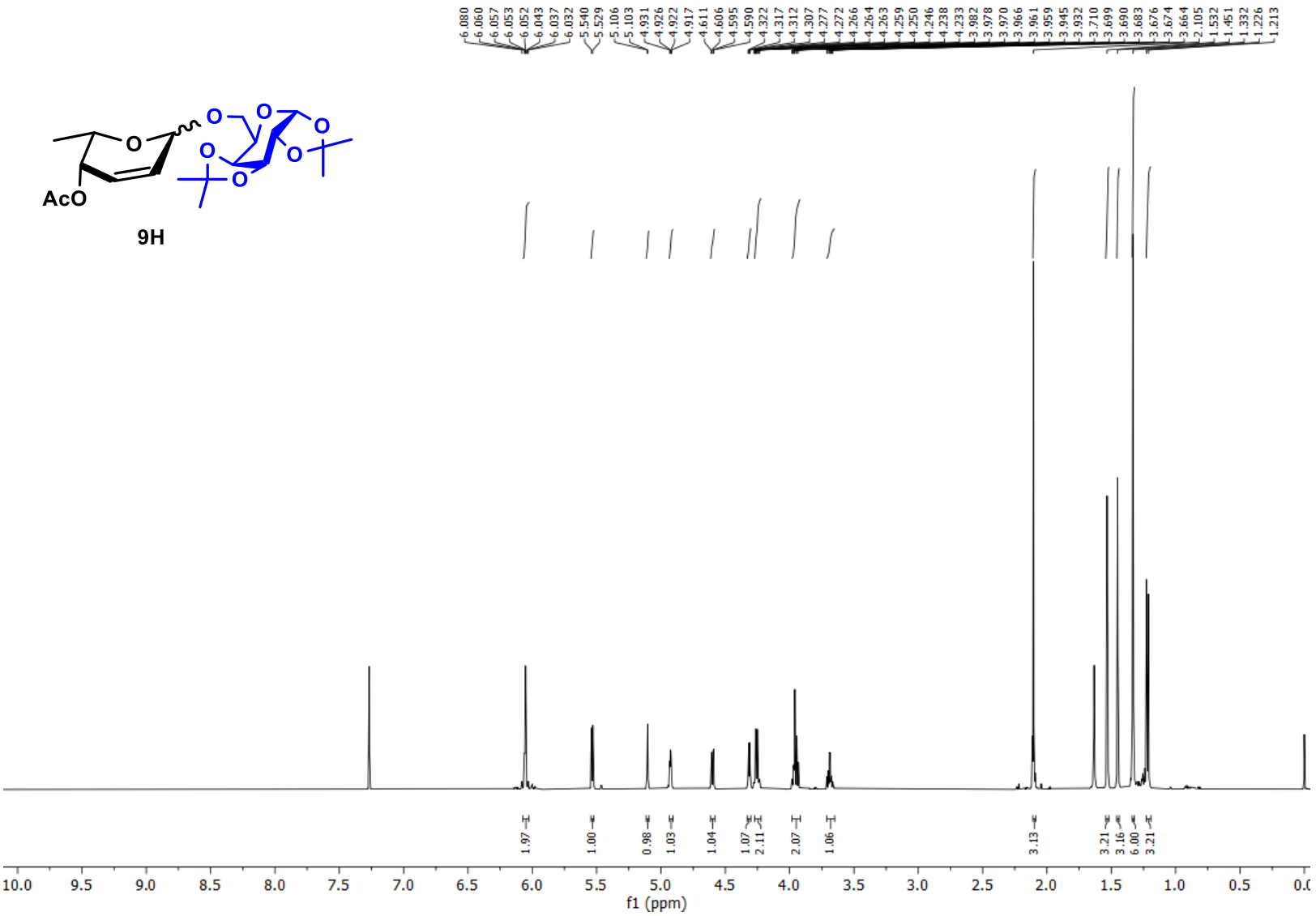


$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (9E)

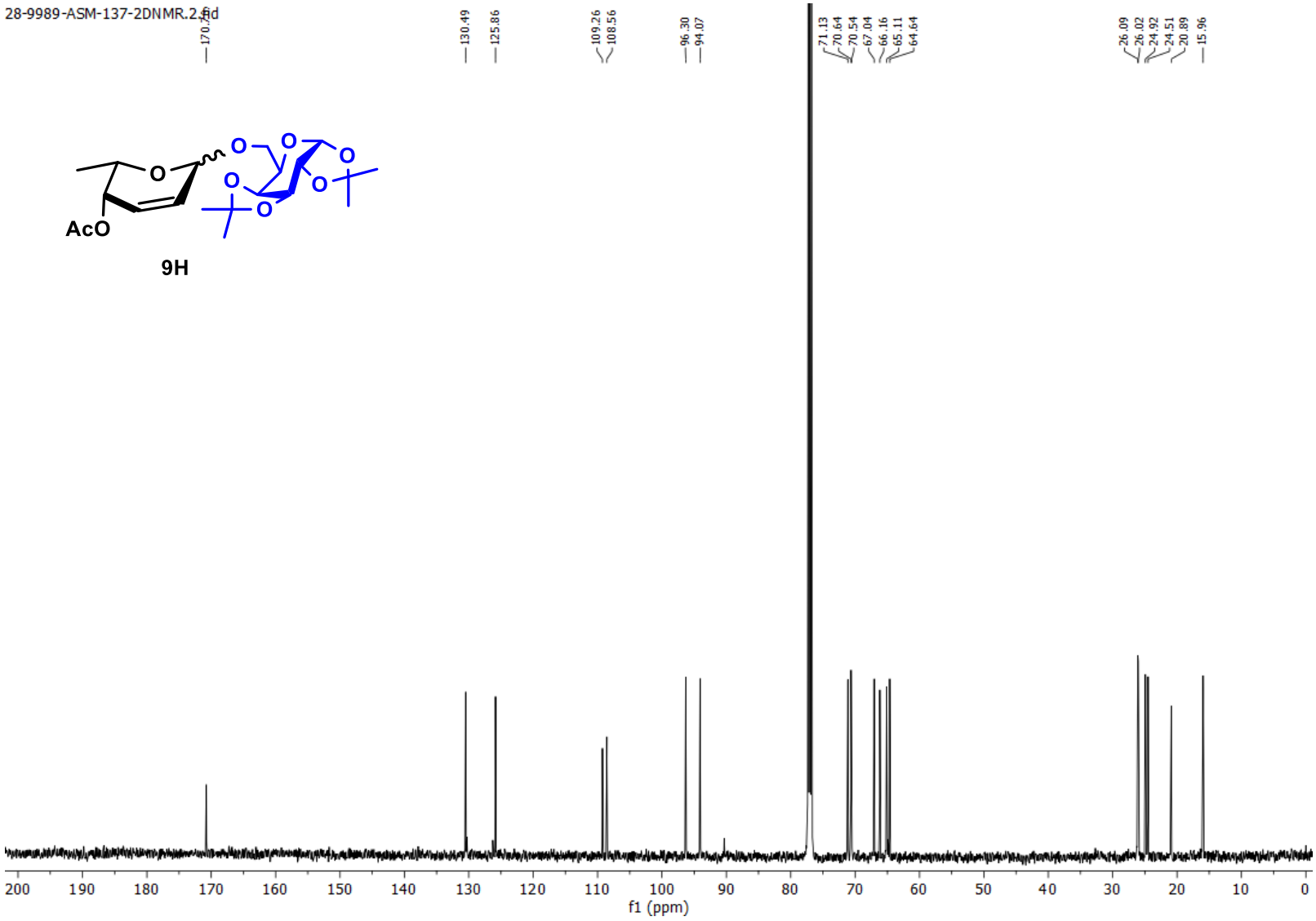
9E



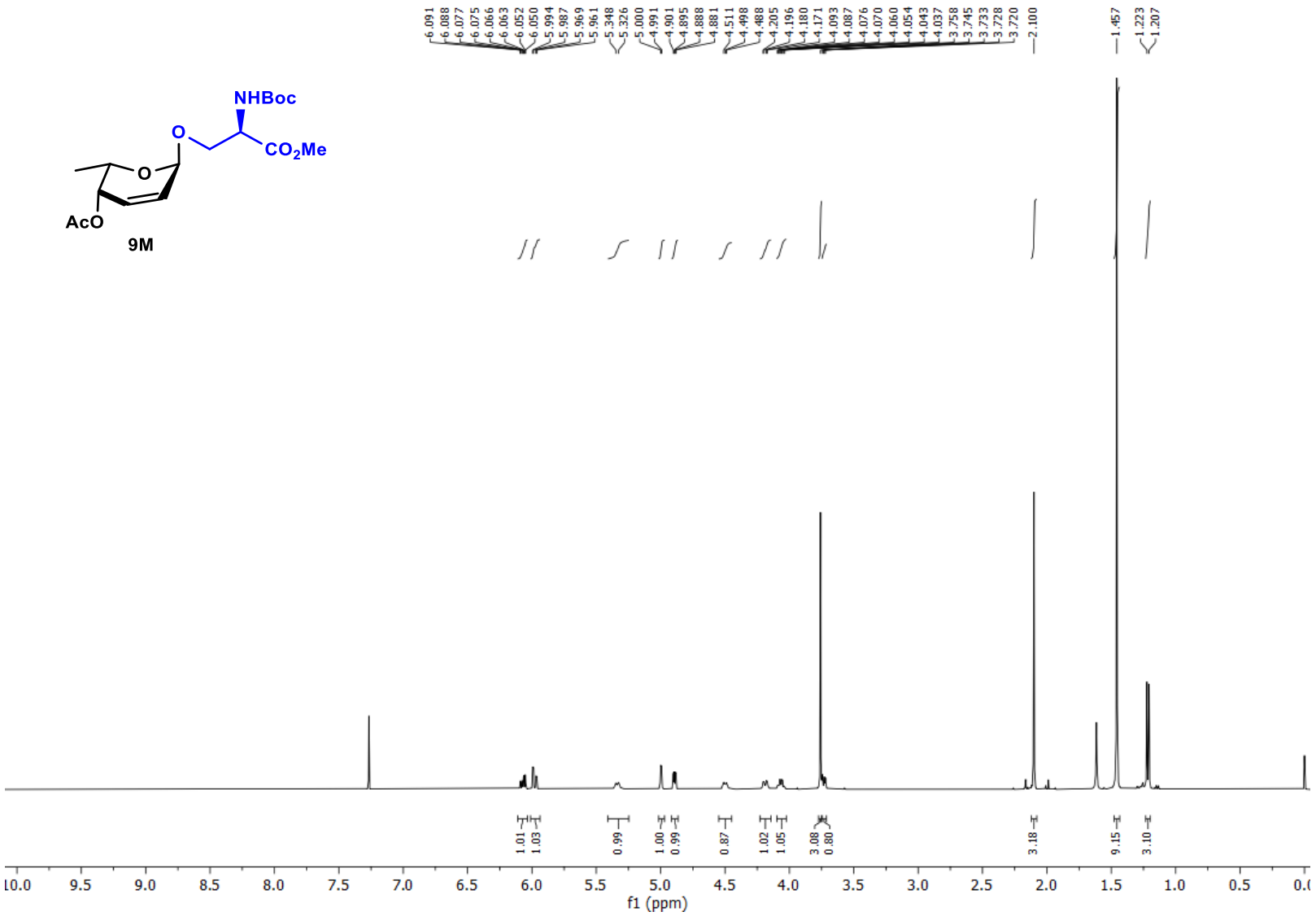
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of compound (9H)



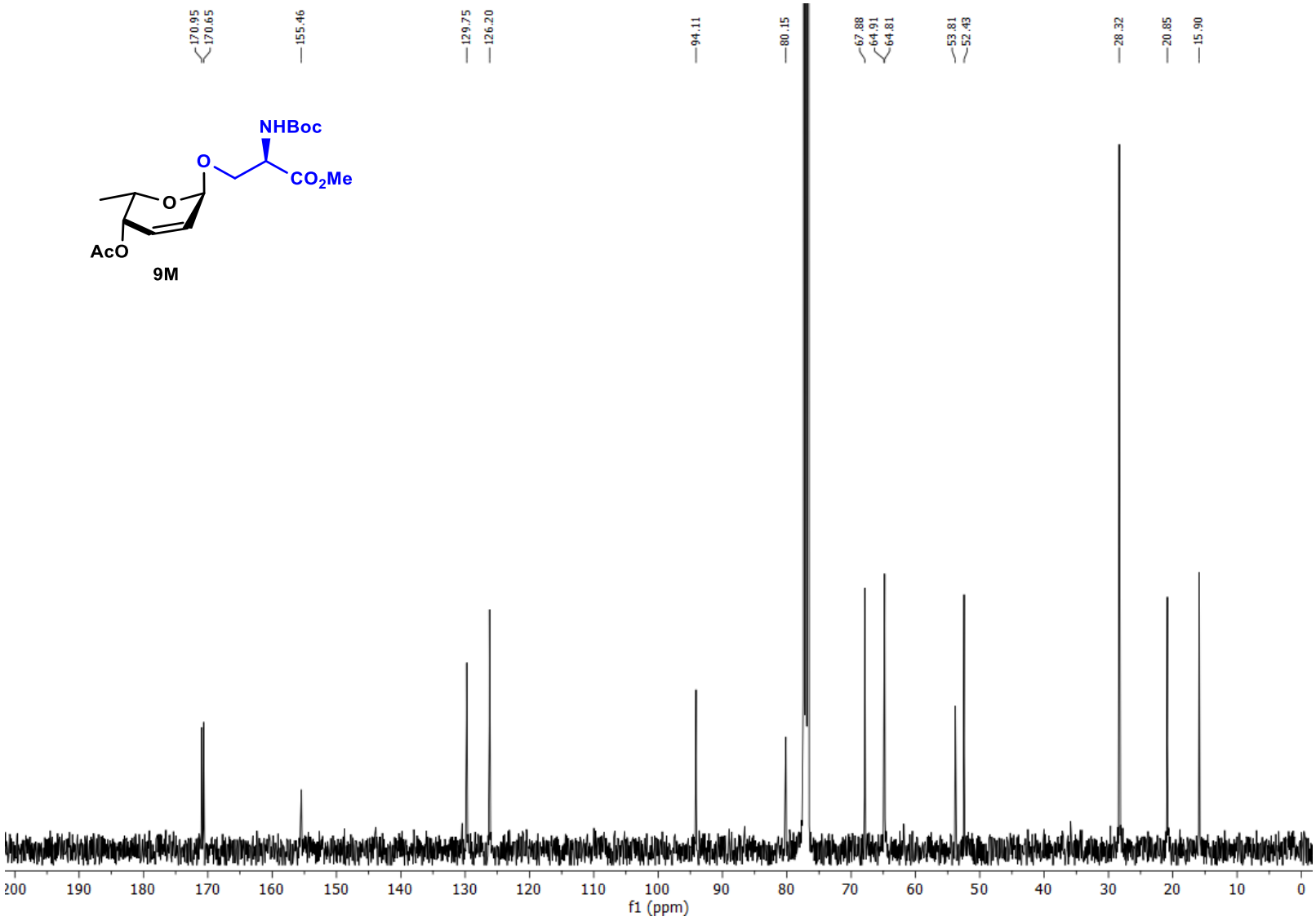
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectrum of compound (9H)



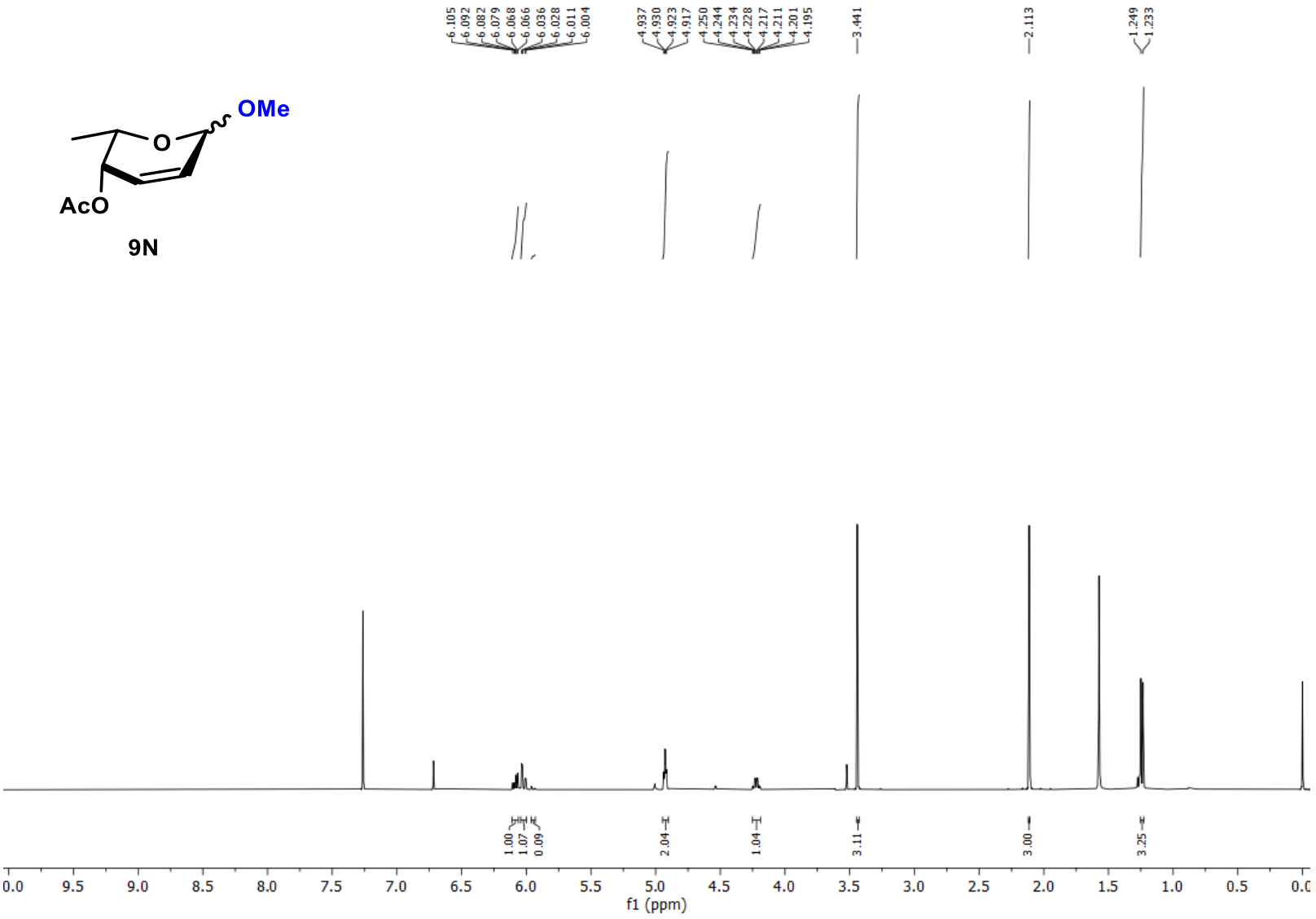
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (9M)



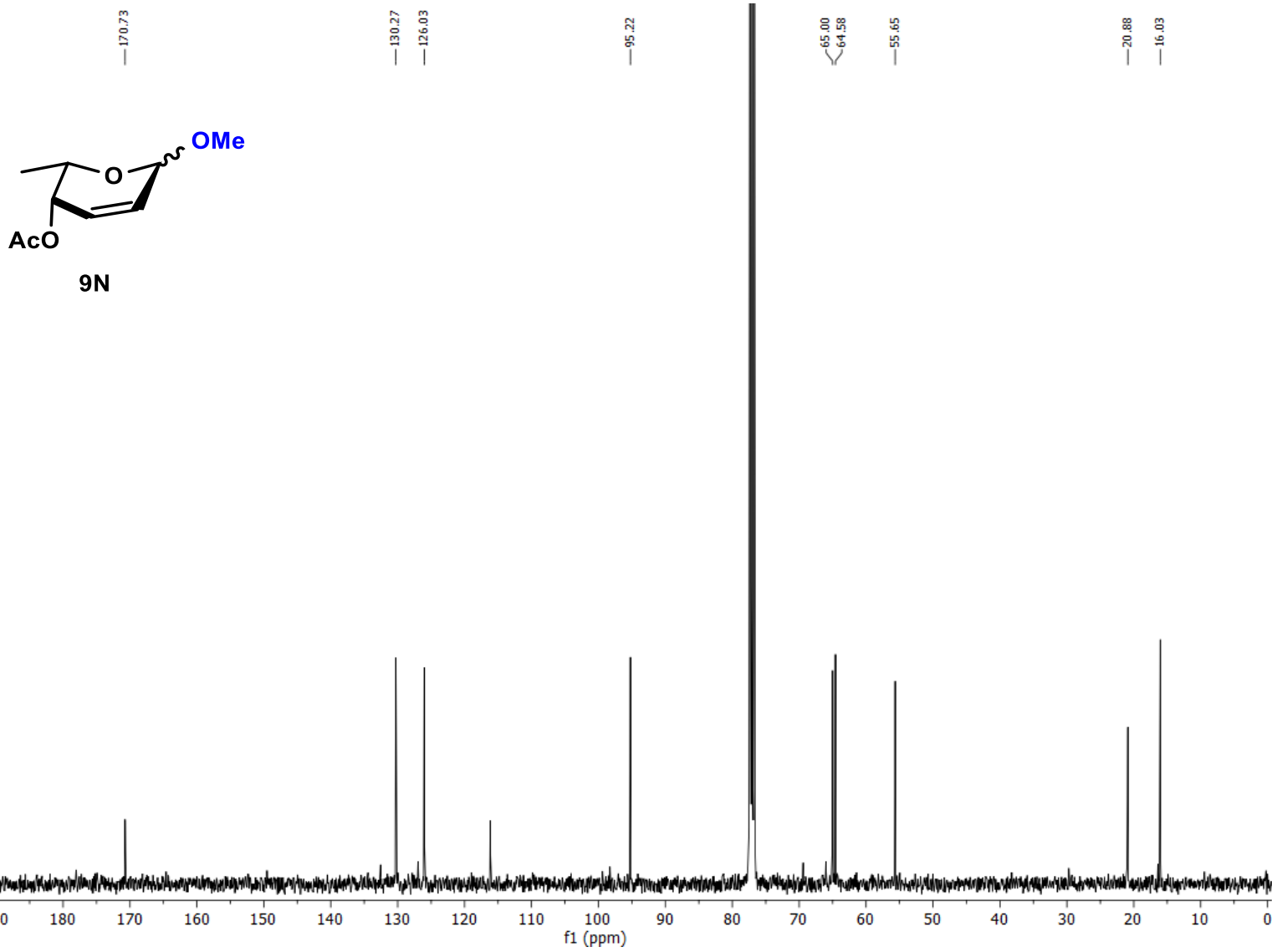
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (9M)



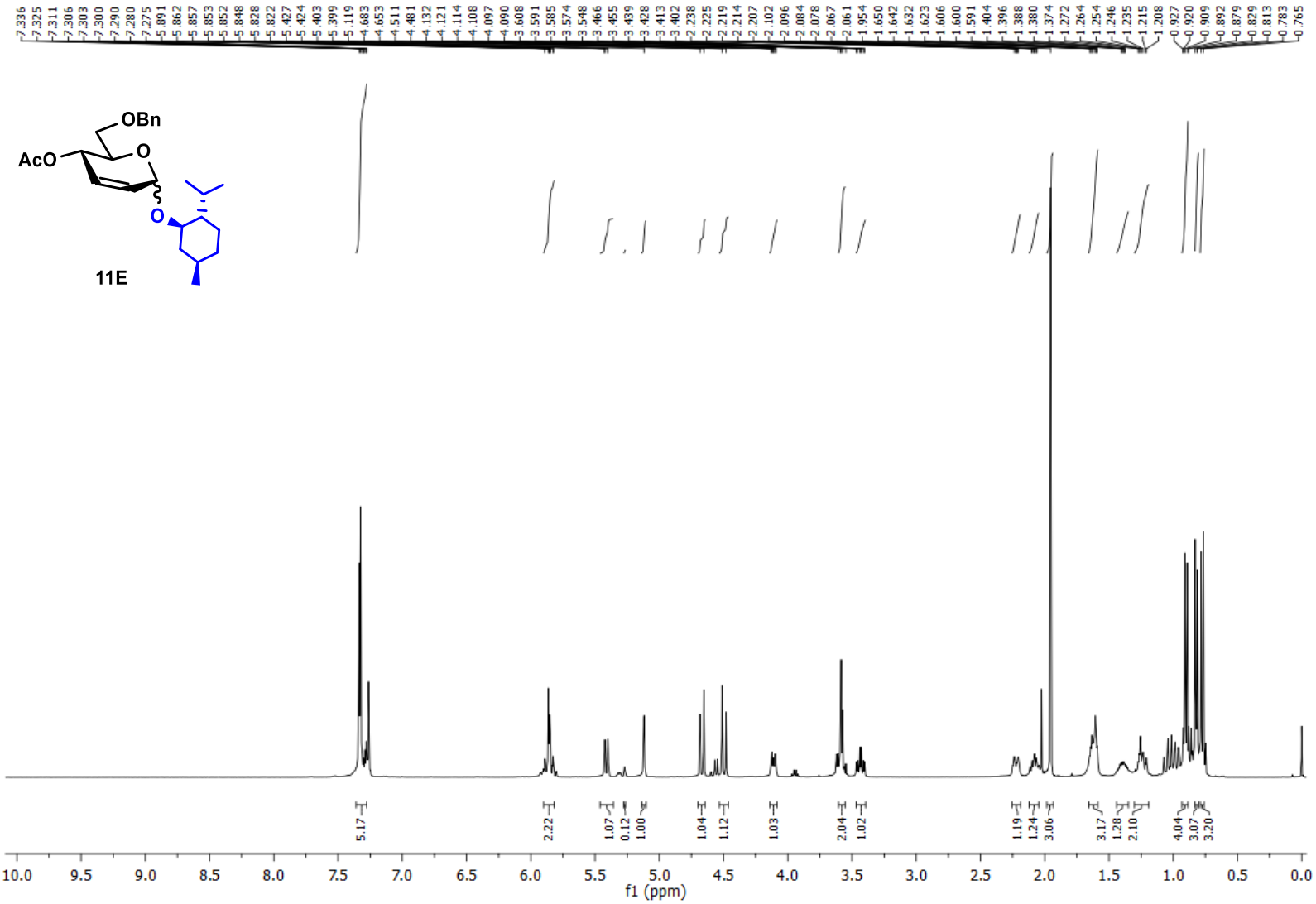
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (9N)



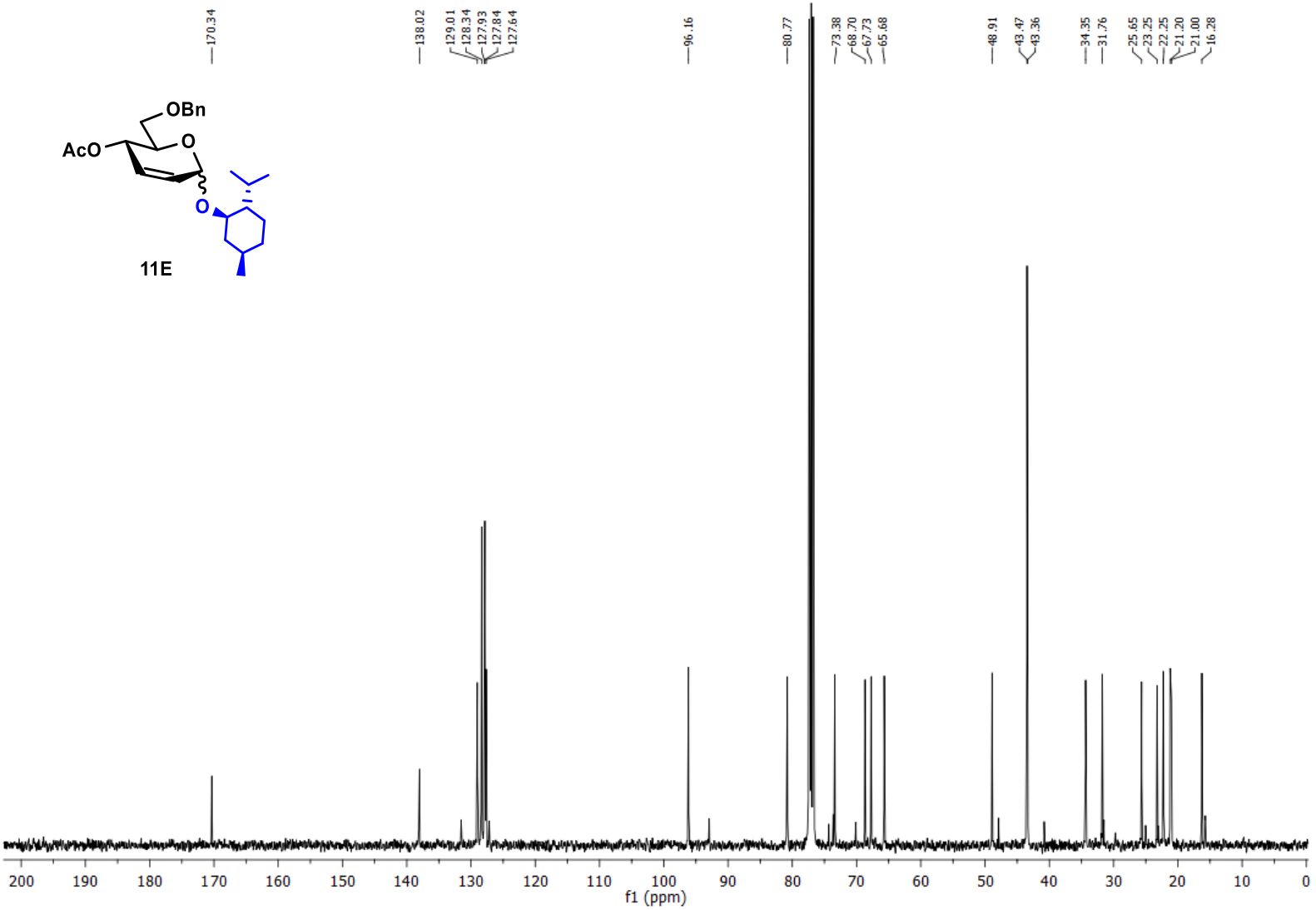
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (9N)



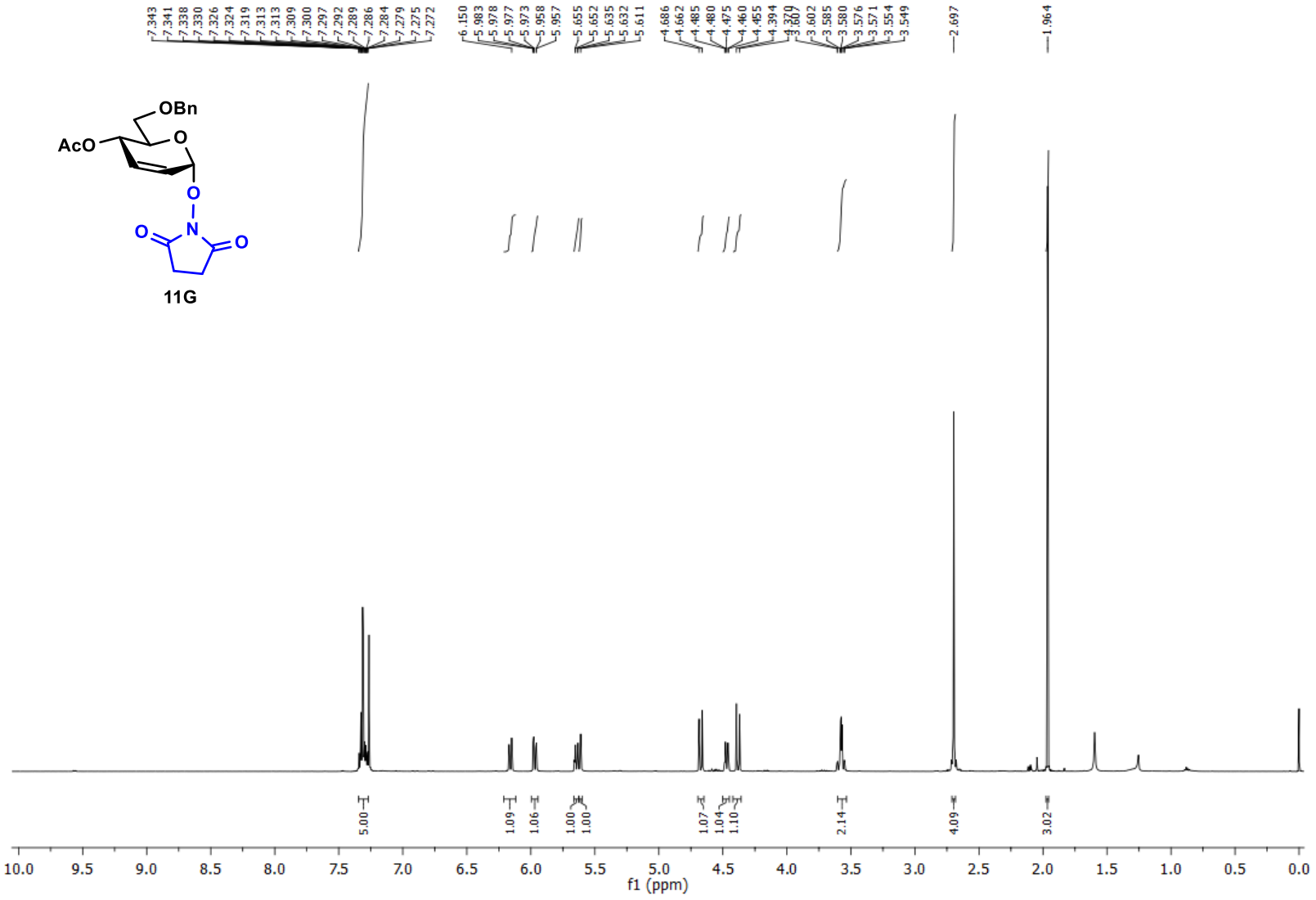
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (11E)



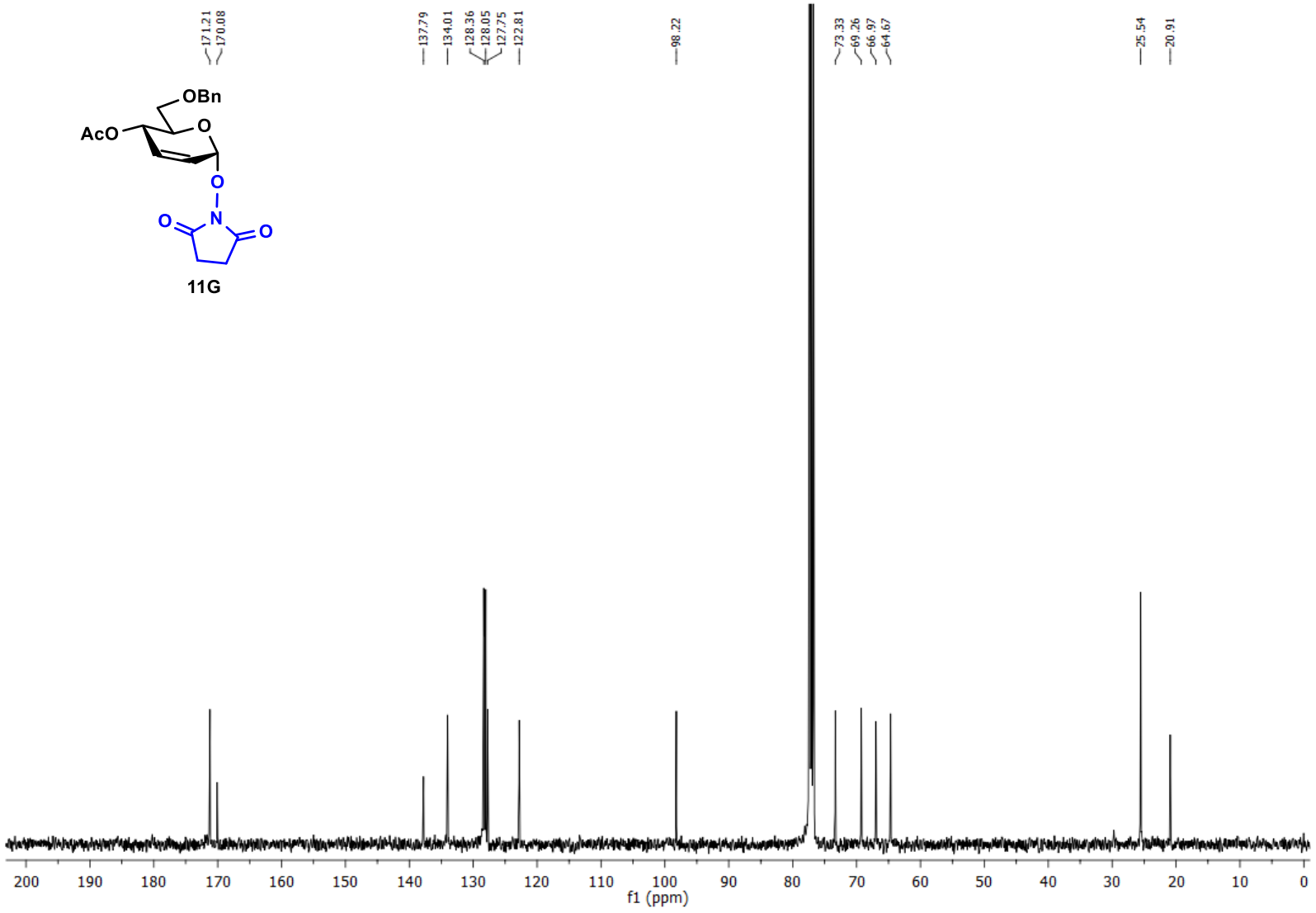
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (11E)



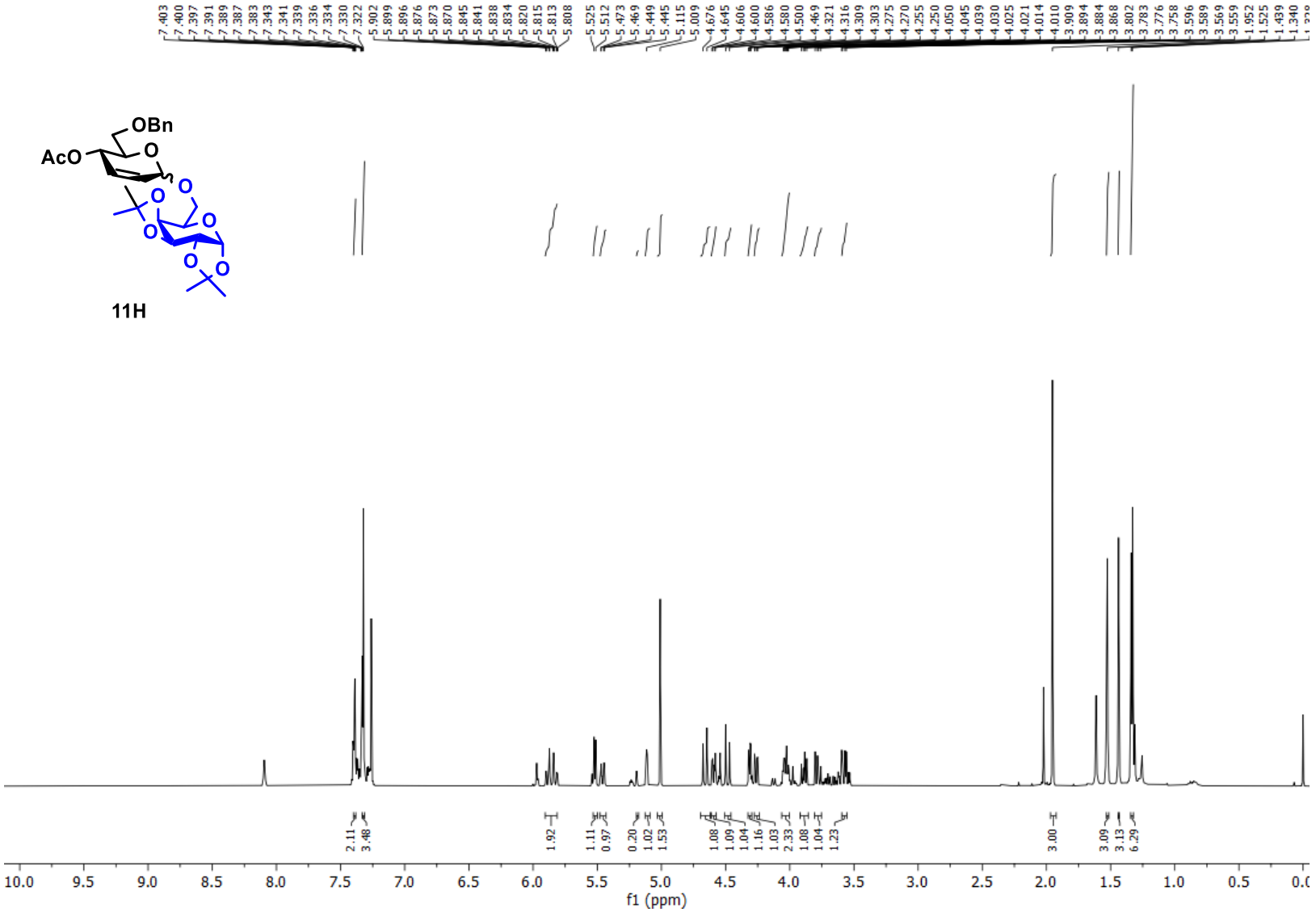
^{1}H (500 MHz, $CDCl_3$ NMR spectrum of compound (11G)



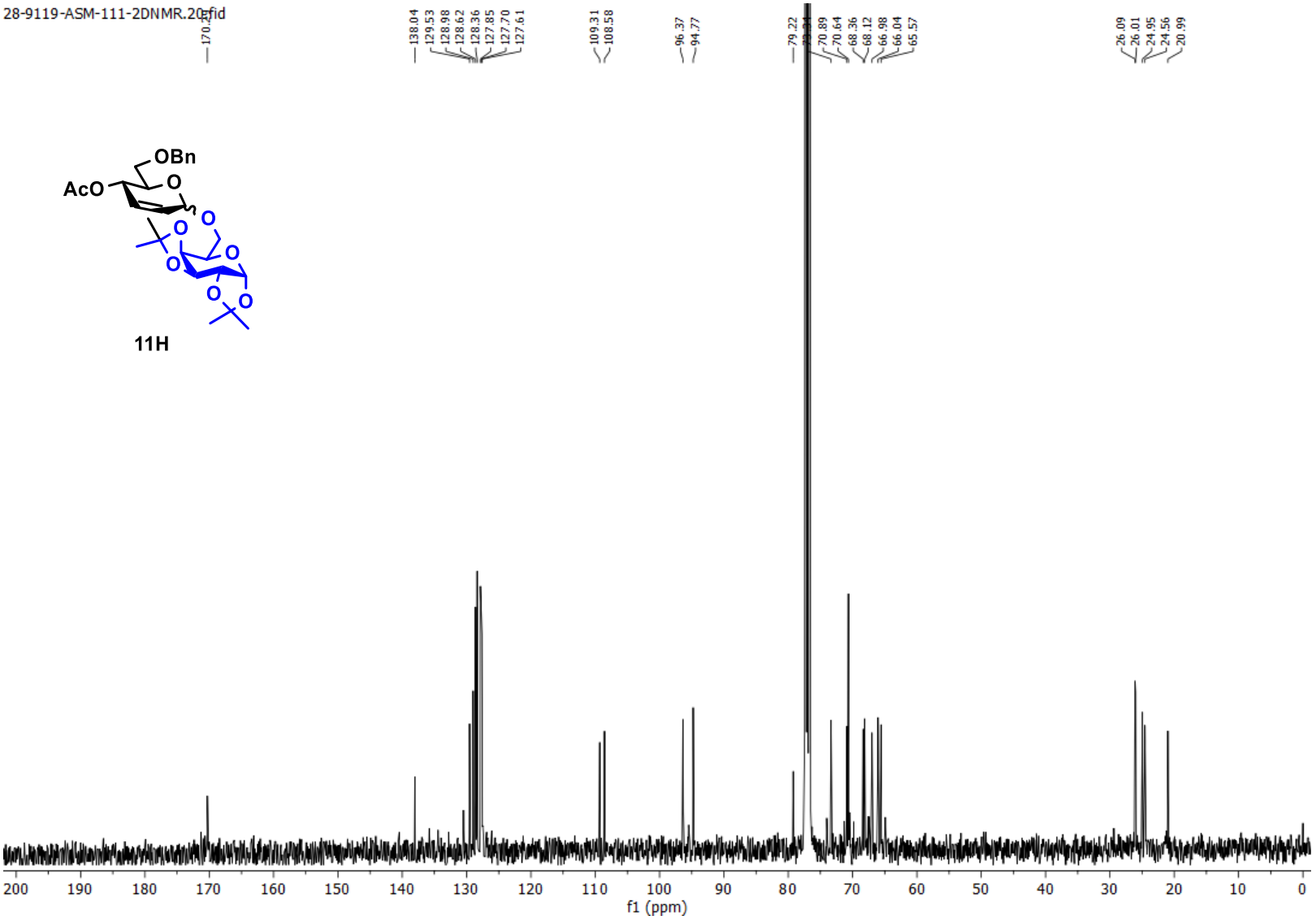
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (11G)



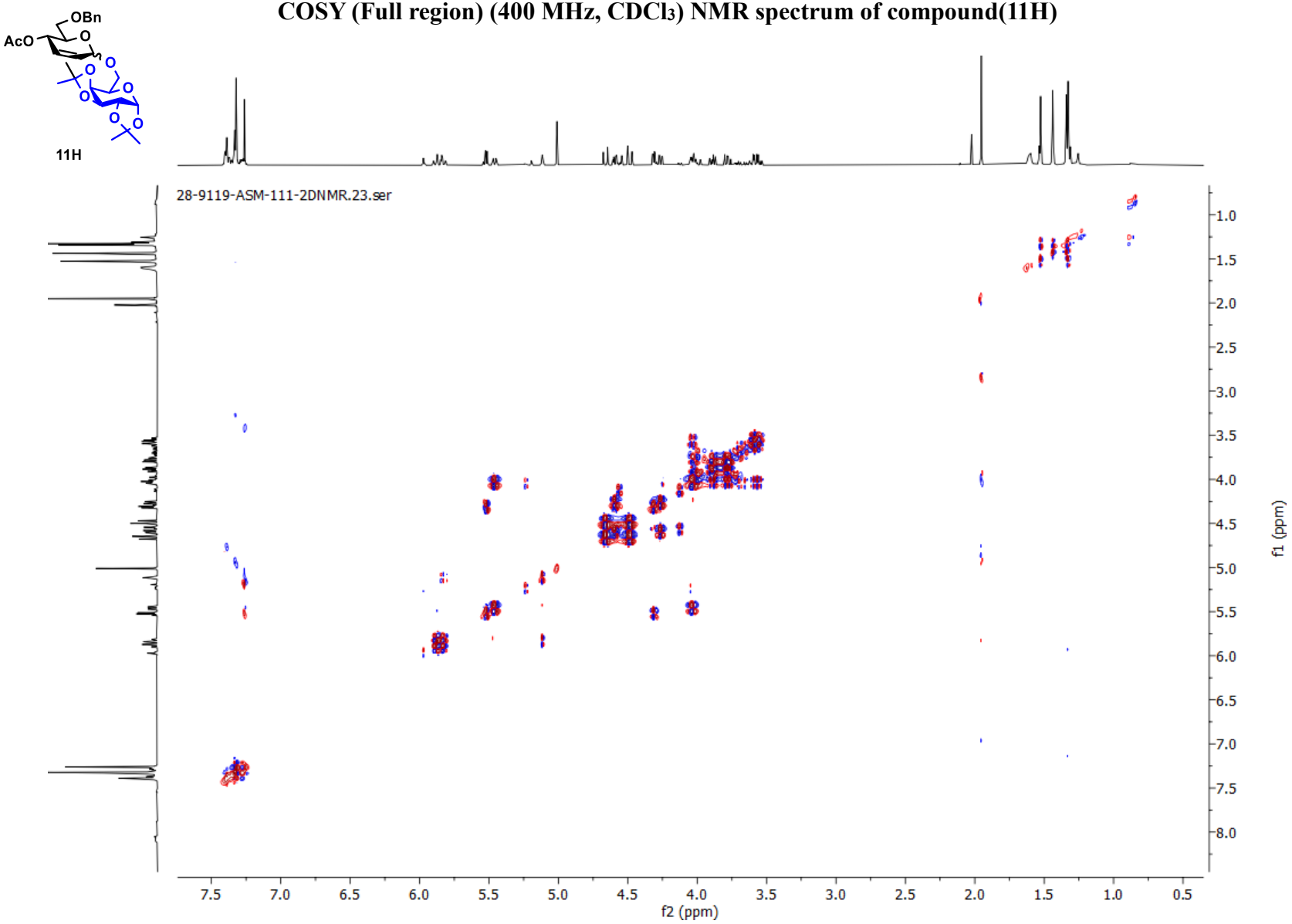
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (11H)



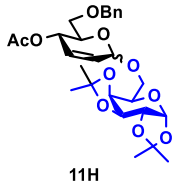
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (11H)



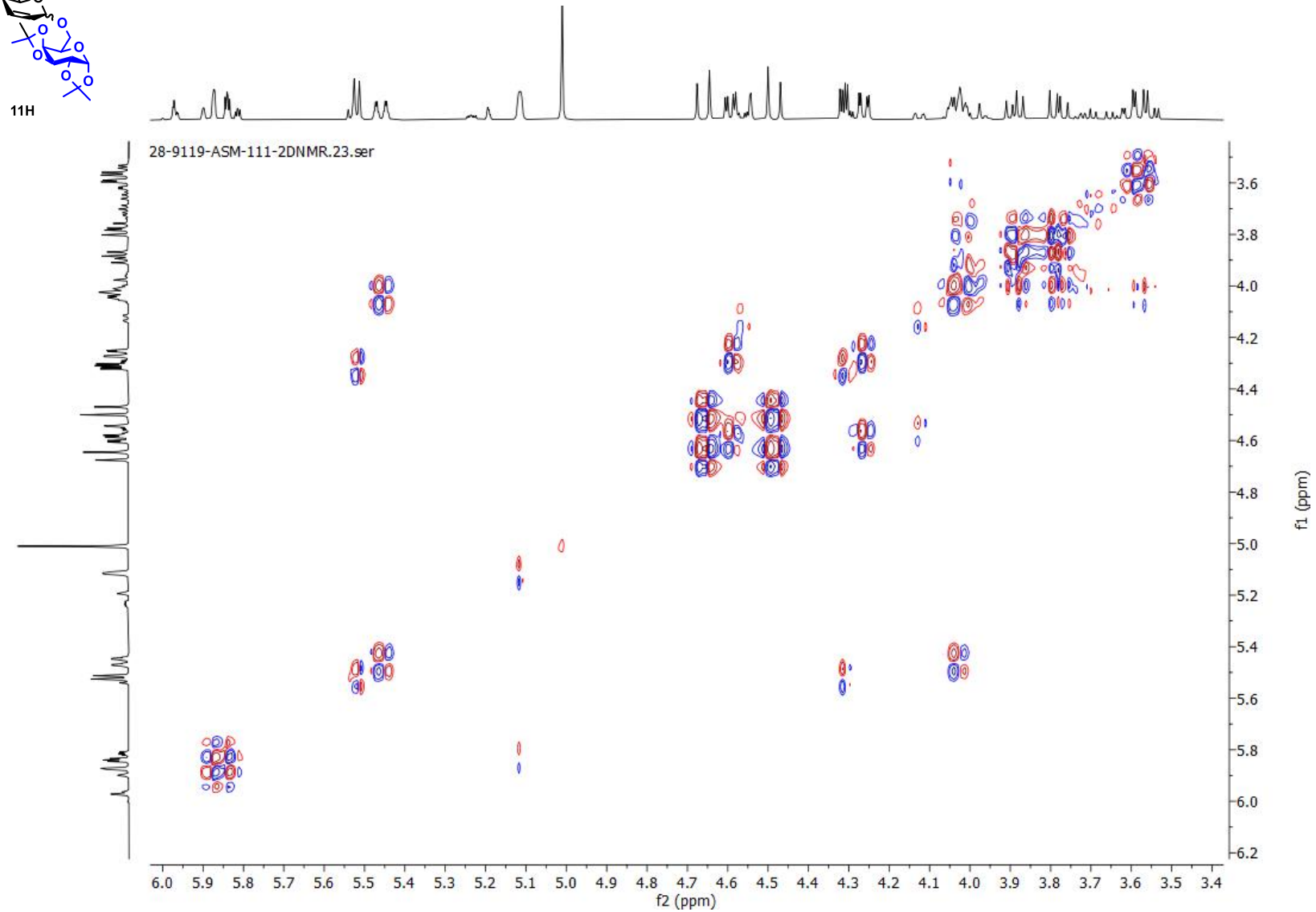
COSY (Full region) (400 MHz, $CDCl_3$) NMR spectrum of compound(11H)



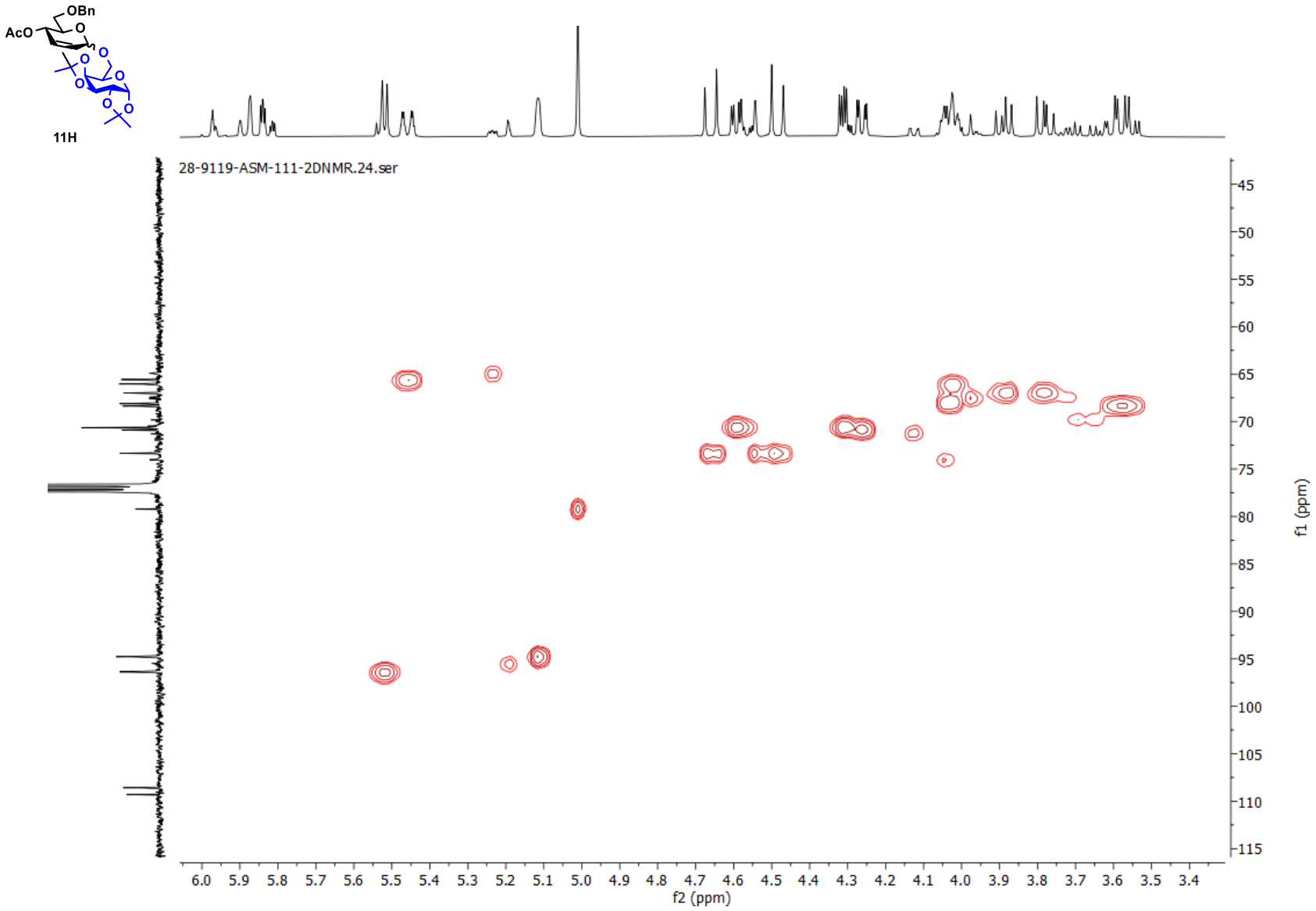
COSY (Expanded region) (400 MHz, $CDCl_3$) NMR spectrum of compound(11H)



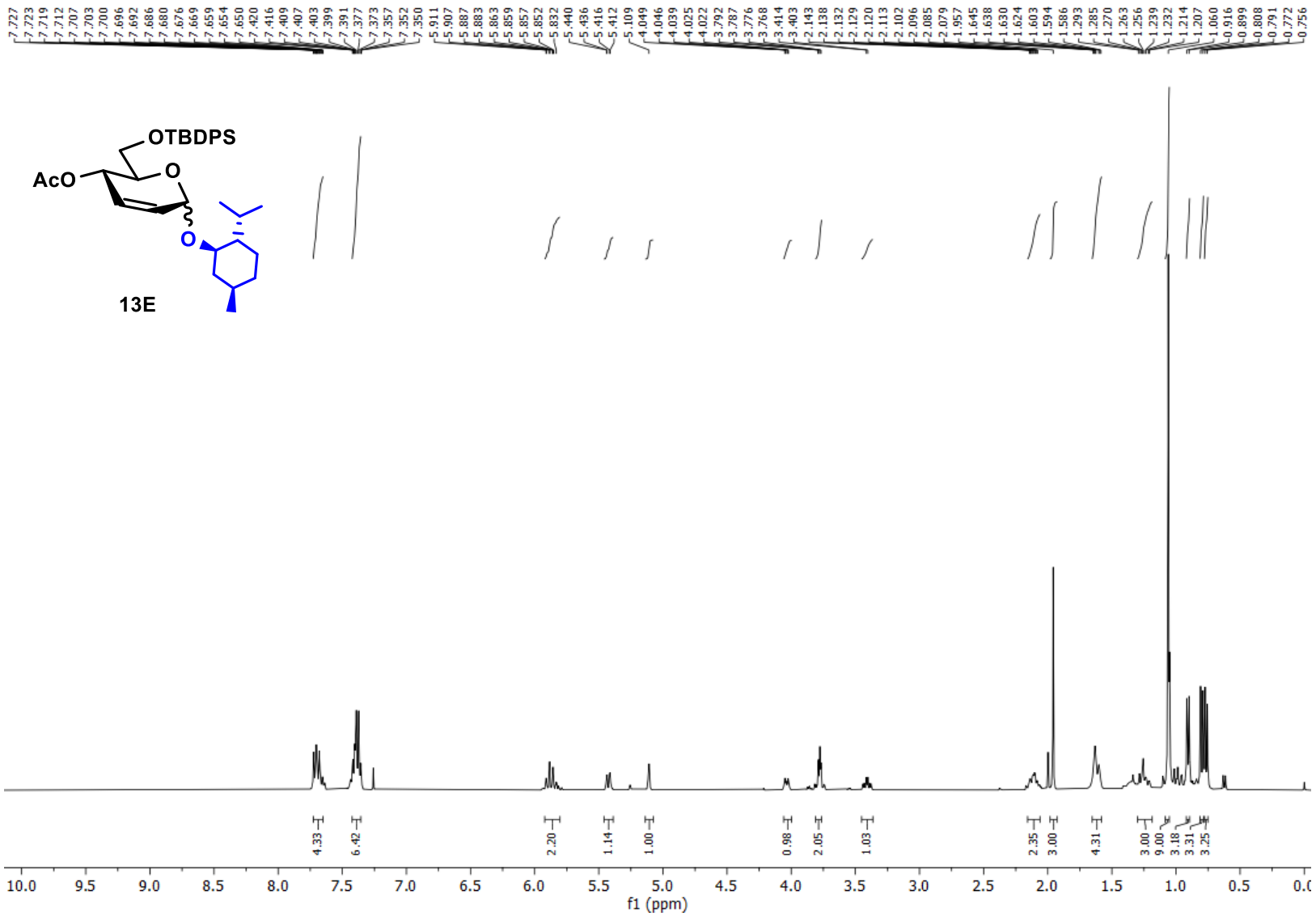
11H



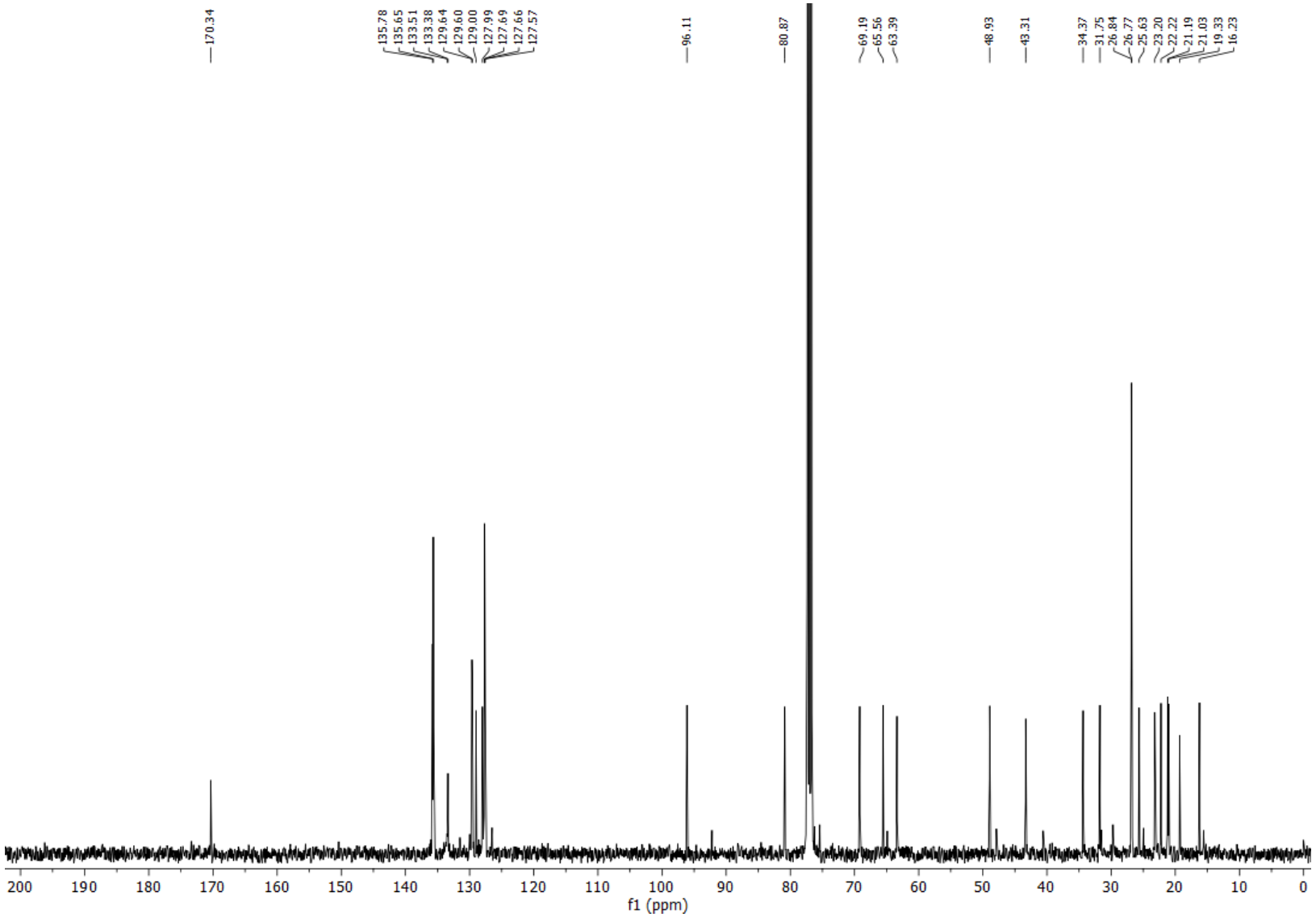
HSQC (Expanded region) (400 MHz, $CDCl_3$) NMR spectrum of compound(11H)



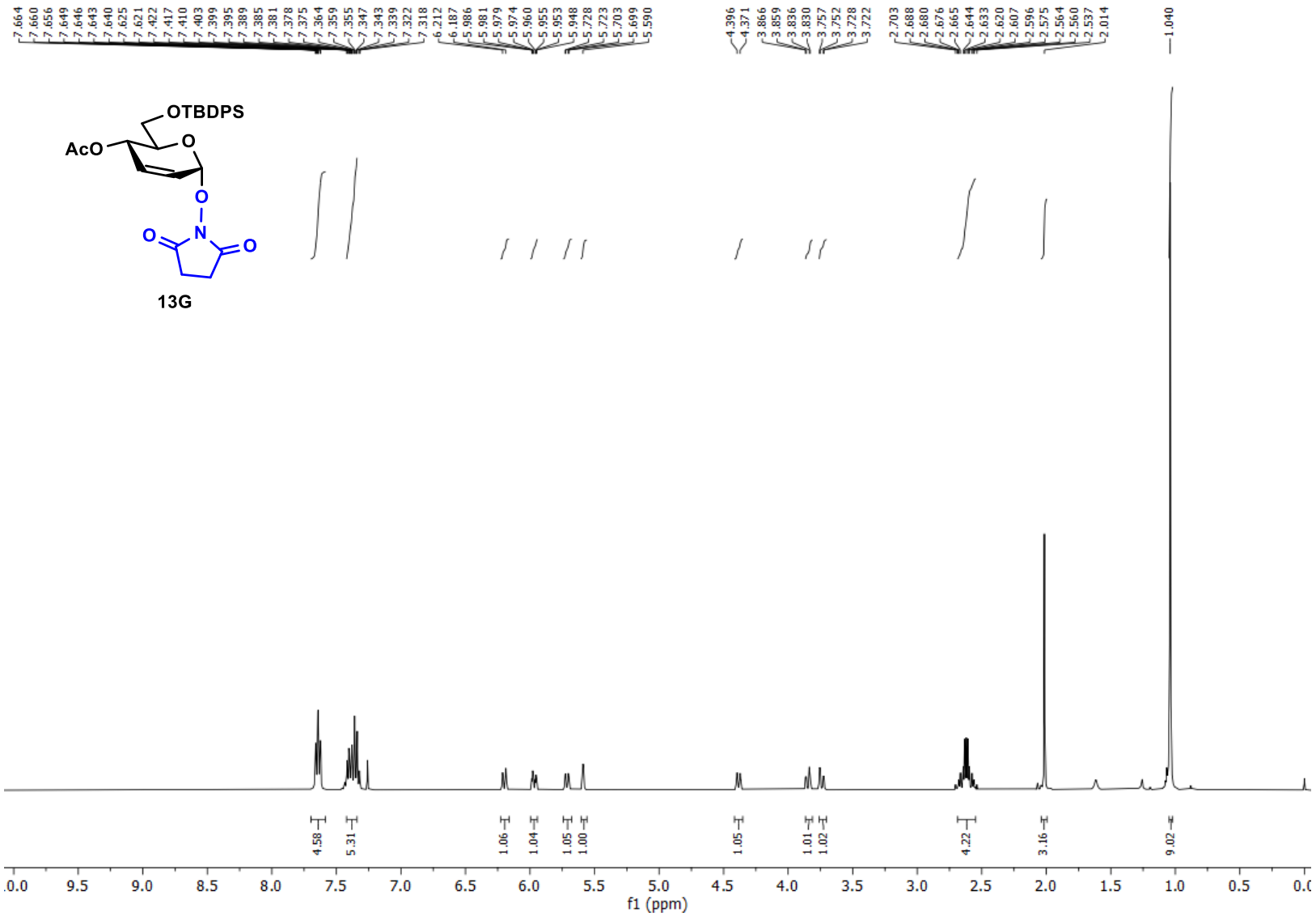
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (13E)



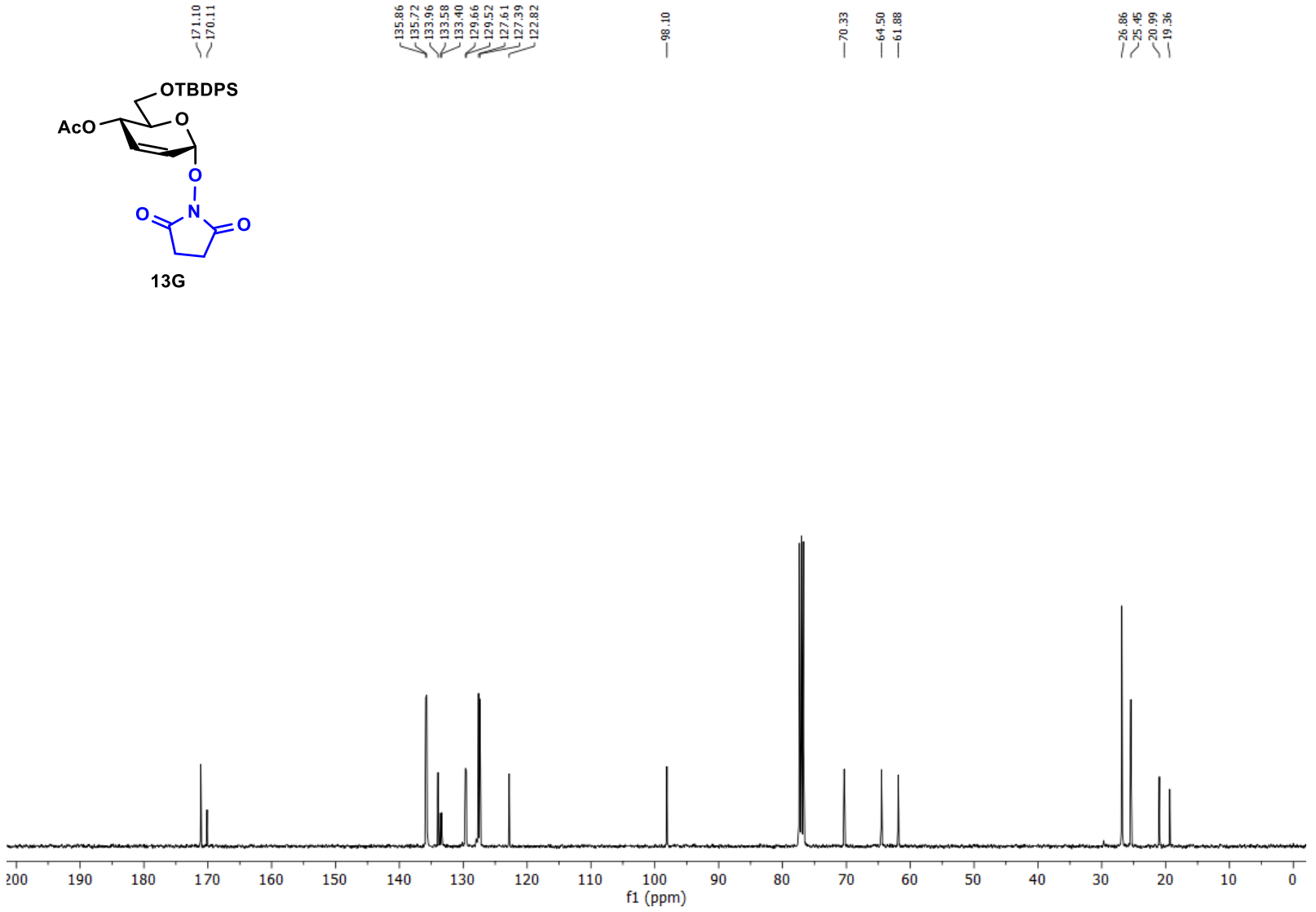
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (13E)



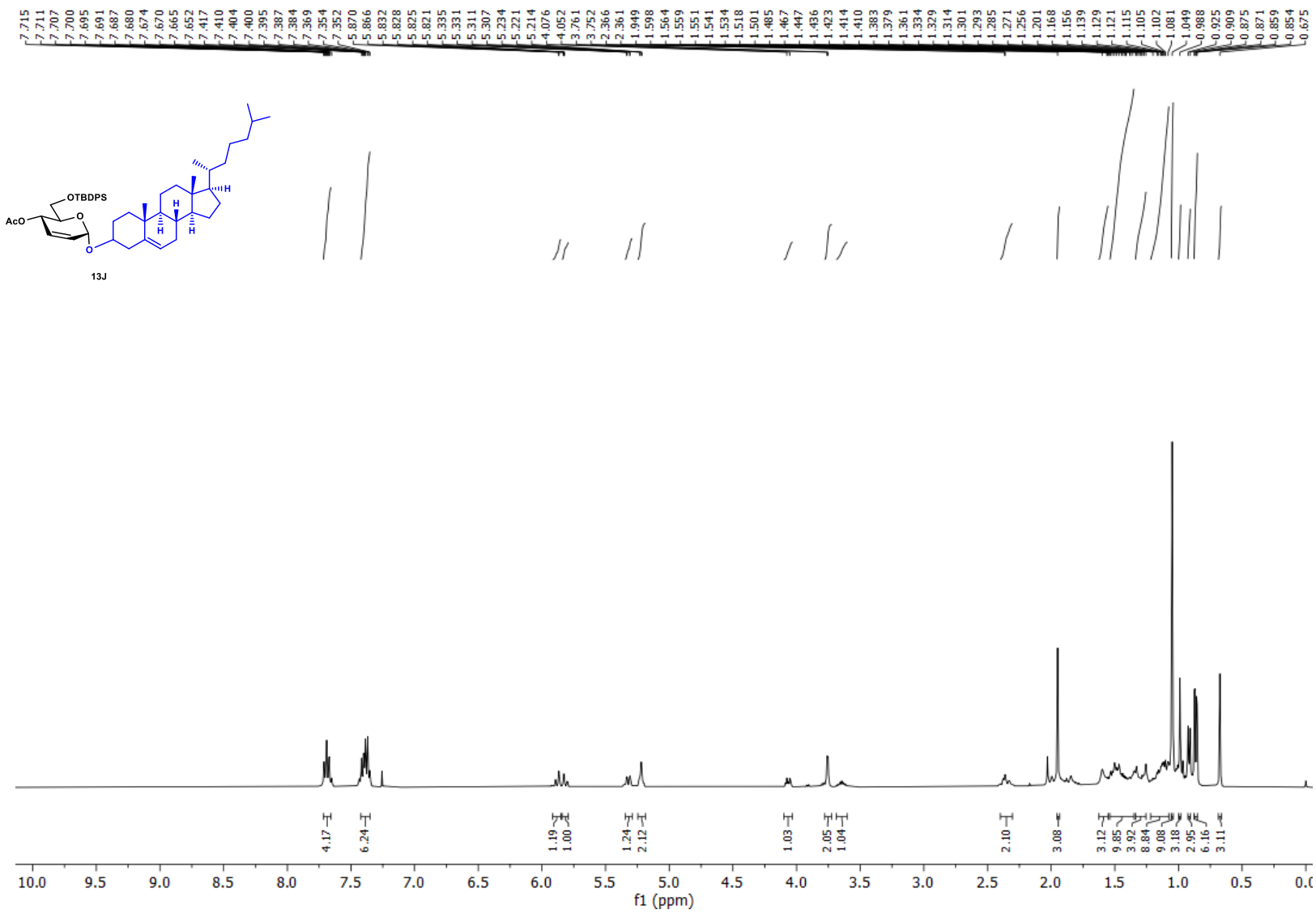
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of compound (13G)



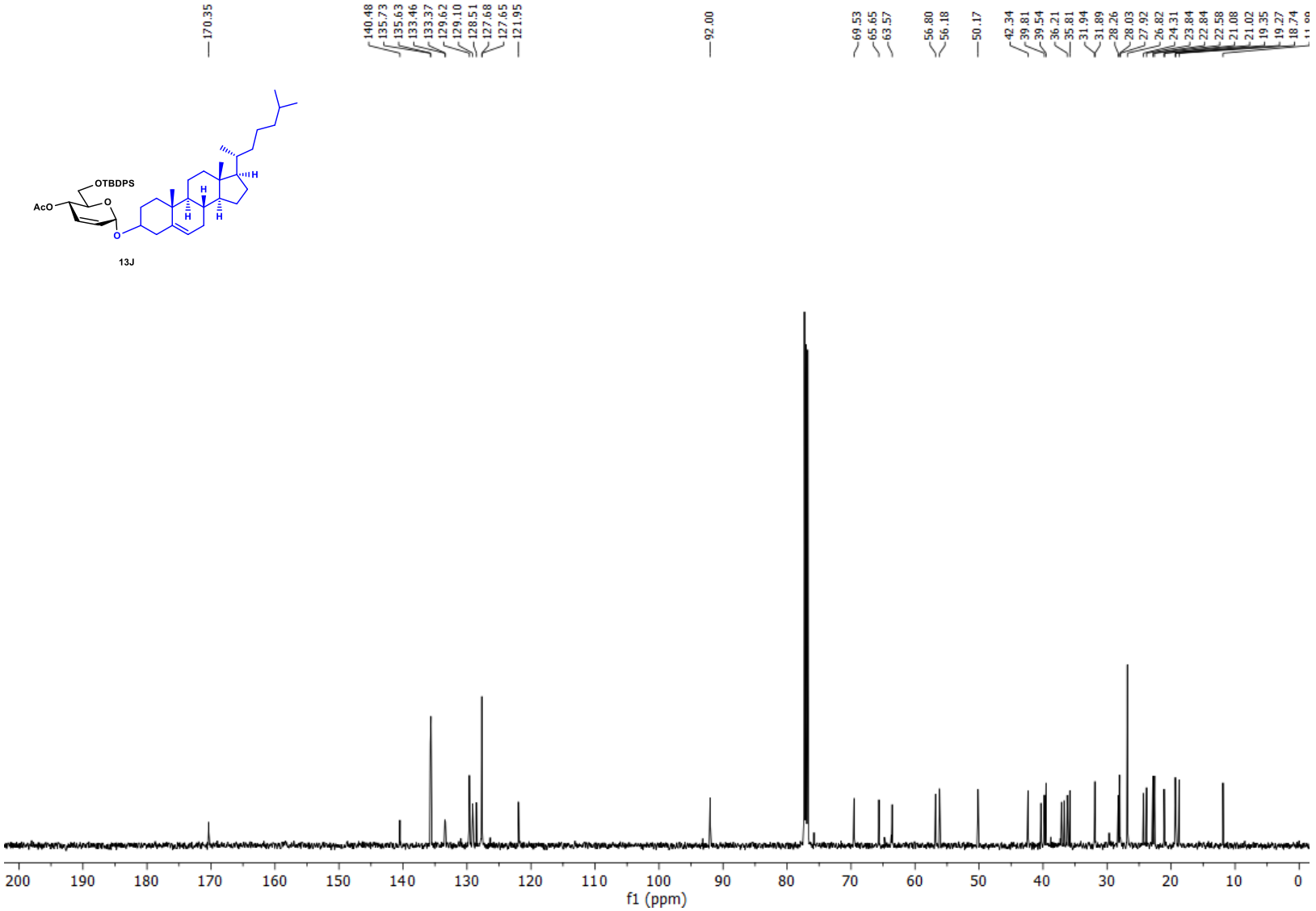
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (13G)



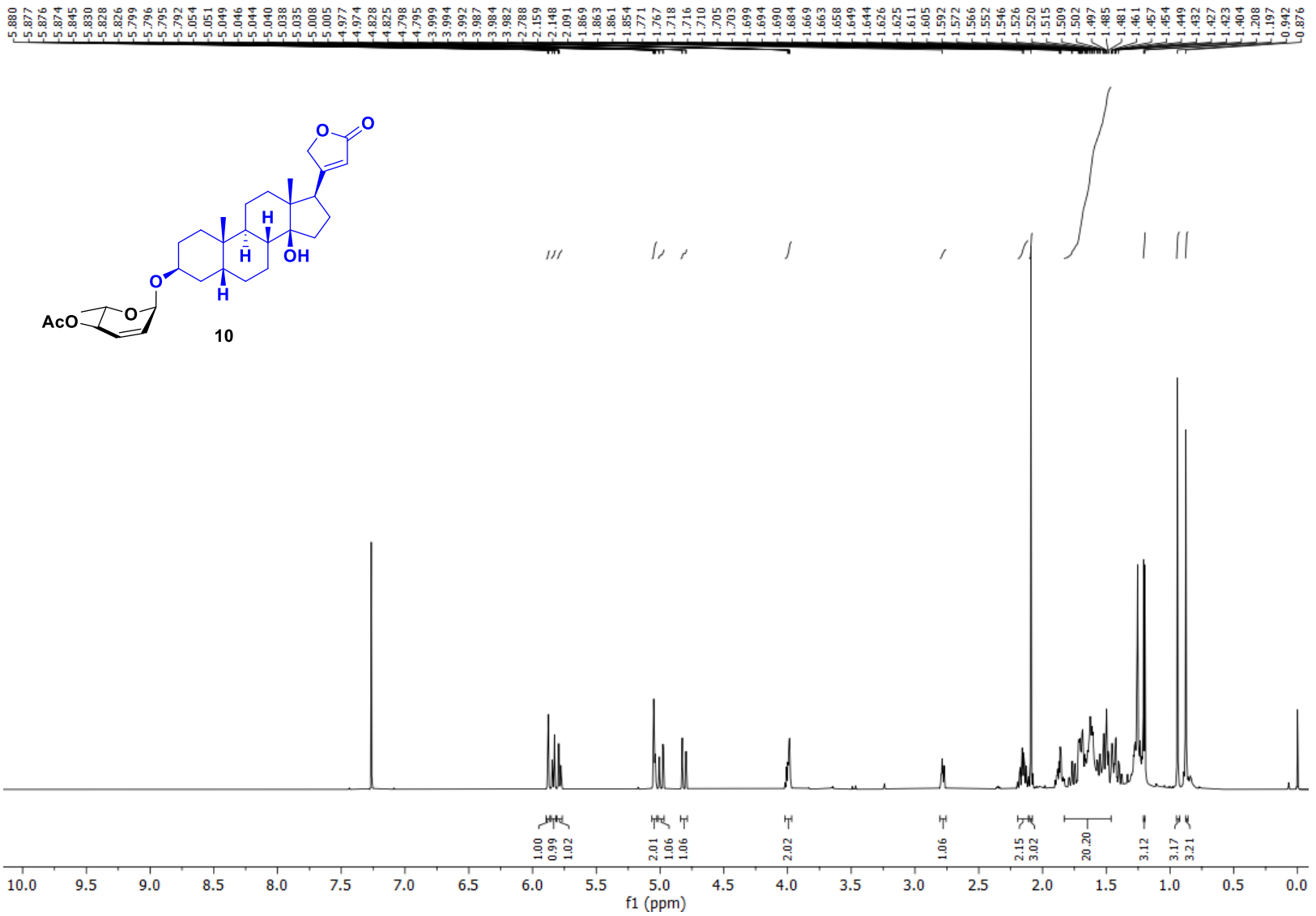
^{1}H (400 MHz, $CDCl_3$) NMR spectra of compound (13J)



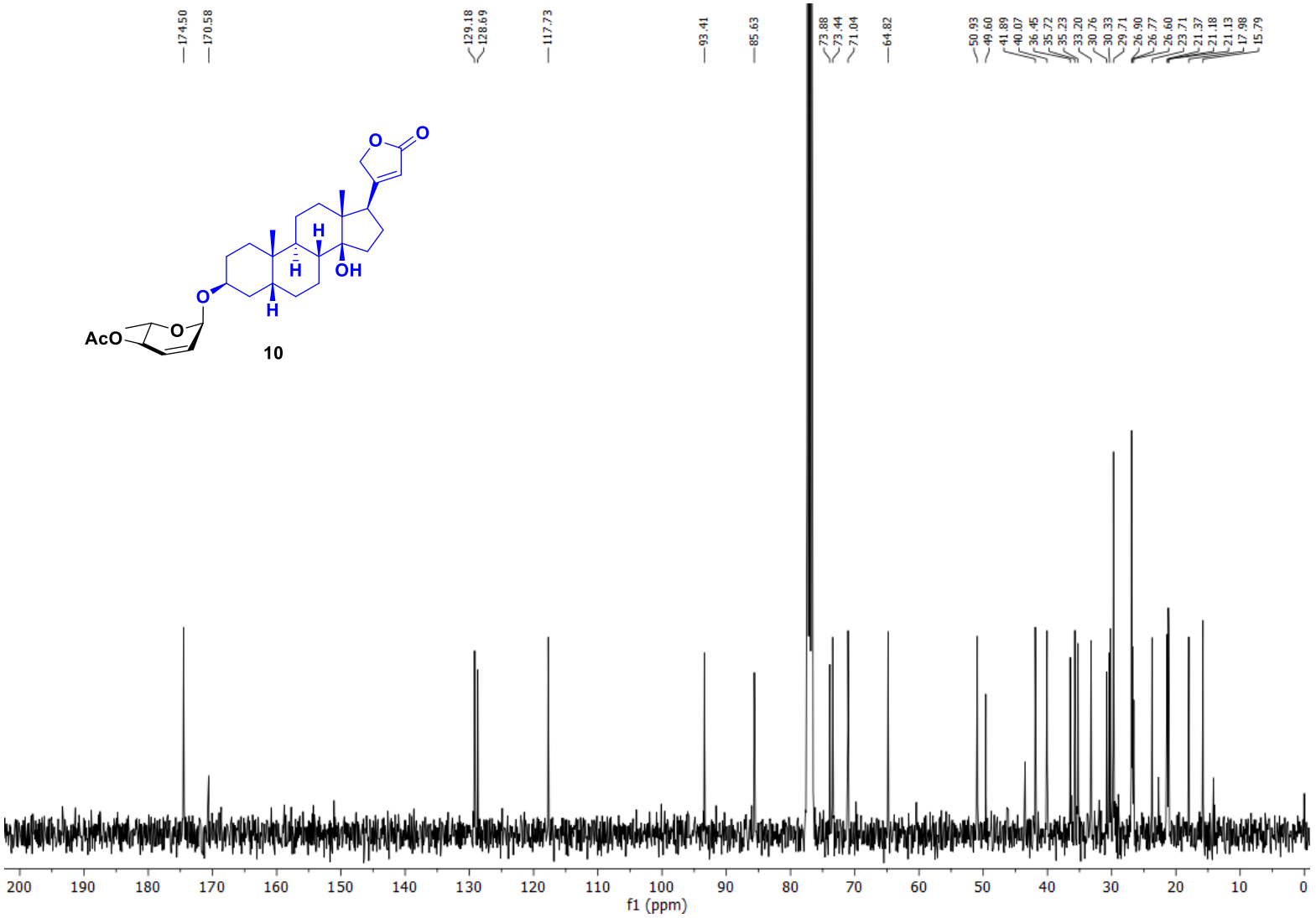
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of compound (13J)



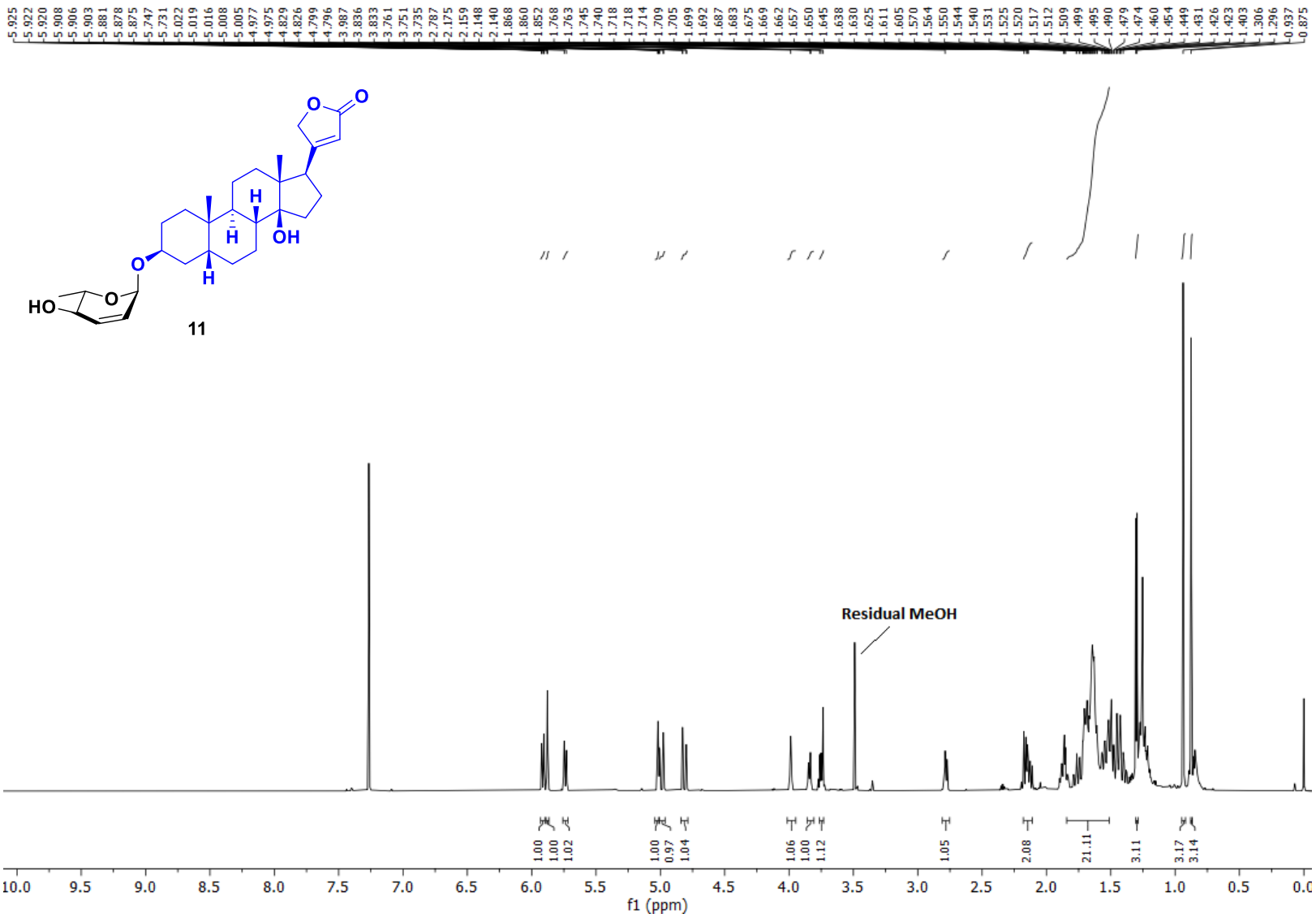
^{1}H (600 MHz, $CDCl_3$) NMR spectrum of compound (10)



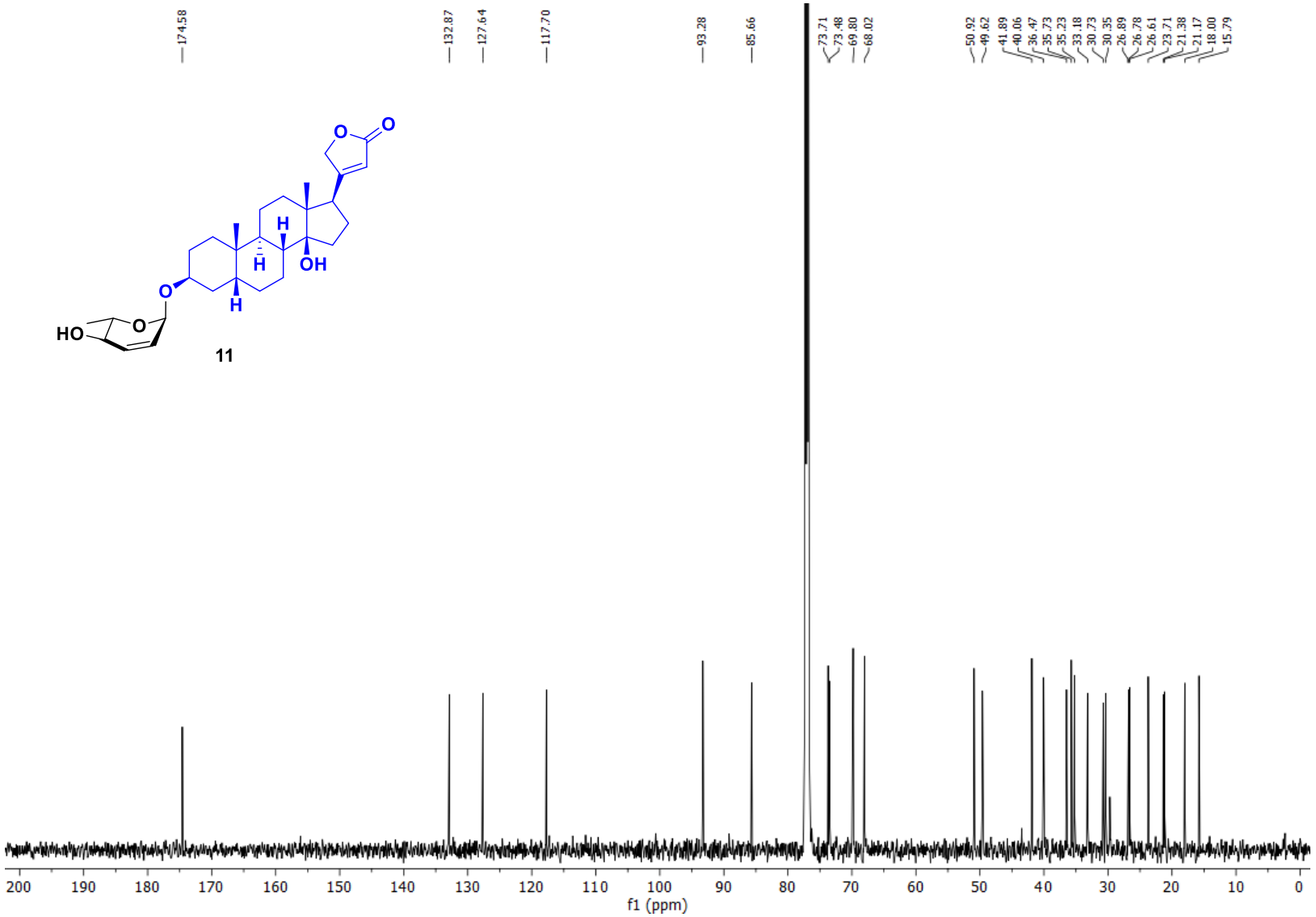
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) NMR spectrum of compound (10)



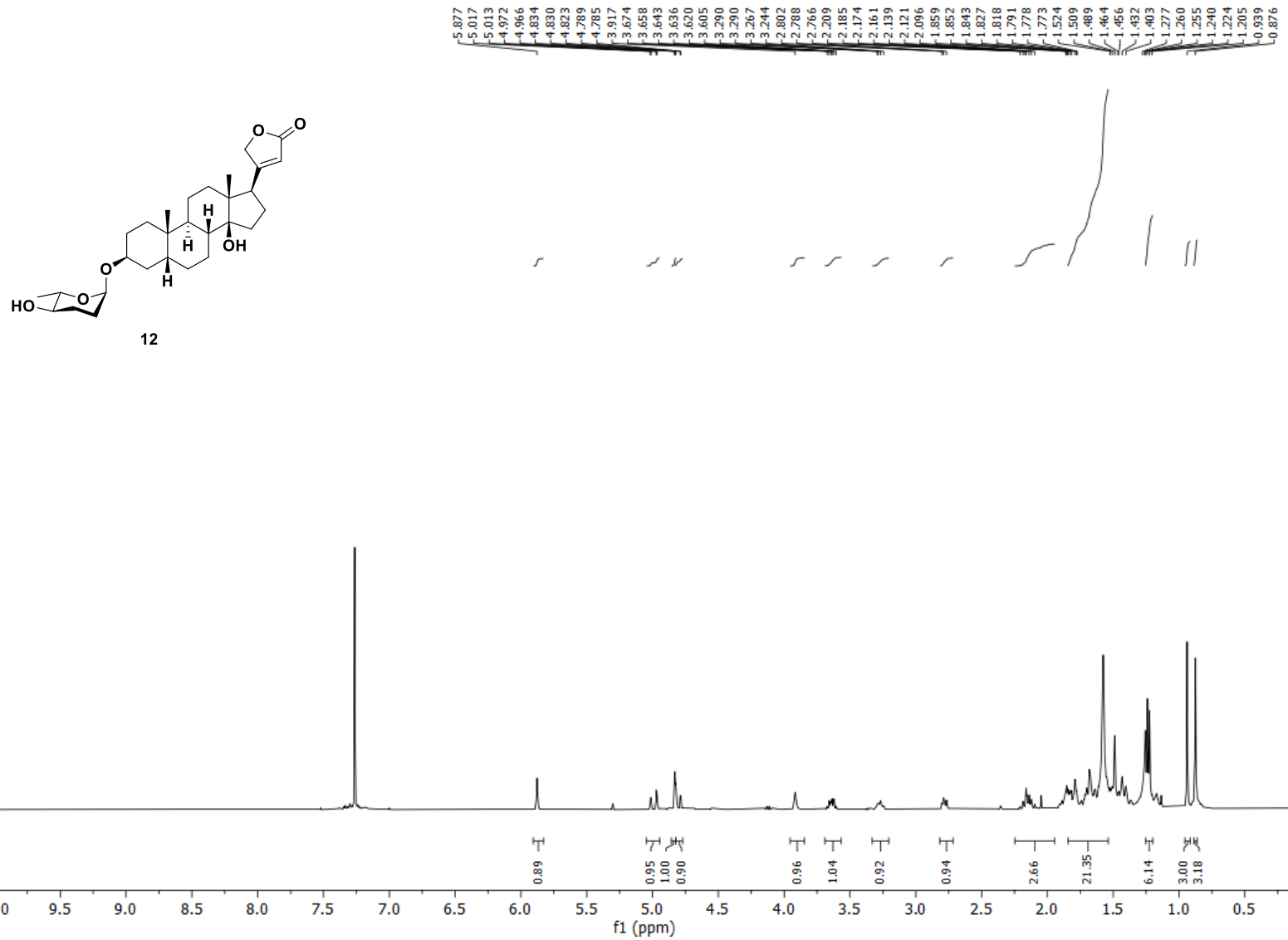
^{1}H (600 MHz, $CDCl_3$) NMR spectrum of compound (11)



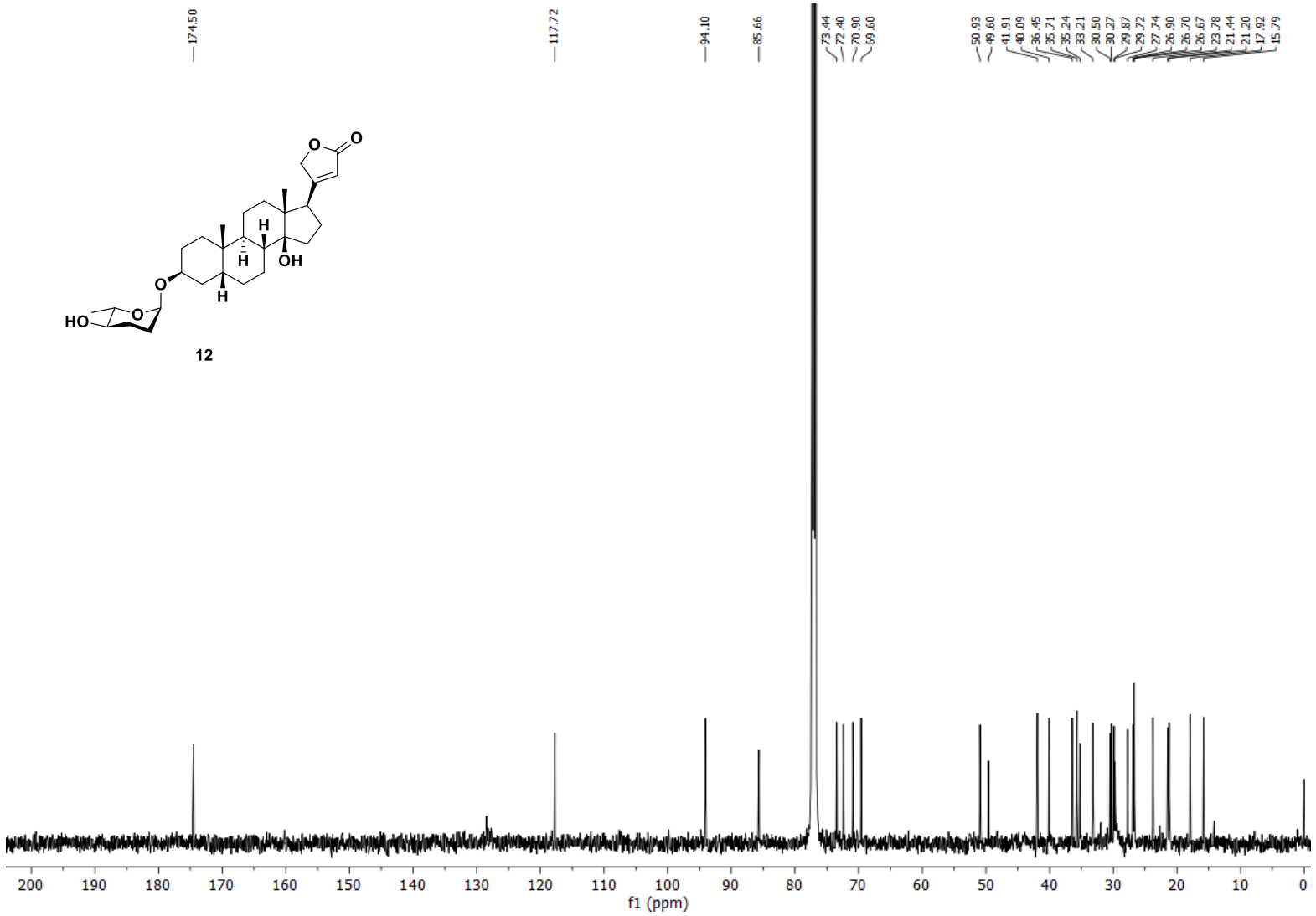
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$) NMR spectrum of compound (11)



^{1}H (400 MHz, $CDCl_3$) NMR spectra of compound (12)



$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of compound (12)



HRMS of compound **12**