Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of Chiral Azides from C-2 Substituted Glycals and their Transformation to C3-Glycoconjugates and α-Triazolo-Naphthalene Polyol

Ram Pratap Pandey [a] Mittali Maheshwari [a], and Nazar Hussain*[a]

Department of Medicinal Chemistry, Institute of Medical Sciences, Banaras Hindu University, Varanasi-221005, India.

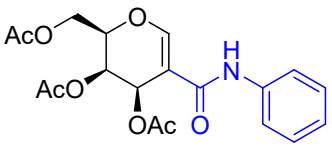
Email: nazar10@bhu.ac.in

General Consideration

^{1}H and ^{13}C NMR spectra were recorded using 400 to 600 MHz spectrometers with TMS as internal standards. Chemical shifts are expressed in parts per million (δ ppm). Silica gel-coated aluminum plates were used for TLC. The products were purified by column chromatography on silica gel (100-200 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. All product's exact masses were derived using HRMS having a QTOF analyzer. Reagents used were mostly purchased from Sigma Aldrich, TCI, and SRL.

Starting material used in the study

All the starting materials were synthesized according to the literature procedures.[1–5]



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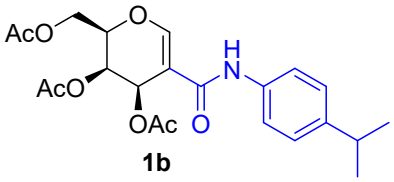

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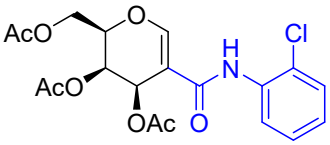

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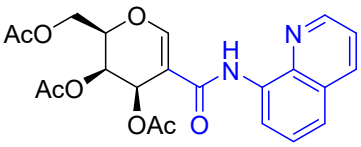

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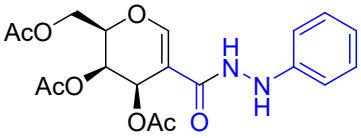

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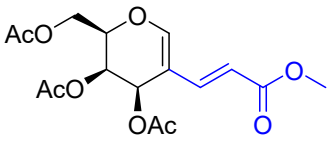

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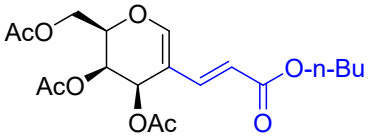

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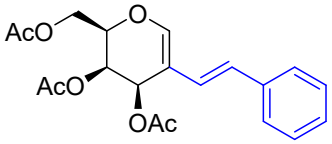

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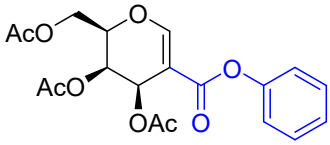

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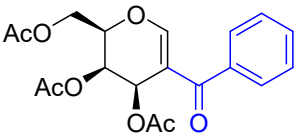

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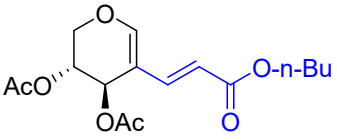

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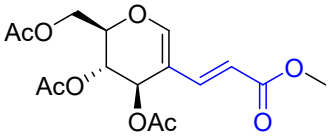

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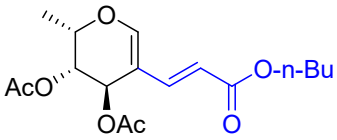

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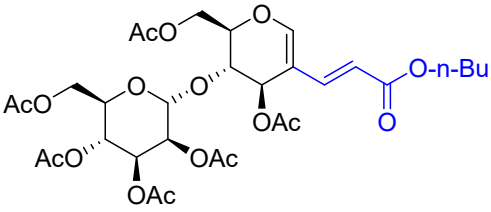

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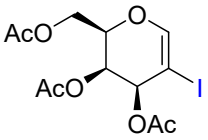

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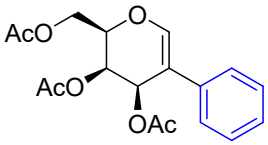

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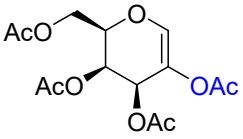
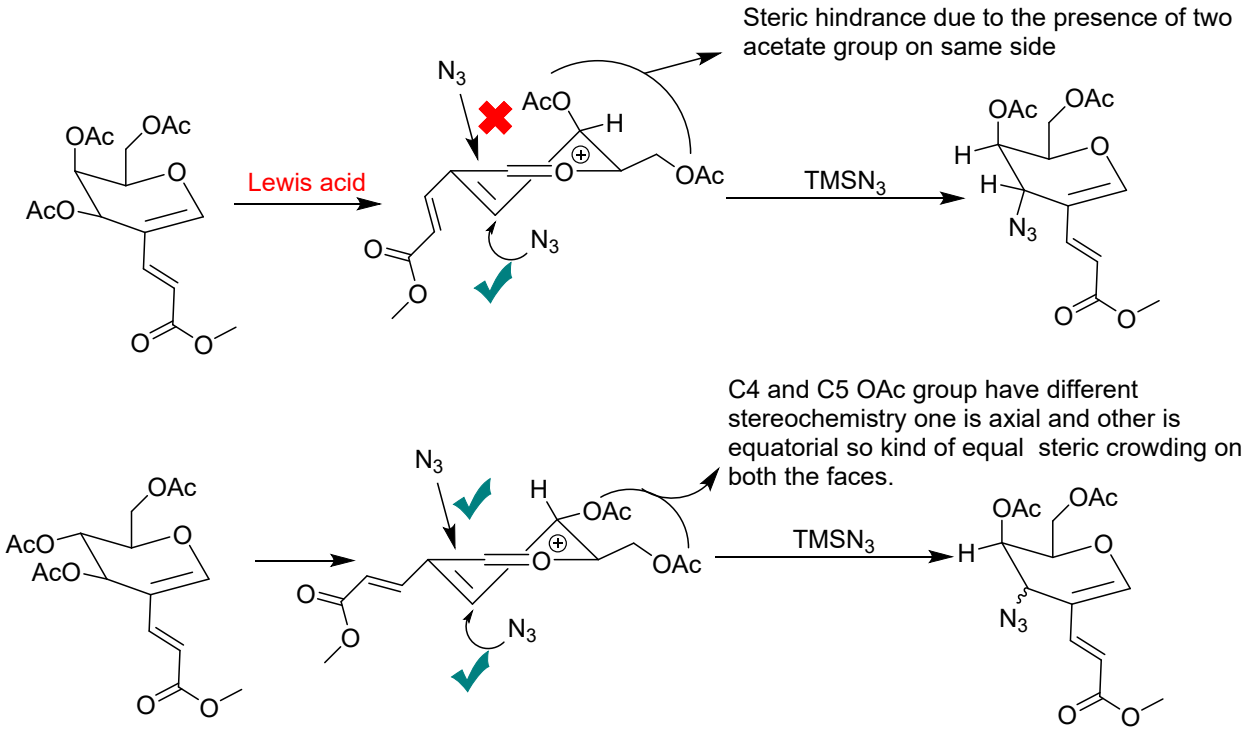
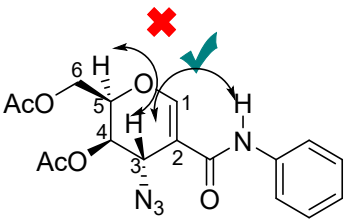


1q

Plausible reaction mechanism and reason for stereoselectivity of azido group at C3-position



2D-NMR Analysis



2a

HSQC Correlations of 2a

	^{1}H	^{13}C
H-1	7.64 (s, 1H)	152.6
H-2		107.1
H-3	4.46 (d, *J* = 1.6 Hz, 1H)	52.7
H-4	5.13 (s, 1H)	65.8
H-5	4.27 (d, *J* = 6.4 Hz, 1H)	71.3
H-6	4.32 (dd, *J* = 12.7, 5.1 Hz, 2H)	61.7

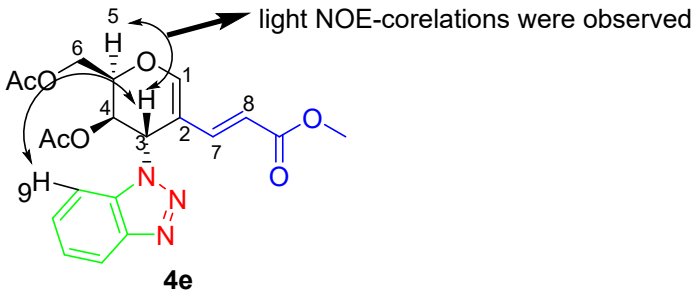
COSY Correlations of 2a

	^{1}H	^{1}H
H-1	7.64 (s, 1H)	
H-3	4.46 (d, *J* = 1.6 Hz, 1H)	5.13 (s, 1H, H4, *bs*)
H-4	5.13 (s, 1H, *bs*)	4.46 (d, *J* = 1.6 Hz, 1H, H3), 4.27 (m, 1H, H5)
H-5	4.27 (d, *J* = 6.4 Hz, 1H)	5.13 (s, 1H, H4, *bs,* 4.32 (dd, *J* = 12.7, 5.1 Hz, 2H, H6)
H-6	4.32 (dd, *J* = 12.7, 5.1 Hz, 2H)	4.27 (m, 1H, H5)

NOESY Correlations of 2a

	^{1}H	^{1}H
H-1	7.64 (s, 1H)	
H-3	4.46 (d, *J* = 1.6 Hz, 1H)	5.13 (s, 1H, H4, *bs*)
H-4	5.13 (s, 1H)	4.46 (d, *J* = 1.6 Hz, 1H), 4.27 (d, *J* = 6.4 Hz, 1H, H5)
H-5	4.27 (d, *J* = 6.4 Hz, 1H)	5.13 (s, 1H, H4), 4.32 (dd, *J* = 12.7, 5.1 Hz, 2H, H6)
H-6	4.32 (dd, *J* = 12.7, 5.1 Hz,	4.27 (d, *J* = 6.4 Hz, 1H, H6)

	2H)	



4e

HSQC Correlations of 4e

	^{1}H	**^{13}C**
H-1/C-1	7.30 (s, 1H)	153.1
C-2		105.3
H-3/C-3	5.44 (s, 1H)	50.4
H-4/C-4	4.99 (s, 1H),	66.2
H-5/C-5	4.57 (t, *J* = 5.7 Hz, 1H)	69.9
H-6/C-6	4.26 – 4.21 (m, 1H), 4.15 – 4. 11 (m,1H)	60.7
H-7/C-7	7.30 (s, 2H, *bs,* H1/H7),	140.3
H-8/C-8	5.06 (d, *J* = 15.8 Hz, 1H)	112.3,

COSY Correlations of 4e

	^{1}H	^{1}H
H-1	7.30 (s, 1H)	
H-3	5.44 (s, 1H),	4.99 (s, 1H)
H-4	4.99 (s, 1H),	5.44 (s, 1H), 4.57 (t, *J* = 5.7 Hz, 1H)
H-5	4.57 (t, *J* = 5.7 Hz, 1H)	4.99 (s, 1H), 4.26 – 4.21 (m, 1H), 4.15 – 4. 11

		(m,1H
H-6	4.26 – 4.21 (m, 1H), 4.15 – 4. 11 (m,1H)	4.57 (t, *J* = 5.7 Hz, 1H)
H-7	7.30 (s, 2H, *bs*),	5.06 (d, *J* = 15.8 Hz, 1H)
H-8	5.06 (d, *J* = 15.8 Hz, 1H)	7.30 (s, 2H, *bs*),

NOESY Correlations of 4e

	^{1}H	^{1}H
H-1	7.30 (s, 1H)	
H-3	5.44 (s, 1H),	4.99 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 1H),
H-4	4.99 (s, 1H),	5.44 (s, 1H), 4.57 (t, *J* = 5.7 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.15 – 4. 11 (m,1H)
H-5	4.57 (t, *J* = 5.7 Hz, 1H)	4.99 (s, 1H), 4.26 – 4.21 (m, 1H), 4.15 – 4. 11 (m,1H), 5.44 (s, 1H, very light NOE with H5).
H-6	4.26 – 4.21 (m, 1H), 4.15 – 4. 11 (m,1H)	4.99 (s, 1H), 4.99 (s, 1H),
H-7	7.30 (s, 2H, *bs*),	5.06 (d, *J* = 15.8 Hz, 1H)
H-8	5.06 (d, *J* = 15.8 Hz, 1H)	7.30 (s, 2H, *bs*),

Experimental procedures for all products

1. General procedure for the products (2a-2e, 3a-3c).

In an oven-dried round bottom flask substituted glycal **1a** (0.13 mmol, 1 equiv.), was dissolved in 2 mL of DCM at rt, and TMS-N_3 (0.19 mmol, 1.5 equiv.) was added. $BF_3.OEt_2$ (0.13 mmol, 1 equiv.) was added slowly at room temperature. Finally, the reaction mixture was stirred at the same temperature for 14 h. After the starting material

was converted as confirmed through TLC, the mixture was quenched with a saturated sodium bicarbonate solution (10 mL), and the organic layer was extracted with DCM (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

2. General procedure for the products (2f-2n).

In an oven-dried round bottom flask substituted glycal **1f** (0.14 mmol, 1 equiv.), was dissolved in 2 mL of DCM at rt, and TMS-N_3 (0.21 mmol, 1.5 equiv.) was added. $BF_3.OEt_2$ (0.14 mmol, 1 equiv.) was added slowly at room temperature. Finally, the reaction mixture was stirred at 60 ^oC for 10 h. After the starting material was converted as confirmed through TLC, the mixture was cooled at room temperature, quenched with saturated sodium bicarbonate (10 mL), and the organic layer was extracted with DCM (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

3. General procedure for the products (4a,4b)

In an oven-dried round bottom flask product **2i** (0.13 mmol, 1 equiv.), was dissolved in 2 mL of dry ACN at rt under Ar. To this mixture was added CsF (0.26 mmol, 2 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate (0.20 mmol, 1.5 equiv.) subsequently. Then the reaction mixture was stirred for 12 h at 60 ^oC. After converting the starting material as confirmed through TLC, the organic layer was extracted with EtOAc (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

4. General procedure for the products (4c,4d)

In an oven-dried round bottom flask product **2b** (0.12 mmol, 1 equiv.), was dissolved in 2 mL of ACN at rt. To this mixture was added ethynyl benzene (0.18 mmol, 1.5 equiv.),

CuI (0.02 mmol, 20 mol %) and N,N- Diisopropylethylamine (0.18 mmol, 1.5 equiv.) subsequently. Then the reaction mixture was stirred for 8 h. After converting the starting material as confirmed through TLC, the organic layer was extracted with EtOAc (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

5. General procedure for the products (4e-4g)

In an oven-dried round bottom flask product **2f** (0.15 mmol, 1 equiv.), was dissolved in 2 mL of ACN at rt. To this mixture, CsF (0.30 mmol, 2 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.23 mmol, 1.5 equiv.), was added and the reaction mixture was stirred at 60 ^{o}C for 12 h. After converting the starting material as confirmed through TLC, the organic layer was extracted with EtOAc (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

6. General procedure for the products (4h)

In an oven-dried round bottom flask product **2a** (0.13 mmol, 1 equiv.), was dissolved in 2 mL of THF: H_2O (5:1) at rt. PPh3 (0.26 mmol, 2 equiv.) was added to this mixture. Finally, the reaction mixture was stirred at 60^{o} C for 2 h. After the complete conversion of starting material as confirmed through TLC, the reaction mixture was diluted with ethyl acetate, and washed with brine solution. The organic layer was extracted with ethyl acetate and dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent. The C_3-amine **2aa** obtained was directly used in the next step without characterization. Again, in an oven-dried round bottom flask product **2aa** (0.14 mmol, 1 equiv.), was dissolved in 2 mL of dry DCM at rt. To this mixture were added indomethacin (0.17 mmol, 1.2 equiv.), EDCI.HCl (0.26 mmol, 1.8 equiv.), DMAP (0.04 mmol, 0.30 equiv.) and DIPEA (0.22 mmol, 1.5equiv.) and the reaction mixture was stirred for 12 h. After the starting material was converted as confirmed through TLC, the organic layer was

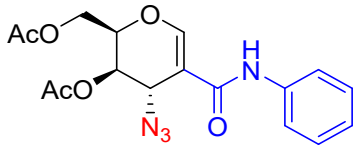
extracted with DCM (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

7. General procedure for the products (4i)

In an oven-dried round bottom flask product **4d** (0.09 mmol, 1 equiv.), was dissolved in 2 mL of dry ACN at rt under Ar. To this mixture was added CsF (0.19 mmol, 2 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.14 mmol, 1.5 equiv.), and the reaction mixture was stirred at 60 ^{o}C for 10 h. After the starting material was converted as confirmed through TLC, the organic layer was extracted with EtOAc (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

Characterization data:

((2R,3R,4S)-3-acetoxy-4-azido-5-(phenylcarbamoyl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate

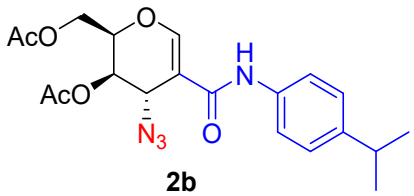


2a

The title compound **2a** was prepared according to the general procedure (1) and purified by column chromatography giving a pale yellow sticky solid (42.6 mg, 89% yield).**R_f** (Hexane/ EtOAc = 60/40): 0.42; $[\alpha]_D^{24}$ = +67.4 (c = 0.6, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)**) δ 7.64 (s, 1H), 7.53(s, 1H), 7.52 (t, *J* = 7.1 Hz, 2H), 7.33 (m, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.13 (s, 1H), 4.46 (d, *J* = 1.6 Hz, 1H), 4.34 – 4.30 (m, 2H), 4.28 – 4.25 (m, 1H), 2.13 (s, 3H), 2.10 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 170.5, 169.7, 163.9, 152.5, 137.5, 129.1, 129.1, 124.7, 120.4, 120.4, 107.1, 71.3, 65.8, 61.7,

52.7, 20.7, 20.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{18}N_4O_6$ 375.1305; found 375.1302.

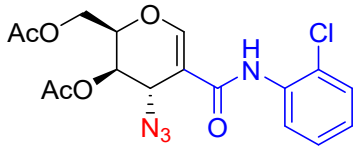
((2R,3R,4S)-3-acetoxy-4-azido-5-((4-isopropylphenyl)carbamoyl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate



2b

The title compound **2b** was prepared according to the general procedure (1) and purified by column chromatography giving a pale yellow sticky solid (39..9 mg, 83% yield).**R_f** (Hexane/ EtOAc = 70/30): 0.52; $[\alpha]^{24.6}$ D = +52.0 (c = 0.9, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.55 (s, 1H), 7.38 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.05 (s, 1H), 4.39 (d, *J* = 1.9 Hz, 1H), 4.27 – 4.22 (m, 2H), 4.21 – 4.16 (m, 1H), 2.83 – 2.79 (m, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 168.7, 162.8, 151.3, 144.5, 134.1, 126.0, 126.0, 119.6, 119.6, 106.1, 70.3, 64.8, 60.7, 51.7, 32.6, 23.0, 23.0, 19.7, 19.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{24}N_4O_6$ 417.1774; found 417.1771.

((2R,3R,4S)-3-acetoxy-4-azido-5-((2-chlorophenyl)carbamoyl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate

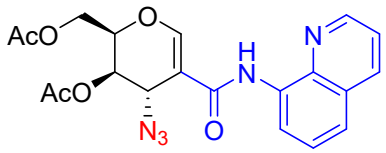


2c

The title compound **2c** was prepared according to the general procedure (1) and purified by column chromatography giving white sticky solid (41.0 mg, 86% yield). **R_f** (Hexane/ EtOAc = 70/30): 0.46**;** $[\alpha]^{24}$ D = +70.4 (c = 0.5, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.99 (s, 1H), 7.63 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 5.08 (s, 1H, bs), 4.39 (s, 1H), 4.24 (s,

3H, bs), 2.04 (s, 3H), 2.02 (s, 3H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 168.7, 162.7, 152.2, 133.4, 128.0, 126.8, 123.8, 121.9, 120.7, 105.9, 70.5, 64.8, 60.7, 51.9, 19.7, 19.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{18}ClN_4O_6$ 409.0915; found 409.0912.

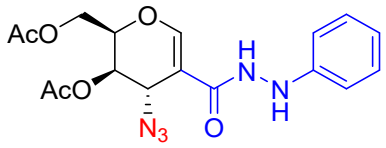
((2R,3R,4S)-3-acetoxy-4-azido-5-(quinolin-8-ylcarbamoyl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate



2d

The title compound **2d** was prepared according to the general procedure (1) and purified by column chromatography giving a pale-yellow sticky solid (37.5 mg, 78% yield). **R_f** (Hexane/ EtOAc = 70/30): 0.59**;** $[\alpha]^{24.3}$ D = +85.8 (c = 0.6, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.25 (s, 1H), 8.74 (d, J= 7.8Hz, 1H), 8.66 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.75 (s, 1H), 7.47 (d, *J* = 6.8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.37 (m, 1H), 5.10 (s, 1H, bs), 4.55 (s, 1H), 4.27 (s, 3H, bs), 2.06 (s, 3H), 2.03 (s, 3H). **^{13}C DEPT NMR (151 MHz, $CDCl_3$)** δ 152.8, 148.4, 136.4, 127.4, 121.8, 121.6, 116.5, 71.3, 66.0, 61.9, 53.0, 20.7, 20.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{19}N_5O_6$ 426.1414; found 426.1411.

((2R,3R,4S)-3-acetoxy-4-azido-5-(2-phenylhydrazine-1-carbonyl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate

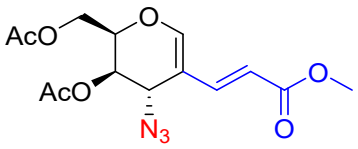


2e

The title compound **2e** was prepared according to the general procedure (1) and purified by column chromatography giving a yellow sticky solid (34.5 mg, 72% yield). **R_f** (Hexane/ EtOAc = 70/30): 0.67**;** $[\alpha]^{24.5}$ D = +65.2 (c = 0.5, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.36 (s, 1H), 7.27 (m, *J* = 7.9 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.06 (s, 1H, bs), 4.38 (d, *J* = 2.2 Hz, 1H), 4.27 – 4.23 (m, 2H),

4.21 – 4. 19 (m, 1H), 2.06 (s, 3H), 2.03 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 168.7, 162.8, 151.5, 136.5, 128.1, 128.1, 123.7, 119.4, 119.4, 106.1, 70.3, 64.8, 60.7, 51.7, 19.7, 19.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{22}N_5O_6$ 390.1414; found 391.0009.

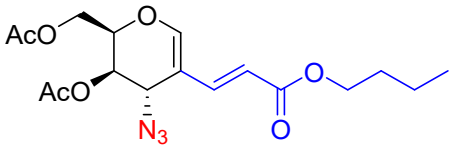
methyl(E)-3-((2R,3R,4S)-3-acetoxy-2-(acetoxymethyl)-4-azido-3,4-dihydro-2H-pyran-5-yl)acrylate



2f

The title compound **2f** was prepared according to the general procedure (2) and purified by column chromatography giving a light bluish gummy solid (41.0 mg, 86% yield). **R_f** (Hexane/ EtOAc = 70/30): 0.39**;** $[\alpha]_{24}$ D = +84.9 (c = 0.8, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.26 (d, *J* = 15.8 Hz, 1H), 7.03 (s, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 5.02 (s, 1H, bs), 4.25 – 4. 18 (m, 3H), 4.00 (s, 1H, bs), 3.69 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 168.7, 166.3, 152.1, 140.6, 113.0, 106.7, 70.4, 65.0, 60.8, 51.4, 50.6, 19.7, 19.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{14}H_{17}N_3O_7$ 340.1145; found 340.1141.

butyl(E)-3-((2R,3R,4S)-3-acetoxy-2-(acetoxymethyl)-4-azido-3,4-dihydro-2H-pyran-5-yl)acrylate

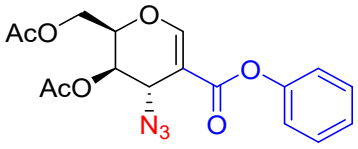


2g

The title compound **2g** was prepared according to the general procedure (2) and purified by column chromatography giving a colorless sticky solid (40.4 mg, 84% yield). **R_f** (Hexane/ EtOAc = 60/40): 0.52**;** $[\alpha]_{25.0}$ D = +83.4 (c = 0.8, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.24 (d, *J* = 15.8 Hz, 1H), 7.03 (s, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 5.01 (s, 1H),

4.25 – 4.21 (m, 3H), 4.11 – 4.08 (m, 2H), 4.00 (s, 1H, bs), 2.05 (s, 3H), 2.01 (s, 3H), 1.60 – 1.57 (m, 2H), 1.36 – 1.32 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). **13C NMR (151 MHz, CDCl3)** δ 169.4, 168.7, 166.0, 152.0, 140.3, 113.5, 106.7, 70.4, 65.1, 63.4, 60.8, 51.5, 29.8, 19.7, 19.6, 18.2, 12.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{24}N_3O_7$ 382.3930; found 382.1611.

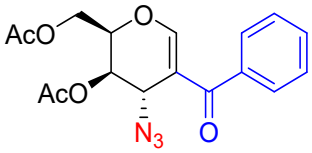
Phenyl (2R,3R,4S)-3-acetoxy-2-(acetoxymethyl)-4-azido-3,4-dihydro-2H-pyran-5-carboxylate



2i

The title compound **2i** was prepared according to the general procedure (2) and purified by column chromatography giving a pale-yellow gummy solid (38 mg, 81% yield). **R_f** (Hexane/ EtOAc = 70/30): 0.41**;** $[\alpha]^{24.6}$ D = +52.4 (c = 0.9, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (s, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.07 (m, 2H), 5.00 (s, 1H, bs), 4.46 (d, *J* = 2.4 Hz, 1H), 4.32 – 4.30 (m, 1H), 4.24 (d, *J* = 5.7 Hz, 2H), 2.05 (s, 6H). **13C NMR (151 MHz, CDCl3)** δ 169.4, 168.5, 163.8, 157.4, 149.3, 128.5, 128.5, 125.0, 120.6, 120.6, 102.3, 70.6, 64.4, 60.6, 51.4, 19.7, 19.6. **HRMS (ESI)** m/z: $[M+NH_4]^+$ calcd for $C_{17}H_{17}N_3O_7$ 393.1410; found 393.1421.

((2R,3R,4S)-3-acetoxy-4-azido-5-benzoyl-3,4-dihydro-2H-pyran-2-yl)methyl acetate

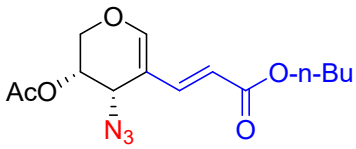


2j

The title compound **2j** was prepared according to the general procedure (2) and purified by column chromatography giving a pastel-yellow sticky solid (37.5 mg, 78% yield). **R_f** (Hexane/ EtOAc = 70/30):0.47; $[\alpha]^{24}$ D = +49.5 (c = 0.5, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 (s, 1H), 7.56 (t, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 6.0 Hz, 1H), 7.39 (m, 2H), 5.06 (s, 1H, bs), 4.70 (d, *J* = 2.4 Hz, 1H), 4.34 (t, *J* = 6.2 Hz, 1H), 4.27 – 4.20 (m, 2H),

2.05 (s, 3H), 2.02 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 193.3, 169.4, 168.4, 159.9, 136.9, 130.9, 127.8, 127.8, 127.5, 127.5, 112.0, 70.8, 64.3, 60.7, 50.4, 19.7, 19.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{17}N_3O_6$ 360.1196; found 360.3243 .

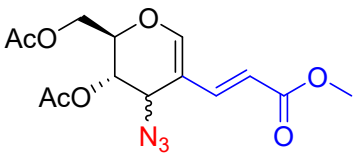
Butyl (E)-3-((3S,4S)-3-acetoxy-4-azido-3,4-dihydro-2H-pyran-5-yl)acrylate



2k

The title compound **2k** was prepared according to the general procedure (2) and purified by column chromatography giving a colorless gummy solid (36.0 mg, 76% yield). **R_f** (Hexane/ EtOAc = 70/30):0.57; $[\alpha]^{24.1}$ D = +81.1 (c = 0.5, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.24 (d, *J* = 15.8 Hz, 1H), 7.03 (s, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 4.97 (s, 1H), 4.29 (d, *J* = 12.8 Hz, 1H), 4.11 – 4.07 (m, 2H), 3.99 – 3.95 (m, 2H), 2.01 (s, 3H), 1.58 (d, *J* = 7.5 Hz, 2H), 1.35 (d, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.8, 166.1, 152.7, 140.7, 112.9, 106.3, 65.6, 63.3, 63.2, 50.8, 29.8, 19.8, 18.2, 12.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{14}H_{19}N_3O_5$ 310.1403; found 310.1404 .

Methyl (E)-3-((2R,3S)-3-acetoxy-2-(acetoxymethyl)-4-azido-3,4-dihydro-2H-pyran-5-yl)acrylate

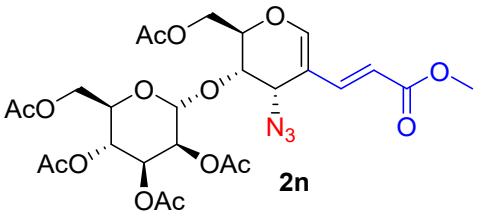


2l

The title compound **2l** was prepared according to the general procedure (2) and purified by column chromatography giving a colourless gummy solid (37.5 mg, 79% yield). **R_f** (Hexane/ EtOAc = 60/40):0.54**; ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.14 (d, *J* = 16.3 Hz, 1H), 6.19 (s, 1H), 6.01 (d, *J* = 16.3 Hz, 1H), 5.70 (s, 1H, bs), 5.46 (d, *J* = 9.6 Hz, 1H), 4.28 (t,

J = 3.9 Hz, 2H), 4.22 – 4. 19 (m, 1H), 3.78 (s, 3H), 2.12 (s, 3H), 2.12 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 170.5, 169.6, 167.3, 152.6, 140.6, 120.6, 114.1, 71.5, 67.3, 61.3, 53.2, 51.6, 20.6, 20.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{14}H_{17}N_3O_7$ 340.1145; found 340.1141.

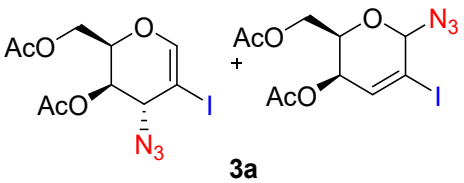
(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-(((2R,3S,4S)-2-(acetoxymethyl)-4-azido-5-((E)-3-butoxy-3-oxoprop-1-en-1-yl)-3,4-dihydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate



2n

The title compound **2n** was prepared according to the general procedure (2) and purified by column chromatography giving a white sticky solid (36.0 mg, 79% yield). **R_f** (Hexane/ EtOAc = 50/50):0.51; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.23 (d, *J* = 15.8 Hz, 1H), 6.93 (m, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 5.42 – 5.37 (m, 1H), 5.31 (d, *J* = 3.7 Hz, 1H), 5.02 (t, *J* = 9.8 Hz, 1H), 4.82 – 4.79 (m, 1H), 4.30 – 4.27 (m, 1H), 4.26 – 4.20 (m, 2H), 4.16 (s, 1H), 4.02 (d, *J* = 11.8 Hz, 2H), 3.99 – 3.91 (m, 2H), 3.70 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.96 (s, 6H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.5, 169.4, 169.1, 168.9, 168.5, 166.2, 152.0, 139.7, 113.1, 107.4, 92.4, 74.6, 72.4, 71.1, 69.4, 68.5, 67.5, 67.1, 60.6, 53.9, 50.7, 19.7, 19.7, 19.7, 19.6, 19.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{33}N_3O_{15}$ 628.1990; found 628.1979.

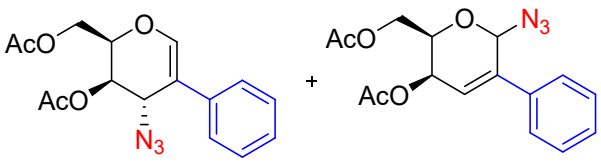
((2R,3R,4R)-3-acetoxy-4-azido-5-iodo-3,4-dihydro-2H-pyran-2-yl)methyl acetate



3a

The title compound **3a** was prepared according to the general procedure (1) and purified by column chromatography giving a white sticky solid (41.2 mg, 86% yield). **R_f** (Hexane/ EtOAc = 70/30):0.37; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.84 (s, 0.58H), 6.66 (d, *J* = 5.6 Hz, 1H), 5.57 (s, 1H), 4.98 (dd, *J* = 2.2, 1.2 Hz, 0.58H), 4.91 (dd, *J* = 5.8, 2.5 Hz, 1H), 4.32 (ddd, *J* = 7.5, 5.1, 2.5 Hz, 1H), 4.20 – 4.10 (m, 4H), 3.87 (d, *J* = 2.2 Hz, 0.58H), 2.06 (s, 1.7H), 2.03 (s, 4.85H), 2.02 (s, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 170.6, 170.4, 170.0, 169.8, 149.8, 134.9, 100.0, 90.4, 69.6, 68.2, 67.9, 64.8, 62.3, 62.3, 61.9, 61.3, 20.7, 20.7, 20.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{10}H_{12}IN_3O_5$ 381.9900; found 381.9923.

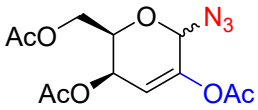
((2R,3R,4S)-3-acetoxy-4-azido-5-phenyl-3,4-dihydro-2H-pyran-2-yl)methyl acetate



3b

The title compound **3b** was prepared according to the general procedure (1) and purified by column chromatography giving a pink gummy solid (39.0 mg, 82% yield). **R_f** (Hexane/ EtOAc = 70/30):0.54; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 3.4 Hz, 3.76H), 7.28 (dd, *J* = 13.0, 7.1 Hz, 3.64H), 7.21 (d, *J* = 7.0 Hz, 0.75H), 7.02 (s, 0.83H), 6.27 (d, *J* = 5.7 Hz, 1H), 6.02 (s, 0.98H), 5.21 (dd, *J* = 5.6, 2.6 Hz, 1H), 5.07 (s, 0.85H), 4.40 (ddd, *J* = 7.4, 4.8, 2.7 Hz, 1H), 4.31 – 4.23 (m, 5H), 4.17 (ddd, *J* = 17.3, 12.2, 6.2 Hz, 2H), 2.07 (s, 2.16H), 2.05 (s, 2.60H), 2.04 (s, 2H), 2.03 (s, 2.88H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.7, 169.5, 169.3, 169.0, 143.4, 139.1, 134.9, 134.3, 129.9, 128.2, 128.0, 127.9, 127.8, 126.3, 125.3, 124.0, 120.5, 108.3, 84.6, 69.1, 67.5, 67.1, 66.2, 62.5, 61.5, 61.2, 53.8, 37.7, 19.8, 19.8. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{16}H_{17}N_3O_5$ 354.1066; found 354.1047.

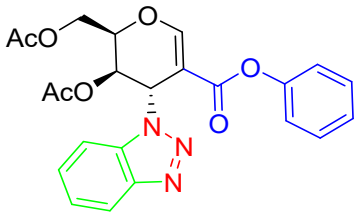
(2R,3R,6S)-2-(acetoxymethyl)-6-iodo-3,6-dihydro-2H-pyran-3,5-diyl diacetate



3c

The title compound **3c** was prepared according to the general procedure (1) and purified by column chromatography giving a yellow gummy solid (36.5.0 mg, 77% yield). **R_f** (Hexane/ EtOAc = 70/30):0.42; **^{1}H NMR (600 MHz, $CDCl_3$** δ 6.93 (dd, *J* = 10.7, 1.7 Hz, H), 6.14 (dd, *J* = 10.7, 2.5 Hz, 1H), 5.94 (d, *J* = 6.2 Hz, 0.76H), 5.56 (s, 0.69H), 5.34 (s, 1H), 5.19 (dd, *J* = 6.2, 2.4 Hz, 0.75H), 4.84 – 4.81 (m, 1H), 4.33 – 4.28 (m, 2H), 4.23 – 4. 16 (m, 3H), 2.13 (s, 3H), 2.04 (s, 3.74H), 2.02 (s, 4.48H) **^{13}C NMR (151 MHz, $CDCl_3$)** δ 185.6, 169.6, 169.6, 169.2, 166.6, 146.7, 146.3, 125.0, 111.4, 86.5, 82.8, 67.8, 67.2, 63.2, 62.9, 61.1, 20.0, 19.7, 19.7. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}N_3O_7$ 336.0808; found 336.0801.

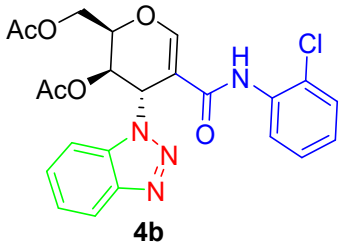
Phenyl (2R,3R,4S)-3-acetoxy-2-(acetoxymethyl)-4-(1H-benzo[d][1,2,3]triazol-1-yl)-3,4-dihydro-2H-pyran-5-carboxylate



4a

The title **4a** compound was prepared according to the general procedure (3) and purified by column chromatography giving pale yellow sticky solid (46.5 mg, 77% yield). **R_f** (Hexane/ EtOAc = 70/30):0.35; $[\alpha]^{24.1}$ D = +82.8 (c = 0.5, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.18 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 5.65 (s, 1H, bs), 5.08 (s, 1H, bs), 4.91 (t, *J* = 6.2 Hz, 1H), 4.32– 4.24 (m, 2H), 2.19 (s, 3H), 1.98 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.3, 169.2, 163.2, 157.9, 149.2, 144.8, 132.1, 128.3, 128.3, 127.4, 124.9, 123.6, 120.5, 120.5, 119.0, 108.9, 100.7, 70.7, 65.9, 60.5, 49.4, 19.8, 19.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{21}N_3O_7$ 452.1458; found 452.1451.

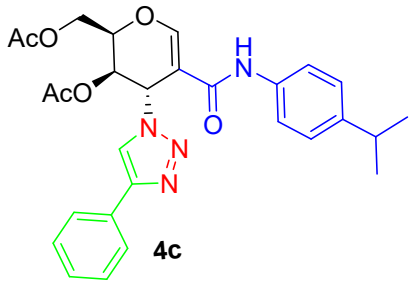
((2R,3R,4S)-3-acetoxy-4-(1H-benzo[d][1,2,3]triazol-1-yl)-5-((2-chlorophenyl)carbamoyl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate



4b

The title compound **4b** was prepared according to the general procedure (3) and purified by column chromatography giving light yellow sticky solid (47.0 mg, 79% yield). **R_f** (Hexane/ EtOAc = 80/20):0.52; $[\alpha]^{24.6}$ D = +77.3 (c = 0.8, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 5.83 (s, 1H, bs), 5.06 (s, 1H), 4.73 (t, *J* = 6.2 Hz, 1H), 4.34 – 4.19 (m, 2H), 2.17 (s, 3H), 1.97 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.3, 169.3, 162.4, 151.4, 133.2, 132.0, 128.0, 127.3, 126.7, 123.8, 121.8, 120.5, 119.0, 109.0, 106.0, 70.2, 65.9, 60.8, 49.5, 19.8, 19.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{21}ClN_4O_6$ 485.1228; found 485.1213.

((2R,3R,4S)-3-acetoxy-5-((4-isopropylphenyl)carbamoyl)-4-(4-phenyl-1H-1,2,3-triazol-1-yl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate

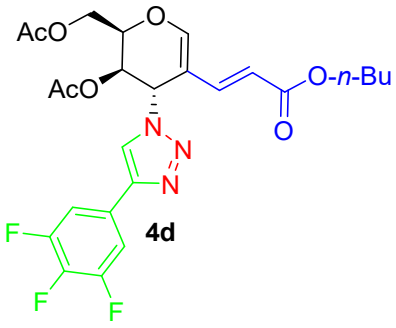


4c

The title compound **4c** was prepared according to the general procedure (4) and purified by column chromatography giving a yellow solid (48.5 mg, 78% yield). **R_f** (Hexane/ EtOAc = 60/40):0.47; $[\alpha]^{24.2}$ D = +25.5 (c = 0.5, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (s, 1H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.58 (s, 1H), 7.38 (s, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.55 (s, 1H, bs), 5.22 (s, 1H), 4.80 (t, *J* = 6.2 Hz, 1H), 4.28 – 4.24 (m, 2H), 2.78 – 2.75 (m, 1H), 2.12 (s, 3H), 2.00

(s, 3H), 1.12 (s, 3H), 1.11 (s, 3H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 169.0, 162.6, 150.3, 146.9, 144.5, 133.9, 129.0, 127.8, 127.8, 127.4, 125.9, 125.9, 124.8, 124.8, 120.1, 119.5, 119.5, 106.6, 70.7, 66.1, 60.6, 51.8, 32.6, 23.0, 22.9, 19.7, 19.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{31}N_4O_6$ 519.2244; found 519.2244.

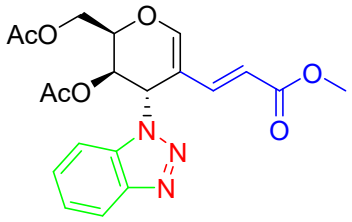
Butyl (E)-3-((2R,3R,4S)-3-acetoxy-2-(acetoxymethyl)-4-(4-(3,4,5-trifluorophenyl)-1H-1,2,3-triazol-1-yl)-3,4-dihydro-2H-pyran-5-yl)acrylate



4d

The title compound **4d** was prepared according to the general procedure (4) and purified by column chromatography giving yellow solid (50.0 mg, 71% yield). **R_f** (Hexane/ EtOAc = 60/40):0.57; $[\alpha]^{24.2}$ D = +29.0 (c = 0.6, $CHCl_3$); **^{1}H NMR (500 MHz,)** δ 7.86 (s, 1H), 7.44 – 7.41 (m, 2H), 7.28 (s, 1H), 5.40 (d, *J* = 15.9 Hz, 1H), 5.33 (s, 2H), 4.37 (t, *J* = 6.1 Hz, 1H), 4.27 – 4.21 (m, 2H), 4.14 – 3.96 (m, 3H), 2.14 (s, 3H), 2.01 (s, 3H), 1.54 – 1.51 (m, 2H), 1.32 – 1.28 (m, 2H), 0.84 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz,)** δ 170.3, 169.9, 166.6, 154.4, 154.4, 145.4, 145.4, 140.5, 120.1, 114.6, 110.1, 110.1, 109.9, 109.9, 105.9, 71.1, 67.0, 64.5, 61.7, 53.4, 30.7, 20.7, 20.7, 19.1, 13.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{25}H_{26}N_3O_7$ 538.1801; found 538.1830.

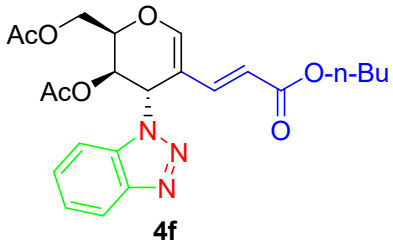
methyl (E)-3-((2R,3R,4S)-3-acetoxy-2-(acetoxymethyl)-4-(1H-benzo[d][1,2,3]triazol-1-yl)-3,4-dihydro-2H-pyran-5-yl)acrylate



4e

The title compound **4e** was prepared according to the general procedure (5) and purified by column chromatography giving light green sticky solid (46.0 mg, 75% yield). **R_f** (Hexane/ EtOAc = 70/30):0.33; $[\alpha]^{24}$ D = +73.4 (c = 0.5, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 (s, 2H, *bs*), 5.44 (s, 1H), 5.06 (d, *J* = 15.8 Hz, 1H), 4.99 (s, 1H), 4.57 (t, *J* = 5.7 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.15 – 4. 11 (m,1H), 3.50 (s, 3H), 2.14 (s, 3H), 1.92 (s, 3H) **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 169.3, 165.9, 153.1, 145.2, 140.3, 131.6, 127.5, 123.8, 119.5, 112.3, 108.4, 105.3, 69.9, 66.2, 60.7, 50.4, 50.1, 19.8, 19.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{21}N_3O_7$ 416.1458; found 416.1450 .

butyl (E)-3-((2R,3R,4S)-3-acetoxy-2-(acetoxymethyl)-4-(1H-benzo[d][1,2,3]triazol-1-yl)-3,4-dihydro-2H-pyran-5-yl)acrylate

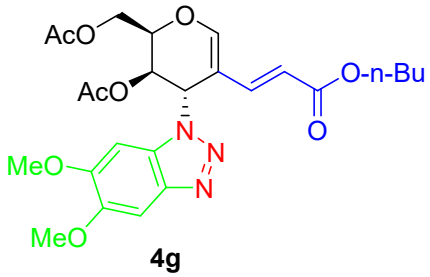


4f

The title compound **4f** was prepared according to the general procedure (5) and purified by column chromatography giving colorless gummy solid (49.0 mg, 82% yield). **R_f** (Hexane/ EtOAc = 70/30):0.39; $[\alpha]^{24}$ D = +69.8 (c = 0.6, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 16.3 Hz, 2H), 5.44 (s, 1H), 5.08 (d, *J* = 15.8 Hz, 1H), 4.98 (s, 1H), 4.55 (m, 1H), 4.23 – 4.15 (m, 2H), 3.98 – 3.90 (m, 2H), 2.15 (s, 3H), 1.94 (s, 3H), 1.47 – 1.43 (m, 2H), 1.21 (m, 2H), 0.80 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (151 MHz,**

$CDCl_3$) δ 169.4, 169.3, 165.6, 152.9, 145.2, 140.0, 131.6, 127.5, 123.8, 119.5, 112.8, 108.5, 105.2, 69.9, 66.1, 63.2, 60.7, 50.1, 29.6, 19.8, 19.6, 18.1, 12.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{27}N_3O_7$ 458.1927; found 458.1921.

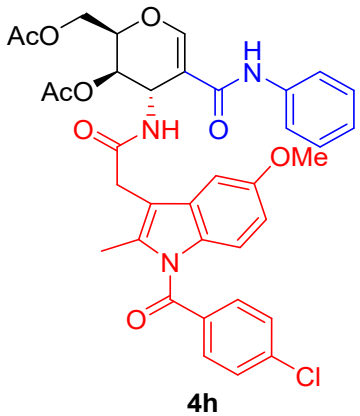
butyl (*E*)-3-((2R,3R,4S)-3-acetoxy-2-(acetoxymethyl)-4-(5,6-dimethoxy-1H-benzo[d][1,2,3]triazol-1-yl)-3,4-dihydro-2H-pyran-5-yl)acrylate



4g

The title compound **4g** was prepared according to the general procedure (5) and purified by column chromatography giving yellow solid (53.0 mg, 78% yield). **R_f** (Hexane/ EtOAc = 60/40):0.49; $[\alpha]^{24.2}$ D = +66.2 (c = 0.7, $CHCl_3$); **^{1}H NMR (500 MHz,)** δ 7.33 (s, 1H), 7.32 (s, 1H), 7.30 (s, 1H), 7.27 (d, *J* = 16.3 Hz, 1H), 5.30 (s, 1H), 5.08 (d, *J* = 15.9 Hz, 1H), 4.94 (s, 1H), 4.49 (t, *J* = 6.1 Hz, 1H), 4.20 – 4.12 (m, 2H), 4.01 (s, 3H), 3.99 – 3.94 (t, 2H), 3.91 (s, 3H), 2.14 (s, 3H), 1.94 (s, 3H), 1.47 (m, 2H), 1.25 – 1.21 (m, 2H), 0.81 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz,)** δ 165.0, 165.6, 161.9, 149.2, 147.5, 144.5, 136.5, 135.9, 123.1, 109.0, 101.6, 94.5, 85.1, 66.0, 62.4, 59.5, 57.1, 51.8, 51.6, 46.2, 26.0, 16.1, 15.9, 14.4, 9.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{25}H_{31}N_3O_9$ 518.2139; found 518.2109.

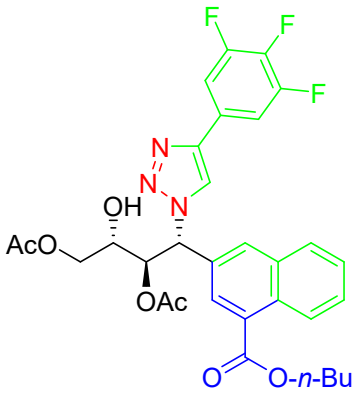
((2R,3R,4S)-3-acetoxy-4-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetamido)-5-(phenylcarbamoyl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate



4h

The title compound **4h** was prepared according to the general procedure (6) and purified by column chromatography giving white solid (72.0 mg, 73% yield). $\mathbf{R_f}$ (Hexane/ EtOAc = 60/40):0.56; $[\alpha]^{24.2}$ D = +11.9 (c = 0.5, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 6.2 Hz, 3H), 7.46 (d, *J* = 8.0 Hz, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.95 (s, 1H), 6.86 (d, *J* = 6.3 Hz, 2H), 6.79 (s, 1H), 6.66 (s, 1H), 5.00 – 4.96 (m, 2H), 4.18 (t, *J* = 5.5 Hz, 2H), 3.83 (s, 3H), 3.71 (s, 1H), 3.68 (s, 2H), 2.39 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.2, 170.4, 169.6, 168.3, 166.3, 156.1, 154.8, 139.7, 139.3, 136.5, 136.2, 133.8, 133.4, 131.2, 131.2, 129.3, 129.2, 129.2, 128.9, 124.1, d119.9, 119.9, 115.0, 112.8, 111.7, 101.3, 100.2, 71.2, 66.3, 61.8, 55.7, 55.6, 42.2, 20.7, 20.6, 13.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{36}H_{34}ClN_3O_9$ 688.2062; found 688.2054.

(2R,3S,4S)-4-(4-hexanoylnaphthalen-2-yl)-2-hydroxy-4-(4-(3,4,5-trifluorophenyl)-1H-1,2,3-triazol-1-yl)butane-1,3-diyl diacetate



4i

The title compound **4i** was prepared according to the general procedure (7) and purified by column chromatography giving light yellow gummy solid (36.0 mg, 63% yield). **R_f** (Hexane/ EtOAc = 80/20):0.39; $[\alpha]^{24.6}$ D = +3.4 (c = 0.5, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.76 (d, *J* = 8.6 Hz, 1H), 7.94 (s, 1H), 7.91 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.63 (s, 1H), 7.50 (s, 1H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.19 (s, 1H), 6.23 (d, *J* = 9.1 Hz, 1H), 5.43 – 5.36 (m, 1H), 4.41 – 4.38 (m, 1H), 4.36 (s, 2H), 4.34 (d, *J* = 6.7 Hz, 2H), 2.04 (s, 3H), 2.03 (s, 3H), 1.73 – 1.70 (m, 2H), 1.39 (d, *J* = 7.5 Hz, 2H), 0.88 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.5, 169.1, 166.0, 137.1, 137.1, 132.6, 132.6, 130.5, 130.0, 128.2, 128.2, 126.4, 126.1, 124.9, 122.3, 120.9, 114.9, 109.2, 109.1, 109.0, 108.99, 67.6, 67.6, 64.5, 63.6 29.7, 19.9, 19.8, 18.3, 12.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{31}H_{30}F_3N_3O_7$ 614.2114; found 614.2198.

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2 S. Dharuman and Y. D. Vankar, *Org Lett*, 2014, **16**, 1172–1175.

3 N. Hussain, K. Jana, B. Ganguly and D. Mukherjee, *Org Lett*, 2018, **20**, 1572–1575.

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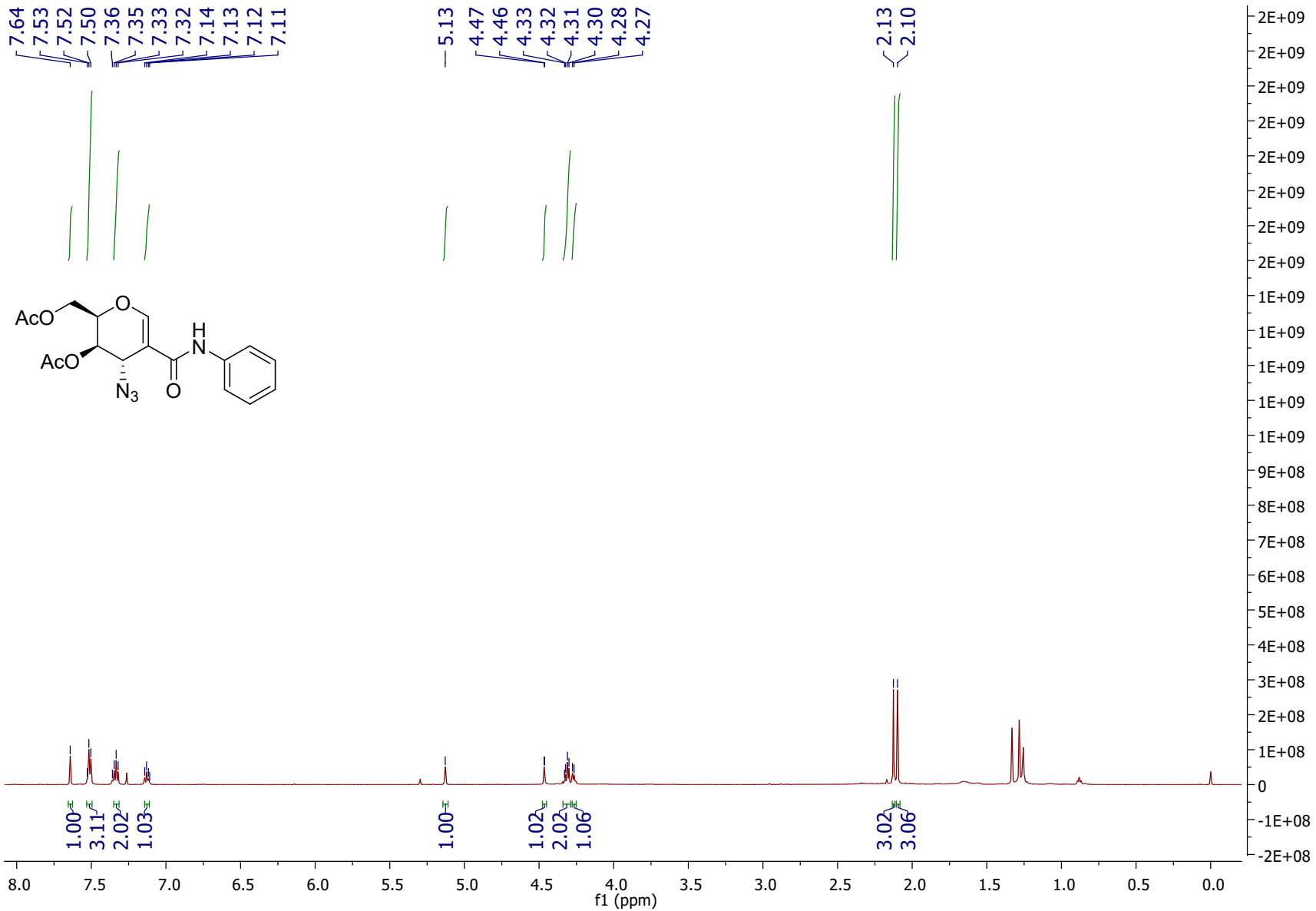
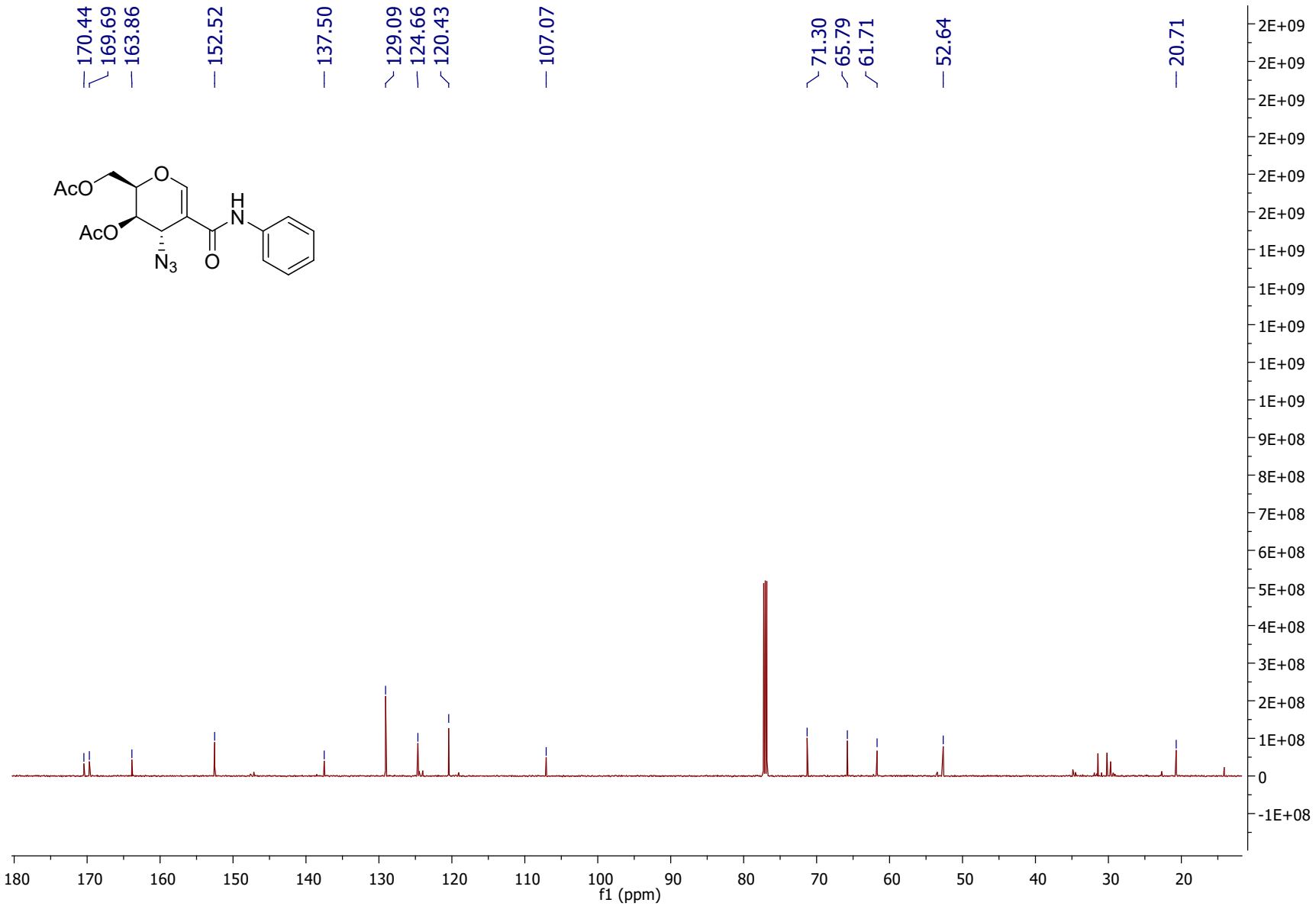
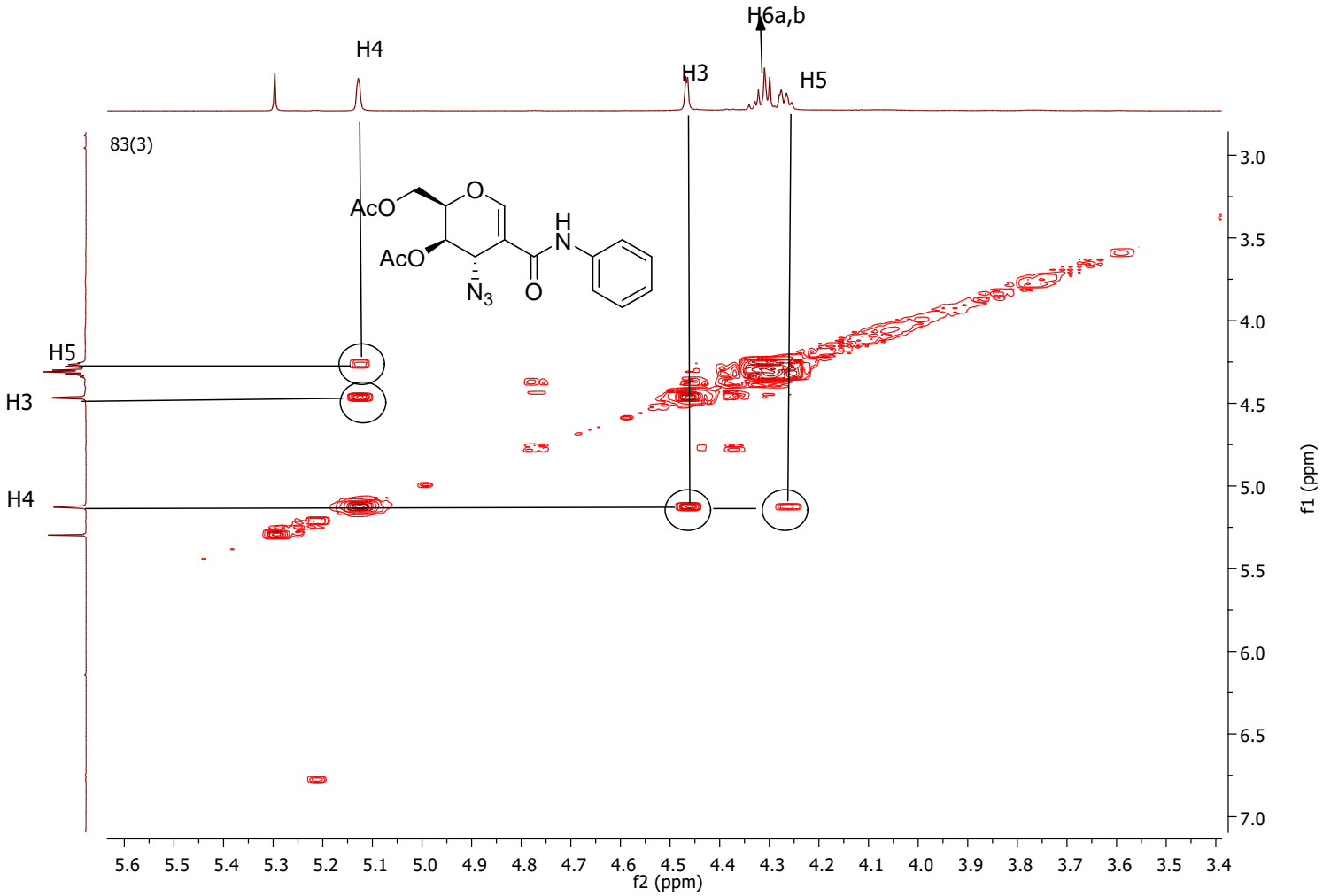
5 N. L. B. Pohl, *Carbohydr Res*, 2015, **412**, 19.



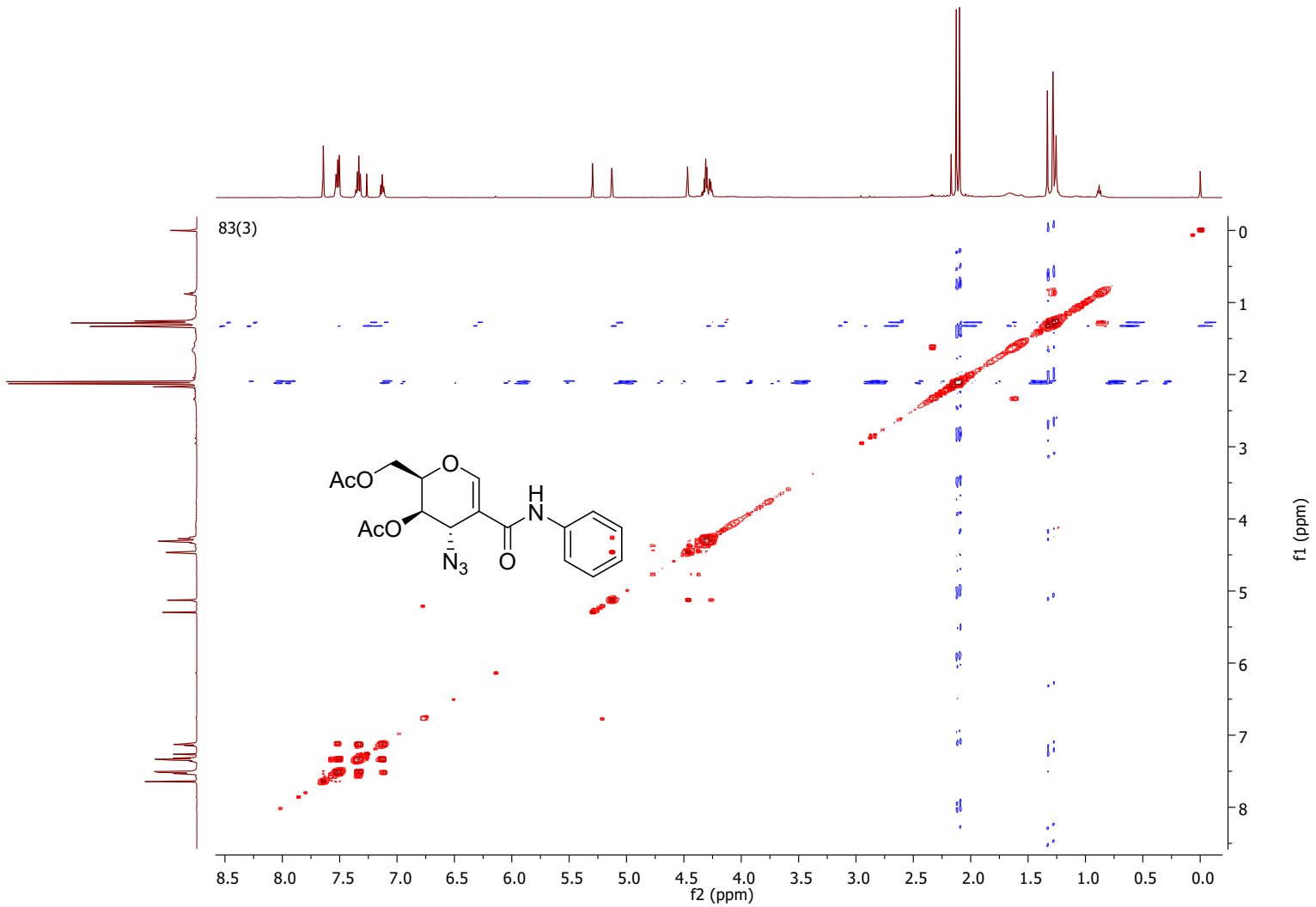
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2a**



^{13}C NMR (151 MHz, $CDCl_3$) of compound **2a**



COSY of compound **2a** (expanded form)



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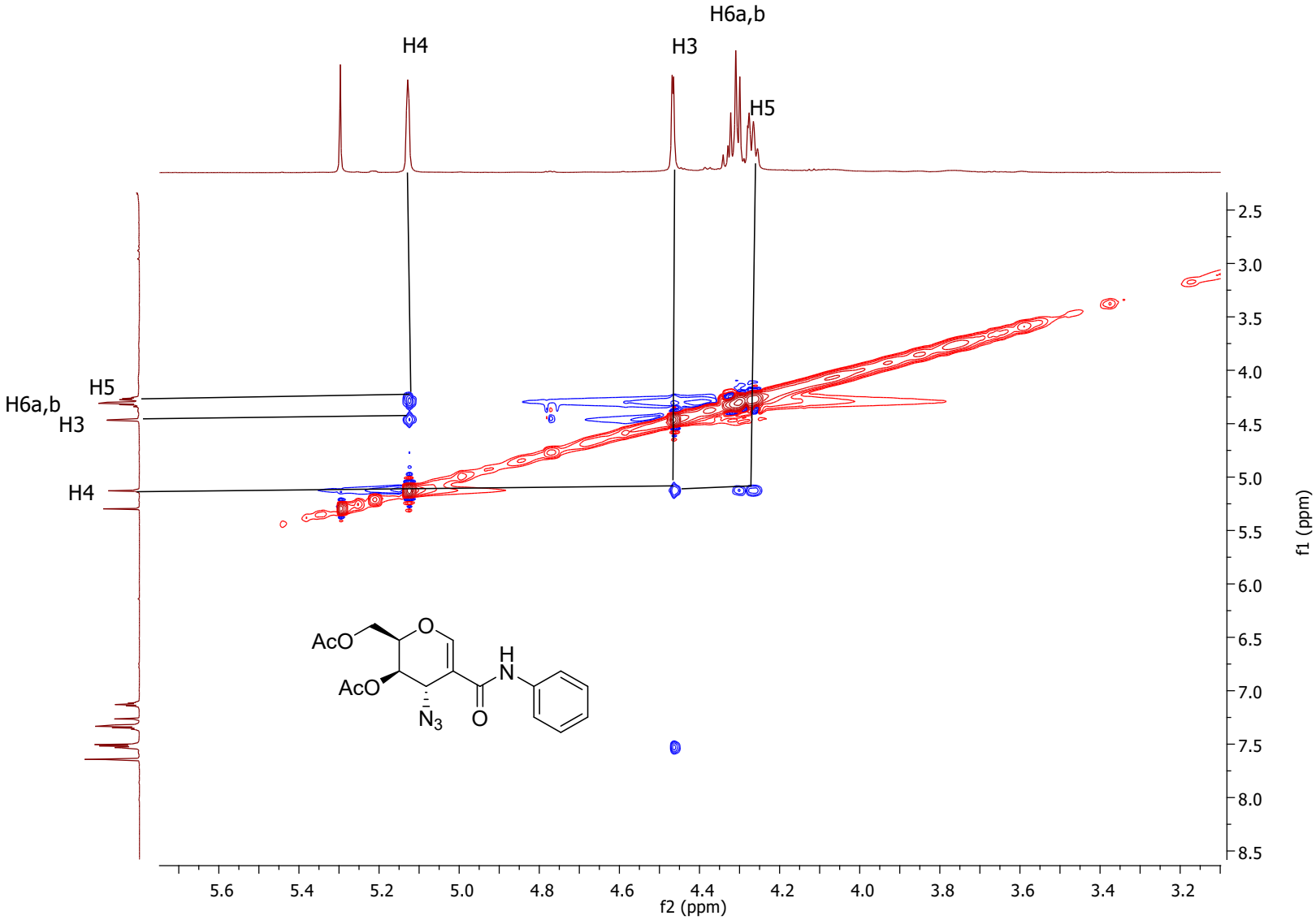
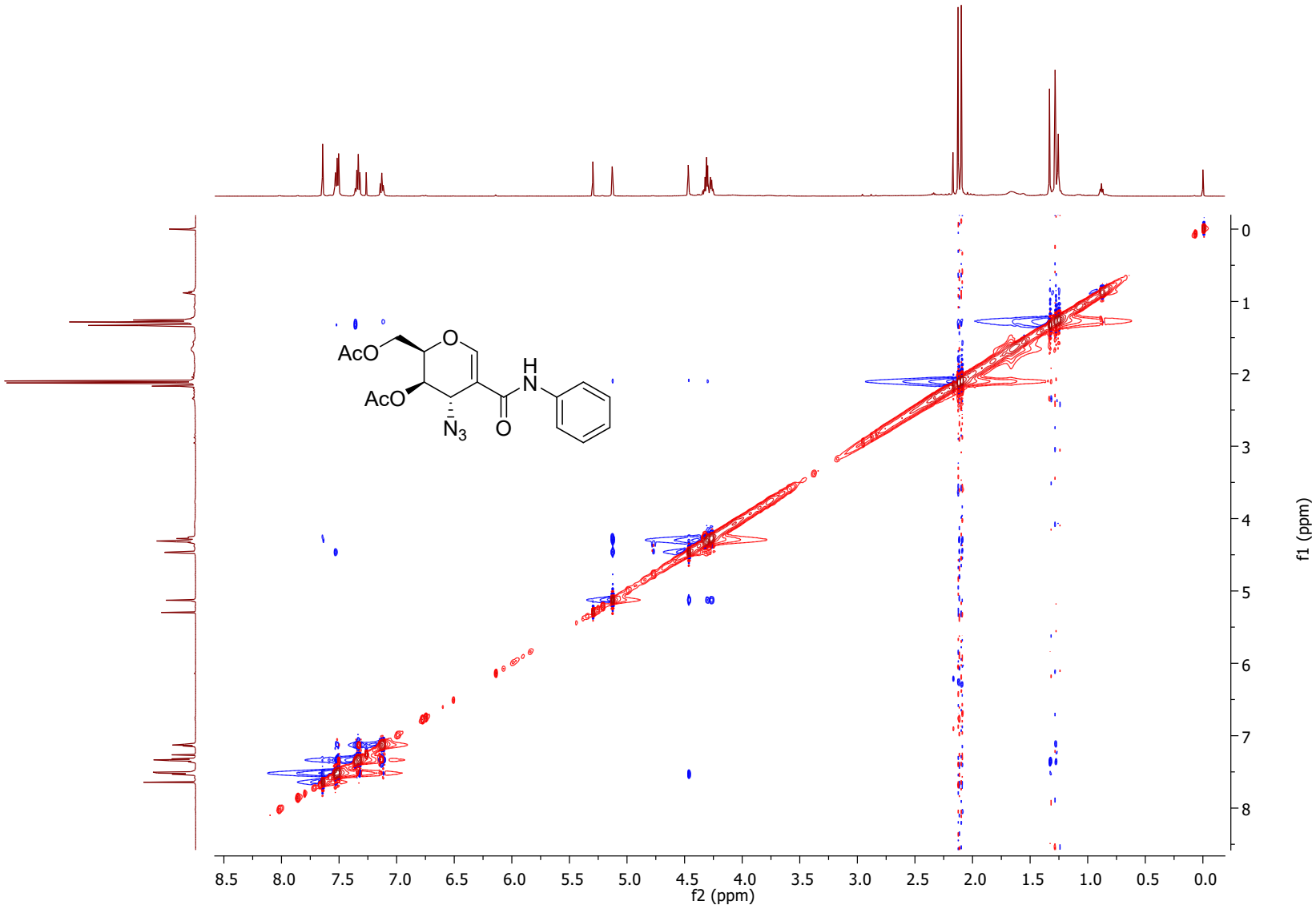
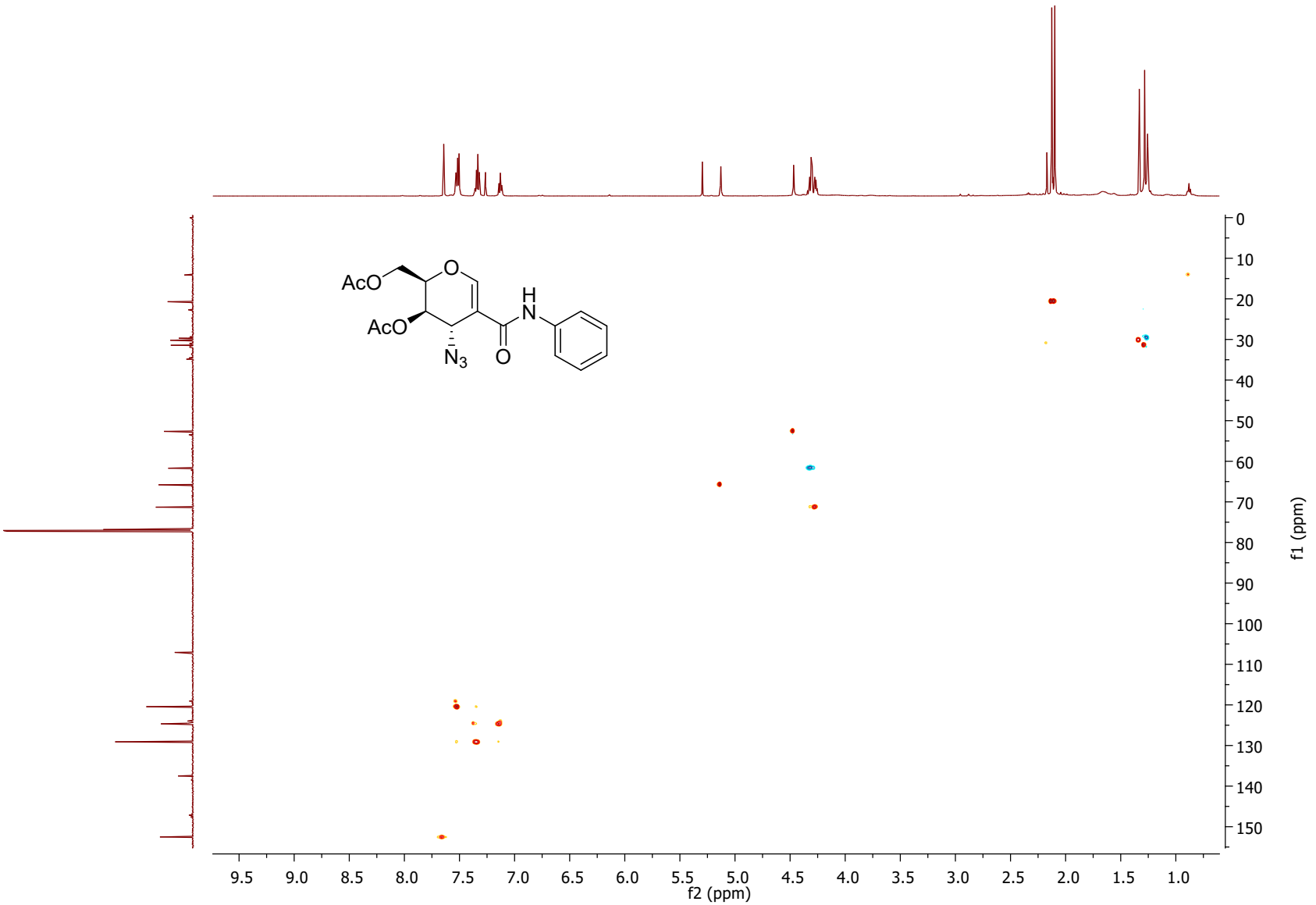


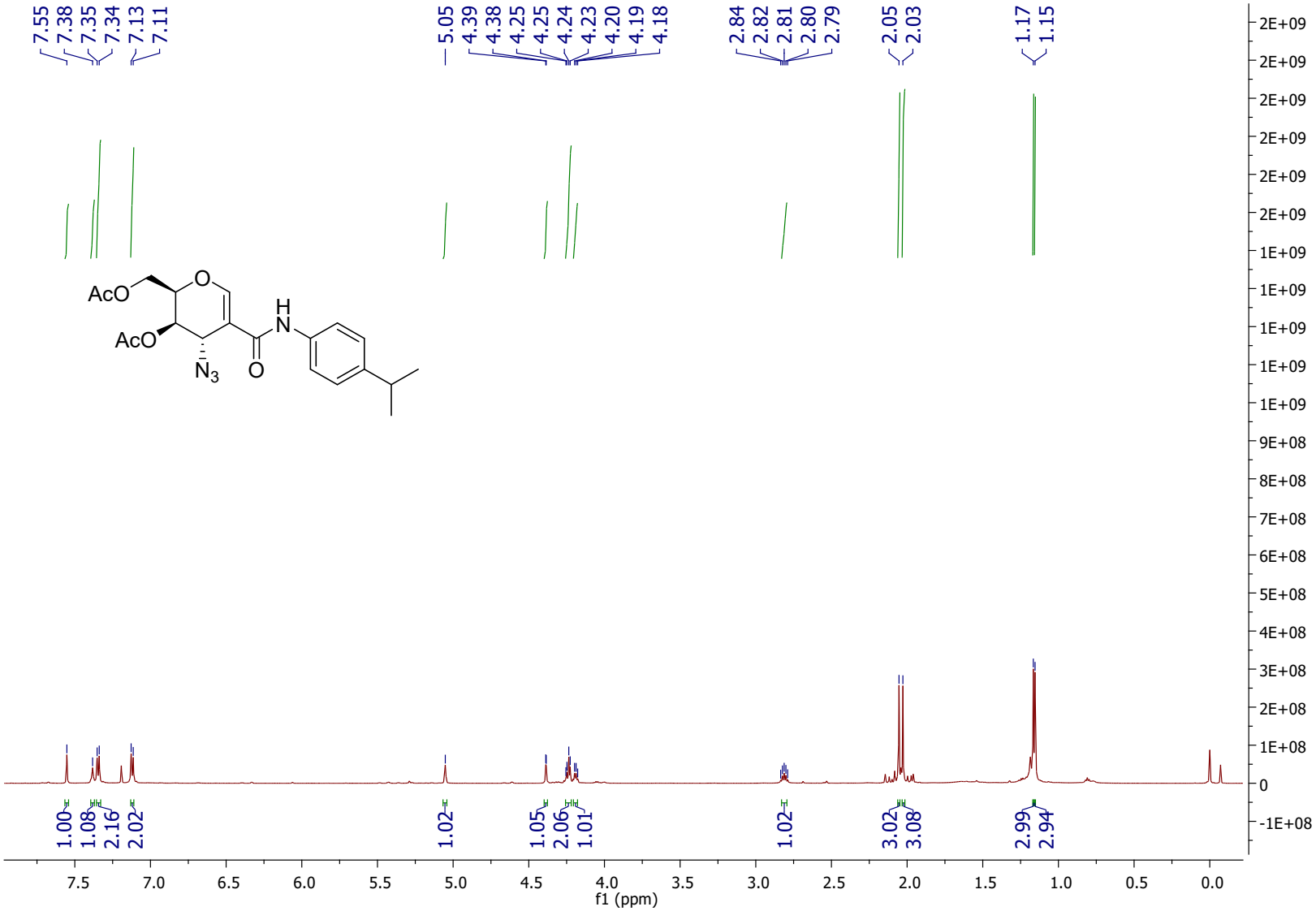
NOESY of compound **2a** (expanded form)



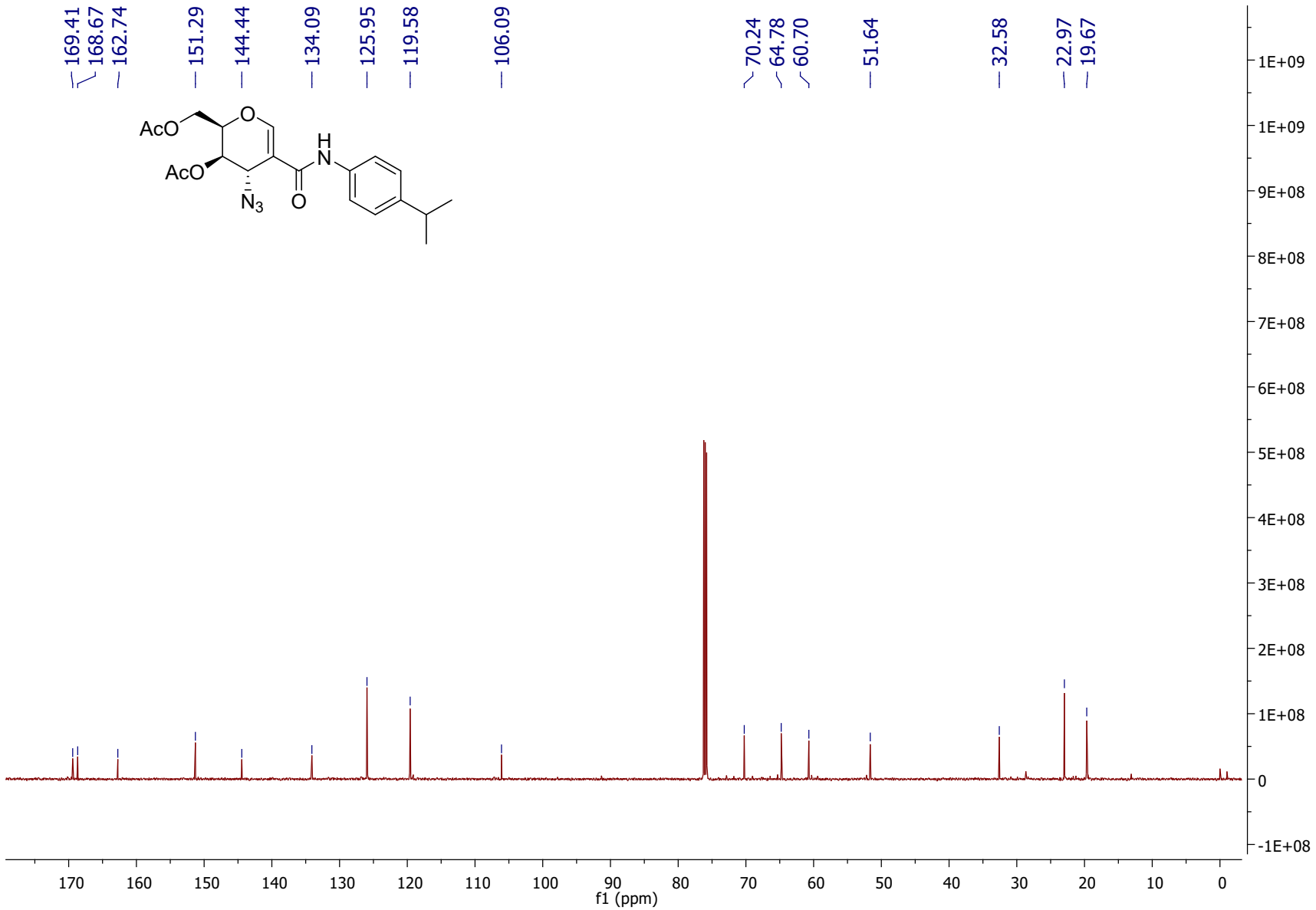
NOESY of compound **2a**



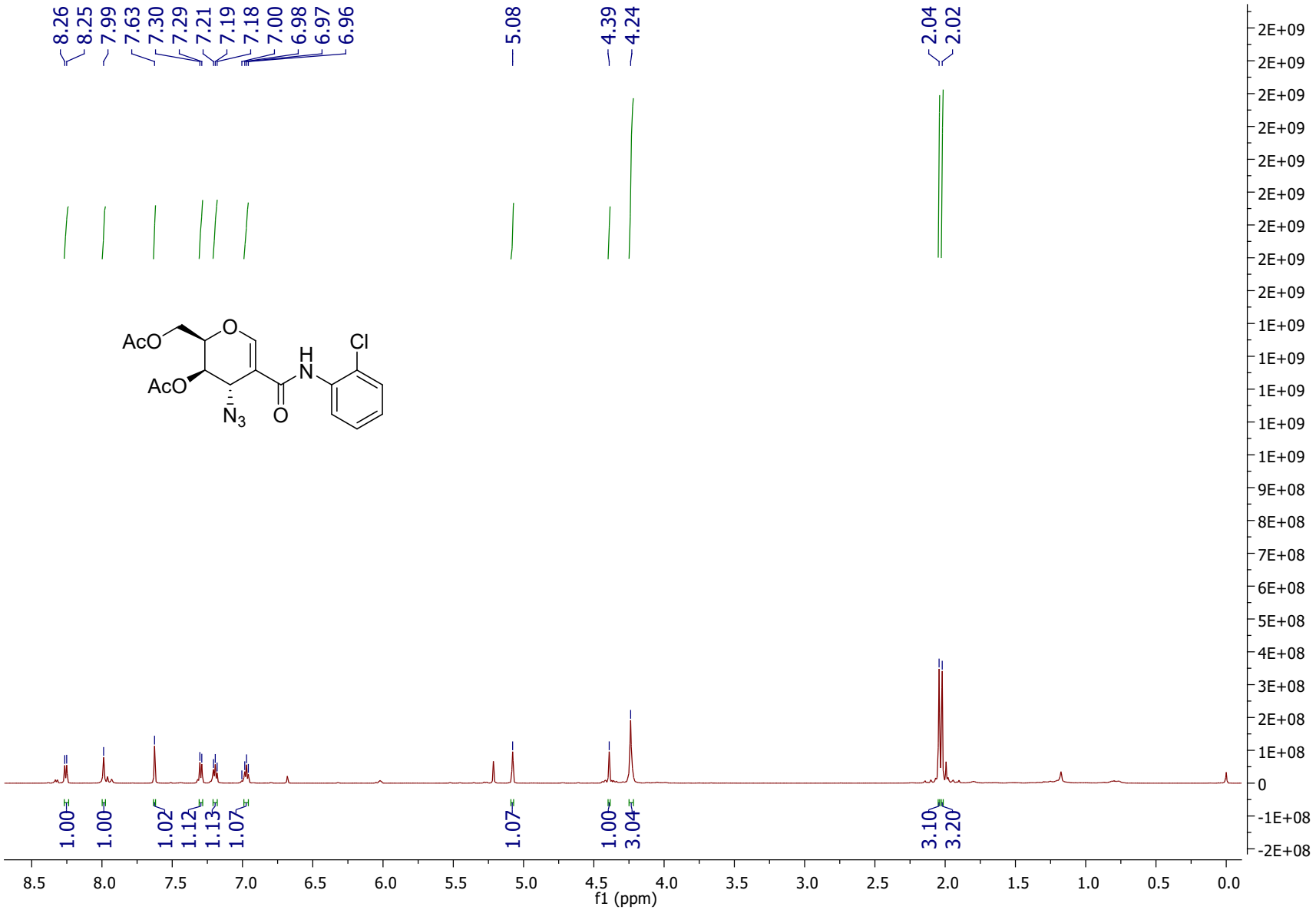
HSQC of compound **2a**



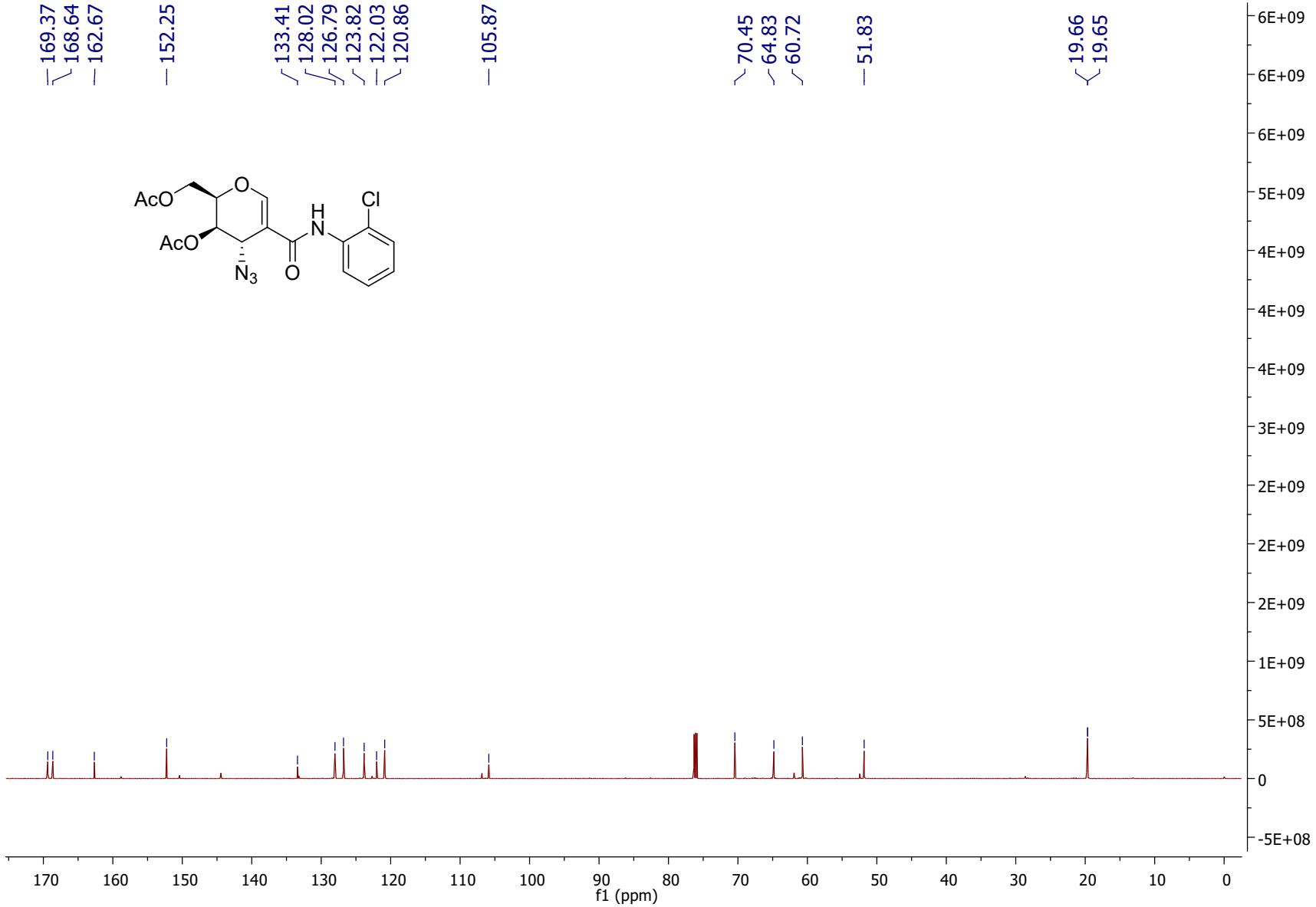
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2b**



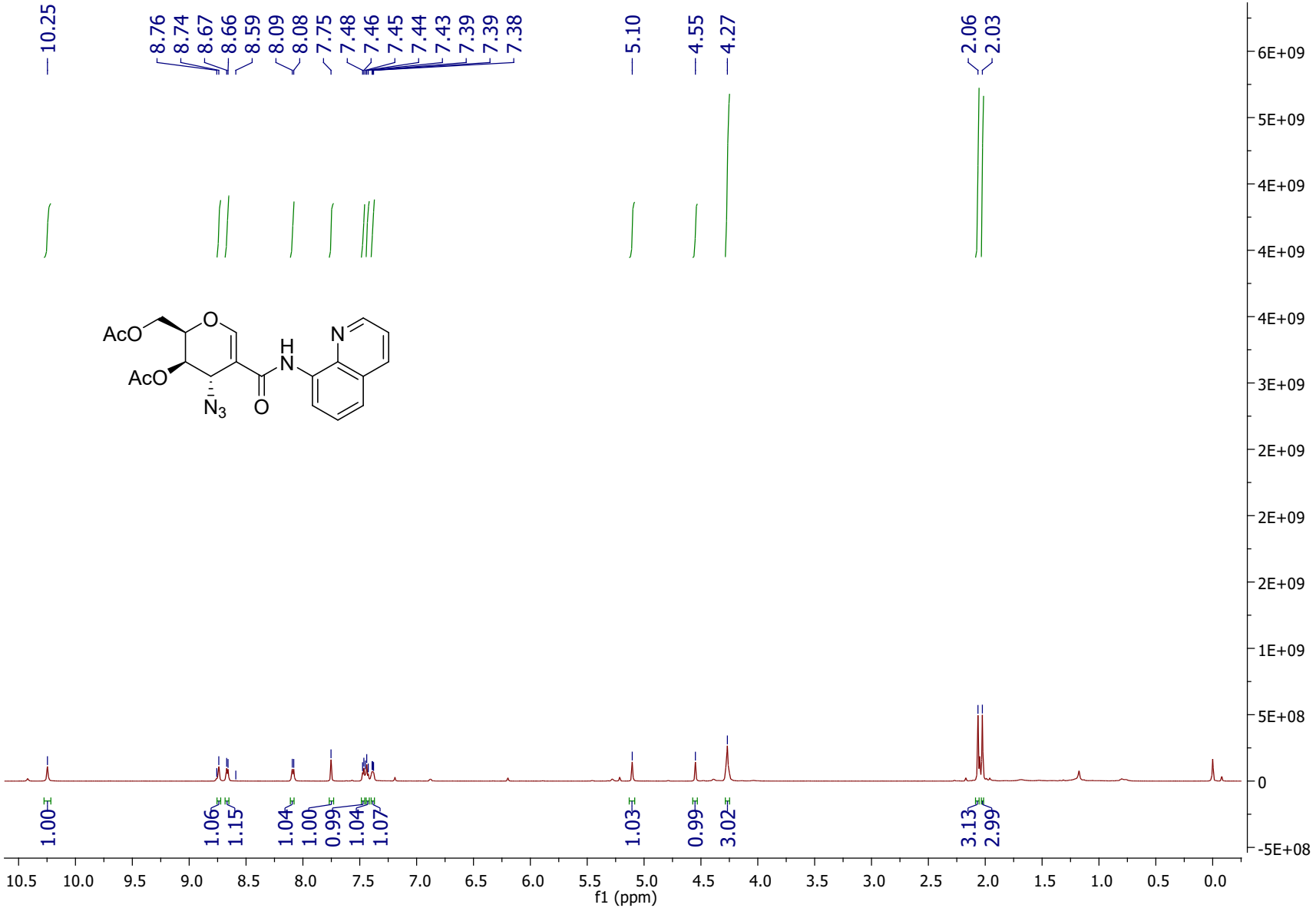
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2b**



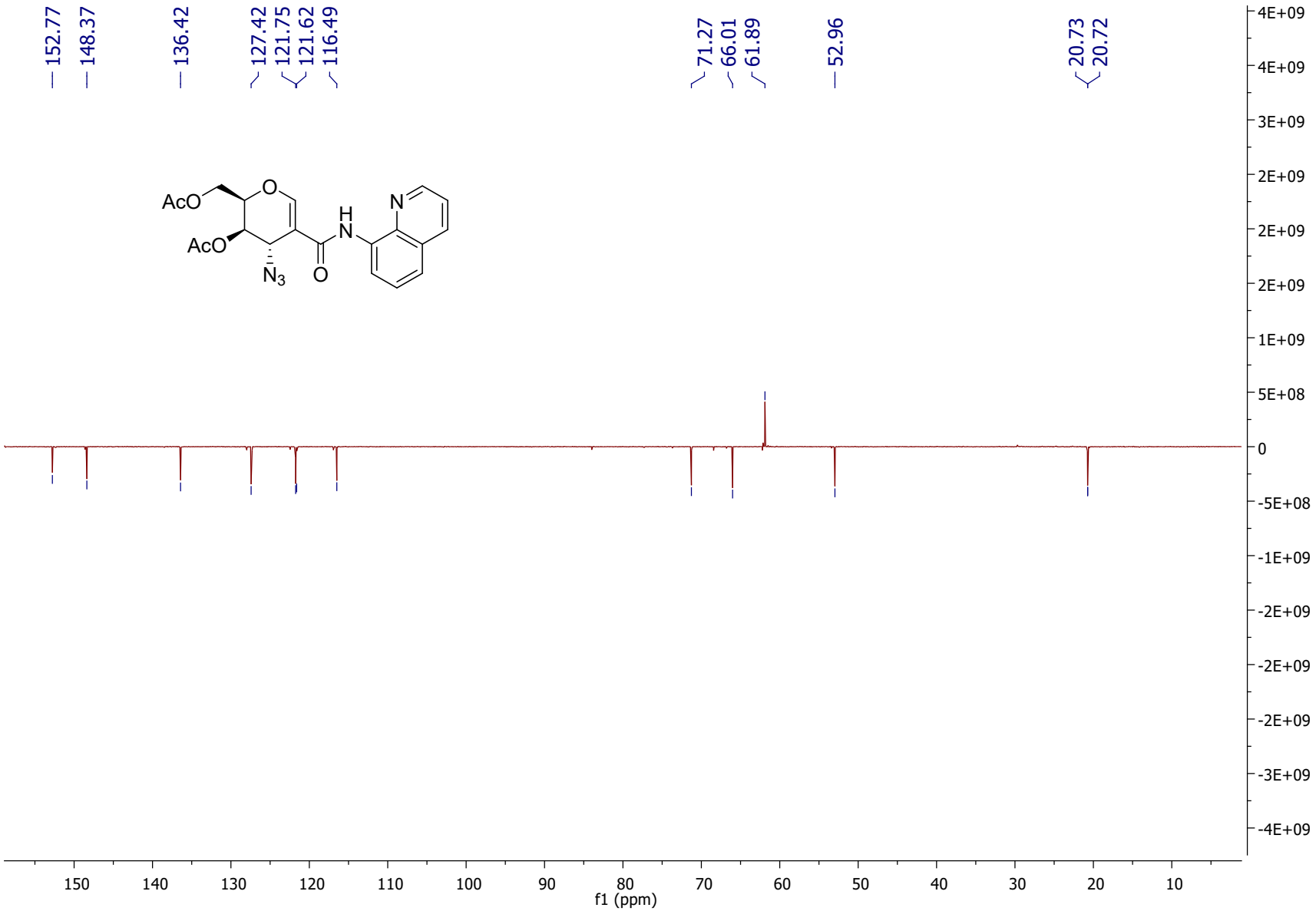
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2c**



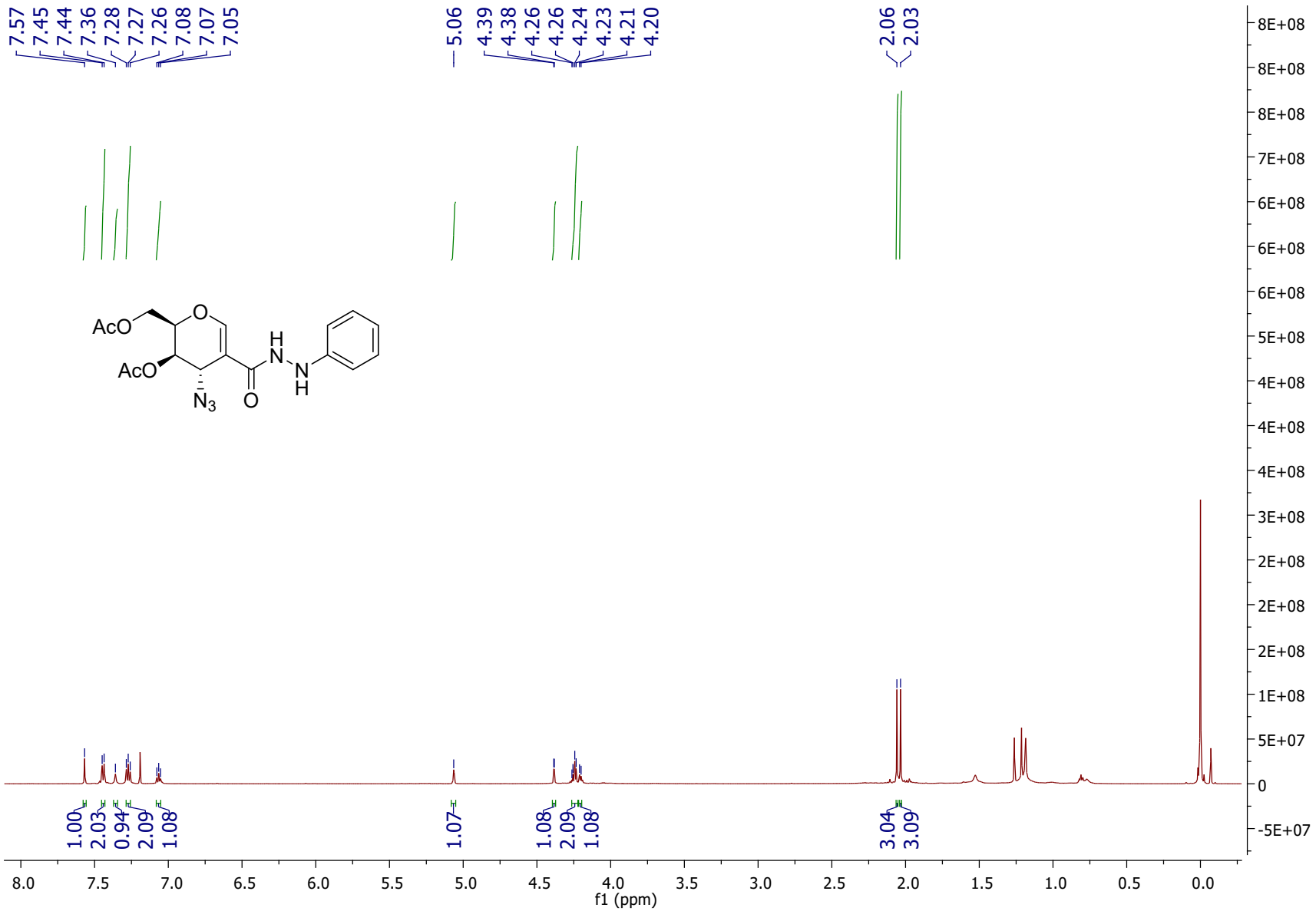
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2c**



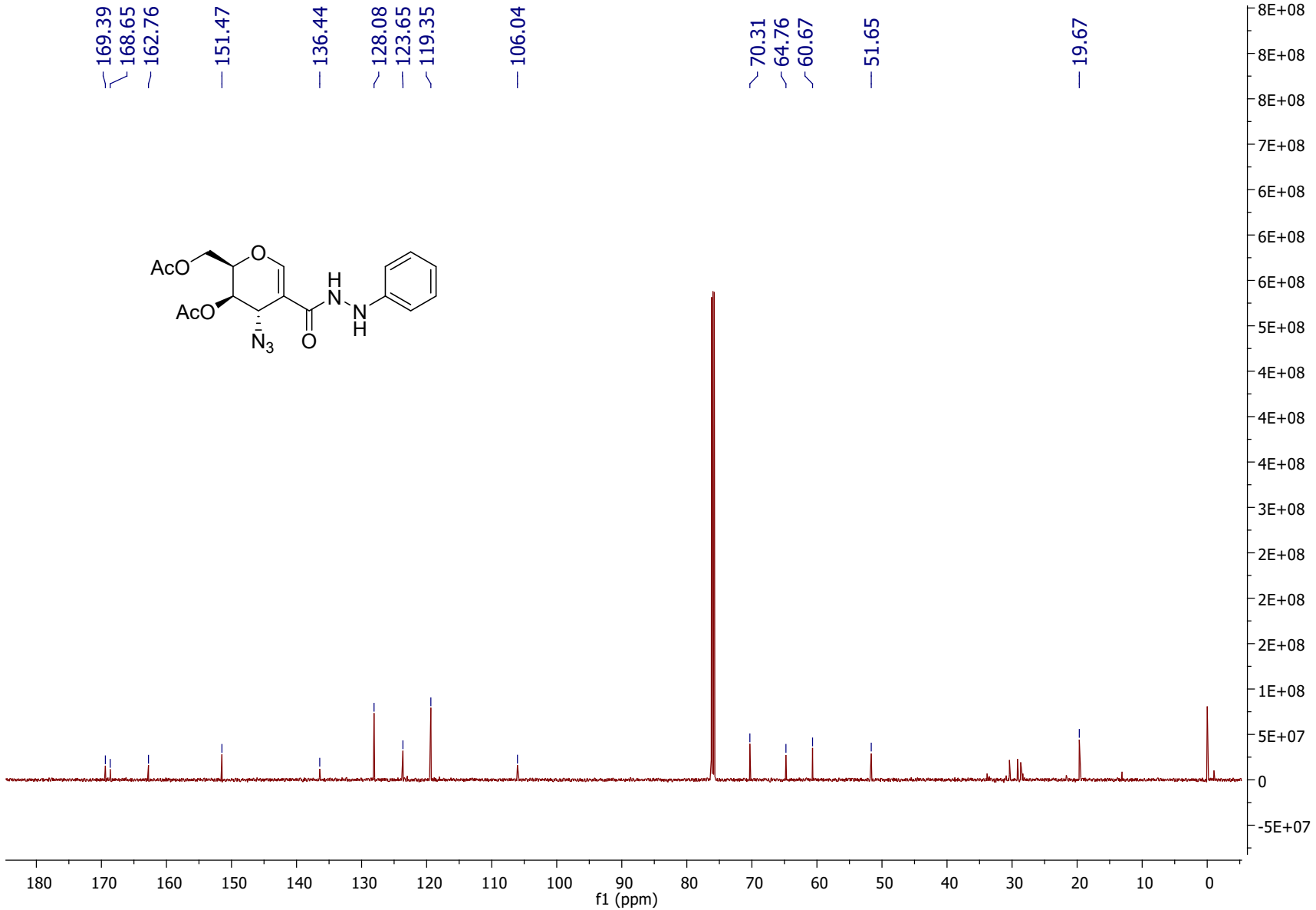
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2d**



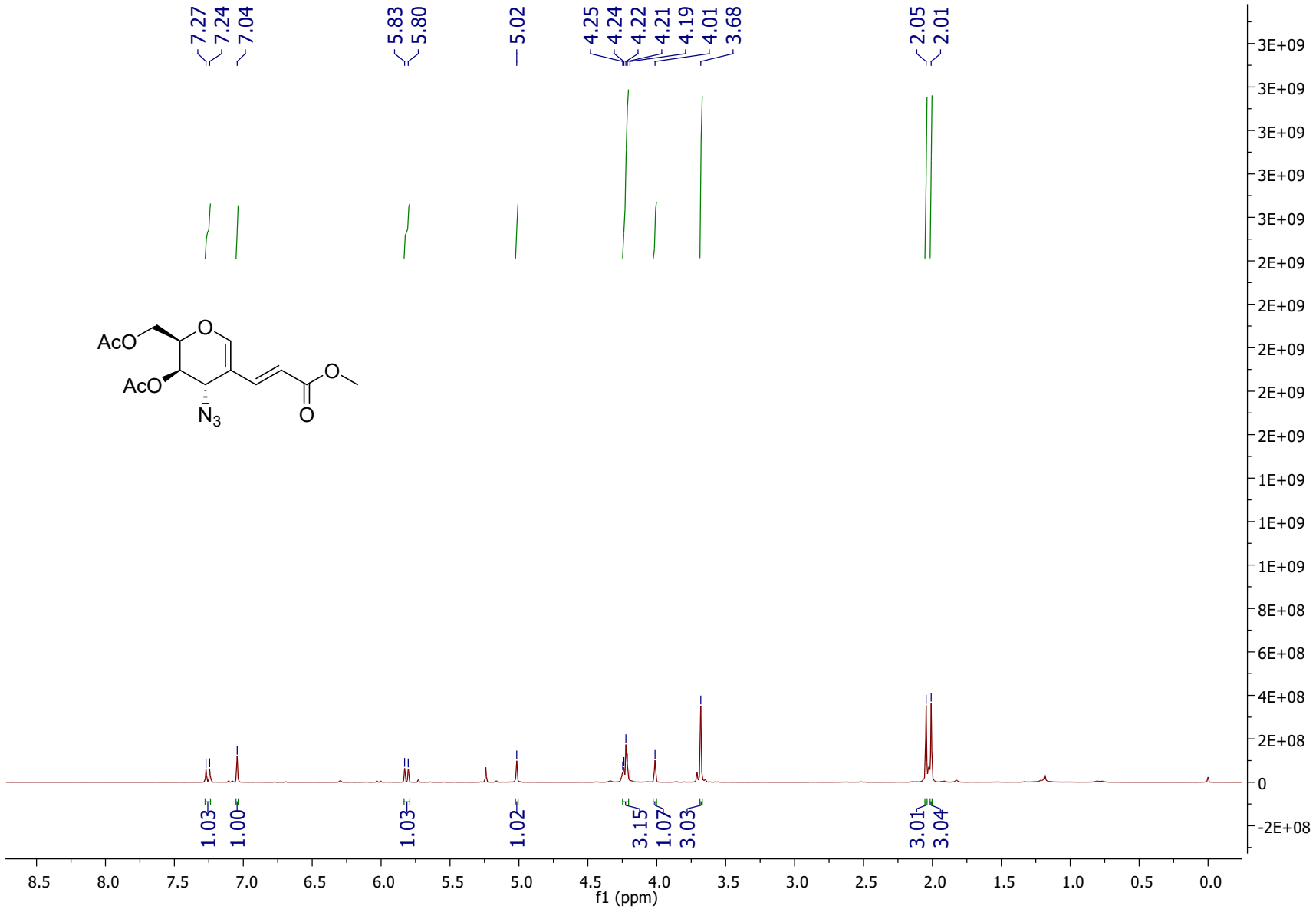
DEPT^{13}C NMR (151 MHz, $CDCl_3$) of compound **2d**



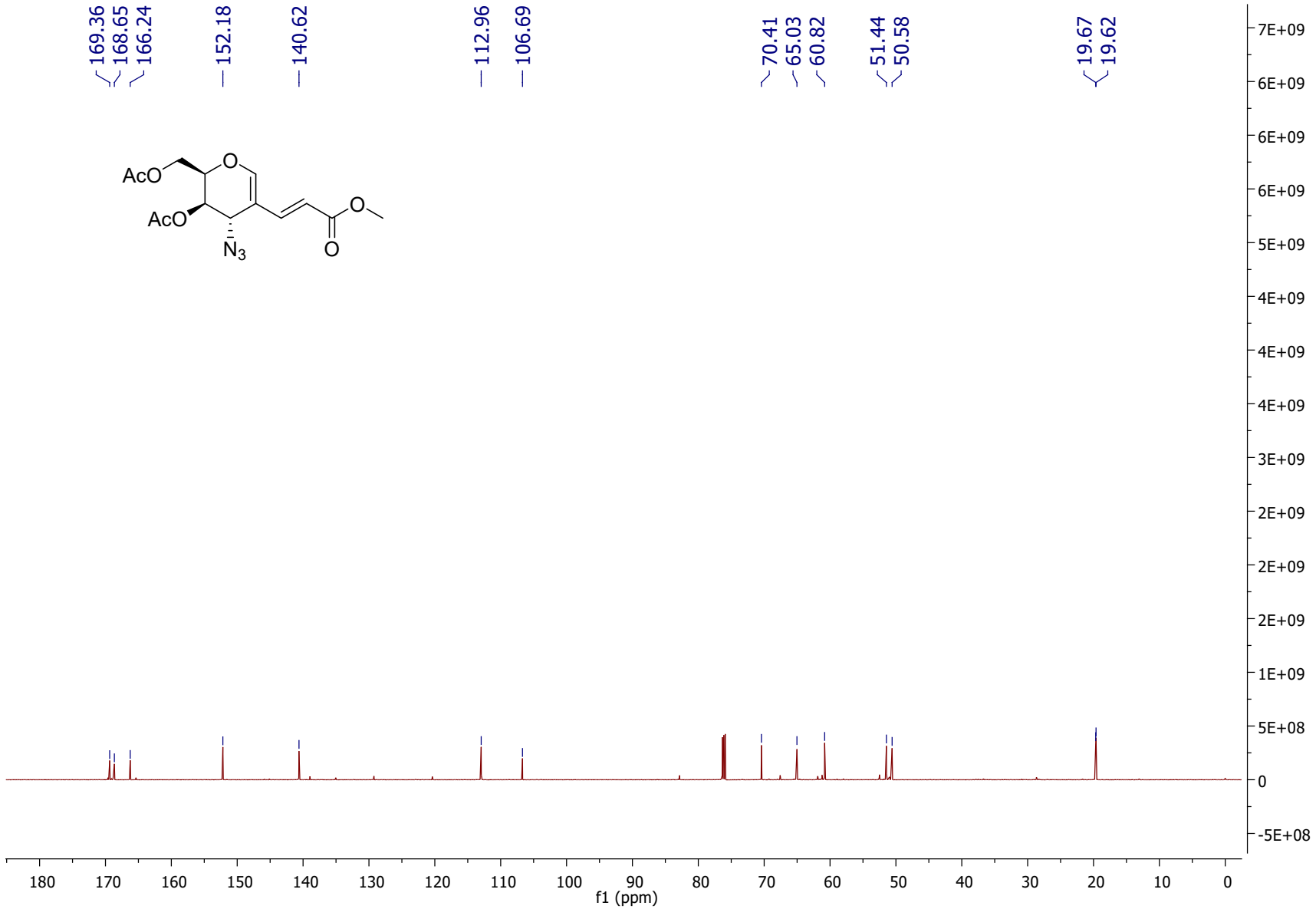
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2e**



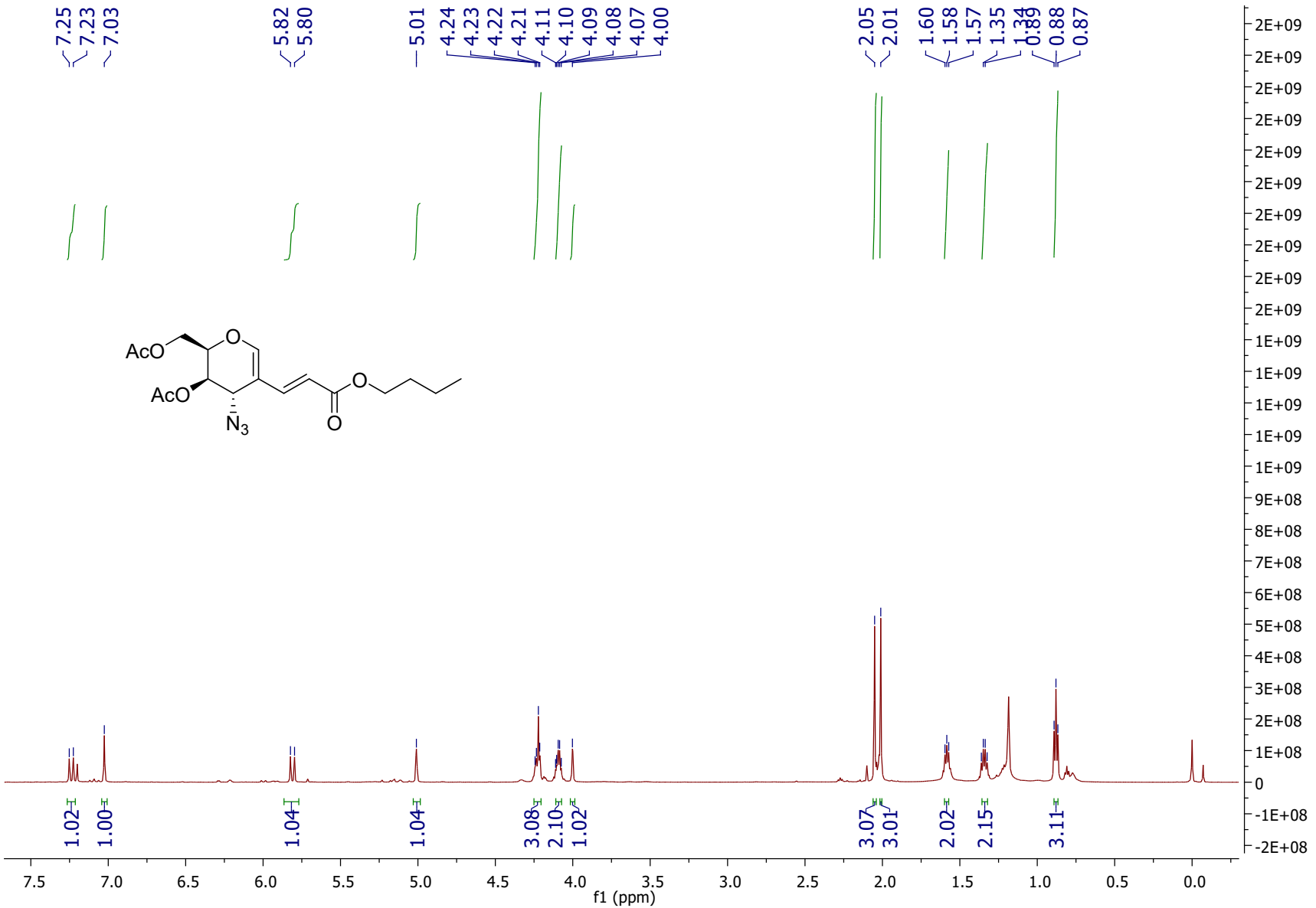
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2e**



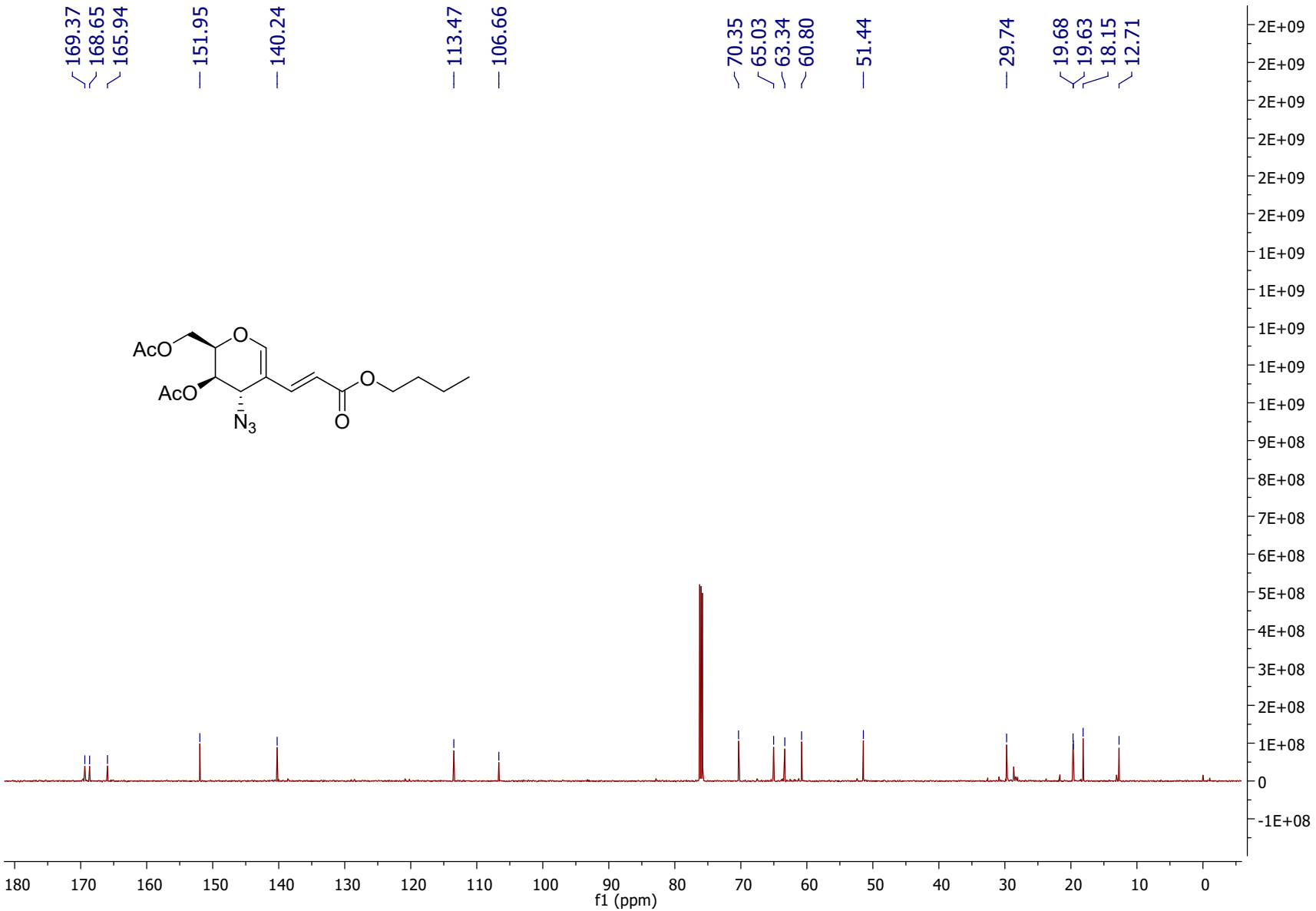
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2f**



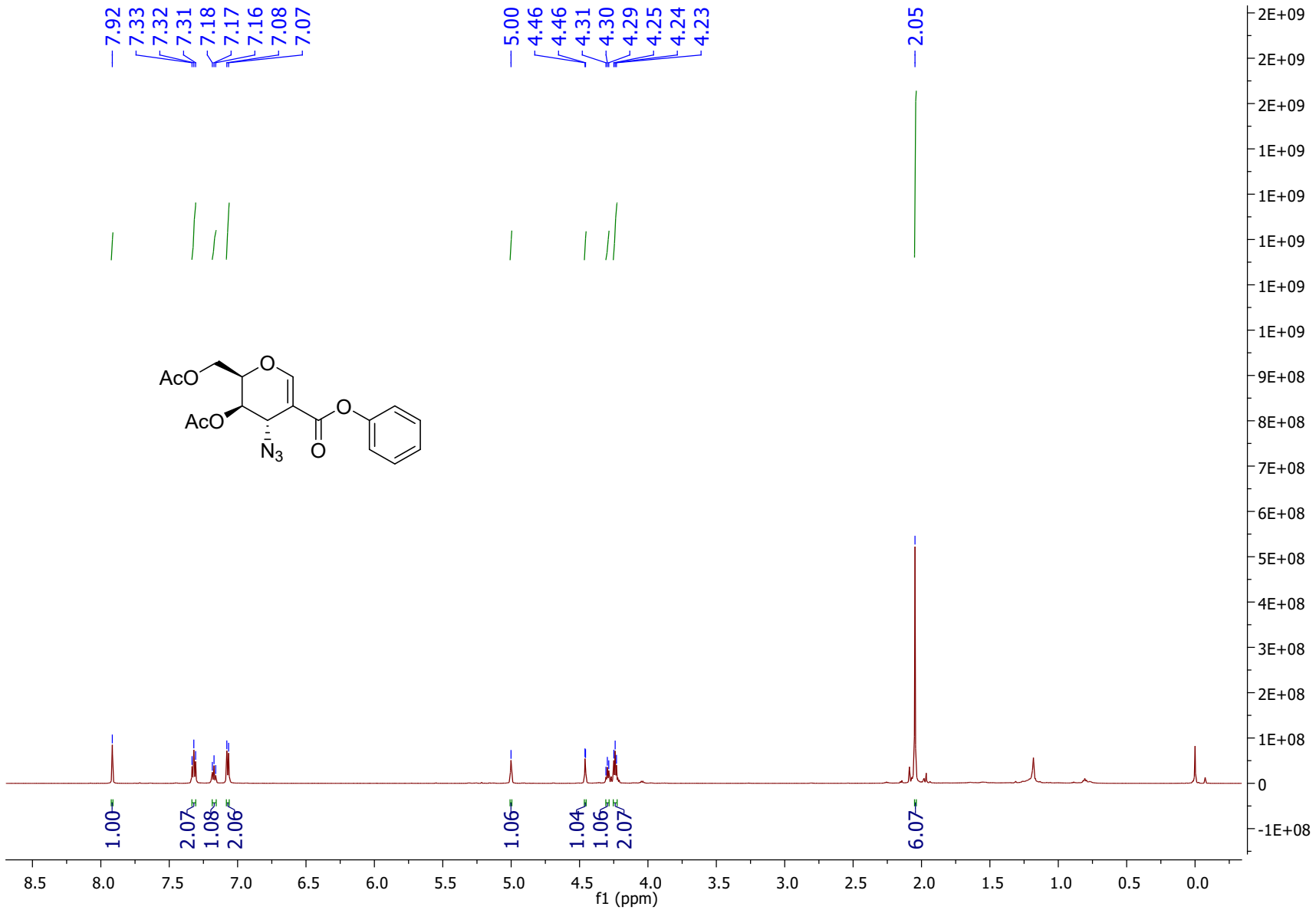
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2f**



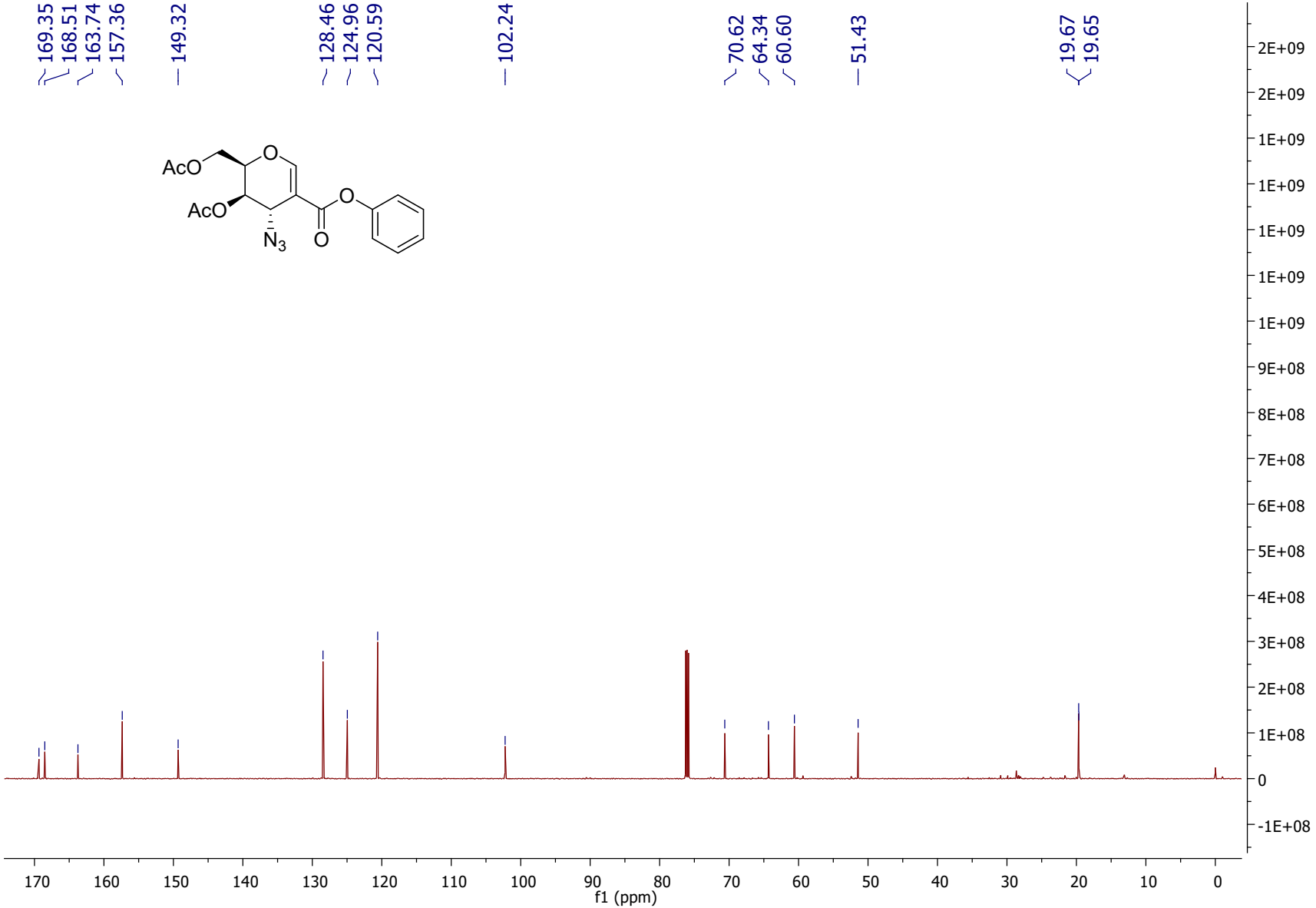
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2g**



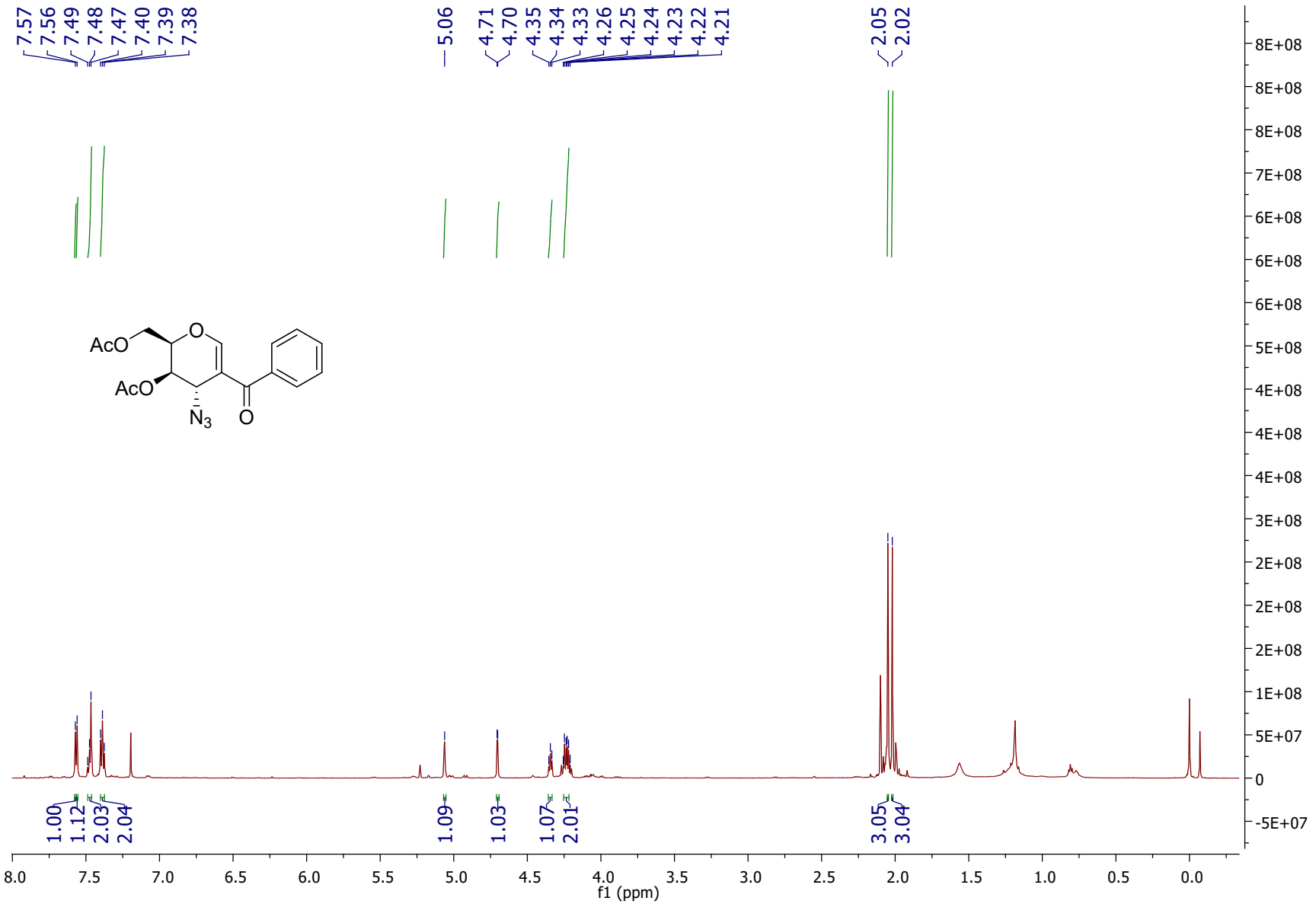
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2g**



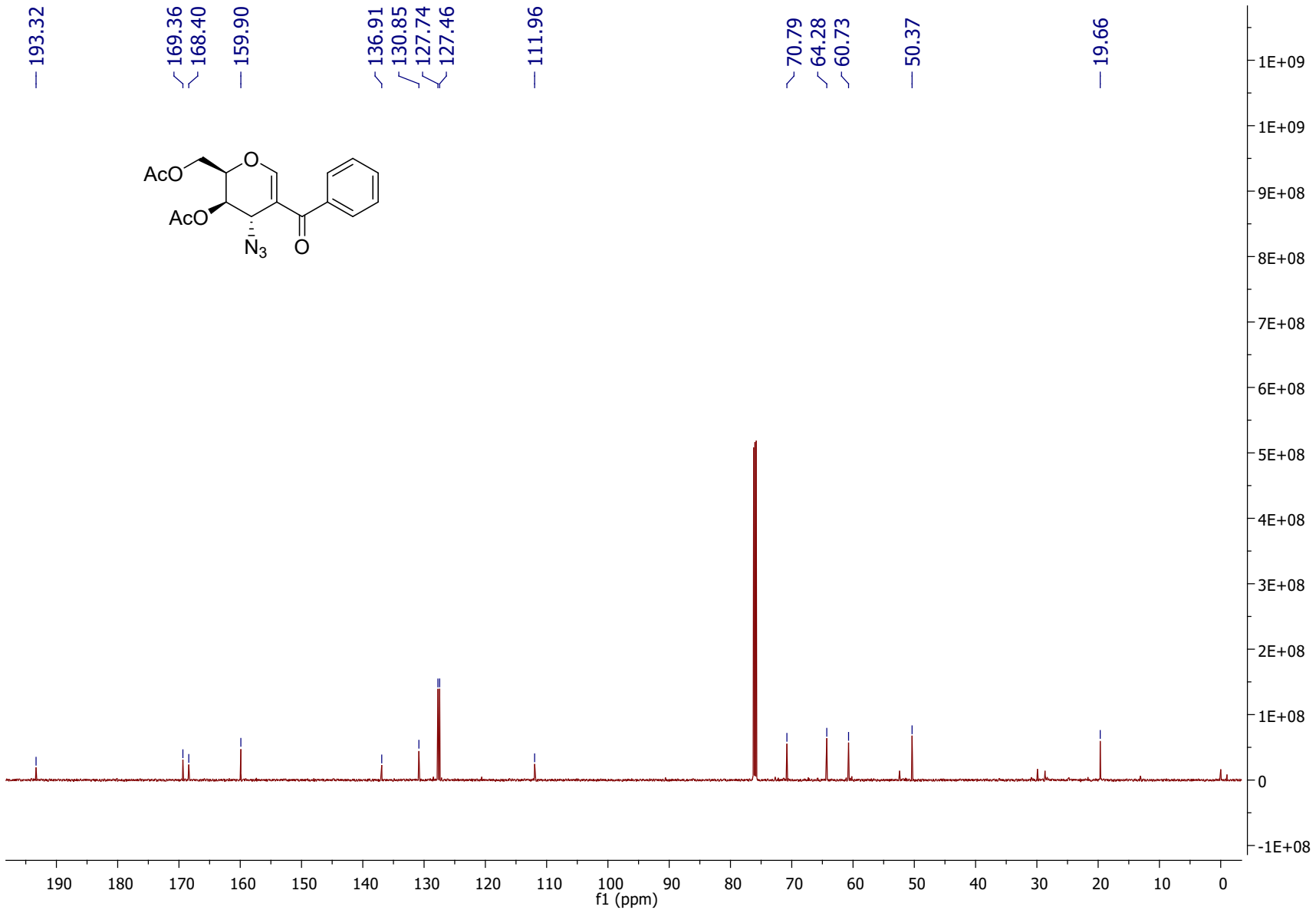
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2i**



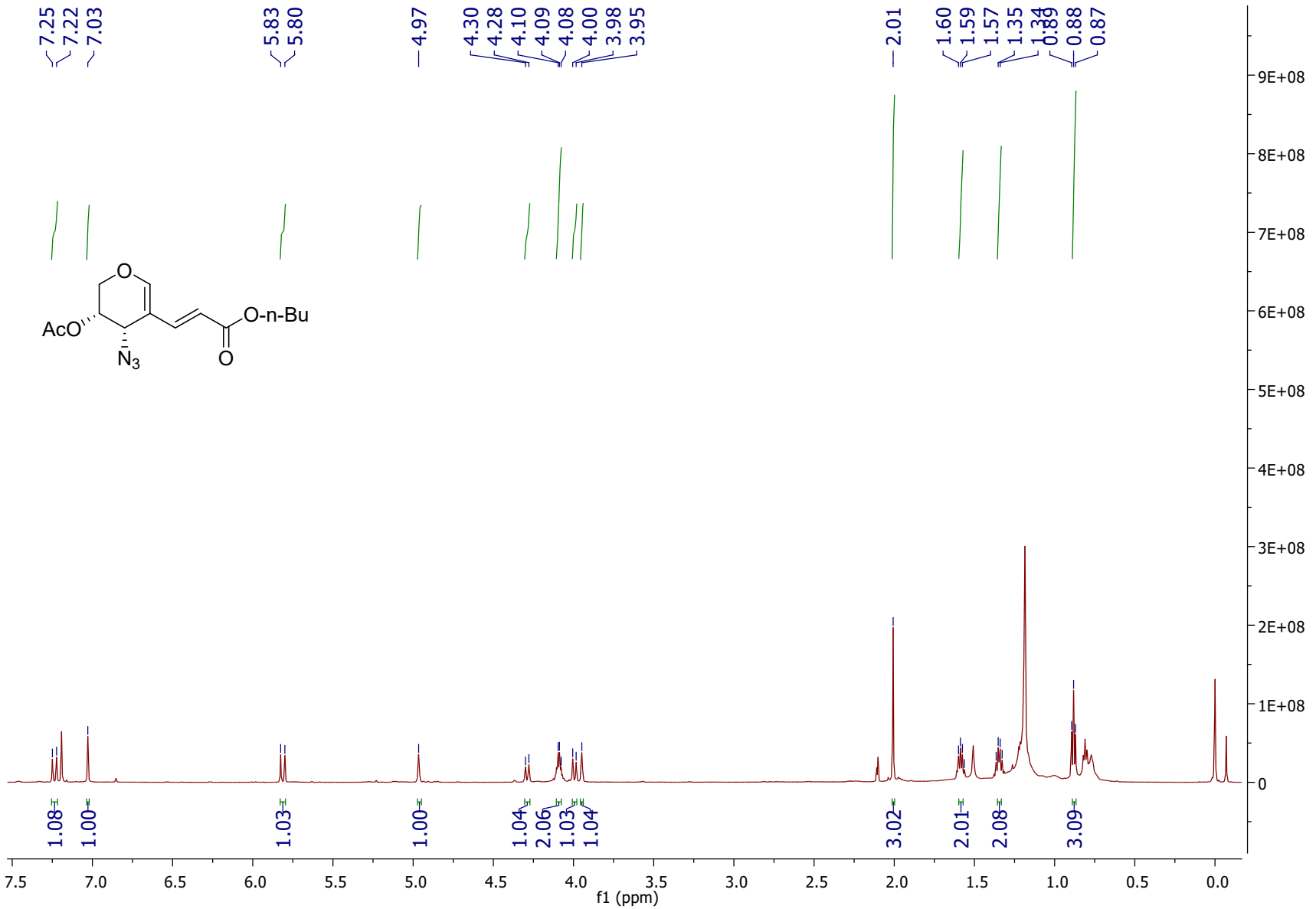
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2i**



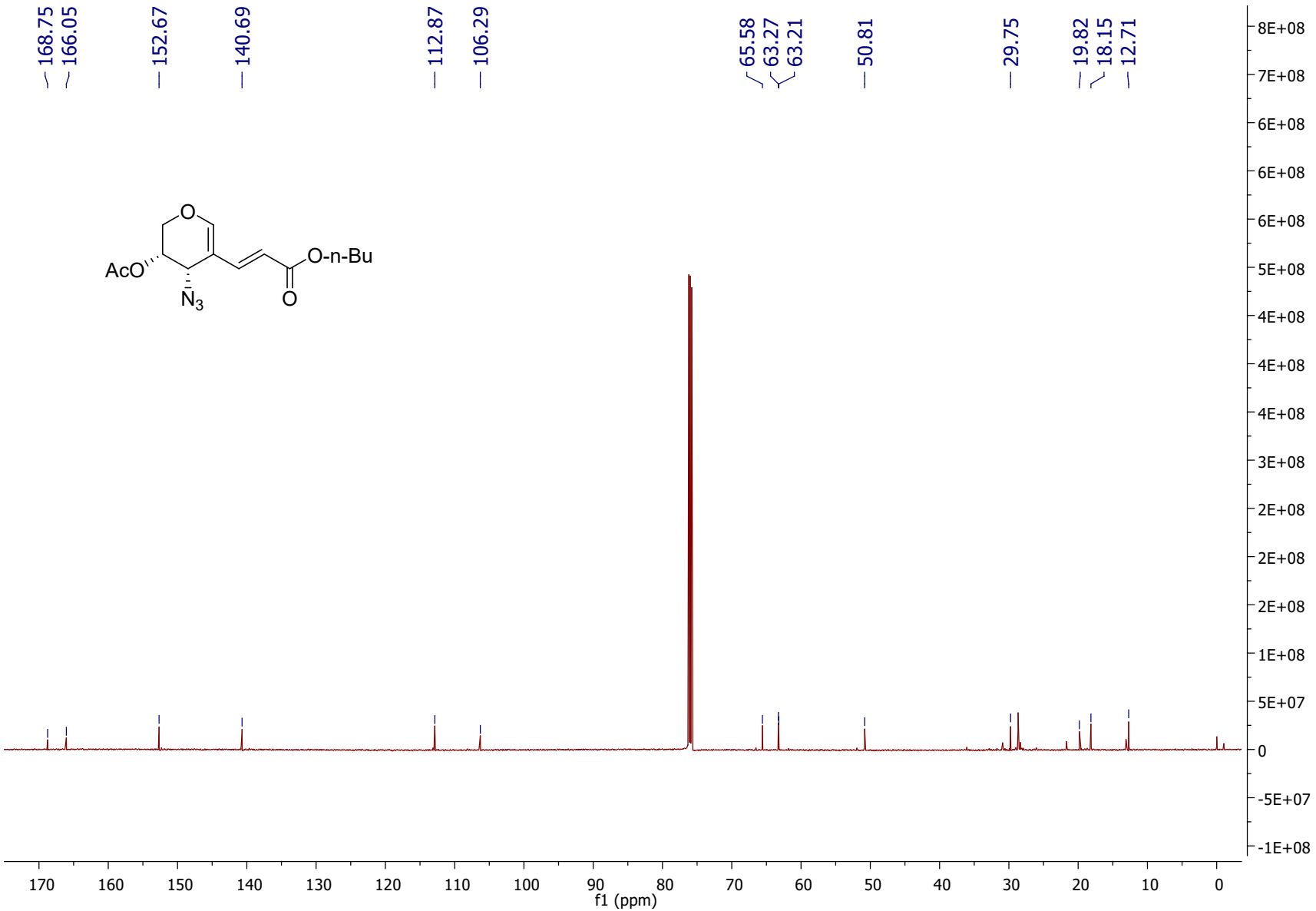
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2j**



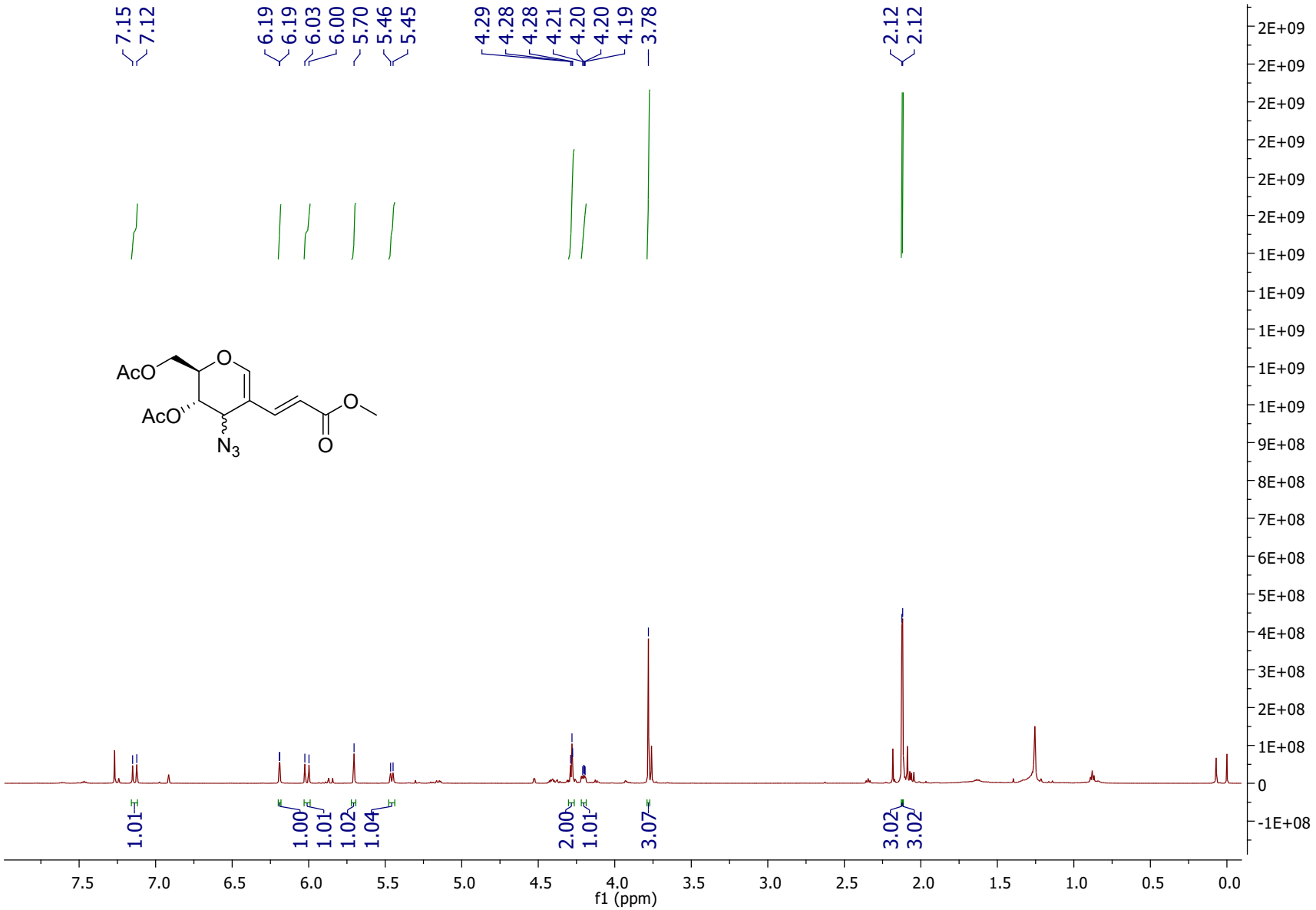
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2j**



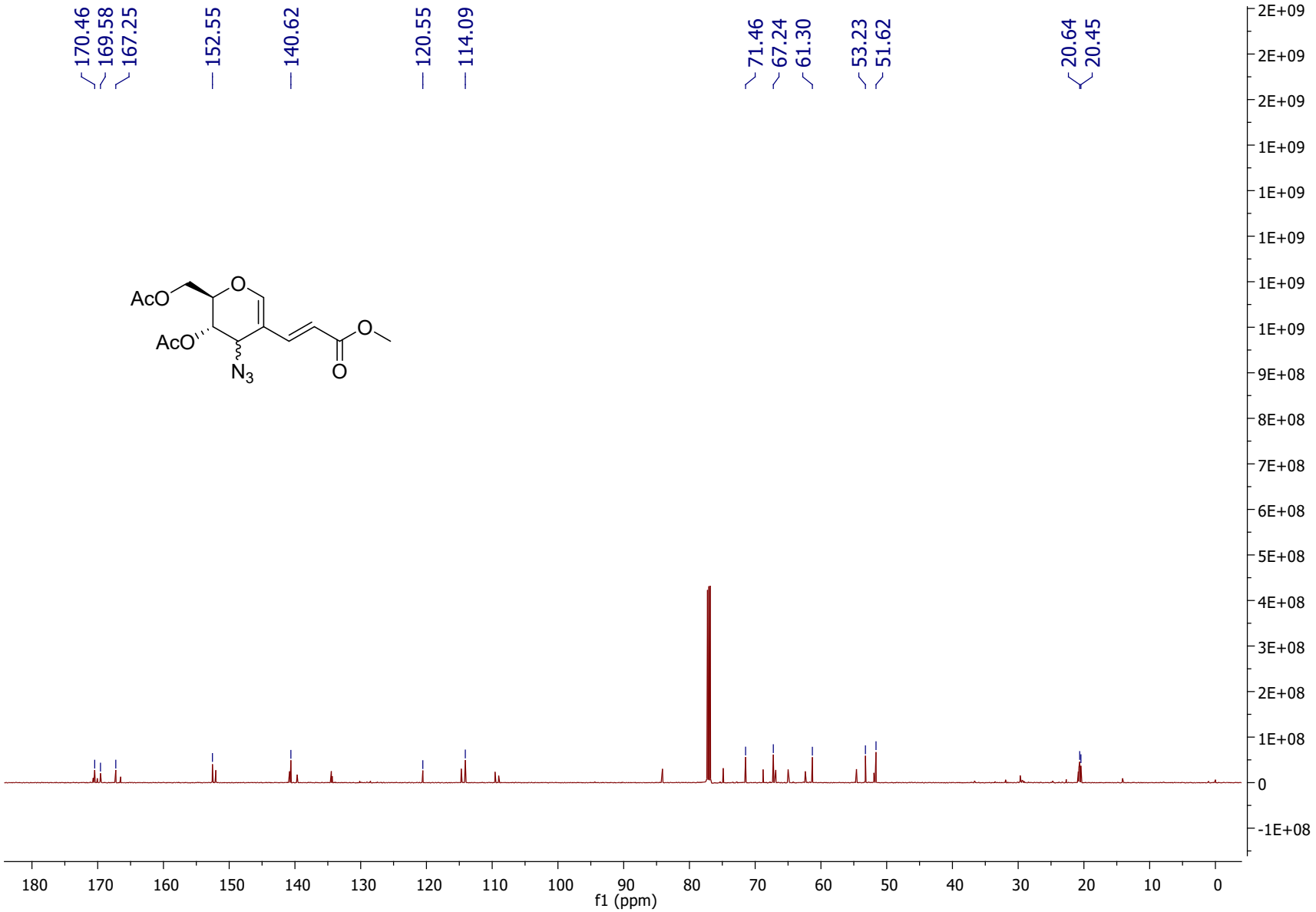
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2k**



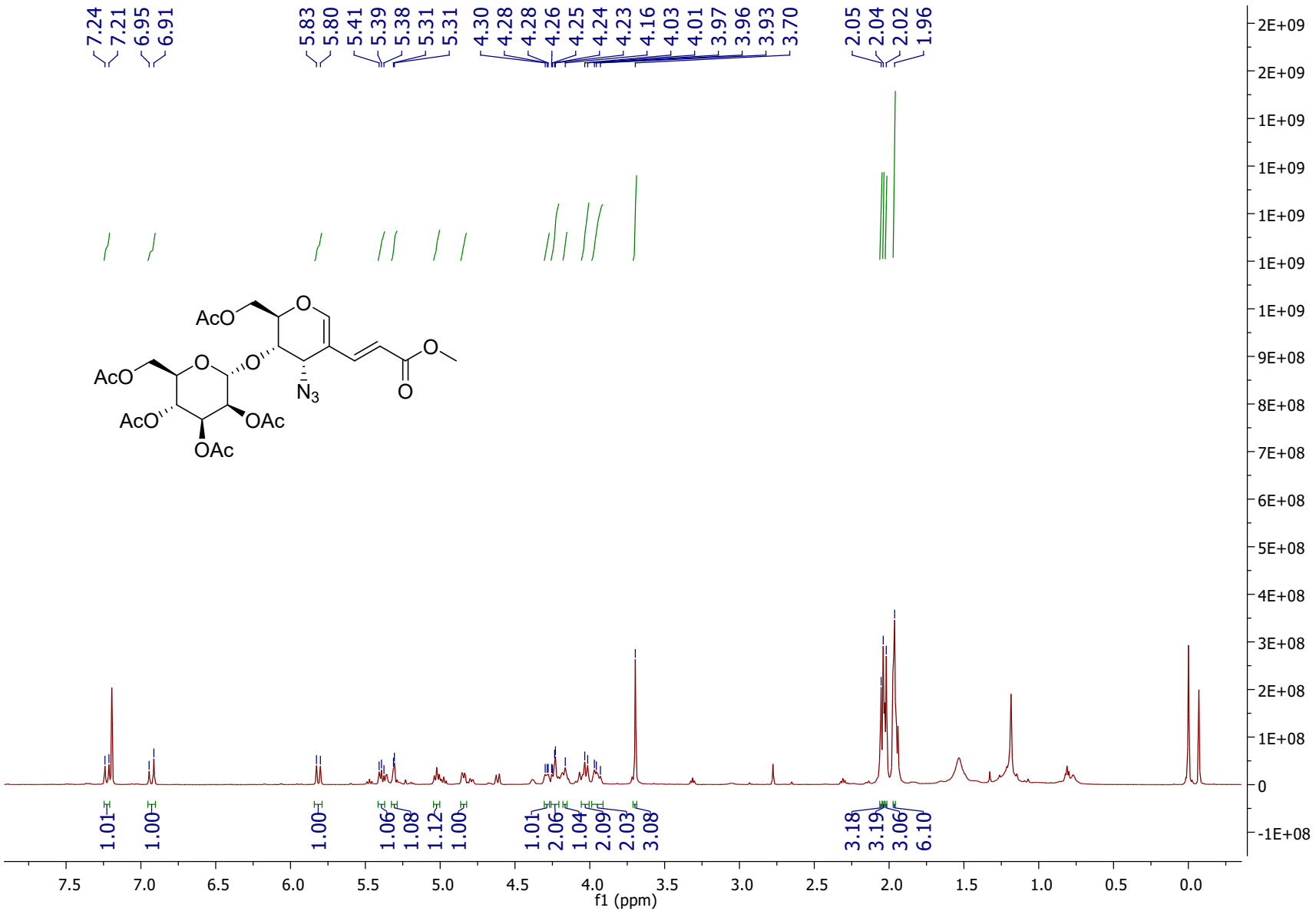
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2k**



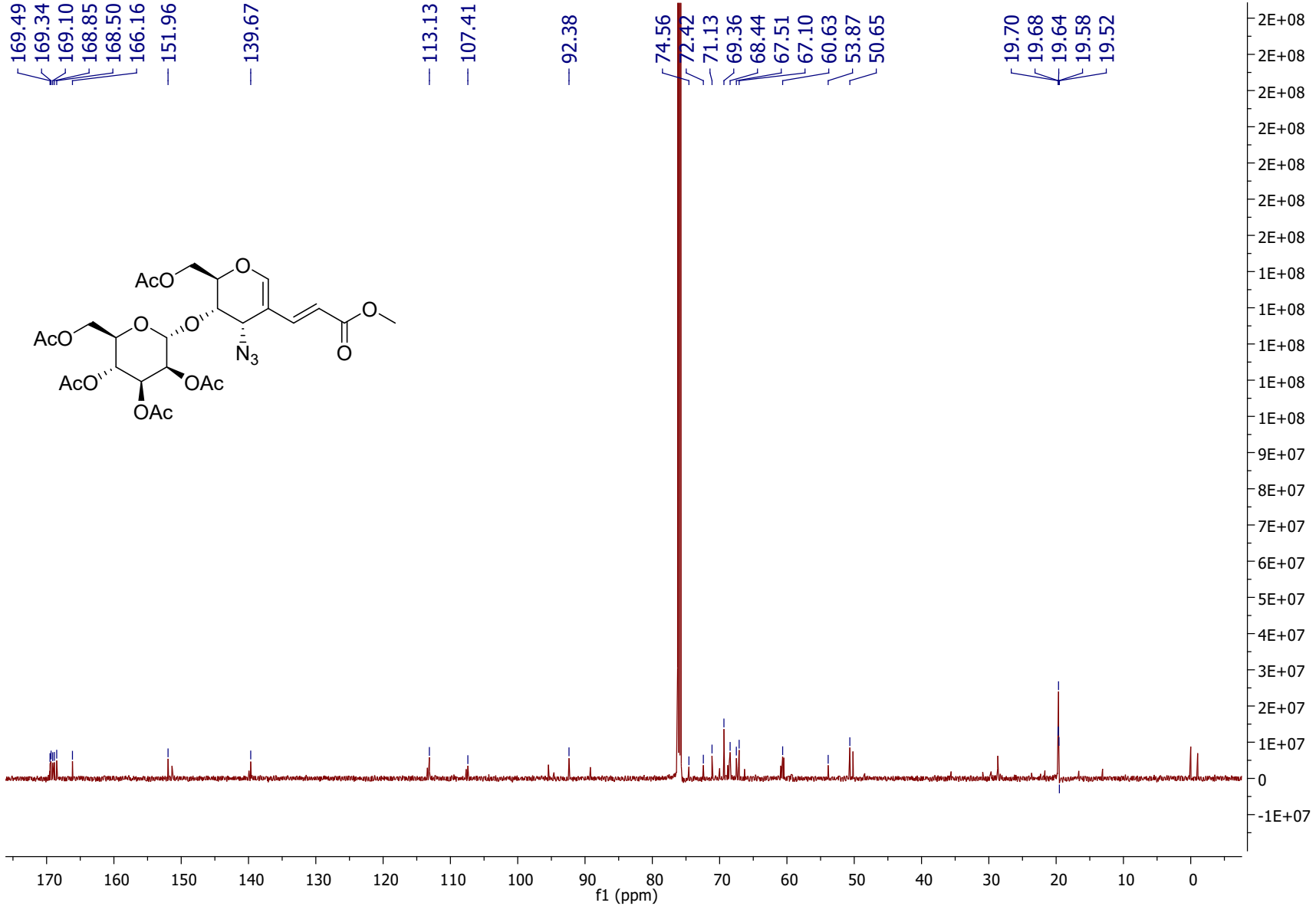
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2l**



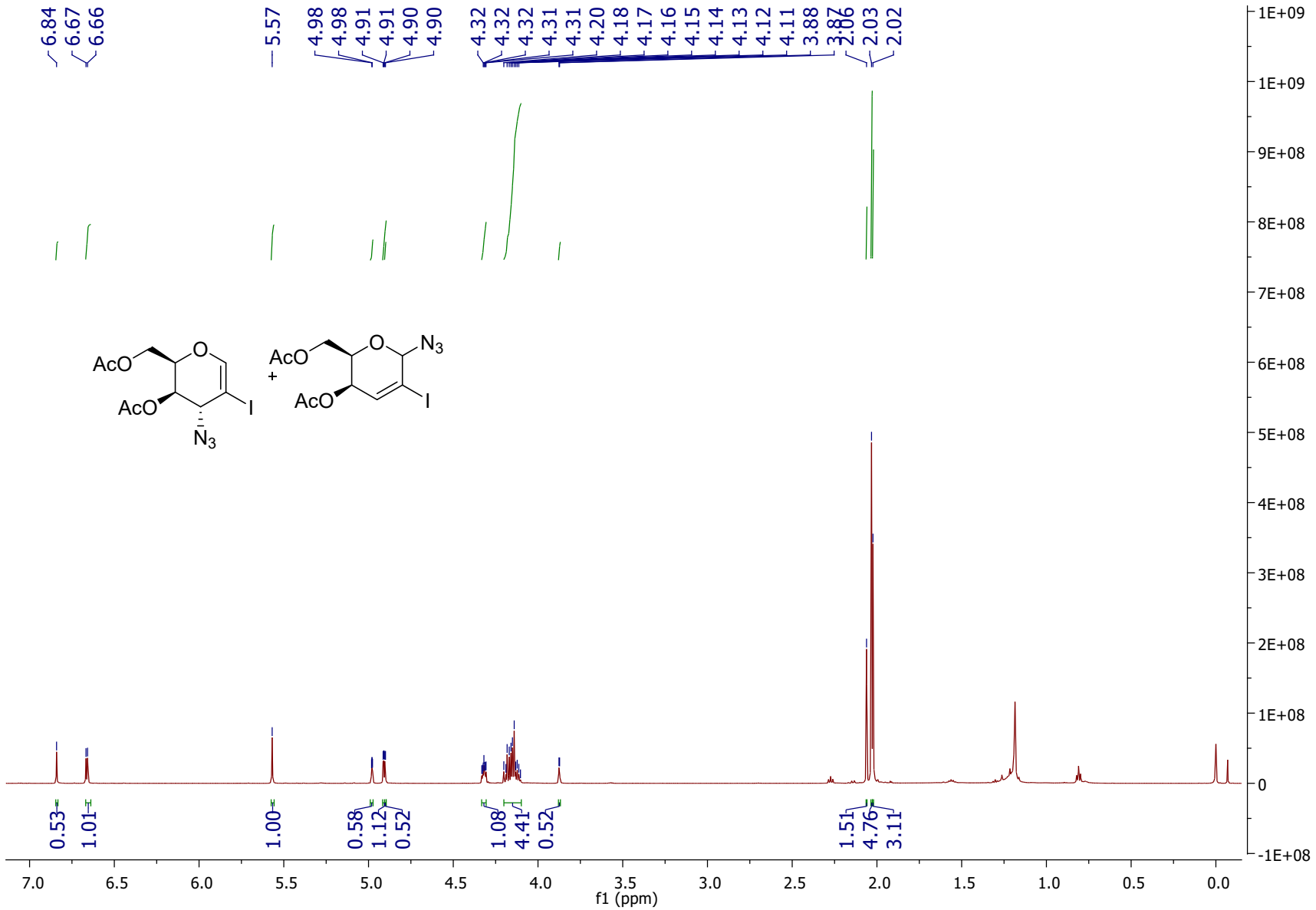
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2l**



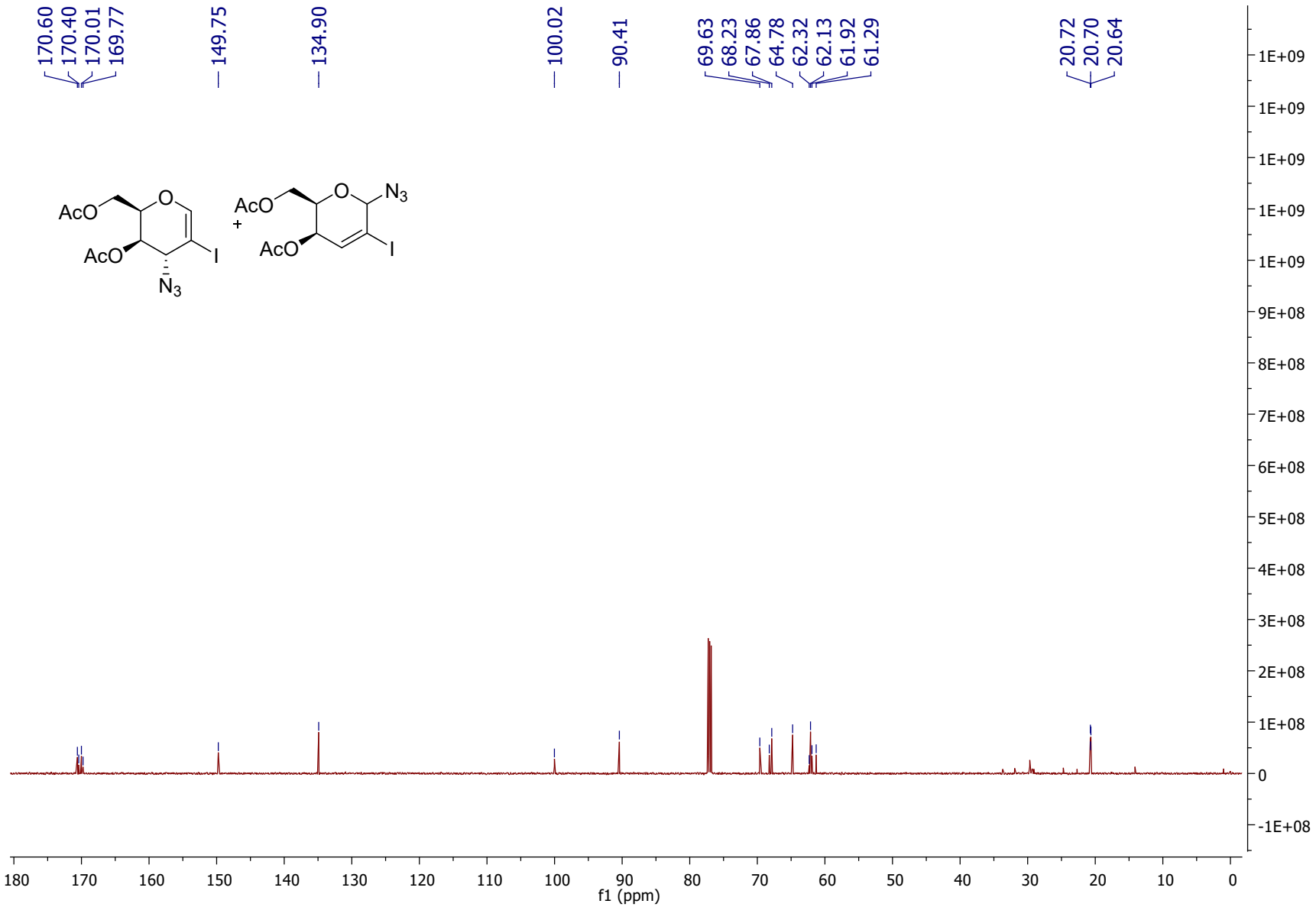
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2n**



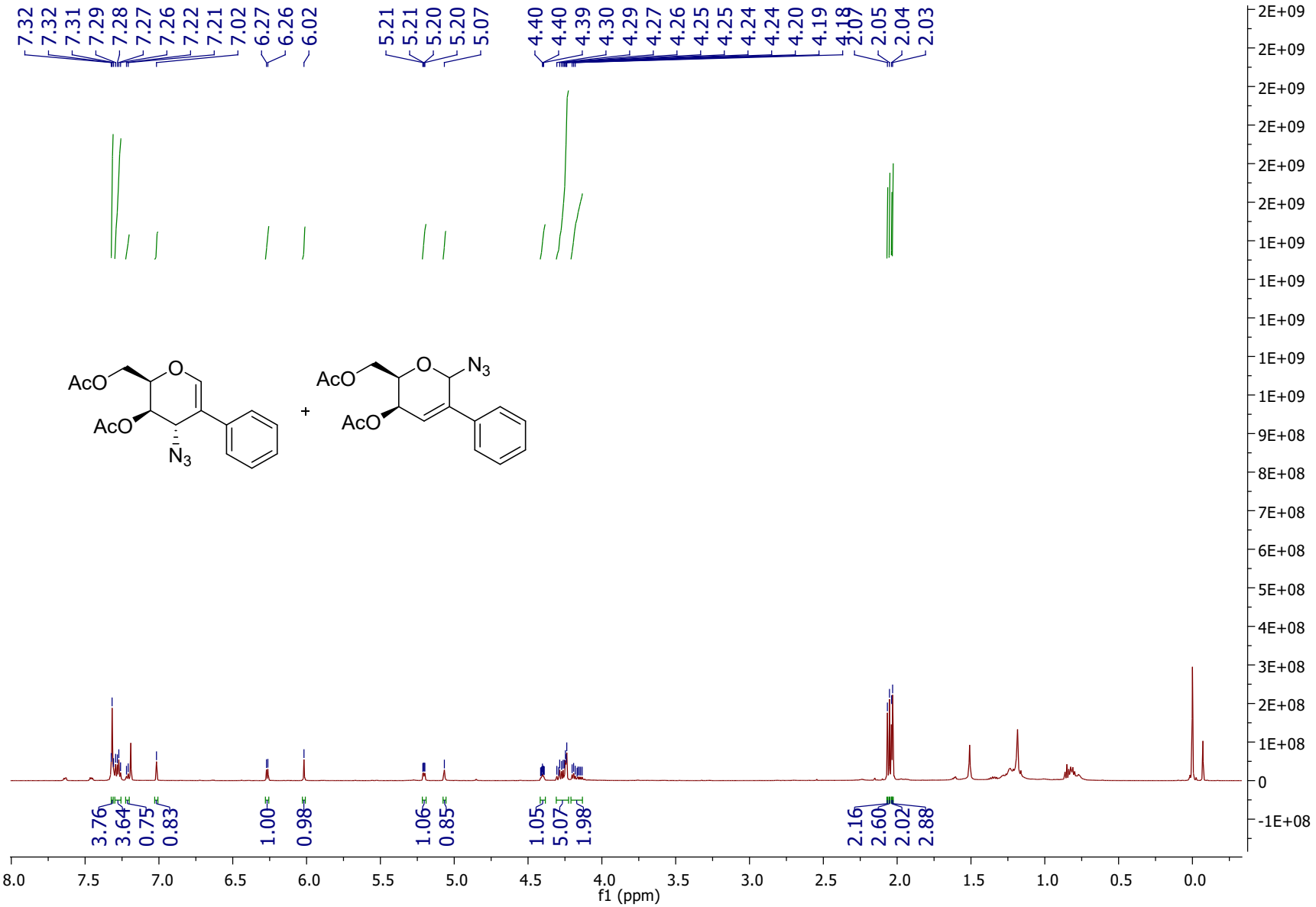
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2n**



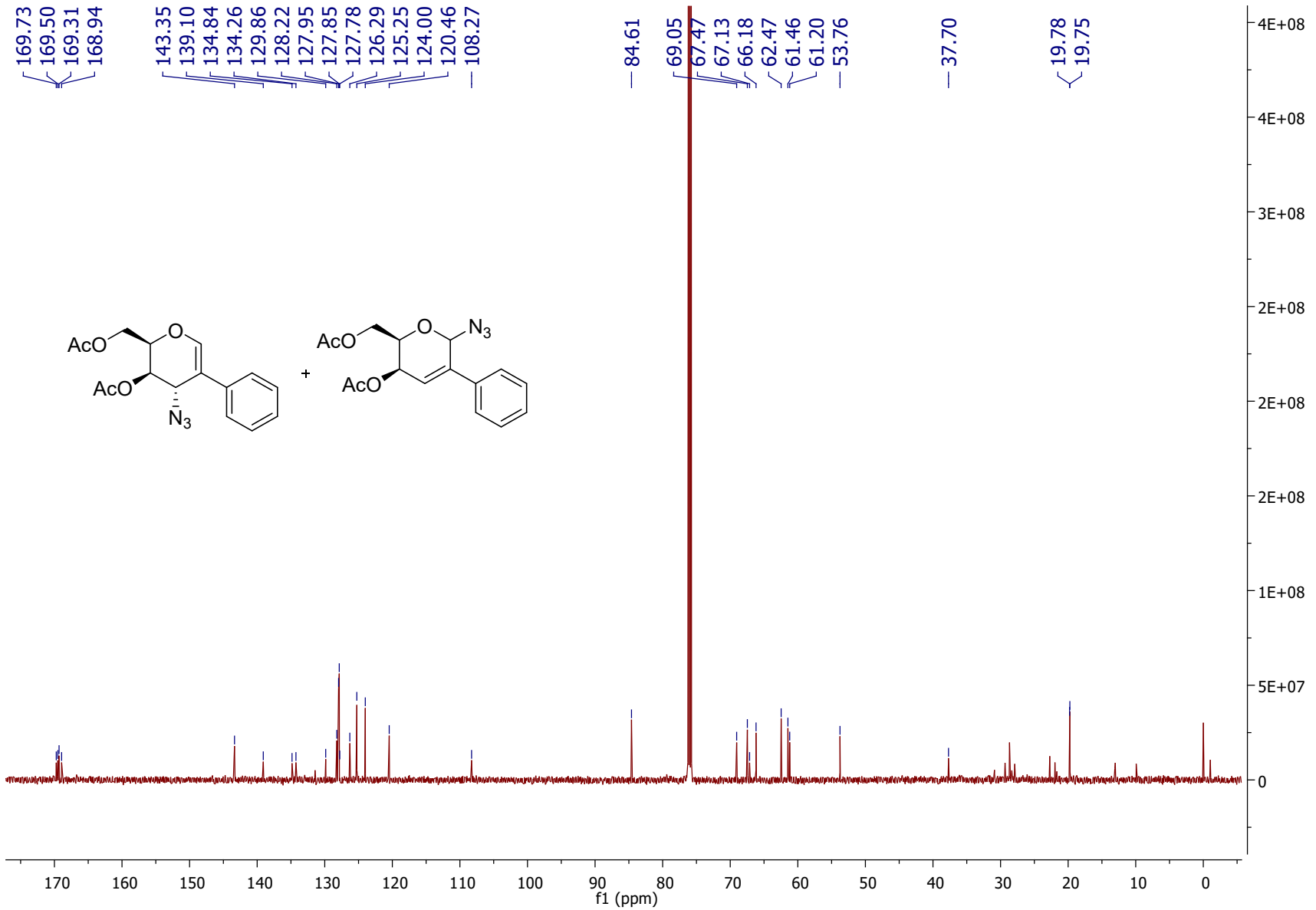
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3a**



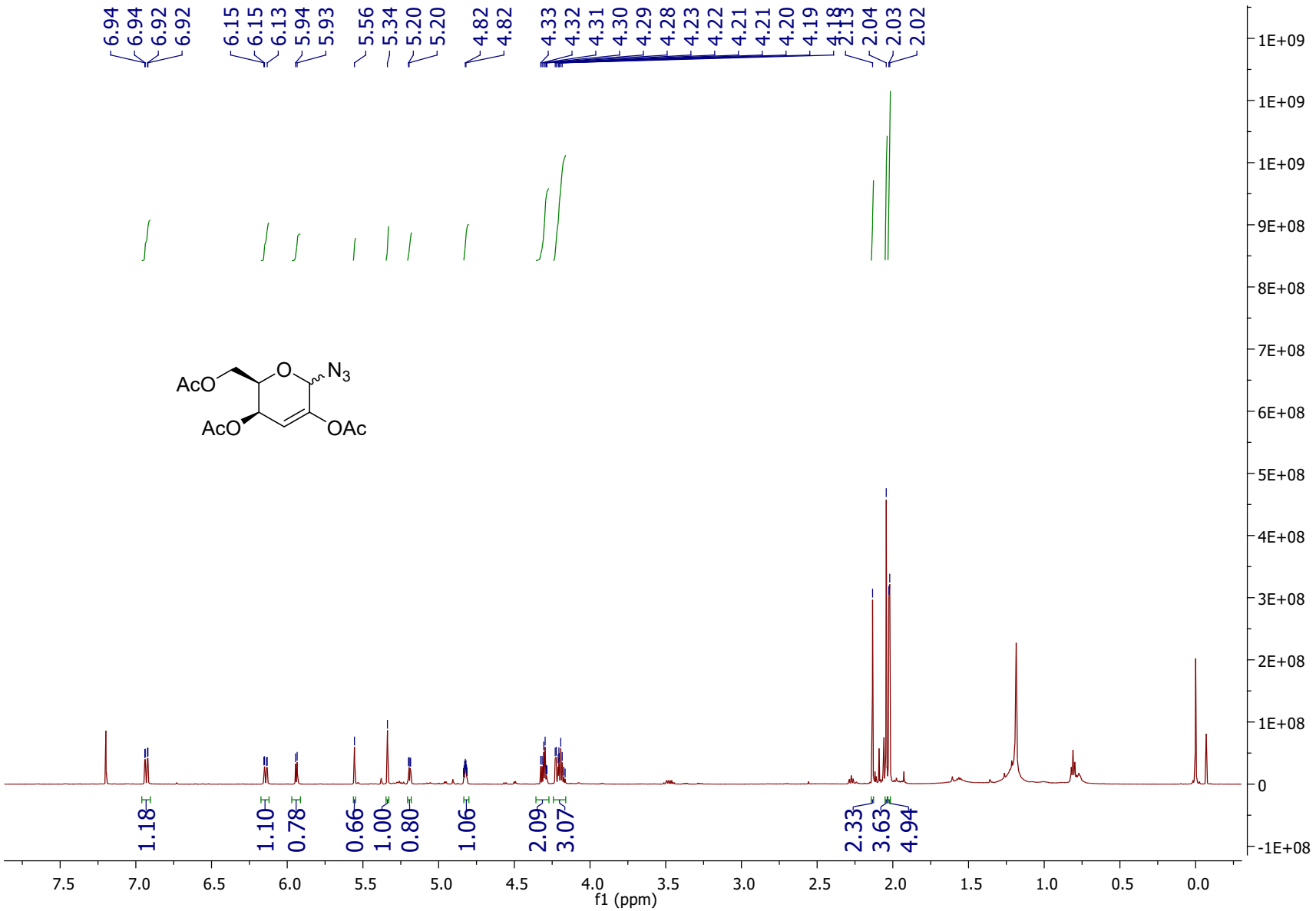
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3a**



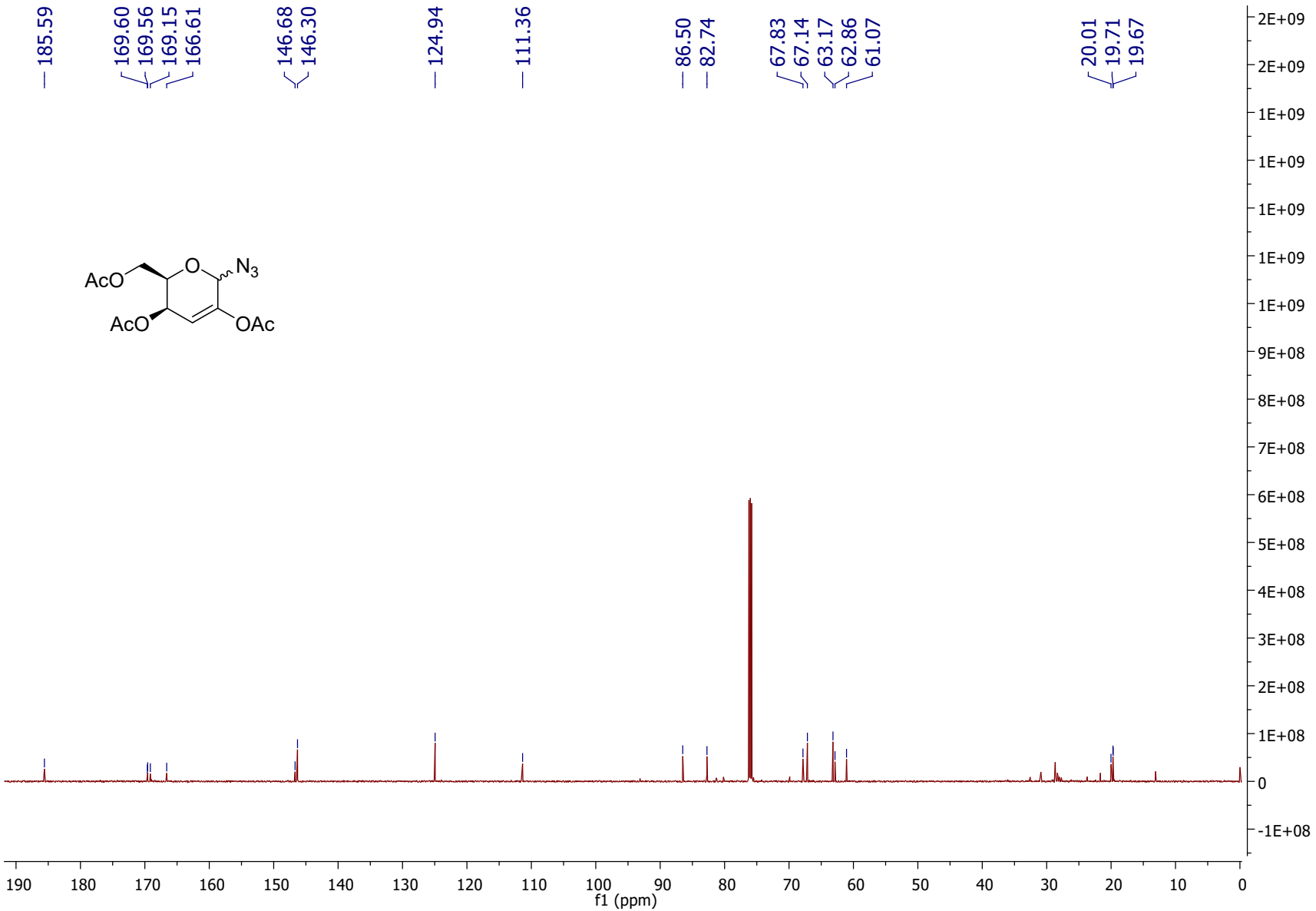
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3b**



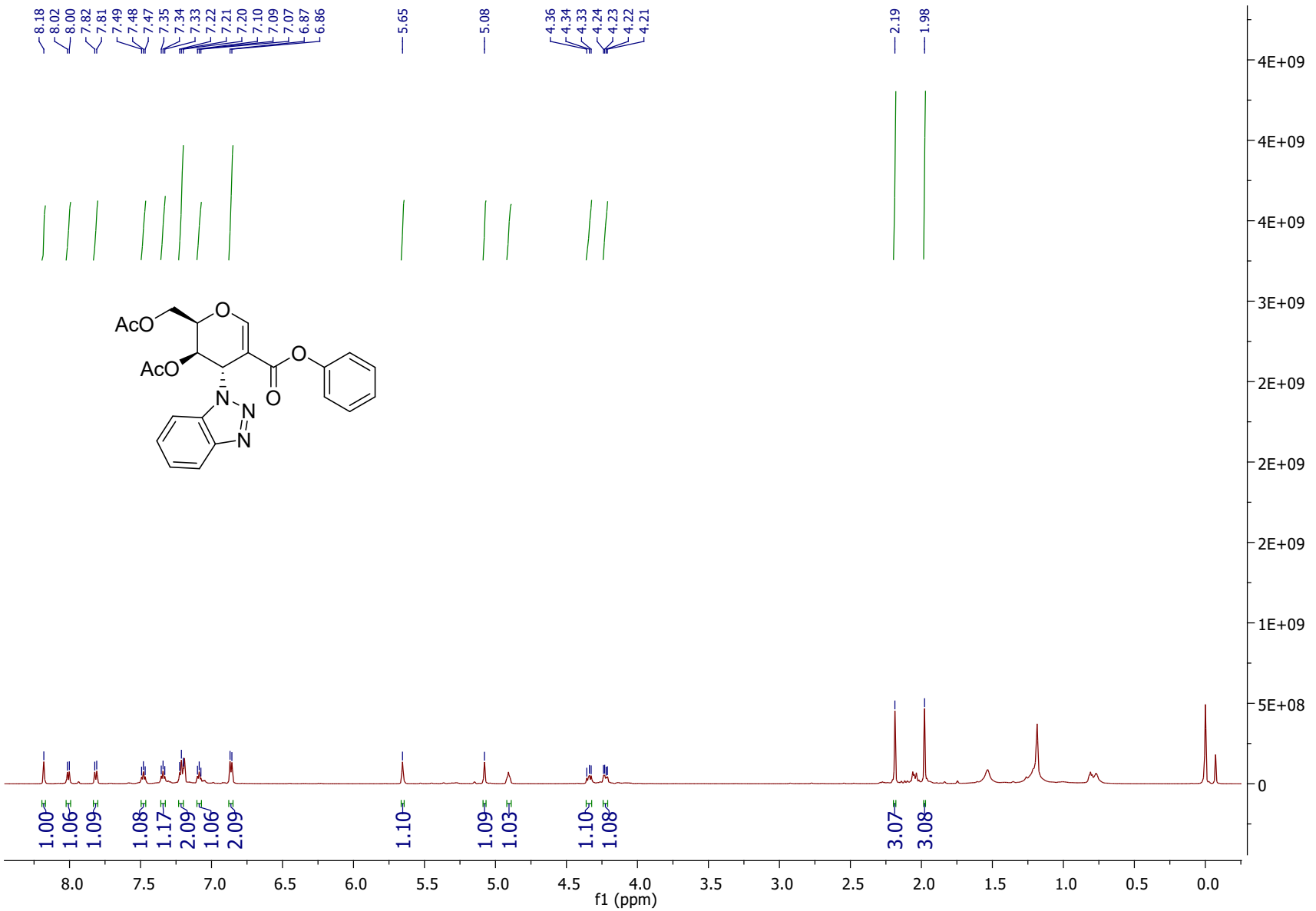
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3b**



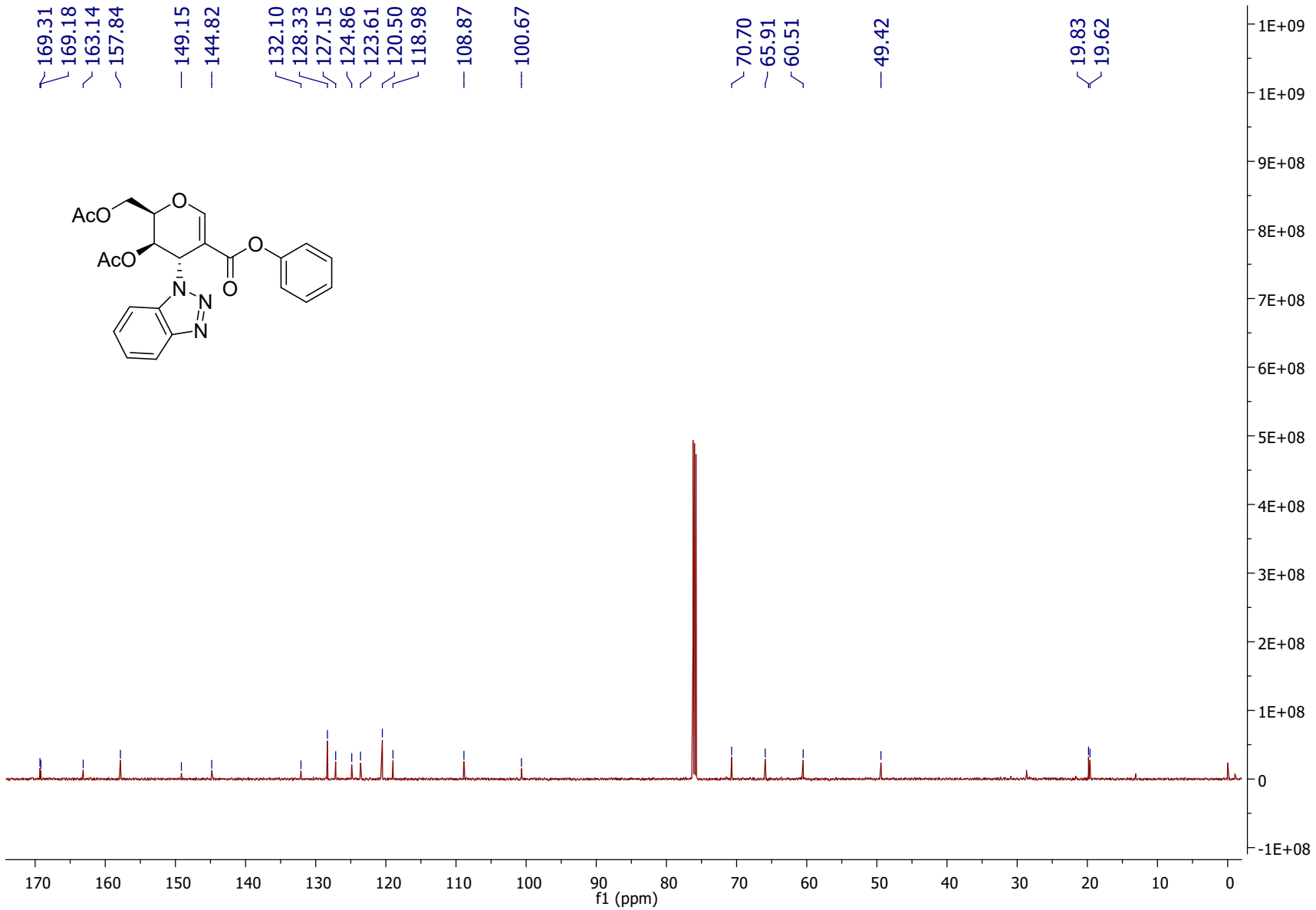
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3c**



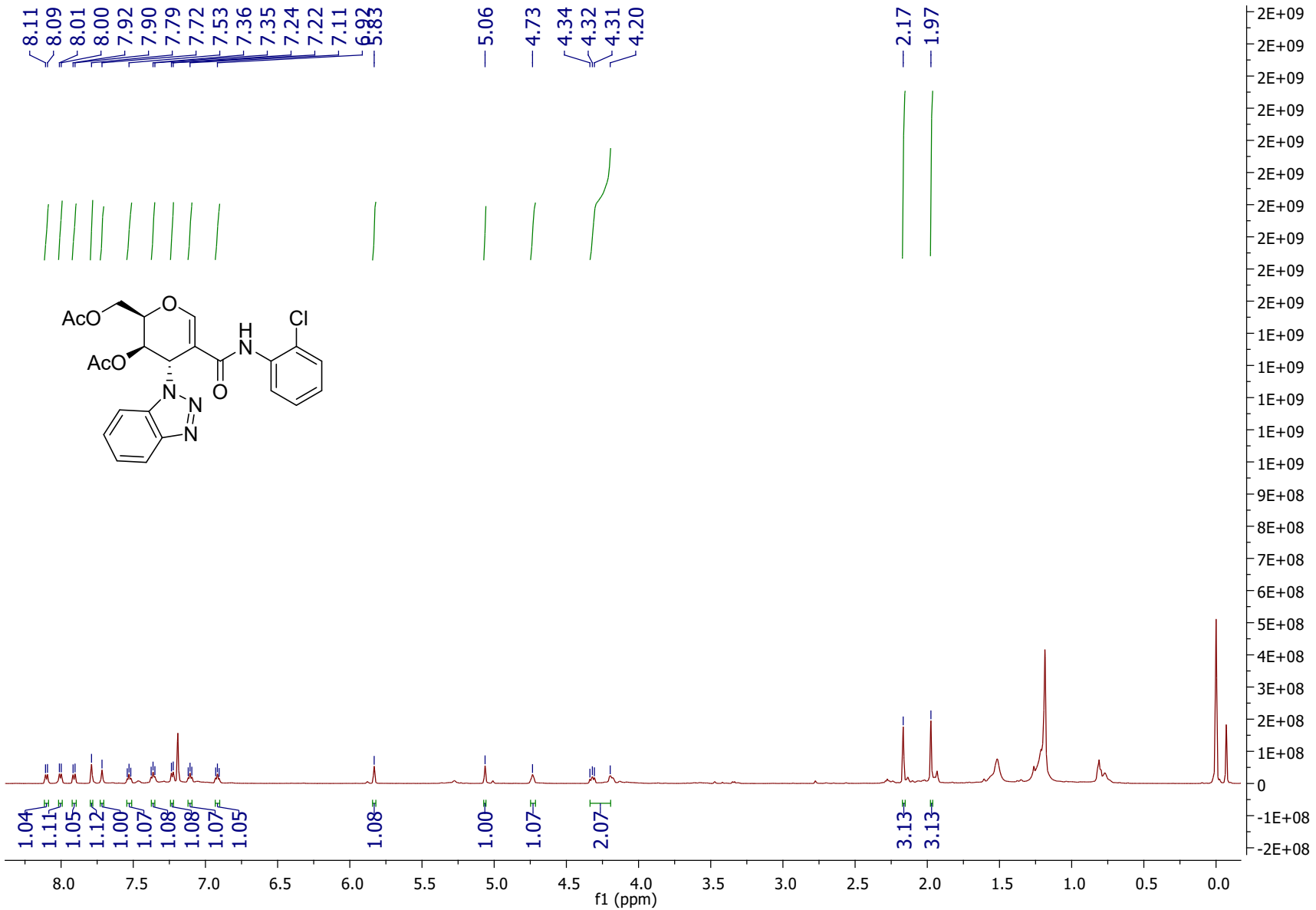
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3c**



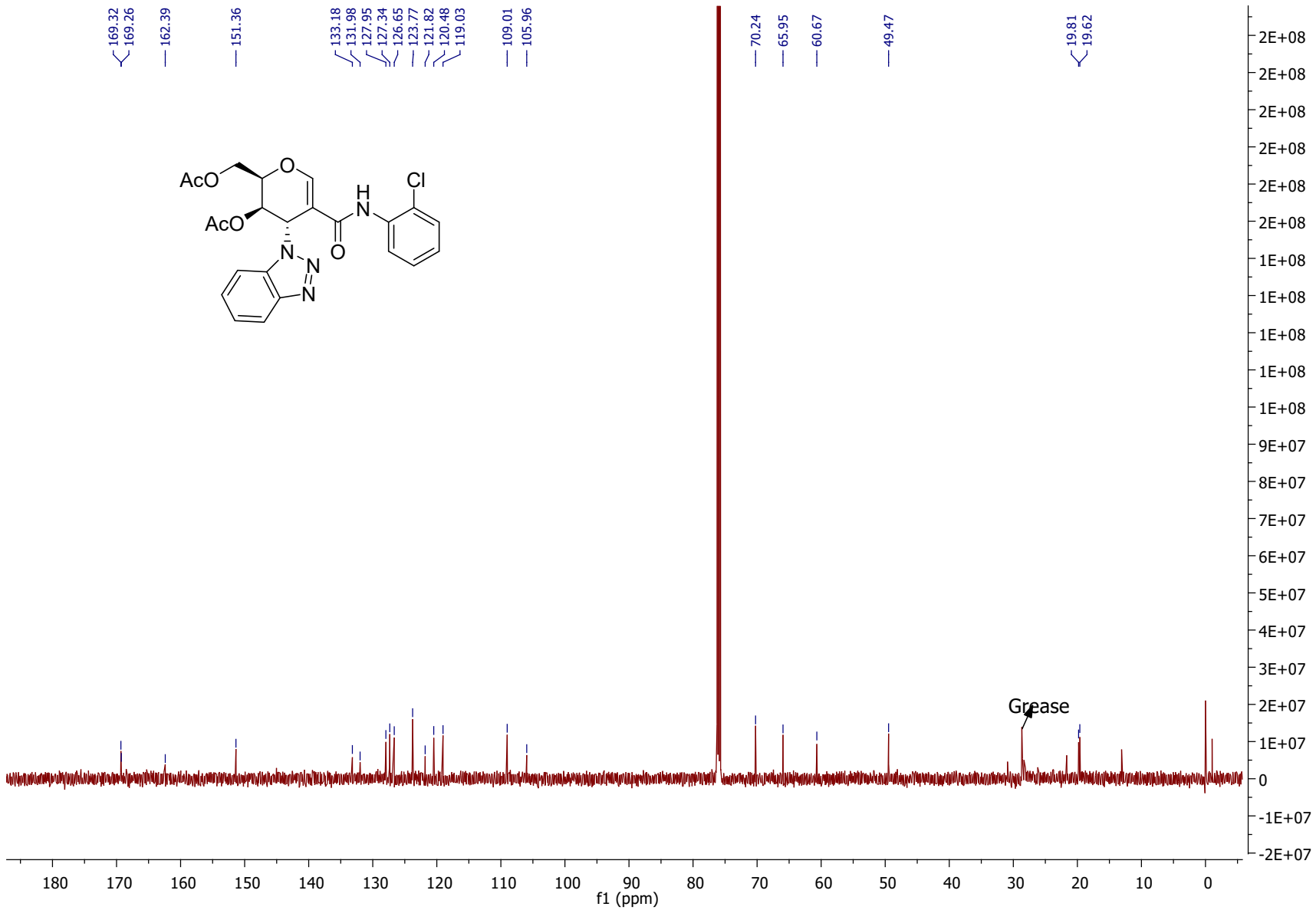
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4a**



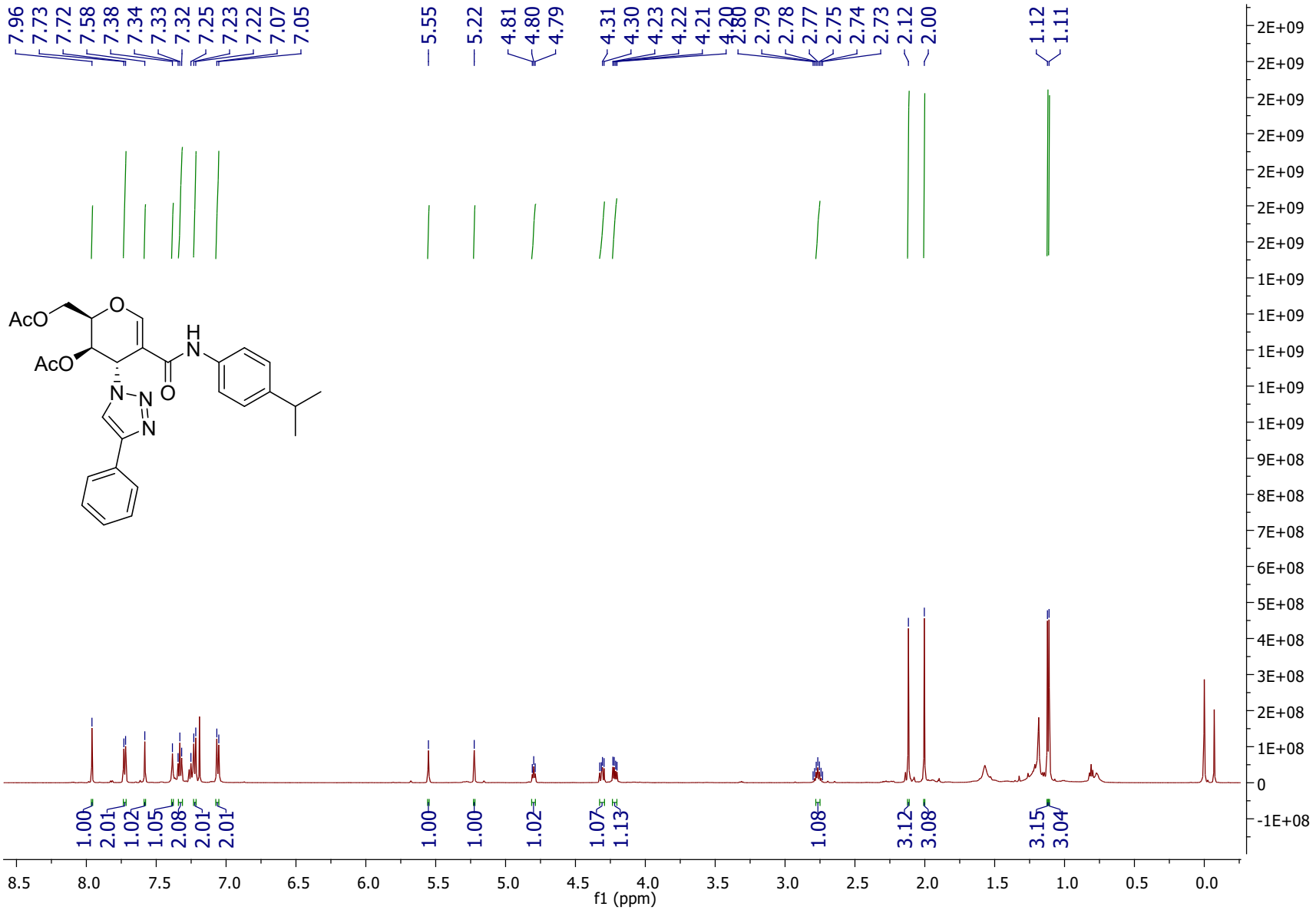
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4a**



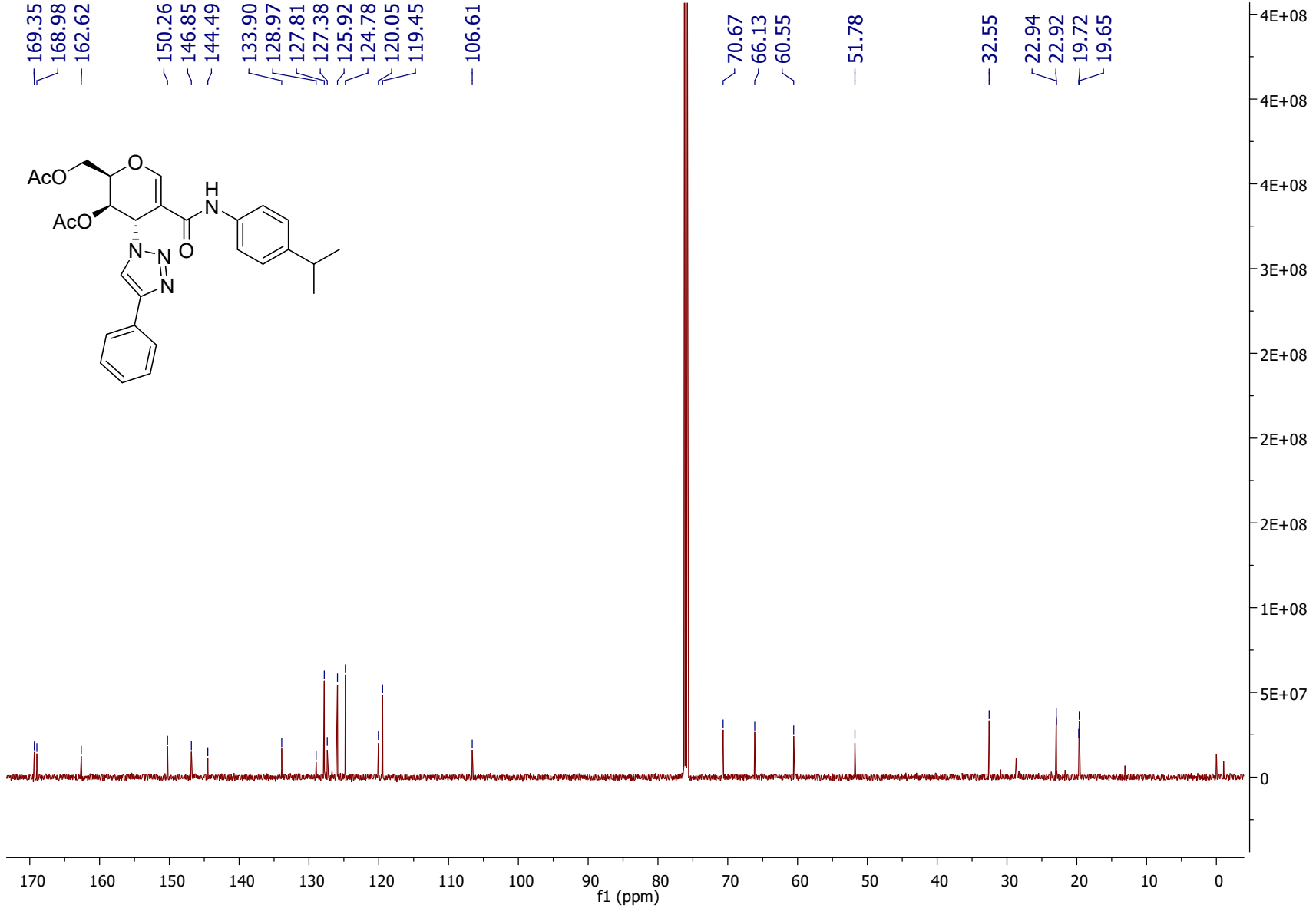
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4b**



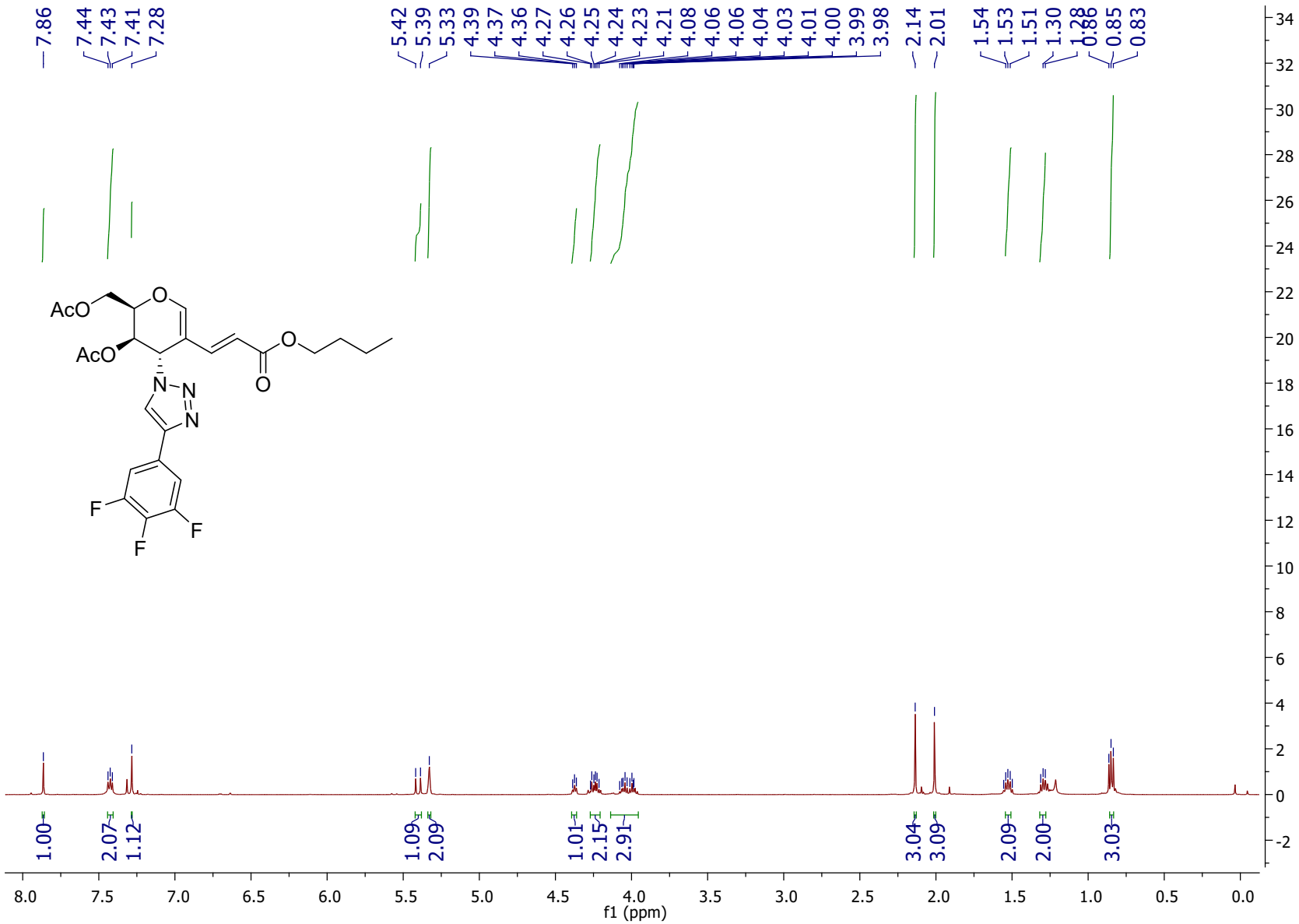
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4b**



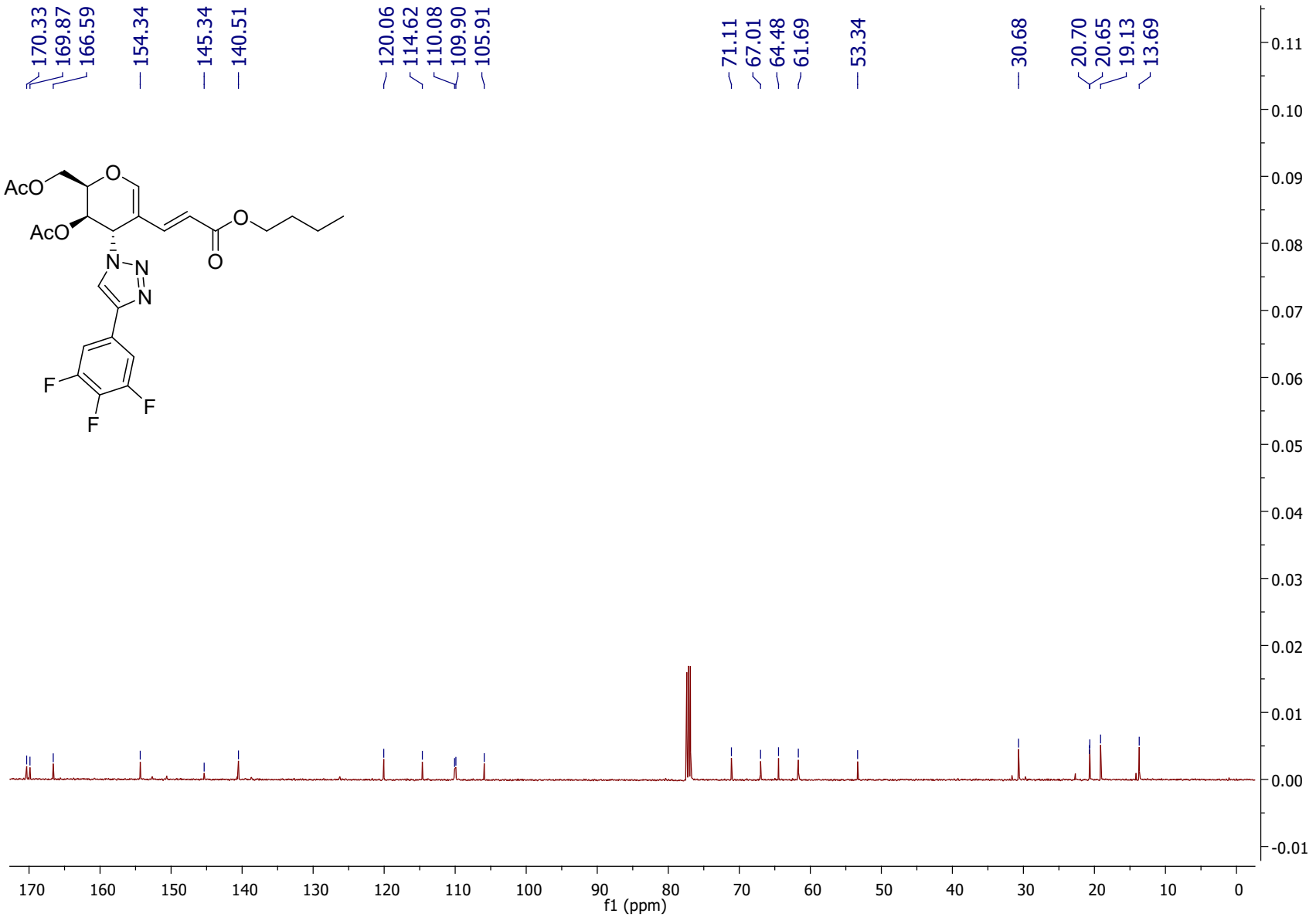
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4c**



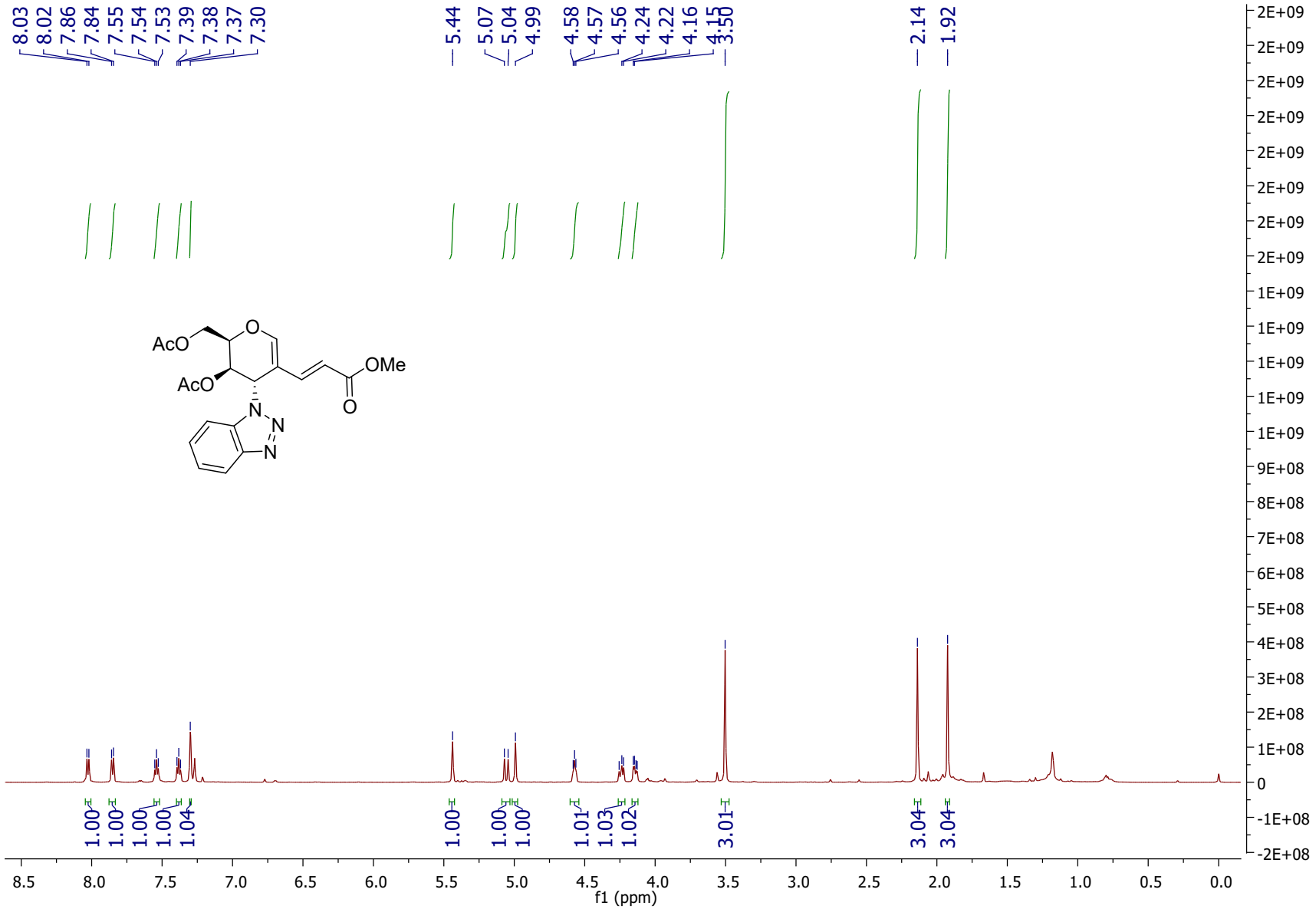
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4c**



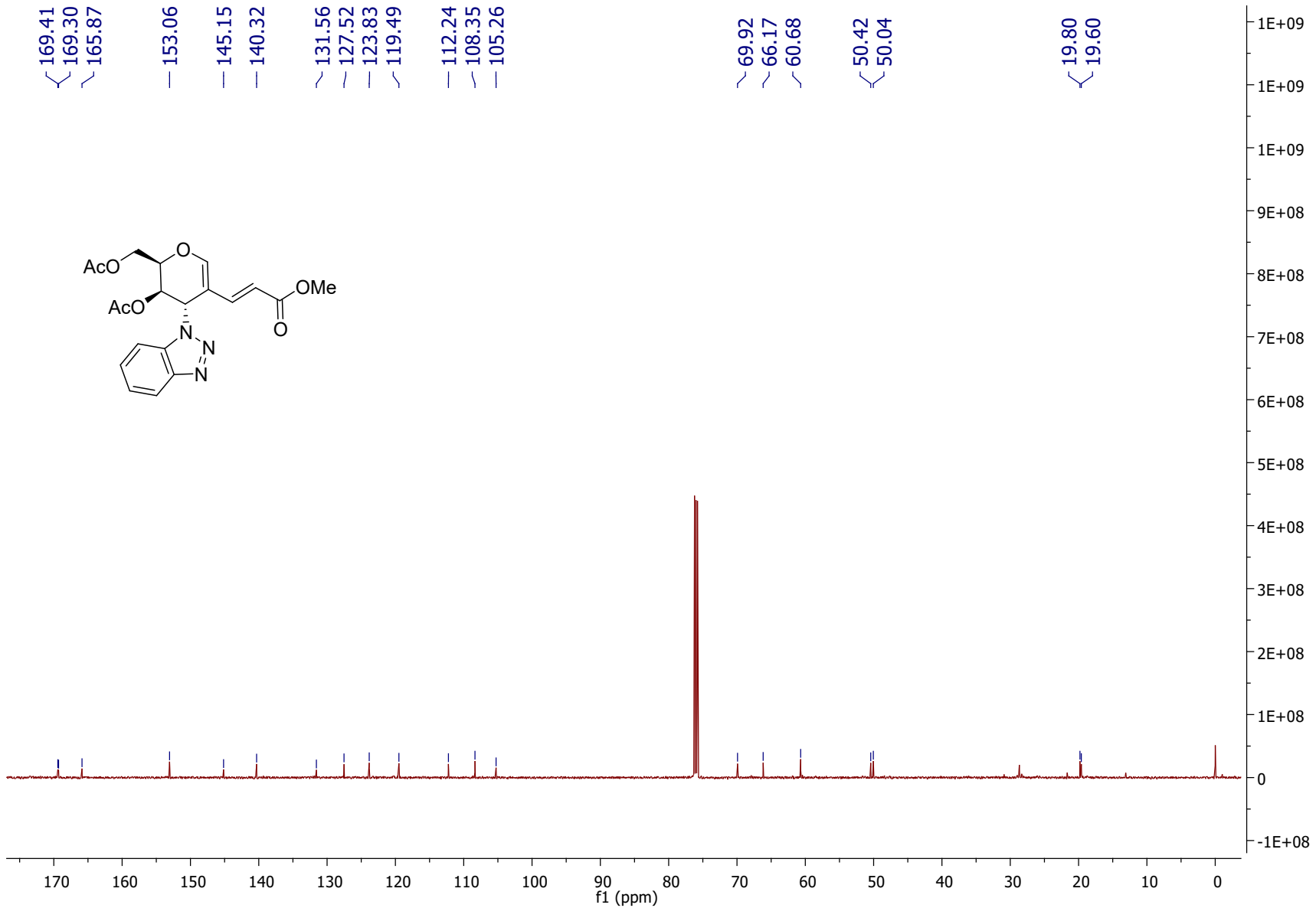
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4d**



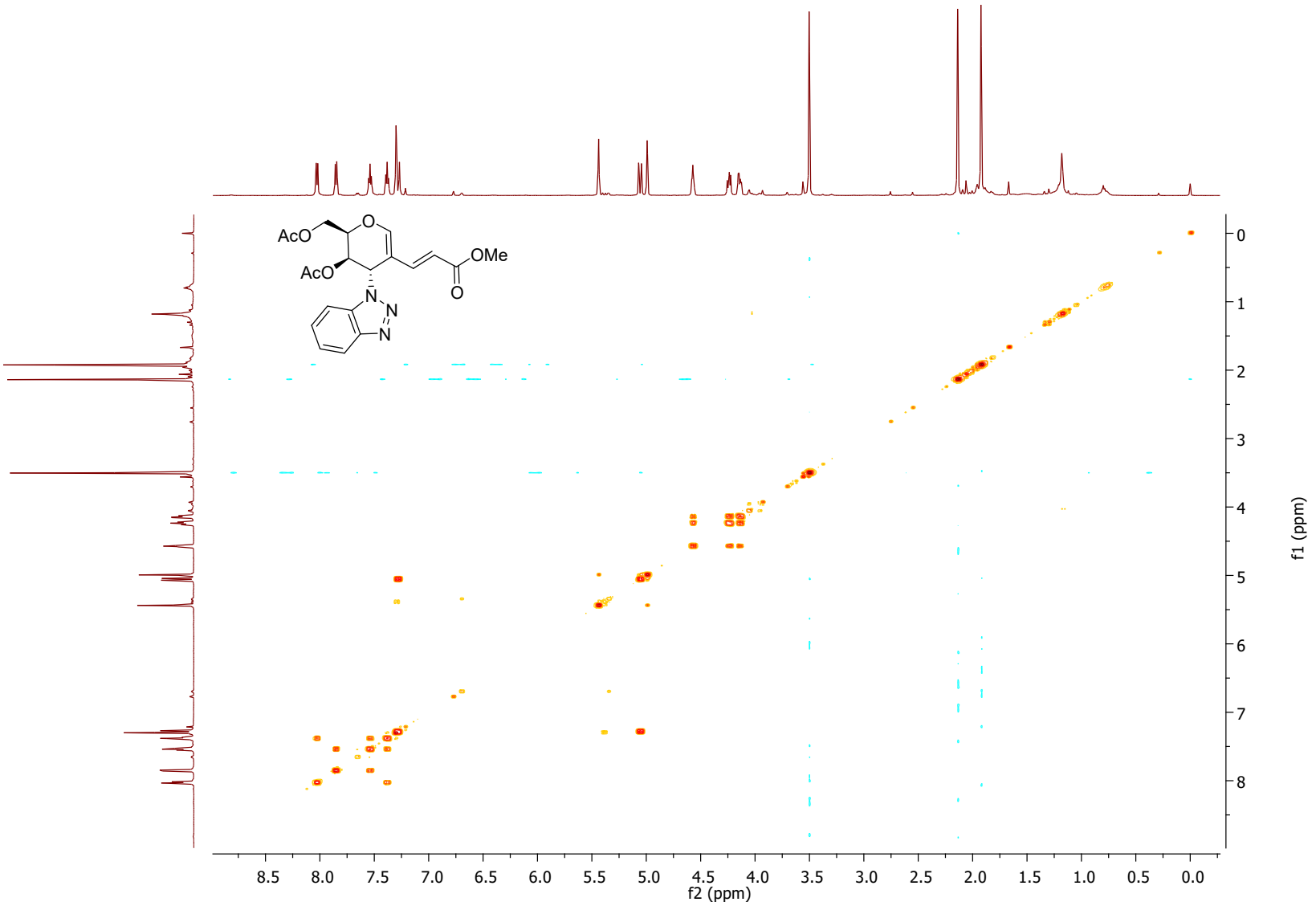
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4d**



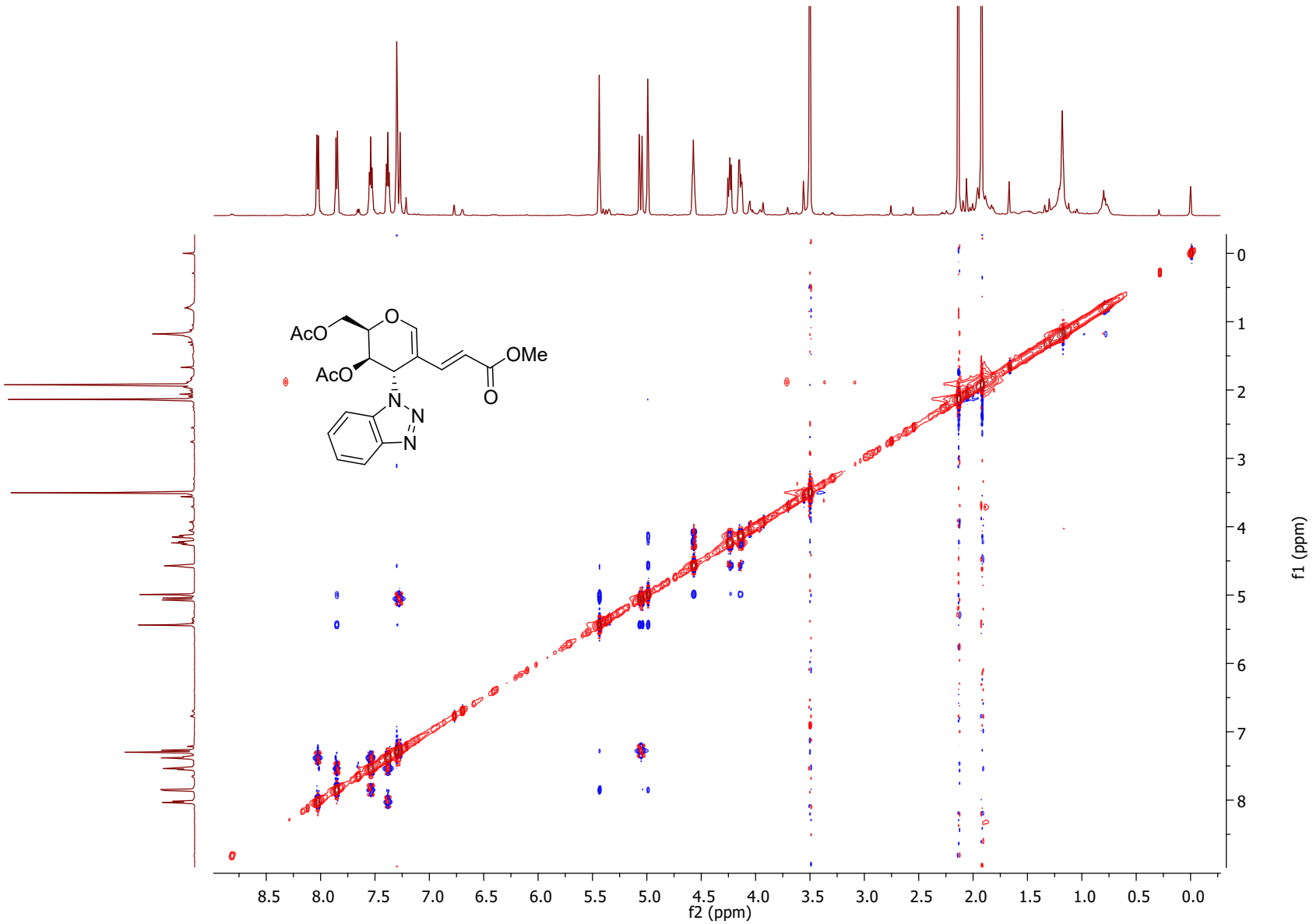
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4e**



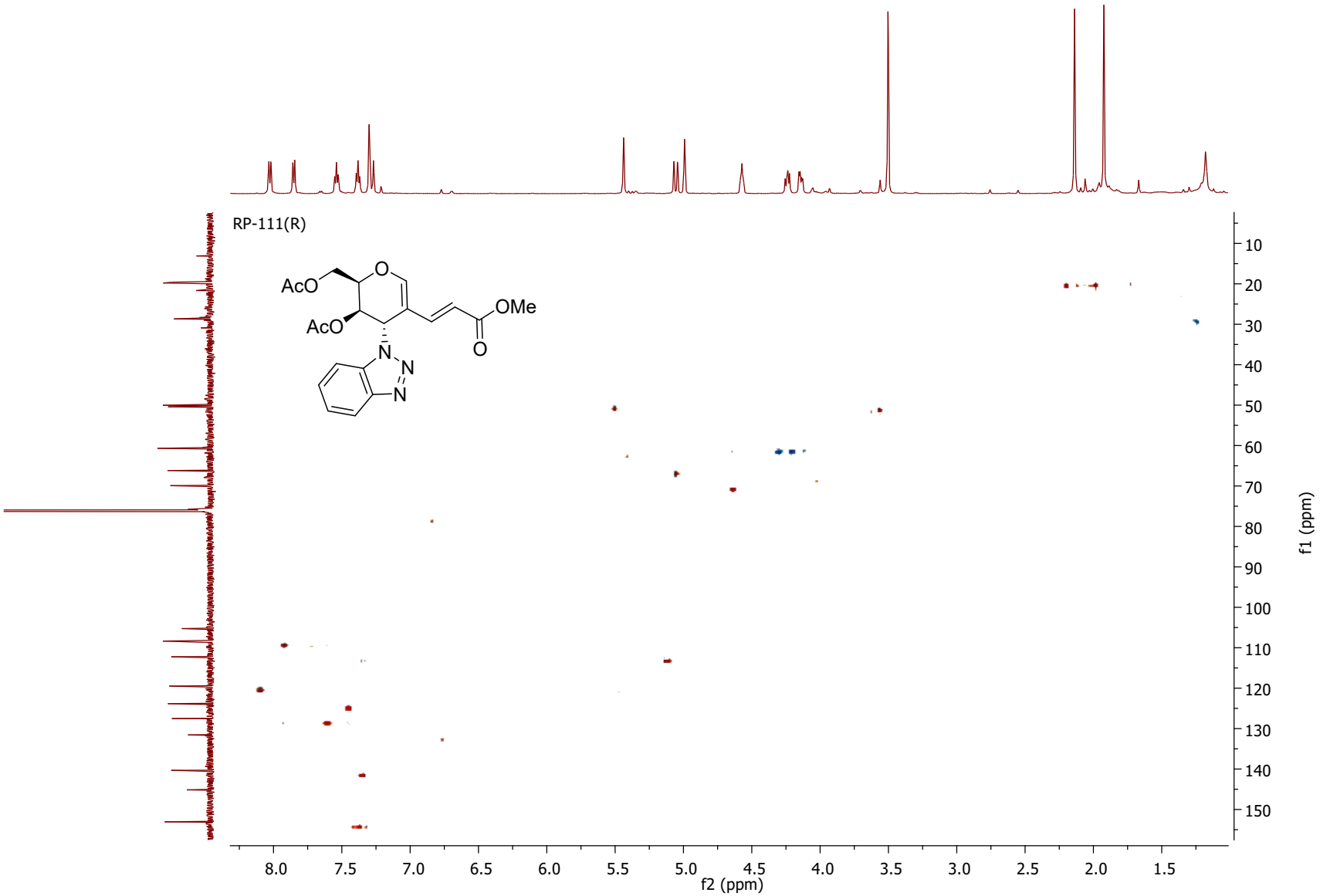
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4e**



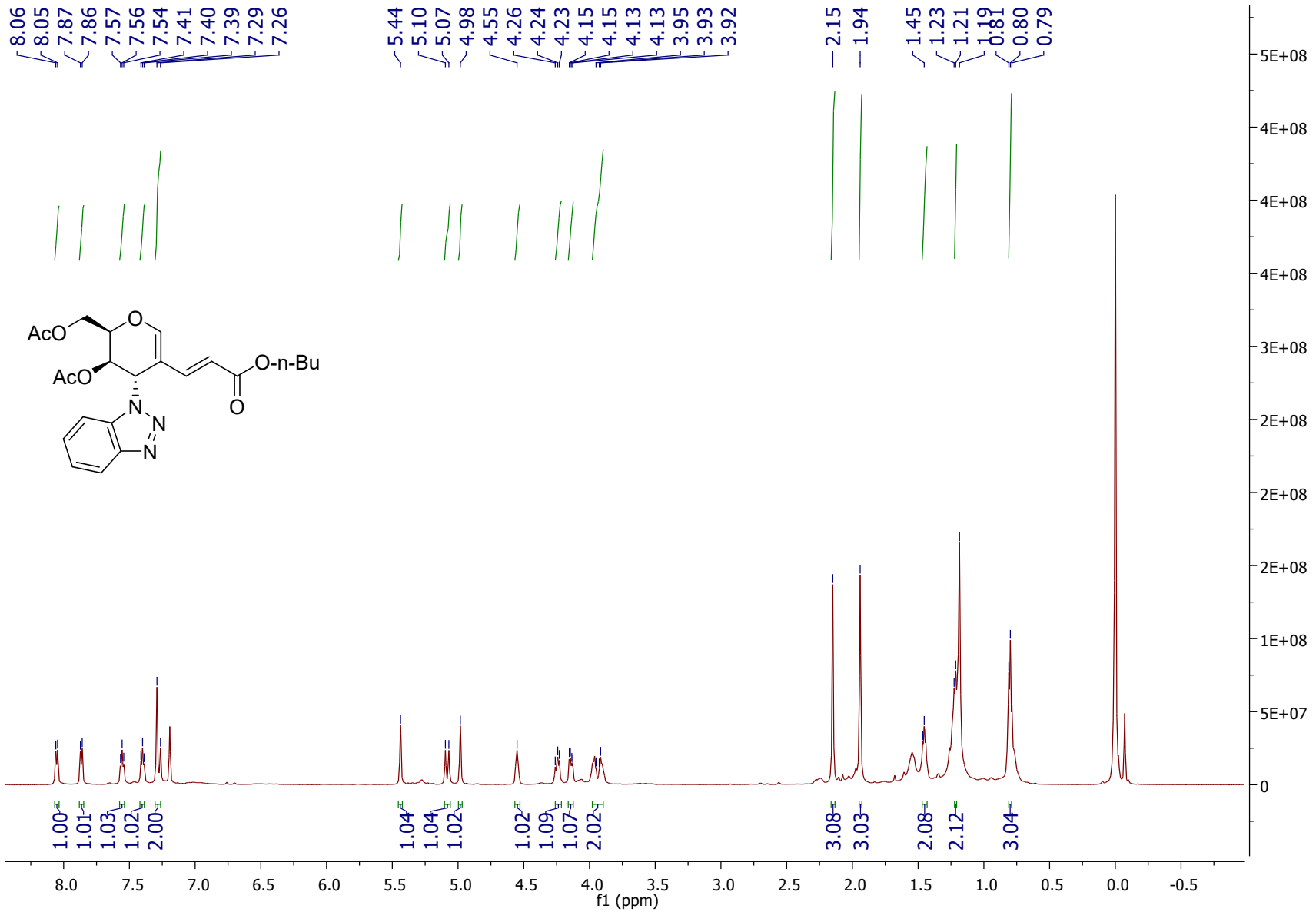
COSY of compound **4e**



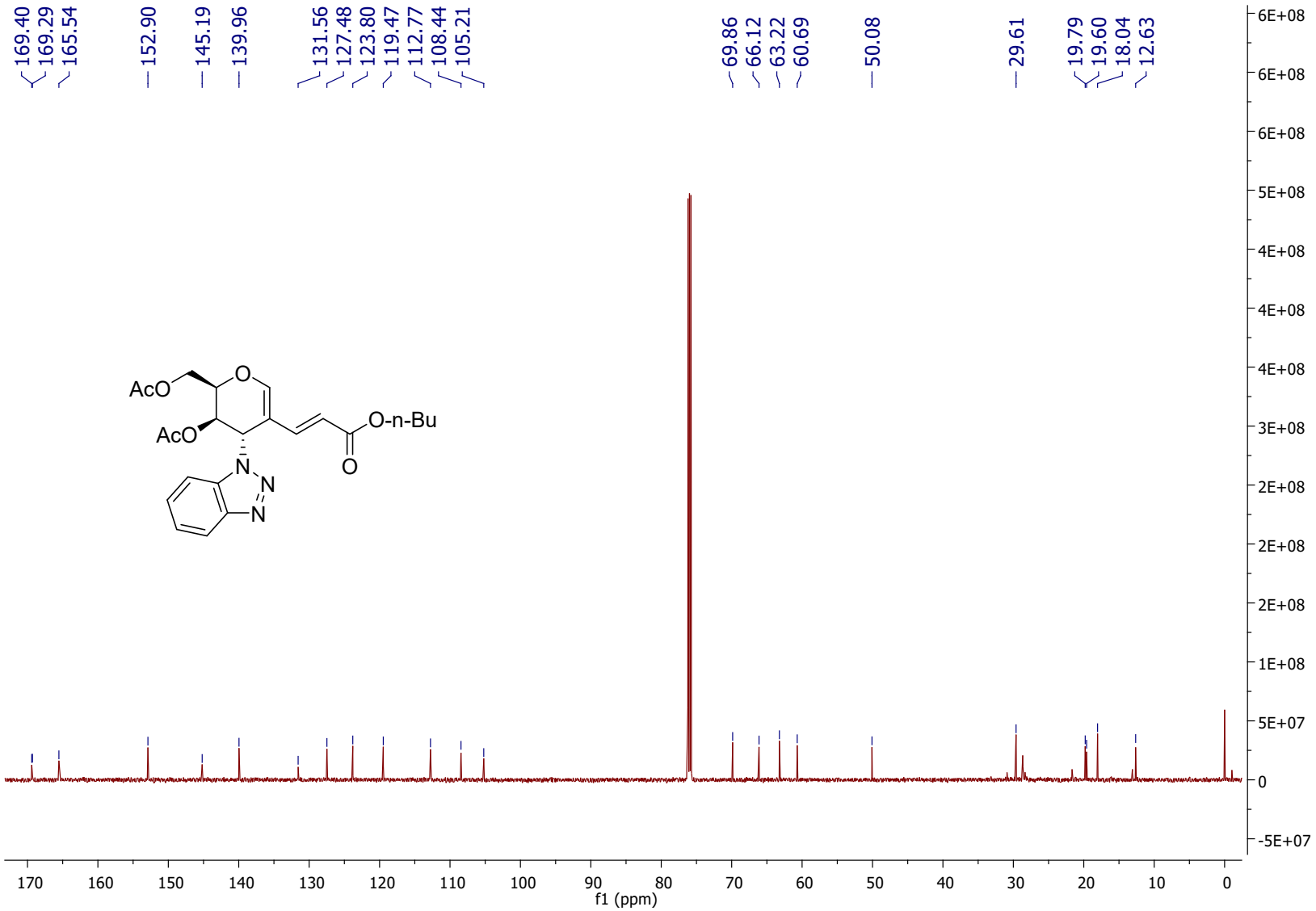
NOESY of compound **4e**



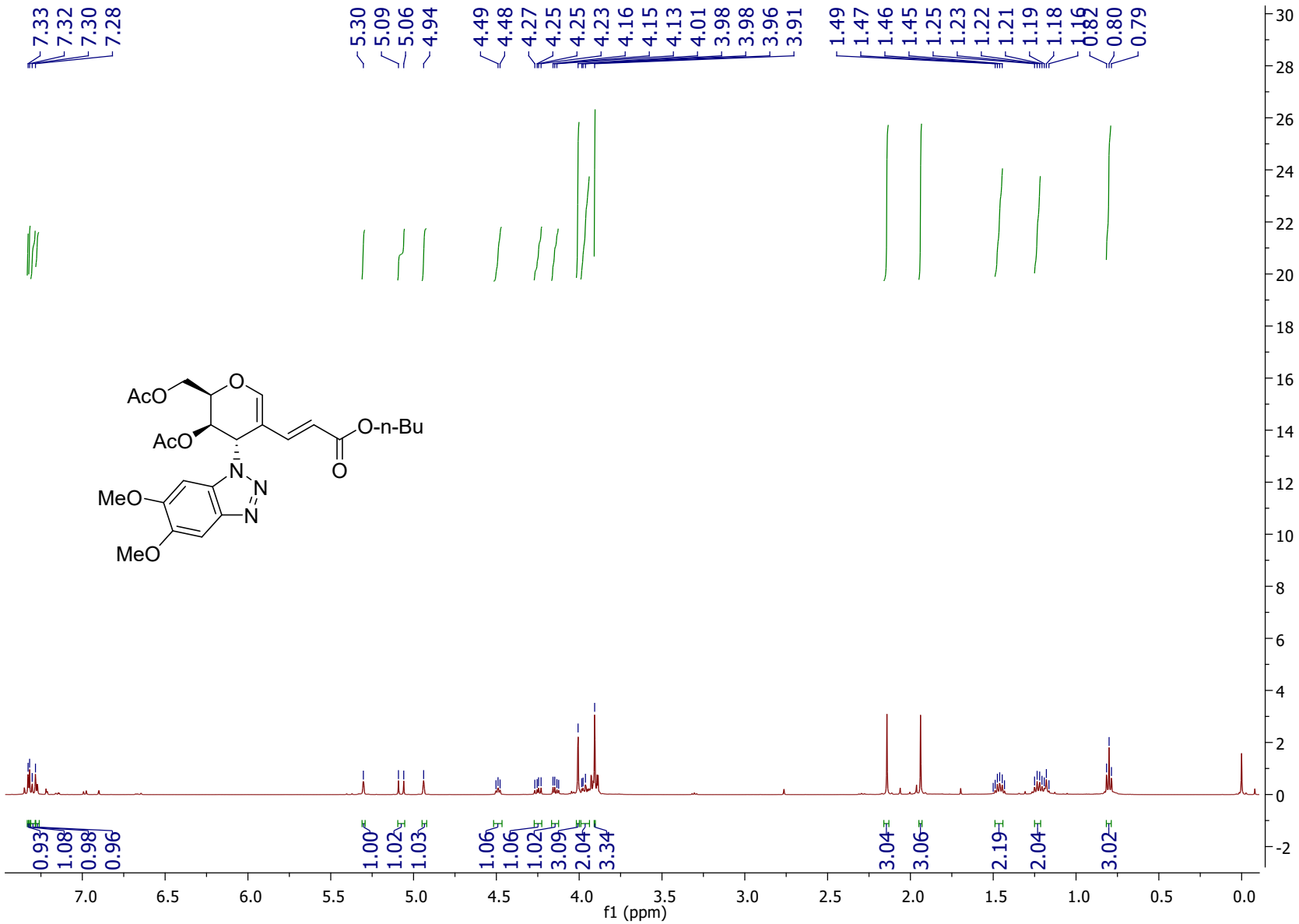
HSQC of compound **4e**



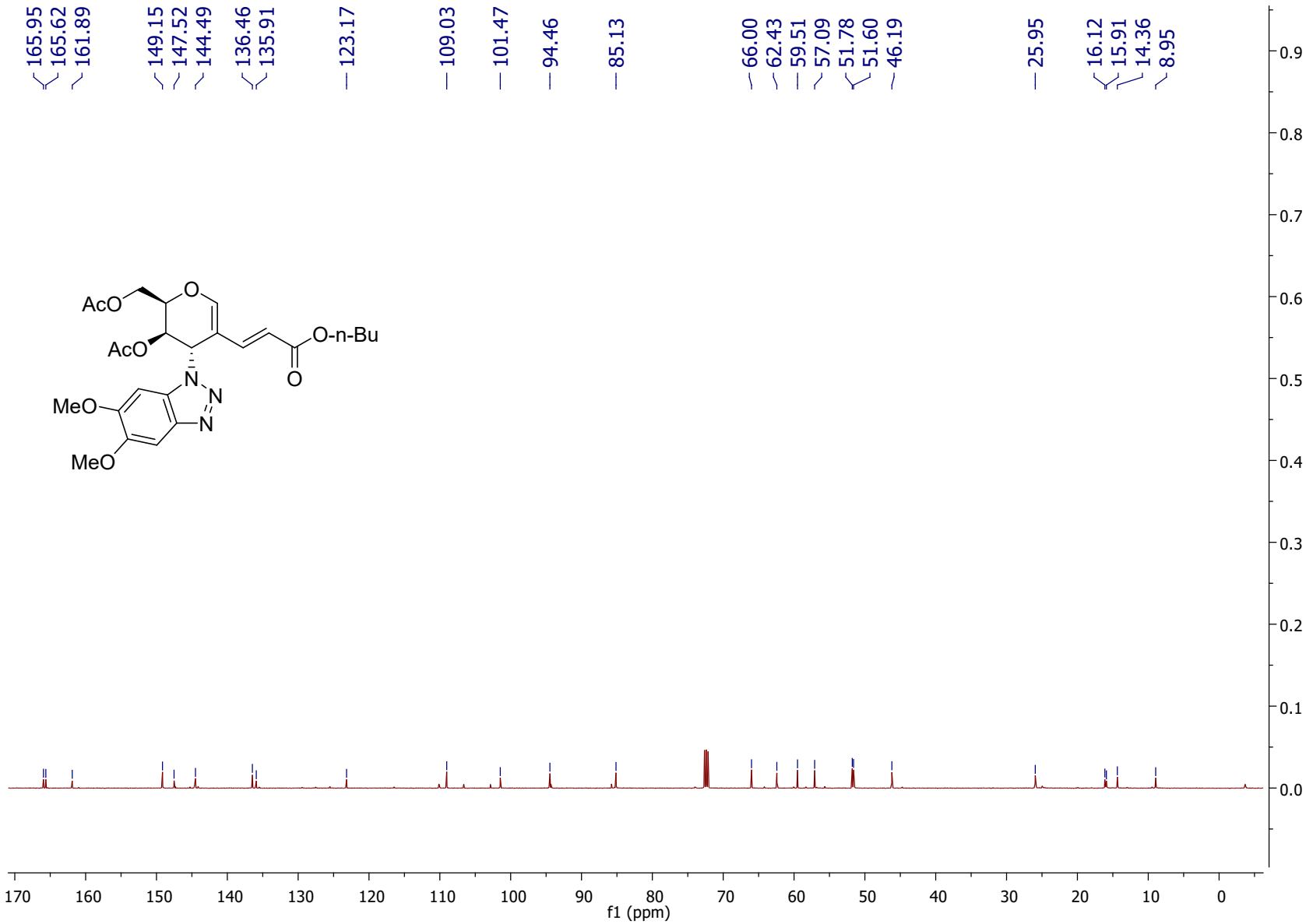
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4f**



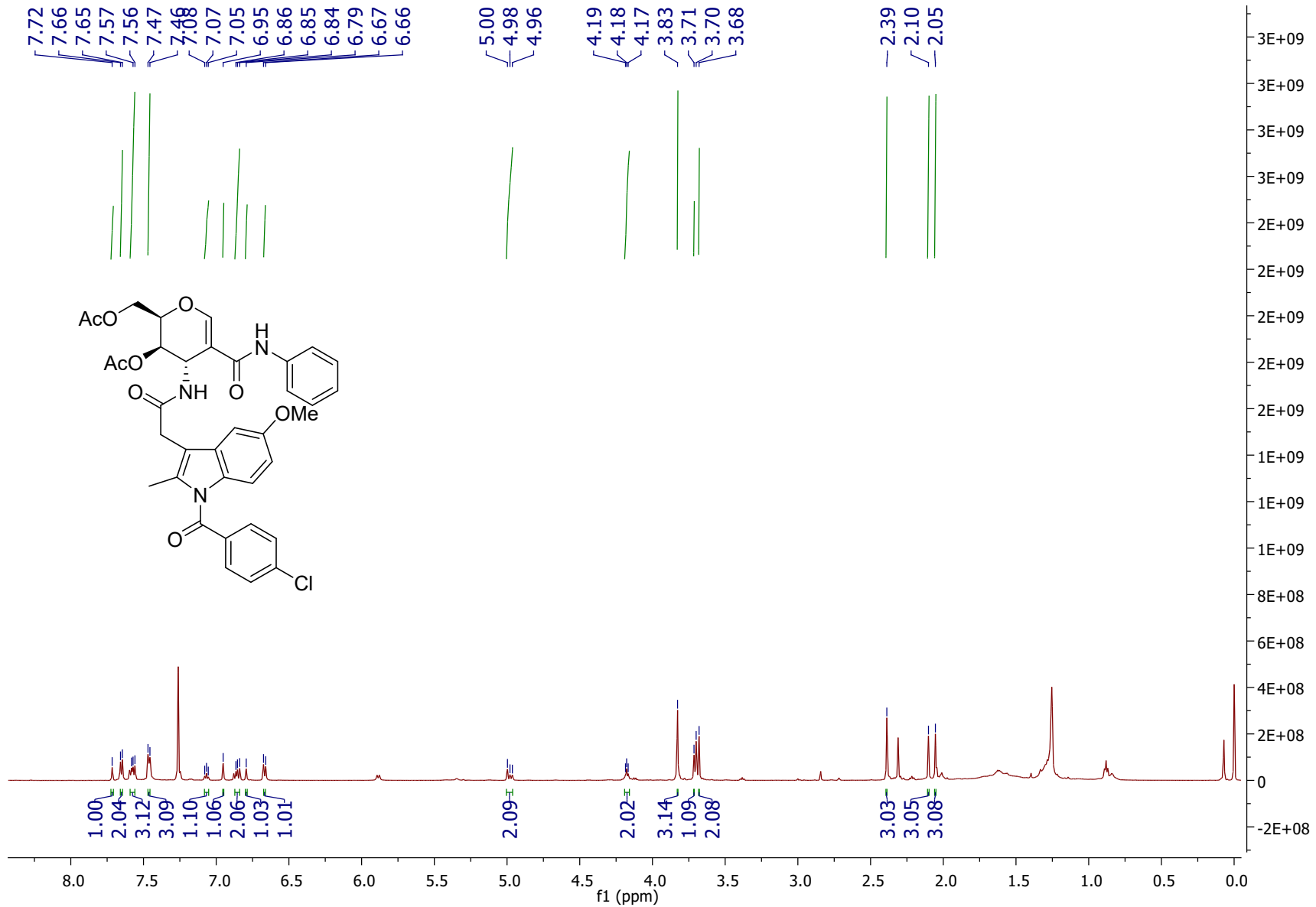
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4f**



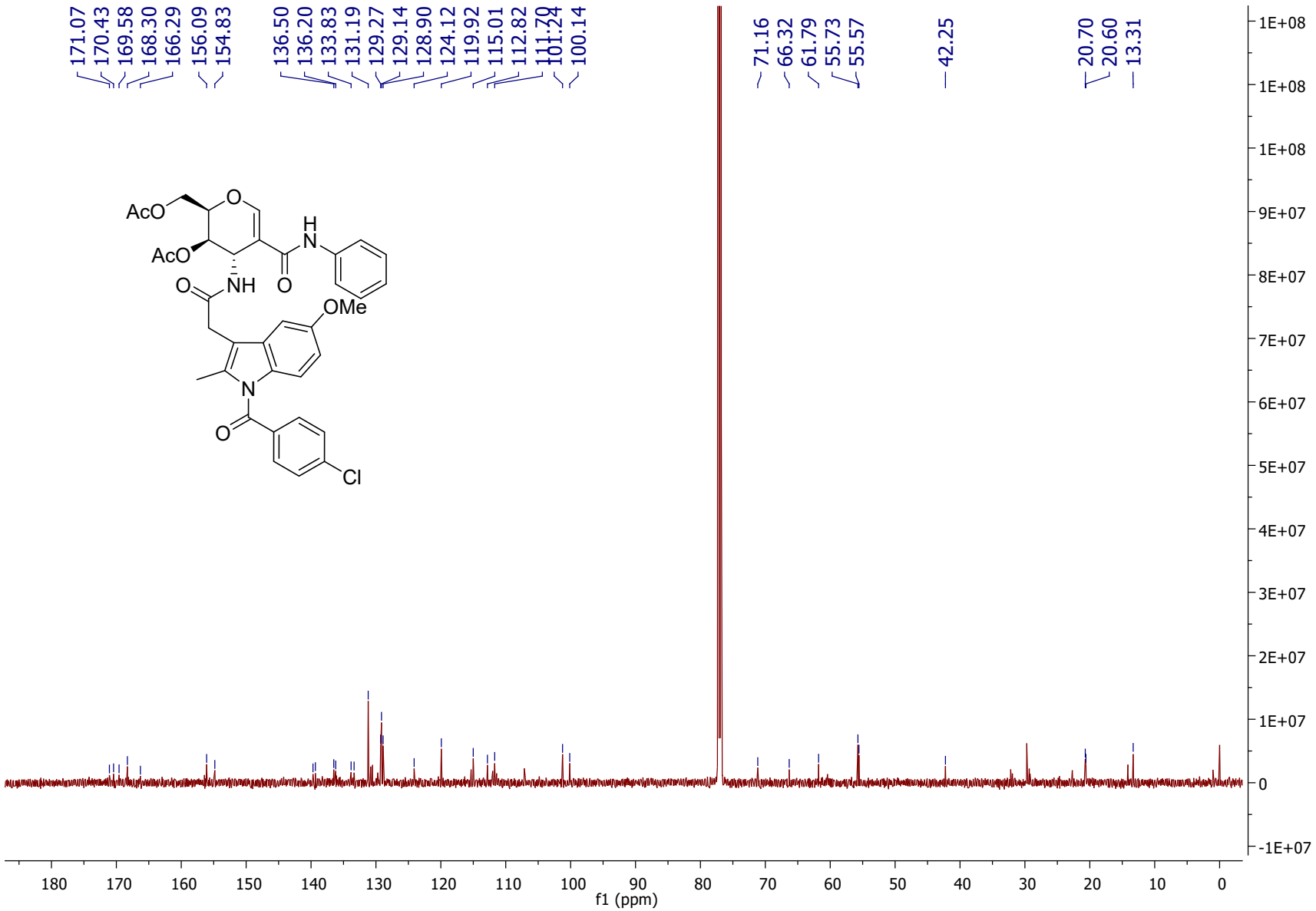
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4g**



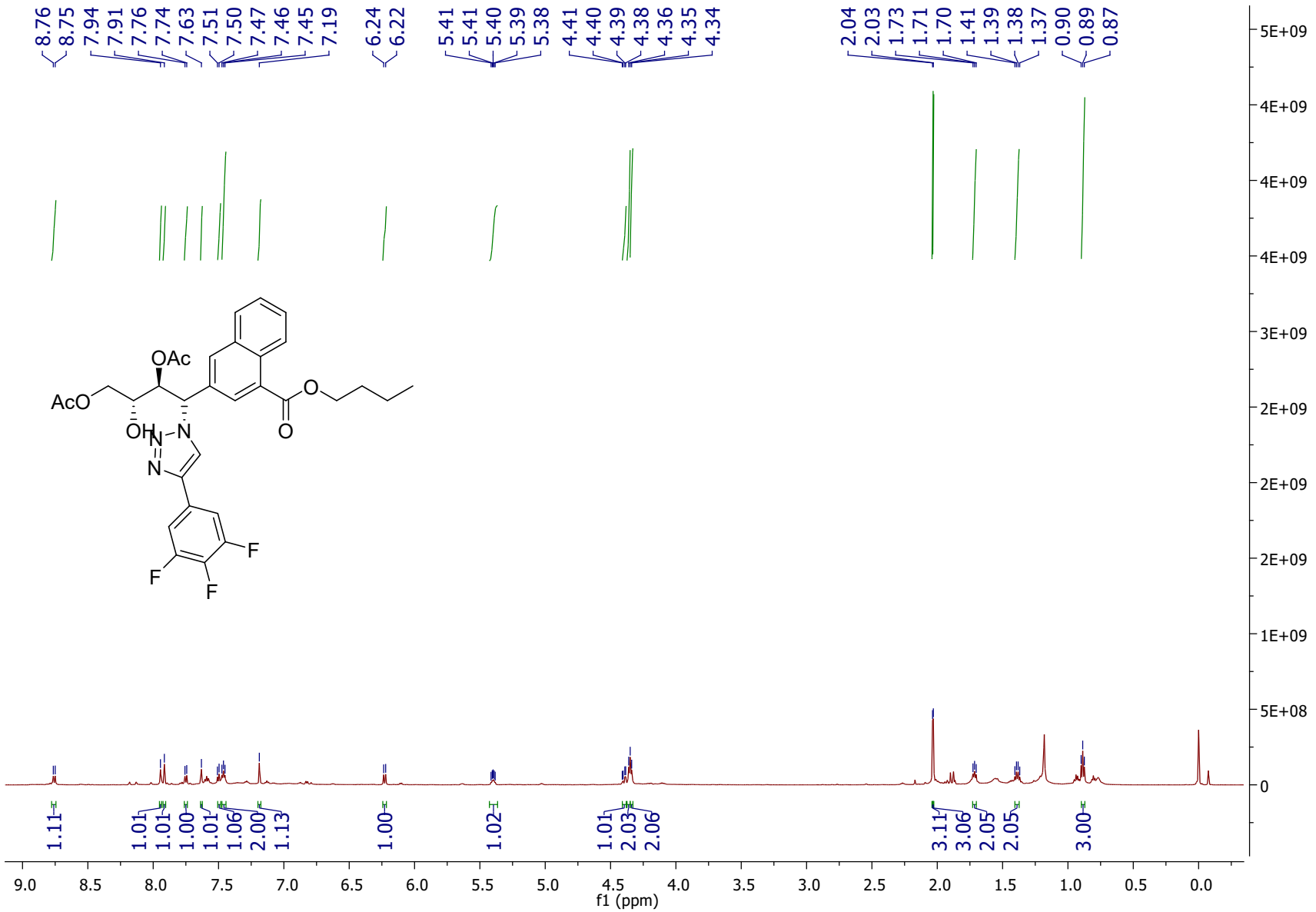
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4g**



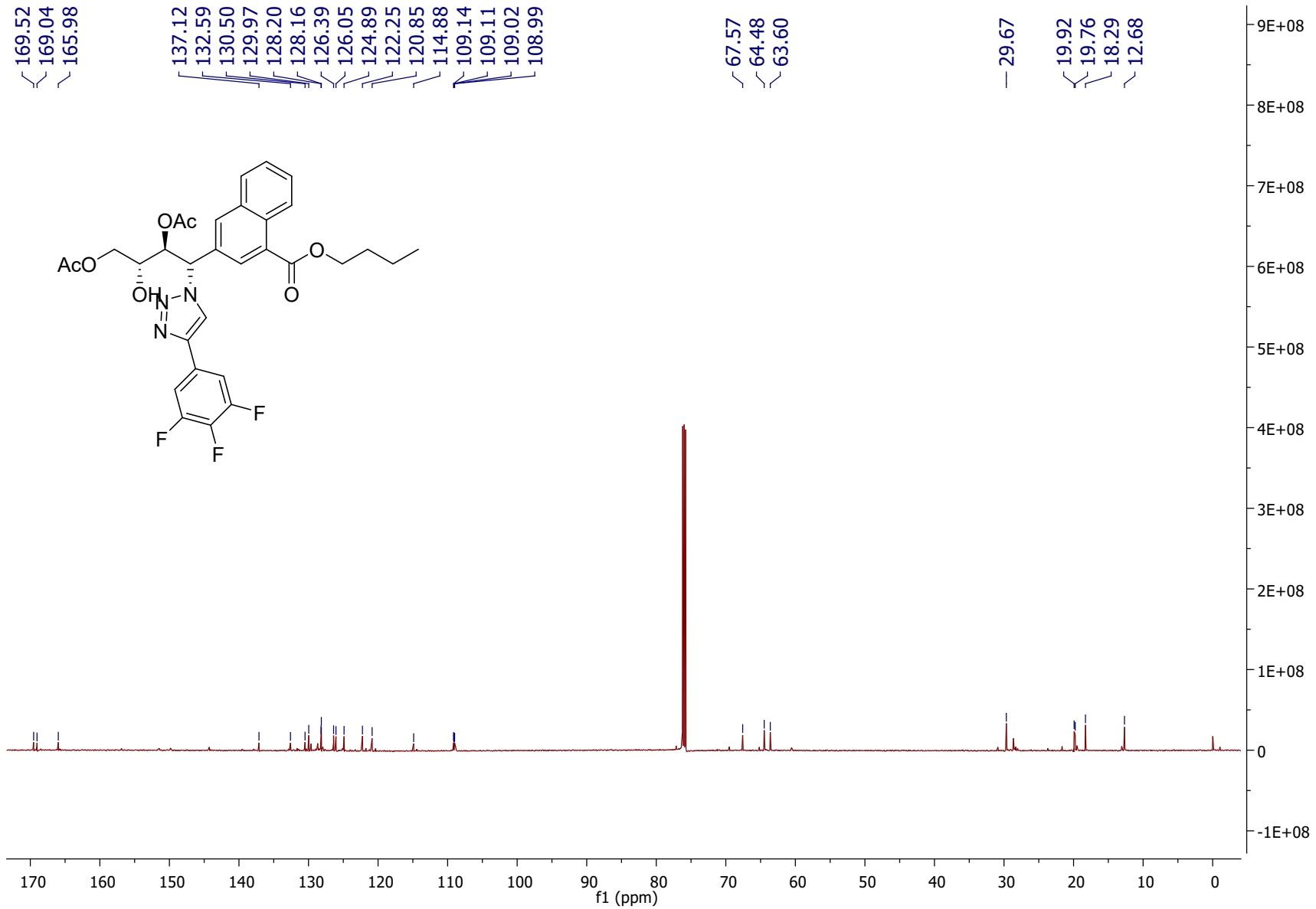
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4h**



^{13}C NMR (151 MHz, $CDCl_3$) of compound **4h**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **4i**



^{13}C NMR (151 MHz, $CDCl_3$) of compound **4i**