Supporting Information

Dehydration of α-Hydroxymethyl Tetrahydrofurans using Burgess' Reagent under Microwave Irradiation

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1. General Information

All reactions were carried out in oven dried 10 mL microwave reaction vials that were sealed with a septum under normal atmosphere. Chemicals were purchased from *Acros* and *Sigma Aldrich* and used without further purification. The substrates that were employed to the dehydration were prepared according to the literature processes and are not described further in the experimental part.[1,2]

The dehydration was carried out in a microwave reactor of the type CEM Discover LabMate. The reaction vial was irradiated for 1 minute with 150 W to heat the reaction mixture to 150 °C. The reaction was carried out for 3 minutes at this temperature whilst being continuously stirred.

All products were purified via flash column chromatography using silica gel (*Fluka* 60 Å, 230-400 mesh). Thin layer chromatography was carried out using Merck Silica Gel F254 plates. The compounds were visualized using UV light or potassium permanganate stain. Concentration of the eluent under reduced pressure was performed by rotary evaporation at 40 °C water bath temperature at the appropriate pressure.

GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5975B VL MSD mass selective detector (30 m x 0.25 mm capillary column, HP5-ms) using helium as carrier gas.

NMR spectra were recorded on a Bruker Avance-600 (600 MHz), Bruker Avance-400 (400 MHz) or Bruker F-300 (300 MHz) instrument at ambient temperature using $CDCl_3$ as the solvent. Chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard relative to $CHCl_3$ (δ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). Coupling constants are reported in Hz.

IR (Infrared) data were obtained on a ATR-FT-IR spectrometer of the type Alpha-P from Bruker with only major peaks being reported.

Mass spectra were recorded on an Agilent 6224 ESI-TOF mass spectrometer.

Melting points (MP) were measured with a Büchi Melting Point M-565 and are uncorrected.

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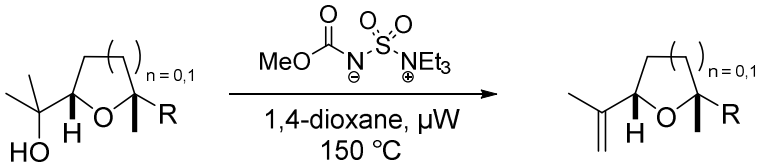
[1] Göhler, S.; Roth, S.; Cheng, H.; Göksel, H.; Rupp, A.; Haustedt, L. O.; Stark, C. B. W. *Synthesis* **2007**, *17*, 2751–2754.

[2] Roth, S.; Göhler, S.; Cheng, H.; Stark, C. B. W. *Eur. J. Chem.* **2005**, *19*, 4109–4118.

2. Syntheses of 2-Vinyl-THF-Products

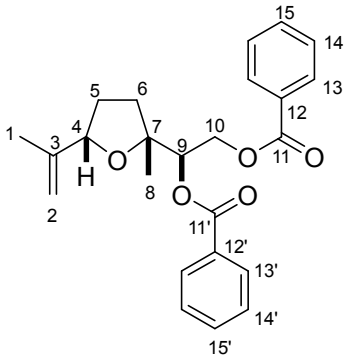
2.1 General Procedure for Dehydration using Burgess‘ Reagent under Microwave Irradiation



The respective alcohol (200 µmol) was dissolved in 1,4-dioxane (1.0 mL). Burgess‘ reagent (96.0 mg, 400 µmol) was added, the reaction vial was sealed with a septum and submitted to the microwave reactor. The reaction mixture was irradiated for 1 minute with a capacity of 150 W to reach a temperature of 150 °C. The reaction was stirred for 3 minutes at this temperature and then cooled down to ambient temperature. The reaction mixture was directly subjected to silica gel flash chromatography using petroleum ether/EtOAc (using the solvent composition or gradient indicated) for purification of the crude product.

2.2 Analytical Data of Dehydration Products

(R)-2-Benzoyl-2-((2R, 5S)-5-(prop-1-en-2-yl)-2-(methyl)-tetrahydrofuran-2-yl)-ethylbenzoat (*13a*)



synthesized according to general procedure: 48.1 mg (122 µmol, 61%) were isolated (eluent: petroleum ether/EtOAc 98:2 → 80:20) as a colorless solid.

R_f - value (PE/EE, 90:10): 0.44.

MP: 80.2-83.5 °C.

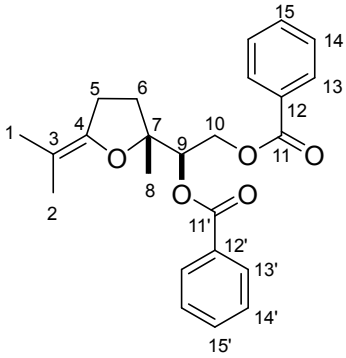
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.12-8.03 (m, 2H, H-13), 7.96-7.88 (m, 2H, H-13‘), 7.60-7.30 (m, 6H, H-15, H-15‘, H-14, H-14‘), 5.62 (dd, 1H, J = 8.8, 2.7 Hz, H-9), 5.11 (s, br, 1H, H-2a), 4.86 (s, br, 1H, H-2b), 4.84-4.76 (m, 1H, H-10a), 4.58 (dd, 1H, J = 11.9, 8.8 Hz, H-10b), 4.41 (t, 1H, J = 7.1 Hz, H-4), 2.26-1.99 (m, 2H, H-6a, H-5a), 1.87-1.70 (m, 5H, H-5b, H-1, H-6b), 1.45 (s, 3H, H-8).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.6 (C-11), 166.2 (C-11‘), 144.9 (C-3), 133.2 (C-12), 133.1 (C-12‘), 130.1 (C-14), 129.9 (C-15), 129.8 (C-15‘), 128.5 (C-13), 128.4 (C-13‘), 110.8 (C-2), 83.1 (C-7), 82.1 (C-4), 76.7 (C-9), 64.3 (C-10), 35.6 (C-6), 31.9 (C-5), 24.7 (C-8), 18.4 (C-1).

IR (ATR): $\tilde{\nu}$ = 3069 (w), 2971 (w), 1718 (s), 1450 (m), 1259 (s), 1095 (s), 1068 (s), 1025 (s), 707 (s).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calculated for $C_{24}H_{26}O_5Na$: 417.1678, found 417.1701.

(R)-2-Benzoyl-2-((2R)-5-(prop-2-yliden)-2-(methyl)-tetrahydrofuran-2-yl)-ethylbenzoat (*13b*)



synthesized according to general procedure: 6.00 mg (15.1 µmol, 7%) were isolated (eluent: petroleum ether/EtOAc 98:2 → 80:20) as a colorless oil.

R_f - value (PE/EE, 90:10): 0.29.

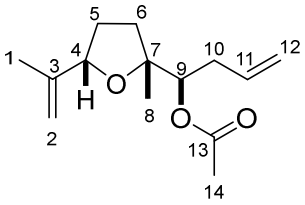
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.09-8.01 (m, 2H, H-13), 7.98-7.89 (m, 2H, H-13‘), 7.62-7.31 (m, 6H, H-15, H-15‘, H-14, H-14‘), 5.61 (dd, 1H, *J* = 8.6, 2.9 Hz, H-9), 4.78-4.73 (m, 1H, H-10a), 4.52 (dd, 1H, *J* = 11.9, 8.6 Hz, H-10b), 2.55 (tt, 2H, *J* = 8.0, 1.8 Hz, H-5), 2.22-2.10 (m, 1H, H-6a), 1.92-1.77 (m, 1H, H-6b), 1.64 (d, 3H, *J* = 1.1 Hz, H-1), 1.56 (s, 3H, H-2), 1.46 (s, 3H, H-8).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.7 (C-11), 166.0 (C-11‘), 148.5 (C-4), 133.3 (C-12), 133.2 (C-12‘), 130.0 (C-15), 129.8 (C-15‘), 129.5 (C-13), 128.6 (C-13‘), 126.7 (C-14), 126.6 (C-14‘), 98.5 (C-3), 84.3 (C-7), 76.4 (C-9), 64.0 (C-10), 33.8 (C-6), 26.5 (C-5), 23.9 (C-8), 19.1 (C-2), 16.8 (C-1).

IR (ATR): $\tilde{\nu}$ = 2974 (w), 1705 (m), 1453 (m), 1265 (s), 1212 (s), 1172 (s), 1126 (s), 967 (m), 929 (m), 710 (s).

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calculated for $C_{24}H_{27}O_5$: 395.1853, found 395.1891.

(R)-4-Acetoxy-4-((2R, 5S)-5-(propen-1-en-2-yl)-2-(methyl)-tetrahydrofuran-2-yl)-but-1-en (*15*)



synthesized according to general procedure: 35.3 mg (150 µmol, 68%) were isolated (eluent: petroleum ether/EtOAc 95:5) as a colorless oil.

R_f - value (PE/EE, 95:5): 0.22.

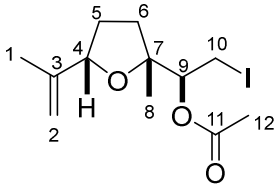
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.75 (dddd, 1H J = 17.0, 10.1, 8.1, 6.0 Hz, H-11), 5.11-4.96 (m, 4H, H-9, H-2a, H-12), 4.81 (s, 1H, H-2b), 4.37 (dd, 1H, J = 8.2, 6.1 Hz, H-4), 2.51-2.40 (m, 1H, H-10a), 2.36-2.24 (m, 1H, H-10b), 2.10-1.88 (m, 5H, H-14, H-5a, H-6a), 1.78-1.62 (m, 5H, H-1, H-5b, H-6b), 1.25 (s, 3H, H-8).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.8 (C-13), 145.2 (C-3), 134.8 (C-11), 117.4 (C-12), 110.8 (C-2), 83.9 (C-7), 81.9 (C-4), 77.6 (C-9), 35.3 (C-10), 35.2 (C-6), 31.7 (C-5), 23.5 (C-1), 21.3 (C-14), 18.2 (C-8).

IR (ATR): $\tilde{\nu}$ = 3078 (w), 2973 (w), 1737 (s), 1371 (m), 1234 (s), 1023 (s), 911 (m).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_{22}O_3Na$: 261.1461, found 261.1444.

(S)-4-Acetoxy-4-((2R, 5S)-5-(prop-1-en-2-yl)-2-(methyl)-tetrahydrofuran-2-yl)-1-iod-ethan (17)



synthesized according to general procedure: 17.3 mg (51.2 µmol, 61%) were isolated (eluent: petroleum ether/EtOAc 95:5) as a colorless oil.

R_f - value (PE/EE, 90:10): 0.23.

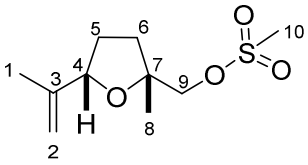
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.21 (dd, 1H, J = 10.8, 2.4 Hz, H-9), 5.02 (s, 1H, H-2a), 4.83 (s, 1H, H-2b), 4.35 (t, 1H, J = 7.1 Hz, H-4), 3.52 (dd, 1H, J = 10.8, 2.4 Hz, H-10a), 3.28 (t, 1H, J = 10.8 Hz, H-10b), 2.15 (s, 3H, H-11), 2.06-1.95 (m, 2H, H-5a, H-6a), 1.75-1.64 (m, 5H, H-1, H-5b, H-6b), 1.27 (s, 3H, H-8).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 207.1 (C-11), 144.7 (C-3), 111.1 (C-2), 84.1 (C-7), 82.1 (C-4), 78.4 (C-9), 35.3 (C-6), 31.7 (C-5), 24.5 (C-8), 21.2 (C-11), 18.2 (C-1), 3.9 (C-10).

IR (ATR): $\tilde{\nu}$ = 2970 (m), 2926 (m), 2854 (w), 1746 (s), 1451 (w), 1372 (m), 1232 (s), 1069 (m), 1021 (m), 901 (w).

MS (EI-TOF) *m/z*: calculated for $C_8H_{13}O$ $(M–C_4H_6IO_2)^+$ 125.0966, found 125.09; calculated for $C_{10}H_{16}IO$ $(M–C_2H_3O_2)^+$ 279.0246, found 279.14.

(2R, 5S)-2-((Methansulfonyl)oxymethyl)-2-methyl-5-(prop-1-en-2-yl)tetrahydrofuran (19)



synthesized according to general procedure: 11.1 mg (47.4 µmol, 94%) were isolated (eluent: petroleum ether/EtOAc 80:20) as a colorless oil.

R_f - value (PE/EE, 80:20): 0.38.

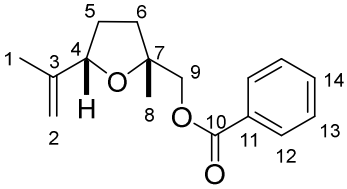
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 5.01 (s, 1H, H-2a), 4.82 (s, 1H, H-2b), 4.42 (t, 1H, J = 7.1 Hz, H-4), 4.12-4.03 (m, 2H, H-9), 3.04 (s, 3H, H-10), 2.13-2.03 (m, 2H, H-5a, H-6a), 1.85-1.69 (m, 5H, H-5b, H-6b, H-1), 1.33 (s, 3H, H-8).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 144.9 (C-3), 110.9 (C-2), 82.6 (C-4), 81.2 (C-7), 74.4 (C-9), 37.6 (C-10), 34.9 (C-6), 31.3 (C-5), 24.1 (C-8), 18.2 (C-1).

IR (ATR): $\tilde{\nu}$ = 2922 (m), 2852 (w), 1722 (s), 1409 (m), 1263 (m), 1175 (s), 1100 (m), 965 (m), 729 (m), 529 (m).

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calculated for $C_{10}H_{19}O_4S$: 235.0999, found 235.0955.

(2R, 5S)-2-(Benzoyloxymethyl)-2-methyl-5-(prop-1-en-2-yl)tetrahydrofuran (21)



synthesized according to general procedure: 29.0 mg (111 µmol, 67%) were isolated (eluent: petroleum ether/EtOAc 80:20) as a colorless oil.

R_f - value (PE/EE, 95:5): 0.49.

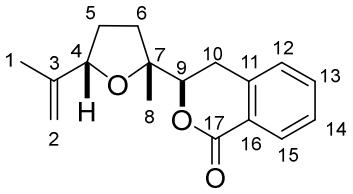
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 (dd, 2H, J = 8.3, 1.4 Hz, H-13), 7.60-7.52 (m, 1H, H-14), 7.44 (dd, 2H, J = 8.3, 7.0 Hz, H-12), 5.05 (s, 1H, H-2a), 4.80 (s, 1H, H-2b), 4.45 (dd, 1H, J = 7.9, 5.8 Hz, H-4), 4.34-4.26 (m, 1H, H-9a), 4.24-4.17 (m, 1H, H-9b), 2.16-2.07 (m, 2H, H-5a, H-6a), 1.89-1.77 (m, 2H, H-5b, H-6b), 1.72 (s, 3H, H-1), 1.39 (s, 3H, H-8).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6 (C-10), 145.4 (C-11), 133.1 (C-14), 130.3 (C-3), 129.8 (C-13), 128.5 (C-12), 110.6 (C-2), 82.5 (C-4), 81.8 (C-7), 70.2 (C-9), 35.2 (C-6), 31.6 (C-5), 24.6 (C-8), 18.2 (C-1).

IR (ATR): $\tilde{\nu}$ = 2972 (m), 2872 (w), 1718 (s), 1451 (m), 1271 (s),1249 (m), 1110 (s), 1069 (m), 1026 (m), 897 (m), 710 (s).

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{20}NaO_3$: 283.1305, found 283.1309.

(S)-3-((2S, 5R)-5-(prop-1-en-2-yl)-2-methyltetrahydrofuran-2-yl)isochroman-1-on (*23*)



synthesized according to general procedure: 17.8 mg (65.4 µmol, 95%) were isolated (eluent: petroleum ether/EtOAc 90:10) as a colorless oil.

R_f - value (PE/EE, 90:10): 0.20.

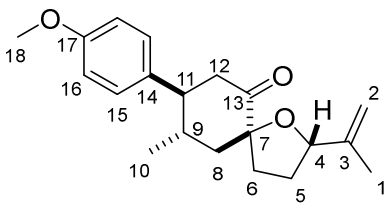
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.09 (dd, 1H, *J* = 7.9, 1.4 Hz, H-15), 7.53 (td, 1H, *J* = 7.5, 1.4 Hz, H-13), 7.41-7.35 (m, 1H, H-14), 7.29-7.26 (m, 1H, H-12), 5.02 (s, 1H, H-2a), 4.83 (s, 1H, H-2b), 4.47-4.39 (m, 2H, H-4, H-9), 3.18 (dd, 1H, *J* = 16.2, 12.7 Hz, H-10a), 3.00 (dd, 1H, *J* = 16.2, 2.9 Hz, H-10b), 2.37 (ddd, 1H, *J* = 12.3, 8.8, 2.9 Hz, H-6a), 2.11-2.04 (m, 1H, H-5a), 1.95-1.86 (m, 1H, H-5b), 1.86-1.78 (m, 1H, H-6b), 1.75 (s, 3H, H-1), 1.41 (s, 3H, H-8).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 165.5 (C-17), 144.9 (C-3), 139.6 (C-16), 133.9 (C-13), 130.4 (C-15), 127.8 (C-12), 127.7 (C-14), 125.2 (C-11), 111.1 (C-2), 83.4 (C-9), 83.0 (C-7), 82.4 (C-4), 34.6 (C-6), 32.1 (C-5), 28.5 (C-10), 25.0 (C-8), 18.2 (C-1).

IR (ATR): $\tilde{\nu}$ = 2970 (m) 2925 (m), 1728 (s), 1608 (w), 1460 (m), 1276 (m) 1232 (m), 1121 (m), 1089 (m), 1030 (m), 900 (w), 744 (m).

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{21}O_3$: 273.1485, found 273.1512.

(2R, 5R, 8R, 9R)-2-(Prop-1-en-2-yl)-8-(4-methoxyphenyl)-9-methyl-1-oxaspiro[4.5]decan-6-on (*25*)



synthesized according to general procedure: 10.2 mg (32.4 µmol, 83%) were isolated (eluent: petroleum ether/EtOAc 90:10) as a colorless oil.

R_f - value (PE/EE, 90:10): 0.28.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.12 (d, 2H, J =8.6 Hz, H-15), 6.85 (d, 2H, J = 8.7 Hz, H-16), 4.96 (s, 1H, H-2a), 4.81 (s, 1H, H-2b), 4.48 (dd, 1H, J = 10.0, 5.8 Hz, H-4), 3.80 (s, 3H, H-18), 3.25-3.11 (m, 1H, H-12a), 2.66 (ddd, 1H, J = 12.3, 7.4, 2.1 Hz, H-6a), 2.45-2.33 (m, 3H, H-9, H-12b, H-11),

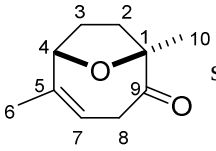
2.11 (dd, 1H, J = 14.3, 3.0 Hz, H-8a), 2.00 (dddd, 1H, J = 12.7, 7.5, 5.9, 2.1 Hz, H-5a), 1.78-1.67 (m, 1H, H-5b), 1.64 (s, 3H, H-1), 1.52-1.44 (m, 2H, H-6b, H-8b), 0.70 (d, 3H, J = 5.6 Hz, H-10).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 209.3 (C-13), 158.4 (C-17), 145.1 (C-3), 135.8 (C-14), 128.4 (C-15), 114.1 (C-16), 111.1 (C-2), 87.6 (C-7), 84.1 (C-4), 55.4 (C-18), 52.0 (C-11), 47.5 (C-8), 46.5 (C-12), 33.9 (C-9), 31.8 (C-6), 31.5 (C-5), 19.2 (C-10), 17.7 (C-1).

IR (ATR): $\tilde{\nu}$ = 2954 (m), 2924 (m), 1720 (s), 1612 (w), 1513 (s), 1457 (m), 1254 (s), 1177 (m), 1037 (m), 831 (m).

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{27}O_3$: 315.1955, found 315.1956.

(1R,5R,6S)-1,5-Dimethyl-5-hydroxy-9-oxabicylco[4.2.1]nonan-2-on (27)



synthesized according to general procedure: 33.4 mg (201 µmol, 93%) were isolated (eluent: petroleum ether/EtOAc 95:5) as a colorless oil.

R_f - value (PE/EE, 95:5): 0.32.

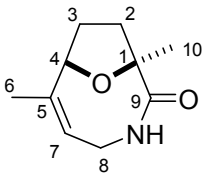
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.14-5.07 (m, 1H, H-7), 4.76-4.67 (m, 1H, H-4), 4.00-3.87 (m, 1H, H-8a), 2.63 (dd, 1H, J = 14.0, 8.9 Hz, H-8b), 2.21-1.96 (m, 2H, H-2a, H-3a), 1.86-1.70 (m, 2H, H-2b, H-3b), 1.62 (s, 3H, H-6), 1.39 (s, 3H, H-10).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 214.6 (C-9), 139.4 (C-5), 113.0 (C-7), 89.0 (C-1), 83.1 (C-4), 40.2 (C-8), 34.5 (C-2), 30.4 (C-3), 23.5 (C-10), 20.4 (C-6).

IR (ATR): $\tilde{\nu}$ = 2972 (m), 2932 (m), 1717 (s), 1446 (m), 1368 (w), 1285 (w), 1189 (m), 1118 (m), 1056 (s), 923 (m), 844 (w), 552 (m).

MS (EI-TOF) *m/z*: $[M]^+$ calculated for $C_{10}H_{14}O_2$: 166.0994, found 166.10.

(1R,7S)-1,6-Dimethyl-6-hydroxy-2-aza-10-oxabicylco[5.2.1]dec-5-en-3-on (29)



synthesized according to general procedure: 13.1 mg (72.3 µmol, 51%) were isolated (eluent: DCM/MeOH 95:5) as a colorless oil.

R_f - value (DCM/MeOH, 95:5): 0.38.

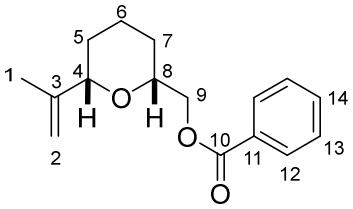
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.99 (s, br, 1H, NH), 5.53-5.41 (m, 1H, H-7), 5.18-5.03 (m, 1H, H-8a), 4.7-4.65 (m, 1H, H-4), 3.11 (ddd, 1H, J = 15.0, 8.8, 7.9 Hz, H-8b), 2.65-2.54 (m, 1H, H-4a), 2.34-2.19 (m, 1H, H-3a), 1.89-1.71 (m, 2H, H-3b, H-4b), 1.61 (s, 3H, H-6), 1.59 (s, 3H, H-10).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 179.2 (C-9), 142.8 (C-5), 120.7 (C-7), 83.9 (C-4), 51.0 (C-1), 40.1 (C-8), 38.2 (C-4), 31.7 (C-3), 24.7 (C-10), 19.9 (C-6).

IR (ATR): $\tilde{\nu}$ = 3219 (br, m), 2974 (m), 1707 (s), 1640 (s), 1462 (m), 1351 (m), 1265 (w), 1128 (w), 766 (w).

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calculated for $C_{10}H_{16}NO_2$: 182.1176, found 182.1174.

(2R, 6S)-2-Benzoyloxymethyl-6-(prop-1-en-2-yl)-tetrahydropyran (31)



synthesized according to general procedure: 25.1 mg (96.4 µmol, 98%) were isolated (eluent: petroleum ether/EtOAc 95:5) as a colorless oil.

R_f - value (PE/EE, 95:5): 0.53.

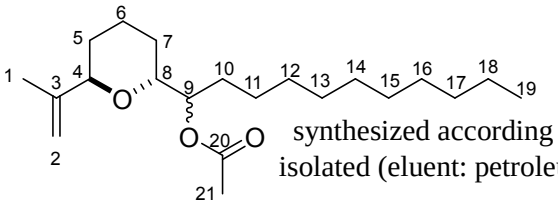
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.06 (dd, 2H, J = 8.3, 1.4 Hz, H-13), 7.59-7.52 (m, 1H, H-14), 7.43 (dd, 2H, J = 8.3, 7.0 Hz, H-12), 5.02-4.94 (m, 2H, H-2), 4.45-4.37 (m, 1H, H-9a), 4.35-4.24 (m, 2H, H-9b, H-4), 3.97 (tdd, 1H, J = 7.5, 4.2, 2.9 Hz, H-8), 1.88-1.64 (m, 8H, H-5, H-6, H-1, H-7a), 1.55-1.43 (m, 1H, H-7b).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7 (C-10), 144.5 (C-11), 133.1 (C-14), 130.3 (C-3), 129.8 (C-13), 128.5 (C-12), 112.5 (C-2), 74.7 (C-4), 69.5 (C-8), 66.7 (C-9), 27.2 (C-7), 26.8 (C-5), 20.1 (C-1), 19.0 (C-6).

IR (ATR): $\tilde{\nu}$ = 2942 (m), 2870 (w), 1717 (s), 1450 (m), 1269 (s), 1111 (m), 1094 (m), 900 (m), 710 (s).

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{20}NaO_3$: 283.1305, found 283.1307.

(2R, 6R)-2-(1-(Acetoxy)undecyl)-6-(prop-1-en-2-yl)-tetrahydropyran (33)



synthesized according to general procedure: 17.9 mg (52.9 µmol, 86%) were isolated (eluent: petroleum ether/EtOAc 95:5) as a colorless oil.

R_f - value (PE/EE, 95:5): 0.42.

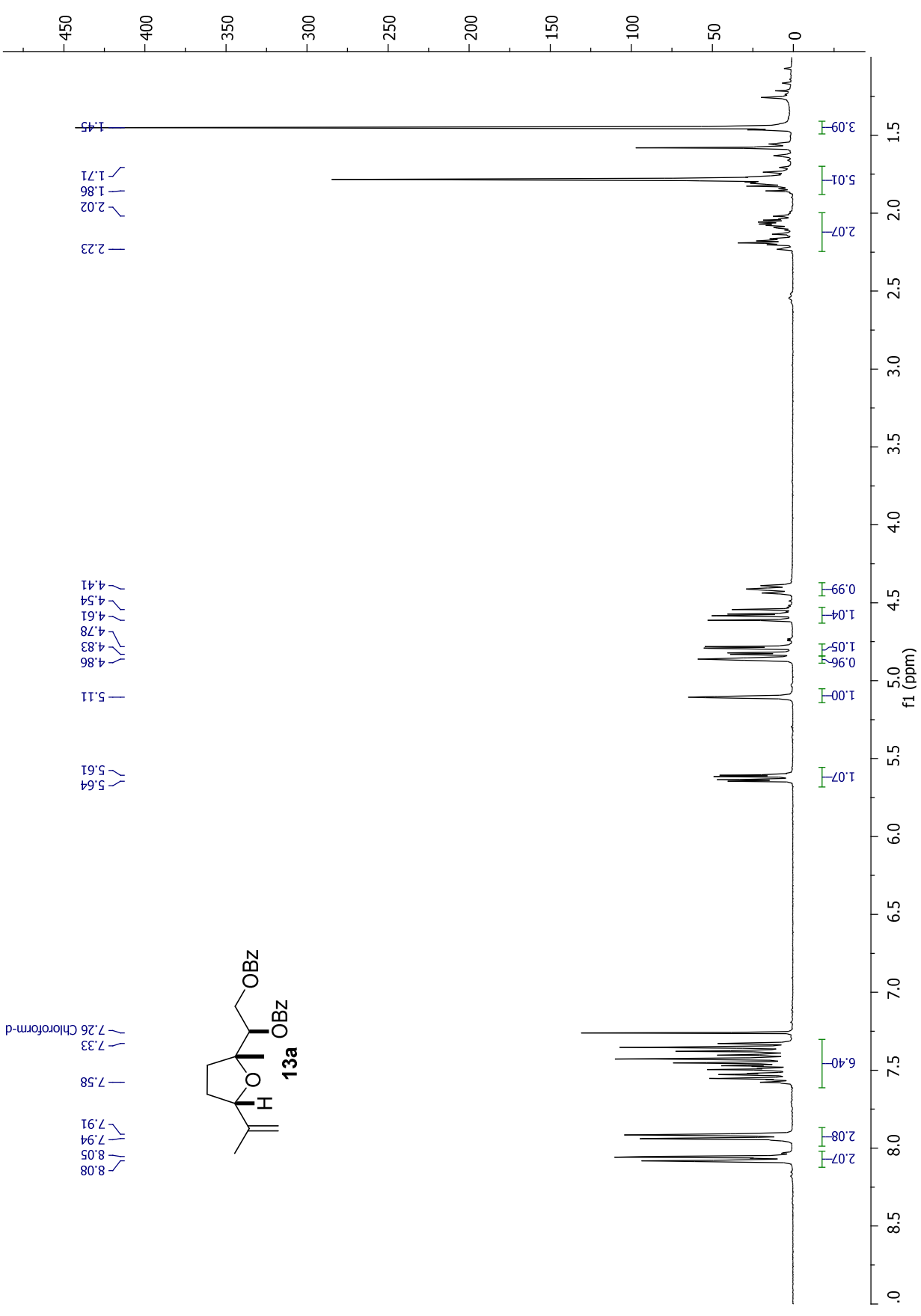
^{1}H-NMR (300 MHz, $CDCl_3$): δ =5.06-4.97 (m, 2H, H-4, H-2a), 4.92 (s, 1H, H-2b), 4.32-4.23 (m, 1H, H-9), 3.53 (ddd, 1H, J = 8.8, 5.6, 3.2 Hz, H-8), 2.09 (s, 3H, H-21), 1.86-1.58 (m, 8H, H-5, H-1, H-7, H-6a), 1.53-1.37 (m, 2H, H-6b, H-10a), 1.36-1.17 (m, 17H, H-10b, H-11, H-12, H-13, H-14, H-15, H-16, H-17, H-18), 0.88 (t, 3H, J = 6.7 Hz, H-19).

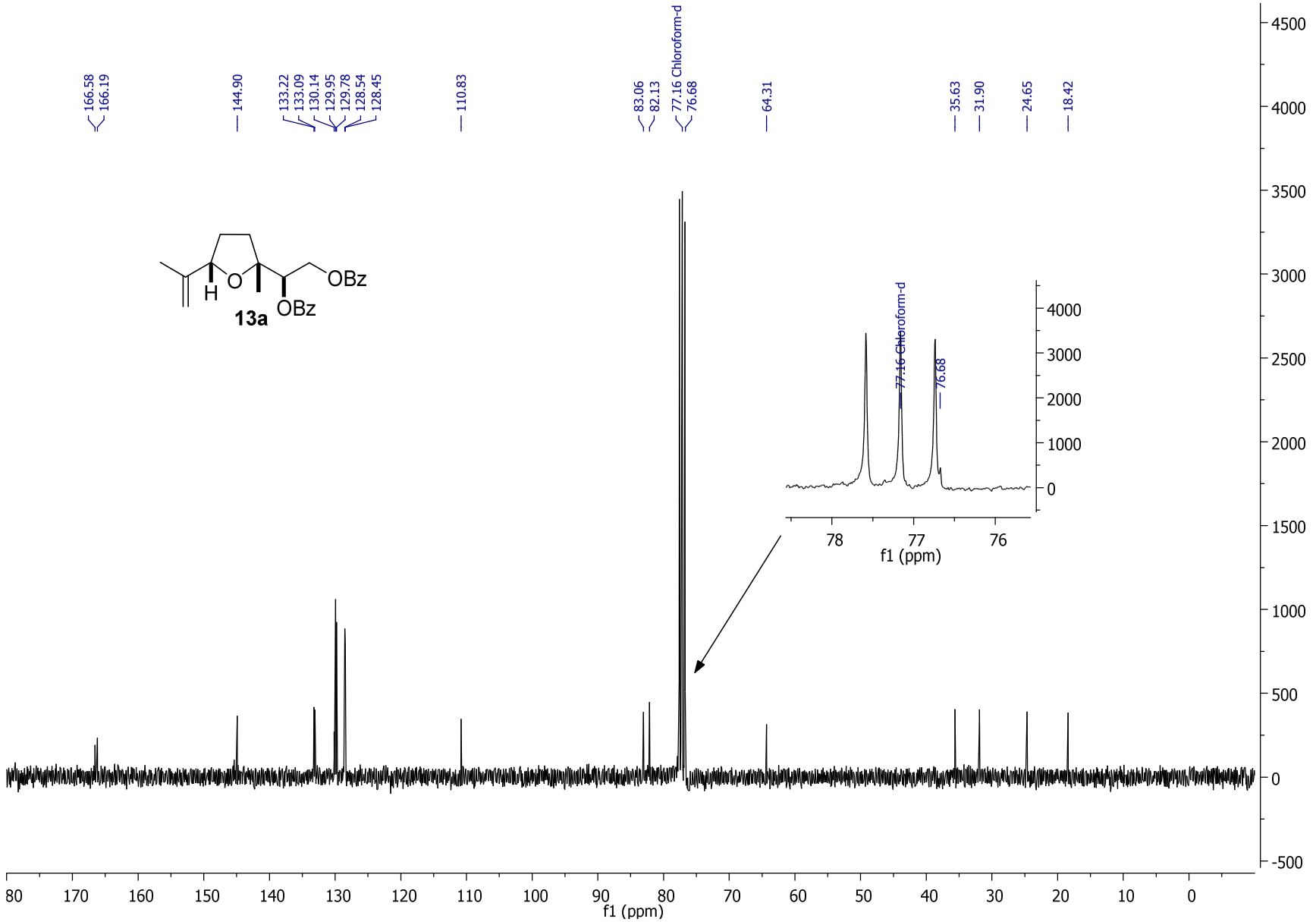
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.1 (C-20), 144.5 (C-3), 112.6 (C-2), 74.9 (C-4), 74.8 (C-9), 72.3 (C-8), 32.1 (CH_2), 30.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 27.2 (CH_2), 26.5 (C-5), 25.5 (CH_2), 22.8 (C-7), 21.3 (C-21), 20.3 (C-1), 19.2 (C-6), 14.3 (C-19).

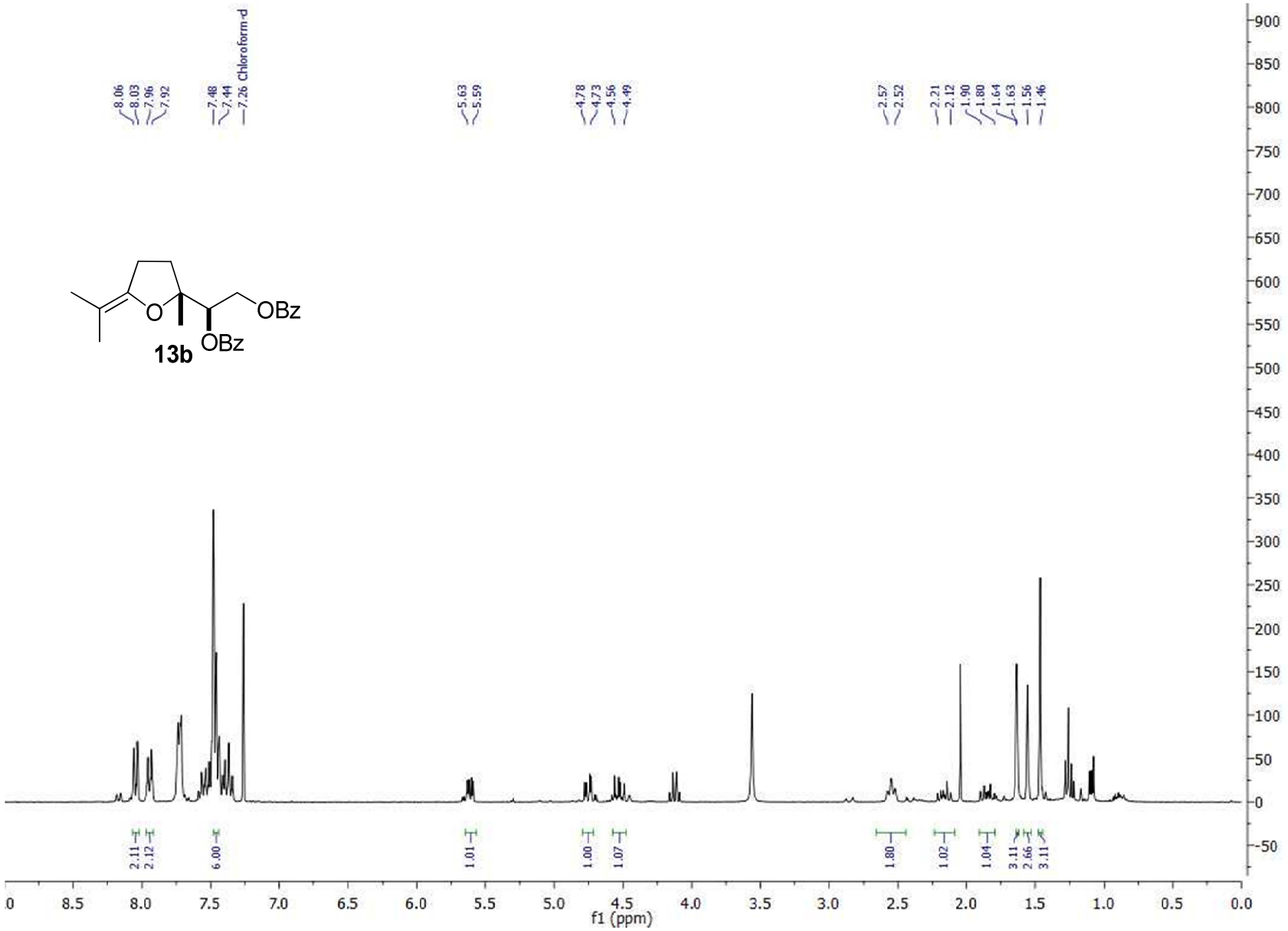
IR (ATR): $\tilde{\nu}$ = 2924 (s), 2854 (m), 1737 (s), 1460 (w), 1372 (m), 1239 (s), 1040 (m), 898 (m).

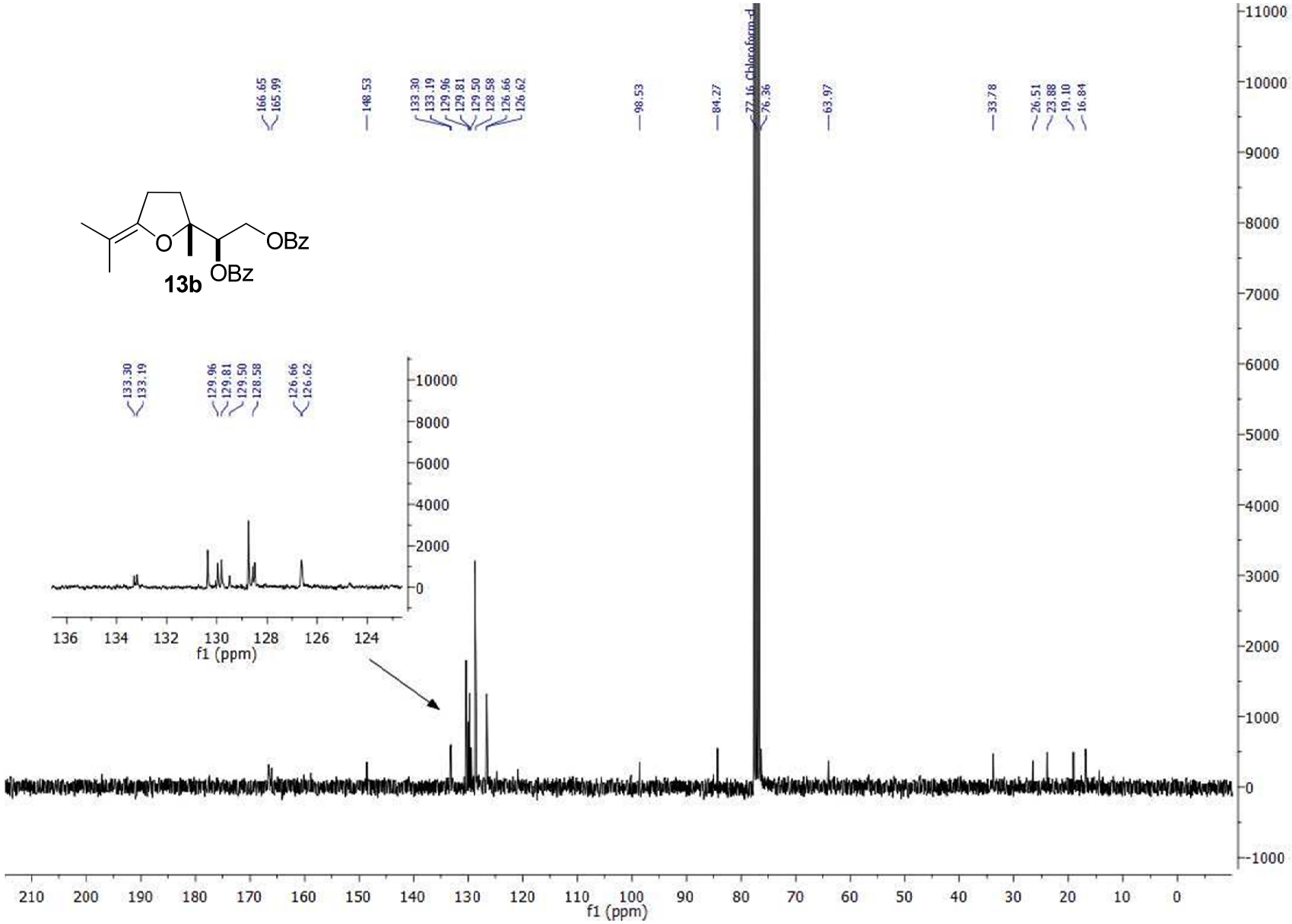
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calculated for $C_{21}H_{38}NaO_3$: 361.2713, found 361.2708.

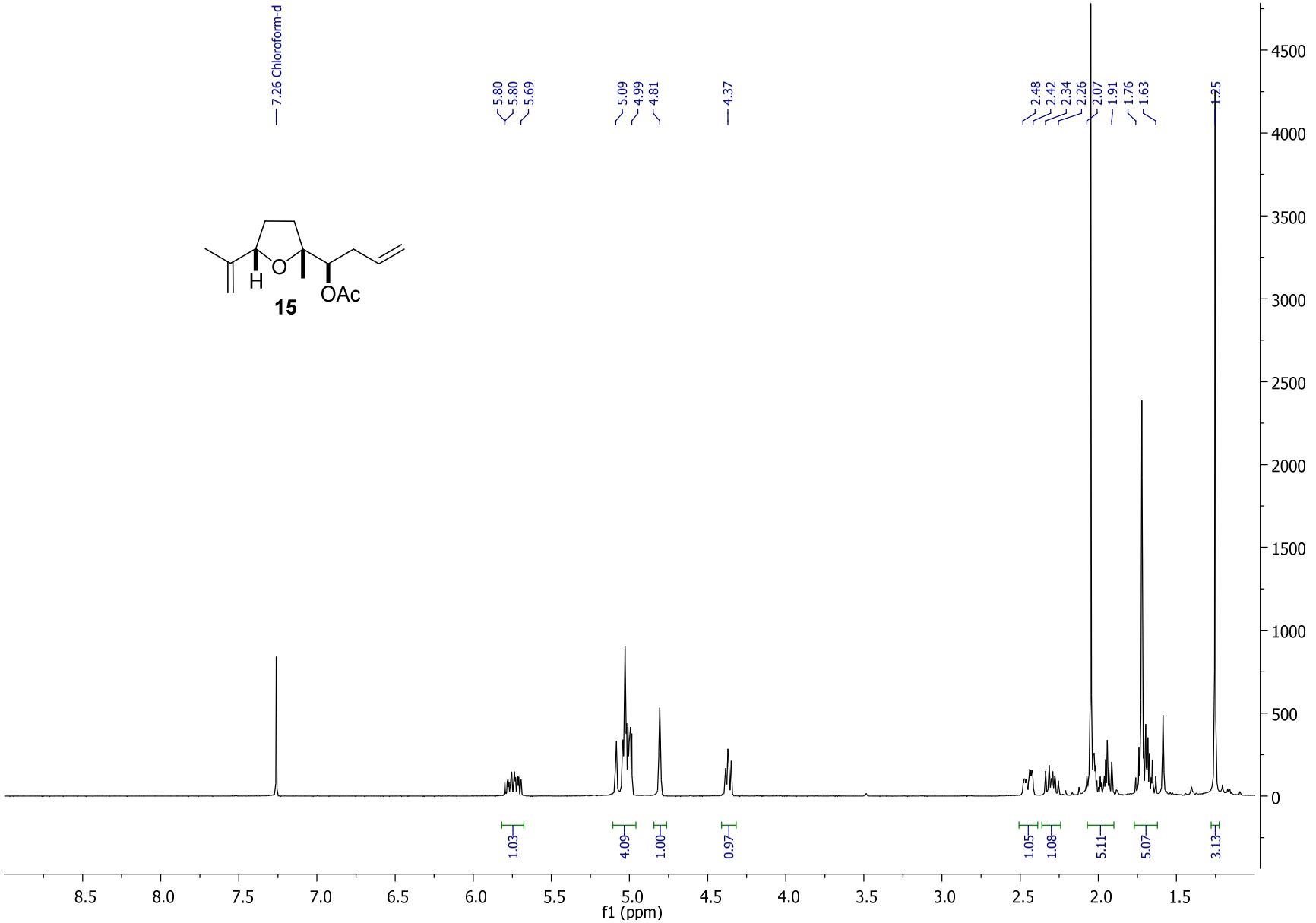
3. ^{1}H and ^{13}C NMR Spectra

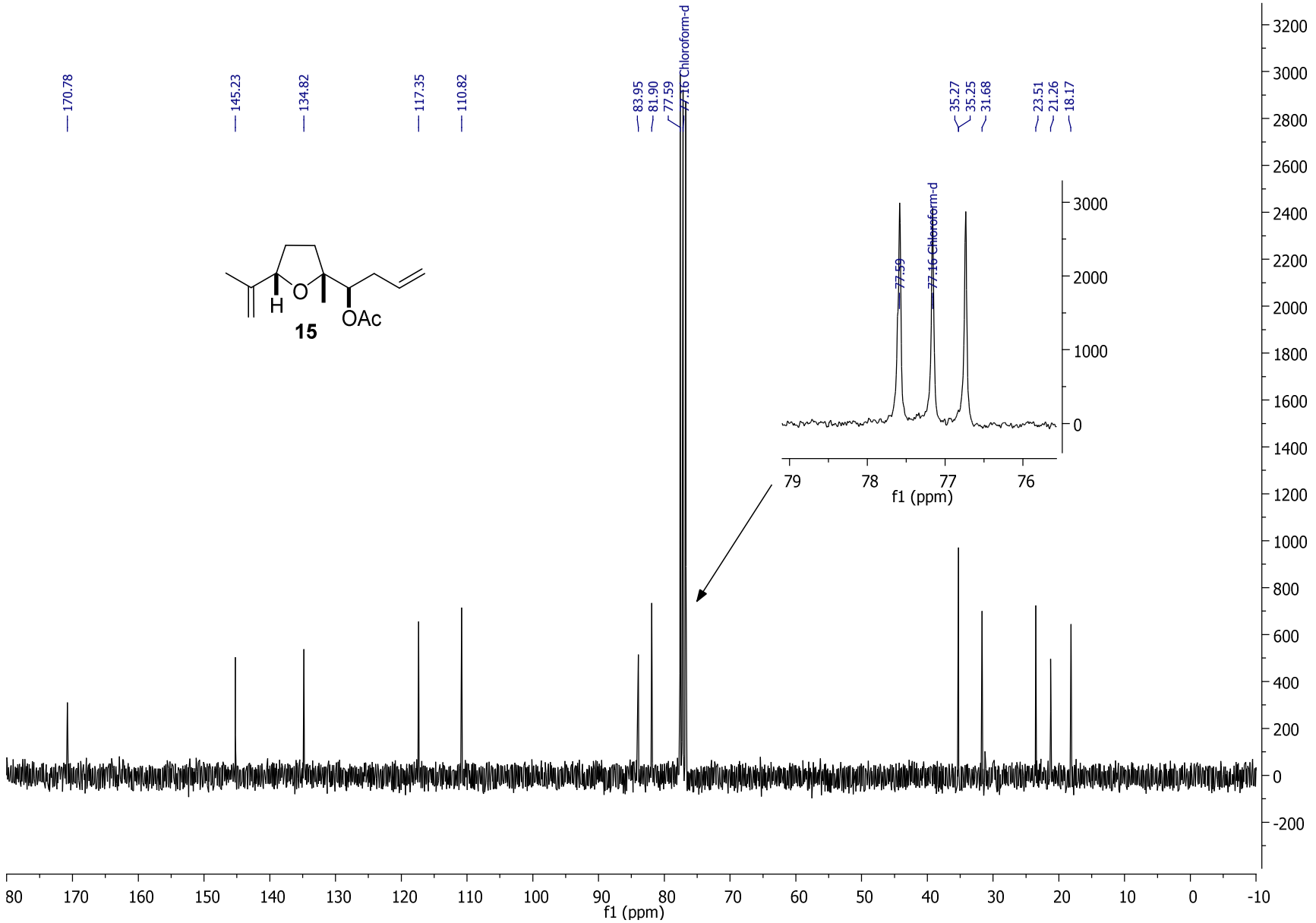


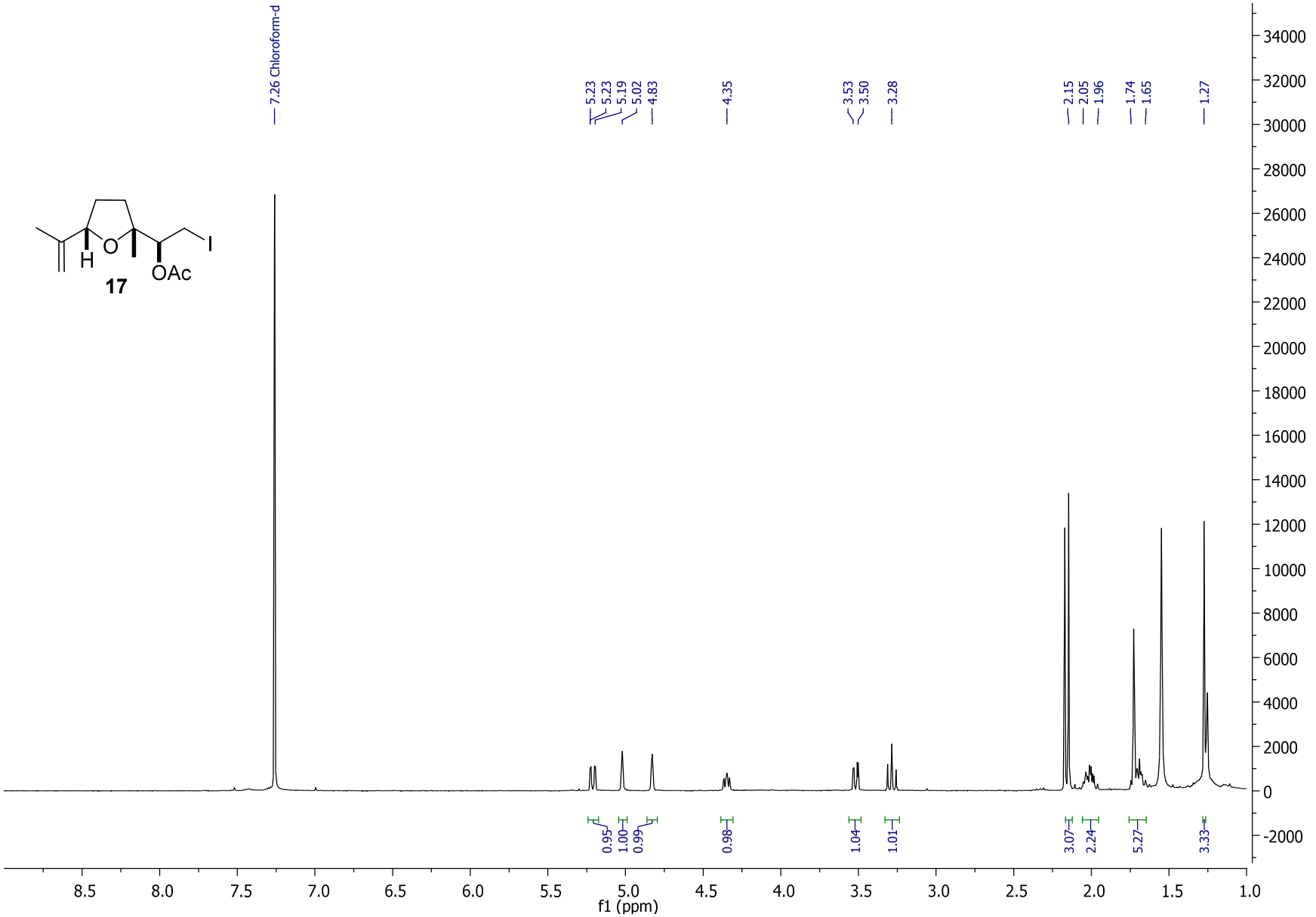

166.58
166.19
144.90
133.22
133.09
130.14
129.95
129.78
128.54
128.45
110.83
83.06
82.13
77.16 Chloroform-d
76.68
64.31
35.63
31.90
24.65
18.42
OBz
O
H
OBz
13a
f1 (ppm)

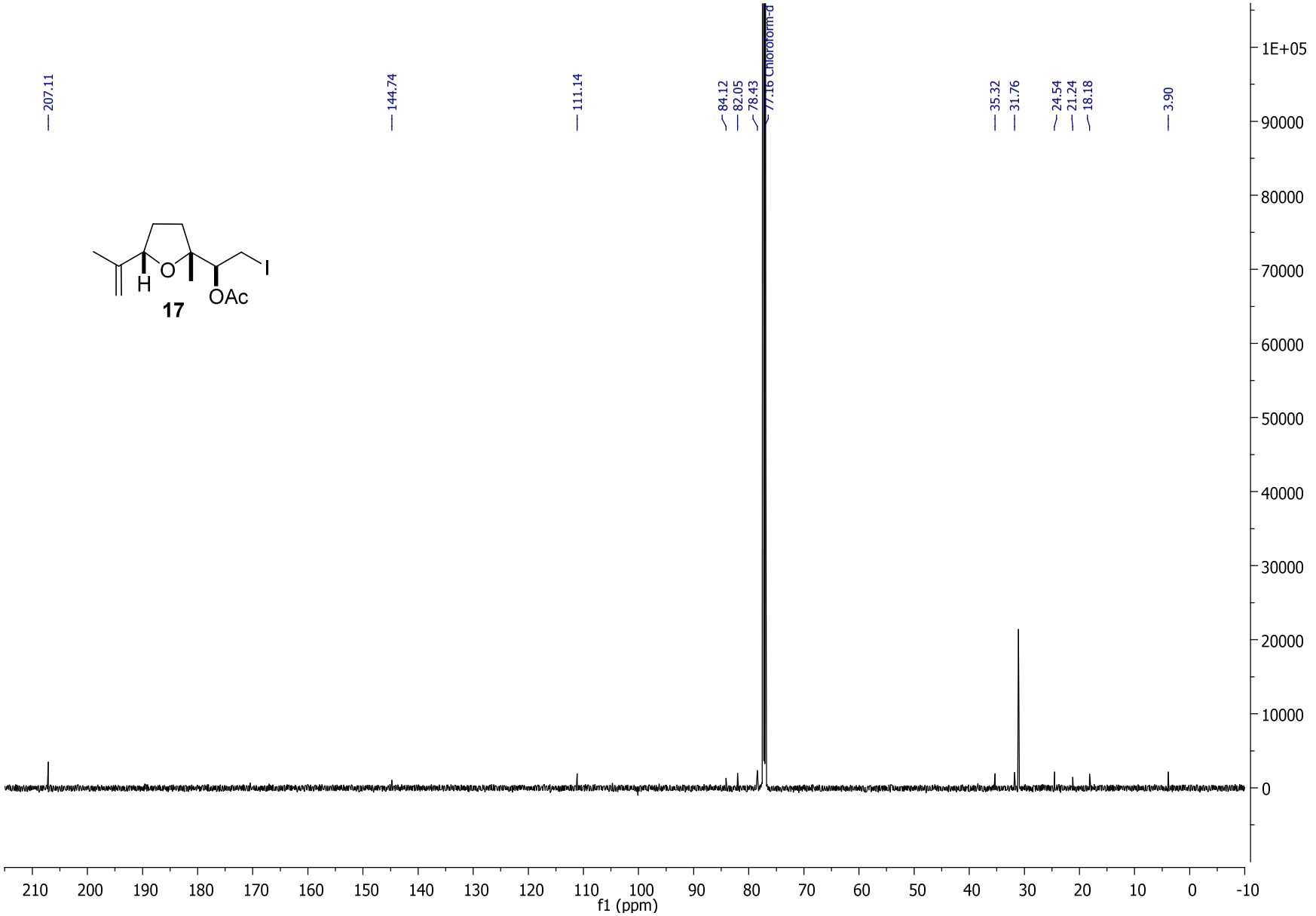

8.06
8.03
7.96
7.92
7.48
7.44
7.26 Chloroform-d
5.63
5.59
4.78
4.73
4.56
4.49
2.57
2.52
2.21
2.12
1.90
1.80
1.64
1.63
1.56
1.46
OBz
OBz
O
13b
2.11
2.12
6.00
1.01
1.00
1.07
1.80
1.02
1.04
3.11
2.66
3.11
f1 (ppm)

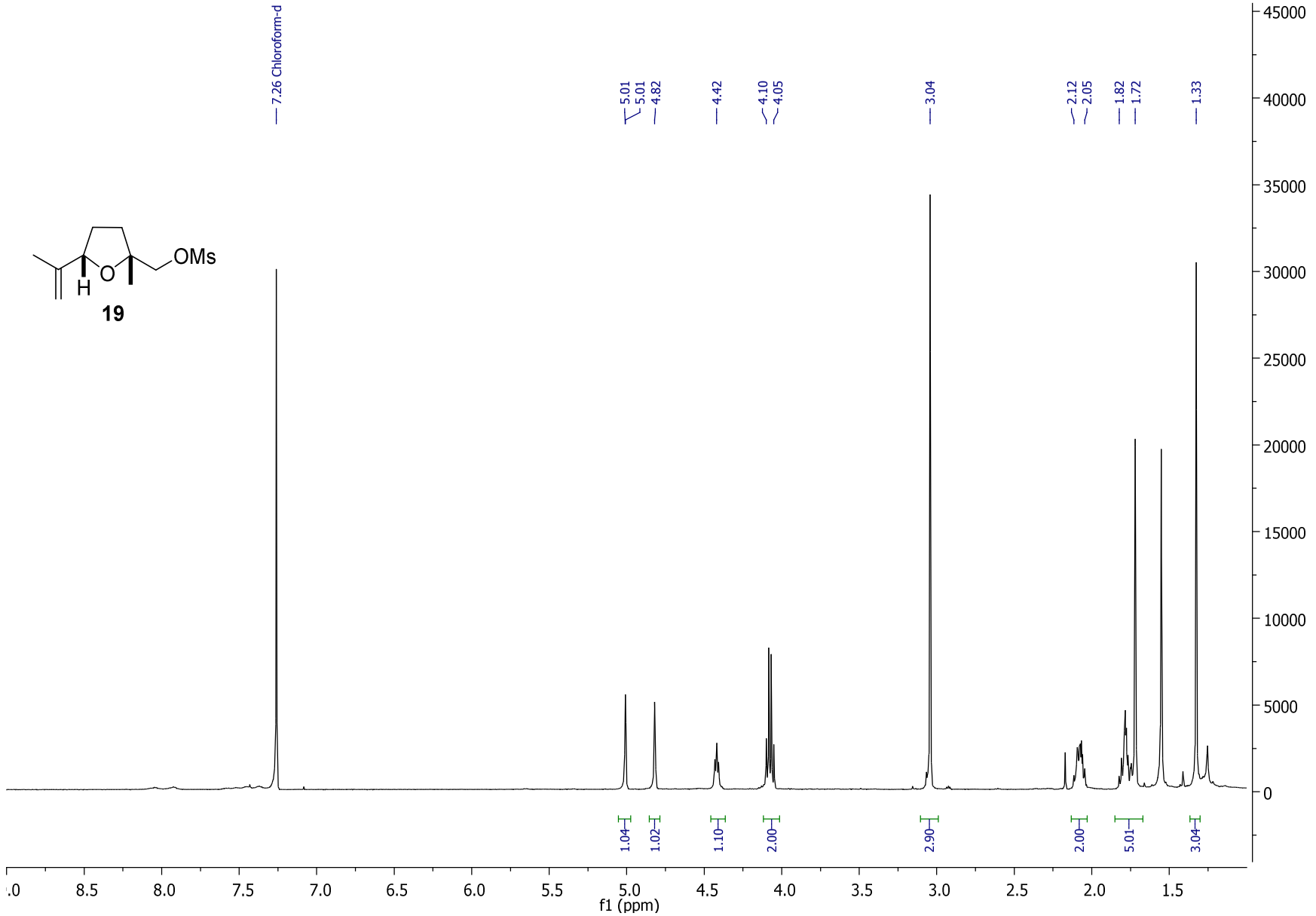

166.65
165.99
148.53
133.30
133.19
129.96
129.81
129.50
128.58
126.66
126.62
98.53
84.27
77.16 Chloroform-d
76.36
63.97
33.78
26.51
23.88
19.10
16.84
OBz
OBz
O
13b
f1 (ppm)
f1 (ppm)

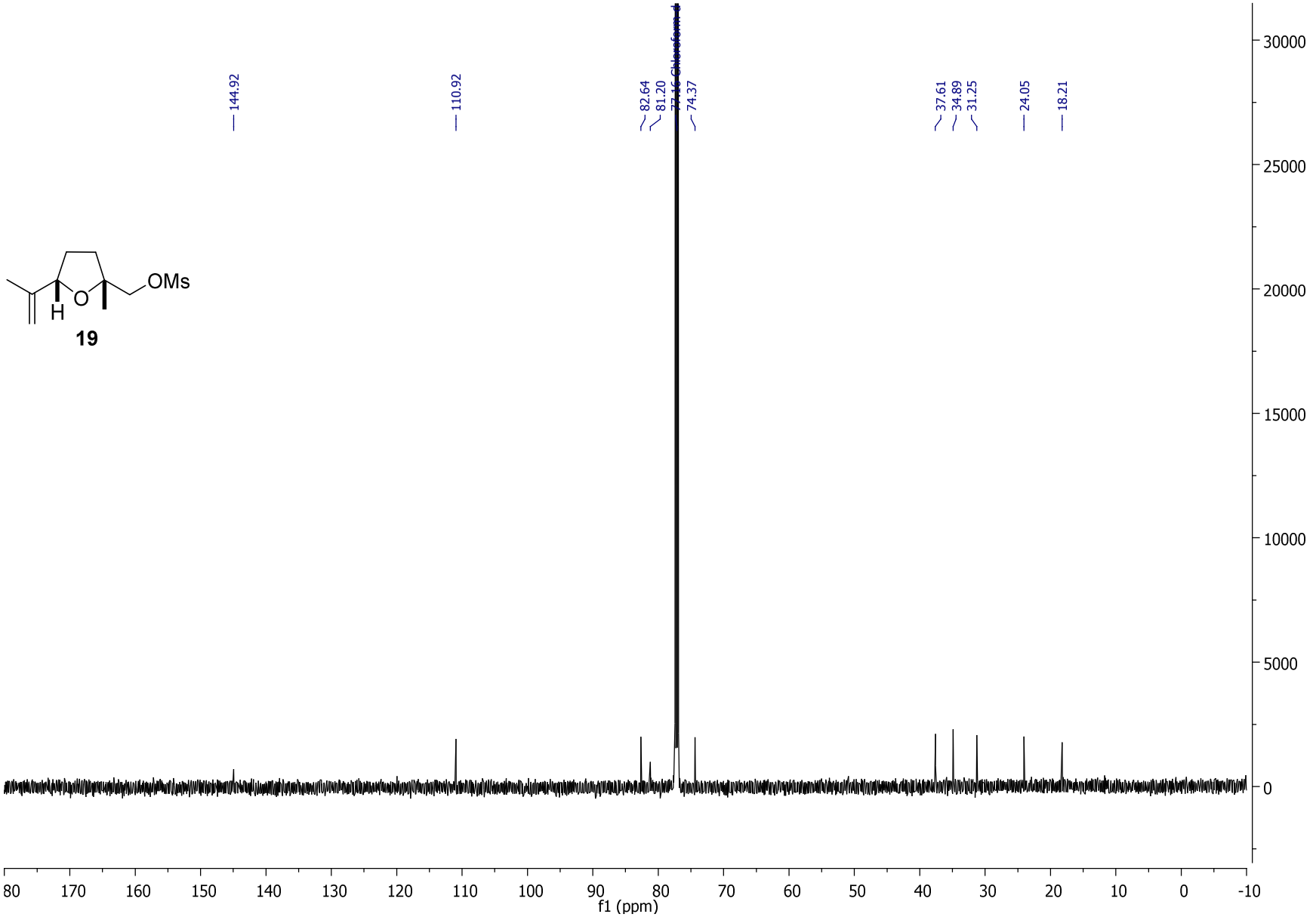

7.26 Chloroform-d
5.80
5.80
5.69
5.09
4.99
4.81
4.37
2.48
2.42
2.34
2.26
2.07
1.91
1.76
1.63
1.25
O
H
OAc
15
1.03
4.09
1.00
0.97
1.05
1.08
5.11
5.07
3.13
f1 (ppm)

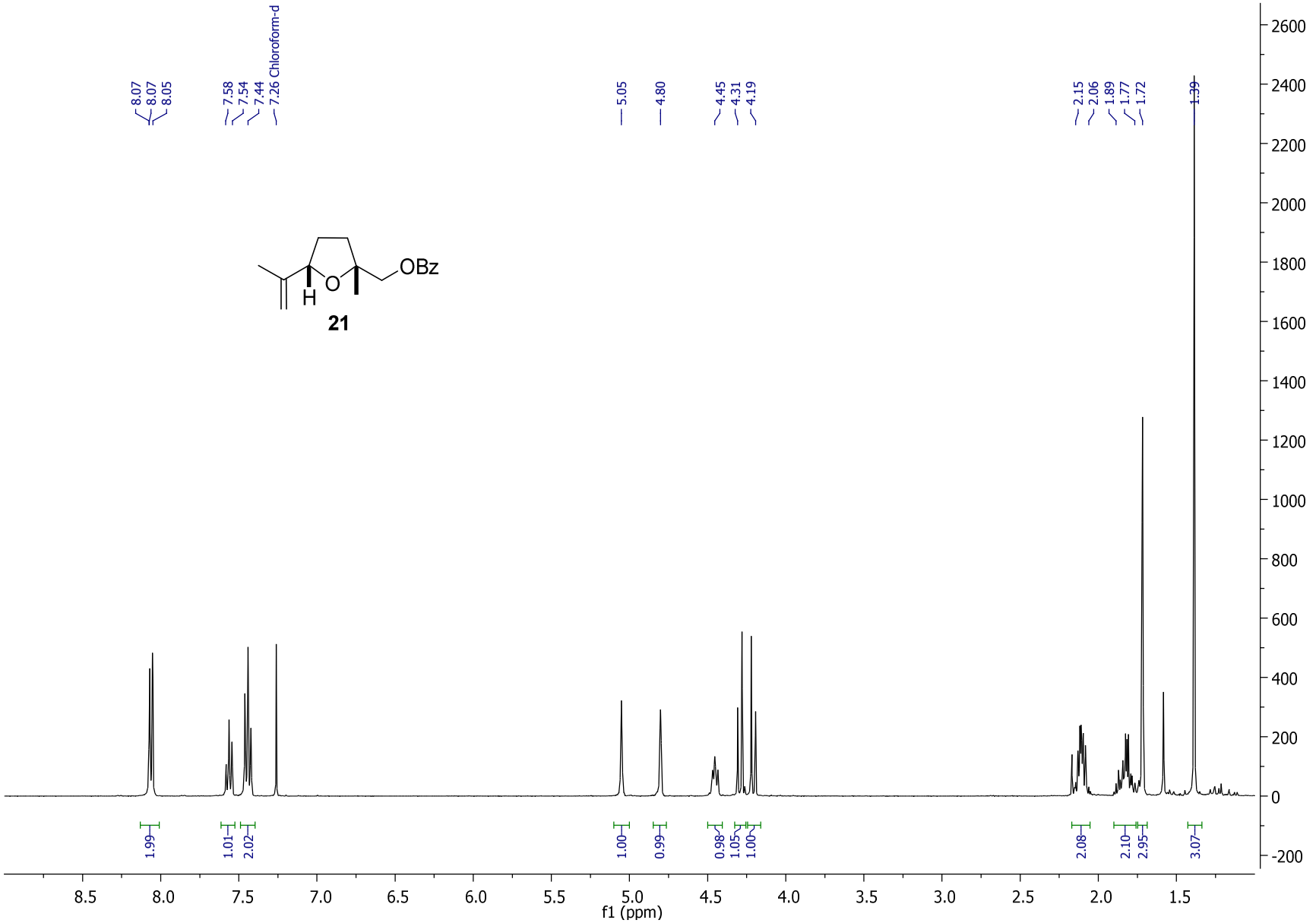

170.78
145.23
134.82
117.35
110.82
83.95
81.90
77.59
77.16 Chloroform-d
35.27
35.25
31.68
23.51
21.26
18.17
H
O
OAc
15
f1 (ppm)

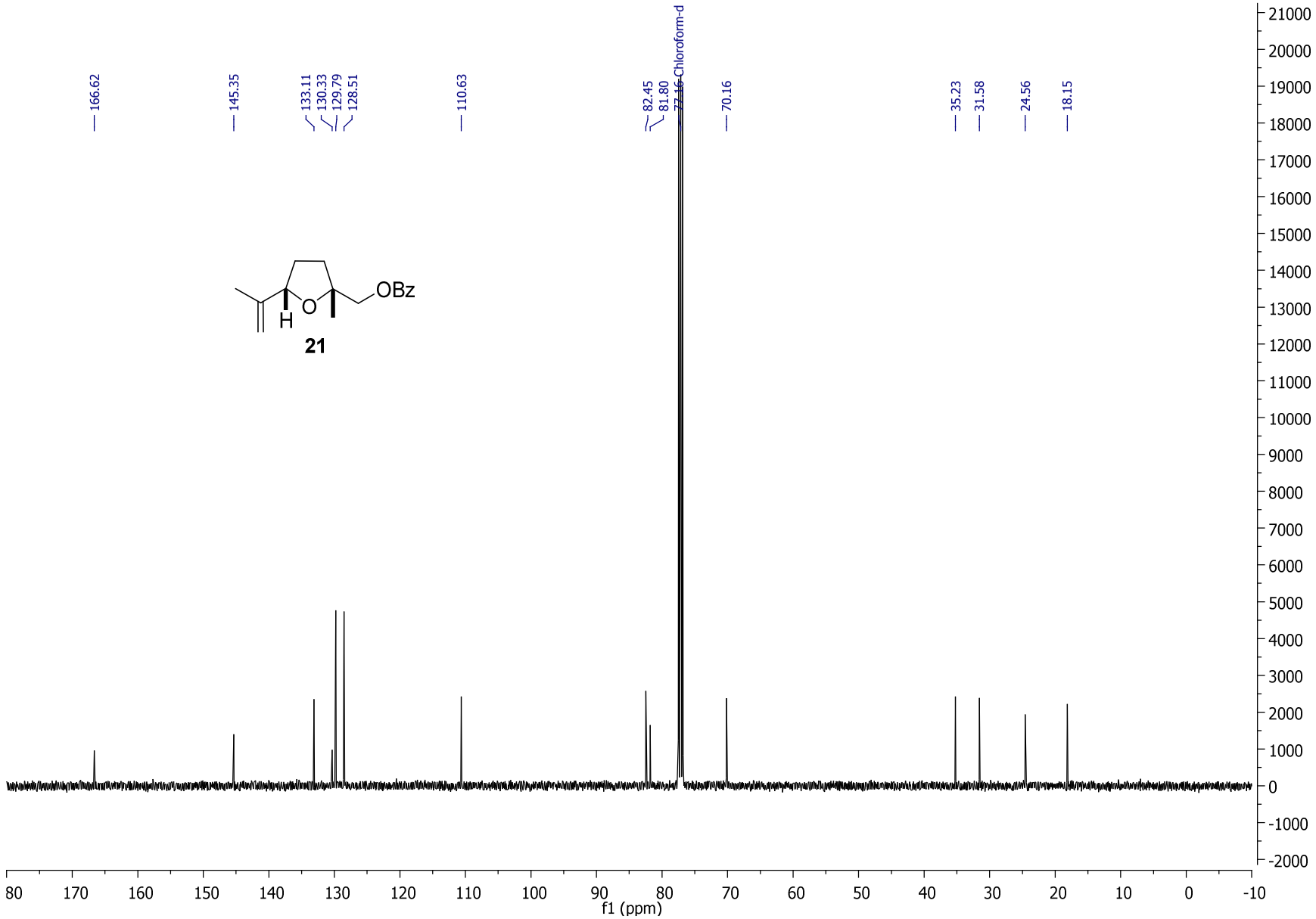

7.26 Chloroform-d
5.23
5.23
5.19
5.02
4.83
4.35
3.53
3.50
3.28
2.15
2.05
1.96
1.74
1.65
1.27
H
O
I
OAc
17
0.95
1.00
0.99
0.98
1.04
1.01
3.07
2.24
5.27
3.33
f1 (ppm)

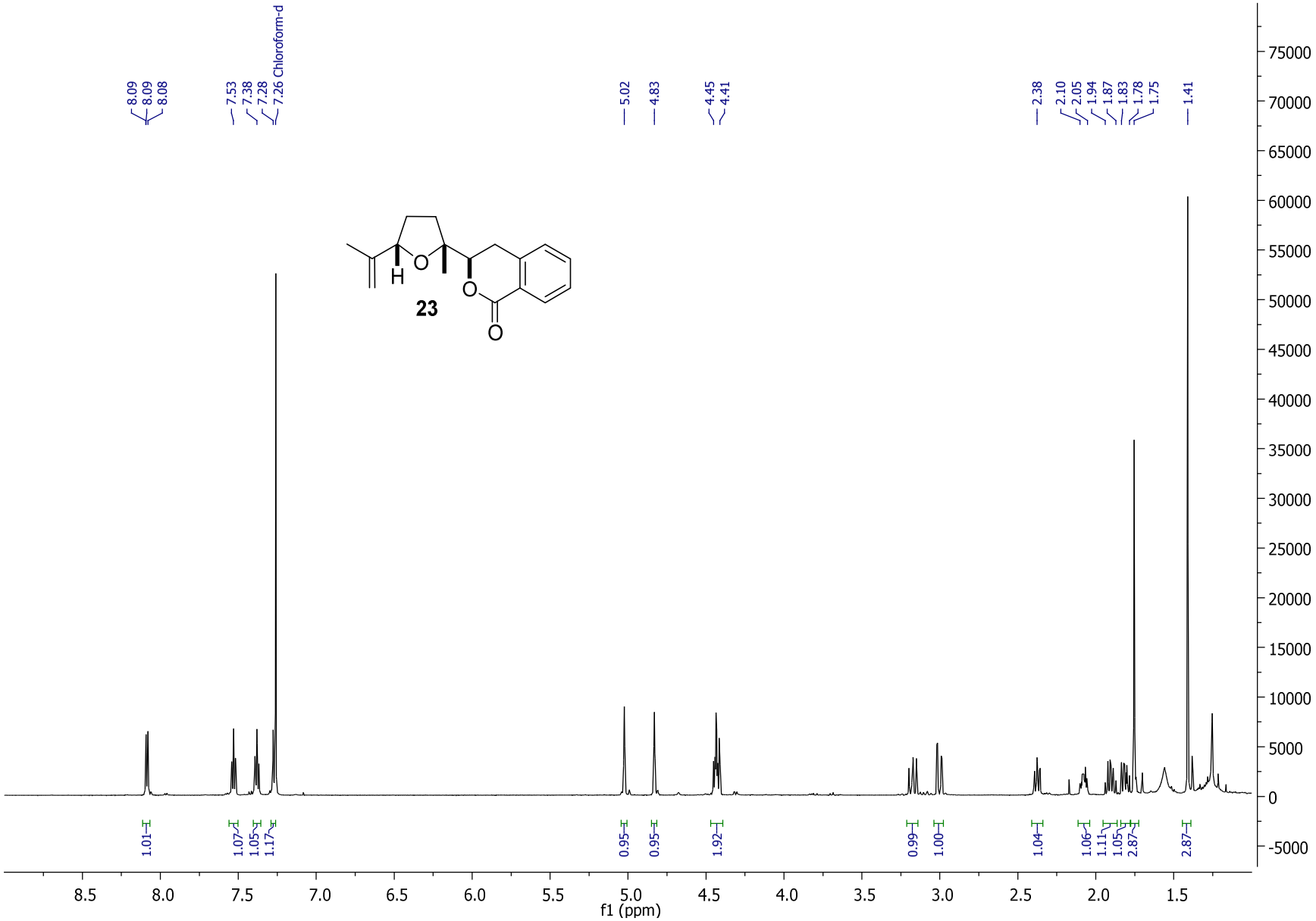

207.11
144.74
111.14
84.12
82.05
78.43
77.16 Chloroform-d
35.32
31.76
24.54
21.24
18.18
3.90
H
O
OAc
I
17
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 Chloroform-d
5.01
5.01
4.82
4.42
4.10
4.05
3.04
2.12
2.05
1.82
1.72
1.33
OMs
O
H
19
1.04
1.02
1.10
2.00
2.90
2.00
5.01
3.04
f1 (ppm)


144.92
110.92
82.64
81.20
77.16 Chloroform-d
74.37
37.61
34.89
31.25
24.05
18.21
OMs
O
H
19
30000
25000
20000
15000
10000
5000
0
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.07
8.07
8.05
7.58
7.54
7.44
7.26 Chloroform-d
5.05
4.80
4.45
4.31
4.19
2.15
2.06
1.89
1.77
1.72
1.39
OBz
O
H
21
1.99
1.01
2.02
1.00
0.99
0.98
1.05
1.00
2.08
2.10
2.95
3.07
f1 (ppm)


166.62
145.35
133.11
130.33
129.79
128.51
110.63
82.45
81.80
77.16 Chloroform-d
70.16
35.23
31.58
24.56
18.15
OBz
O
H
21
f1 (ppm)


8.09
8.09
8.08
7.53
7.38
7.28
7.26 Chloroform-d
5.02
4.83
4.45
4.41
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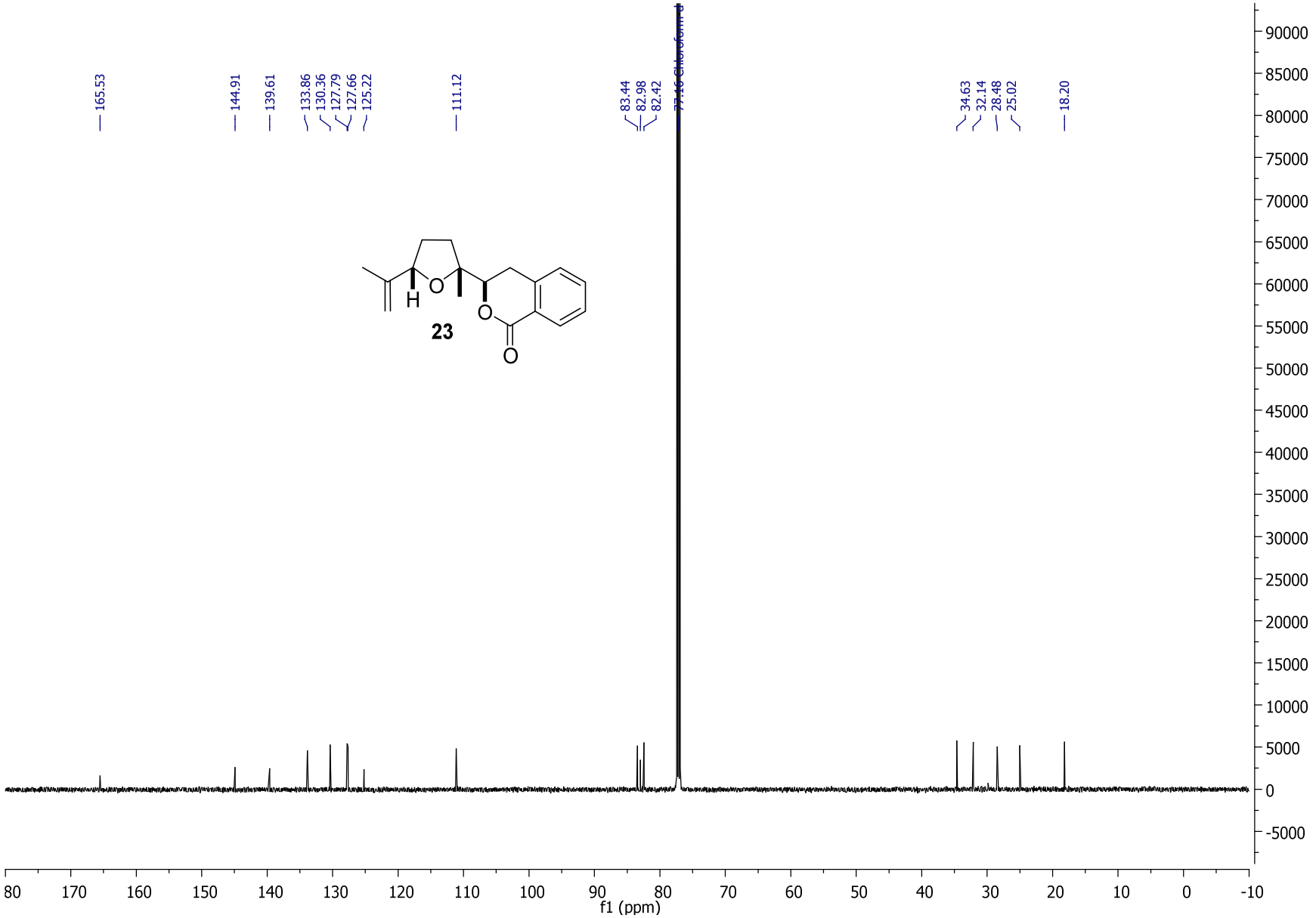
2.10
2.05
1.94
1.87
1.83
1.78
1.75
1.41
23
O
H
O
O
1.01
1.07
1.05
1.17
0.95
0.95
1.92
0.99
1.00
1.04
1.06
1.11
1.05
2.87
2.87
f1 (ppm)


165.53
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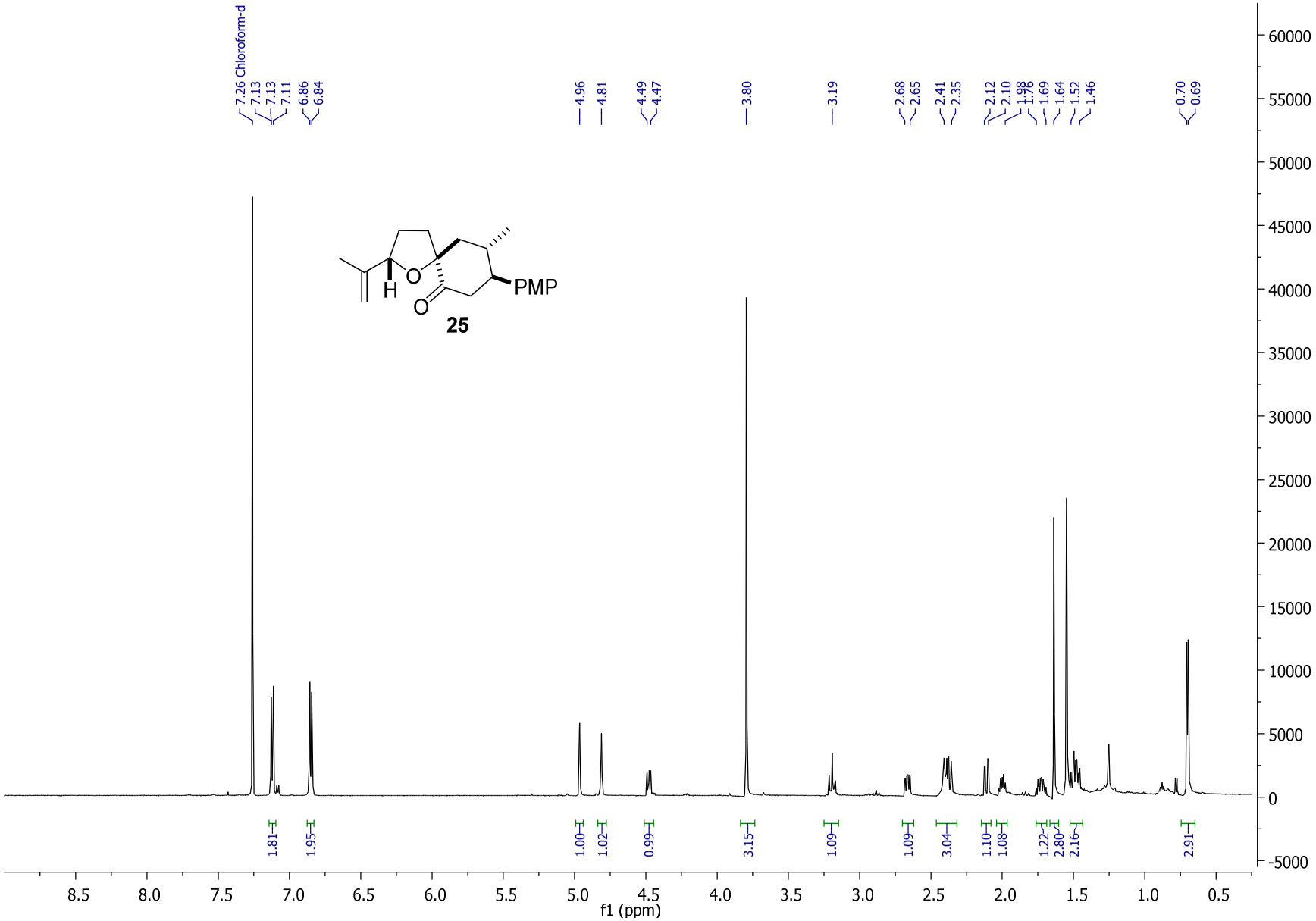
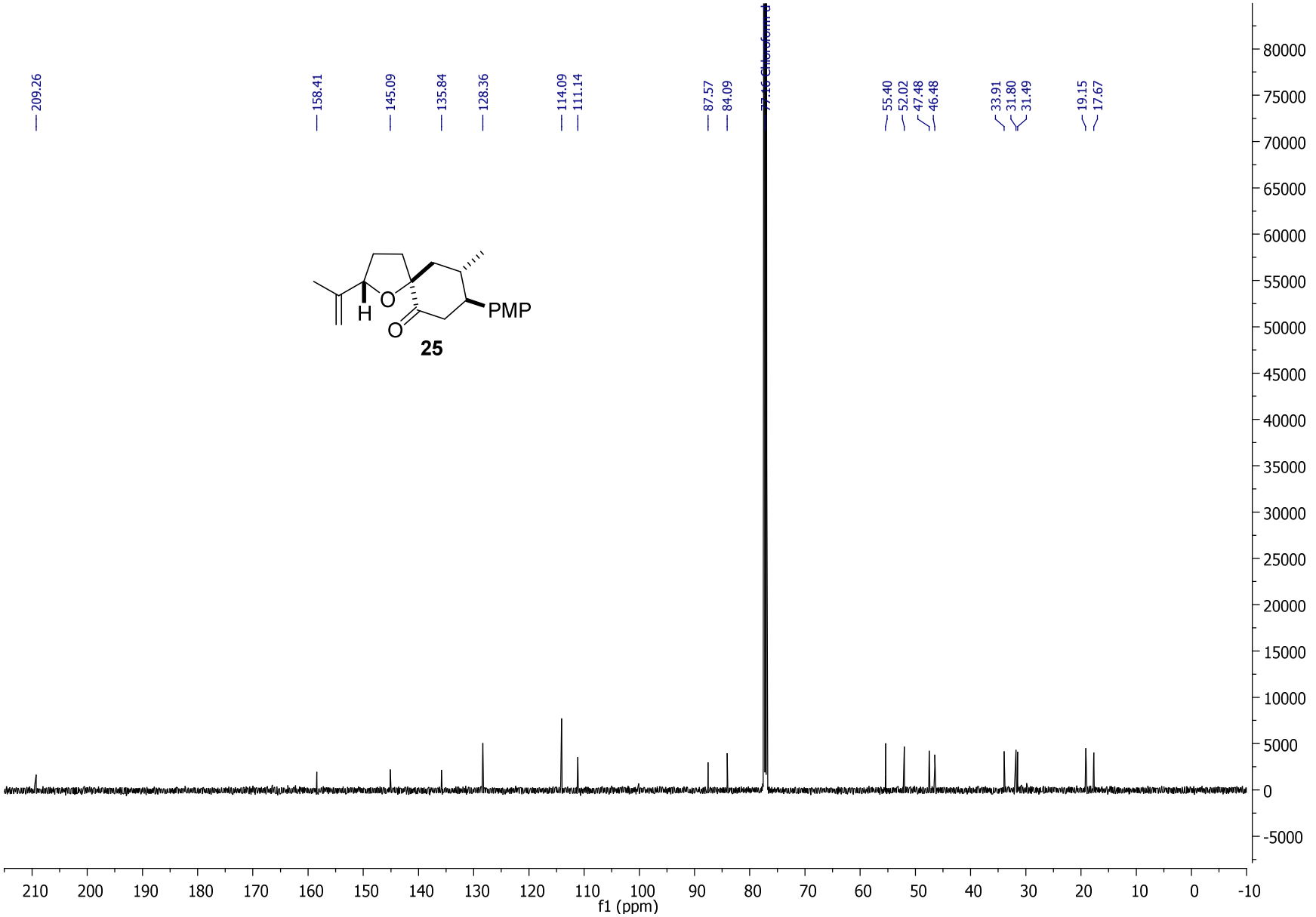
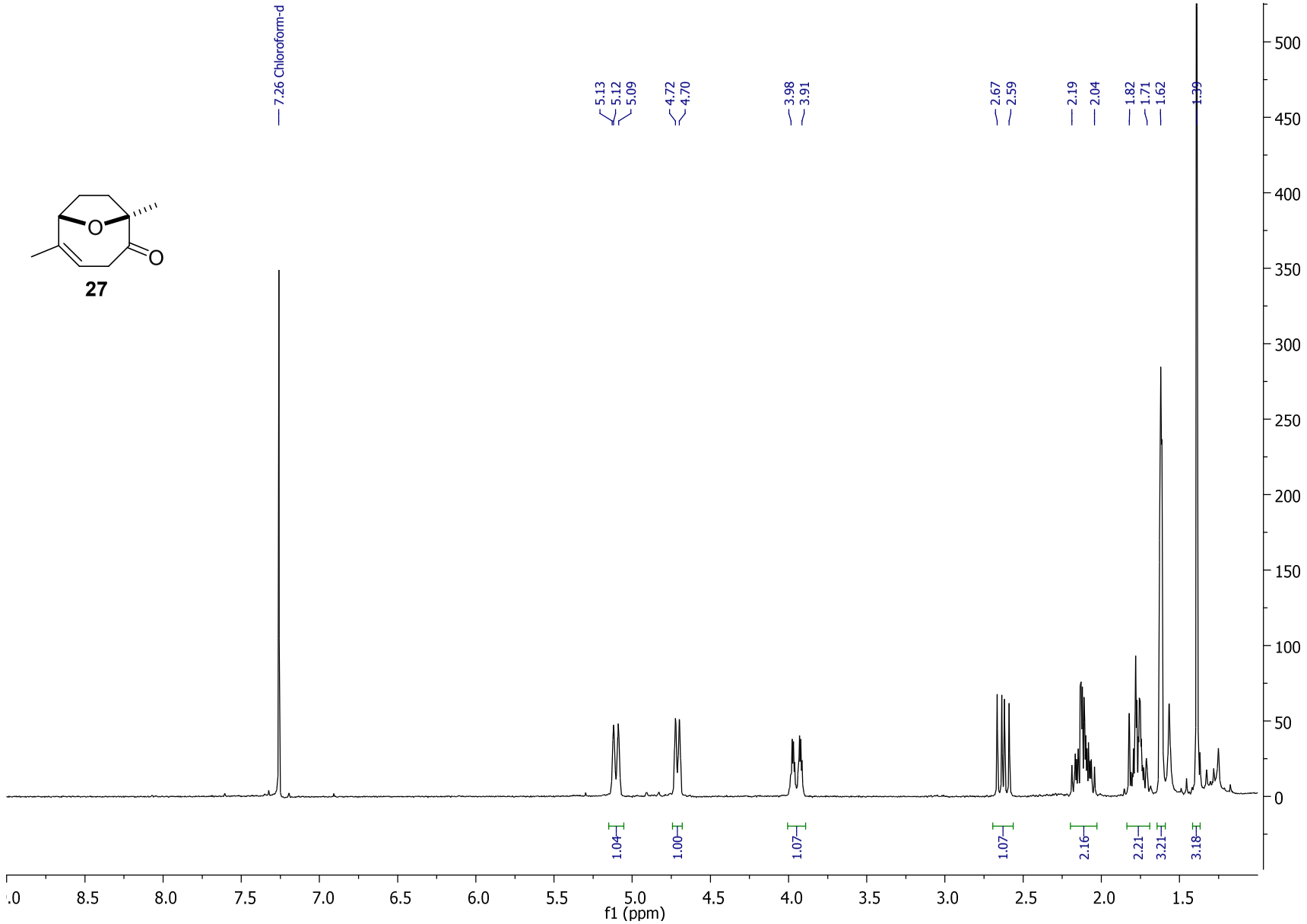
133.86
130.36
127.79
127.66
125.22
111.12
83.44
82.98
82.42
77.16 Chloroform-d
34.63
32.14
28.48
25.02
18.20
H
O
O
O
23
f1 (ppm)


7.26 Chloroform-d
7.13
7.13
7.11
6.86
6.84
4.96
4.81
4.49
4.47
3.80
3.19
2.68
2.65
2.41
2.35
2.12
2.10
1.98
1.76
1.69
1.64
1.52
1.46
0.70
0.69
PMP
O
H
O
25
1.81
1.95
1.00
1.02
0.99
3.15
1.09
1.09
3.04
1.10
1.08
1.22
2.80
2.16
2.91
f1 (ppm)


209.26
158.41
145.09
135.84
128.36
114.09
111.14
87.57
84.09
77.16 Chloroform-d
55.40
52.02
47.48
46.48
33.91
31.80
31.49
19.15
17.67
H
O
O
PMP
25
f1 (ppm)


7.26 Chloroform-d
5.13
5.12
5.09
4.72
4.70
3.98
3.91
2.67
2.59
2.19
2.04
1.82
1.71
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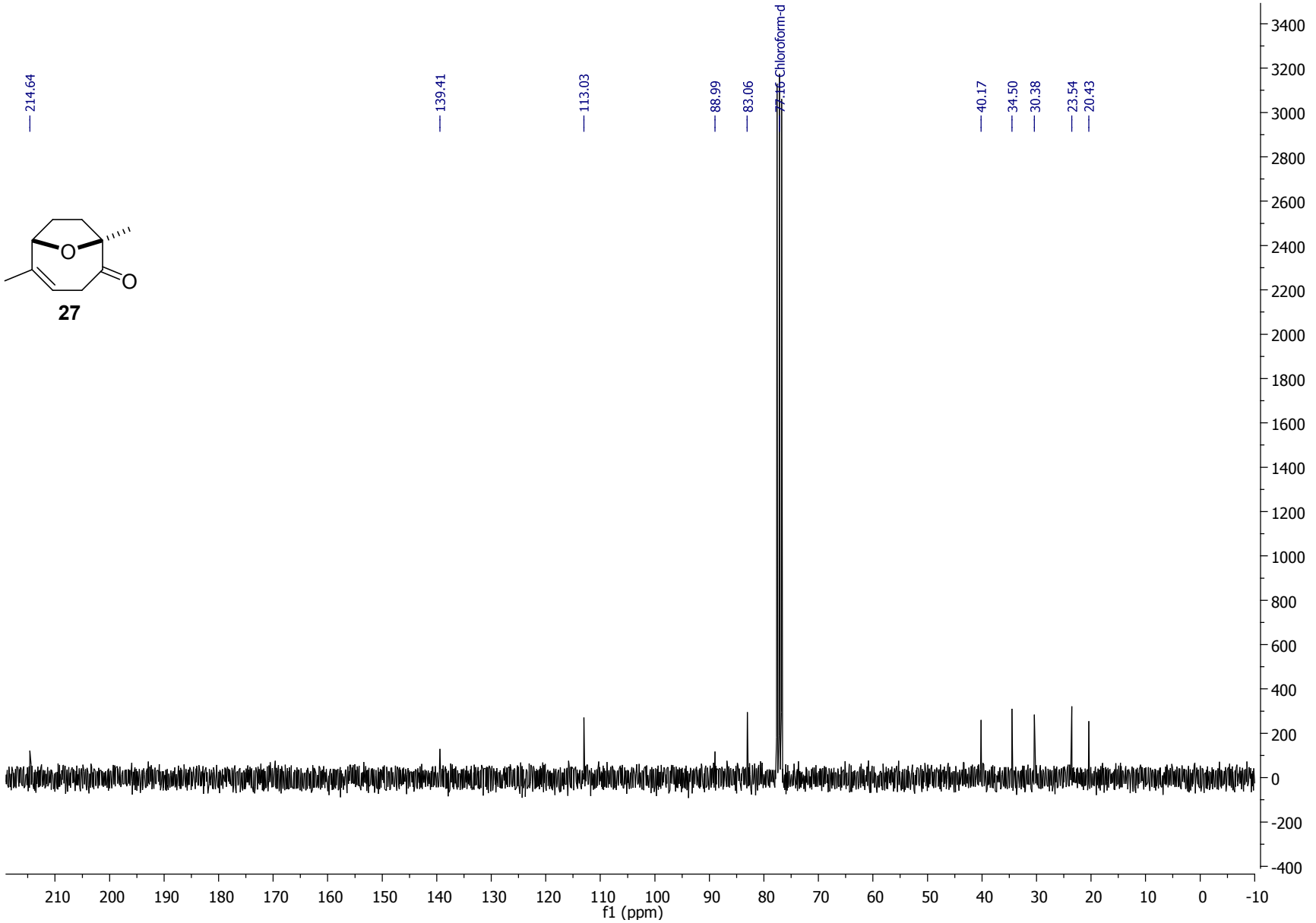
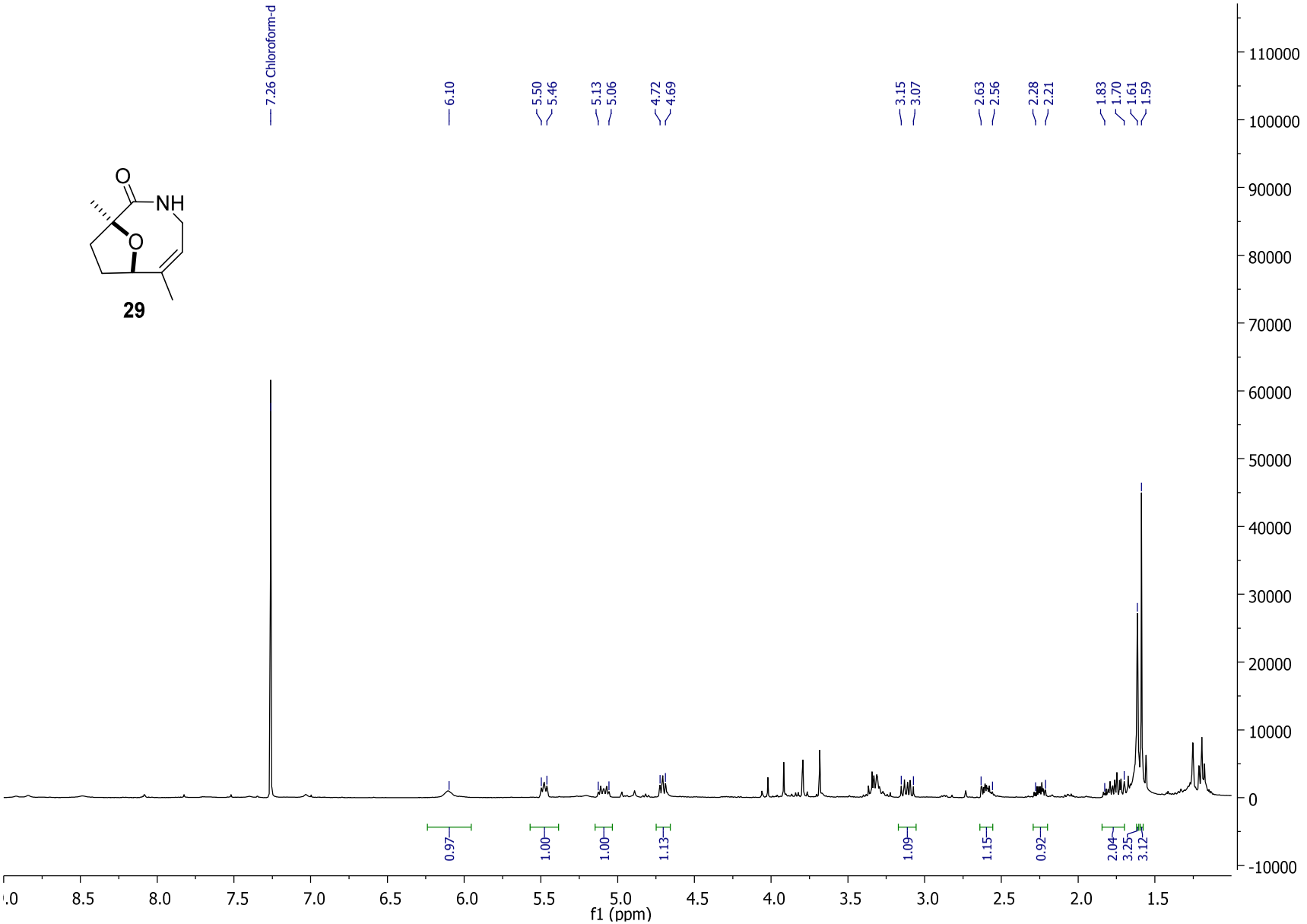
2.16
2.21
3.21
3.18
f1 (ppm)

27


214.64
139.41
113.03
88.99
83.06
77.16 Chloroform-d
40.17
34.50
30.38
23.54
20.43
O
O
27
f1 (ppm)


7.26 Chloroform-d
6.10
5.50
5.46
5.13
5.06
4.72
4.69
3.15
3.07
2.63
2.56
2.28
2.21
1.83
1.70
1.61
1.59
O
NH
O
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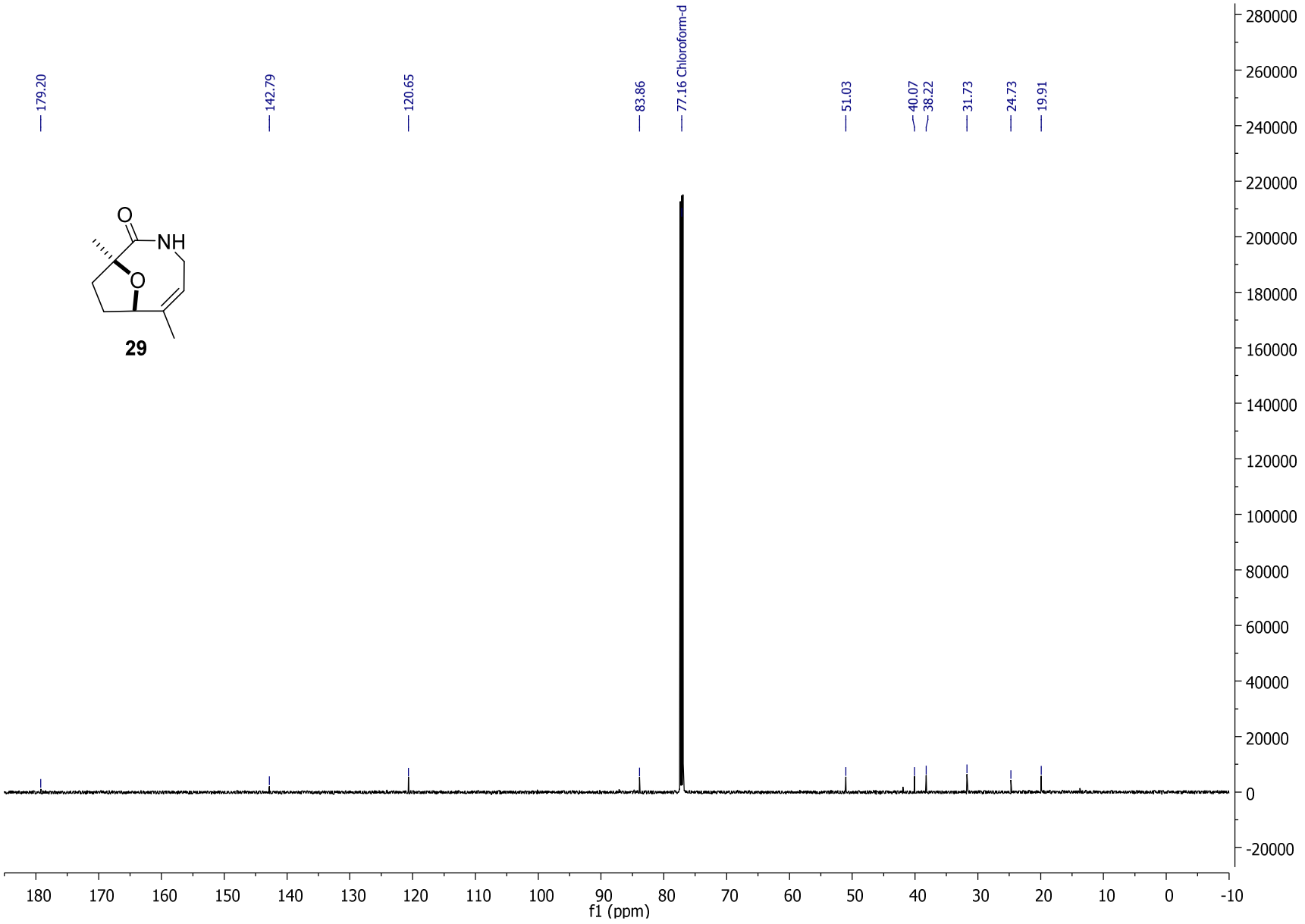
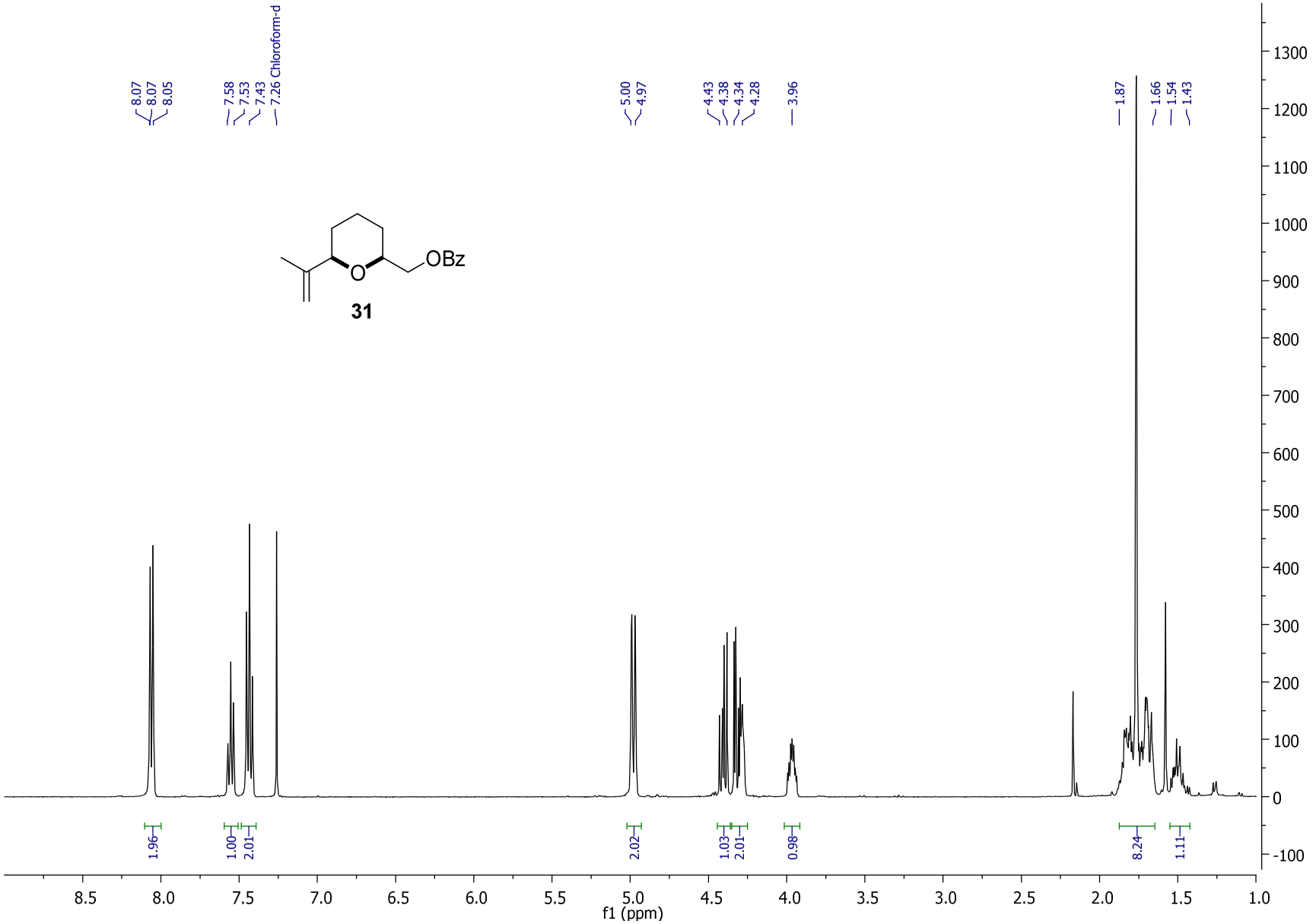
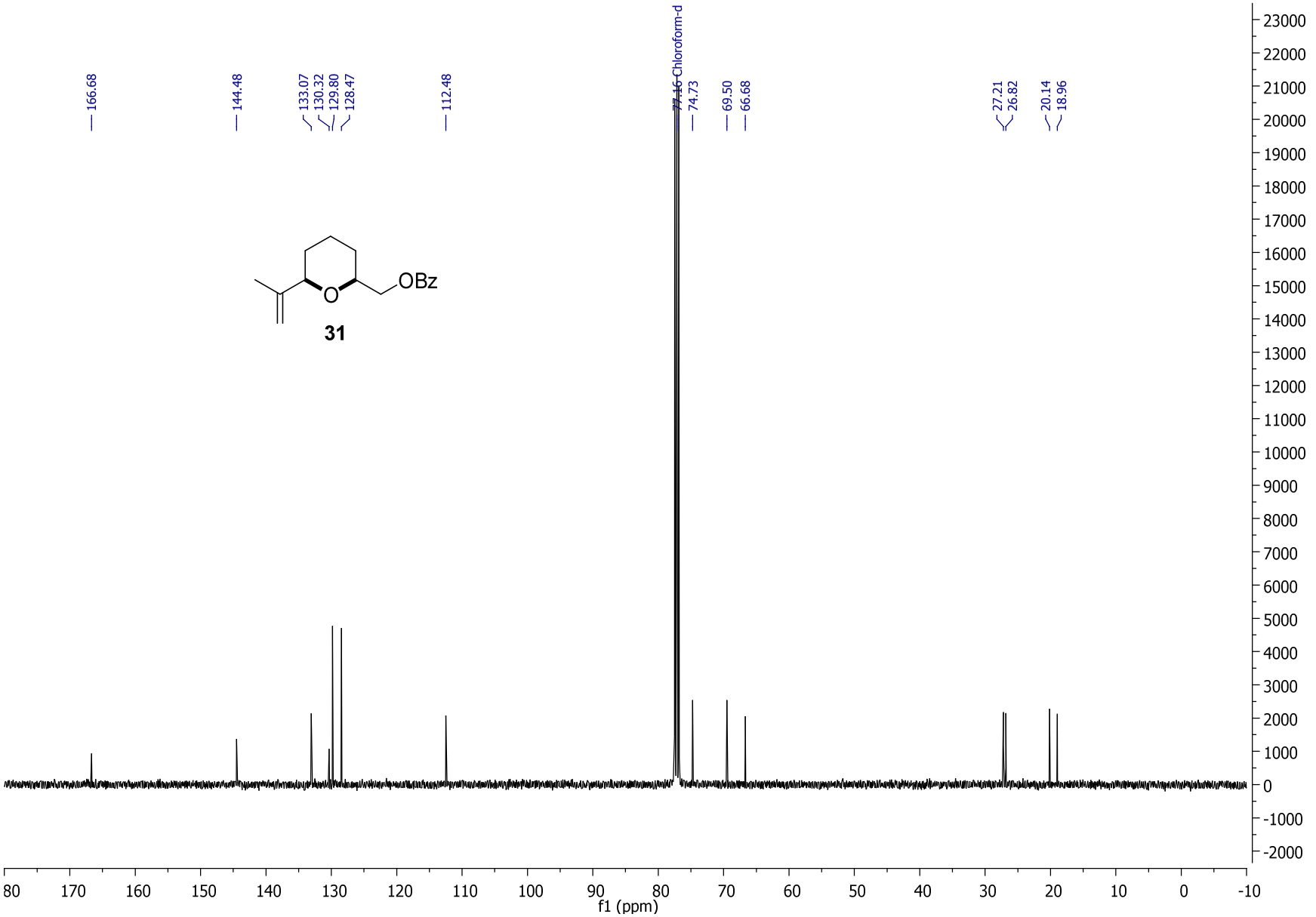
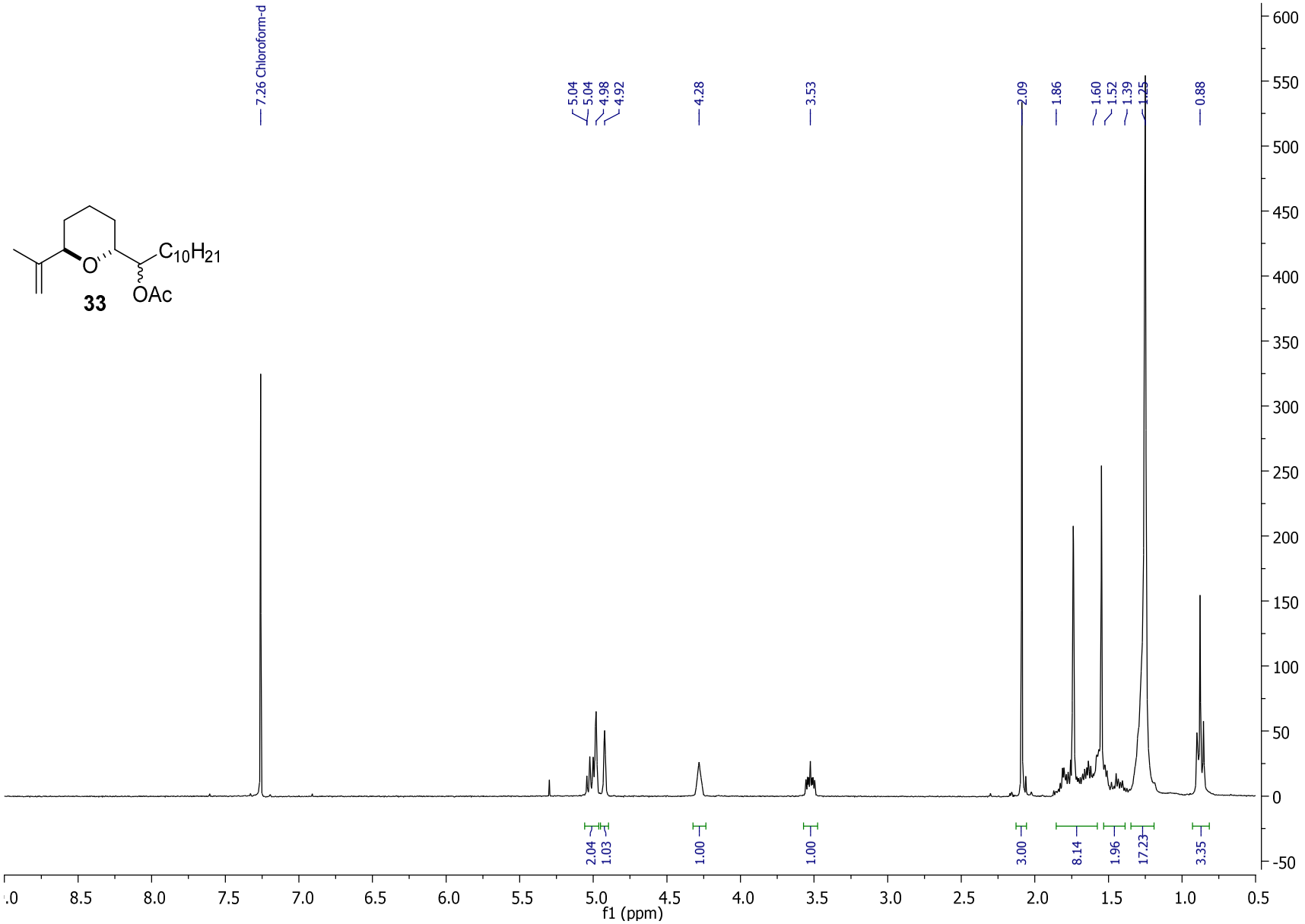
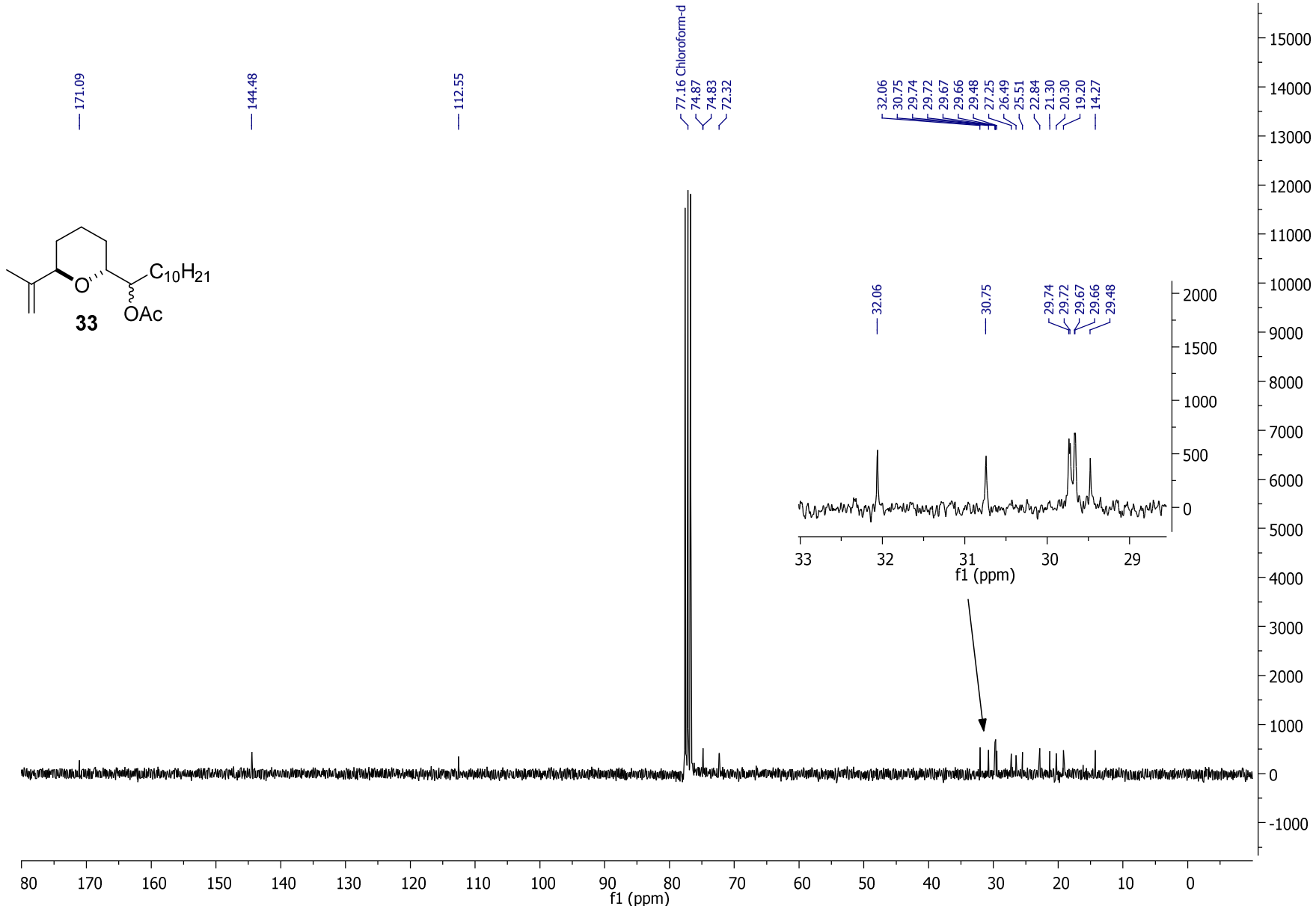
1.00
1.13
1.09
1.15
0.92
2.04
3.25
3.12
f1 (ppm)


179.20
142.79
120.65
83.86
77.16 Chlororform-d
51.03
40.07
38.22
31.73
24.73
19.91
O
NH
O
29
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.07
8.07
8.05
7.58
7.53
7.43
7.26 Chloroform-d
5.00
4.97
4.43
4.38
4.34
4.28
3.96
1.87
1.66
1.54
1.43
OBz
O
31
1.96
1.00
2.01
2.02
1.03
2.01
0.98
8.24
1.11
f1 (ppm)


166.68
144.48
133.07
130.32
129.80
128.47
112.48
77.16 Chloroform-d
74.73
69.50
66.68
27.21
26.82
20.14
18.96
OBz
O
31
f1 (ppm)


7.26 Chloroform-d
5.04
5.04
4.98
4.92
4.28
3.53
2.09
1.86
1.60
1.52
1.39
1.25
0.88
$C_{10}H_{21}$
O
OAc
33
2.04
1.03
1.00
1.00
3.00
8.14
1.96
17.23
3.35
f1 (ppm)


171.09
144.48
112.55
77.16 Chloroform-d
74.87
74.83
72.32
32.06
30.75
29.74
29.72
29.67
29.66
29.48
27.25
26.49
25.51
22.84
21.30
20.30
19.20
14.27
C10H21
O
OAc
33
f1 (ppm)