Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting informations
# for
# Stereoselective synthesis and application of isopulegol-based bi- and trifunctional ligands

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# Contents

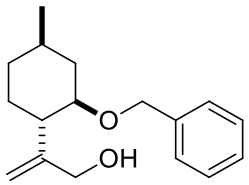
## 1. General methods

Commercially available solvents were used as obtained from suppliers (Molar Chemicals Ltd, Halásztelek, Hungary; Merck Ltd., Budapest, Hungary and VWR International Ltd., Debrecen, Hungary), while applied solvents were dried according to standard procedures. Optical rotations were measured in MeOH at 20 °C with a Perkin-Elmer 341 polarimeter (PerkinElmer Inc., Shelton, CT, USA). Chromatographic separations and monitoring of reactions were carried out on Merck Kieselgel 60 (Merck Ltd., Budapest, Hungary). Elemental analyses for all prepared compounds were performed on a Perkin-Elmer 2400 Elemental Analyzer (PerkinElmer Inc., Waltham, MA, USA). GC measurements for direct separation of commercially available enantiomers of isopulegol to determine the enantiomeric purity of starting material **1** and separation of *O*-acetyl derivatives of enantiomers were performed on a Chirasil-DEX CB column (2500 × 0.25 mm I.D.) on a Perkin-Elmer Autosystem XL GC consisting of a Flame Ionization Detector (Perkin-Elmer Corporation, Norwalk, CT, USA) and a Turbochrom Workstation data system (Perkin-Elmer Corp., Norwalk, CT, USA). Melting points were determined on a Kofler apparatus (Nagema, Dresden, Germany) and are uncorrected. $^{1}$H- and $^{13}$C-NMR were recorded on Brucker Avance DRX 500 spectrometer [500 MHz ($^{1}$H) and 125 MHz ($^{13}$C), δ = 0 (TMS)]. Chemical shifts are expressed in ppm (δ) relative to TMS as the internal reference. *J* values are given by Hz. Microbiological cultivations were carried out in ferment broths containing 10 g/L peptone, 5 g/L NaCl, 5 g/L yeast extract for bacteria as well as 20 g/L peptone, 10 g/L yeast extract, 20 g/L glucose for yeast. The ampicillin and nystatin were purchased from Merck Ltd. (Budapest, Hungary). For the measurements of both antioxidant and antimicrobiological activity, a SPECTROstar®Nano microplate reader (BMG LABTECH, Ortenberg, Germany) were used controlled by the MARS Ver. 2.2 software (BMG LABTECH, Ortenberg, Germany).

(–)-Isopulegol **1** is available commercially from Merck Co with *ee* = 95%. (–)-Isopulegol acetate **2**, diol **3** and (–)-$\alpha$-methylene-$\gamma$-butyrolactone **4** were prepared according to literature procedures, and all spectroscopic data were similar to those described therein.[1] The nucleophilic addition of amines to $\alpha$-methylene-$\gamma$-butyrolactone were carried out according to our literature procedures with all spectroscopic data of compounds **5**–**8** being consistent with their literature values.[2]

## 2. Experimental section and compound characterisations

**2-((1*S*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)prop-2-en-1-ol (41)**




**41**

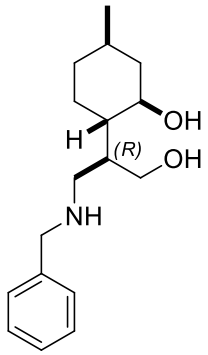
To a solution of *t*-BuOOH (70% purity in $H_2O$, 32.80 mmol) in $CHCl_3$ (50 mL), dried briefly by ($Na_2SO_4$), was added finely powdered $SeO_2$ (1.96 mmol) followed by addition of **33** (8.20 mmol) after 30 minutes stirring. After stirring for 20 h at 60°C, saturated $NaHCO_3$ solution (50 mL) was added to the mixture and the organic phase was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 x 50 mL). The organic layer was dried ($Na_2SO_4$) and concentrated in vacuo to afford colorless oil, which was added to a suspension of $LiAlH_4$ (24.60 mmol) in dry ether (50 mL) at 0 °C. The reaction mixture was stirred for 6 h at same temperature while the reaction progress was monitored by TLC. A mixture of $H_2O$ (2 mL) and THF (8 mL) was then added dropwise to decompose excess $LiAlH_4$ with cooling. The inorganic material was filtered off and washed with $Et_2O$. The filtrate was dried ($Na_2SO_4$) and evaporated to dryness. The crude product was purified by column chromatography on silica gel using *n*-hexane:EtOAc = 4:1.

Yield: 60%, colorless oil. $[\alpha]_D^{20}$ = -95.0 (c 0.23, MeOH). Found: C, 78.40; H, 9.27. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.89-1.01 (2H, m), 0.96 (3H, d, *J* = 6.6 Hz), 1.35-1.50 (2H, m), 1.64-1.76 (2H, m), 2.05-2.11 (1H, m), 2.17-2.20 (1H, m), 2.70 (1H, brs), 3.25 (1H, td, *J* = 10.6, 4.0 Hz), 4.04 (2H, t, *J* = 14.3 Hz), 4.38 (1H, d, *J* = 11.5 Hz), 4.63 (1H, d, *J* = 11.5 Hz), 4.92 (1H, s), 5.08 (1H, d, *J* = 0.8 Hz), 7.23-7.33 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 31.6, 31.9, 34.7, 40.3, 46.8, 67.1, 70.8, 82.4, 110.6, 127.7, 128.0, 128.4, 138.3, 152.1.

### 2.1. General procedure for reduction with $LiAlH_4$

To the stirred suspension of $LiAlH_4$ (8.0 mmol) in dry $Et_2O$ or dry THF (16 mL), *β*-aminolactones **5**–**8**, carbonates **40a–b** or epoxide **63a** (4.0 mmol) in dry ether or dry THF (20 mL) was added at 0 °C. The reaction mixture was stirred for 4 h at room temperature (**5**–**8**), 0 °C (**40a–b**) or for 6 h at 0 °C (**63a**). When the reaction was comleted (TLC monitoring), a mixture of $H_2O$ (2 mL) and THF (8 mL) was added dropwise to the solution with cooling. The inorganic material was filtered off and washed with $Et_2O$ (for compounds **9**–**12**) or EtOAc (for compound **39a–b** and **22a**–**b**). The filtrate was dried ($Na_2SO_4$) and evaporated to dryness. The crude product was purified by column chromatography on silica gel using $CHCl_3$:MeOH = 9:1 then recrystallized in $Et_2O$ (for **9**–**12**) or *n*-hexane:EtOAc (1:1 for **39a–b** and 1:2 for **22a**).

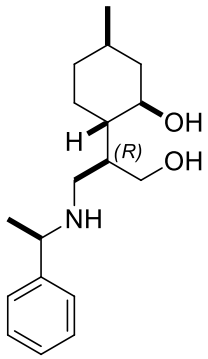
**(1*R*,2*S*,5*R*)-2-((*R*)-1-(Benzylamino)-3-hydroxypropan-2-yl)-5-methylcyclohexanol (9)**




**9**

Yield: 50%, white crystals, m.p.: 214–215 °C. $[\alpha]_D^{20}$ = -33.0 (c 0.20, MeOH). Found: C, 73.65; H, 9.80; N, 5.10. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.73-0.79 (1H, m), 0.80-0.89 (1H, m), 0.85 (3H, d, *J* = 6.3 Hz), 0.94-1.01 (1H, m), 1.25-1.40 (2H, m), 1.53 (2H, t, *J* = 12.9 Hz), 1.81 (1H , d, *J* = 11.9 Hz), 2.26 (1H, s), 2.87 (1H, t, *J* = 9.3 Hz), 3.04 (1H, d, *J* = 11.3 Hz), 3.21 (1H, t, *J* = 7.5 Hz), 3.53 (2H, d, *J* = 6.3 Hz), 4.08 (1H, d, *J* = 13.0 Hz), 4.17 (1H, d, *J* = 13.0 Hz), 4.90 (1H, s), 5.09 (1H, brs), 7.41-7.56 (5H, m), 8.67 (1H, brs), 9.22 (1H, brs). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 22.2, 26.4, 30.9, 34.2, 38.1, 44.6, 44.8, 47.8, 50.4, 61.7, 68.7, 128.6, 128.9, 130.0, 132.1.

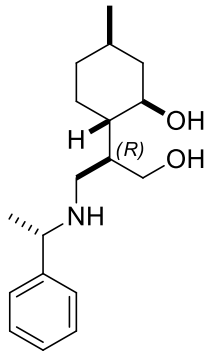
**(1*R*,2*S*,5*R*)-2-((*R*)-1-Hydroxy-3-(((*R*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (10)**




**10**

Yield: 60%, white crystals, m.p.: 196–197 °C. $[\alpha]_D^{20}$ = +3.0 (c 0.225, MeOH). Found: C, 74.20; H, 10.00; N, 4.83. Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.71-0.78 (1H, m), 0.80-0.87 (1H, m), 0.82 (3H, d, *J* = 6.2 Hz), 0.91-0.98 (1H, m), 1.27-1.32 (2H, m), 1.48-1.52 (2H, m), 1.58 (3H, d, *J* = 6.6 Hz), 2.16 (1H, s), 2.77 (2H, t, *J* = 4.7 Hz), 3.08 (1H, td, *J* = 10.2, 6.9 Hz), 3.52 (2H, d, *J* = 6.0 Hz), 4.36 (1H, q, *J* = 6.7 Hz), 4.90 (1H, brs), 7.37-7.59 (5H, m), 8.97 (1H, brs). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 19.2, 22.1, 26.8, 30.8, 34.1, 38.8, 44.5, 44.6, 46.2, 46.2, 57.6, 61.1, 68.9, 127.8, 128.7, 128.8, 137.5.

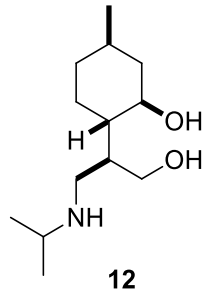
**(1*R*,2*S*,5*R*)-2-((*R*)-1-Hydroxy-3-(((*S*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (11)**




**11**

Yield: 65%, white crystals, m.p.: 196–197 °C. $[\alpha]_D^{20}$ = -40.0 (c 0.225, MeOH). Found: C, 74.15; H, 10.05; N, 4.79. Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.71-0.76 (1H, m), 0.83 (3H, d, *J* = 6.2 Hz), 0.82-0.90 (2H, m), 1.23-1.32 (2H, m), 1.44-1.52 (2H, m), 1.59 (3H, d, *J* =6.7 Hz), 1.80 (1H, d, *J* = 11.7 Hz), 2.22 (1H, d, *J* = 5.2 Hz), 2.98 (1H, d, *J* = 10.4 Hz), 3.22 (1H, td, *J* = 10.2, 6.7 Hz), 3.42-3.49 (2H, m), 4.32 (1H, q, *J* = 6.2 Hz), 5.01 (1H, brs), 7.37-7.57 (5H, m). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 19.6, 22.2, 26.2, 30.8, 34.1, 38.3, 44.4, 44.6, 46.3, 57.8, 61.2, 68.6, 127.6, 128.8, 128.9, 137.6.

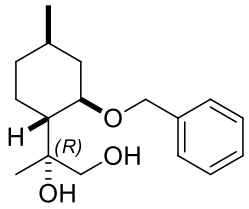
**(1*R*,2*S*,5*R*)-2-((*R*)-1-Hydroxy-3-(isopropylamino)propan-2-yl)-5-methylcyclohexanol (12)**




**12**

Yield: 67%, colorless oil. $[\alpha]_D^{20}$ = -22.0 (c 0.24, MeOH). Found: C, 68.10; H, 11.90; N, 6.15. Anal. Calcd for $C_{13}H_{27}NO_2$: C, 68.08; H, 11.87; N, 6.11. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.84-0.97(3H, m), 0.90 (3H, d, *J* = 6.6 Hz), 1.05-1.17 (2H, m), 1.10 (3H, d, *J* = 2.5 Hz), 1.11 (3H, d, *J* = 2.5 Hz), 1.25-1.32 (2H, m), 1.37-1.43 (1H, m), 1.56-1.64 (2H, m), 1.96-2.02 (2H, m), 2.57 (1H, q, *J* = 6.6 Hz), 2.80 (1H, quin, *J* = 6.3 Hz), 3.03 (1H, dd, *J* = 11.9, 3.7 Hz), 3.34 (1H, td, *J* = 10.5, 4.2 Hz), 3.70 (1H, dd, *J* = 10.6, 4.3 Hz), 3.79 (1H, t, *J* = 9.2 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 22.4, 22.6, 28.9, 31.5, 34.7, 42.5, 44.9, 47.4, 48.4, 49.5, 64.7, 70.2, 82.7.

**(*R*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)propane-1,2-diol (39a)**

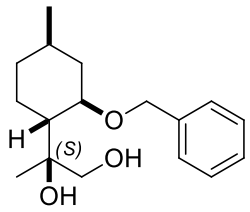



**40a**

Yield: 95%, colorless oil. $[\alpha]_D^{20}$ = -40.0 (c 0.15, MeOH). Found: C, 73.37; H,9.38. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.86-1.08 (3H, m), 0.96 (3H, d, *J* = 6.5 Hz), 1.03 (3H, s), 1.37-1.42 (1H, m), 1.63-1.70 (1H, m), 1.73-1.77 (1H, m), 1.81-1.86 (1H, m), 2.28-2.33 (1H, m), 3.30 (1H, d, *J* = 11.1 Hz), 3.44 (1H, d, *J* = 11.1 Hz), 3.61 (1H, td, *J* = 10.6, 3.9 Hz), 4.43 (1H, d, *J* = 10.8 Hz), 4.72 (1H, d, *J* = 10.9 Hz), 7.26-

7.37 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 20.0, 22.2, 26.6, 31.4, 34.3, 39.6, 47.0, 68.8, 70.3, 75.5, 80.6, 128.2, 128.4, 128.7, 137.4.

**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)propane-1,2-diol (39b)**

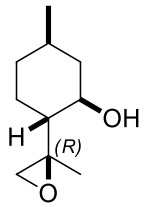



Yield: 56%, colorless oil. $[\alpha]_D^{20}$ = -67.0 (c 0.22, MeOH). Found: C, 73.29; H,9.43. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87-1.05 (3H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.02 (3H, s), 1.36-1.40 (1H, m), 1.62-1.68 (1H, m), 1.73-1.76 (1H, m), 1.80-1.86 (1H, m), 2.25-2.33 (1H, m), 2.45-2.55 (1H, m), 3.30 (1H, d, *J* = 11.1 Hz), 3.43 (1H, t, *J* = 9.8 Hz), 3.59 (1H, td, *J* = 10.6 , 3.9 Hz), 4.41 (1H, d, *J* = 10.9 Hz), 4.70 (1H, d, *J* = 10.9 Hz), 5.25 (1H, s), 7.26-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 20.0, 22.2, 26.6, 31.3, 34.2, 39.6, 47.0, 68.8, 70.2, 75.5, 80.5, 128.1, 128.3, 128.7, 137.4.

## 2.2. General procedure of epoxidation

To the solution of allylic alcohol derivatives **1**, **3**, **33**, **41**, **50a,b** (11.9 mmol) in $CH_2Cl_2$ (50 mL), $Na_2HPO_4 \cdot 12H_2O$ (35.7 mmol) in water (130 mL) and *m*-chloroperbenzoic acid (70% purity, 23.8 mmol) was added at 0 °C then the mixture was stirred at room temperature. When the reaction was complete (2 h), the mixture was separated and the aqueous phase was extracted with $CH_2Cl_2$ (100 mL). The organic layer was washed with 5% KOH solution (3 × 50 mL), dried ($Na_2SO_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel with an appropriate solvent mixture to afford epoxides.

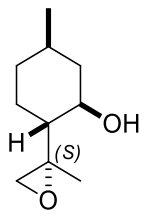
**(1*R*,2*R*,5*R*)-5-Methyl-2-((*R*)-2-methyloxiran-2-yl)cyclohexanol (23a)**




**23a**

Prepared from **1** and eluted by *n*-hexane: EtOAc = 4:1. Yield: 29%, white crystals, m.p.: 50−55 °C. $[\alpha]_D^{20}$ = +23.0 (c 0.22, MeOH). All spectroscopic data of compound **23a** was consistent with literature data.[3]

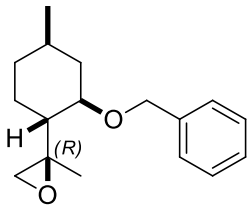
**(1*R*,2*R*,5*R*)-5-Methyl-2-((*S*)-2-methyloxiran-2-yl)cyclohexanol (23b)**




**23b**

Prepared from **1** and eluted by *n*-hexane: EtOAc = 4:1. Yield: 43%, colorless oil. $[\alpha]_D^{20}$ = -37.0 (c 0.26, MeOH). All spectroscopic data of compound **23b** was consistent with literature data.[3]

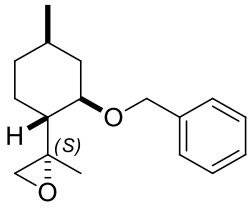
**(*R*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (34a)**




**34a**

Prepared from **33** and eluted by *n*-hexane: EtOAc = 9:1. Yield: 43%, colorless oil. $[\alpha]_D^{20}$ = -56.0 (c 0.16, MeOH). Found: C, 78.45; H, 9.27. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87-0.95 (2H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.08-1.14 (1H, m), 1.13 (3H, s), 1.21-1.33 (1H, m), 1.37-1.45 (1H, m), 1.67-1.71 (1H, m), 1.86-1.91 (1H, m), 2.19-2.24 (1H, m), 2.68 (1H, d, *J* = 5.0 Hz), 2.76 (1H, d, *J* = 5.0 Hz), 3.26 (1H, td, *J* = 10.6, 4.2 Hz), 4.40 (1H, d, *J* = 11.7 Hz), 4.67 (1H, d, *J* = 11.7 Hz), 7.25-7.35 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 16.7, 22.3, 26.4, 31.5, 33.9, 39.9, 50.8, 56.8, 57.9, 70.3, 78.8, 127.6, 128.4, 139.0.

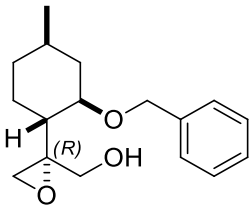
**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (34b)**




**34b**

Prepared from **33** and eluted by *n*-hexane: EtOAc = 9:1. Yield: 25%, colorless oil. $[\alpha]_D^{20}$ = -66.0 (c 0.19, MeOH). Found: C, 78.39; H, 9.31. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.85-0.99 (2H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.12-1.20 (1H, m), 1.25 (3H, s), 1.27-1.42 (2H, m), 1.65-1.75 (2H, m), 2.19-2.25 (1H, m), 2.50 (2H, t, *J* = 5.7 Hz), 3.29 (1H, td, *J* = 10.6, 4.1 Hz), 4.44 (1H, d, *J* = 11.7 Hz), 4.72 (1H, d, *J* = 11.7 Hz), 7.23-7.42 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 18.8, 22.2, 27.8, 31.3, 34.2, 39.6, 49.2, 52.0, 58.4, 69.7, 78.3, 127.4, 127.7, 128.3, 138.9.

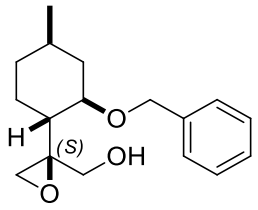
**((*R*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)oxiran-2-yl)methanol (42a)**




**42a**

Prepared from **41** and eluted by *n*-hexane: EtOAc = 2:1. Yield: 64%, colorless oil. $[\alpha]_D^{20}$ = -88.0 (c 0.32, MeOH). Found: C, 73.87; H, 8.80. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.82-0.96 (2H, m), 0.94 (3H, d, *J* = 6.6 Hz), 1.25-1.33 (1H, m), 1.36-1.48 (2H, m), 1.65-1.70 (1H, m), 1.83-1.88 (1H, m), 2.00 (1H, dd, *J* = 8.1, 4.3 Hz), 2.21-2.25 (1H, m), 2.78 (1H, d, *J* = 4.9 Hz), 2.94 (1H, d, *J* = 4.8 Hz), 3.33 (1H, td, *J* = 10.7, 4.2 Hz), 3.53 (1H, dd, *J* = 12.0, 8.1 Hz), 3.76 (1H, dd, *J* = 12.0, 4.2 Hz), 4.42 (1H, d, *J* = 11.4 Hz), 4.66 (1H, d, *J* = 11.4 Hz), 7.25-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 27.0, 31.3, 34.1, 40.1, 47.5, 52.3, 60.5, 61.2, 70.4, 78.2, 127.7, 127.8, 128.5, 138.6.

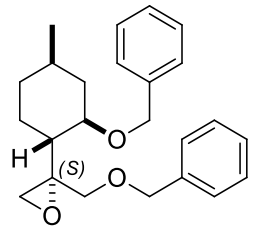
**((*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)oxiran-2-yl)methanol (42b)**




**42b**

Prepared from **41** and eluted by *n*-hexane: EtOAc = 2:1. Yield: 15%, colorless oil. $[\alpha]_D^{20}$ = -81.0 (c 0.23, MeOH). Found: C, 73.90; H, 8.70. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.86-1.03 (3H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.32-1.41 (1H, m), 1.64-1.69 (2H, m), 1.70-1.76 (1H, m), 2.20-2.24 (1H, m), 2.52 (1H, d, *J* = 4.6 Hz), 2.76 (1H, d, *J* = 4.6 Hz), 3.20 (1H, td, *J* = 10.4, 4.1 Hz), 3.66 (1H, dd, *J* = 11.9, 2.7 Hz), 3.74 (1H, dd, *J* = 11.9, 7.7 Hz), 7.25-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 26.3, 31.2, 34.0, 39.7, 44.6, 47.8, 61.1, 64.0, 70.0, 79.1, 127.8, 128.0, 128.5, 138.3.

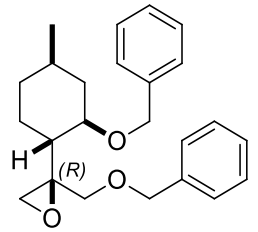
**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-2-((benzyloxy)methyl)oxirane (51a)**




**51a**

Prepared from **50b** and eluted by *n*-hexane: EtOAc = 9:1. Yield: 38%, colorless oil. $[\alpha]_D^{20}$ = -46.0 (c 0.27, MeOH). Found: C, 78.70; H, 8.23. Anal. Calcd for $C_{24}H_{30}O_3$: C, 78.65; H, 8.25. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.80-0.94 (2H, m), 0.93 (3H, d, *J* = 6.5 Hz), 1.28-1.45 (3H, m), 1.66 (1H, d, *J* = 12.8 Hz), 1.90-1.97 (1H, m), 2.19 (1H, d, *J* = 12.1 Hz), 2.76 (1H, d, *J* = 5.1 Hz), 2.92 (1H, d, *J* = 5.1 Hz), 3.41 (1H, td, *J* = 10.6, 4.1 Hz), 3.54 (1H, d, *J* = 11.2 Hz), 3.61 (1H, d, *J* = 11.2 Hz), 4.33 (1H, d, *J* = 11.5 Hz), 4.47 (2H, q, *J* = 12.0 Hz), 4.61 (1H, d, *J* = 11.5 Hz), 7.24-7.32 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 27.0, 31.4, 34.3, 40.3, 49.0, 52.9, 59.4, 70.3, 70.4, 73.4, 78.6, 127.5, 127.6, 127.7, 127.8, 128.4, 128.5, 138.2, 139.1.

**(*R*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-2-((benzyloxy)methyl)oxirane (51b)**

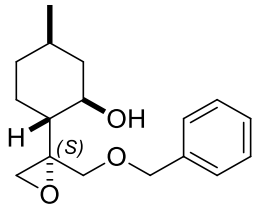



**51b**

Prepared from **50b** and eluted by *n*-hexane: EtOAc = 9:1. Yield: 28%, colorless oil. $[\alpha]_D^{20}$ = -60.0 (c 0.16, MeOH). Found: C, 78.62; H, 8.27. Anal. Calcd for $C_{24}H_{30}O_3$: C, 78.65; H, 8.25. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.85-0.97 (2H, m), 0.94 (3H, d, *J* = 6.6 Hz), 1.15 (1H, qt, *J* = 13.2, 3.5 Hz), 1.30-1.40 (1H, m), 1.64-1.79 (3H, m), 2.20 (1H, d, *J* = 11.8 Hz), 2.57 (1H, d, *J* = 4.8 Hz), 2.76 (1H, d, *J* = 4.8 Hz), 3.21 (1H, td, *J* = 10.6, 4.0 Hz), 3.62

(2H, q, *J* = 11.1 Hz), 4.34 (1H, d, *J* = 11.6 Hz), 4.44 (1H, d, *J* = 12.6 Hz), 4.52 (1H, d, *J* = 12.0 Hz), 4.67 (1H, d, *J* = 11.6 Hz), 7.25-7.32 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 26.8, 31.2, 34.2, 39.8, 44.6, 48.5, 60.0, 69.8, 72.1, 73.3, 78.8, 127.5, 127.6, 127.8, 128.4, 138.9.

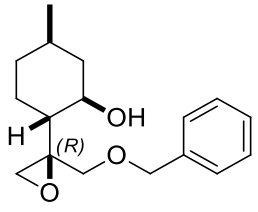
**(1*R*,2*R*,5*R*)-2-((*S*)-2-((Benzyloxy)methyl)oxiran-2-yl)-5-methylcyclohexanol (57a)**




**51a**

Prepared from **50a** and eluted by *n*-hexane: EtOAc = 2:1. Yield: 38%, colorless oil. $[\alpha]_D^{20}$ = -29.0 (c 0.26, MeOH). Found: C, 73.84; H, 8.78. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.85-1.03 (2H, m), 0.92 (3H, d, *J* = 6.5 Hz), 1.11 (1H, qt, *J* = 13.0, 3.5 Hz), 1.37-1.45 (1H, m), 2.63-2.73 (2H, m), 1.83-1.87 (1H, m), 1.95 (1H, d, *J* = 12.5 Hz), 2.80 (1H, d, *J* = 4.2 Hz), 2.91 (1H, d, *J* = 4.2 Hz), 3.37 (1H, td, *J* = 10.1, 3.3 Hz), 3.50 (2H, d, *J* = 10.9 Hz), 3.66 (1H, d, *J* = 11.2 Hz), 4.51 (1H, d, *J* =11.9 Hz), 4.61 (1H, d, *J* = 11.9 Hz), 7.25-7.37 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 27.6, 31.3, 33.9, 42.6, 45.4, 49.2, 61.6, 70.0, 71.8, 73.5, 127.9, 128.0, 128.6, 137.8.

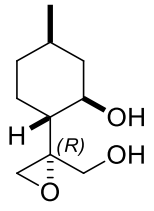
**(1*R*,2*R*,5*R*)-2-((*R*)-2-((Benzyloxy)methyl)oxiran-2-yl)-5-methylcyclohexanol (57b)**




**57b**

Prepared from **50a** and eluted by *n*-hexane: EtOAc = 2:1. Yield: 15%, colorless oil. $[\alpha]_D^{20}$ = -27.0 (c 0.20, MeOH). Found: C, 73.90; H, 8.73. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.84-0.97 (2H, m), 0.92 (3H, d, *J* = 6.6 Hz), 1.19-1.25 (2H, m), 1.40-1.44 (1H, m), 1.63-1.73 (2H, m), 1.97-2.01 (1H, m), 2.60 (1H, d, *J* = 4.8 Hz), 2.73 (1H, d, *J* = 4.8 Hz), 3.48 (1H, d, *J* = 10.8 Hz), 3.68 (1H, t, *J* = 6.9 Hz), 3.74 (1H, d, *J* = 10.8 Hz), 4.56 (2H, q, *J* = 11.9 Hz), 7.26-7.37 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 27.3, 31.2, 34.1, 43.7, 49.7, 49.8, 60.0, 71.6, 72.0, 73.8, 127.9, 128.0, 128.6, 137.6.

**(1*R*,2*R*,5*R*)-2-((*R*)-2-(Hydroxymethyl)oxiran-2-yl)-5-methylcyclohexanol (63a)**

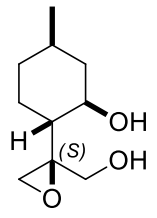



**63a**

Prepared from **3** and eluted by *n*-hexane: EtOAc = 1:4. Yield: 33%, white crystals, m.p.: 83–85 °C. $[\alpha]_D^{20}$ = -27.0 (c 0.24, MeOH). Found: C, 64.52; H, 9.76. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87-1.03 (2H, m), 0.93 (3H, d, *J* = 6.6 Hz), 1.06-1.15 (1H, m), 1.37-1.45 (1H, m), 1.64-1.76 (2H, m), 1.82-1.87 (1H, m), 1.92-1.97 (1H, m), 2.63 (1H, brs), 2.94 (2H, q, *J* = 4.1 Hz), 3.35 (1H, td, *J* = 10.4, 4.4 Hz), 3.60-

3.70 (2H, m), 3.84 (1H, d, *J* = 12.3 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 27.8, 31.1, 33.8, 42.6, 44.3, 48.6, 63.2, 63.3, 69.9.

**(1*R*,2*R*,5*R*)-2-((*S*)-2-(Hydroxymethyl)oxiran-2-yl)-5-methylcyclohexanol (63b)**



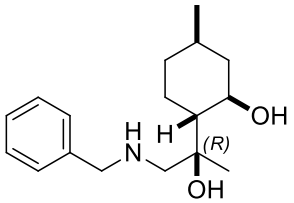

**63b**

Prepared from **3** and eluted by *n*-hexane: EtOAc = 1:4. Yield: 7%, white crystals, m.p.: 117–119 °C. $[\alpha]_D^{20}$ = -38.0 (c 0.16, MeOH). Found: C, 64.47; H, 9.70. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.83-0.99 (2H, m), 0.93 (3H, d, *J* = 6.6 Hz), 1.15-1.30 (2H, m), 1.41-1.49 (1H, m), 1.66-1.76 (2H, m), 1.97-2.02 (1H, m), 2.45 (1H, brs), 2.62 (1H, d, *J* = 4.6 Hz), 2.78 (1H, brs), 2.88 (1H, d, *J* = 4.6 Hz), 3.64-3.71 (2H, m), 3.93 (1H, d, *J* = 11.0 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 26.9, 31.2, 34.0, 44.1, 49.1, 49.3, 61.4, 62.1, 72.0.

### 2.3. General procedure for ring-opening of epoxides with primary amines

A solution of the appropriate epoxides (2.9 mmol) in MeCN (30 mL) was added to the appropriate amines (5.8 mmol) in MeCN (10 mL) and $LiClO_4$ (2.9 mmol). The mixture was kept at reflux temperature for 6−20 h. When the reaction was completed (indicated by TLC), the mixture was evaporated to dryness, the residue was redissolved in water (15 mL) and extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic phase was dried ($Na_2SO_4$), filtered and concentrated. The crude product was purified by column chromatography on silica gel with an appropriate solvent mixture, resulting in aminodiol and aminotriol derivatives, respectively.

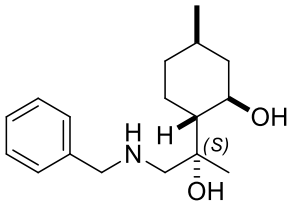
**(1*R*,2*R*,5*R*)-2-((*R*)-1-(Benzylamino)-2-hydroxypropan-2-yl)-5-methylcyclohexanol (24a)**




**24a**

Prepared from **23a** and benzylamine at reflux for 8 h and eluted by $CHCl_3$:MeOH = 19:1. Yield: 75%, colorless oil. $[\alpha]_D^{20}$ = -9.0 (c 0.27, MeOH). Found: C, 73.65; H, 9.78; N, 5.08. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.33-1.05 (3H, m), 0.91 (3H, d, *J* = 6.5 Hz), 1.17 (3H, s), 1.34-1.42 (1H, m), 1.49-1.55 (1H, m), 1.62-1.71 (2H, m), 1.92-1.97 (1H, m), 2.70 (1H, d, *J* = 12.0 Hz), 2.78 (1H, d, *J* = 12.0 Hz), 3.61 (1H, td, *J* = 10.5, 4.3 Hz), 3.81-3.87 (2H, m), 7.26-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 26.2, 26.4, 31.5, 34.8, 44.3, 52.7, 54.3, 54.5, 71.8, 75.2, 127.5, 128.3, 128.7, 139.4.

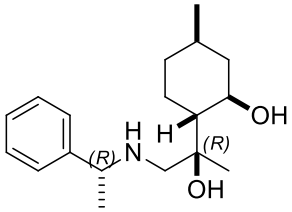
**(1*R*,2*R*,5*R*)-2-((*S*)-1-(Benzylamino)-2-hydroxypropan-2-yl)-5-methylcyclohexanol (24b)**



**24b**

Prepared from **23b** and benzylamine at reflux for 8 h and eluted by $CHCl_3$:MeOH = 19:1. Yield: 50%, colorless oil. $[\alpha]_D^{20}$ = -4.0 (c 0.25, MeOH). Found: C, 73.58; H, 9.83; N, 5.04. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.83-1.04 (3H, m), 0.91 (3H, d, *J* = 6.5 Hz), 1.16 (3H, s), 1.25-1.29 (1H, m), 1.40-1.46 (2H, m), 1.51-1.55 (1H, m), 1.60-1.63 (1H, m), 1.96-2.00 (1H, m), 2.49 (1H, d, *J* = 12.2 Hz), 2.73 (1H, d, *J* = 12.2 Hz), 3.74 (1H, td, *J* = 10.5, 4.3 Hz), 3.81-3.87 (2H, m), 7.26-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 20.9, 22.2, 26.4, 31.2, 34.5, 44.3, 49.8, 54.3, 57.1, 71.7, 75.3, 127.5, 128.3, 128.7, 139.5.

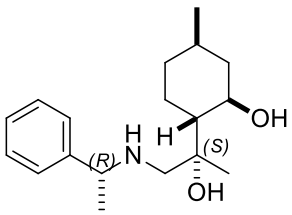
**(1*R*,2*R*,5*R*)-2-((*R*)-2-Hydroxy-1-(((*R*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (25a)**



**25a**

Prepared from **23a** and (*R*)-methylbenzylamine at reflux for 8 h and eluted by $CHCl_3$:MeOH = 19:1. Yield: 70%, colorless oil. $[\alpha]_D^{20}$ = +32.0 (c 0.28, MeOH). Found: C, 74.22; H, 10.05; N, 4.78. Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.80-1.03 (3H, m), 0.88 (3H, d, *J* = 6.5 Hz), 1.15 (3H, s), 1.24-1.32 (1H, m), 1.37-1.47 (1H, m), 1.41 (3H, d, *J* = 6.6 Hz), 1.58-1.64 (1H, m), 1.85-1.89 (1H, m), 2.55 (1H, d, *J* = 17.8 Hz), 2.56 (1H, d, *J* = 17.9 Hz), 3.42 (1H, td, *J* = 10.5, 4.3 Hz), 3.78 (1H, q, *J* = 6.6 Hz), 7.24-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 24.1, 26.1, 26.6, 31.4, 34.8, 44.2, 52.5, 52.9, 58.8, 71.6, 75.0, 126.8, 127.5, 128.7, 144.5.

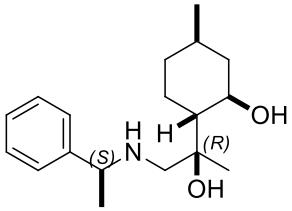
**(1*R*,2*R*,5*R*)-2-((*S*)-2-Hydroxy-1-(((*R*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (25b)**



**25b**

Prepared from **23b** and (*R*)-methylbenzylamine at reflux for 8 h and eluted by $CHCl_3$:MeOH = 19:1. Yield: 70%, colorless oil. $[\alpha]_D^{20}$ = +25.0 (c 0.22, MeOH). Found: C, 74.16; H, 10.07; N, 4.85. Anal. Calcd or $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.86-0.94 (2H, m), 0.91 (3H, d, *J* = 6.5 Hz), 0.97-1.05 (1H, m), 1.08 (3H, s), 1.37-1.40 (2H, m), 1.38 (3H, d, *J* = 6.6 Hz), 1.50-1.55 (1H, m), 1.60-1.63 (1H, m), 1.96-2.01 (1H, m), 2.31 (1H, d, *J* = 12.3 Hz), 2.61 (1H, d, *J* = 12.2 Hz), 3.69-3.76 (2H, m), 7.24-7.35 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 20.7, 22.2, 24.3, 26.3, 31.1, 34.6, 44.2, 50.1, 55.5, 58.6, 71.6, 75.1, 126.6, 127.3, 128.7, 145.1.

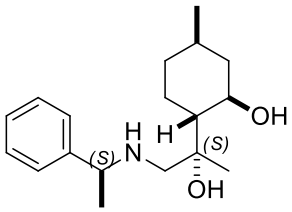
**(1*R*,2*R*,5*R*)-2-((*R*)-2-Hydroxy-1-(((S)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (26a)**




**26a**

Prepared from **23a** and (*S*)-methylbenzylamine at reflux for 8 h and eluted by $CHCl_3$:MeOH = 19:1. Yield: 70%, colorless oil. $[\alpha]_D^{20}$ = -41.0 (c 0.20, MeOH). Found: C, 74.17; H, 10.07; N, 4.83. Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.84-0.90 (2H, m), 0.89 (3H, d, *J* = 6.5 Hz), 0.97-1.05 (1H, m), 1.13 (3H, s), 1.23-1.30 (1H, m), 1.35-1.40 (1H, m), 1.40 (3H, d, *J* = 6.6Hz), 1.49-1.55 (1H, m), 1.59-1.64 (2H, m), 1.92-1.97 (1H, m), 2.47 (1H, d, *J* = 12.0 Hz), 2.63 (1H, d, *J* = 12.0 Hz), 3.63 (1H, td, *J* = 10.4, 4.3 Hz), 3.75 (1H, q, *J* = 6.6 Hz), 7.24-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ =22.1, 24.1, 26.1, 26.6, 31.4, 34.8, 44.4, 52.5, 52.6, 59.0, 71.9, 75.1, 126.4, 127.3, 128.8.

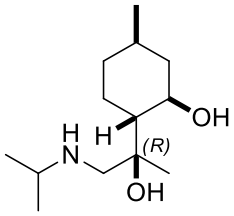
**(1*R*,2*R*,5*R*)-2-((*S*)-2-Hydroxy-1-(((*S*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (26b)**




**26b**

Prepared from **23b** and (*S*)-methylbenzylamine at reflux for 8 h and eluted by $CHCl_3$:MeOH = 19:1. Yield: 81%, colorless oil. $[\alpha]_D^{20}$ = -3.0 (c 0.21, MeOH). Found: C, 74.13; H, 10.05; N, 4.87. Anal. Calcd or $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81-0.91 (2H, m), 0.90 (3H, d, *J* = 6.5 Hz), 0.96-1.05 (1H, m), 1.13 (3H, s), 1.24-1.27 (1H, m), 1.35-1.45 (3H, m), 1.39 (3H, d, *J* = 6.6 Hz), 1.57-1.60 (1H, m), 1.95-1.99 (1H, m), 2.33 (1H, d, *J* = 12.2 Hz), 2.52 (1H, d, *J* = 12.2 Hz), 2.69-3.76 (2H, m), 7.26-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.0, 22.2, 24.4, 26.4, 31.2, 34.5, 44.4, 49.4, 55.7, 58.9, 71.8, 75.2, 126.5, 127.3, 128.7.

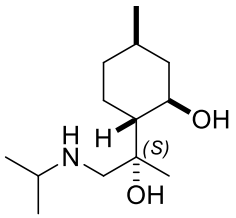
**(1*R*,2*R*,5*R*)-2-((*R*)-2-Hydroxy-1-(isopropylamino)propan-2-yl)-5-methylcyclohexanol (27a)**




**27a**

Prepared from **23a** and isopropylamine at reflux for 8 h and eluted by $CHCl_3$:MeOH = 19:1. Yield: 95%, white crystals, m.p.: 125-130 °C. $[\alpha]_D^{20}$ = -6.0 (c 0.26, MeOH). Found: C, 68.10; H, 11.82; N, 6.13. Anal. Calcd for $C_{13}H_{27}NO_2$: C, 68.08; H, 11.87; N, 6.11. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.75-0.83 (1H, m), 0.87 (3H, d, *J* = 6.5 Hz), 0.89-1.03 (2H, m), 1.12 (3H, s), 1.22 (6H, d, *J* = 6.5 Hz), 1.32-1.42 (2H, m), 1.60-1.67 (1H, m), 1.80-1.87 (1H, m), 3.00 (1H, d, *J* = 12.4 Hz), 3.09 (1H, d, *J* = 12.3 Hz), 3.26-3.32 (1H, m), 3.41 (1H, td, *J* = 10.4, 4.0 Hz), 5.32 (1H, s). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 18.2, 18.3, 21.4, 21.9, 24.7, 31.0, 32.5, 34.1, 45.2, 50.3, 51.2, 52.8, 70.4, 71.6.

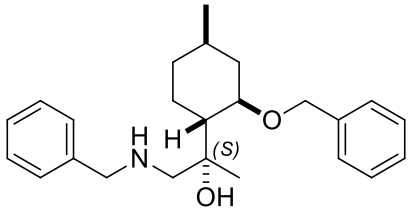
**(1*R*,2*R*,5*R*)-2-((*S*)-2-Hydroxy-1-(isopropylamino)propan-2-yl)-5-methylcyclohexanol (27b)**




**27b**

Prepared from **23b** and isopropylamine at reflux for 8 h and eluted by $CHCl_3$:MeOH = 19:1. Yield: 90%, colorless oil. $[\alpha]_D^{20}$ = -10.0 (c 0.26, MeOH). Found: C, 68.13; H, 11.90; N, 6.09. Anal. Calcd for $C_{13}H_{27}NO_2$: C, 68.08; H, 11.87; N, 6.11. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.92 (3H, d, *J* = 6.5 Hz), 1.00-1.06 (1H, m), 1.11-1.18 (1H, m), 1.33 (3H, s), 1.40-1.50 (1H, m), 1.44 (3H, d, *J* = 6.3 Hz), 1.45 (3H, d, *J* = 6.3 Hz), 1.58-1.64 (1H, m), 1.67-1.70 (2H, m), 1.95-2.00 (1H, m), 2.86-2.91 (1H, m), 3.12-3.18 (1H, m), 3.51-3.56 (1H, m), 3.82 (1H, td, *J* = 10.5, 4.3 Hz), 6.91 (1H, brs), 7.52 (1H, brs). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.1, 19.3, 21.9, 22.8, 26.4, 31.4, 33.6, 44.5, 48.6, 52.6, 53.0, 72.3, 73.0.

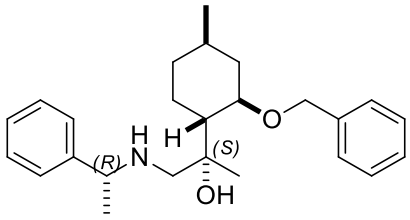
**(*S*)-1-(Benzylamino)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)propan-2-ol (35b)**




**35b**

Prepared from **34b** with benzylamine at reflux for 20 h and eluted by *n*-hexane:EtOAc = 1:1. Yield: 36%, white crystals, m.p.: 65−68 °C. $[\alpha]_D^{20}$ = -34.0 (c 0.26, MeOH). Found: C, 78.40; H, 9.07; N, 3.79. Anal. Calcd for $C_{24}H_{33}NO_2$: C, 78.43; H, 9.05; N, 3.81. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.79-0.87 (1H, m), 0.96 (3H, d, *J* = 6.5 Hz), 0.94-1.06 (2H, m), 1.06 (3H, s), 1.36-1.42 (1H, m), 1.621-1.72 (2H, m), 1.86 (1H, brs), 1.91-1.96 (1H, m), 2.25-2.28 (1H, m), 2.45 (1H, d, *J* = 17.9 Hz), 2.48 (1H, d, *J* = 17.9 Hz), 3.60 (1H, td, *J* = 10.6, 3.9 Hz), 4.41 (1H, d, *J* = 10.9 Hz), 4.70 (1H, d, *J* = 10.9 Hz), 5.11 (1H, brs), 7.19-7.35 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 26.8, 31.5, 34.5, 39.7, 48.1, 54.2, 57.8, 70.2, 75.2, 81.0, 126.8, 128.1, 128.2, 128.3, 128.7, 137.6, 141.0.

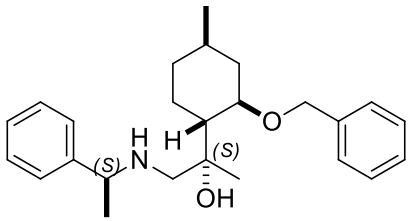
**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-1-(((R)-1-phenylethyl)amino)propan-2-ol (36b)**



**36b**

Prepared from **34b** and (*R*)-methylbenzylamine at reflux for 20 h and eluted by *n*-hexane:EtOAc = 1:1. Yield: 41%, colorless oil. $[\alpha]_D^{20}$ = -31.0 (c 0.26, MeOH). Found: C, 78.68; H, 9.23; N, 3.70. Anal. Calcd for $C_{25}H_{35}NO_2$: C, 78.70; H, 9.25; N, 3.67. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.80-0.85 (1H, m), 0.91-1.08 (2H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.08 (3H, s), 1.30 (3H, d, *J* = 6.5 Hz), 1.34-1.44 (1H, m), 1.68-1.74 (1H, m), 1.81-1.87 (1H, m), 2.22-2.30 (1H, m), 2.30 (1H, d, *J* = 11.2 Hz), 2.44 (1H, d, *J* = 11.2 Hz), 3.59 (1H, td, *J* = 10.6, 3.9 Hz), 3.67 (1H, q, *J* = 6.5 Hz), 4.40 (1H, d, *J* = 10.9 Hz), 4.70 (1H, d, *J* = 10.9 Hz), 7.17-7.34 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.8, 22.3, 24.6, 26.7, 31.5, 34.5, 39.6, 49.0, 56.5, 58.7, 70.2, 75.0, 81.0, 126.6, 126.7, 128.1, 128.3, 128.4, 128.7, 137.6.

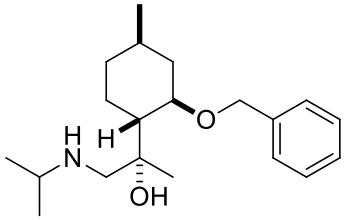
**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-1-(((S)-1-phenylethyl)amino)propan-2-ol (37b)**



**37b**

Prepared from **34b** and (*S*)-methylbenzylamine at reflux for 20 h and eluted by *n*-hexane:EtOAc = 1:1. Yield: 31%, colorless oil. $[\alpha]_D^{20}$ = -48.0 (c 0.26, MeOH). Found: C, 78.73; H, 9.27; N, 3.70. Anal. Calcd for $C_{25}H_{35}NO_2$: C, 78.70; H, 9.25; N, 3.67. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.63-0.72 (1H, m), 0.93-1.09 (2H, m), 0.96 (3H, d, *J* = 6.6 Hz), 0.98 (3H, s), 1.29 (3H, d, *J* = 6.6 Hz), 1.33-1.39 (1H, m), 1.47-1.52 (1H, m), 1.55-1.60 (1H, m), 1.72 (1H, brs), 2.00-2.06 (1H, m), 2.23-2.30 (2H, m), 2.33 (1H, d, *J* = 11.6 Hz), 3.57 (1H, td, *J* = 10.6, 3.9 Hz), 3.63 (1H, q, *J* = 6.5 Hz), 4.40 (1H, d, *J* = 109 Hz), 4.70 (1H, d, *J* = 10.9 Hz), 5.20 (1H, brs), 7.17-7.34 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 22.6, 25.4, 26.7, 31.6, 34.4, 39.8, 47.4, 56.8, 59.1, 70.3, 75.3, 81.0, 126.7, 127.0, 128.1, 128.2, 128.3, 128.7, 137.6, 146.8.

**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-1-(isopropylamino)propan-2-ol (38b)**

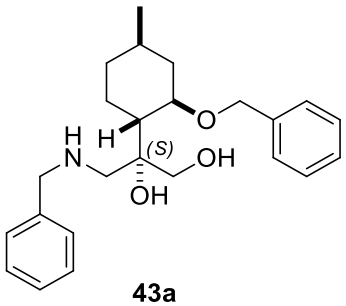


**38b**

Prepared from **34b** and isopropylamine at reflux for 20 h and eluted by *n*-hexane:EtOAc = 1:1. Yield: 45%, colorless oil. $[\alpha]_D^{20}$ = -37.0 (c 0.39, MeOH). Found: C, 75.15; H, 10.43; N, 4.37. Anal. Calcd for $C_{20}H_{33}NO_2$: C, 75.19; H, 10.41; N, 4.38. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.94-1.11 (4H, m), 0.97 (3H, d, *J* = 6.5 Hz), 1.21 (3H, s), 1.35-1.43 (1H, m), 1.38 (3H, d, *J* = 2.8 Hz), 1.39 (3H, d, *J* = 2.9 Hz), 1.65-1.72 (3H, m), 2.25-2.35 (1H, m), 2.99 (2H, s), 3.48 (1H, quin, *J* = 6.6 Hz), 3.63 (1H, td, *J* = 10.5, 3.9 Hz), 4.40 (1H, d, *J* = 10.9 Hz), 4.72 (1H, d, *J* = 10.9

Hz), 7.26-7.39 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.1, 19.2, 21.2, 22.0, 26.4, 31.1, 33.6, 39.1, 49.0, 52.9, 53.3, 70.3, 72.5, 80.2, 128.5, 128.6, 128.9, 136.8.

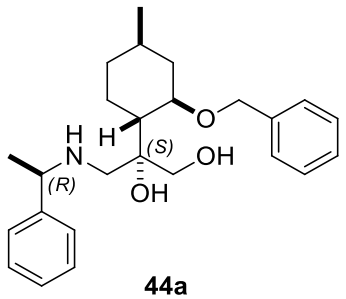
**((*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)oxiran-2-yl)methanol (43a)**



**43a**

Prepared from **42a** and benzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 46%, colorless oil. $[\alpha]_D^{20}$ = -48.0 (c 0.22, MeOH). Found: C, 75.13; H, 8.70; N, 3.66. Anal. Calcd for $C_{24}H_{33}NO_3$: C, 75.16; H, 8.67; N, 3.65. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.77-0.94 (3H, m), 0.90 (3H, d, *J* = 6.5 Hz), 1.30-1.40 (1H, m), 1.56-1.64 (3H, m), 2.15-2.25 (1H, m), 2.96 (1H, t, *J* = 10.9 Hz), 3.30 (1H, td, *J* = 10.4, 3.8 Hz), 3.38-3.44 (1H, m), 3.45-3.50 (1H, m), 3.78 (1H, d, *J* = 11.1 Hz), 4.15-4.17 (1H, m), 4.19-4.25 (1H, m), 4.49 (1H, d, *J* = 11.1 Hz), 7.20-7.42 (10H, m), 7.86 (1H, brs). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.0, 25.3, 30.9, 34.0, 39.6, 48.5, 52.1, 52.6, 68.9, 69.8, 73.5, 79.1, 128.3, 128.5, 128.8, 129.6, 129.9, 130.1, 130.3, 137.1.

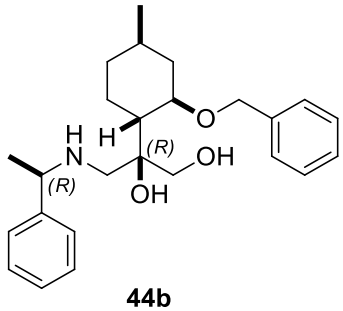
**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-3-(((*R*)-1-phenylethyl)amino)propane-1,2-diol (44a)**



**44a**

Prepared from **42a** and (*R*)-methylbenzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 54%, white crystals, m.p = 88−93 °C. $[\alpha]_D^{20}$ = -22.0 (c 0.22, MeOH). Found: C, 75.57; H, 8.83; N, 3.50. Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.53; H, 8.87; N, 3.52. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.77-0.96 (3H, m), 0.88 (3H, d, *J* = 6.5 Hz), 1.25-1.33 (1H, m), 1.57-1.70 (3H, m), 1.70 (3H, d, *J* = 6.8 Hz), 1.86 (1H, s), 2.10-2.15 (1H, m), 2.81 (1H, d, *J* = 11.7 Hz), 3.14 (1H, td, *J* = 10.5, 3.9 Hz), 3.50-3.60 (2H, m), 3.87 (1H, d, *J* = 10.9 Hz), 3.91 (1H, d, *J* = 11.1 Hz), 4.10 (1H, brs), 4.37 (2H, d, *J* = 10.9 Hz), 5.50 (1H, s), 7.17-7.41 (10H, m)7.85 (1H, brs). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.8, 21.9, 25.2, 30.9, 34.0, 39.7, 48.6, 52.6, 60.3, 68.4, 70.0, 73.3, 79.8, 127.8, 128.1, 128.3, 128.8, 129.8, 129.9, 135.4, 137.1.

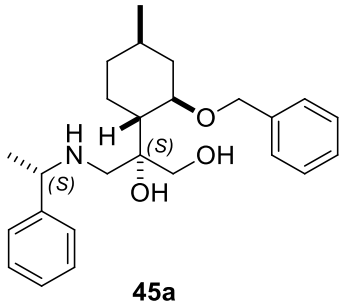
**(*R*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-3-(((*R*)-1-phenylethyl)amino)propane-1,2-diol (44b)**



**44b**

Prepared from **42b** and (*R*)-methylbenzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 14%, colorless oil. $[\alpha]_D^{20}$ = -35.0 (c 0.20, MeOH). Found: C, 75.50; H, 8.93; N, 3.56. Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.53; H, 8.87; N, 3.52. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81-0.97 (3H, m), 0.91 (3H, d, *J* = 6.6 Hz), 1.29-1.39 (1H, m), 1.38 (3H, d, *J* = 6.6 Hz), 1.56-1.65 (3H, m), 2.20-2.30 (1H, m), 2.63 (2H, dd, *J* = 1.5, 11.2 Hz), 3.46 (1H, td, *J* = 11.0, 4.4 Hz), 3.60 (1H, dd, *J* = 11.1, 1.4 Hz), 3.67-3.72 (2H, m), 7.23-7.36 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 26.0, 31.2, 34.5, 39.9, 50.1, 54.9, 59.4, 67.9, 70.1, 74.9, 80.3, 126.9, 127.5, 128.2, 128.7, 128.8.

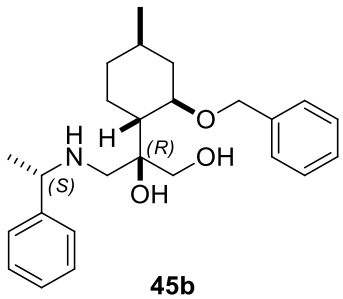
**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-3-(((*S*)-1-phenylethyl)amino)propane-1,2-diol (45a)**



**45a**

Prepared from **42a** and *(S)*-methylbenzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 54%, white crystals, m.p = 82−85 °C. $[\alpha]_D^{20}$ = -60.0 (c 0.22, MeOH). Found: C, 75.51; H, 8.82; N, 3.49. Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.53; H, 8.87; N, 3.52. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.71-0.94 (3H, m), 0.90 (3H, d, *J* = 6.6 Hz), 1.20-1.40 (2H, m), 1.57 (3H, d, *J* = 6.8 Hz), 1.56-1.65 (3H, m), 2.17-2.25 (1H, m), 3.02 (2H, dd, *J* = 17.8, 12.5 Hz), 3.34 (1H, td, *J* = 10.3, 3.8 Hz), 3.56 (1H, d, *J* = 11.5 Hz), 3.60 (1H, d, *J* = 11.3 Hz), 4.14 (1H, q, *J* = 6.7 Hz), 4.37 (1H, d, *J* = 11.2 Hz), 4.56 (1H, d, *J* = 11.3 Hz), 7.26-7.40 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 20.0, 22.0, 25.4, 30.9, 34.0, 39.7, 48.8, 52.4, 59.6, 68.6, 69.5, 73.7, 78.7, 127.5, 128.2, 128.5, 128.7, 129.6, 136.3, 137.5.

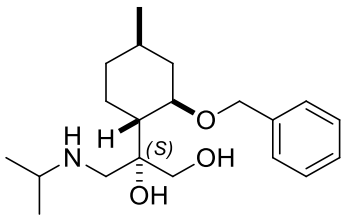
**(*R*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-3-(((*S*)-1-phenylethyl)amino)propane-1,2-diol (45b)**



**45b**

Prepared from **42b** and (*S*)-methylbenzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 14%, white crystals, m.p = 100−103 °C. $[\alpha]_D^{20}$ = -64.0 (c 0.12, MeOH). Found: C, 75.48; H, 8.84; N, 3.57. Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.53; H, 8.87; N, 3.52. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81-1.02 (3H, m), 0.93 (3H, d, *J* = 6.6 Hz), 1.25 (1H, s), 1.34-1.39 (1H, m), 1.42 (3H, d, *J* = 6.6 Hz), 1.52-1.55 (1H, m), 1.57-1.65 (1H, m), 1.67-1.75 (1H, m), 2.24-2.27 (1H, m), 2.42 (1H, d, *J* = 11.3 Hz), 2.89 (1H, d, *J* = 11.3 Hz), 3.57 (1H, td, *J* = 10.6, 4.0 Hz), 3.64 (2H, q, *J* = 11.3 Hz), 3.77 (1H, q, *J* = 6.6 Hz), 4.37 (1H, d, *J* = 10.8 Hz), 4.69 (1H, d, *J* = 10.8 Hz), 7.24-7.37 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 25.9, 31.2, 34.5, 39.9, 49.1, 53.7, 59.0, 70.3, 75.1, 80.4, 126.7, 127.7, 128.3, 128.8, 137.3.

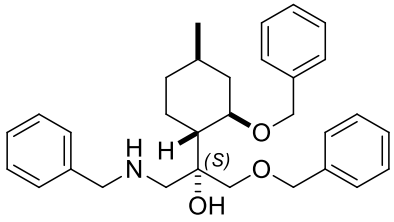
**(*S*)-2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-3-(isopropylamino)propane-1,2-diol (46a)**




**46a**

Prepared from **42a** and isopropylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 58%, colorless oil. $[\alpha]_D^{20}$ = -53.0 (c 0.29, MeOH). Found: C, 71.63; H, 9.89; N, 4.16. Anal. Calcd for $C_{20}H_{33}NO_3$: C, 71.60; H, 9.91; N, 4.18. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.84-1.01 (3H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.16 (3H, d, *J* = 9.4 Hz), 1.17 (3H, d, *J* = 9.4 Hz), 1.35-1.45 (1H, m), 1.65-1.73 (2H, m), 1.80-1.87 (1H, m), 2.31 (1H, d, *J* = 12.3 Hz), 2.95 (1H, t, *J* = 10.2 Hz), 3.15-3.25 (1H, m), 3.38-3.46 (2H, m), 3.67 (1H, dd, *J* = 10.2, 1.1 Hz), 3.88 (1H, d, *J* = 11.3 Hz), 4.42 (1H, d, *J* = 11.0 Hz), 4.70 (1H, d, *J* = 11.0 Hz), 6.92 (1H, brs), 7.26-7.36 (5H, m), 7.43 (1H, brs). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 18.8, 18.9, 20.0, 25.4, 31.1, 34.1, 39.7, 49.3, 51.9, 52.0, 67.9, 69.8, 73.6, 78.9, 128.3, 128.7, 128.9, 137.3.

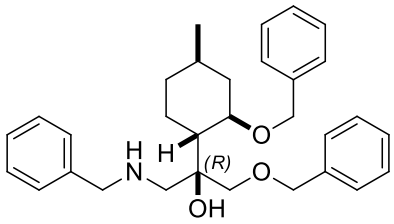
**(*S*)-1-(Benzylamino)-3-(benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)propan-2-ol (52a)**




**52a**

Prepared from **51a** and benzylamine at reflux for 6 h and eluted by *n*-hexane:EtOAc = 2:1. Yield: 32%, colorless oil. $[\alpha]_D^{20}$ = -66.0 (c 0.23, MeOH). Found: C, 78.57; H, 8.33; N, 2.93. Anal. Calcd for $C_{31}H_{39}NO_3$: C, 78.61; H, 8.30; N, 2.96. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.86-0.98 (2H, m), 0.93 (3H, d, *J* = 6.5 Hz), 1.17-1.25 (1H, m), 1.34-1.41 (1H, m), 1.60-1.65 (1H, m), 1.69-1.73 (1H, m), 2.18-2.22(1H, m), 2.64 (2H, s), 3.45 (2H, s), 3.65 (1H, td, *J* = 10.7, 3.9 Hz), 3.73 (1H, d, *J* = 13.5 Hz), 3.81 (1H, d, *J* = 13.5 Hz), 4.17 (1H, d, *J* = 10.8 Hz), 4.42 (1H, d, *J* = 12.0 Hz), 4.49 (1H, d, *J* = 12.0 Hz), 4.55 (1H, d, *J* = 10.8 Hz), 7.19-7.35 (15H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 26.4, 31.5, 34.8, 40.2, 48.3, 45.2, 70.1, 73.8, 74.3, 76.1, 81.1, 126.8, 127.7, 127.9, 128.1, 128.2, 128.3, 128.4, 128.6, 137.9, 138.6.

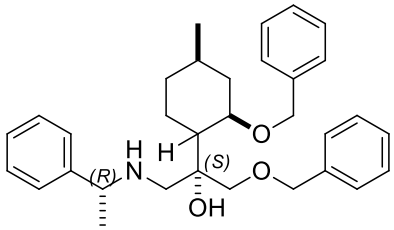
**(*R*)-1-(Benzylamino)-3-(benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)propan-2-ol (52b)**



**52b**

Prepared from **51b** and benzylamine at reflux for 6 h and eluted by *n*-hexane:EtOAc = 2:1. Yield: 32%, colorless oil. $[\alpha]_D^{20}$ = -30.0 (c 0.26, MeOH). Found: C, 78.63; H, 8.29; N, 2.94. Anal. Calcd for $C_{31}H_{39}NO_3$: C, 78.61; H, 8.30; N, 2.96. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.88-1.01 (3H, m), 0.93 (3H, d, *J* = 6.5 Hz), 1.35-1.45 (1H, m), 1.60-1.65 (1H, m), 1.75-1.80 (1H, m), 1.85-1.93 (1H, m), 2.20-2.27 (1H, m), 2.79 (1H, q, *J* = 11.6 Hz), 3.43 (1H, d, *J* = 9.5 Hz), 3.59 (1H, d, *J* = 9.5 Hz), 3.64 (1H, td, *J* = 10.6, 4.0 Hz), 3.77 (2H, q, *J* = 13.3 Hz), 4.26 (1H, d, *J* = 11.0 Hz), 4.26 (1H, d, *J* = 11.8 Hz), 4.60 (1H, t, *J* = 10.6 Hz), 7.20-7.33 (15H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 26.3, 31.4, 34.5, 40.0, 47.9, 53.5, 53.9, 70.0, 73.8, 75.4, 75.8, 80.0, 127.7, 127.8, 128.0, 128.3, 128.5, 128.6, 128.7, 137.7.

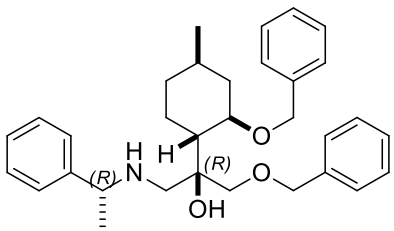
**(*S*)-1-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-3-(((*R*)-1-phenylethyl)amino)propan-2-ol (53a)**



**53a**

Prepared from **51a** and (*R*)-methylbenzylamine at reflux for 6 h and eluted by *n*-hexane:EtOAc = 2:1. Yield: 35%, colorless oil. $[\alpha]_D^{20}$ = -74.0 (c 0.21, MeOH). Found: C, 78.77; H, 8.52; N, 2.90. Anal. Calcd for $C_{32}H_{41}NO_3$: C, 78.81; H, 8.47; N, 2.87. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81-0.95 (3H, m), 0.92 (3H, d, *J* = 6.6 Hz), 1.16-1.36 (2H, m), 1.29 (3H, d, *J* = 6.5 Hz), 1.59 (1H, d, *J* = 13.2 Hz), 1.65-1.71 (1H, m), 1.75-1.80 (1H, m), 2.18 (1H, d, *J* = 11.7 Hz), 2.46-2.58 (2H, m), 3.49 (2H, t, *J* = 9.8 Hz), 3.60-3.70 (2H, m), 4.14 (1H, d, *J* = 10.7 Hz), 4.40 (1H, d, *J* = 11.8 Hz), 4.48 (1H, d, *J* = 11.8 Hz), 4.53 (1H, d, *J* = 10.7 Hz), 7.17-7.33 (15H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 24.6, 26.2, 31.4, 34.8, 40.1, 49.1, 52.9, 58.8, 70.1, 73.8, 74.1, 75.8, 81.1, 126.7, 127.6, 127.8, 128.1, 128.4, 128.6, 137.9, 138.6.

**(*R*)-1-(benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-3-(((*R*)-1-phenylethyl)amino)propan-2-ol (53b)**

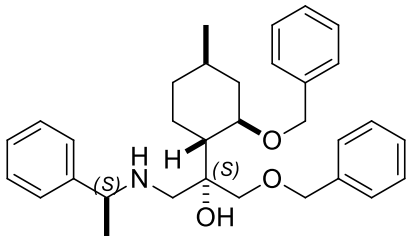


**53b**

Prepared from **51b** and (*R*)-methylbenzylamine at reflux for 6 h and eluted by *n*-hexane:EtOAc = 2:1. Yield: 35%, colorless oil. $[\alpha]_D^{20}$ = -58.0 (c 0.30, MeOH). Anal. Calcd for $C_{32}H_{41}NO_3$: C, 78.81; H, 8.47; N, 2.87. Found: C,

78.83; H, 8.43; N, 2.89. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81-0.98 (3H, m), 0.92 (3H, d, *J* = 6.6 Hz), 1.19-1.32 (3H, m), 1.31 (3H, d, *J* = 6.5 Hz), 1.56-1.67 (2H, m), 1.92-1.99 (1H, m), 2.19 (1H, d, *J* = 11.9 Hz), 2.47 (2H, s), 3.36 (1H, d, *J* = 10.1 Hz), 3.47 (1H, d, *J* = 10.1 Hz), 3.60 (1H, q, *J* = 6.5 Hz), 3.73 (1H, td, *J* = 10.6, 3.5 Hz), 4.21 (1H, d, *J* = 10.9 Hz), 4.43 (1H, d, *J* = 12.2 Hz), 4.57 (1H, d, *J* = 10.9 Hz), 4.65 (1H, d, *J* = 12.2 Hz), 7.18-7.33 (15H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 26.4, 31.5, 34.6, 40.1, 47.6, 51.8, 59.1, 70.0, 73.6, 74.9, 80.8, 126.8, 127.1, 127.6, 127.8, 127.9, 128.4, 128.5, 128.6, 138.0, 138.7.

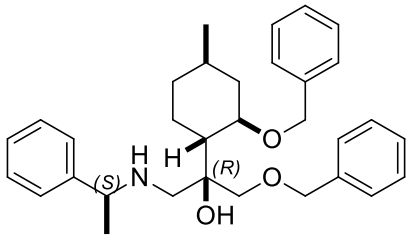
**(*S*)-1-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-3-(((*S*)-1-phenylethyl)amino)propan-2-ol (54a)**



**54a**

Prepared from **51a** and (*S*)-methylbenzylamine at reflux for 6 h and eluted by *n*-hexane:EtOAc = 2:1. Yield: 40%, colorless oil. Found: C, 78.84; H, 8.50; N, 2.83. Anal. Calcd for $C_{32}H_{41}NO_3$: C, 78.81; H, 8.47; N, 2.87. $[\alpha]_D^{20}$ = -75.0 (c 0.22, MeOH). $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.88-1.02 (3H, m), 1.25-1.59 (2H, m), 1.28 (3H, d, *J* = 6.5 Hz), 1.51 (1H, dd, *J* = 12.7, 2.9 Hz), 1.57 (1H, d, *J* = 12.5 Hz), 2.00 (1H, td, *J* = 11.4, 2.4 Hz), 2.19 (1H, d, *J* = 11.6 Hz), 2.37 (1H, d, *J* = 11.6 Hz), 2.47 (1H, d, *J* = 11.6 Hz), 3.35 (2H, q, *J* = 9.6 Hz), 3.61-3.69 (2H, m), 4.16 (1H, d, *J* = 10.7 Hz), 4.44 (2H, q, *J* = 12.0 Hz), 4.54 (1H, d, *J* = 10.7 Hz), 7.17-7.32 (15H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 25.2, 26.4, 31.5, 34.7, 40.3, 47.3, 52.8, 59.0, 70.2, 73.8, 74.5, 76.5, 81.3, 126.7, 126.9, 127.6, 127.9, 128.1, 128.2, 128.4, 128.6, 137.9, 138.5.

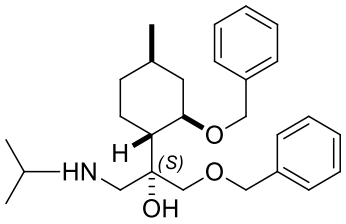
**(*R*)-1-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-3-(((*S*)-1-phenylethyl)amino)propan-2-ol (54b)**



**54b**

Prepared from **51b** and (*S*)-methylbenzylamine at reflux for 6 h and eluted by *n*-hexane:EtOAc = 2:1. Yield: 42%, colorless oil. Found: C, 78.79; H, 8.44; N, 2.90. Anal. Calcd for $C_{32}H_{41}NO_3$: C, 78.81; H, 8.47; N, 2.87. $[\alpha]_D^{20}$ = -81.0 (c 0.23, MeOH). $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.86-0.98 (4H, m), 0.91 (3H, d, *J* = 6.5 Hz), 1.23-1.33 (3H, m), 1.30 (3H, d, *J* = 6.6 Hz), 1.57-1.60 (1H, m), 1.67-1.75 (1H, m), 1.92 (1H, t, *J* = 10.6 Hz), 2.20 (1H, d, *J* = 11.9 Hz), 2.45 (1H, d, *J* = 11.5 Hz), 2.56 (1H, d, *J* = 11.2 Hz), 3.36 (1H, d, *J* = 10.1 Hz), 3.52-3.61 (3H, m), 4.26 (1H, d, *J* = 11.1 Hz), 4.46 (1H, d, *J* = 11.9 Hz), 4.60 (1H, d, *J* = 11.5 Hz), 7.20-7.34 (15H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 24.1, 26.3, 31.3, 34.5, 40.0, 48.0, 52.3, 59.1, 69.8, 73.7, 75.1, 75.9, 79.8, 126.8, 127.3, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, 128.6, 137.8, 138.5.

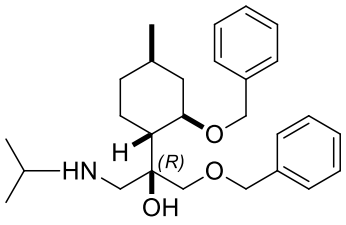
**(*S*)-1-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-3-(isopropylamino)propan-2-ol (55a)**




**55a**

Prepared from **51a** and isopropylamine at reflux for 6 h and eluted by *n*-hexane:EtOAc = 1:1. Yield: 25%, colorless oil. Found: C, 76.17; H, 9.27; N, 3.30. Anal. Calcd for $C_{27}H_{39}NO_3$: C, 76.20; H, 9.24; N, 3.29. $[\alpha]_D^{20}$ = -48.0 (c 0.21, MeOH). $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.91-1.01 (2H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.06-1.12 (1H, m), 1.17 (3H, d, *J* = 6.5 Hz), 1.23 (3H, d, *J* = 6.5 Hz), 1.35-1.41 (1H, m), 1.65-1.70 (3H, m), 2.23-2.30 (1H, m), 3.00-3.05 (1H, m), 3.36-3.47 (4H, m), 3.70 (1H, d, *J* = 9.6 Hz), 4.24 (1H, d, *J* = 11.0 Hz), 4.43 (1H, d, *J* = 11.3 Hz), 4.56 (1H, d, *J* = 11.3 Hz), 4.65 (1H, d, *J* = 11.0 Hz), 5.35 (1H, s), 6.80 (1H, brs), 7.12 (1H, brs), 7.23-7.39 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.1, 19.2, 22.0, 25.7, 31.0, 34.0, 39.5, 49.7, 52.1, 52.3, 70.1, 73.1, 74.2, 79.7, 128.5, 128.6, 128.7, 128.8, 128.9, 136.9, 137.1.

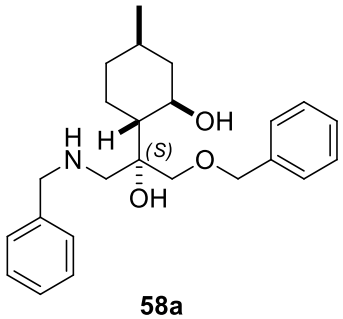
**(*R*)-1-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-3-(isopropylamino)propan-2-ol (55b)**




**55b**

Prepared from **51b** and isopropylamine at reflux for 6 h and eluted by *n*-hexane:EtOAc = 1:1. Yield: 29%, colorless oil. Found: C, 76.23; H, 9.27; N, 3.33. Anal. Calcd for $C_{27}H_{39}NO_3$: C, 76.20; H, 9.24; N, 3.29. $[\alpha]_D^{20}$ = -49.0 (c 0.20, MeOH). $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.86-1.07 (3H, m), 0.95 (3H, d, *J* = 6.5 Hz), 0.98 (3H, d, *J* = 6.5 Hz), 1.06 (3H, d, *J* = 6.5 Hz), 1.39-1.48 (1H, m), 1.68-1.76 (3H, m), 1.84-1.88 (1H, m), 2.30-2.33 (1H, m), 3.06-3.14 (1H, m), 3.20-3.25 (1H, m), 3.28-3.34 (1H, m), 3.54-3.62 (2H, m), 3.77 (1H, d, *J* = 9.5 Hz), 3.35 (1H, d, *J* = 10.6 Hz), 4.49 (1H, d, *J* =10.8 Hz), 4.55 (1H, d, *J* = 10.7 Hz), 6.91 (2H, brs), 7.26-7.38 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 18.8, 19.4, 22.0, 25.6, 31.1, 34.1, 39.8, 49.0, 51.9, 52.3, 70.2, 73.2, 74.5, 76.3, 79.4, 128.3, 128.6, 128.7, 128.8, 128.9, 136.8, 137.5.

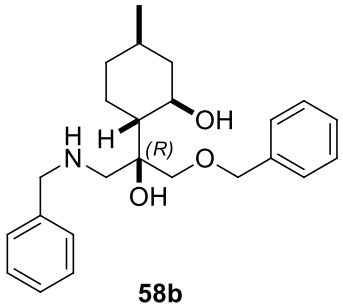
**(1*R*,2*R*,5*R*)-2-((*S*)-1-(Benzylamino)-3-(benzyloxy)-2-hydroxypropan-2-yl)-5-methylcyclohexanol (58a)**



**58a**

Prepared from **57a** and benzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 39%, colorless oil. $[\alpha]_D^{20}$ = -12.0 (c 0.20, MeOH). Found: C, 75.17; H, 8.63; N, 3.68. Anal. Calcd for $C_{24}H_{33}NO_3$: C, 75.16; H, 8.67; N, 3.65. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.79-0.87 (1H, m), 0.89 (3H, d, *J* = 6.5 Hz), 0.95-1.04 (2H, m), 1.33-1.41 (1H, m), 1.49-1.62 (3H, m), 1.96 (1H, d, *J* = 12.4 Hz), 2.69 (1H, d, *J* = 12.0 Hz), 3.00 (1H, d, *J* = 11.9 Hz), 3.60 (2H, q, *J* = 9.7 Hz), 3.67 (1H, td, *J* = 10.4, 4.3 Hz), 3.85 (2H, q, *J* = 13.3 Hz), 4.48 (1H, d, *J* = 11.8 Hz), 4.55 (1H, d, *J* = 11.8 Hz), 7.25-7.35 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 25.5, 31.1, 34.5, 44.5, 50.6, 53.8, 54.4, 71.5, 74.0, 74.3, 75.2, 127.7, 127.8, 128.0, 128.5, 128.6, 128.8, 137.9.

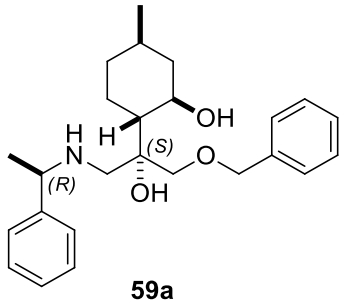
**(1*R*,2*R*,5*R*)-2-((*R*)-1-(Benzylamino)-3-(benzyloxy)-2-hydroxypropan-2-yl)-5-methylcyclohexanol (58b)**



**58b**

Prepared from **57b** and benzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 21%, colorless oil. $[\alpha]_D^{20}$ = -9.0 (c 0.26, MeOH). Found: C, 75.13; H, 8.70; N, 3.69. Anal. Calcd for $C_{24}H_{33}NO_3$: C, 75.16; H, 8.67; N, 3.65. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.78-0.92 (2H, m), 0.88 (3H, d, *J* = 6.5 Hz), 1.05 (1H, q, *J* = 12.2 Hz), 1.33-1.43 (1H, m), 1.59-1.66 (2H, m), 1.92 (1H, d, *J* = 12.4 Hz), 2.98 (1H, d, *J* = 12.1 Hz), 3.30 (1H, d, *J* = 12.1 Hz), 3.48 (1H, d, *J* = 9.5 Hz), 3.67 (1H, d, *J* = 9.5 Hz), 3.78 (1H, td, *J* = 10.4, 4.2 Hz), 3.94 (1H, d, *J* = 13.0 Hz), 4.16 (1H, d, *J* = 13.1 Hz), 4.48 (1H, d, *J* = 11.4 Hz), 4.55 (1H, d, *J* = 11.4 Hz), 7.19-7.33 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.9, 25.7, 31.2, 34.3, 44.7, 48.7, 51.8, 53.0, 71.4, 74.2, 74.9, 128.2, 128.3, 128.8, 128.9, 129.1, 129.2, 137.3.

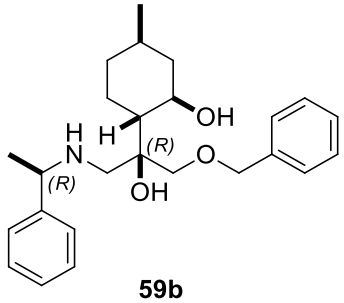
**(1*R*,2*R*,5*R*)-2-((*S*)-1-(Benzyloxy)-2-hydroxy-3-(((*R*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (59a)**



**59a**

Prepared from **57a** and (*R*)-methylbenzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 34%, colorless oil. $[\alpha]_D^{20}$ = +7.0 (c 0.15, MeOH). Found: C, 75.50; H, 8.89; N, 3.57. Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.53; H, 8.87; N, 3.52. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.75-1.00 (3H, m), 0.89 (3H, d, *J* = 6.5 Hz), 1.34 (3H, d, *J* = 6.6 Hz), 1.32-1.37 (1H, m), 1.41-1.46 (1H, m), 1.52-1.59 (2H, m), 1.94-1.98 (1H, m), 2.40 (1H, d, *J* = 11.9 Hz), 2.78 (1H, d, *J* = 11.9 Hz), 3.55 (2H, q, *J* = 9.6 Hz), 3.61-3.68 (2H, m), 4.45 (1H, d, *J* = 11.8 Hz), 4.54 (1H, d, *J* = 11.8 Hz), 7.17-7.34 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 24.1, 25.5, 31.1, 34.6, 44.5, 51.5, 53.5, 58.8, 71.5, 73.9, 74.2, 75.1, 126.4, 127.2, 127.7, 127.9, 128.6, 128.7, 138.1.

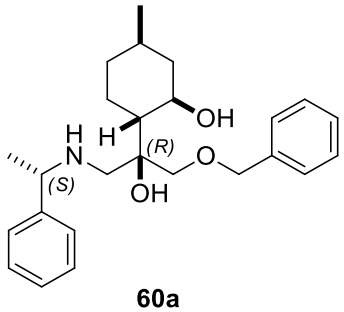
**(1*R*,2*R*,5*R*)-2-((*R*)-1-(Benzyloxy)-2-hydroxy-3-(((*R*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (59b)**



**59b**

Prepared from **57b** and (*R*)-methylbenzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 16%, colorless oil. $[\alpha]_D^{20}$ = +10.0 (c 0.24, MeOH). Found: C, 75.57; H, 8.90; N, 3.48. Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.53; H, 8.87; N, 3.52. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.79-0.83 (2H, m), 0.87 (3H, d, *J* = 6.5 Hz), 0.96 (1H, q, *J* = 12.3 Hz), 1.25-1.33 (1H, m), 1.35 (3H, d, *J* = 6.6 Hz), 1.55-1.63 (3H, m), 1.87-1.91 (1H, m), 2.64 (2H, q, *J* = 12.0 Hz), 3.39 (1H, d, *J* = 9.6 Hz), 3.44 (1H, td, *J* = 10.3, 4.3 Hz), 3.56 (1H, d, *J* = 9.6 Hz), 3.77 (1H, q, *J* = 6.6 Hz), 4.54 (2H, s), 7.24-7.37 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 25.6, 31.2, 34.5, 44.2, 49.7, 50.3, 58.5, 70.8, 73.8, 75.9, 126.8, 127.5, 127.8, 128.0, 128.6, 128.7.

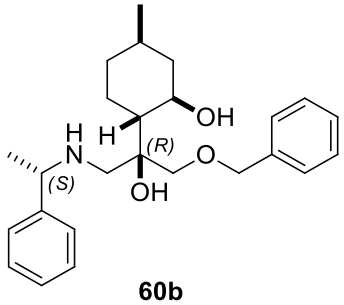
**(1*R*,2*R*,5*R*)-2-((*S*)-1-(Benzyloxy)-2-hydroxy-3-(((*S*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (60a)**



**60a**

Prepared from **57a** and (*S*)-methylbenzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 43%, colorless oil. $[\alpha]_D^{20}$ = -25.0 (c 0.20, MeOH). Found: C, 75.55; H, 8.83; N, 3.55. Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.53; H, 8.87; N, 3.52. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.75-0.99 (3H, m), 0.88 (3H, d, *J* = 6.5 Hz), 1.32 (3H, d, *J* = 6.5 Hz), 1.31-1.37 (1H, m), 1.45-1.58 (3H, m), 1.92-1.97 (1H, m), 2.36 (1H, d, *J* = 11.9 Hz), 2.83 (1H, d, *J* = 11.9 Hz), 3.53 (1H, d, *J* = 9.6 Hz), 3.59 (1H, d, *J* = 9.6 Hz), 3.66 (1H, td, *J* = 10.5, 4.3 Hz), 3.75 (1H, q, *J* = 5.2 Hz), 4.50 (1H, d, *J* = 11.8 Hz), 4.56 (1H, d, *J* = 11.8 Hz), 7.24-7.37 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 24.6, 25.5, 31.2, 34.6, 44.5, 50.1, 53.0, 58.5, 71.7, 73.9, 74.0, 75.7, 126.8, 127.2, 127.7, 127.9, 128.6, 128.6.

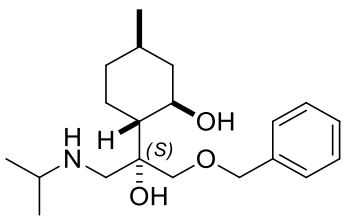
**(1*R*,2*R*,5*R*)-2-((*R*)-1-(Benzyloxy)-2-hydroxy-3-(((*S*)-1-phenylethyl)amino)propan-2-yl)-5-methylcyclohexanol (60b)**



**60b**

Prepared from **57b** and (*S*)-methylbenzylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 16%, colorless oil. $[\alpha]_D^{20}$ = -12.0 (c 0.20, MeOH). Found: C, 75.57; H, 8.91; N, 3.50. Anal. Calcd for $C_{25}H_{35}NO_3$: C, 75.53; H, 8.87; N, 3.52. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.79-0.82 (3H, m), 0.88 (3H, d, *J* = 6.7 Hz), 1.02 (1H, q, *J* = 12.2 Hz), 1.33-1.41 (2H, m), 1.39 (3H, d, *J* = 6.6 Hz), 1.51-1.58 (2H, m), 1.61-1.67 (1H, m), 1.93-1.98 (1H, m), 2.58 (1H, d, *J* = 12.0 Hz), 2.78 (1H, brs), 3.38 (1H, d, *J* = 9.6 Hz), 3.55 (1H, d, *J* = 9.6 Hz), 3.67 (1H, td, *J* = 10.3, 4.2 Hz), 3.75-3.80 (1H, m), 4.52 (2H, s), 7.16-7.36 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 25.6, 31.2, 34.5, 44.4, 48.7, 50.0, 59.1, 71.2, 73.9, 76.5, 126.6, 127.9, 128.1, 128.6, 128.9.

**(1*R*,2*R*,5*R*)-2-((*S*)-1-(Benzyloxy)-2-hydroxy-3-(isopropylamino)propan-2-yl)-5-methylcyclohexanol (61a)**

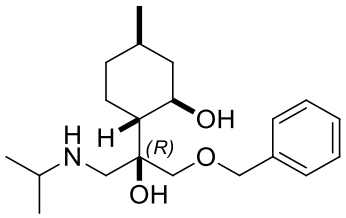


**61a**

Prepared from **57a** and isopropylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 50%, colorless oil. $[\alpha]_D^{20}$ = -12.0 (c 0.20, MeOH). Found: C, 71.65; H, 9.87; N, 4.17. Anal. Calcd for $C_{20}H_{33}NO_3$: C, 71.60; H, 9.91; N, 4.18. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.86-0.93 (1H, m), 0.89 (3H, d, *J* = 6.5 Hz), 1.02-1.10

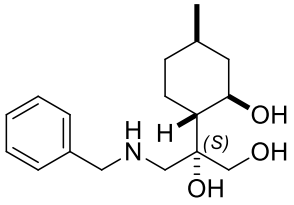
(2H, m), 1.19 (3H, d, *J* = 6.5 Hz), 1.24-1.31 (1H, m), 1.28 (3H, d, *J* = 6.5 Hz), 1.35-1.44 (1H, m), 1.59-1.65 (3H, m), 1.96 (1H, d, *J* = 12.1 Hz), 3.22 (2H, q, *J* = 12.2 Hz), 3.37 (1H, quin, *J* = 6.5 Hz), 3.71-3.80 (3H, m), 4.52 (1H, d, *J* = 11.1 Hz), 4.61 (1H, d, *J* = 11.1 Hz), 7.30-7.38 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.1, 19.3, 21.9, 25.5, 31.1, 34.0, 44.7, 49.6, 51.7, 51.8, 71.6, 73.5, 74.3, 75.0, 128.4, 128.5, 128.8, 137.2.

**(1*R*,2*R*,5*R*)-2-((*R*)-1-(Benzyloxy)-2-hydroxy-3-(isopropylamino)propan-2-yl)-5-methylcyclohexanol (61b)**




Prepared from **57b** and isopropylamine at reflux for 8 h and eluted by *n*-hexane:EtOAc = 1:2. Yield: 17%, colorless oil. $[\alpha]_D^{20}$ = -9.0 (c 0.20, MeOH). Found: C, 71.57; H, 9.93; N, 4.14. Anal. Calcd for $C_{20}H_{33}NO_3$: C, 71.60; H, 9.91; N, 4.18. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.82-0.97 (2H, m), 0.90 (3H, d, *J* = 6.5 Hz), 1.07-1.14 (1H, m), 1.14 (3H, d, *J* = 6.5 Hz), 1.25-1.29 (1H, m), 1.28 (3H, d, *J* = 6.5 Hz), 1.40-1.50 (1H, m), 1.64-1.74 (3H, m), 1.94 (1H, d, *J* = 12.1 Hz), 3.14 (1H, t, *J* = 10.0 Hz), 3.38 (1H, quin, *J* = 6.3 Hz), 3.50-3.57 (1H, m), 3.61 (1H, d, *J* = 9.5 Hz), 3.84 (1H, d, *J* = 9.5 Hz), 3.88 (1H, td, *J* = 10.5, 4.2 Hz), 4.52 (1H, d, *J* = 10.8 Hz), 4.63 (1H, d, *J* = 10.8 Hz), 6.98 (1H, brs), 7.32-7.39 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.1, 19.6, 21.8, 25.7, 31.2, 34.1, 45.1, 48.5, 50.0, 51.8, 71.6, 73.9, 74.5, 77.3, 128.6, 128.7, 128.9, 136.9.

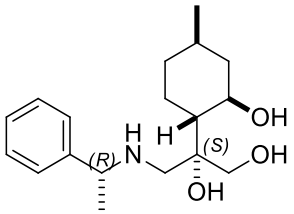
**(*S*)-3-(Benzylamino)-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)propane-1,2-diol (64a)**




**64a**

Prepared from **63a** and benzylamine at reflux for 6 h and eluted by $CHCl_3$:MeOH = 9:1. Yield: 67%, white crystals, m.p.: 159–163 °C. $[\alpha]_D^{20}$ = -11.0 (c 0.23, MeOH). Found: C, 69.55; H, 9.31; N, 4.80. Anal. Calcd for $C_{17}H_{27}NO_3$: C, 69.59; H, 9.28; N, 4.77. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.70-0.78 (1H, m), 0.85 (3H, d, *J* = 6.5 Hz), 0.88-0.95 (2H, m), 1.32-1.46 (2H, m), 1.59 (1H, d, *J* = 12.0 Hz), 1.81-1.85 (2H, m), 3.04 (1H, d, *J* = 12.7 Hz), 3.15 (1H, d, *J* = 12.7 Hz), 3.41-3.46 (2H, m), 3.56 (1H, d, *J* = 11.2 Hz), 4.15 (2H, q, *J* = 13.3 Hz), 5.50 (1H, brs), 7.41-7.53 (5H, m). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 21.9, 24.7, 30.8, 34.1, 45.2, 49.2, 50.9, 52.4, 64.7, 69.8, 73.5, 128.7, 128.9, 130.0, 131.8.

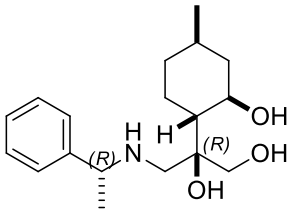
**(*S*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)-3-(((*R*)-1-phenylethyl)amino)propane-1,2-diol (65a)**



**65a**

Prepared from **63a** and (*R*)-methylbenzylamine at reflux for 6 h and eluted by $CHCl_3$:MeOH = 9:1. Yield: 67%, white crystals, m.p.: 172–175 °C. $[\alpha]_D^{20}$ = +16.0 (c 0.20, MeOH). Found: C, 70.30; H, 9.48; N, 4.55. Anal Calcd for $C_{18}H_{29}NO_3$: C, 70.32; H, 9.51; N, 4.56. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.72-0.83 (2H, m), 0.87 (3H, d, *J* = 6.5 Hz), 1.03 (1H, q, *J* = 11.9 Hz), 1.25-1.40 (1H, m), 1.45-1.65 (6H, m), 1.76 (3H, d, *J* = 6.8 Hz), 1.86 (1H, d, *J* = 12.3 Hz), 3.11 (1H, d, *J* = 12.5 Hz), 3.21 (1H, d, *J* = 12.5 Hz), 3.48 (1H, td, *J* = 10.1, 3.9 Hz), 3.52 (1H, d, *J* = 11.7 Hz), 3.77 (1H, d, *J* = 11.3 Hz), 4.46 (1H, q, *J* = 6.7 Hz), 7.41-7.47 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.4, 27.8, 25.3, 31.3, 34.0, 44.9, 49.0, 50.2, 59.8, 68.8, 71.9, 74.2, 127.8, 129.8, 129.9.

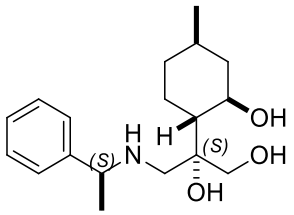
**(*R*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)-3-(((*R*)-1-phenylethyl)amino)propane-1,2-diol (65b)**



**65b**

Prepared from **63b** and (*R*)-methylbenzylamine at reflux for 6 h and eluted by $CHCl_3$:MeOH = 9:1. Yield: 87%, colorless oil. $[\alpha]_D^{20}$ = +10.0 (c 0.35, MeOH). Found: C, 70.33; H, 9.54; N, 4.55. Anal. Calcd for $C_{18}H_{29}NO_3$: C, 70.32; H, 9.51; N, 4.56. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.77-0.85 (1H, m), 0.87 (3H, d, *J* = 6.5 Hz), 0.99 (1H, q, *J* = 12.2 Hz), 1.32-1.58 (5H, m), 1.51 (3H, d, *J* = 6.6 Hz), 1.91-1.97 (1H, m), 2.77 (2H, t, *J* = 12.0 Hz), 3.56 (1H, d, *J* = 11.3 Hz), 3.68 (1H, td, *J* = 10.3, 4.3 Hz), 3.81 (1H, d, *J* = 11.3 Hz), 3.89 (1H, q, *J* = 6.6 Hz), 4.52 (3H, brs), 7.29-7.39 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.0, 23.2, 25.5, 31.1, 34.4, 44.7, 50.0, 54.2, 59.2, 66.4, 71.7, 75.4, 127.0, 128.1, 129.0, 142.0.

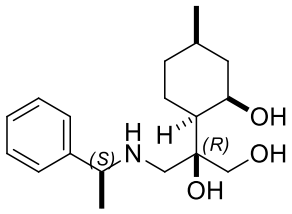
**(*S*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)-3-(((*S*)-1-phenylethyl)amino)propane-1,2-diol (66a)**



**66a**

Prepared from **63a** and (*S*)-methylbenzylamine at reflux for 6 h and eluted by $CHCl_3$:MeOH = 9:1. Yield: 62%, colorless oil. $[\alpha]_D^{20}$ = -21.0 (c 0.30, MeOH). Found: C, 70.27; H, 9.48; N, 4.52. Anal. Calcd for $C_{18}H_{29}NO_3$: C, 70.32; H, 9.51; N, 4.56. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.65-0.85 (2H, m), 0.87 (3H, d, *J* = 6.5 Hz), 1.05 (1H, q, *J* = 12.2 Hz), 1.34-1.41 (1H, m), 1.44-1.60 (3H, m), 1.69 (3H, d, *J* = 6.8 Hz), 1.85-1.95 (1H, m), 2.77 (1H, d, *J* = 12.3 Hz), 3.33 (1H, dd, *J* = 12.3, 1.2 Hz), 3.57 (1H, dd, *J* = 11.2, 1.4 Hz), 3.65 (1H, d, *J* = 11.3 Hz), 3.76 (1H, td, *J* = 10.5, 4.2 Hz), 4.26 (1H, q, *J* = 6.7 Hz), 7.36-7.45 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 21.9, 25.4, 31.1, 34.1, 44.8, 48.8, 51.1, 59.9, 69.7, 71.8, 74.6, 127.3, 129.3, 129.6, 138.0.

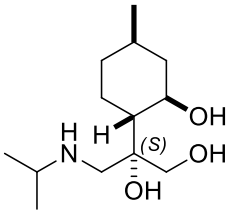
**(*R*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)-3-(((*S*)-1-phenylethyl)amino)propane-1,2-diol (66b)**




**66b**

Prepared from **63b** and (*S*)-methylbenzylamine at reflux for 6 h and eluted by $CHCl_3$:MeOH = 9:1. Yield: 93%, colorless oil. $[\alpha]_D^{20}$ = -5.2 (c 0.32, MeOH). Found: C, 70.27; H, 9.49; N, 4.58. Anal. Calcd for $C_{18}H_{29}NO_3$: C, 70.32; H, 9.51; N, 4.56. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.77-1.01 (9H, m), 0.88 (3H, d, *J* = 6.5 Hz), 1.30-1.50 (4H, m), 1.51 (3H, d, *J* = 6.7 Hz), 1.55-1.60 (1H, m), 1.90-1.96 (1H, m), 2.58 (1H, d, *J* = 11.9 Hz), 2.94 (1H, d, *J* = 12.1 Hz), 3.64 (1H, d, *J* = 11.4 Hz), 3.72 (1H, td, *J* = 10.5, 4.3 Hz), 3.82 (1H, d, *J* = 11.3 Hz), 3.93 (1H, q, *J* = 6.6 Hz), 7.29-7.39 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.0, 23.0, 25.4, 29.8, 31.1, 34.4, 44.7, 49.6, 53.5, 59.1, 65.9, 71.8, 75.5, 126.8, 128.1, 129.1.

**(*S*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)-3-(isopropylamino)propane-1,2-diol (67a)**



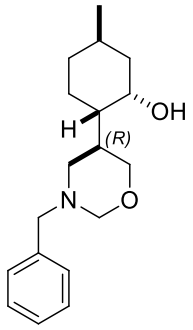

**67a**

Prepared from **63a** and isopropylamine at reflux for 6 h and eluted by $CHCl_3$:MeOH = 9:1. Yield: 77%, colorless oil. $[\alpha]_D^{20}$ = -7.0 (c 0.23, MeOH). Found: C, 63.60; H, 11.12; N, 5.68. Anal. Calcd for $C_{13}H_{27}NO_3$: C, 63.64; H, 11.09; N, 5.71. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.79-0.81 (1H, m), 0.86 (3H, d, *J* = 6.5 Hz), 0.89-1.05 (2H, m), 1.22 (6H, d, *J* = 6.5 Hz), 1.35-1.45 (1H, m), 1.46-1.52 (1H, m), 1.60 (1H, d, *J* = 12.3 Hz), 1.82-1.87 (2H, m), 3.09 (2H, q, *J* = 12.6 Hz), 3.44 (1H, d, *J* = 11.2 Hz), 3.56 (1H, d, *J* = 11.2 Hz), 3.58 (1H, td, *J* = 10.6, 4.1 Hz), 5.56 (1H, brs). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 18.2, 18.4, 21.9, 24.7, 30.7, 34.1, 45.2, 48.7, 49.3, 50.3, 64.7, 69.9, 73.6.

### 2.4. General procedure for ring closure of aminodiols with formaldehyde

A solution of aminodiols **9**–**12** or **20**–**23** (1.8 mmol) in $Et_2O$ (5 mL) was added to 35% aqueous formaldehyde solution (20 mL). After stirring at room temperature for 1 h, the mixture was made alkaline with 10% aqueous KOH (20 mL) and extracted with $Et_2O$ (3 × 50 mL). After drying ($Na_2SO_4$) and solvent evaporation, crude products **14**–**17** or **25**–**28** were purified by column chromatography ($CHCl_3$:MeOH = 19:1).

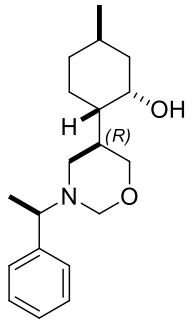
**(1*S*,2*S*,5*R*)-2-((*R*)-3-Benzyl-1,3-oxazinan-5-yl)-5-methylcyclohexanol (14)**




**14**

Yield: 74%, colorless oil. $[\alpha]_D^{20}$ = +3.0 (c 0.25, MeOH). Found: C, 74.68; H, 9.43; N, 4.80. Anal. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40; N, 4.84. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.84-1.00 (2H, m), 0.90 (3H, d, *J* = 6.5 Hz), 1.18-1.28 (1H, m), 1.32-1.41 (2H, m), 1.47-1.51 (1H, m), 1.62 (1H, d, *J* = 12.7 Hz), 2.00 (1H, d, *J* = 12.6 Hz), 2.01 (1H, brs), 2.92 (1H, d, *J* = 9.5 Hz), 3.17 (1H, dd, *J* = 11.9, 5.4 Hz), 3.51 (1H, td, *J* = 10.0, 6.4 Hz), 3.76 (1H, s), 3.87-4.00 (3H, m), 4.44 (1H, d, *J* = 8.2 Hz), 7.28-7.43 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 29.7, 31.2, 34.4, 44.3, 47.4, 55.2, 56.8, 68.7, 69.8, 83.8, 128.4, 128.9, 129.8, 133.7.

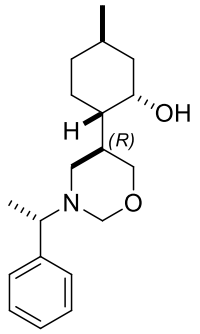
**(1*S*,2*S*,5*R*)-5-Methyl-2-((*R*)-3-((*R*)-1-phenylethyl)-1,3-oxazinan-5-yl)cyclohexanol (15)**




**15**

Yield: 64%, colorless oil. $[\alpha]_D^{20}$ = +8.0 (c 0.22, MeOH). Found: C, 75.23; H, 9.60; N, 4.65. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.89-1.01 (2H, m), 0.93 (3H, d, *J* = 6.5 Hz), 1.25-1.35 (1H, m), 1.37-1.50 (3H, m), 1.44 (3H, d, *J* = 6.7 Hz), 1.61-1.66 (1H, m), 1.70 (1H, s), 2.03-2.08 (1H, m), 2.60 (1H, dd, *J* = 11.6, 4.5 Hz), 3.19 (1H, d, *J* = 11.7 Hz), 3.43 (1H, q, *J* = 6.6 Hz), 3.48-3.53 (2H, m), 3.60 (1H, td, *J* = 10.6, 4.4 Hz), 4.00 (1H, d, *J* = 11.9 Hz), 4.36 (1H, dd, *J* = 8.0, 0.9 Hz), 7.23-7.33 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 20.2, 22.3, 31.0, 31.3, 34.7, 38.5, 44.1, 49.4, 54.6, 61.2, 67.7, 69.4, 83.9, 127.4, 127.7, 128.8, 141.9.

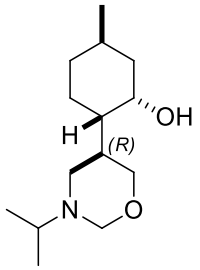
**(1*S*,2*S*,5*R*)-5-Methyl-2-((*R*)-3-((S)-1-phenylethyl)-1,3-oxazinan-5-yl)cyclohexanol (16)**




**16**

Yield: 64%, colorless oil. $[\alpha]_D^{20}$ = -18.0 (c 0.18, MeOH). Found: C, 75.19; H, 9.65; N, 4.64. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.83-0.97 (2H, m), 0.90 (3H, d, *J* = 6.5 Hz), 1.18-1.22 (2H, m), 1.36-1.43 (2H, m), 1.43 (3H, d, *J* = 6.7 Hz), 1.57-1.61 (1H, m), 1.71 (1H, s), 1.97-2.02 (1H, m), 2.44 (1H, dd, *J* = 12.0, 4.3 Hz), 2.76 (1H, dd, *J* = 12.0, 4.0 Hz), 3.46-3.51 (1H, m), 3.57 (1H, dd, *J* = 11.6, 3.6 Hz), 3.89-3.95 (2H, m), 4.62 (1H, d, *J* = 8.0 Hz), 7.25-7.35 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.3, 22.2, 30.5, 31.2, 34.6, 44.2, 48.4, 52.7, 60.3, 68.3, 69.5, 83.9, 127.6, 127.8, 128.6, 141.6.

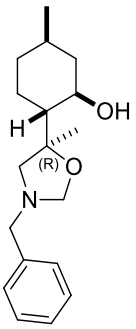
**(1*S*,2*S*,5*R*)-2-((*R*)-3-Isopropyl-1,3-oxazinan-5-yl)-5-methylcyclohexanol (17)**




**17**

Yield: 70%, colorless oil. $[\alpha]_D^{20}$ = -18.0 (c 0.10, MeOH). Anal. Calcd for $C_{14}H_{27}NO_2$: C, 69.66; H, 11.27; N, 5.80. Found: C, 69.70; H, 11.29; N, 5.77. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.88-0.98 (3H, m), 0.91 (3H, d, *J* = 6.5 Hz), 1.12 (3H, d, *J* = 10.1 Hz), 1.13 (3H, d, *J* = 10.1 Hz), 1.25-1.49 (6H, m), 1.61-1.65 (1H, m), 1.76 (1H, s), 1.98-2.04 (1H, m), 2.87-2.96 (3H, m), 3.56-3.63 (2H, m), 3.95-4.05 (2H, m), 4.54 (1H, d, *J* = 7.7 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 18.1, 18.5, 22.3, 30.8, 31.3, 34.7, 38.4, 44.0, 48.4, 51.8, 52.0, 68.0, 69.4, 82.3.

**(1*R*,2*R*,5*R*)-2-((*R*)-3-Benzyl-5-methyloxazolidin-5-yl)-5-methylcyclohexanol (29a)**

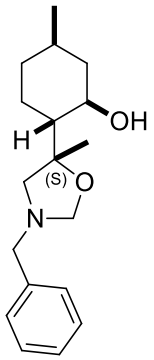



**29a**

Yield: 97%, colorless oil. $[\alpha]_D^{20}$ = -4.0 (c 0.24, MeOH). Found: C, 74.67; H, 9.43; N, 4.85. Anal. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40; N, 4.84. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81-093 (2H, m), 0.92 (3H, d, *J* = 6.5 Hz),

0.97-1.05 (1H, m), 1.33 (3H, s), 1.35-1.43 (1H, m), 1.57-1.64 (2H, m), 1.70-1.74 (1H, m), 1.95-2.00 (1H, m), 2.55 (1H, d, *J* = 9.9 Hz), 2.88 (1H, d, *J* = 9.9 Hz), 3.64-3.69 (1H, m), 3.71 (2H, d, *J* = 1.7 Hz), 4.28 (1H, d, *J* = 3.4 Hz), 4.34 (1H, d, *J* = 3.4 Hz), 7.24-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 25.8, 27.1, 31.2, 34.5, 43.8, 51.8, 57.3, 59.4, 71.1, 85.1, 86.9, 127.4, 128.5, 128.6, 138.6.

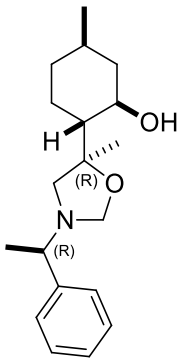
**(1*R*,2*R*,5*R*)-2-((*S*)-3-Benzyl-5-methyloxazolidin-5-yl)-5-methylcyclohexanol (29b)**




**29b**

Yield: 88%, colorless oil. $[\alpha]_D^{20}$ = +9.0 (c 0.24, MeOH). Found: C, 74.73; H, 9.39; N, 4.80. Anal. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40; N, 4.84. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.83-0.89 (1H, m), 0.92 (3H, d, *J* = 6.5 Hz), 0.95-1.05 (2H, m), 1.32 (3H, s), 1.42-1.49 (3H, m), 1.61-1.65 (1H, m), 1.98-2.03 (1H, m), 2.77 (2H, t, *J* = 10.2 Hz), 3.69-3.78 (3H, m), 4.30 (1H, d, *J* = 4.0 Hz), 4.40 (1H, d, *J* = 4.0 Hz), 7.25-7.33 (5H, m) . $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 22.2, 26.9, 31.2, 34.6, 43.7, 51.9, 57.8, 64.5, 71.3, 85.6, 85.7, 127.5, 128.6, 128.7.

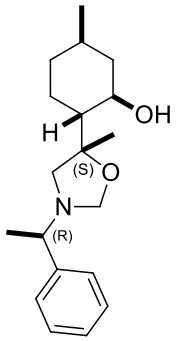
**(1*R*,2*R*,5*R*)-5-methyl-2-((*R*)-5-methyl-3-((*R*)-1-phenylethyl)oxazolidin-5-yl)cyclohexanol (30a)**




**30a**

Yield: 95%, colorless oil. $[\alpha]_D^{20}$ = +20.0 (c 0.25, MeOH). Found: C, 75.19; H, 9.67; N, 4.58. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81-0.87 (2H, m), 0.91 (3H, d, *J* = 6.5 Hz), 1.00 (1H, q, *J* = 12.3 Hz), 1.31 (3H, s), 1.34-1.41 (1H, m), 1.35 (3H, d, *J* = 6.5 Hz), 1.52-1.58 (1H, m), 1.60-1.63 (1H, m), 1.68-1.73 (1H, m), 1.95-1.99 (1H, m), 2.45 (1H, d, *J* = 9.4 Hz), 2.79 (1H, d, *J* = 9.4 Hz), 3.36 (1H, q, *J* = 6.4 Hz), 3.64 (1H, td, *J* = 10.3, 4.4 Hz), 4.15 (1H, d, *J* = 2.8 Hz), 4.30 (1H, d, *J* = 2.7 Hz), 7.22-7.35 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 23.6, 26.0, 27.2, 31.3, 34.6, 43.8, 52.0, 58.2, 62.8, 71.3, 84.3, 87.1, 127.0, 127.5, 128.7, 144.8.

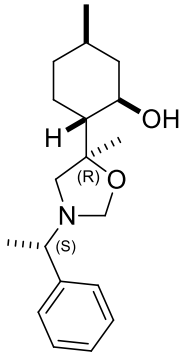
**(1*R*,2*R*,5*R*)-5-Methyl-2-((*S*)-5-methyl-3-((*R*)-1-phenylethyl)oxazolidin-5-yl)cyclohexanol (30b)**




**30b**

Yield: 96%, colorless oil. $[\alpha]_D^{20}$ = -23.0 (c 0.21, MeOH). Found: C, 75.24; H,9.59; N, 4.67. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.82-0.92 (2H, m), 0.91 (3H, d, *J* = 6.5 Hz), 0.95-1.05 (2H, m), 1.29 (3H, s), 1.35 (3H, d, *J* = 6.5 Hz), 1.39-1.50 (3H, m), 1.61-1.65 (1H, m), 1.97-2.02 (1H, m), 2.63 (1H, d, *J* = 9.5 Hz), 2.69 (1H, d, *J* = 9.5 Hz), 3.38-3.42 (1H, m), 3.71 (1H, td, *J* = 10.0, 4.4 Hz), 4.27 (2H, s), 7.24-7.32 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.4, 22.2, 23.4, 26.9, 31.2, 34.6, 43.8, 51.8, 62.4, 63.1, 71.2, 85.0, 86.2, 127.1, 127.5, 128.7, 144.5.

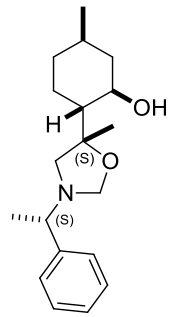
**(1*R*,2*R*,5*R*)-5-Methyl-2-((*R*)-5-methyl-3-((*S*)-1-phenylethyl)oxazolidin-5-yl)cyclohexanol (31a)**




**31a**

Yield: 88%, colorless oil. $[\alpha]_D^{20}$ = -52.0 (c 0.24, MeOH). Found: C, 75.25; H, 9.60; N, 4.67. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.77-0.91 (3H, m), 0.91 (3H, d, *J* = 6.5 Hz), 1.00 (1H, q, *J* = 12.3 Hz), 1.32 (3H, s), 1.35 (3H, d, *J* = 6.5 Hz), 1.37-1.44 (1H, m), 1.52-1.69 (7H, m), 1.95-2.00 (1H, m), 2.36 (1H, d, *J* = 9.4 Hz), 2.80 (1H, d, *J* = 9.3 Hz), 3.34 (1H, q, *J* = 6.4 Hz), 3.70 (1H, td, *J* = 10.2, 4.4 Hz), 4.16 (1H, d, *J* = 2.5 Hz), 4.36 (1H, d, *J* = 2.6 Hz), 7.23-7.35 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 23.6, 27.2, 31.2, 34.5, 43.7, 51.6, 58.1, 62.7, 71.1, 84.3, 87.3, 127.0, 127.4, 128.7.

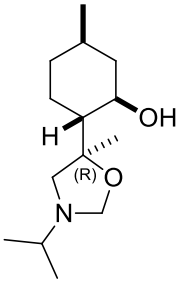
**(1*R*,2*R*,5*R*)-5-Methyl-2-((*S*)-5-methyl-3-((*S*)-1-phenylethyl)oxazolidin-5-yl)cyclohexanol (31b)**




**31b**

Yield: 87%, colorless oil. $[\alpha]_D^{20}$ = +18.0 (c 0.25, MeOH). Found: C, 75.23; H, 9.58; N, 4.65. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.80-0.94 (2H, m), 0.91 (3H, d, *J* = 6.5 Hz), 0.95-1.03 (2H, m), 1.29 (3H, s), 1.34 (3H, d, *J* = 6.5 Hz), 1.38-1.47 (3H, m), 1.58-1.63 (1H, m), 1.97-2.02 (1H, m), 2.56 (1H, d, *J* = 9.4 Hz), 2.71 (1H, d, *J* = 9.4 Hz), 3.36 (1H, q, *J* = 6.5 Hz), 3.69 (1H, td, *J* = 10.6, 4.3 Hz), 4.17 (1H, d, *J* = 2.8 Hz), 4.39 (1H, d, *J* = 2.8 Hz), 7.24-7.34 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.9, 22.2, 23.4, 26.8, 31.2, 34.6, 43.7, 52.1, 62.5, 63.5, 71.2, 85.1, 86.1, 127.0, 127.4, 128.7, 144.6.

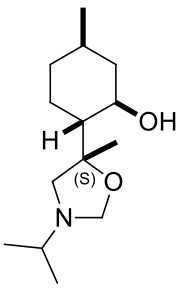
**(1*R*,2*R*,5*R*)-2-((*R*)-2-Hydroxy-1-(isopropylamino)propan-2-yl)-5-methylcyclohexanol (32a)**




**32a**

Yield: 95%, colorless oil. $[\alpha]_D^{20}$ = -7.0 (c 0.21 MeOH). Found: C, 69.69; H, 11.25; N, 5.83. Anal. Calcd for $C_{14}H_{27}NO_2$: C, 69.66; H, 11.27; N, 5.80. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87-0.92 (2H, m), 0.92 (3H, d, *J* = 6.5 Hz), 1.00 (1H, q, *J* = 12.3 Hz), 1.08 (3H, d, *J* = 2.5 Hz), 1.10 (3H, d, *J* = 2.4 Hz), 1.31 (3H, s), 1.37-1.45 (1H, m), 1.53-1.59 (1H, m), 1.74-1.78 (1H, m), 1.93-1.98 (1H, m), 2.47 (1H, q, *J* = 6.2 Hz), 2.51 (1H, d, *J* = 9.2 Hz), 2.88 (1H, d, *J* = 9.2 Hz), 3.65 (1H, td, *J* = 10.3, 4.6 Hz), 4.29 (1H, d, *J* = 2.5 Hz), 4.33 (1H, d, *J* = 2.5 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.8, 21.9, 22.2, 25.6, 27.2, 31.4, 34.6, 44.0, 52.0, 52.7, 52.8, 71.2, 83.9, 86.8.

**(1*R*,2*R*,5*R*)-2-(S)-2-Hydroxy-1-(isopropylamino)propan-2-yl)-5-methylcyclohexanol (32b)**



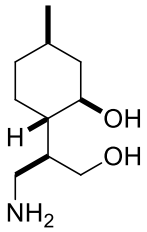

**32b**

Yield: 95%, colorless oil. $[\alpha]_D^{20}$ = +5.0 (c 0.24, MeOH). Found: C, 69.62; H, 11.22; N, 5.77. Anal. Calcd for $C_{14}H_{27}NO_2$: C C, 69.66; H, 11.27; N, 5.80. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.83-0.89 (1H, m), 0.95-1.06 (2H, m), 1.08 (6H, d, *J* = 6.3 Hz), 1.29 (3H, s), 1.38-1.46 (2H, m), 1.55-1.60 (1H, m), 1.63-1.67 (1H, m), 1.95-2.00 (1H, m), 2.45 (1H, quin, *J* = 6.3 Hz), 2.63 (1H, d, *J* = 9.1 Hz), 2.83 (1H, d, *J* = 9.1 Hz), 3.69 (1H, td, *J* = 10.6, 4.3 Hz), 4.34 (2H, s). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.8, 21.9, 22.1, 26.7, 31.1, 34.6, 43.7, 52.1, 52.4, 62.9, 71.0, 84.9, 85.8.

### 2.5. General procedure for debenzylation

A solution of isopulegol-based benzyl derivatives (14.0 mmol) in MeOH (100 mL) was added to a suspension of palladium-on-carbon (5% Pd, 0.22 g) in MeOH or *n*-hexane:EtOAc = 9 : 1 (50 mL) and the mixture was stirred under a $H_2$ atmosphere (1 atm) at room temperature. After completion of the reaction (as monitored by TLC, 24 h), the mixture was filtered through a Celite pad and the solution was evaporated to dryness. The crude products were recrystallized in diethyl ether, resulting in primary aminodiols and aminotriols, together with tri- and tetraols.

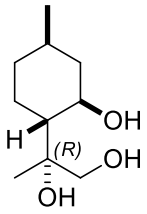
**(1*R*,2*S*,5*R*)-2-((*R*)-1-Amino-3-hydroxypropan-2-yl)-5-methylcyclohexanol (13)**




**13**

Prepared from **9–11**. Yield: 50% (with **9**), 67% (with **10**), 65% (with **11**), white crystals, m.p.: 124-125 °C. $[\alpha]_D^{20}$ = -13.0 (c 0.27, MeOH). Found: C, 64.15; H, 11.33; N, 7.47. Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.71-0.81 (1H, m), 0.79-0.86 (1H, m), 0.84 (3H, d, *J* = 6.5 Hz), 0.95-1.04 (1H, m), 1.24-1.30 (1H, m), 1.31-1.39 (1H, m), 1.51-1.55 (2H, m), 1.81 (1H, d, *J* = 12.0 Hz), 2.13 (1H, s), 2.74 (1H, dd, *J* = 12.1, 8.7 Hz), 2.89 (1H, dd, *J* = 12.6, 4.0 Hz), 3.23 (1H, td, *J* = 10.5, 4.1 Hz), 3.49-3.55 (2H, m), 6.70 (4H, brs). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 22.2, 26.3, 30.8, 34.3, 39.1, 44.7, 61.6, 68.8.

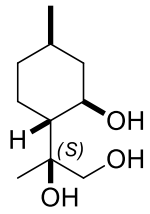
**(*R*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)propane-1,2-diol (22a)**




**22a**

Prepared from **39a**. Yield: 95%. All physical and spectroscopic properties was mentioned in dihydroxylation part.

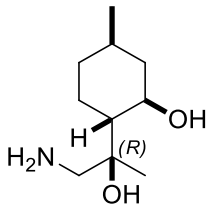
**(*S*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)propane-1,2-diol (22b)**




**22b**

Prepared from **39b**. Yield: 91%. All physical and spectroscopic properties was mentioned in dihydroxylation part.

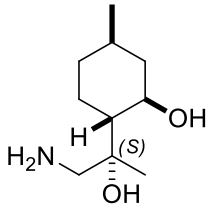
**(1*R*,2*R*,5*R*)-2-((*R*)-1-Amino-2-hydroxypropan-2-yl)-5-methylcyclohexanol (28a)**




**28a**

Prepared from **24–26a**. Yield: 87% (with **24a**), 95% (with **25a**), 90% (with **26a**), white crystals, m.p.: 100−110 °C. $[\alpha]_D^{20}$ = -17.0 (c 0.17, MeOH). Found: C, 64.10; H, 11.27; N, 7.53. Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.85-1.06 (3H, m), 0.91 (3H, d, *J* = 6.6 Hz), 1.14 (3H, s), 1.38-1.44 (1H, m), 1.52-1.57 (1H, m), 1.65-1.73 (2H, m), 1.93-1.96 (1H, m), 2.71 (1H, d, *J* = 12.5 Hz), 2.83 (1H, d, *J* = 12.5 Hz), 3.10 (3H, brs), 3.67 (1H, td, *J* = 10.4, 4.2 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 25.5, 26.3, 31.5, 34.8, 44.5, 46.1, 52.5, 71.9, 75.4.

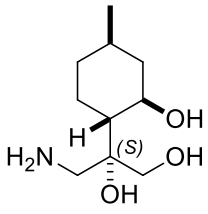
**(1*R*,2*R*,5*R*)-2-((*S*)-1-Amino-2-hydroxypropan-2-yl)-5-methylcyclohexanol (28b)**




**28b**

Prepared from **24–26b** or **35–38b**. Yield: 85% (with **24b**), 90% (with **25b**), 87% (with **26b**), 70% (with **35b**), 67% (with **36b**), 65% (with **37b**), white crystals, m.p.: 102−105 °C. $[\alpha]_D^{20}$ = -12.0 (c 0.21, MeOH). Found: C, 64.14; H, 11.33; N, 7.52. Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.86 (3H, d, *J* = 6.2 Hz), 0.85-0.98 (3H, m), 1.15 (3H, s), 1.30-1.50 (2H, m), 1.50-1.65 (1H, m), 1.80-1.90 (1H, m), 2.64 (1H, d, *J* = 12.8 Hz), 2.84 (1H, d, *J* = 12.8 Hz), 3.63 (1H, td, *J* = 9.2, 2.3 Hz), 5.82 (1H, brs), 5.98 (1H, s), 7.94 (1H, s). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 21.3, 22.0, 25.5, 30.6, 33.7, 44.7, 46.6, 48.0, 70.7, 72.6.

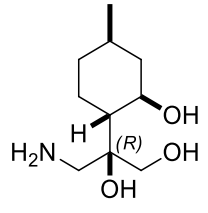
**(*S*)-3-Amino-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)propane-1,2-diol (47a)**




**47a**

Prepared from **43–45a**, **52–54a, 58–60a** or **64–66a**. Yield: 87% (with **43a**), 95% (with **44a**), 90% (with **45a**), 95% (with **52a**), 98% (with **53a**), 95% (with **54a**), 93% (with **58a**), 90% (with **59a**), 90% (with **60a**), 67% (with **64a**), 71% ( with **65a**), 75% (with **66a**), white crystals, m.p.: 210–212 °C. $[\alpha]_D^{20}$ = -9.0 (c 0.28, MeOH). Found: C, 59.07; H, 10.44; N, 6.93. Anal. Calcd for $C_{10}H_{21}NO_3$: C, 59.08; H, 10.41; N, 6.89. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.71-0.80 (1H, m), 0.86 (3H, d, *J* = 6.5 Hz), 0.90-1.00 (2H, m), 1.37-1.48 (2H, m), 1.59 (1H, d, *J* = 12.2 Hz), 1.80-1.87 (2H, m), 2.93 (1H, d, *J* = 12.8 Hz), 3.05 (1H, d, *J* = 12.5 Hz), 3.39 (1H, d, *J* = 11.3 Hz), 3.51 (1H, d, *J* = 11.3 Hz), 3.53 (1H, td, *J* = 10.4, 4.0 Hz), 5.43 (1H, brs), 7.45 (2H, brs). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 22.0, 24.7, 30.8, 34.2, 44.3, 45.3, 48.7, 64.5, 70.0, 73.5.

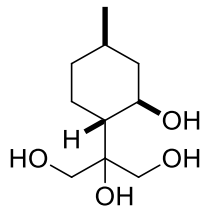
**(*R*)-3-Amino-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)propane-1,2-diol (47b)**




**47b**

Prepared from **52–54b** or **58–60b**. Yield: 95% (with **52b**), 95% (with **53b**), 98% (with **54b**), 90% (with **58b**), 93% (with **59b**), 93% (with **60b**), white crystals, m.p.: 263–265 °C. Found: C, 59.13; H, 10.38; N, 6.85. Anal. Calcd for $C_{10}H_{21}NO_3$: C, 59.08; H, 10.41; N, 6.89. $[\alpha]_D^{20}$ = -23.0 (c 0.21, MeOH). $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.75-0.94 (2H, m), 0.85 (3H, d, *J* = 6.5 Hz), 1.07-1.18 (1H, m), 1.30-1.42 (2H, m), 1.56 (1H, d, *J* = 12.5 Hz), 1.60-1.67 (1H, m), 1.82 (1H, d, *J* = 11.9 Hz), 2.88 (1H, q, *J* = 12.8 Hz), 3.44 (1H, d, *J* = 11.4 Hz), 3.55 (1H, d, *J* = 11.3 Hz), 3.63 (1H, td, *J* = 10.4, 4.1 Hz). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 22.0, 24.9, 30.6, 34.1, 43.8, 45.2, 47.9, 64.4, 70.2, 73.9.

**2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)propane-1,2,3-triol (49)**

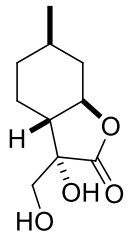



Prepared from **48**, **56a** or **62a**. Yield: 86% (with **48**), 83% (with **56a**), 97% (with **62a**), 95% (with **62b**) colorless oil. $[\alpha]_D^{20}$ = -11.0 (c 0.33, MeOH). Found: C, 58.77; H, 9.85. Anal. Calcd for $C_{10}H_{20}O_4$: C, 58.80; H, 9.87. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.84-0.91 (1H, m), 0.91 (3H, d, *J* = 6.5 Hz), 0.97-1.06 (2H, m), 1.39-1.47 (1H, m), 1.64-1.71 (3H, m), 1.94 (1H, d, *J* = 12.1 Hz), 3.53 (1H, d, *J* = 11.5 Hz), 3.60 (1H, d, *J* = 11.5 Hz), 3.70 (1H, d, *J* = 11.5 Hz), 3.77 (1H, d, *J* = 11.5 Hz), 3.83 (1H, td, *J* = 10.4, 4.1 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 25.7, 31.3, 34.4, 45.0, 47.6, 64.2, 65.9, 72.2, 77.6.

### 2.6. General procedure for dihydroxylation

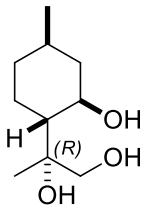
A solution of the appropriate allylic alcohol derivative (14.0 mmol) in acetone (60 mL) was added to an aqueous solution of NMO (12.0 mL, 50% aqueous solution) and $OsO_4$ in *t*-BuOH (6.0 mL, 2% *t*-BuOH solution) in one portion. The reaction mixture was stirred at room temperature for 24 h then quenched by the addition of a saturated aqueous solution of $Na_2SO_3$ (100 mL) and extracted with EtOAc (3 x 100 mL). The organic layer was dried and evaporated. The crude products were purified by chromatography on silica gel with an appropriate solvent mixture. The products after purification were recrystallized in diethyl ether resulting in di-, tri- and tetraols.

**(3*S*,3a*R*,6*R*,7a*R*)-3-Hydroxy-3-(hydroxymethyl)-6-methylhexahydrobenzofuran-2(3*H*)-one (18)**




Prepared from **4** and eluted with *n*-hexane:EtOAc = 1:2. Yield: 28%, white crystals, m.p.: 132-135 °C. $[\alpha]_D^{20}$ = +65.0 (c 0.265, MeOH). Found: C, 60.03; H, 8.07. Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.95 (3H, d, *J* = 6.6 Hz), 0.94-0.99 (1H, m), 1.05-1.14 (1H, m), 1.30-1.37 (1H, m), 1.50-1.60 (1H, m), 1.63-1.66 (1H, m), 1.72 (1H, d, *J* = 13.0 Hz), 1.80 (1H, td, *J* = 12.7, 2.6 Hz), 2.13 (1H, d, *J* = 11.1 Hz), 3.61 (1H, dd, *J* = 10.8, 6.1 Hz), 4.07 (1H, td, *J* = 11.4, 3.6 Hz), 4.84 (1H, t, *J* = 5.3 Hz), 5.63 (1H, s). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 20.8, 21.8, 30.6, 33.5, 38.3, 47.0, 60.7, 75.7, 79.3, 176.8.

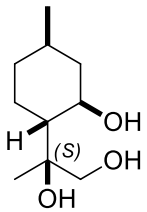
**(*R*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)propane-1,2-diol (22a)**




**22a**

Prepared from **1** and eluted with *n*-hexane:EtOAc = 1:2. Yield: 33%, colorless oil. $[\alpha]_D^{20}$ = -5.0 (c 0.26, MeOH). Found: C, 63.83; H, 10.67. Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.80; H, 10.71. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.73-0.94 (3H, m), 0.85 (3H, d, *J* = 6.5 Hz), 0.97 (3H, s), 1.31-1.39 (1H, m), 1.44-1.49 (1H, m), 1.54-1.64 (2H, m), 1.78-1.83 (1H, m), 3.16 (1H, dd, *J* = 11.2, 5.1 Hz), 3.26 (1H, dd, *J* = 11.2, 6.9 Hz), 3.54-3.59 (1H, m), 4.38 (1H, dd, *J* = 6.8, 5.0 Hz), 5.20 (1H, s), 5.49 (1H, d, *J* = 2.6 Hz). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 19.8, 22.1, 25.7, 30.7, 34.2, 44.7, 47.5, 68.1, 70.9, 75.7.

**(*S*)-2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)propane-1,2-diol (22b)**

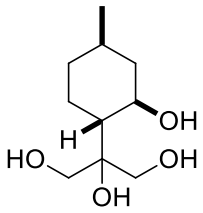



**22b**

Prepared from **1** and eluted with *n*-hexane:EtOAc = 1:2. Yield: 33%, white crystals, m.p.: 65–70 °C. $[\alpha]_D^{20}$ = -16.0 (c 0.26, MeOH). Found: C, 63.79; H, 10.73. Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.80; H, 10.71. $^1$H NMR (500 MHz,

DMSO-$d_6$): δ = 0.70-0.78 (1H, m), 0.82-0.89 (1H, m), 0.85 (3H, d, *J* = 6.5 Hz), 1.01 (3H, s), 1.03-1.12 (1H, m), 1.22-1.27 (1H, m), 1.31-1.38 (1H, m), 1.55-1.60 (1H, m), 1.69-1.74 (1H, m), 1.76-1.81 (1H, m), 3.34 (1H, dd, *J* = 10.3, 5.5 Hz), 3.41 (1H, dd, *J* = 10.8, 6.2 Hz), 3.50-3.58 (1H, m), 4.51 (1H, t, *J* = 5.6 Hz), 4.83 (1H, s), 5.30 (1H, d, *J* = 3.5 Hz). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 22.1, 23.2, 25.8, 30.9, 34.6, 45.2, 52.1, 67.6, 71.0, 74.8.

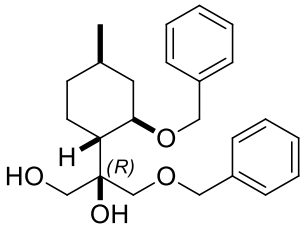
**2-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)propane-1,2,3-triol (48)**




**48**

Prepared from **41** and eluted with *n*-hexane:EtOAc = 1:4. Yield: 60%, white crystals, m.p.: 75−77 °C. $[\alpha]_D^{20}$ = -77.0 (c 0.28, MeOH). Found: C, 69.40; H, 8.87. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.88-1.09 (3H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.37-1.44 (1H, m), 1.66-1.78 (2H, m), 1.87-1.93 (1H, m), 2.10-2.50 (3H, m), 3.46 (2H, q, *J* = 10.1 Hz), 3.56 (2H, q, *J* = 11.3 Hz), 3.74 (1H, td, *J* = 10.6, 4.0 Hz), 4.40 (1H, d, *J* = 10.9 Hz), 4.71 (1H, d, *J* = 10.9 Hz), 5.52 (1H, s), 7.26-7.38 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 26.1, 31.3, 34.4, 40.0, 46.0, 64.1, 65.6, 70.2, 77.0, 80.4, 128.2, 128.3, 128.8, 137.4.

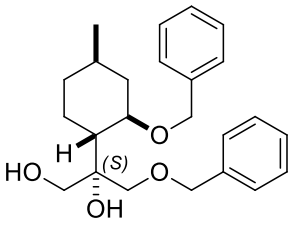
**(*R*)-3-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)propane-1,2-diol (56a)**




**56a**

Prepared from **50b** and eluted with *n*-hexane:EtOAc = 1:1. Yield: 50%, colorless oil. $[\alpha]_D^{20}$ = -43.0 (c 0.20, MeOH). Found: C, 74.93; H, 8.34. Anal. Calcd for $C_{24}H_{32}O_4$: C, 74.97; H, 8.39. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.85-0.98 (2H, m), 0.94 (3H, d, *J* = 6.5 Hz), 1.25-1.40 (2H, m), 1.64 (1H, d, *J* = 12.9 Hz), 1.71-1.80 (2H, m), 2.22 (1H, d, *J* = 11.2 Hz), 3.44 (2H, t, *J* = 10.2 Hz), 3.55 (2H, q, *J* = 11.1 Hz), 3.68 (1H, td, *J* = 10.6, 3.9 Hz), 4.20 (1H, d, *J* = *10.7* Hz), 4.43 (1H, d, *J* = 11.9 Hz), 4.52 (1H, d, *J* = 11.9 Hz), 4.58 (1H, d, *J* = 10.8 Hz), 5.23 (1H, brs), 7.24-7.36 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 26.2, 31.4, 34.7, 40.1, 47.5, 66.2, 70.2, 72.7, 73.9, 76.2, 80.8, 127.8, 128.1, 128.2, 128.5, 128.7, 137.7, 138.3.

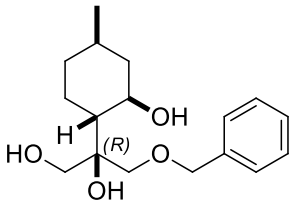
**(*S*)-3-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)propane-1,2-diol (56b)**




**56b**

Prepared from **50b** and eluted with *n*-hexane:EtOAc = 1:1. Yield: 15%, colorless oil. $[\alpha]_D^{20}$ = -30.0 (c 0.12, MeOH). Found: C, 74.98; H, 8.42. Anal. Calcd for $C_{24}H_{32}O_4$: C, 74.97; H, 8.39$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.88-1.04 (4H, m), 0.95 (3H, d, *J* = 6.5 Hz), 1.35-1.45 (1H, m), 1.64 (1H, d, *J* = 12.5 Hz), 1.78 (1H, dd, *J* = 13.0, 3.2 Hz), 1.96 (1H, td, *J* = 12.3, 3.0 Hz), 2.26 (1H, d, *J* = 11.5 Hz), 3.39 (1H, d, *J* = 10.0 Hz), 3.42-3.50 (2H, m), 3.56 (1H, d, *J* = 11.2 Hz), 3.65 (1H, td, *J* = 10.6, 3.8 Hz), 4.36 (1H, d, *J* = 11.0 Hz), 4.46 (1H, d, *J* = 12.2 Hz), 4.62 (1H, d, *J* = 12.2 Hz), 4.70 (1H, d, *J* = 11.0 Hz), 5.09 (1H, brs), 7.26-7.35 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2, 26.3, 31.4, 34.6, 40.1, 47.2, 65.3, 70.2, 73.7, 74.0, 80.3, 127.7, 127.9, 128.2, 128.5, 128.7.

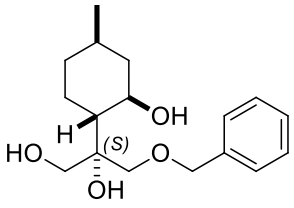
**(*R*)-3-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)propane-1,2-diol (62a)**




**62a**

Prepared from **50a** and eluted with *n*-hexane:EtOAc = 1:2. Yield: 59%, colorless oil. $[\alpha]_D^{20}$ = -11.0 (c 0.22, MeOH). Found: C, 69.40; H, 8.87. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.82-0.92 (1H, m), 0.90 (3H, d, *J* = 6.5 Hz), 0.97-1.08 (2H, m), 1.35-1.43 (1H, m), 1.60-1.68 (3H, m), 1.92-1.97 (1H, m), 3.10 (3H, brs), 3.52 (1H, d, *J* = 11.3 Hz), 3.60 (1H, d, *J* = 9.5 Hz), 3.65 (1H, d, *J* = 9.5 Hz), 3.72 (1H, d, *J* = 11.3 Hz), 3.74 (1H, td, *J* = 10.6, 4.3 Hz), 3.55 (2H, q, *J* = 11.8 Hz), 7.29-7.38 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 25.6, 31.2, 34.5, 44.7, 48.3, 66.9, 72.0, 72.8, 74.1, 76.7, 127.8, 128.1, 128.7, 137.7.

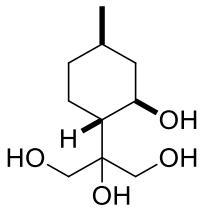
**(*S*)-3-(Benzyloxy)-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)propane-1,2-diol (62b)**




**62b**

Prepared from **50a** and eluted with *n*-hexane:EtOAc = 1:2. Yield: 29%, white crystal, m.p.: 81−85 °C. $[\alpha]_D^{20}$ = -6.0 (c 0.23, MeOH). Found: C, 69.33; H, 8.93. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81-1.04 (3H, m), 0.91 (3H, d, *J* = 6.5 Hz), 1.35-1.45 (1H, m), 1.58-1.73 (3H, m), 1.96 (1H, d, *J* = 12.3 Hz), 3.23 (3H, brs), 3.48 (1H, d, *J* = 9.6 Hz), 3.61 (1H, d, *J* = 11.6 Hz), 3.63 (1H, d, *J* = 8.6 Hz), 3.76 (1H, d, *J* = 11.2 Hz), 3.77 (1H, td, *J* = 10.2, 4.4 Hz), 4.52 (1H, d, 11.9 Hz), 4.61 (1H, d, *J* = 11.9 Hz), 7.26-7.37 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.1, 25.8, 31.2, 34.5, 44.7, 48.1, 64.5, 71.7, 73.9, 74.4, 127.9, 128.1, 128.7, 137.7.

**2-((1*R*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)propane-1,2,3-triol (49)**

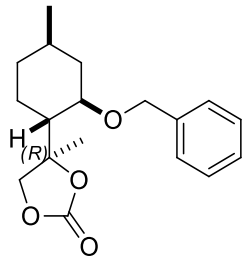



Prepared from **50a** and eluted with *n*-hexane:EtOAc = 1:9. Yield: 53%. All properties of compound **49** was mentioned above.

### 2.7. General procedures for carbonation with triphosgene

A solution of mixture **39a** and **39b** (2.0 mmol) in dry $CH_2Cl_2$ (20 mL) was added to the mixture of dry pyridine (8.2 mmol) and triphosgene (1.0 mmol) in dry $CH_2Cl_2$ (5 mL) under cooling in an ice bath. After stirring at room temperature for 2 h under Ar atmosphere, water (20 mL) was added to the solution, the phases were separated and the organic layer was washed with saturated aqueous $NH_4Cl$ solution (20 mL). The organic layer was collected, dried over anhydrous $Na_2SO_4$ and filtered. After evaporation the crude product was purified by column chromatography on silica gel (*n*-hexane:EtOAc = 9:1) to obtain **40a** and **40b**.

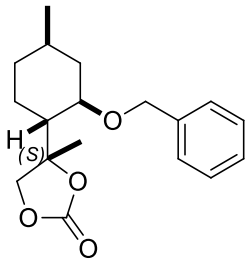
**(*R*)-4-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-4-methyl-1,3-dioxolan-2-one (40a)**




**40a**

Yield: 36 %, colorless oil. $[\alpha]_D^{20}$ = -207.0 (c 0.20, MeOH). Found: C, 71.07; H, 7.92. Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.90-0.98 (2H, m), 0.98 (3H, d, *J* = 6.6 Hz), 1.12-1.20 (1H, m), 1.25 (3H, s), 1.43-1.46 (1H, m), 1.72-1.77 (1H, m), 1.83-1.88 (1H, m), 2.00-2.05 (1H, m), 2.26-2.30 (1H, m), 3.21 (1H, td, *J* = 10.6, 3.9 Hz), 4.02 (1H, d, *J* = 9.4 Hz), 4.22 (1H, d, *J* = 11.2 Hz), 4.32 (1H, d, *J* = 9.4 Hz), 4.64 (1H, d, *J* = 11.1 Hz), 7.24-7.37 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 19.3, 22.1, 25.3, 31.4, 33.8, 39.3, 51.7, 70.2, 78.0, 78.9, 86.1, 128.1, 128.2, 128.7, 137.8, 154.8.

**(*S*)-4-((1*R*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)-4-methyl-1,3-dioxolan-2-one (40b)**




**40b**

Yield: 36 %, colorless oil. $[\alpha]_D^{20}$ = -56.0 (c 0.23, MeOH). . Found: C, 71.05; H, 7.98. Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87-1.01 (2H, m), 0.96 (3H, d, *J* = 6.5 Hz), 1.10-1.19 (1H, m), 4.40-4.46 (1H, m), 1.49 (3H, s), 1.70-1.75 (2H, m), 1.86-1.90 (1H, m), 2.28-2.32 (1H, m), 3.41 (1H, td, *J* = 10.6, 3.9 Hz), 3.88 (1H, d, *J* = 7.9 Hz), 4.34 (1H, d, *J* = 10.9 Hz), 4.58 (1H, d, *J* = 7.9 Hz), 4.61 (1H, d, *J* = 10.8 Hz), 7.25-7.36 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.0, 25.7, 26.1, 31.1, 34.1, 39.8, 48.9, 70.3, 74.2, 78.2, 85.0, 127.8, 128.3, 128.5, 138.0, 155.3.

### 2.8. General procedure for hydrolysis of epoxides in alkaline condition

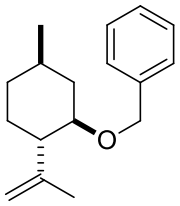
Compound **51a** or **57a** (0.60 mmol) was treated with DMSO (3.0 mL) and 3 M NaOH (3.0 mL). The resulting homogenous solution was stirred at 80 °C for 2 h (**57a**) or 24 h (**51a**). After being cooled to room temperature, EtOAc (20 mL) was added and the aqueous layer was washed with EtOAc (3 x 20 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated in vacuo. The crude material was purified by column

chromatography on silica gel (*n*-hexane:EtOAc = 2:1 or 1:2) to provide compound **56a** (33%) or **62a** (57%), respectively. All spectroscopic data of **56a** and **62a** was shown in dihydroxylation section.

### 2.9. General procedure for benzylation

A suspension of NaH (60% purity, 6.6 mmol) in dry THF (10 mL) was added to a solution of the appropriate alcohol (6.6 mmol) in dry THF (20 mL). The reaction mixture was stirred at 25 °C for 30 min before benzyl bromide (9.9 or 19.8 mmol) and KI (6.6 mmol) were added to the mixture. Stirring was continued for 12−48 h at 60 °C. When the reaction was complete, the mixture was poured into saturated $NH_4Cl$ solution (30 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phase was dried over anhydrous $Na_2SO_4$. The solvent was evaporated in vacuo and the crude product was purified by column chromatography on silica to provide **33** or **50a–b**, respectively.

**Benzyl-protected isopulegol (33)**

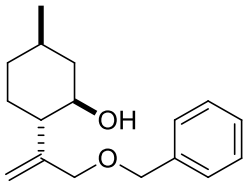



**33**

Prepared from **1** and benzyl bromide (9.9 mmol) at reflux for 12 h and eluted by *n*-hexane:EtOAc = 19:1. Yield: 70%, colorless oil. All physical properties and spectroscopic data of compound **33** was consistent with literature data. [4]

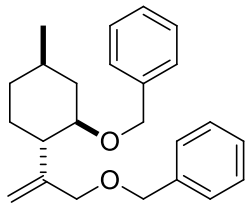
**(1*R*,2*S*,5*R*)-2-(3-(Benzyloxy)prop-1-en-2-yl)-5-methylcyclohexanol (50a) and (((2-((1*S*,2*R*,4*R*)-2-(Benzyloxy)-4-methylcyclohexyl)allyl)oxy)methyl)benzene (50b)**

Prepared from **3** and benzyl bromide (19.8 mmol) at reflux for 48 h and eluted by *n*-hexane:EtOAc = 19:1 to 9:1 to give **50a** (19%) and **50b** (40%)




**50a**

Compound **50a**: colorless oil. $[\alpha]_D^{20}$ = -7.0 (c 0.25, MeOH). Found: C, 78.39; H, 9.33. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87-1.02 (2H, m), 0.94 (3H, d, *J* = 6.6 Hz), 1.32 (1H, qt, *J* = 13.2, 3.5 Hz), 1.45-1.55 (1H, m), 1.63-1.71 (2H, m), 1.93-2.04 (2H, m), 2.45 (1H, brs), 3.53 (1H, td, *J* = 10.5, 4.1 Hz), 3.98 (2H, q, *J* = 11.5 Hz), 4.55 (2H, s), 5.12 (1H, s), 5.23 (1H, s), 7.25-7.37 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.3, 31.3, 31.6, 34.6, 43.1, 51.2, 72.6, 72.7, 72.8, 115.4, 127.8, 127.9, 128.6, 137.9, 147.6.



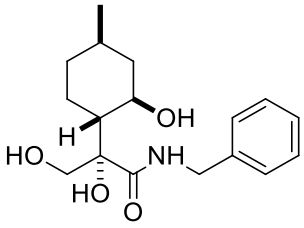
**50b**

Compound **50b**: colorless oil. $[\alpha]_D^{20}$ = -48.0 (c 0.35, MeOH). Found: C, 82.19; H, 8.67. Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.88-0.99 (2H, m), 0.94 (3H, d, *J* = 6.5 Hz), 1.34-1.47 (2H, m), 1.65 (1H, d, *J* = 12.6 Hz), 1.73-1.77 (1H, m), 2.02-2.09 (1H, m), 2.17 (1H, d, *J* = 11.6 Hz), 3.34 (1H, td, *J* = 10.6, 4.0 Hz), 3.98 (1H, d, *J* = 13.1 Hz), 4.07 (1H, d, *J* = 13.1 Hz), 4.37 (1H, d, *J* = 11.5 Hz), 4.48 (2H, q, *J* = 11.5 Hz), 4.59 (1H, d, *J* = 11.5 Hz), 5.01 (1H,.s), 5.17 (1H, d, *J* = 1.1 Hz), 7.23-7.32 (10H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.4, 31.6, 31.9, 40.6, 47.7, 70.8, 72.1, 73.4, 81.2, 111.0, 127.4, 127.5, 127.7, 127.8, 128.3, 128.4, 138.7, 139.1, 149.0.

### 2.10. General procedure for the preparation of *α,β*-dihydroxyamides

A solution of *α,β*-dihydroxylactone **18** (1.2 mmol) in dry THF (5 mL) was added to the appropriate amine (4.8 mmol) in dry THF (3 mL). The mixture was stirred at 60 °C for 24–72 h. When the reaction was completed (indicated by TLC), the mixture was evaporated to dryness. The crude product was purified by column chromatography on silica gel ($CHCl_3$:MeOH = 4:1) then recrystallized in $CH_2Cl_2$ resulting in compounds **19–21**.

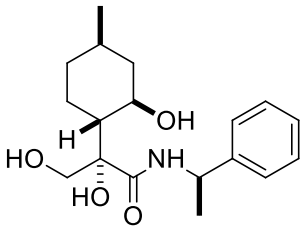
**(*S*)-*N*-Benzyl-2,3-dihydroxy-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)propanamide (19)**



**19**

Prepared with benzylamine at reflux for 24 h. Yield: 56%, white crystals, m.p.: 210-212 °C. $[\alpha]_D^{20}$ = -2.0 (c 0.285, MeOH). Found: C, 66.47; H, 8.18; N, 4.57. Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.68-0.75 (1H, m), 0.83 (3H, d, *J* = 6.4 Hz), 0.82-0.90 (1H, m), 0.94-1.02 (1H, m), 1.29 (1H, s), 1.50-1.60 (2H, m), 1.70-1.85 (2H, m), 3.52 (1H, dd, *J* = 10.8, 4.1 Hz), 3.60-3.69 (1H, m), 3.73 (1H, q, *J* = 7.6 Hz), 4.22-4.30 (2H, m), 4.50 (1H, dd, *J* = 6.5, 4.4 Hz), 4.84 (1H, d, *J* = 4.7 Hz), 4.45 (1H, s), 7.19-7.28 (5H, m), 8.01 (1H, t, *J* = 5.9 Hz). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 22.1, 25.0, 30.8, 34.1, 42.0, 45.2, 49.2, 65.5, 69.5, 79.1, 126.5, 127.1, 128.1, 139.8, 174.5.

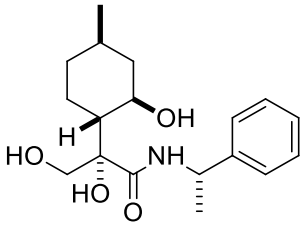
**(*S*)-2,3-Dihydroxy-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)-*N*-((*R*)-1-phenylethyl)propanamide (20)**



**20**

Prepared with (*R*)-methylbenzylamine at reflux for 72 h. Yield: 41%, white crystals, m.p.: 182-183 °C. $[\alpha]_D^{20}$ = +48.0 (c 0.285, MeOH). Found: C, 67.24; H, 8.53; N, 4.33. Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.26; H, 8.47; N, 4.36. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.74 (1H, q, *J* = 11.6 Hz), 0.84 (3H, d, *J* = 6.5 Hz), 0.83-0.90 (1H, m), 0.97-1.05 (1H, m), 1.30-1.37 (1H, m), 1.36 (3H, d, *J* = 6.9 Hz), 1.55-1.65 (2H, m), 1.75-1.85 (2H, m), 3.48 (1H, dd, *J* = 10.8, 4.0 Hz), 3.60-3.70 (2H, m), 4.60 (1H, q, *J* = 4.1 Hz), 4.73 (1H, d, *J* = 5.1 Hz), 4.91 (1H, quin, *J* = 7.4 Hz), 5.43 (1H, s), 7.19-7.36 (5H, m), 7.63 (1H, d, *J* = 8.3 Hz). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 22.1, 24.8, 30.8, 34.1, 45.2, 47.5, 49.0, 65.6, 69.3, 78.8, 126.1, 126.5, 128.1, 144.4, 173.7.

**(*S*)-2,3-Dihydroxy-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)-*N*-((*S*)-1-phenylethyl)propanamide (21)**




**21**

Prepared with (*S*)-methylbenzylamine at reflux for 72 h. Yield: 35%, white crystals, m.p.: 121-122 °C. $[\alpha]_D^{20}$ = -59.0 (c 0.255, MeOH). Found: C, 67.30; H, 8.48; N, 4.40. Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.26; H, 8.47; N, 4.36. $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 0.60-0.70 (1H, m), 0.81 (3H, d, *J* = 6.5 Hz), 0.80-0.90 (2H, m), 1.15-1.30 (1H, m), 1.37 (3H, d, *J* = 7.0 Hz), 1.46-1.55 (2H, m), 1.66 (1H, dd, *J* = 13.2, 2.6 Hz), 1.75 (1H, d, *J* = 11.7 Hz), 3.50 (1H, dd, *J* = 10.9, 4.3 Hz), 3.55-3.65 (1H, m), 3.73 (1H, dd, *J* = 10.9, 7.2 Hz), 4.50 (1H, t, *J* = 6.5 Hz), 4.85-4.95 (2H, m), 5.51 (1H, s), 7.18-7.34 (5H, m), 7.78 (1H, d, *J* = 8.0 Hz). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 22.1, 22.2, 25.0, 30.8, 34.1, 45.2, 47.7, 49.2, 65.2, 69.6, 79.0, 126.0, 126.5, 128.1, 144.7, 173.4.

### 2.11. General procedure for antioxidant activity (DPPH Radical Scavenging Activity)

The analysis of free radical scavenging activity was carried out by the modified assay of Osorio et al.[5] performed on a 96-well microplate using DPPH (2,2′-diphenyl-1-picrylhydrazyl) method. The compounds were dissolved in methanol and dissolutions (4–32 mg/mL) were prepared with the same solvent, while DPPH solution was also prepared in methanol in a concentration of 0.127 μmol/mL. For the reaction, 50 μL of each dissolution and 250 μL of DPPH solution were added into the wells of the 96-well plate. MeOH and gallic acid were used as blank and as positive control, respectively. The mixtures were left for 120 minutes in the dark at room temperature and the absorbances were measured at λ = 517 nm. The radical scavenging activity was calculated as follows: Inhibition% = [(blank absorbance − sample absorbance) / blank absorbance] × 100. The IC50 values (concentrations causing 50% inhibition) were calculated graphically.

### 2.12. General procedure for antimicrobial assays

For the antimicrobial analyses, the pure compounds were first dissolved in MeOH and diluted with $H_2O$ to both 400 µg/ml and 40 µg/ml keeping the final MeOH content at 10%. Then these solutions were investigated in microdilution assay with two Gram-positive bacteria including *Bacillus subtilis* SZMC 0209 and *Staphylococcus aureus* SZMC 14611, two Gram-negative bacteria *Escherichia coli* SZMC 6271 and *Pseudomonas aeruginosa* SZMC 23290, as well as two yeast strains *Candida albicans* SZMC 1533 and *C. krusei* SZMC 1352 according to the M07-A10 CLSI guideline [6] and our previous work.[7] Suspensions of the test microbes were prepared in ferment broth overnight at 37 ºC, where the cultured suspensions were set finally at the concentration of 2 x $10^5$ cells/mL with sterile media. The assays were composed by dispensing 100 µL of microbial suspension and 50 µL of sterile broth as well as 50 µL of the test solutions into the wells of 96-well plates and incubated during 24 h at 37 ºC. The mixture of 150 µL broth and 50 µL of 10% methanol was used as the blank sample for the background correction and the mixture of 100 µL of microbial suspension, 50µL sterile broth and 50 µL of 10% methanol was applied as negative control. The ampicillin or nystatin at two concentration levels (100 µg/mL and 10 µg/mL) was used as positive control for bacteria or yeasts, respectively. The assays were measured spectrophotometrically at 620 nm and the inhibitory effects was calculated as the percentage of the negative control after blank correction.

## 3. Reference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## 4. Complete results of antimicrobial activities

| | | Inhibitory effect (%) ± RSD (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Gram positive | | Gram negative | | Yeast | |
| **Analit** | **Conc. (µg/mL)** | ***B. subtilis* SZMC0209** | ***S. aureus* SZMC14611** | ***E. coli* SZMC6271** | ***P. aeruginosa* SZMC23290** | ***C. albicans* SZMC1533** | ***C. krusei* SZMC1352** |
| Ampicillin | 100 | 92.82 ± 3.28 | 86.27 ± 1.30 | 98.20 ± 5.95 | 28.75 ± 0.87 | - | - |

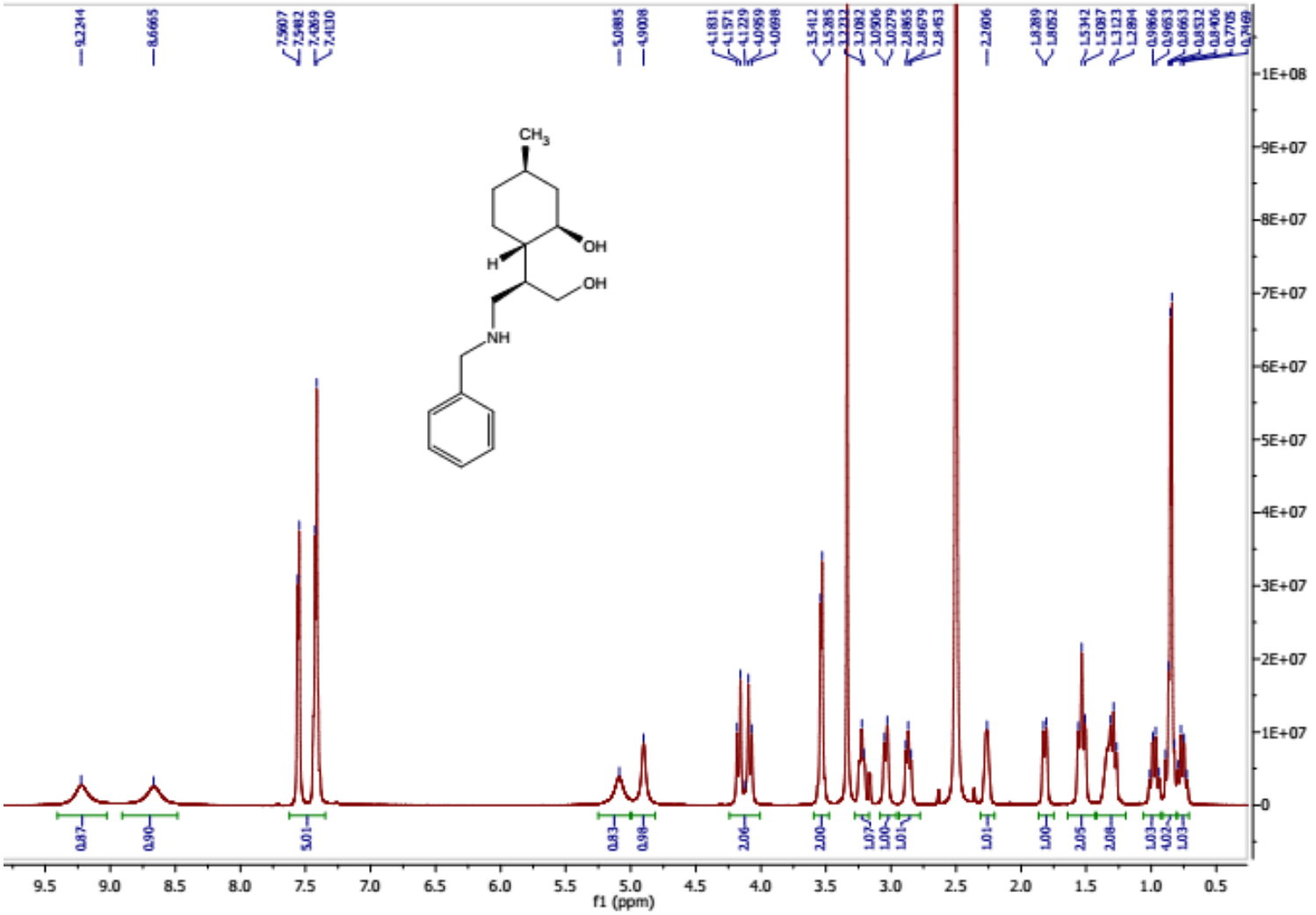
| Inhibitory effect (%) ± RSD (%) | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Gram positive | | Gram negative | | Yeast | |
| **Analit** | **Conc. (μg/mL)** | ***B. subtilis* SZMC0209** | ***S. aureus* SZMC14611** | ***E. coli* SZMC6271** | ***P. aeruginosa* SZMC23290** | ***C. albicans* SZMC1533** | ***C. krusei* SZMC1352** |
| | 10 | 88.54 ± 2.06 | 76.83 ± 1.54 | 89.43 ± 3.27 | - | - | - |
| Nystatin | 100 | - | - | - | - | 92.87 ± 3.43 | 93.86 ± 1.25 |
| | 10 | - | - | - | - | 91.93 ± 2.94 | 90.25 ± 3.50 |
| **4** | 100 | 31.51 ± 4.58 | - | - | - | 94.30 ± 5.46 | 88.22 ± 5.36 |
| | 10 | - | - | - | - | 8.44 ± 4.05 | - |
| **18** | 100 | - | - | 8.39 ± 3.79 | 2.83 ± 2.67 | - | 3.37 ± 4.33 |
| | 10 | - | 4.99 ± 9.19 | 8.18 ± 4.26 | - | 2.39 ± 2.49 | - |
| **19** | 100 | 48.00 ± 7.97 | - | 6.05 ± 4.06 | - | 15.85 ± 8.99 | - |
| | 10 | - | - | - | - | 15.53 ± 8.21 | 5.85 ± 2.59 |
| **9** | 100 | 15.83 ± 12.98 | - | 11.55 ± 3.21 | 6.99 ± 1.12 | 7.97 ± 7.76 | 2.61 ± 14.59 |
| | 10 | 31.67 ± 4.46 | - | - | - | 3.98 ± 1.69 | - |
| **14** | 100 | 19.58 ± 12.87 | - | 12.04 ± 4.94 | 11.71 ± 2.09 | 6.43 ± 4.17 | - |
| | 10 | 30.17 ± 5.46 | - | - | 4.24 ± 3.11 | 4.64 ± 3.29 | - |
| **13** | 100 | 23.70 ± 9.23 | - | 10.22 ± 3.98 | - | - | - |
| | 10 | 3.28 ± 8.93 | - | 12.58 ± 9.42 | - | 5.48 ± 2.97 | 4.96 ± 2.40 |
| **1** | 100 | - | - | - | - | - | - |
| | 10 | 18.49 ± 2.52 | - | 4.58 ± 0.88 | - | 3.51 ± 1.17 | - |
| **24b** | 100 | - | - | 10.75 ± 1.47 | 4.87 ± 3.07 | 7.91 ± 2.68 | - |
| | 10 | 42.04 ± 4.39 | - | - | 4.48 ± 2.94 | 4.72 ± 5.46 | - |
| **24a** | 100 | 32.85 ± 0.77 | - | 9.86 ± 6.44 | 8.14 ± 4.92 | 6.15 ± 3.94 | - |
| | 10 | 26.73 ± 3.96 | - | - | - | 7.56 ± 3.47 | - |
| **28b** | 100 | 9.09 ± 4.53 | - | 20.62 ± 3.18 | 4.72 ± 1.96 | - | 1.97 ± 3.75 |
| | 10 | 4.59 ± 0.57 | - | 1.57 ± 6.61 | 2.57 ± 1.75 | - | 4.10 ± 2.23 |
| **28a** | 100 | 40.66 ± 3.65 | - | 5.17 ± 5.82 | - | - | - |
| | 10 | - | 7.96 ± 5.14 | 1.08 ± 2.49 | - | - | - |
| **22a** | 100 | 1.84 ± 4.03 | - | - | 2.57 ± 8.17 | 5.33 ± 3.47 | - |
| | 10 | 24.45 ± 7.70 | - | - | 9.53 ± 6.18 | 5.90 ± 3.54 | - |
| **22b** | 100 | 2.44 ± 5.34 | - | - | - | 2.59 ± 3.68 | - |
| | 10 | 2.50 ± 1.37 | - | - | - | 7.21 ± 5.16 | - |
| **33** | 100 | 5.93 ± 6.53 | - | 5.73 ± 3.94 | 1.89 ± 3.48 | 3.55 ± 1.19 | 22.21 ± 2.42 |
| | 10 | - | - | - | - | 4.33 ± 3.09 | 9.30 ± 3.41 |
| **35b** | 100 | 92.04 ± 1.18 | - | 16.81 ± 0.76 | 3.22 ± 4.39 | 25.86 ± 1.43 | 12.40 ± 4.30 |
| | 10 | 57.37 ± 6.13 | - | - | - | 15.16 ± 4.84 | 2.88 ± 3.13 |
| **28b** | 100 | 36.98 ± 10.15 | - | - | 7.31 ± 0.69 | 2.51 ± 2.47 | - |
| | 10 | 32.26 ± 2.72 | - | - | 2.96 ± 0.41 | 6.88 ± 3.77 | - |
| **39b** | 100 | - | - | - | 9.92 ± 0.91 | 17.73 ± 9.18 | - |
| | 10 | 3.75 ± 13.63 | - | - | - | 10.07 ± 3.72 | 2.90 ± 3.19 |
| **39a** | 100 | - | - | 7.95 ± 2.38 | - | 5.33 ± 3.28 | - |
| | 10 | - | - | 4.18 ± 2.08 | - | 11.69 ± 5.07 | 4.08 ± 1.81 |
| **48** | 100 | - | - | 4.04 ± 2.84 | 2.70 ± 0.94 | 10.66 ± 2.60 | - |

| Inhibitory effect (%) ± RSD (%) | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Gram positive | | Gram negative | | Yeast | |
| **Analit** | **Conc. (µg/mL)** | ***B. subtilis* SZMC0209** | ***S. aureus* SZMC14611** | ***E. coli* SZMC6271** | ***P. aeruginosa* SZMC23290** | ***C. albicans* SZMC1533** | ***C. krusei* SZMC1352** |
| | 10 | - | - | - | - | 6.33 ± 4.35 | - |
| **49** | 100 | 16.93 ± 11.41 | - | - | - | 5.78 ± 4.90 | - |
| | 10 | 4.37 ± 3.25 | - | - | - | 5.66 ± 0.60 | 4.10 ± 0.74 |
| **43a** | 100 | 91.72 ± 3.98 | - | 1.99 ± 3.87 | 30.58 ± 1.51 | 22.64 ± 6.99 | 2.33 ± 1.83 |
| | 10 | 17.58 ± 7.06 | - | - | 6.42 ± 3.49 | 5.09 ± 4.71 | - |
| **45a** | 100 | 91.29 ± 1.86 | - | 6.24 ± 1.99 | 23.37 ± 2.81 | 12.56 ± 0.71 | 5.91 ± 0.37 |
| | 10 | 7.78 ± 6.78 | - | 4.44 ± 3.55 | - | 10.83 ± 8.98 | 4.76 ± 3.29 |
| **45b** | 100 | 77.98 ± 6.27 | - | 9.61 ± 5.13 | 9.88 ± 1.37 | 13.97 ± 4.35 | - |
| | 10 | 1.53 ± 2.93 | - | - | - | 13.30 ± 7.23 | 2.44 ± 3.13 |
| **41** | 100 | 76.58 ± 11.68 | - | 5.17 ± 0.83 | 12.84 ± 2.74 | 23.49 ± 7.28 | - |
| | 10 | 25.17 ± 6.00 | - | - | 4.72 ± 1.24 | 16.00 ± 1.45 | - |
| **50b** | 100 | 76.30 ± 16.90 | - | - | - | 18.81 ± 7.07 | 9.24 ± 8.76 |
| | 10 | 45.25 ± 11.25 | - | - | - | 8.80 ± 3.30 | 2.19 ± 5.76 |
| **52a** | 100 | 77.67 ± 3.81 | 73.44 ± 1.78 | 2.81 ± 3.62 | - | 86.64 ± 2.54 | 84.92 ± 4.20 |
| | 10 | 93.88 ± 1.77 | - | - | - | 13.07 ± 4.55 | 5.54 ± 2.99 |
| **52b** | 100 | 87.23 ± 4.17 | 68.03 ± 4.74 | 14.19 ± 1.70 | - | 81.47 ± 5.04 | 81.00 ± 4.03 |
| | 10 | 94.63 ± 1.01 | - | - | - | 41.25 ± 9.35 | 7.22 ± 5.98 |
| **56a** | 100 | 78.20 ± 7.98 | - | 6.29 ± 2.63 | - | 16.10 ± 4.46 | 10.39 ± 1.84 |
| | 10 | 10.06 ± 1.88 | - | - | 1.98 ± 11.01 | 15.51 ± 6.93 | - |
| **56b** | 100 | 10.09 ± 3.34 | - | - | 20.37 ± 4.23 | 13.50 ± 3.85 | 1.73 ± 5.65 |
| | 10 | - | - | - | - | 15.06 ± 4.11 | 2.04 ± 0.64 |
| **47b** | 100 | 3.22 ± 3.34 | - | 4.56 ± 5.04 | 10.75 ± 0.77 | 7.56 ± 8.70 | 1.26 ± 0.60 |
| | 10 | 9.71 ± 2.02 | - | - | 5.03 ± 0.46 | 1.02 ± 2.64 | 3.70 ± 3.60 |
| **50a** | 100 | 11.74 ± 3.52 | - | - | 5.40 ± 1.96 | 10.79 ± 2.40 | 4.67 ± 3.19 |
| | 10 | 14.77 ± 5.29 | - | - | - | 8.80 ± 2.23 | - |
| **58b** | 100 | 68.93 ± 6.85 | - | 9.21 ± 5.24 | 15.87 ± 5.13 | 11.81 ± 5.55 | 1.64 ± 1.25 |
| | 10 | 34.63 ± 7.99 | - | - | 7.01 ± 3.06 | 10.58 ± 6.08 | - |
| **58a** | 100 | 60.52 ± 2.49 | - | 7.88 ± 3.97 | 26.09 ± 4.61 | 2.49 ± 5.59 | - |
| | 10 | 5.68 ± 1.49 | - | 3.90 ± 10.14 | 11.66 ± 2.61 | 5.25 ± 3.34 | - |
| **62a** | 100 | 15.40 ± 6.89 | - | - | 6.86 ± 1.85 | 9.56 ± 4.22 | 6.89 ± 3.35 |
| | 10 | 4.62 ± 7.60 | - | 4.23 ± 3.49 | - | 6.17 ± 3.86 | 3.41 ± 6.09 |
| **62b** | 100 | 1.50 ± 6.19 | - | - | 17.82 ± 4.29 | 5.72 ± 3.75 | 10.76 ± 10.82 |
| | 10 | 45.44 ± 3.20 | - | 9.21 ± 1.18 | - | 1.53 ± 0.33 | 5.67 ± 4.33 |
| **3** | 100 | - | - | 4.82 ± 5.52 | - | 11.52 ± 5.83 | 5.83 ± 0.78 |
| | 10 | - | - | 2.27 ± 1.57 | 5.72 ± 2.40 | 6.50 ± 2.11 | 1.40 ± 4.79 |
| **64a** | 100 | - | - | 6.97 ± 2.09 | 12.75 ± 1.22 | 7.60 ± 5.64 | 2.99 ± 9.25 |
| | 10 | 22.02 ± 1.09 | - | 1.71 ± 4.45 | 5.16 ± 0.69 | 4.09 ± 1.84 | - |
| **66a** | 100 | 31.48 ± 11.69 | - | - | 11.23 ± 1.36 | 7.52 ± 6.97 | 39.76 ± 3.24 |
| | 10 | 14.43 ± 9.09 | - | 10.05 ± 2.49 | 3.59 ± 0.61 | 5.60 ± 2.95 | - |
| **66b** | 100 | - | - | - | 22.79 ± 7.42 | 7.13 ± 4.44 | - |

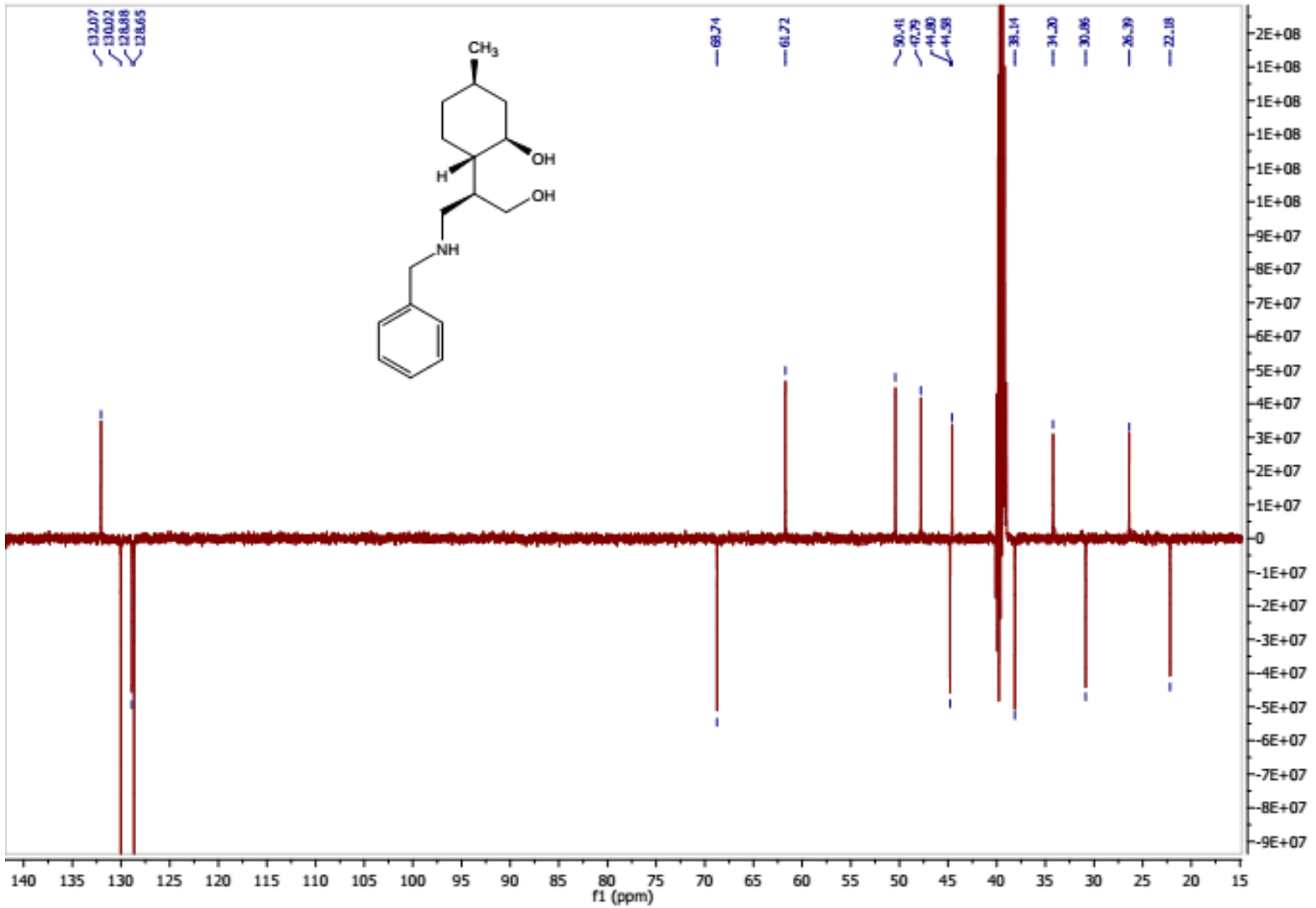
| Inhibitory effect (%) ± RSD (%) | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Gram positive | | Gram negative | | Yeast | |
| **Analit** | **Conc. (μg/mL)** | ***B. subtilis* SZMC0209** | ***S. aureus* SZMC14611** | ***E. coli* SZMC6271** | ***P. aeruginosa* SZMC23290** | ***C. albicans* SZMC1533** | ***C. krusei* SZMC1352** |
| | 10 | 3.15 ± 1.47 | - | 7.32 ± 4.10 | - | 4.04 ± 2.91 | - |
| **47a** | 100 | 25.61 ± 9.22 | - | 6.69 ± 3.89 | - | 11.77 ± 3.43 | 3.88 ± 9.15 |
| | 10 | 26.30 ± 5.69 | - | 10.45 ± 8.73 | 3.96 ± 2.54 | 9.27 ± 1.01 | 3.81 ± 7.29 |
| **30b** | 100 | 52.97 ± 8.35 | - | 8.95 ± 6.18 | 23.00 ± 9.26 | 6.23 ± 4.42 | - |
| | 10 | 41.69 ± 10.35 | - | - | 6.70 ± 2.06 | 5.15 ± 6.52 | - |
| **30a** | 100 | 46.53 ± 2.55 | - | 4.63 ± 7.30 | 10.29 ± 2.09 | 9.29 ± 2.29 | - |
| | 10 | 34.92 ± 6.84 | - | 6.26 ± 5.73 | 2.94 ± 2.79 | 8.48 ± 3.21 | 5.71 ± 7.72 |

# 1. $^{1}$H- and $^{13}$C-NMR spectra of new compounds

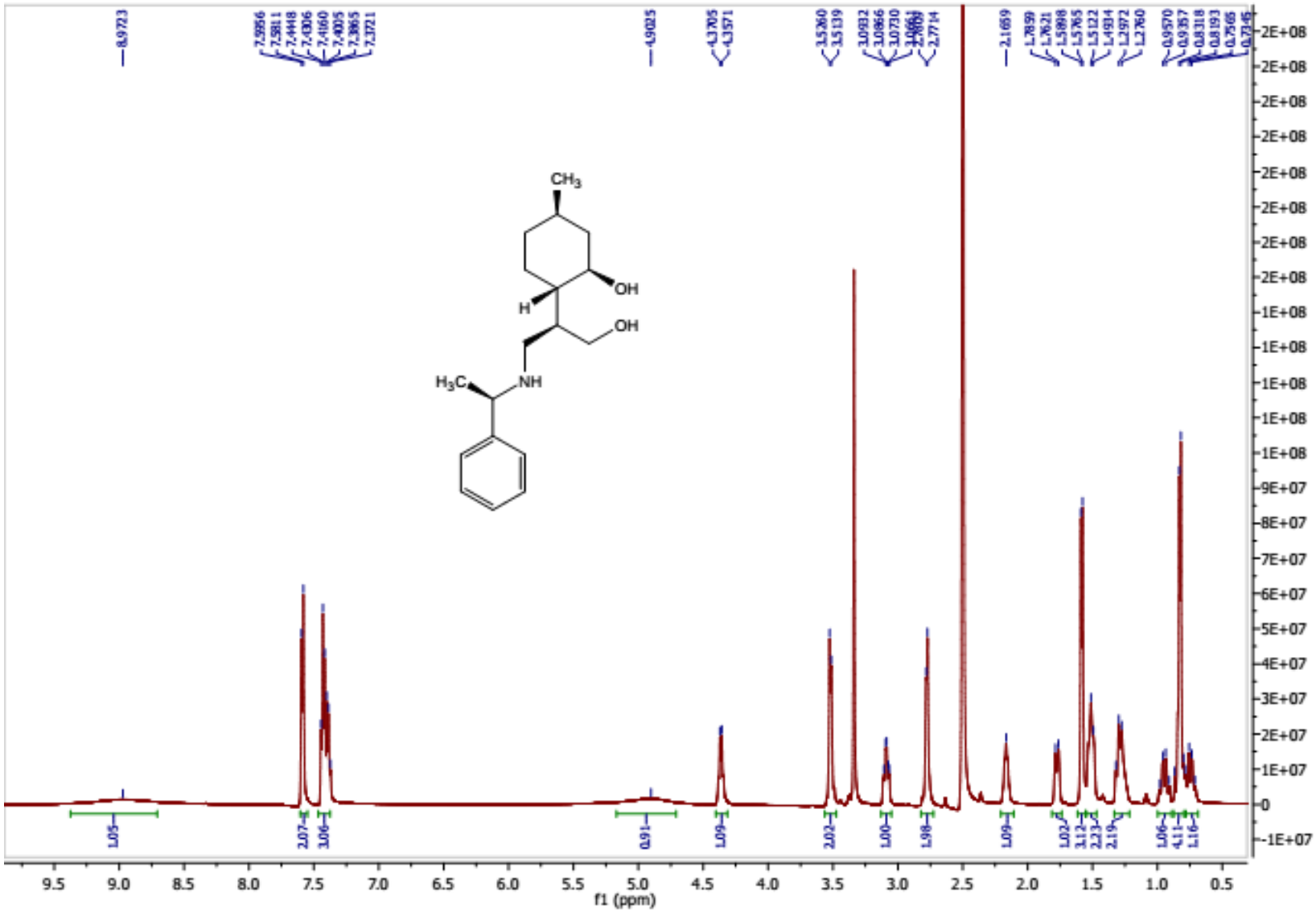
$^{1}$H-NMR of compound **9**



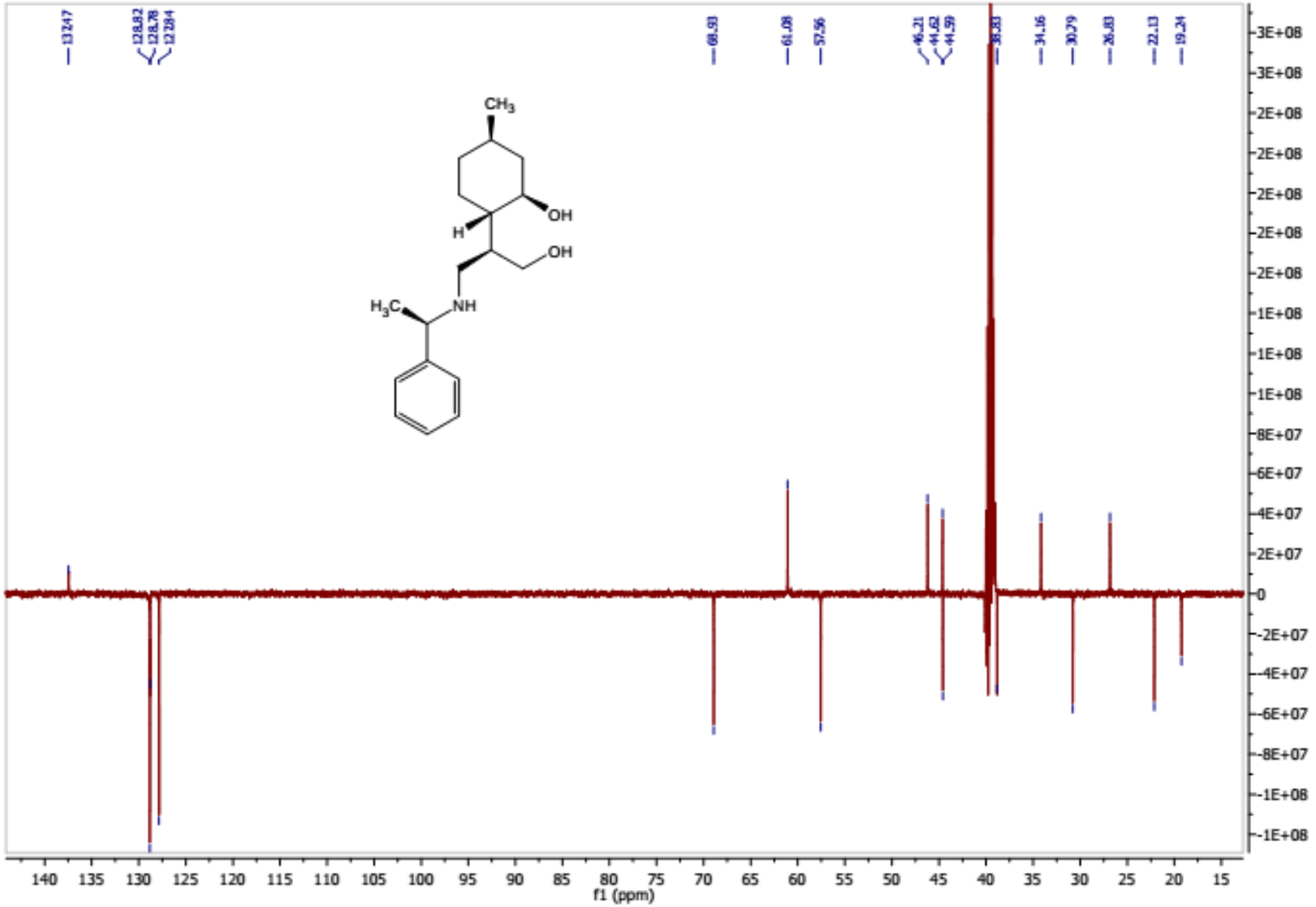
$^{13}$C-NMR of compound **9**



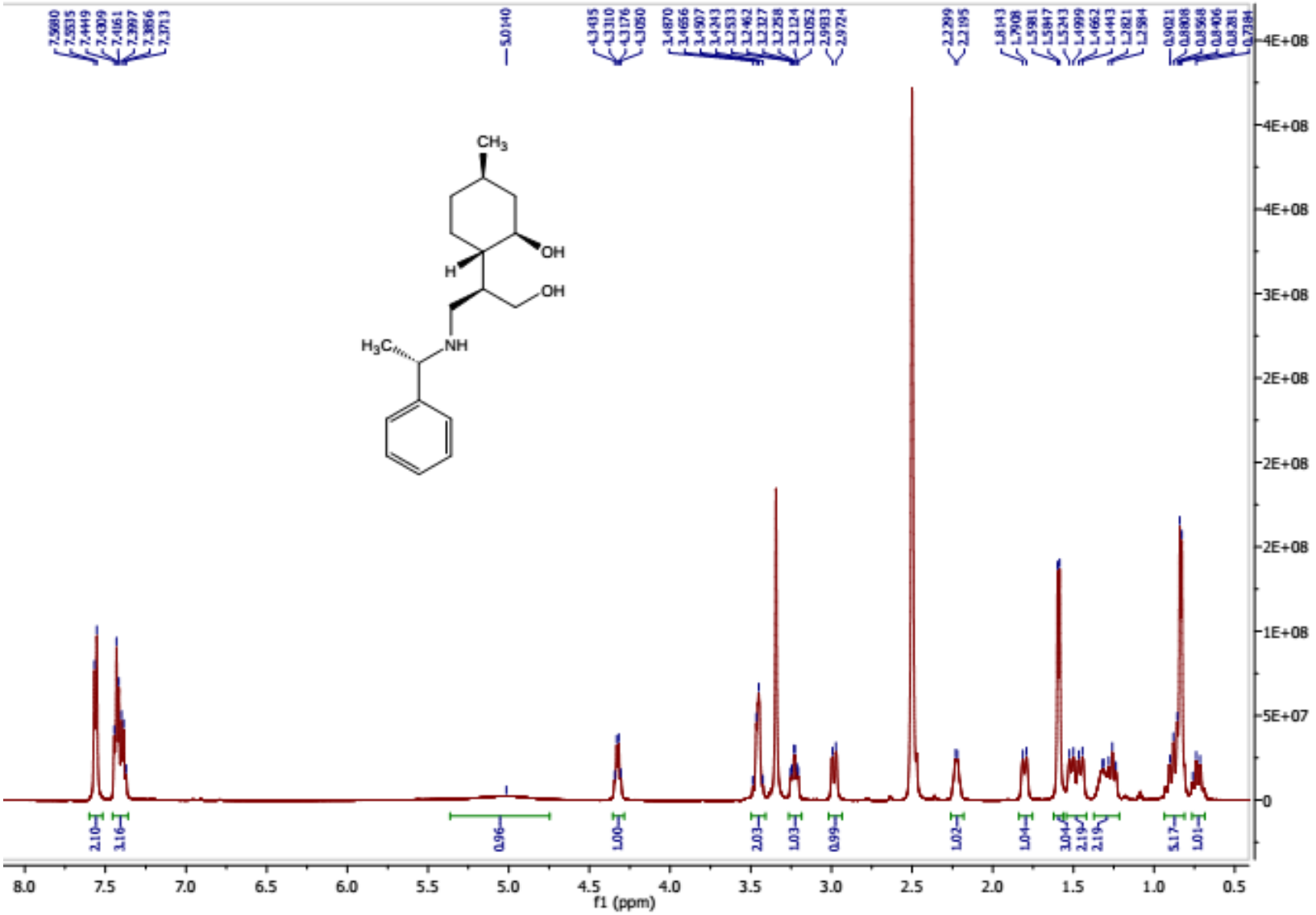
[1]H-NMR of compound **10**



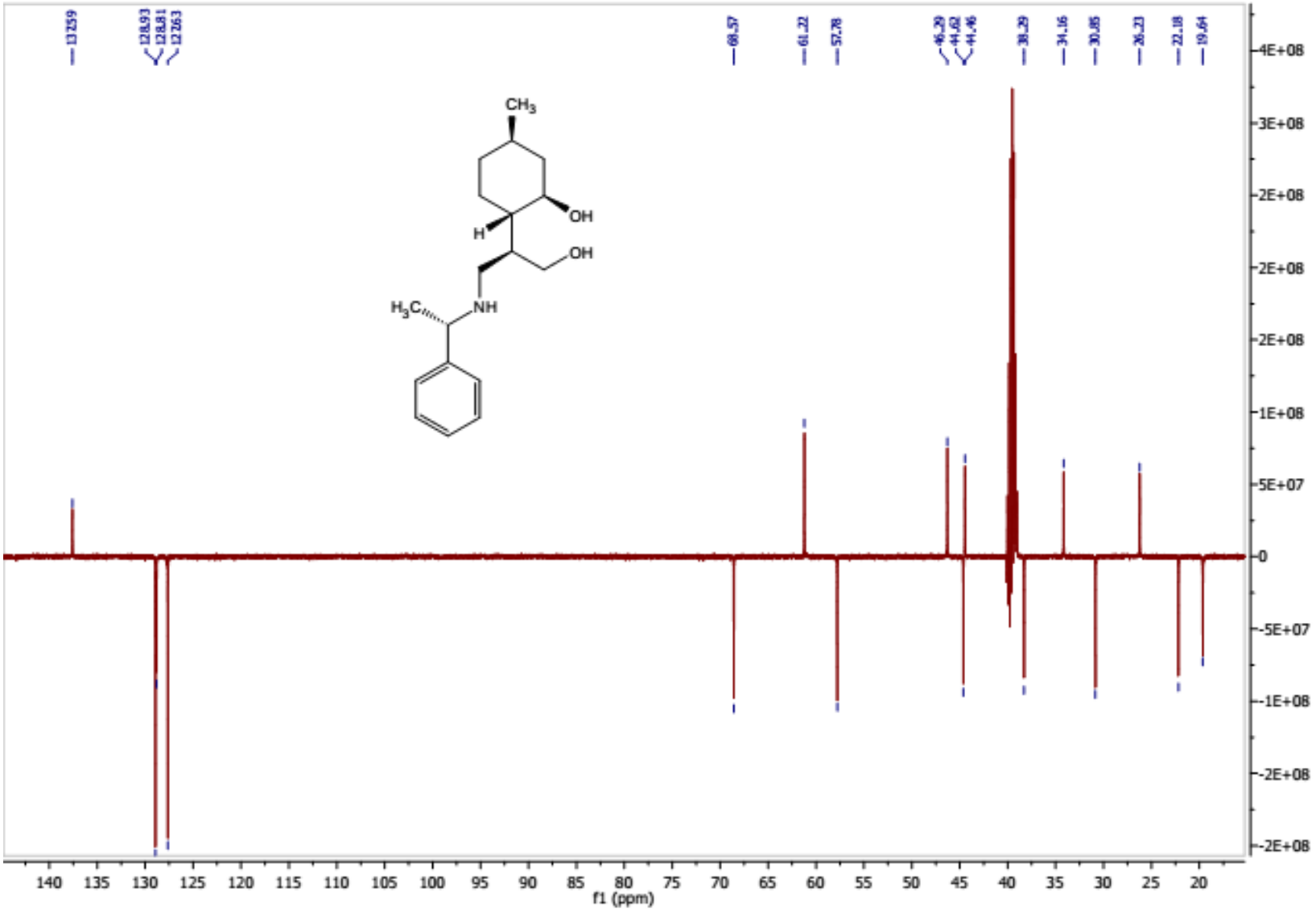
$^{13}$C-NMR of compound **10**



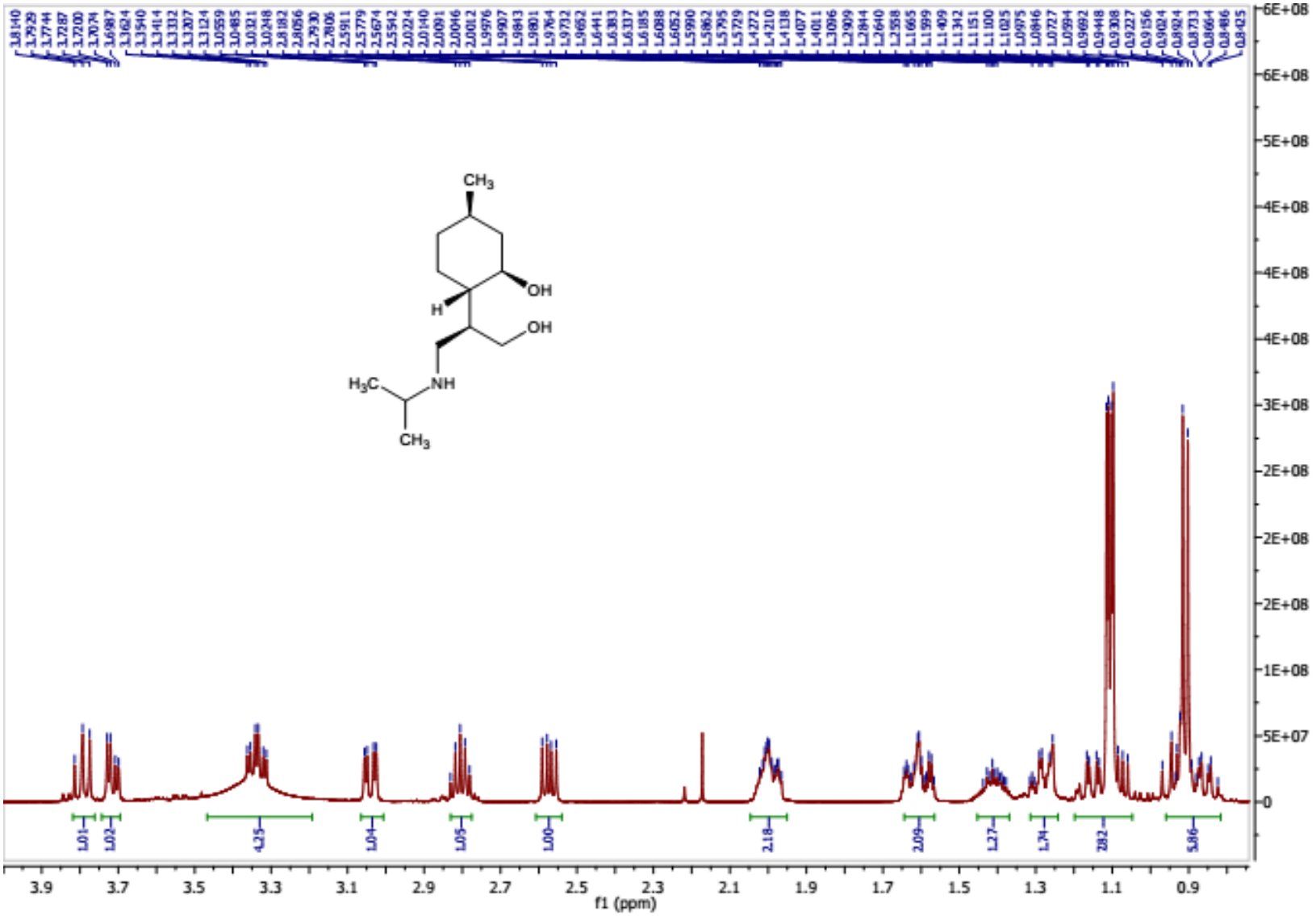
[1]H-NMR of compound **11**



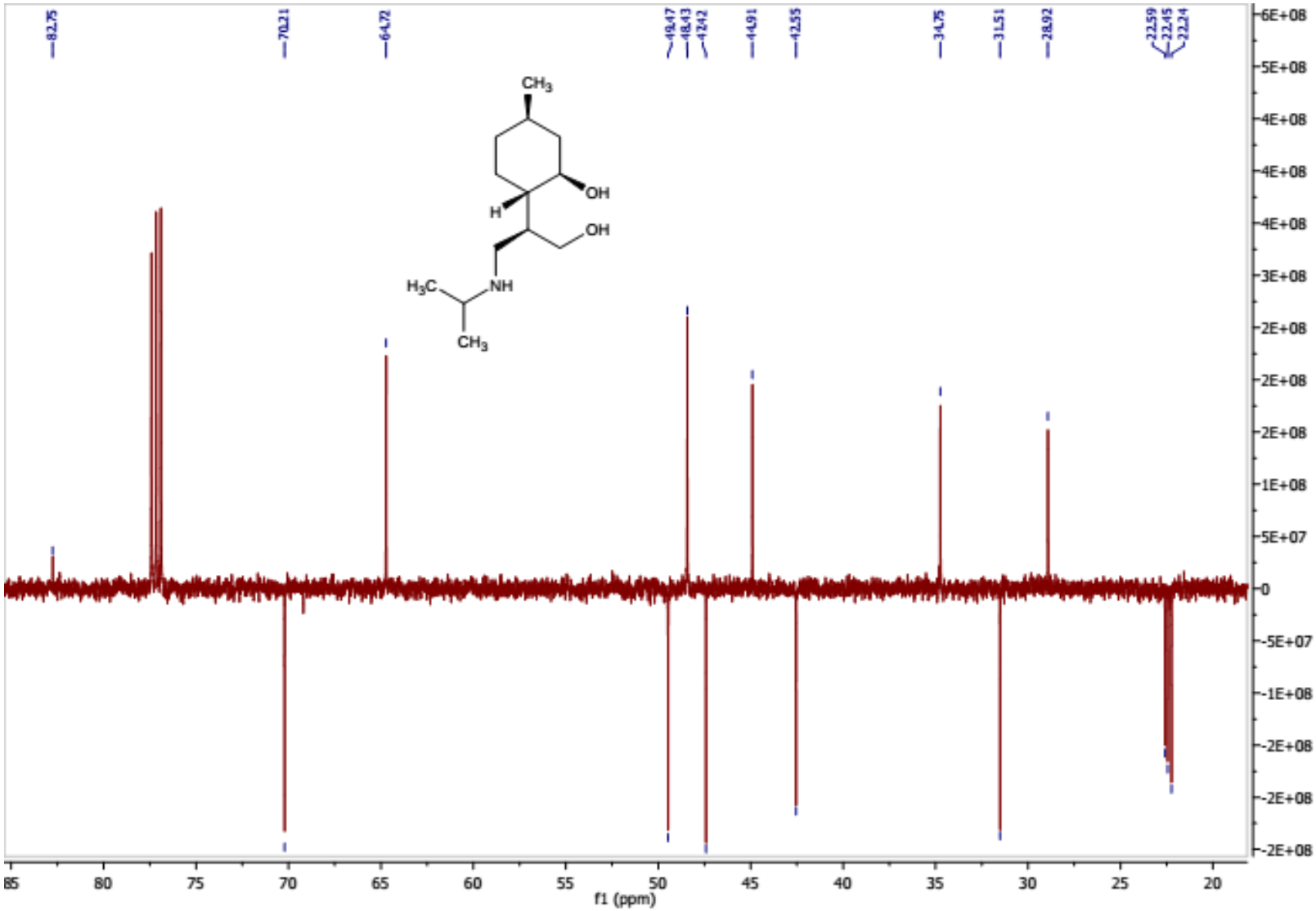
$^{13}$C-NMR of compound **11**



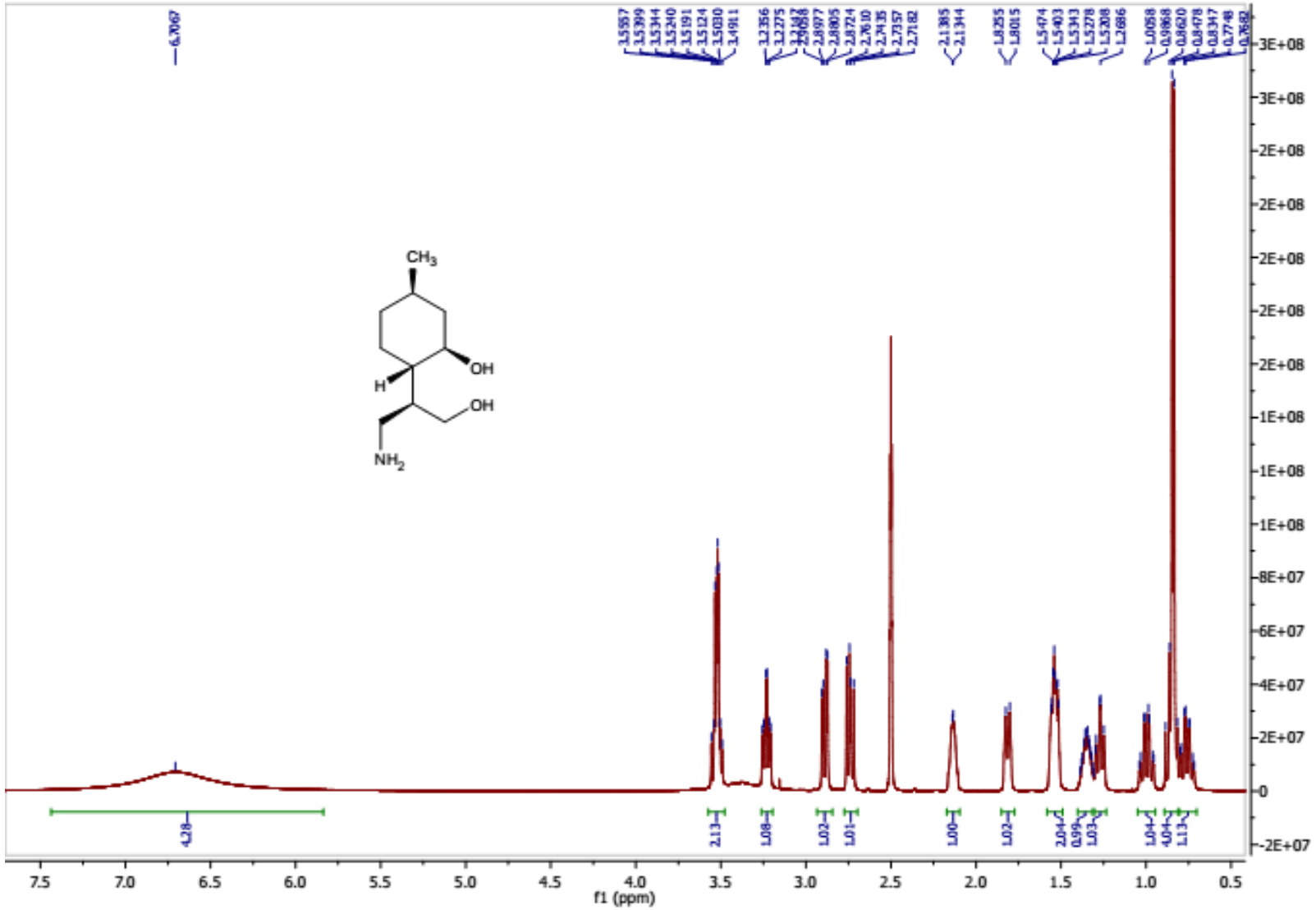
[1]H-NMR of compound **12**



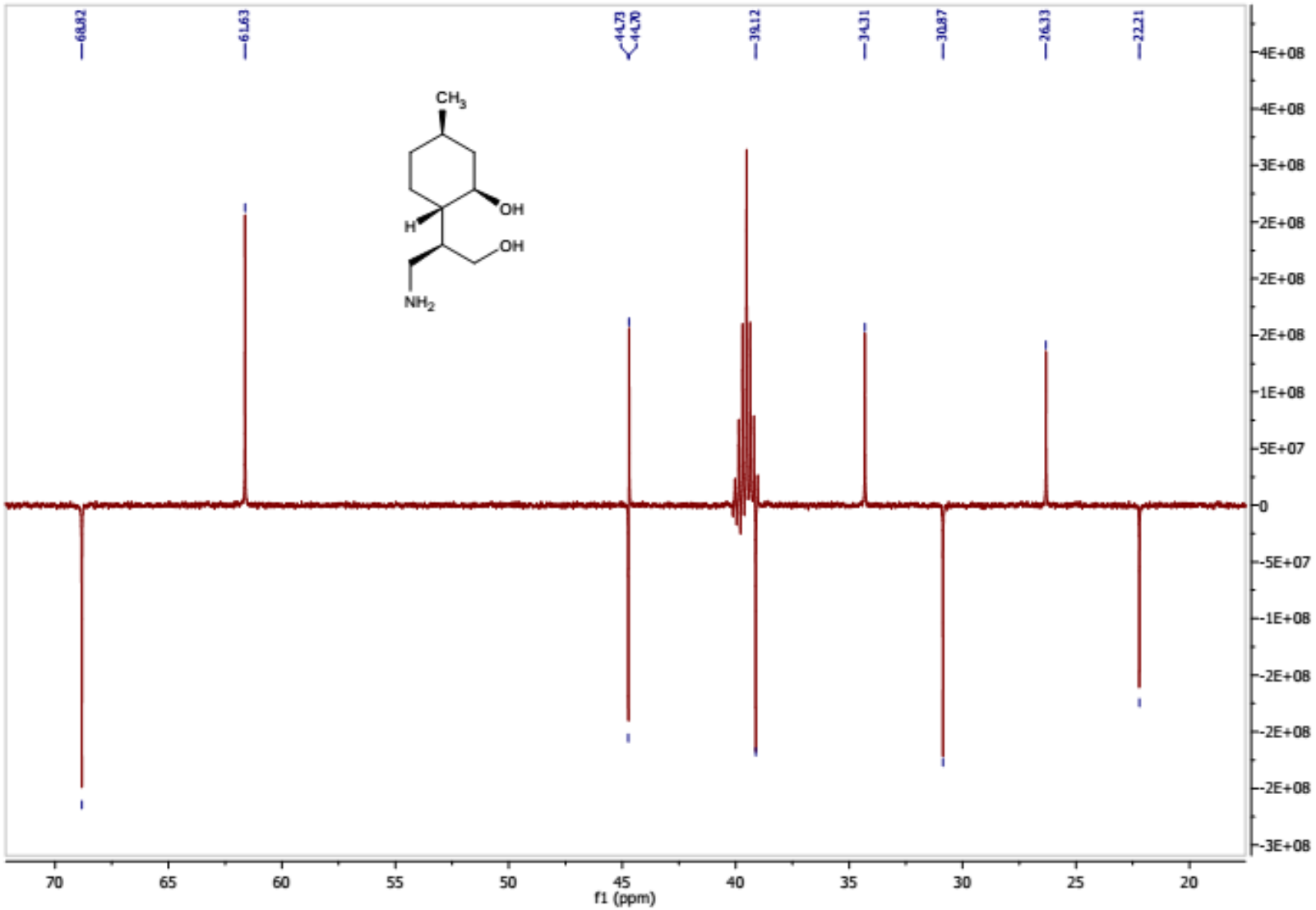
$^{13}$C-NMR of compound **12**



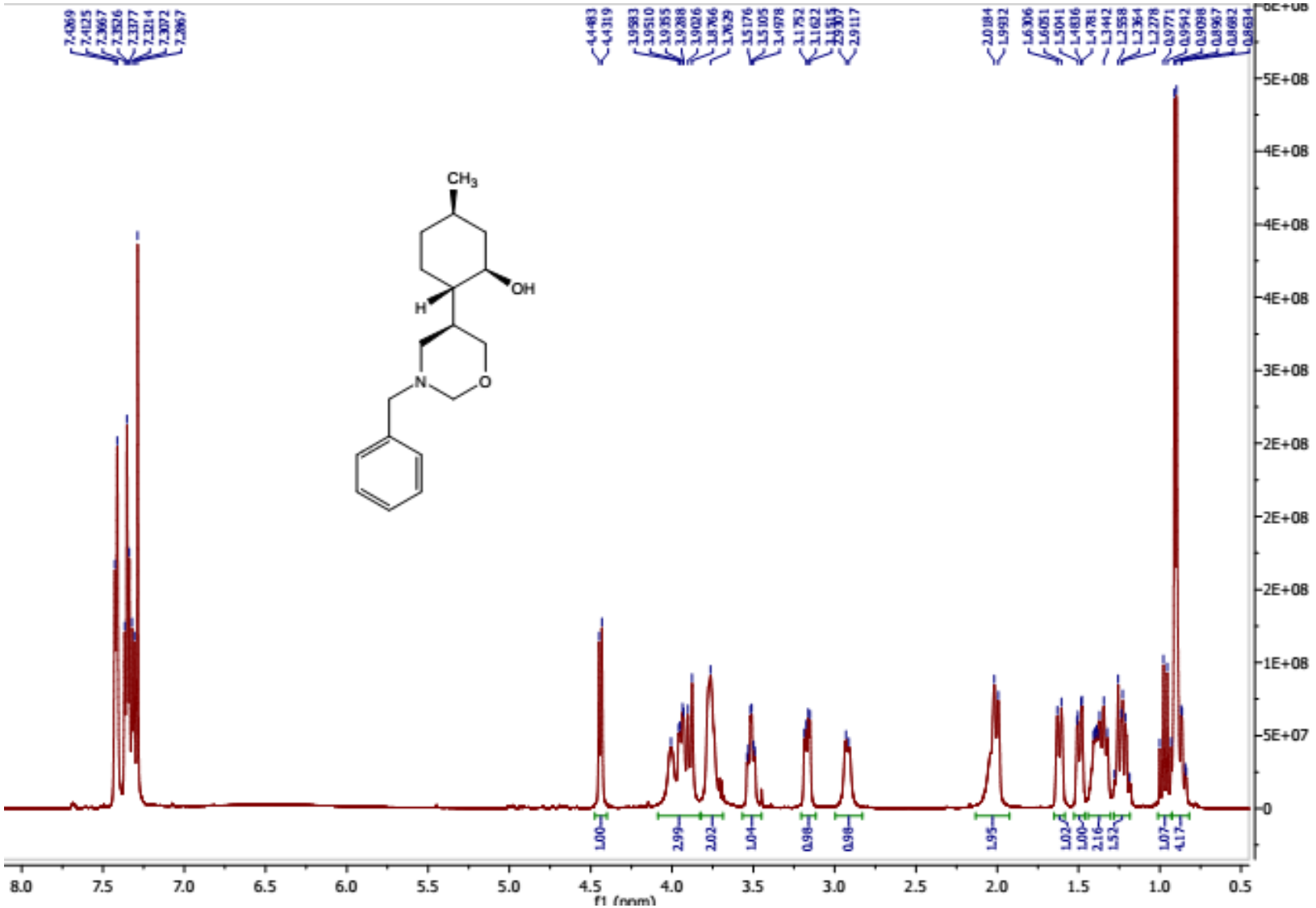
$^{1}$H-NMR of compound **13**



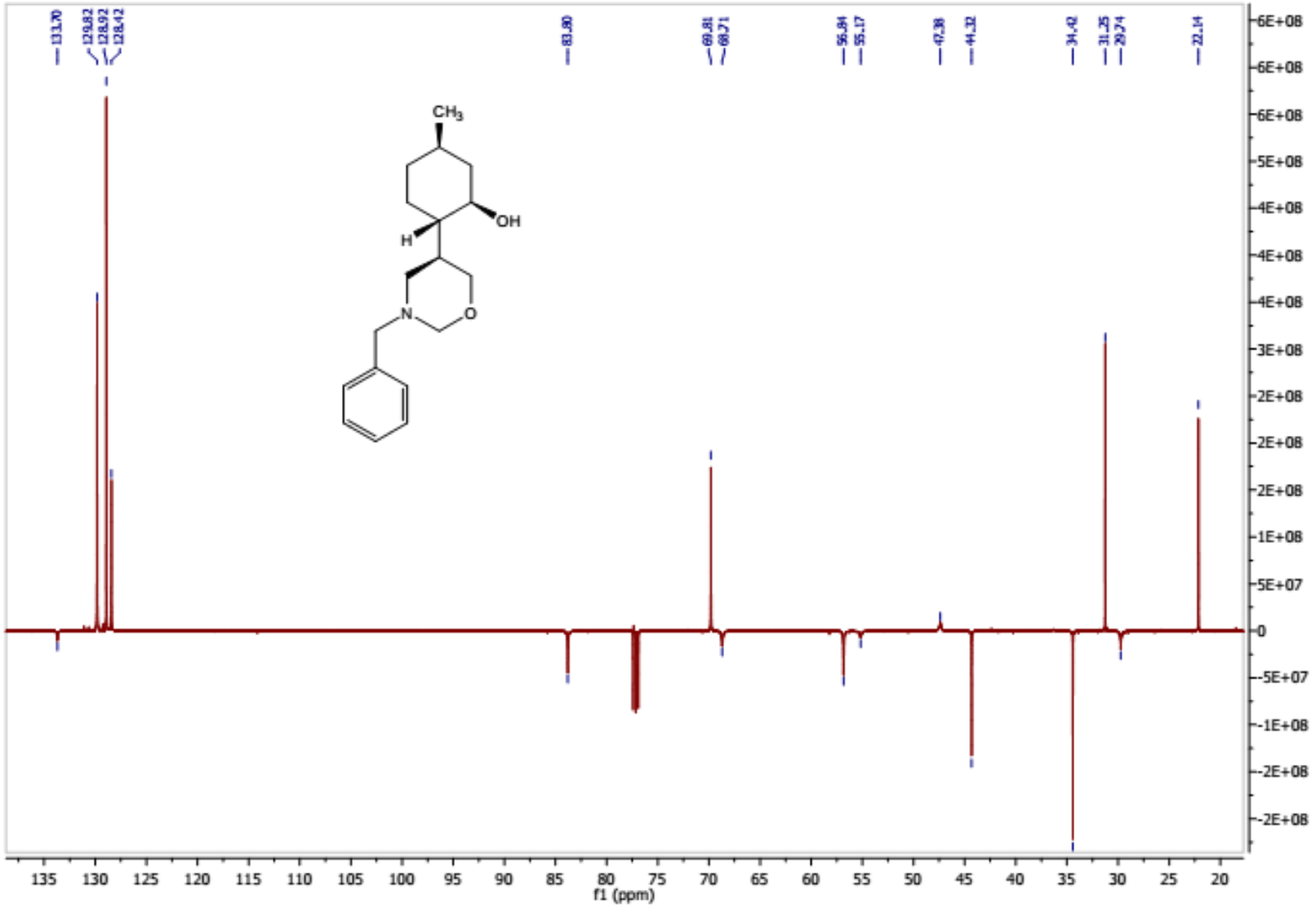
$^{13}$C-NMR of compound **13**



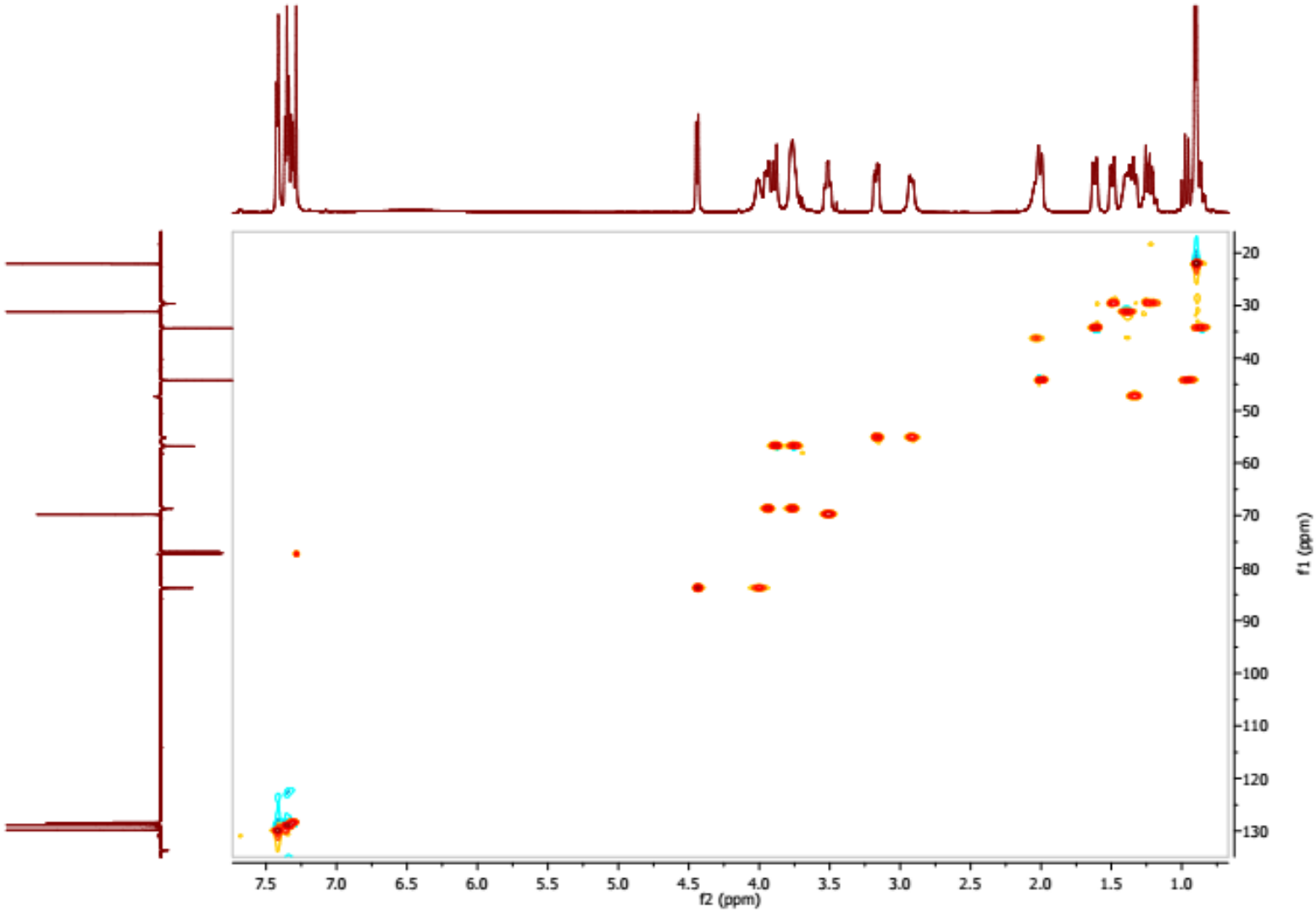
[1]H-NMR of compound **14**



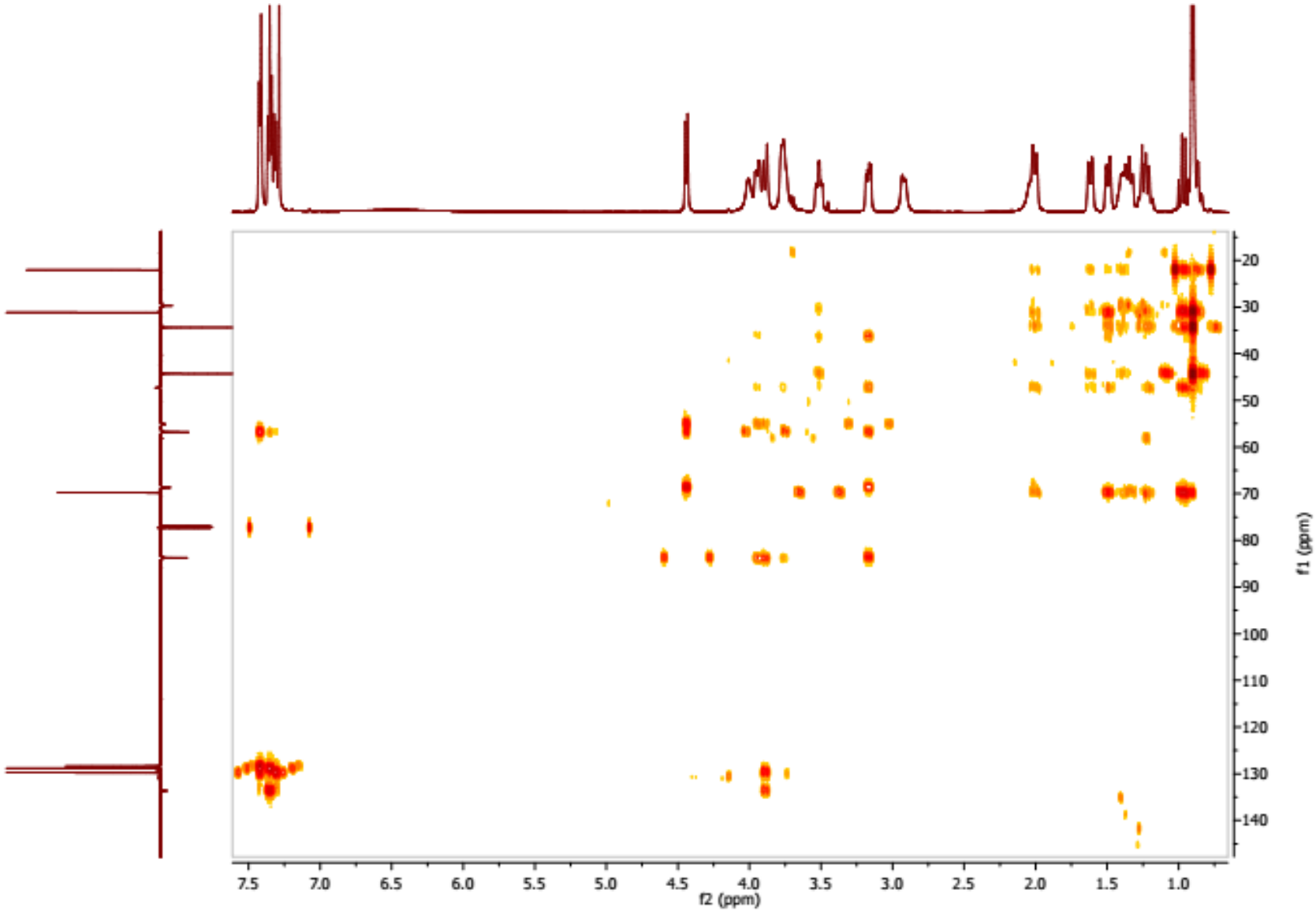
$^{13}$C-NMR of compound **14**



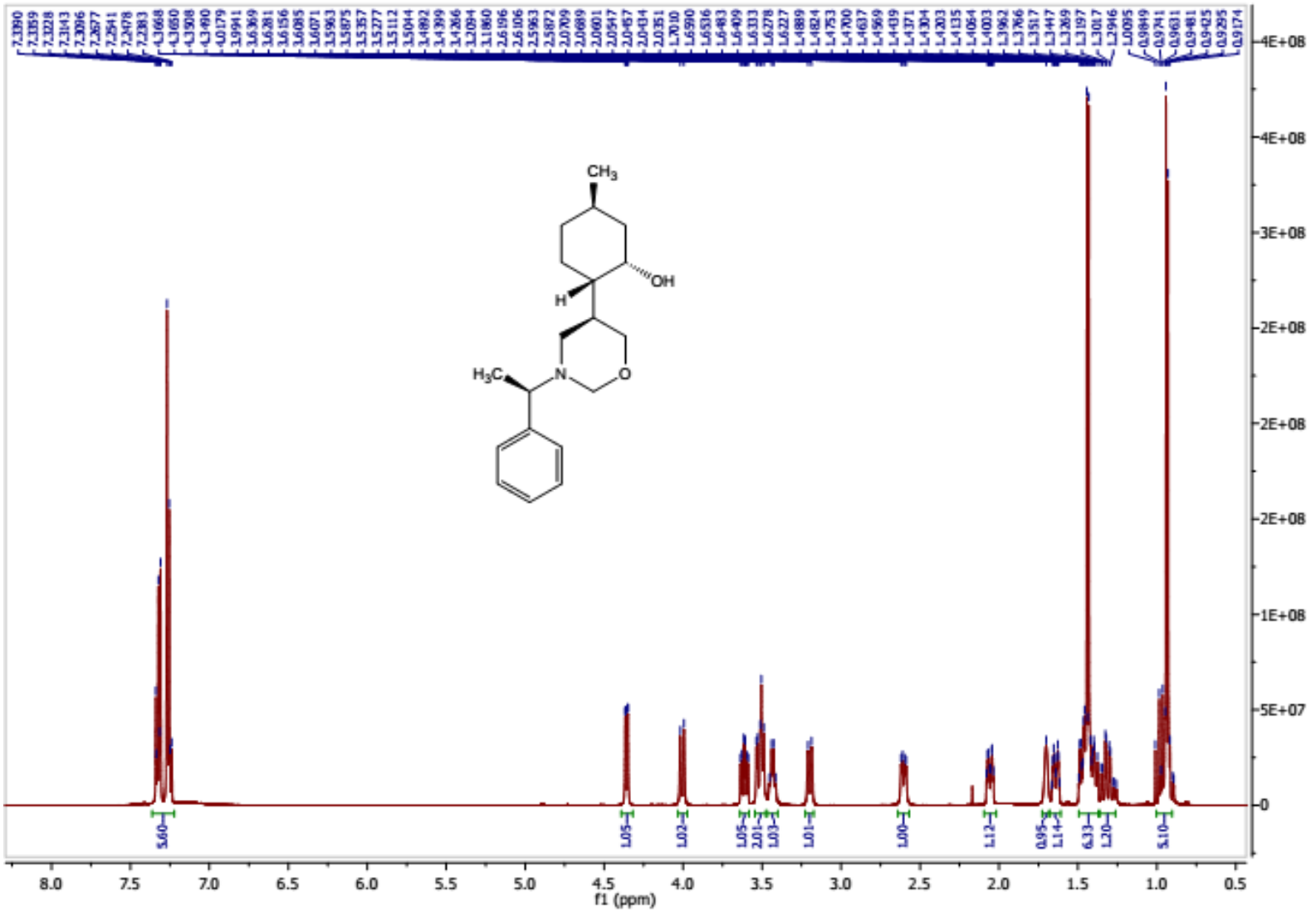
HSQC of compound**14**



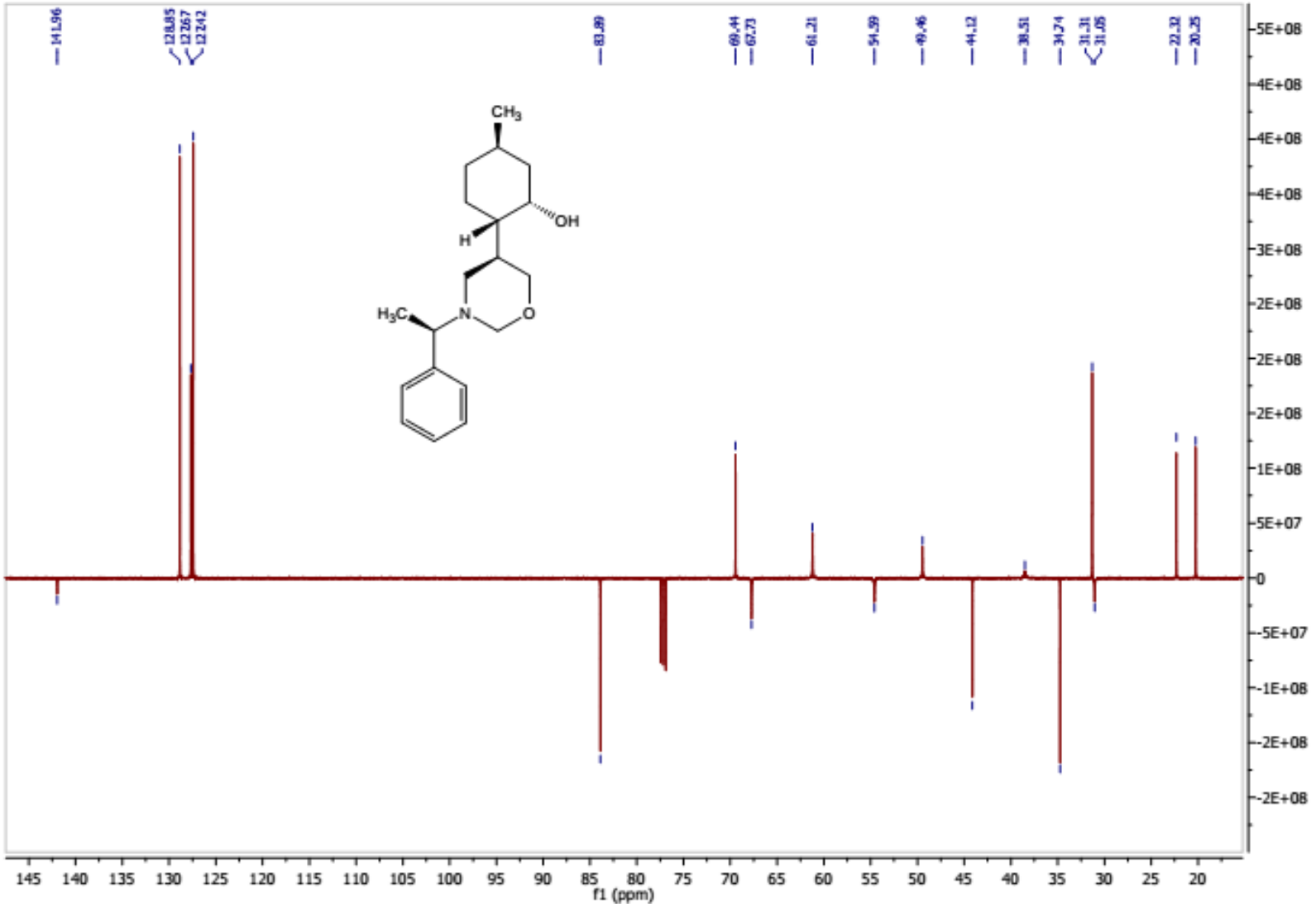
HMBC of compound **14**



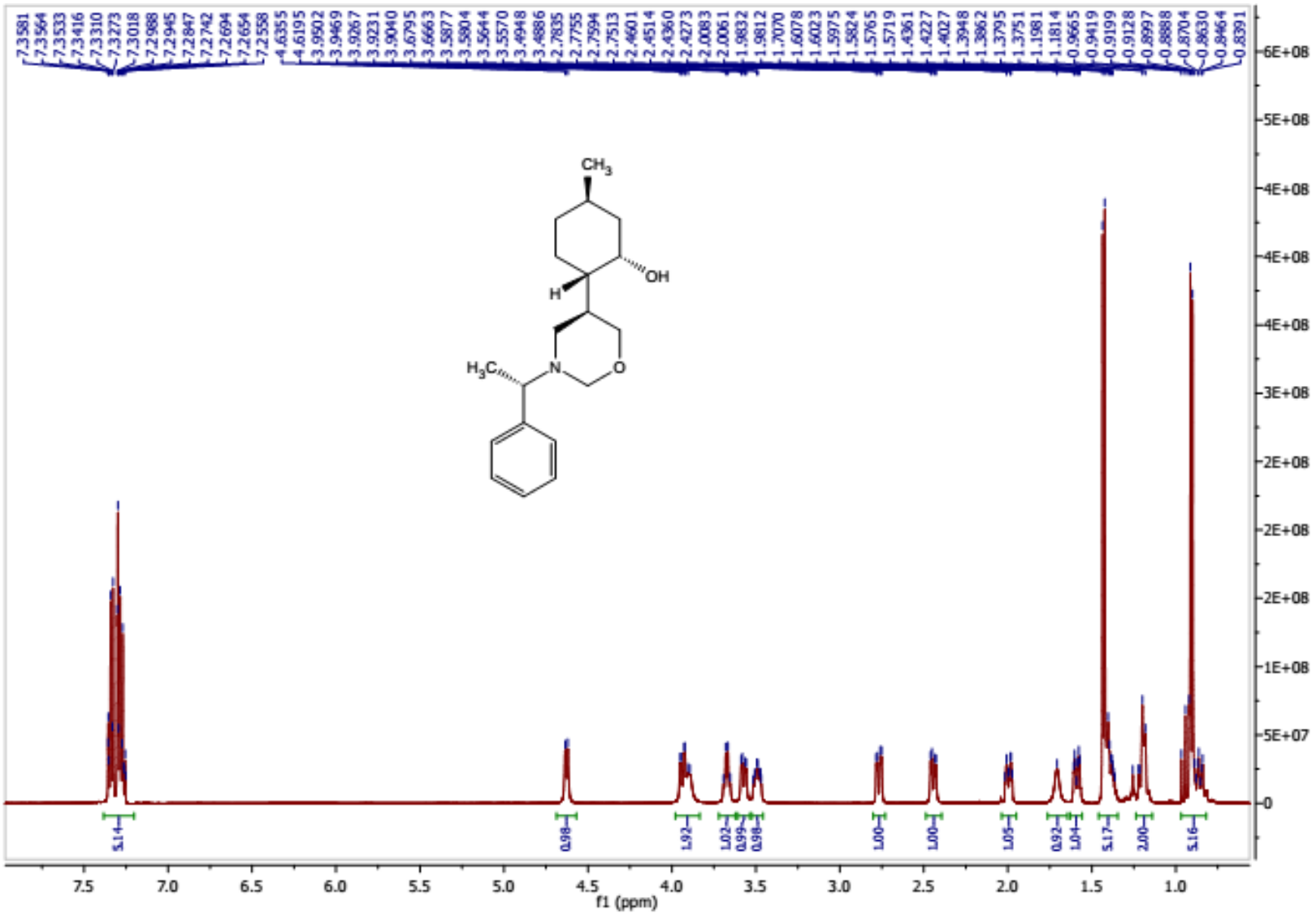
[1]H-NMR of compound **15**



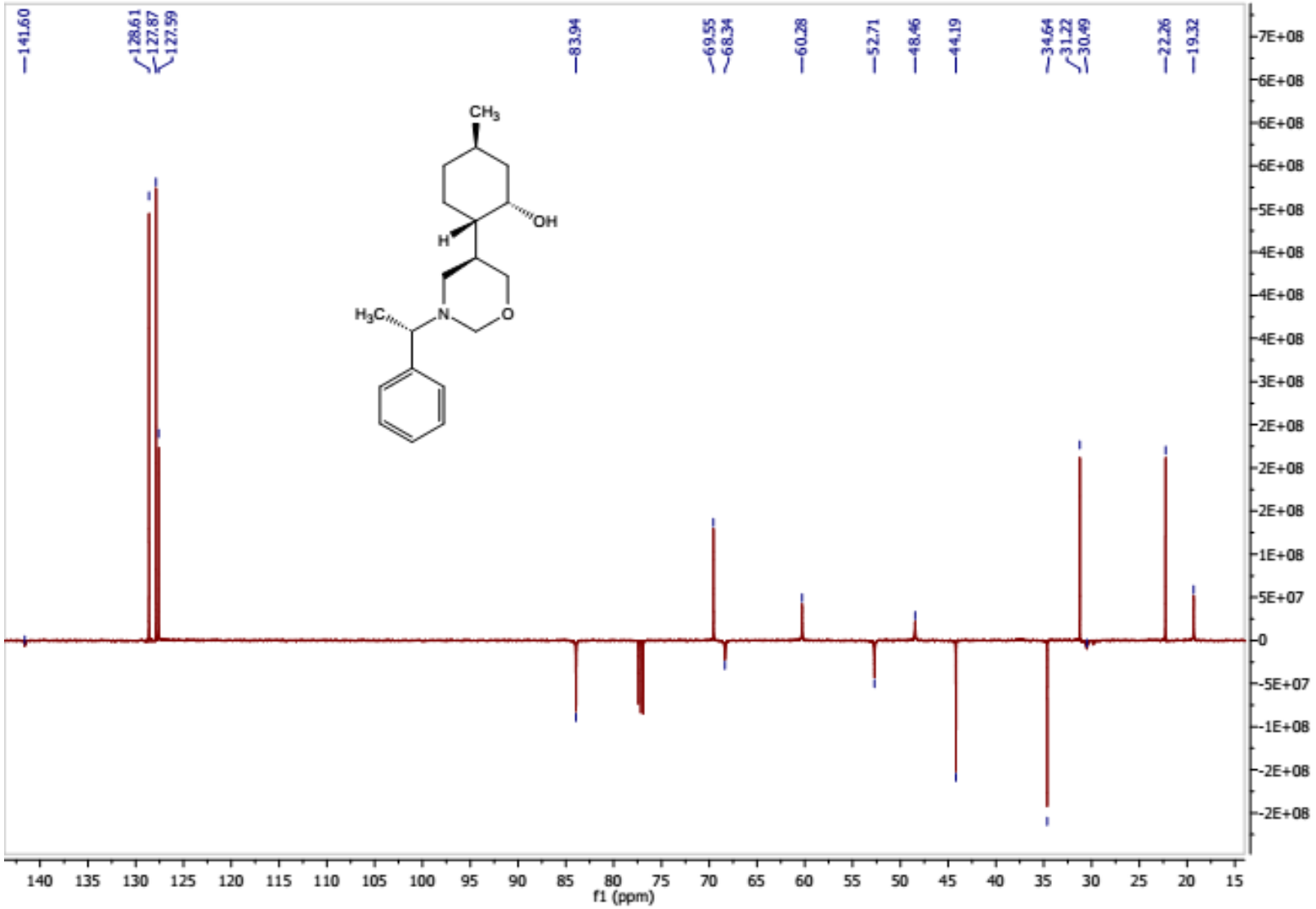
$^{13}$C-NMR of compound **15**



[1]H-NMR of compound **16**



$^{13}$C-NMR of compound **16**



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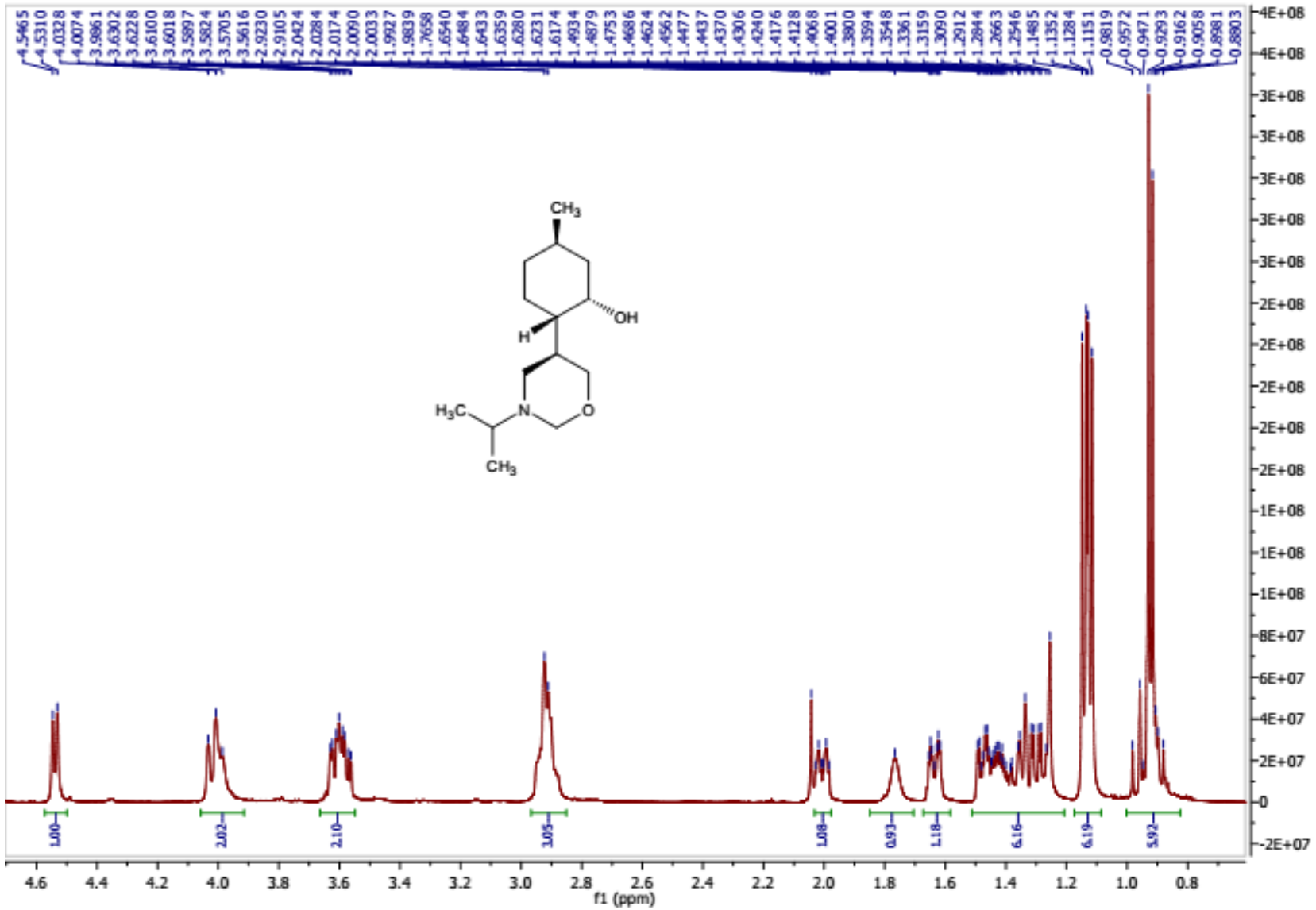
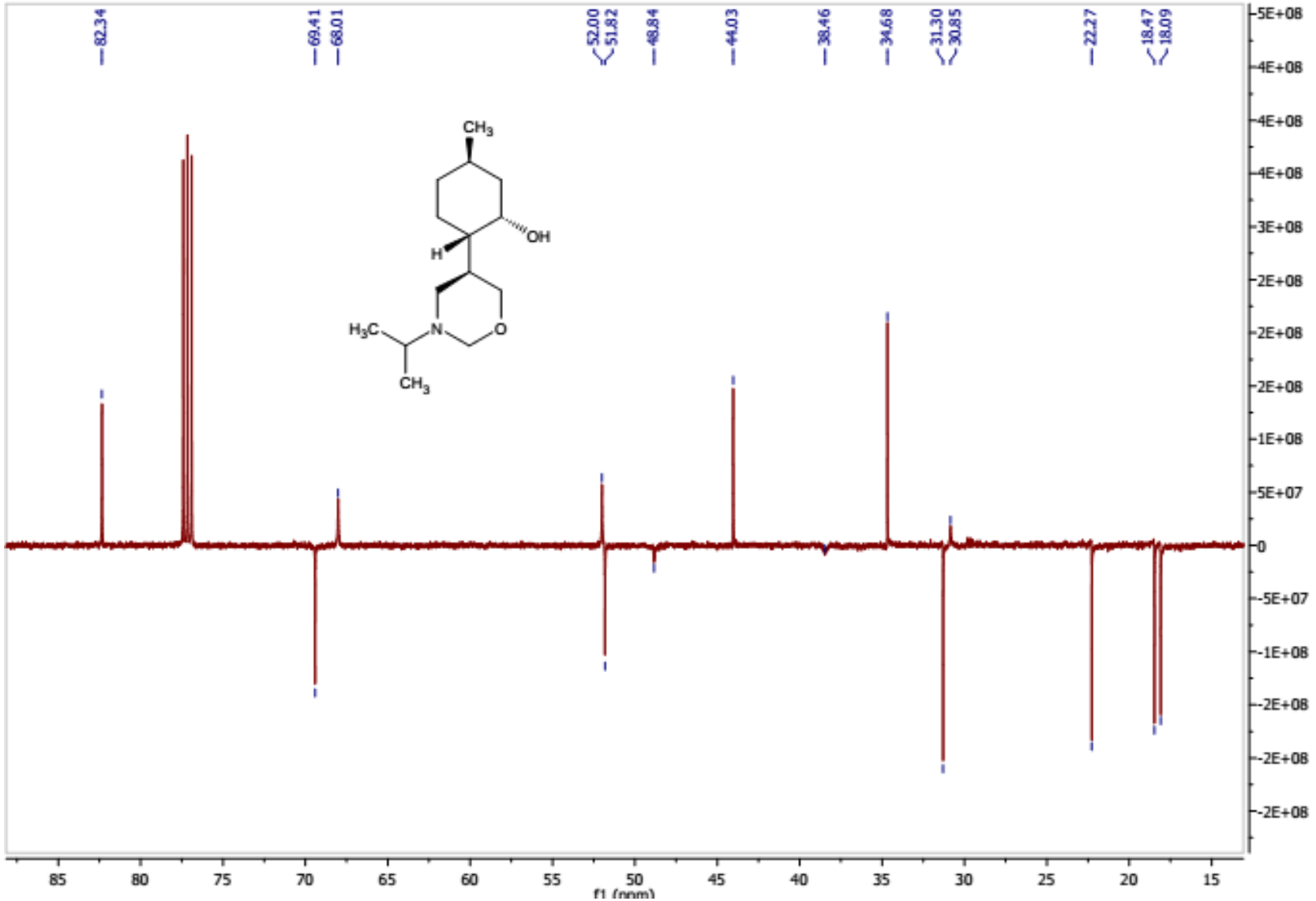
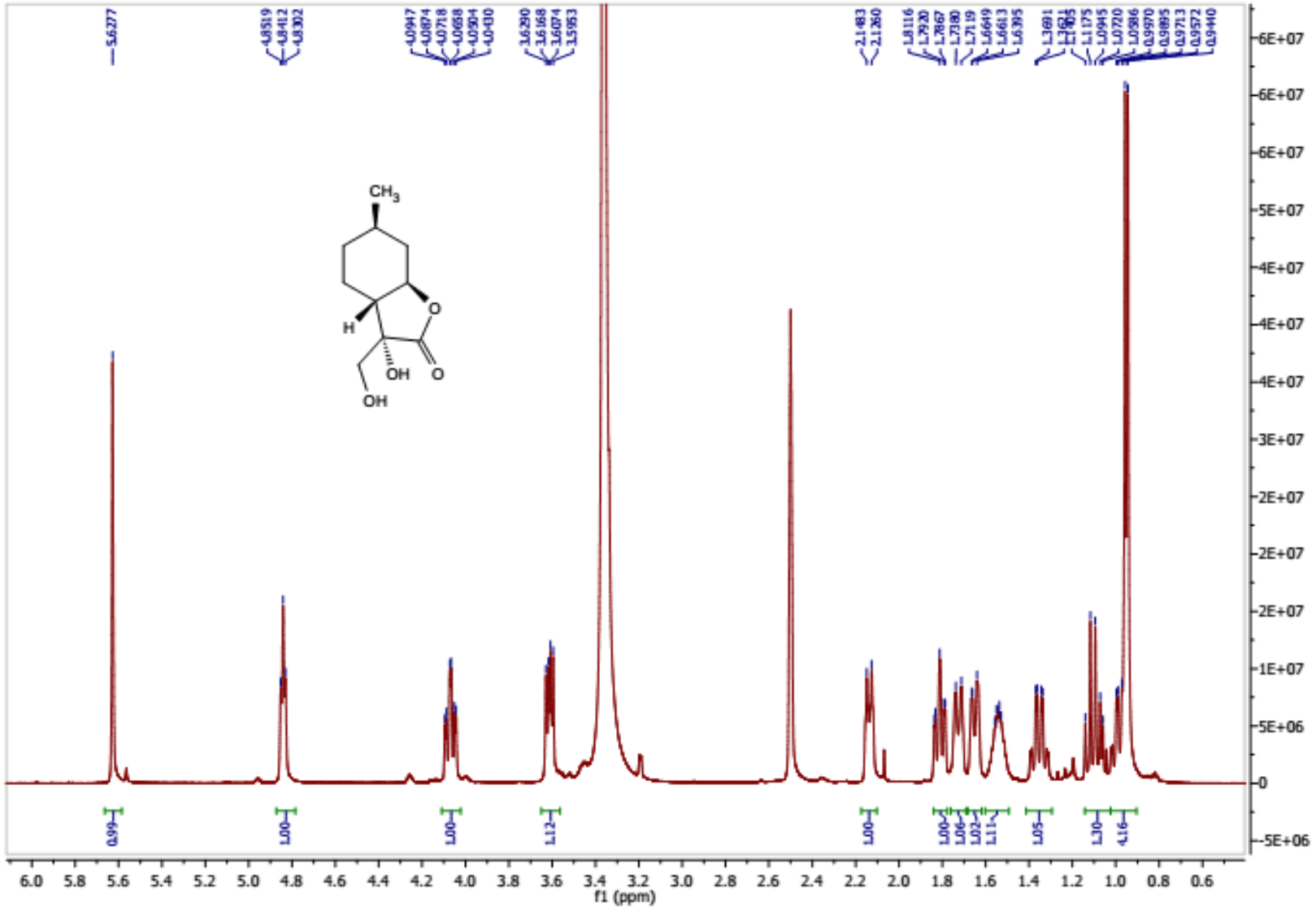


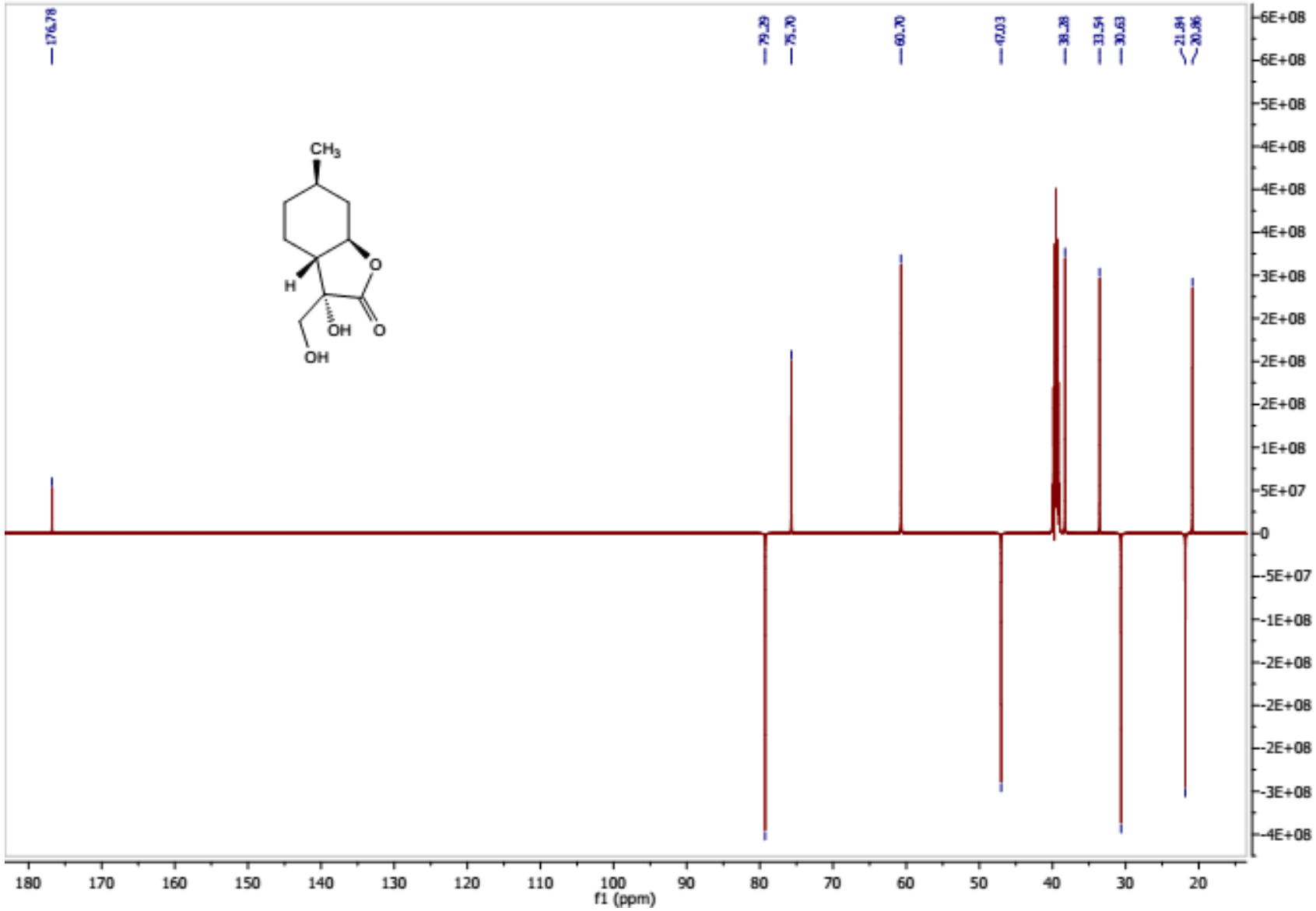
$^{13}$C-NMR of compound **17**



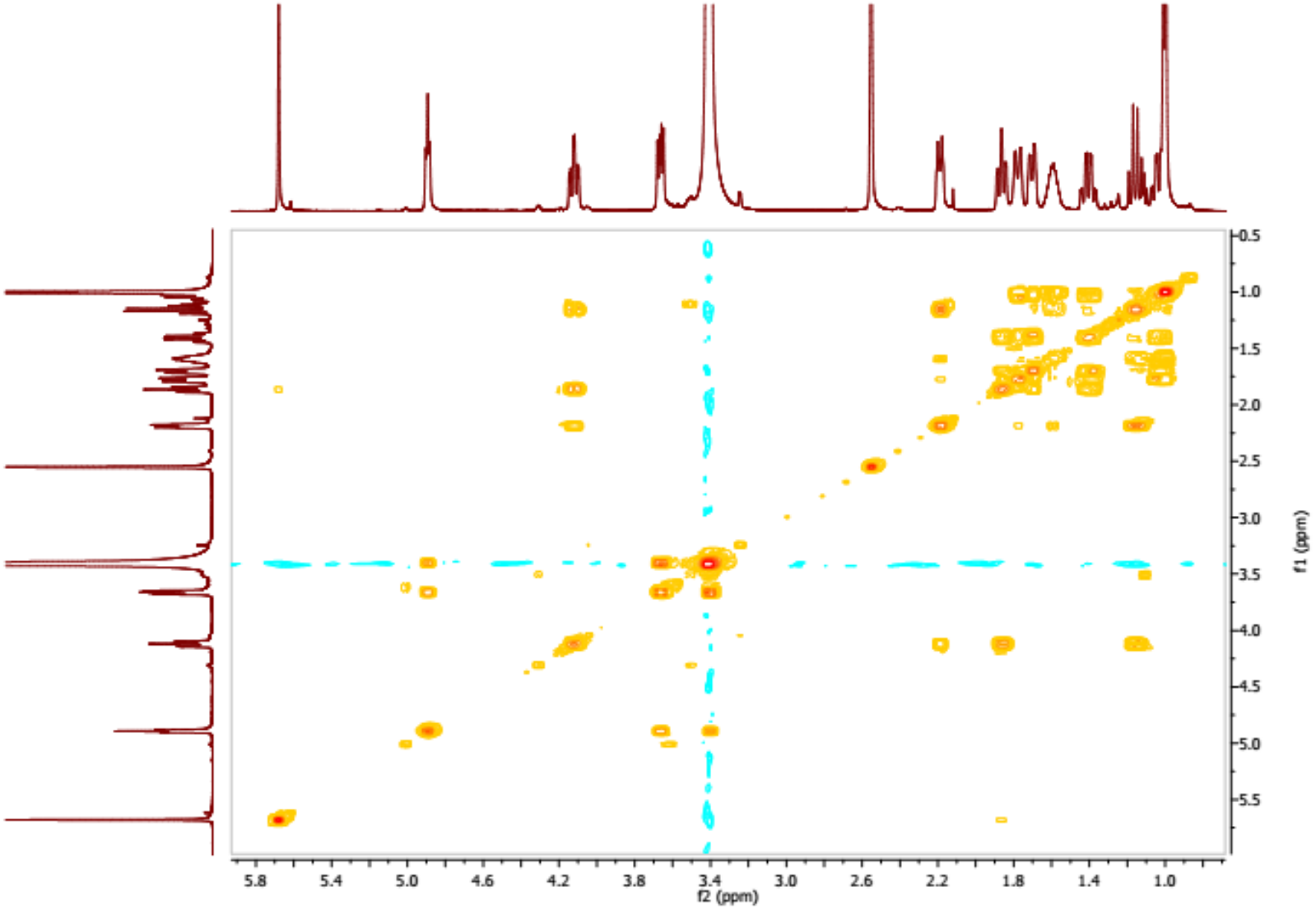
[1]H-NMR of compound **18**



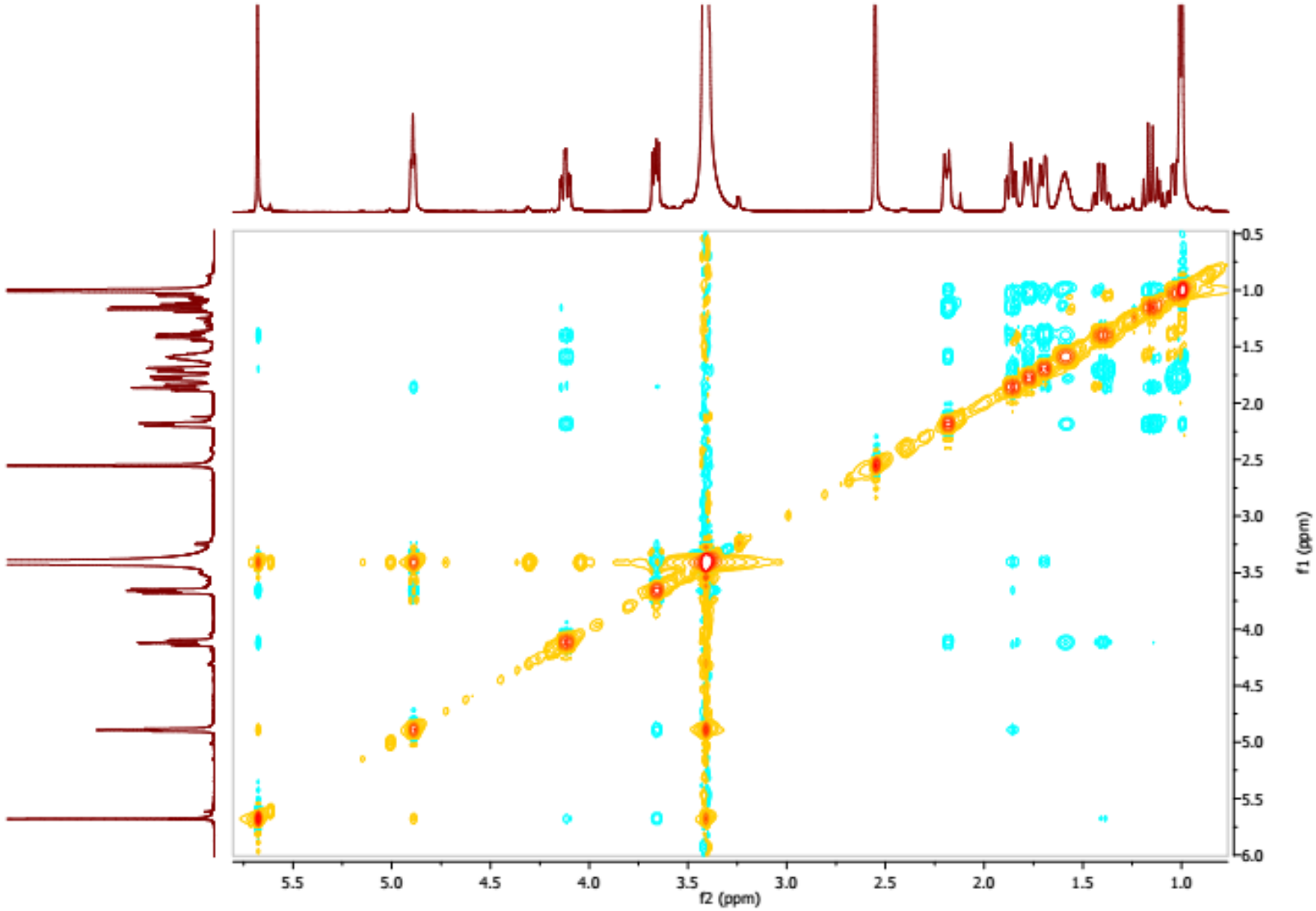
$^{13}$C-NMR of compound **18**



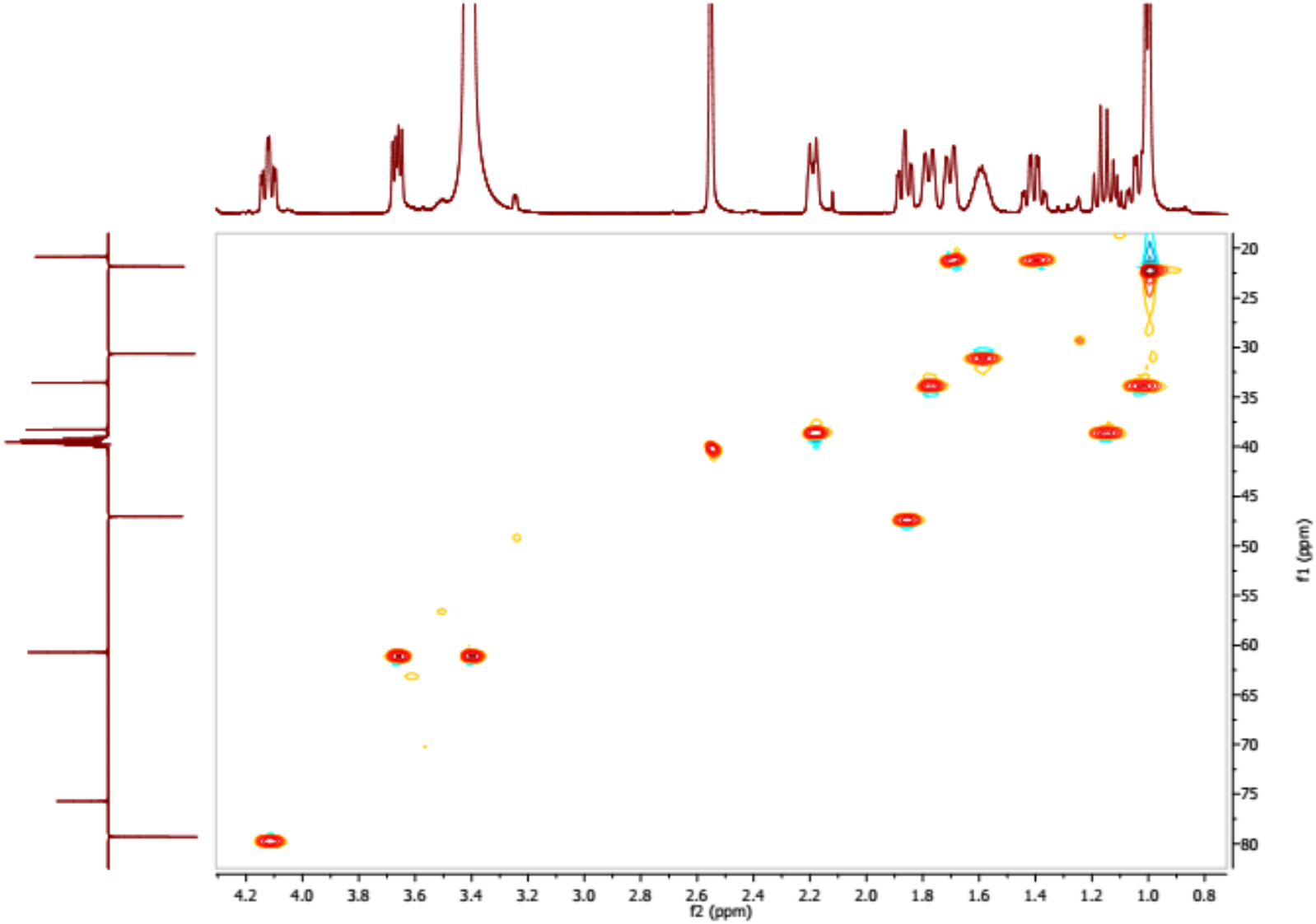
COSY of counpound **18**



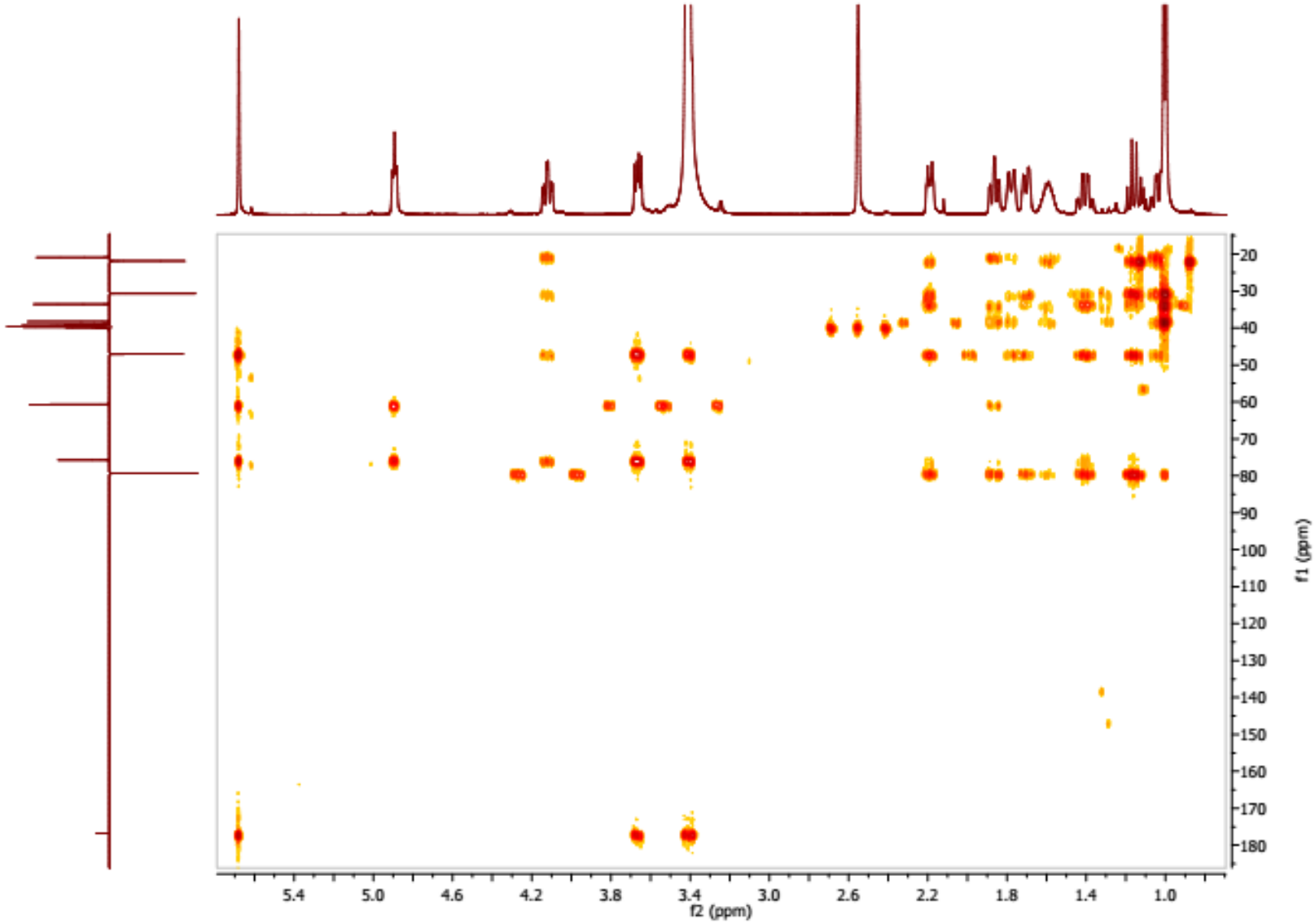
NOESY of compound **18**



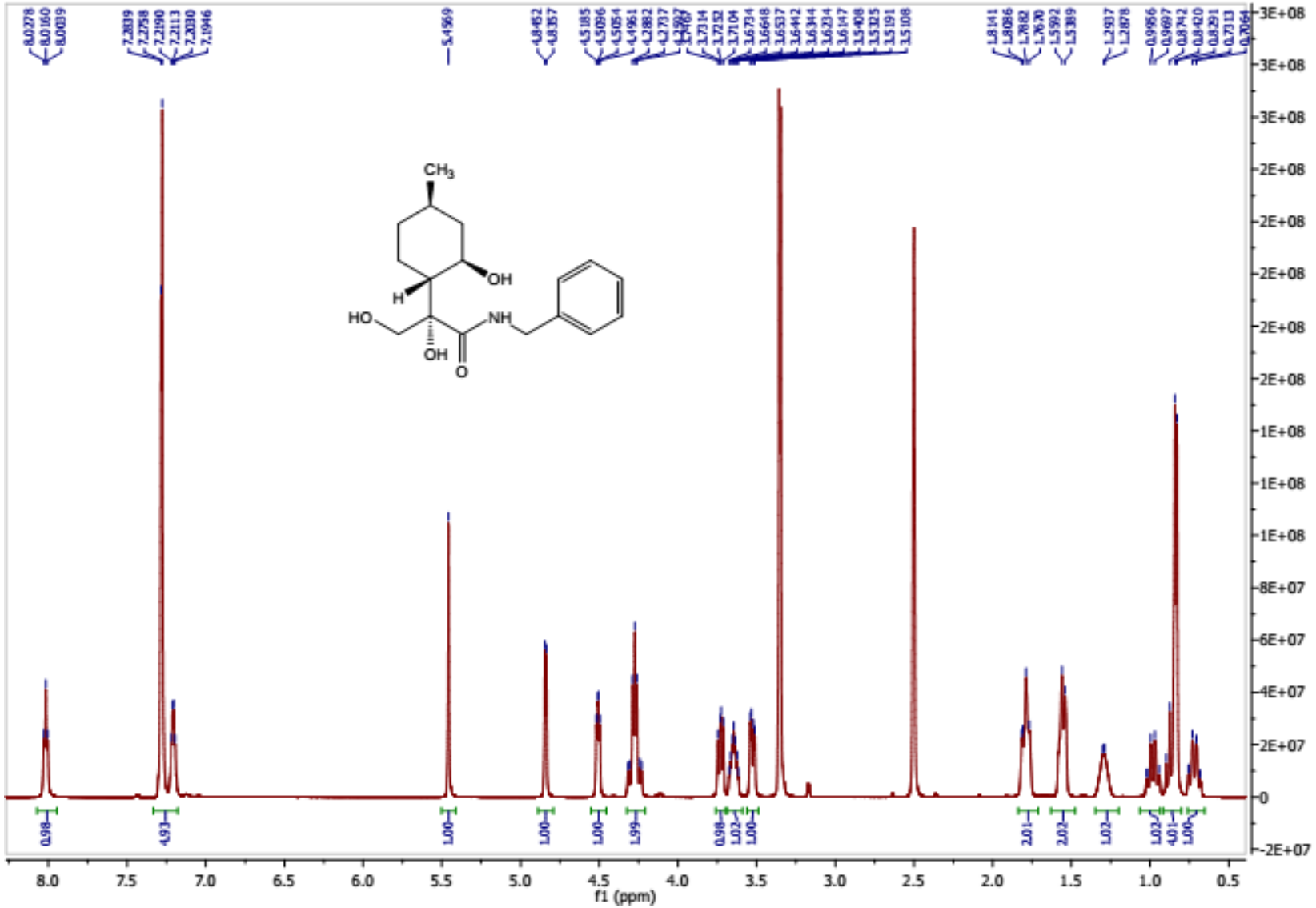
HSQC of compound **18**



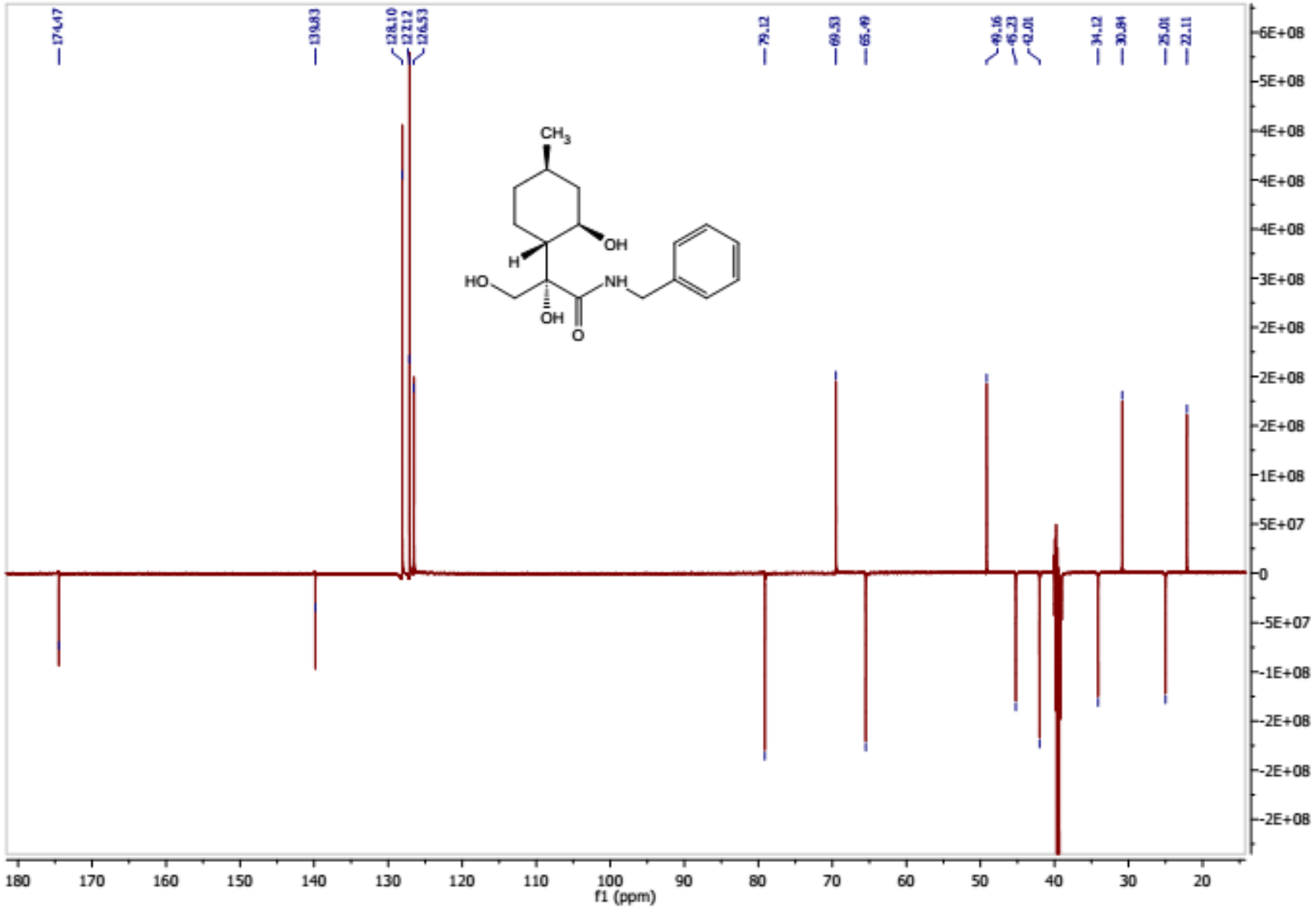
HMBC of compound **18**



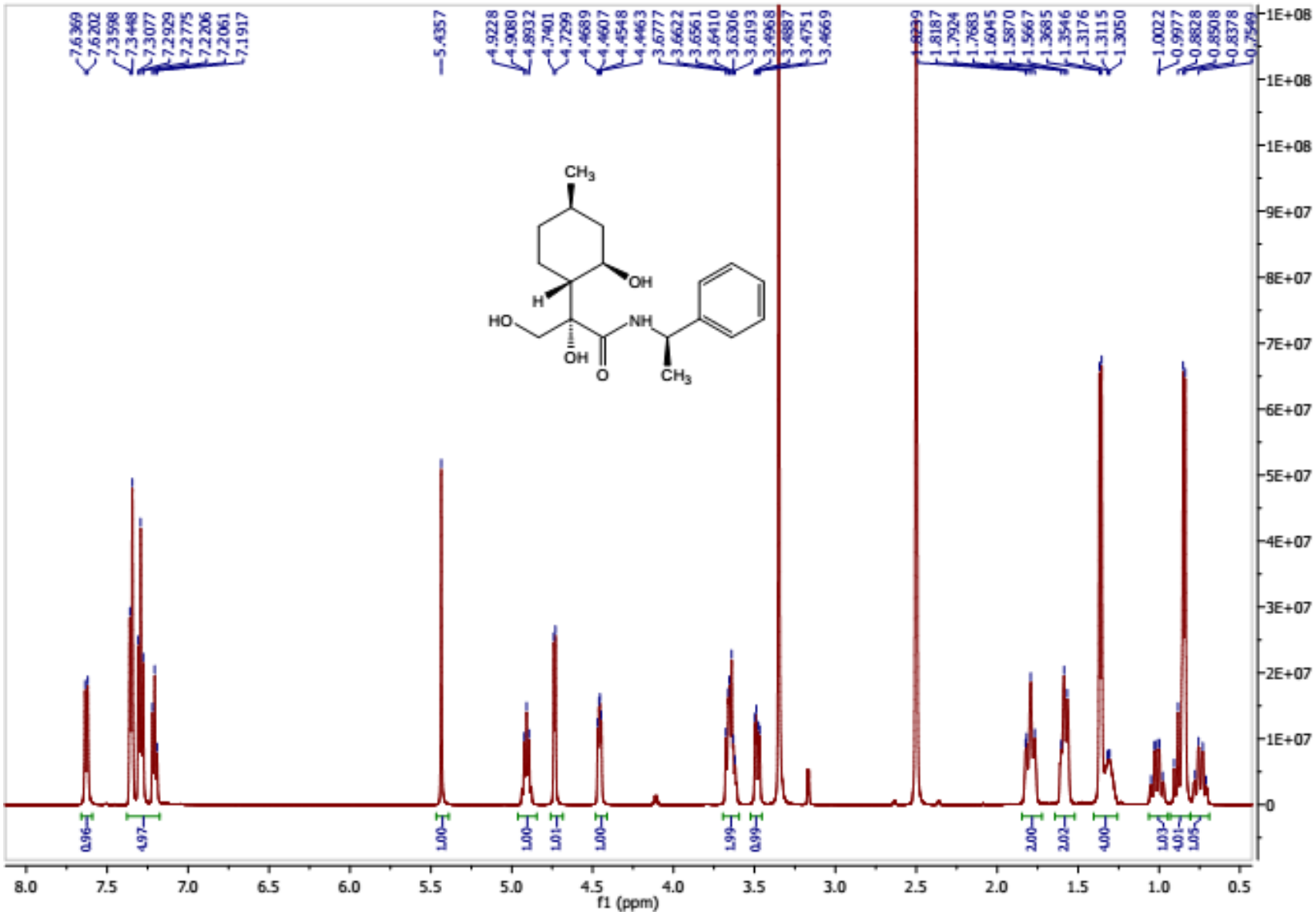
[1]H-NMR of compound **19**



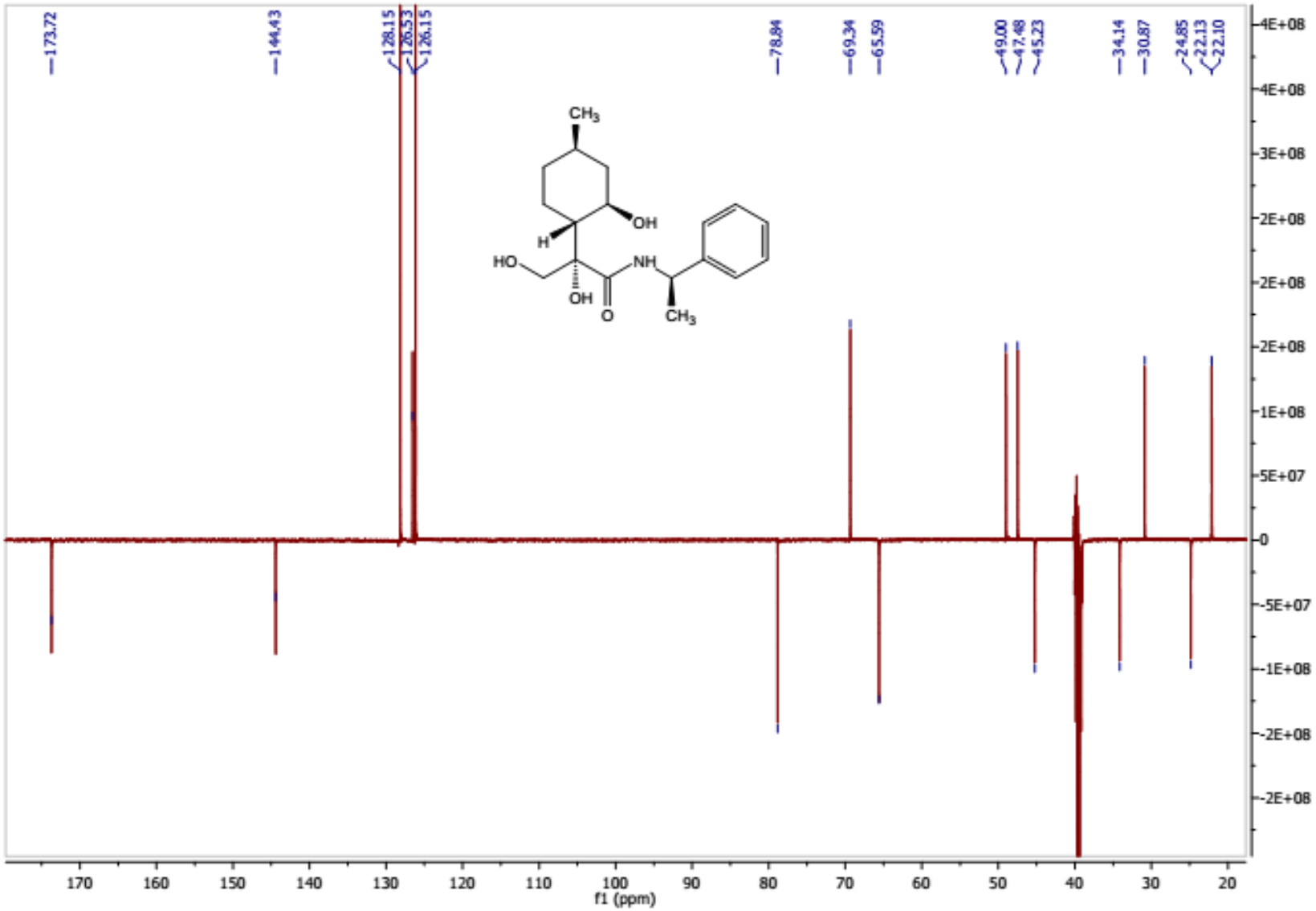
$^{13}$C-NMR of compound **19**



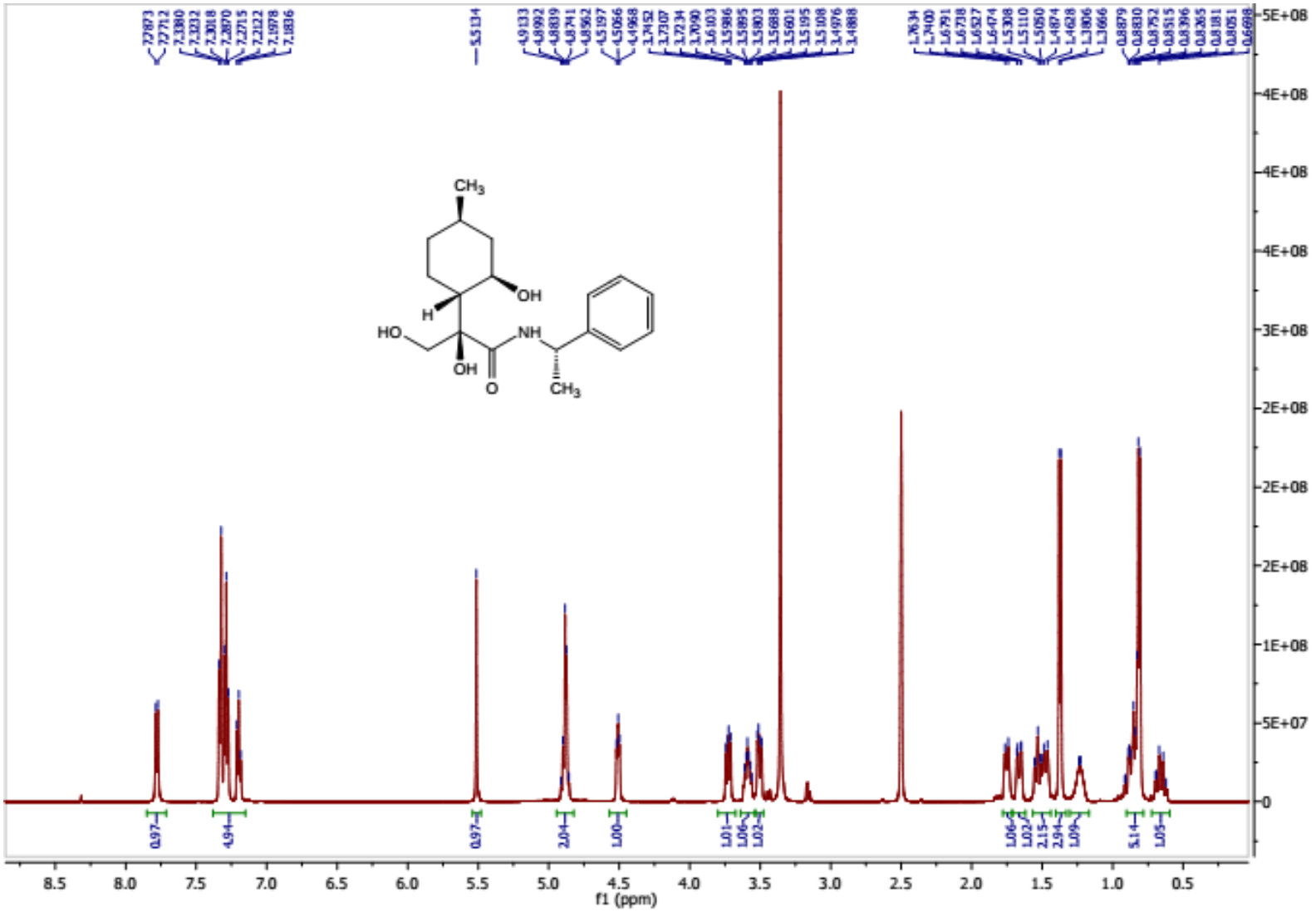
[1]H-NMR of compound **20**



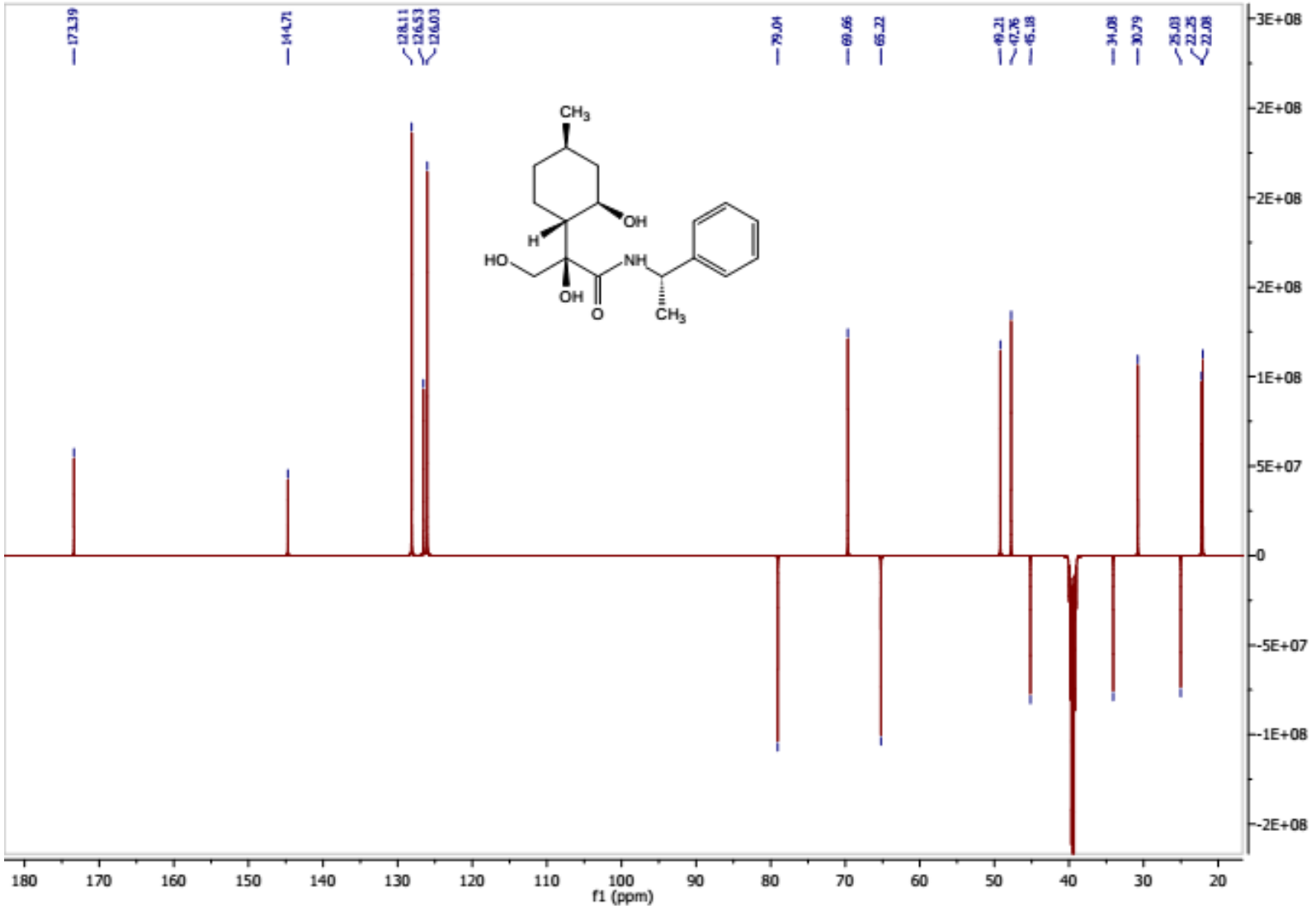
$^{13}$C-NMR of compound **20**



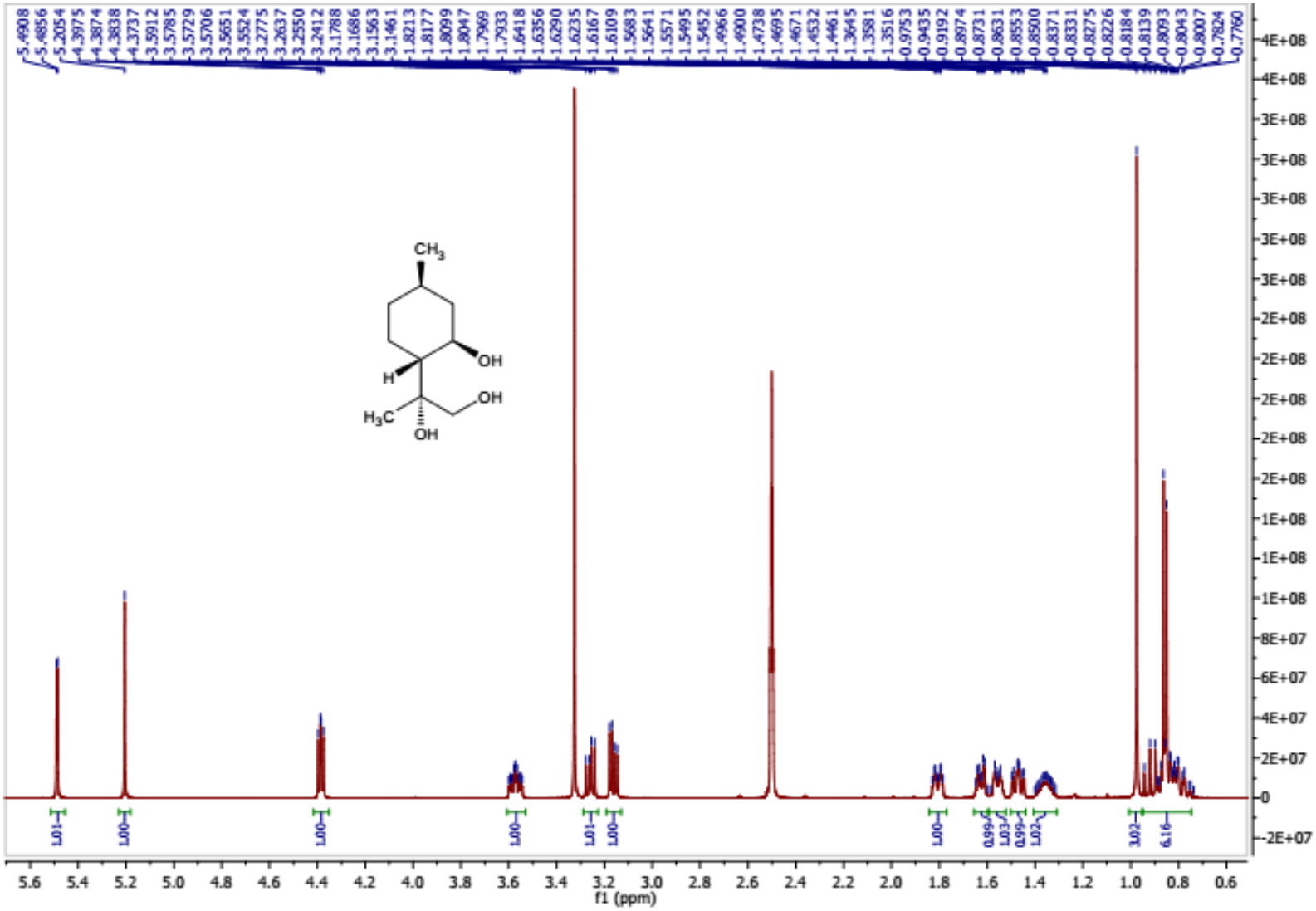
[1]H-NMR of compound **21**



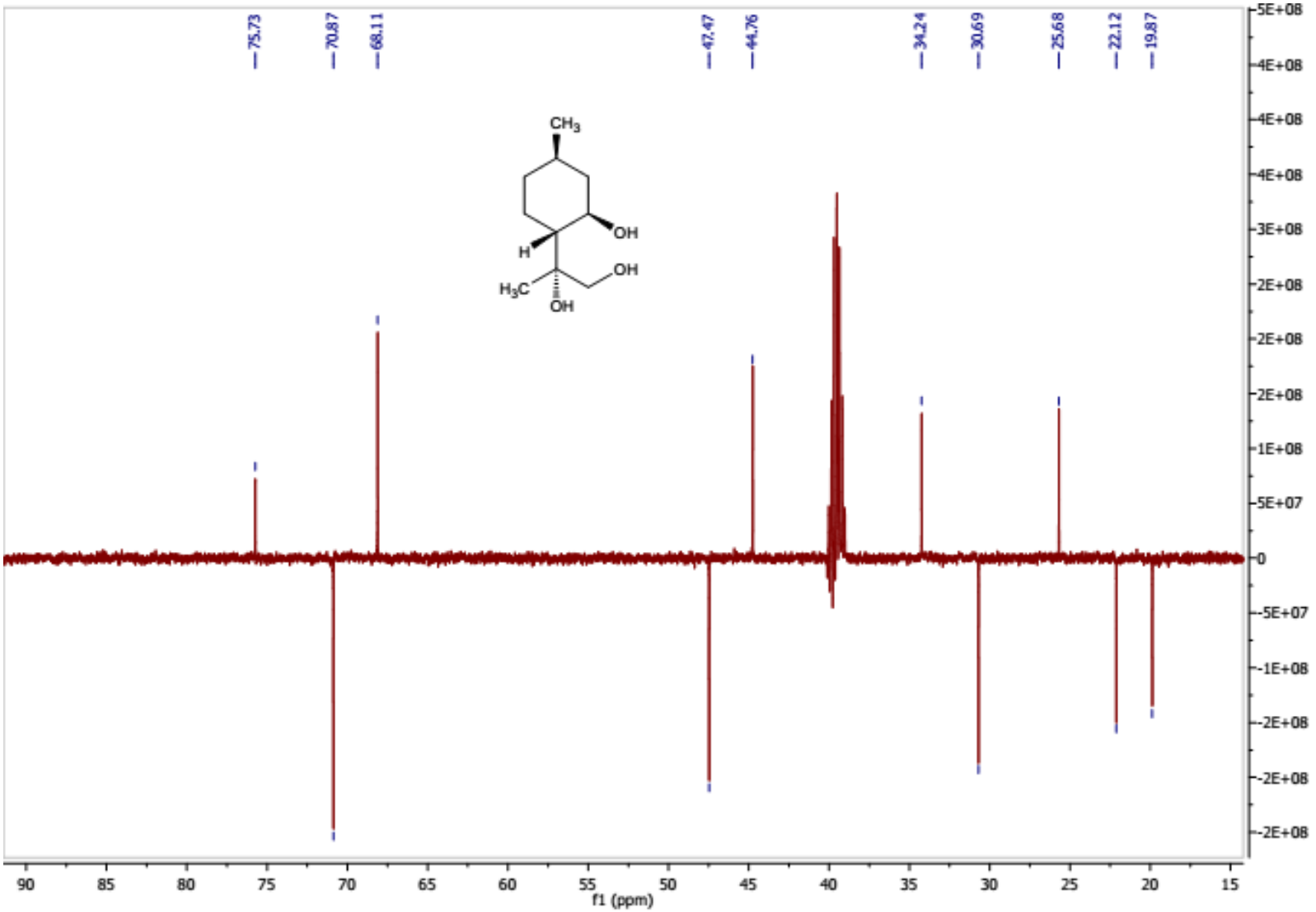
$^{13}$C-NMR of compound **21**



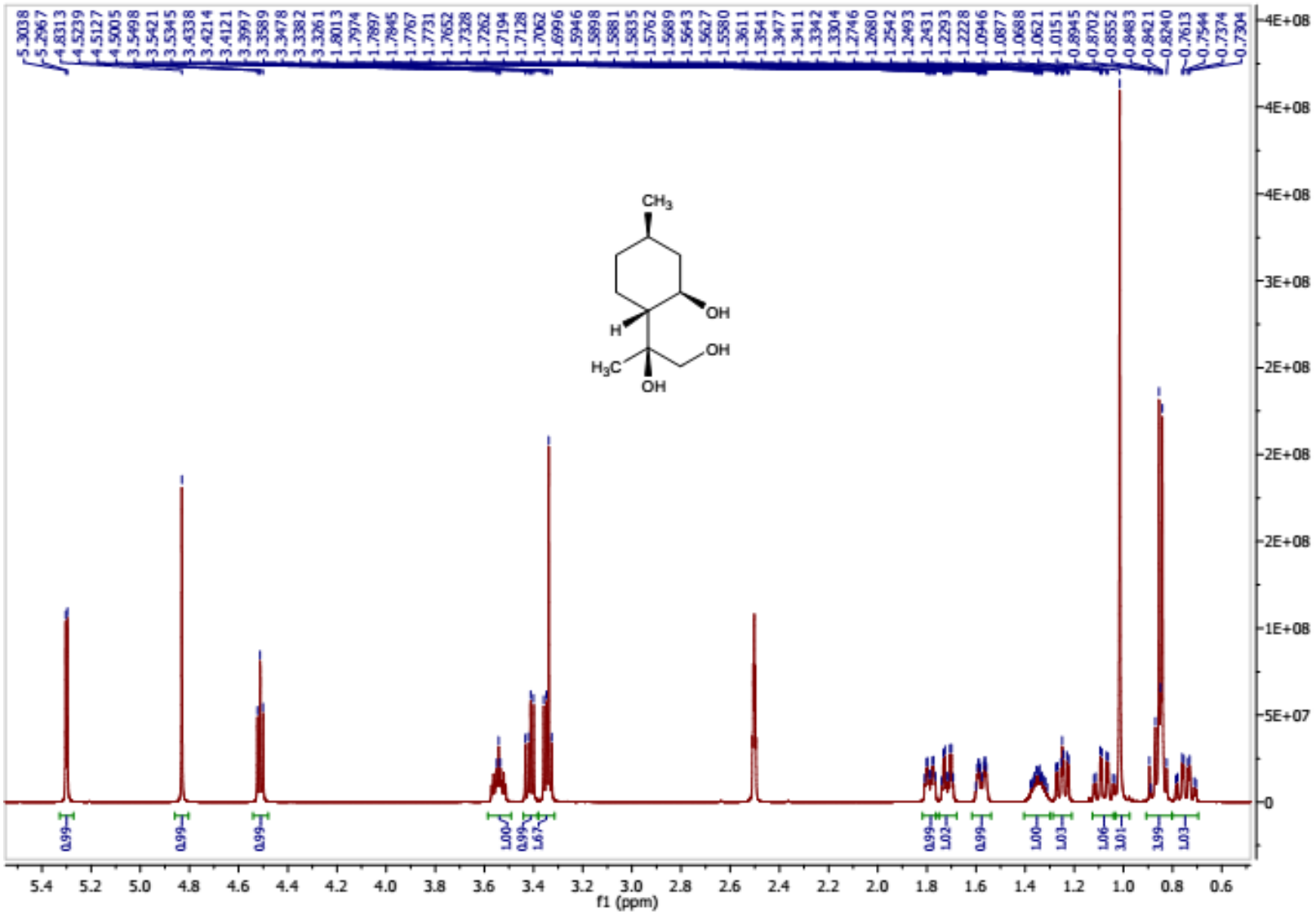
[1]H-NMR of compound **22a**



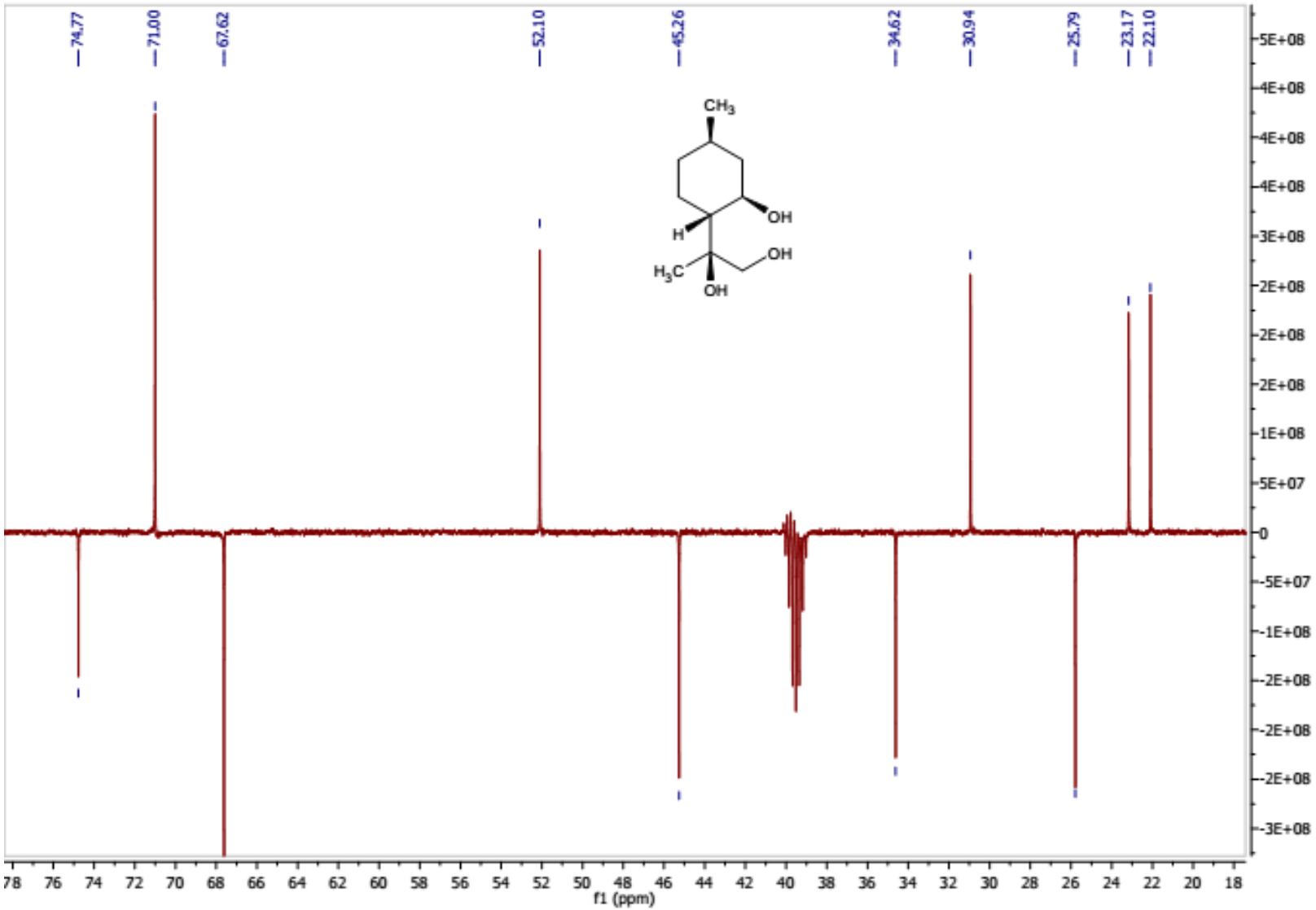
$^{13}$C-NMR of compound **22a**



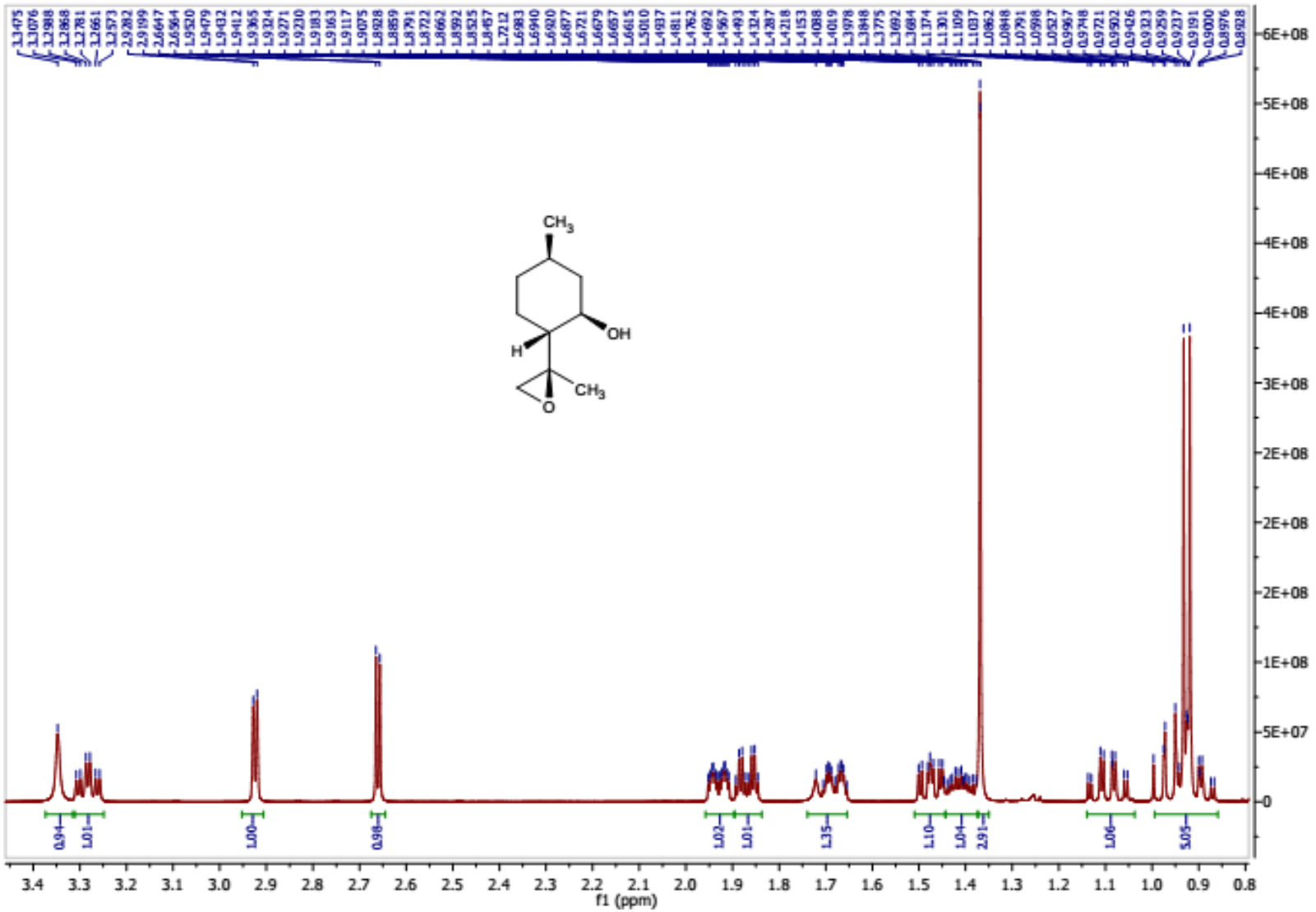
[1]H-NMR of compound **22b**



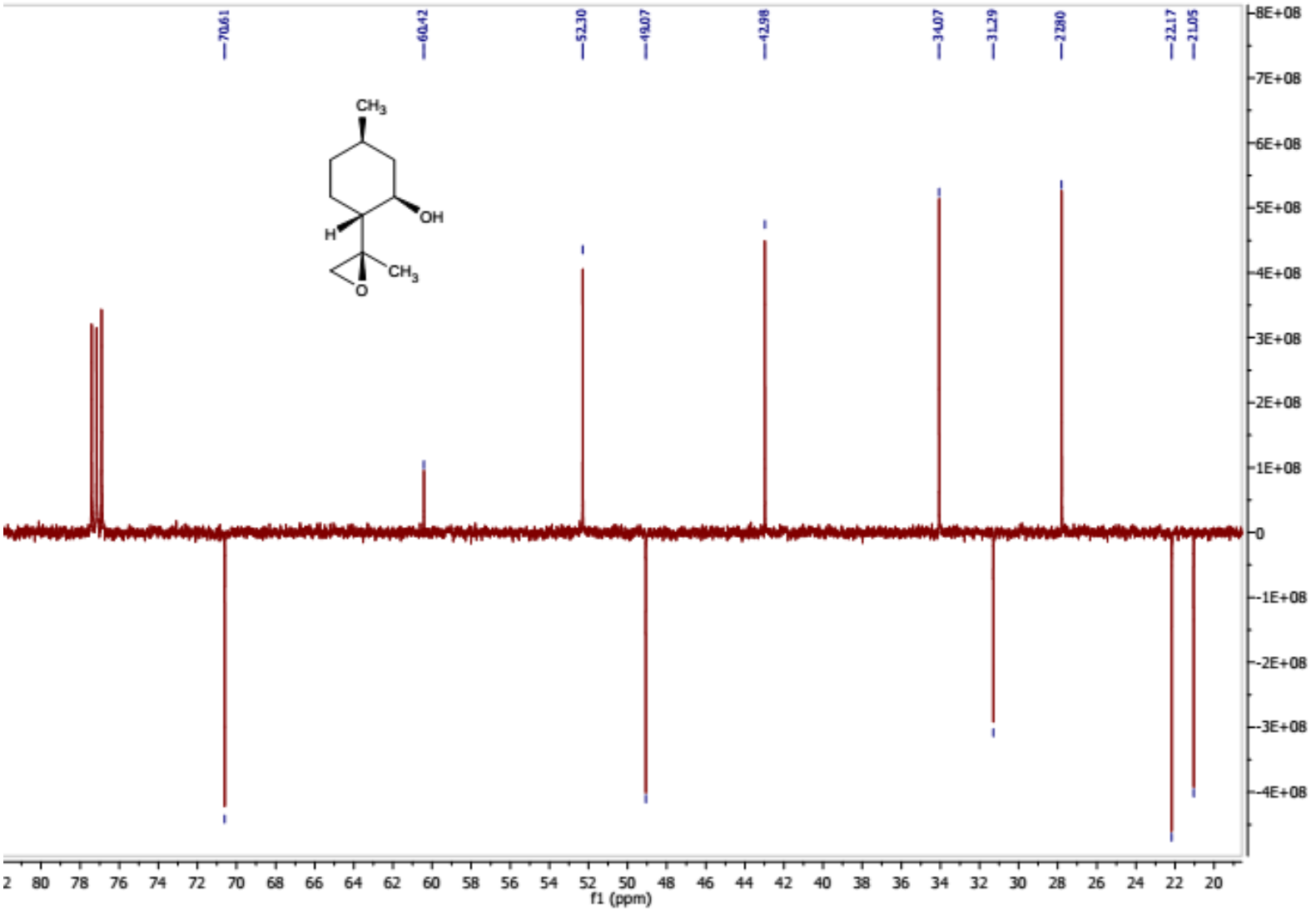
$^{13}$C-NMR of compound **22b**



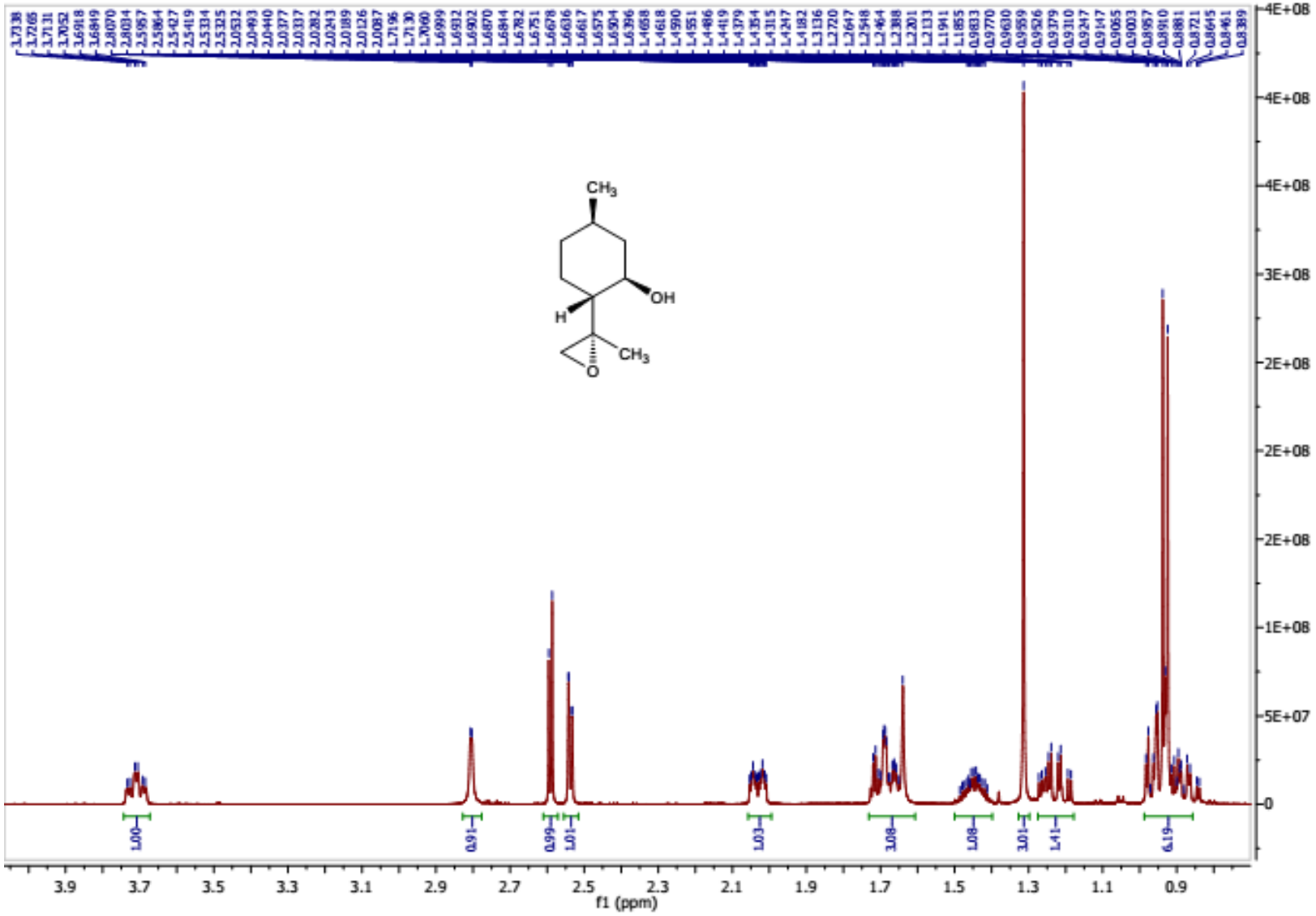
$^{1}$H-NMR of compound **23a**



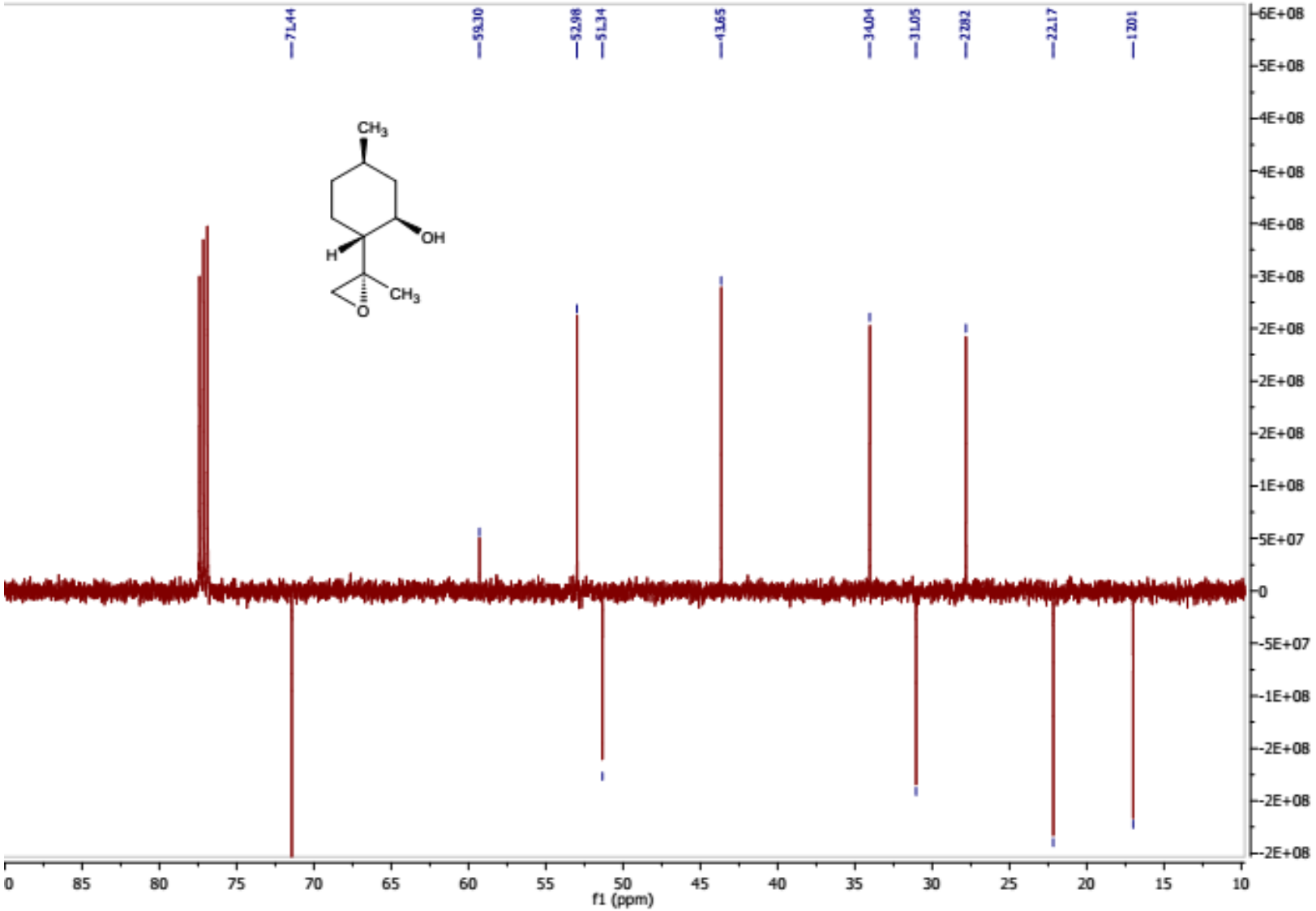
$^{13}$C-NMR of compound **23a**



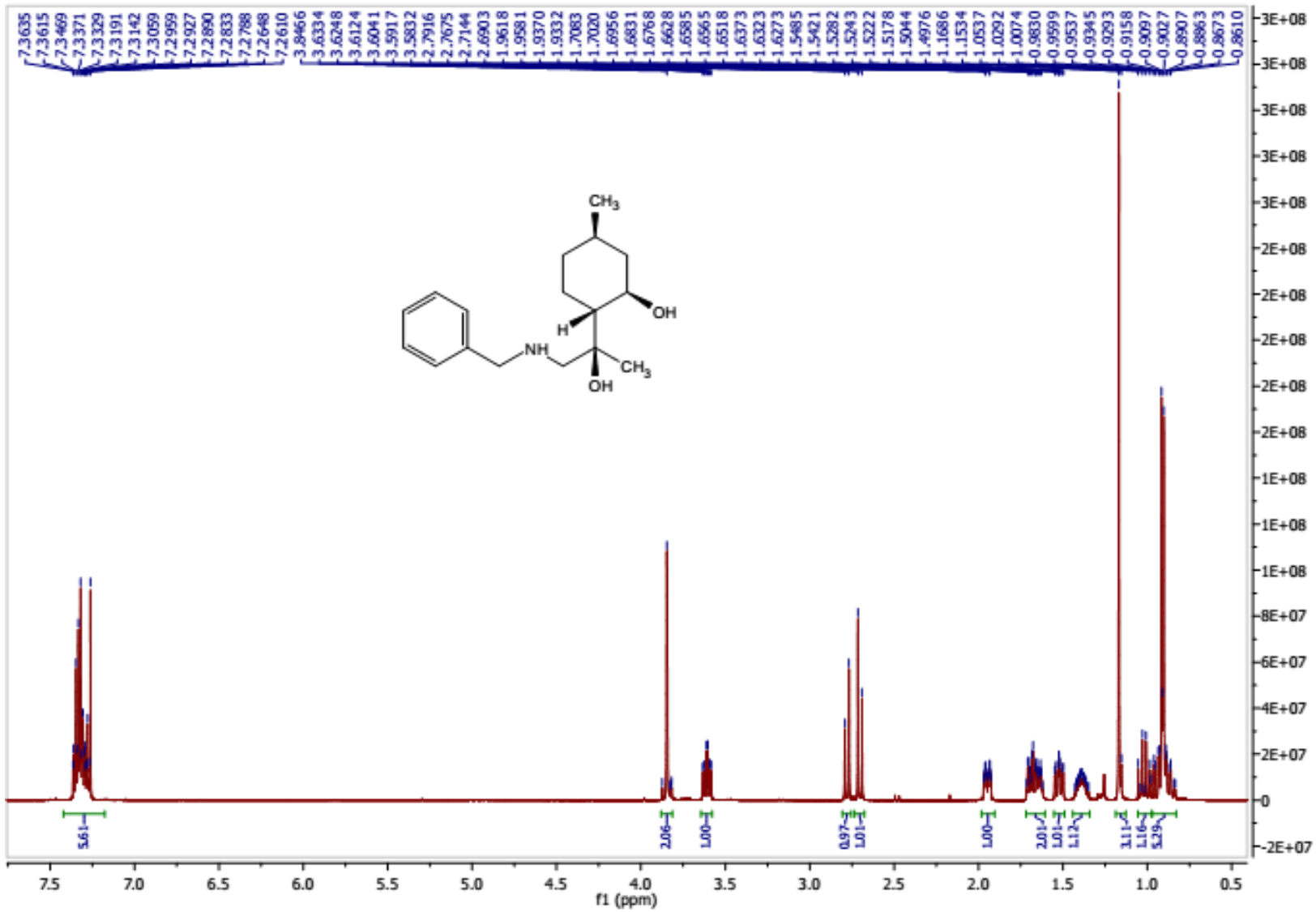
$^{1}$H-NMR of compound **23b**



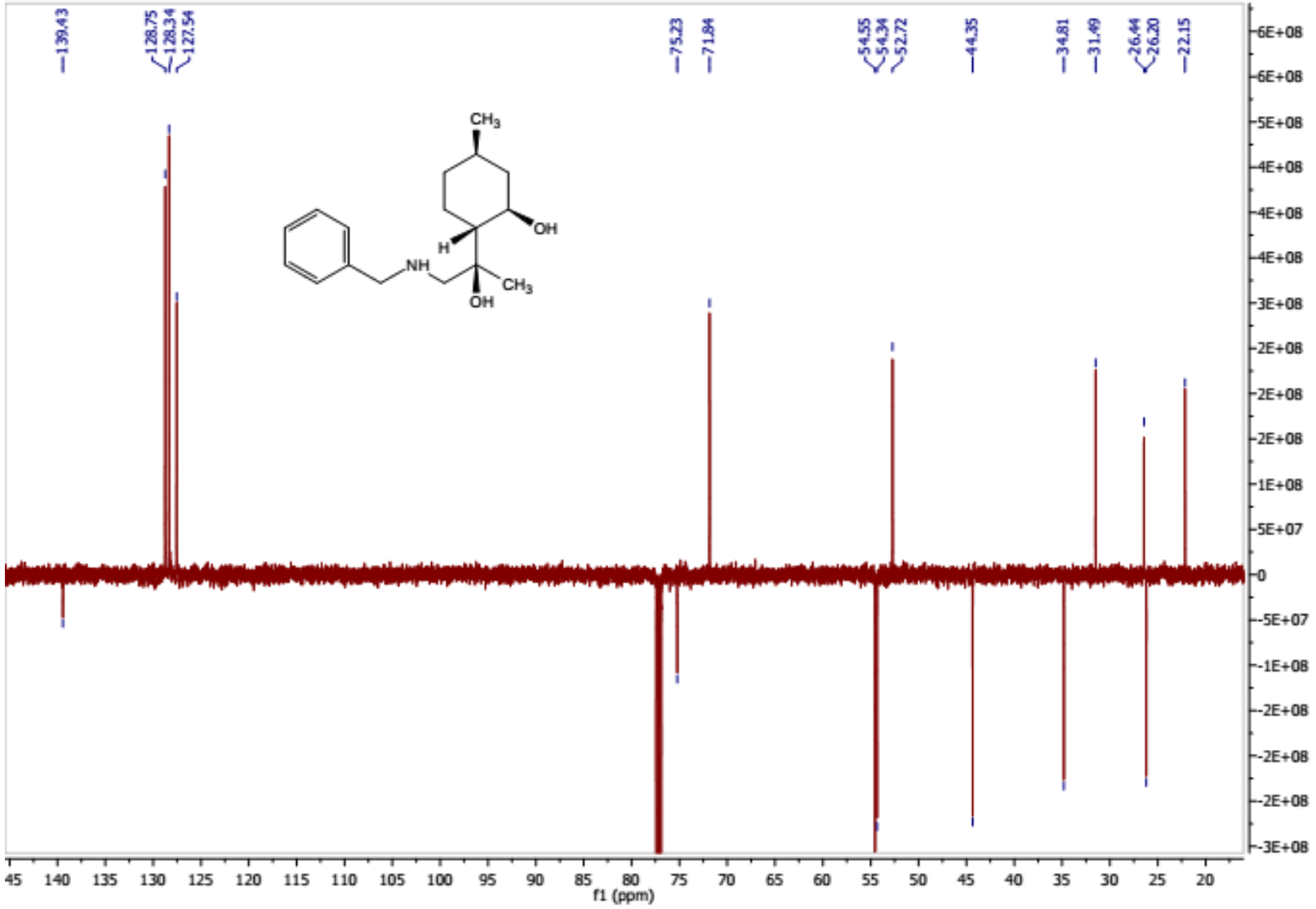
$^{13}$C-NMR of compound **23a**



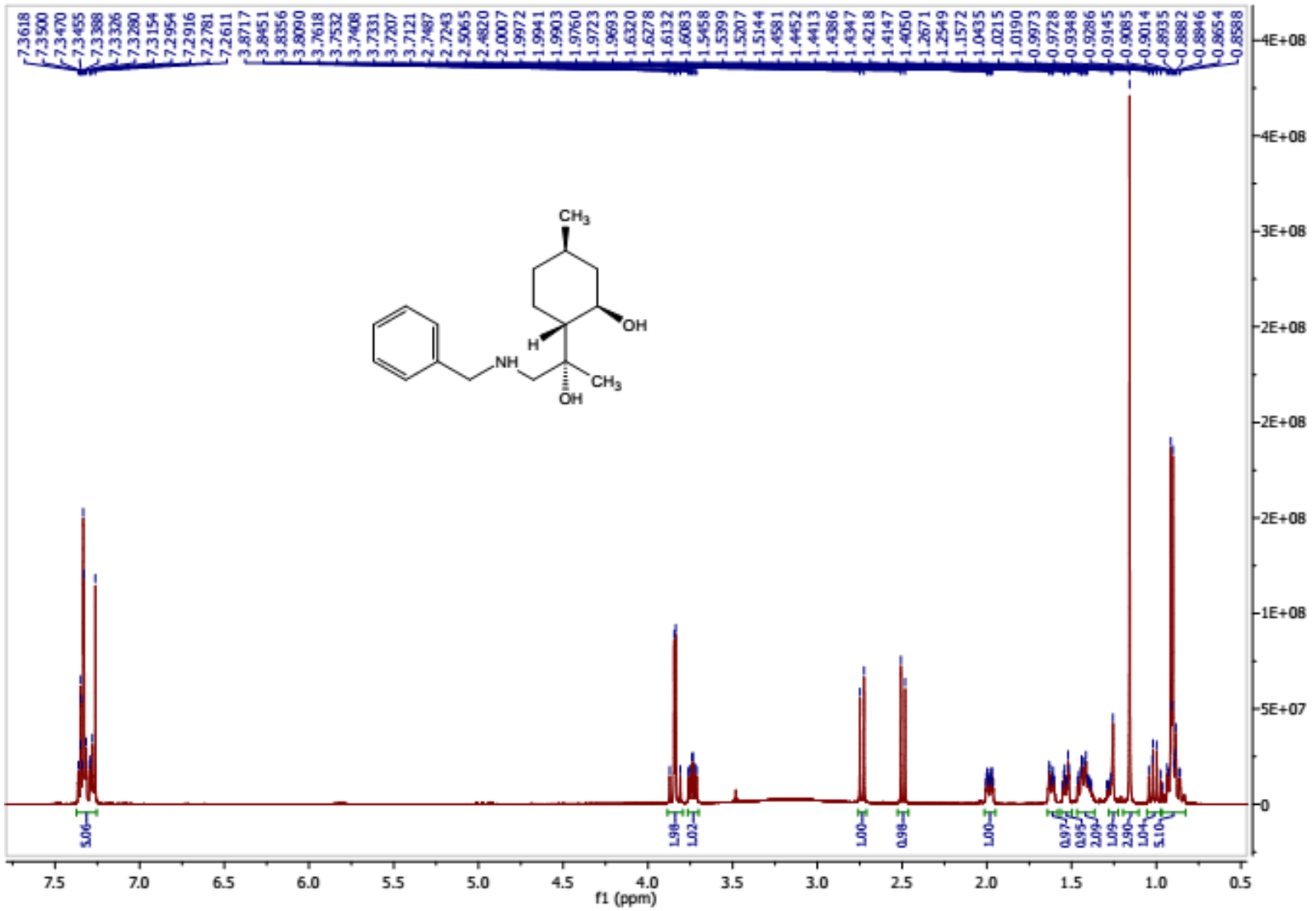
[1]H-NMR of compound **24a**



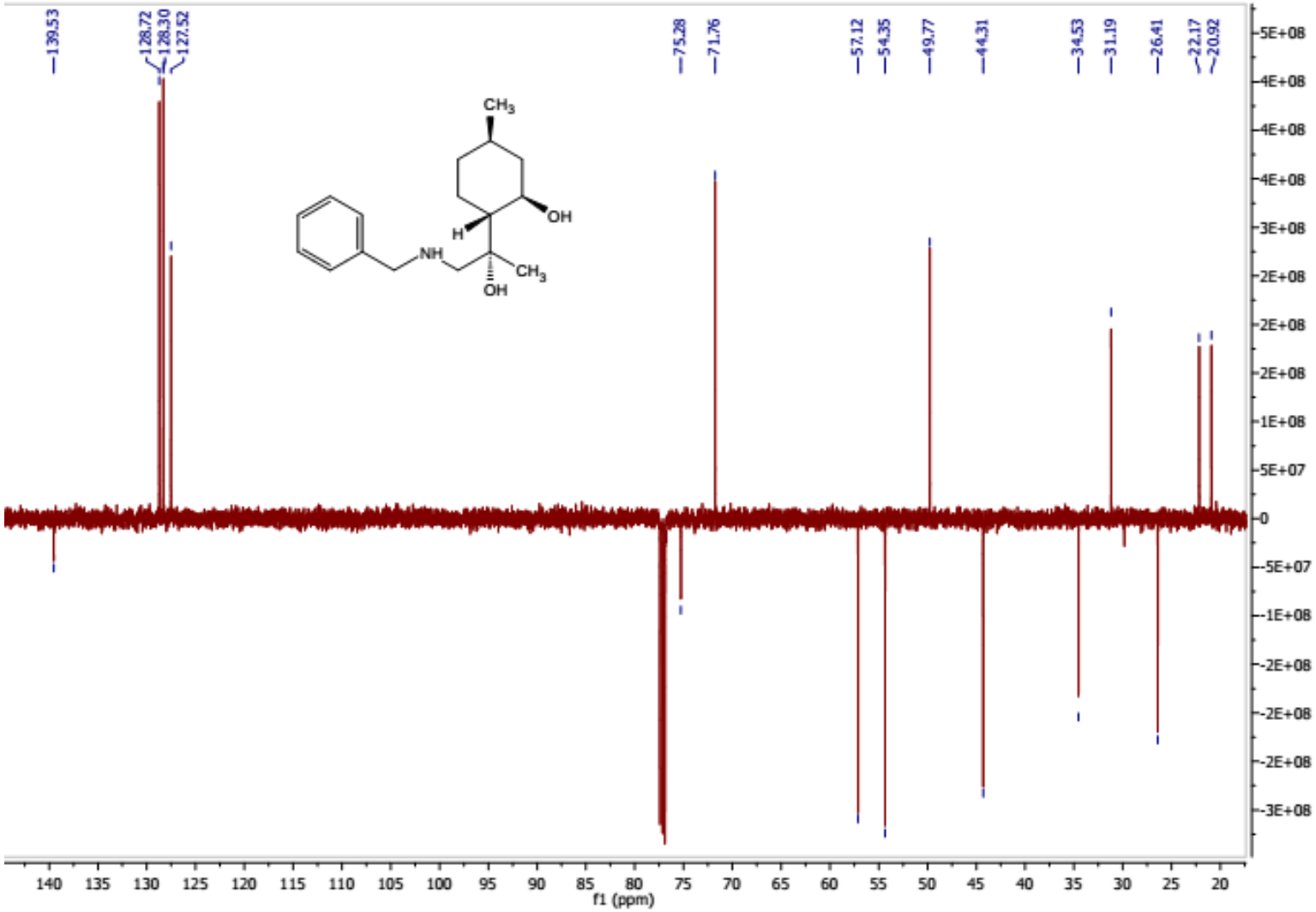
$^{13}$C-NMR of compound **24a**



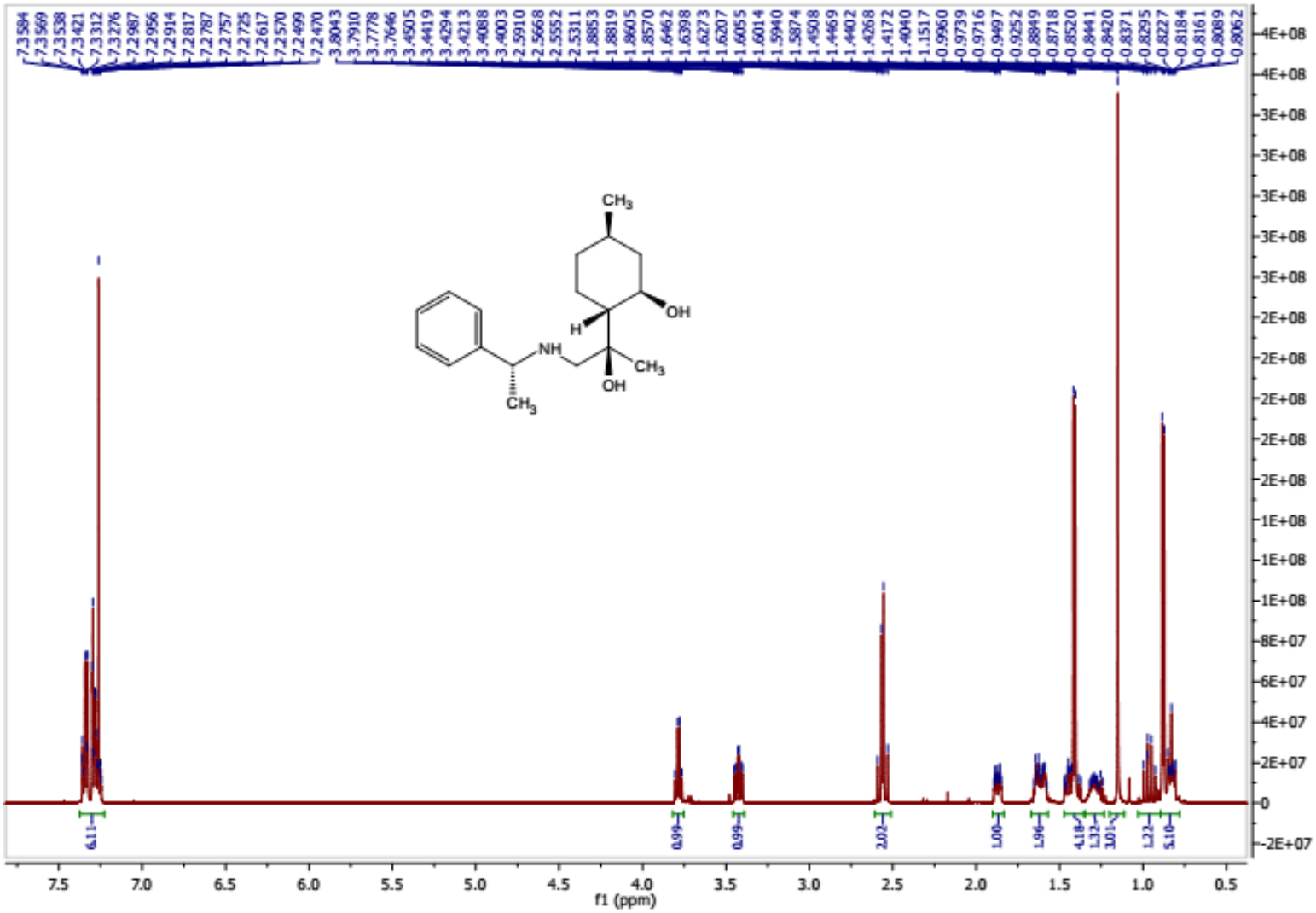
[1]H-NMR of compound **24b**



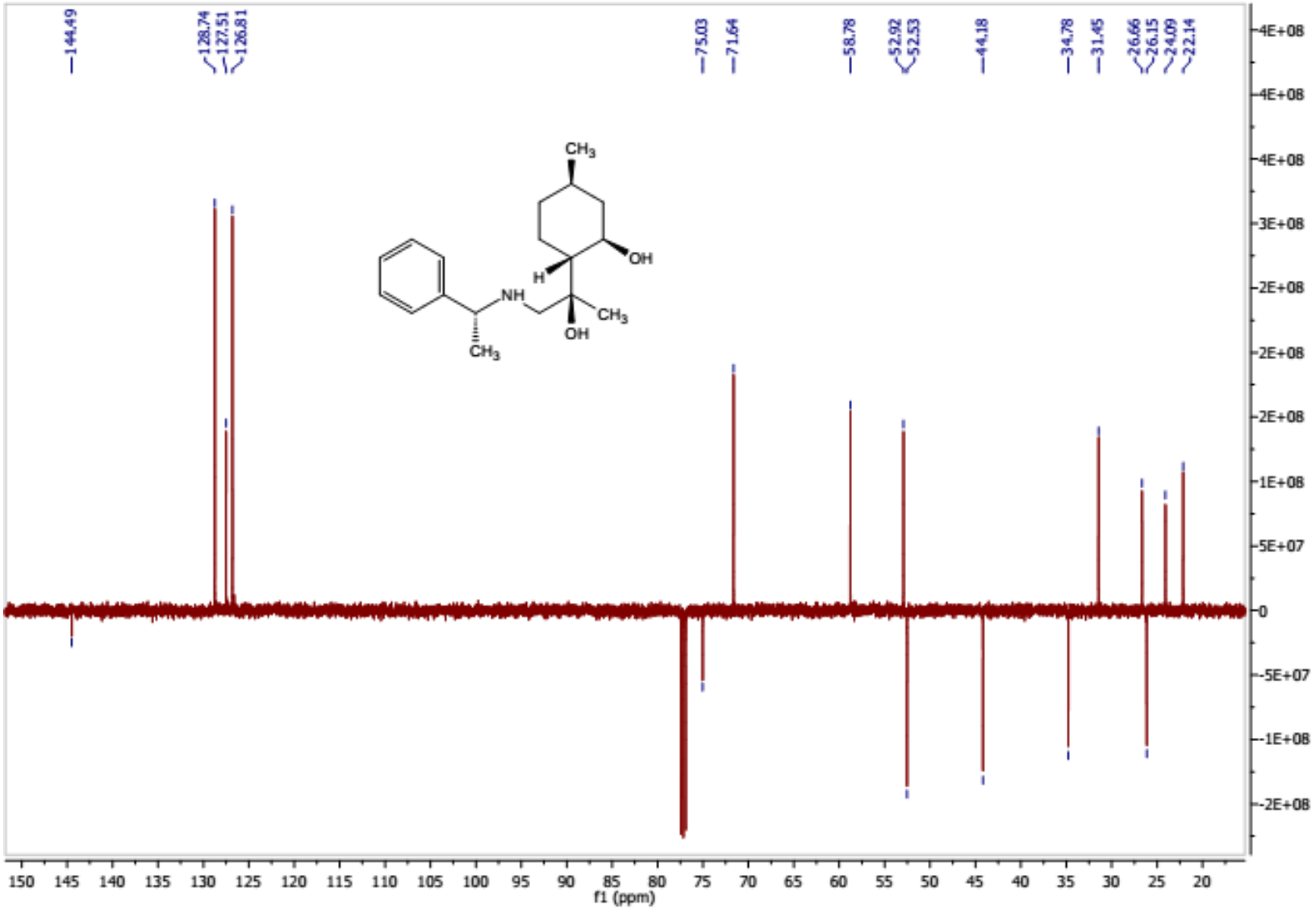
$^{13}$C-NMR of compound **24b**



[1]H-NMR of compound **25a**



$^{13}$C-NMR of compound **25a**



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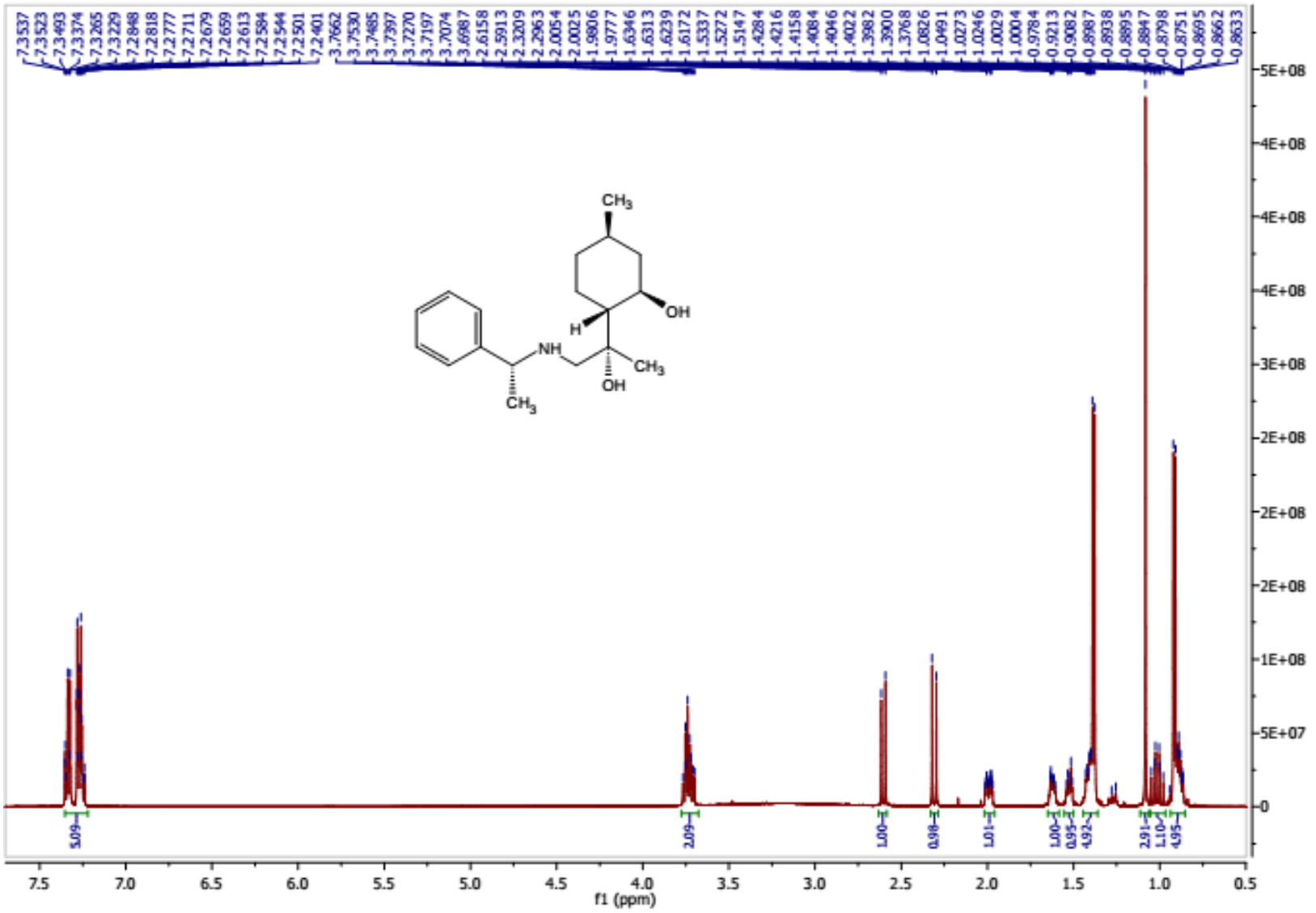
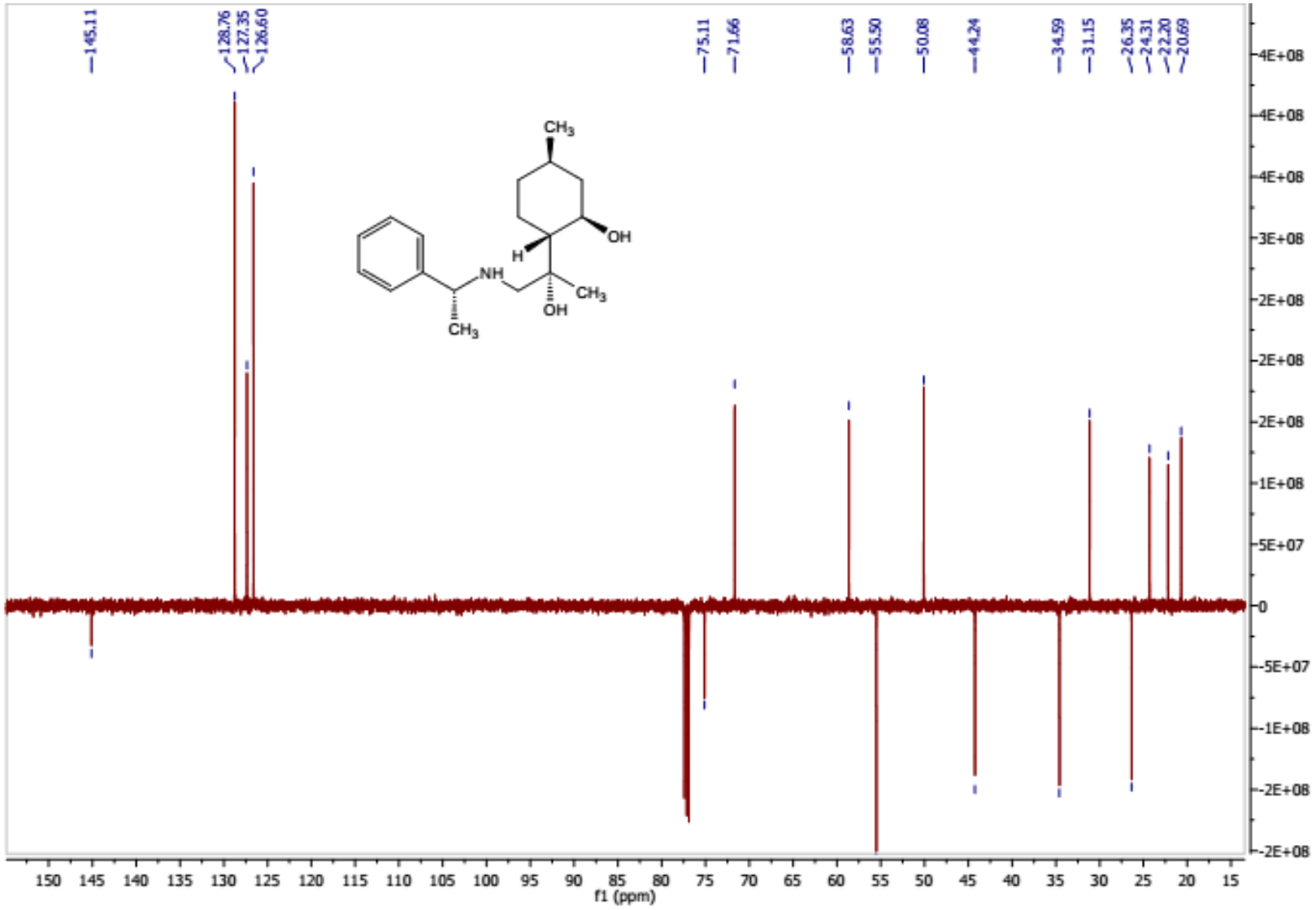
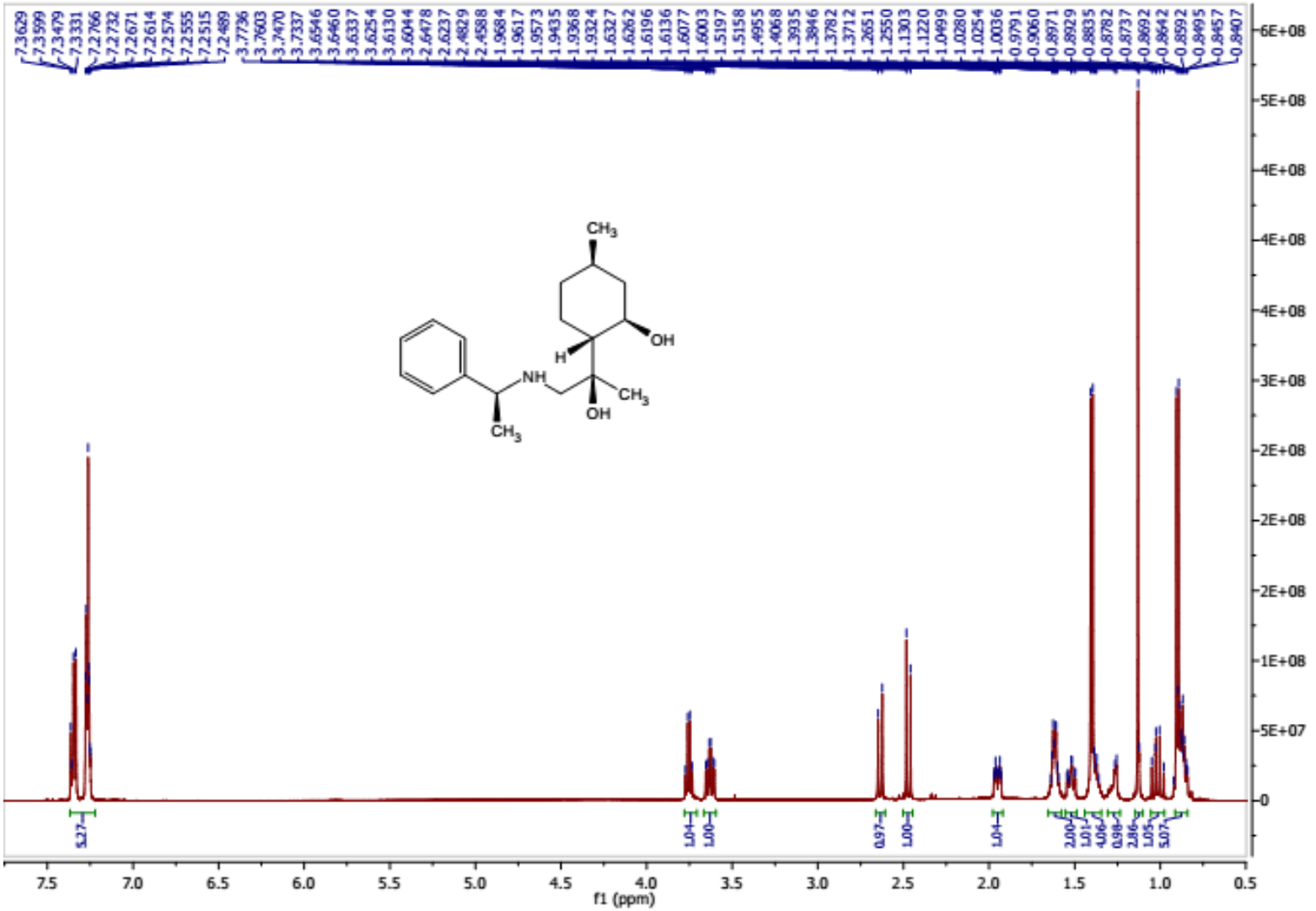


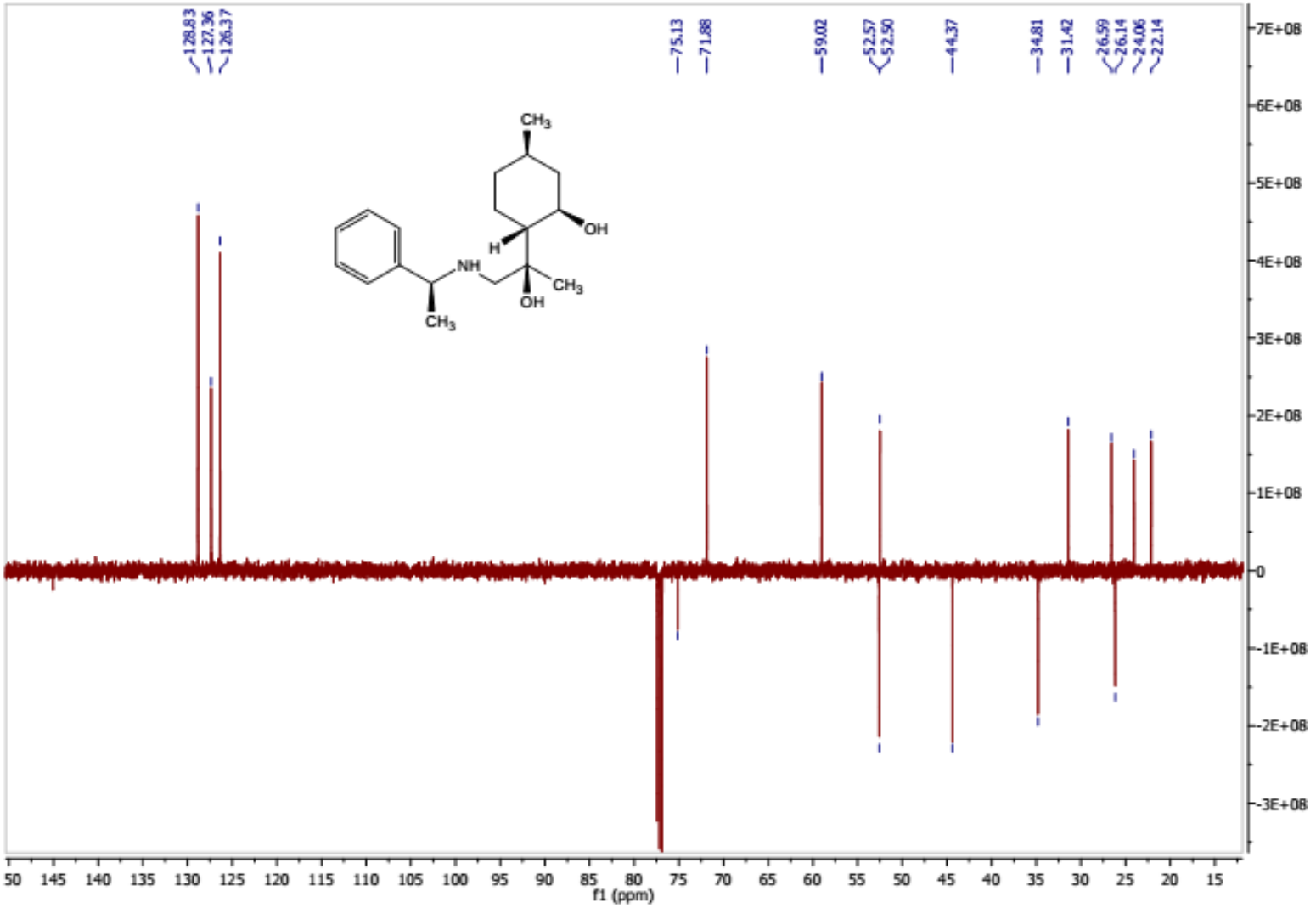
$^{13}$C-NMR of compound **25b**



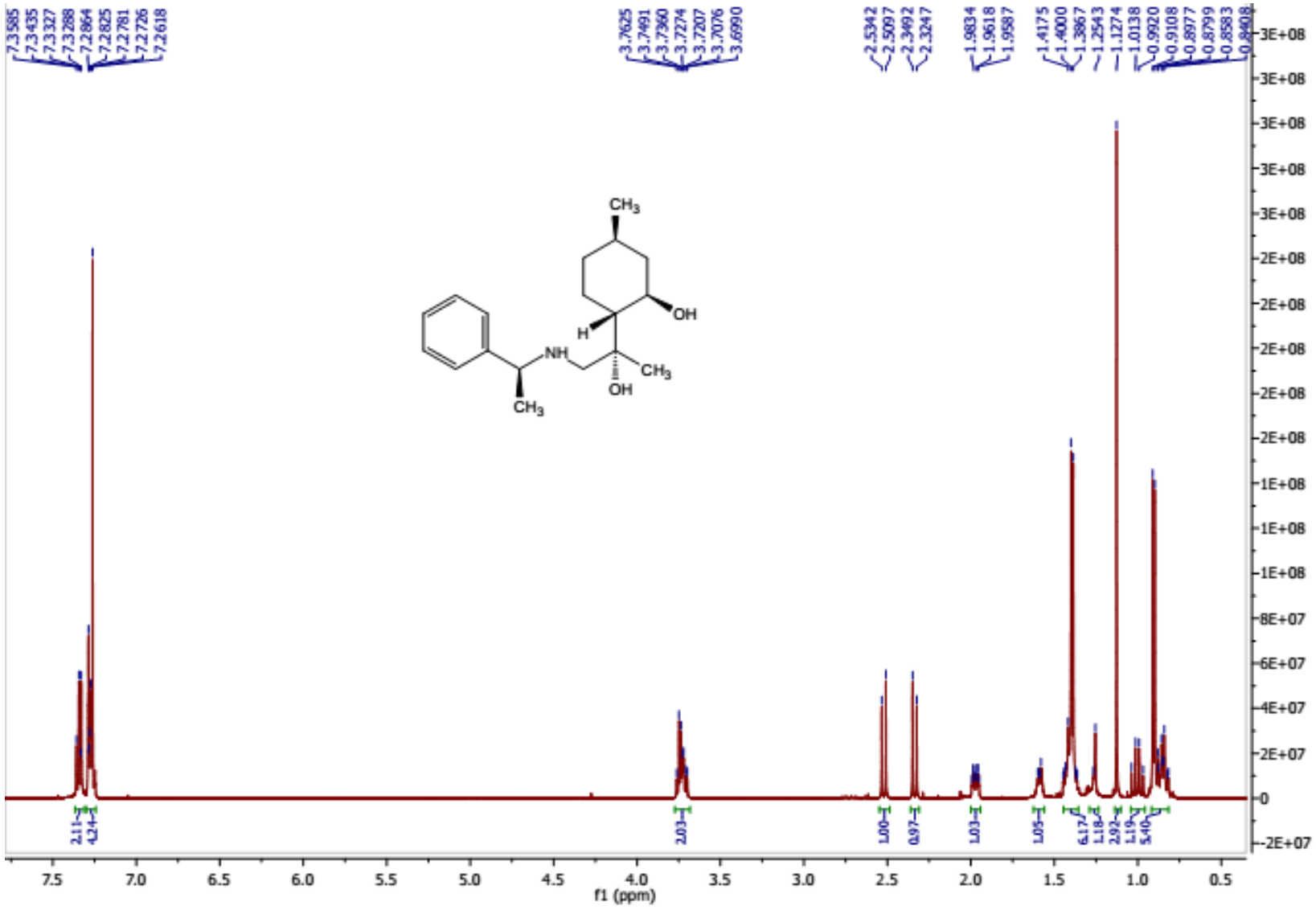
[1]H-NMR of compound **26a**



$^{13}$C-NMR of compound **26a**



$^{1}$H-NMR of compound **26b**



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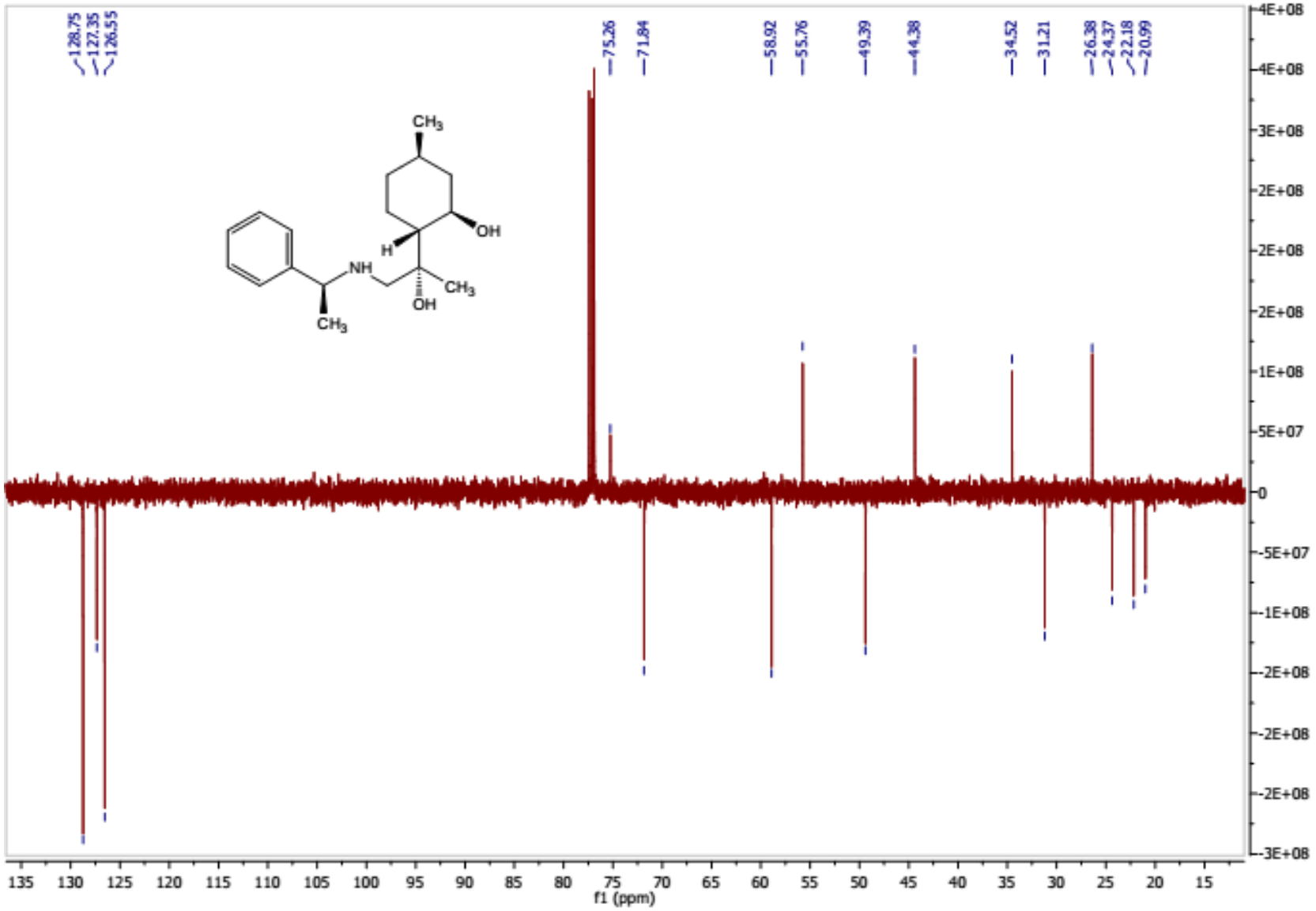

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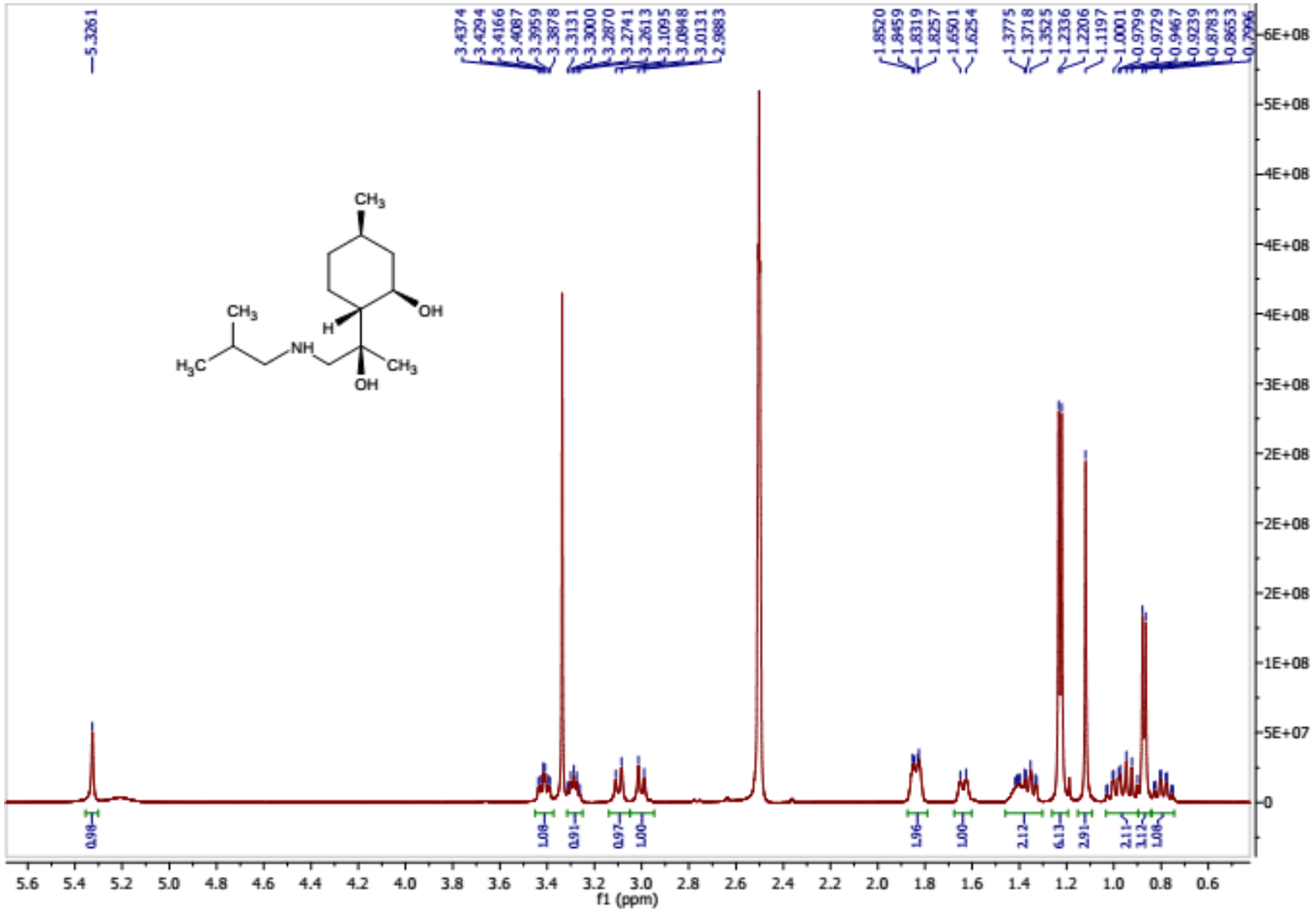
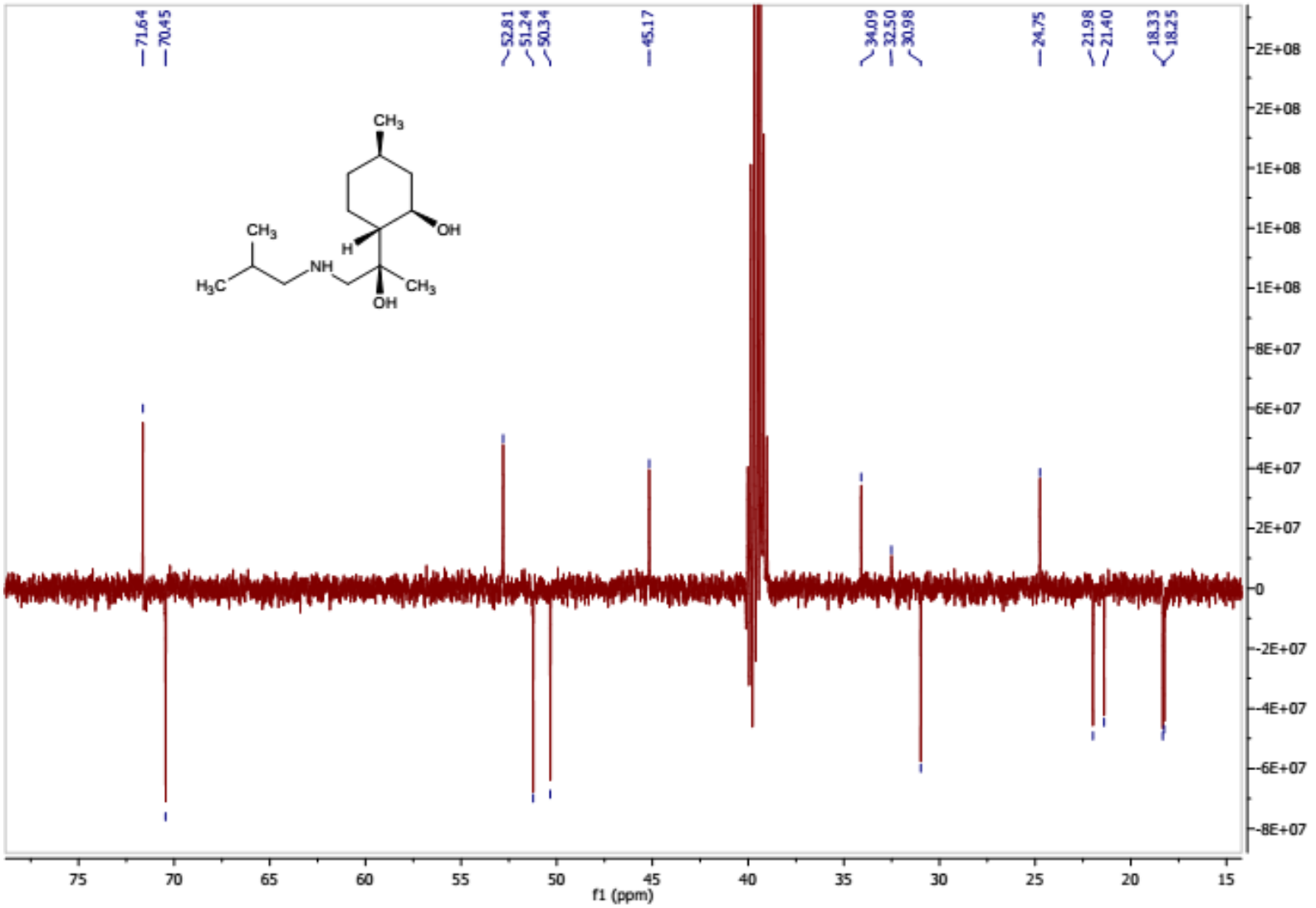


$^{13}$C-NMR of compound **27a**



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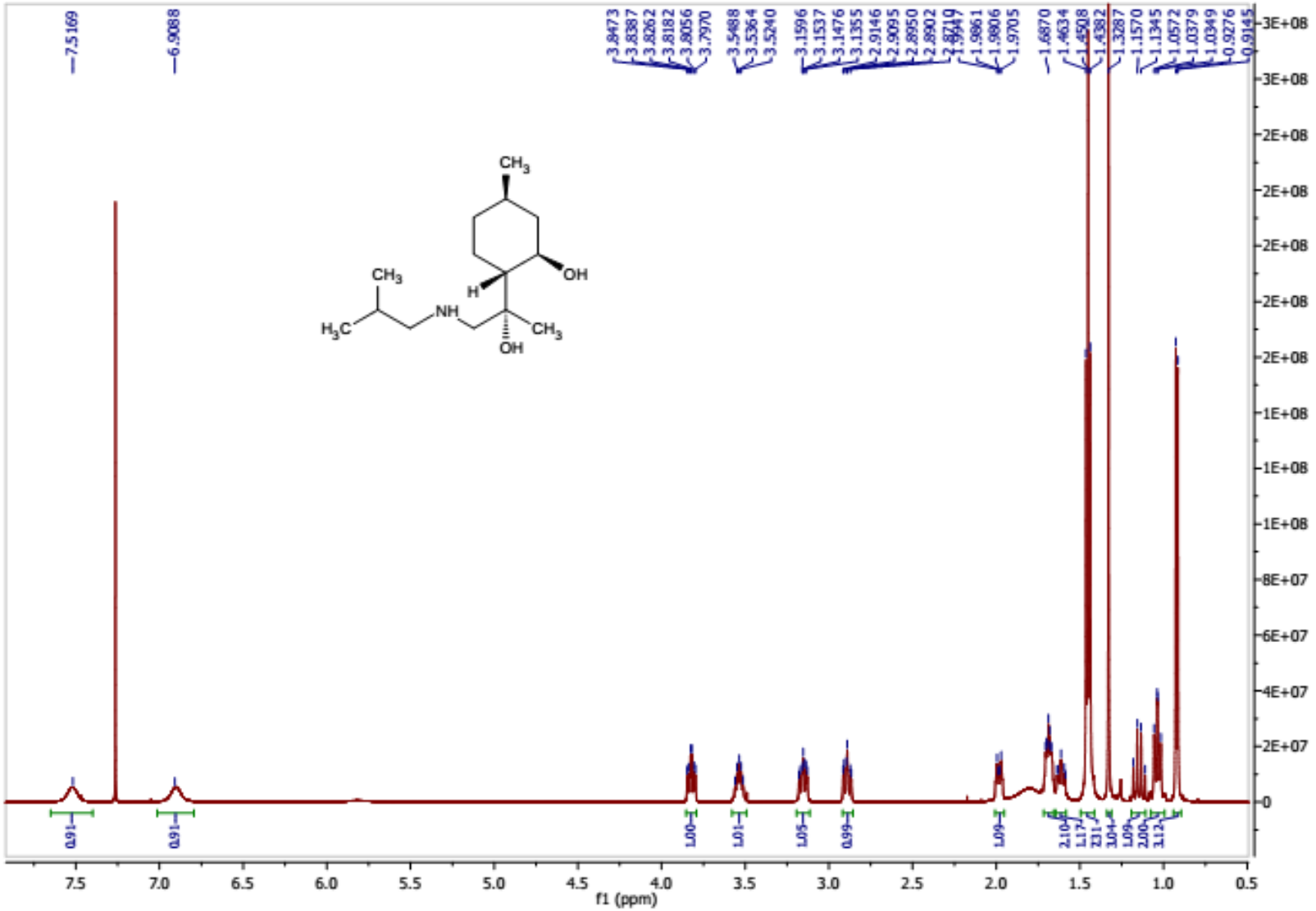
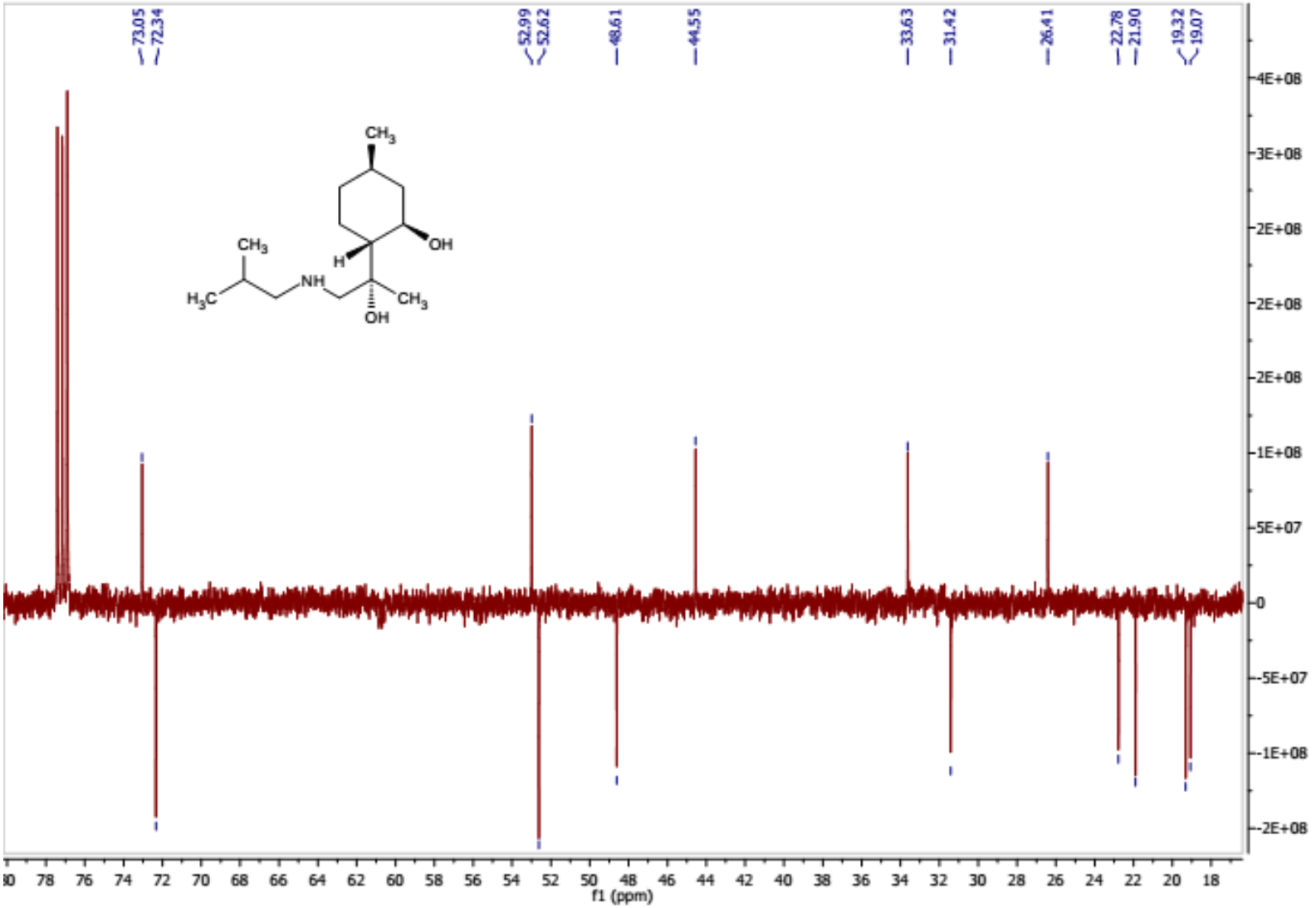


$^{13}$C-NMR of compound **27b**



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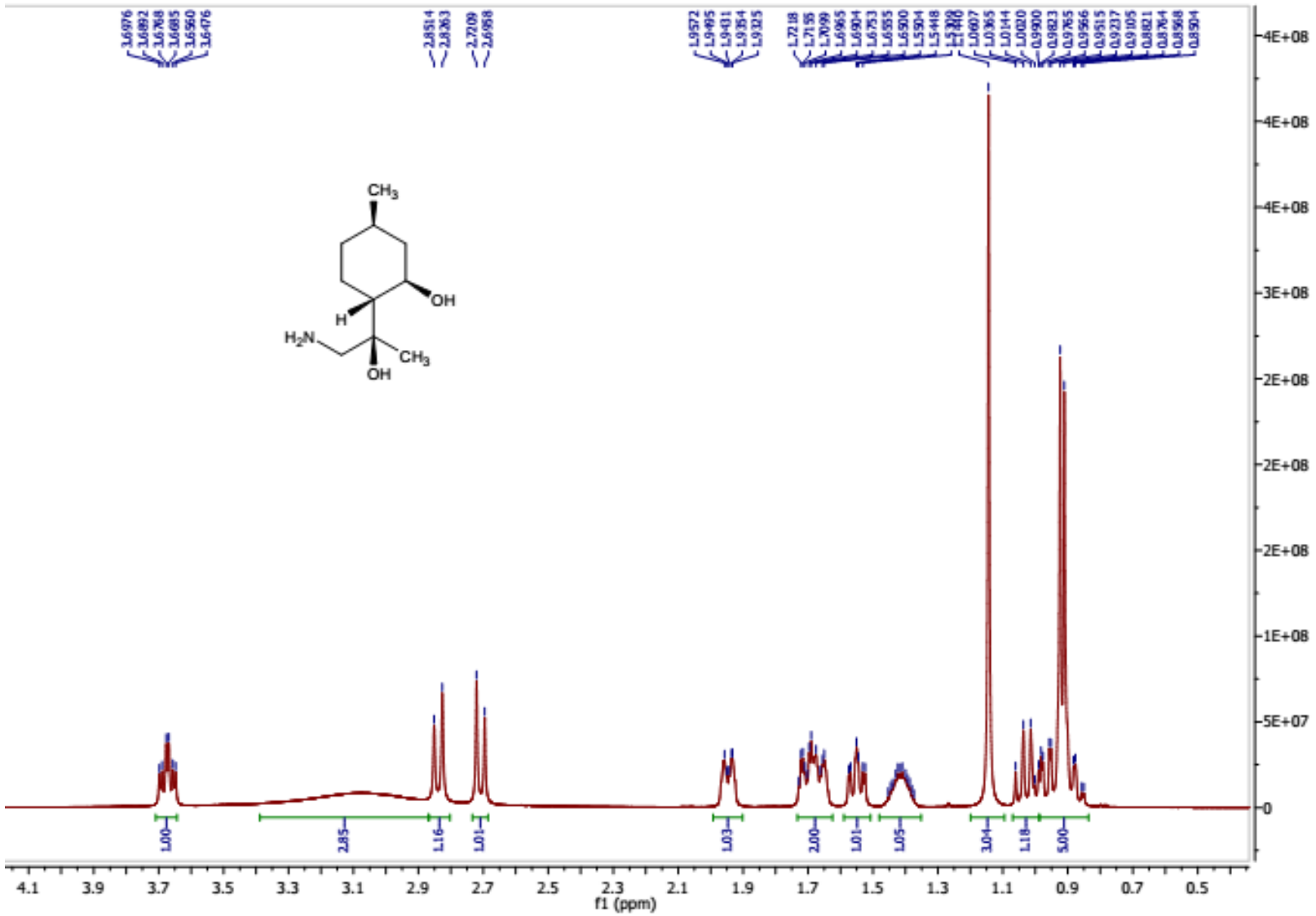

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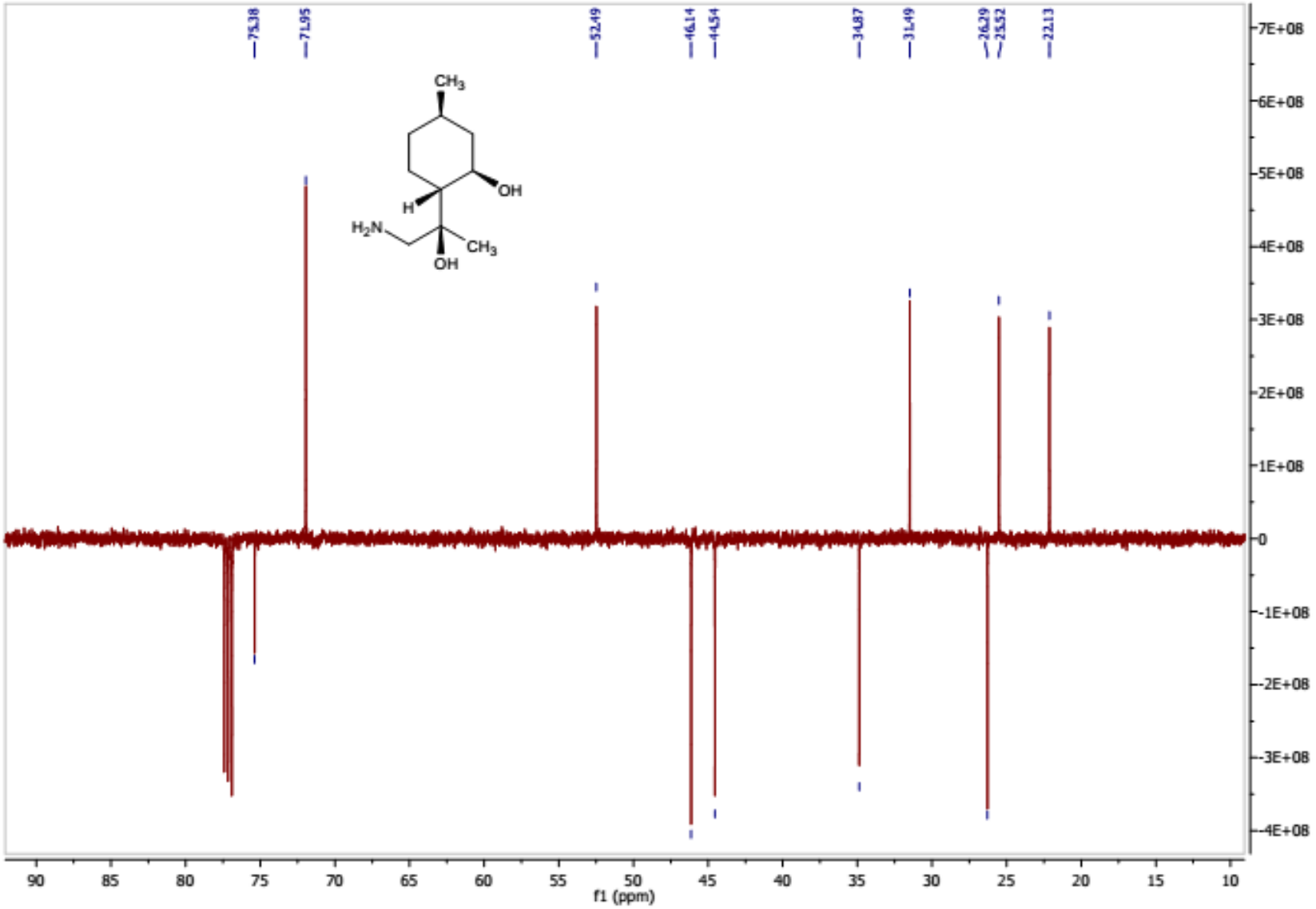

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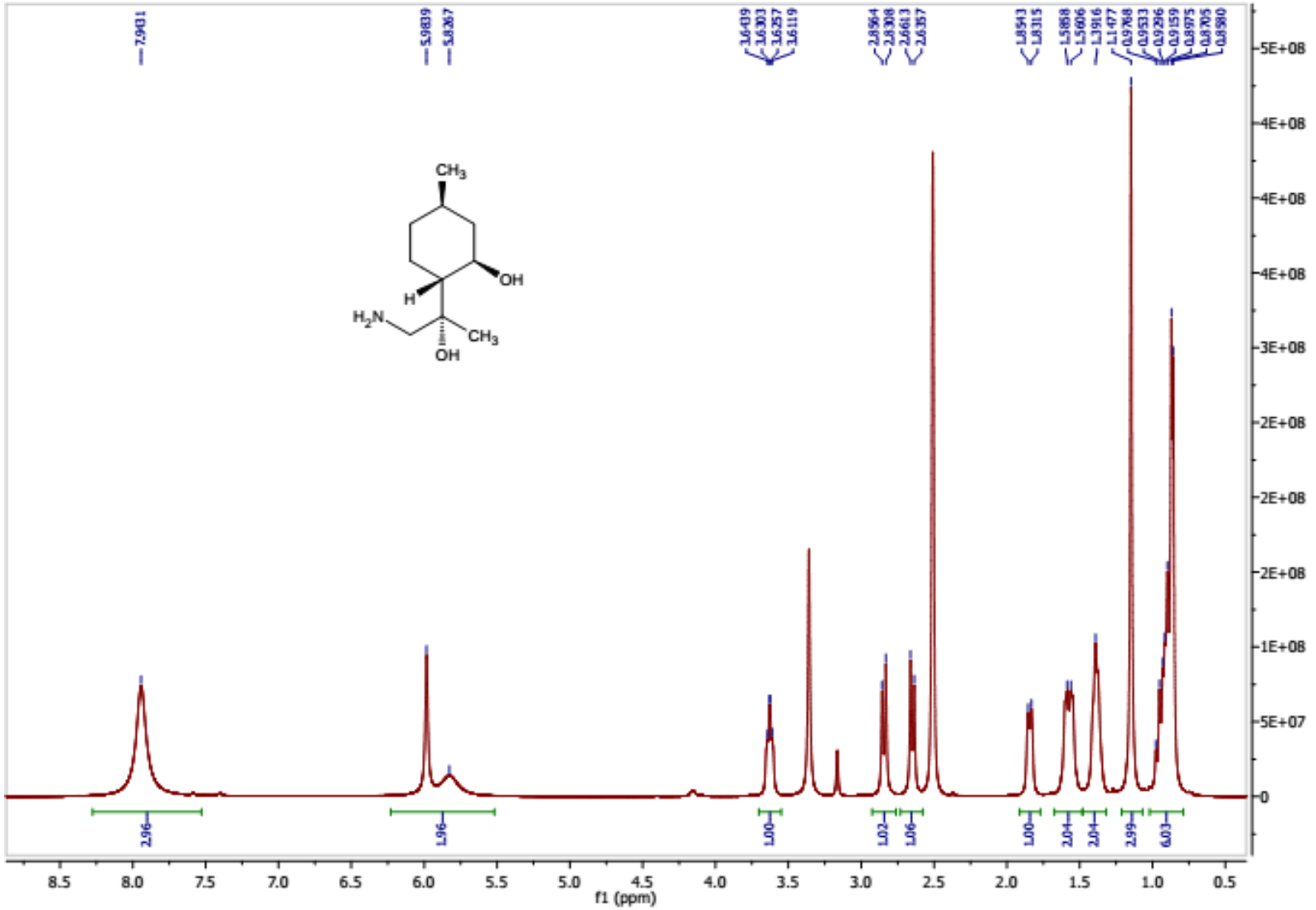

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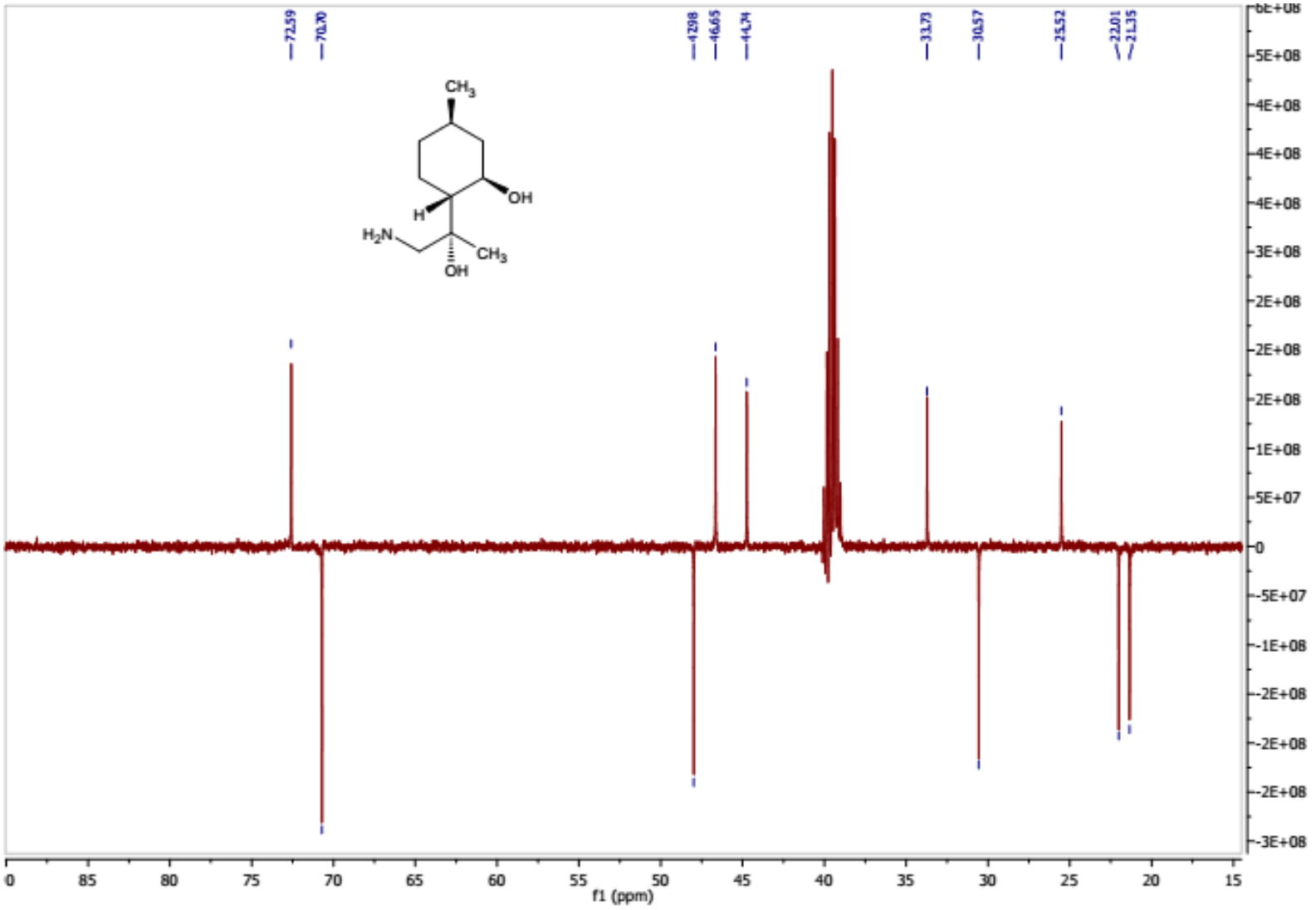

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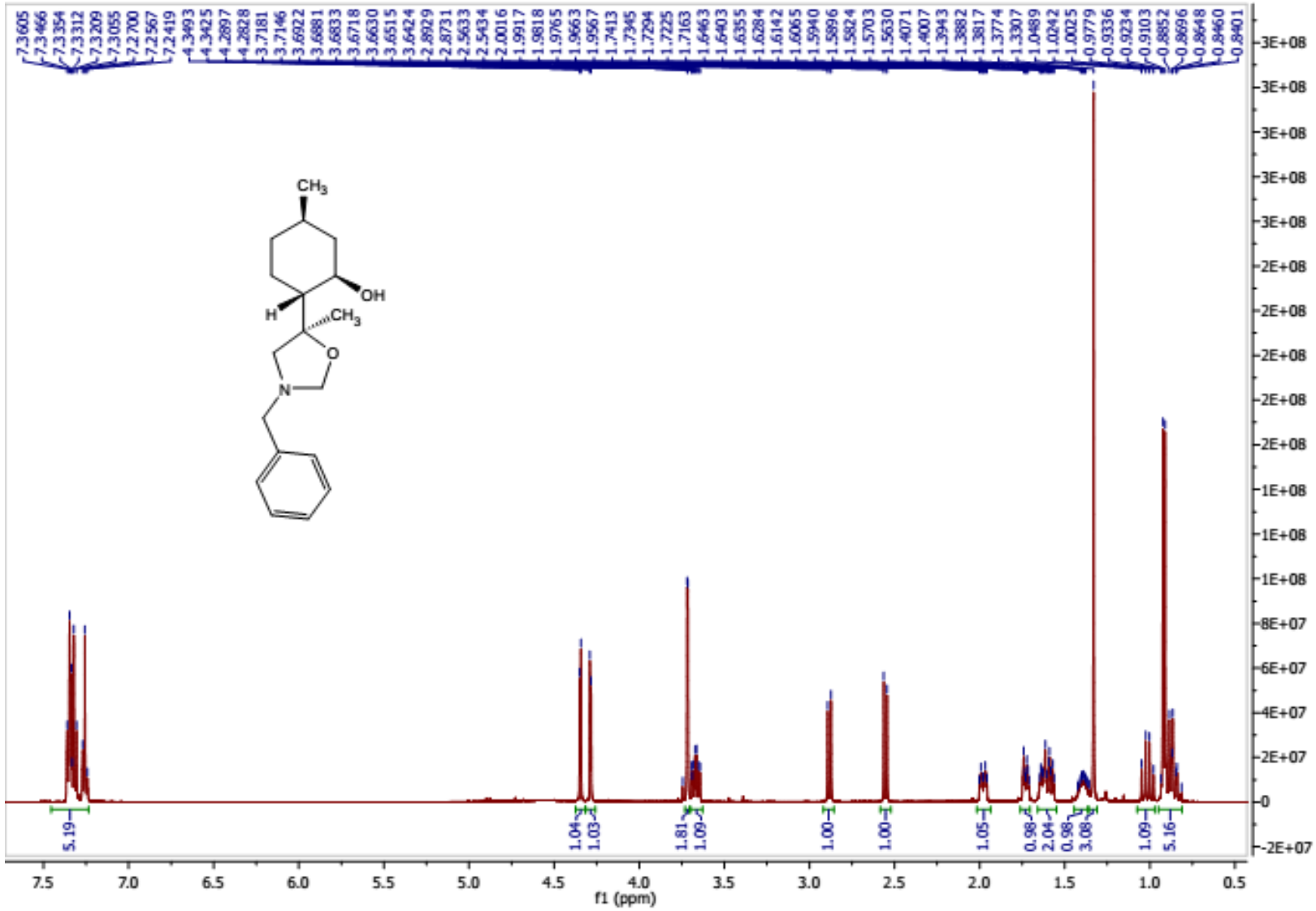
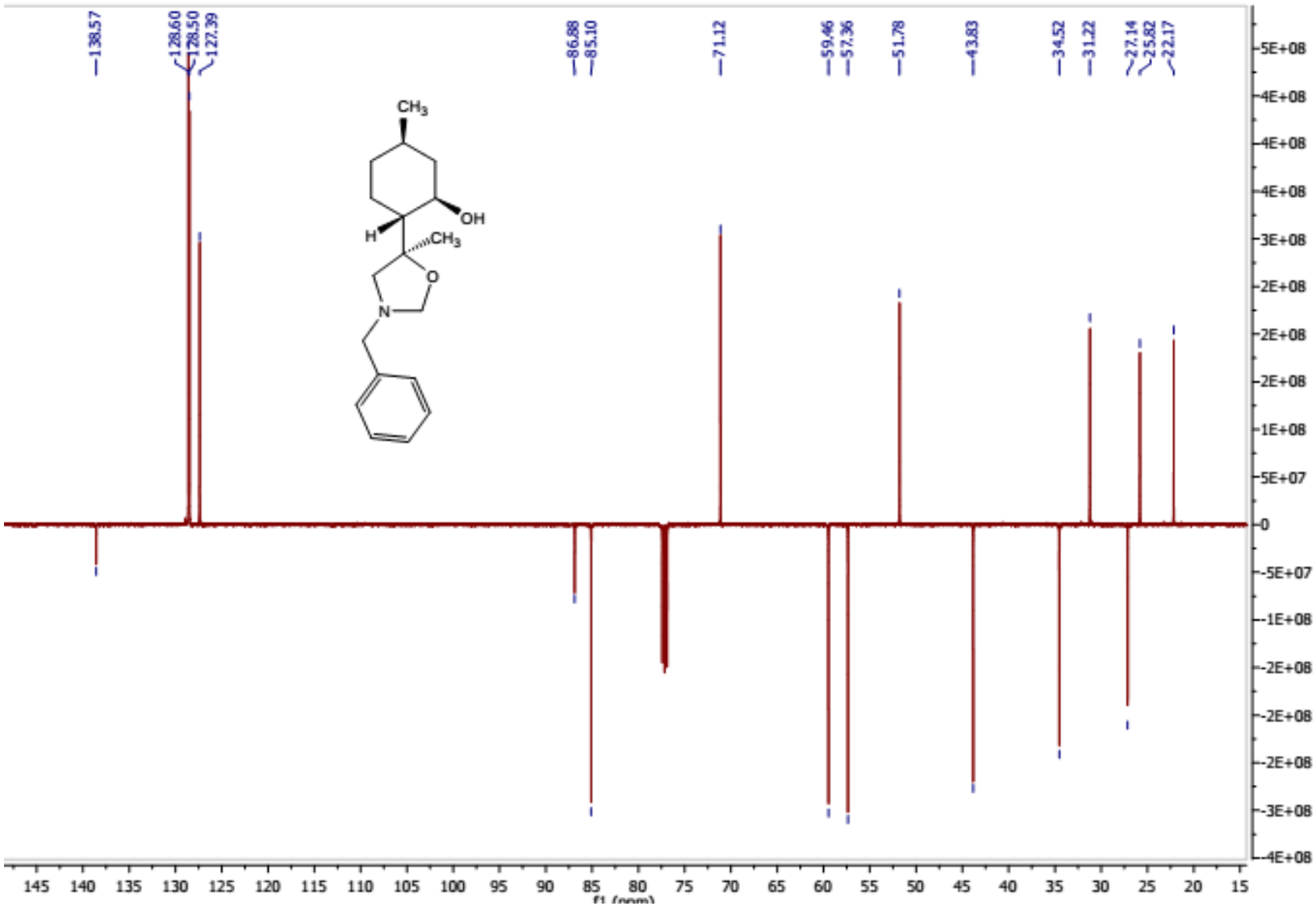
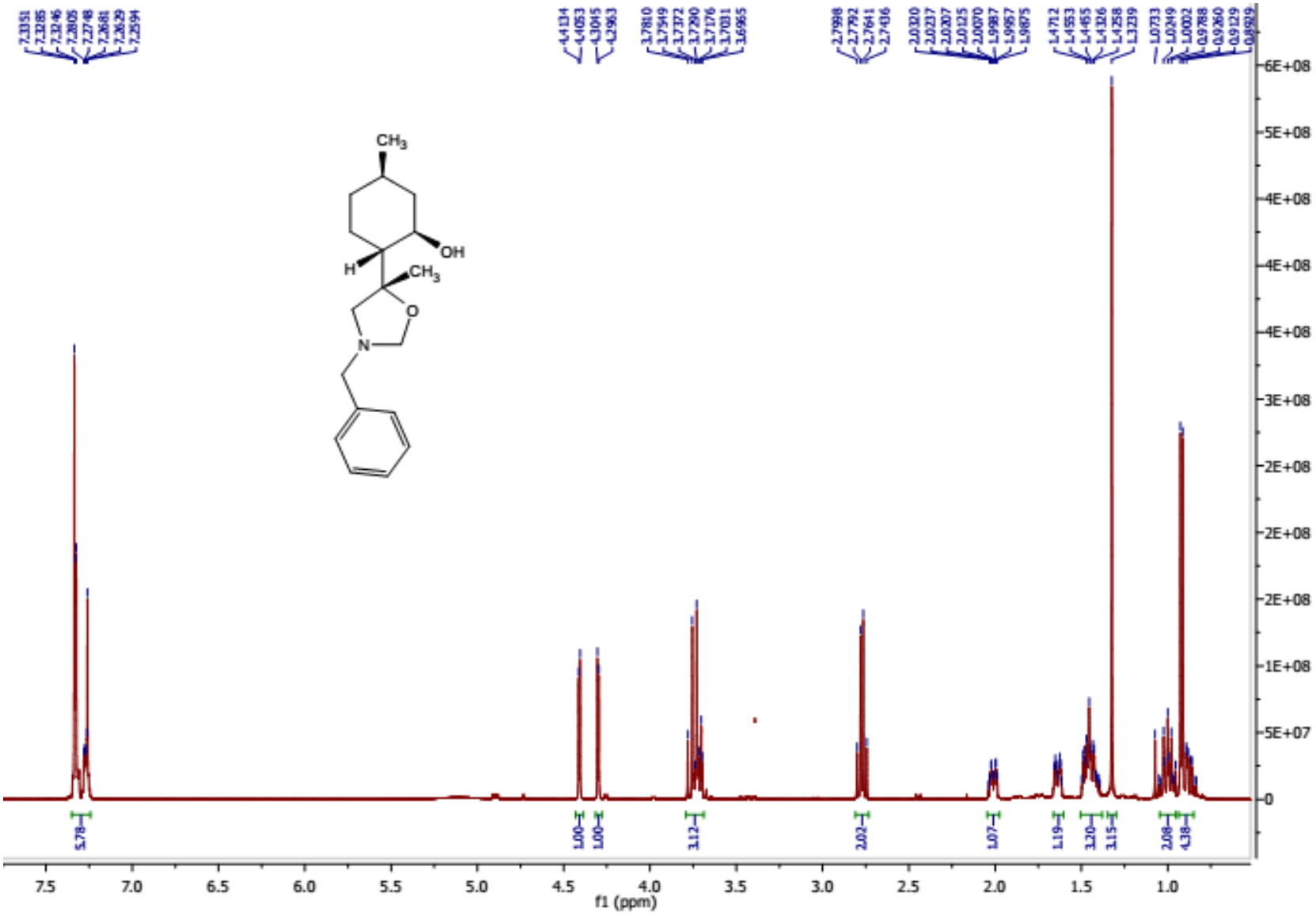


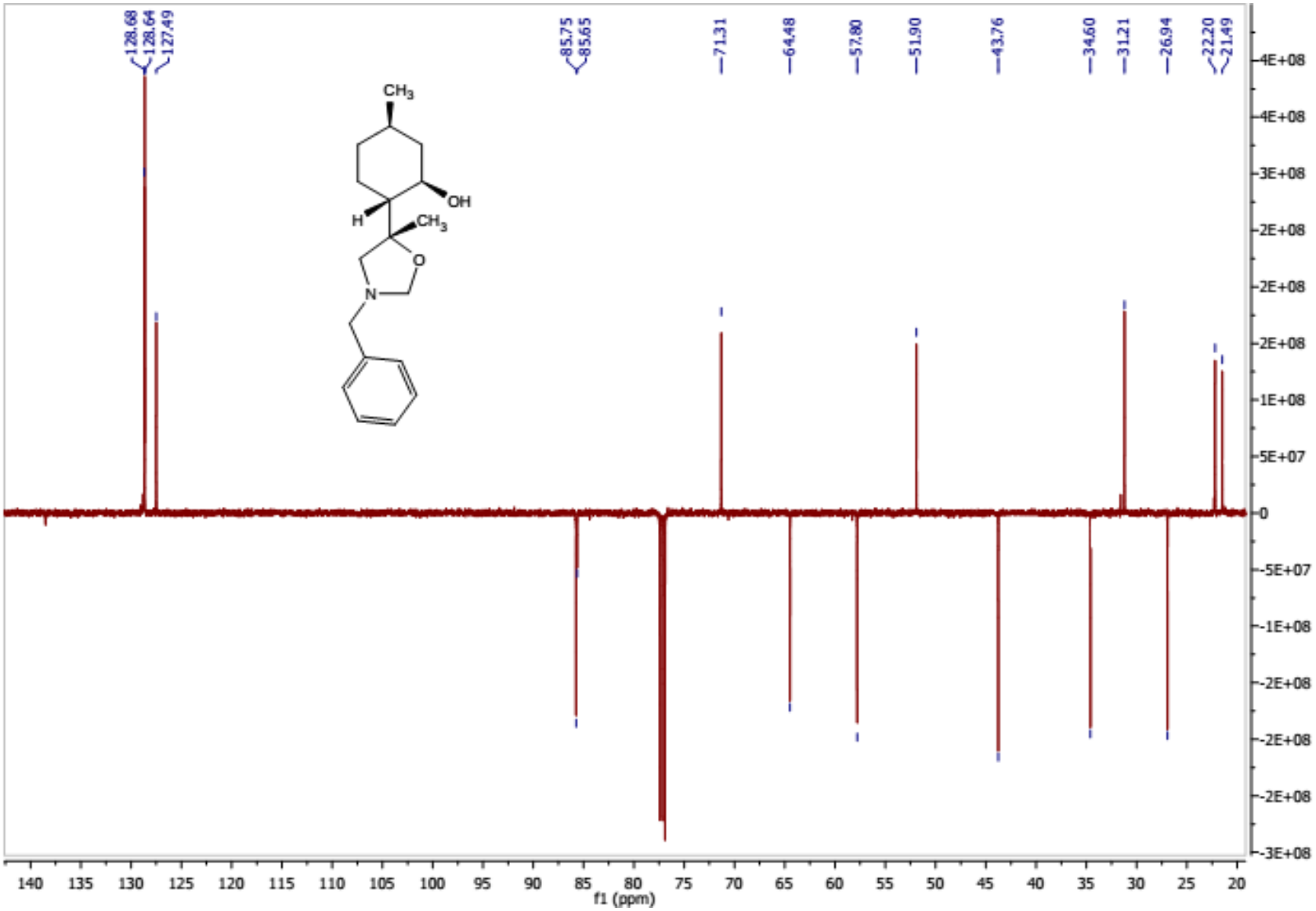
$^{13}$C-NMR of compound **29a**



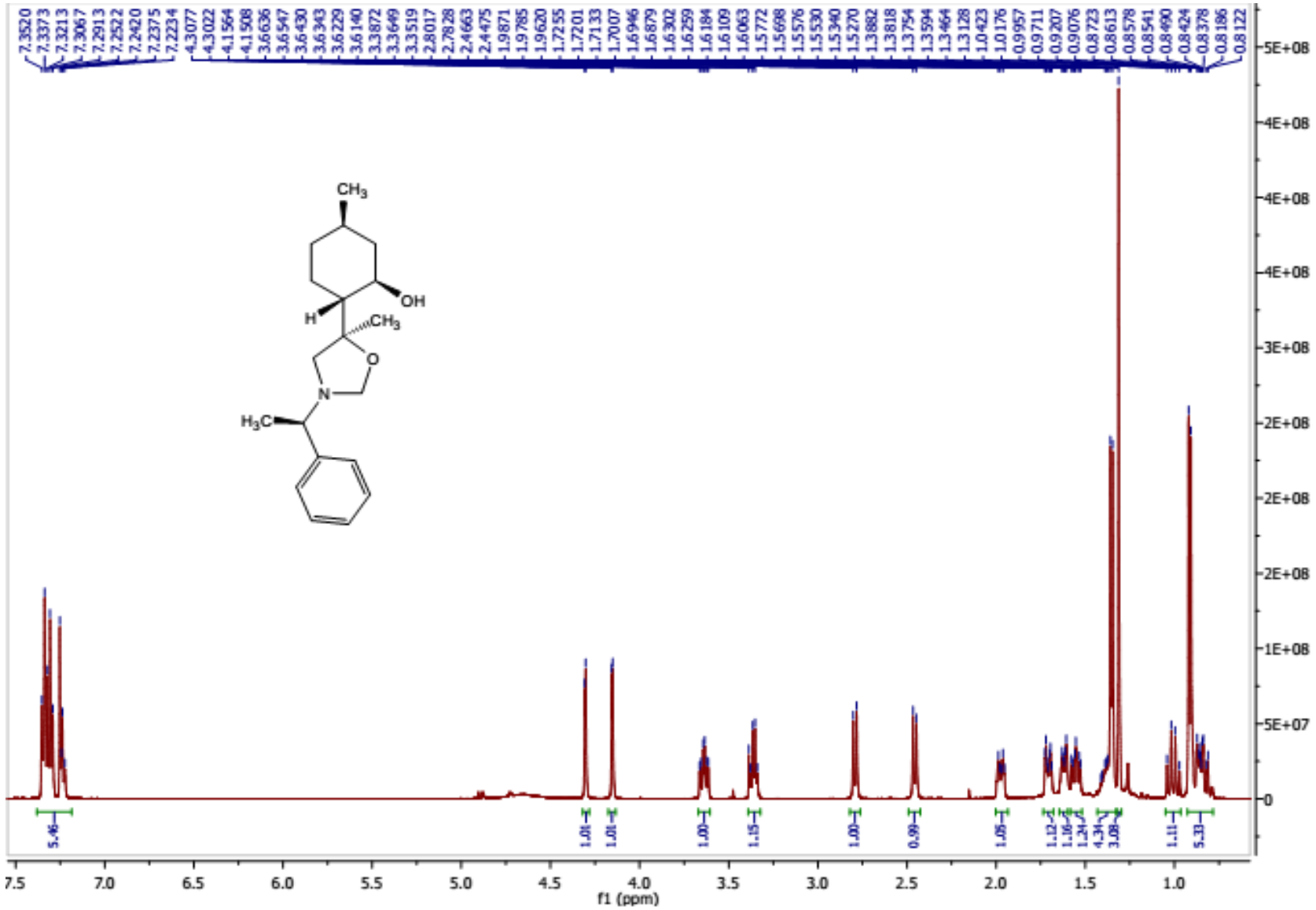
[1]H-NMR of compound **29b**



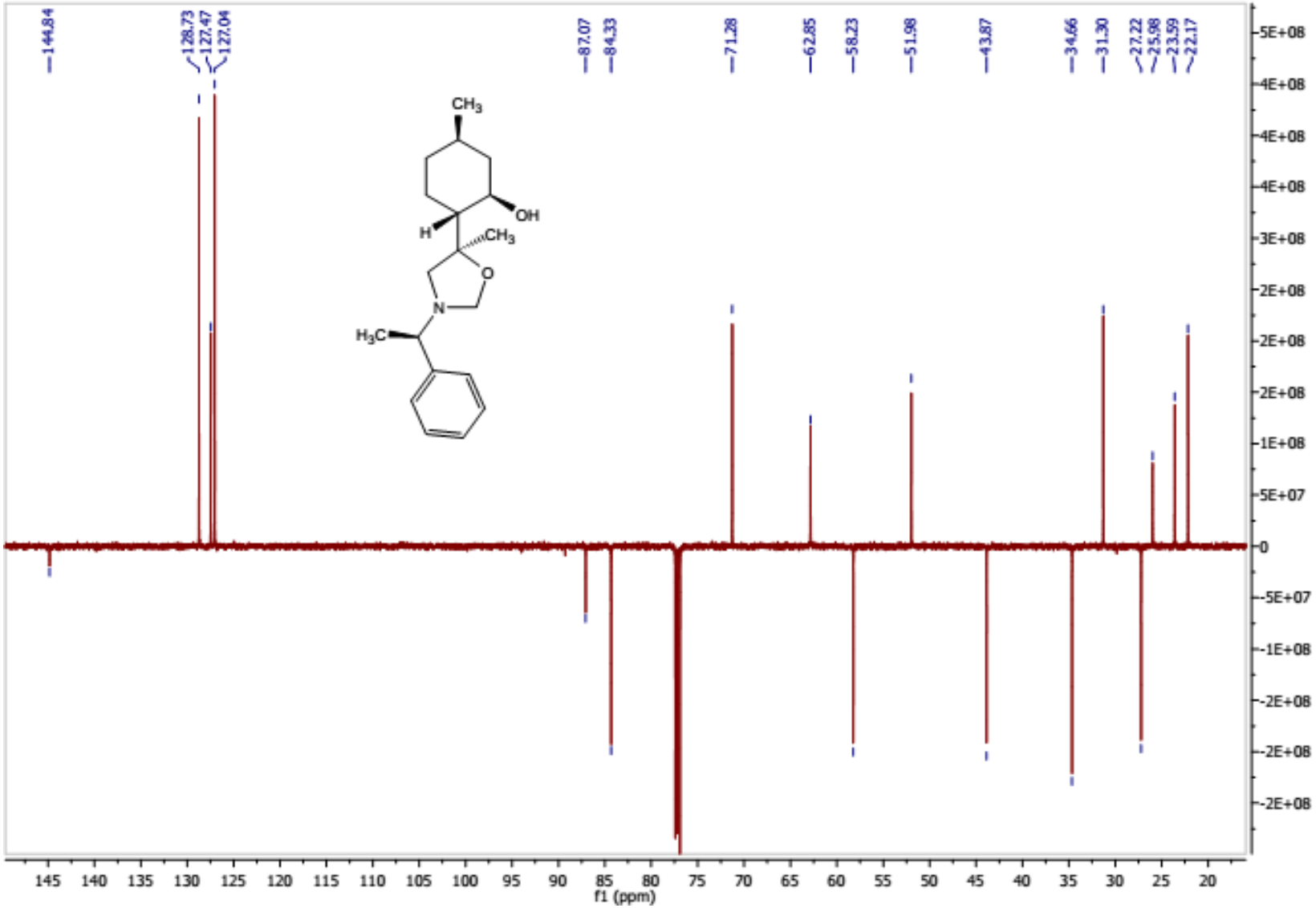
$^{13}$C-NMR of compound **29b**



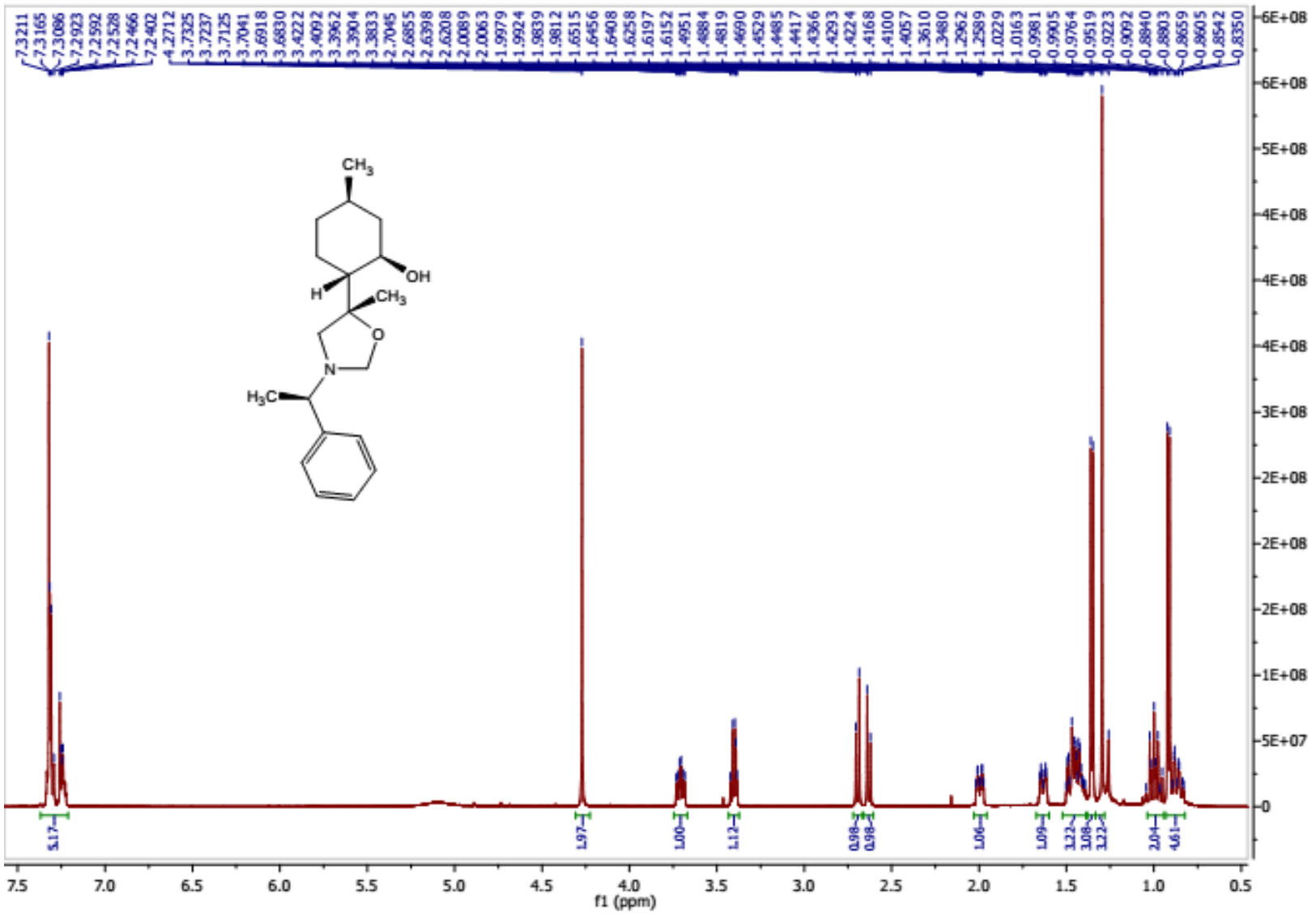
[1]H-NMR of compound **30a**



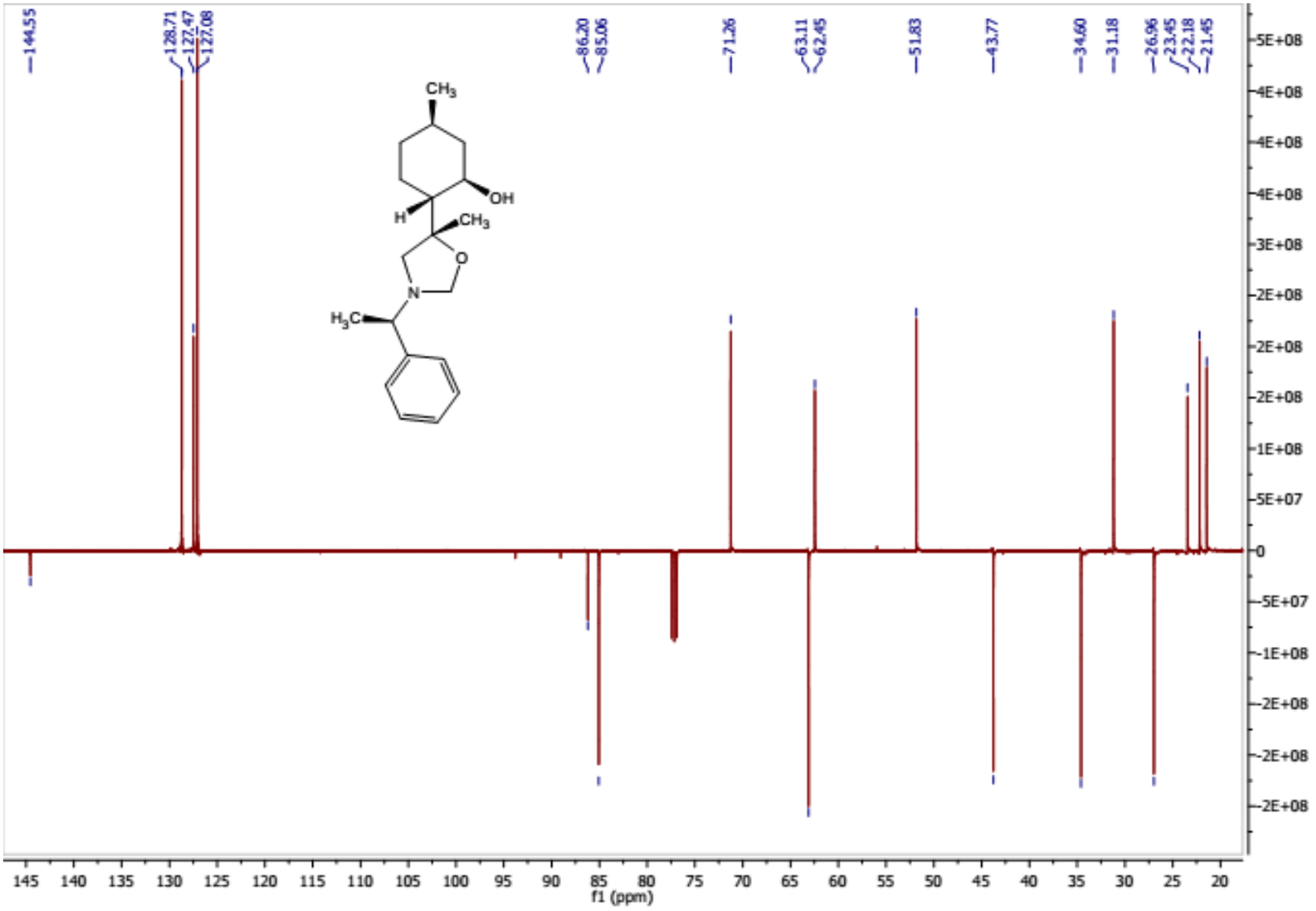
$^{13}$C-NMR of compound **30a**



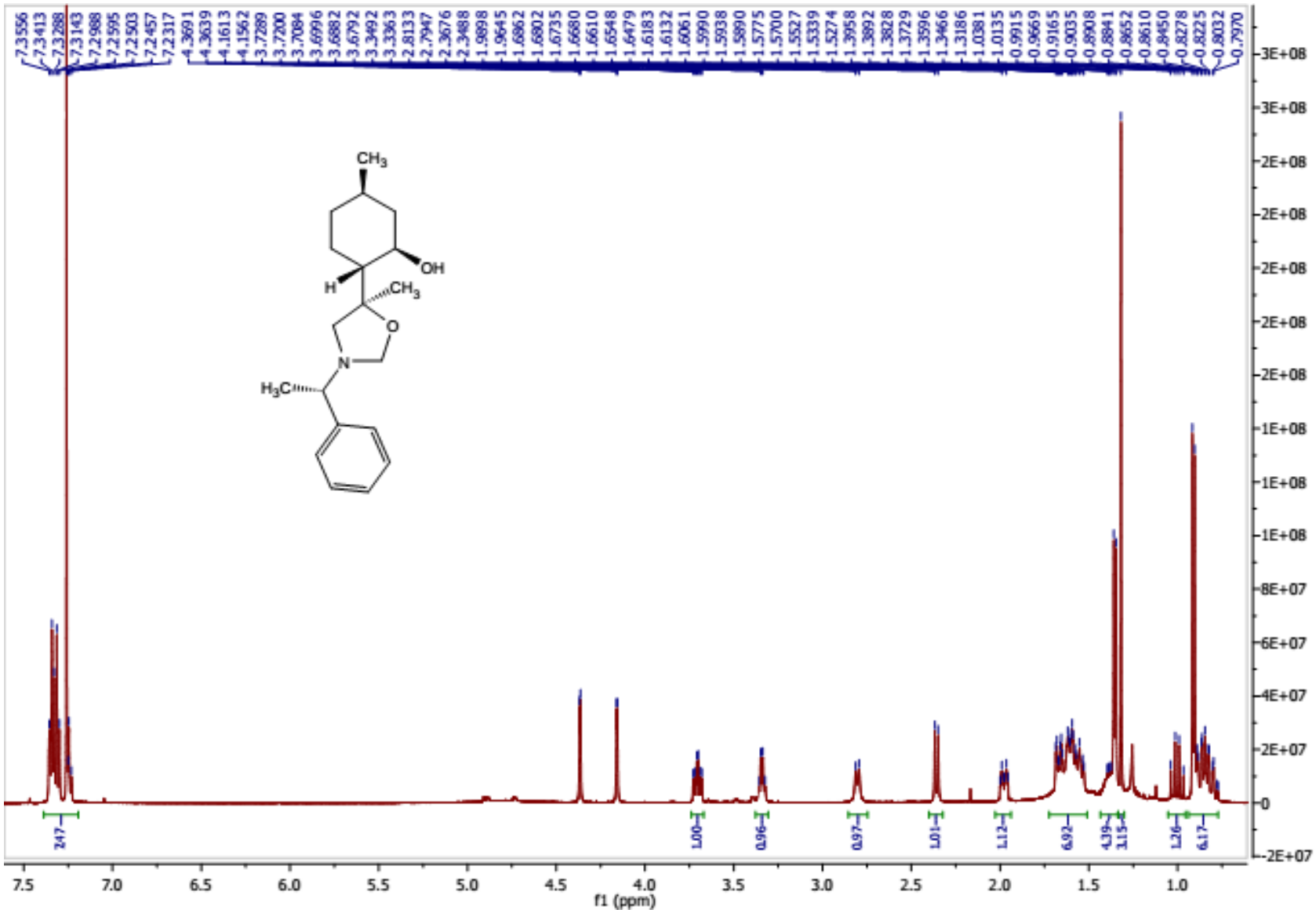
[1]H-NMR of compound **30b**



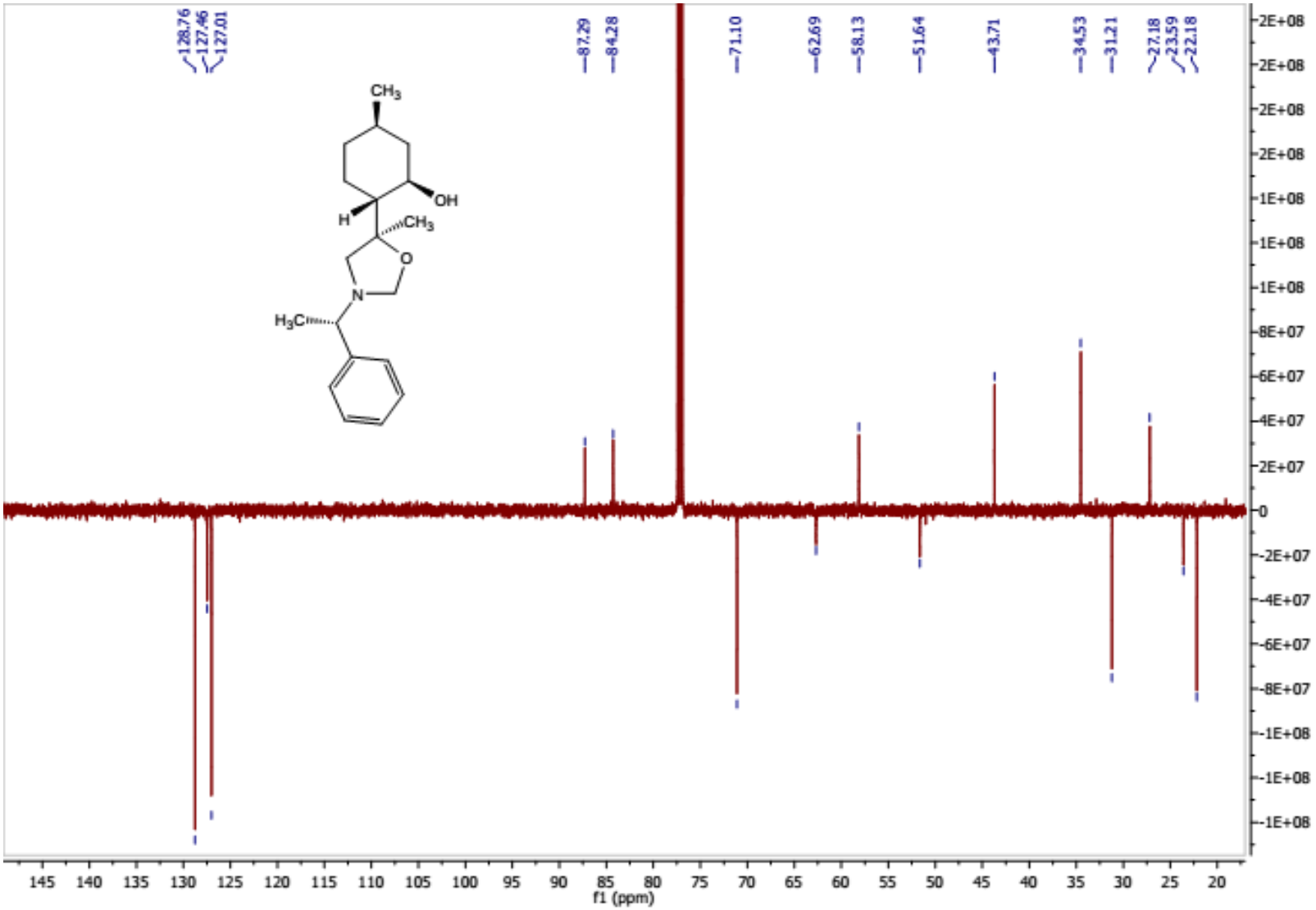
$^{13}$C-NMR of compound **30b**



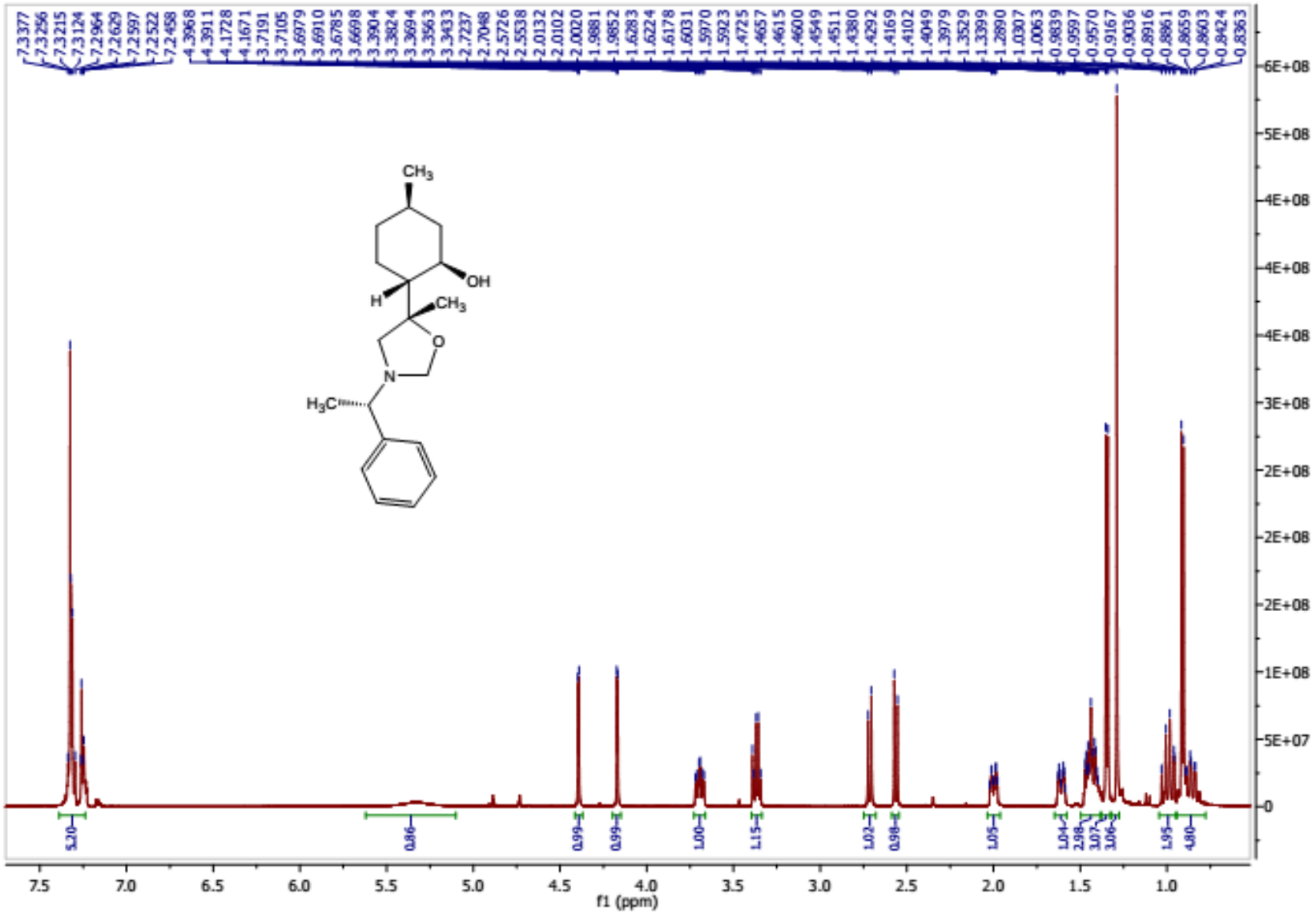
[1]H-NMR of compound **31b**



$^{13}$C-NMR of compound **31b**



[1]H-NMR of compound **31b**



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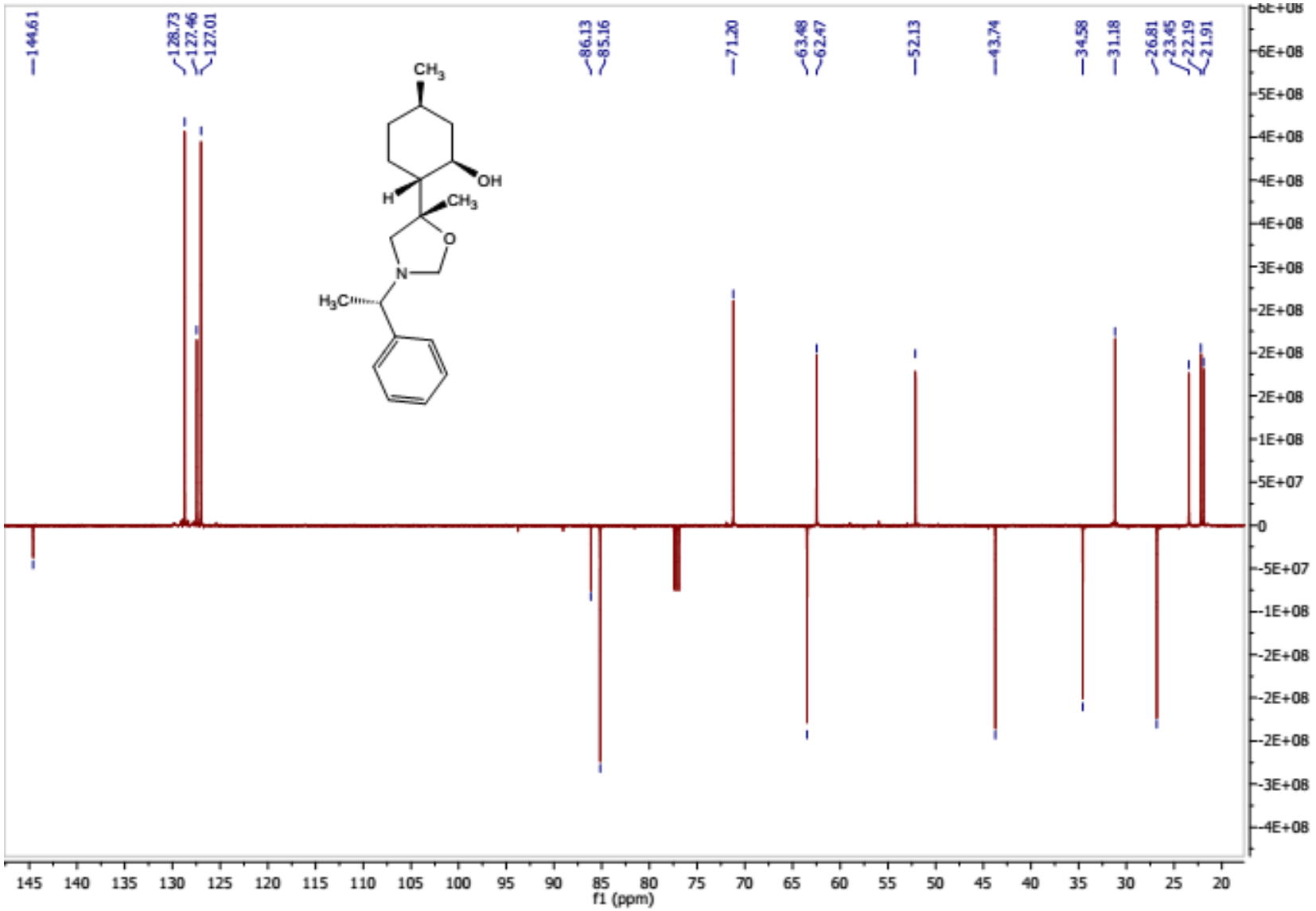
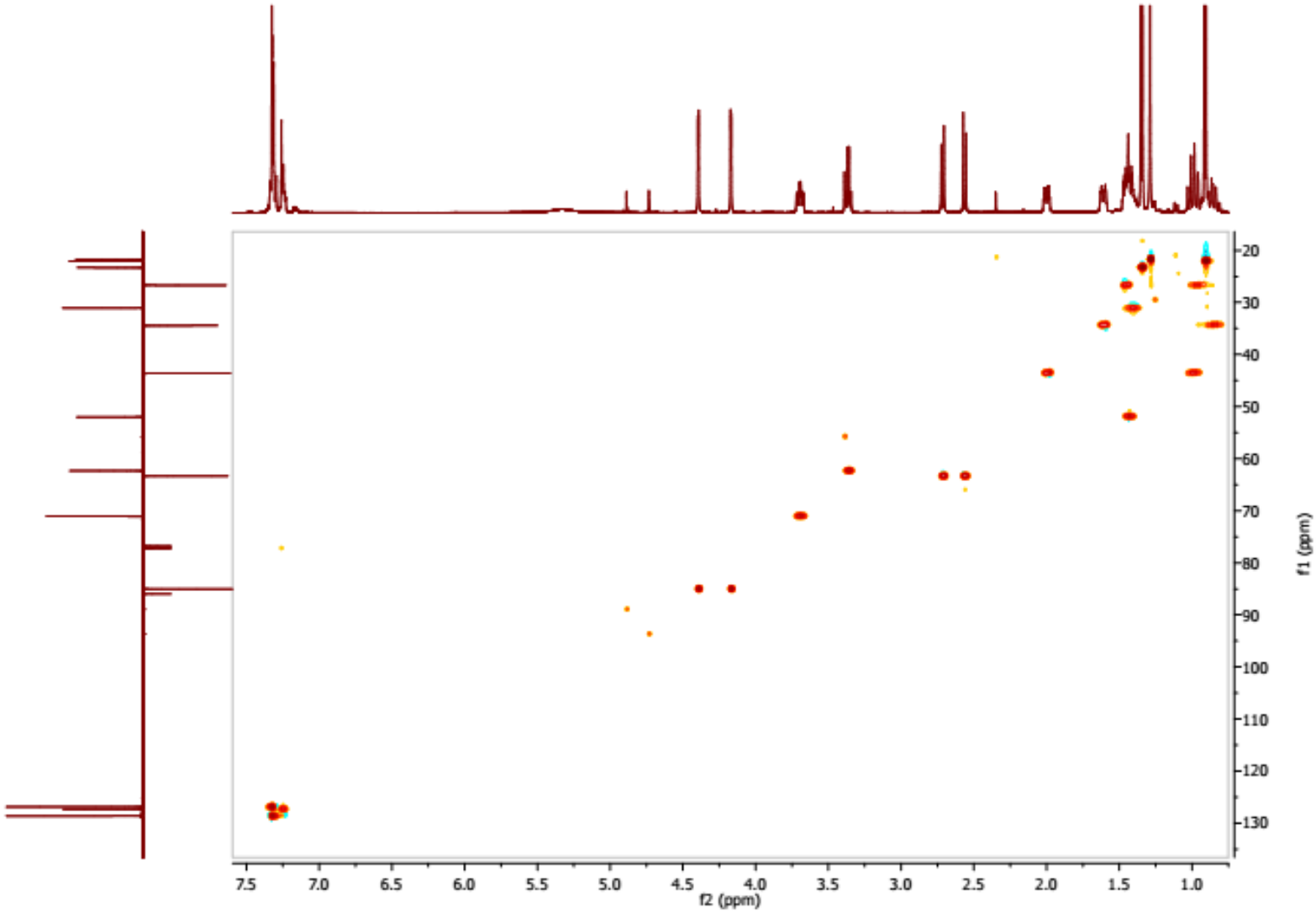
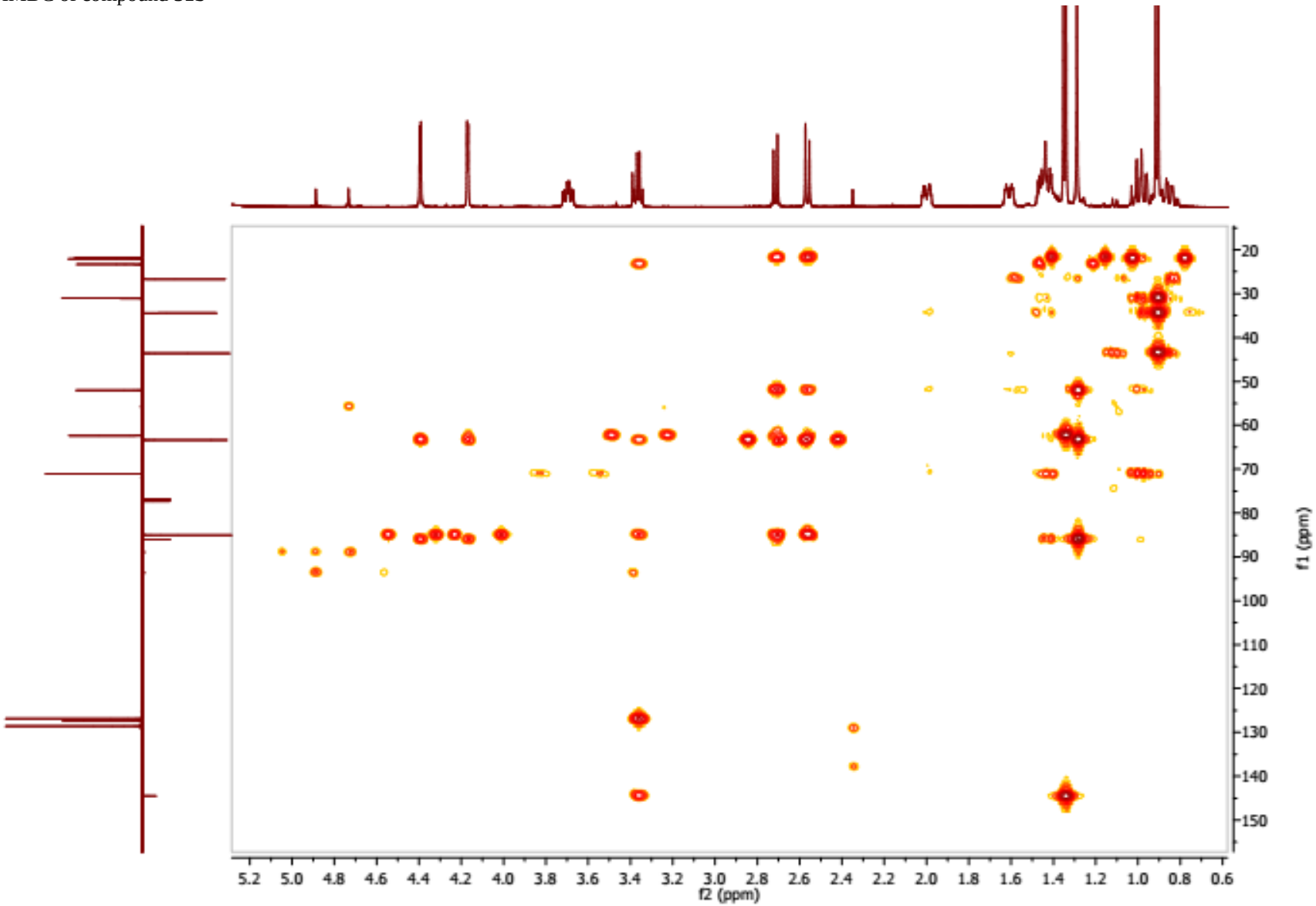


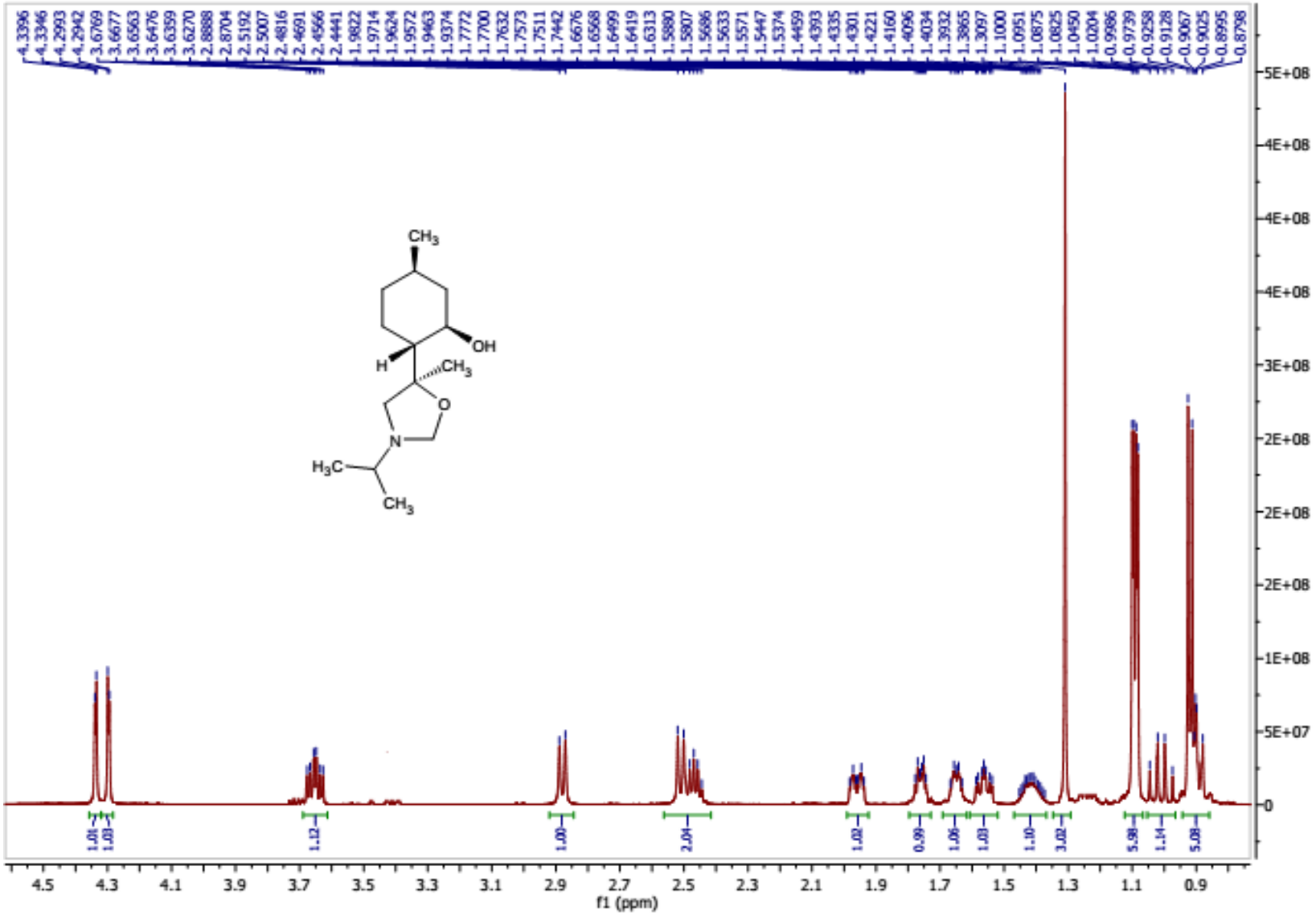
HSQC of compound **31b**



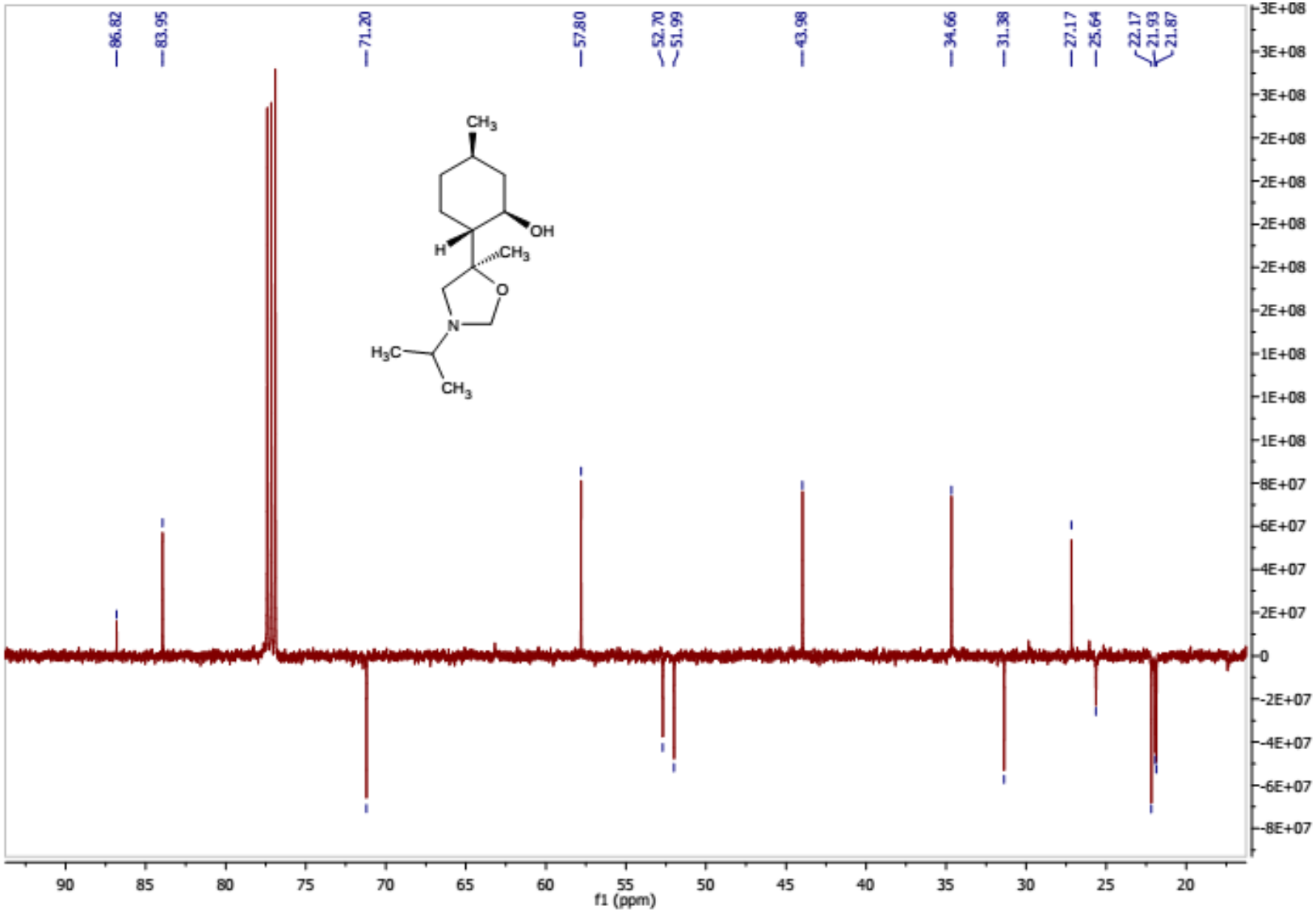
HMBC of compound **31b**



[1]H-NMR of compound **32a**



$^{13}$C-NMR of compound **32a**



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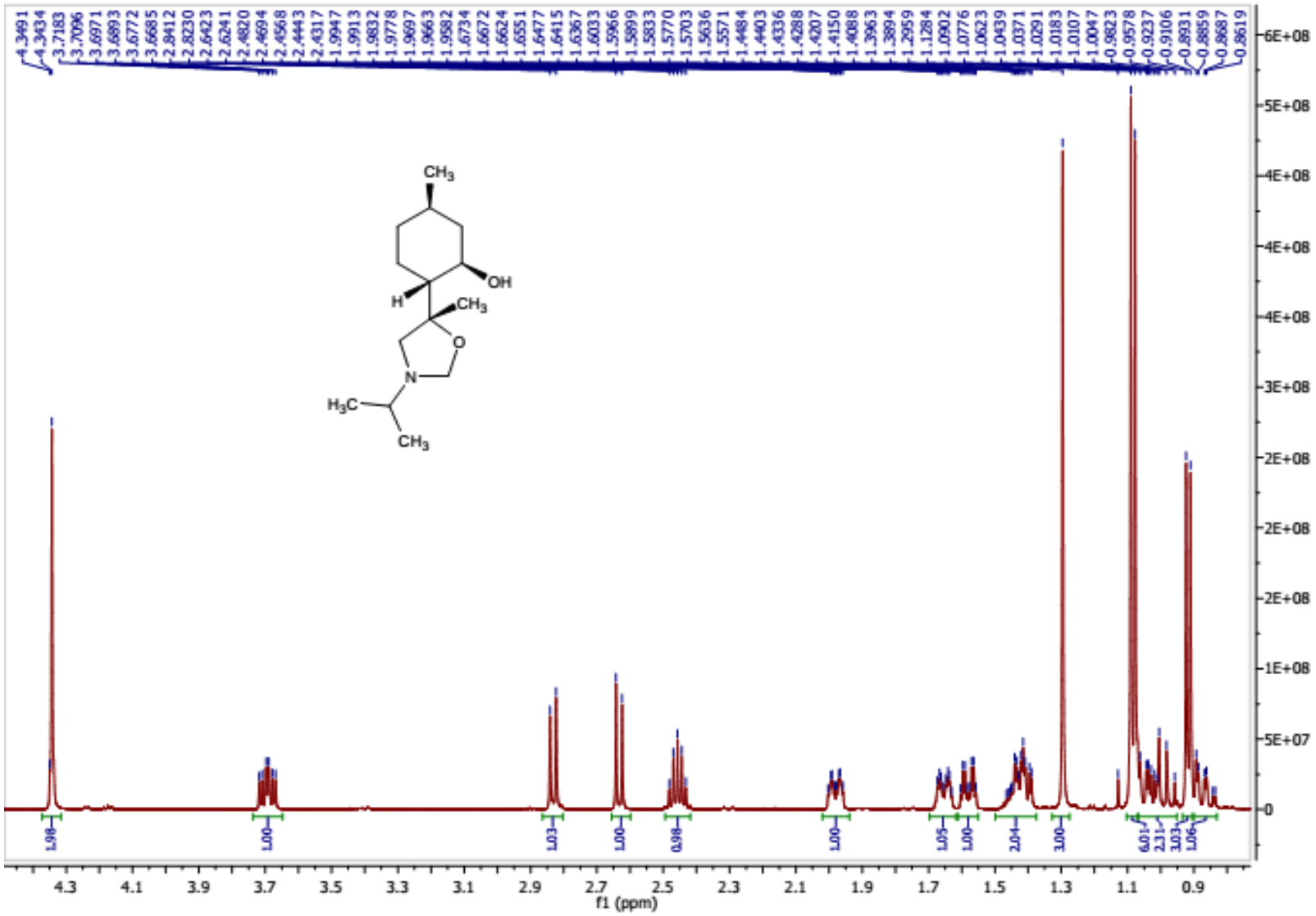
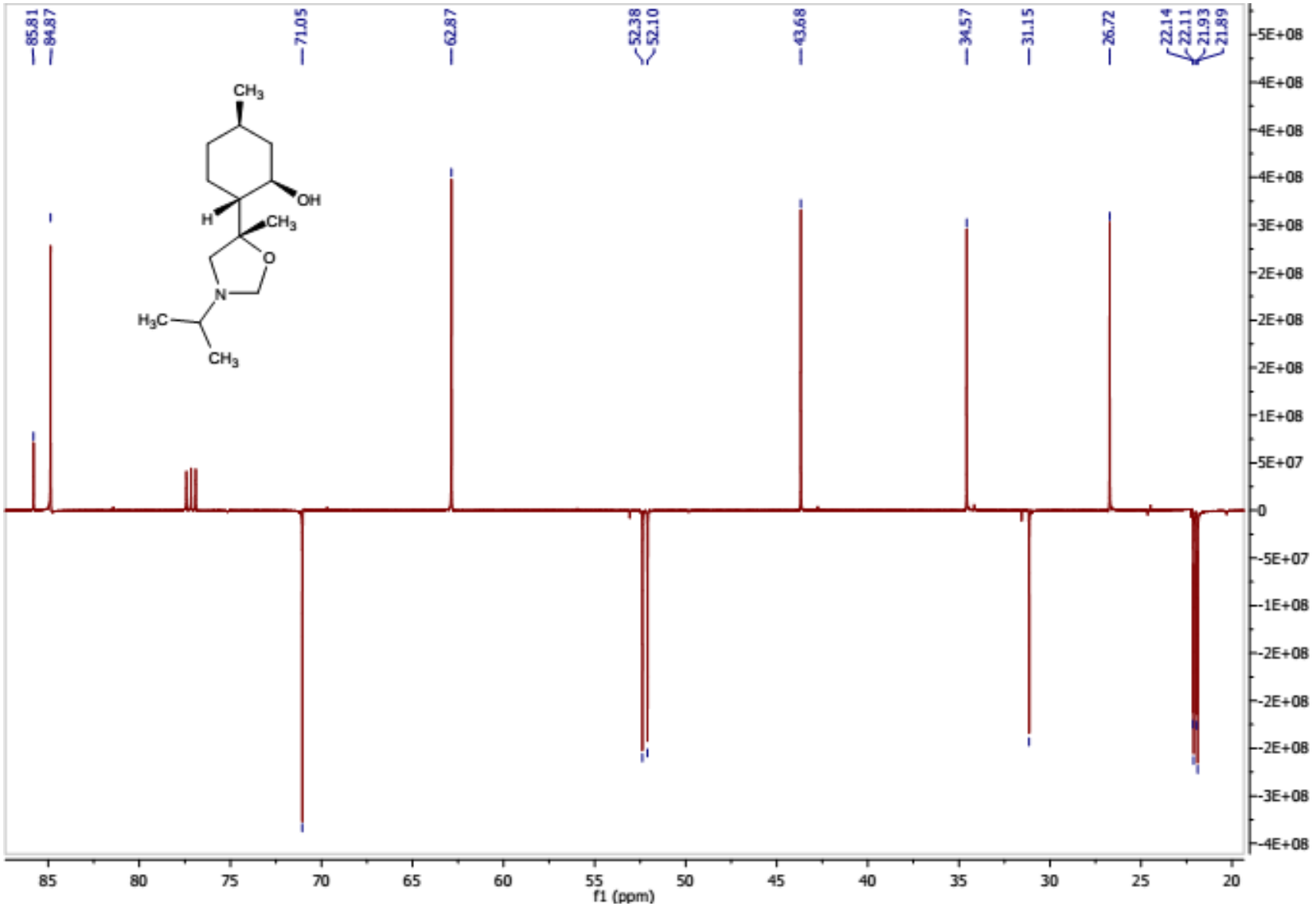
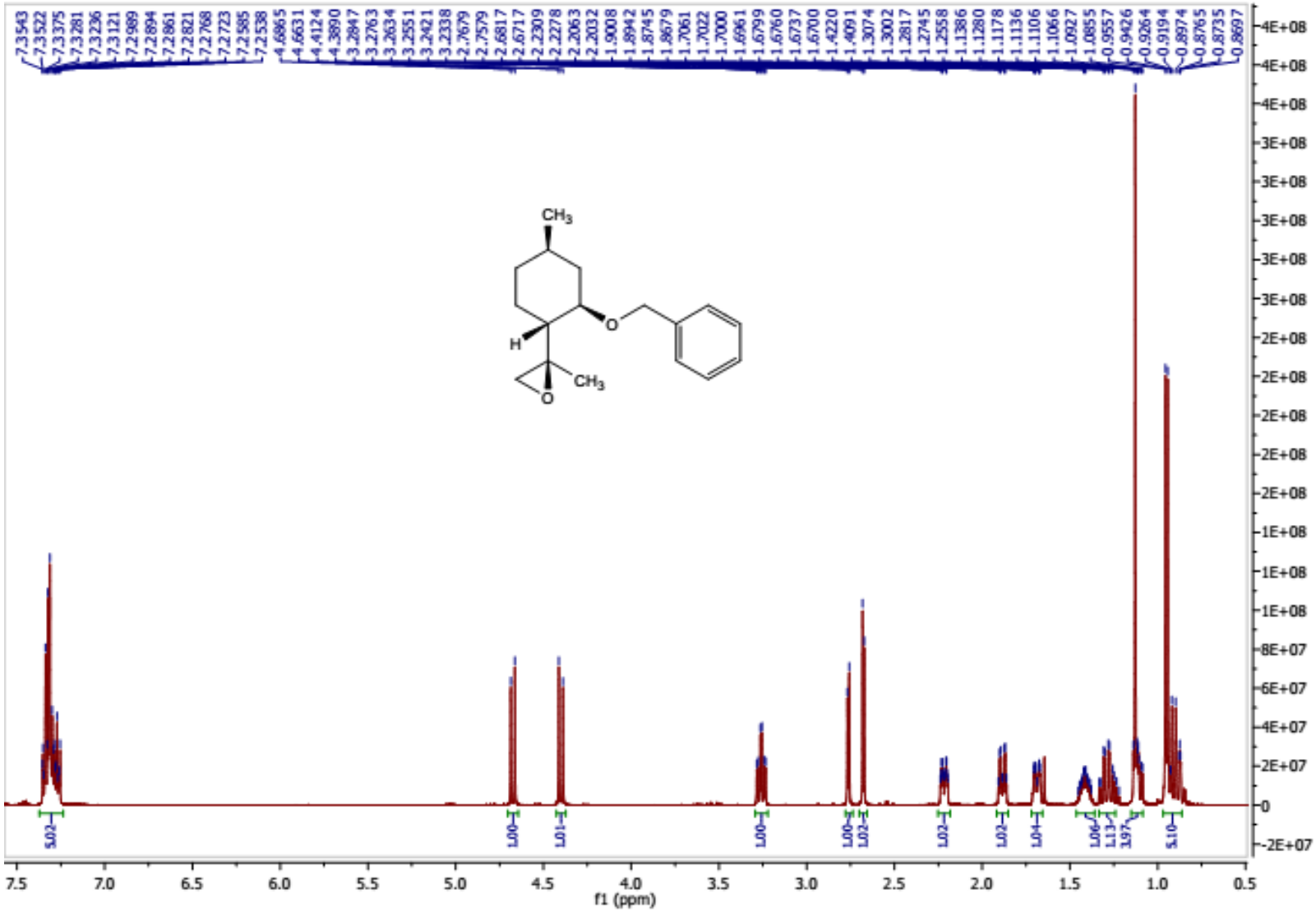


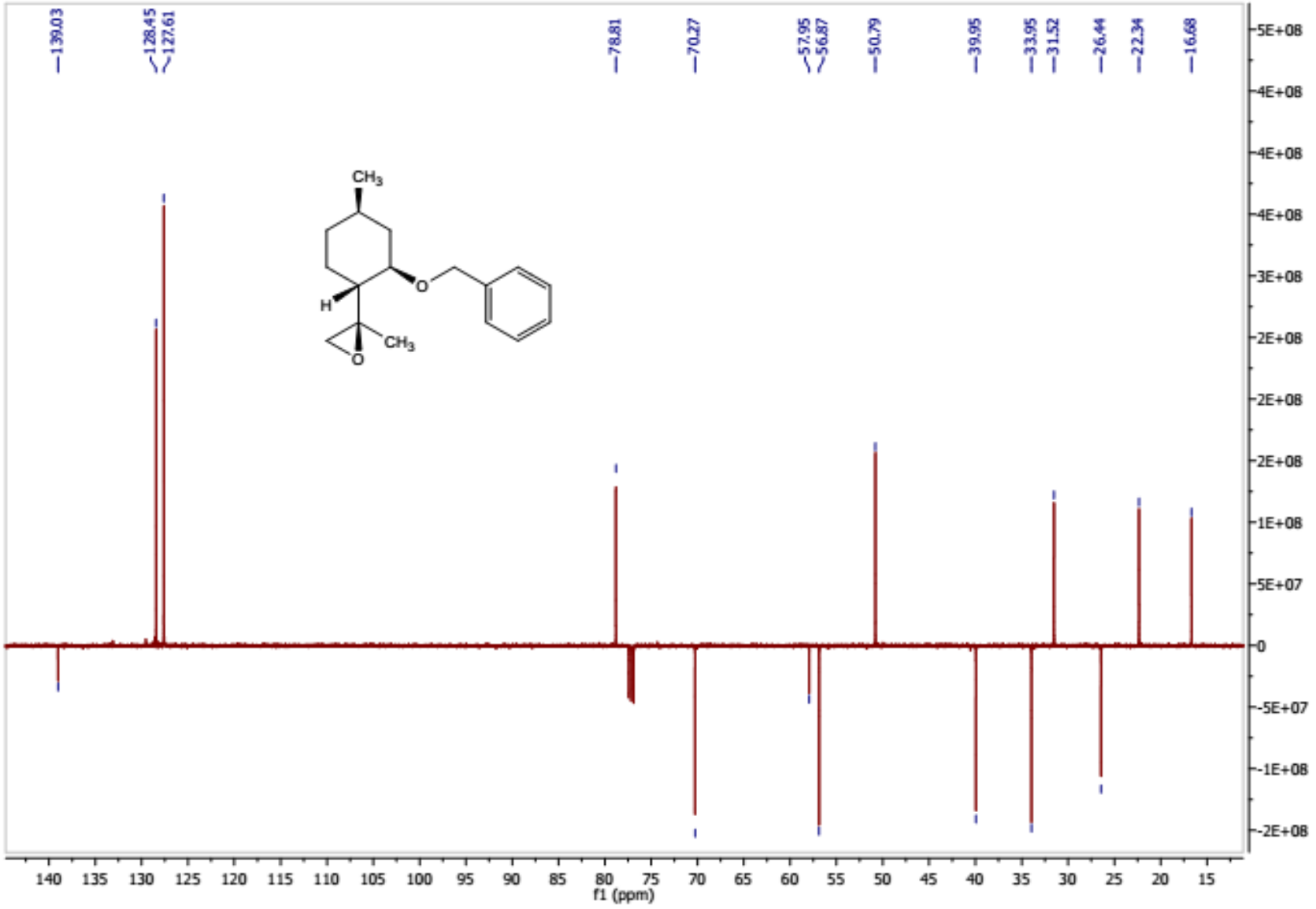
$^{13}$C-NMR of compound **32b**



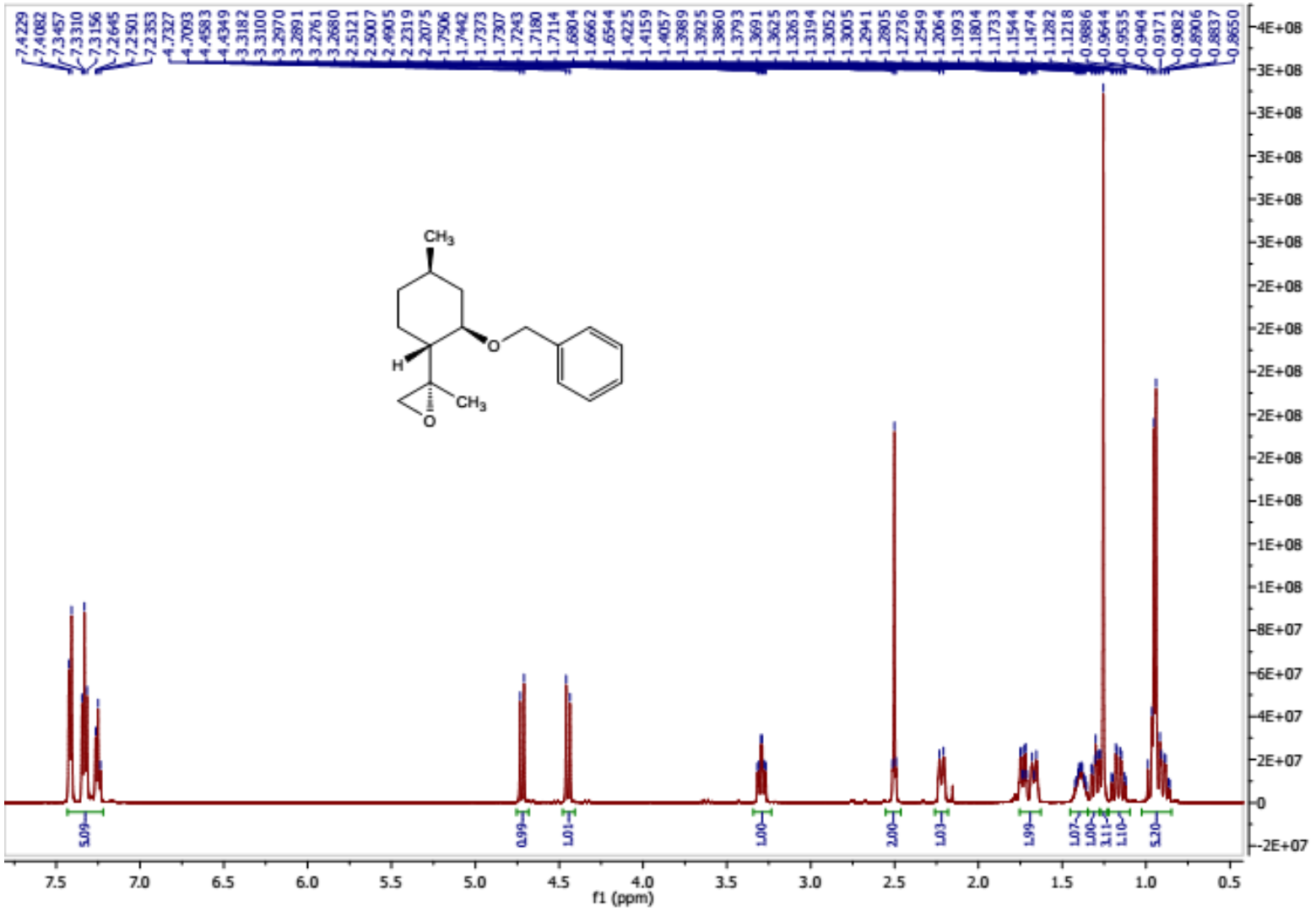
[1]H-NMR of compound **34a**



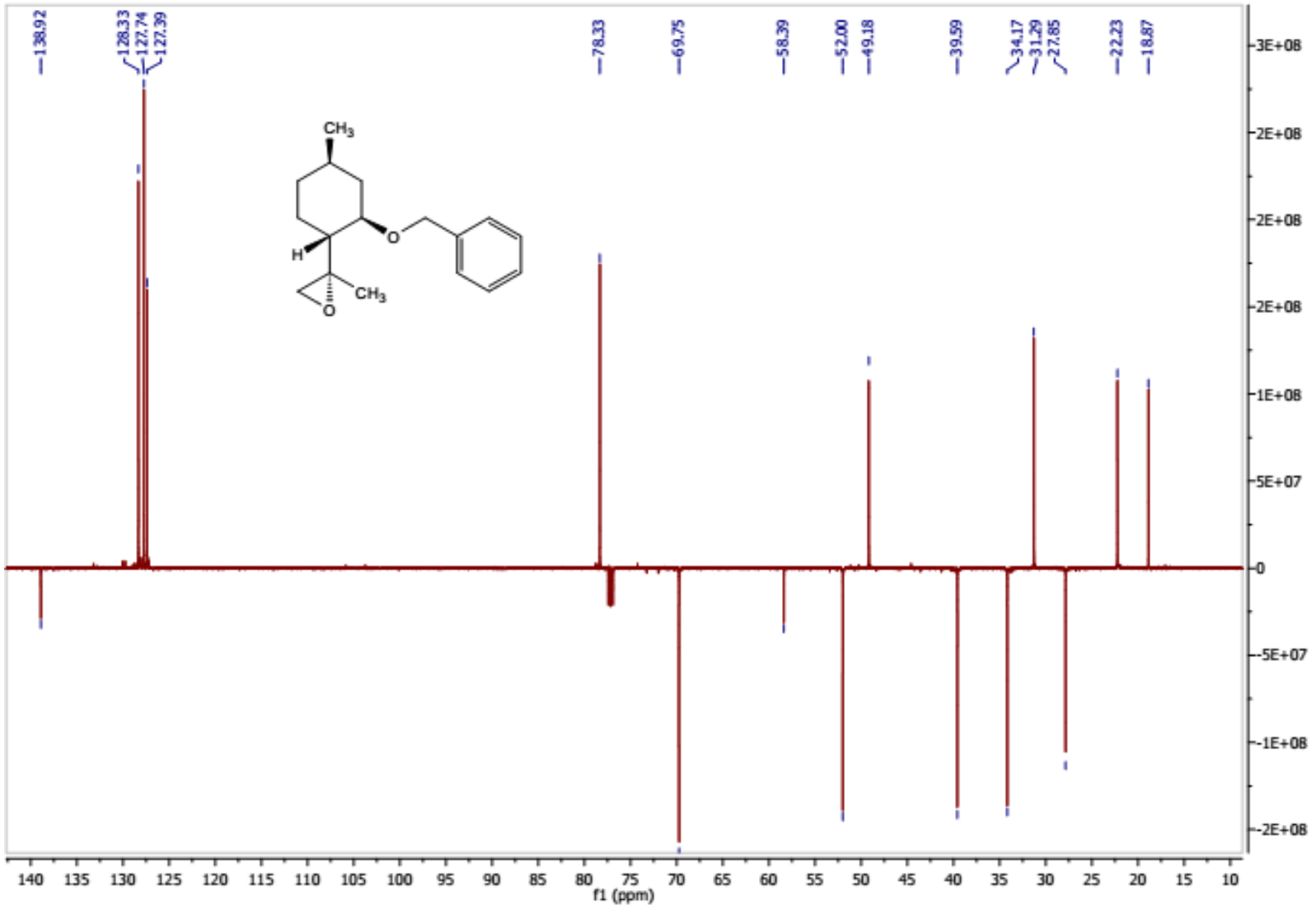
$^{13}$C-NMR of compound **34a**



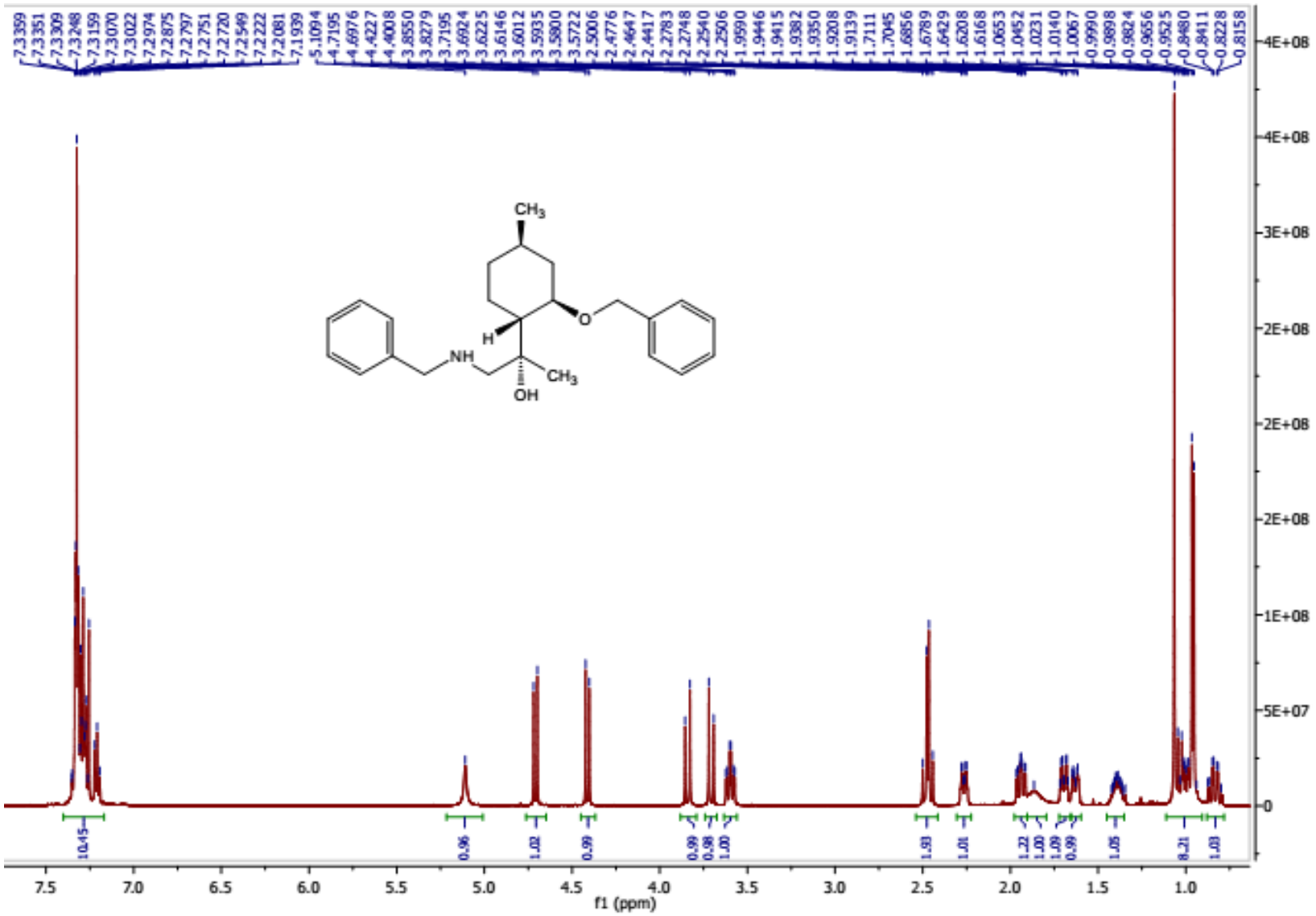
$^{1}$H-NMR of compound **34b**



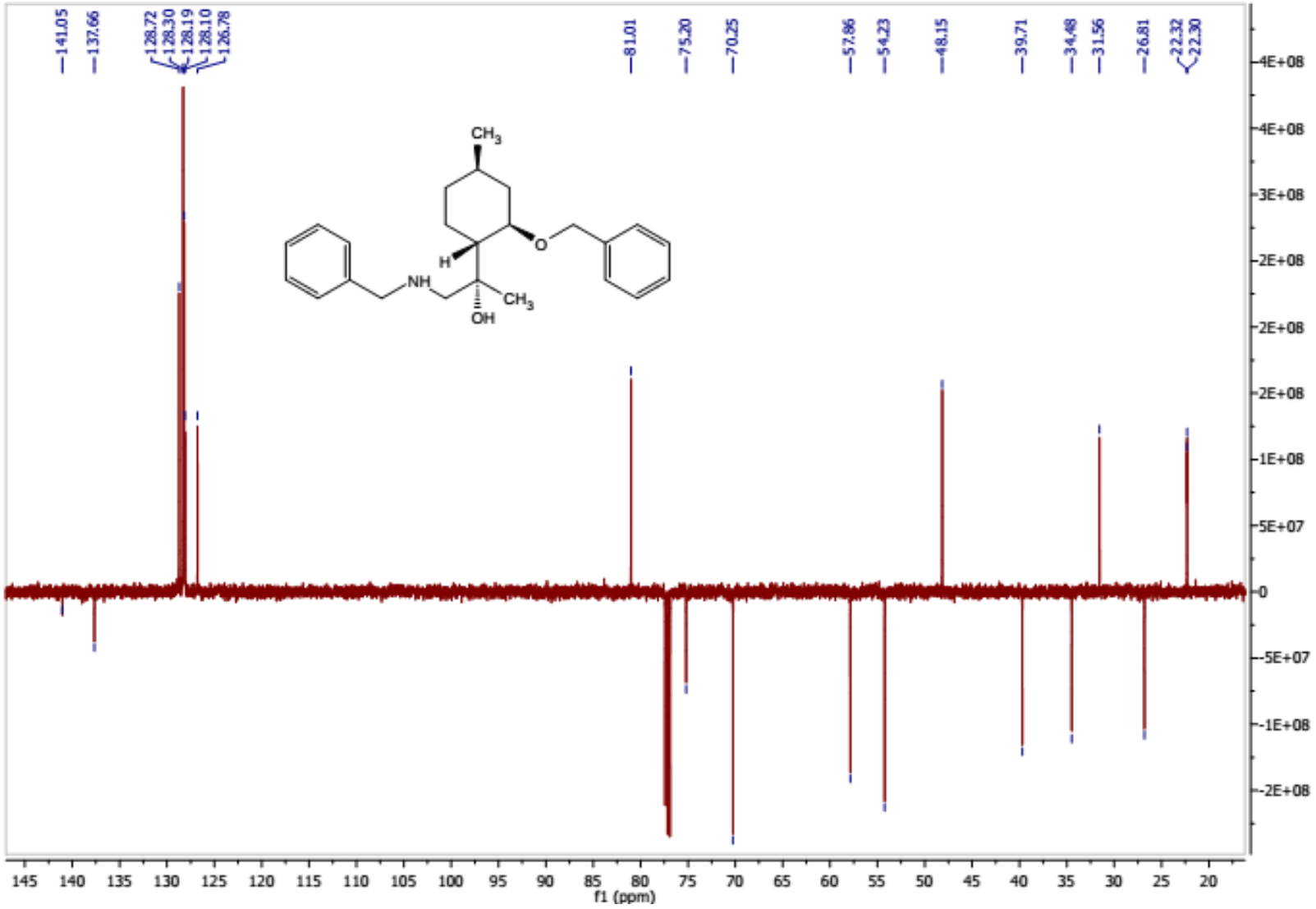
$^{13}$C-NMR of compound **34b**



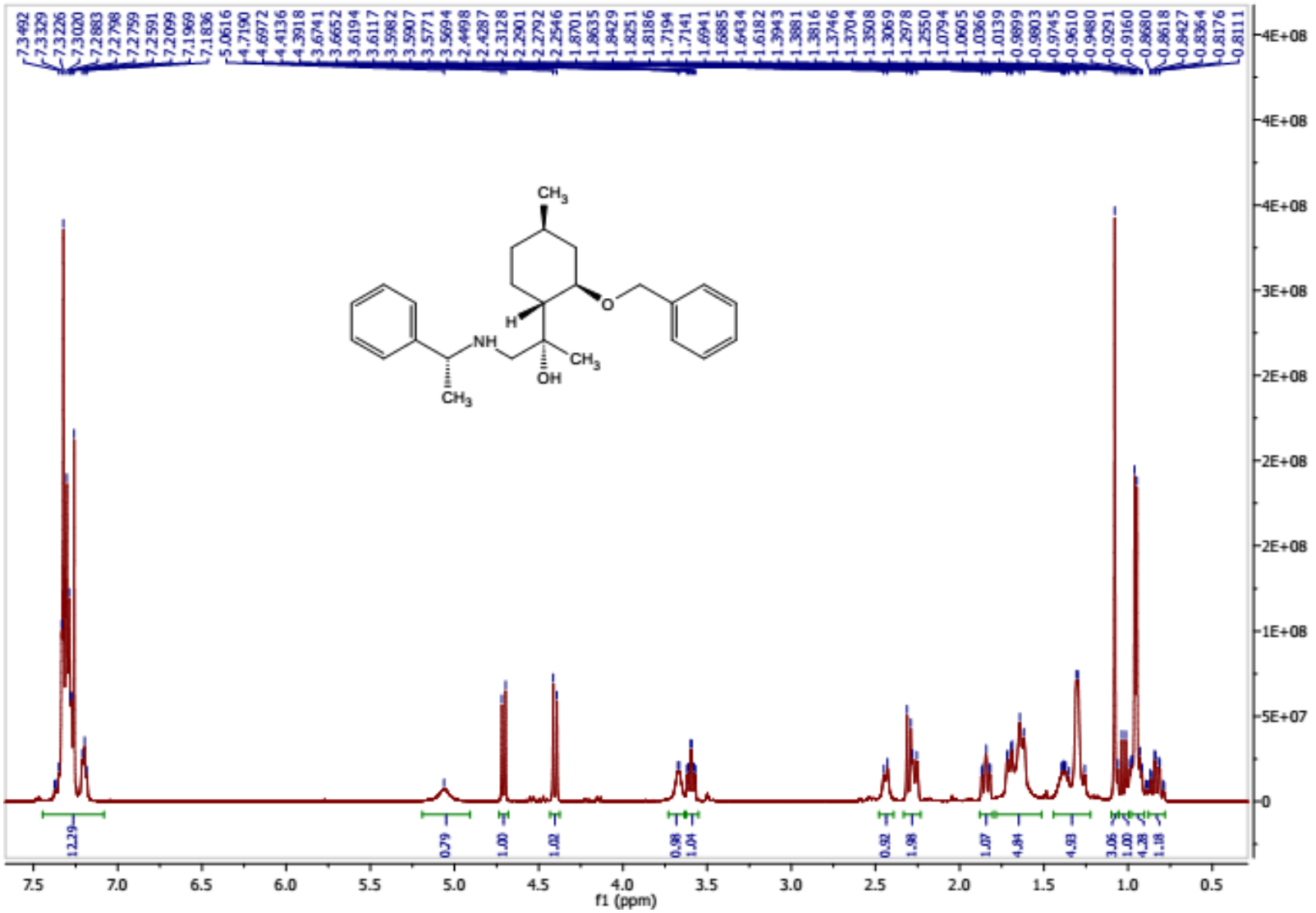
[1]H-NMR of compound **35b**



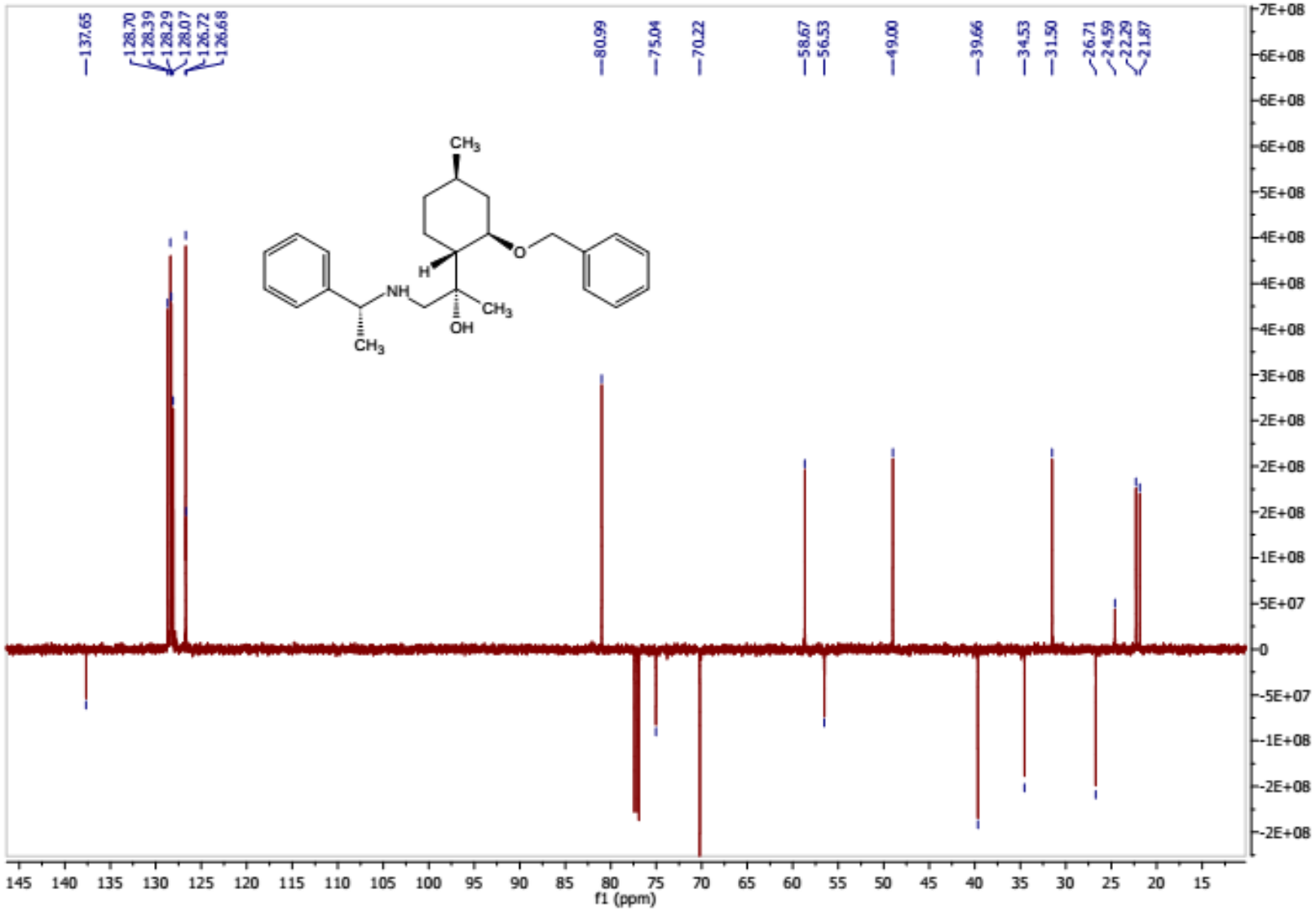
$^{13}$C-NMR of compound **35b**



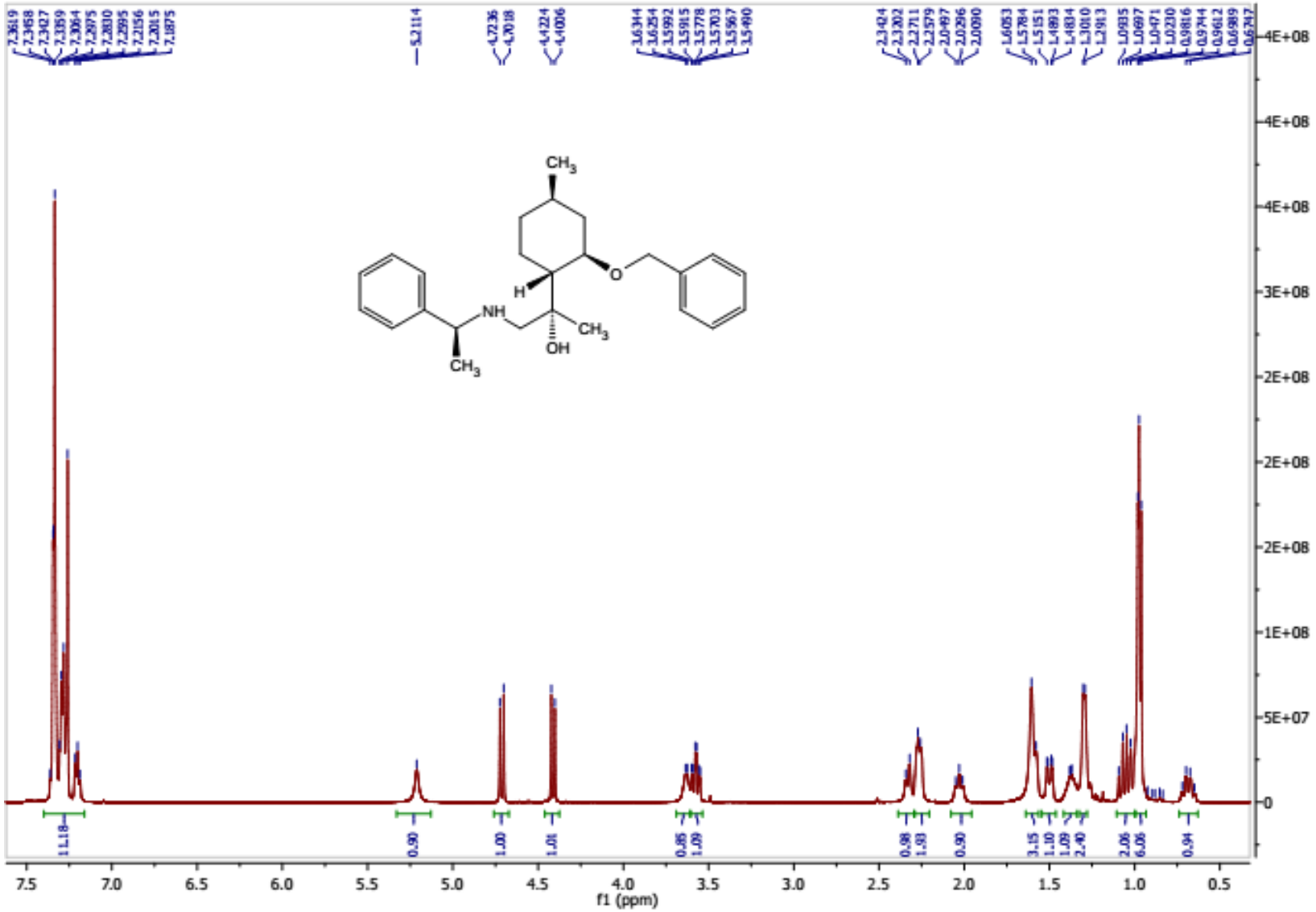
[1]H-NMR of compound **36b**



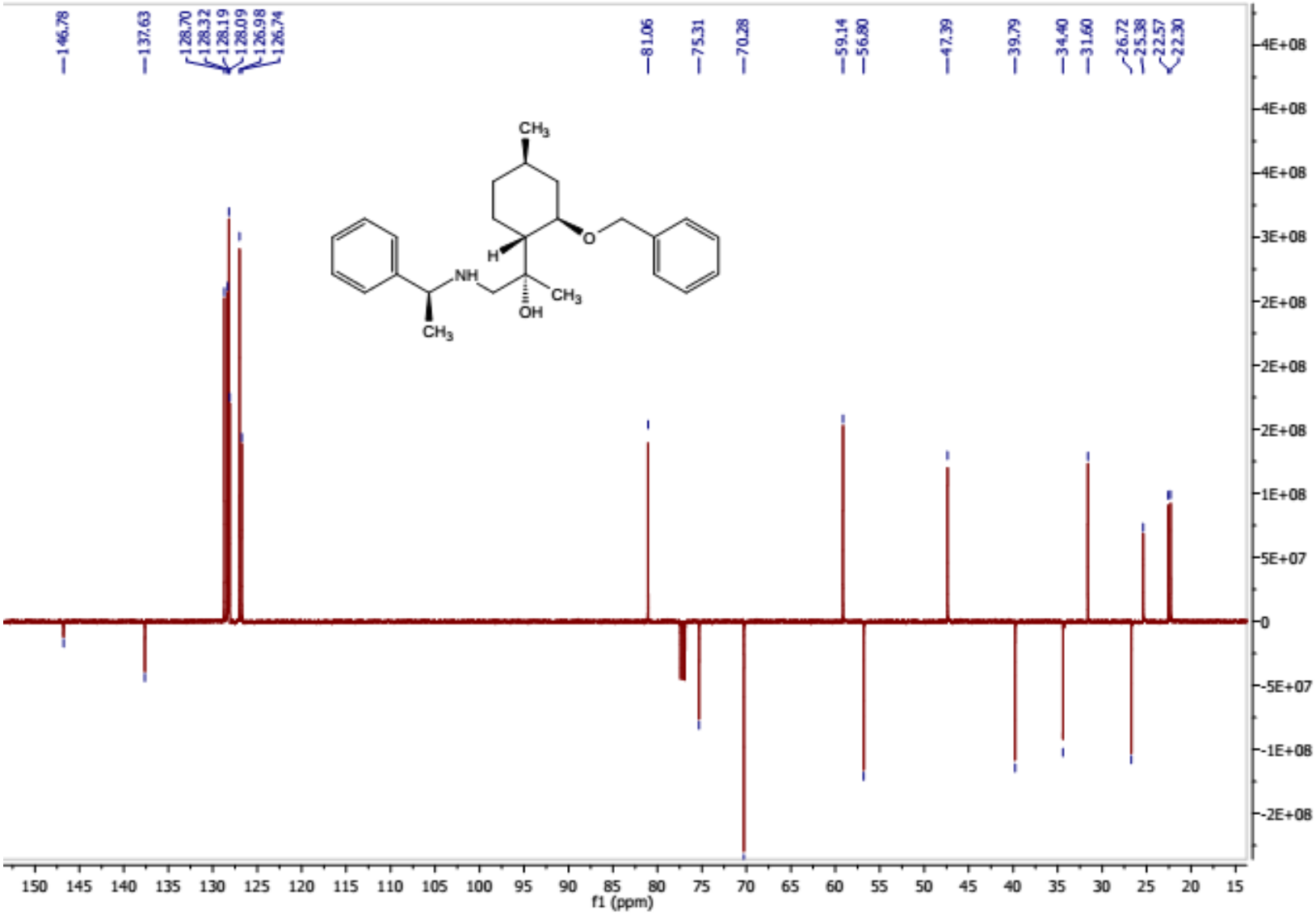
$^{13}$C-NMR of compound **36b**



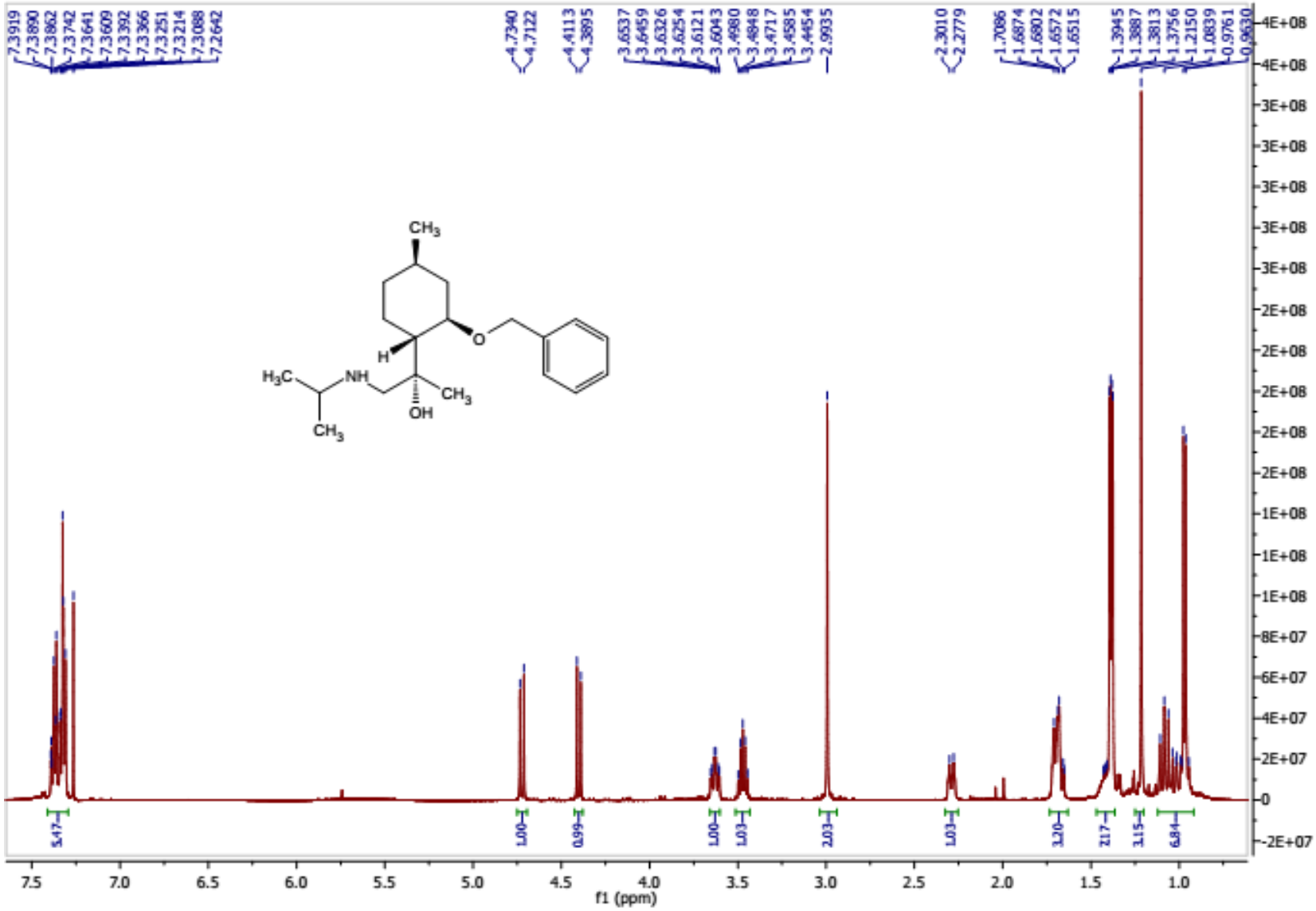
[1]H-NMR of compound **37b**



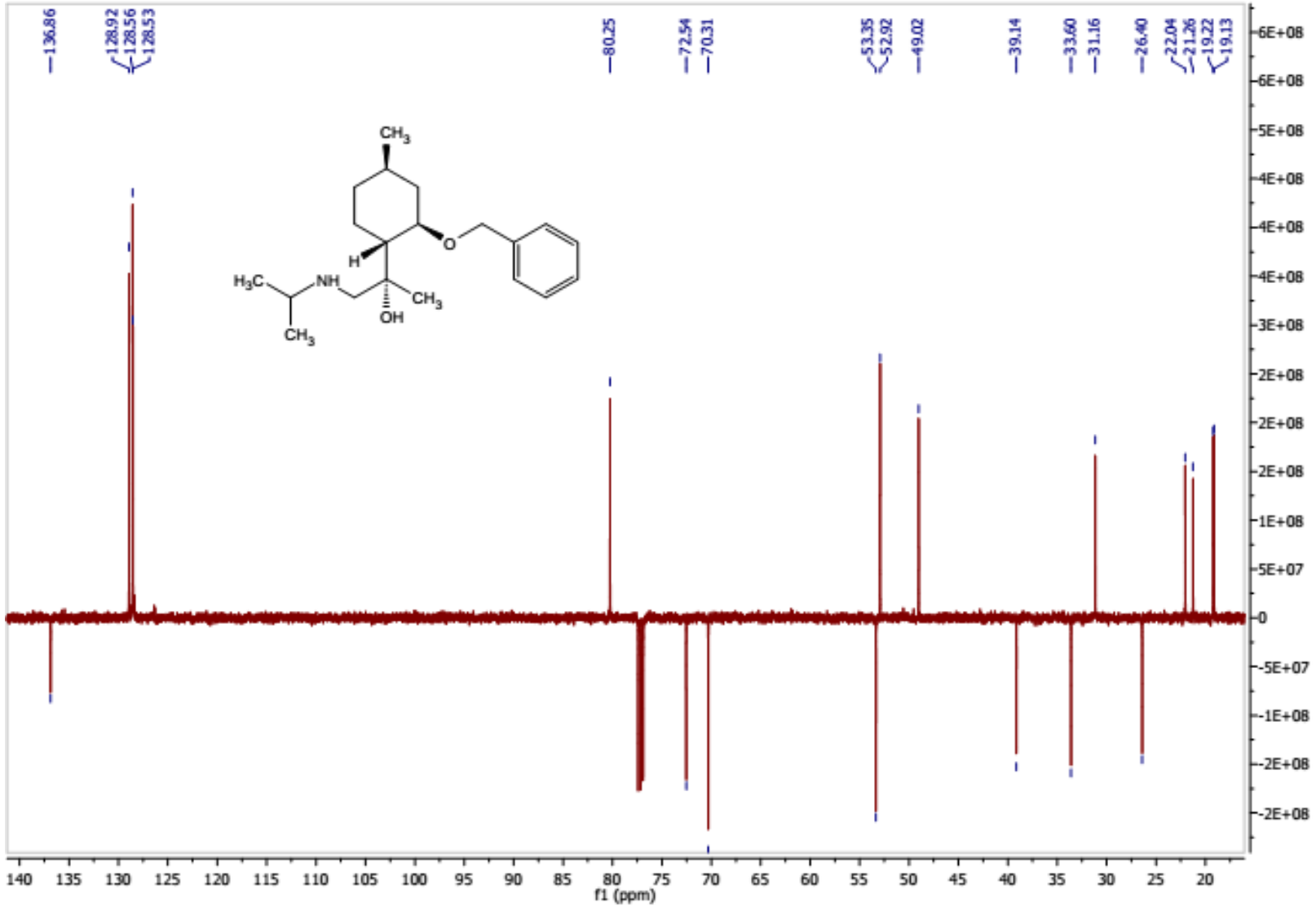
$^{13}$C-NMR of compound **37b**



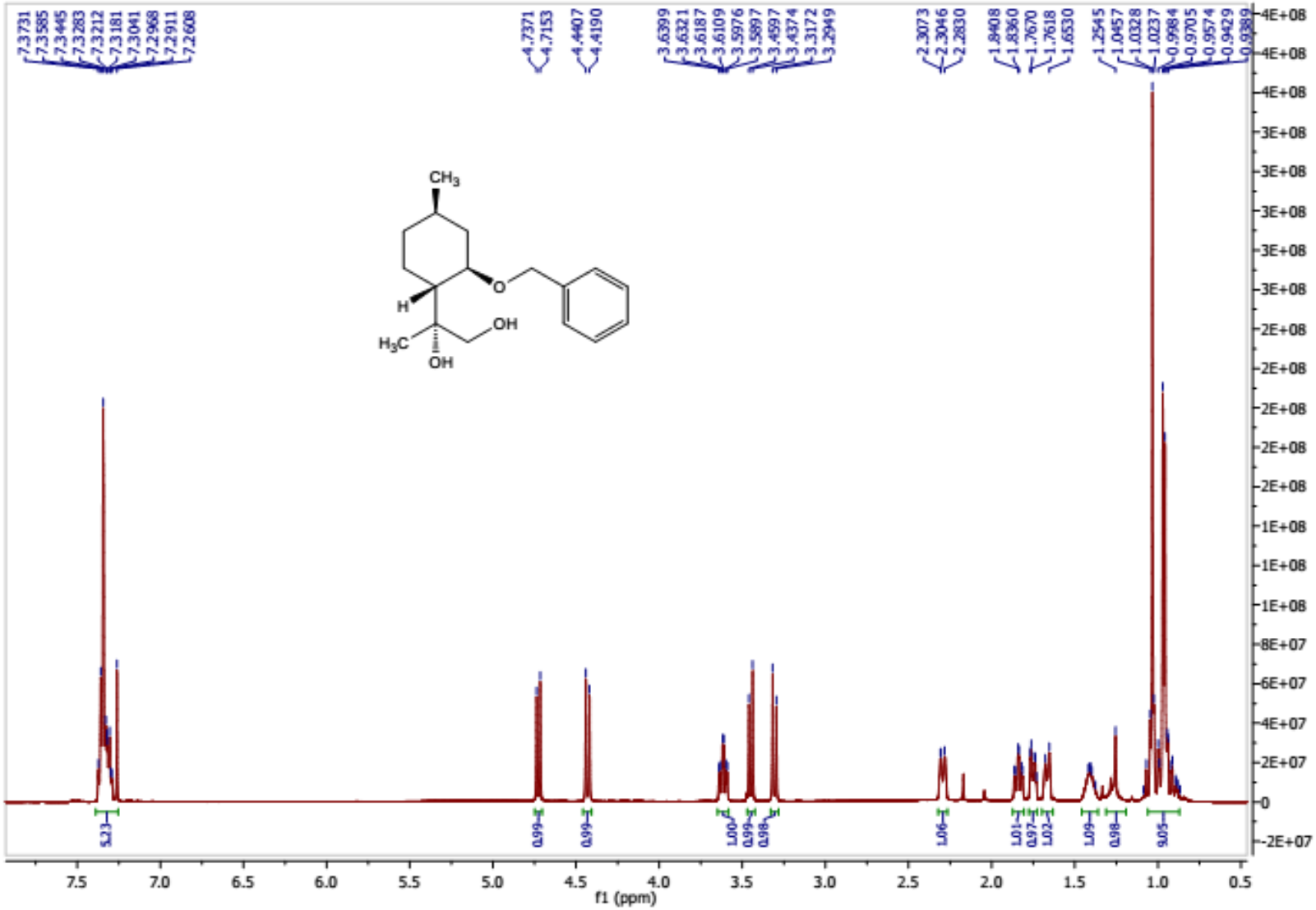
[1]H-NMR of compound **38b**



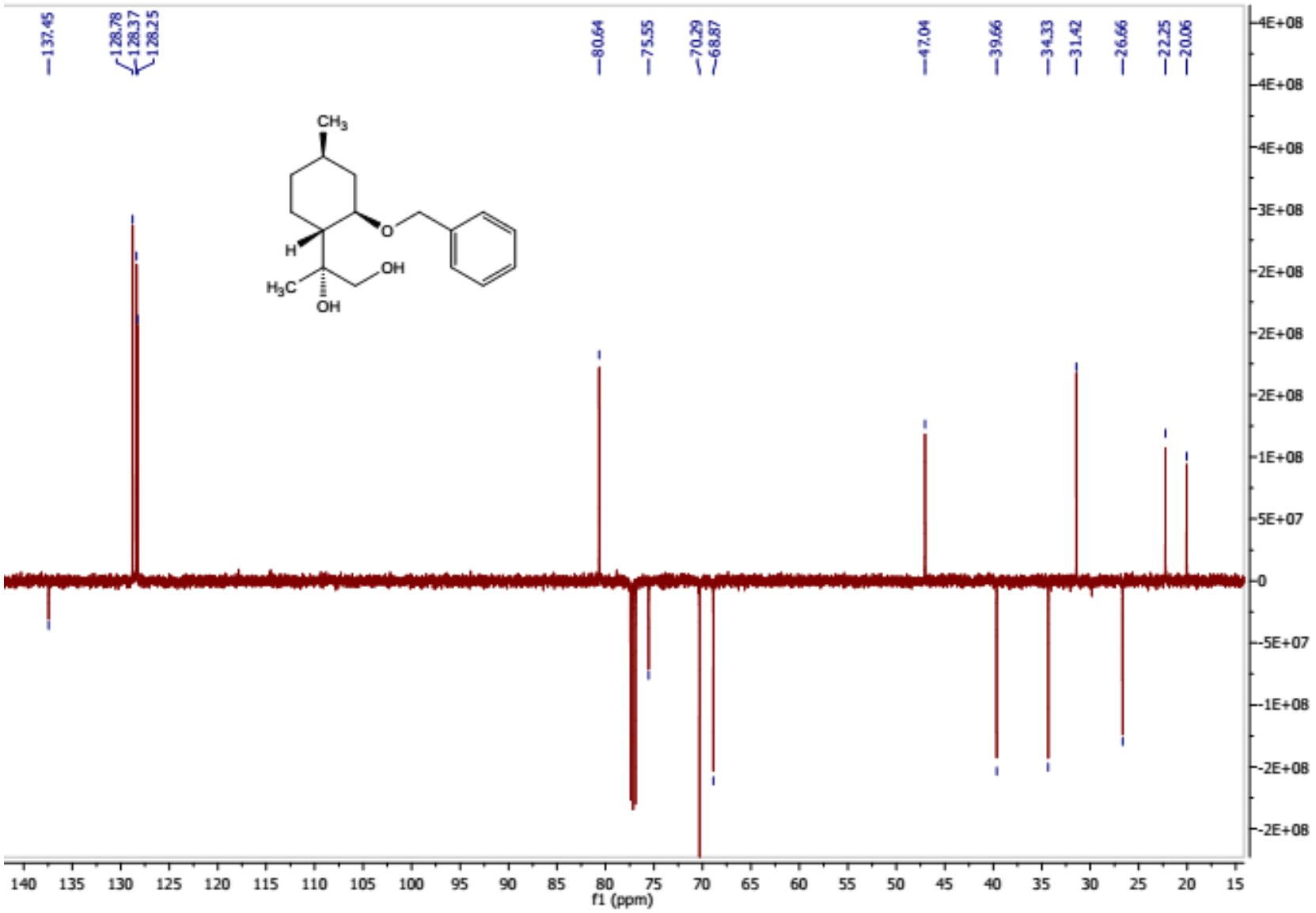
$^{13}$C-NMR of compound **38b**



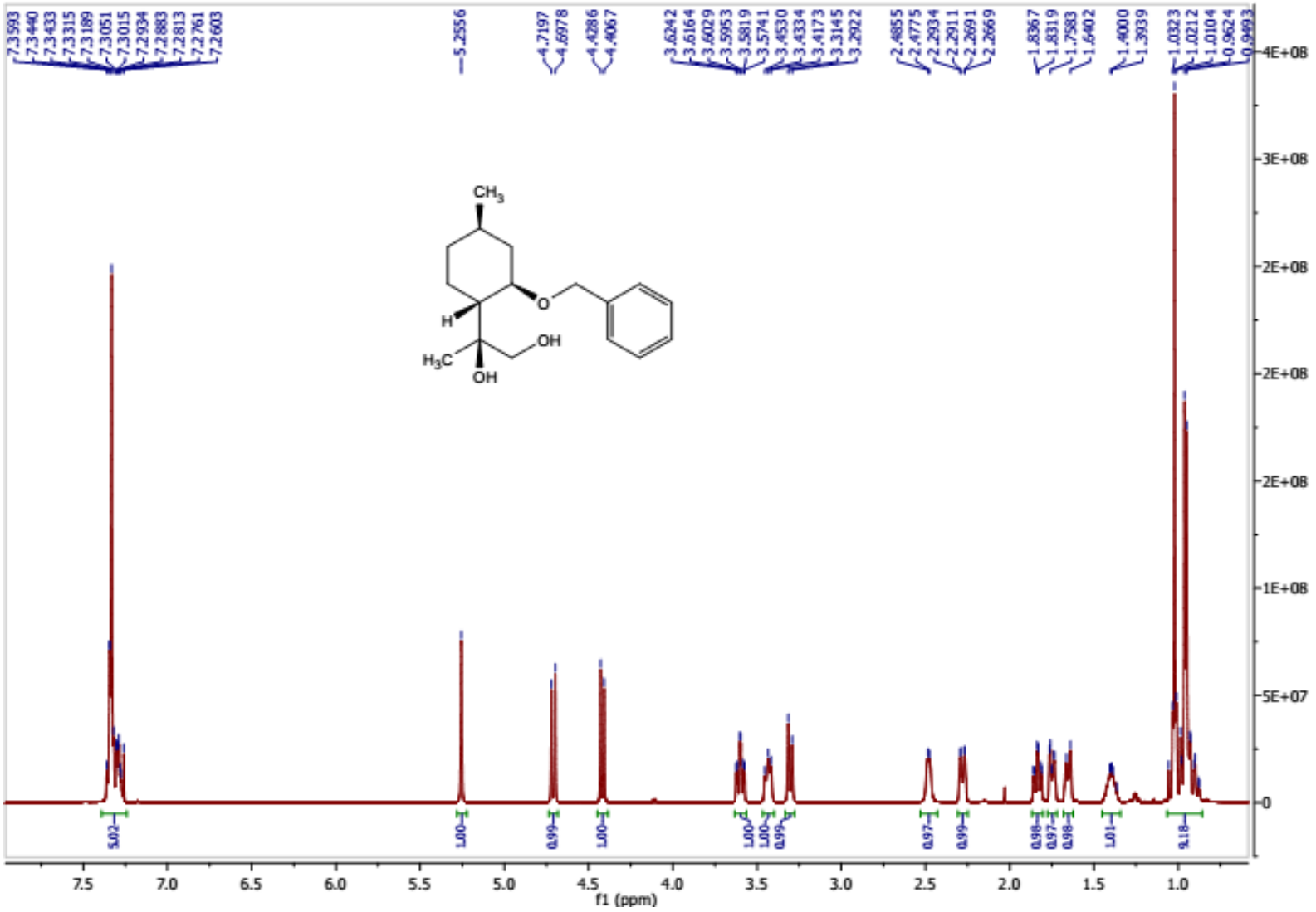
[1]H-NMR of compound **39a**



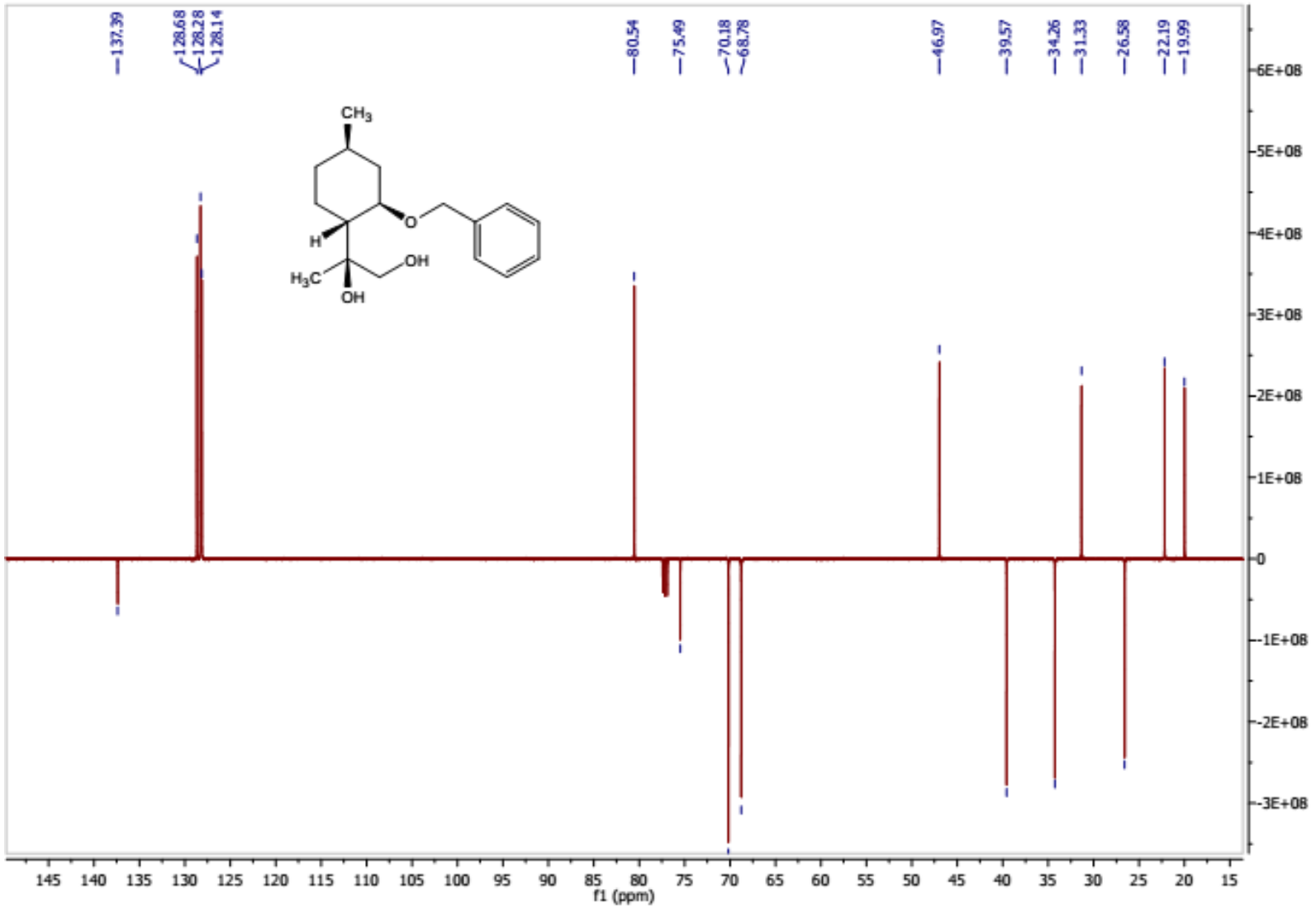
$^{13}$C-NMR of compound **39a**



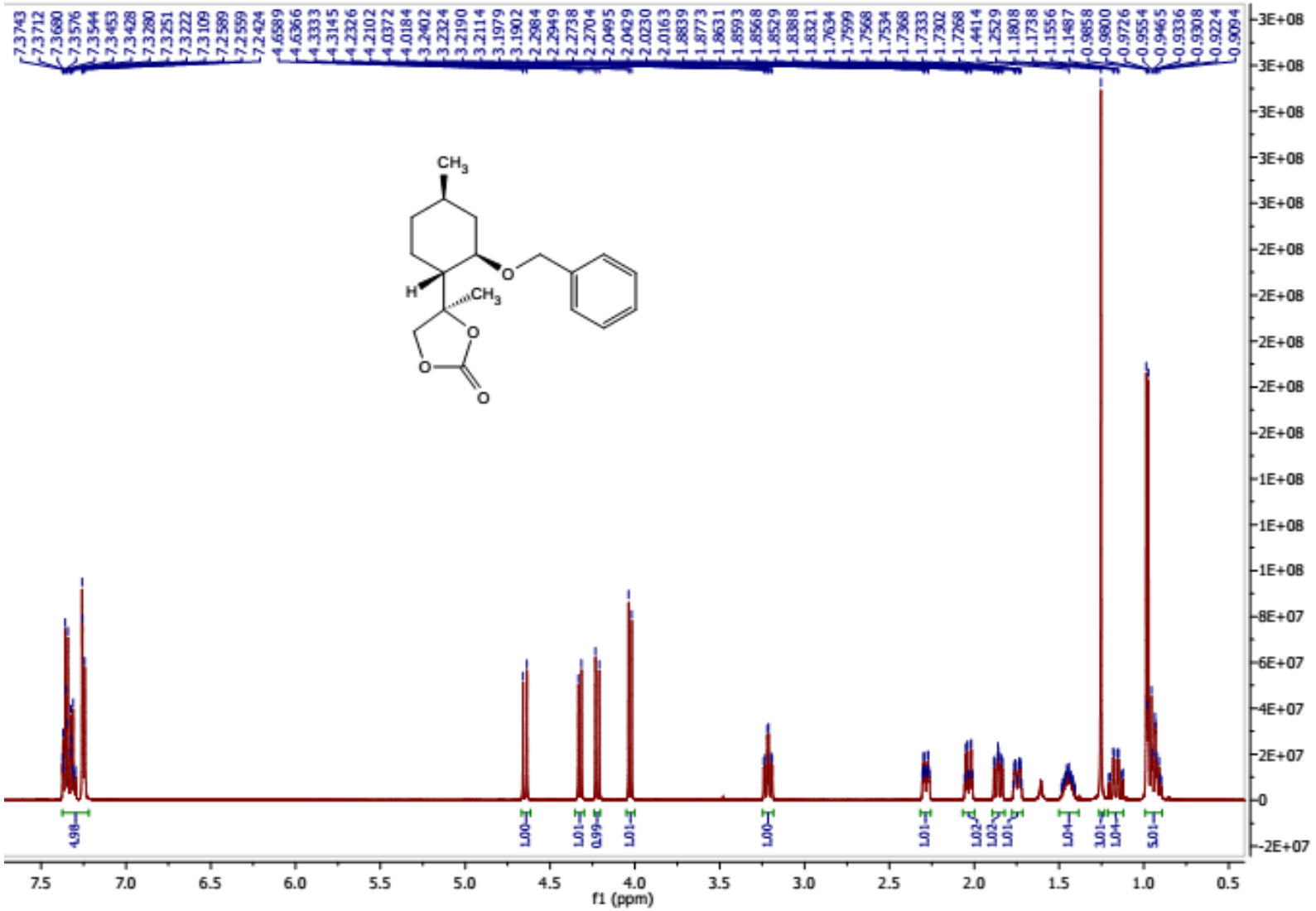
[1]H-NMR of compound **39b**



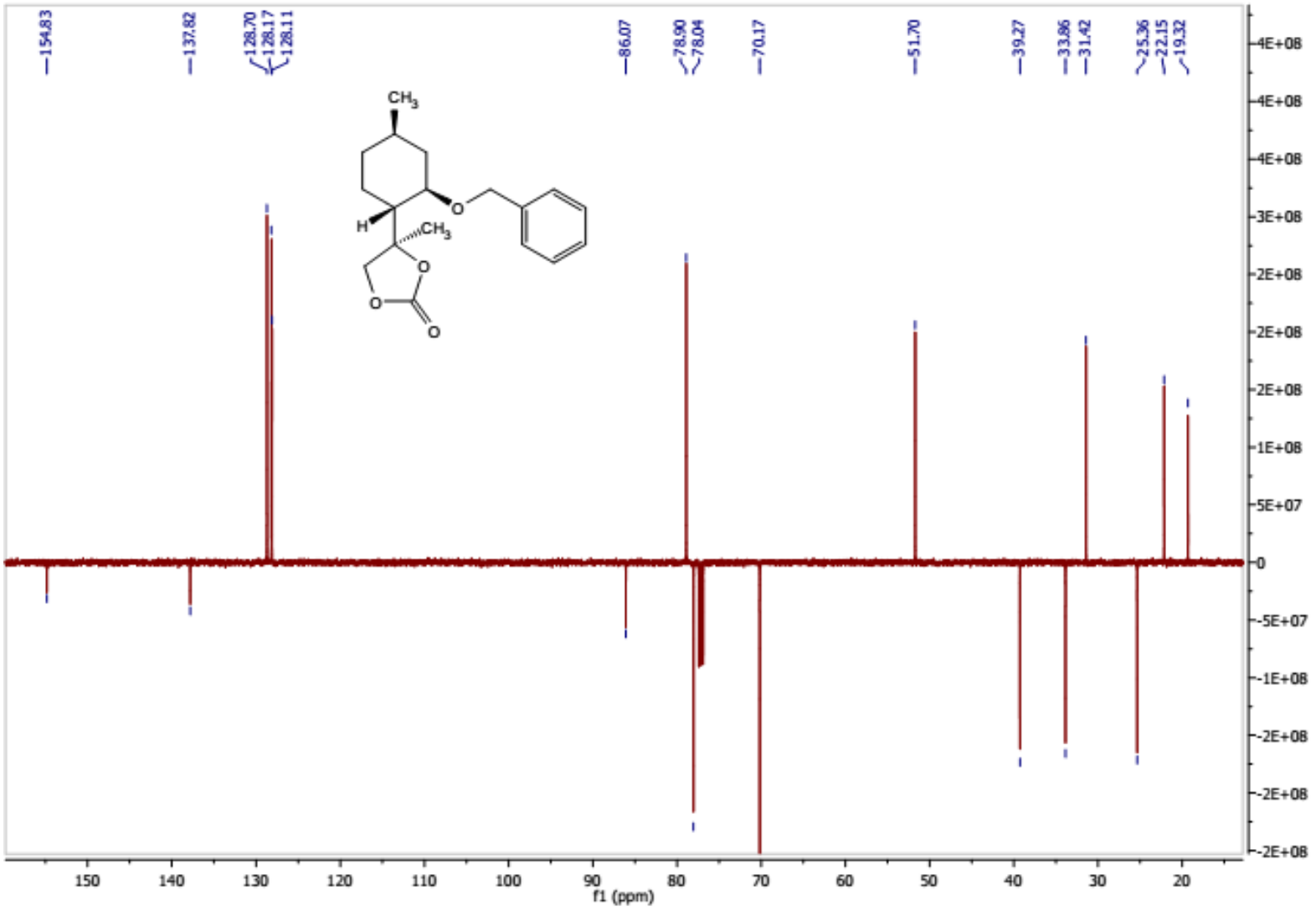
$^{13}$C-NMR of compound **39b**



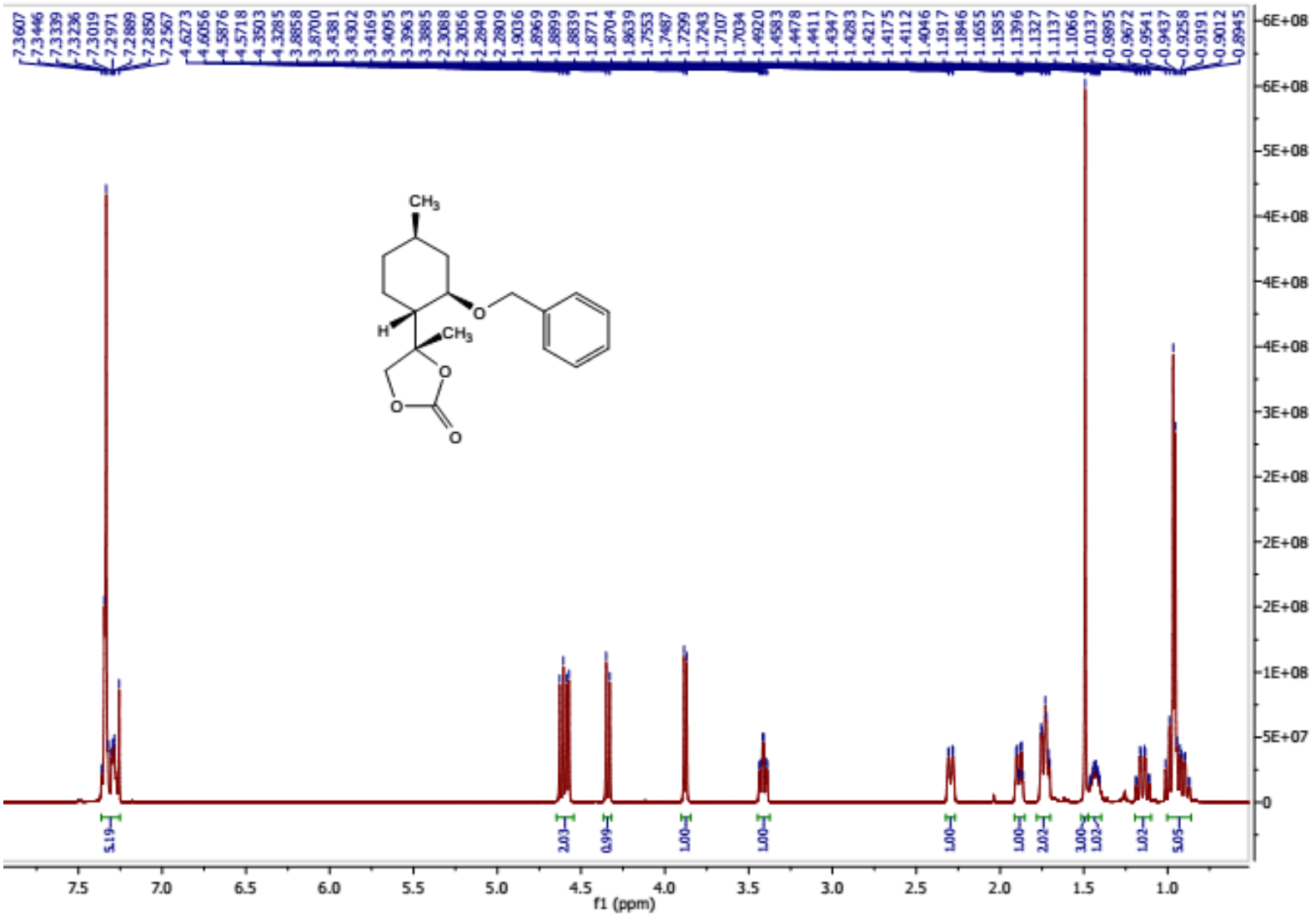
$^{1}$H-NMR of compound **40a**



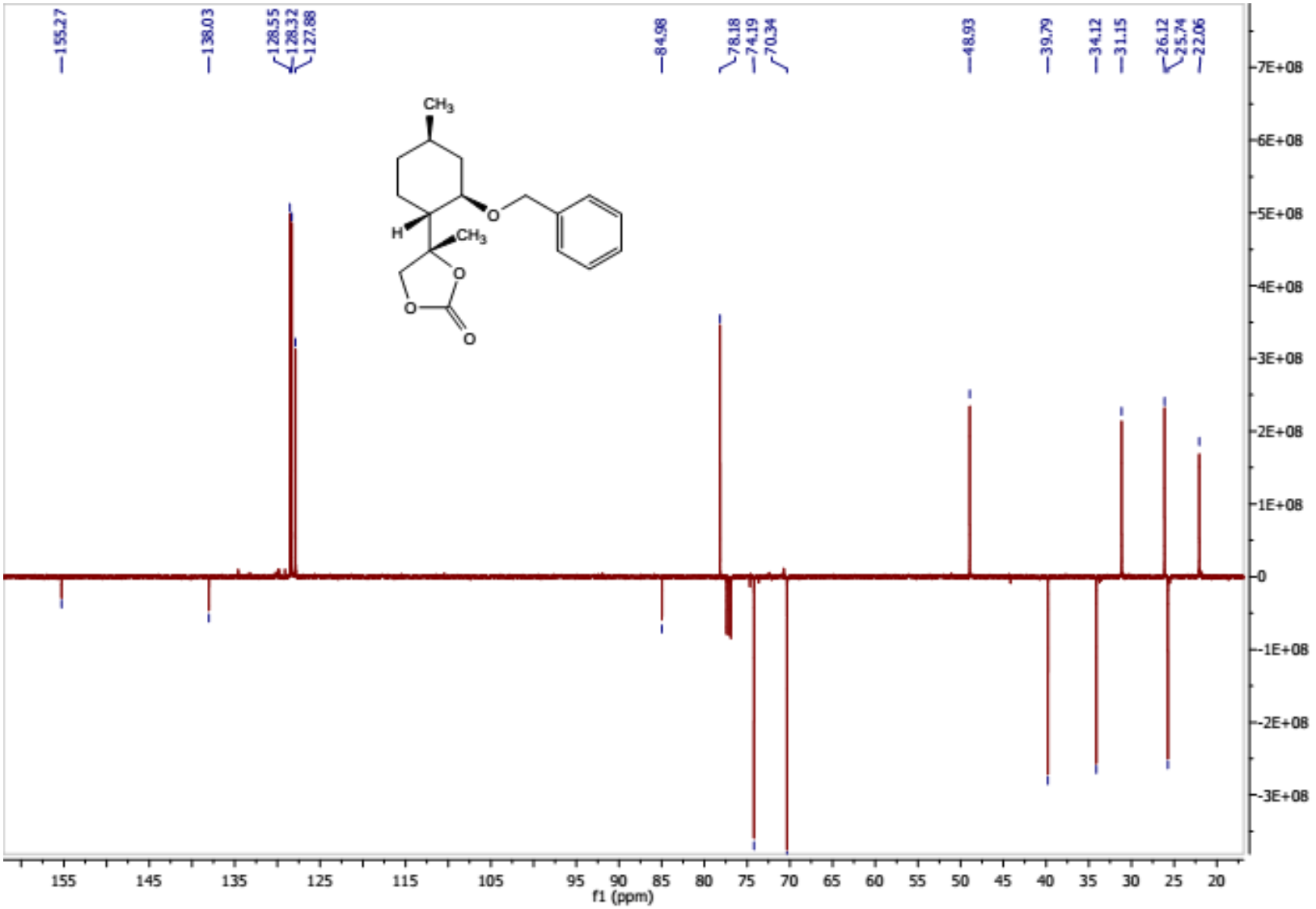
$^{13}$C-NMR of compound **40a**



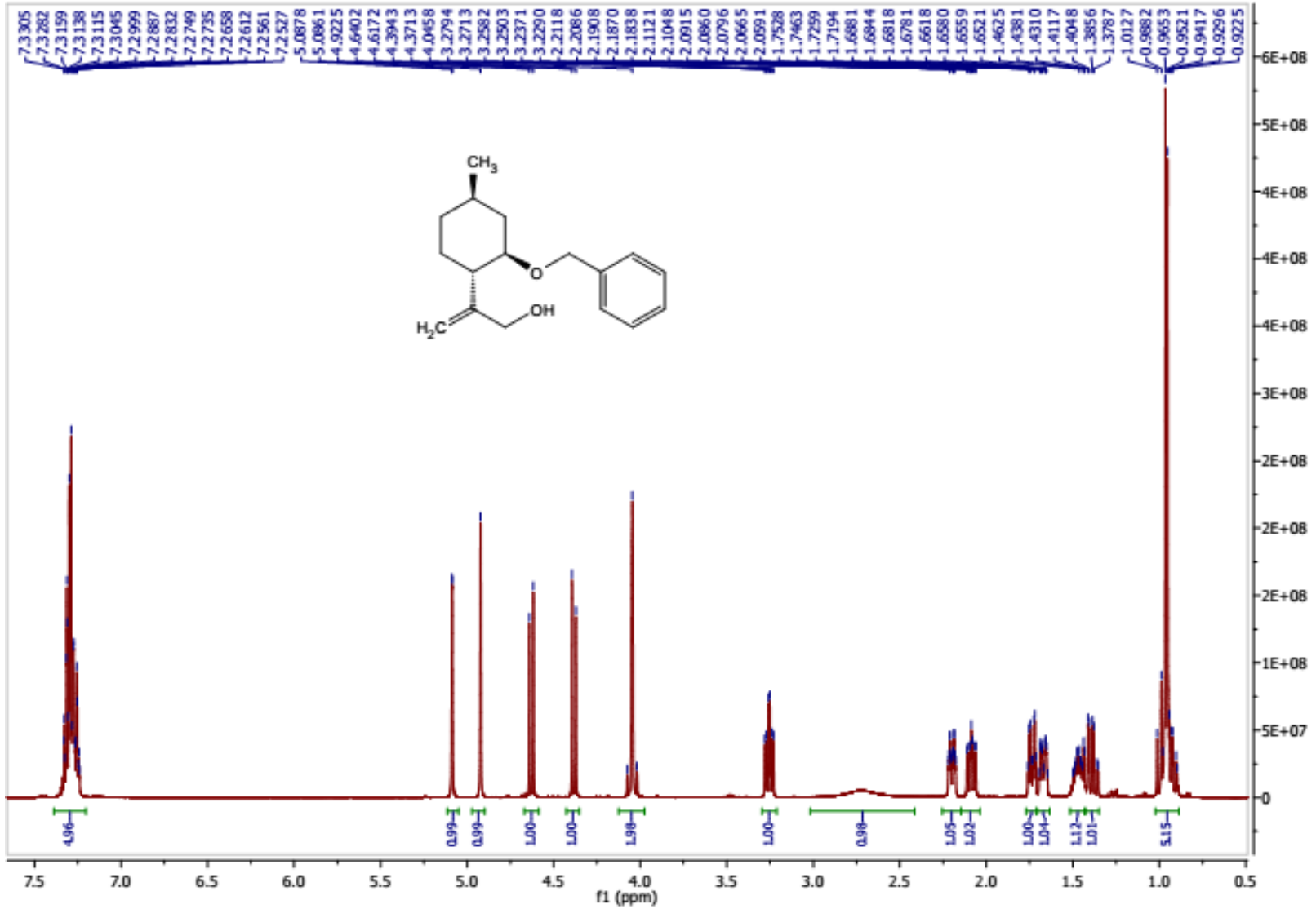
[1]H-NMR of compound **40b**



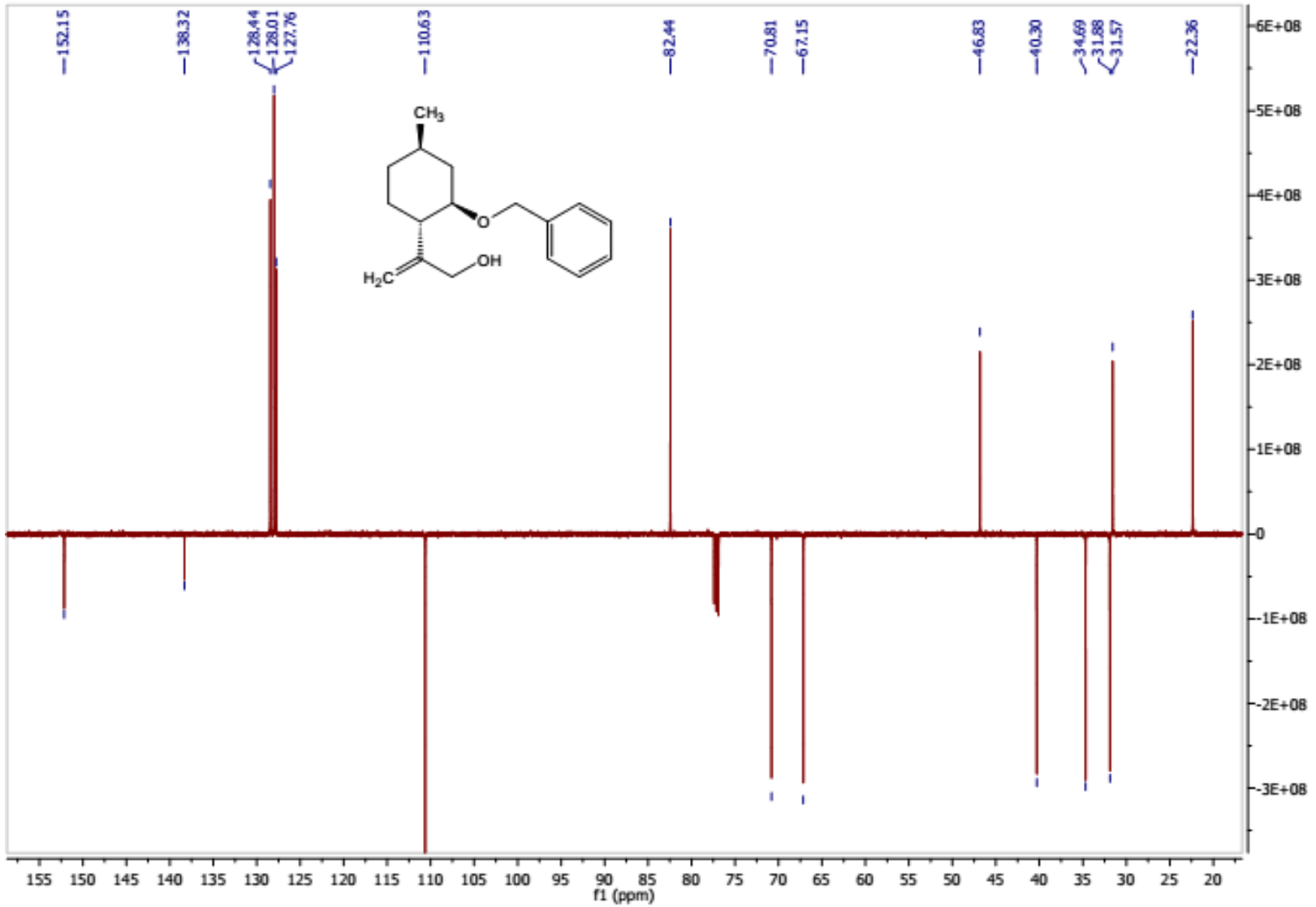
$^{13}$C-NMR of compound **40b**



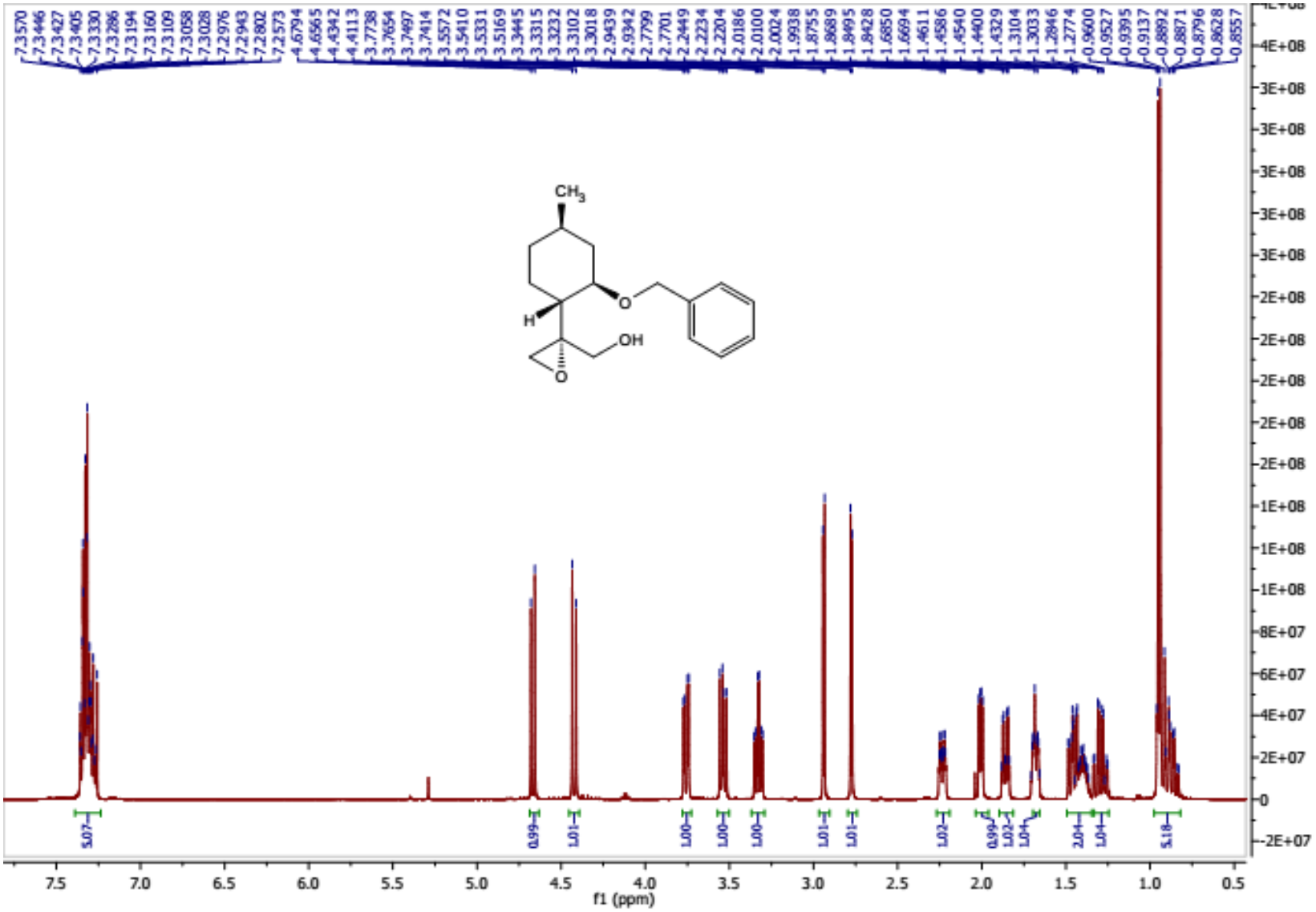
[1]H-NMR of compound **41**



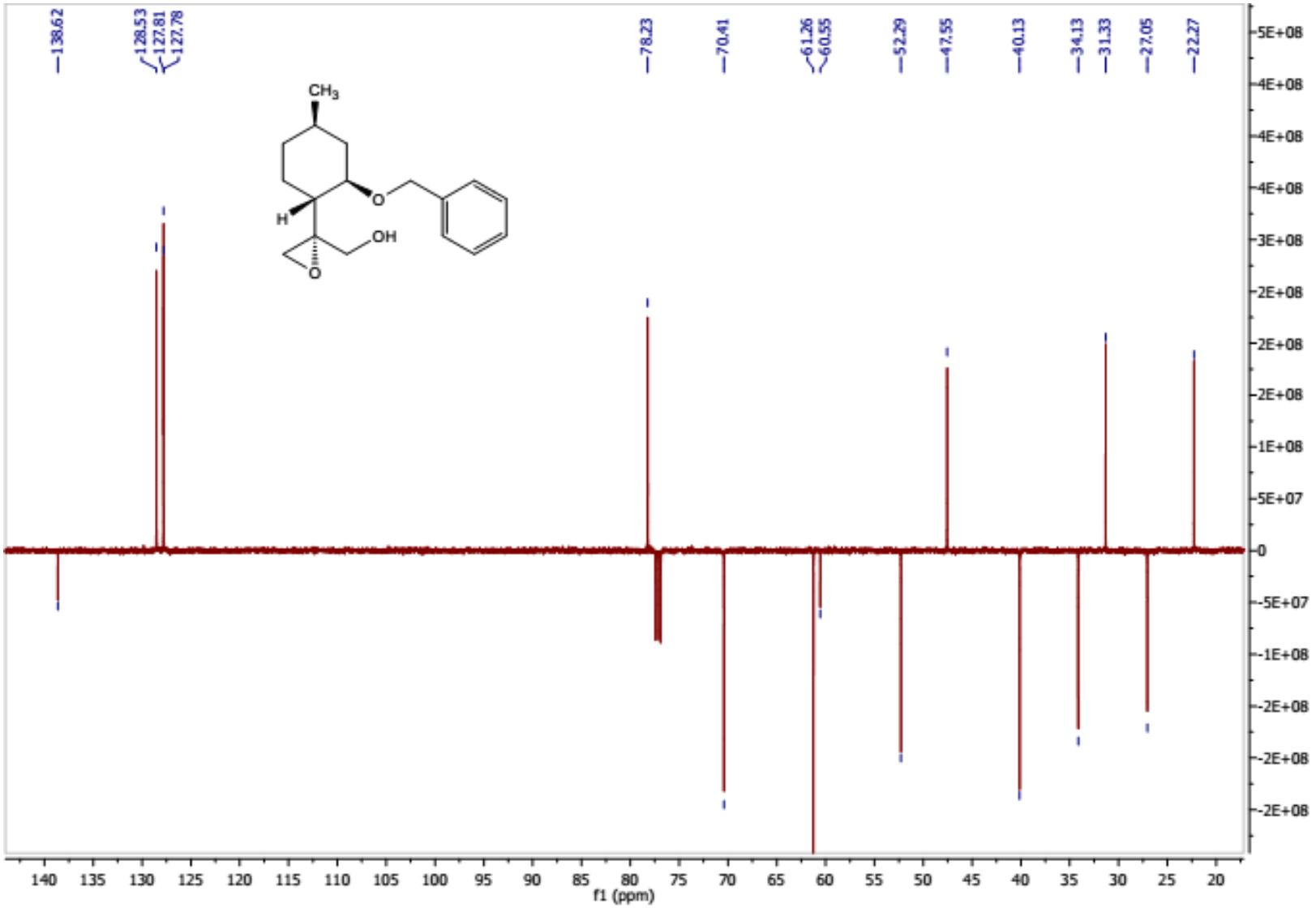
$^{13}$C-NMR of compound **41**



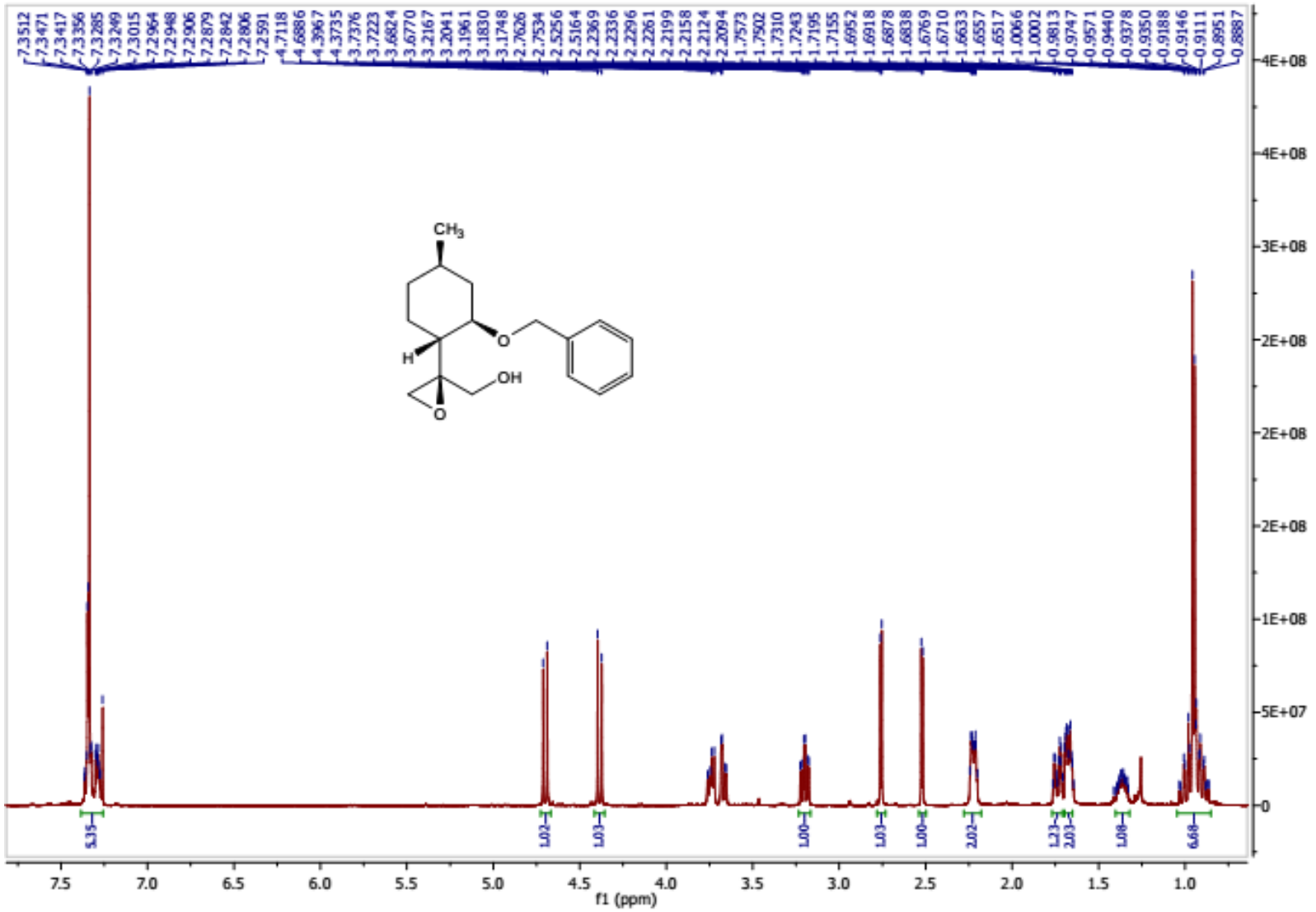
[1]H-NMR of compound **42a**



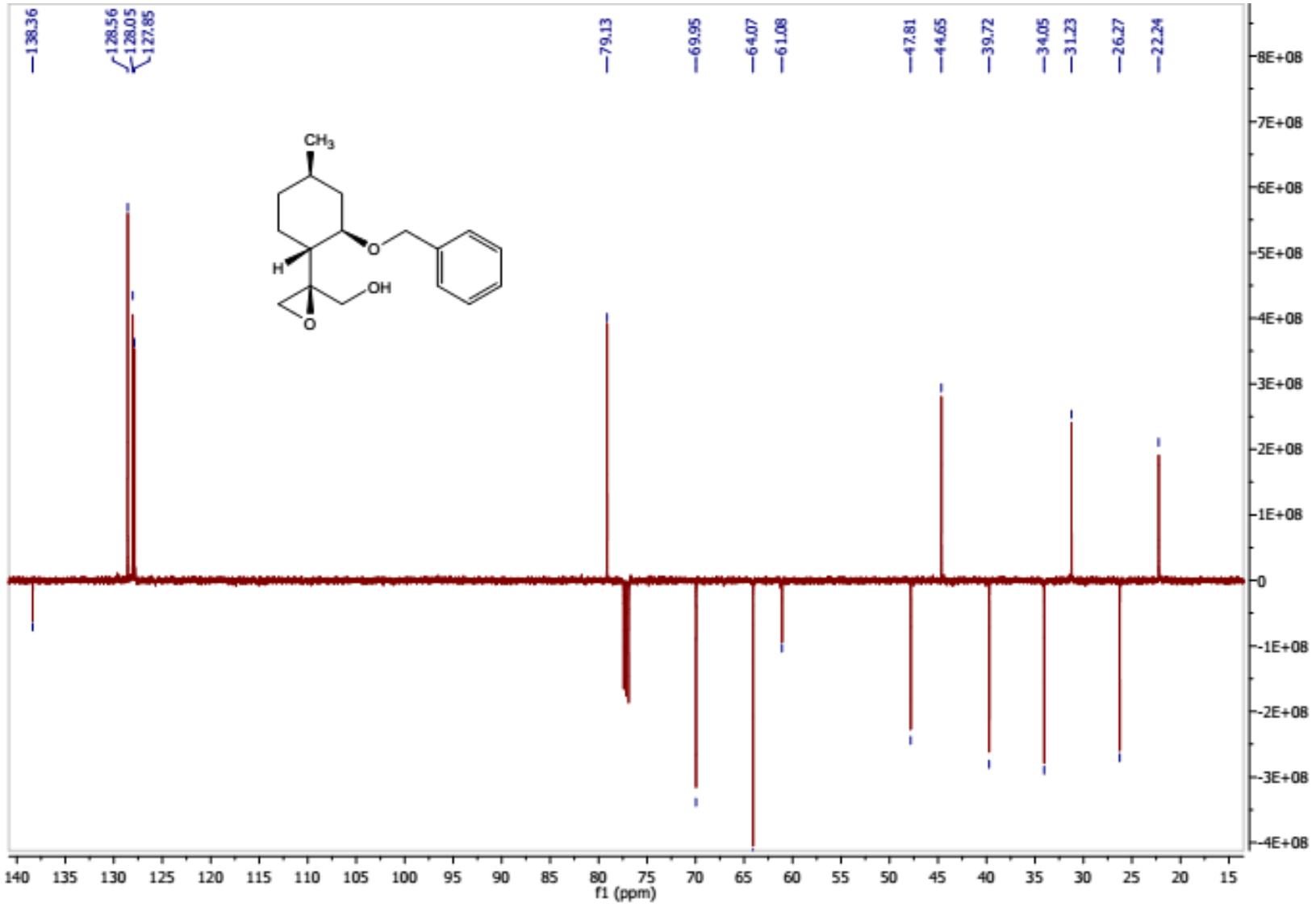
$^{13}$C-NMR of compound **42a**



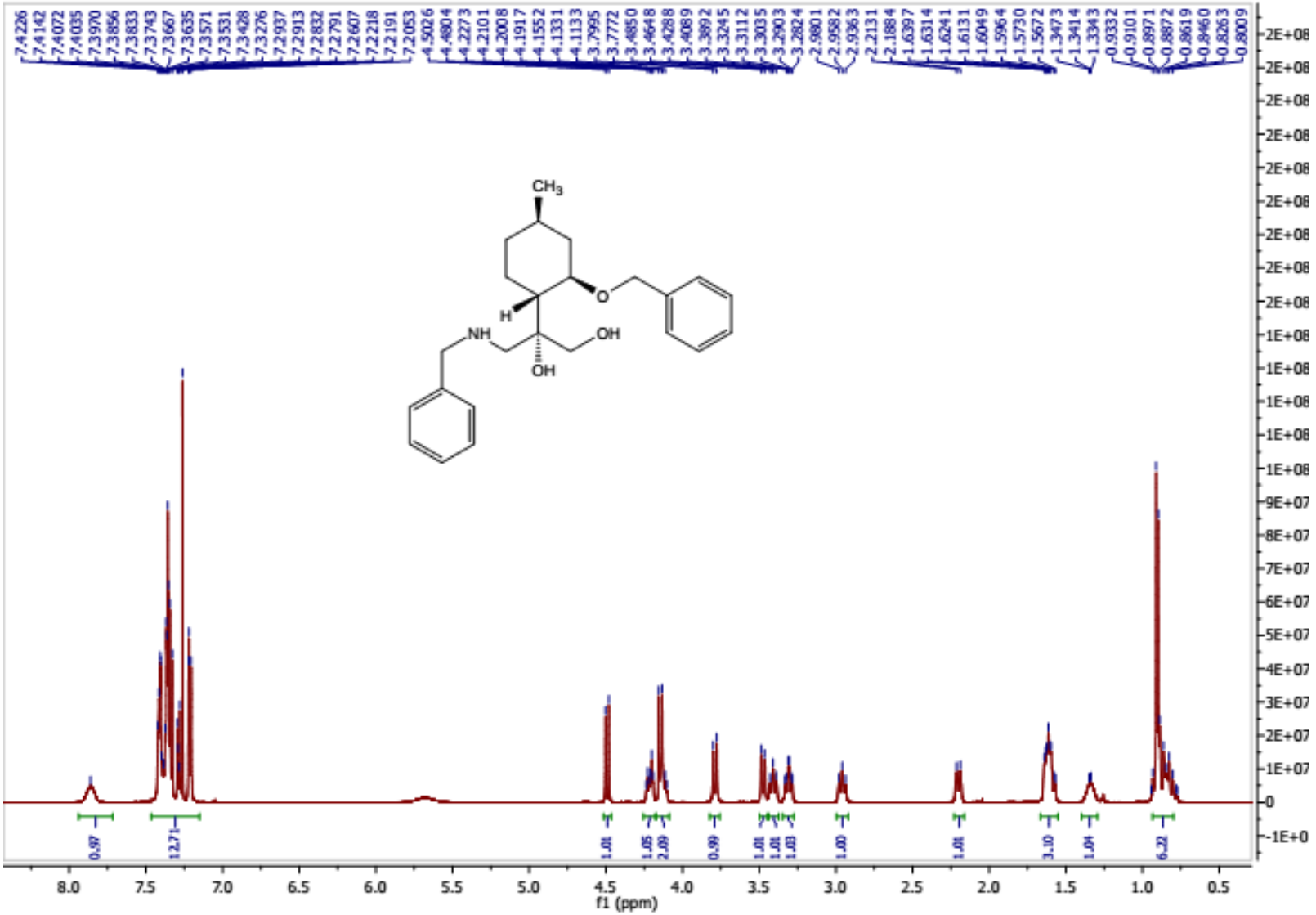
[1]H-NMR of compound **42b**



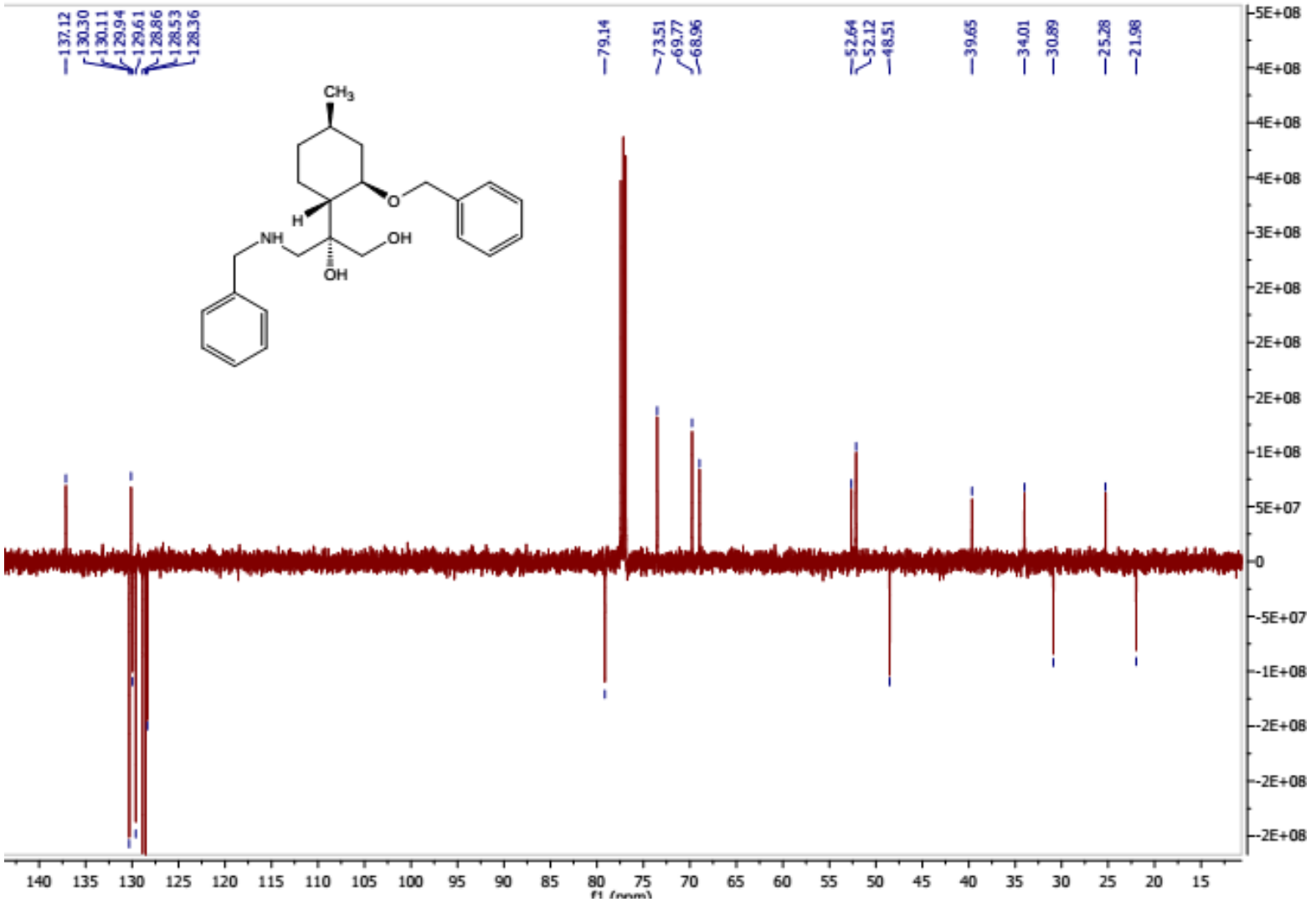
$^{13}$C-NMR of compound **42b**



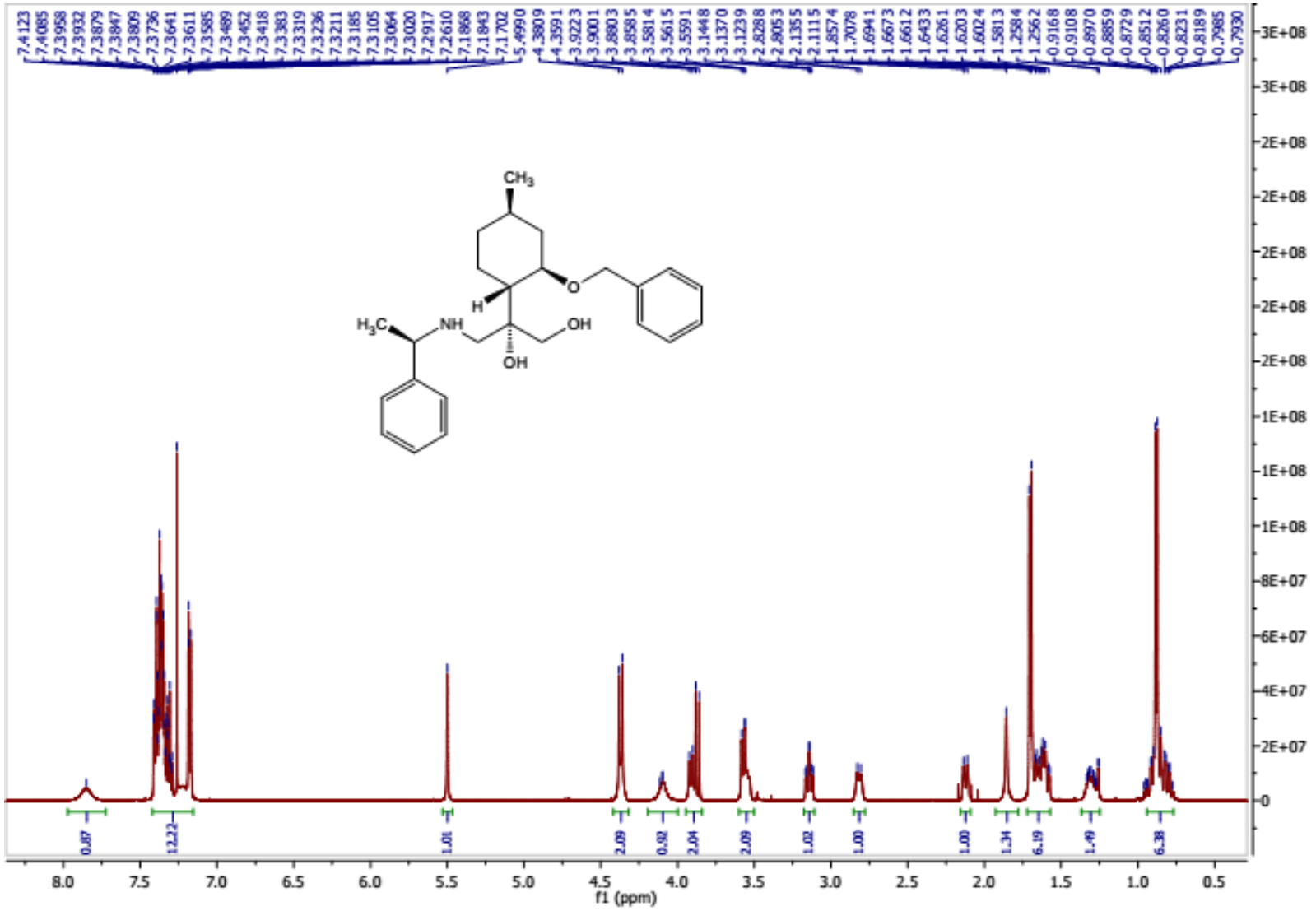
$^{1}$H-NMR of compound **43a**



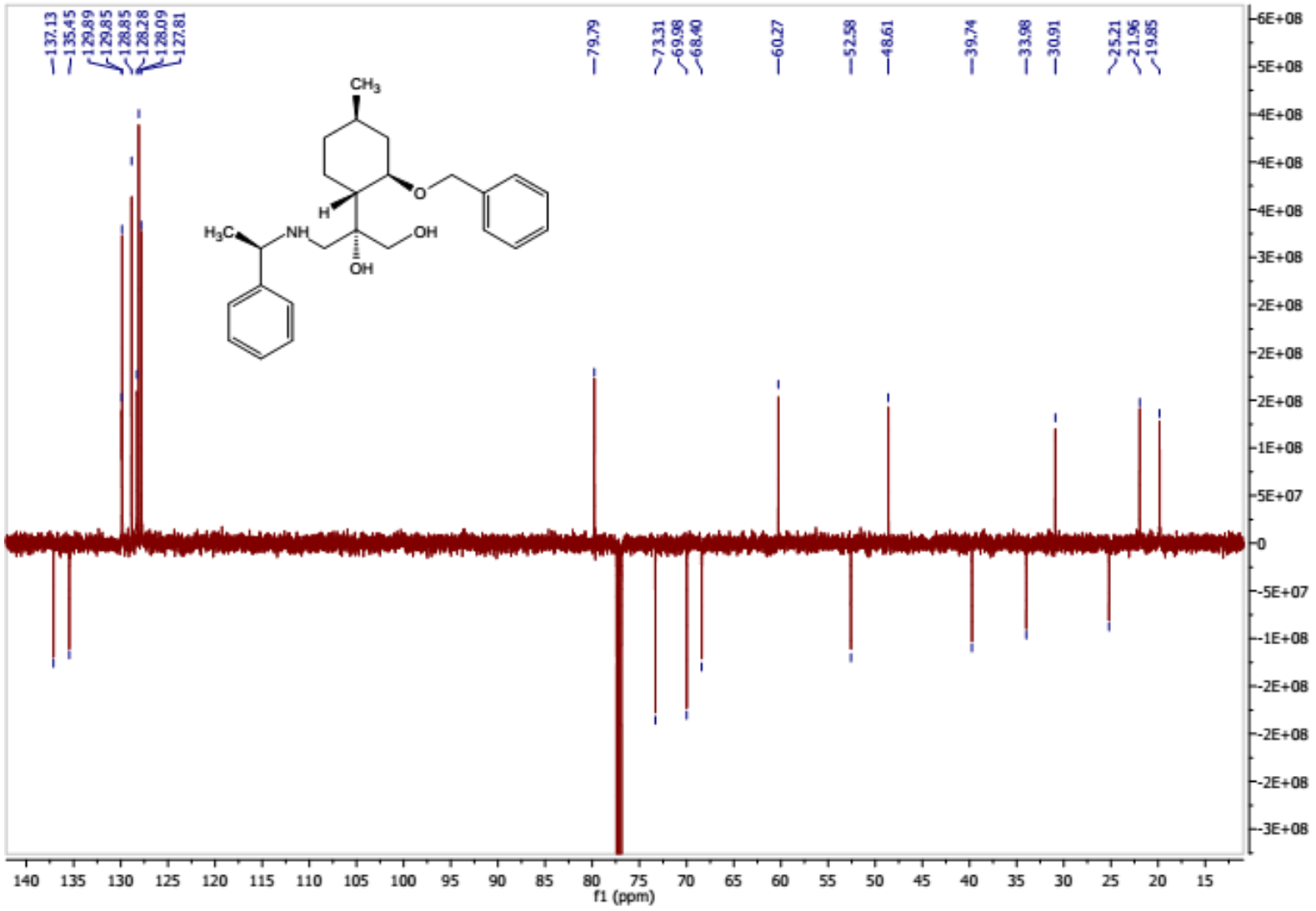
$^{13}$C-NMR of compound **43a**



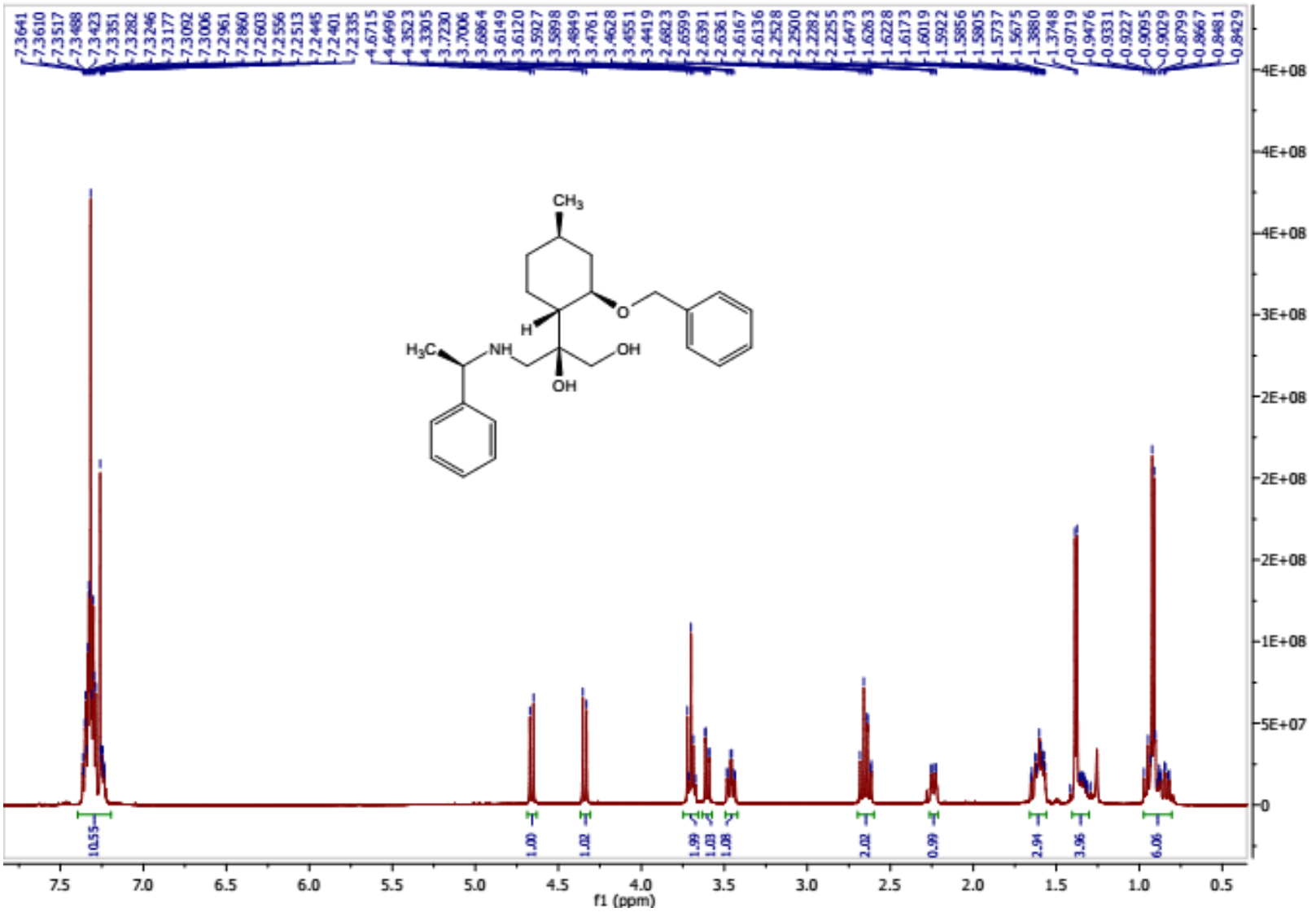
[1]H-NMR of compound **44a**



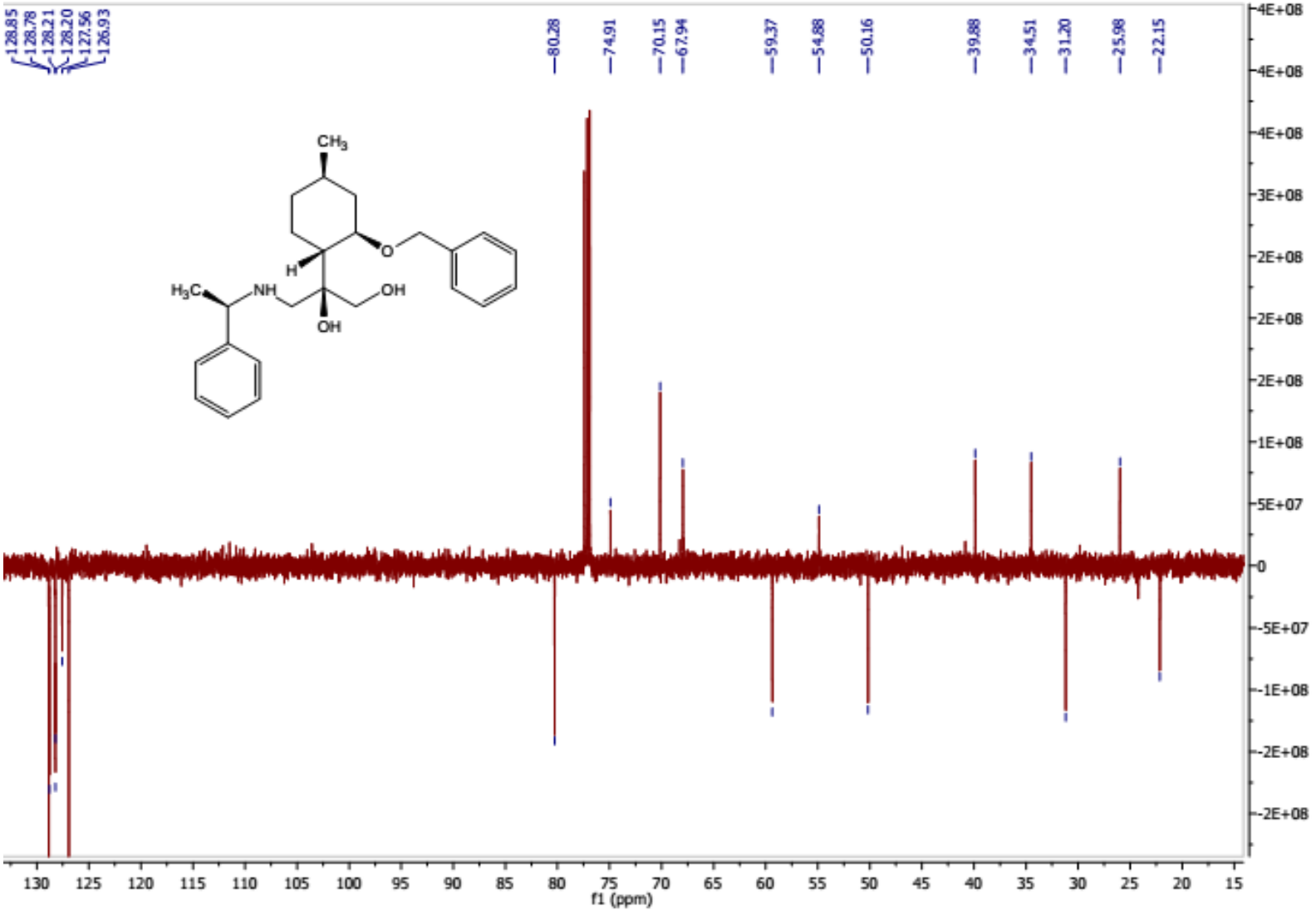
$^{13}$C-NMR of compound **44a**



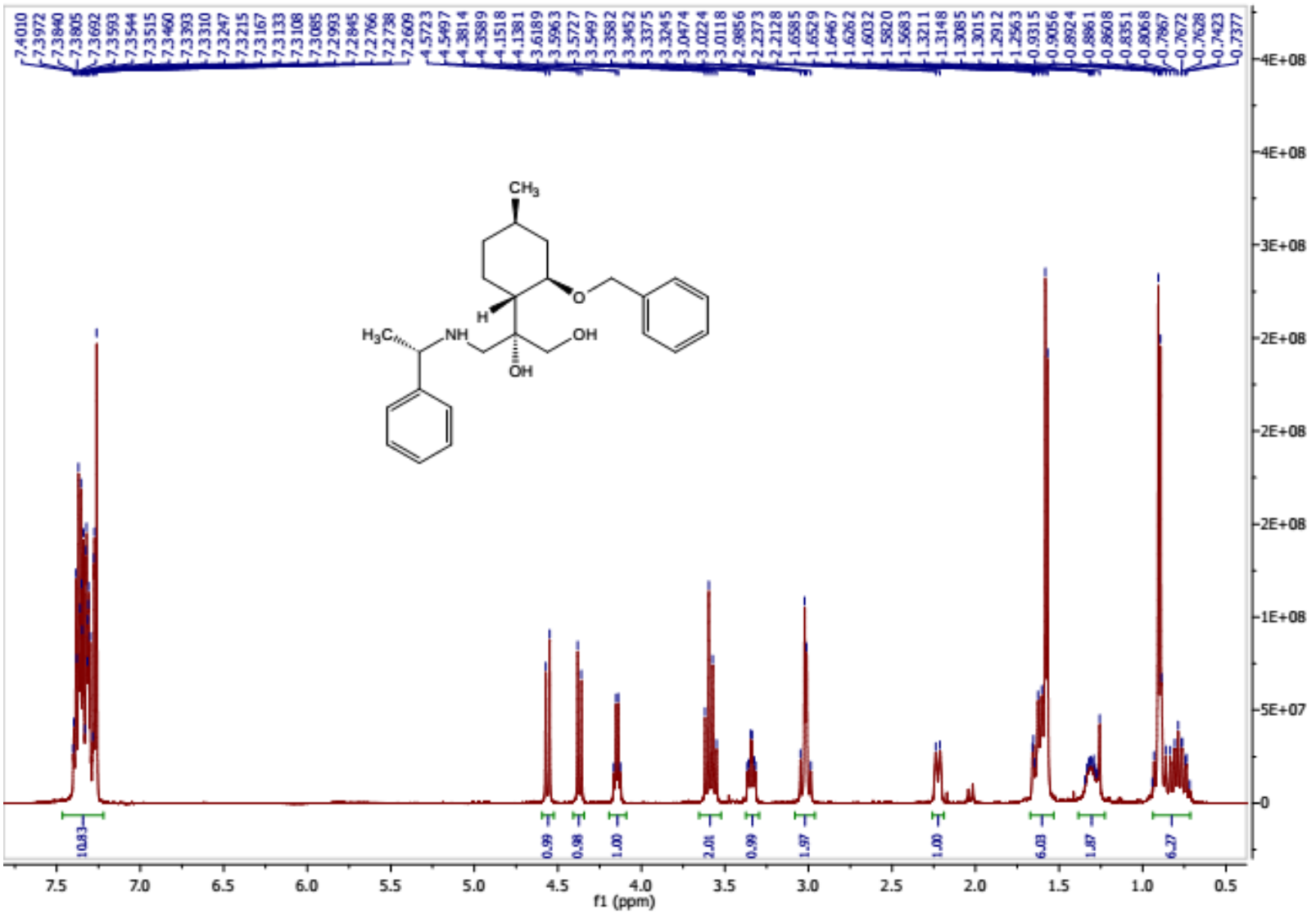
[1]H-NMR of compound **44b**



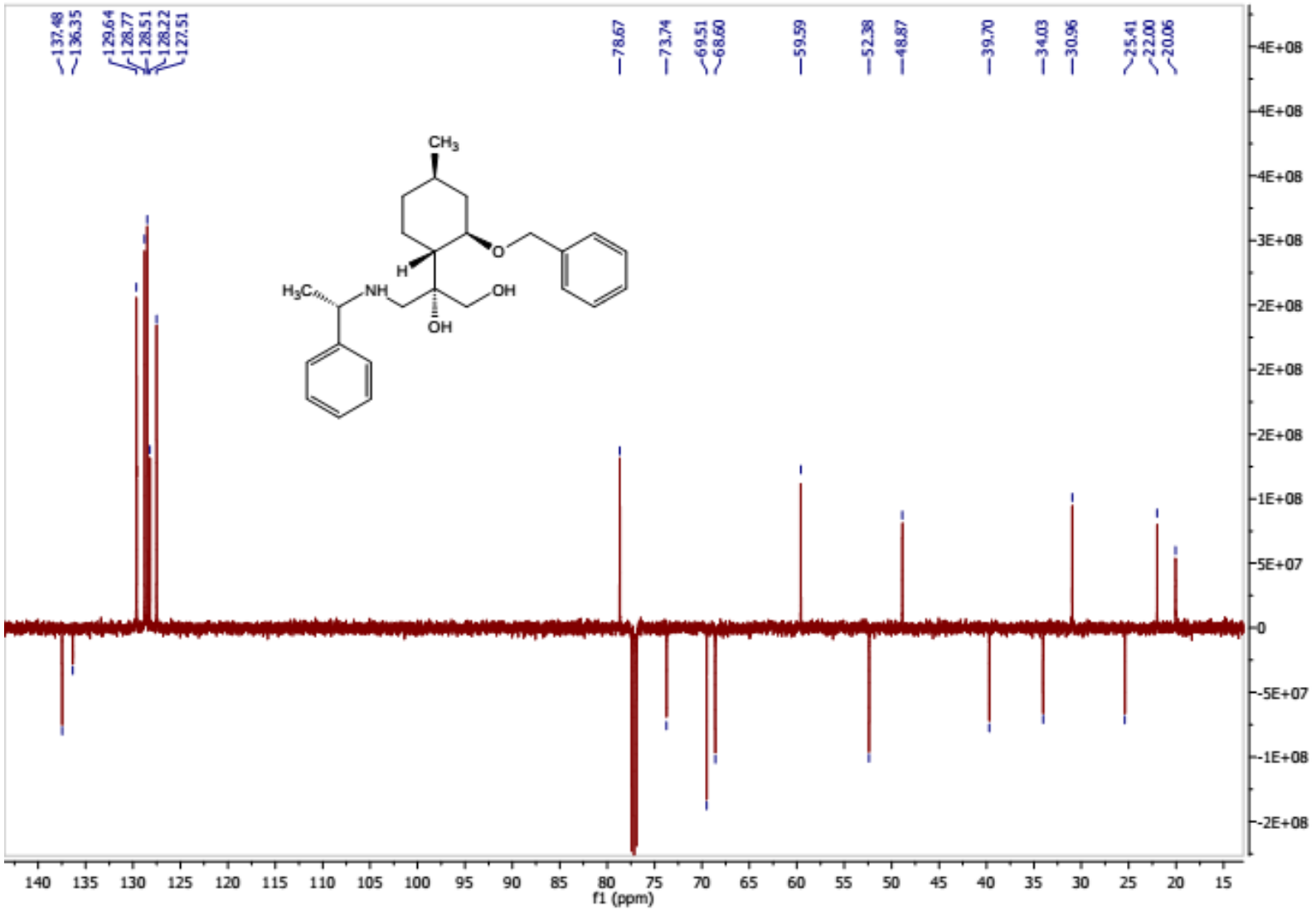
$^{13}$C-NMR of compound **44b**



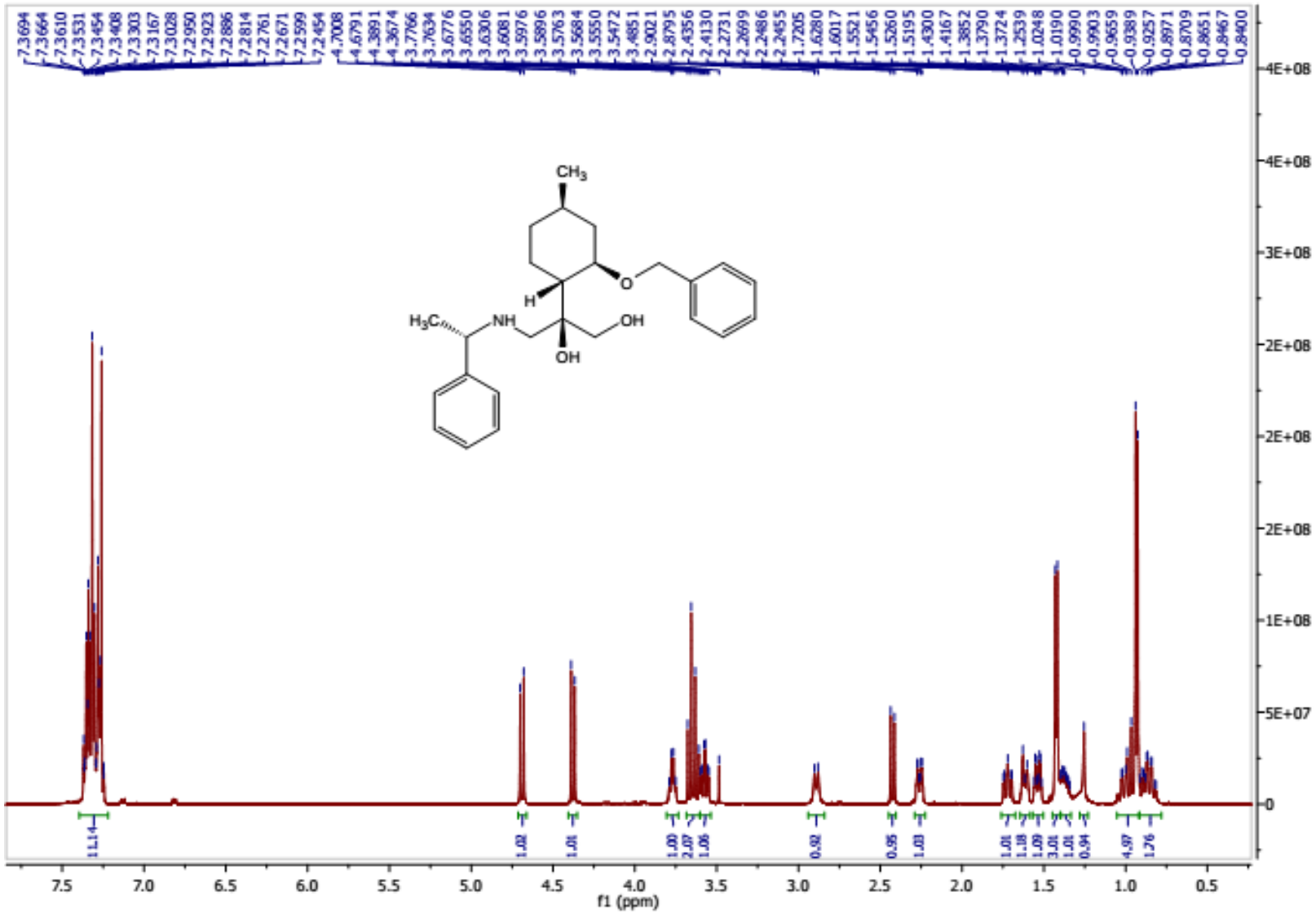
[1]H-NMR of compound **45a**



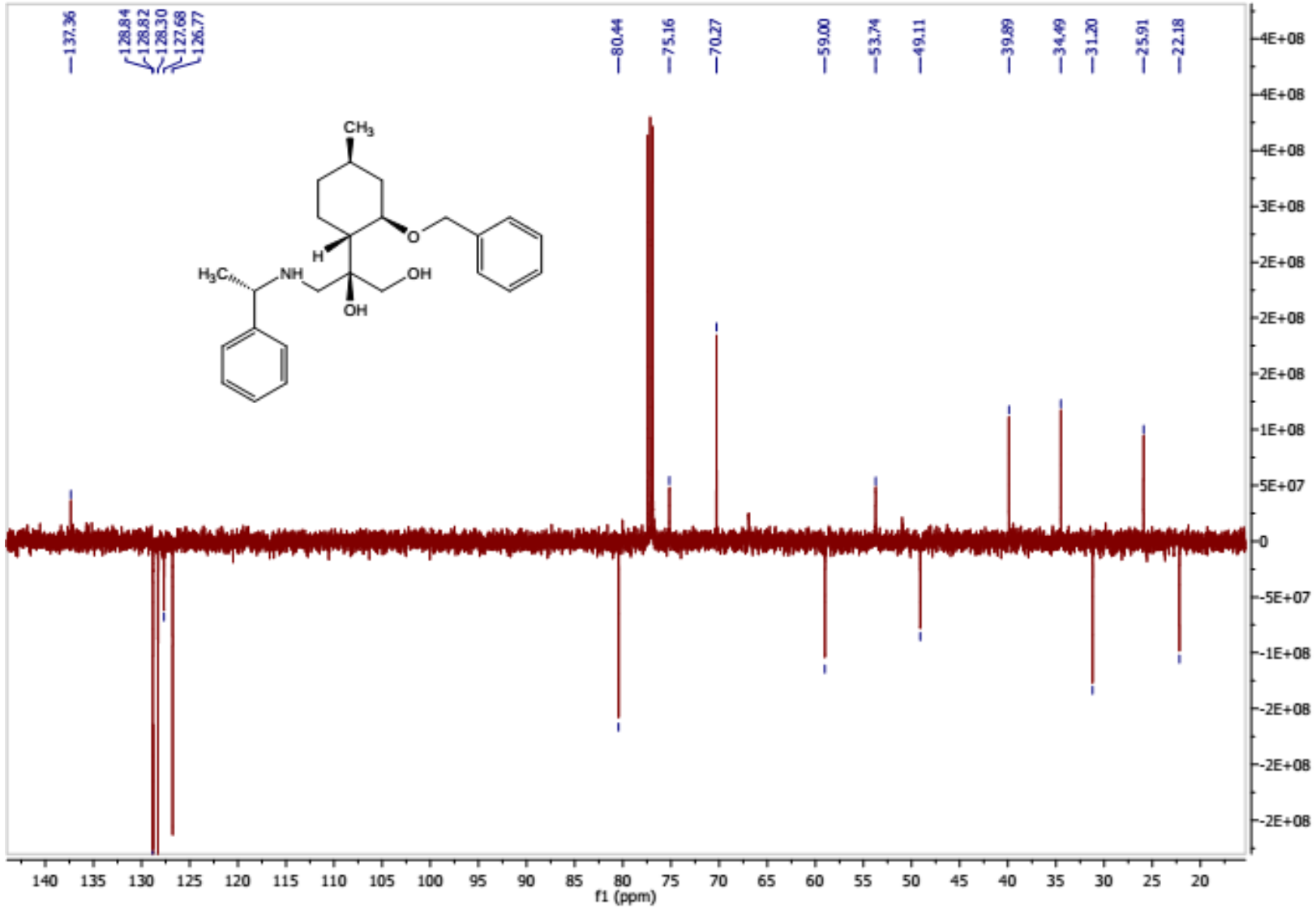
$^{13}$C-NMR of compound **45a**



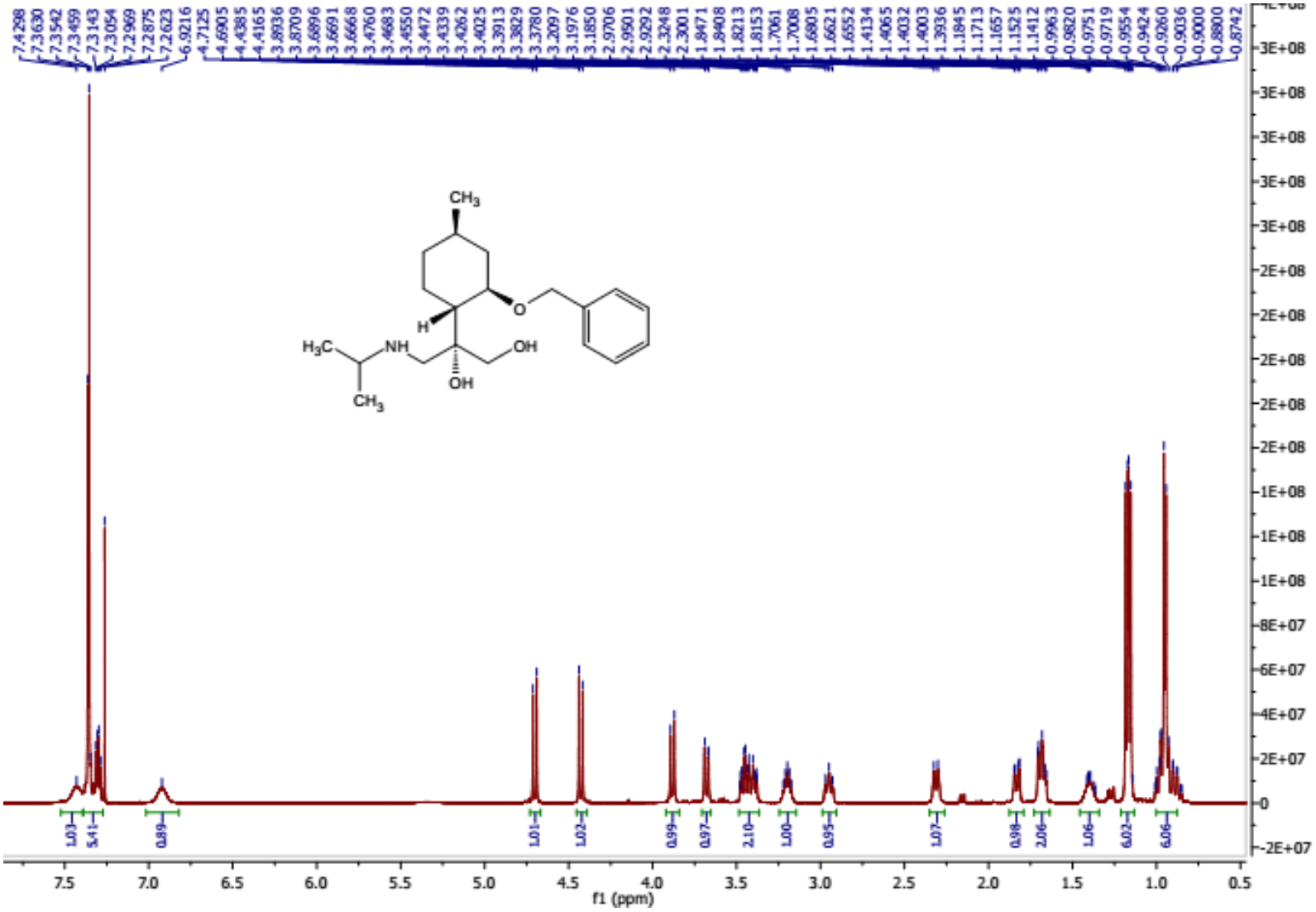
[1]H-NMR of compound **45b**



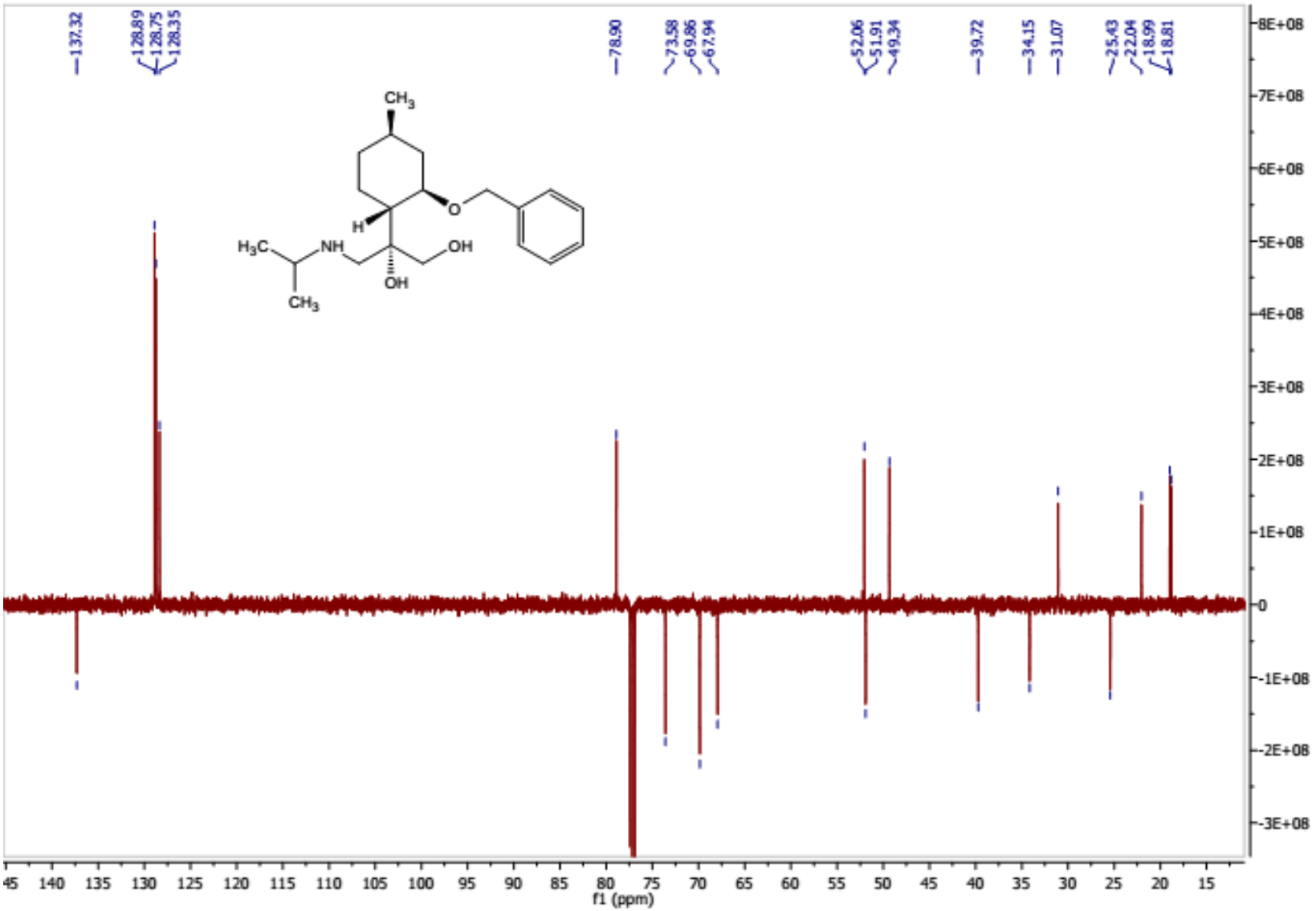
$^{13}$C-NMR of compound **45b**



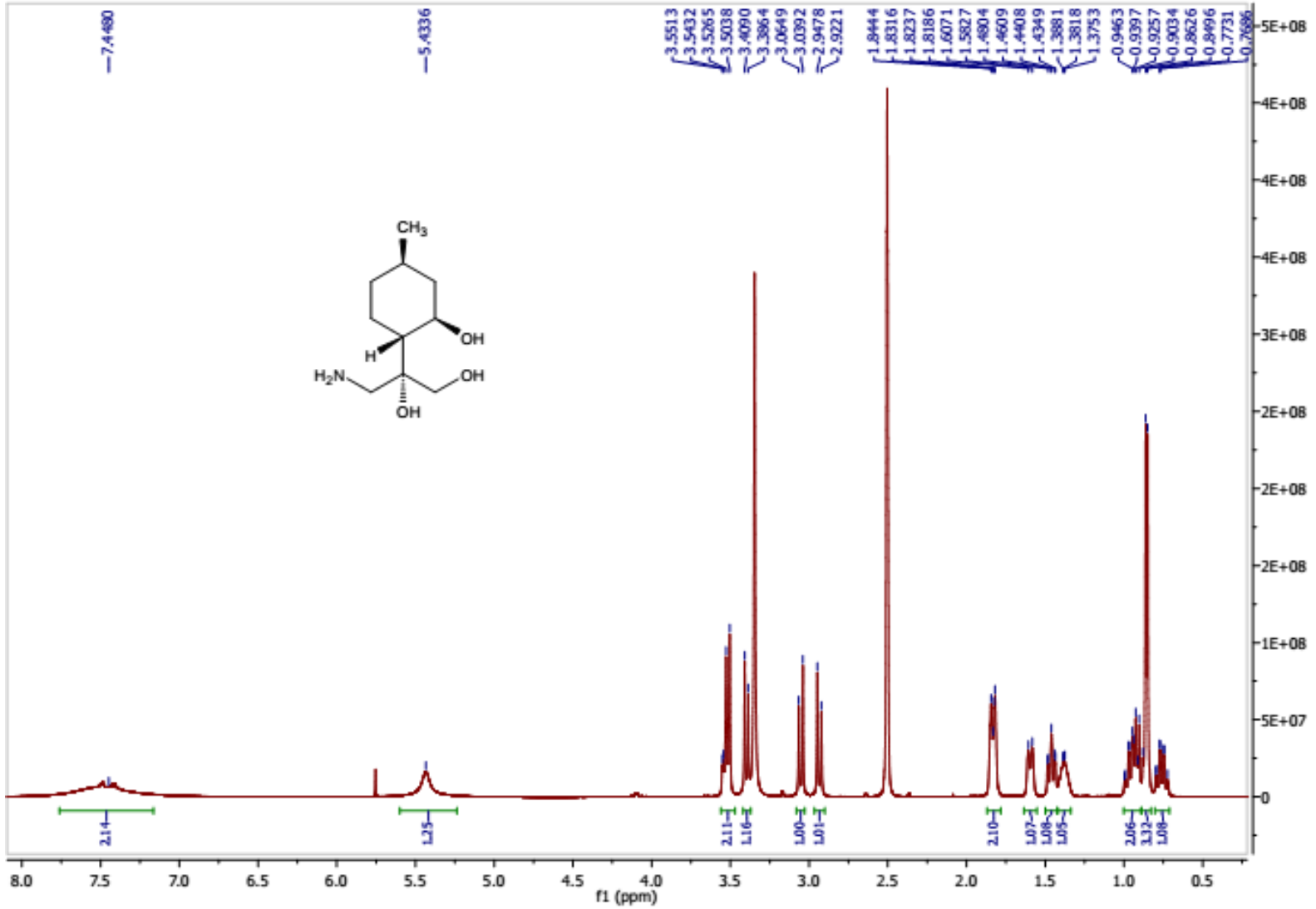
[1]H-NMR of compound **46a**



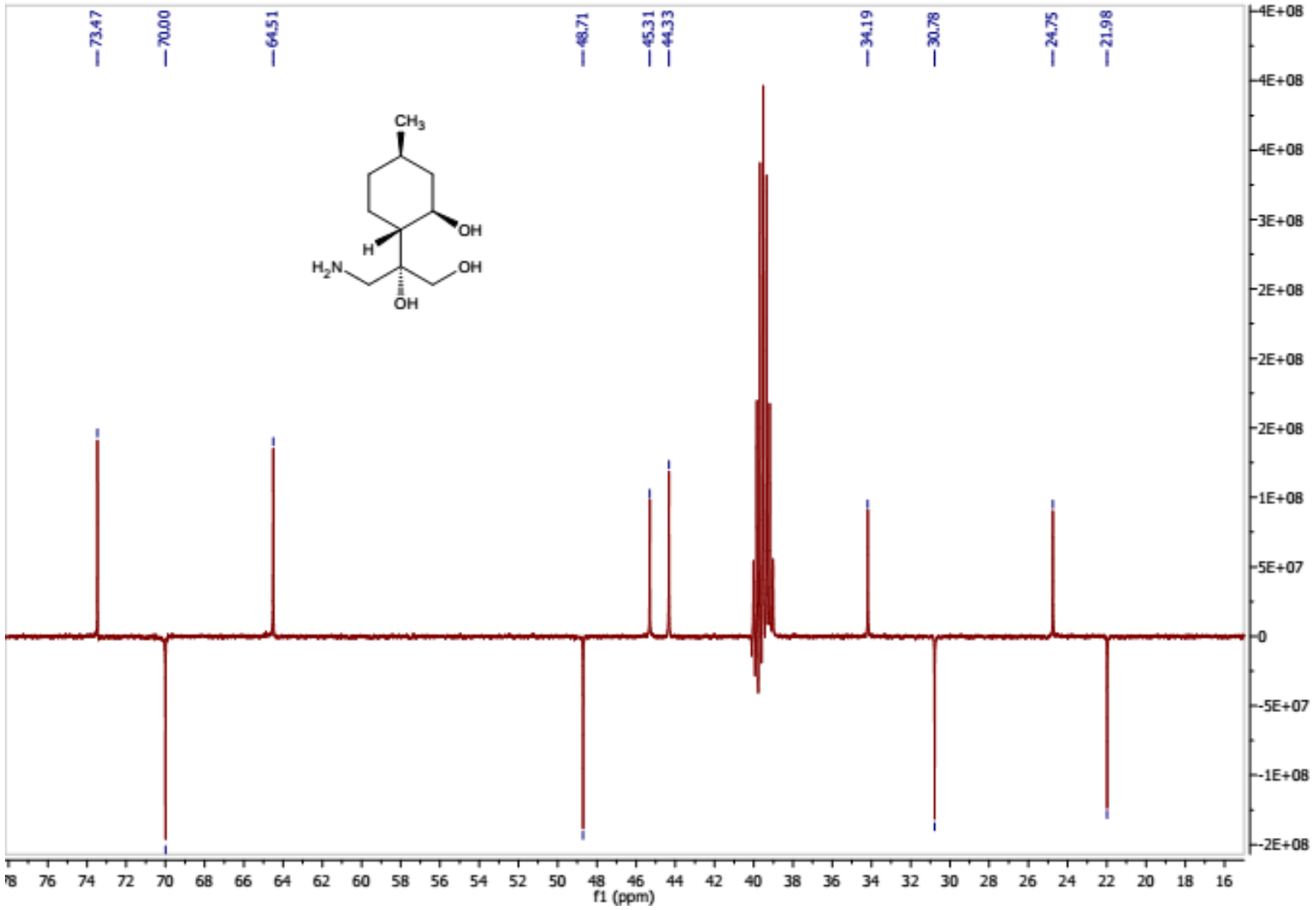
$^{13}$C-NMR of compound **46a**



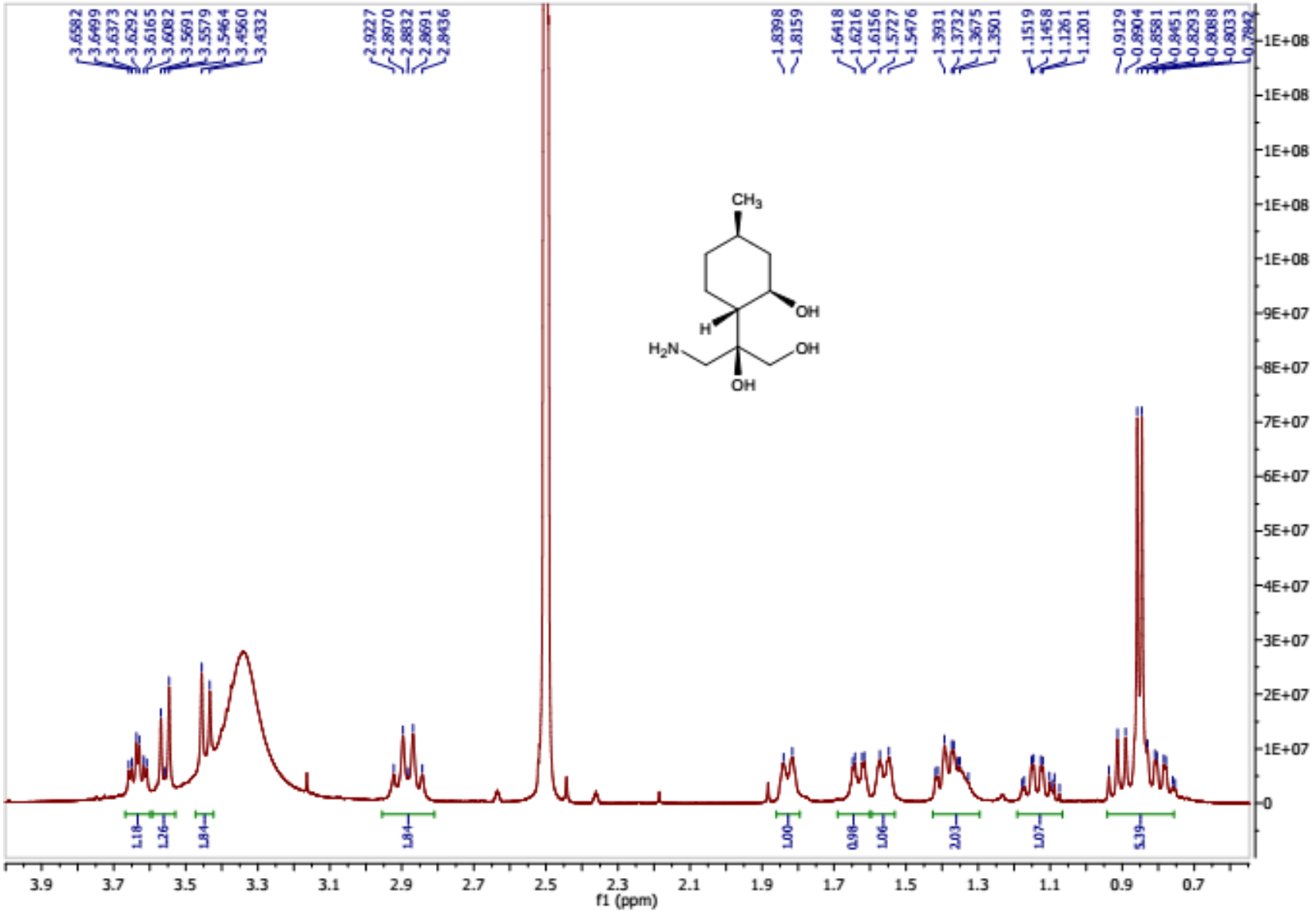
[1]H-NMR of compound **47a**



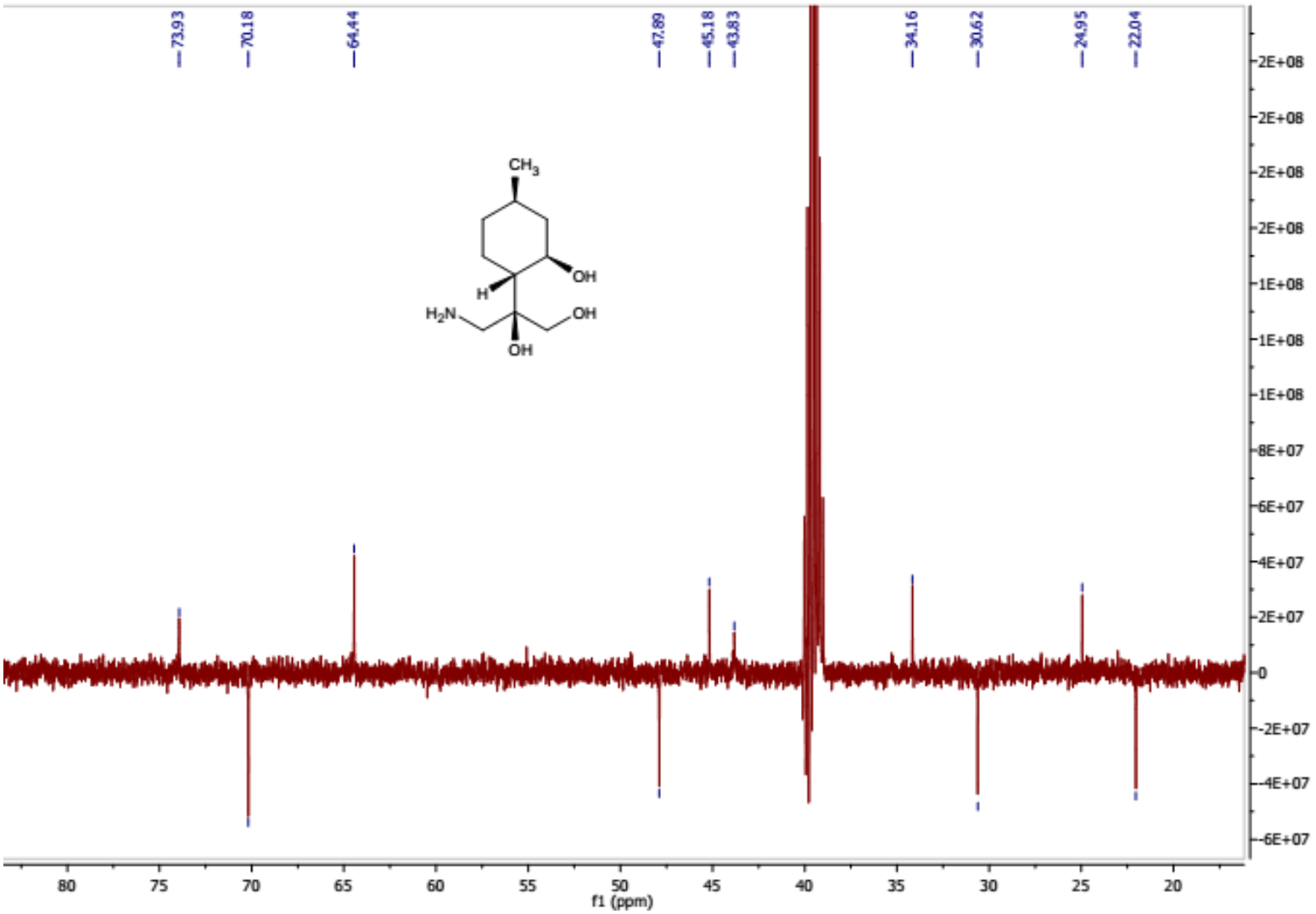
$^{13}$C-NMR of compound **47a**



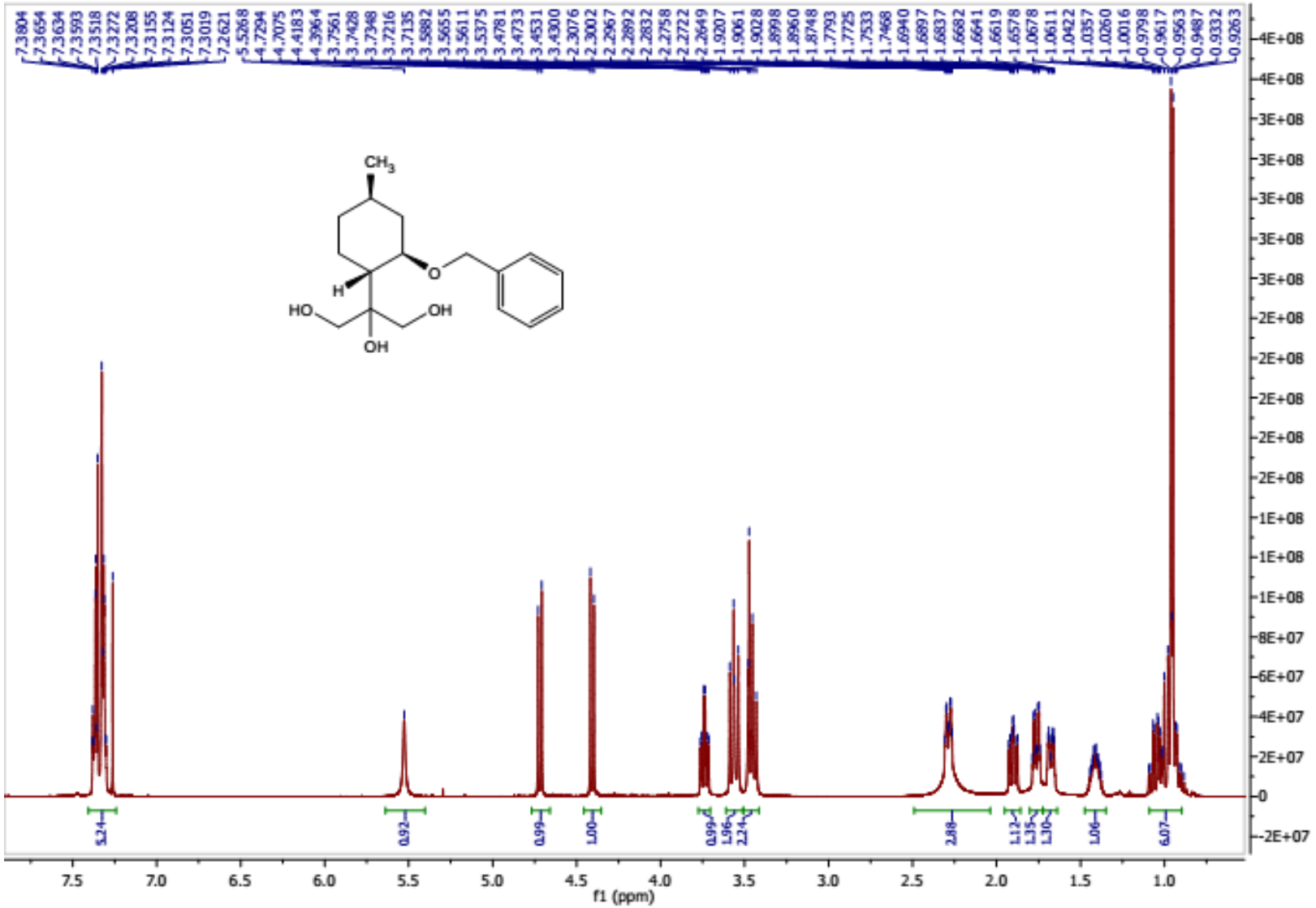
[1]H-NMR of compound **47b**



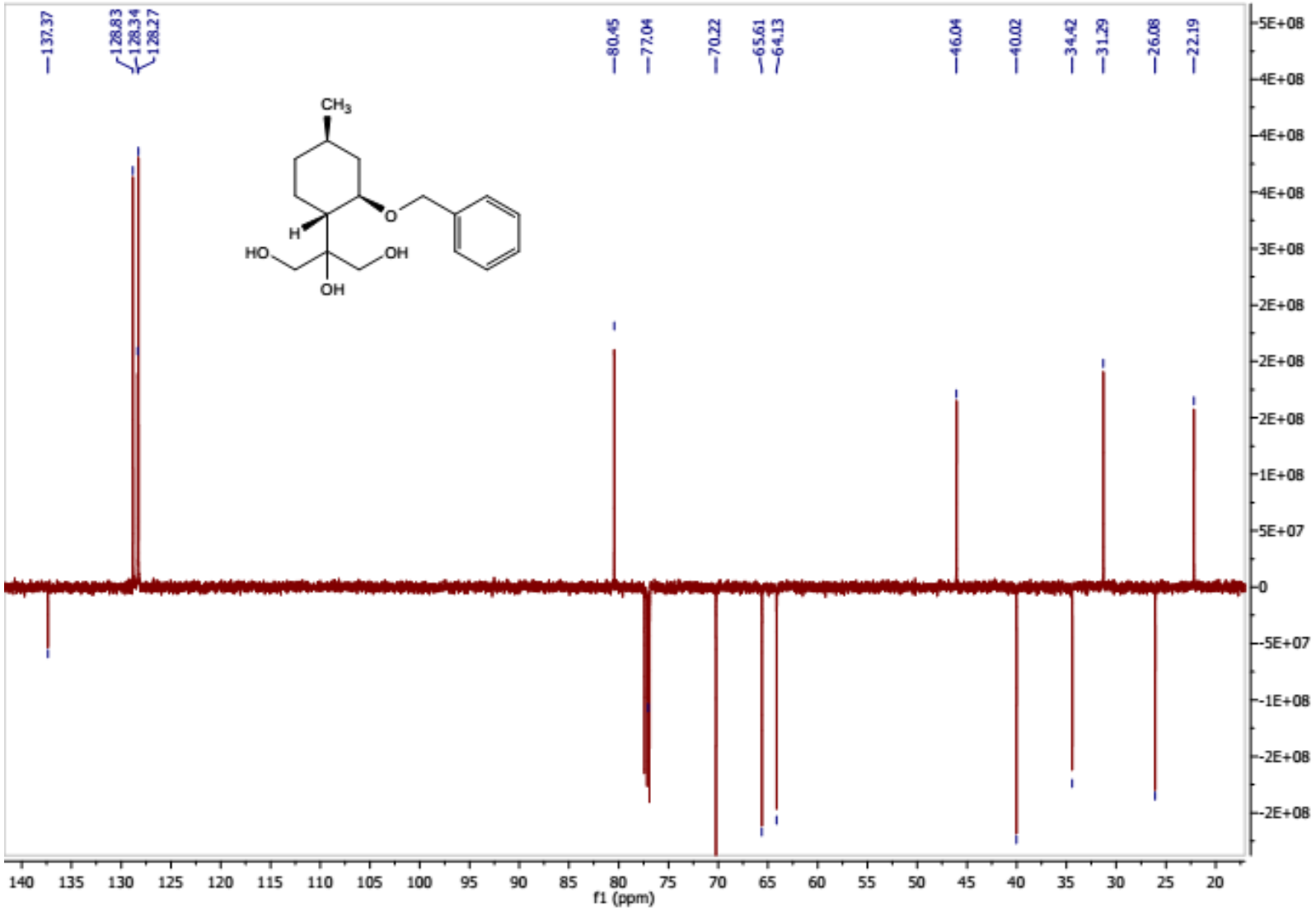
$^{13}$C-NMR of compound **47b**



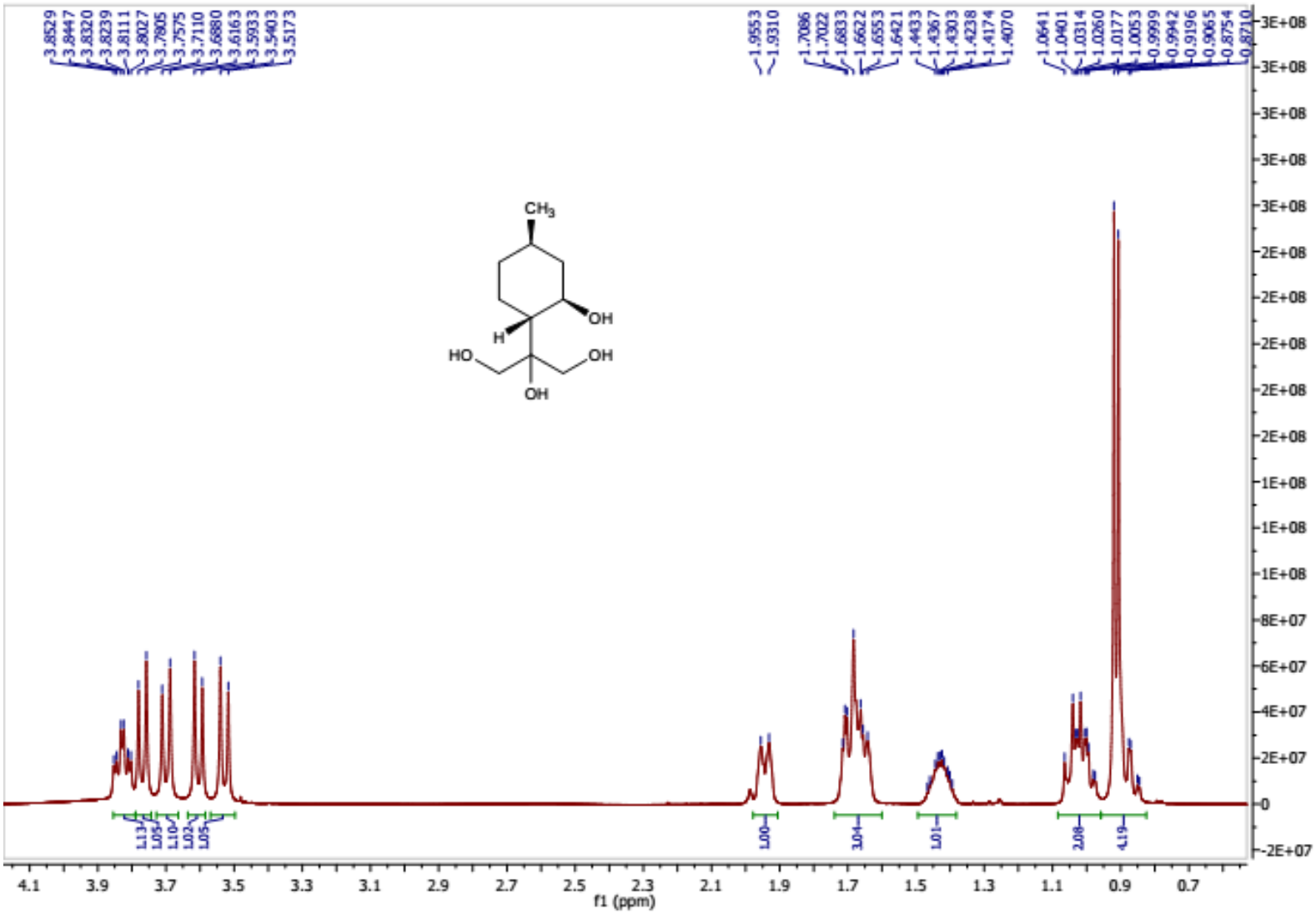
[1]H-NMR of compound **48**



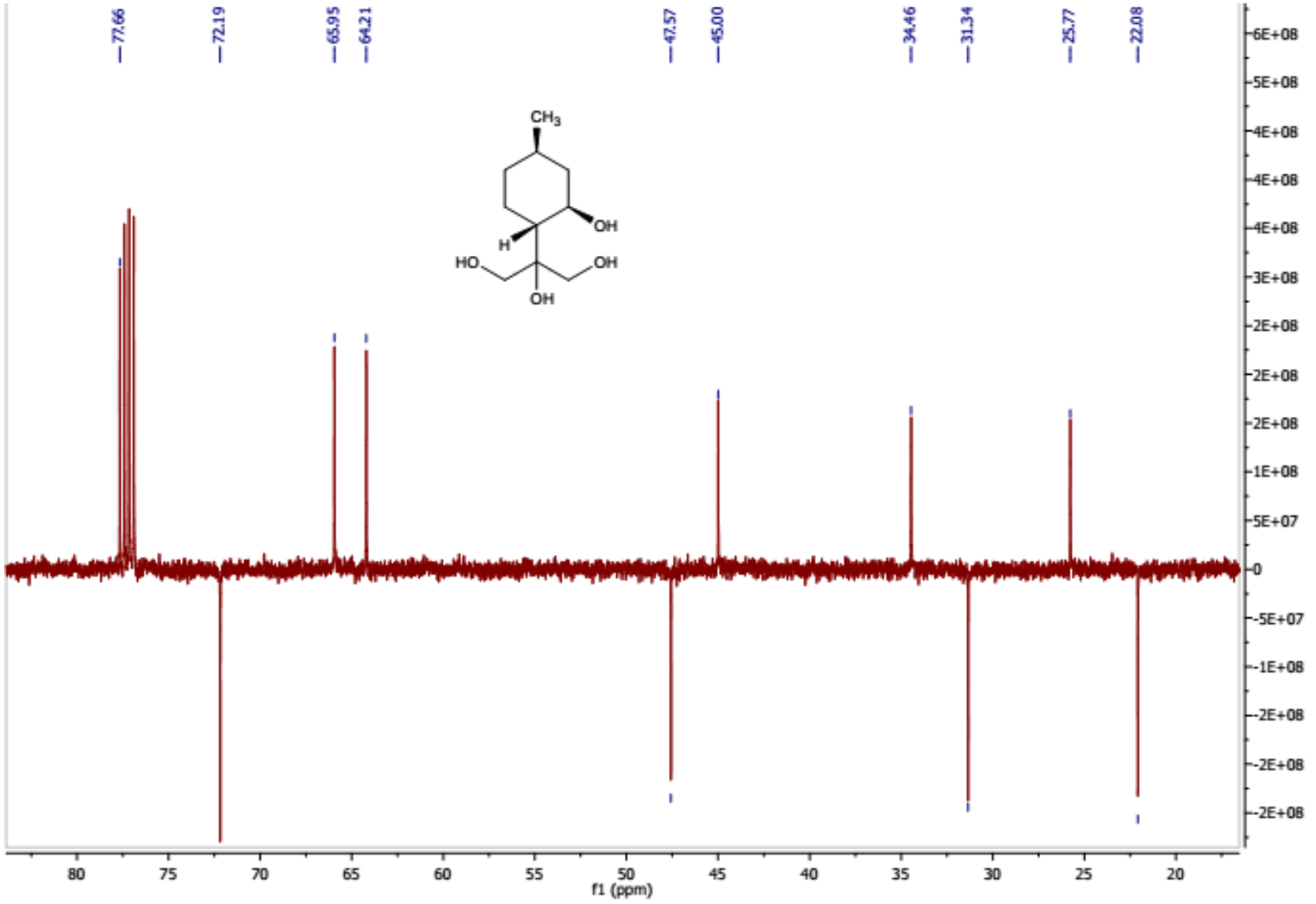
$^{13}$C-NMR of compound **48**



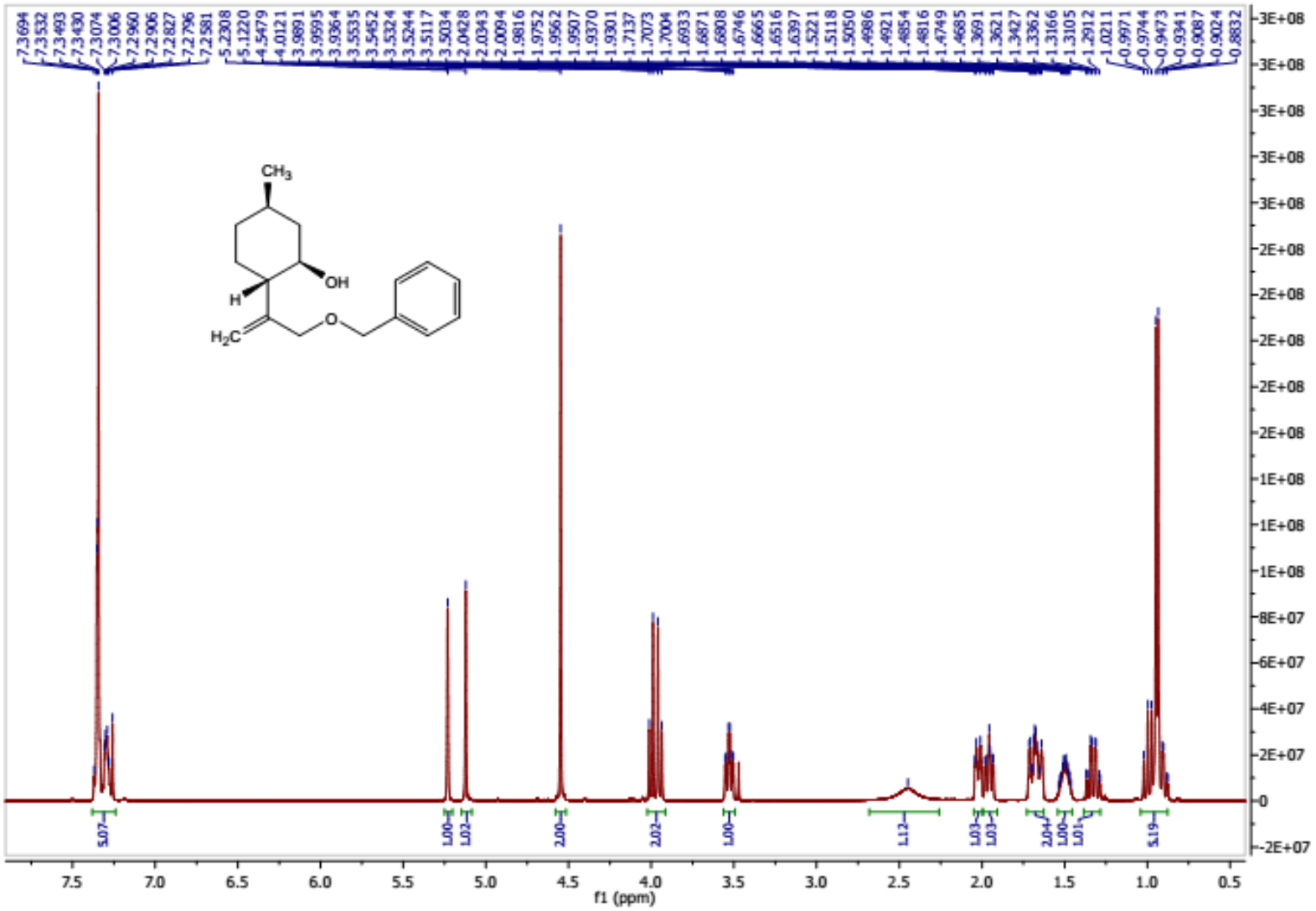
[1]H-NMR of compound **49**



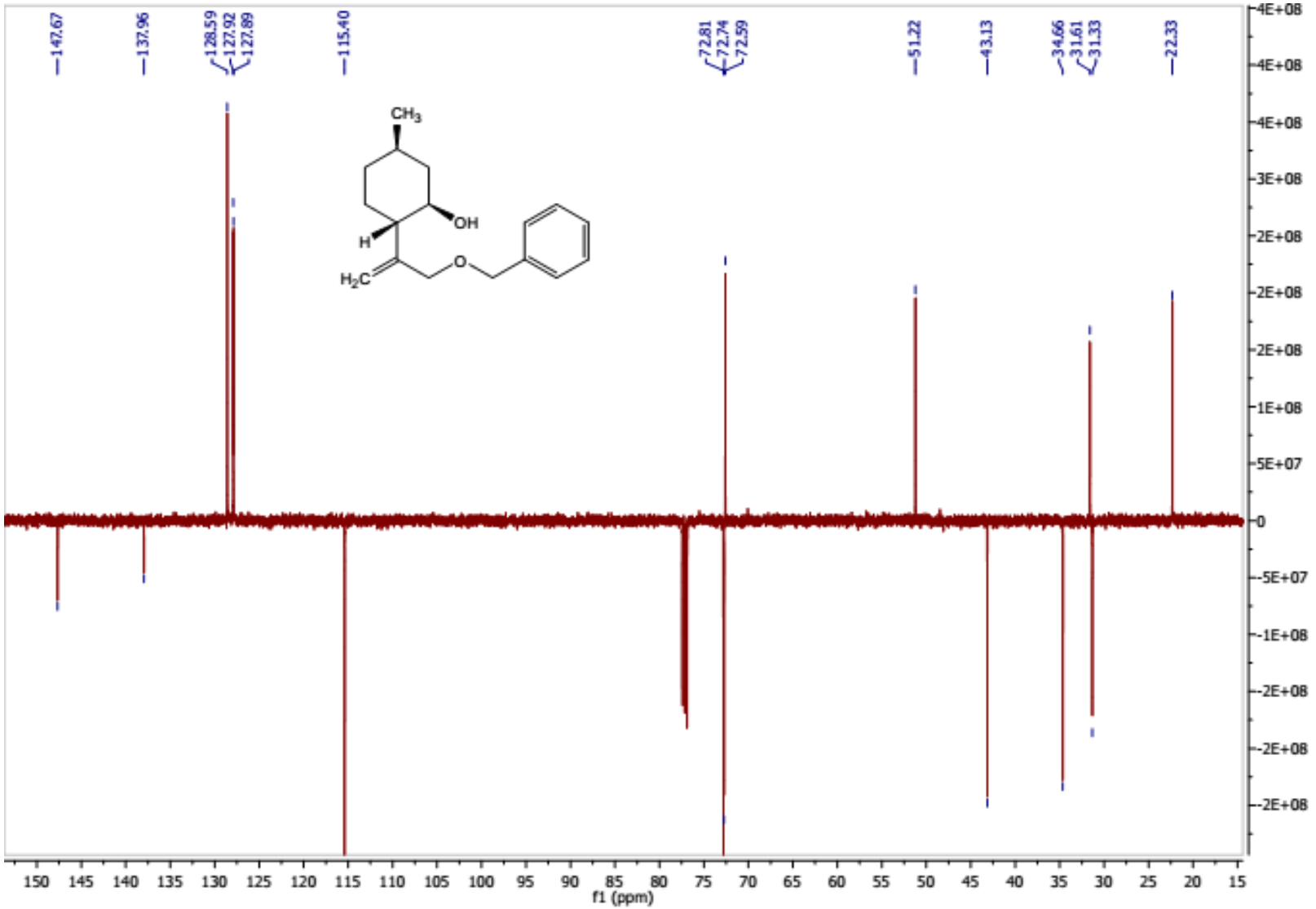
$^{13}$C-NMR of compound **49**



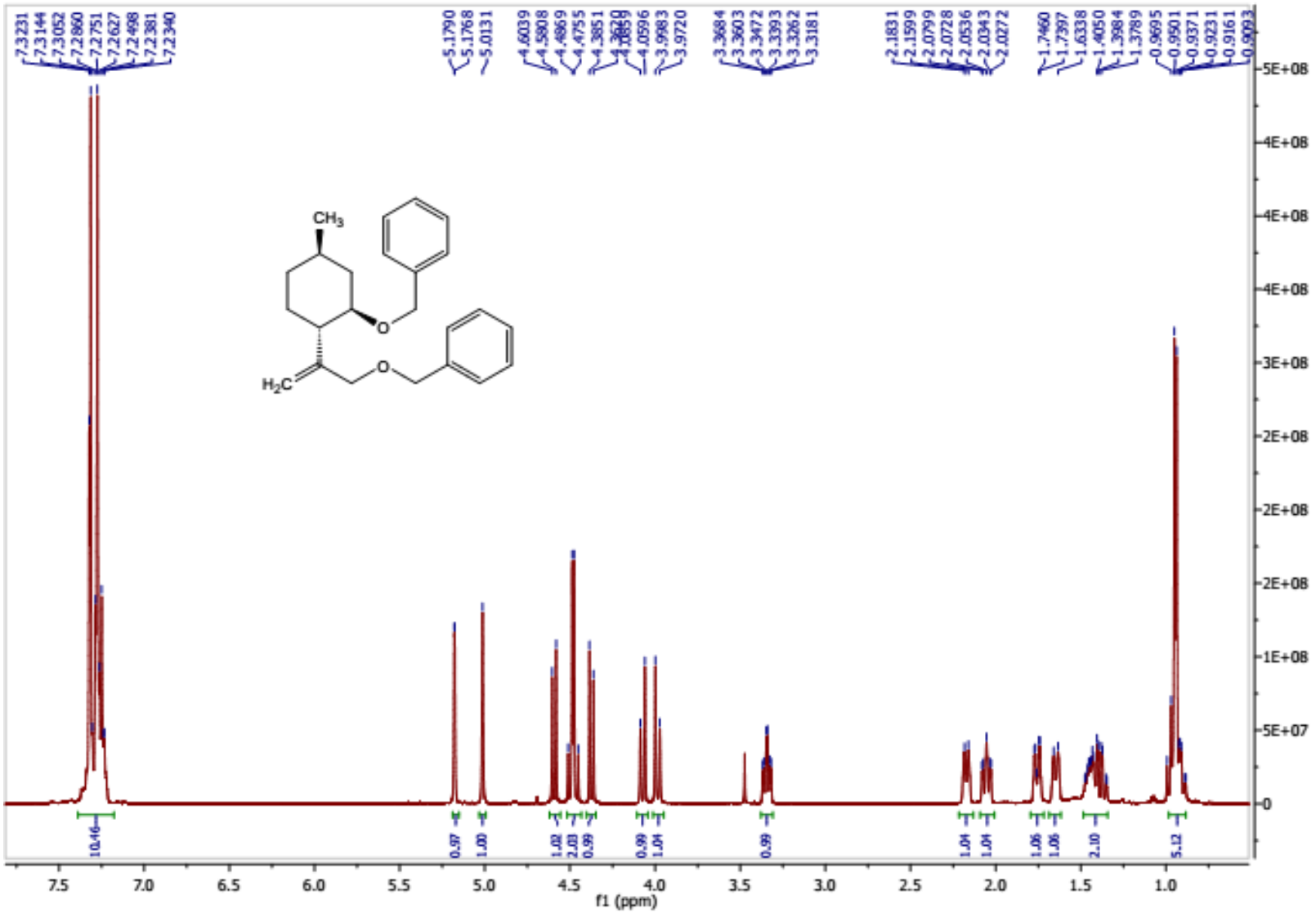
[1]H-NMR of compound **50a**



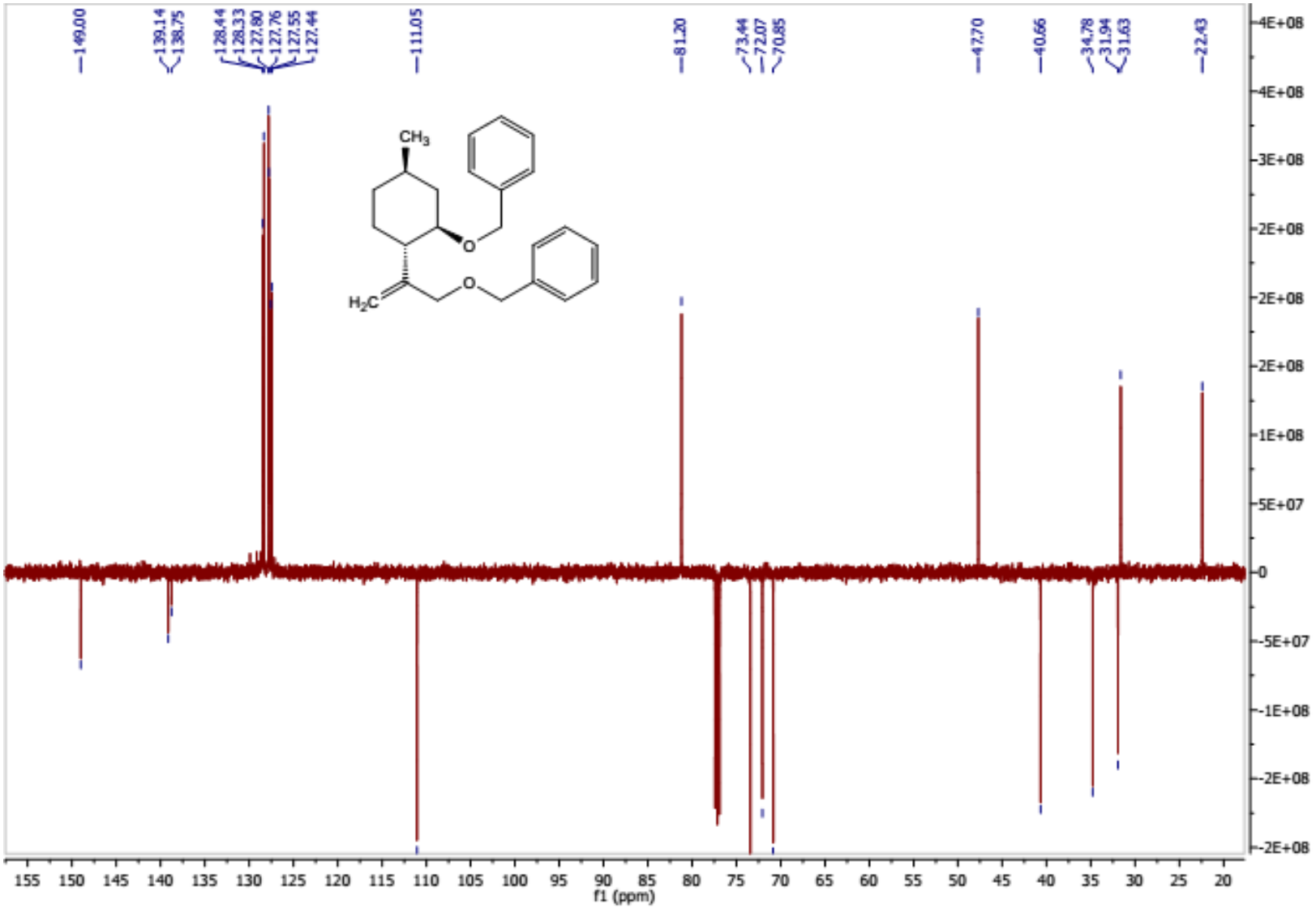
$^{13}$C-NMR of compound **50a**



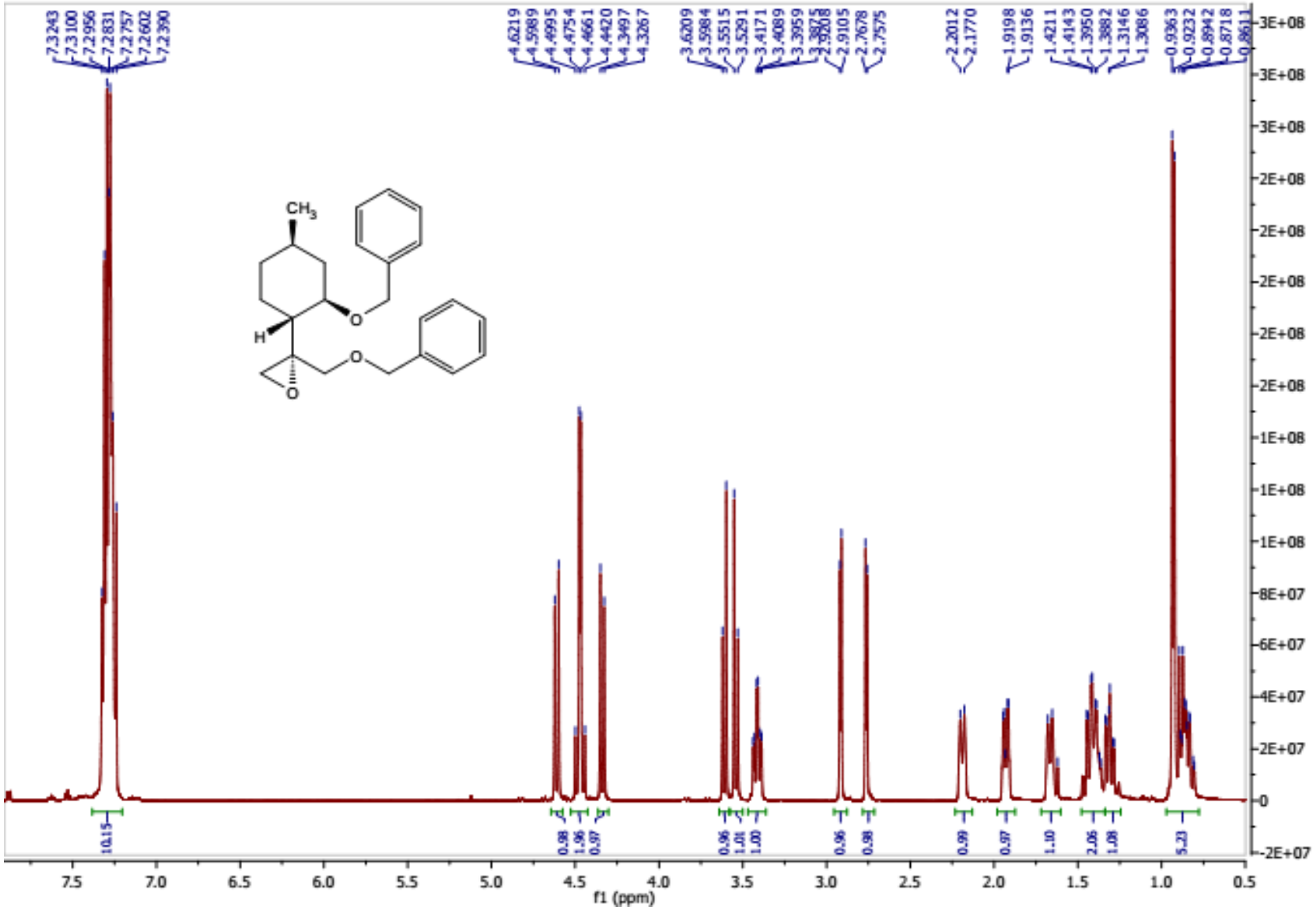
[1]H-NMR of compound **50b**



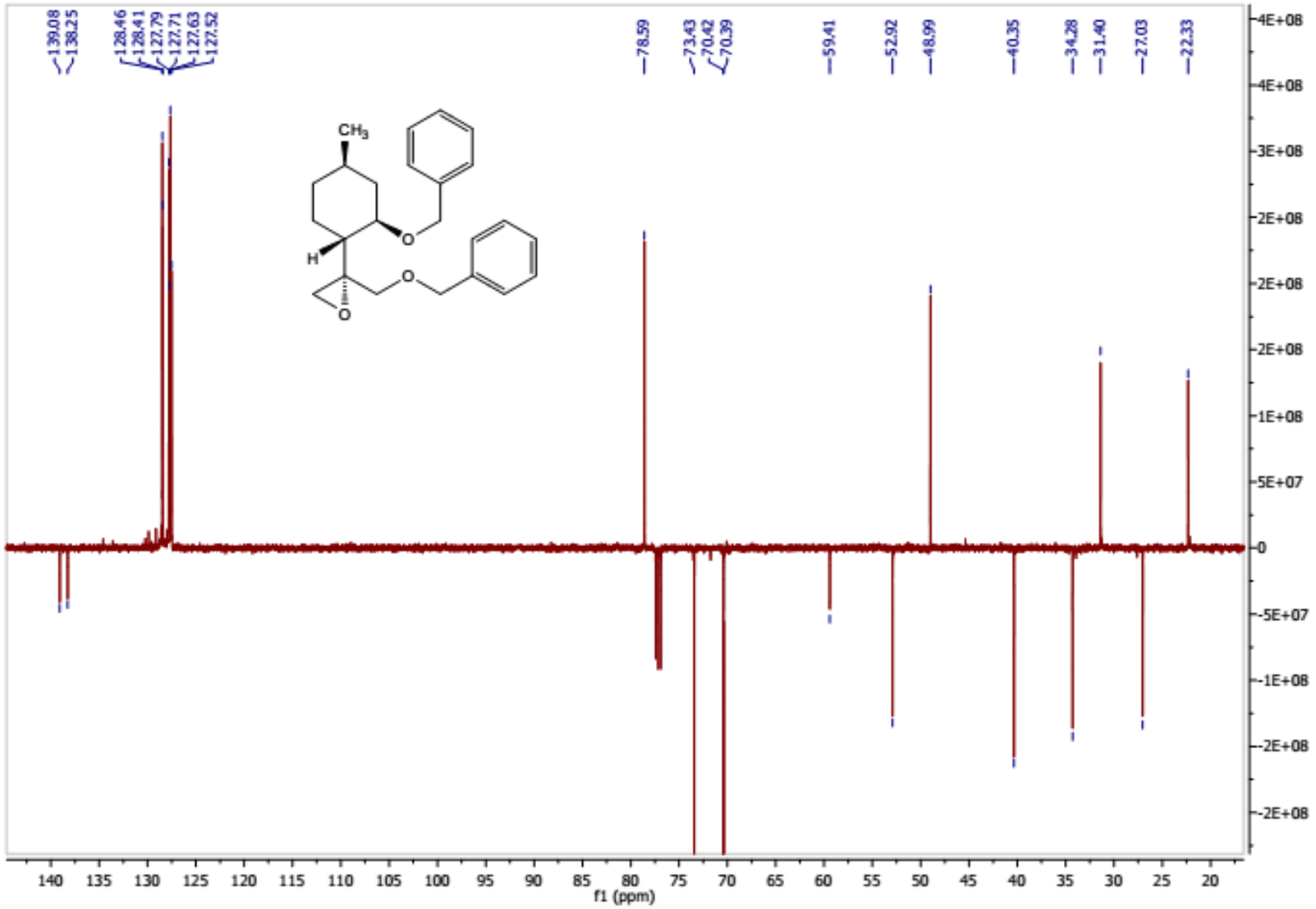
$^{13}$C-NMR of compound **50b**



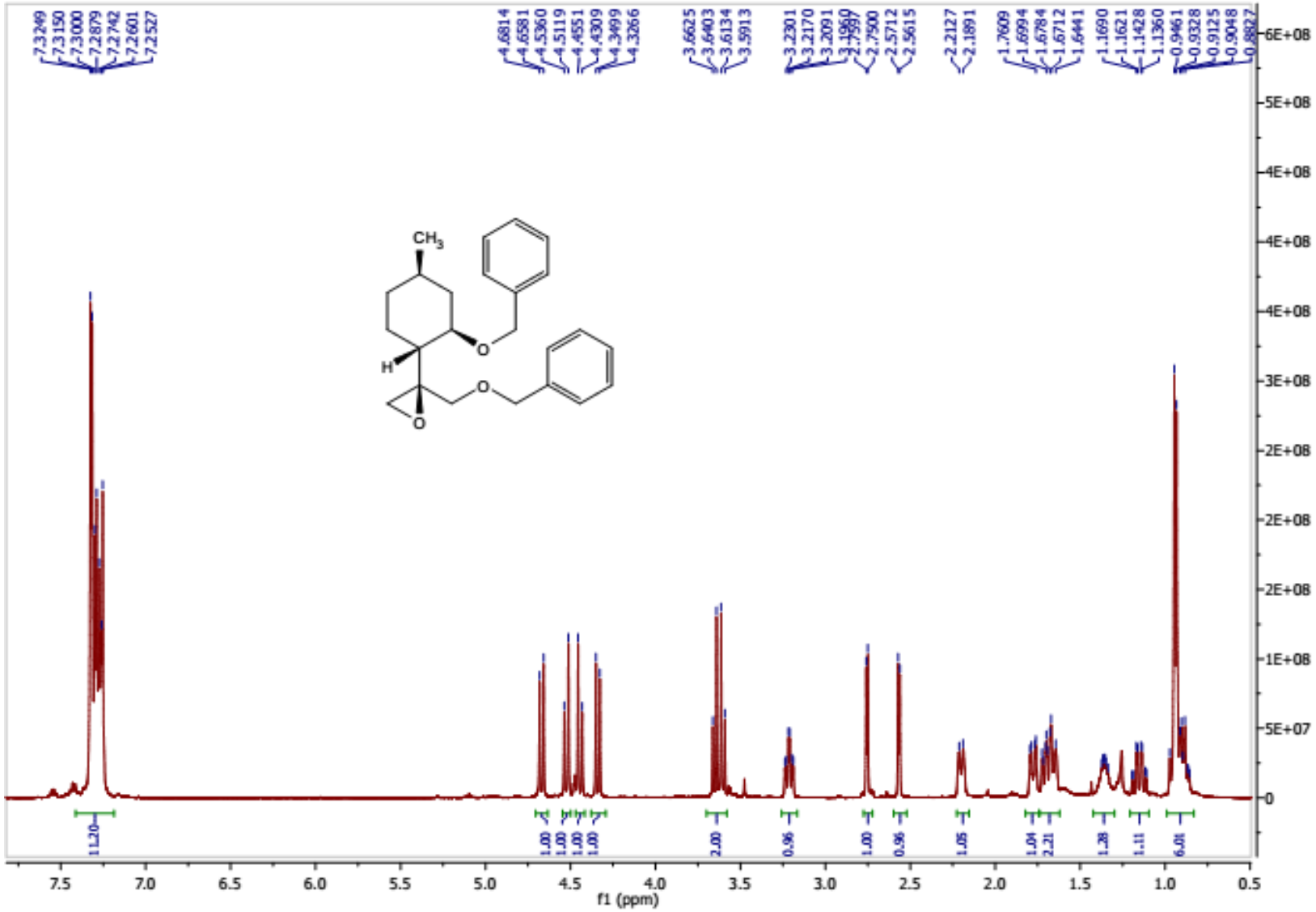
[1]H-NMR of compound **51a**



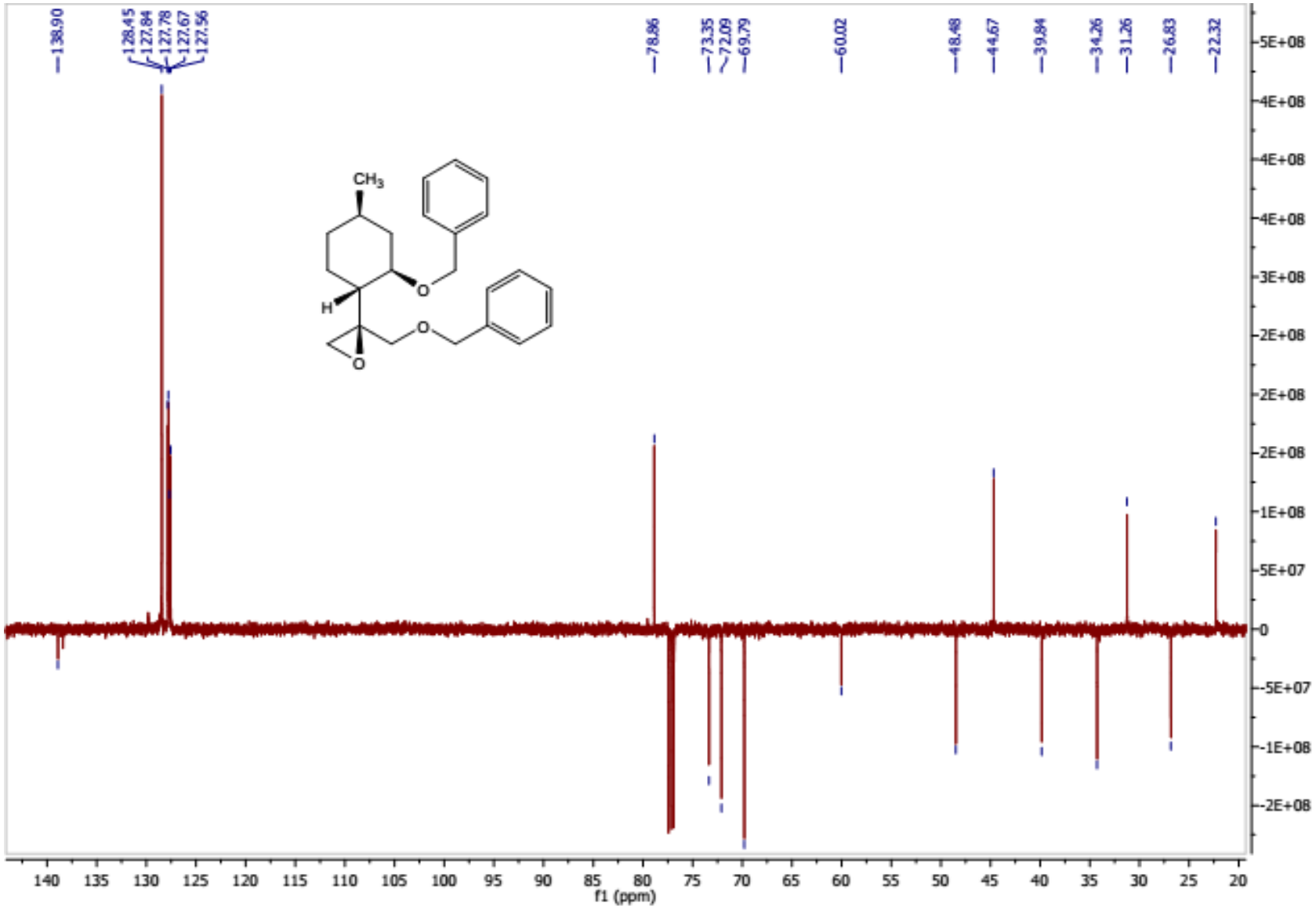
$^{13}$C-NMR of compound **51a**



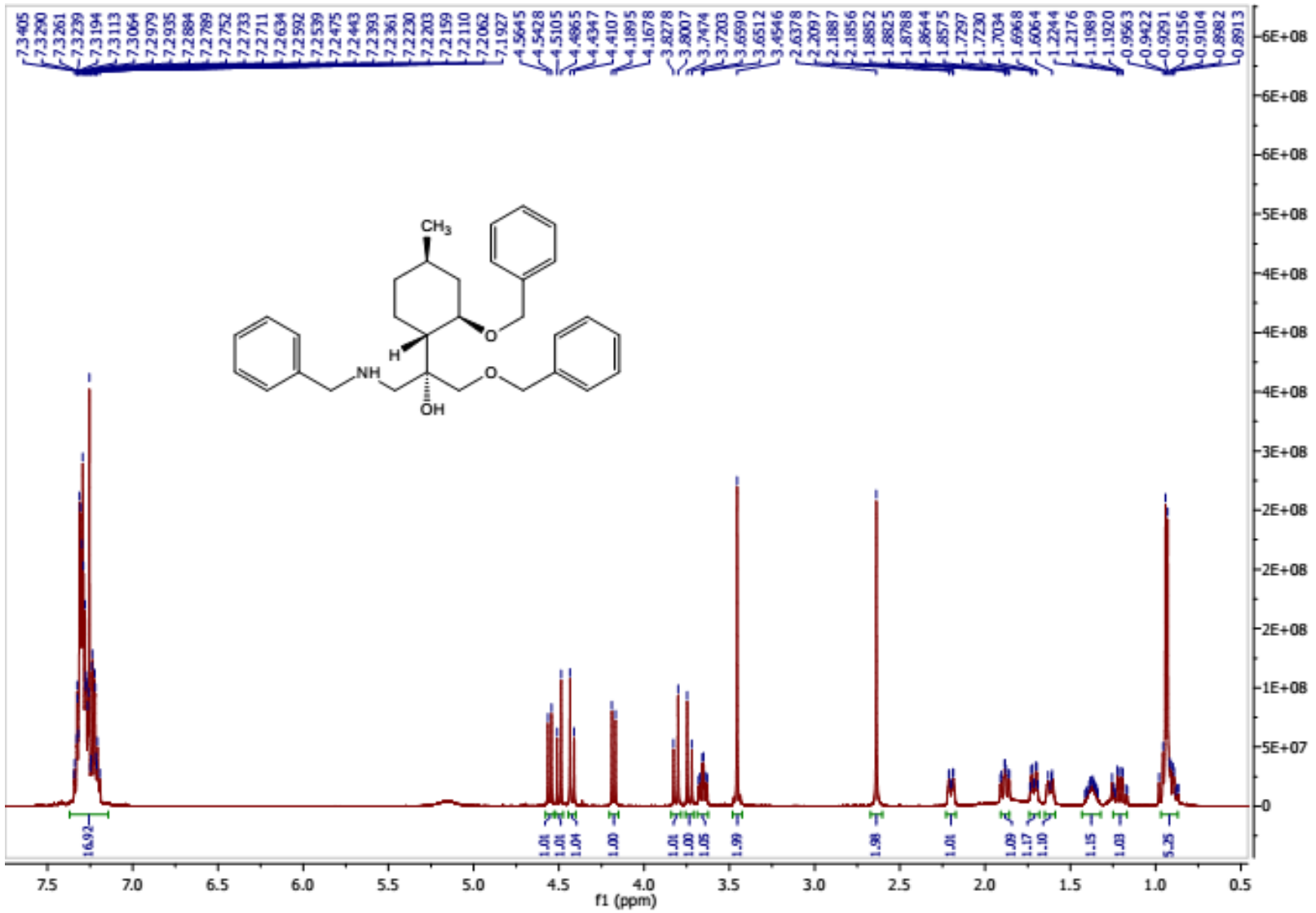
[1]H-NMR of compound **51b**



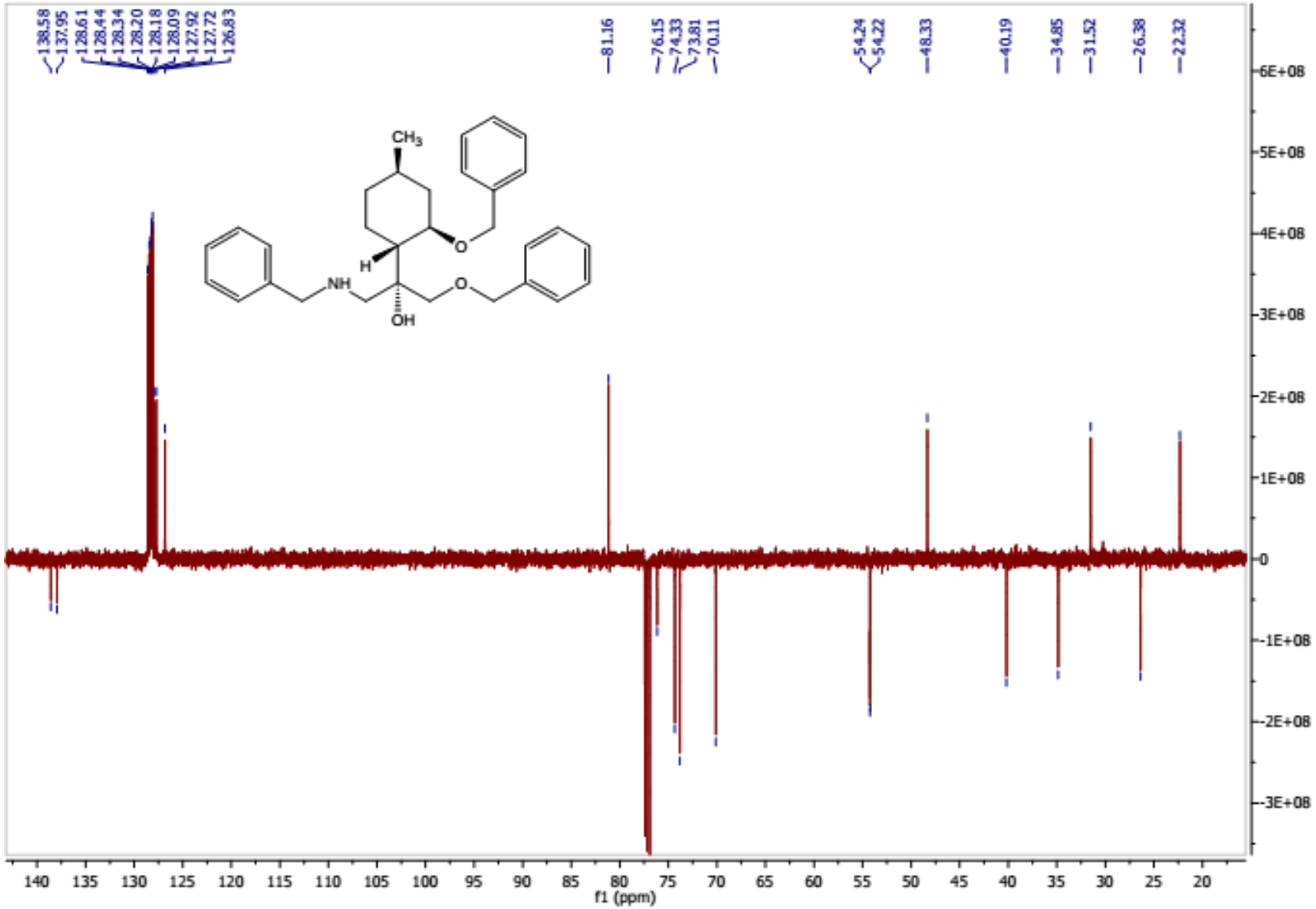
$^{13}$C-NMR of compound **51b**



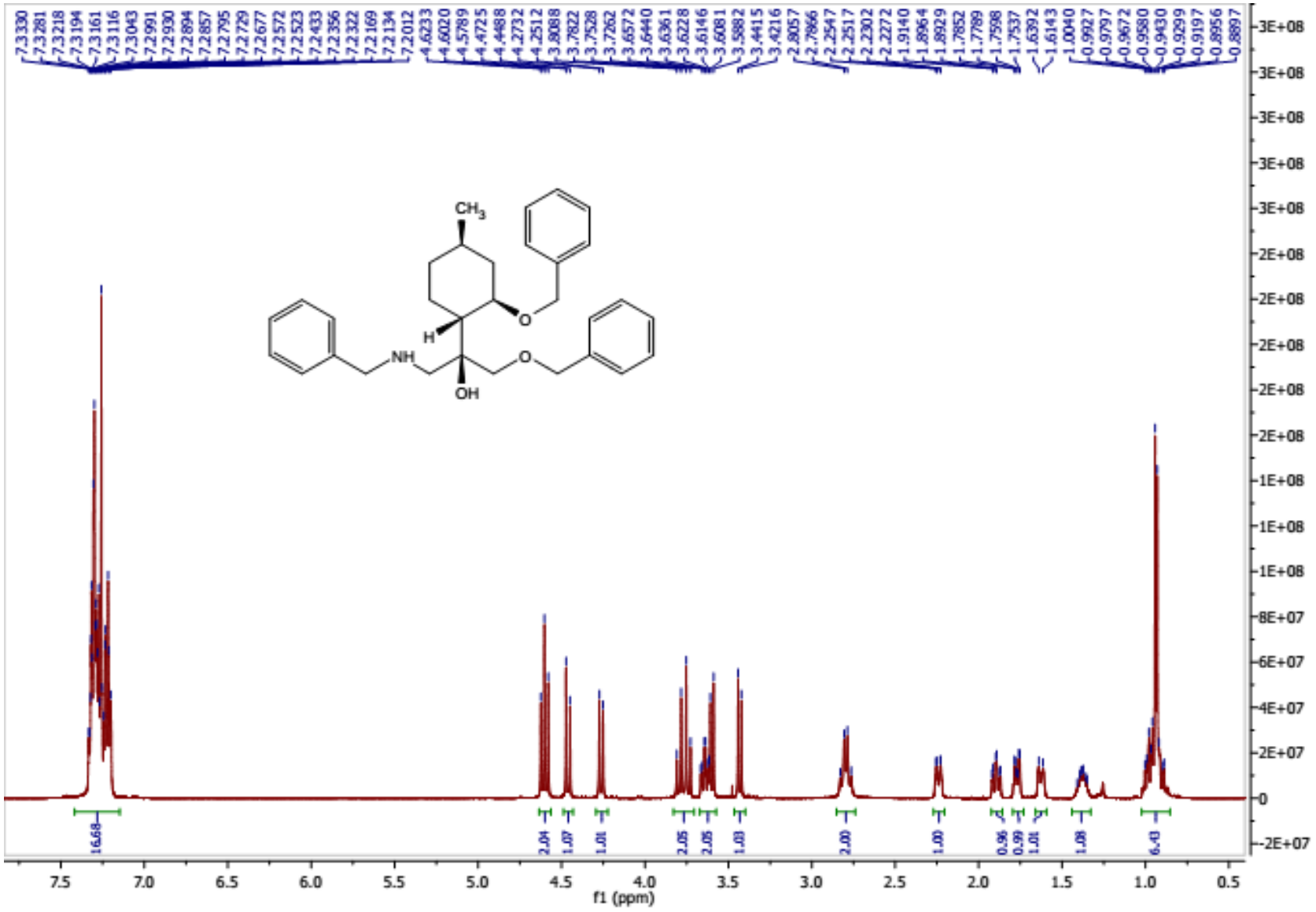
[1]H-NMR of compound **52a**



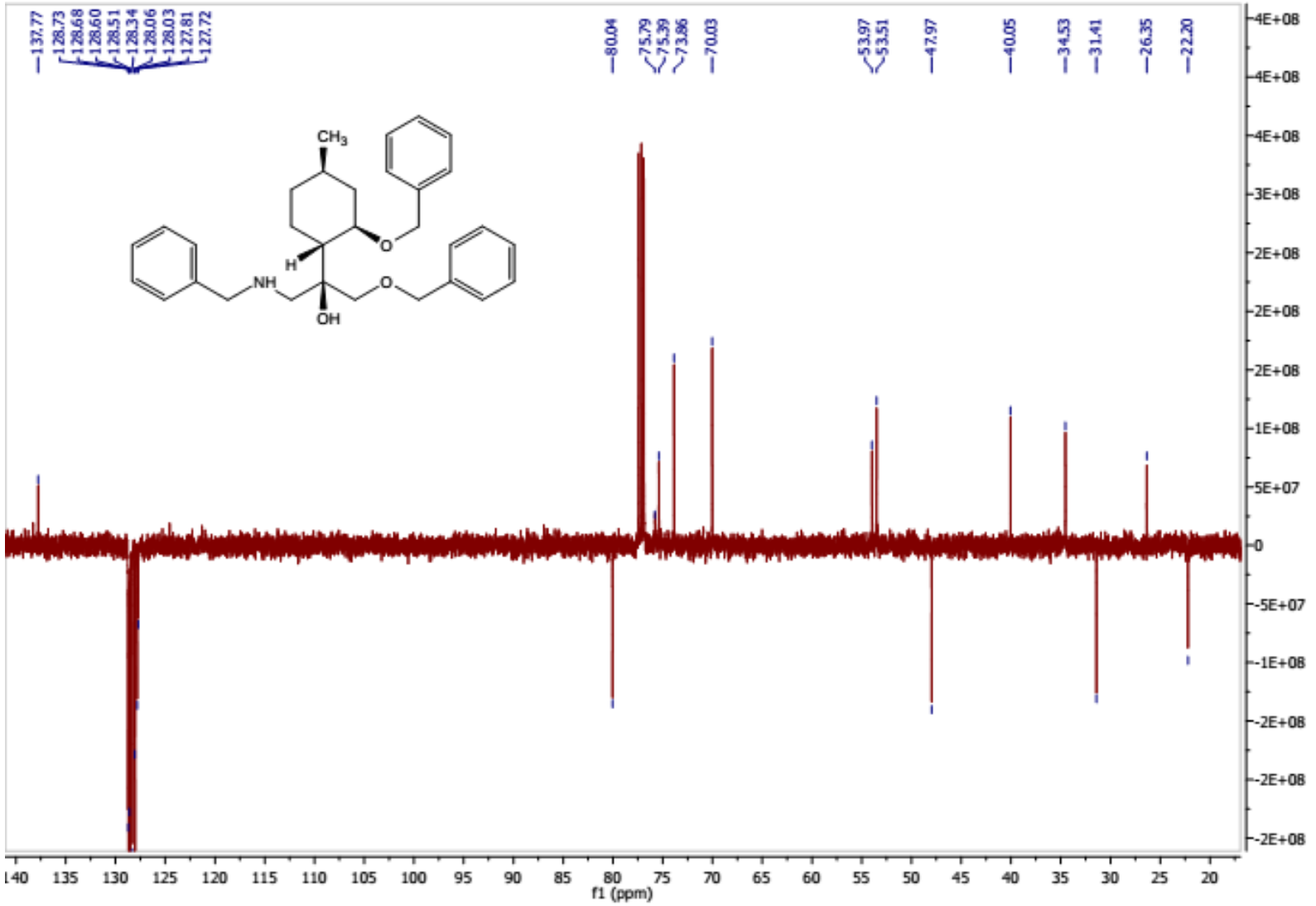
$^{13}$C-NMR of compound **52a**



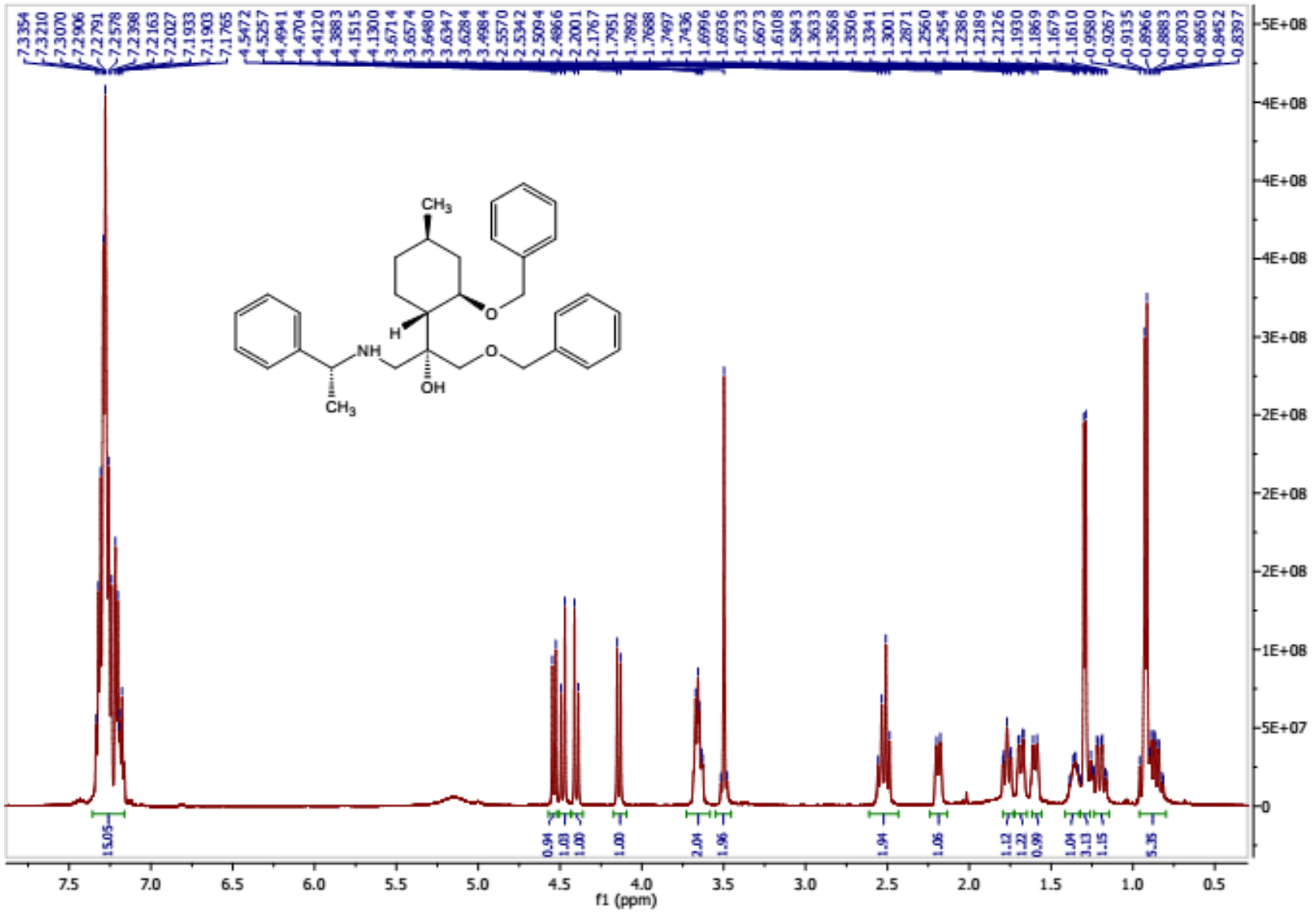
[1]H-NMR of compound **52b**



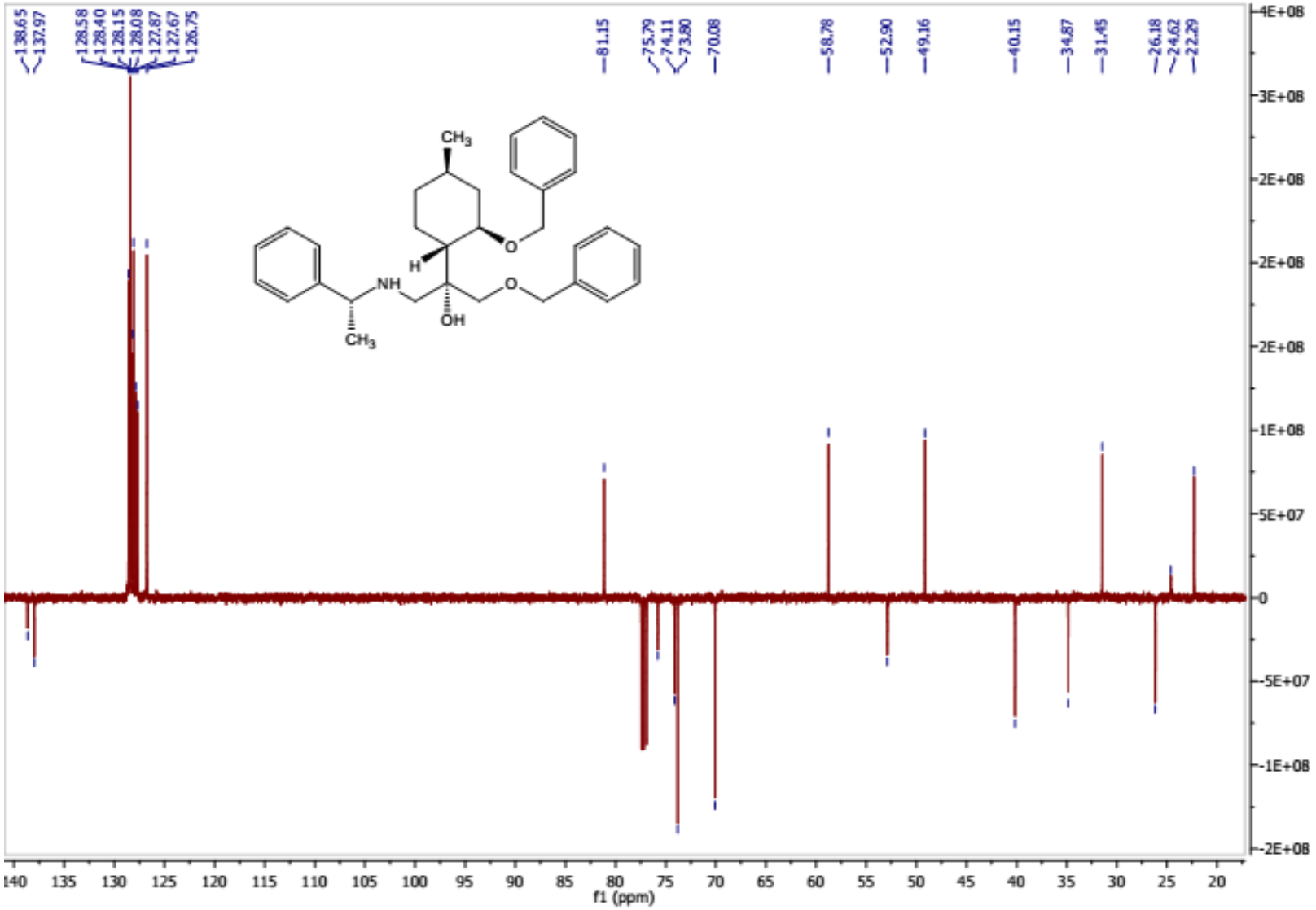
$^{13}$C-NMR of compound **52b**



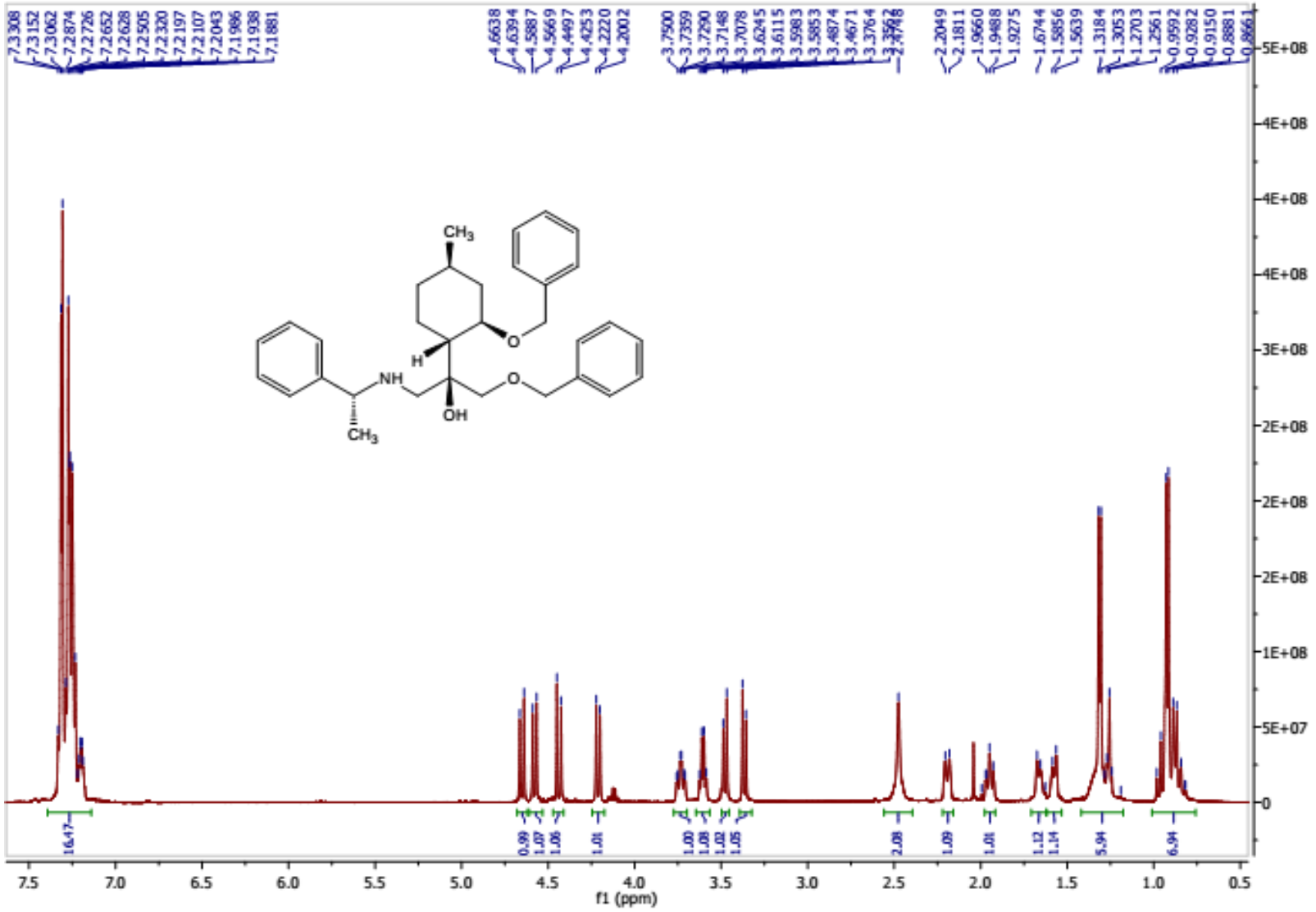
[1]H-NMR of compound **53a**



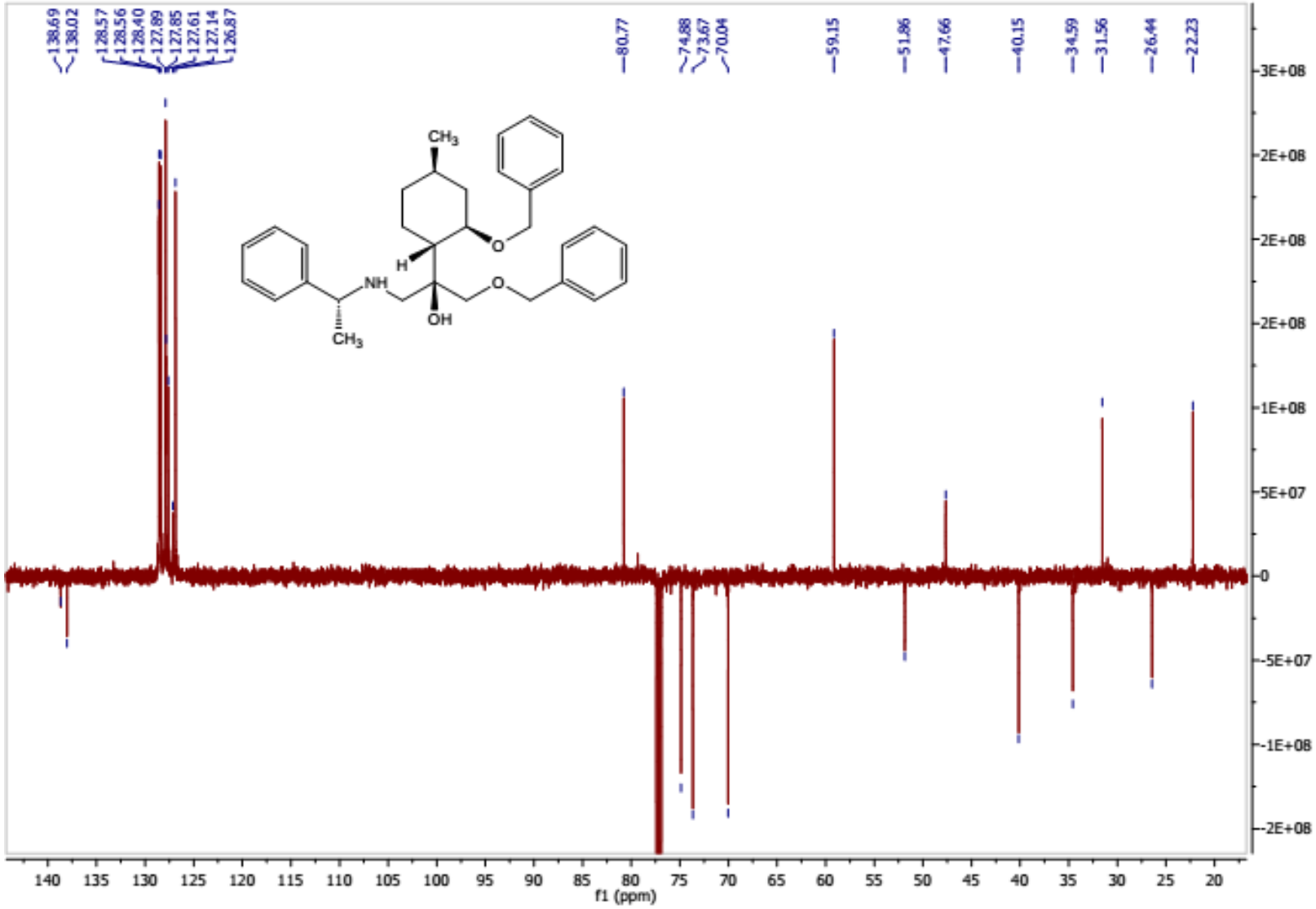
$^{13}$C-NMR of compound **53a**



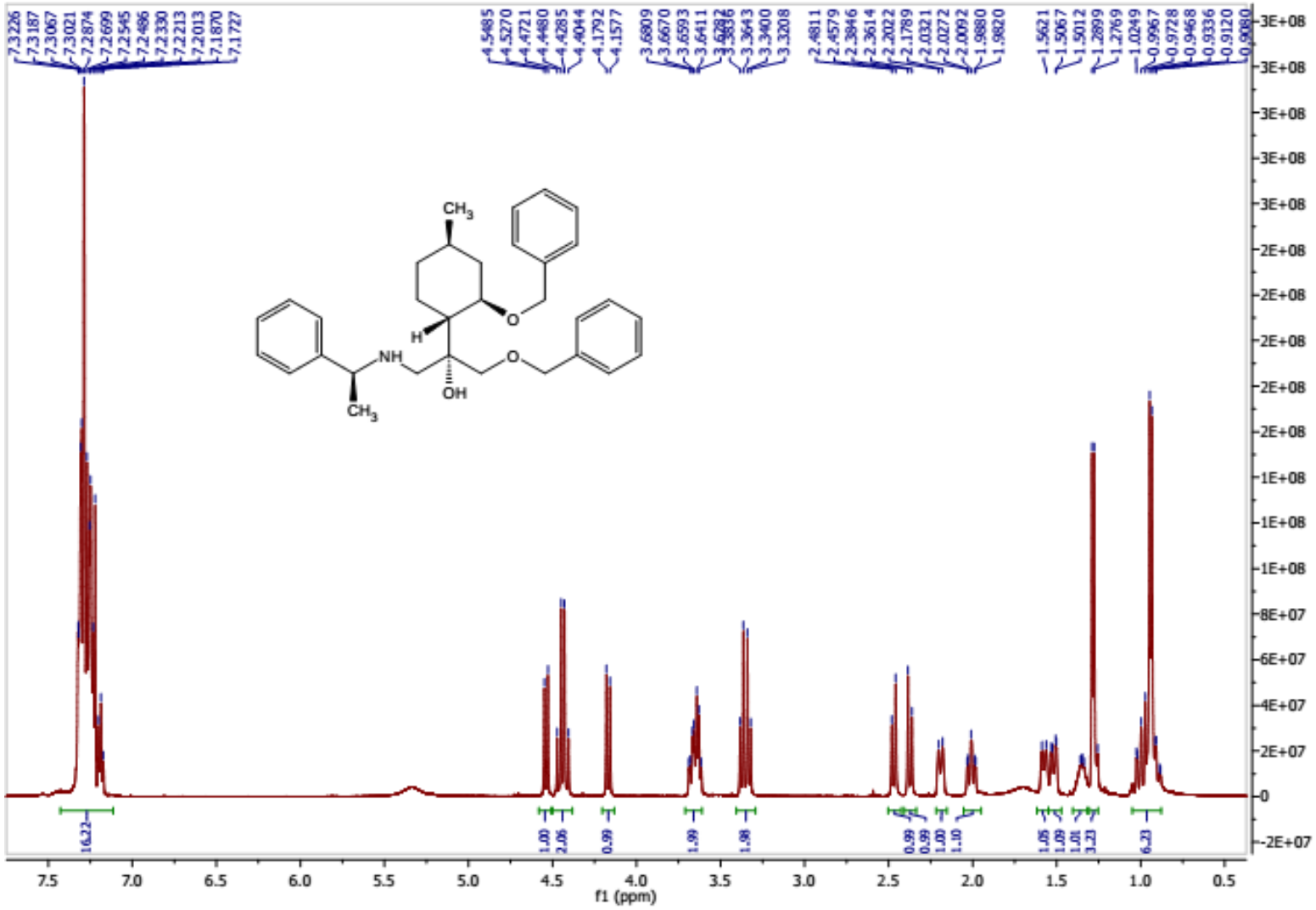
[1]H-NMR of compound **53b**



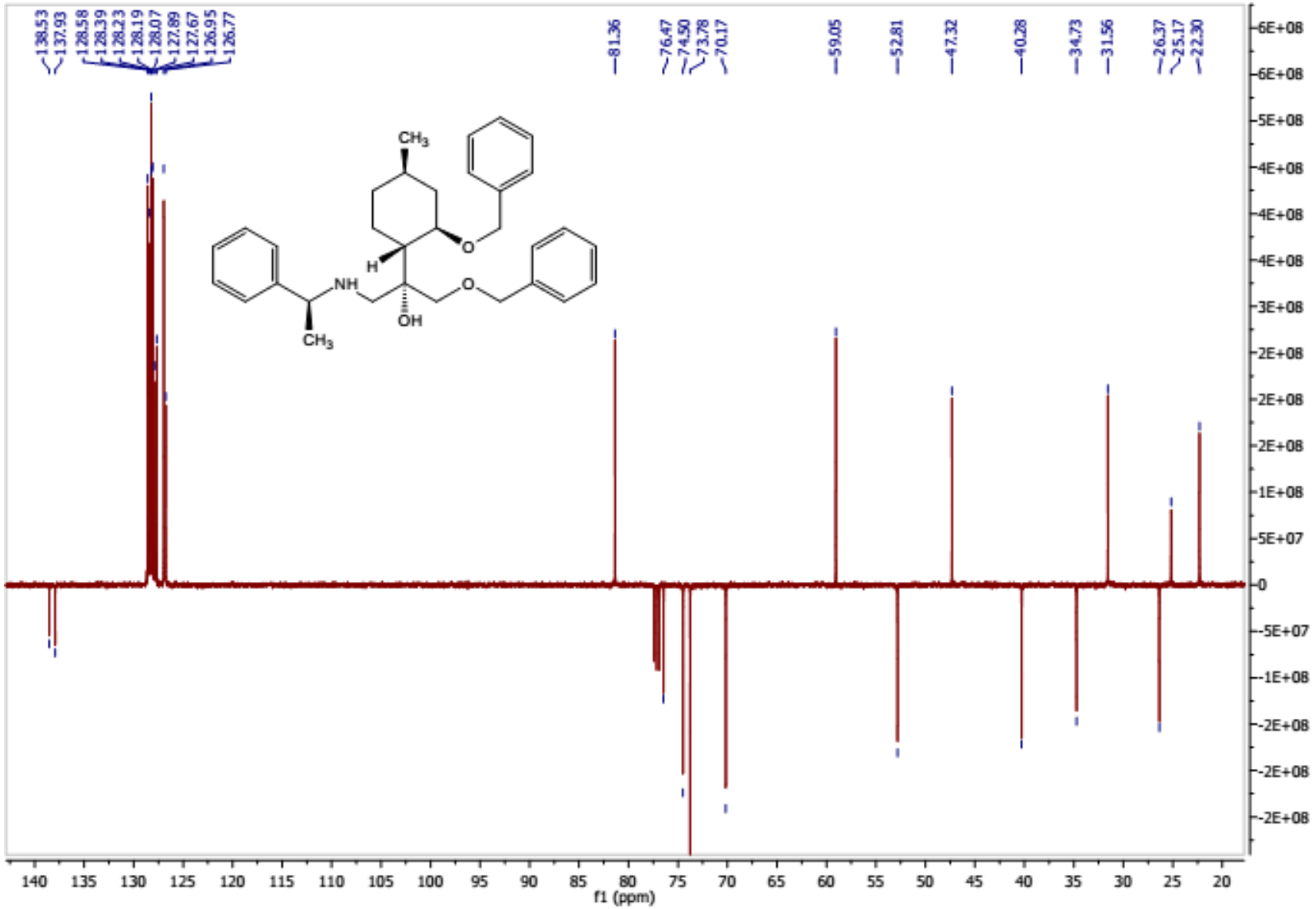
$^{13}$C-NMR of compound **53b**



[1]H-NMR of compound **54a**



$^{13}$C-NMR of compound **54a**



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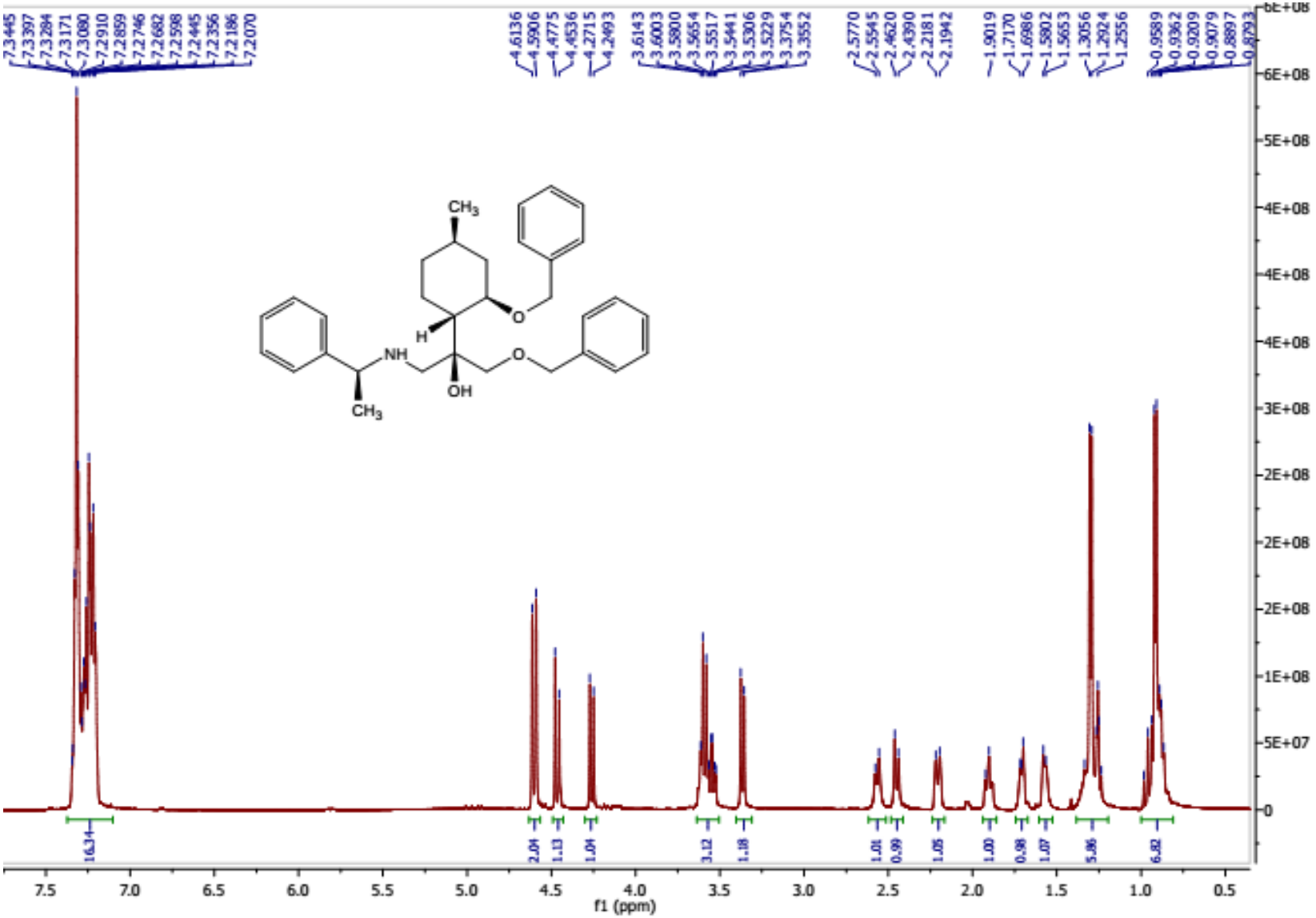
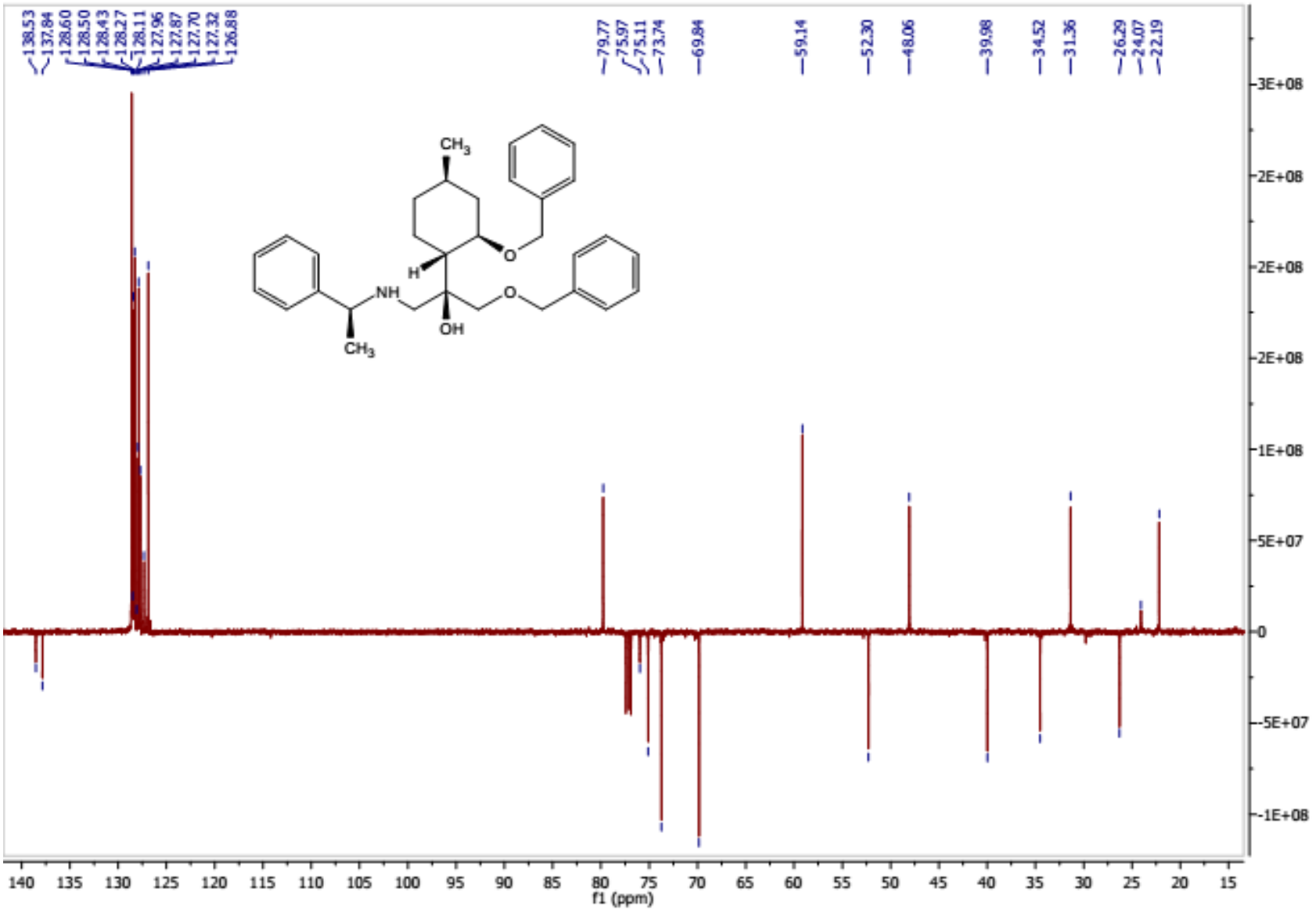


$^{13}$C-NMR of compound **54b**



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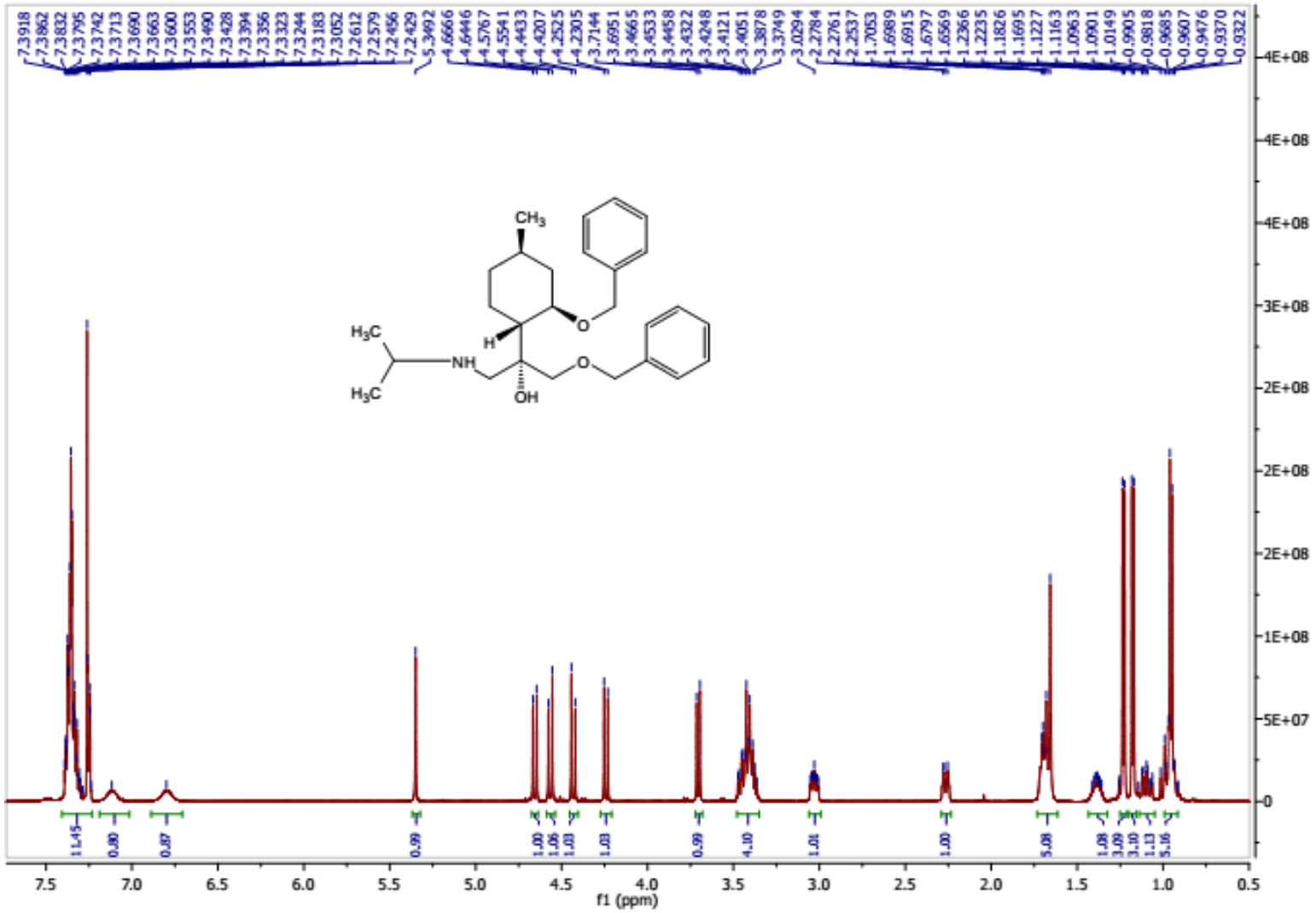
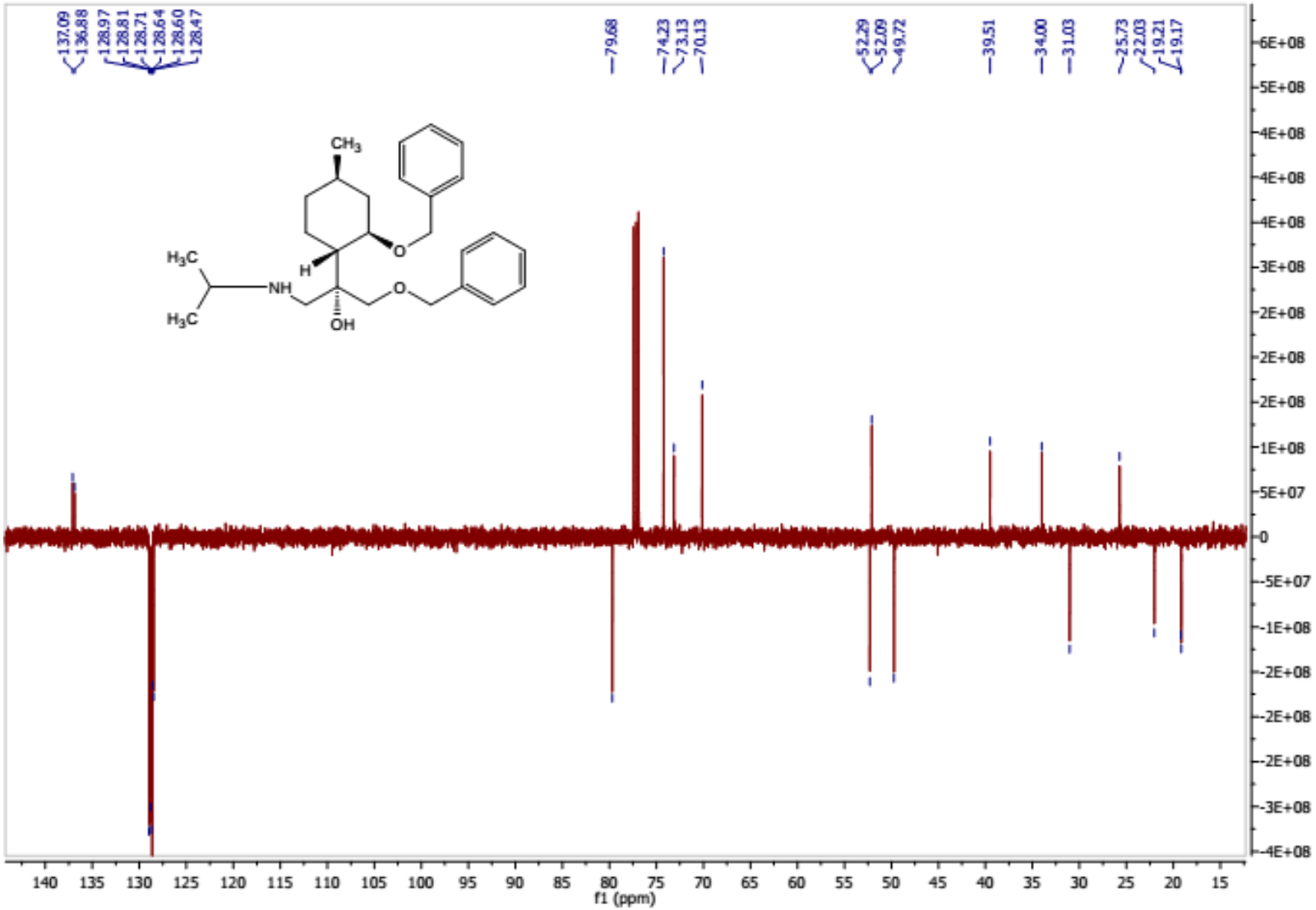
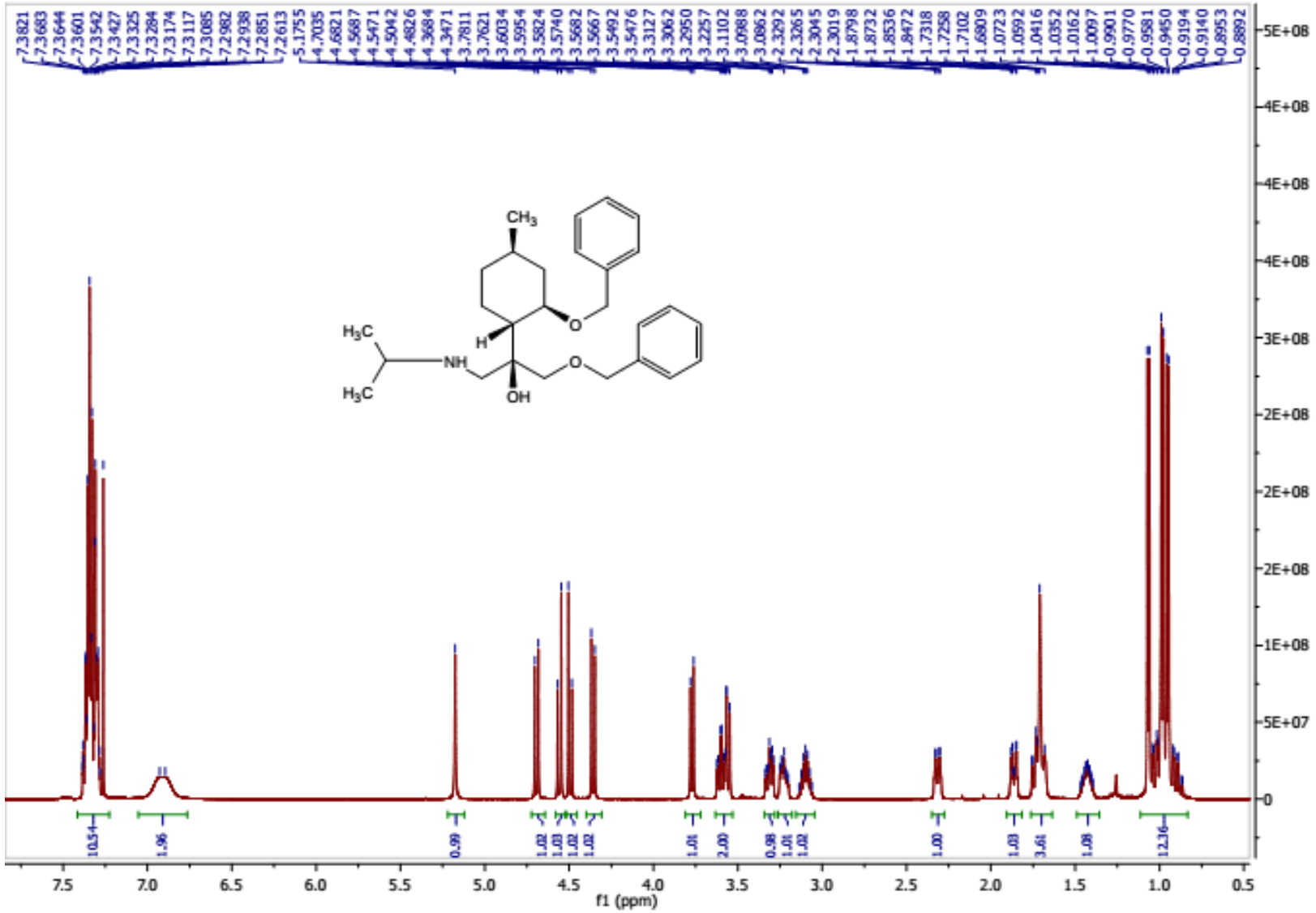


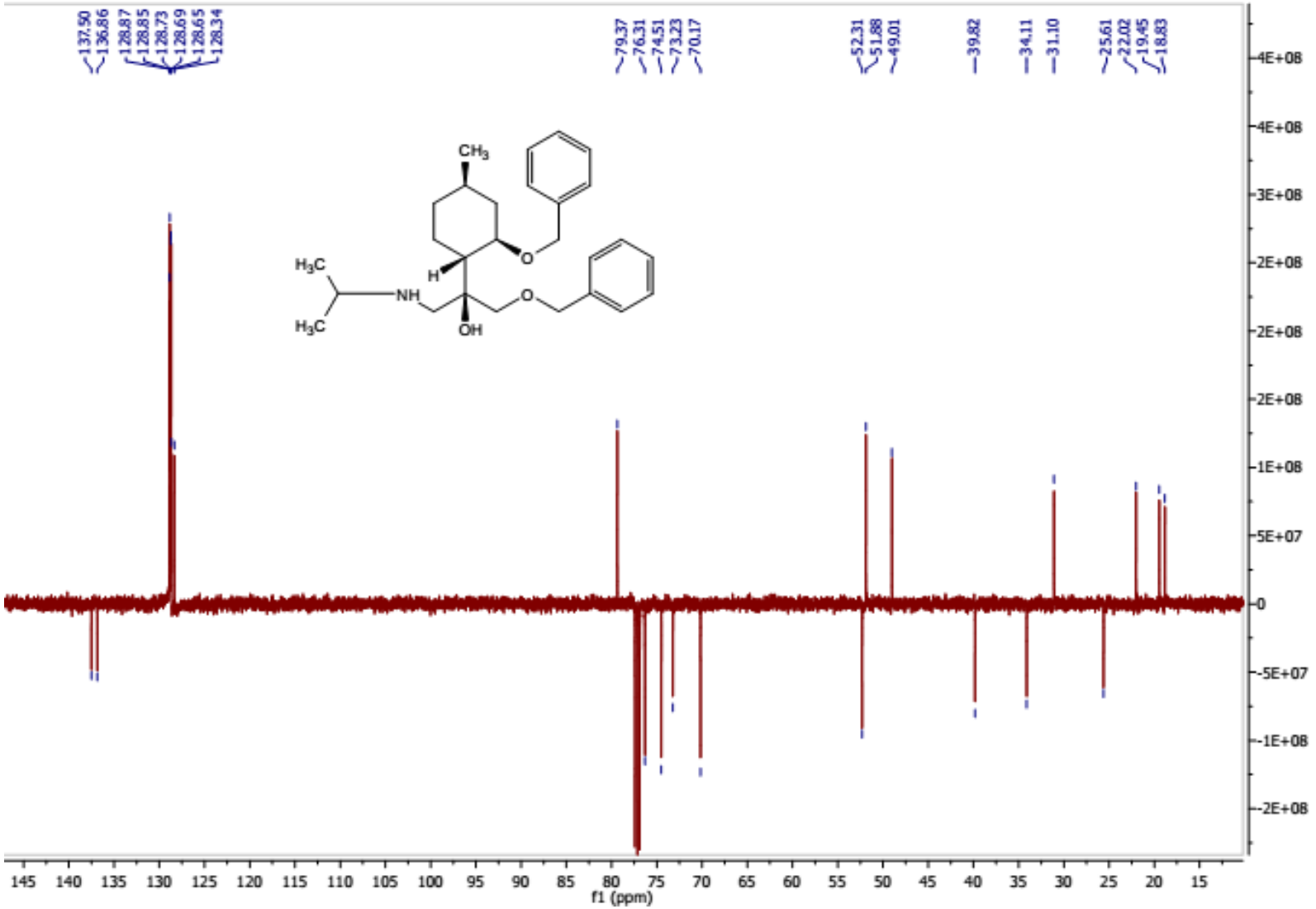
$^{13}$C-NMR of compound **55a**



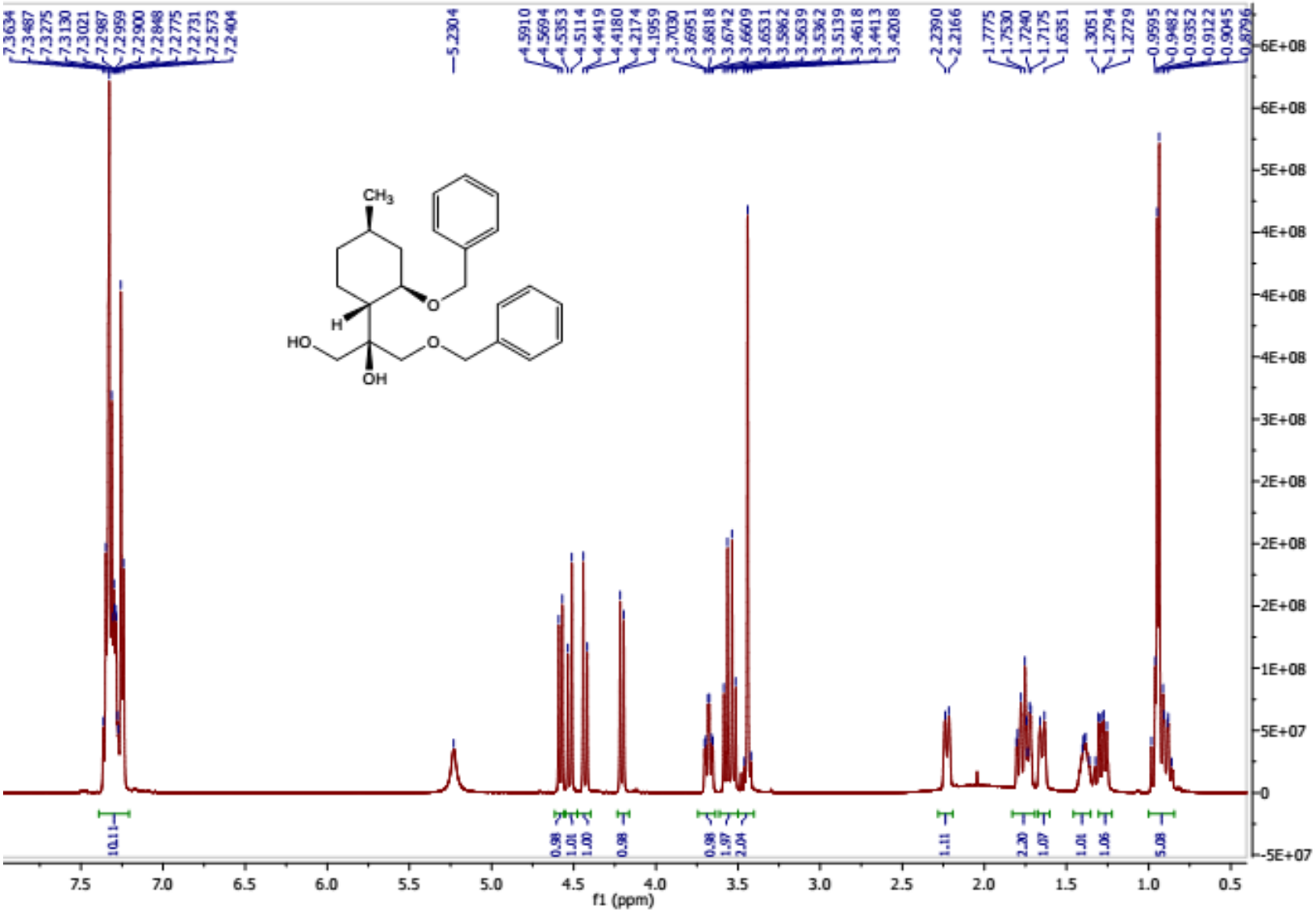
[1]H-NMR of compound **55b**



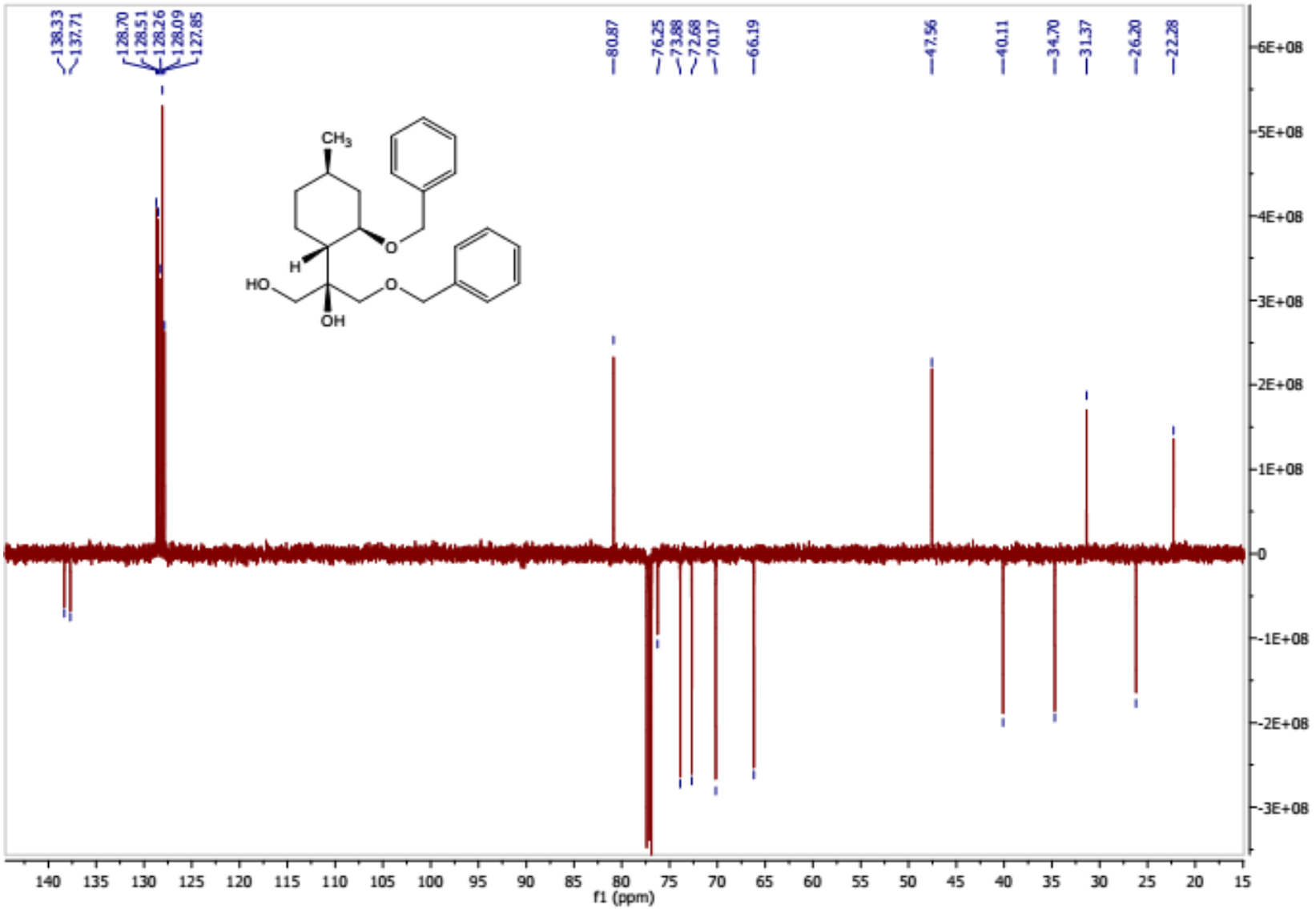
$^{13}$C-NMR of compound **55b**



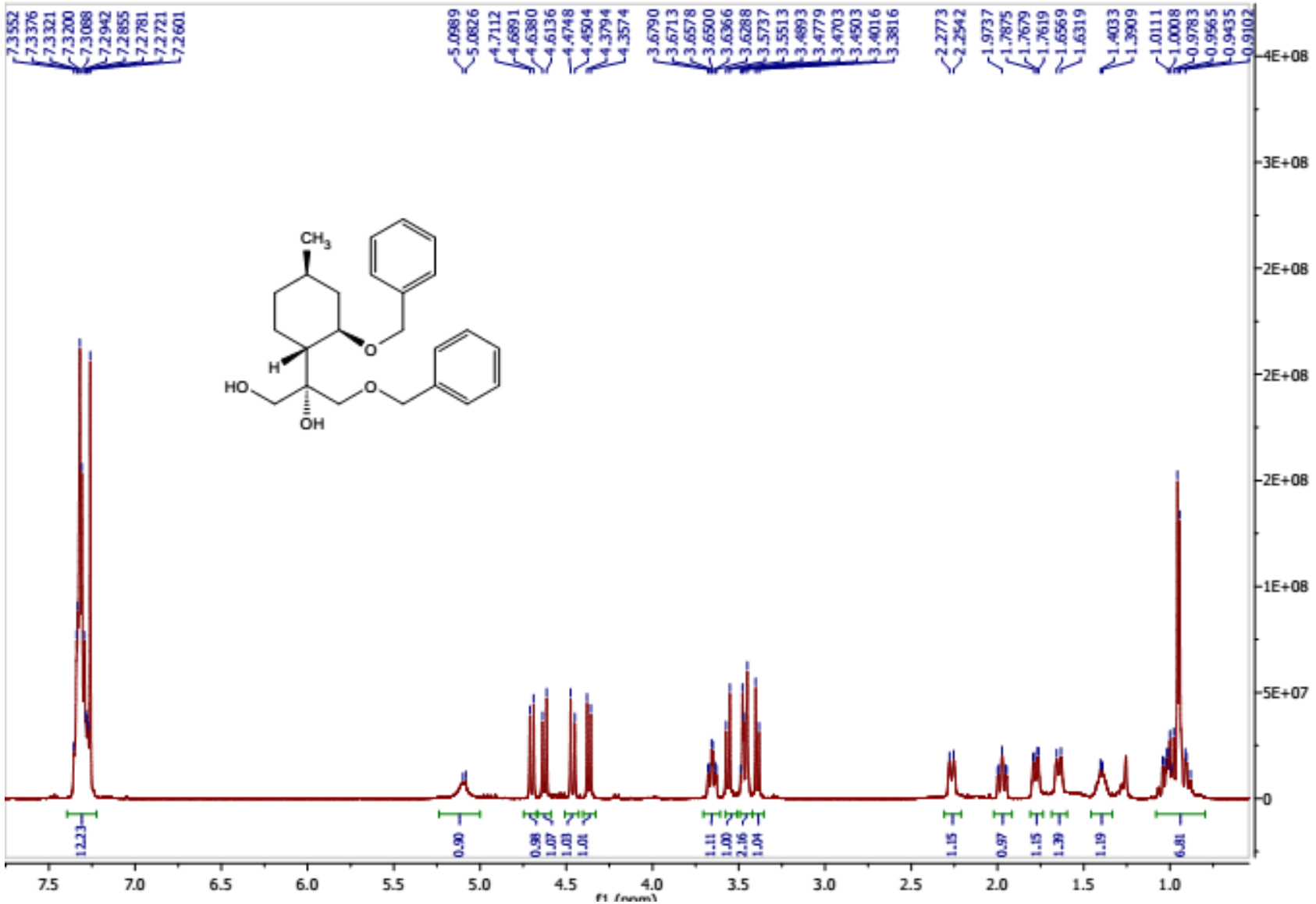
[1]H-NMR of compound **56a**



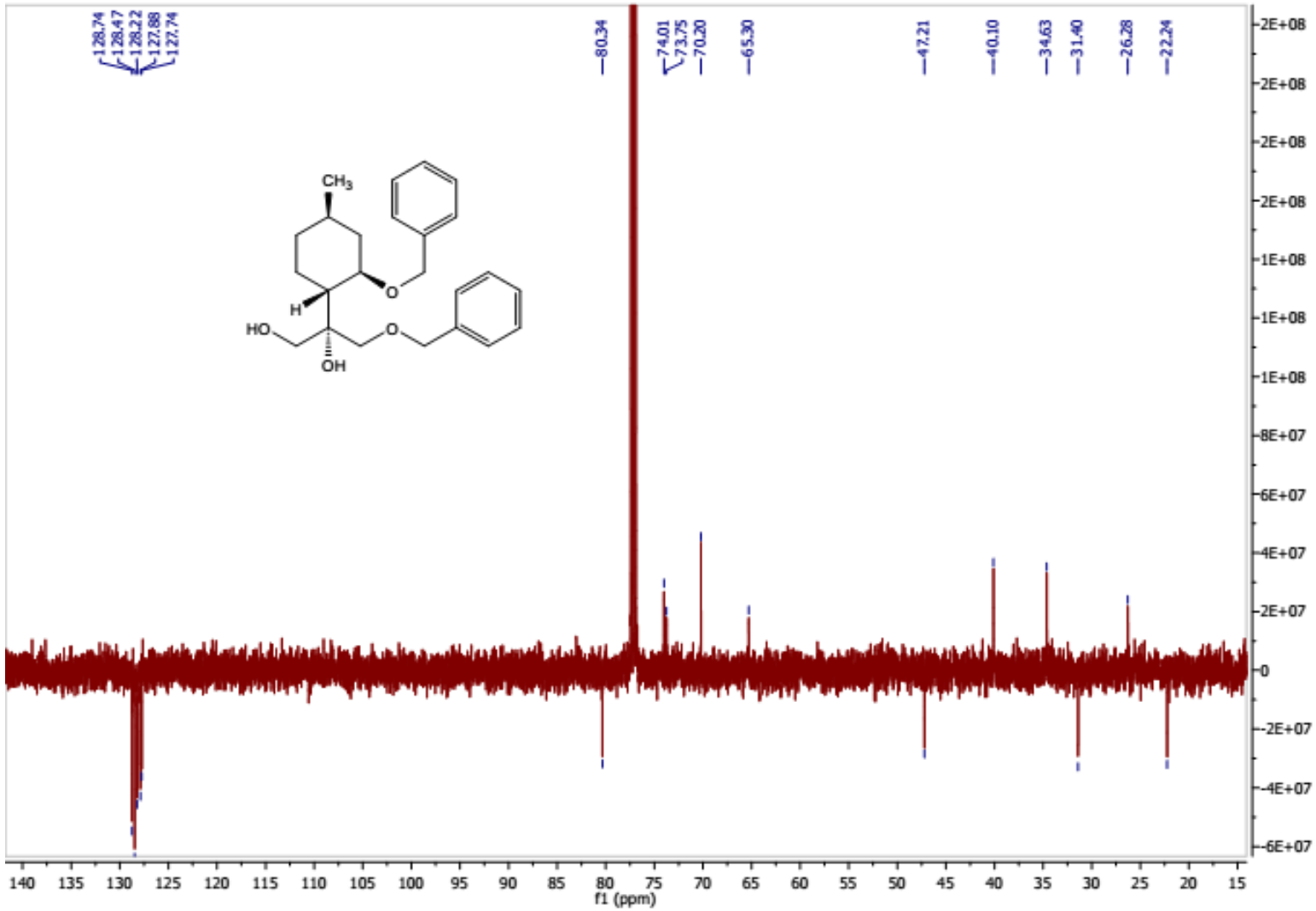
$^{13}$C-NMR of compound **56a**



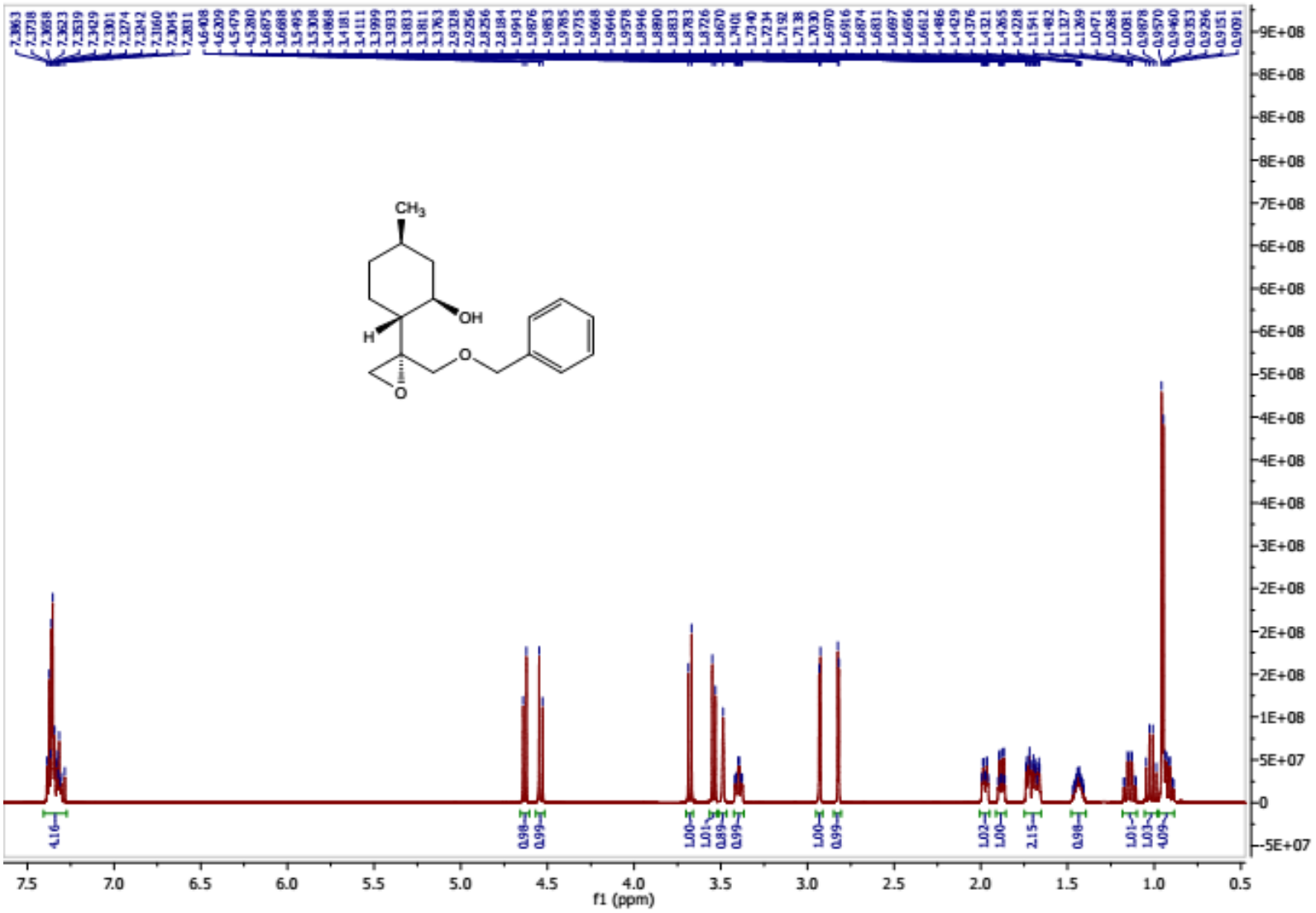
$^{1}$H-NMR of compound **56b**



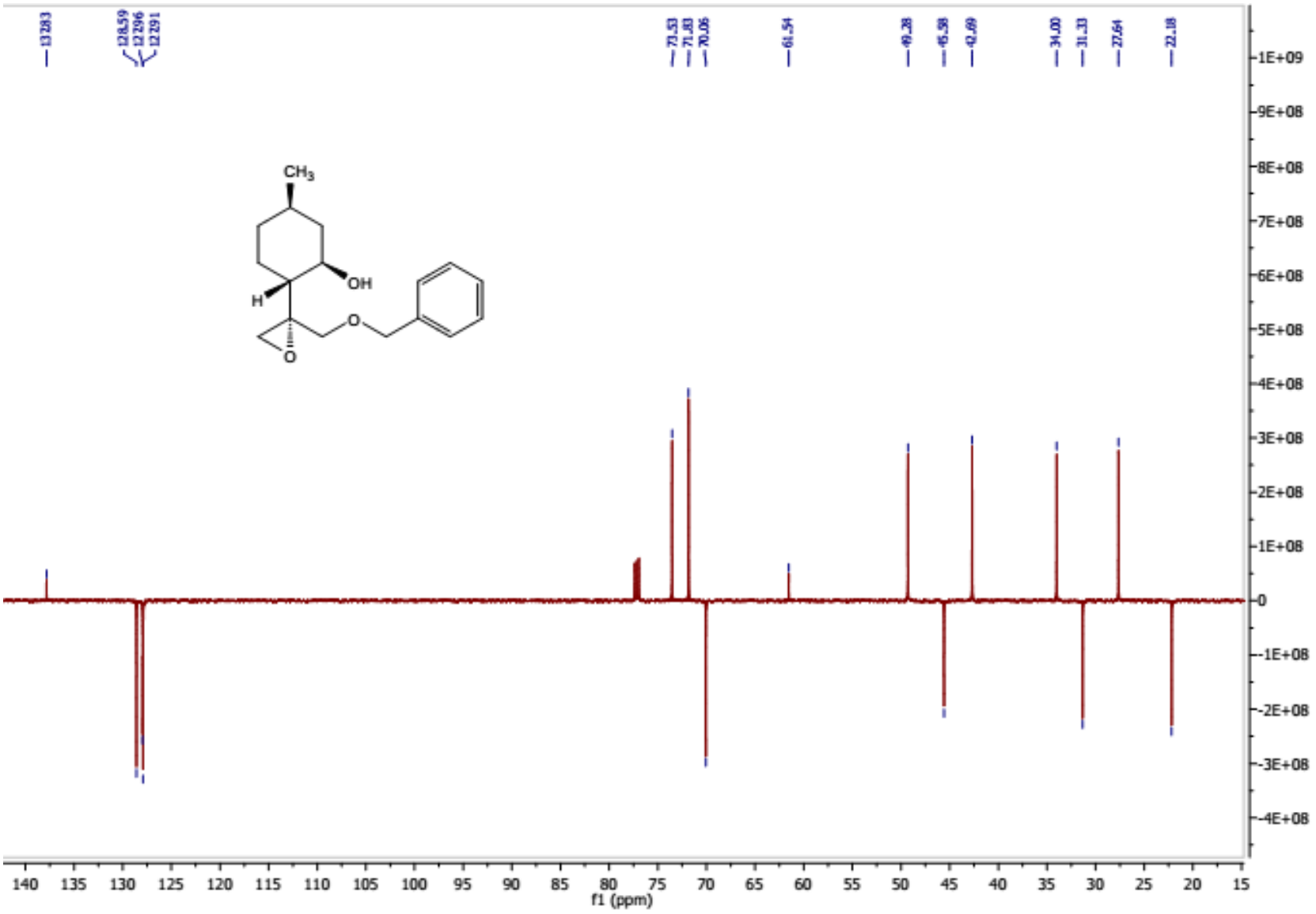
$^{13}$C-NMR of compound **56b**



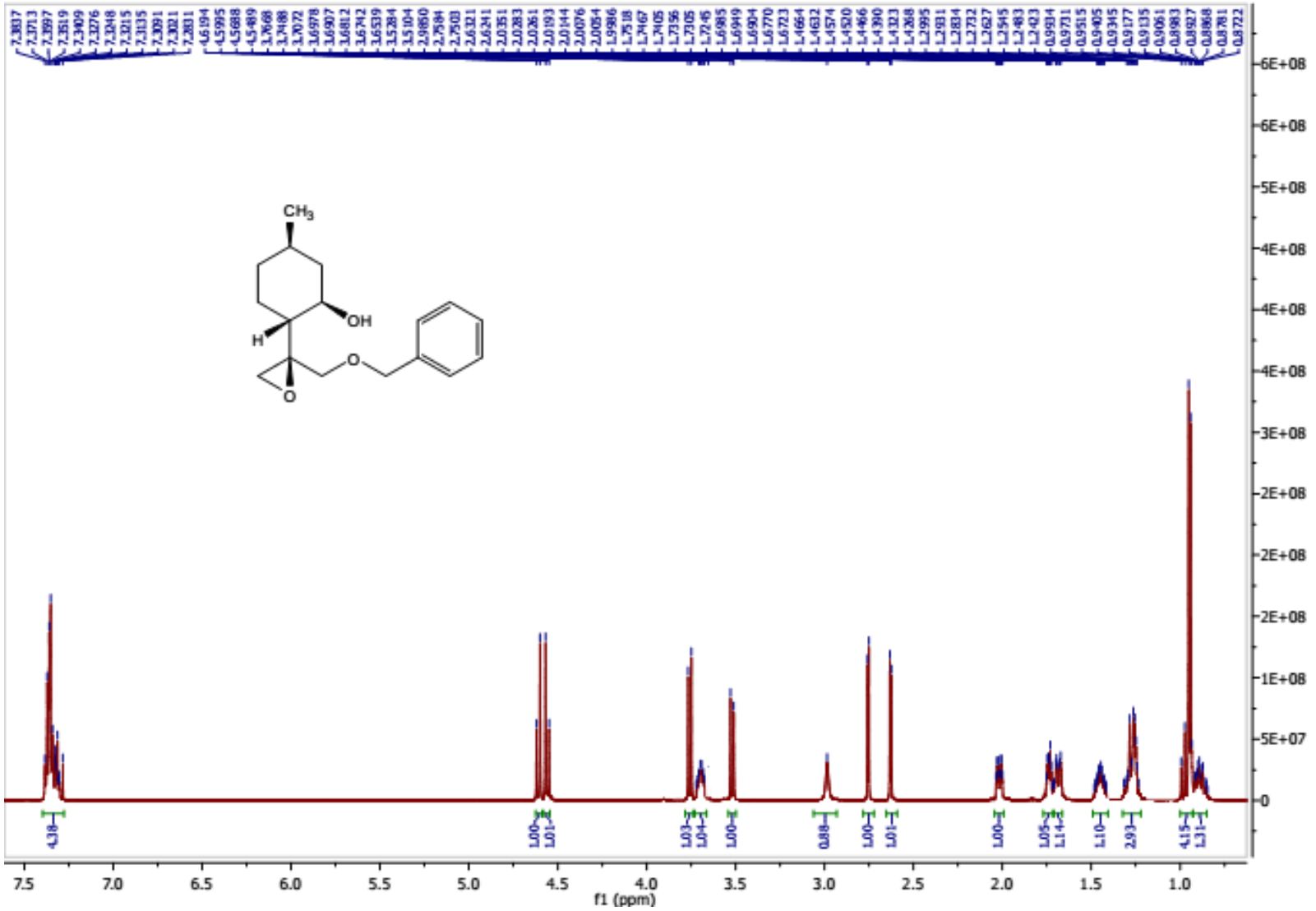
[1]H-NMR of compound **57a**



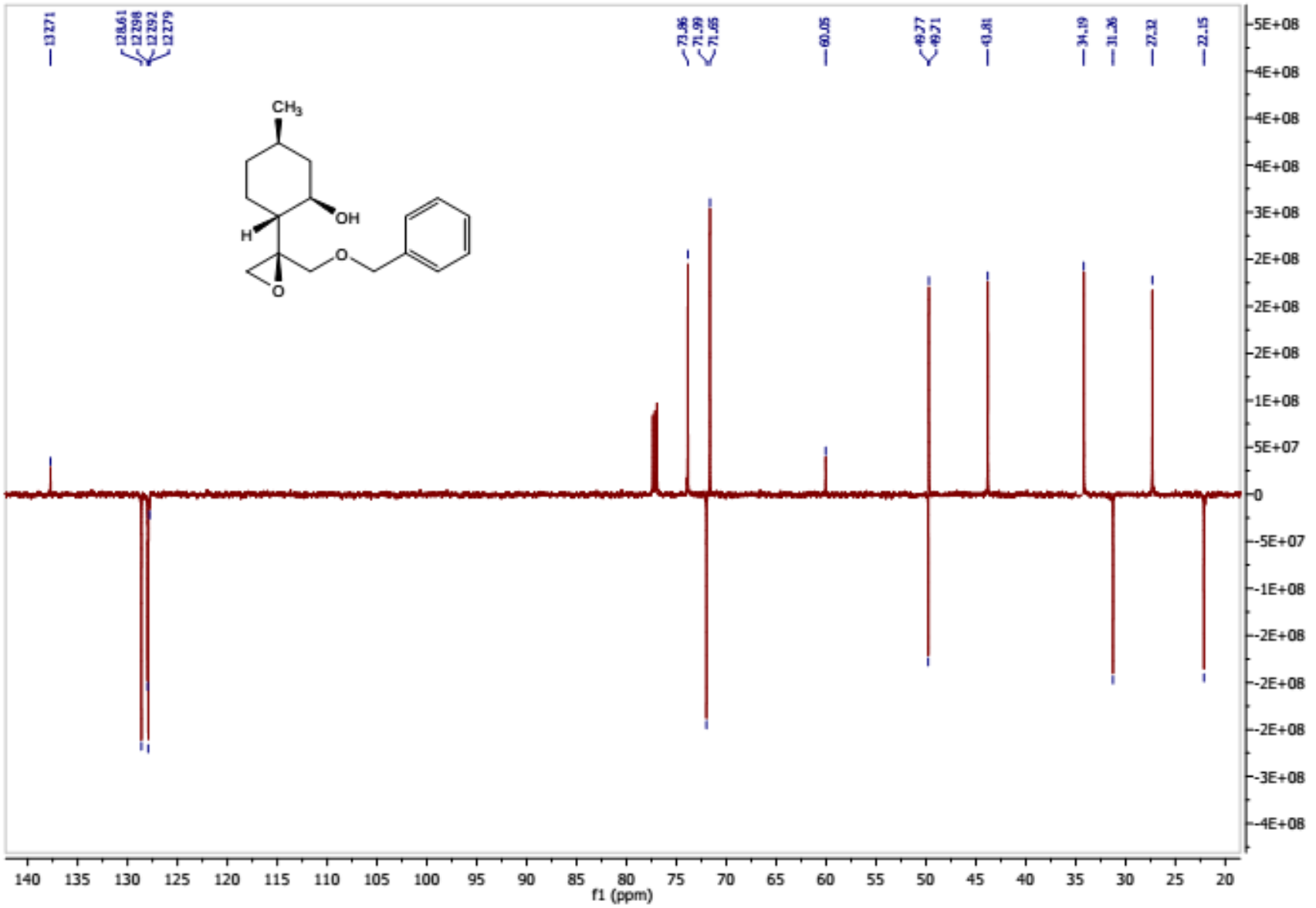
$^{13}$C-NMR of compound **57a**



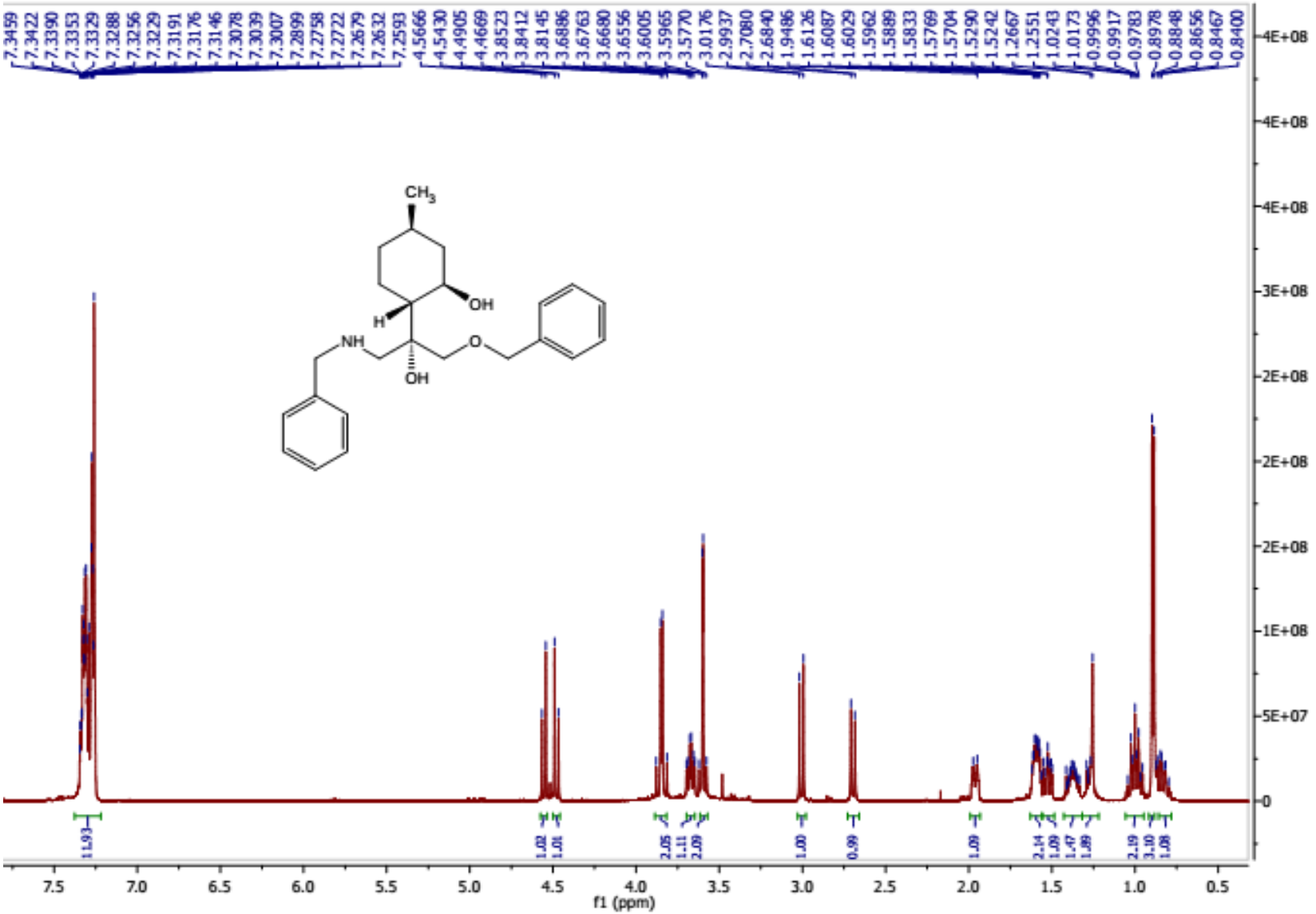
$^{1}$H-NMR of compound **57b**



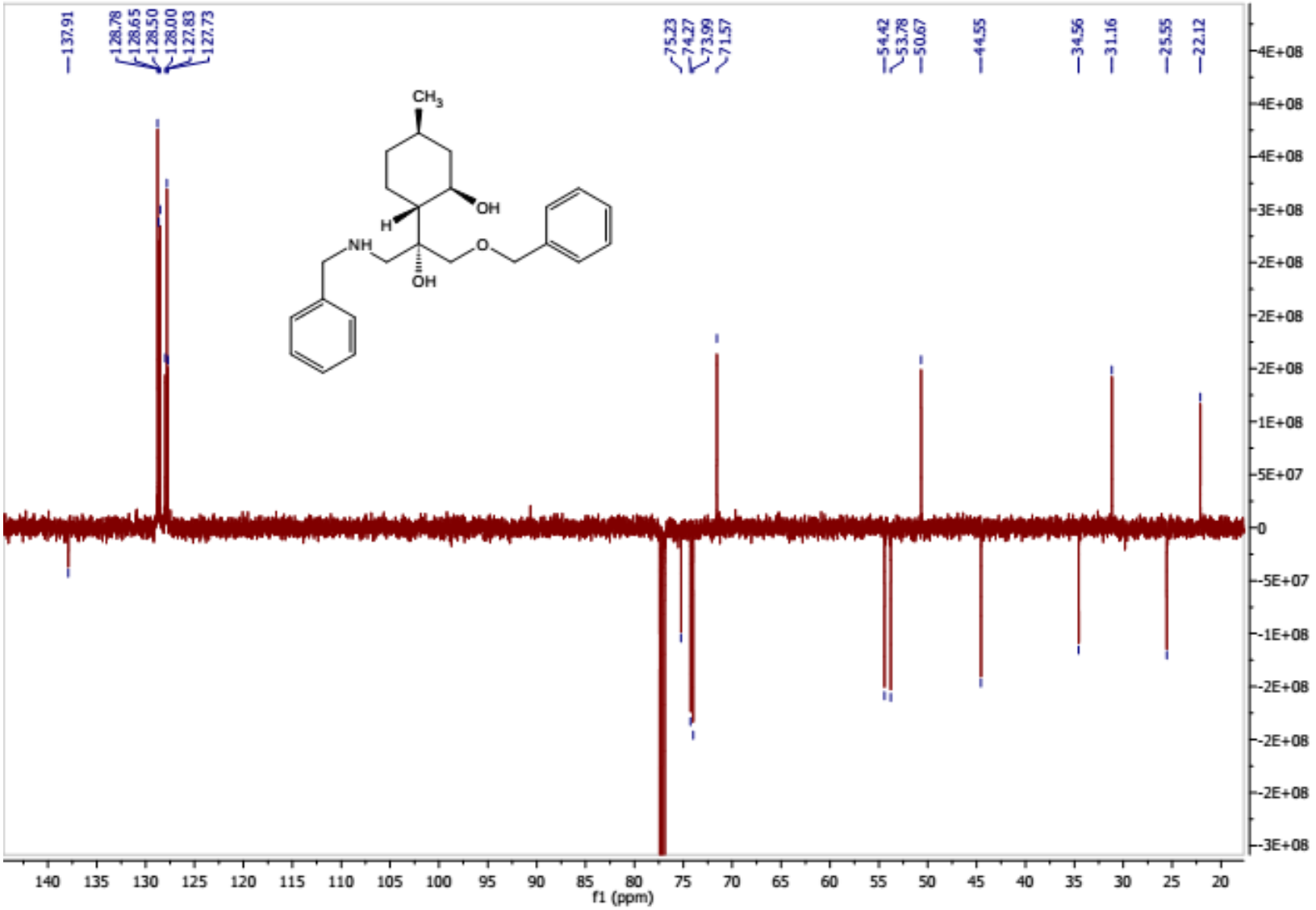
$^{13}$C-NMR of compound **57b**



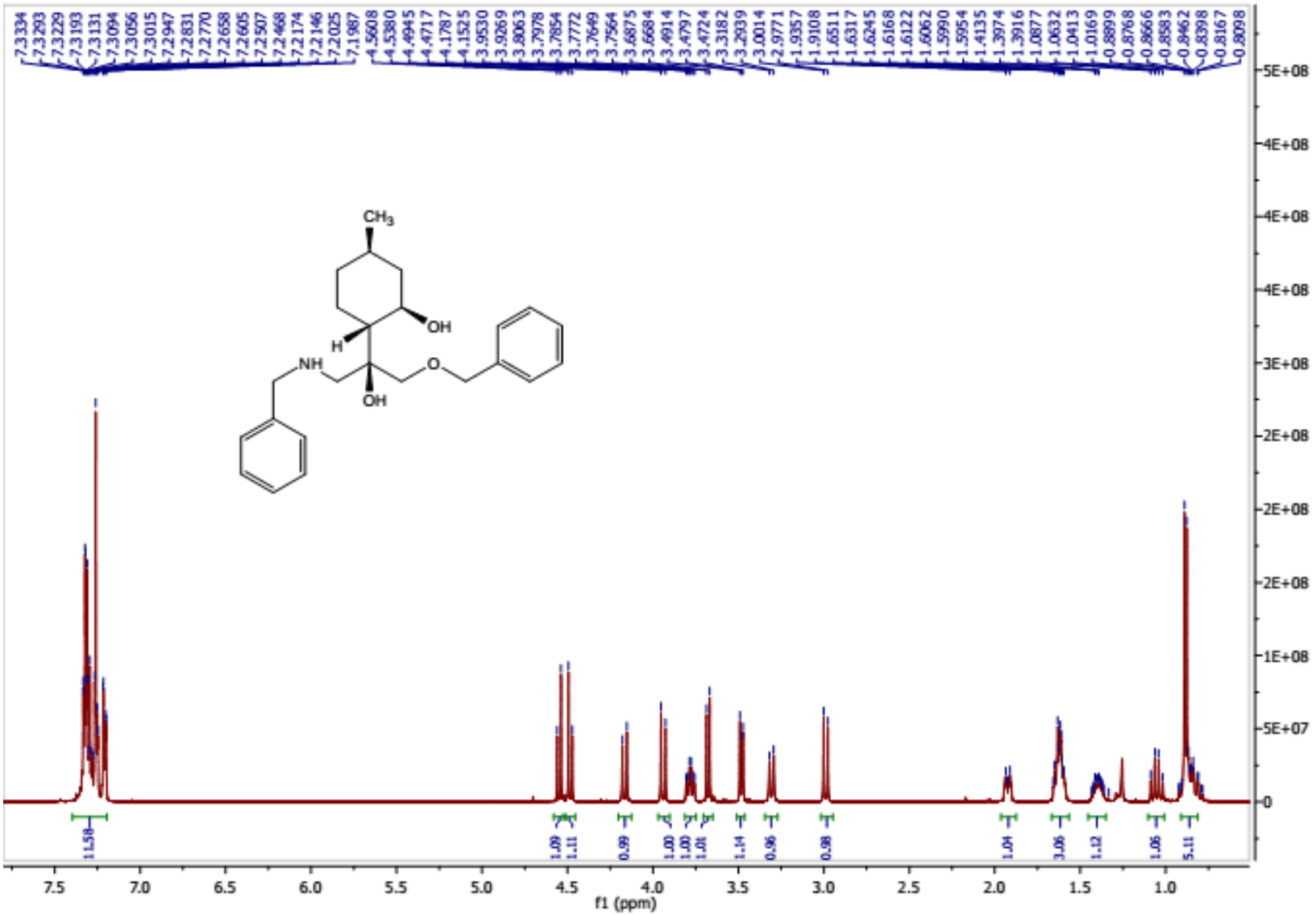
[1]H-NMR of compound **58a**



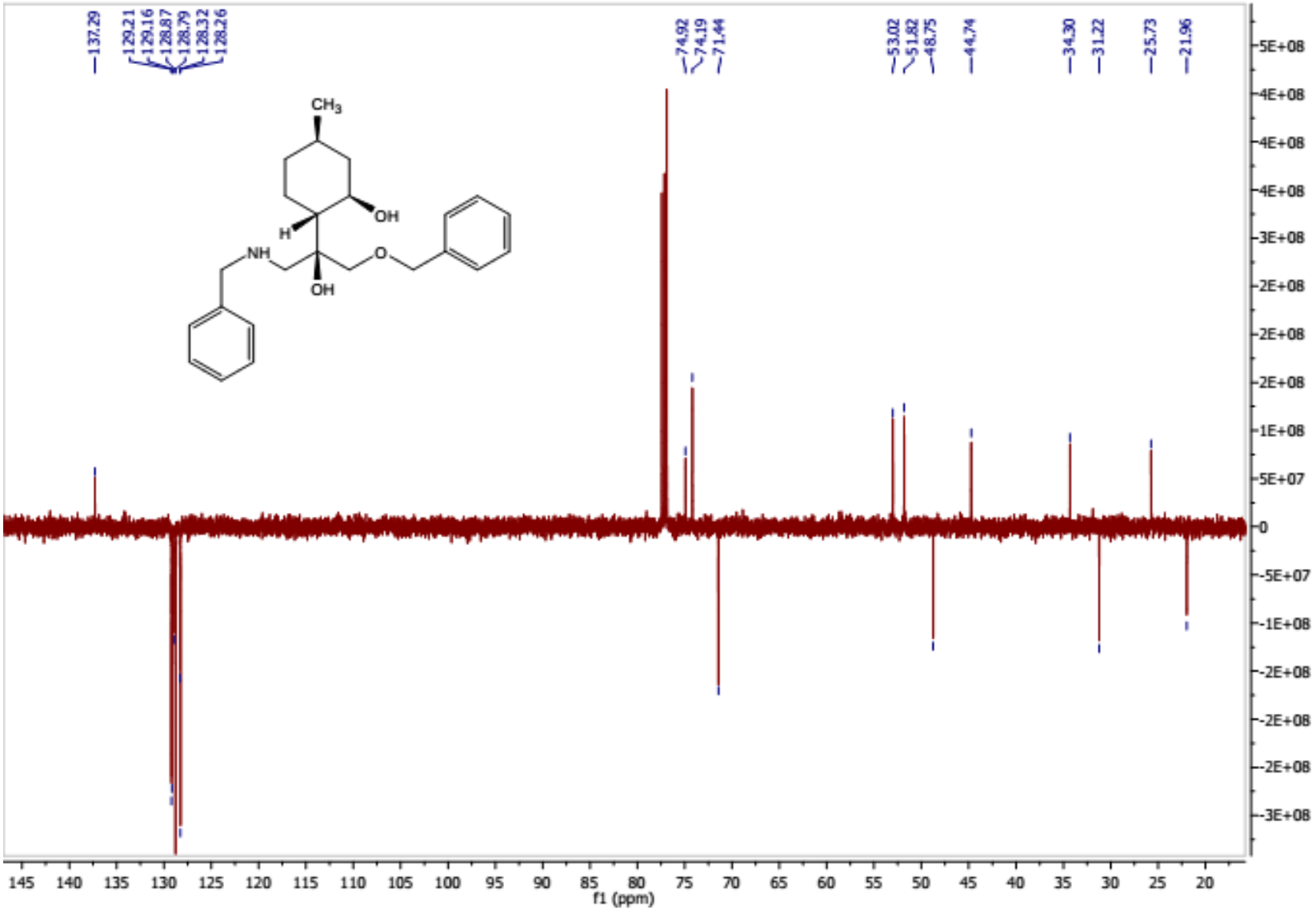
$^{13}$C-NMR of compound **58a**



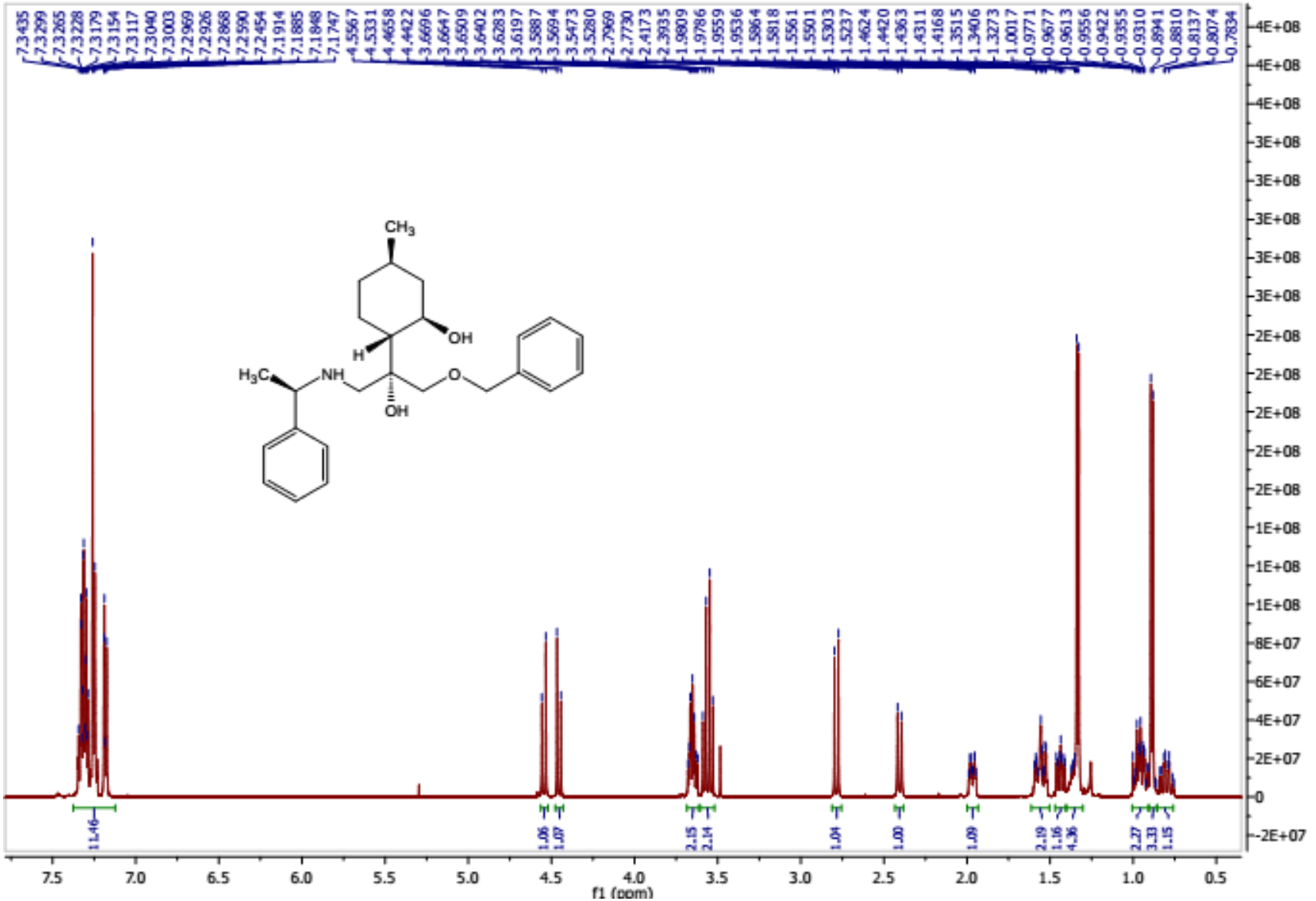
[1]H-NMR of compound **58b**



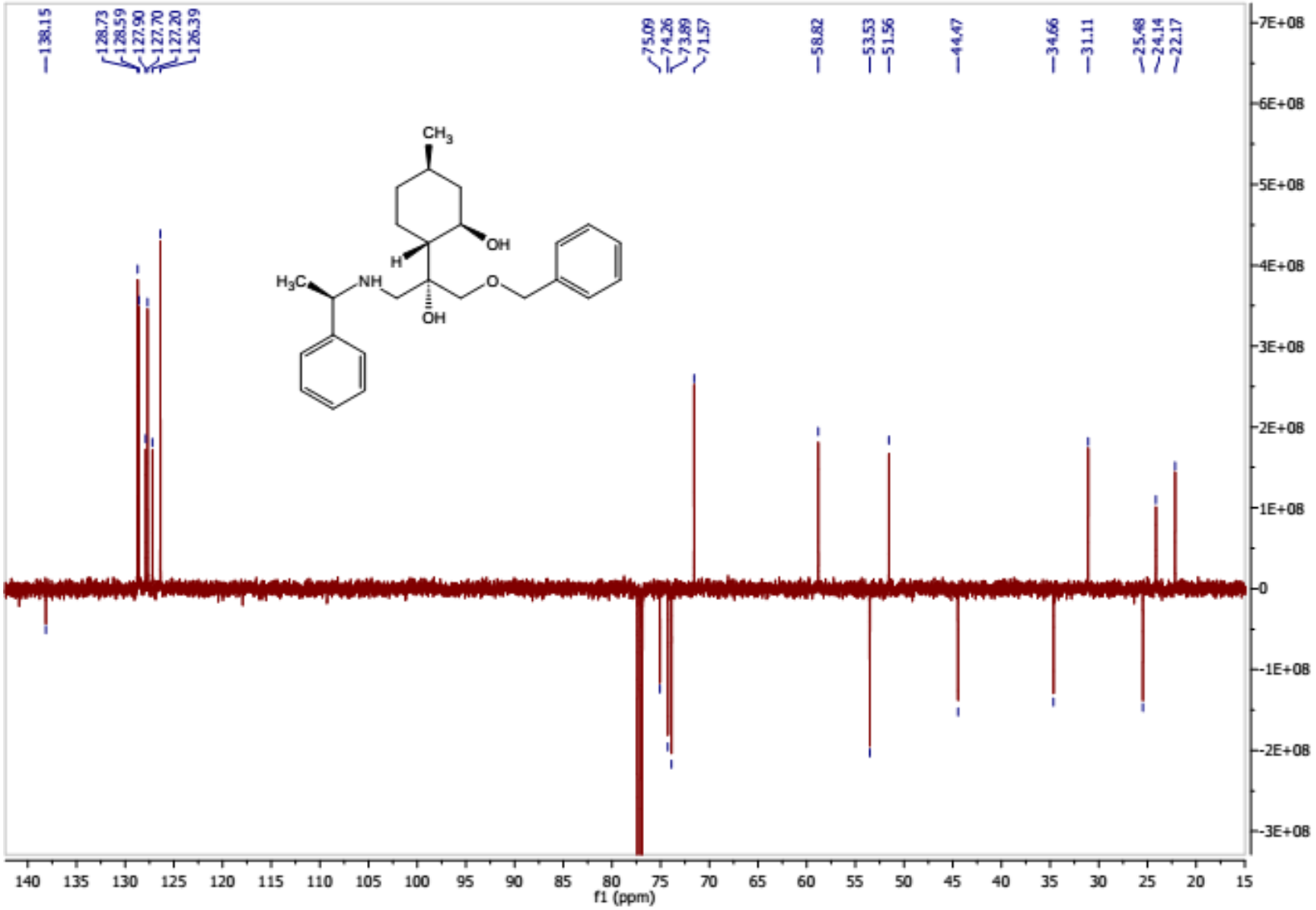
$^{13}$C-NMR of compound **58b**



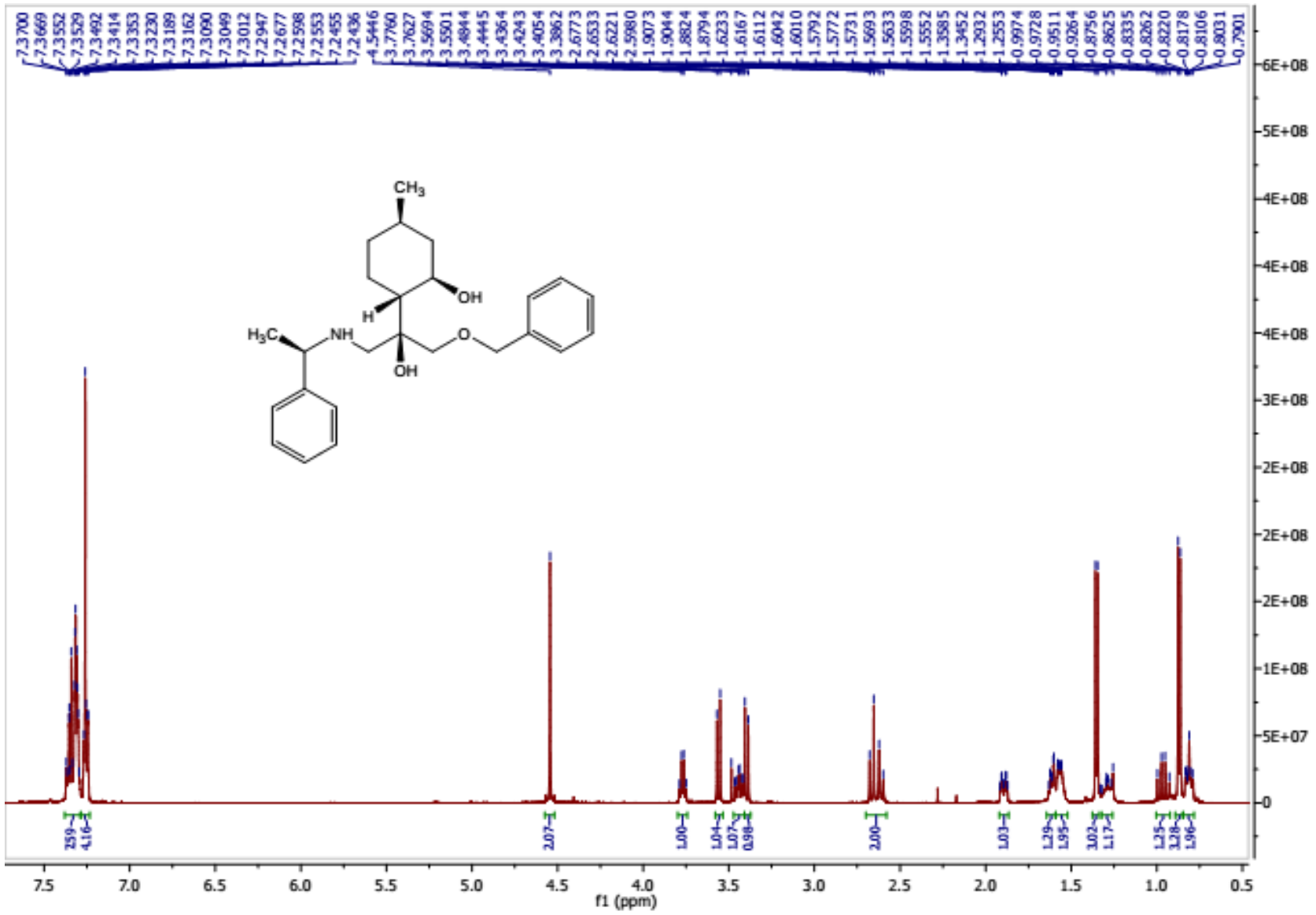
[1]H-NMR of compound **59a**



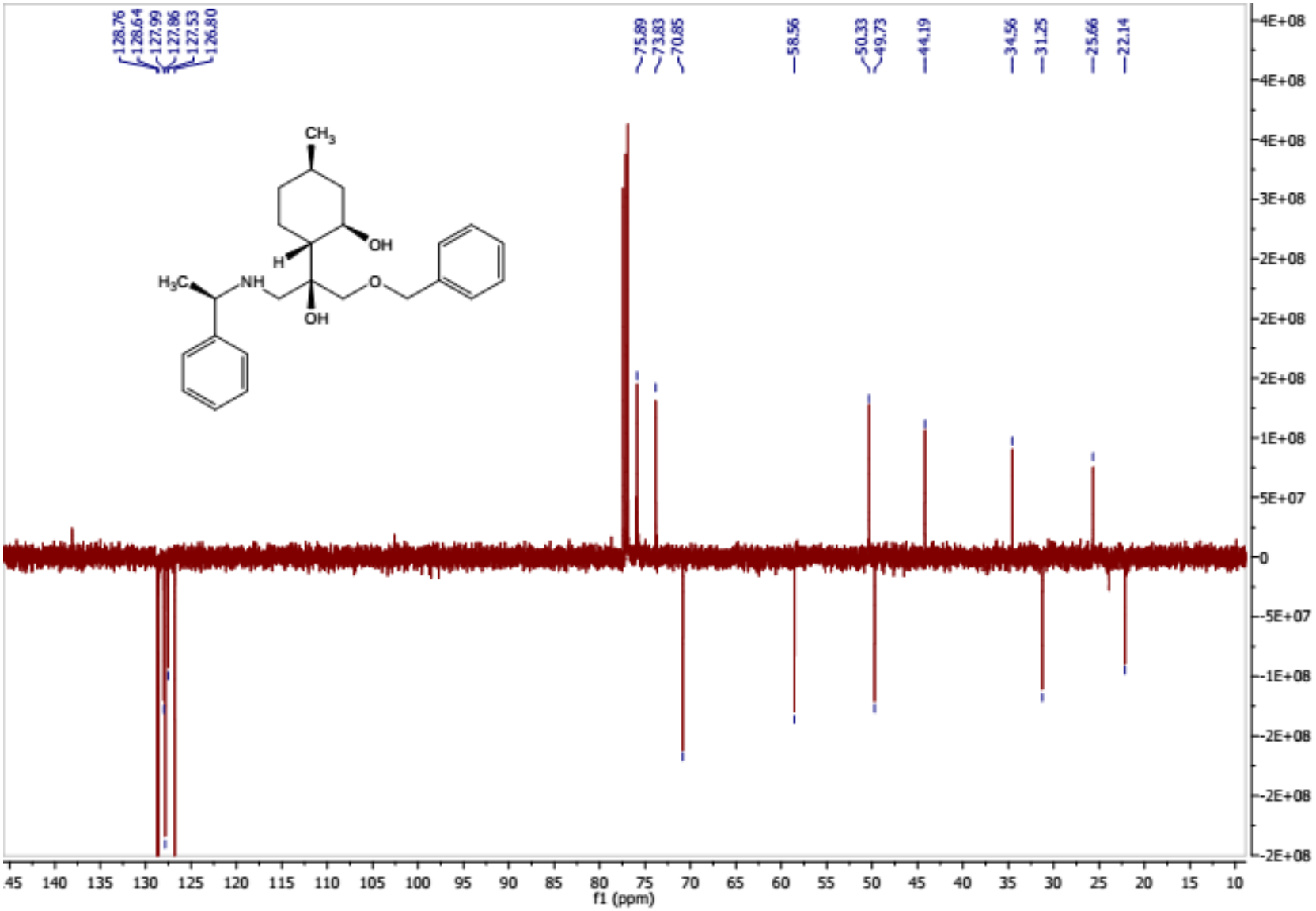
$^{13}$C-NMR of compound **59a**



[1]H-NMR of compound **59b**



$^{13}$C-NMR of compound **59b**



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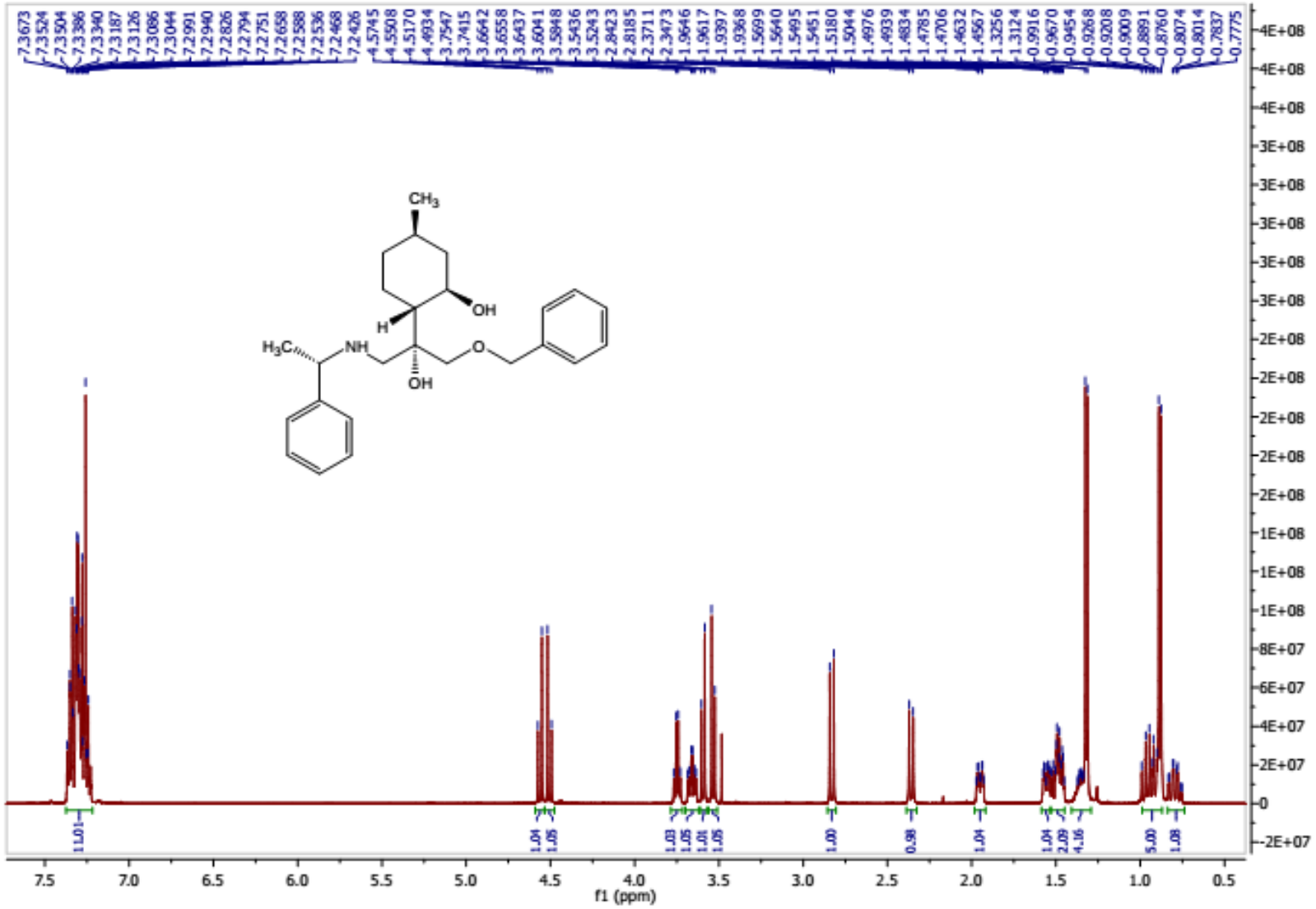

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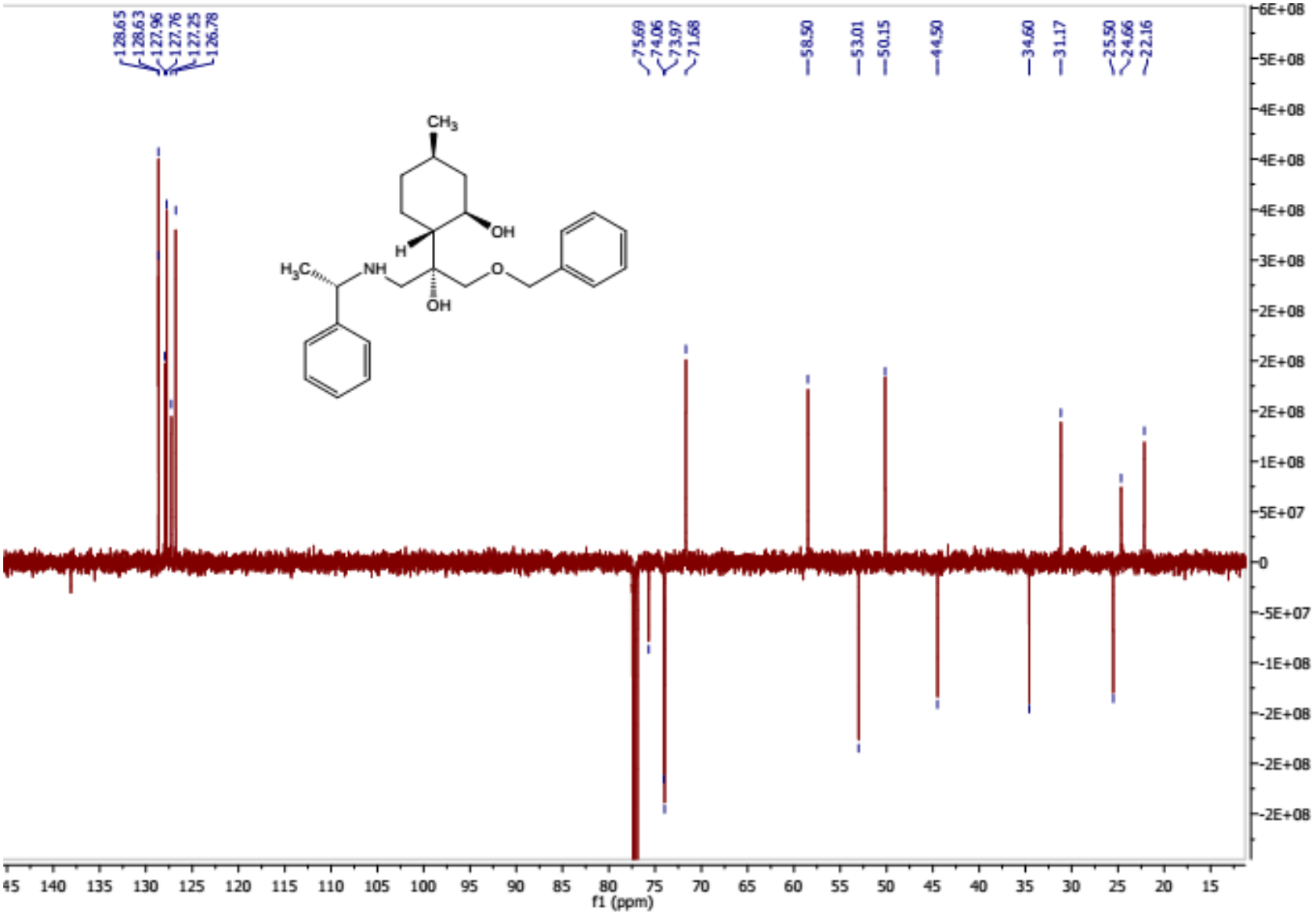

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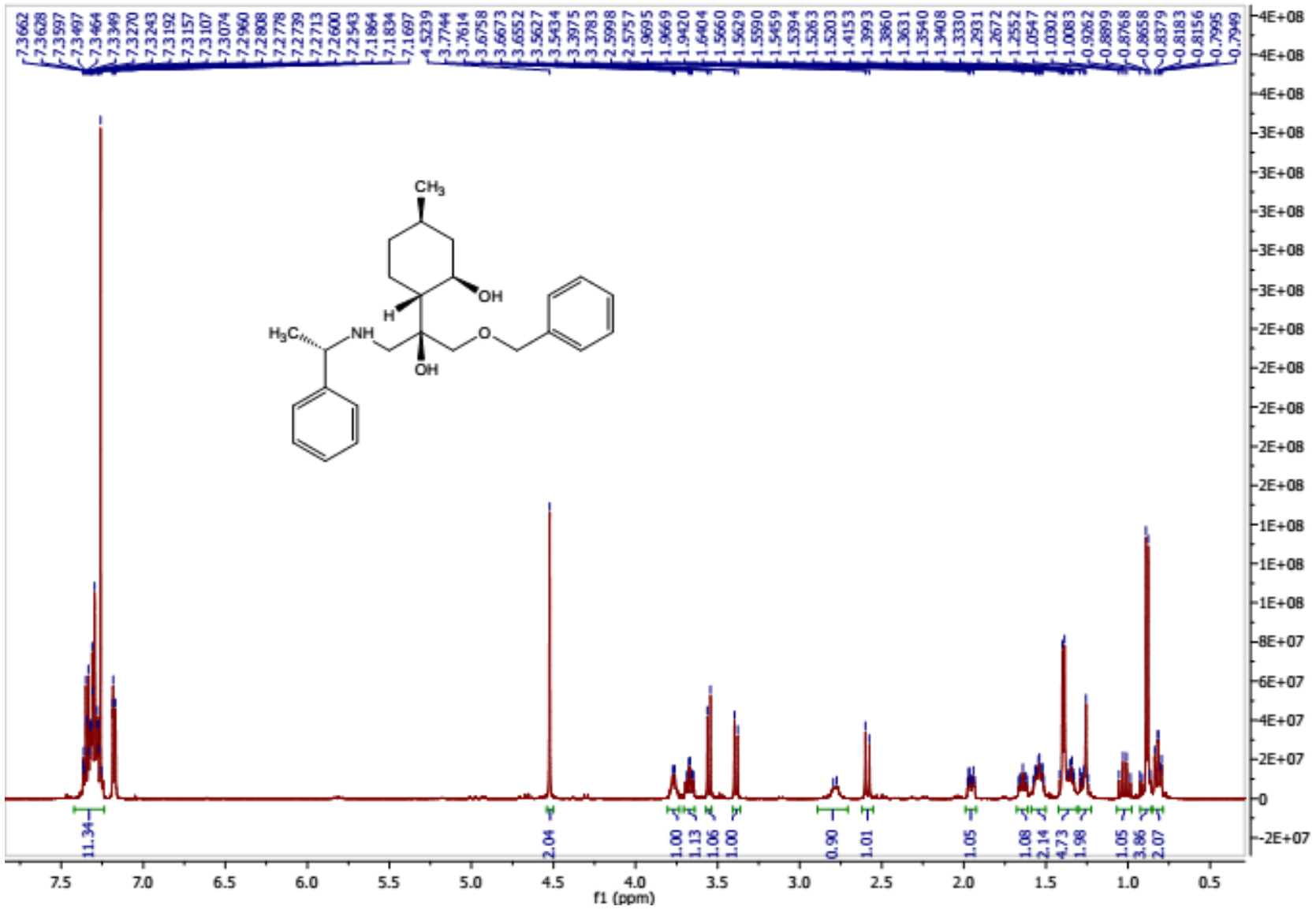
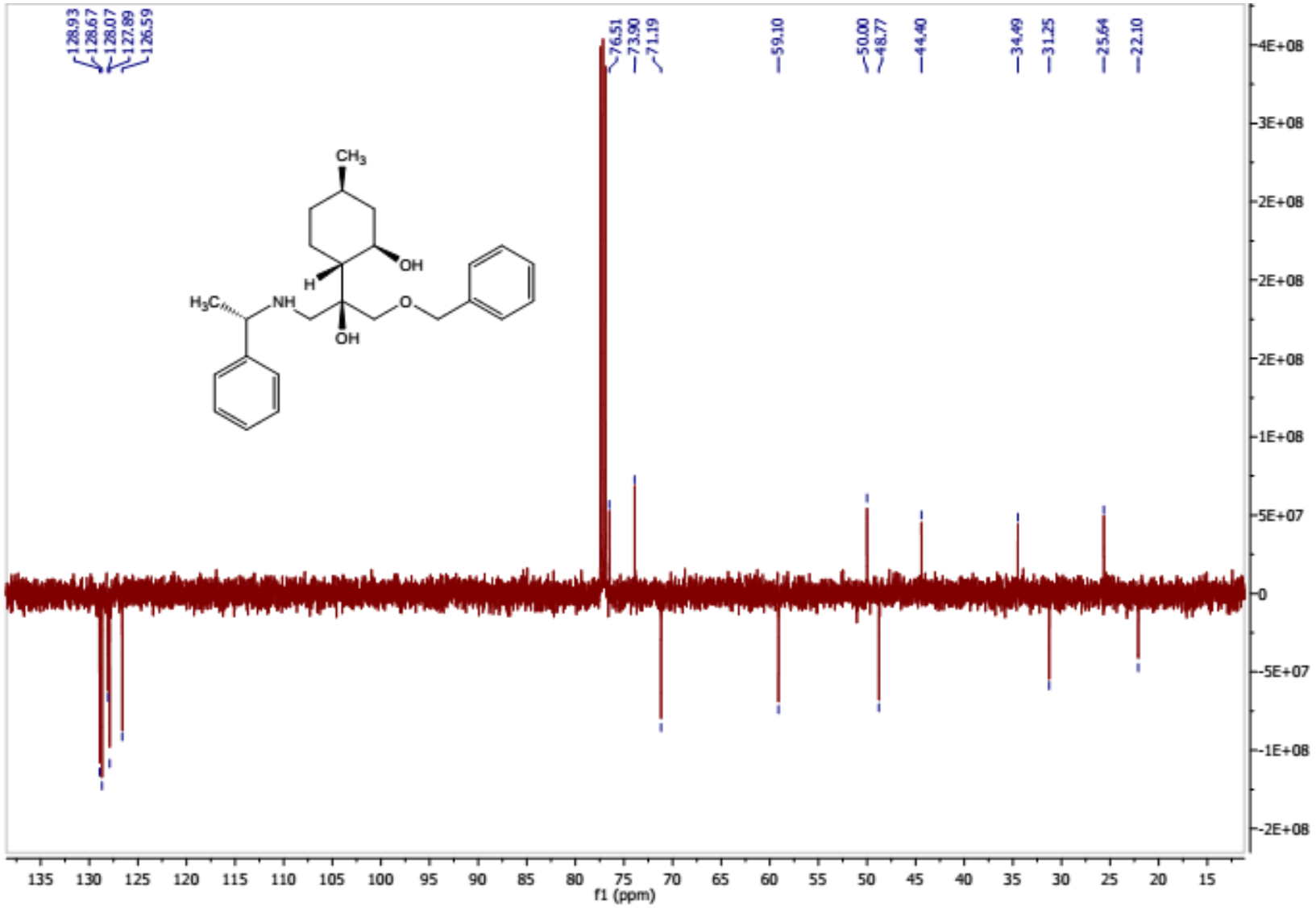


$^{13}$C-NMR of compound **60b**



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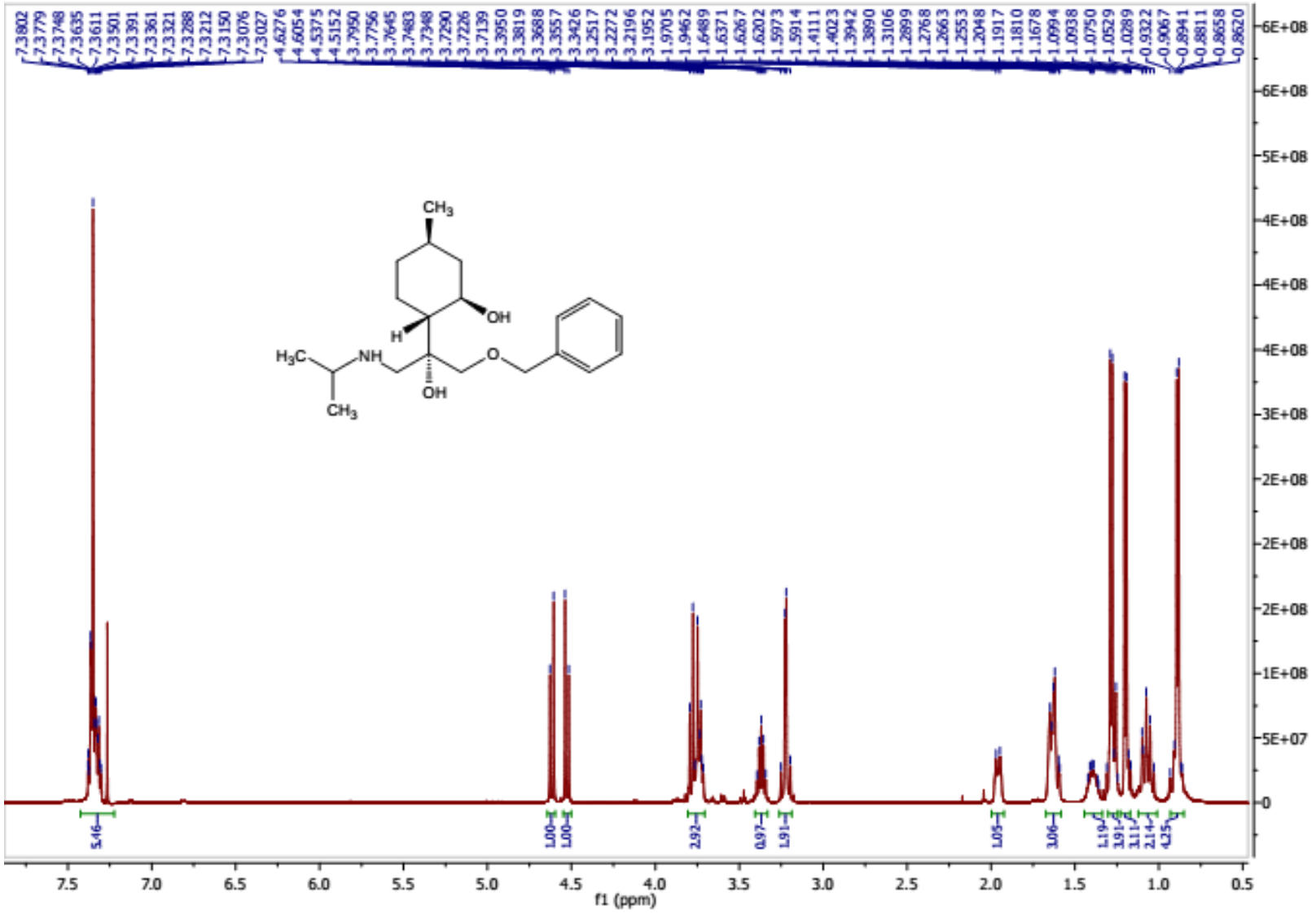
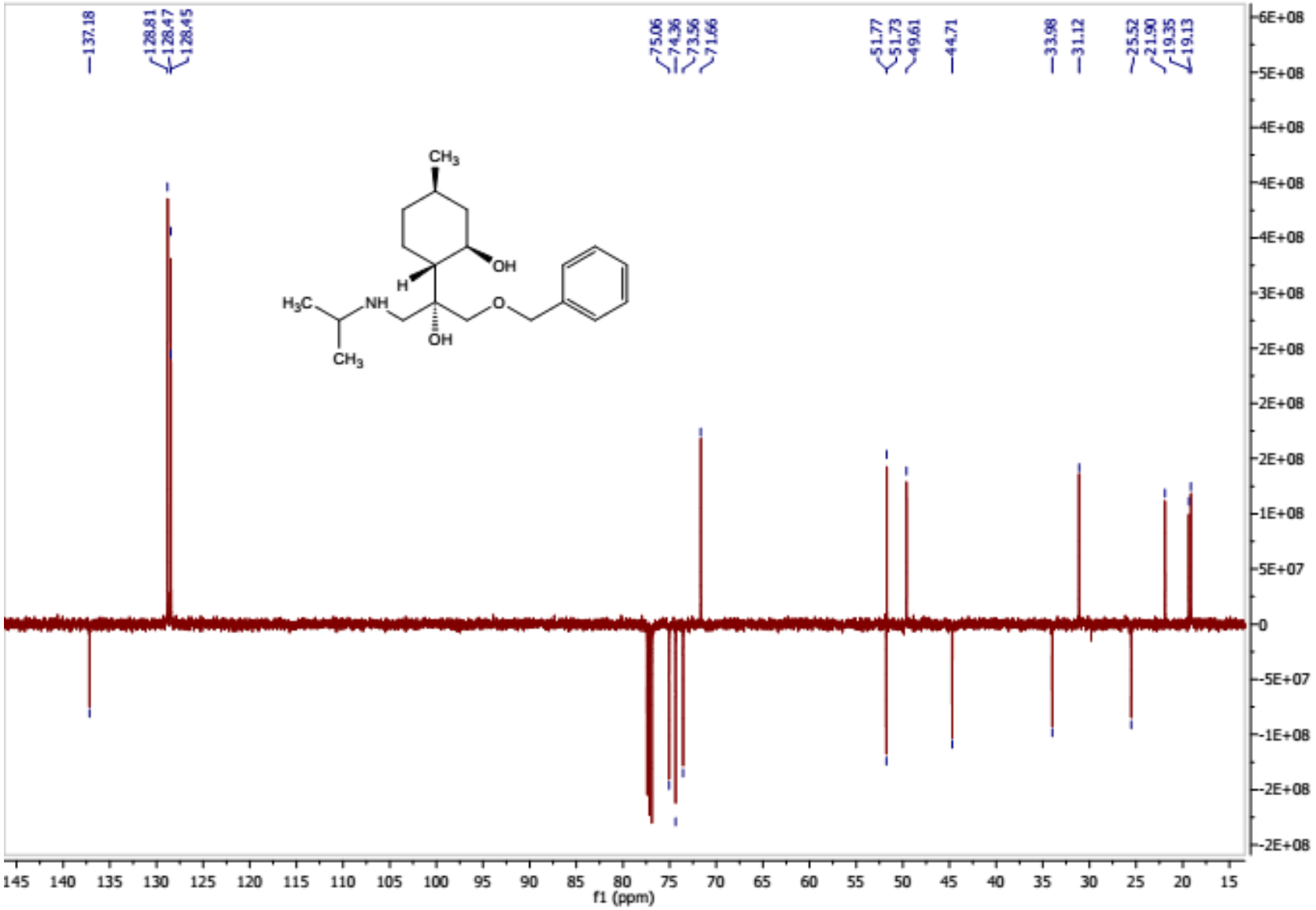


$^{13}$C-NMR of compound **61a**



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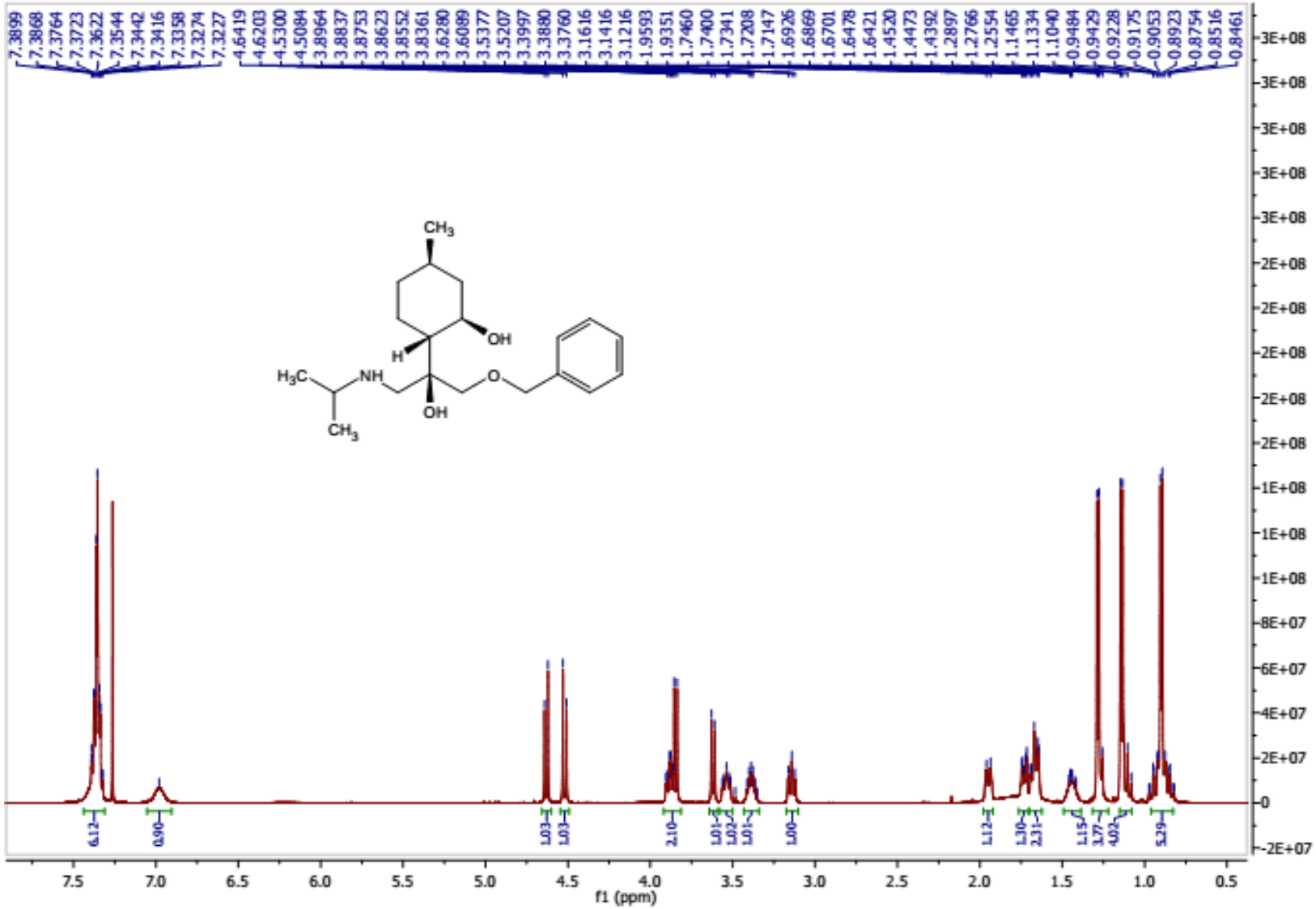

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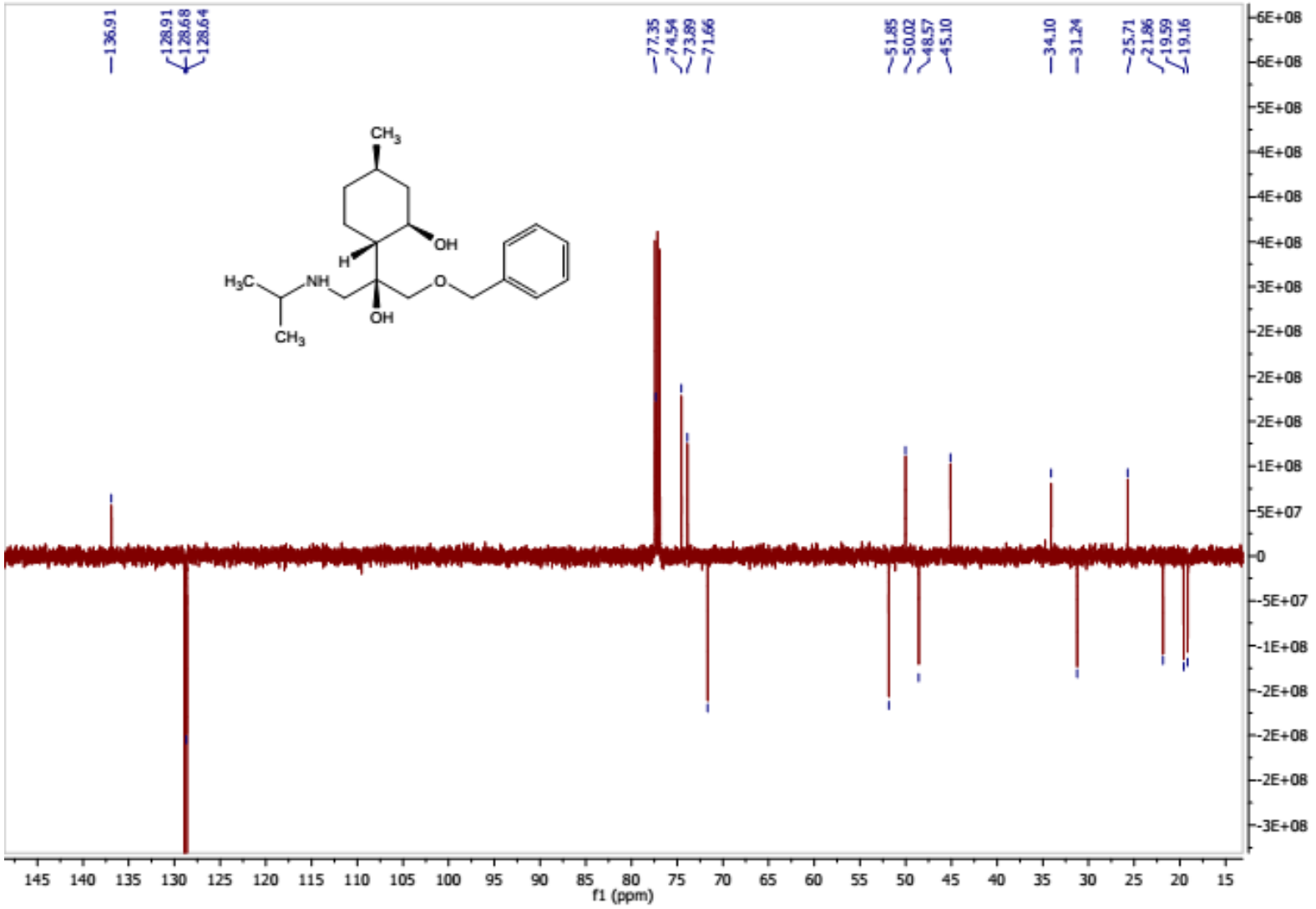

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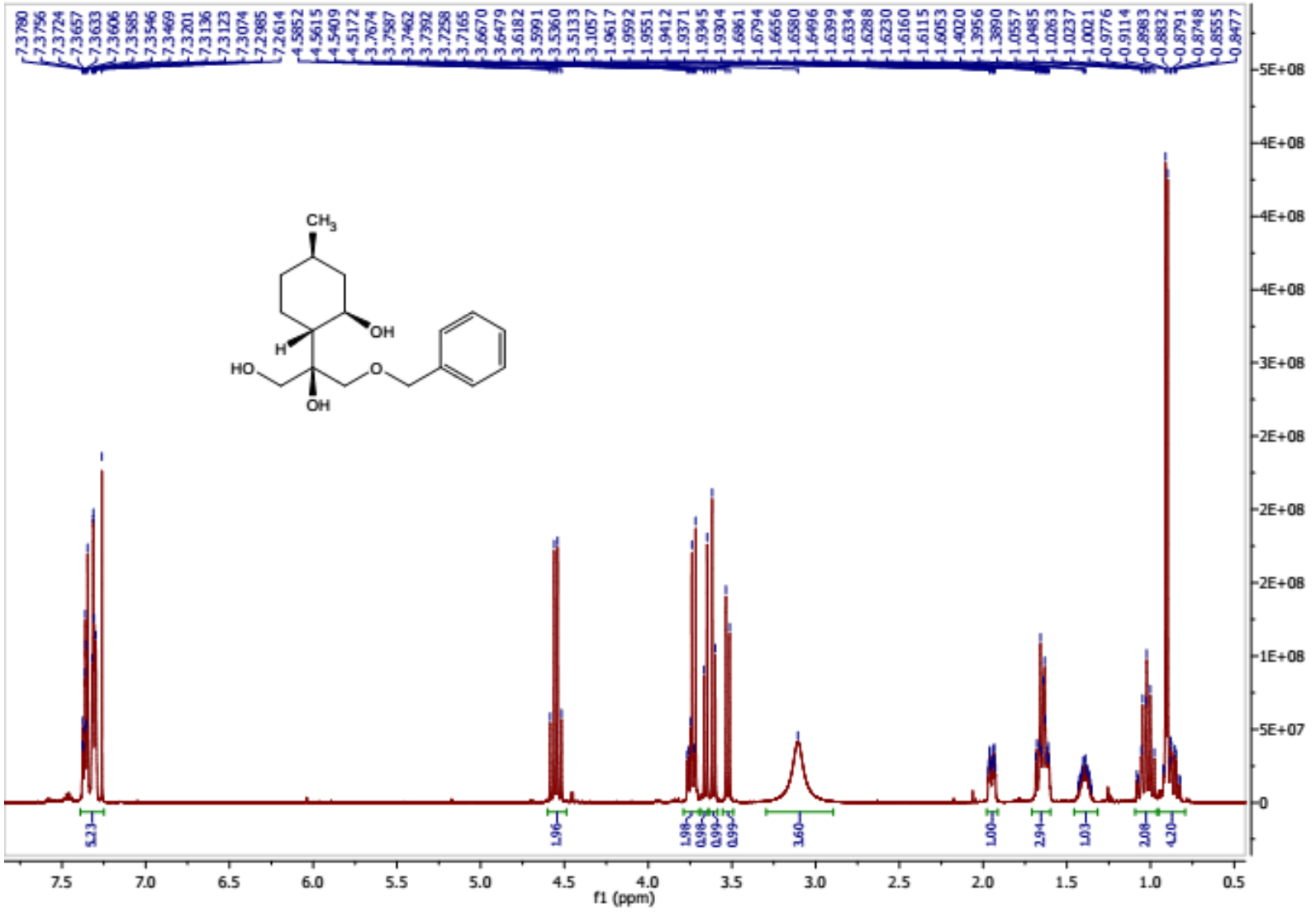

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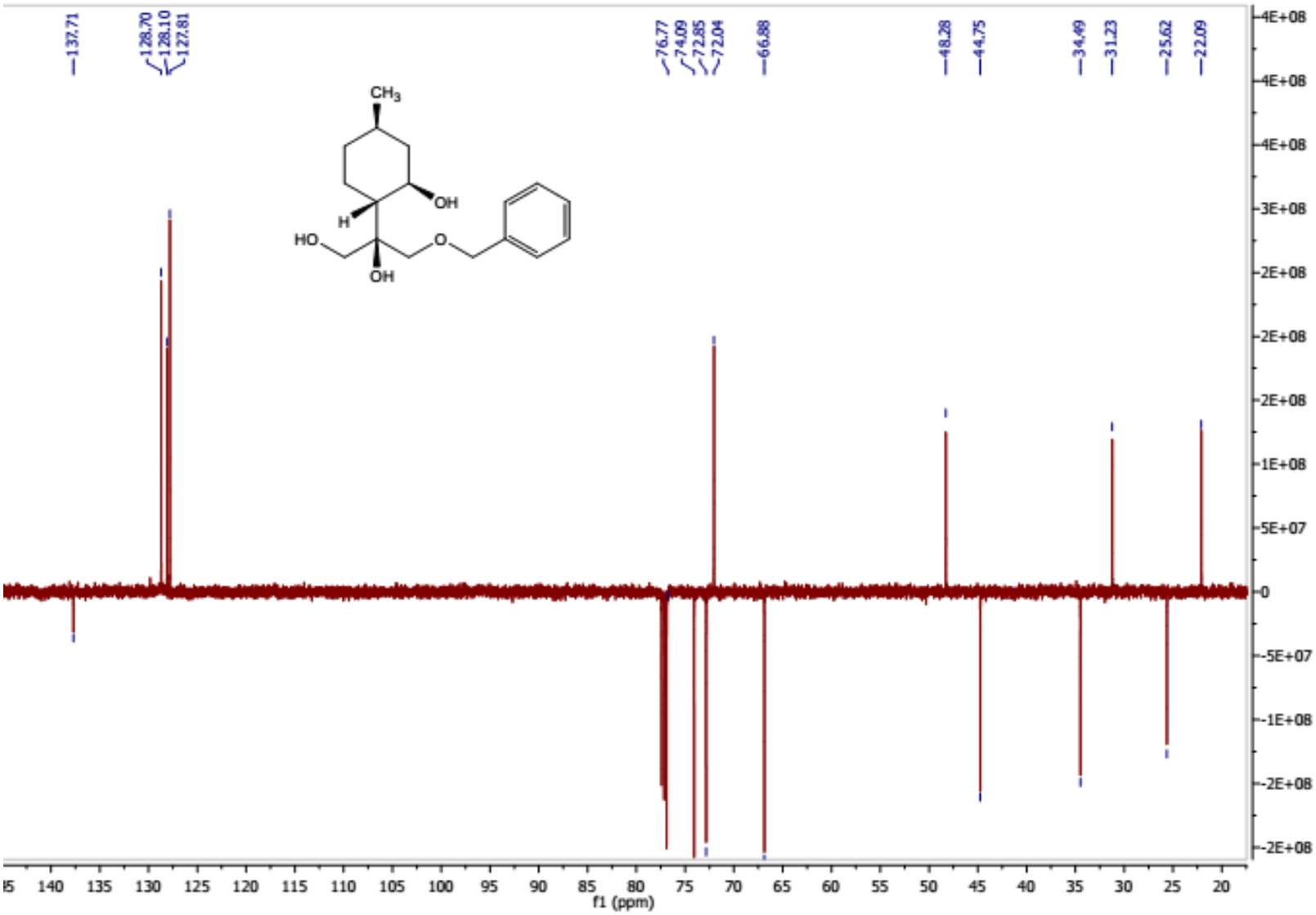

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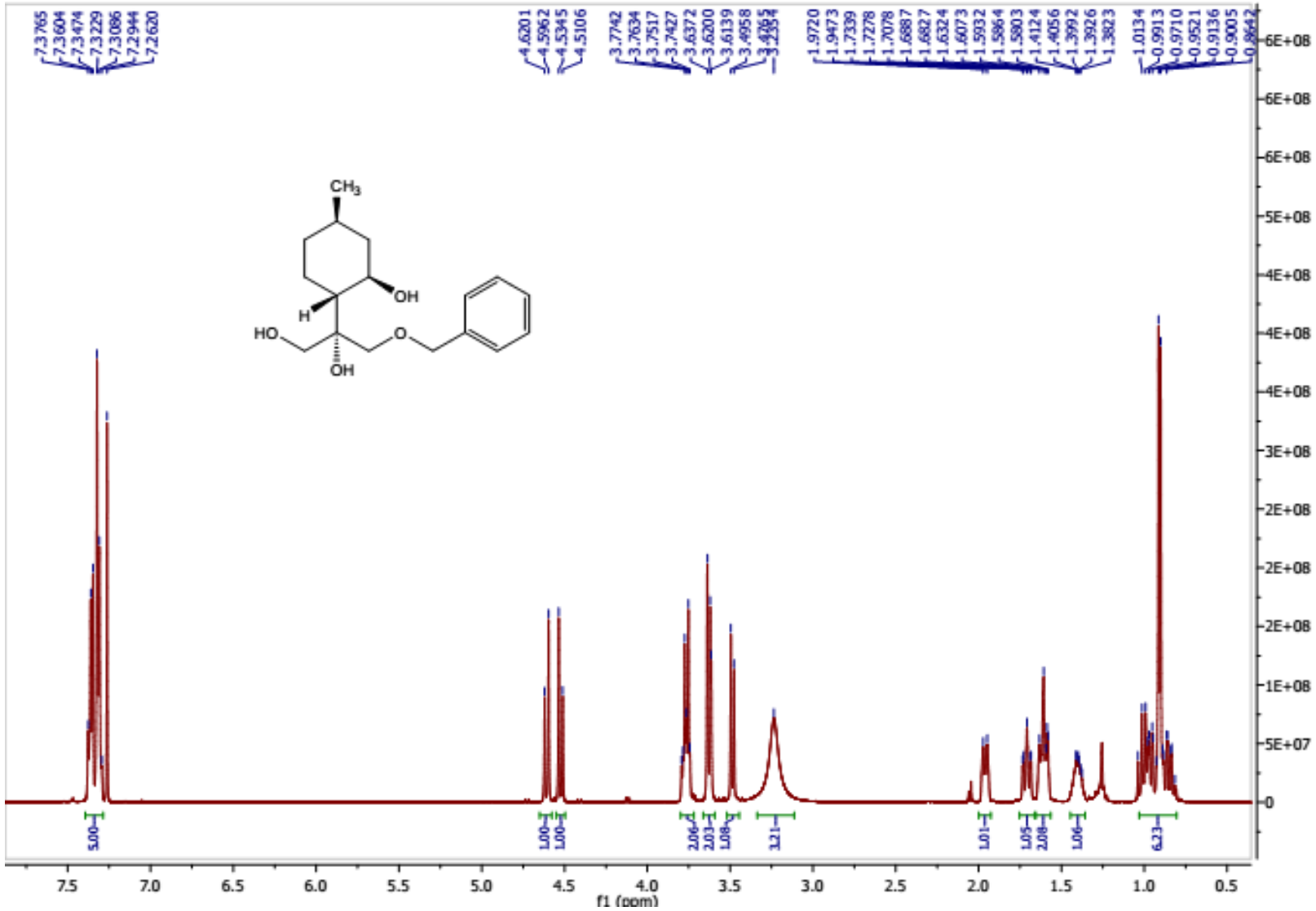

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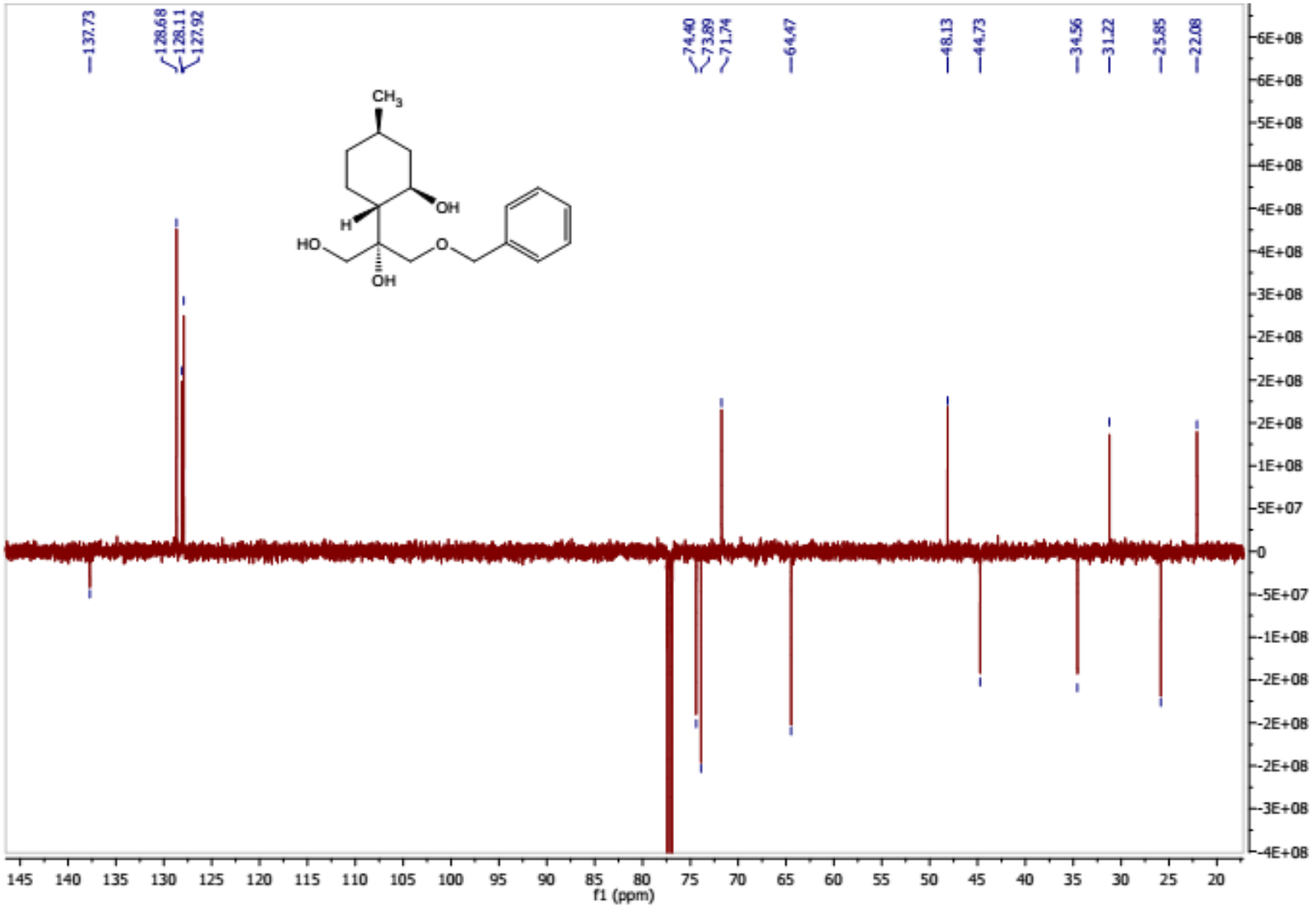

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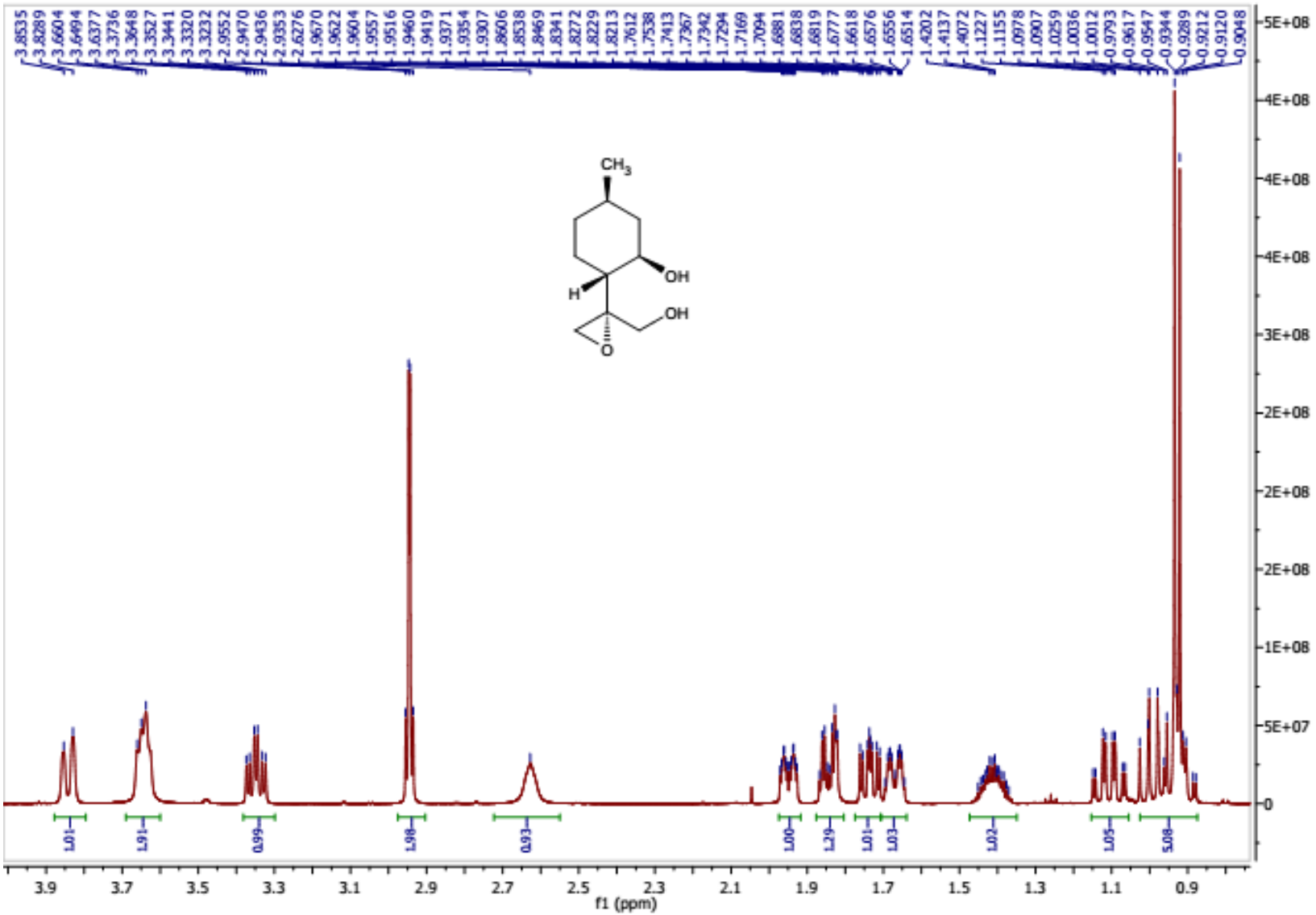

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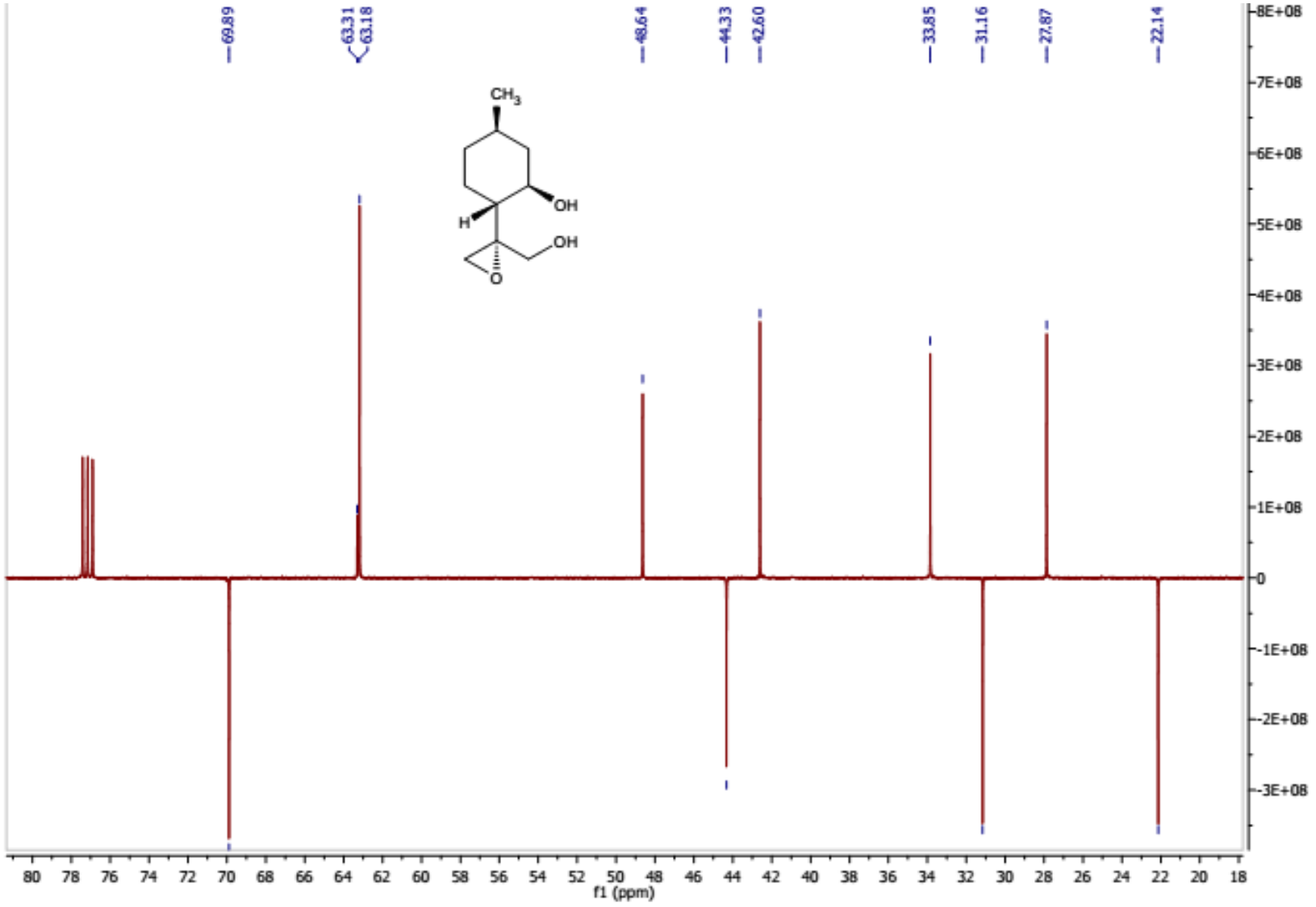

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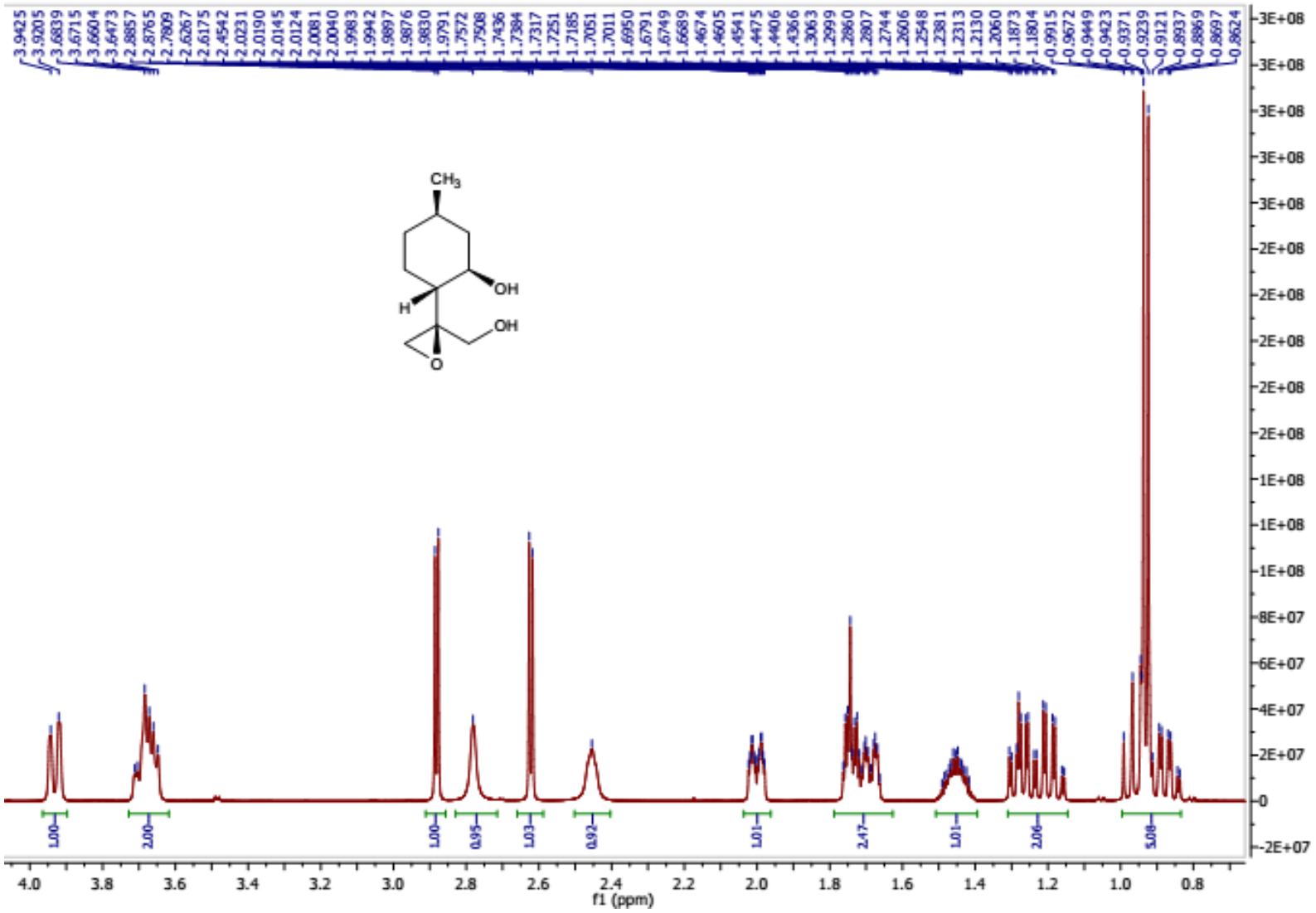
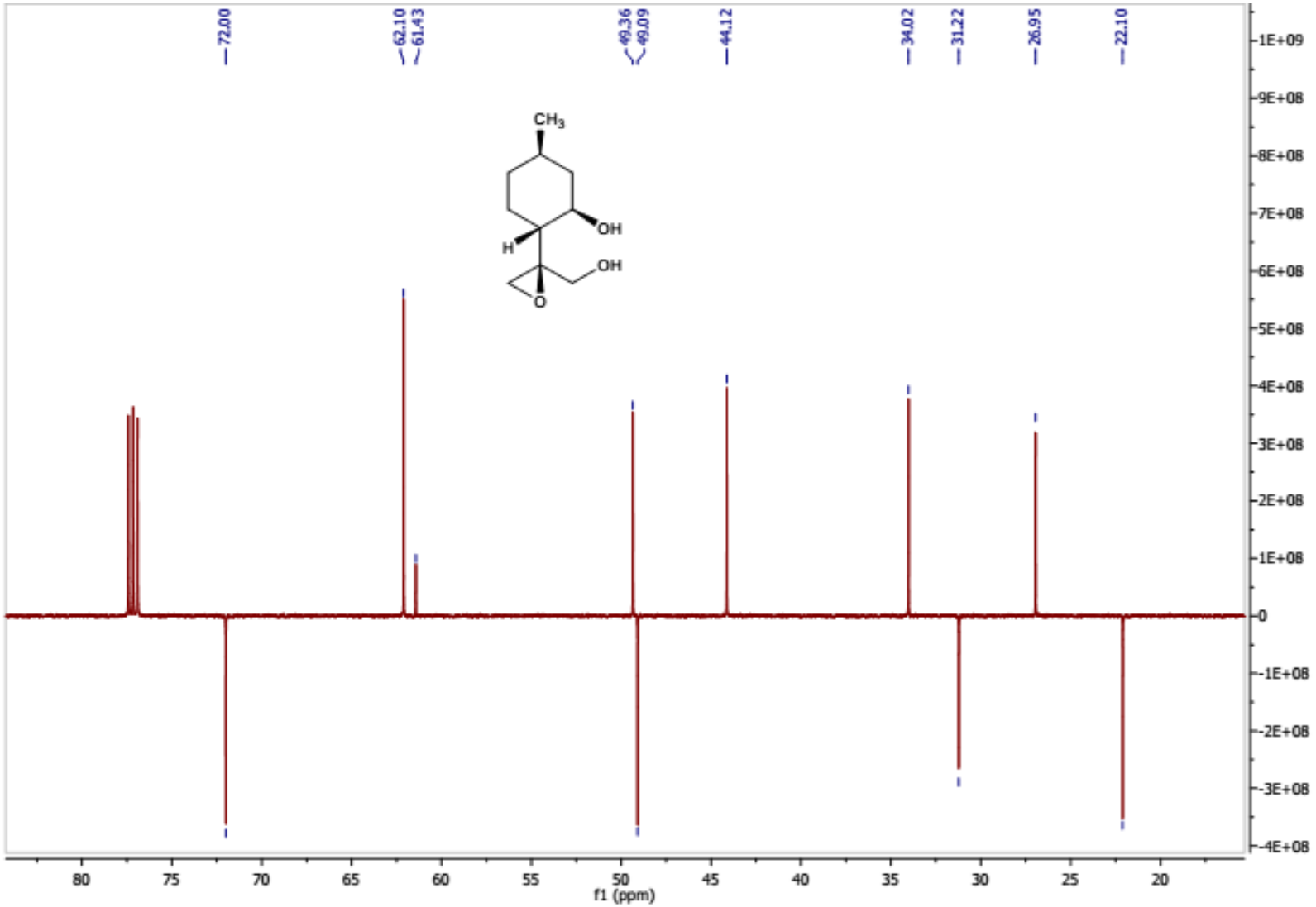


$^{13}$C-NMR of compound **63b**



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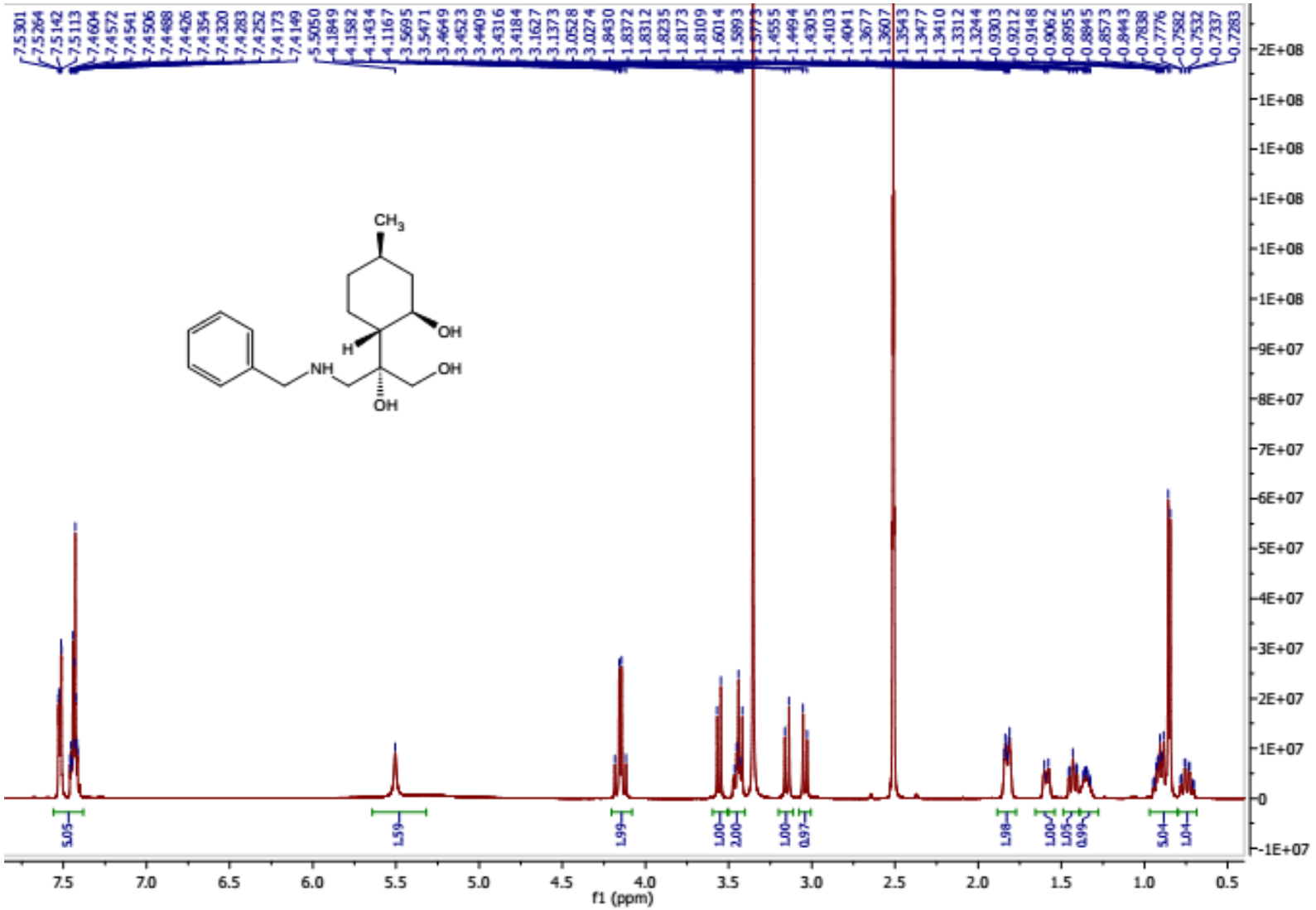

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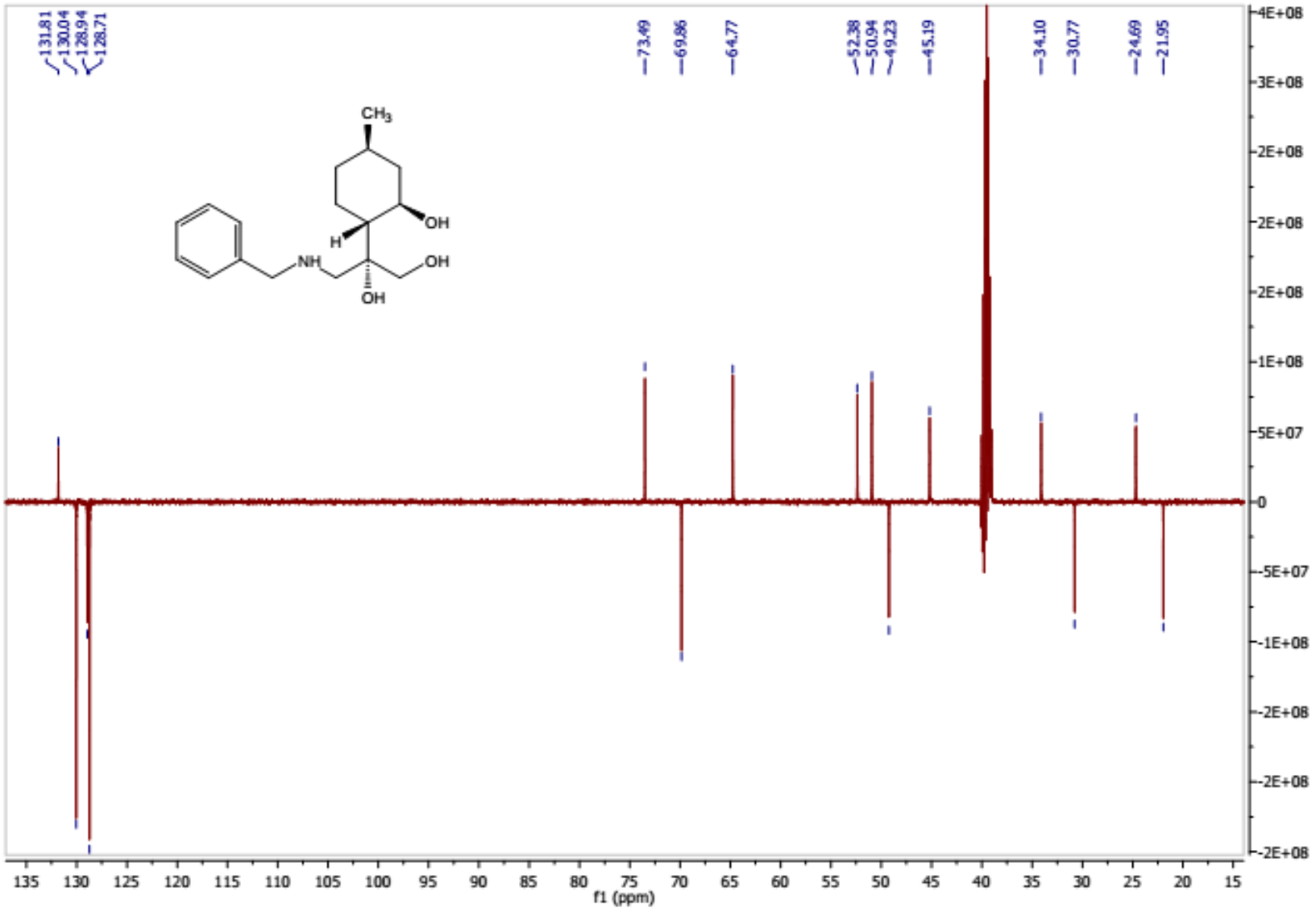

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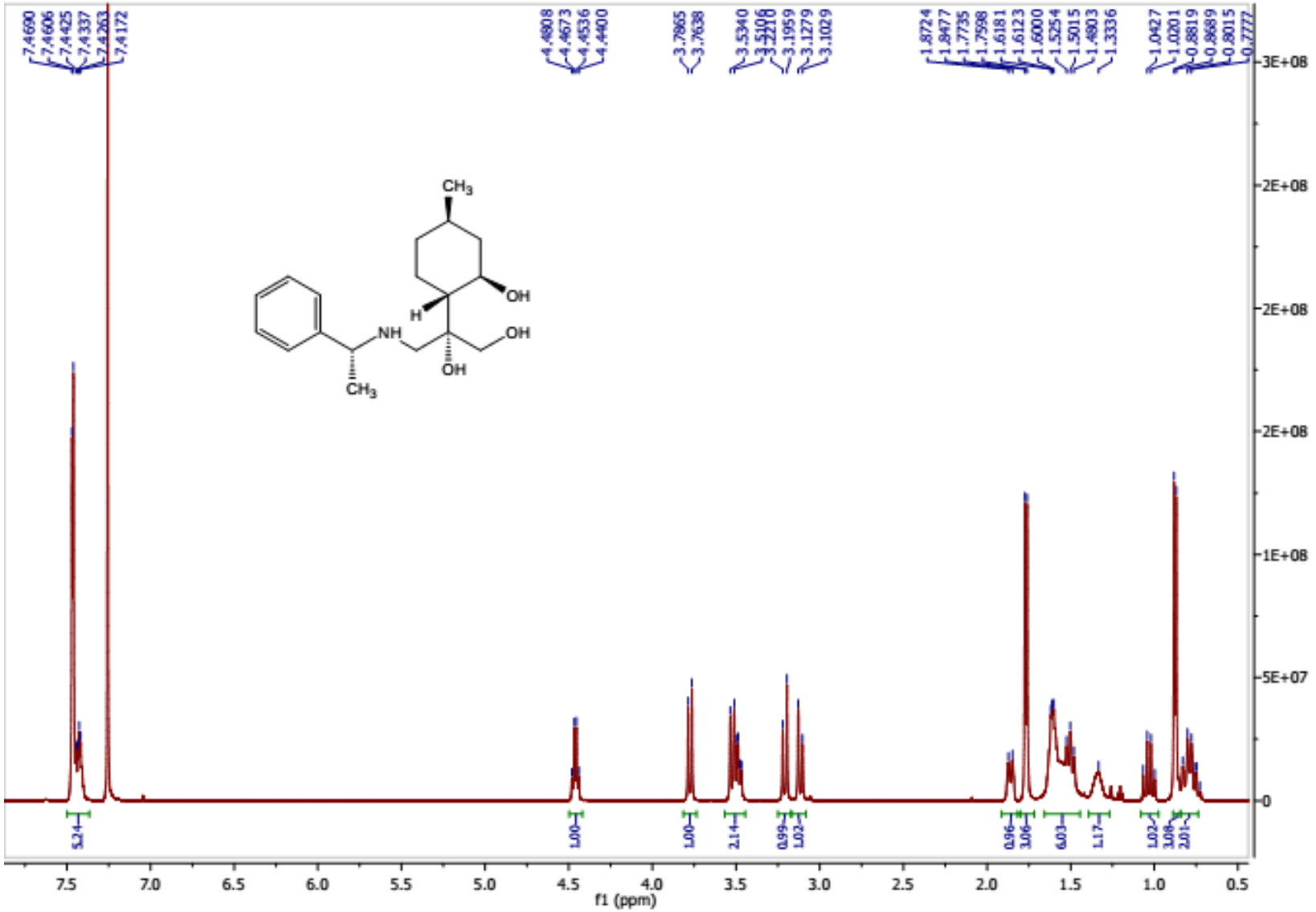

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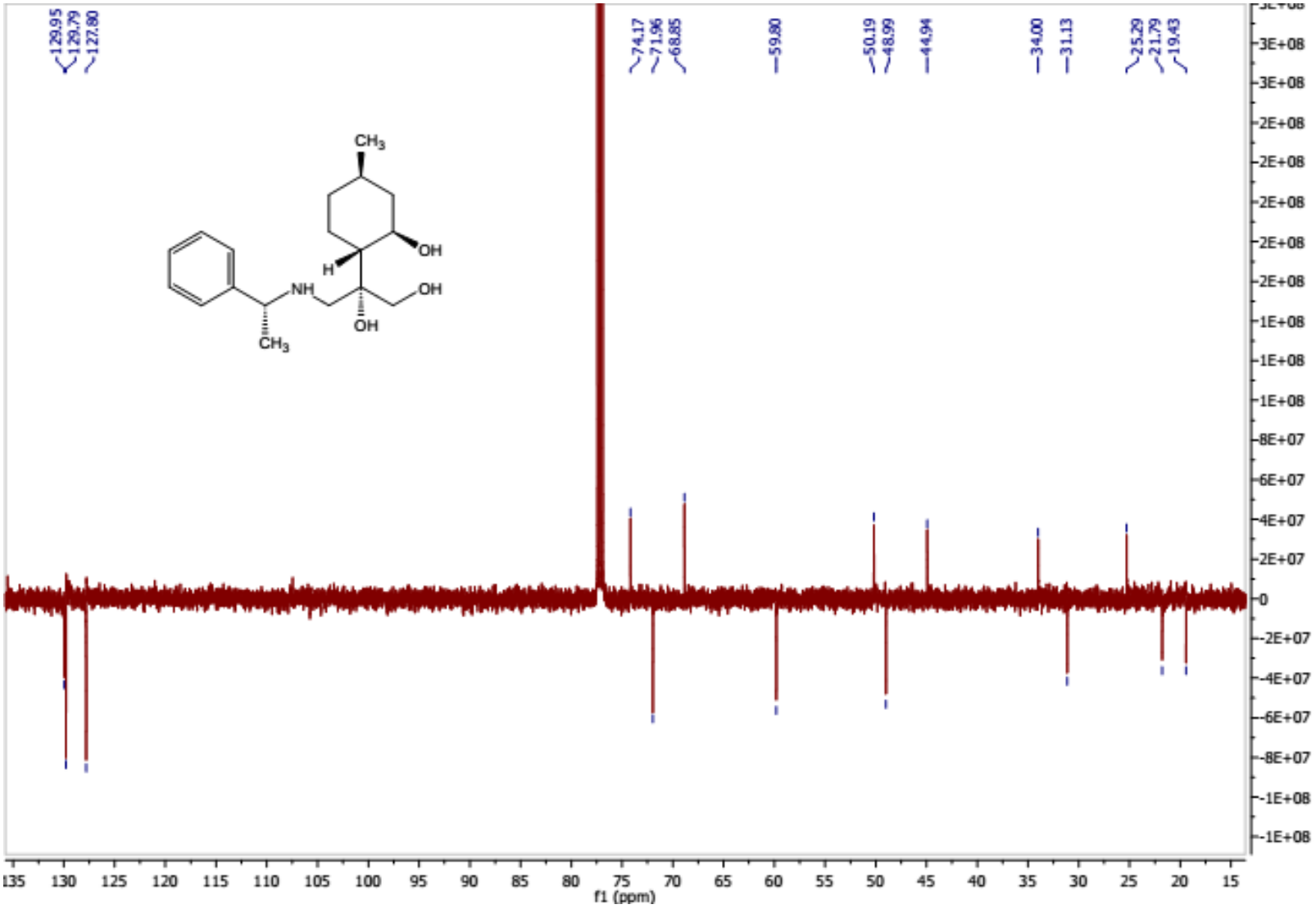

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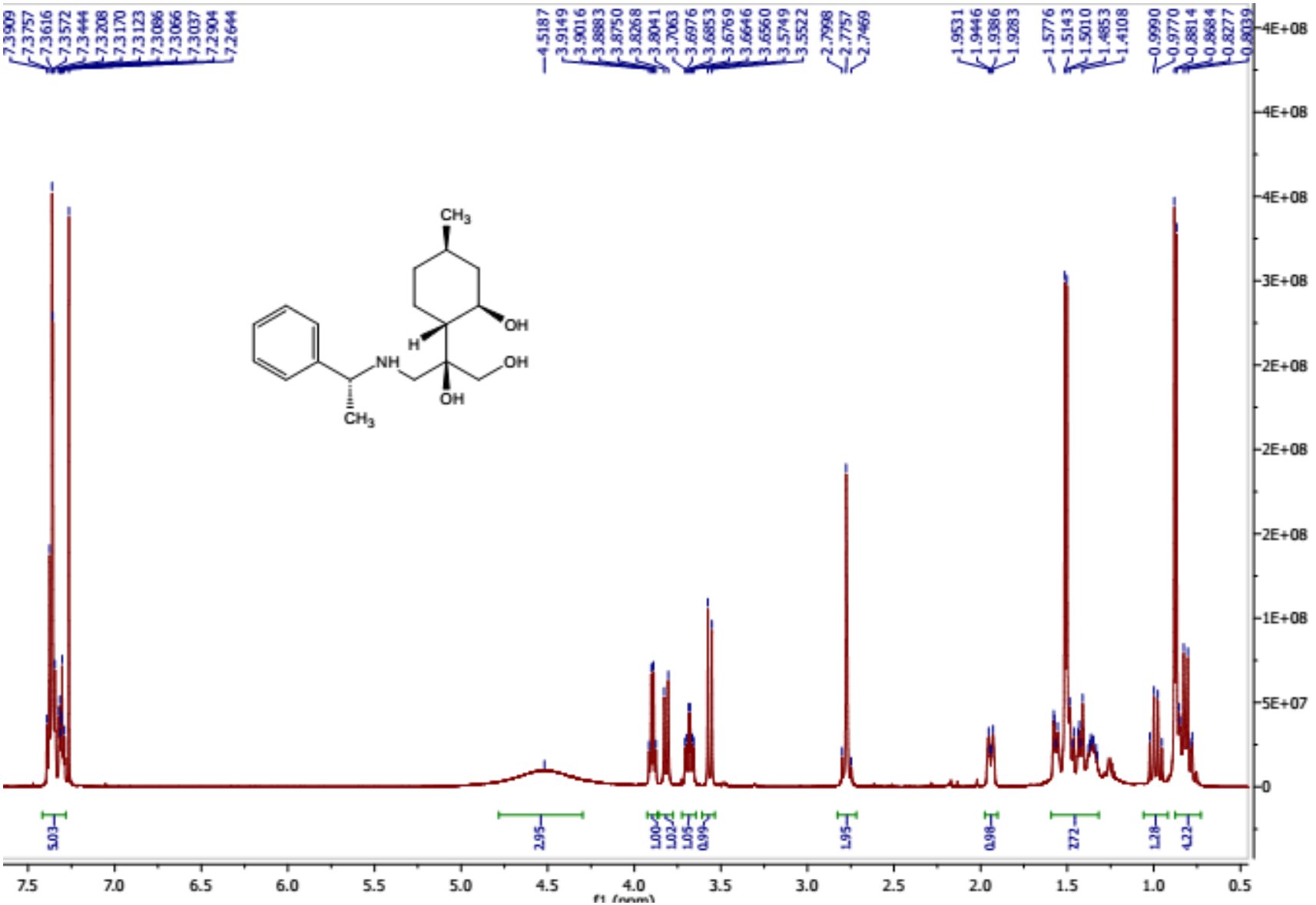

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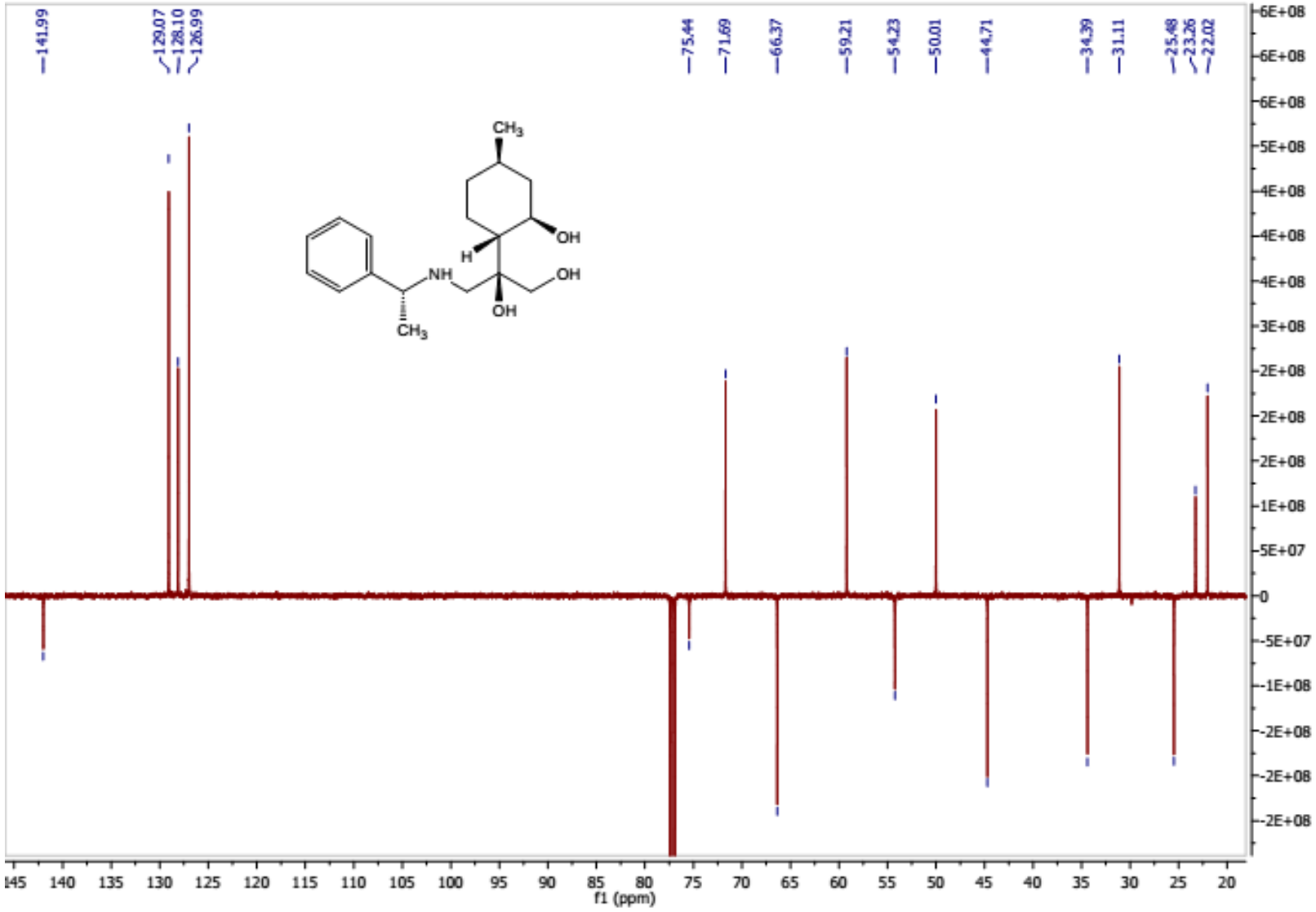

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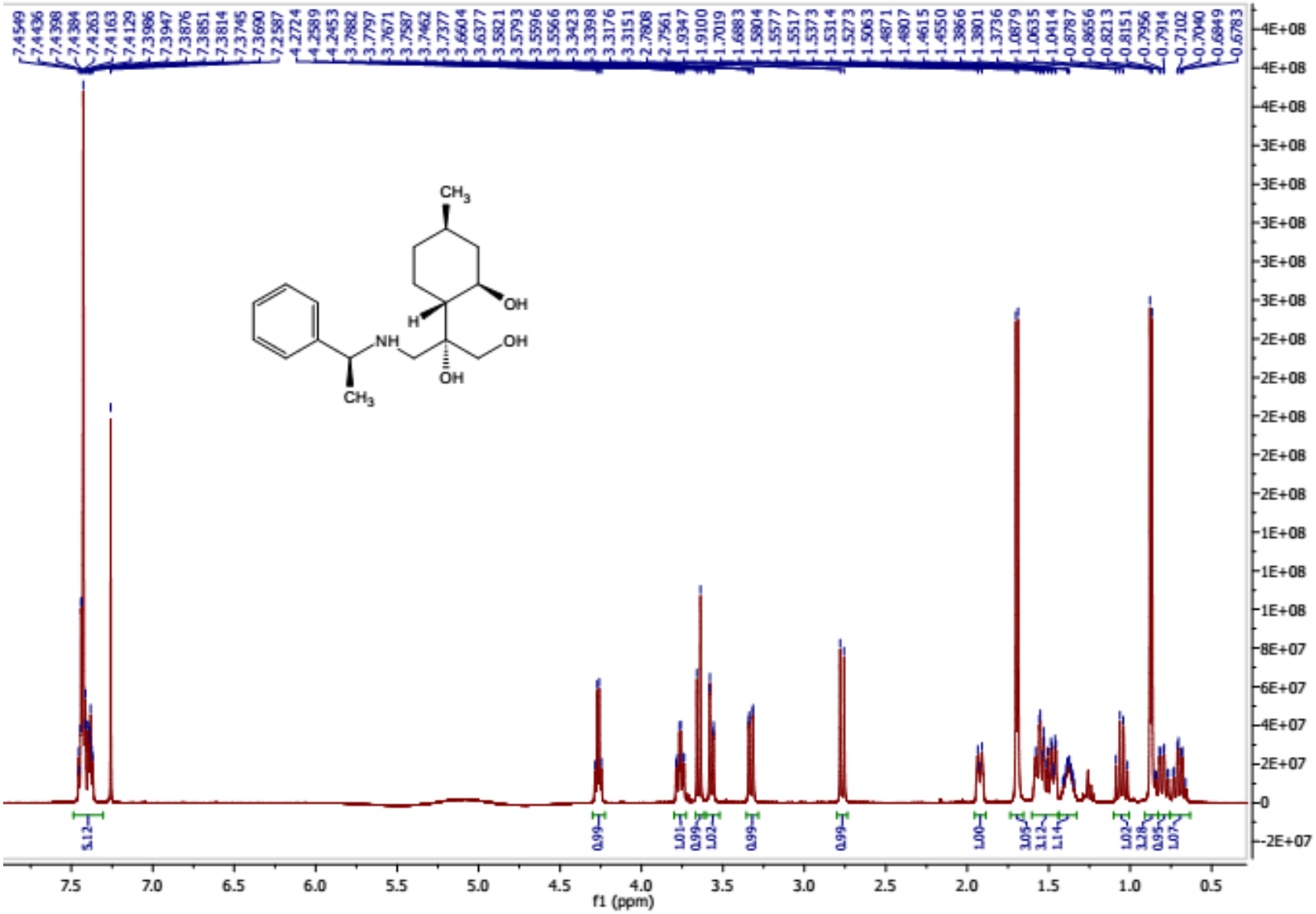

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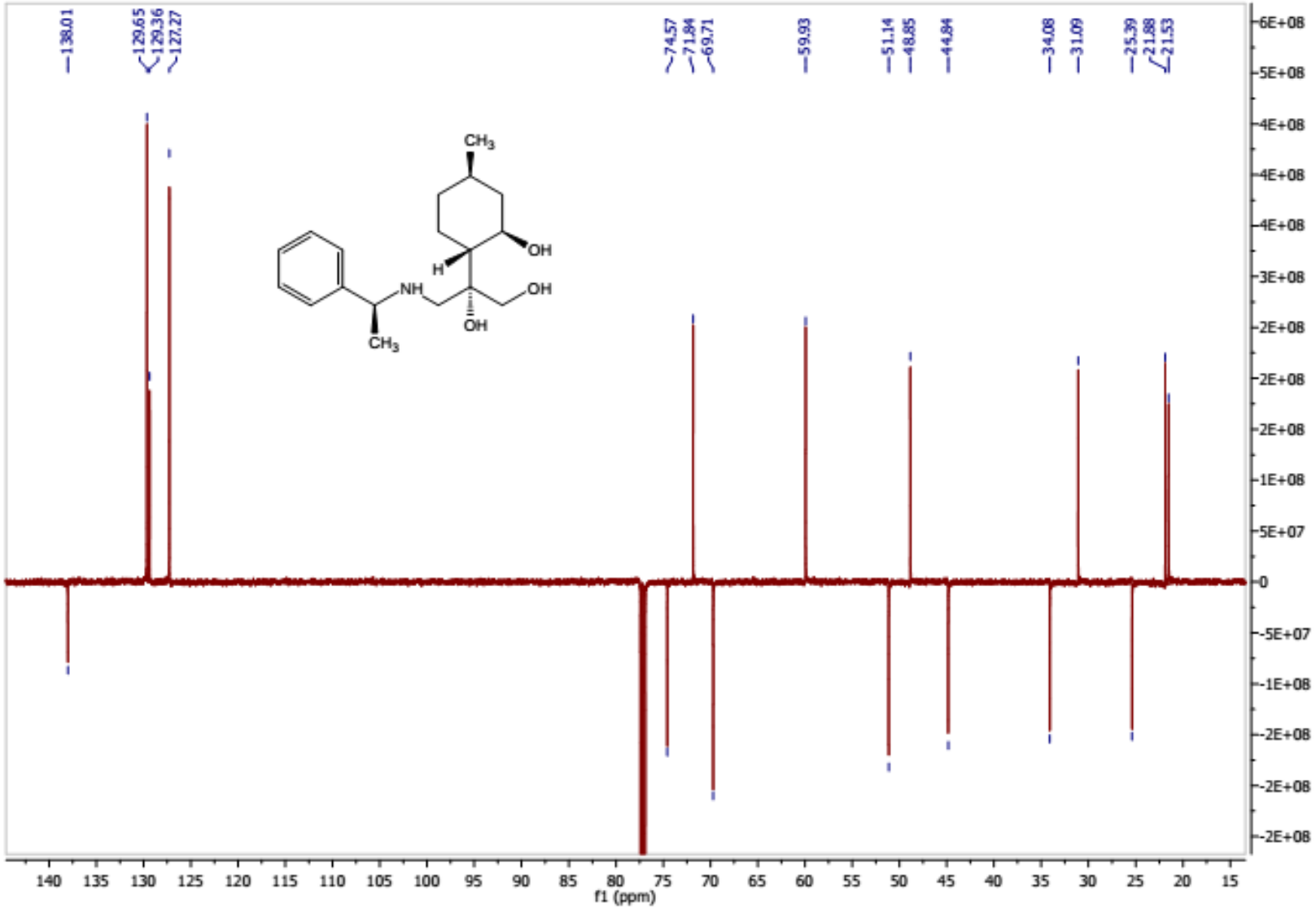

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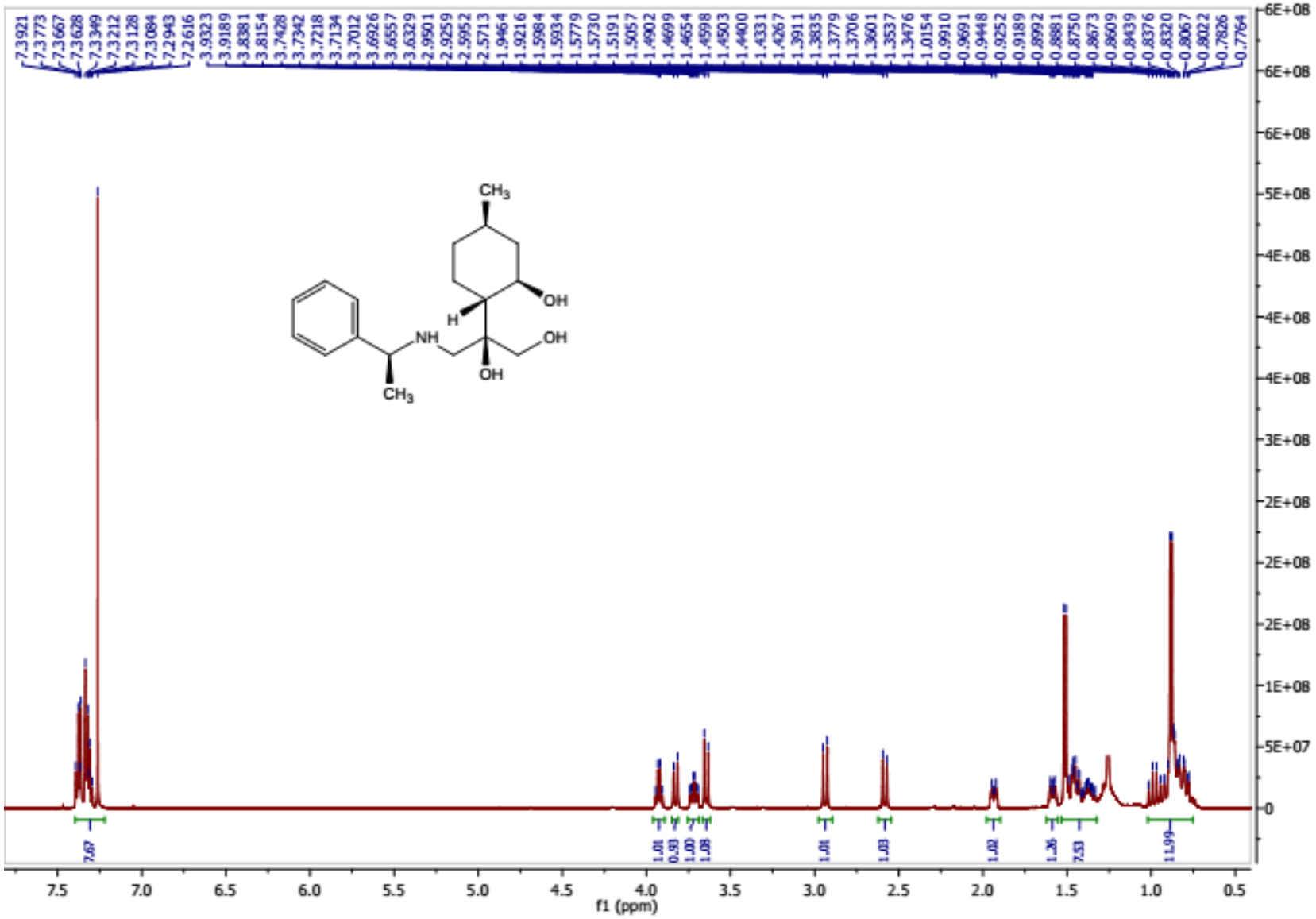

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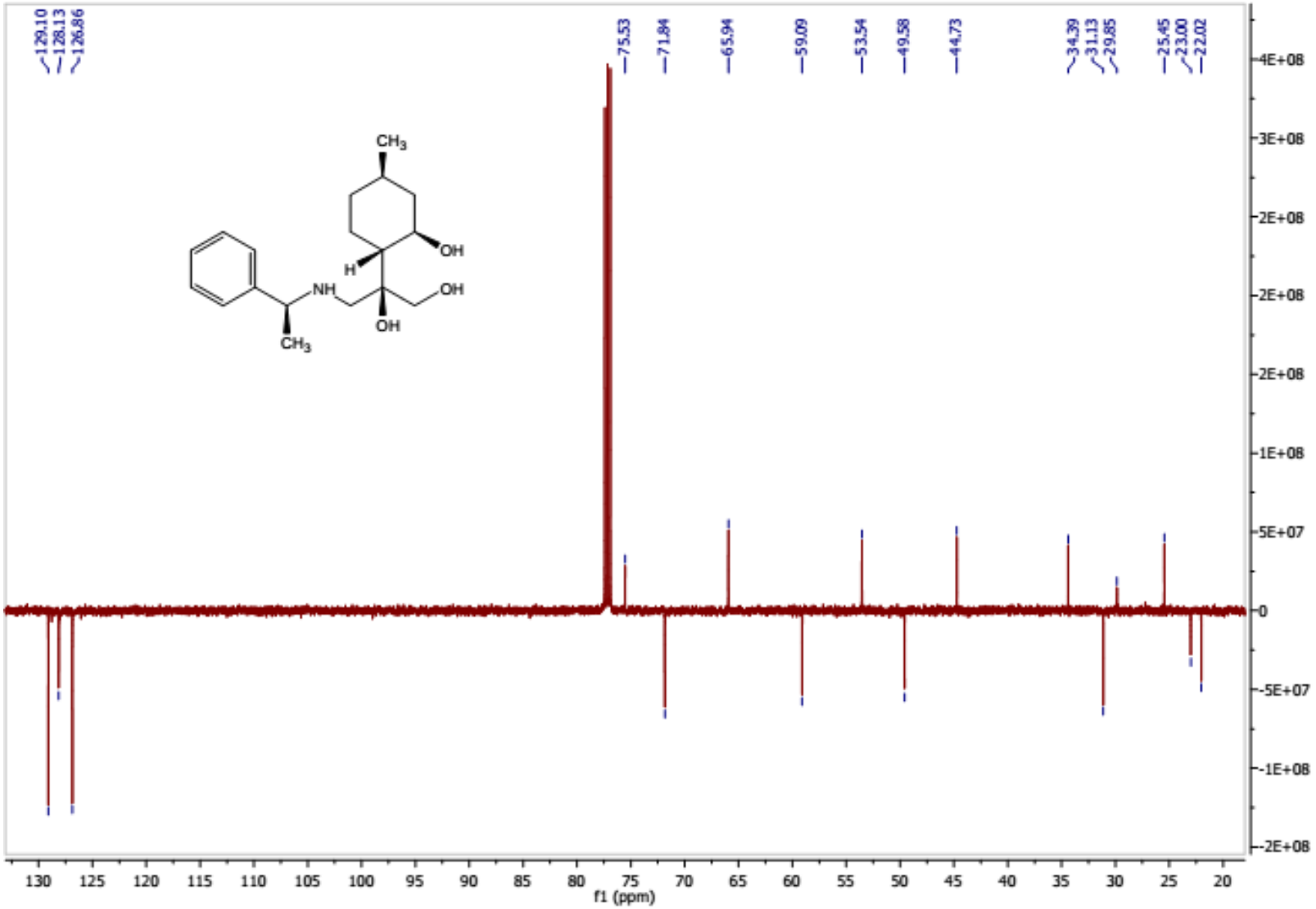

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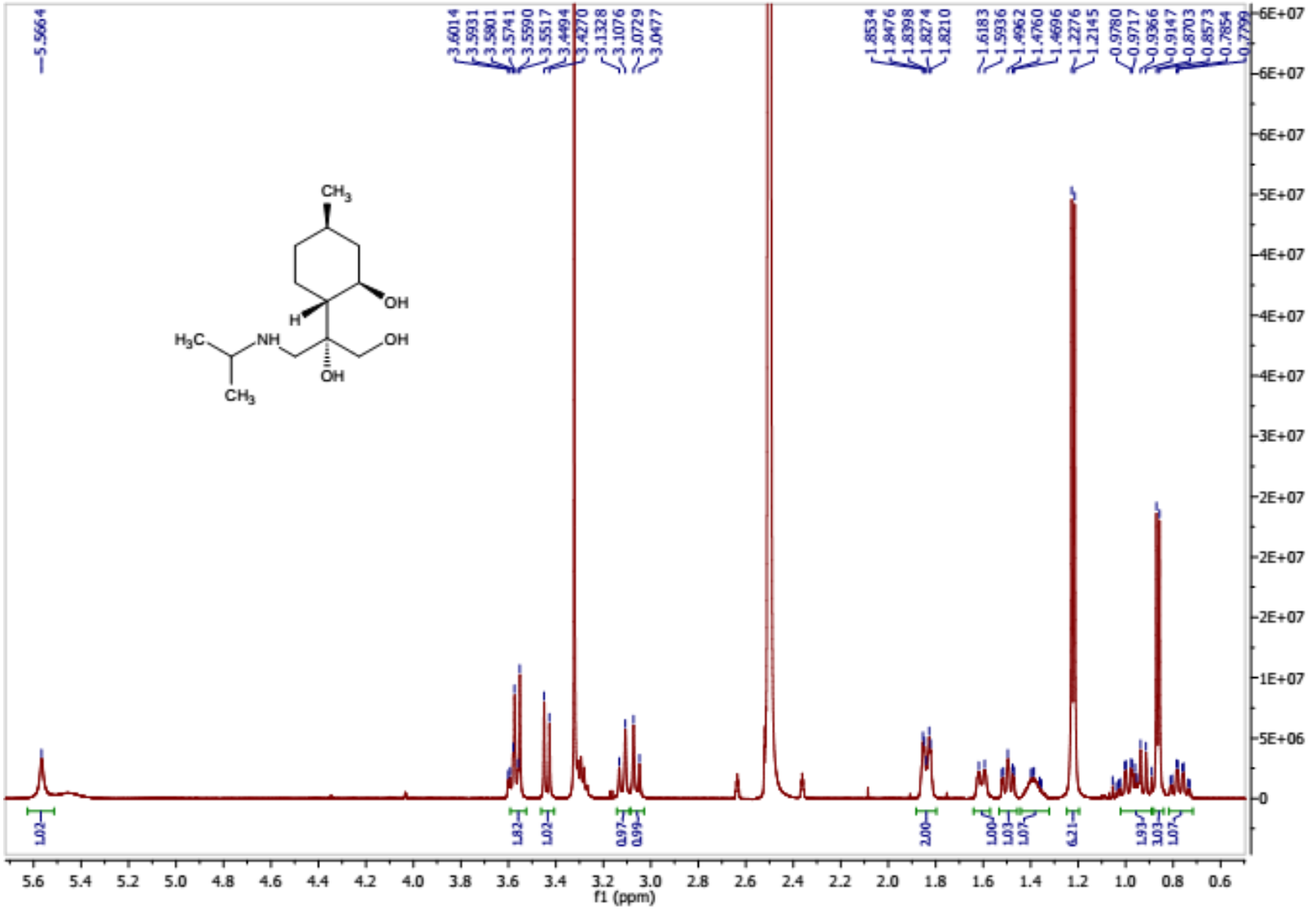

$^{13}$C-NMR of compound **67a**