SUPPORTING INFORMATION

Using Stereoretention for the Synthesis of *E*-Macrocycles with Ruthenium-based Olefin Metathesis Catalysts

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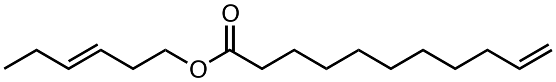
General Information

Unless otherwise specified, all manipulations were carried out under air-free conditions in dry glassware in a Vacuum Atmospheres Glovebox filled with N_2. General solvents were purified by passing through solvent purification columns. Commercially available substrates were used as received. All solvents and substrates were sparged with Ar before bringing into the glovebox and filtered over basic alumina (Brockmann I) prior to use. **2**−**4**,[1] *trans*-3-penten-1-ol,[2] *trans*-4-hexen-1-ol,[3] 5-heptyn-1-ol,[4] 6-octyn-1-ol,[5] 7-nonyn-1-ol,[6] 10-dodecyn-1-ol[7] were synthesized according to literature procedure.

Kinetic NMR experiments were performed on a Varian 600 MHz spectrometer with an AutoX probe. Spectra were analyzed using MestReNova Ver. 8.1.2. ^{1}H and ^{13}C NMR characterization data were obtained on a Bruker 400 with Prodigy broadband cryoprobe and referenced to residual protio-solvent.

GC conversion data was obtained using an HP-5 capillary column with an Agilent 6850 FID gas chromatograph. High-resolution mass spectrometry (HRMS) was performed using FAB+ ionization on a JEOL MSRoute mass spectrometer. Some accurate masses were determined by electrospray ionization, in the positive ion mode, using a Waters LCT Premier XE time-of-flight mass spectrometer.

Synthesis of (*E*)-hex-3-en-1-yl undec-10-enoate (5)



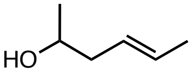
To a round-bottom flask charged with a stir bar were added 20 mL dichloromethane, undecenoyl chloride (2.37 mL, 11.0 mmol), and pyridine (0.89 mL, 11.0 mmol). *Trans*-3-hexenol (1.22 mL, 10.0 mmol) was then added dropwise at 0 °C. The reaction mixture was brought to room temperature and stirred for 4 h. The reaction mixture was extracted with 1M aq. HCl (200 mL) and saturated aq. $NaHCO_3$ (200 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and solvents were removed *in vacuo*. The product was purified by column chromatography on silica gel (5:95 Et_2O: pentane) to yield a colorless oil (2.53 g, 95% yield).

^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.55 (dtt, *J* = 15.3, 6.3, 1.3 Hz, 1H), 5.36 (dtt, *J* = 15.2, 6.8, 1.5 Hz, 1H), 4.99 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 4.07 (t, *J* = 6.9 Hz, 2H), 2.36 – 2.24 (m, 4H), 2.12 – 1.95 (m, 4H), 1.68 – 1.59 (m, 2H), 1.41 – 1.33 (m, 2H), 1.32 – 1.22 (m, 8H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.04, 139.33, 135.14, 124.24, 114.28, 64.04, 34.52, 33.94, 32.13, 29.44, 29.36, 29.27, 29.21, 29.04, 25.77, 25.15, 13.89.

HRMS (EI+): $[M]^+$ $C_{17}H_{30}O_2$ Calculated – 266.2246, Found – 266.2239.

Synthesis of *trans*-4-hexen-2-ol



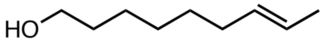
To an oven-dried, round-bottomed flask equipped with a magnetic stir bar was added 4-pentyn-2-ol (500 mg, 5.94 mmol) and THF (8.87 mL) under an argon atmosphere. The flask was placed in a dry ice/acetone bath at −78 °C, and *n*-butyllithium (8.92 mL, 12.48 mmol) was added slowly. The reaction mixture was stirred at −78 °C for 1.5 h. Methyl iodide (1.11 mL, 17.82

mmol) was added to the reaction mixture. The reaction was warmed to ambient temperature and stirred for 8 h. The reaction was quenched with a saturated aq. $NaHCO_3$ solution and extracted with diethyl ether (3 x 20 mL). The organic extracts were combined and washed with a saturated aq. NH_4Cl solution. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the methylated alkyne product as colorless oil.

Adapted from Sigman *et al. J. Am. Chem. Soc.* **2015**, *137*, 3462.

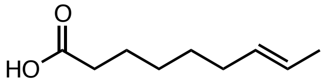
To an oven-dried round-bottomed flask equipped with a magnetic stir bar and charged with lithium aluminum hydride (557 mg, 14.7 mmol), toluene (6.5 mL), and THF (3.5 mL) was added the crude alcohol product (450 mg). The round-bottomed flask was equipped with a condenser and stirred at 90 °C for 24 h. The reaction was cooled to ambient temperature, diluted with diethyl ether, and quenched with water (**dropwise 1 mL, as this results in vigorous release of hydrogen gas, *Extreme Caution* should be taken**). A 20 wt% solution of potassium hydroxide in water was added followed by excess water. The aqueous phase was extracted with diethyl ether (2 x 30 mL). The combined organic extracts were washed with brine (2 x 20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified *via* flash column chromatography (diethyl ether:pentane, 1:7) to furnish the desired product as a colorless oil (120 mg, 20% yield). *Note*: The product is slightly volatile, so concentration to remove solvent should be slow.
^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.61 – 5.50 (m, 1H), 5.43 (dddq, *J* = 15.6, 8.0, 6.4, 1.5 Hz, 1H), 3.86 – 3.71 (m, 1H), 2.27 – 2.13 (m, 1H), 2.07 (dtt, *J* = 13.8, 7.7, 1.0 Hz, 1H), 1.78 – 1.66 (m, 3H), 1.66 – 1.57 (m, 1H), 1.18 (dd, *J* = 6.2, 0.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 129.16, 127.25, 67.32, 42.69, 22.80, 18.23.
HRMS (EI+): $[M]^+$ $C_6H_{12}O$ Calculated – 100.0888, Found – 100.0901.

Synthesis of *trans*-7-nonen-1-ol



To an oven-dried, three-necked flask equipped with a condenser and charged with glass-coated stir bar was added a solution of 7-nonyn-1-ol (500 mg, 3.56 mmol) in *t*BuOH/THF (10:16 mL, 26 mL) under argon atmosphere. The flask was placed in a dry ice/acetone bath at −78 °C, and ammonia (30 mL) was condensed into the flask. Lithium metal (259 mg) was added and the reaction was stirred for 1.5 h. The ammonia was allowed to evaporate while bringing to room temperature, and the reaction was quenched with saturated aq. NH_4Cl solution immediately upon disappearance of the blue color. The aqueous layer was extracted with pentane (4 × 100 mL) and washed with brine (2 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as colorless oil (453 mg, 90% yield) *Note*: If reaction did not reach full conversion to reduced product, the crude mixture was resubject to reaction conditions.
^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.64 – 5.23 (m, 2H), 3.65 (t, *J* = 6.6 Hz, 2H), 2.06 – 1.92 (m, 2H), 1.66 (dq, *J* = 4.0, 1.3 Hz, 3H), 1.58 (dq, *J* = 8.4, 6.3 Hz, 2H), 1.47 – 1.24 (m, 7H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.61, 124.83, 63.18, 32.89, 32.64, 29.67, 29.07, 25.74, 18.07.
HRMS (EI+): $[M]^+$ $C_9H_{18}O$ Calculated – 142.1358, Found – 142.1310.

Synthesis of *trans*-7-nonenoic acid



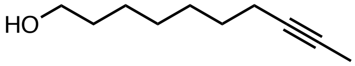
To a vial charged with a stir bar was added *trans*-7-nonen-1-ol (200.0 mg, 1.41 mmol) and acetone (2.80 mL). Jones reagent (1.05 mL, 2.0 M, 2.11 mmol) was added dropwise at 0 °C, and the reaction was stirred for 1.5 h. 5 mL Et_2O was added and the product was extracted with saturated aq. $NaHCO_3$ solution (4 × 5 mL). The aqueous phase was then acidified dropwise with concentrated H_2SO_4 at 0 °C. The product was extracted with ethyl acetate (3 × 5 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as a colorless oil (188 mg, 85% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 9.34 (s, 1H)' 5.61 – 5.28 (m, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 1.99 (tddd, *J* = 6.1, 5.3, 3.7, 2.6, 1.4 Hz, 2H), 1.74 – 1.58 (m, 5H), 1.37 (pt, *J* = 4.0, 2.3 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.31, 131.33, 125.07, 34.18, 32.47, 29.29, 28.67, 24.68, 18.07.

HRMS (FAB+): $[M+H]^+$ $C_9H_{17}O_2$ Calculated – 157.1229, Found – 157.1234.

Synthesis of 8-decyn-1-ol



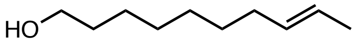
To a vial charged with a stir bar and KO^{t}Bu (1.5 g, 13.0 mmol) and sealed with a septum cap under argon atmosphere was added anhydrous DMSO (22 mL) and 9-decyn-1-ol (1.15 mL, 6.5 mmol). After stirring for 3 h, the reaction was quenched with 1M aq. HCl. After extraction with diethyl ether (3 × 100 mL) and washing with water (1 × 100 mL), the organic phase was dried over anhydrous $MgSO_4$ and filtered. Solvents were removed *in vacuo* to yield the product as a colorless oil (901 mg, 90% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 3.69 – 3.55 (m, 2H), 2.10 (ddt, *J* = 7.1, 4.7, 2.5 Hz, 2H), 1.77 (q, *J* = 2.5 Hz, 3H), 1.64 – 1.51 (m, 2H), 1.51 – 1.42 (m, 2H), 1.42 – 1.20 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 79.43, 75.54, 63.12, 32.86, 29.11, 29.09, 28.95, 25.76, 18.82, 3.61.

HRMS (EI+): $[M]^+$ $C_{10}H_{17}O$ Calculated – 153.1279, Found – 153.1320.

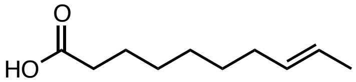
Synthesis of *trans*-8-decen-1-ol



To an oven-dried, three-necked flask equipped with a condenser and charged with glass-coated stir bar was added a solution of 8-decyn-1-ol (100 mg, 0.65 mmol) in *t*BuOH/THF (2 mL: 3 mL, 5 mL) under argon atmosphere. The flask was placed in a dry ice/acetone bath at −78 °C, and ammonia (10 mL) was condensed into the flask. Lithium metal (22 mg, 3.24 mmol) was added and the reaction was stirred for 1.5 h. The ammonia was allowed to evaporate while bringing to room temperature, and the reaction was quenched with saturated aq. NH_4Cl solution immediately upon disappearance of the blue color. The aqueous layer was extracted with pentane (4 × 25 mL) and washed with brine (2 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as colorless oil (74 mg, 73% yield) *Note*: If reaction did not reach full conversion to reduced product, the crude mixture was resubject to reaction conditions.

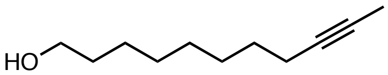
^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.49 – 5.30 (m, 2H), 3.63 (t, *J* = 6.7 Hz, 2H), 2.06 – 1.86 (m, 2H), 1.63 (dt, *J* = 4.7, 1.4 Hz, 3H), 1.61 – 1.51 (m, 2H), 1.37 – 1.28 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.70, 124.77, 63.23, 32.93, 32.72, 29.67, 29.44, 29.26, 25.85, 18.09.
HRMS (EI+): $[M]^+$ $C_{10}H_{20}O$ Calculated – 156.1514, Found – 156.1504.

Synthesis of *trans*-8-decenoic acid



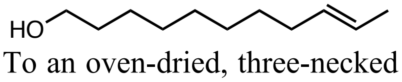
To a vial equipped with a magnetic stir bar was added *trans*-8-decen-1-ol (74 mg, 0.47 mmol) and acetone (1 mL). The reaction mixture was cooled to 0 °C and Jones reagent (0.355 mL, 0.71 mmol) was added dropwise. The reaction was stirred at ambient temperature for 1.5 h. Diethyl ether (10 mL) was added and the mixture was extracted with saturated aq. Na HCO_3 solution (5 x 10 mL). The aqueous extracts were combined, acidified with H_2SO_4, and extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried with Na_2SO_4, and concentrated to deliver the desired product as a colorless oil (47 mg, 59% yield).
^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 11.42 (s, 1H), 5.40 (dq, *J* = 4.6, 2.1 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 3H), 1.96 (ddd, *J* = 8.6, 5.2, 3.1 Hz, 2H), 1.64 (dt, *J* = 4.9, 1.4 Hz, 5H), 1.35 – 1.22 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.24, 131.54, 124.90, 34.17, 32.63, 29.49, 29.05, 28.87, 24.78, 18.08.
HRMS (EI+): $[M]^+$ $C_{10}H_{18}O_2$ Calculated: 170.1307, Found: 170.1309.

Synthesis of 9-undecyn-1-ol



To a vial charged with a stir bar and KO^{t}Bu (0.63 g, 5.6 mmol) and sealed with a septum cap under argon atmosphere was added anhydrous DMSO (11 mL) and 10-undecyn-1-ol (0.53 mL, 2.8 mmol). After stirring for 3 h, the reaction was quenched with 1M aq. HCl. After extraction with diethyl ether (3 × 50 mL) and washing with water (1 × 100 mL), the organic phase was dried over anhydrous $MgSO_4$ and filtered. Solvents were removed *in vacuo* to yield the product as a colorless oil (450 mg, 96% yield).
^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 3.63 (t, *J* = 6.6 Hz, 2H), 2.10 (ddq, *J* = 9.6, 7.3, 2.5 Hz, 2H), 1.77 (t, *J* = 2.6 Hz, 3H), 1.62 – 1.51 (m, 2H), 1.51 – 1.40 (m, 3H), 1.40 – 1.19 (m, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 79.49, 75.50, 63.17, 32.89, 29.44, 29.26, 29.17, 28.94, 25.82, 18.84, 3.61.
HRMS (FAB+): $[M+H]^+$ $C_{11}H_{21}O$ Calculated – 169.1591, Found – 169.1592.

Synthesis of *trans*-9-undecen-1-ol



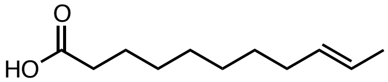
To an oven-dried, three-necked flask equipped with a condenser and charged with glass-coated stir bar was added a solution of 9-undecyn-1-ol (300 mg, 1.78 mmol) in *t*BuOH/THF (5 mL: 8 mL, 13 mL) under argon atmosphere. The flask was placed in a dry ice/acetone bath at −78 °C, and ammonia (15 mL) was condensed into the flask. Lithium metal (130 mg) was added and the reaction was stirred for 1.5 h. The ammonia was allowed to evaporate while bringing to room temperature, and the reaction was quenched with saturated aq. NH_4Cl solution immediately upon disappearance of the blue color. The aqueous layer was extracted with pentane (4 × 50 mL) and washed with brine (2 × 25 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as colorless oil (268 mg, 89% yield) *Note*: If reaction did not reach full conversion to reduced product, the crude mixture was resubject to reaction conditions.

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.50 – 5.32 (m, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.95 (dddd, *J* = 7.9, 5.0, 3.1, 1.6 Hz, 2H), 1.67 – 1.50 (m, 6H), 1.39 – 1.23 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.76, 124.72, 63.24, 32.94, 32.74, 29.73, 29.62, 29.54, 29.25, 25.87, 18.09.

HRMS (EI+): $[M]^+$ $C_{11}H_{22}O$ Calculated – 170.1671, Found – 170.1681.

Synthesis of *trans*-9-undecenoic acid



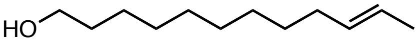
To a vial charged with a stir bar was added *trans*-9-undecen-1-ol (200.0 mg, 1.17 mmol) and acetone (2.16 mL). Jones reagent (0.88 mL, 2.0 M, 1.76 mmol) was added dropwise at 0 °C, and the reaction was brought to room temperature and stirred for 1.5 h. 5 mL Et_2O was added and the product was extracted with saturated aq. $NaHCO_3$ solution (4 × 5 mL). The aqueous phase was then acidified dropwise with concentrated H_2SO_4 at 0 °C. The product was extracted with ethyl acetate (3 × 5 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as a colorless solid (190 mg, 88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 9.14 (s, 1H), 5.61 – 5.21 (m, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 1.98 (dddd, *J* = 7.3, 4.6, 2.8, 1.4 Hz, 2H), 1.74 – 1.59 (m, 5H), 1.38 – 1.28 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.00, 131.68, 124.80, 34.13, 32.70, 29.66, 29.25, 29.16, 29.08, 24.80, 18.09.

HRMS (EI+): $[M]^+$ $C_{11}H_{20}O_2$ Calculated – 184.1463, Found – 184.1469.

Synthesis of *trans*-10-dodecen-1-ol



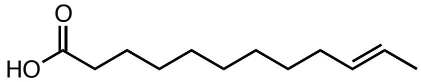
To an oven-dried, three-necked flask equipped with a condenser and charged with glass-coated stir bar was added a solution of 10-dodecyn-1-ol (500 mg, 2.75 mmol) in *t*BuOH/THF (7.5 mL: 12.5 mL, 20 mL) under argon atmosphere. The flask was placed in a dry ice/acetone bath at −78 °C, and ammonia (30 mL) was condensed into the flask. Lithium metal (200 mg) was added and the reaction was stirred for 1.5 h. The ammonia was allowed to evaporate while bringing to room temperature, and the reaction was quenched with saturated aq. NH_4Cl solution immediately upon disappearance of the blue color. The aqueous layer was extracted with pentane (4 × 100 mL) and washed with brine (2 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as colorless oil (417 mg, 83% yield) *Note*: If reaction did not reach full conversion to reduced product, the crude mixture was resubject to reaction conditions.

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.55 – 5.25 (m, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.95 (dtd, *J* = 7.9, 5.1, 2.5 Hz, 2H), 1.69 – 1.61 (m, 3H), 1.56 (dq, *J* = 8.3, 6.8 Hz, 2H), 1.40 – 1.23 (m, 13H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.79, 124.69, 63.23, 32.94, 32.75, 29.75, 29.71, 29.59, 29.56, 29.31, 25.87, 18.08.

HRMS (FAB+): $[M+H]^+$ $C_{12}H_{25}O$ Calculated – 185.1905, Found – 185.1912.

Synthesis of *trans*-10-dodecenoic acid



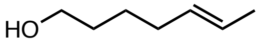
To a vial charged with a stir bar was added *trans*-10-dodecen-1-ol (200.0 mg, 1.08 mmol) and acetone (2.16 mL). Jones reagent (0.81 mL, 2.0 M, 1.62 mmol) was added dropwise at 0 °C, and the reaction was brought to room temperature and stirred for 1.5 h. 5 mL Et_2O was added and the product was extracted with saturated aq. $NaHCO_3$ solution (4 × 5 mL). The aqueous phase was then acidified dropwise with concentrated H_2SO_4 at 0 °C. The product was extracted with ethyl acetate (3 × 5 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as a white solid (179 mg, 84% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.52 – 5.34 (m, 2H), 2.37 (t, *J* = 7.5 Hz, 3H), 1.97 (dqt, *J* = 7.7, 2.7, 1.5 Hz, 2H), 1.73 – 1.52 (m, 5H), 1.44 – 1.21 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.57, 131.75, 124.74, 34.08, 32.73, 29.71, 29.43, 29.34, 29.24, 29.19, 24.82, 18.09.

HRMS (EI+): $[M]^+$ $C_{12}H_{22}O_2$ Calculated – 198.1620, Found – 198.1640.

Synthesis of *trans*-5-hepten-1-ol



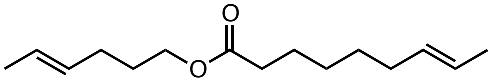
To an oven-dried, three-necked flask equipped with a condenser and charged with glass-coated stir bar was added a solution of 5-heptyn-1-ol (125 mg, 1.14 mmol) in *t*BuOH/THF (3 mL: 5 mL, 8 mL) under argon atmosphere. The flask was placed in a dry ice/acetone bath at −78 °C, and ammonia (20 mL) was condensed into the flask. Lithium metal (83 mg, 11.4 mmol) was added and the reaction was stirred for 1.5 h. The ammonia was allowed to evaporate while bringing to room temperature, and the reaction was quenched with saturated aq. NH_4Cl solution immediately upon disappearance of the blue color. The aqueous layer was extracted with pentane (4 × 25 mL) and washed with brine (2 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as colorless oil (97 mg, 76% yield) *Note*: If reaction did not reach full conversion to reduced product, the crude mixture was resubject to reaction conditions.

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.52 – 5.34 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.00 (dddd, *J* = 7.2, 6.1, 4.0, 1.2 Hz, 2H), 1.64 (dt, *J* = 5.0, 1.3 Hz, 3H), 1.62 – 1.50 (m, 2H), 1.46 – 1.35 (m, 2H), 1.34 – 1.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.22, 125.27, 63.07, 32.41, 32.37, 25.78, 18.07.

HRMS (EI+): $[M+H]^+$ $C_7H_{13}O$ Calculated – 113.0966, Found – 113.0987.

Synthesis of (*E*)-(*E*)-hex-4-en-1-yl non-7-enoate (7)



To a vial charged with a stir bar was added *trans*-7-nonenoic acid (143.7 mg, 0.9198 mmol), DMAP (23.0 mg, 0.184 mmol), EDC hydrochloride (352.1 mg, 1.840 mmol), and 7.5 mL dry dichloromethane under argon atmosphere. *Trans*-4-hexen-1-ol (216 µL, 1.840 mmol) was added, and the reaction was stirred for 3 h. 1 M aq. HCl (15 mL) was added to quench the reaction, the product was extracted with DCM (4 x 15 mL). This organic phase was dried over

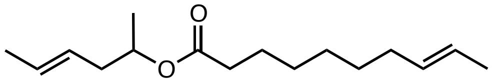
$MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (5:95 Et_2O:pentane) to yield the product as a colorless oil (201.7 mg, 92% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.52 – 5.36 (m, 4H), 4.08 (t, *J* = 6.7 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.11 – 2.03 (m, 2H), 1.99 (dddd, *J* = 8.7, 6.5, 3.0, 1.3 Hz, 2H), 1.74 – 1.59 (m, 10H), 1.42 – 1.26 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.95, 131.28, 129.97, 125.81, 124.86, 63.78, 34.37, 32.39, 29.21, 28.88, 28.66, 28.47, 24.91, 17.94, 17.93.

HRMS (EI+): $[M]^+$ $C_{15}H_{26}O_2$ Calculated – 238.1933, Found – 238.1935.

Synthesis of (*E*)-(*E*)-hex-4-en-2-yl dec-8-enoate



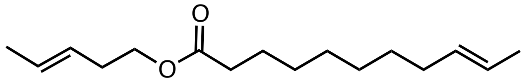
To a vial charged with a stir bar was added *trans*-8-decenoic acid (47.0 mg, 0.276 mmol), DMAP (6.74 mg, 0.0552 mmol), EDC hydrochloride (105.8 mg, 0.5520 mmol), and 2.3 mL dry dichloromethane under argon atmosphere. *Trans*-4-hexen-2-ol (55.3 mg, 0.552 mmol) was added, and the reaction was stirred for 3 h at ambient temperature. 1 M aq. HCl (10 mL) was added to quench the reaction, the product was extracted with DCM (4 x 10 mL). The organic extracts were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (5:95 Et_2O:pentane) to yield the product as a colorless oil (47 mg, 67% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.54 – 5.43 (m, 1H), 5.42 – 5.29 (m, 3H), 4.90 (h, *J* = 6.3 Hz, 1H), 2.30 – 2.22 (m, 3H), 2.22 – 2.12 (m, 1H), 2.00 – 1.90 (m, 2H), 1.69 – 1.55 (m, 8H), 1.39 – 1.24 (m, 6H), 1.18 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.54, 131.60, 128.33, 126.29, 124.83, 70.39, 39.26, 34.86, 32.65, 29.54, 29.14, 28.94, 25.20, 19.62, 18.15, 18.08.

HRMS (EI+): $[M]^+$ $C_{16}H_{28}O_2$ Calculated – 252.2089, Found – 252.2074.

Synthesis of (*E*)-(*E*)-pent-3-en-1-yl undec-9-enoate



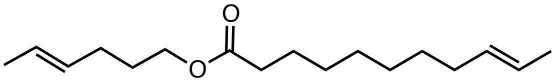
To a vial charged with a stir bar was added *trans*-9-undecenoic acid (53.4 mg, 0.290 mmol), DMAP (7.1 mg, 0.0580 mmol), EDC hydrochloride (111.1 mg, 0.580 mmol), and 2.3 mL dry dichloromethane under argon atmosphere. *Trans*-3-penten-1-ol (59.3 µL, 0.580 mmol) was added, and the reaction was stirred for 3 h. 1M aq. HCl (5 mL) was added to quench the reaction, the product was extracted with DCM (4 x 5 mL). This organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (5:95 Et_2O:pentane) to yield the product as a colorless oil (65.7 mg, 90% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.60 – 5.31 (m, 1H), 4.06 (t, *J* = 6.9 Hz, 1H), 2.36 – 2.22 (m, 1H), 1.99 – 1.89 (m, 1H), 1.72 – 1.51 (m, 2H), 1.39 – 1.23 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.04, 131.69, 127.97, 126.52, 124.76, 64.00, 34.51, 32.70, 32.15, 29.67, 29.28, 29.24, 29.11, 25.14, 18.14, 18.08.

HRMS (EI+): $[M]^+$ $C_{16}H_{28}O_2$ Calculated – 252.2089, Found – 252.2095.

Synthesis of (*E*)-(*E*)-hex-4-en-1-yl undec-9-enoate



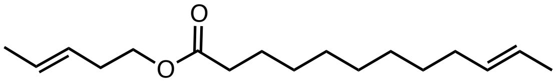
To a vial charged with a stir bar was added *trans*-9-undecenoic acid (51.4 mg, 0.280 mmol), DMAP (6.8 mg, 0.0560 mmol), EDC hydrochloride (106.9 mg, 0.560 mmol), and 2.2 mL dry dichloromethane under argon atmosphere. *Trans*-4-hexen-1-ol (65.6 µL, 0.560 mmol) was added, and the reaction was stirred for 3 h. 1M aq. HCl (5 mL) was added to quench the reaction, the product was extracted with DCM (4 x 5 mL). This organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (5:95 Et_2O:pentane) to yield the product as a colorless oil (68.3 mg, 92% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.46 – 5.25 (m, 4H), 3.99 (t, *J* = 6.7 Hz, 2H), 2.27 – 2.15 (m, 2H), 1.97 (tdd, *J* = 7.6, 5.9, 1.5 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.65 – 1.49 (m, 10H), 1.32 – 1.13 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.12, 131.69, 130.10, 125.93, 124.76, 63.90, 34.53, 32.70, 29.66, 29.27, 29.26, 29.11, 29.02, 28.60, 25.15, 18.08, 18.06.

HRMS (EI+): $[M]^+$ $C_{17}H_{30}O_2$ Calculated – 266.2237, Found – 266.2246.

Synthesis of (*E*)-(*E*)-pent-3-en-1-yl dodec-10-enoate



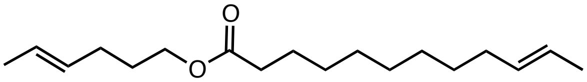
To a vial charged with a stir bar was added *trans*-10-dodecenoic acid (45.8 mg, 0.231 mmol), DMAP (5.6 mg, 0.0462 mmol), EDC hydrochloride (88.6 mg, 0.462 mmol), and 1.8 mL dry dichloromethane under argon atmosphere. *Trans*-3-penten-1-ol (47.3 µL, 0.462 mmol) was added, and the reaction was stirred for 3 h. 1M aq. HCl (5 mL) was added to quench the reaction, the product was extracted with DCM (4 x 5 mL). This organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (5:95 Et_2O:pentane) to yield the product as a colorless oil (51.4 mg, 84% yield).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.60 – 5.29 (m, 4H), 4.06 (t, *J* = 6.9 Hz, 2H), 2.37 – 2.22 (m, 4H), 1.95 (dtt, *J* = 7.9, 5.1, 1.5 Hz, 2H), 1.72 – 1.56 (m, 8H), 1.40 – 1.24 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.05, 131.76, 127.98, 126.53, 124.73, 64.01, 34.52, 32.74, 32.16, 29.73, 29.48, 29.39, 29.30, 29.28, 29.26, 25.16, 18.16, 18.10.

HRMS (EI+): $[M]^+$ $C_{17}H_{30}O_2$ Calculated – 266.2237, Found – 266.2261.

Synthesis of (*E*)-(*E*)-hex-4-en-1-yl dodec-10-enoate



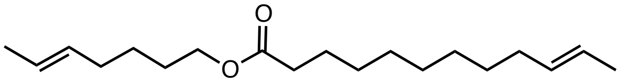
To a vial charged with a stir bar was added *trans*-10-dodecenoic acid (45.6 mg, 0.230 mmol), DMAP (5.6 mg, 0.0460 mmol), EDC hydrochloride (88.2 mg, 0.460 mmol), and 1.4 mL dry dichloromethane under argon atmosphere. *Trans*-4-hexen-1-ol (41.3 mg, 0.460 mmol) was added, and the reaction was stirred for 3 h. 1M aq. HCl (5 mL) was added to quench the reaction, the product was extracted with DCM (4 x 5 mL). This organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (5:95 Et_2O:pentane) to yield the product as a colorless oil (47.2 mg, 73% yield).

^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.53 – 5.32 (m, 4H), 4.05 (t, *J* = 6.7 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.04 (dtd, *J* = 7.9, 6.1, 1.5 Hz, 2H), 1.98 – 1.91 (m, 2H), 1.73 – 1.52 (m, 11H), 1.33 – 1.22 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.13, 131.76, 130.11, 125.93, 124.72, 63.90, 34.54, 32.73, 29.72, 29.47, 29.38, 29.29, 29.26, 29.02, 28.60, 25.16, 18.09, 18.06.

HRMS (EI+): $[M]^+$ $C_{18}H_{32}O_2$ Calculated – 280.2402, Found – 280.2379.

Synthesis of (*E*)-(*E*)-hept-5-en-1-yl dodec-10-enoate



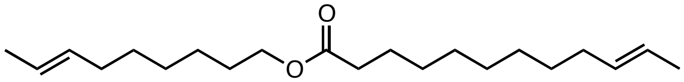
To a vial charged with a stir bar was added *trans*-10-dodecenoic acid (35.9 mg, 0.181 mmol), DMAP (4.4 mg, 0.0362 mmol), EDC hydrochloride (69.4 mg, 0.362 mmol), and 1.4 mL dry dichloromethane under argon atmosphere. *Trans*-5-hepten-1-ol (41.3 mg, 0.362 mmol) was added, and the reaction was stirred for 3 h. 1M aq. HCl (5 mL) was added to quench the reaction, the product was extracted with DCM (4 x 5 mL). This organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (5:95 Et_2O:pentane) to yield the product as a colorless oil (41.0 mg, 77% yield).

^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.52 – 5.31 (m, 4H), 4.05 (t, *J* = 6.7 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.06 – 1.86 (m, 4H), 1.67 – 1.55 (m, 10H), 1.47 – 1.35 (m, 2H), 1.35 – 1.20 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.15, 131.74, 130.98, 125.41, 124.71, 64.38, 34.53, 32.73, 32.25, 29.72, 29.47, 29.37, 29.29, 29.25, 28.25, 25.99, 25.15, 18.08, 18.06.

HRMS (EI+): $[M]^+$ $C_{19}H_{34}O_2$ Calculated – 294.2559, Found – 294.2578.

Synthesis of (*E*)-(*E*)-non-7-en-1-yl dodec-10-enoate



To a vial charged with a stir bar was added *trans*-10-dodecenoic acid (35.9 mg, 0.188 mmol), DMAP (4.6 mg, 0.0376 mmol), EDC hydrochloride (72.1 mg, 0.376 mmol), and 1.5 mL dry dichloromethane under argon atmosphere. *Trans*-7-nonen-1-ol (53.5 mg, 0.376 mmol) was added, and the reaction was stirred for 3 h. 1M aq. HCl (5 mL) was added to quench the reaction, the product was extracted with DCM (4 x 5 mL). This organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (5:95 Et_2O:pentane) to yield the product as a colorless oil (42.4 mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.41 (ddt, *J* = 5.0, 3.7, 1.7 Hz, 4H), 4.05 (t, *J* = 6.7 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.03 – 1.88 (m, 4H), 1.69 – 1.54 (m, 10H), 1.34 – 1.23 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.16, 131.76, 131.54, 124.89, 124.71, 64.51, 34.55, 32.74, 32.62, 29.72, 29.59, 29.48, 29.38, 29.30, 29.26, 28.90, 28.76, 25.96, 25.17, 18.09.

HRMS (EI+): $[M]^+$ $C_{21}H_{38}O_2$ Calculated – 322.2872, Found – 322.2896.

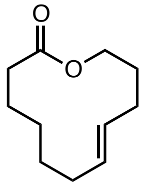
Procedure for Synthesis of 6 from 5

In an N_2-filled glovebox, **5** (5.0 mg, 18.8 µmol) and 2.8 mL THF were added to a vial charged with a stir bar. A solution of catalyst (1.4 µmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. 0.5 mL aliquots were taken out of the box at 2 and 5 h, and solvents were removed *in vacuo*. Conversions were determined by ^1H NMR of these aliquots, and stereoselectivity was determined by GC.

Procedure for Synthesis of 8 from 7

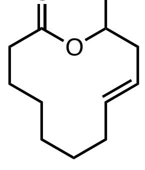
In an N_2-filled glovebox, **7** (10.0 mg, 42.0 µmol) and 7.4 mL THF were added to a vial charged with a stir bar. A solution of catalyst (3.1 µmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. 0.5 mL aliquots were taken out of the box, and solvents were removed *in vacuo*. Conversions were determined by ^1H NMR of these aliquots, and stereoselectivity was determined by GC.

Synthesis of (*E*)-oxacyclododec-8-en-2-one (8)



In an N_2-filled glovebox, (*E*)-(*E*)-hex-4-en-1-yl non-7-enoate (20.0 mg, 83.9 µmol) and 15.8 mL THF were added to a vial charged with a stir bar. A solution of catalyst (6.3 µmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. The vial was taken out of the glovebox and quenched with 0.5 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified with column chromatography on silica gel (1:49 Et_2O:pentane) to yield the product as a colorless oil (7.2 mg, 47% yield with **2**; 9.1 mg, 60 % yield with **4**).
^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.50 (dtt, *J* = 15.3, 7.1, 1.3 Hz, 1H), 5.24 – 5.10 (m, 1H), 4.14 – 4.04 (m, 2H), 2.36 – 2.26 (m, 2H), 2.24 – 2.18 (m, 2H), 2.14 – 2.07 (m, 2H), 1.84 – 1.76 (m, 2H), 1.55 (tdd, *J* = 9.6, 8.5, 4.3, 2.4 Hz, 2H), 1.48 – 1.39 (m, 2H), 1.28 – 1.19 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.92, 133.38, 127.22, 66.38, 35.35, 32.60, 29.67, 28.12, 25.16, 24.99, 21.10.
HRMS (EI+): $[M]^+$ $C_{11}H_{18}O_2$ Calculated – 182.1307, Found – 182.1308.

Synthesis of (*E*)-12-methyloxacyclododec-9-en-2-one (9)



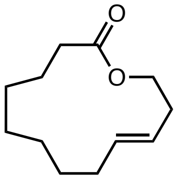
In an N_2-filled glovebox, (*E*)-hex-4-en-2-yl (*E*)-dec-8-enoate (20.0 mg, 79.2 µmol) and 14.8 mL THF were added to a vial charged with a stir bar. A solution of catalyst (5.9 µmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. The vial was taken out of the glovebox and quenched with 0.5 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified with column chromatography on silica gel (1:49 Et_2O:pentane) to yield the product as a colorless oil (9.4 mg, 61% yield with **2**; 12.4 mg, 80% yield with **4**).

^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.36 – 5.21 (m, 2H), 5.16 (dqd, *J* = 11.2, 6.3, 2.9 Hz, 1H), 2.37 (ddd, *J* = 14.1, 11.5, 4.0 Hz, 1H), 2.33 – 2.27 (m, 1H), 2.23 (ddd, *J* = 14.0, 5.5, 4.5 Hz, 1H), 2.20 – 2.06 (m, 2H), 2.03 – 1.91 (m, 1H), 1.88 – 1.75 (m, 1H), 1.57 – 1.46 (m, 3H), 1.46 – 1.32 (m, 2H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.21 – 1.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.58, 133.55, 127.16, 68.63, 41.09, 33.04, 30.34, 25.04, 24.74, 24.33, 23.27, 20.70.

HRMS (EI+): $[M]^+$ $C_{12}H_{20}O_2$ Calculated – 196.1463, Found – 196.1451.

Synthesis of (*E*)-oxacyclotridec-10-en-2-one (10)



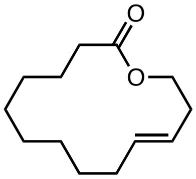
In an N_2-filled glovebox, (*E*)-(*E*)-pent-3-en-1-yl undecen-9-enoate (22.6 mg, 89.7 µmol) and 17.0 mL THF were added to a vial charged with a stir bar. A solution of catalyst (6.7 µmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. The vial was taken out of the glovebox and quenched with 0.5 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified with column chromatography on silica gel (1:49 Et_2O:pentane) to yield the product as a colorless oil (10.0 mg, 57% yield with **2**; 13.2 mg, 75% yield with **4**).

^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.56 (dtt, *J* = 15.6, 7.1, 1.3 Hz, 1H), 5.34 (dtt, *J* = 15.1, 6.9, 1.3 Hz, 1H), 4.18 – 4.11 (m, 2H), 2.40 – 2.24 (m, 4H), 2.02 (dddd, *J* = 10.5, 5.9, 2.2, 1.1 Hz, 2H), 1.72 – 1.60 (m, 2H), 1.42 (dq, *J* = 5.7, 2.7 Hz, 2H), 1.38 – 1.23 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.24, 134.87, 126.58, 63.06, 34.08, 32.73, 32.14, 27.52, 27.51, 27.43, 27.09, 24.33.

HRMS (EI+): $[M]^+$ $C_{12}H_{20}O_2$ Calculated – 196.1463, Found – 196.1488.

Synthesis of (*E*)-oxacyclotetradec-11-en-2-one (6)

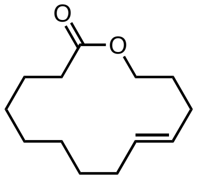


In an N_2-filled glovebox, (*E*)-(*E*)-pent-3-en-1-yl dodecen-10-enoate (20.8 mg, 78.1 µmol) and 14.6 mL THF were added to a vial charged with a stir bar. A solution of catalyst (5.8 µmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. The vial was taken out of the glovebox and quenched with 0.5 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified with column chromatography on silica gel (1:49 Et_2O:pentane) to yield the product as a colorless oil (9.5 mg, 58% yield with **2**; 10.6 mg, 65% yield with **4**).

^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.55 – 5.27 (m, 2H), 4.16 – 4.07 (m, 2H), 2.41 – 2.31 (m, 4H), 2.05 – 1.95 (m, 2H), 1.65 – 1.53 (m, 2H), 1.45 – 1.17 (m, 10H).

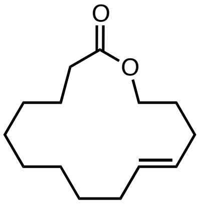
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.22, 132.98, 127.93, 64.48, 35.25, 32.01, 31.42, 26.79, 26.29, 25.99, 25.77, 24.00, 23.92.
HRMS (EI+): $[M]^+$ $C_{13}H_{22}O_2$ Calculated – 210.1620, Found – 210.1592.

Synthesis of *(E)*-oxacyclotetradec-10-en-2-one (11)



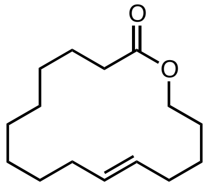
In an N_2-filled glovebox, (*E*)-(*E*)-hex-4-en-1-yl undecen-9-enoate (24.4 mg, 91.6 μmol) and 17.3 mL THF were added to a vial charged with a stir bar. A solution of catalyst (6.9 μmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. The vial was taken out of the glovebox and quenched with 0.5 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified with column chromatography on silica gel (1:49 Et_2O:pentane) to yield the product as a colorless oil (11.5 mg, 60% yield with **2**; 12.9 mg, 67 % yield with **4**).
^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.51 (dtt, J = 15.1, 7.0, 1.3 Hz, 1H), 5.37 (dtt, J = 15.2, 7.0, 1.3 Hz, 1H), 4.17 – 4.07 (m, 2H), 2.36 – 2.30 (m, 2H), 2.22 (dddd, J = 11.0, 5.8, 2.4, 1.2 Hz, 2H), 2.13 – 2.01 (m, 2H), 1.80 – 1.63 (m, 4H), 1.46 – 1.37 (m, 2H), 1.34 – 1.25 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.41, 130.76, 130.54, 64.94, 33.14, 31.55, 31.05, 28.31, 27.19, 26.77, 26.66, 25.11, 24.22.
HRMS (EI+): $[M]^+$ $C_{13}H_{22}O_2$ Calculated – 210.1620, Found – 210.1614.

Synthesis of (*E*)-oxacyclopentadec-11-en-2-one (12)



In an N_2-filled glovebox, (*E*)-(*E*)-hex-4-en-1-yl dodecen-10-enoate (22.4 mg, 79.9 μmol) and 15.0 mL THF were added to a vial charged with a stir bar. A solution of catalyst (6.0 μmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. The vial was taken out of the glovebox and quenched with 0.5 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified with column chromatography on silica gel (1:49 Et_2O:pentane) to yield the product as a colorless oil (11.3 mg, 63% yield with **2**; 12.5 mg, 70% yield with **4**).
^{1}H NMR (400 MHz, Chloroform-d_1) δ 5.51 – 5.32 (m, 2H), 4.18 – 4.09 (m, 2H), 2.38 – 2.29 (m, 2H), 2.25 – 2.15 (m, 2H), 2.08 – 1.99 (m, 2H), 1.81 – 1.73 (m, 2H), 1.67 – 1.58 (m, 2H), 1.39 – 1.22 (m, 10H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.49, 131.98, 129.88, 64.31, 35.02, 31.02, 30.33, 27.86, 27.57, 27.04, 26.83, 26.64, 25.04, 24.58.
HRMS (EI+): $[M]^+$ $C_{14}H_{24}O_2$ Calculated – 224.1776, Found – 224.1791.

Synthesis of (*E*)-oxacyclohexadec-11-en-2-one (13)



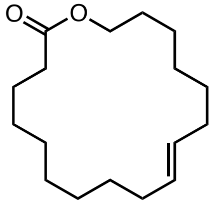
In an N_2-filled glovebox, (*E*)-(*E*)-hept-5-en-1-yl dodecen-10-enoate (20.5 mg, 69.6 μmol) and 12.9 mL THF were added to a vial charged with a stir bar. A solution of catalyst (5.2 μmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. The vial was taken out of the glovebox and quenched with 0.5 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified with column chromatography on silica gel (1:49 Et_2O:pentane) to yield the product as a colorless oil (11.0 mg, 66% yield with **2**; 11.6 mg, 70% yield with **4**).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.37 – 5.23 (m, 2H), 4.12 (t, *J* = 7.2 Hz, 2H), 2.39 – 2.24 (m, 2H), 2.03 (dtd, *J* = 10.4, 5.8, 1.9 Hz, 4H), 1.70 – 1.55 (m, 4H), 1.42 – 1.21 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.09, 131.96, 130.47, 64.10, 34.91, 32.17, 32.13, 28.47, 28.42, 28.35, 28.15, 27.35, 26.69, 25.61, 25.31.

HRMS (EI+): $[M]^+$ $C_{15}H_{26}O_2$ Calculated – 238.1933, Found – 238.1950.

Synthesis of (*E*)-oxacyclooctadec-11-en-2-one (14)



In an N_2-filled glovebox, (*E*)-(*E*)-non-7-en-1-yl dodecen-10-enoate (23.7 mg, 73.5 μmol) and 13.7 mL THF were added to a vial charged with a stir bar. A solution of catalyst (5.5 μmol) in 1 mL of THF was then added to this mixture. The vial was loosely capped, and the reaction was stirred at 35 °C for the reported amount of time. The vial was taken out of the glovebox and quenched with 0.5 mL butyl vinyl ether. Solvents were removed *in vacuo*, and the product was purified with column chromatography on silica gel (1:49 Et_2O:pentane) to yield the product as a colorless oil (12.5 mg, 64% yield with **2**; 12.3 mg, 63% yield with **4**).

^{1}H NMR (400 MHz, Chloroform-*d*$_1$) δ 5.43 – 5.20 (m, 2H), 4.11 (t, *J* = 5.9 Hz, 2H), 2.38 – 2.25 (m, 2H), 2.00 (p, *J* = 6.6 Hz, 4H), 1.71 – 1.56 (m, 4H), 1.47 – 1.15 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.22, 130.95, 130.89, 63.85, 34.51, 31.96, 31.76, 29.32, 29.32, 28.87, 28.68, 28.46, 28.20, 27.39, 27.28, 25.65, 25.53.

HRMS (EI+): $[M]^+$ $C_{17}H_{30}O_2$ Calculated – 266.2246, Found – 266.2226.

GC Methods

HP-5 Agilent Column 30m × 0.25mm (ID) × 0.25μm film thickness
Injector temperature: 250 °C
Detector temperature: 350 °C
Oven temperature: Starting temperature: 50 °C, hold time: 1 min.
Ramp rate: 20 °C/min to 150 °C, hold time: 3 min., 10 °C/min to 210 °C hold time: 0 min., 35 °C/min to 300 °C, hold time: 3 min.
Carrier gas: He

Average velocity: 31 cm/s
Split ratio: 48.9:1

References:

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2. Patel, H. H.; Sigman, M. S. *J. Am. Chem. Soc.* **2015**, *137* (10), 3462.
3. Denmark, S. E.; Forbes, D. C.; Hays, D. S.; DePue, J. S.; Wilde, R. G. *J. Org. Chem.* **1996**, 60, 1391.
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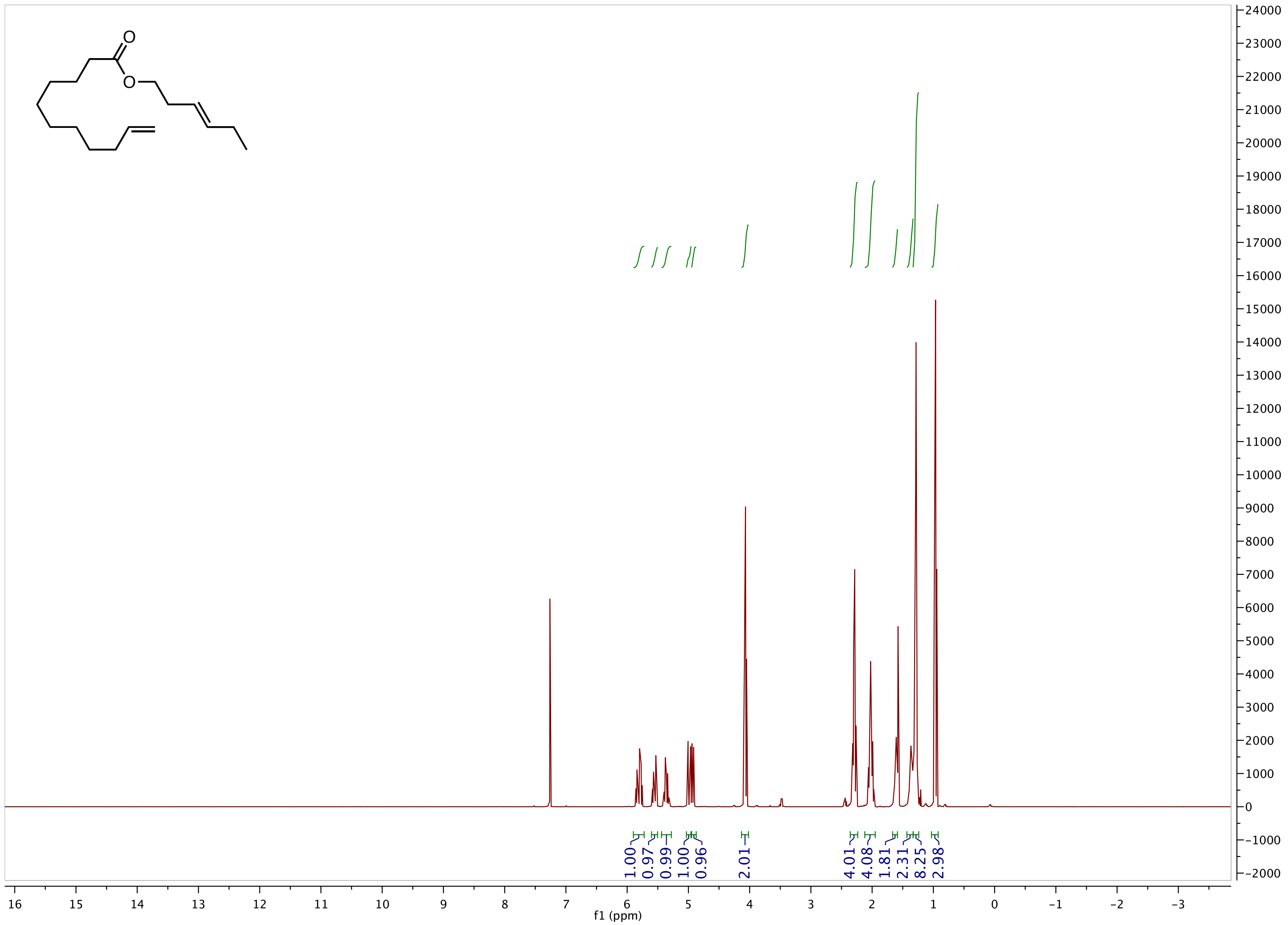
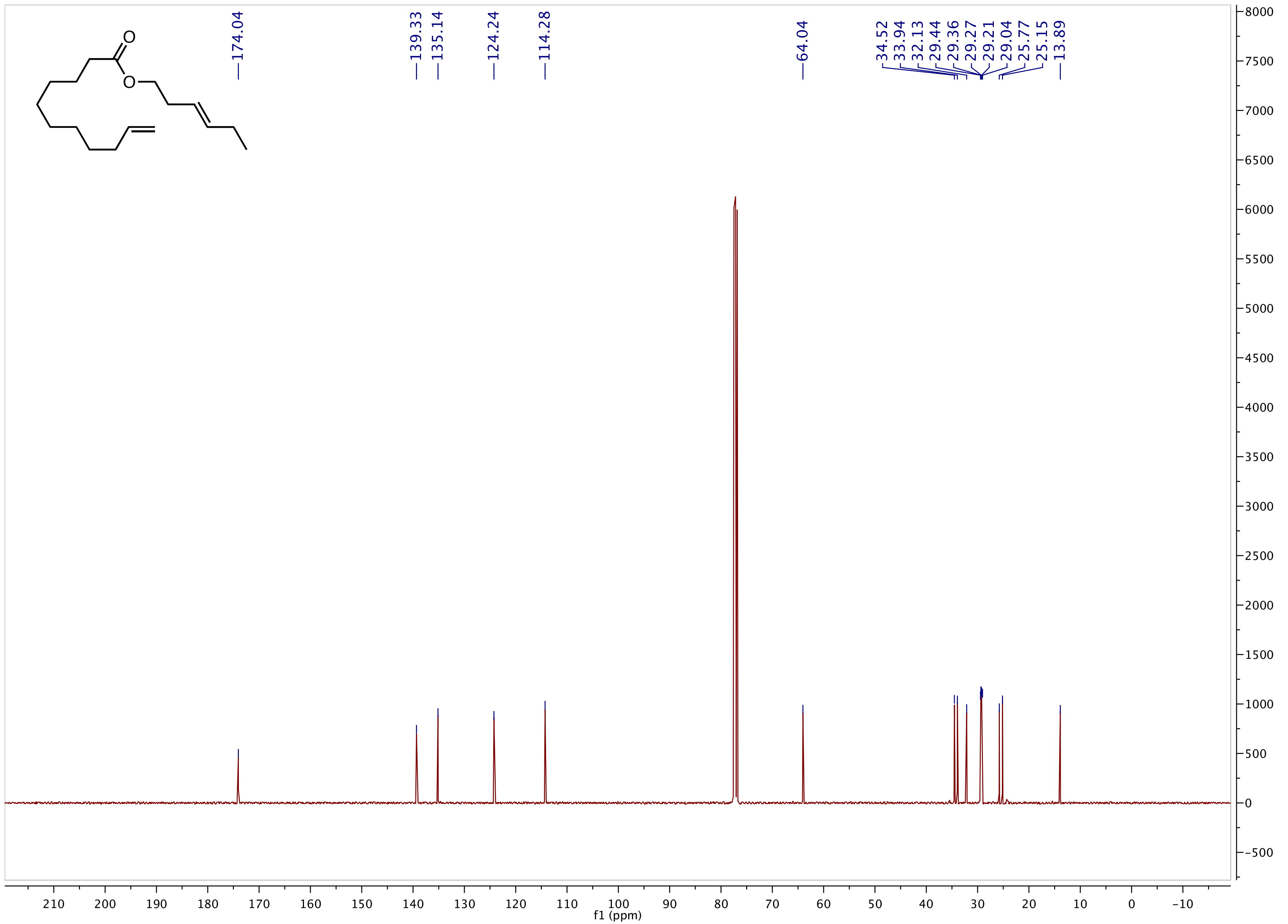
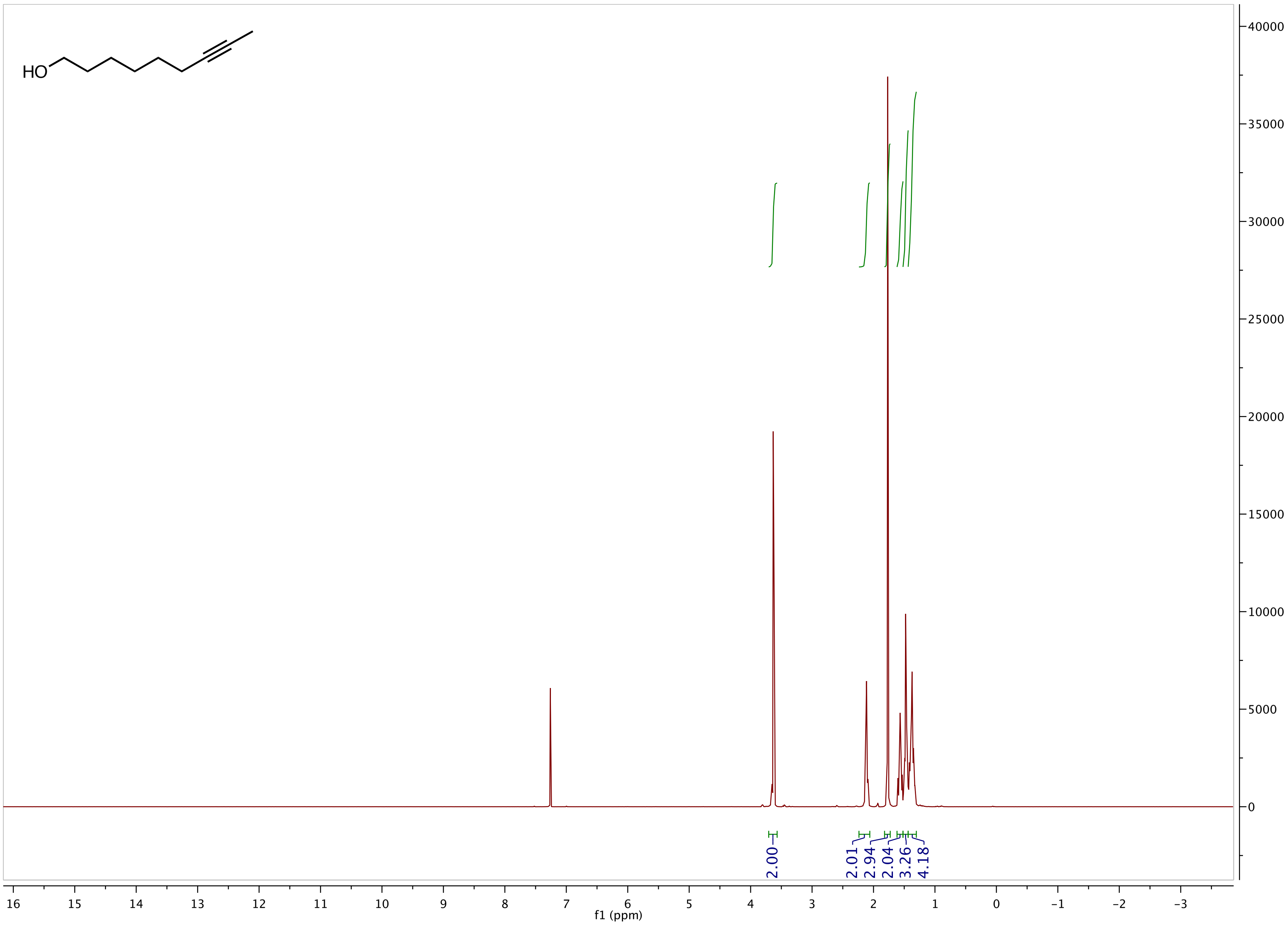
6. Robinson, J. A.; Flohr, H.; Kempe, U. M.; Panhorst, W.; Rétey, J. *Liebigs Annalen der Chemie*, **1983**, *2*, 181.
7. Cryle, M. J.; Hayes, P. Y.; De Voss, J. J. *Chem. Eur. J.* **2012**, *18*, 15994.



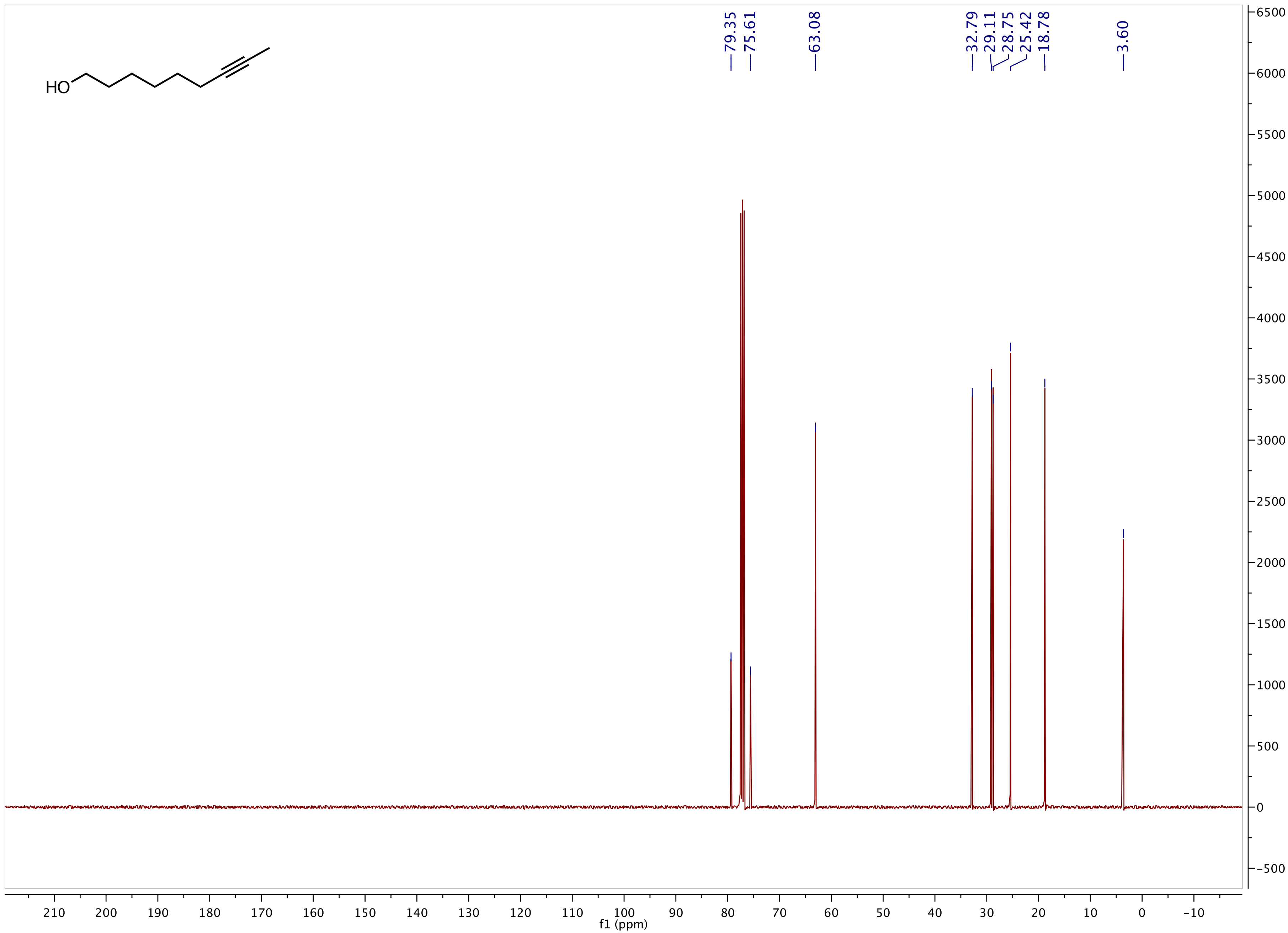
^{1}H NMR of (*E*)-hex-3-en-1-yl undec-10-enoate **5** (400 MHz, $CDCl_3$)



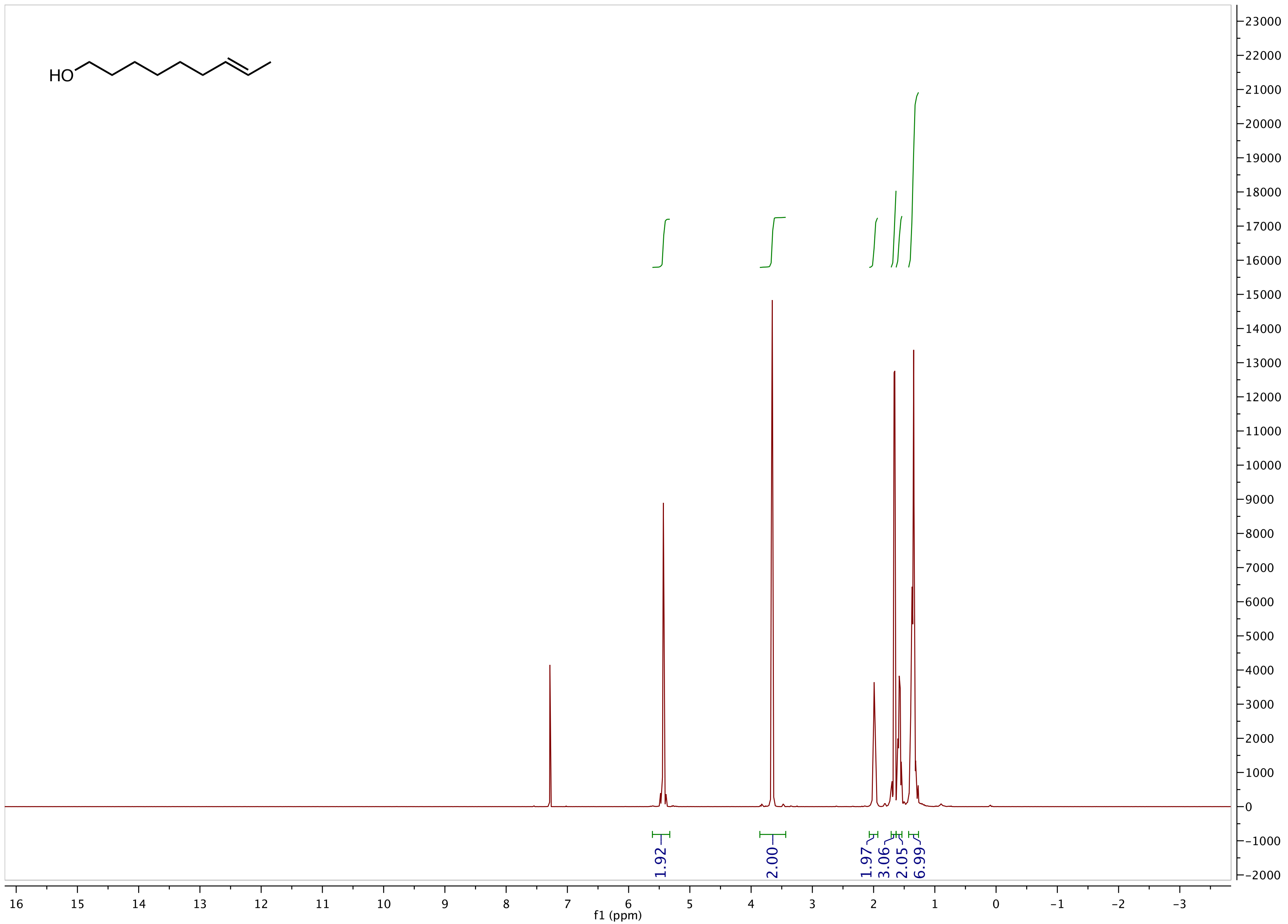
^{13}C NMR of (*E*)-hex-3-en-1-yl undec-10-enoate **5** (101 MHz, CDCl$_3$)



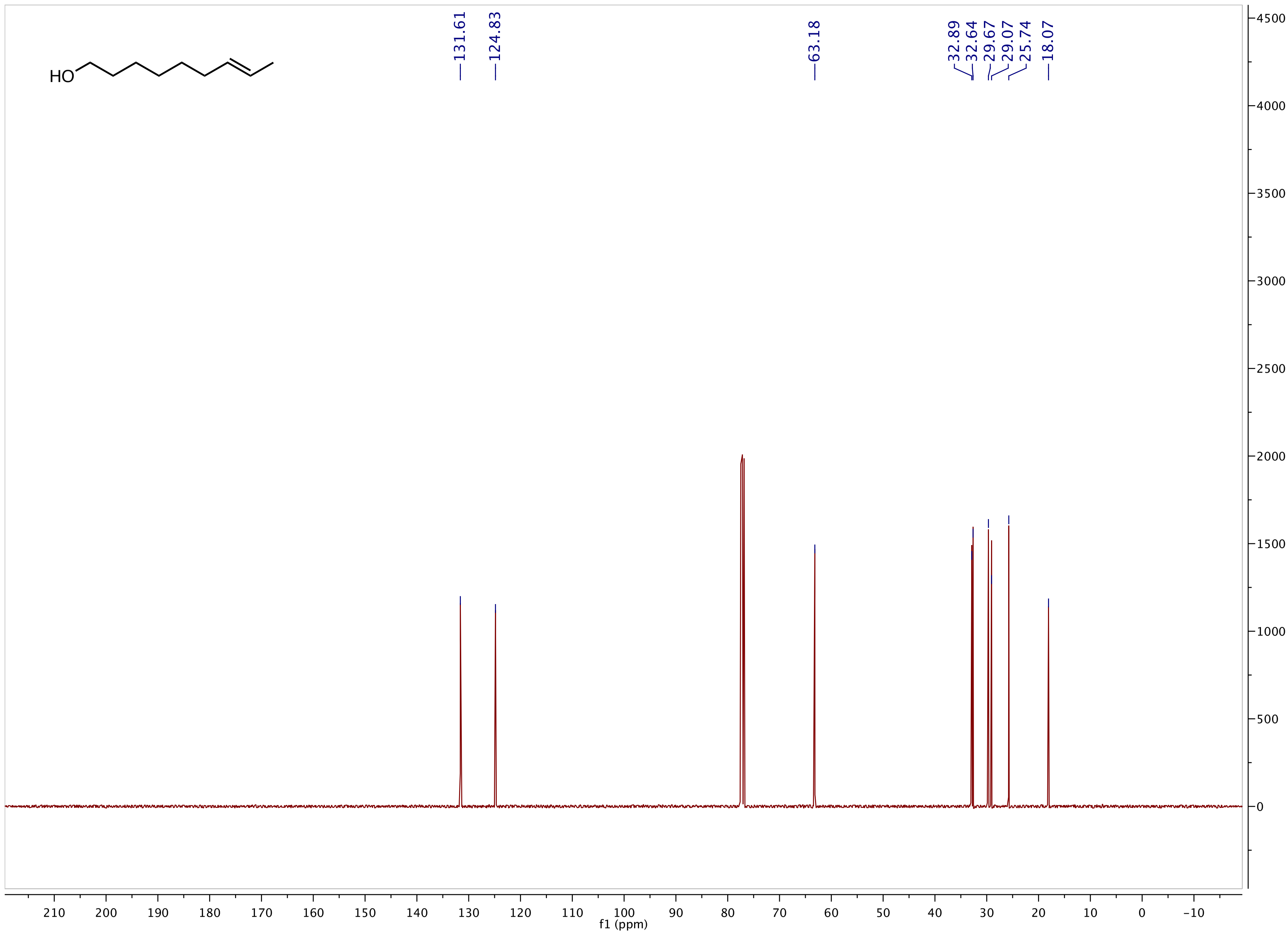
^{1}H NMR of non-7-yn-1-ol (400 MHz, $CDCl_3$)



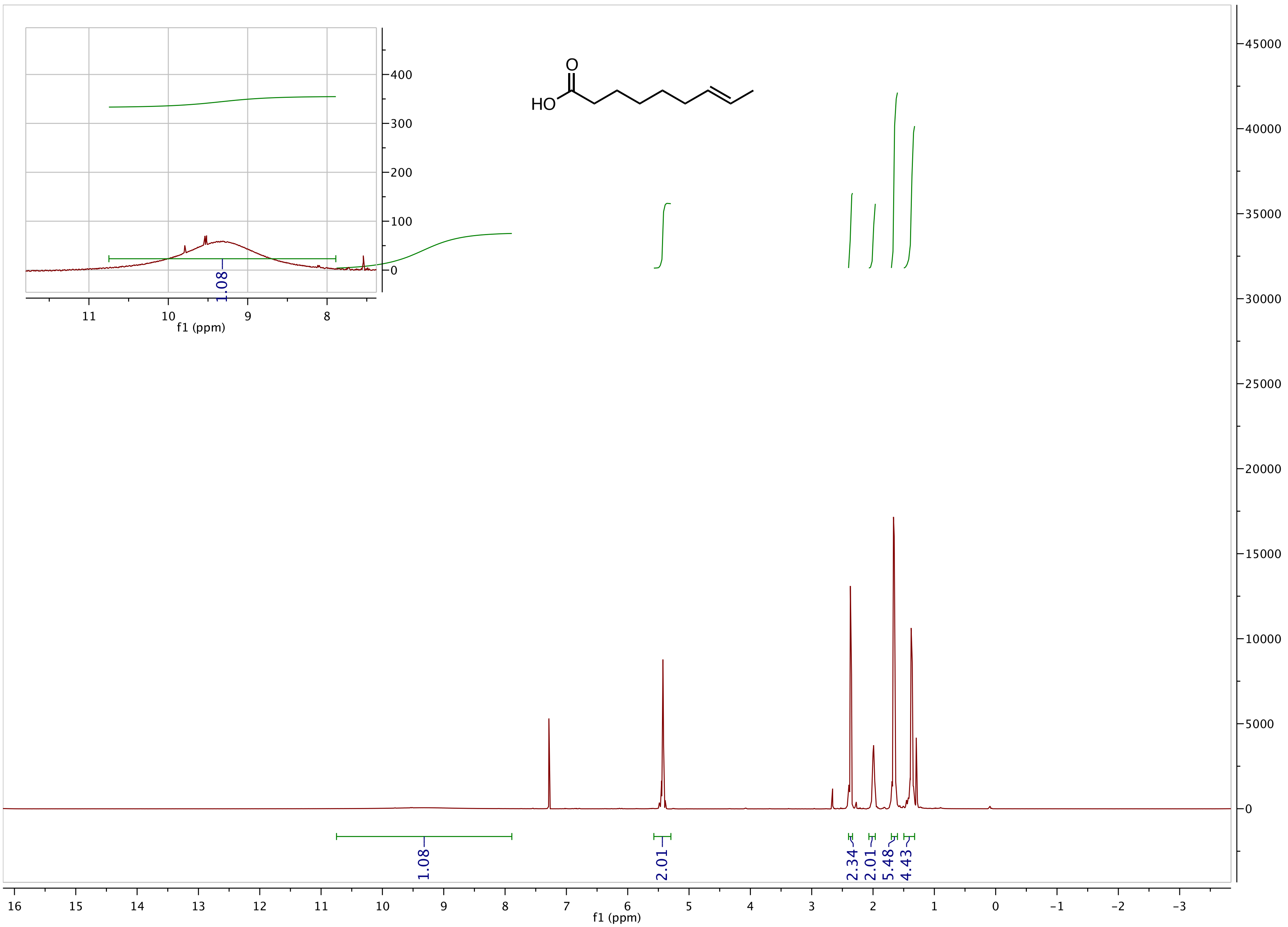
^{13}C NMR of non-7-yn-1-ol (101 MHz, CDCl$_3$)



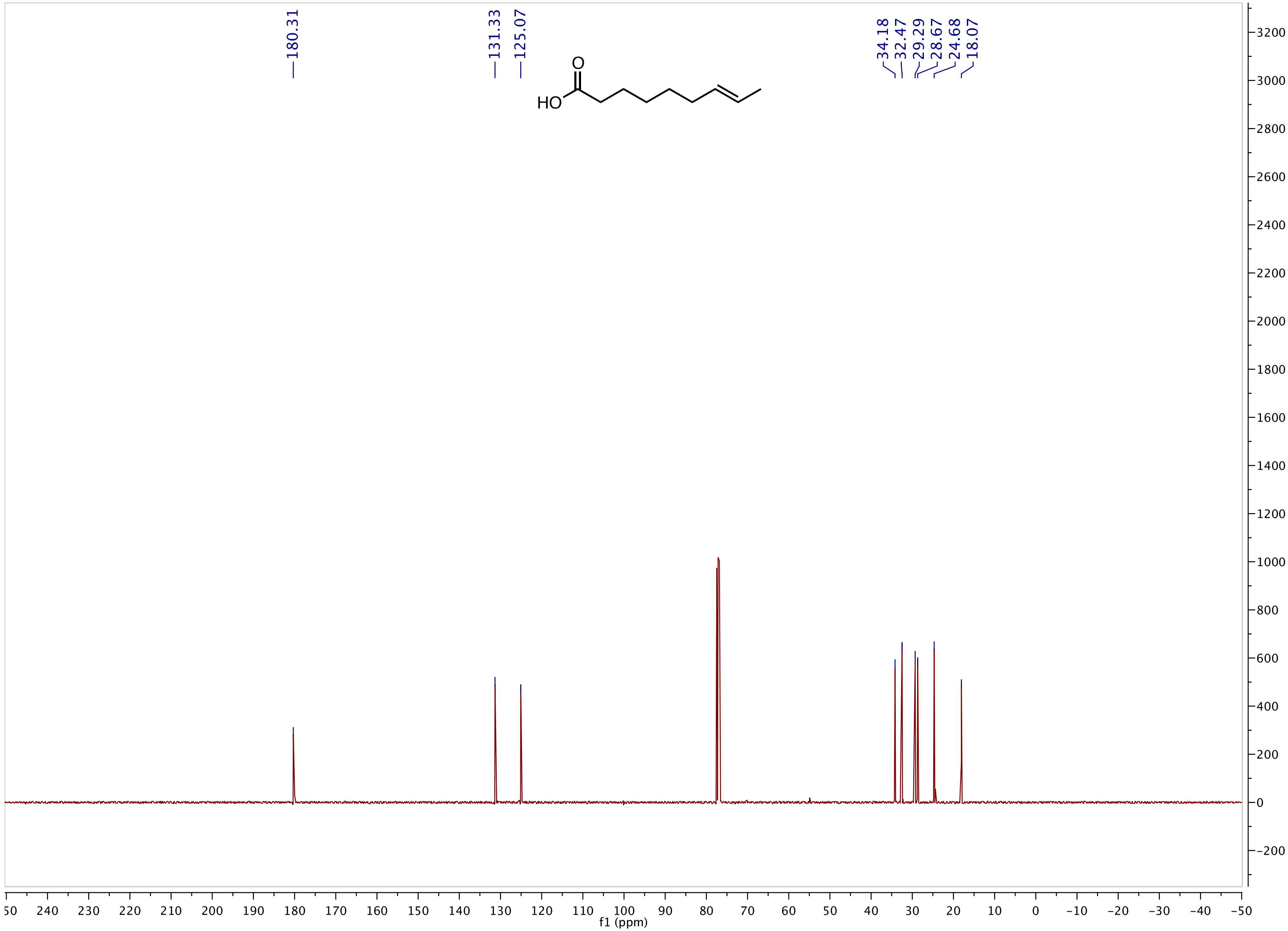
^{1}H NMR of *trans*-7-nonen-1-ol (400 MHz, CDCl$_3$)



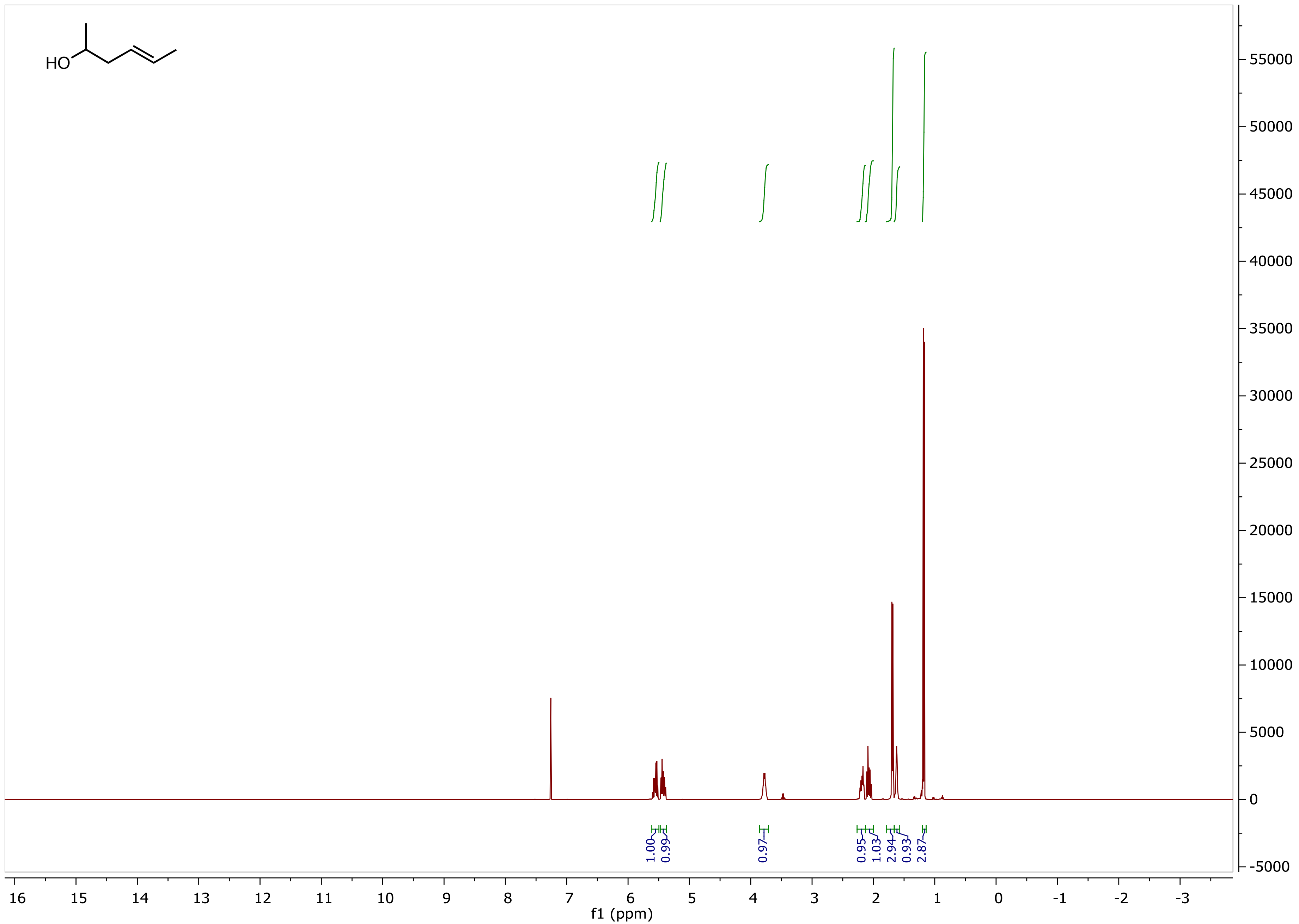
^{13}C NMR of *trans*-7-nonen-1-ol (101 MHz, $CDCl_3$)



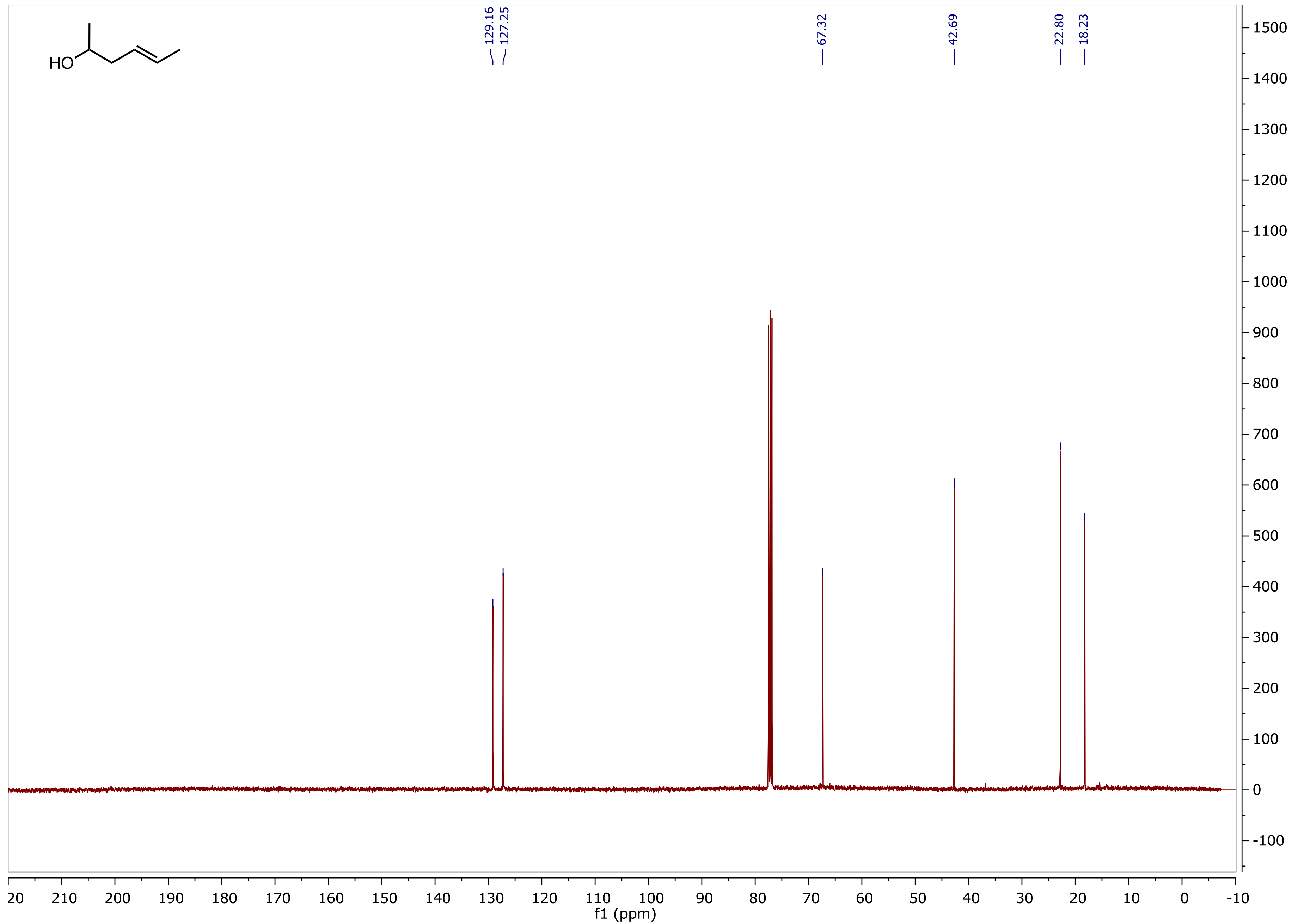
^{1}H NMR of *trans*-7-nonenoic acid (400 MHz, $CDCl_3$)



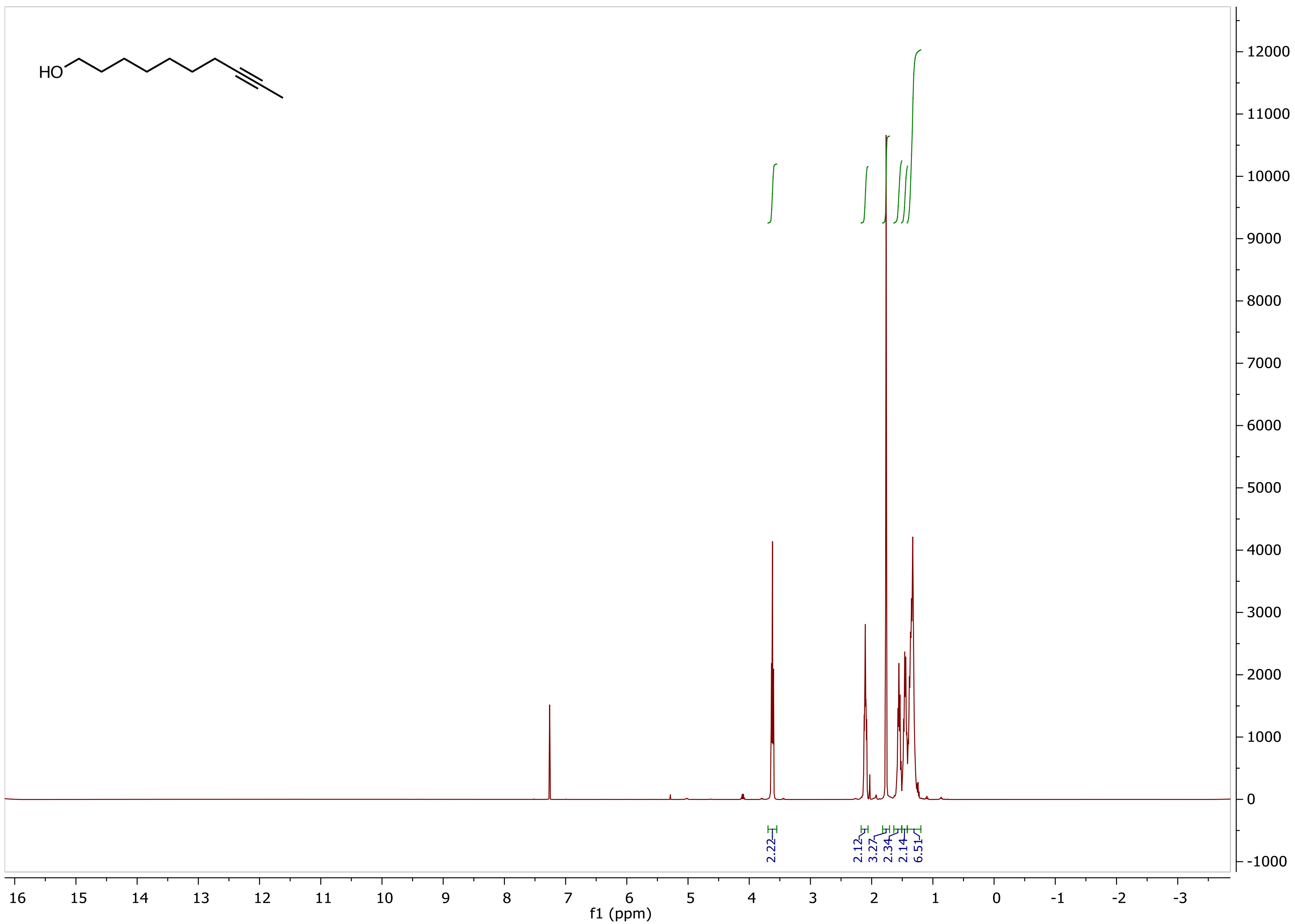
^{13}C NMR of *trans*-7-nonenoic acid (101 MHz, $CDCl_3$)



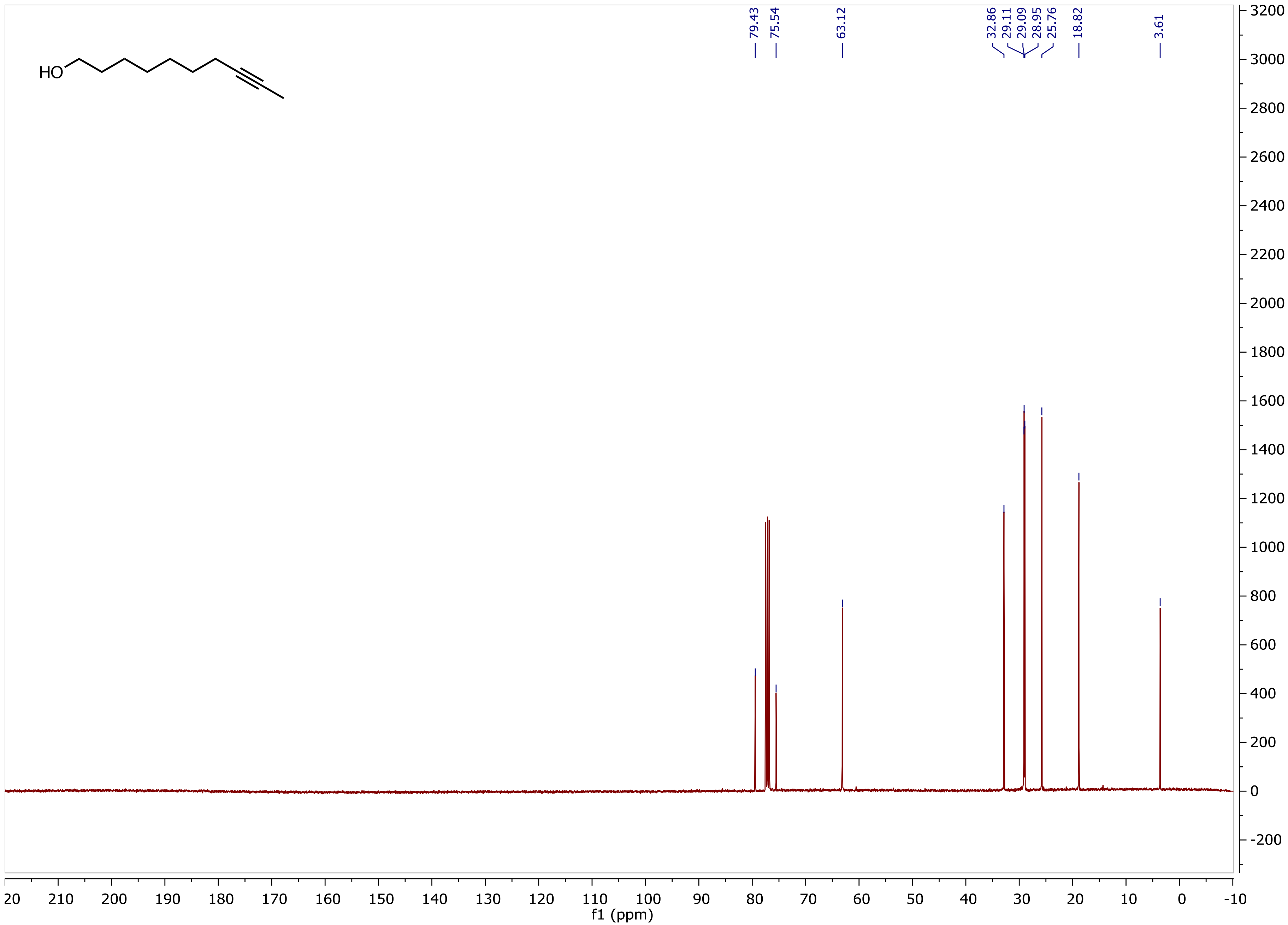
^{1}H NMR of *trans*-4-hexen-2-ol (400 MHz, $CDCl_3$)



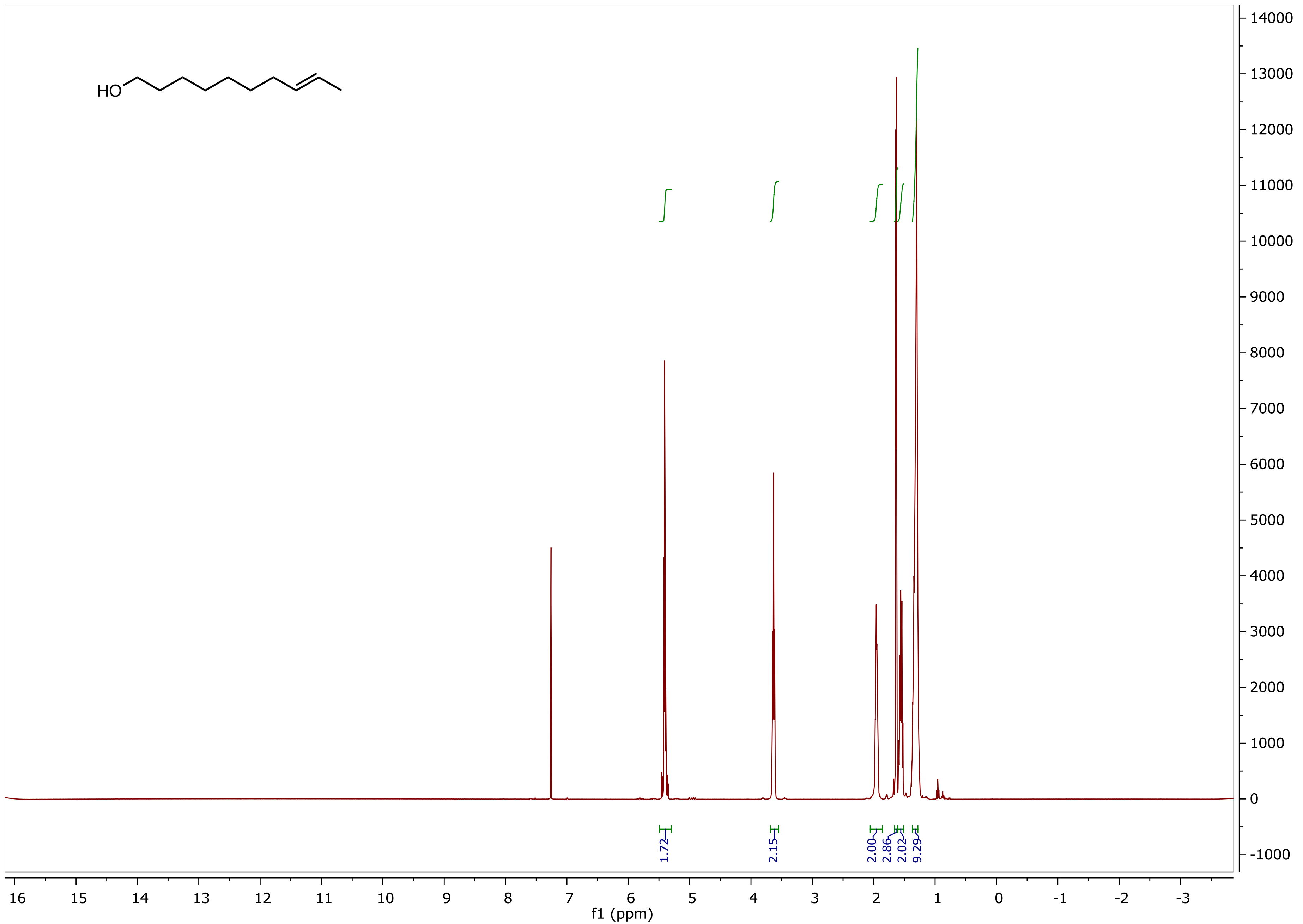
^{13}C NMR of *trans*-4-hexen-2-ol (101 MHz, $CDCl_3$)



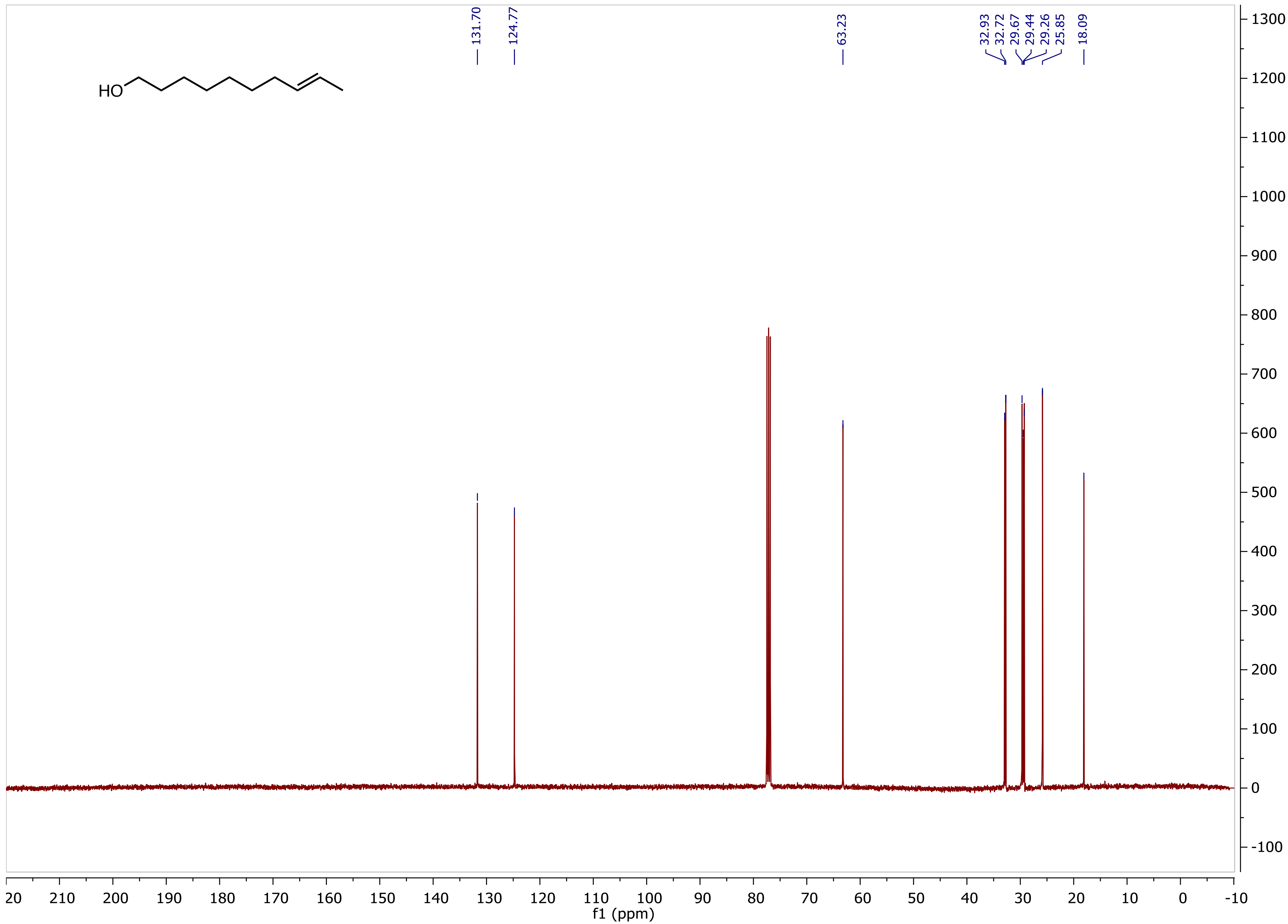
^{1}H NMR of 8-decyn-1-ol (400 MHz, $CDCl_3$)



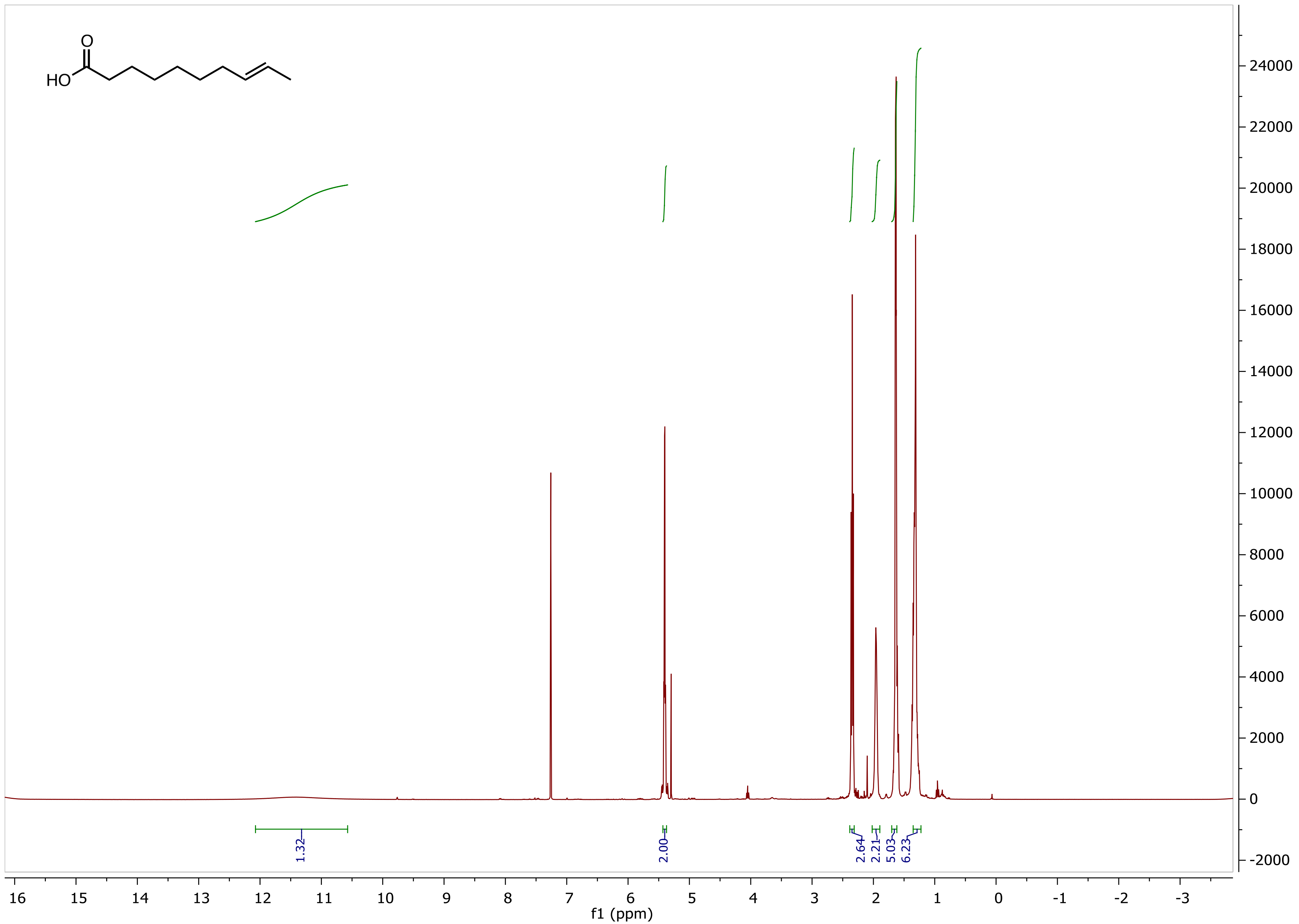
^{13}C NMR of 8-decyn-1-ol (101 MHz, CDCl$_3$)



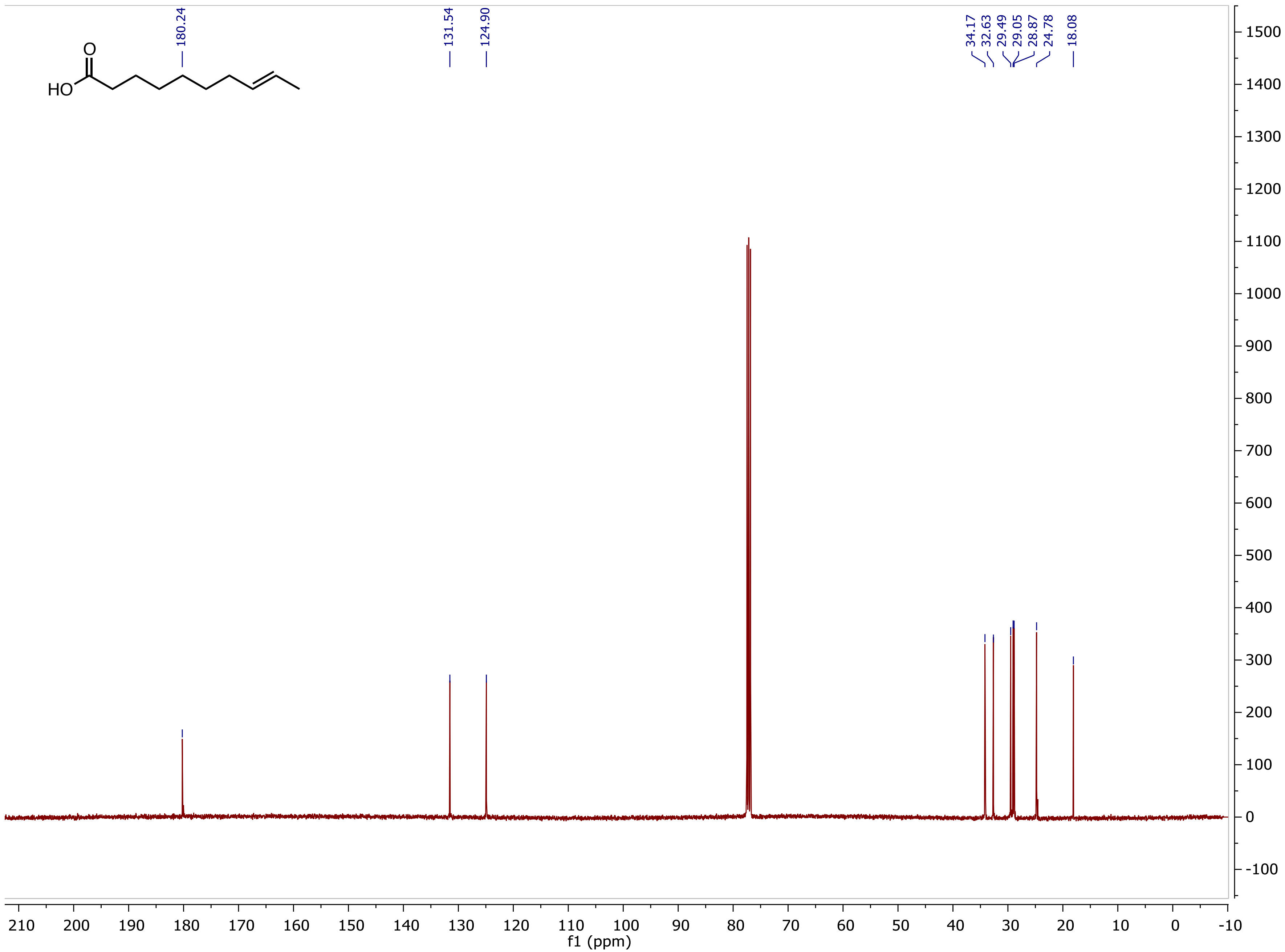
^{1}H NMR of *trans*-8-decen-1-ol (400 MHz, $CDCl_3$)



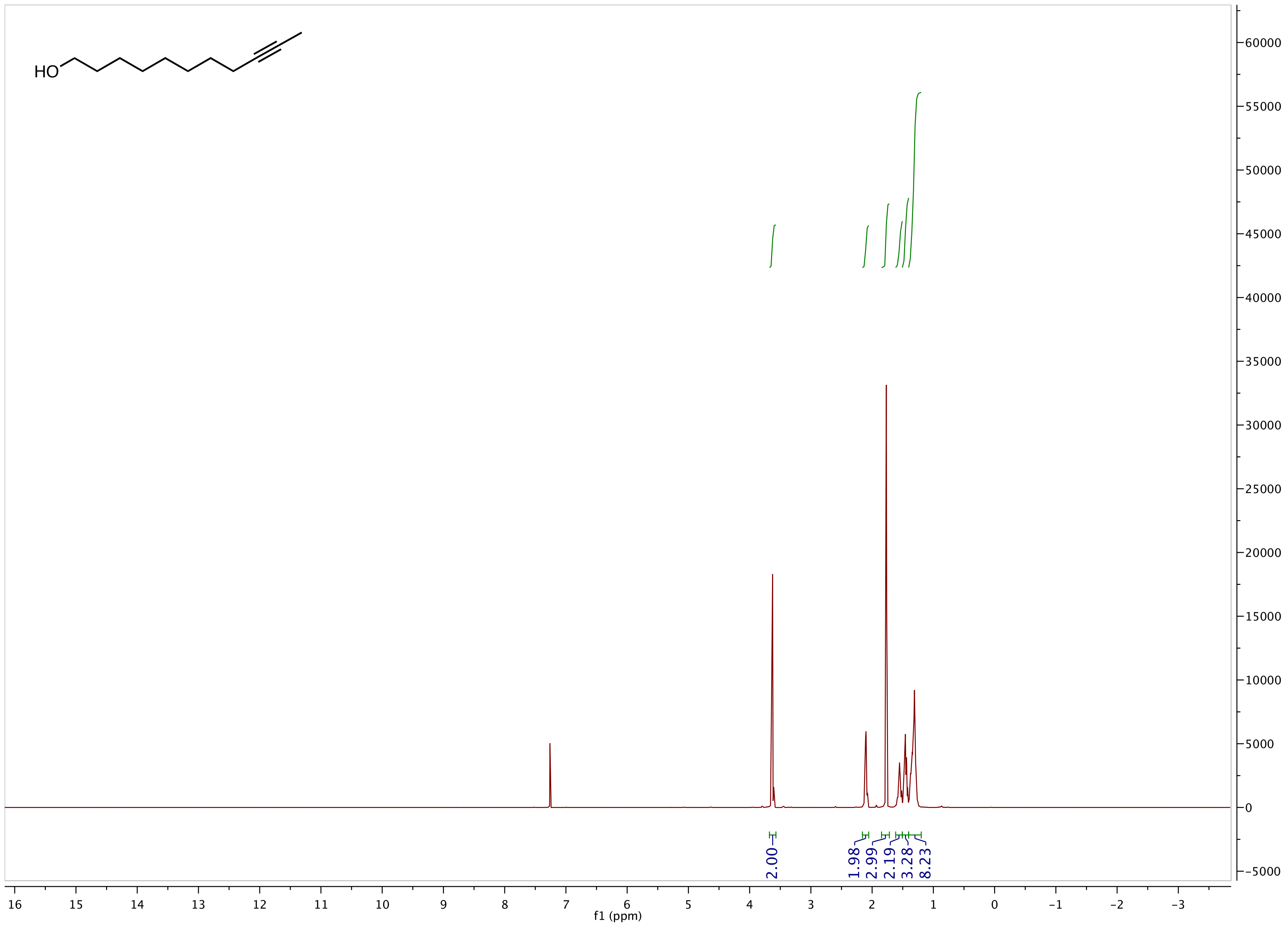
^{13}C NMR of *trans*-8-decen-1-ol (101 MHz, $CDCl_3$)



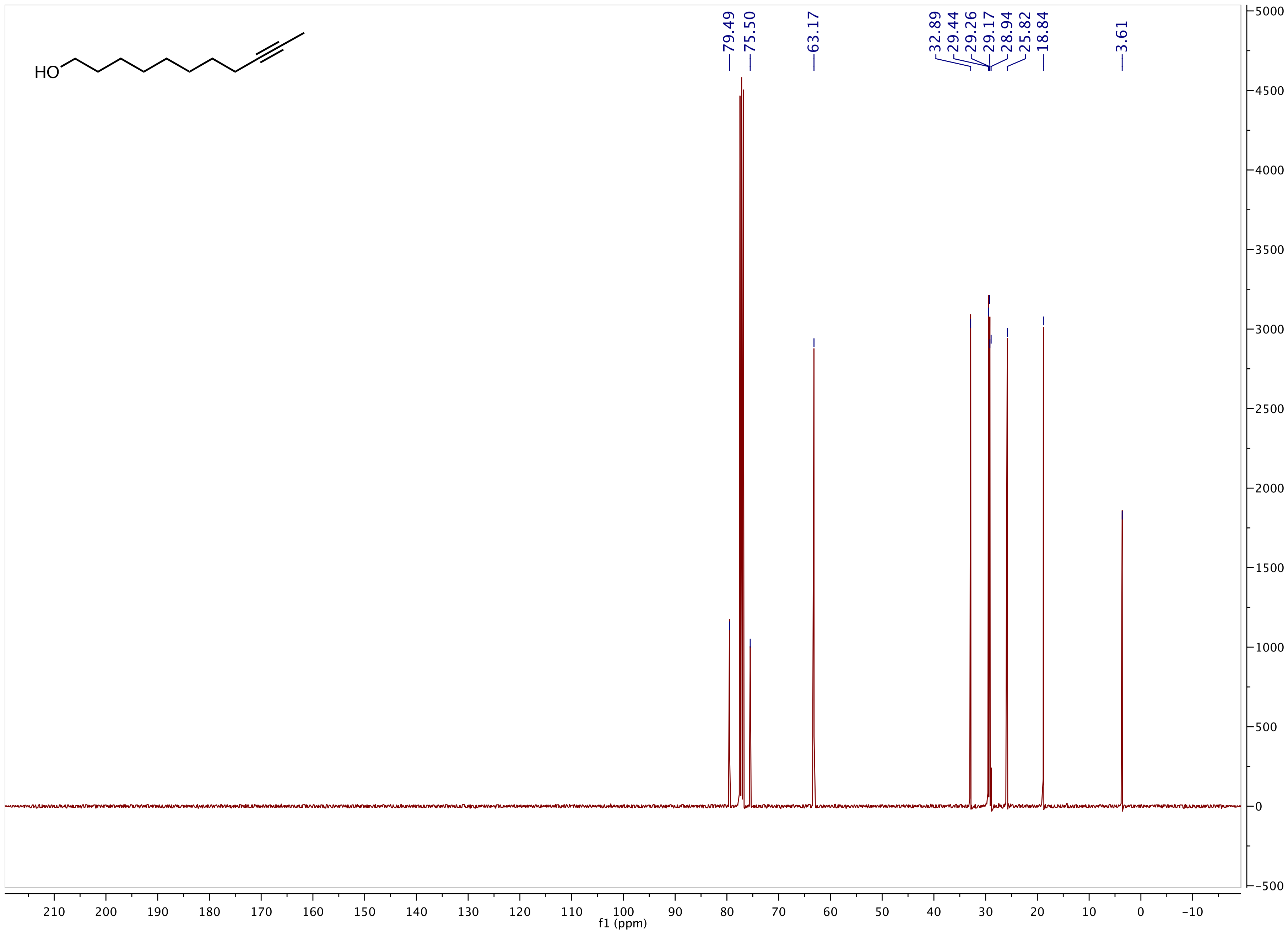
^{1}H NMR of *trans*-8-decenoic acid (400 MHz, $CDCl_3$)



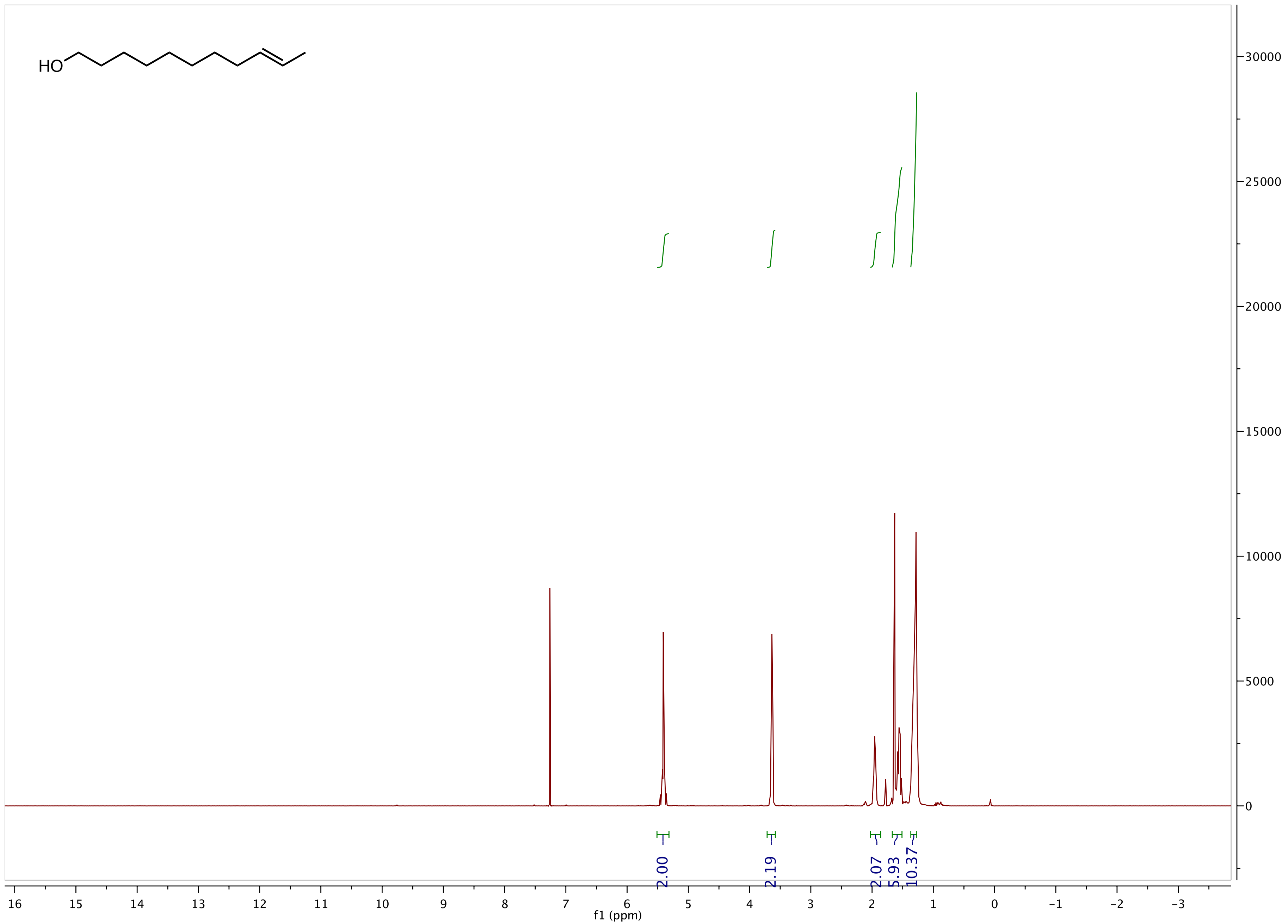
^{13}C NMR of *trans*-8-decenoic acid (101 MHz, $CDCl_3$)



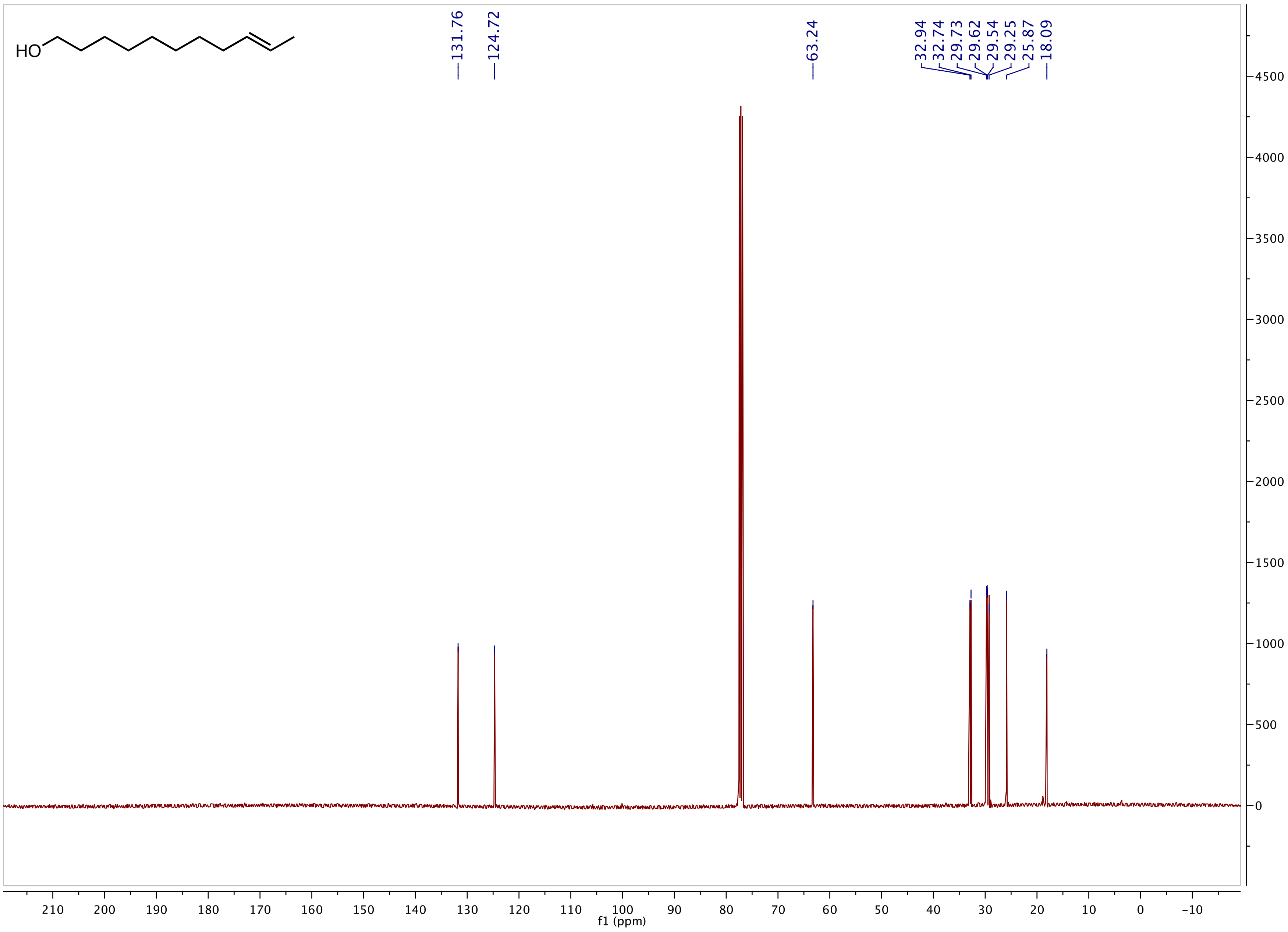
^{1}H NMR of undec-9-yn-1-ol (400 MHz, CDCl$_3$)



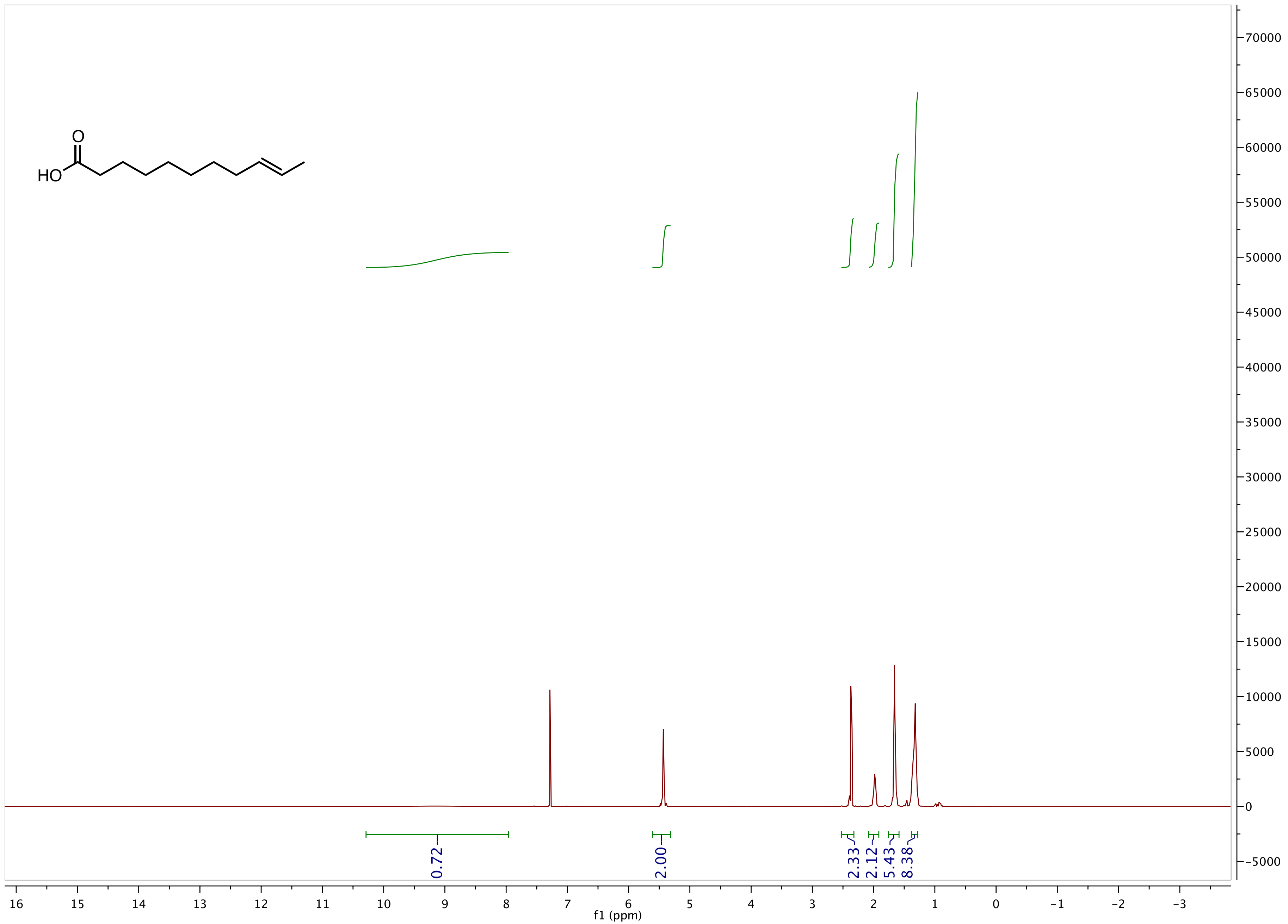
^{13}C NMR of undec-9-yn-1-ol (101 MHz, $CDCl_3$)



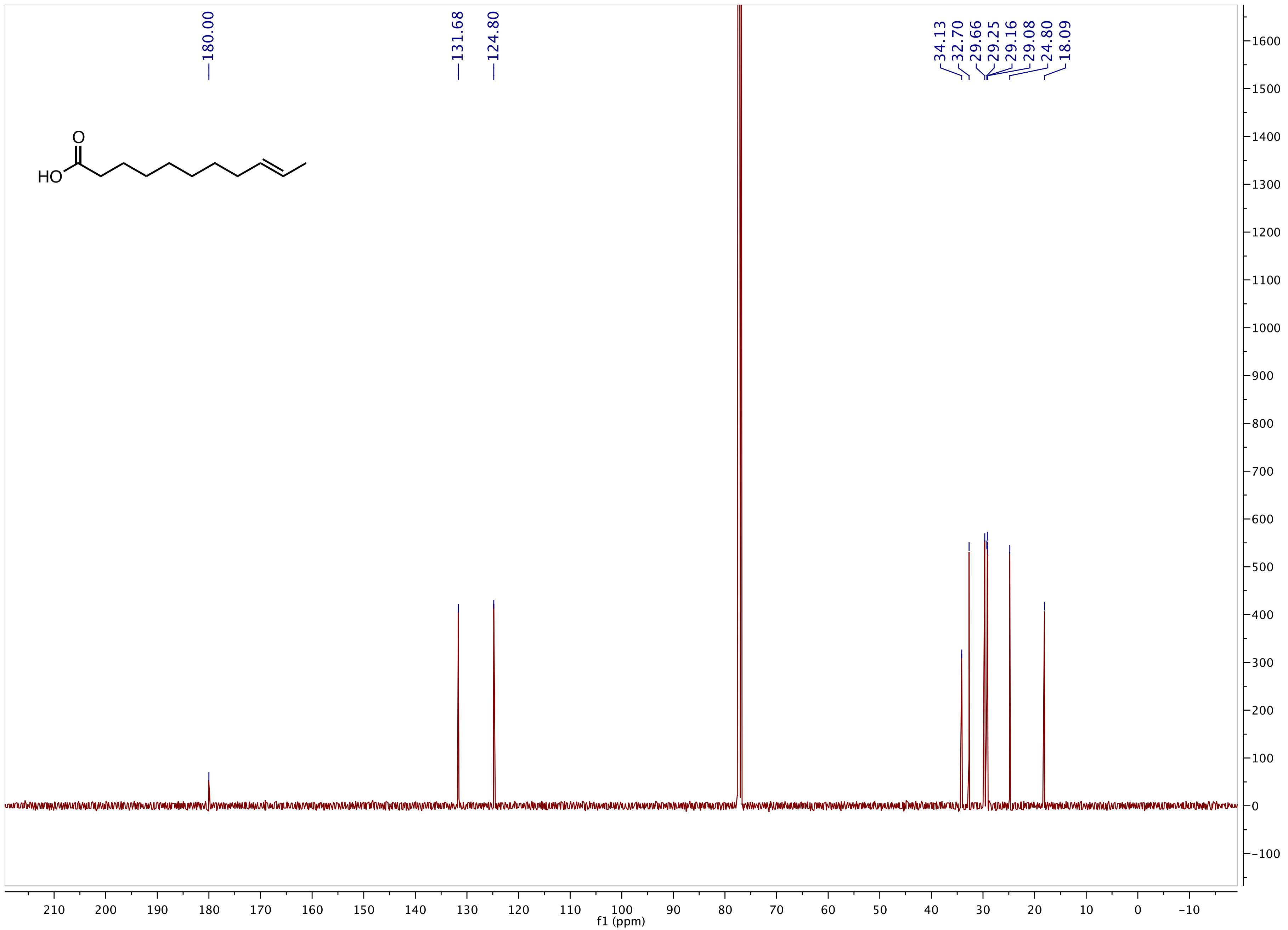
^{1}H NMR of *trans*-9-undecen-1-ol (400 MHz, $CDCl_3$)



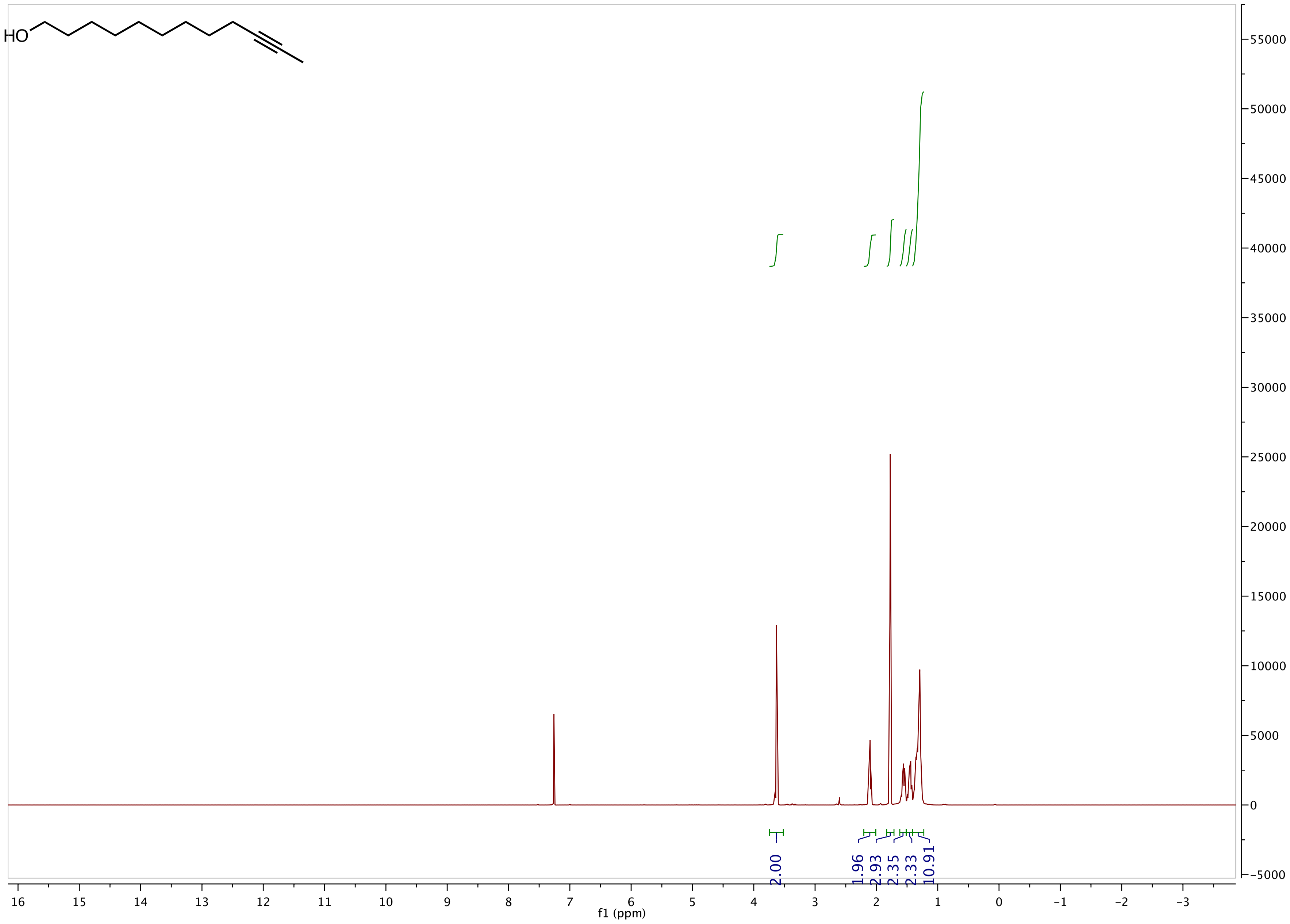
^{13}C NMR of *trans*-9-undecen-1-ol (101 MHz, $CDCl_3$)



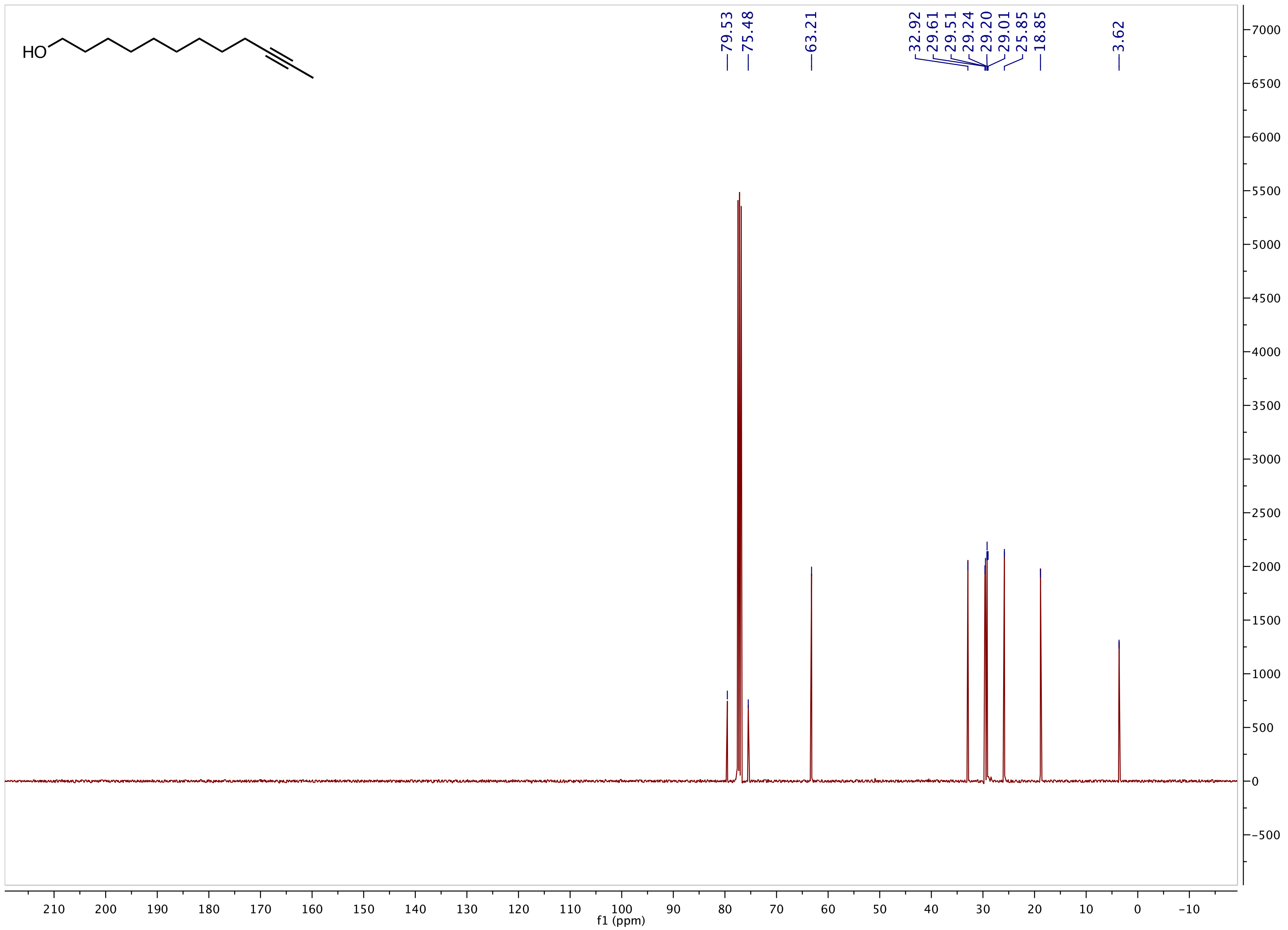
^{1}H NMR of *trans*-9-undecenoic acid (400 MHz, CDCl$_3$)



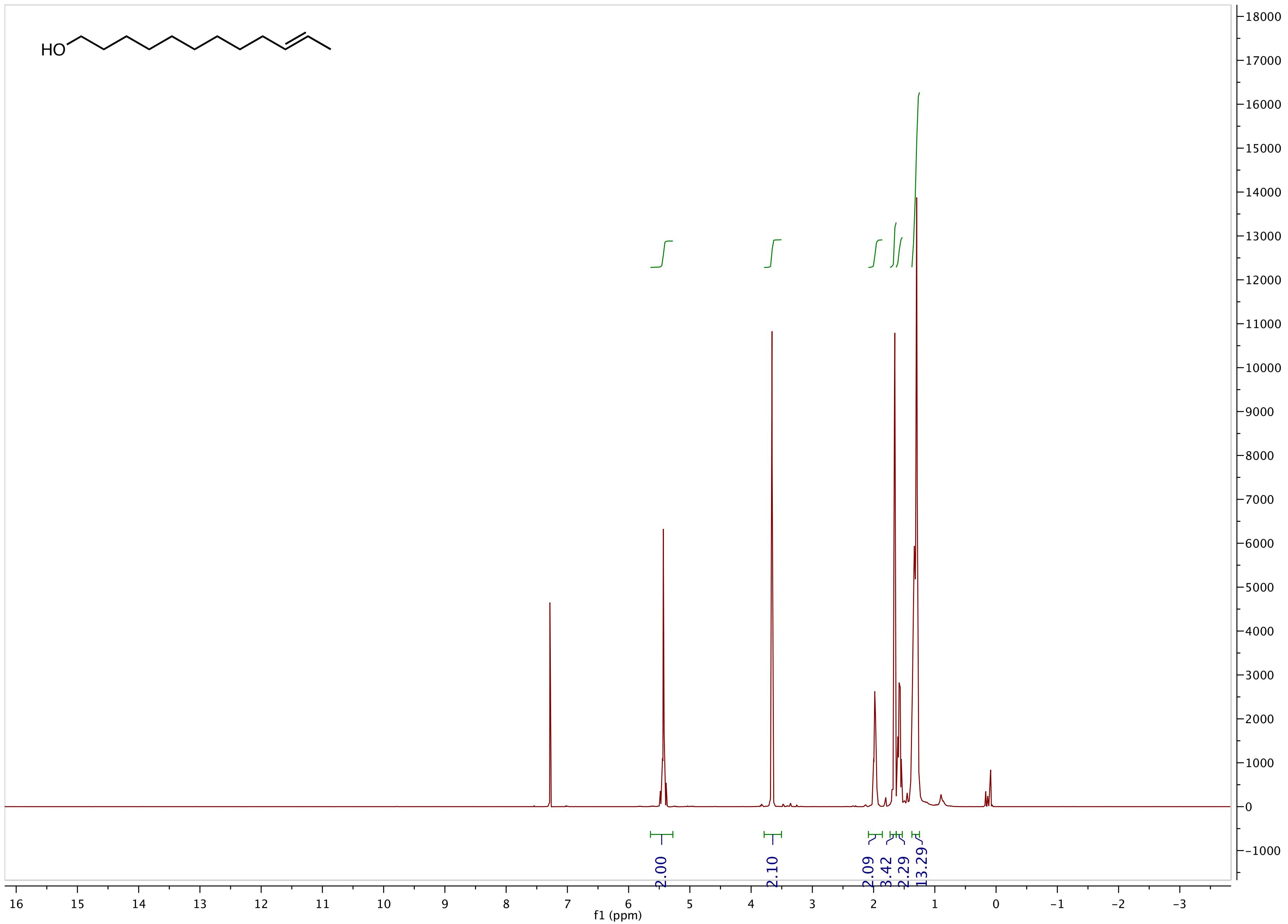
^{13}C NMR of *trans*-9-undecenoic acid (101 MHz, CDCl$_3$)



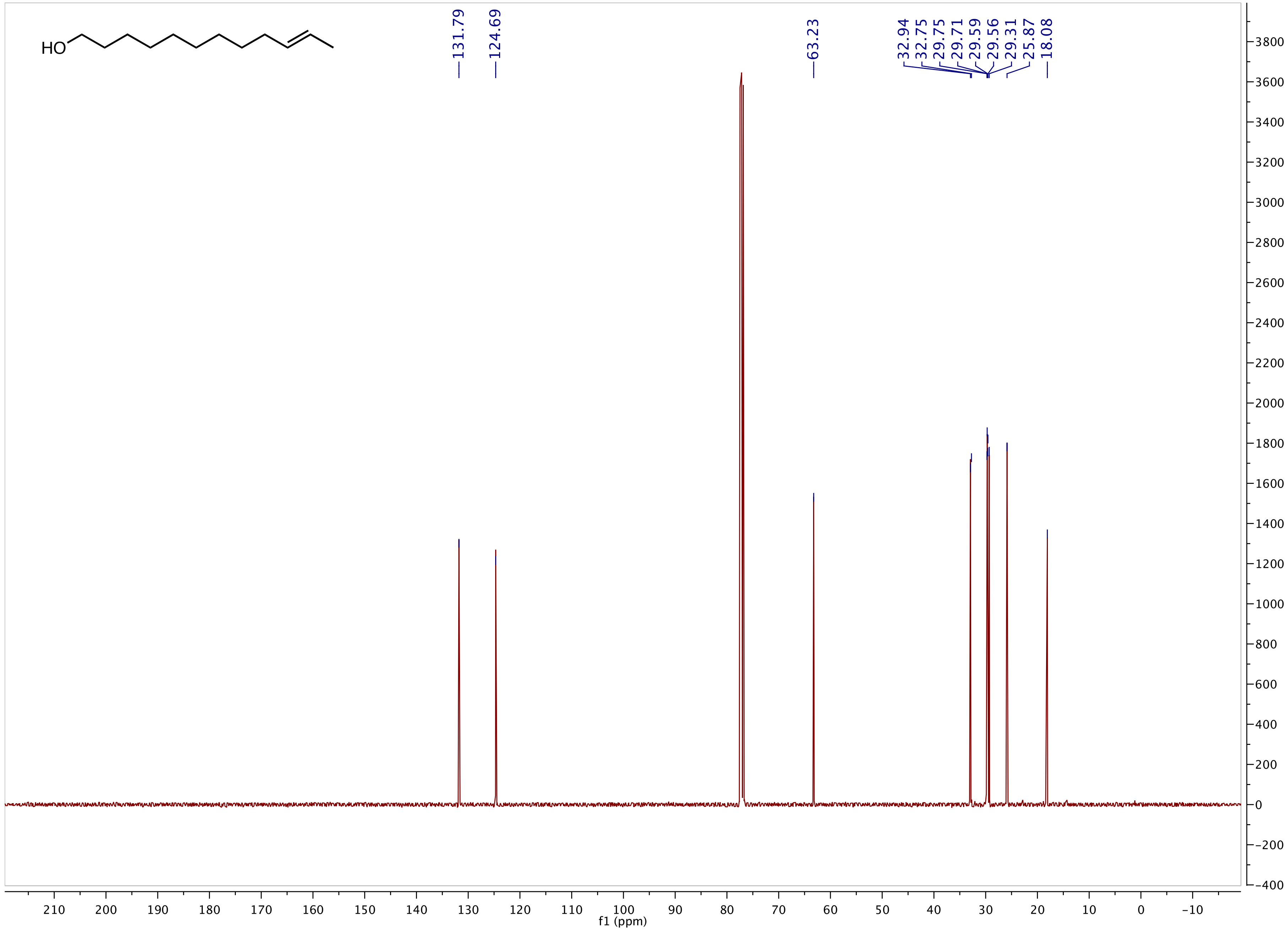
^{1}H NMR of dodec-10-yn-1-ol (400 MHz, $CDCl_3$)



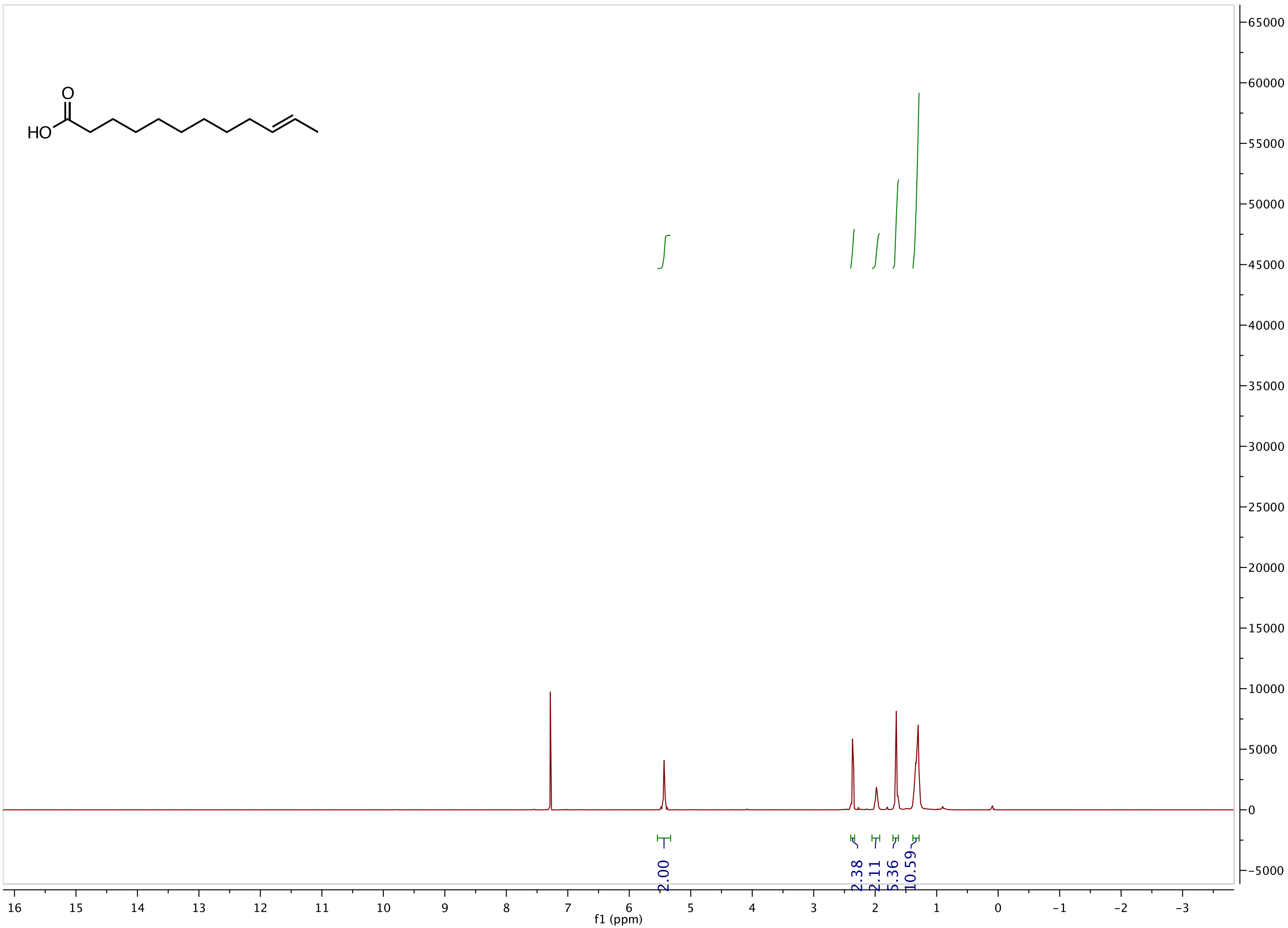
^{13}C NMR of dodec-10-yn-1-ol (101 MHz, $CDCl_3$)



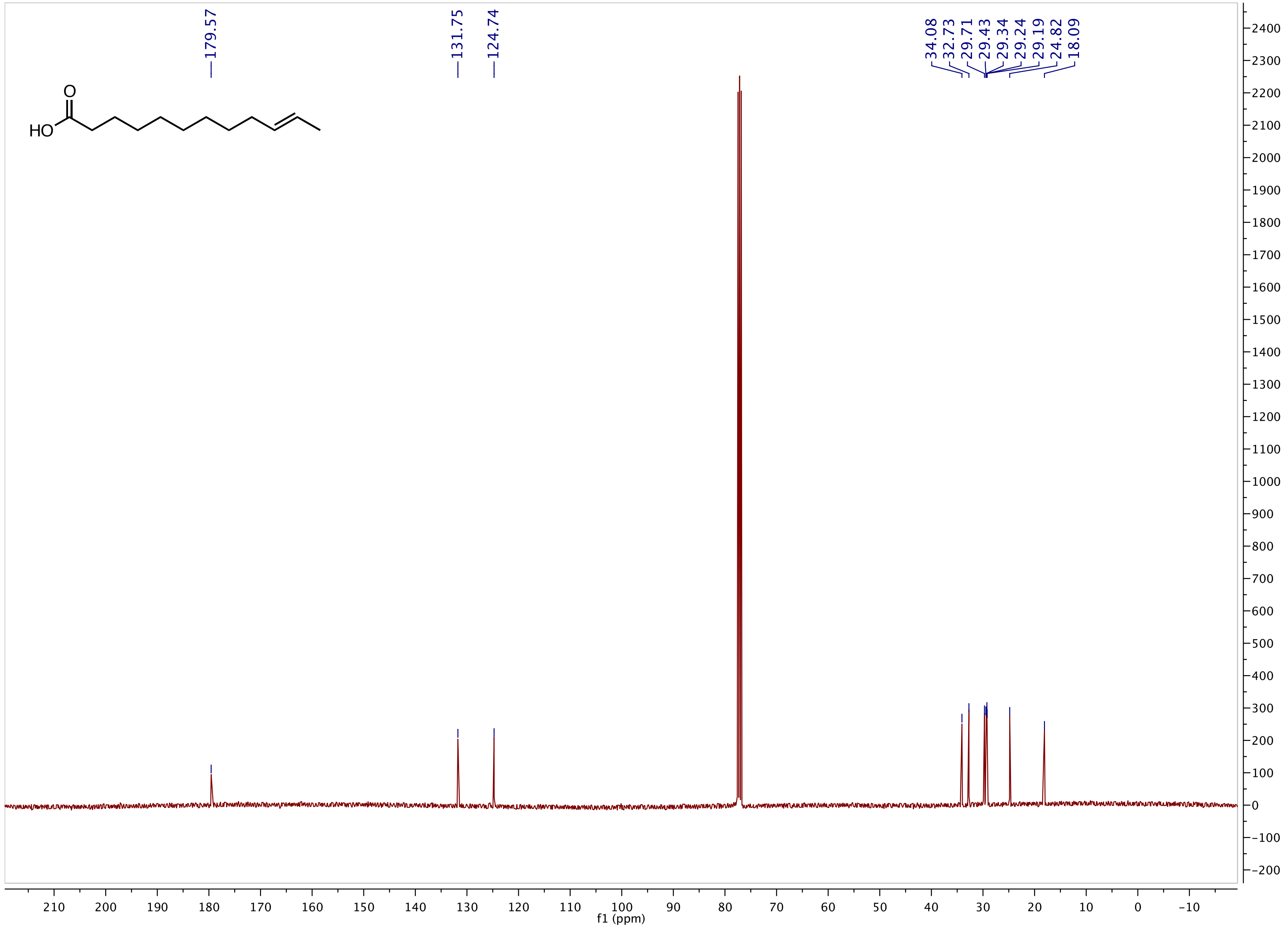
^{1}H NMR of *trans*-10-dodecen-1-ol (400 MHz, $CDCl_3$)



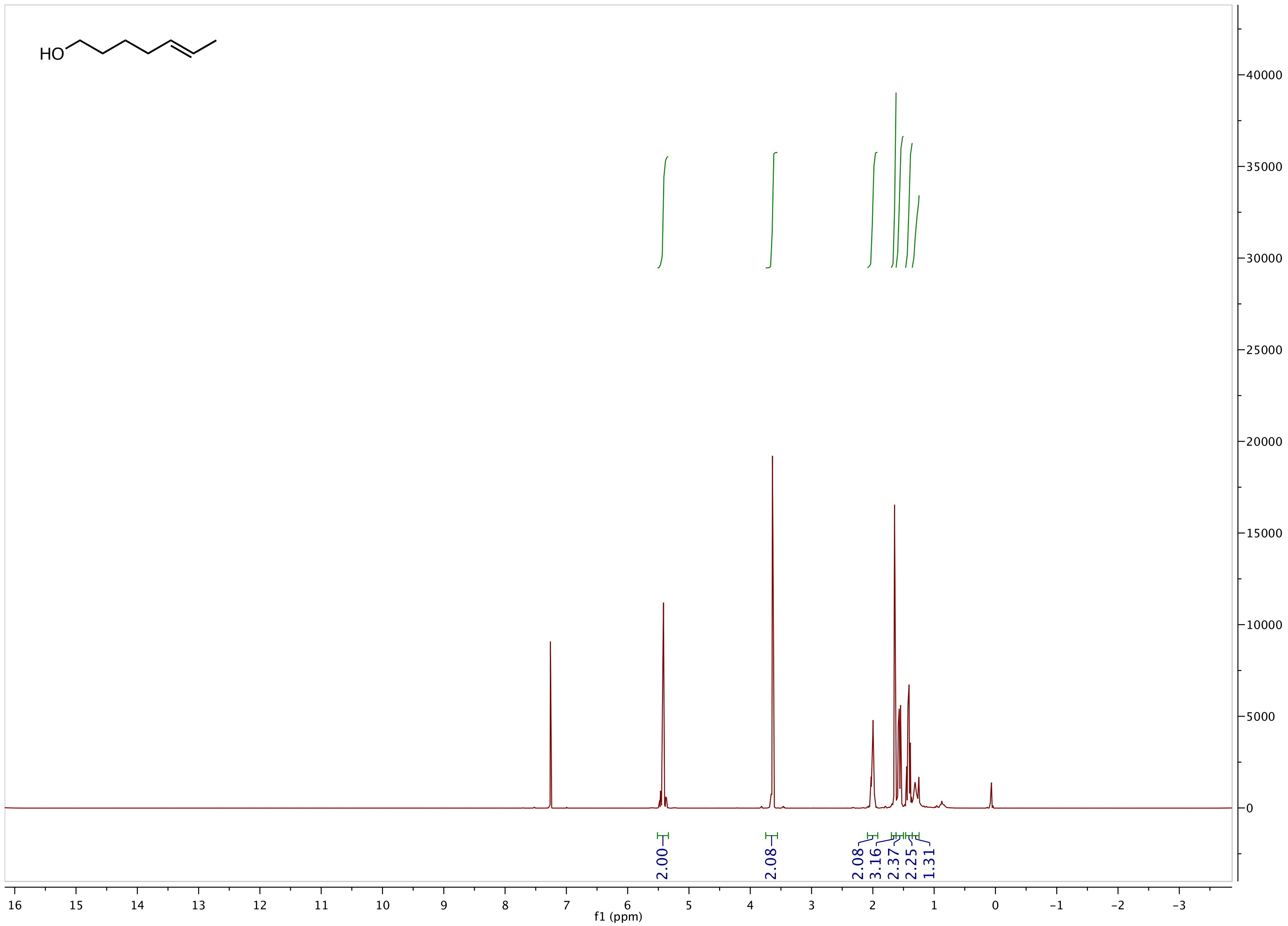
^{13}C NMR of *trans*-10-dodecen-1-ol (101 MHz, $CDCl_3$)



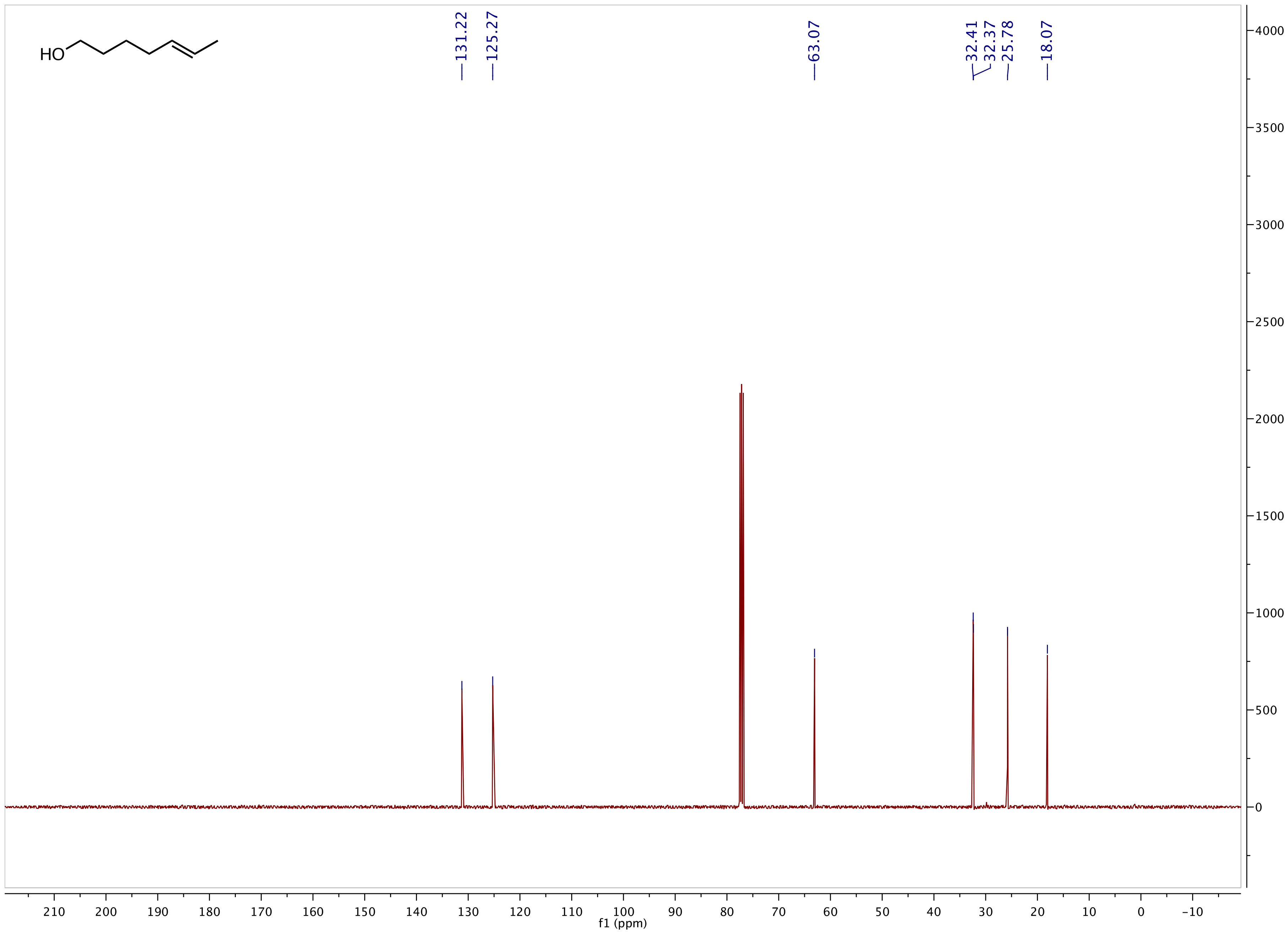
^{1}H NMR of *trans*-10-dodecenoic acid (400 MHz, $CDCl_3$)



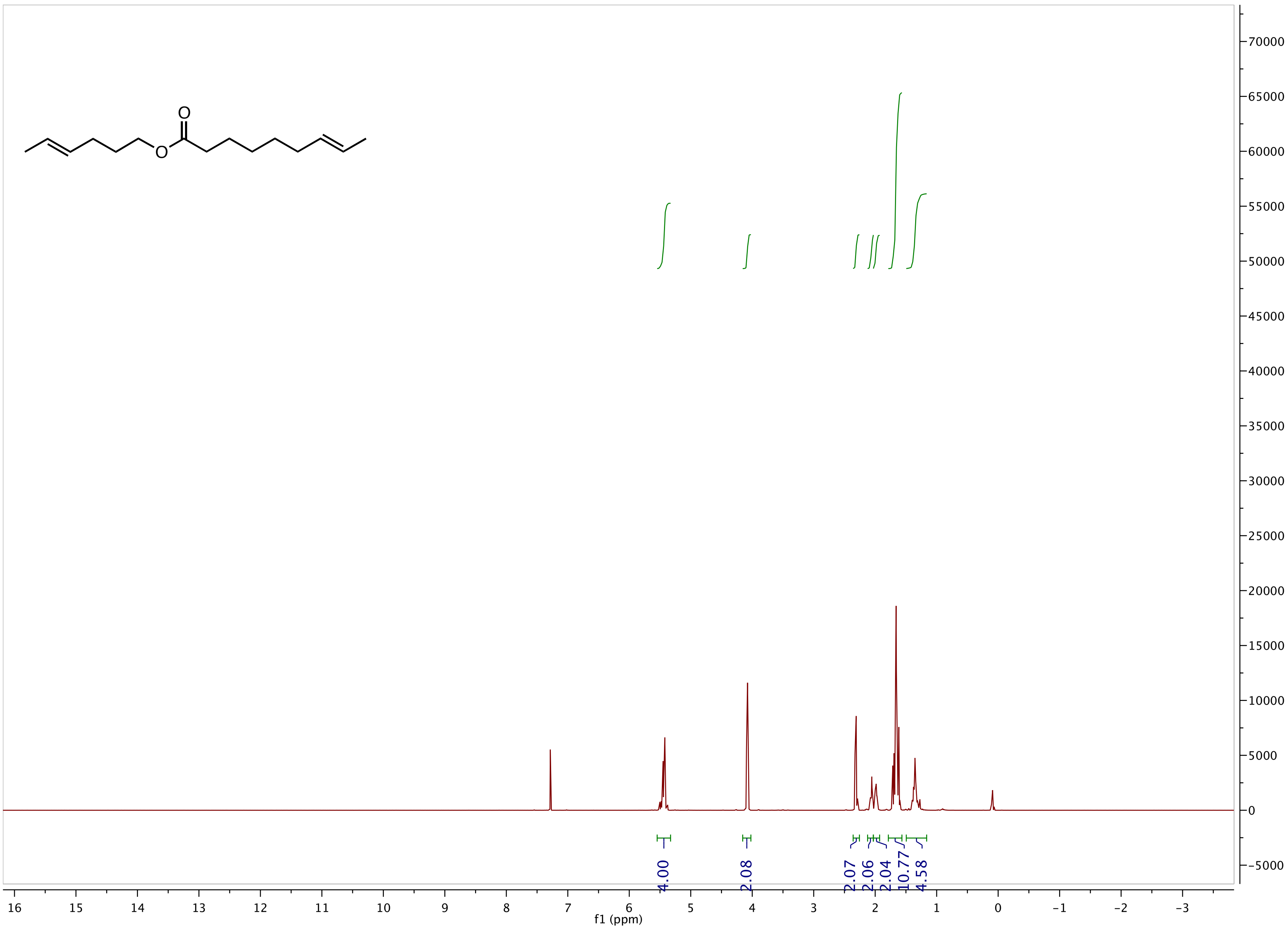
^{13}C NMR of *trans*-10-dodecenoic acid (101 MHz, $CDCl_3$)



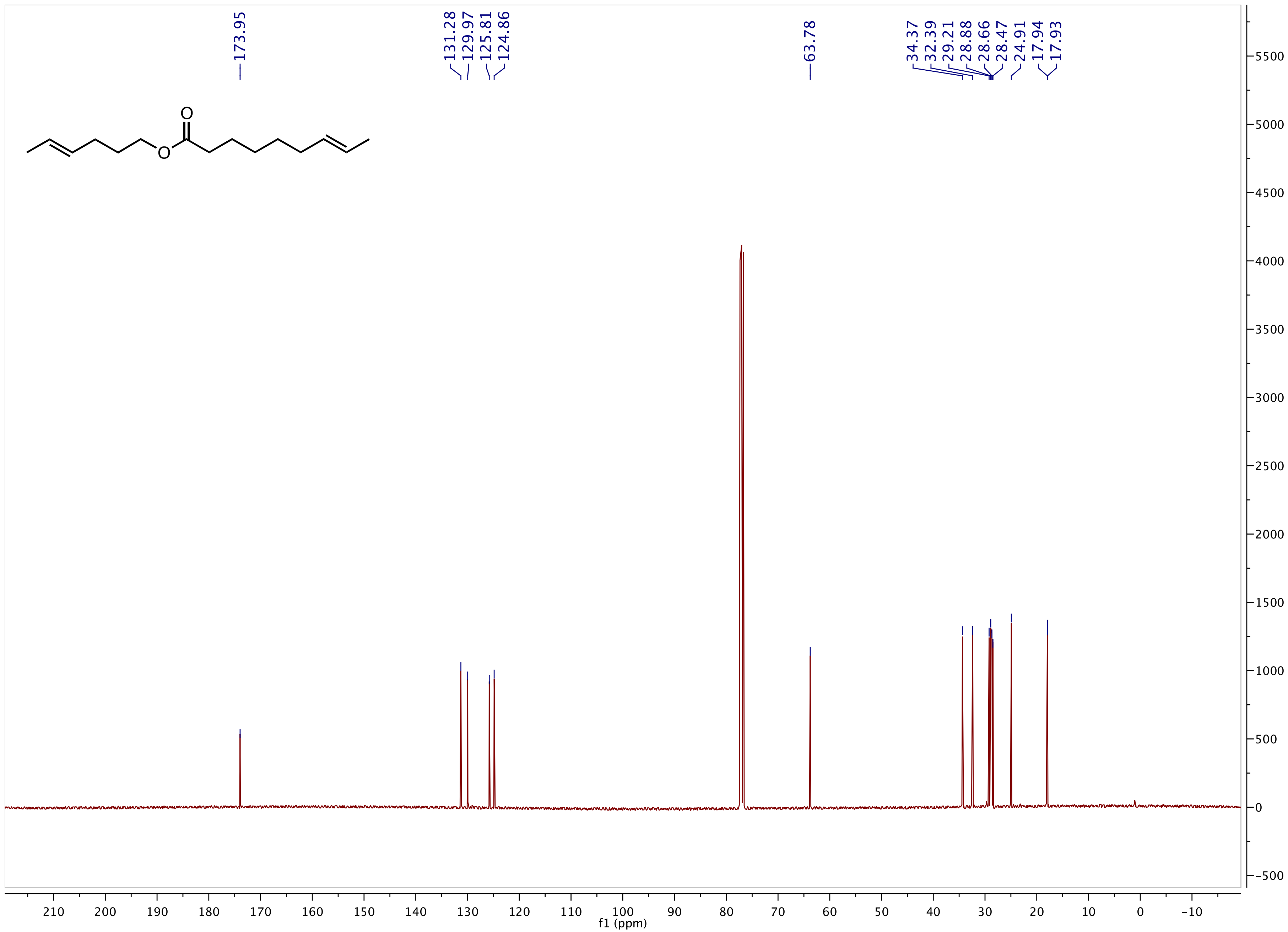
^{1}H NMR of *trans*-5-hepten-1-ol (400 MHz, $CDCl_3$)



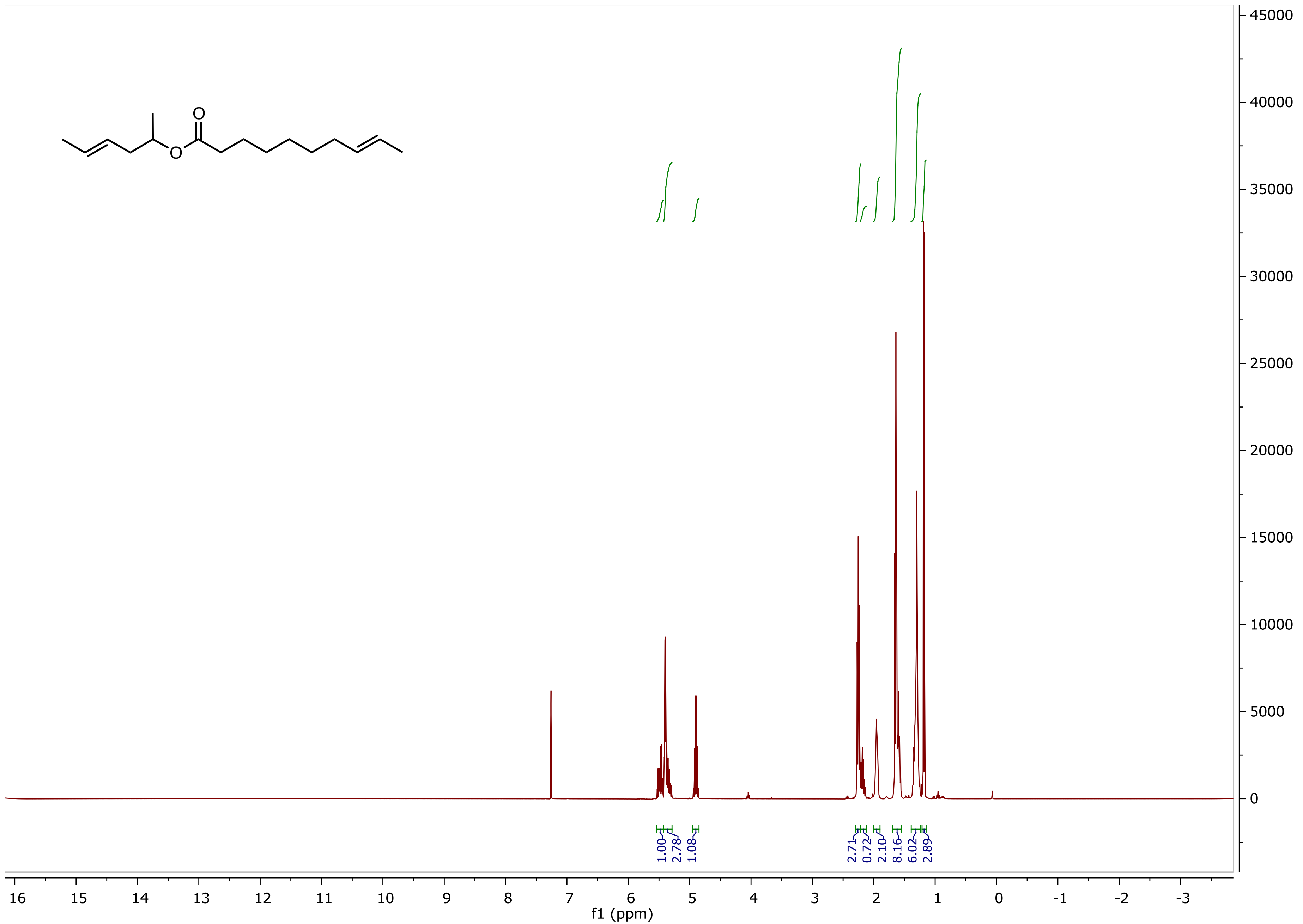
^{13}C NMR of *trans*-5-hepten-1-ol (101 MHz, $CDCl_3$)



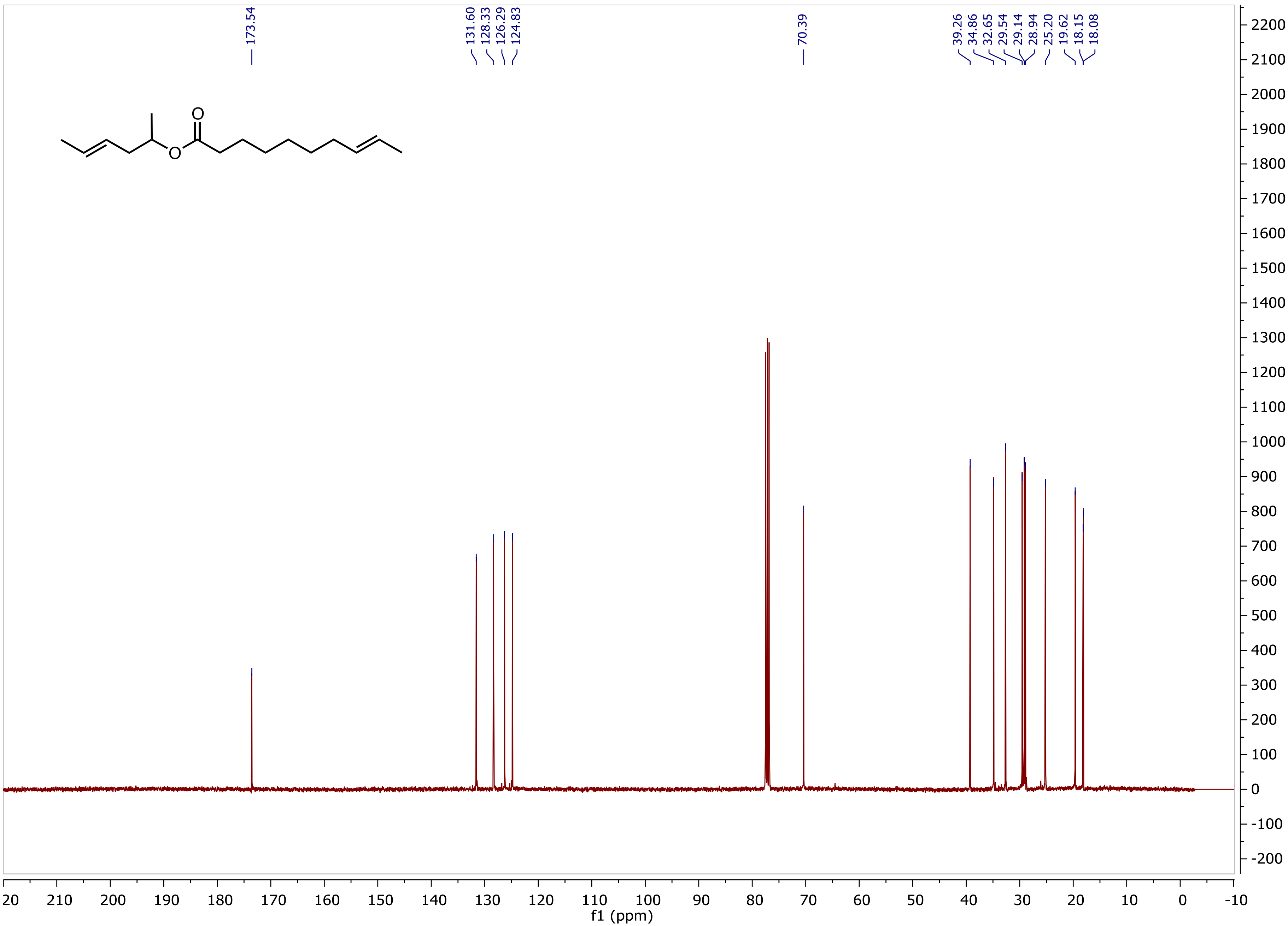
^{1}H NMR of (*E*)-(*E*)-hex-4-en-1-yl non-7-enoate **7** (400 MHz, $CDCl_3$)



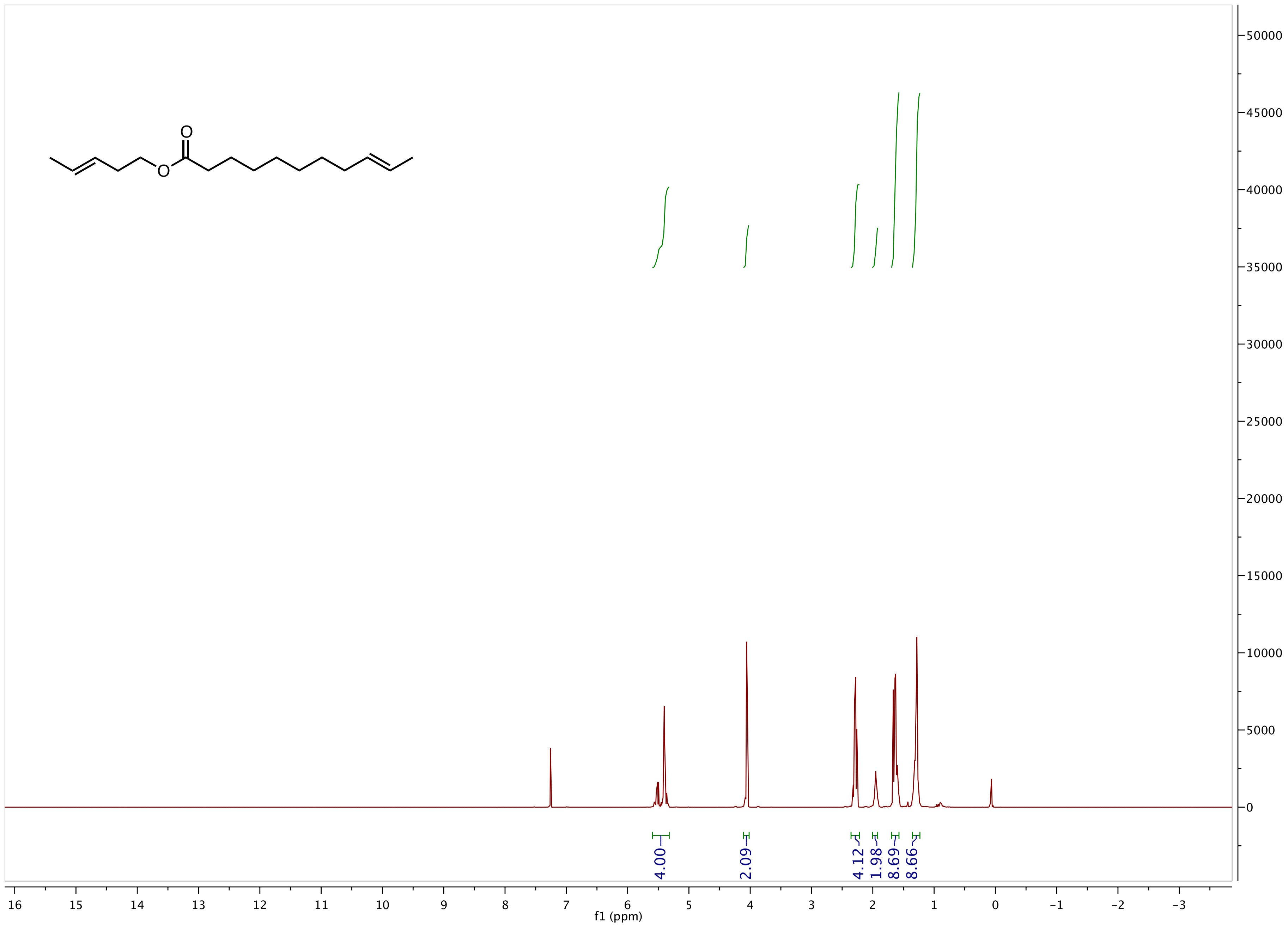
^{13}C NMR of (*E*)-(*E*)-hex-4-en-1-yl non-7-enoate **7** (101 MHz, CDCl$_3$)



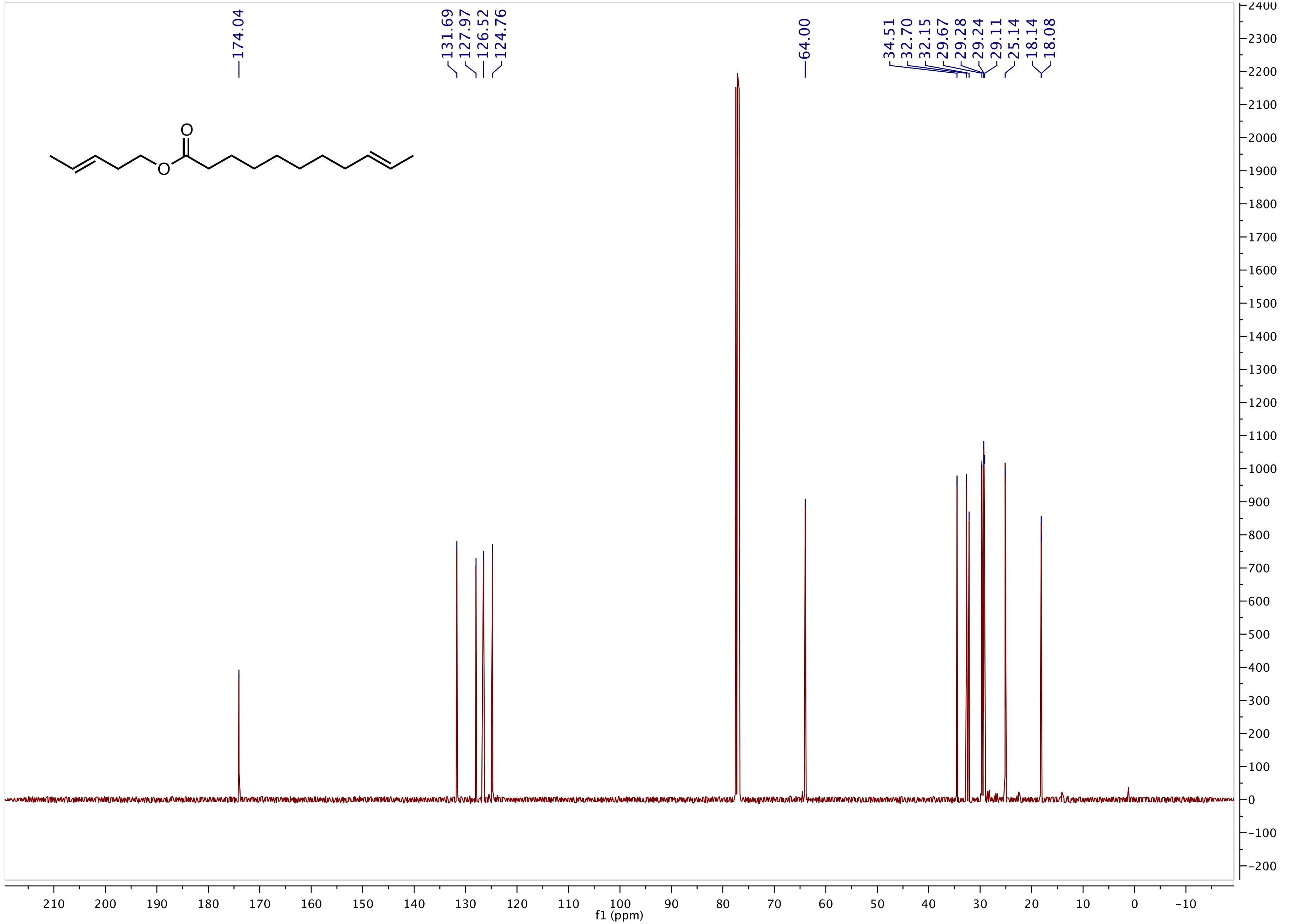
^{1}H NMR of (*E*)-(*E*)-hex-4-en-2-yl dec-8-enoate (400 MHz, $CDCl_3$)



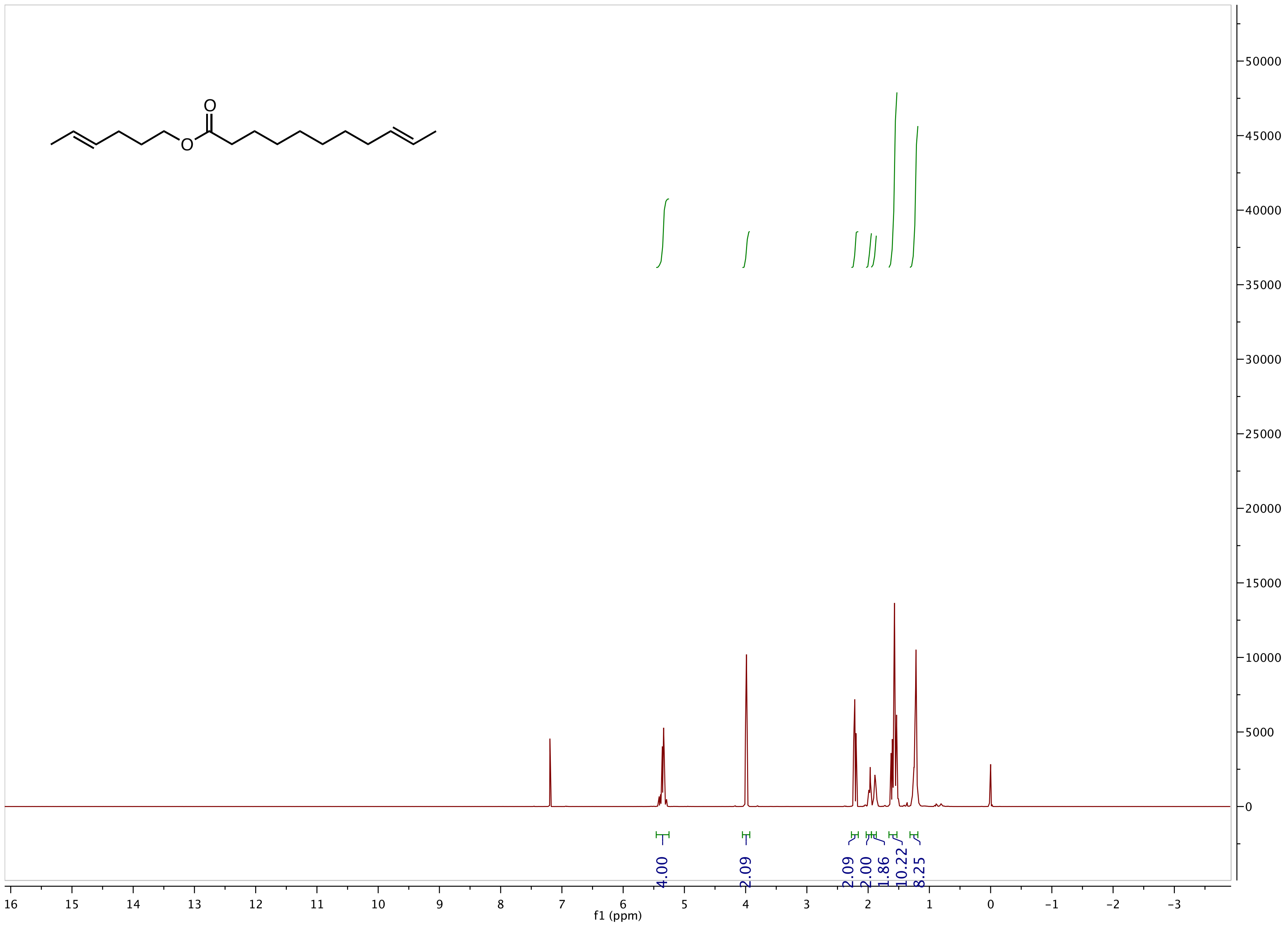
^{13}C NMR of (*E*)-(*E*)-hex-4-en-2-yl dec-8-enoate (101 MHz, $CDCl_3$)



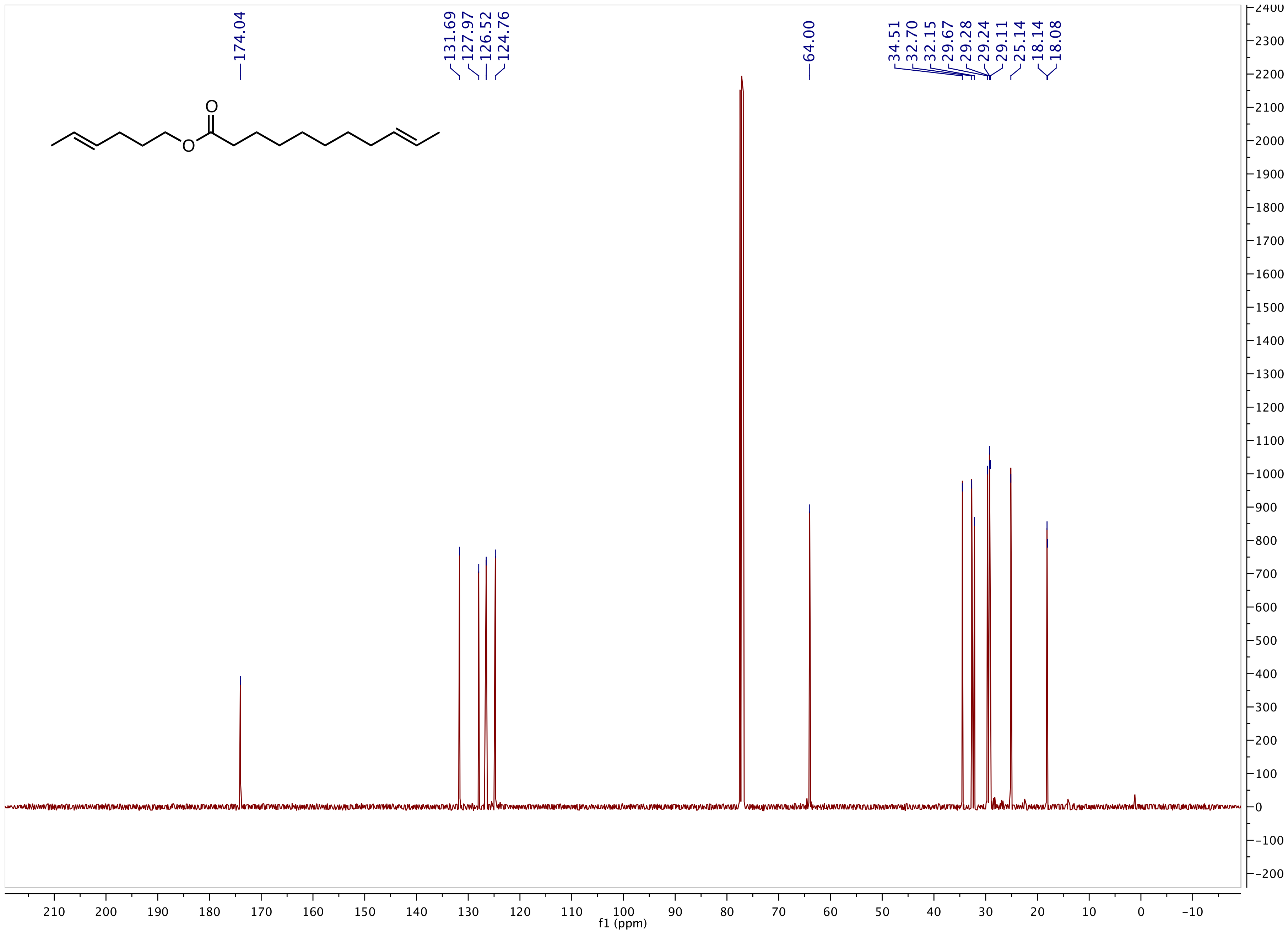
^{1}H NMR of (*E*)-(*E*)-pent-3-en-1-yl undec-10-enoate (400 MHz, $CDCl_3$)



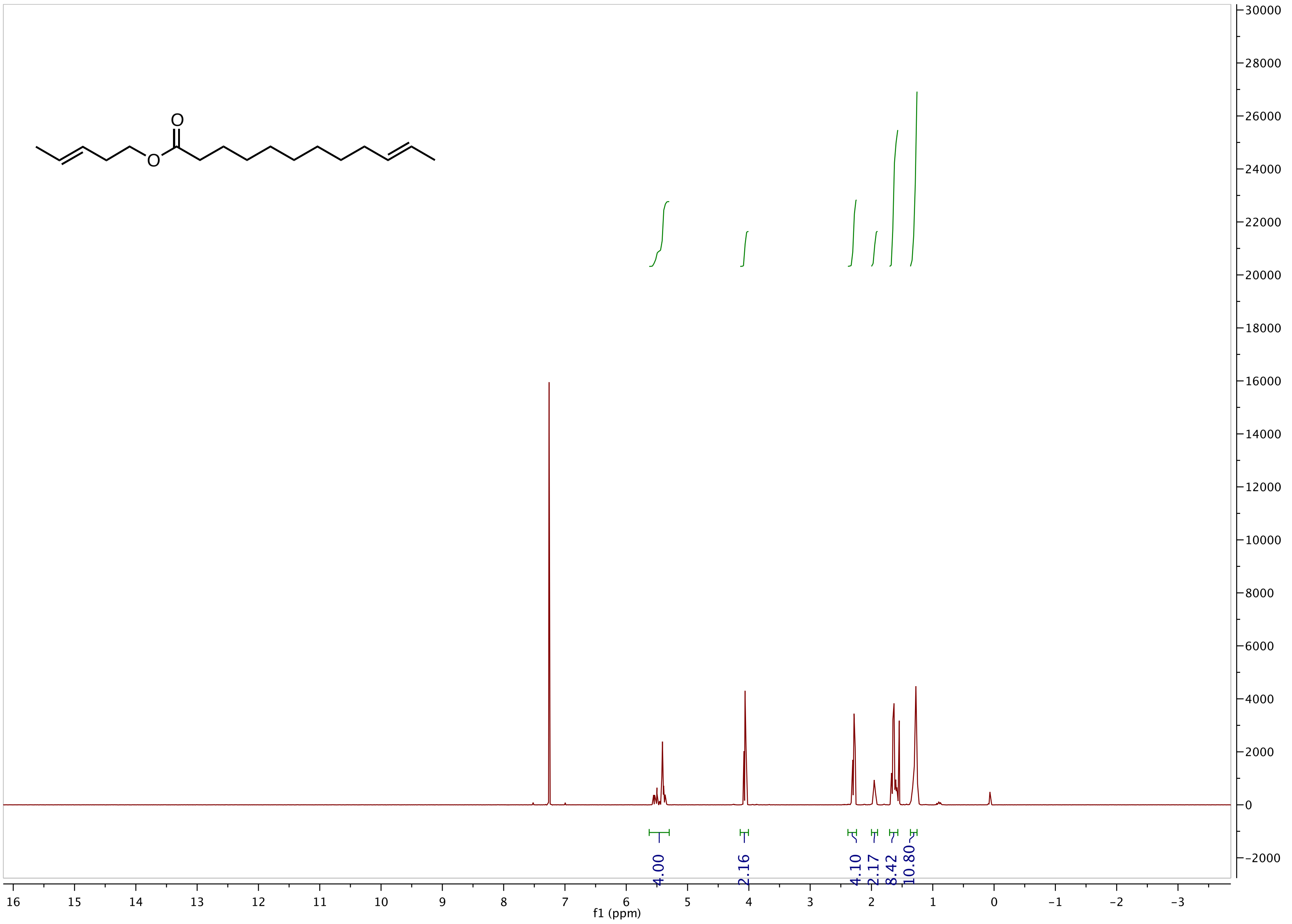
^{13}C NMR of (*E*)-(*E*)-pent-3-en-1-yl undec-10-enoate (101 MHz, $CDCl_3$)



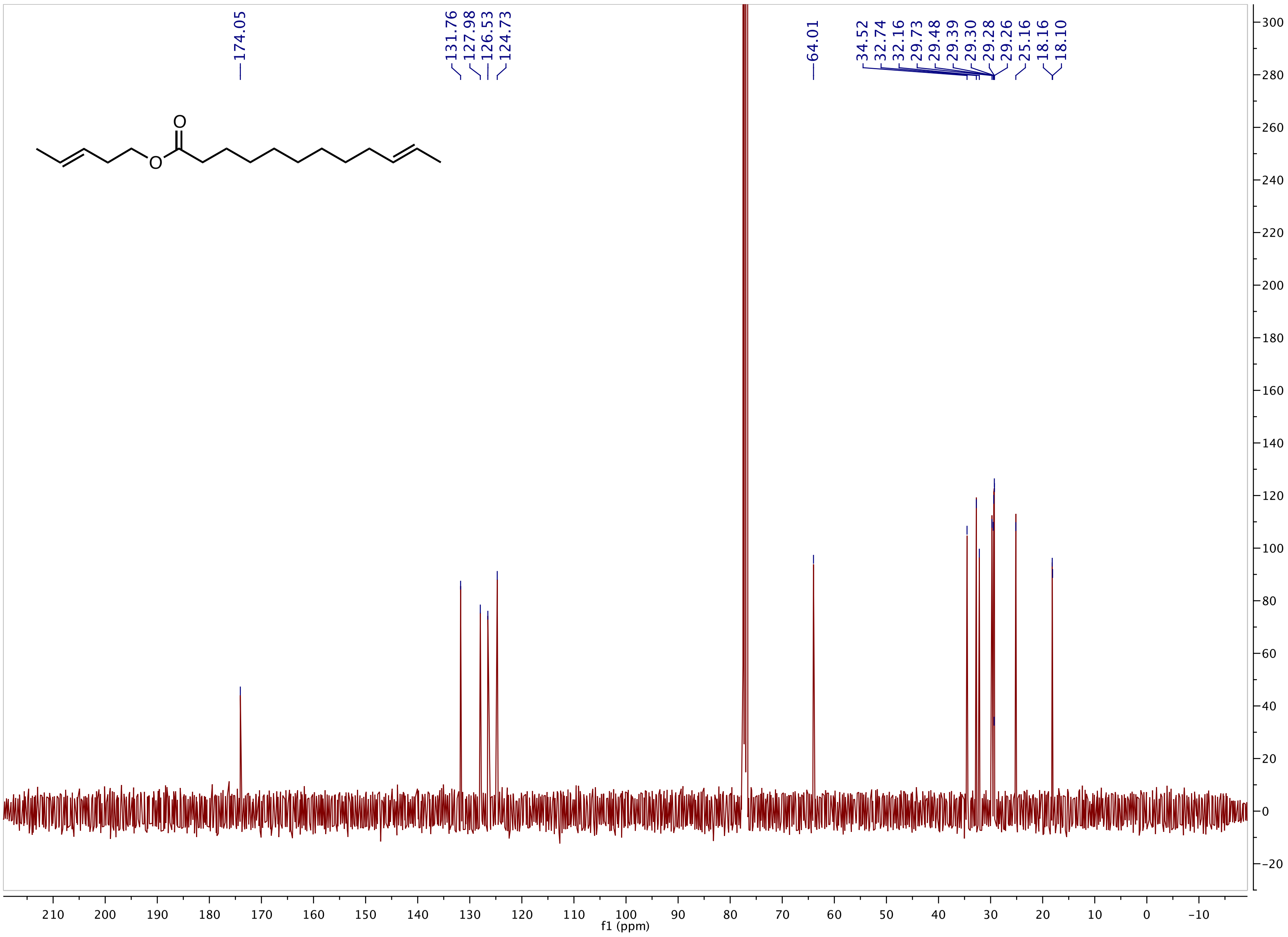
^{1}H NMR of (*E*)-(*E*)-hex-4-en-1-yl undec-10-enoate (400 MHz, $CDCl_3$)



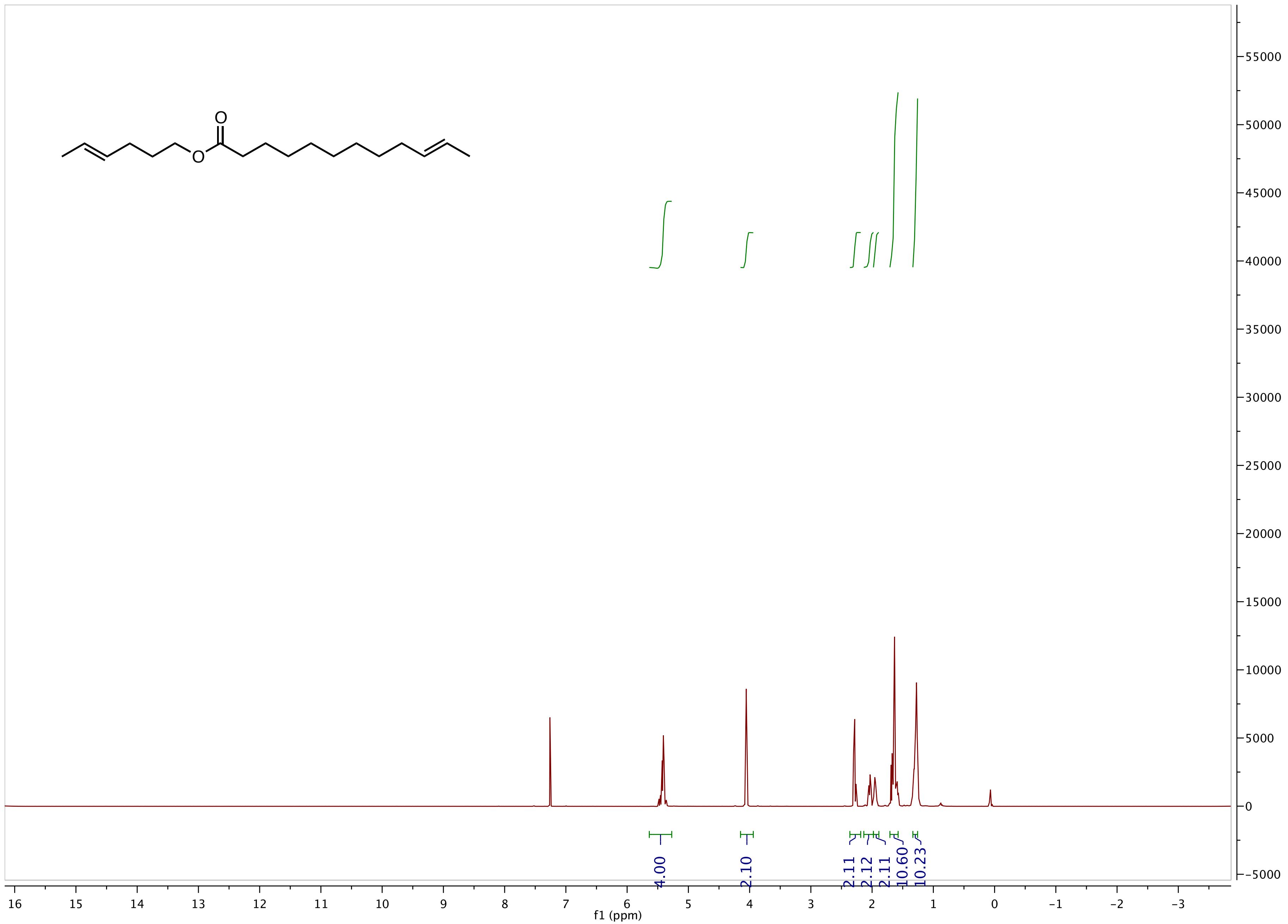
^{13}C NMR of (*E*)-(*E*)-hex-4-en-1-yl undec-10-enoate (101 MHz, $CDCl_3$)



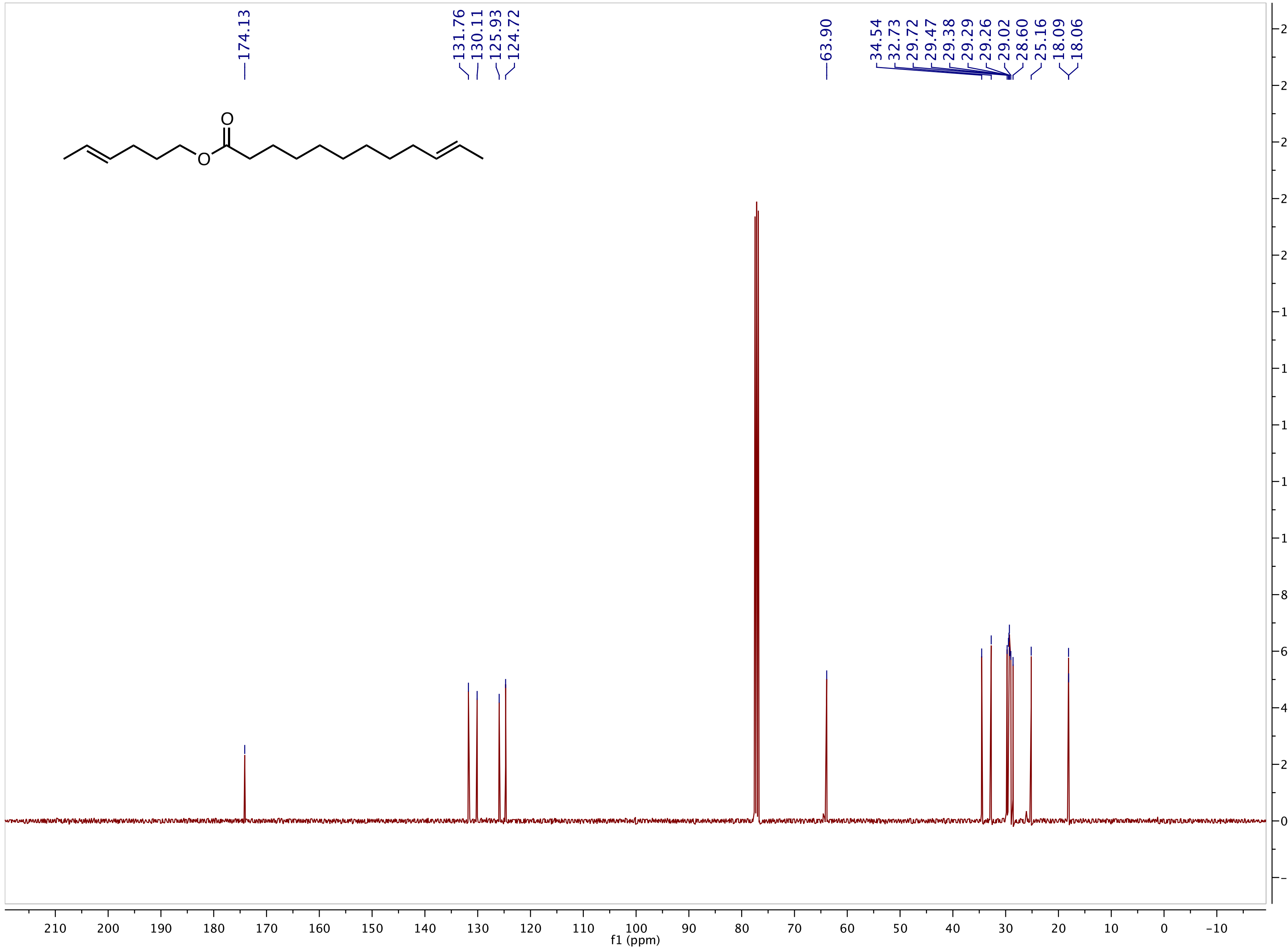
^{1}H NMR of (*E*)-(*E*)-pent-3-en-1-yl dodec-10-enoate (400 MHz, $CDCl_3$)



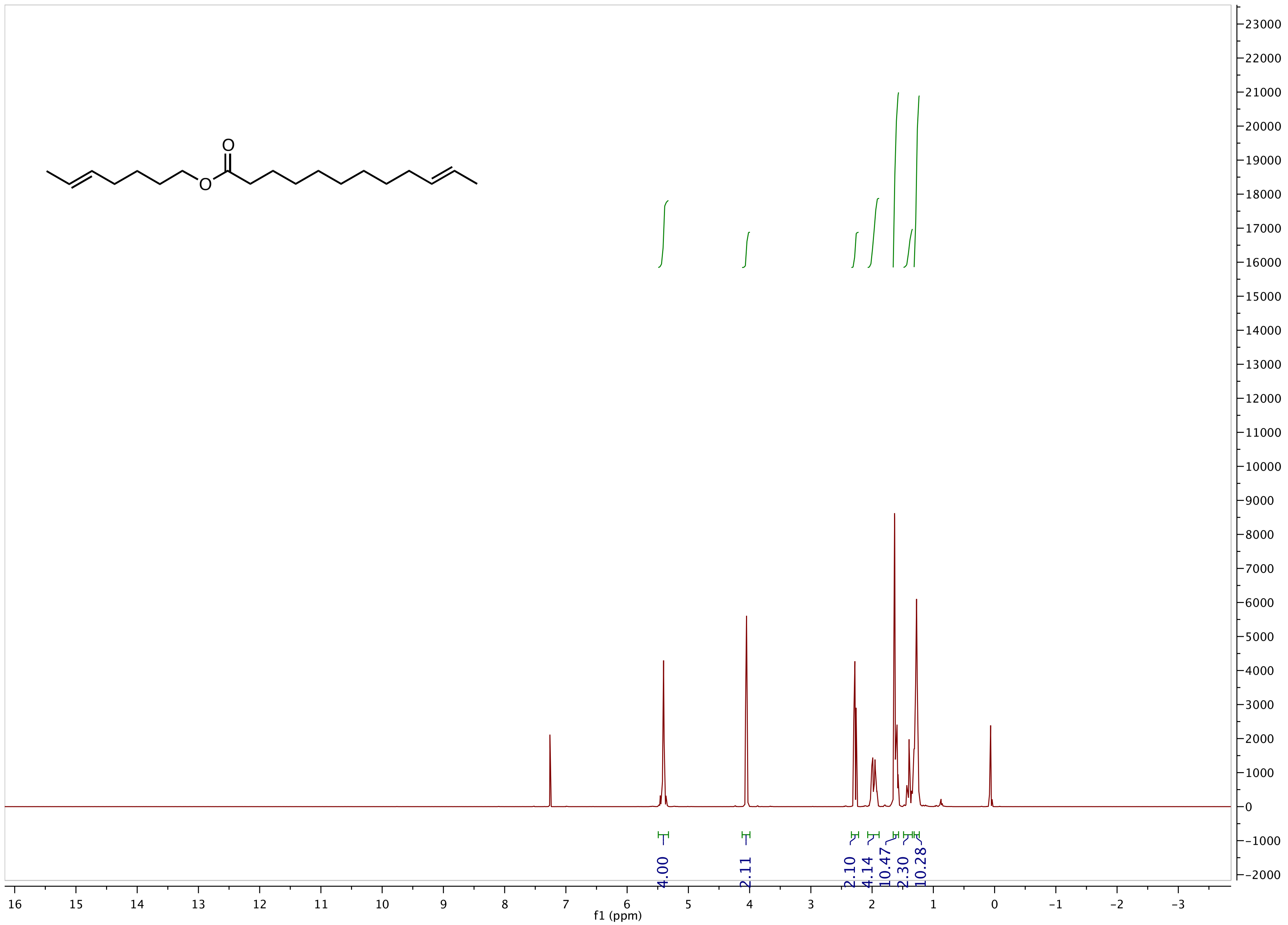
^{13}C NMR of (*E*)-(*E*)-pent-3-en-1-yl dodec-10-enoate (101 MHz, $CDCl_3$)



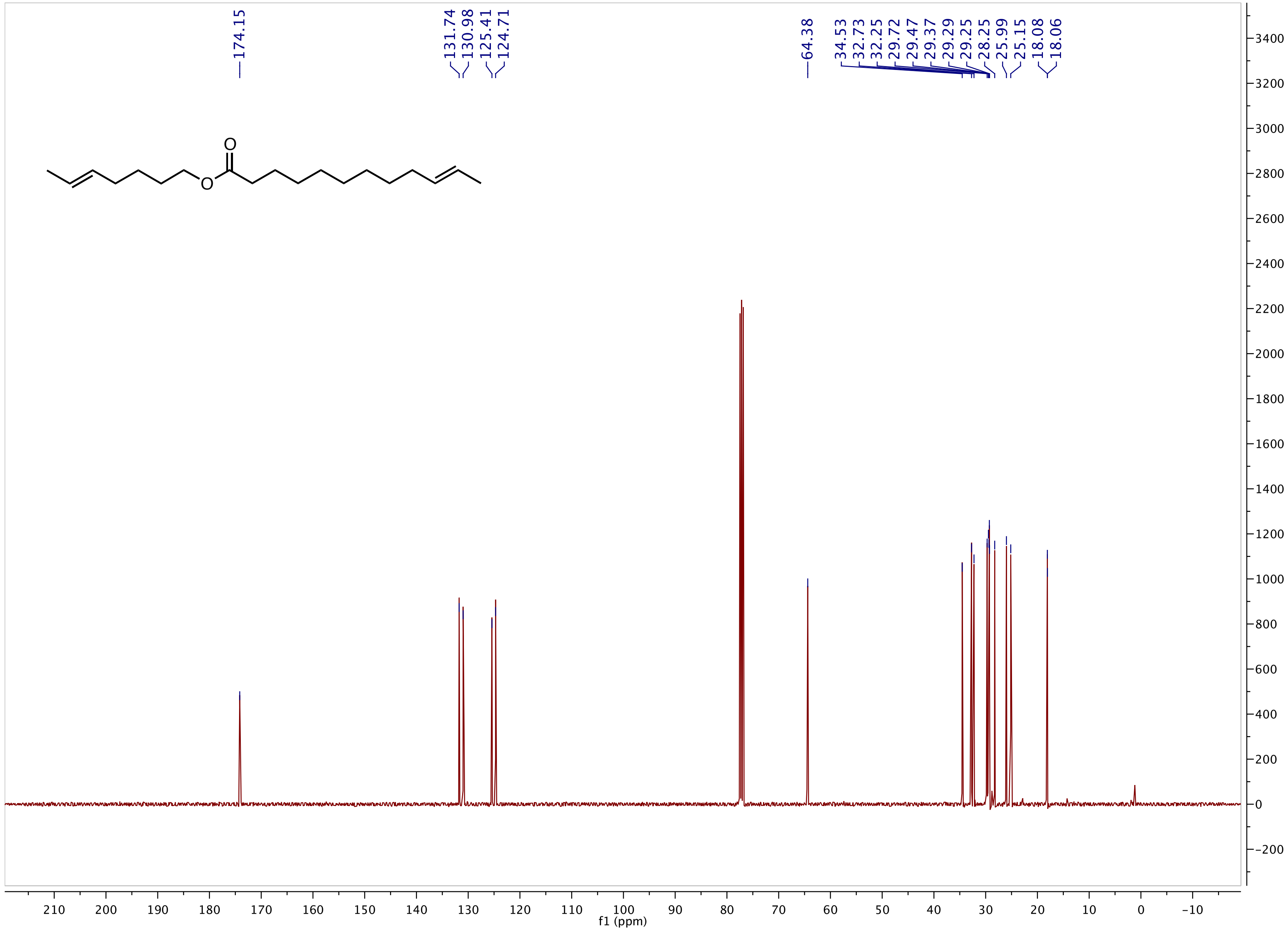
^{1}H NMR of (*E*)-(*E*)-hex-4-en-1-yl dodec-10-enoate (400 MHz, $CDCl_3$)



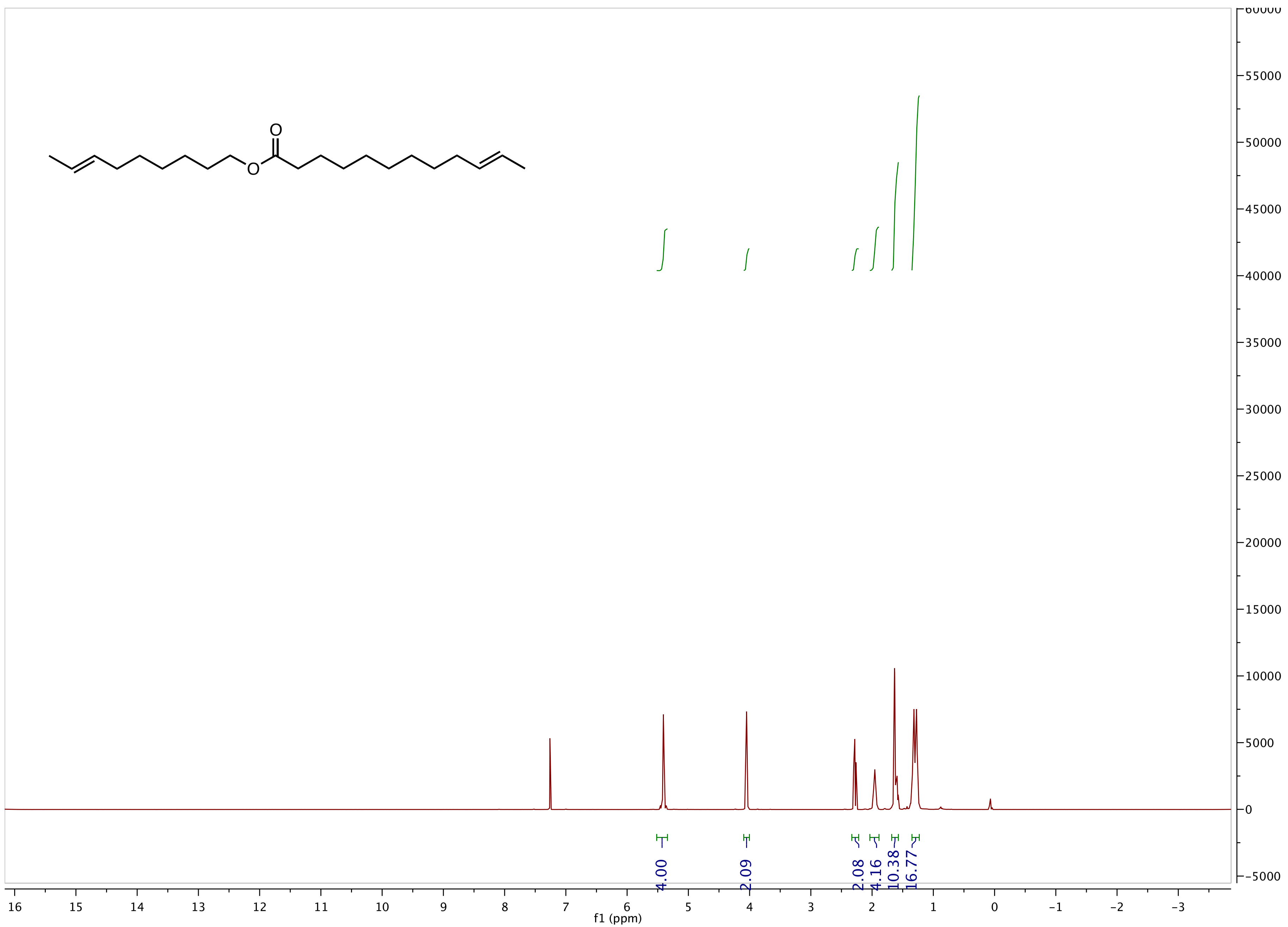
^{13}C NMR of (*E*)-(*E*)-hex-4-en-1-yl dodec-10-enoate (101 MHz, CDCl$_3$)



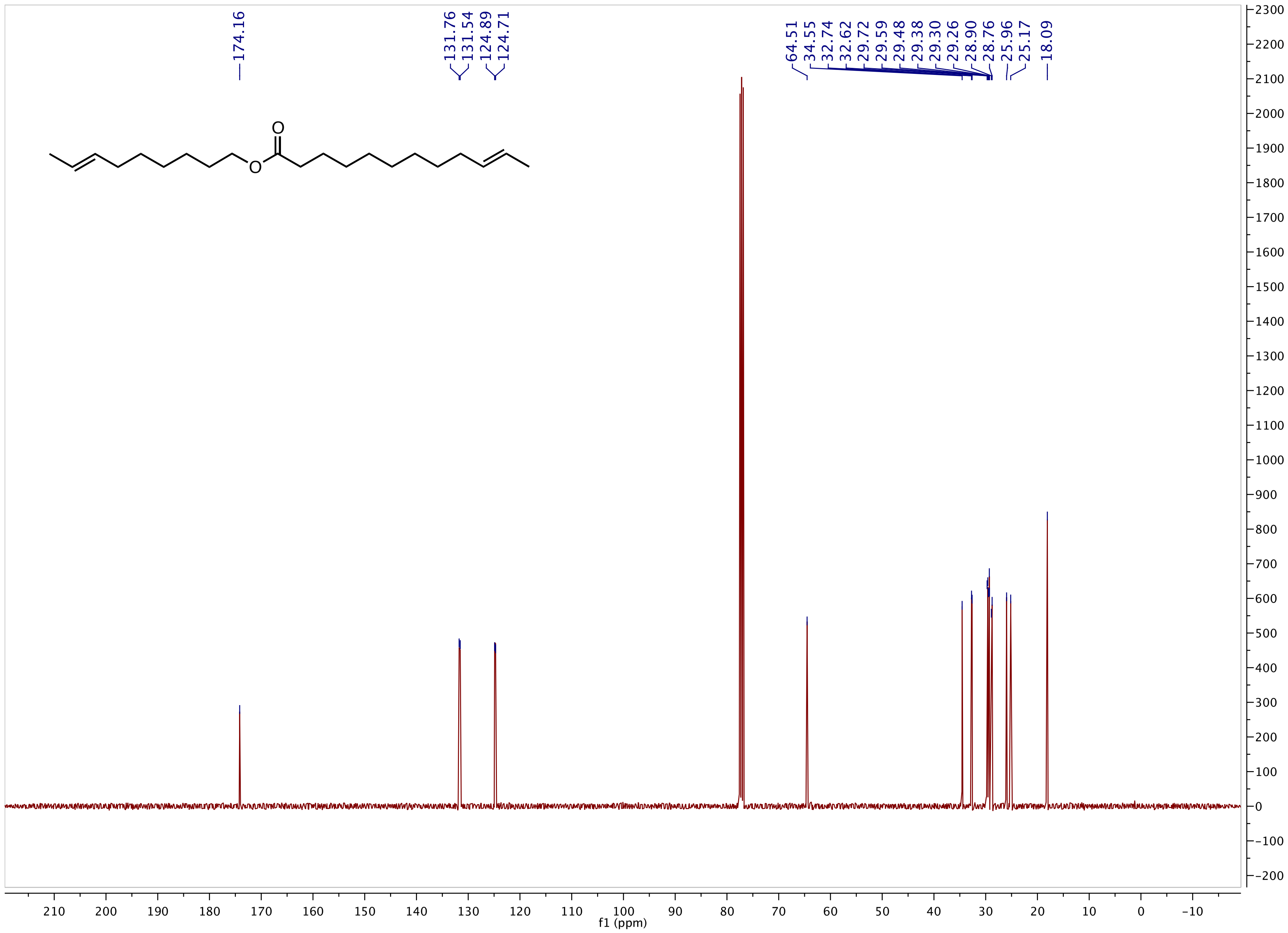
^{1}H NMR of (*E*)-(*E*)-hept-5-en-1-yl dodec-10-enoate (400 MHz, CDCl$_3$)



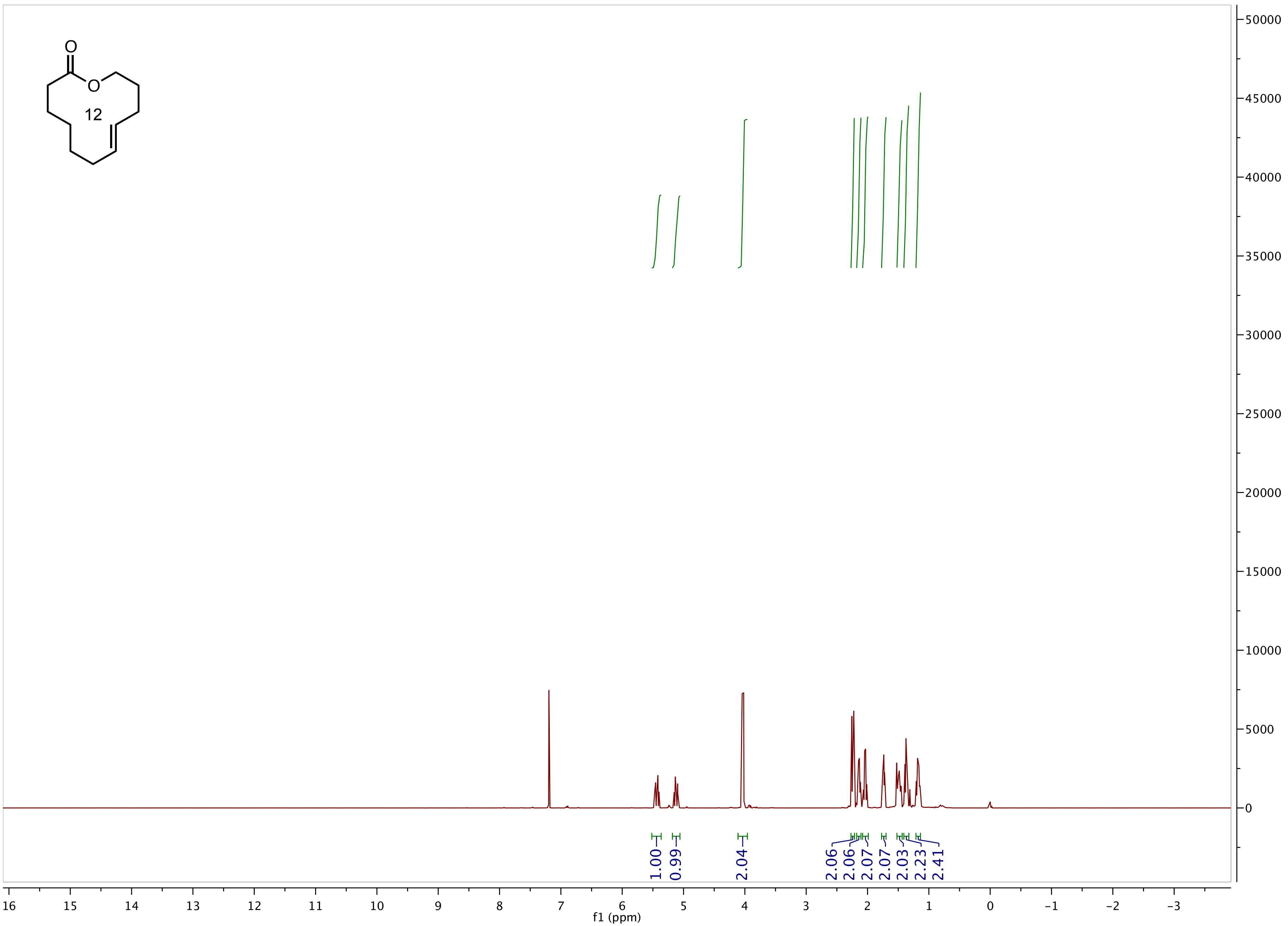
^{13}C NMR of (*E*)-(*E*)-hept-5-en-1-yl dodec-10-enoate (101 MHz, $CDCl_3$)



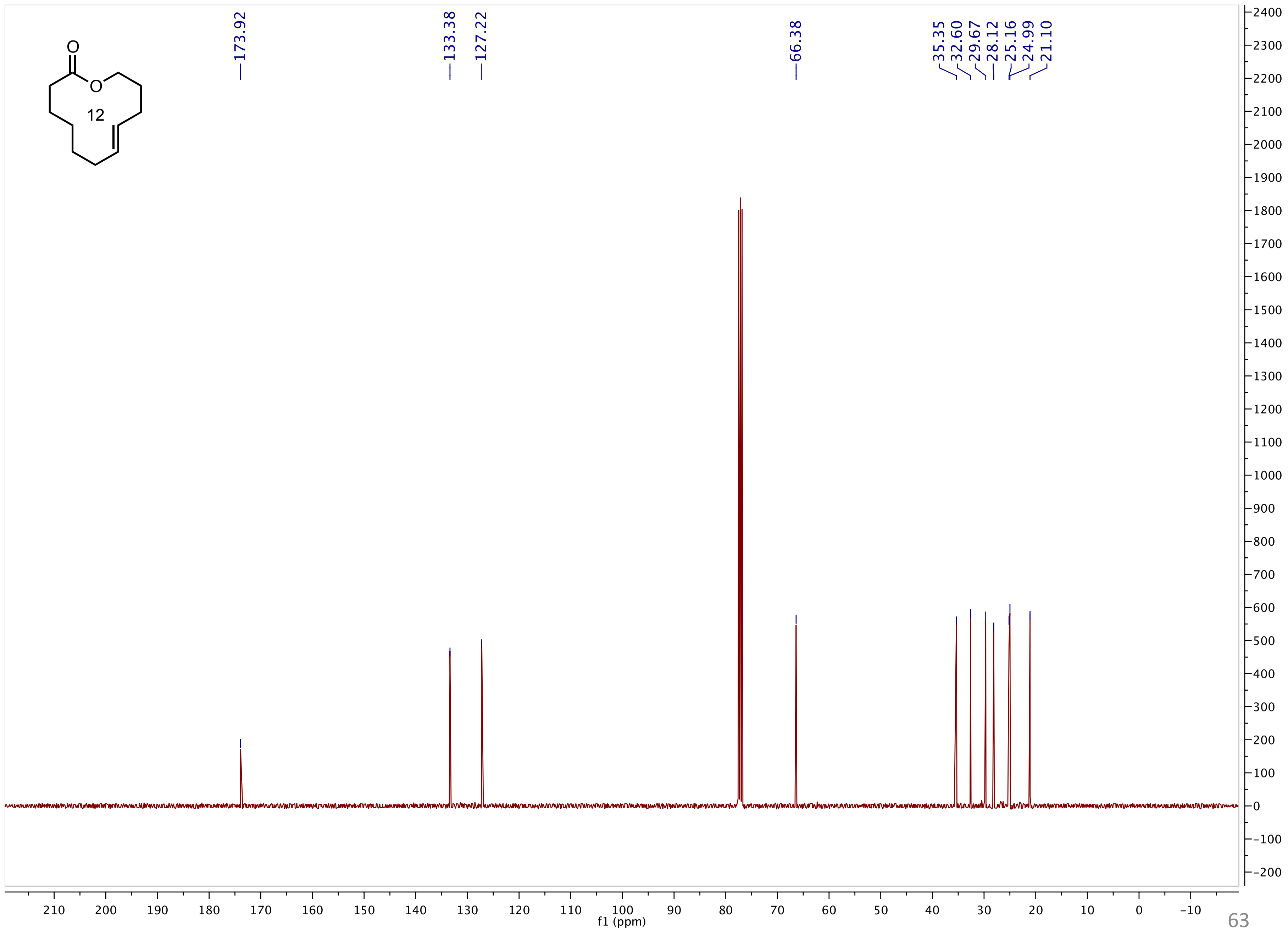
^{1}H NMR of (*E*)-(*E*)-non-7-en-1-yl dodec-10-enoate (400 MHz, $CDCl_3$)



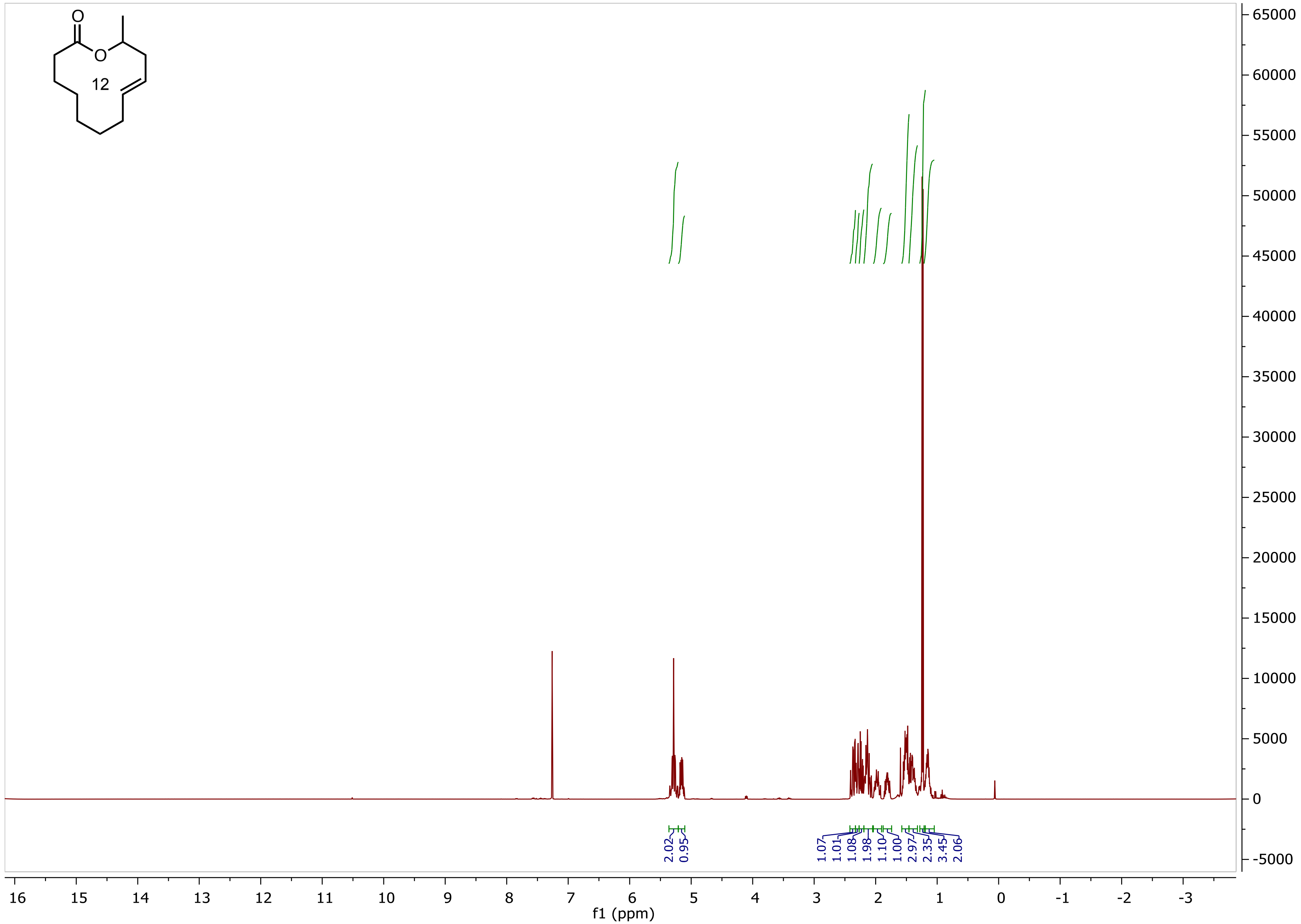
^{13}C NMR of (*E*)-(*E*)-non-7-en-1-yl dodec-10-enoate (101 MHz, $CDCl_3$)



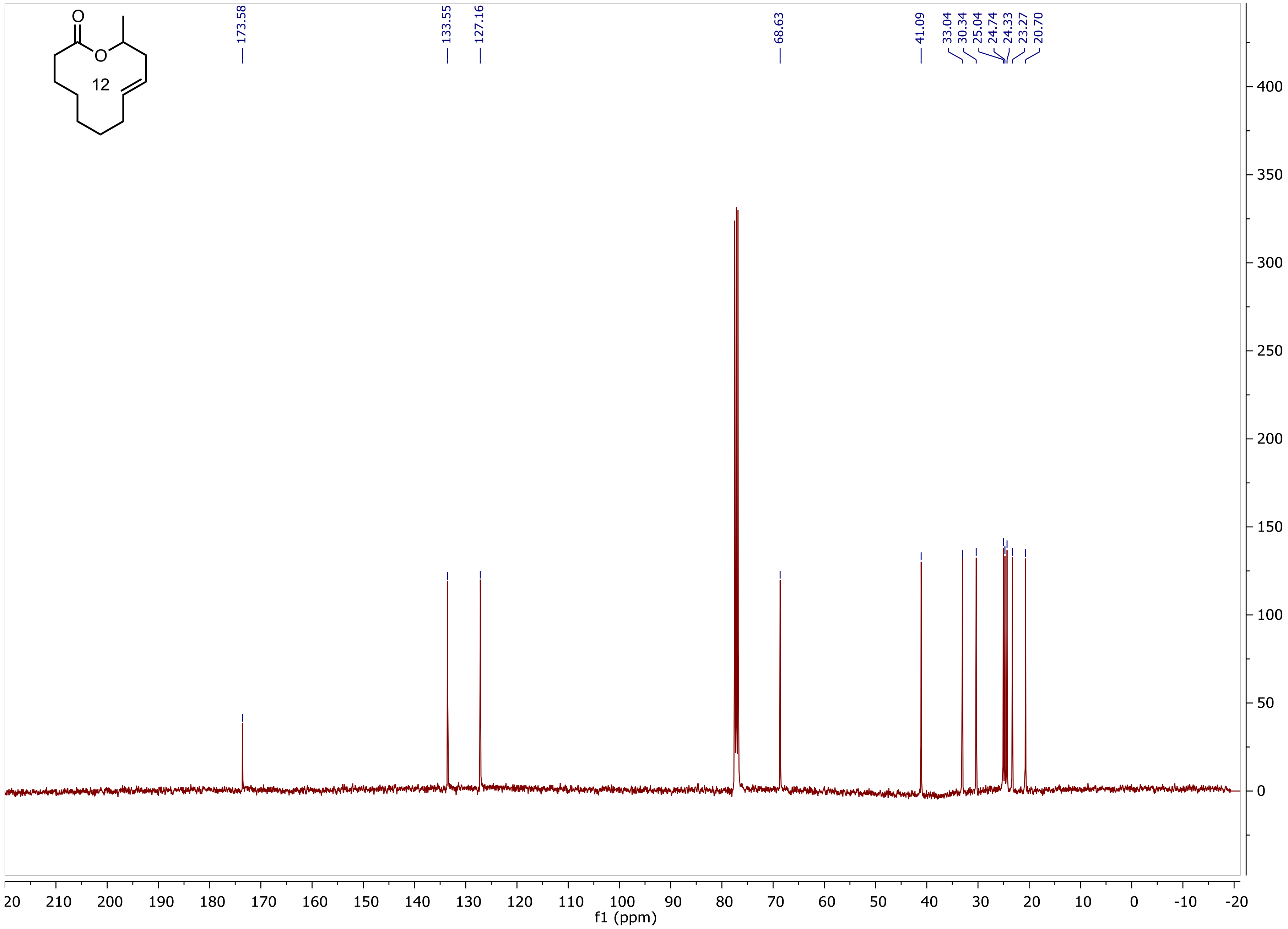
^{1}H NMR of *(E)*-oxacyclodec-8-en-2-one **8** (400 MHz, $CDCl_3$)



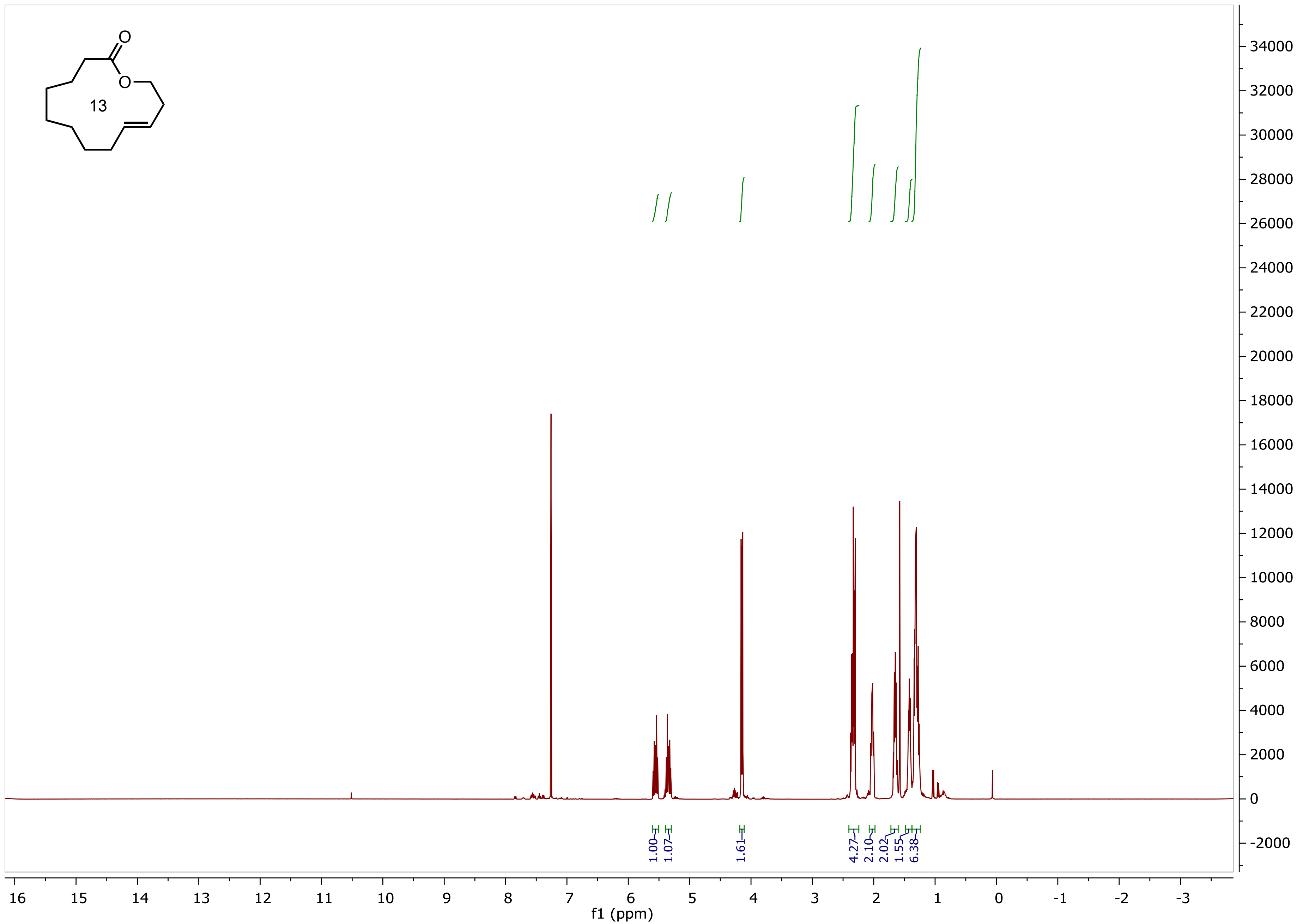
^{13}C NMR of *(E)*-oxacyclodec-8-en-2-one **8** (101 MHz, $CDCl_3$)



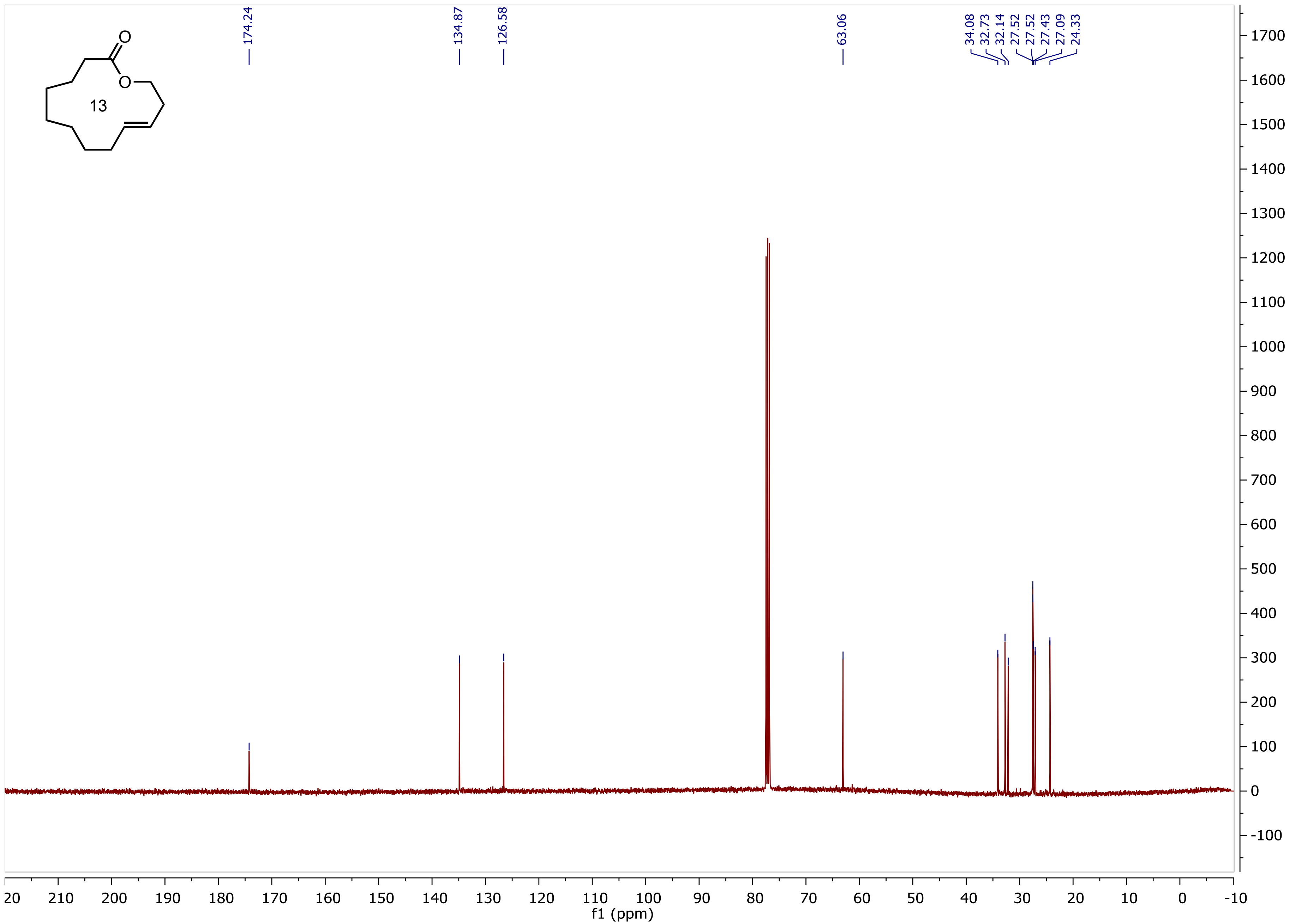
^{1}H NMR of (*E*)-12-methyloxacyclododec-9-en-2-one **9** (400 MHz, $CDCl_3$)



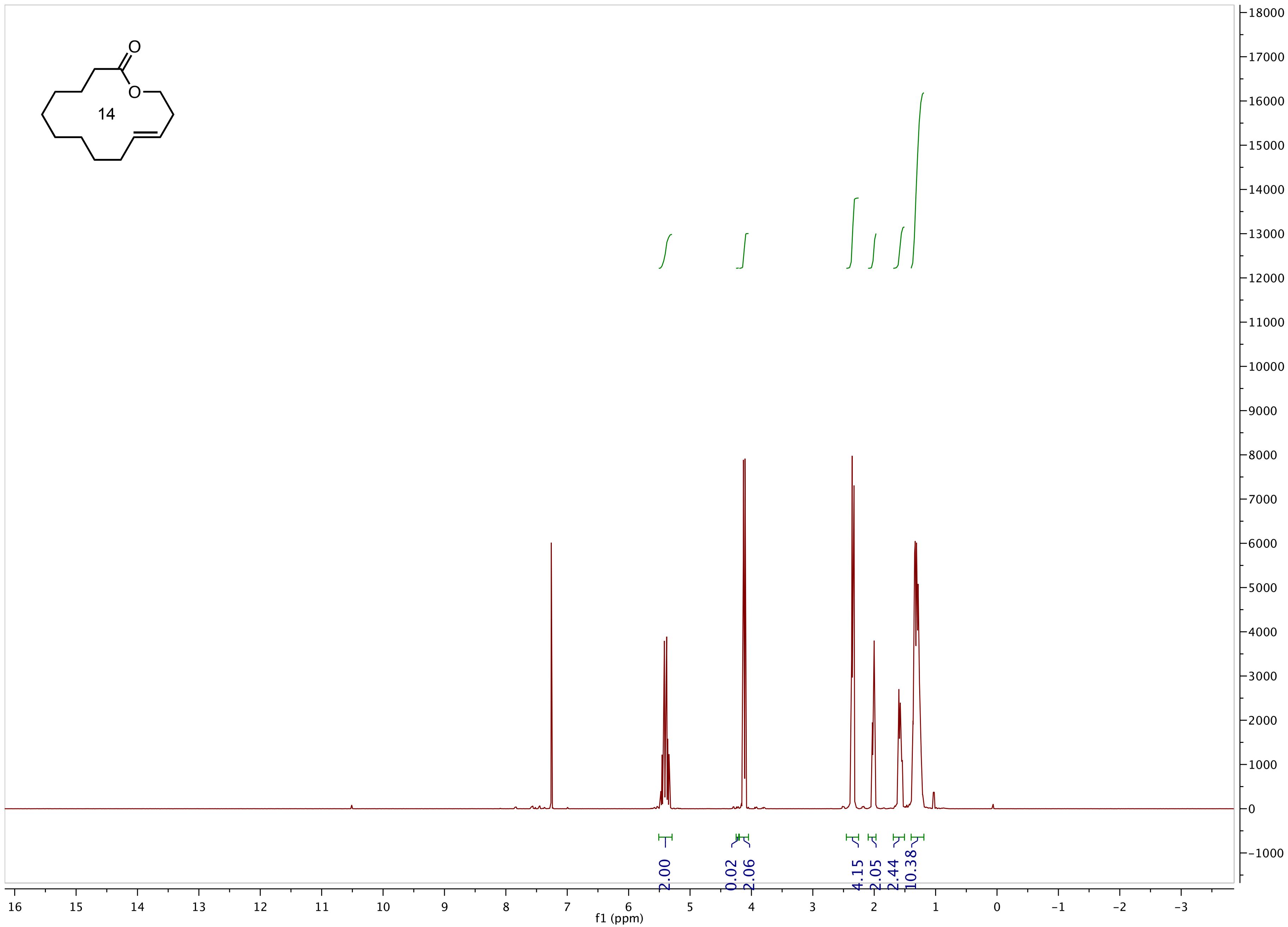
^{13}C NMR of (*E*)-12-methyloxacyclododec-9-en-2-one **9** (101 MHz, $CDCl_3$)



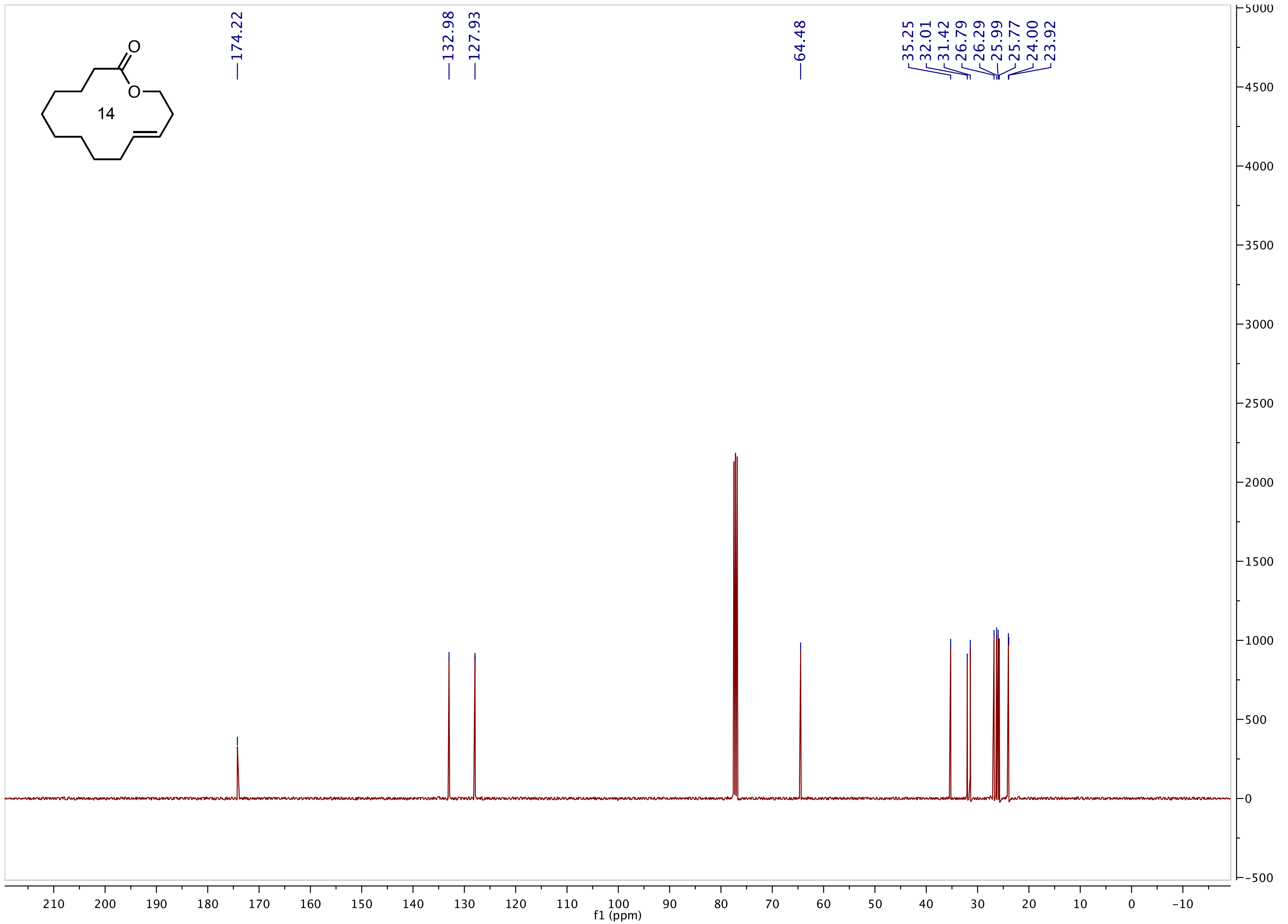
^{1}H NMR of (*E*)-oxacyclotridec-10-en-2-one **11** (400 MHz, $CDCl_3$)



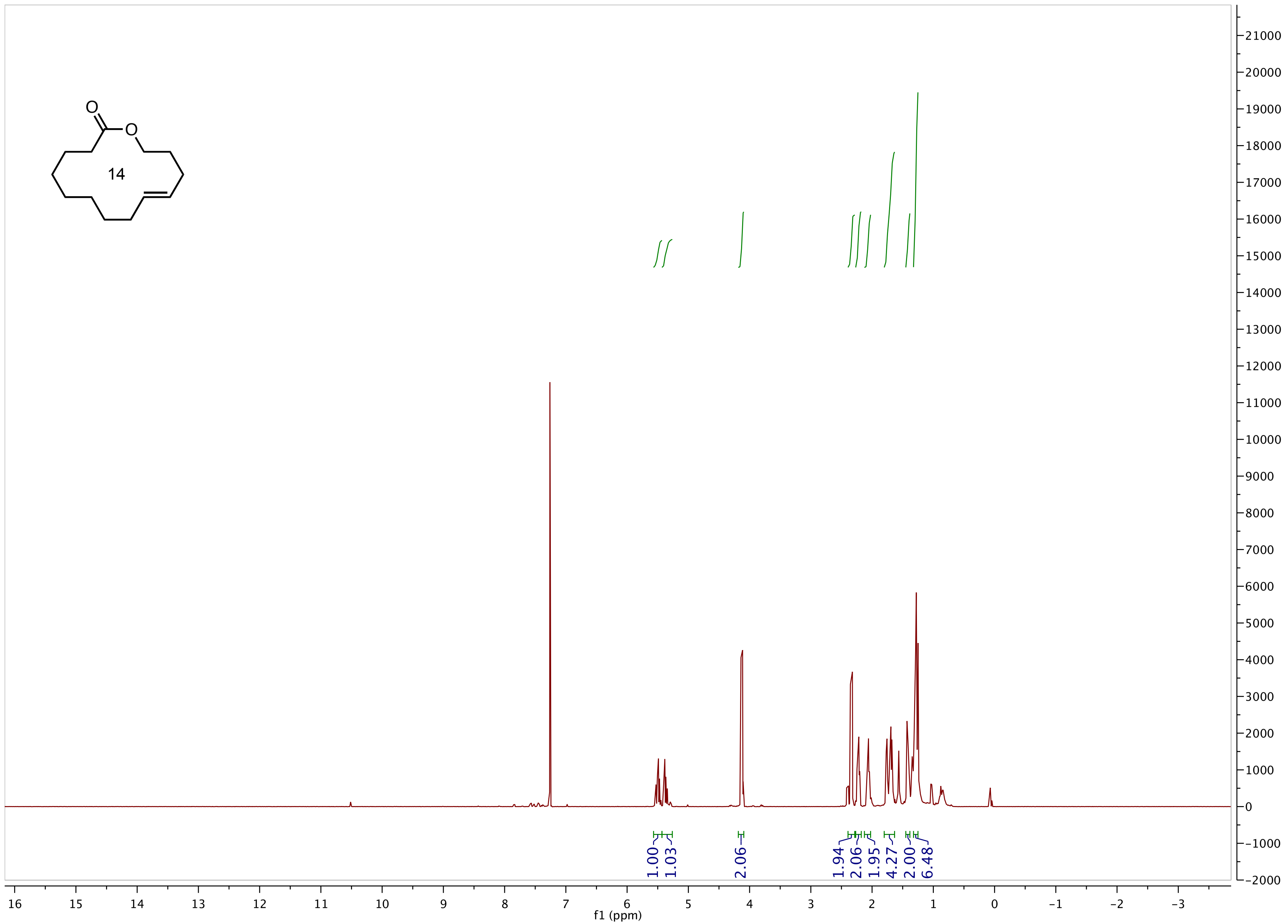
^{13}C NMR of (*E*)-oxacyclotridec-10-en-2-one **11** (101 MHz, CDCl$_3$)



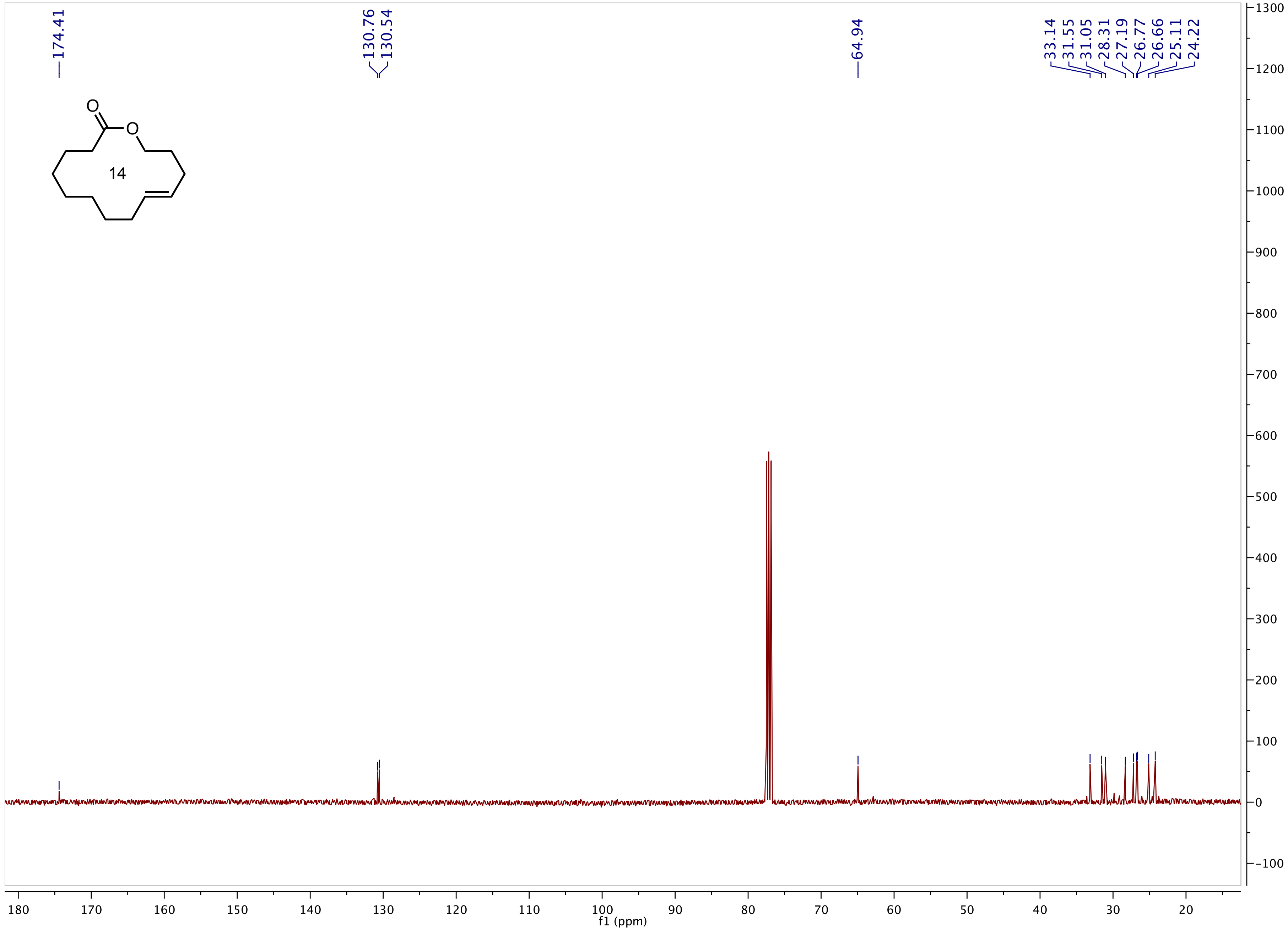
^{1}H NMR of (*E*)-oxacyclotetradec-11-en-2-one **6** (400 MHz, $CDCl_3$)



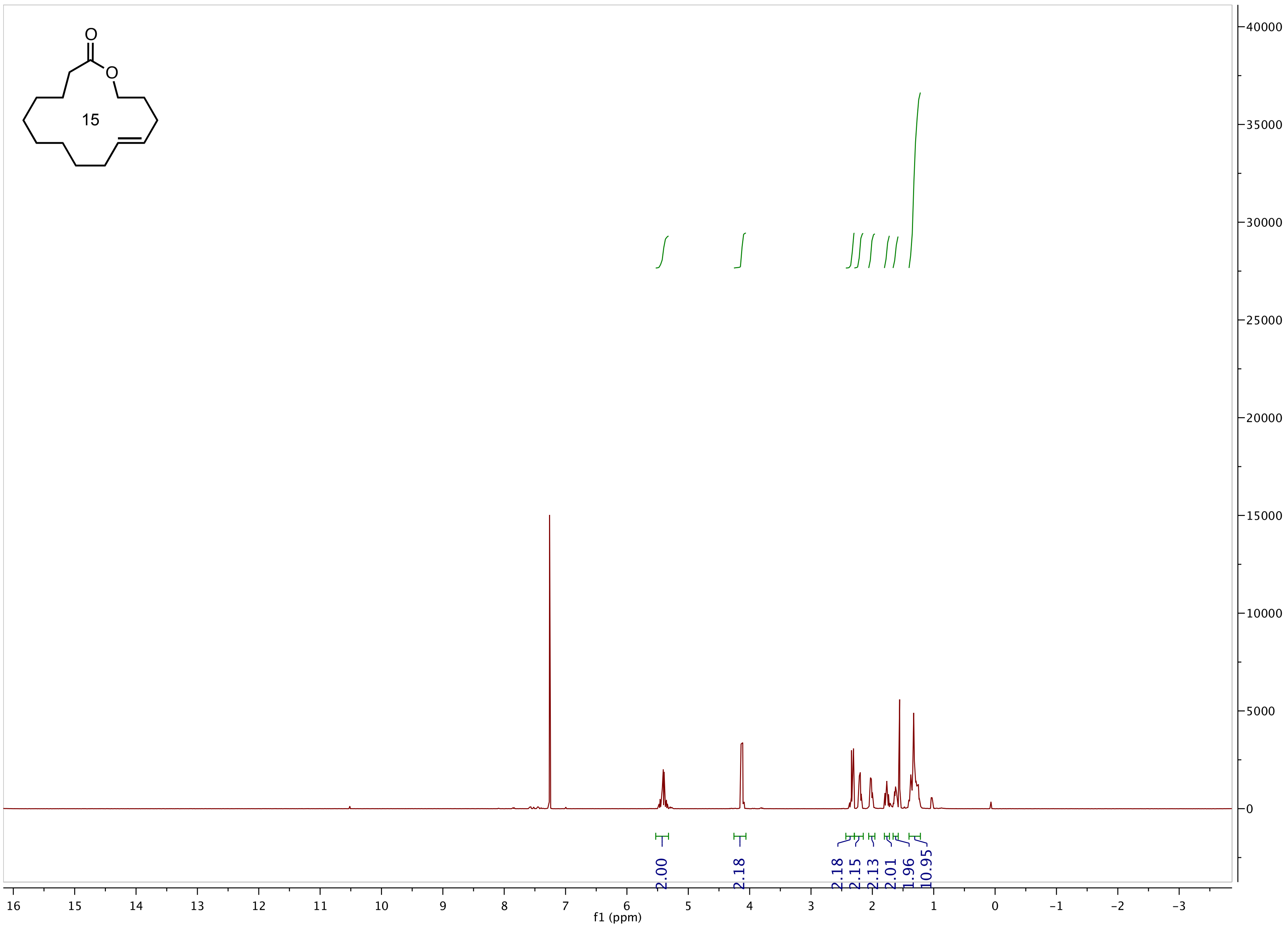
^{13}C NMR of (*E*)-oxacyclotetradec-11-en-2-one **6** (101 MHz, $CDCl_3$)



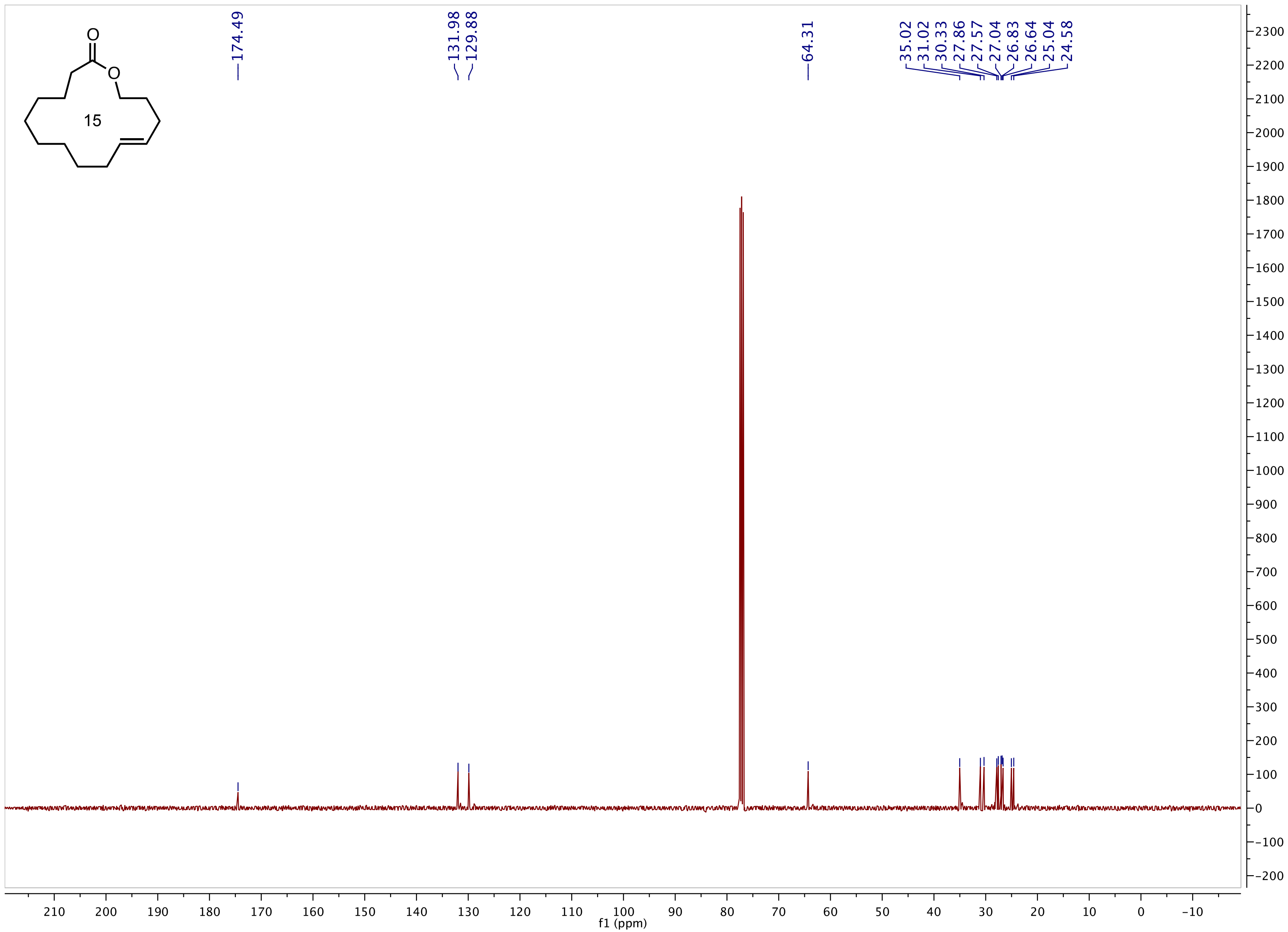
^{1}H NMR of *(E)*-oxacyclotetradec-10-en-2-one **11** (400 MHz, $CDCl_3$)



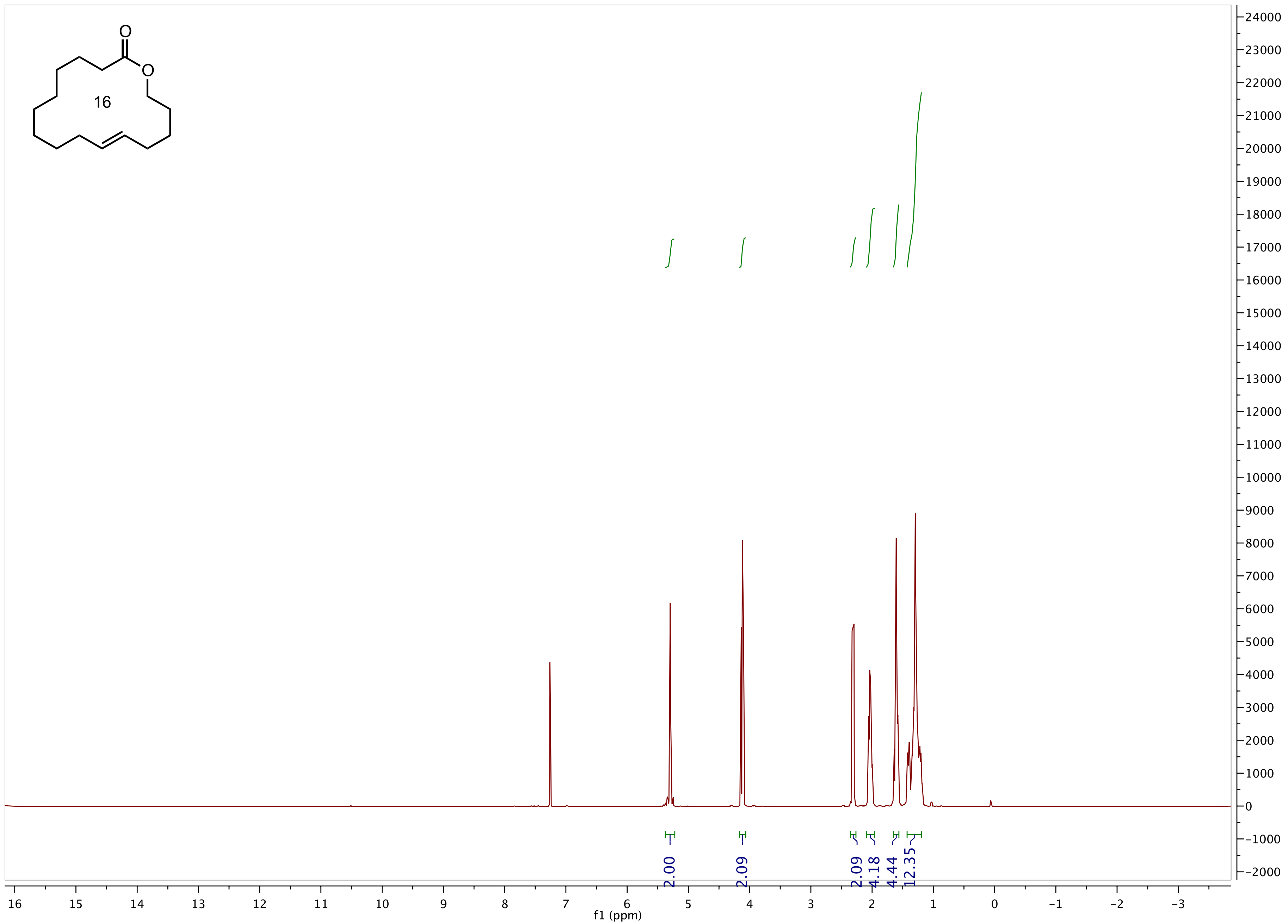
^{13}C NMR of (*E*)-oxacyclotetradec-10-en-2-one **11** (101 MHz, $CDCl_3$)



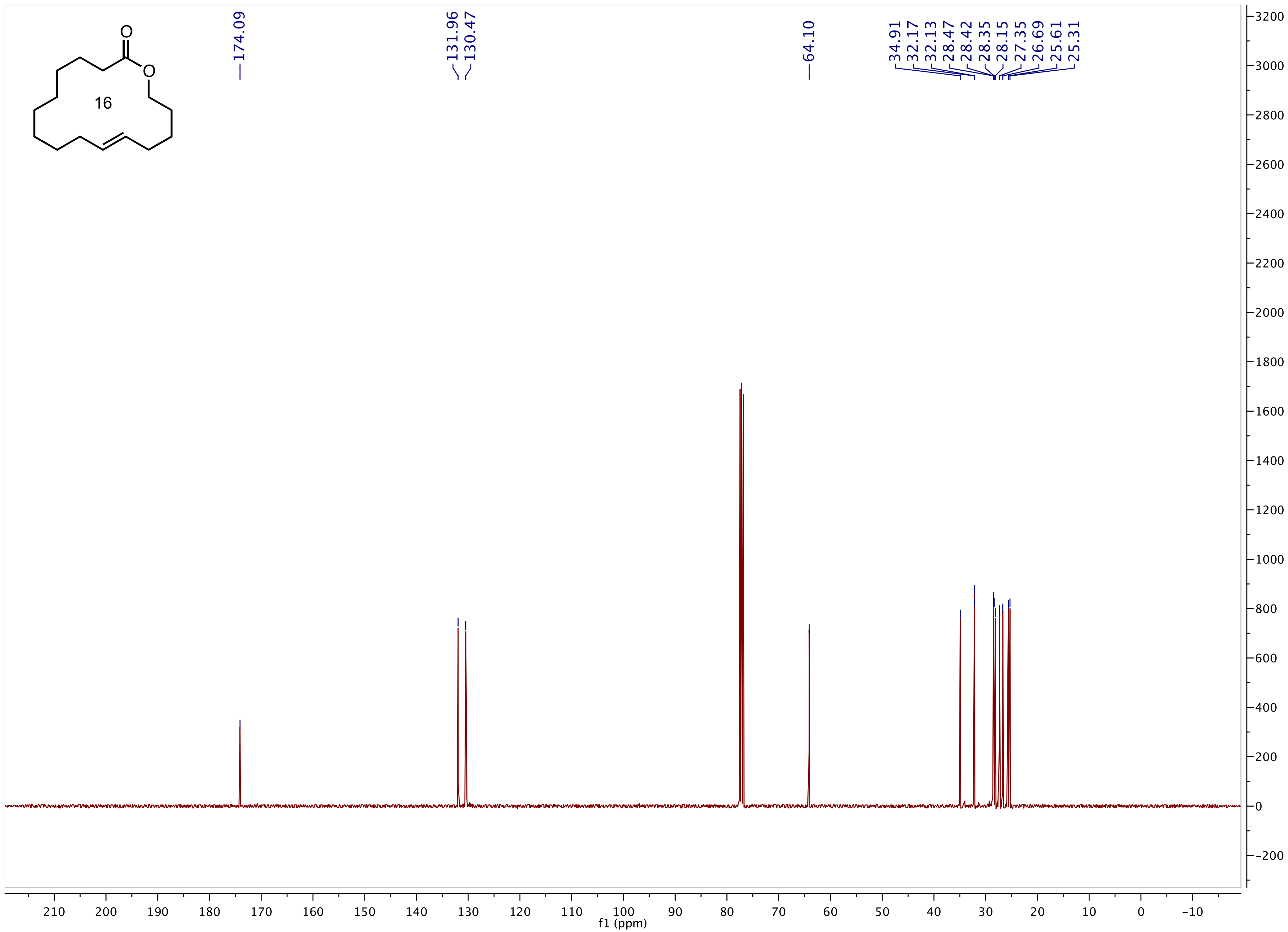
^{1}H NMR of (*E*)-oxacyclopentadec-11-en-2-one **12** (400 MHz, $CDCl_3$)



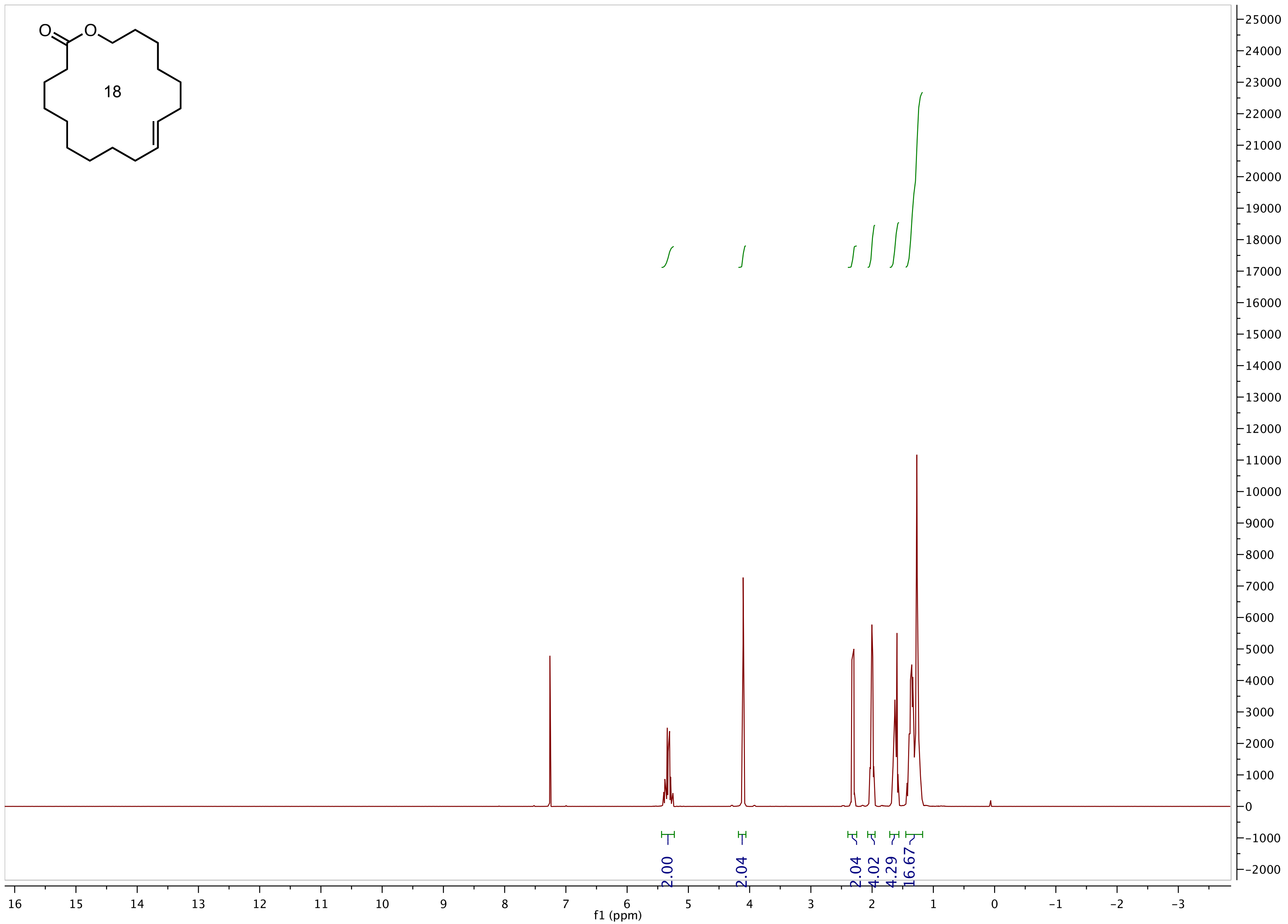
^{13}C NMR of (*E*)-oxacyclopentadec-11-en-2-one **12** (101 MHz, $CDCl_3$)



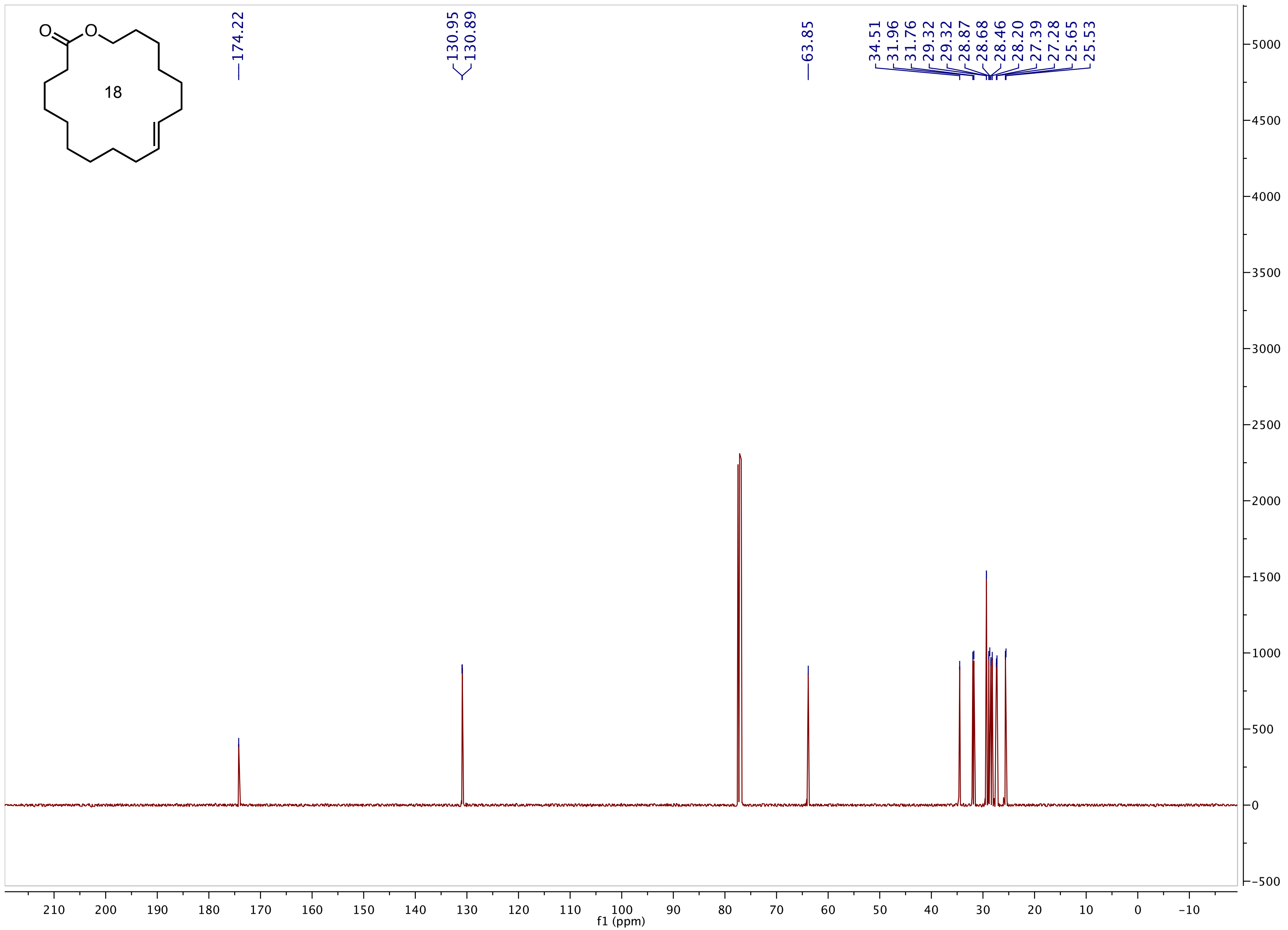
^{1}H NMR of **(***E***)**-oxacyclohexadec-11-en-2-one **13** (400 MHz, CDCl$_3$)



^{13}C NMR of (*E*)-oxacyclohexadec-11-en-2-one **13** (101 MHz, $CDCl_3$)



^{1}H NMR of (*E*)-oxacyclooctadec-11-en-2-one **14** (400 MHz, CDCl$_3$)



^{13}C NMR of (*E*)-oxacyclooctadec-11-en-2-one **14** (101 MHz, $CDCl_3$)