Stereoselective Access to *Z*- and *E*-Macrocycles by Ruthenium-Catalyzed *Z*-Selective Ring-Closing Metathesis and Ethenolysis

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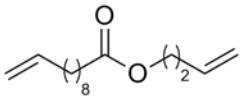
General methods

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk line techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified. All solvents were purified by passage through solvent purification columns,[1] with the exception of anhydrous 1,2-dichloroethane which was used as received from Sigma Aldrich, and further degassed with argon. Ruthenium complex **2** was obtained from Materia Inc. ^{1}H-NMR spectra were acquired at 500 MHz and ^{13}C-NMR spectra at 125 MHz as $CDCl_3$ solutions. Quantitative ^{13}C measurements were acquired at 125 MHz (decoupled, without NOE, 13 second delay time). All HRMS were by positive-ion EI or FAB.

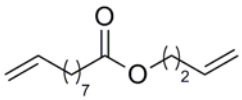
But-3-en-1-yl undec-10-enoate (1a)



1a

10-Undecenoyl chloride (4.5 mL, 21 mmol) was dissolved in CH_2Cl_2 (40 mL), and pyridine (1.7 mL, 21 mmol), then 3-butenol (1.6 mL, 19 mmol), were added dropwise at 0 °C. The solution was warmed to room temperature, and stirred for four hours. The mixture was then washed sequentially with 1M HCl (*aq.*), saturated $NaHCO_3$ (*aq.*), brine, dried with Na_2SO_4, and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, using 5% EtOAc in hexanes) provided **1a** (4.4 g, 88%) as a colourless oil; ^{1}H NMR δ 5.79 (2H, m), 5.11 (1H, m), 5.07 (1H, m), 4.99 (1H, m), 4.93 (1H, m), 4.12 (2H, t, *J* = 6.7 Hz), 2.38 (2H, m), 2.29 (2H, t, *J* = 7.6 Hz), 2.03 (2H, m), 1.61 (2H, m), 1.26-1.40 (10H, m); ^{13}C NMR δ 173.8, 139.2, 134.1, 117.1, 114.2, 63.3, 34.3, 33.8, 33.1, 29.3, 29.2, 29.1 (2C), 28.9, 25.0; HRMS (EI) 238.1932, $[C_{15}H_{26}O_2]^+$ requires 238.1933.

But-3-en-1-yl dec-9-enoate (4a)



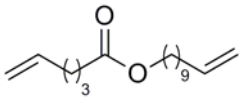
4a

Oxalyl chloride (2.1 mL, 25 mmol) was added dropwise to a solution of 9-decenoic acid (3.9 mL, 21 mmol) and pyridine (0.20 mL, 2.1 mmol) in CH_2Cl_2 (100 mL), and the solution was let to stir for fifteen hours, then concentrated. The residue was dissolved in CH_2Cl_2 (40 mL), and pyridine (1.7 mL, 21 mmol),

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics.* **1996**, *15*, 1518.

then 3-butenol (1.6 mL, 19 mmol), were added dropwise at 0 °C. The solution was warmed to room temperature, and stirred for four hours. The mixture was then washed sequentially with 1M HCl (*aq.*), saturated $NaHCO_3$ (*aq.*), brine, dried with Na_2SO_4, and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, using 5% EtOAc in hexanes) provided **4a** (4.0 g, 85%) as a colourless oil; ^{1}H NMR δ 5.79 (2H, m), 5.11(1H), 5.07 (1H, m), 4.99 (1H, m), 4.93 (1H, m), 4.13 (2H, t, *J* = 7.1 Hz), 2.38 (2H, m), 2.30 (2H, t, *J* = 7.5 Hz), 2.04 (2H, m), 1.62 (2H, m), 1.22-1.41 (8H, m); ^{13}C NMR δ 173.8, 139.1, 134.1, 117.1, 114.2, 63.3, 34.3, 33.8, 33.1, 29.1 (2C), 28.9 (2C), 25.0; HRMS (EI) 224.1773, $[C_{14}H_{24}O_2]^+$ requires 224.1776.

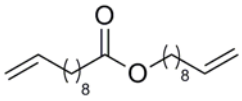
Undec-10-en-1-yl hex-5-enoate (5a)



5a

According to the procedure for compound **4a**, 5-hexenoic acid (1.65 mL, 14 mmol) was reacted with oxalyl chloride (1.4 mL, 17 mmol) and pyridine (0.12 mL, 1.4 mmol), then 10-undecenol (2.6 mL, 13 mmol) and pyridine (1.2 mL, 14 mmol), to provide **5a** (0.86 g, 23%) as a colourless oil; ^{1}H NMR δ 5.80 (2H, m), 5.01 (2H, m), 4.96 (2H, m), 4.06 (2H, t, *J* = 6.8 Hz), 2.31 (2H, t, *J* = 7.6 Hz), 2.09 (2H, m), 2.04 (2H, m), 1.73 (2H, m), 1.61 (2H, m), 1.24-1.41 (12H, m); ^{13}C NMR δ 173.7, 139.2, 137.7, 115.3, 114.1, 64.5, 33.8, 33.6, 33.1, 29.5, 29.4, 29.2, 29.1, 28.9, 28.7, 25.9, 24.1; HRMS (EI) 266.2245, $[C_{17}H_{30}O_2]^+$ requires 266.2246.

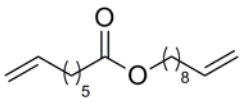
Dec-9-en-1-yl undec-10-enoate (6a)



6a

According to the procedure for compound **1a**, 10-undecenoyl chloride (4.5 mL, 21 mmol) was reacted with 9-decenol (3.4 mL, 19 mmol) and pyridine (1.7 mL, 21 mmol), to provide **6a** (6.4 g, 94%) as a colourless oil; ^{1}H NMR δ 5.81 (2H, m), 4.99 (2H, m), 4.93 (2H, m), 4.05 (2H, t, *J* = 6.7 Hz), 2.29 (2H, t, *J* = 7.5 Hz), 2.04 (2H, m), 1.61 (2H, m), 1.25-1.41 (20H, m); ^{13}C NMR δ 174.0, 139.2, 139.1, 114.2, 114.1, 64.4, 34.4, 33.8 (2C), 29.4, 29.3, 29.2 (2C), 29.1 (2C), 29.0, 28.9 (2C), 28.7, 25.9, 25.0; HRMS (EI) 322.2884, $[C_{21}H_{38}O_2]^+$ requires 322.2872.

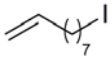
Dec-9-en-1-yl oct-7-enoate (7a)



7a

According to the procedure for compound **4a**, 7-octenoic acid (3.2 mL, 21 mmol) was reacted with oxalyl chloride (2.1 mL, 25 mmol) and pyridine (0.20 mL, 2.1 mmol), then 9-decenol (3.4 mL, 19 mmol) and pyridine (1.7 mL, 21 mmol), to provide **7a** (4.8 g, 81%) as a colourless oil; ^{1}H NMR δ 5.80 (2H, m), 4.99 (2H, m), 4.93 (2H, m), 4.06 (2H, t, *J* = 6.7 Hz), 2.29 (2H, t, *J* = 7.5 Hz), 2.04 (2H, m), 1.62 (2H, m), 1.26-1.44 (14H, m); ^{13}C NMR δ 173.9, 139.1, 138.8, 114.4, 114.2, 64.4, 34.3, 33.8, 33.6, 29.4, 29.2, 29.0, 28.9, 28.7, 28.6, 28.5, 25.9, 24.9; HRMS (EI) 280.2406, $[C_{18}H_{32}O_2]^+$ requires 280.2402.

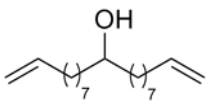
9-Iodonon-1-ene (16)



16

Methanesulponyl chloride (3.3 mL, 42 mmol) was added dropwise to a 0 °C solution of 8-nonenol (5.9 mL, 35 mmol) and triethylamine (5.9 mL, 42 mmol) in CH_2Cl_2 (35 mL). The mixture was let to stir at room temperature for two hours, and was then washed sequentially with 1M HCl (*aq.*) (x2), saturated $NaHCO_3$ (*aq.*), brine, and dried with Na_2SO_4. The solvent was removed *in vacuo*, the residue was taken in acetone (125 mL), and NaI (13 g, 88 mmol) was added. The mixture was stirred at room temperature for 24 hours, then concentrated. Flash chromatography of the residue (SiO_2, using hexanes) provided **16** (6.9 g, 78%) as a colourless oil; ^{1}H NMR δ 5.81 (1H, m), 4.99 (1H, m), 4.93 (1H, m), 3.19 (2H, t, *J* = 7.0 Hz), 2.04 (2H, m), 1.82 (2H, m), 1.39 (4H, m), 1.31 (4H, m); ^{13}C NMR δ 139.0, 114.3, 33.7, 33.5, 30.5, 28.9, 28.8, 28.4, 7.3; HRMS (EI) 252.0373, $[C_9H_{17}I]^+$ requires 252.0375.

Nonadeca-1,18-dien-10-ol (10a)

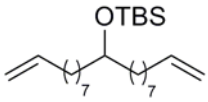


10a

A solution of iodide **16** (6.9 g, 27 mmol) in Et_2O (50 mL) was cooled to -78 °C, and *tert*-butyl lithium

(32 mL, 1.7M in pentanes) was added dropwise. The solution was warmed to room temperature over 1 hour, then re-cooled to -78 °C, and 9-decenal[2] (3.9 g, 25 mmol) was added dropwise. The solution was warmed to room temperature over one hour, then washed with saturated $NaHCO_3$ (*aq.*), then brine, dried with Na_2SO_4, and concentrated. The residue was taken in hexanes, and recrystallized at -20 °C to provide **10a** (5.0 g, 71%) as a colourless solid; ^{1}H NMR δ 5.81 (2H, m), 4.99 (2H, m), 4.93 (2H, m), 3.58 (1H, m), 2.04 (4H, m), 1.25-1.48 (25H, m); ^{13}C NMR δ 139.2 (2C), 114.1 (2C), 72.0, 37.5 (2C), 33.8 (2C), 29.6 (2C), 29.5 (2C), 28.9 (2C), 25.6 (2C); HRMS (EI) 280.2759, $[C_{19}H_{36}O]^+$ requires 280.2766.

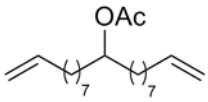
***tert*-Butyldimethyl(nonadeca-1,18-dien-10-yloxy)silane (11a)**



11a

tert-Butyldimethylsilyl chloride (0.18 g, 1.2 mmol) was added to a solution of alcohol **10a** (0.30 g, 1.1 mmol), imidazole (0.14 g, 2.1 mmol), and 4-dimethylaminopyridine (0.012 g, 0.10 mmol) in CH_2Cl_2 (5 mL), and the solution was let to stir for 24 hours at room temperature. The solution was washed with saturated $NaHCO_3$ (*aq.*), brine, and dried with Na_2SO_4. The solvent was removed *in vacuo*, and flash chromatography of the residue (SiO_2, using pentanes) provided **11a** (0.42 g, 98%) as a colourless oil; ^{1}H NMR δ 5.81 (2H, m), 4.99 (2H, m), 4.93 (2H, m), 3.61 (1H, m), 2.04 (4H, m), 1.38 (8H, m), 1.28 (16H, m), 0.88 (9H, s), 0.03 (6H, s); ^{13}C NMR δ 139.2 (2C), 114.1 (2C), 72.4, 37.1 (2C), 33.8 (2C), 29.8 (2C), 29.5 (2C), 29.1 (2C), 28.9 (2C), 26.0 (3C), 25.3 (2C), 18.2, -4.4 (2C); HRMS (EI) 393.3545, $[C_{25}H_{49}OSi\text{-}H]^+$ requires 393.3553.

Nonadeca-1,18-dien-10-yl acetate (12a)



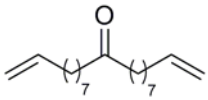
12a

Acetic anhydride (0.13 mL, 1.4 mmol) was added to a solution of alcohol **10a** (0.19 g, 0.68 mmol) and pyridine (0.070 mL, 0.87 mmol) in CH_2Cl_2 (1.5 mL), and the solution was let to stir for 17 hours at room temperature. The mixture was diluted with diethyl ether, washed with saturated $NaHCO_3$ (*aq.*), brine, and dried with Na_2SO_4. The solvent was removed *in vacuo*, and flash chromatography of the residue

[2] Prepared from 9-decenol according to: Berube, M.; Laplante, Y.; Poirier, D. *Med. Chem.* **2006**, *4*, 329.

(SiO_2, using 10% Et_2O in pentanes) provided **12a** (0.21 g, 95%) as a colourless oil; ^{1}H NMR δ 5.80 (2H, m), 4.99 (2H, m), 4.92 (2H, m), 4.85 (1H, m), 2.03 (3H, s), 2.03 (4H, m), 1.49 (4H, m), 1.36 (4H, m), 1.22-1.31 (16H, m); ^{13}C NMR δ 170.9, 139.2 (2C), 114.2 (2C), 74.4, 34.1 (2C), 33.8 (2C), 29.5 (2C), 29.4 (2C), 29.0 (2C), 28.9 (2C), 25.3 (2C), 21.3 (2C); HRMS (FAB) 321.2794, $[C_{21}H_{38}O_2\text{-}H]^+$ requires 321.2794.

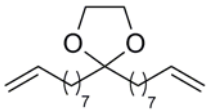
Nonadeca-1,18-dien-10-one (8a)



8a

Tetrapropylammonium perruthenate (0.21 g, 0.60 mmol) was added to a solution of alcohol **8a** (3.5 g, 12 mmol) and *N*-methylmorpholine *N*-oxide (2.1 g, 18 mmol) in CH_2Cl_2 (25 mL). The mixture was let to stir at room temperature for one hour, then loaded directly onto a silica gel column. Purification by flash chromatography (using 10% EtOAc in hexanes) provided **8a** (3.2 g, 97%) as a colourless solid; ^{1}H NMR δ 5.80 (2H, m), 4.98 (2H, m), 4.93 (2H, m), 2.38 (4H, t, *J* = 7.5 Hz), 2.03 (4H, m), 1.56 (4H, m), 1.37 (4H, m), 1.29 (12H, m); ^{13}C NMR δ 211.7, 139.1 (2C), 114.2 (2C), 42.8 (2C), 33.8 (2C), 29.3 (2C), 29.2 (2C), 28.9 (4C), 23.9 (2C); HRMS (EI) 278.2607, $[C_{19}H_{34}O]^+$ requires 278.2610.

2,2-Di(non-8-en-1-yl)-1,3-dioxolane (9a)

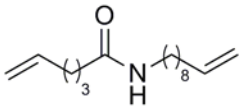


9a

para-Toluenesulphonic acid (0.010 g, 0.055 mmol) was added to a solution of ketone **9a** (0.30 g, 1.1 mmol) and ethylene glycol (0.60 mL, 11 mmol) in benzene (10 mL), and refluxed using a Dean-Stark apparatus for 21 hours. The solution was then cooled, diluted with Et_2O, washed sequentially with 10% NaOH (*aq.*), saturated $NaHCO_3$ (*aq.*), then brine, dried with Na_2SO_4, and concentrated. In order to facilitate separation of **9a** from unreacted **8a**, the residue was dissolved in MeOH (5 mL), and stirred with $NaBH_4$ (10 mg) for *ca.* 30 minutes. The mixture was then diluted with Et_2O, washed with brine, then dried with Na_2SO_4. The solvent was removed *in vacuo*, and flash chromatography of the residue (SiO_2, using 2% Et_2O in pentanes) provided **9a** (0.30 g, 86%) as a colourless oil; ^{1}H NMR δ 5.81 (2H, m), 4.99 (2H,

m), 4.92 (2H, m), 3.92 (4H, s), 2.04 (4H, m), 1.59 (4H, m), 1.25-1.40 (20H, m); ^{13}C NMR δ 139.2 (2C), 114.1 (2C), 111.9, 64.9 (2C), 37.1 (2C), 33.8 (2C), 29.9 (2C), 29.5 (2C), 29.1 (2C), 28.9 (2C), 24.9 (2C); HRMS (EI) 322.2862, $[C_{21}H_{38}O_2]^+$ requires 322.2872.

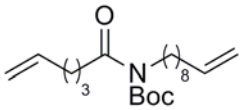
***N*-(Dec-9-en-1-yl)hex-5-enamide (13a)**



13a

5-Hexenoic acid (1.5 mL, 13 mmol), then triethylamine (3.3 mL, 24 mmol), were added to a solution of 9-decenamine[3] (1.9 g, 12 mmol), 1-hydroxybenzotriazole hydrate (2.0 g, 13 mmol), and *N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (2.5 g, 13 mmol) in CH_2Cl_2 (60 mL), and the mixture was stirred at room temperature overnight. The solution was diluted with EtOAc, and washed sequentially with 0.5M citric acid (*aq.*), saturated $NaHCO_3$, then brine, dried with Na_2SO_4, and concentrated. Purification by flash chromatography (using a gradient of CH_2Cl_2 to 5% MeOH in CH_2Cl_2) provided **13a** (2.6 g, 87%) as a pale yellow oil; ^{1}H NMR δ 5.79 (2H, m), 5.47 (1H, br s), 4.98 (4H, m), 3.23 (2H, m), 2.16 (2H, t, *J* = 7.5 Hz), 2.09 (2H, m), 2.03 (2H, m), 1.74 (2H, m), 1.48 (2H, m), 1.37 (2H, m), 1.29 (8H, m); ^{13}C NMR δ 172.7, 139.2, 138.0, 115.3, 114.2, 39.5, 36.0, 33.8, 33.2, 29.7, 29.4, 29.2, 29.0, 28.9, 26.9, 24.8; HRMS (EI) 251.2240, $[C_{16}H_{29}ON]^+$ requires 251.2249.

***tert*-Butyl dec-9-en-1-yl(hex-5-enoyl)carbamate (14a)**



14a

A solution of amide **13a** (1.0 g, 4.0 mmol) in THF (15 mL) was cooled to -78 °C, and *n*-butyl lithium (15 mL, 2.5M in hexanes) was added dropwise. After 30 minutes of stirring, a solution of di-*tert*-butyl dicarbonate (0.89 g, 4.1 mmol) in THF (4 mL) was added dropwise, and the mixture was let to warm to 0 °C over two hours. The solution was then diluted with Et_2O, washed with saturated NH_4Cl (*aq.*), dried with Na_2SO_4, and concentrated. Purification by flash chromatography (using 2% Et_2O in pentanes) provided **13a** (1.1 g, 79%) as a colourless oil; ^{1}H NMR δ 5.79 (2H, m), 4.96 (4H, m), 3.62 (2H, t, *J* = 7.5

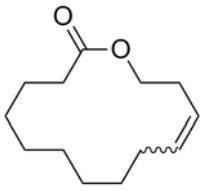
[3] Prepared from 10-undecenoyl chloride according to: Kaur, N.; Delcros, J.-G.; Martin, B.; Phanstiel, O. *J. Med. Chem.* **2005**, *48*, 3832.

Hz), 2.81 (2H, t, *J* = 7.5 Hz), 2.08 (2H, m), 2.01 (2H, m), 1.72 (2H, m), 1.51 (9H, s), 1.48 (2H, m), 1.35 (2H, m), 1.26 (8H, m); ^{13}C NMR δ 175.8, 153.4, 139.2, 138.3, 114.9, 114.1, 82.6, 44.5, 37.7, 33.8, 33.2, 29.4, 29.3, 29.0, 28.9, 28.7, 28.1 (3C), 27.4, 26.9, 24.4; HRMS (EI) 351.2783, $[C_{21}H_{37}O_3N]^+$ requires 351.2773.

***General procedure 1: Z*-selective macrocyclizations catalyzed by Ru-complex 2**

In a glovebox, a 500 mL Strauss flask was charged with a solution of diene (1 equiv, *ca.* 0.45 mmol) in dichloroethane (5 mM, 90 mL), and a solution of **2** (7.5 mol%) dissolved in dichloroethane (1 mL) was added. The flask was sealed, brought out of the glovebox, and subjected to a single freeze/pump/thaw/cycle. The flask was kept under a static vacuum of 20 mtorr, and heated at 60 °C. After 24 hours (except for ***Z*-8** which was quenched after 8 hours), the mixture was cooled, quenched with excess ethyl vinyl ether, and concentrated. Flash chromatography of the residue (SiO_2, using 2% Et_2O in pentanes for compounds **1, 4** – **9**, **12**, and **14**, 10% Et_2O in pentanes for compound **10**, pentanes for compound **11**, and 66% Et_2O in pentanes for compound **13**) provided the product.

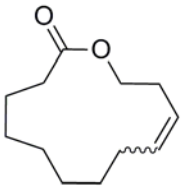
***Z*-Oxacyclotetradec-11-en-2-one (1)**



***Z*-1**

According to *General Procedure 1*, diene **1a** (0.11 g, 0.46 mmol) was reacted with **2** (0.022 g, 0.035 mmol) to provide ***Z*-1** (0.056 g, 58% yield, 85% *Z* as determined by ^{1}H-NMR) as a colourless oil; ^{1}H NMR δ 5.54 (1H, m), 5.38 (1H, m), 4.23 (2H, t, *J* = 5.3 Hz), 2.41 (2H, m), 2.35 (2H, t, *J* = 6.3 Hz), 2.03 (2H, m), 1.64 (2H, m), 1.24-1.39 (10H, m); ^{13}C NMR δ 174.0, 132.3, 127.1, 63.7, 33.3, 27.7, 27.5, 26.1, 26.0, 25.5, 25.4, 25.2, 23.5; HRMS (EI) 210.1623, $[C_{13}H_{22}O_2]^+$ requires 210.1620.

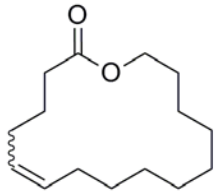
***Z*-Oxacyclotridec-10-en-2-one (4)**



***Z*-4**

According to *General Procedure 1*, diene **4a** (0.10 g, 0.45 mmol) was reacted with **2** (0.021 g, 0.033 mmol) to provide ***Z*-4** (0.035 g, 40% yield, 86% *Z* as determined by ^{1}H-NMR) as a colourless oil; ^{1}H NMR δ 5.40 (2H, m), 4.23 (2H, t, *J* = 4.5 Hz), 2.43 (2H, m), 2.28 (2H, t, *J* = 6.0 Hz), 2.09 (2H, m), 1.67 (2H, m), 1.49 (2H, m), 1.38 (2H, m), 1.27 (2H, m), 1.21 (2H, m); ^{13}C NMR δ 174.7, 132.3, 127.1, 64.2, 35.4, 29.7, 27.5, 27.3, 26.0, 25.9, 24.6, 23.5; HRMS (EI) 196.1424, $[C_{12}H_{20}O_2]^+$ requires 196.1463.

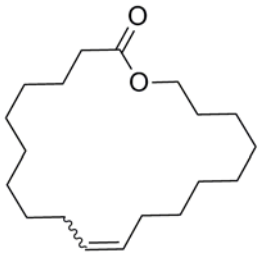
***Z*-Oxacyclohexadec-6-en-2-one (5)**



***Z*-5**

According to *General Procedure 1*, diene **5a** (0.11 g, 0.43 mmol) was reacted with **2** (0.022 g, 0.035 mmol) to provide ***Z*-5** (79 mg, 77% yield, 84% *Z* as determined by ^{1}H-NMR) as a colourless oil; ^{1}H NMR δ 5.35 (2H, m), 4.14 (2H, t, *J* = 5.5 Hz), 2.35 (2H, t, *J* = 6.6 Hz), 2.02-2.12 (4H, m), 1.61-1.74 (4H, m), 1.28-1.44 (12H, m); ^{13}C NMR δ 174.0, 131.2, 129.0, 64.5, 34.3, 28.0, 27.9, 27.4, 27.0, 26.9, 26.8, 26.6, 26.2, 25.6, 25.5; HRMS (EI) 238.1933, $[C_{15}H_{26}O_2]^+$ requires 238.1943.

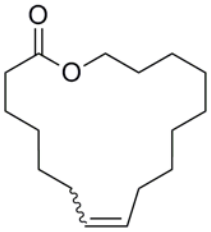
***Z*-Oxacycloicos-11-en-2-one (6)**



***Z*-6**

According to *General Procedure 1*, diene **6a** (0.14 g, 0.43 mmol) was reacted with **2** (0.021 g, 0.033 mmol) to provide ***Z*-6** (0.98 g, 75% yield, 94% *Z* as determined by quantitative ^{13}C-NMR) as a colourless oil; ^{1}H NMR δ 5.35 (2H, m), 4.12 (2H, t, *J* = 5.8 Hz), 2.31 (2H, t, *J* = 6.9 Hz), 2.03 (4H, m), 1.63 (4H, m), 1.22-1.43 (20H, m); ^{13}C NMR δ 174.0, 130.1, 130.0, 64.3, 34.8, 29.3, 29.1, 29.0, 28.8 (2C), 28.7 (2C), 28.5, 28.4, 28.1, 26.5, 26.4, 26.3, 25.1; HRMS (EI) 294.2552, $[C_{19}H_{34}O_2]^+$ requires 294.2559.

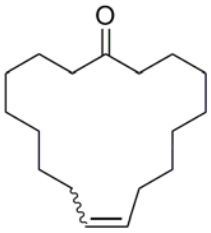
***Z*-Oxacycloheptadec-8-en-2-one (7)**



***Z*-7**

According to *General Procedure 1*, diene **7a** (0.13 g, 0.46 mmol) was reacted with **2** (0.022 g, 0.035 mmol) to provide ***Z*-7** (0.085 g, 71% yield, 89% *Z* as determined by quantitative ^{13}C-NMR) as a colourless oil; ^{1}H NMR δ 5.32 (2H, m), 4.14 (2H, t, *J* = 5.4 Hz), 2.33 (2H, t, *J* = 6.5 Hz), 2.04 (4H, m), 1.63 (4H, m), 1.21-1.43 (14H, m); ^{13}C NMR δ 173.9, 130.2, 130.1, 63.7, 34.6, 29.4, 28.8, 28.7, 28.5 (2C), 28.4, 27.7, 27.0, 26.8, 25.3 (2C); HRMS (EI) 252.2089, $[C_{16}H_{28}O_2]^+$ requires 252.2100.

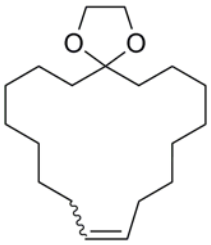
***Z*-Cycloheptadec-9-enone (8)**



***Z*-8**

According to *General Procedure 1*, diene **8a** (0.12 g, 0.43 mmol) was reacted with **2** (0.021 g, 0.033 mmol) for 8 hours to provide ***Z*-8** (0.068 g, 62% yield, 50% *Z* as determined by ^{1}H-NMR) as a colourless solid; ^{1}H NMR δ 5.34 (2H, m), 2.39 (4H, t, *J* = 6.7 Hz), 2.01 (4H, m), 1.61 (4H, m), 1.21-1.39 (16H, m); ^{13}C NMR δ 212.95, 130.2 (2C), 42.5 (2C), 29.0 (2C), 28.6 (2C), 28.2 (4C), 26.7 (2C), 23.9 (2C); HRMS (EI) 250.2299, $[C_{17}H_{30}O]^{+}$ requires 250.2297.

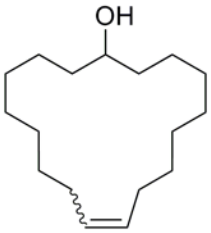
***Z*-1,4-Dioxaspiro[4.16]henicos-13-ene (9)**



***Z*-9**

According to *General Procedure 1*, diene **9a** (0.14 g, 0.43 mmol) was reacted with **2** (0.021 g, 0.033 mmol) to provide ***Z*-9** (0.075 g, 60% yield, 85% *Z* as determined by quantitative ^{13}C-NMR) as a colourless oil; ^{1}H NMR δ 5.33 (2H, m), 3.91 (4H, s), 2.05 (4H, m), 1.57 (4H, m), 1.24-1.38 (20H, m); ^{13}C NMR δ 130.1 (2C), 112.2, 64.3 (2C), 35.7 (2C), 29.2 (2C), 28.8 (2C), 27.8 (2C), 27.7 (2C), 27.1 (2C), 22.8 (2C); HRMS (EI) 294.2545, $[C_{19}H_{34}O_2]^{+}$ requires 294.2559.

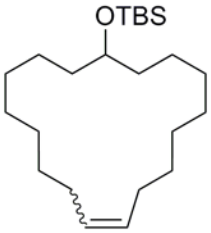
***Z*-Cycloheptadec-9-enol (10)**



***Z*-10**

According to *General Procedure 1*, diene **10a** (0.12 g, 0.43 mmol) was reacted with **2** (0.021 g, 0.033 mmol) to provide ***Z*-10** (0.062 g, 56% yield, 65% *Z* as determined by quantitative ^{13}C-NMR) as a colourless solid; ^{1}H NMR δ 5.34 (2H, m), 3.72 (1H, m), 2.04 (4H, m), 1.50 (4H, m), 1.22-1.40 (21H, m); ^{13}C NMR δ 130.2 (2C), 70.4, 35.6 (2C), 29.0 (2C), 28.2 (2C), 28.0 (2C), 27.9 (2C), 26.8 (2C), 23.5 (2C); HRMS (EI) 252.2451, $[C_{17}H_{32}O]^{+}$ requires 252.2453.

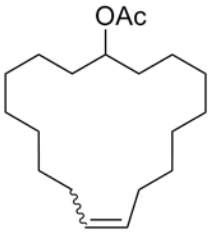
***Z*-*tert*-Butyl(cycloheptadec-9-en-1-yloxy)dimethylsilane (11)**



***Z*-11**

According to *General Procedure 1*, diene **11a** (0.17 g, 0.43 mmol) was reacted with **2** (0.021 g, 0.033 mmol) to provide ***Z*-11** (0.090 g, 56% yield, 75% *Z* as determined by quantitative ^{13}C-NMR) and recovered **11a** (0.022 g, 13%) as an inseperable mixture; for ***Z*-11**: ^{1}H NMR δ 5.34 (2H, m), 3.68 (1H, m), 2.04 (4H, m), 1.18-1.53 (24H, m), 0.88 (9H, s), 0.03 (6H, s); ^{13}C NMR δ 130.2 (2C), 71.3, 35.9 (2C), 29.1 (2C), 28.5 (2C), 28.1 (2C), 27.9 (2C), 26.9 (2C), 25.9 (3C), 23.4 (2C), 18.2, 4.5 (2C); HRMS (EI) 365.3252, $[C_{23}H_{46}OSi\text{-}H]^{+}$ requires 365.3240.

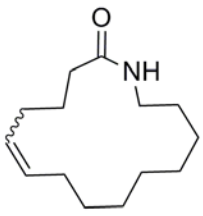
***Z*-Cycloheptadec-9-en-1-yl acetate (12)**



***Z*-12**

According to *General Procedure 1*, diene **12a** (0.14 g, 0.43 mmol) was reacted with **2** (0.022 g, 0.035 mmol) to provide ***Z*-12** (0.074 g, 59% yield, 75% *Z* as determined by quantitative ^{13}C-NMR) as a colourless oil; ^{1}H NMR δ 5.34 (2H, m), 4.86 (1H, m), 2.03 (4H, m), 2.01 (3H, s), 1.55 (4H, m), 1.22-1.40 (20H, m); ^{13}C NMR δ 170.8, 130.2, 73.5, 32.2 (2C), 29.1 (2C), 28.2 (2C), 27.8 (2C), 26.8 (2C), 23.4 (2C), 21.4 (2C); HRMS (FAB) 295.2633, $[C_{19}H_{34}O_2+H]^+$ requires 295.2637.

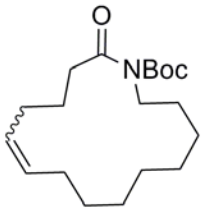
***Z*-Azacyclopentadec-6-en-2-one (13)**



***Z*-13**

According to *General Procedure 1*, diene **13a** (0.11 g, 0.44 mmol) was reacted with **2** (0.022 g, 0.035 mmol) to provide **(*Z*)-13** (0.029 g, 30% yield, 84% *Z* as determined by ^{1}H-NMR) as a colourless solid; ^{1}H NMR δ 5.41 (2H, m), 5.28 (1H, m), 3.32 (2H, m), 2.02 (2H, t, *J* = 6.1 Hz), 2.13 (2H, m), 1.99 (2H, m), 1.75 (2H, m), 1.52 (2H, m), 1.25-1.39 (10H, m); ^{13}C NMR δ 172.7, 131.2, 129.4, 38.9, 35.3, 28.4, 27.9, 27.3, 26.9, 26.7 (2C), 25.8, 25.4, 25.3; HRMS (EI) 223.1930, $[C_{14}H_{25}ON]^+$ requires 223.1936.

***Z-tert*-Butyl 2-oxoazacyclopentadec-6-ene-1-carboxylate (14)**



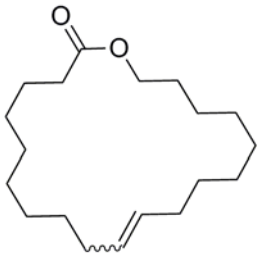
***Z*-14**

According to *General Procedure 1*, diene **14a** (0.15 g, 0.43 mmol) was reacted with **2** (0.022 g, 0.035 mmol) to provide ***Z*-14** (0.082 g, 59% yield, 83% *Z* as determined by ^{1}H-NMR) as a colourless oil; ^{1}H NMR δ 5.37 (1H, m), 5.27 (1H, m), 3.83 (2H, t, *J* = 5.8 Hz), 2.86 (2H, t, *J* = 5.8 Hz), 2.16 (2H, m), 1.96 (2H, m), 1.75 (2H, m), 1.58 (2H, m), 1.51 (9H, m), 1.20-1.35 (10H, m); ^{13}C NMR δ 176.0, 153.6, 131.3, 129.6, 82.5, 43.9, 36.2, 28.4, 28.1 (3C), 28.0, 27.6, 27.1, 27.0, 26.3, 25.9, 25.8, 24.4; HRMS (EI) 323.2447, $[C_{19}H_{33}O_3N]^+$ requires 323.2460.

***General procedure* 2: Synthesis of *E*-enriched macrocycles[4]**

A solution of diene (1 equiv, 1.8 mmol) and benzylidene-bis*(*tricyclohexylphosphine*)*dichlororuthenium (0.074 g, 0.090 mmol) in CH_2Cl_2 (6 mM, 300 mL) was refluxed for six hours, then quenched with ethyl vinyl ether, and concentrated. Flash chromatography of the residue (SiO_2, using 2% Et_2O in pentanes for compounds **6** and **8**, 10% Et_2O in pentanes for compound **10**, and 66% Et_2O in pentanes for compound **13**) provided the product.

***E*-O*xacycloicos*-11-en-2-one (6)**



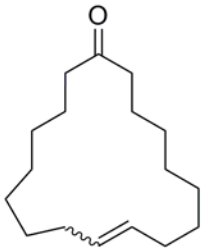
***E*-6**

According to *General Procedure 2*, diene **6a** provided ***E*-6** (0.31 g, 58% yield, 69% *E* as determined by quantitative ^{13}C-NMR) as a colourless oil; ^{1}H NMR δ 5.32 (m, 2H), 4.09 (t, *J* = 5.6 Hz,

[4] Prepared in a manner similar to: Lee, C.-W.; Grubbs, R. H. *Org. Lett.* **2000**, *Org. Lett., 2*, 2145-2147.

2H), 2.31 (t, *J* = 6.7 Hz, 2H), 2.01 (m, 4H), 1.63 (m, 4H), 1.26-1.41 (m, 20H); ^{13}C NMR δ 174.2, 130.8, 130.8, 64.4, 34.2, 32.0, 31.9, 29.4, 29.2, 28.9 (2C), 28.8 (2C), 28.7, 28.3, 27.7, 27.6, 26.2, 25.1.

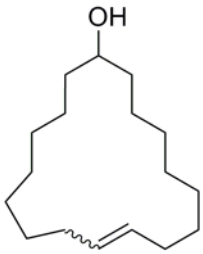
***E*-Cycloheptadec-9-enone (8)**



***E*-8**

According to *General Procedure 2*, diene **8a** provided ***E*-8** (0.20 g, 44% yield, 80% *E* as determined by ^{1}H-NMR) as a colourless solid; ^{1}H NMR δ 5.31 (m, 2H), 2.37 (t, *J* = 7.1 Hz, 4H), 2.01 (m, 4H) 1.60 (m, 4H), 1.22-1.37 (m, 16H); ^{13}C NMR δ 213.4, 131.2 (2C), 42.6 (2C), 32.1 (2C), 29.0 (2C), 28.9 (2C), 28.5 (2C), 27.6 (2C), 24.2 (2C).

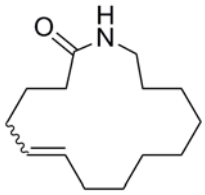
***E*-Cycloheptadec-9-enol (10)**



***E*-10**

According to *General Procedure 2*, diene **10a** provided ***E*-10** (0.18 g, 40% yield, 80% *E* as determined by quantitative ^{13}C-NMR) as a colourless solid; ^{1}H NMR δ 5.34 (m, 2H), 3.71 (m, 1H), 2.02 (m, 4H), 1.50 (m, 4H), 1.23-1.36 (m, 20H); ^{13}C NMR δ 131.0 (2C), 71.4, 35.6 (2C), 32.4 (2C), 29.2 (2C), 28.7 (2C), 28.2 (2C), 27.4 (2C), 22.9 (2C).

***E*-Azacyclopentadec-6-en-2-one (13)**



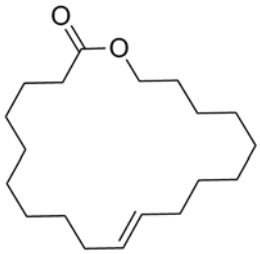
***E*-13**

Similar to *General Procedure 2*, except after 6 hours a second aliquot of 5 mol% bis(tricyclohexylphosphine)benzylidine ruthenium(IV) was added and the solution refluxed for an additional six hours, diene **13a** provided ***E*-13** (0.13 g, 33% yield, 55% *E* as determined by ^{1}H-NMR) as a colourless solid. ^{1}H NMR δ 5.36 (m, 2H), 5.32 (1H, *overlapped*), 3.27 (q, *J* = 5.7 Hz, 2H), 2.21 (t, *J* = 6.3 Hz, 2H), 2.13 (m, 2H), 2.01 (m, 2H), 1.78 (m, 2H), 1.45 (m, 2H), 1.34 (m, 8H), 1.26 (m, 2H); ^{13}C NMR δ 172.9, 130.4, 130.1, 38.9, 34.6, 31.5 (2C), 27.8, 27.6, 26.4, 26.2, 25.2, 23.8, 23.4.

***General procedure* 3: *Z*-selective ethenolysis of *E*-dominant macrocycles**

A solution of *E*-enriched macrocycle (1 equiv.) in THF (1M) was prepared in a 4 mL vial in a glovebox and sealed with a septum cap. Catalyst **2** (2 mol %) was added as a solution in a minimal amount of THF. The sealed vial was removed from the glovebox and stirred under an ethylene atmosphere. The reaction was heated (35 °C for **6** and **9**, 40 °C for **12**, 75 °C for **7**) for 2 hours, then quenched with ethyl vinyl ether and concentrated. Flash chromatography of the residue (SiO_2, using 2% Et_2O in pentanes for compounds **6** and **7**, 10% Et_2O in pentanes for compound **9**, and 66% Et_2O in pentanes for compound **12**) provided the product as the pure *E*-isomer. Isolated yields of the pure *E*-macrocycles and recovered diene were calculated based on the assumption that only the *Z*-isomer underwent ethenolysis and that it reacted completely.

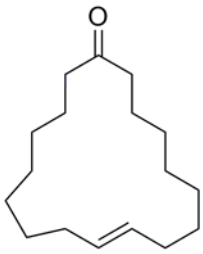
***E*-Oxacycloicos-11-en-2-one (6)**



***E*-6**

According to *General Procedure 3*, macrocycle **6** (97 mg, 0.33 mmol, 69% *E*) was reacted with **2** (4.2 mg, 7.0 μmol) and provided the pure *E*-isomer of **6** (47 mg, 69% yield) and diene **6a** (27 mg, 81% yield) as colourless oils; ^{1}H NMR δ 5.32 (m, 2H), 4.09 (t, *J* = 5.6 Hz, 2H), 2.31 (t, *J* = 6.7 Hz, 2H), 2.01 (m, 4H), 1.63 (m, 4H), 1.26-1.41 (m, 20H); ^{13}C NMR δ 174.2, 130.8, 130.8, 64.4, 34.2, 32.0, 31.9, 29.4, 29.2, 28.9 (2C), 28.8 (2C), 28.7, 28.3, 27.7, 27.6, 26.2, 25.1. HRMS (EI) 294.2549, $[C_{19}H_{34}O_2]^+$ requires 294.2559.

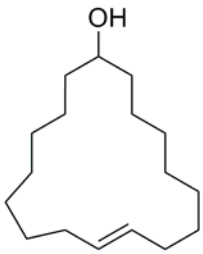
***E*-Cycloheptadec-9-enone (8)**



***E*-8**

According to *General Procedure 3*, macrocycle **8** (156 mg, 0.62 mmol, 80% *E*) was reacted with **2** (7.9 mg, 12 μmol) and provided the pure *E*-isomer of **8** (50 mg, 40% yield) and diene **8a** (16 mg, 46% yield) as colourless solids; ^{1}H NMR δ 5.31 (m, 2H), 2.37 (t, *J* = 7.1 Hz, 4H), 2.01 (m, 4H) 1.60 (m, 4H), 1.22-1.37 (m, 16H); ^{13}C NMR δ 213.4, 131.2, 42.6, 32.1, 29.0, 28.9, 28.5, 27.6, 24.2. HRMS (FAB) 251.2372, $[C_{17}H_{30}O+H]^+$ requires 251.2375.

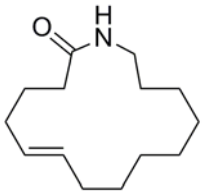
***E*-Cycloheptadec-9-enol (10)**



***E*-10**

According to *General Procedure 3*, macrocycle **10** (108 mg, 0.43 mmol, 80% *E*) was reacted with **2** (5.4 mg, 9.0 μmol) and provided the pure *E*-isomer of **10** (68 mg, 78% yield) and diene **10a** (19 mg, 79% yield) as colourless solids; ^{1}H NMR δ 5.34 (m, 2H), 3.71 (m, 1H), 2.02 (m, 4H), 1.50 (m, 4H), 1.23-1.36 (m, 20H); ^{13}C NMR δ 131.0 (2C), 71.4, 35.6 (2C), 32.4 (2C), 29.2 (2C), 28.7 (2C), 28.2 (2C), 27.4 (2C), 22.9 (2C). HRMS (FAB) 251.2371, $[C_{17}H_{32}O_2\text{-}H]^+$ requires 251.2375.

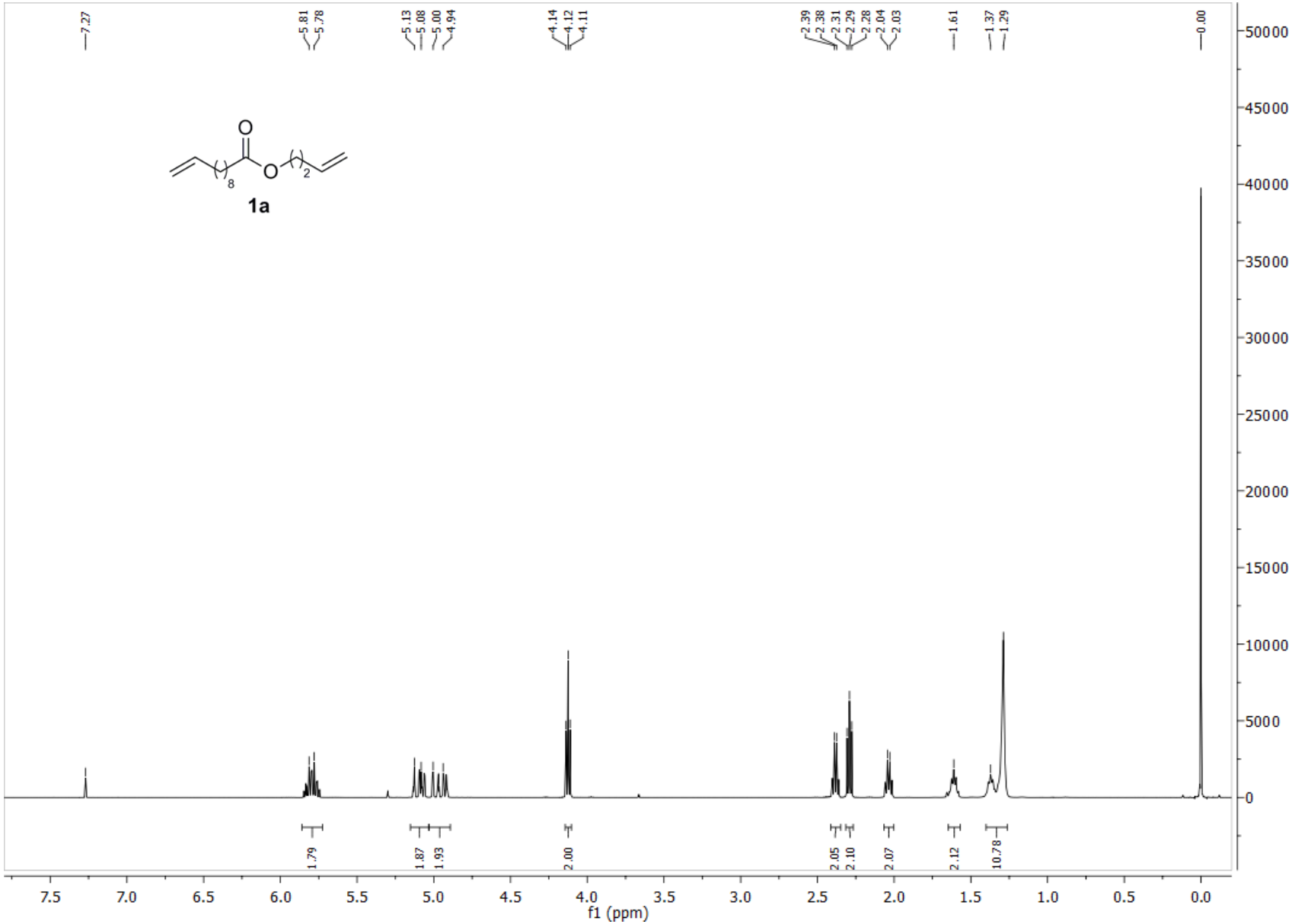
***E*-Azacyclopentadec-6-en-2-one (13)**



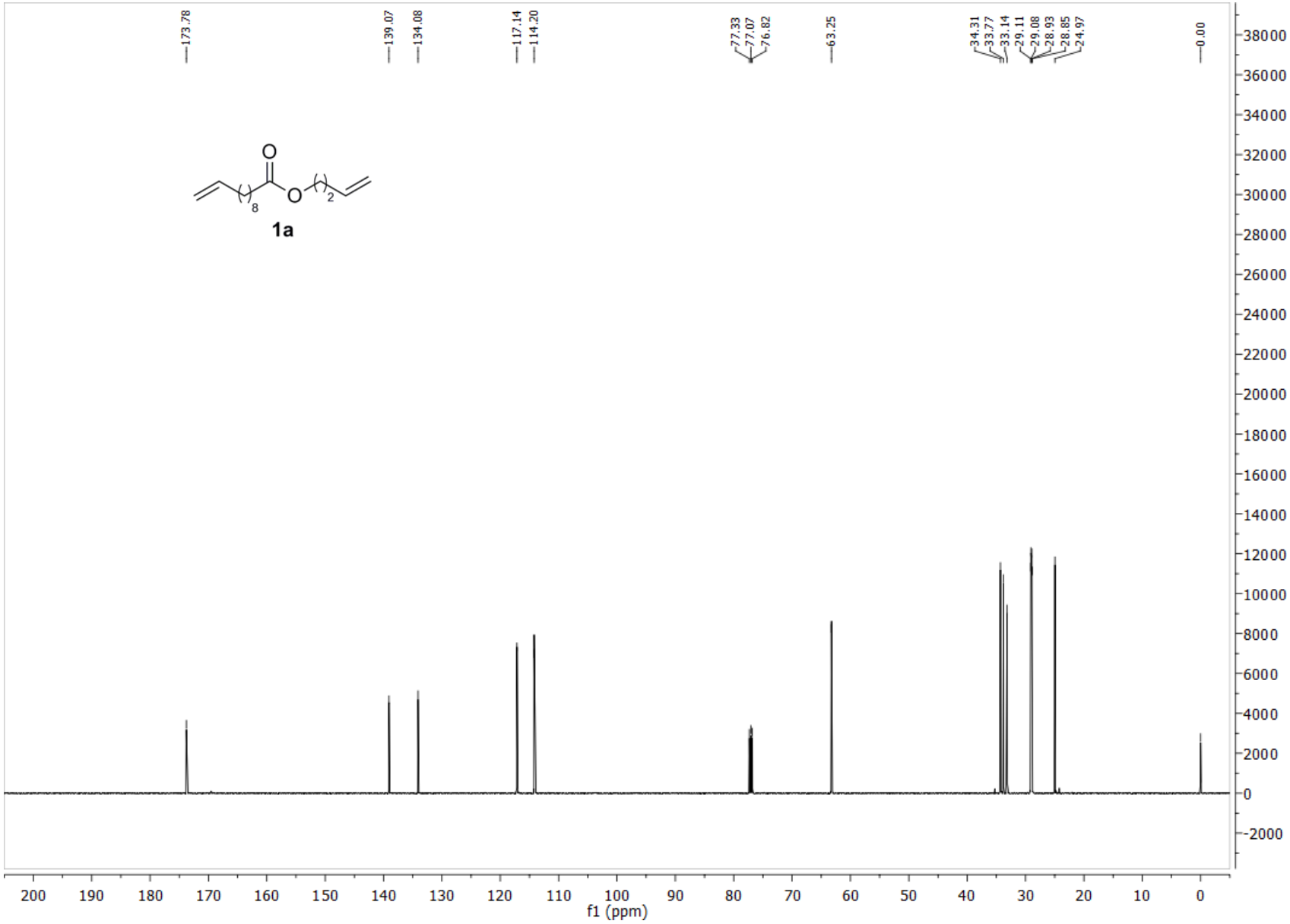
***E*-13**

According to *General Procedure 3*, macrocycle **13** (51 mg, 0.22 mmol, 55% *E*) was reacted with **2** (2.8 mg, 4.4 μmol) and provided the pure *E*-isomer of **13** (21 mg, 75% yield) as a colourless solid, and diene **13a** (21 mg, 86% yield) as a pale yellow oil; ^{1}H NMR δ 5.36 (m, 2H), 5.32 (1H, *overlapped*), 3.27 (q, *J* = 5.7 Hz, 2H), 2.21 (t, *J* = 6.3 Hz, 2H), 2.13 (m, 2H), 2.01 (m, 2H), 1.78 (m, 2H), 1.45 (m, 2H), 1.34 (m, 8H), 1.26 (m, 2H); ^{13}C NMR δ 172.9, 130.4, 130.1, 38.9, 34.6, 31.5 (2C), 27.8, 27.6, 26.4, 26.2, 25.2, 23.8, 23.4. HRMS (FAB) 224.2014, $[C_{14}H_{25}NO\text{+}H]^+$ requires 224.2014.

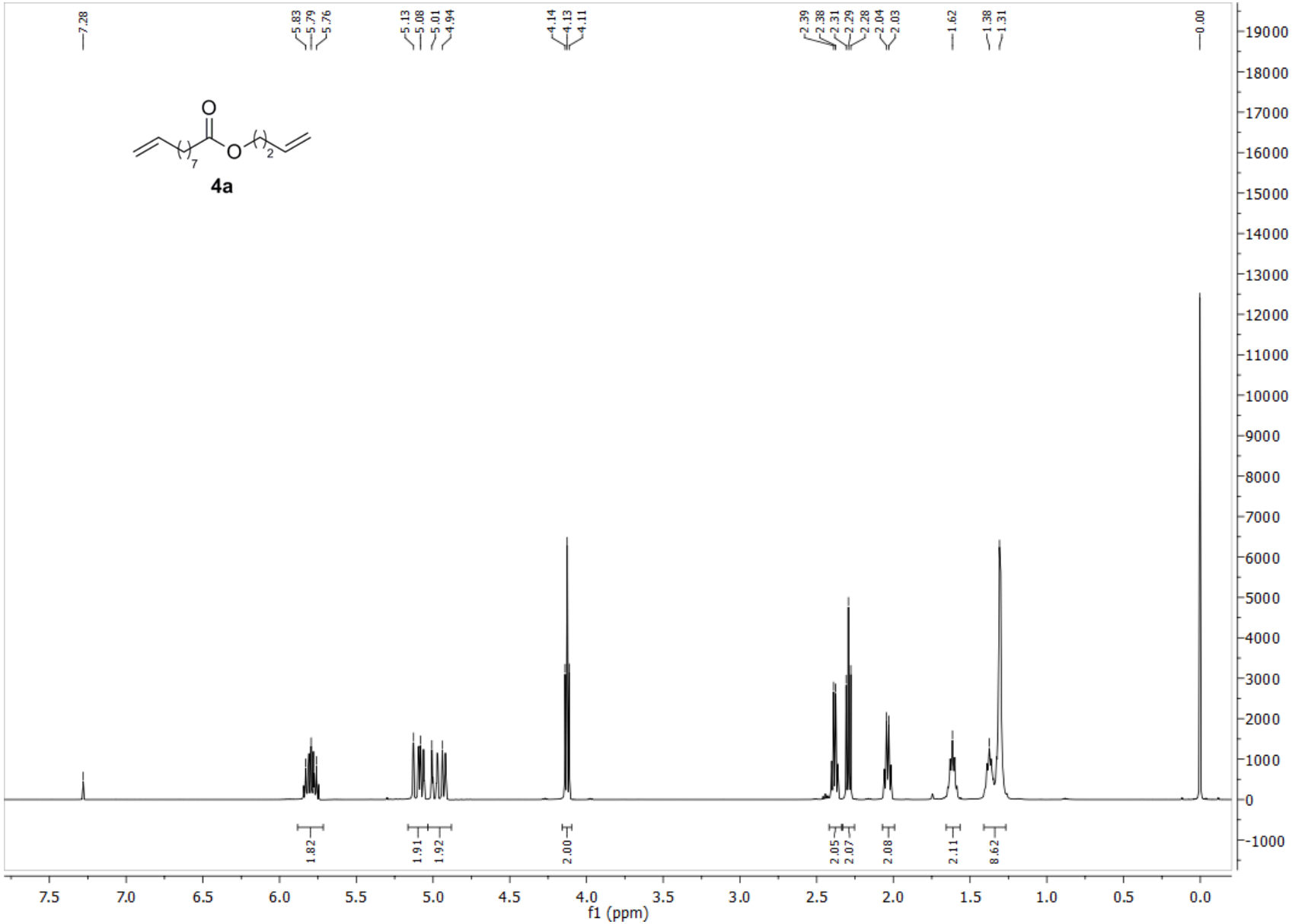
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of but-3-en-1-yl undec-10-enoate (1a)



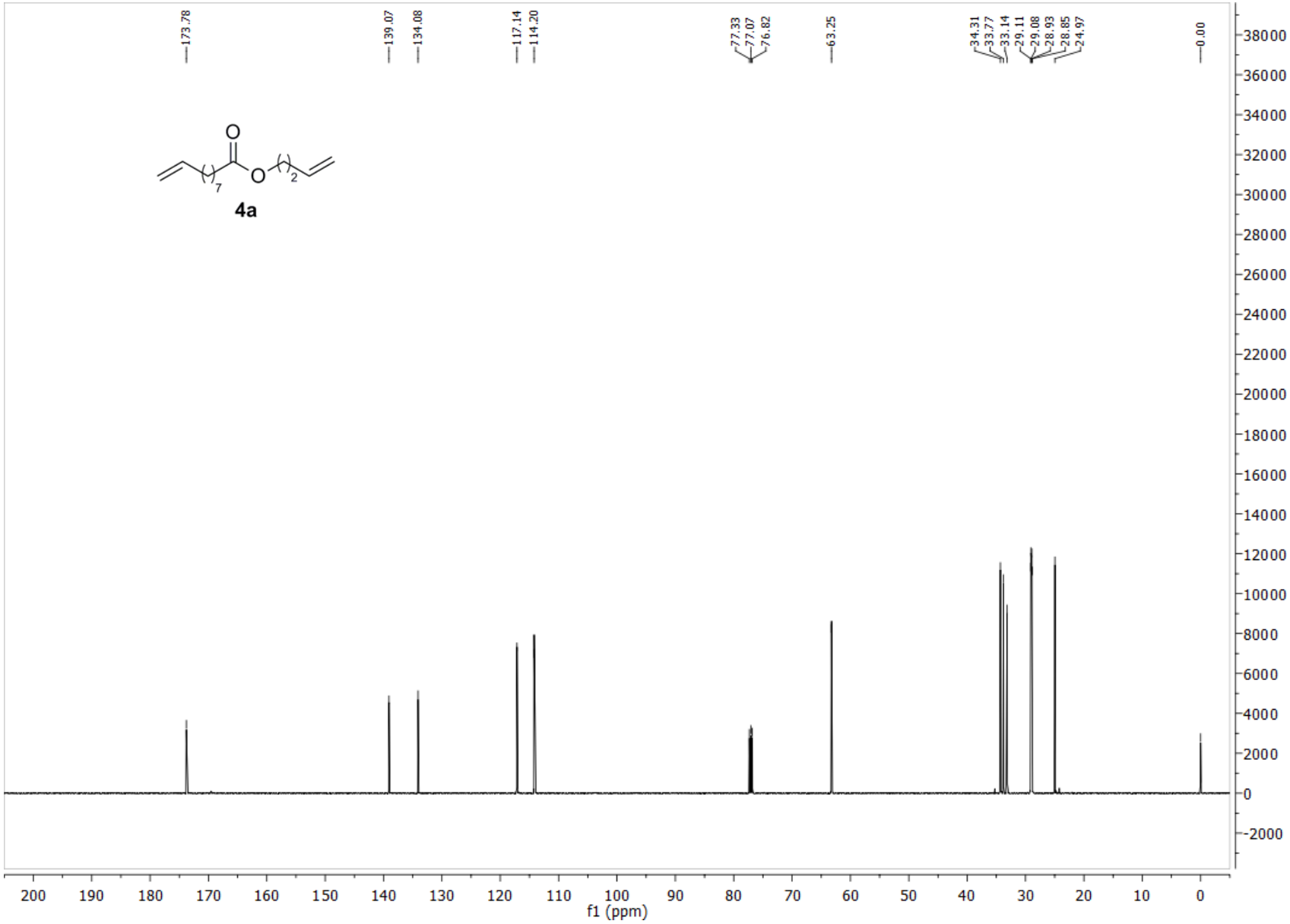
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of but-3-en-1-yl undec-10-enoate (1a)



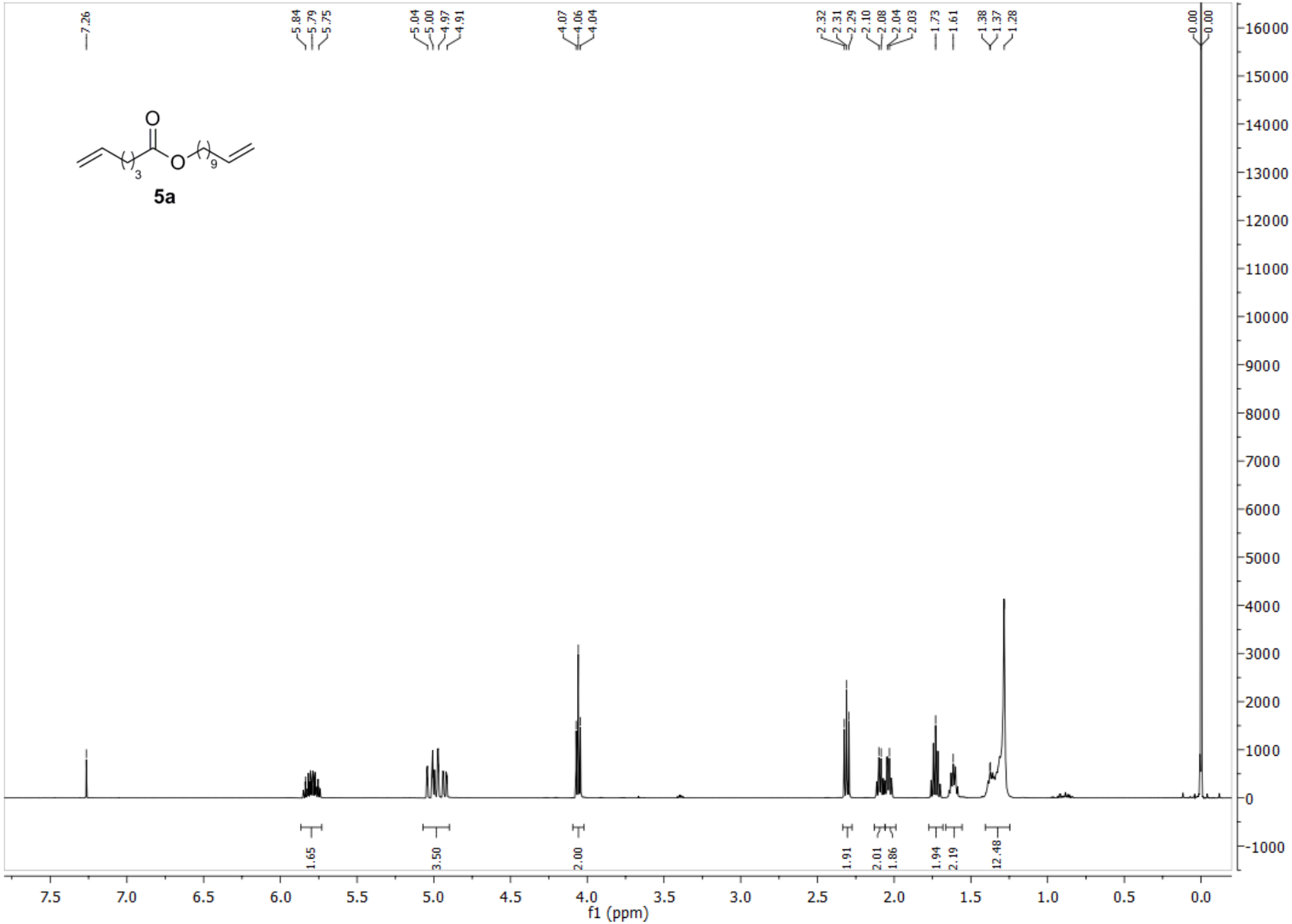
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of but-3-en-1-yl dec-9-enoate (4a)



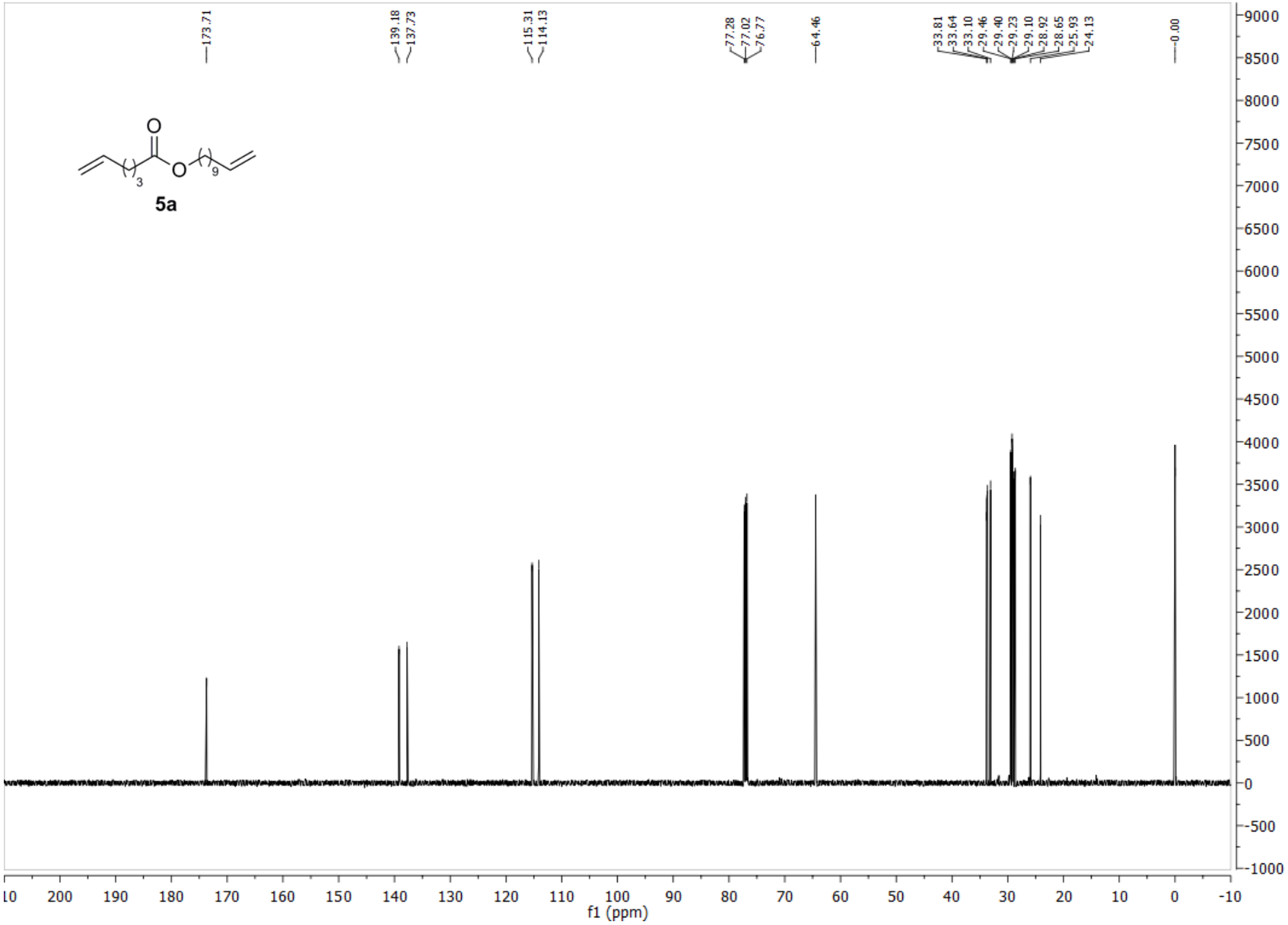
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of but-3-en-1-yl dec-9-enoate (4a)



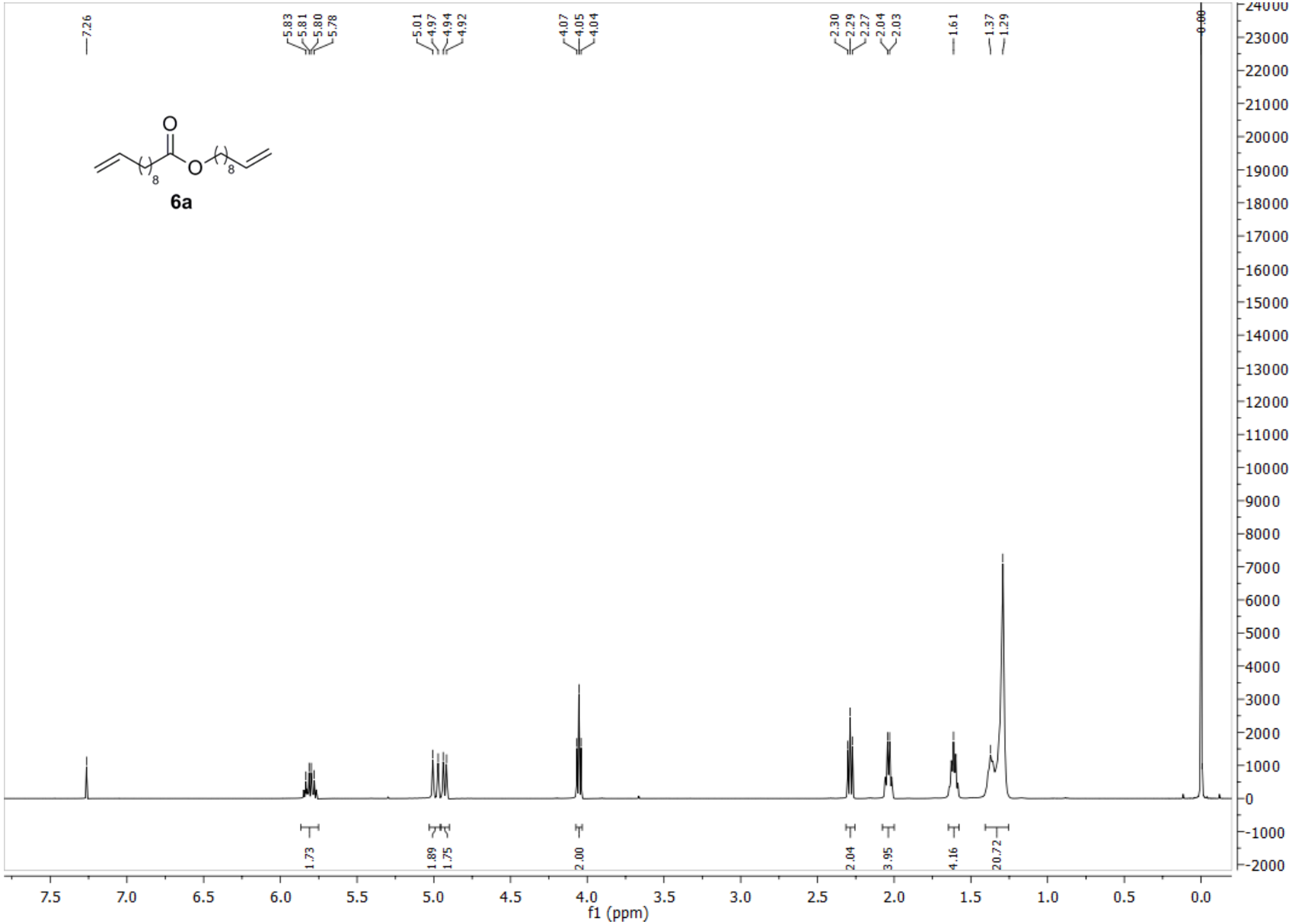
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of undec-10-en-1-yl hex-5-enoate (5a)



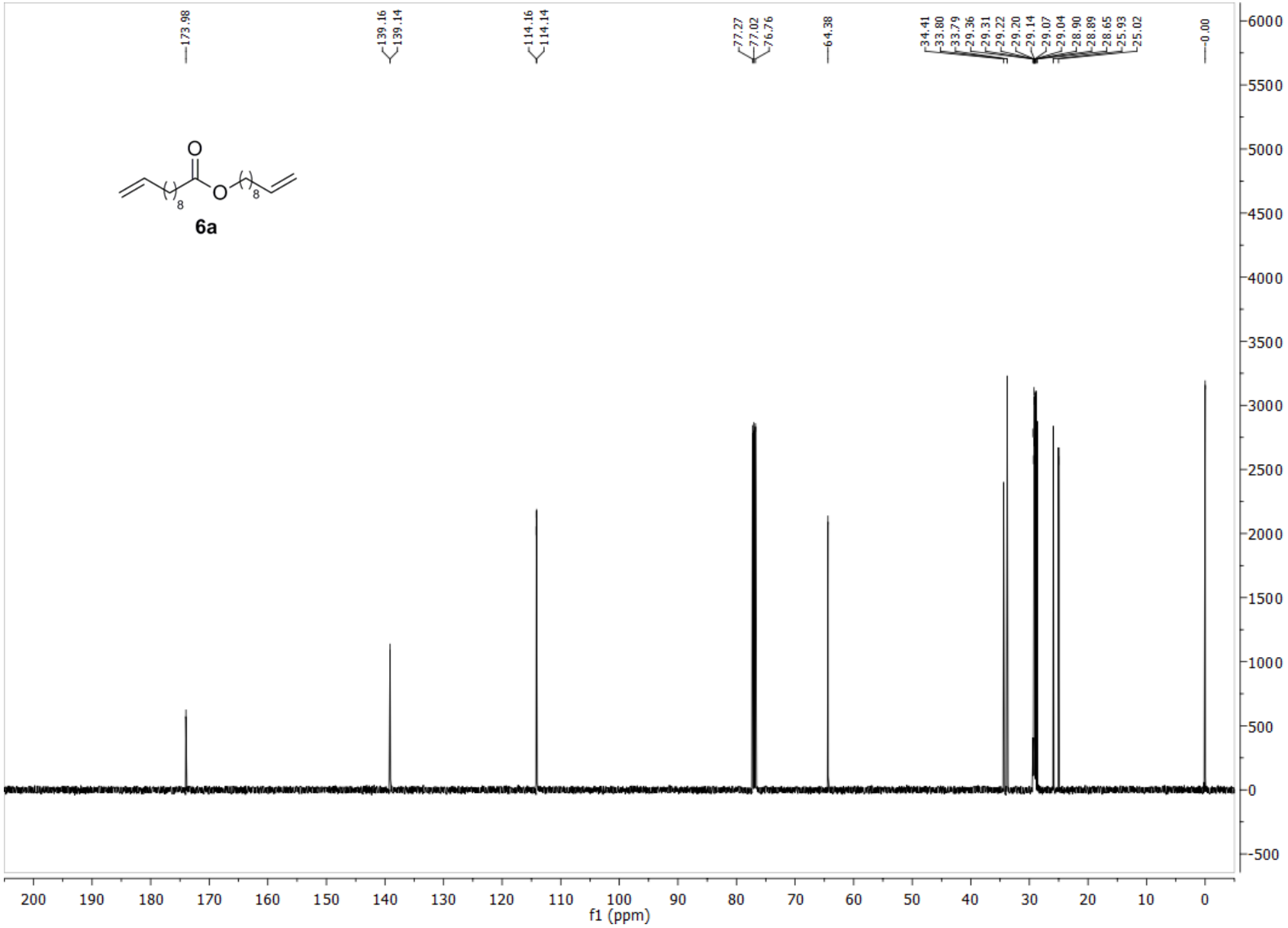
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of undec-10-en-1-yl hex-5-enoate (5a)



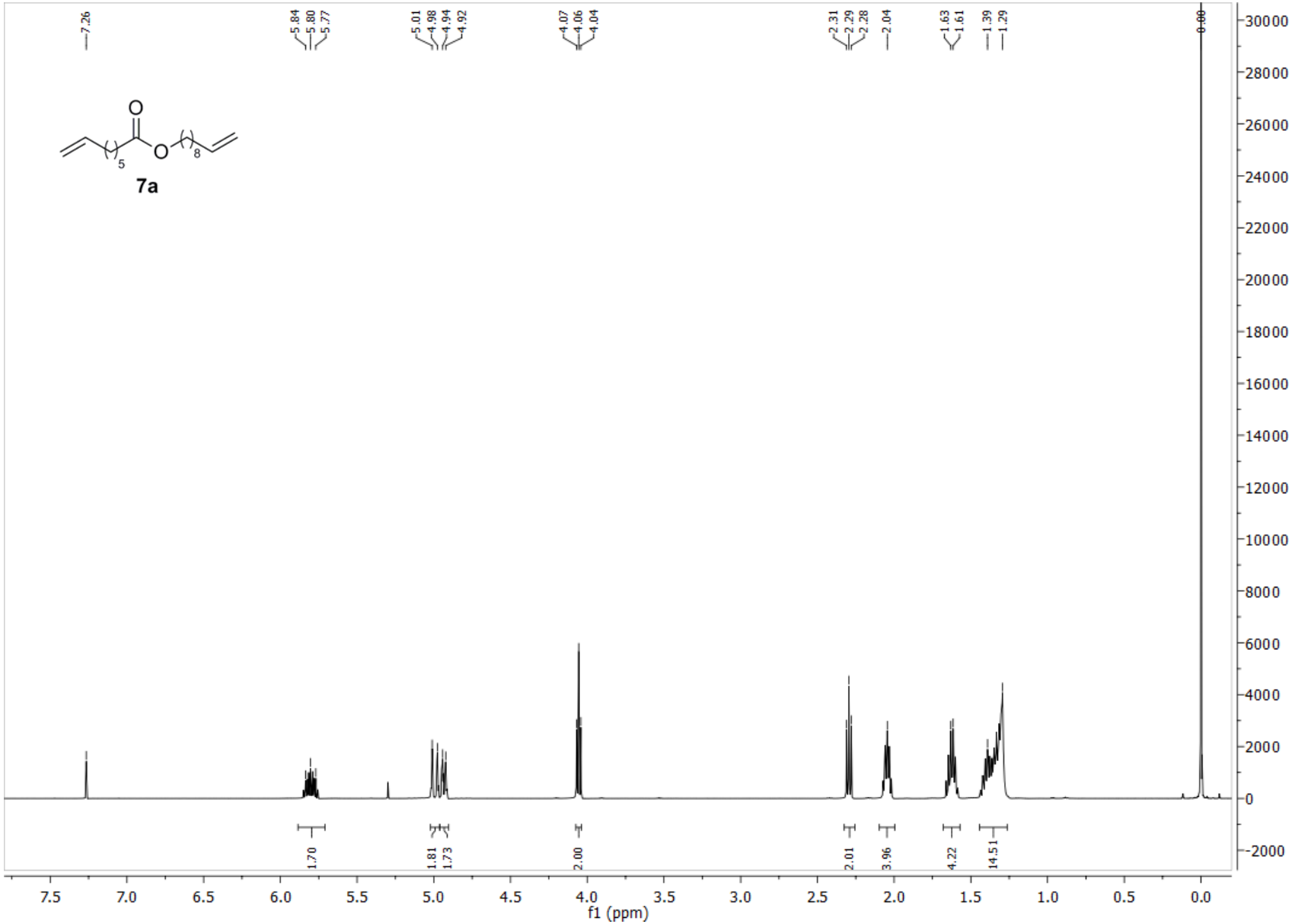
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of dec-9-en-1-yl undec-10-enoate (6a)



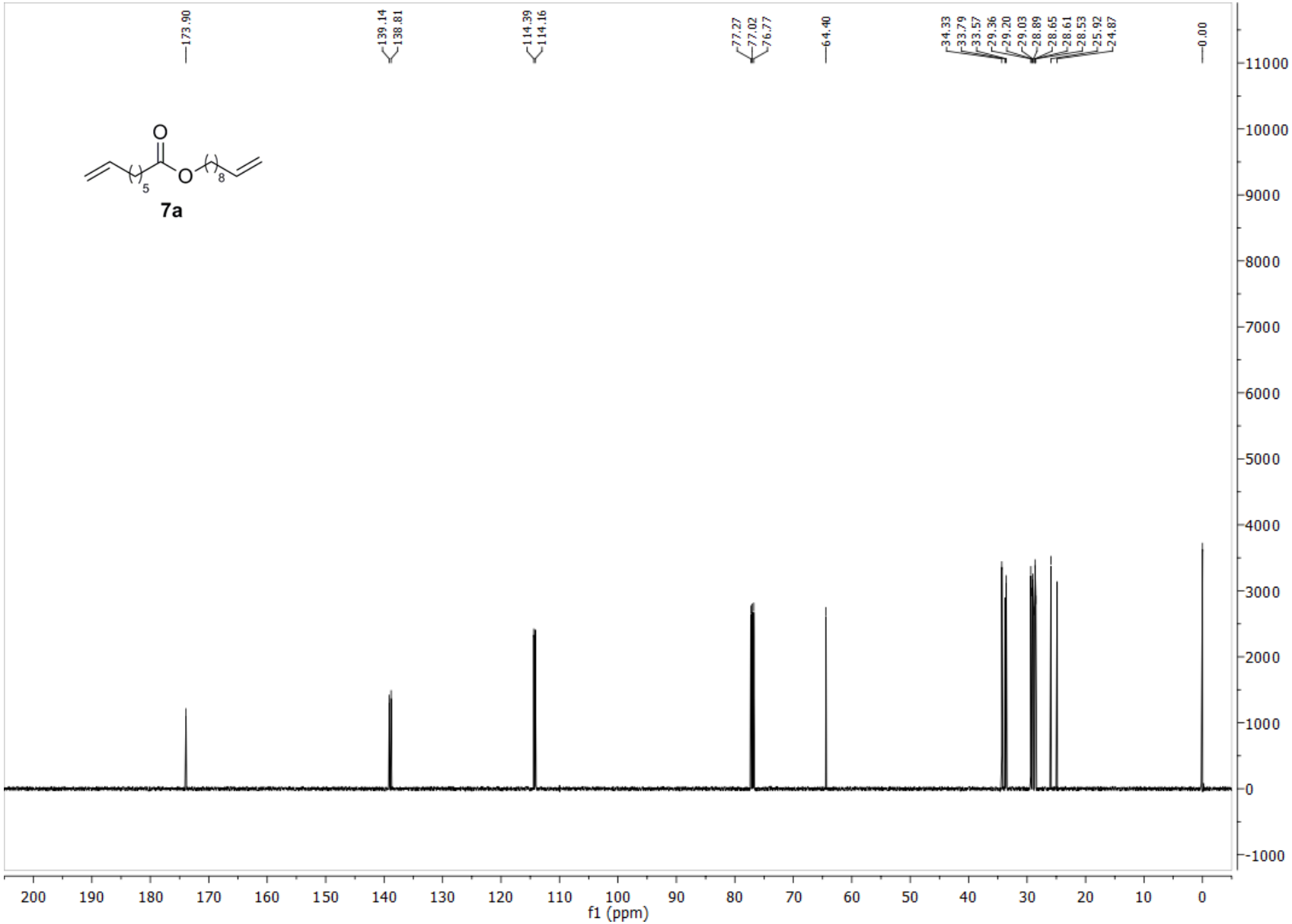
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of dec-9-en-1-yl undec-10-enoate (6a)



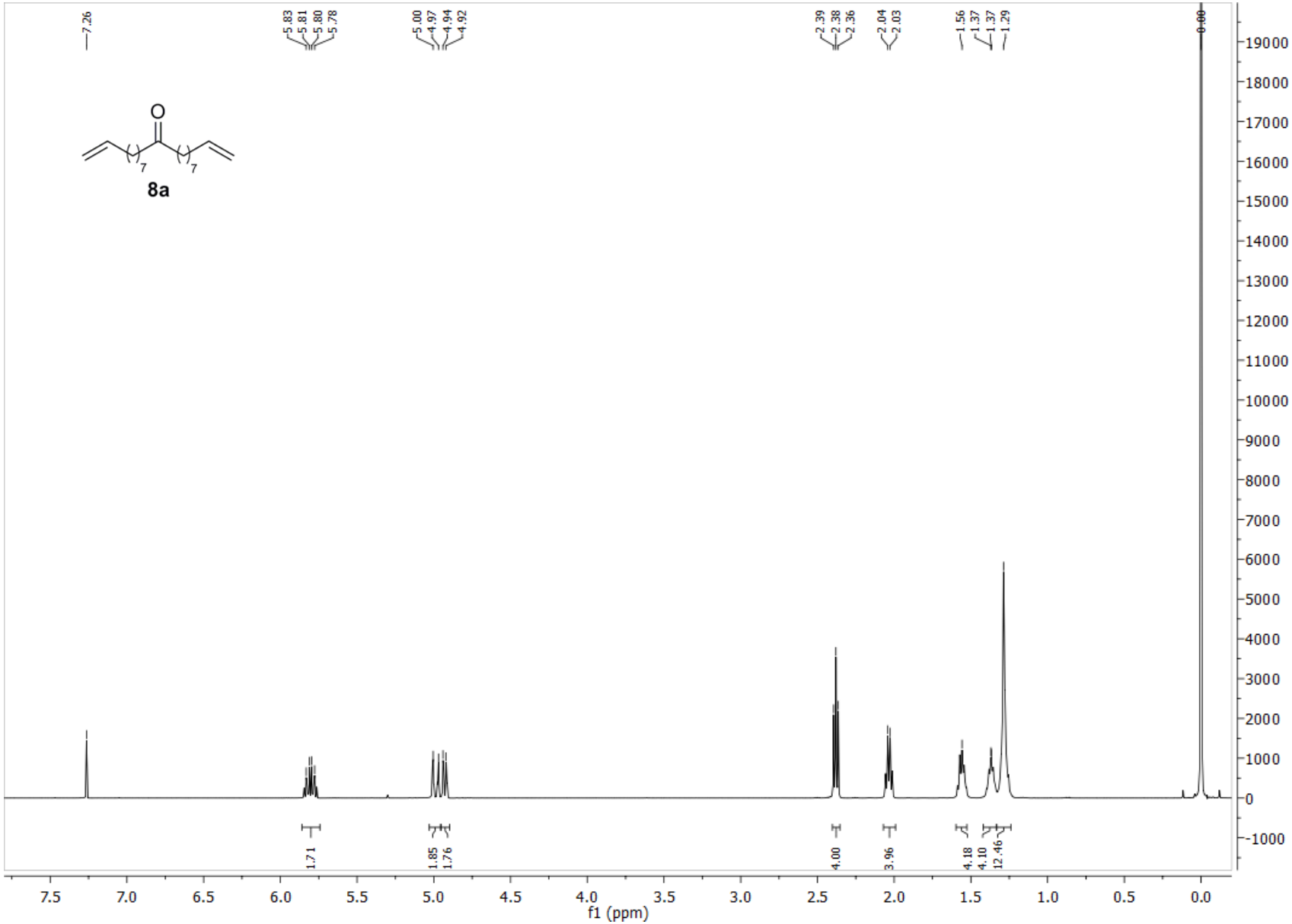
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of dec-9-en-1-yl oct-7-enoate (7a)



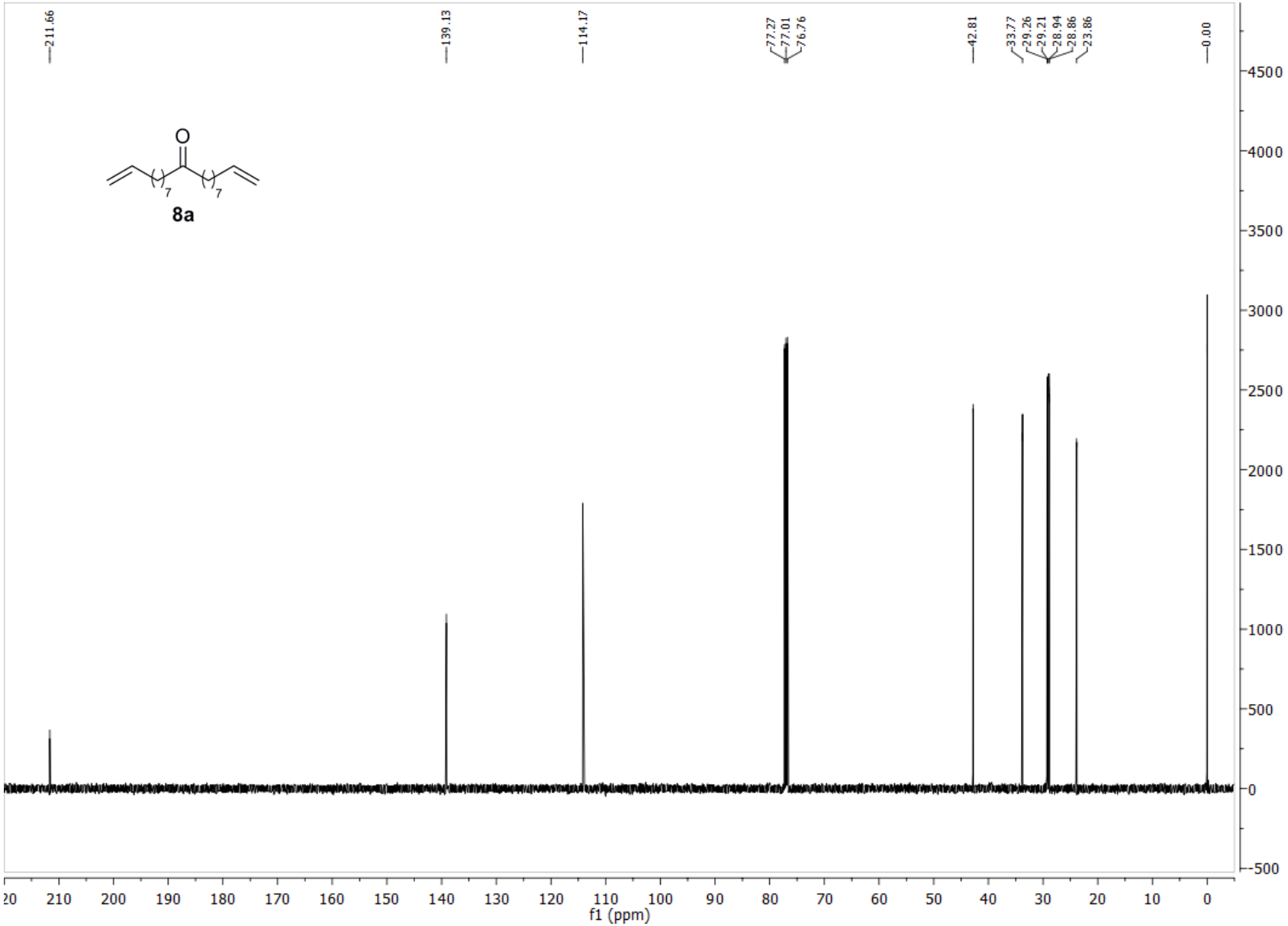
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of dec-9-en-1-yl oct-7-enoate (7a)



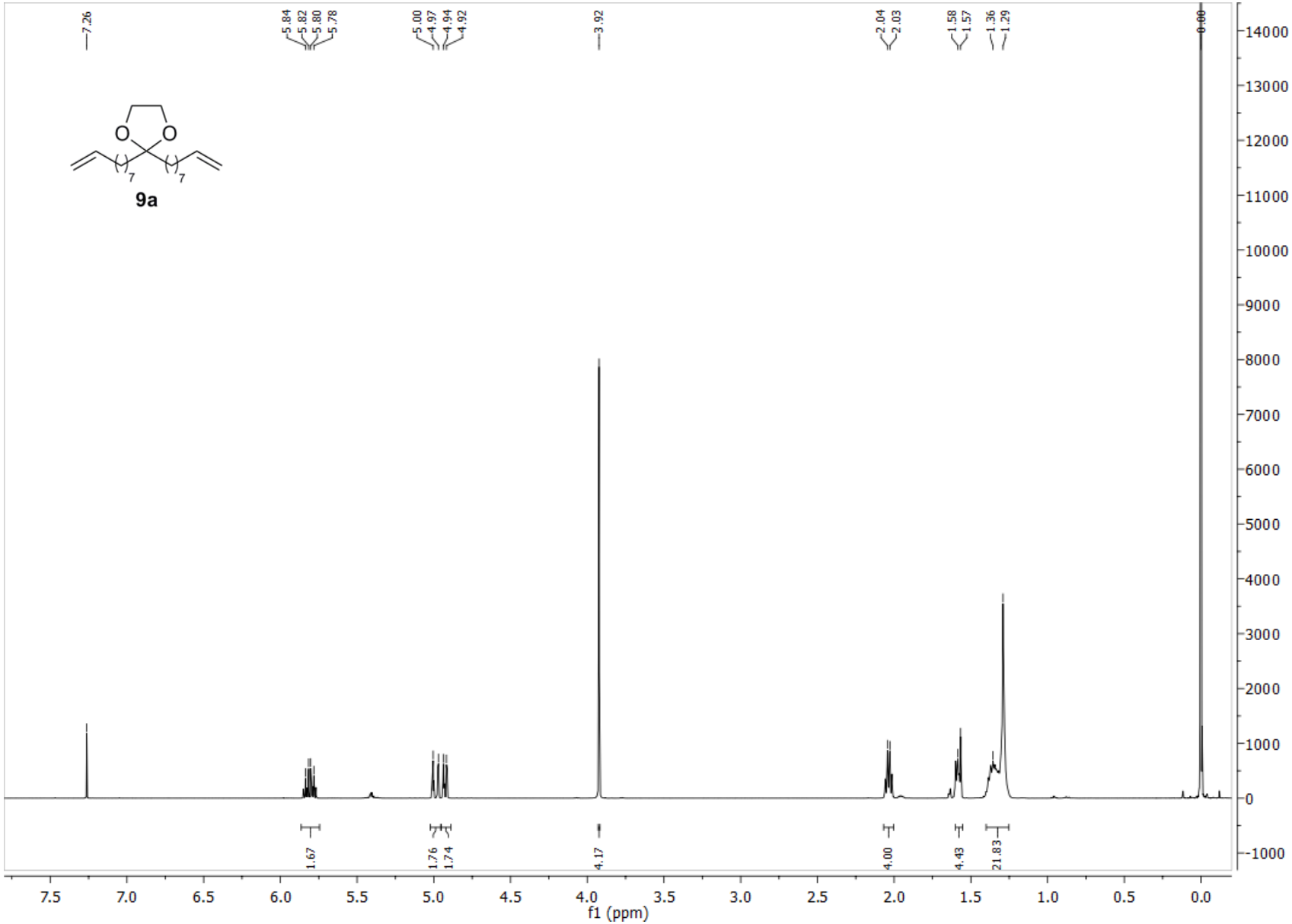
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of nonadeca-1,18-dien-10-one (8a)



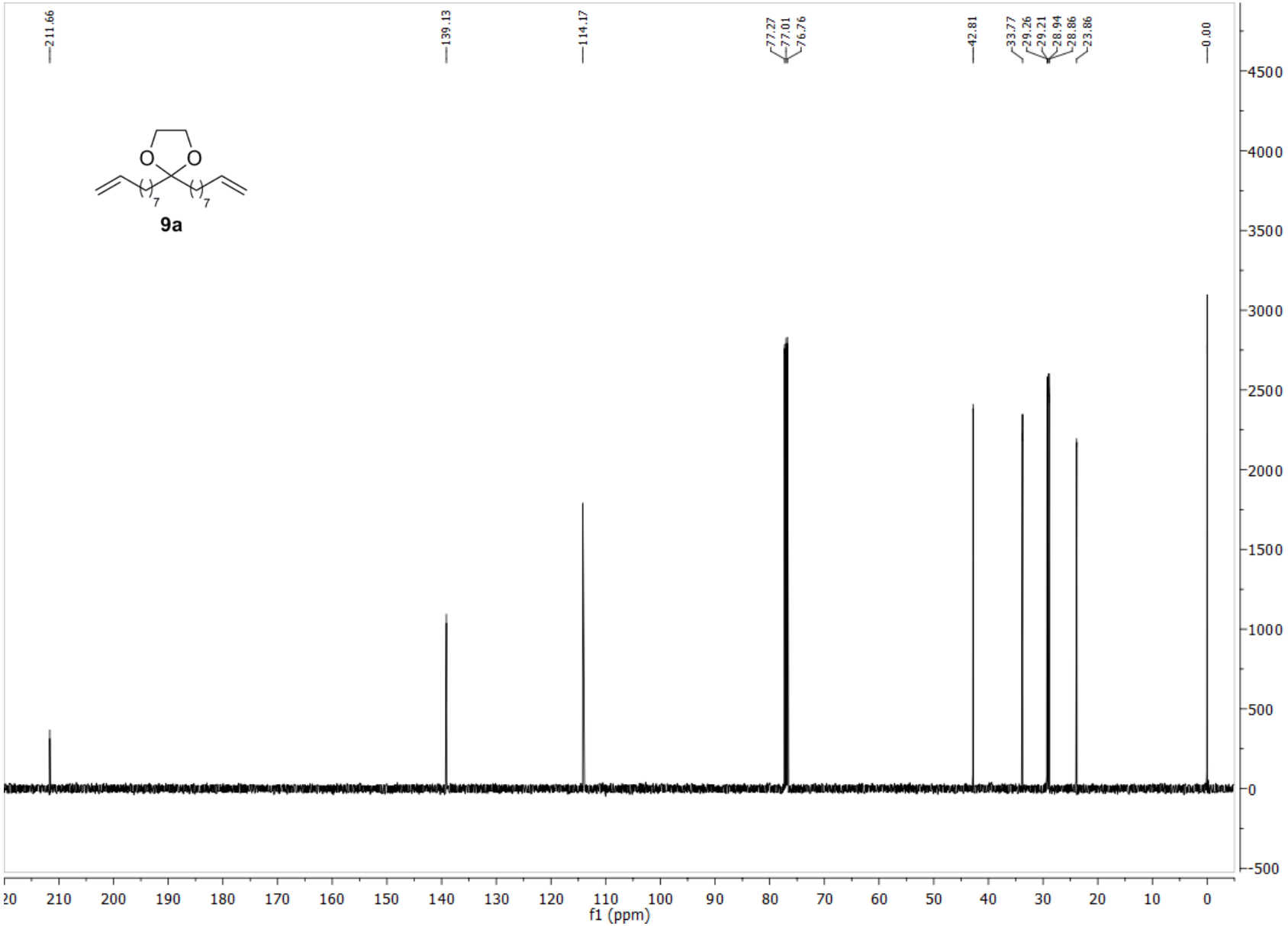
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of nonadeca-1,18-dien-10-one (8a)



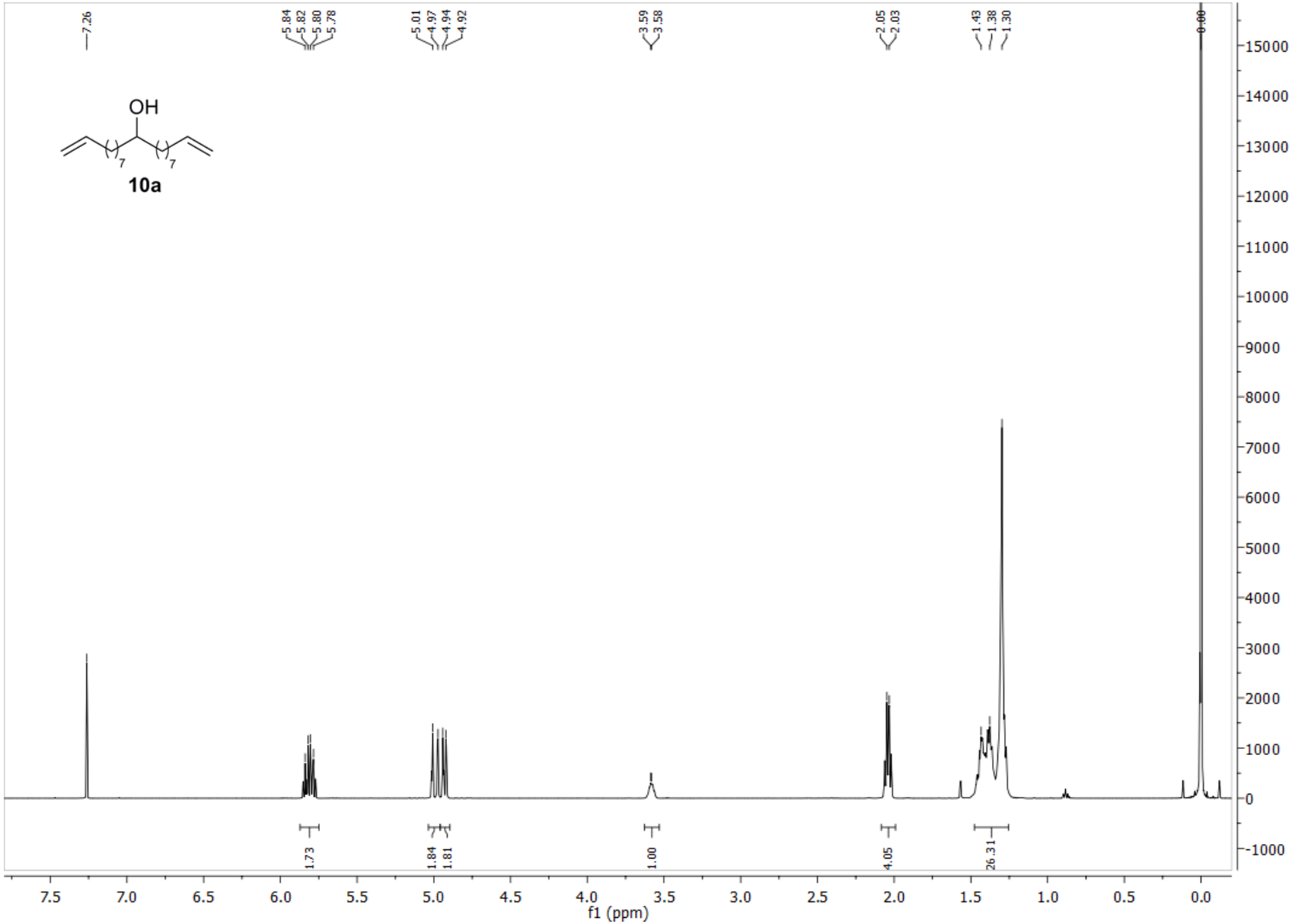
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2,2-di(non-8-en-1-yl)-1,3-dioxolane (9a)



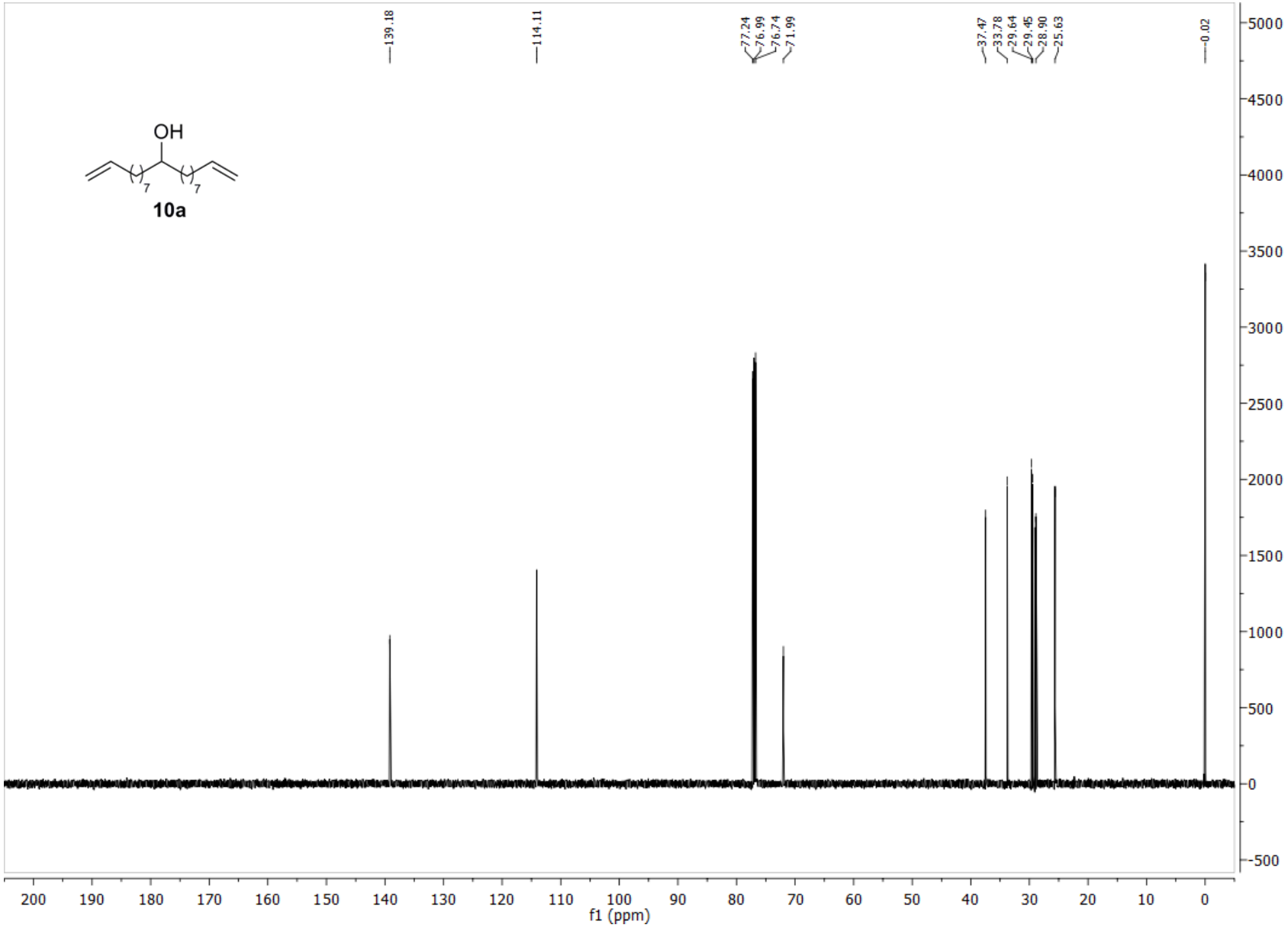
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of 2,2-di(non-8-en-1-yl)-1,3-dioxolane (9a)



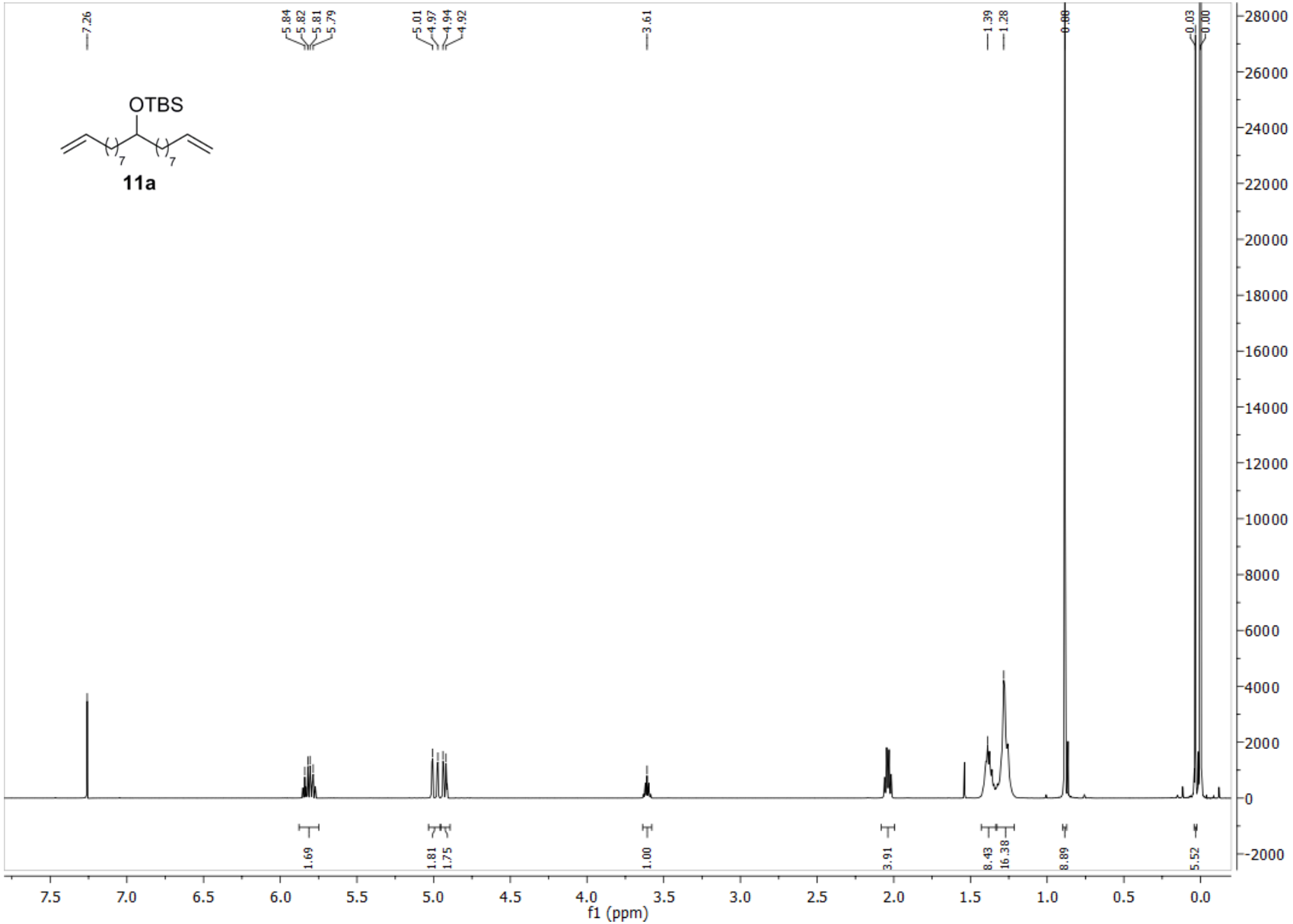
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of nonadeca-1,18-dien-10-ol (10a)



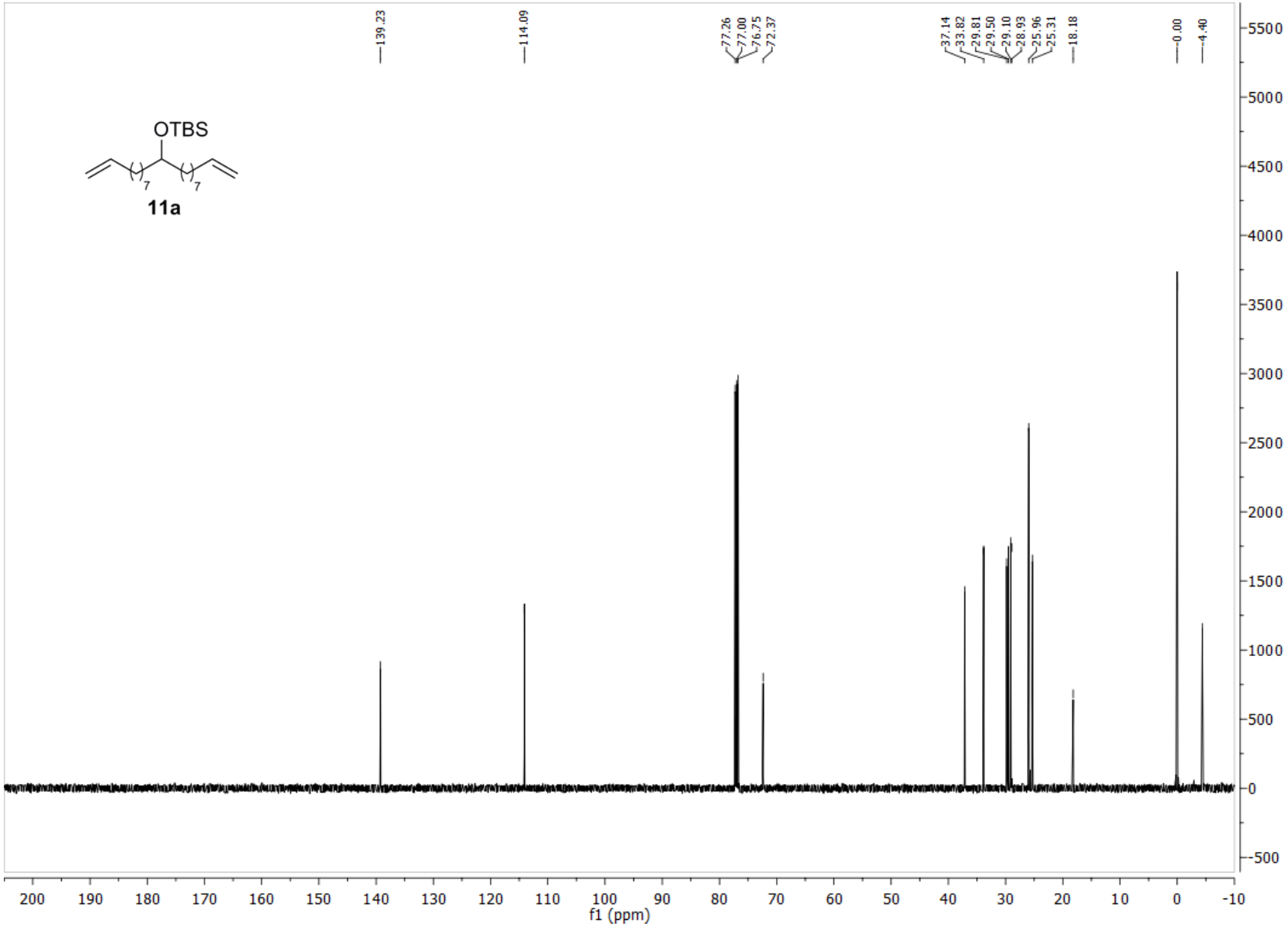
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of nonadeca-1,18-dien-10-ol (10a)



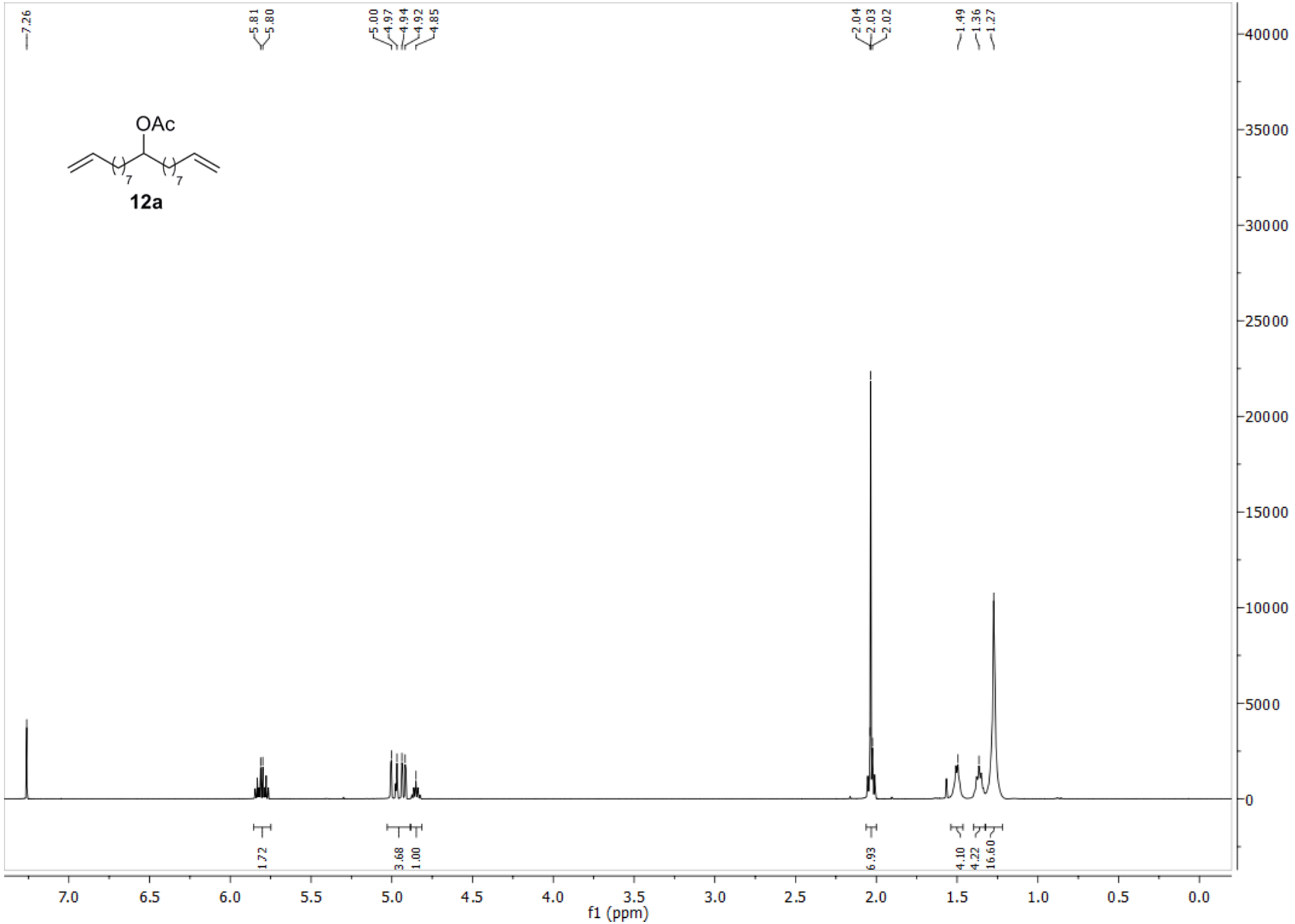
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *tert*-butyldimethyl(nonadeca-1,18-dien-10-yloxy)silane (11a)



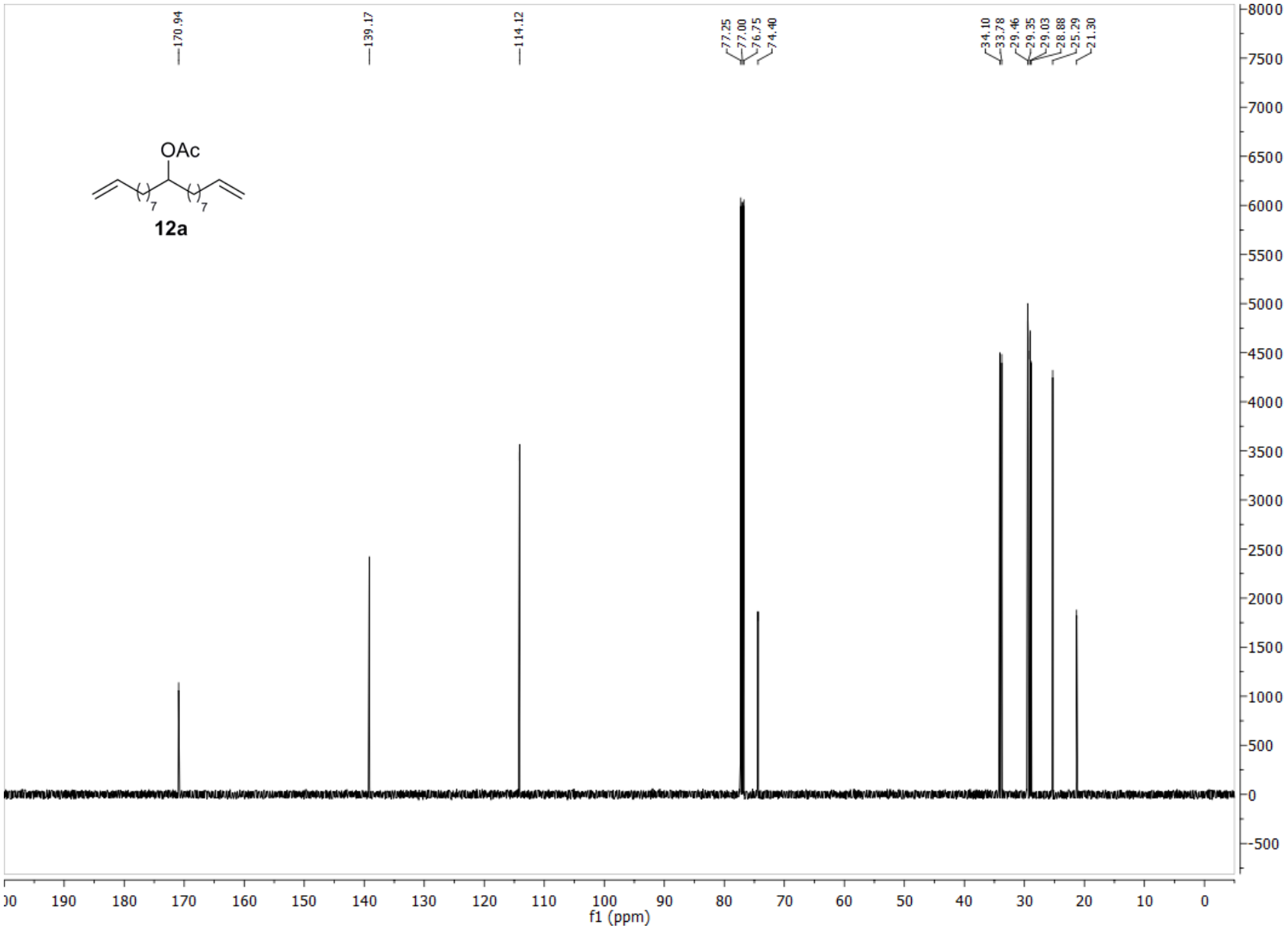
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *tert*-butyldimethyl(nonadeca-1,18-dien-10-yloxy)silane (11a)



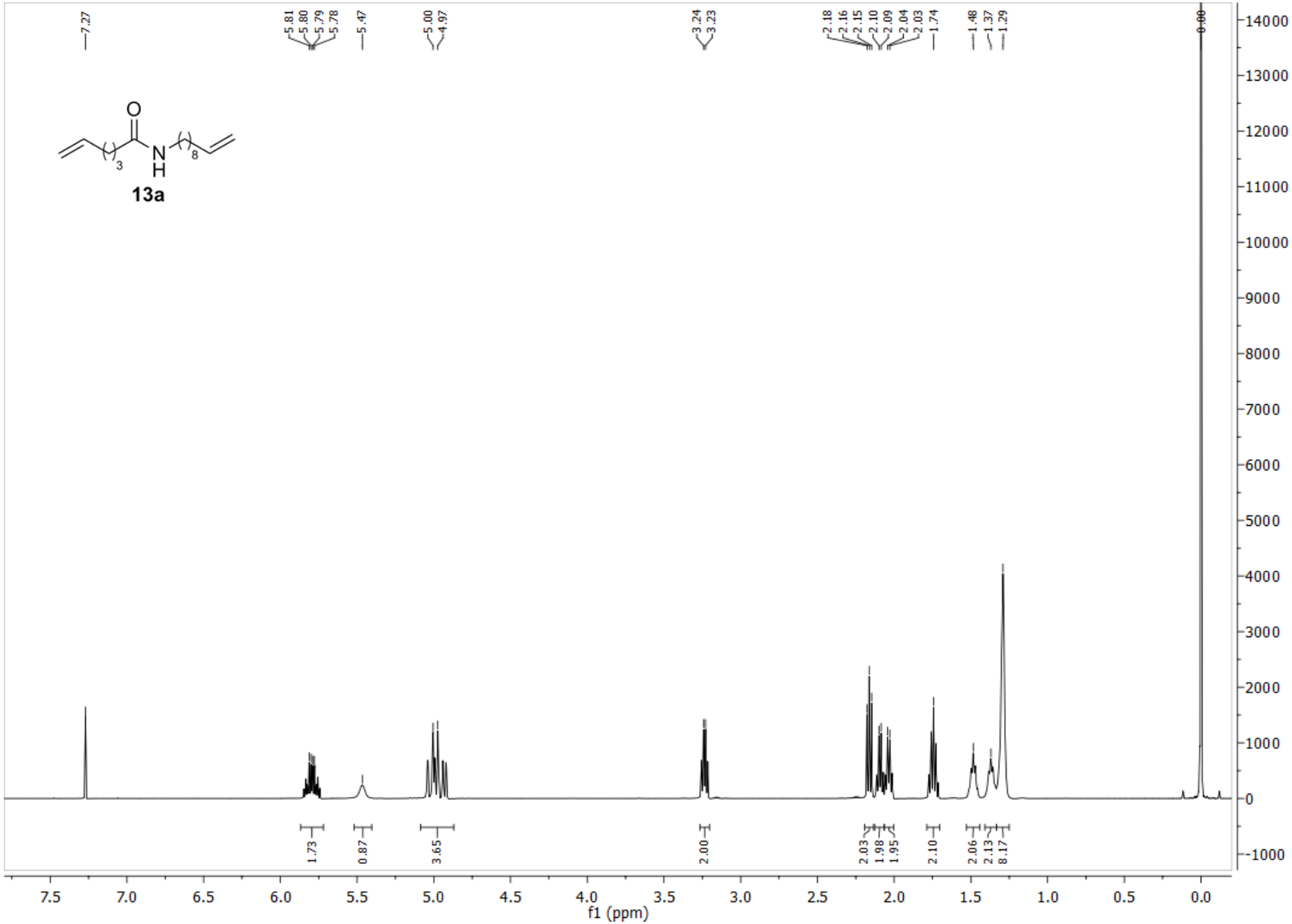
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of nonadeca-1,18-dien-10-yl acetate (12a)



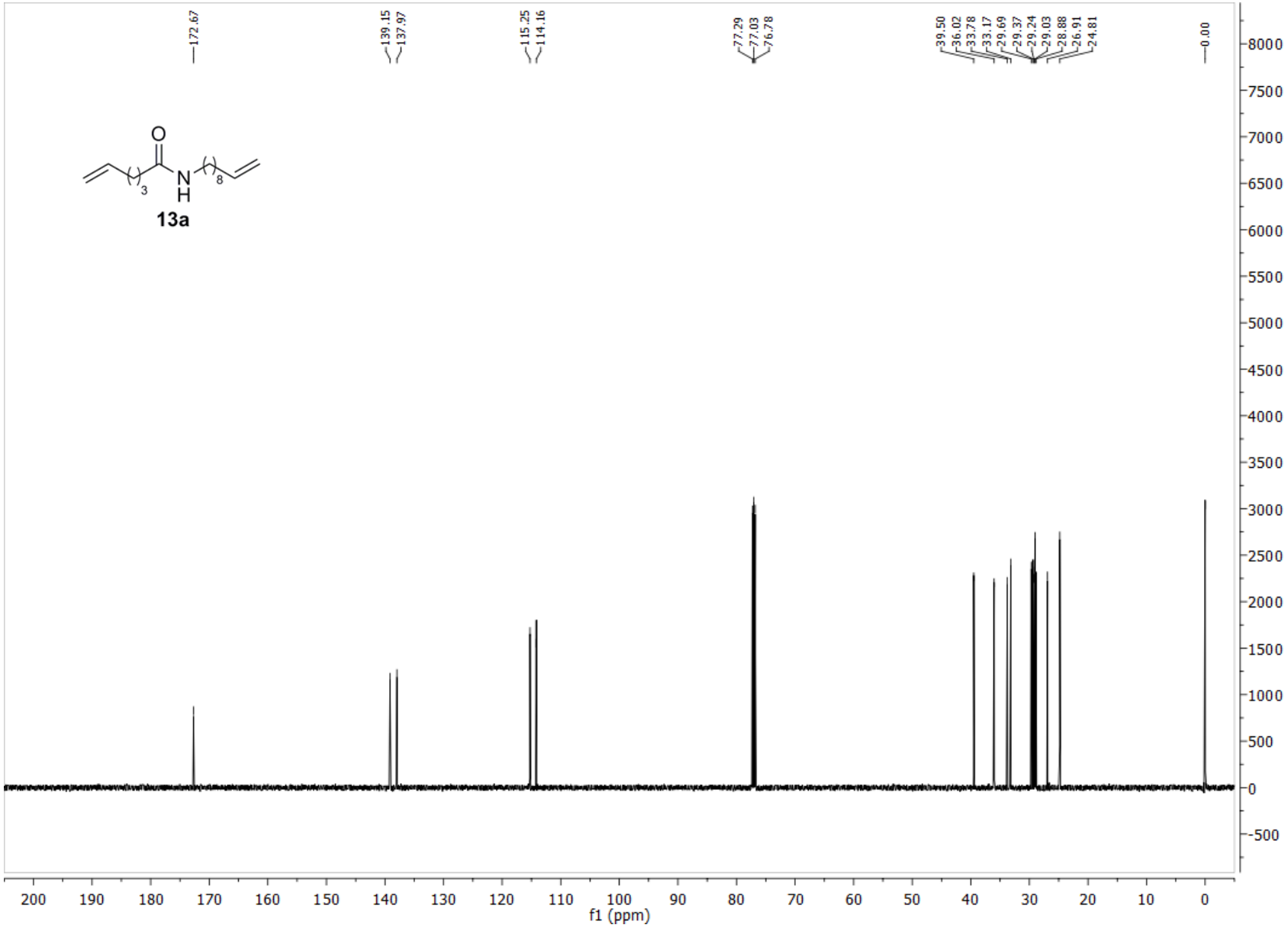
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of nonadeca-1,18-dien-10-yl acetate (12a)



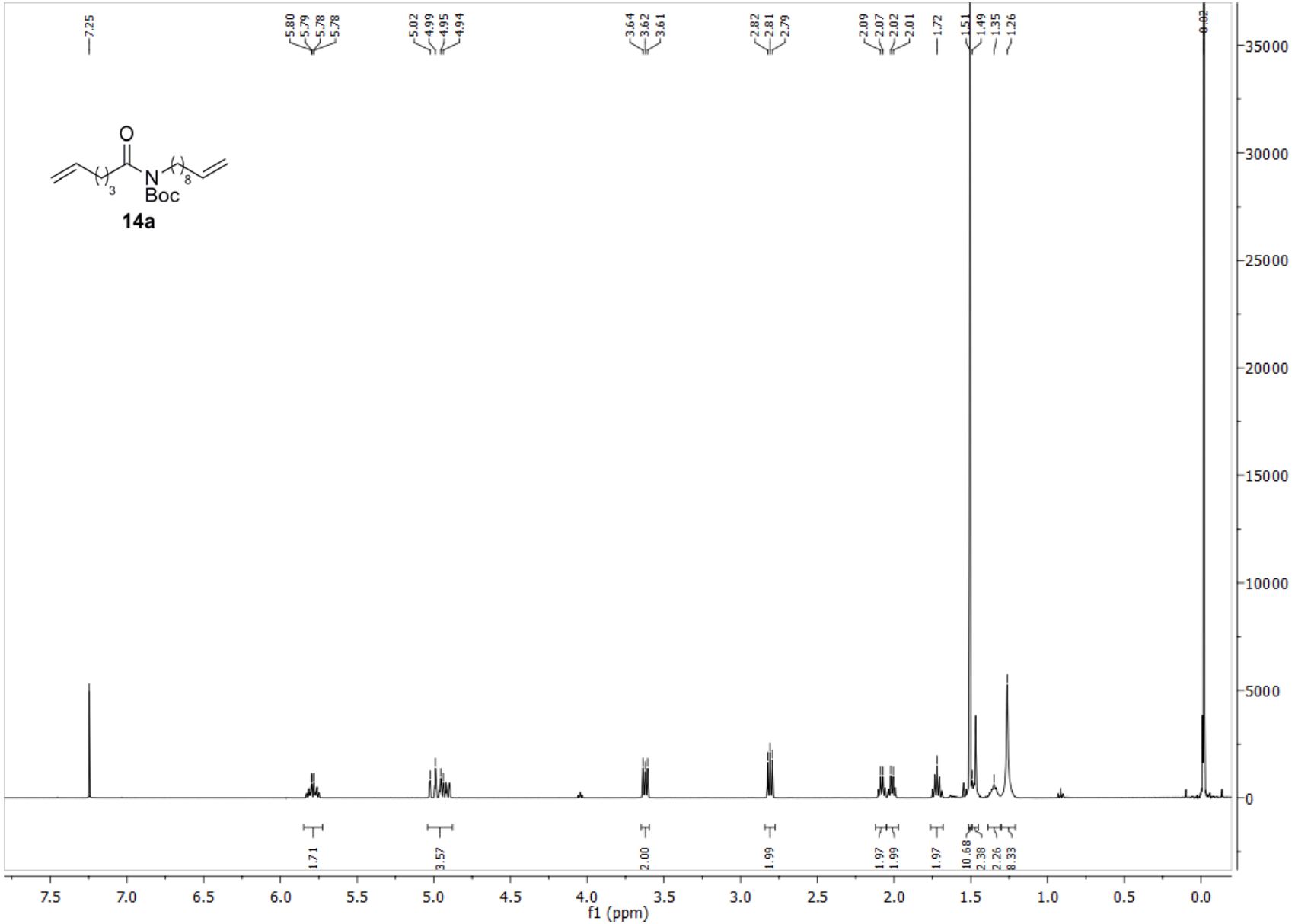
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *N*-(dec-9-en-1-yl)hex-5-enamide (13a)



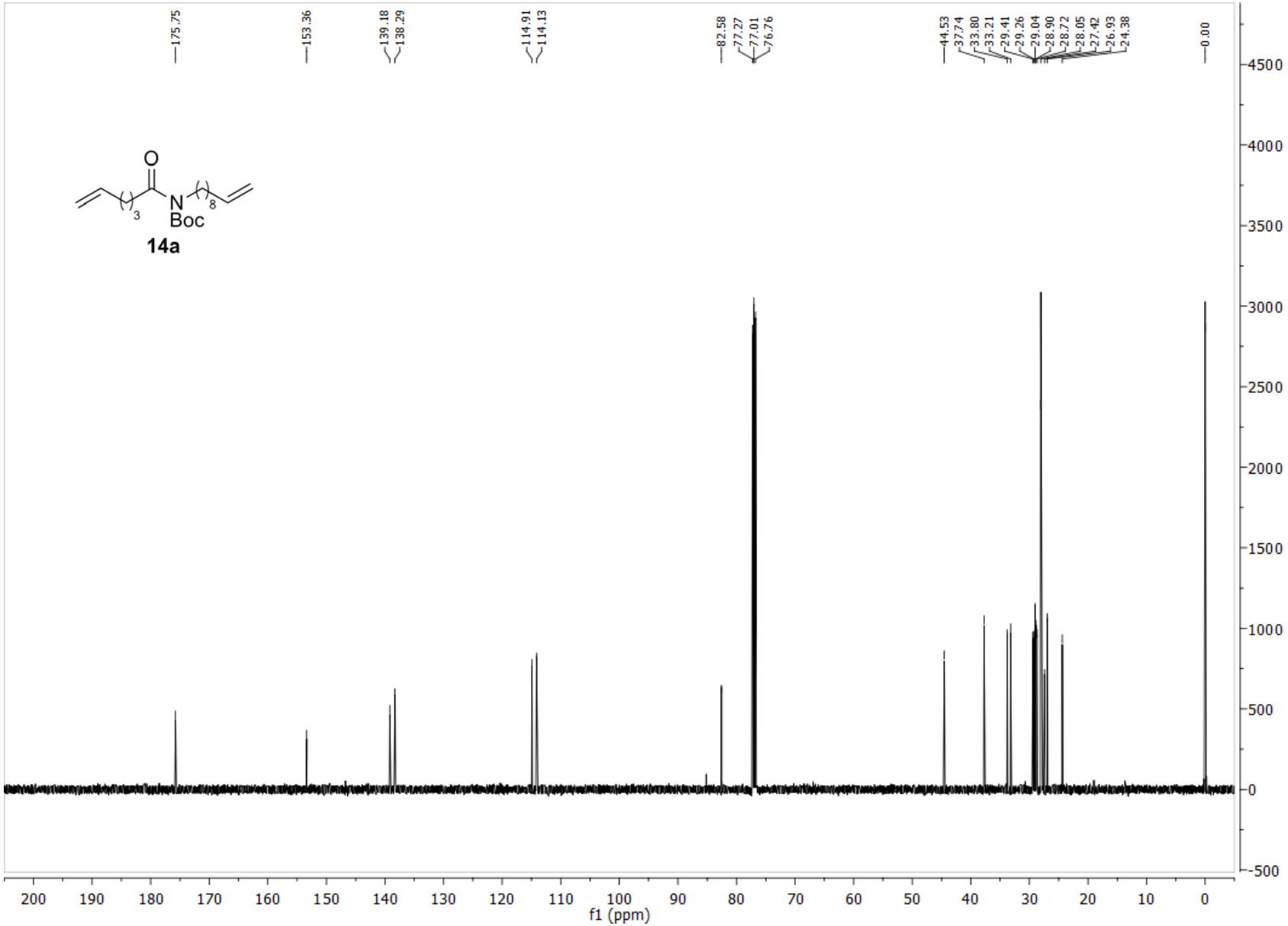
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *N*-(dec-9-en-1-yl)hex-5-enamide (13a)



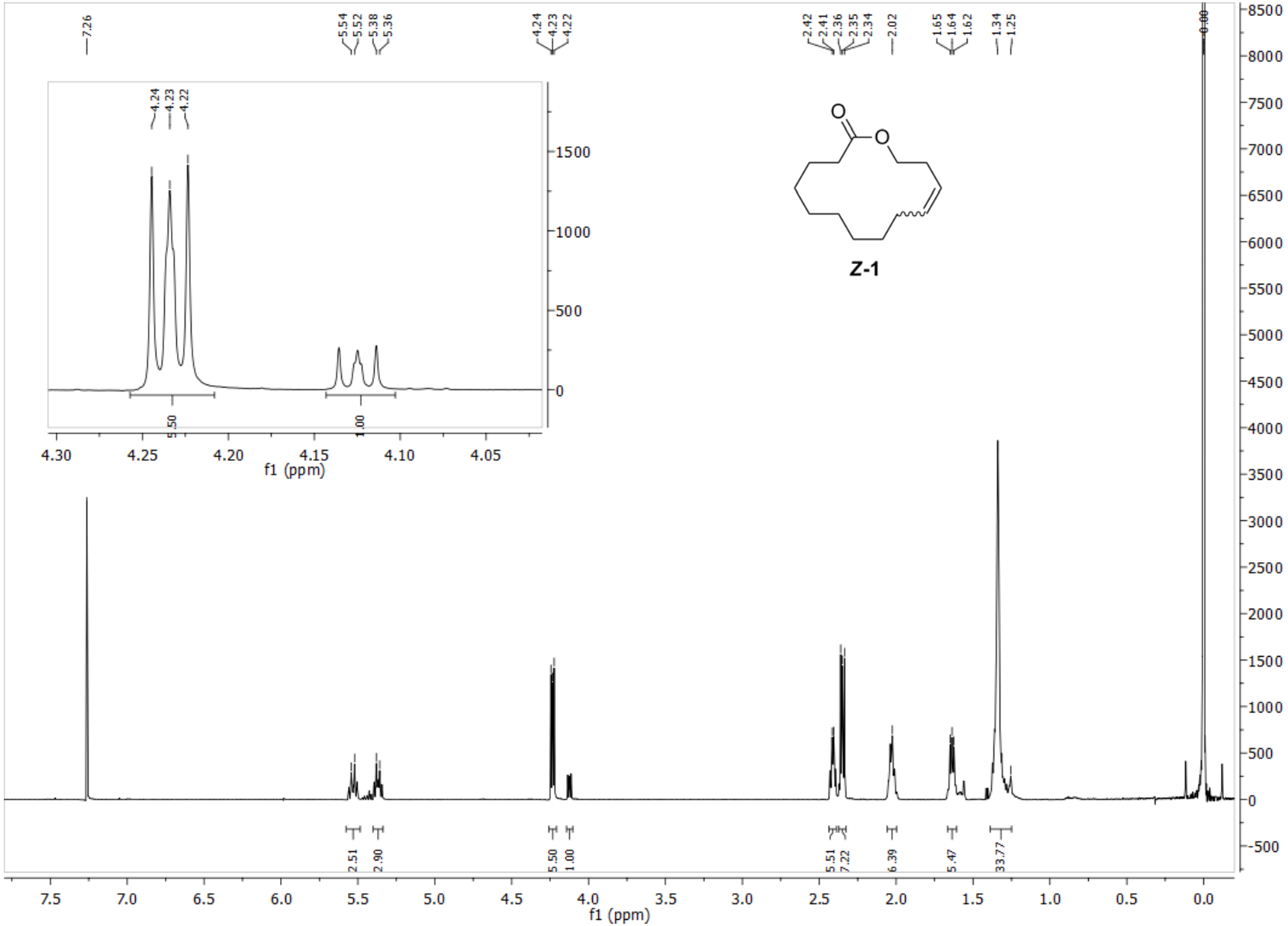
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *tert*-butyl dec-9-en-1-yl(hex-5-enoyl)carbamate (14a)



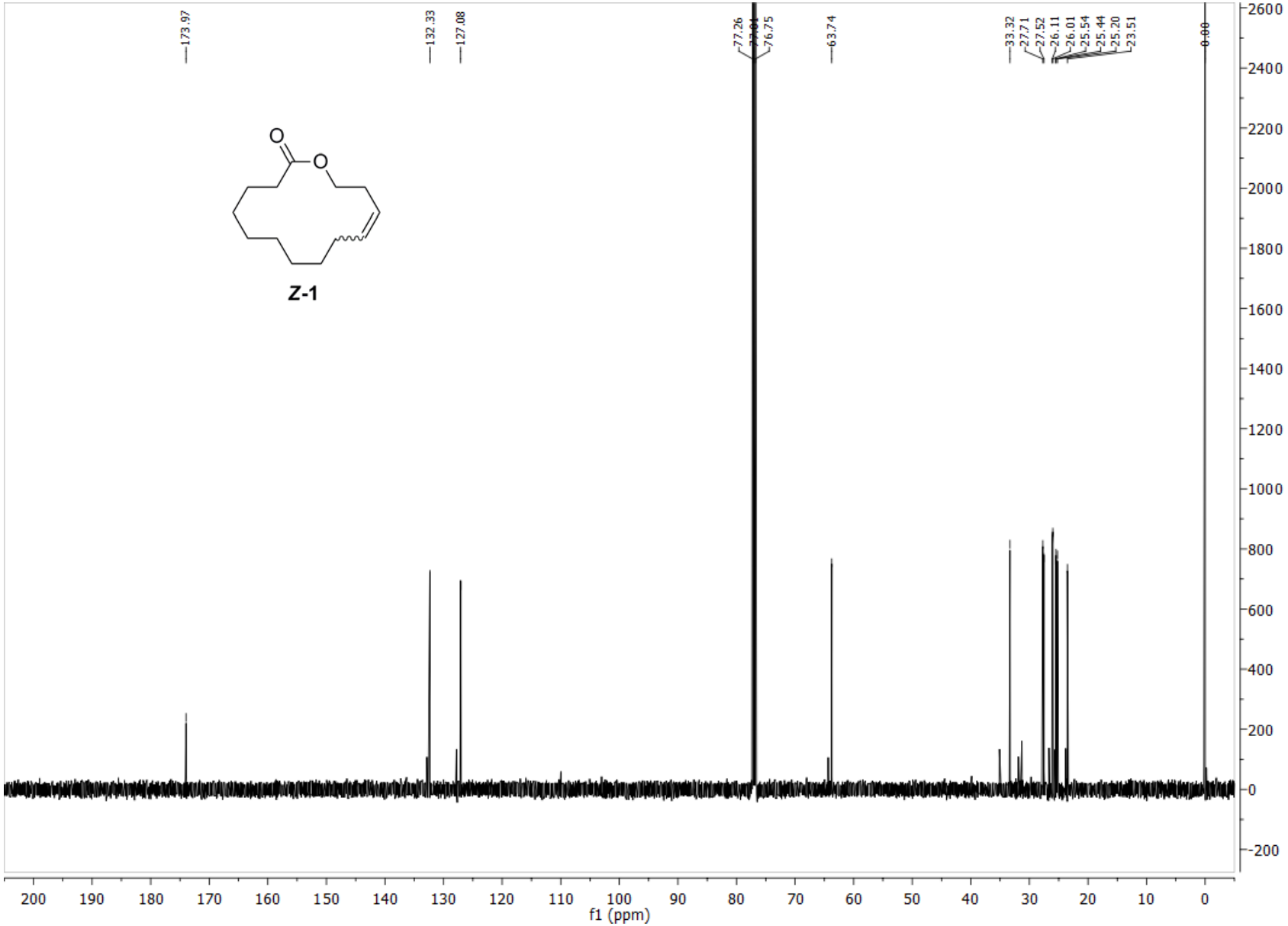
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *tert*-butyl dec-9-en-1-yl(hex-5-enoyl)carbamate (14a)



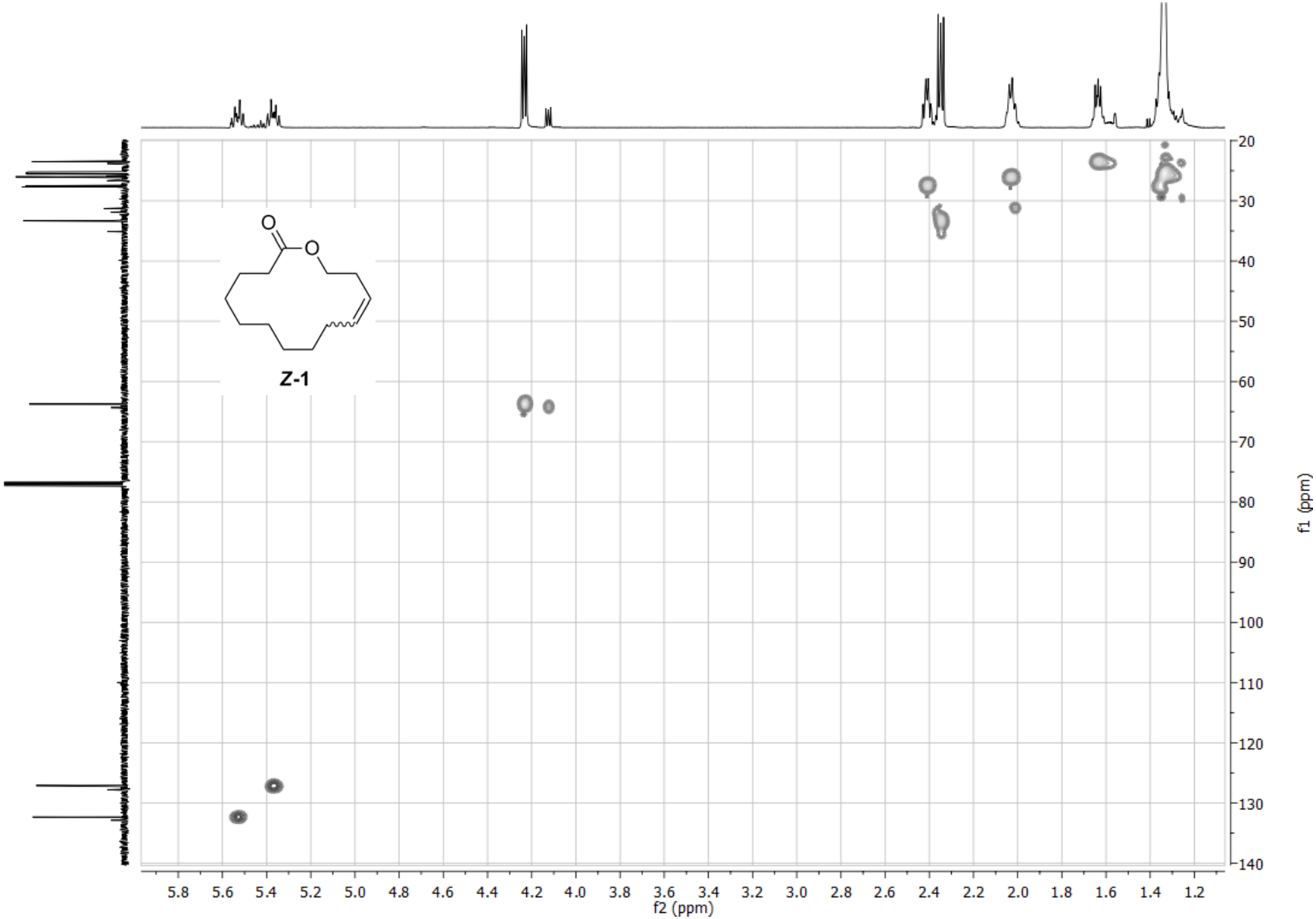
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-oxacyclotetradec-11-en-2-one (1)



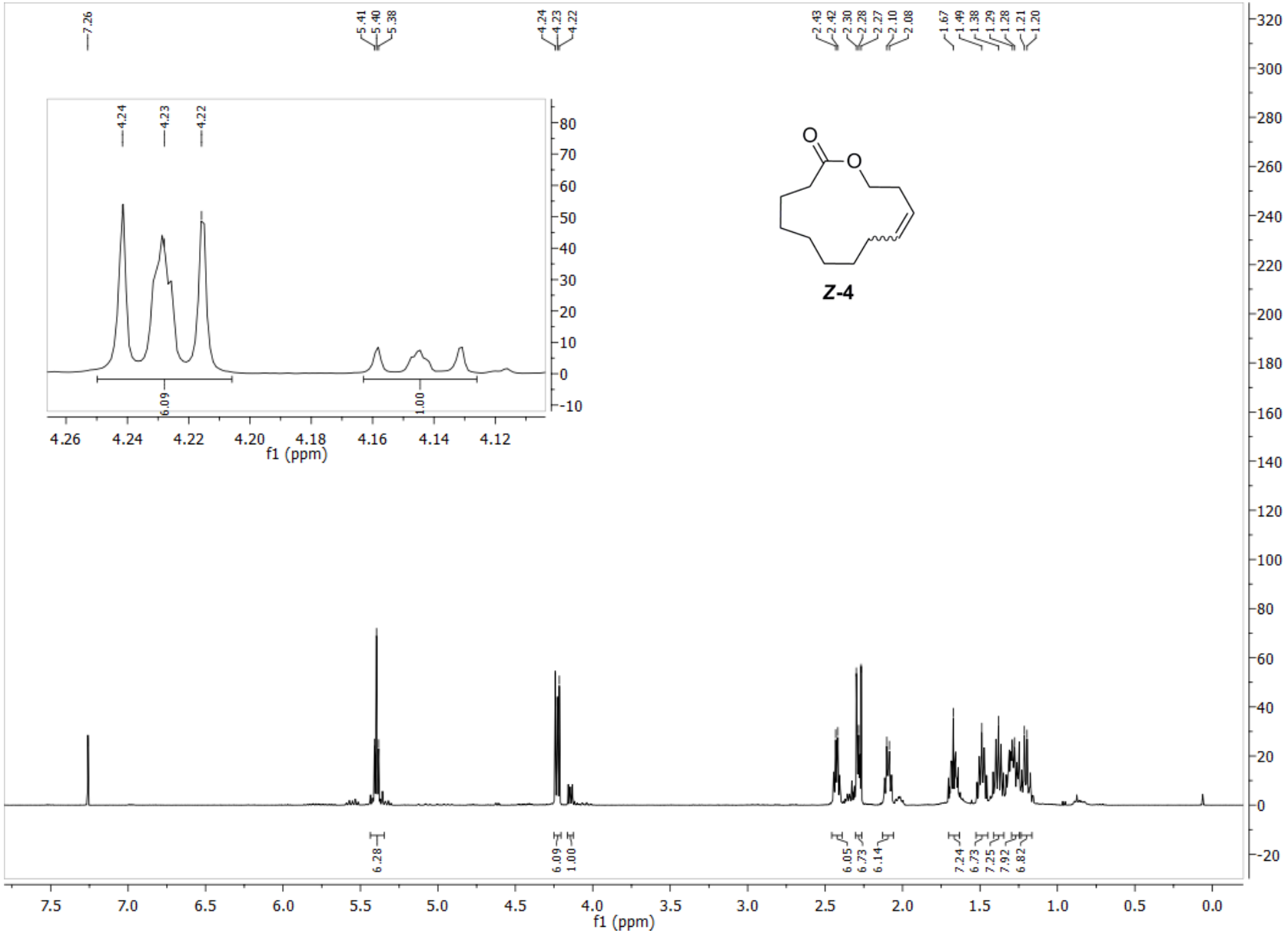
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-oxacyclotetradec-11-en-2-one (1)



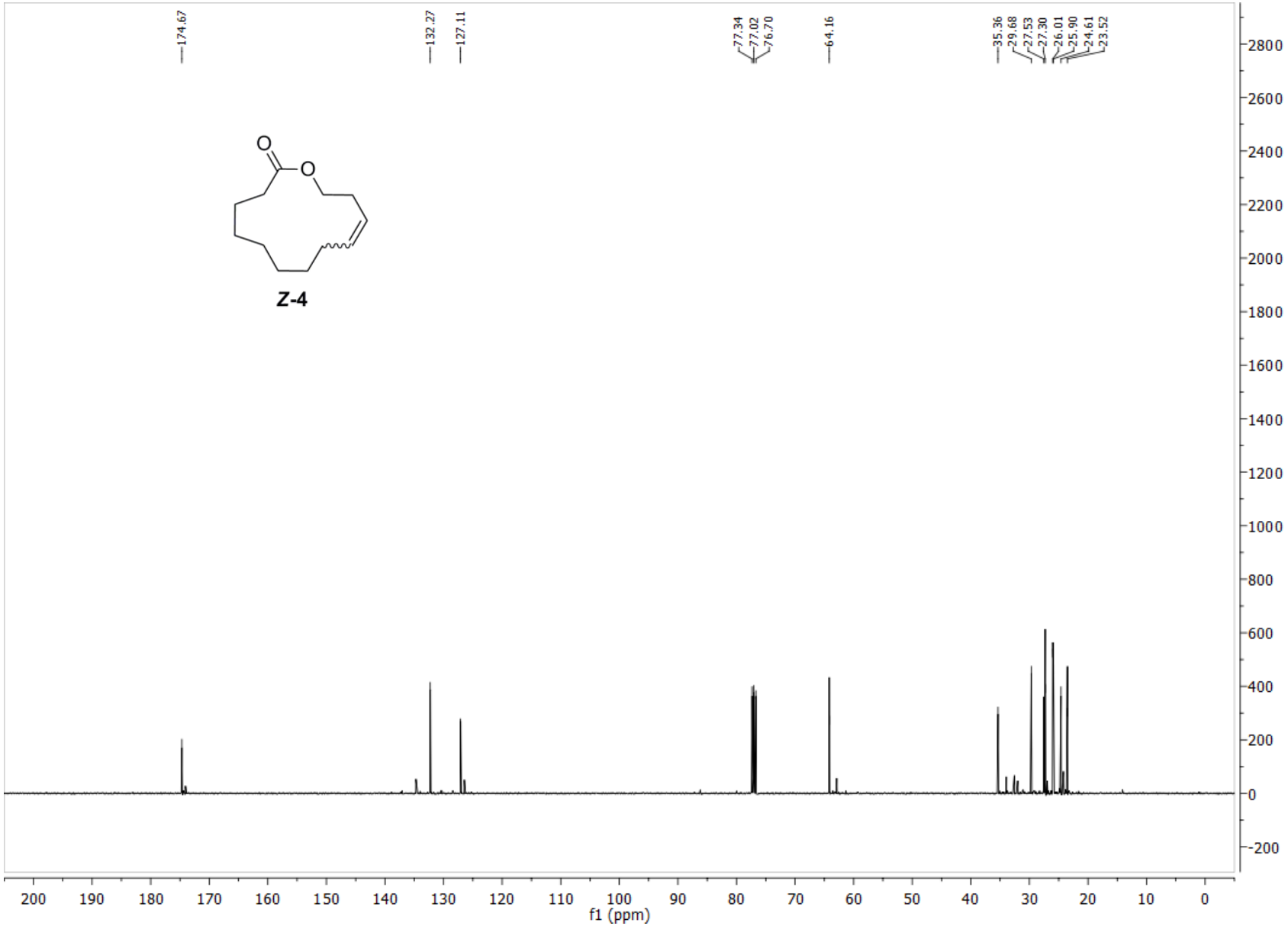
HSQC spectrum of *Z*-oxacyclotetradec-11-en-2-one (1)



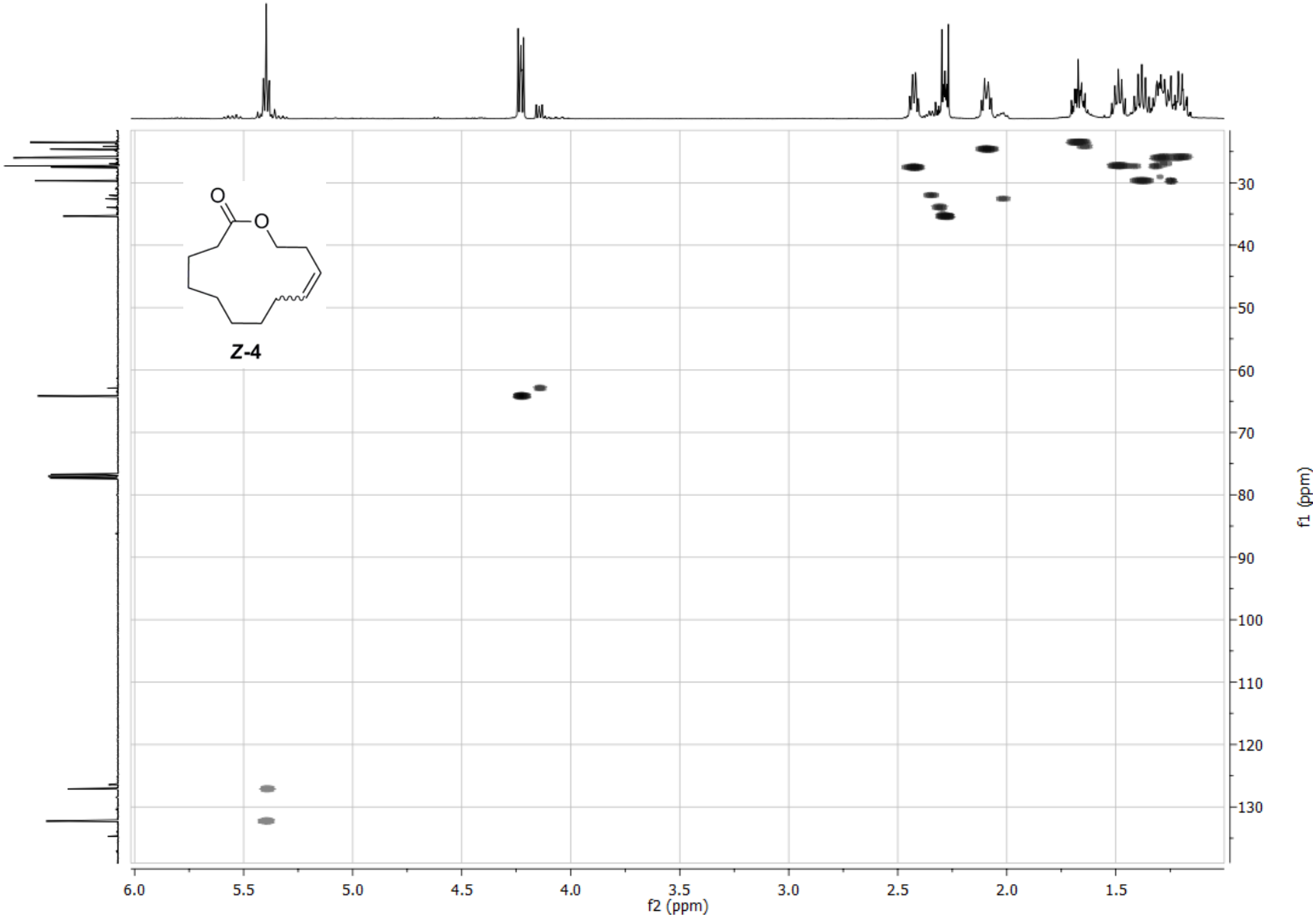
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-oxacyclotridec-10-en-2-one (4)



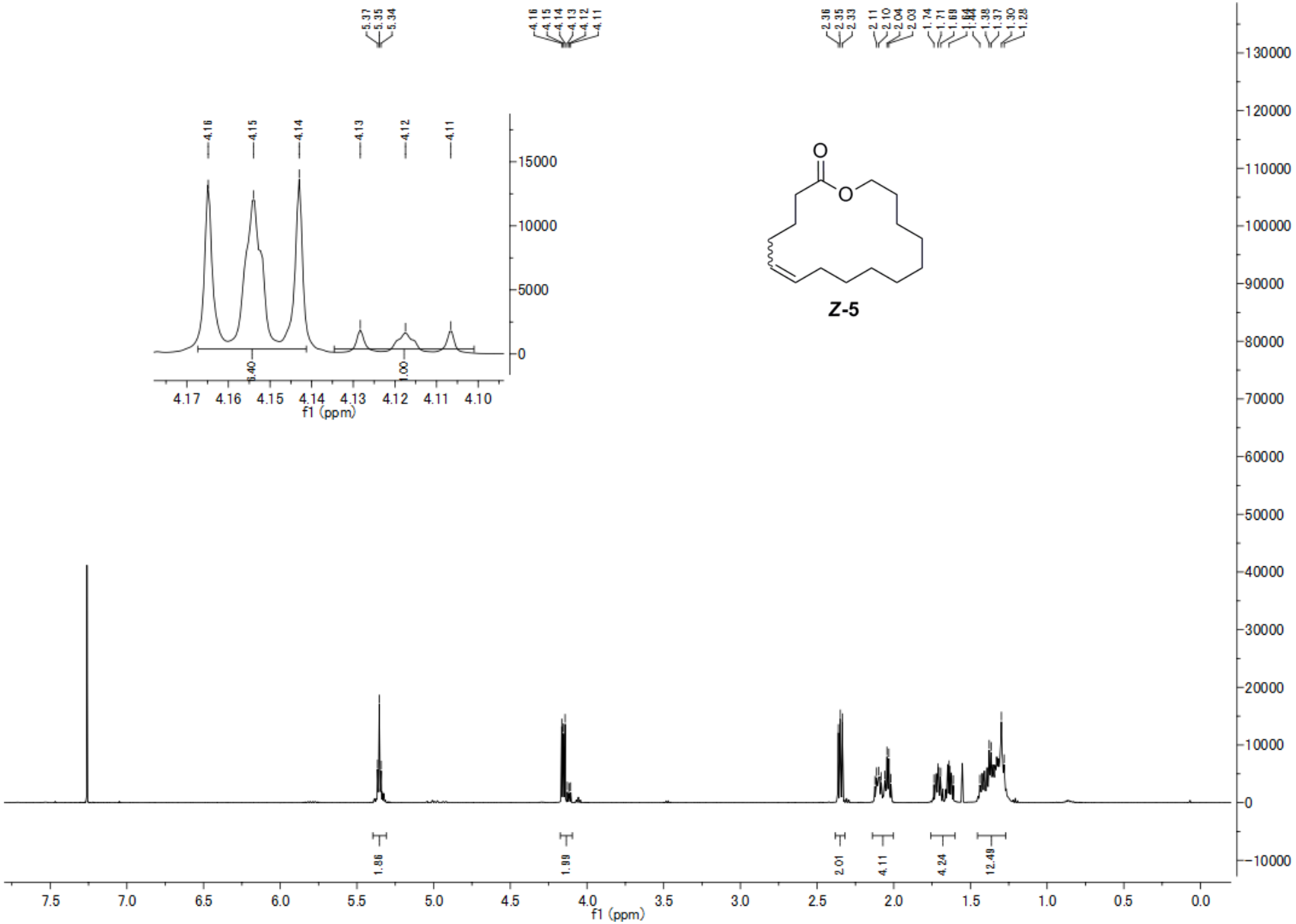
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-oxacyclotridec-10-en-2-one (4)



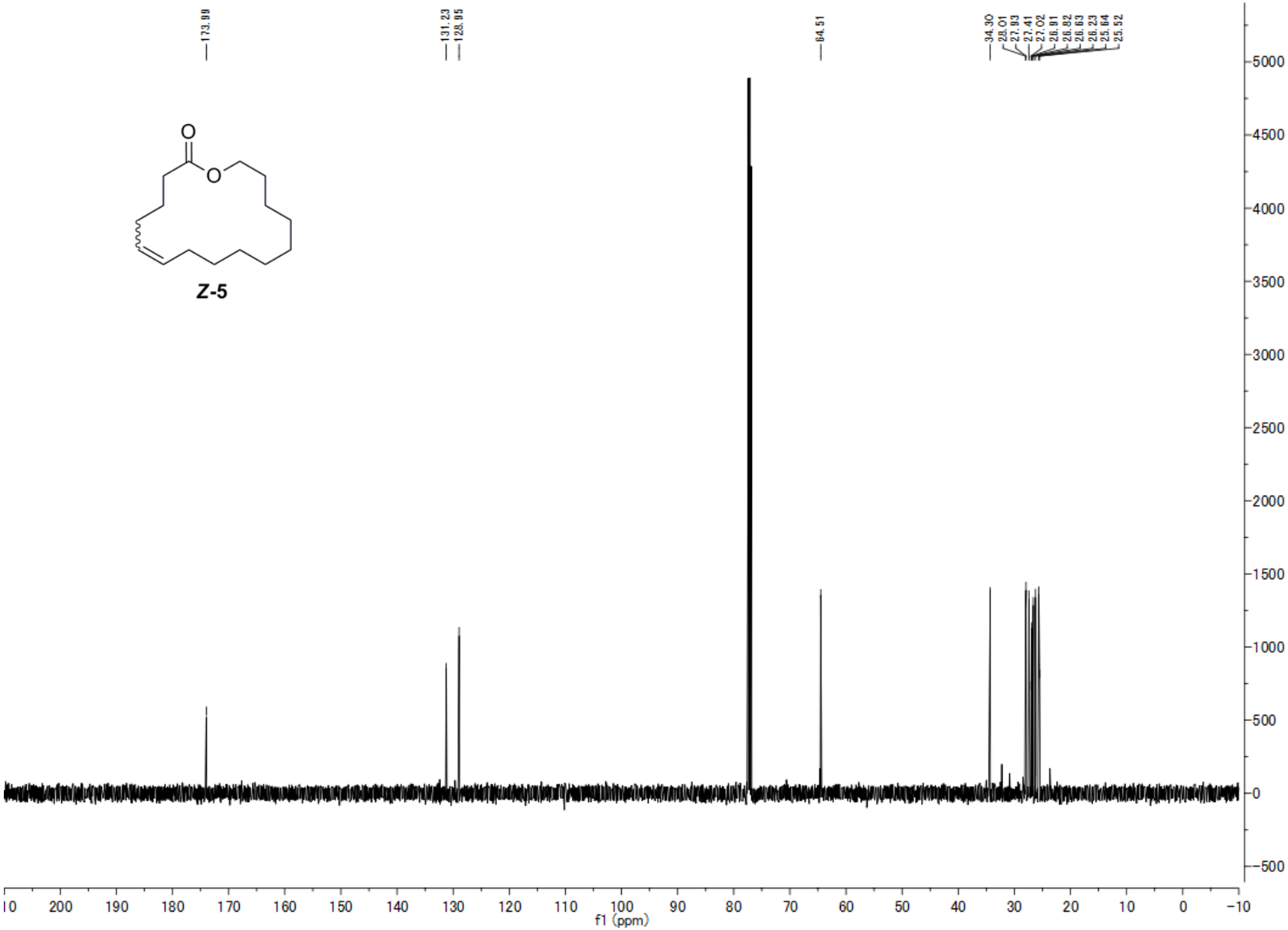
HSQC spectrum of *Z*-oxacyclotridec-10-en-2-one (4)



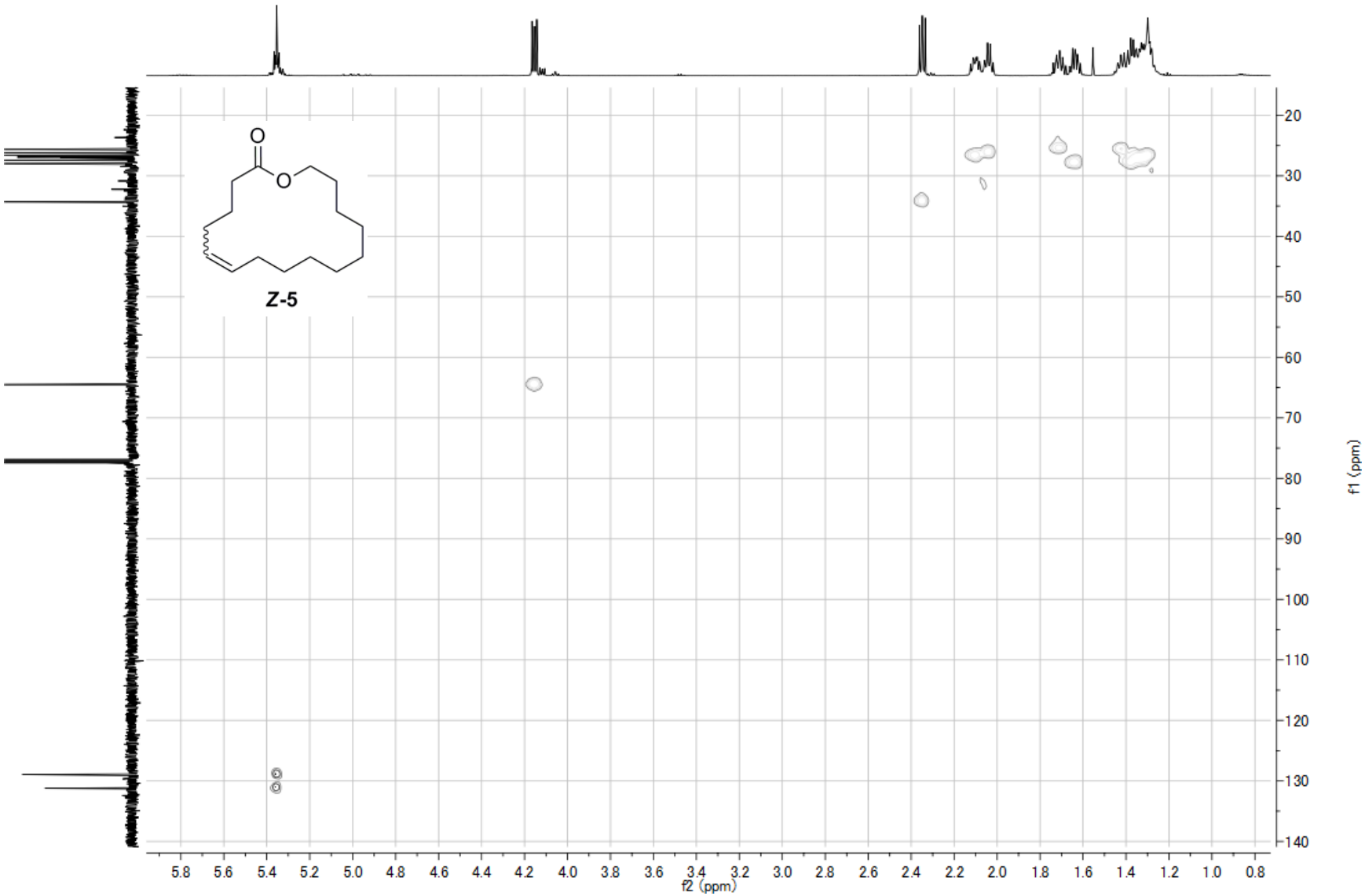
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-oxacyclohexadec-6-en-2-one (5)



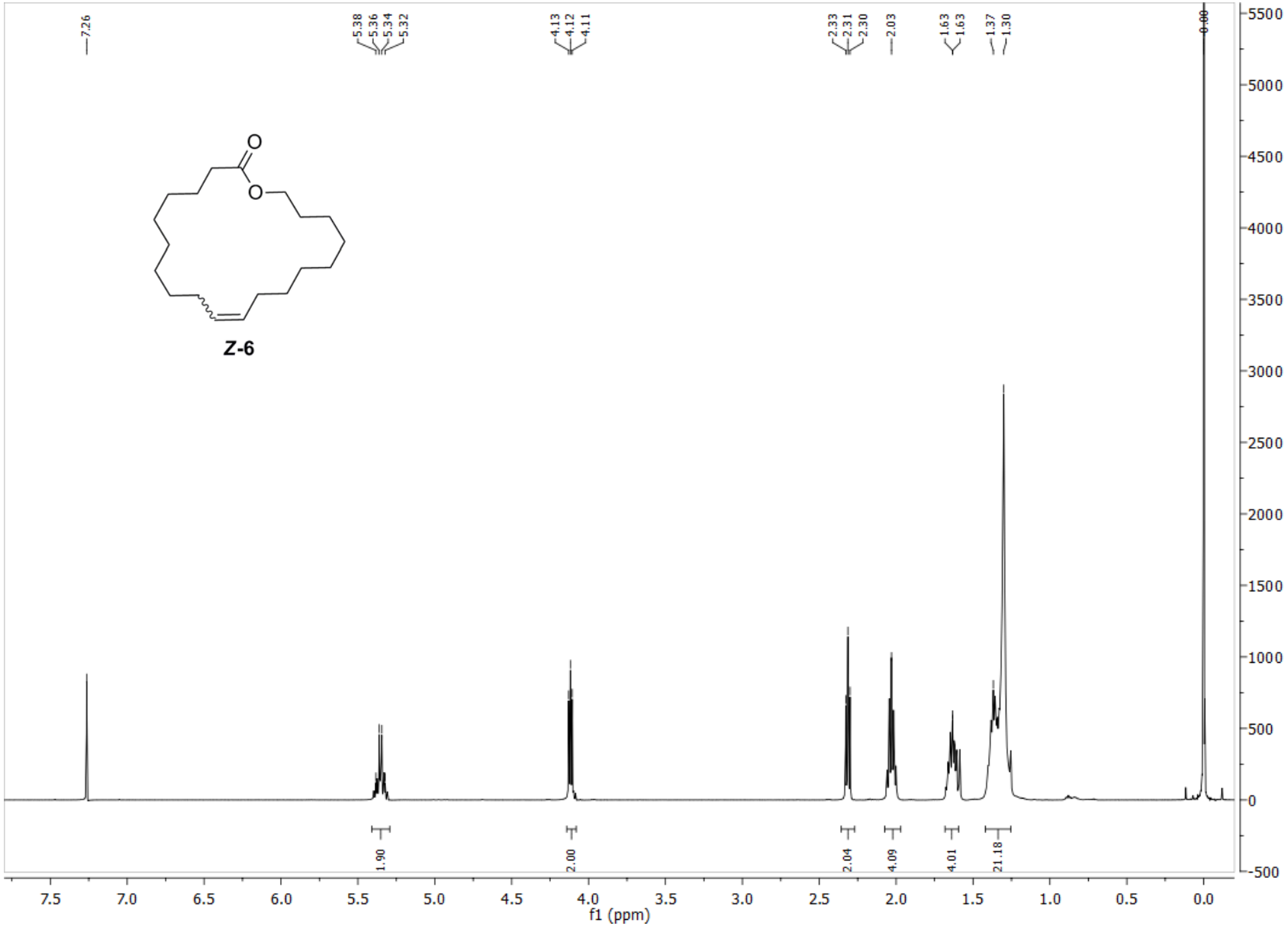
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*- oxacyclohexadec-6-en-2-one (5)



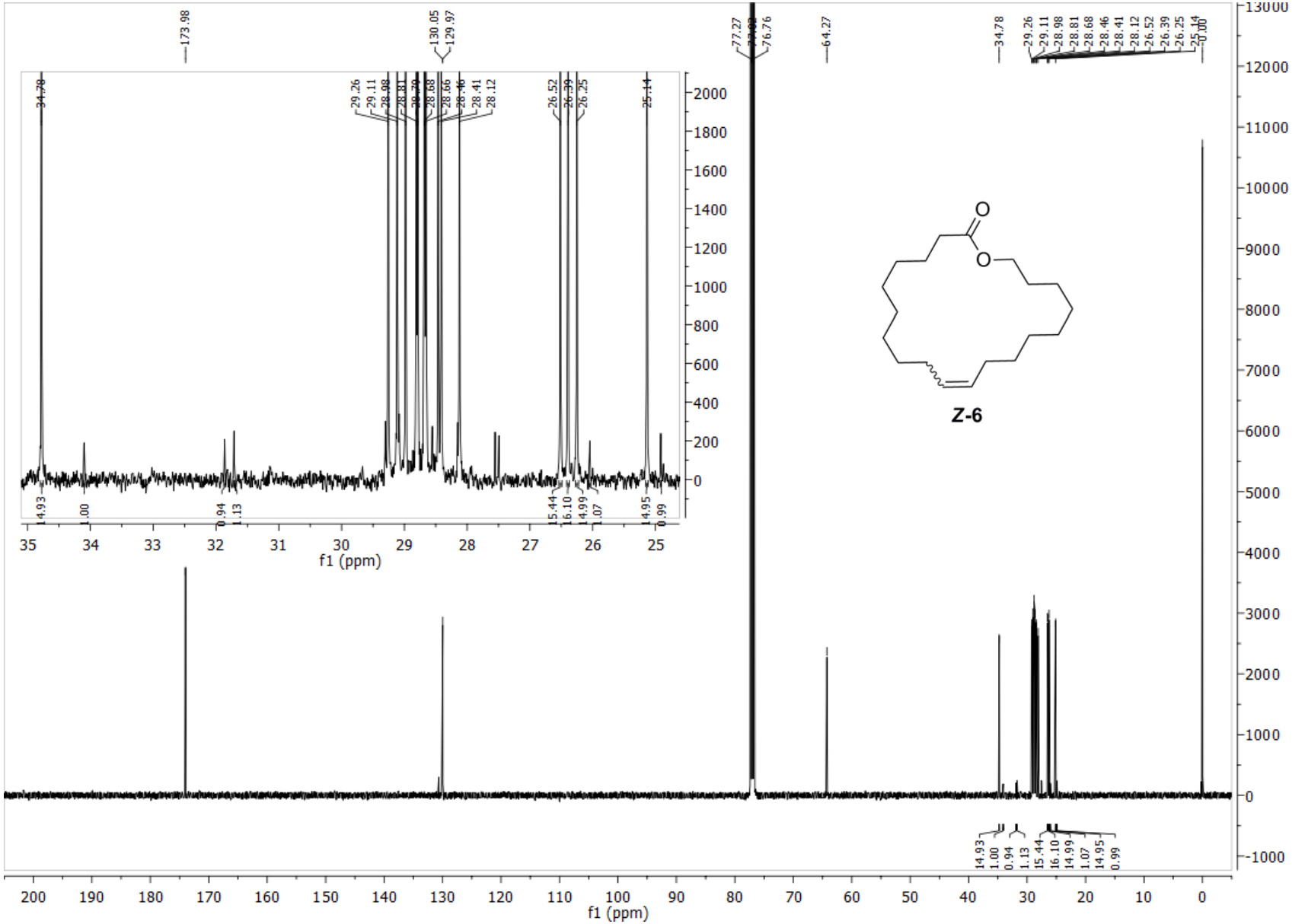
HSQC spectrum of *Z*- oxacyclohexadec-6-en-2-one (5)



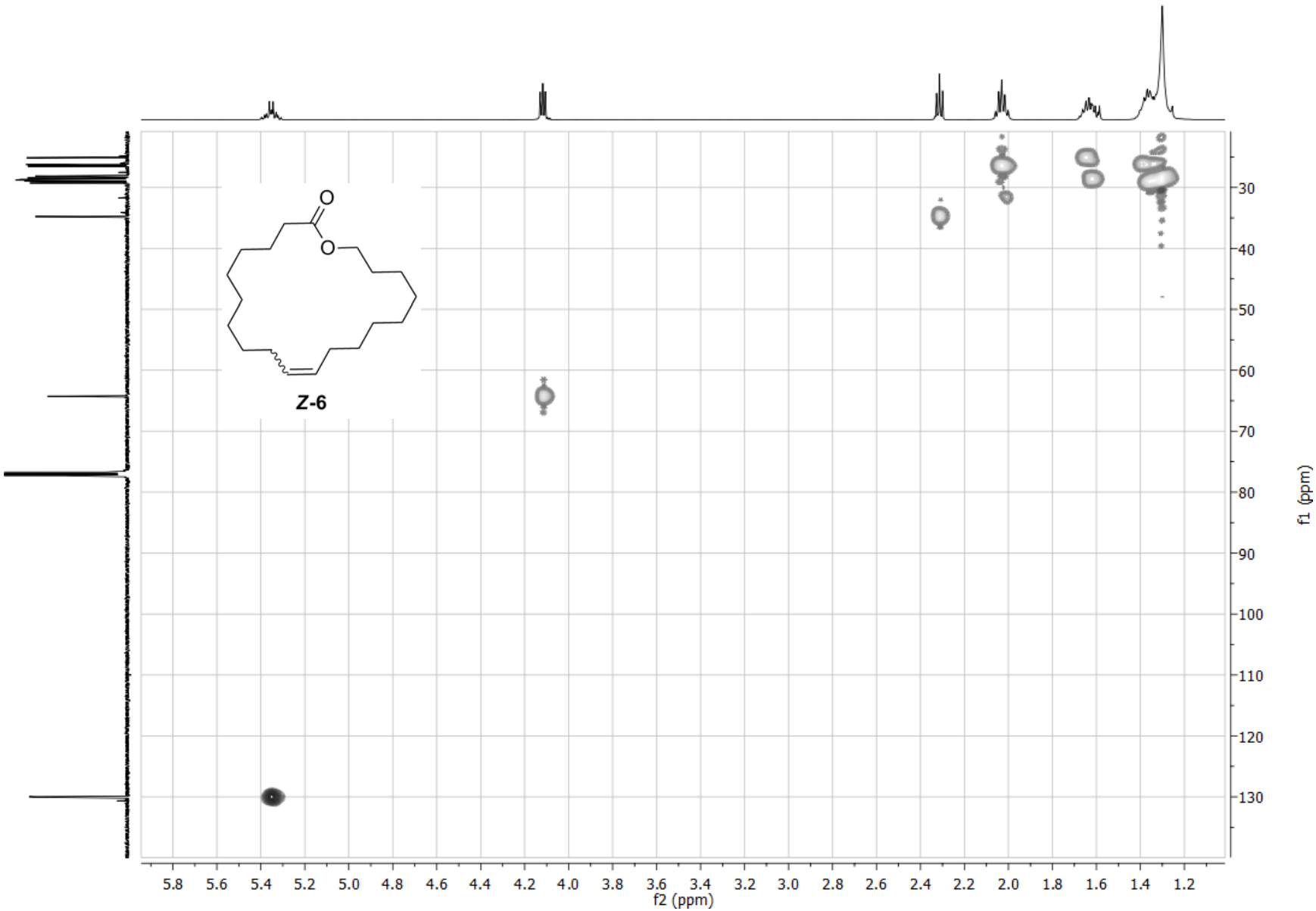
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-oxacycloicos-11-en-2-one (6)



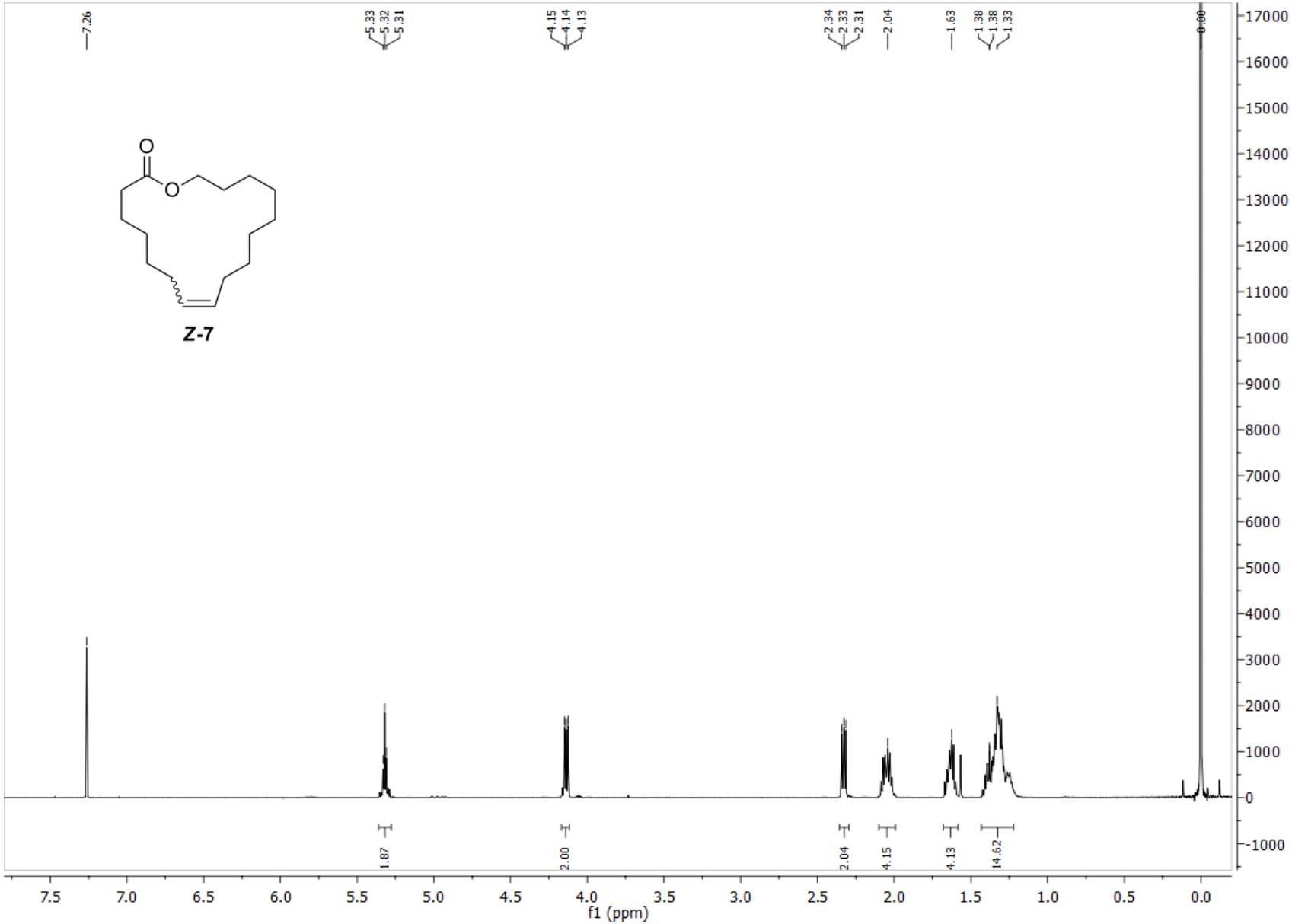
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-oxacycloicos-11-en-2-one (6)



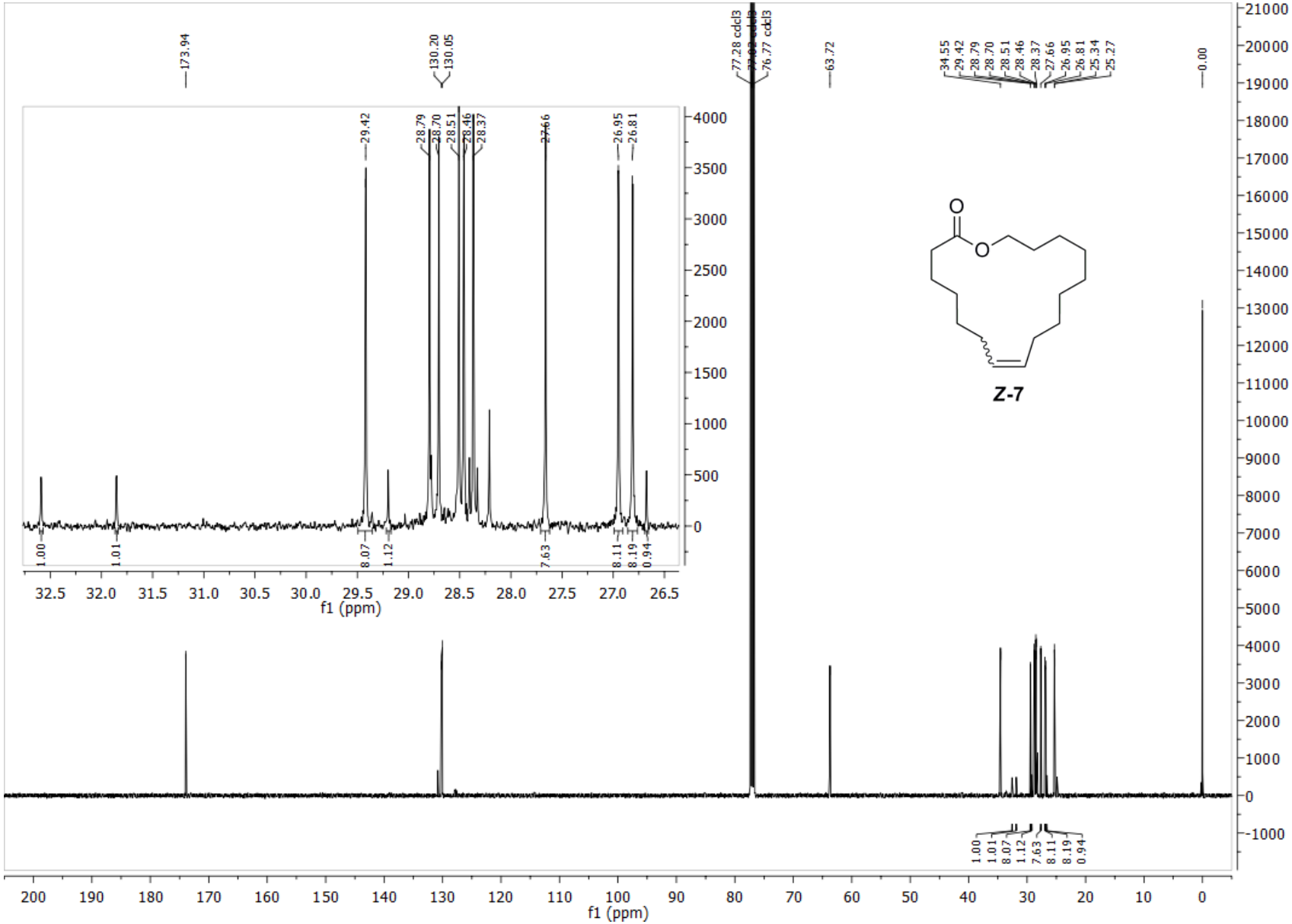
HSQC spectrum of *Z*-oxacycloicos-11-en-2-one (6)



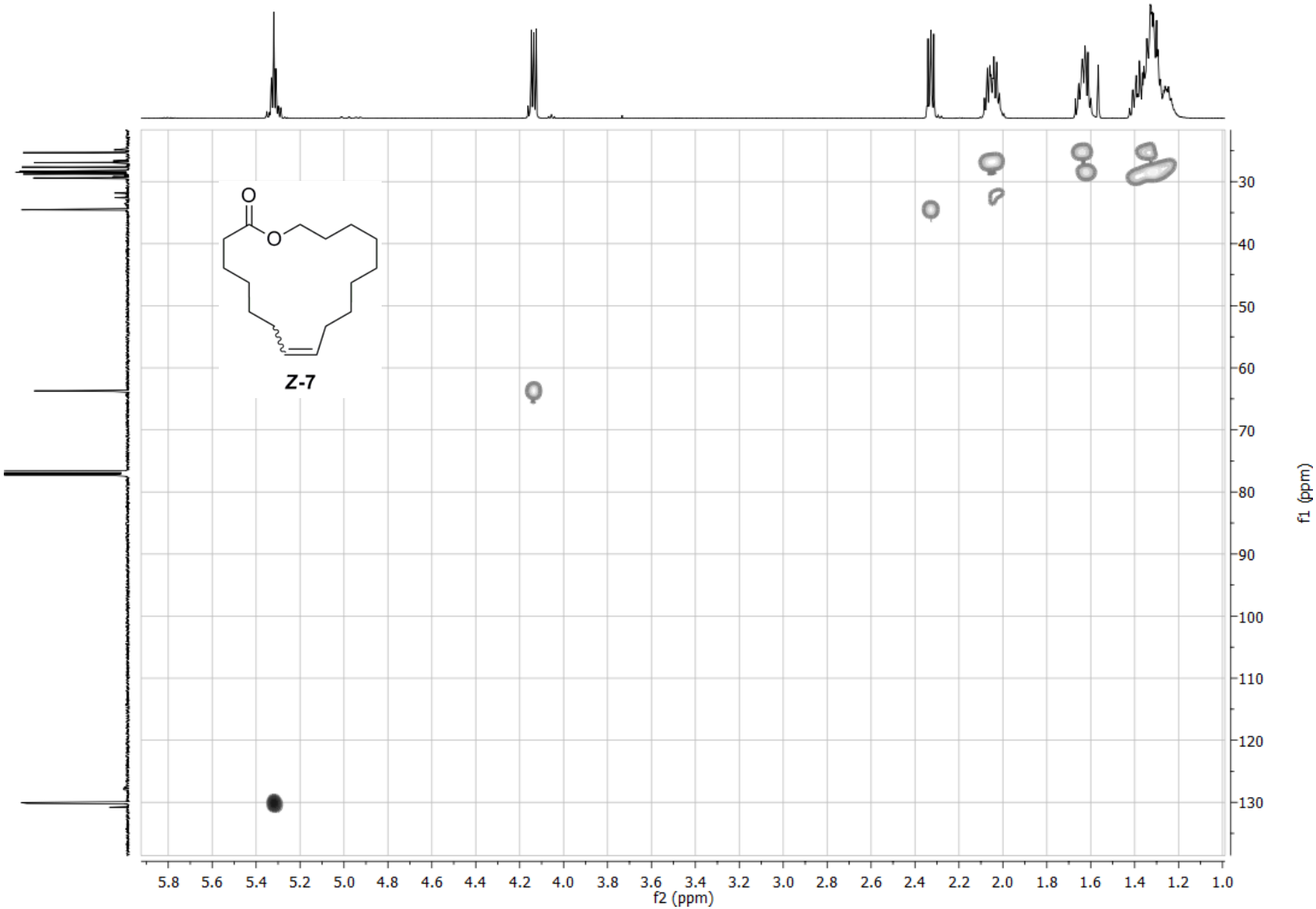
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-oxacycloheptadec-8-en-2-one (7)



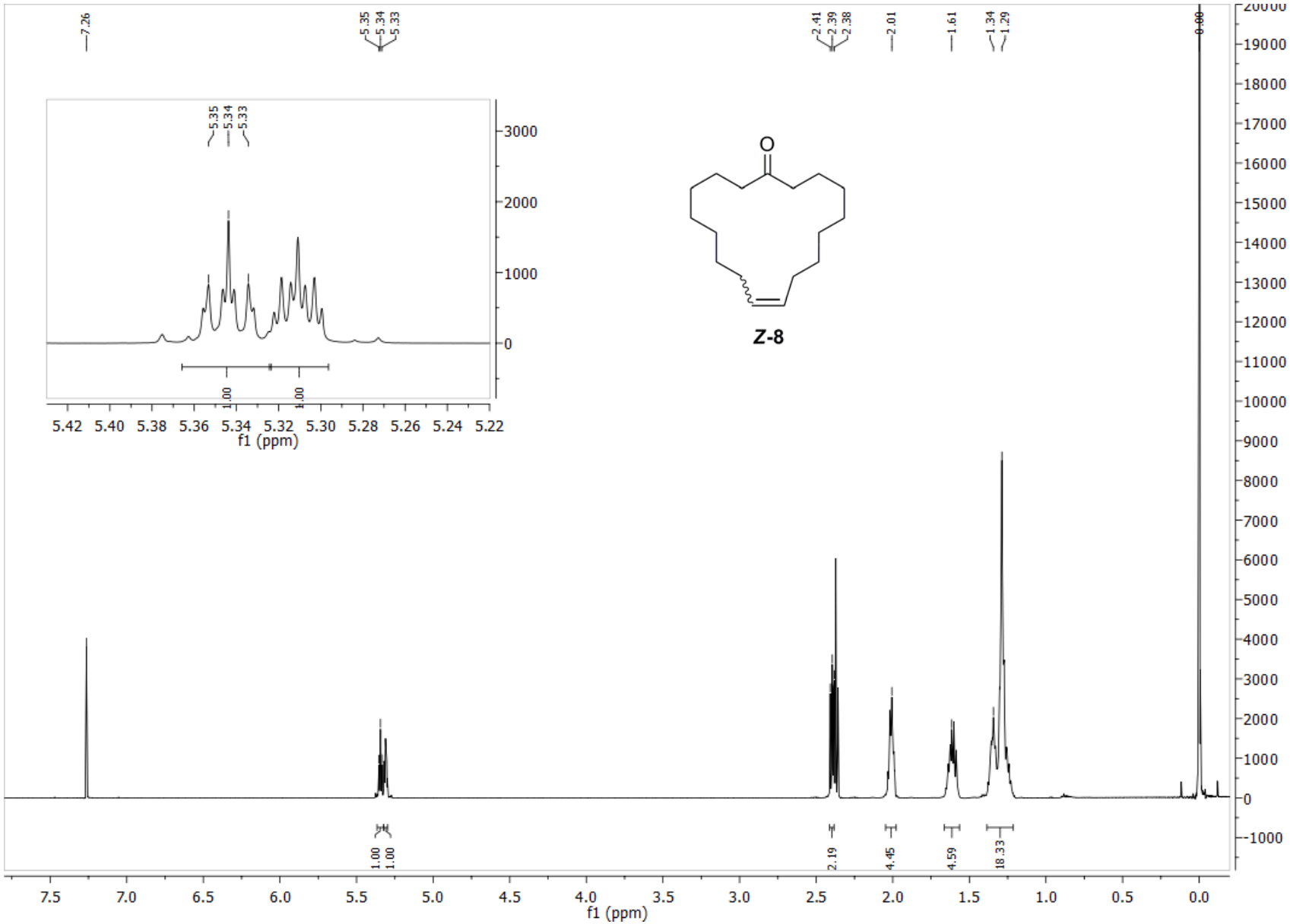
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-oxacycloheptadec-8-en-2-one (7)



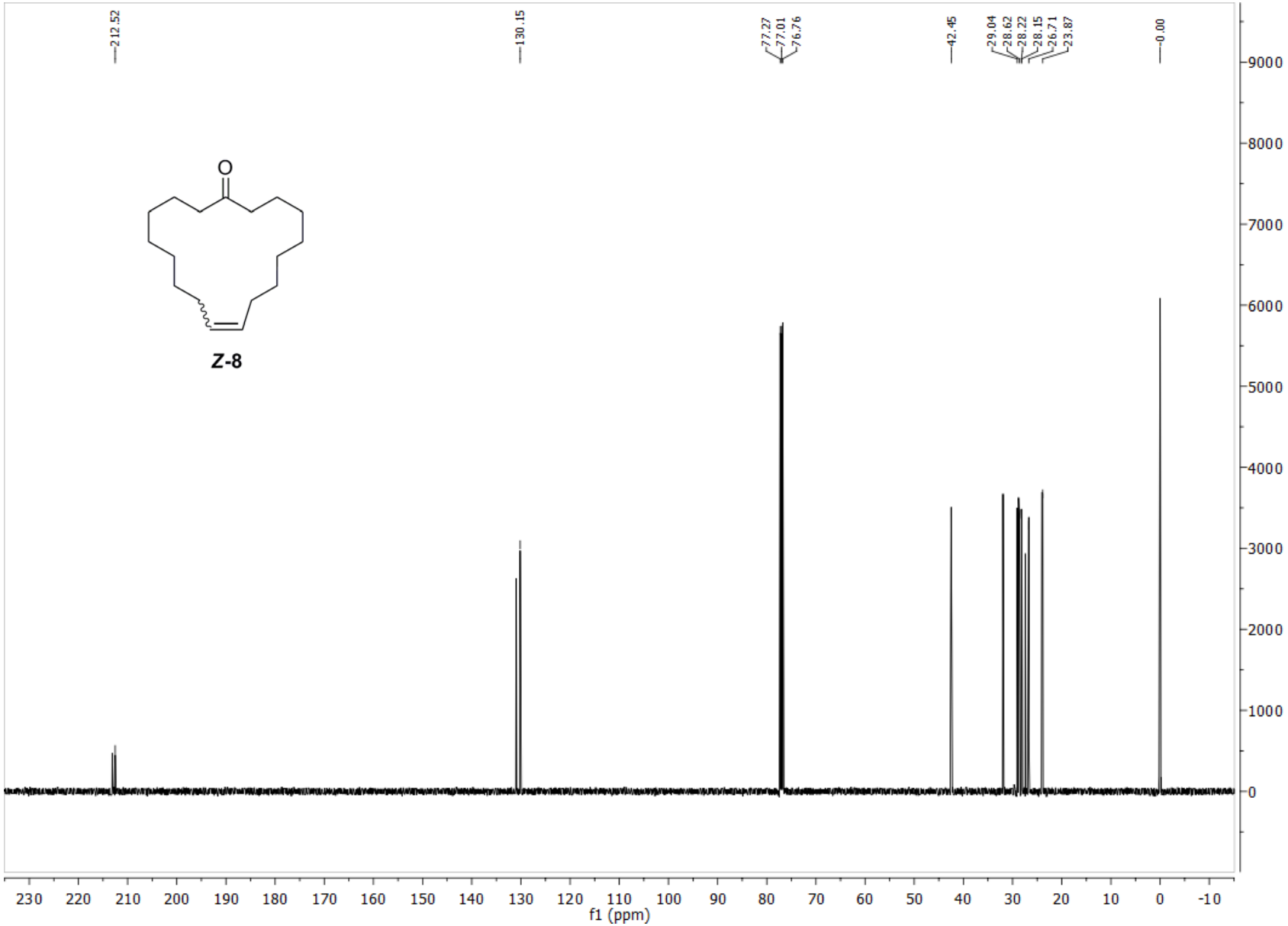
HSQC spectrum of *Z*-oxacycloheptadec-8-en-2-one (7)



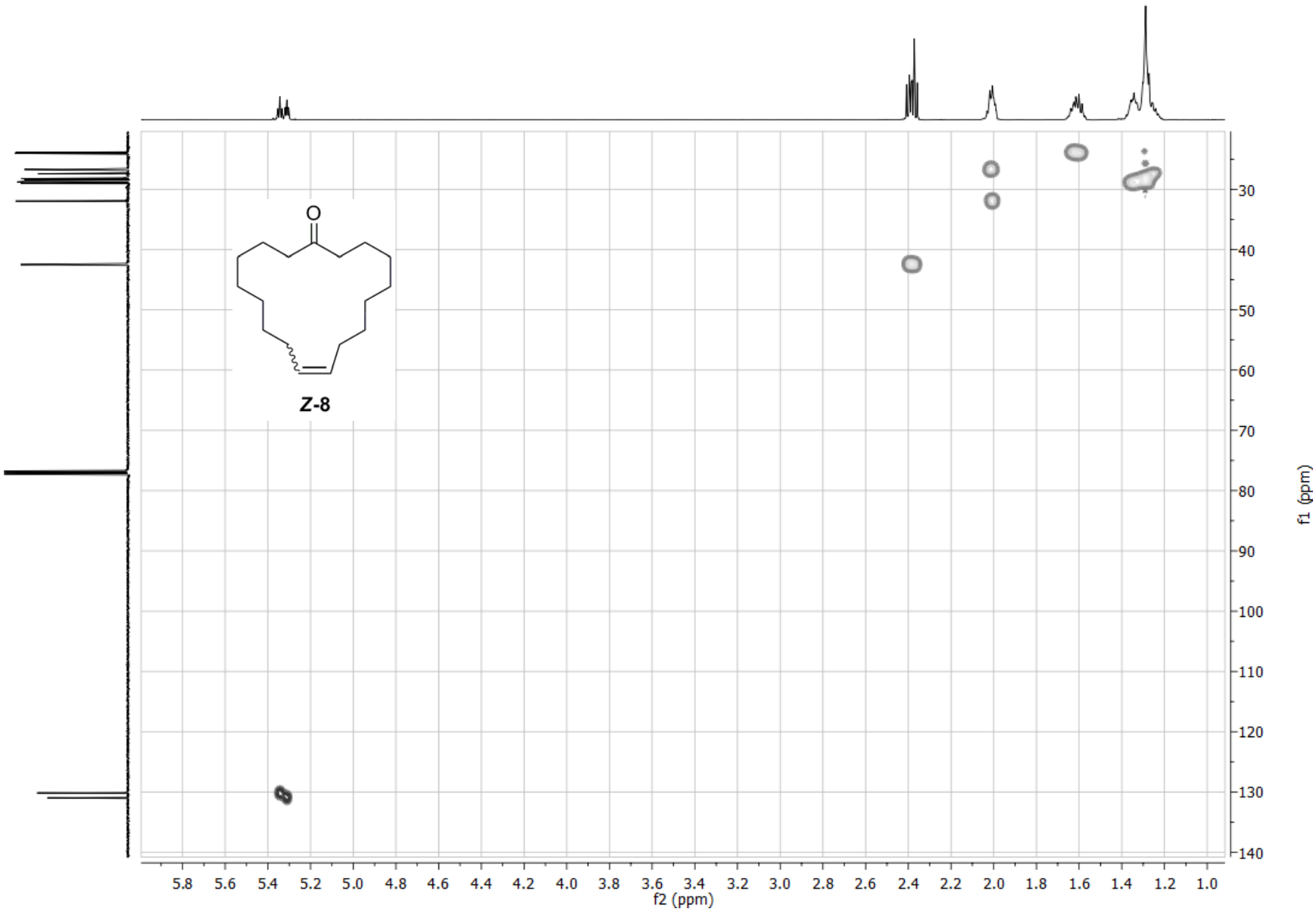
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-cycloheptadec-9-enone (8)



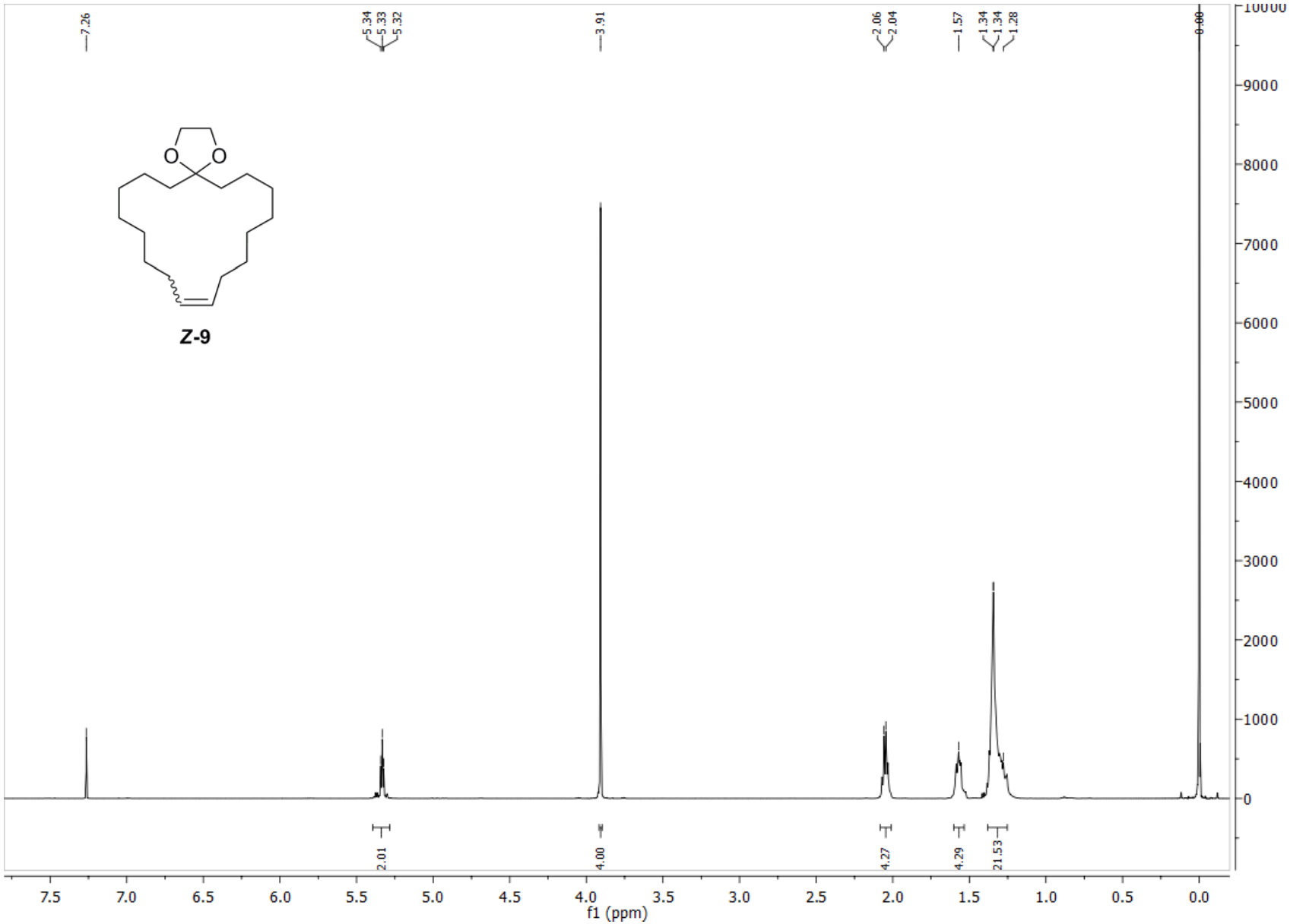
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-cycloheptadec-9-enone (8)



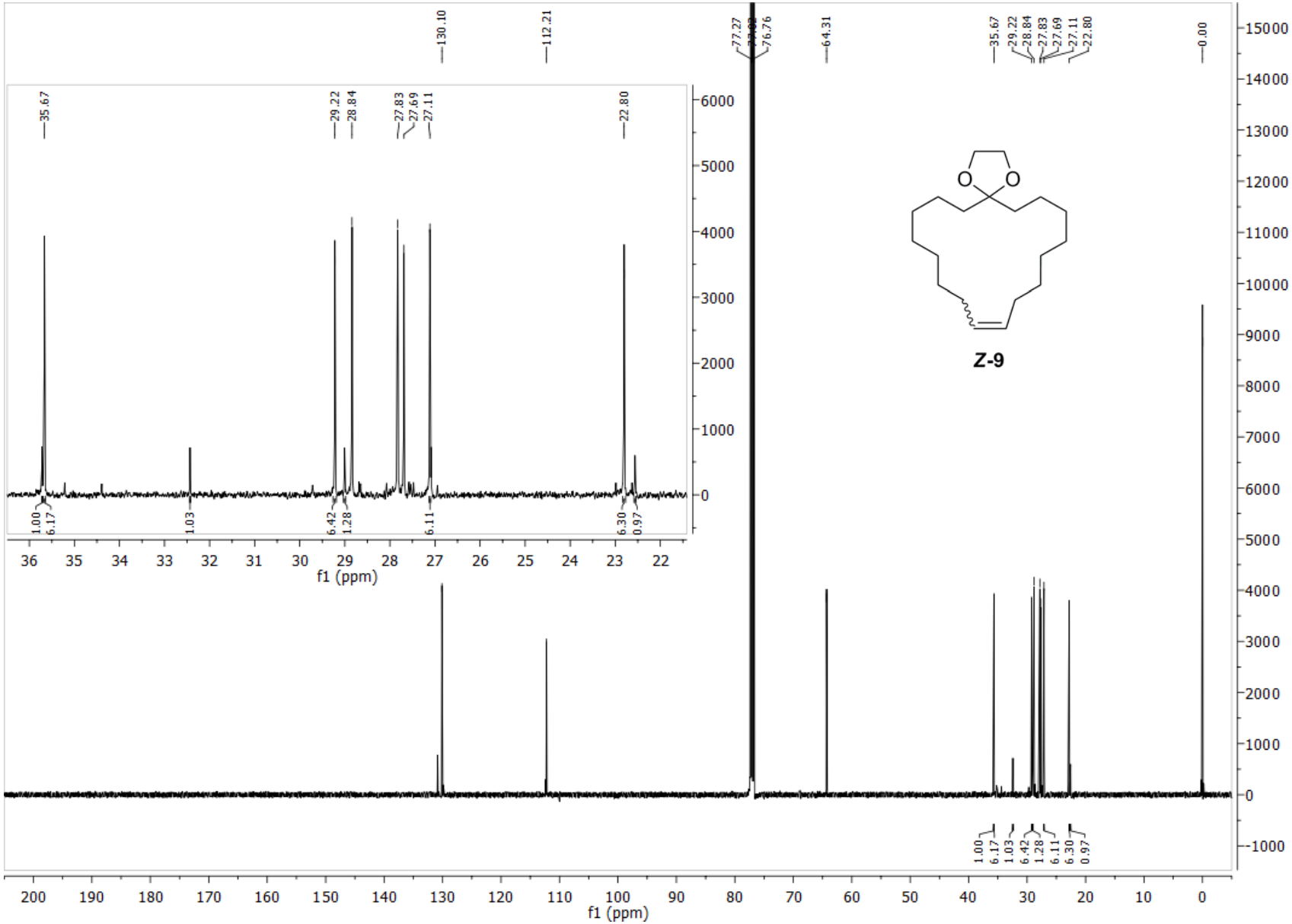
HSQC spectrum of *Z*-cycloheptadec-9-enone (8)



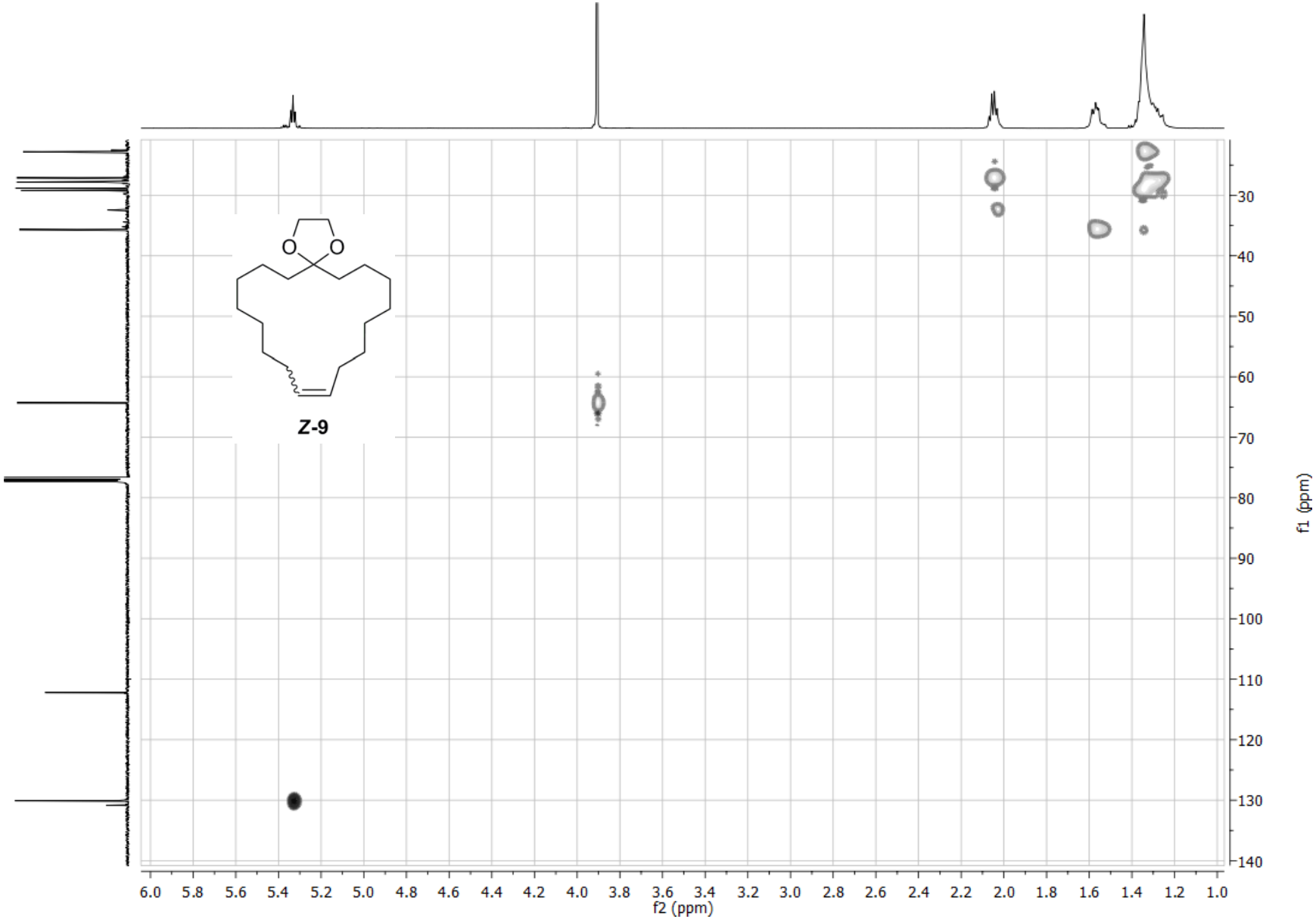
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-1,4-dioxaspiro[4.16]henicos-13-ene (9)



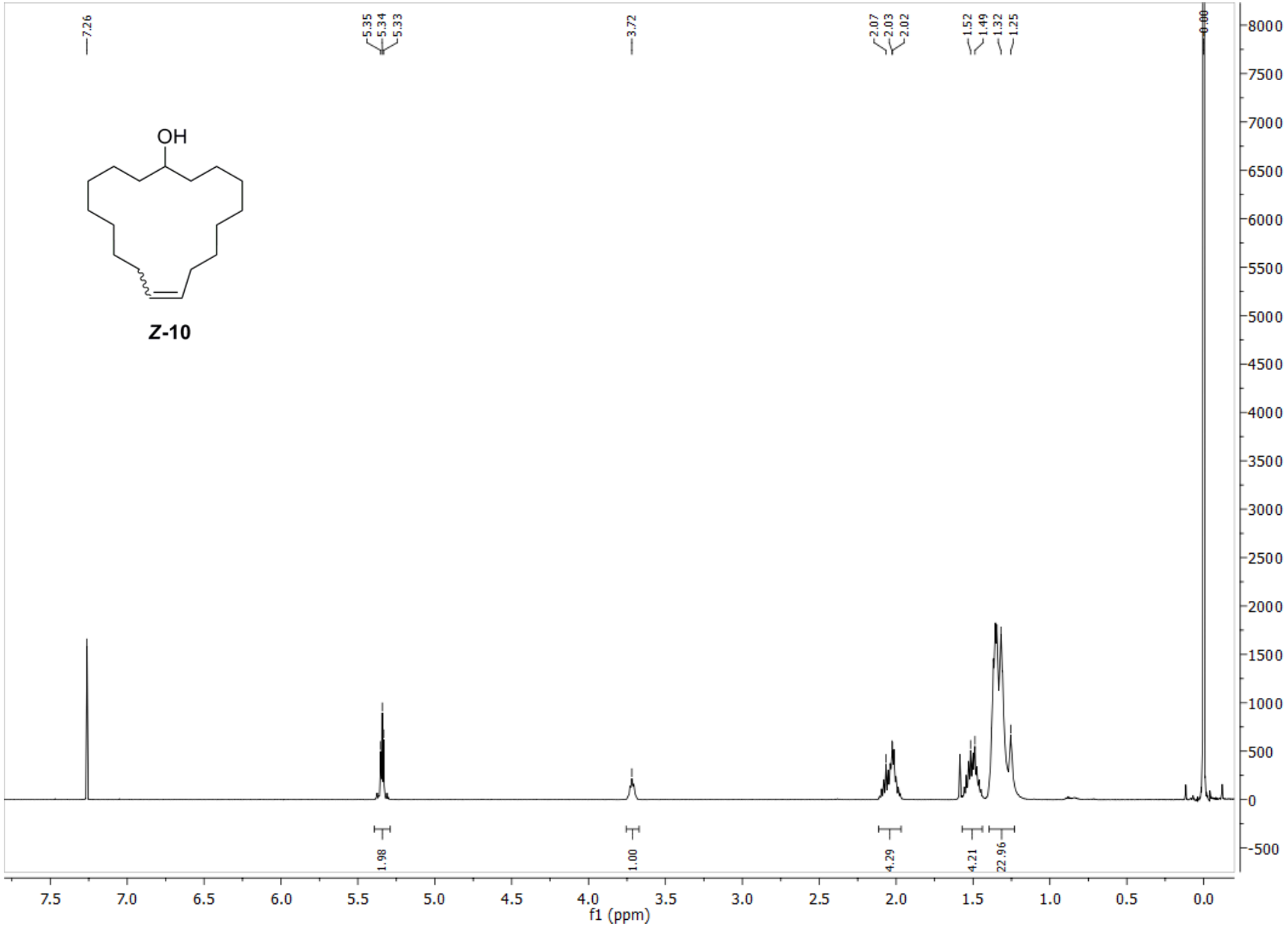
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-1,4-dioxaspiro[4.16]henicos-13-ene (9)



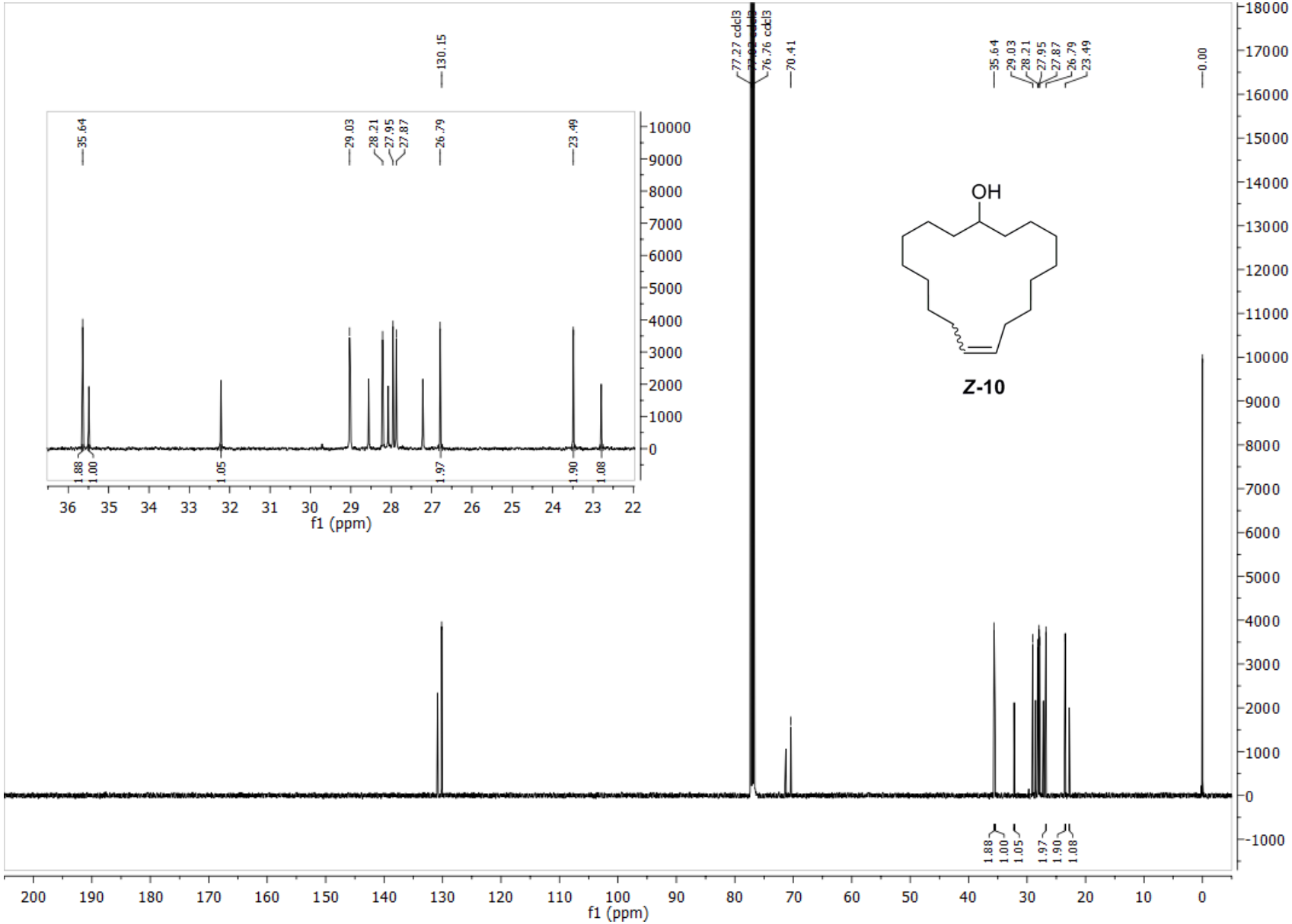
HSQC spectrum of *Z*-1,4-dioxaspiro[4.16]henicos-13-ene (9)



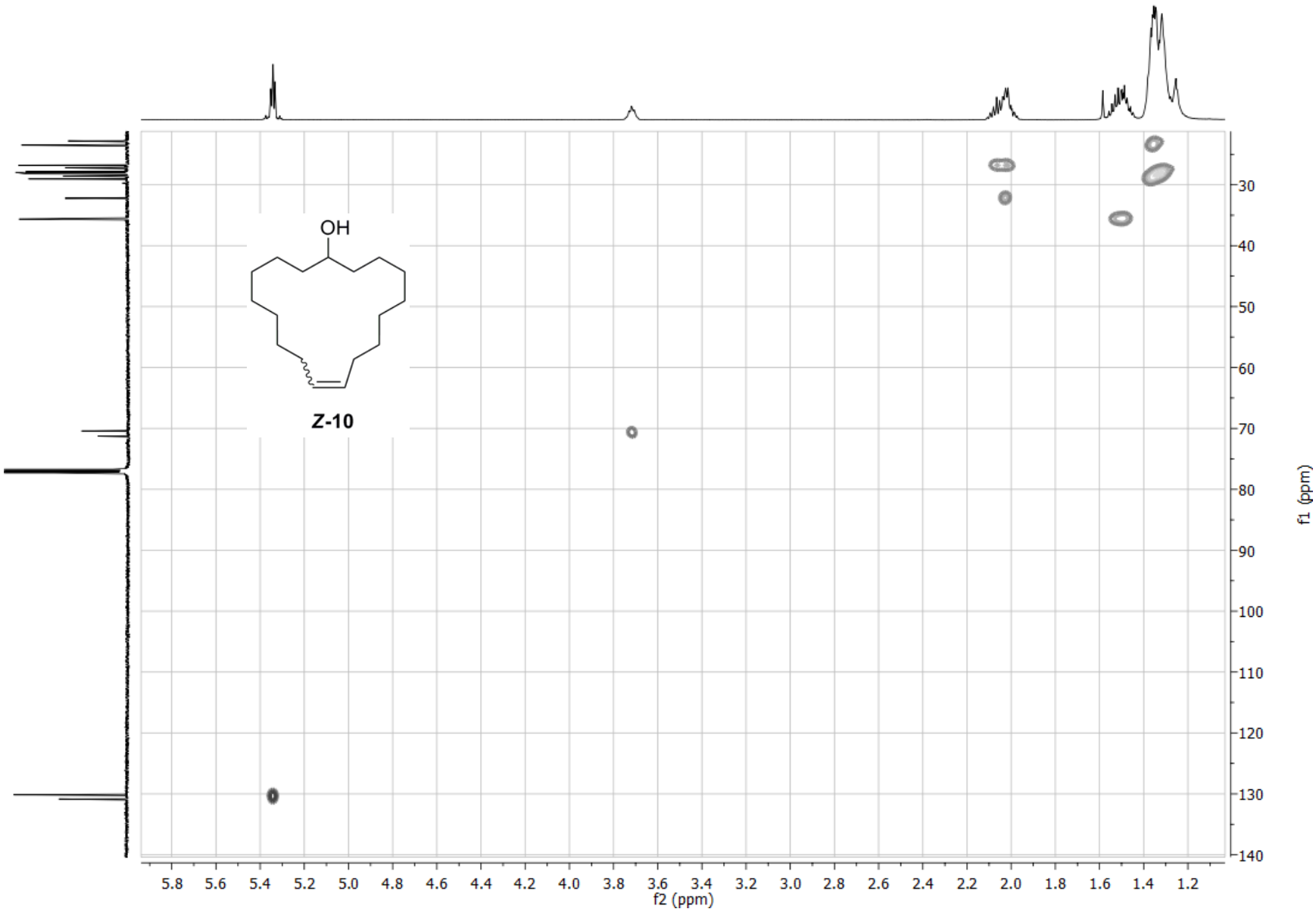
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-cycloheptadec-9-enol (10)



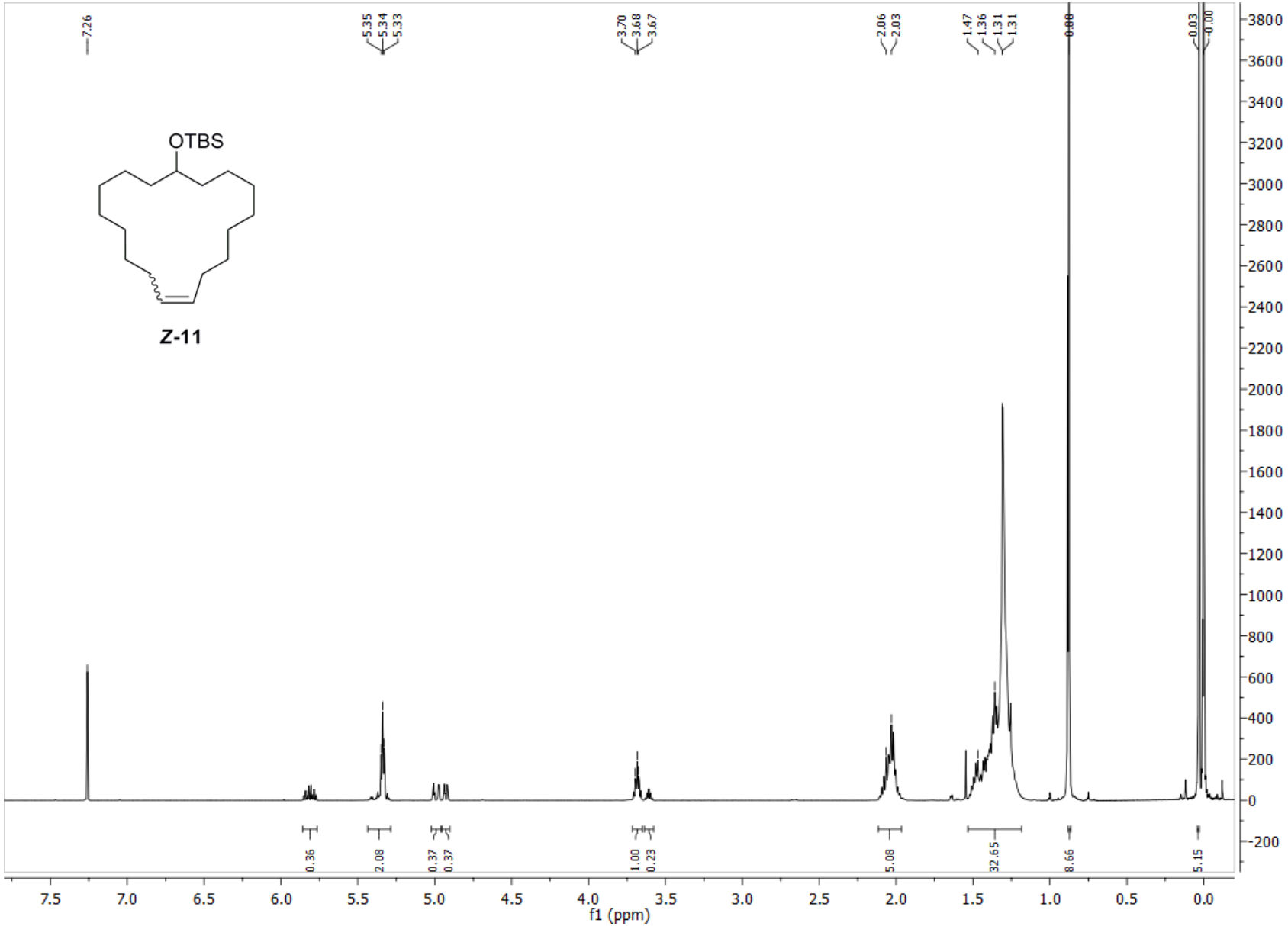
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-cycloheptadec-9-enol (10)



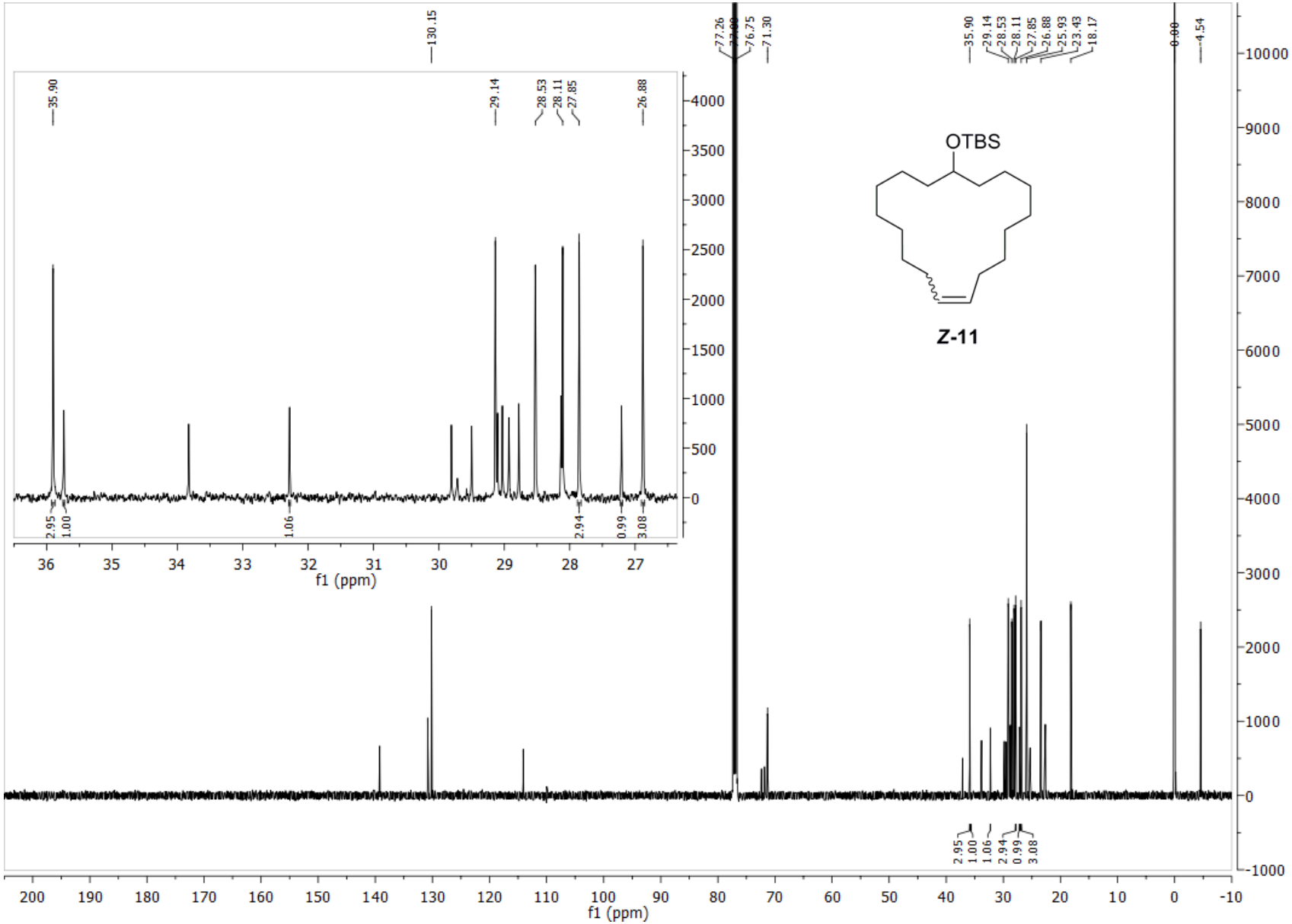
HSQC spectrum of *Z*-cycloheptadec-9-enol (10)



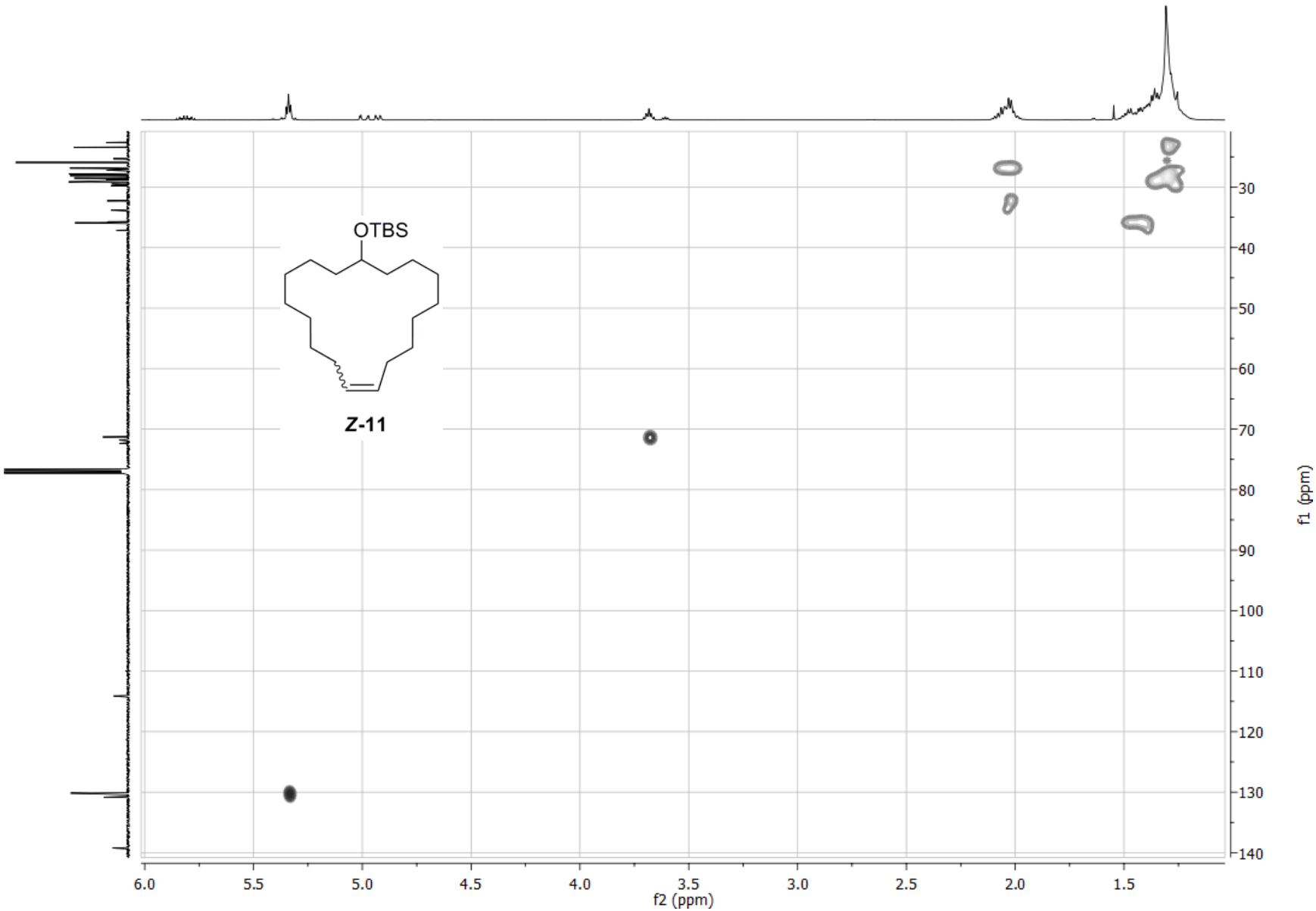
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-*tert*-butyl(cycloheptadec-9-en-1-yloxy)dimethylsilane (11)



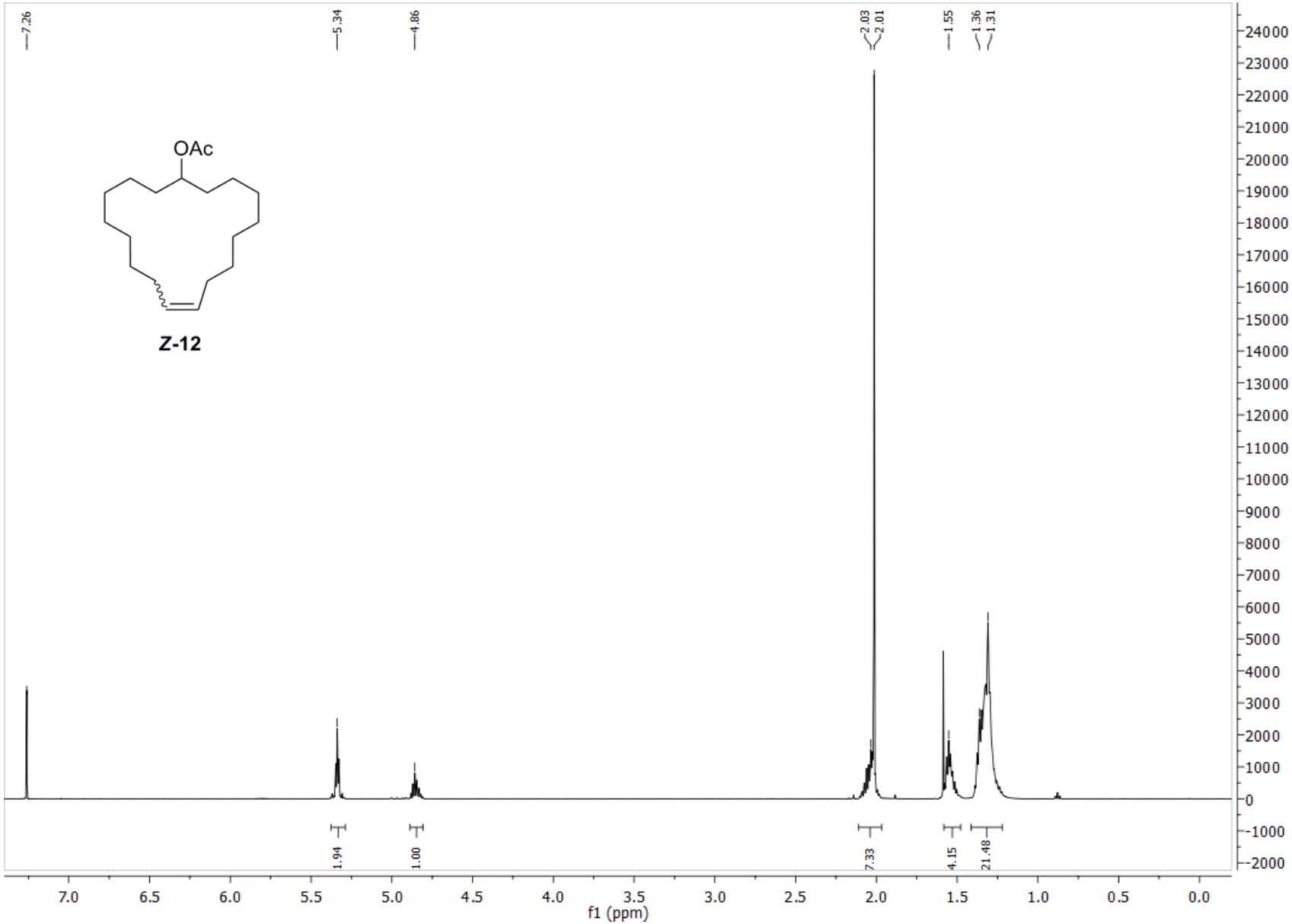
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z-tert*-butyl(cycloheptadec-9-en-1-yloxy)dimethylsilane (11)



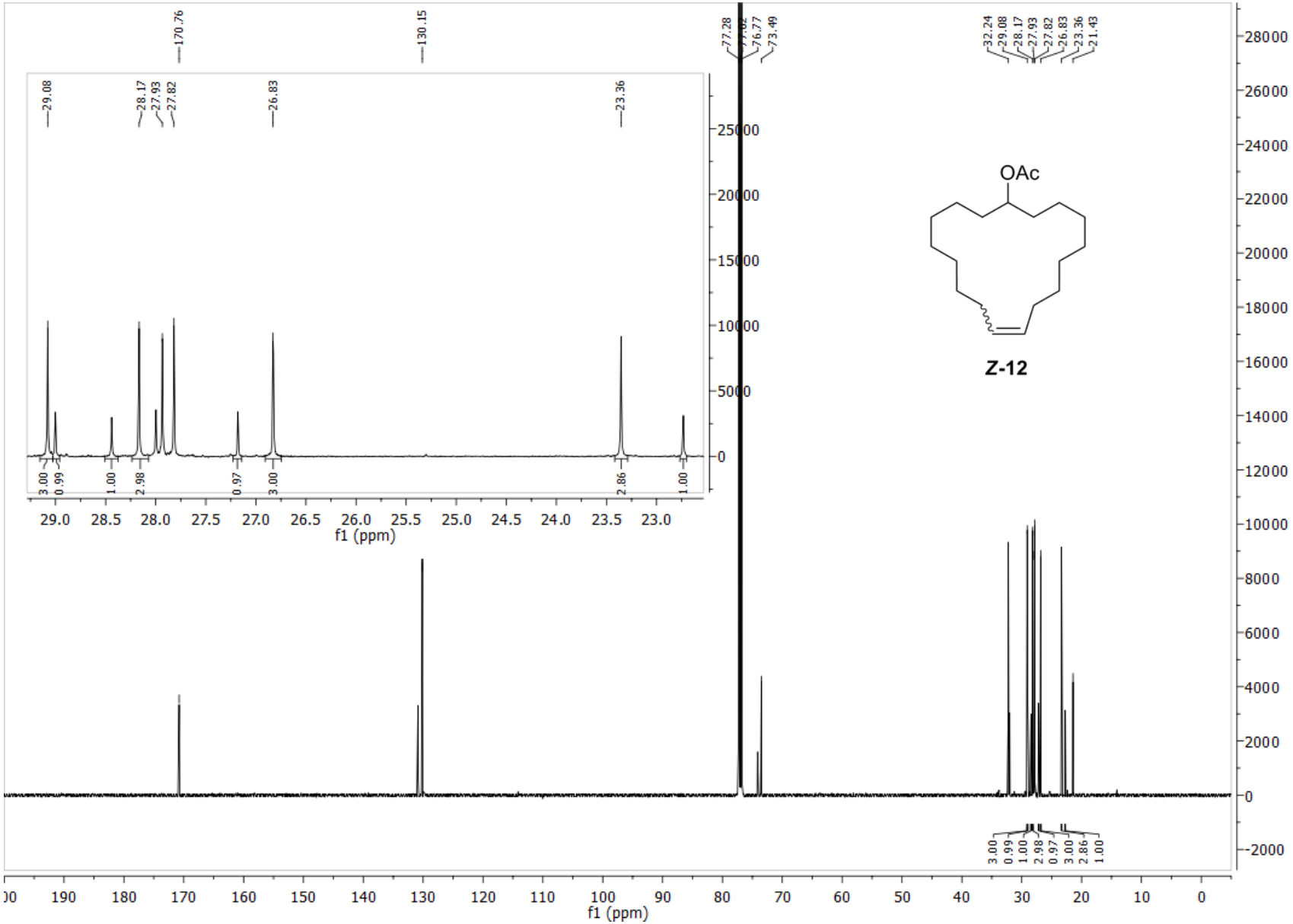
HSQC spectrum of *Z-tert*-butyl(cycloheptadec-9-en-1-yloxy)dimethylsilane (11)



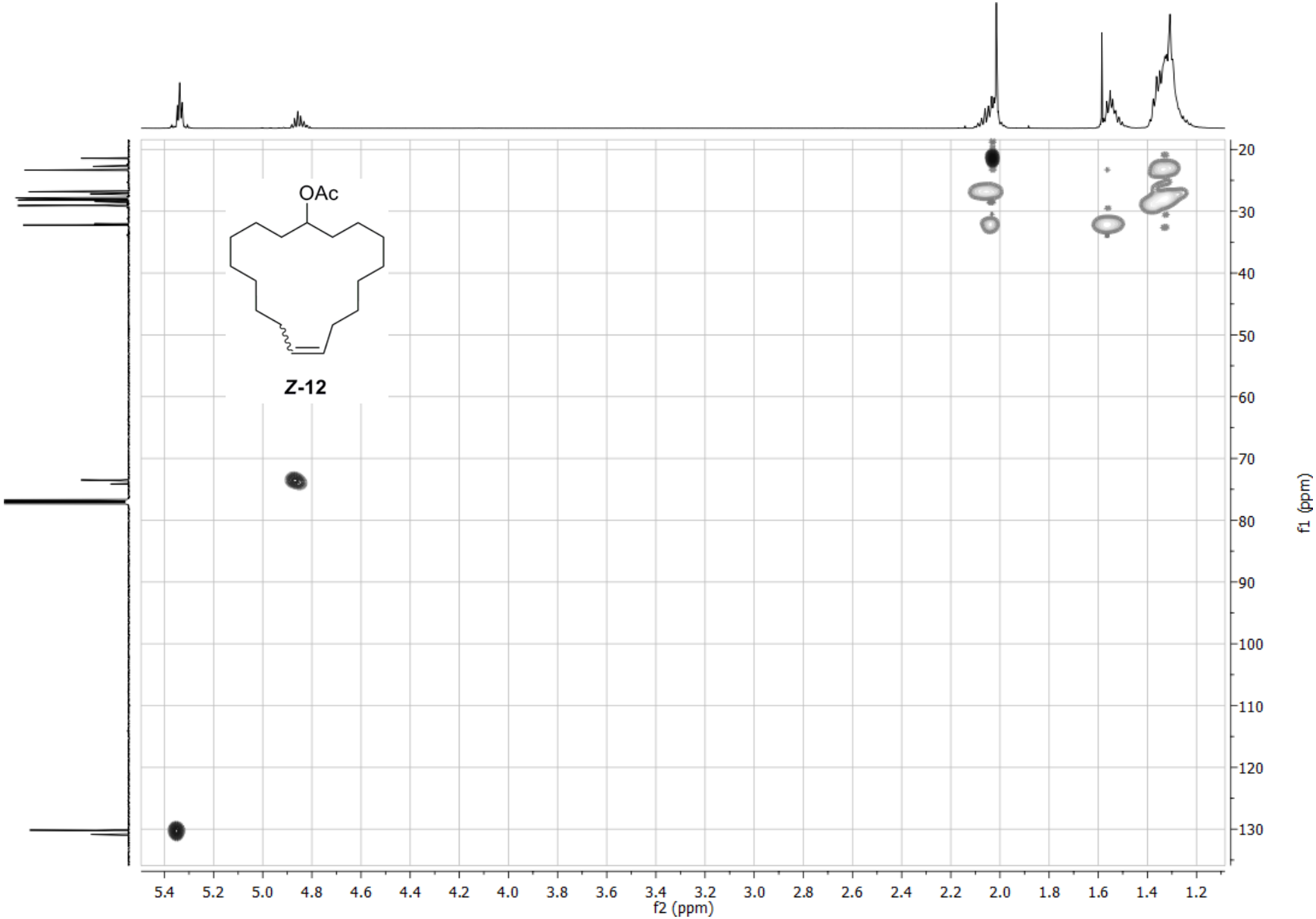
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-cycloheptadec-9-en-1-yl acetate (12)



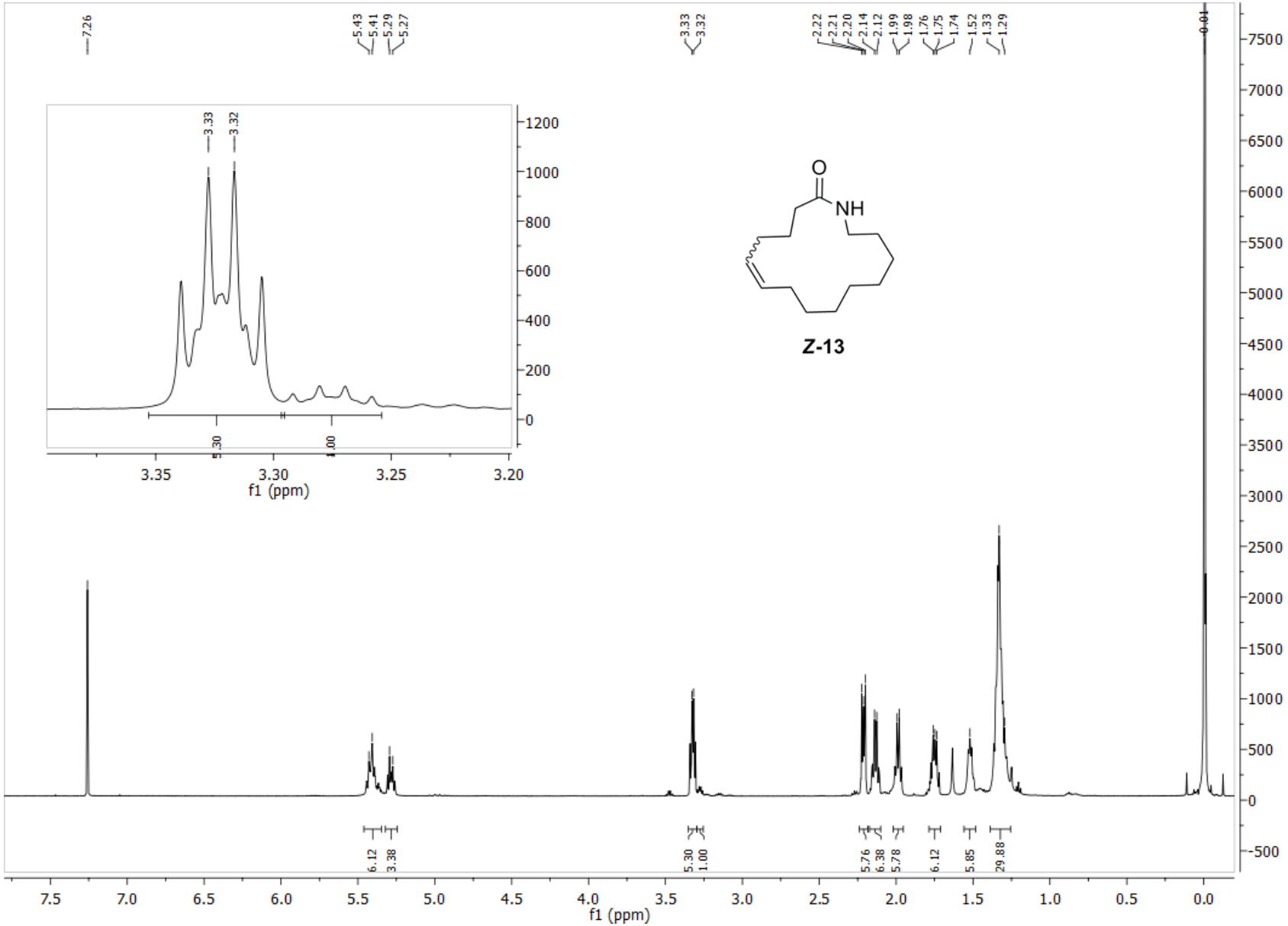
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-cycloheptadec-9-en-1-yl acetate (12)



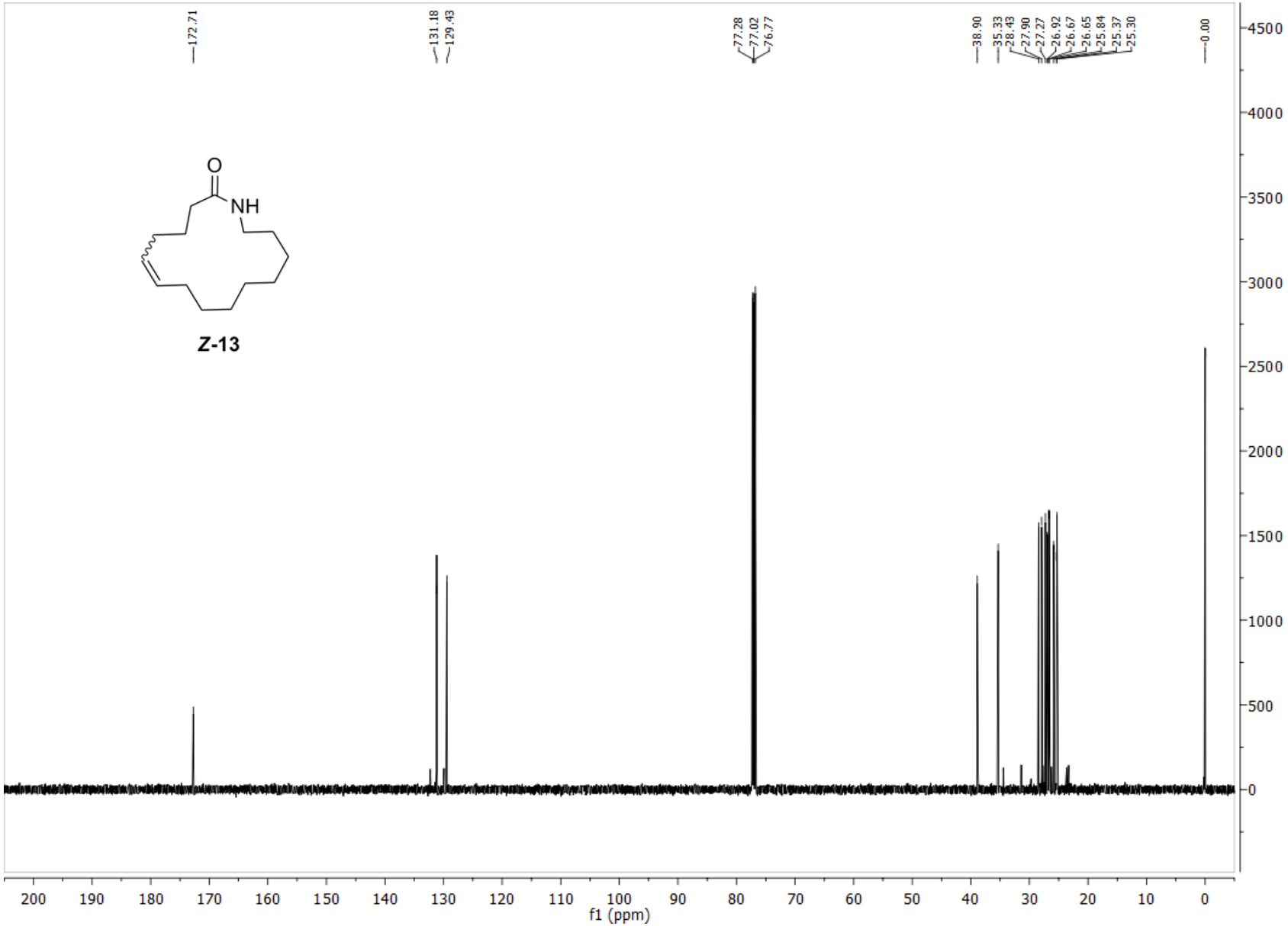
HSQC spectrum of *Z*-cycloheptadec-9-en-1-yl acetate (12)



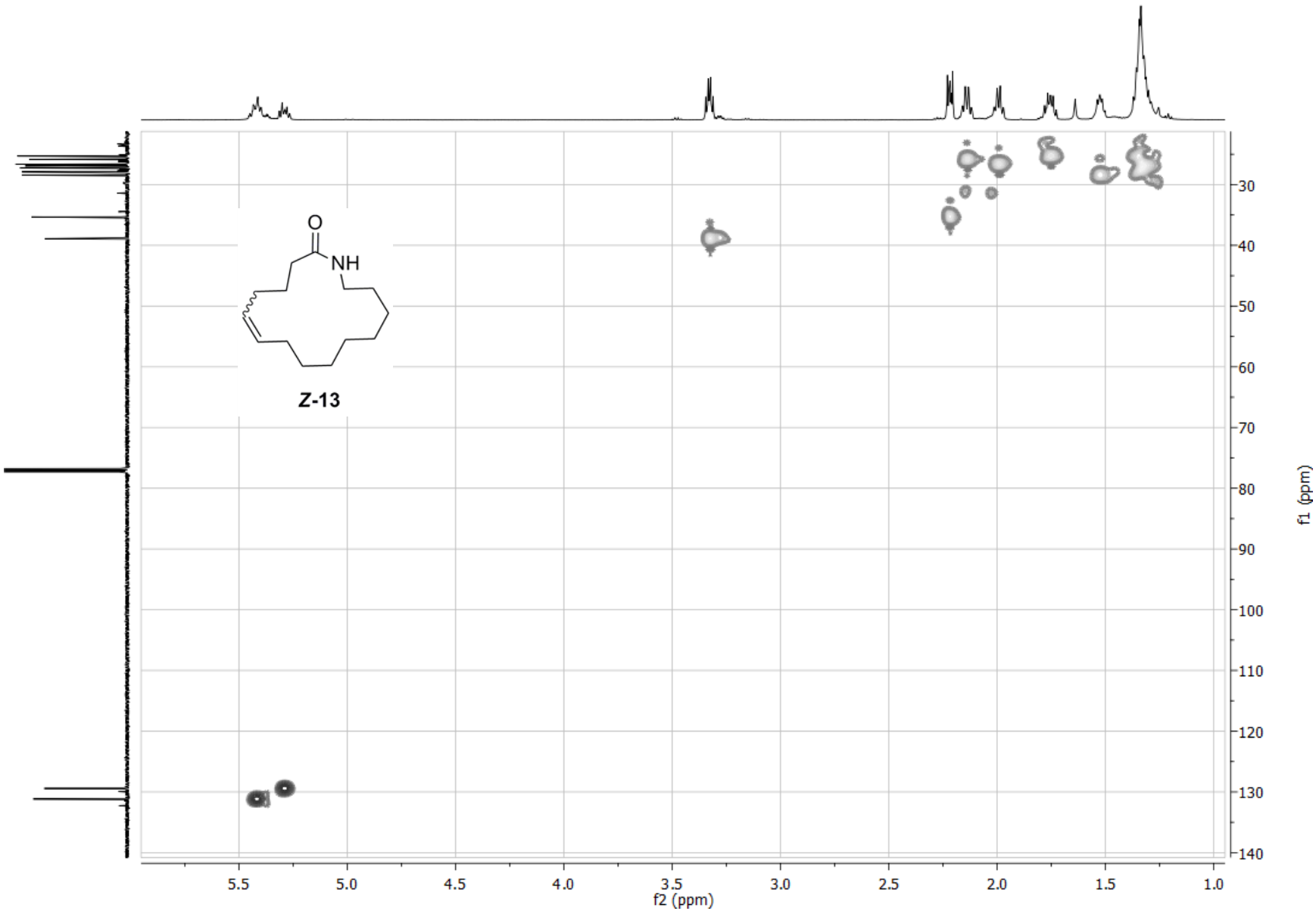
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-azacyclopentadec-6-en-2-one (13)



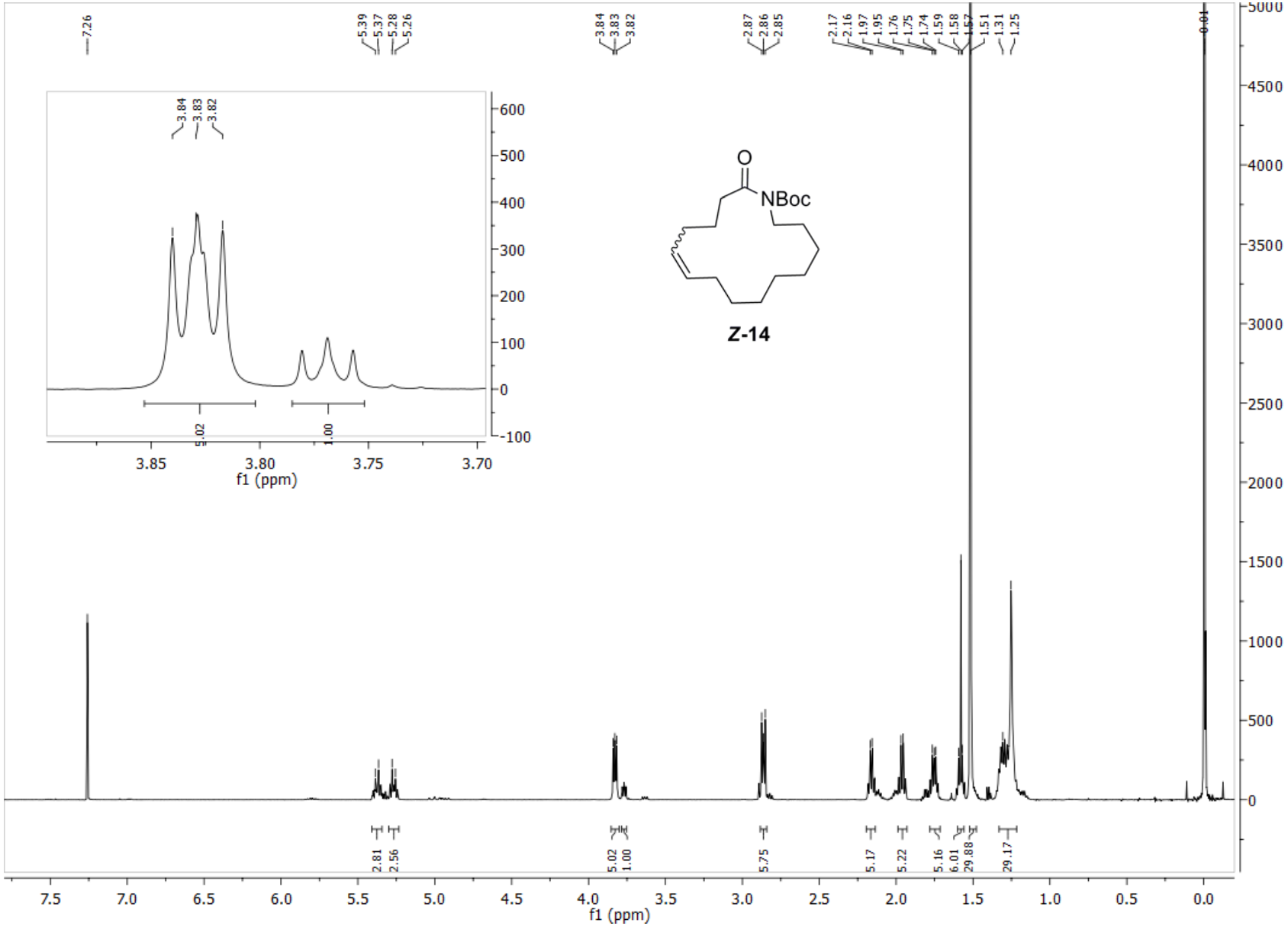
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z*-azacyclopentadec-6-en-2-one (13)



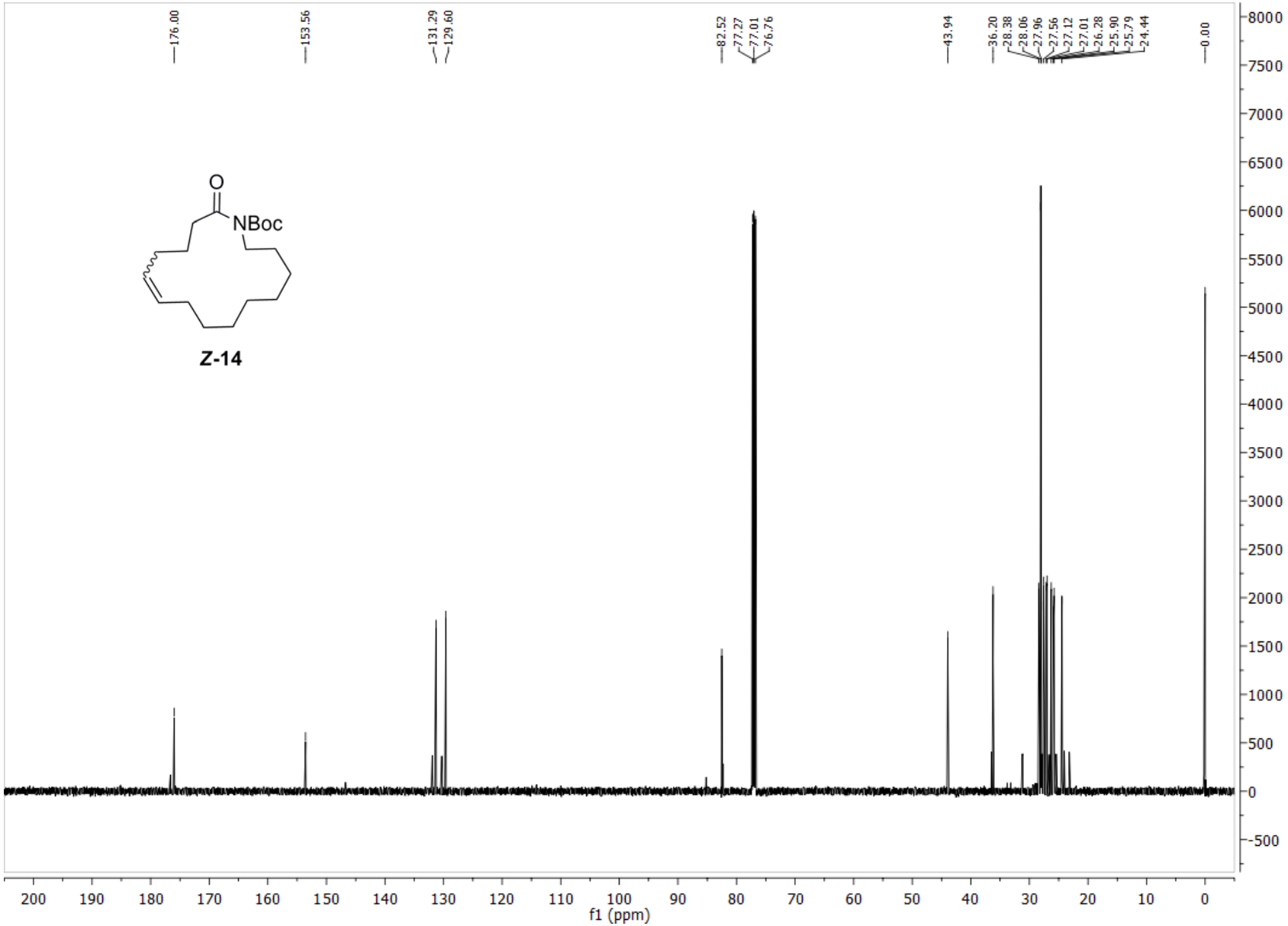
HSQC spectrum of *Z*-azacyclopentadec-6-en-2-one (13)



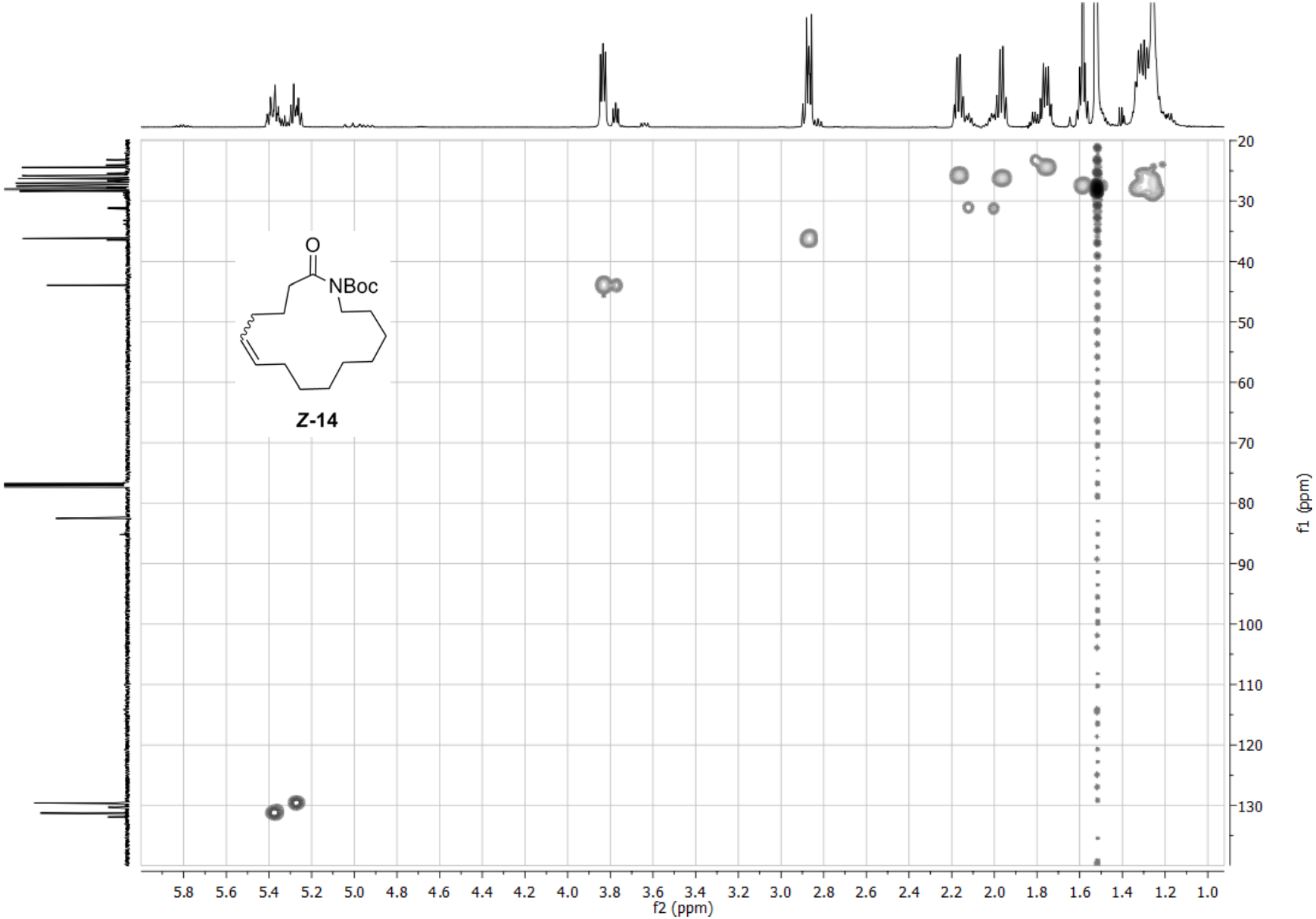
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *Z*-*tert*-butyl 2-oxoazacyclopentadec-6-ene-1-carboxylate (14)



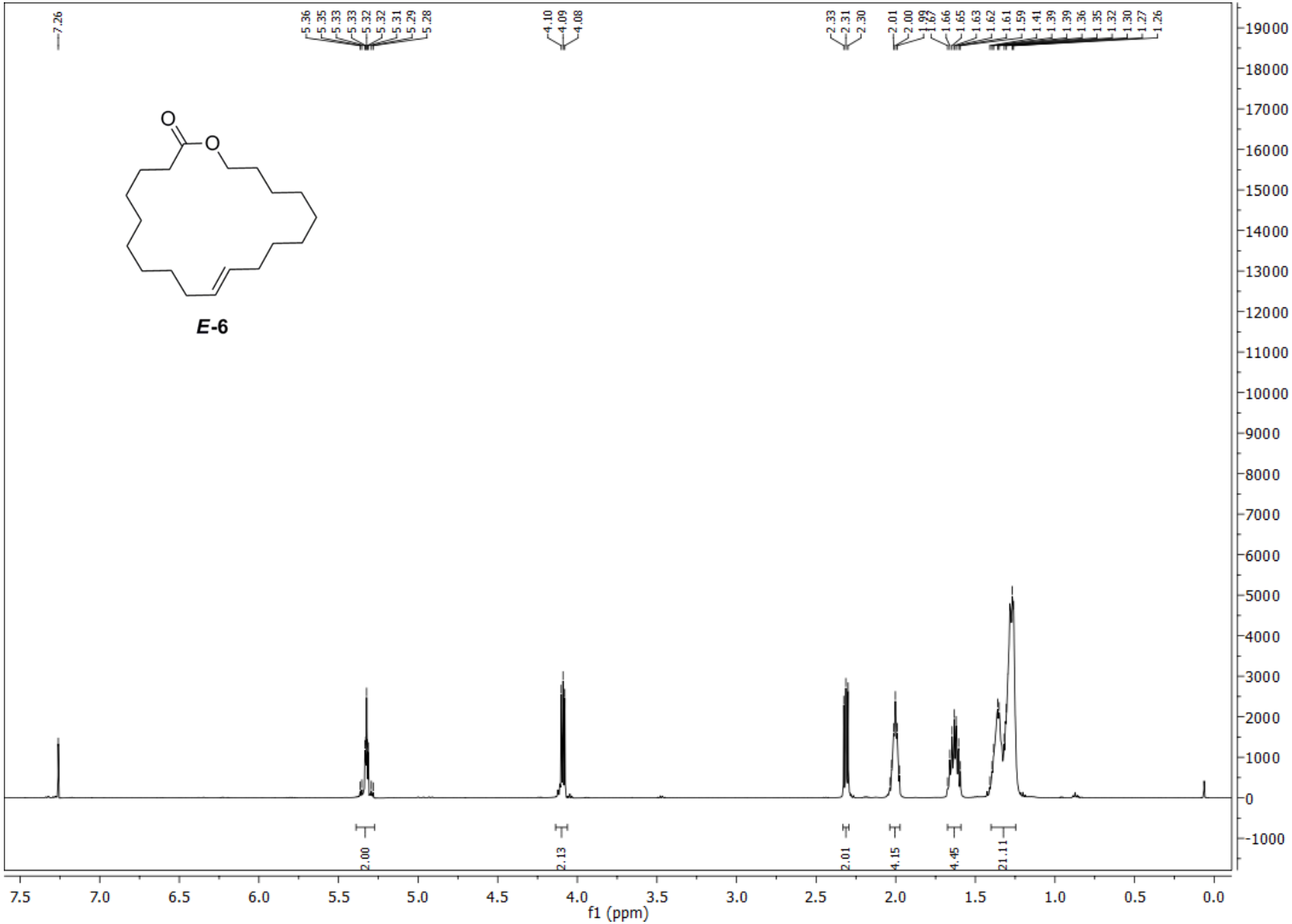
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *Z-tert*-butyl 2-oxoazacyclopentadec-6-ene-1-carboxylate (14)



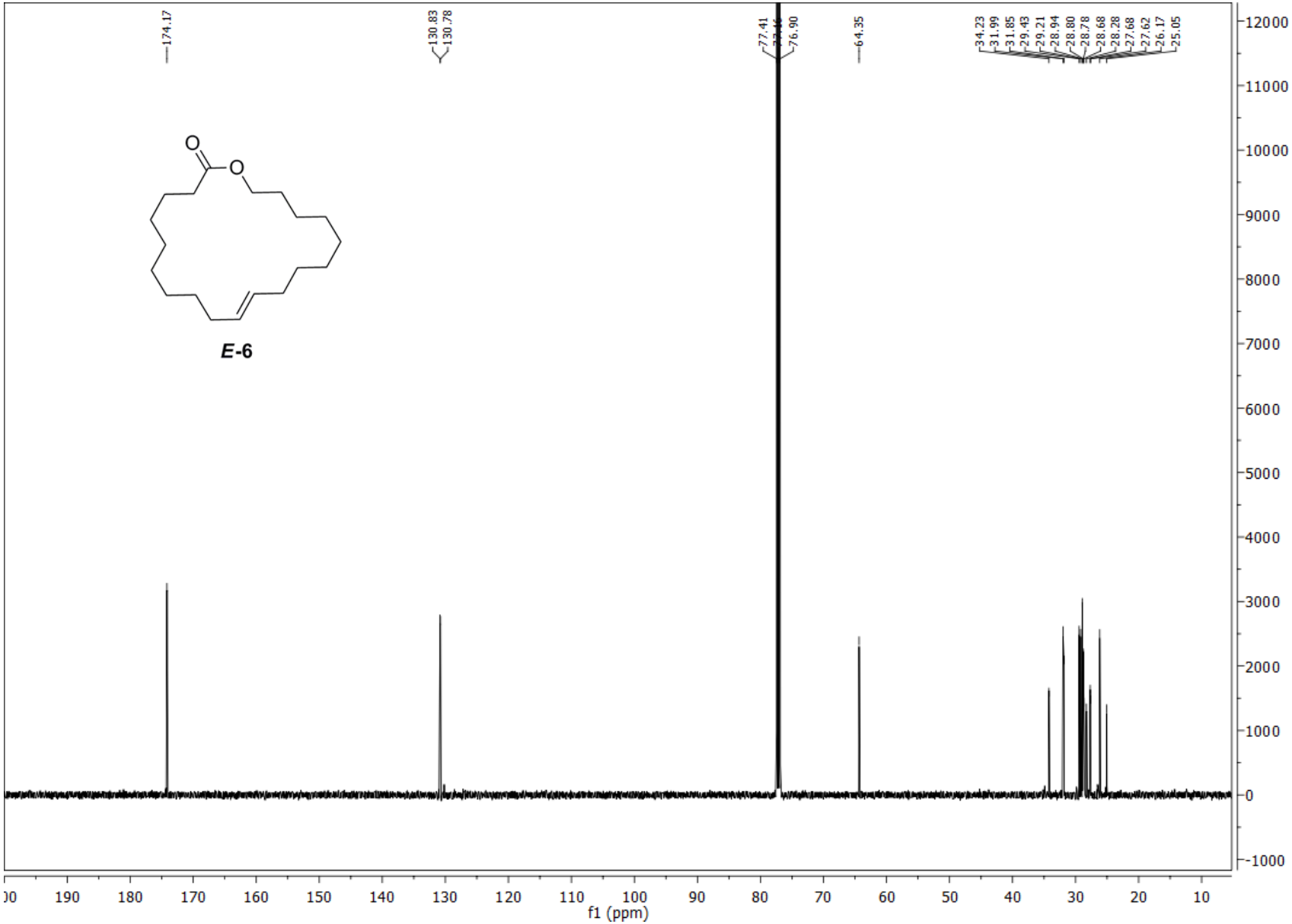
HSQC spectrum of *Z-tert*-butyl 2-oxoazacyclopentadec-6-ene-1-carboxylate (14)



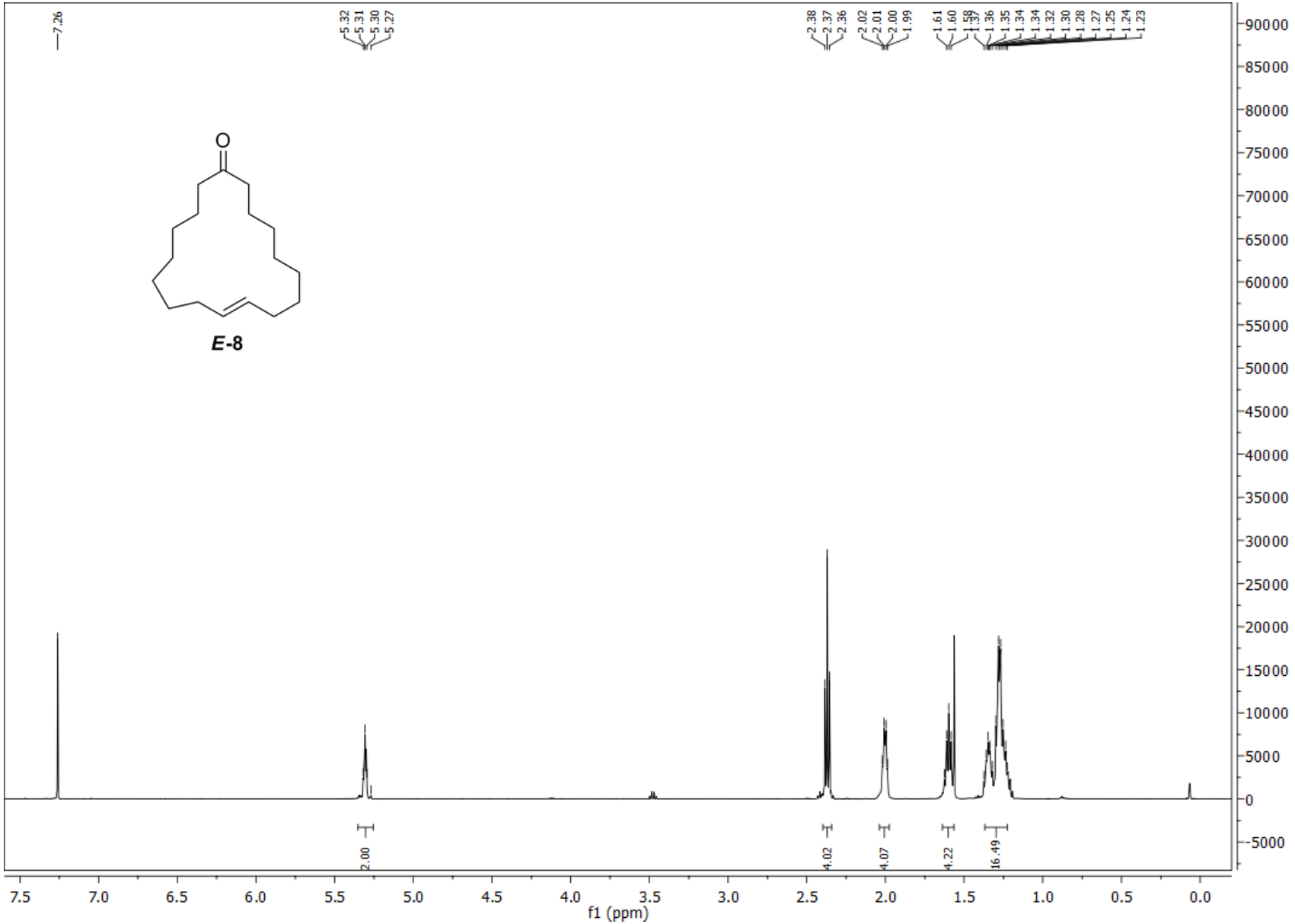
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *E*-oxacycloicos-11-en-2-one (6)



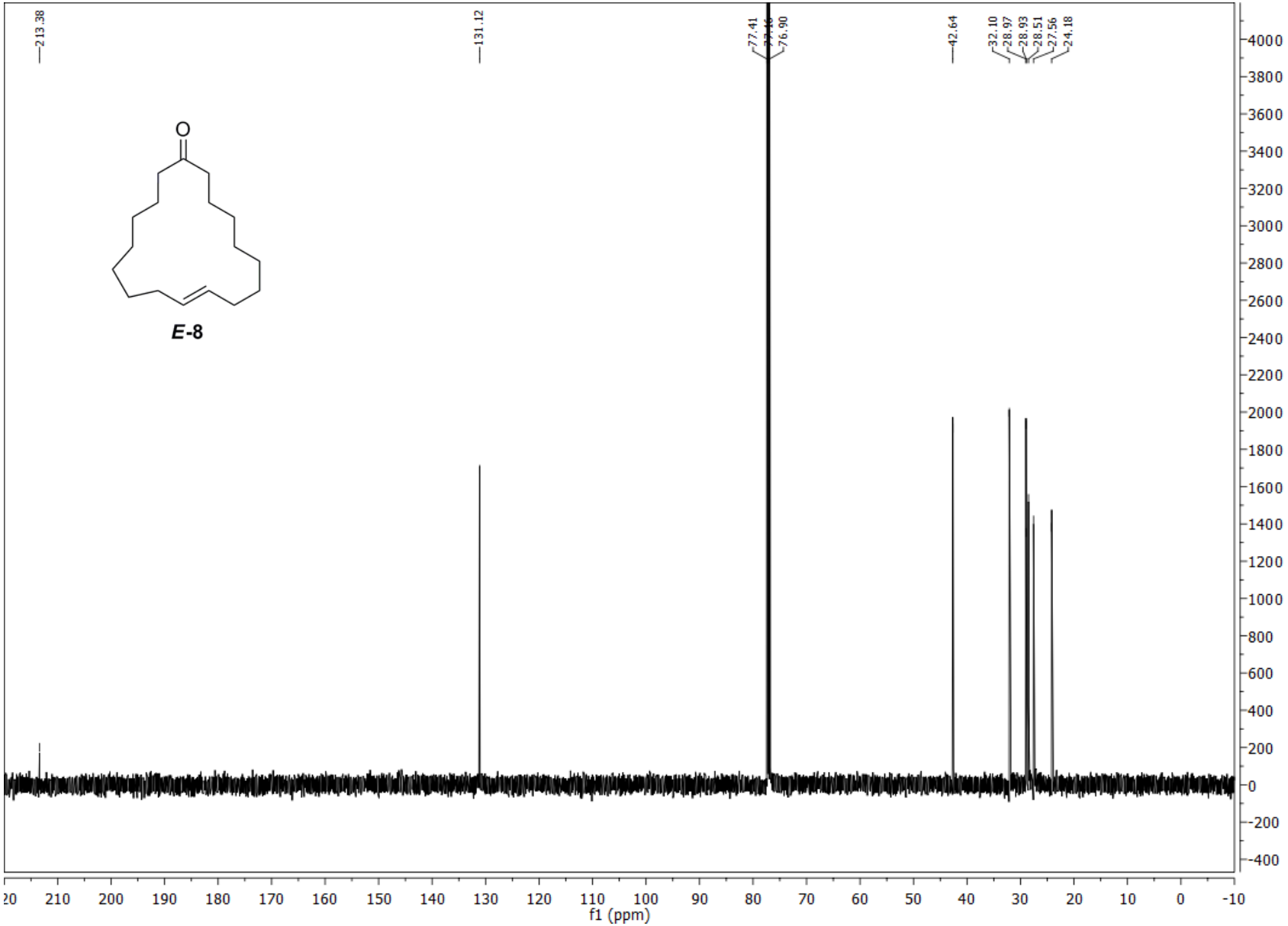
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *E*-oxacycloicos-11-en-2-one (6)



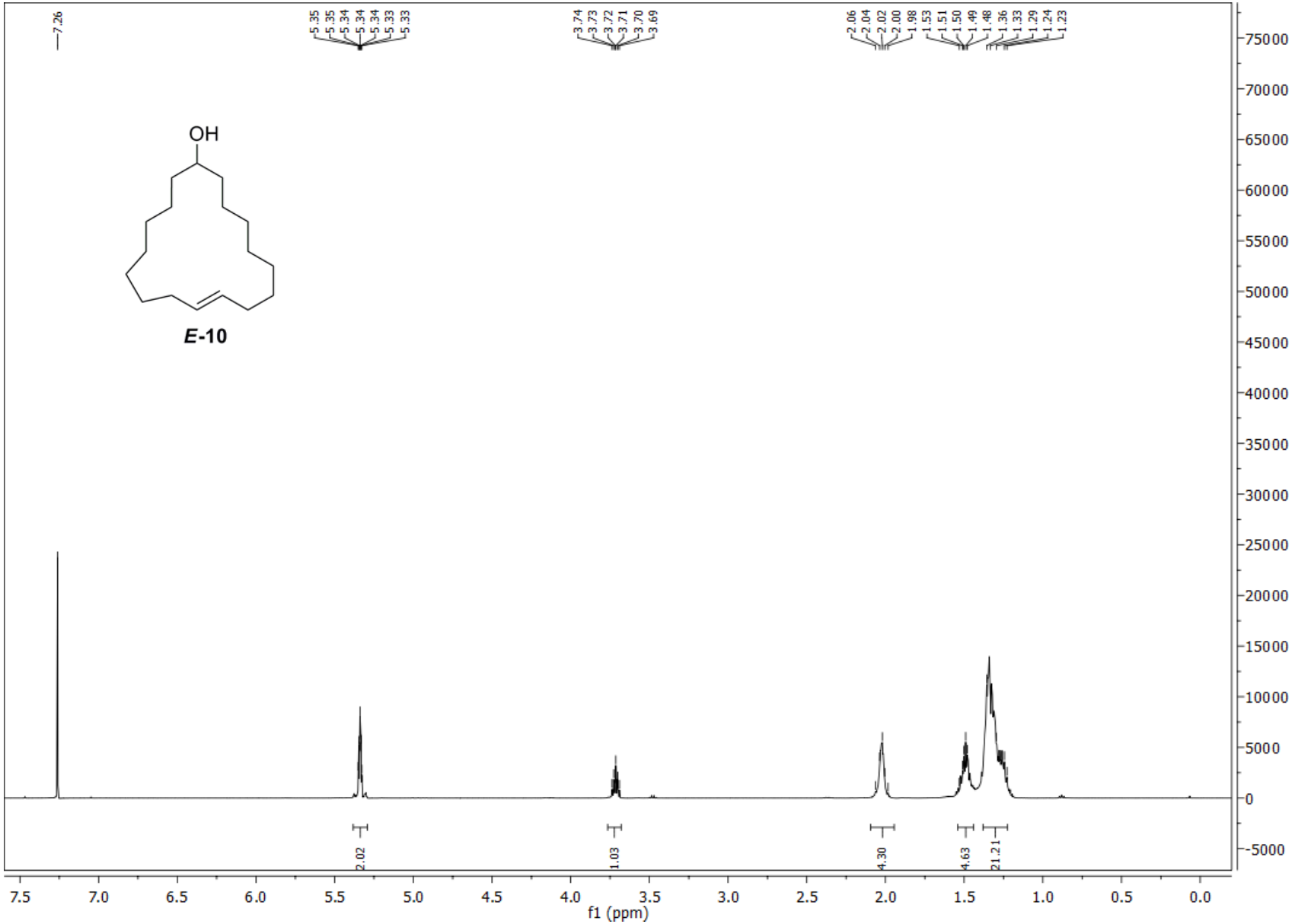
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *E*-cycloheptadec-9-enone (8)



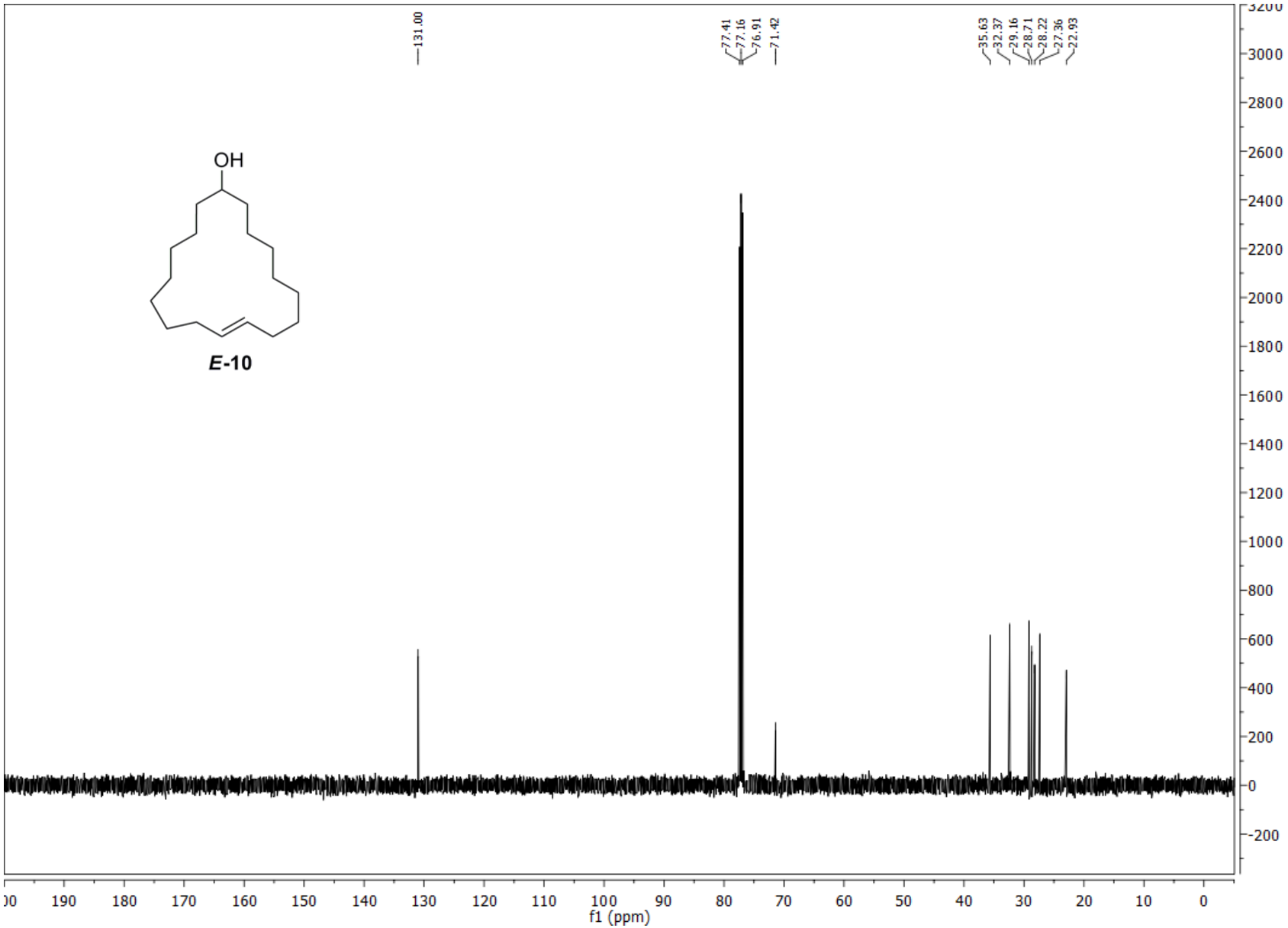
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *E*-cycloheptadec-9-enone (8)



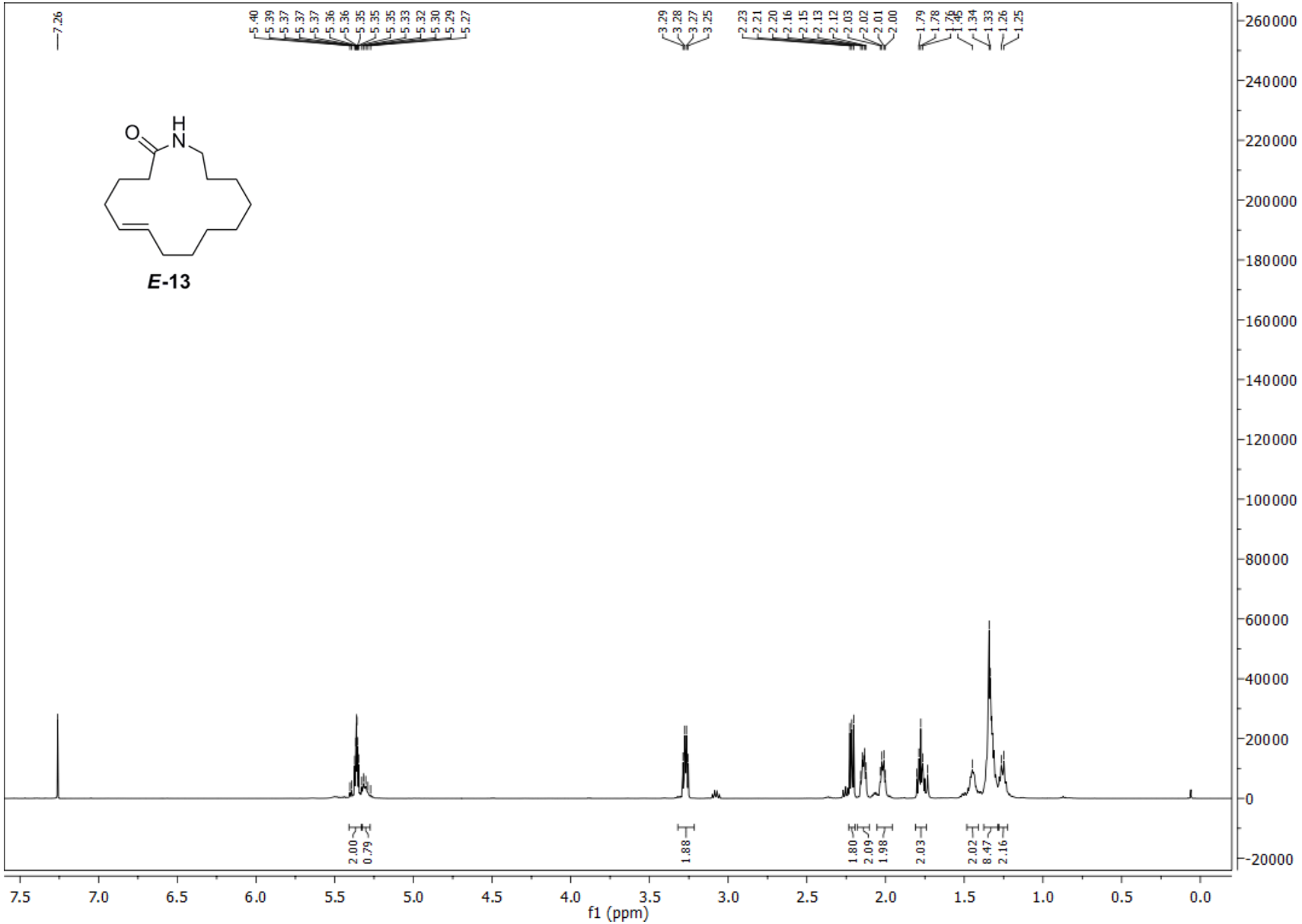
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *E*-cycloheptadec-9-enol (10)



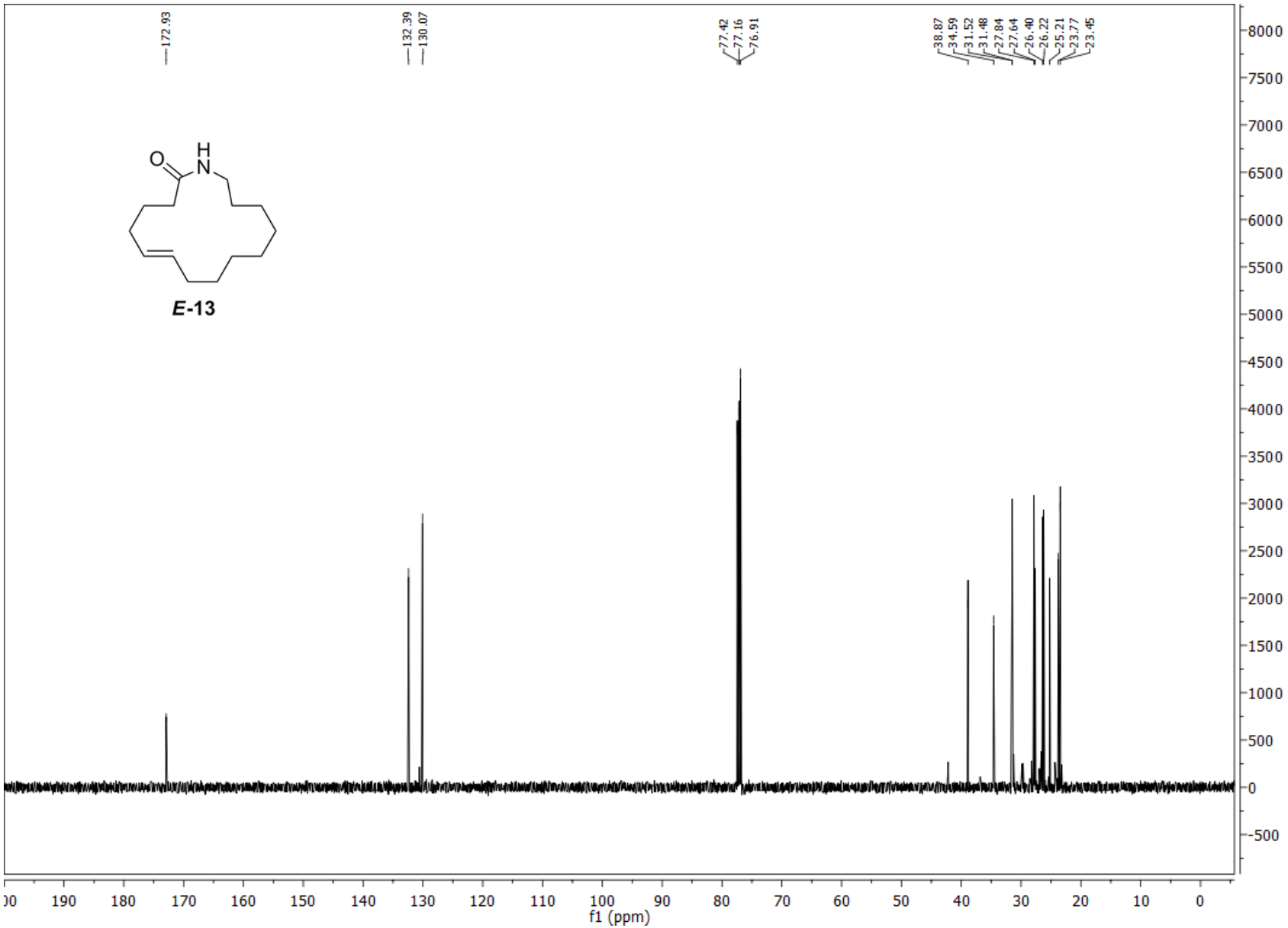
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *E*-cycloheptadec-9-enol (10)



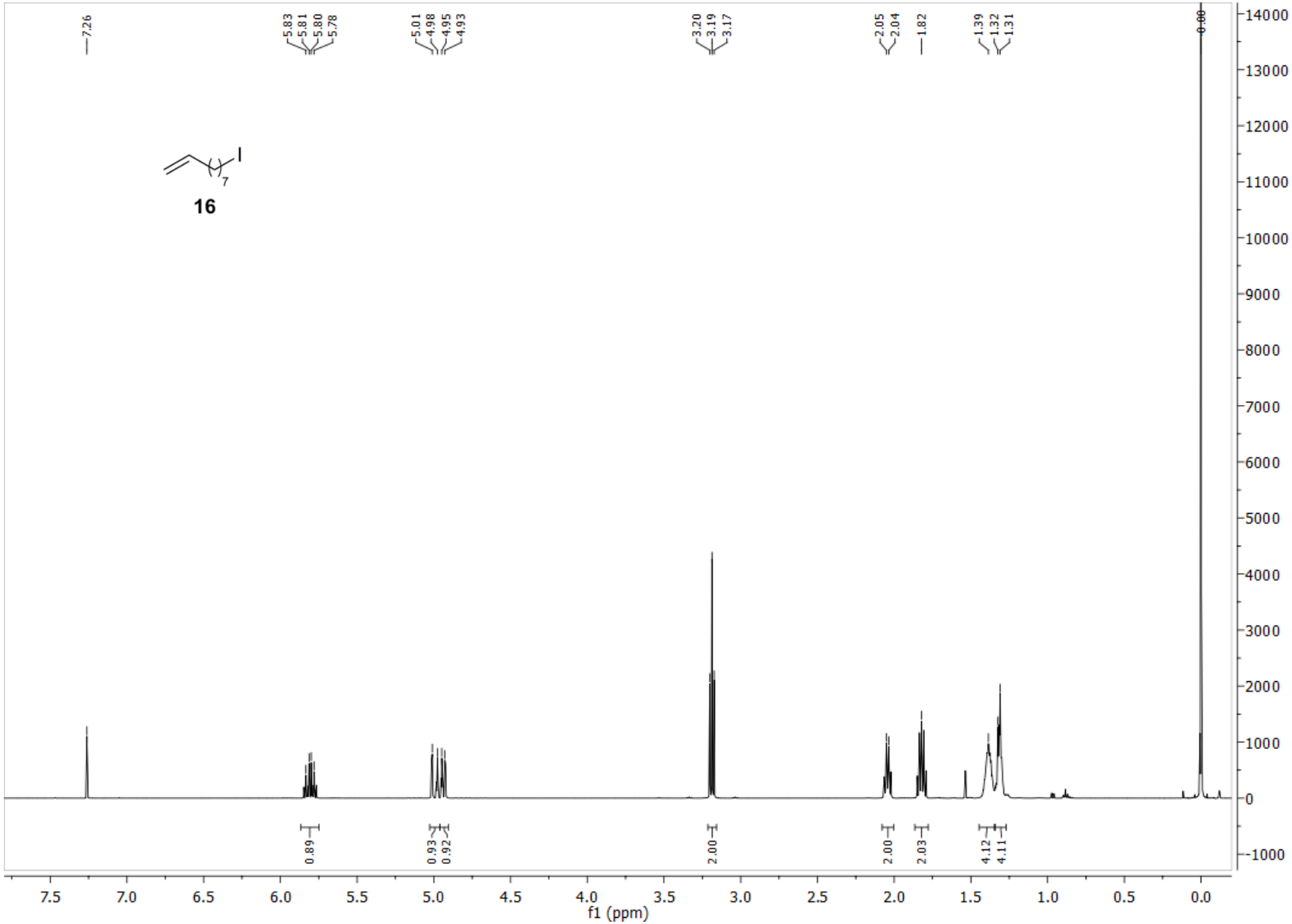
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *E*-azacyclopentadec-6-en-2-one (13)



^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *E*-azacyclopentadec-6-en-2-one (13)



^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 9-iodonon-1-ene (16)



^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of 9-iodonon-1-ene (16)