Supporting Information

Part 1. Experimental Procedures

General Experimental Procedures

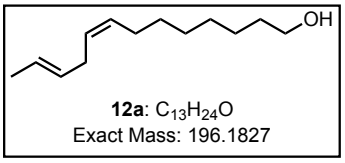
All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere, unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed by bubbling argon. NMR solvents were dried over CaH_2 and vacuum transferred to a dry Schlenk flask and subsequently degassed with bubbling argon. C_6D_6 was purified by passage through a solvent purification column. $CDCl_3$ was used as received. All α-olefins were filtered through a plug of basic alumina prior to use. Ruthenium complexes **1**, **2**, **5**, and **6** were obtained from Materia Inc. Dienes **13a**,[1] and **13c**,[2] **13d**,[3] **13e**,[4] and **13f**[5] were prepared according to their previously reported procedures. Other commercially available reagents and silica gel were used as received.

^{1}H NMR spectra were acquired at 500 MHz and ^{13}C NMR spectra at 125 MHz as $CDCl_3$ solutions unless otherwise noted. High-resolution mass spectra (HRMS) were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer. All HRMS were by positive-ion EI or ESI. Gas chromatography data was obtained using an Agilent 6850 FID gas chromatography system equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (length: 30 m, diameter: 0.25 mm, film: 0.25 μm) (Agilent). Temperature gradient: 50 °C for 2 min; 21 °C/min to 300 °C; 300 °C for 3 min).

(1) Trost, B. M.; Conway, W. P.; Strege, P. E.; Dietsche, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7165–7167.
(2) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *J. Org. Chem.* **2004**, *69*, 1038–1052.
(3) Ranu, B. C.; Majee, A. *Chem. Commun.* **1997**, 1225–1226.
(4) Ishikura, M.; Kato, H. *Tetrahedron* **2002**, *58*, 9827–9838.
(5) Hodgson, D. M.; Fleming, M. J.; Stanway, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 12250–12251.

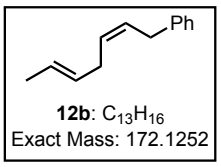
General Procedure for Reaction with *trans*-1,4-hexadiene.

(*Z*,*E*)-8,10-tridecadien-1-ol (12a).



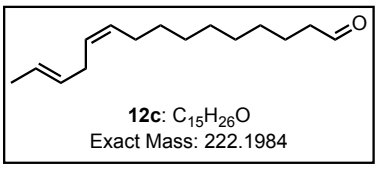
In a glovebox, a 4 mL vial was charged with 28 mg (0.20 mmol) of 8-nonen-1-ol. *Trans*-1,4-pentadiene (0.20 mL) and THF (0.16 mL) were added, followed by a solution of catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol). The resulting solution was stirred in an open vial for 5 h before being removed from the glovebox and quenched with excess ethyl vinyl ether (~0.1 mL). The solvent was removed *in vacuo* and the residue purified by column chromatography (SiO_2; 0% to 25% EtOAc in hexane) to provide 31 mg (80%) of diene **12a** as a clear, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 – 5.32 (m, 4H), 3.63 (t, J = 6.7 Hz, 2H), 2.71 (appt, J = 6.3, Hz, 2H), 2.03 (appq, J = 7.9 Hz, 2H), 1.65 (dt, J = 4.5, 1.3 Hz, 3H), 1.60 – 1.52 (m, 3H), 1.40 – 1.27 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.54, 129.79, 127.89, 125.28, 63.22, 32.95, 30.63, 29.77, 29.49, 29.41, 27.26, 25.91, 18.10; HRMS (EI) m/z calcd for $C_{13}H_{24}O$ (M^+) 196.1827, found 196.1825.

(*Z*,*E*)-1-phenyl-2,5-heptadiene (12b)



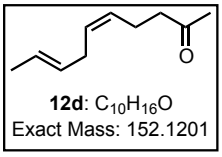
Following the procedure for **12a**, **12b** was obtained as 56 mg of a 4:1 molar (63% **12b**) mixture with (*E*,*Z*,*E*)-2,5,8-pentatriene when allyl benzene (24 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 5.58 – 5.38 (m, 4H), 3.45 (d, J = 6.8 Hz, 2H), 2.89 (ddt, J = 6.3, 3.0, 1.5 Hz, 2H), 1.74 – 1.66 (m, 3H).

(*Z*,*E*)-10,13-pentadecadienal (12c)



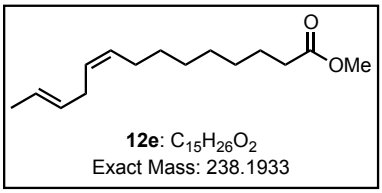
Following the procedure for **12a**, **12c** (31 mg, 70%) was obtained as a clear, colorless oil when undecenal (33 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.9 Hz, 1H), 5.50 – 5.32 (m, 4H), 2.72 (ddd, *J* = 6.8, 5.0, 1.6 Hz, 2H), 2.42 (td, *J* = 7.4, 1.9 Hz, 2H), 2.03 (q, *J* = 6.8 Hz, 2H), 1.65 (dt, *J* = 4.6, 1.3 Hz, 3H), 1.62 (q, *J* = 7.3 Hz, 2H), 1.37 – 1.24 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.10, 130.55, 129.80, 127.89, 125.28, 44.12, 30.64, 29.81, 29.53, 29.49, 29.38, 29.35, 27.27, 22.28, 18.11; HRMS (EI) m/z calcd for $C_{15}H_{26}O$ (M^+) 222.1984, found 222.1976.

(*Z*,*E*)-deca-5,8-dien-2-one (12d).



Following the procedure of **12a**, **12d** (15 mg, 49%) was obtained as a clear, colorless oil when 5-hexen-2-one (20 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 – 5.31 (m, 4H), 2.73 (tdd, *J* = 5.7, 3.2, 1.4 Hz, 2H), 2.48 (t, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.3 Hz, 2H), 2.14 (s, 3H), 1.68 – 1.62 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.6, 129.4, 129.2, 128.4, 125.6, 43.7, 30.6, 30.2, 21.8, 18.1; HRMS (EI) m/z calcd for $C_{10}H_{16}O$ (M^+) 152.1201, found 152.1164.

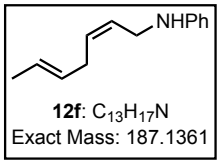
methyl (*Z*,*E*)-9,12-tetradecadienoate (12e)



Following the procedure for **12a**, **12e** (39 mg, 82%) was obtained as a clear, colorless oil when methyl 10-undecenoate (39 mg,

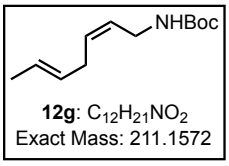
0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 – 5.32 (m, 4H), 3.67 (s, 3H), 2.71 (tt, *J* = 5.1, 1.1 Hz, 2H), 2.33 – 2.27 (m, 2H), 2.06 – 1.99 (m, 2H), 1.65 (dt, *J* = 4.5, 1.2 Hz, 3H), 1.64 – 1.57 (m, 2H), 1.38 – 1.24 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.49, 130.52, 129.79, 127.89, 125.28, 51.63, 34.30, 30.63, 29.77, 29.33, 29.32, 29.26, 27.25, 25.14, 18.10; HRMS (EI) m/z calcd for $C_{15}H_{26}O_2$ (M^+) 238.1933, found 238.1932.

phenyl (*Z*,*E*)-2,5-heptadien-1-ylamine (12f)



Following the procedure for **12a**, **12f** (25 mg, 68%) was obtained as a clear, colorless oil when *N*-allyl aniline (27 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.6, 7.4 Hz, 2H), 6.74 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.64 (dd, *J* = 8.6, 1.1 Hz, 2H), 5.66 – 5.57 (m, 2H), 5.57 – 5.42 (m, 2H), 3.81 – 3.77 (m, 2H), 3.65 (bs, 1H), 2.84 (tdd, *J* = 4.7, 2.6, 1.2 Hz, 2H), 1.70 (dd, *J* = 6.1, 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.20, 130.94, 129.21, 128.71, 127.24, 125.82, 117.49, 112.96, 41.03, 30.71, 17.93. HRMS (EI) m/z calcd for $C_{13}H_{17}N$ (M^+) 187.1361, found 187.1331.

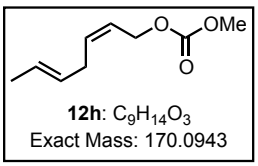
***tert*-butyl (*Z*,*E*)-hepta-2,5-dien-1-ylcarbamate (12g)**



Following the procedure for **12a**, **12g** (23 mg, 54%) was obtained as a clear, colorless oil when *tert*-butyl allylcarbamate (31 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52 (dddd, *J* = 12.7, 8.4, 7.1, 5.6 Hz, 1H), 5.48 – 5.35 (m, 3H), 4.49 (bs, 1H), 3.82 – 3.72 (m, 2H), 2.80 – 2.72 (m, 2H), 1.69 – 1.62 (m, 3H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.00, 131.21, 128.87, 126.51,

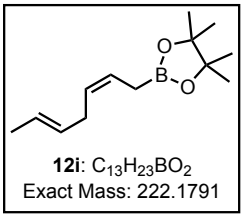
126.00, 79.49, 37.75, 30.65, 28.63, 18.09; HRMS (ESI) m/z calcd for $C_{12}H_{21}NO_2Na$ ($M + Na^+$) 234.1470, found 234.1451.

(*Z*,*E*)-hepta-2,5-dien-1-yl methyl carbonate (12h).



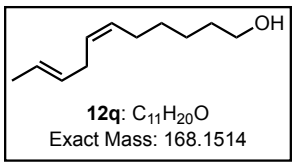
Following the procedure of **12a**, **12h** (27 mg, 79%) was obtained as a clear, colorless oil when allyl methyl carbonate (23 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68 (dtt, *J* = 10.9, 7.3, 1.2 Hz, 1H), 5.59 (dtt, *J* = 10.9, 6.8, 1.4 Hz, 1H), 5.52 – 5.35 (m, 2H), 4.69 (ddt, *J* = 6.7, 1.1, 0.6 Hz, 2H), 3.79 (s, 3H), 2.81 (appt, *J* = 7.6 Hz, 2H), 1.66 (dq, *J* = 6.2, 1.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 134.0, 128.4, 126.4, 123.3, 63.8, 54.9, 30.9, 18.1; HRMS (EI) m/z calcd for $C_9H_{14}O_3$ (M^+) 170.0943, found 170.0921.

2-((*Z*,*E*)-hepta-2,5-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12i)



Following the procedure for **12a**, **12i** (29 mg, 65%) was obtained as a clear, colorless oil when allyl pinacolboronate (34 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 (dtt, *J* = 11.0, 7.9, 1.6 Hz, 1H), 5.50 – 5.35 (m, 3H), 2.75 – 2.68 (m, 2H), 1.68 (d, *J* = 7.0 Hz, 2H), 1.64 (d, *J* = 4.7 Hz, 3H), 1.25 (s, 12H); ^{13}C NMR (126 MHz, $cdcl_3$) δ 129.71, 127.89, 125.17, 124.92, 83.42, 30.46, 24.96, 18.10; HRMS (EI) m/z calcd for $C_{13}H_{22}O_2B$ (M^+) 221.1713, found 221.1715.

(*Z*,*E*)-undeca-6,9-dien-1-ol (12q)

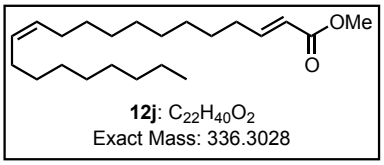


Following the procedure for **12a**, **12q** (22 mg, 65%) was obtained as a clear, colorless oil when *cis*-6-nonen-1-ol (28 mg, 0.20 mmol) was

reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 *trans*-1,4-hexadiene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52 – 5.29 (m, 4H), 3.65 (t, J = 6.7 Hz, 2H), 2.76 – 2.69 (m, 2H), 2.06 (q, J = 6.1 Hz, 2H), 1.66 (d, J = 5.5 Hz, 3H), 1.59 (p, J = 6.7 Hz, 3H), 1.38 (dd, J = 6.9, 3.6 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.08, 129.52, 127.88, 125.13, 63.01, 32.66, 30.43, 29.40, 27.02, 25.34, 17.91; HRMS (EI) m/z calcd for $C_{11}H_{20}O$ (M^+) 168.1514, found 168.1522.

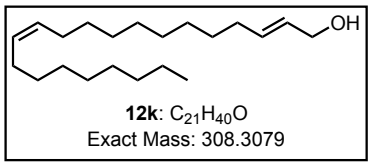
General procedure for the reaction with 1-decene.

methyl (*E*,*Z*)-2,12-henicosadienoate (12j)



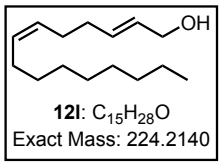
In a glovebox, diene methyl *E*-2,12-tridecadienoate (**13a**, 40 mg, 0.20 mmol) was dissolved in THF (0.16 mL) and 1-decene (0.2 mL). A solution of catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) was added and the reaction was maintained at room temperature in an open vial for 5 h. The solution was then removed from the glovebox and quenched with ethyl vinyl ether (~0.1 mL). The reaction mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2, 0% to 25% EtOAc in hexanes) to provide 54 mg (80%) of diene **12j** as a clear, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (dt, J = 15.6, 7.0 Hz, 1H), 5.82 (dt, J = 15.6, 1.6 Hz, 1H), 5.40 – 5.30 (m, 2H), 3.73 (s, 3H), 2.20 (qd, J = 7.1, 1.6 Hz, 2H), 2.02 (td, J = 6.9, 5.4 Hz, 5H), 1.49 – 1.40 (m, 2H), 1.38 – 1.21 (m, 21H), 0.88 (appt, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 150.3, 130.4, 130.3, 121.3, 51.8, 32.7, 32.4, 30.2, 30.2, 30.0, 29.9, 29.8, 29.80, 29.79, 29.7, 29.6, 28.5, 27.7, 27.7, 23.2, 14.6; HRMS (EI) m/z calcd for $C_{22}H_{40}O_2$ (M^+) 336.3028, found 336.3026.

(*E*,*Z*)-2,12-henicosadien-1-ol (12k)



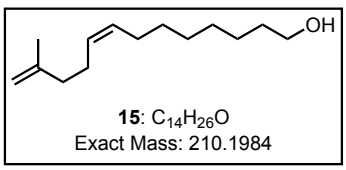
Following the general procedure for **12j**, **12k** (37 mg, 60%) was obtained as a clear, colorless oil when *E*-2,12-tridecadien-1-ol (34 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 1-decene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 – 5.60 (m, 2H), 5.40 – 5.32 (m, 2H), 4.09 (t, *J* = 4.5 Hz, 2H), 2.08 – 1.99 (m, 6H), 1.43 – 1.22 (m, 25H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $cdcl_3$) δ 133.8, 130.1, 130.1, 129.0, 64.1, 32.4, 32.1, 30.0, 30.0, 29.7, 29.7, 29.7, 29.5, 29.5, 29.5, 29.4, 29.4, 27.4, 27.4, 22.9, 14.3; HRMS (EI) m/z calcd for $C_{21}H_{40}O$ (M^+) 308.3079, found 308.3066.

(*E*,*Z*)-2,6-pentadecadien-1-ol (12l)



Following the general procedure for **12j**, **12l** (23 mg, 51%) was obtained as a clear, colorless oil when *E*-2,6-heptadiene-1-ol (22 mg, 0.20 mmol) was reacted with catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in 1:1 1-decene:THF (0.4 mL); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 – 5.63 (m, 2H), 5.43 – 5.31 (m, 2H), 4.09 (d, *J* = 5.1 Hz, 2H), 2.17 – 2.07 (m, 4H), 2.02 (q, *J* = 7.0 Hz, 2H), 1.37 – 1.22 (m, 13H), 0.89 (appt, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.01, 130.83, 129.43, 128.84, 63.98, 32.52, 32.11, 29.90, 29.73, 29.54, 29.52, 27.49, 27.03, 22.89, 14.32; HRMS (EI) m/z calcd for $C_{15}H_{28}O$ (M^+) 224.2140, found 224.2144.

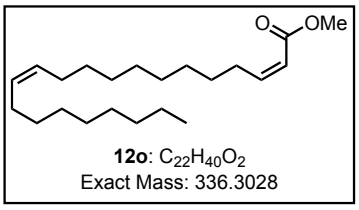
(*Z*)-12-methyltrideca-8,12-dien-1-ol (15)



In a glovebox, 2-methyl-1,5-hexadiene (**14**, 19 mg, 0.20 mmol) and 8-nonen-1-ol (**9a**, 142 mg, 1.0 mmol) was dissolved in THF (0.16 mL). A solution of catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) was added and the reaction was maintained at room temperature in an open vial for 5 h. The solution was then removed from the glovebox and quenched with ethyl

vinyl ether (~0.1 mL). The reaction mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2, 0% to 25% EtOAc in hexanes) to provide 19 mg (45%) of diene **15** as a clear, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 – 5.32 (m, 2H), 4.75 – 4.68 (m, 2H), 3.65 (td, *J* = 6.6, 4.0 Hz, 2H), 2.22 – 2.15 (m, 2H), 2.10 – 2.01 (m, 4H), 1.76 – 1.72 (m, 3H), 1.57 (appp, *J* = 6.7 Hz, 2H), 1.41 – 1.29 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 130.4, 129.4, 110.1, 63.3, 38.0, 33.0, 29.9, 29.5, 29.5, 27.4, 25.9, 25.7, 22.7; HRMS (EI) m/z calcd for $C_{14}H_{26}O$ (M^+) 210.1984, found 210.1994.

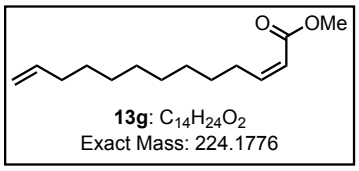
methyl (*Z*,*Z*)-henicosa-2,12-dienoate (12p)



In a glovebox, methyl (*Z*)-2,12-tridecadienoate (**13g**, 40 mg, 0.20 mmol) was dissolved in THF (0.16 mL) and 1-decene (0.2 mL). A solution of catalyst **6** (40 μL of a 0.05M THF stock solution, 0.002 mmol) in THF (40 μL) was added and the reaction was maintained at room temperature in an open vial for 5 h. The solution was then removed from the glovebox and quenched with ethyl vinyl ether (~0.1 mL). The reaction mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2, 0% to 10% EtOAc in hexanes) to provide 53 mg (79%) of diene **12p** as a clear, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (dt, *J* = 11.5, 7.5 Hz, 1H), 5.77 (dt, *J* = 11.5, 1.7 Hz, 1H), 5.40 – 5.30 (m, 2H), 3.71 (s, 3H), 2.65 (qd, *J* = 7.5, 1.7 Hz, 2H), 2.02 (td, *J* = 6.7, 4.8 Hz, 4H), 1.48 – 1.40 (m, 2H), 1.38 – 1.21 (m, 22H), 0.88 (appt, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 151.3, 130.13, 130.05, 119.3, 51.2, 32.1, 30.00, 29.98, 29.8, 29.7, 29.63, 29.55, 29.54, 29.52, 29.49, 29.25, 29.24, 27.43, 27.42, 22.9, 14.3; HRMS (EI) m/z calcd for $C_{22}H_{40}O_2$ (M^+) 336.3028, found 336.3025.

Synthesis of new diene substrates.

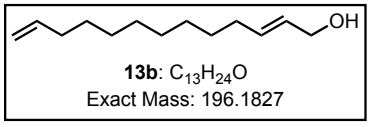
methyl (*Z*)-2,12-tridecadienoate (13g)



13g: $C_{14}H_{24}O_2$
Exact Mass: 224.1776

Methyl *P*,*P*-bis(2,2,2-trifluoroethyl)phosphonoacetate (2.3 mL, 10.7 mmol) and 18-crown-6 (11.3 g, 42.8 mmol) were dissolved in THF (90 mL) and cooled to 0 °C. Potassium bis(trimethylsilyl)amide (2.1 g, 10.7 mmol) was added and the mixture was stirred at 0 °C for 30 minutes before addition of 10-undecenal. The solution was allowed to warm to room temperature for 2 h. The solution was then poured into saturated aqueous ammonium chloride (50 mL) and extracted with diethyl ether (3×50 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, concentrated and purified by column chromatography (SiO_2, 2% ether in pentane) to provide 1.3 g (66%) of diene **13g** as a clear, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (dt, *J* = 11.5, 7.5 Hz, 1H), 5.86 – 5.74 (m, 2H), 4.99 (ddt, *J* = 17.1, 2.2, 1.6 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 3.71 (s, 3H), 2.65 (qd, *J* = 7.5, 1.7 Hz, 2H), 2.04 (dtt, *J* = 8.1, 6.7, 1.4 Hz, 2H), 1.48 – 1.24 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 151.3, 139.4, 119.3, 114.3, 51.2, 34.0, 29.60, 29.57, 29.49, 29.30, 29.22, 29.21, 29.13; HRMS (EI) m/z calcd for $C_{14}H_{24}O_2$ (M^+) 224.1776, found 224.1783.

(*E*,*Z*)-2,12-tridecadien-1-ol (13b).

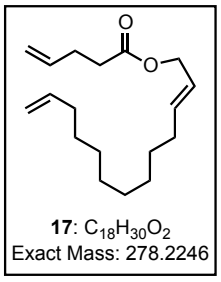


13b: $C_{13}H_{24}O$
Exact Mass: 196.1827

Methyl (*E*)-2,12-tridecadienoate (**13a**, 1.0 g, 4.46 mmol) was dissolved in THF (23 mL) and cooled to 0 °C. Diisobutylaluminum hydride (2.0 mL, 11.1 mmol) was added dropwise. The solution was allowed to warm to ambient temperature. After 1.5 h, methanol (5 mL) was slowly added. The solution was then poured into saturated aqueous ammonium chloride (25 mL) and extracted with diethyl ether (3×30 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, concentrated and purified by column chromatography (SiO_2, 25% EtOAc in hexanes) to provide 0.84 g (96%) of **13b** as a clear, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ

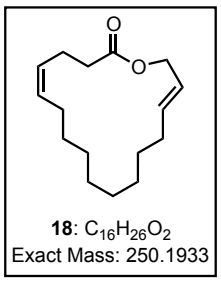
5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.74 – 5.60 (m, 2H), 5.00 (dq, *J* = 17.1, 1.8 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.3 Hz, 1H), 4.09 (dd, *J* = 5.4, 1.2 Hz, 2H), 2.04 (tdd, *J* = 7.9, 5.9, 1.4 Hz, 4H), 1.42 – 1.33 (m, 6H), 1.28 (d, *J* = 3.0 Hz, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 133.8, 129.0, 114.3, 64.1, 34.0, 32.4, 29.6, 29.4, 29.3, 29.1; HRMS (EI) m/z calcd for $C_{13}H_{24}O$ (M^+) 196.1827, found 196.1825.

(*E*)-trideca-2,12-dien-1-yl pent-4-enoate (17)



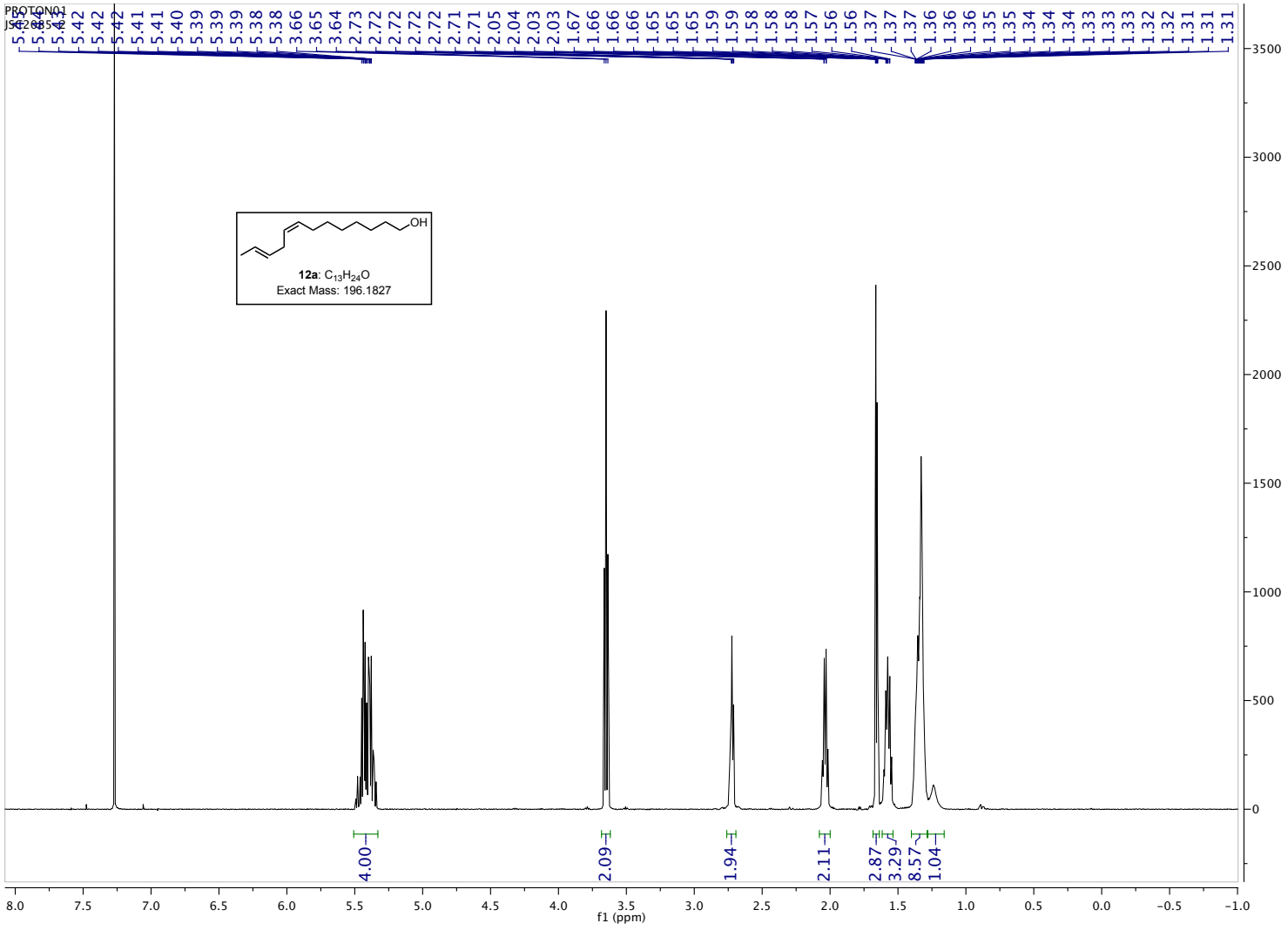
Alcohol **13b** (74 mg, 0.38 mmol) was dissolved in dichloromethane (3.8 mL) with 4-pentenoic acid (58 μL, 0.57 mmol), triethylamine (0.2 mL, 1.5 mmol), and 4-(dimethylamino)pyridine (2 mg, 0.019 mmol). *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (108 mg, 0.57 mmol) was added and the solution was maintained at room temperature for 5 h. The solution was then poured into saturated aqueous ammonium chloride (5 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, concentrated and chromatographed (SiO_2, 10% EtOAc in hexanes) to provide 60 mg (57%) of triene **17** as a clear, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 – 5.73 (m, 3H), 5.60 – 5.52 (m, 1H), 5.07 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.03 – 5.01 (m, 1H), 5.01 – 4.97 (m, 1H), 4.94 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.53 (dq, *J* = 6.5, 1.0 Hz, 2H), 2.46 – 2.35 (m, 4H), 2.04 (dddt, *J* = 10.5, 6.7, 2.9, 1.6 Hz, 4H), 1.38 (p, *J* = 6.8 Hz, 4H), 1.33 – 1.24 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 139.4, 136.9, 136.9, 123.9, 115.7, 114.3, 65.5, 34.0, 33.8, 32.5, 29.6, 29.6, 29.4, 29.3, 29.1, 29.1, 29.1; HRMS m/z calcd for $C_{18}H_{30}O_2$ (M^+) 278.2246, found 278.2233.

(*Z*,*E*)-oxacycloheptadeca-5,15-dien-2-one (18)

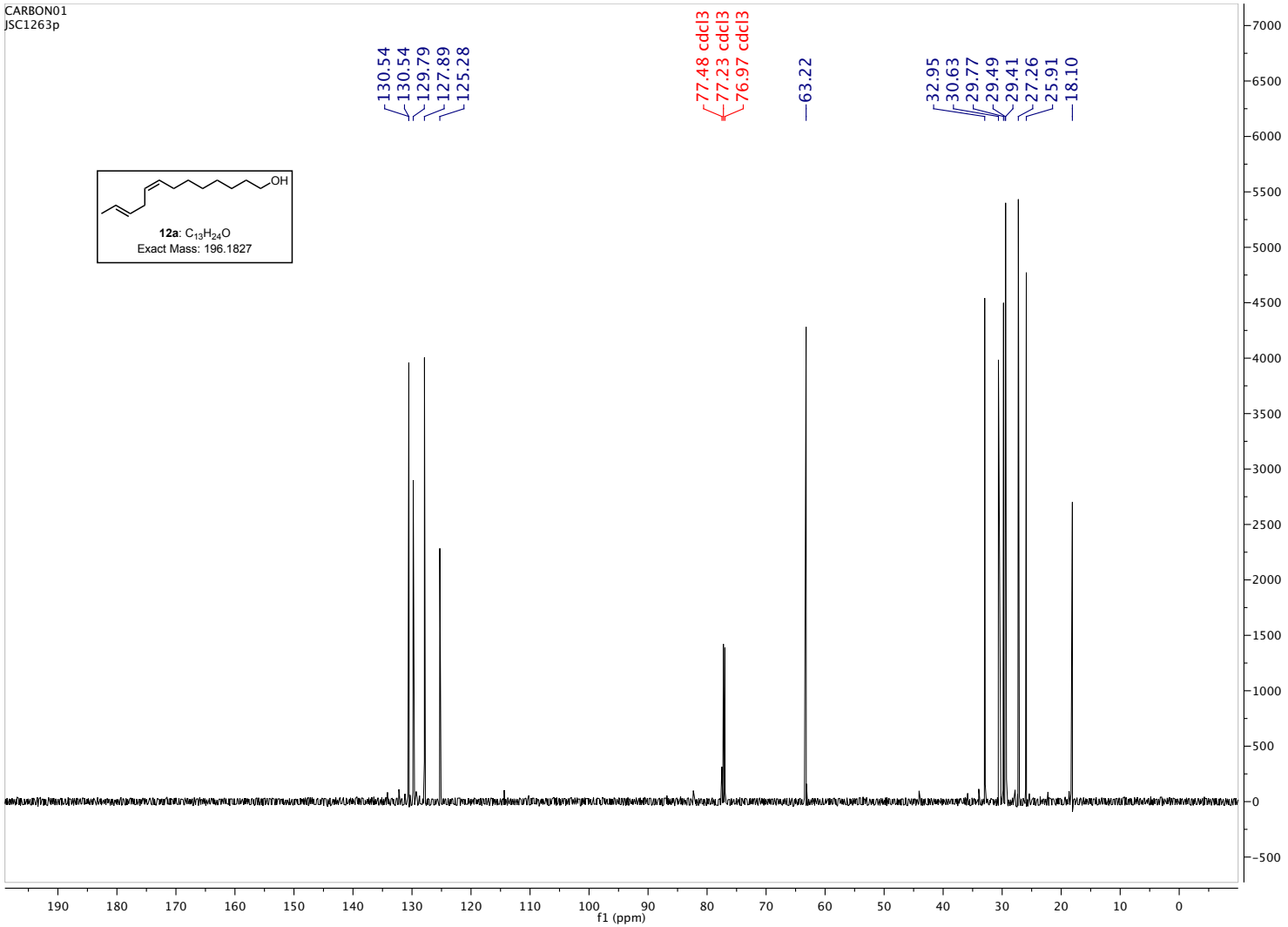


In a glovebox, triene **17** (15 mg, 0.054 mmol) was dissolved in 1,2-dichloroethane (17 mL) in a Schlenk tube. A solution of ruthenium catalyst **2** (2.6 mg, 0.040 mmol) in 1,2-dichloroethane (1 mL) was added, the reaction vessel was sealed, removed from the glovebox, and subjected to a single freeze/pump/thaw cycle. The flask was kept under a static vacuum of *ca* 100 mTorr and heated to 60 °C. After 24 hours, the mixture was cooled, quenched with excess ethyl vinyl ether, concentrated. The crude oil was chromatographed (SiO_2, 2% Et_2O in pentane) to provide 3 mg (22%) of macrolactone **18** as a clear, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (dtt, J = 15.2, 7.0, 1.1 Hz, 1H), 5.57 (dtt, J = 15.4, 6.5, 1.3 Hz, 1H), 5.47 – 5.33 (m, 2H), 4.53 (dq, J = 6.4, 0.9 Hz, 2H), 2.44 – 2.36 (m, 4H), 2.12 – 2.01 (m, 4H), 1.47 – 1.38 (m, 2H), 1.37 – 1.18 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 136.9, 131.6, 128.2, 125.1, 65.0, 35.1, 31.1, 28.8, 28.7, 28.1, 27.8, 27.6, 27.2, 26.5, 23.2; HRMS m/z calcd for $C_{16}H_{26}O_2$ (M^+) 250.1933, found 250.1929.

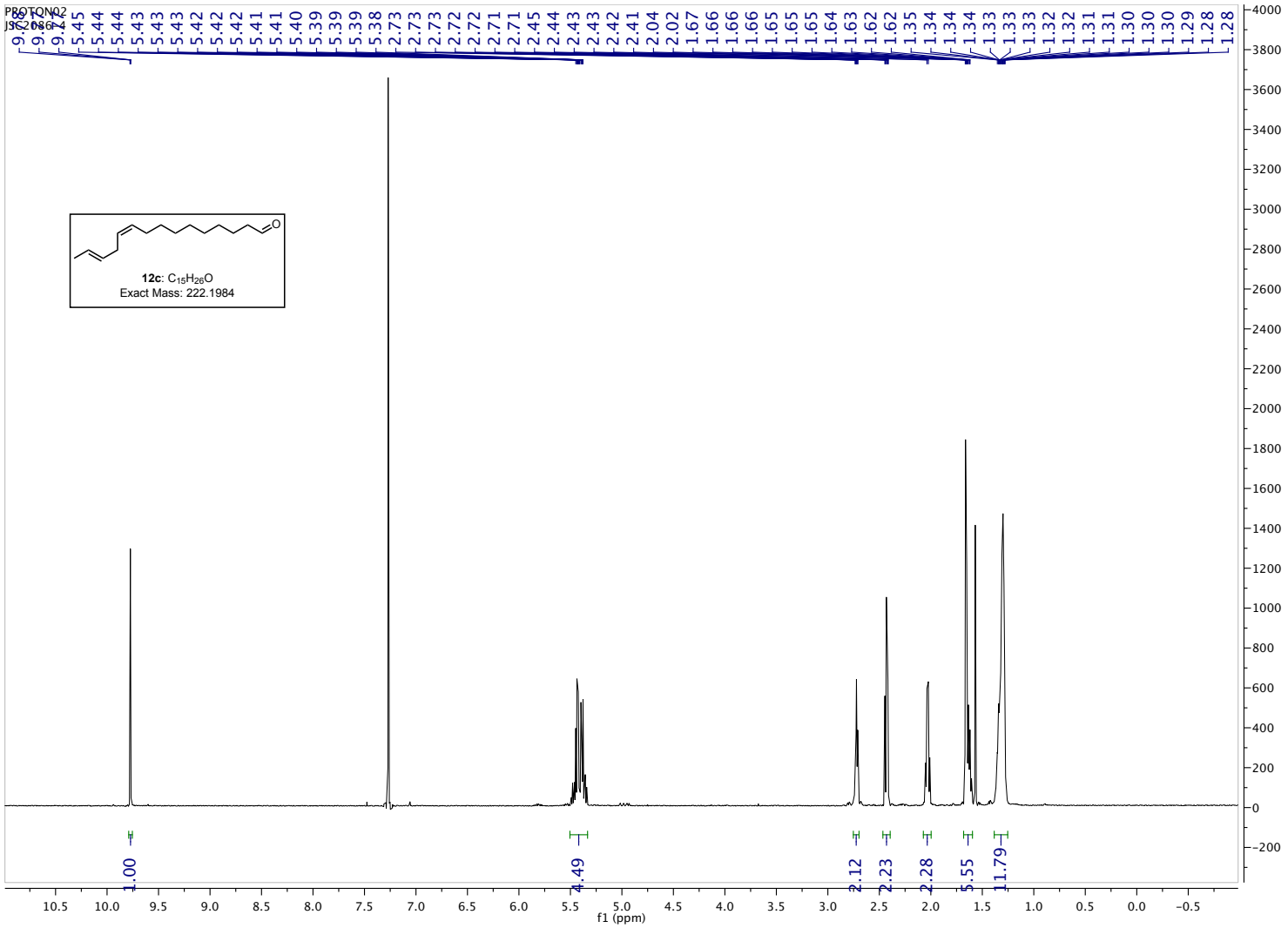
Part 2. Spectral data of new compounds: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12a**.



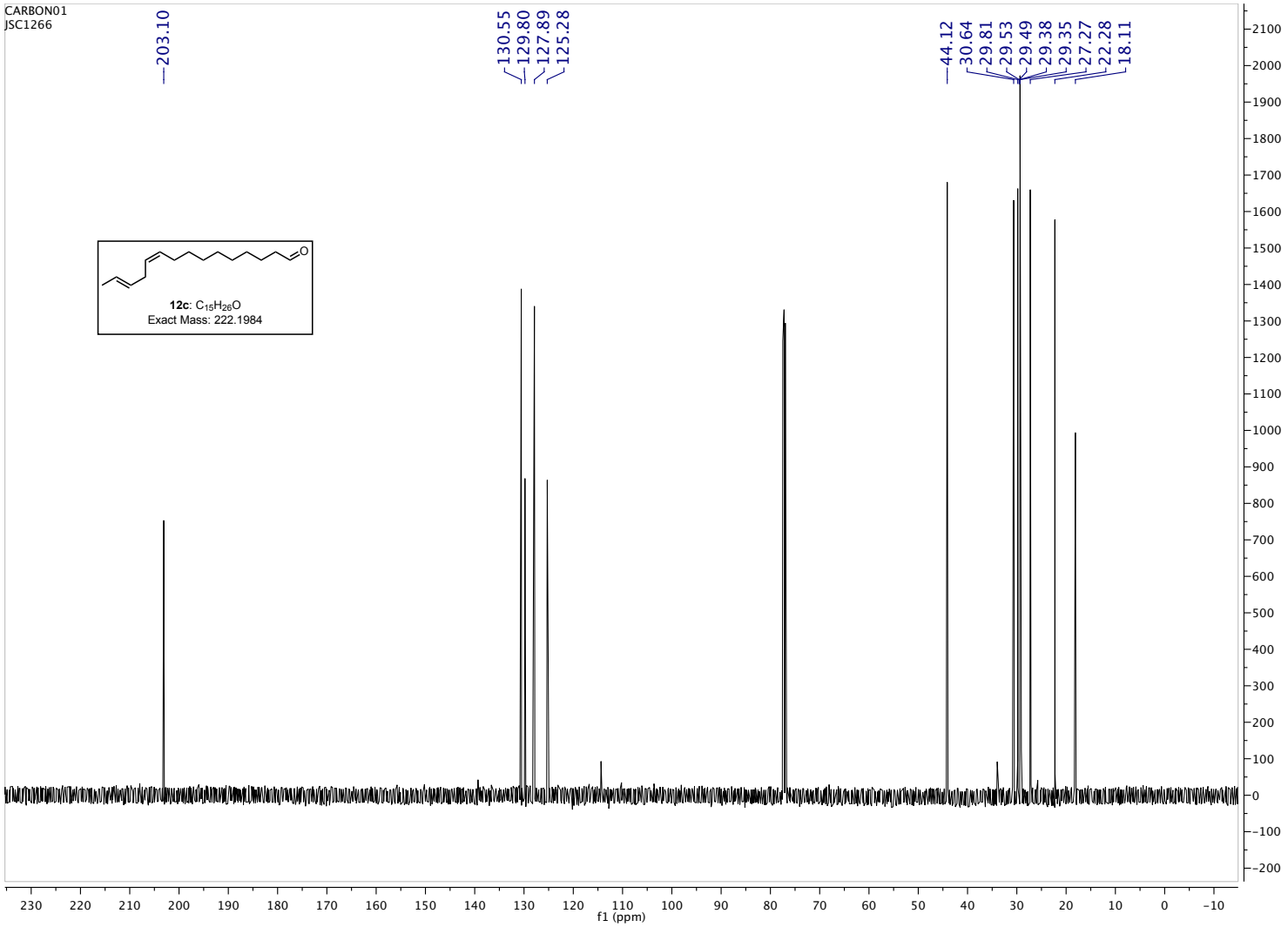
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12a**.



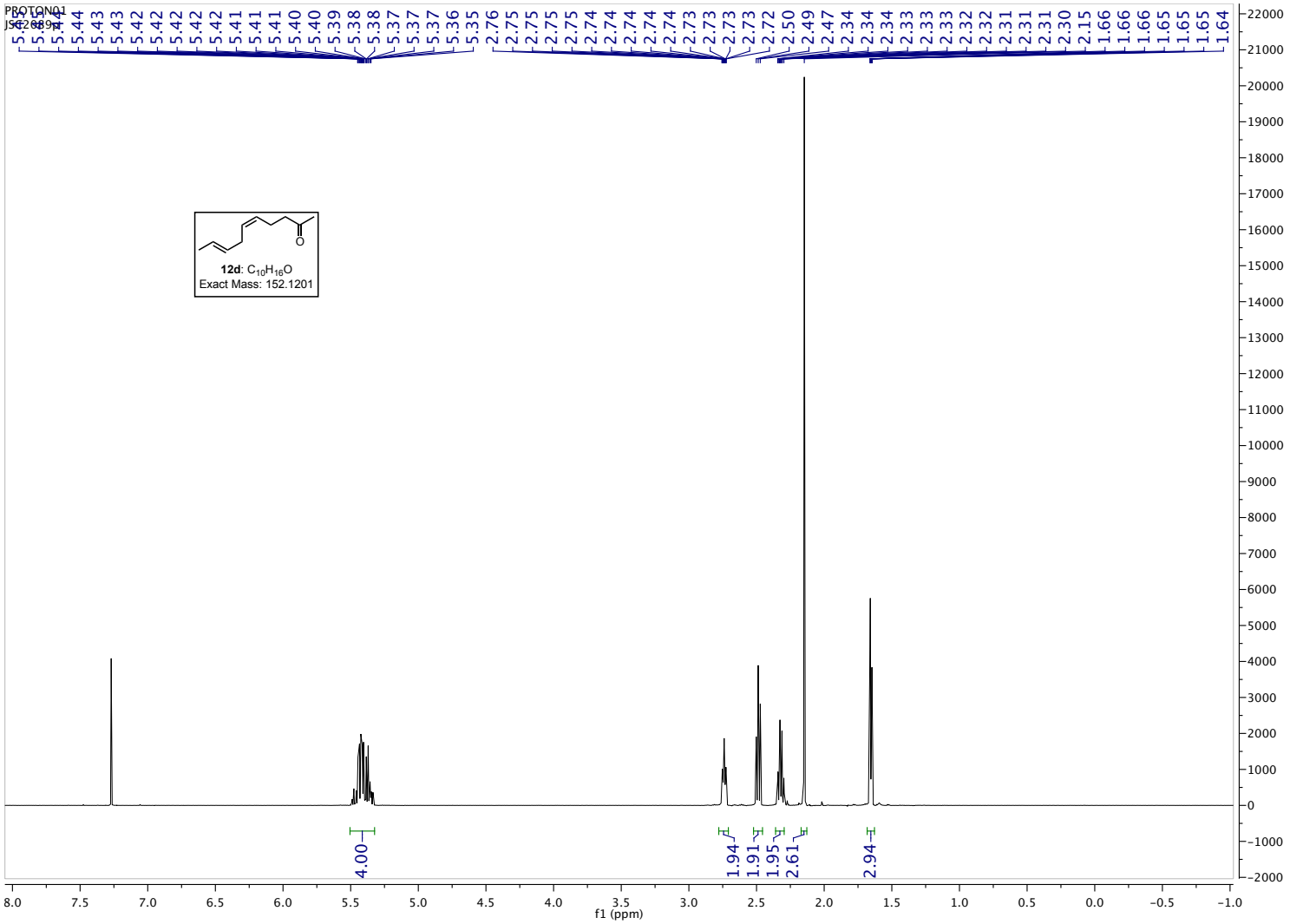
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12c**.



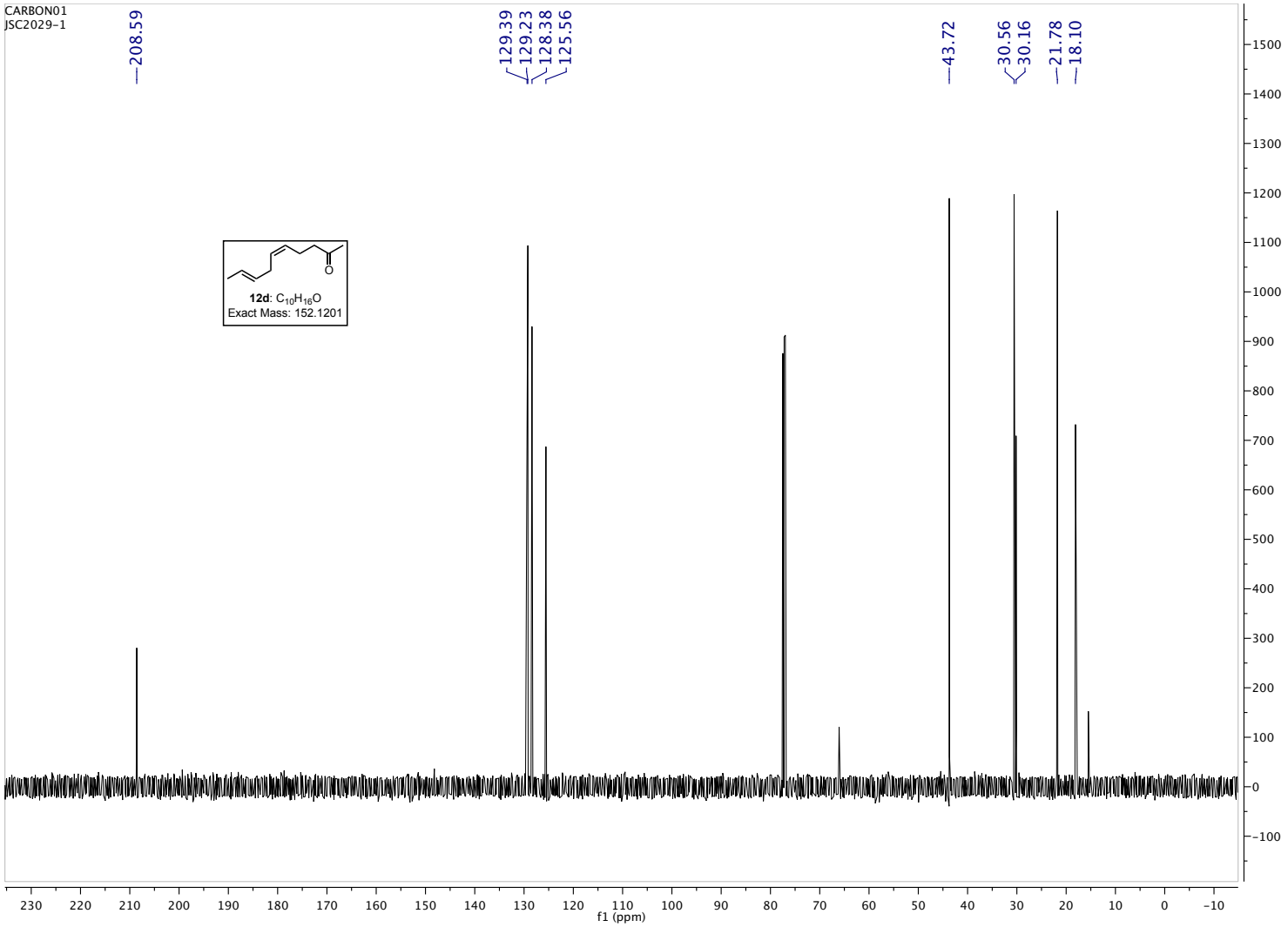
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12c**.



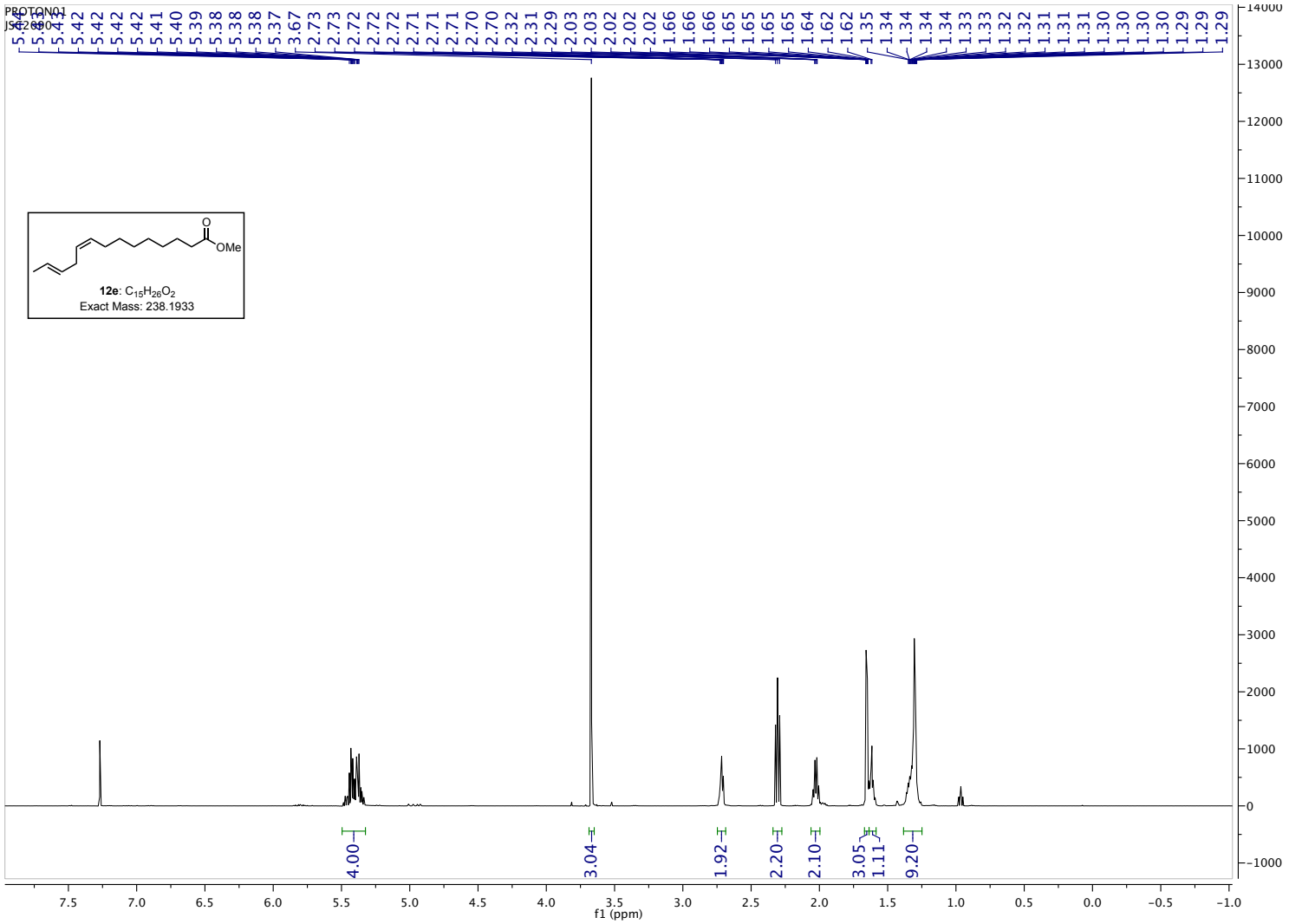
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12d**.



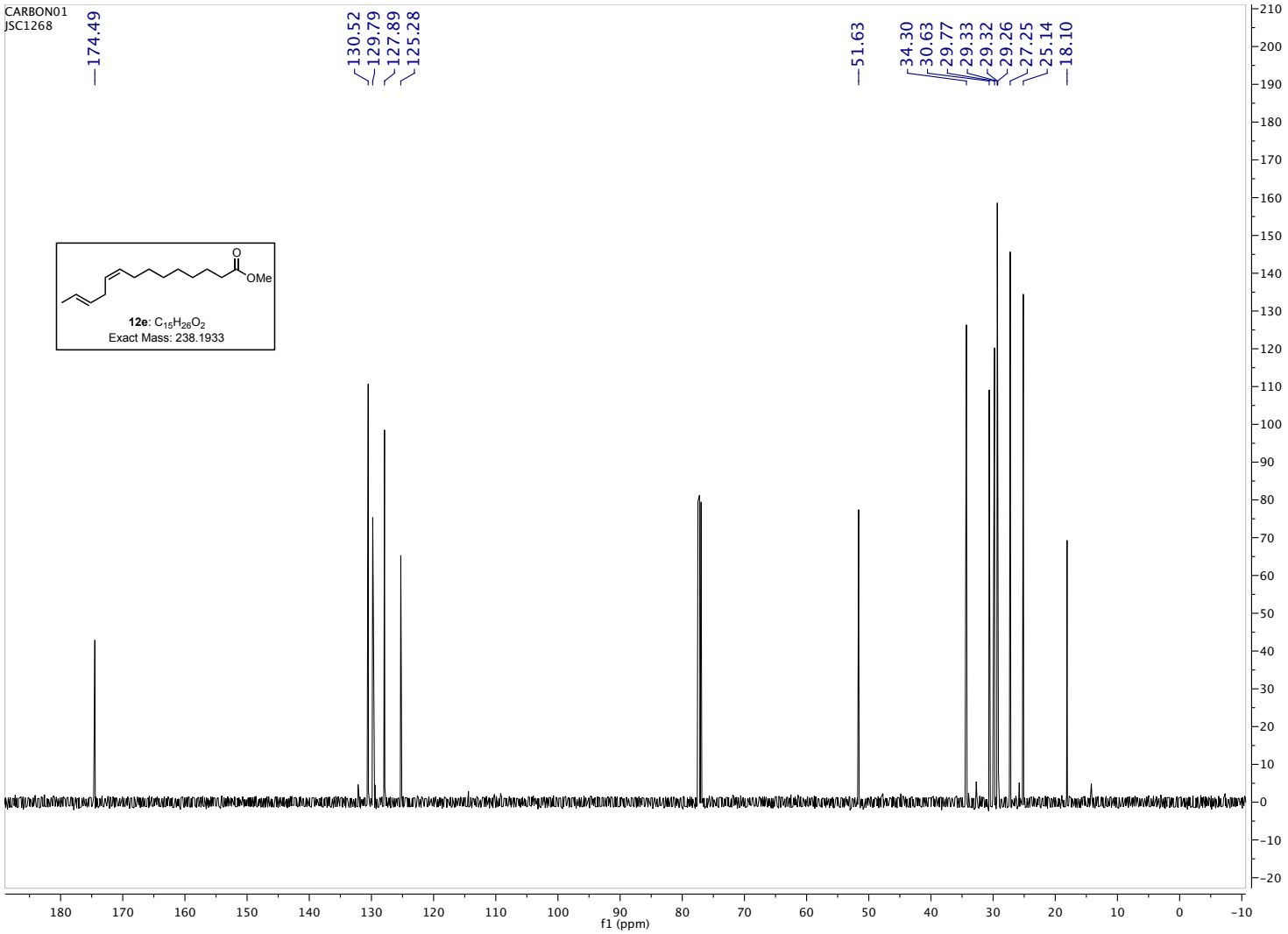
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12d**.



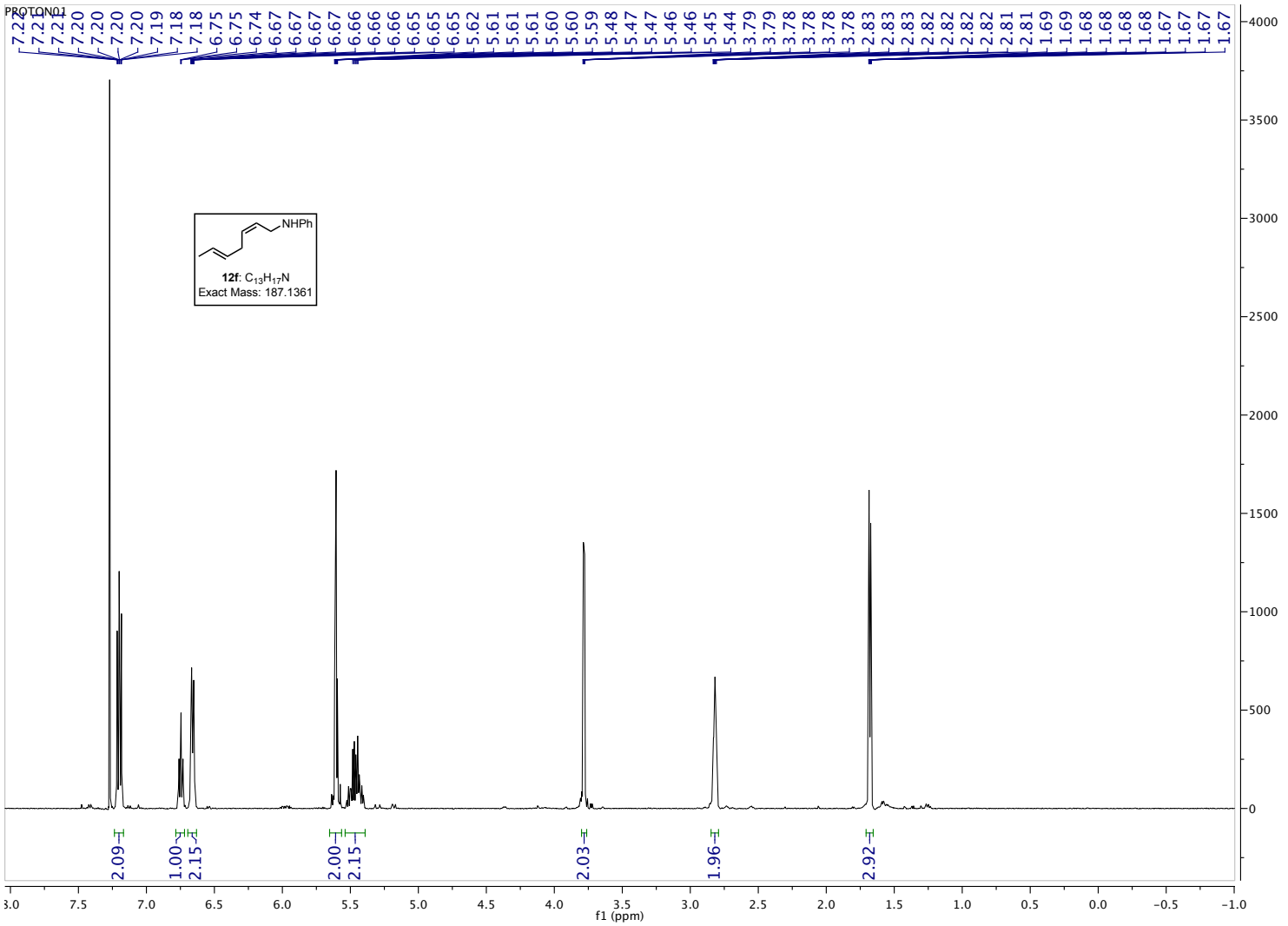
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12e**.



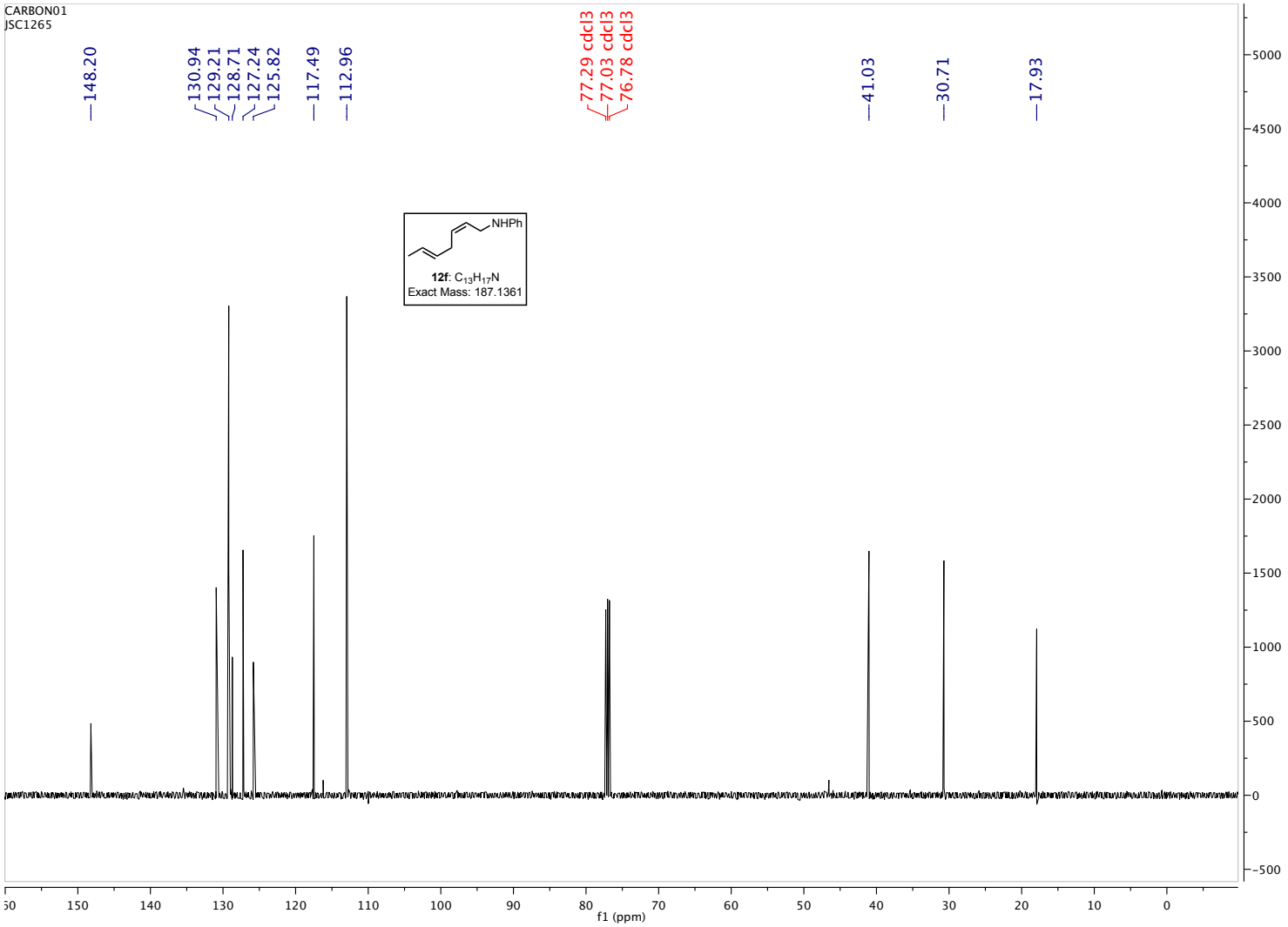
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12e**.



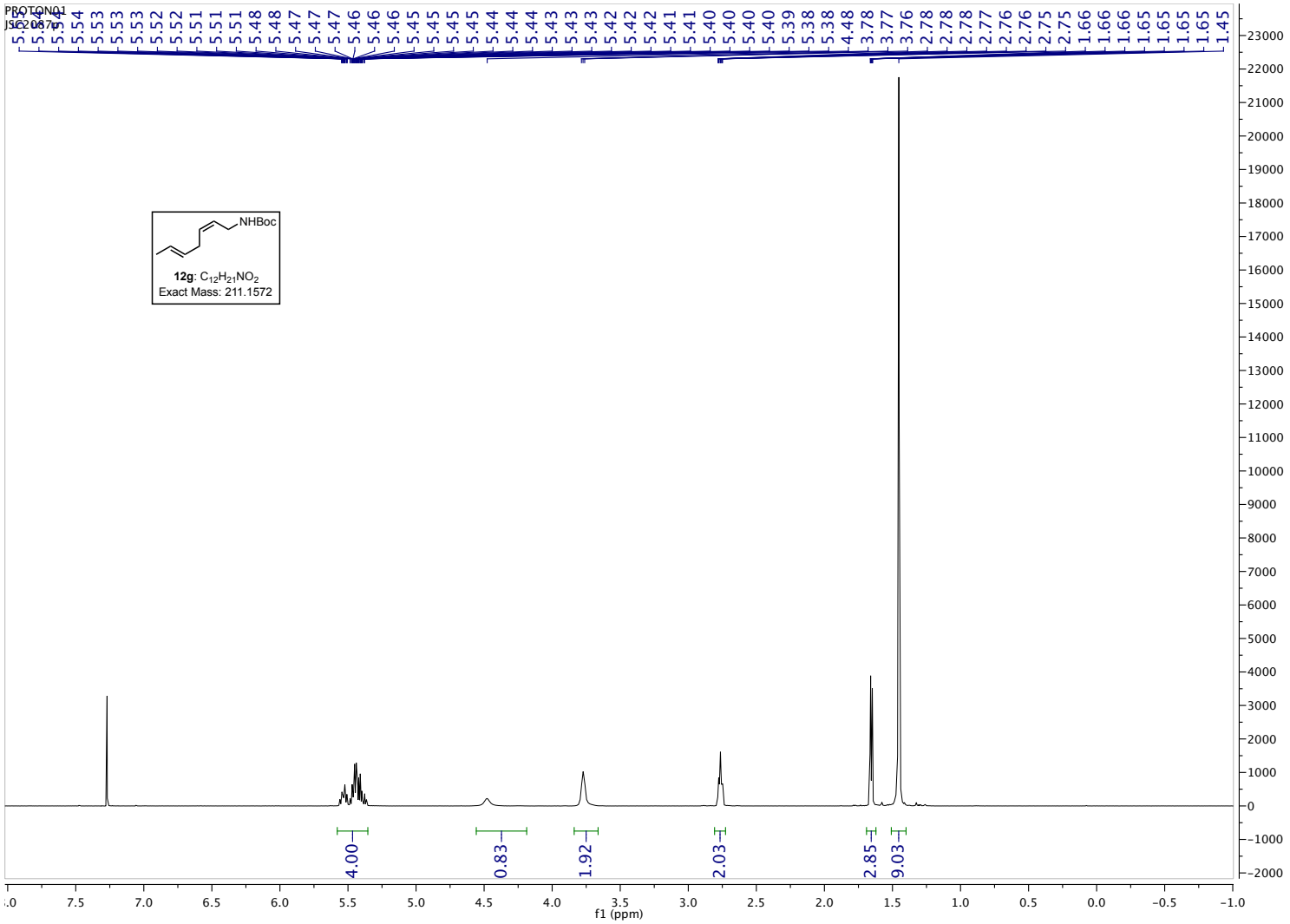
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12f**.



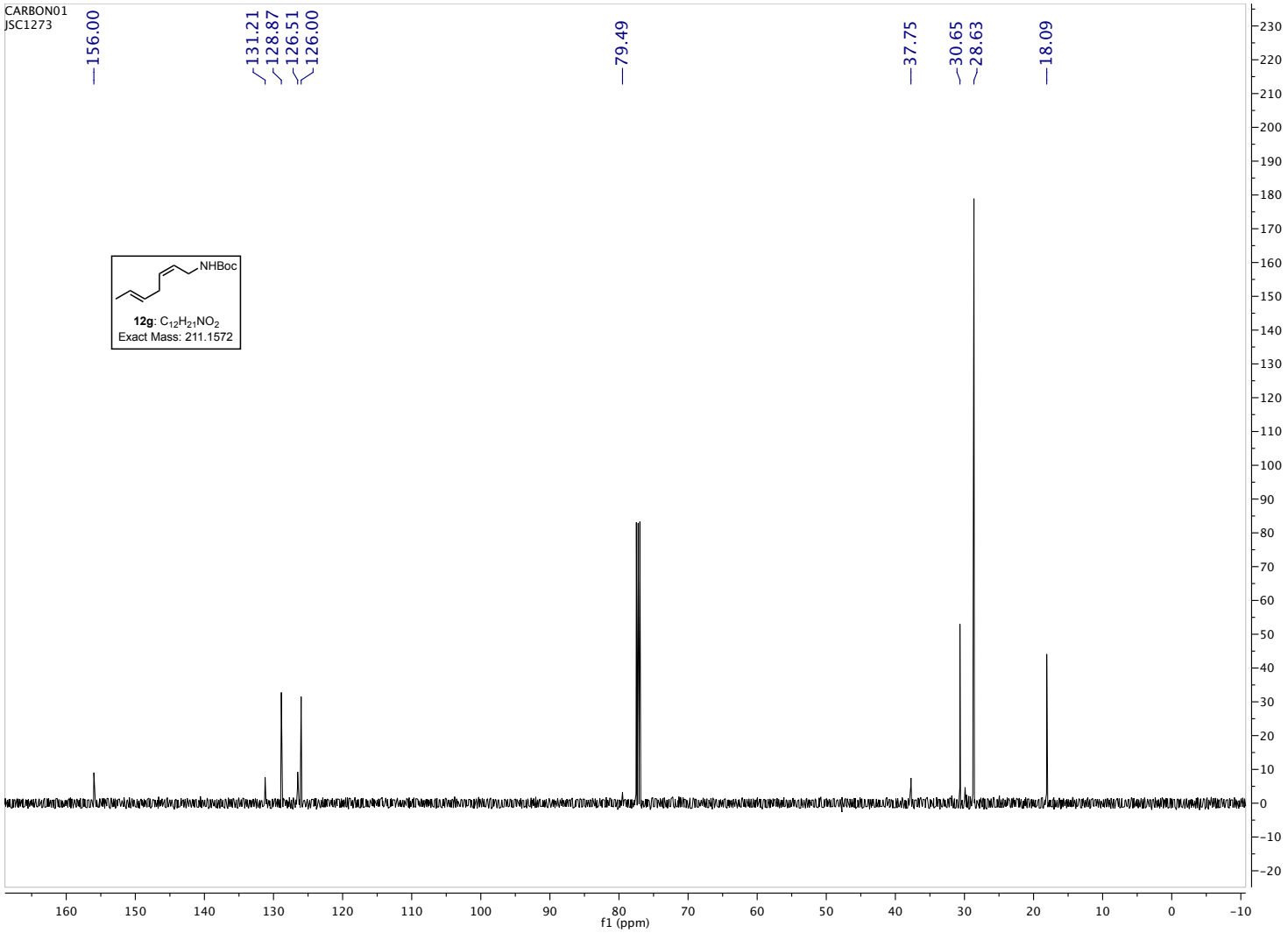
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12f**.



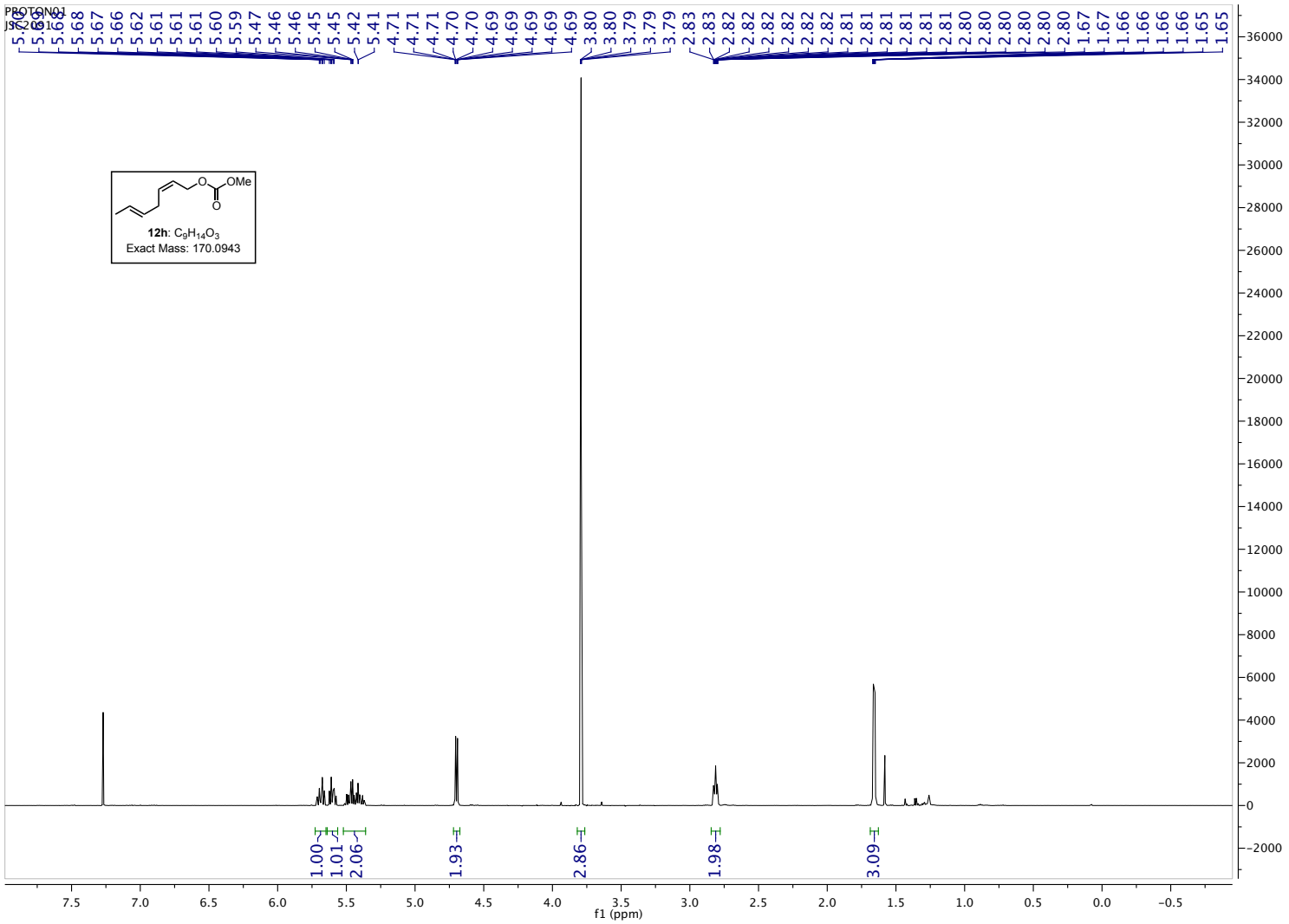
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12g**.



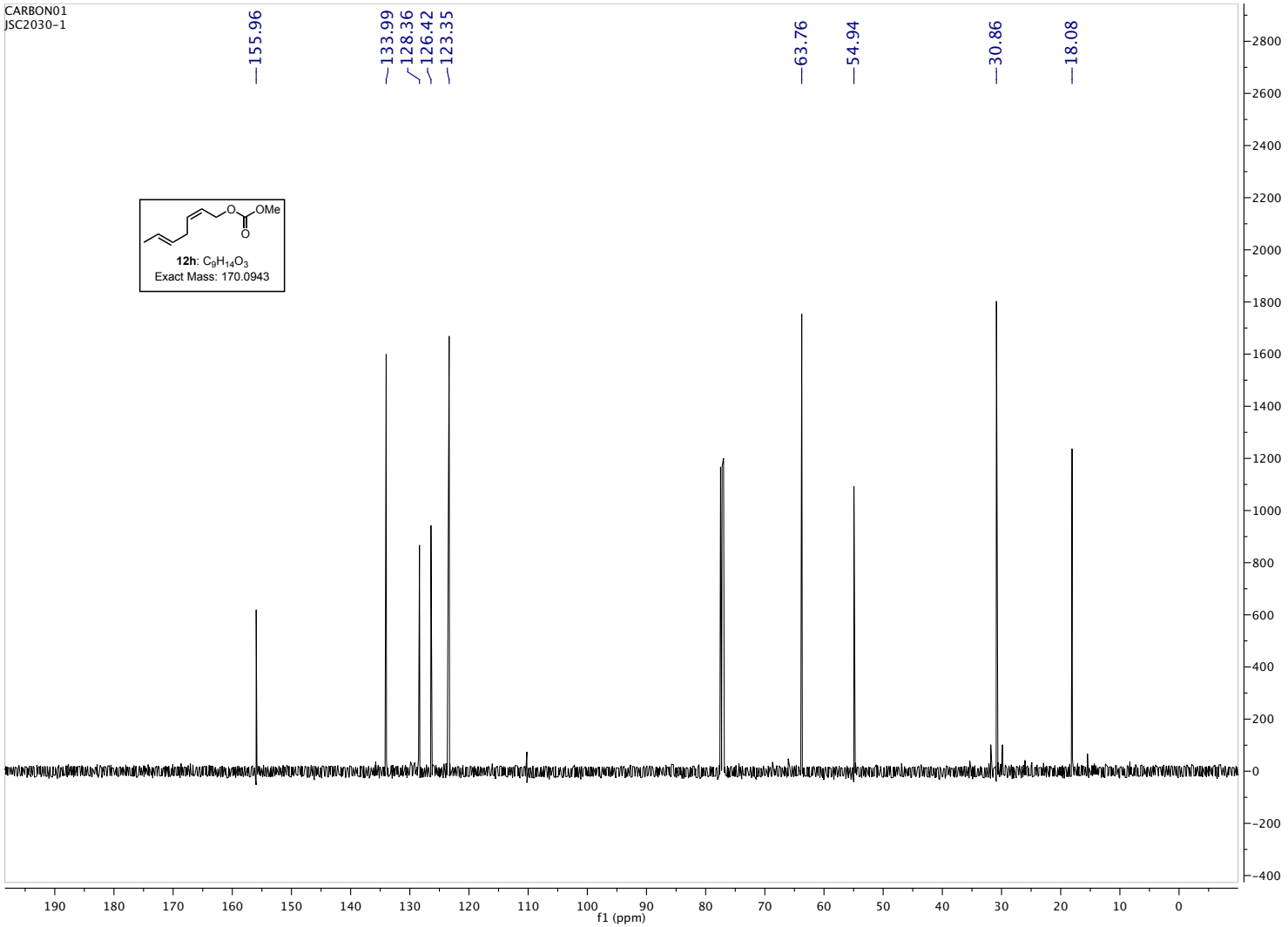
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12g**.



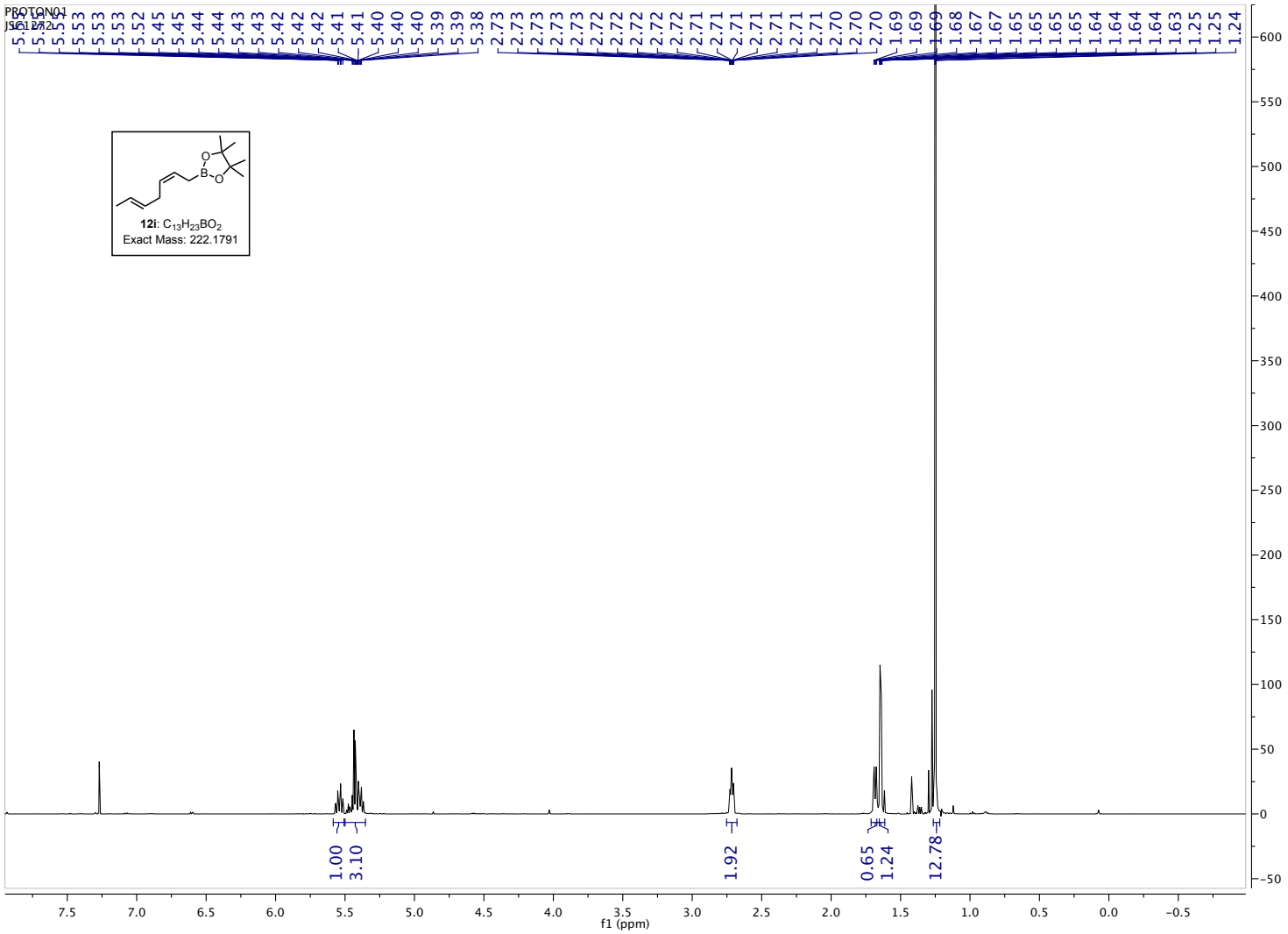
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12h**.



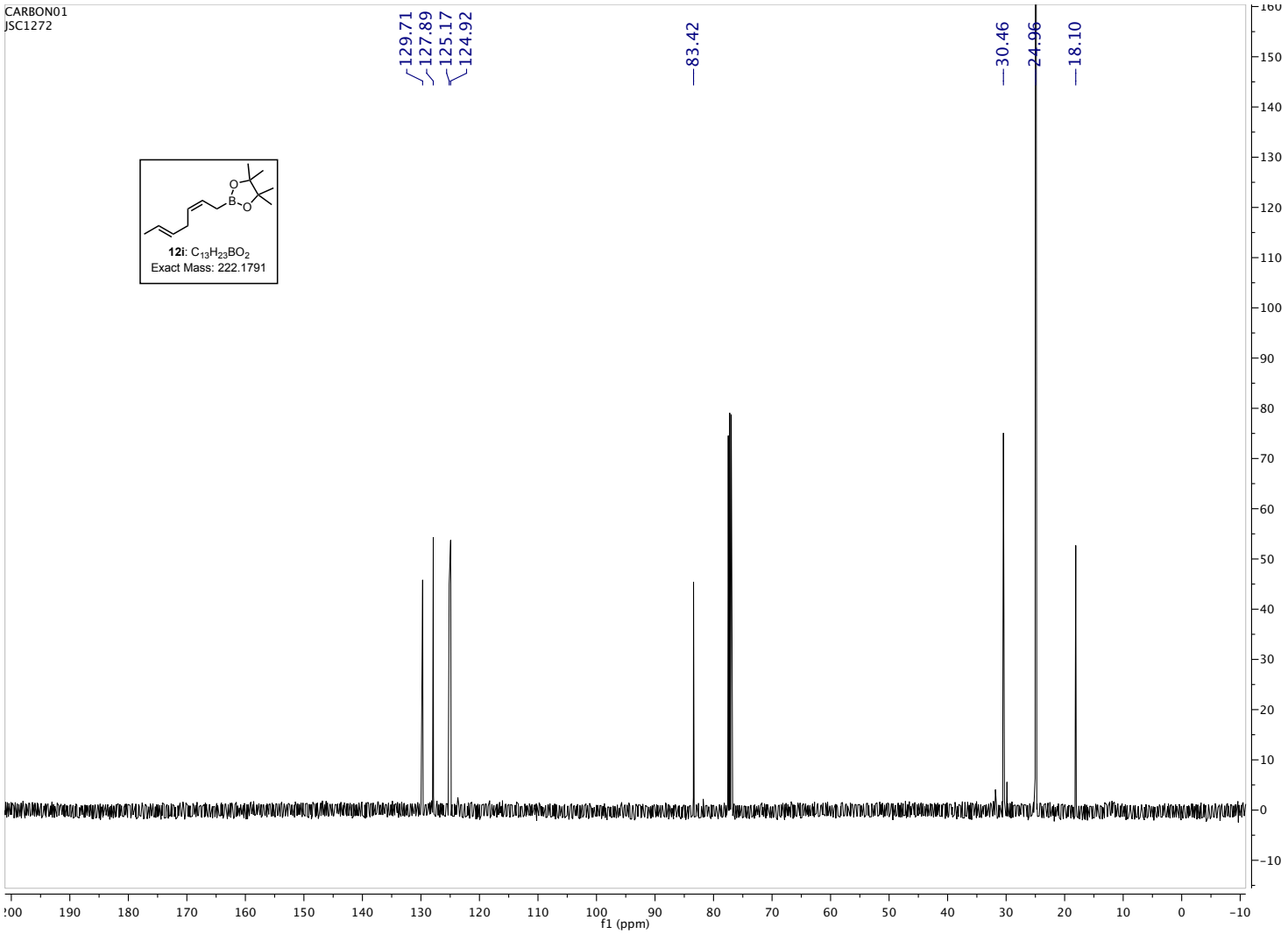
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12h**.



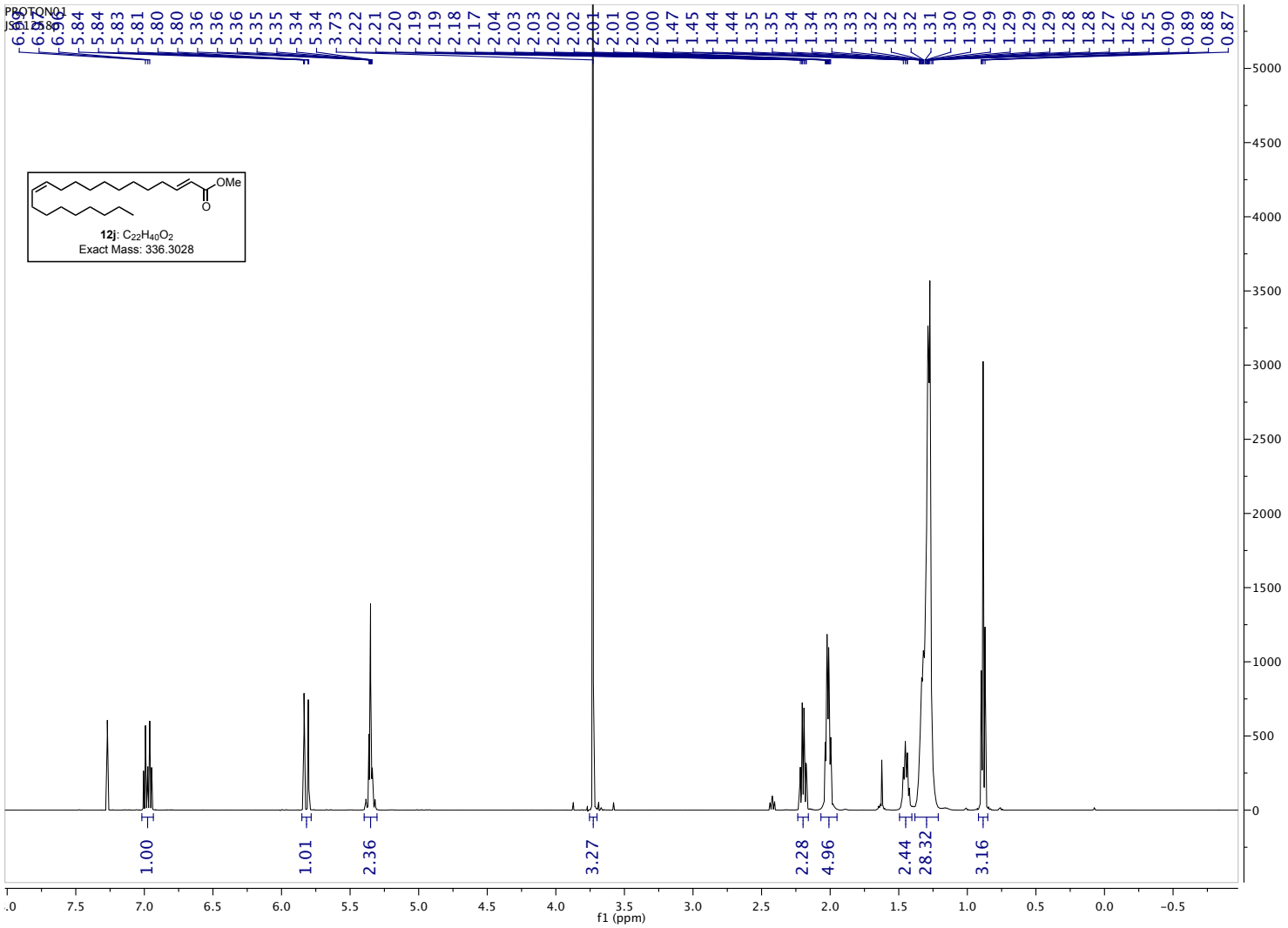
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12i**.



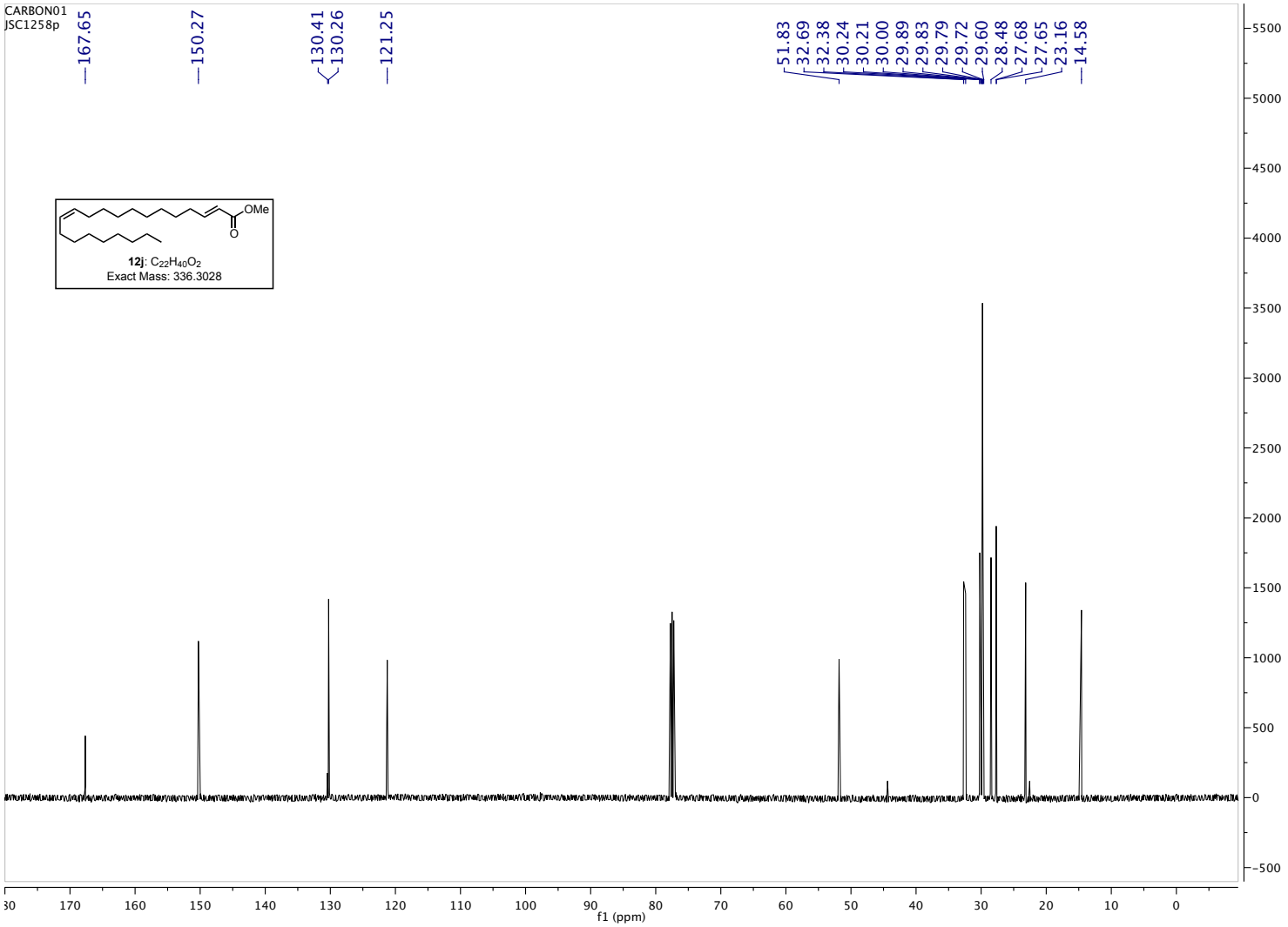
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12i**.



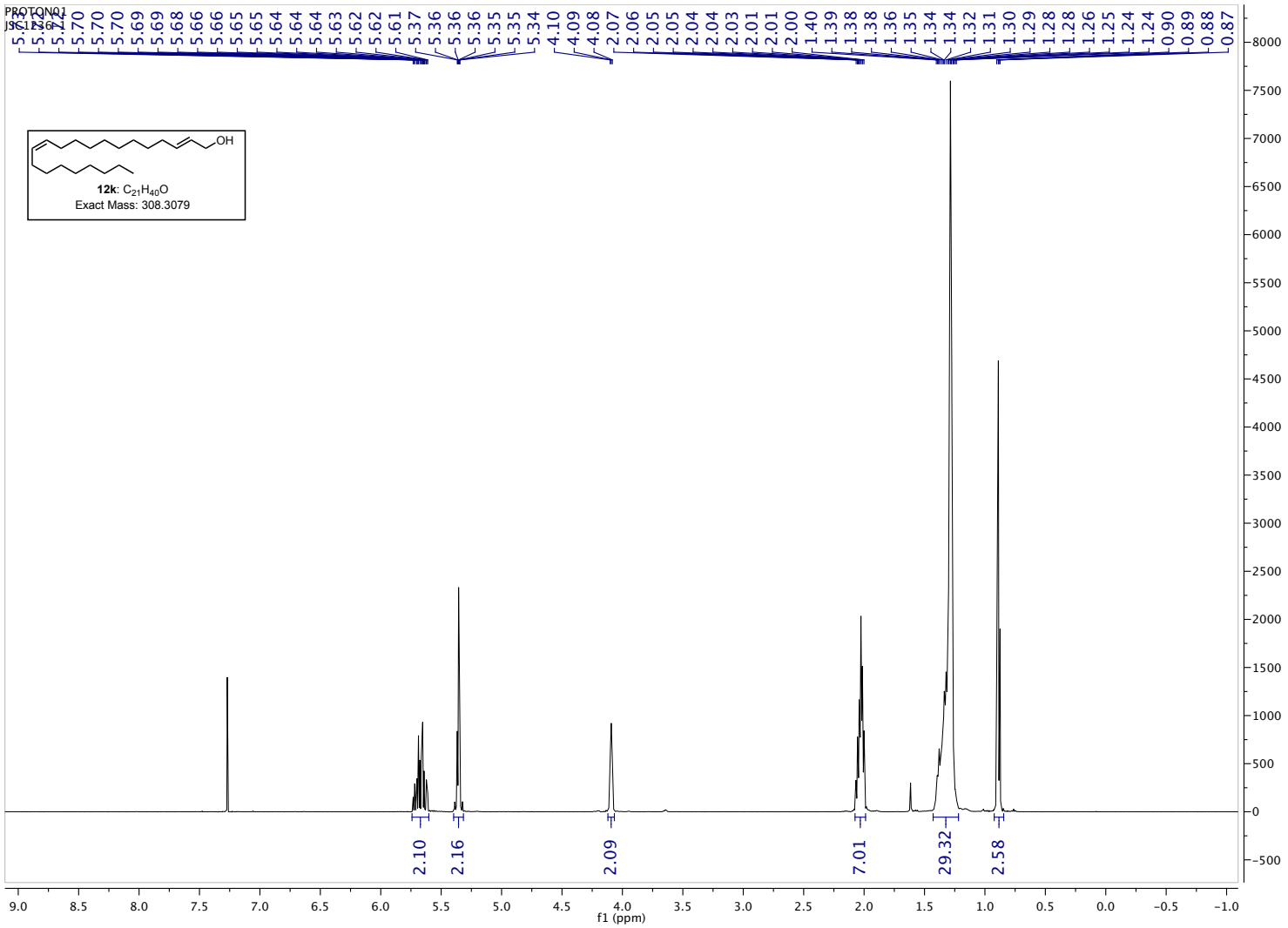
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12j**.



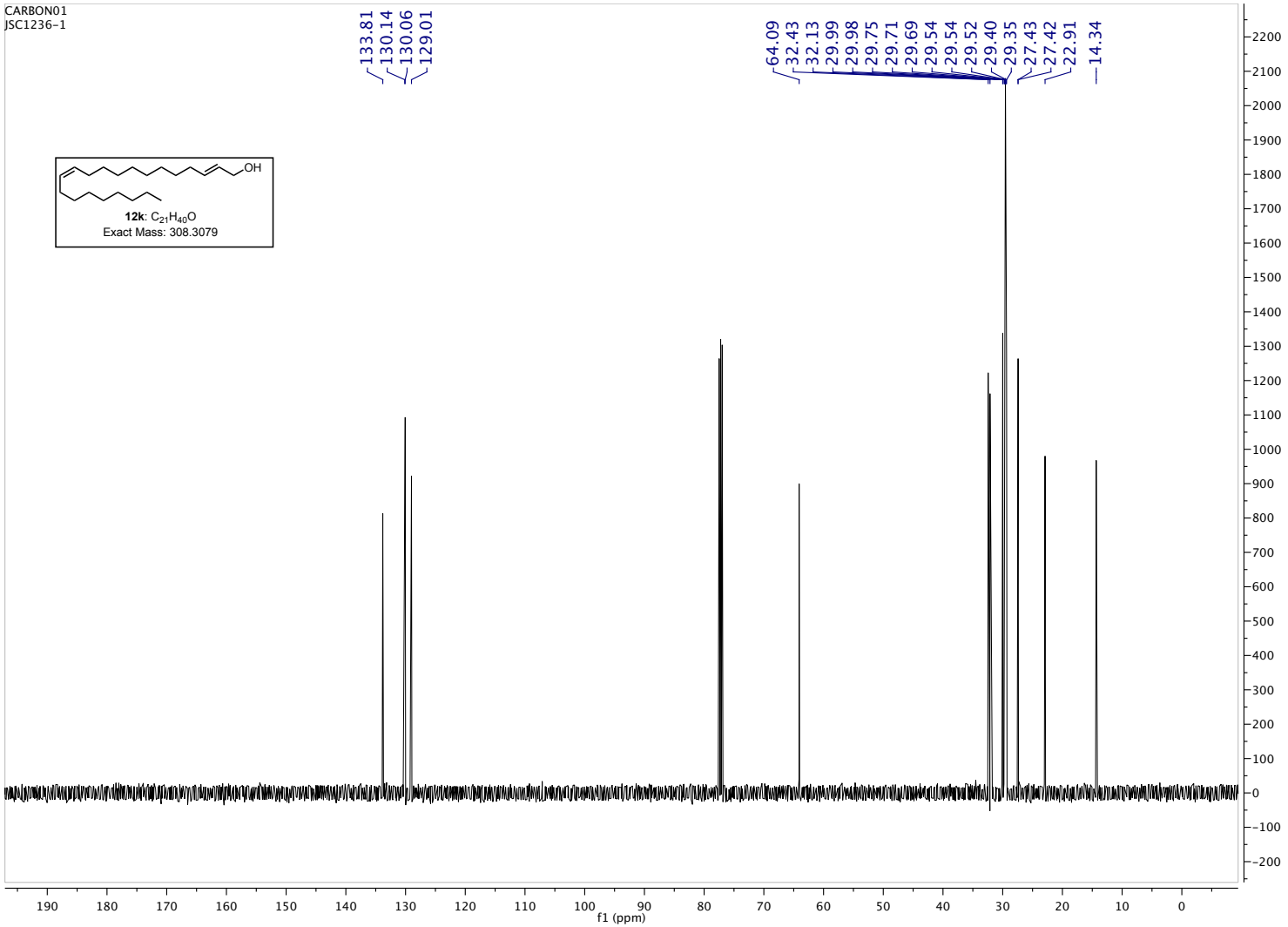
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12j**.



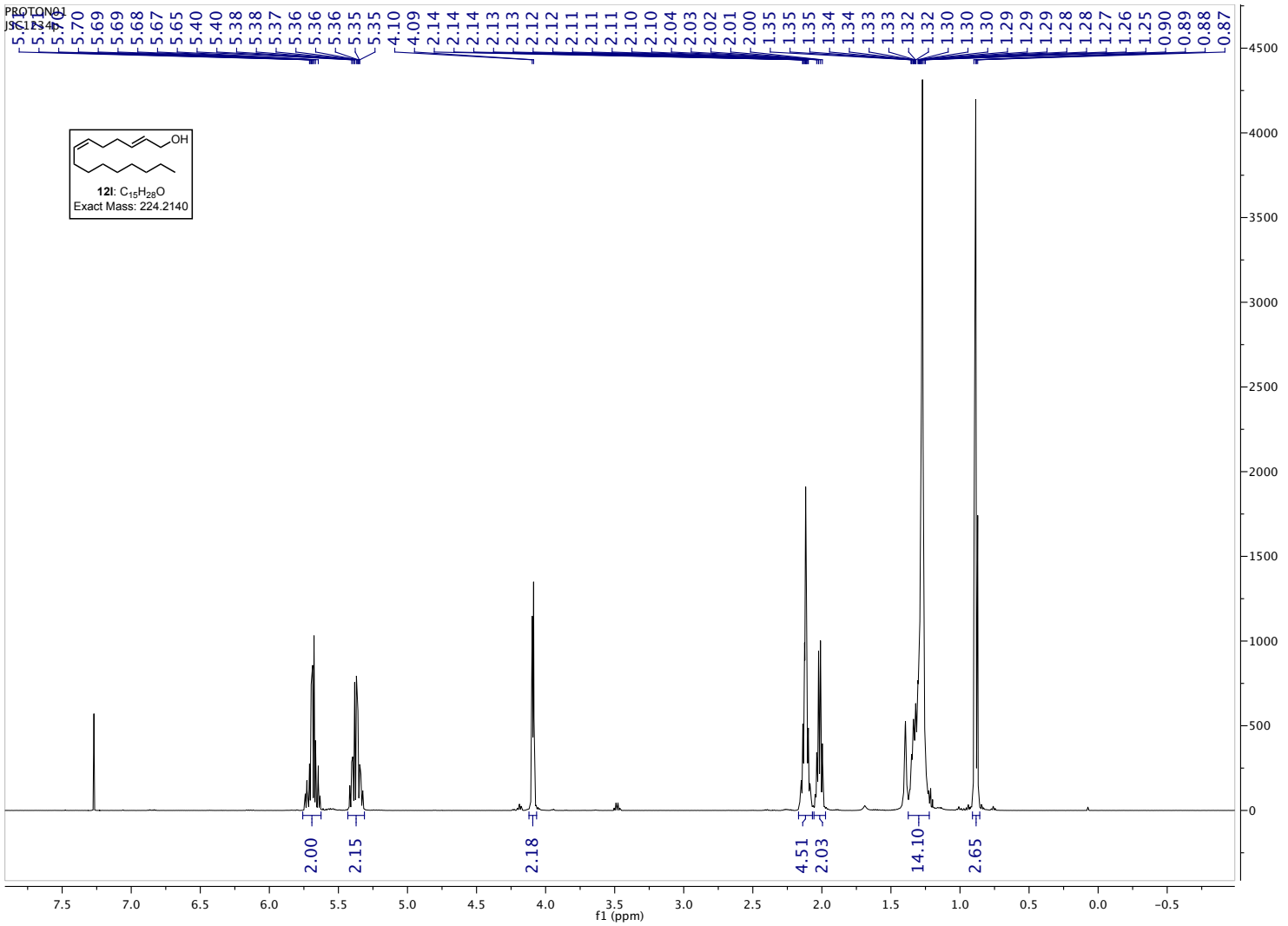
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12k**.



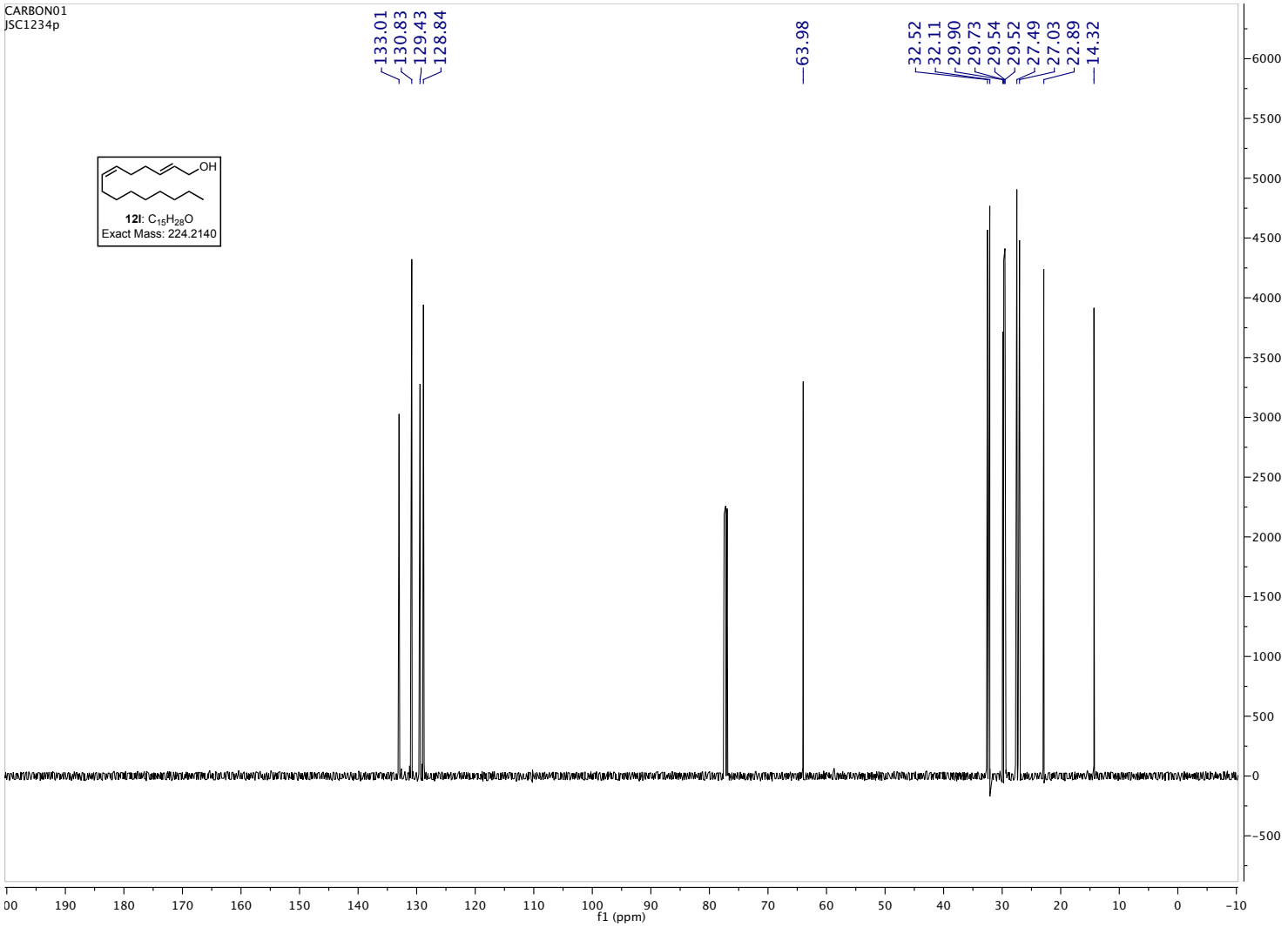
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12k**.



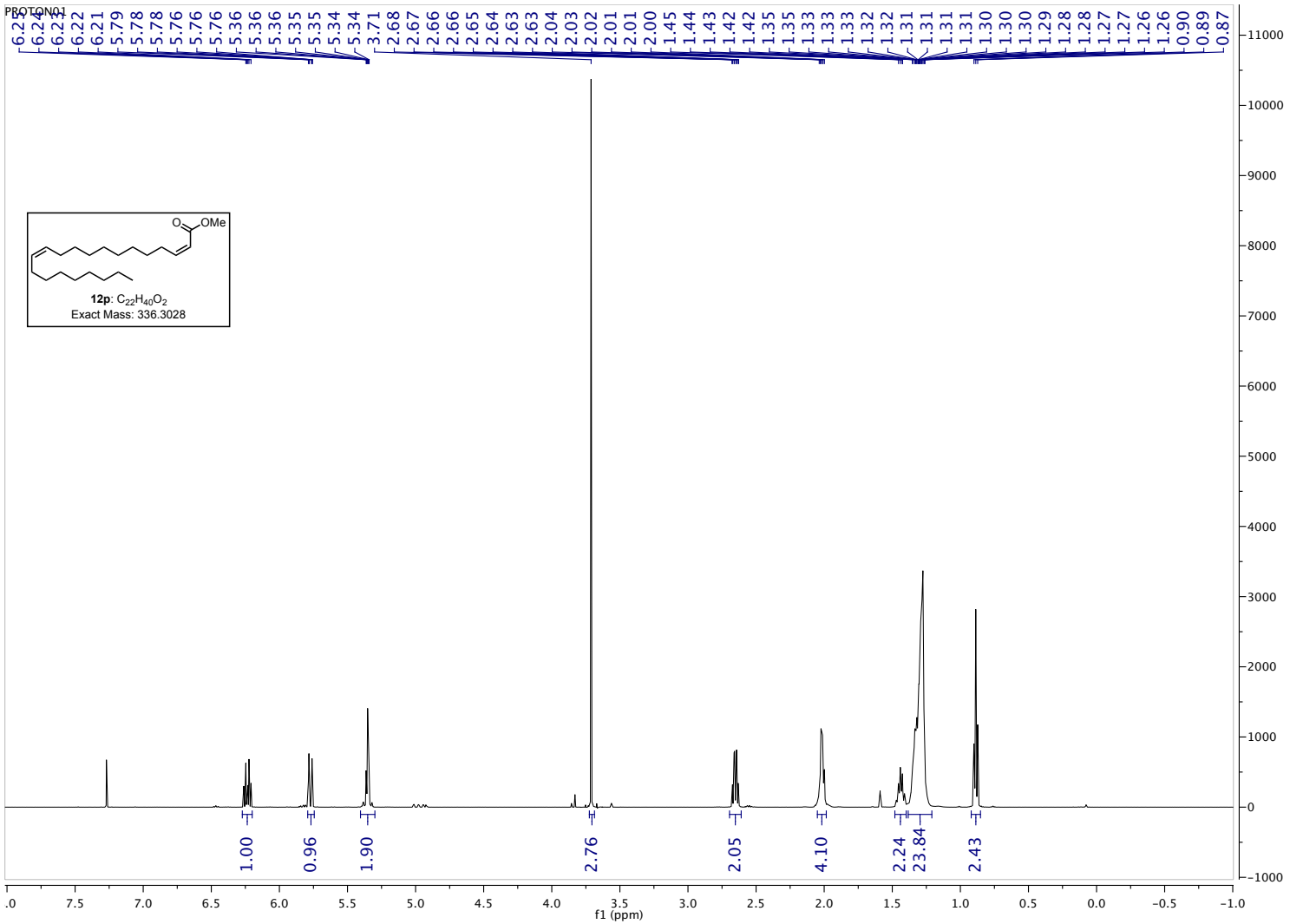
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12l**.



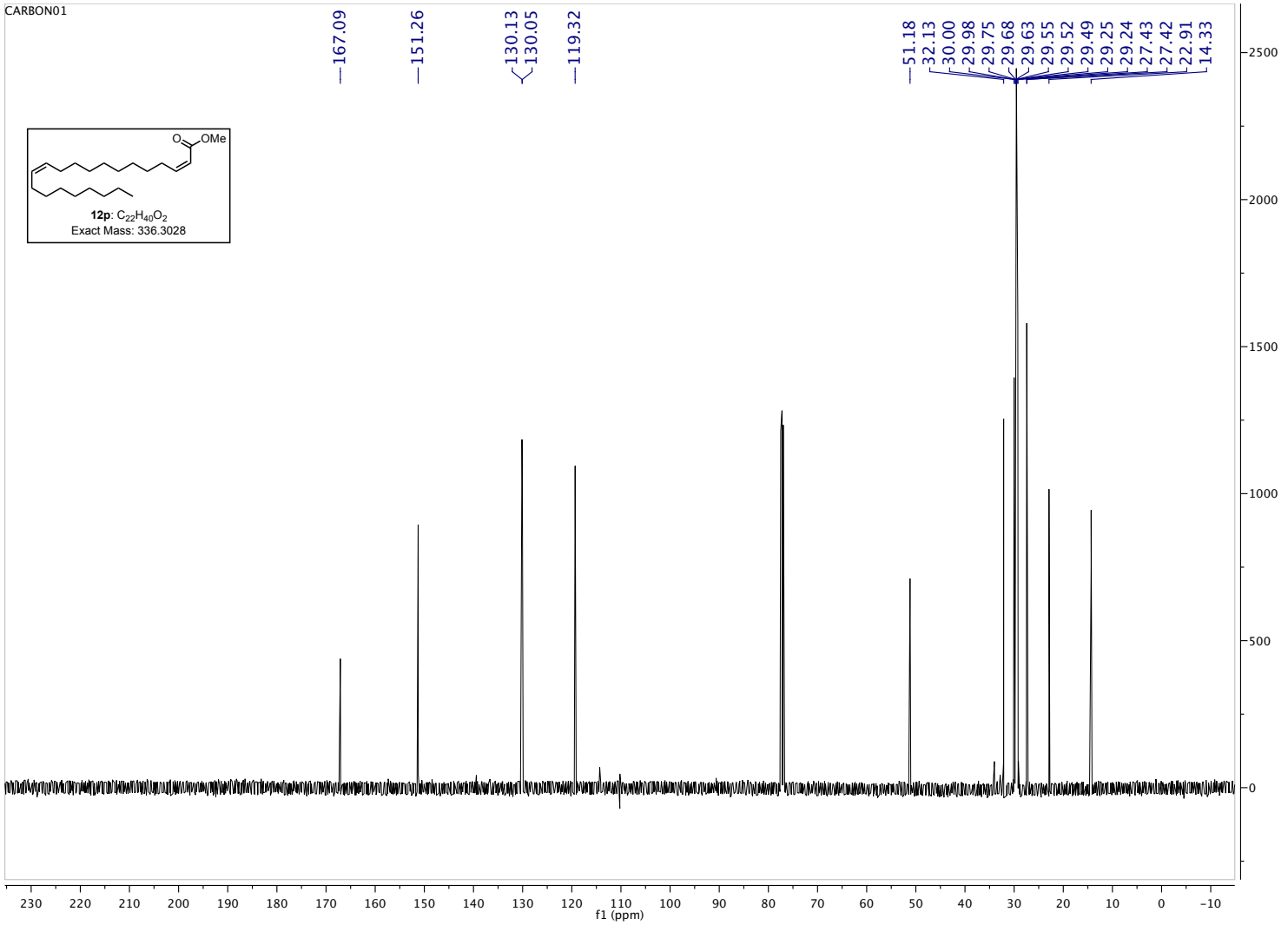
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12l**.



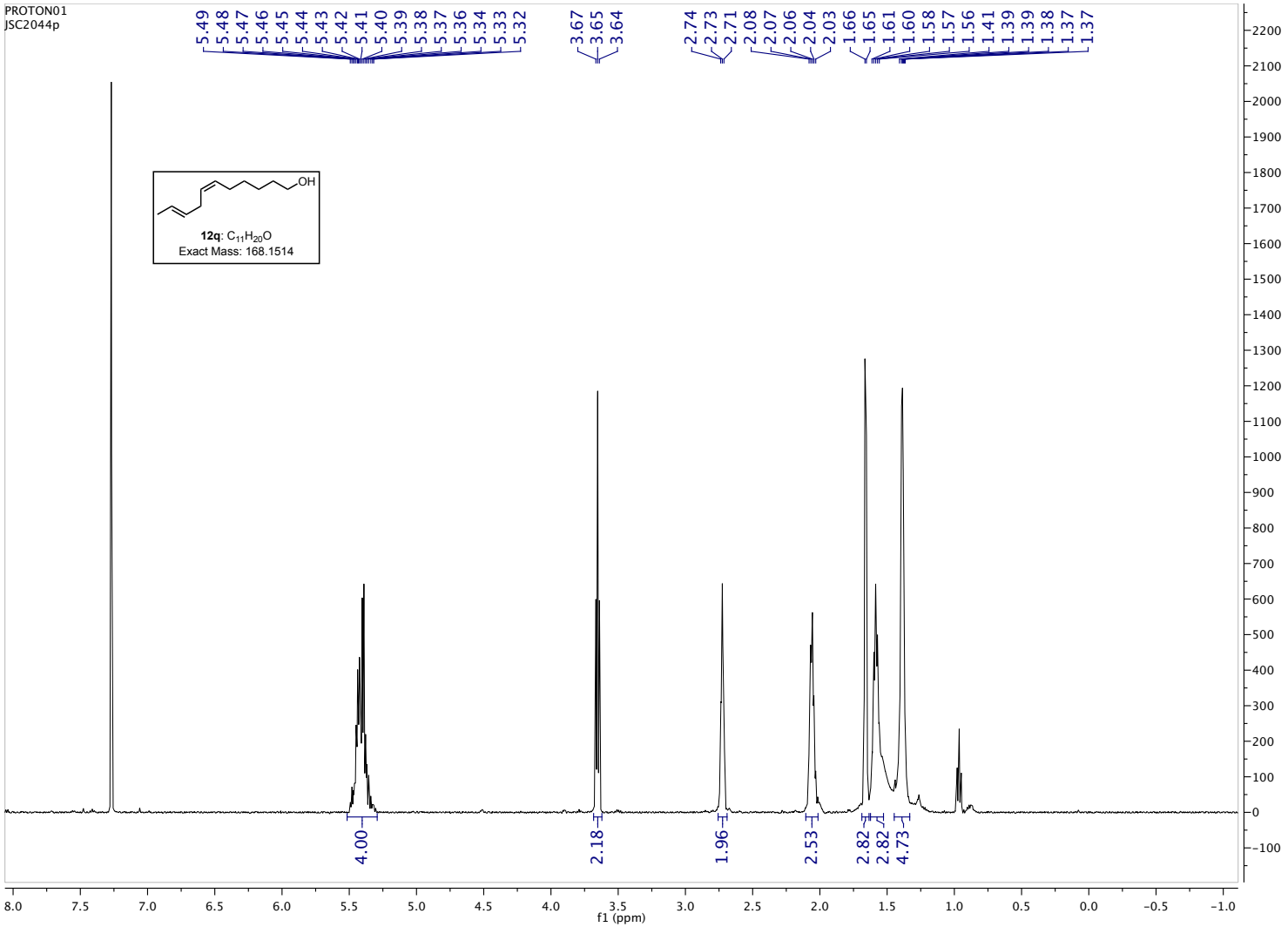
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12p**.



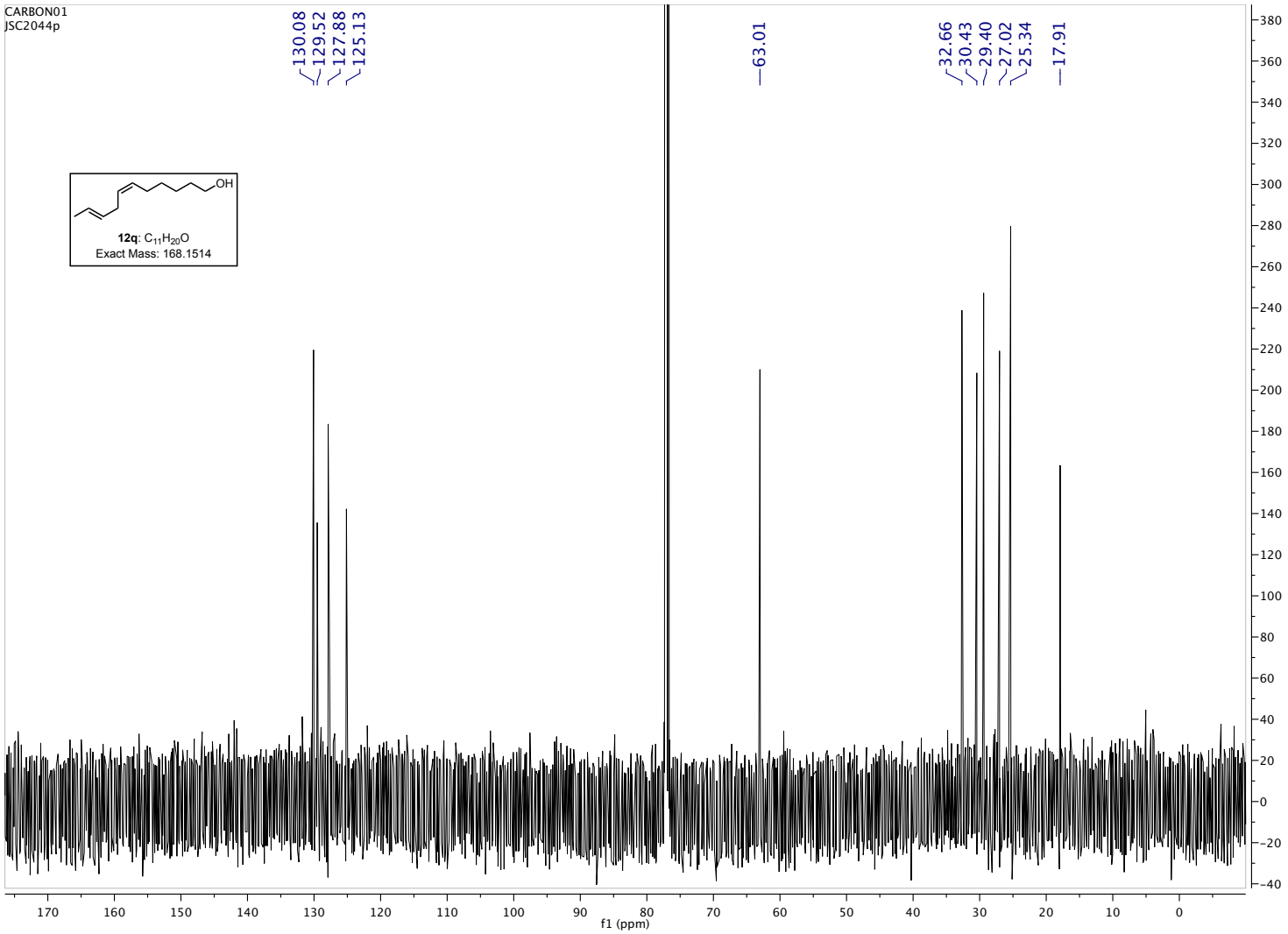
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12p**.



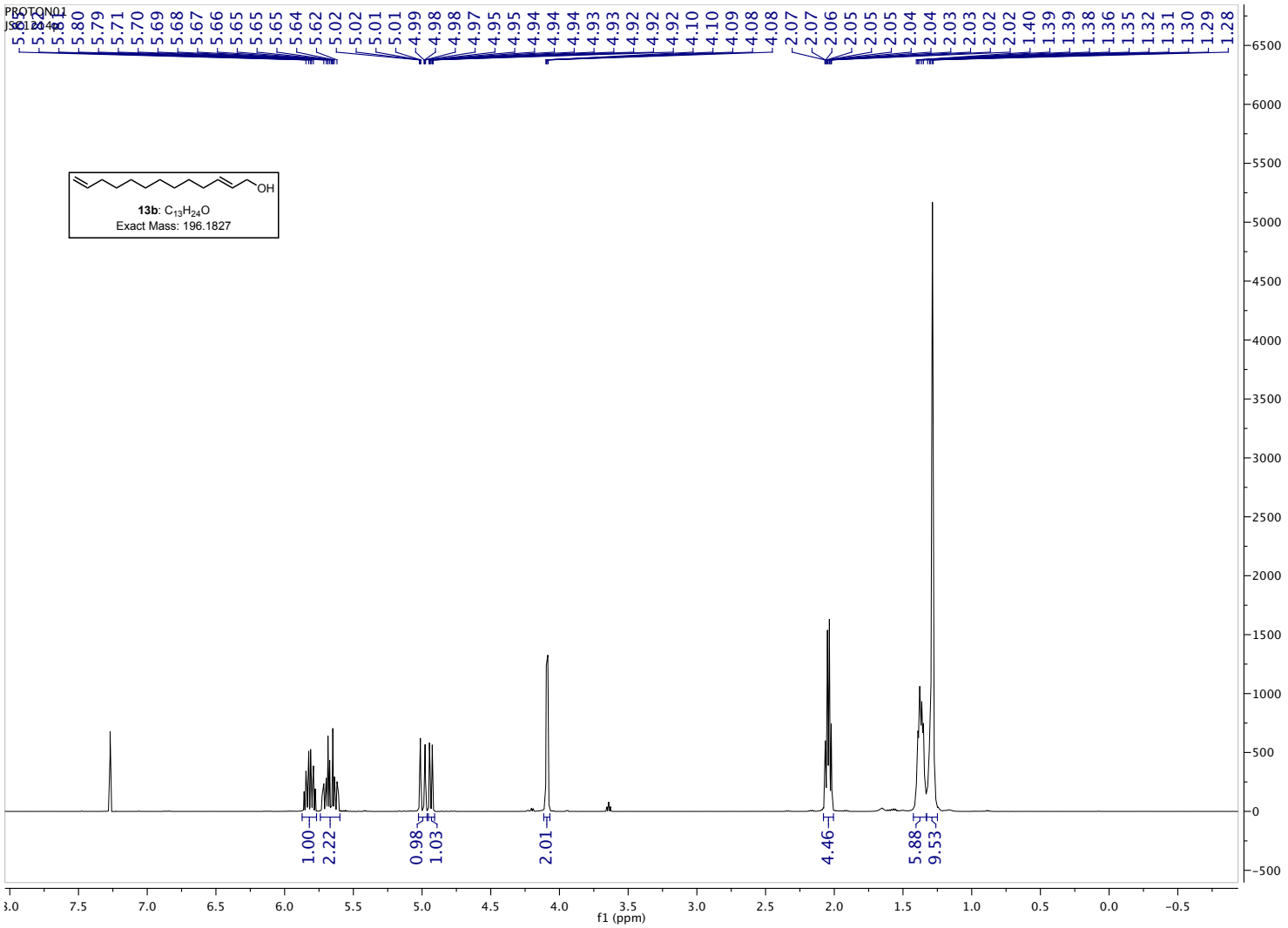
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **12q**.



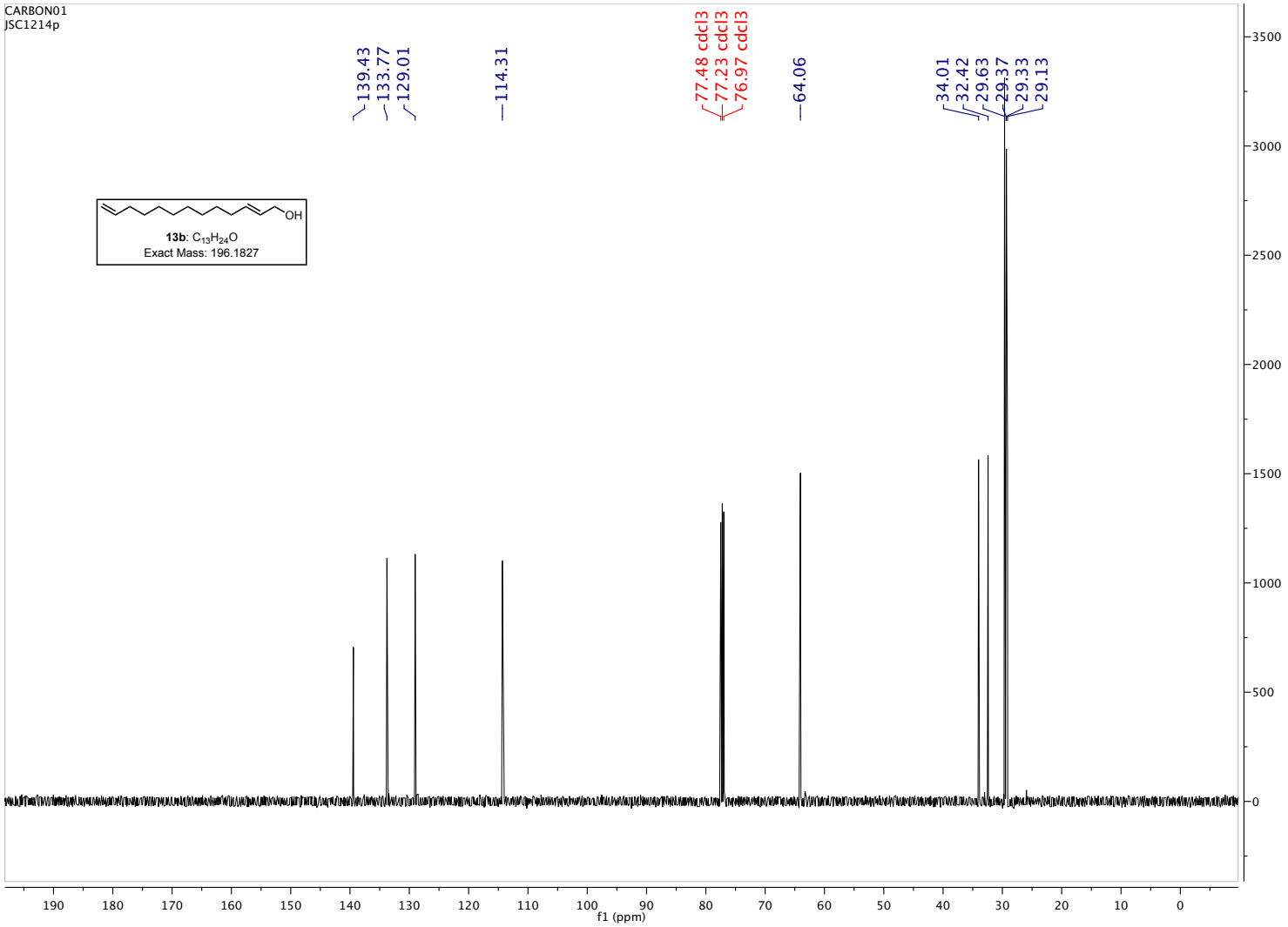
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **12q**.



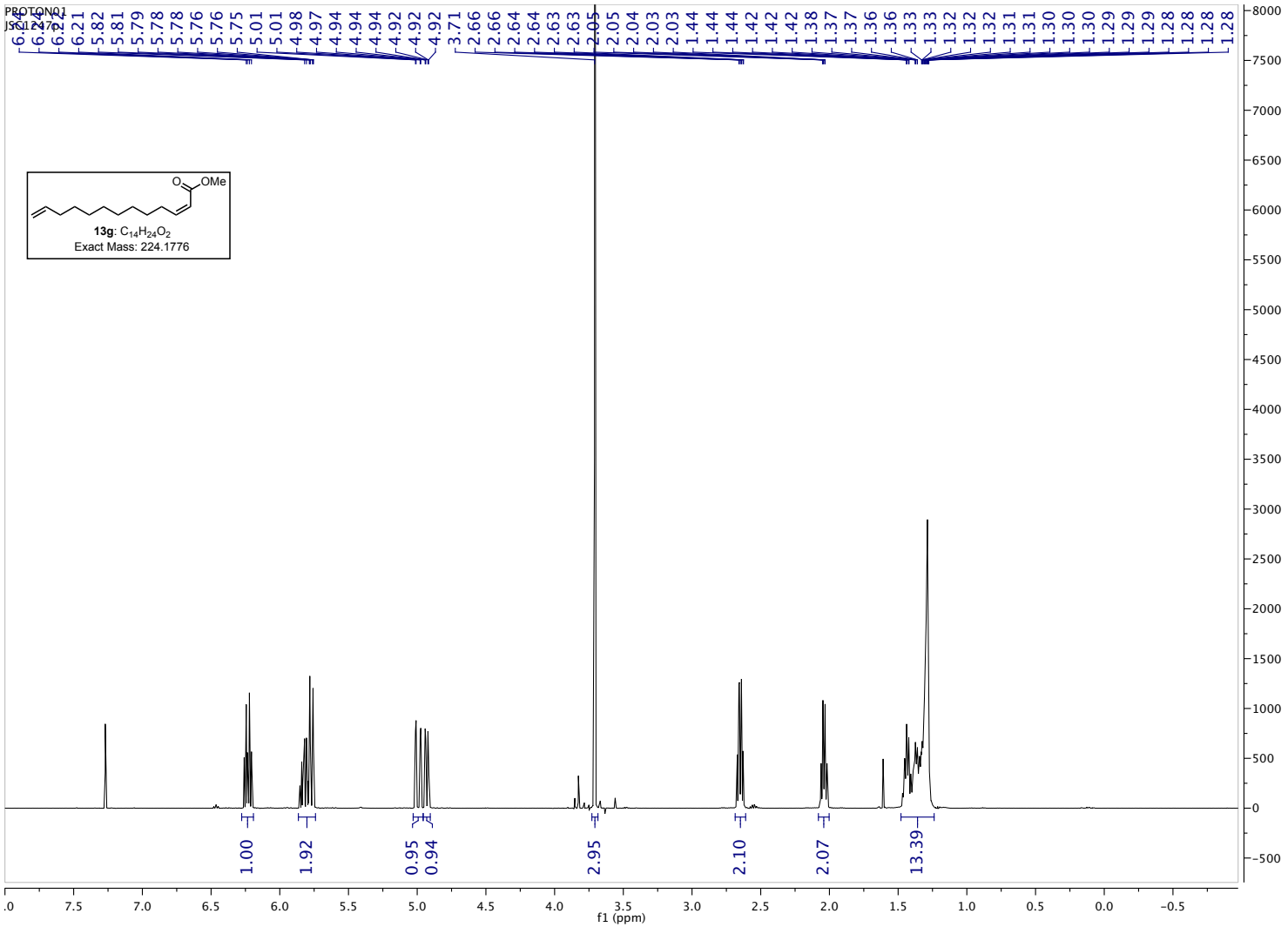
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **13b**.



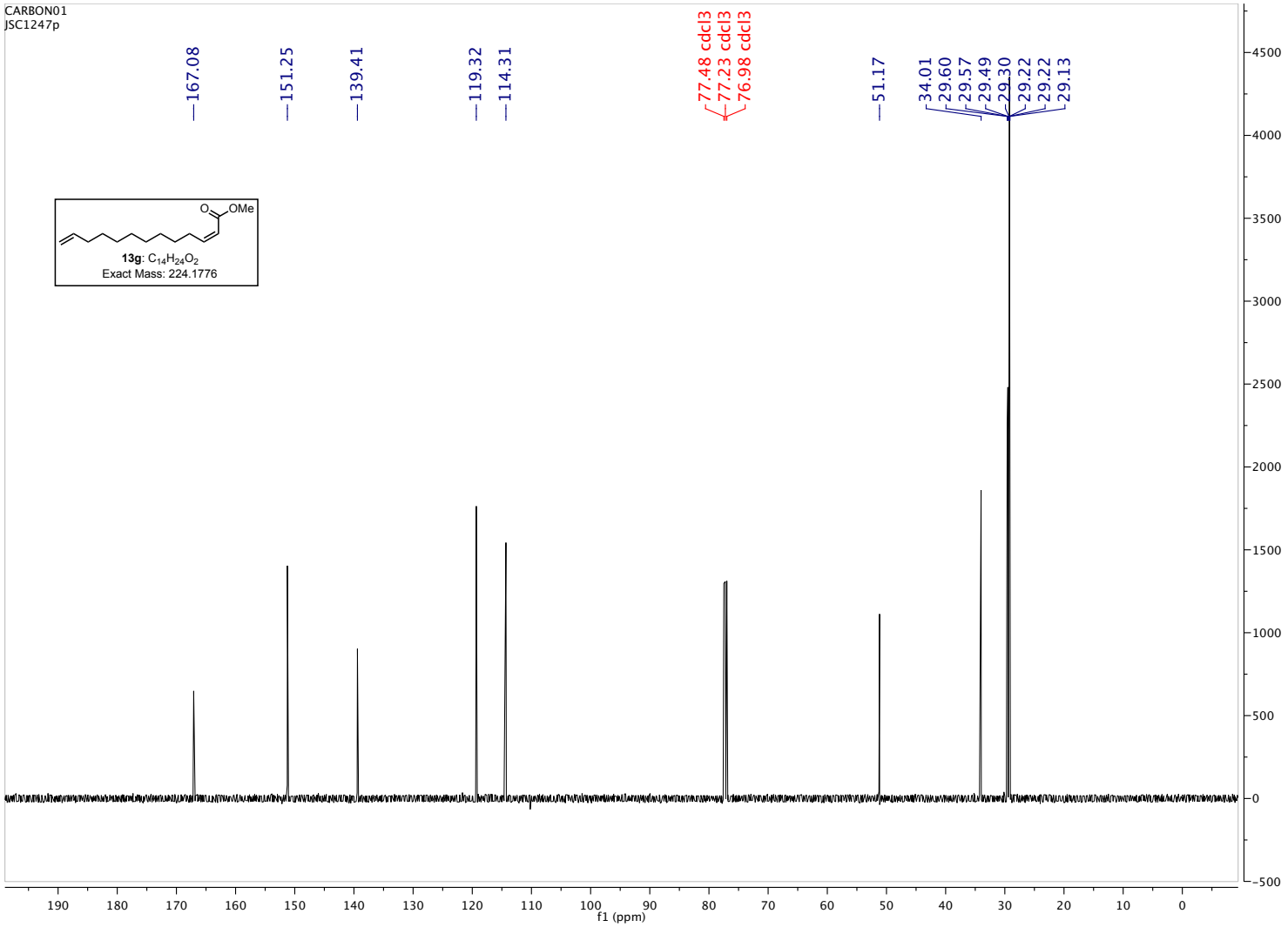
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **13b**.



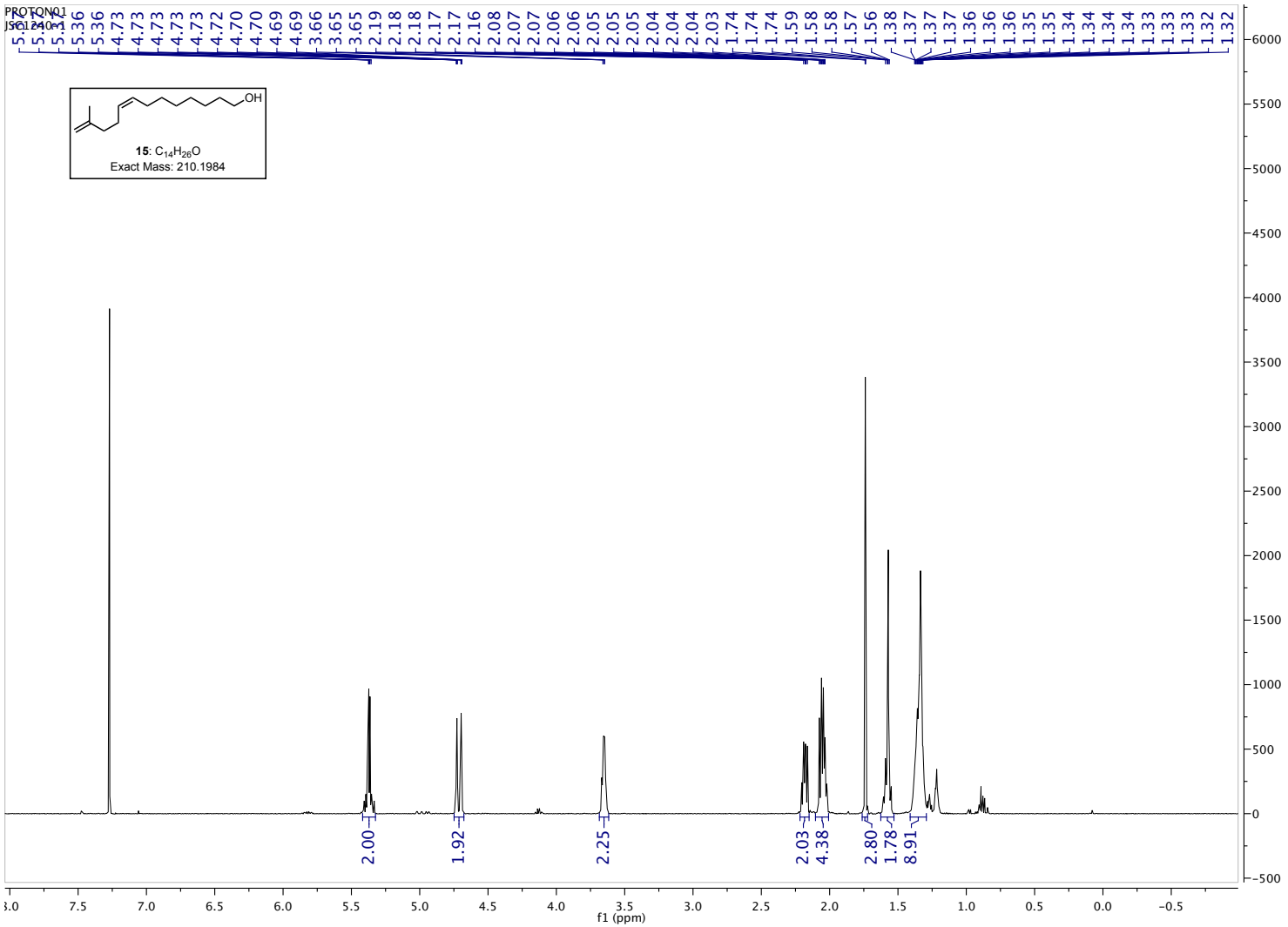
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **13g**.



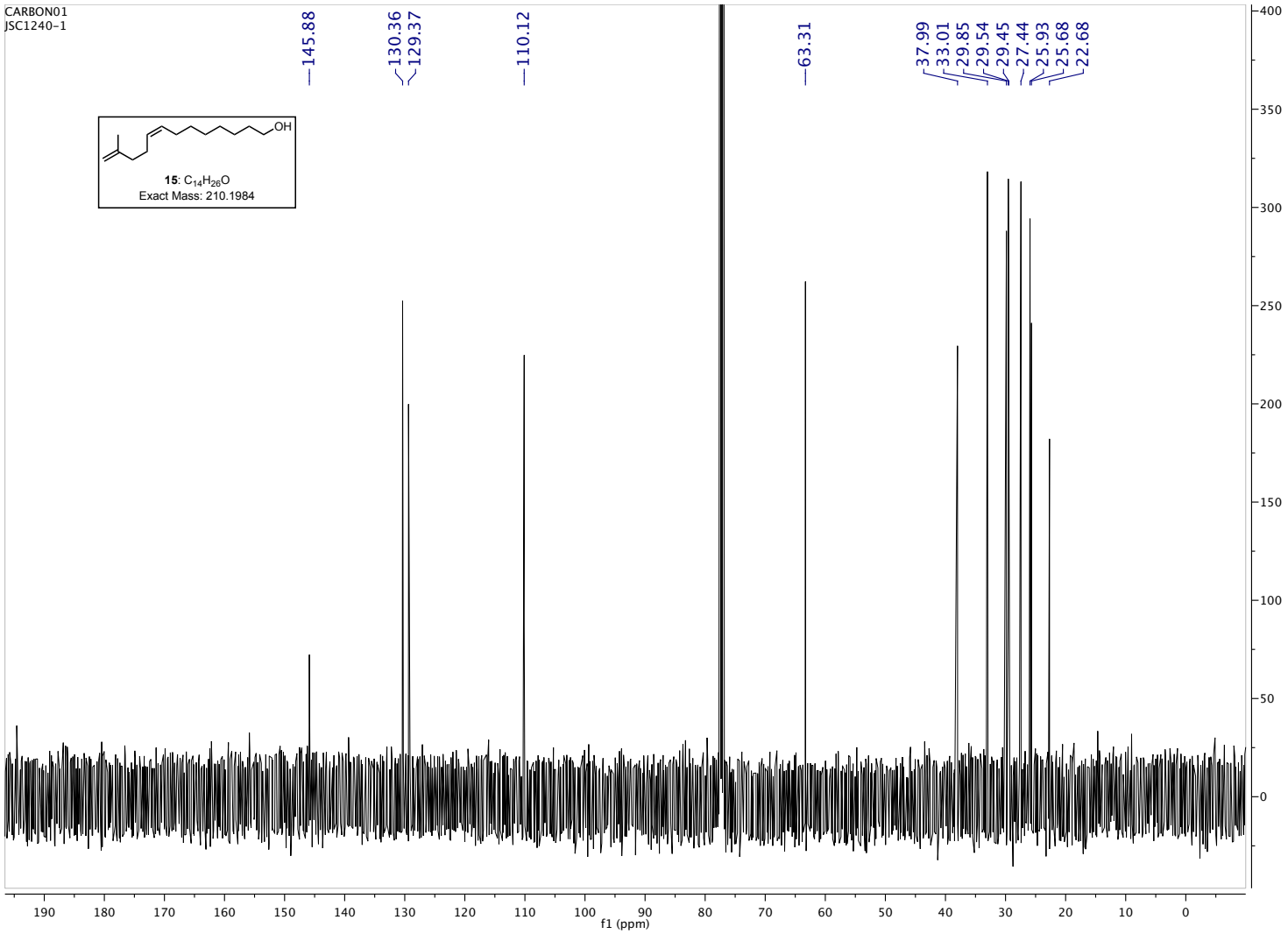
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **13g**.



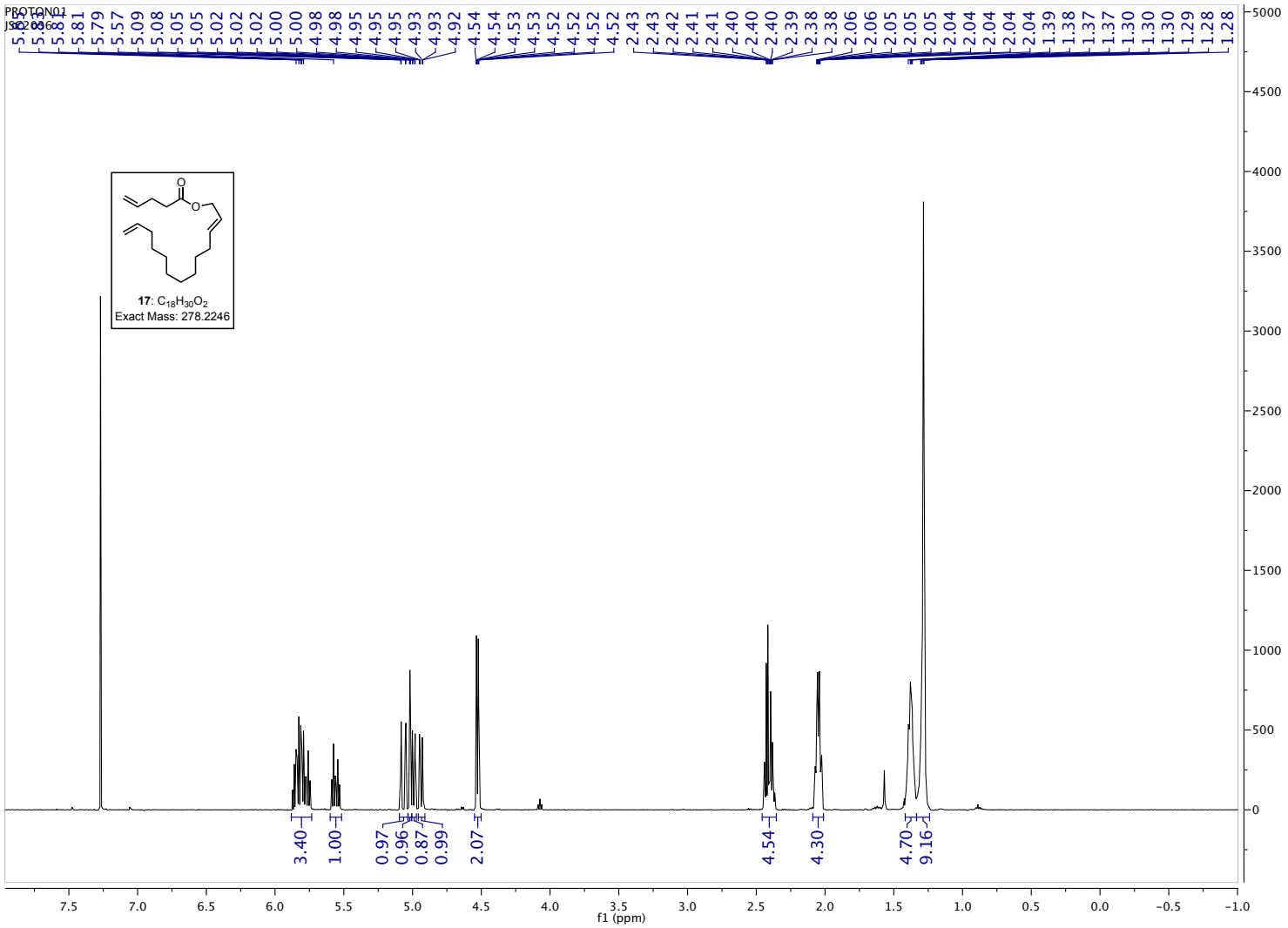
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **15**.



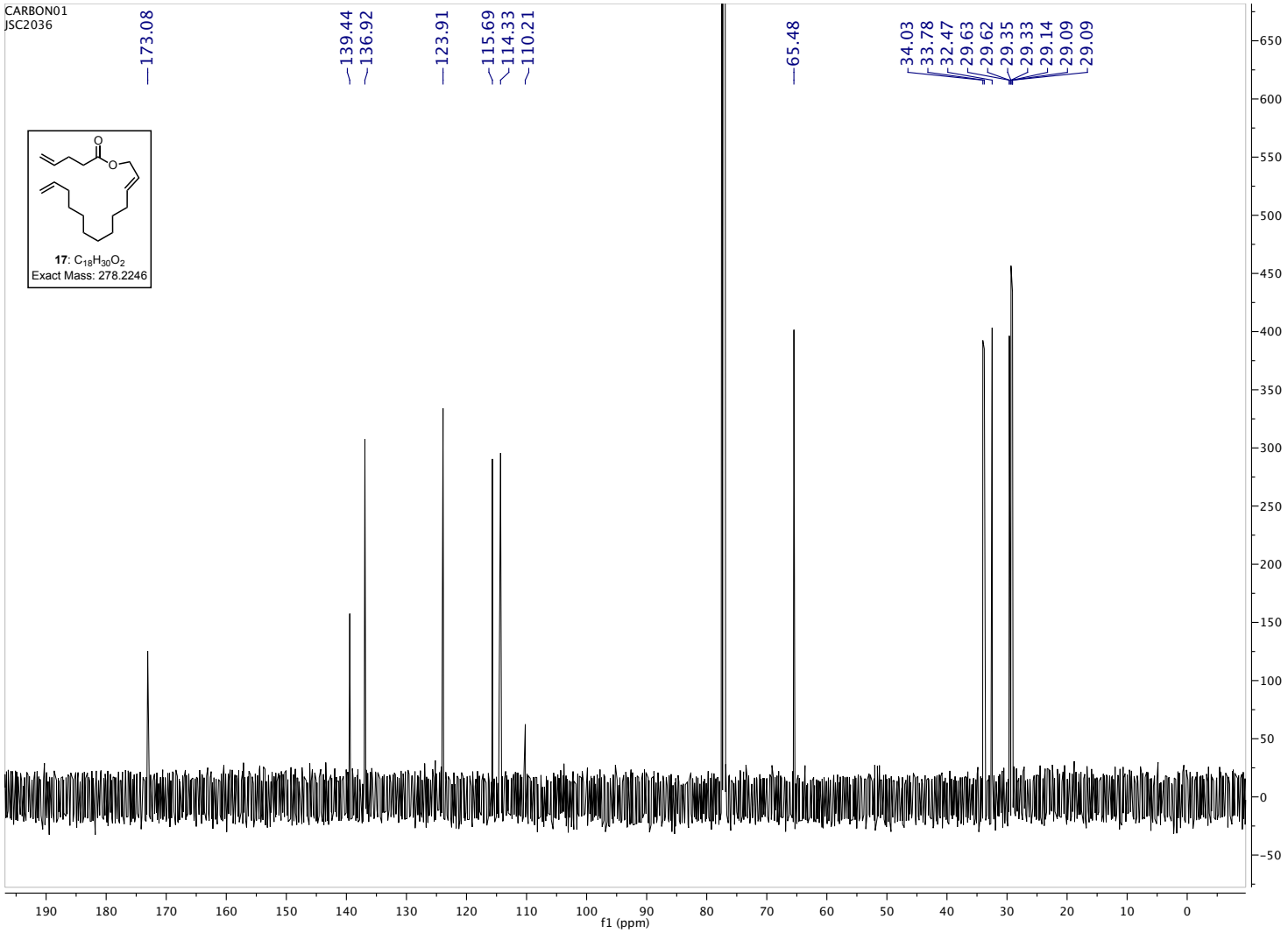
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **15**.



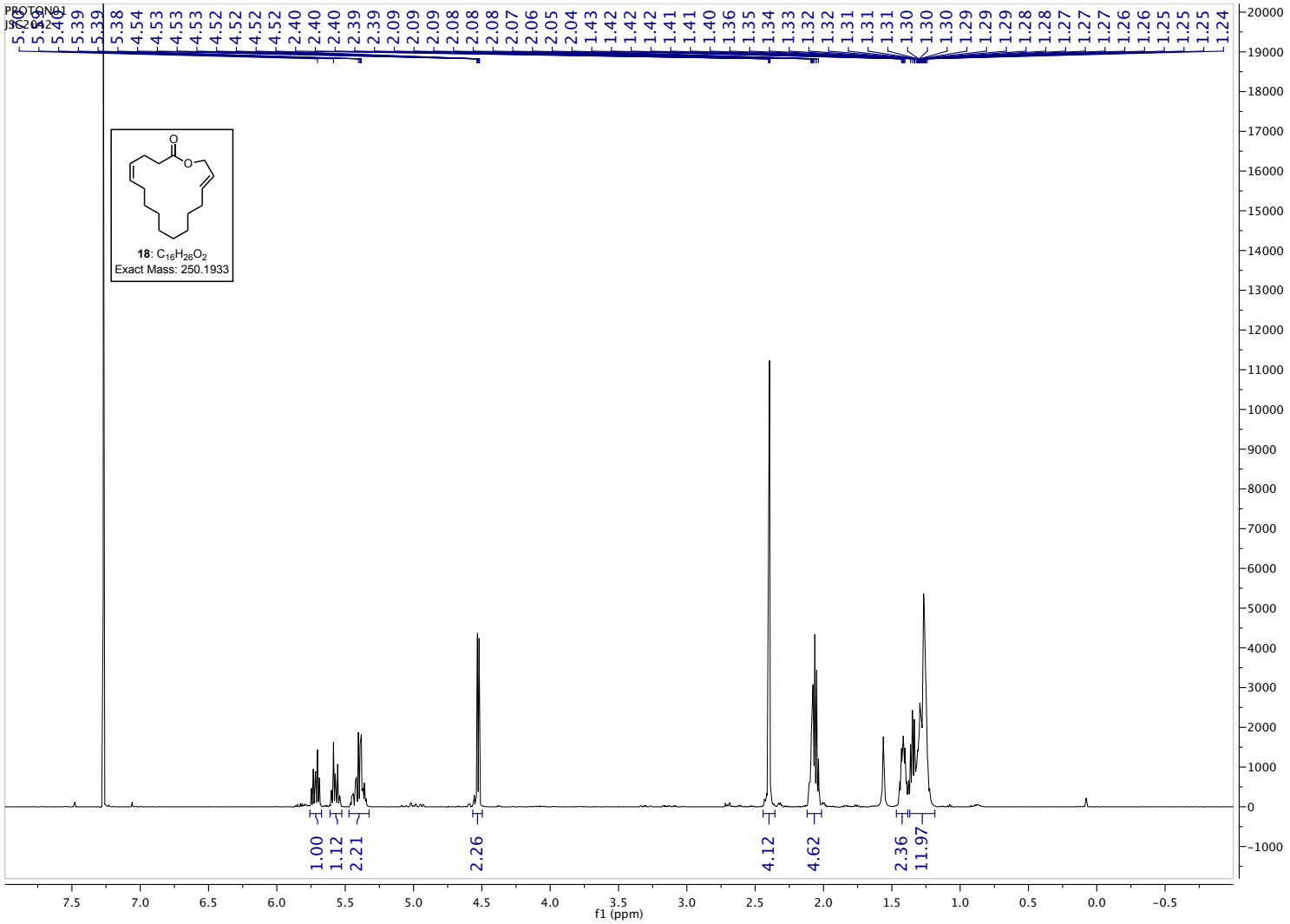
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **17**.



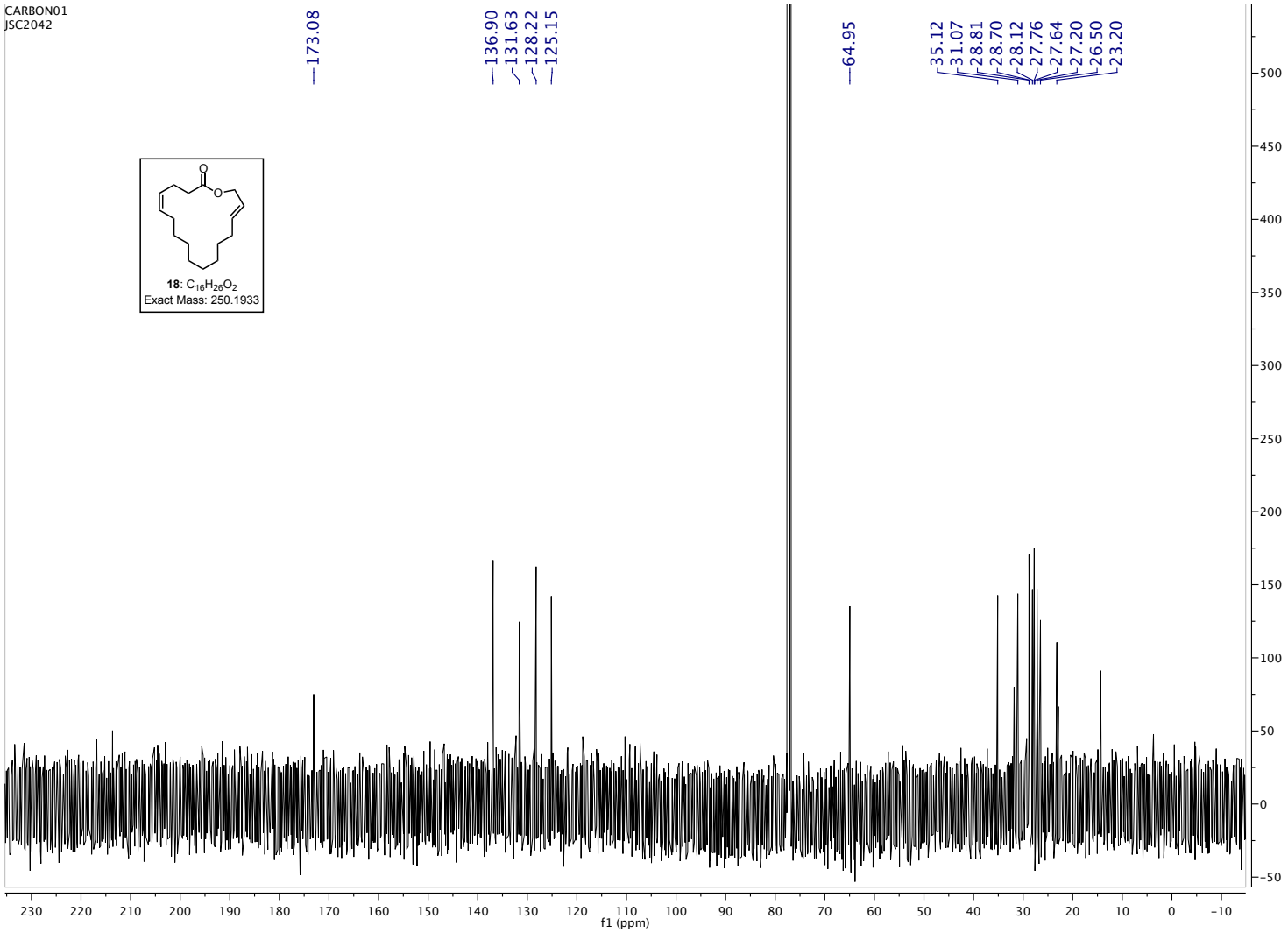
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **17**.



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **18**.

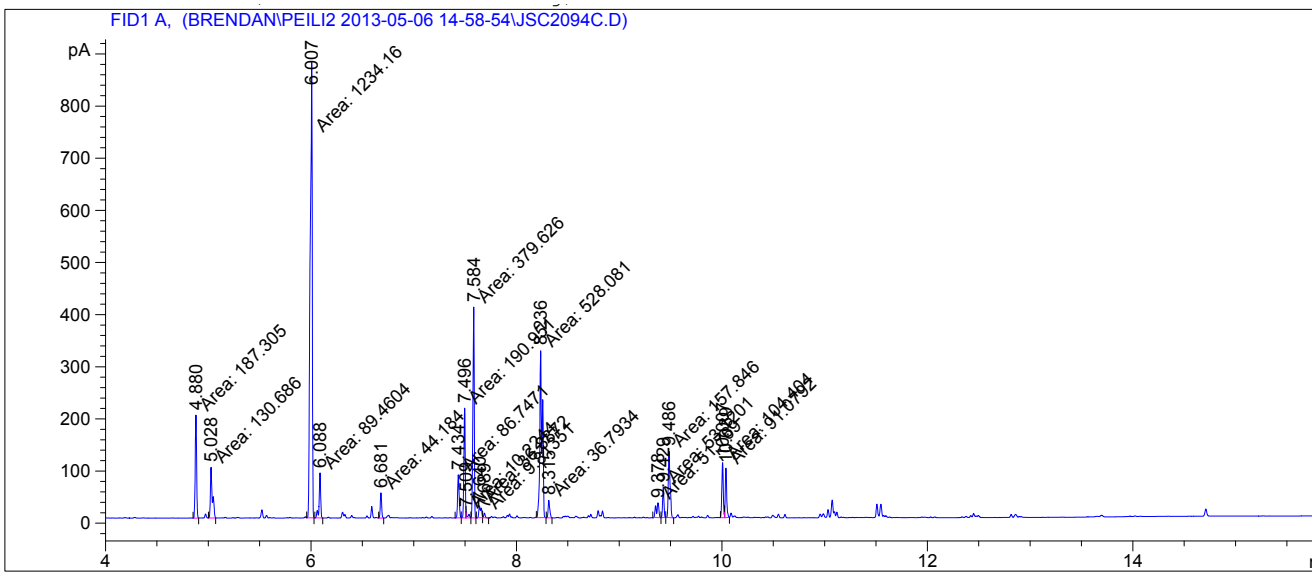


^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **18**.



Part 3. Gas Chromatograms of unpurified reaction mixtures:

Reaction of allyl methyl carbonate with catalyst **2**:

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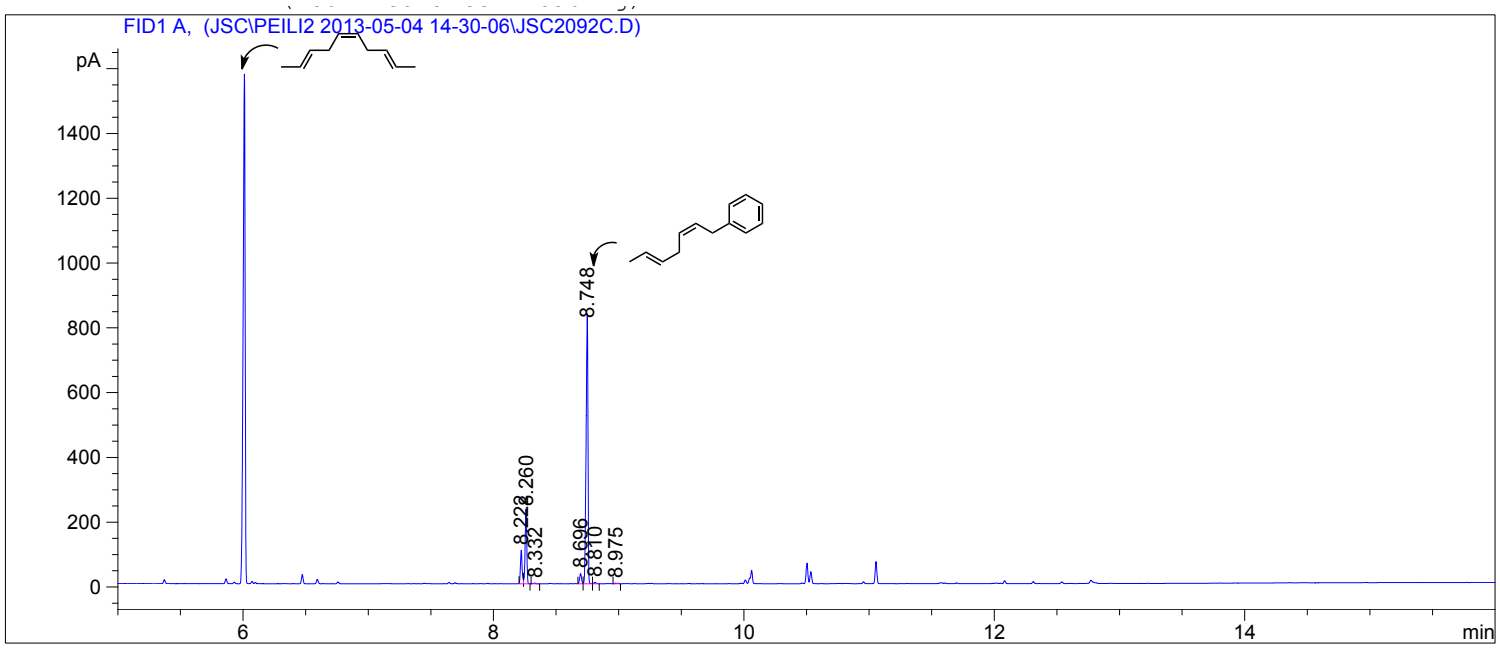
========================================================================
                        Area Percent Report
========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   4.880 MM    0.0157  187.30486  198.48436  5.47173
   2   5.028 MM    0.0223  130.68591   97.57375  3.81772
   3   6.007 MM    0.0235 1234.16125  876.37933 36.05351
   4   6.088 MM    0.0171   89.46044   86.94088  2.61340
   5   6.681 MM    0.0152   44.18403   48.47345  1.29075
   6   7.434 MM    0.0174   86.74712   83.08228  2.53414
   7   7.496 MM    0.0150  190.95100  211.46515  5.57824
   8   7.509 MM    0.0153   10.22445   11.14959  0.29869
   9   7.584 MM    0.0156  379.62555  405.07065 11.08999
  10   7.640 MM    0.0266   36.88715   23.07720  1.07758
  11   7.689 MM    0.0178    9.81351    9.19254  0.28668
  12   8.236 MM    0.0274  528.08093  320.63898 15.42681
  13   8.315 MM    0.0181   36.79343   33.88400  1.07484
  14   9.378 MM    0.0302   51.76898   28.55096  1.51233
  15   9.429 MM    0.0151   53.12011   58.72219  1.55180
  16   9.486 MM    0.0206  157.84572  127.74446  4.61114
  17  10.007 MM    0.0164  104.40427  106.17732  3.04996
  18  10.039 MM    0.0158   91.07923   95.94094  2.66069
```

Compound **12b**

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   8.222 BV    0.0140   96.11469  101.92526  7.90367
   2   8.260 VB    0.0151  211.75037  223.46384 17.41259
   3   8.332 BB    0.0181    2.21064    1.83542  0.18178
   4   8.696 BV    0.0164   32.63651   30.82909  2.68376
   5   8.748 VV    0.0176  865.78290  803.49988 71.19481
   6   8.810 VB    0.0185    4.77008    3.84769  0.39225
   7   8.975 BB    0.0259    2.81074    1.49441  0.23113
```
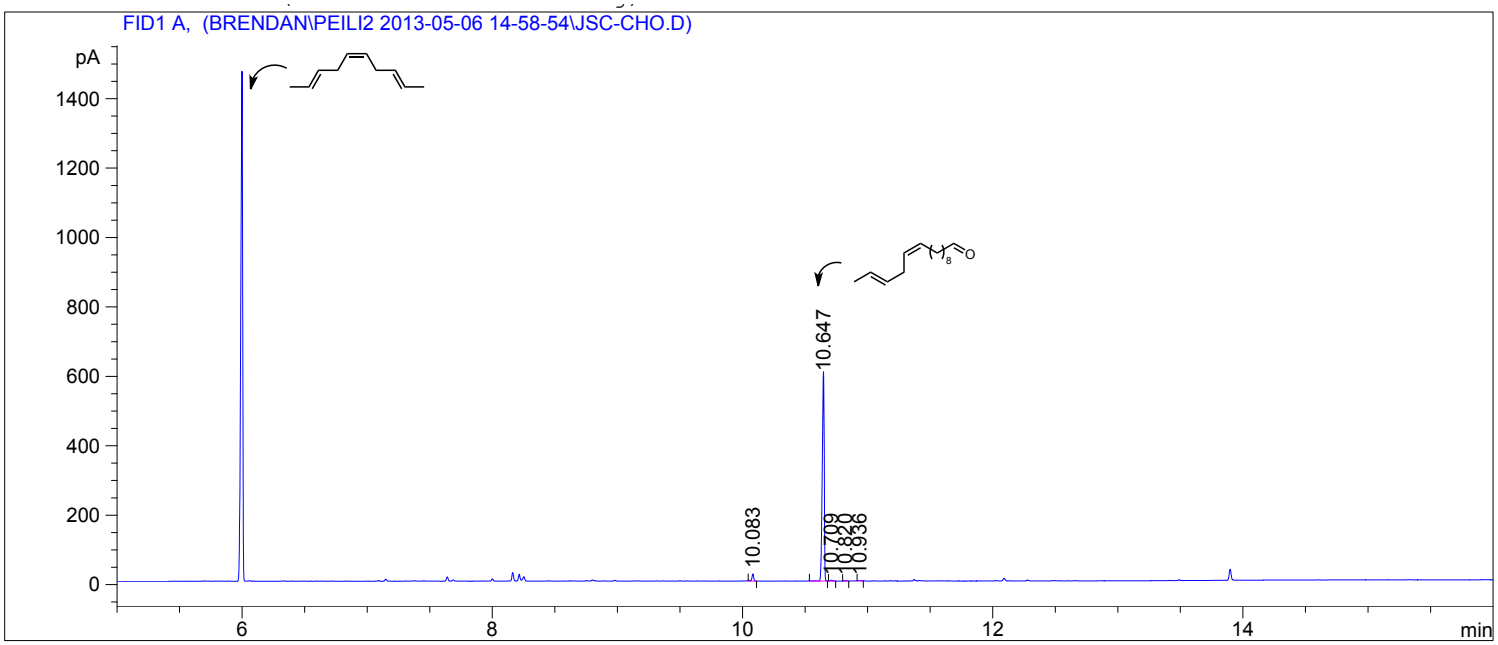

Compound **12c**.

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                        Area Percent Report
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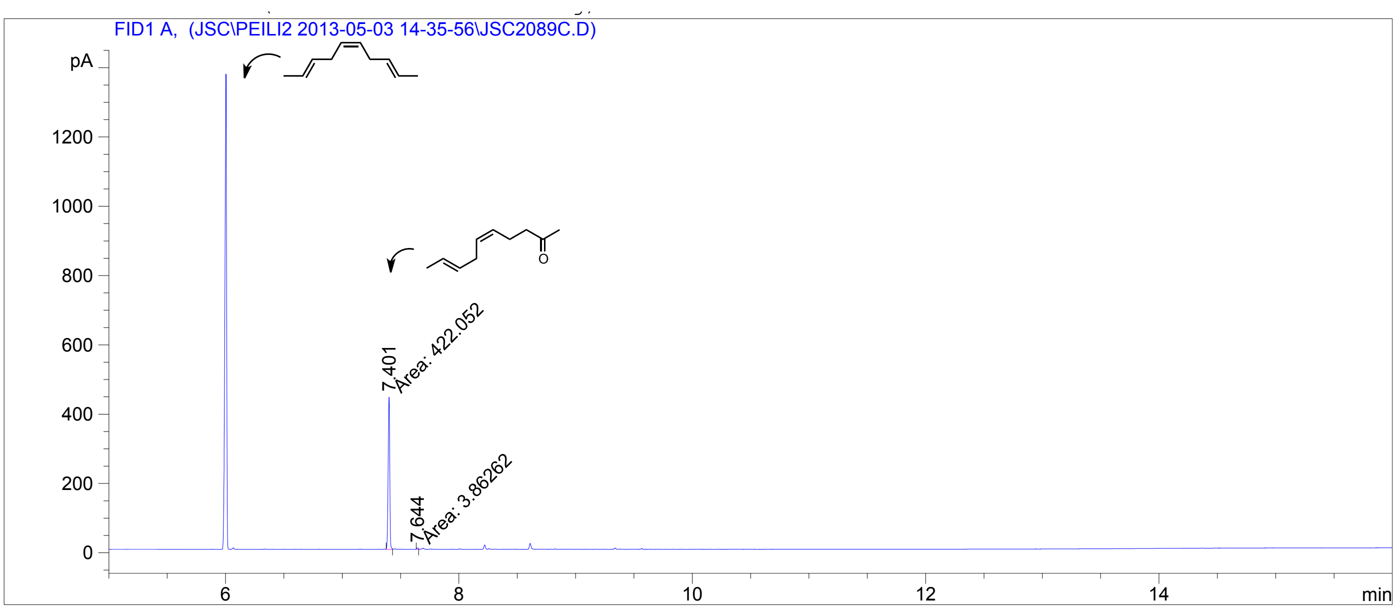
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  10.083 BB    0.0165   21.23759   19.88708  3.06365
   2  10.647 BB    0.0172  665.04510  588.68805 95.93679
   3  10.709 BB    0.0200    3.11192    2.42401  0.44891
   4  10.820 BB    0.0155    1.76482    1.79816  0.25459
   5  10.936 BB    0.0193    2.05235    1.56559  0.29606

Totals :                   693.21179  614.36289
```

Compound **12d**

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=====================================================================
                     Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   7.401 MM    0.0160  422.05228  440.50253 99.09310
   2   7.644 MM    0.0142    3.86262    4.52266  0.90690

Totals :                   425.91489  445.02519
```
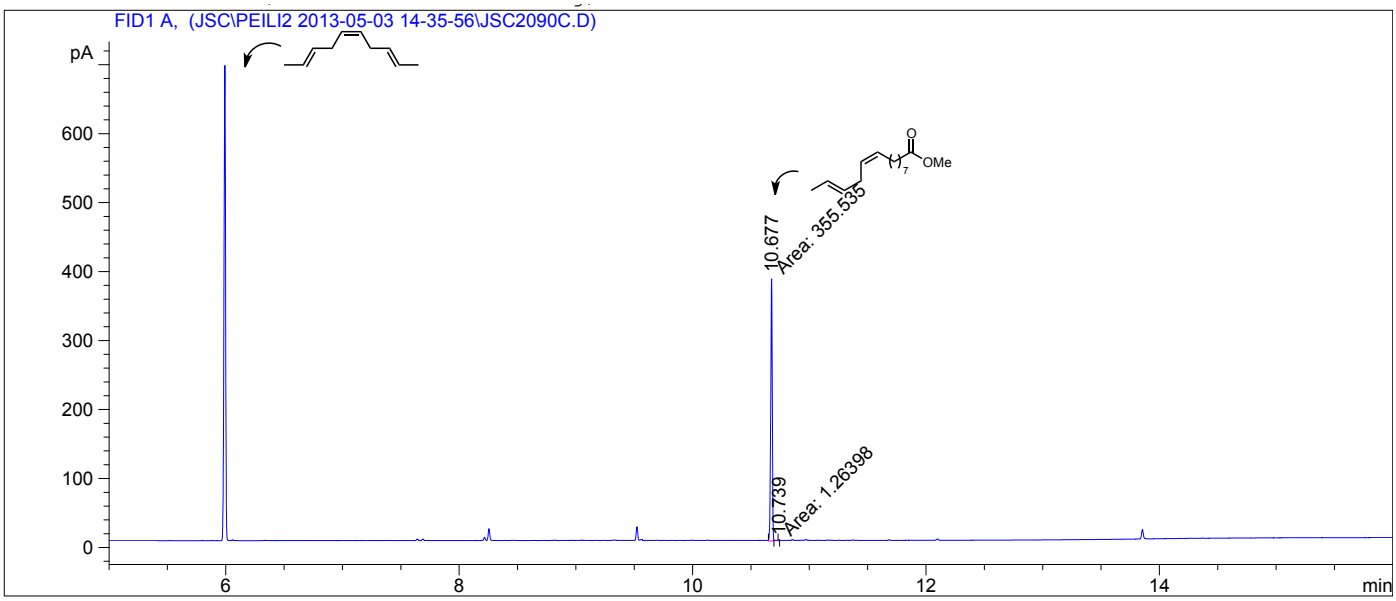

Compound **12e**

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                      Area Percent Report
=====================================================================

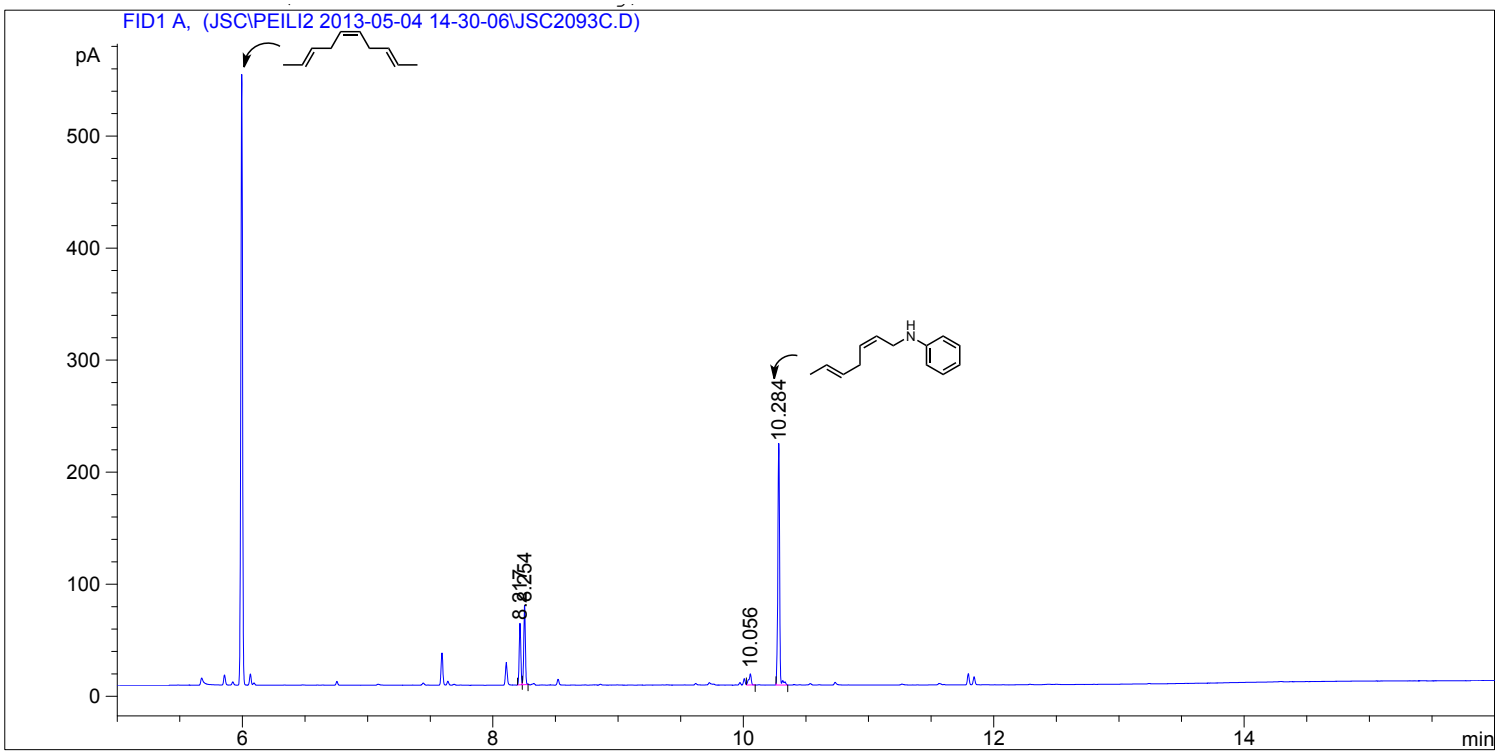
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  10.677 MM    0.0155  355.53497  381.70740 99.64574
   2  10.739 MM    0.0121    1.26398    1.74760  0.35426

Totals :                   356.79896  383.45499
```

Compound **12f**

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                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   8.217 BV    0.0148   49.03390   53.11898 14.52418
   2   8.254 VB    0.0147   62.72197   68.66196 18.57868
   3  10.056 VB    0.0199   13.20779    9.69418  3.91224
   4  10.284 BB    0.0157  212.63818  212.74730 62.98490
```
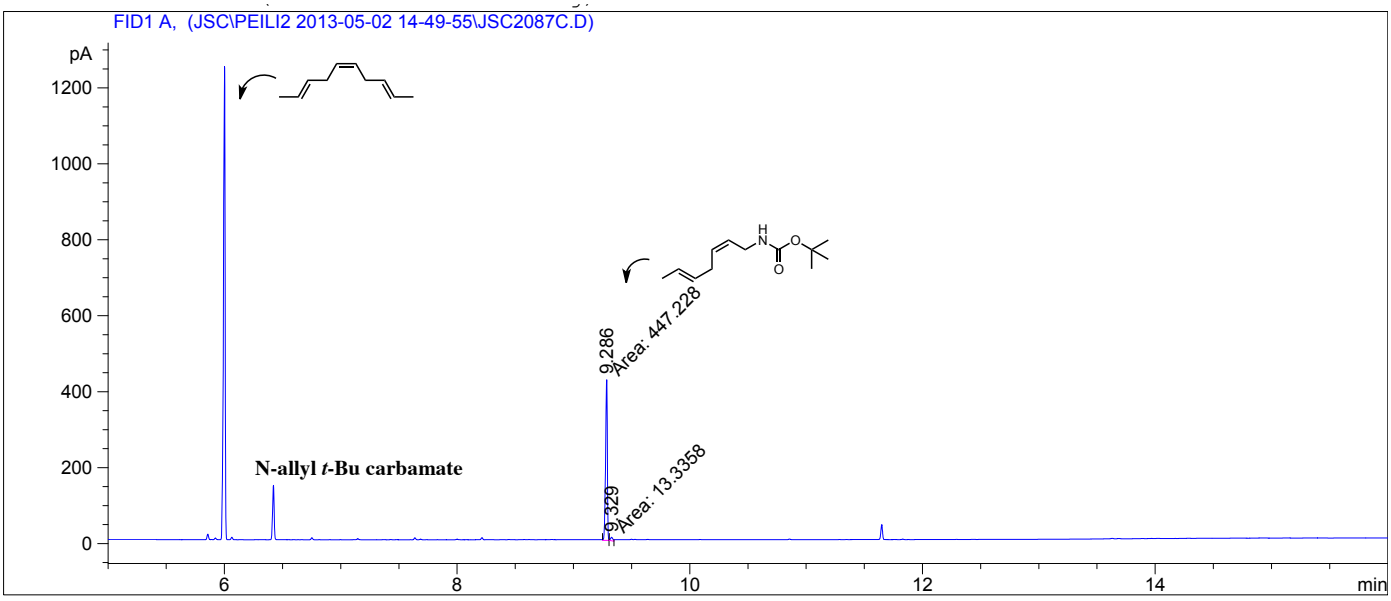

Compound **12g**

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                      Area Percent Report
=====================================================================

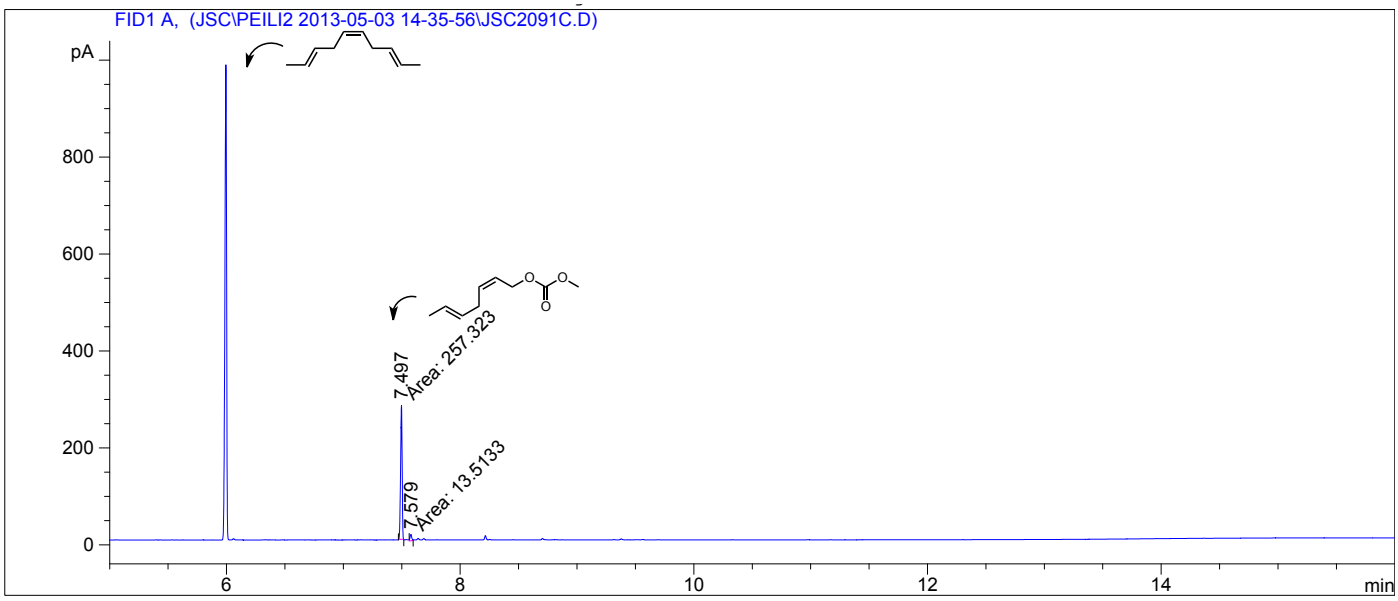
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   9.286 MM    0.0176  447.22815  423.34912 97.10447
   2   9.329 MM    0.0237   13.33575    9.37145  2.89553

Totals :                   460.56390  432.72057
```

Compound **12h**




```
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                      Area Percent Report
=====================================================================

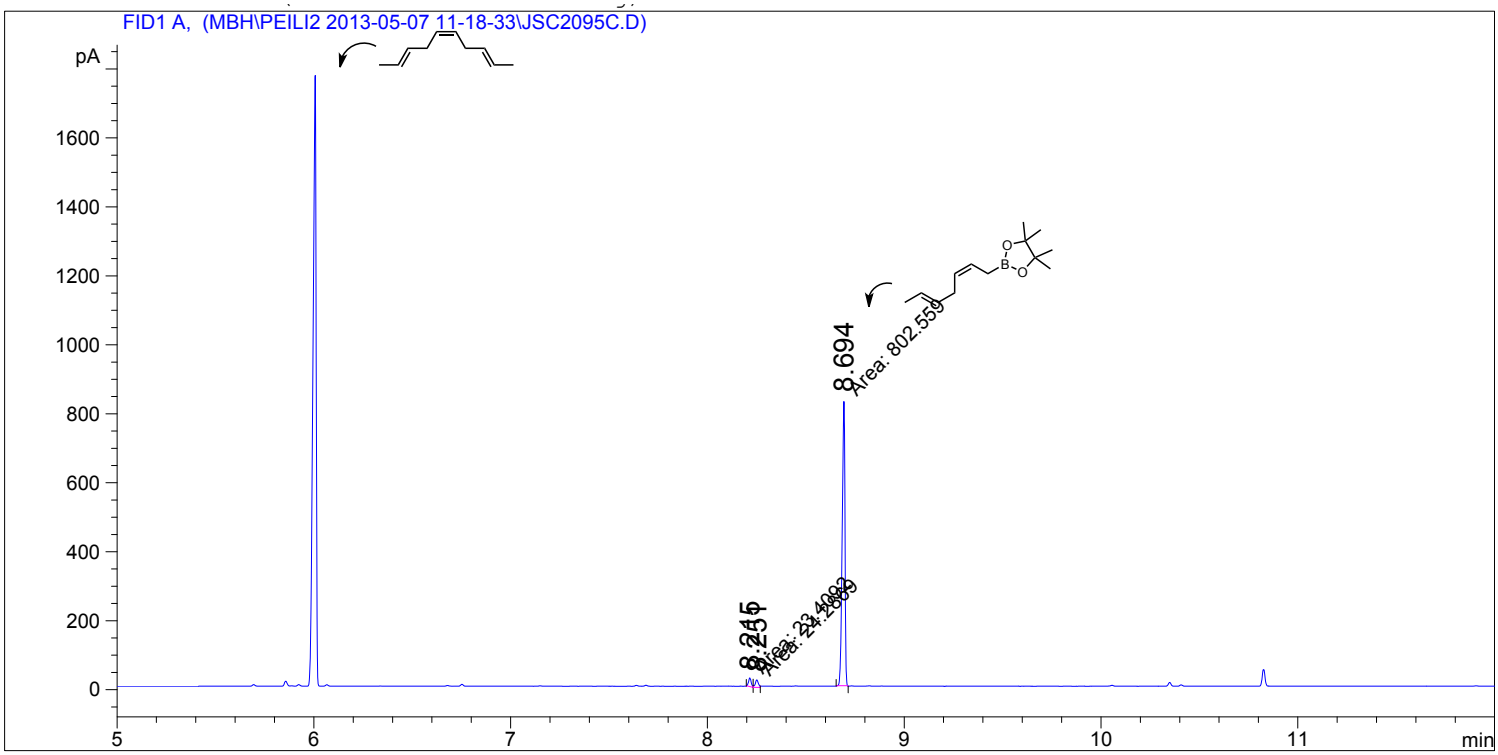
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   7.497 MM    0.0154  257.32266  278.86462 95.01052
   2   7.579 MM    0.0168   13.51332   13.40776  4.98948

Totals :                   270.83598  292.27239
```

Compound **12i**

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   8.215 MM    0.0155   23.40919   25.09799  2.75320
   2   8.251 MM    0.0188   24.28689   21.54846  2.85642
   3   8.694 MM    0.0161  802.55859  829.74054 94.39038

Totals :                   850.25467  876.38698
```