Supporting Information for:

Diastereoselective Au-catalyzed allene cycloisomerizations to highly substituted cyclopentenes

Ryan D. Reeves, Alicia M. Phelps, William A. T. Raimbach, and Jennifer M. Schomaker

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI, 53706-1396

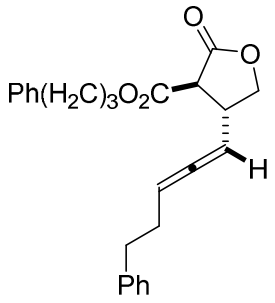
I. General Information.

All glassware was either oven dried at 130 °C or flame dried under vacuum and purged with nitrogen immediately prior to use. Unless otherwise specified, reagents were used as obtained from the supplier without further purification. Ph_3PAuCl was obtained from Strem Chemicals; Cy_3PAuCl was obtained from Sigma-Aldrich and used without additional purification. Tetrahydrofuran was passed through an alumina column before use or freshly distilled from Na/benzophenone ketyl. Dichloromethane was freshly distilled from calcium hydride or passed through an alumina column before use. Acetonitrile, toluene, and benzene were freshly distilled from calcium hydride immediately prior to use. Other solvents were purified using accepted procedures from the sixth edition of "Purification of Laboratory Chemicals".[1] Air- and moisture- sensitive reactions were performed using standard Schlenk techniques under an inert nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel 60 F24 plates containing a fluorescent indicator. Either ceric ammonium molybdate (CAM stain) or $KMnO_4$ were used to visualize the reaction products, unless otherwise specified. Preparative chromatography using a gradient method with mixtures of EtOAc and hexanes, unless otherwise specified, was performed using SilicaFlash P60 silica gel (230-400 mesh) via Still's method.[2]

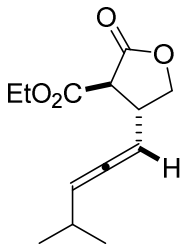
^1H NMR and ^{13}C NMR spectra were obtained using Bruker Avance-500 spectrometers. Chemical shifts are reported relative to the tetramethylsilane peak (δ 0.00 ppm). Accurate mass measurements were acquired at the University of Wisconsin, Madison, using a Micromass LCT (electrospray ionization or electron impact methods). The NMR and Mass Spectrometry facilities are funded by the NSF (CHE-1048642, CHE-0342998, CHE-9304546 and CHE-9208463), the University of Wisconsin as well as a generous gift by Paul J. Bender.

II. Experimental Procedures for C-H Insertion Reactions.

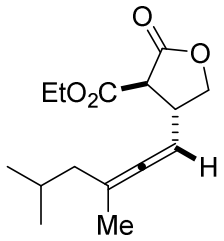
C-H insertion products **2a-m** were prepared and characterized according to procedures previously published in the literature.[3] Characterization data for new C-H insertion compounds **2e-f**, **2i**, **2k**, and **2m** is provided below.



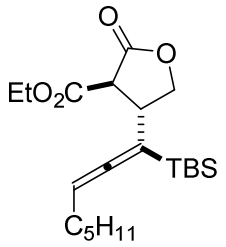
Compound 2e. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 1.05 g (2.68 mmol, 80%) of **2e** as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.22 – 7.14 (m, 6H), 5.41 – 5.34 (m, 1H), 5.16 (tq, *J* = 6.3, 3.1 Hz, 1H), 4.38 (ddd, *J* = 14.3, 8.8, 7.5 Hz, 1H), 4.28 – 4.15 (m, 2H), 3.84 (dt, *J* = 20.6, 8.6 Hz, 1H), 3.47 – 3.39 (m, 1H), 3.26 (dd, *J* = 18.8, 9.2 Hz, 1H), 2.75 – 2.66 (m, 4H), 2.45 – 2.27 (m, 2H), 2.04 – 1.96 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.81, 203.73, 171.30, 171.25, 167.00, 166.96, 141.04, 141.00, 140.88, 128.51, 128.47, 128.44, 128.41, 128.39, 128.38, 128.29, 126.22, 126.15, 126.07, 94.65, 94.51, 88.94, 88.90, 71.21, 71.11, 65.42, 65.39, 52.12, 51.74, 39.06, 39.02, 34.97, 34.85, 31.92, 31.90, 30.10, 30.08, 29.95. HRMS (ESI) *m/z* calculated for $C_{25}H_{26}O_4$ $[M + NH_4]^+$ 408.2169, found 408.2166.



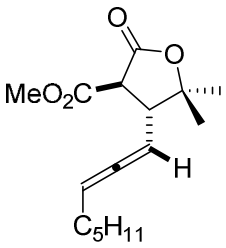
Compound 2f. Purified on silica gel using a 2-10% gradient of EtOAc in hexanes as eluent to afford 242 mg (1.02 mmol, 54%) of **2f** as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (td, *J* = 6.0, 2.6 Hz, 1H), 5.24 (dtd, *J* = 7.3, 5.9, 3.1 Hz, 1H), 4.54 (ddd, *J* = 8.8, 7.5, 5.0 Hz, 1H), 4.30 – 4.24 (m, 2H), 4.04 (ddd, *J* = 8.9, 7.9, 3.2 Hz, 1H), 3.62 – 3.51 (m, 1H), 3.44 (t, *J* = 8.6 Hz, 1H), 2.40 – 2.26 (m, 1H), 1.32 (td, *J* = 7.2, 2.2 Hz, 3H), 1.00 (ddd, *J* = 6.7, 3.3, 1.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 201.9, 171.5, 171.5, 167.1, 167.1, 102.9, 102.7, 90.0, 89.8, 71.5, 71.4, 62.3, 62.2, 52.0, 52.0, 39.5, 39.1, 27.8, 27.7, 22.2, 22.1, 14.1, 14.1. HRMS (ESI) *m/z* calculated for $C_{13}H_{18}O_4$ $[M + Na]^+$ 261.1097, found 261.1096.



Compound 2i. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 523 mg (1.96 mmol, 58%) of **2i** as a clear, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.07 (dqd, *J* = 5.5, 2.7, 1.5 Hz, 1H), 4.53 (dd, *J* = 8.8, 7.5 Hz, 1H), 4.26 (qt, *J* = 7.0, 1.9 Hz, 2H), 4.02 (ddd, *J* = 8.8, 7.9, 6.2 Hz, 1H), 3.52 (dddd, *J* = 11.5, 5.8, 3.1, 1.5 Hz, 1H), 3.41 (dd, *J* = 8.9, 0.9 Hz, 1H), 1.91 – 1.79 (m, 2H), 1.71 (ddd, *J* = 13.4, 6.9, 2.3 Hz, 1H), 1.67 (dd, *J* = 2.9, 1.6 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.92 – 0.87 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.8, 201.8, 171.7, 171.6, 167.2, 167.2, 103.2, 103.2, 87.2, 87.0, 71.8, 71.7, 62.2, 62.2, 52.2, 52.2, 43.5, 43.4, 40.1, 39.9, 26.3, 26.2, 22.5, 22.5, 22.5, 19.0, 18.9, 14.1, 14.1. HRMS (ESI) *m/z* calculated for $C_{15}H_{22}O_4$ $[M + Na]^+$ 289.1410, found 289.1407.



Compound 2k. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 307 mg (0.81 mmol, 53%) of **2k** of a 2:1 mixture of diastereomers as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) Major diastereomer: δ 5.13 (td, *J* = 6.9, 1.7 Hz, 1H), 4.56 – 4.52 (m, 1H), 4.24 (tdd, *J* = 8.1, 6.7, 1.0 Hz, 2H), 3.89 (td, *J* = 8.6, 4.2 Hz, 1H), 3.58 (d, *J* = 9.1 Hz, 1H), 3.49 – 3.40 (m, 1H), 2.02 – 1.96 (m, 2H), 1.37 (dtd, *J* = 8.6, 6.7, 1.9 Hz, 2H), 1.30 (td, *J* = 7.1, 3.1 Hz, 7H), 0.97 – 0.92 (m, 3H), 0.89 (overlapping signals, 9H), 0.07 (d, *J* = 4.6 Hz, 6H). Minor diastereomer: δ 5.07 (td, *J* = 7.0, 1.6 Hz, 1H), 4.53 – 4.47 (m, 1H), 4.33 – 4.27 (m, 2H), 3.89 (td, *J* = 8.6, 4.2 Hz, 1H), 3.61 (d, *J* = 9.8 Hz, 1H), 3.54 – 3.40 (m, 1H), 1.96 – 1.89 (m, 2H), 1.37 (dtd, *J* = 8.6, 6.7, 1.9 Hz, 2H), 1.30 (tt, *J* = 8.4, 3.1 Hz, 7H), 0.95 – 0.92 (m, 3H), 0.90 (overlapping signals, 9H), 0.08 – 0.06 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.8, 206.7, 171.8, 167.3, 167.3, 93.5, 90.5, 73.5, 73.1, 62.1, 62.0, 52.6, 52.6, 41.0, 40.8, 31.6, 31.5, 31.5, 29.4, 29.3, 28.5, 28.2, 26.7, 26.6, 26.6, 26.5, 26.3, 22.5, 22.5, 22.4, 17.9, 17.7, 14.1, 14.1, 14.0, 14.0, 14.0, -0.0, -5.5, -5.6, -5.7, -5.8. HRMS (ESI) *m/z* calculated for $C_{21}H_{36}O_4Si$ $[M + Na]^+$ 403.2275, found 403.2275.

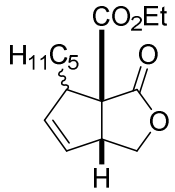


Compound 2m. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 3.00 g (10.7 mmol, 68%) of **2m** as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (qd, *J* = 6.7, 2.6 Hz, 1H), 5.06 (tq, *J* = 6.5, 3.2 Hz, 1H), 3.80 (s, 3H), 3.65 (d, *J* = 12.5 Hz, 1H), 3.61 (d, *J* = 12.4 Hz, 1H), 3.34 (dddd, *J* = 12.5, 9.8, 6.3, 2.6 Hz, 1H), 1.99 (dtdd, *J* = 15.6, 8.1, 5.0, 2.0 Hz, 2H), 1.52 (s, 3H), 1.43 – 1.34 (m, 1H), 1.34 – 1.26 (overlapping signals, 7H), 0.92 – 0.86 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.5, 204.5, 170.2, 170.2, 167.7, 167.7, 94.7, 94.5, 86.2, 86.2, 85.8, 85.7, 52.9, 52.9, 51.6, 51.3, 49.5, 49.3, 31.4, 31.3, 28.7, 28.6, 28.5, 28.5, 27.0, 27.0, 23.2, 23.2, 22.5, 22.5, 14.0, 14.0. HRMS (ESI) *m/z* calculated for $C_{16}H_{24}O_4$ [M + NH_4]$^+$ 298.2013, found 298.2010.

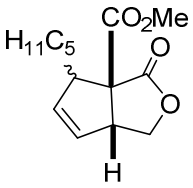
III. Experimental Procedures for Au-catalyzed Carbocyclizations.

General Procedure for Au-catalyzed Carbocyclizations:

A 250 mL round bottom flask equipped with a reflux condenser was charged with 92 mg PCy_3AuCl (0.025 equiv, 0.18 mmol) and 651 mg $Cu(OTf)_2$ (0.25 equiv, 1.81 mmol) in 35 mL dry toluene and allowed to stir for *ca.* 15 minutes at room temperature under N_2. To this was added 2.00 g of allene substrate **2m** (1.00 equiv, 7.10 mmol) in 35 mL toluene, and the reaction mixture heated to reflux for 24 h. The resulting dark brown solution was cooled to room temperature and 75 mL saturated aqueous NH_4Cl was added. The biphasic solution was stirred at room temperature for 2h, then diluted in EtOAc and washed with additional saturated aqueous NH_4Cl, followed by dilute NH_4OH, and then brine. The organics were dried over Na_2SO_4 and the volatiles removed *in vacuo* to afford crude carbocyclization products typically as yellow oils. Final purification was done *via* flash column chromatography on silica gel using 0-10% EtOAc in hexanes as eluent, unless indicated otherwise.

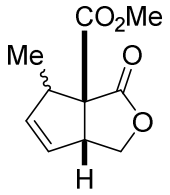


Compound 3a. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 72 mg (0.27 mmol, 63%) of **3a** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$), Major diastereomer: δ 5.84 (dt, *J* = 5.5, 2.0 Hz, 1H), 5.53 (dt, *J* = 5.3, 2.3 Hz, 1H), 4.44 (dd, *J* = 8.7, 7.3 Hz, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 4.17 (dd, *J* = 8.9, 1.8 Hz, 1H), 3.80 (dt, *J* = 7.1, 2.1 Hz, 1H), 3.51 (ddd, *J* = 9.2, 5.4, 2.4 Hz, 1H), 2.01 – 1.92 (m, 1H), 1.48 – 1.17 (m, 10H), 0.96 – 0.82 (m, 3H). Minor diastereomer: δ 5.89 (dt, *J* = 5.3, 2.4 Hz, 1H), 5.63 (dt, *J* = 5.8, 1.5 Hz, 1H), 4.41 (dd, *J* = 9.1, 6.0 Hz, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 4.23 (m, 1H), 4.02 – 3.94 (m, 1H), 3.37 – 3.27 (m, 1H), 1.58 (dt, *J* = 11.0, 4.2 Hz, 1H), 1.50 – 1.18 (m, 10H), 0.91 – 0.86 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 173.1, 169.6, 166.8, 136.3, 136.0, 129.2, 127.5, 70.3, 70.2, 63.8, 62.2, 62.2, 61.7, 53.4, 52.1, 51.4, 49.1, 31.9, 31.8, 31.6, 30.0, 28.4, 26.3, 22.6, 22.5, 14.1, 14.1, 14.0. HRMS (ESI) *m/z* calculated for $C_{15}H_{22}O_4$ $[M + H]^+$ 267.1591, found 267.1595.

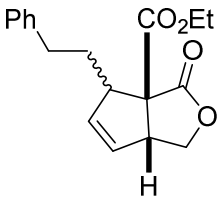


Compound 3b. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 128 mg (0.57 mmol, 68%) of **3b** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) Major diastereomer: δ 5.85 (dt, *J* = 5.8, 2.0 Hz, 1H), 5.54 (dt, *J* = 5.7, 2.3 Hz, 1H), 4.44 (dd, *J* = 9.0, 7.3 Hz, 1H), 4.16 (dd, *J* = 8.9, 2.0 Hz, 1H), 3.83 – 3.81 (m, 1H), 3.80 (s, 3H), 3.51 (ddt, *J* = 9.5, 5.1, 2.4 Hz, 1H), 2.01 – 1.90 (m, 1H), 1.48 – 1.17 (m, 8H), 0.91 – 0.86 (m, 3H). Minor diastereomer: δ 5.90 (dt, *J* = 5.8, 2.4 Hz, 1H), 5.63 (dt, *J* = 5.8, 1.5 Hz, 1H), 4.43 (s, 1H), 4.24 (d, *J* = 9.2 Hz,

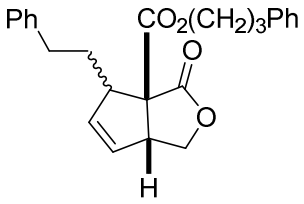
1H), 4.02 – 3.97 (m, 1H), 3.80 (s, 3H), 3.33 (dtd, *J* = 9.4, 3.7, 1.8 Hz, 1H), 1.55 – 1.47 (m, 1H), 1.49 – 1.17 (m, 8H), 0.96 – 0.73 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 173.0, 170.2, 167.3, 136.2, 135.9, 129.2, 127.6, 70.3, 70.2, 63.8, 61.6, 53.3, 53.2, 52.9, 52.4, 51.6, 49.1, 31.9, 31.8, 31.7, 30.0, 28.4, 26.4, 22.6, 22.5, 14.1, 13.9. HRMS (ESI) *m/z* calculated for $C_{14}H_{20}O_4$ $[M + NH_4]^+$ 270.1700, found 270.1696.



Compound 3c. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 210 mg (1.08 mmol, 60%) of **3c** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$), Major diastereomer: δ 5.73 – 5.67 (m, 1H), 5.52 (dt, *J* = 4.8, 2.3 Hz, 1H), 4.47 (ddd, *J* = 8.5, 7.3, 0.9 Hz, 1H), 4.16 (ddd, *J* = 8.9, 2.1, 0.8 Hz, 1H), 3.85 (dtd, *J* = 7.3, 2.1, 0.9 Hz, 1H), 3.80 (d, *J* = 1.2 Hz, 3H), 3.69 – 3.61 (m, 1H), 1.30 (dd, *J* = 7.5, 1.3 Hz, 3H). Minor diastereomer: δ 5.81 – 5.78 (m, 1H), 5.58 (dp, *J* = 5.8, 0.9 Hz, 1H), 4.43 (ddd, *J* = 9.2, 5.9, 1.0 Hz, 1H), 4.25 (dd, *J* = 9.2, 0.8 Hz, 1H), 4.03 (ddq, *J* = 5.1, 2.0, 1.0 Hz, 1H), 3.81 (d, *J* = 1.2 Hz, 3H), 3.44 – 3.38 (m, 1H), 1.04 (dd, *J* = 7.1, 1.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 172.9, 169.9, 167.3, 137.9, 137.5, 128.3, 127.3, 70.4, 70.3, 64.0, 61.7, 53.2, 53.2, 53.0, 48.6, 47.5, 46.1, 16.8, 15.5. HRMS (ESI) *m/z* calculated for $C_{10}H_{12}O_4$ $[M + H]^+$ 197.0808, found 197.0808.

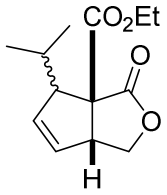


Compound 3d. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 89 mg (0.29 mmol, 72%) of **3d** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) Major diastereomer: δ 7.30 – 7.21 (m, 3H), 7.21 – 7.11 (m, 2H), 5.82 (dt, *J* = 5.7, 2.0 Hz, 1H), 5.55 (dt, *J* = 5.8, 2.4 Hz, 1H), 4.44 (overlapping t, *J* = 6.4 Hz, 1H), 4.29 – 4.21 (m, 3H), 4.19 (dd, *J* = 8.9, 1.7 Hz, 1H), 3.80 (dt, *J* = 7.1, 2.0 Hz, 1H), 3.57 (ddq, *J* = 8.7, 6.3, 2.3 Hz, 1H), 2.86 – 2.73 (m, 1H), 2.59 (dd, *J* = 9.2, 7.5 Hz, 1H), 2.31 (ddt, *J* = 13.3, 9.8, 6.5 Hz, 1H), 1.75 (dtd, *J* = 13.8, 9.4, 5.7 Hz, 1H), 1.28 (overlapping t, 3H). Minor diastereomer: δ 7.30 – 7.21 (m, 3H), 7.21 – 7.11 (m, 2H), 5.96 (dt, *J* = 5.8, 2.4 Hz, 1H), 5.69 (dt, *J* = 5.8, 1.5 Hz, 1H), 4.44 (overlapping t, *J* = 6.4 Hz, 1H), 4.29 – 4.21 (m, 3H), 4.02 (dt, *J* = 5.8, 2.0 Hz, 1H), 3.41 (ddq, *J* = 9.3, 3.5, 1.8 Hz, 1H), 2.86 – 2.73 (m, 1H), 2.59 (dd, *J* = 9.2, 7.5 Hz, 1H), 1.94 (dtd, *J* = 12.9, 8.6, 8.0, 4.3 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.28 (overlapping t, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 173.1, 169.5, 166.7, 141.9, 141.5, 135.9, 135.7, 134.2, 134.1, 129.8, 129.3, 129.2, 128.5, 128.5, 128.3, 128.2, 127.9, 126.0, 125.8, 70.3, 70.1, 63.7, 62.3, 62.3, 61.7, 53.4, 51.9, 50.9, 49.2, 34.9, 33.7, 33.0, 31.9, 14.1, 14.0. HRMS (ESI) *m/z* calculated for $C_{18}H_{20}O_4$ $[M + NH_4]^+$ 318.1700, found 318.1699.

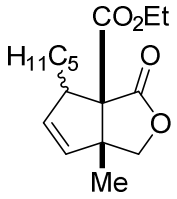


Compound 3e. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 180 mg (0.49 mmol, 69%) of **3e** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) Major diastereomer: δ 7.36 – 7.03 (m, 10H), 5.82 (dt, *J* = 5.8, 2.1 Hz, 1H), 5.55 (dt, *J* = 5.7, 2.4 Hz, 1H), 4.43 (dt, *J* = 9.1, 6.6 Hz, 1H), 4.20 (d, *J* = 2.1 Hz, 2H), 4.20 – 4.15 (m, 1H), 3.78 (dp, *J* = 6.3, 2.1 Hz, 1H), 3.57 (ddq, *J* = 8.6, 6.4, 2.3 Hz, 1H), 2.79 (qdd, *J* = 13.7, 9.7, 6.1 Hz, 1H), 2.68

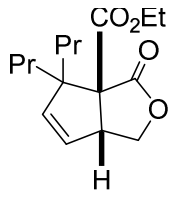
(td, J = 8.2, 7.7, 2.5 Hz, 2H), 2.60 (dd, J = 9.7, 7.0 Hz, 1H), 2.33 (ddt, J = 13.2, 9.9, 6.5 Hz, 1H), 2.02 – 1.93 (m, 2H), 1.76 (dtd, J = 13.8, 9.4, 5.6 Hz, 1H). Minor diastereomer: δ 7.31 – 7.07 (m, 10H), 5.97 (dt, J = 5.8, 2.4 Hz, 1H), 5.70 (dt, J = 5.9, 1.5 Hz, 1H), 4.43 (dt, J = 9.1, 6.6 Hz, 2H), 4.26 (d, J = 9.2 Hz, 1H), 4.22 – 4.15 (m, 2H), 4.02 – 3.96 (m, 1H), 3.43 (ddd, J = 9.7, 4.1, 2.0 Hz, 1H), 2.79 (qdd, J = 13.7, 9.7, 6.1 Hz, 1H), 2.68 (td, J = 8.2, 7.7, 2.5 Hz, 2H), 2.60 (dd, J = 9.7, 7.0 Hz, 1H), 2.03 – 1.93 (m, 2H), 1.94 – 1.90 (m, 1H), 1.65 – 1.55 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 172.9, 169.5, 166.7, 141.8, 141.4, 140.7, 140.7, 135.9, 135.7, 129.8, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 127.9, 126.1, 126.1, 126.1, 125.9, 70.2, 70.1, 65.4, 65.4, 63.8, 61.7, 53.4, 51.9, 50.9, 49.2, 34.9, 33.8, 33.1, 31.9, 31.9, 30.0, 29.9. HRMS (ESI) *m/z* calculated for $C_{25}H_{26}O_4$ $[M + NH_4]^+$ 408.2169, found 408.2167.



Compound 3f. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 18 mg (0.08 mmol, 36%) of **3f** as a yellow oil. Isolated as a single diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) Major diastereomer: δ 5.91 (dt, J = 5.8, 2.0 Hz, 1H), 5.55 (ddd, J = 5.9, 2.8, 2.0 Hz, 1H), 4.38 (dd, J = 9.0, 7.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 4.18 (dd, J = 9.0, 1.7 Hz, 1H), 3.74 (dt, J = 7.0, 2.1 Hz, 1H), 3.38 (ddt, J = 8.5, 4.5, 2.1 Hz, 1H), 2.18 (dp, J = 8.6, 6.7 Hz, 1H), 1.30 (t, J = 7.2 Hz, 3H), 1.08 (d, J = 6.6 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 170.3, 135.1, 127.7, 69.4, 62.2, 62.2, 59.0, 54.4, 27.5, 23.0, 21.2, 14.1. HRMS (ESI) *m/z* calculated for $C_{13}H_{18}O_4$ $[M + H]^+$ 239.1278, found 239.1274.

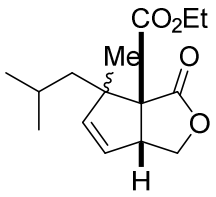


Compound 3g. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 204 mg (0.73 mmol, 54%) of **3g** as a light brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) Major diastereomer: δ 5.75 (dd, *J* = 5.7, 1.6 Hz, 1H), 5.40 (dd, *J* = 5.7, 2.7 Hz, 1H), 4.33 – 4.16 (m, 2H), 4.21 (d, *J* = 8.8 Hz, 1H), 4.05 (d, *J* = 8.8 Hz, 1H), 3.58 (dddd, *J* = 9.2, 6.0, 2.8, 1.7 Hz, 1H), 1.87 (ddt, *J* = 12.7, 8.6, 5.9 Hz, 1H), 1.48 (ddd, *J* = 13.0, 9.2, 5.0 Hz, 1H), 1.44 – 1.38 (m, 1H), 1.36 – 1.26 (m, 8H), 1.12 (s, 3H), 0.92 – 0.85 (m, 3H). Minor diastereomer: δ 5.95 (dd, *J* = 5.7, 2.6 Hz, 1H), 5.52 (dd, *J* = 5.7, 1.3 Hz, 1H), 4.28 (d, *J* = 7.2 Hz, 2H), 4.33 – 4.16 (m, 1H), 4.24 (d, *J* = 7.1 Hz, 1H), 3.27 (dq, *J* = 6.4, 3.4 Hz, 1H), 1.87 (ddt, *J* = 12.7, 8.6, 5.9 Hz, 1H), 1.48 (ddd, *J* = 13.0, 9.2, 5.0 Hz, 1H), 1.44 – 1.38 (m, 2H), 1.36 – 1.26 (m, 8H), 1.12 (s, 3H), 0.92 – 0.85 (m, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 173.8, 168.3, 166.6, 135.5, 134.6, 134.3, 132.9, 75.1, 74.5, 64.9, 61.9, 61.5, 58.3, 56.3, 51.9, 49.5, 32.4, 31.9, 31.9, 28.9, 28.6, 27.5, 22.6, 19.4, 17.9, 14.2, 14.2, 14.1, 14.0. HRMS (ESI) *m/z* calculated for $C_{16}H_{24}O_4$ $[M + H]^+$ 281.1747, found 281.1746.

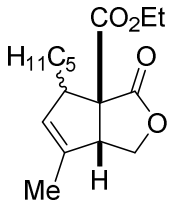


Compound 3h. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 31 mg (0.11 mmol, 49%) of **3h** as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65 (dd, *J* = 5.9, 2.3 Hz, 1H), 5.56 (dd, *J* = 5.9, 1.8 Hz, 1H), 4.32 (dd, *J* = 8.8, 6.5 Hz, 1H), 4.31 – 4.17 (m, 2H), 4.14 (dd, *J* = 8.8, 1.1 Hz, 1H), 4.04 (dtd, *J* = 6.6, 2.1, 1.1 Hz, 1H), 1.91 – 1.74 (m, 2H), 1.67

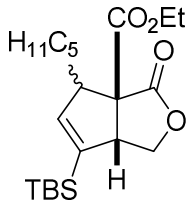
(tqd, J = 12.2, 7.1, 5.0 Hz, 1H), 1.51 – 1.45 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.29 – 1.16 (m, 2H), 1.15 – 1.03 (m, 1H), 0.93 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 167.6, 139.9, 127.3, 69.2, 66.2, 62.1, 58.4, 50.9, 39.0, 36.8, 18.6, 17.4, 14.9, 14.7, 14.0. HRMS (ESI) *m/z* calculated for $C_{16}H_{24}O_4$ $[M + H]^+$ 281.1747, found 281.1744.



Compound 3i. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 13 mg (0.05 mmol, 26%) of **3i** as a brown oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.91 (dd, J = 5.9, 2.3 Hz, 1H), 5.52 (ddd, J = 7.9, 5.8, 1.8 Hz, 1H), 4.30 (dddd, J = 16.5, 13.1, 6.9, 1.8 Hz, 2H), 4.15 (dd, J = 8.9, 1.1 Hz, 1H), 4.08 – 4.04 (m, 1H), 1.79 – 1.61 (m, 2H), 1.36 – 1.30 (m, 5H), 1.07 (s, 3H), 1.00 (d, J = 6.5 Hz, 3H), 0.96 (d, J = 6.5 Hz, 3H). Minor diastereomer: δ 5.75 (dd, J = 5.8, 2.4 Hz, 1H), 5.52 (ddd, J = 7.9, 5.8, 1.8 Hz, 1H), 4.22 (dqd, J = 10.8, 7.1, 1.0 Hz, 2H), 4.15 (dd, J = 8.9, 1.1 Hz, 1H), 4.09 – 4.04 (m, 1H), 1.80 – 1.62 (m, 2H), 1.48 (s, 3H), 1.36 – 1.29 (m, 5H), 0.92 (d, J = 6.7 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 172.1, 167.2, 167.0, 141.5, 140.9, 127.1, 126.9, 68.9, 68.8, 67.0, 66.9, 62.1, 62.0, 54.9, 54.8, 49.7, 48.9, 48.0, 43.0, 25.6, 25.4, 25.2, 25.1, 24.6, 24.6, 23.1, 20.3, 14.1, 14.1. HRMS (ESI) *m/z* calculated for $C_{15}H_{22}O_4$ $[M + H]^+$ 267.1591, found 267.1588.

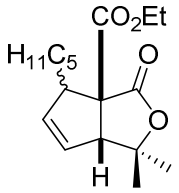


Compound 3j. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 12 mg (0.04 mmol, 30%) of **3j** as a brown oil. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 523 mg (1.96 mmol, 58%) as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$), Major diastereomer: δ 5.46 (q, *J* = 1.7 Hz, 1H), 4.41 – 4.19 (m, 4H), 3.61 (dt, *J* = 7.5, 1.8 Hz, 1H), 3.44 (ddd, *J* = 9.8, 5.2, 2.5 Hz, 1H), 1.98 – 1.87 (m,1H), 1.72 (dt, *J* = 2.5, 1.3 Hz, 3H), 1.36 – 1.22 (m, 10H), 0.93 – 0.82 (m, 3H). Minor diastereomer: δ 5.52 (q, *J* = 1.9 Hz, 1H), 4.41 – 4.19 (m, 4H), 3.80 (ddt, *J* = 5.0, 2.7, 1.4 Hz, 1H), 3.24 – 3.18 (m, 1H), 1.97 – 1.88 (m, 1H), 1.76 (q, *J* = 1.4 Hz, 3H), 1.36 – 1.18 (m, 10H), 0.93 – 0.83 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 173.3, 169.7, 167.0, 136.5, 134.9, 130.2, 130.1, 68.1, 68.0, 64.2, 62.1, 62.1, 62.0, 56.0, 51.7, 51.0, 50.6, 31.9, 31.9, 31.8, 30.5, 28.4, 26.3, 22.6, 22.5, 14.1, 14.1, 14.1, 14.0. HRMS (ESI) *m/z* calculated for $C_{16}H_{24}O_4$ $[M + H]^+$ 281.1747, found 281.1749.

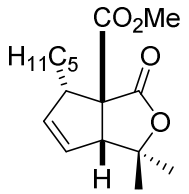


Compound 3k. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 22 mg (0.06 mmol, 42%) of **3k** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) Major diastereomer: δ 6.04 (t, *J* = 1.9 Hz, 1H), 4.47 (dd, *J* = 8.9, 7.8 Hz, 1H), 4.25 (p, *J* = 6.7 Hz, 3H), 4.13 (dd, *J* = 8.9, 3.5 Hz, 1H), 3.90 (ddt, *J* = 7.8, 3.5, 1.6 Hz, 1H), 3.56 (ddt, *J* = 9.5, 5.7, 1.8 Hz, 1H), 1.94 – 1.84 (m, 1H), 1.68 (dtd, *J* = 8.3, 6.2, 2.1 Hz, 1H), 1.49 – 1.38 (m, 2H), 1.36 – 1.24 (m, 5H), 0.90 – 0.88 (m, 4H), 0.87 (s, 9H), 0.07 (d, *J* = 6.2 Hz, 6H). Minor diastereomer: δ 6.09 (t, *J* = 2.3 Hz, 1H), 4.42 (dd, *J* = 9.3, 5.9 Hz, 1H), 4.32 – 4.25 (m, 3H), 4.03 (ddt, *J* = 6.3, 2.0, 1.0 Hz, 1H), 3.63 – 3.57 (m, 1H), 2.03 – 1.94 (m, 1H), 1.68 (dtd, *J* = 8.3, 6.2, 2.1 Hz, 1H), 1.46 – 1.39 (m, 2H), 1.36 – 1.22 (m, 5H), 0.91 – 0.89 (m, 4H), 0.87 (s, 9H), 0.09 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 173.4, 170.2, 170.0, 168.0, 147.5, 147.5, 140.6, 139.2, 70.9, 63.0, 62.2, 62.0, 58.5, 53.4, 37.3, 36.1, 31.9, 31.5, 30.5, 28.3, 26.6, 26.3, 23.7, 22.5, 22.5, 22.4, 18.8, 17.1, 16.9, 14.1, 14.1, 14.0, 14.0, 13.9, 1.0, -4.7, -5.6, -5.9, -6.3. HRMS (ESI) *m/z* calculated for $C_{21}H_{36}O_4Si$ $[M + H]^+$ 381.2456, found 381.2455.



Compound 3l. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 501 mg (1.70 mmol, 81%) of a 6:1 mixture of **3l** as a brown oil. Partial separation of the major diastereomer was achieved *via* purification of the mixture of diastereomers on silica gel using a 0-20% gradient of Et_2O in hexanes to afford 370 mg of the major diastereomer in >19:1 *dr*. ^{1}H NMR (500 MHz, $CDCl_3$), Major diastereomer: δ 5.83 (dt, *J* = 5.8, 2.1 Hz, 1H), 5.54 (dt, *J* = 5.8, 2.4 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.64 (q, *J* = 2.1 Hz, 1H), 3.45 (ddq, *J* = 9.8, 5.8, 2.1 Hz, 1H), 1.97 (m, 1H), 1.50 (s, 3H), 1.40 (d, *J* = 7.2 Hz, 3H), 1.36 – 1.24 (m, 10H), 0.93 – 0.84 (m, 3H). Minor diastereomer: δ 5.86 (dt, *J* = 5.9, 2.3 Hz, 1H), 5.65 (dt, *J* = 5.9, 1.7 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.82 (q, *J* = 2.1 Hz, 1H), 3.36 (dtt, *J* = 10.9, 4.3, 1.9 Hz, 1H), 1.97 (m, 1H), 1.50 (s, 3H), 1.40 (d, *J* = 7.2 Hz, 3H), 1.36 – 1.24 (m, 10H), 0.92 – 0.84 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 171.7, 170.9, 168.5, 135.4, 135.4, 127.4, 125.8, 84.9, 84.0, 65.7, 64.5, 62.5, 62.3, 62.2, 58.6, 53.8, 53.4, 32.1, 31.9, 31.8, 30.8, 29.6, 28.8, 28.1, 26.8, 25.2, 24.9, 22.5, 22.5, 22.5, 14.2, 14.0, 14.0. HRMS (ESI) *m/z* calculated for $C_{17}H_{26}O_4$ $[M + H]^+$ 295.1904, found 295.1901.

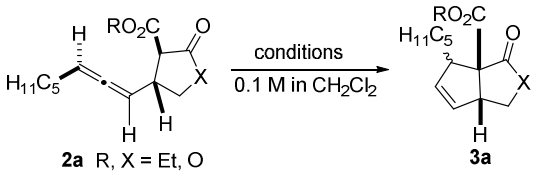


Compound 3m. Purified on silica gel using a 0-10% gradient of EtOAc in hexanes as eluent to afford 1.67 g (6.00 mmol, 85%) of a 6:1 mixture of **3m** as a brown oil. Partial separation of the major diastereomer was achieved *via* purification of the mixture of diastereomers on silica gel using a 0-20% gradient of Et_2O in hexanes to afford 754 mg of the major diastereomer in >19:1 *dr*. ^{1}H NMR (500 MHz, $CDCl_3$), Major diastereomer: δ 5.84 (dt, *J* = 5.8, 2.1 Hz, 1H), 5.54 (dt, *J* = 5.8, 2.3 Hz, 1H), 3.82 (s, 3H), 3.65 (q, *J* = 2.1 Hz, 1H), 3.47 – 3.40 (m, 1H), 2.02 – 1.93 (m, 1H), 1.49 (s, 3H), 1.44 – 1.37 (m, 1H), 1.34 (s, 3H), 1.33 – 1.24 (m, 4H), 0.88 (tt, *J* = 4.8, 2.5 Hz, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 171.5, 135.3, 125.8, 84.0, 64.4, 62.5, 53.6, 53.3, 31.8, 30.8, 29.6, 28.1, 25.2, 22.5, 14.0. HRMS (ESI) *m/z* calculated for $C_{16}H_{24}O_4$ $[M + H]^+$ 281.1747, found 281.1747.

IV. Additional Screening Results for Au(I) Carbocyclizations.

Early carbocyclization conditions utilizing lactone-containing **3a** and a mixed Au/Ag system failed to yield the desired cyclopentene **3a** (Table S1, entries 1, 2); upon addition of camphorsulfonic acid (CSA), some conversion to 3a was observed (entry 3). Addition of $Bi(OTf)_3$ promoted complete conversion of **2a** to **3a**, albeit with low *dr* (entry 4). The addition of triflic acid promoted cyclization of **2a** to cyclopentene **3a** in 90% yield and 2.5:1 *dr* (entry 5). Although the addition of triflic acid with a mixed Au(I)/Ag(I) system did provide good conversion with moderate diastereoselectivity, these results could not be replicated when a new bottle of Ph_3PAuCl was used. The observed reactivity was presumably due to an unidentified contaminant present in the original bottle of PPh_3AuCl.

Table S1. Initial catalyst screening conditions.

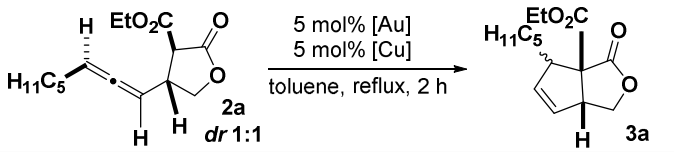


2a R, X = Et, O **3a**

entry	R, X	catalyst	additive	conversion	*dr*
1	Et, O	$(Ph_3P)AuCl$	AgOTf	0%	---
2	Et, O	$(Ph_3P)AuCl$	AgOTf, Tf_2NH	0%	---
3	Et, O	$(Ph_3P)AuCl$	AgOTf, CSA	10%	1:1
4	Et, O	$(Ph_3P)AuCl$	AgOTf, $Bi(OTf)_3$	100%	1:1
5	Et, O	$(Ph_3P)AuCl$	AgOTf, TfOH	90%	2.5:1

Initial studies on gold carbocyclizations of allenes using gold catalysts with varying degrees of steric and electronic properties and copper additives are shown in Table S2. Treatment of a 1:1 mix of stereoisomers **2a** with Ph_3PAuCl and $Cu(OTf)_2$ resulted in cyclopentene **3a** with excellent conversion as a 1.1:1 mix of diastereomers. Changing the ligands on the Au species resulted in slightly diminished yields and 1:1 *dr* (entries 4 and 5). Electron rich alkyl phosphine ligands (entry 7) improved the *dr* of the reaction, however a reduction of yield was observed. Phosphite ligands also resulted in an increase in *dr* with decreased yields (entry 9). Au(III) catalysts were not capable of converting the allene to the desired cyclopentene (entry 10). Using a copper salt with electron rich ligands (entry 11) also resulted in no conversion to cyclopentene **3a**. In addition to a variety of different gold catalysts, chiral phosphoric acids were also utilized as additives, however no appreciable increase in the *dr* of cyclopentene **3a** was observed. As with the bulky phosphine gold catalysts (entries 2, 4, and 5), it was hypothesized that the chirality induced by the chiral phosphoric acid species was too far removed from the reactive sites on the molecule to induce a noticeable increase in *dr*.[4]

Table S2. Additional Au Catalysts Screened.



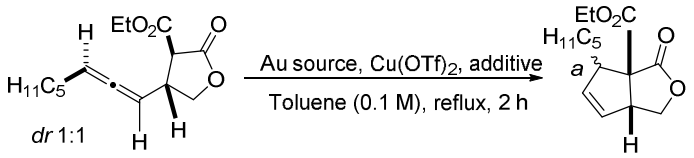
entry	Au source	Cu source	conversion[a]	*dr*
1	Ph_3PAuCl	$Cu(OTf)_2$	100%	1.1:1
2	$dppm(AuCl)_2$	$Cu(OTf)_2$	100%	1.1:1
3	AuIPrCl	$Cu(OTf)_2$	88%	1.3:1
4	$^tBu_2$JohnPhosAuCl	$Cu(OTf)_2$	81%	1:1
5	Cy_2JohnPhosAuCl	$Cu(OTf)_2$	100%	1:1
6	$^tBu_3PAuCl$	$Cu(OTf)_2$	100%	1:1
7	$(o\text{-tolyl})_3PAuCl$	$Cu(OTf)_2$	70%	1:1
8	Cy_3PAuCl	$Cu(OTf)_2$	85%	1.3:1
9	$(PhO)_3PAuCl$	$Cu(OTf)_2$	55%	1.6:1
10	$AuCl_3$	$Cu(OTf)_2$	0%	--
11	Ph_3PAuCl	$Cu(OAc)_2$	0%	--
12	Ph_3PAuCl	(CuOTf)-toluene	82%	1:1

[a] Mesitylene used as an internal standard.

To further improve the observed diastereoselectivity of the carbocyclization reaction, a series of Au sources were screened with copper additives (Table S3). Chiral digold sources (entries 1 and 2) resulted in no conversion to cyclopentene **3a**. The use of (*S*)-MonoPhosAuCl resulted in some conversion to cyclopentene **3a** (entry 3); however, there was no noticeable increase in observed *dr* when compared to Ph_3PAuCl or Cy_3PAuCl. Adding a chiral phosphoric acid additive had no noticeable improvement on the observed *dr* of the carbocyclization reaction (entries 4-8) when compared to the standardized conditions employing 2.5 mol% Ph_3PAuCl and 25 mol% $Cu(OTf)_2$ in refluxing toluene. In accord with Toste's observations, these results suggest that the chirality introduced in either the Au(I) ligand or *via* chiral phosphoric acid additives is too far removed from the reactive sites within the molecule and the newly formed stereocenter to impart control over the diastereoselectivity of the carbocyclization reactions.[4]

Once a competent Au(I) source was found, modifications to the original reaction conditions were explored (Table S4). Treatment of allene **2a** with 5 mol% Ph_3PAuCl and 5 mol% $Cu(OTf)_2$ resulted in 72% yield of cyclopentene **3a** as a 1.3:1 mixture of diastereomers

Table S3. Chiral Au(I) Sources and Chiral Additives.

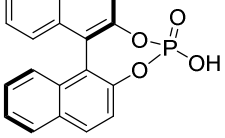


2a **3a**

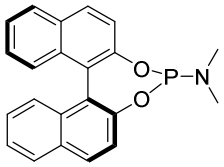
entry	Au source	additive	NMR yield	*dr*
1	*R*-DTBM-SEGPHOS(AuCl)$_2$	none	0%	--
2	*R*-SEGPHOS(AuCl)$_2$	none	0%	--
3	*S*-MonoPhosAuCl	none	46%	1.6:1
4	AuPPh$_3$Cl	1 equiv. **A**	76%	1.6:1
5	dppm(AuCl)$_2$	1 equiv. **A**	22%	1.5:1
6	*S*-MonoPhosAuCl	1 equiv. **A**	83%	1.8:1
7	*R*-MonoPhosAuCl	1 equiv. **A**	53%	1.5:1
8	*S*-MonoPhosAuCl	5 mol% **A**	76%	1.7:1

[a] *dr* of the stereocenter *a*

A:

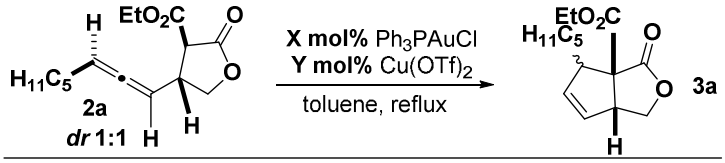


S-MonoPhos:



(entry 1). Decreasing the amount of gold to 1 mol% increased the *dr* to 1.7:1, however the yield of the reaction was reduced (entry 2). Increasing the catalyst loading to 5 mol% Ph$_3$PAuCl and 25 mol% Cu(OTf)$_2$ resulted in a slight increase in *dr*, which continued to improve as more Cu was employed relative to Au (entries 3 and 4). Extending the reaction time from 2 h to 12 h compensated for the loss in yield due to lower Au loading while maintaining the *dr* (entry 5). Ultimately, 2.5 mol% Ph$_3$PAuCl and 25 mol% Cu(OTf)$_2$ resulted in 68% yield of cyclopentene **3a** as a 1.6:1 mixture of diastereomers when the reaction time was further extended to 24 hours (entry 7). As a final step to increase the overall yield, Cy$_3$PAuCl carried out the conversion of allene **2a** to cyclopentene **3a** in 93% yield as a 1.8:1 mixture of diastereomers (entry 8).

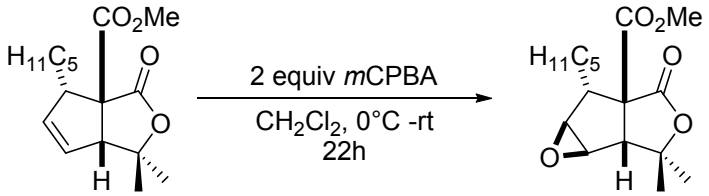
Table S4. Studies on the impact of the Au:Cu Ratio.



entry	X	Y	time (h)	NMR yield[a]	*dr*
1	5	5	2	72%	1.3 : 1
2	1	5	2	35%	1.7 : 1
3	5	25	2	41%	1.8 : 1
4	1	10	2	34%	2.0 : 1
5	1	10	12	50%	1.9 : 1
6	1	25	2	36%	1.4 : 1
7	2.5	25	24	68%	1.6 : 1
8[b]	2.5	25	24	93%	1.8 : 1

[a]Yield determined by relative integration to mesitylene internal standard.
[b]$Au(PCy_3)Cl$ used in place of $Au(PPh_3)Cl$.

V. Experimental Procedures for Olefin Functionalization.

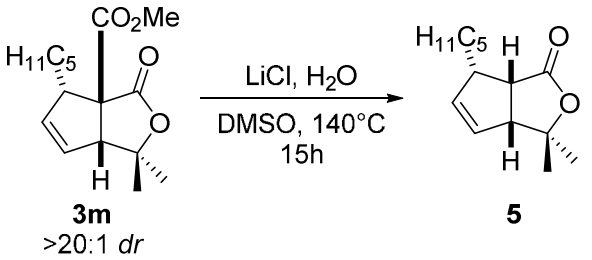


3m
>20:1 dr

4

Epoxide 4. A 50 mL round bottom flask was charged with 284 mg (1.01 mmol, 1.00 equiv) cyclopentene **3m** in 10.1 mL CH_2Cl_2 and cooled to 0 °C. A portion of 453 mg (2.02 mmol, 2.00 equiv) ≥77% *m*CPBA (obtained from Sigma Aldrich; used without additional purification) was added slowly in one portion and the resulting solution slowly warmed to room temperature and stirred for 22 h. A 10 mL portion of saturated aqueous $Na_2S_2O_3$ was added and the mixture stirred at room temperature for an additional 30 minutes. The biphasic solution was poured into a separatory funnel containing 25 mL saturated aqueous $NaHCO_3$ and extracted with 3 x 25 mL portions of CH_2Cl_2. The combined organics were dried over Na_2SO_4, and the volatiles removed *in vacuo* to afford the crude epoxide. The crude material was purified via column

chromatography using 0-20% EtOAc in hexanes as eluent to give 207 mg (0.70 mmol, 69% yield) epoxide **4** as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.61 (ddd, *J* = 11.8, 2.7, 1.5 Hz, 2H), 2.97 (d, *J* = 1.7 Hz, 1H), 2.74 (ddd, *J* = 9.6, 5.7, 1.2 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.87 – 1.77 (m, 1H), 1.64 (s, 3H), 1.48 – 1.40 (m, 2H), 1.37 (s, 3H), 1.36 – 1.29 (m, 4H), 0.89 (ddt, *J* = 7.2, 4.3, 2.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 170.6, 81.6, 60.0, 59.2, 56.3, 56.2, 53.5, 51.1, 31.7, 28.7, 28.2, 25.6, 25.2, 22.5, 14.0. HRMS (ESI) *m/z* calculated for $C_{16}H_{24}O_5$ $[M + H]^+$ 297.1697, found 297.1692.

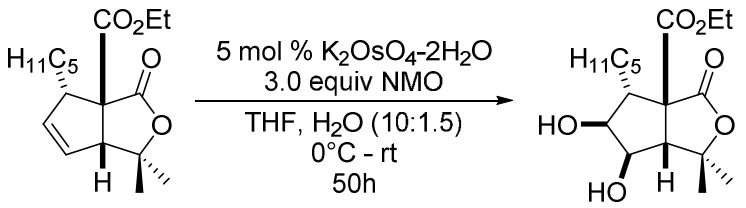


3m
>20:1 *dr*

5

Cyclopentene 5. A round bottom flask equipped with a reflux condenser was charged with 292 mg (1.04 mmol, 1.00 equiv) methyl ester **3m** in 10.4 mL DMSO. A portion of 132 mg (3.12 mmol, 3.00 equiv) LiCl was added, followed by 0.52 mL of H_2O. The resulting solution was heated to 140°C for 15 h, cooled to room temperature and poured into a separatory funnel containing 25 mL H_2O and extracted with 3 x 25 mL portions EtOAc. The combined organics were washed with brine, dried over Na_2SO_4, and the volatiles removed *in vacuo*. The crude residue was purified *via* flash chromatography using a 0-10% gradient of EtOAc in hexanes to afford 198 mg (0.89 mmol, 86% yield) decarboxylated product **5** as a clear, pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (dt, *J* = 5.8, 2.0 Hz, 1H), 5.64 (dt, *J* = 5.8, 2.3 Hz, 1H), 3.33 (t, *J* = 8.2 Hz, 1H), 3.29 (dq, *J* = 8.0, 2.4 Hz, 1H), 2.97 (dddd, *J* = 13.0, 8.6, 5.8, 1.7 Hz, 1H), 1.99 – 1.90 (m, 1H), 1.51 – 1.42 (m, 2H), 1.42 (s, 3H), 1.38 (s, 3H), 1.36 – 1.24 (m, 5H), 0.89 (td, *J* = 6.0, 5.1, 2.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 137.4, 127.3, 83.5, 57.1, 48.3, 46.0,

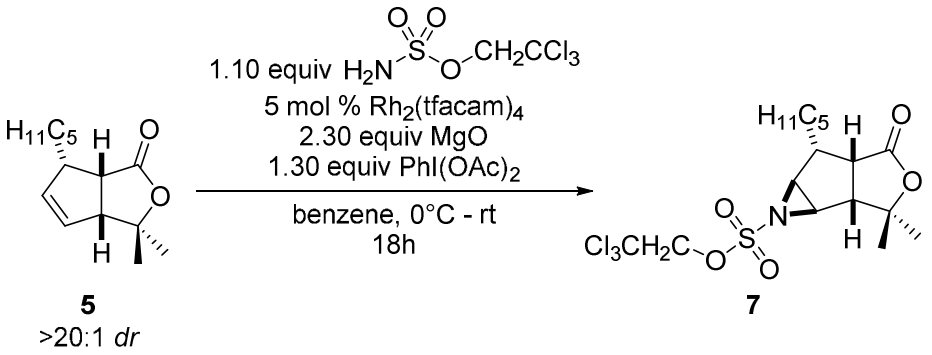
31.9, 30.2, 29.7, 28.6, 24.5, 22.6, 14.1. HRMS (ESI) *m/z* calculated for $C_{14}H_{22}O_2$ $[M + H]^+$ 223.1693, found 223.1691.



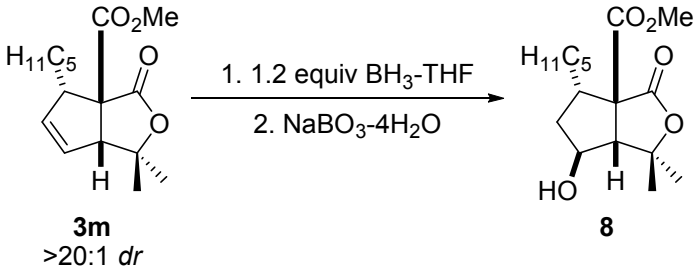
3l
>20:1 *dr*

6

Compound 6. A round bottom flask was charged with 56 mg (0.19 mmol, 1.00 equiv) cyclopentene **3l** in 1.9 mL THF. A portion of 67 mg (0.57 mmol, 3.00 equiv) NMO was added, followed by 0.29 mL of H_2O. The resulting solution was cooled to 0 °C, 3.7 mg (0.01 mmol, 0.05 equiv) $K_2OsO_4 \cdot 2H_2O$ was added, and the reaction mixture slowly warmed to rt and stirred for 50 h. The crude reaction mixture was poured into 15 mL H_2O and extracted with 3 x 15 mL portions of EtOAc. The combined organics were dried over Na_2SO_4 and the volatiles removed *in vacuo*. The crude material was purified via column chromatography using a 0-50% gradient of EtOAc in hexanes as eluent to afford 44 mg (0.13 mmol, 70% yield) diol **6** as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34 – 4.23 (m, 2H), 4.20 (q, *J* = 4.3 Hz, 1H), 3.80 (td, *J* = 6.6, 4.2 Hz, 1H), 2.87 – 2.80 (m, 2H), 2.70 (dd, *J* = 19.8, 5.7 Hz, 2H), 1.78 (dddd, *J* = 13.7, 10.6, 6.9, 5.4 Hz, 1H), 1.53 (s, 3H), 1.47 (s, 3H), 1.42 (dddd, *J* = 13.3, 10.4, 6.8, 4.1 Hz, 2H), 1.35 – 1.24 (m, 8H), 0.92 – 0.84 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 171.4, 83.1, 77.8, 74.2, 62.9, 62.8, 60.1, 49.0, 32.0, 31.2, 28.5, 27.9, 24.6, 22.5, 14.0, 13.9. HRMS (ESI) *m/z* calculated for $C_{17}H_{28}O_6$ $[M + NH_4]^+$ 346.2224, found 346.2220.



Aziridine 7. A portion of 171 mg (0.77 mmol, 1.00 equiv) decarboxylated cyclopentene **5** was converted to aziridine **7** using conditions previously described by DuBois.[5] The crude material was purified via column chromatography using a 0-10% gradient of EtOAc in hexanes ($KMnO_4$ stain) to give 227 mg (0.51 mmol, 66% yield) aziridine as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (s, 2H), 4.65 – 4.56 (m, 2H), 3.77 (d, *J* = 8.6 Hz, 1H), 3.69 (d, *J* = 8.5 Hz, 1H), 2.14 (ddd, *J* = 14.1, 11.4, 4.5 Hz, 1H), 1.74 (ddd, *J* = 16.1, 9.9, 3.5 Hz, 1H), 1.60 – 1.52 (m, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.35 – 1.30 (m, 5H), 0.91 – 0.86 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 133.8, 133.7, 93.4, 84.1, 78.2, 74.2, 56.6, 55.2, 37.4, 31.8, 30.5, 25.0, 24.5, 22.5, 14.0. HRMS (ESI) *m/z* calculated for $C_{16}H_{24}Cl_3NO_5S$ $[M + H]^+$ 448.0514, found 448.0509.

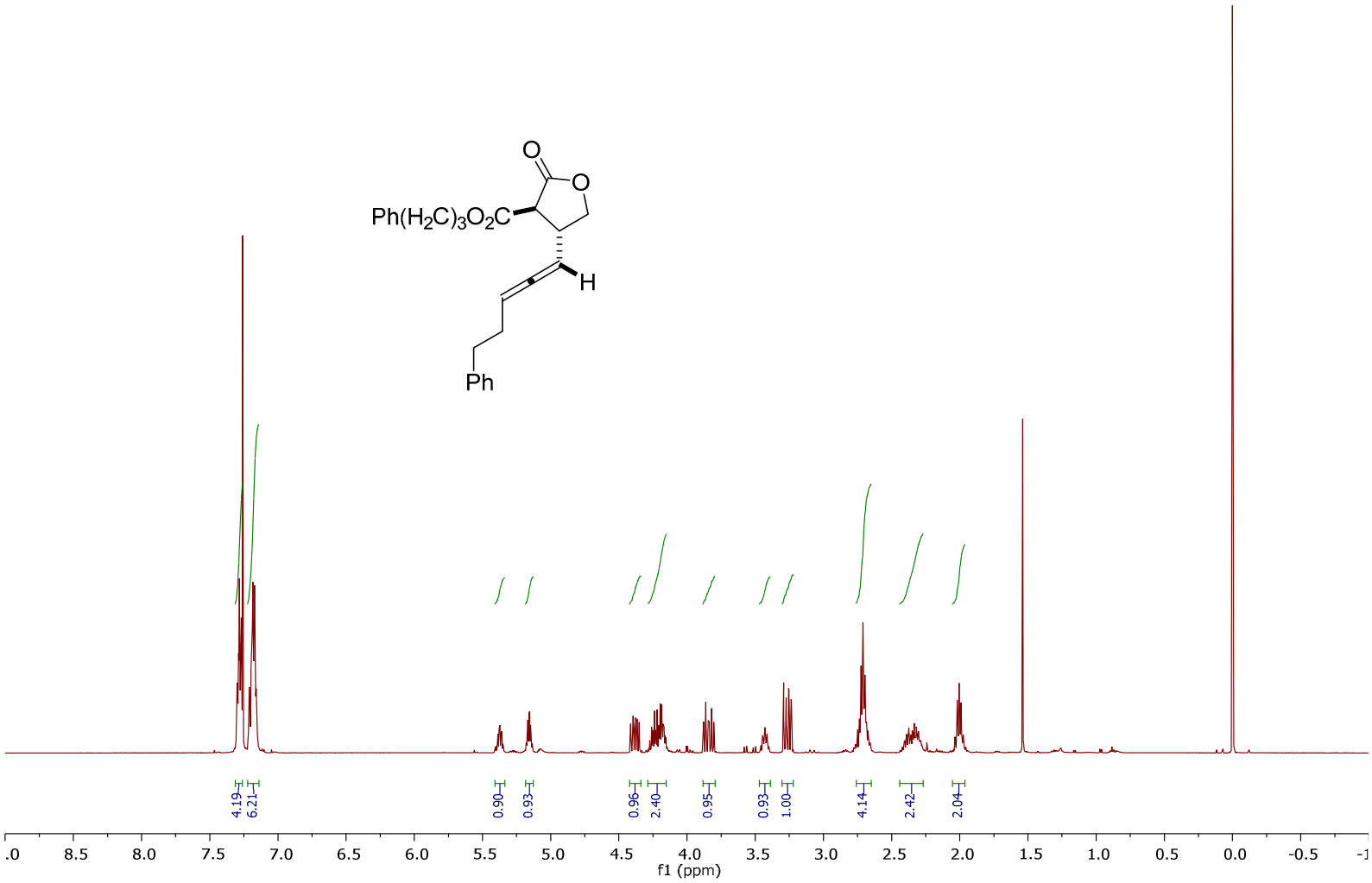


Alcohol 8. A 50 mL round bottom flask was charged with 242 mg (0.86 mmol, 1 equiv) cyclopentene **3m** in 8.60 mL dry THF and cooled to 0°C. 1.29 mL (1.29 mmol, 1.5 equiv) BH_3·THF was added dropwise and the resulting solution stirred at 0°C for 2h. 400 mg (2.60 mmol, 3.00 equiv) $NaBO_3$·$4H_2O$ was added in one portion, followed by 8.60 mL H_2O. The

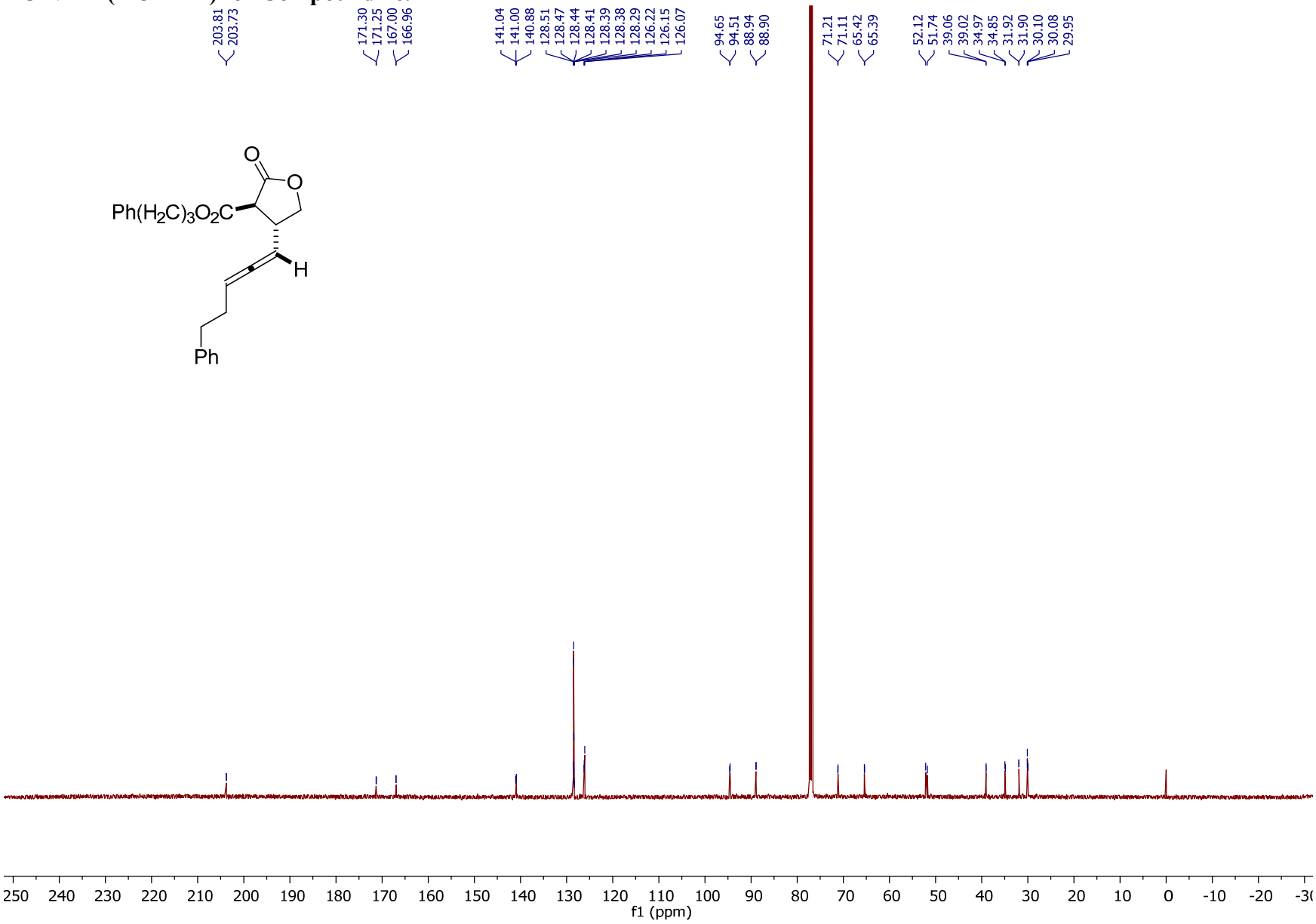
resulting suspension was stirred at 0C for 1.5 hours. The reaction mixture was poured into a separatory funnel containing 50 mL H_2O and extracted with 3x50 mL portions of EtOAc. The combined organics were dried over Na_2SO_4 and the volatiles removed *in vacuo*. Final purification was completed *via* column chromatography using a 0-30% gradient of EtOAc in hexanes to afford 164 mg (0.55 mmol, 64%) alcohol **8** as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (s, 2H), 5.40 (s, 1H), 4.65 – 4.56 (m, 2H), 3.77 (d, *J* = 8.6 Hz, 1H), 3.69 (d, *J* = 8.5 Hz, 1H), 2.14 (ddd, *J* = 14.1, 11.4, 4.5 Hz, 1H), 1.74 (ddd, *J* = 16.1, 9.9, 3.5 Hz, 1H), 1.60 – 1.52 (m, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.35 – 1.30 (m, 4H), 0.91 – 0.86 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 171.4, 83.5, 73.2, 64.8, 64.3, 53.2, 45.1, 41.0, 31.9, 31.4, 29.9, 28.5, 24.4, 22.5, 14.0. HRMS (ESI) *m/z* calculated for $C_{16}H_{26}O_5$ $[M + Na]^+$ 321.1673, found 321.1666.

VI. NMR Spectra.

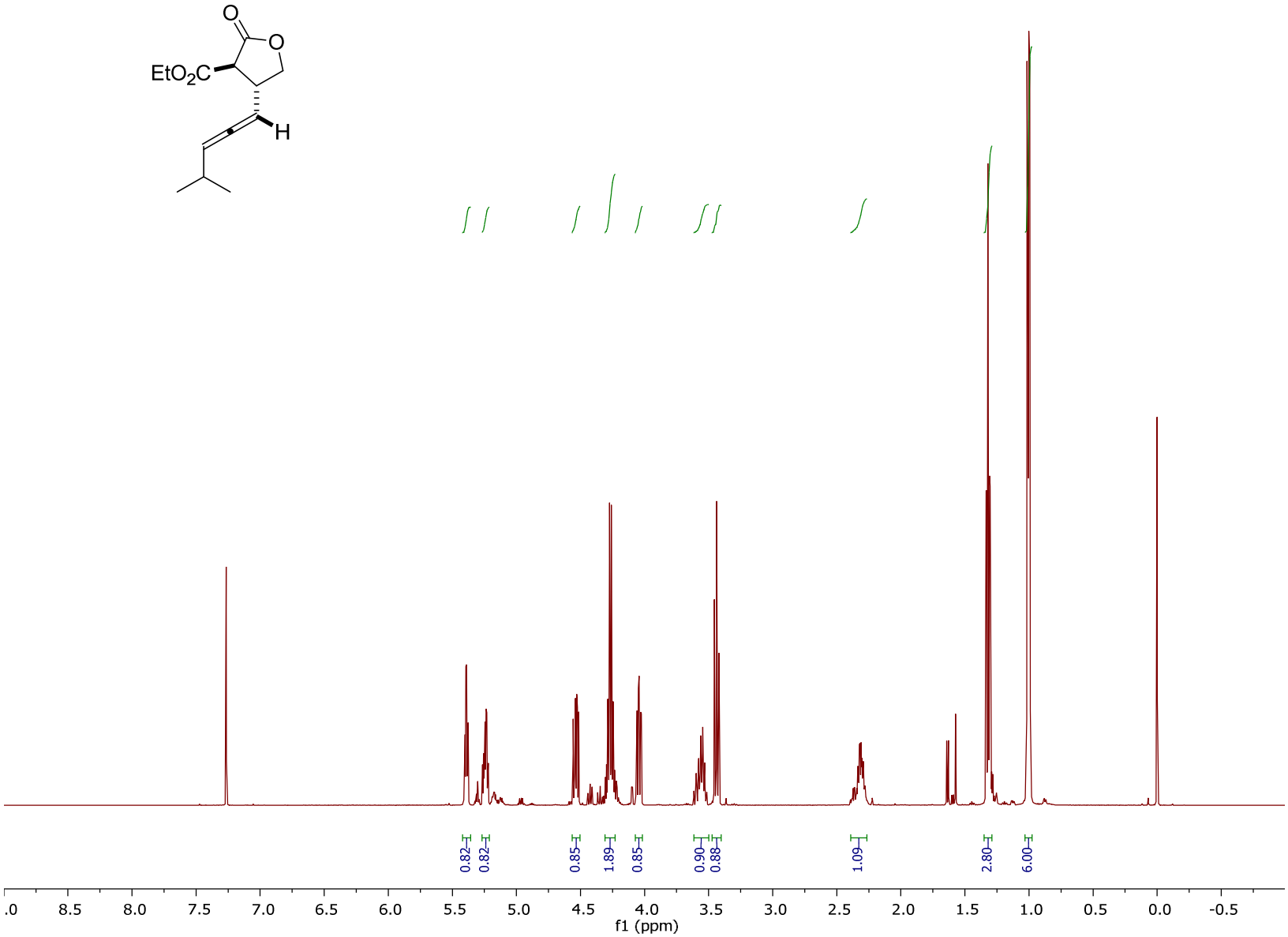
^{1}H NMR (500 MHz) for Compound 2e.



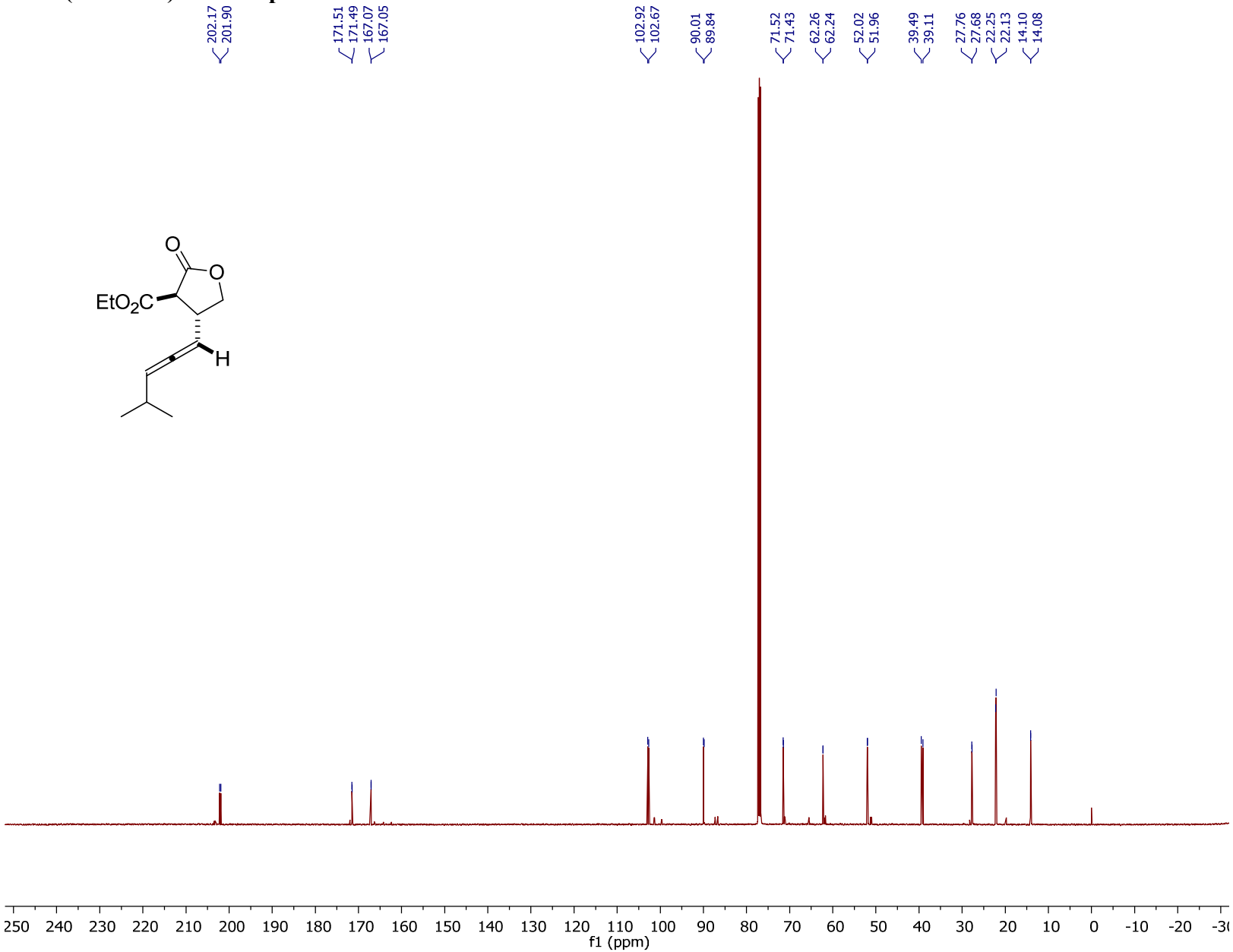
^{13}C NMR (125 MHz) for Compound 2e.



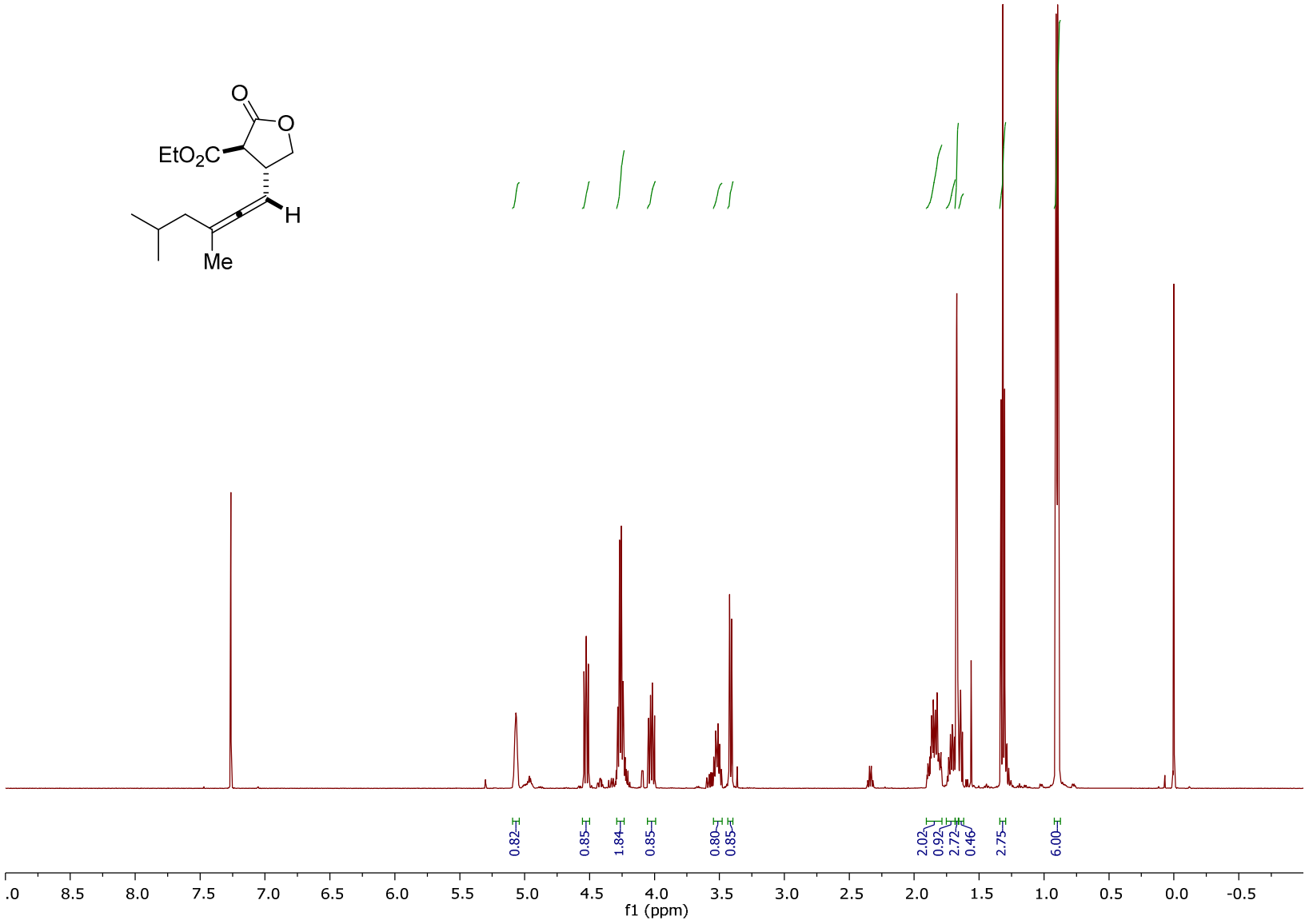
^{1}H NMR (500 MHz) for Compound 2f.



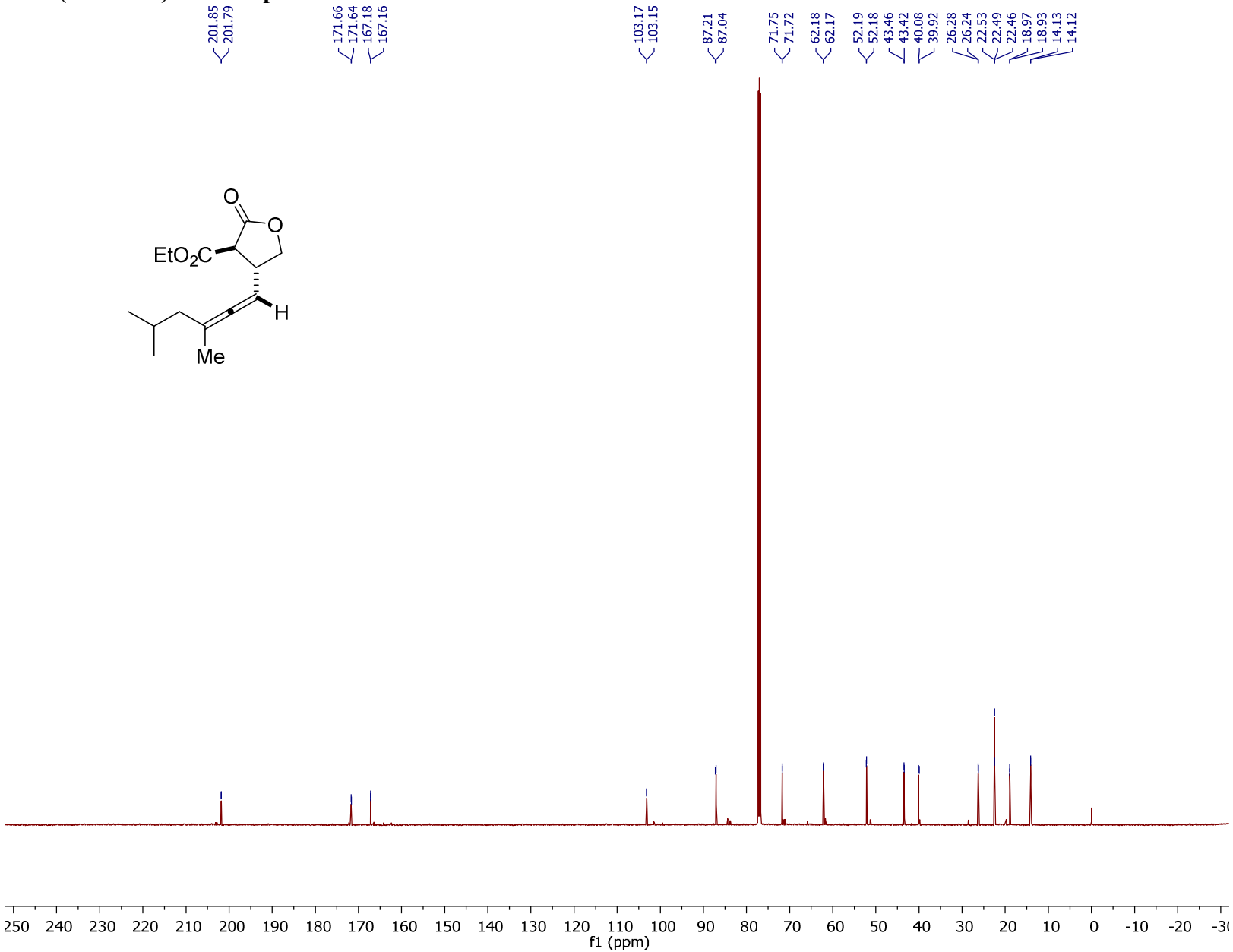
^{13}C NMR (125 MHz) for Compound 2f.



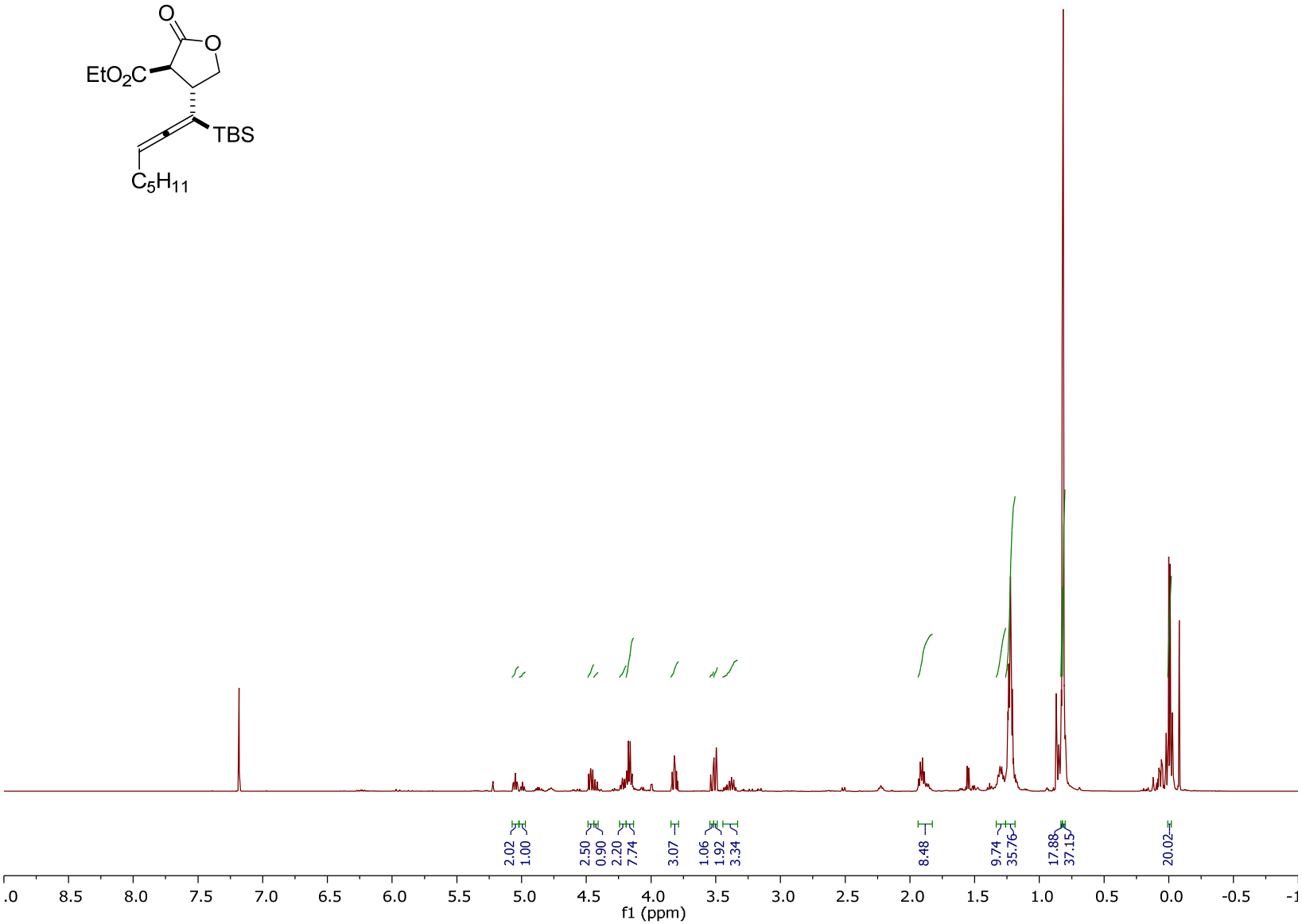
^{1}H NMR (500 MHz) for Compound 2i.



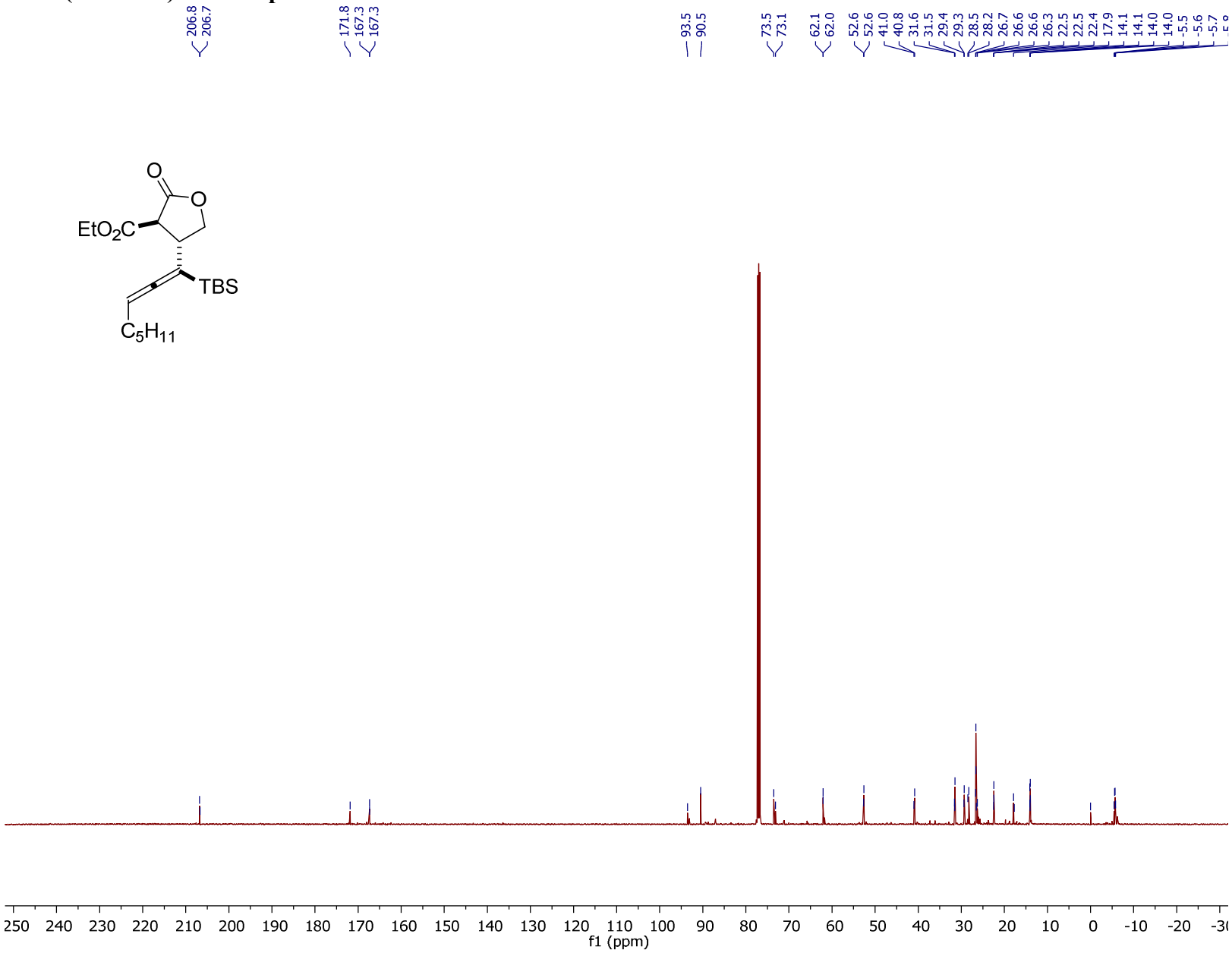
^{13}CNMR (125 MHz) for Compound 2i.



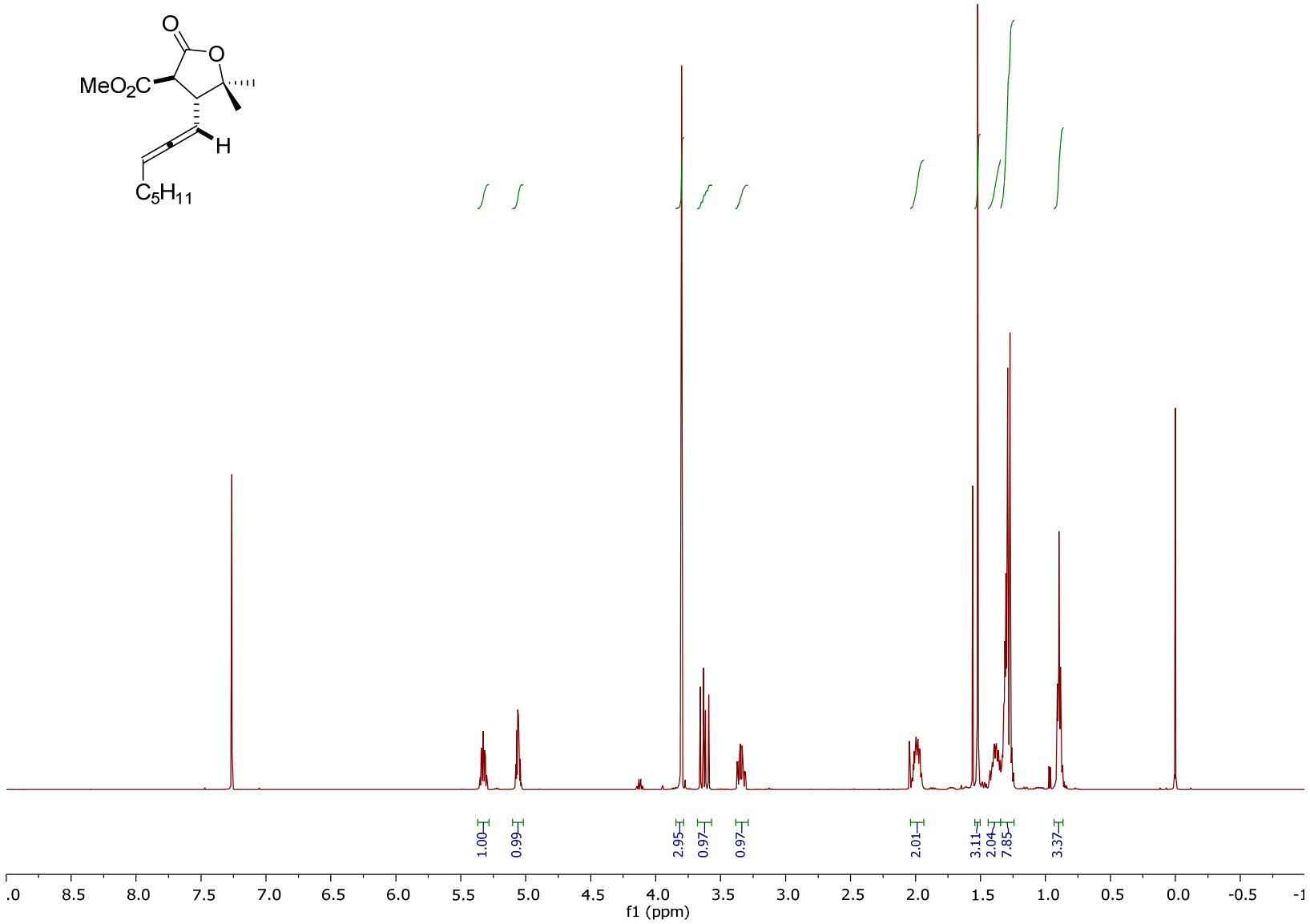
^{1}H NMR (500 MHz) for Compound 2k.



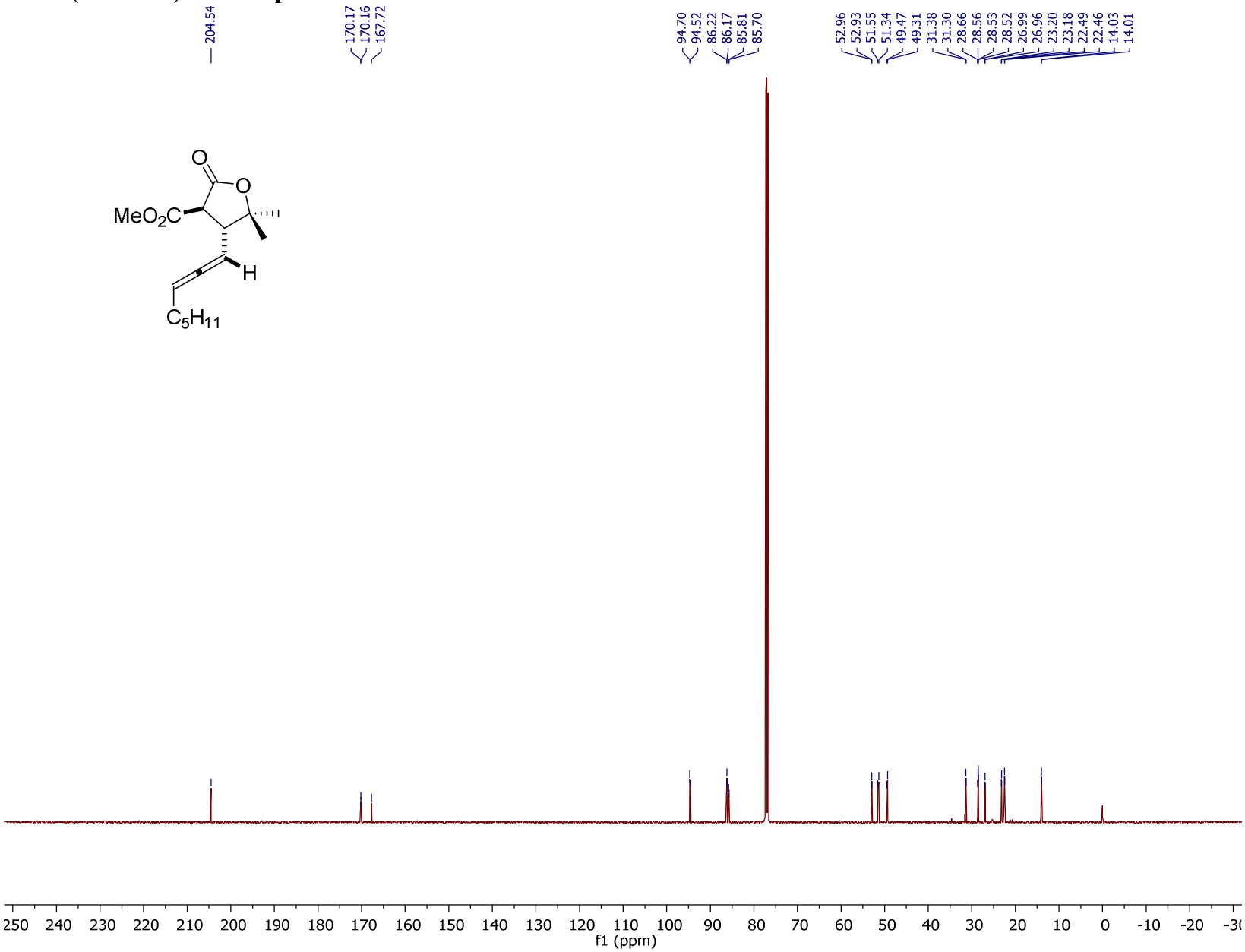
^{13}C NMR (125 MHz) for Compound 2k.



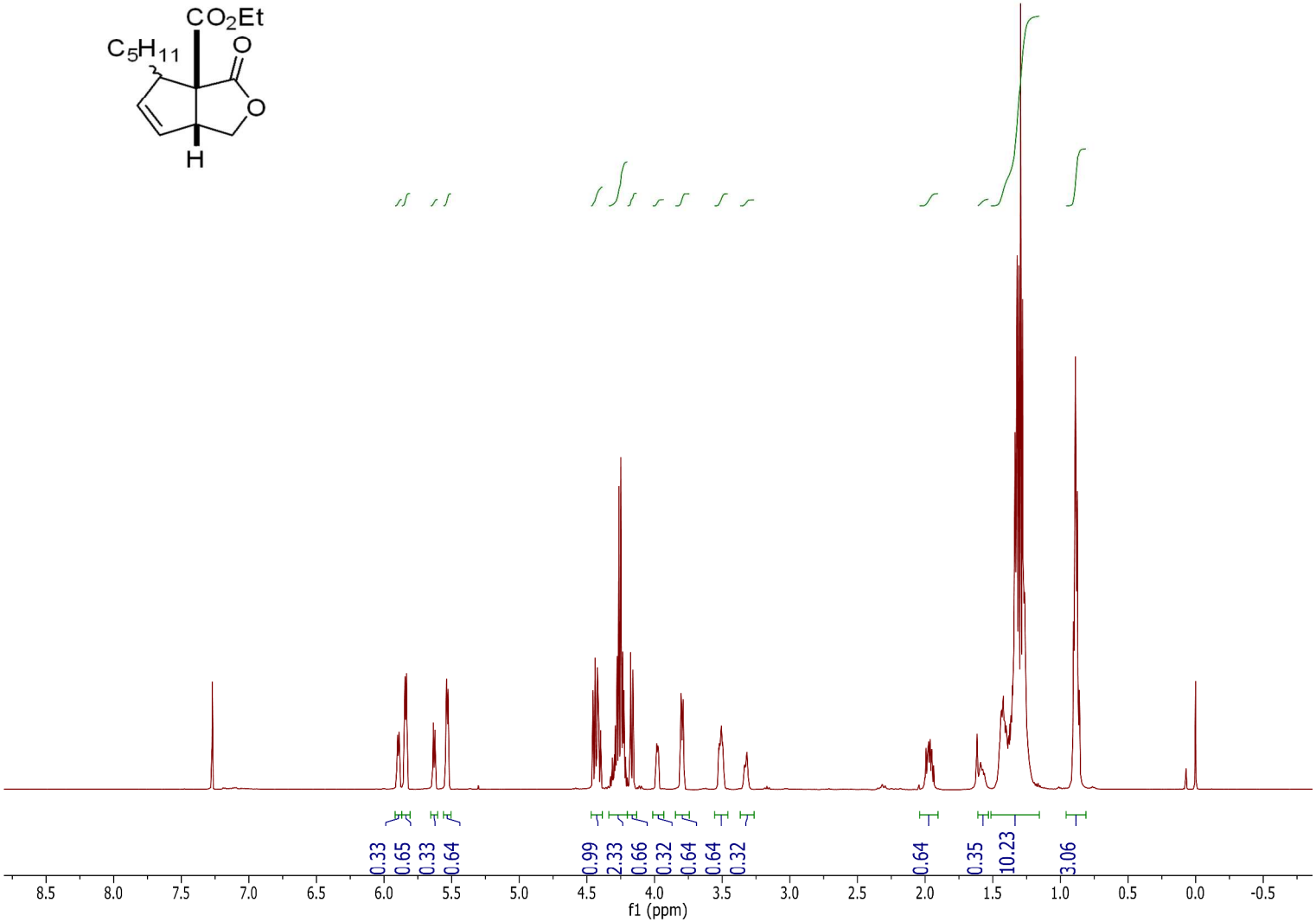
^{1}H NMR (500 MHz) for Compound 2m.



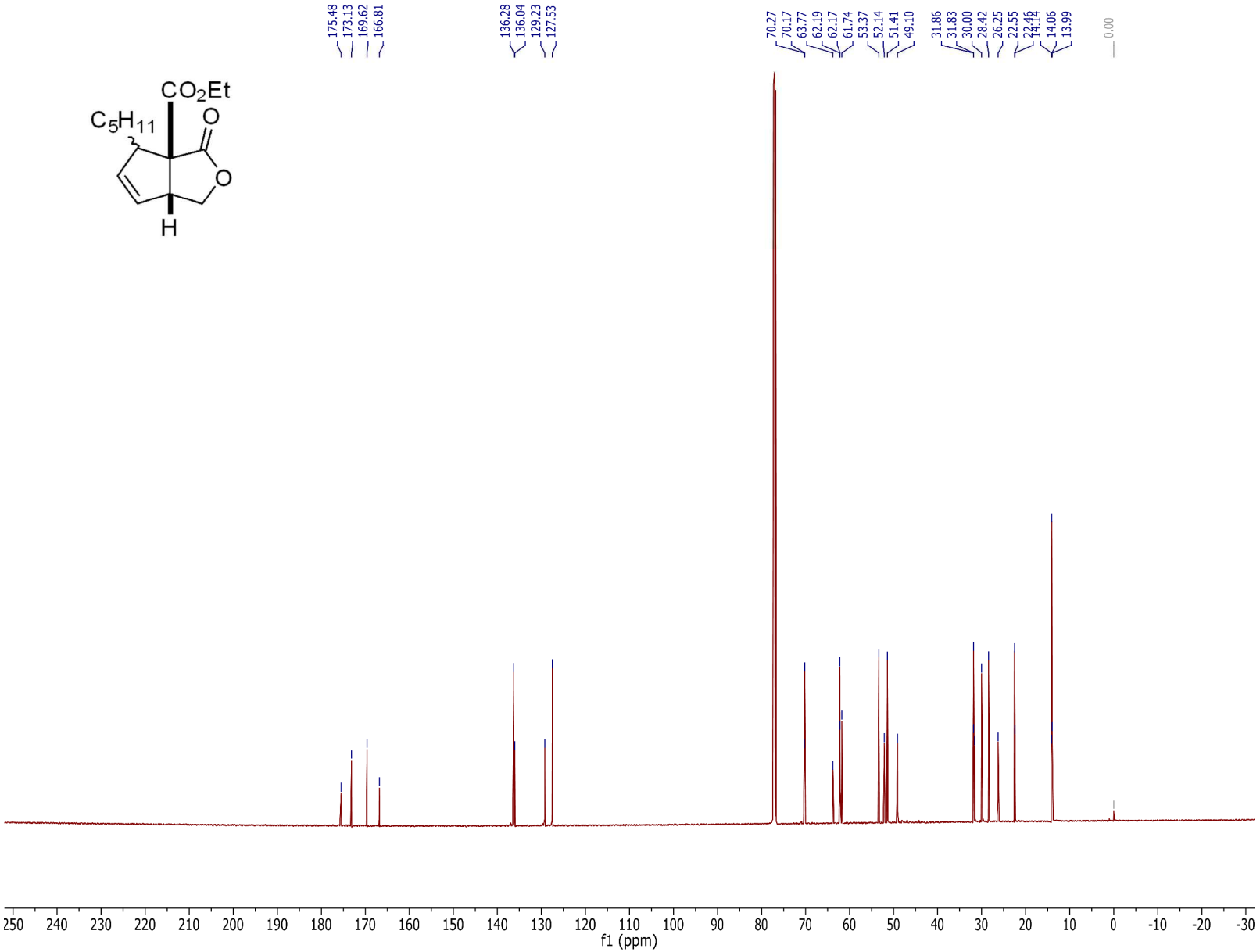
^{13}C NMR (125 MHz) for Compound 2m.



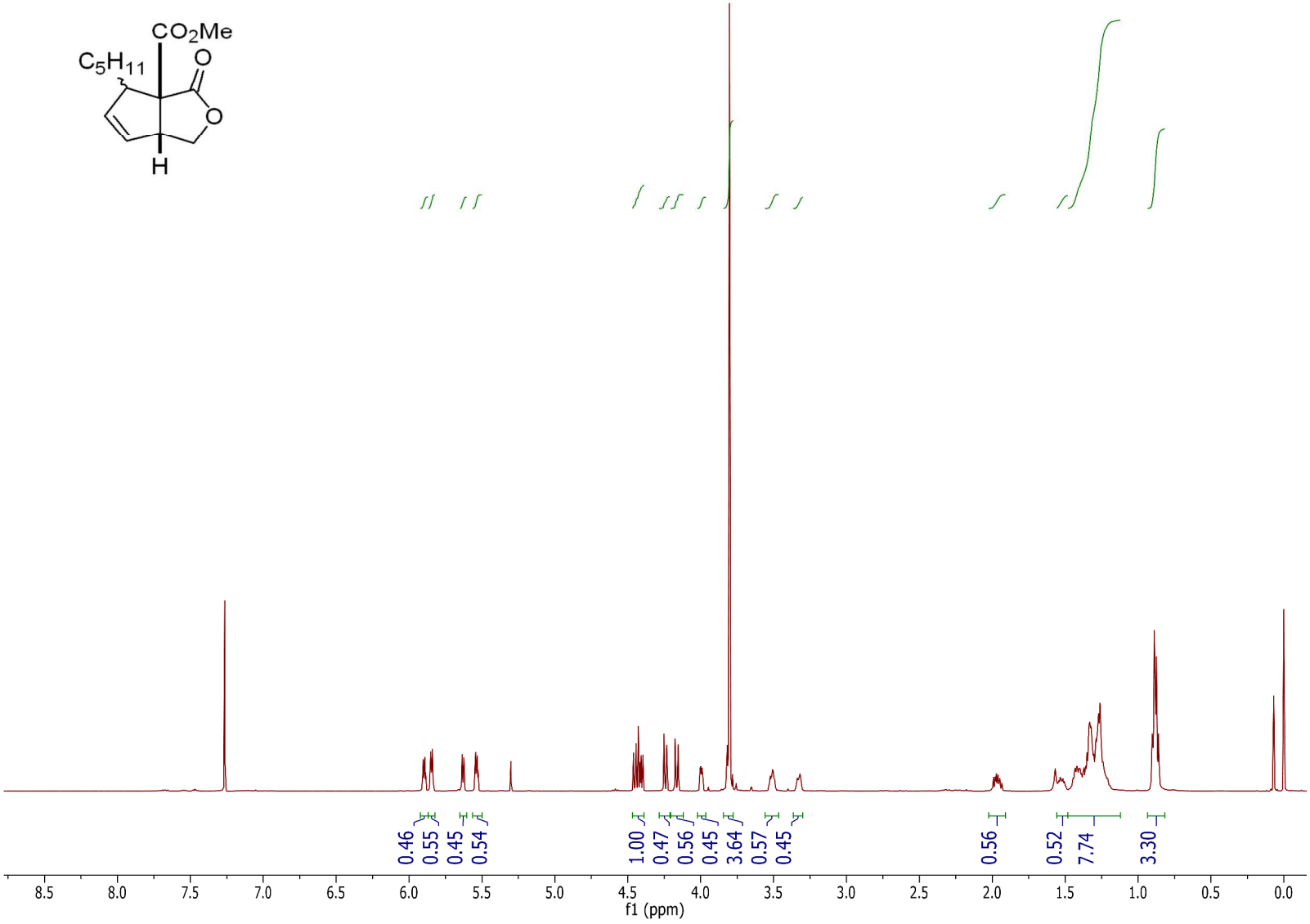
^{1}H NMR (500 MHz) for Compound 3a.



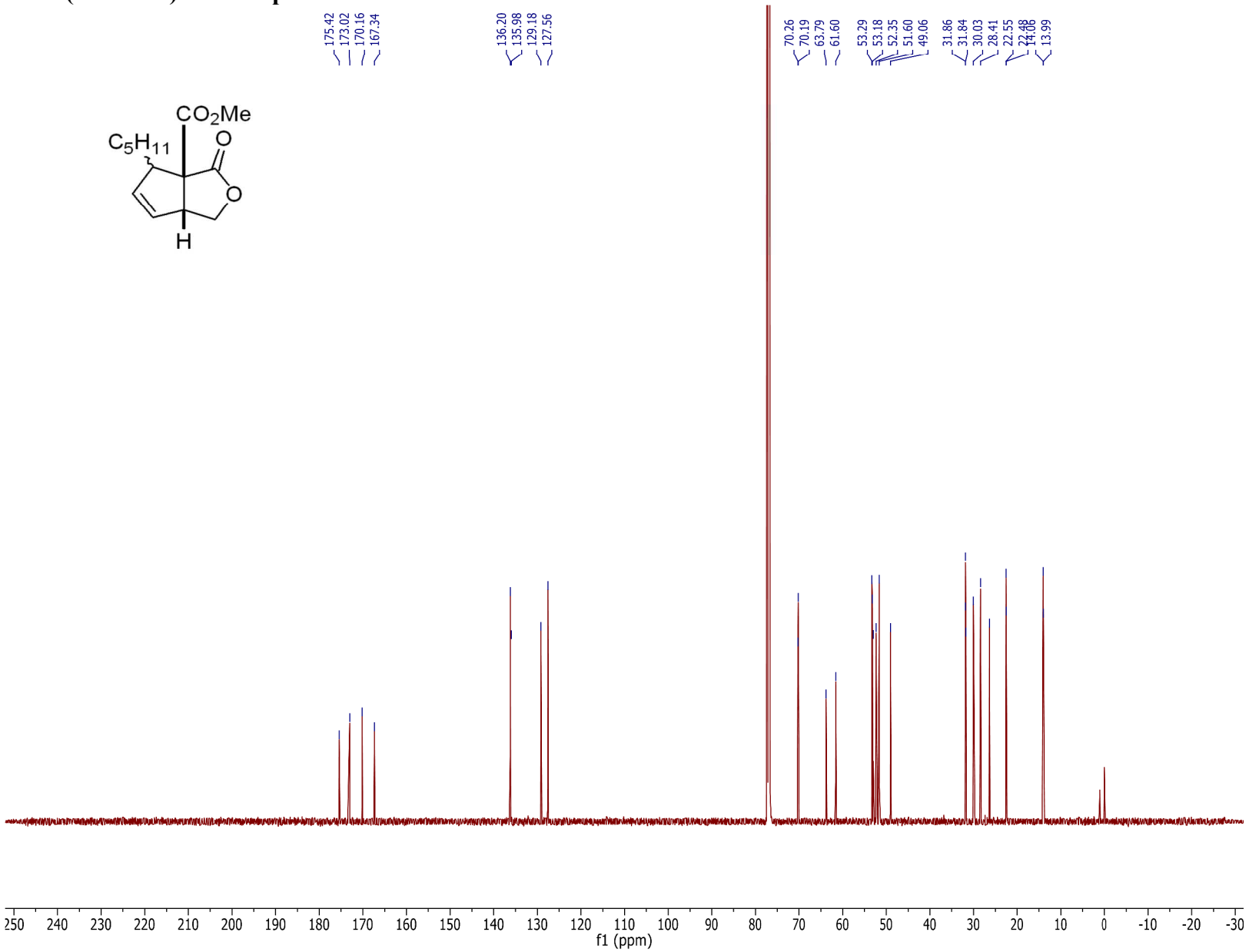
^{13}C NMR (125 MHz) for Compound 3a.



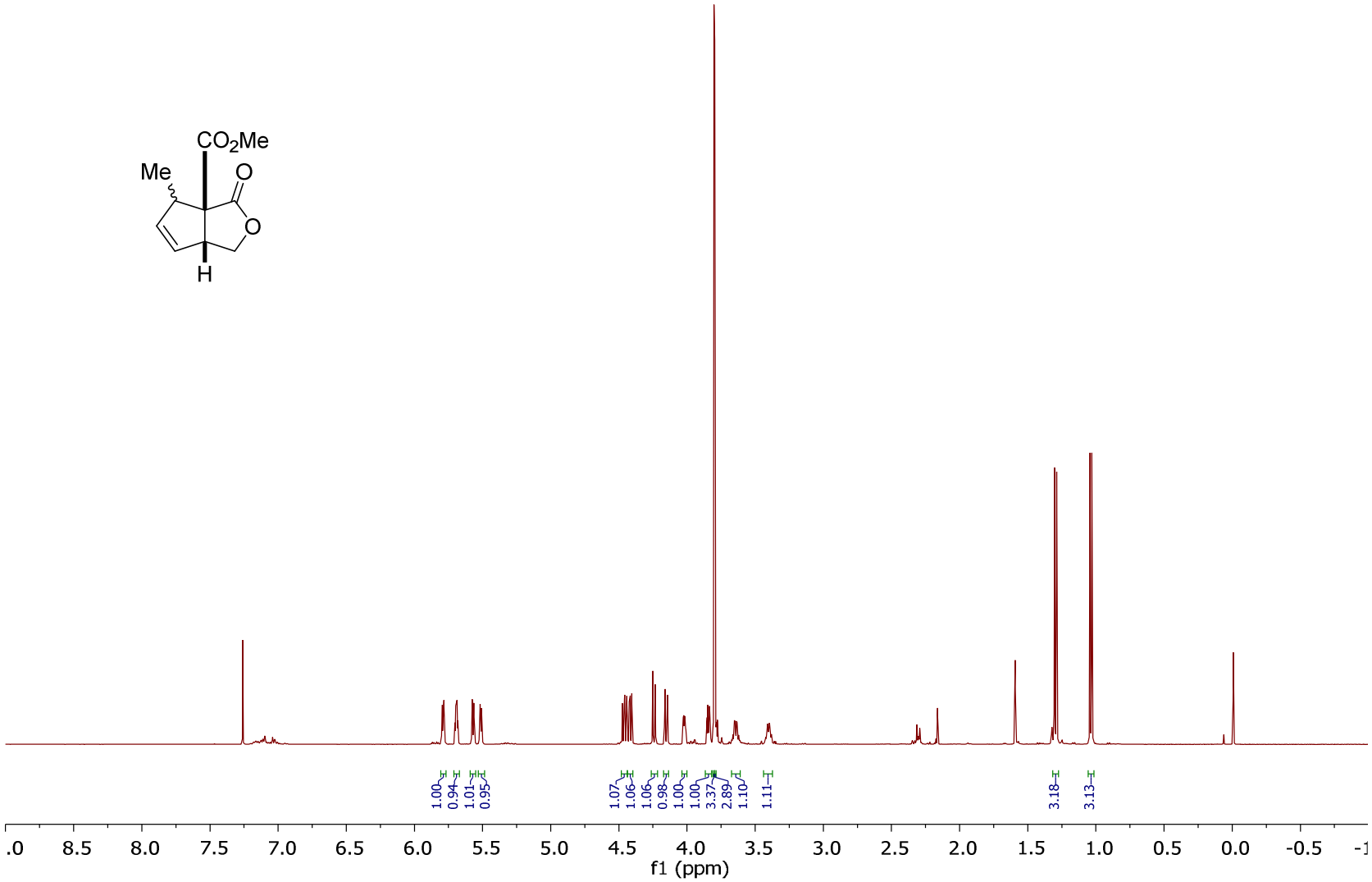
^{1}H NMR (500 MHz) for Compound 3b.



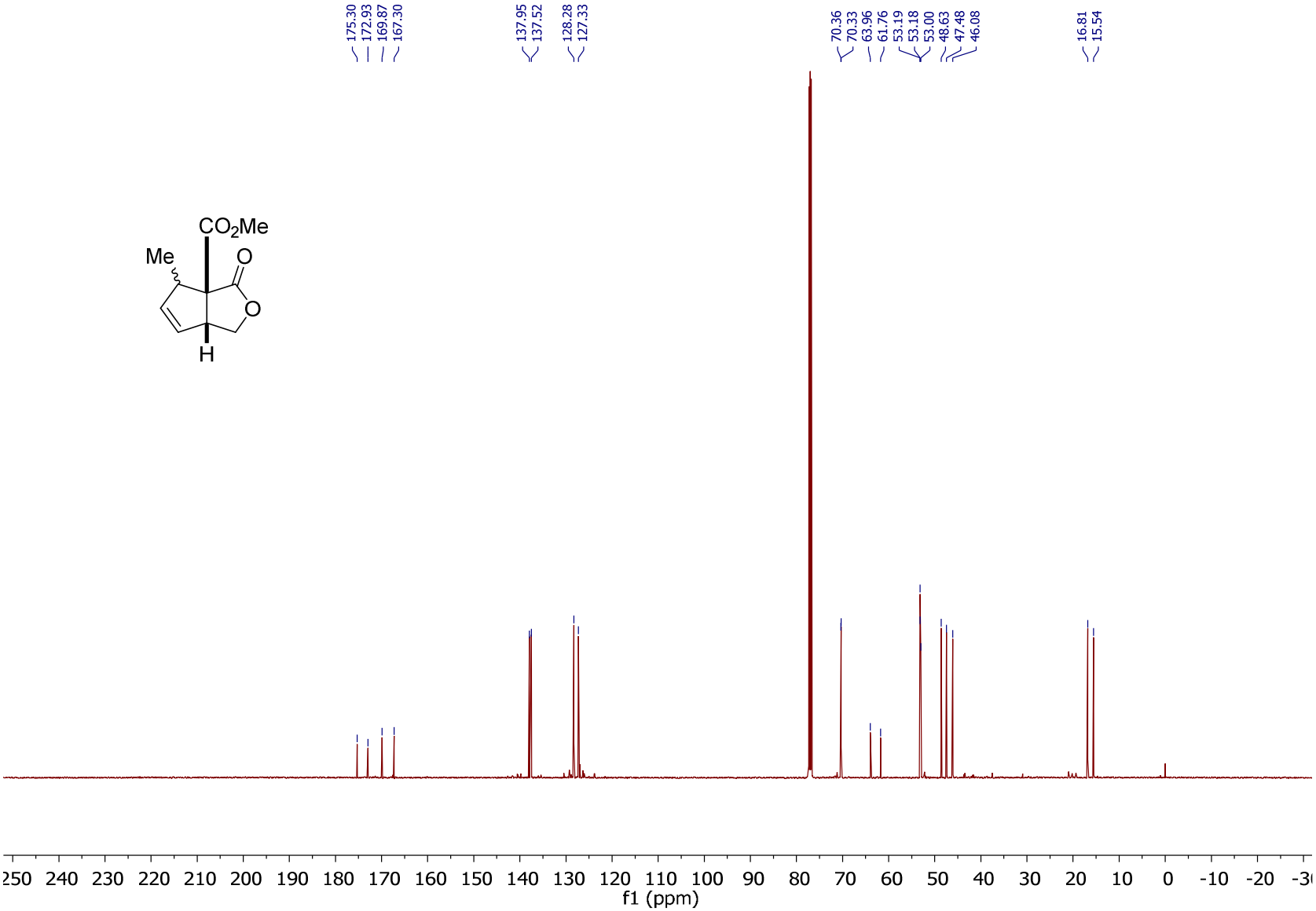
^{13}C NMR (125 MHz) for Compound 3b.



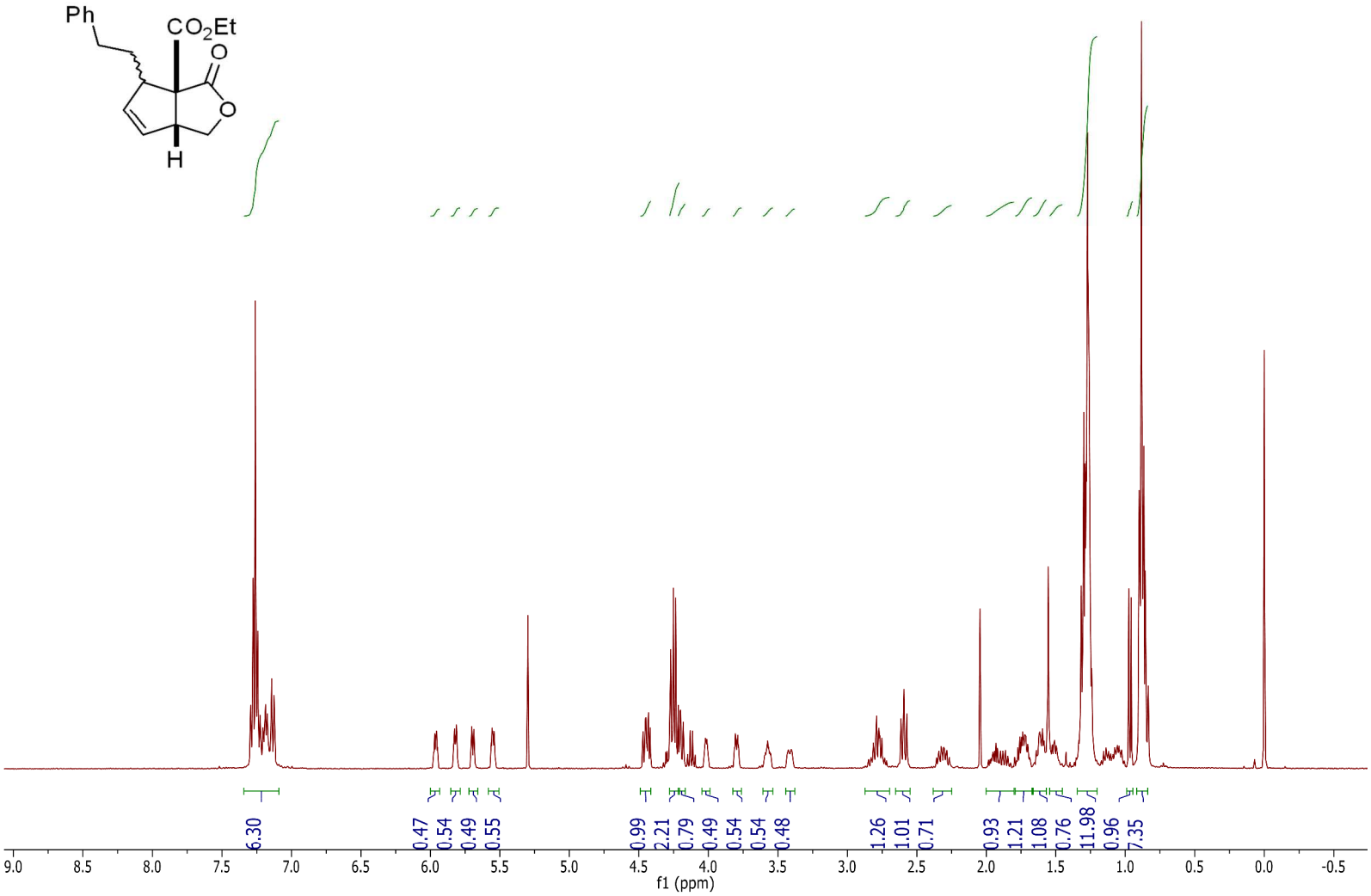
^{1}H NMR (500 MHz) for Compound 3c.



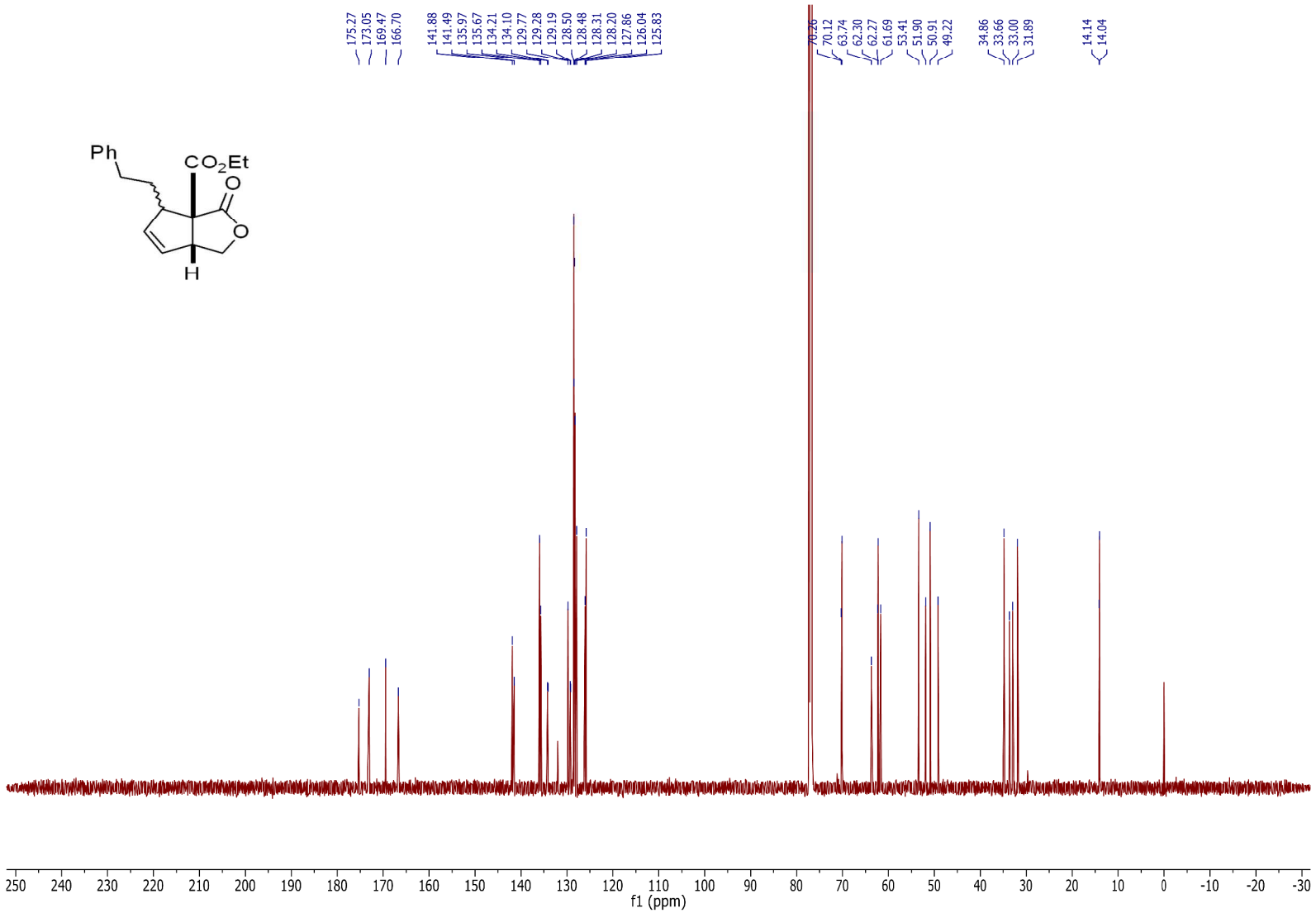
^{13}C NMR (125 MHz) for Compound 3c.



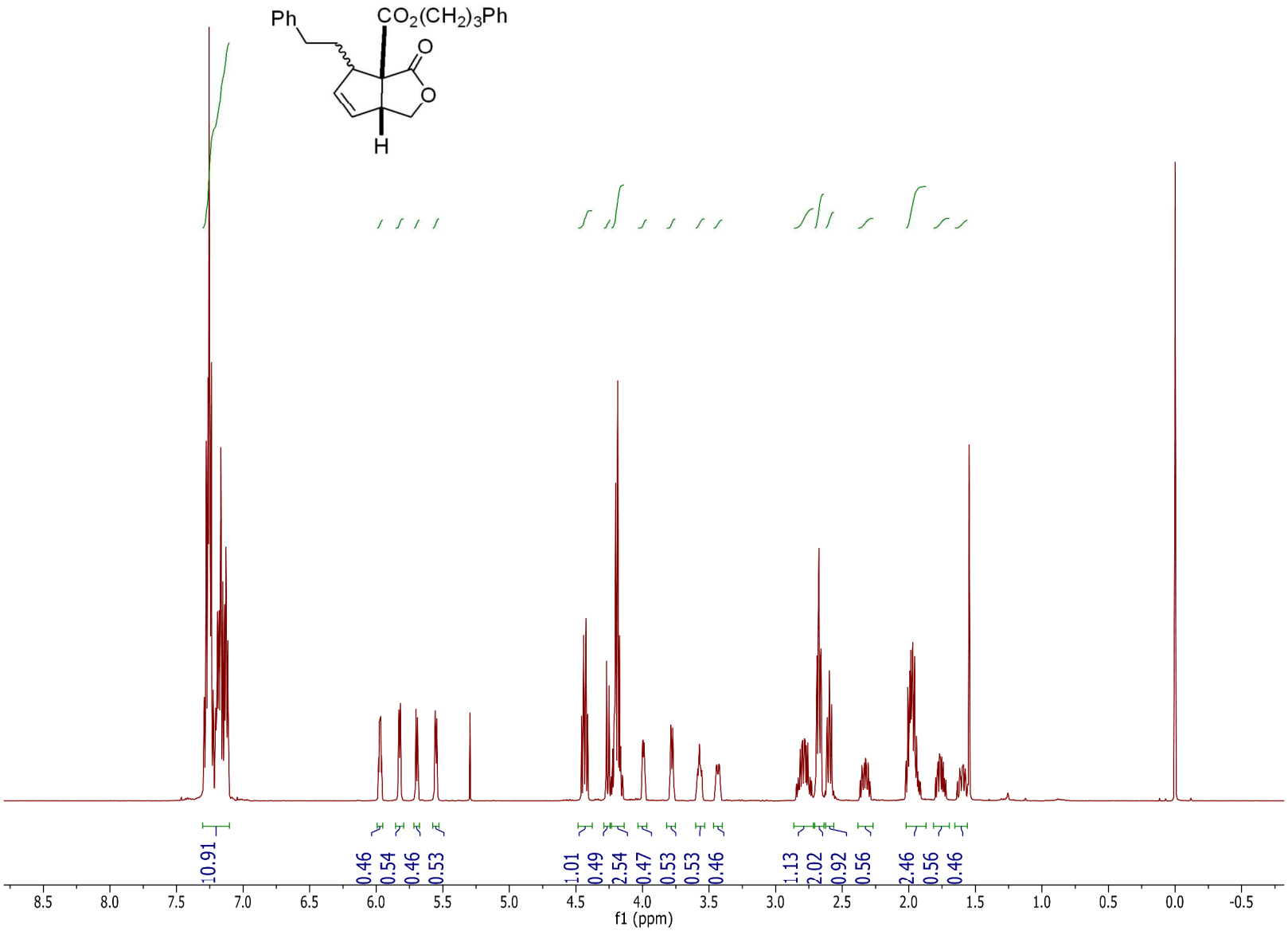
^{1}H NMR (500 MHz) for Compound 3d.



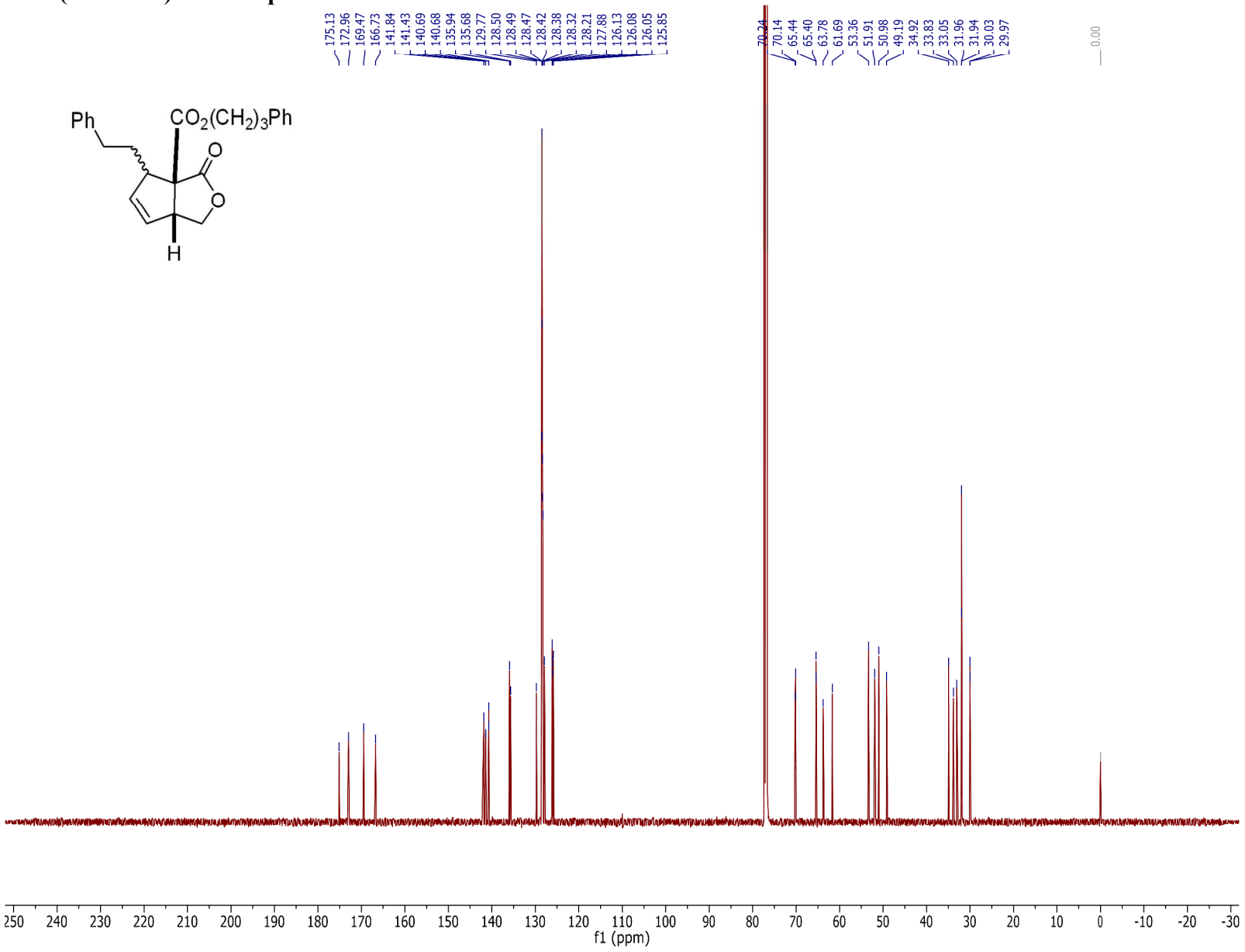
^{13}C NMR (125 MHz) for Compound 3d.



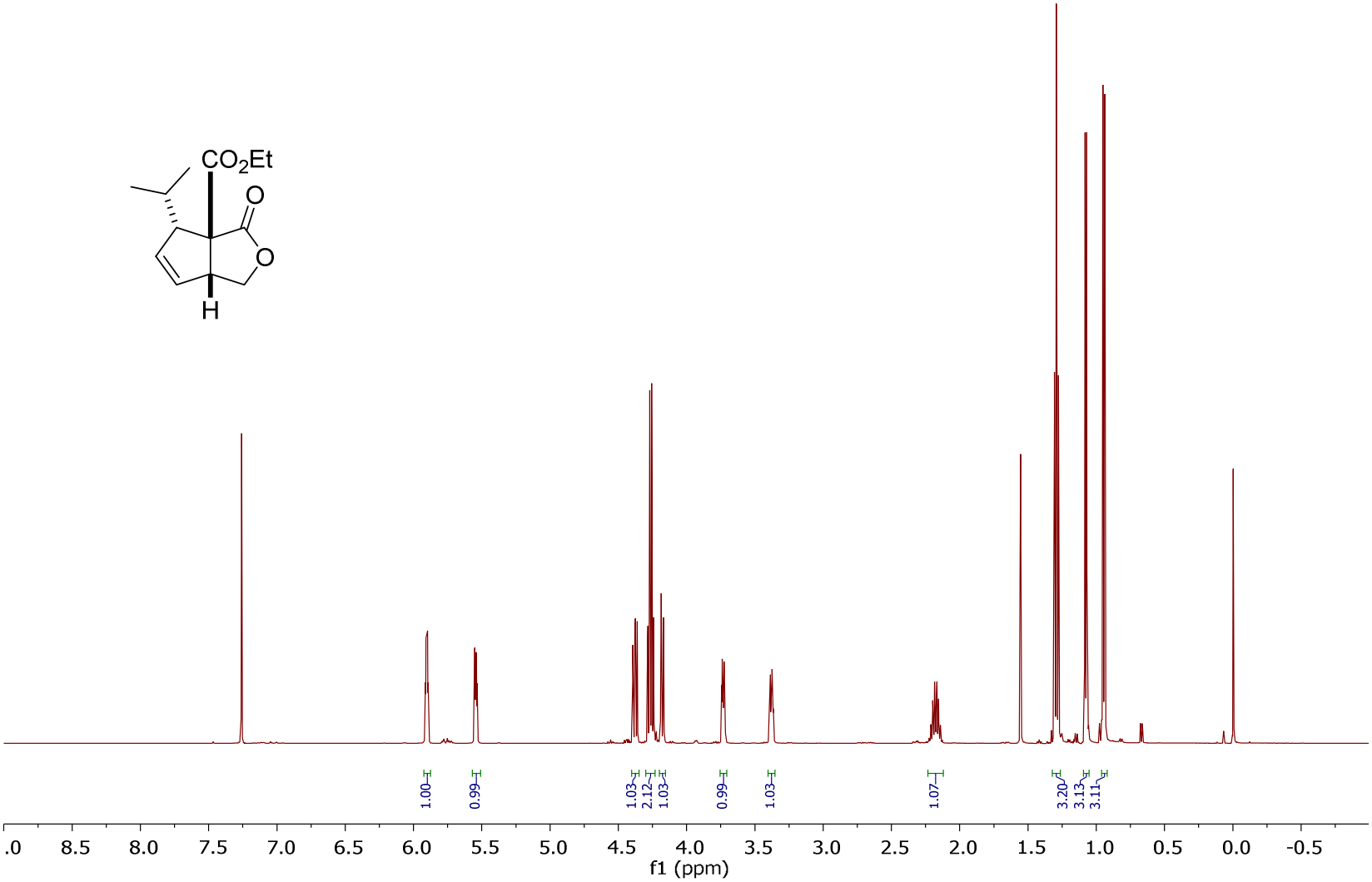
[1]H NMR (500 MHz) for Compound 3e.



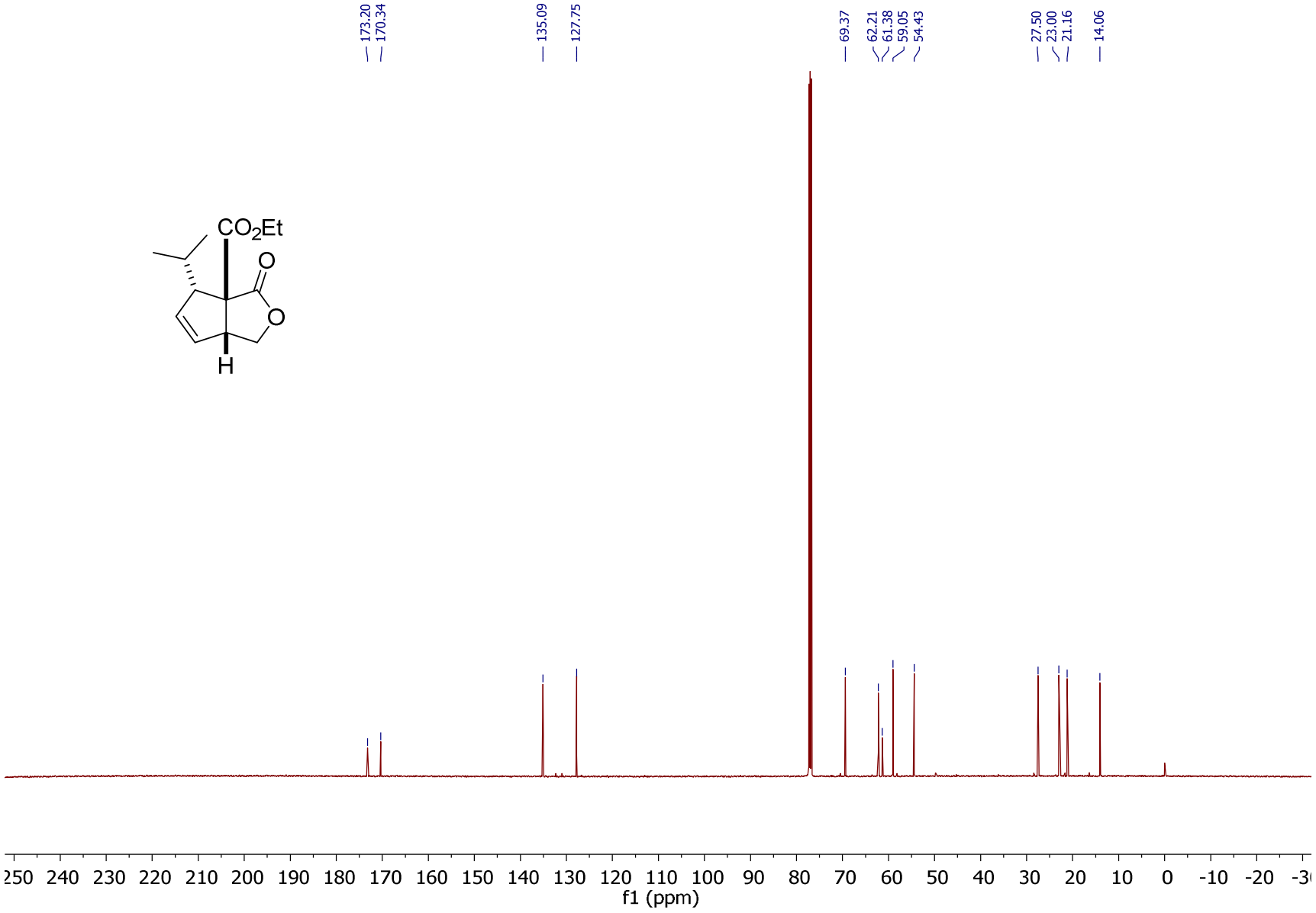
^{13}C NMR (125 MHz) for Compound 3e.



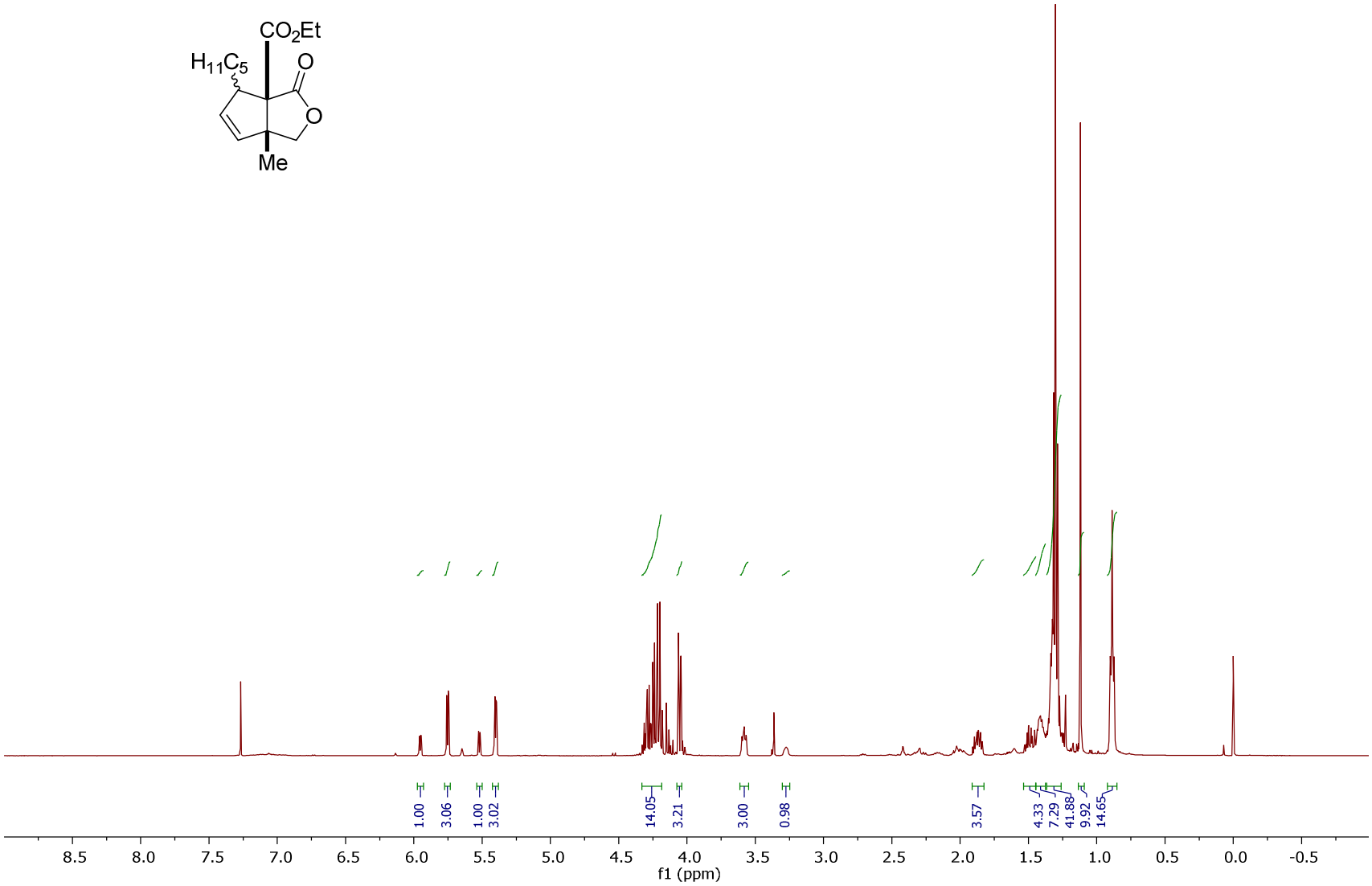
^{1}H NMR (500 MHz) for Compound 3f.



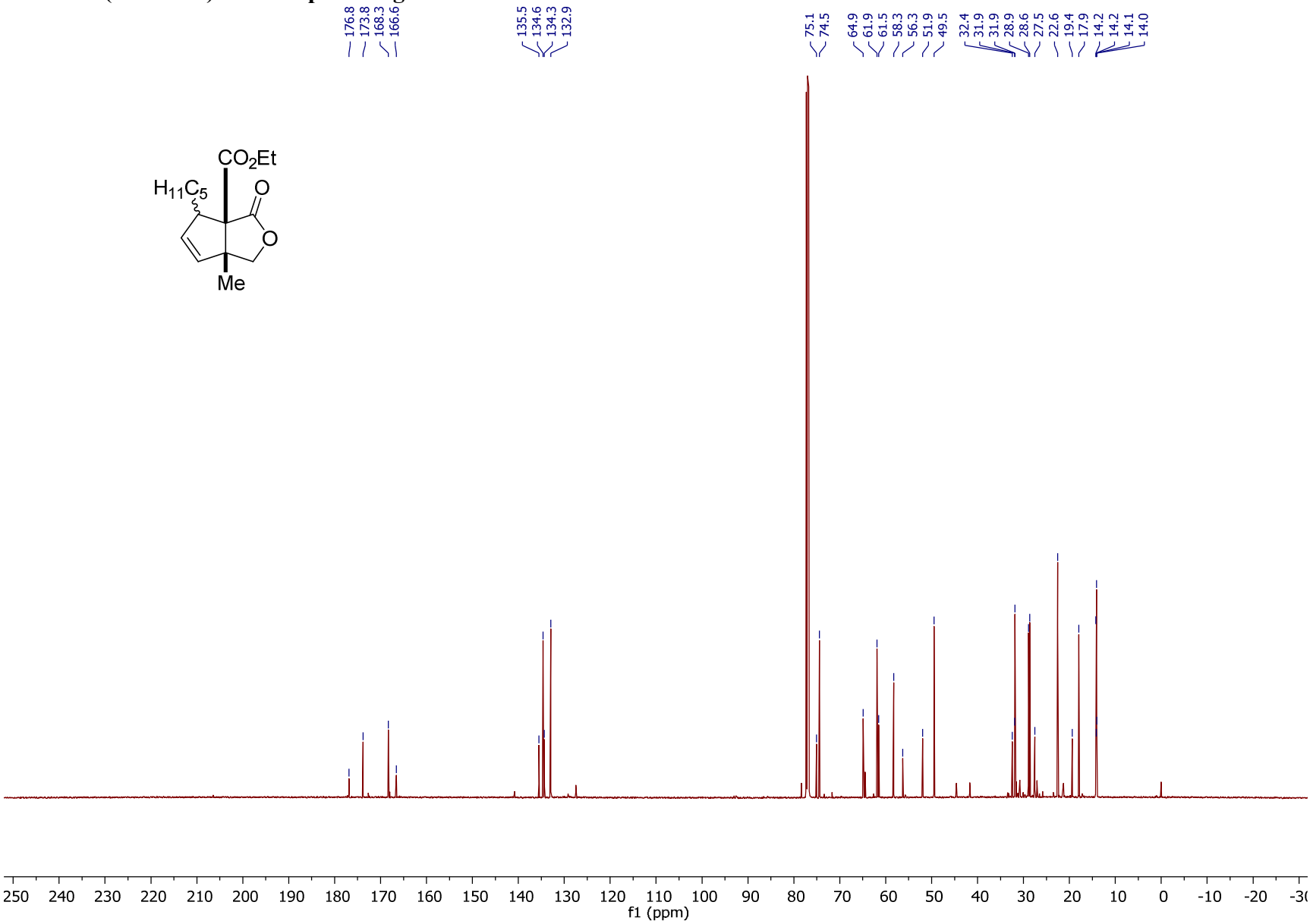
^{13}C NMR (125 MHz) for Compound 3f.



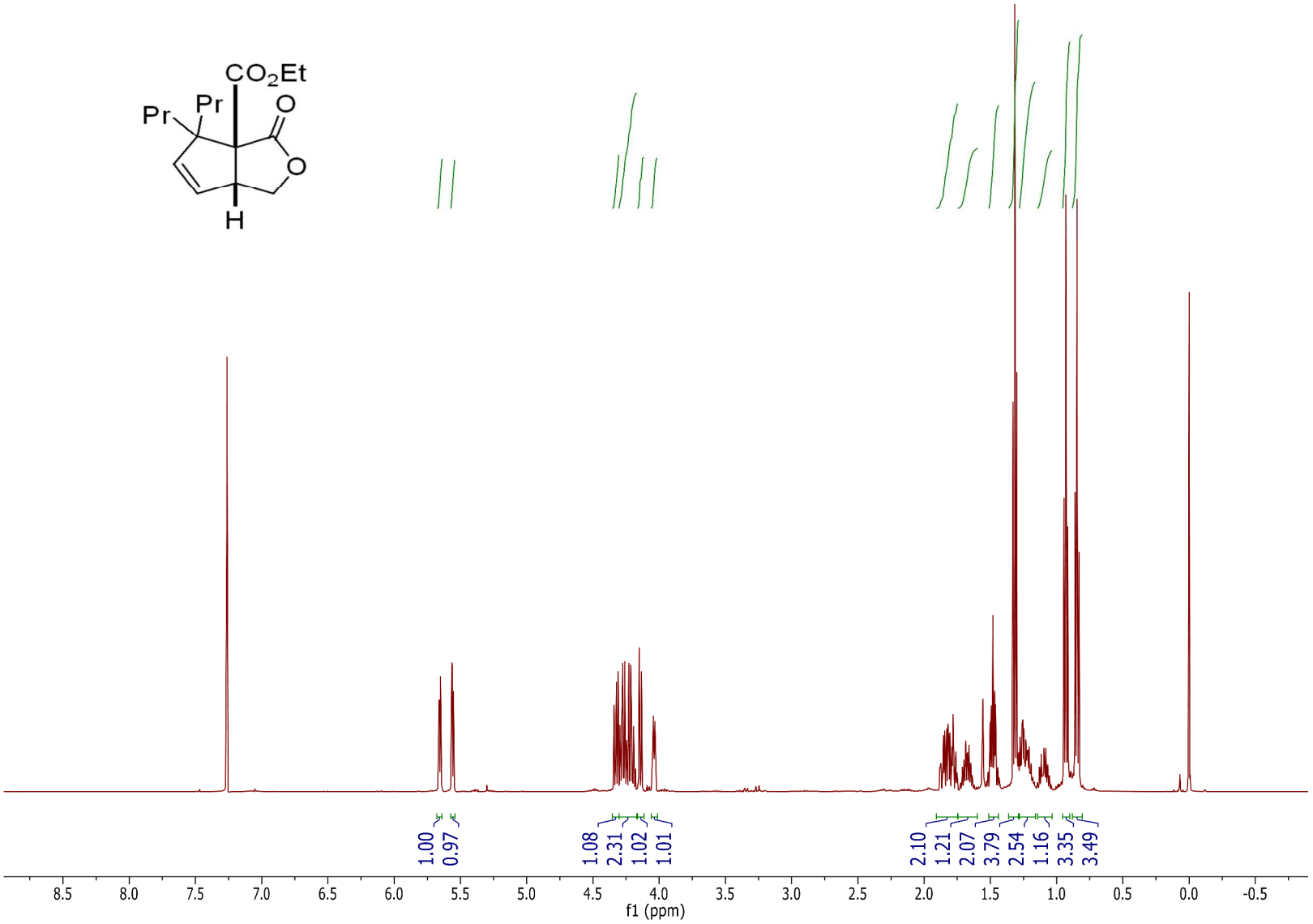
^{1}H NMR (500 MHz) for Compound 3g.



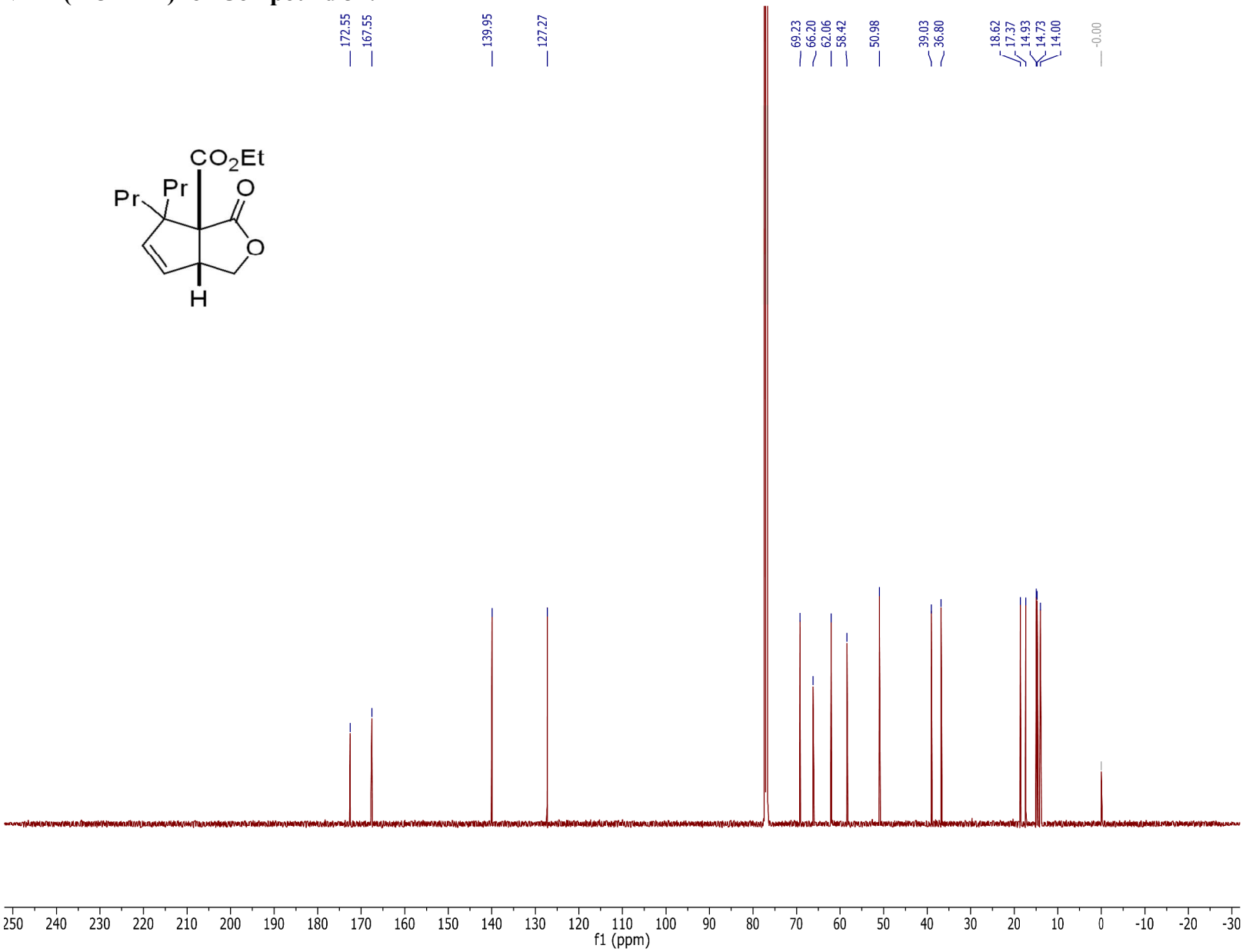
^{13}C NMR (125 MHz) for Compound 3g.



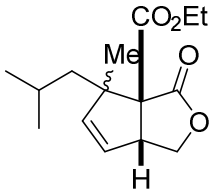
^{1}H NMR (500 MHz) for Compound 3h.



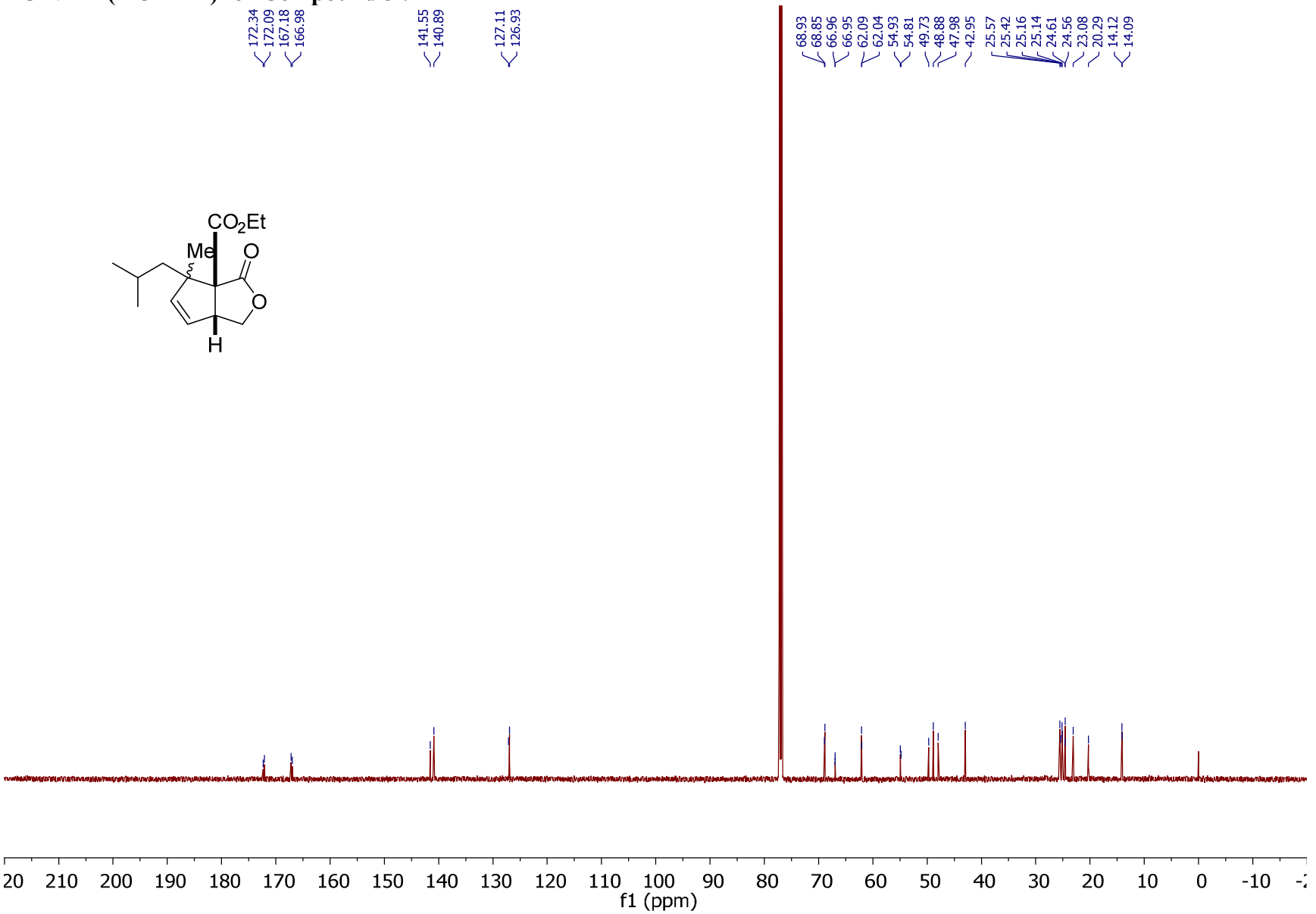
^{13}C NMR (125 MHz) for Compound 3h.



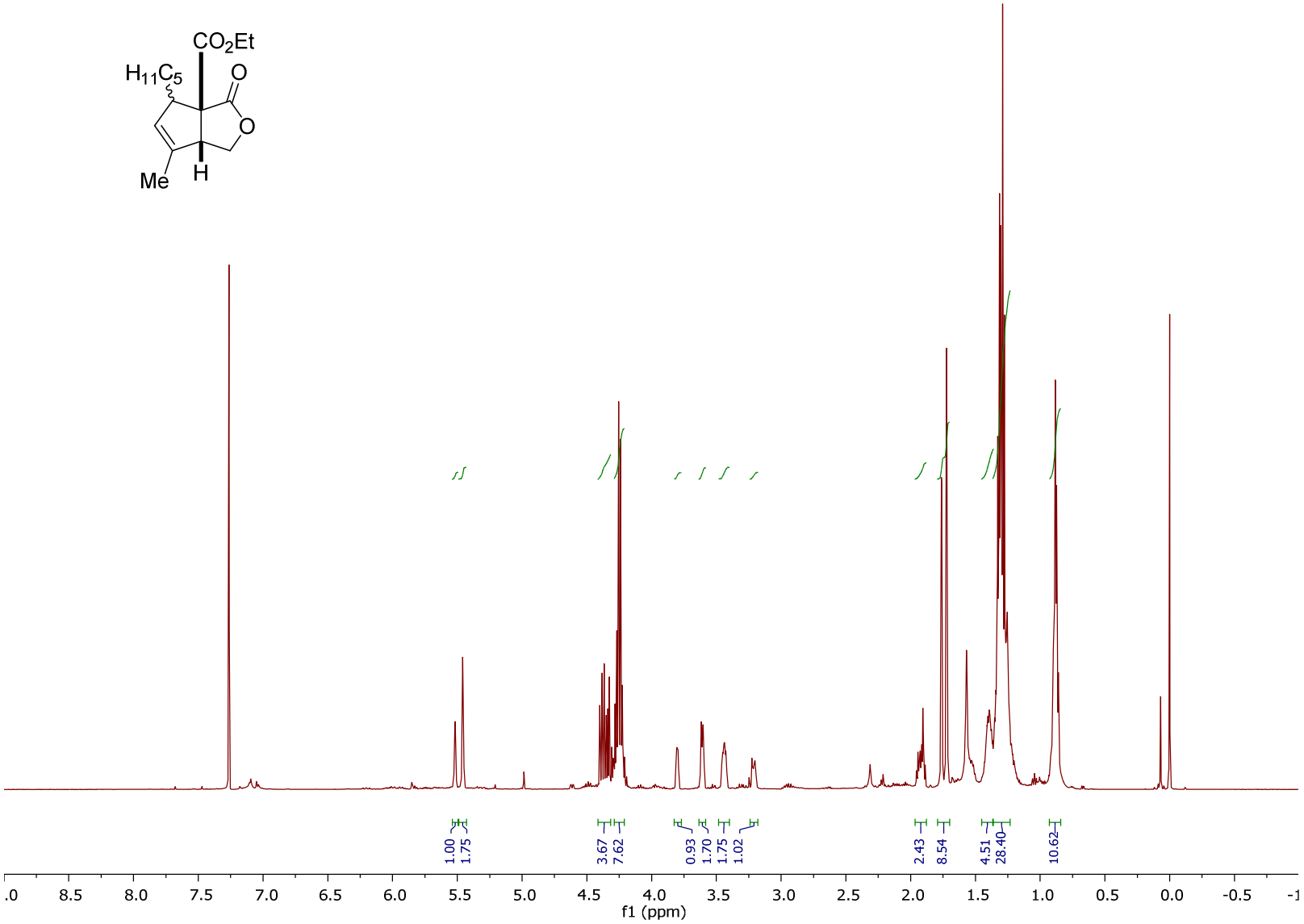
^{1}H NMR (500 MHz) for Compound 3i.



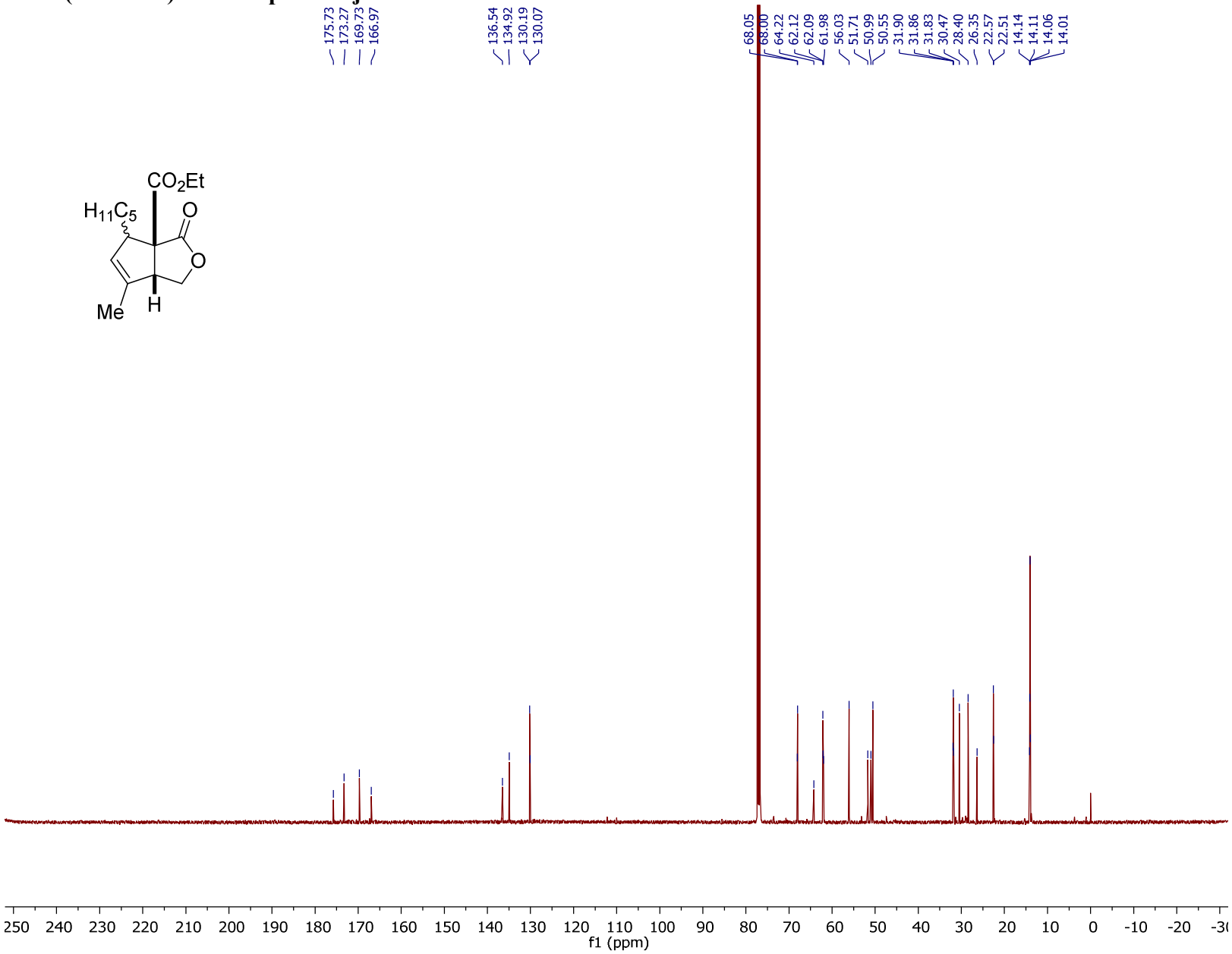
^{13}C NMR (125 MHz) for Compound 3i.



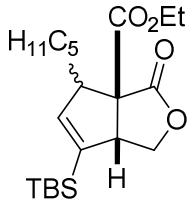
^{1}H NMR (500 MHz) for Compound 3j.



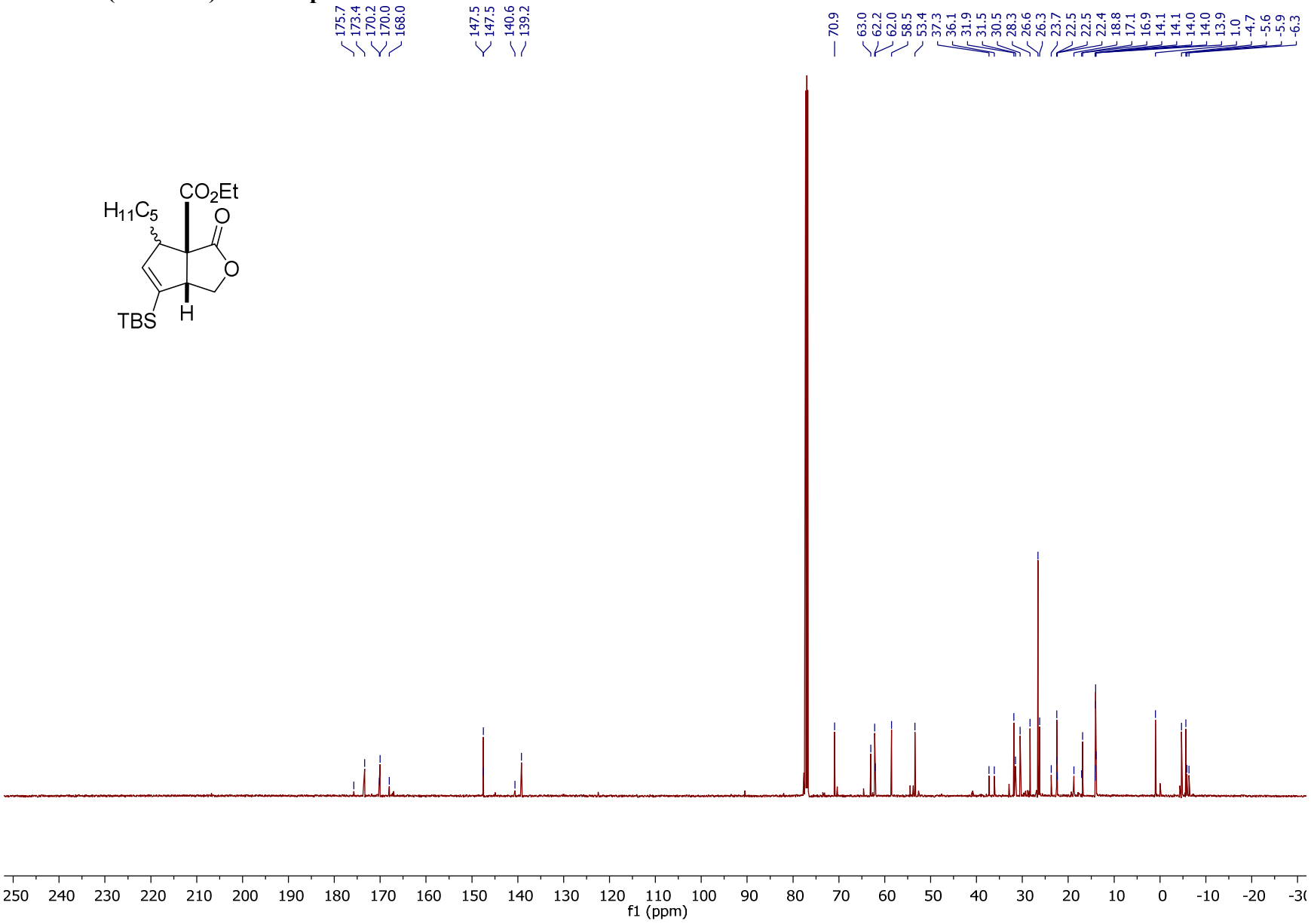
^{13}C NMR (125 MHz) for Compound 3j.



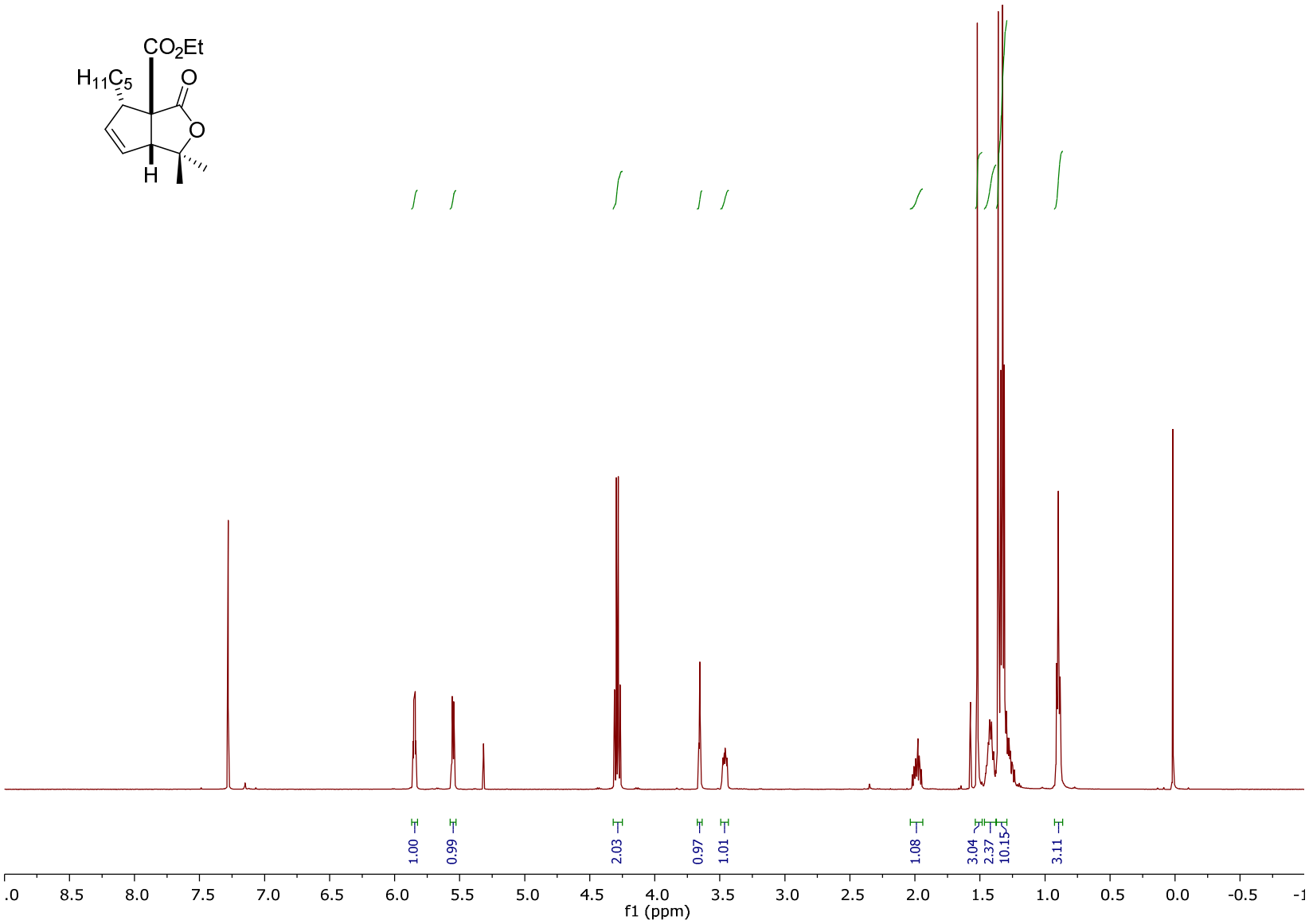
^{1}H NMR (500 MHz) for Compound 3k.



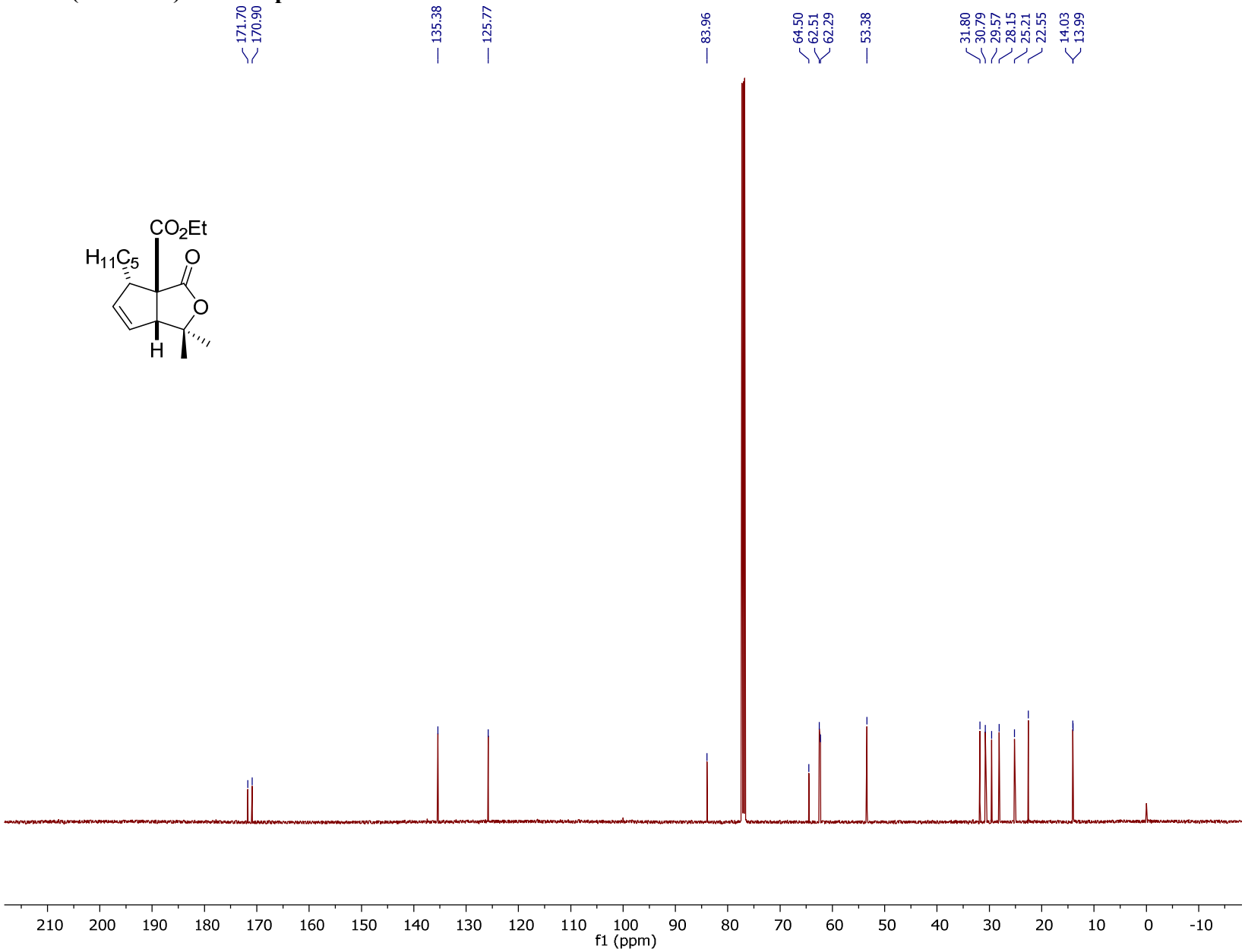
^{13}C NMR (125 MHz) for Compound 3k.



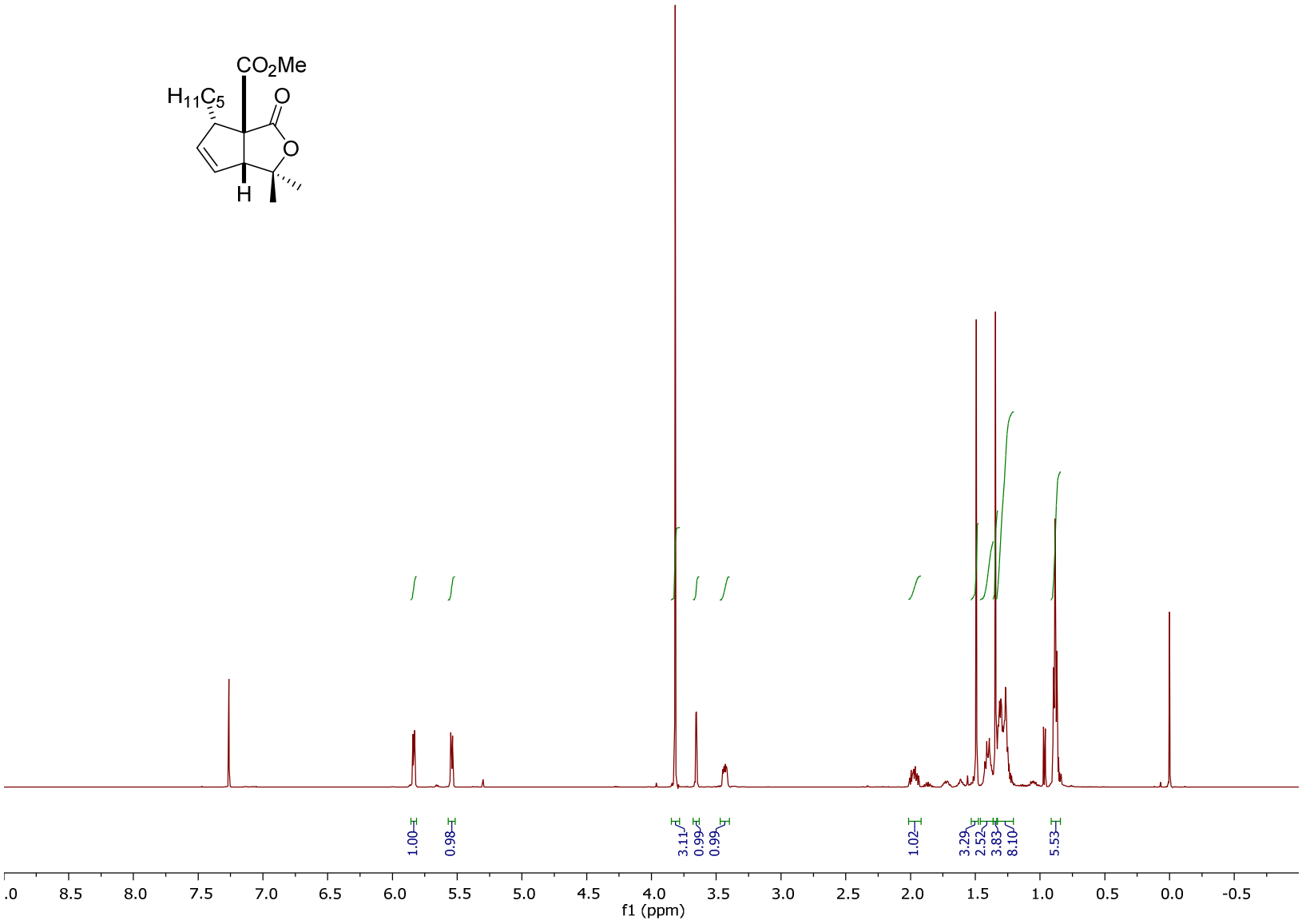
^{1}H NMR (500 MHz) for Compound 3l.



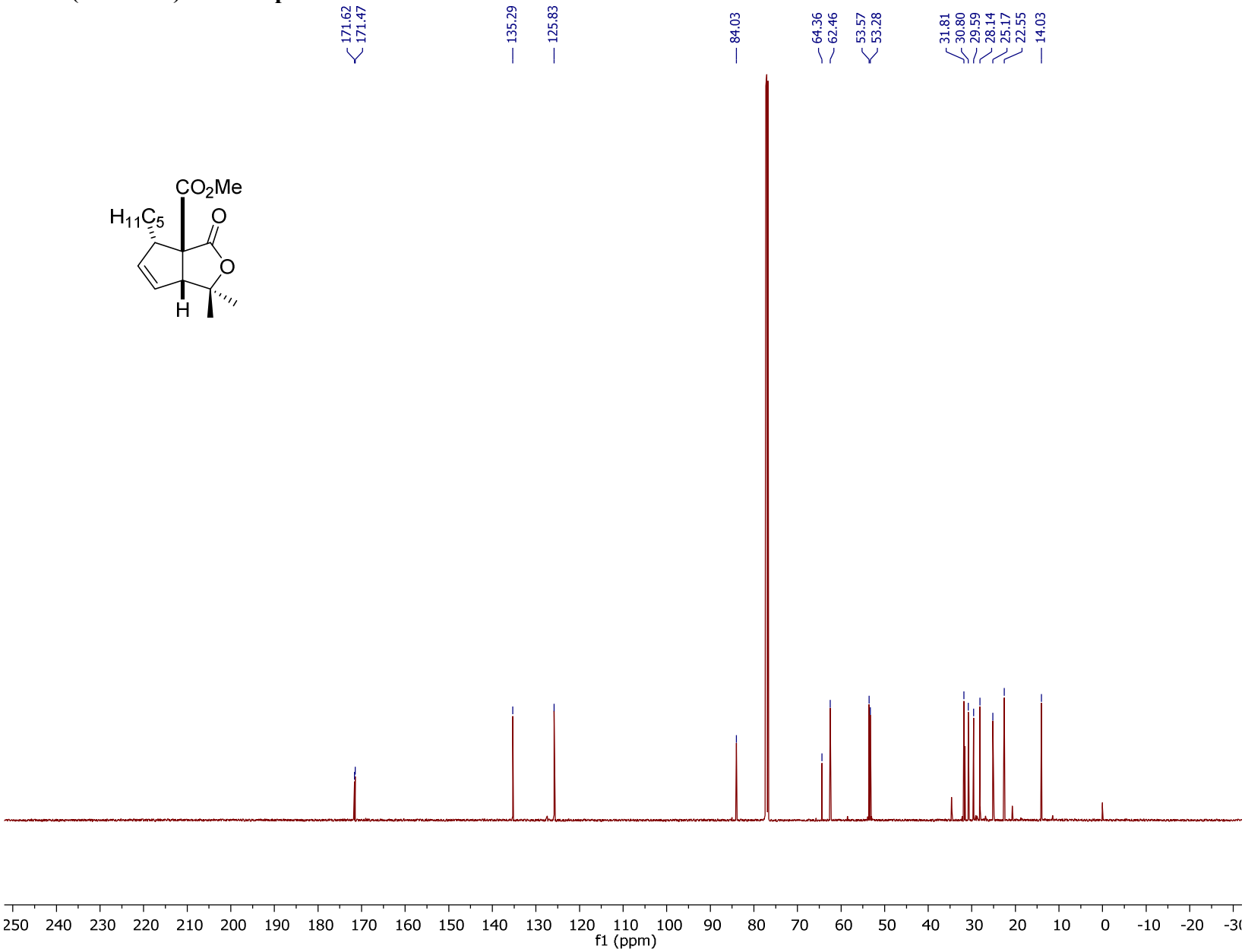
^{13}C NMR (125 MHz) for Compound 3l.



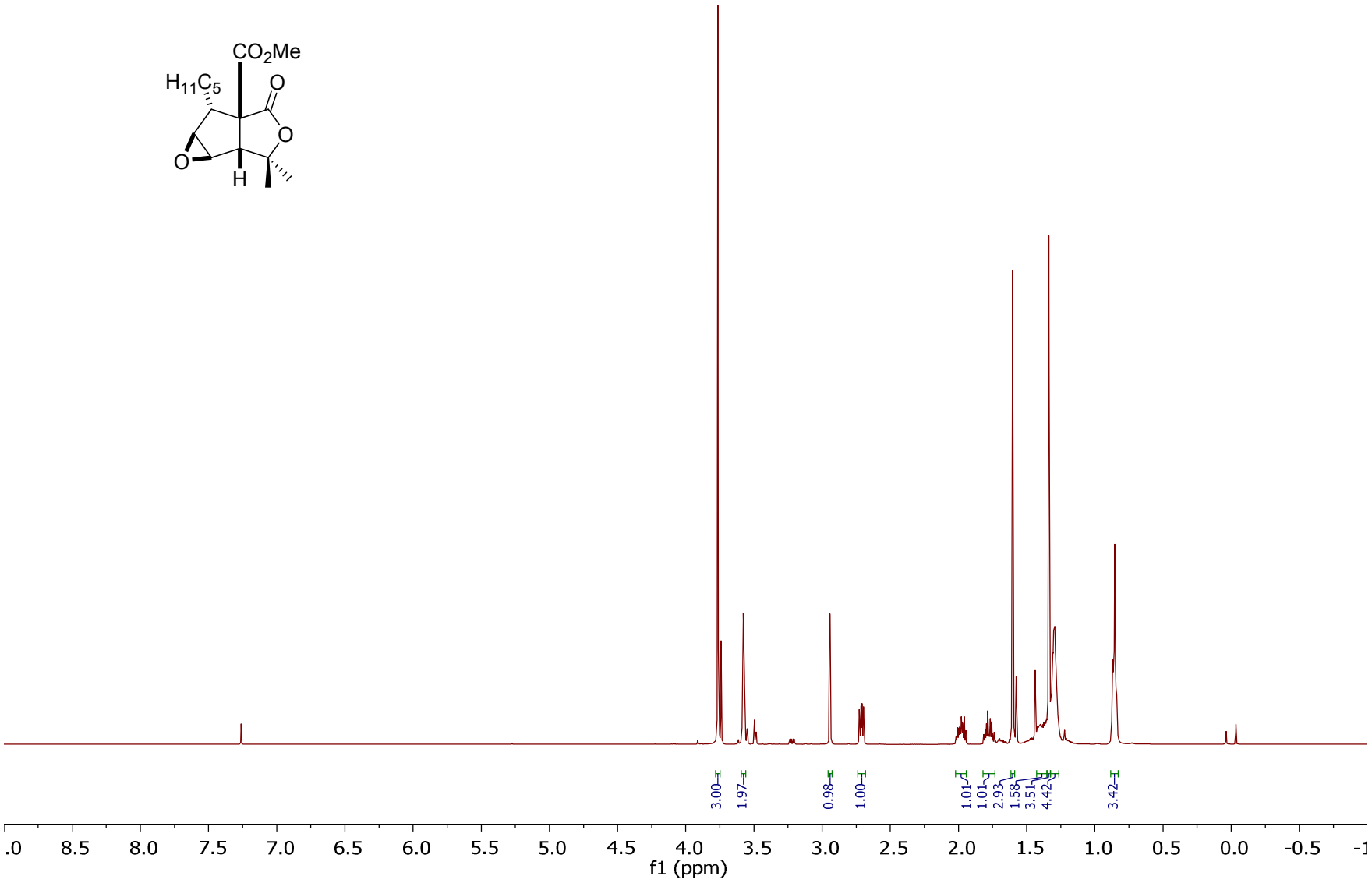
^{1}H NMR (500 MHz) for Compound 3m.



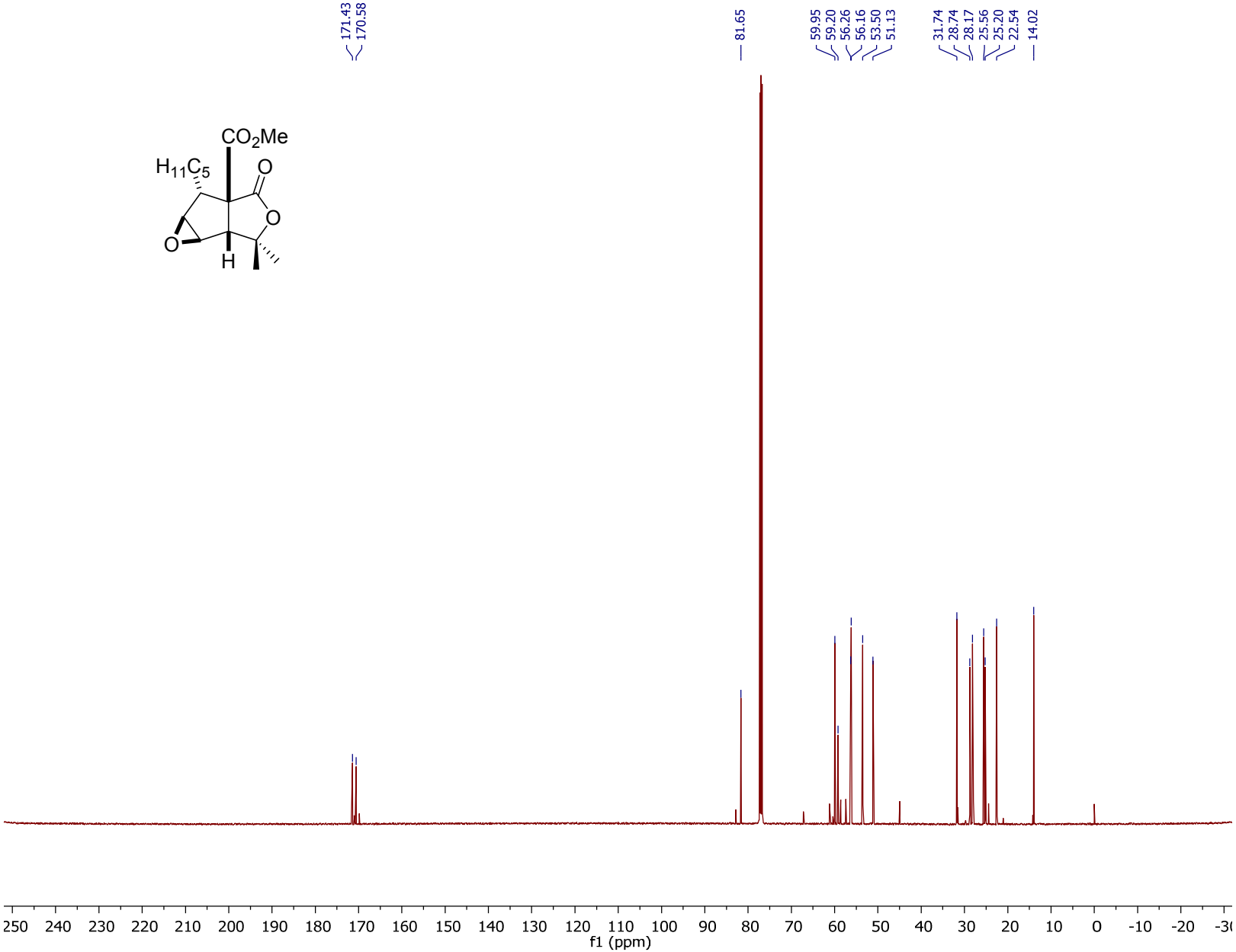
^{13}C NMR (125 MHz) for Compound 3m.



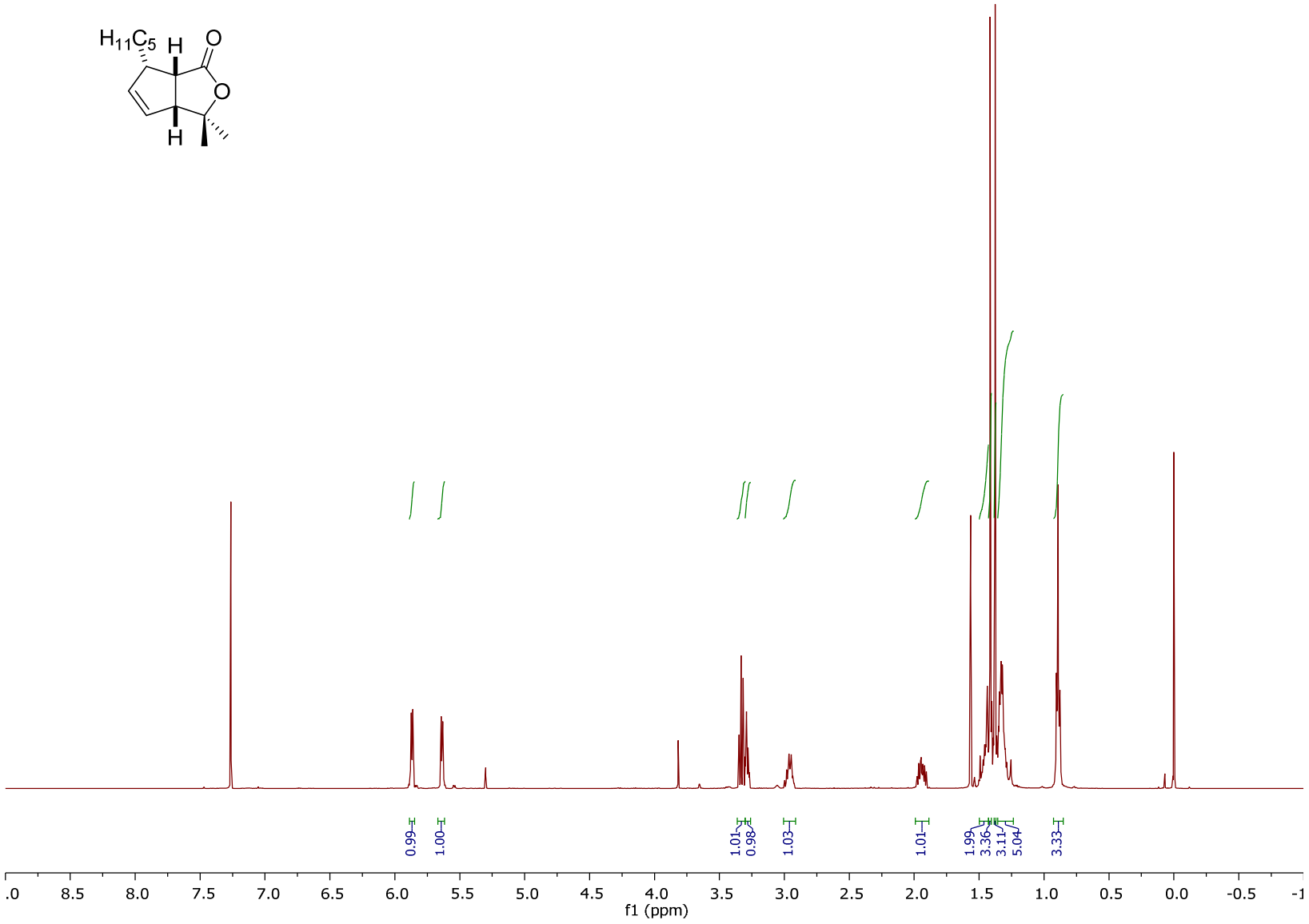
^{1}H NMR (500 MHz) for Compound 4.



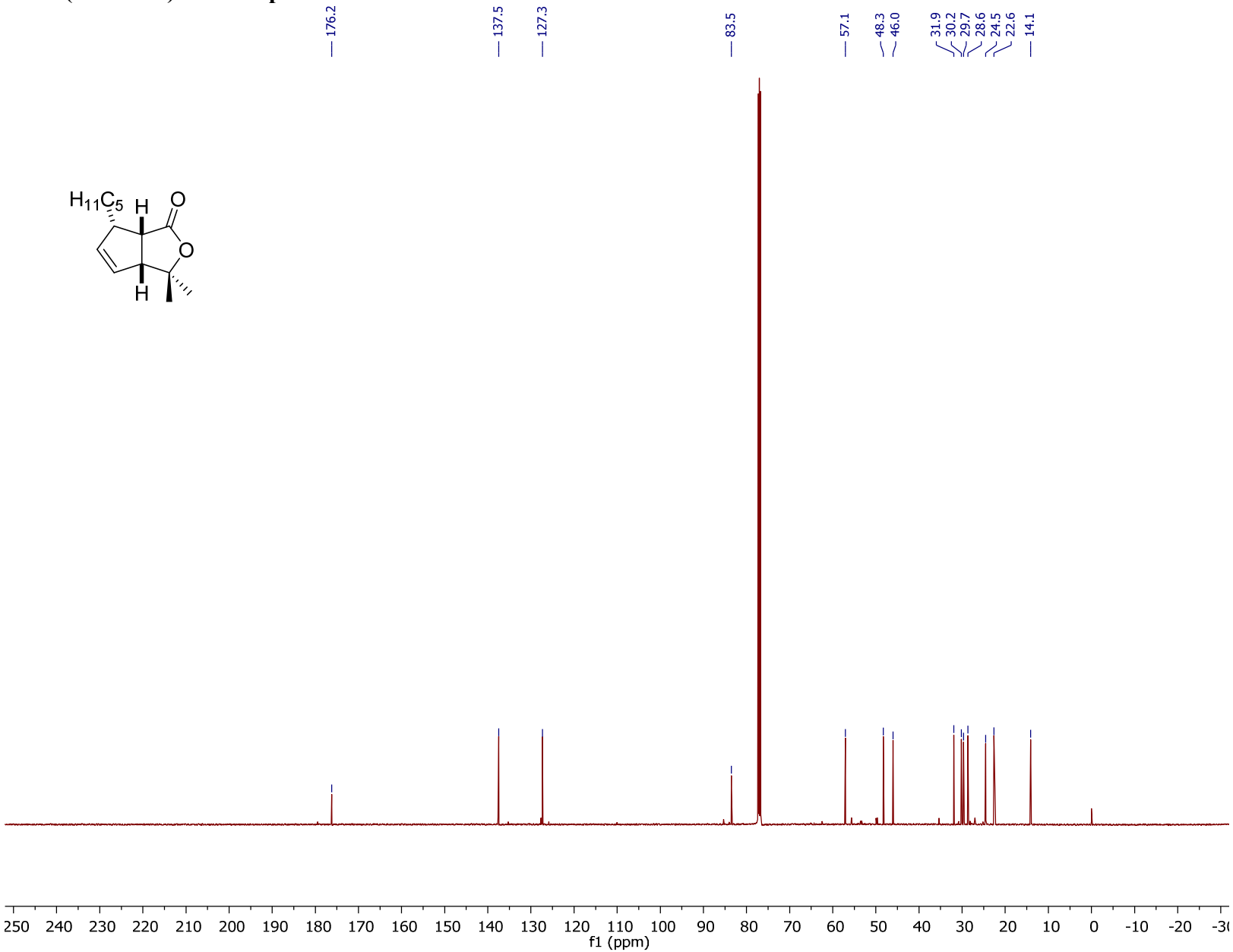
^{13}C NMR (125 MHz) for Compound 4.



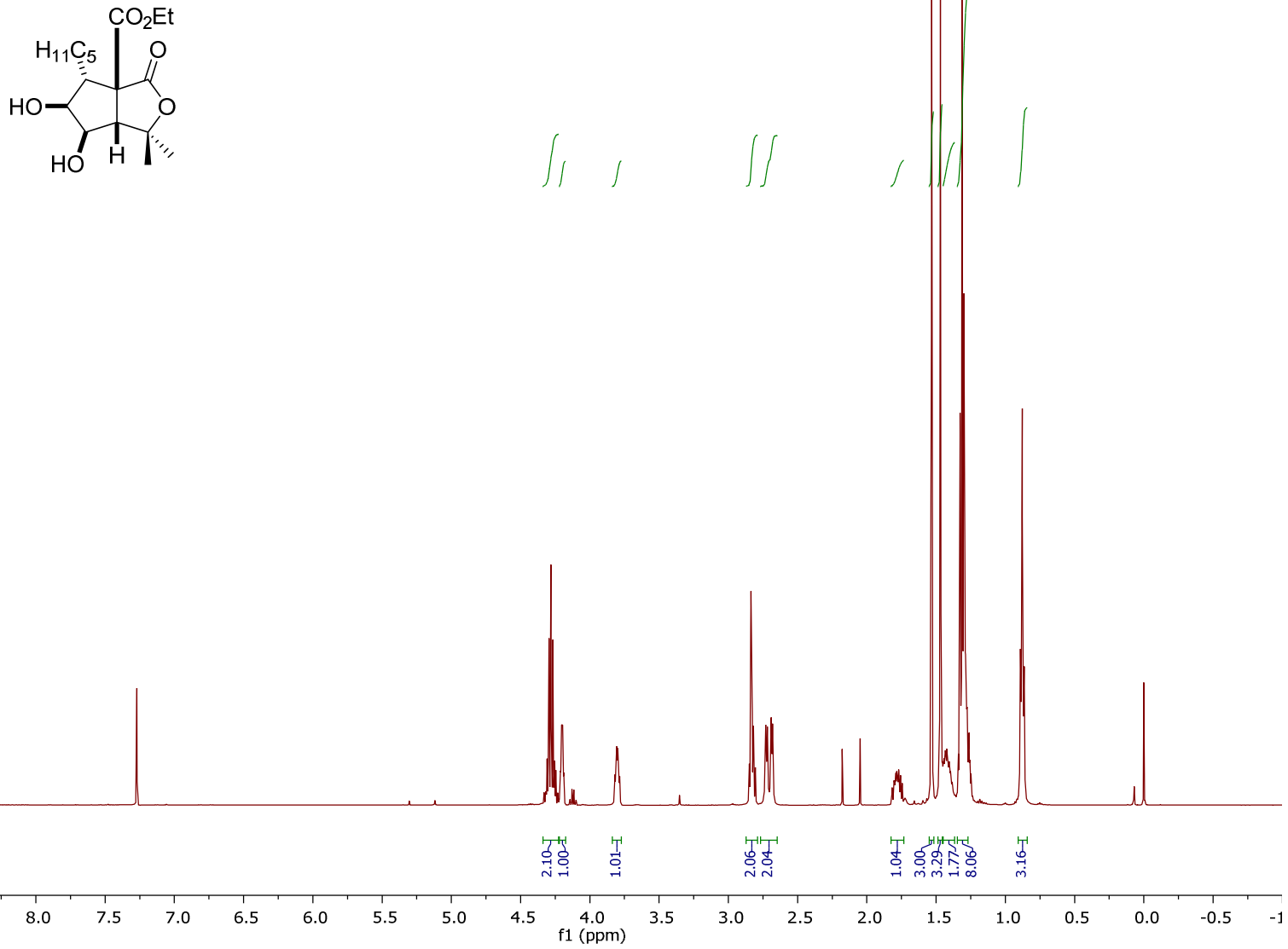
^{1}H NMR (500 MHz) for Compound 5.



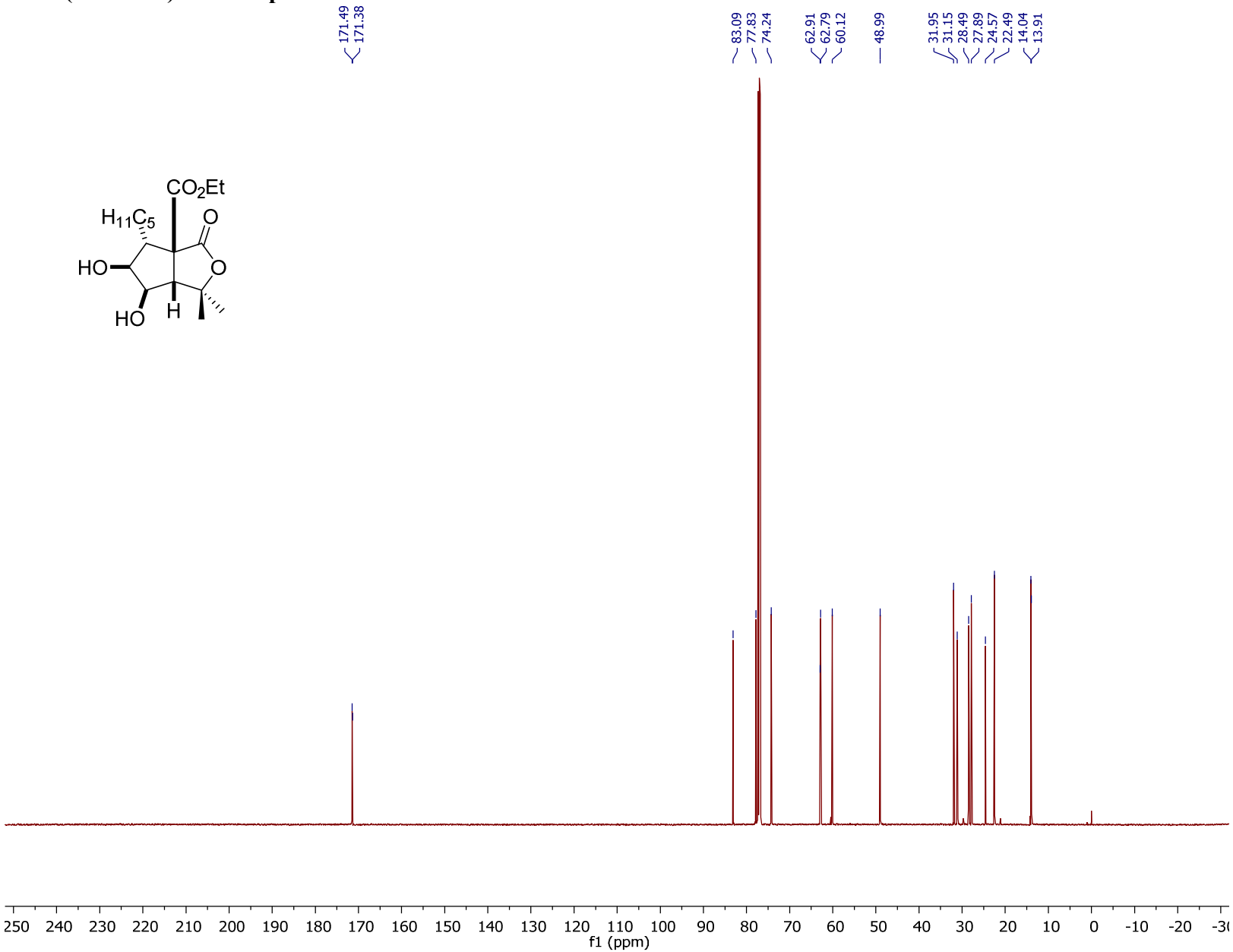
^{13}C NMR (125 MHz) for Compound 5.



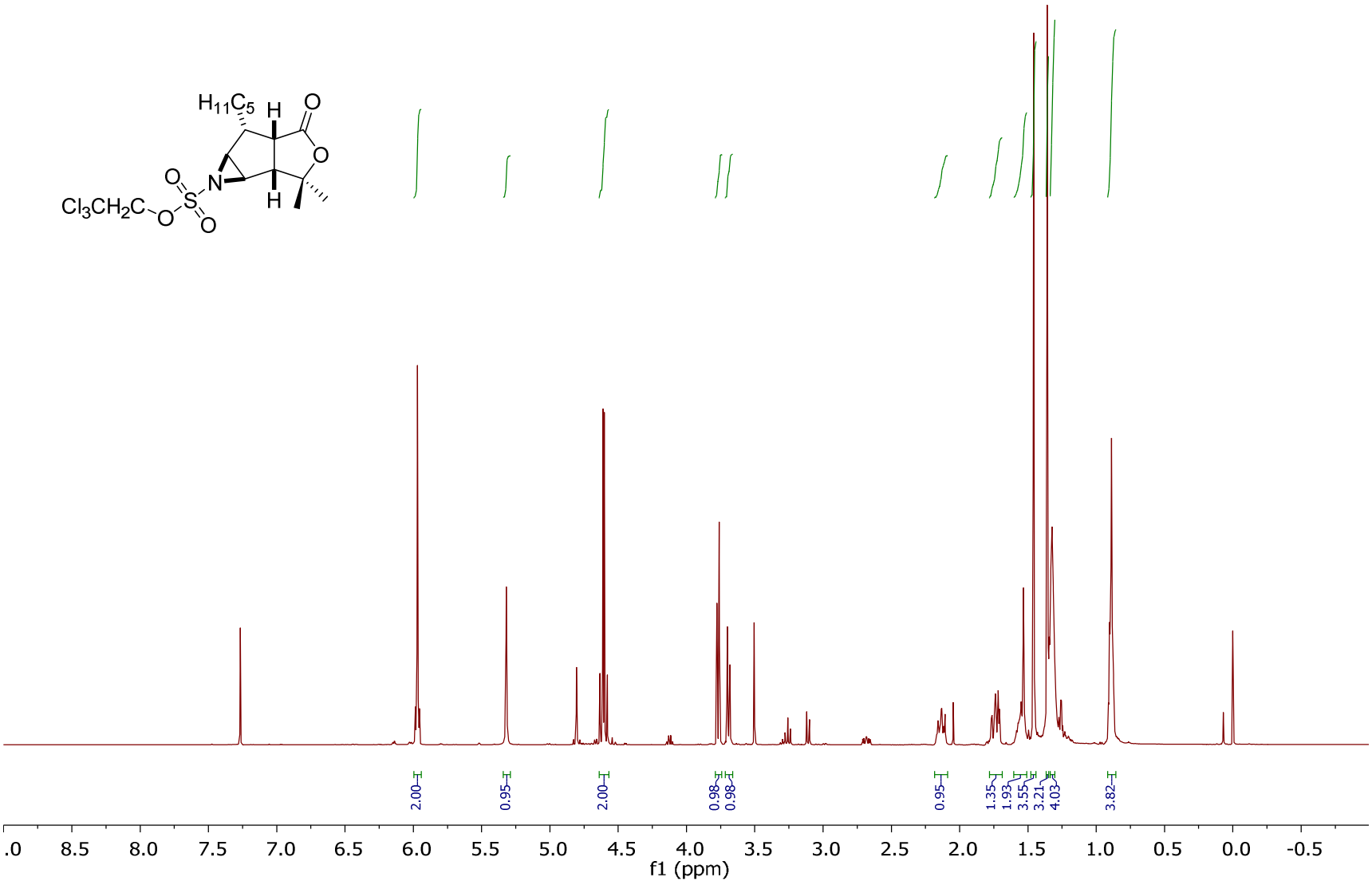
^{1}H NMR (500 MHz) for Compound 6.



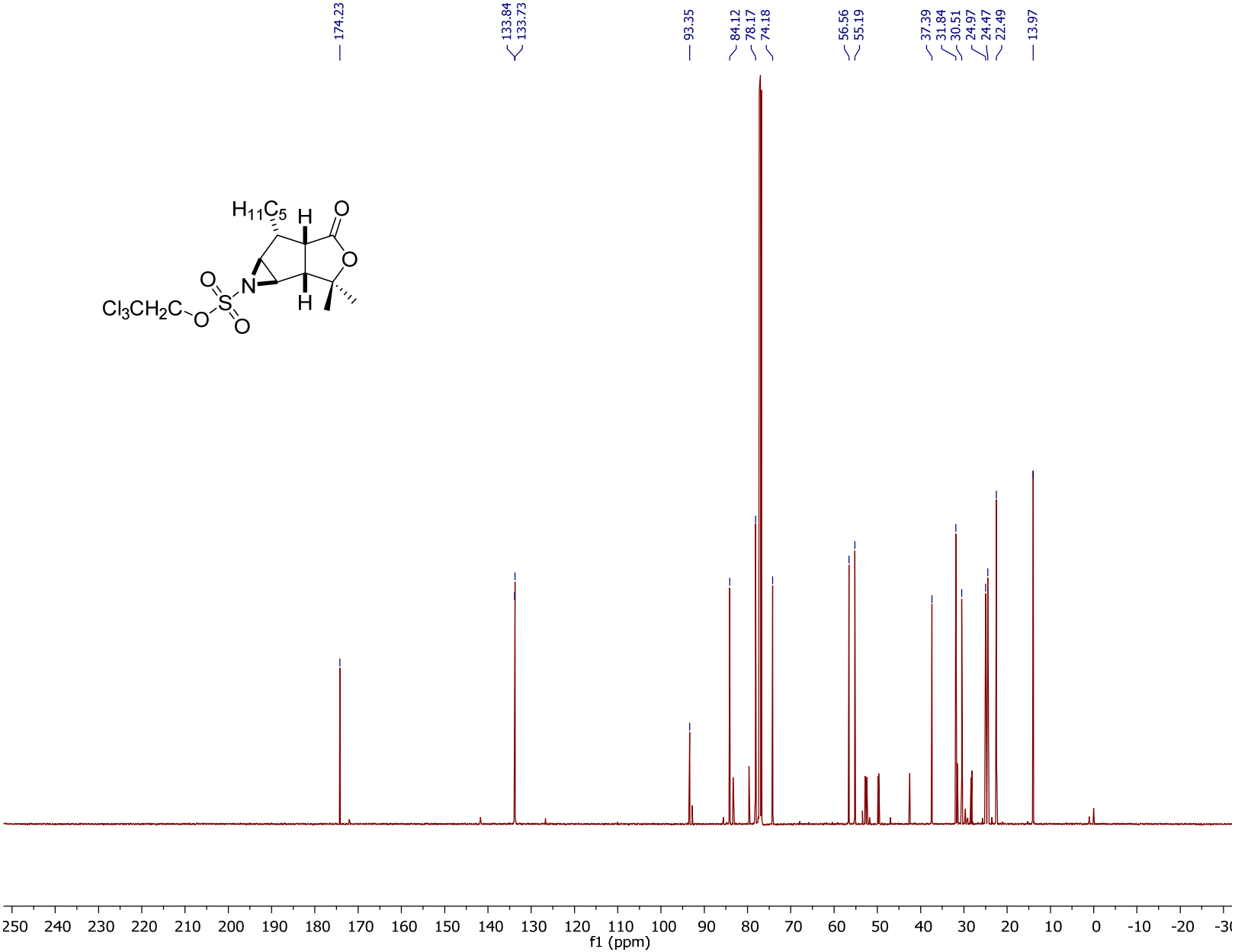
^{13}C NMR (125 MHz) for Compound 6.



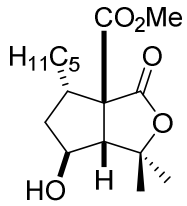
^{1}H NMR (500 MHz) for Compound 7.



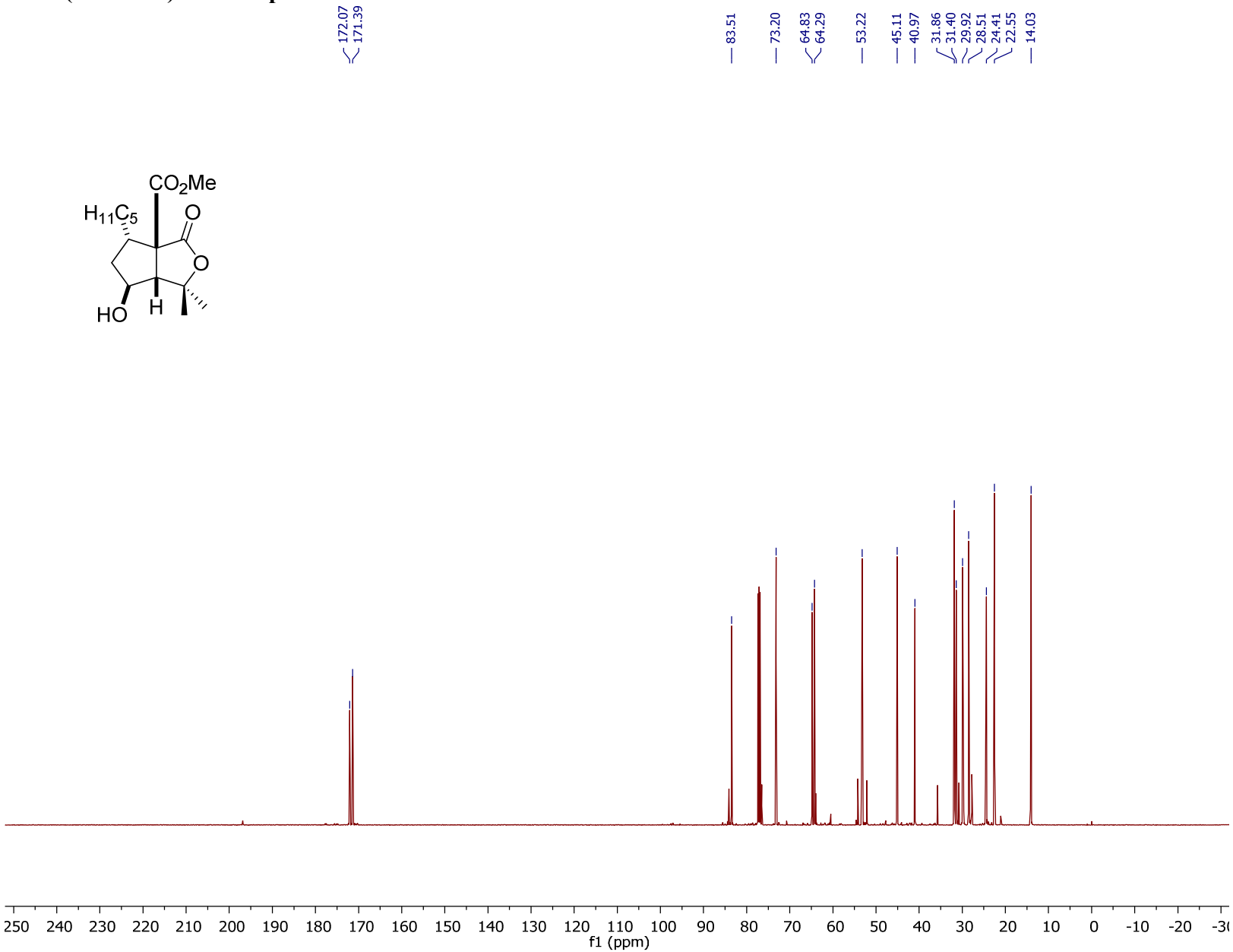
^{13}C NMR (125 MHz) for Compound 7.



^{1}H NMR (500 MHz) for Compound 8.



^{13}C NMR (125 MHz) for Compound 8.



VII. References

1. Armarego, W. L. F.; Chai, C. L. L., Chapter 4 - Purification of Organic Chemicals. In *Purification of Laboratory Chemicals (Sixth Edition)*, Butterworth-Heinemann: Oxford, 2009; pp 88-444.
2. Still, W. C.; Kahn, M.; Mitra, A., *J. Org. Chem.* **1978,** *43* (14), 2923-5.
3. Phelps, A. M.; Dolan, N. S.; Connell, N. T.; Schomaker, J. M., *Tetrahedron* **2013,** *69* (27-28), 5614-5621.
4. Corkey, B. K.; Toste, F. D., *J. Am. Chem. Soc.* **2005,** *127* (49), 17168-17169.
5. Guthikonda, K.; DuBois, J., *J. Am. Chem. Soc.* **2002,** *124* (46), 13672-13673.