

Supporting Information For:

A Novel Condensation, Fragmentation, and Elimination Reaction of
Bicyclo[2.2.1]heptenone Ring Systems

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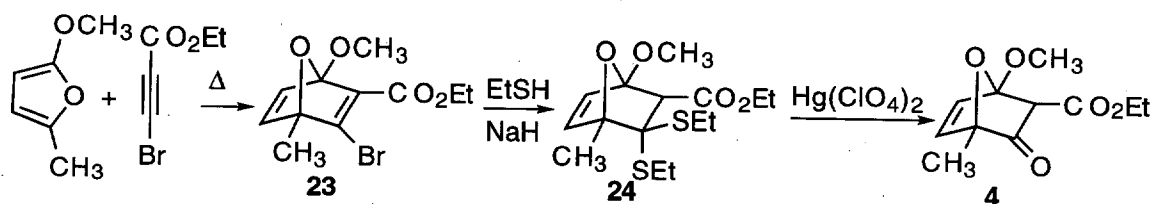
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Experimental procedure (including characterization data) as well as copies of the ^1H and ^{13}C NMR spectra for **4-12** and nOe data for **15** and **16**.

Experimental

General Information.

NMR spectra were recorded on either a Bruker AM-250 or a Varian 300 spectrophotometer. Chemical shifts were reported in δ , parts per million (ppm), relative to chloroform ($\delta = 7.24$ ppm) as an internal standard. Coupling constants, J , were reported in Hertz (Hz) and refer to apparent peak multiplicities and not true coupling constants. Mass spectra were recorded at the Mass Spectrometry Facility at the Department of Chemistry of the University of Arizona on a Jeol HX-110A and are reported as % relative intensity to the molecular base peak. IR spectra were recorded on a Nicolet Impact 410. Ether, THF, hexanes, benzene, and toluene were distilled from sodium/benzophenone. CH_2Cl_2 , CHCl_3 , TMEDA, $(i\text{-Pr})_2\text{NEt}$, Et_3N , and Et_2NH were distilled from CaH_2 . All other reagents were used without purification. Unless otherwise stated, all reactions were run under an atmosphere of argon in flame-dried glassware. Concentration refers to removal of solvent under reduced pressure (house vacuum at ca. 20 mm Hg) with a Büchi Rotavapor.

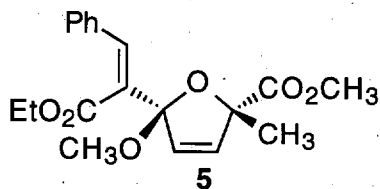


Representative procedure for the formation of Keto-ester. Preparation of ($\pm$)-ethyl-1-methoxy-4-methyl-7-oxabicyclo[2.2.1]hepta-5-ene-3-one-2-carboxylate (4**).** A solution of ethyl 3-bromopropiolate (0.25 g, 1.4 mmol), 2-methoxy-

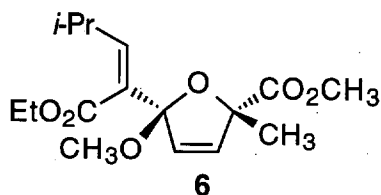
5-methyl furan (0.39 g, 3.5 mmol), and benzene (4 mL) was heated to 80°C for 8 hr. After cooling to rt, the mixture was concentrated. Purification by flash chromatography (7:1 hexanes/ethyl acetate) gave 0.18 g of **23** (45%). ¹H NMR (250MHz, CDCl₃) δ 6.89 (d, *J* = 5.3 Hz, 1H), 6.82 (d, *J* = 5.2 Hz, 1H), 4.19 (m, 2H), 3.46 (s, 3H), 1.61 (s, 3H), 1.24 (t, *J* = 7.1Hz, 3H); ¹³C NMR (250MHz, CDCl₃) δ 162.2, 153.7, 146.5, 142.9, 141.6, 116.5, 88.6, 60.6, 54.4, 15.5, 14.0 ppm; IR (CCl₄) 1715, 1320 cm⁻¹; MS (FAB⁺) 289(MH⁺), 291(MH⁺), 210 m/z; HRMS calcd for C₁₁H₁₃O₄Br (MH⁺) 289.0075, found 289.0081.

A solution of **23** (0.78 g, 2.7 mmol) and THF (20 mL) was added over 2 hrs to a solution of EtSNa (20 mL of a 0.27 M solution in THF, 5.4 mmol) at 0°C. After the addition was completed, the reaction was immediately quenched with NaHCO₃ (sat., 20 mL) extracted with ether, dried (MgSO₄), and concentrated. Flash chromatography (5:1 hexanes/ethyl acetate) afforded 0.86 g (96%) of **24** as a single diastereomer. ¹H NMR (250MHz, CDCl₃) δ 6.63 (d, *J* = 5.6 Hz, 1H), 6.39 (d, *J* = 5.6Hz, 1H), 4.12 (m, 2H), 3.47 (s, 3H), 3.40(s, 1H), 2.76 (m, 4H), 1.60 (s, 3H), 1.24(m, 6H), 1.12 (t, *J* = 7.5Hz, 3H); ¹³C NMR (62.5MHz, CDCl₃) δ 168.8, 140.2, 134.6, 113.1, 88.5, 73.7, 63.3, 61.0, 53.9, 25.8, 24.8, 16.3, 14.0, 13.8, 13.3; IR (CCl₄) 1739cm⁻¹; HRMS (FAB) calcd for C₁₅H₂₄O₄S₂(M+Cs⁺) 465.0170, found 465.0165.

To a solution of **24** (0.20 g, 0.88 mmol) and THF (4mL) at 0°C was added water (0.8 mL, 44 mmol) and CaCO₃ (0.12 g, 1.2 mmol) followed by Hg(ClO₄)₂ (0.54 g, 1.3 mmol). The reaction mixture was immediately diluted with ether (25 ml) and phosphate buffer (pH 7.0, 25 ml). The aqueous phase was extracted with ether (3 X 25 mL); the extracts were dried (Na₂SO₄), and concentrated. Chromatography (5:1) gave 82 mg (61%) of **4** as thick oil. ¹H NMR (250MHz, CDCl₃) δ 6.84 (d, *J* = 5.6 Hz, 1H), 6.19 (d, *J* = 5.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.55, (s, 3H), 3.40 (s, 1H), 1.55 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (250MHz, CDCl₃) δ 198.1, 166.7, 140.0, 133.9, 111.3, 88.1, 61.6, 53.9, 53.3, 14.0, 12.5; IR (CCl₄) 1777, 1734 cm⁻¹; HRMS (FAB) calcd for C₁₁H₁₄O₅ (M+H⁺) 227.0919, found 227.0915.

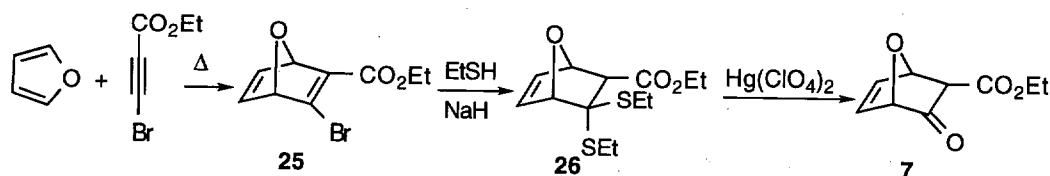


Representative procedure for the condensation, fragmentation, and elimination reaction. Preparation of (±)-5-methoxycarbonyl-5-methyl-2-methoxy-2-Z-[ethyl-3-phenylprop-2-enoate]-2,5-dihydrofuran (5). A solution of **4** (0.050 g, 0.20 mmol) and DMF (1 mL) was added dropwise to a slurry of NaH (0.006 g, 0.2 mmol) and DMF (0.5 mL) at 0°C. After stirring for 1 h at 0°C, benzaldehyde (0.04 mL, 0.4 mmol) was added. The mixture was allowed to slowly warm to room temperature, stirred for 1 h, and quenched with methyl iodide (0.3 mL, 5 mmol). NaHCO₃ (sat., 10 mL) was added, the mixture was separated and the aqueous phase was extracted with ether (3 X 15 mL). The extracts were dried (MgSO₄) and concentrated. Flash chromatography (5:1 hexane/ethyl acetate) provided 0.060 g (83%) of furan **5** as a colorless oil. ¹H NMR (250MHz, CDCl₃) δ 7.31 (s, 1H), 7.18 (s, 5H), 6.16 (d, *J* = 5.8 Hz, 1H), 6.04 (d, *J* = 5.7 Hz), 4.11 (m, 2H), 3.61 (s, 3H), 3.22 (s, 3H), 1.59 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (62.5MHz, CDCl₃) δ 172.0, 168.1, 135.1, 133.9, 133.8, 132.7, 130.4, 128.3, 128.2, 128.1, 113.6, 90.0, 60.9, 52.4, 50.4, 24.9, 13.6; IR (CCl₄) 1758, 1727, 1258, 1215 cm⁻¹; HRMS (FAB) calcd for C₁₉H₂₂O₆ (M+Cs⁺) 479.0471, found 479.0483.



Preparation of (±)-5-methoxycarbonyl-5-methyl-2-methoxy-2-Z-[ethyl-4-methylpent-2-enoate]-2,5-dihydrofuran (6). Prepared according to the procedure outlined for the formation of **5** using **4** (0.080 g, 0.4 mmol), NaH (0.01 g, 0.4 mmol), isobutyraldehyde (0.07 mL, 0.8 mmol), DMF (3 mL), and methyl iodide (0.3 mL, 5 mmol) to give 0.091 g (78%) of **6** as a colorless oil. ¹H NMR (250MHz, CDCl₃) δ 6.37 (d, *J* = 10.2 Hz, 1H), 6.21 (d, *J* = 5.8 Hz, 1H), 6.05 (d, *J* = 5.7 Hz, 1H), 4.18 (m, 2H), 3.70 (s, 3H), 3.20 (s, 3H), 2.85 (m, 1H), 1.62 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (62.5MHz, CDCl₃) δ 172.2, 167.2, 146.7, 132.6, 130.7, 130.4, 113.6, 89.5, 60.5, 52.2, 50.3, 28.7, 24.8, 22.6,

22.5, 14.2; IR (CCl₄) 1764, 1721, 1449 cm⁻¹; HRMS (FAB) calcd for C₁₆H₂₄O₆ (M+Cs⁺) 445.0627, found 445.0614.



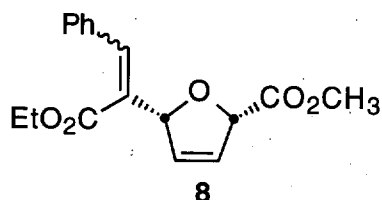
Preparation of (±)-ethyl-7-oxabicyclo[2.2.1]hepta-5-ene-3-one-2-carboxylate (7).

A solution of ethyl 3-bromopropiolate (1.5 g, 8.0 mmol) and furan (6 mL, 82 mmol) was heated at 80 °C in a pressure tube for 24 h. After cooling and concentrating, the resulting oil was purified by flash chromatography (5:1 hexanes/ethyl acetate) to give 0.47 g (24%) of **25** as a colorless oil. ¹H NMR (250MHz, CDCl₃) δ 7.20 (dd, *J* = 5.4, 1.8 Hz, 1H), 7.14 (dd, *J* = 5.3, 1.8 Hz, 1H), 5.65 (t, *J* = 1.6 Hz, 1H), 5.28 (t, *J* = 1.6 Hz, 1H), 4.20 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (62.5MHz, CDCl₃) δ 162.3, 148.7, 144.2, 143.1, 141.2, 89.5, 84.5, 60.8, 14.1; IR (CCl₄) 1703, 1314 cm⁻¹.

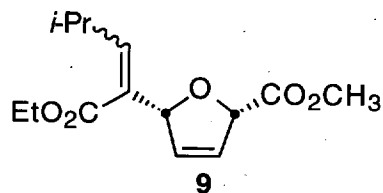
Prepared according to the procedure for **24** using **25** (0.47 g, 1.9 mmol), THF (15 mL), and EtSNa (15 mL of a 0.25 M solution in THF, 3.8 mmol) to give 0.49 g (89%) of **26** as a 3:1 mixture of endo:exo isomers. **26** (endo isomer) ¹H NMR (250MHz, CDCl₃) δ 6.60 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.40 (dd, *J* = 5.8, 1.8 Hz, 1H), 5.04 (d, *J* = 4.3 Hz, 1H), 4.74 (s, 1H), 4.02 (m, 2H), 3.34 (d, *J* = 4.3 Hz, 1H), 2.74 (m, 3H), 2.54 (m, 1H), 1.18 (q, *J* = 7.1 Hz, 6H), 1.09 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (62.5MHz, CDCl₃) δ 168.8, 136.0, 133.9, 86.6, 80.3, 66.6, 60.8, 58.9, 25.0, 24.6, 13.8, 13.4, 13.3; IR (CCl₄) 1734, 1172 cm⁻¹; HRMS (FAB) calcd for C₁₃H₂₀O₃S₂ (M+H⁺) 289.0932, found 289.0942. **26** (exo isomer) ¹H NMR (250MHz, CDCl₃) δ 6.43 (s, 2H), 5.21 (s, 1H), 4.90 (s, 1H), 4.20 (dq, *J* = 7.2, 1.8 Hz, 2H), 2.84-2.66 (m, 5H), 1.30-1.13 (m, 9H); ¹³C NMR (62.5MHz, CDCl₃) δ 170.3, 135.7, 135.5, 85.3, 81.1, 65.2, 61.1, 58.2, 25.4, 25.2, 14.0, 13.7, 13.3; IR (CCl₄) 1734, 1178 cm⁻¹; HRMS (FAB) calcd for C₁₃H₂₀O₃S₂ (M+H⁺) 289.0932, found 289.0942.

Prepared according to the procedure outlined for the formation of **4** using **26** (0.23 g, 0.8 mmol), Hg(ClO₄)₂ (0.64 g, 1.6 mmol), CaCO₃ (0.3 g, 3.0 mmol), H₂O (0.8 mL, 44 mmol), and THF (4 mL) to afford 0.8 g (55%) of **7** as a colorless oil and as a 2:1 mixture of endo:exo isomers. ¹H NMR (250MHz, CDCl₃) (endo isomer) δ 6.94 (dd, *J* = 5.8, 1.7 Hz, 1H), 6.40 (dd, *J* = 5.8, 2.0 Hz, 1H), 5.32 (d, *J* = 4.0 Hz, 1H), 4.73 (d, *J* = 1.8 Hz, 1H), 4.12 (q, *J* = 7.3 Hz, 2H), 3.35 (d, *J* = 4.0 Hz, 1H), 1.24 (t, *J* = 7.3 Hz,

3H), (*exo isomer*) δ 6.72 (dd, $J = 5.8, 1.6$ Hz, 1H), 6.54 (dd, $J = 5.8, 1.9$ Hz, 1H), 5.54 (s, 1H), 4.66 (s, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 2.87 (s, 1H), 1.24 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (62.5MHz, CDCl_3) δ 199.3, 198.1, 166.9, 166.5, 141.7, 141.2, 132.6, 127.8, 82.7, 81.5, 81.5, 79.5, 61.8, 61.6, 50.0, 48.0, 14.0; IR (CCl_4) 1777, 1734 cm^{-1} ; ; HRMS(FAB) calcd for $\text{C}_9\text{H}_{10}\text{O}_4(\text{M}+\text{H}^+)$ 183.0657, found 183.0656.

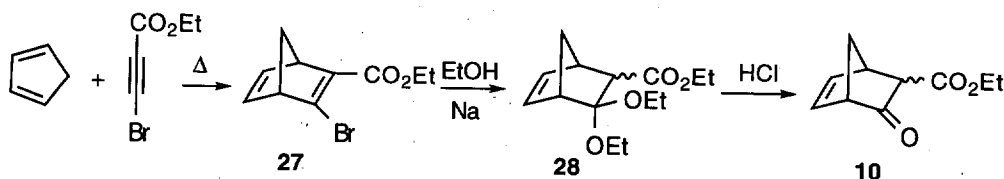


Preparation of (±)-5-methoxycarbonyl-2-[ethyl-3-phenylprop-2-enoate]-2,5-dihydrofuran (8). Prepared according to the procedure outlined for the formation of **5** using **7** (0.14 g, 0.77 mmol), NaH (0.02 g, 0.8 mmol), benzaldehyde (0.17 mL, 1.6 mmol), DMF (6 mL), and methyl iodide (0.6 mL, 10 mmol) to give 0.13 g (56%) of **8** as a 3:1 mixture of *E*- and *Z*-alkenes. **8E-alkene isomer:** ^1H NMR (250MHz, CDCl_3) δ 7.81 (s, 1H), 7.38-7.32 (m, 5H), 5.90 (m, 2H), 5.83 (m, 1H), 5.28(m, 1H), 4.19 (m, 2H), 3.74 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (62.5MHz, CDCl_3) δ 170.7, 166.5, 143.5, 134.3, 130.7, 129.4, 128.9, 128.4, 128.3, 124.8, 84.3, 82.7, 60.6, 52.0, 14.0; IR (CCl_4) 1767, 1720, 1243 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_5 (\text{M}+\text{H}^+)$ 303.1232, found 303.1235. **8Z- alkene isomer:** ^1H NMR (250MHz, CDCl_3) δ 7.34 (s, 1H), 7.27 (s, 5H), 6.13 (m, 1H), 5.94 (m, 1H), 5.70 (m, 1H), 5.34 (m, 1H), 4.11 (dq, $J = 7.2, 2.1$ Hz, 2H), 3.74 (s, 3H), 1.08 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (62.5MHz, CDCl_3) δ 170.7, 167.5, 135.8, 135.7, 132.6, 131.4, 128.6, 128.1, 127.9, 124.8, 88.2, 84.6, 60.8, 52.2, 13.7; IR (CCl_4) 1765, 1703, 1216 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_5 (\text{M}+\text{H}^+)$ 303.1232, found 303.1228.



Preparation of (±)-5-methoxycarbonyl-2-[ethyl-4-methylpent-2-enoate]-2,5-dihydrofuran (9). Prepared according to the procedure outlined for the formation of **5** using **7** (0.16 g, 0.89 mmol), NaH (0.02 g, 0.9 mmol), isobutyraldehyde (0.14 mL, 1.8 mmol), DMF (6 mL), and methyl iodide (0.6 mL, 10 mmol) to give 0.11 g (45%) of **9**

as a 1:2 mixture of *E*- and *Z*-alkenes. **9Z**: ^1H NMR (250MHz, CDCl_3) δ 6.37 (d, $J = 9.9$ Hz, 1H), 6.02 (m, 1H), 5.83 (m, 1H), 5.57 (br. s, 1H), 5.25 (m, 1H), 4.17 (dq, $J = 7.2$, 2.6 Hz, 2H), 3.70 (s, 3H), 3.23 (m, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 0.98 (t, $J = 6.5$ Hz, 6H); ^{13}C NMR (62.5MHz, CDCl_3) δ 170.9, 166.4, 150.8, 132.1, 128.4, 124.2, 87.1, 84.3, 60.2, 51.9, 28.1, 22.4, 22.3, 14.1; IR (CCl_4) 1762, 1719 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{20}\text{O}_5$ ($\text{M}+\text{Cs}^+$) 401.0365, found 401.0374. **9E**: ^1H NMR (300MHz, CDCl_3) δ 6.67 (d, $J = 10.5$, 1H), 5.99 (m, 1H), 5.92 (m, 1H), 5.83 (m, 1H), 5.24 (m, 1H), 4.11 (m, 2H), 3.72 (s, 3H), 2.90 (m, 1H), 1.20 (t, $J = 6.9$ Hz, 3H), 1.00 (dd, $J = 6.0$, 4.2 Hz, 6H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 170.6, 166.6, 153.8, 131.2, 127.7, 125.0, 84.1, 82.5, 60.4, 52.0, 27.1, 22.5, 22.4, 14.0; IR (CCl_4) 1765, 1721, 1258 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{20}\text{O}_5$ ($\text{M}+\text{Cs}^+$) 401.0365, found 401.0357.



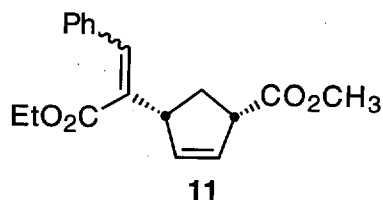
Preparation of (±)-3-ethoxycarbonylbicyclo[2.2.1]hepta-5-ene-2-one (10).

Prepared according to the procedure outlined for the formation of **23** using cyclopentadiene (0.84 g, 12.7 mmol), ethyl-3-bromopropiolate (1.84 g, 10.4 mmol), and benzene (20 mL) to afford 2.06 g (91%) of **27** as a colorless oil. ^1H NMR (250MHz, CDCl_3) δ 6.85 (m, 1H), 6.79 (m, 1H), 4.17 (m, 2H), 3.94 (m, 1H), 3.62 (s, 1H), 2.26 (d, $J = 6.6$ Hz, 1H), 2.07 (d, $J = 6.6$ Hz, 1H), 1.26 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (62.5MHz, CDCl_3) δ 163.7, 148.3, 142.9, 142.0, 140.3, 71.6, 61.6, 60.4, 52.0, 14.1; HRMS (FAB) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ ($\text{M}+\text{H}^+$) 243.0021, found 243.0029.

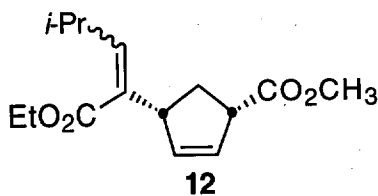
A solution of **27** (0.60 g, 2.7 mmol) and ethanol (2 mL) was added to a solution of sodium ethoxide (1 mL of a 5.4 M solution in ethanol, 5.4 mmol) at rt. The resulting mixture was heated to 85°C for 0.2 h. After cooling to rt, the reaction was quenched with NaHCO_3 (sat., 40 mL), extracted with ether (3×50 mL), dried (MgSO_4), and concentrated. Flash chromatography (5:1 hexanes/ethyl acetate) gave 0.4 g (63%) of **28** as yellow oil. ^1H NMR (250MHz, CDCl_3) δ (endo isomer) 6.55(m, 1H), 5.95(m, 1H), 4.15 (m, 1H), 3.97 (m, 1H), 3.79-3.43 (m, 3H), 3.25 (m, 1H), 2.98 (d, $J = 3.3$ Hz, 1H), 2.88 (m, 2H), 1.67 (m, 1H), 1.55 (m, 1H), 1.24-1.02 (m, 9H); (exo isomer) 6.15 (m, 1H), 6.12 (m, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 4.15 (m, 1H), 3.97 (m, 1H), 3.79-3.43 (m, 3H), 3.25 (m, 1H), 2.42 (d, $J = 2.6$ Hz, 1H), 2.14 (d, $J = 8.2$ Hz, 1H), 1.55 (m,

1H), 1.24-1.02 (m, 9H); ^{13}C NMR (62.5MHz, CDCl_3) δ 172.3, 171.3, 138.7, 137.4, 136.2, 130.1, 128.2, 112.4, 112.1, 59.9, 59.8, 58.9, 58.3, 57.7, 56.5, 55.0, 53.1, 50.9, 47.2, 47.1, 46.0, 44.6, 43.8, 15.3, 15.2, 15.1, 14.8, 14.2, 14.1; IR (CCl_4) 1740, 1178, 1060 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4$ ($\text{M}+\text{H}^+$) 255.1596, found 255.1602.

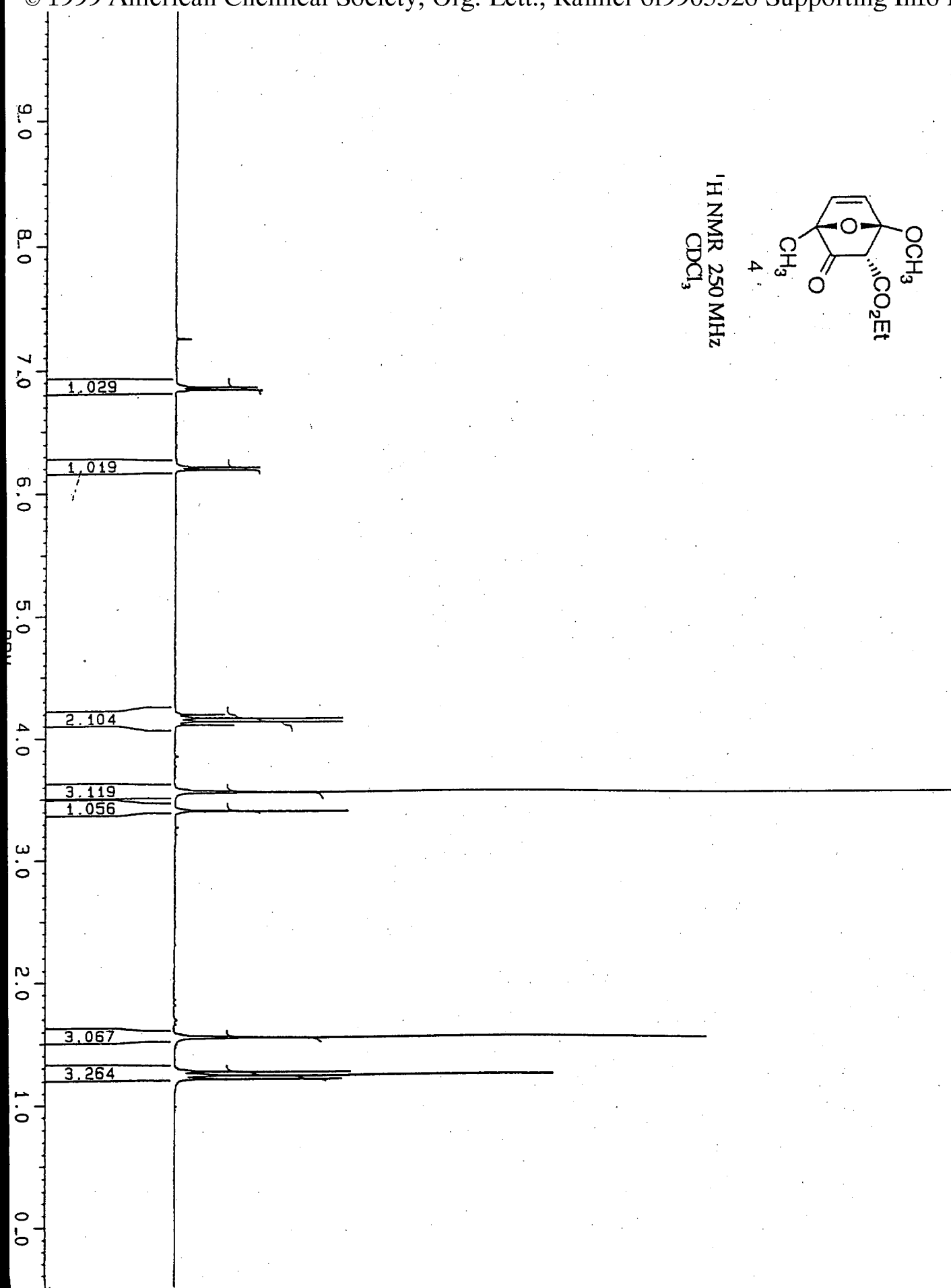
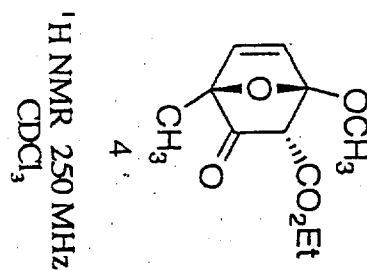
A solution **28** (0.35 g, 1.4 mmol) and THF (2 mL) was added dropwise to a solution of HCl (2 mL of a 2M (aq) solution) and THF (2 mL). After 0.2 h the reaction mixture was extracted with ether (3 X 10 mL), the extracts were dried (MgSO_4), and concentrated to give 0.24 g (95%) of **10** as a colorless oil. ^1H NMR (250MHz, CDCl_3)(endo isomer) δ 6.67 (m, 1H), 5.97 (m, 1H), 4.07 (m, 2H), 3.25 (s, 1H), 3.10 (s, 1H), 3.06 (d, $J = 3.0$ Hz, 1H), 2.04 (d, $J = 9.7$ Hz, 1H), 1.84 (d, $J = 9.5$ Hz, 1H), 1.19 (m, 3H); (exo isomer) δ 6.51 (m, 1H), 6.14 (m, 1H), 4.07 (m, 2H), 3.28 (s, 1H), 3.03 (s, 1H), 2.78 (d, $J = 3.8$ Hz, 1H), 2.42 (d, $J = 9.8$ Hz, 1H), 2.12 (s, 1H), 1.19 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl_3) δ 207.1, 204.5, 168.7, 168.3, 142.4, 142.0, 133.0, 128.2, 61.2, 61.0, 55.7, 54.8, 52.9, 50.4, 47.9, 47.8, 44.0, 42.6, 14.0; IR (CCl_4) 1764, 1721, 1313; HRMS (FAB) calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3$ ($\text{M}+\text{H}^+$) 181.0865, found 181.0856.

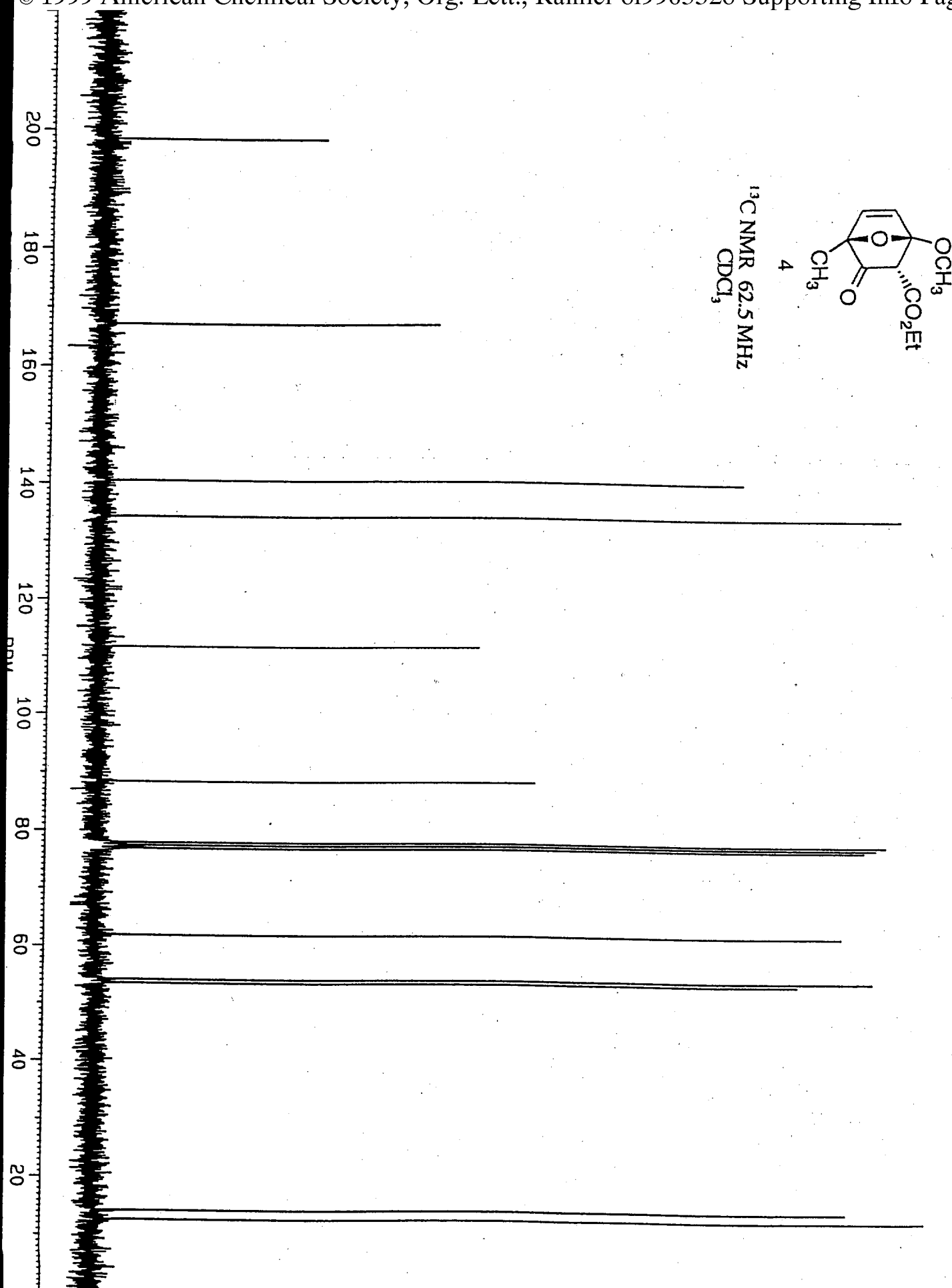


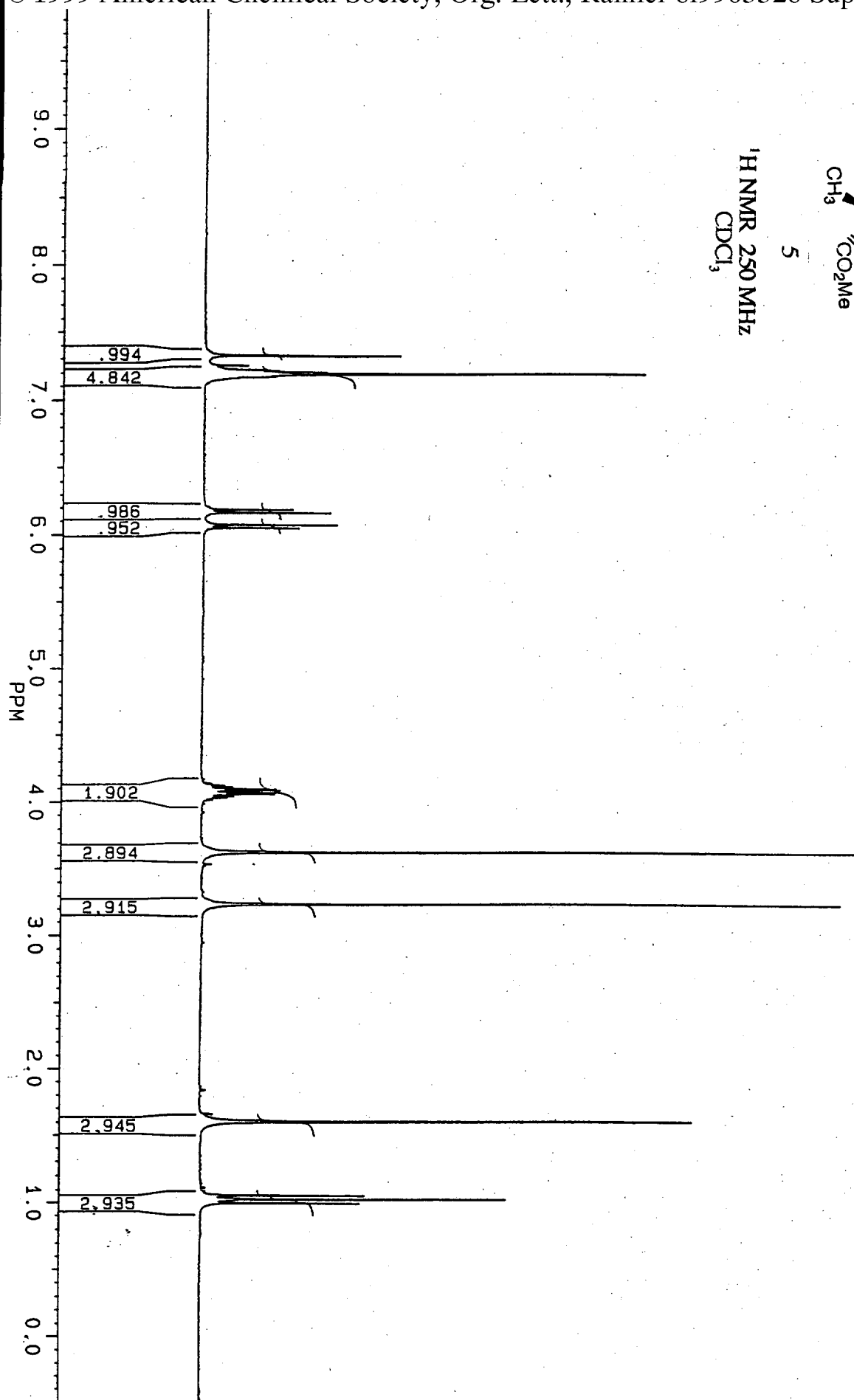
Preparation of (±)-2-methoxycarbonyl-4-E-[ethyl-3-phenylprop-2-enoate]-1-cyclopentene (11). Prepared according to the procedure outlined for the formation of **5** using **10** (0.090 g, 0.50 mmol), $\text{KO}^t\text{-Bu}$ (0.083 g, 0.75 mmol), benzaldehyde (0.06 mL, 0.6 mmol), DMF (3 mL), and methyl iodide (0.3 mL, 5 mmol) to give 0.13 g (91%) of **11**. ^1H NMR (300MHz, CDCl_3) δ 7.71 (s, 1H), 7.40-7.33 (m, 5H), 5.81 (m, 1H), 5.70 (m, 1H), 4.21 (q, $J = 6.9$ Hz, 2H), 4.05 (m, 1H), 3.72 (s, 3H), 3.61 (m, 1H), 2.41 (m, 2H), 1.27 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75.0MHz, CDCl_3) δ 174.3, 167.4, 139.9, 135.6, 135.4, 134.2, 128.9, 128.3, 128.2, 128.0, 60.5, 51.8, 50.4, 44.0, 33.0, 14.0; IR (CCl_4) 1740, 1715, 1233 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4$ ($\text{M}+\text{Cs}^+$) 433.0416, found 433.0400.



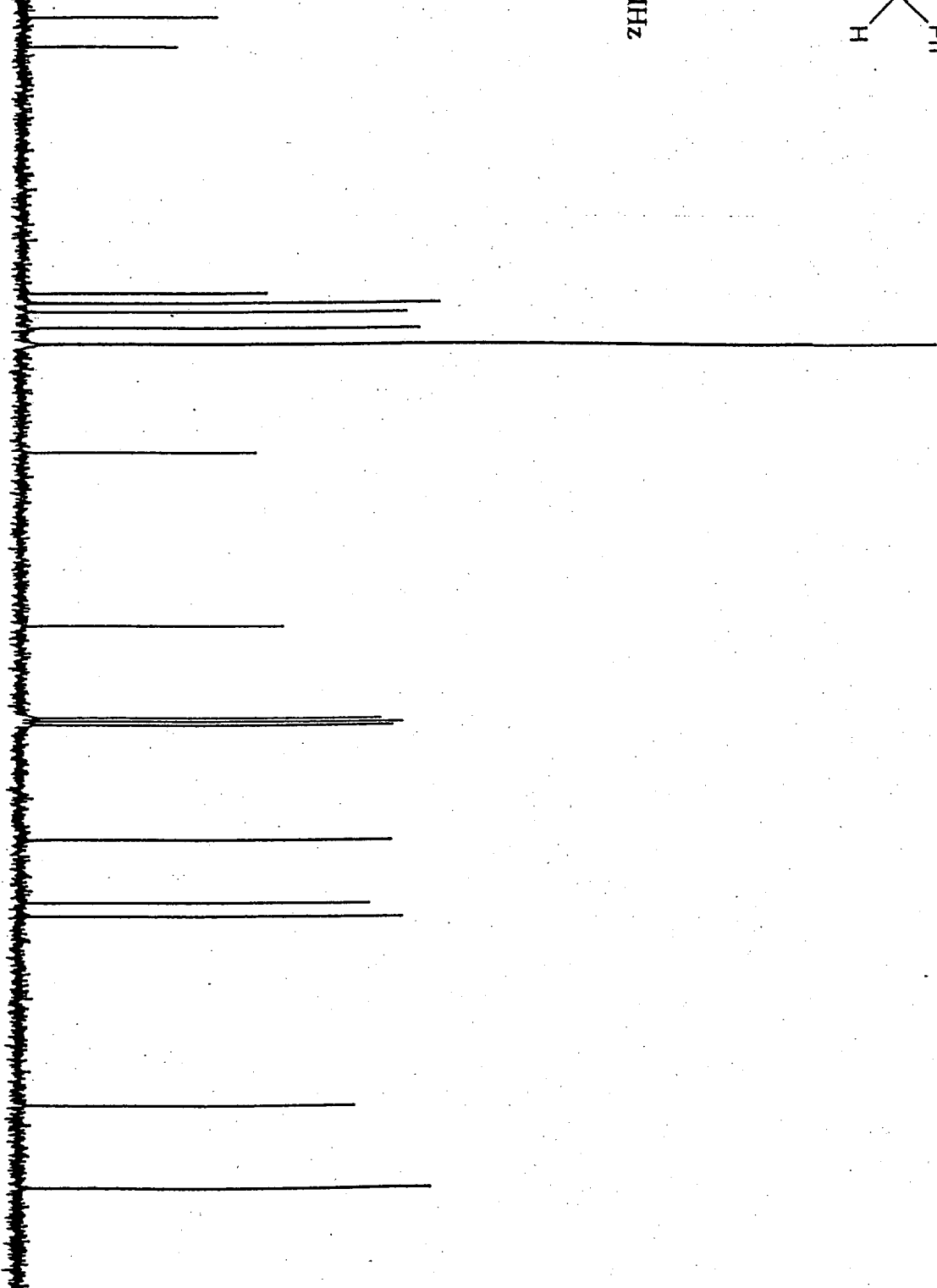
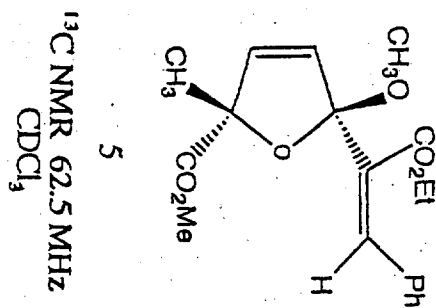
Preparation of (±)-2-methoxycarbonyl-4-[ethyl-4-methylpent-2-enoate]-1-cyclopentene (12). Prepared according to the procedure outlined for the formation of **5** using **10** (0.22 g, 1.2 mmol), NaH (0.043 g, 1.8 mmol), isobutyraldehyde (0.22 mL, 2.4 mmol), DMF (6 mL), and methyl iodide (0.6 mL, 10 mmol) to give 0.28 g (94%) of **12** as a colorless oil and as a 1:3 mixture of *Z*:*E* alkene isomers. **12Z**: ^1H NMR (300MHz, CDCl_3) δ 5.82 (m, 1H), 5.71 (m, 1H), 5.56 (d, $J = 9.6$ Hz), 4.17 (q, $J = 7.2$ Hz, 2H), 3.65 (s, 3H), 3.53 (m, 1H), 3.07 (m, 1H), 2.53 (m, 1H), 1.80 (m, 1H), 1.27 (t, $J = 7.2$ Hz, 3H), 0.95 (d, $J = 6$ Hz, 3H), 0.93 (d, $J = 6$ Hz, 3H); ^{13}C NMR (75.0MHz, CDCl_3) δ 174.6, 168.2, 146.9, 135.5, 132.7, 129.8, 60.2, 51.8, 50.2, 47.8, 35.0, 28.4, 22.7, 22.6, 14.2; IR (CCl_4) 1740, 1715, 1215 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4$ ($\text{M}+\text{Cs}^+$) 399.0572, found 399.0566. **12E**: ^1H NMR (300MHz, CDCl_3) δ 6.54 (d, $J = 10.5$ Hz, 1H), 5.75 (s, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.89 (m, 1H), 3.67 (s, 3H), 3.57 (m, 1H), 2.83 (m, 1H), 2.44 (m, 1H), 2.03 (m, 1H), 1.22 (t, $J = 6.9$ Hz, 3H), 0.97 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (75.0MHz, CDCl_3) δ 174.6, 167.9, 150.6, 136.6, 130.9, 127.8, 60.4, 51.8, 50.4, 43.7, 34.2, 27.2, 22.5, 22.2, 14.1; IR (CCl_4) 1740, 1709, 1246 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4$ ($\text{M}+\text{Cs}^+$) 399.0572, found 399.0566.

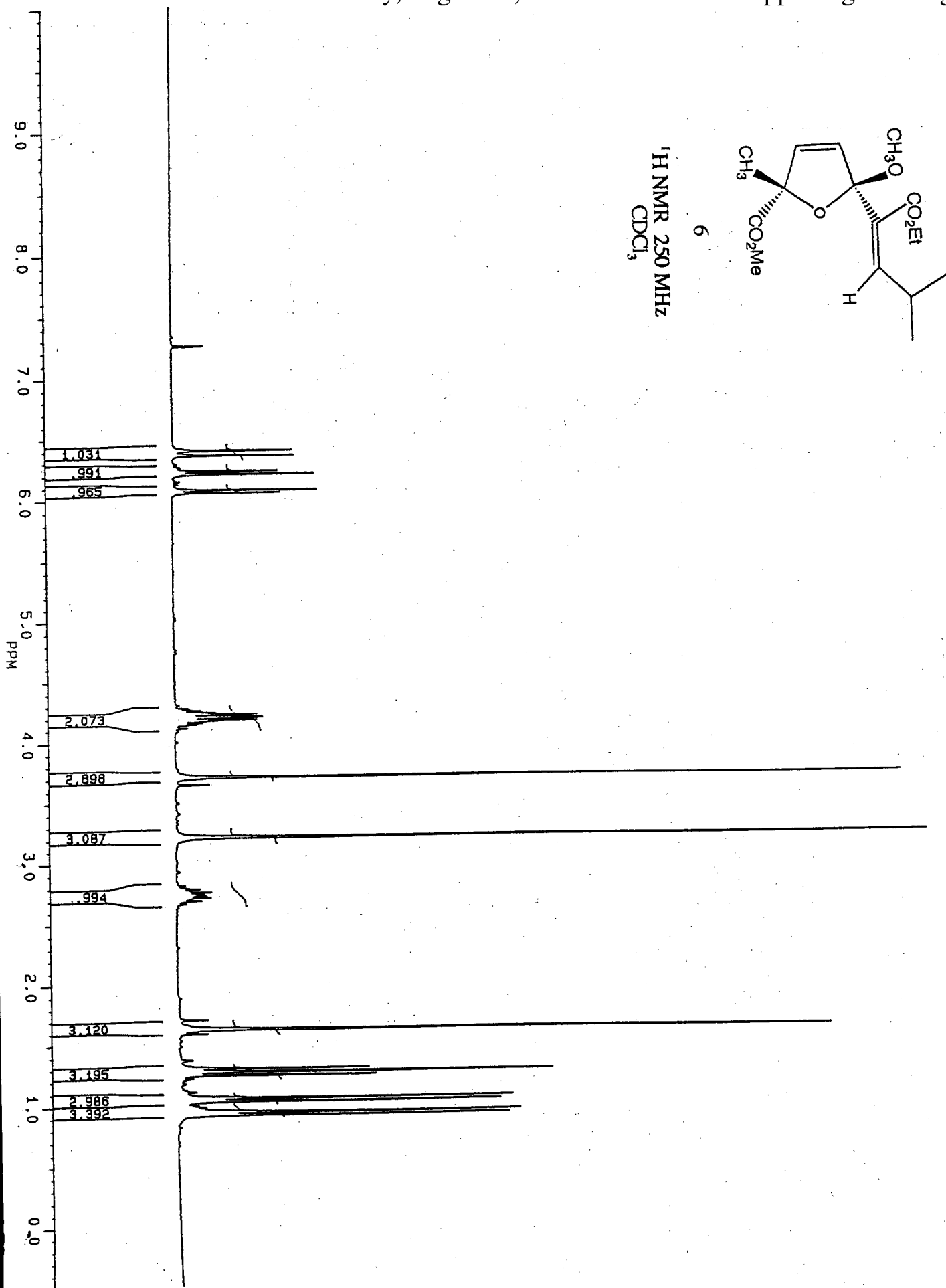


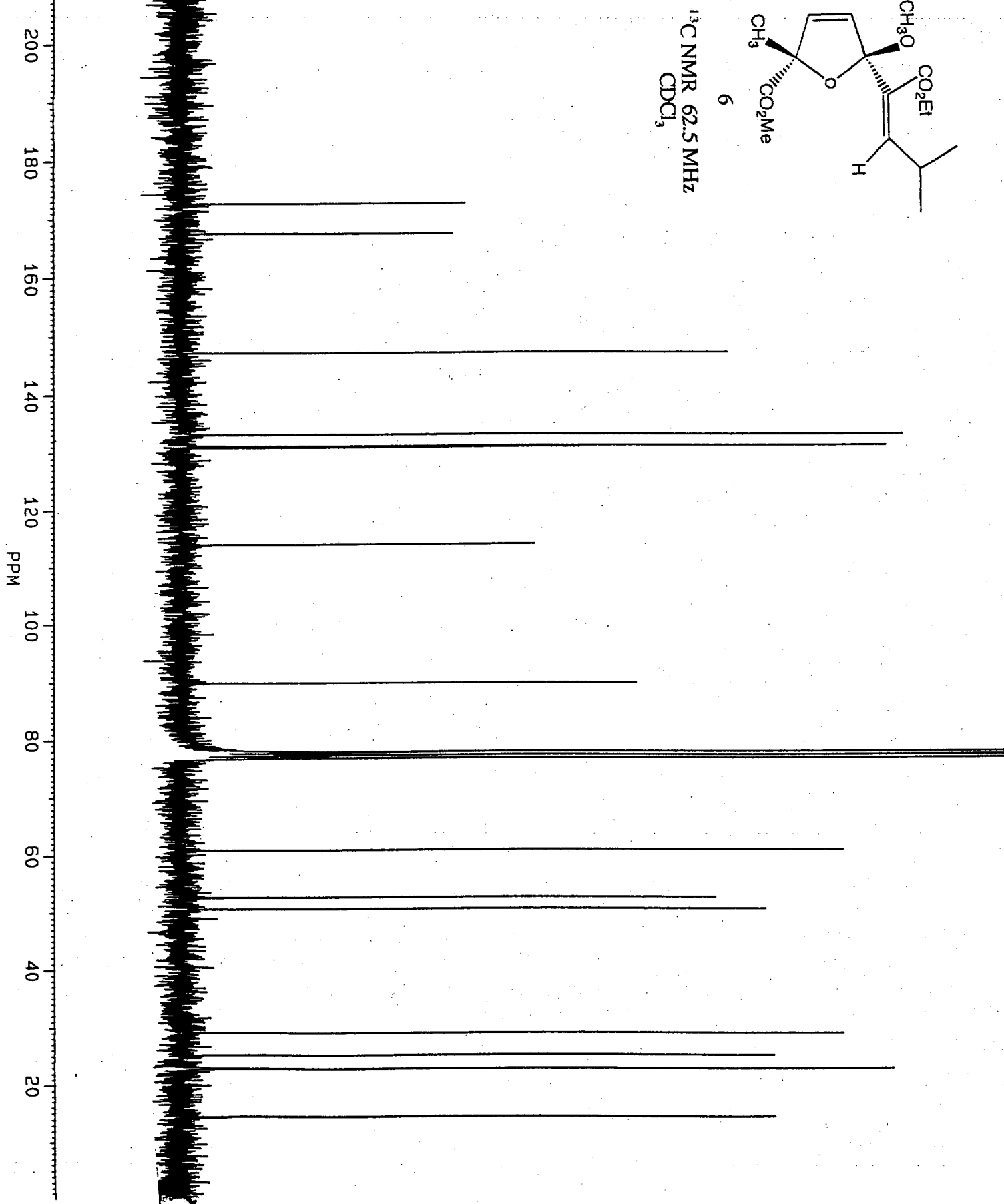


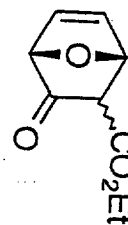


200
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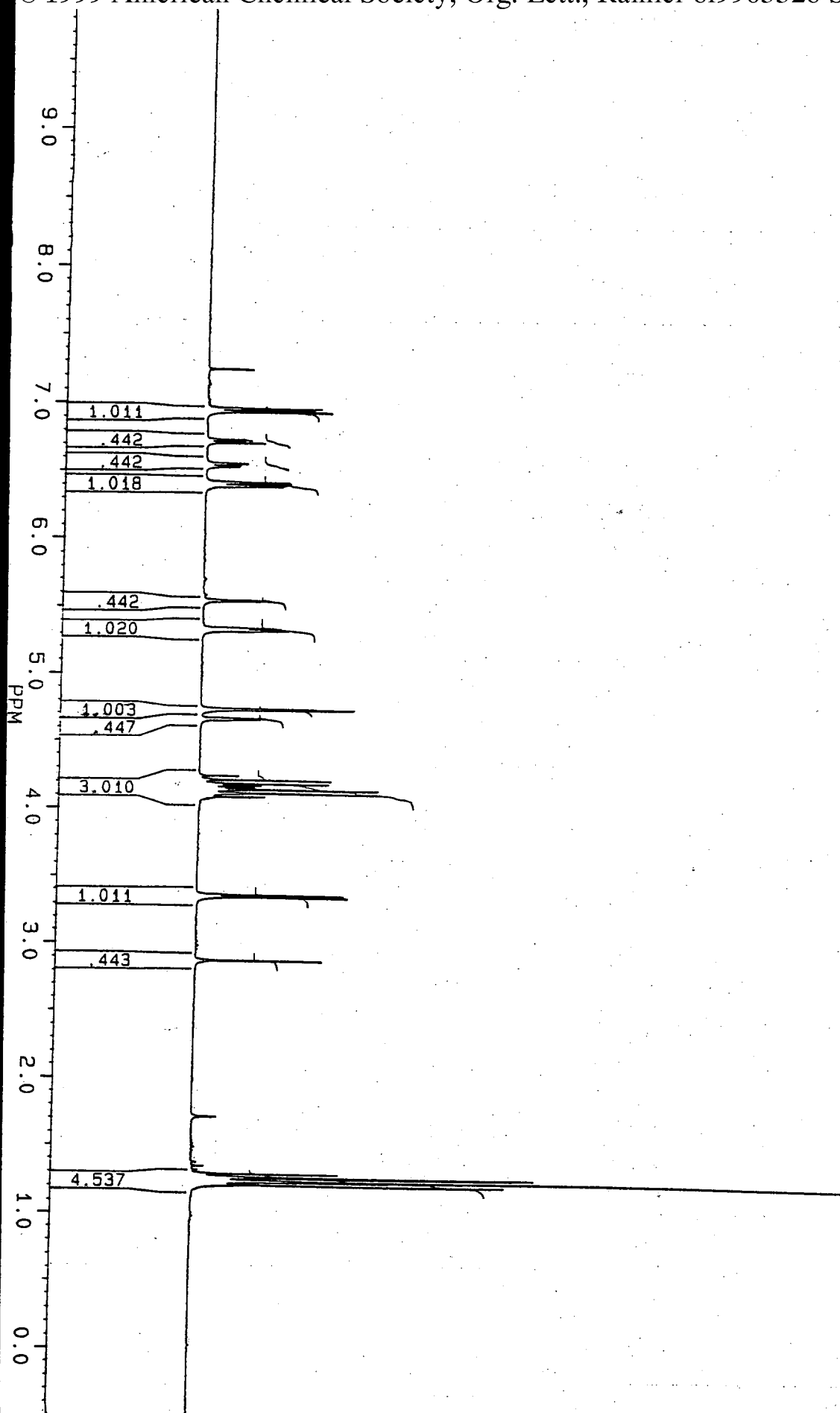


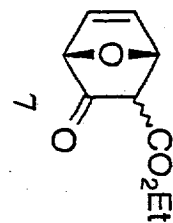




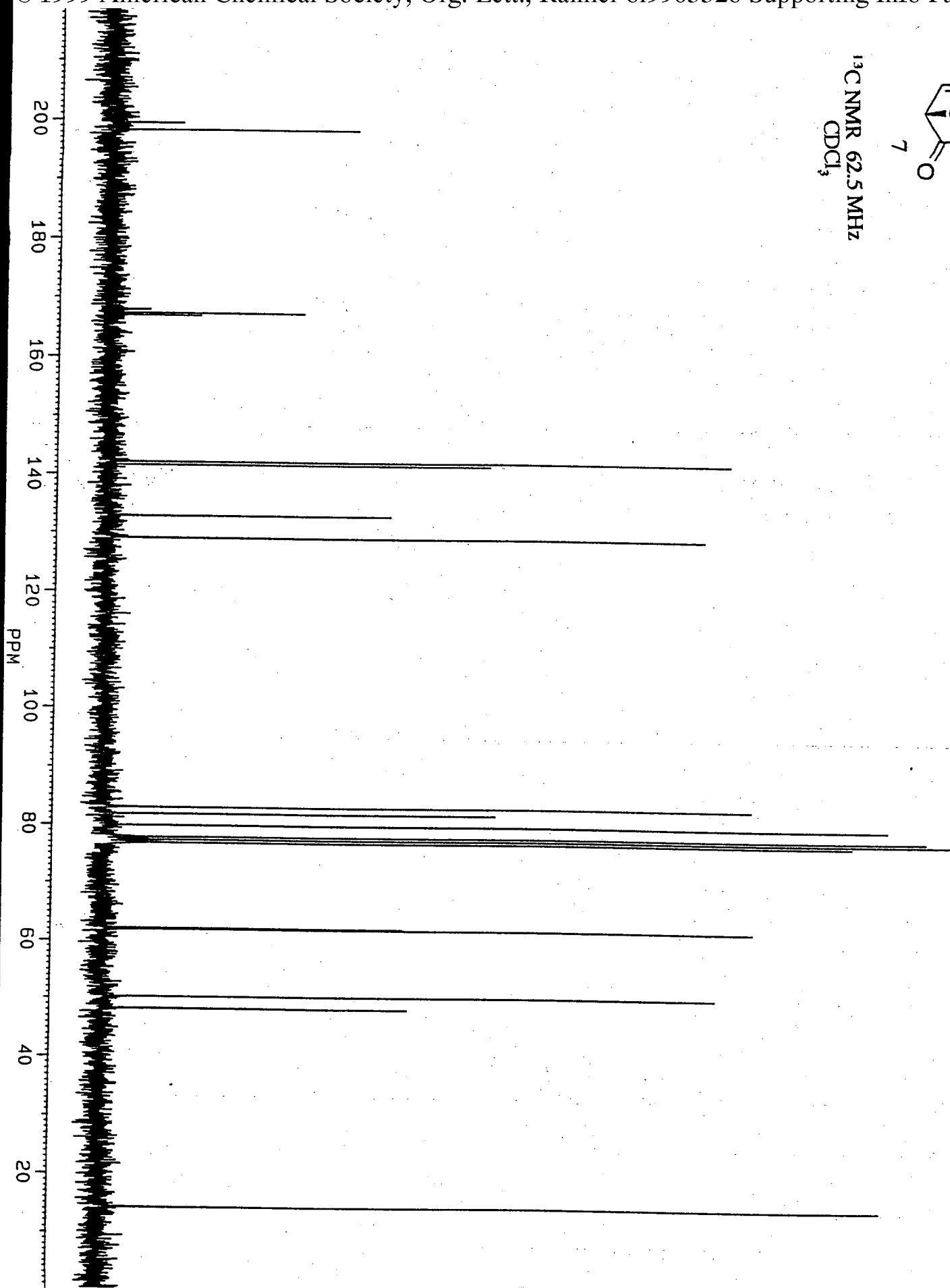


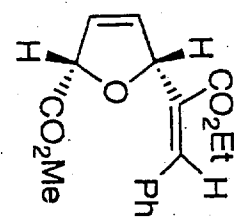
$^1\text{H NMR}$ 250 MHz
 CDCl_3





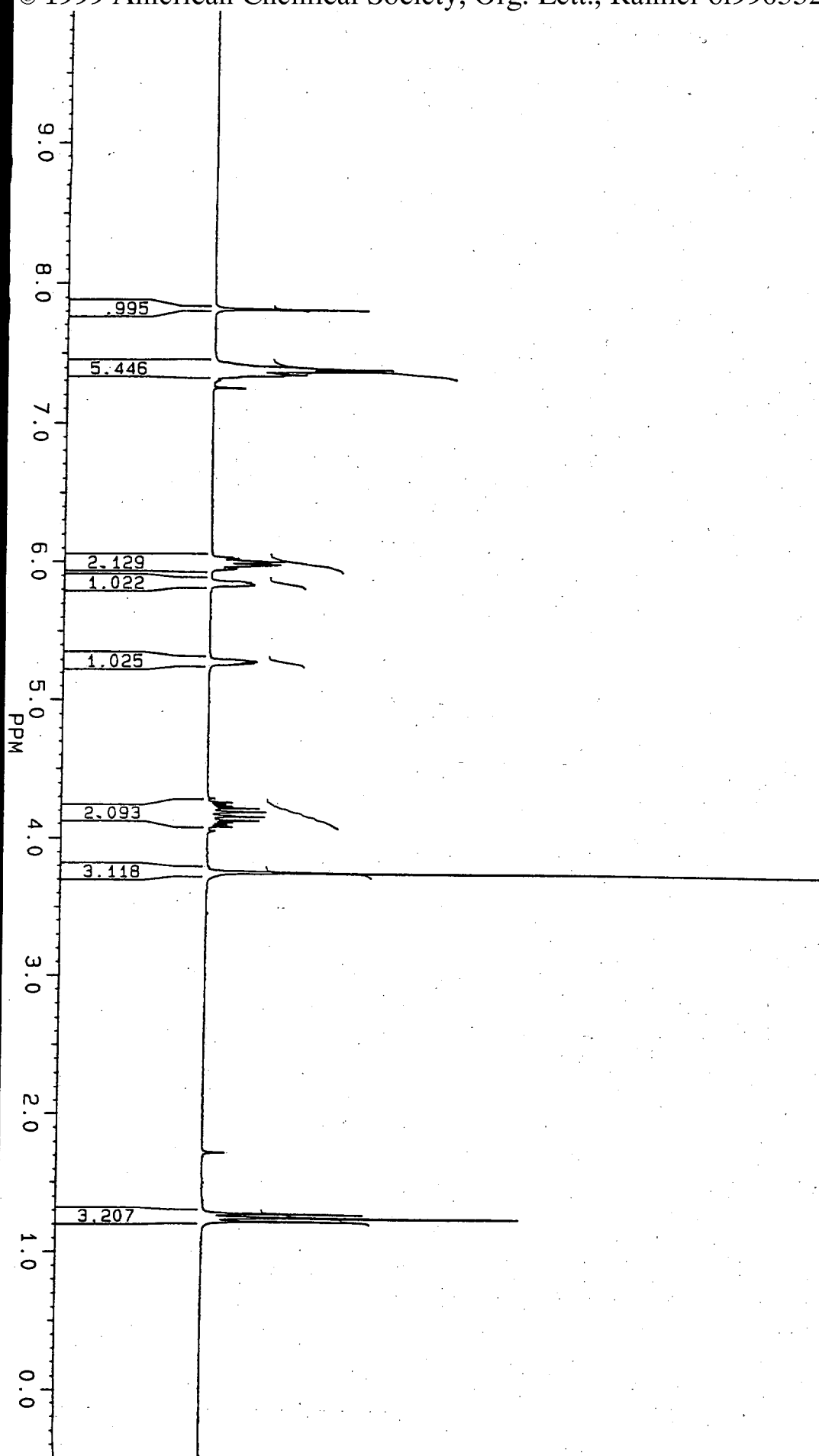
^{13}C NMR 62.5 MHz
 CDCl_3

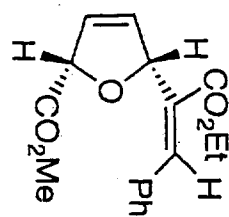




8 (*E*-alkene isomer)

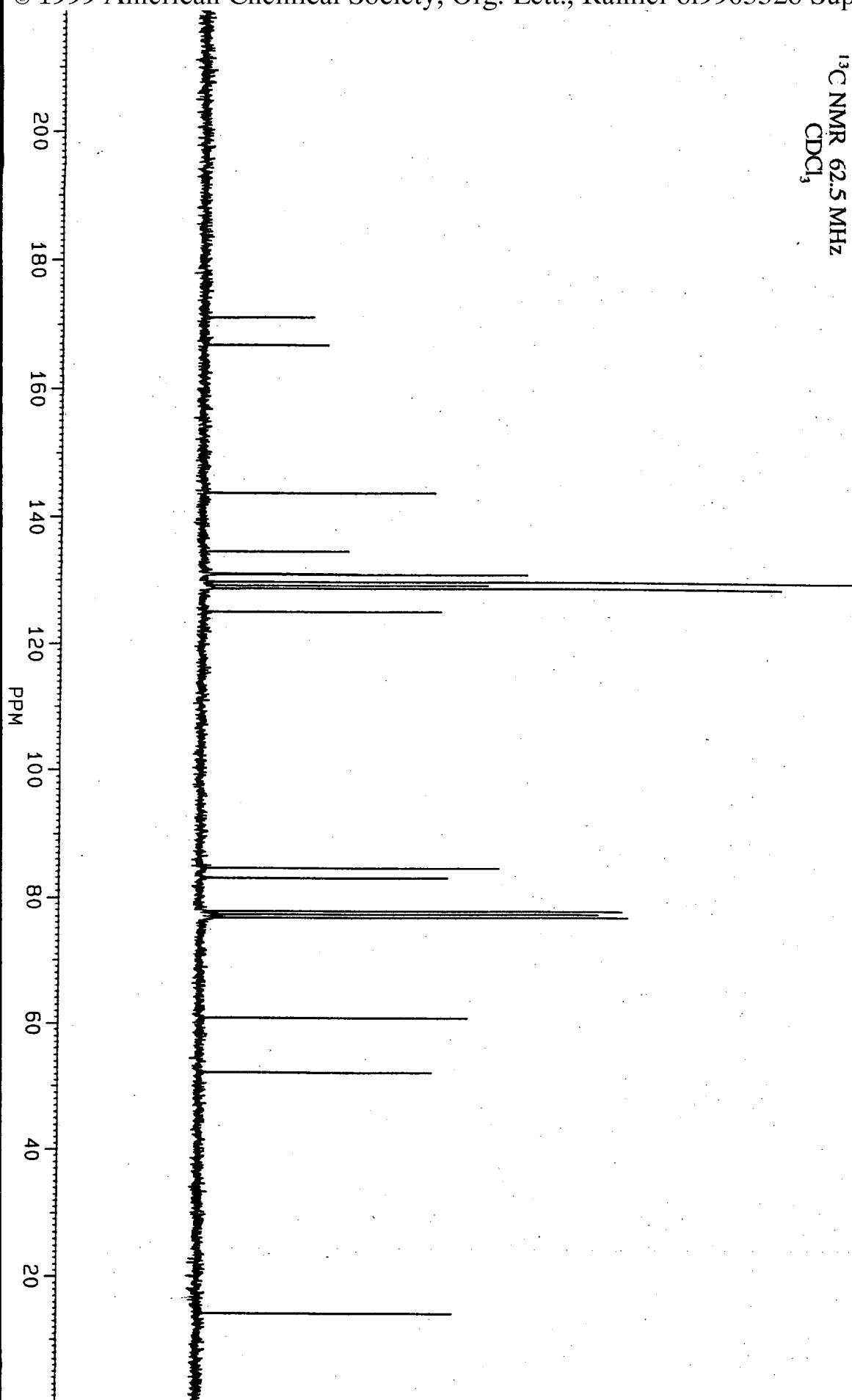
^1H NMR 250 MHz
 CDCl_3

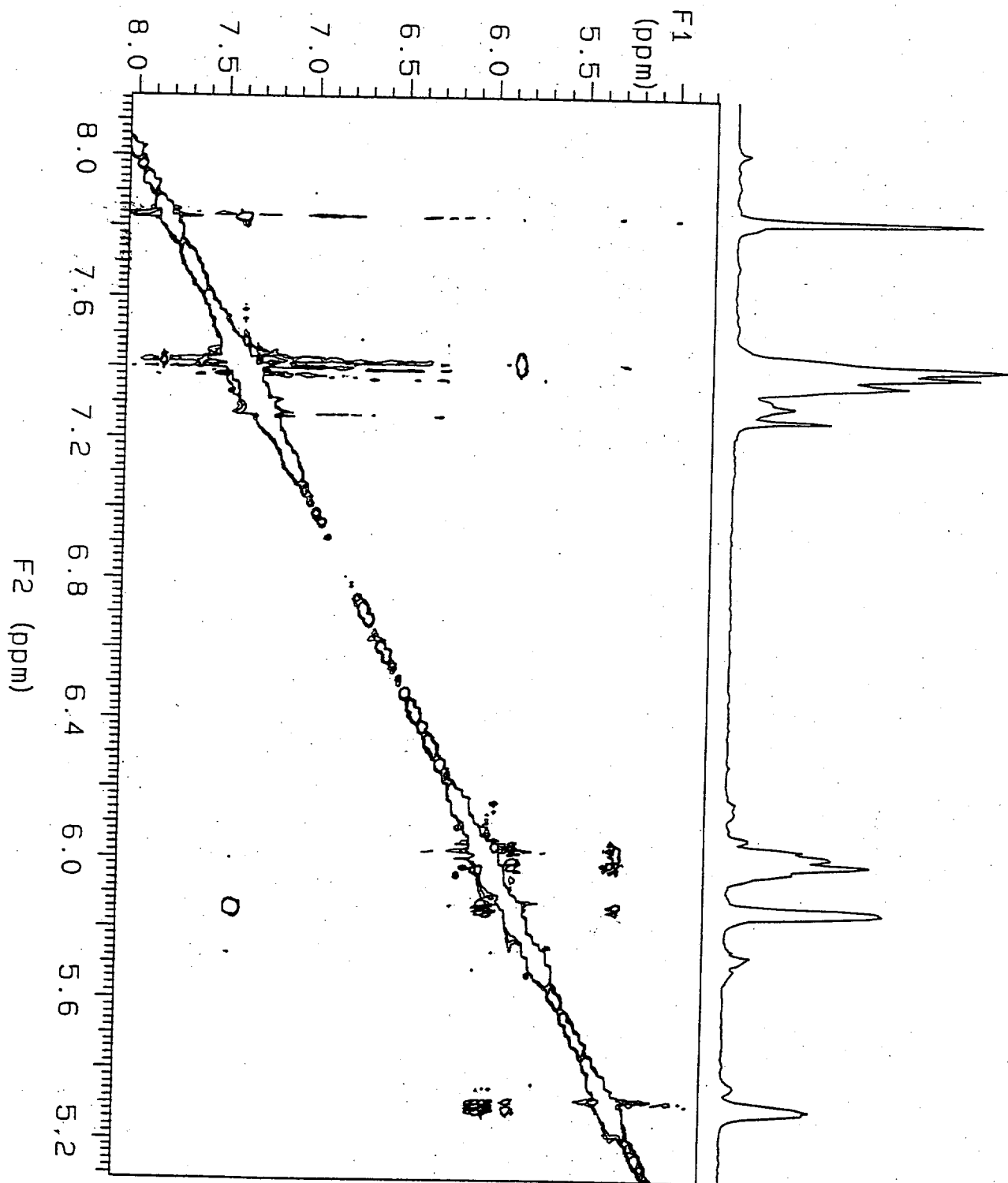
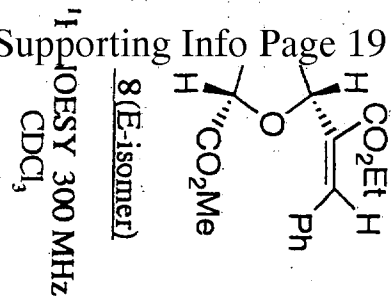


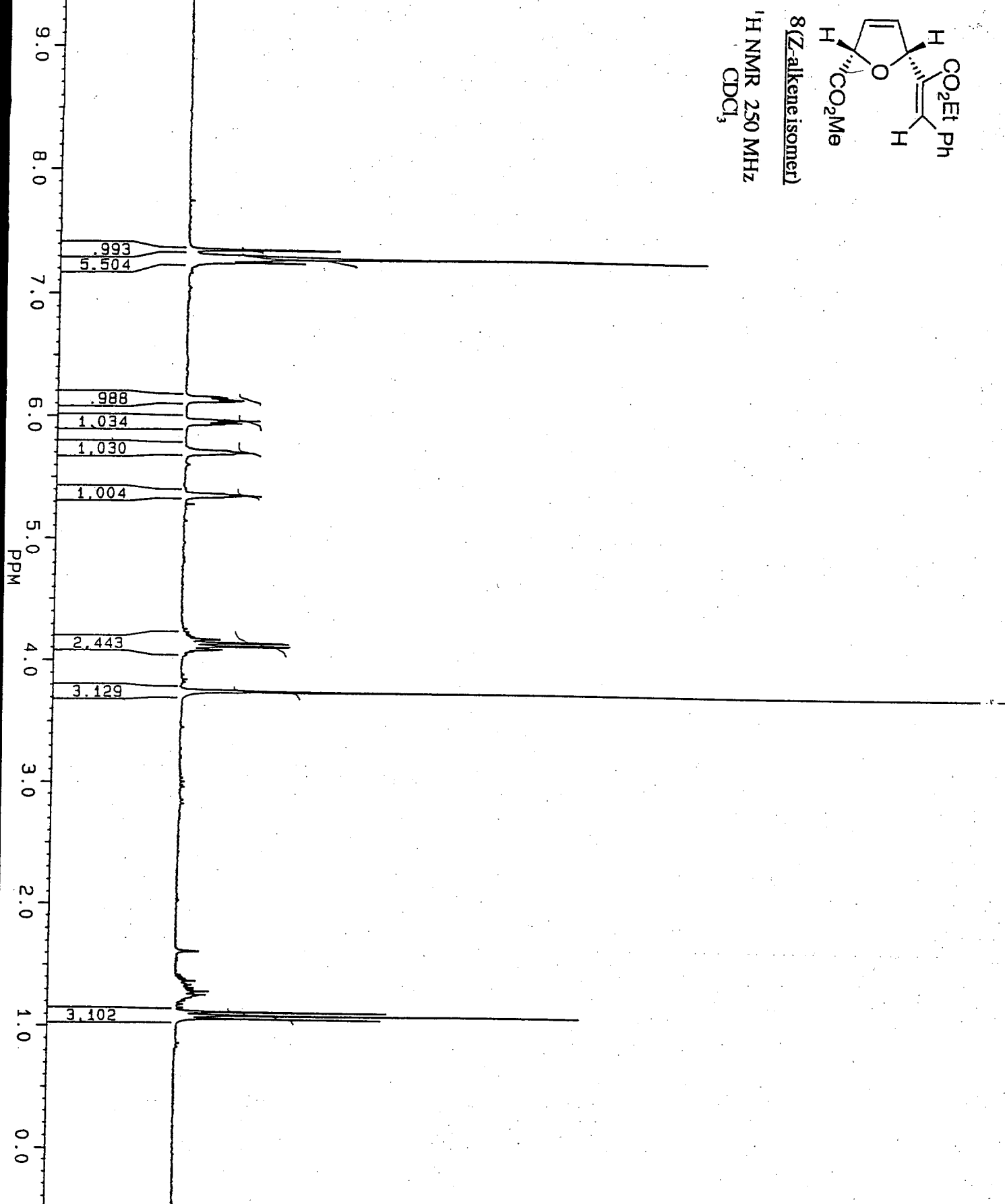


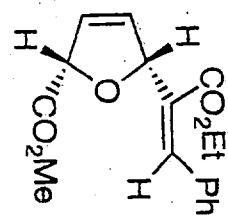
8(E)-alkene isomer

^{13}C NMR 62.5 MHz
 CDCl_3



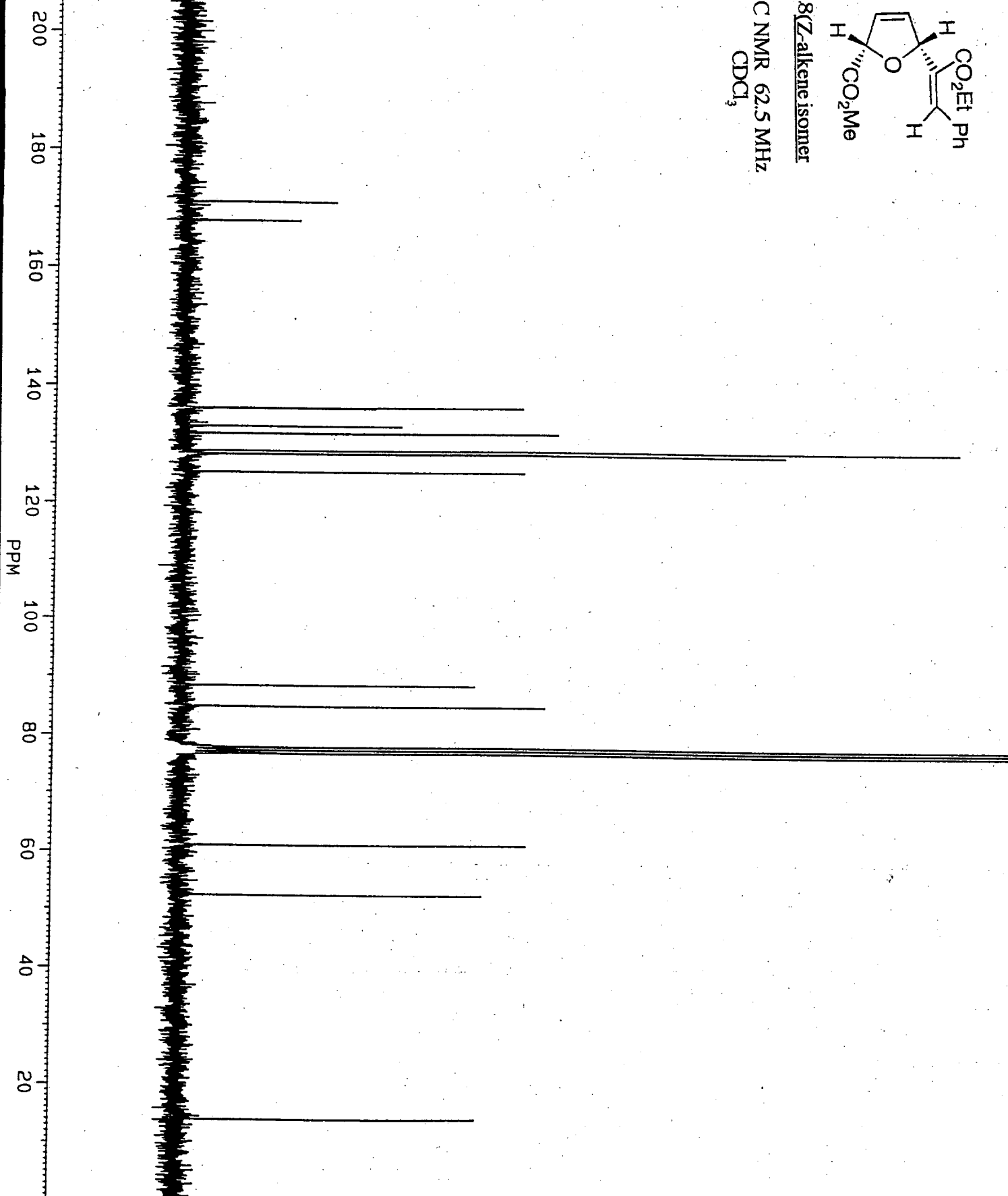


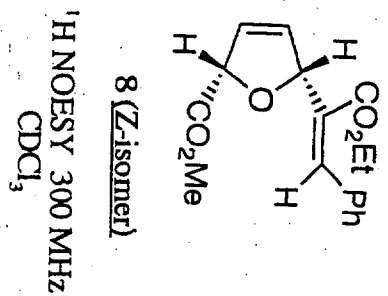
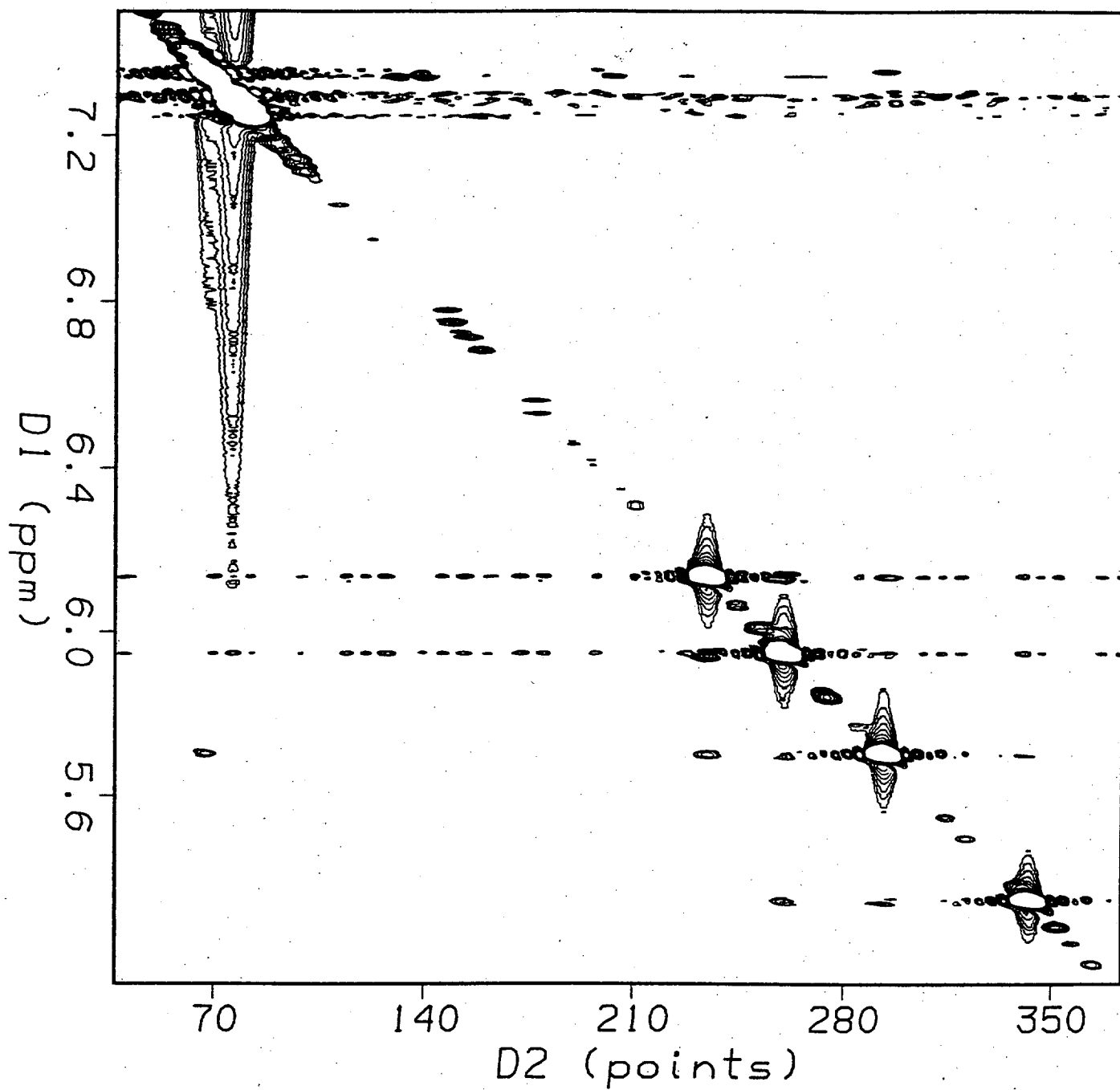


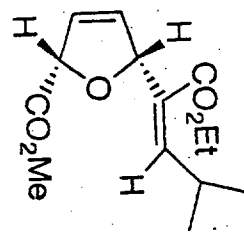


8(Z)-alkene isomer

^{13}C NMR 62.5 MHz
 CDCl_3

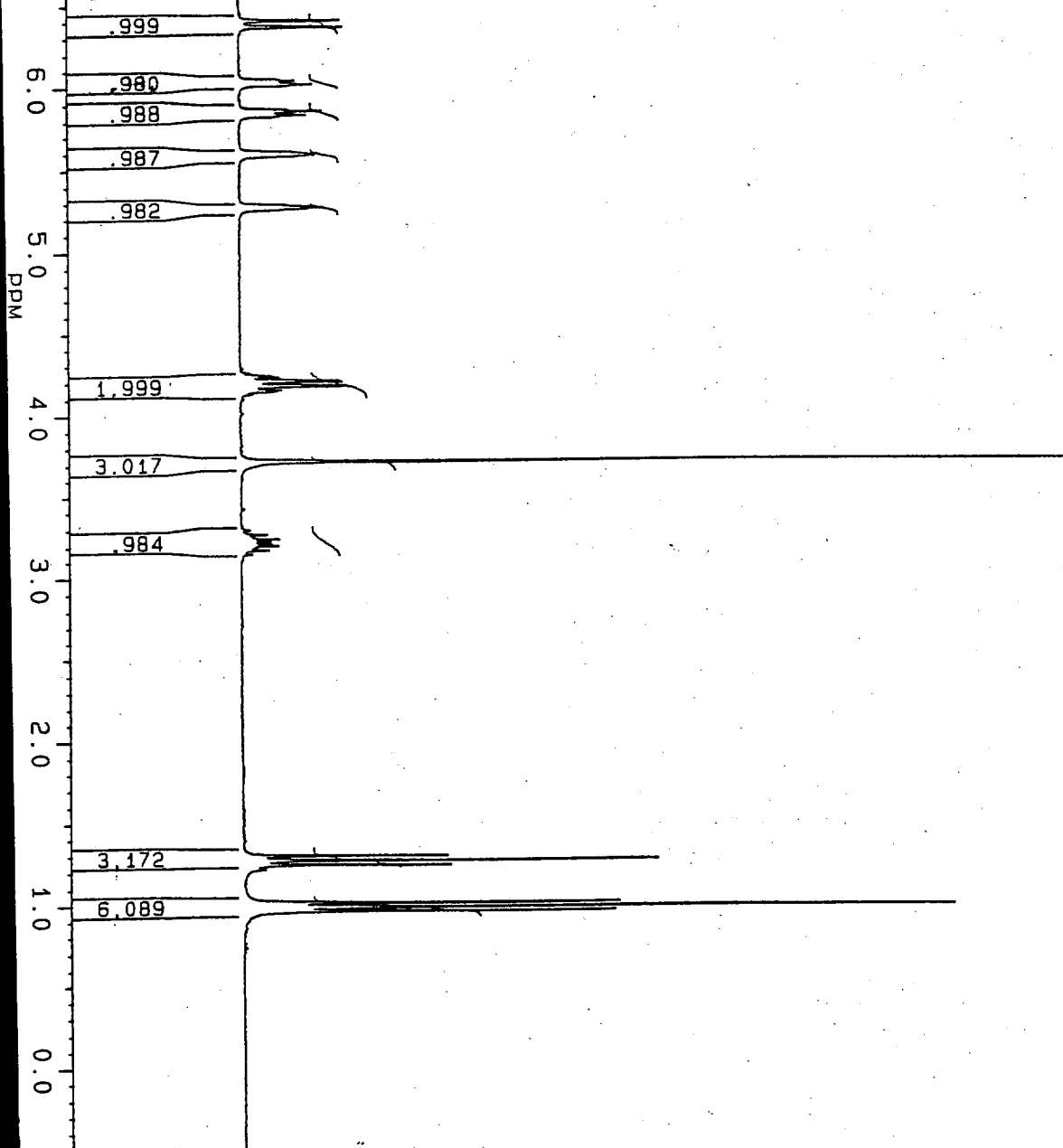


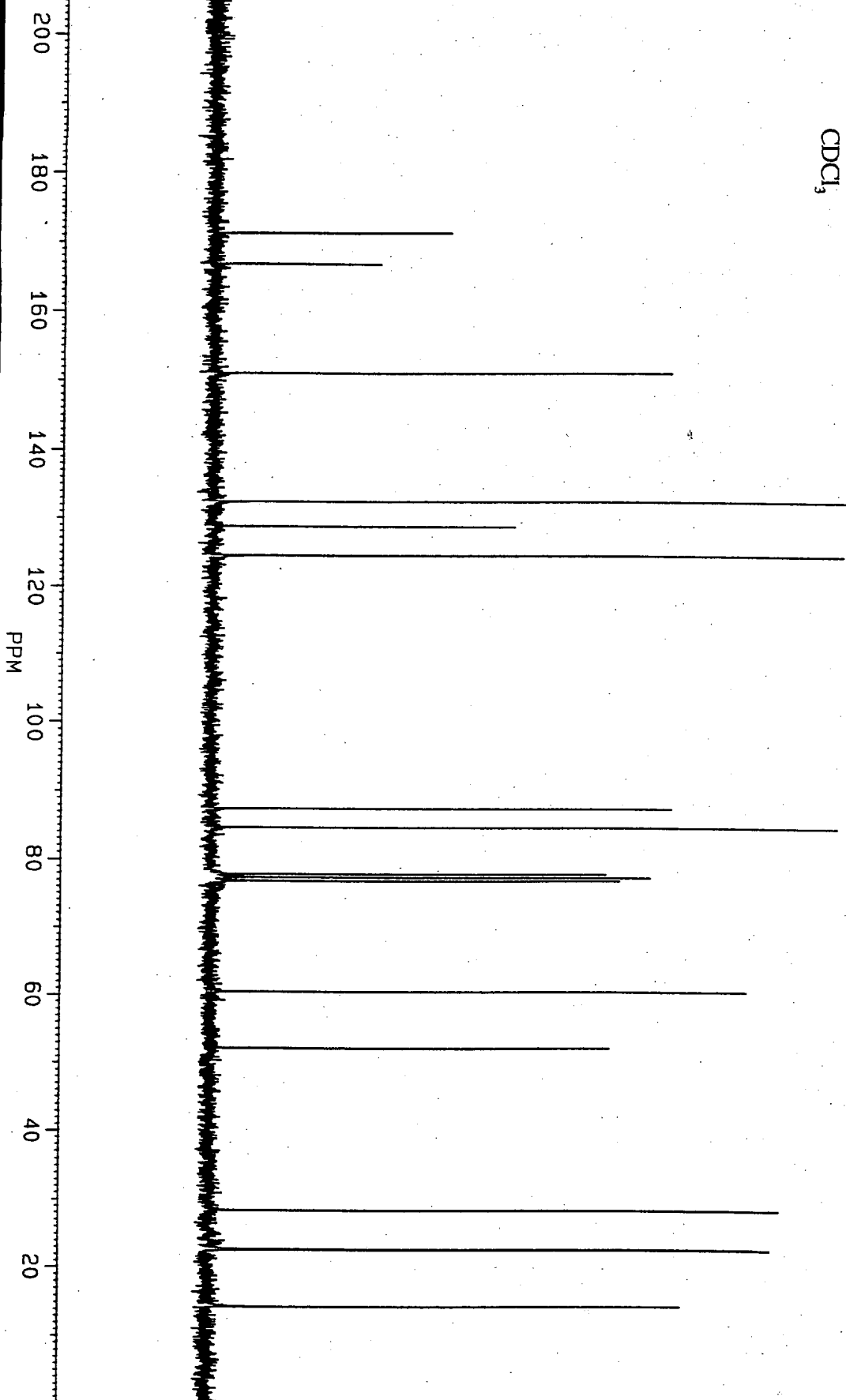
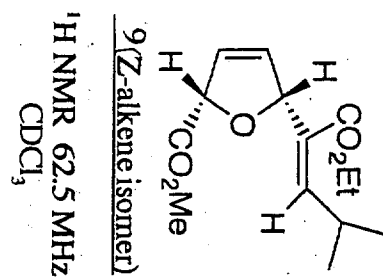


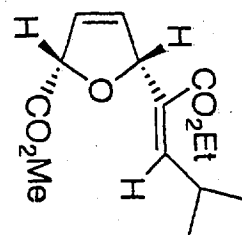


9 (Z-alkene isomer)

¹H NMR 250 MHz
CDCl₃

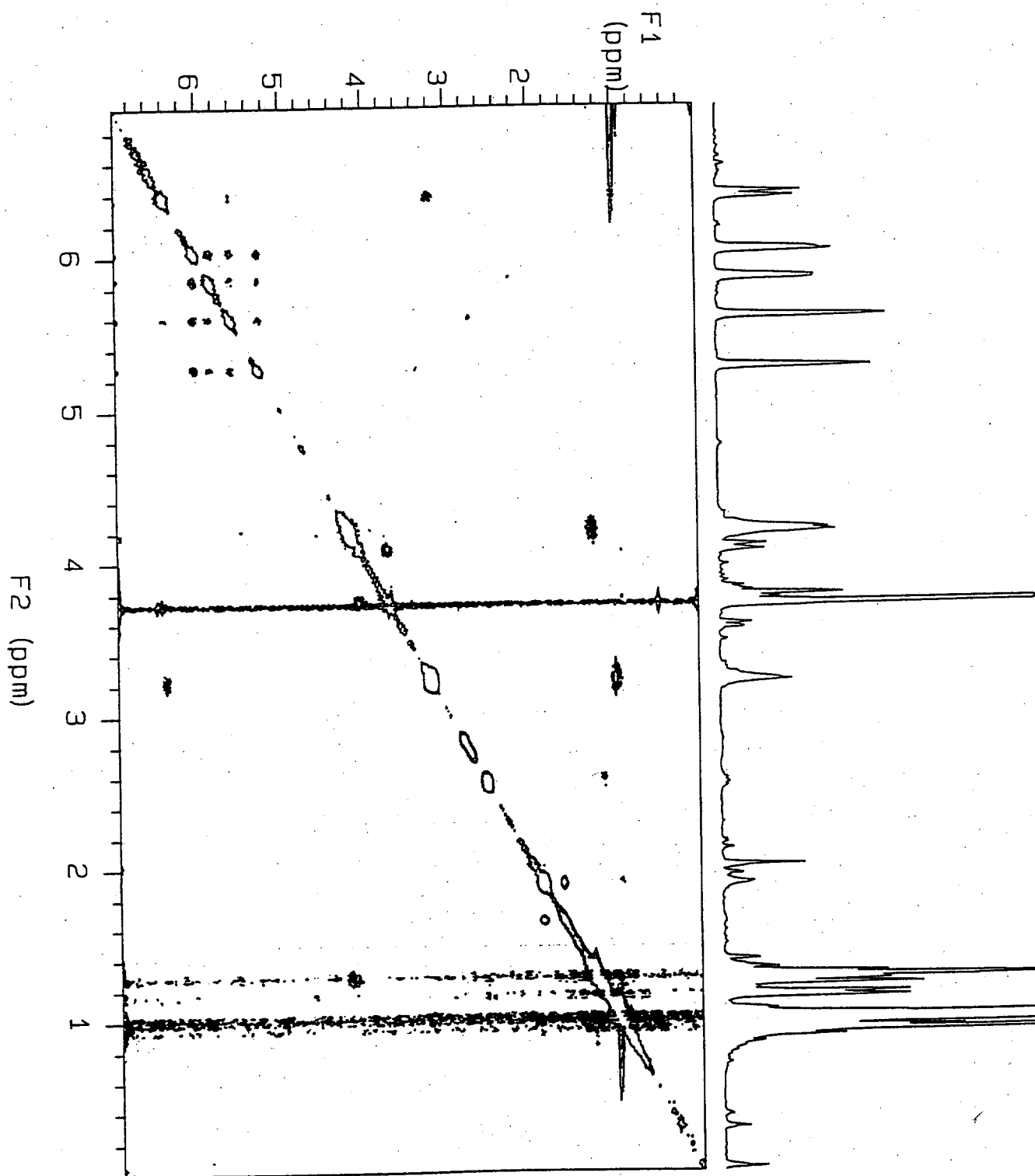


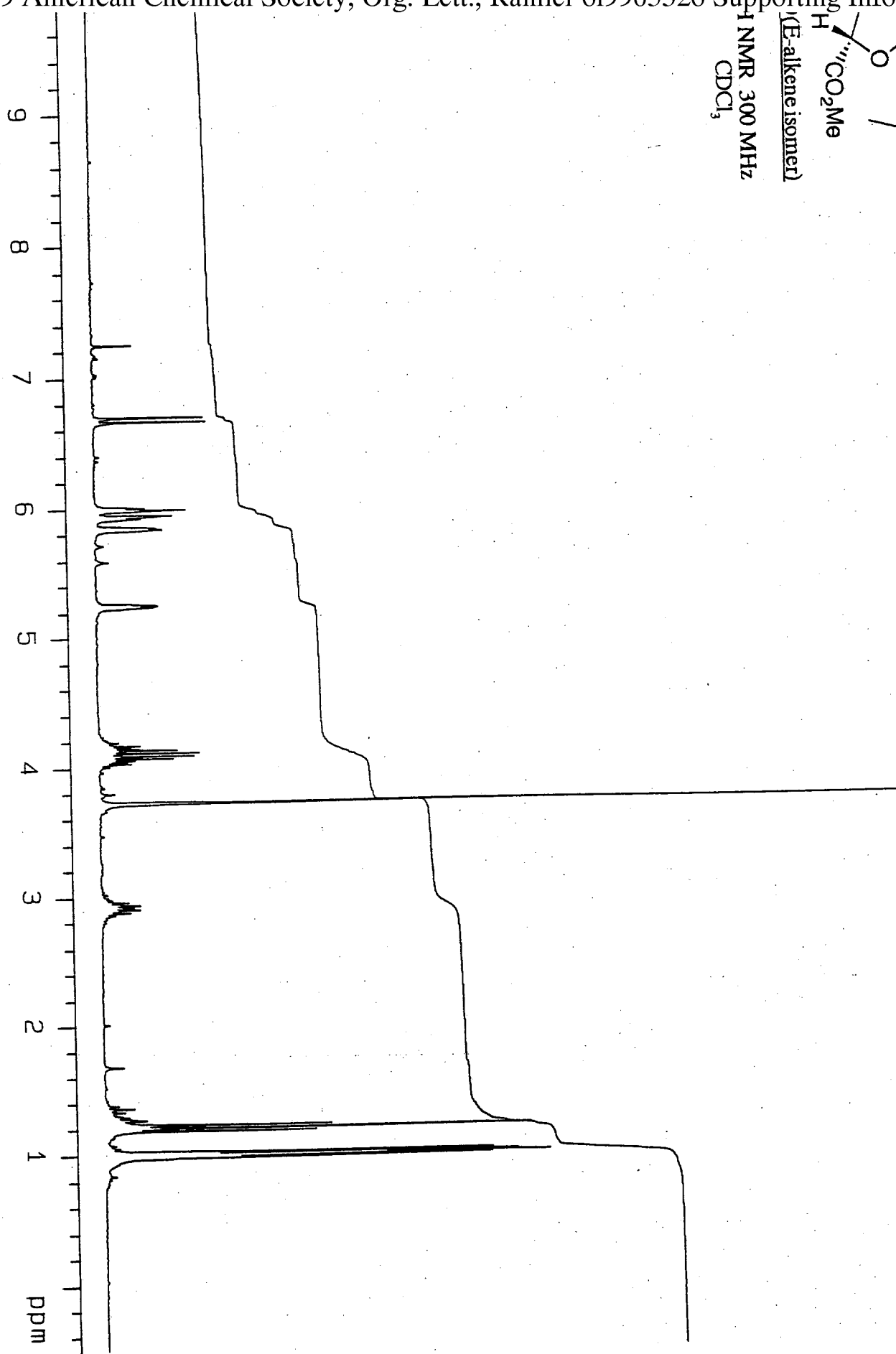
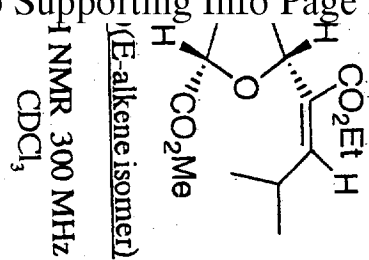


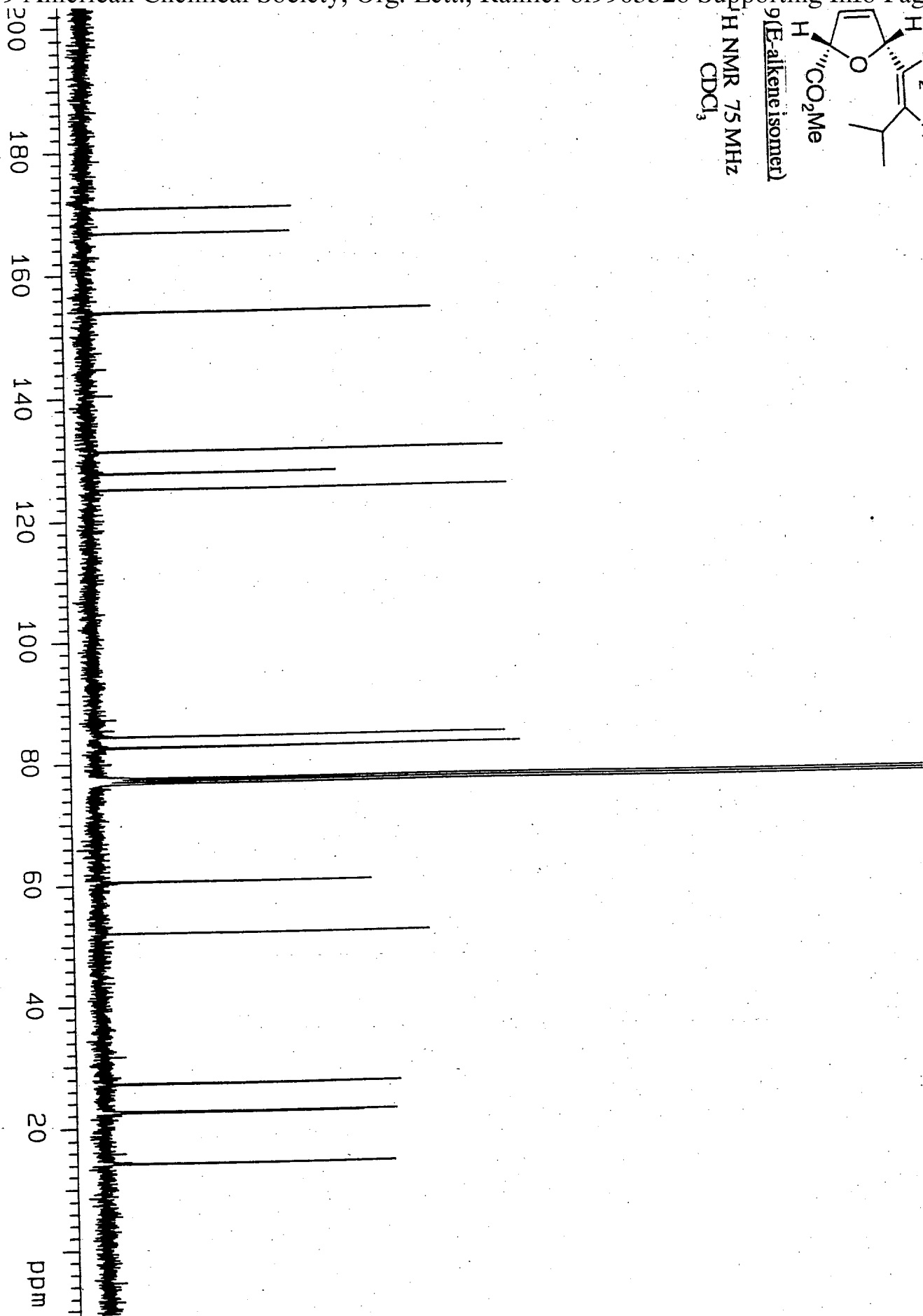
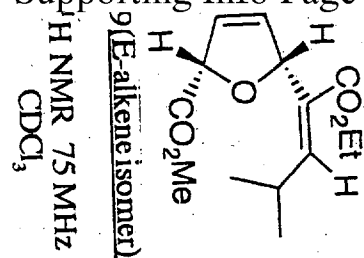


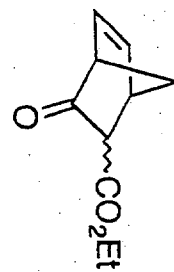
2 (Z-isomer)

1NOESY 300 MHz
CDCl₃



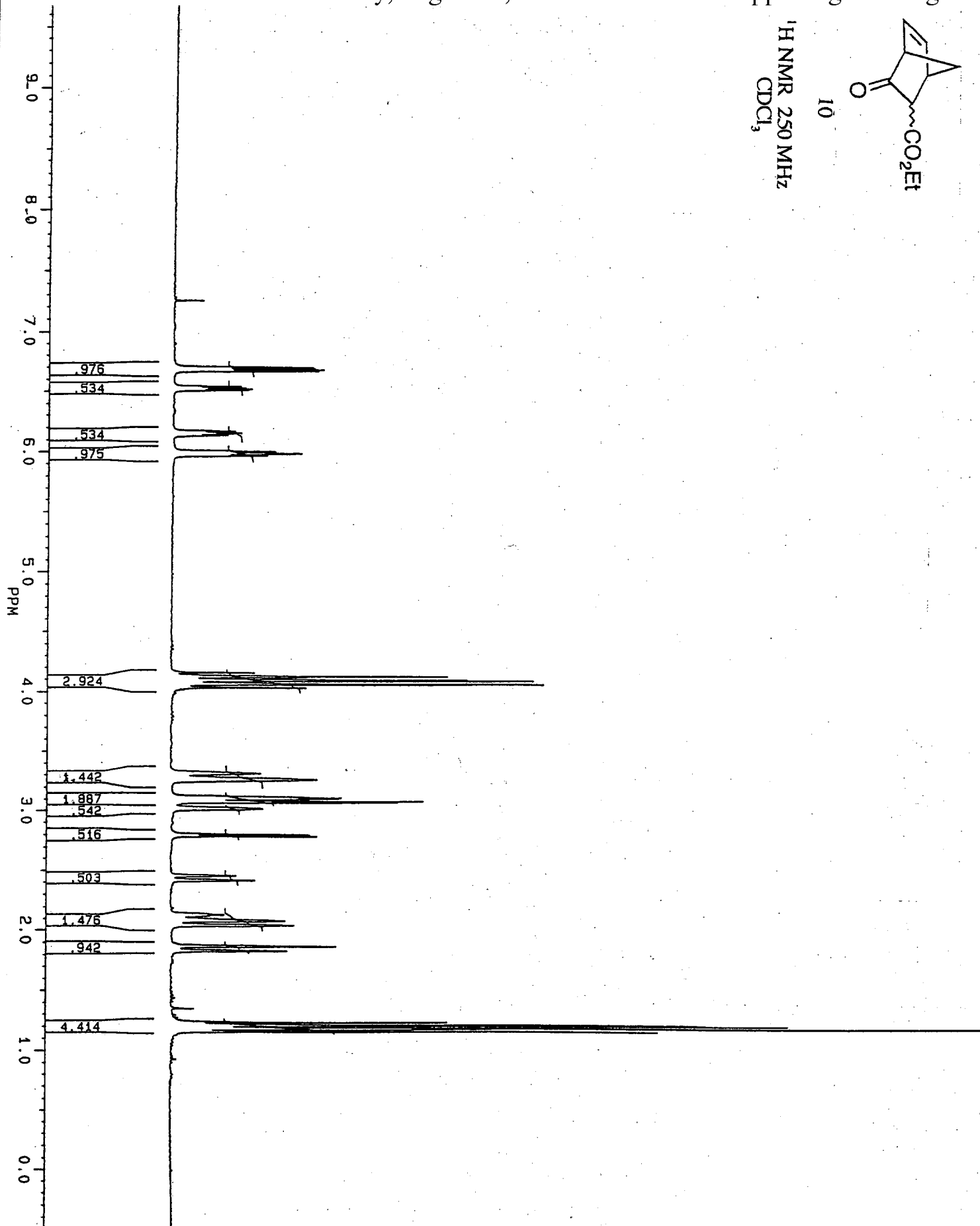


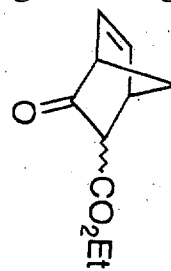




10

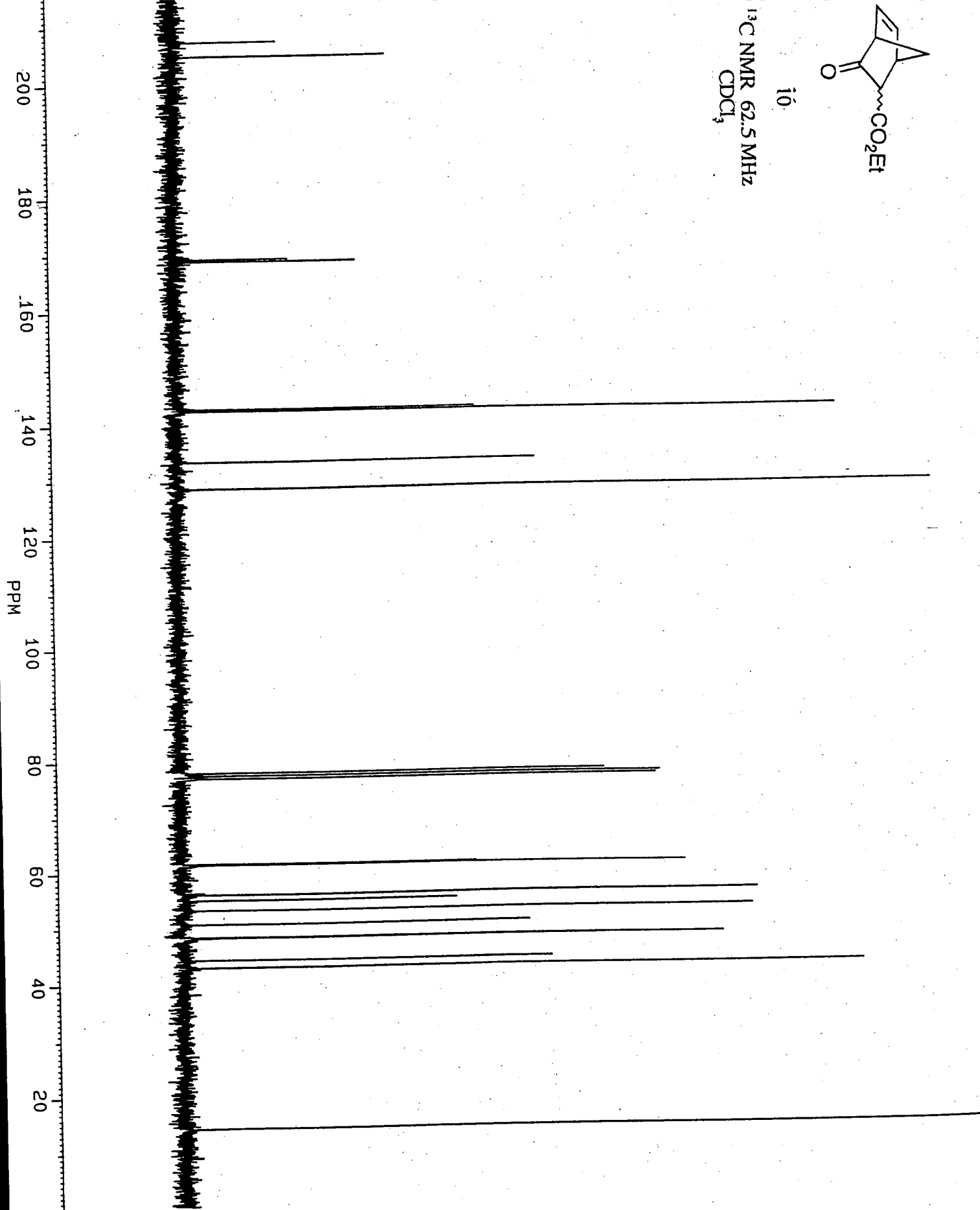
$^1\text{H NMR}$ 250 MHz
 CDCl_3

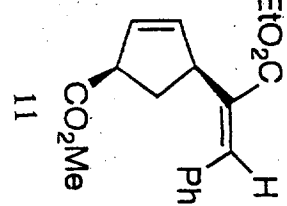




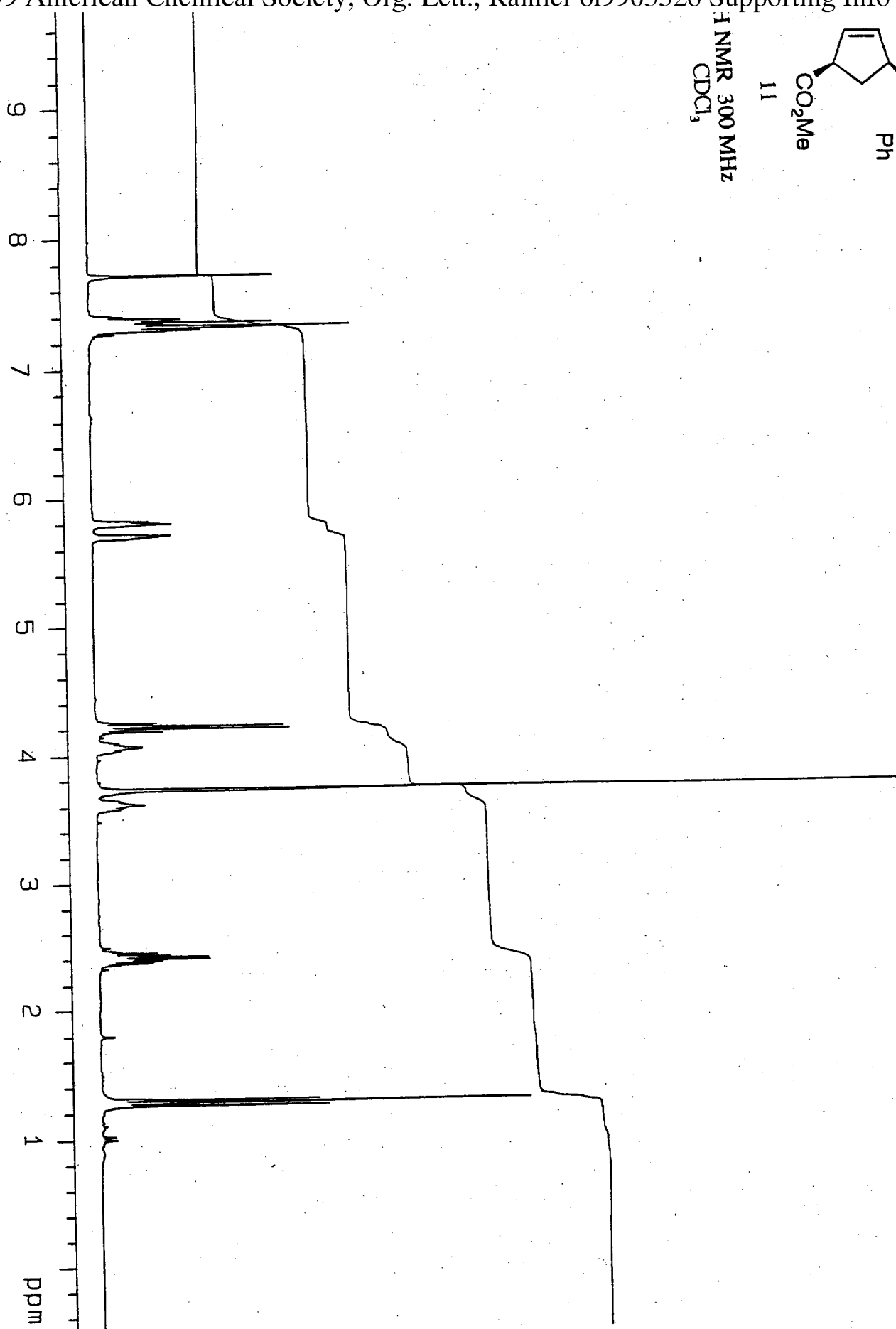
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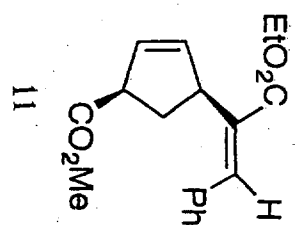
^{13}C NMR 62.5 MHz
 CDCl_3



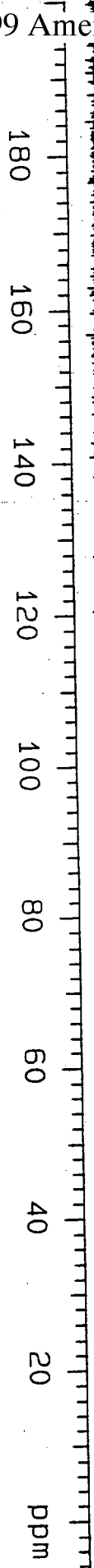


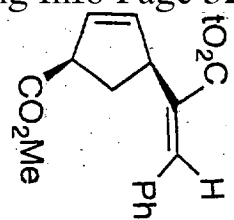
¹H NMR 300 MHz
CDCl₃



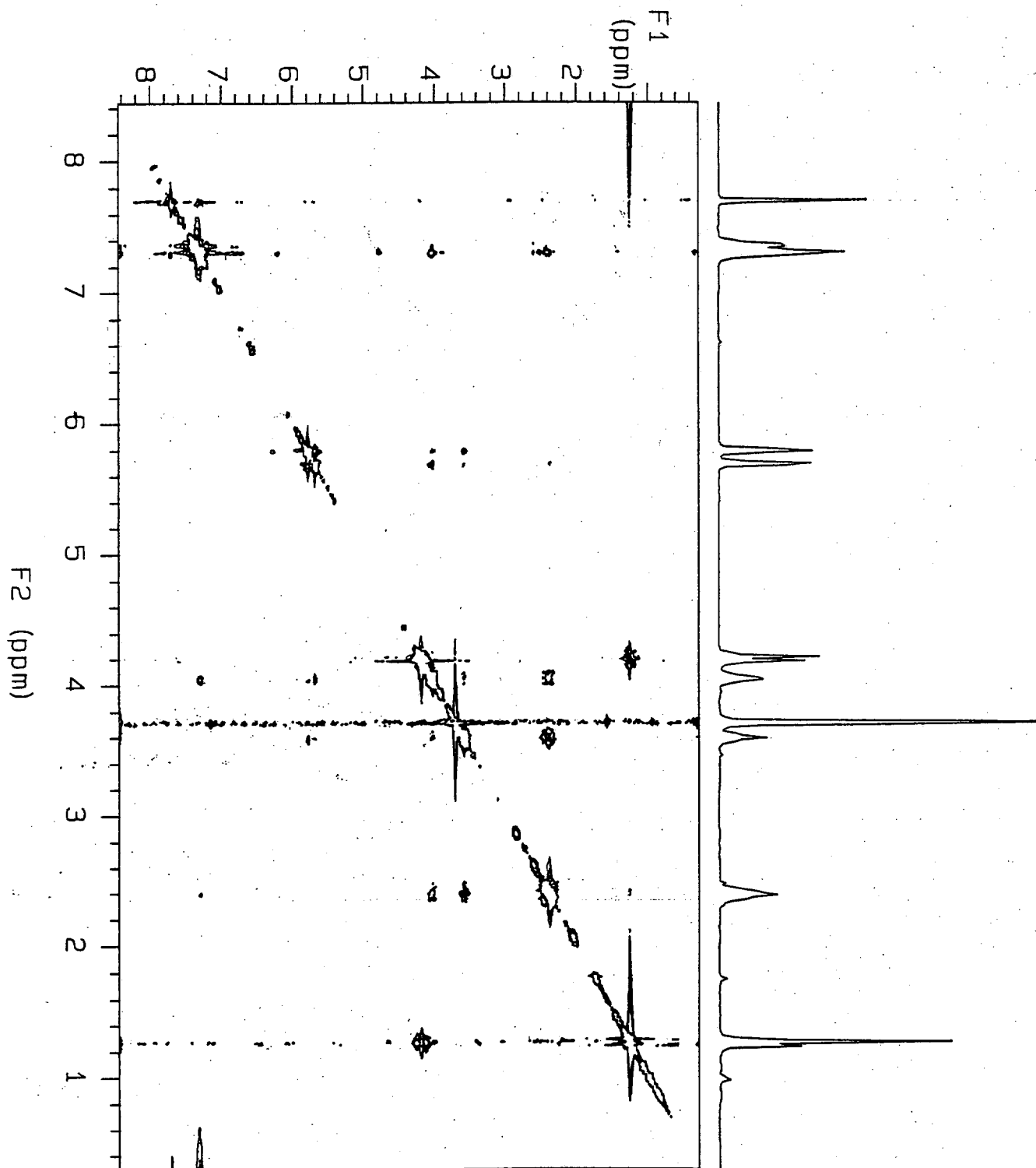


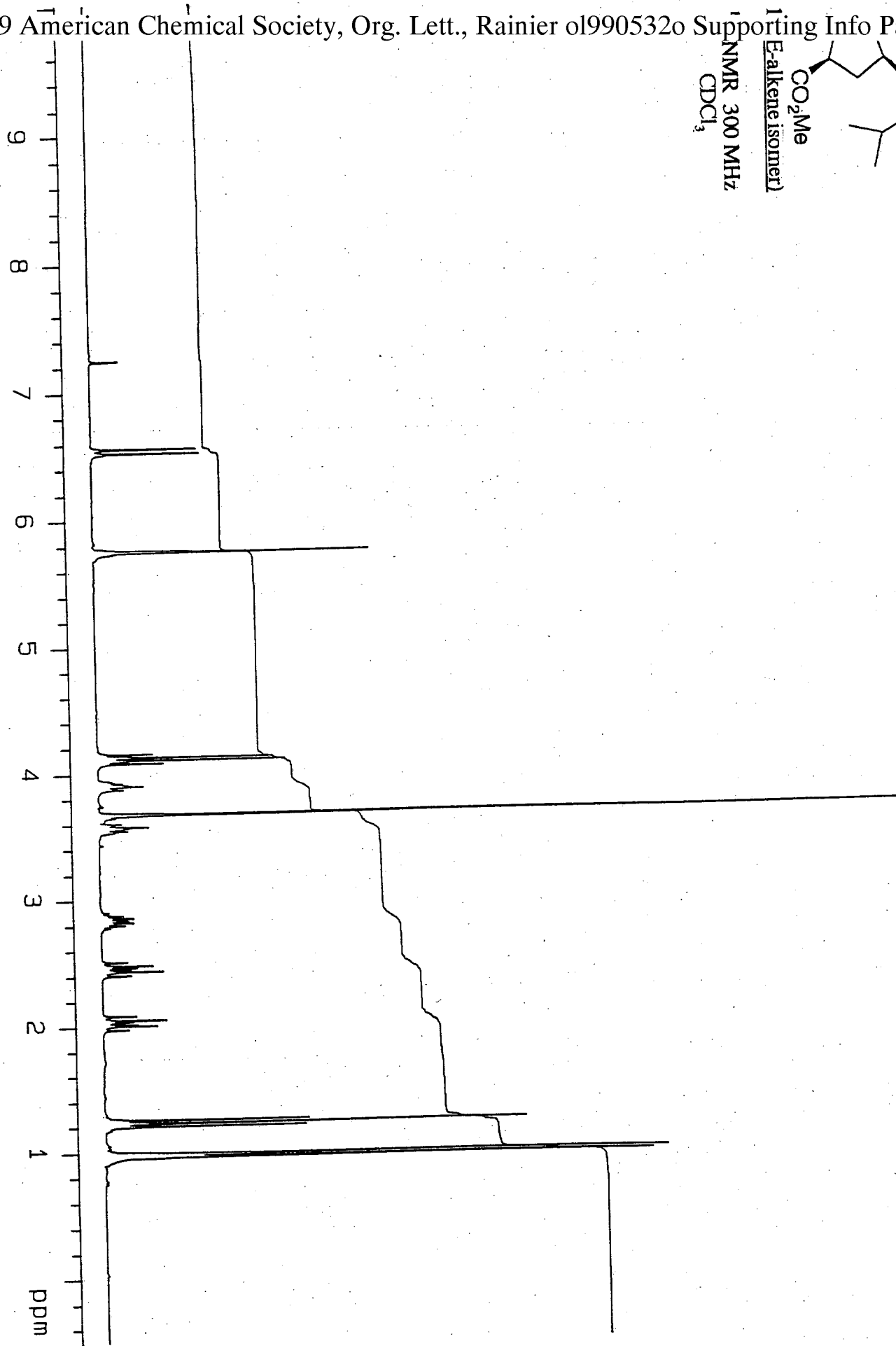
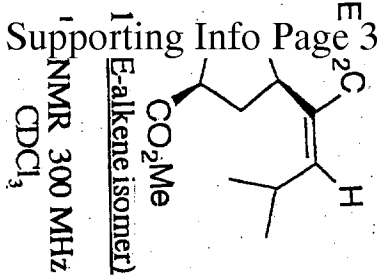
¹H NMR 75 MHz
CDCl₃

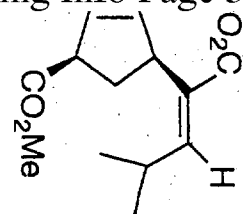




NOESY 300 MHz
CDCl₃

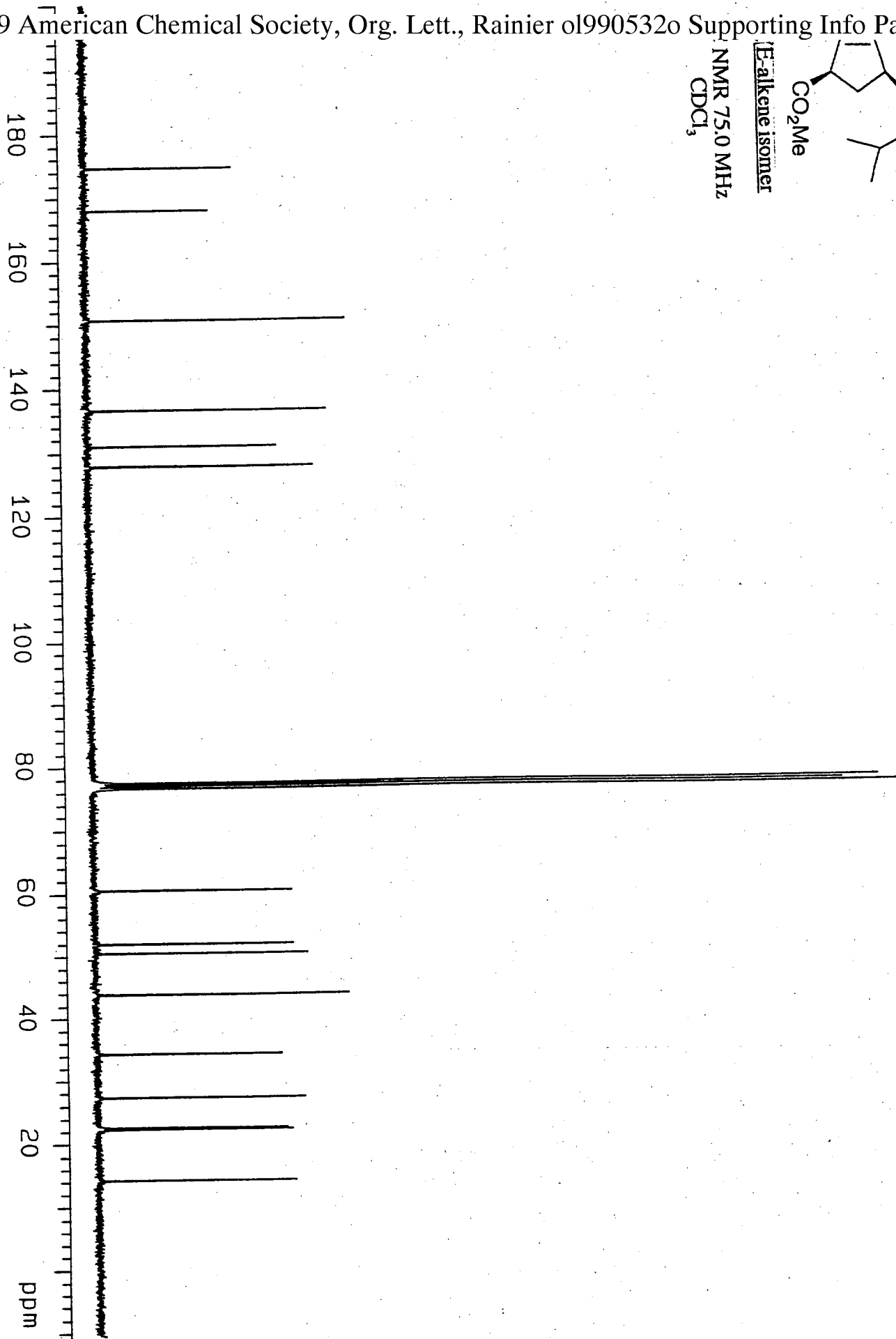


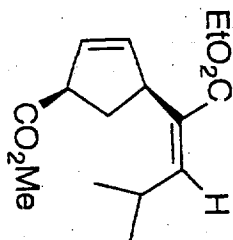




(E)-alkene isomer

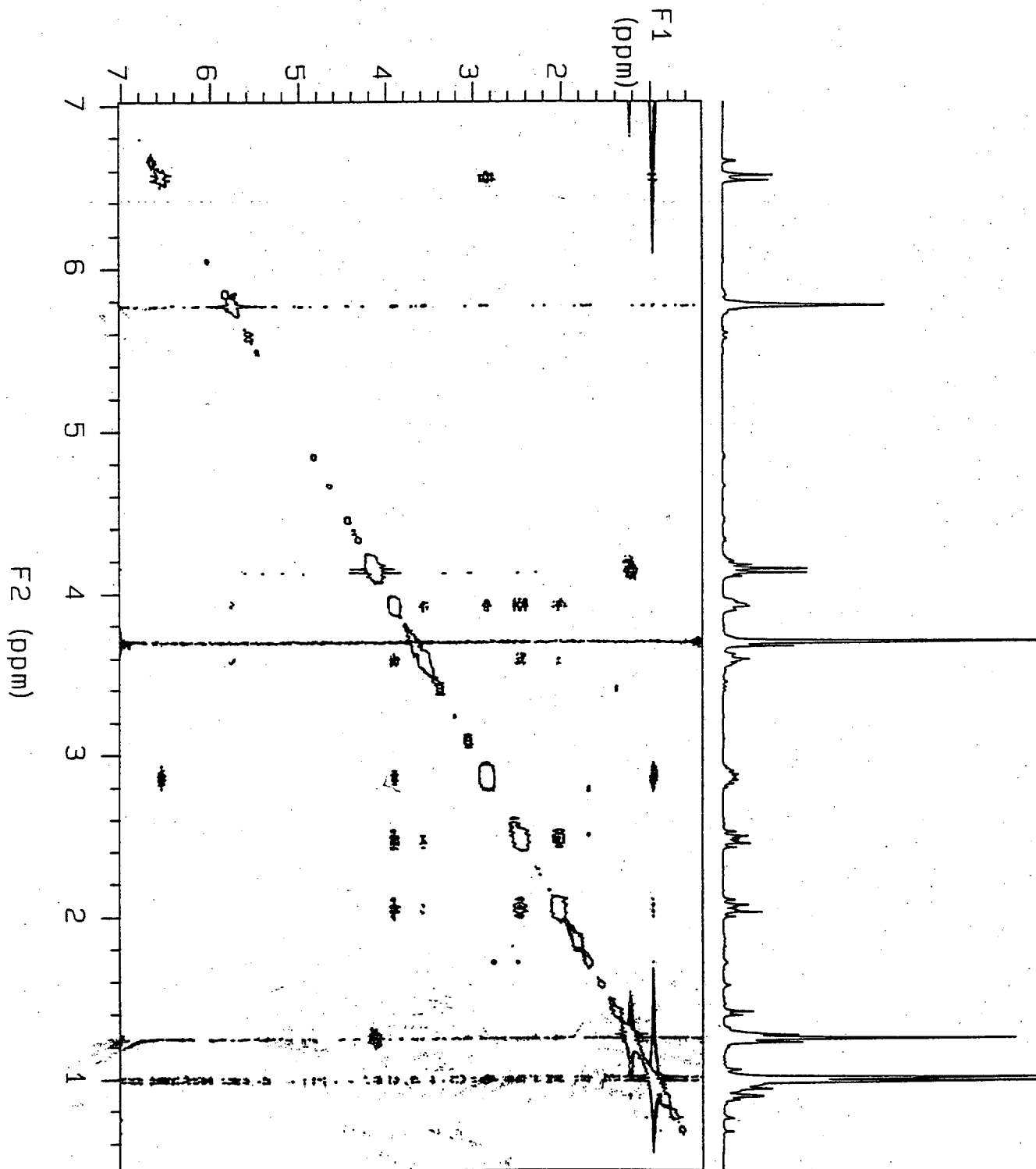
NMR 75.0 MHz
CDCl₃

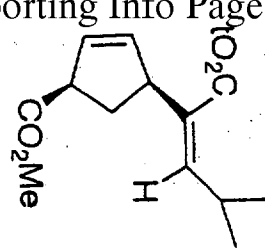




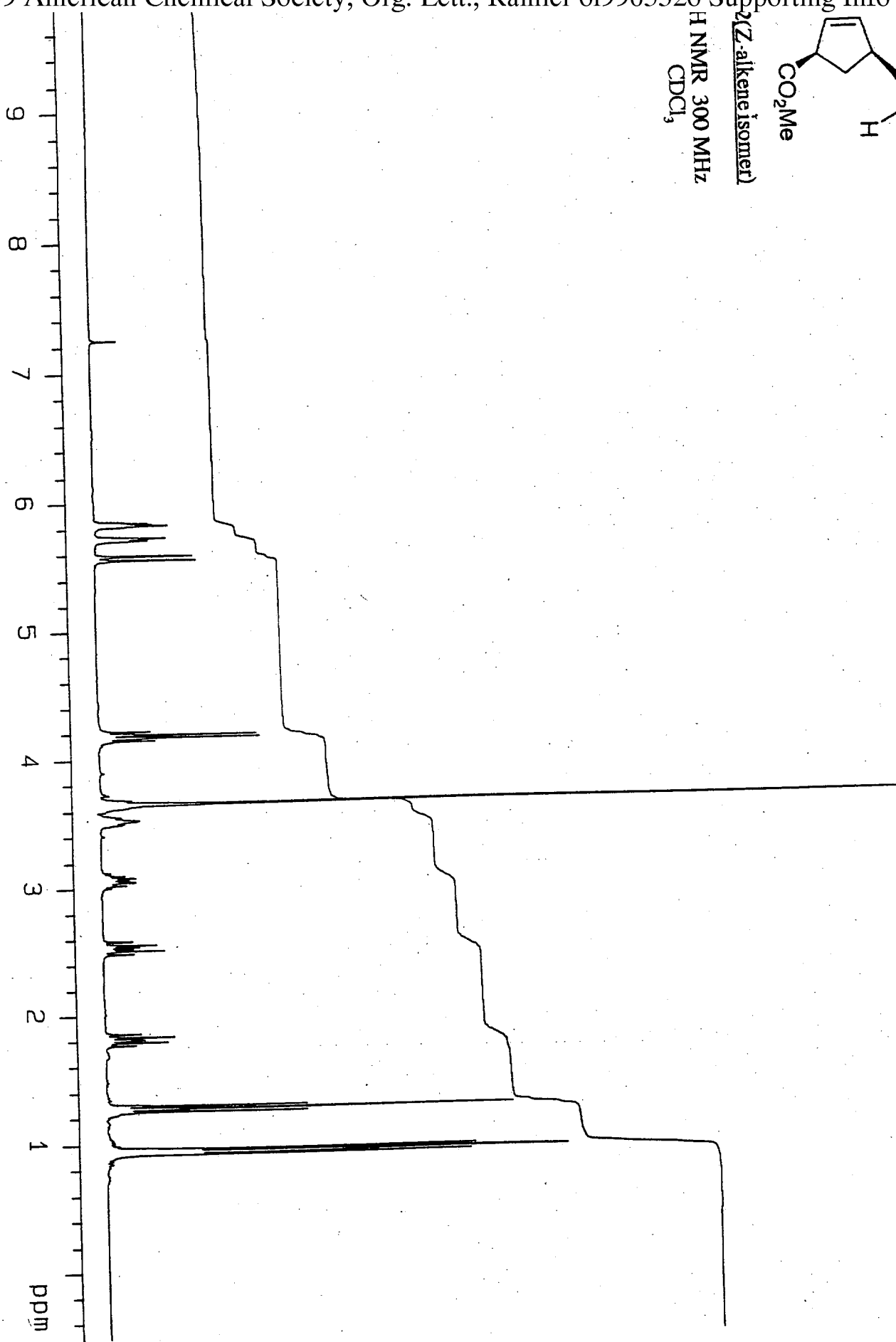
12(E-isomer)

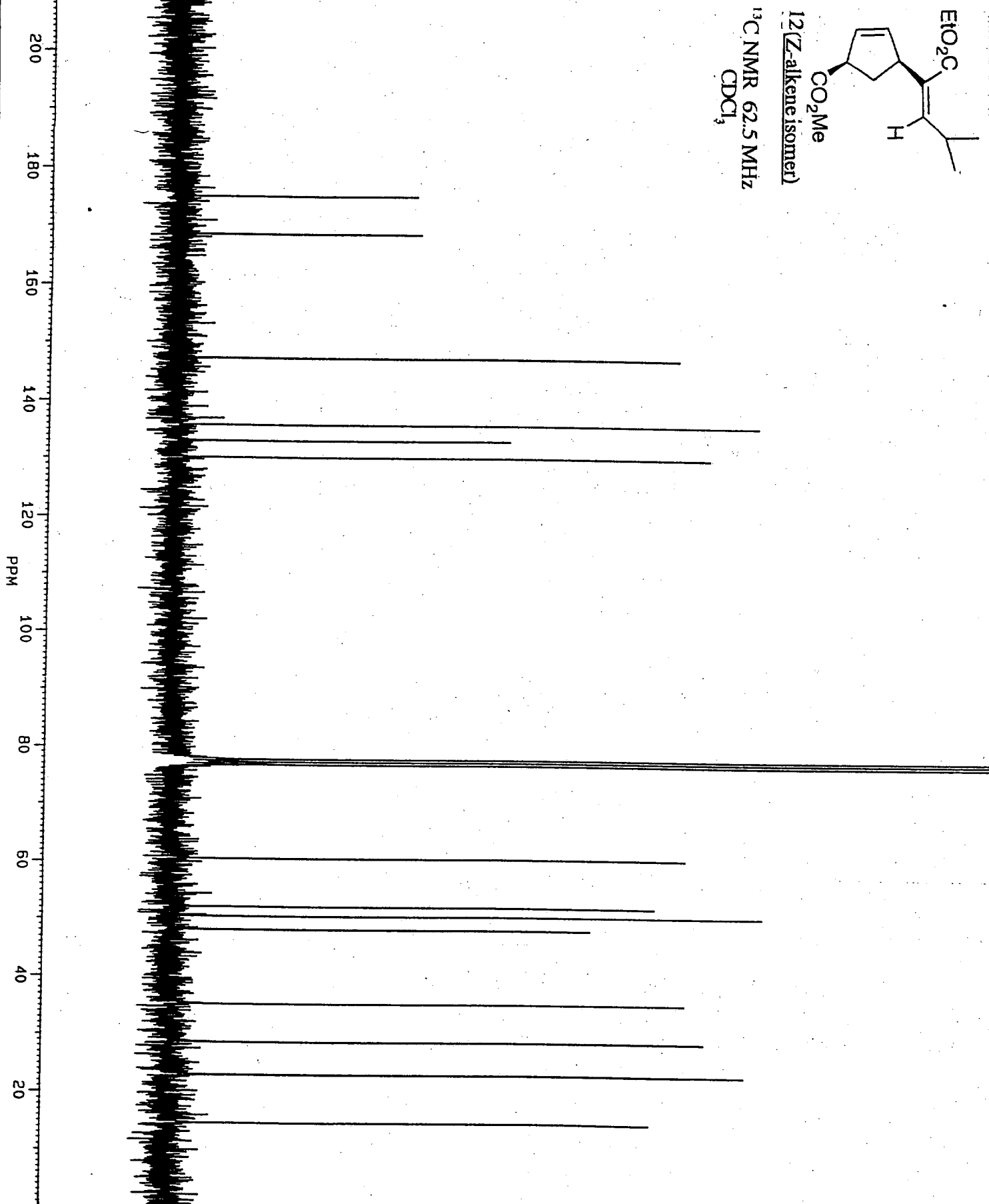
¹H NMR 300 MHz
CDCl₃

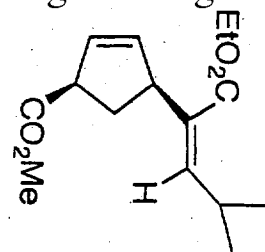




(Z)-alkene isomer 2
¹H NMR 300 MHz
 CDCl₃

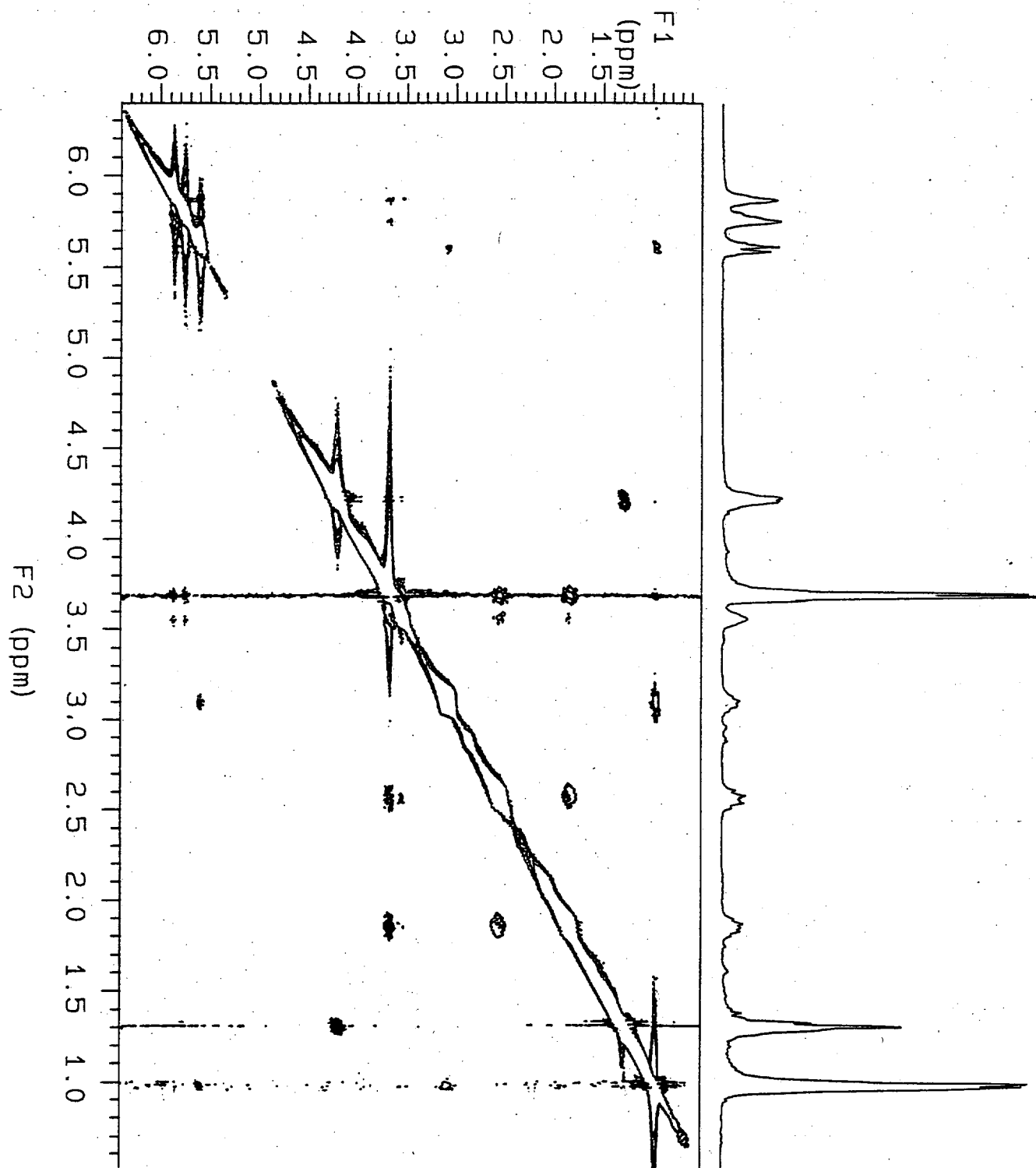




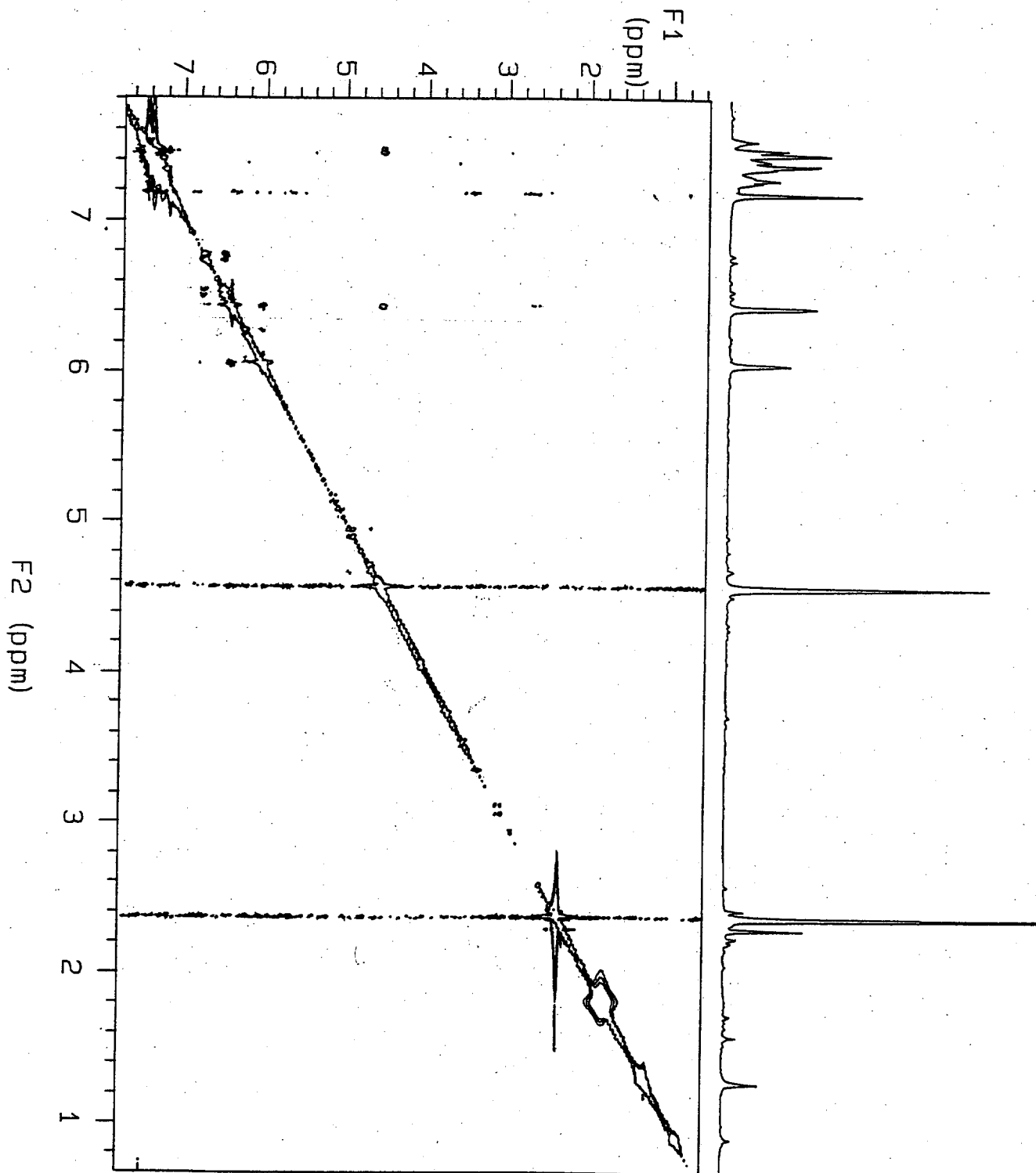
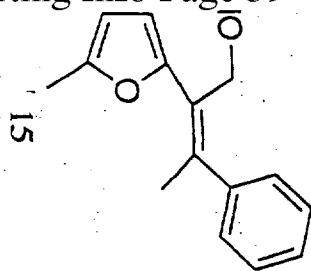


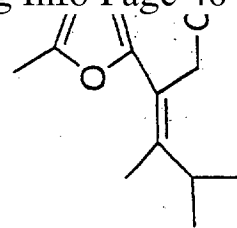
12 (Z-isomer)

NOESY 300 MHz
CDCl₃



¹H NOESY 300 MHz
CDCl₃





16

NOESY 300 MHz
CDCl₃

