Supporting Information For:

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

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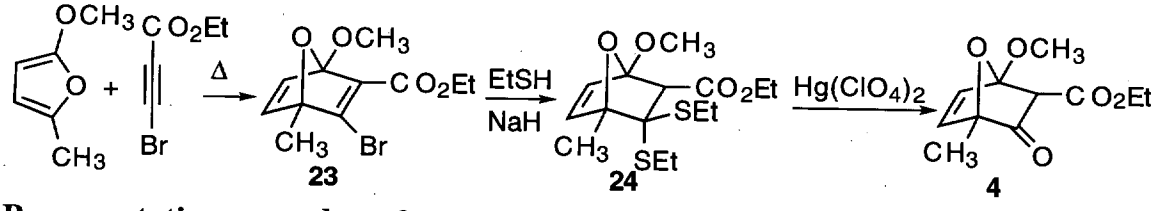
Experimental procedure (including characterization data) as well as copies of the ^{1}H and ^{13}C NMR spectra for **4-12** and nOe data for **15** and **16**.

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 (δ = 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, $(i\text{-}Pr)_2NEt$, 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.

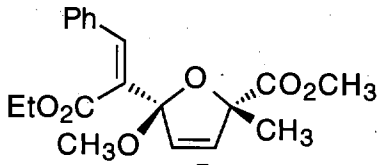


Representative procedure for the formation of Keto-ester. Preparation of (±)-ethyl-1-methoxy-4-methyl-7-oxabicyclo[2.2.1]hepta-5-ene-3-one-2-carboxylate (4). A solution of ethyl 3-bromopropiolate (0.25 g, 1.4 mmol), 2-methoxy-

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%). ^{1}H NMR (250MHz, $CDCl_3$) 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); ^{13}C NMR (250MHz, $CDCl_3$) 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 (CCl_4) 1715, 1320 cm-1; MS (FAB^+) 289(MH^+), 291(MH^+), 210 m/z; HRMS calcd for $C_{11}H_{13}O_4Br$ (MH^+) 289.0075, found 289.0081.

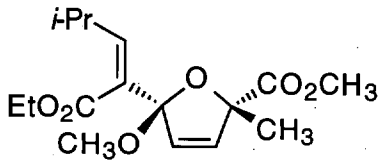
A solution of **23** (0.78 g, 2.7 mmol) and THF (20 mL) was added over 2 hrs to a solution of EtSNa (20 mL of a 0.27 M solution in THF, 5.4 mmol) at 0°C. After the addition was completed, the reaction was immediately quenched with $NaHCO_3$ (sat., 20 mL) extracted with ether, dried ($MgSO_4$), and concentrated. Flash chromatography (5:1 hexanes/ethyl acetate) afforded 0.86 g (96%) of **24** as a single diastereomer. ^{1}H NMR (250MHz, $CDCl_3$) 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); ^{13}C NMR (62.5MHz, $CDCl_3$) 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 $C_{15}H_{24}O_4S_2$(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 $CaCO_3$ (0.12 g, 1.2 mmol) followed by $Hg(ClO_4)_2$ (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 (Na_2SO_4), and concentrated. Chromatography (5:1) gave 82 mg (61%) of **4** as thick oil. ^{1}H NMR (250MHz, $CDCl_3$) 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); ^{13}C NMR (250MHz, $CDCl_3$) δ 198.1, 166.7, 140.0, 133.9, 111.3, 88.1, 61.6, 53.9, 53.3, 14.0, 12.5; IR (CCl_4) 1777, 1734 cm^{-1}; HRMS (FAB) calcd for $C_{11}H_{14}O_5$ (M+H^+) 227.0919, found 227.0915.



5

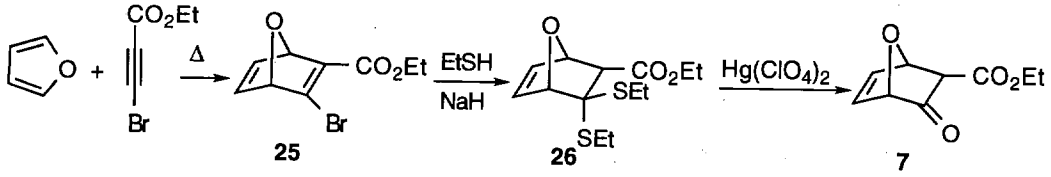
Representative procedure for the condensation, fragmentation, and elimination reaction. Preparation of (±)-5-methoxycarbonyl-5-methyl-2-methoxy-2-*Z*-[ethyl-3-phenylprop-2-enoate]-2,5-dihydrofuran (5). A solution of **4** (0.050 g, 0.20 mmol) and DMF (1 mL) was added dropwise to a slurry of NaH (0.006 g, 0.2 mmol) and DMF (0.5 mL) at 0°C. After stirring for 1h 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). $NaHCO_3$ (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 ($MgSO_4$) and concentrated. Flash chromatography (5:1 hexane/ethyl acetate) provided 0.060 g (83%) of furan **5** as a colorless oil. ^{1}H NMR (250MHz, $CDCl_3$) 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); ^{13}C NMR (62.5MHz, $CDCl_3$) 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 (CCl_4) 1758, 1727, 1258, 1215 cm^{-1}; HRMS (FAB) calcd for $C_{19}H_{22}O_6$ (M+Cs$^+$) 479.0471, found 479.0483.



6

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. ^{1}H NMR (250MHz, $CDCl_3$) 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); ^{13}C NMR (62.5MHz, $CDCl_3$) 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 (CCl_4) 1764, 1721, 1449 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{24}O_6$ ($M+Cs^+$) 445.0627, found 445.0614.

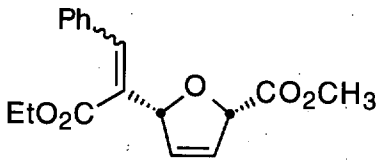


Preparation of (±)-ethyl-7-oxabicyclo[2.2.1]hepta-5-ene-3-one-2-carboxylate (7). A solution of ethyl 3-bromopropiolate (1.5 g, 8.0 mmol) and furan (6 mL, 82 mmol) was heated at 80 °C in a pressure tube for 24 h. After cooling and concentrating, the resulting oil was purified by flash chromatography (5:1 hexanes/ethyl acetate) to give 0.47 g (24%) of **25** as a colorless oil. ^1H NMR (250MHz, $CDCl_3$) 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); ^{13}C NMR (62.5MHz, $CDCl_3$) δ 162.3, 148.7, 144.2, 143.1, 141.2, 89.5, 84.5, 60.8, 14.1; IR (CCl_4) 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, $CDCl_3$) 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); ^{13}C NMR (62.5MHz, $CDCl_3$) 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 (CCl_4) 1734, 1172 cm^{-1}; HRMS(FAB) calcd for $C_{13}H_{20}O_3S_2$ ($M+H^+$) 289.0932, found 289.0942. **26 (exo isomer)** ^1H NMR (250MHz, $CDCl_3$) δ 6.43 (s, 2H), 5.21 (s, 1H), 4.90 (s, 1H), 4.20 (dq, J = 7.2, 1.8Hz, 2H), 2.84-2.66 (m, 5H), 1.30-1.13 (m, 9H); ^{13}C NMR (62.5MHz, $CDCl_3$) 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 (CCl_4) 1734, 1178 cm^{-1}; HRMS(FAB) calcd for $C_{13}H_{20}O_3S_2$ ($M+H^+$) 289.0932, found 289.0942.

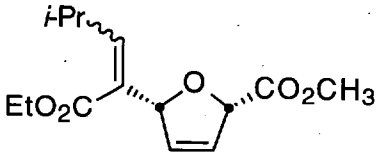
Prepared according to the procedure outlined for the formation of **4** using **26** (0.23 g, 0.8 mmol), $Hg(ClO_4)_2$ (0.64 g, 1.6 mmol), $CaCO_3$ (0.3 g, 3.0 mmol), H_2O (0.8 mL, 44 mmol), and THF (4 mL) to afford 0.8 g (55%) of **7** as a colorless oil and as a 2:1 mixture of endo:exo isomers. ^1H NMR (250MHz, $CDCl_3$) **(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* = 7.2Hz, 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 $C_9H_{10}O_4$(M+H$^+$) 183.0657, found 183.0656.



8

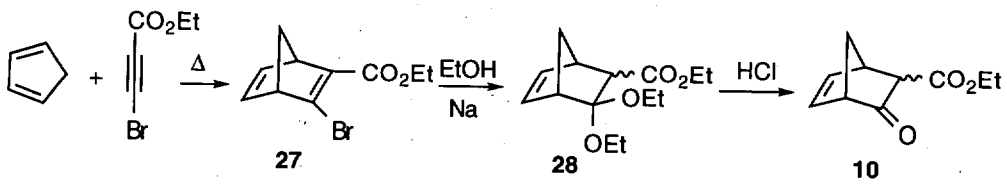
Preparation of (±)-5-methoxycarbonyl-2-[ethyl-3-phenylprop-2-enoate]-2,5-dihydrofuran (8). Prepared according to the procedure outlined for the formation of **5** using **7** (0.14 g, 0.77 mmol), NaH (0.02 g, 0.8 mmol), benzaldehyde (0.17 mL, 1.6 mmol), DMF (6 mL), and methyl iodide (0.6 mL, 10 mmol) to give 0.13 g (56%) of **8** as a 3:1 mixture of *E*- and *Z*-alkenes. **8*E*-alkene isomer:** ^{1}H 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 $C_{17}H_{18}O_5$ (M+H$^+$) 303.1232, found 303.1235. **8*Z*- alkene isomer:** ^{1}H 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 $C_{17}H_{18}O_5$ (M+H$^+$) 303.1232, found 303.1228.



9

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**: ^{1}H 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 $C_{14}H_{20}O_5$ ($M+Cs^+$) 401.0365, found 401.0374. **9E**: ^{1}H 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 $C_{14}H_{20}O_5$ ($M+Cs^+$) 401.0365, found 401.0357.



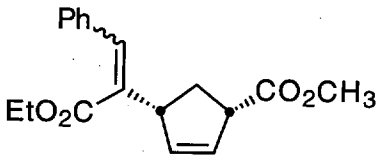
27 28 10

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. ^{1}H 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, 3 H); ^{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 $C_{10}H_{11}O_2Br$ ($M+H^+$) 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. ^{1}H 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,

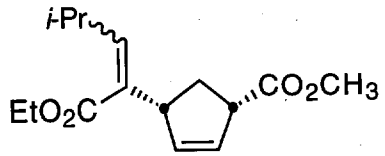
1H), 1.24-1.02 (m, 9H); ^{13}C NMR (62.5MHz, $CDCl_3$) δ 172.3, 171.3, 138.7, 137.4, 136.2, 130.1, 128.2, 112.4, 112.1, 59.9, 59.8, 58.9, 58.3, 57.7, 56.5, 55.0, 53.1, 50.9, 47.2, 47.1, 46.0, 44.6, 43.8, 15.3, 15.2, 15.1, 14.8, 14.2, 14.1; IR (CCl_4) 1740, 1178, 1060 cm^{-1}; HRMS(FAB) calcd for $C_{14}H_{22}O_4$ ($M+H^+$) 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. ^{1}H 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 $C_{10}H_{12}O_3$ ($M+H^+$) 181.0865, found 181.0856.



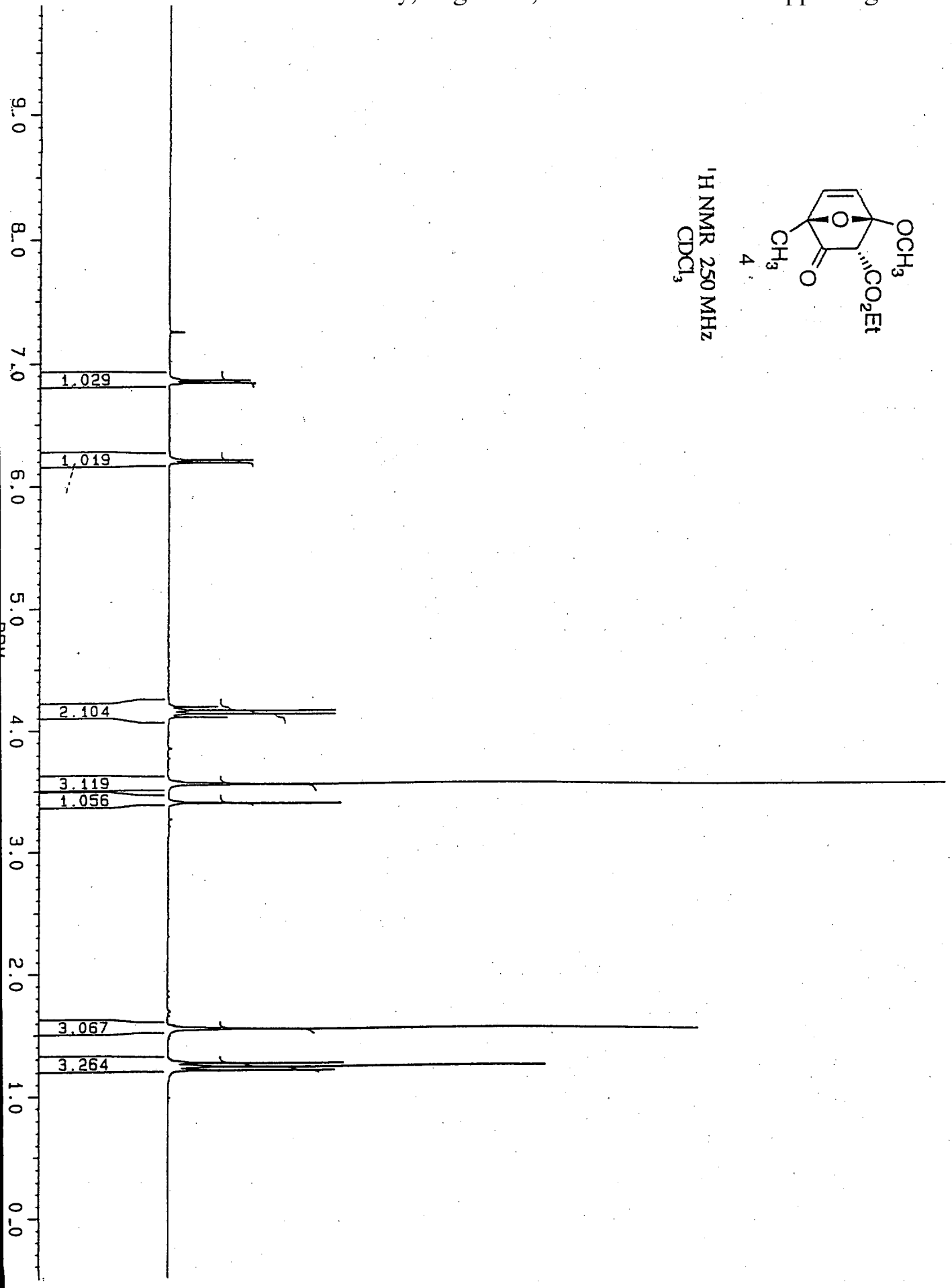
11

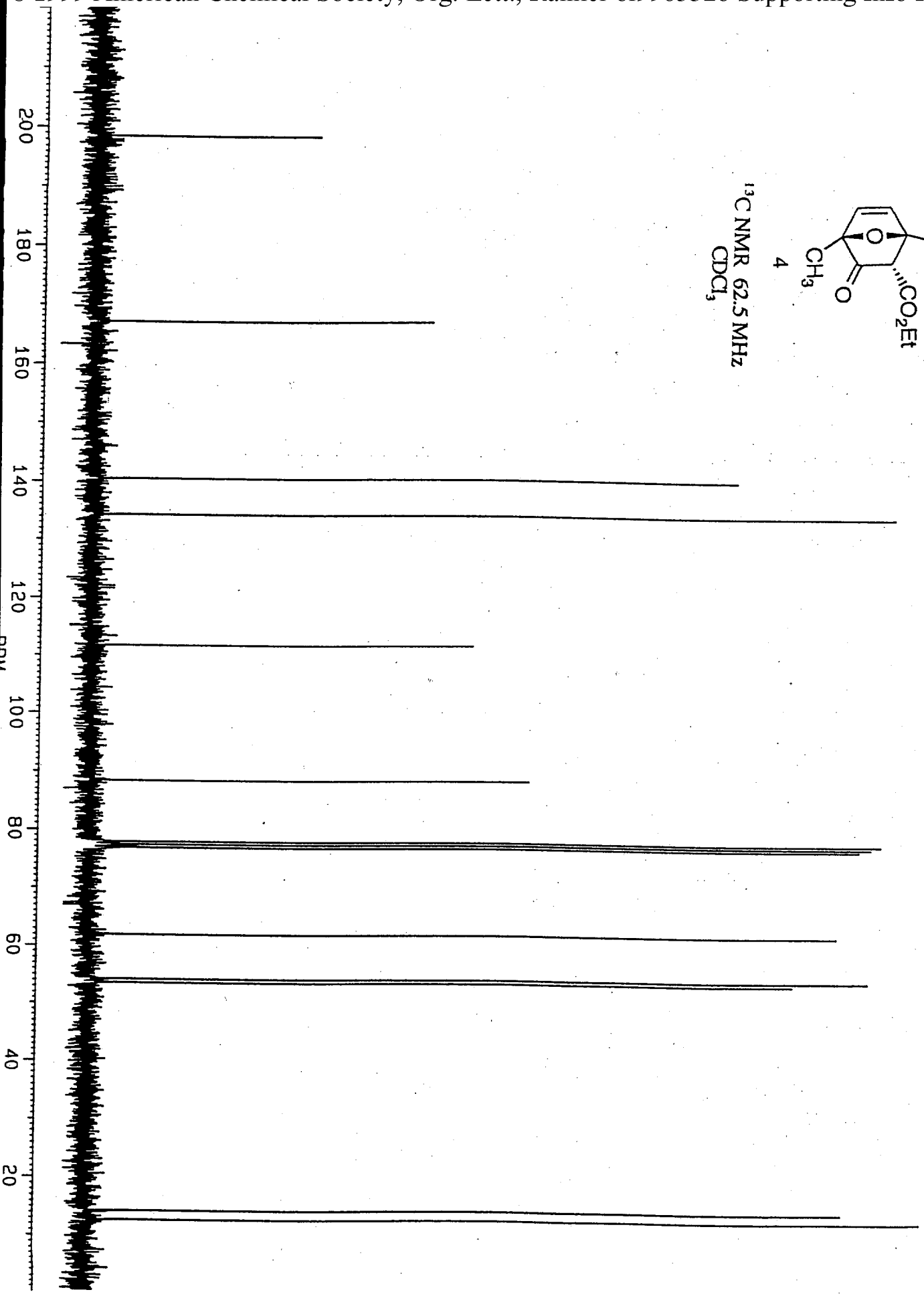
Preparation of (±)-2-methoxycarbonyl-4-*E*-[ethyl-3-phenylprop-2-enoate]-1-cyclopentene (11). Prepared according to the procedure outlined for the formation of **5** using **10** (0.090 g, 0.50 mmol), KO*t*-Bu (0.083 g, 0.75 mmol), benzaldehyde (0.06 mL, 0.6 mmol), DMF (3 mL), and methyl iodide (0.3 mL, 5 mmol) to give 0.13 g (91%) of **11**. ^{1}H 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 $C_{18}H_{20}O_4$ ($M+Cs^+$) 433.0416, found 433.0400.

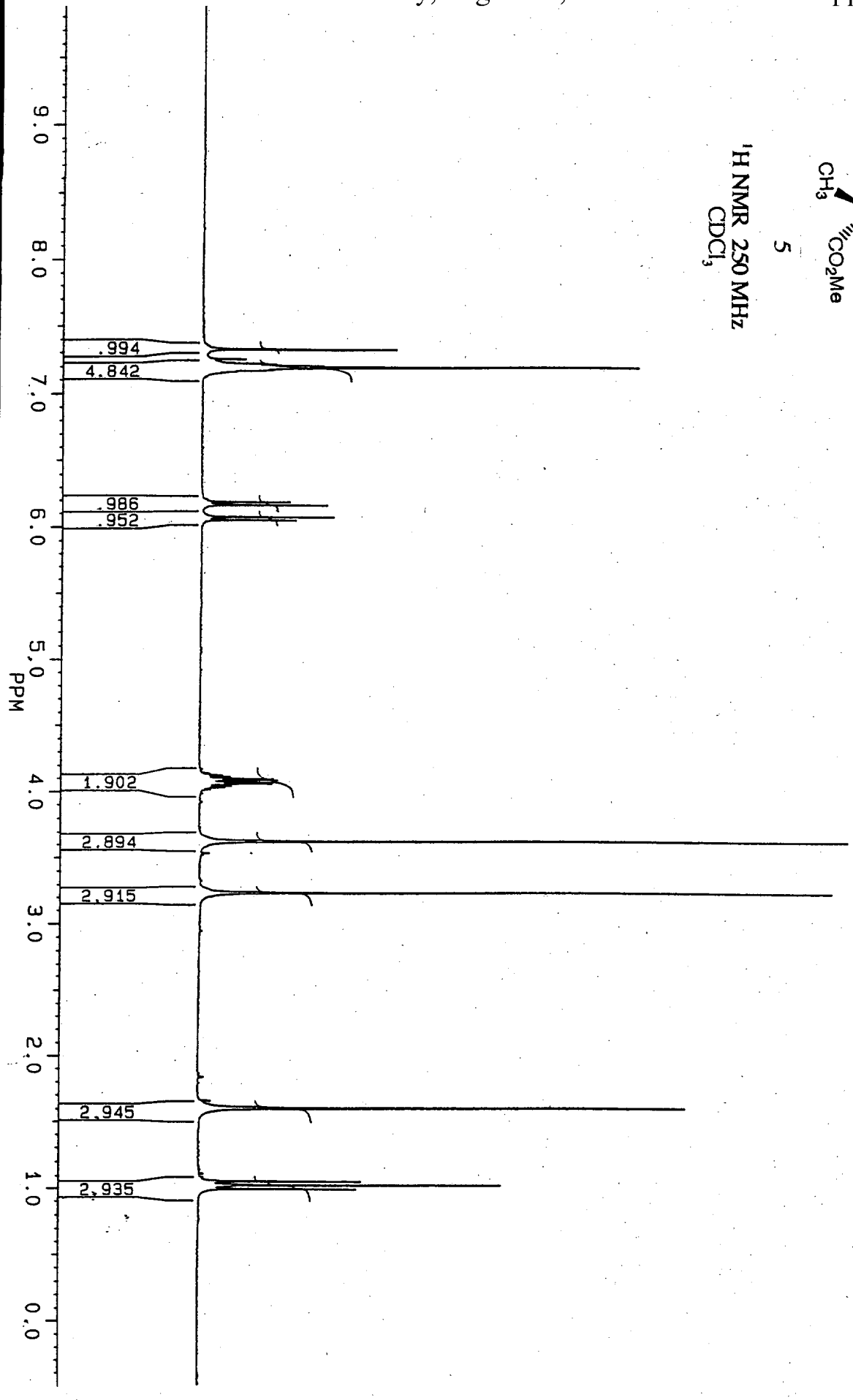


12

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. **12*Z*:** ^{1}H 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, $CDCl_3$) δ174.6, 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 $C_{15}H_{22}O_4$ (M+Cs^+) 399.0572, found 399.0566. **12*E*:** ^{1}H 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 $C_{15}H_{22}O_4$ (M+Cs^+) 399.0572, found 399.0566.

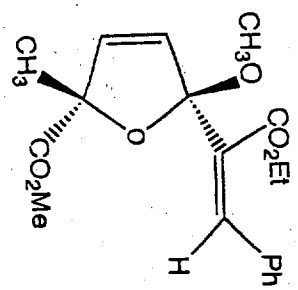

^{1}H NMR 250 MHz
$CDCl_3$
4
CH_3
O
O
OCH_3
CO_2Et
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.029
1.019
2.104
3.119
1.056
3.067
3.264

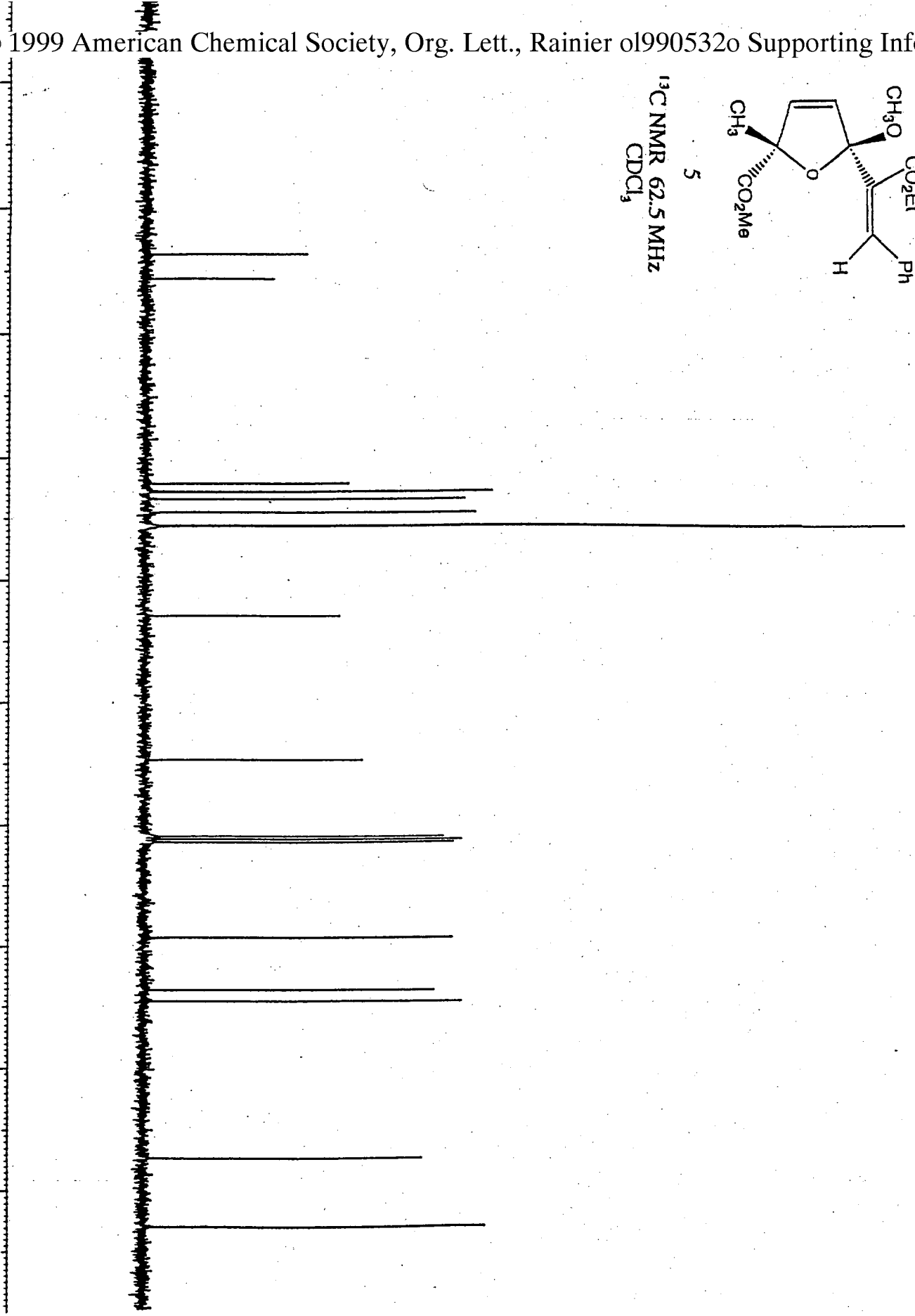




^{1}H NMR 250 MHz
$CDCl_3$

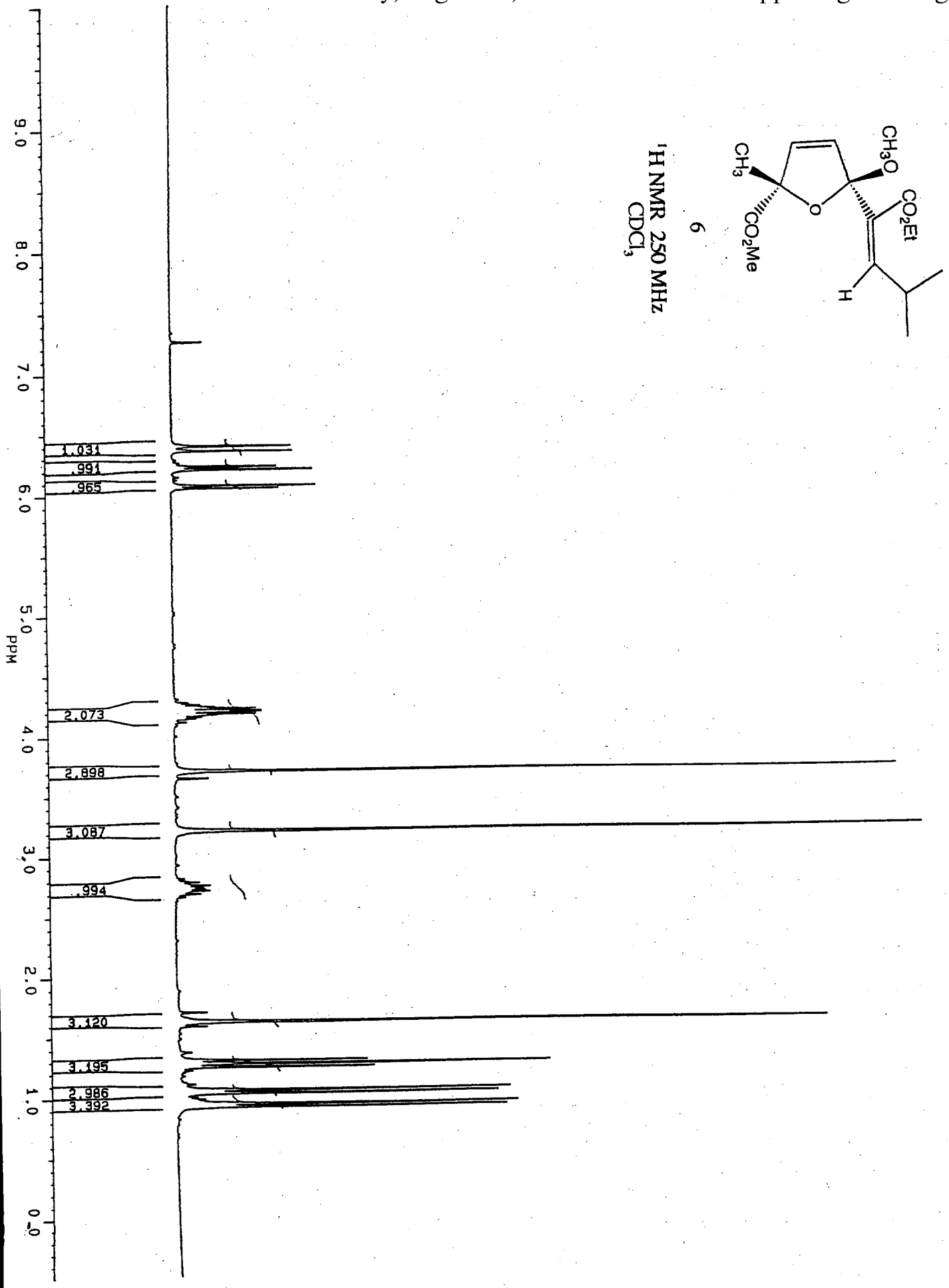
5

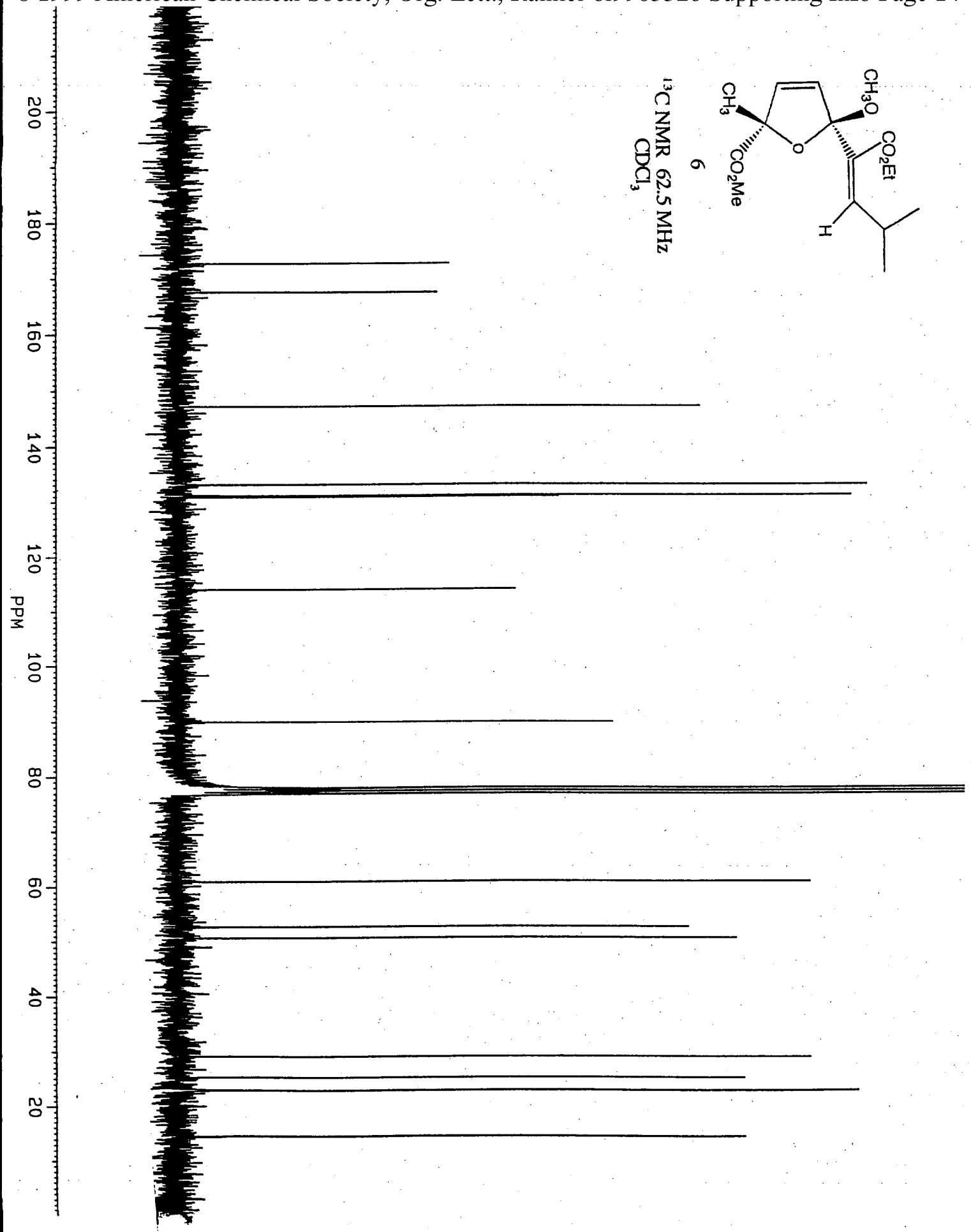


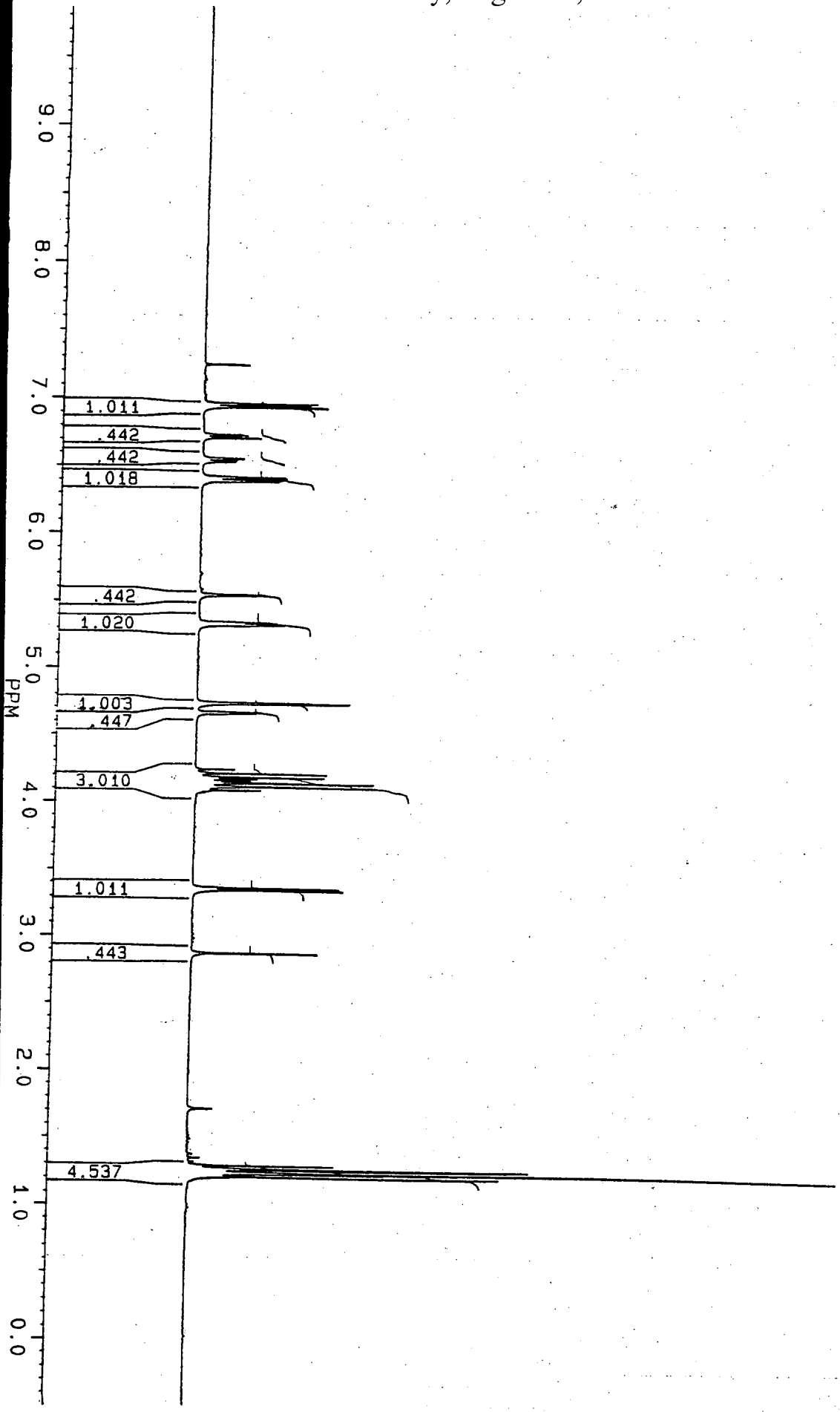


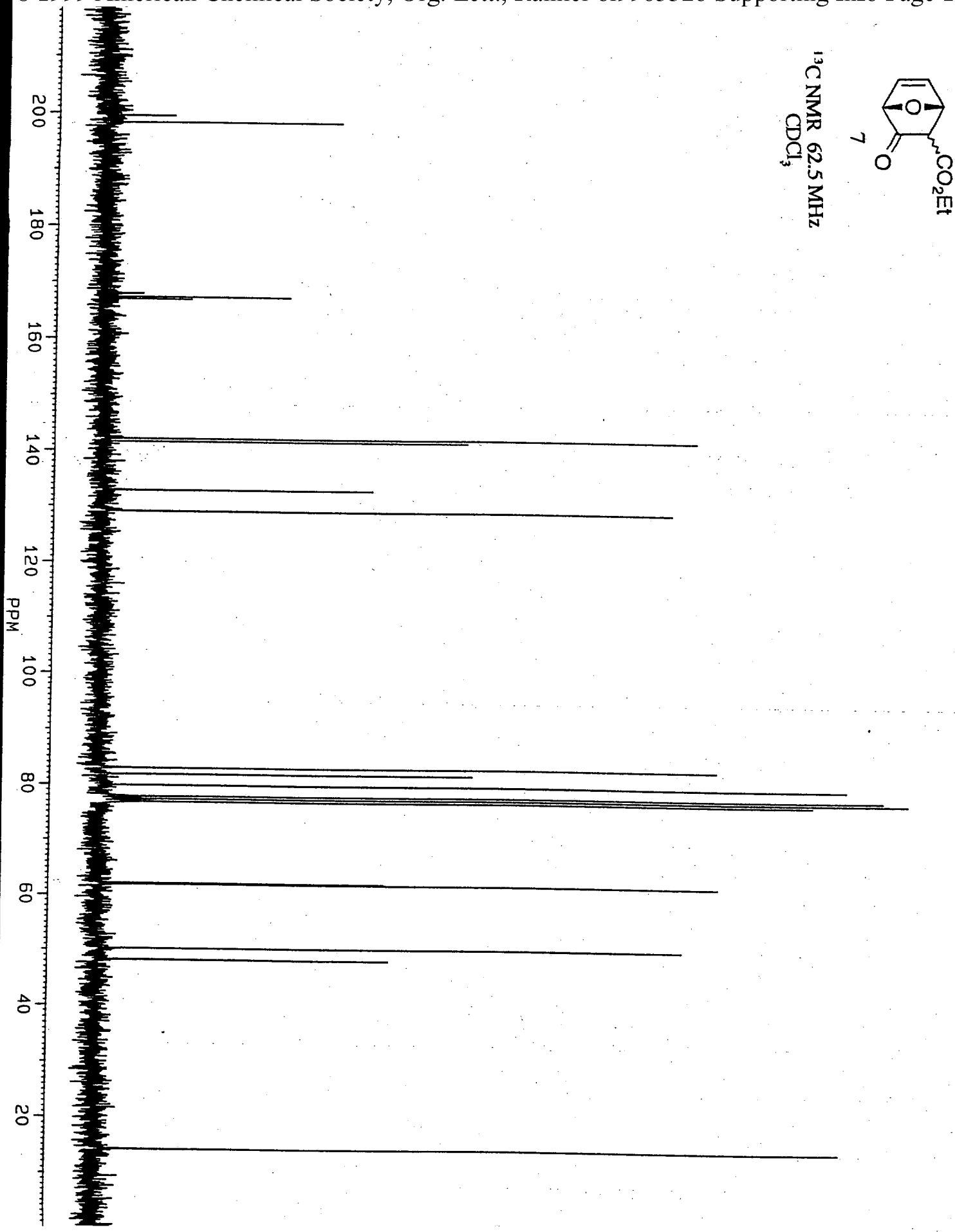
^{13}C NMR 62.5 MHz
$CDCl_3$

5



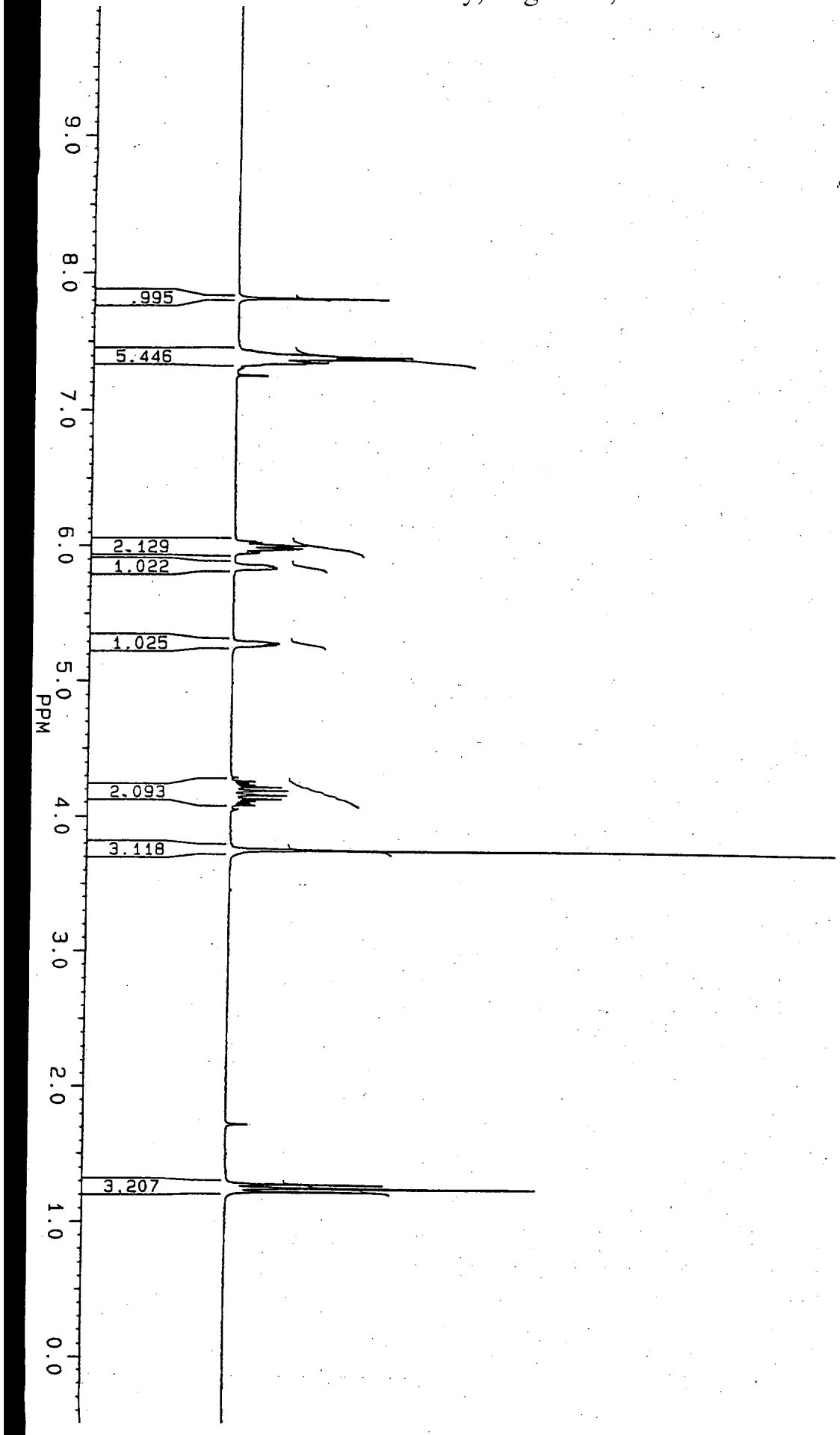

^{13}C NMR 62.5 MHz
$CDCl_3$
6
CH_3O
CO_2Et
CH_3
CO_2Me
O
H
200
180
160
140
120
100
80
60
40
20
PPM

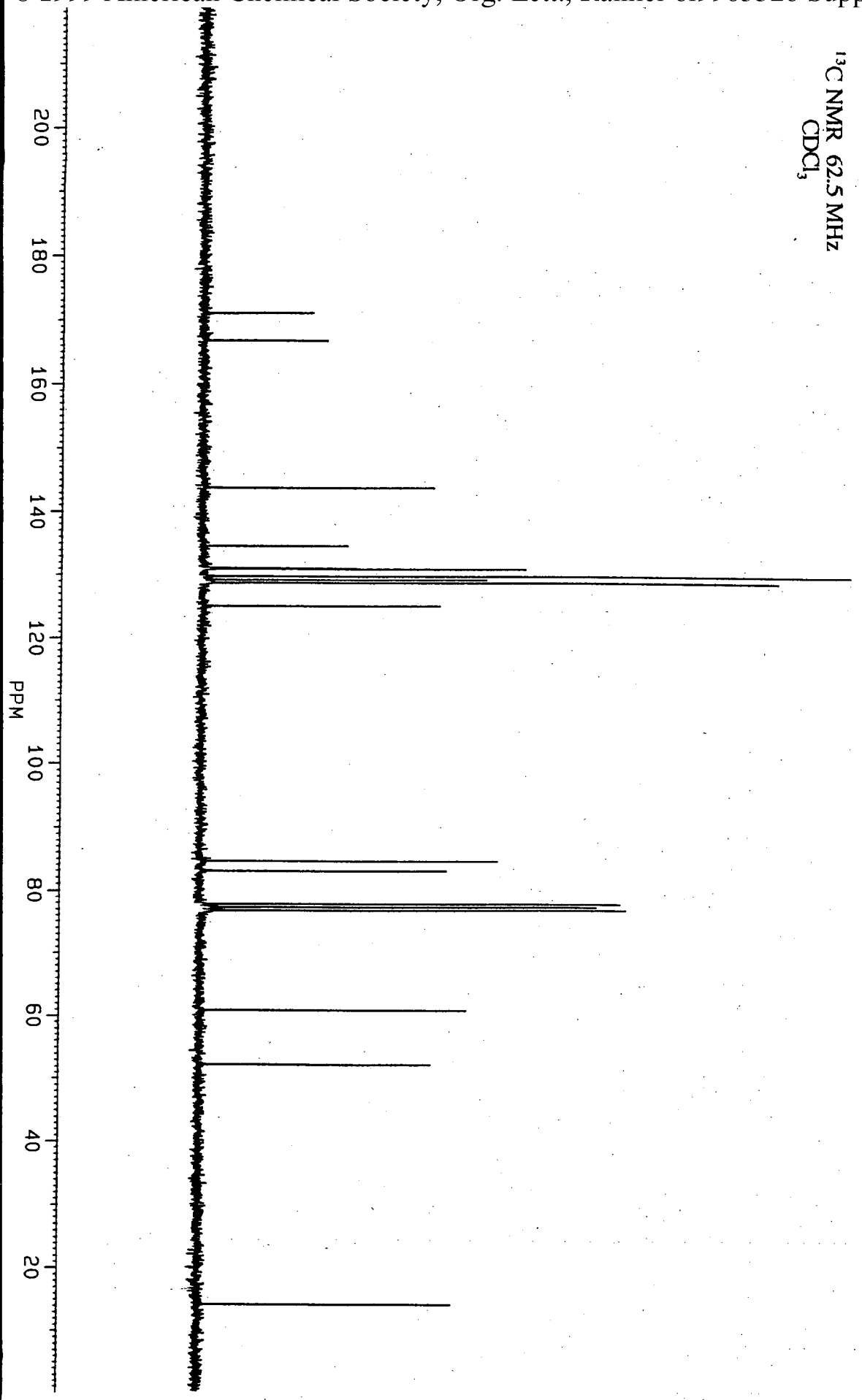

^{1}H NMR 250 MHz
$CDCl_3$
7
CO_2Et
O
O
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
1.011
.442
.442
1.018
.442
1.020
1.003
.447
3.010
1.011
.443
4.537


^{13}C NMR 62.5 MHz
$CDCl_3$
7
CO_2Et
O
O
200
180
160
140
120
100
80
60
40
20
PPM

8 (E-alkene isomer)

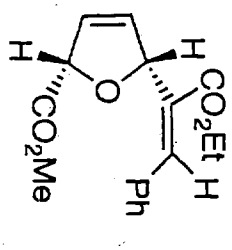
^{1}H NMR 250 MHz
$CDCl_3$





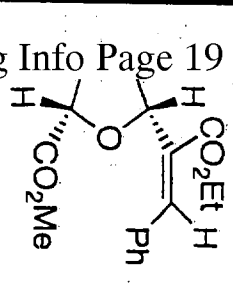
^{13}C NMR 62.5 MHz
$CDCl_3$

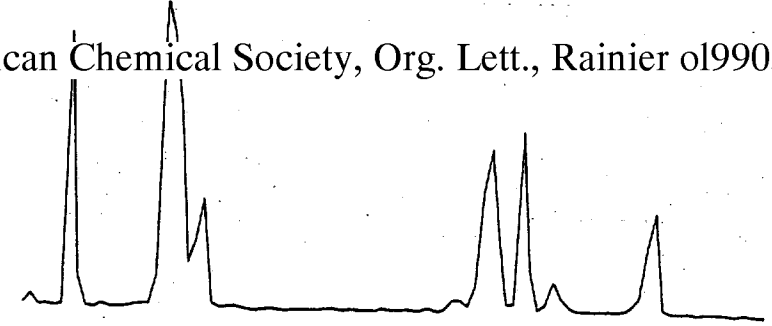
8(E-alkene isomer

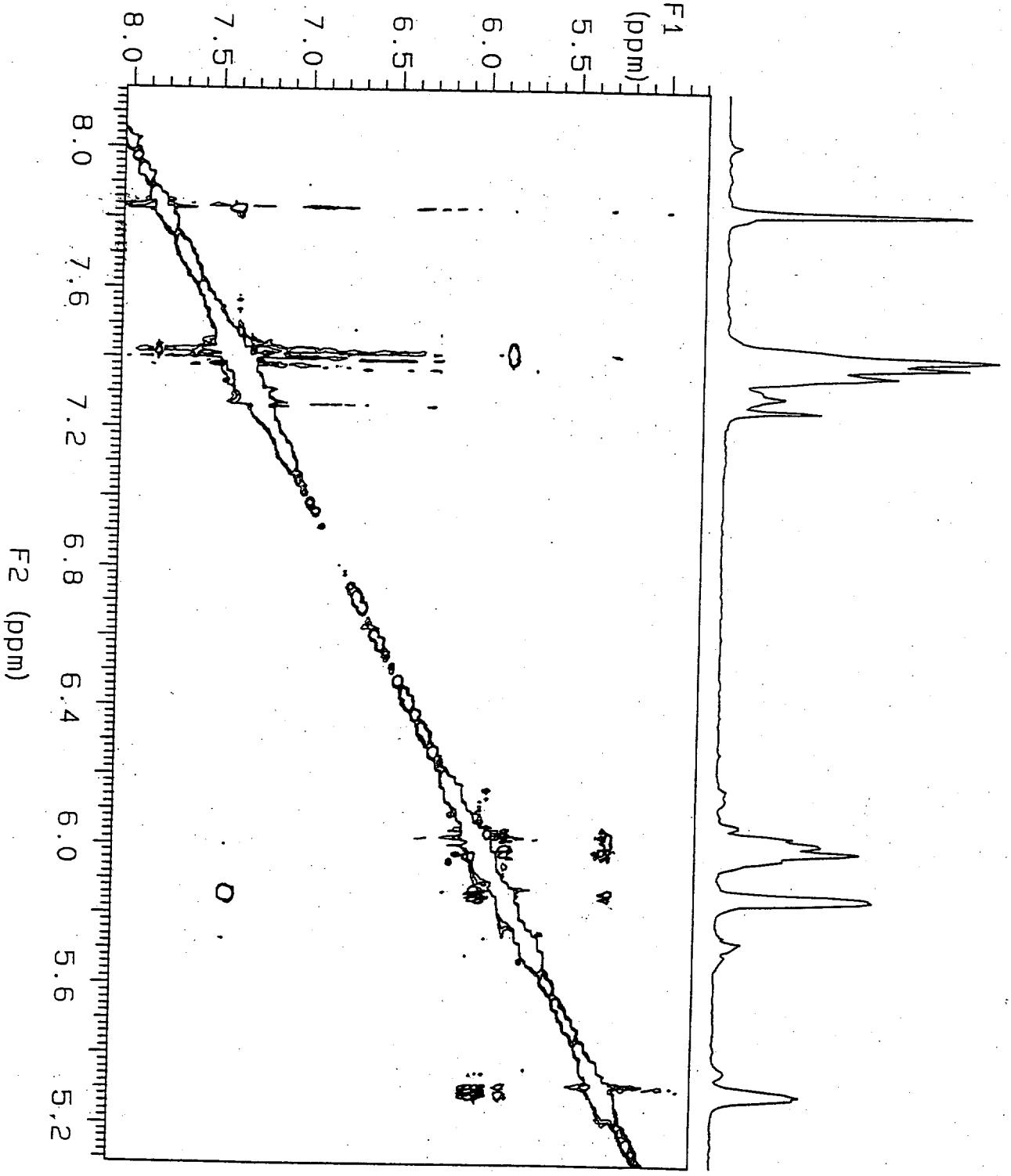


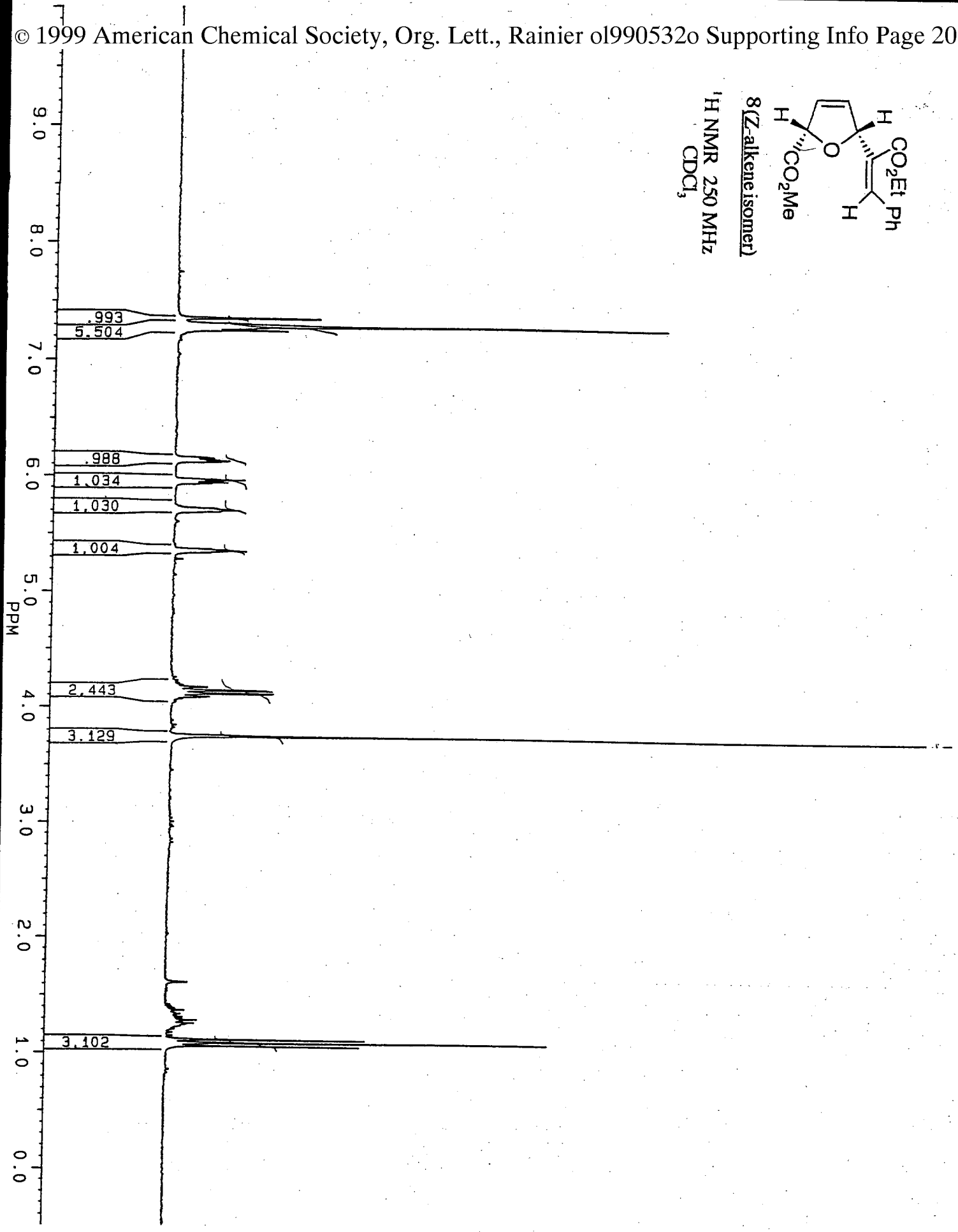
^{1}H NOESY 300 MHz
$CDCl_3$

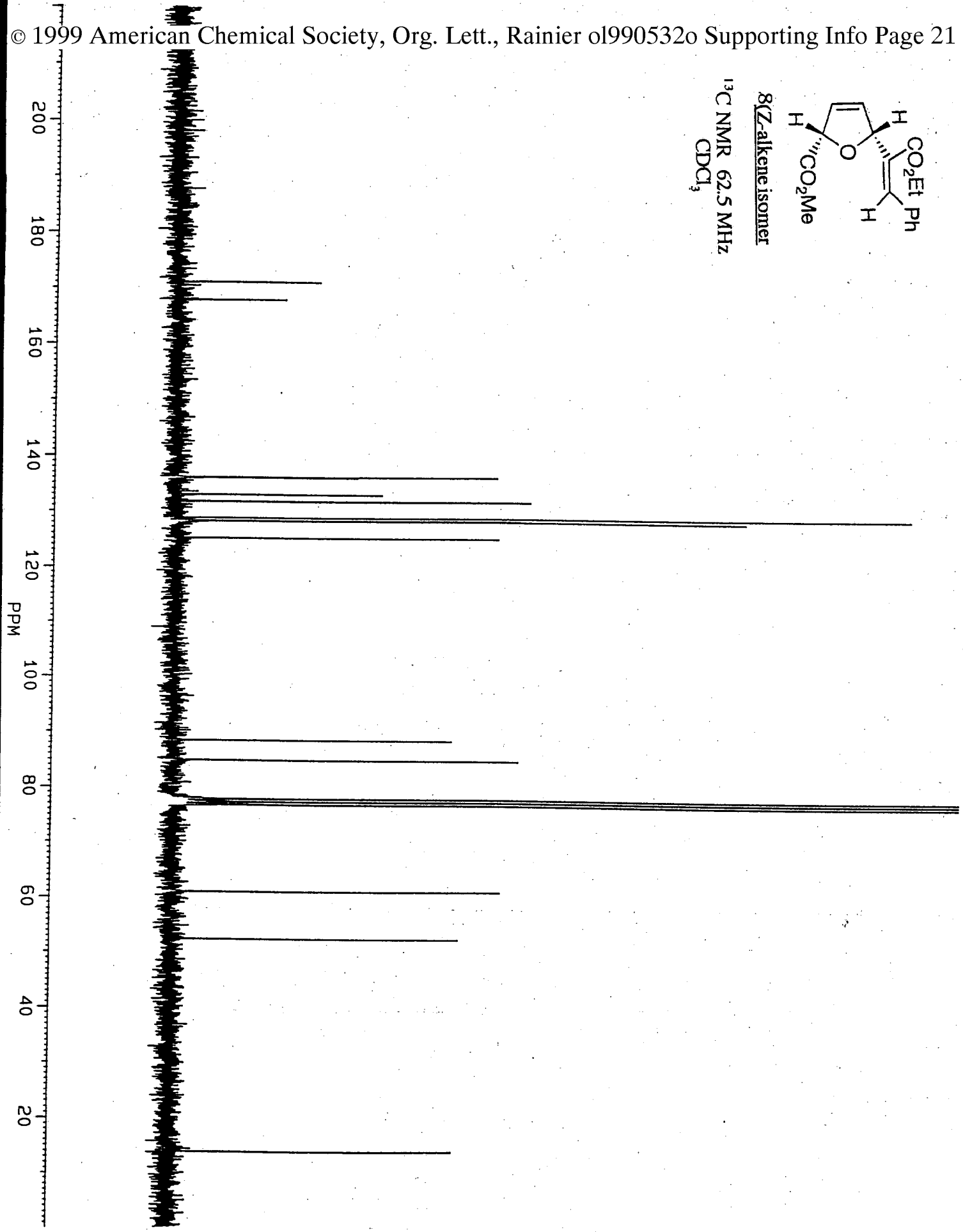
8 (E-isomer)

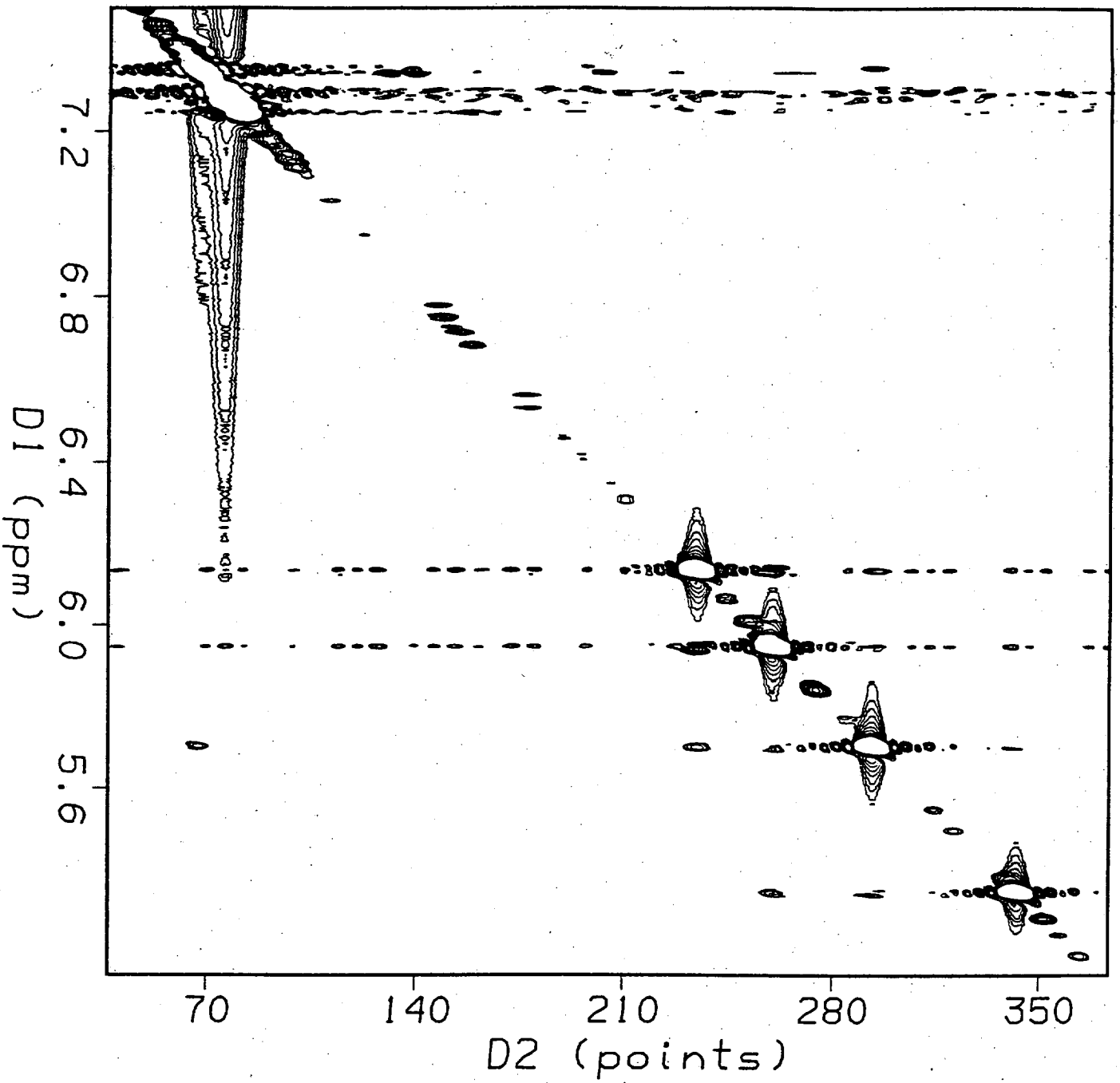






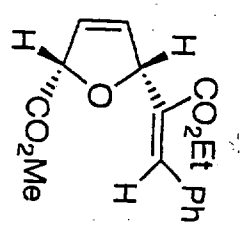



8(Z-alkene isomer
^{13}C NMR 62.5 MHz
$CDCl_3$
H
CO_2Et
Ph
O
CO_2Me
H
H
200
180
160
140
120
100
80
60
40
20
PPM



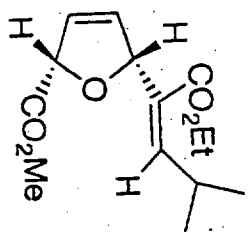
^{1}H NOESY 300 MHz
$CDCl_3$

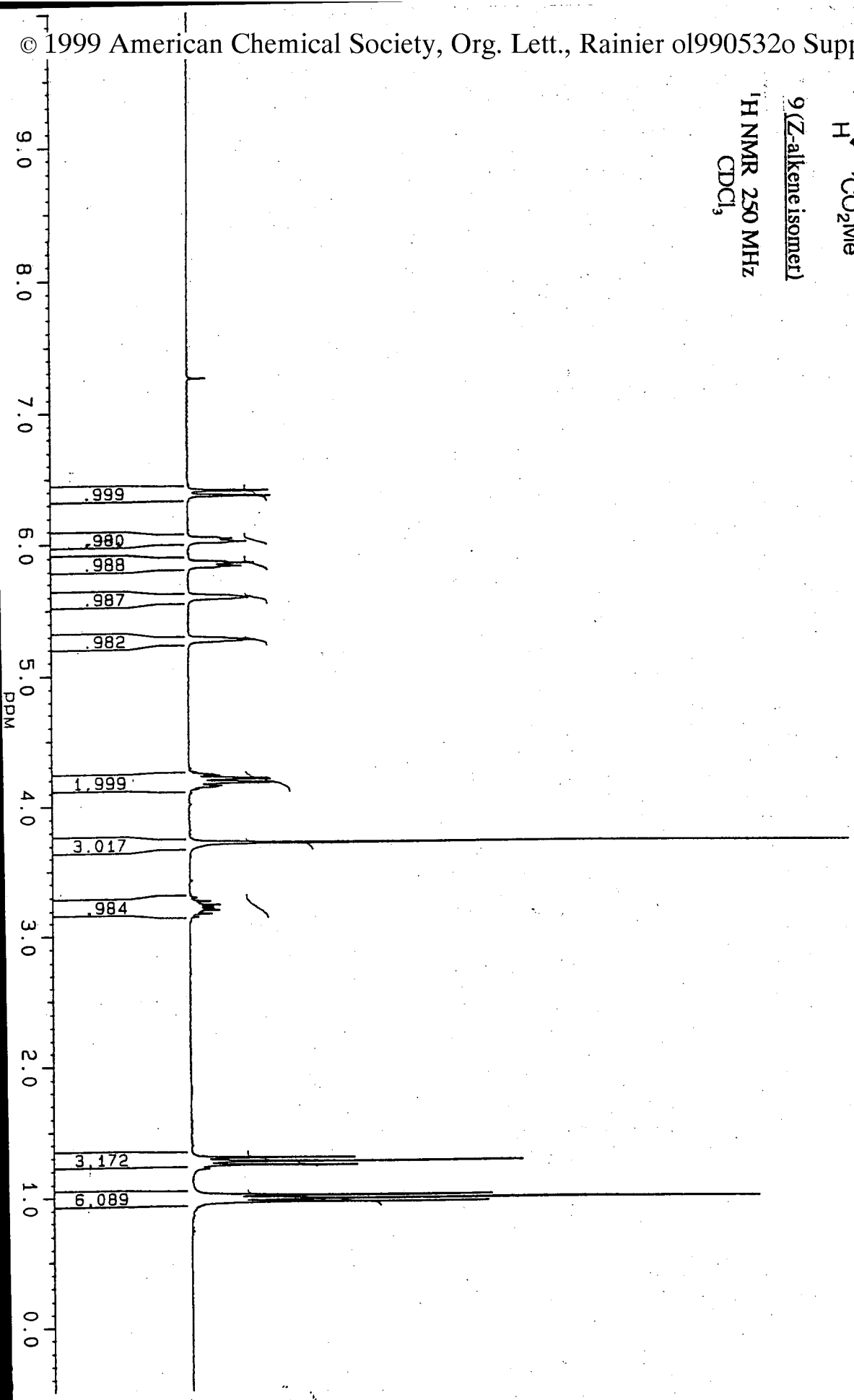
8 (Z-isomer)

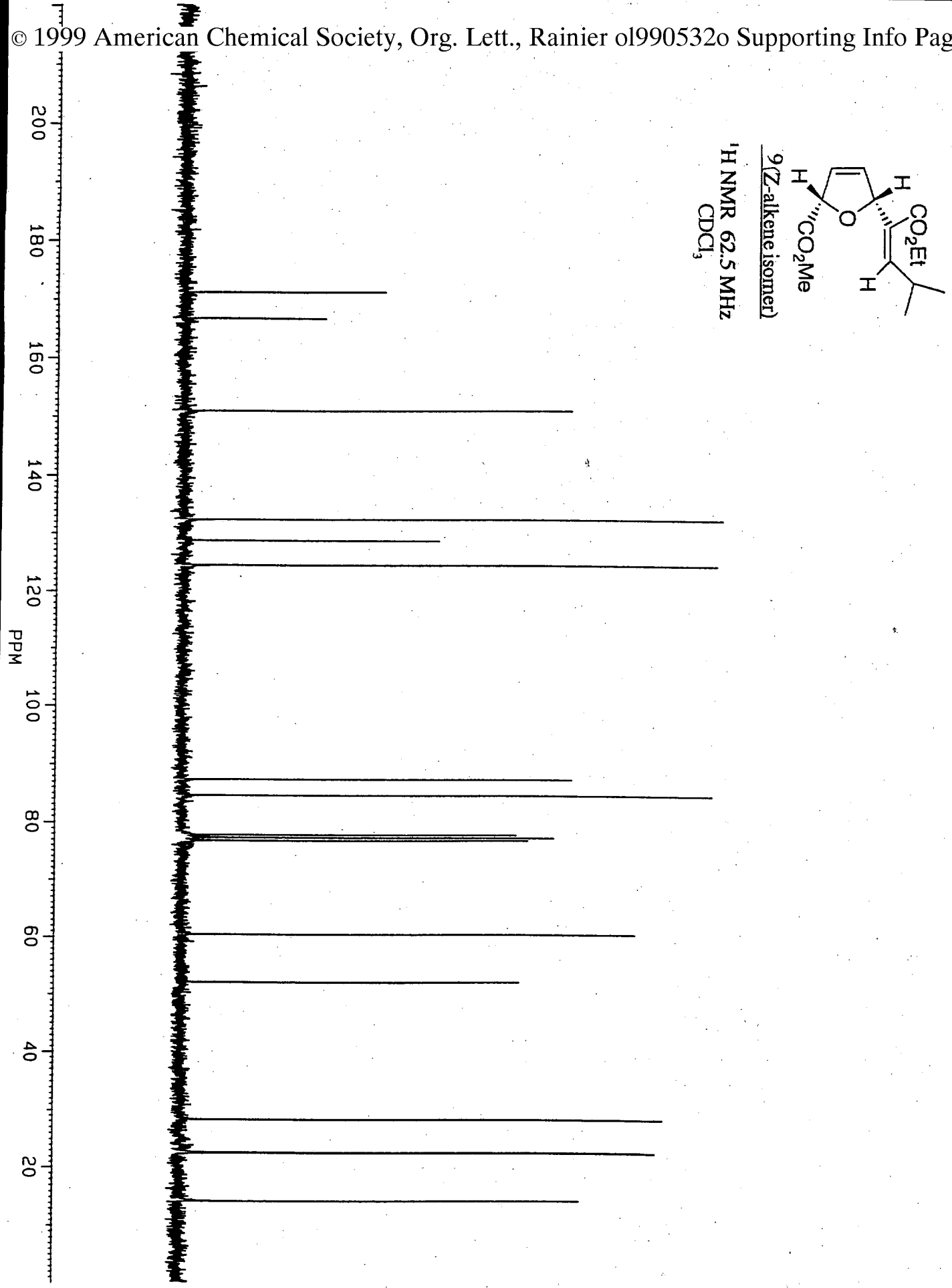


9 (Z-alkene isomer)

^{1}H NMR 250 MHz
$CDCl_3$

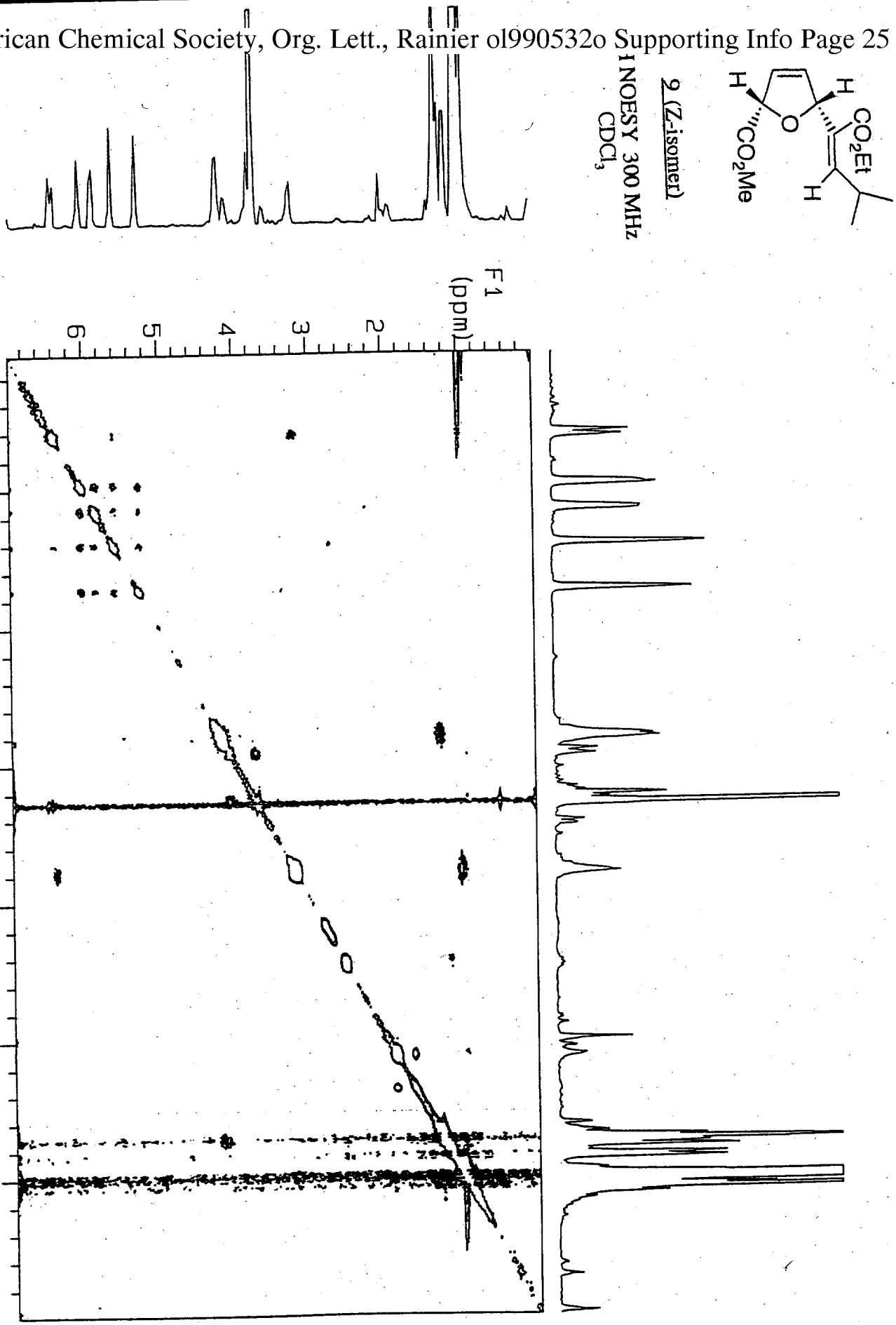


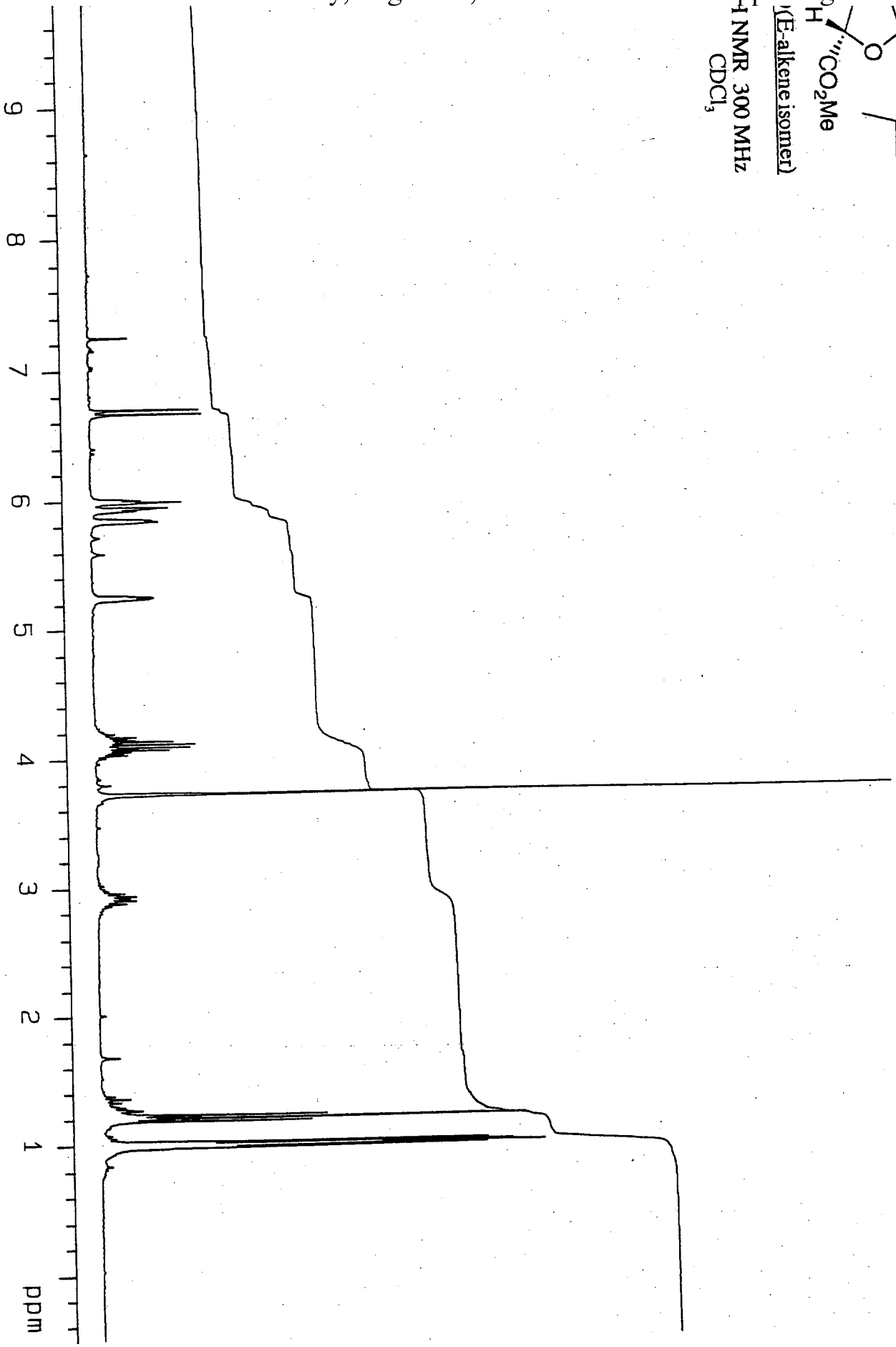


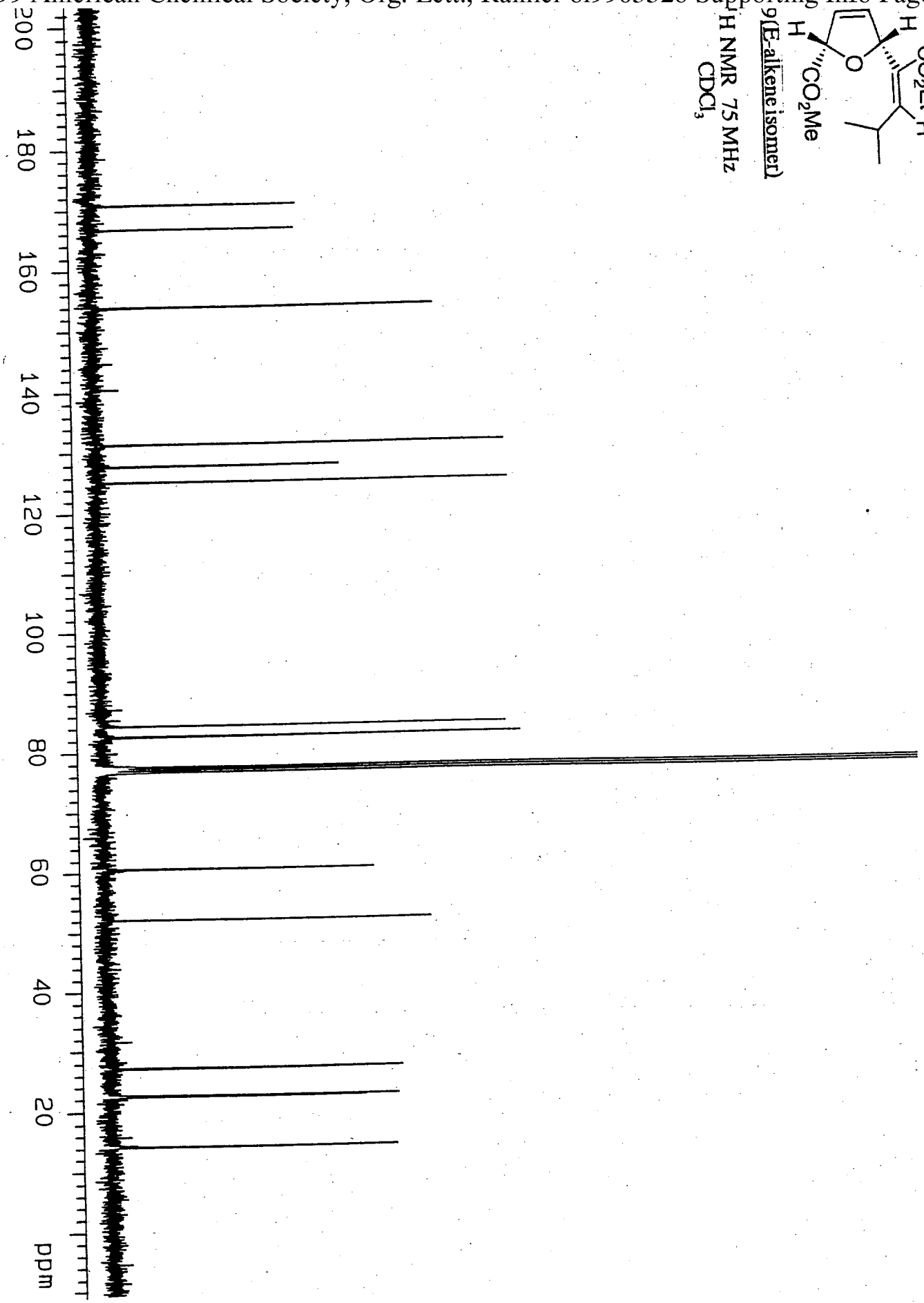


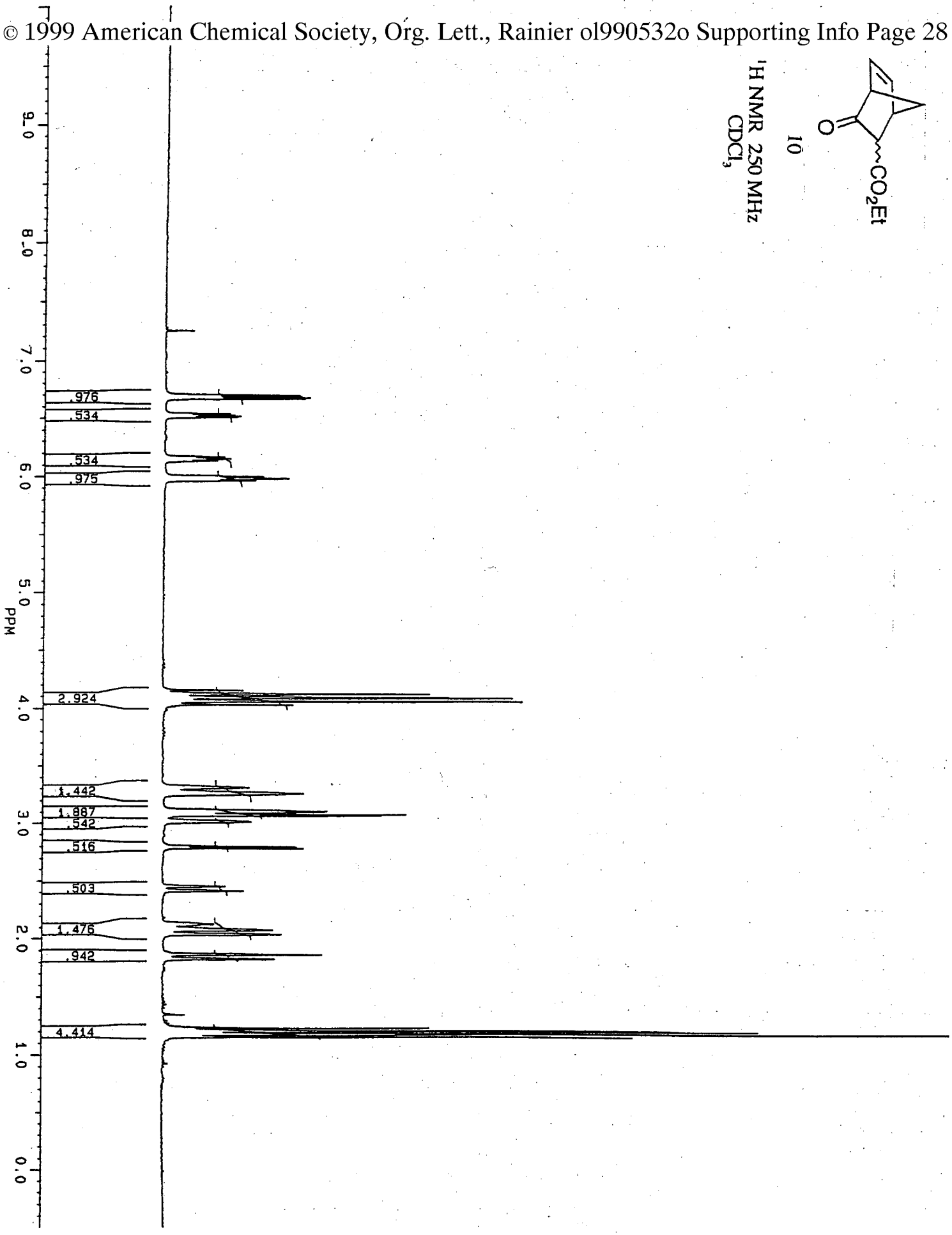
^{1}H NMR 62.5 MHz
$CDCl_3$

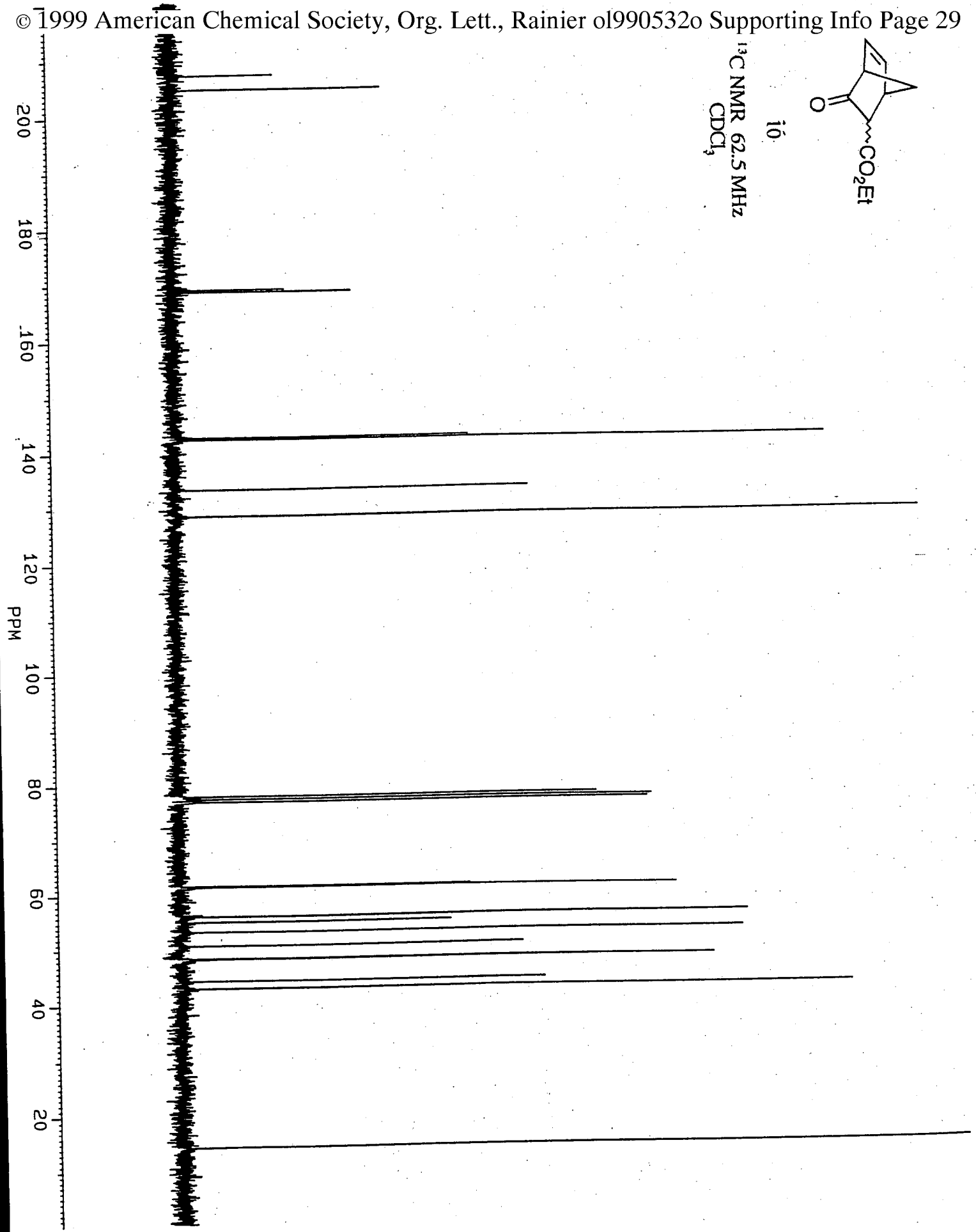
9(Z-alkene isomer)

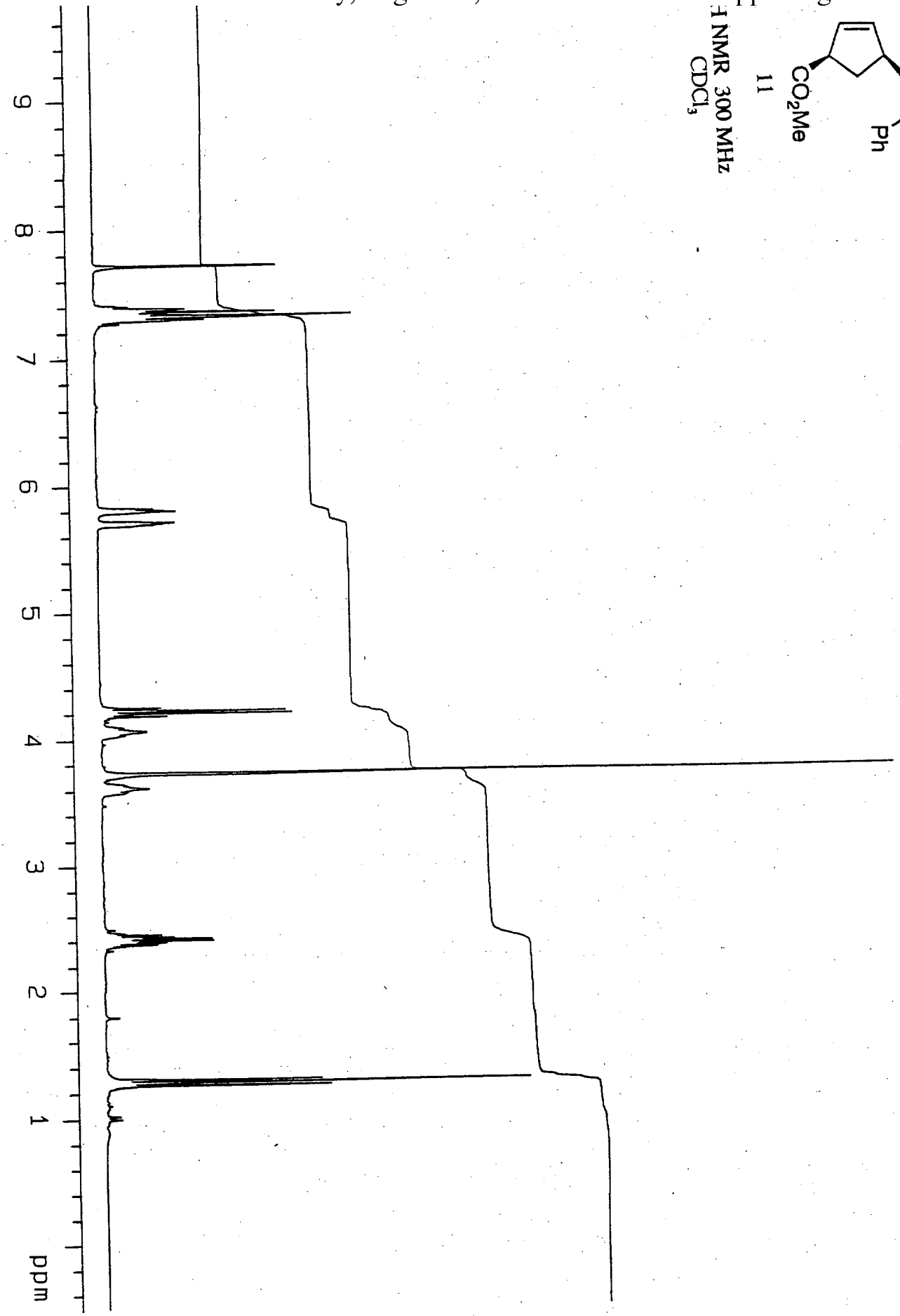


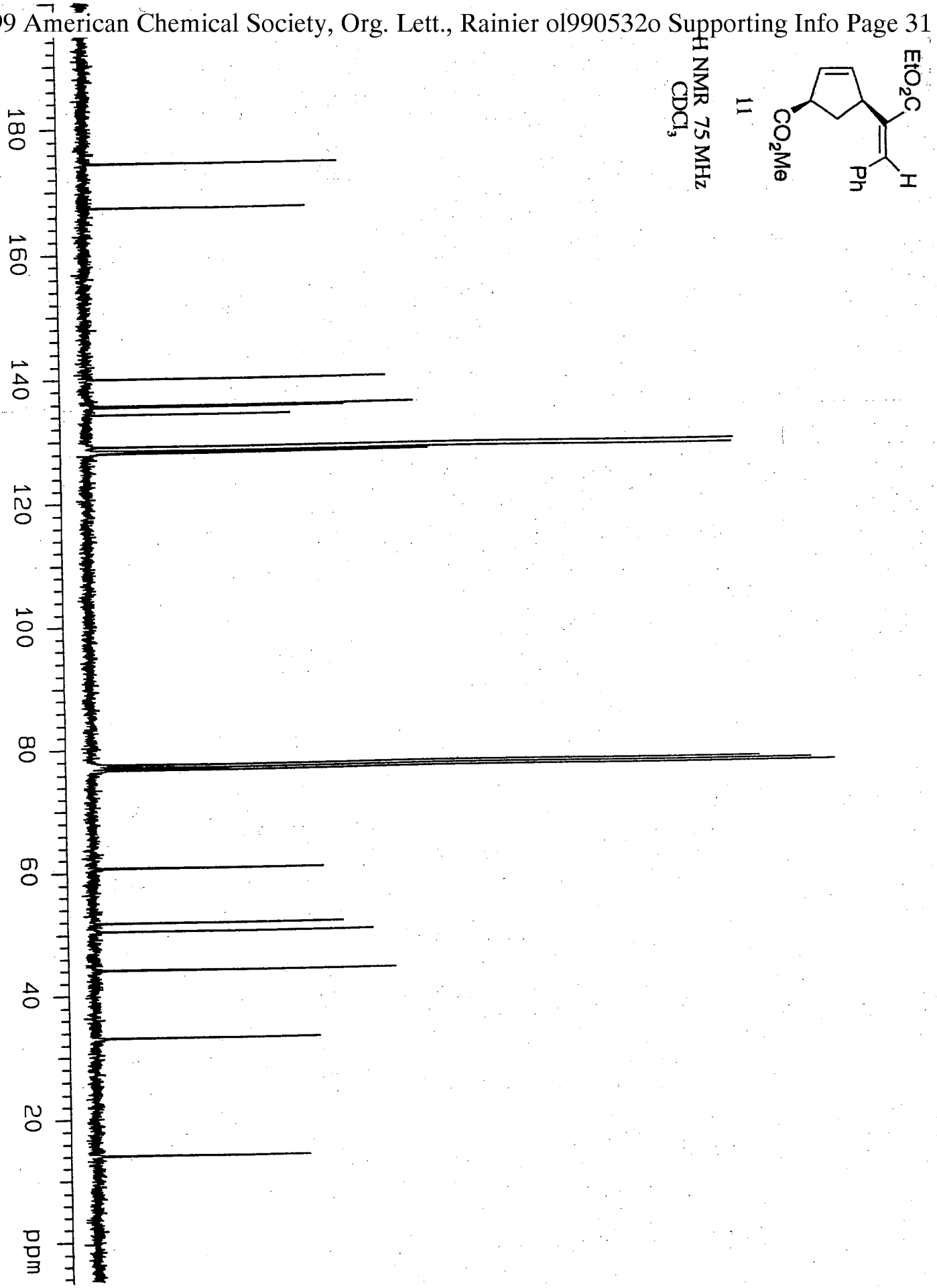

(E-alkene isomer)
H NMR 300 MHz
CDCl3
CO2Et H
CO2Me
O
9
8
7
6
5
4
3
2
1
ppm

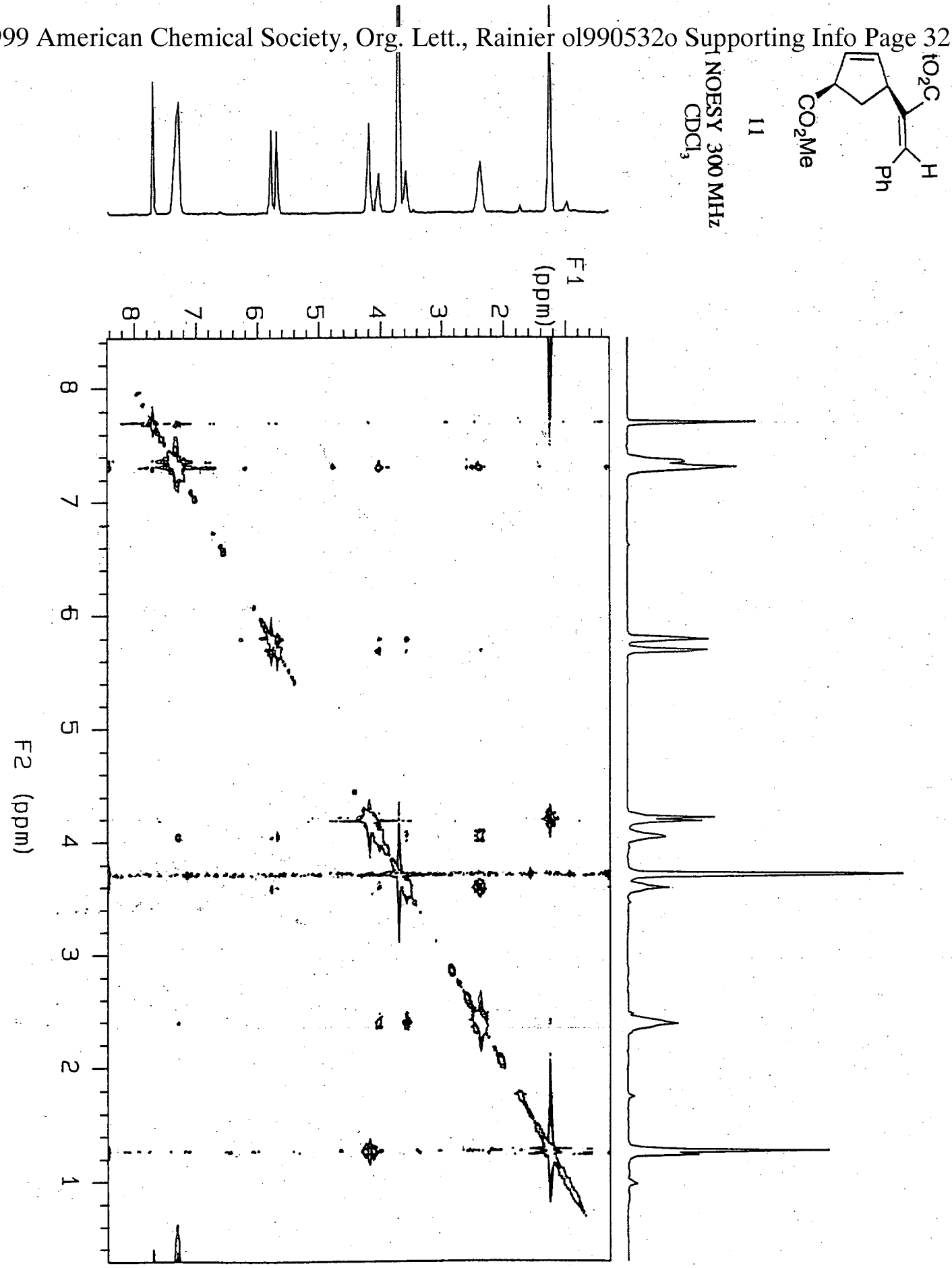

9(E-alkene isomer)
^{1}H NMR 75 MHz
$CDCl_3$
H
H
O
CO_2Me
CO_2Et H
200
180
160
140
120
100
80
60
40
20
ppm

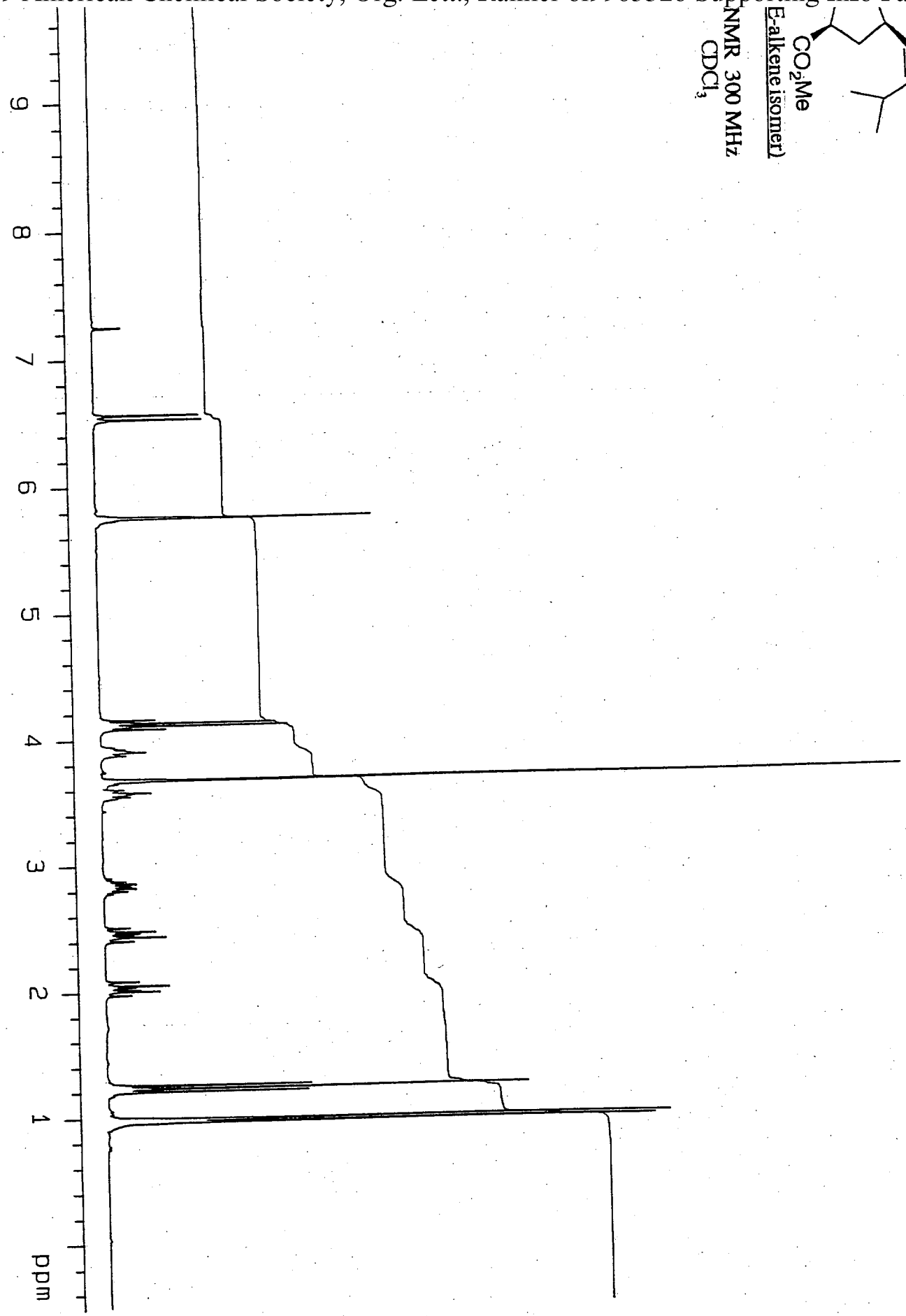


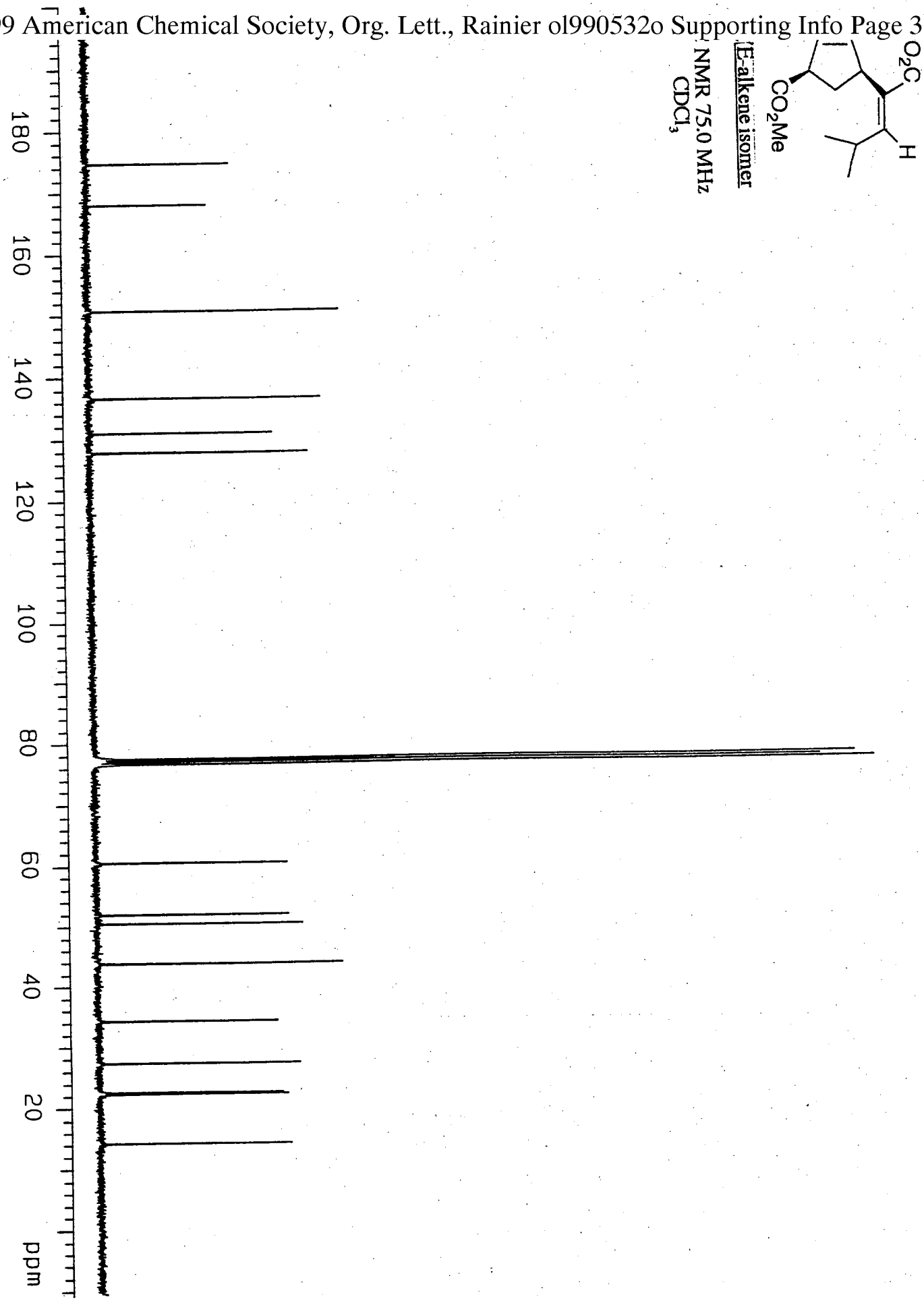

^{13}C NMR 62.5 MHz
$CDCl_3$
10
CO_2Et
O
200
180
160
140
120
100
80
60
40
20
PPM

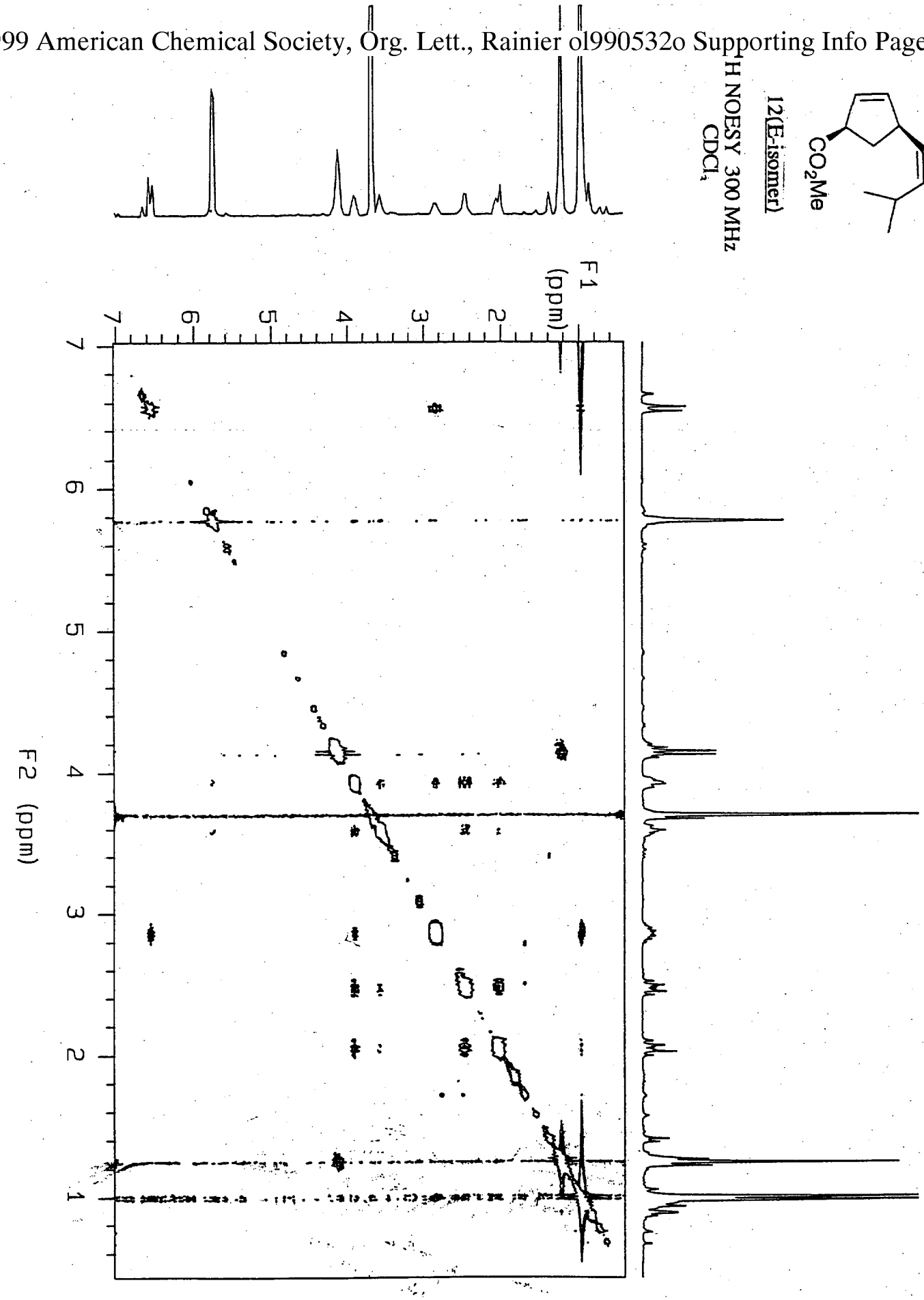

^{1}H NMR 300 MHz
$CDCl_3$
11
CO_2Me
Ph
H
EtO_2C
9
8
7
6
5
4
3
2
1
ppm

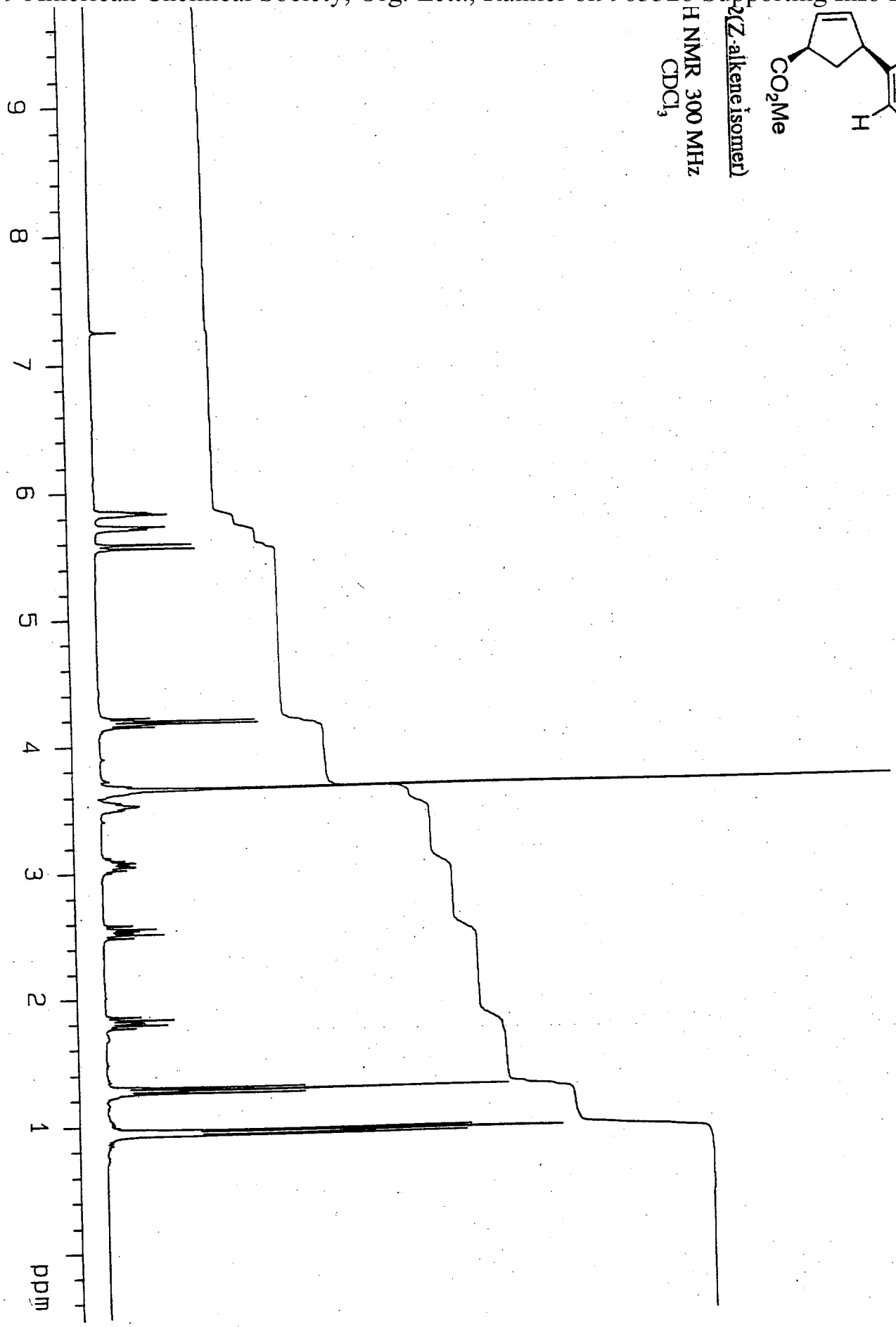

^{1}H NMR 75 MHz
$CDCl_3$
11
EtO_2C
CO_2Me
Ph
H
180
160
140
120
100
80
60
40
20
ppm

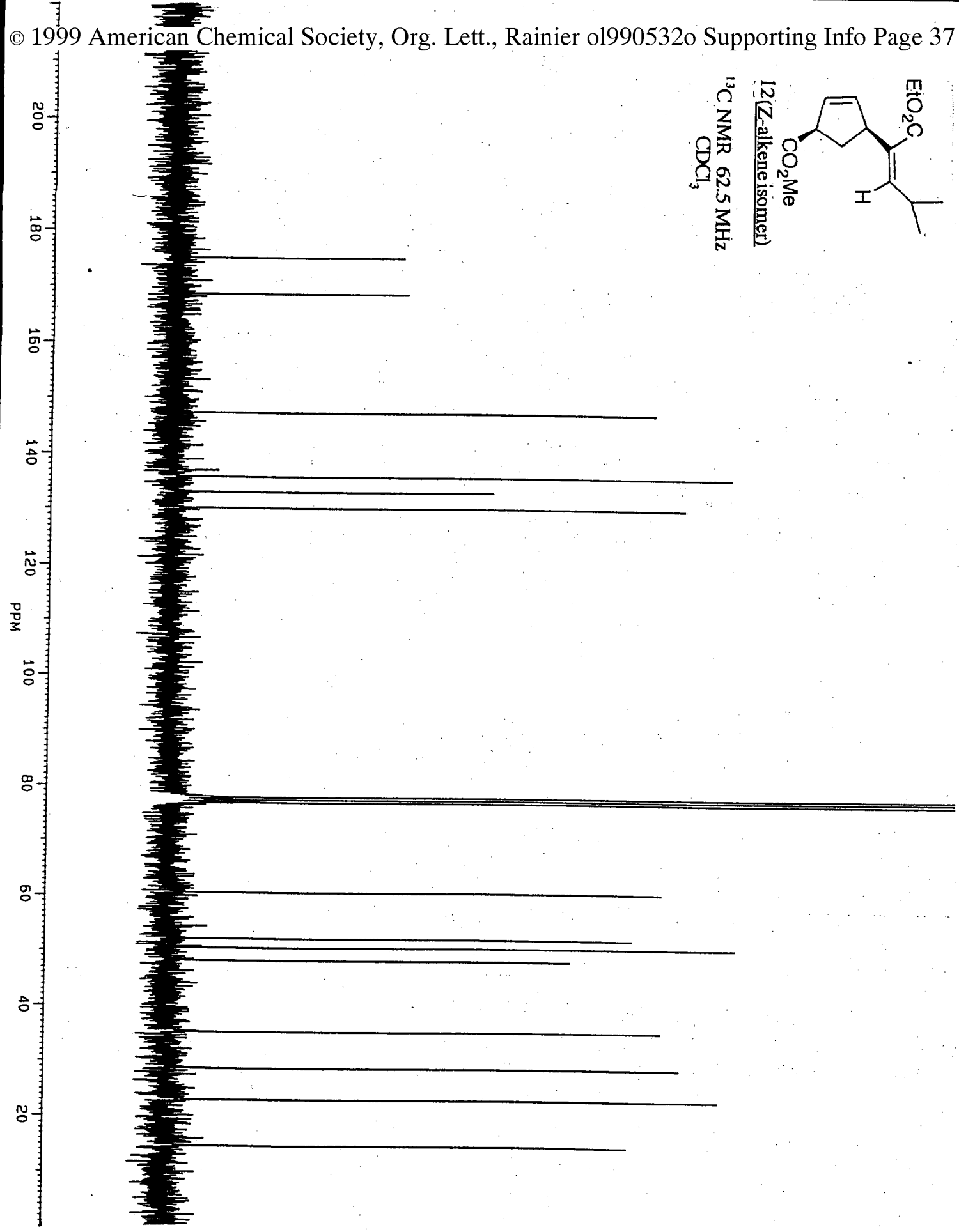

NOESY 300 MHz
$CDCl_3$
11
CO_2Me
tO_2C
H
Ph
F1 (ppm)
F2 (ppm)
8
7
6
5
4
3
2
1

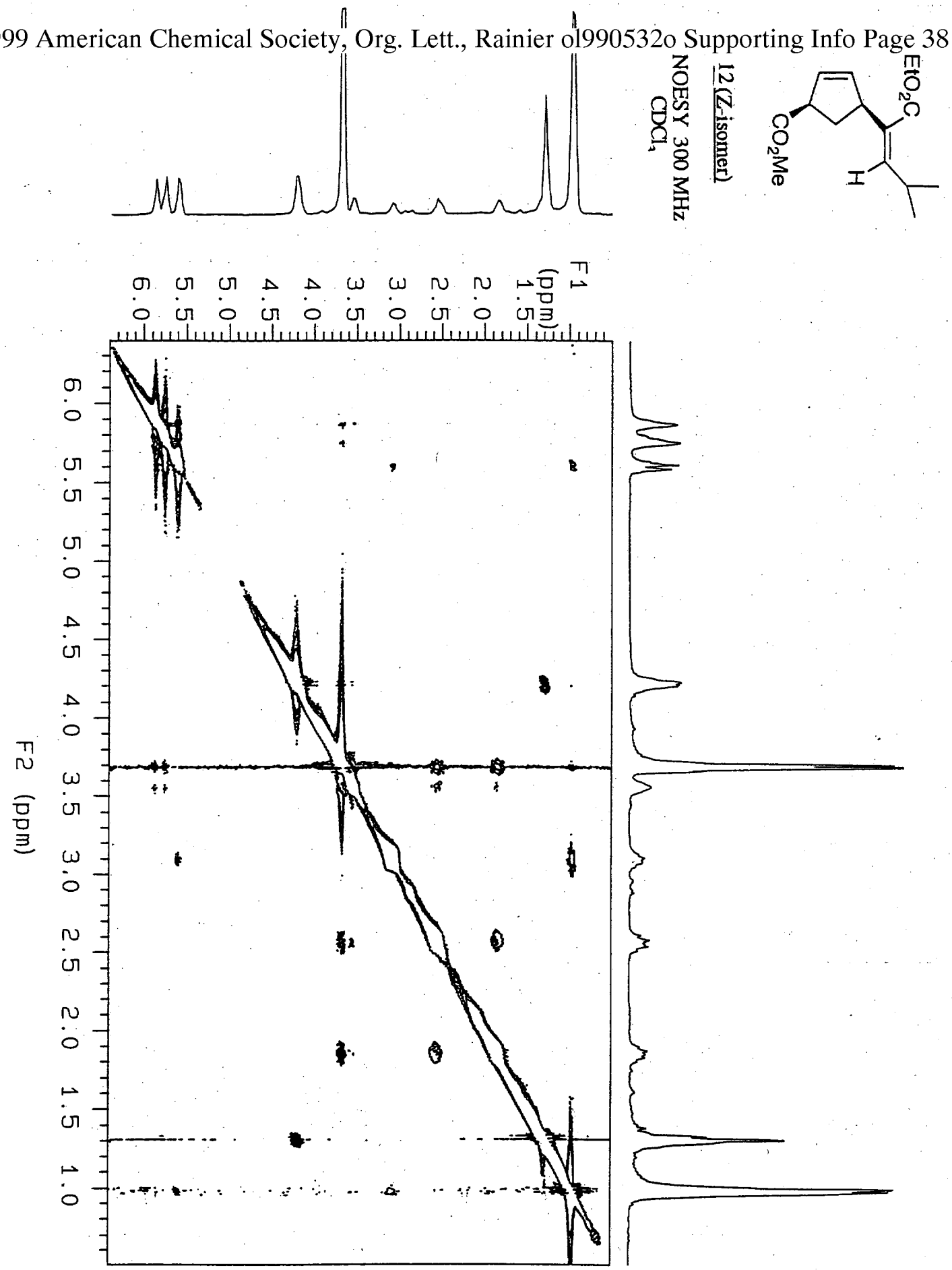

E
CO_2C
CO_2Me
H
E-alkene isomer
NMR 300 MHz
$CDCl_3$
9
8
7
6
5
4
3
2
1
ppm

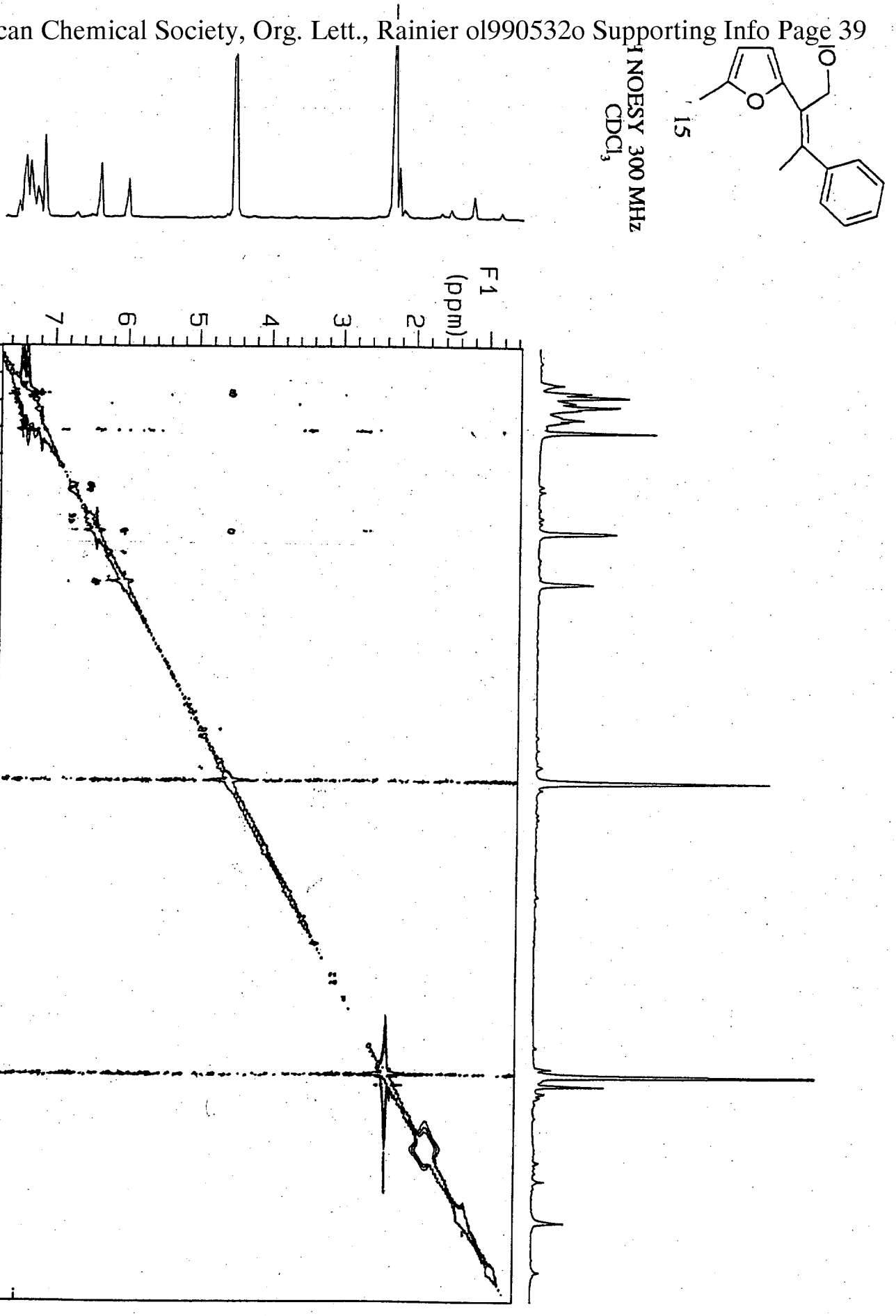

E-alkene isomer
NMR 75.0 MHz
$CDCl_3$
CO_2Me
O_2C
H
180
160
140
120
100
80
60
40
20
ppm

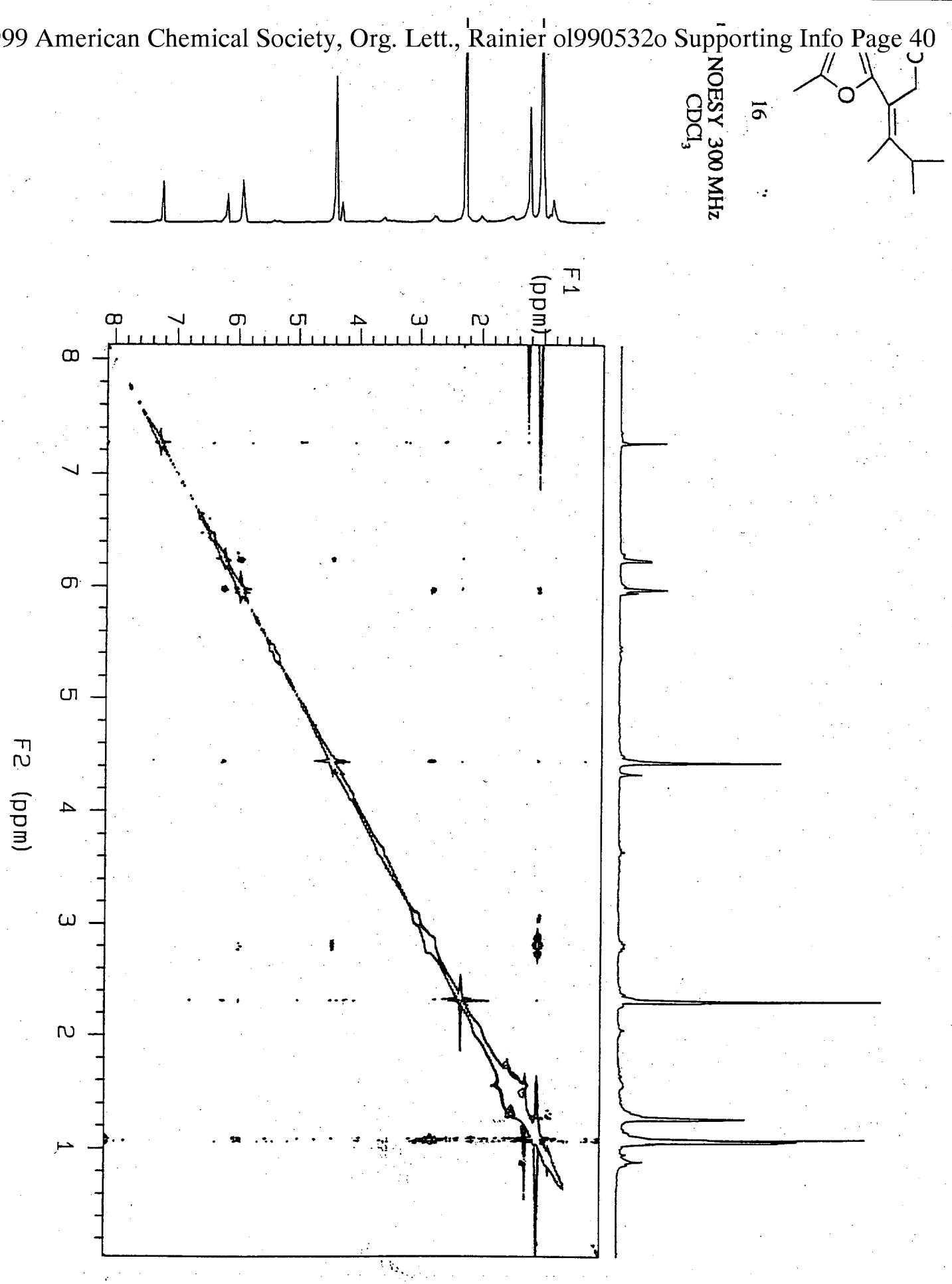

EtO2C
CO2Me
H
12(E-isomer)
1H NOESY 300 MHz
CDCl3
F1 (ppm)
F2 (ppm)
7
6
5
4
3
2
1


2(Z-alkene isomer)
H NMR 300 MHz
CDCl3
CO2Me
iPrO2C
H
9
8
7
6
5
4
3
2
1
ppm






15
1H NOESY 300 MHz
CDCl3
F1 (ppm)
F2 (ppm)
7
6
5
4
3
2
1


NOESY 300 MHz
$CDCl_3$
16
O
F1 (ppm)
F2 (ppm)
8
7
6
5
4
3
2
1