Supporting Information for

First Direct Evidence of Radical Intermediates in Samarium Diiodide-induced Cyclization by ESR Spectra

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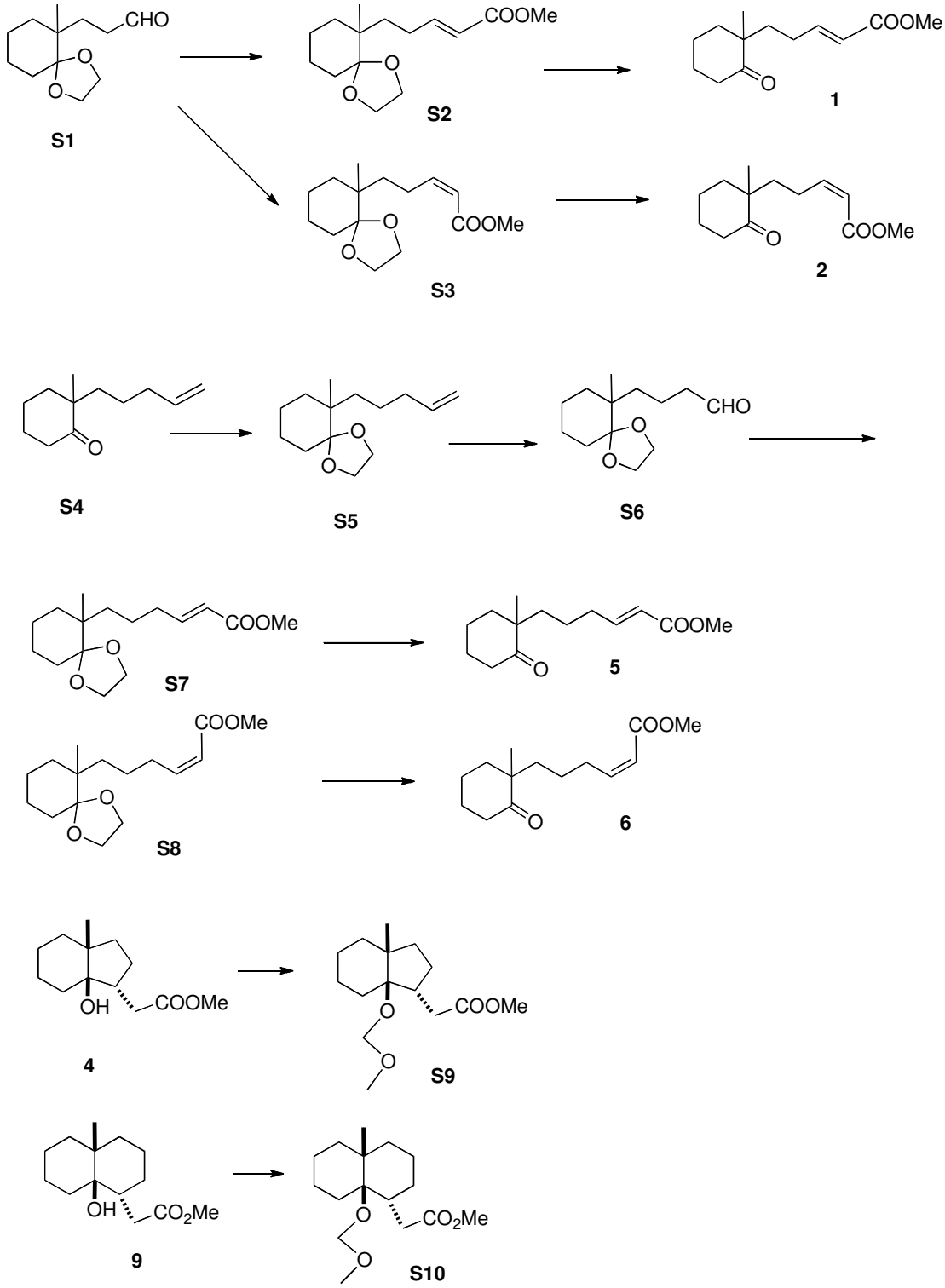
Contents

Experimental

General

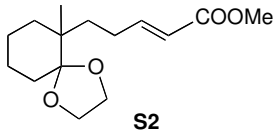
IR spectra, on a JASCO FT/IR-5300 spectrophotometer; ^{1}H and ^{13}C NMR spectra, on a Varian Unity 600 (600 MHz and 150 MHz, respectively) and a Varian Unity 200 (200 MHz and 50 MHz, respectively) spectrometer. Mass spectra, including high-resolution ones, were recorded on a JEOL JMS-700 MStation. ESR was measured on a JES-FR30EX. The simulation was carried out using WINEPR SimFonia. Chemcopak Nucleosil 50-5 (4.6×250 mm) with a solvent system of hexane-ethyl acetate was used for HPLC (JASCO pump system). Silica gel 60 (300 mesh, Fuji Sylisia) was used for column chromatography. Silica gel 60 F_{254} plates (Merck) were used for TLC.



Synthesis of **S2**

To a mixture of NaH (82.0 mg, 2.2 mmol) and $(MeO)_2POCH_2CO_2Me$ (458.0 mg, 2.2

mmol) in THF was added a solution of **S1** (365.7 mg, 1.7 mmol) in THF and the mixture was stirred overnight. Wet Et_2O was added and extracted. The organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford a residue. The residue was purified by silica-gel column chromatography (hexane-EtOAc, 1-40%) to give **S3** (5.2 mg, 4.0%) and **S2** (52.5 mg, 41.5%).

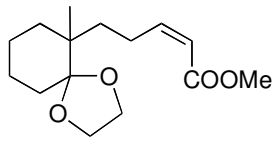


S2

S2: oil: FT-IR: 1720, 1660 cm^{-1}; ^1H NMR (200MHz, $CDCl_3$) δ 0.93 (3H, s), 1.37-1.62 (10H, m), 2.05-2.21 (2H, m), 3.73 (3H, s), 3.90-4.00 (4H, m), 5.83 (1H, dt, *J* = 15.7, 1.0 Hz), 7.01 (1H, dt, *J* = 15.7, 6.2 Hz); ^{13}C NMR (50MHz, $CDCl_3$) δ 19.3, 20.8, 23.5, 26.7, 30.4, 33.0, 34.3, 41.1, 51.3, 64.7, 64.9, 112.7 (C), 120.4 (CH), 150.8 (CH), 167.3 (CO); MS *m/z* 268 $[M]^+$, 169 (base), 113, 99; EI-HRMS Found *m/z* 268.1686 $[M]^+$ $C_{15}H_{24}O_4$ requires 268.1674.

Synthesis of S**3**

To a stirred mixture of 18-crown-6-ether (983.8 mg, 3.7 mmol), K_2CO_3 (516.2 mg, 3.7 mmol) in toluene at -20°C was added a THF solution of aldehyde **S1** (329.1 mg, 1.5 mmol), $(CF_3CH_2O)_2POCH_2CO_2CH_3$ (591.7 mg, 1.2 mmol). The mixture was stirred for 3 h. Sat. NH_4Cl solution was added 0°C and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford a residue. The residue was purified by silica-gel column chromatography (hexane-EtOAc, 0-10%) to give cis **S3** (80.0 mg, 19.2%) and trans **S2** (19.5 mg, 4.7%).

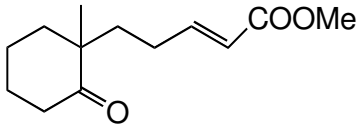


S3

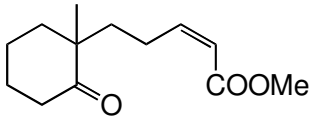
S3: oil: FT-IR: 1720, 1640 cm^{-1}; ^1H NMR (200MHz, $CDCl_3$) δ 0.98 (3H, s), 1.39-1.65 (10H, m), 2.60 (2H, m), 3.68 (3H, s), 3.90-4.00 (4H, m), 5.77 (1H, dt, *J* = 11.0, 1.4 Hz), 6.24 (1H, dt, *J* = 11.0, 7.1 Hz); ^{13}C NMR (50MHz, $CDCl_3$) δ 19.3, 20.8, 23.6 (X2), 30.5, 33.7, 34.1, 41.3, 51.0, 64.8, 65.0, 112.9 (C), 118.8 (CH), 151.9 (CH), 166.9 (CO); MS *m/z* 268 $[M]^+$, 169 (base), 113, 99; EI-HRMS Found *m/z* 268.1676 $[M]^+$ $C_{15}H_{24}O_4$ requires 268.1675.

Synthesis of **1** and **2**

A solution of **S3** (68.5 mg, 0.3 mmol) in THF was treated with 1M HCl (1 ml) at rt overnight. The solvent was evaporated and aq. $NaHCO_3$ soln. was added. The mixture was extracted with ether. The organic solution was washed with brine, dried ($MgSO_4$), and evaporated to afford a residue. The residue was purified by silica-gel column chromatography (hexane-EtOAc, 1-40%) to give **2** (38.5 mg, 67.2%).
Similarly **S2** (52.5 mg, 0.2 mmol) was hydrolyzed to give **1** (33.8 mg, 77.0%).



1; oil: FT-IR: 1720, 1700, 1650 cm^{-1}; ^1H NMR (200MHz, $CDCl_3$) δ 1.08 (3H, s), 1.48-1.62 (3H, m), 1.65-1.85 (5H, m), 1.90-2.30 (2H, m), 2.38 (2H, t, *J* = 6.8 Hz), 3.75 (3H, s), 5.92 (1H, dt, *J* = 16.7, 1.0 Hz), 6.97 (1H, dt, *J* = 16.7, 7.2 Hz); ^{13}C NMR (50MHz, $CDCl_3$) δ 20.9, 22.5, 26.7, 27.3, 35.8, 38.7, 39.1, 48.2, 51.4 (CH_3), 121.0 (CH), 149.1 (CH), 167.1 (CO), 215.4 (CO); MS *m/z* 224 $[M]^+$, 112 (base), 97; EI-HRMS Found *m/z* 224.1406 $[M]^+$ $C_{13}H_{20}O_3$ requires 224.1412.

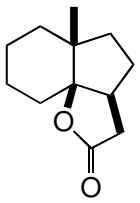


2; oil: FT-IR: 1720, 1700, 1640 cm^{-1}; ^1H NMR (200MHz, $CDCl_3$) δ 1.10 (3H, s), 1.50-1.90 (8H, m), 2.38-2.66 (4H, m), 3.70 (3H, s), 5.78 (1H, dt, *J* = 10.0, 1.0 Hz), 6.10 (1H, dt, *J* = 10.0, 8.0 Hz); ^{13}C NMR (50MHz, $CDCl_3$) δ 21.0, 22.5, 23.7, 27.4, 36.4, 38.7, 38.9, 48.4, 51.1 (CH_3), 119.5 (CH), 150.1 (CH), 166.7 (CO), 215.5 (CO); MS *m/z* 224 $[M]^+$, 112 (base), 97; EI-HRMS Found *m/z* 224.1442 $[M]^+$ $C_{13}H_{20}O_3$ requires 224.1412.

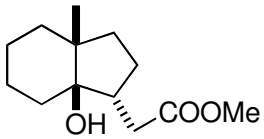
General procedure for SmI_2-induced cyclization of **1** and **2** (Table 1)
A THF solution of **1** or **2** (15 mg-30 mg, 0.07 mmol-0.14 mmol) was treated with SmI_2 in THF (3.0 mL, 0.3 mmol-15 mL, 1.5 mmol) with or without the additive at rt for a certain period specified in Table 1. The reaction was worked up as before and the mixture was separated by silica-gel column chromatography (hexane-EtOAc, 0-30%).

The results for Table 1.
Entry 1: Compound **1** (22.7 mg) was treated with SmI_2 to afford compound **4** (17.2 mg, 75.1%).
Entry 2: Compound **1** (24.6 mg) was treated with SmI_2 to afford compound **4** (19.1 mg, 77.0%).

Entry 3: Compound **1** (22.1 mg) was treated with SmI_2 to afford compound **4** (20.3 mg, 91.0%).
Entry 4: Compound **1** (18.2 mg) was treated with SmI_2 to afford compound **3** (3.2 mg, 20.3%) and compound **4** (13.5 mg, 73.5%).
Entry 5: Compound **2** (19.4 mg) was treated with SmI_2 to afford compound **3** (14.8 mg, 88.1%) and compound **4** (1.8 mg, 9.2%).
Entry 6: Compound **2** (19.0 mg) was treated with SmI_2 to afford compound **3** (14.0 mg, 85.1%) and compound **4** (2.3 mg, 12.0%).
Entry 7: Compound **2** (19.0 mg) was treated with SmI_2 to afford compound **3** (11.0 mg, 66.8%) and compound **4** (2.8 mg, 14.6%).
Entry 8: Compound **2** (20.0 mg) was treated with SmI_2 to afford compound **3** (1.2 mg, 6.9%) and compound **4** (18.6 mg, 92.2%).



3; oil: FT-IR: 1770 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.75-0.83 (1H, m), 0.84-0.93 (2H, m), 0.97 (1H, m), 1.01 (3H, s), 1.03 (1H, dd, *J* = 14.4, 5.4 Hz), 1.07-1.14 (2H, m), 1.22 (1H, dt, *J* = 13.8, 2.4 Hz), 1.30 (1H, m), 1.44 (1H, td, *J* = 13.8, 4.8 Hz), 1.59 (1H, td, *J* = 6.6, 4.2 Hz), 1.62-1.69 (1H, m), 1.91 (1H, d, *J* = 18.0 Hz), 2.02 (1H, td, *J* = 8.4, 3.6 Hz), 2.26 (1H, ddd, *J* = 18.0, 8.4, 0.6 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 19.3 (CH_3), 21.1 (CH_2), 23.7 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 34.8 (CH_2), 37.2 (CH_2), 38.6 (CH_2), 39.4 (CH_2), 45.1 (C), 97.2 (C), 175.4 (CO); MS *m/z* 194 $[M]^+$,179, 1665, 151, 135, 112 (base); EI-HRMS Found *m/z* 194.1307 $[M]^+$ $C_{12}H_{18}O_2$ requires194.1307.

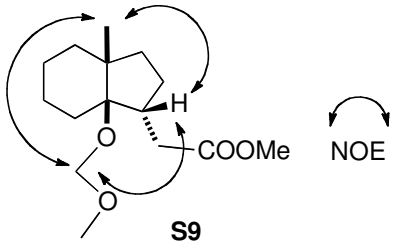


4; oil: FT-IR: 3500, 1720 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.85-0.94 (2H, m), 0.97 (3H, s), 1.01 (1H, ddd, *J* = 13.8, 10.2, 3.6 Hz), 1.20 (1H, qt, *J* = 13.8, 4.2 Hz), 1.26 (1H, m), 1.28 (1H, m), 1.39 (1H, m), 1.42 (1H, m), 1.47 (1H, td, *J* = 18.0, 4.2 Hz), 1.55-1.65 (2H, m), 1.82 (1H, dtd, *J* = 13.8, 10.2, 6.6 Hz), 2.03 (1H, dd, *J* = 16.2, 7.8 Hz), 2.29 (1H, dd, *J* = 16.2, 7.8 Hz), 2.49 (1H, tt, *J* = 10.2, 7.8 Hz), 3.29 (3H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 21.5 (CH_2), 22.0 (CH_2), 25.2 (CH_3), 25.4 (CH_2), 30.4 (CH_2), 30.8 (CH_2), 33.4

(CH_2), 34.5 (CH), 43.3 (CH), 43.8 (C), 51.1 (CH_3), 78.1 (C), 174.5 (CO); MS *m/z* 226 $[M]^+$, 169, 151, 135, 112 (base); EI-HRMS Found *m/z* 226.1560 $[M]^+$ $C_{13}H_{22}O_3$ requires 226.1569.

Preparation of **S9**

To a CH_2Cl_2 solution of **4** (20.8 mg, 0.09 mmol) was added $^iPr_2NEt$ (0.05 mL, 0.28 mmol) and MOMCl (0.02 mg, 0.22 mmol) at 0°C and the mixture was stirred at rt overnight. Sat. $NaHCO_3$ soln. was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford a residue. The residue was purified by silica-gel column chromatography (hexane-EtOAc, 0-20%) to give **S9** (0.8 mg). The stereochemistry was established by the NOESY spectrum (in the figure).



S9

S9: oil: FT-IR: 1740 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.99 (3H, s), 1.11-1.21 (3H, m), 1.33-1.41 (4H, m), 1.44-1.50 (2H, m), 1.72 (1H, br d, *J* = 12.6 Hz), 1.81 (1H, td, *J* = 12.0, 7.2 Hz), 2.05 (1H, dd, *J* = 15.0, 10.8 Hz), 2.13 (1H, tdd, *J* = 13.8, 10.2, 7.8 Hz), 2.69 (1H, tdd, *J* = 10.8, 8.4, 3.0 Hz), 2.84 (1H, dd, *J* = 15.0, 3.0 Hz), 3.38 (3H, s), 3.66 (3H, s), 4.67 (1H, d, *J* = 7.4 Hz), 4.76 (1H, d, *J* = 7.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.1 (CH_2), 21.5 (CH_2), 24.8 (CH_3), 25.5 (CH_2), 26.4 (CH_2), 30.7 (CH_2), 33.0 (CH_2), 35.7 (CH_2), 40.7 (CH), 45.3(C), 51.4 (CH_3), 55.2 (CH_3), 83.8 (C), 90.8 (CH_2), 174.3 (CO); MS: *m/z* 270 $[M]^+$, 238, 225, 209, 193, 183, 165, 156, 135, 112 (base); EI-HRMS Found *m/z* 270.1826 $C_{15}H_{26}O_4$ requires 270.1831

Preparation of **S6**

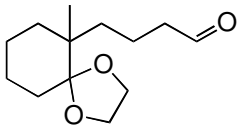
A solution of 2-methylcyclohexanone (112.2 mg, 1 mmol) in THF (10 mL), was treated with ^tBuOK (158.5 mg, 1.2 mmol) at rt for 30 min. 5-bromopent-1-ene (178.8 mg, 1.2 mmol) was added and the mixture was further stirred for 5 h at rt. Sat. NH_4Cl soln. was added at 0°C and the mixture was extracted with ether. The organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford a residue. The residue was purified by silica-gel column chromatography to give **S4**.

A solution of **S4** (1.80 g, 10.0 mmol) in benzene was treated with ethylene glycol (744

mg, 12 mmol) and TsOH (150 mg) under reflux for 7 h with the aid of the Dean-Stark water separator. Sat. $NaHCO_3$ soln was added and the mixture was extracted with ether. The organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford **S5** (1.86 g).

Preparation of **S6**

Ozone was bubbled through a solution of **S5** (1.03 g, 4.6 mmol) in CH_2Cl_2at -78°C for 1 h. Zn (3.0 g, 46 mmol) and acetic acid (2.8 g, 46 mmol) was added at -78-0°C and the mixture was stirred for 5 h. The mixture was filtered and $NaHCO_3$ soln. was added. The mixture was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford **S6** (1.40 g).

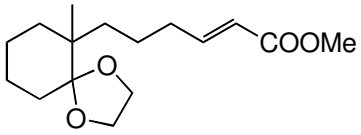


S6: oil ; FT-IR: 1720 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.94 (3H, s), 1.35-1.65 (12H, m), 2.41 (2H, td, *J* = 7.5, 1.5 Hz), 3.85-3.95 (4H,m), 9.77 (1H, t, *J* = 2.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.3, 19.3, 20.8, 23.5, 30.4, 34.2, 64.7 (CH_2), 64.9 (CH_2), 112.9 (C), 203.1 (CO); MS (CI) *m/z* 227 $[M+H]^+$, 198, 165, 129, 89 (base); CI-HRMS Found m/z 227.1630$[M+H]^+$ $C_{13}H_{23}O_3$ requires 227.1647.

Preparation of **S7** and **S8**

To a mixture of 18-crown-6-ether (158.3 mg, 0.6 mmol) and K_2CO_3 (80.9 mg, 0.6 mmol) was added a solution of **S6** (55.5 mg, 0.2 mmol) and $(CF_3CH_2O)_2POCH_2CO_2CH_3$ (92.3 mg, 0.3 mmol) in THF at -20°C and the mixture was stirred at rt overnight. Sat. NH_4Cl soln. was added at 0°C and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford **S7** and **S8** 1:4.5.

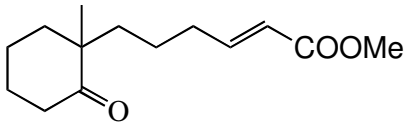
To a suspension of NaH (47.3 mg, 1.3 mmol) in THF was added $(MeO)_2POCH_2CO_2Me$ (209.4 mg, 1.2 mmol) at rt for 1 h. Then a solution of **S6** (217.5 mg, 1.0 mmol) in THF was added and the mixture was stirred overnight. Wet Et_2O was added and extracted. The organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford **S7** and **S8** in the ratio of 5: 1.



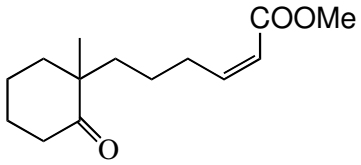
S7: oil; FT-IR: 1660 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (3H, s), 1.35-1.65 (12H, m), 2.18 (2H, dt, *J* = 7.0, 5.6 Hz), 3.73 (3H, s), 3.85-4.00 (4H, m), 6.83 (1H, d, *J* = 15.7 Hz), 6.99 (1H, dt, *J* = 15.7, 6.7 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.4, 20.8, 22.2, 23.6, 30.4, 33.3, 34.1, 34.2, 41.2, 51.4 (CH_3), 64.7 (CH_2), 64.9 (CH_2), 112.9 (C), 120.8 (CH), 149.8 (CH), 167.2 (CO); MS *m/z* 282 $[M]^+$, 183, 113, 99 (base), 86; EI-HRMS Found *m/z* 282.1827 $[M]^+$ $C_{16}H_{26}O_4$ requires282.1831.

Preparation of **5** and **6**

A solution of **S7** and **S8** (201.4 mg, 0.7 mmol) in THF was treated with 1M HCl (2 mL) at rt overnight. The solvent was evaporated and $NaHCO_3$ soln. was added. The mixture was extracted with ether and the organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford a residue. The residue was purified by silica-gel column chromatography (hexane-EtOAc, 0-30%) to give **5** (22.1 mg) and **6** (122.4 mg), respectively.



5: oil; FT-IR: 1720, 1700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.05 (3H, s), 1.20-1.90 (10H, m), 2.20 (2H, m), 2.34 (2H, t, *J* = 8.5 Hz), 3.71 (3H, s), 5.82 (1H, d, *J* = 13.0 Hz), 6.92 (1H, dt, *J* = 13.0, 6.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.1, 22.4, 22.7, 27.4, 32.7, 37.1, 38.8, 39.2, 48.5 (C), 51.4 (CH_3), 121.3 (CH), 149.0 (CH), 167.1 (CO), 215.7 (CO); MS *m/z* 238 $[M]^+$, 206, 189, 112 (base); EI-HRMS Found *m/z* 238.1561 $[M]^+$ $C_{13}H_{22}O_3$ requires 238.1569.

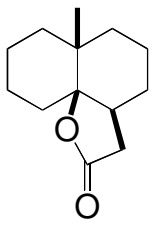


6: oil; FT-IR: 1720, 1700, 1640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.04 (3H, s), 1.35-2.00 (10H, m), 2.34 (2H, m), 2.64 (2H, m), 3.70 (3H, s), 5.79 (1H, d, *J* = 11.2 Hz), 6.20 (1H, dt, *J* = 11.2, 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.0, 22.5, 23.3, 27.4, 29.3, 37.1, 38.7, 39.3, 48.5, 51.0 (CH_3), 119.6 (CH), 150.2 (CH), 166.5 (CO), 215.9 (CO); MS *m/z* 238 $[M]^+$, 206, 189, 112 (base); EI-HRMS Found 238.1560 $[M]^+$ $C_{14}H_{22}O_3$ requires 238.1569.

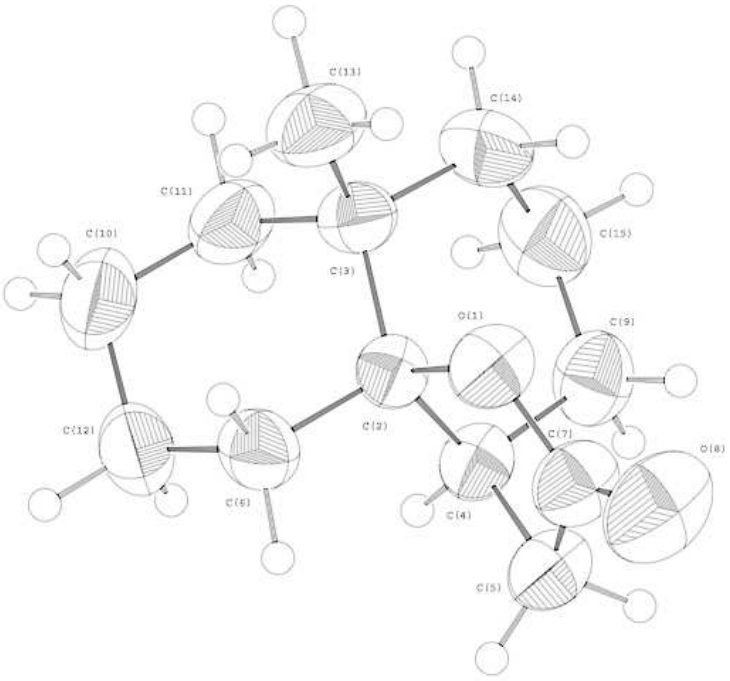
General procedure for SmI_2-induced cyclization of compounds **5** and **6** (Table 2)

To a stirred solution of SmI_2 in THF (3.6 mL, 0.36 mmol) was added a solution of **5** or **6** in THF at the temperature for a certain period specified in the Table 2. The reaction was worked up as before and the mixture was separated by silica-gel column chromatography (hexane-EtOAc, 0-30%).

The results for Table 2.
Entry 1: Compound **5** (29.8 mg) was treated with SmI_2 to afford compound **8** (18.8 mg, 72.2%).
Entry 2: Compound **5** (29.5 mg) was treated with SmI_2 to afford compound **8** (25.2 mg, 97.7%).
Entry 3: Compound **5** (18.8 mg) was treated with SmI_2 to afford compound **8** (11.5 mg, 70.0%) and compound **9** (2.5 mg, 13.2%).
Entry 4: Compound **5** (21.8 mg) was treated with SmI_2 to afford compound **8** (15.7 mg, 82.4%).
Entry 5: Compound **6** (29.2 mg) was treated with SmI_2 to afford compound **7** (23.0 mg, 90.1%).
Entry 6: Compound **6** (23.8 mg) was treated with SmI_2 to afford compound **7** (15.4 mg, 74.0%).
Entry 7: Compound **6** (19.6 mg) was treated with SmI_2 to afford compound **7** (14.8 mg, 86.4%).
Entry 8: Compound **6** (22.4 mg) was treated with SmI_2 to afford compound **7** (14.7 mg, 75.1%) and compound **8** (3.4 mg, 17.4%).



7: crystal; mp. 48.8-50.2°C ($CHCl_3$); FT-IR: 1760 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.10 (3H, s), 1.16-1.27 (3H, m), 1.30-1.38 (1H, m), 1.41-1.46 (1H, m), 1.50-1.58 (4H, m), 1.65-1.76 (3H, m), 1.78-1.84 (2H, m), 2.06 (1H, dd, *J* = 17.0, 1.2 Hz), 2.43 (1H, dtd, *J* = 11.2, 6.6, 1.2 Hz), 2.81 (1H, dd, *J* = 17.0, 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.4 (CH_2), 20.8 (CH_2), 23.2 (CH_3), 24.0 (CH_2), 29.6 (CH_2), 30.9 (CH_2), 34.5 (CH_2), 34.7 (CH_2), 35.5 (CH_2), 35.7 (C), 38.4 (CH_2), 89.7 (C), 177.2 (CO); MS *m/z* 208 $[M]^+$, 193, 179, 165, 152, 151 (base), 123, 112; EI-HRMS Found *m/z* 208.1459 $[M]^+$ $C_{13}H_{20}O_2$ requires 208.1463.



Crystal data

$C_{13}H_{20}O_2$

$C_{13}H_{20}O_2$

$M_r = 208.301$

Monoclinic

$P2_1/c$

a = 11.8390 (9)Å

b = 6.6930 (4)Å

c = 15.221 (2)Å

$\alpha = 90.00°$

$\beta = 99.424\ (3)°$

$\gamma = 90.00°$

$V = 1189.8\ (2)Å^3$

$Z = 4$

$D_x = 1.163\ Mg\ m^{-3}$

Density measured by: not measured

fine-focus sealed tube

Mo *K*α radiation
$\lambda = 0.71073$
$\mu = 0.076\ mm^{-1}$
T = 298 K
Needle
Colorless
Crystal source: Local laboratory

Data collection
DIP Image plate
IP
Absorption correction: cylinder
$T_{min} = 0.975$, $T_{max} = 0.975$
2393 measured reflections
2195 independent reflections
1655 observed reflections
Criterion: >2sigma(I)
$\theta_{max} = 25.74$ °
h = 0 →14
k = 0 →7
l = -18 →18

Refinement
Refinement on F^2
full matrix least squares refinement
R(all) = 0.0745
R(gt) = 0.0566
wR(ref) = 0.1700
wR(gt)= 0.1493
S(ref) = 1.060
2195 reflections
137 parameters
0 restraints
Only coordinates of H atoms refined
Calculated weights calc
$\Delta/\sigma_{max} = 0.000$

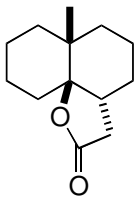
$\Delta\rho_{max}$ = 0.201eÅ^3

$\Delta\rho_{min}$ = -0.213eÅ^3

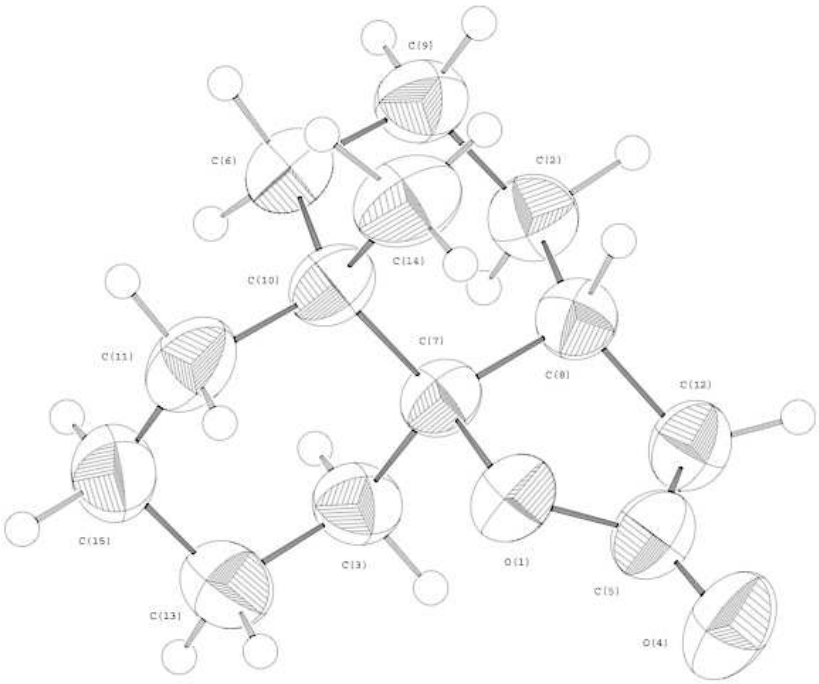
Extinction correction: *SHELXL*

$Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient = 0.037 (6)



8: crystal; mp. 92.8-94.2°C (C_6H_6-EtOAc); FT-IR: 1770cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.03 (3H, s), 1.12 (1H, dd, *J* = 9.9, 4.8 Hz), 1.27 (1H, dt, *J* = 11.5, 3.0 Hz), 1.44 (1H, m), 1.47 (1H, qd, *J* = 12.6, 4.7 Hz), 1.50-1.56 (2H, m), 1.58-1.67 (3H, m), 1.68-1.71 (2H, m), 1.73 (1H, m), 1.86 (1H, ddd, *J* = 14.0, 6.0, 5.2 Hz), 2.00 (1H, td, *J* = 14.4, 6.0 Hz), 2.34 (1H, dd, *J* = 16.5, 8,5 Hz), 2.38 (1H, dd, *J* = 16.5, 12.6 Hz), 2.58 (1H, tdd, *J* = 12.6, 8.5, 3.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.1 (CH_2), 21.2 (CH_3), 21.2 (CH_2), 21.8 (CH_2), 24.7 (CH_2), 25.8 (CH_2), 32.3 (CH_2), 33.3 (CH_2), 36.5 (CH_2), 36.7 (C), 39.8 (CH), 89.4 (CO), 176.7 (CO); MS: *m/z* 208 $[M]^+$, 193, 179, 165, 152 (base), 151, 125; HR-MS: Found *m/z* 208.1454 $[M]^+$ $C_{13}H_{20}O_2$ requires 208.1463.



Crystal data

$C_{13}H_{20}O_2$

$C_{13}H_{20}O_2$

$M_r = 208.301$

Monoclinic

C2/c

a = 12.6700 (11)Å

b = 8.5820 (6)Å

c = 21.582 (2)Å

$\alpha = 90.00°$

$\beta = 100.405\ (4)°$

$\gamma = 90.00°$

$V = 2308.1\ (4)Å^3$

Z = 8

$D_x = 1.199\ Mg\ m^{-3}$

Density measured by: not measured

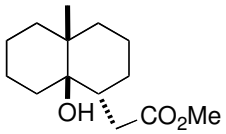
fine-focus sealed tube

Mo *K*a radiation
$\lambda = 0.71073$
$\mu = 0.079\ mm^{-1}$
T = 298 K
Plate
Colorless
Crystal source: Local laboratory

Data collection
DIP Image plate
IP
Absorption correction: cylinder
$T_{min} = 0.974$, $T_{max} = 0.974$
2079 measured reflections
1950 independent reflections
1656 observed reflections
Criterion: >2sigma(I)
$\theta_{max} = 25.85$ °
h = 0 →15
k = 0 →9
l = -26 →25

Refinement
Refinement on F^2
full matrix least squares refinement
R(all) = 0.0618
R(gt) = 0.0555
wR(ref) = 0.1633
wR(gt)= 0.1558
S(ref) = 1.060
1950 reflections
137 parameters
0 restraints
Only coordinates of H atoms refined
Calculated weights calc
$\Delta/\sigma_{max} = 0.000$

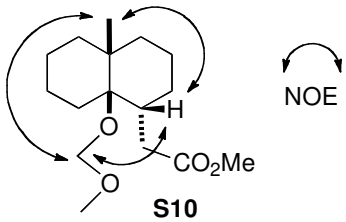
$\Delta\rho_{max}$ = 0.217eÅ^3
$\Delta\rho_{min}$ = -0.215eÅ^3
Extinction correction: *SHELXL*
$Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient = 0.0115 (19)



9: oil; FT-IR: 3500, 1730cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.99 (3H, s), 1.07 (1H, m), 1.12 (1H, m), 1.20 (1H, dd, *J* = 13.0, 4.7 Hz), 1.25-1.85 (11H, m), 1.91 (1H, td, *J* = 13.7, 4.4 Hz), 1.96 (1H, dd, *J* = 15.1, 9.3 Hz), 227 (1H, m), 2.68 (1H, dd, *J* = 15.1, 4.4 Hz), 3.67 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.8, 21.2, 21.3, 22.2, 26.3, 30.2, 33.8, 34.9, 36.8, 38.2, 40.4, 51.6 (CH_3), 74.8 (C), 175.1(CO); MS (GC): *m/z* 240 $[M]^+$, 208, 184, 152, 151, 112 (base); HR-MS: Found *m/z* 240.0720 $[M]^+$ $C_{14}H_{24}O_3$ requires 240.1726.

Preparation of **S10**

To a stirred solution of **8** (12.6 mg, 0.05 mmol) in CH_2Cl_2 was added ^{i}Pr$_2$NEt (0.09 mL, 0.48 mmol) and MOMCl (0.03 mL, 0.39 mmol) at 0°C. The reaction mixture was stirred overnight at rt. Sat. $NaHCO_3$ was added and the organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford a residue (36.1 mg). The residue was purified by a silica-gel column chromatography (hexane-EtOAc, 0-30 %) to give **S10** (10.6 mg). The stereochemistry was established by the NOESY spectrum (in the figure).



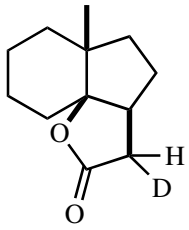
S10

S10: oil; FT-IR: 1735 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.02 (3H, s), 1.15 (1H, qd, *J* = 13.5, 4.4 Hz), 1.22-1.44 (5H, m), 1.45-1.52 (4H, m), 1.67-1.73 (2H, m), 1.78-1.85 (1H, m), 1.90 (1H, dd, *J* = 15.4, 11.0 Hz), 1.92 (1H, td, *J* = 14.0, 4.1 Hz), 2.47 (1H, tdd, *J* = 11.0, 4.4, 2.2 Hz), 2.81 (1H, dd, *J* = 15.4, 2.2 Hz), 3.37 (3H, s), 3.66 (3H, s), 4.71 (1H, d, *J* = 6.9 Hz), 4.82 (1H, d, *J* = 6.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.6, 21.0, 21.2, 23.2, 24.5, 30.9, 34.8, 35.3, 36.8, 37.0, 39.3, 51.4 (CH_3), 55.0 (CH_3), 82.0 (C),

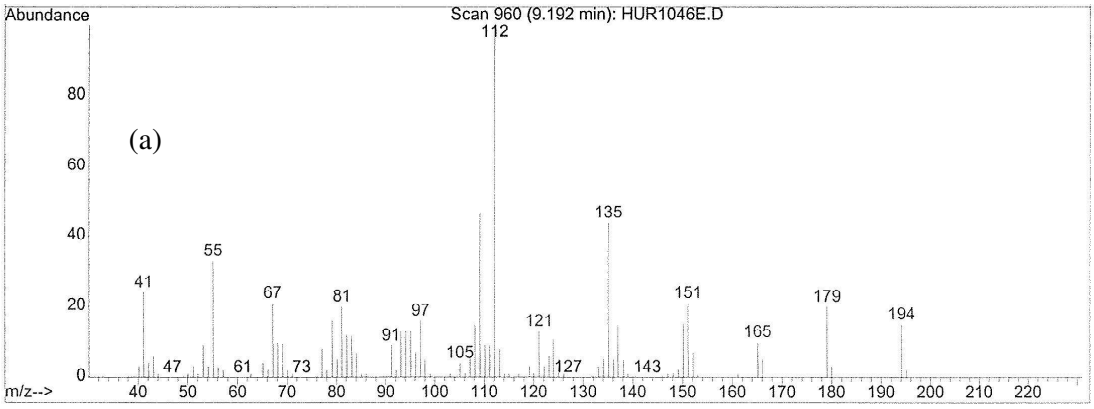
90.9 (CH_2), 174.7 (CO); MS *m/z* 284 $[M]^+$, 252, 239, 223, 173, 156, 147, 112 (base); EI-HRMS Found *m/z* 284.1990 $[M]^+$ $C_{16}H_{28}O_4$ requires 284.1988.

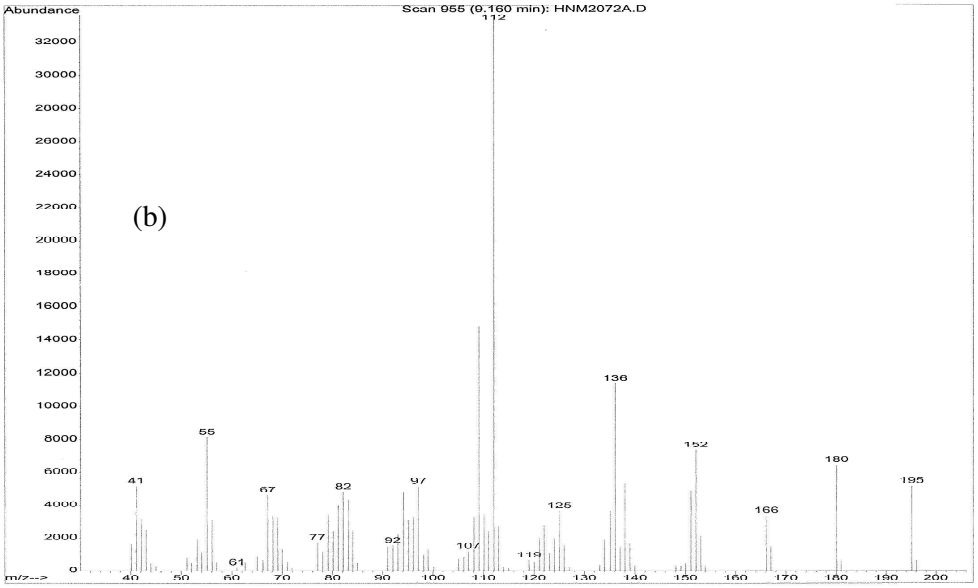
Trapping with D_2O

A solution of **1** (20.0 mg, 0.090 mmol) and D_2O (9.0 mg, 0.45 mmol) in THF was treated with SmI_2 (0.1 M in THF, 1.8 ml, 0.18 mmol) at rt for 1 h. Ether and Rochell's salt were added and the organic layer was washed with brine, dried ($MgSO_4$), and was evaporated to afford a residue. The residue was purified by a silica-gel column chromatography (hexane-EtOAc, 0–25%) to give **3a** (1.7 mg, 9.8%) and **4a** (1.6 mg, 7.9%). Compounds **3a** (1.7 mg, 9.7%) and **4a** (1.6 mg, 7.8%) were obtained from compound **2**.

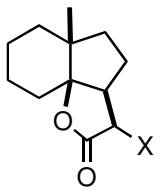


3a: oil; MS *m/z* 195 $[M]^+$, 180, 166, 152, 136, 112 (base).

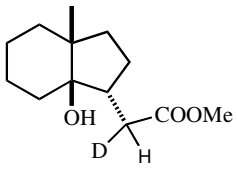




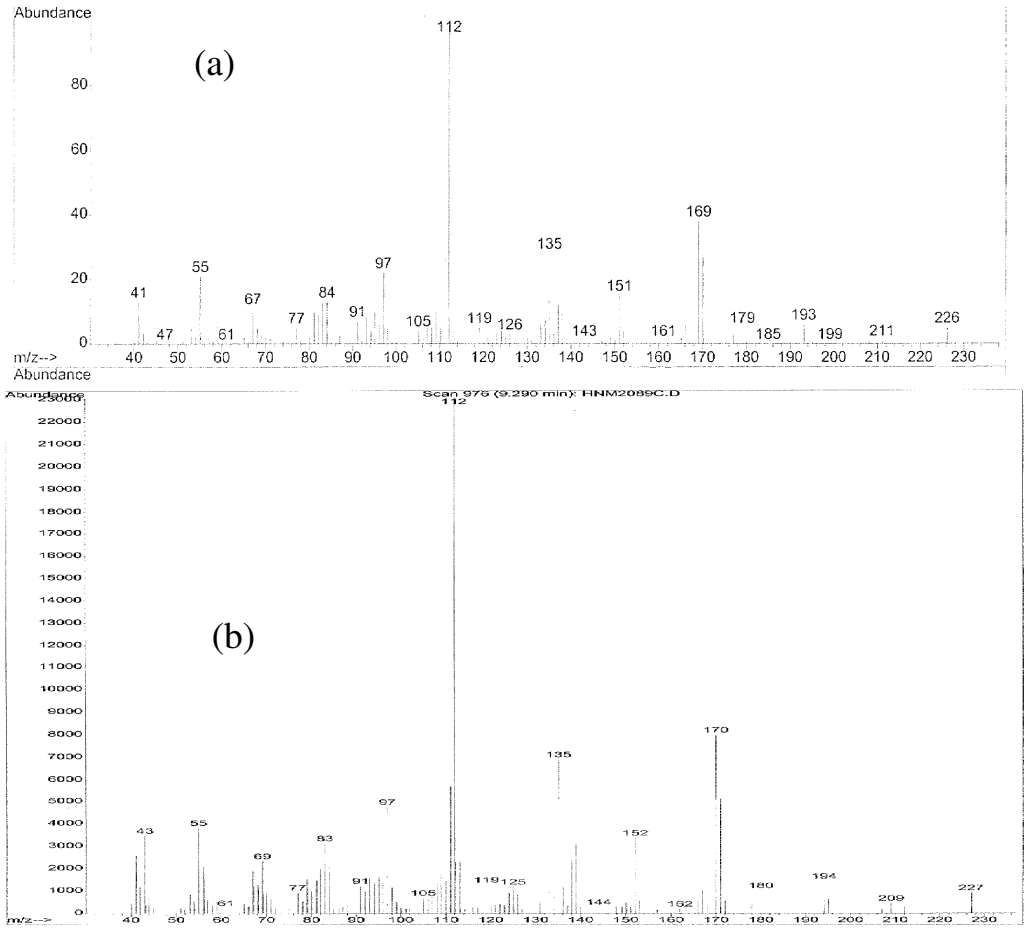
MS spectra for compound **3** (a) and compound **3a** (b) **.**



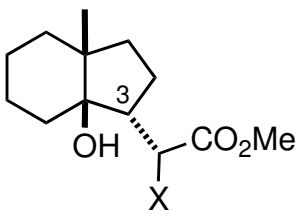
3 X=H
3a X=D



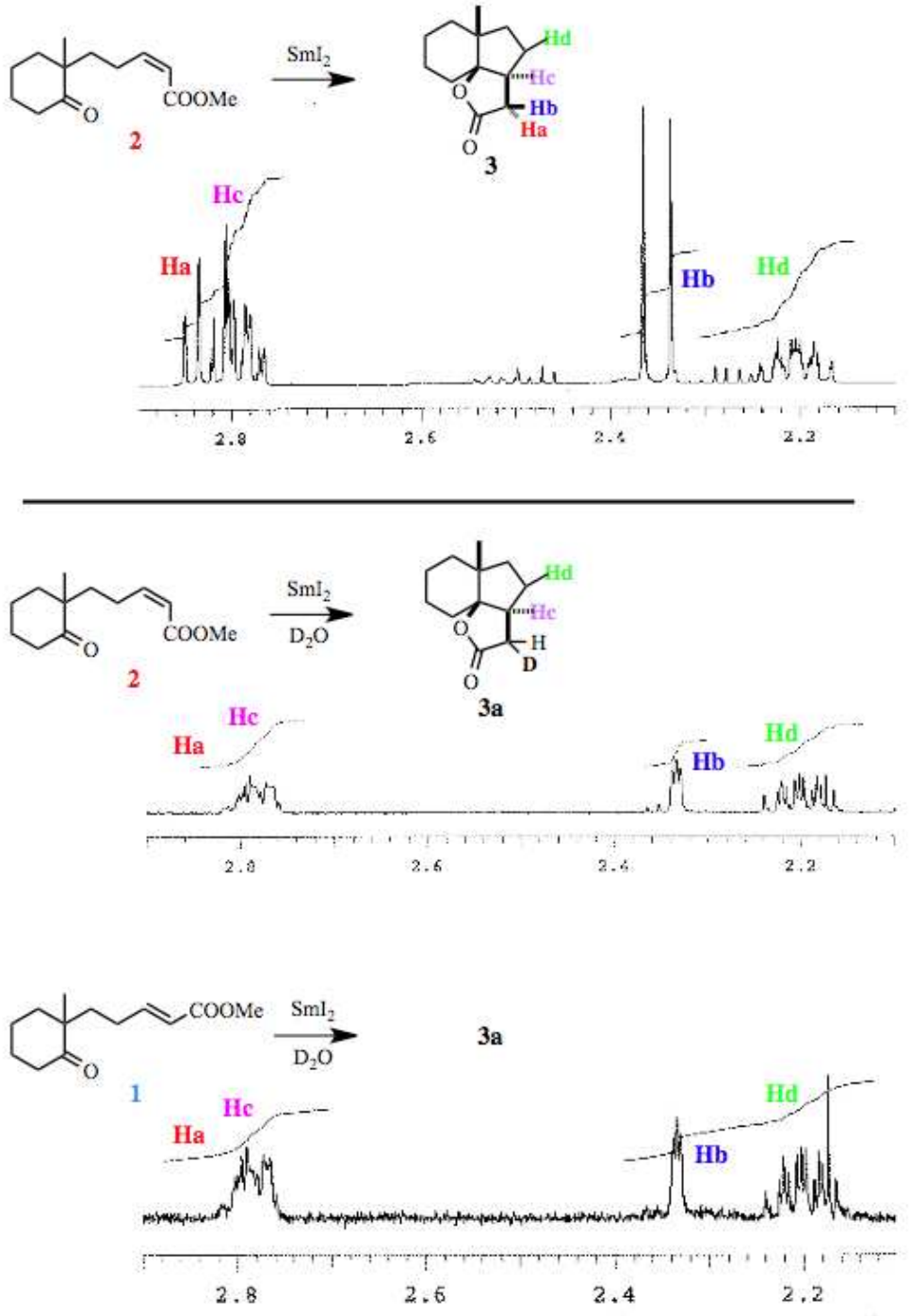
4a: oil: MS *m/z* 227 $[M]^+$, 209, 194, 180, 170, 152, 135, 112 (base).



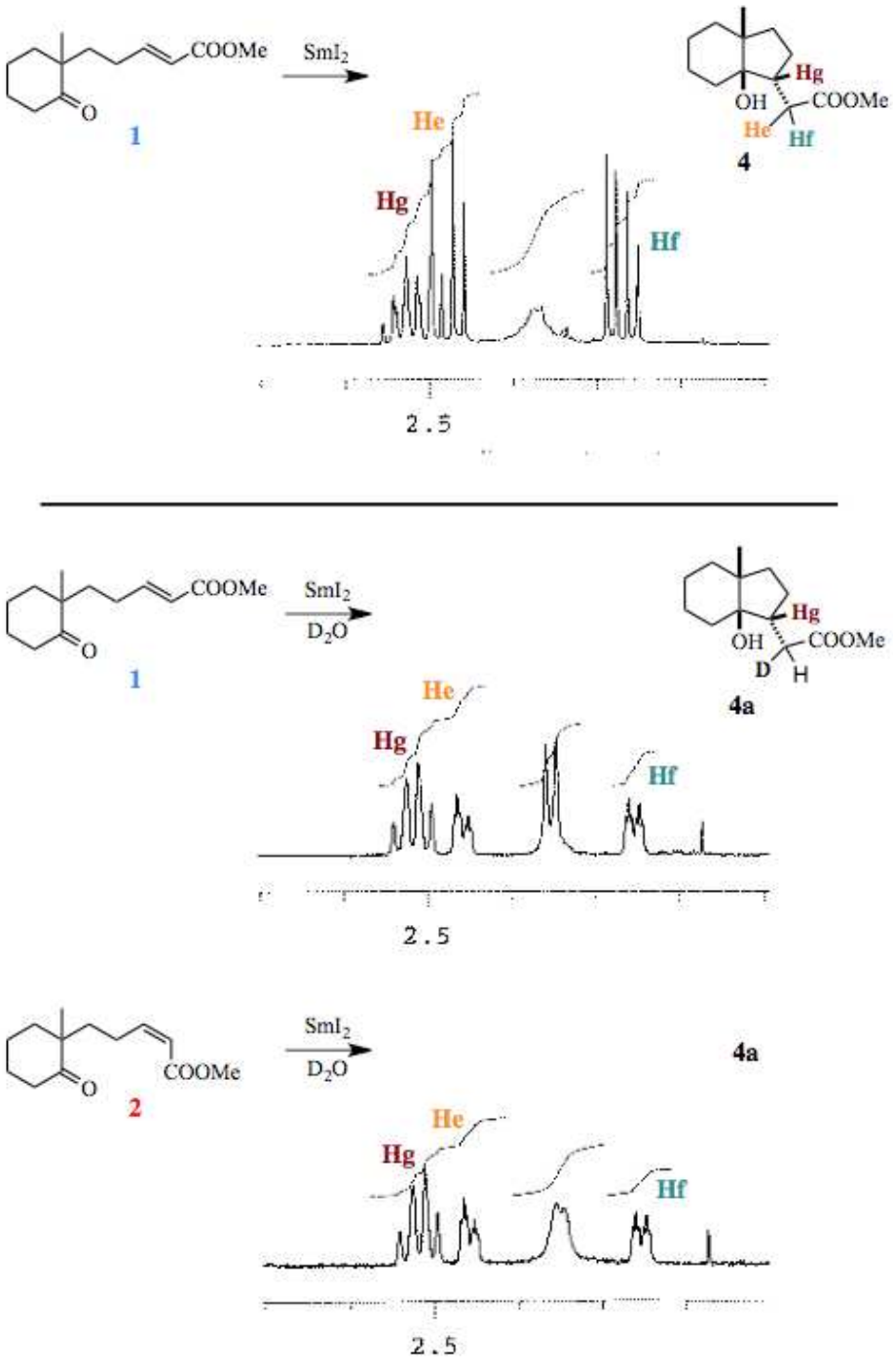
MS spectra for compound **4** (a) and compound **4a** (b) **.**



4 X=H
4a X=D



Assignment of Ha, Hb, Hc, and Hd in compound **3**. ^{1}H NMR spectra of compound **3a** derived from **1** and **2** by quenching with D_2O. Ha and Hb significantly diminished.



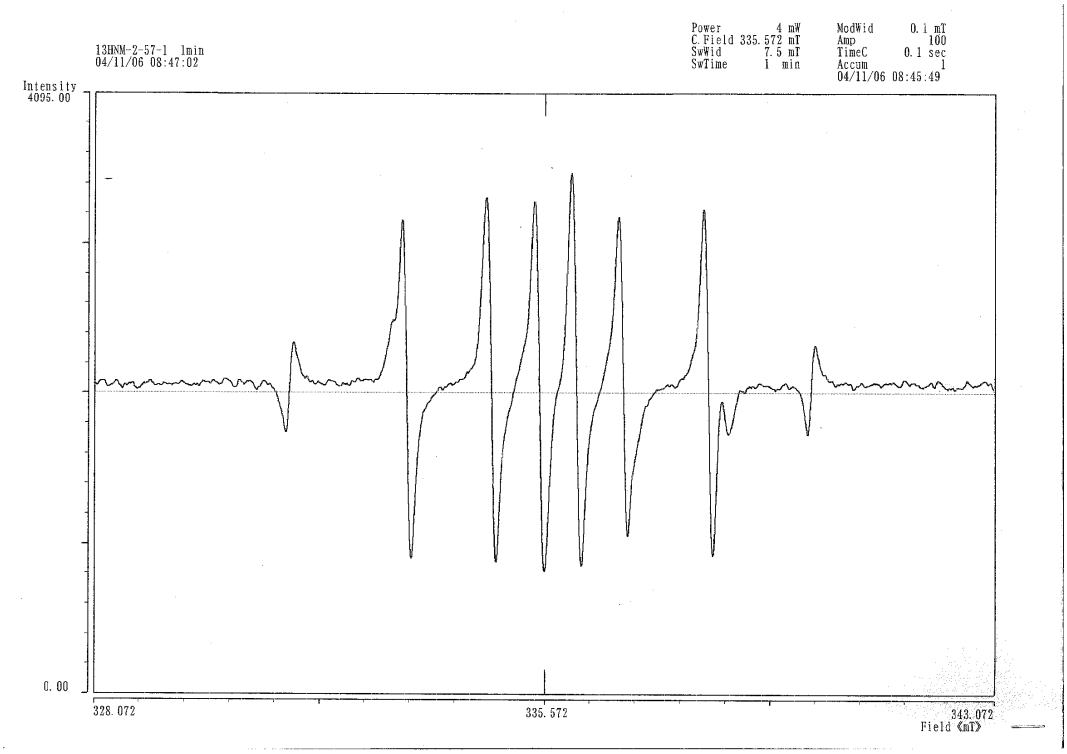
Assignment of He, Hf, and Hg in compound **4**. ^{1}H NMR spectra of compound **4a** derived from **1** and **2** by quenching with D_2O. He and Hf significantly diminished.

General procedures of trapping experiment of the substrates and DMPO

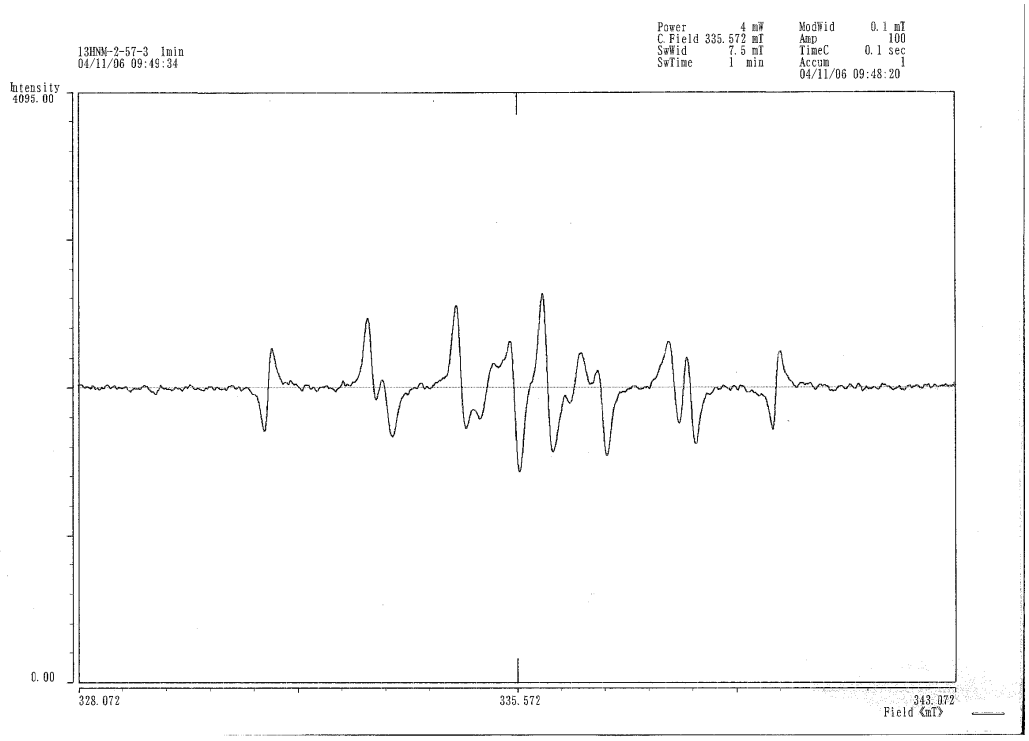
To a solution of the substrate and DMPO in a test tube, SmI_2 in THF was added with stirring, and in 1 min (the blue color faded), the ESR was measured (when the substrate was not added, no signal was detected). Isolation of the adduct **11**, **12**, or **13** was not attempted.

The ESR spectra of the reactions and simulations

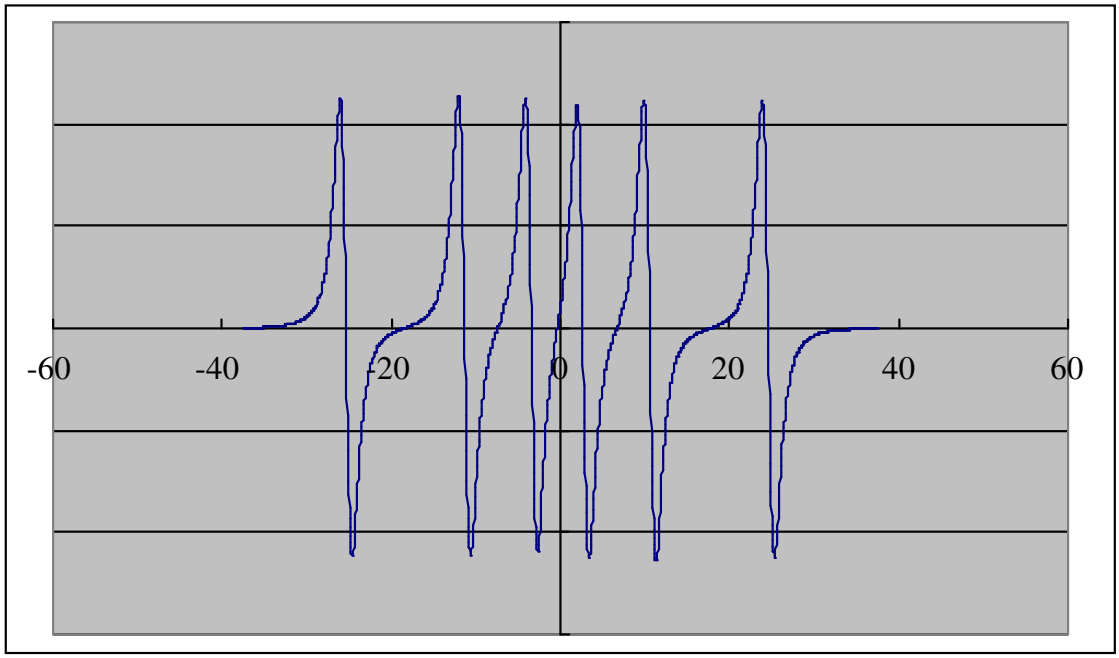
(1) The ESR for the reaction of compound **1** with SmI_2 in the presence of DMPO.



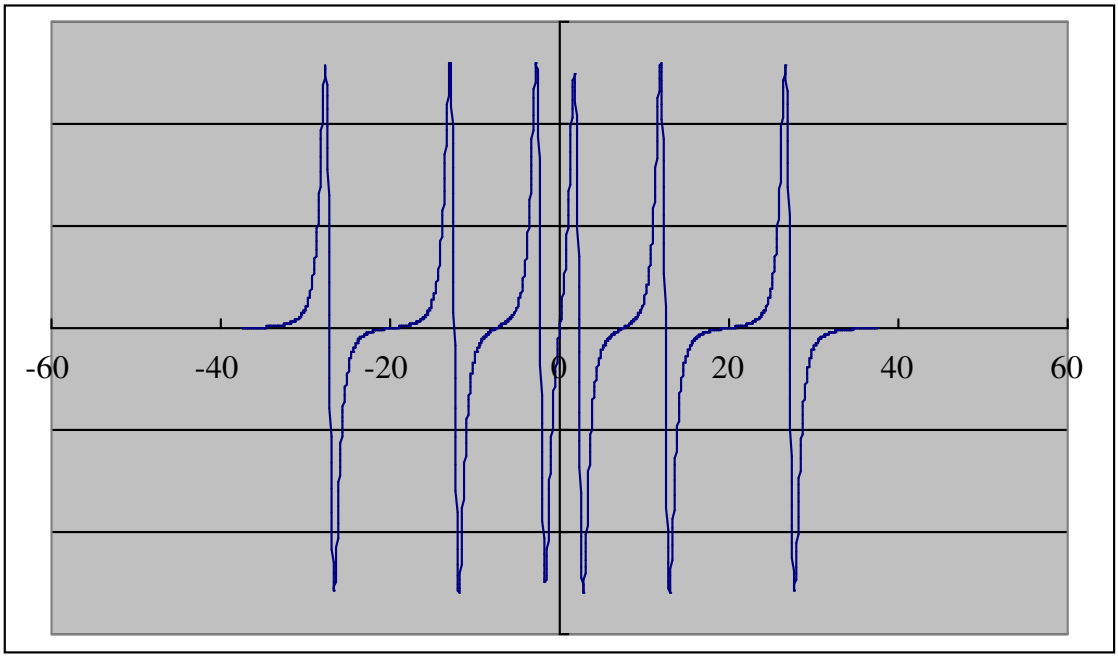
(2) The ESR for the reaction of compound **2** with SmI_2 in the presence of DMPO.



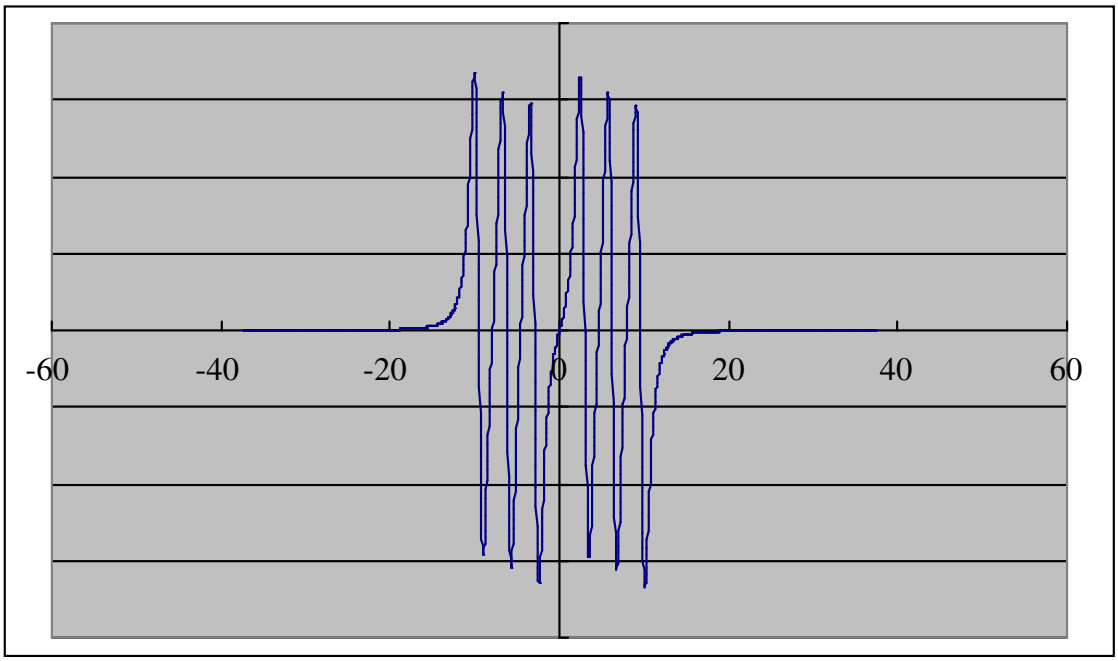
(3) The species **12**: *a*(N)/mT = 1.40, *a*(H)/mT = 2.19, ΔB/mT = 0.14



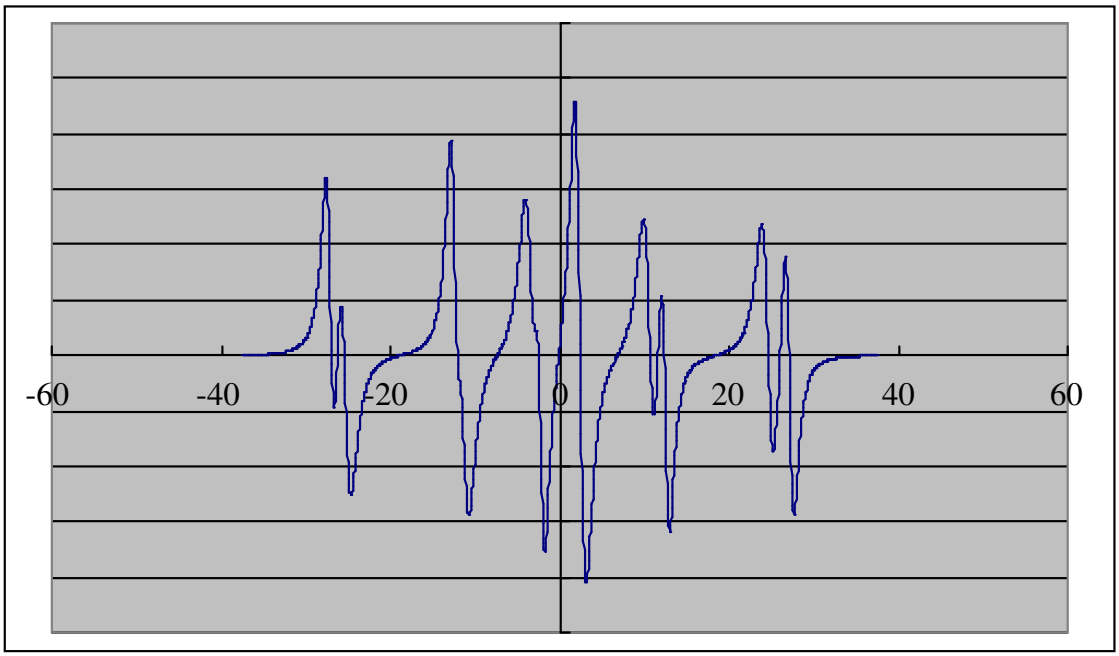
(4) The species **13**: *a*(N)/mT = ca. 1.47, *a*(H)/mT = ca. 2.49, ΔB/mT = ca. 0.10



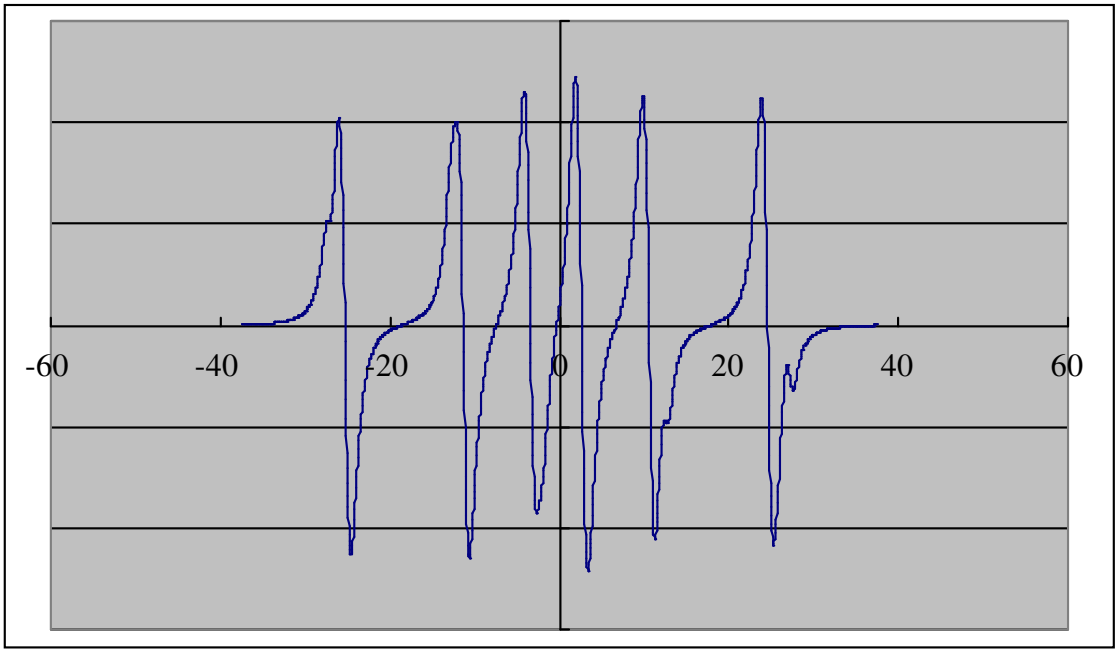
(5) The unknown species: *a*(N)/mT = ca. 0.33, *a*(H)/mT = ca. 1.25



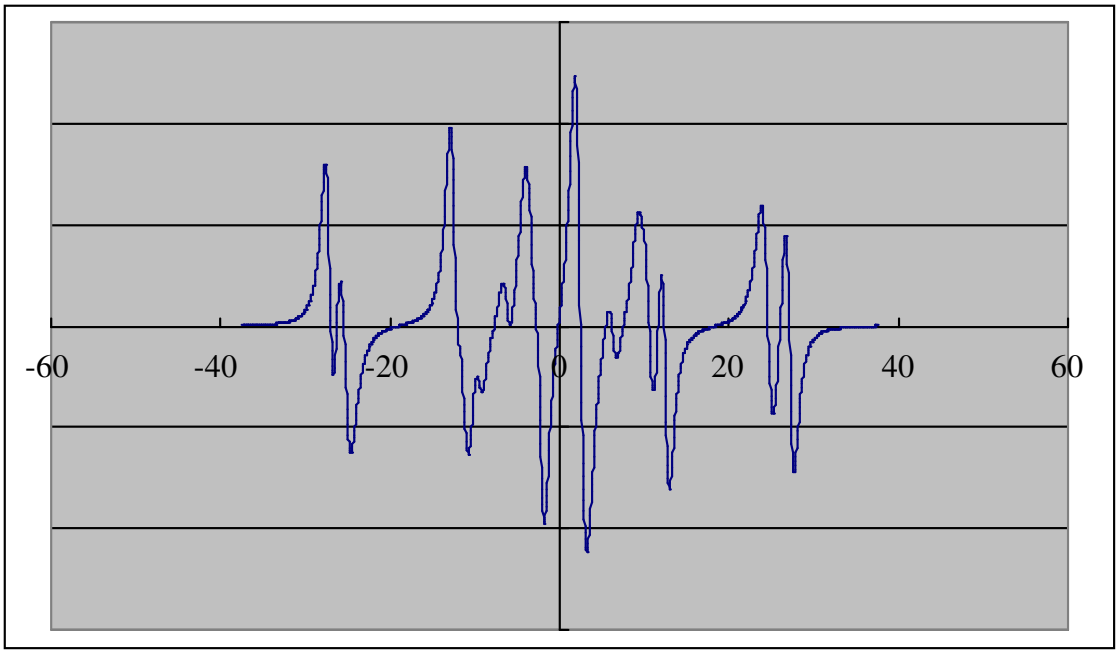
(6) The spectrum of **12** and **13** (1:1)



(7) The spectrum of **12** and **13** (100:12)

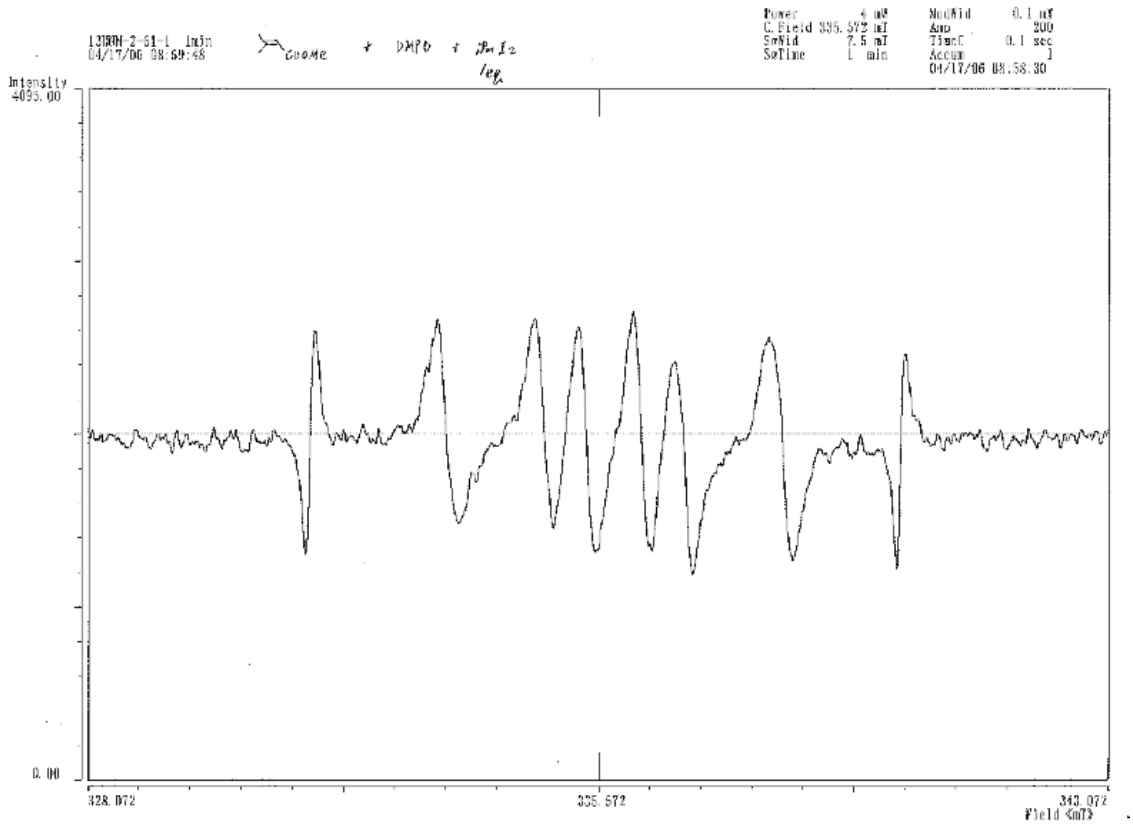


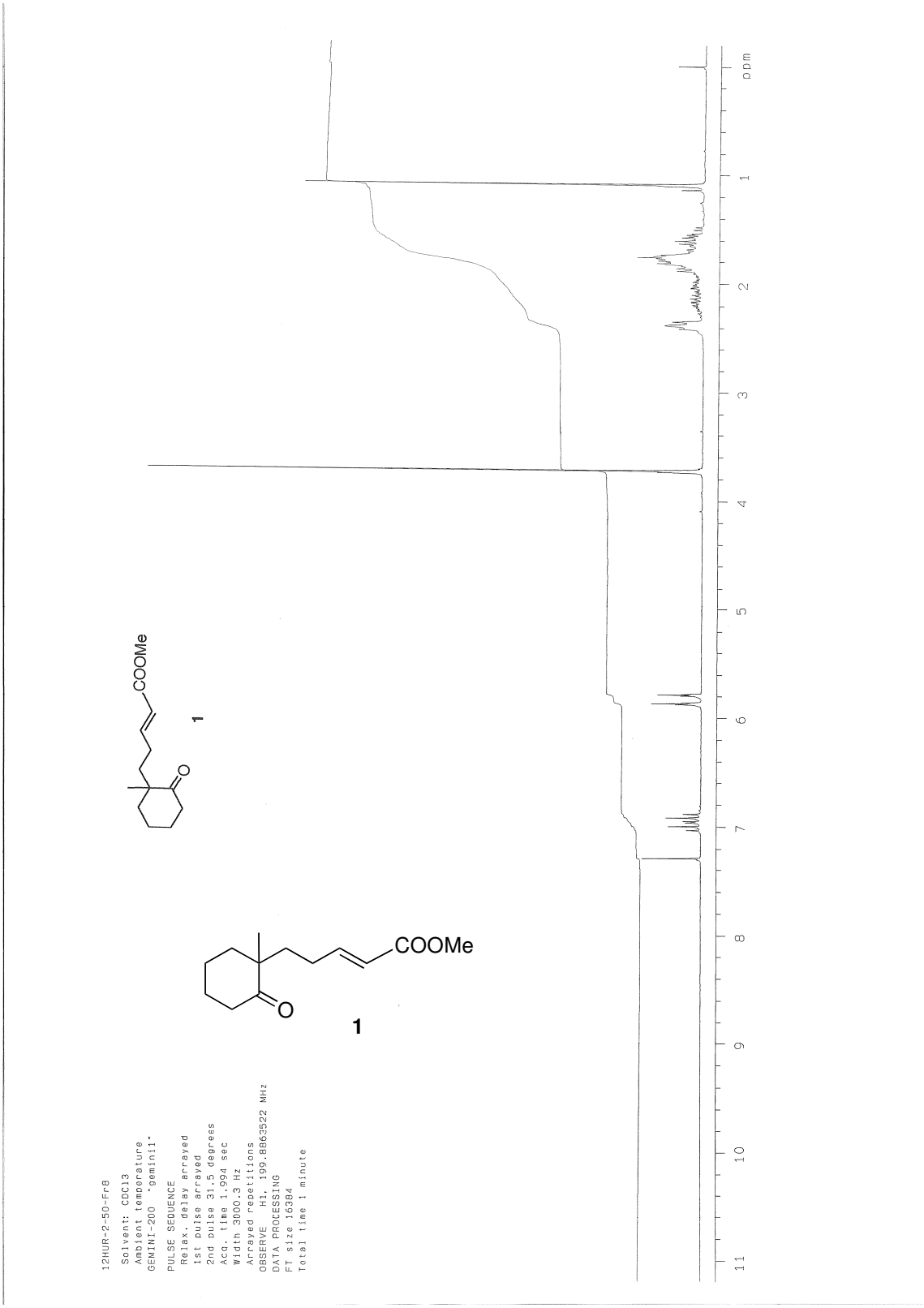
(8) The spectrum of **12** and **13** (1:1) and the unknown species.



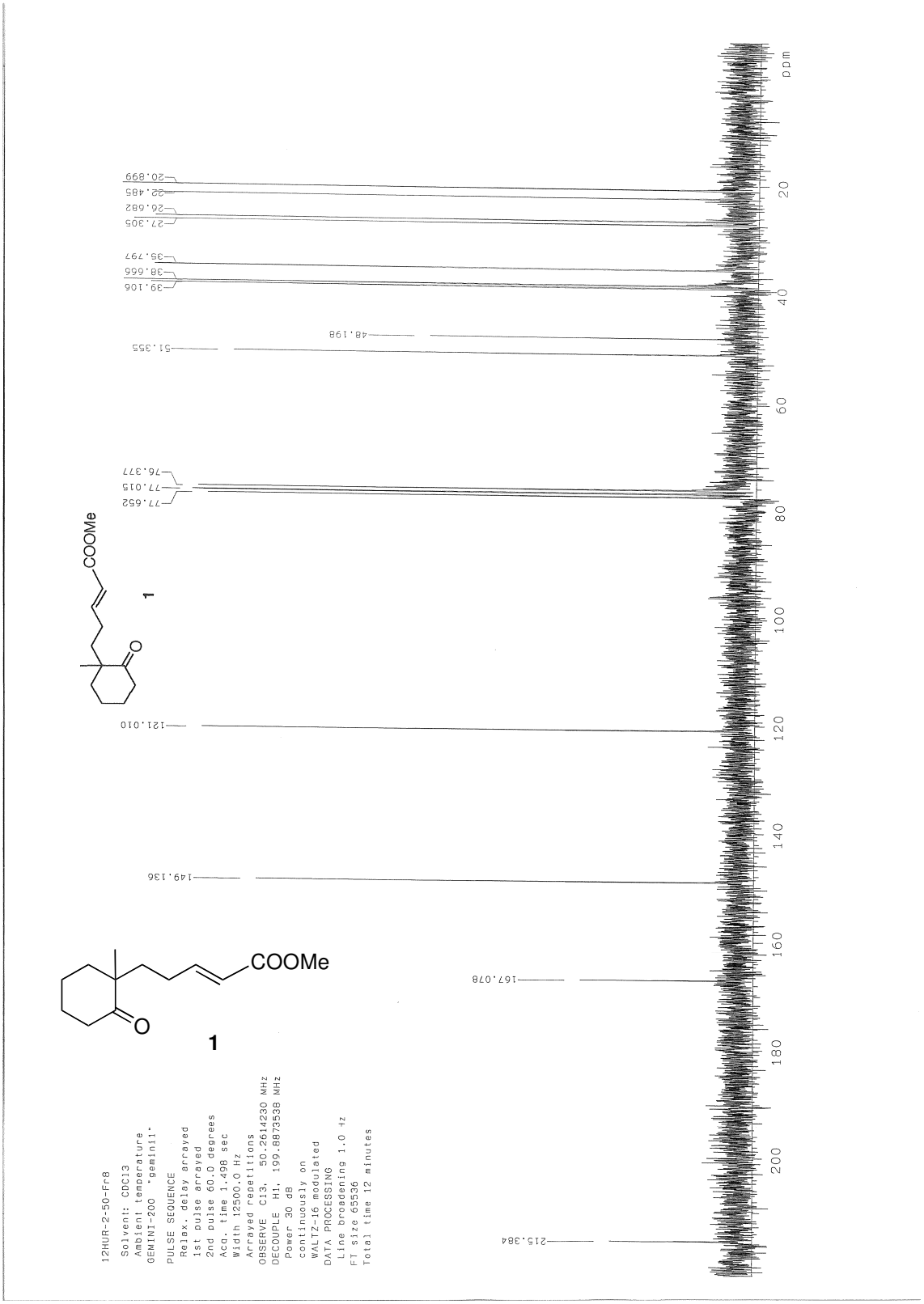
In this system the simulation with a(N)/mT = 0.79, a(H)/mT = 0.33 can also resulted in a similar spectrum. Therefore, it was not possible to identify the radical species. However, the signal intensities are very weak and presumably due to a by-product or an impurity.

(9) The ESR for the reaction of compound **10** with SmI_2 in the presence of DMPO.

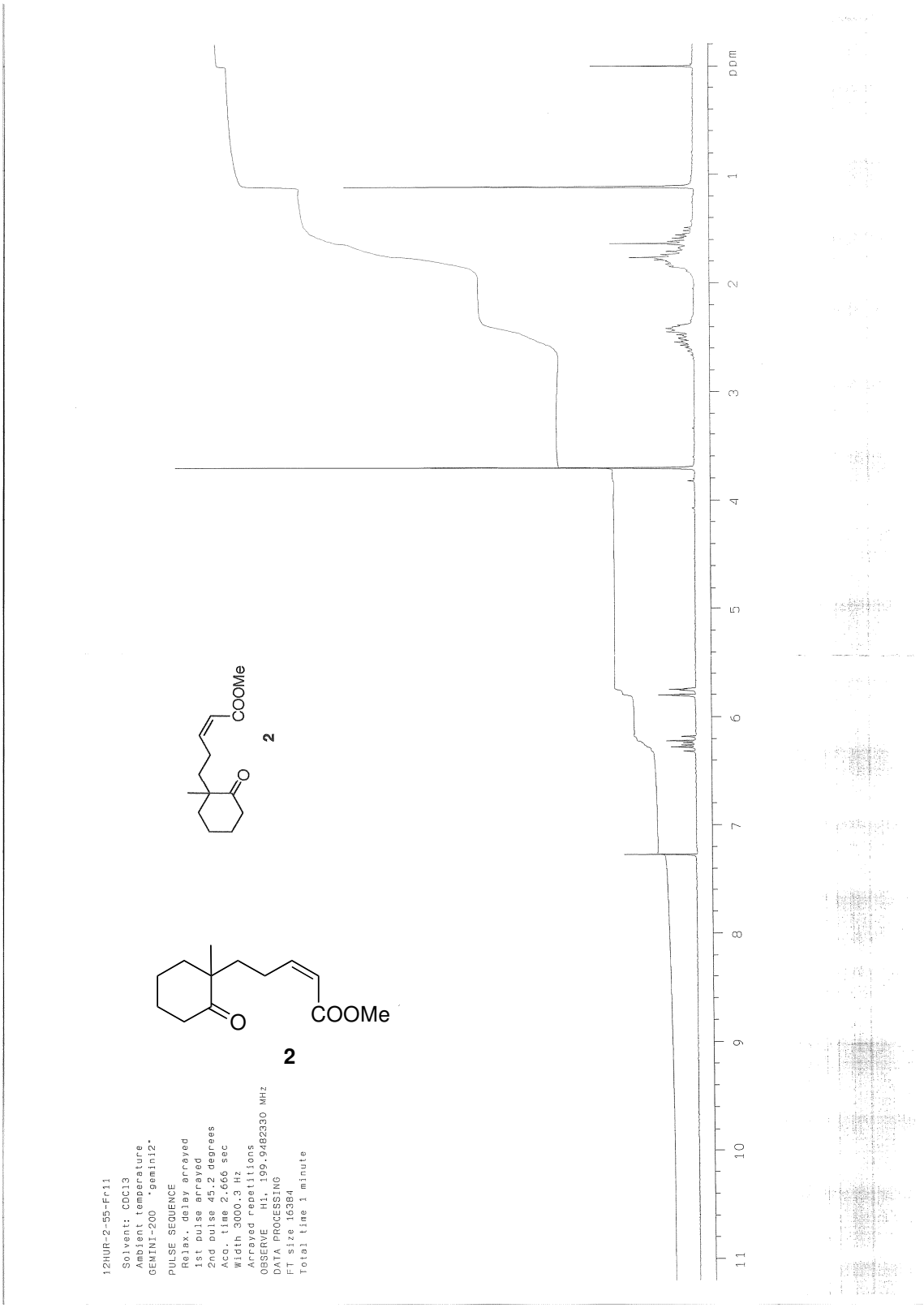




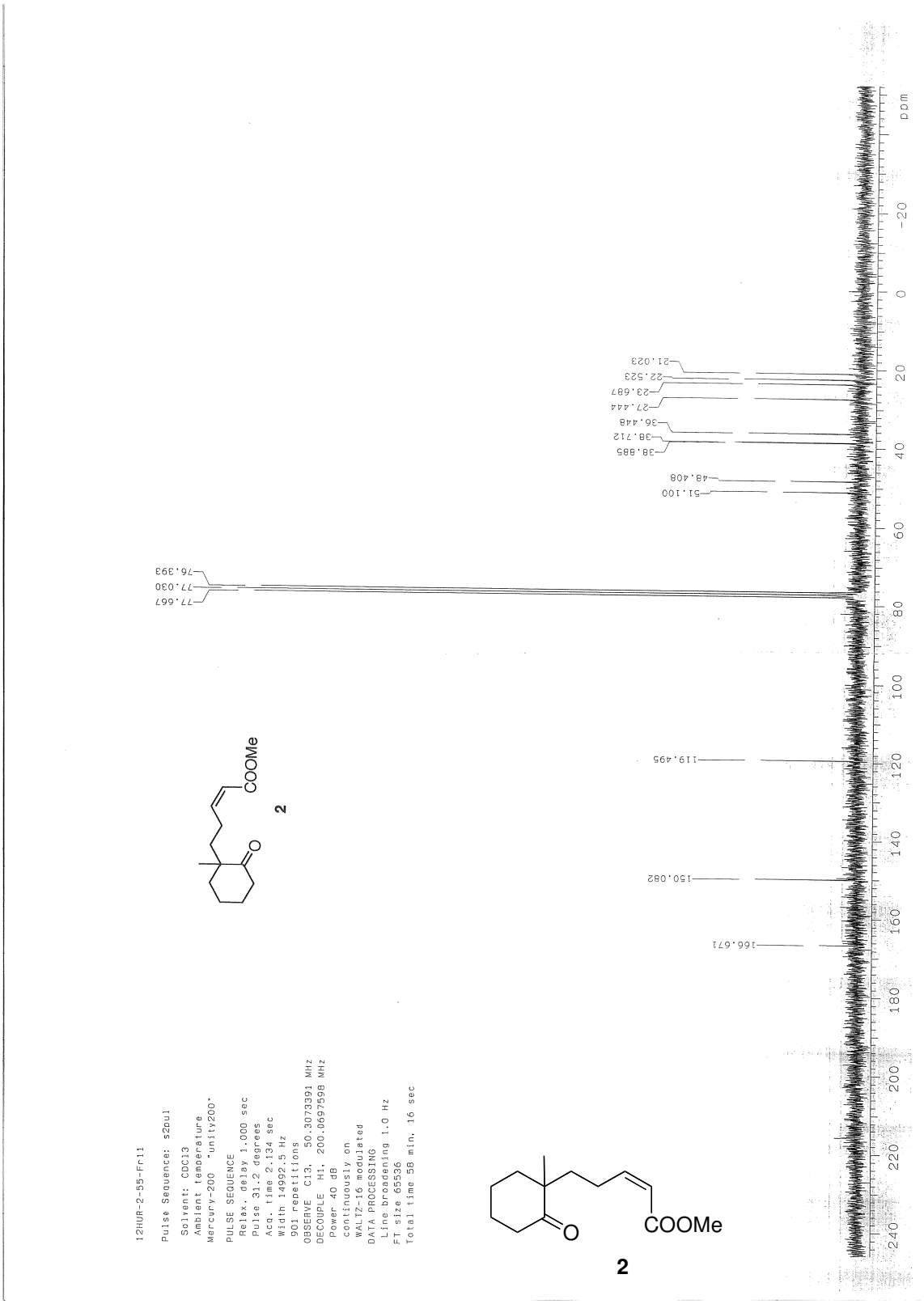
^{1}H NMR of Compound **1**



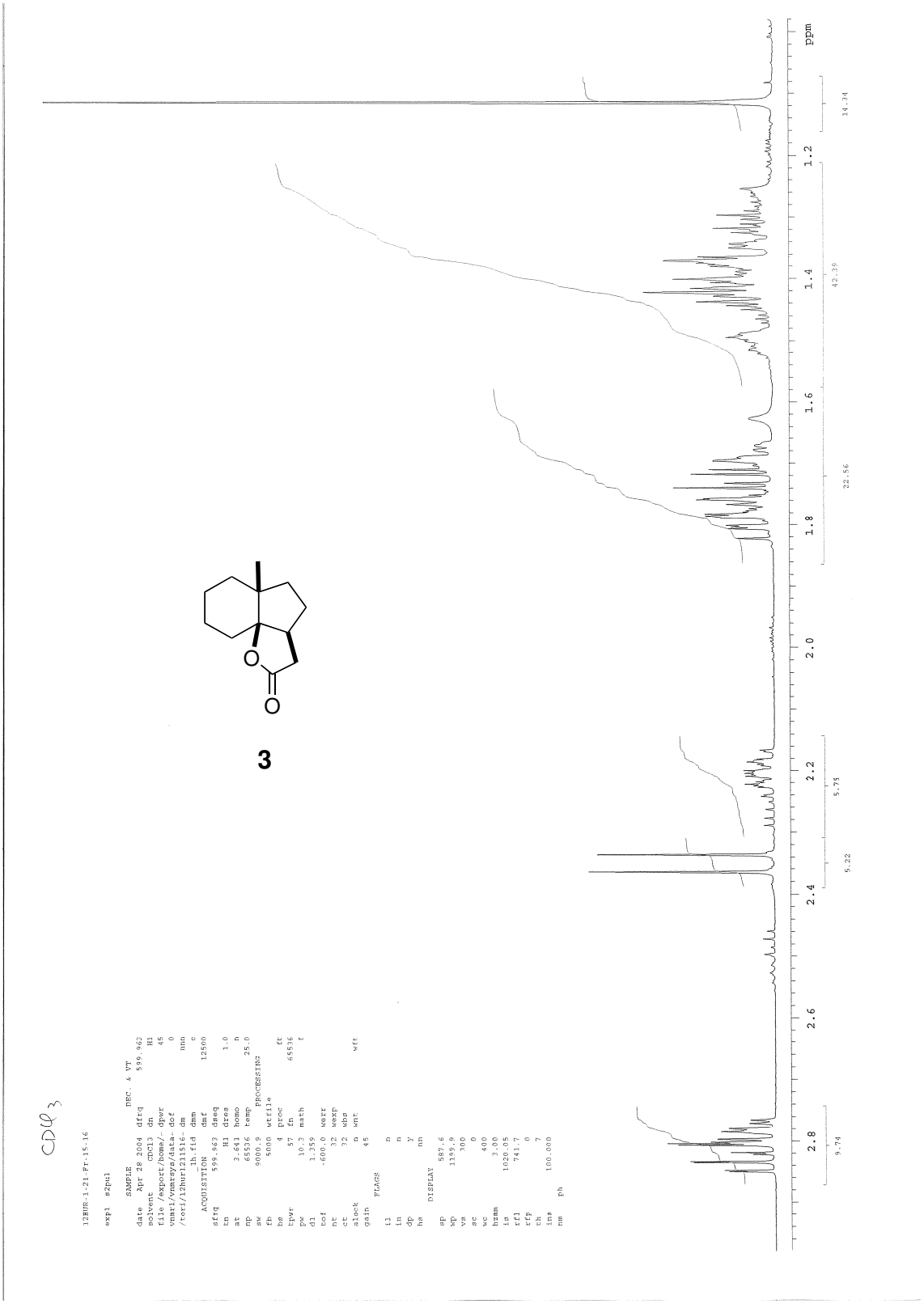
^{13}C NMR of Compound **1**



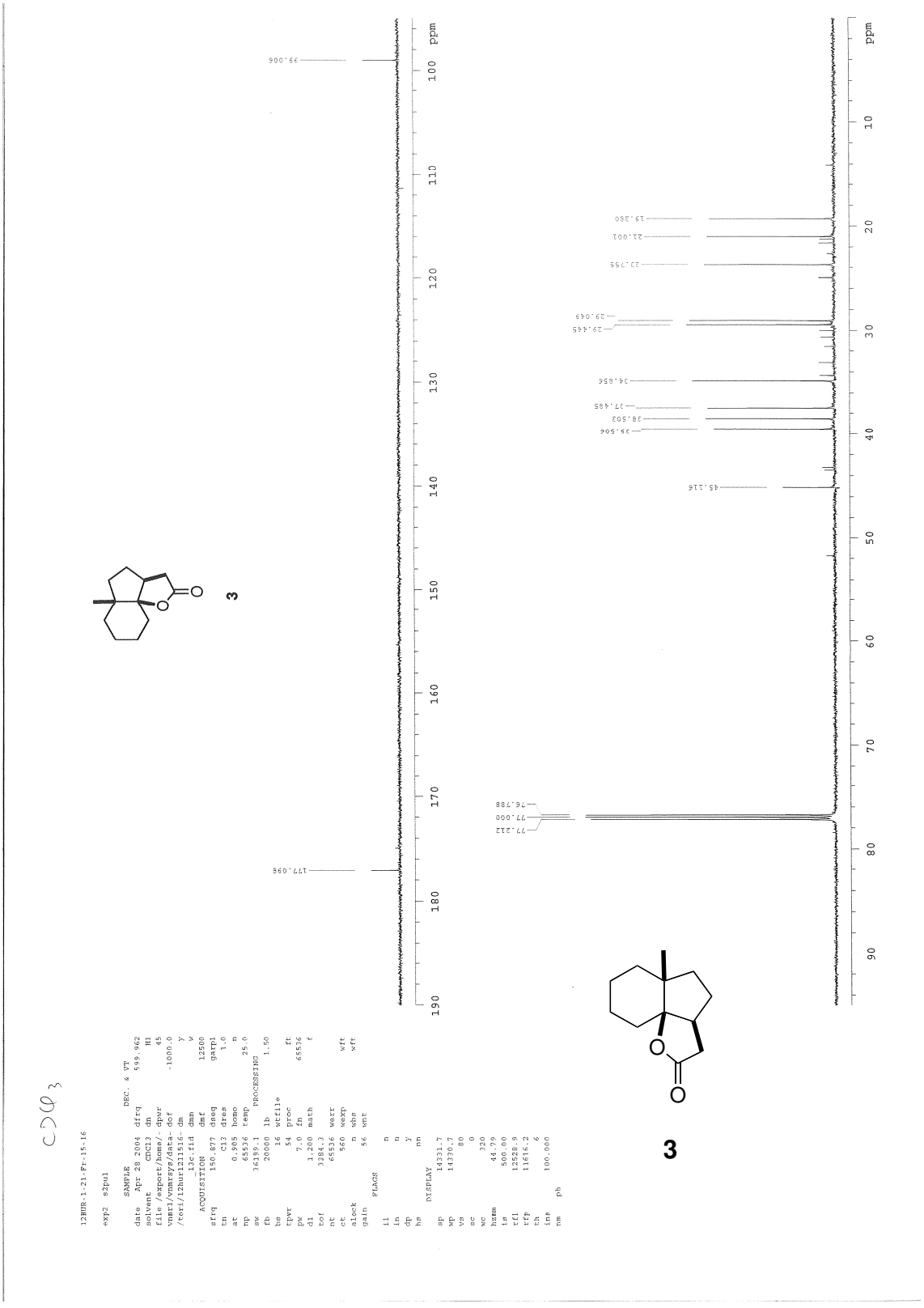
^{1}H NMR of Compound **2**



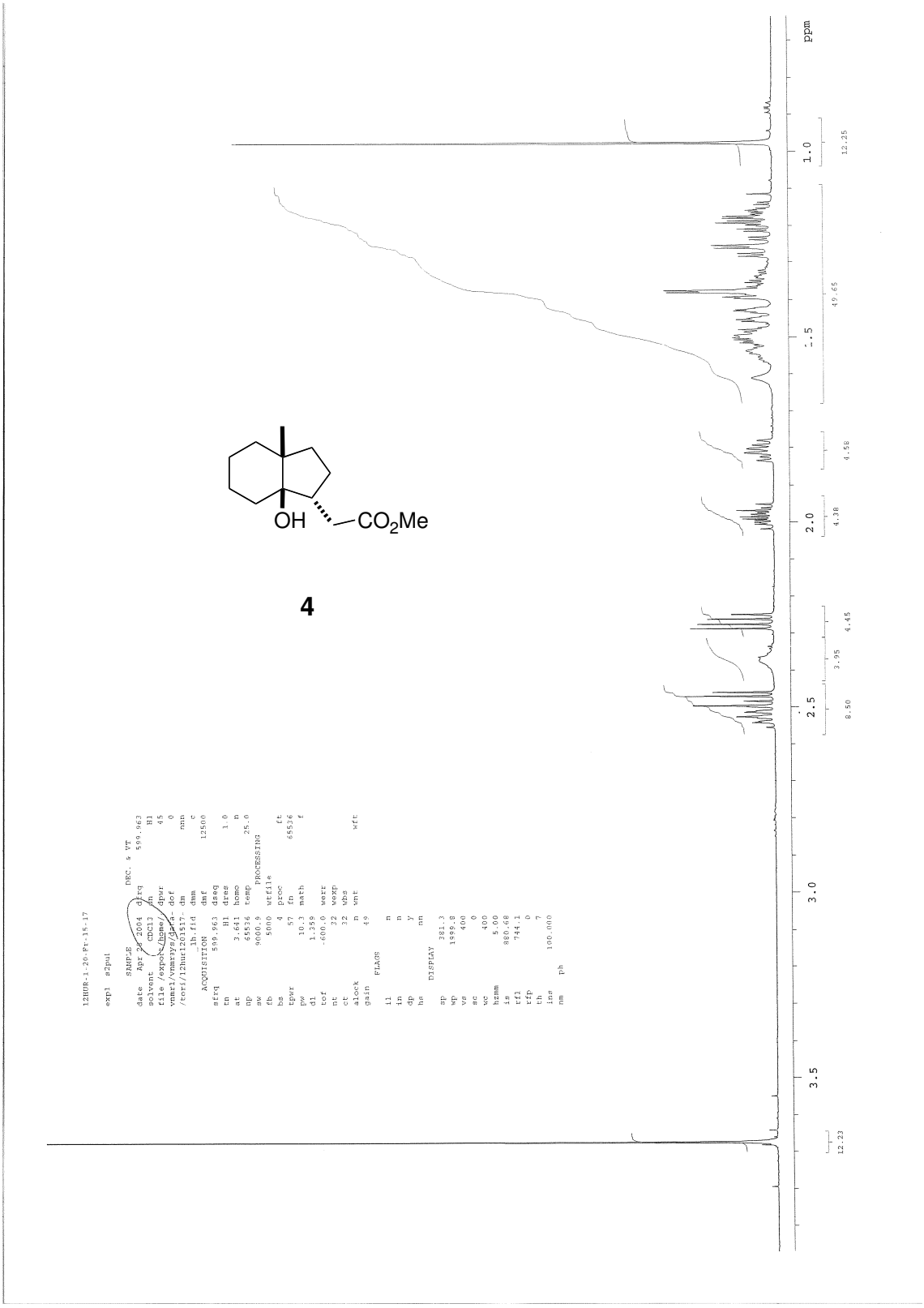
^{13}C NMR of Compound **2**



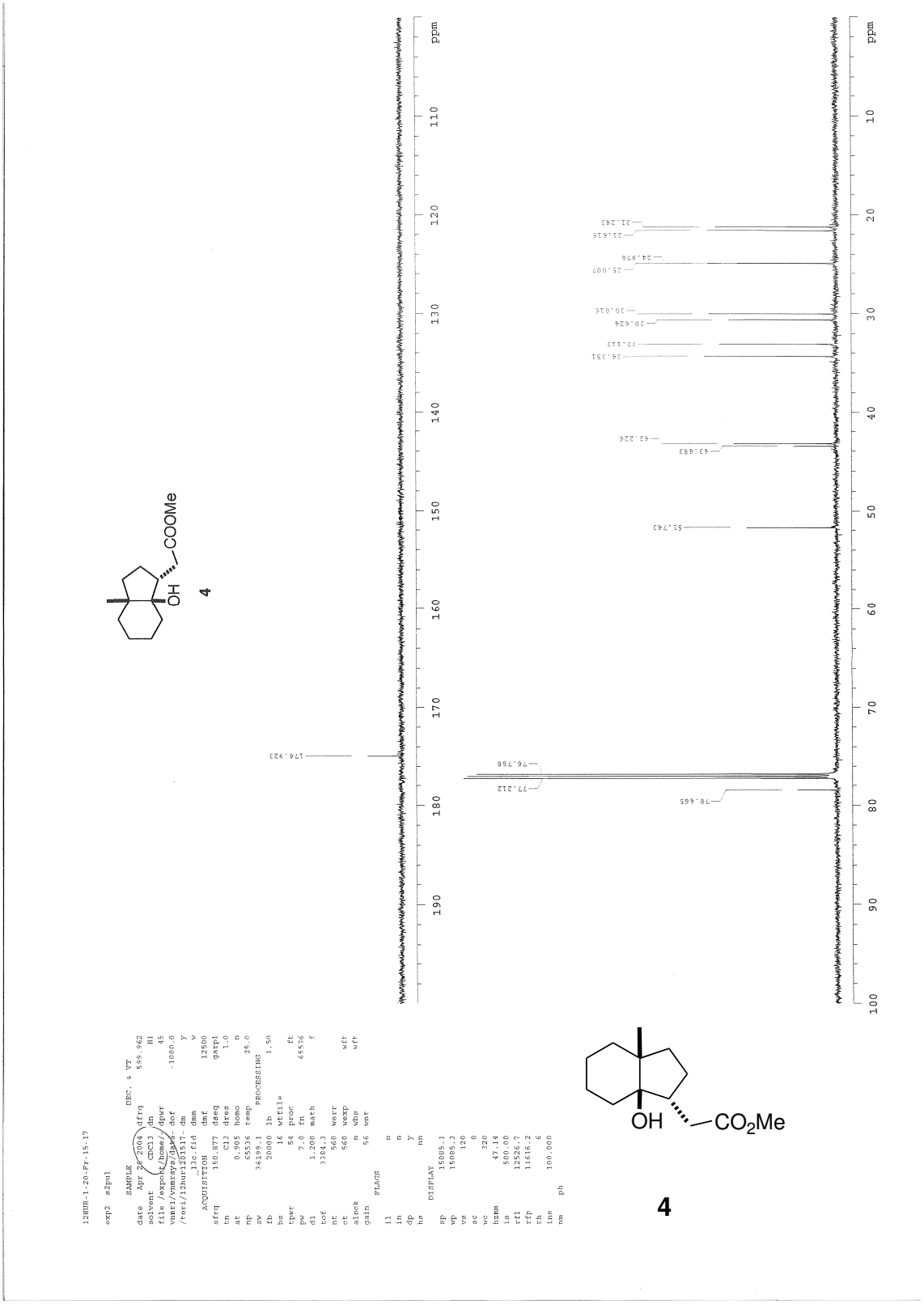
600MHz ^{1}H NMR of Compound **3**



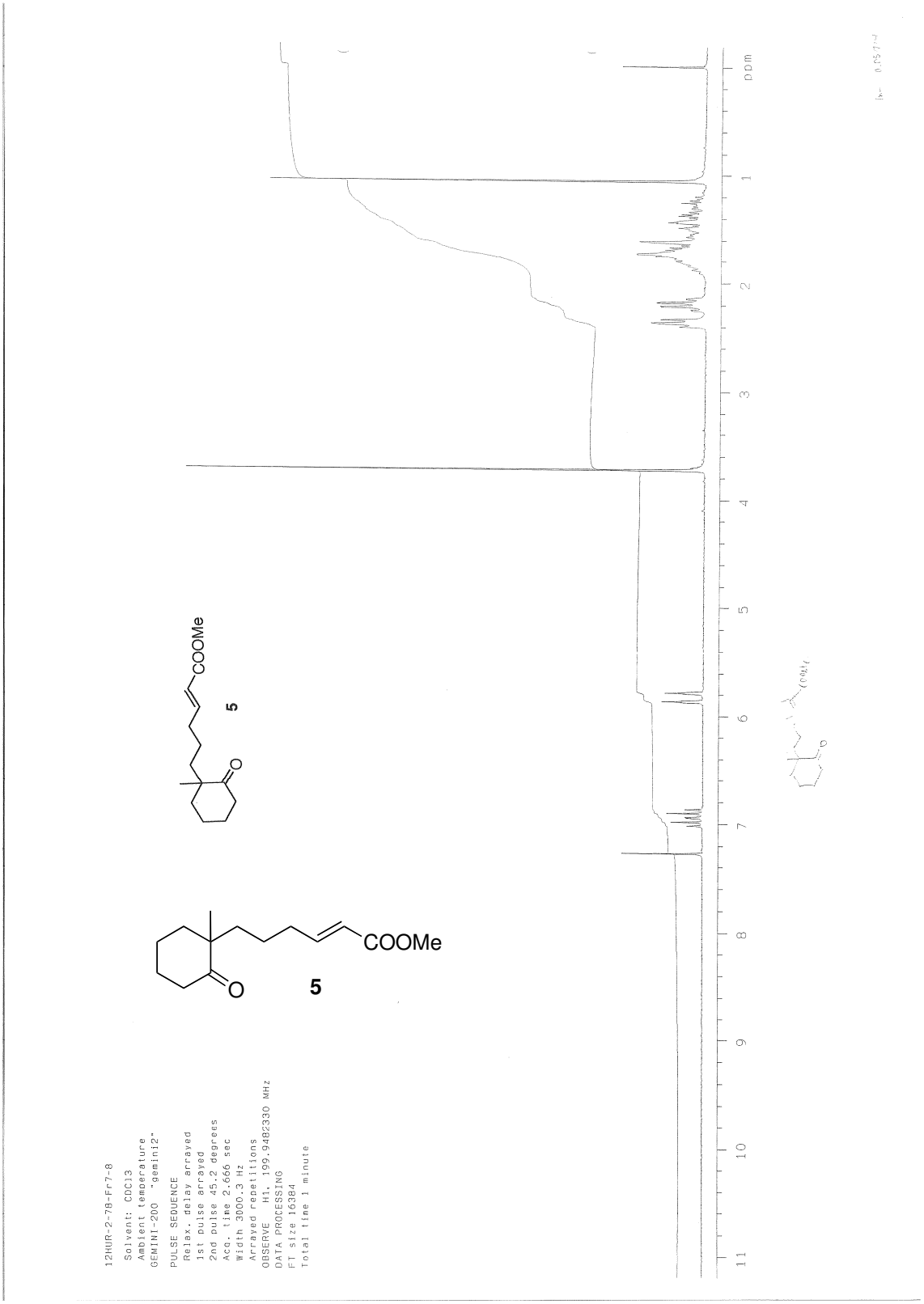
150MHz ^{13}C NMR of Compound **3**



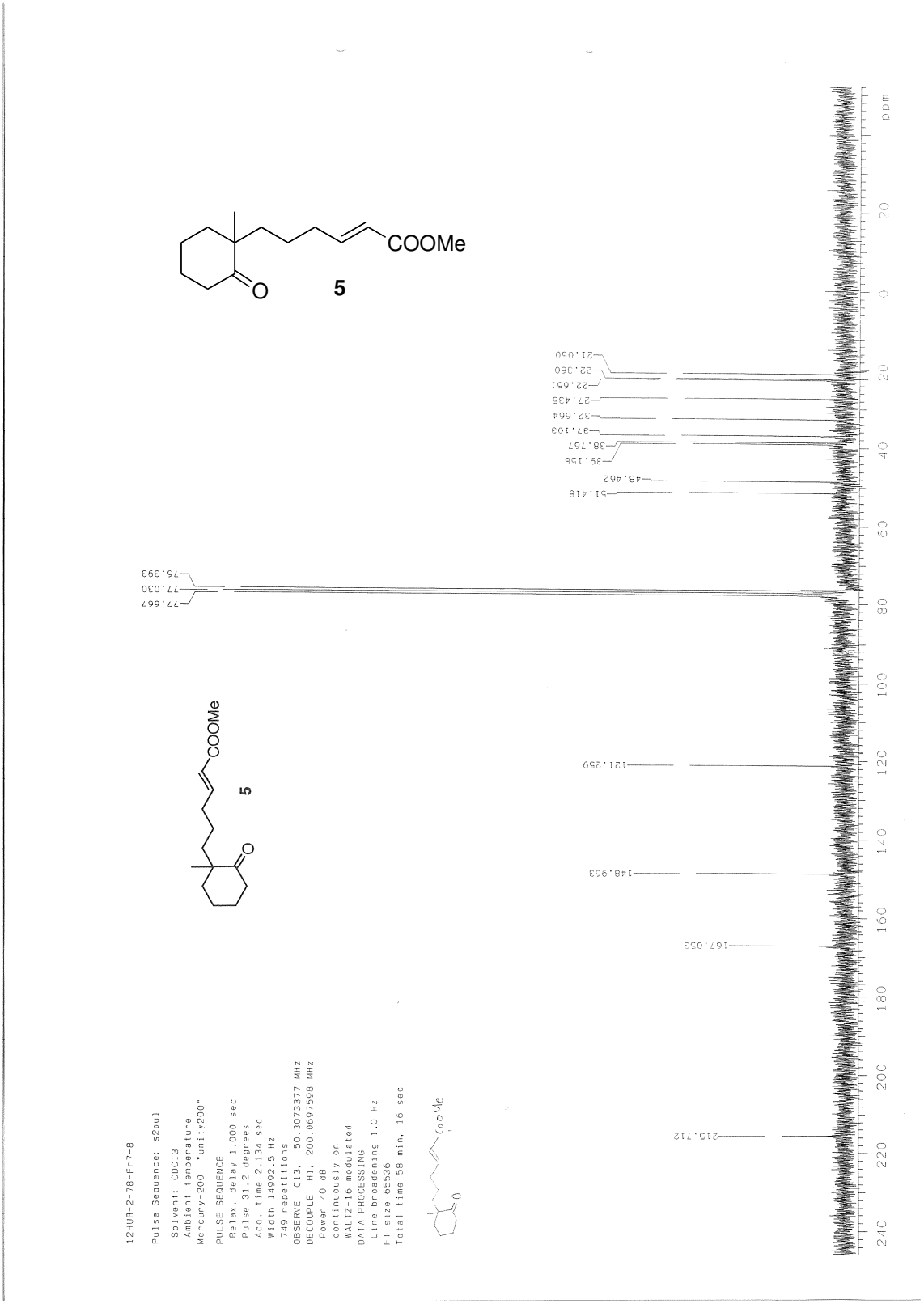
600MHz ^{1}H NMR of Compound **4**



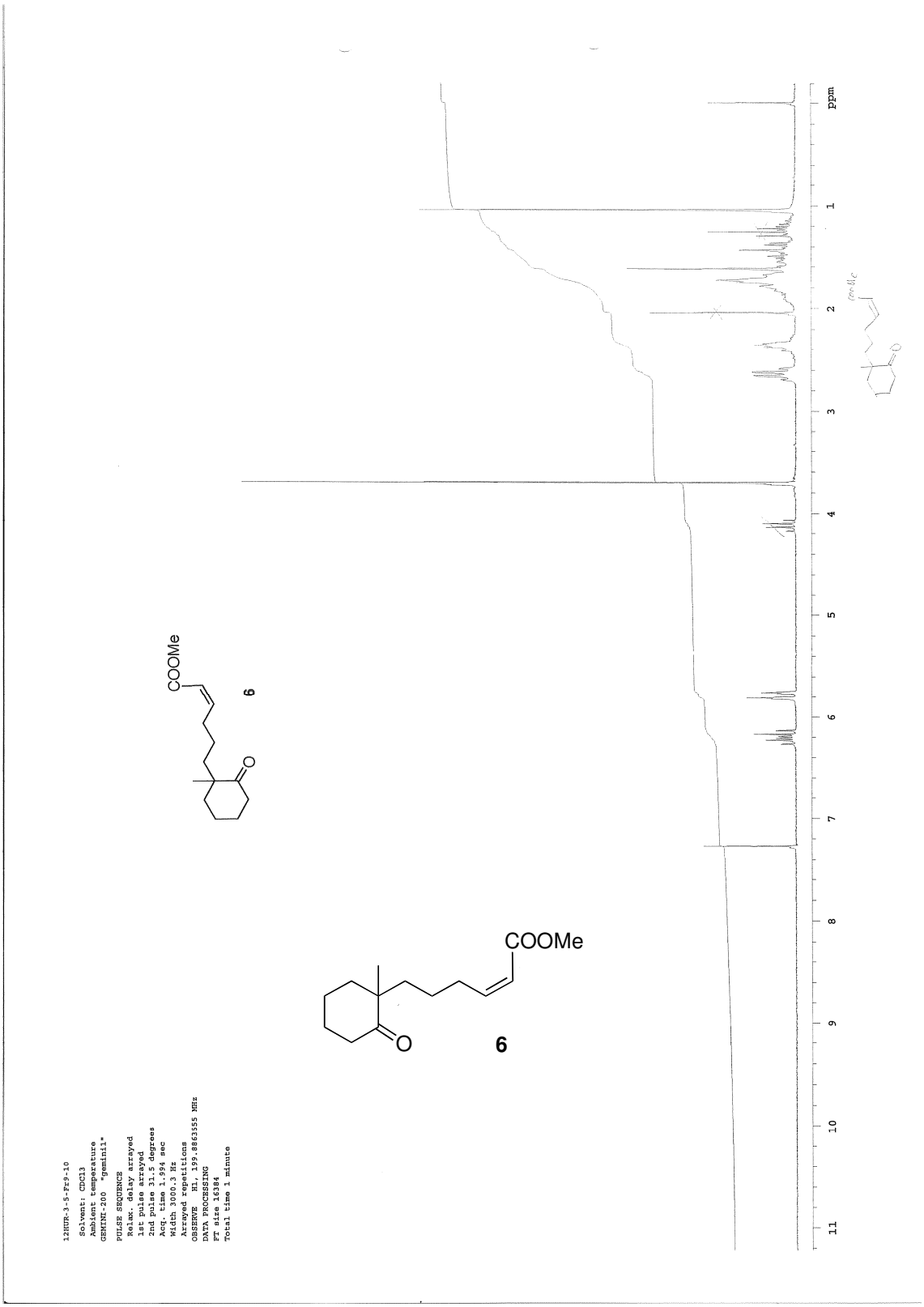
150MHz ^{13}C NMR of Compound **4**



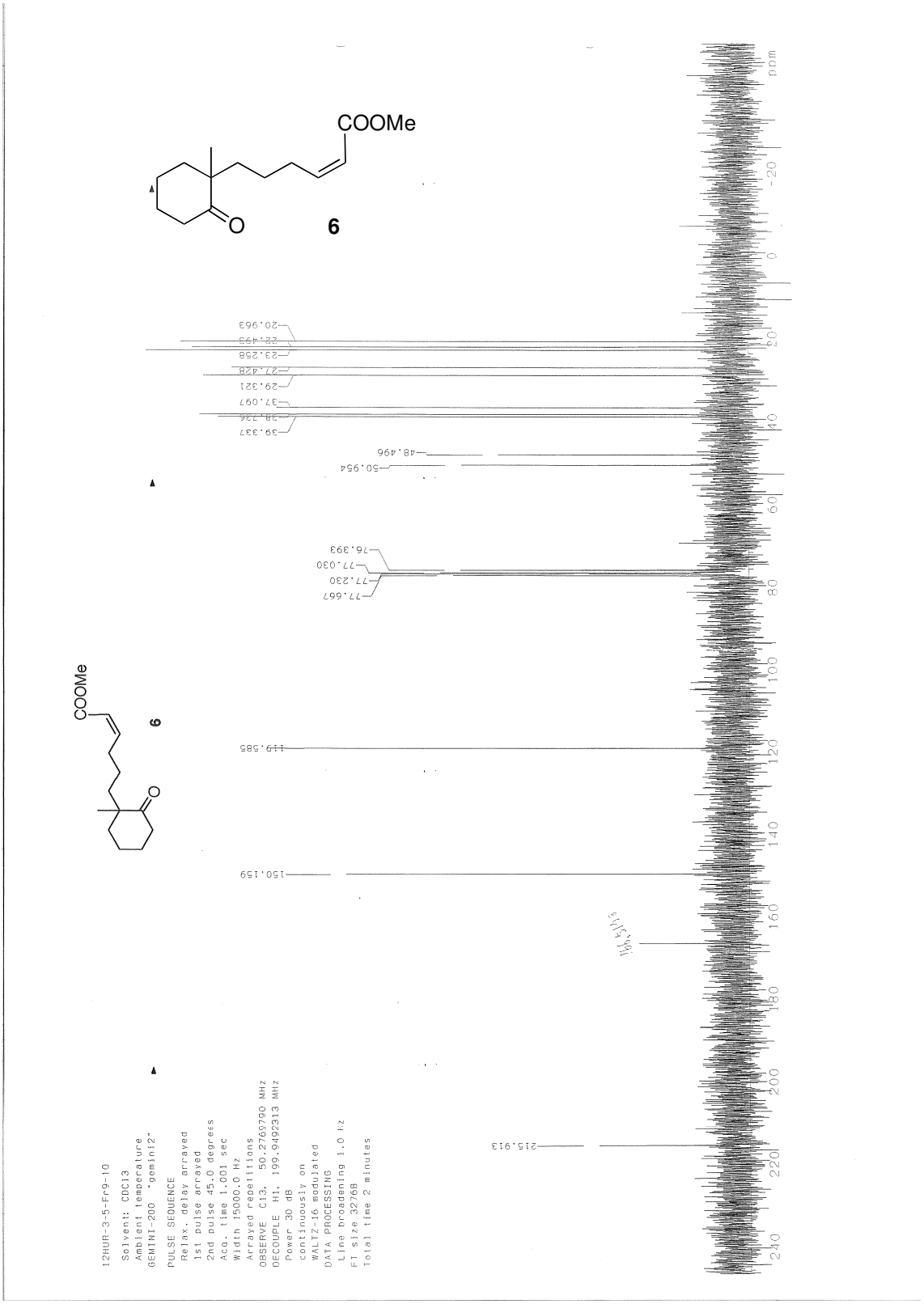
200MHz ^{1}H NMR of Compound **5**



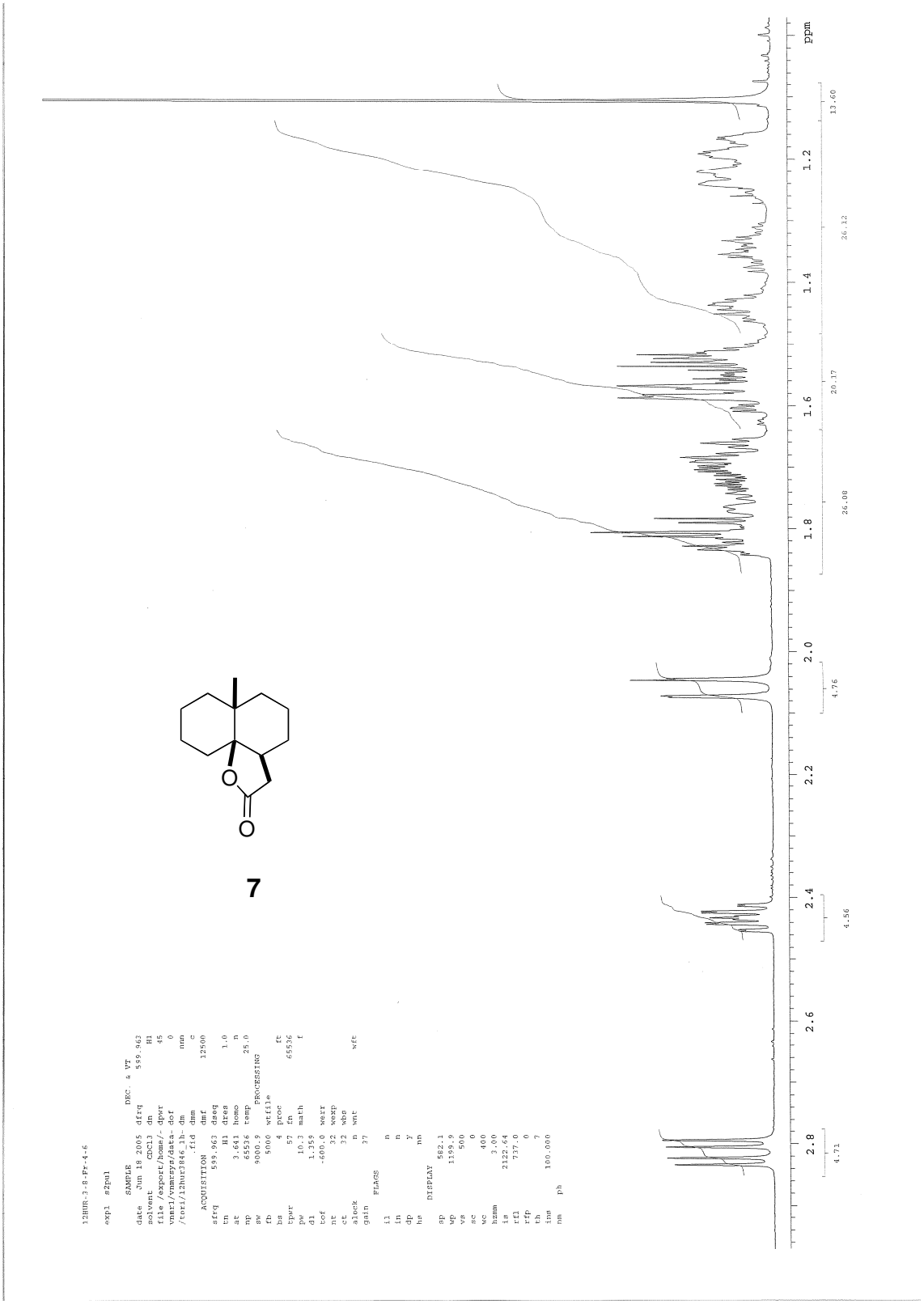
50MHz ^{13}C NMR of Compound **5**



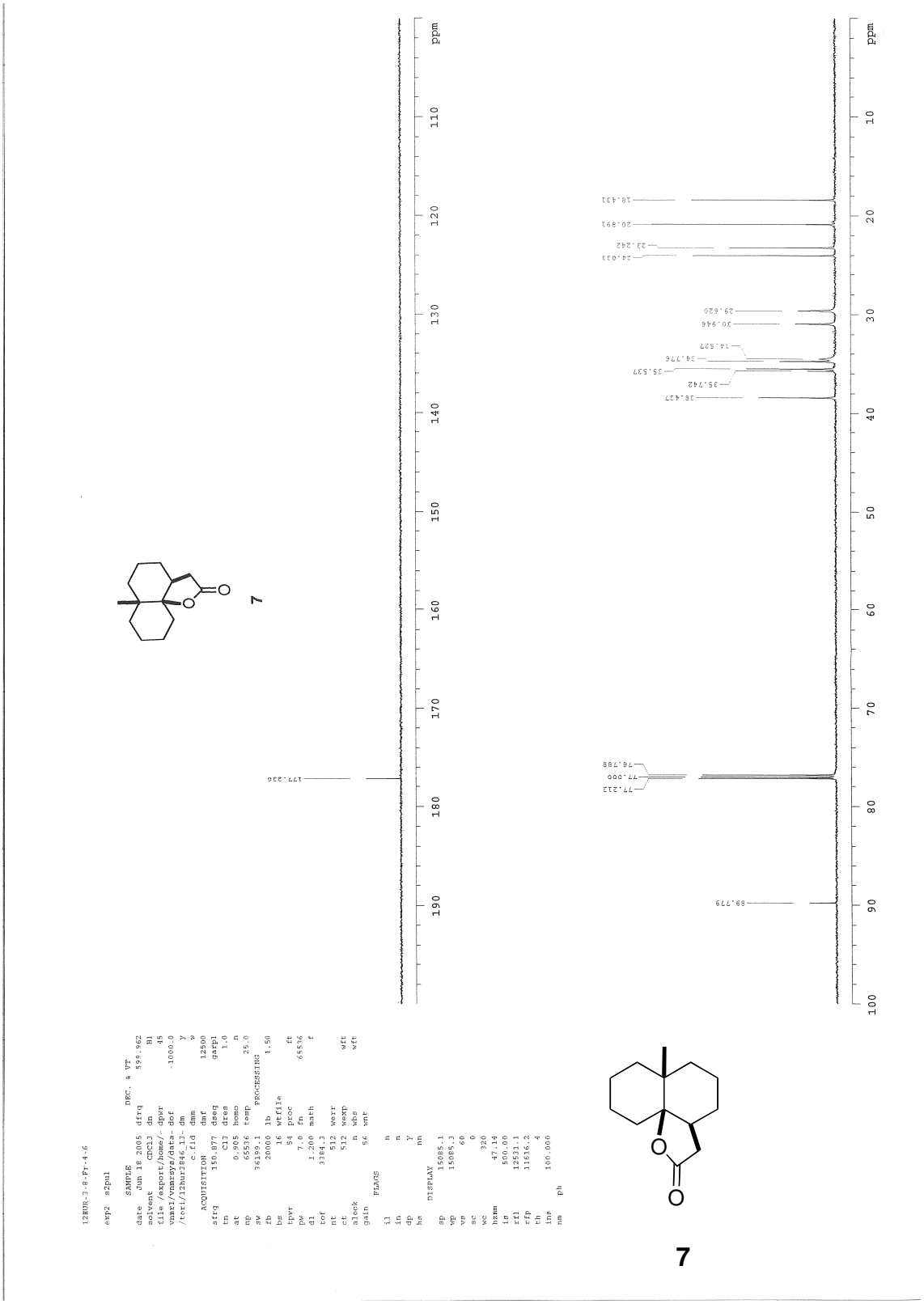
200MHz ^{1}H NMR of Compound **6**



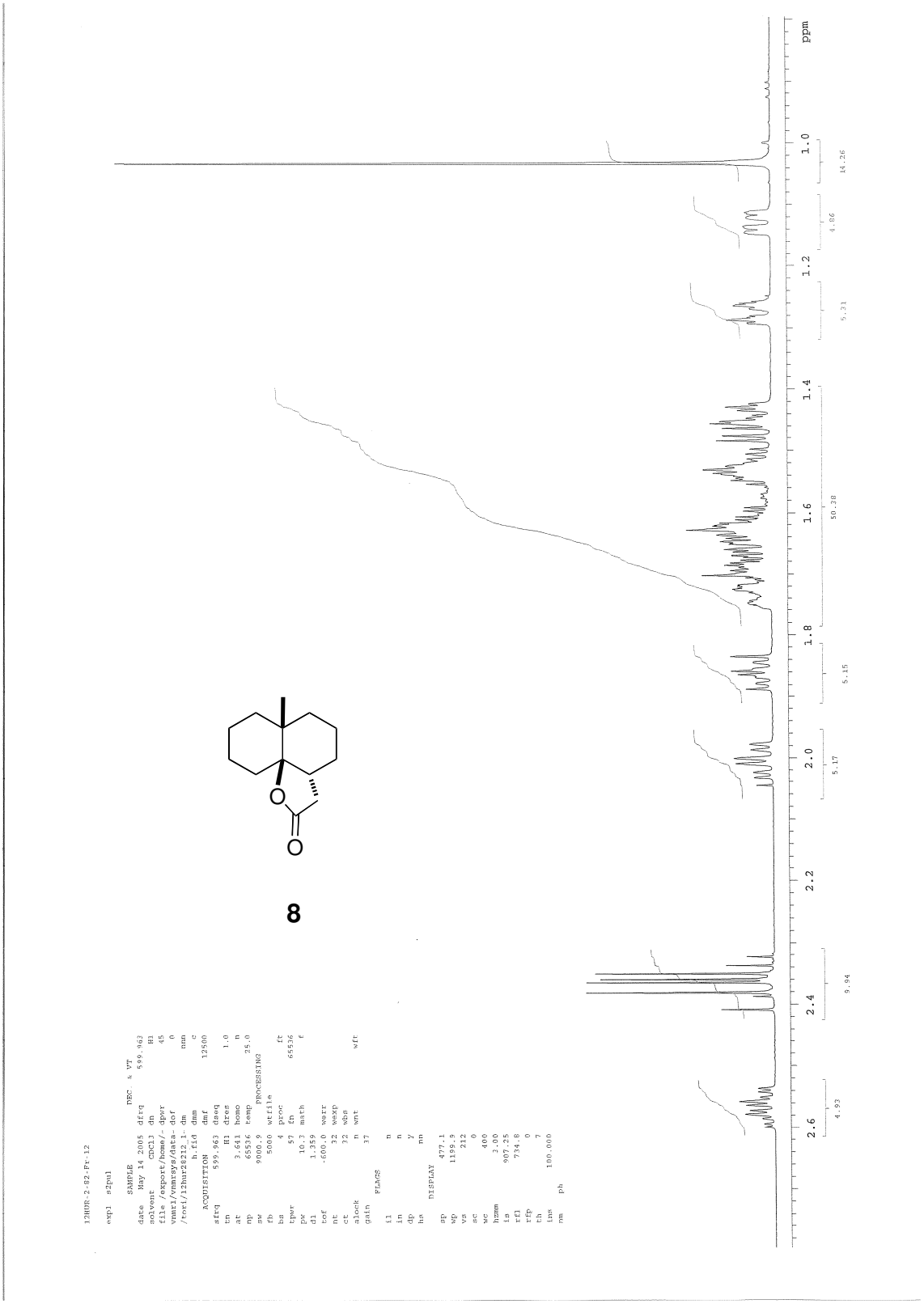
50MHz ^{13}C NMR of Compound **6**



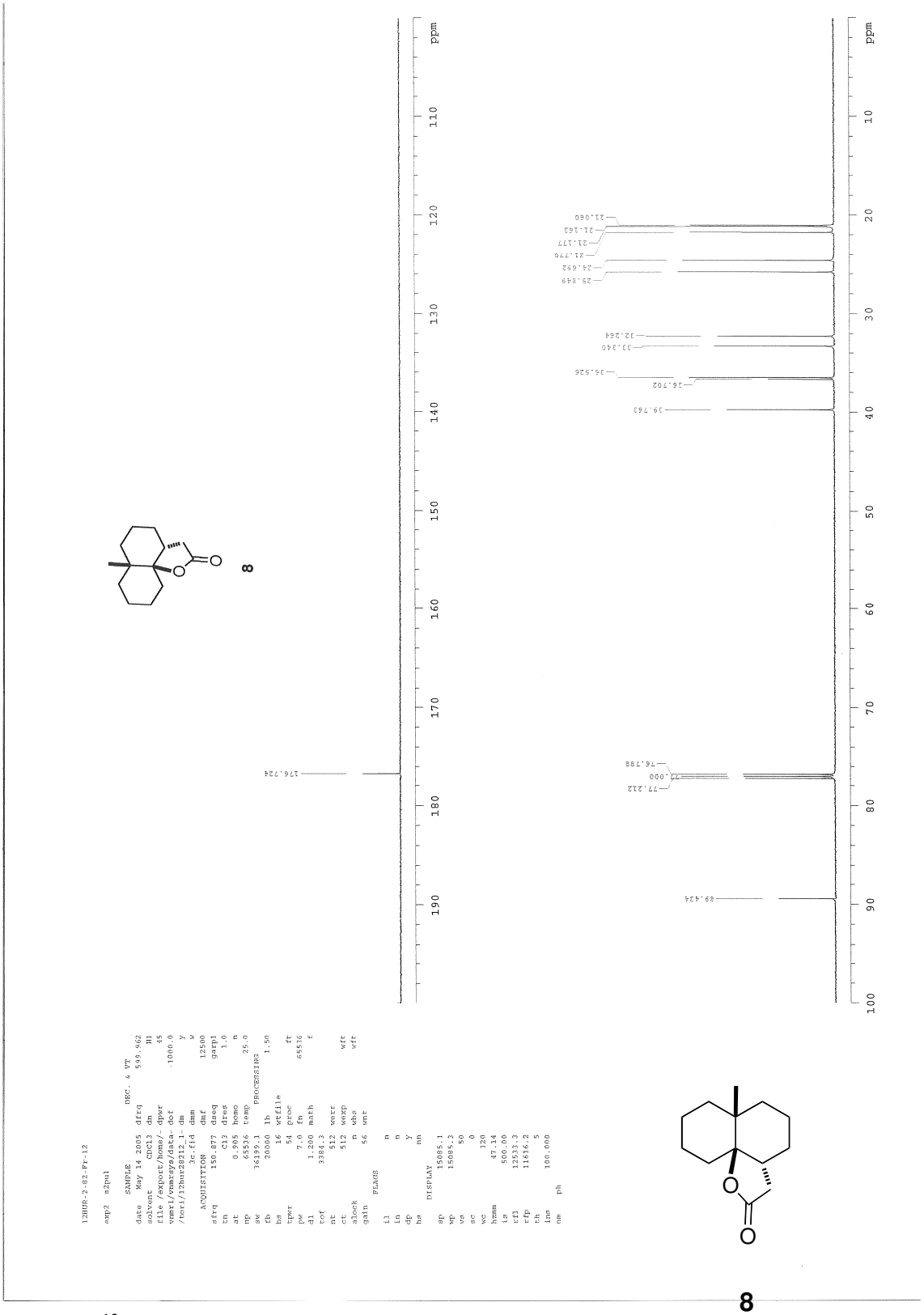
600MHz ^{1}H NMR of Compound **7**



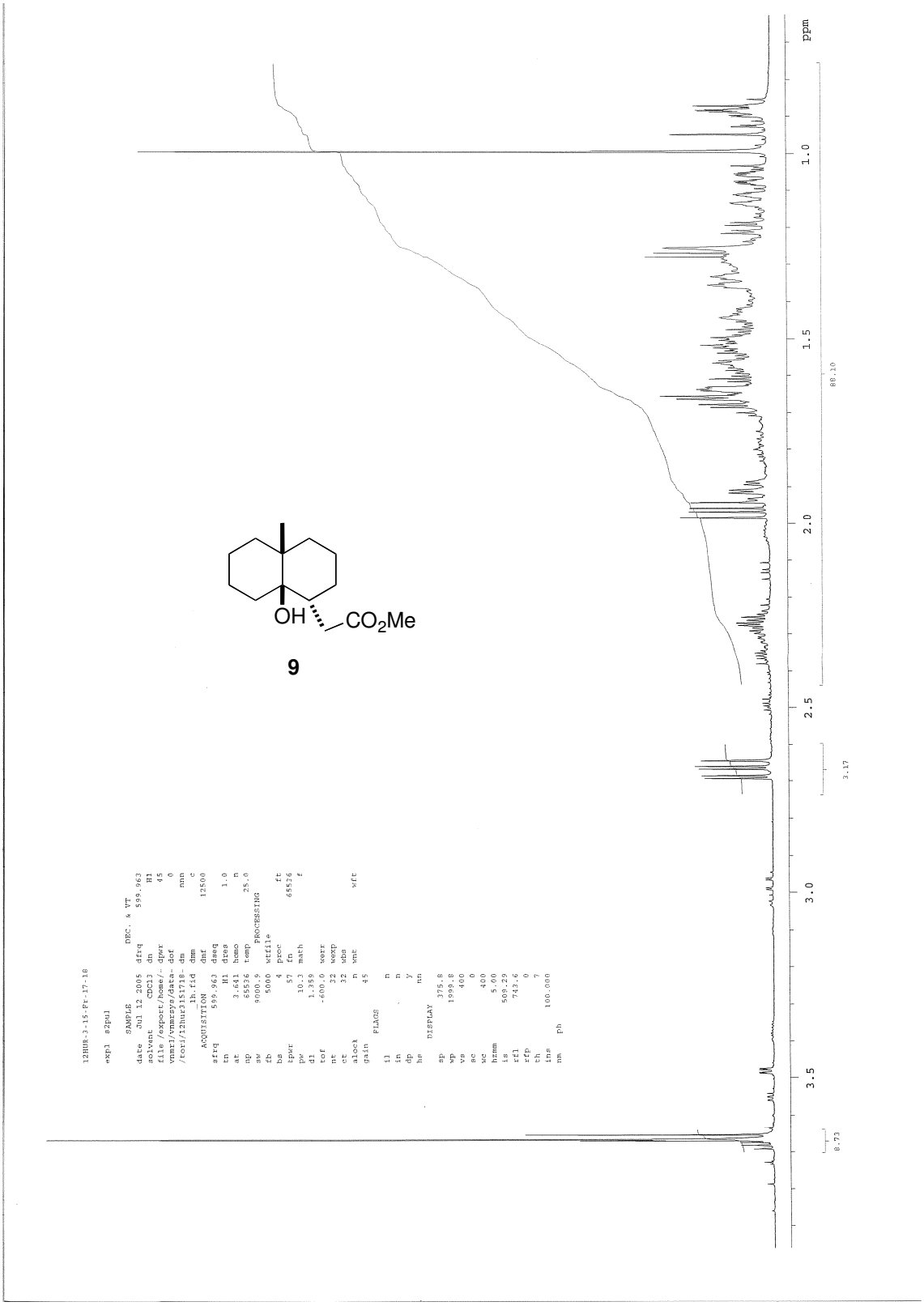
150MHz ^{13}C NMR of Compound **7**



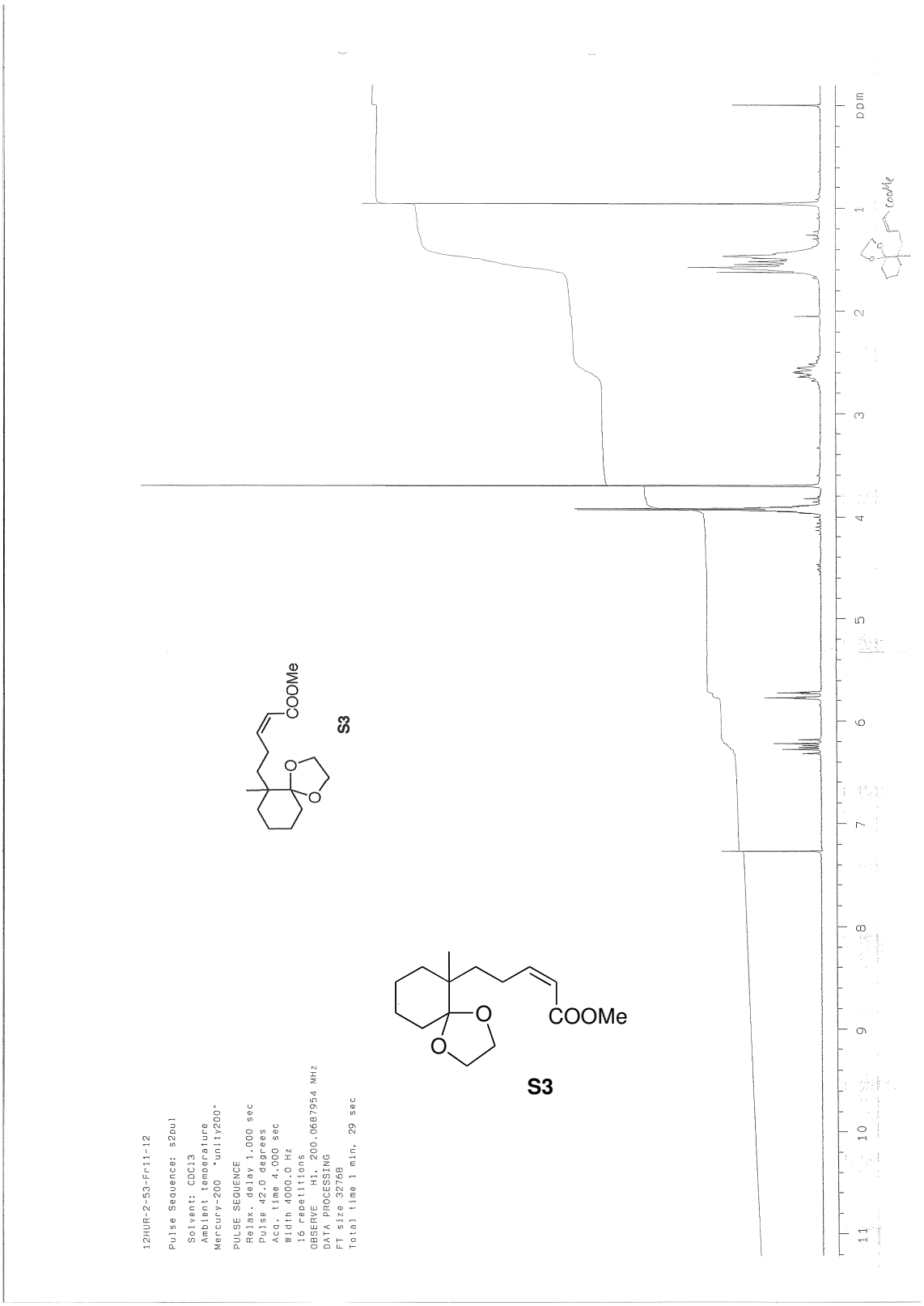
600MHz ^{1}H NMR of Compound **8**



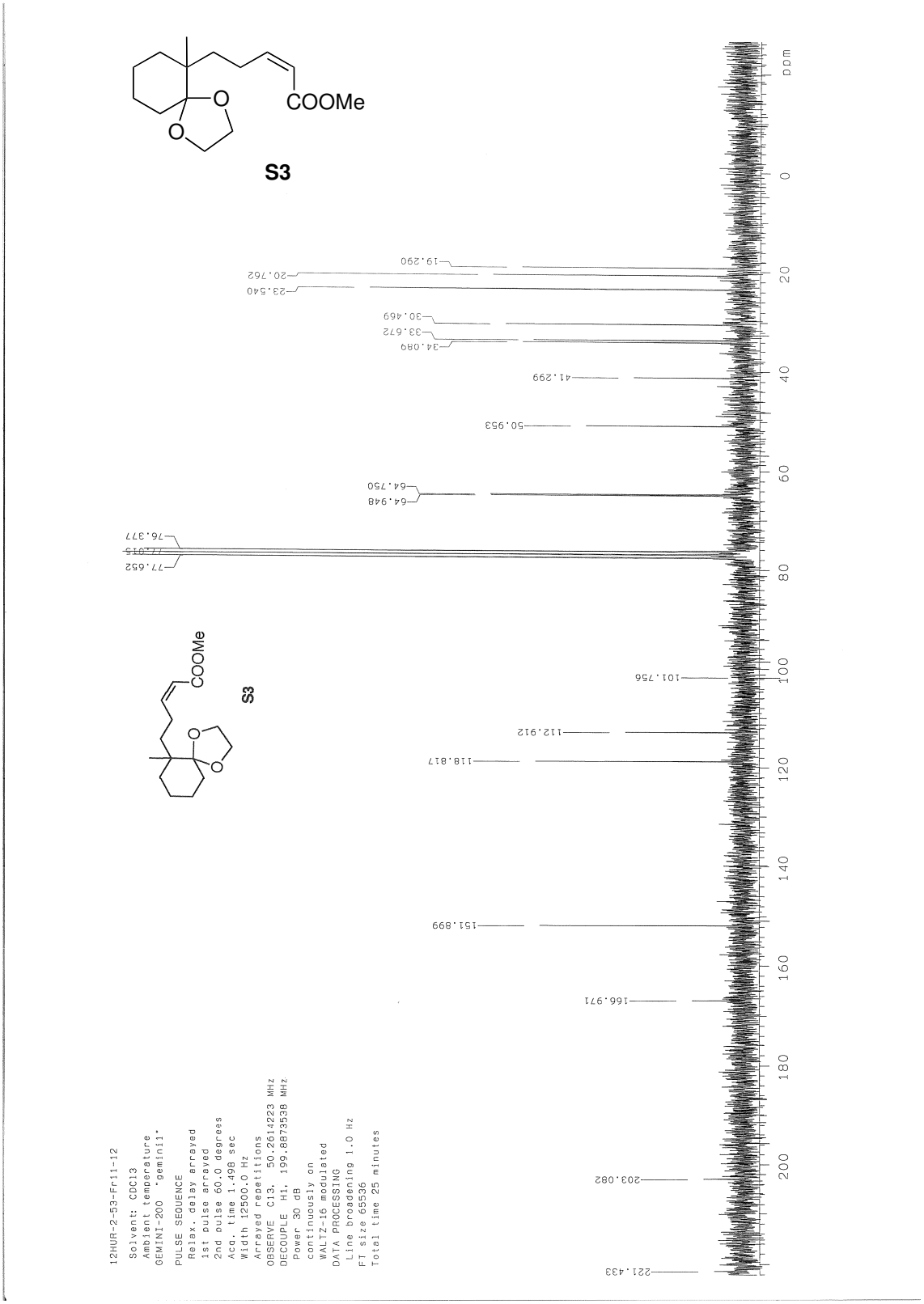
150MHz ^{13}C NMR of Compound **8**



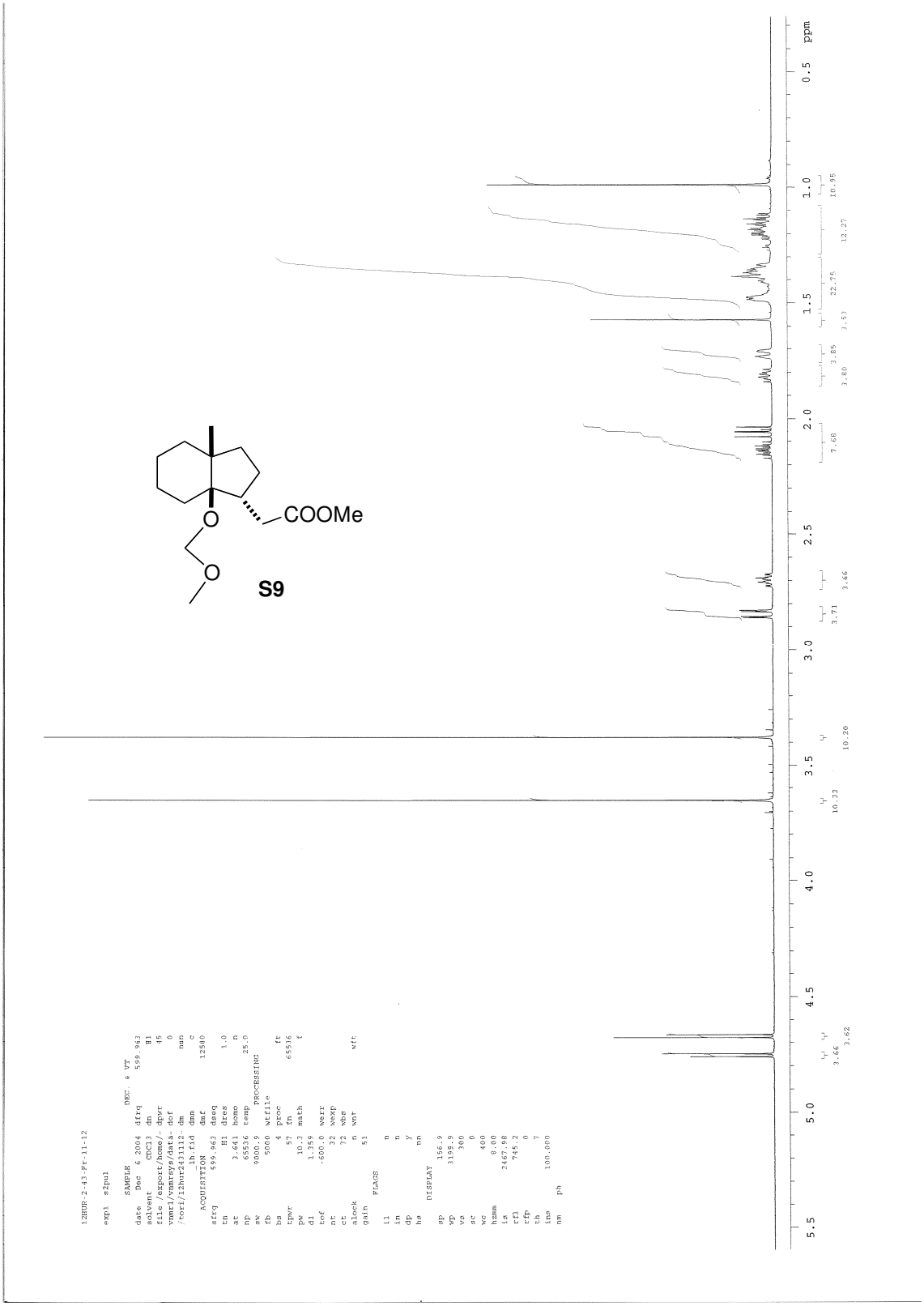
600MHz ^{1}H NMR of Compound **9**



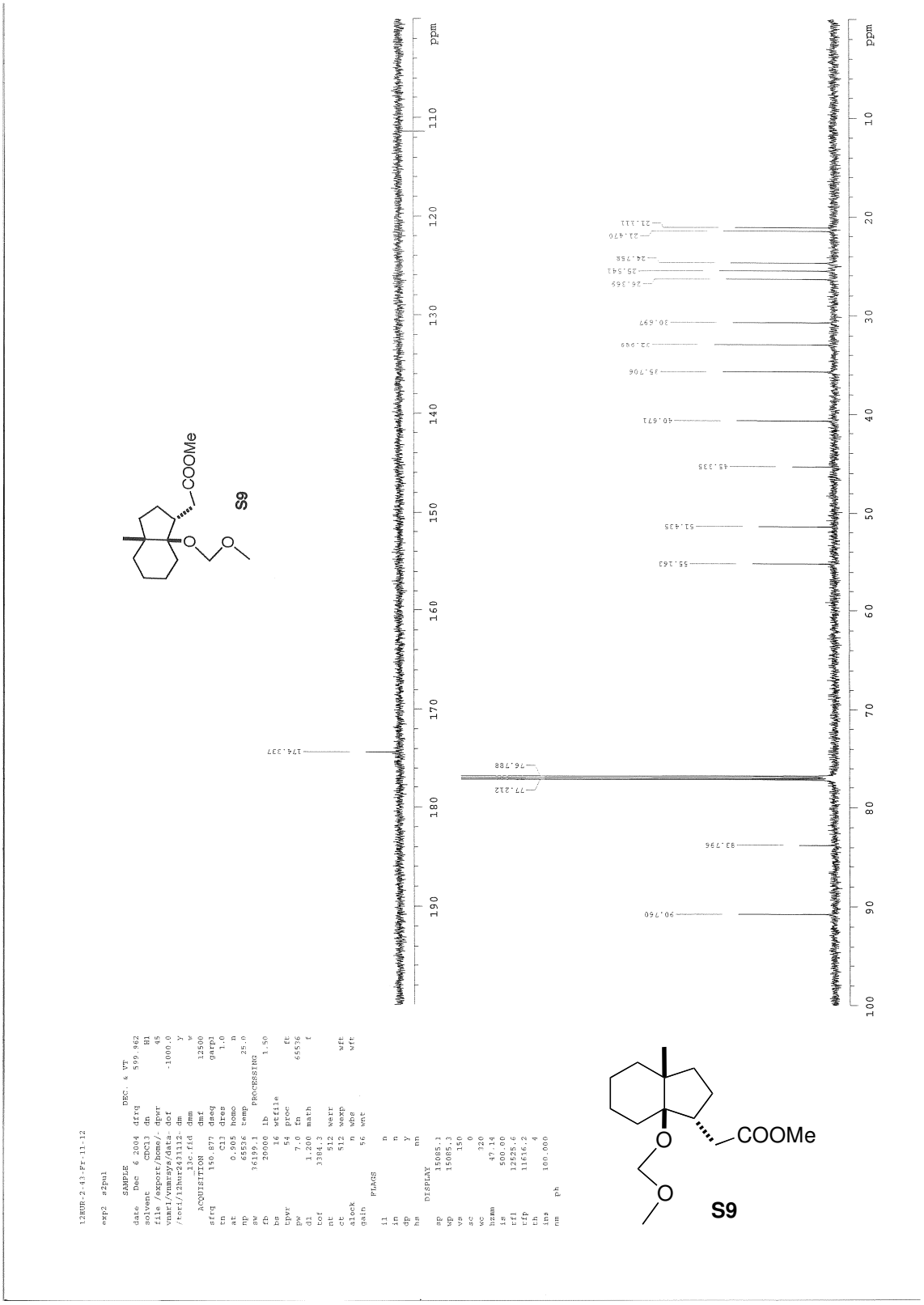
200MHz ^{1}H NMR of Compound **S3**



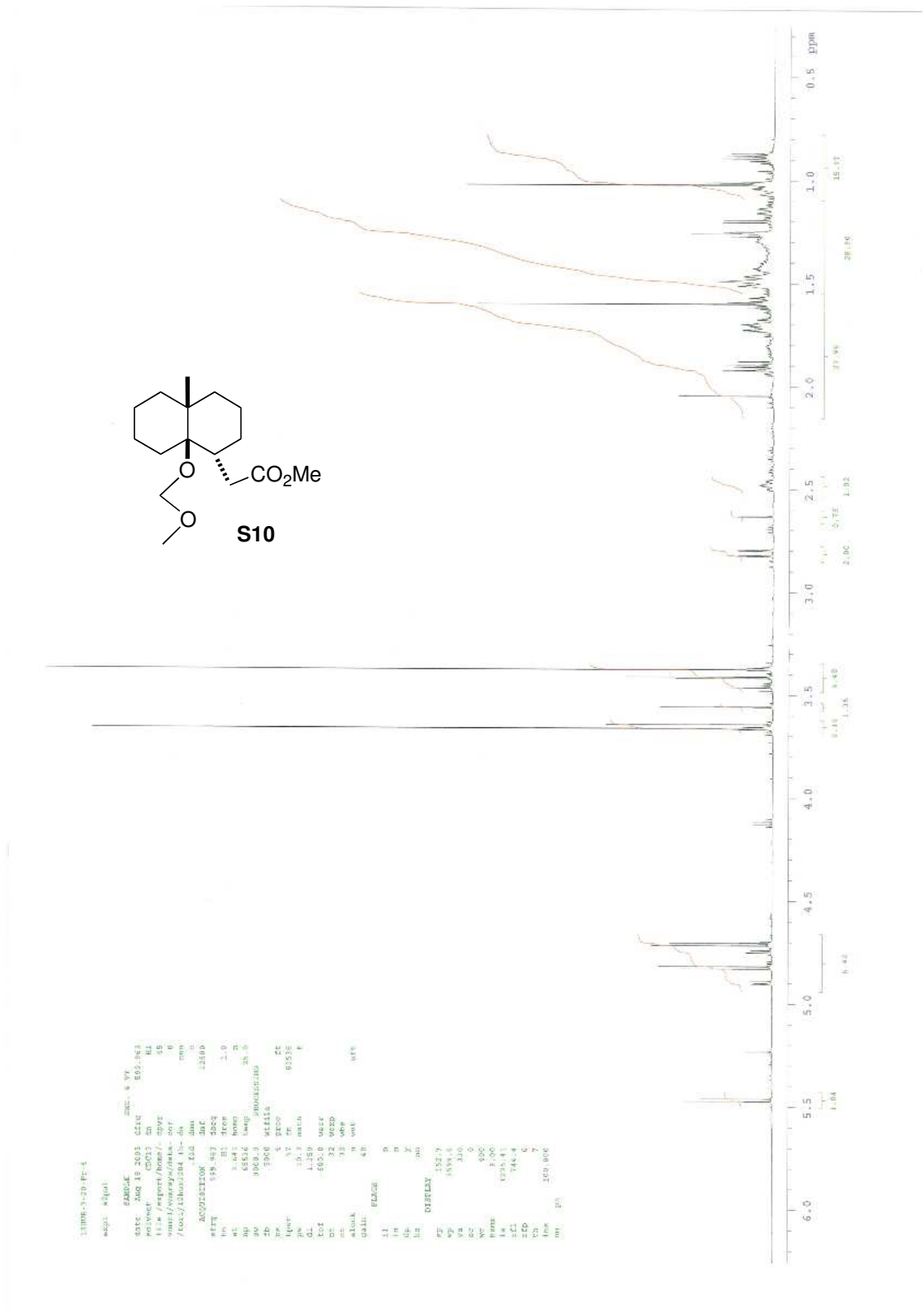
50MHz ^{13}C NMR of Compound **S3**



600MHz ^{1}H NMR of Compound **S9**



150MHz ^{13}C NMR of Compound **S9**



600MHz ^{1}H NMR of Compound **S10**