

Supporting Information

The Total Synthesis of (±)-Montanin A and (±)-Teuscorolide

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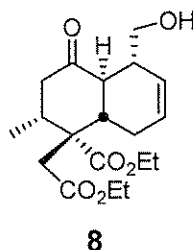
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1) General remarks

All of starting materials and reagents were obtained from commercial suppliers (Merck or Aldrich) and used without further purification. Reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF) and ethyl ether were distilled from sodium-benzophenone, ethanol was distilled from magnesium/iodine, benzene and dichloromethane (CH_2Cl_2) was distilled from calcium hydride before use. TLC analysis was carried out on Merck 25 DC-Alufolien Kieselgel 60F₂₅₄ aluminum-backed plates visualised by using UV light, or by means of ethanolic solution of vanillin (5%) with sulphuric acid (5%). All of the products were purified by flash chromatography using Merck Art.9385 Kieselgel 60 silica gel (230-400 mesh). NMR spectra (^1H , ^{13}C) were recorded on a Brücker 400 spectrometer using deuteriochloroform (CDCl_3) as solvent. Chemical shifts measurements are reported in delta (δ) units. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). Coupling constants (J) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Bomem MB-100FT spectrophotometer (KBr pellets) and resonances are reported in wave numbers (cm^{-1}). High resolution mass spectra (HRMS) were determined by using a A. E. I. model MS-50 mass spectrometer in electron impact (EI) or fast atom bombardment (FAB) modes.

2) Experimental Section and Characterization of Compound 8-16, 20, 5, 6

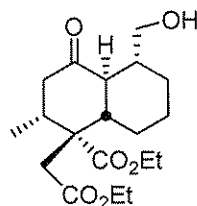
(1*R**,4*R**,5*R**,6*S**,10*R**)-5-carbethoxy-5-(carbethoxymethyl)-10-(hydroxymethyl)-4-methylbicyclo[4.4.0]dec-8-en-2-one (8)



To a solution of compound 7 (182 mg, 0.48 mmol) in ethanol (10 mL) at room temperature under nitrogen was added NaH (60% purity, 39 mg, 0.97 mmol) in one portion. The resulting mixture was stirred for 12 h, and then quenched with saturated aqueous NH_4Cl (10 mL). The mixture was extracted with ether (3 x 20 mL). The combined organic extracts were washed with water (2 x 20 mL) and brine (30 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude

product thus obtained was purified with flash chromatography on silica gel (ethyl acetate:*n*-hexane=1:4) to give compound **8** (161 mg, 0.46 mmol, 95%) as a pale yellow liquid. IR (film): ν 3467, 1712, 1196 cm^{-1} . ^1H -NMR (CDCl_3 , 400 MHz): δ 5.58-5.60 (m, 1H), 5.47 (br d, $J = 10.5$ Hz, 1H), 4.11 (qd, $J = 7.1, 0.9$ Hz, 2H), 3.90-4.00 (m, 2H), 3.47 (dd, $J = 10.5, 4.4$ Hz, 1H), 3.36 (dd, $J = 10.5, 5.0$ Hz, 1H), 3.02 (dd, $J = 12.0, 9.62$ Hz, 1H), 2.69-2.84 (m, 3H), 2.61-2.62 (m, 1H), 2.47 (br s, 1H), 2.22-2.32 (m, 2H), 2.12 (dd, $J = 13.1, 4.46$ Hz, 1H), 2.05 (td, $J = 12.2, 4.6$ Hz, 1H), 1.64-1.72 (m, 1H), 1.17 (t, $J = 7.1$ Hz, 3H), 1.06 (t, $J = 7.1$, 3H), 0.88 (d, $J = 6.7$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 100MHz): δ 211.5 (C), 171.9 (C), 170.4 (C), 127.7 (CH_3), 125.7 (CH_3), 65.5 (CH_2), 60.8 (CH_2), 60.2 (CH_2), 51.9 (C), 47.0 (CH), 46.2 (CH_2), 42.5 (CH), 37.9 (CH), 37.2 (CH), 35.7 (CH_2), 27.1 (CH_2), 17.1 (CH), 14.0 (CH), 13.8 (CH). HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{28}\text{O}_6$: 352.1886, found: 352.1878.

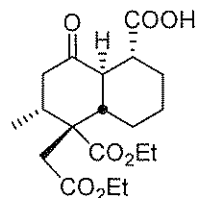
(1*R,4*R**,5*R**,6*S**,10*R**)-5-Carbethoxy-5-(carbethoxymethyl)-10-(hydroxymethyl)-4-methylbicyclo[4.4.0]dec-8-en-2-one (9)**



9

The mixture of compound **8** (120 mg, 0.34 mmol) and catalytic amount of Pd/C (10% w/w, 10 mg) was stirred in ethyl acetate (50 mL) at room temperature under high pressure of hydrogen (50 psi). After 2 h, the reaction mixture was filtered with celite and then concentrated. The crude product thus obtained was purified with flash chromatography on silica gel (ethyl acetate:*n*-hexane=1:4) to give compound **9** (118 mg, 0.33 mmol, 98%) as a colorless liquid. IR (film): ν 3446, 2929, 1723, 1190 cm^{-1} . ^1H -NMR (CDCl_3 , 400 MHz): δ 4.06-4.12 (m, 2H), 3.89-3.99 (m, 2H), 3.41 (dd, $J = 12.0, 3.9$ Hz, 1H), 3.27 (dd, $J = 12.0, 4.7$ Hz, 1H), 2.78-2.86 (m, 2H), 2.77 (d, $J = 14.8, 1\text{H}$), 2.62 (d, $J = 14.8, 1\text{H}$), 2.20-2.24 (m, 1H), 2.03 (dd, $J = 12.0, 4.6$ Hz, 1H), 1.18-1.91 (m, 1H), 1.58-1.71 (m, 4H), 1.17 (t, $J = 7.1$ Hz, 3H), 1.07 (t, $J = 7.3$ Hz, 3H), 0.85 (d, $J = 5.9$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 100MHz): δ 213.1 (C), 171.9 (C), 170.4 (C), 66.5 (CH_2), 60.7 (CH_2), 60.2 (CH_2), 52.1 (C), 51.1 (CH), 47.5 (CH), 46.9 (CH_2), 38.7 (CH), 38.5 (CH), 35.8 (CH_2), 28.6 (CH_2), 27.9 (CH_2), 24.8 (CH_2), 17.1 (CH_3), 14.1 (CH_3), 13.9 (CH_3). HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{30}\text{O}_6$: 354.2042, found: 354.2061. Anal. calcd. for $\text{C}_{19}\text{H}_{30}\text{O}_6$: C, 64.38; H, 8.53. Found: C, 64.08; H, 8.54.

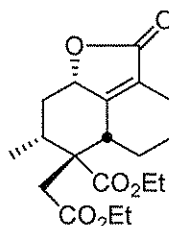
(1*R,4*R**,5*R**,6*S**,10*R**)-5-Carbethoxy-5-(carbethoxymethyl)-4-methyl-2-oxo-10-bicyclo[4.4.0]decanecarboxylic acid (10)**



10

To a solution of compound **9** (366 mg, 1.03 mmol) in acetone (35 mL) at 0 °C was added Jones reagent (5 mL) dropwise. After the reaction was complete, the mixture was diluted with CH₂Cl₂ (40 mL), quenched with water (20 mL) and allowed to warm to room temperature. The aqueous layer was separated and extracted with CH₂Cl₂ (3 x 10 mL). The combined organic extracts was washed with water (30 mL) and brine, dried over anhydrous magnesium sulfate, filtered and concentrated. The crude residue was purified with flash chromatography on silica gel (methanol:CH₂Cl₂=1:1) to give compound **10** (365 mg, 98.88 μmol, 96%) as a colorless liquid. IR (film): ν 2500-3500, 2938, 1715 and 1191 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ 4.24 (q, *J* = 6.6 Hz, 1H), 4.23 (q, *J* = 6.7 Hz, 1H), 4.08 (m, 2H), 3.24 (dd, *J* = 12.1, 12.0 Hz, 1H), 2.85-2.97 (m, 1H), 2.90 (d, *J* = 14.6 Hz, 1H), 2.79 (d, *J* = 14.7 Hz, 1H), 2.17-2.42 (m, 3H), 1.98-2.09 (m, 3H), 1.78-1.89 (m, 2H), 1.31 (t, *J* = 6.8 Hz, 3H), 1.16-1.34 (m, 2H), 1.20 (t, *J* = 6.6 Hz, 3H) and 0.98 (d, *J* = 6.5 Hz, 3H). ¹³C-NMR (CDCl₃, 100MHz): δ 209.7 (C), 181.2 (C), 171.9 (C), 170.7 (C), 61.0 (CH₂), 60.5 (CH₂), 51.9 (C), 50.5 (CH), 45.8 (C), 45.3 (CH₂), 43.2 (CH), 37.4 (CH), 35.8 (CH₂), 29.1 (CH₂), 27.7 (CH₂), 25.0 (CH₂), 17.2 (CH₃), 14.3 (CH₃), 14.1 (CH₃). HRMS (EI) calcd. for C₁₉H₂₈O₇: 368.1835, found: 368.1832.

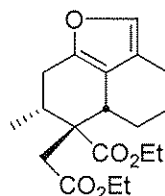
(4*S,6*R**,7*R**,8*S**)-7-Carbethoxy-7-(carbethoxymethyl)-6-methyl-3-oxatricyclo[6.3.1.0^{4,12}]dodec-1-en-2-one (11)**



11

To a solution of *p*-toluenesulfonyl acid (684 mg, 3.80 mmol) in benzene (20 mL) under nitrogen was added compound **10** (350 mg, 0.95 mmol) at room temperature. The resulting mixture was heated to reflux with Dean-Stark separator for 12 h, and then cooled to room temperature, diluted with CH₂Cl₂ (20 mL) and neutralized with saturated aqueous NaHCO₃ (25 mL). The aqueous layer was separated and extracted with CH₂Cl₂ (3 x 15 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product thus obtained was purified with flash chromatography on silica gel (ethyl acetate; methanol:CH₂Cl₂=1:1) to afford compound **11** (283 mg, 3.23 mmol, 85%) as a colorless liquid. IR (film): ν 2939, 1755 and 1721 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ 4.76 (m, 1H), 4.17 (q, *J* = 6.7, 1.9 Hz, 2H), 4.09 (q, *J* = 6.6 Hz, 2H), 3.17 (m, 1H), 3.04 (d, *J* = 14.6, 1H), 2.70 (d, *J* = 14.8 Hz, 1H), 1.79-2.37 (m, 8H), 1.45-1.61 (m, 1H), 1.28 (t, *J* = 6.7 Hz, 3H), 1.20 (t, *J* = 6.6 Hz, 3H) and 0.99 (d, *J* = 6.7 Hz, 3H). ¹³C-NMR (CDCl₃, 100MHz): δ 173.2 (C), 171.3 (C), 171.0 (C), 164.4 (C), 124.7 (C), 78.0 (CH), 60.8 (CH₂), 60.5 (CH₂), 54.5 (C), 36.7 (CH₃), 36.1 (CH₂), 35.6 (CH₂), 32.9 (CH), 23.8 (CH₂), 21.8 (CH₂), 19.4 (CH₂), 16.3 (CH₃), 14.0 (CH₃), 13.9 (CH₃). HRMS (EI) calcd. for C₁₉H₂₆O₆: 350.1729, found: 350.1723.

(6*R,7*R**,8*S**)-7-Carbethoxy-7-(hydroxyethyl)-6-methyl-3-oxatricyclo[6.3.1.0^{4,12}]dodec-1,4-diene (**12**)**

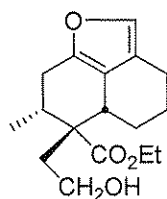


12

To a solution of compound **11** (232 mg, 0.66 mmol) in THF (15 mL) at -40 °C under an atmosphere of nitrogen was added Dibal-H (1.0M in hexane, 0.99 mmol, 1 mL) slowly. The resulting mixture was stirred at -40 °C for 25 min, quenched with aqueous 6*N* HCl carefully to reach PH=2, and the mixture was allowed to warm to room temperature. The aqueous layer was extracted with ether (2 x 10 mL). The combined organic extracts were washed with water (2 x 10 mL) and brine (30 mL), dried over anhydrous magnesium sulfate, filtered and concentrated. The crude residue was purified with flash chromatography on silica gel (ethyl acetate: *n*-hexane =1:10) to provide compound **12** (156 mg, 0.53 mmol, 80%) as a colorless liquid. IR (film): ν 3439, 2933, 1722, 1188 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ 7.00 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.39-4.03 (m, 2H), 2.94-2.97 (m, 1H), 2.98 (d, *J* = 14.9 Hz, 1H), 2.84 (d, *J* = 14.9 Hz, 1H), 2.60-2.66 (m, 1H), 2.54 (td, *J* = 10.4, 2.3 Hz, 1H), 2.25-2.44 (m,

3H), 1.94-2.02 (m, 3H), 1.48-1.59 (m, 1H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.12 (d, $J = 6.7$ Hz, 3H), 1.12 (d, $J = 6.7$ Hz, 3H), 1.05 (t, $J = 7.1$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 100MHz): δ 172.0 (C), 171.4 (C), 147.4 (C), 135.5 (CH), 120.2 (C), 118.2 (C), 60.4 (CH_2), 60.1 (CH_2), 51.3 (C), 38.1 (CH), 36.6 (CH_2), 35.5 (CH), 31.0 (CH_2), 24.9 (CH_2), 23.9 (CH_2), 19.3 (CH_2), 17.2 (CH_3), 14.2 (CH_3), 14.1 (CH_3). HRMS (FAB) calcd. for $\text{C}_{19}\text{H}_{27}\text{O}_5$ $[\text{M}+1]^+$: 335.1859, found: 335.1857.

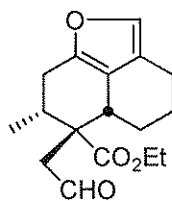
(6*R,7*R**,8*S**)-7-Carbethoxy-7-(hydroxyethyl)-6-methyl-3-oxatricyclo[6.3.1.0^{4,12}]dodec-1,4-diene (13)**



13

To a solution of compound **11** (232 mg, 0.66 mmol) in THF (15 mL) at -40 °C under an atmosphere of nitrogen was added Dibal-H (1.0M in hexane, 2.64 mmol, 2.6 mL) slowly. The resulting mixture was stirred at -40 °C for 25 min, quenched with aqueous 6N HCl carefully to reach PH=2, and the mixture was allowed to warm to room temperature. The aqueous layer was extracted with ether (2 x 10 mL). The combined organic extracts were washed with water (2 x 10 mL) and brine (30 mL), dried over anhydrous magnesium sulfate, filtered and concentrated. The crude residue was purified with flash chromatography on silica gel (ethyl acetate: *n*-hexane =1:10) to provide compound **13** (164 mg, 0.56 mmol, 85%) as a colorless liquid. IR (film): ν 2927, 1736, 1179 cm^{-1} . ^1H -NMR (CDCl_3 , 400 MHz): δ 6.99 (s, 1H), 3.90-4.02 (m, 2H), 3.77 (t, $J = 7.4$ Hz, 2H), 2.50-2.72 (m, 4H), 2.33 (td, $J = 13.4, 5.04$ Hz, 1H), 2.01-2.22 (m, 3H), 1.96 (dd, $J = 10.96, 4.2$ Hz, 2H), 1.72 (br s, 1H), 1.52 (qd, $J = 12.8, 6.2$ Hz, 1H), 1.08 (d, $J = 6.8$ Hz, 3H), 1.04 (t, $J = 7.0$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 100MHz): δ 173.4 (C), 147.5 (C), 135.6 (C), 120.2 (C), 118.4 (C), 59.9 (CH_2), 58.9 (CH_2), 51.0 (C), 38.1 (CH), 35.9 (CH), 34.9 (CH_2), 31.0 (CH_2), 25.3 (CH_2), 24.0 (CH_2), 19.3 (CH_2), 17.1 (CH_3), 14.1 (CH_3). HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_4$: 292.1675, found: 292.1670.

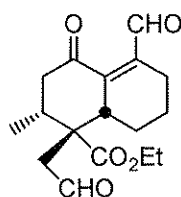
(6*R,7*R**,8*S**)-7-Carbethoxy-7-(formylethyl)-6-methyl-3-oxatricyclo[6.3.1.0^{4,12}]dodec-1,4-diene (14)**



14

To a solution of compound **13** (106 mg, 0.36 mmol) in benzene (12 mL) at room temperature under a nitrogen atmosphere was added silver carbonate on celite (1.65 g, 1.76 mmol/g, 2.90 mmol). The resulting slurry was heated under reflux for 2 days, allowed to cool to room temperature and filtered. The cake was washed well with ether, and the solvents were removed from the combined filtrates to give the crude product. The crude residue was submitted to flash chromatography on silica gel (ethyl acetate: *n*-hexane =1:5), giving compound **14** (93 mg, 0.32 mmol, 88%) as a colorless liquid. ¹H-NMR (CDCl₃, 400 MHz): δ 9.85 (t, *J* = 2.32 Hz, 1H), 6.97 (s, 1H), 3.93-4.02 (m, 2H), 2.82 (s, 2H), 2.54-2.74 (m, 4H), 2.24-2.35 (m, 2H), 1.87-1.97 (m, 2H), 1.49 (qd, *J* = 12.8, 4.8 Hz, 1H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.04 (t, *J* = 7.14 Hz, 3H). ¹³C-NMR (CDCl₃, 100MHz): δ 201.9 (CH), 171.7 (C), 147.6 (C), 135.8 (CH), 120.1 (C), 117.8 (C), 60.3 (CH₂), 51.3 (C), 47.5 (CH₂), 40.1 (CH), 37.3 (CH), 31.0 (CH₂), 25.4 (CH₂), 23.9 (CH₂), 19.2 (CH₂), 17.4 (CH₃), 14.1 (CH₃). HRMS (EI) calcd. for C₁₇H₂₂O₄: 290.1518, found: 290.1514.

(4*R,5*R**,6*S**)-5-Carbethoxy-5-(formylmethyl)-4-methylbicyclo-[4.4.0]dec-10-en-2-one (**15**) :**

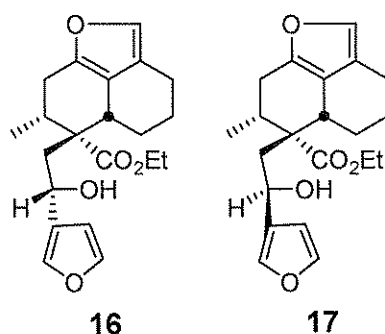


15

To a solution of compound **13** (32 mg, 0.11 mmol) in CH₂Cl₂ (5 mL) at 0 °C was added PCC (95 mg, 0.44 mmol) under a nitrogen atmosphere. The resulting mixture was stirred for 12 h, filtered with celite, and the solvent was removed from the filtrate to provide the crude product. Purification with flash chromatography on silica gel (ethyl acetate: *n*-hexane =1:5) gave the compound **15** (32 mg, 0.06 mmol, 50%) as a colorless liquid and **14** (6 mg, 0.02 mmol, 16%). The spectral data of compound **15**: ¹H-NMR (CDCl₃, 400 MHz) : δ 9.84 (s, 1H), 9.68 (s, 1H), 4.09-4.21 (m, 2H), 3.11 (dd, *J* = 14.2, 1.1 Hz, 1H), 3.01 (dd, *J* = 14.1, 1.4 Hz, 1H), 2.55-2.71 (m, 3H),

2.00-2.04 (m, 1H), 1.84-1.97 (m, 3H), 1.58 (br d, $J = 5.6$ Hz, 3H), 1.21 (t, $J = 5.8$ Hz, 3H), 1.03 (d, $J = 5.1$ Hz, 3H).

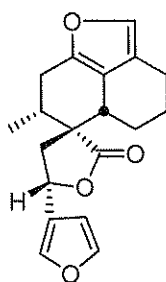
(8*R,9*R**,10*S**,12*S**)-7-Carbethoxy-7-((3-furyl)hydroxyethyl)-6-mehtyl-3-oxatricyclo[6.3.1.0^{4,12}]dodec-1,4-diene (16) and (8*R**,9*R**,10*S**,12*R**)-7-carbethoxy-7-((3-furyl)hydroxyethyl)-6-mehtyl-3-oxatricyclo[6.3.1.0^{4,12}]dodec-1,4-diene (17)**



To a solution of compound **14** (52 mg, 0.18 mmol) in ether (8 mL) at -78°C under an atmosphere of nitrogen was added freshly prepared solution of 3-lithiofuran (0.236M in diethyl ether, 1.5 mL, 0.36 mmol), and the mixture was stirred for 40 min. The reaction was quenched with water (4 mL) dropwise and allowed to warm to room temperature. The aqueous layer was separated and extracted with ether (3 x 4 mL). The combined extracts were washed with brine (10 mL), dried over anhydrous magnesium sulfate, and the solvents were evaporated under reduced pressure. The resulting residue was submitted to flash chromatography on silica gel (ethyl acetate: *n*-hexane = 1:10) to provide separated diastereomers **16** (26 mg, 0.07 mmol, 40%) and **17** (27 mg, 0.07 mmol, 42%) as colorless liquid. The spectral data of compound **17**: ¹H-NMR (CDCl₃, 400 MHz): δ 7.39 (s, 1H), 7.36 (d, $J = 0.9$ Hz, 1H), 7.00 (s, 1H), 6.42 (s, 1H), 4.90 (d, $J = 7.6$ Hz, 1H), 3.92-4.01 (m, 2H), 3.13 (br d, $J = 9.4$ Hz, 1H), 2.83 (br s, 1H), 2.68 (td, $J = 13.0, 4.7$ Hz, 2H), 2.57 (d, $J = 1.71$ Hz, 1H), 2.48-2.57 (m, 3H), 2.30-2.36 (m, 3H), 2.13-2.19 (m, 2H), 2.00 (dd, $J = 12.3, 1.4$ Hz, 1H), 1.95-1.99 (m, 2H), 1.52-1.63 (m, 2H), 1.03 (t, $J = 5.6$ Hz, 3H), 1.02 (d, $J = 5.4$ Hz, 3H). ¹³C-NMR (CDCl₃, 100MHz): δ 174.4 (C), 147.2 (C), 143.4 (CH), 138.5 (CH), 130.8 (CH), 63.5 (CH), 60.1 (CH₂), 51.6 (C), 41.3 (CH₂), 38.4 (CH), 36.4 (CH), 31.1 (CH₂), 25.9 (CH₂), 24.0 (CH₂), 19.3 (CH₂), 17.3 (CH₃), 14.0 (CH₃). HRMS (FAB) calcd. for C₁₅H₂₇O₅[M+1]⁺: 259.1859, found: 259.1863. The spectral data of compound **16**: ¹H-NMR (CDCl₃, 400 MHz): δ 7.40 (s, 1H), 7.38 (s, 1H), 6.98 (s, 1H), 6.46 (s, 1H), 4.90 (dd, $J = 5.7, 3.2$ Hz, 1H), 3.89-4.00 (m, 2H), 2.67-2.71 (m,

4H), 2.45-2.59 (m, 6H), 2.39(dd, $J = 12.4, 5.9$ Hz, 2H), 2.25-2.33 (m, 4H), 1.80-1.92 (m, 4H), 1.34-1.48 (m, 2H), 1.17 (d, $J = 5.2$ Hz, 3H), 1.03 (t, $J = 5.7$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 100MHz): δ 173.6 (C), 147.7 (C), 143.6 (CH), 138.7 (CH), 135.5 (CH), 130.5 (C), 120.2 (C), 118.3 (C), 63.8 (CH), 59.9 (CH_2), 51.8 (C), 40.1 (CH_2), 37.8 (CH), 36.2 (CH), 31.3 (CH_2), 25.0 (CH_2), 23.9 (CH_2), 19.3 (CH_2), 17.6 (CH_3), 14.1 (CH_3). HRMS (FAB) calcd. for $\text{C}_{15}\text{H}_{27}\text{O}_5[\text{M}+1]^+$: 259.1859, found: 259.1859.

(\pm)-Montanin A {(4*S,4'*S**,6*R**,7*R**,8*S**)-6-Methyl-3-oxatricyclo-[6.3.1.0^{4,12}]dodec-1,4-diene-7-spiro-1'-[4'-(3-furyl)-3'-oxacyclopetan-2'-one] (5)}**

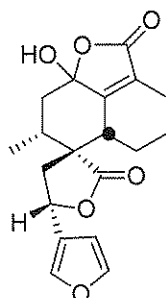


(\pm)-Montanin A (**5**)

To a solution of compound **15** (7 mg, 0.02 mmol) in THF (7 mL) at room temperature under nitrogen was added quickly lithium hydride (0.2 mg, 0.03 mmol). The resulting mixture was heated to reflux for 2 h, and allowed to cool to room temperature. The reaction was quenched with water (3 mL) and the aqueous layer was separated and extracted with ether (2 x 3 mL). The combined organic layers were washed with brine (6 mL), dried over anhydrous magnesium sulfate and the solvents were removed. The crude product thus obtained was placed onto flash chromatography column and eluted (ethyl acetate: *n*-hexane = 1:15), giving natural product **5** (6 mg, 0.02 mmol, 95%) as a colorless liquid. IR (film): ν 3055, 1762, 1423, 1265, 896, 741 cm^{-1} . ^1H -NMR (CDCl_3 , 400 MHz): δ 7.42 (m, 1H), 7.45 (s, 1H), 7.04 (bs, 1H), 6.39 (m, 1H), 5.42 (t, $J = 8.5$ Hz, 1H), 2.78 (m, 2H), 2.38-2.69 (m, 5H), 2.21-2.28 (m, 2H), 2.05-2.17 (m, 3H), 1.13 (d, $J = 6.8$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 100MHz): δ 175.5 (C), 147.9 (C), 144.1 (CH), 139.6 (CH), 136.2 (CH), 125.5 (C), 119.7 (C), 116.9 (C), 108.1 (CH), 71.6 (CH), 50.7 (C), 43.2 (CH), 39.7 (CH_2), 36.1 (CH), 30.0 (CH_2), 25.6 (CH_2), 23.9 (CH_2), 23.9 (CH_2), 17.7 (CH_3). HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_4$: 312.1362, found: 312.1362.

(4'*S,6*R**,7*R**,8*S**)-6-Methyl-4-hydroxy-3-oxatricyclo[6.3.1.0^{4,12}]dode**

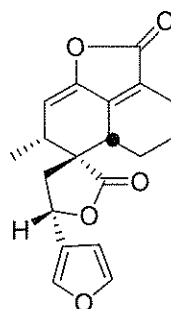
c-1-en-2-one-7-spiro-1'-[4'-(3-furyl)-3'-oxacyclopetan-2'-one] (21)



21

To a solution of compound **5** (6 mg, 0.02 mmol) in DMF (3 mL) at room temperature was added PDC (29 mg, 0.08 mmol) under a nitrogen atmosphere. The resulting mixture was stirred for 4 h, filtered with celite, and the solvent was removed from the filtrate to provide the crude product. Purification with flash chromatography on silica gel (ethyl acetate: *n*-hexane =1:2) gave the compound **21** (3 mg, 0.01 mmol, 45%) as a colorless liquid. ¹H-NMR (CDCl₃, 400 MHz): δ 7.44 (s, 1H), 7.43 (m, 1H), 6.37 (m, 1H), 5.42 (t, *J* = 8.5 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 1H), 2.53 (t, *J* = 8.0 Hz, 2H), 2.47 (t, *J* = 12.8 Hz, 1H), 2.18-2.35 (m, 1H), 2.08-2.17 (m, 4H), 1.90-2.05 (m, 4H), 1.01 (d, *J* = 7.6 Hz, 3H). ¹³C-NMR (CDCl₃, 100MHz): δ 174.6 (C), 169.5 (C), 150.9 (C), 147.9 (C), 144.3 (CH), 139.5 (CH), 125.1 (C), 124.4 (C), 107.8 (CH), 107.2 (CH), 71.6 (CH), 53.4 (C), 40.0 (CH), 39.4 (CH), 39.3 (CH₂), 23.4 (CH₂), 22.4 (CH₂), 19.4 (CH₂), 17.2 (CH₃). HRMS (FAB) calcd. for C₁₉H₂₁O₆ [M+1]⁺: 345.1337, found: 345.1338.

(±)-Teuscoloride {(4'*S,6*R**,7*R**,8*S**)-6-Methyl-3-oxatricyclo [6.3.1.0^{4,12}]dodec-1,3-dien-2-one-7-spiro-1'-[4'-(3-furyl)-3'-oxacyclopetan-2'-one] (6)}**

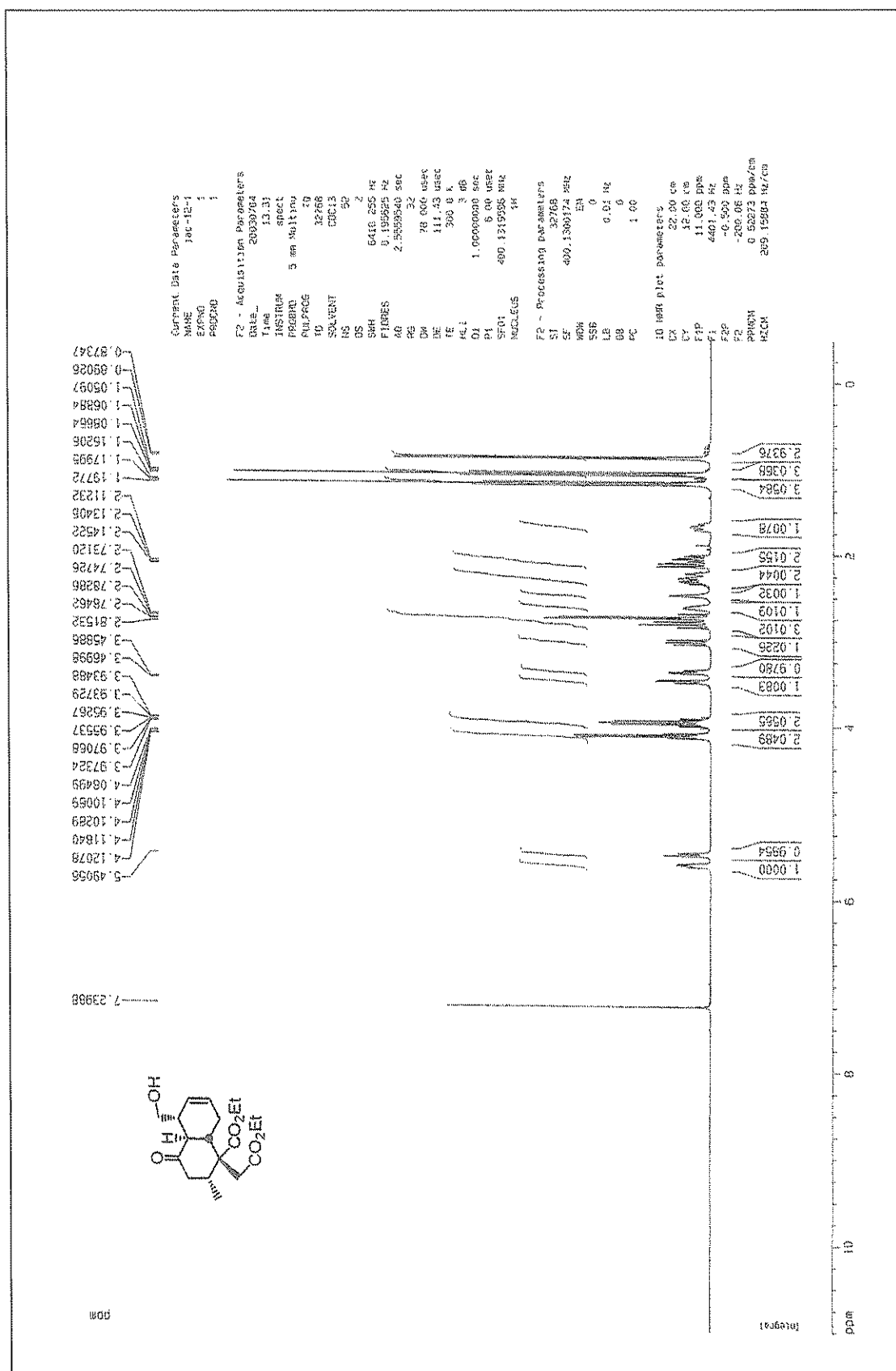


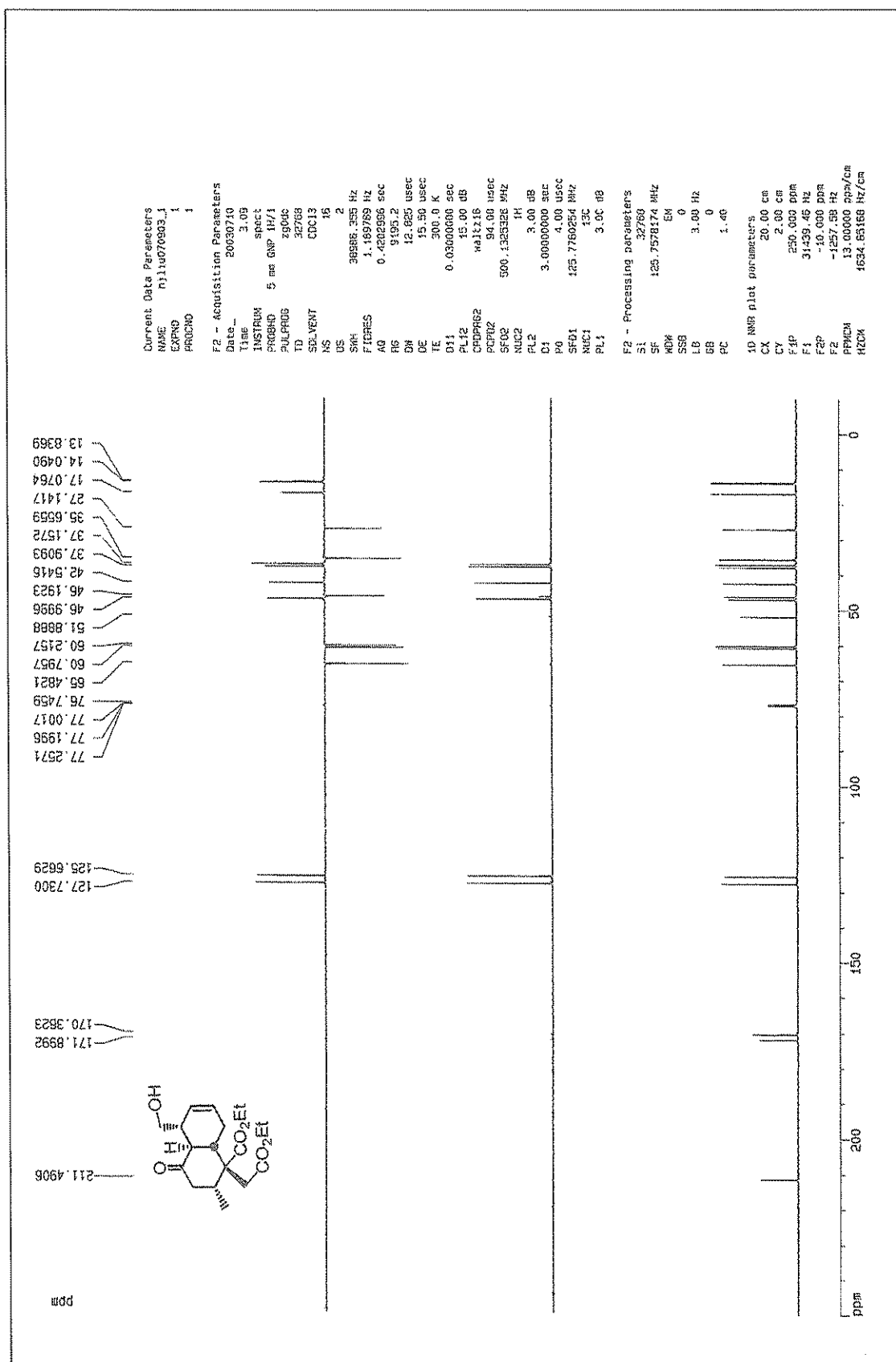
(±)-Teuscoloride (6)

To a solution of *p*-toluenesulfonyl acid (1.6 mg, 0.01mmol) in benzene (3 mL) at room temperature was added the solution of compound **21** (2 mg, 0.006 mmol) in benzene (2 mL) under nitrogen. The resulting mixture was then heated to reflux for 15 min, allowed to cool to room temperature, diluted with CH₂Cl₂ (3 mL), and quenched

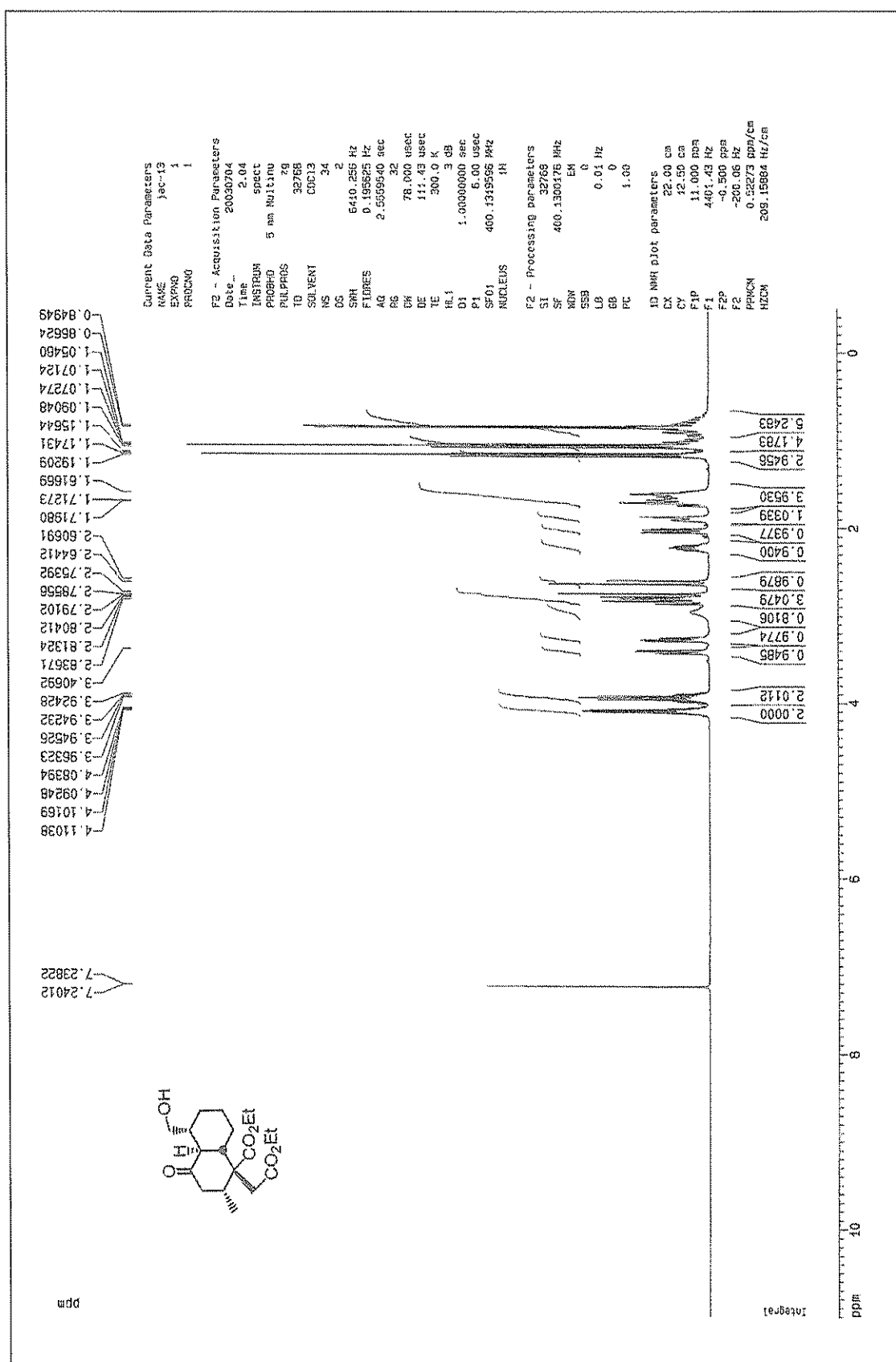
with dilute aqueous sodium bicarbonate (3 mL). The aqueous layer was separated and extracted with CH₂Cl₂ (3 x 3 mL), and the combined organic layers was washed with brine (5 mL), dried over anhydrous magnesium sulfate. Filtration, concentration, and purification with flash chromatography on silica gel (ethyl acetate: *n*-hexane =1:1) gave the desired product **6** (2 mg, 0.006 mmol, 99%) as a colorless liquid. IR (film): ν 3055, 1762, 1710 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ 7.46 (m, 1H), 7.44 (dd, *J* = 1.7, 1.6 Hz, 1H), 6.38 (m, 1H), 5.39 (t, *J* = 8.5 Hz, 1H), 5.31 (d, *J* = 2.1 Hz, 1H), 2.70-2.90 (m, 2H), 2.68 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.44 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.22-2.40 (m, 6H), 1.21 (d, *J* = 7.2 Hz, 3H). ¹³C-NMR (CDCl₃, 100MHz): δ 174.4 (C), 169.5 (C), 150.1 (C), 147.3 (C), 144.3 (CH), 139.6 (CH), 124.7 (C), 124.2 (C), 108.0 (CH), 107.9 (CH), 71.5 (CH), 53.5 (C), 41.0 (CH), 39.8 (CH₂), 37.4 (CH), 29.6 (CH₂), 22.4 (CH₂), 19.4 (CH₂), 16.8 (CH₃). HRMS (FAB) calcd. for C₁₉H₁₉O₅ [M+1]⁺: 327.1229, found: 327.1232.

3) ^1H , ^{13}C , DEPT NMR Spectra of Compounds 8-16, 20, 5, 6

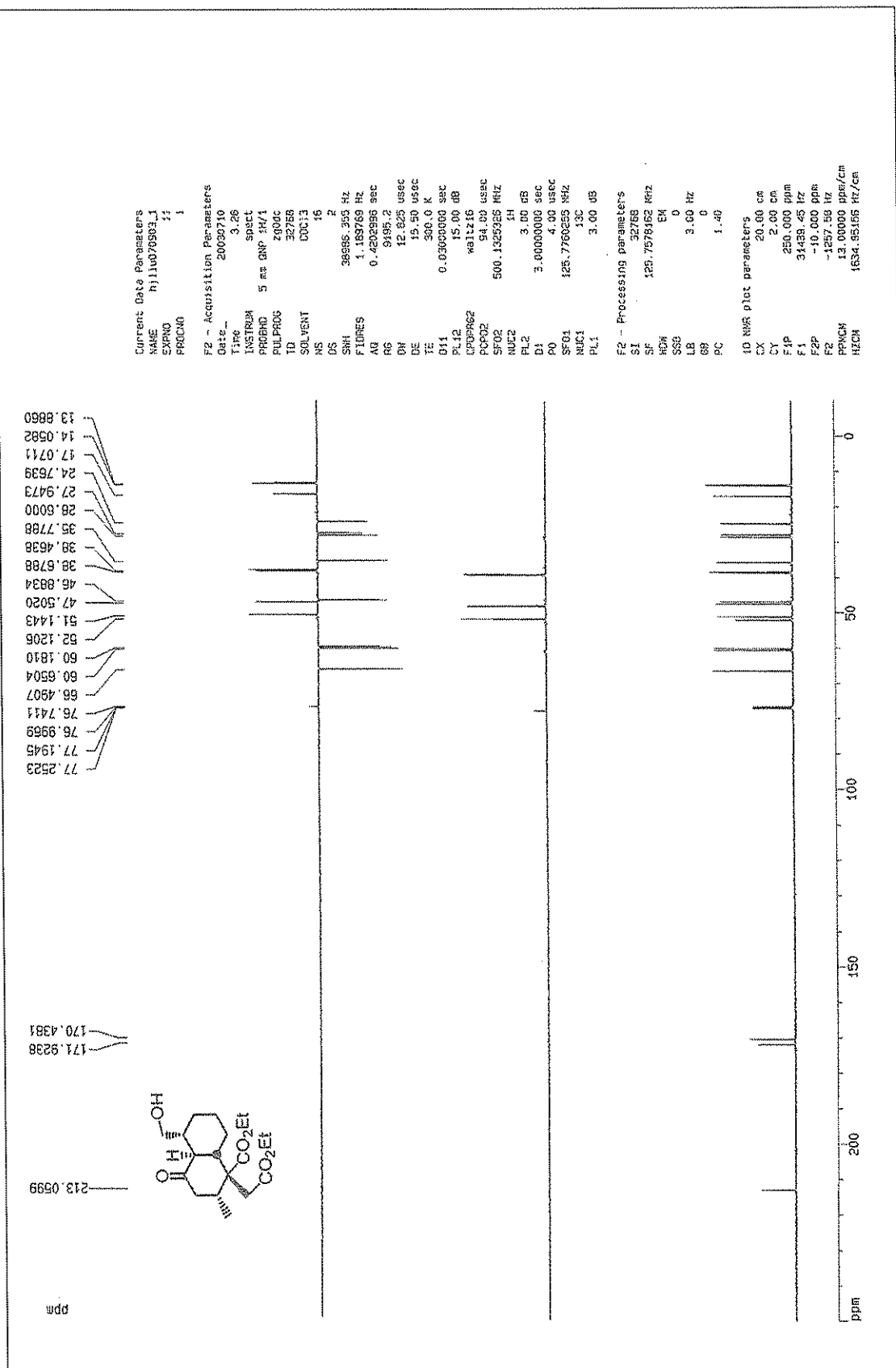




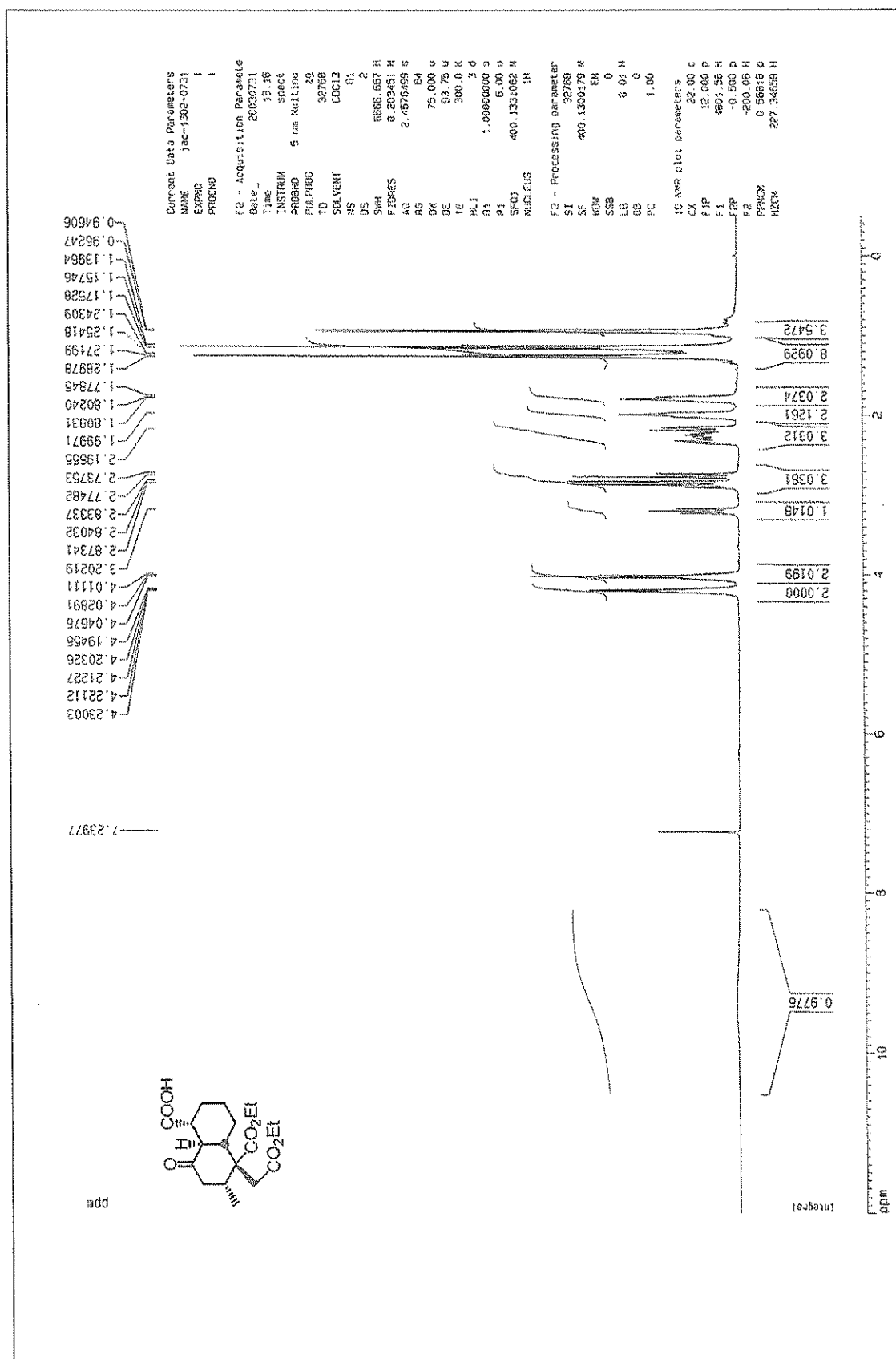
¹³C NMR of compound 8

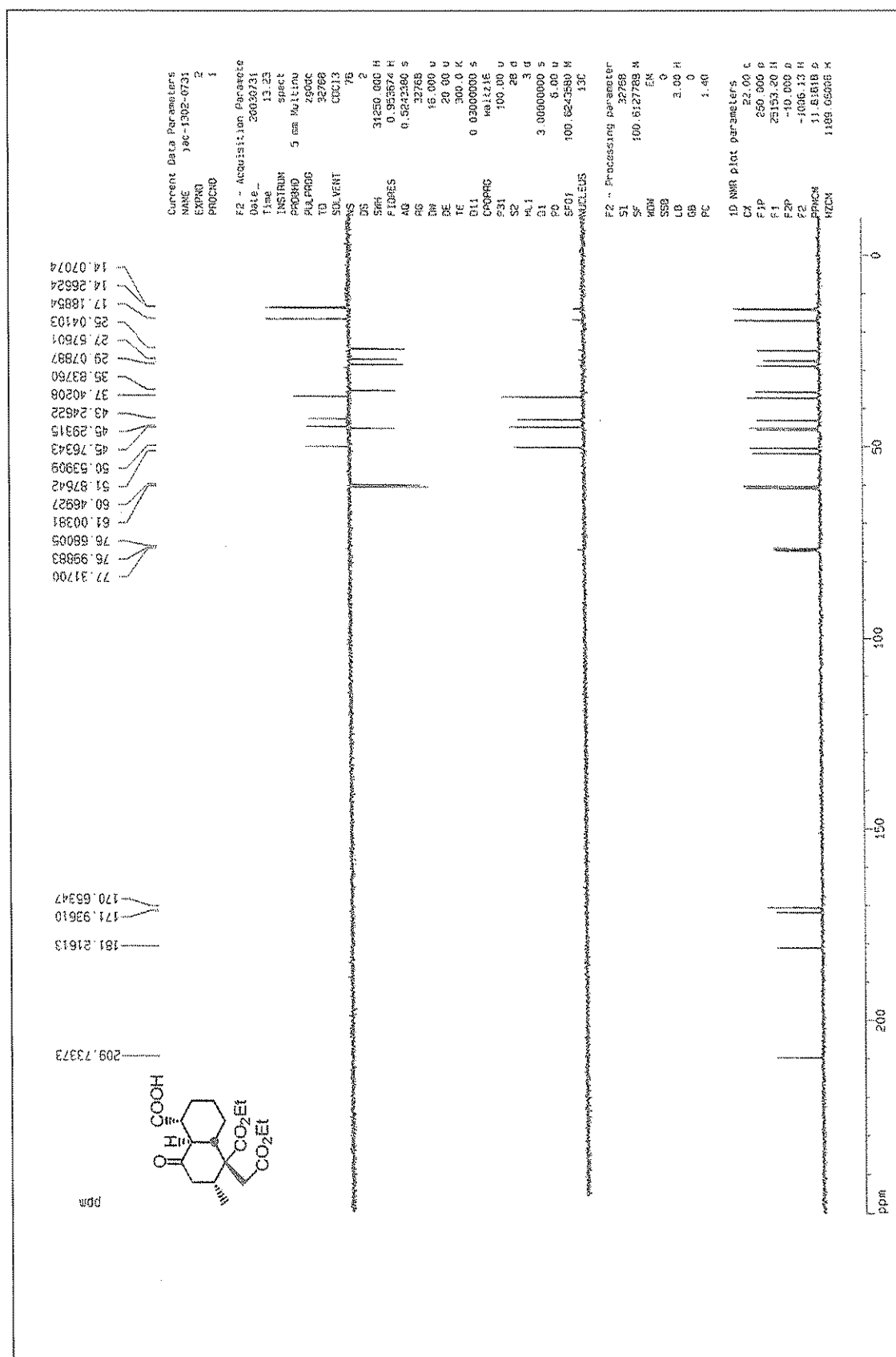


¹H NMR of compound 9



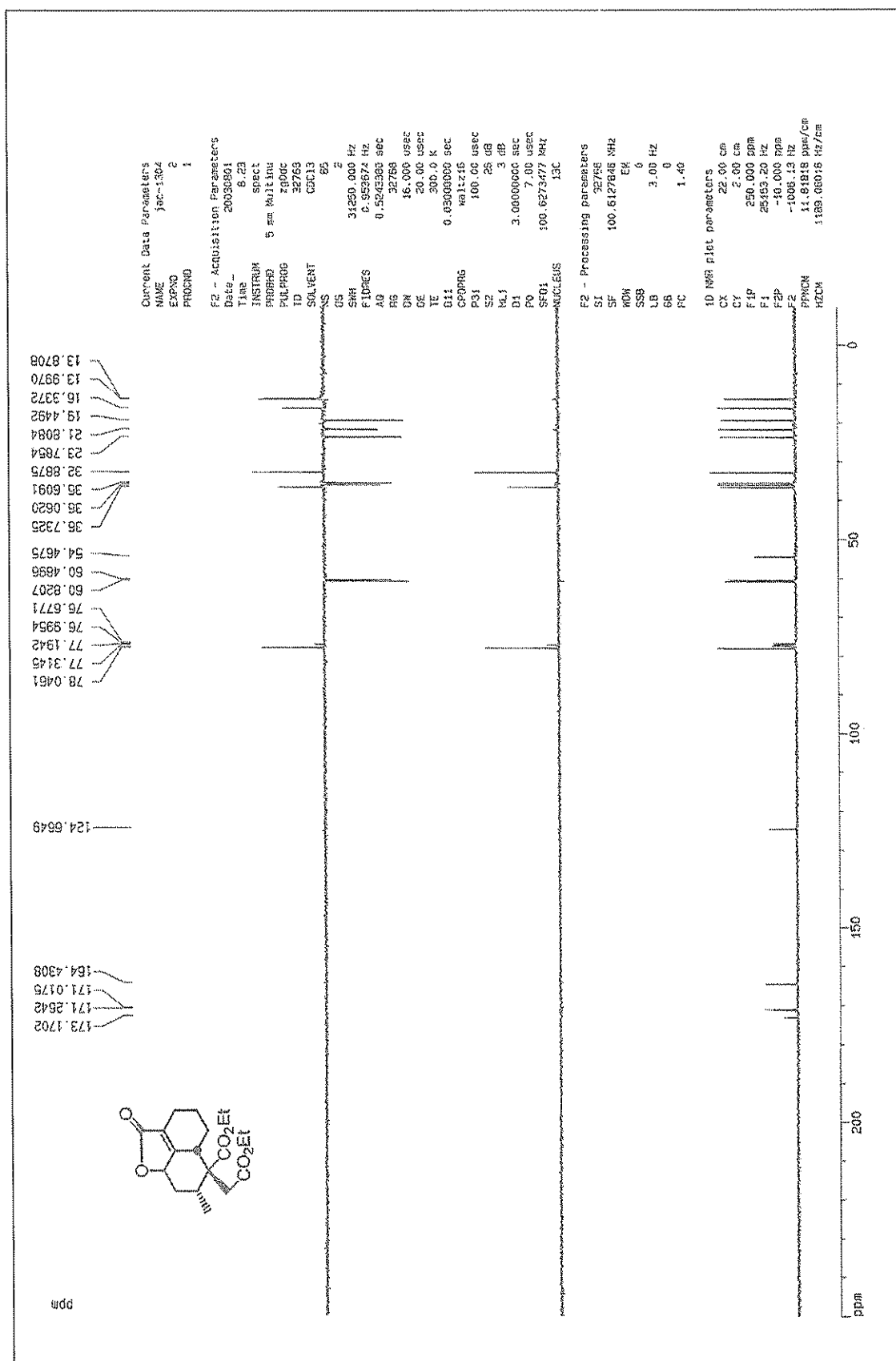
¹³C NMR of compound 9



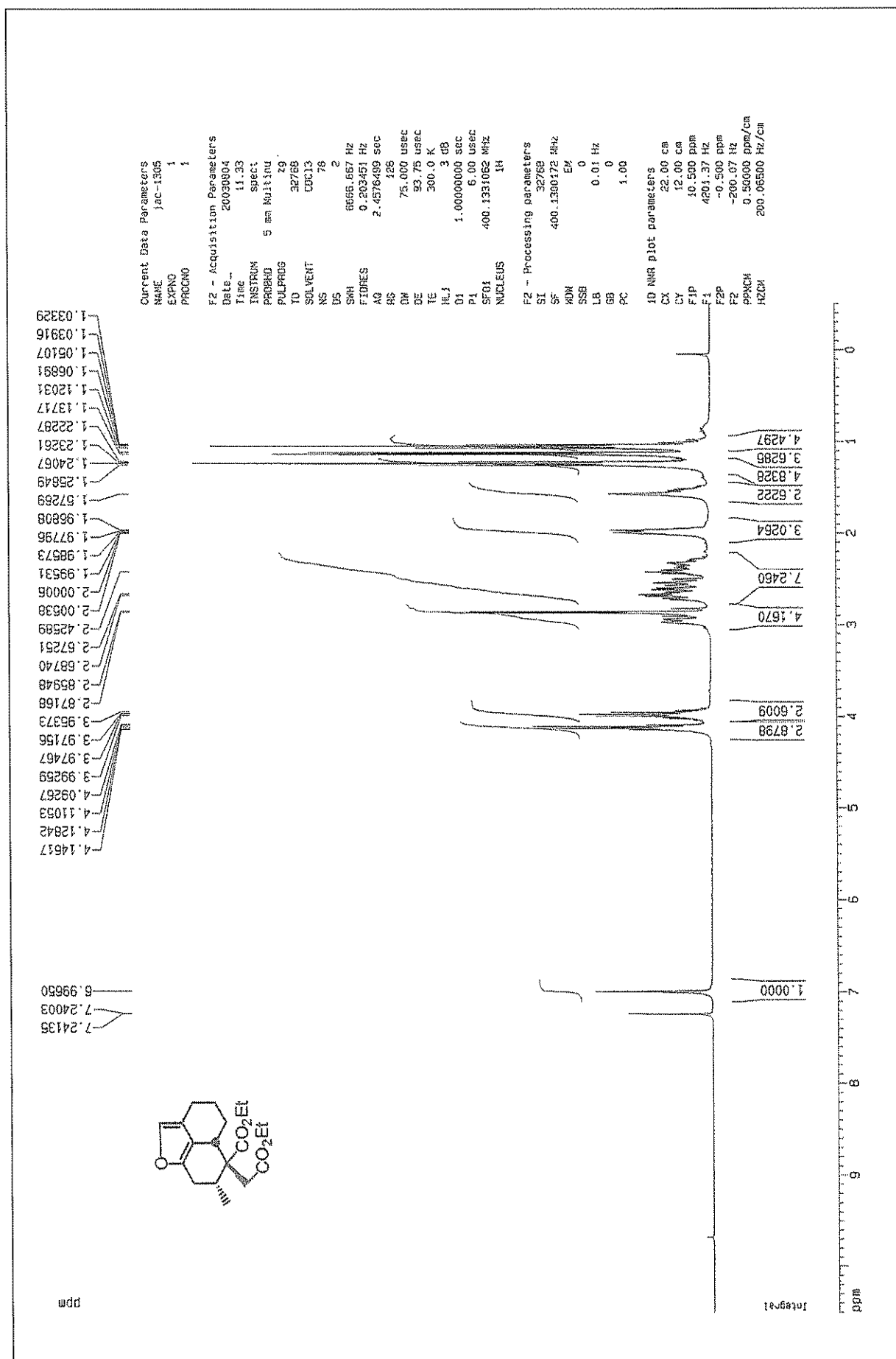


¹³C NMR of compound 10

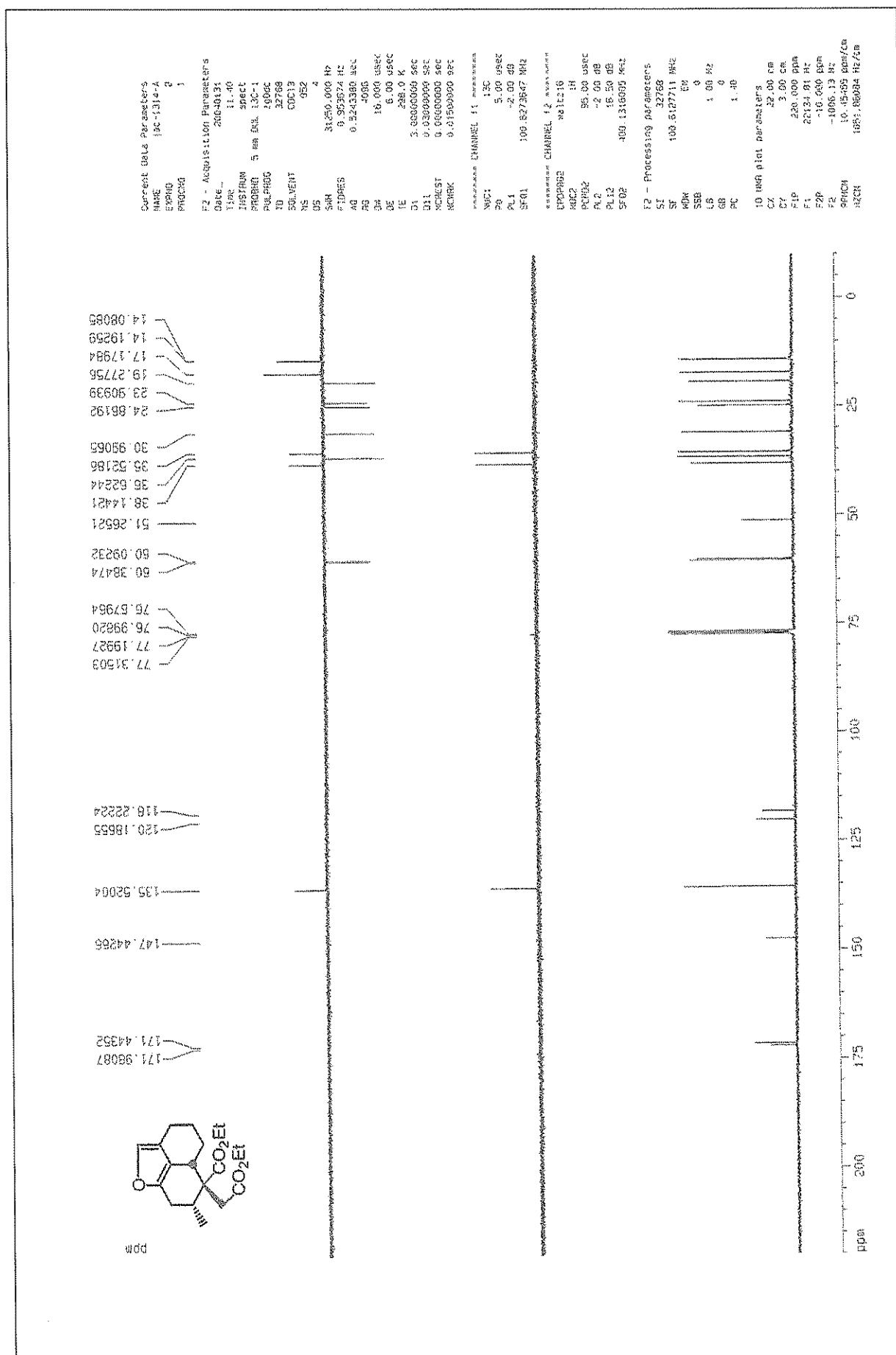




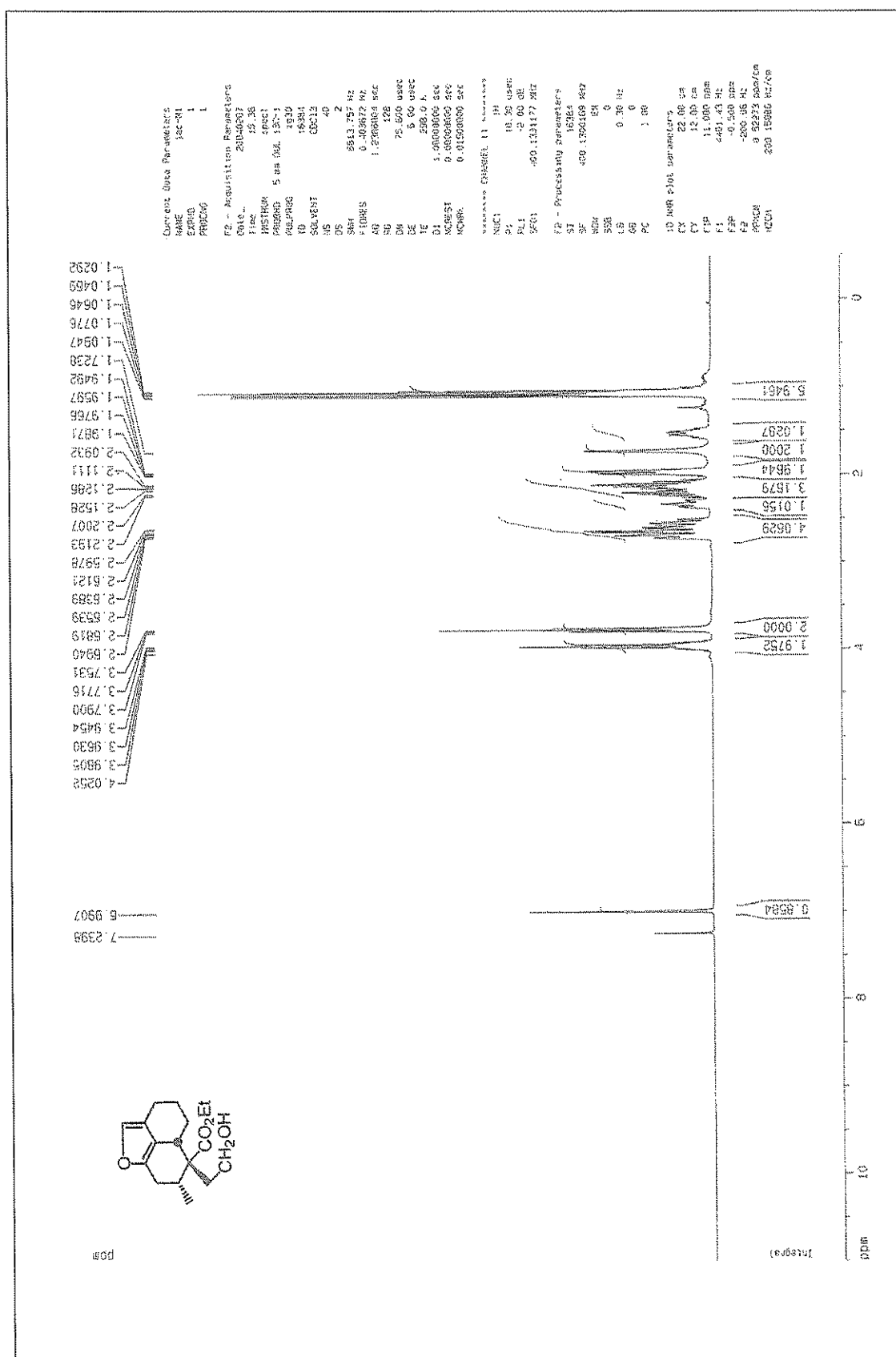
¹³C NMR of compound 11

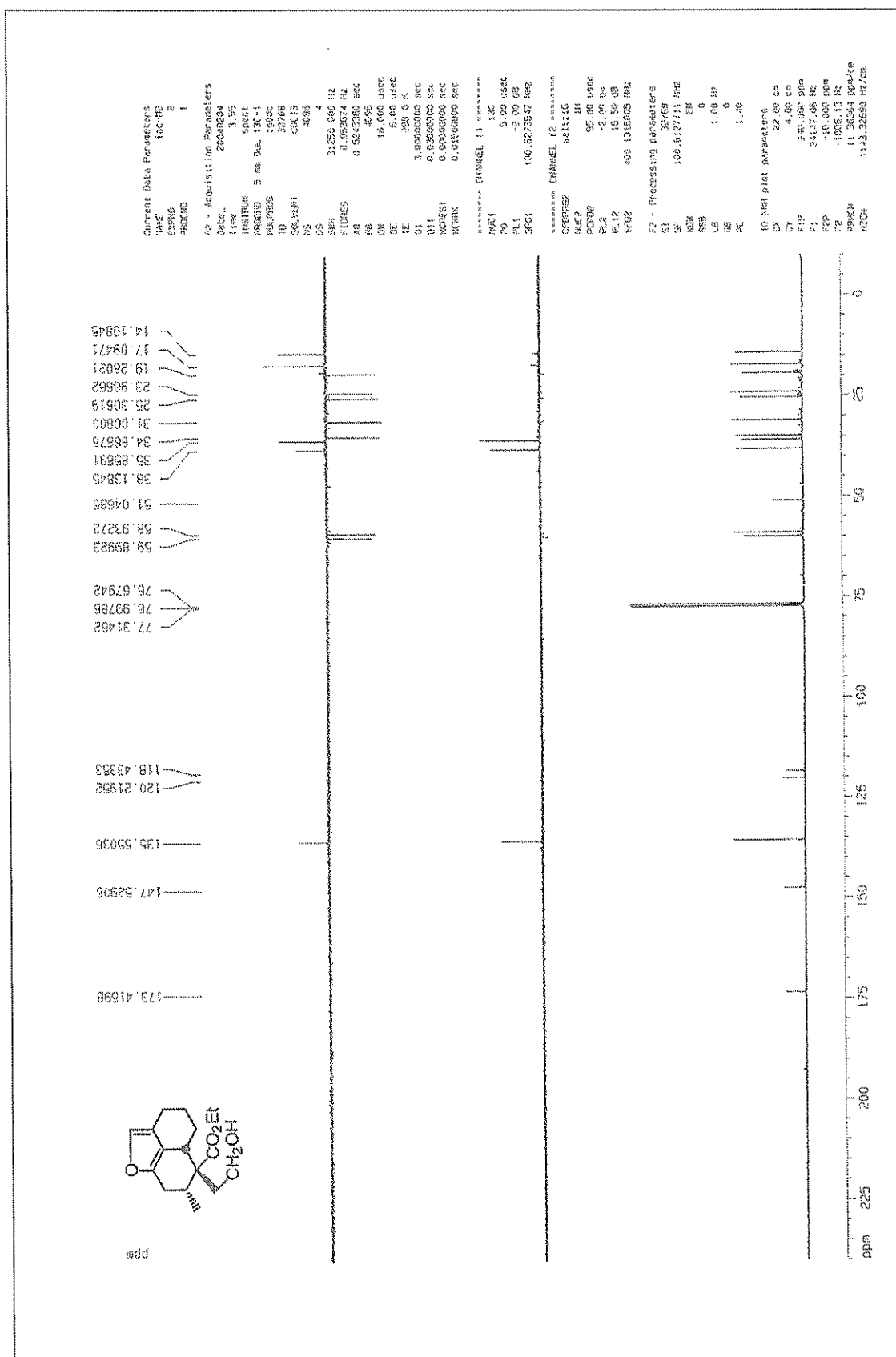


¹H NMR of compound 12

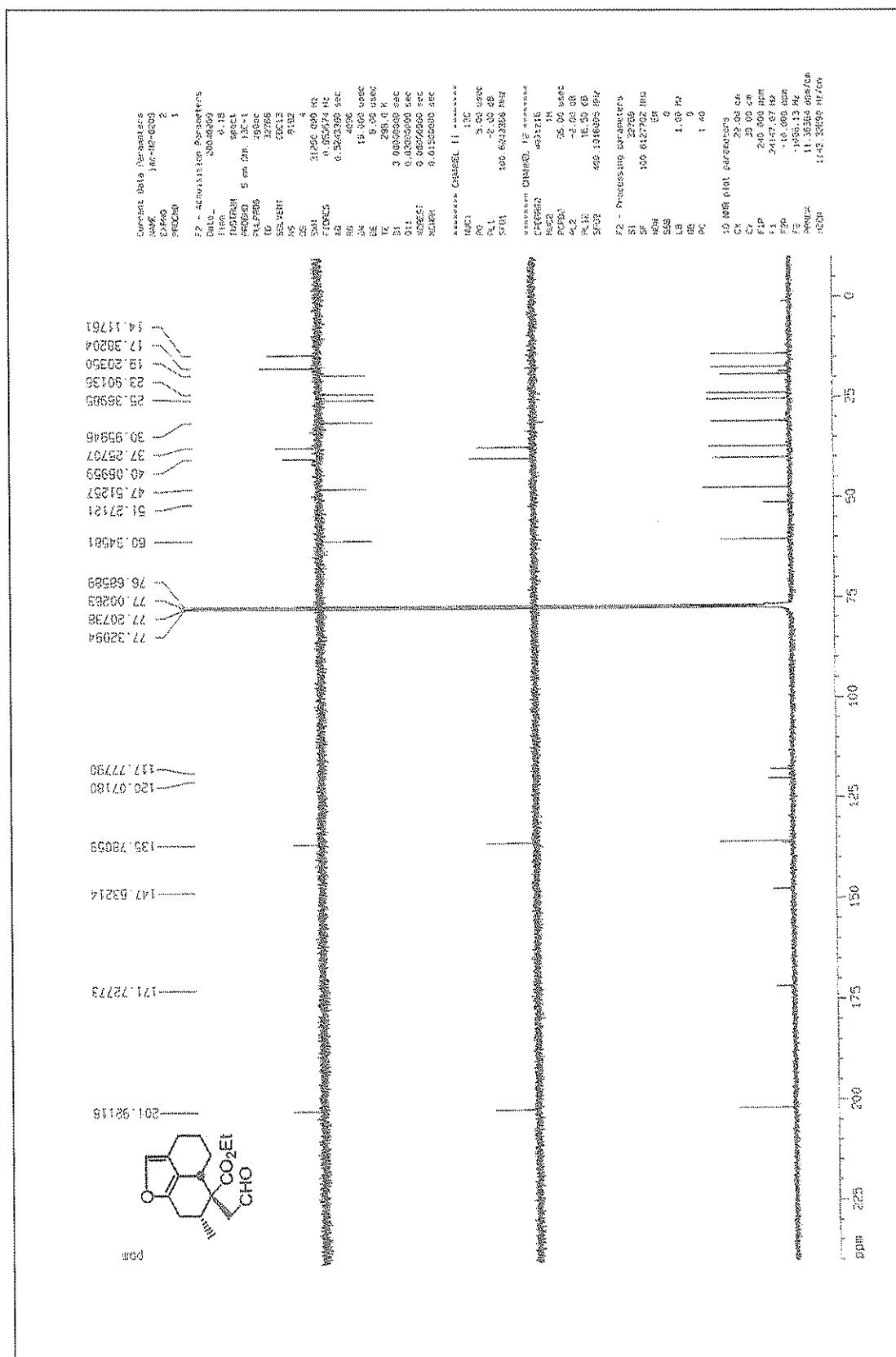


¹³C NMR of compound 12









¹³C NMR of compound 14



