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Supplementary Material

Diastereoselective Total Synthesis of Both Enantiomers of Epolactaene

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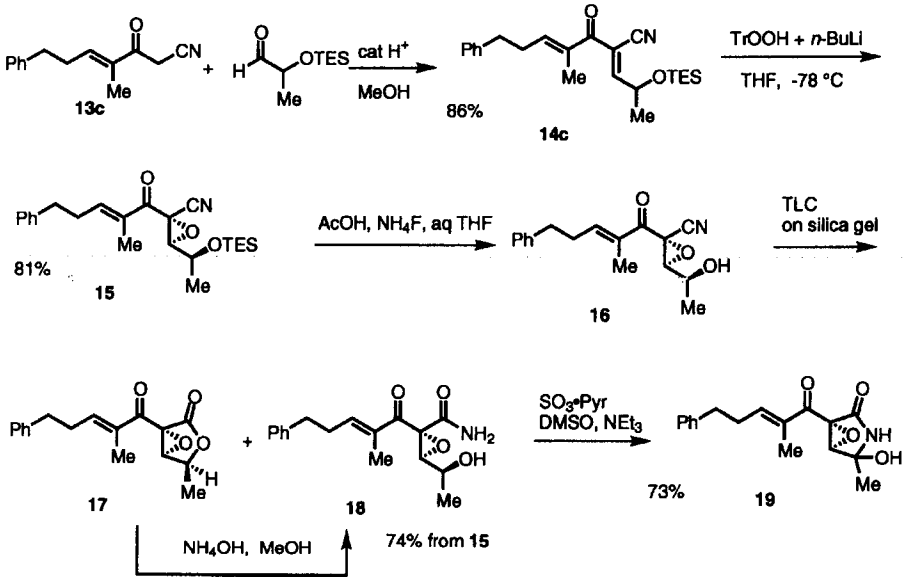
Experimental Section

Model Study



2-Triethylsiloxypropanal

To a CH_2Cl_2 (2 mL) solution of methyl 2-triethylsiloxypropanate (429 mg, 1.97 mmol) was added DIBAL-H solution (5.9 mL, 0.95 M in hexane, 5.60 mmol) at –78 °C. The temperature of the reaction mixture was gradually raised from –78 °C to –20 °C over 2 h with stirring. To the reaction mixture was added MeOH (0.33 mL, 7.9 mmol) and then Na_2SO_4 •$10H_2O$ (3.8 g, 11.8 mmol), which was stirred at rt for 30 minuts. After filtration of the inorganic materials, the solvent was removed under reduced pressure and crude 2-triethylsiloxy-1-propanol (234.9 mg, 63% yield) was obtained. To a CH_2Cl_2 (1.2 mL) solution of the crude 2-triethylsiloxy-1-propanol (234.9 mg) was added Et_3N (3.7 mL, 3.7 mmol), DMSO (1.2 mL), and SO_3•pyridine (588 mg, 3.7 mmol) at 0 °C and the reaction mixture was stired for 1.5 h at this temperature. Buffer solution was added, and the organic materials were extracted with ethyl acetate three times, and the combined organic extracts were washed with saturated NaCl solution

three times, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Rapid purification by flash column chromatography on florisil gel (ethyl acetate: hexane=1:3) gave 127 mg (55%) of 2-triethylsiloxypropanal, which was used in the next step in the same day.

4-Methyl-3-oxo-7-phenyl-2-(2-triethylsiloxypropylidene)hept-4-enenitrile (**14C**)

To a benzene solution (0.3 mL) of 4-methyl-3-oxo-7-phenylhept-4-enenitrile (57.5 mg, 0.270 mmol) and 2-triethylsiloxypropanal (127 mg, 0.674 mmol) was added ethylenediammonium diacetate (2.4 mg, 0.013 mmol, 5 mol%), and the reaction mixture was stirred at rt for 3 h. After removing benzene at reduced pressure, the residue was purified by rapid flash column chromatography on florisil gel (ethyl acetate: hexane=1:3) to afford 89.2 mg (86%) of 4-methyl-3-oxo-7-phenyl-2-(2-triethylsiloxypropylidene)hept-4-enenitrile (**14c**). As the purification of silica gel causes decomposition, **14c** was used directly after the above rough purification.
^{1}H NMR($CDCl_3$) δ=0.56 (6H, q, *J*=8.0 Hz), 0.86 (9H, t, *J*= 8.0 Hz), 1.20 (3H, d, *J*=7.2 Hz), 1.72 (3H, s), 2.54-2.58 (2H, m), 2.72-2.74 (2H, m), 4.75 (1H, dq, *Jd*=8.0 Hz, *Jq*=7.2 Hz), 6.48 (1H, dt, *Jd*= 1.5 Hz, *Jt*= 7.0 Hz), 6.92 (1H, d, *J*=8.0 Hz), 7.12-7.45 (5H, m); ^{13}C NMR($CDCl_3$) δ=4.8, 6.6, 12.2, 23.3, 30.9, 34.4, 67.4, 113.2, 114.3, 126.3, 128.3, 128.6, 135.6, 140.5, 145.3, 162.5, 188.9.

(1*S**, 2*S**, 3*S**)-1-(2-Methyl-5-phenylpent-2-enoyl)-3-triethylsiloxy-1,2-epoxybutanecarbonitrile (**15**)

To a THF (1.5 mL) solution of TrOOH (253 mg, 0.676 mmol) was added *n*-BuLi (0.39 mL, 0.56 mmol, 1.45 M in hexane) at -78 °C. After the reaction mixture was stirred for 1 h at this temperature, a THF solution (2 mL) of 4-methyl-3-oxo-7-phenyl-2-(2-triethylsiloxypropylidene)hept-4-enenitrile (**14C**) was added to the reaction mixture, which was stirred at –78 °C for another 1 h. Buffer solution was added, and the organic materials were extracted with ethyl acetate three times, and the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Purification by TLC (ethyl acetate: hexane=1:5) gave 40.1 mg (81%) of (1*S**, 2*S**, 3*S**)-1-(2-methyl-5-phenylpent-2-enoyl)-3-triethylsiloxy-1,2-epoxybutanecarbonitrile (**15**).
^{1}H NMR($CDCl_3$) δ=0.62 (6H, q, *J*= 8.0 Hz), 0.91 (9H, t, *J*= 8.0 Hz), 1.32 (3H, d, *J*= 6.3 Hz), 1.68 (3H, s), 2.50-2.58 (2H, m), 2.75 (2H, t, *J*= 7.5 Hz), 3.03 (1H, d, *J*=6.8 Hz), 3.88-3.91 (1H, m), 6.97 (1H, t, *J*= 7.5 Hz), 7.12-7.25 (5H, m); ^{13}C NMR($CDCl_3$) δ= 5.4, 7.1, 11.4, 21.8, 31.8, 34.7, 54.7, 66.9, 67.4, 115.4, 126.8, 128.7, 129.0, 135.0, 140.8, 147.8, 187.7; IR (neat) 2956, 2877, 2240, 1693, 1454, 1116, 746 cm^{-1}; HRMS: Calcd for $C_{23}H_{34}O_3Si$: M, 400.2309. Found: m/z 400.2305.

(2*S**,3*S**,4*S**)-4-Hydroxy-2-(2-methyl-5-phenylpent-2-enoyl)-2,3-epoxypentamide (**18**)

To a THF solution (0.4 mL) of (1*S**, 2*S**, 3*S**)-1-(2-methyl-5-phenylpent-2-enoyl)-3-triethylsiloxy-1,2-epoxybutanecarbonitrile (**15**) (29.5 mg, 0.0737 mmol) was added H_2O (20 μL), acetic acid (86 μL) and NH_4F (14 mg). After the reaction mixture was stirred for 1.5 h at rt, sat. $NaHCO_3$ solution was added. The organic materials were extracted with ethyl acetate three times, and the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Crude materials were charged on TLC and developed by mixed solvent

of ethyl acetate and hexane (1:1). (1*S**, 4*S**, 5*S**)-4-Methyl-1-(2-methyl-5-phenylpent-2-enoyl)-3,6-dioxabicyclo[3.1.0]hexan-2one (**17**) (Rf = 0.5, ethyl acetate/hexane = 1:1) and (2*S**, 3*S**, 4*S**)-4-hydroxy-2-(2-methyl-5-phenylpent-2-enoyl)-2,3-epoxypentamide (**18**) (Rf = 0.1, ethyl acetate/hexane = 1:1) could be separated, but eluted together, affording 1:1 mixture of lactone (**17**) and amide (**18**). To a MeOH solution (2 mL) of the above mixture was added NH_4OH solution (0.4 mL, 30% concentration), and the reaction mixture was stirred for 0.5 h at rt. Buffer solution was added, and the organic materials were extracted with chloroform three times, and the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Purification by TLC (ethyl acetate: hexane=3:1) gave 16.5 mg of amide **18** (74% three steps from **15**).

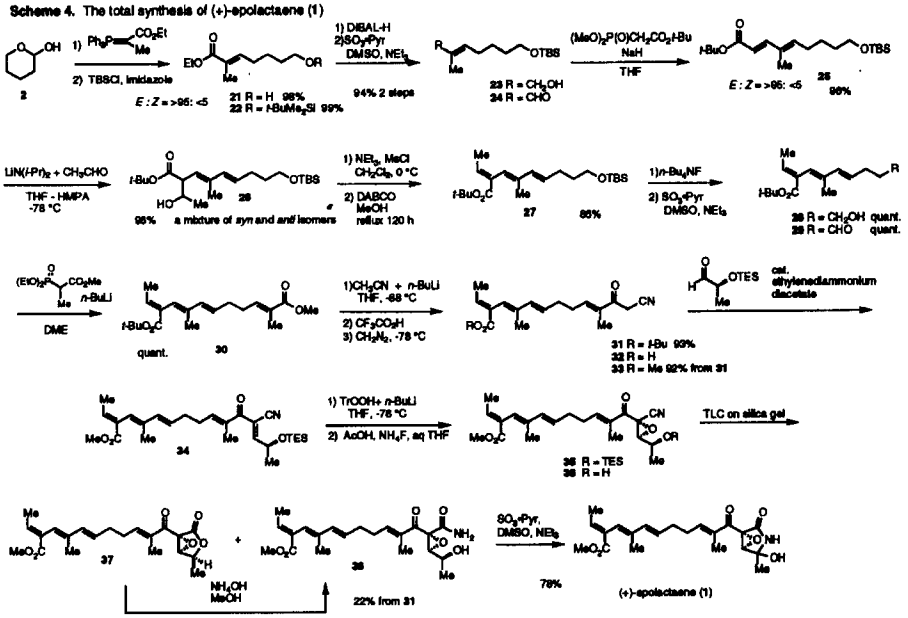
18: ^{1}H NMR($CDCl_3$) δ=1.31 (3H, d, *J*=7.8 Hz), 1.64 (3H, s), 2.53-2.58 (2H, m), 2.73-2.77 (2H, m), 3.04 (1H, d, *J*= 7.9 Hz), 3.64 (1H, dq, *Jd*= 7.9 Hz, *Jq*= 7.8 Hz), 6.21 (1H, bs), 6.50 (1H, bs), 7.02-7.23 (6H, m); ^{13}C NMR($CDCl_3$) δ=11.1, 20.3, 31.2, 34.3, 65.4, 66.0, 126.2, 128.4, 128.4, 128.5, 135.2, 140.7, 149.6, 167.6, 192.9; IR 3343, 2927, 1687, 1454, 1072, 700 cm^{-1}; HRMS, Found: m/z. 303.1468, Calcd for $C_{17}H_{21}NO_4$: M, 303.1471.

(1*S**,5*S**)-4-Hydroxy-4-methyl-1-(2-methyl-5-phenylpent-2-enoyl)-6-oxa-3-azabicyclo-[3.1.0]hexan-2-one (**19**)

To a CH_2Cl_2 solution (70 μL) of **18** (16.5 mg, 0.0539 mmol) was added DMSO (70 μL), Et_3N (37 μL, 0.267 mmol) and SO_3•pyridine (25.7 mg, 0.162 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, buffer was added, and the organic materials were extracted with ethyl acetate three times, and the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Purification by TLC (ethyl acetate: hexane=3:1) gave 11.8 mg (73%) of (1*S**, 5*S**)-4-hydroxy-4-methyl-1-(2-methyl-5-phenylpent-2-enoyl)-6-oxa-3-azabicyclo[3.1.0]hexan-2-one (**19**).

^{1}H NMR($CDCl_3$) δ=1.58 (3H, s), 1.77 (3H, s), 2.61-2.71 (2H, m), 2.83 (2H, t, *J*= 7.0 Hz), 3.90 (1H, d, *J*= 2.5 Hz), 4.37 (1H, bs), 6.66 (1H, bs), 7.06 (1H, dt, *Jd*= 1.5 Hz, *Jt*= 7.0 Hz), 7.20-7.35 (5H, m); ^{13}C NMR($CDCl_3$) δ= 11.0, 21.8, 31.4, 34.3, 62.3, 63.8, 83.7, 126.3, 128.5, 128.6, 136.6, 140.7, 149.8, 169.7, 190.7; HRMS, Found: m/z. 306.1116, Calcd for [$C_{17}H_{19}NO_4$-H_2O+Na]: M, 306.1107.

Total Synthesis of (+)-epolactaene



(E)-Ethyl 7-hydroxy-2-methyl-2-heptenate (**21**)

To a benzene (300 mL) solution of ethoxycarbonylethylidene triphenylphosphorane (64.4 g, 0.178 mol) was added tetrahydropyran-2-ol (**2**) (14.0 g, 0.138 mol), and the reaction mixture was stirred for 1.5 h at 90 °C. After allowing the reaction mixture to cool to rt, the solvent was removed *in vacuo*, affording the crude material. Purification by flash column chromatography (ethyl acetate: hexane=1:5) gave 25.2 g (98%) of ester **21**.

^{1}H NMR($CDCl_3$) δ=1.27 (3H, t, *J*=7.2 Hz), 1.48-1.61 (4H, m), 1.82 (3H, s), 1.99 (1H, bs), 2.20 (2H, q, *J*=7.3 Hz), 3.64 (2H, t, *J*=6.3 Hz), 4.17 (2H, q, *J*=7.2 Hz), 6.74 (1H, dt, *J*=1.3, 7.3Hz); ^{13}C NMR($CDCl_3$) δ=12.3, 14.2, 24.7, 28.3, 32.2, 60.4, 62.4, 127.9, 141.9, 168.3; IR (neat) 3421, 2935, 1712, 1649, 1271, 1095 cm^{-1}, Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%. found C,64.39 ;H,9.75%.

(E)-Ethyl 7-(*tert*-butyldimethylsiloxy)-2-methyl-2-heptenate (**22**)

To a CH_2Cl_2(300 mL) and DMF (43 mL) solution of ester **21** (13.9 g, 74.8 mol), imidazole (7.60 g, 112 mol) and *t*-butyldimethylsilylchloride (13.5 g, 89.7 mol) were added in succession, and the reaction mixture was stirred for 20 minutes. Buffer solution was added, and the organic materials were extracted with ethyl acetate three times, and the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Purification by flash column chromatography (ethyl acetate: hexane=1:1) gave 22.2 g (99%) of ester **22**.

^{1}H NMR($CDCl_3$)) δ=0.01 (6H, s), 0.86 (9H, s), 1.26 (3H, t, *J*=7.1 Hz), 1.40-1.56 (4H, m), 1.79 (3H, s), 2.15 (2H, q, *J*=7.1 Hz), 3.58 (2H, t, *J*=6.0 Hz), 4.15 (2H, q, *J*=7.1 Hz), 6.72 (1H, dt, *J*=1.3, 7.5 Hz); ^{13}C NMR($CDCl_3$) δ= -5.3, 12.3, 14.3, 18.3, 24.9, 25.7, 28.4, 32.4, 60.4, 62.8, 127.8,142.1, 168.3; IR (neat) 2952, 2931, 1712, 1651, 1255,

1101, 837, 775 cm^{-1}; Anal. Calcd for $C_{16}H_{32}O_3Si$: C, 63.95; H, 10.73%. found C, 63.72; H,10.48%.

(E)-7-(*tert*-Butyldimethylsiloxy)-2-methylhept-2-en-1-ol (**23**)

To a CH_2Cl_2 (200 mL) solution of ester **22** (15.8g, 52.8 mmol) was added DIBAL-H (0.95 M in hexane, 139 mL, 132 mmol) at 0 °C, and the reaction mixture was stirred for 1 h. MeOH (7 mL, 160 mmol) and $Na_2SO_4 \cdot 10H_2O$ (68.0 g, 211 mmol) were added to the reaction mixture, which was then stirred for 30 minutes. After filtering off the inorganic materials with $CHCl_3$, the solvent was removed *in vacuo* to give the crude alcohol **23** (13.6 g), which was used directly in the next reaction.
^1H NMR($CDCl_3$) δ= 0.02 (6H, s), 0.86 (9H, s), 1.32-1.43 (2H, m), 1.43-1.60 (2H, m), 1.63 (3H, s), 1.76 (1H, d, *J*=0.8 Hz), 2.01 (2H, q, *J*=7.3 Hz), 3.58 (2H, t, *J*=6.5 Hz), 3.97 (2H, s), 5.38 (1H, dt *J*=0.8, 7.0 Hz); ^{13}C NMR($CDCl_3$) δ= -5.3, 13.7, 18.4, 25.7, 26.0, 27.2, 32.3, 63.1, 68.9, 126.3, 134.8; IR (neat) 3307, 2929, 2858, 1649, 1101, 837, 775 cm^{-1}; HRMS(FAB$^+$) Calcd for $C_{14}H_{31}O_2Si$:(M+H$^+$), 259.2093. Found:m/z 259.2101.

(E)-7-(*tert*-Butyldimethylsiloxy)-2-methylhept-2-enal (**24**)

To a CH_2Cl_2 (53 mL) solution of alcohol **23** (13.6g) was added triethylamine (36.5 mL) and a DMSO (53 mL) solution of SO_3•pyridine (25.0 g) at 0 °C, and the reaction mixture was stirred for 1.5 h. After buffer solution had been added, the organic materials were extracted with ethyl acetate three times, and the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. Purification by TLC (ethyl acetate: hexane=1:10) gave 12.8 g (94%, 2 steps) of aldehyde **24**.
^1H NMR($CDCl_3$) δ= 0.02 (6H, s), 0.86 (9H, s), 1.51-1.55 (4H, m), 1.70 (3H, s), 2.35 (2H, q, *J*=6.6 Hz), 3.54-3.65 (2H, m), 6.46 (1H, dt, *J*=1.3, 7.4 Hz) , 9.36 (1H, s); ^{13}C NMR ($CDCl_3$) δ= 5.3, 9.2, 18.3, 24.8, 25.9, 28.7, 32.4, 62.7, 139.5, 154.6, 195.2; IR (neat) 2952, 2929, 1691, 1644, 1255, 1101, 837, 775 cm^{-1}; HRMS(FAB$^+$) Calcd for $C_{14}H_{29}O_2Si$: (M+H$^+$), 257.1937. Found: m/z 257.1932.

(2*E*,4*E*)-*tert*-Butyl 9-(*tert*-butyldimethylsiloxy)-4-methylnona-2,4-dienate (**25**)

To a THF (5 mL) suspension of NaH (155 mg, 3.88 mmol) was added a THF (5 mL) solution of *tert*-butyldimethylphosphono acetate (1.26 g, 4.94 mmol) at 0 °C, and the reaction mixture was stirred for 0.5 h at rt. A THF solution (5 mL) of aldehyde **24** (504 mg, 1.97 mmol) was added to this reaction mixture at 0 °C, which was stirred for 0.5 h at the same temperature. A buffer solution was added and the organic materials were extracted with ethyl acetate three times. The combined organic phases were dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Purification by flash column chromatography (ethyl acetate: hexane=1:20) gave 666 mg (96%) of ester **25**.
^1H NMR($CDCl_3$) δ= 0.02 (6H, s), 0.86 (9H, s), 1.35-1.58 (4H ,m), 1.47 (9H, s), 1.72 (3H, s), 2.18 (2H, q, *J*=7.2 Hz), 3.58 (2H, t, *J*=6.0 Hz), 5.68 (1H, d, *J*=15.6 Hz), 5.85 (1H, t, *J*=7.2 Hz), 7.19 (1H, d, *J*=15.6 Hz); ^{13}C NMR($CDCl_3$) δ= 5.3, 12.2, 18.3, 25.4, 25.9, 28.0, 28.2, 32.4, 62.9, 79.9, 117.4, 132.8, 141.4, 148.6, 167.0; IR (neat) 2929, 2858, 1709, 1622, 1255, 1151, 1101, 835, 775 cm^{-1}; HRMS Calcd for $C_{20}H_{38}O_3Si$: M, 354.2590. Found: m/z 354.2488.

(3*E*,5*E*)-*tert*-Butyl 9-(*tert*-butyldimethylsiloxy)-2-[1-hydroxyethyl]-

4-methylnona-3,5-dienate (**26**)

To a THF (5 mL) and HMPA (1.6 mL) solution of diisopropylamine (401 mg, 3.96 mmol) was added *n*-BuLi (1.53 M in hexane, 2.2 mL, 3.37 mmol) at 0 °C, and the reaction mixture was stirred for 10 minutes. To this mixture was added a THF (6 mL) solution of ester **25** (666 mg, 1.88 mmol) at -78 °C. The reaction mixture was stirred for 1.5 h at this temperature, then freshly distilled acetaldehyde (2 mL, 35.8 mmol) was added and stirring continued for a further 3 h at –78 °C. Then buffer solution was added and the organic materials were extracted with ethyl acetate three times, and the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. Rough purification by column chromatography (ethyl acetate: hexane=1:20) afforded a mixture of *syn*- and *anti*-aldols (**26a,b**), which was used in the next reaction. Careful purification by flash column chromatography (ethyl acetate: hexane=1:50) gave 269 mg of *syn*-aldol **26a** and 449 mg of *anti*-aldol **26b**.

Syn-aldol **26a**: ^{1}H NMR($CDCl_3$) δ= 0.02 (6H, s), 0.87 (9H, s), 1.12 (3H, d, *J*=6.3 Hz), 1.42 (9H, s), 1.55-1.61 (2H, m), 1.77 (3H, s), 2.14 (2H, q, *J*=7.0 Hz), 2.80 (1H, d, *J*=3.0 Hz), 3.2 3(1H, dd, *J*=4.8, 10.0 Hz), 3.59 (2H, t, *J*=6.3 Hz), 4.02-4.05 (1H, m), 5.47 (1H, d, *J*=10.0 Hz), 5.65 (1H, dt, *J*=15.6, 7.0 Hz), 6.1(1H, d, *J*=15.6 Hz); ^{13}C NMR($CDCl_3$) δ= 5.3, 13.2, 18.3, 19.9, 25.9, 28.0, 29.1, 32.5, 52.5, 62.5, 68.3, 81.4, 122.8, 129.3, 134.4, 138.5, 172.9; IR (neat) 3456, 2954, 2929, 1725, 1706, 1255, 1153, 1103, 835, 775 cm^{-1}; HRMS Calcd for $C_{22}H_{42}O_4Si$: M, 398.2852. Found: m/z 398.2840.

Anti-aldol **26b**: ^{1}H NMR($CDCl_3$) δ= 0.02 (6H, s), 0.8 (9H, s), 1.13 (3H, d, *J*=6.3 Hz), 1.41 (9H, s), 1.53-1.60 (2H, m), 1.78 (3H ,s), 2.13(2H, q, *J*=7.0 Hz), 2.69 (1H, d, *J*=5.2 Hz), 3.24 (1H, dd, *J*=7.8, 10.0 Hz), 3.59 (2H, t, *J*=6.3 Hz), 3.93-3.98 (1H, m), 5.26 (1H, d, *J*=10.0 Hz), 5.64 (1H, dt, *J*=15.6, 7.0 Hz), 6.05 (1H, d, 15.6Hz); ^{13}C NMR($CDCl_3$) δ= 5.3, 13.2, 18.3, 20.7, 25.9, 28.0, 29.1, 32.4, 53.9, 62.5, 69.2, 81.3, 123.9, 129.3, 134.4, 137.4, 172.9; IR (neat) 3446, 2954, 2931, 1730, 1709, 1255, 1155, 1101, 835, 775 cm^{-1}; HRMS Calcd for $C_{22}H_{42}O_4Si$: M, 398.2852. Found: m/z398.2860

(3*E*,5*E*)-*tert*-Butyl 9-(*tert*-butyldimethylsiloxy)-2-[(*E*)-ethylidene]-4-methylnona-3,5-dienate (**27**)

To a CH_2Cl_2 (15 mL) solution of aldol **26** (4.03 g, 10.1 mmol) was added cat.DMAP, triethylamine (4.60 mL, 33.0 mmol) and a CH_2Cl_2 (20 mL) solution of MsCl (2.30 g, 20.2 mmol) at 0 °C, after which the reaction mixture was stirred for 1.5 h at rt. Buffer solution was added and the organic materials were extracted with ethyl acetate three times, then the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. To a MeOH (50 mL) solution of this mesylate, DABCO (5.67 g, 50.6 mmol) was added and the reaction mixture was stirred at 100 °C for 120 h. Buffer solution was added and the organic materials were extracted with ethyl acetate three times, then the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Purification by flash column chromatography (ethyl acetate: hexane=1:3) gave 3.31 g of triene **27**.

^{1}H NMR($CDCl_3$) δ= 0.03 (6H ,s), 0.88 (9H, s), 1.45 (9H, s), 1.56-1.64 (2H, m), 1.60 (3H, d, *J*=0.7 Hz), 1.67 (3H, dd, *J*=1.0, 7.0 Hz), 2.16 (2H, q, *J*=7.0 Hz), 3.61 (2H, t, *J*=6.4 Hz), 5.68 (1H, dt, *J*=15.6, 7.0 Hz), 5.89 (1H, s), 6.18 (1H, d, *J*=15.6Hz), 6.78 (1H, q, *J*=7.0 Hz); ^{13}C NMR($CDCl_3$) δ= -5.3, 14.6, 15.7, 18.3, 26.0, 28.1, 29.1,

32.5, 62.6, 80.3, 122.7 129.6, 132.4, 134.5, 137.5, 137.9, 166.8; IR (neat) 2929, 2858, 1712, 1635, 1254, 1173, 1101, 837, 775 cm^{-1}; HRMS Calcd for $C_{22}H_{40}O_3Si$:M, 380.2747. Found: m/z 380.2727.

(3*E*,5*E*)-*tert*-Butyl [(2*E*)-ethylidene]-9-hydroxy-4-methylnona-3,5-dienate (**28**)

To triene **27** (1.30 g, 3.41 mol) was added tetra-*n*-butylammoniumfluoride (1 M in THF, 10.0 mL, 10.0 mmol), and the reaction mixture was stirred at 0 °C for 3 h. Buffer solution was added and the organic materials were extracted with ethyl acetate three times, then the extracts were combined and dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. Purification by flash column chromatography (ethyl acetate: hexane=1:5) gave 894 mg of alchol **28** quantitatively.

^1H NMR($CDCl_3$) δ= 1.45 (9H, s), 1.60 (3H, s), 1.65-1.71 (6H, m), 2.20 (2H, q, *J*=7.2 Hz), 3.64 (2H, t, *J*=6.5 Hz), 5.68 (1H, dt, *J*=15.5, 7.2Hz), 5.90 (1H, s), 6.20 (1H, d, *J*=15.6 Hz), 6.77 (1H ,q, *J*=7.2 Hz); ^{13}C NMR($CDCl_3$) δ= 14.5, 15.7, 28.1, 29.1, 32.3, 62.4, 80.3, 122.9, 129.1, 132.3, 134.7, 137.4, 138.0, 166.7; IR (neat) 3440, 2978, 2933, 1709, 1633, 1367, 1254, 1171, 1134 cm^{-1}; HRMS Calcd for $C_{16}H_{26}O_3$: M,266.1882. Found: m/z 266.1880.

(3*E*,5*E*)-*tert*-Butyl [(2*E*)-ethylidene]-4-methyl-9-formylocta-3,5-dienate (**29**)

To a CH_2Cl_2 (10 mL) solution of alcohol **28** (379 mg, 1.42 mmol) was added triethylamine (0.60 mL, 4.30 mmol) and a DMSO (6 mL) solution of SO_3•pyridine (452.1 mg, 2.84 mmol) at 0 °C, and the reaction mixture was stirred for 1.5 h. Buffer solution was added and the organic materials were extracted with ethyl acetate three times, then the combined organic extracts were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. Purification by flash column chromatography (ethyl acetate: hexane=1:10) gave 377 mg of aldehyde **29** quantitatively.

^1H NMR($CDCl_3$) δ= 1.45 (9H, s), 1.59 (3H, d, *J*=1.0 Hz), 1.66 (3H, dd, *J*=1.2, 7.4 Hz), 2.45 (2H, q, *J*=7.4 Hz), 2.55 (2H, t, *J*=7.4 Hz), 5.65 (1H, dt, *J*=15.5, 6.5Hz), 5.92 (1H, s), 6.21 (1H, d,*J*=15.5Hz), 6.78 (1H, q, *J*=7.4 Hz), 9.77(1H, t, *J*=1.4 Hz); ^{13}C NMR($CDCl_3$) δ= 14.5, 15.6, 28.1, 29.2, 31.4, 80.4, 123.8, 127.4, 132.2, 135.6, 137.0, 138.0, 166.7, 188.24; IR (neat) 2979, 1724, 1699, 1633, 1279, 1255, 1173, 1134 cm^{-1}; HRMS Calcd for $C_{16}H_{24}O_3$: M, 264.1725. Found: m/z 264.1734.

(3*E*,5*E*,9*E*)-*tert*-Butyl [(2*E*)-ethylidene]-4,10-dimethyl-11-oxo-11-methoxyundeca-3,5,9-trienoate (**30**)

To a DME (30 mL) solution of methyl 2-(diethylphosphono)propanate (3.37 g, 15.1 mmol) was added *n*-BuLi (1.50 M in hexane, 8.00 mL, 12.0 mmol) at 0 °C. After 10 minutes, a DME (15 mL) solution of aldehyde **29** (1.59 g, 6.02 mmol) was added at rt, after which the reaction mixture was stirred for 0.5 h. Buffer solution was added and the organic materials were extracted with ethyl acetate three times, then the combined organic extracts was dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. Purification by flash column chromatography (ethyl acetate: hexane=1:10) gave 2.01 g of ester **30** quantitatively.

^1H NMR($CDCl_3$) δ=1.45 (9H, s), 1.60 (3H, d, *J*=0.8 Hz), 1.67 (3H, dd, *J*=1.1, 7.2 Hz), 1.82 (3H, s), 2.23-2.31 (4H, m), 3.71 (3H, s), 5.66 (1H, dt, *J*=15.5 6.5 Hz), 5.92 (1H, s), 6.21 (1H, d, *J*=15.5 Hz), 6.73-6.81 (2H, m); ^{13}C NMR($CDCl_3$) δ=12.5, 14.5, 15.7,

28.1, 28.7, 31.7, 51.7, 80.3, 123.3, 127.9, 128.4, 132.3, 135.0, 137.3, 138.0, 141.6, 166.6, 168.6; IR (neat) 2979, 2852, 1714, 1704, 1650, 1633, 1173, 1133 cm^{-1}; HRMS Calcd for $C_{20}H_{30}O_4$: M, 334.2144. Found: m/z 334.2139; Anal. Calcd for $C_{20}H_{30}O$: C, 71.82; H, 9.04%. found C, 72.00; H, 8.64%.

(3*E*,5*E*,9*E*)-*tert*-Butyl 12-cyano-[(2*E*)-ethylidene]-4,10-dimethyl-11-oxododeca-3,5,9-trienoate (**31**)

To a THF (10 mL) solution of CH_3CN (0.322 mL, 6.17 mmol) was added *n*-BuLi (1.46 M in hexane, 2.11 mL, 3.09 mmol) at –78 °C after which the reaction mixture was stirred for 1 h. A THF (5 mL) solution of ester **30** (500 mg, 1.54 mmol) was added dropwise to the reaction mixture at –88 °C. After 1 minute, buffer solution was added and the organic materials were extracted with ethyl acetate, then the organic phase was dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. Purification by flash chromatography (ethyl acetate: hexane=1:10) gave 491 mg (93%) of ketonitrile **31**.

^1H NMR($CDCl_3$) δ=1.45 (9H, s), 1.60 (3H, d, *J*=0.6 Hz), 1.67 (3H, dd, *J*=1.0, 7.1 Hz), 1.82 (3H, d, *J*=0.6 Hz), 2.31 (2H, q, *J*=7.2 Hz), 2.41 (2H, q, *J*=7.2 Hz), 3.75 (2H, s), 5.64 (1H, dt, *J*=15.6, 6.8 Hz), 5.92 (1H, s), 6.21 (1H, d, *J*=15.6 Hz), 6.74 (1H, dt, *J*=1.0, 7.2 Hz), 6.77 (1H, q, *J*=7.2 Hz); ^{13}C NMR($CDCl_3$) δ= 11.5, 14.5, 15.8, 28.1, 28.3, 29.2, 31.4, 80.43, 114.2, 123.9, 127.4, 132.1, 135.7, 136.3, 137.0, 138.2, 145.5, 166.5, 188.2; IR (neat) 2979, 2929, 2256, 1705, 1681, 1639, 1281, 1254, 1169, 1134 cm^{-1}; HRMS Calcd for $C_{21}H_{29}NO_3$: M, 343.2147. Found: m/z 343.2153; Anal. Calcd for $C_{21}H_{29}NO_3$: C, 73.44; H, 8.51; N, 4.08%. found C, 73.53; H, 8.79; N, 4.08%.

(3*E*,5*E*,9*E*)-12-Cyano-[(2*E*)-ethylidene]-4,10-dimethyl-11-oxododeca-3,5,9-trienoic acid (**32**)

To a CH_2Cl_2 (1.0 mL) solution of ketonitrile **31** (97.0 mg, 0.282 mmol) was added CF_3COOH (0.6 mL) at 0 °C and the reaction mixture was stirred for 5 minutes at 0 °C, then for 15 minutes at 23 °C. The solvent and CF_3COOH were removed *in vacuo*, to give carboxylic acid **32**, which was used in the next step. An analytical sample was recrystallized from benzene.

^1H NMR($CDCl_3$) δ= 1.63 (3H, s), 1.74 (3H, d, *J*=7.0 Hz), 1.82 (3H, s), 2.32 (2H, q, *J*=7.0 Hz), 2.42 (2H, q, *J*=7.0 Hz), 3.75 (2H, s), 5.69 (1H, dt, *J*=15.6, 6.8 Hz), 5.94 (1H, s), 6.24 (1H, d, *J*=15.6 Hz), 6.58 (1H, t, *J*=6.7 Hz), 7.06 (1H, q, *J*=7.0 Hz); ^{13}C NMR($CDCl_3$) δ= 11.5, 14.4, 16.1, 28.2, 29.1, 31.4, 114.22, 122.6, 128.3, 129.9, 135.3, 136.4, 138.2, 142.3, 145.4, 172.0, 188.3; IR (neat) 2924, 2854, 2258, 1681, 1633, 1281, 1219, 914, 773cm^{-1}; Mp.64.0-66.0 °C; HRMS Calcd for $C_{17}H_{21}NO_3$: M, 287.1521. Found: m/z 287.1529; Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87%. Found C, 71.24; H, 7.36; N, 4.42%.

(3*E*,5*E*,9*E*)-Methyl 12-cyano-[(2*E*)-ethylidene]-4,10-dimethyl-11-oxododeca-3,5,9-trienoate (**33**)

To an Et_2O (3 mL) solution of the above carboxylic acid **32** was added an ether solution of CH_2N_2 at –78 °C until the yellow color of CH_2N_2 persisted. After addition had been completed, the solvent was removed *in vacuo*. Purification by TLC (ethyl acetate: hexane=1:1) gave 78.0 mg (92% for 2 steps) of ketonitrile **33**.

^1H NMR($CDCl_3$) δ= 1.60 (3H, d, *J*=0.7 Hz), 1.69 (3H, dd, *J*=1.1, 7.2 Hz), 1.81

(3H, s), 2.31 (2H, q, J=7.1 Hz), 2.41 (2H, q, J=7.2 Hz), 3.70 (3H, s), 3.75 (2H, s), 5.67 (1H, dt, J= 15.6 ,6.8 Hz), 5.94 (1H, s), 6.22 (1H, d, J=15.6 Hz), 6.58 (1H, dt, J=1.1, 7.0 Hz), 6.91 (1H, dq, J=0.7, 7.2 Hz); ^{13}C NMR($CDCl_3$) δ= 11.5, 14.3, 15.8, 28.2, 29.2, 31.4, 51.8, 114.2, 123.2, 127.9, 130.5, 135.4, 136.3, 137.5, 139.7, 145.3, 167.7, 188.2; IR (neat) 2951, 2929, 2256, 1716, 1684, 1637, 1435, 1252, 1134cm^{-1}; HRMS Calcd for $C_{18}H_{23}NO_3$: M, 301.1678. Found: m/z 301.1673.

(14*S*)-(3*E*,5*E*,9*E*,12*E*)-Methyl 12-cyano-[(2*E*)-ethylidene]-4,10-dimethyl-11-oxo-14-triethylsiloxypentadeca-3,5,9,12-tetraenoate (**34**)

To a benzene (1 mL) solution of ketonitrile **33** (36.6 mg, 0.365 mmol) was added (*S*)-2-(triethylsiloxy)propanal and ethylenediammonium diacetate (1.7 mg, 0.0094 mmol) and the reaction mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo*. Very rapid flash column chromatography of florisil gel in order to remove ammonium salt (ethyl acetate: hexane = 1:3) gave crude olefin **34** with some aldehyde impurity, which was used immediately in the next reaction.

(12*S*,13*S*,14*S*)-(3*E*,5*E*,9*E*)-Methyl 12-cyano-[(2*E*)-ethylidene]-4,10-dimethyl-11-oxo-14-triethylsiloxy12,13-epoxypentadeca-3,5,9-trienoate (**35**)

To a THF (4 mL) solution of TrOOH (400 mg, 1.45 mmol) was added *n*-BuLi (1.49 M in hexane, 0.85 mL, 1.22 mmol) at –78 °C and the reaction mixture was stirred for 1 h at the same temperature. To this mixture was added a THF (3mL) solution of crude olefin **34**, and the mixture was stirred for 1 h at –78 °C. After buffer solution had been added, the organic materials were extracted with ethyl acetate three times, and the combined organic phases were dried over anhydrous Na_2SO_4, which was concentrated *in vacuo* after filtration. Crude epoxide **35** was used directly in the next reaction.

(12*R*,13*S*,14*S*)-(3*E*,5*E*,9*E*)-Methyl 12-carbamoyl- [(2*E*)-ethylidene]-14-hydroxy-4,10-dimethyl-11-oxo-12,13-epoxypentadeca-3,5,9-trienoate (**38**)

To the crude epoxide **35** was added THF (0.3 mL), H_2O (70 μL), acetic acid (0.21 mL, 3.64 mmol) and NH_4F (50.0 mg, 1.35 mmol) and the reaction mixture was stirred for 1.5 h at room temperature. A saturated $NaHCO_3$ solution was added to the reaction mixture and the organic materials were extracted with ethyl acetate three times, then the combined organic phases were dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. Rapid flash column chromatography (ethyl acetate: hexane=1:5, then $CHCl_3$: MeOH=10:1) gave the crude hydroxynitrile **36**, which was charged on thin layer chromatography plate and developed by an ethyl acetate/hexane mixed solvent (1/2). Lactone **37** and hydroxyamide **38** could be separated but were eluted together with 10% MeOH/$CHCl_3$. After evaporation of the solvent, a MeOH (1 mL) solution of the mixture **37** and **38** was treated with an NH_4OH solution (concentration 30%, 0.5 mL) at 0 °C and the reaction mixture was stirred for 0.5 h at this temperature. Buffer solution was added and the organic materials were extracted with $CHCl_3$ three times, then the combined organic phases were dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. Purification by flash column chromatography (ethyl acetate: hexane=3:1) gave 10.7 mg (22% for 5 steps) of hydroxyamide **38**.

^{1}H NMR($CDCl_3$) δ= 1.34 (3H, d, J=6.3 Hz), 1.59 (3H, s) , 1.69 (3H, dd, J=0.8, 7.0 Hz), 1.77 (3H, s), 2.33 (2H, q, J=6.7 Hz), 2.42 (2H, q, J=6.9 Hz), 3.14 (1H, d, J=7.9 Hz), 3.26 (1H, bs), 3.69-3.71 (1H ,m), 3.70 (3H, s), 5.67 (1H, dt, J=15.6, 6.9 Hz), 5.92 (1H, s), 6.22 (1H, d, J=15.6 Hz), 6.33 (1H, bs), 6.47 (1H, bs), 6.91 (1H, q, J=7.1 Hz),

7.06 (1H, dt, J=0.7, 6.9 Hz); ^{13}C NMR($CDCl_3$) δ= 11.2, 14.3, 15.7, 20.3, 29.0, 31.3, 51.9, 65.3, 65.5, 66.1, 122.8, 128.3, 130.4, 135.0, 135.5, 138.1, 139.8, 149.6, 167.4, 167.9, 192.9; IR (neat) 3425, 3332, 2951, 2927, 1712, 1689, 1635, 1435, 1263, 1211, 1136, 1058, 1024, 966 cm^{-1}; HRMS Calcd for $C_{21}H_{29}NO_6$:M, 391.1995. Found: m/z 391.1995.

(3*E*,5*E*,9*E*)-Methyl [(2*E*)-ethylidene]-4,10-dimethyl-11-((1*R*,4*S*,5*S*)-4-methyl-2-oxo-3,6-dioxabicyclo[3.1.0]hex-1-yl)-11-oxoundeca-3,5,9-trienoate (**37**)

^{1}H NMR($CDCl_3$) δ= 1.47 (3H, d, J=6.7 Hz), 1.60 (3H, s), 1.70 (3H, d, J=6.2 Hz), 1.84 (3H, s), 2.33 (2H, q, J=6.7 Hz), 2.40-2.50 (2H, m), 3.70 (3H, s), 4.05 (1H, s), 4.68 (1H, q, J=6.7 Hz), 5.69 (1H, dt, J=15.5, 7.2 Hz), 5.94 (1H, s), 6.23(1H, d, J=15.5 Hz), 6.87-6.95 (2H, m); ^{13}C NMR($CDCl_3$) δ= 11.2, 14.3, 15.8, 17.8, 29.2, 31.3, 51.8, 60.4, 64.0, 75.4, 123.1, 128.0, 130.5, 135.5, 136.1, 137.7, 139.7, 149.4, 167.8, 168.2, 188.3; IR (neat) 2981, 2927, 1782, 1718, 1680, 1637, 1437, 1252, 1072 cm^{-1}; HRMS Calcd for $C_{21}H_{26}O_6$: M, 374.1729. Found: m/z 374.1737.

(+)-epolactaene (**1**)

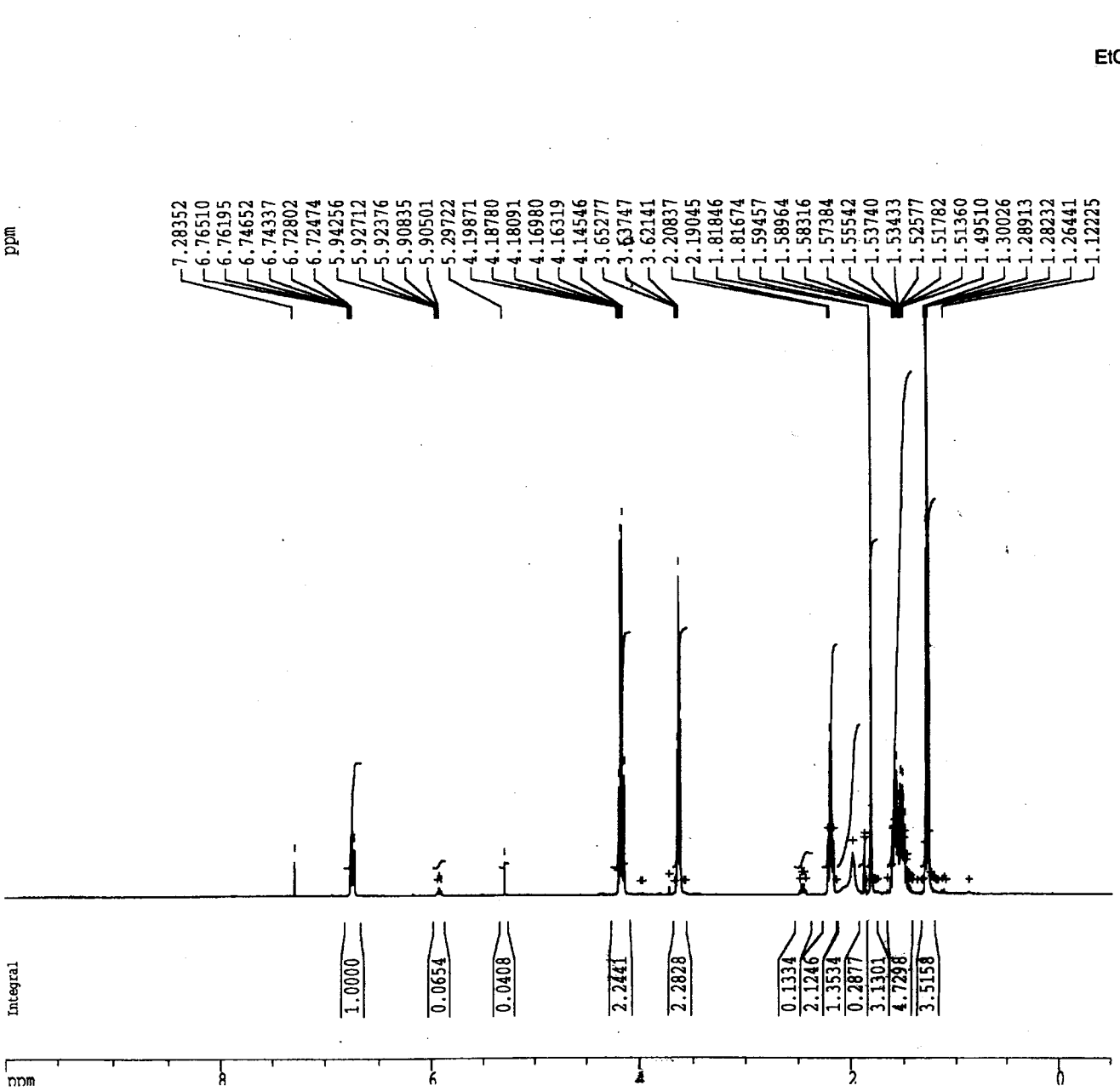
To a CH_2Cl_2 (0.1 mL) solution of hydroxyamide **38** (9.7 mg, 0.0248 mmol) was added triethylamine (67μL, 0.49 mmol) and a DMSO (0.1 mL) solution of SO_3•pyridine (52.7 mg, 0.331 mmol) at 0 °C, and the reaction mixture was stirred for 2 h. Buffer solution was added and the organic materials were extracted with ethyl acetate, then the combined organic extracts were washed with a saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. Flash column chromatography (ethyl acetate: hexane = 3:1) gave 7.5 mg (78%) of (+)-epolactaene (**1**).

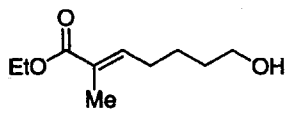
^{1}H NMR(500 MHz, CD_3OD) δ= 1.51 (3H, s), 1.61 (3H, d, J=1.0 Hz), 1.71 (3H, dd, J=1.5, 7.0 Hz), 1.85 (3H, s), 2.30-2.40 (2H, m), 2.40-2.55 (2H, m), 3.71 (3H, s), 3.97 (1H, s), 5.77 (1H, dt, J=15.6, 7.0 Hz), 5.94 (1H, bs), 6.28 (1H, d, J=15.4 Hz), 6.92 (1H, dq, J=0.9, 7.0 Hz), 7.01 (1H, dt, J=1.0, 7.0 Hz); ^{13}C NMR(125 MHz, CD_3OD) δ= 11.1, 14.6, 16.0, 22.2, 30.2, 32.5, 52.4, 63.9, 66.0, 84.7, 123.6, 129.7, 131.9, 136.6, 137.2, 139.6, 140.8, 150.0, 169.6, 172.2, 192.1; IR (neat) 3440, 3315, 2950, 2925, 1720, 1682, 1633, 1435, 1271,1136, 1061, 964, 951 cm^{-1}; $[\alpha]_D^{26}$ +31 (C=0.12, MeOH); lit $[\alpha]_D^{26}$ +32 (C=0.1, MeOH); HRMS Calcd for $C_{21}H_{27}NO_6$:M, 389.1838. Found: m/z 389.1853.

(-)-epolactaene

All the analytical data including ^{1}H, ^{13}C and IR are the same as those of (+)-epolacatene except for the optical rotation.

$[\alpha]_D^{26}$ -28 (C=0.09, MeOH)





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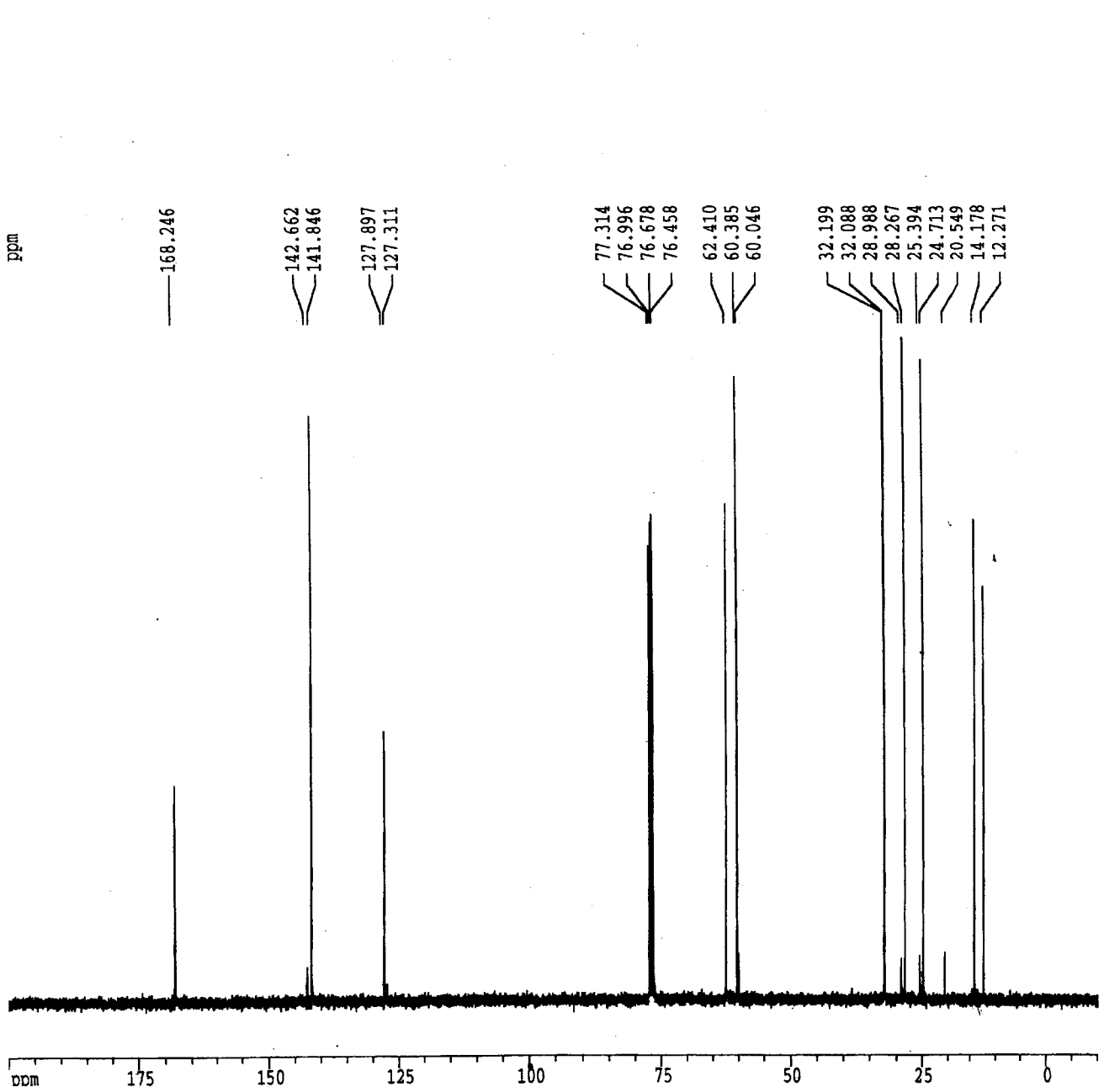

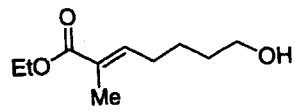

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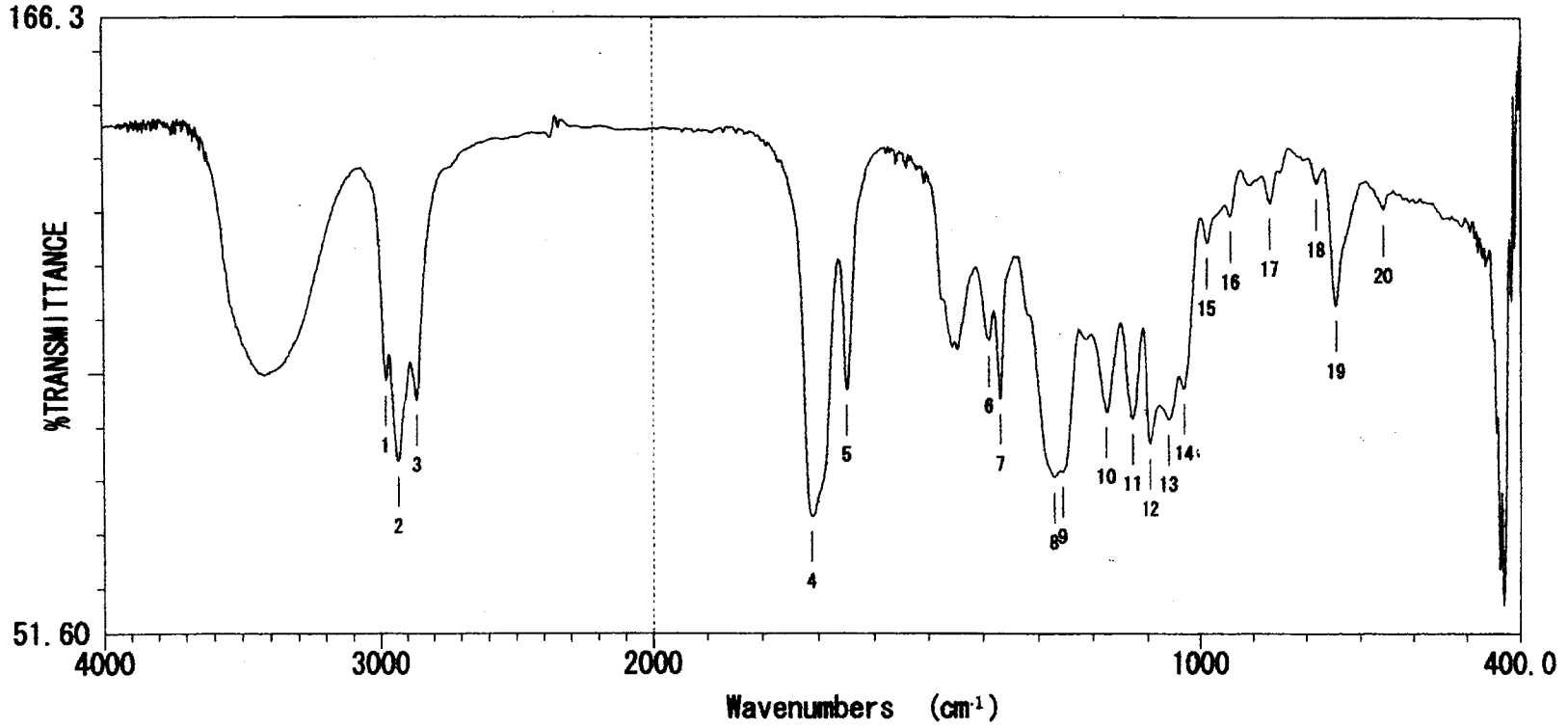
FTIR system for Windows



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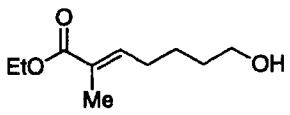

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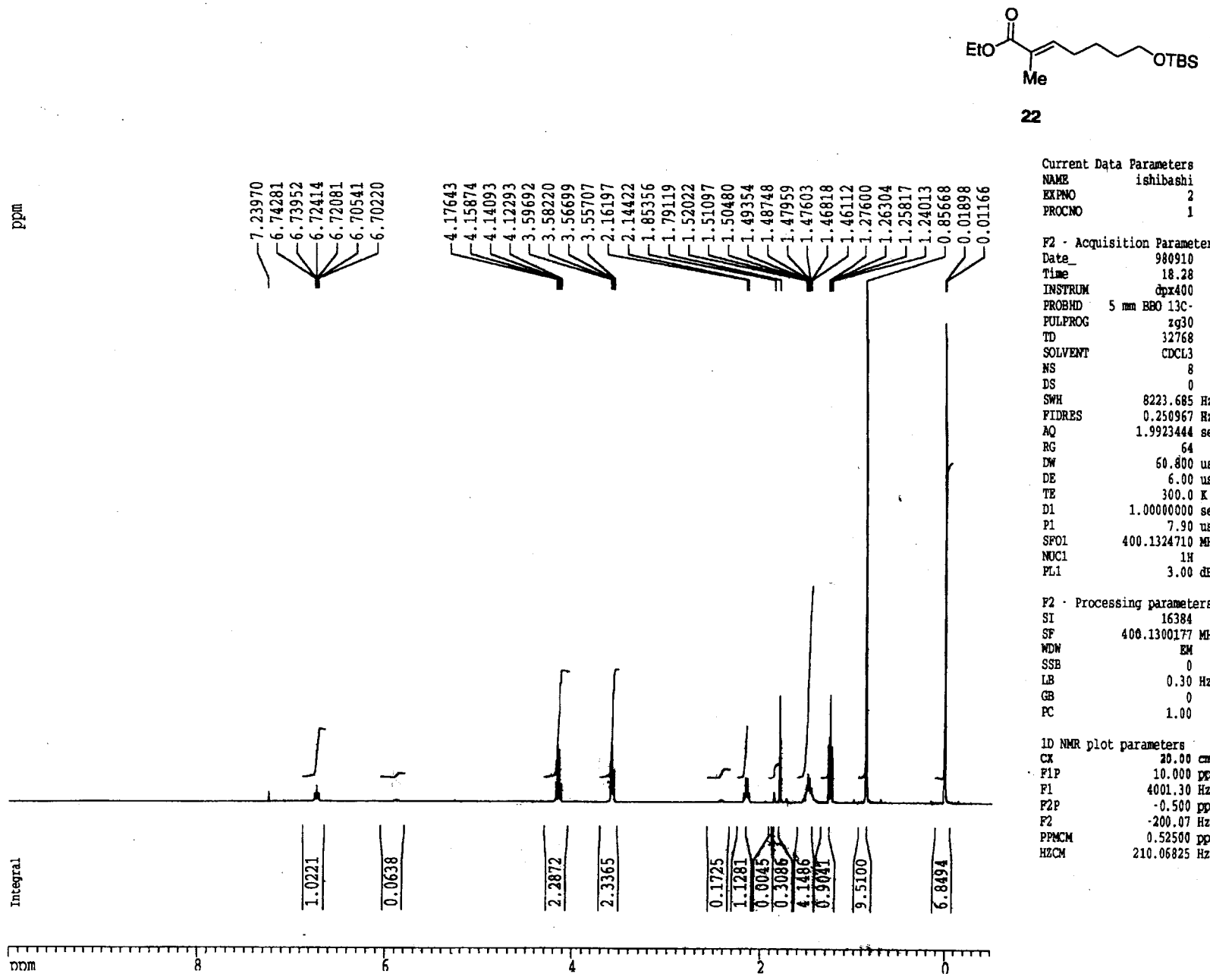

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FIDRES	0.250967 Hz
AQ	1.9923444 sec
RG	64
DW	60.800 usec
DE	6.00 usec
TE	300.0 K
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P1	7.90 usec
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NUC1	1H
PL1	3.00 dB

F2 - Processing parameters

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1D NMR plot parameters

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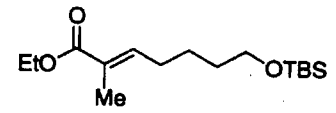

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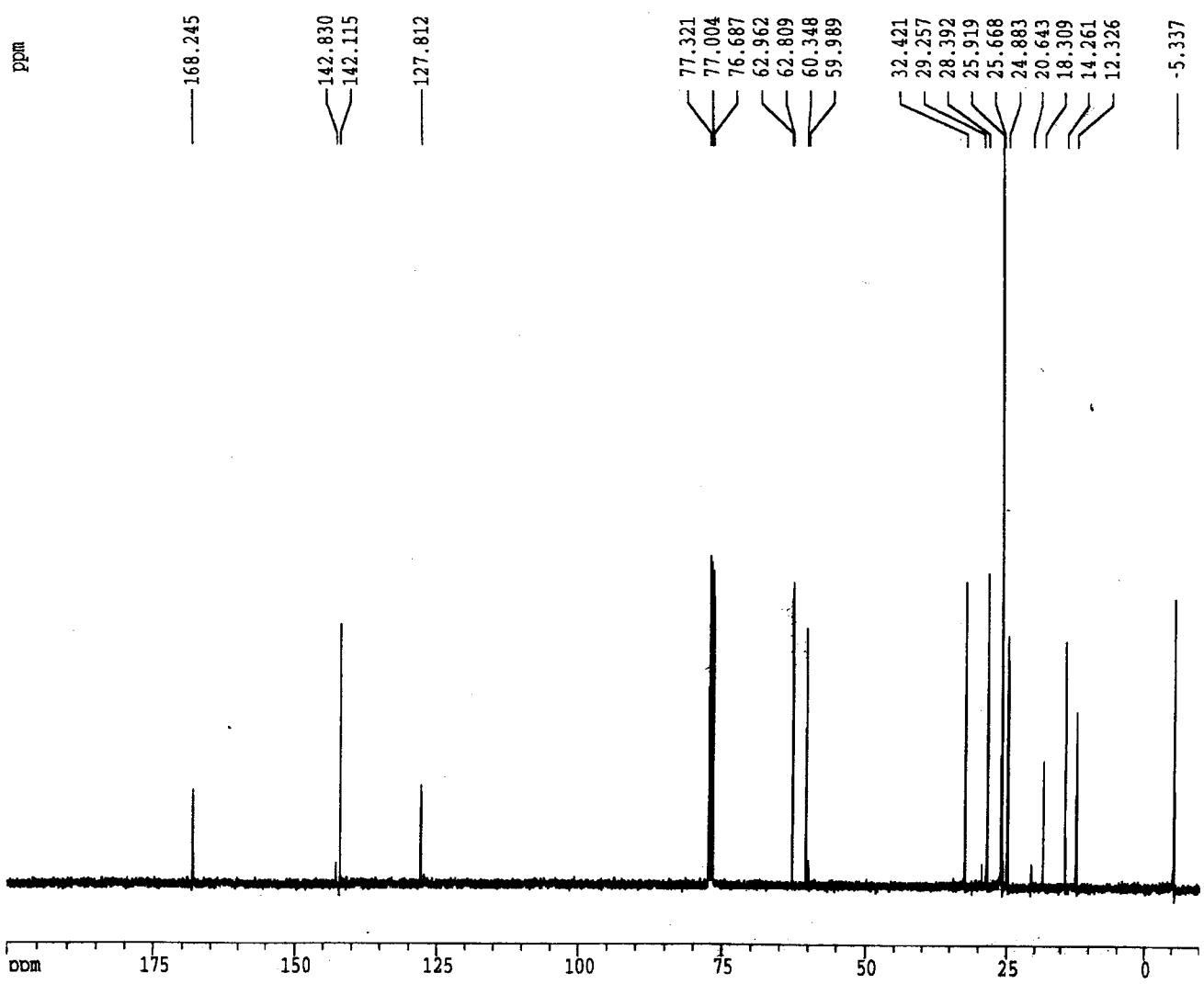


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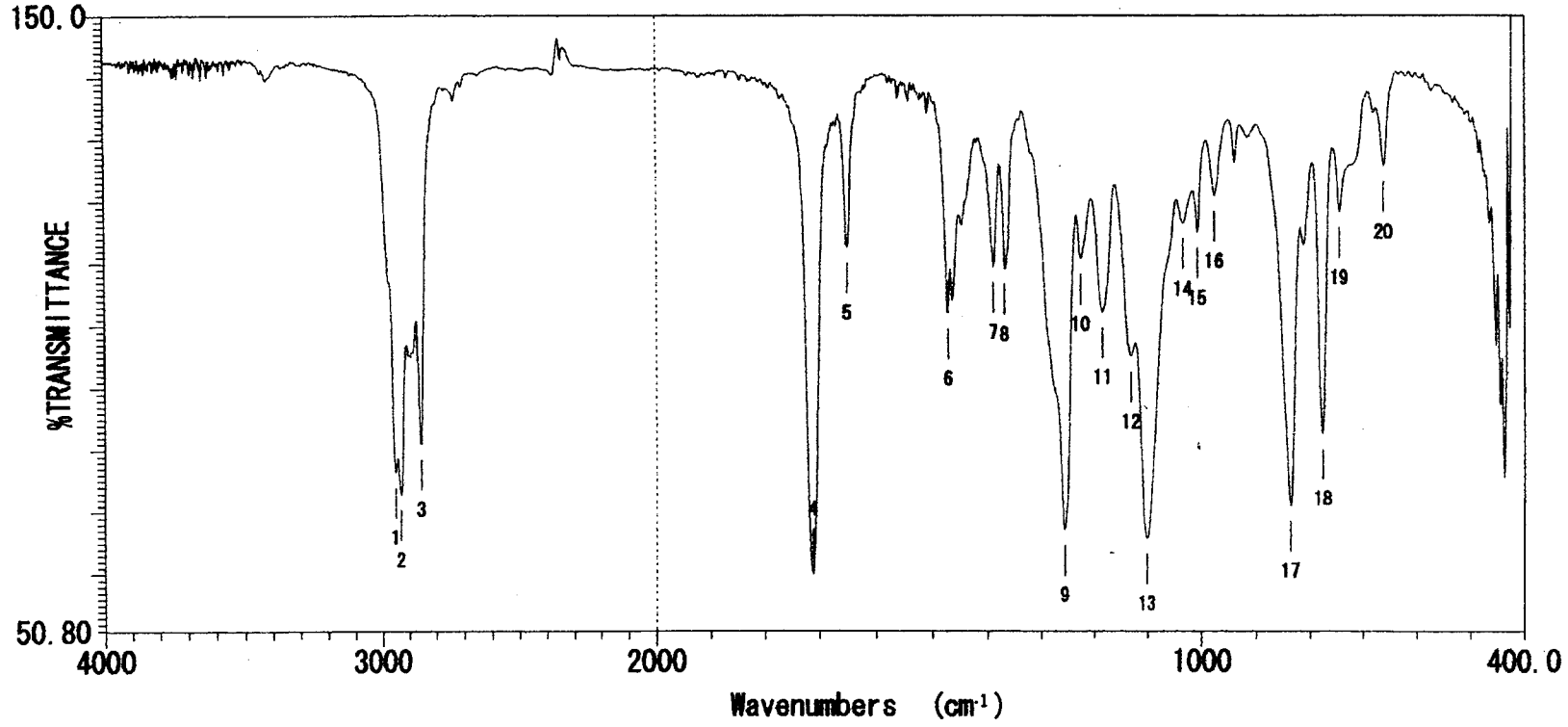
FIDRES         0.485949 Hz
AQ             1.0289652 sec
RG                  8192
DW                15.700 usec
DE                 6.00 usec
TE                300.0 K
d11           0.03000000 sec
d12           0.00002000 sec
PL13              22.00 dB
D1            2.00000000 sec
CPDPRG2          waltz16
PCPD2             80.00 usec
SFO2         400.1316005 MHz
NUC2                 1H
PL2                3.00 dB
PL12              22.00 dB
P1                 9.30 usec
SFO1         100.6254358 MHz
NUC1                13C
PL1                3.00 dB

F2 - Processing parameters
SI                 32768
SF           100.6127727 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

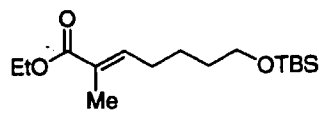
1D NMR plot parameters
CX                 20.00 cm
F1P               200.000 ppm
F1              20122.55 Hz
F2P               -10.000 ppm
F2              -1006.13 Hz
PPMCM             10.50000 ppm/cm
```

HORIBA FT-IR for Windows(TM) Ver.3.12
FTIR system for Windows

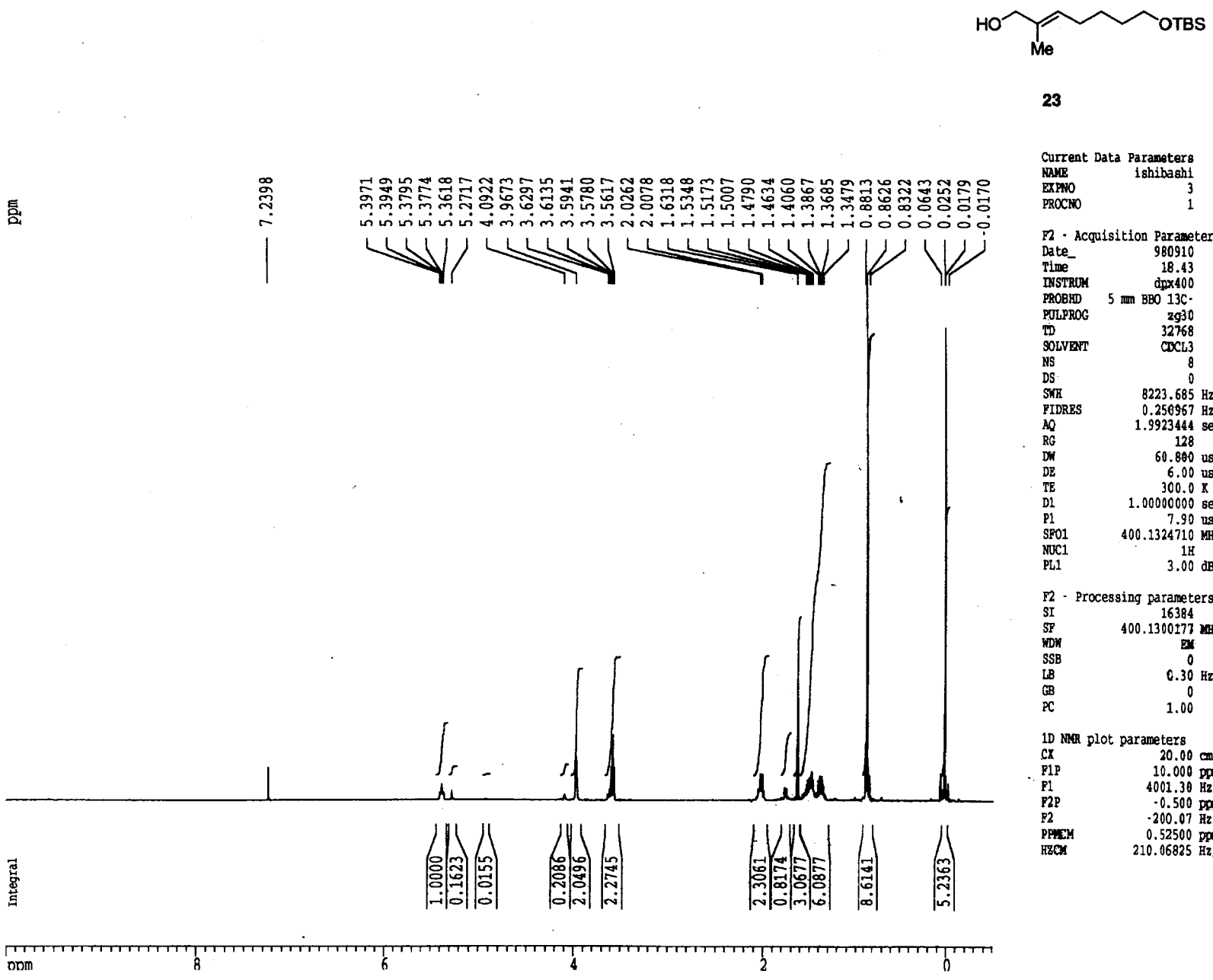


ファイル名	2mate
タイトル	
測定日時	2000年12月21日 14時38分35秒
測定分解能	4 cm-1
スキャン回数	10 回
測定ゲイン	1
コメント	

ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)
01	2952.48	76.4337	11	1184.08	102.428
02	2931.27	72.8504	12	1132.01	95.2695
03	2857.99	80.9404	13	1101.15	65.7866
04	1712.48	59.9552	14	1033.66	116.652
05	1650.77	112.680	15	1006.66	115.151
06	1471.42	102.185	16	975.804	121.115
07	1388.50	109.656	17	836.955	71.0730
08	1367.28	109.339	18	775.244	82.8881
09	1256.43	67.1757	19	744.388	118.480
10	1224.58	110.915	20	661.464	125.848



22



Current Data Parameters

NAME	ishibashi
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

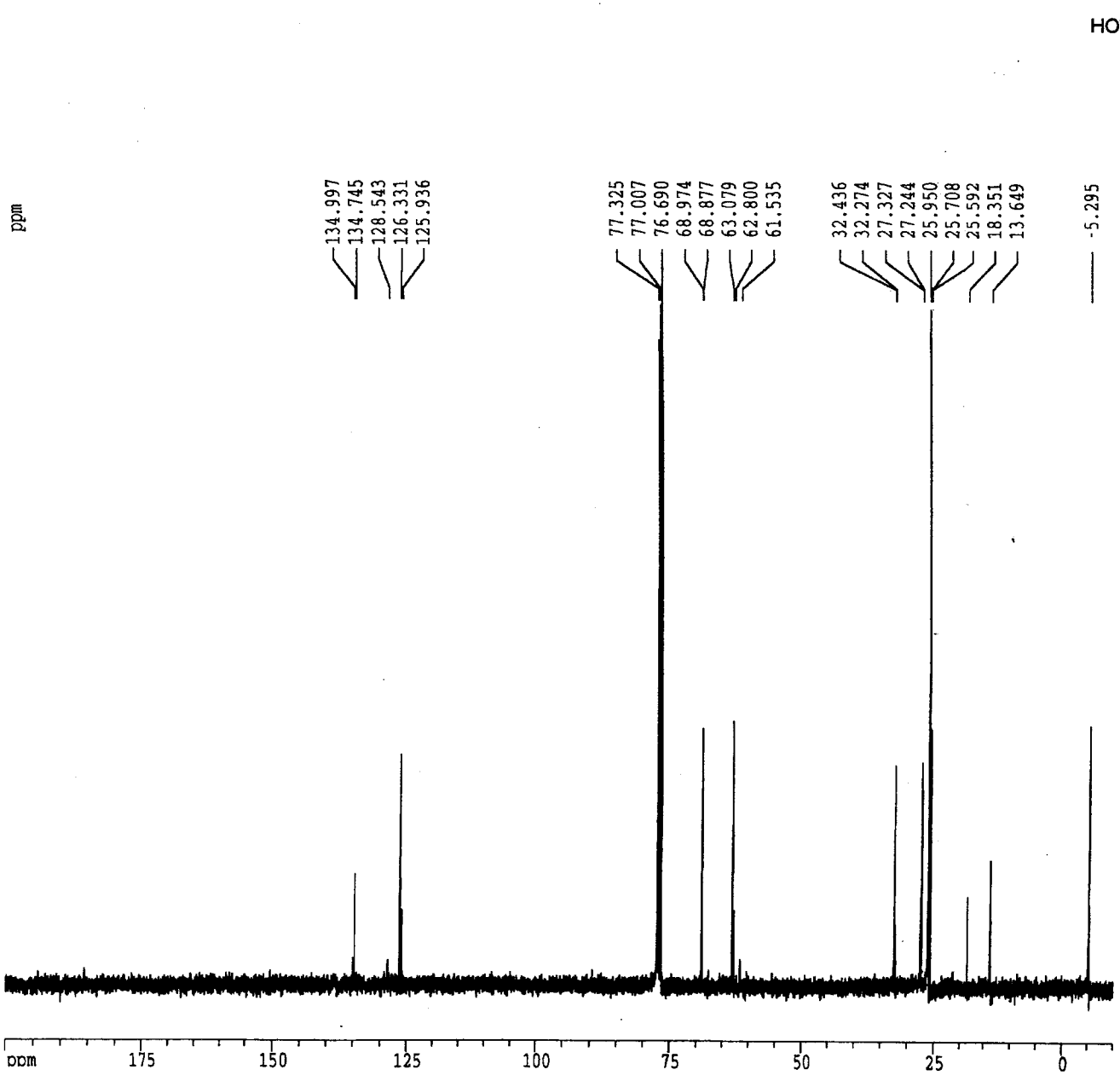
Date_	980910
Time	18.43
INSTRUM	dpx400
PROBHD	5 mm BBO 13C-
PULPROG	zg30
TD	32768
SOLVENT	CDCL3
NS	8
DS	0
SWH	8223.685 Hz
FIDRES	0.250967 Hz
AQ	1.9923444 sec
RG	128
DW	60.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.90 usec
SFO1	400.1324710 MHz
NUC1	1H
PL1	3.00 dB

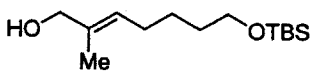
F2 - Processing parameters

SI	16384
SF	400.1300177 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.000 ppm
F1	4001.30 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.52500 ppm/cm
HZCM	210.06825 Hz/cm





23

Current Data Parameters

NAME	ishibashi-C
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	980910
Time	18.53
INSTRUM	dpx400
PROBHD	5 mm BBO 13C-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	179
DS	2
SWH	31847.133 Hz
FIDRES	0.485949 Hz
AQ	1.0289652 sec
RG	16384
DW	15.700 usec
DE	6.00 usec
TE	300.0 K
d11	0.03000000 sec
d12	0.00002000 sec
PL13	22.00 dB
D1	2.00000000 sec
CPDPRG2	waltz16
PCPD2	80.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	3.00 dB
PL12	22.00 dB
P1	9.30 usec
SFO1	100.6254358 MHz
NUC1	13C
PL1	3.00 dB

F2 - Processing parameters

SI	32768
SF	100.6127727 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	200.000 ppm
F1	20122.55 Hz
F2P	-10.000 ppm
F2	-1006.13 Hz
PPMCM	10.50000 ppm/cm

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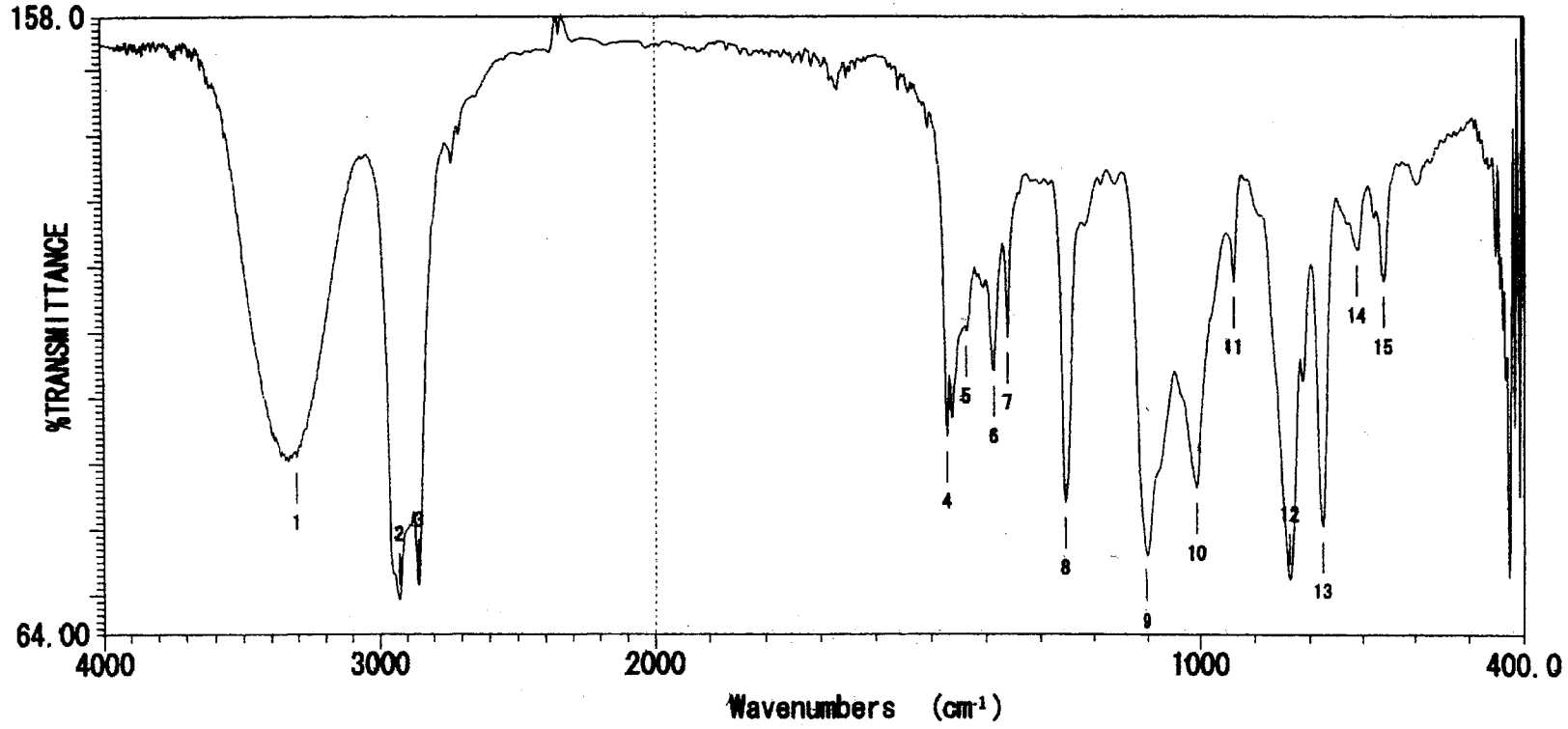
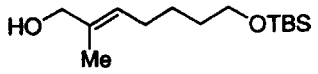
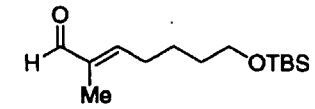


ファイル名	jk-etooh
タイトル	
測定日時	2000年12月21日 15時20分44秒
測定分解能	4 cm-1
スキャン回数	10 回
測定ゲイン	1
コメント	

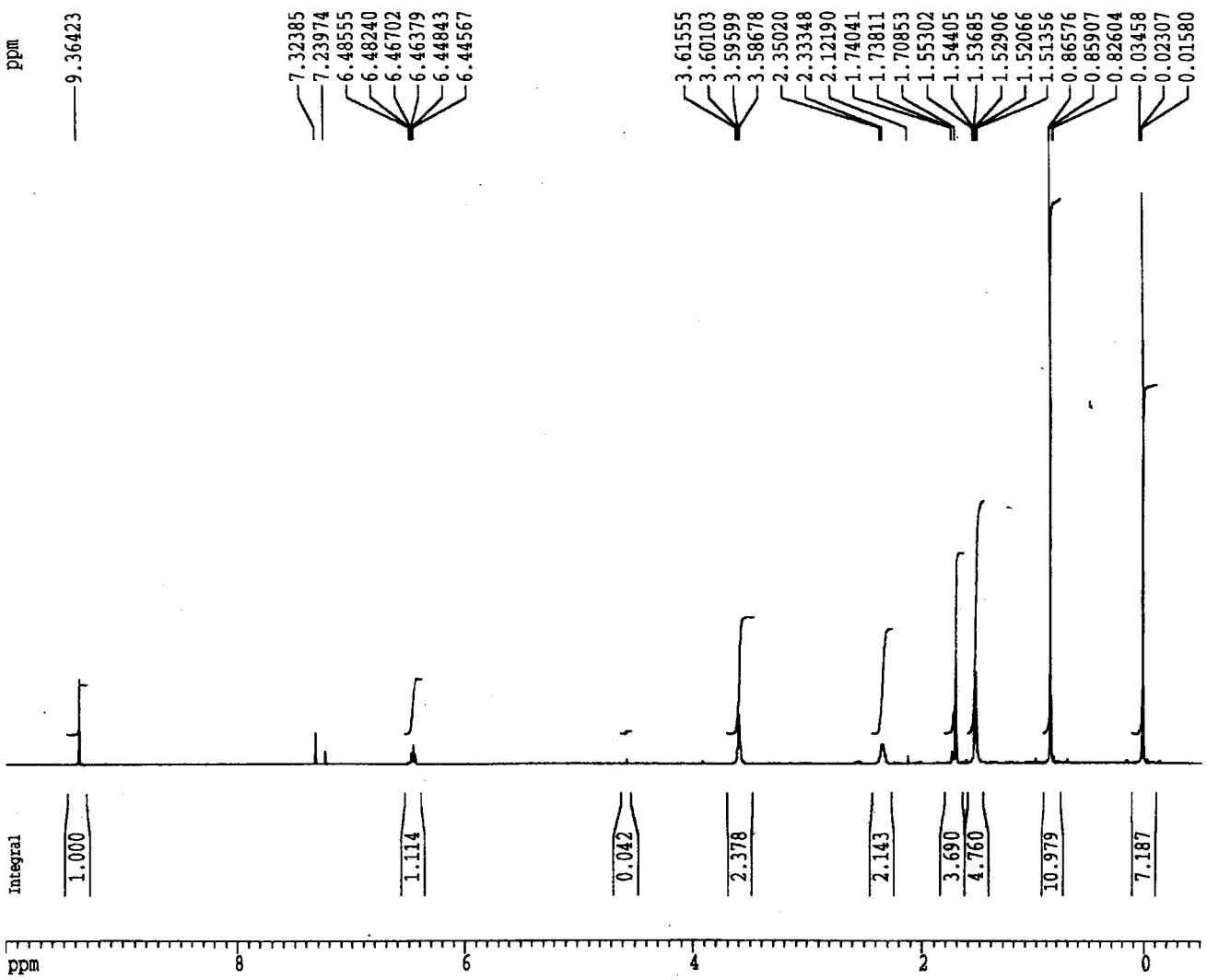
ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)
01	3307.32	90.9997	11	939.163	117.878
02	2929.34	69.2589	12	836.955	72.4982
03	2857.99	71.4044	13	775.244	80.6407
04	1471.42	94.2908	14	711.604	122.792
05	1436.71	110.340	15	661.484	117.977
06	1386.57	104.291			
07	1361.50	109.391			
08	1255.43	84.2105			
09	1101.15	76.0382			
10	1006.66	86.3888			



23



24



Current Data Parameters

NAME	ishibashi
EXPNO	4
PROCNO	1

F2 - Acquisition Parameters

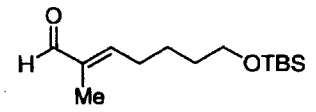
Date_	980912
Time	17.16
INSTRUM	dpx400
PROBHD	5 mm BBO 13C-
PULPROG	zg30
TD	32768
SOLVENT	CDCL3
NS	8
DS	0
SWH	8223.685 Hz
FIDRES	0.250967 Hz
AQ	1.9923444 sec
RG	64
DW	60.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.90 usec
SFO1	400.1324710 MHz
NUC1	1H
PL1	3.00 dB

F2 - Processing parameters

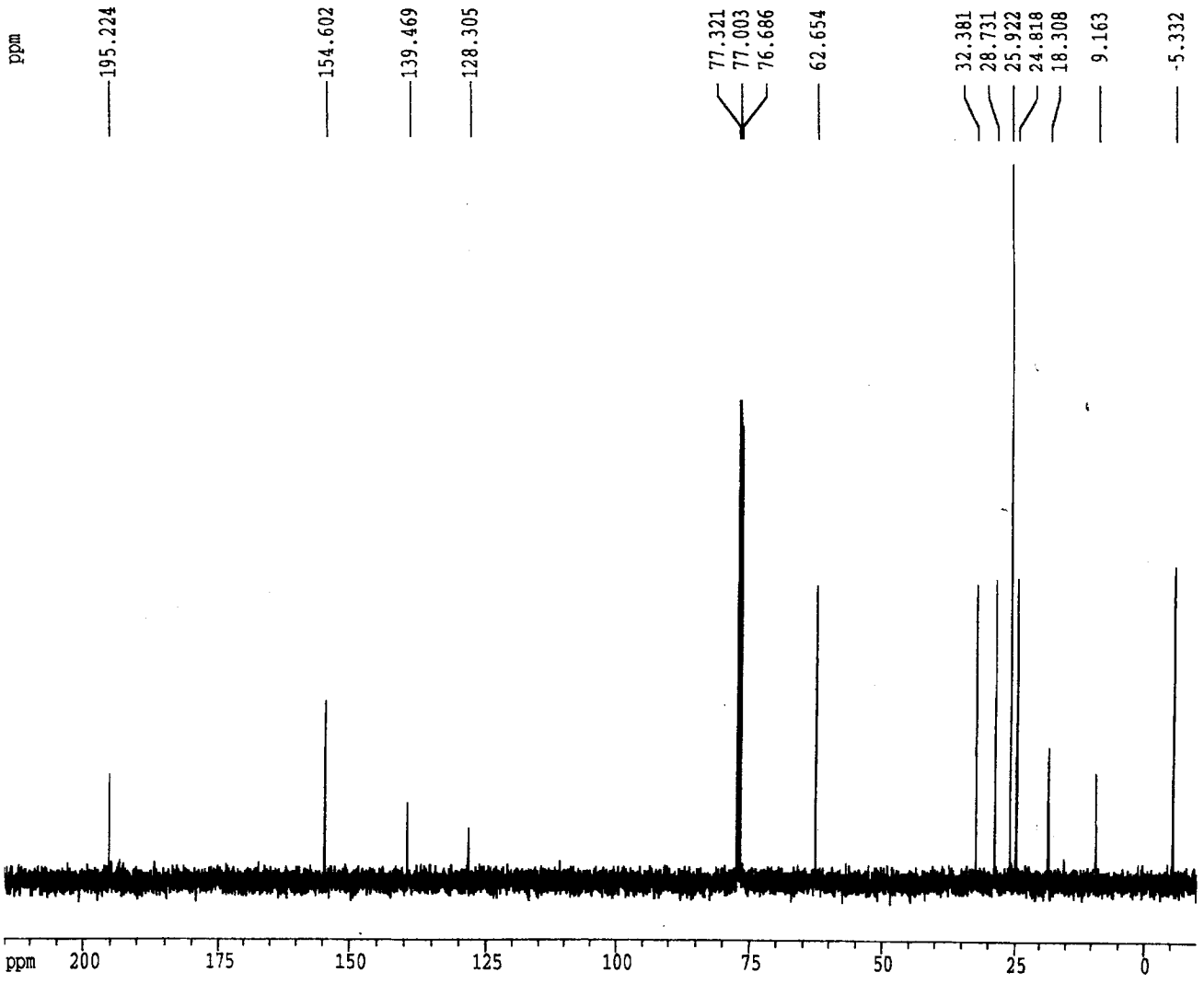
SI	16384
SF	400.1300177 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.000 ppm
F1	4001.30 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.52500 ppm/cm
HZCM	210.06825 Hz/cm



24



Current Data Parameters
NAME Jan09-01-hayash
EXPNO 103
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010109
Time 21.23
INSTRUM dpx400
PROBHD 5 mm BBO 13C-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 84
DS 2
SWH 31847.133 Hz
FIDRES 0.485949 Hz
AQ 1.0289652 sec
RG 4096
DW 15.700 usec
DE 6.00 usec
TE 300.0 K
d11 0.03000000 sec
d12 0.00002000 sec
PL13 22.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 80.00 usec
SFO2 400.1316005 MHz
NUC2 1H
PL2 3.00 dB
PL12 22.00 dB
P1 9.30 usec
SFO1 100.6254358 MHz
NUC1 13C
PL1 3.00 dB

F2 - Processing parameters
SI 32768
SF 100.6127688 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 21631.75 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 11.25000 ppm/cm
HZCM 1131.89380 Hz/cm

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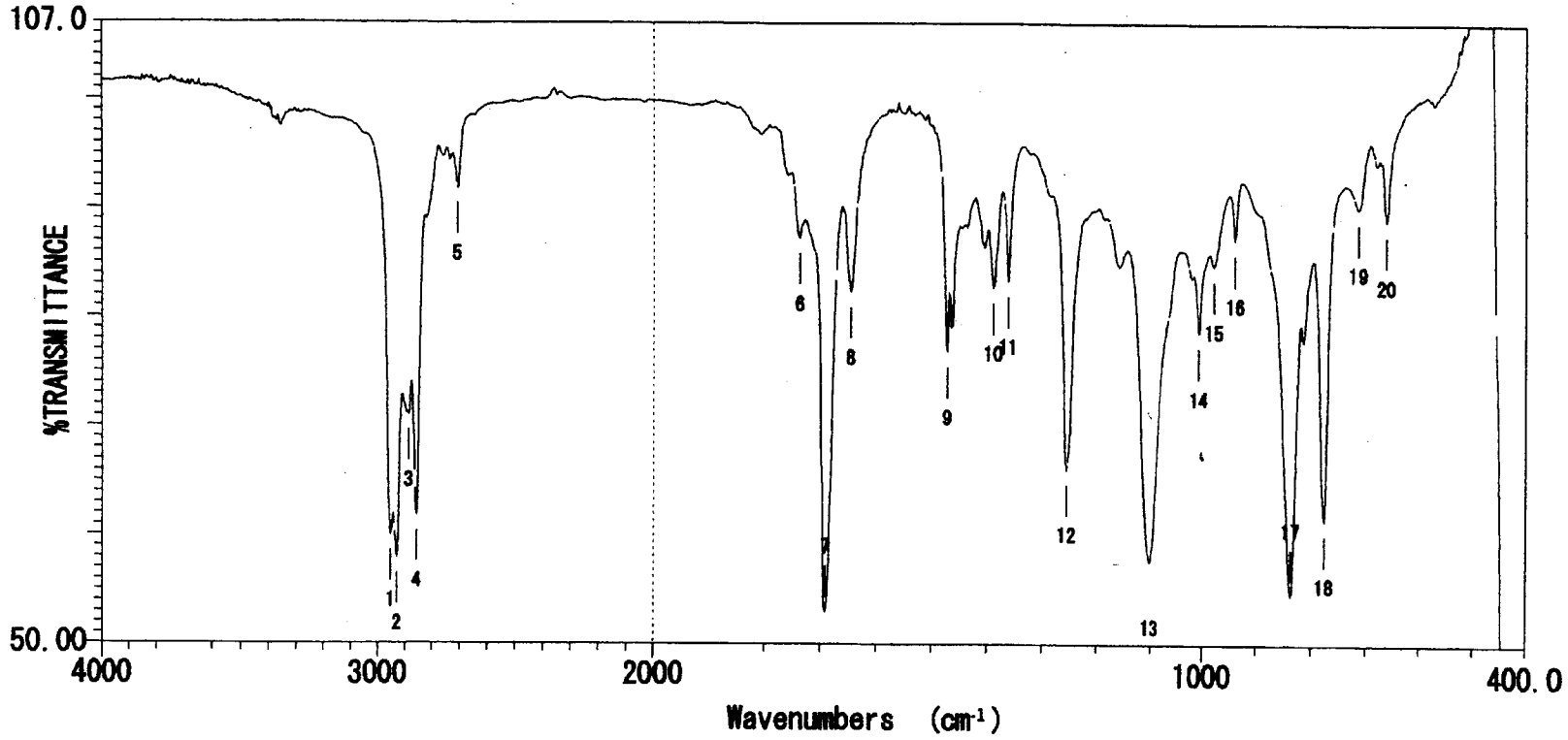
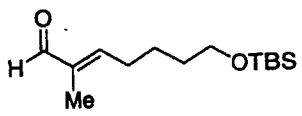
FTIR system for Windows

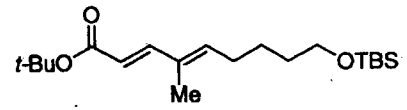


ファイル名	jk-23-2
タイトル	jk-23-2
測定日時	2001年01月10日 16時07分29秒
測定分解能	4 cm-1
スキャン回数	10 回
測定ゲイン	1
コメント	

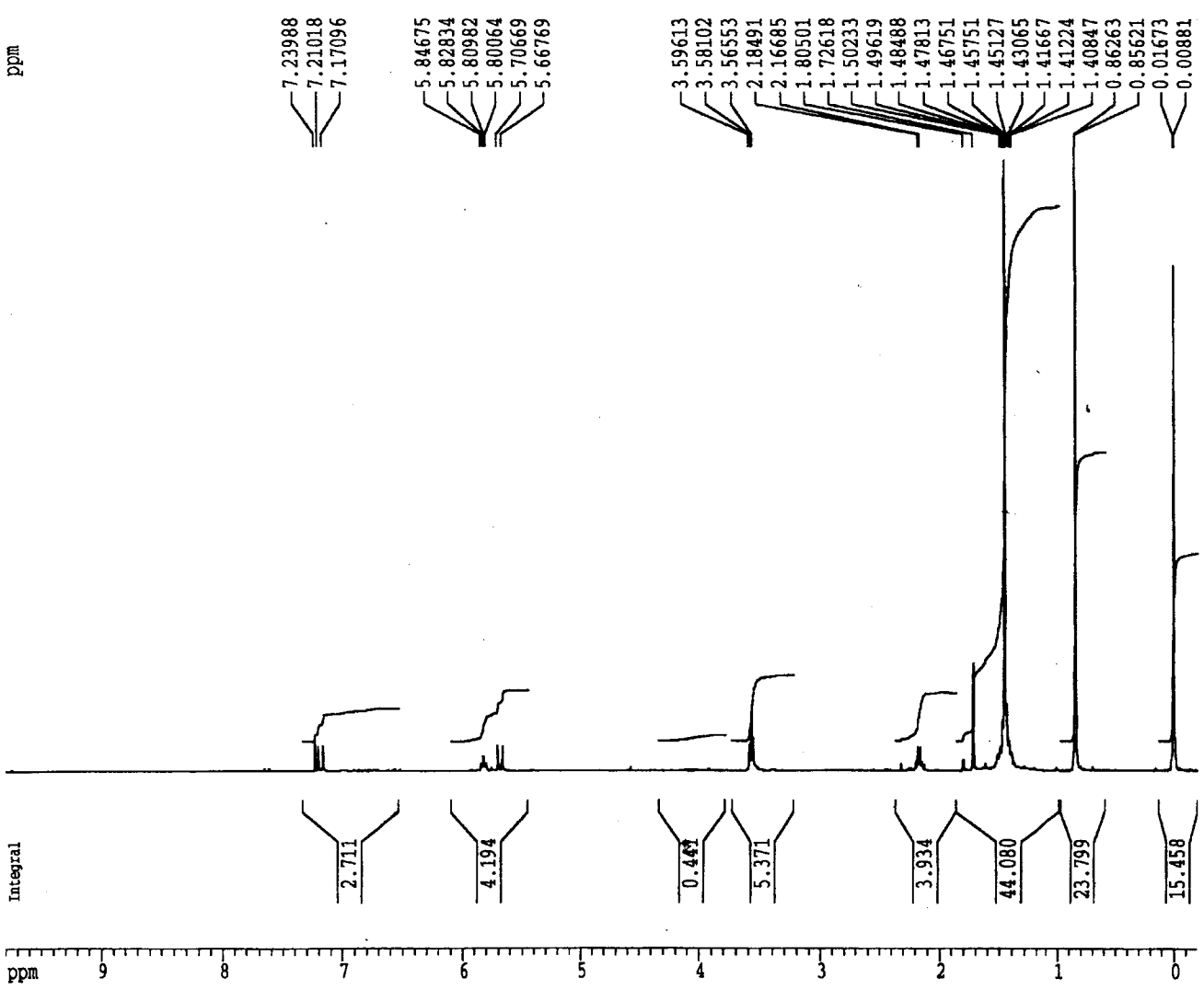
ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)
01	2952.48	59.9856	11	1361.50	83.4480
02	2929.34	57.8709	12	1256.43	66.1907
03	2886.92	71.0346	13	1101.15	57.6781
04	2857.99	61.7779	14	1006.66	78.7596
05	2709.50	91.8101	15	977.733	84.8833
06	1737.55	87.3328	16	939.163	87.2881
07	1691.27	52.9529	17	836.955	54.5194
08	1644.98	82.4227	18	775.244	61.5110
09	1471.42	76.9891	19	713.533	90.2036
10	1388.50	82.8670	20	661.464	89.0079



24



25

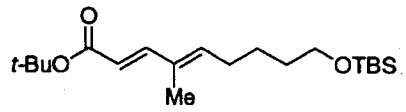


Current Data Parameters
NAME Dec09-98-hayash
EXPNO 10
PROCNO 1

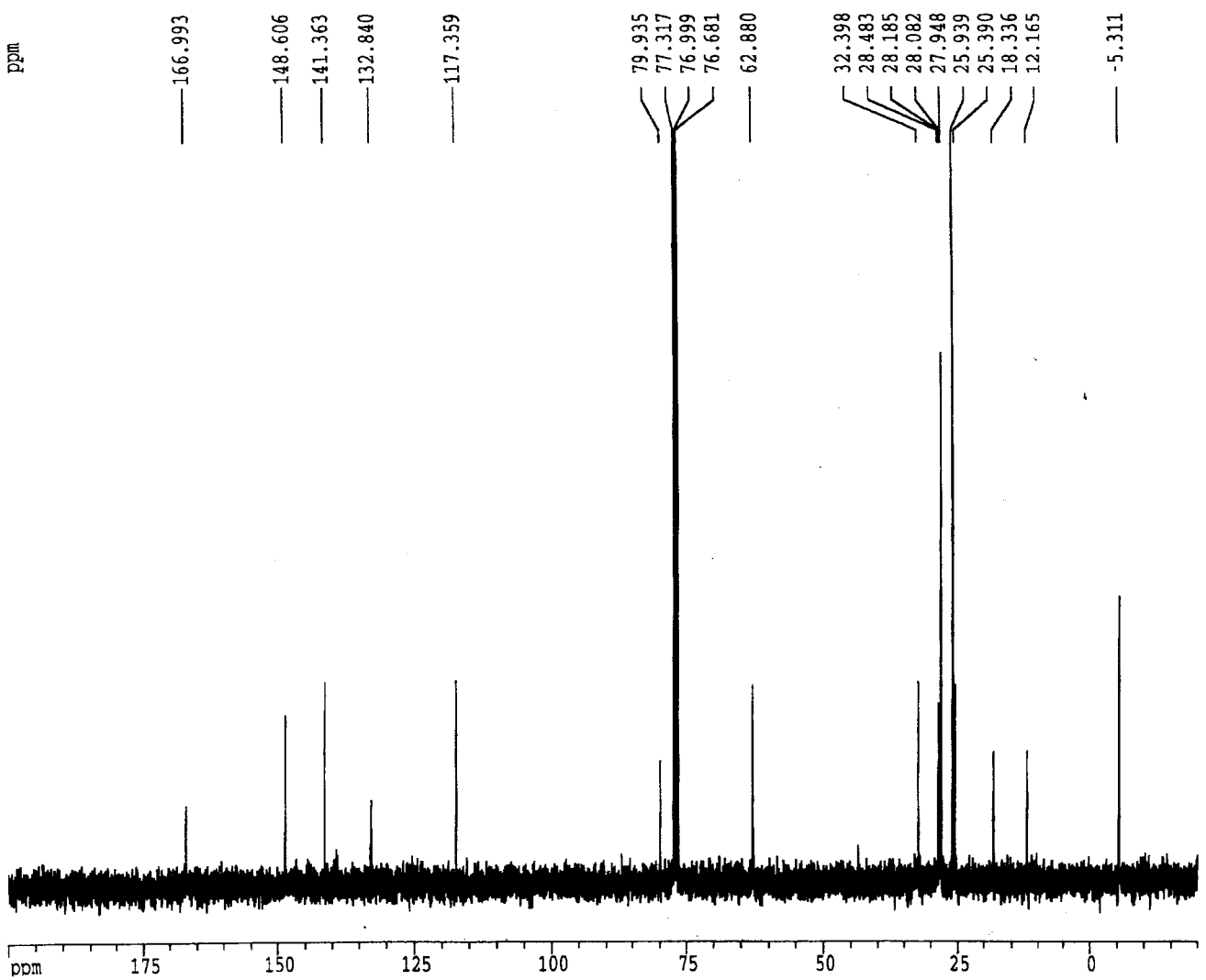
F2 - Acquisition Parameters
Date_ 981209
Time 9.31
INSTRUM dpx400
PROBHD 5 mm BBO 13C-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 101.6
DW 60.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 8.30 usec
SFO1 400.1324710 MHz
NUC1 1H
PL1 3.00 dB

F2 - Processing parameters
SI 16384
SF 400.1300177 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 9.800 ppm
F1 3921.27 Hz
F2P -0.200 ppm
F2 -80.03 Hz
PPMCM 0.50000 ppm/cm
HZCM 200.06500 Hz/cm



25




```
Current Data Parameters
NAME       Dec19-98-hayash
EXPNO                  50
PROCNO                  1

F2 - Acquisition Parameters
Date_              981219
Time                17.52
INSTRUM           dpx400
PROBHD    5 mm BBO 13C-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                   168
DS                     2
SWH            31847.133 Hz
FIDRES         0.485949 Hz
AQ             1.0289652 sec
RG                  8192
DW                15.700 usec
DE                 6.00 usec
TE                300.0 K
d11            0.03000000 sec
d12            0.00002000 sec
PL13              22.00 dB
D1             2.00000000 sec
CPDPRG2          waltz16
PCPD2             80.00 usec
SFO2          400.1316005 MHz
NUC2                 1H
PL2                3.00 dB
PL12              22.00 dB
P1                 9.30 usec
SFO1          100.6254358 MHz
NUC1                13C
PL1                3.00 dB

F2 - Processing parameters
SI                 32768
SF            100.6127718 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              200.000 ppm
F1             20122.55 Hz
F2P              -20.000 ppm
F2             -2012.26 Hz
PPMCM          11.00000 ppm/cm
```

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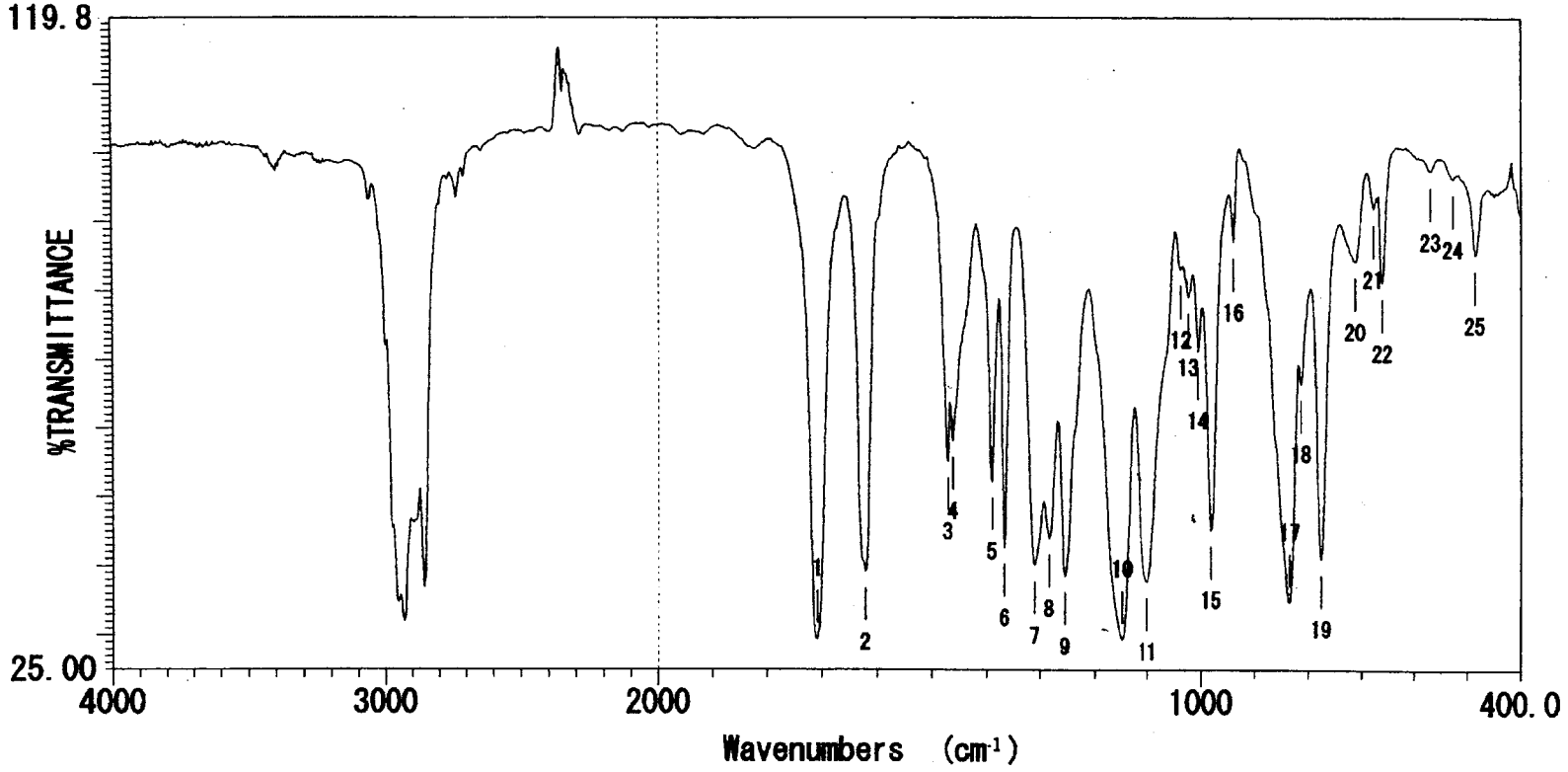
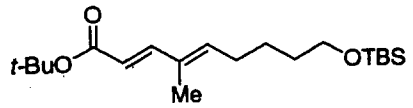
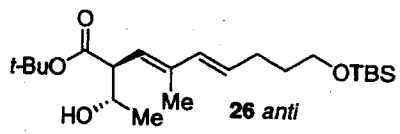


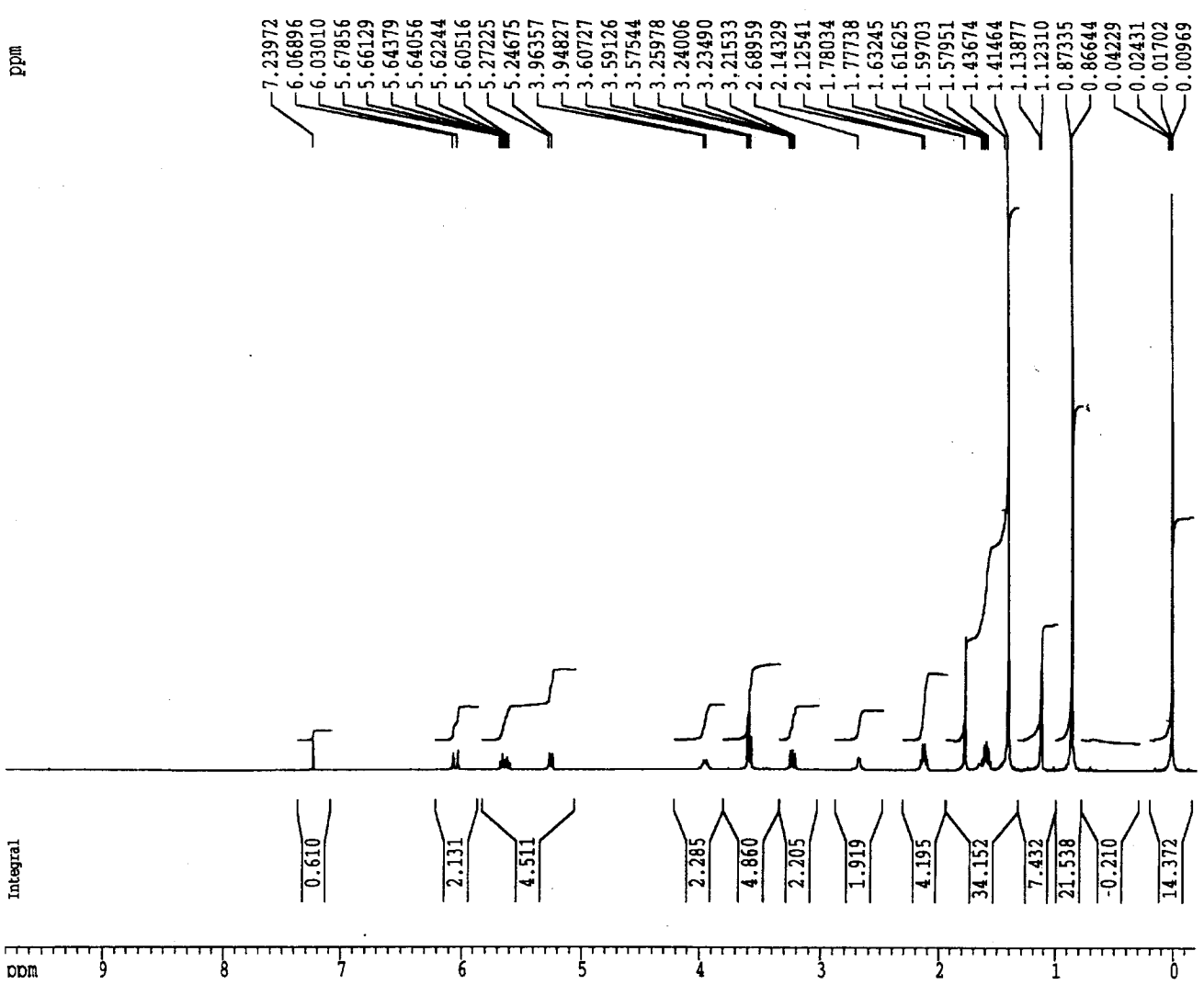
ファイル名 : JK-24
タイトル : epo24
測定日時 : 1999年12月17日 13時12分57秒
測定分解能 : 4 cm-1
スキャン回数 : 10 回
測定ゲイン : 1
コメン



25

ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)
01	1708.62	29.3926	10	1151.29	29.4336	19	775.244	41.1537
02	1621.84	39.1904	11	1101.15	37.8376	20	713.533	84.4424
03	1471.42	55.2521	12	1037.52	83.2983	21	678.820	92.0702
04	1461.78	58.2220	13	1024.02	79.2585	22	661.464	81.3574
05	1390.42	52.3376	14	1006.66	71.5024	23	570.826	97.4423
06	1367.28	42.7344	15	981.590	45.3483	24	528.400	96.3923
07	1311.36	40.1902	16	939.163	87.2417	25	485.974	85.4099
08	1284.36	44.0937	17	835.026	34.8424			
09	1255.43	38.6126	18	813.813	66.6714			



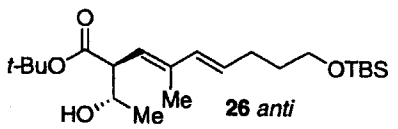



```
Current Data Parameters
NAME      Dec19-98-hayash
EXPNO              31
PROCNO             1

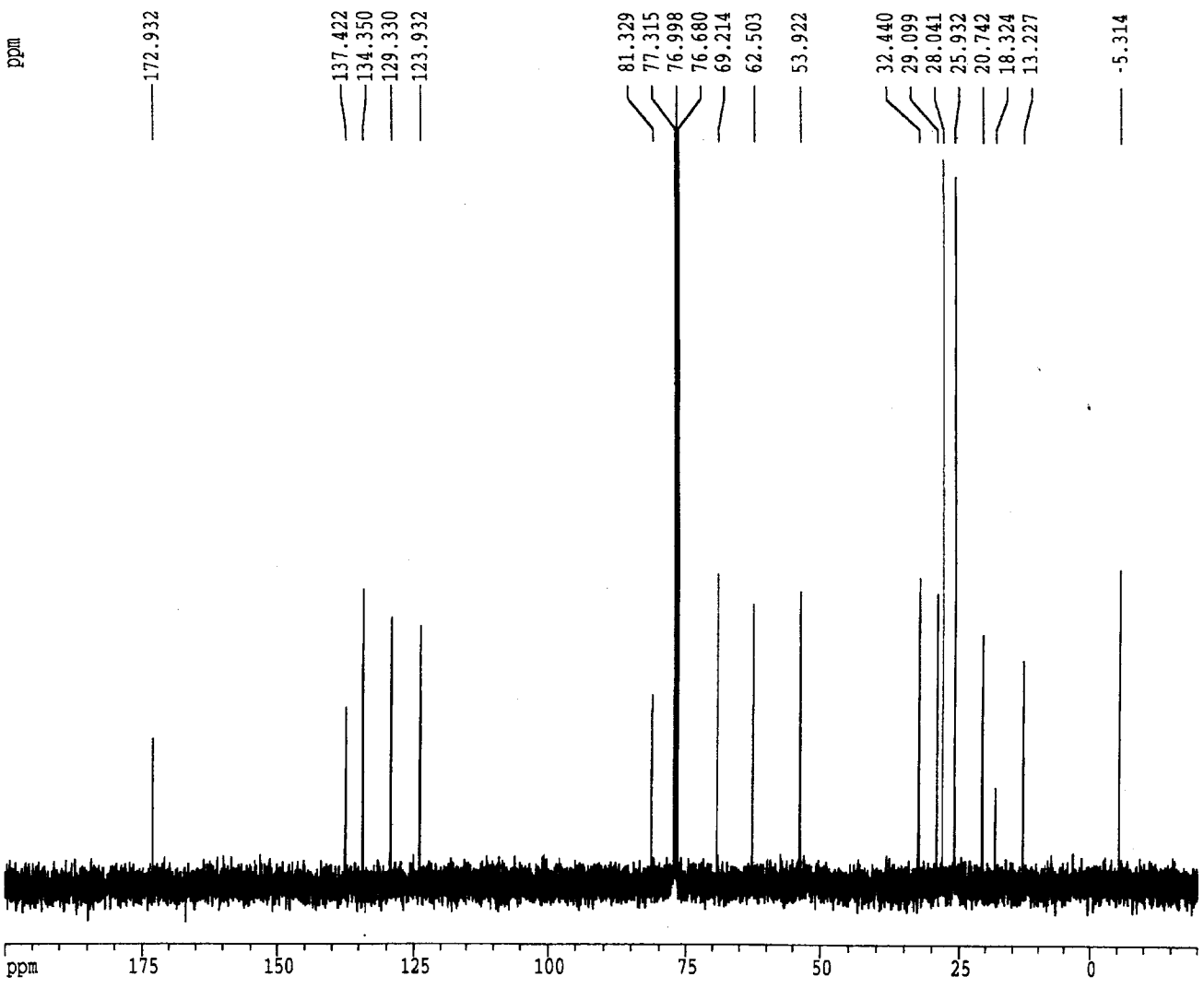
F2 - Acquisition Parameters
Date_           981219
Time            15.46
INSTRUM         dpx400
PROBHD    5 mm BBO 13C-
PULPROG         zg30
TD              32768
SOLVENT         CDCl3
NS              8
DS              0
SWH          8223.685 Hz
FIDRES       0.250967 Hz
AQ           1.9923444 sec
RG              114
DW           60.800 usec
DE           6.00 usec
TE           300.0 K
D1           1.00000000 sec
P1           8.30 usec
SFO1         400.1324710 MHz
NUC1         1H
PL1          3.00 dB

F2 - Processing parameters
SI              16384
SF         400.1300177 MHz
WDW             EM
SSB             0
LB           0.30 Hz
GB              0
PC           1.00

1D NMR plot parameters
CX           20.00 cm
F1P          9.800 ppm
F1           3921.27 Hz
F2P          -0.200 ppm
F2           -80.03 Hz
PPMCM        0.50000 ppm/cm
HZCM         200.06500 Hz/cm
```



26 *anti*



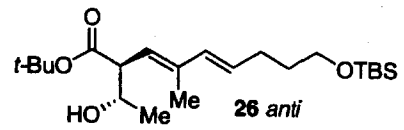

```
Current Data Parameters
NAME      Dec19-98-hayash
EXPNO               32
PROCNO               1

F2 - Acquisition Parameters
Date_           981219
Time             15.48
INSTRUM          dpx400
PROBHD    5 mm BBO 13C-
PULPROG          zgpg30
TD               65536
SOLVENT          CDCl3
NS                 117
DS                   2
SWH          31847.133 Hz
FIDRES         0.485949 Hz
AQ           1.0289652 sec
RG               16384
DW              15.700 usec
DE               6.00 usec
TE              300.0 K
d11          0.03000000 sec
d12          0.00002000 sec
PL13            22.00 dB
D1           2.00000000 sec
CPDPRG2        waltz16
PCPD2           80.00 usec
SFO2        400.1316005 MHz
NUC2               1H
PL2              3.00 dB
PL12            22.00 dB
P1               9.30 usec
SFO1        100.6254358 MHz
NUC1               13C
PL1              3.00 dB

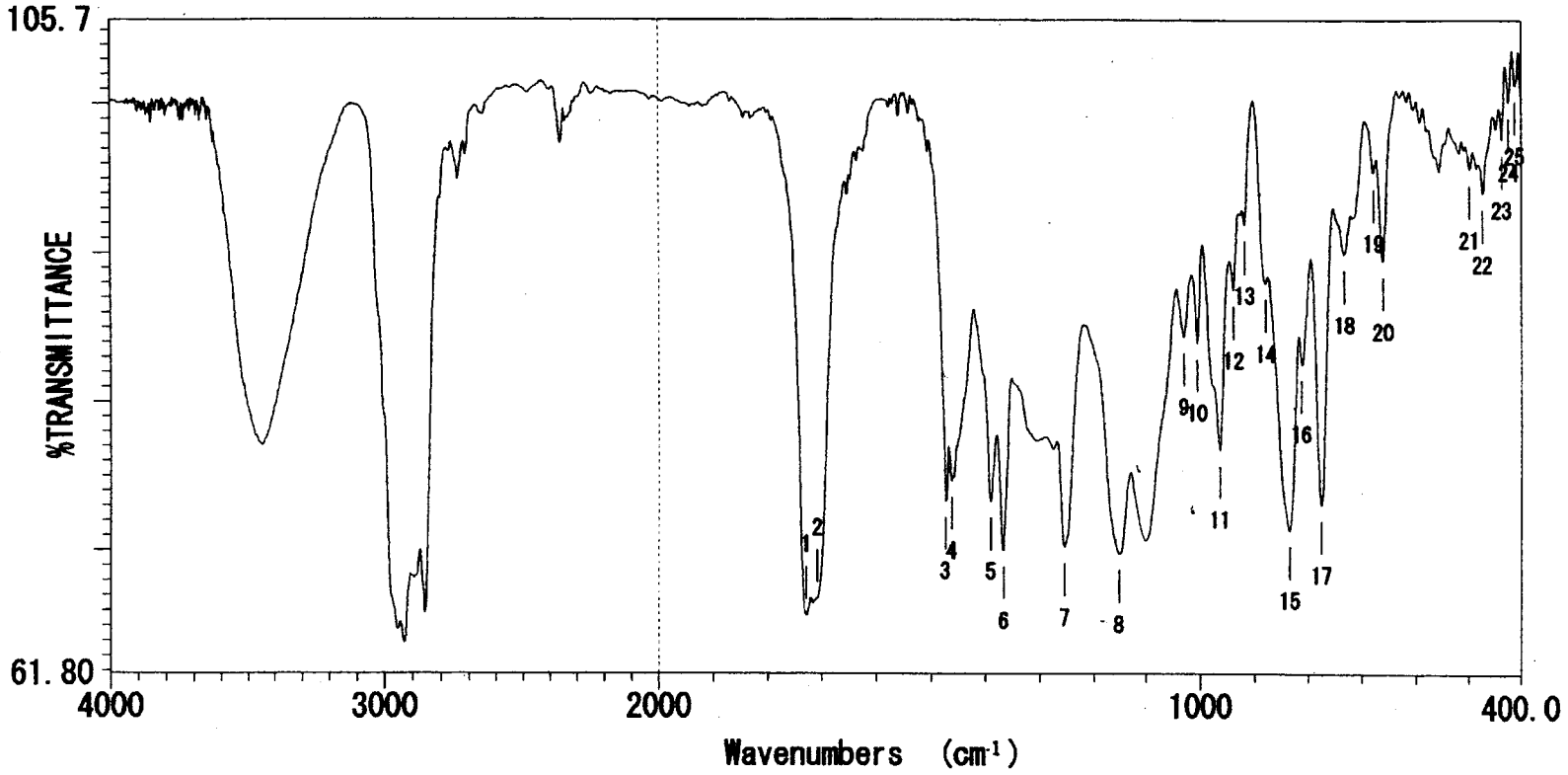
F2 - Processing parameters
SI                32768
SF          100.6127727 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40

1D NMR plot parameters
CX              20.00 cm
F1P            200.000 ppm
F1           20122.55 Hz
F2P           -20.000 ppm
F2           -2012.26 Hz
PPMCM         11.00000 ppm/cm
HZCM          1106.74048 Hz/cm
```

HORIBA FT-IR for Windows(TM) Ver.3.12
FTIR system for Windows

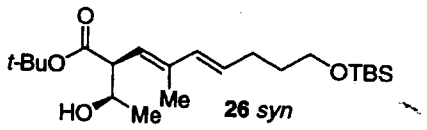


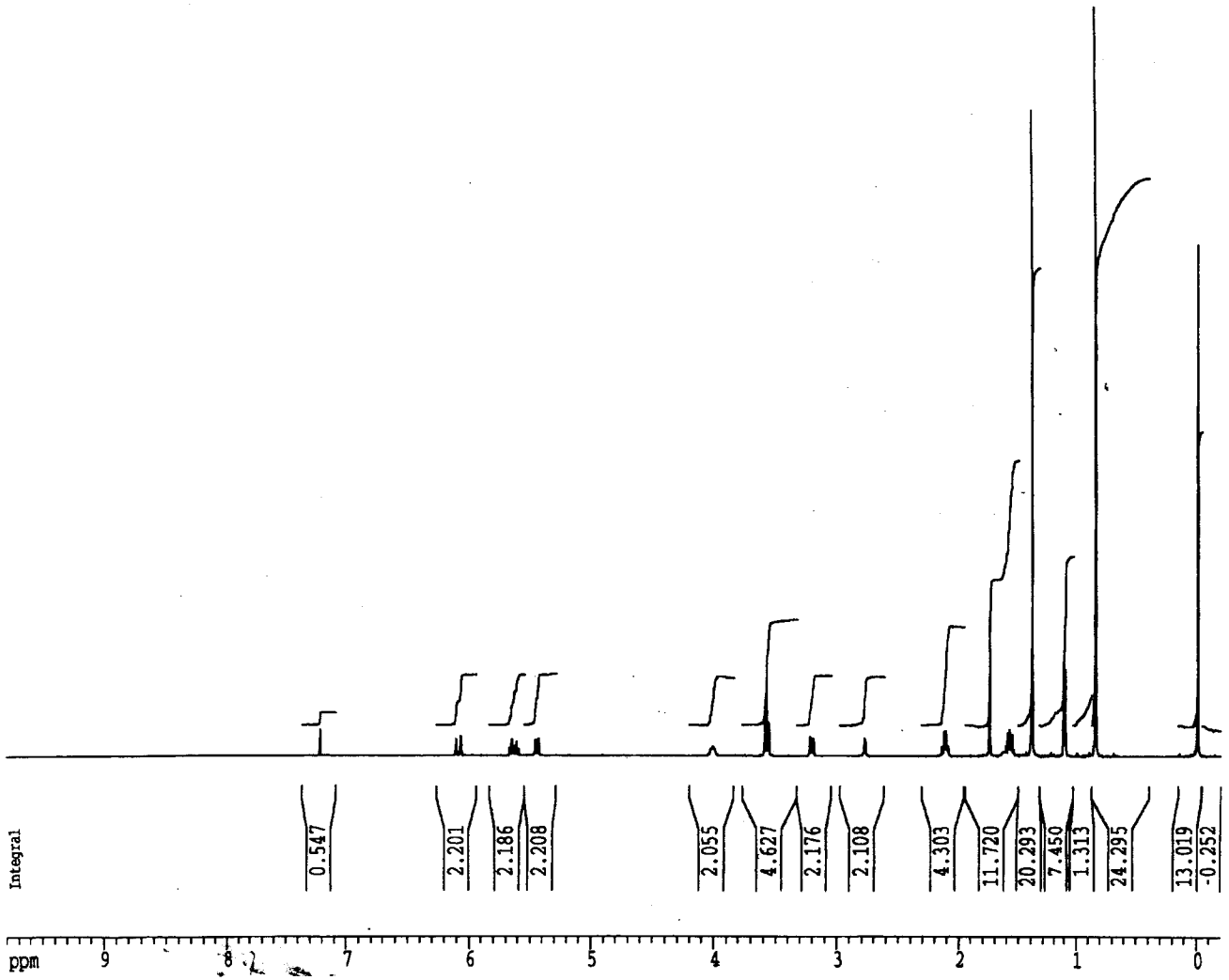
26 *anti*



ファイル名	JK-25shi
タイトル	epo-25-2
測定日時	1999年12月22日 12時04分03秒
測定分解能	4 cm-1
スキャン回数	10 回
測定ゲイン	1
コメント	

ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)
01	1729.83	65.6536	10	1006.66	84.0651	19	678.820	95.4070
02	1708.62	66.7911	11	964.233	76.8333	20	661.464	89.5212
03	1473.35	73.3451	12	939.163	87.5620	21	499.473	95.6242
04	1461.78	74.7087	13	917.950	91.9069	22	474.403	93.9964
05	1390.42	73.3003	14	879.381	88.0381	23	437.762	97.6059
06	1367.28	70.0390	15	835.026	71.4059	24	424.263	100.133
07	1255.43	70.2372	16	813.813	82.6160	25	412.692	101.213
08	1155.15	69.7815	17	775.244	73.0952			
09	1031.73	84.4622	18	732.817	89.9811			



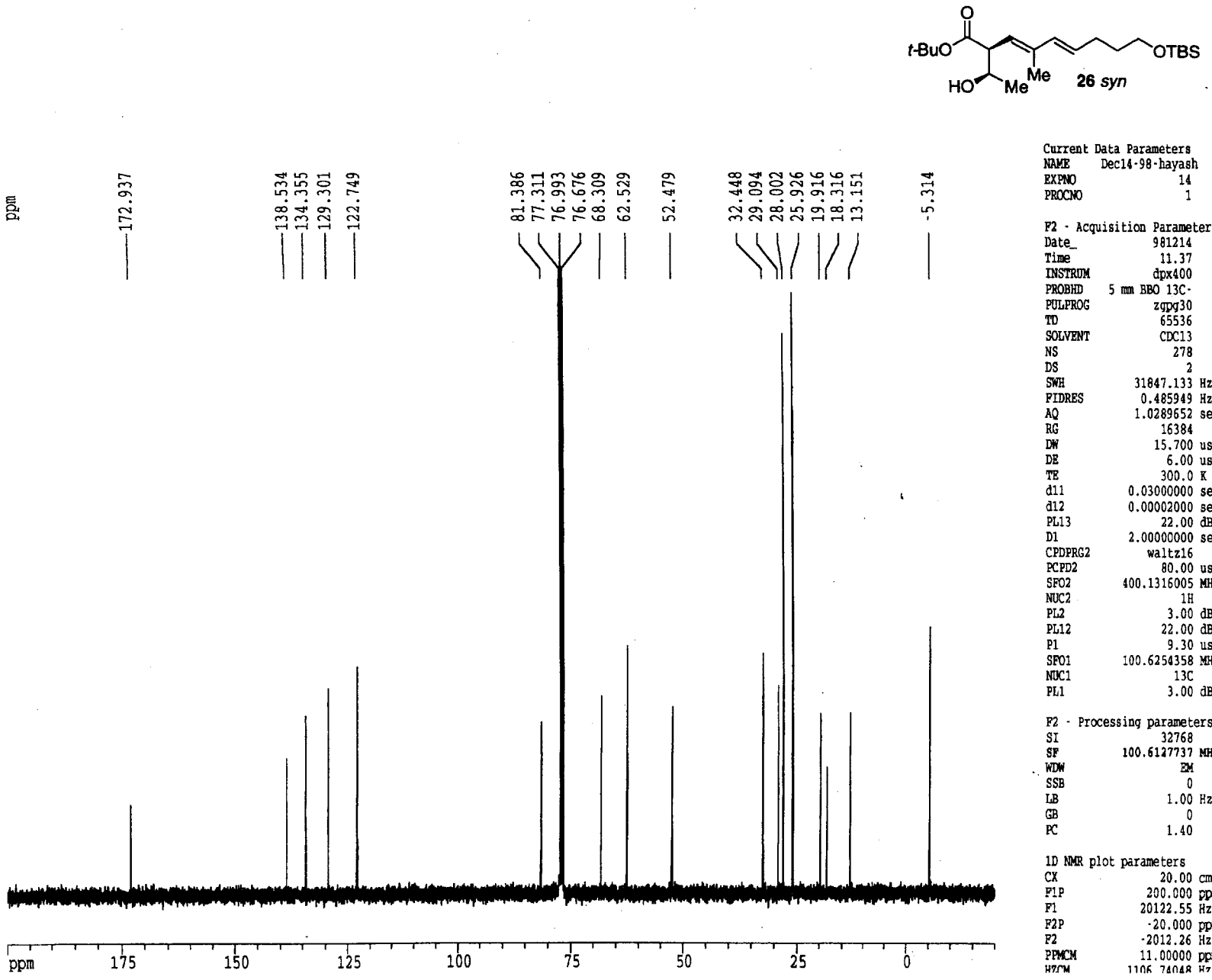



```
Current Data Parameters
NAME      Dec12-98-hayash
EXPNO                  52
PROCNO                  1

F2 - Acquisition Parameters
Date_              981212
Time                17.41
INSTRUM            dpx400
PROBHD    5 mm BBO 13C-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9923444 sec
RG                   101.6
DW                  60.800 usec
DE                   6.00 usec
TE                  300.0 K
D1               1.00000000 sec
P1                   8.30 usec
SFO1          400.1324710 MHz
NUC1                   1H
PL1                  3.00 dB

F2 - Processing parameters
SI                   16384
SF            400.1300254 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.800 ppm
F1                3921.27 Hz
F2P                -0.200 ppm
F2                 -80.03 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06502 Hz/cm
```



Current Data Parameters

NAME	Dec14-98-hayash
EXPNO	14
PROCNO	1

F2 - Acquisition Parameters

Date_	981214
Time	11.37
INSTRUM	dpx400
PROBHD	5 mm BBO 13C-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	278
DS	2
SWH	31847.133 Hz
FIDRES	0.485949 Hz
AQ	1.0289652 sec
RG	16384
DW	15.700 usec
DE	6.00 usec
TE	300.0 K
d11	0.03000000 sec
d12	0.00002000 sec
PL13	22.00 dB
D1	2.00000000 sec
CPDPRG2	waltz16
PCPD2	80.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	3.00 dB
PL12	22.00 dB
P1	9.30 usec
SFO1	100.6254358 MHz
NUC1	13C
PL1	3.00 dB

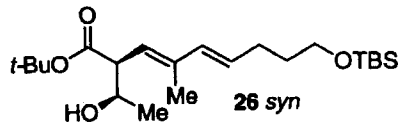
F2 - Processing parameters

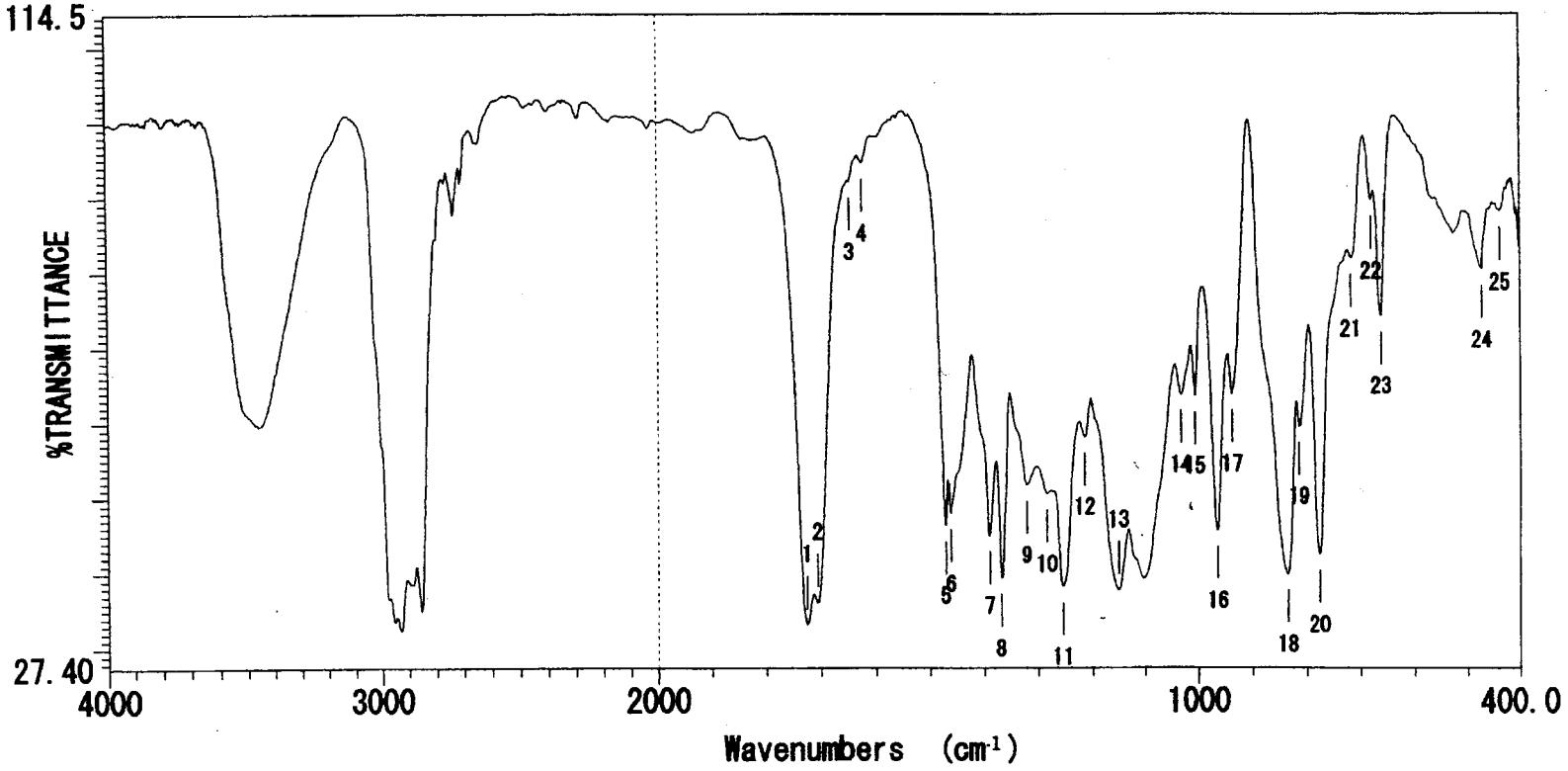
SI	32768
SF	100.6127737 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	200.000 ppm
F1	20122.55 Hz
F2P	-20.000 ppm
F2	-2012.26 Hz
PPMCM	11.00000 ppm/cm
HZCM	1106.74048 Hz/cm

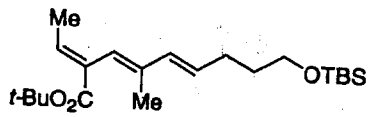
HORIBA FT-IR for Windows(TM) Ver.3.12
FTIR system for Windows





ファイル名 : JK-25ue
タイトル : epo-25-1
測定日時 : 1999年12月22日 11時57分20秒
測定分解能 : 4 cm-1
スキャン回数 : 10 回
測定ゲイン : 1
コメント :

ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)	ピーク番号	波数(cm-1)	透過率(%)
01	1725.98	33.1743	10	1284.36	50.6306	19	813.813	59.6396
02	1706.69	36.0985	11	1255.43	38.2386	20	775.244	42.5655
03	1646.91	92.1165	12	1214.93	58.2222	21	717.390	82.0355
04	1623.77	94.6352	13	1153.22	37.7998	22	678.820	89.6724
05	1471.42	46.4001	14	1033.66	63.9048	23	661.464	74.4175
06	1461.78	47.9296	15	1006.66	63.7343	24	472.474	80.6109
07	1390.42	45.0518	16	964.233	45.7176	25	437.762	88.1367
08	1369.21	39.4084	17	937.235	63.9416			
09	1321.00	51.8229	18	835.026	39.9243			



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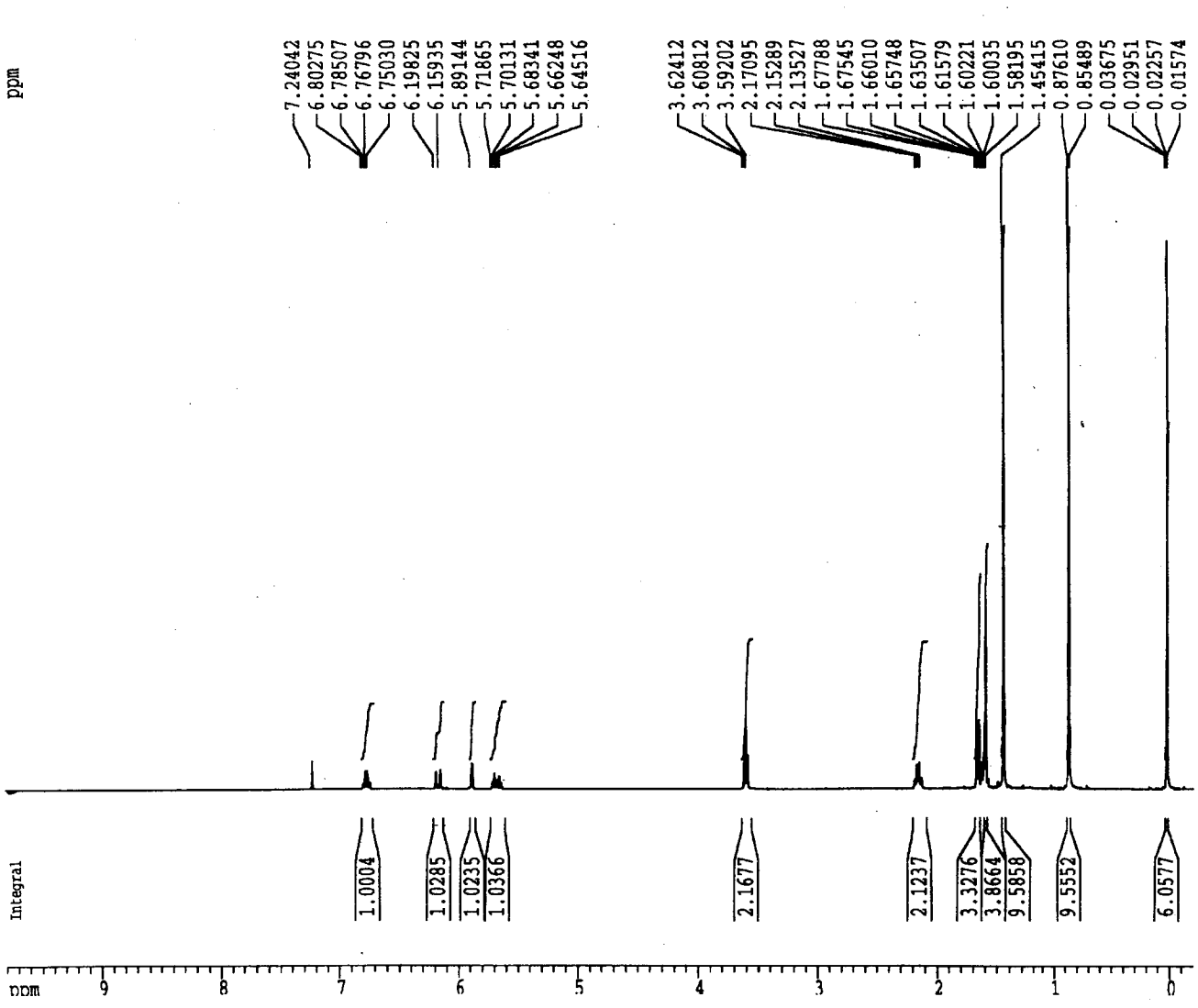

Current Data Parameters
NAME Oct27-99-hayash
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 991027
Time 9.36
INSTRUM dpx400
PROBHD 5 mm BBO 13C-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 143.7
DW 60.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 8.30 usec
SFO1 400.1324710 MHz
NUC1 1H
PL1 3.00 dB

F2 - Processing parameters
SI 16384
SF 400.1300172 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 9.800 ppm
F1 3921.27 Hz
F2P -0.200 ppm
F2 -80.03 Hz
PPMCM 0.50000 ppm/cm
HZCM 200.06500 Hz/cm