Supporting Information for

Studies in Marine Polypropionate Synthesis: Total Synthesis of (-)-Baconipyrone C

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General Experimental

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded using internal deuterium lock for the indicated reference at ambient temperatures on the following instruments: Bruker DRX 500 Fourier Transform instrument (500 MHz), Bruker AM 400 Fourier Transform instrument (400 MHz), Bruker DPX 400 Fourier Transform instrument (400 MHz), and Bruker DPX 250 Fourier Transform instrument (250 MHz). Data are presented as follows: chemical shift (in ppm on the δ scale relative to $\delta_{TMS} = 0$), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, spt = septet, m = multiplet, br = broad), coupling constant and assignment. Assignments were made either on the basis of unambiguous chemical shift or coupling pattern, or by comparison to fully interpreted spectra for enantiomeric, identical or related compounds. ^{13}C NMR spectra were recorded using internal deuterium lock for the indicated reference at ambient probe temperatures on the above instruments, and are reported in ppm on the δ scale. An internal reference of δ_C 77.0 was used for $CDCl_3$.

Infra-red (IR) spectra were recorded on a Perkin-Elmer 1620 (FT-IR) spectrophotometer calibrated relative to polystyrene using 5 mm sodium chloride plates or a sodium chloride solution cell. Wavelengths of maximum absorbance (ν_{max}) are quoted in cm^{-1}; the abbreviations s, m, br, and w indicate strong, medium, broad and weak absorbances respectively.

High resolution mass spectra (HRMS) and low resolution mass spectra were recorded either by the SERC Mass Spectrometry Service at Swansea or by the Departmental Service at Cambridge using either chemical ionisation (CI), electron impact (EI) or fast atom bombardment (FAB). The parent ion is quoted, followed by significant fragments with relative intensities.

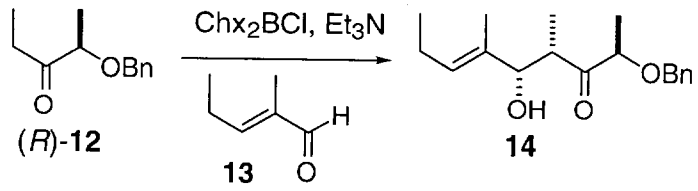
Optical rotations were measured on a Perkin Elmer 241 polarimeter at the sodium D line (589 nm) and are reported as follows: $[\alpha]_D^{20}$ concentration (c in g/100 ml) and solvent (all the rotations were measured at a temperature of 20°C).

Analytical thin layer chromatography (t.l.c) was carried out on Merck Kieselgel 60 F_{254} plates with visualisation by ultraviolet, anisaldehyde, potassium permanganate, and/or phosphomolybdic acid dips. Flash column chromatography was carried out on Merck Kieselgel 60 (230-400 mesh) under a positive pressure by means of hand bellows or by means of compressed air line (the use of the term in this work also implies removal of the solvent in *vacuo* afterwards).

Reagents and solvents were purified by standard means. Dichloromethane, hexane, acetonitrile, toluene, and methanol were distilled from calcium hydride and stored under an argon atmosphere; tetrahydrofuran and diethyl ether were distilled from sodium wire/benzophenone and subsequently stored under an argon atmosphere; carbon tetrachloride was distilled from calcium chloride and stored under an argon atmosphere. Triethylamine and diisopropylethylamine were distilled from and stored over calcium hydride; 3-pentanone was stored over 4Å molecular sieves after distillation from potassium carbonate; the achiral aldehydes used were distilled from calcium chloride immediately prior to use. Triphenylphosphine was recrystalised from distilled ethanol and subsequently stored under argon atmosphere. All other chemicals were used as received, except where otherwise quoted in the experimental text. Solvents used for extractions in work-up and flash column chromatography were distilled.

All experiments were performed under anhydrous conditions in an atmosphere of argon, except where stated, using oven-dried apparatus and employing standard techniques for handling air-sensitive materials.

Preparation of (2*R*,4*S*,5*S*,6*E*)-2-benzyloxy-4,6-dimethyl-5-hydroxynon-6-en-3-one, 14.

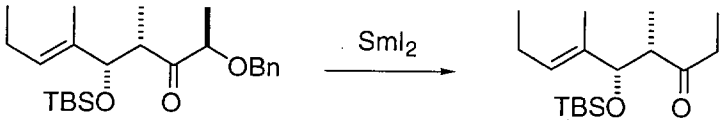


A solution of (*R*)-**12** (1.63 g, 8.47 mmol) in Et_2O (3 x 10 ml) was added *via* cannula to a stirred mixture of Chx_2BCl (2.39 ml, 11.03 mmol) and Et_3N (1.77 ml, 12.70 mmol) in Et_2O (40 ml) at –78°C. The reaction mixture was stirred at –78°C for 1 hour and then at 0°C for 15 minutes to allow complete enolisation. The reaction mixture was then re-cooled to –78°C and freshly distilled (*E*)-2-methyl-2-pentenal **13** (2.90 ml, 25.41 mmol) was added, after which stirring was continued for a further hour at –78°C before being transferred to the freezer (–26°C) for 16 hours. The reaction was quenched at 0°C by the addition of pH7 buffer (35 ml). The aqueous layer was extracted with Et_2O (3 x 250 ml), and the combined organics concentrated in *vacuo*. MeOH (35 ml) and water (35 ml) were added and the mixture was cooled to 0°C before adding H_2O_2 (35 ml, 30% aq.).

The reaction mixture was further stirred at 0°C for one hour before being quenched by addition of water (60 ml) and extracted with CH_2Cl_2 (3 x 300 ml). The combined organics were dried ($MgSO_4$) and concentrated *in vacuo*. Flash column chromatography (50% Et_2O/hexane) afforded **14** as a colourless oil (2.46 g, 100%).

R_f (50% Et_2O/hexane) = 0.34; $[\alpha]_D^{20}$ = +37.3 (*c* = 2.8, $CHCl_3$); **IR** (FT, liquid film) 3600-3200 (br, OH), 1710 (C=O) cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 7.37-7.25 (5H, m, $C_6\mathbf{H}_5$), 5.46 (1H, t, *J* = 7.2 Hz, C**H**=C), 4.55 (1H, d, *J* = 11.7 Hz, $OC\mathbf{H}_AH_BPh$), 4.51 (1H, d, *J* = 11.7 Hz, $OCH_A\mathbf{H}_BPh$), 4.27 (1H, br, C**H**OH), 4.03 (1H, q, *J* = 6.8 Hz, C**H**(CH_3)OBn), 3.17 (1H, qd, *J* = 7.1 & 4.4 Hz, C**H**(CH_3)CHOH), 2.68 (1H, d, *J* = 2.4 Hz, O**H**), 2.01 (2H, qd, *J* = 7.5 & 7.2 Hz, $C\mathbf{H}_2CH_3$), 1.51 (3H, s, $CC\mathbf{H}_3$), 1.35 (3H, d, *J* = 6.8 Hz, $CH(C\mathbf{H}_3)$OBn), 1.04 (3H, d, *J* = 7.1 Hz, $CH(C\mathbf{H}_3)$CHOH), 0.94 (3H, t, *J* = 7.5 Hz, $CH_2C\mathbf{H}_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 216.5, 137.9, 133.2, 128.9, 128.8, 128.3, 128.2, 79.9, 75.6, 72.2, 44.2, 21.2, 17.3, 14.4, 13.4, 11.1; **HRMS** (CI) $[M+NH_4]^+$ found 308.2226, $C_{18}H_{30}NO_3$ requires 308.2226; **m/z** 308 ($[M+NH_4]^+$ 2), 273 (2), 210 (63), 116 (100%).

Preparation of (4*S*,5*S*,6*E*)-5-*tert*-butyldimethylsilyloxy-4,6-dimethyl-non-6-en-3-one, 15.



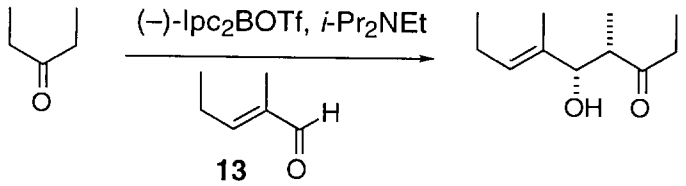
15

SmI_2 (0.48 M solution in THF, ~ 20 ml, ~9.6 mmol) was added to a stirred solution of α-benzyloxy ketone (892 mg, 2.20 mmol) in THF/MeOH (2:1, 45 ml) at 0°C where the addition was stopped until a deep green colour was remained in the reaction mixture. The reaction was quenched at 0°C with the addition of K_2CO_3 (sat. aq., 120 ml) and allowed to warm up to room temperature. The aqueous layer was extracted with CH_2Cl_2 (3 x 300 ml), the combined organics dried ($MgSO_4$) and concentrated in *vacuo*. Flash column chromatography (5% Et_2O/hexane) afforded **15** as a colourless oil (621 mg, 94%).

R_f (5% Et_2O/hexane) = 0.33; $[\alpha]_D^{20}$ = +14.1 (*c* = 0.6, $CHCl_3$); **IR** (FT, liquid film) 1716 (C=O) cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 5.23 (1H, t, *J* = 7.2 Hz, C**H**=C), 4.01 (1H, d, *J* = 8.3 Hz, C**H**OTBS), 2.74 (1H, dq, *J* = 8.2 & 6.8 Hz, C**H**CH_3), 2.34 (2H, dq, *J* = 14.6 & 7.3 Hz, $C\mathbf{H}_A\mathbf{H}_BC$=O), 1.93 (2H, qd, *J* = 7.5 & 7.2 Hz, $C\mathbf{H}_2C$=C), 1.54 (3H, s, C=$CC\mathbf{H}_3$), 1.06 (3H, d, *J* = 6.8 Hz, $CHC\mathbf{H}_3$), 0.94 (3H, t, *J* = 7.2 Hz, $C\mathbf{H}_3CH_2$), 0.88 (3H, t, *J* = 7.5 Hz, $C\mathbf{H}_3CH_2$), 0.85 (9H, s, $C(C\mathbf{H}_3)_3$), 0.00 (3H, s, $SiC\mathbf{H}_3$), -0.06 (3H, s,

$SiCH_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 214.3, 135.1, 130.0, 80.6, 51.6, 36.4, 26.2, 21.1, 18.5, 14.1, 13.9, 11.5, 7.7, -4.2, -4.8. **HRMS** (CI) $[M+H]^+$ found 299.2408, $C_{17}H_{35}SiO_2$ requires 299.2406; **m/z** 299 ($[M+H]^+$ 12), 215 (21), 184 (39), 167 (100), 132 (16%).

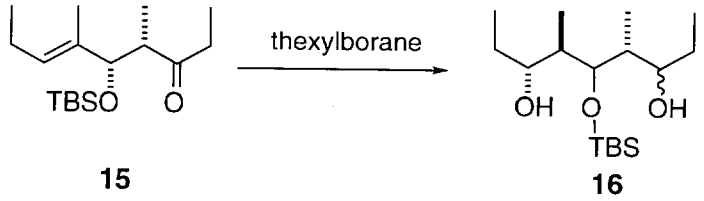
Preparation of (4*S*,5*S*,6*E*)-4,6-dimethyl-5-hydroxynon-6-en-3-one.



A solution of (–)-Ipc_2BOTf (25 mmol) in hexane was added to CH_2Cl_2 (100 ml) at –78°C, followed by *i*-Pr_2NEt (8.9 ml, 51 mmol) and 3-pentanone (1.73 ml, 17 mmol). The reaction was stirred at –78°C for 4 hours before the addition of freshly distilled (*E*)-2-methyl-2-pentenal **13** (9.75 ml, 85 ml), then transferred to the freezer (–26°C) overnight before being poured into pH7 buffer (250 ml) and extracted with Et_2O (3 x 150 ml). The extracts were concentrated in vacuo, resuspended in MeOH (75 ml) and pH7 buffer (10 ml), then cooled to 0°C. H_2O_2 (30 ml, 30% aq.) was added dropwise and the reaction stirred at room temperature for 4 hours before being quenched with water (150 ml) and extracted with CH_2Cl_2 (3 x 150 ml). The extracts were washed with sat. aq. $NaHCO_3$ (150 ml) and brine (150 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Flash column chromatography (10% Et_2O/CH_2Cl_2) followed by HPLC (10% EtOAc/hexane) afforded the title compound as a colourless oil (1.80 g, 57%). ^{1}H NMR analysis showed the presence of a single diastereomer, whilst Mosher ester formation indicated 85% ee.

R_f (30% EtOAc/hexane) = 0.35; **HPLC R_t** (35% EtOAc/hexane) = 13.5 min; $[\alpha]_D^{20}$ = –9.1 (*c* = 1.0, $CHCl_3$); **IR** (FT, liquid film) 3600-3100 (br, OH), 1705 (C=O) cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 5.45 (1H, tdq, *J* = 7.2, 1.4 & 1.4 Hz, C**H**=C), 4.26 (1H, br dd, *J* = 3.6 & 3.3 Hz, C**H**OH), 2.74 (1H, qd, *J* = 7.1 & 4.7 Hz, C**H**CH_3), 2.52 (1H, dq, *J* = 18.0 & 7.3 Hz, CH_AH_BC=O), 2.46 (1H, dq, *J* = 18.0 & 7.3 Hz, CH_A**H**$_B$C=O), 2.01 (2H, dq, *J* = 7.4 & 7.4 Hz, C**H**$_2$C=C), 1.57 (3H, s, C=CC**H**$_3$), 1.06 (3H, d, *J* = 7.1 Hz, CHC**H**$_3$), 1.03 (3H, t, *J* = 7.3 Hz, CH_2C**H**$_3$), 0.95 (3H, t, *J* = 7.5 Hz, CH_2C**H**$_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 215.9, 132.9, 128.4, 75.8, 48.3, 35.1, 20.8, 14.0, 12.9, 10.6, 7.5; **HRMS** (CI, NH_3) $[M]^+$ found 184.1463, $C_{11}H_{20}O_2$ requires 184.1463; **m/z** 184 ($[M]^+$ 9), 167 (100), 116 (5), 98 (5%).

Preparation of (3*R*,4*R*,6*R*)-5-*tert*-butyldimethylsilyloxy-4,6-dimethyl-nonan-3,7-diol, 16.

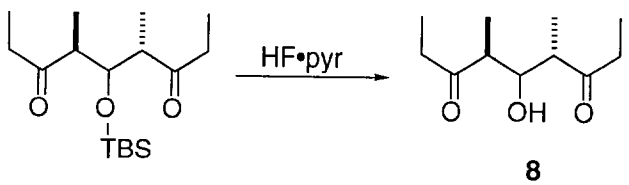


15 **16**

Thexylborane (0.50 M solution in THF, 3.45 ml, 1.73 mmol) was added dropwise to a stirred solution of **15** (17.2 mg, 0.058 mmol) in THF (1 ml) at 40°C. The reaction was further stirred at 40°C for 16 hours. The mixture was cooled to 0°C and H_2O_2 (1 ml, 30 % aq.), NaOH (1 ml, 10 % aq.) and THF (10 ml) were added, allowed to warm up to room temperature and further stirred for 1 hour. The reaction was quenched by addition of water (10 ml) and the aqueous layer extracted with EtOAc (3 x 25 ml). The combined organics were dried ($MgSO_4$) and concentrated in *vacuo*. Flash column chromatography (20% Et_2O/CH_2Cl_2) afforded **16** as a colourless syrupy oil (10 mg, 59 %).

$\mathbf{R_f}$ (20% Et_2O/CH_2Cl_2) = 0.40; $[\alpha]_D^{20}$ = +5.8 (*c* = 3.5, $CHCl_3$); **IR** (FT, liquid film) 3600-3200 (br, OH) cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 3.85 (1H, dd, *J* = 4.9 & 3.2 Hz, C**H**OTBS), 3.67 (1H, td, *J* = 4.8 & 2.2 Hz, C**H**OH), 3.41 (1H, td, *J* = 8.8 & 2.7 Hz, C**H**OH), 1.99 (1H, dqd, *J* = 8.9, 7.0 & 3.1 Hz, C**H**CH_3), 1.73 (1H, qdd, *J* = 7.1, 4.9 & 2.3 Hz, C**H**CH_3), 1.63 (1H, dqd, *J* = 10.2, 7.4 & 2.7 Hz, $CH_ACH_BCH_3$), 1.48-1.27 (3H, m, CH_AC**H**$_B$$CH_3$, C**H**$_2$$CH_3$), 0.93 (3H, t, *J* = 7.4 Hz, CH_2C**H**$_3$), 0.90 (3H, t, *J* = 7.4 Hz, CH_2C**H**$_3$), 0.89 (9H, s, C(C**H**$_3$)$_3$), 0.87 (3H, d, *J* = 7.0 Hz, CHC**H**$_3$), 0.83 (3H, d, *J* = 7.0 Hz, CHC**H**$_3$), 0.08 (3H, s, SiC**H**$_3$), 0.05 (3H, s, SiC**H**$_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 78.7, 76.2, 73.2, 42.1, 41.1, 27.8, 27.6, 26.3, 18.5, 16.7, 11.3, 10.0, 9.9, -3.9, -4.2. **HRMS** (CI) $[M+H]^+$ found 319.2672, $C_{17}H_{39}SiO_3$ requires 319.2668; **m/z** 319 ($[M+H]^+$ 31), 299 (44), 261 (67), 259 (71), 201 (80), 173 (52), 167 (100), 144 (63), 132 (84), 104 (62%).

Preparation of (4*S*,6*S*)-4,6-dimethyl-5-hydroxynonan-3,7-dione, 8.



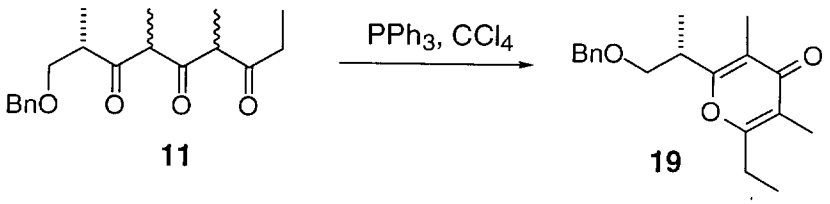
8

HF•pyr (~2 ml) was added cautiously to a stirred solution of TBS ether (77 mg, 0.24 mmol) in THF (2 ml) at 0°C. The reaction mixture was further stirred at 0°C for 1 hour before being quenched with $NaHCO_3$ (sat. aq.) until no further effervescence and neutral

pH was obtained. The reaction was extracted with EtOAc (3 x 30 ml), dried ($MgSO_4$) and concentrated in *vacuo*. Flash column chromatography (30% EtOAc/hexane) afforded **8** as a colourless oil (47 mg, 97%).

$\mathbf{R_f}$(30% EtOAc/hexane) = 0.18; $[\alpha]_D^{20}$ = –16.4 (*c* = 1.1, $CHCl_3$); **IR** (FT, liquid film) 3600-3200 (br, OH), 1708 (C=O) cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 4.02 (1H, ddd, *J* = 8.1, 4.5 & 3.8 Hz, C**H**OH), 3.22 (1H, d, *J* = 4.6, O**H**), 2.71-2.60 (2H, m, C**H**CH_3, C**H**CH_3), 2.60-2.43 (4H, m, C$\mathbf{H_2}CH_3$, C$\mathbf{H_2}CH_3$), 1.14 (3H, d, *J* = 7.2 Hz, CHC$\mathbf{H_3}$), 1.04 (3H, t, *J* = 7.3 Hz, $CH_2C\mathbf{H_3}$), 1.03 (3H, d, *J* = 7.1 Hz, CHC$\mathbf{H_3}$), 1.03 (3H, t, *J* = 7.2 Hz, $CH_2C\mathbf{H_3}$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 215.7, 215.6, 73.5, 47.5, 47.4, 36.3, 34.8, 13.9, 10.0, 7.6, 7.4. **HRMS** (CI) $[M+H]^+$ found 201.1487, $C_{11}H_{20}O_3$ requires 201.1490; **m/z** 201 ($[M+H]^+$ 12), 116 (51), 104 (100), 86 (18%).

Preparation of (*S*)-2-(1'-benzyloxyprop-2'-yl)-3,5-dimethyl-6-ethylpyran-4-one, 19.

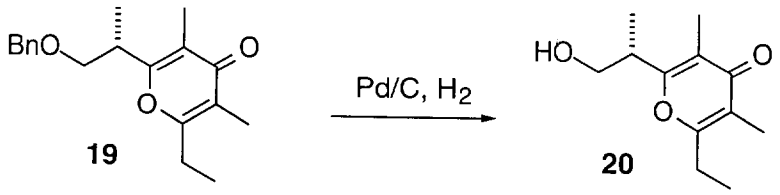


11 **19**

A solution of **11** (3.964 g, 12.5 mmol) in THF (5 ml + 10 ml) was added *via* cannula to a stirred solution of PPh_3 (8.19 g, 31.2 mmol) and CCl_4 (3.01 ml, 31.2 mmol) in THF (100 ml). The reaction mixture was stirred at room temperature for 3 days before being quenched by pouring into brine (200 ml), extracted with EtOAc (3 x 200 ml), dried ($MgSO_4$) and concentrated in *vacuo*. Flash column chromatography (20% Et_2O/CH_2Cl_2) gave **19** as a crystalline solid (3.333 g, 88%).

$\mathbf{R_f}$(20% Et_2O/CH_2Cl_2) = 0.27; $[\alpha]_D^{20}$ = +2.0 (*c* = 2.1, $CHCl_3$); **mp** 23-24 °C; **IR** (FT, liquid film) 1723 (C=O), 1659, 1608 cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 7.33-7.22 (5H, m, $C_6\mathbf{H_5}$), 4.52 (1H, d, *J* = 12.2 Hz, $C\mathbf{H_X}H_YPh$), 4.45 (1H, d, *J* = 12.2 Hz, $CH_X\mathbf{H_Y}Ph$), 3.66 (1H, dd, *J* = 9.1 & 8.1 Hz, $C\mathbf{H_A}H_BOBn$), 3.53 (1H, dd, *J* = 9.2 & 6.2 Hz, $CH_A\mathbf{H_B}OBn$), 3.33 (1H, dqd, *J* = 8.1, 7.0 & 6.2 Hz, C**H**CH_3), 2.57 (1H, dq, *J* = 15.0 & 7.6 Hz, $C\mathbf{H_\alpha}H_\beta CH_3$), 2.55 (1H, dq, *J* = 14.8 & 7.7 Hz, $CH_\alpha\mathbf{H_\beta}CH_3$), 1.99 (3H, s, $CC\mathbf{H_3}$), 1.95 (3H, s, $CC\mathbf{H_3}$), 1.19 (3H, d, *J* = 7.0 Hz, CHC$\mathbf{H_3}$), 1.16 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H_3}$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 179.9, 164.2, 163.8, 138.1, 128.3, 127.6, 127.4, 119.0, 117.9, 73.0, 72.3, 36.0, 24.7, 14.7, 11.2, 9.5; **HRMS** (CI, NH_3) $[M+H]^+$ found 301.1804, $C_{19}H_{25}O_3$ requires 301.1804; **m/z** 301 ($[M+H]^+$ 100), 108 (9), 52 (9%).

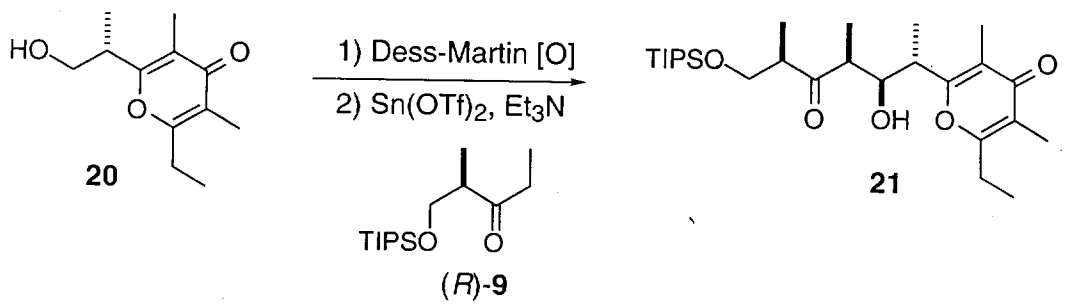
Preparation of (*R*)-3,5-dimethyl-6-ethyl-2-(1'-hydroxyprop-2'-yl)-pyran-4-one, 20.



Palladium on activated carbon (1.5 g, 10% Pd) was added to a stirred solution of **19** (4.221 g, 14.1 mmol) in ethanol (100 ml). The reaction flask was flashed thoroughly first with argon, then hydrogen and finally placed under a hydrogen atmosphere (by means of a hydrogen filled double balloon). The reaction mixture was stirred vigorously for 8 hours, filtered through a pad of silica and concentrated in *vacuo*. Flash column chromatography (100% EtOAc) gave **20** as a white crystalline solid (2.803 g, 95%).

$\mathbf{R_f}$(100% EtOAc) = 0.22; $[\alpha]_D^{20}$ = +37.9 (*c* = 1.7, $CHCl_3$); **mp** 84-85°C; **IR** (FT, liquid film) 3600-3200 (br, OH), 1655 (C=O), 1593 cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 3.82 (1H, dd, *J* = 10.3 & 8.2 Hz, CH_AH_BOH), 3.69 (1H, dd, *J* = 10.7 & 6.0 Hz, CH_AH_BOH), 3.21 (1H, dqd, *J* = 8.1, 7.0 & 6.0 Hz, $CHCH_3$), 3.10 (1H, br s, OH), 2.58 (1H, dq, *J* = 15.0 & 7.5 Hz, $CH_\alpha H_\beta CH_3$), 2.57 (1H, dq, *J* = 15.2 & 7.6 Hz, $CH_\alpha H_\beta CH_3$), 1.93 (3H, s, CCH_3), 1.86 (3H, s, CCH_3), 1.19 (3H, t, *J* = 7.6 Hz, CH_2CH_3), 1.18 (3H, d, *J* = 7.0 Hz, $CHCH_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 179.9, 164.4, 164.2, 119.3, 117.8, 65.3, 38.5, 24.8, 14.2, 11.1, 9.5, 9.4; **HRMS** (EI) $[M]^+$ found 210.1256, $C_{12}H_{18}O_3$ requires 210.1256; **m/z** 210 ($[M]^+$, 48), 195 (52), 193 (100), 179 (47), 151 (21), 83 (21), 67 (22), 57 (53%); Analysis found C, 68.26%, H, 8.54%; $C_{12}H_{18}O_3$ requires C, 68.55%, H, 8.63%.

Preparation of (2'*S*,3'*R*,4'*S*,6'*R*)-3,5-dimethyl-6-ethyl-2-(4',6'-dimethyl-3'-hydroxy-7'-triisopropylsilyloxy-5'-oxo-hept-2'-yl)-pyran-4-one, 21.



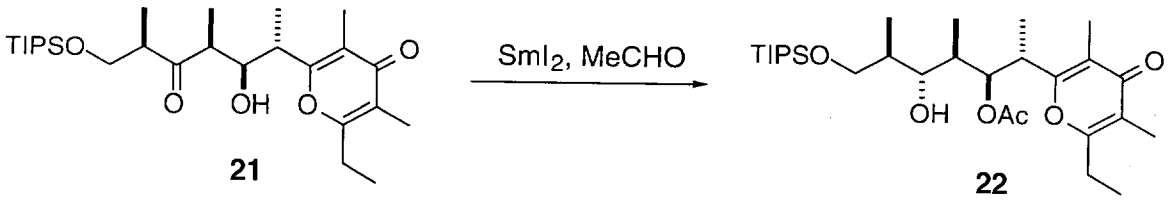
A solution of **20** (1.068 g, 5.08 mmol) in CH_2Cl_2 (5 ml + 10 ml) was added *via* cannula to a stirred suspension of Dess-Martin periodinane (4.312 g, 10.2 mmol) in CH_2Cl_2

(40 ml) at room temperature. The reaction mixture was stirred for 1.5 hour at room temperature before being quenched with a mixture of $Na_2S_2O_3$ and $NaHCO_3$ solution (1:1 sat. aq., 150 ml) and the cloudy two phase mixture stirred until it became clear (15 min). CH_2Cl_2 was removed in *vacuo* and the remaining residue was extracted with Et_2O (3 x 200 ml), the combined organics dried ($MgSO_4$) and concentrated in *vacuo*. The crude **10** was directly used in the subsequent aldol reaction.

Et_3N (3.19 ml, 22.8 mmol) was added to a stirred suspension of $Sn(OTf)_2$ (8.263 g, 19.8 mmol) in CH_2Cl_2 (100 ml) at room temperature and the resulting $Et_3N/Sn(OTf)_2$ mix was then immediately cooled to –78°C. A solution of **9** (4.152 g, 15.3 mmol) in CH_2Cl_2 (5 ml + 10 ml) was added *via* cannula and the reaction mixture was stirred at –78°C for 3 hours before the addition of a solution of freshly prepared **10** (ex. 1.068 mg, **20**, ~5.1 mmol) in CH_2Cl_2 (5 ml + 10 ml). After a further 1.5 hour at –78°C, the reaction mixture was quenched with pH7 buffer (150 ml) and extracted with EtOAc (5 x 150 ml). The combined organics were dried ($MgSO_4$) and concentrated in *vacuo*. Flash column chromatography (50% EtOAc/hexane) afforded two colourless oils, unreacted **9** and aldol products (1.965 g, 2 steps from 20, 80%). Further flash column chromatography purifications (50% EtOAc/hexane) afforded desired *syn-syn* aldol product **21** as a white crystalline solid (1.814 g, 74%), and a mixture of *syn-anti* and *anti-anti* aldol products as a colourless oil (151 mg, 6%).

R_f (50% EtOAc/hexane) = 0.29; $[\alpha]_D^{20}$ = –78.3 (*c* = 1.4, $CHCl_3$); **mp** 77-78°C; **IR** (FT, liquid film) 3600-3200 (br, OH), 1698 (C=O), 1654, 1592 cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 4.29 (1H, ddd, *J* = 10.0, 2.1 & 2.0 Hz, C**H**OH), 3.82 (1H, dd, *J* = 9.3 & 9.2 Hz, C**H**$_A$H$_B$OTIPS), 3.68 (1H, dd, *J* = 9.3 & 4.6 Hz, CH$_A$**H**$_B$OTIPS), 3.24 (1H, d, *J* = 2.5 Hz, O**H**), 3.14-3.09 (1H, m, C**H**CH$_3$CH$_2$OTIPS), 3.04 (1H, dq, *J* = 10.0 & 7.1 Hz, C=CC**H**CH$_3$), 2.87 (1H, qd, *J* = 7.3 & 1.6 Hz, CHOHC**H**CH$_3$C=O), 2.62-2.49 (2H, m, C**H**$_2$CH$_3$), 1.95 (3H, s, CC**H**$_3$), 1.91 (3H, s, CC**H**$_3$), 1.19 (3H, d, *J* = 7.3 Hz, CHC**H**$_3$), 1.16 (3H, t, *J* = 7.7 Hz, CH$_2$C**H**$_3$), 1.08 (3H, d, *J* = 7.0 Hz, CHC**H**$_3$), 1.01 (21H, s, Si(C**H**(CH$_3$)$_2$)$_3$), 0.99 (3H, d, *J* = 7.0 Hz, CHC**H**$_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 219.0, 179.8, 164.2, 163.9, 119.4, 117.8, 71.3, 67.3, 47.9, 46.6, 37.8, 24.7, 17.9, 14.2, 13.5, 11.8, 11.3, 9.6, 9.5, 7.3; **HRMS** (CI, NH_3) $[M+H]^+$ found 481.3349, $C_{27}H_{49}O_5Si$ requires 481.3349; **m/z** 481 ($[M+H]^+$ 9), 273(18), 209 (93), 181 (100), 153 (21), 58 (74%); Analysis found C, 67.44%, H, 10.07%; $C_{27}H_{48}O_5Si$ requires C, 67.46%, H, 10.06%.

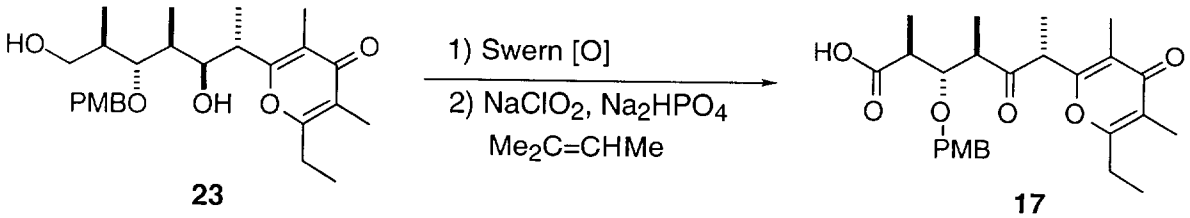
Preparation of (2'*S*,3'*R*,4'*R*,5'*R*,6'*R*)-2-(3'-acetoxy-4',6'-dimethyl-5'-hydroxy-7'-triisopropylsilyloxyhept-2'-yl)-3,5-dimethyl-6-ethylpyran-4-one, 22.



SmI_2 (35.56 ml, 3.56 mmol, 0.1 *M* in THF) was added dropwise to a stirred solution of acetaldehyde (3.18 ml, 56.9 mmol) in THF (40 ml) at –10°C and the resulting SmI_2/acetaldehyde complex was further stirred for 5~10 minutes. A solution of 21 (1.366 g, 2.84 mmol) in THF (5 ml + 10 ml) was added *via* cannula to the SmI_2/acetaldehyde complex and the resulting reaction mixture was further stirred at –10°C for 1 hour before being transferred to the freezer (–26°C) for 16 hours. The reaction was quenched with $NaHCO_3$ (sat. aq., 100 ml), the aqueous phase extracted with Et_2O (3 x 150 ml) and the combined organics dried ($MgSO_4$) and concentrated in *vacuo*. Flash column chromatography (50% EtOAc/hexane) afforded **22** as a colourless oil (1.490 g, 100%).

R_f (50% EtOAc/hexane) = 0.29; $[\alpha]_D^{20}$ = –16.7 (*c* = 2.1, $CHCl_3$); **IR** (FT, liquid film) 3600-3200 (br, OH), 1728 (C=O), 1654, 1592 cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 5.57 (1H, dd, *J* = 10.4 & 1.1 Hz, C**H**OAc), 3.79 (2H, d, *J* = 4.8 Hz, C**H**$_2$OTIPS), 3.55 (1H, d, *J* = 6.2 Hz, C**H**OH), 3.27 (1H, dq, *J* = 10.4 & 6.9 Hz, C=CC**H**CH$_3$), 3.15-3.11 (1H, m, C**H**CH$_3$), 2.64-2.49 (2H, m, C**H**$_2$CH$_3$), 2.08 (1H, qd, *J* = 7.2 & 7.2 Hz, C**H**CH$_3$), 1.94 (3H, s, CC**H**$_3$), 1.89 (3H, s, CC**H**$_3$), 1.79 (3H, s, C**H**$_3$C=O), 1.19 (3H, t, *J* = 7.5 Hz, CH$_2$C**H**$_3$), 1.16 (3H, d, *J* = 6.9 Hz, CHC**H**$_3$), 1.08-1.02 (24H, m, CHC**H**$_3$, Si(C**H**(CH$_3$)$_2$)$_3$), 0.95 (3H, d, *J* = 6.9 Hz, CHC**H**$_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 180.1, 170.8, 165.1, 163.6, 119.6, 118.1, 76.9, 74.8, 66.1, 37.9, 37.6, 36.3, 25.1, 21.0, 18.4, 16.3, 14.6, 12.2, 11.5, 10.0, 9.9, 9.9; **HRMS** (CI, NH_3) $[M+H]^+$ found 525.3610, $C_{29}H_{53}O_6Si$ requires 525.3611; **m/z** 525 ($[M+H]^+$ 100), 481 (21), 281 (67), 228 (21), 209 (64), 186 (27), 181 (28), 136 (21), 58 (22), 52 (61%).

Preparation of (2*S*,3*R*,4*R*,6*S*)-6-(3',5'-dimethyl-6'-ethyl-4'-oxopyran-2'-yl)-2,4-dimethyl-3-*p*-methoxybenzyloxy-5-oxoheptanoic acid, 17.



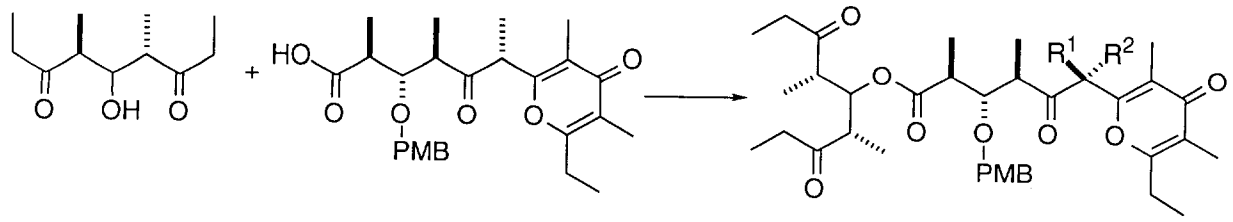
23 **17**

DMSO (63 µl, 0.89 mmol) was added cautiously to a stirred solution of $(COCl)_2$ (2.0 M solution in CH_2Cl_2, 222 µl, 0.44 mmol) in CH_2Cl_2 (2 ml) at –78°C. The reaction mixture was stirred for 30 minutes before adding a solution of **23** (40 mg, 0.09 mmol) in CH_2Cl_2 (3 x 0.5 ml) *via* cannula. The reaction was stirred at -78°C for 1.5 hour before the addition of Et_3N (186 µl, 1.33 mmol). The reaction was stirred at –78°C for 30 minutes then warmed to –30°C and further for 30 minutes. Hexane/toluene (3:1, 10 ml) was added to the reaction mixture at –30°C, the resulting suspension was filtered through a pad of celite and the filtrate was concentrated in *vacuo*. The resulting crude ketoaldehyde was submitted for further oxidation to the corresponding acid.

A solution of $NaClO_2$ (100 mg, 1.11 mmol) and Na_2HPO_4 (139 mg, 0.89 mmol) in water (1.8 ml) was added dropwise to a solution of crude ketoaldehyde (ex. 40 mg, **23**, ~0.09 mmol) and 2-methyl-2-butene (few drops) in *tert*-butanol (1.8 ml) at room temperature. The reaction mixture was stirred for 1 hour then poured into brine (10 ml) and extracted with Et_2O (6 x 15 ml). The combined organics were dried ($MgSO_4$) and concentrated in *vacuo*. Flash column chromatography (50% Et_2O/CH_2Cl_2 + 1% AcOH) afforded **17** as a colourless oil (39 mg, 96%).

R_f (50% Et_2O/CH_2Cl_2 + 1% AcOH) = 0.38; $[\alpha]_D^{20}$ = –96.5 (*c* = 0.4, $CHCl_3$); **IR** (FT, liquid film) 3400-2500 (br, CO_2H), 1723 (C=O), 1652, 1698 cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 7.15 (2H, d, *J* = 8.6 Hz, *m*-C**H**), 6.83 (2H, d, *J* = 8.6 Hz, *o*-C**H**), 4.53 (1H, d, *J* = 10.5 Hz, C$\mathbf{H}_A$$H_B$Ar), 4.23 (1H, d, *J* = 10.5 Hz, $CH_A$$\mathbf{H}_B$Ar), 3.91 (1H, q, *J* = 6.9 Hz, C=CC**H**CH_3), 3.84 (1H, dd, *J* = 9.8 & 2.5 Hz, C**H**OPMB), 3.78 (3H, s, OC$\mathbf{H}_3$), 3.05 (1H, dq, *J* = 9.8 & 6.8 Hz, C**H**CH_3), 2.82 (1H, qd, *J* = 7.0 & 2.5 Hz, C**H**CH_3), 2.52 (2H, qd, *J* = 7.4 & 2.2 Hz, C$\mathbf{H}_2$$CH_3$), 1.93 (3H, s, CC$\mathbf{H}_3$), 1.91 (3H, s, CC$\mathbf{H}_3$), 1.21 (6H, d, *J* = 6.9 Hz, CHC$\mathbf{H}_3$, CHC$\mathbf{H}_3$), 1.12 (3H, t, *J* = 7.6 Hz, CH_2C$\mathbf{H}_3$), 0.85 (3H, d, *J* = 6.8 Hz, CHC$\mathbf{H}_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 210.0, 180.5, 177.3, 165.5, 161.5, 159.7, 130.2, 129.8, 120.9, 118.8, 114.1, 85.1, 74.3, 55.6, 51.3, 46.7, 41.6, 25.1, 13.9, 13.1, 12.8, 11.7, 10.3, 10.0; **HRMS** (CI, NH_3) $[M+H]^+$ found 459.2383, $C_{26}H_{35}O_7$ requires 459.2383; **m/z** 459 ($[M+H]^+$ 100), 443 (20), 277 (40), 237 (43), 181 (38), 154 (21), 138 (24), 121 (80%).

p-Methoxybenzyl protected baconipyrone C, 24.

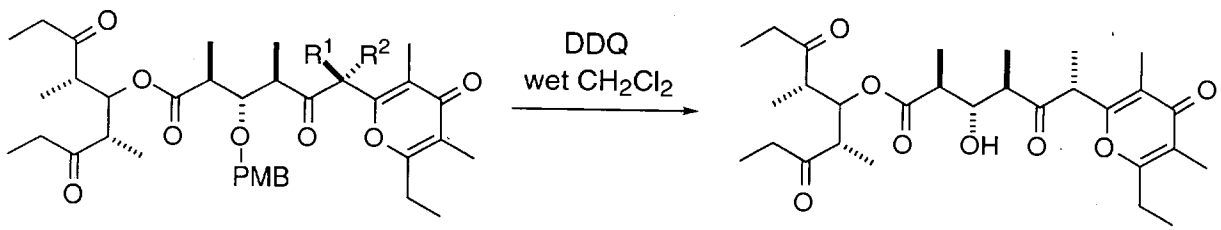


8 **17** **24** R^1 = H, R^2 = Me; **25** R^1 = Me, R^2 = H

2,4,6-Trichlorobenzoyl chloride (494 µl, 3.164 mmol) was added to a stirred solution of **8** (37.6 mg, 0.187 mmol), **17** (65.9 mg, 0.144 mmol), DMAP (878 mg, 7.191 mmol) and Et_3N (461 µl, 3.308 mmol) in toluene (14 ml) at –78°C. The reaction was warmed to 0°C and the resulted white slurry was stirred at 0°C for 10 minutes before being quenched with $NaHCO_3$ (sat. aq., 10 ml). The aqueous layer was extracted with EtOAc (4 x 15 ml), dried ($MgSO_4$) and concentrated in *vacuo*. Flash column chromatography (50% EtOAc/hexane) afforded an unseparable mixture of **24** and **25** (**24**:**25**, ~10:1) as a colourless oil (67.5 mg, 73%).

R_f (60% EtOAc/hexane) = 0.29; $[\alpha]_D^{20}$ = –30.5 (*c* = 0.4, $CHCl_3$); **IR** (FT, liquid film) 1717 (C=O), 1663, 1599 cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 7.14 (2H, d, *J* = 8.6 Hz, *m*-C**H**), 6.85 (2H, d, *J* = 8.6 Hz, *o*-C**H**), 5.49 (1H, dd, *J* = 7.6 & 5.0 Hz, C**H**O(C=O)), 4.46 (1H, d, *J* = 10.7 Hz, C$\mathbf{H}_A$$H_B$Ar), 4.21 (1H, d, *J* = 10.7 Hz, C$H_A$$\mathbf{H}_B$Ar), 3.94 (1H, q, *J* = 6.9 Hz, C=CC**H**CH_3), 3.86-3.78 (1H, m, C**H**OPMB), 3.80 (3H, s, OC$\mathbf{H}_3$), 2.95-2.67 & 2.56-2.34 (5H & 5H, m & m, C$\mathbf{H}_A$CH_BCH_3, CH_AC$\mathbf{H}_B$CH_3, C$\mathbf{H}_X$CH_YCH_3, CH_XC$\mathbf{H}_Y$CH_3, C**H**CH_3, C**H**CH_3, C**H**CH_3, C**H**CH_3, C$\mathbf{H}_2$CH_3), 1.97 (3H, s, CC$\mathbf{H}_3$), 1.93 (3H, s, CC$\mathbf{H}_3$), 1.25 (3H, d, *J* = 6.9 Hz, CHC$\mathbf{H}_3$), 1.13 (3H, t, *J* = 7.6 Hz, CH_2C$\mathbf{H}_3$), 1.11 (3H, d, *J* = 7.2 Hz, CHC$\mathbf{H}_3$), 1.07 (3H, d, *J* = 7.1 Hz, CHC$\mathbf{H}_3$), 1.02-0.98 (9H, m, CHC$\mathbf{H}_3$, CH_2C$\mathbf{H}_3$, CH_2C$\mathbf{H}_3$), 0.76 (3H, d, *J* = 6.9 Hz, CHC$\mathbf{H}_3$); **^{13}C NMR** δ (100.6 MHz, $CDCl_3$) 211.5, 209.4, 179.6, 172.3, 164.7, 160.6, 159.3, 130.0, 129.4, 120.2, 118.3, 113.7, 83.3, 74.4, 73.1, 55.3, 50.6, 47.5, 46.3, 46.2, 41.2, 35.4, 34.9, 24.7, 13.2, 13.1, 12.9, 11.5, 11.3, 10.8, 9.8, 9.8, 7.7, 7.6.

Baconipyrone C, 3.



24 R^1 = H, R^2 = Me

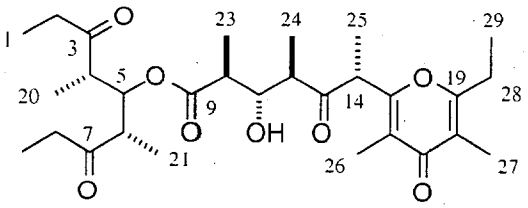
25 R^1 = Me, R^2 = H

3

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (4 mg, 0.018 mmol) was added to a stirred solution of a 10:1 mixture of **24** and **25** (8 mg, 0.011 mmol) in CH_2Cl_2/pH7 buffer mixture (10:1, 1 ml) at room temperature. The reaction mixture was stirred at room temperature for 1 hour and concentrated in *vacuo*. Flash column chromatography (70% EtOAc/hexane) afforded baconipyrone C (**3**) (4.4 mg, 67 %) and 14-*epi*-baconipyrone C (0.4 mg, 7%) both as colourless oils.

R_f (60% EtOAc/hexane) = 0.22; $[\alpha]_D^{20}$ = –73.3 (*c* = 0.77, MeOH); **IR** (FT, liquid film) 3800-3500 (br, OH), 1719 (C=O), 1650, 1600 cm^{-1}; **^{1}H NMR** δ (400 MHz, $CDCl_3$) 5.47 (1H, dd, *J* = 8.9 & 3.7 Hz, C**H**O(C=O)), 4.15 (1H, q, *J* = 6.9 Hz, C=CC**H**CH_3), 3.55 (1H, ddd, *J* = 10.3, 8.7 & 7.2 Hz, C**H**OH), 3.38 (1H, d, *J* = 10.4 Hz, O**H**), 2.85 (1H, dq, *J* = 8.7 & 7.0 Hz, C**H**CH_3), 2.83 (1H, m, C**H**CH_3), 2.83 (1H, m, C**H**CH_3), 2.75 (1H, dq, *J* = 18.1 & 7.2 Hz, C$\mathbf{H}_A$C$H_B$$CH_3$), 2.55 (2H, q, *J* = 7.6 Hz, C$\mathbf{H}_2$$CH_3$), 2.55 (1H, m, C**H**$CH_3$), 2.51 (1H, dq, *J* = 18.2 & 7.2, C$\mathbf{H}_X$C$H_Y$$CH_3$), 2.39 (1H, dq, *J* = 18.0 & 7.2 Hz, CH_AC$\mathbf{H}_B$$CH_3$), 2.34 (1H, dq, *J* = 18.3 & 7.3 Hz, CH_XC$\mathbf{H}_Y$$CH_3$), 2.09 (3H, s, CC$\mathbf{H}_3$), 1.93 (3H, s, CC$\mathbf{H}_3$), 1.39 (3H, d, *J* = 7.0 Hz, CHC$\mathbf{H}_3$), 1.22 (3H, d, *J* = 7.2 Hz, CHC$\mathbf{H}_3$), 1.16 (3H, t, *J* = 7.6 Hz, CH_2C$\mathbf{H}_3$), 1.09 (3H, d, *J* = 7.2 Hz, CHC$\mathbf{H}_3$), 1.02 (3H, d, *J* = 6.9 Hz, CHC$\mathbf{H}_3$), 1.01 (3H, t, *J* = 7.3 Hz, CH_2C$\mathbf{H}_3$), 0.91 (3H, t, *J* = 7.2 Hz, CH_2C$\mathbf{H}_3$), 0.86 (3H, d, *J* = 6.8 Hz, CHC$\mathbf{H}_3$); **^{13}C NMR** δ (62.5 MHz, $CDCl_3$) 211.9, 210.8, 210.4, 179.7, 174.1, 164.6, 160.6, 120.4, 118.3, 77.5, 73.8, 51.0, 48.6, 47.3, 45.8, 41.1, 35.1, 24.7, 15.1, 14.1, 13.4, 13.1, 11.3, 9.9, 9.7, 9.5, 7.7, 7.3. **HRMS** (CI) $[M+H]^+$ found 521.3120, $C_{29}H_{44}O_8$ requires 521.3114; **m/z** 521 ($[M+H]^+$ 11), 302 (21), 237 (100), 200 (53), 183 (17%).

Table 1: ^{1}H NMR data of synthetic *versus* authentic baconipyrone C



baconipyrone C

	Baconipyrone C * (authentic, $CDCl_3$, 360 MHz)		Baconipyrone C (synthetic,$CDCl_3$, 500 MHz)	
H no.	δ (ppm)	*J* (Hz)	δ (ppm)	*J* (Hz)
1	0.91	t (7.2)	0.91	t (7.2)
2	2.34	dq (18.3 & 7.2)	2.34	dq (18.3 & 7.3)
2	2.56	dq (18.3 & 7.2)	2.51	dq (18.2 & 7.2)
4	2.83	m	2.83	m
5	5.46	dd (9.0 & 3.5)	5.47	dd (8.9 & 3.7)
6	2.83	m	2.83	m
8	2.39	dq (18.1 & 7.2)	2.39	dq (18.0 & 7.2)
8	2.76	dq (18.1 & 7.2)	2.75	dq (18.1 & 7.2)
10	2.55	dq (7.2 & 2.7)	2.55	m
11	3.54	ddd (10.5, 9.0 & 7.2)	3.55	ddd (10.3, 8.7 & 7.2)
OH	3.64	d (10.5)	3.38	d (10.4)
12	2.86	dq (9.0 & 7.2)	2.85	dq (8.7 & 7.0)
14	4.16	q (6.9)	4.15	q (6.9)
20	0.85	d (6.8)	0.86	d (6.8)
21	1.02	d (6.9)	1.02	d (6.9)
22	1.01	t (7.2)	1.01	t (7.2)
23	1.22	d (7.2)	1.22	d (7.2)
24	1.09	d (7.2)	1.09	d (7.2)
25	1.38	d (6.9)	1.39	d (7.0)
26	2.03	s	2.09	s
27	1.93	s	1.93	s
28	2.56	q (7.6)	2.55	q (7.6)
29	1.16	t (7.6)	1.16	t (7.6)

*Authentic baconipyrone C: $[\alpha]_D^{20} = -82$ (*c* = 0.16, MeOH)

Synthetic baconipyrone C: $[\alpha]_D^{20} = -73.3$

(*c* = 0.77, MeOH)

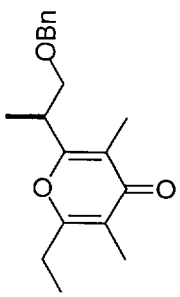
*See footnote 23 for explanation of discrepancy in the specific rotation measured at Cambridge relative to that reported in the original isolation paper: Manker, D. C.; Faulkner, D. J; Stout, T. J.; Clardy, J. *J. Org. Chem.* **1989**, *54*, 5371.

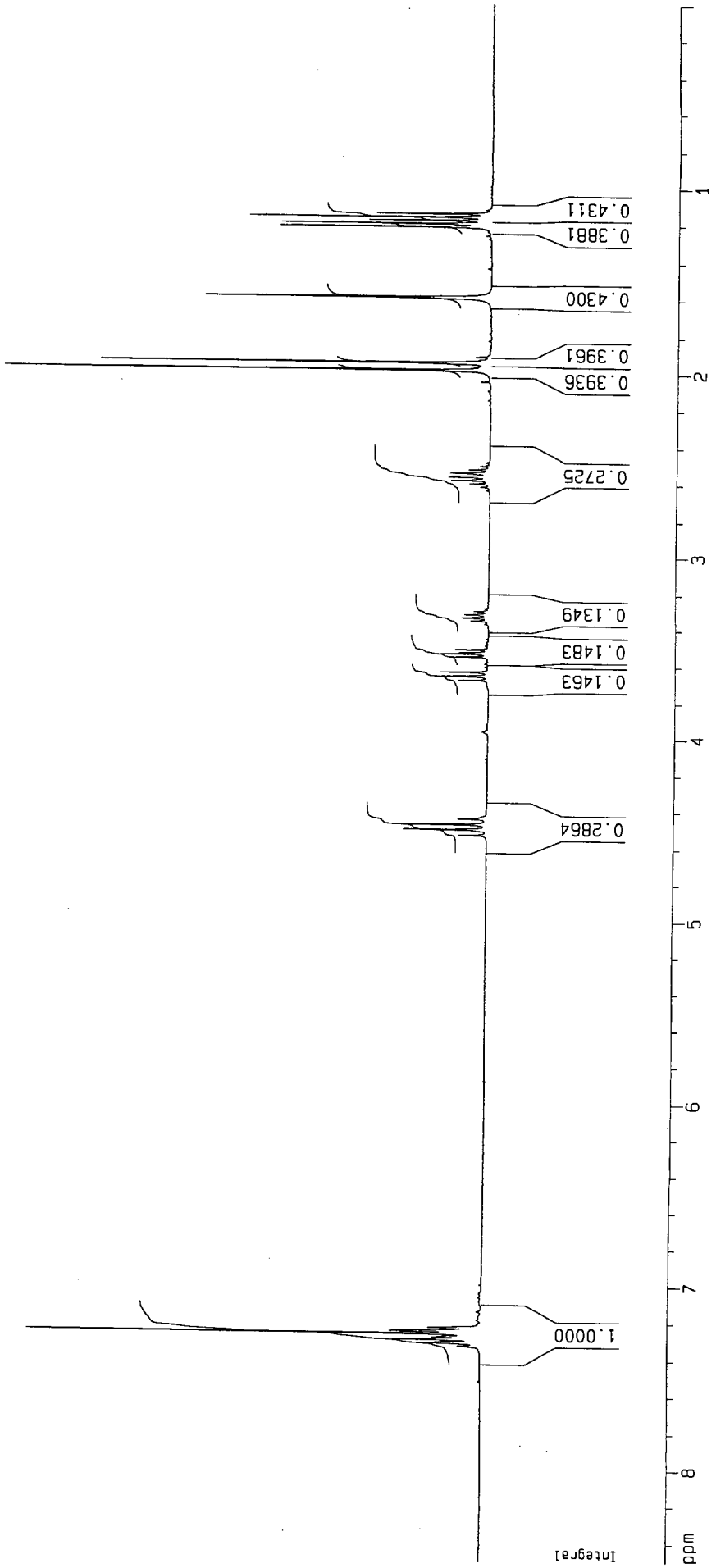
Table 2: ^{13}C NMR data of synthetic *versus* authentic baconipyrone C

Baconipyrone C* (authentic, $CDCl_3$)	**Baconipyrone C (synthetic, $CDCl_3$, 62.9 MHz)**
δ (ppm)	δ (ppm)
211.9	211.9
210.9	210.8
210.4	210.4
179.7	179.7
174.0	174.1
164.7	164.6
160.6	160.6
120.4	120.4
118.2	118.3
77.5	77.5
73.7	73.8
50.9	51.0
48.6	48.6
47.2	47.3
45.7	45.8
41.1	41.1
35.1	35.1
24.7	24.7
15.0	15.1
14.1	14.1
13.8	13.4
13.1	13.1
11.3	11.3
9.9	9.9
9.6	9.7
9.5	9.5
7.7	7.7
7.2	7.3

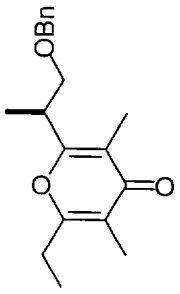
*Manker, D. C.; Faulkner, D. J; Stout, T. J.; Clardy, J. *J. Org. Chem.* **1989**, *54*, 5371.

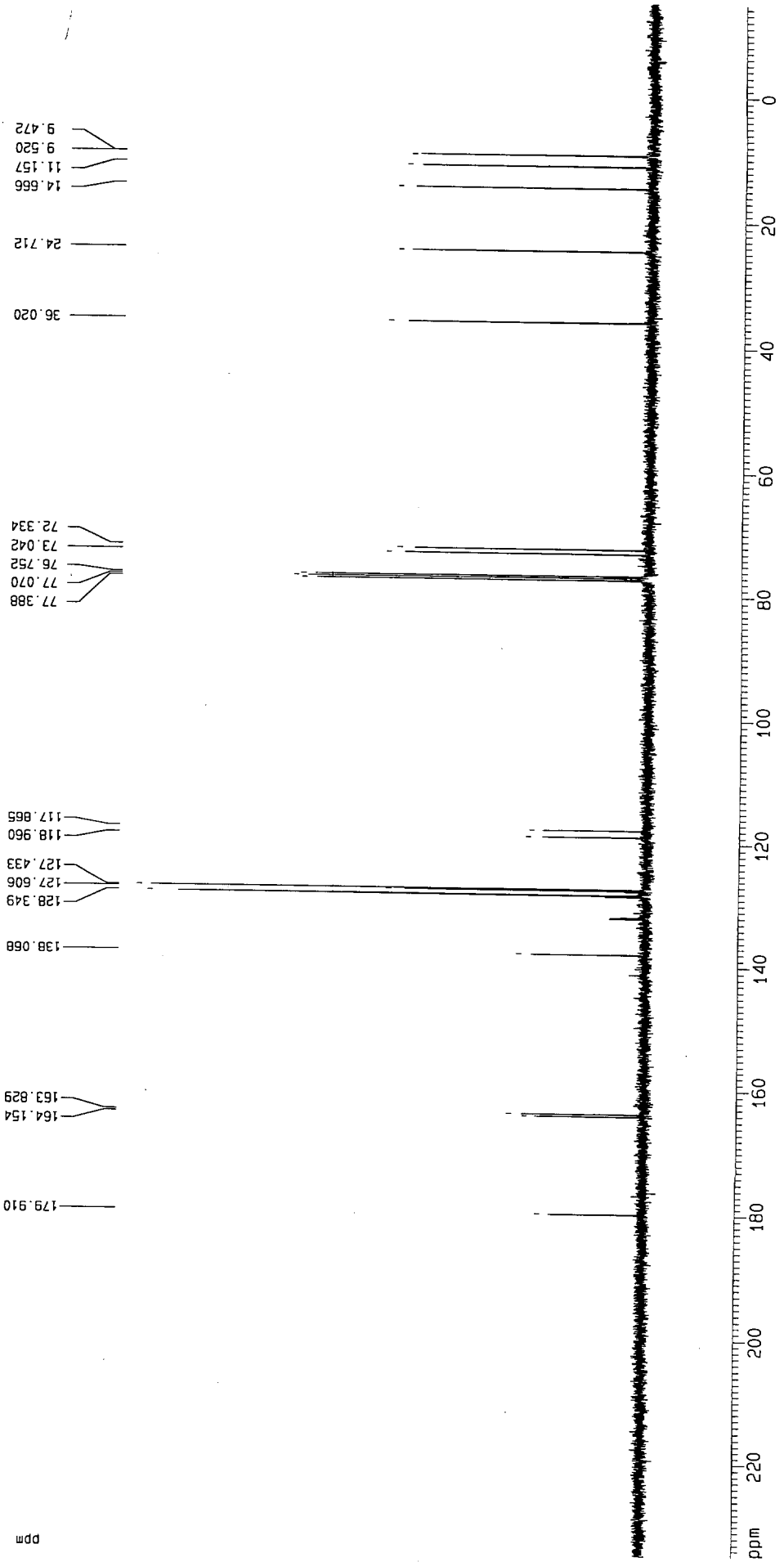
(i) ^{1}H NMR (400 MHz, $CDCl_3$)



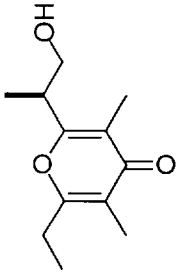


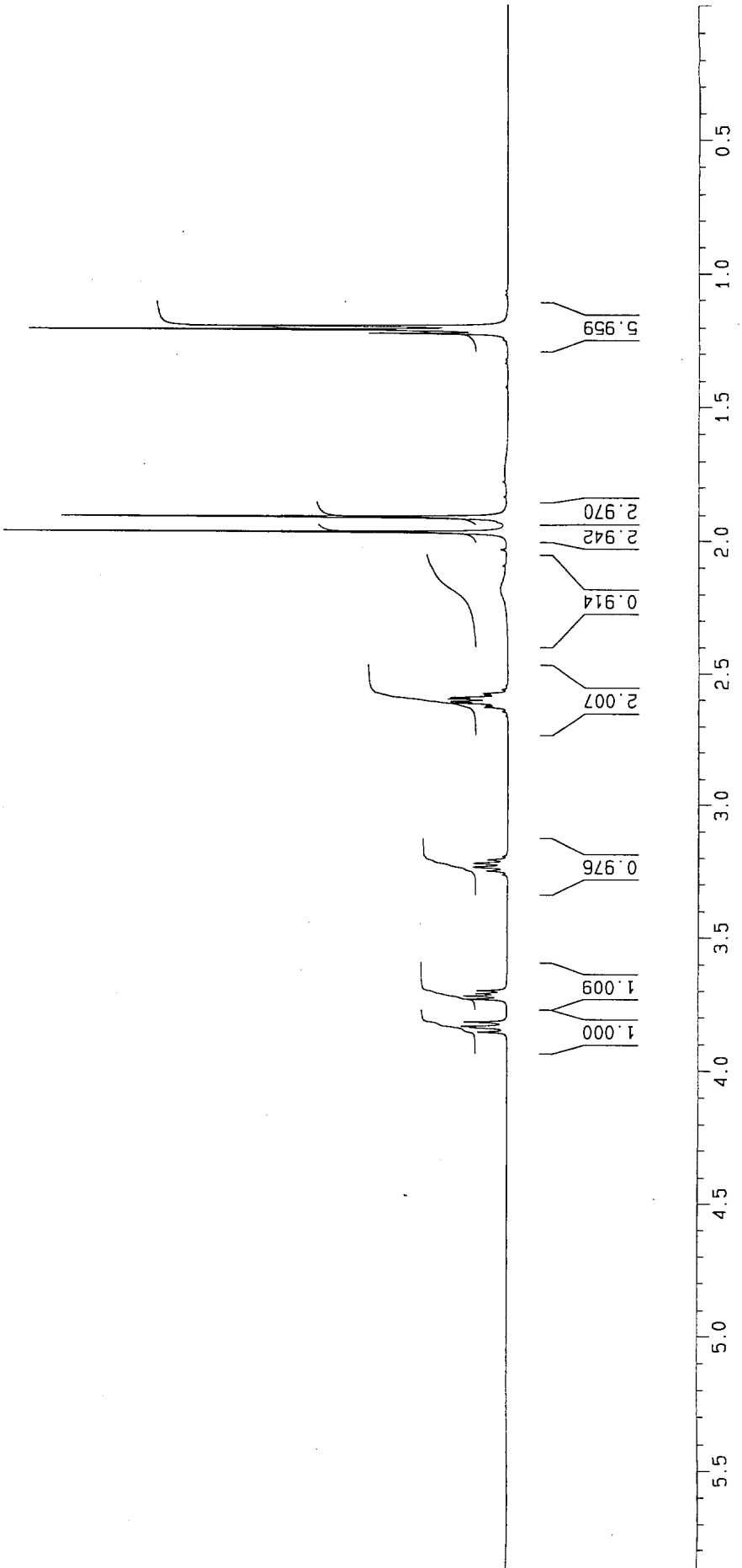
(ii) ^{13}C NMR (100.6 MHz, $CDCl_3$)



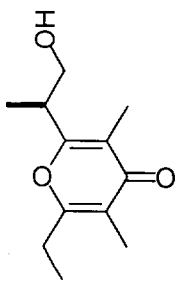


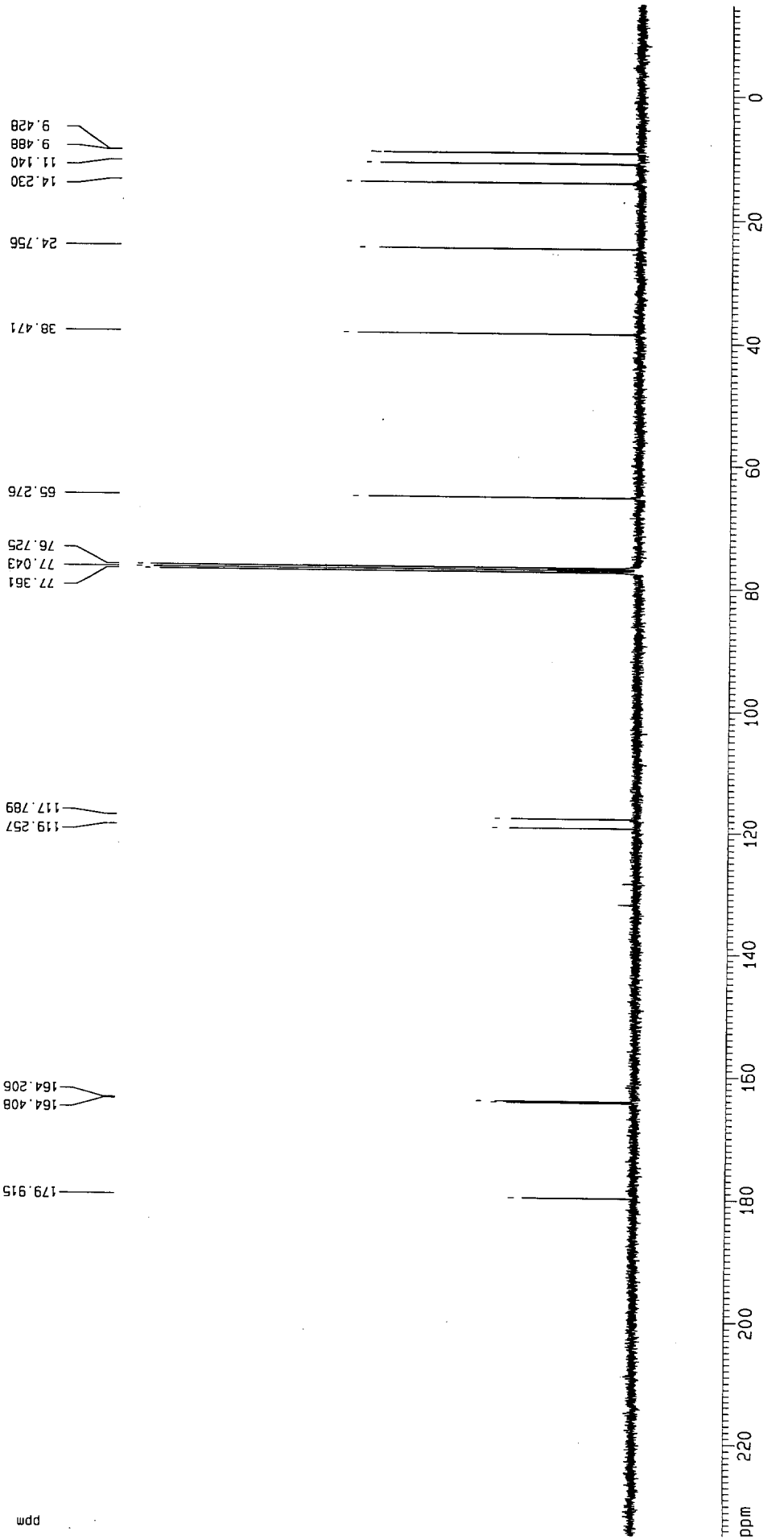
(i) ^{1}H NMR (400 MHz, $CDCl_3$)



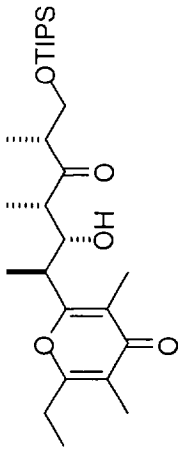


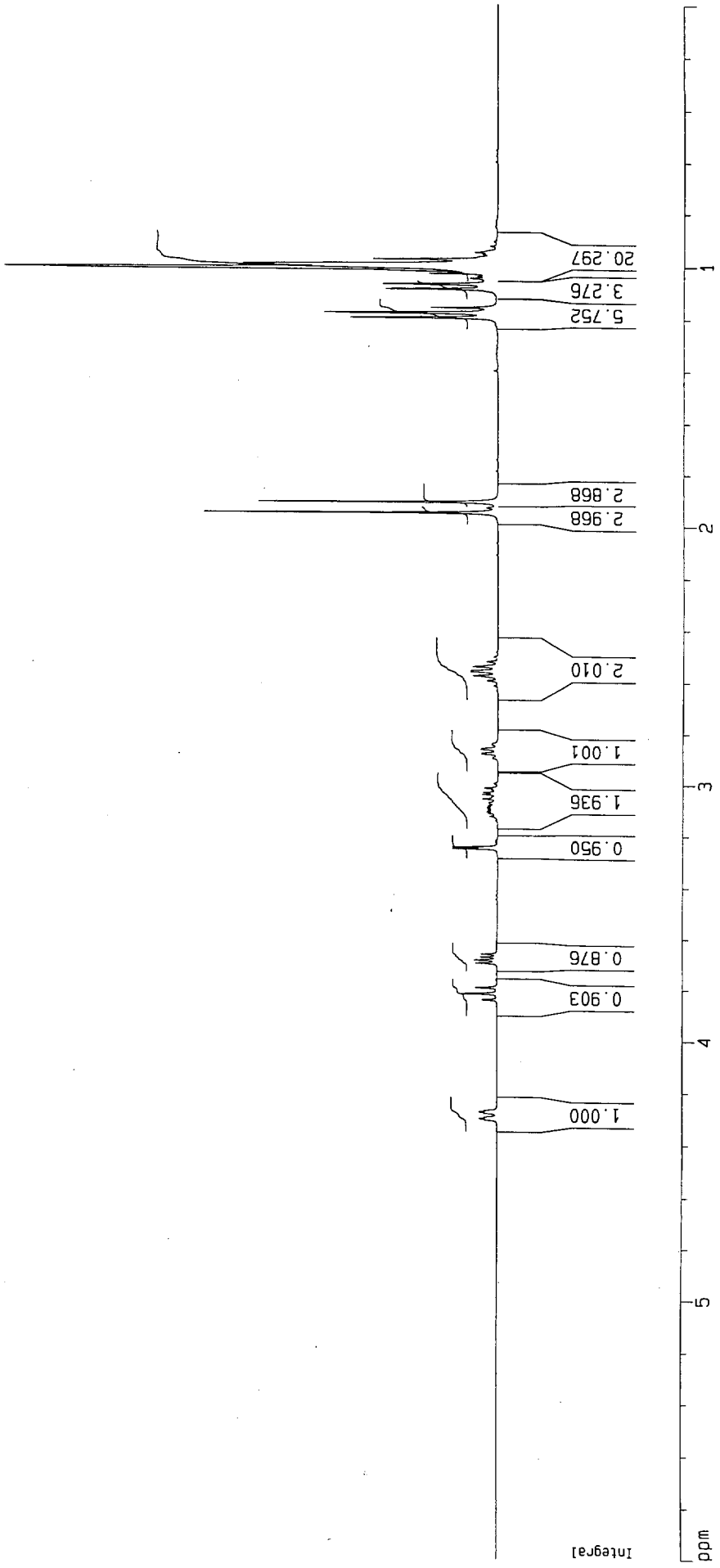
(ii) ^{13}C NMR (100.6 MHz, $CDCl_3$)



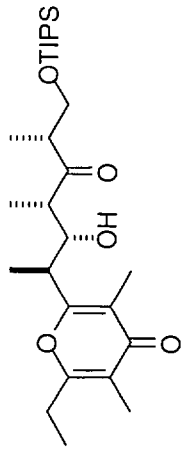


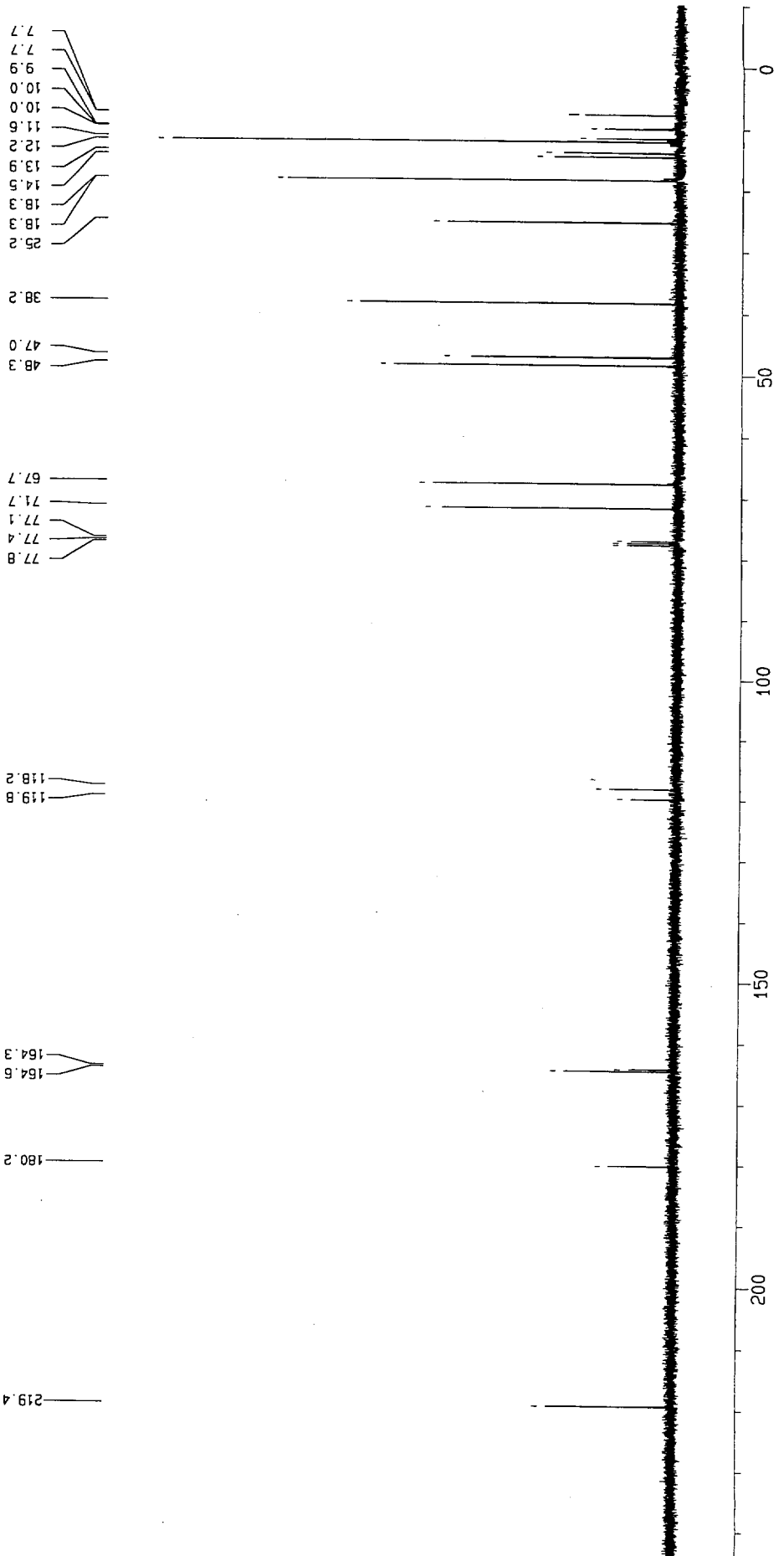
(i) ^{1}H NMR (400 MHz, $CDCl_3$)



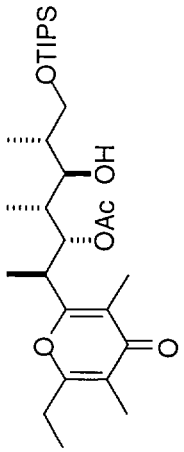


(ii) ^{13}C NMR (100.6 MHz, $CDCl_3$)

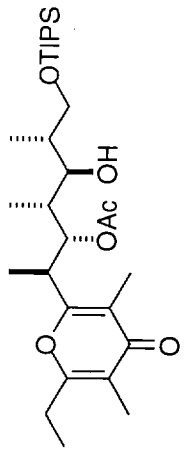


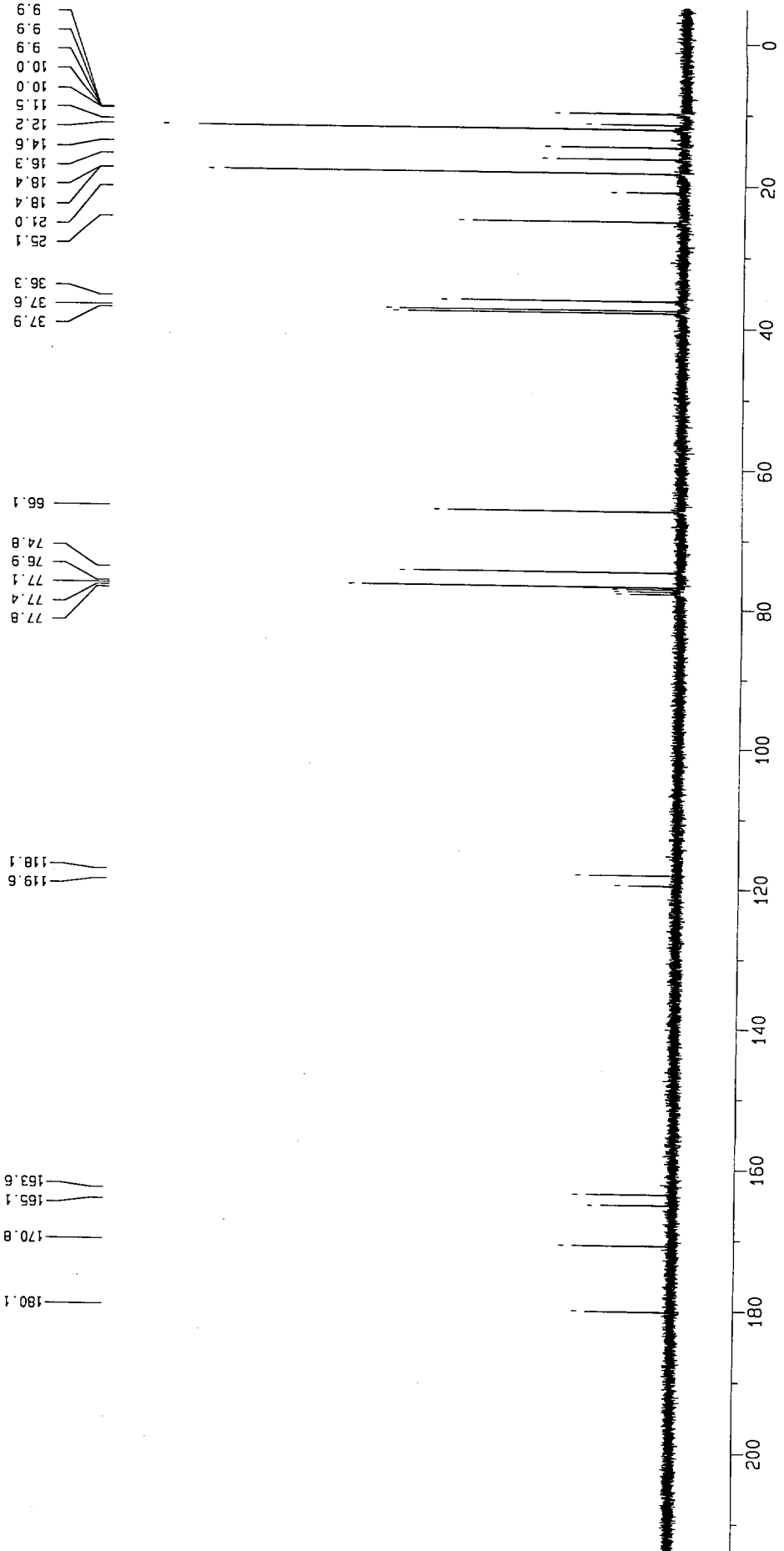


(i) ^{1}H NMR (400 MHz, $CDCl_3$)

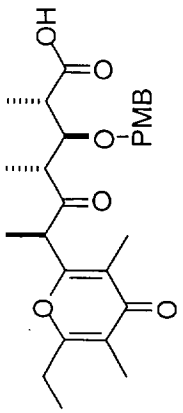


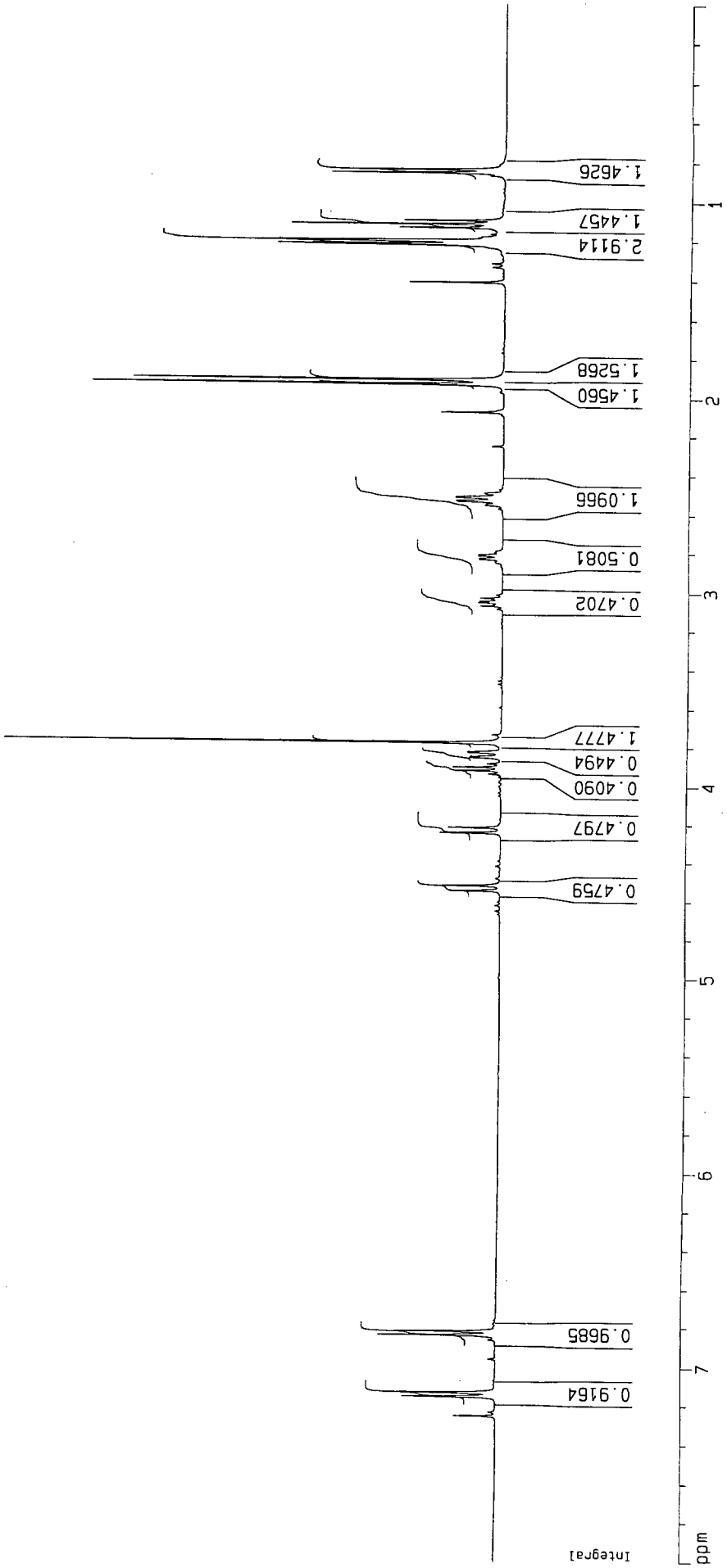
(ii) ^{13}C NMR (100.6 MHz, $CDCl_3$)



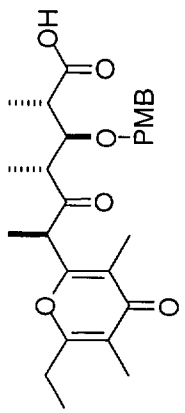


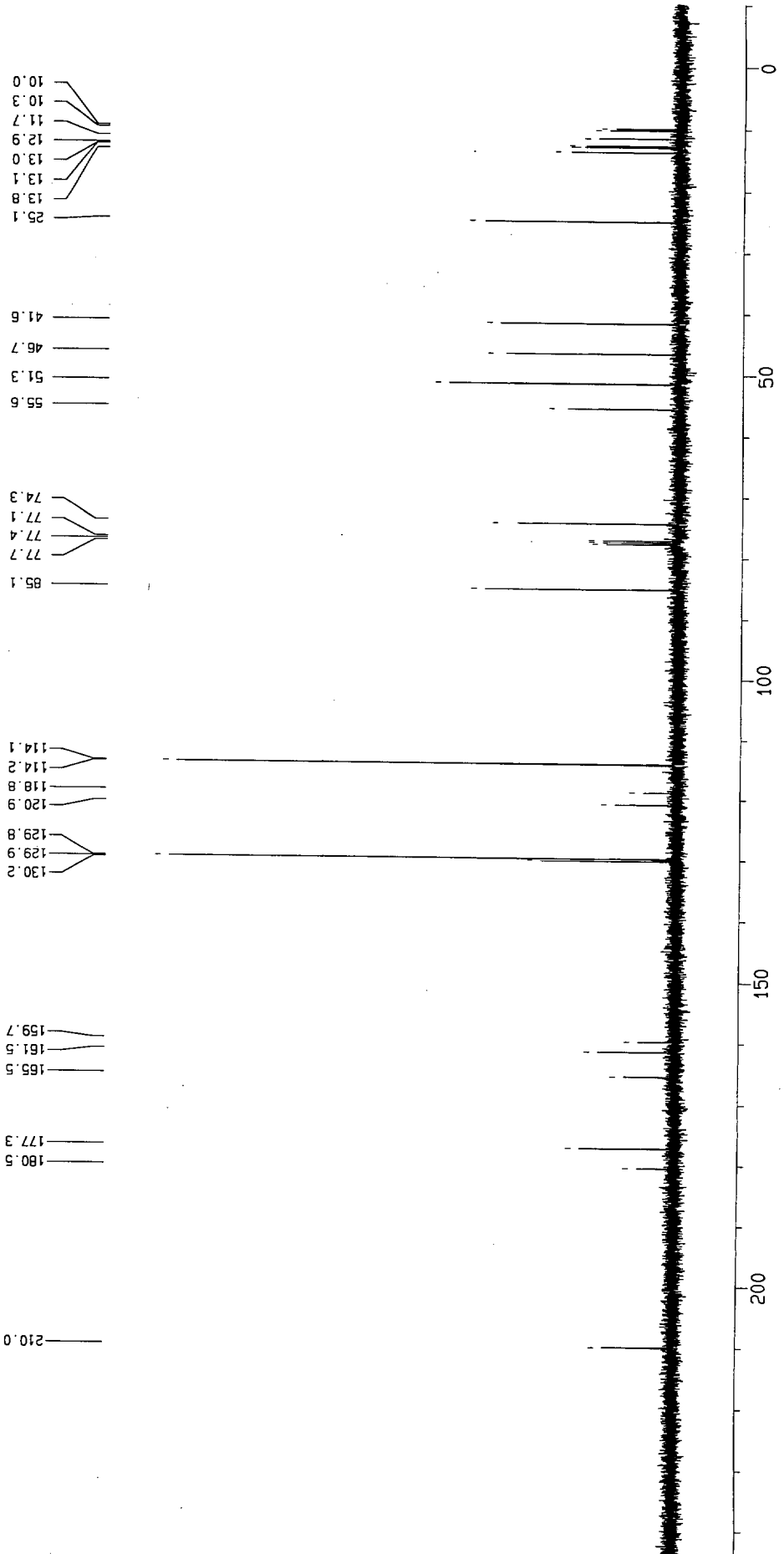
(i) ^{1}H NMR (400 MHz, $CDCl_3$)



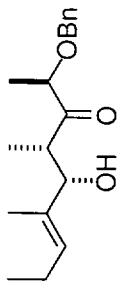


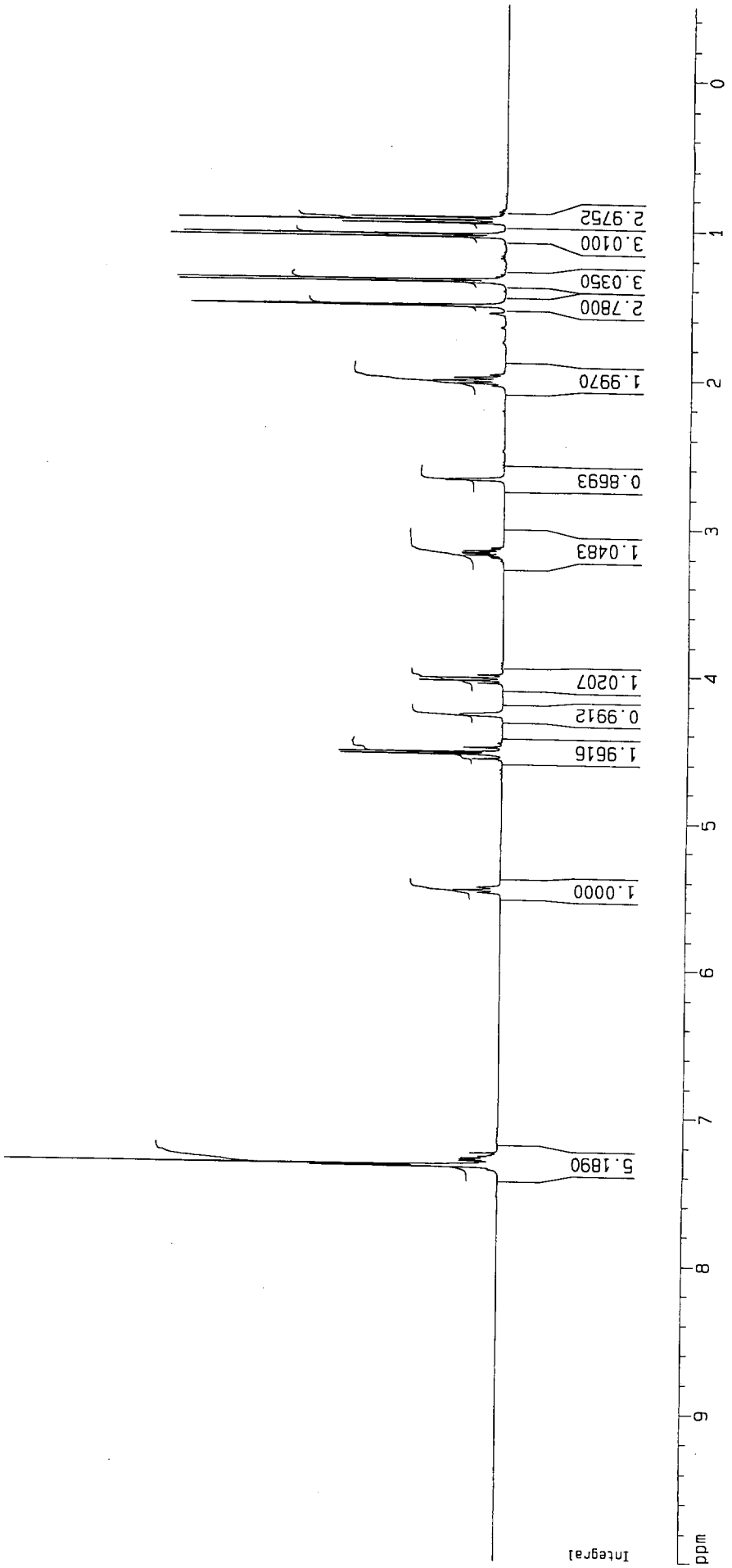
(ii) ^{13}C NMR (100.6 MHz, $CDCl_3$)

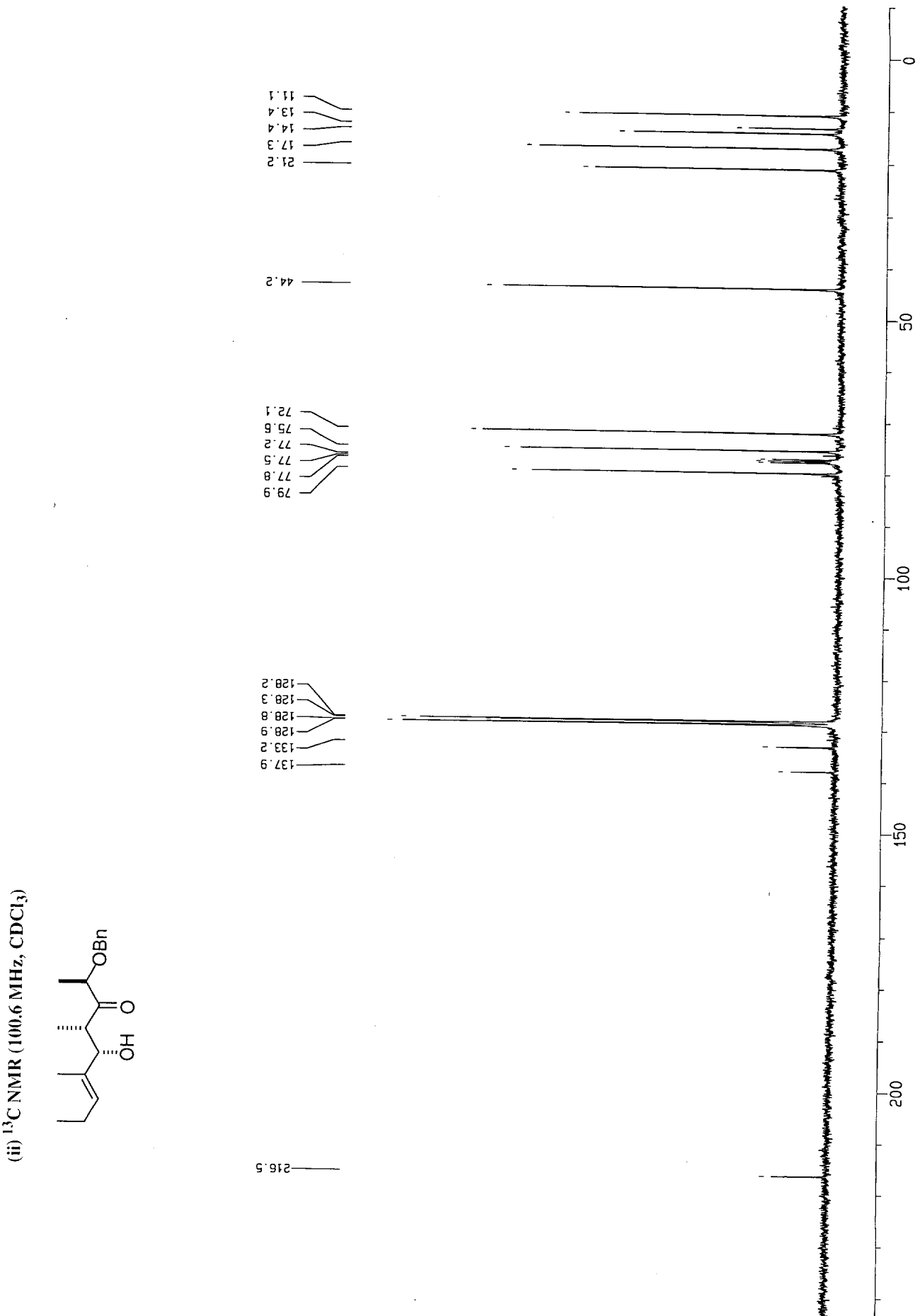


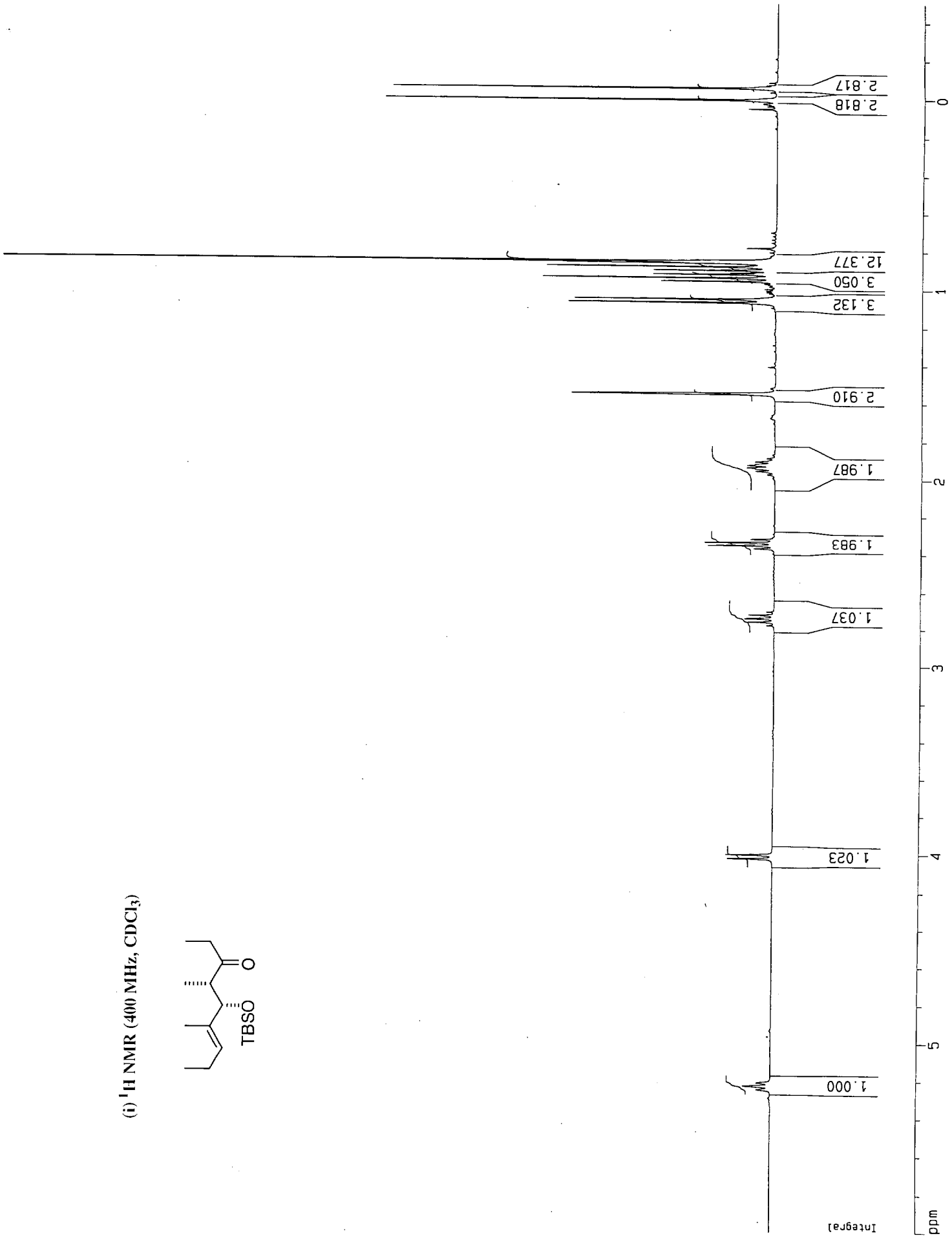


(i) ^{1}H NMR (400 MHz, $CDCl_3$)



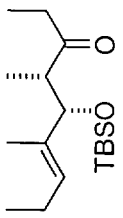


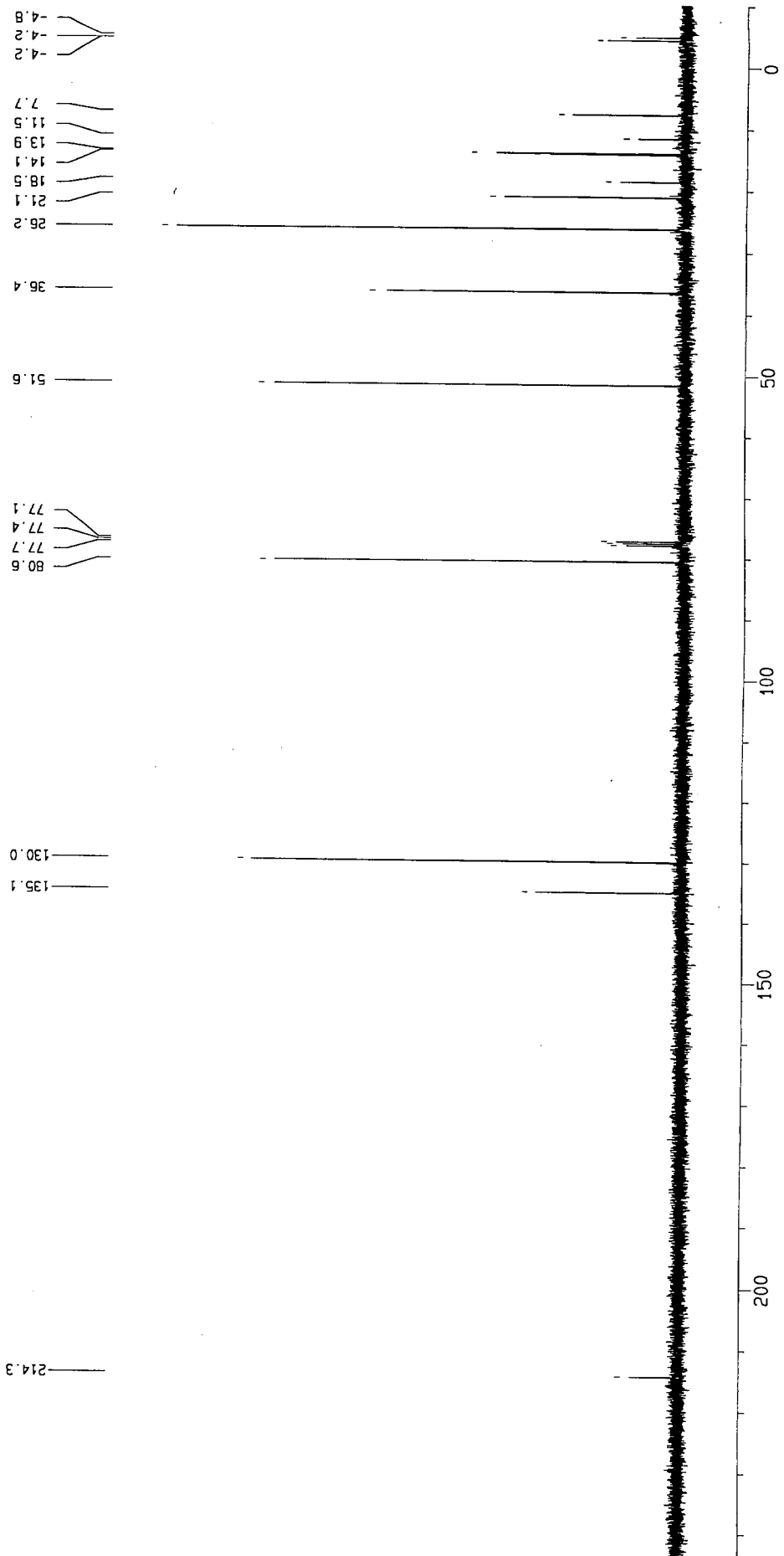




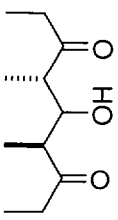
(i) ^{1}H NMR (400 MHz, $CDCl_3$)

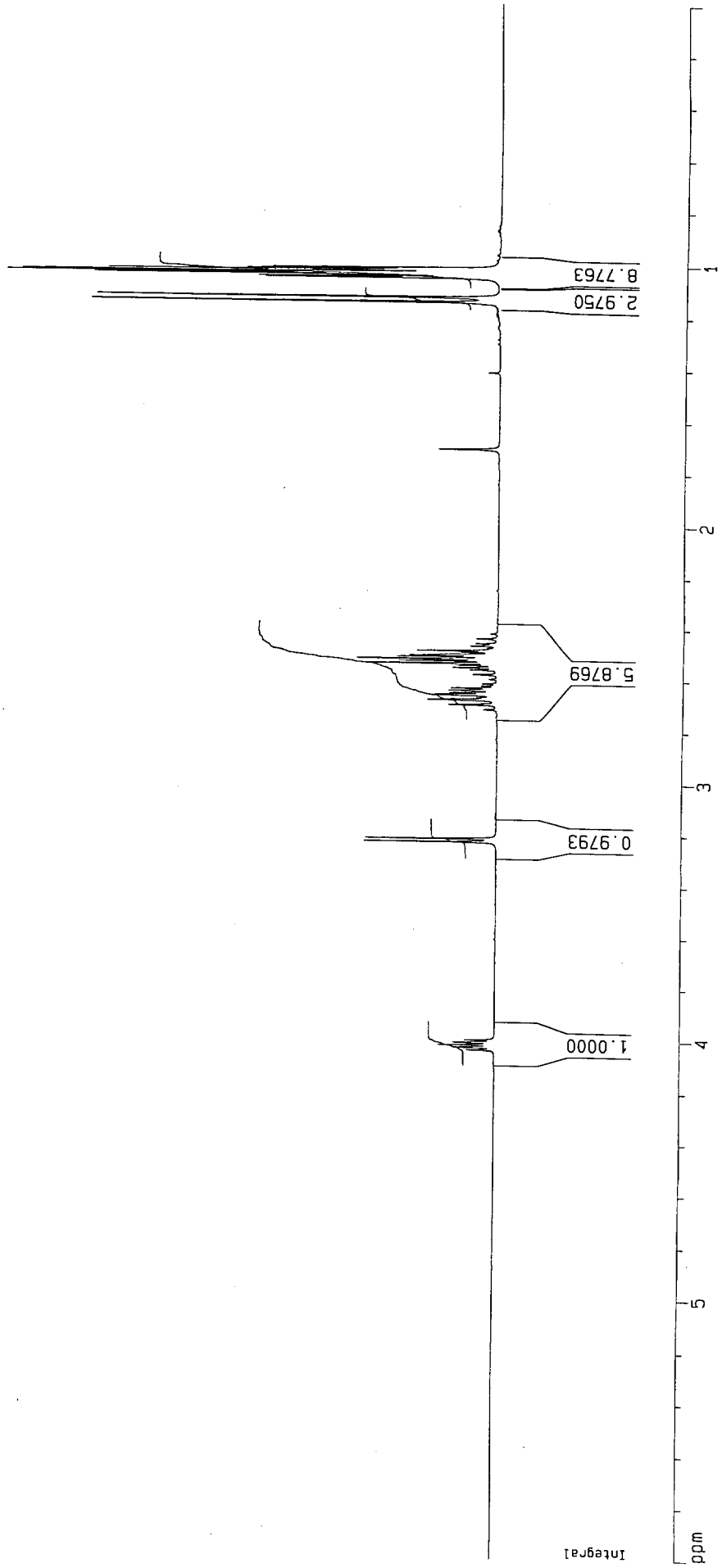
(ii) ^{13}C NMR (100.6 MHz, $CDCl_3$)



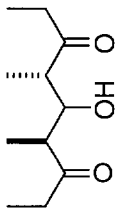


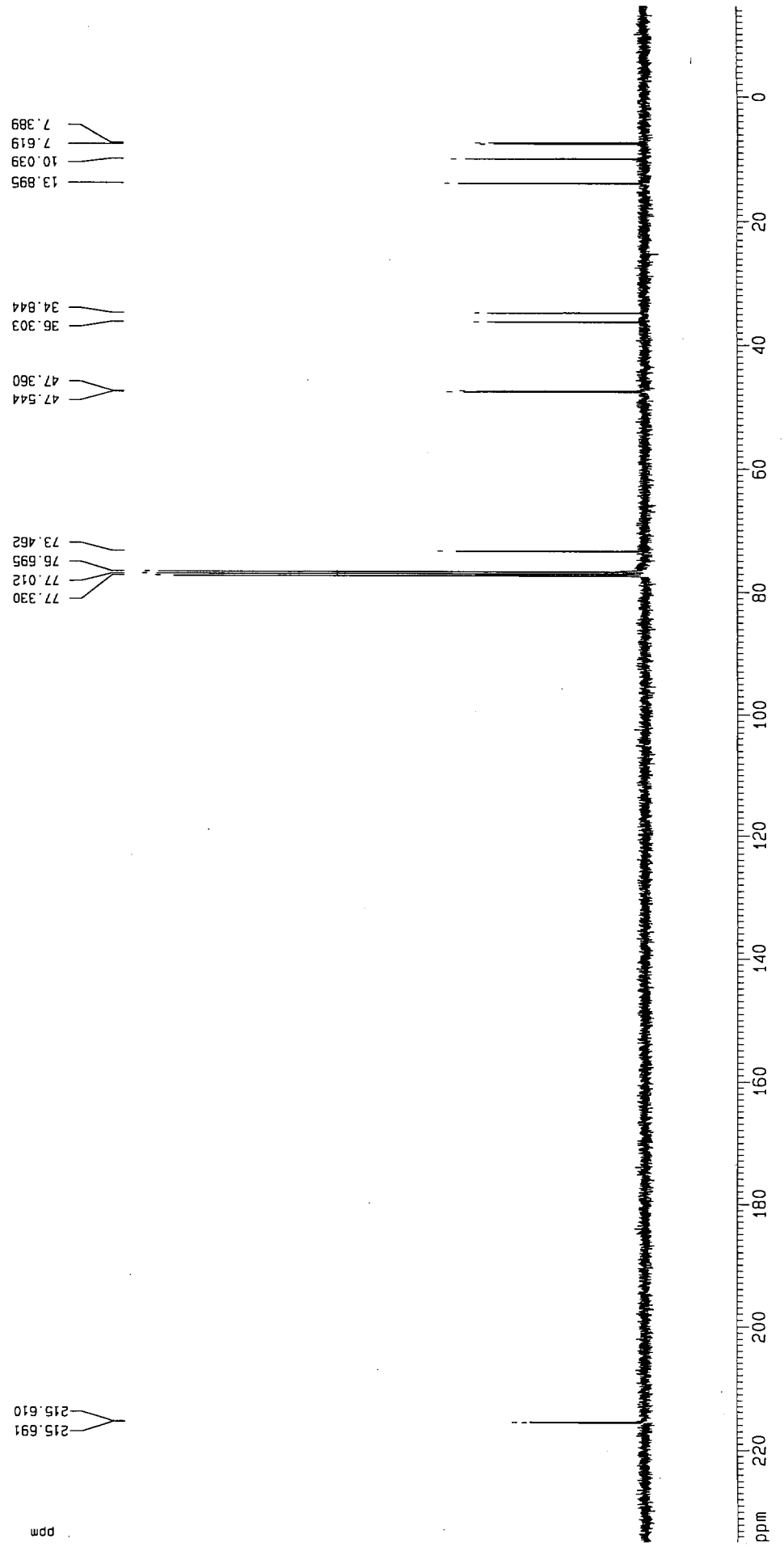
(i) ^{1}H NMR (400 MHz, $CDCl_3$)

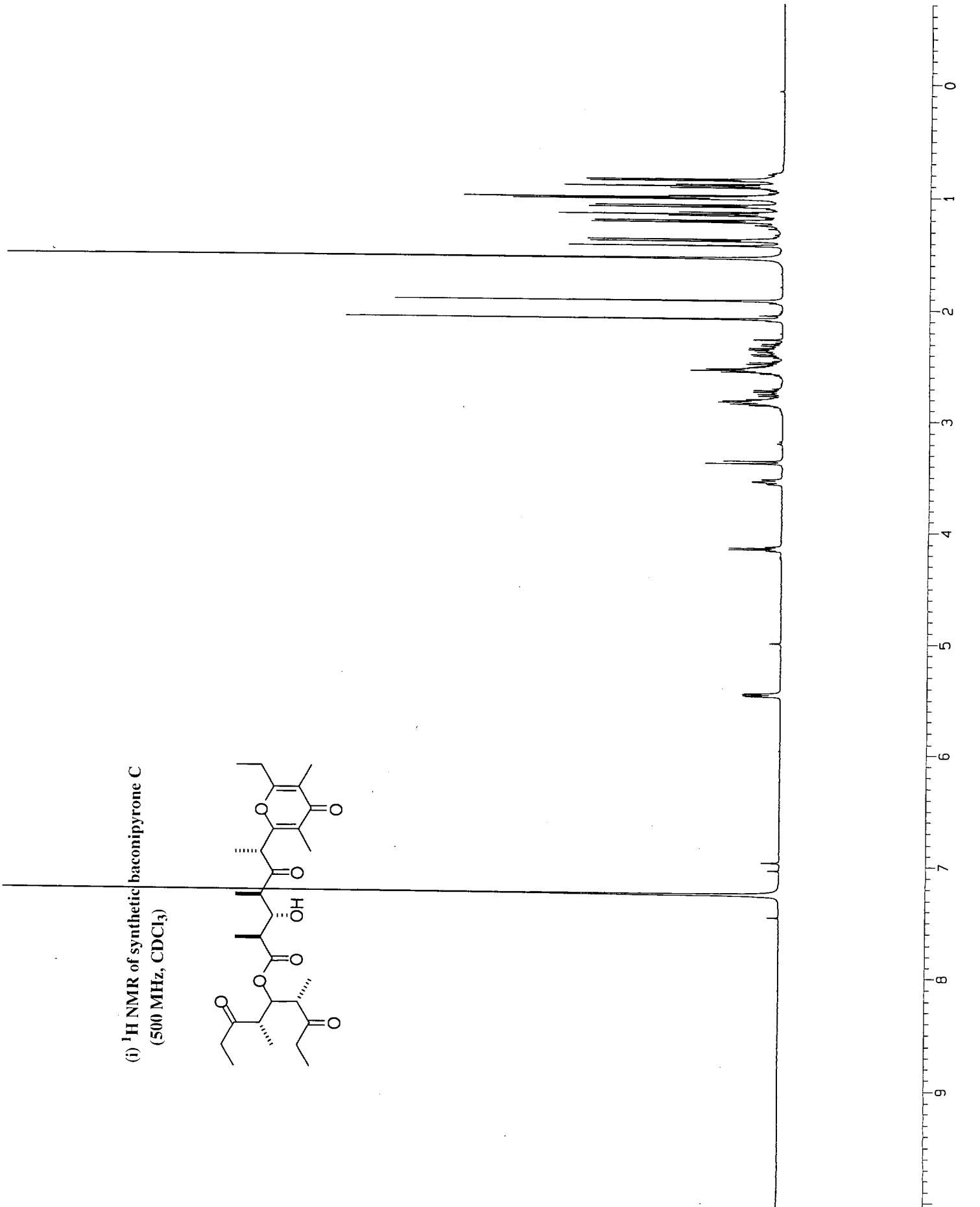




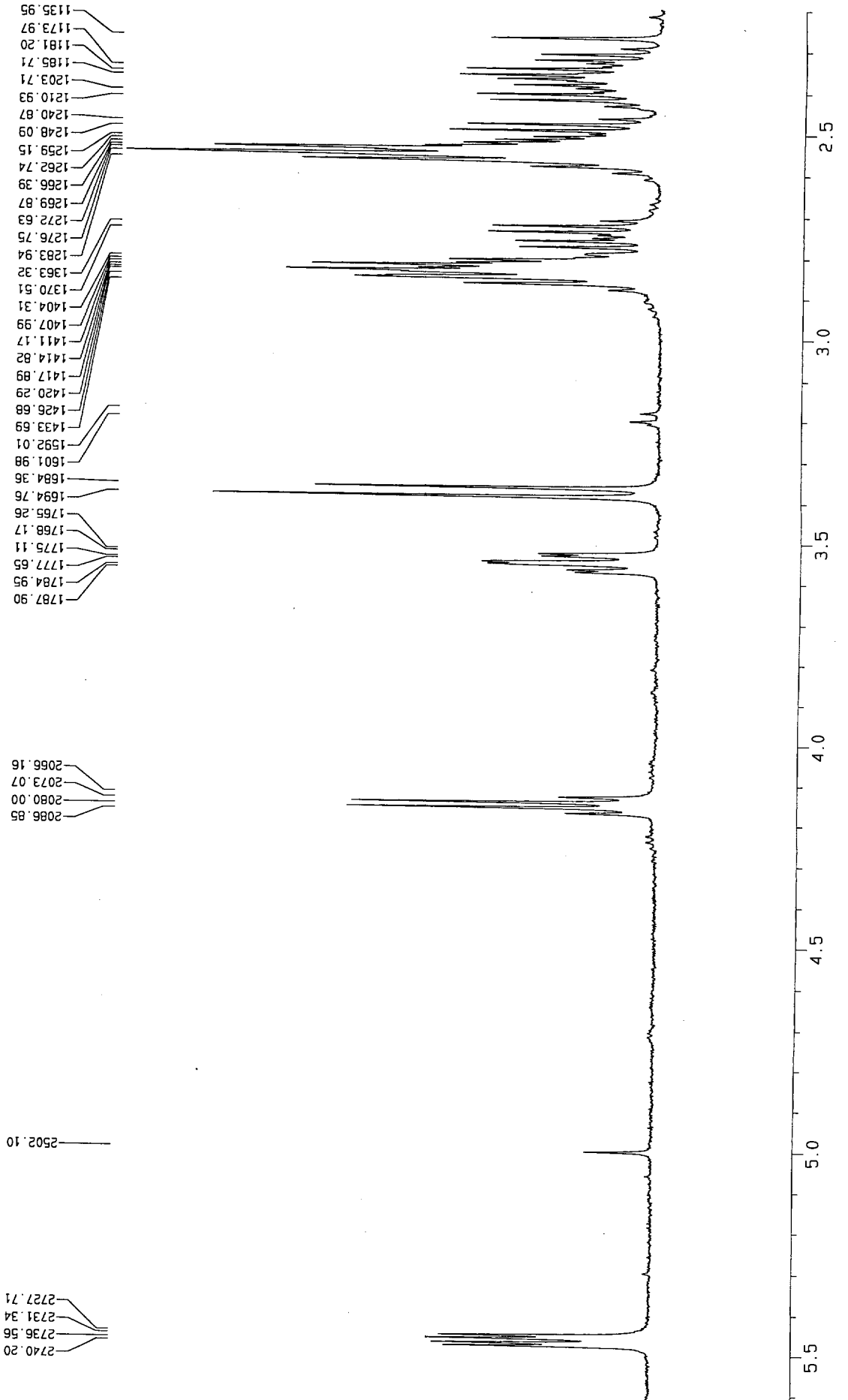
(ii) ^{13}C NMR (100.6 MHz, $CDCl_3$)

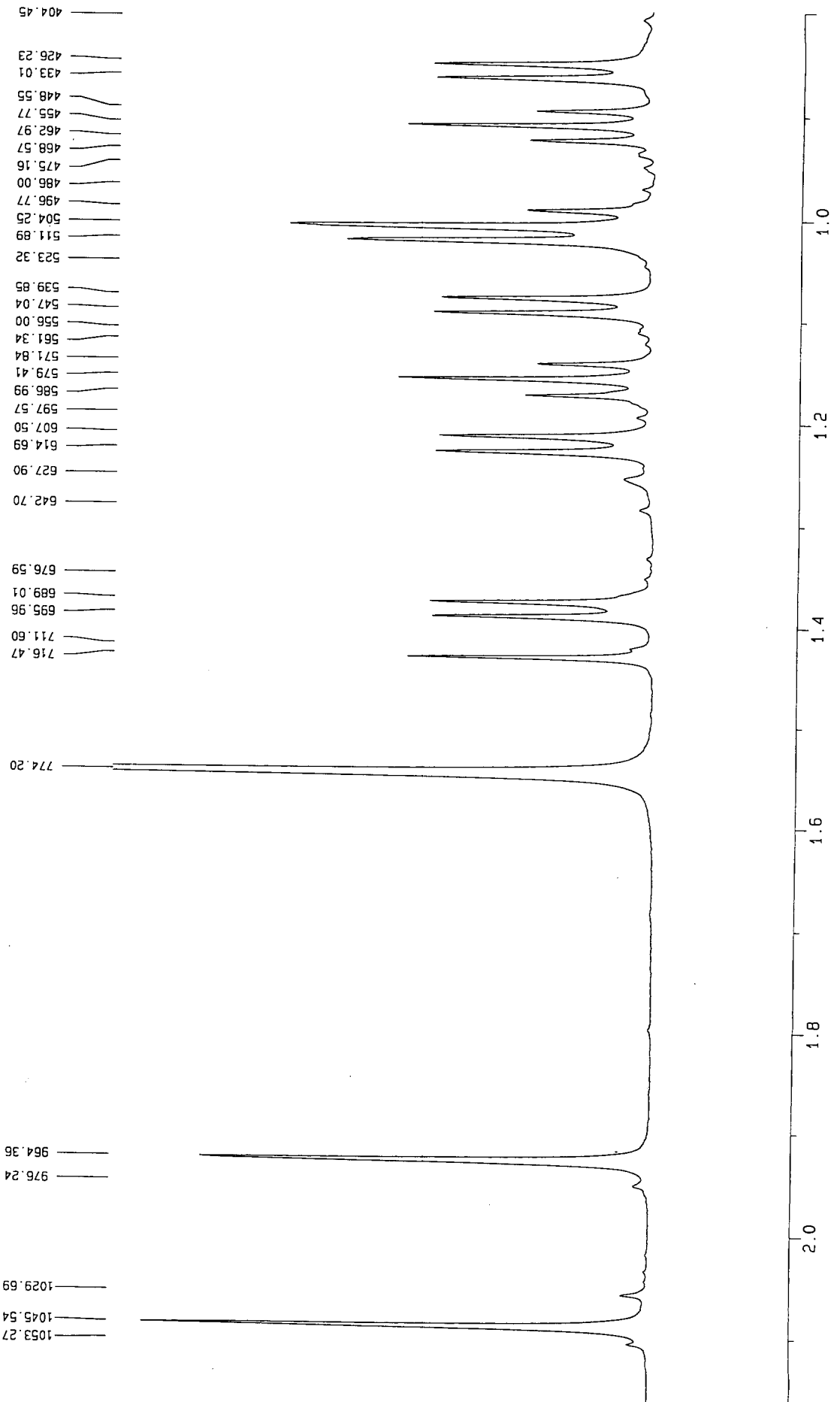


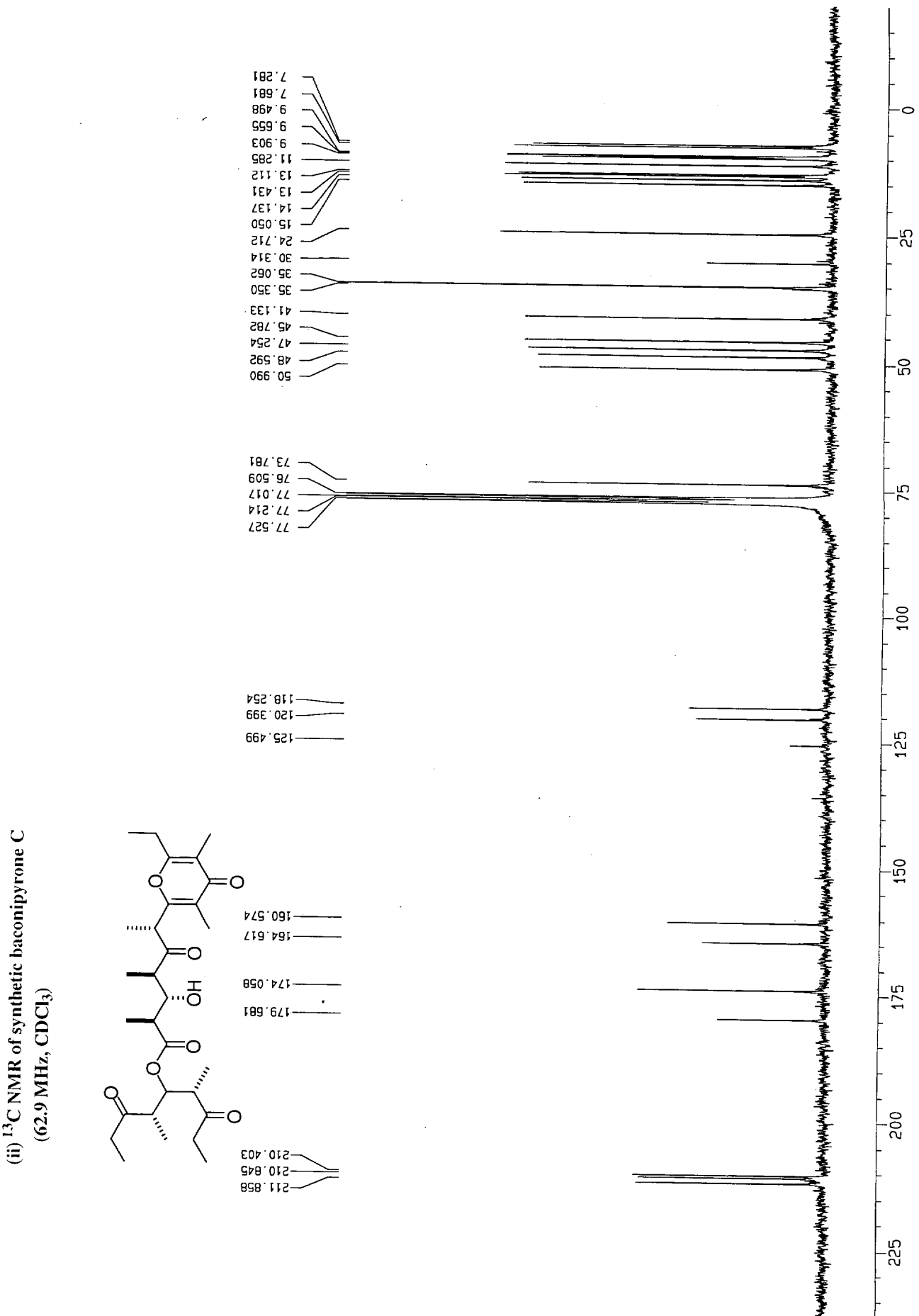




(i) ^{1}H NMR of synthetic baconipyrone C
(500 MHz, $CDCl_3$)







(ii) ^{13}C NMR of synthetic baconipyrone C
(62.9 MHz, $CDCl_3$)

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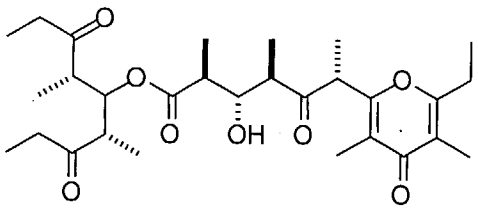
(i) ^{1}H NMR of authentic baconipyrone C
(360 MHz, $CDCl_3$)



(ii) ^{13}C NMR of authentic baconipyrone C ($CDCl_3$)