

Supporting information

Asymmetric total synthesis of Paecilomycin E, 10'-epi-Paecilomycin E and 6'-epi-Cochliomycin C

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Content

Experimental details for the synthesis of few compounds	PP2-PP18
NMR spectrum of compounds	PP 19-PP 188
HPLC chromatogram	PP 189- PP 191

General Information: Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. THF and diethylether were distilled from sodiumbenzophenone ketyl. Dichloromethane (CH_2Cl_2), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were distilled from CaH_2 . Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates (Merck) with UV light, ethanolic anisaldehyde and phosphomolybdic acid/heat as developing agents. Silicagel 100-200 mesh was used for column chromatography. Yields refer to chromatographically and spectroscopically homogeneous materials unless otherwise stated. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) and carbon nuclear magnetic resonance ($^{13}\text{C-NMR}$) spectra were acquired in CDCl_3 unless otherwise mentioned. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, $\delta = 0.00$ ppm), and are referenced to residual solvent (CDCl_3 , $\delta = 7.26$ ppm (^1H), 77.16 ppm (^{13}C) and CD_3COCD_3 , $\delta = 2.09$ ppm (^1H)). Coupling constants (J) are reported in hertz (Hz) and the resonance multiplicity abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; dt, doublet of triplets; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet; comp, overlapping multiplets of magnetically non-equivalent protons. Optical rotations were measured on a JASCO P1020 digital polarimeter. Mass spectrometric analysis was performed in the CRF, IIT-Kharagpur (TOF analyzer). HPLC analysis was performed with the help of PDA detector (200-800 nm)

(*R*)-6-(4-methoxybenzyloxy)hexan-2-yl acetate (12**)**

In a typical resolution experiment, a solution of racemic alcohol **11** (4.0 g, 16.8 mmol) in anhydrous diisopropyl ether (75 ml) was stirred with vinyl acetate (1 equiv, 1.7 mL) and powdered molecular sieves (25 mg, 4 Å) followed by the addition of CAL-B (1.0 g). The reaction mixture was stirred in an orbit shaker (250 rpm) at room temperature for 1 h. After 50% conversion (by TLC analysis), the reaction mixture was filtered through a pad of celite and evaporated to dryness. The alcohol and the acetate were isolated by column chromatography. The undesired acetate (**12**) was deprotected and converted to the desired alcohol **13** by Mitsunobu inversion. The spectral ($^1\text{H}/^{13}\text{C-NMR}$, HRMS) and optical data for (*R*)-**12** is in perfect agreement with those of reported one.^{12a}

(S)-6-(4-methoxybenzyloxy)hexan-2-ol (13)

To a stirring solution of (*R*)-acetate (**12**) (5.9g, 21 mmol) in 50 mL MeOH was added K₂CO₃ (869 mg, 6.3 mmol) and stirred for 4 h. Methanol was evaporated in *vacuo* and 300 mL diethyl ether was added to it. The organic part was washed with water (50 mL), saturated NH₄Cl solution (50 mL) and then with brine solution (50 mL). The organic part was dried over anhydrous MgSO₄ and solvent was removed in *vacuo* to afford the crude alcohol which was used for the next step without further purification.

Mitsunobu inversion: To the stirring solution of the alcohol (5.0 g, 21 mmol) in 90 mL of anhydrous THF was added TPP (8.0 g, 31 mmol), DIAD (6.18 mL, 31 mmol) and benzoic acid (3.7 g, 31 mmol) at 0 °C. The reaction was stirred overnight at room temperature. THF was removed in *vacuo* and the residue was taken in ethyl acetate (200 mL). The organic part was washed with saturated NaHCO₃ (2 × 30 mL) and brine (50 mL) solution and then dried over anhydrous MgSO₄. The organic solvent was evaporated in *vacuo* and purification was accomplished by flash column chromatography eluting with EtOAc/hexane (1:15) to afford the (*S*)-benzoate (6.1 g, 17.8) as a colorless liquid in 85% yield.

R_f = 0.20 (EtOAc/hexane, 1:15).

¹H NMR of benzoate derivative of compound (*S*)-**13** (400 MHz, CDCl₃): δ: 7.97-7.95 (m, 2H), 7.48-7.47 (m, 1H), 7.37-7.33 (m, 2H), 7.18-7.15 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 5.12-5.01 (m, 1H), 4.33 (s, 2H), 3.71 (s, 3H), 3.36 (t, *J* = 6.4 Hz, 2H), 1.71-1.50 (m, 4H), 1.45-1.34 (m, 2H), 1.26 (d, *J* = 6.4 Hz, 3H) .

¹³C NMR of benzoate derivative of compound (*S*)-**13** (100 MHz, CDCl₃): δ: 166.4, 159.3, 132.9, 131.0, 130.8, 129.7, 129.4, 128.4, 113.9, 72.7, 71.8, 69.9, 55.45, 36.0, 29.8, 22.3, 20.3.

Benzoate hydrolysis: To the stirring solution of the benzoate (6.1 g, 17.8 mmol) in 200 mL MeOH was added NaOH (2.2 g, 53 mmol) at room temperature and stirred for 12 h at room temperature. After completion of the reaction MeOH was evaporated in *vacuo* and the crude residue was diluted with 250 mL diethyl ether. The organic part was washed with (2 × 50 mL) water, brine solution (50 mL) and then dried over anhydrous MgSO₄. The organic solvent was evaporated in *vacuo* and purification through flash column chromatography eluting with

EtOAc/hexane (1:5) to afford the (*S*)-alcohol (**13**) (4.2 g, 17.8) as a colorless liquid in 100% yield.

(*S*)-tert-butyl(6-(4-methoxybenzyloxy)hexan-2-yloxy)dimethylsilane (14)

To a stirred solution of alcohol (*S*)-**13** (7.29 g, 30.65 mmol) and imidazole (4.16 g, 61.3 mmol) in dry CH₂Cl₂ (91 mL), TBSCl (4.62 g, 36.78 mmol) was added portion wise at 0°C. The reaction mixture was stirred at the same temperature for 2 h and then quenched with water (50 mL). The dichloromethane (CH₂Cl₂) layer was separated, and the aqueous layer was extracted with additional CH₂Cl₂ (2 × 60 mL). The combined organic layers were washed with water, saturated Na₂CO₃ solution and brine solution and then dried over anhydrous MgSO₄. The organic solvent was removed in *vacuo*, and purification was accomplished by flash column chromatography eluting with EtOAc/hexane (1:20) to afford the (*S*)-**14** (10.24 g, 95%) as a colorless liquid.

R_f = 0.55 (EtOAc/hexane, 1:10).

¹H NMR (200 MHz, CDCl₃): δ: 7.26 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.42 (s, 2H), 3.79 (s, 3H), 3.75-3.69 (m, 1H), 3.43 (t, *J* = 6.4 Hz, 2H), 1.63-1.53 (m, 2H), 1.44-1.36 (m, 4H), 1.12 (d, *J* = 6 Hz, 3H), 0.892 (s, 9H), 0.05 (s, 6H).

¹³C NMR (50 MHz, CDCl₃, 77.23): δ: 159.3, 129.4, 113.9, 72.7, 70.3, 68.8, 55.4, 39.7, 30.0, 26.1, 23.9, 22.6, 18.3, -4.2, -4.5.

[α]_D²⁸ = -6.62 (c = 1.26, CHCl₃).

HRMS (ESI) for C₂₀H₃₆O₃SiNa [M + Na]⁺, calculated: 375.2331, found: 375.2325.

(*S*)-5-(tert-Butyl-dimethyl-silanyloxy)-hexan-1-ol (15)

Compound **14** (10.24 g, 29.09 mmol) was dissolved in 116 mL of CH₂Cl₂/phosphate buffer (pH = 7; 19:1) and the solution was cooled to 0 °C. DDQ (7.92g, 34.91mmol) was added portion wise to the solution and the mixture was stirred at this temperature for 1 h. Then, the reaction mixture was filtered through a pad of celite. The residue was then washed with 70 mL of CH₂Cl₂. The combined organic solution was washed successively with 5% NaHCO₃ solution, water and brine solution. The organic layer was then dried with anhydrous MgSO₄ and evaporated in *vacuo*.

Purification by flash column chromatography (EtOAc:hexane = 1:12) afforded compound **15** (6.47 g, 27.92 mmol) as colorless oil in 96% yield.

$R_f = 0.45$ (EtOAc/hexane, 1:5).

$^1\text{H NMR}$ (200 MHz, CDCl_3): δ : 3.82-3.74 (m, 1H), 3.63 (t, $J = 6.4$ Hz, 2H), 1.59-1.52 (m, 4H), 1.44-1.35 (m, 4H), 1.11 (d, $J = 6$ Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H).

$^{13}\text{C NMR}$ (50 MHz, CDCl_3): δ : 68.7, 62.9, 39.5, 32.9, 26.1, 23.9, 22.0, 18.3, -4.2, -4.5.

$[\alpha]_D^{28} = -8.53$ ($c = 0.8$, CHCl_3).

HRMS (ESI) for $\text{C}_{12}\text{H}_{28}\text{O}_2\text{SiNa}$ $[\text{M} + \text{Na}]^+$, calculated: 255.1756, found: 255.1750.

(S)-5-(tert-butyl dimethylsilyloxy)hexyl methanesulfonate (16)

To a cooled solution (0 °C) of the alcohol **15** (6.47 g, 27.92 mmol) in 111 mL of dry CH_2Cl_2 was added 4.6 mL (33.5 mmol) of Et_3N and 2.6 mL (33.5 mmol) of methanesulfonyl chloride and the mixture was stirred for 12 h. The reaction was then quenched with addition of 50 mL of cold water. The CH_2Cl_2 layer was separated and the aqueous layer was extracted with additional CH_2Cl_2 (2×50 mL). The combined organic layer was washed with saturated NaHCO_3 and brine solution and dried over anhydrous MgSO_4 . Total solvent was evaporated in *vacuo* to afford the crude product, which was then purified by flash column chromatography (EtOAc/hexane, 1:10) to yield compound **16** (8.31 g, 26.80 mmol) as colorless oil.

$R_f = 0.45$ (EtOAc/hexane, 1:5).

$^1\text{H NMR}$ (200 MHz, CDCl_3 , 7.26): δ : 4.22 (t, $J = 6.6$ Hz, 2H), 3.83-3.74 (m, 1H), 3.00 (s, 3H), 1.78-1.71 (m, 2H), 1.41-1.41 (m, 4H), 1.12 (d, $J = 6$ Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H).

$^{13}\text{C NMR}$ (50 MHz, CDCl_3 , 77.23): δ : 77.2, 68.4, 39.1, 37.5, 29.3, 26.1, 23.9, 21.8, 18.3, -4.1, -4.6.

$[\alpha]_D^{28} = -7.82$ ($c = 1.06$, CHCl_3).

HRMS (ESI) for $\text{C}_{13}\text{H}_{30}\text{O}_4\text{SSiNa}$ $[\text{M} + \text{Na}]^+$, calculated: 333.1532, found: 333.1525.

(S)-tert-butyl(6-iodohexan-2-yloxy)dimethylsilane (17)

The mesylate **16** (8.31 g, 26.80 mmol) was dissolved in 170 mL anhydrous acetone. To this solution was added **36** g of anhydrous NaI, 1.48g of NaHCO₃, and few drops of diisopropylethylamine. After protecting the reaction from light by aluminum foil, the reaction was allowed to stir at room temperature for 6 h. The acetone was then removed in *vacuo* and the residue was taken up in diethyl ether. After filtration through celite the solvent was removed in *vacuo*. Purification through flash chromatography (EtOAc/hexane, 1: 30) furnished the iodo compound **17** (8.43 g, 24.65 mmol) as colorless liquid.

R_f = 0.25 (EtOAc/hexane, 1:40).

¹H NMR (200 MHz, CDCl₃): δ: 3.83- 3.74 (m, 1H), 3.19 (t, *J* = 7 Hz, 3H), 1.89-1.79 (m, 2H), 1.49-1.42 (m, 4H), 1.13 (d, *J* = 6 Hz, 3H), 0.89 (s, 9H), 0.05(s, 6H).

¹³C NMR (50 MHz, CDCl₃): δ: 68.5, 38.7, 33.8, 27.0, 26.1, 24.0, 18.3, 7.2, -4.1, -4.5.

[α]_D²⁸ = -7.74 (c = 1.2, CHCl₃).

HRMS (ESI) for C₁₂H₂₇IOSiNa [M + Na]⁺, calculated: 365.0773, found: 365.0770.

(S)-2-(5-(*tert*-butyldimethylsilyloxy)hexylthio)pyridine (18)

To a cooled solution (0 °C) of the 2-mercaptopyridine (203 mg, 1.83 mmol) in 3.0 mL anhydrous DMF was added 73.2 mg NaH (60 % in mineral oil, 1.83 mmol) portion wise and stirred for 20 minute at same temperature. Mesylate **16** (633 mg, 2 mmol) in 2.0 mL anhydrous DMF was added drop wise to the previous solution at 0 °C. The reaction solution was then stirred for 10 h. Saturated solution of ammonium chloride was added to it and then it was poured into 150 mL diethyl ether. The organic layer was washed with (3×50 mL) water and then with 40 mL brine solution. The organic layer was dried over anhydrous MgSO₄ and concentrated in *vacuo*. Purification was done by flash column chromatography (EtOAc/hexane = 1:10) to afford the sulfide **18** (552 mg, 1.7 mmol) in 83% yield.

R_f = 0.45 (EtOAc/hexane, 1:15).

¹H NMR (200 MHz, CDCl₃): δ: 8.43-8.39 (m, 1H); 7.49-7.41 (m, 1H); 7.17-7.13 (m, 1H); 6.98-6.92 (m, 1H); 3.78 (q, *J* = 6.0 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 1H); 1.74-1.63 (m, 2H); 1.49-1.40 (m, 4H); 1.11 (d, *J* = 6.2 Hz, 3H); 0.88 (s, 9H); 0.04 (s, 6H).

^{13}C NMR (50 MHz, CDCl_3): δ : 159.5, 149.6, 135.7, 122.1, 119.1, 68.3, 39.1, 29.9, 29.3, 25.8, 25.1, 23.8, 18.1, -4.5, -4.8.

$[\alpha]_{\text{D}}^{28} = -15.8$ ($c = 0.9$, CHCl_3).

HRMS (ESI) for $\text{C}_{17}\text{H}_{31}\text{NOSSiNa}$ $[\text{M} + \text{Na}]^+$, calculated: 348.1793, found: 348.1787.

(S)-2-(5-(*tert*-butyldimethylsilyloxy)hexylsulfonyl)pyridine (8)

To a stirring solution of sulfide **18** (425 mg, 1.31 mmol) in ethanol (11.0 mL) was added a mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (242 mg, 0.2 mmol) and 30% H_2O_2 solution (1.1 mL) at 0 °C. The mixture was stirred at room temperature for 6 h, and after that the reaction mixture was poured into 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution and extracted with ethyl acetate (100 mL). The organic layer was washed with saturated NaHCO_3 solution and brine, dried over anhydrous MgSO_4 and concentrated in *vacuo*. The crude product was then purified by flash column chromatography (EtOAc/hexane = 1:10) to give sulphone **8** (420 mg, 1.17 mmol) as colorless gummy oil in 90% yield.

$R_f = 0.45$ (EtOAc/hexane, 1:15).

^1H NMR (200 MHz, CDCl_3): δ : 8.74 (d, $J = 4.4$ Hz, 1H); 8.11-8.06 (m, 1H); 8.01-7.92 (m, 1H); 7.58-7.52 (m, 1H); 3.77-3.67 (m, 1H); 3.37 (t, $J = 8$ Hz, 2H); 1.77-1.69 (m, 2H); 1.43-1.36 (m, 4H); 1.07 (d, $J = 6$ Hz, 3H); 0.84 (s, 9H); 0.00 (s, 6H).

^{13}C NMR (50 MHz, CDCl_3): δ : 154.2, 150.2, 138.1, 127.2, 122.1, 67.9, 51.8, 38.8, 25.8, 24.4, 23.7, 22.1, 17.9, -4.5, -4.9.

$[\alpha]_{\text{D}}^{28} = -17$. ($c = 0.6$, CHCl_3).

HRMS (ESI) for $\text{C}_{17}\text{H}_{31}\text{NO}_3\text{SSiNa}$ $[\text{M} + \text{Na}]^+$, calculated: 380.1691, found: 380.1686.

(S)-5-(*tert*-butyldimethylsilyloxy)hexyltriphenylphosphonium iodide (9)

To a solution of the iodide (8.43 g, 24.65 mmol) in anhydrous toluene (66 mL) was added TPP (12.9 g, 49.3 mmol) and Hünig's base (21.6 mL, 123.25 mmol). The mixture was refluxed for 12 h. The solution was then cooled to room temperature and concentrated under reduced pressure to afford the crude phosphonium salt **9**. It is then triturated with anhydrous pentane (5×20 mL) and

dried under high vacuum to get the Wittig salt **9** (13.5 g, 22.43 mmol) as a off white solid which was used without farther purification.

$R_f = 0.15$ (EtOAc).

(S)-tert-butyl(5-(4-methoxybenzyloxy)pent-1-en-3-yloxy)diphenylsilane (20)

To a cooled (0 °C) solution of optically pure alcohol (*S*)-**19** (5.55 g, 25 mmol) in dry CH₂Cl₂ (100 mL) was added imidazole (2.55 g, 37.5 mmol) and TBDPSCl (7.71 mL, 30 mmol). The mixture was stirred for 6 h at room temperature and then quenched with 50 mL of water. The organic layer was separated and the aqueous part was extracted with CH₂Cl₂ (2×30 mL). The combined organic part was washed with saturated NaHCO₃ solution and brine solution and then dried over anhydrous MgSO₄. The solution was then concentrated in *vacuo* and purified via flash chromatography (EtOAc:hexane = 1:20) to yield compound **20** (10.92 g, 23.75 mmol) as colorless oil in 95% yield.

$R_f = 0.30$ (EtOAc/hexane, 1:15).

¹H NMR (200 MHz, CDCl₃): δ: 7.78-7.72 (m, 4H), 7.45- 7.38 (m, 6H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.2$ Hz, 2H), 5.88 (ddd, $J = 17.4, 10.4, 6.8$ Hz, 1H), 5.16-5.03 (m, 1H), 4.9 (s, 1H), 4.44- 4.41(m, 1H), 4.36 (s, 2H), 3.8 (s,3H), 3.56- 3.50 (m, 2H), 1.98-1.77 (m, 2H), 1.14 (s, 9H).

¹³C NMR (50 MHz, CDCl₃): δ: 159.2, 140.7, 136.2, 136.1, 134.4, 134.3, 130.8, 129.7, 129.6, 129.4, 127.8, 127.7, 127.5, 114.7, 113.8, 72.5, 72.5, 66.3, 55.4, 37.8, 27.2, 19.5.

$[\alpha]_D^{28} = 11.76$ (c = 0.86, CHCl₃).

HRMS (ESI) for C₂₉H₃₆O₃SiNa [M + Na]⁺, calculated: 483.2331, found: 483.2321.

(S)-2-(tert-butylidiphenylsilyloxy)-4-(4-methoxybenzyloxy)butanal (10)

To a stirring solution of the olefin **20** (10.92 g, 23.75 mmol) in 92 mL of THF/H₂O (3:1) at room temperature was sequentially added NMO (3.33 g, 28.5 mmol), 0.05 M solution of OsO₄ in toluene (47.5 mL, 2.37 mmol) and NaIO₄ (1.12 g, 47.5 mmol). The mixture was stirred vigorously at room temperature for 12 h. The reaction was quenched by the addition of saturated aq. Na₂SO₃ solution (18 mL) and further stirred for 1 h at room temperature. The reaction mixture is then filtered through a celite pad and washed with 150 mL of EtOAc. The organic

layer was separated and the aqueous part was washed with EtOAc (2×50 mL). The combined organic layers were successively washed with 5% aq. NaHCO₃ solution, saturated aq. Na₂SO₃ and with brine solution. Total organic solution was then dried over anhydrous MgSO₄ and concentrated under reduced pressure to furnish the crude product, which on purification by flash chromatography (EtOAc/hexane = 1:15) afforded the aldehyde **10** (8.77 g, 19 mmol) in 80% yield.

R_f = 0.35 (EtOAc/hexane, 1:10).

¹H NMR (200 MHz, CDCl₃): δ: 9.58 (s, 1H), 7.65- 7.62 (m, 4H), 7.44- 7.32 (m, 6H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.36 (s, 2H), 4.22- 4.17 (m, 1H), 3.81 (s, 3H), 2.10-1.90 (m, 1H), 1.90-1.77 (m, 1H), 1.11 (s, 9H).

¹³C NMR (50 MHz, CDCl₃): δ: 203.4, 159.2, 136.2, 136.1, 134.5, 132.7, 130.93, 130.3, 129.6, 129.6, 129.2, 127.7, 127.5, 113.8, 72.5, 68.6, 67.3, 66.8, 55.5, 39.5, 38.5, 31.3, 29.9, 27.6, 27.2, 26.1, 25.8, 23.9, 19.5, 18.3, -4.2, -4.5.

[α]_D²⁸ = 15.21 (c = 1.06, CHCl₃).

HRMS (ESI) for C₂₈H₃₄O₄SiNa [M + Na]⁺, calculated: 485.2123, found: 485.2115.

2-bromo-3,5-dimethoxybenzaldehyde (27)

To a solution of compound **26** (5.04 g, 30.2 mmol) in acetic acid (140 mL) was added a solution of bromine (1.56 mL, 30.2 mmol) in acetic acid (20 mL) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 8 h. The reaction mixture was poured into 300 mL ice water and the crude product got precipitated. The precipitate was collected by filtration and washed by ice cold water. The crude product was then purified by recrystallization from hexane to afford compound **27** (6.26 g, 25.67 mmol) in 85% yield as white solid.

R_f = 0.35 (EtOAc/hexane, 1:10).

¹H NMR of compound **27** (200 MHz, CDCl₃): δ: 10.45, 7.07 (d, *J* = 2.8 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H).

¹³C NMR of compound **27** (50 MHz, CDCl₃): δ: 191.9, 159.8, 156.9, 134.6, 108.9, 105.7, 103.3, 56.5, 55.7.

HRMS (ESI) for C₉H₉BrO₃Na [M + Na]⁺, calculated: 266.9632, found: 266.9625.

2-(2-bromo-3,5-dimethoxyphenyl)-1,3-dioxolane (28)

A solution of compound **27** (5.5 g, 22.5 mmol), *p*-toluenesulfonic acid (0.5 g) and 1,2 ethanediol (6.15 mL, 112.25 mmol) were taken in 75 mL anhydrous benzene and refluxed in Dean-stark apparatus for 3 h. The benzene was then removed in *vacuo* and the residue was purified by flash column chromatography (EtOAc/hexane/ triethylamine = 1:7: 0.07) to furnish compound **28** (6.35g, 22.05 mmol) in 98% yield.

R_f = 0.25 (EtOAc/hexane, 1:10).

¹H NMR of compound **28** (200 MHz, CDCl₃): δ: 6.80 (d, *J* = 2.8 Hz, 1H), 6.51 (d, *J* = 2.8 Hz, 1H), 6.12 (s, 1H), 4.16-4.12 (m, 2H), 4.09-4.01 (m, 2H), 3.86 (s, 3H), 3.74 (s, 3H).

¹³C NMR of compound **28** (50 MHz, CDCl₃): δ: 159.8, 156.7, 138.4, 128.2, 103.5, 103.4, 102.5, 100.6, 65.4, 56.4, 55.6 .

HRMS (ESI) for C₁₁H₁₃BrO₄Na [M + Na]⁺, calculated: 310.9894, found: 310.9899.

ethyl 2-formyl-4,6-dimethoxybenzoate (5)

To a stirring solution of compound **28** (1.44 g, 5 mmol) in 20 mL anhydrous THF was added *n*-BuLi (1.6 M in hexane, 3.1 mL, 5 mmol) at -78 °C drop wise and stirred for further 1 h. Ethyl chloroformate (0.7 mL, 7.5 mmol) in 5 mL anhydrous THF was slowly added to the reaction mixture and stirred for 1 h. The reaction solution was then quenched by adding water (25 mL) and *p*-toluenesulfonic acid (1 g). The resulting solution was stirred for 4 h at 40 °C and extracted with EtOAc. The combined organic extracts was dried over anhydrous MgSO₄ and concentrated in *vacuo*. The crude product was then purified by flash column chromatography (EtOAc/hexane = 1:10) to afford compound **5** (952 mg, 4 mmol) as white solid in 80% yield.

R_f = 0.4 (EtOAc/hexane, 1:10).

¹H NMR of compound **5** (200 MHz, CDCl₃): δ: 9.94 (s, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.68 (d, *J* = 2.2 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 1H).

¹³C NMR of compound **5** (50 MHz, CDCl₃): δ: 189.9, 166.3, 161.7, 158.2, 135.5, 118.1, 104.5, 104.2, 61.8, 56.2, 55.6, 14.0.

HRMS (ESI) for C₁₂H₁₄BrO₅Na [M + Na]⁺, calculated: 261.0738, found: 261.0731.

Ethyl 3-chloro-2-formyl-4,6-dimethoxybenzoate (6)

To a stirring solution of compound **5** (952 mg, 4 mmol) in 26 mL anhydrous CH₂Cl₂ at 0 °C was added sulfonyl chloride (0.32 mL, 4 mmol, dissolved in 3 mL of CH₂Cl₂). After 20 min the reaction was quenched by addition of water (10 mL). The organic layer was then separated and

the aqueous layer was further washed by CH₂Cl₂. The combined extract was dried over anhydrous MgSO₄ and concentrated in *vacuo*. The crude product was then purified by flash column chromatography (EtOAc/hexane = 1:10) to give compound **6** (783 mg, 2.88 mmol) as off white solid in 72% yield.

R_f = 0.35 (EtOAc/hexane, 1:10).

¹H NMR of compound **6** (200 MHz, CDCl₃): δ: 10.48 (s, 1H), 6.72 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.98 (s, 3H), 3.89 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H),

¹³C NMR of compound **6** (50 MHz, CDCl₃): δ: 189.5, 166.6, 157.6, 156.2, 131.2, 117.9, 116.7, 101.6, 61.9, 56.8, 56.6, 14.0.

HRMS (ESI) for C₁₂H₁₃ClO₅Na [M + Na]⁺, calculated: 295.0349, found: 295.0344.

(5*S*,11*R*,*Z*)-5-(2-(4-methoxybenzyloxy)ethyl)-2,2,11,13,13,14,14-heptamethyl-3,3-diphenyl-4,12-dioxa-3,13-disilapentadec-6-ene (36)

Compound **36** was prepared from the Wittig reaction between enantiomer of **9** and the aldehyde **10** in 76% yield as described earlier.

R_f = 0.65 (EtOAc/hexane, 1:20).

¹H NMR of compound **36** (400 MHz, CDCl₃): δ: 7.70-7.63 (m, 4H), 7.41-7.30 (m, 6H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.40-5.35 (m, 1H), 5.19-5.13 (m, 1H), 4.65-4.57 (m, 1H), 4.35 (s, 2H), 3.80 (s, 3H), 3.65-3.61 (m, 1H), 3.50-3.38 (m, 2H), 1.95-1.94 (m, 1H), 1.87 (m, 1H), 1.74-1.66 (m, 1H), 1.58-1.51 (m, 3H), 1.25-1.17 (m, 3H), 1.03 (comp. 3H), 1.03 (s, 9H), 0.87 (s, 9H), 0.01 (s, 6H).

¹³C NMR of compound **36** (50 MHz, CDCl₃): δ: 159.2, 136.2, 136.1, 134.5, 132.7, 130.9, 130.3, 129.6, 129.5, 129.2, 127.6, 127.5, 113.8, 72.5, 68.6, 67.2, 66.7, 55.3, 39.5, 38.5, 27.6, 27.2, 26.1, 25.9, 23.9, 19.5, 18.3, -4.2, -4.5.

[α]_D²⁸ = - 2.2 (c = 0.05, CHCl₃).

HRMS (ESI) for C₄₀H₆₀O₄Si₂Na [M + Na]⁺, calculated: 683.3927, found: 683.3923.

(5*S*,6*S*,7*S*,11*R*)-5-(2-(4-methoxybenzyloxy)ethyl)-2,2,11,13,13,14,14-heptamethyl-3,3-diphenyl-4,12-dioxa-3,13-disilapentadecane-6,7-diol (37)

The dihydroxylation reaction of compound **36** was performed as described previously to afford compound **37** and **38** in 1:9 ratio .

R_f of **37** = 0.32 (EtOAc/hexane, 1:5).

¹H NMR of compound **37** (400 MHz, CDCl₃): δ: 7.71-7.65 (m, 4H), 7.46-7.35 (m, 6H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.21 (s, 2H), 4.15-4.13 (m, 1H), 3.80 (s, 3H), 3.79-3.76 (m, 1H), 3.51-3.49 (m, 1H), 3.35-3.34 (m, 1H), 3.27-3.25 (m, 1H), 3.21-3.19 (m, 1H), 2.10-2.01 (m, 1H), 1.78-1.73 (m, 2H), 1.67-1.66 (m, 2H), 1.46-1.44 (m, 2H), 1.32-1.35 (m, 4H), 1.11 (d, *J* = 6 Hz, 3H), 1.03 (s, 9H), 0.91 (s, 9H), 0.04 (s, 6H).

¹³C NMR of compound **37** (50 MHz, CDCl₃): δ: 159.2, 136.0, 133.6, 132.9, 130.2, 130.0, 129.3, 128.0, 127.7, 113.8, 75.0, 72.48, 72.2, 72.0, 68.7, 66.3, 55.3, 39.8, 33.8, 27.2, 26.1, 24.0, 21.91, 19.0, 18.2, -4.2, -4.5.

$[\alpha]_D^{28} = 12.0$ (c = 0.8, CHCl₃).

HRMS (ESI) for C₄₀H₆₂O₆Si₂Na [M + Na]⁺, calculated: 717.3982, found: 717.3988.

(5*S*,6*R*,7*R*,11*R*)-5-(2-(4-methoxybenzyloxy)ethyl)-2,2,11,13,13,14,14-heptamethyl-3,3-diphenyl-4,12-dioxa-3,13-disilapentadecane-6,7-diol (38)

¹H NMR of compound **38** (200 MHz, CDCl₃): δ: 7.67-7.60 (m, 4H), 7.44-7.37 (m, 6H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.28 (s, 2H), 4.21-4.00 (m, 1H), 3.80 (s, 3H), 3.75-3.69 (m, 1H), 3.59- 3.56 (m, 3H), 3.19-3.15 (m, 1H), 1.86-1.83 (m, 2H), 1.42-1.32 (m, 6H), 1.11 (comp. 3H), 1.08 (s, 9H), 0.88 (s, 9H), 0.04 (s, 6H).

¹³C NMR of compound **38** (50 MHz, CDCl₃): δ: 159.3, 135.9, 133.9, 133.4, 130.0, 129.9, 129.6, 129.5, 127.8, 127.7, 113.9, 72.8, 72.5, 71.8, 68.8, 66.3, 55.2, 39.9, 32.6, 32.3, 27.2, 26.1, 23.7, 21.9, 19.4, 18.2, -4.3, -4.5.

$[\alpha]_D^{28} = -1.1$ (c = 1.6, CHCl₃).

HRMS (ESI) for C₄₀H₆₂O₆Si₂Na [M + Na]⁺, calculated: 717.3982, found: 717.3991.

***tert*-butyl((*S*)-1-((4*R*,5*R*)-5-((*R*)-4-(*tert*-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(4-methoxybenzyloxy)propoxy)diphenylsilane (39)**

Compound **39** was prepared in 94% yield when the diol **38** was treated with catalytic amount of PPTS and 2,2-DMP in acetone as described earlier.

¹H NMR of compound **39** (400 MHz, CDCl₃): 7.68-7.63 (m, 4H), 7.42-7.33 (m, 6H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.26 (s, 2H), 4.06-4.03 (m, 1H), 3.97-3.89 (m, 2H), 3.80 (s, 3H), 3.67-3.62 (m, 1H), 3.52- 3.47 (m, 2H), 1.99- 1.77 (m, 2H), 1.36 (s, 3H), 1.26 (s, 3H), 1.22-1.15 (comp. 4H), 1.05- 1.01 (comp. 4H), 1.01 (s, 9H), 0.88 (s, 9H), 0.01 (s, 6H).

^{13}C NMR of compound **39** (50 MHz, CDCl_3): δ : 159.1, 136.1, 133.9, 133.9, 130.9, 129.9, 129.8, 127.7, 127.7, 113.8, 107.6, 80.6, 77.8, 72.5, 69.8, 68.7, 66.5, 35.3, 39.6, 34.9, 29.9, 27.9, 27.1, 26.1, 25.7, 23.7, 22.4, 21.1, 19.5, 18.3, -4.2, -4.5.

$[\alpha]_{\text{D}}^{28} = -0.1$ ($c = 0.05$, CHCl_3).

HRMS (ESI) for $\text{C}_{43}\text{H}_{66}\text{O}_6\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$, calculated: 757.4295, found: 757.4287.

(S)-3-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(tert-butyldiphenylsilyloxy)propan-1-ol (40)

Compound **40** was prepared in 96% yield from compound **39** as presented earlier.

^1H NMR of compound **40** (200 MHz, CDCl_3): δ : 7.68-7.64 (m, 4H), 7.48-7.36 (m, 6H), 4.18-4.10 (m, 2H), 3.89-3.86 (m, 1H), 3.74-3.66 (m, 2H), 3.55-3.43 (m, 1H), 1.91-1.82 (comp. 5H), 1.37 (s, 3H), 1.33 (s, 3H), 1.30-1.15 (m, 3H), 1.08 (d, $J = 6$ Hz, 3H), 1.03 (s, 9H), 0.88 (s, 9H), -0.04 (s, 6H).

^{13}C NMR of compound **40** (50 MHz, CDCl_3): δ : 135.9, 135.8, 133.7, 133.4, 129.8, 127.6, 107.8, 80.3, 77.9, 76.5, 70.4, 68.6, 58.7, 38.5, 38.6, 29.8, 28.1, 27.0, 25.9, 23.6, 22.1, 19.3, 18.1, -4.3, -4.6.

$[\alpha]_{\text{D}}^{28} = -2.23$ ($c = 0.5$, CHCl_3).

HRMS (ESI) for $\text{C}_{35}\text{H}_{58}\text{O}_5\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$, calculated: 637.3720, found: 637.3715.

5-((S)-3-((4R,5R)-5-((R)-4-(tert-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(tert-butyldiphenylsilyloxy)propylthio)-1-phenyl-1H-tetrazole (41)

Compound **41** was prepared from primary alcohol **40** in the same way as compound **25** was prepared.

^1H NMR of compound **41** (200 MHz, CDCl_3): δ : 7.67-7.63 (m, 4H), 7.55-7.54 (m, 5H), 7.41-7.32 (m, 6H), 4.16-4.10 (m, 1H), 4.04-3.99 (m, 1H), 3.89-3.86 (m, 1H), 3.71-3.62 (m, 1H), 3.59-3.43 (m, 2H), 2.20-1.99 (m, 2H), 1.35 (s, 3H), 1.29 (s, 3H), 1.17-1.16 (m, 3H), 1.07 (comp. 3H), 1.04 (s, 9H), 0.87 (s, 9H), 0.03 (s, 6H).

^{13}C NMR of compound **41** (50 MHz, CDCl_3): δ : 154.0, 135.9, 133.7, 133.3, 133.2, 129.9, 129.7, 127.7, 127.6, 123.6, 107.8, 80.2, 76.6, 70.5, 68.5, 39.4, 34.0, 29.9, 29.3, 27.9, 27.0, 25.9, 25.6, 23.6, 22.2, 19.3, 18.1, -4.3, -4.6.

$[\alpha]_{\text{D}}^{28} = +1.5$ ($c = 0.3$, CHCl_3).

HRMS (ESI) for $\text{C}_{42}\text{H}_{62}\text{N}_4\text{O}_4\text{SSi}_2\text{Na}$ $[\text{M} + \text{Na}]^+$, calculated: 797.3927, found: 797.3932.

5-((S)-3-((4R,5R)-5-((R)-4-(tert-butyl dimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(tert-butyl diphenylsilyloxy)propylsulfonyl)-1-phenyl-1H-tetrazole (42)

Sulfone **42** was prepared from sulfide **41** as described earlier.

¹H NMR of compound **42** (400 MHz, CDCl₃): δ: 7.65-7.59 (m, 9H), 7.58-7.36 (m, 6H), 4.08-4.00 (m, 1H), 3.98-3.96 (m, 1H), 3.89-3.38 (m, 2H), 3.66-3.63 (m, 2H), 2.23-2.15 (m, 2H), 1.33 (s, 3H), 1.29 (s, 3H), 1.25 (comp. 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.05 (s, 9H), 0.88 (s, 9H), 0.01 (s, 6H).

¹³C NMR of compound **42** (50 MHz, CDCl₃): δ: 153.4, 135.9, 135.9, 133.2, 133.0, 132.8, 131.4, 130.3, 130.2, 129.7, 128.0, 127.9, 125.2, 108.0, 80.4, 77.5, 69.7, 68.6, 52.5, 39.4, 32.0, 30.0, 29.7, 27.9, 27.5, 27.1, 26.0, 25.7, 23.7, 22.2, 19.3, 18.2, -4.3, -4.6.

$[\alpha]_D^{28} = 2.5$ (c = 0.3, CHCl₃).

HRMS (ESI) for C₄₂H₆₂N₄O₆SSi₂Na [M + Na]⁺, calculated: 829.3826, found: 829.3819.

Ethyl 2-((S,E)-4-((4R,5R)-5-((R)-4-(tert-butyl dimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tert-butyl diphenylsilyloxy)but-1-enyl)-4,6-dimethoxybenzoate (43)

The olefin **43** was prepared by JK-olefination reaction of aldehyde **5** and sulfone **42** in 82% yield as described previously.

¹H NMR of compound **43** (400 MHz, CDCl₃): δ: 7.68-7.66 (m, 4H), 7.41-7.33 (m, 6H), 6.45 (s, 1H), 6.34 (s, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.25- 6.20 (m, 1H), 4.36-4.28 (m, 2H), 4.10-4.07 (m, 1H), 4.04-4.02 (m, 1H), 3.89-3.86 (m, 1H), 3.79 (s, 3H), 3.79 (s, 3H), 3.69-3.64 (m, 1H), 2.47-2.44 (m, 2H), 1.39 (comp. 3H), 1.36 (s, 3H), 1.28 (s, 3H), 1.19-1.09 (m, 3H), 1.06 (comp. 3H), 1.04 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H).

¹³C NMR of compound **43** (100 MHz, CDCl₃): δ: 167.9, 161.3, 158.1, 137.6, 136.1, 135.9, 133.8, 133.6, 129.9, 129.9, 129.8, 129.0, 127.7, 127.7, 115.9, 107.6, 101.4, 97.6, 79.8, 77.7, 71.8, 68.7, 61.0, 55.9, 55.3, 39.6, 68.4, 30.2, 28.2, 26.0, 25.9, 23.7, 22.2, 19.4, 18.2, 14.4, -4.3, -4.6.

$[\alpha]_D^{28} = 6.2$ (c = 0.03, CHCl₃).

HRMS (ESI) for C₄₇H₇₀O₈Si₂Na [M + Na]⁺, calculated: 841.4506, found: 841.4498.

Ethyl 2-((S,E)-4-((4R,5R)-5-((R)-4-(tert-butyl dimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tert-butyl diphenylsilyloxy)but-1-enyl)-3-chloro-4,6-dimethoxybenzoate (44)

The olefin **44** was prepared by JK-olefination reaction between aldehyde **6** and sulfone **42** in 78% yield as described earlier.

¹H NMR of compound **44** (400 MHz, CDCl₃): δ: 7.73-7.52 (m, 4H), 7.52-7.34 (m, 6H), 6.46 (d, *J* = 16.8 Hz, 1H), 6.44 (s, 1H), 6.14-6.07 (m, 1H), 4.30-4.20 (m, 1H), 4.18-4.11 (m, 1H), 4.04-4.02 (m, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.67-3.63 (m, 1H), 2.45 (s, 2H), 1.39 (s, 3H), 1.37 (s, 3H), 1.34-1.22 (comp. 4H), 1.20-1.16 (m, 2H), 1.09 (comp. 3H), 1.05 (s, 9H), 0.93 (s, 9H), 0.07 (s, 6H).

¹³C NMR of compound **44** (100 MHz, CDCl₃): δ: 167.4, 156.4, 155.9, 136.4, 136.2, 133.6, 133.6, 132.8, 129.9, 129.9, 127.9, 127.7, 127.7, 117.0, 113.6, 107.8, 95.2, 79.2, 77.8, 71.1, 68.8, 61.4, 56.5, 56.3, 39.7, 38.9, 30.4, 28.4, 27.2, 27.1, 26.2, 26.0, 23.8, 23.7, 22.2, 19.4, 18.2, 14.3, -4.2, -4.5.

$[\alpha]_{\text{D}}^{28} = 5.2$ (c = 0.03, CHCl₃).

HRMS (ESI) for C₄₇H₆₉ClO₈Si₂Na [M + Na]⁺, calculated: 875.4116, found: 875.4110.

(2-((*S,E*)-4-((*4R,5R*)-5-((*R*)-4-(*tert*-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(*tert*-butyldiphenylsilyloxy)but-1-enyl)-4,6-dimethoxyphenyl)methanol (45)

Compound **43** was reduced to compound **45** with DIBAL-H in 95% yield as presented earlier.

¹H NMR of compound **45** (400 MHz, CDCl₃): δ: 7.77-7.67 (m, 4H), 7.46-7.36 (m, 6H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.47 (s, 1H), 6.38 (d, *J* = 2.0 Hz, 1H), 6.20-6.16 (m, 1H), 6.68 (d, *J* = 4.0 Hz, 2H), 4.19-4.17 (m, 1H), 4.15-4.10 (m, 1H), 3.97-3.96 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.74-3.68 (m, 1H), 2.54 (s, 2H), 1.51 (s, 3H), 1.39-1.33 (m, 1H), 1.33 (s, 3H), 1.29-1.18 (comp. 4H), 1.13-1.11 (m, 1H), 1.10 (comp. 3H), 1.08 (s, 9H), 0.91 (s, 9H), 0.06 (s, 6H).

¹³C NMR of compound **45** (100 MHz, CDCl₃): δ: 160.3, 159.3, 139.6, 136.2, 136.2, 134.0, 133.8, 130.1, 130.1, 130.0, 129.7, 127.9, 127.8, 127.8, 119.4, 107.9, 102.5, 97.6, 80.0, 78.0, 71.9, 68.9, 55.8, 55.4, 39.8, 38.8, 30.4, 28.4, 27.3, 26.2, 23.9, 22.4, 19.6, 18.4, -4.1, -4.4.

$[\alpha]_{\text{D}}^{28} = 6.2$ (c = 0.05, CHCl₃).

HRMS (ESI) for C₄₅H₆₈O₇Si₂Na [M + Na]⁺, calculated: 799.4401, found: 799.4395.

(2-((*S,E*)-4-((*4R,5R*)-5-((*R*)-4-(*tert*-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(*tert*-butyldiphenylsilyloxy)but-1-enyl)-3-chloro-4,6-dimethoxyphenyl)methanol (46)

The ester functionality in compound **44** was reduced with DIBAL-H to afford compound **46** in 92% yield as stated previously.

¹H NMR of compound **46** (400 MHz, CDCl₃): δ: 7.77-7.68 (m, 4H), 7.42-7.35 (m, 6H), 6.46 (s, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.06 (td, *J* = 15.2, 6.8 Hz, 1H), 4.67 (d, *J* = 3.6 Hz, 1H), 4.24-4.21 (m, 1H), 4.11-4.07 (m, 1H), 4.08 (s, 3H), 3.95 (s, 3H), 3.68 (q, *J* = 6.0 Hz, 1H), 2.59-2.57 (m, 2H), 1.48-1.41 (m, 3H), 1.36 (s, 3H), 1.32 (s, 3H), 1.19-1.11 (m, 3H), 1.08-1.06 (comp. 3H), 1.05 (s, 9H), 0.89 (s, 9H), 0.04 (s, 6H).

¹³C NMR of compound **46** (100 MHz, CDCl₃): δ: 157.8, 155.2, 139.3, 136.2, 136.1, 133.8, 133.6, 130.0, 129.9, 127.7, 121.0, 113.7, 167.9, 95.1, 79.8, 78.0, 71.3, 67.9, 58.0, 56.5, 56.0, 39.7, 39.0, 30.2, 28.5, 27.1, 26.1, 23.7, 22.2, 19.4, 18.3.

[α]_D²⁸ = 7.2 (c = 0.04, CHCl₃).

HRMS (ESI) for C₄₅H₆₇ClO₇Si₂Na [M + Na]⁺, calculated: 833.4011, found: 833.4016.

2-((*S,E*)-4-((*4R,5R*)-5-((*R*)-4-(*tert*-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(*tert*-butyldiphenylsilyloxy)but-1-enyl)-4,6-dimethoxybenzaldehyde (47**)**

Compound **45** was oxidized to aldehyde **47** by MnO₂ in 95% yield as stated earlier.

¹H NMR of compound **47** (400 MHz, CDCl₃): δ: 10.43 (s, 1H), 7.70-7.69 (m, 4H), 7.41-7.33 (m, 6H), 7.27 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 6.19 (ddd, *J* = 15.6, 8.8, 4.4 Hz, 1H), 4.15-4.09 (m, 1H), 4.08-4.06 (m, 1H), 4.05-4.04 (m, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.71-3.67 (m, 1H), 2.62-2.49 (m, 2H), 1.39 (s, 3H), 1.29-1.26 (m, 3H), 1.25 (s, 3H), 1.19-1.10 (comp. 4H), 0.89 (comp. 3H), 0.88 (s, 9H), 0.03 (s, 6H).

¹³C NMR of compound **47** (100 MHz, CDCl₃): δ: 190.4, 164.7, 164., 143.6, 136.1, 136.1, 133.9, 133.8, 131.2, 131.0, 129.9, 129.9, 127.7, 127.7, 116.1, 107.8, 104.0, 96.9, 80.0, 77.8, 71.9, 68.8, 55.9, 55.5, 39.7, 38.5, 30.3, 28.3, 27.2, 28.1, 28.0, 23.7, 22.3, 19.54, 18.3, -4.2, -4.5.

[α]_D²⁸ = 5.1 (c = 0.1, CHCl₃).

HRMS (ESI) for C₄₅H₆₆O₇Si₂Na [M + Na]⁺, calculated: 797.4244, found: 797.4235.

2-((*S,E*)-4-((*4R,5R*)-5-((*R*)-4-(*tert*-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(*tert*-butyldiphenylsilyloxy)but-1-enyl)-3-chloro-4,6-dimethoxybenzaldehyde (48**)**

Alcohol **46** was oxidized by MnO₂ to afford aldehyde **48** in 90% yield as presented earlier.

¹H NMR of compound **48** (400 MHz, CDCl₃): δ: 10.05 (s, 1H), 7.73-7.61 (m, 4H), 7.42-7.34 (m, 6H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.46 (s, 1H), 5.92-5.84 (m, 1H), 4.18-4.15 (m, 1H), 4.08-4.06 (m, 1H), 4.04 (s, 3H), 3.97 (s, 3H), 3.97 (comp. 1H), 3.69-3.64 (m, 1H), 2.59-2.56 (m, 2H), 1.42-1.41 (m, 1H), 1.37 (s, 3H), 1.29 (s, 3H), 1.26-1.25 (m, 1H), 1.11-1.06 (m, 3H), 1.05 (comp. 3H), 1.05 (comp. 1H), 1.02 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H).

¹³C NMR of compound **48** (100 MHz, CDCl₃): δ: 189.7, 160.6, 159.3, 142.7, 137.4, 136.1, 136.1, 133.7, 133.6, 130.0, 129.9, 127.7, 120.5, 118.7, 114.0, 107.9, 94.7, 79.6, 77.9, 71.1, 68.9, 56.5, 56.4, 39.7, 39.0, 30.0, 28.4, 27.1, 26.2, 26.1, 23.7, 22.2, 19.4, 18.3, -4.2, -4.5.

[α]_D²⁸ = 5.1 (c = 0.1, CHCl₃).

HRMS (ESI) for C₄₅H₆₅ClO₇Si₂Na [M + Na]⁺, calculated: 831.3854, found: 831.3859.

2-((*S,E*)-4-((*4R,5R*)-5-((*R*)-4-(*tert*-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(*tert*-butyldiphenylsilyloxy)but-1-enyl)-4,6-dimethoxybenzoic acid (49**)**

Pinnick oxidation of aldehyde **47** was performed to furnish the acid **49** in 80% yield as described earlier.

¹H NMR of compound **49** (400 MHz, CDCl₃): δ: 7.69-7.67 (m, 4H), 7.41- 7.35 (m, 6H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.51 (s, 1H), 6.38 (s, 1H), 6.22-6.15 (m, 1H), 4.13- 4.10 (m, 1H), 4.07- 4.04 (m, 1H), 3.94-3.92 (m, 1H), 3.90 (s, 3H), 3.70 (s, 3H), 3.68-3.65 (m, 1H), 2.50-2.46 (m, 2H), 1.48-1.46 (m, 2H), 1.36 (s, 3H), 1.33 (comp. 1H), 1.28 (s, 3H), 1.28 (comp. 1H), 1.27- 1.21 (m, 2H), 1.06 (comp., 3H), 1.05 (s, 9H), 0.02 (s, 6H).

¹³C NMR of compound **49** (100 MHz, CDCl₃): δ: 169.8, 162.1, 158.9, 136.2, 136.1, 133.9, 130.2, 130.1, 130.0, 129.9, 127.8, 127.7, 113.1, 107.8, 97.7, 79.9, 77.9, 71.9, 68.9, 56.4, 55.5, 39.7, 38.5, 30.4, 28.3, 27.2, 26.1, 26.0, 23.7, 22.3, 19.6, 18.3, -4.2, -4.5.

[α]_D²⁸ = 6.9 (c = 0.03, CHCl₃).

HRMS (ESI) for C₄₅H₆₆O₈Si₂Na [M + Na]⁺, calculated:813.4193, found: 813.4187.

2-((*S,E*)-4-((*4R,5R*)-5-((*R*)-4-(*tert*-butyldimethylsilyloxy)pentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(*tert*-butyldiphenylsilyloxy)but-1-enyl)-3-chloro-4,6-dimethoxybenzoic acid (50**)**

Pinnick oxidation of aldehyde **48** was performed as described earlier to furnish acid **50** in 80% yield.

¹H NMR of compound **50** (400 MHz, CDCl₃): δ: 7.69- 7.66 (m, 4H), 7.40-7.33 (m, 6H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.44 (s, 1H), 4.18- 4.16 (m, 1H), 4.15-4.12 (m, 1H), 3.99 (s, 1H), 3.99 (comp. 1H), 3.68-3.63 (m, 1H), 2.50-2.47 (m, 2H), 1.31 (s, 3H), 1.31 (s, 3H), 1.29-1.21 (comp. 5H), 1.06 (s, 3H), 1.04 (s, 9H), 0.08 (s, 9H), 0.02 (s, 6H).

¹³C NMR of compound **50** (100 MHz, CDCl₃): δ: 170.2, 156.7, 156.1, 137.0, 136.3, 136.1, 133.7, 133.7, 133.4, 130.0, 129.9, 127.8, 127.7, 116.1, 113.9, 107.9, 95.2, 79.2, 77.9, 71.2, 68.9, 58.6, 56.5, 39.7, 38.9, 35.10, 30.5, 28.5, 27.1, 26.2, 23.7, 22.3, 19.5, 18.3, -4.2, -4.4.

[α]_D²⁸ = 6.9 (c = 0.03, CHCl₃).

HRMS (ESI) for C₄₅H₆₅ClO₈Si₂Na [M + Na]⁺, calculated:831.3854, found: 831.3859.

2-((*S,E*)-4-(*tert*-butyldiphenylsilyloxy)-4-((*4R,5R*)-5-((*R*)-4-hydroxypentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)but-1-enyl)-4,6-dimethoxybenzoic acid (51**)**

Seco-acid **51** was prepared from **49** in 85% yield as stated earlier.

¹H NMR of compound **51** (400 MHz, CDCl₃): δ: 7.69-7.67 (m, 4H), 7.41-7.35 (m, 6H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.50 (d, *J* = 2 Hz, 1H), 6.38 (d, *J* = 1.6 Hz, 1H), 6.25-6.17 (m, 1H), 4.13-4.10 (m, 1H), 4.05-4.02 (m, 1H), 3.90-3.84 (m, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.71-3.65 (m, 1H), 2.56-2.42 (m, 2H), 1.39 (s, 3H), 1.36-1.33 (m, 2H), 1.28 (s, 3H), 1.25-1.21(comp. 4H), 1.10 (d, *J* = 6.0 Hz, 3H), 1.05 (s, 9H).

¹³C NMR of compound **51** (100 MHz, CDCl₃): δ: 169.7, 161.8, 158.6, 139.6, 136.1, 136.1, 133.8, 133.6, 130.1, 130.0, 129.9, 127.8, 127.7, 107.8, 102.5, 97.7, 79.9, 77.6, 72.2, 68.0, 56.3, 55.6, 38.8, 38.4, 30.1, 28.0, 27.4, 27.2, 27.1, 25.8, 23.2, 23.1, 22.2, 19.5.

[α]_D²⁸ = 5.1 (c = 0.02, CHCl₃).

HRMS (ESI) for C₃₉H₅₂O₈SiNa [M + Na]⁺, calculated:699.3328, found: 699.3323.

2-((*S,E*)-4-(*tert*-butyldiphenylsilyloxy)-4-((*4R,5R*)-5-((*R*)-4-hydroxypentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)but-1-enyl)-3-chloro-4,6-dimethoxybenzoic acid (52**)**

Selective deprotection of TBS group in compound **50** was performed as stated earlier to afford seco-acid **52** in 82% yield.

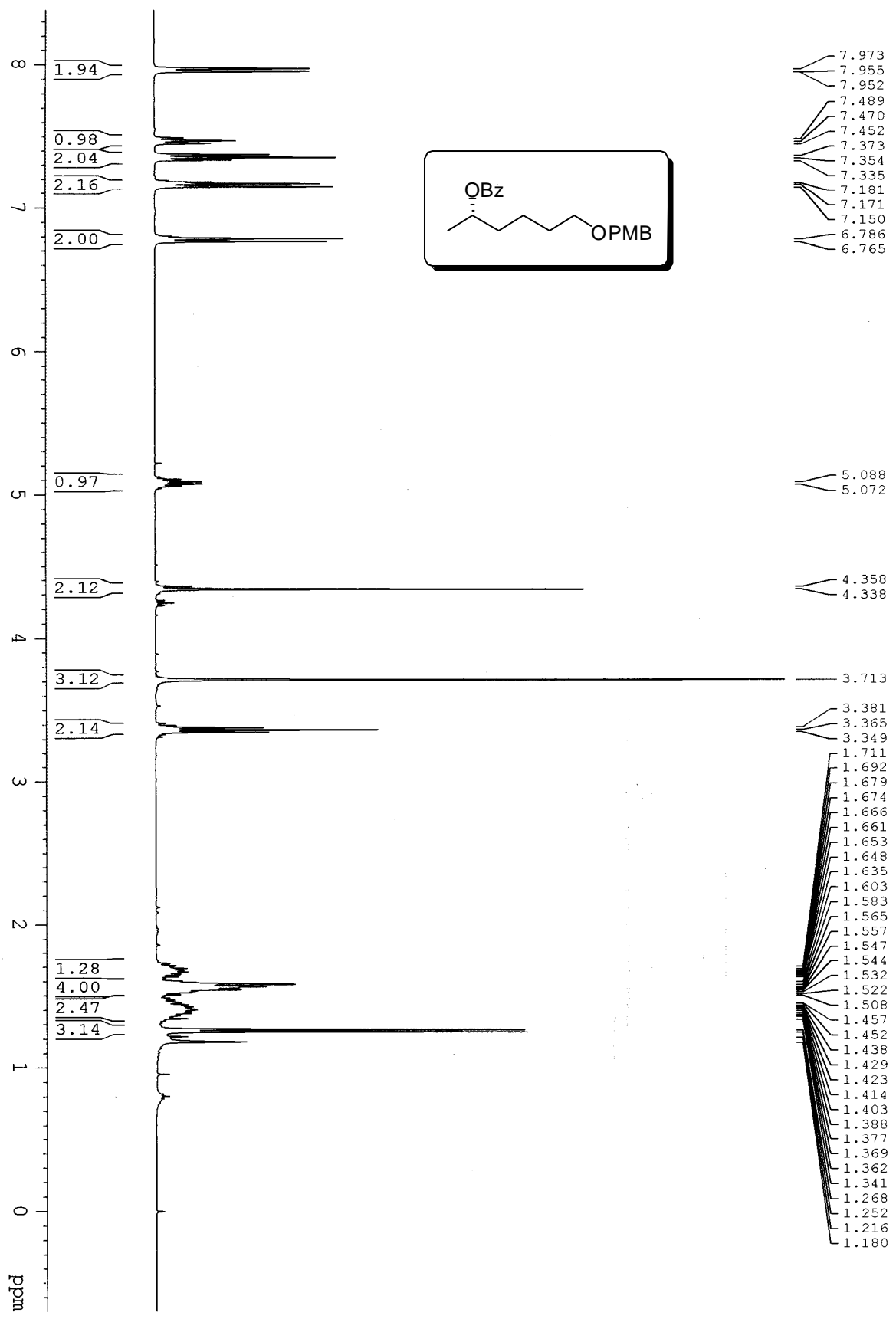
¹H NMR of compound **52** (400 MHz, CDCl₃): δ: 7.69-7.68 (m, 4H), 7.41-7.35 (m, 6H), 6.46 (d, *J* = 16.4 Hz, 1H), 6.44 (s, 1H), 6.19-6.14 (m, 1H), 4.18-4.16 (m, 1H), 4.05-4.03 (m, 1H), 3.92 (s, 3H), 3.88 (comp. 1H), 3.85 (s, 3H), 3.66-3.65 (m, 1H), 2.51-2.50 (m, 2H), 1.31 (s, 3H), 1.30 (s, 3H), 1.25-1.23 (m, 2H), 1.18-1.16 (m, 3H), 1.11 (d, *J* = 6.0 Hz, 3H), 1.07-1.06 (m, 1H), 1.03 (s, 9H).

¹³C NMR of compound **52** (50 MHz, CDCl₃): δ: 169.9, 156.6, 156.1, 136.9, 136.3, 130.2, 134.0, 133.7, 130.0, 129.8, 127.9, 127.7, 116.5, 113.9, 107.9, 95.3, 79.7, 77.9, 71.6, 68.3, 56.6, 56.5, 39.1, 38.8, 30.2, 28.1, 27.1, 25.9, 23.4,22.1, 19.5.

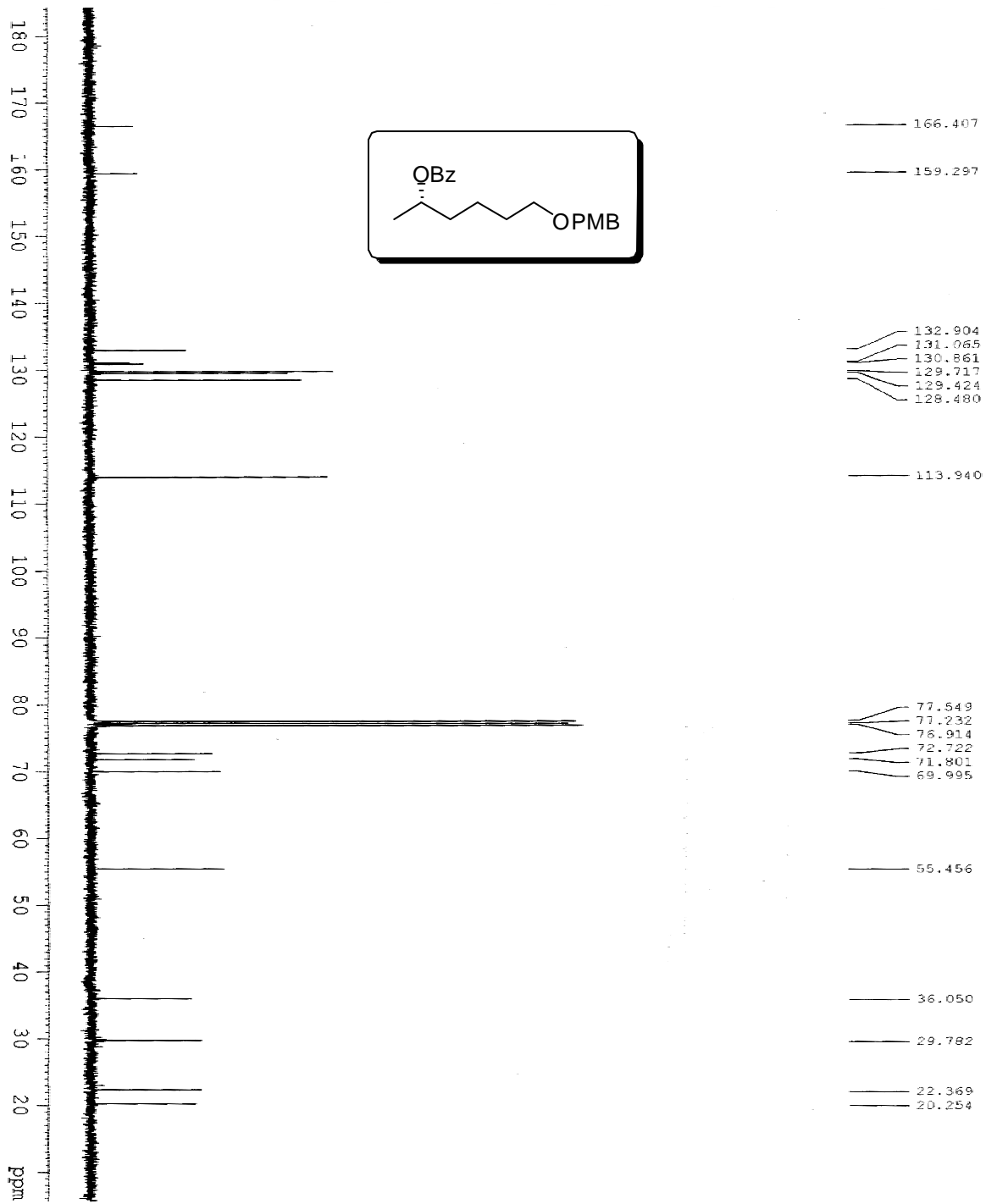
[α]_D²⁸ = 5.1 (c = 0.02, CHCl₃).

HRMS (ESI) for C₃₉H₅₁ClO₈SiNa [M + Na]⁺, calculated:733.2939, found: 733.2932.

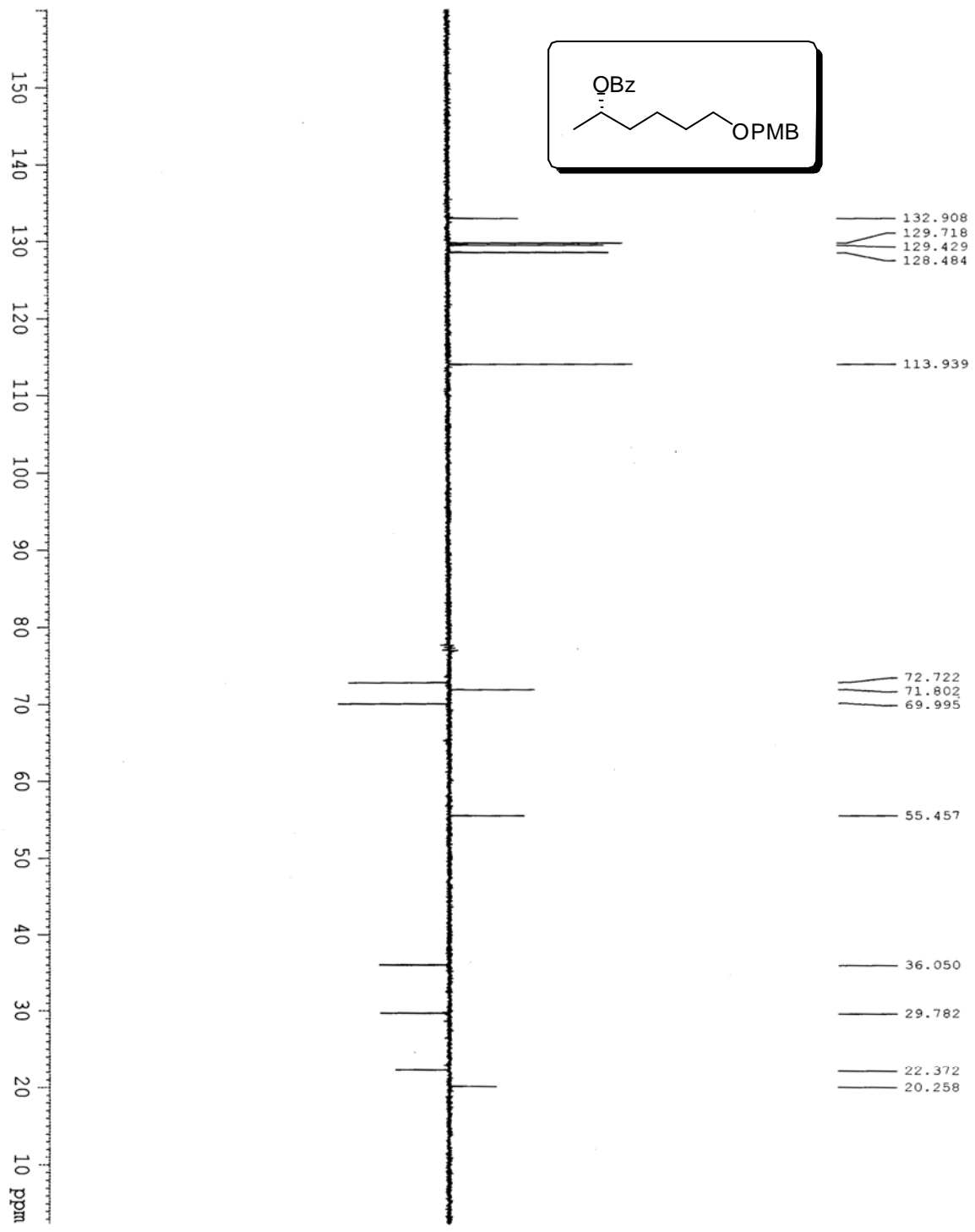
¹H- NMR of Benzoate of compound (S)-13 (400MHz, CDCl₃)



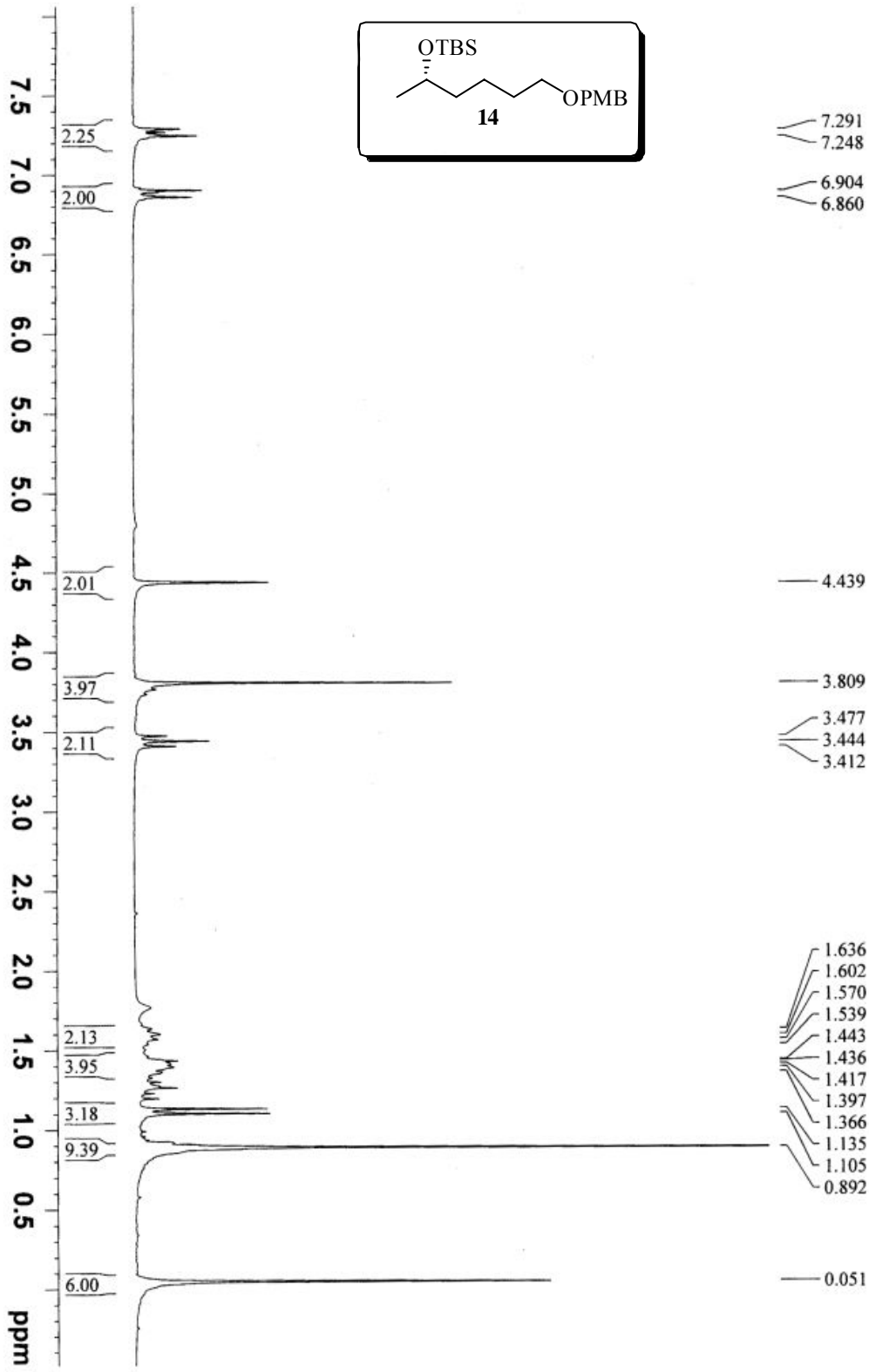
¹³C-NMR of Benzoate of compound (S)-13 (100MHz, CDCl₃)



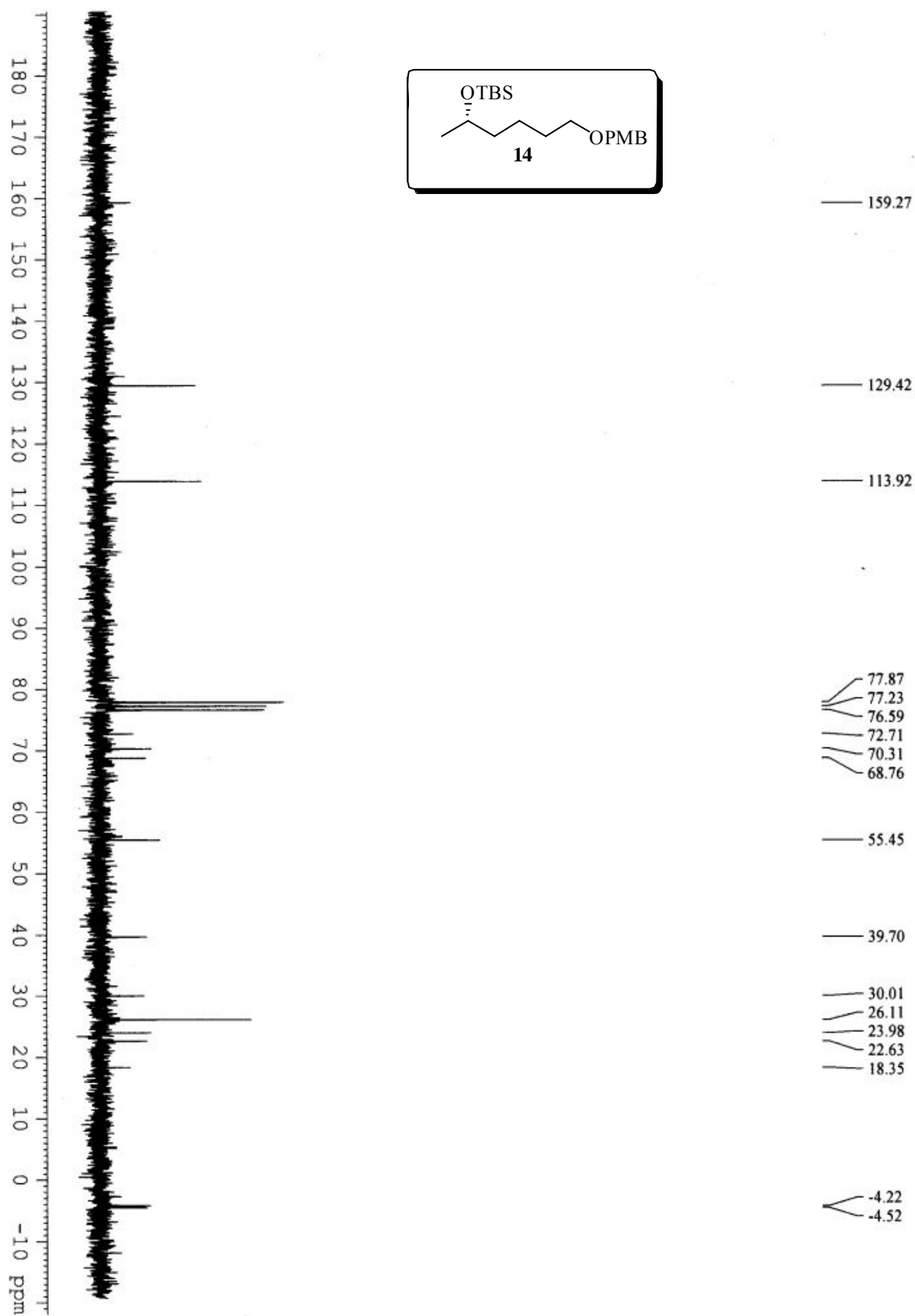
DEPT- NMR of Benzoate of compound (S)-13 (100MHz, CDCl₃)



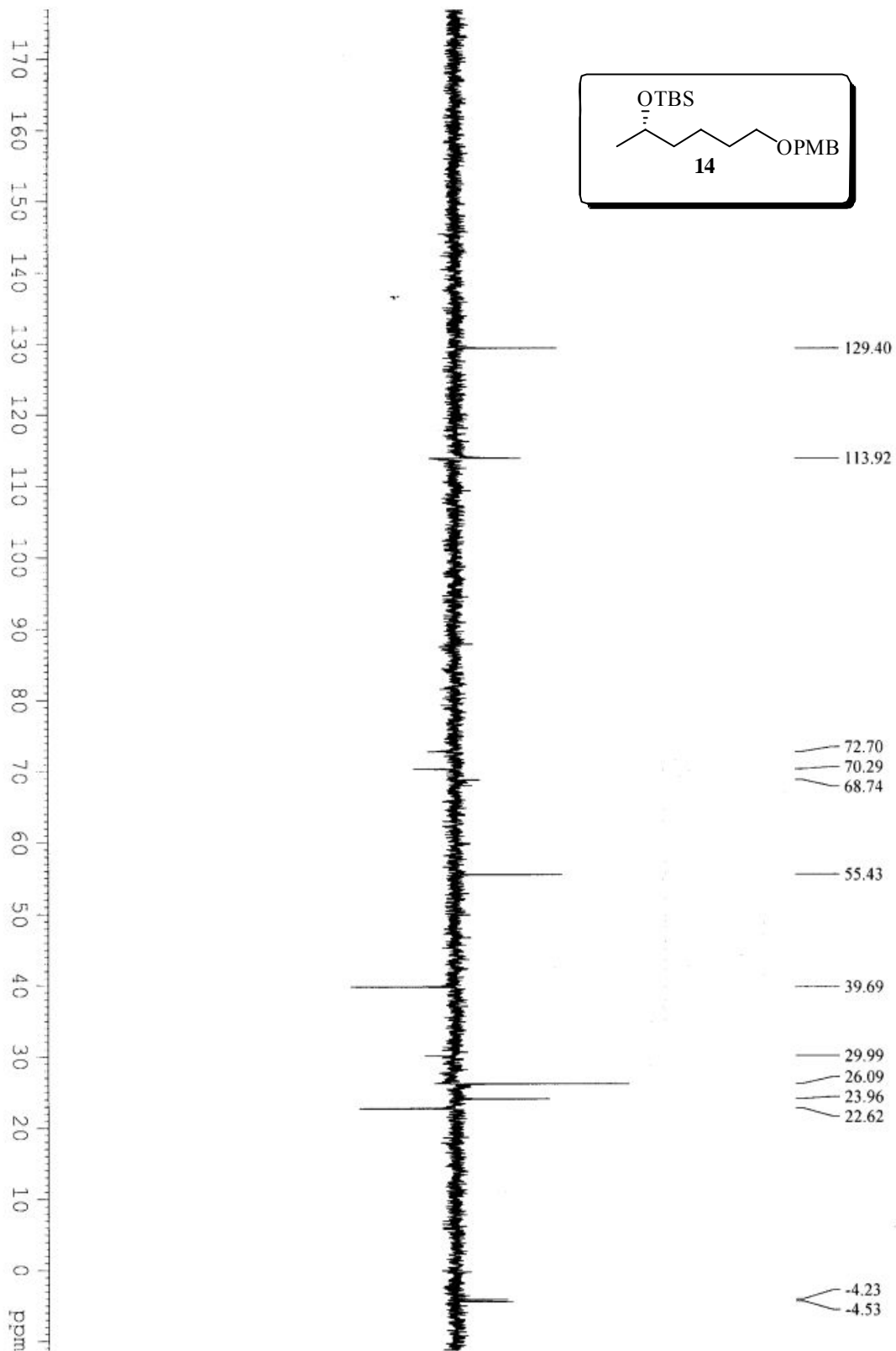
¹H- NMR of compound 14 (200MHz, CDCl₃)



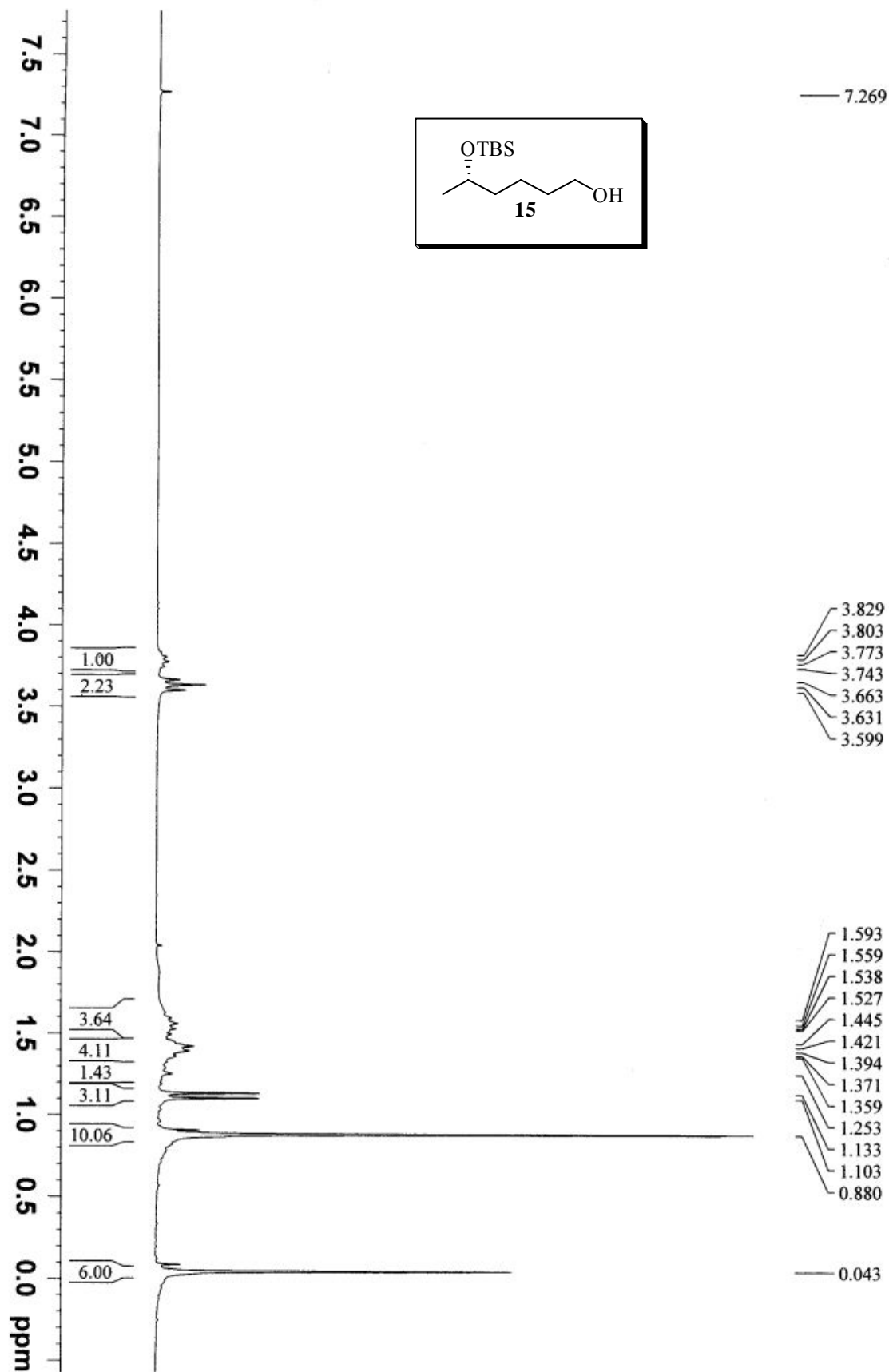
¹³C-NMR of compound 14 (50MHz, CDCl₃)



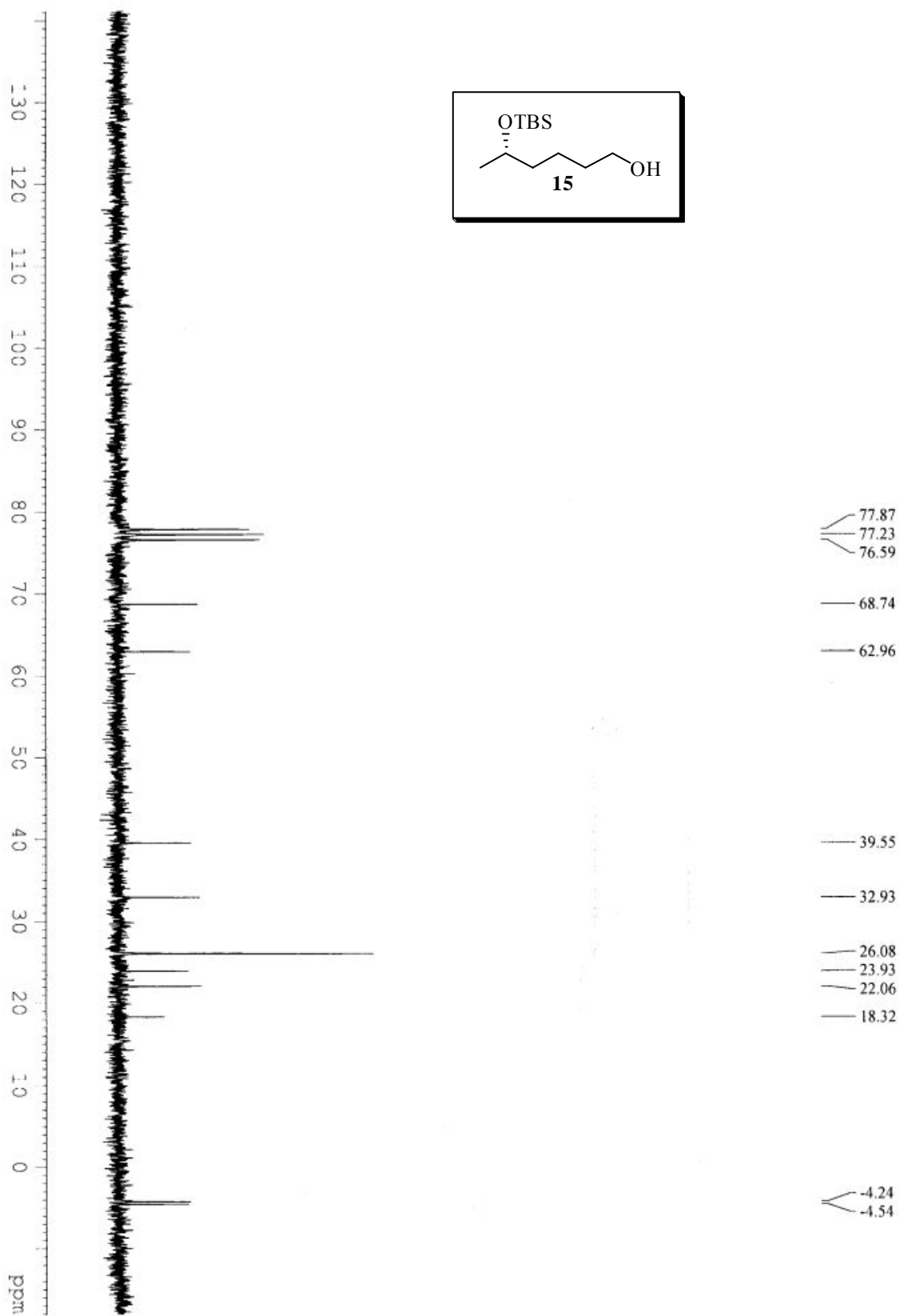
DEPT- NMR of compound 14 (50MHz, CDCl₃)



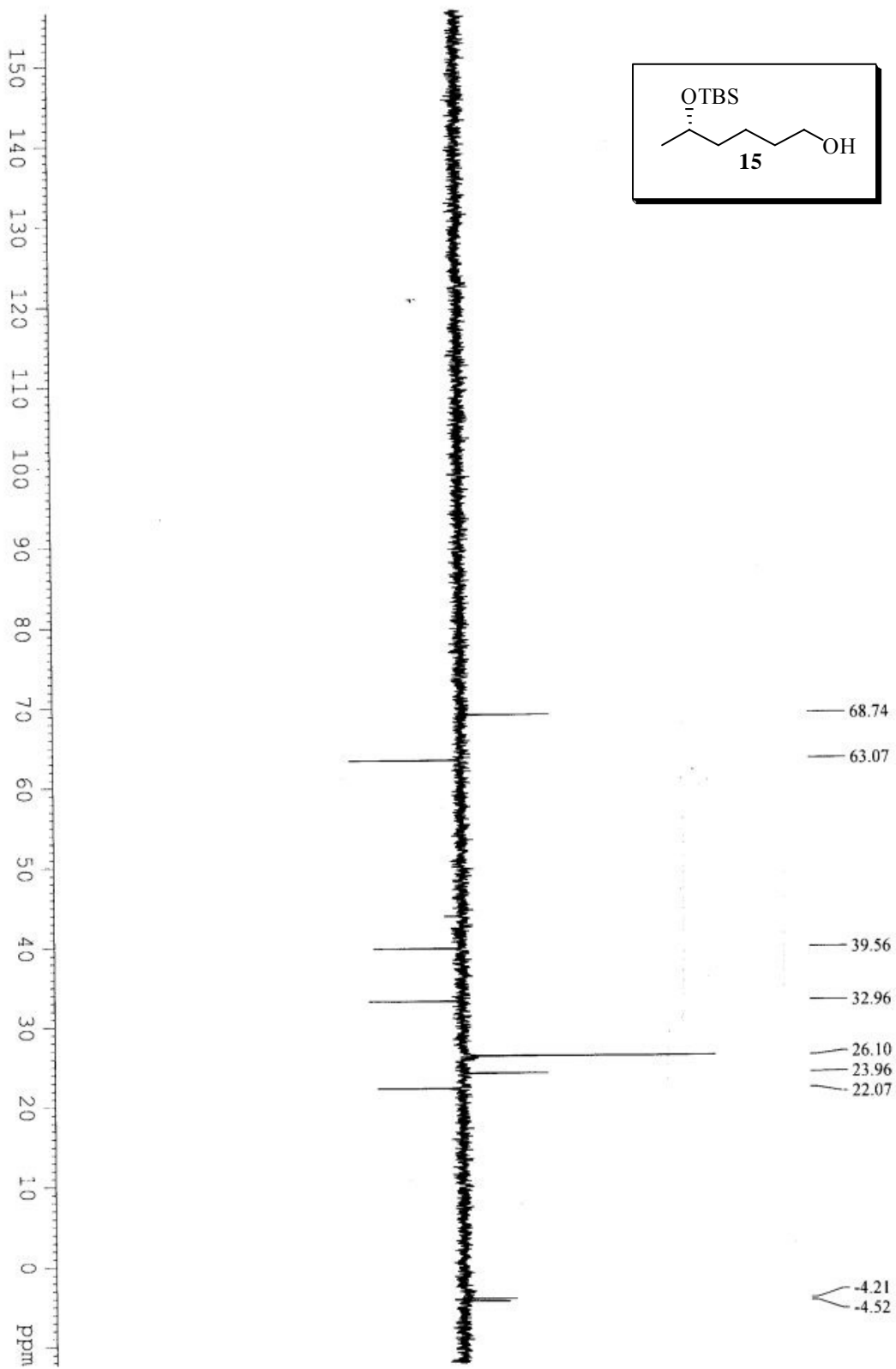
¹H-NMR of compound 15 (200MHz, CDCl₃)



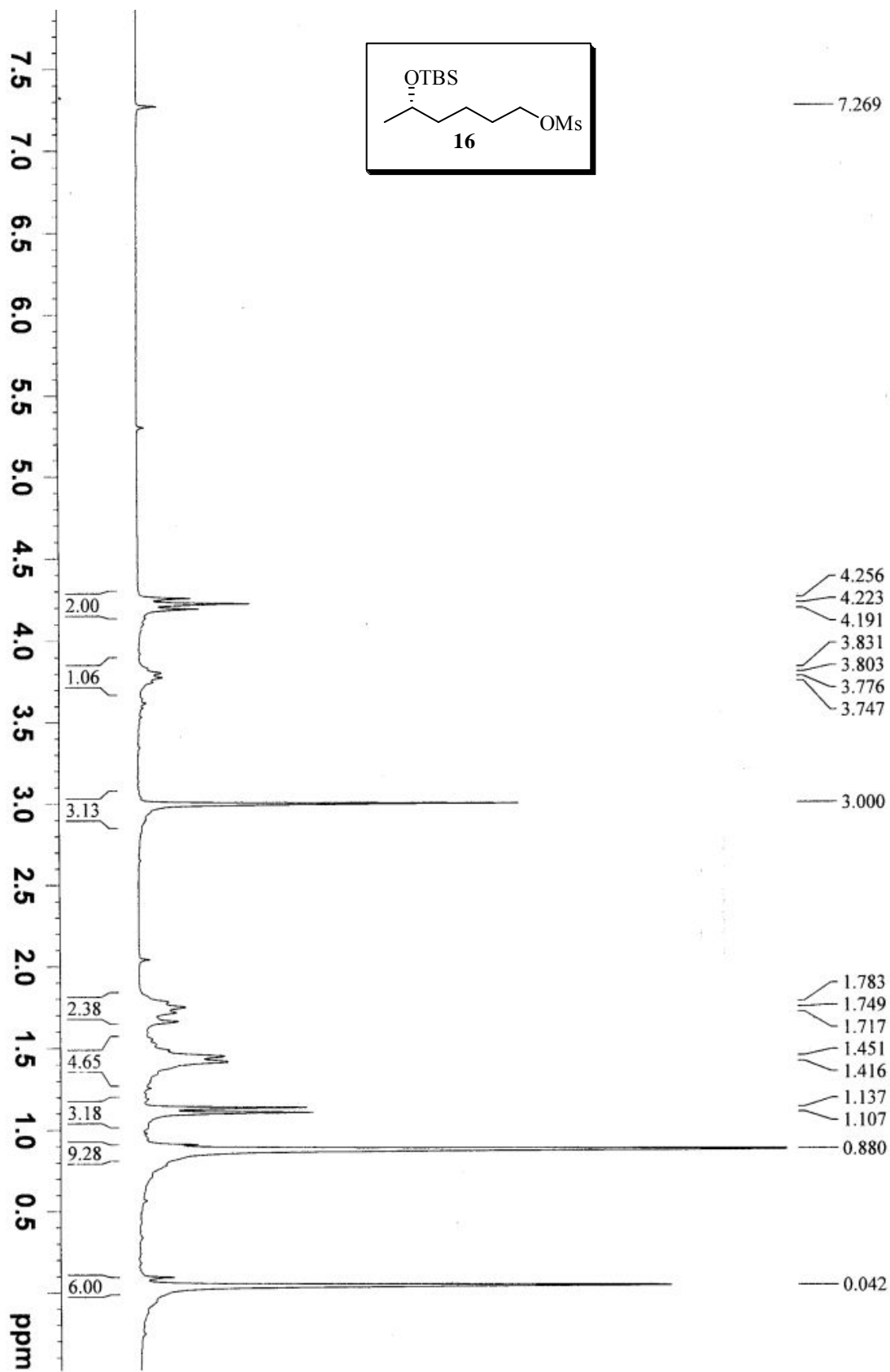
^{13}C -NMR of compound 15 (50MHz, CDCl_3)



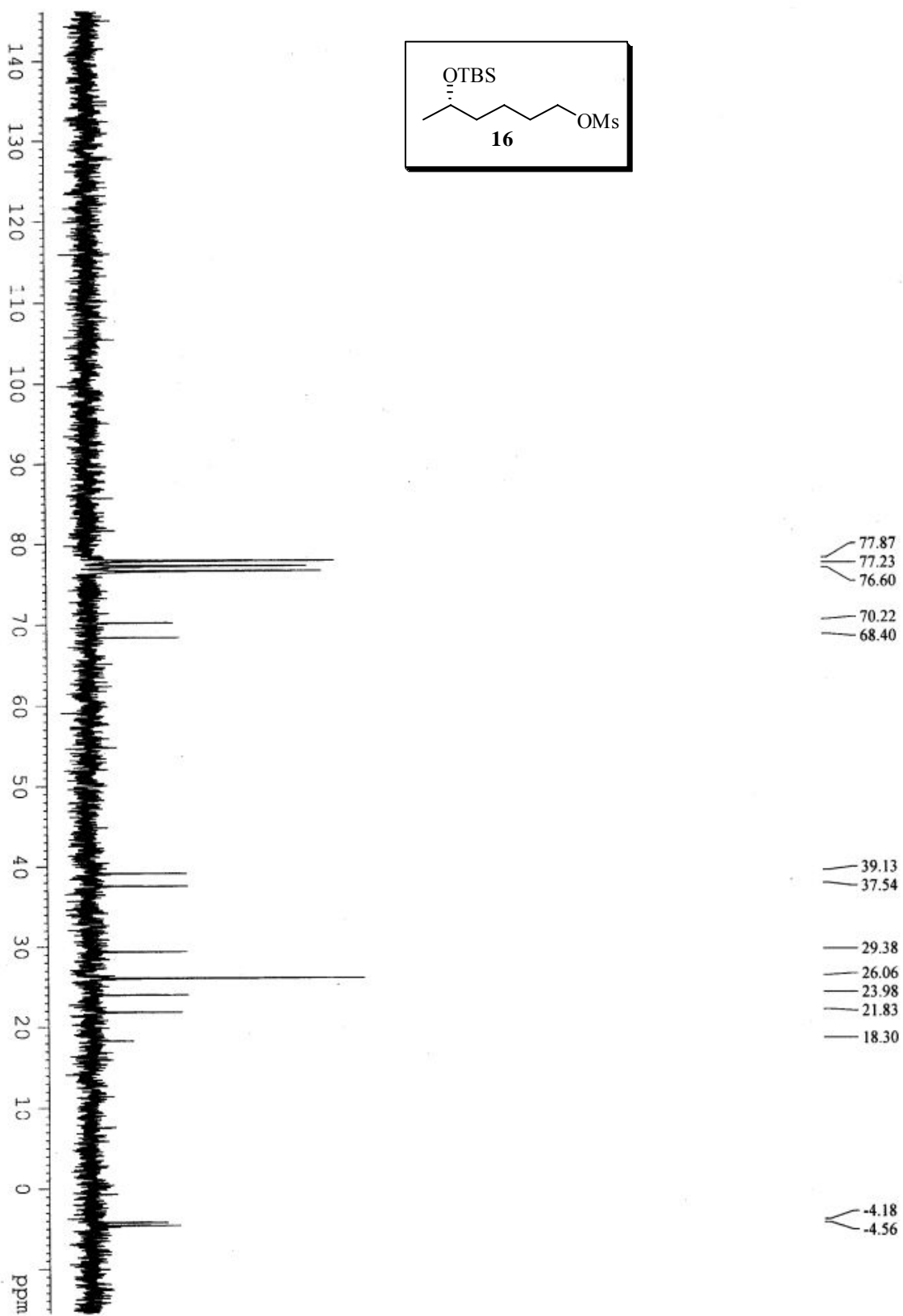
DEPT- NMR of compound 15 (50MHz, CDCl₃)



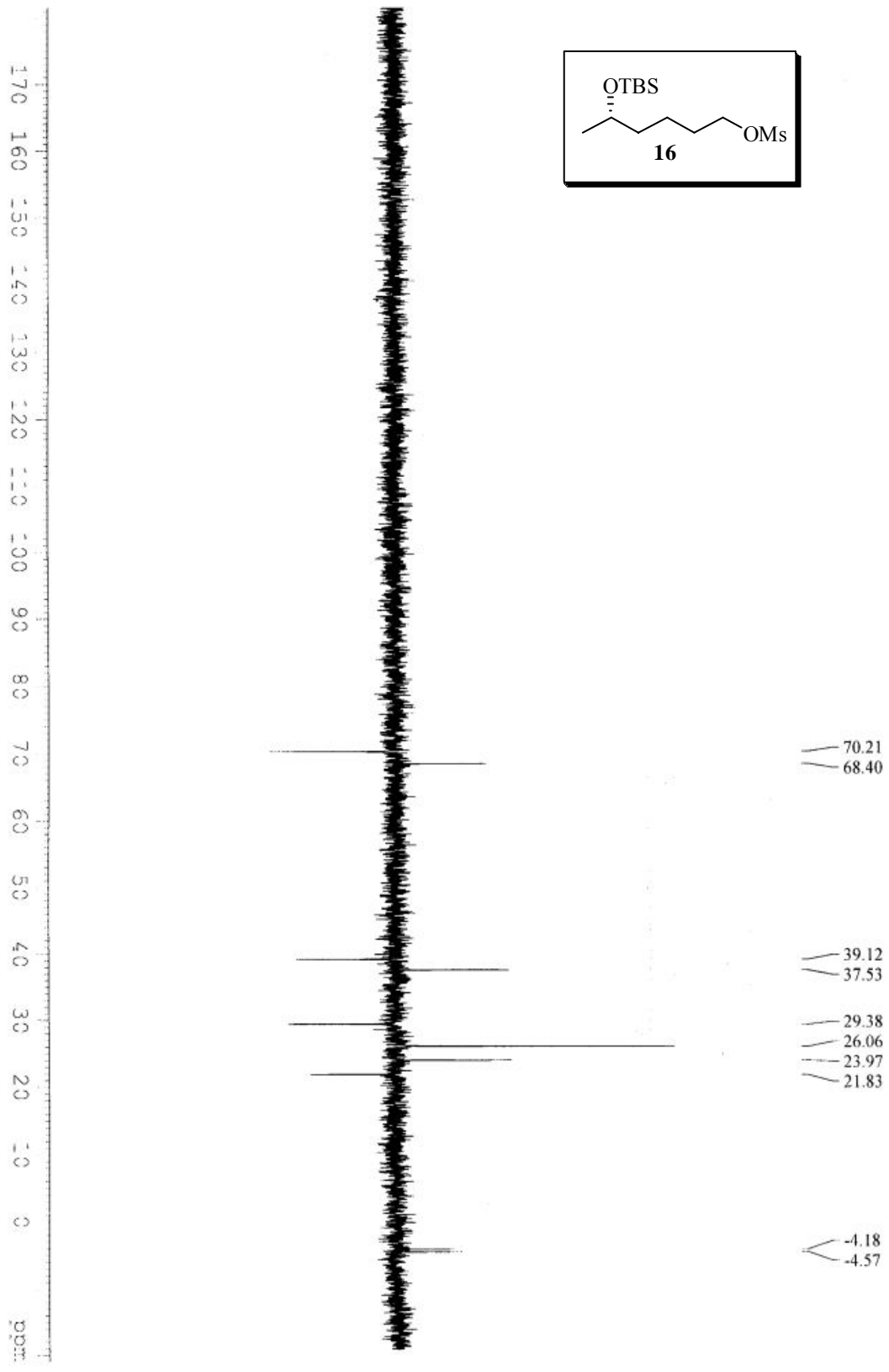
¹H- NMR of compound 16 (200MHz, CDCl₃)



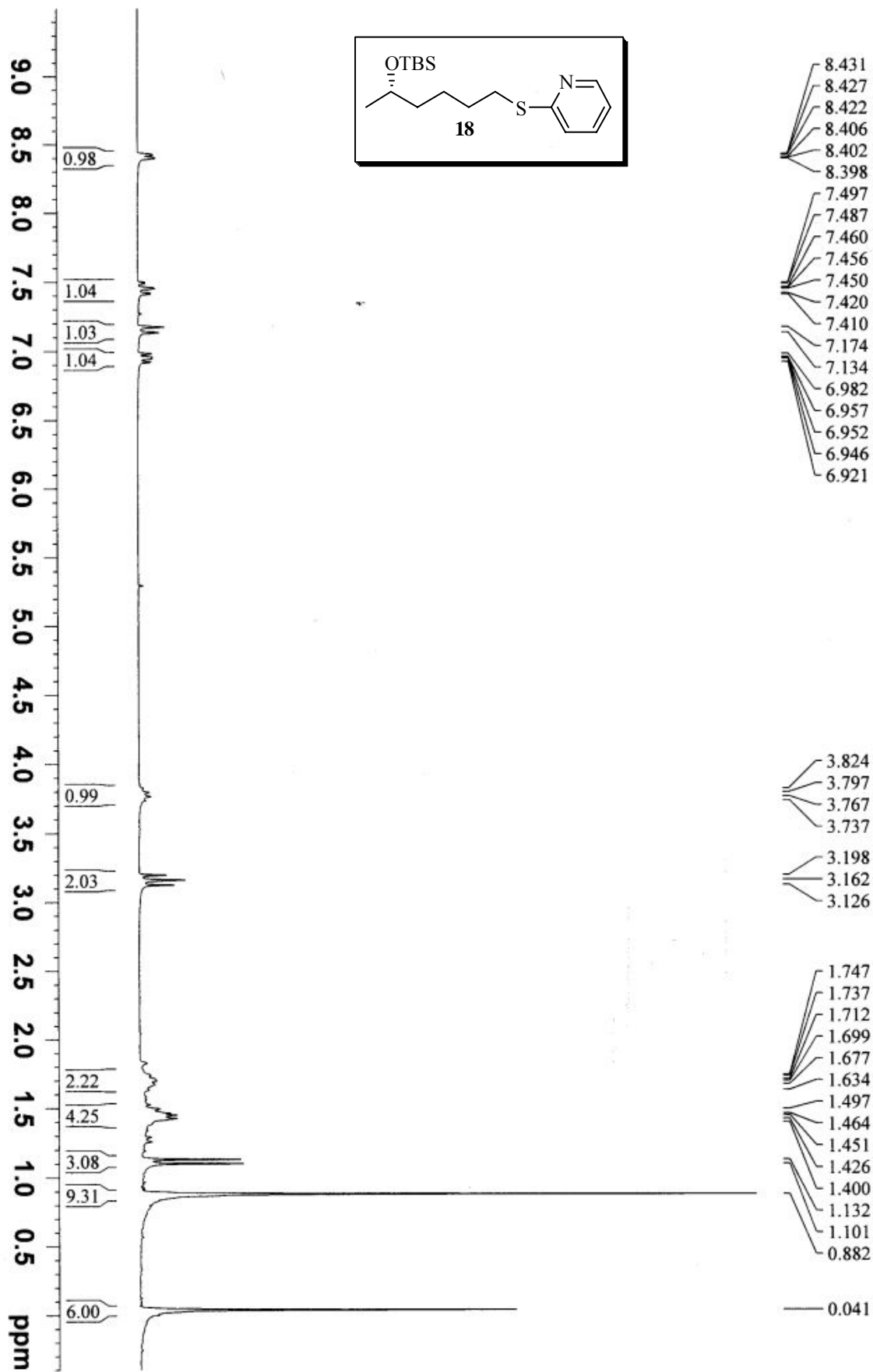
^{13}C -NMR of compound 16 (50MHz, CDCl_3)



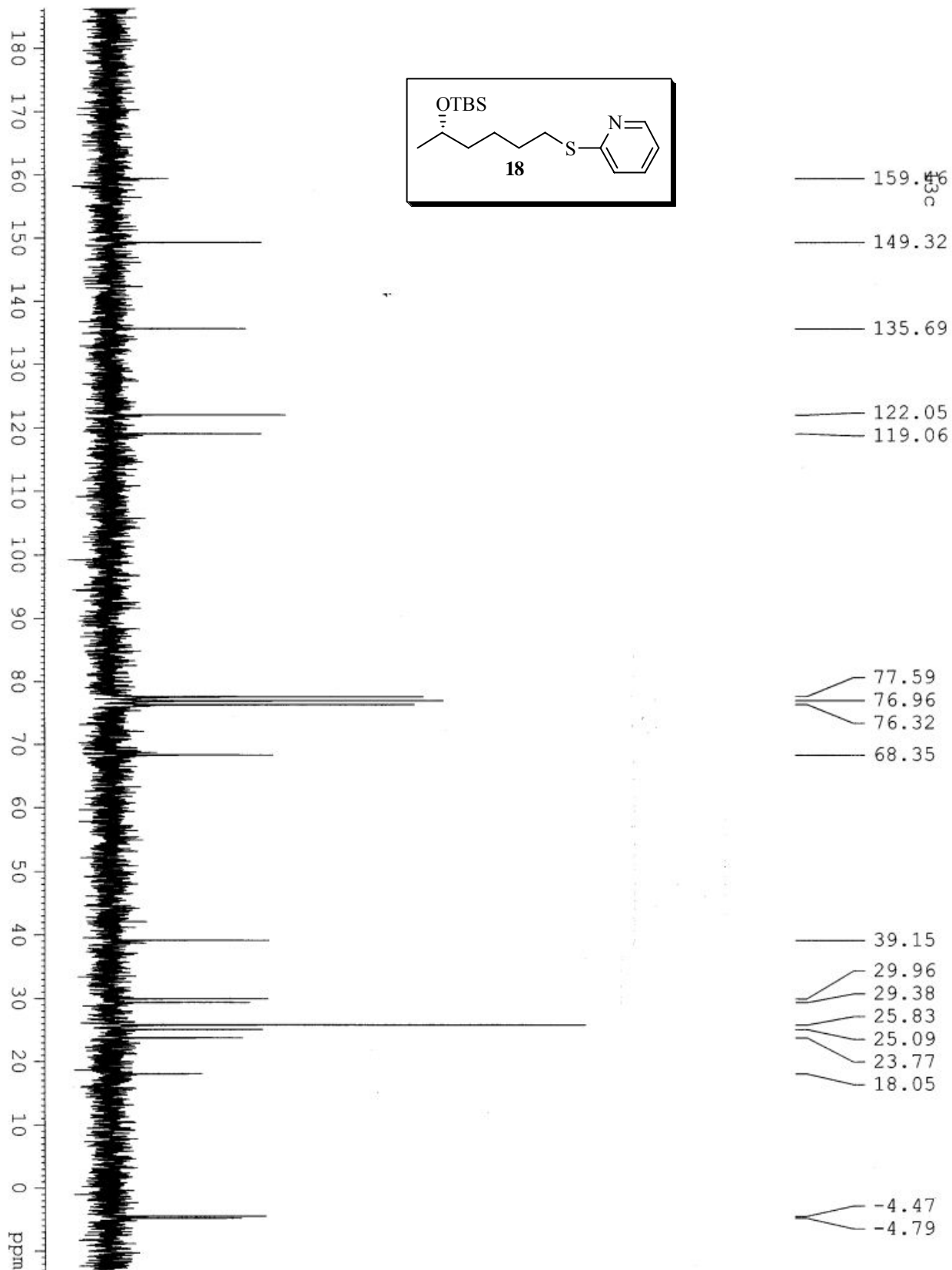
DEPT- NMR of compound 16 (50MHz, CDCl₃)



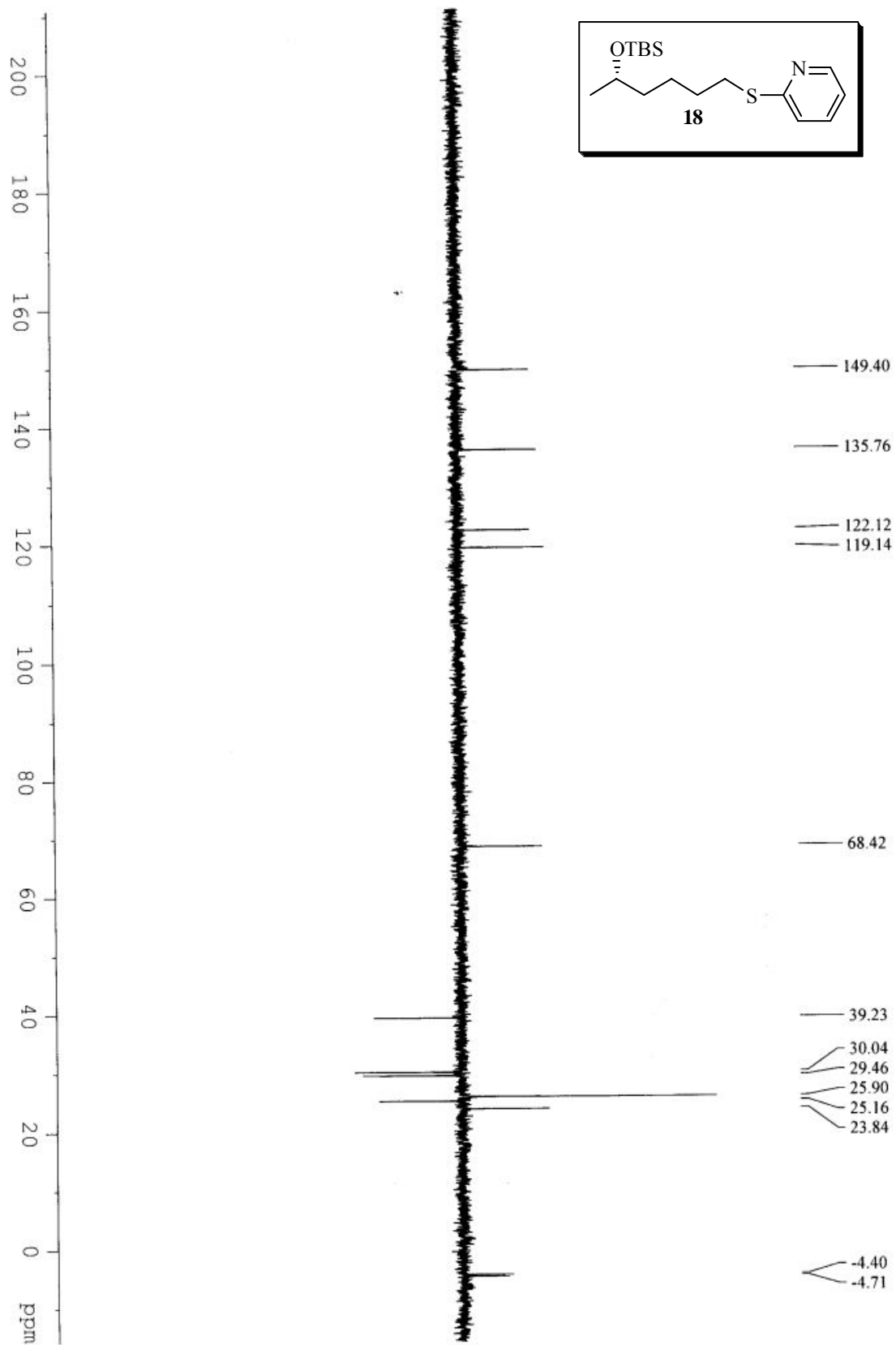
¹H-NMR of compound 18 (200MHz, CDCl₃)



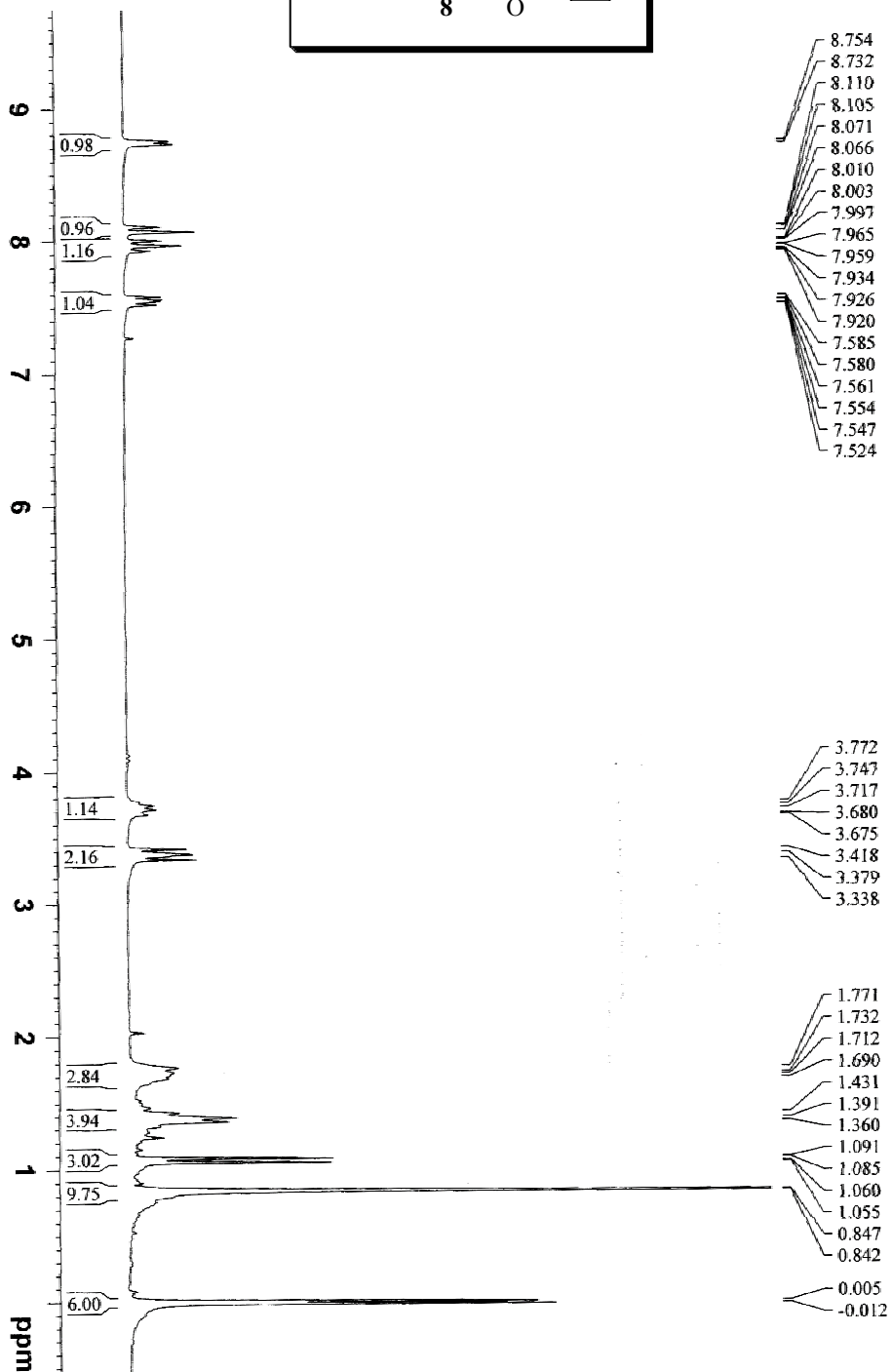
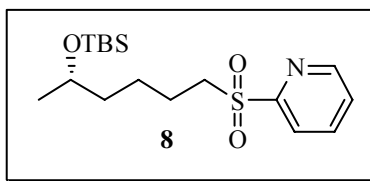
^{13}C -NMR of compound 18 (50MHz, CDCl_3)



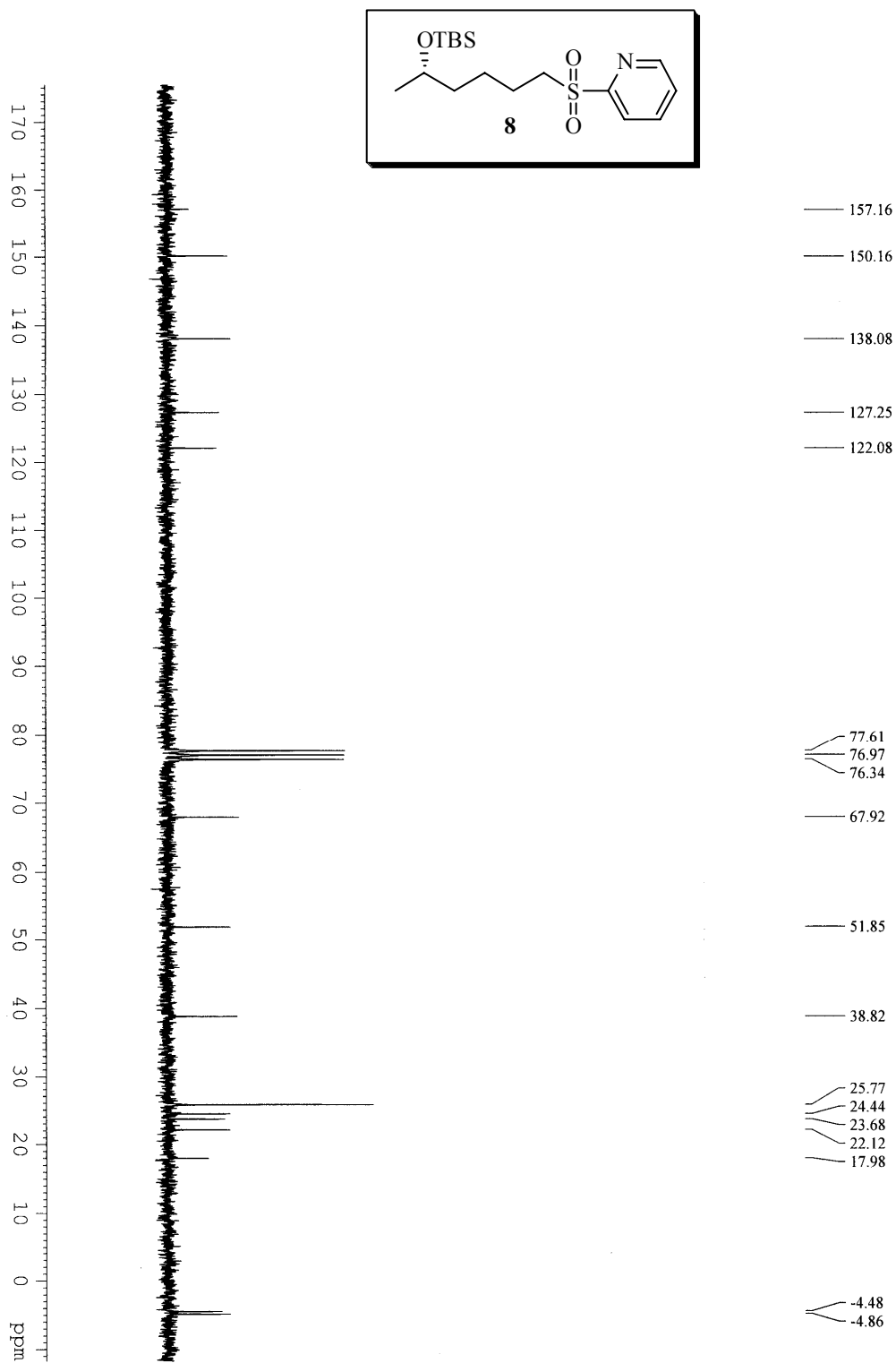
DEPT- NMR of compound 18 (50MHz, CDCl₃)



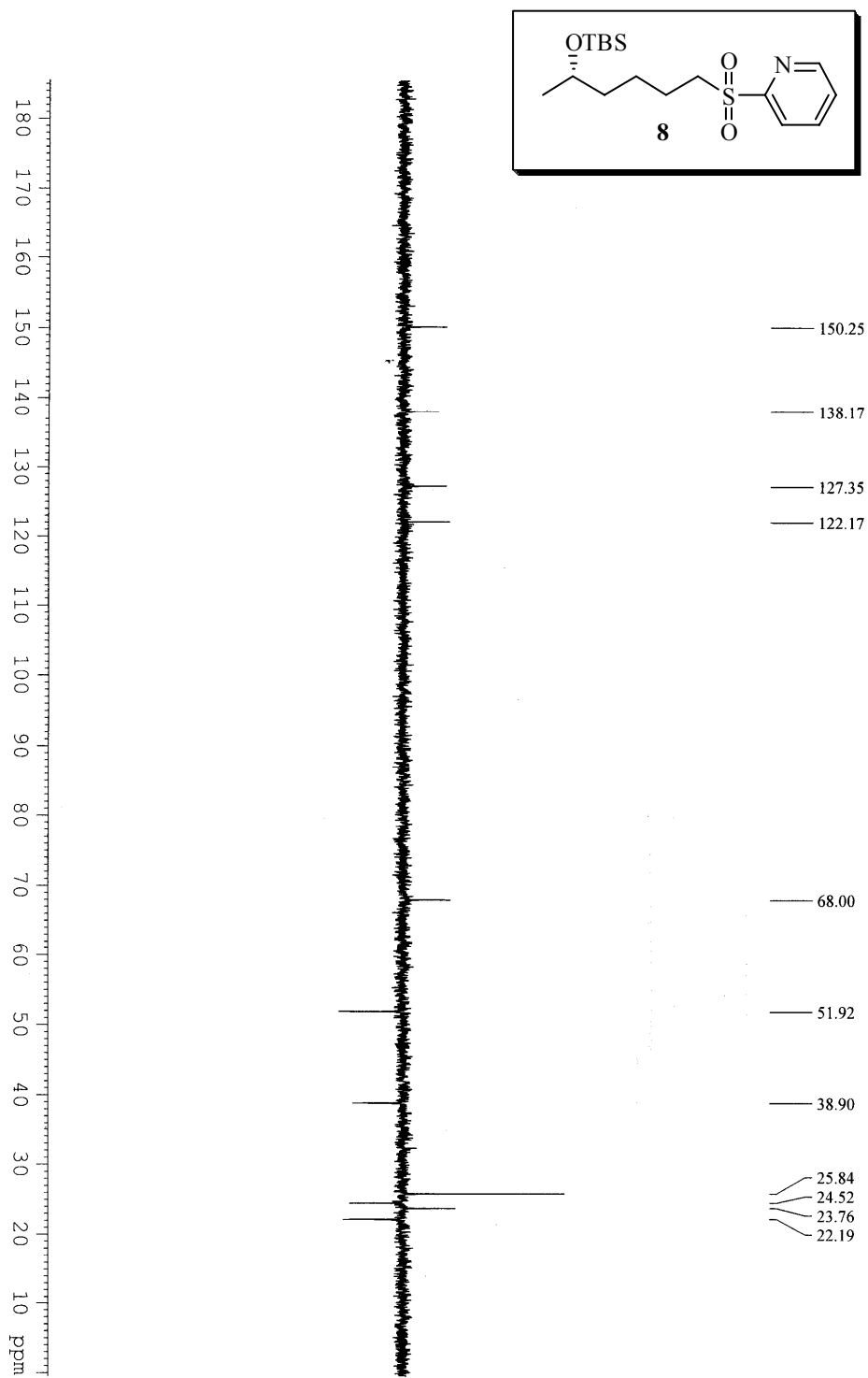
¹H-NMR of compound 8 (200MHz, CDCl₃)



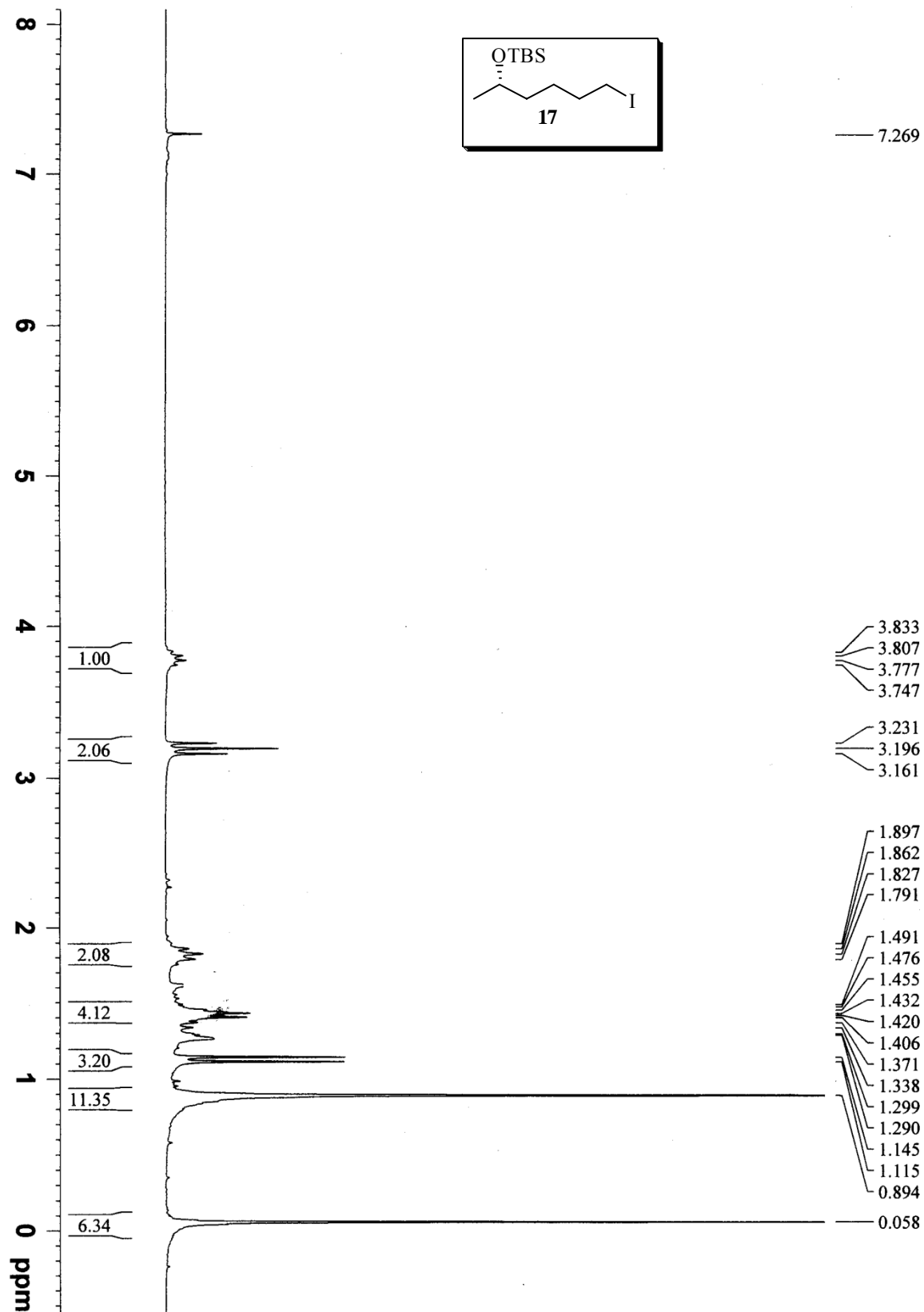
¹³C-NMR of compound 8 (50MHz, CDCl₃)



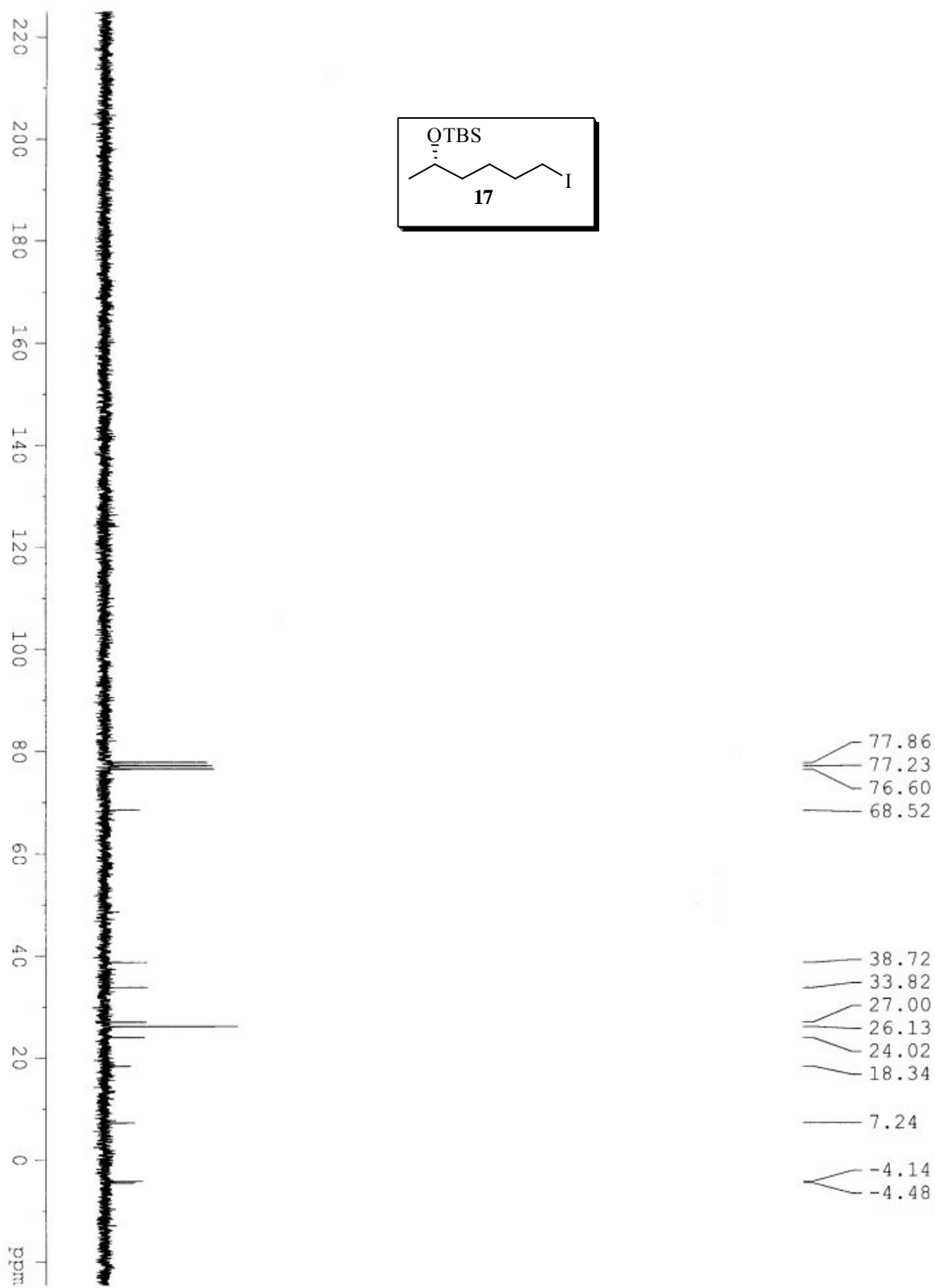
DEPT-NMR of compound 8 (50MHz, CDCl₃)



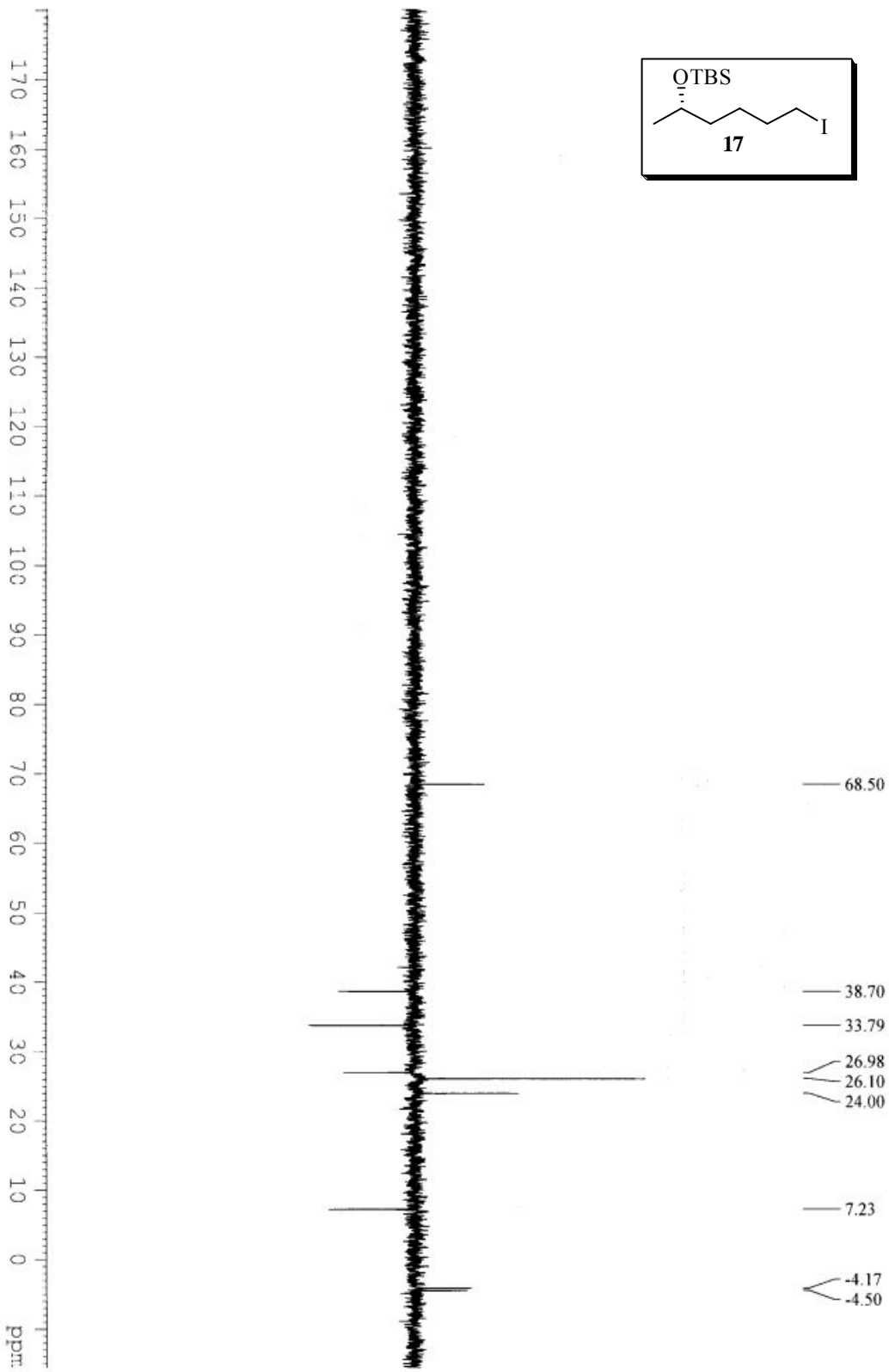
¹H- NMR of compound 17 (200MHz, CDCl₃)



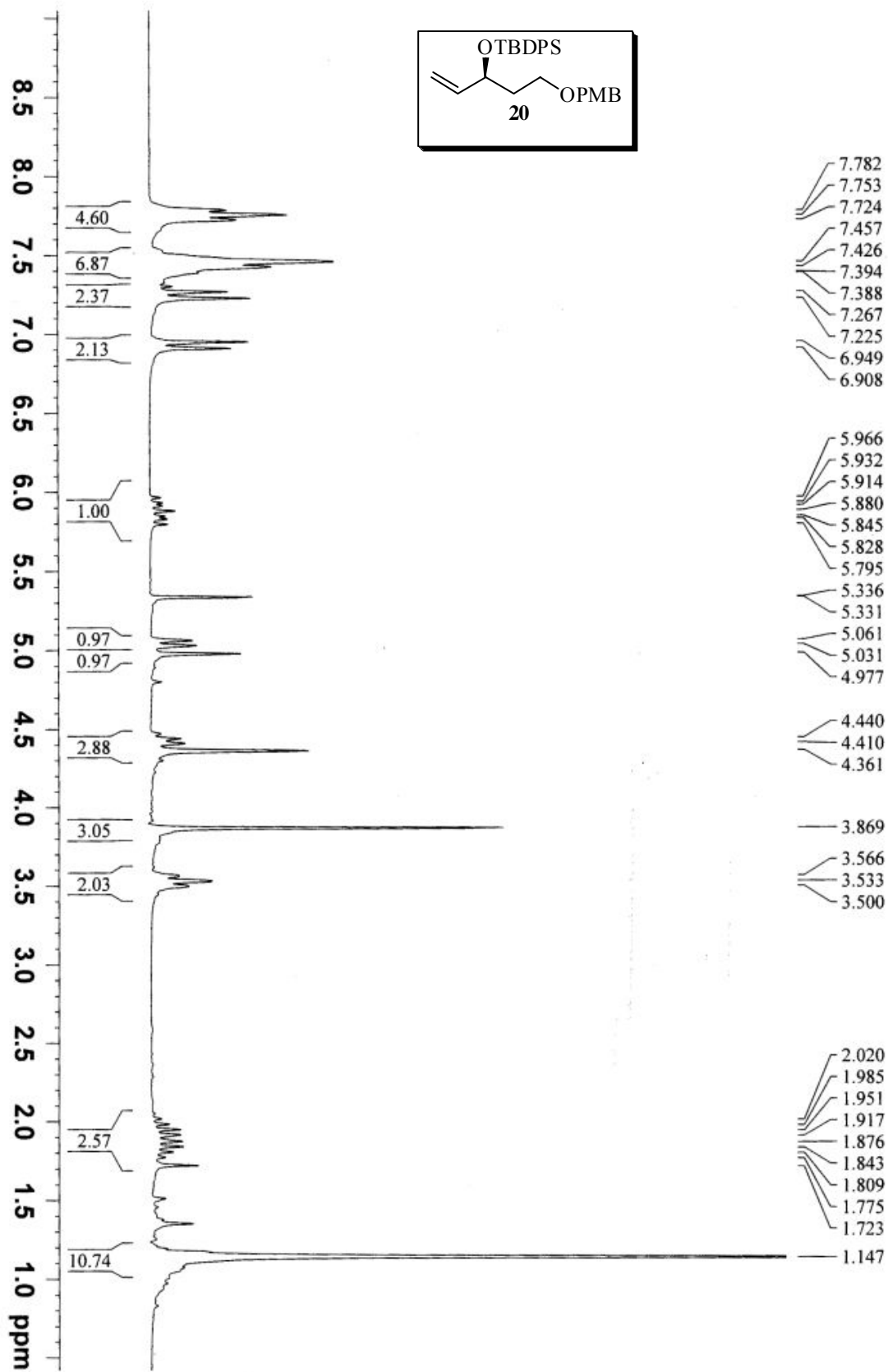
^{13}C -NMR of compound 17 (50MHz, CDCl_3)



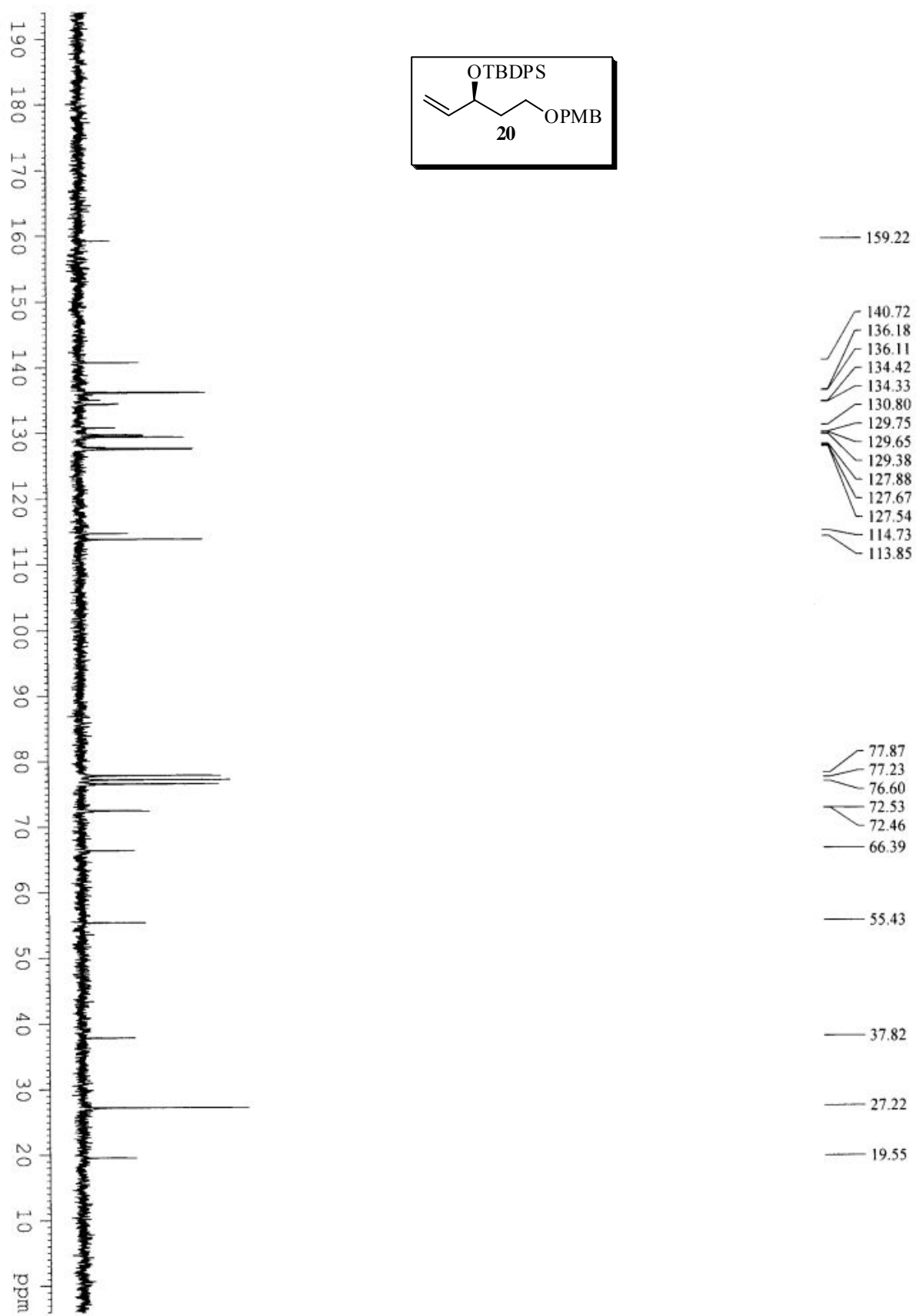
DEPT- NMR of compound 17 (50MHz, CDCl₃)



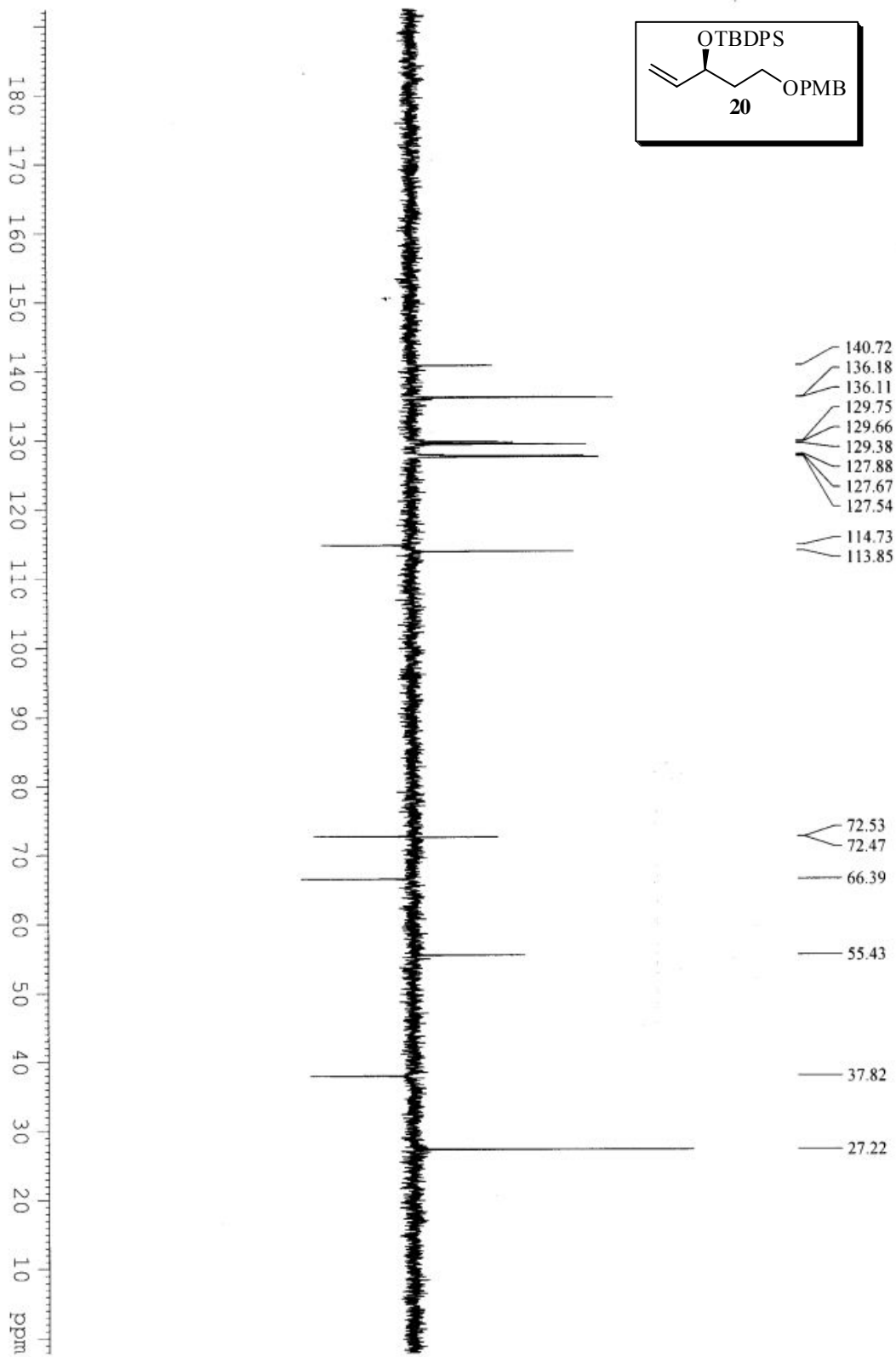
¹H- NMR of compound 20 (200MHz, CDCl₃)



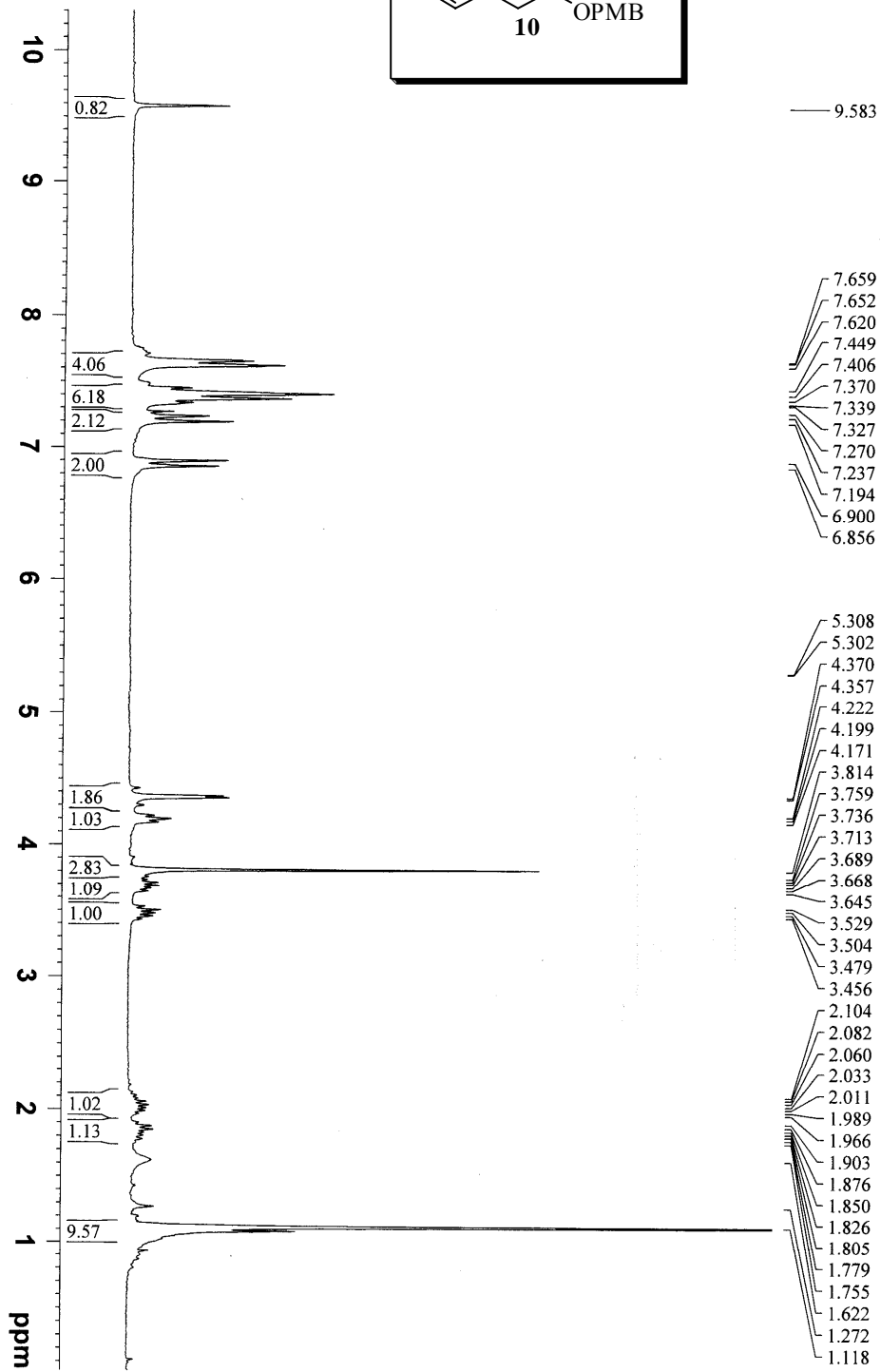
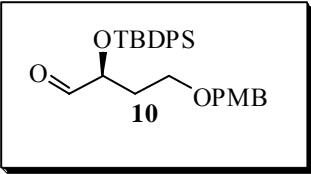
¹³C-NMR of compound 20 (50MHz, CDCl₃)



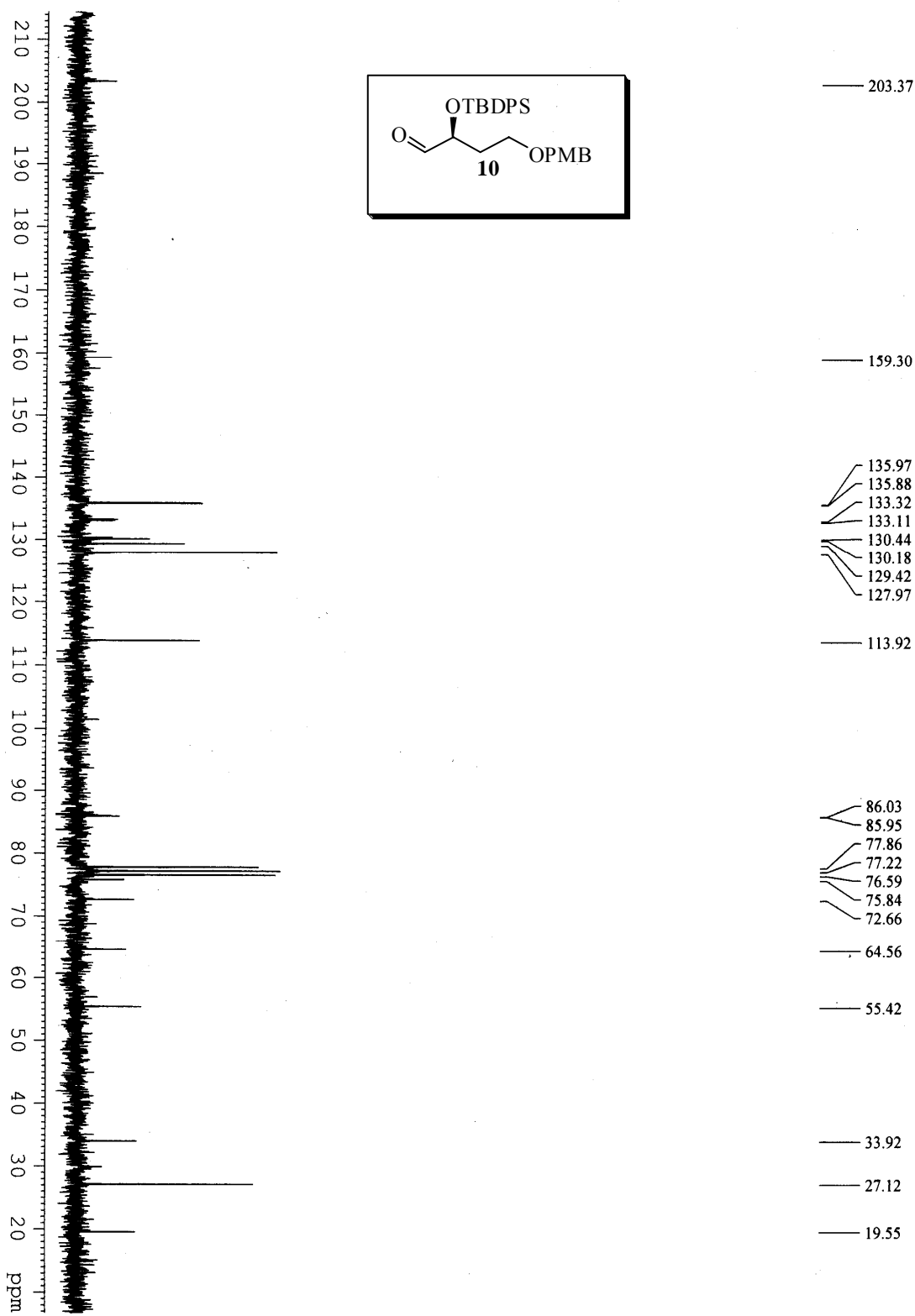
DEPT- NMR of compound 20 (50MHz, CDCl₃)



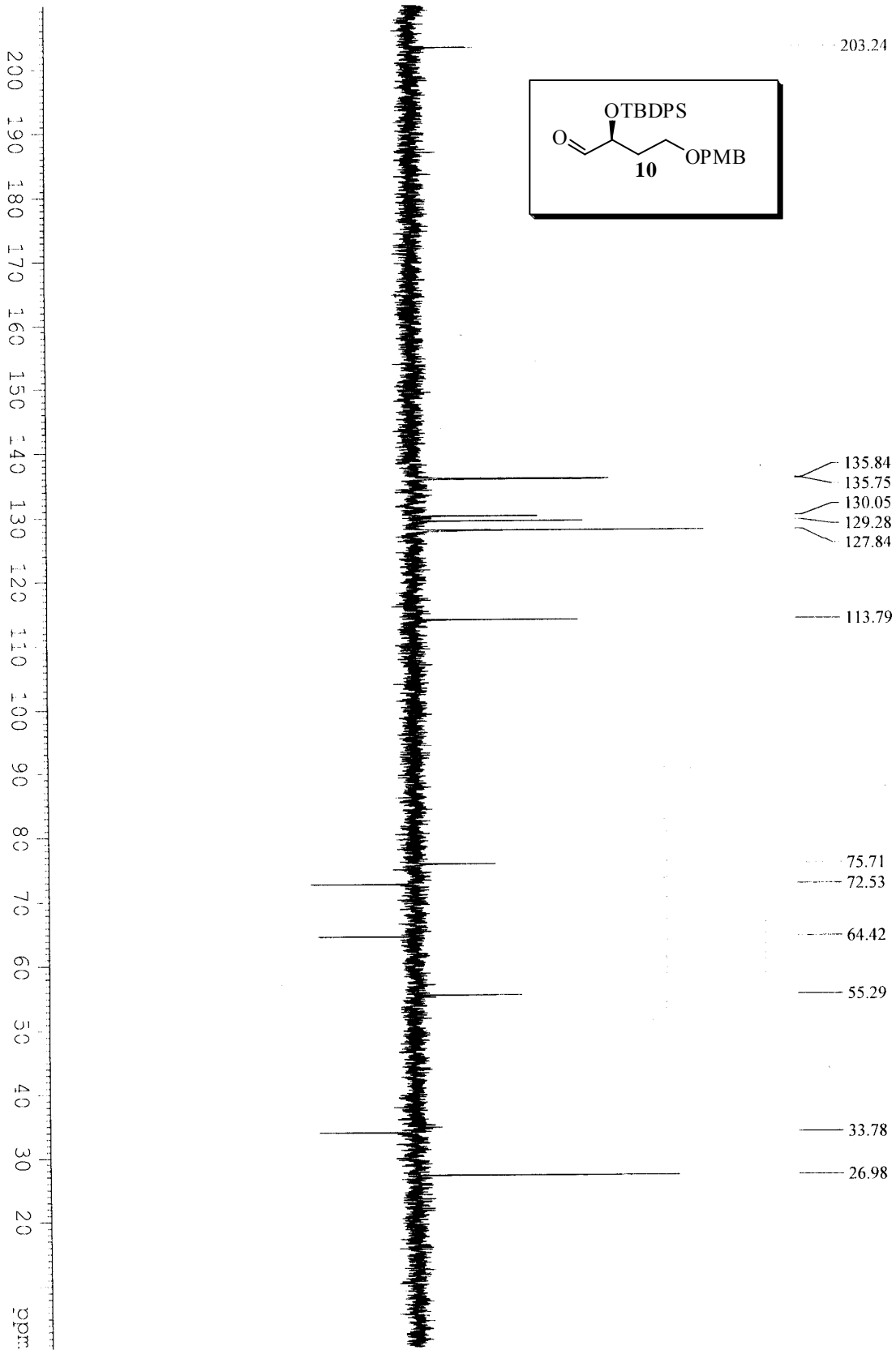
¹H- NMR of compound 10 (200MHz, CDCl₃)



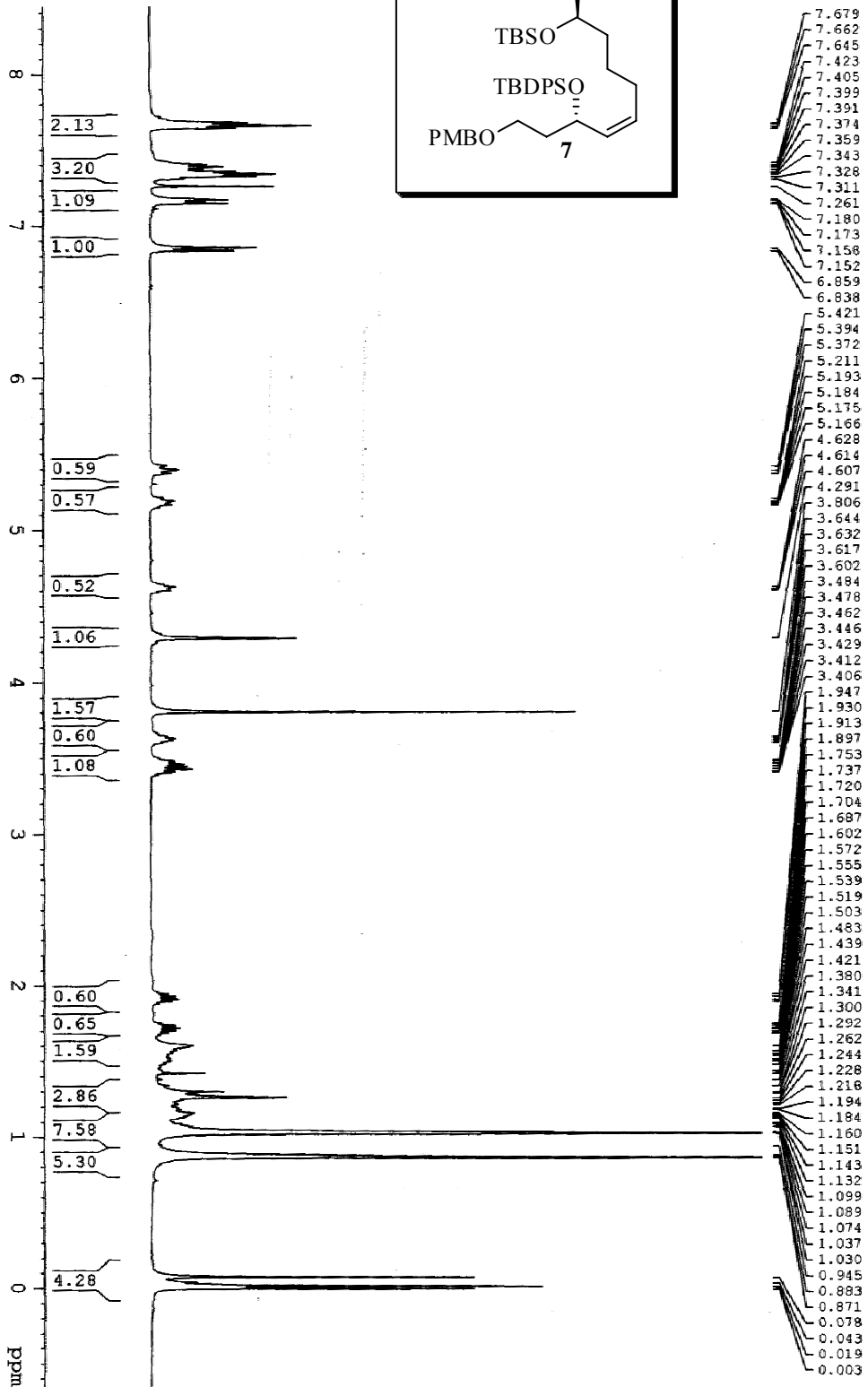
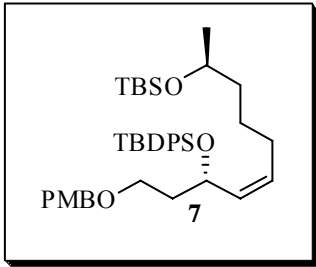
¹³C-NMR of compound 10 (50MHz, CDCl₃)



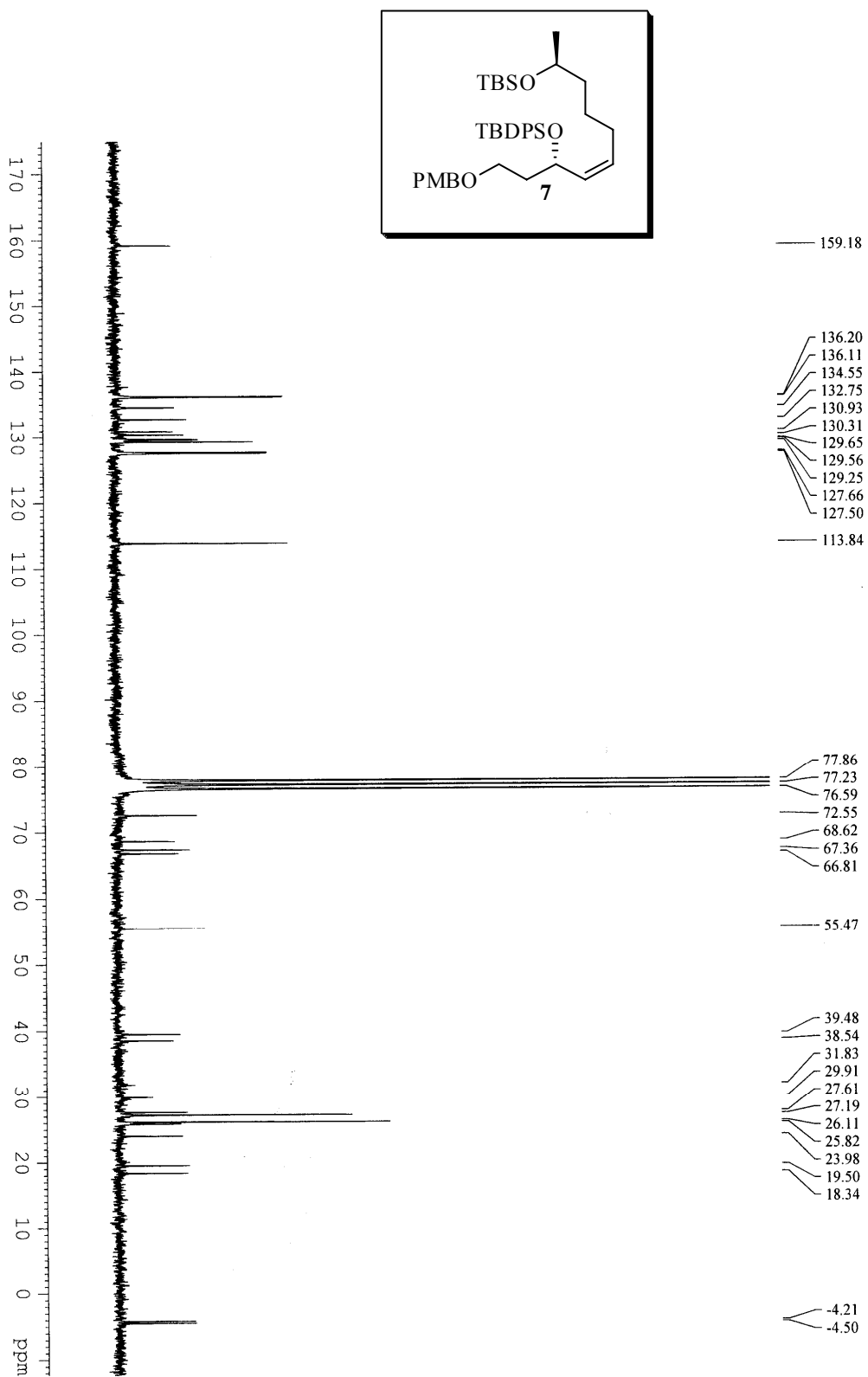
DEPT- NMR of compound 10 (50MHz, CDCl₃)



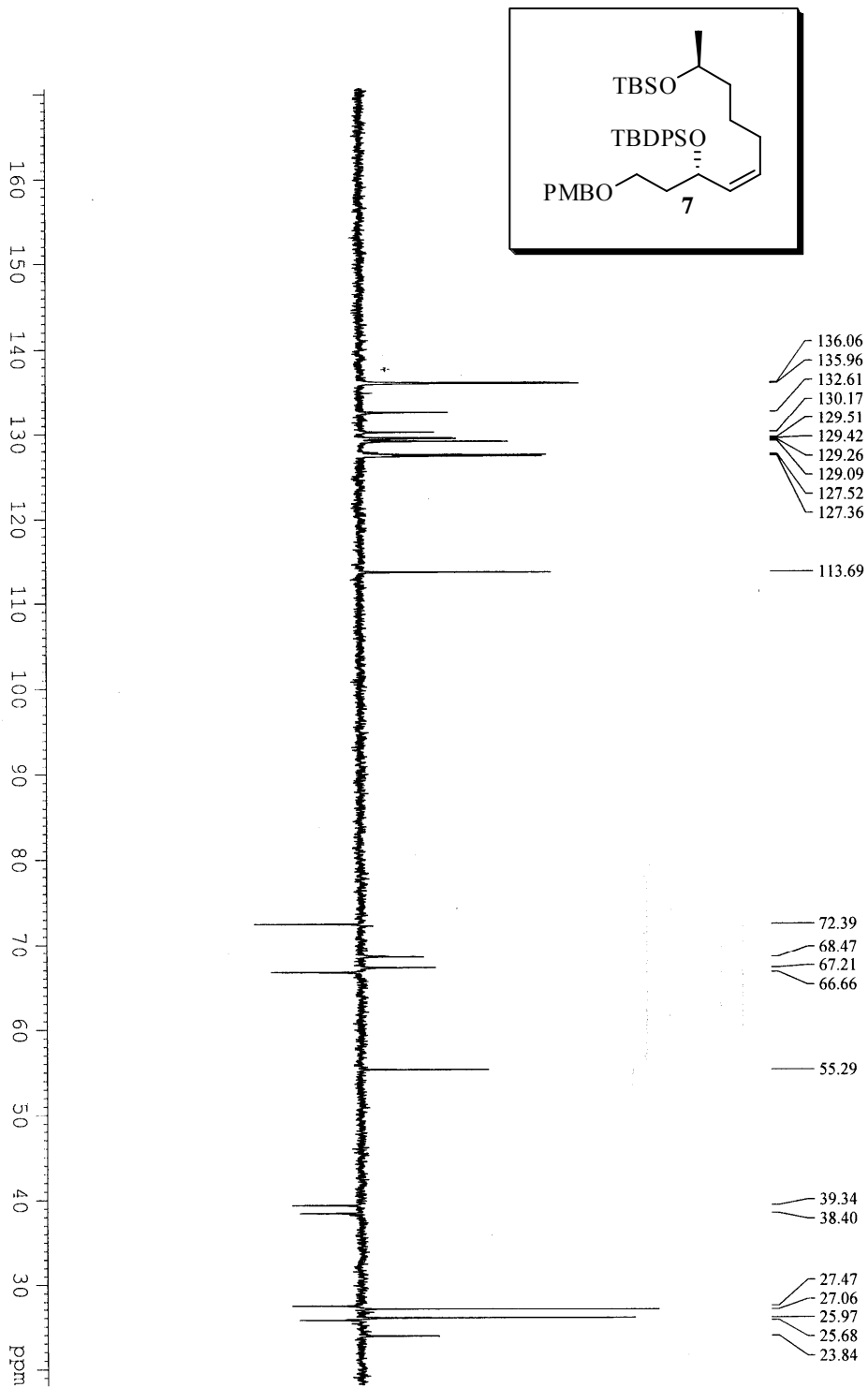
¹H-NMR of compound 7 (400MHz, CDCl₃)



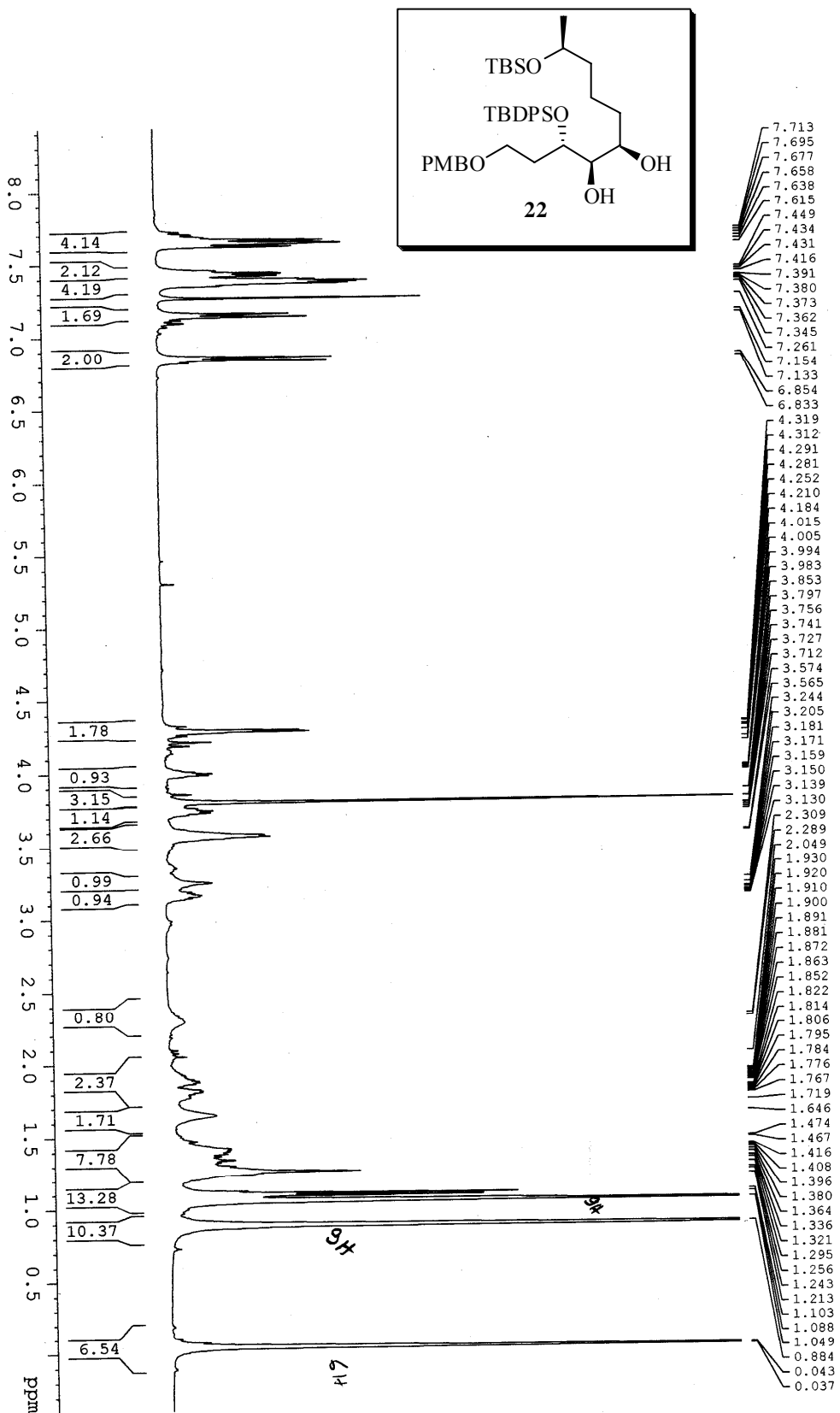
¹³C-NMR of compound 7 (50MHz, CDCl₃)



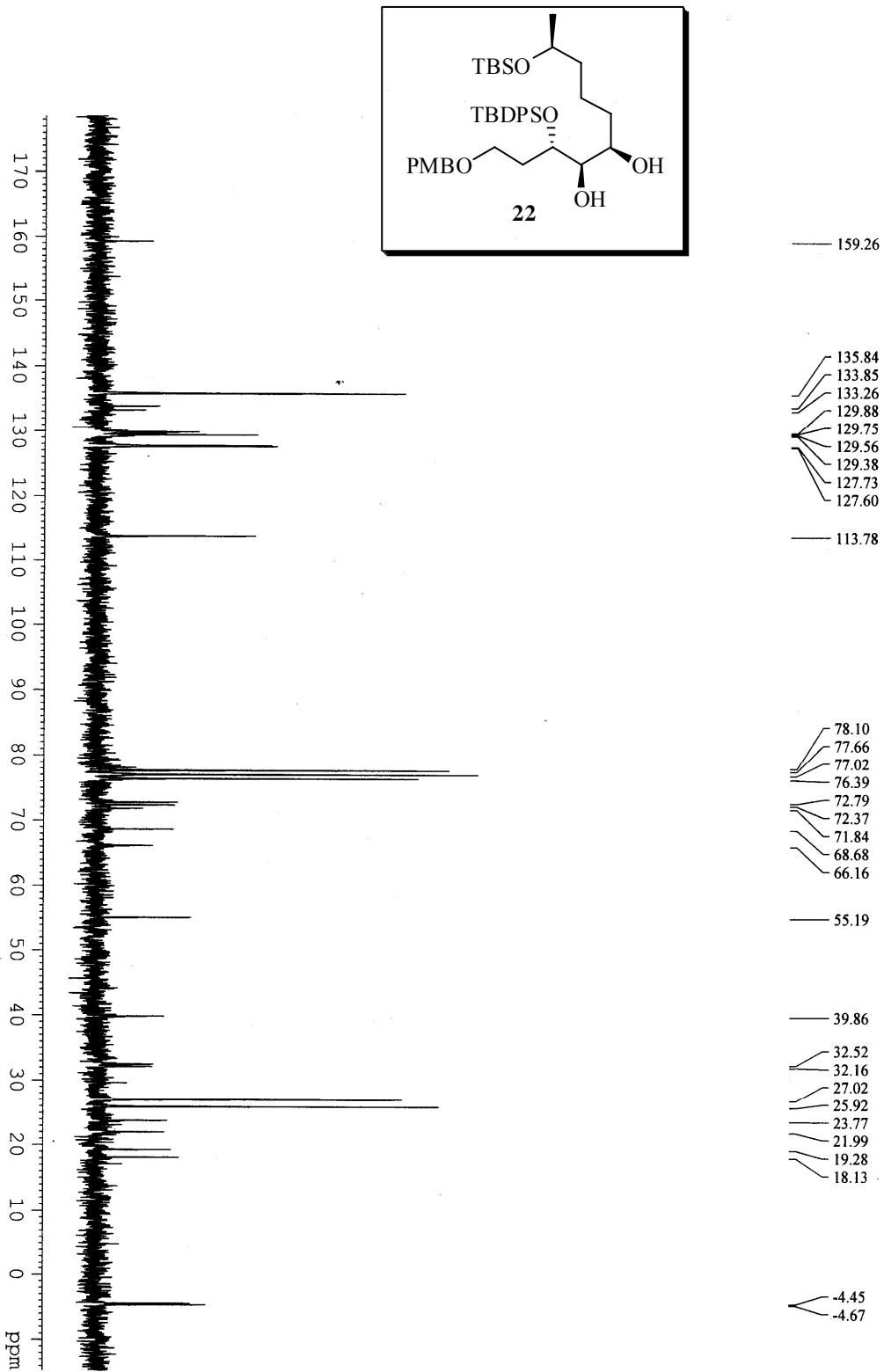
DEPT- NMR of compound 7 (50MHz, CDCl₃)



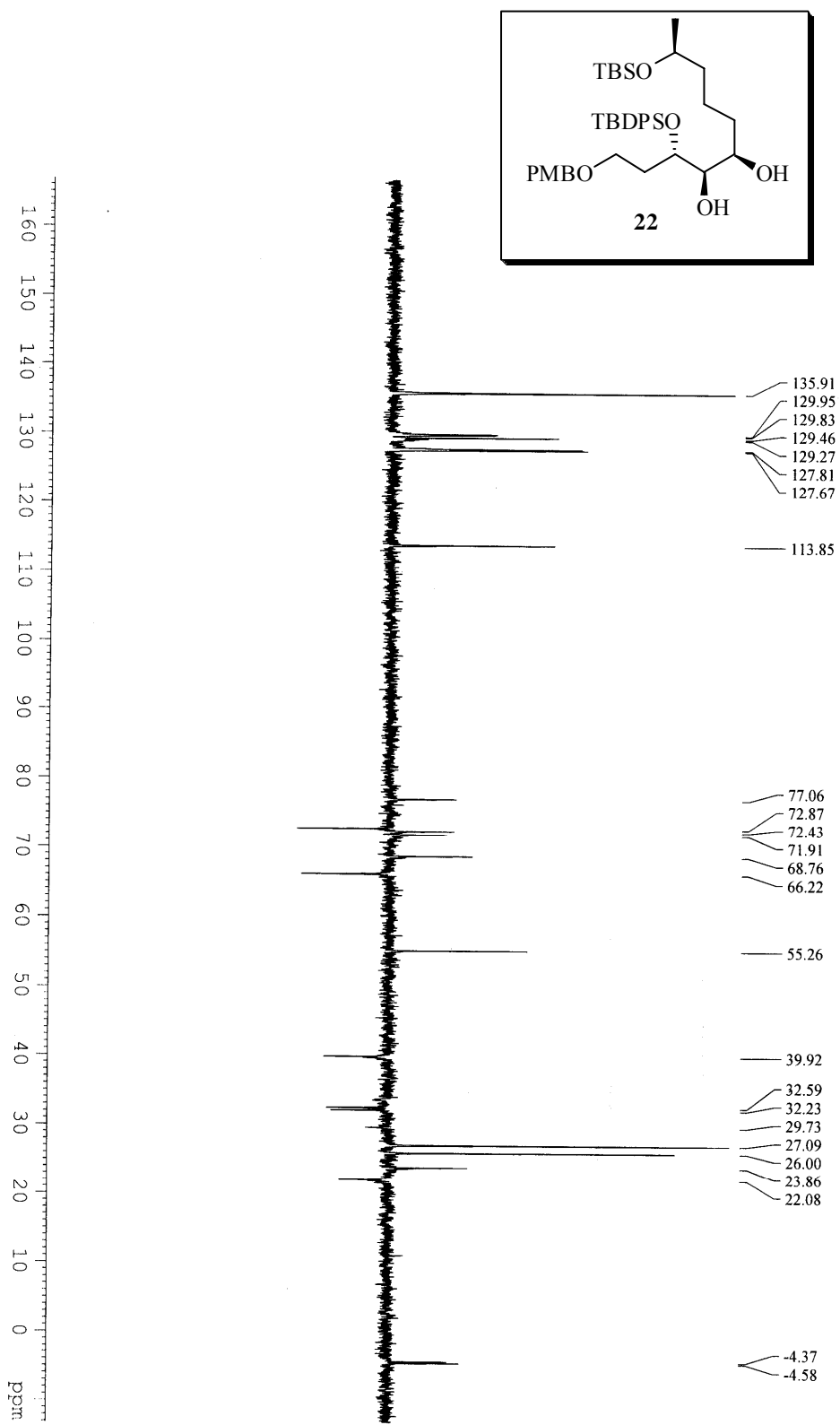
¹H-NMR of compound 22 (400MHz, CDCl₃)



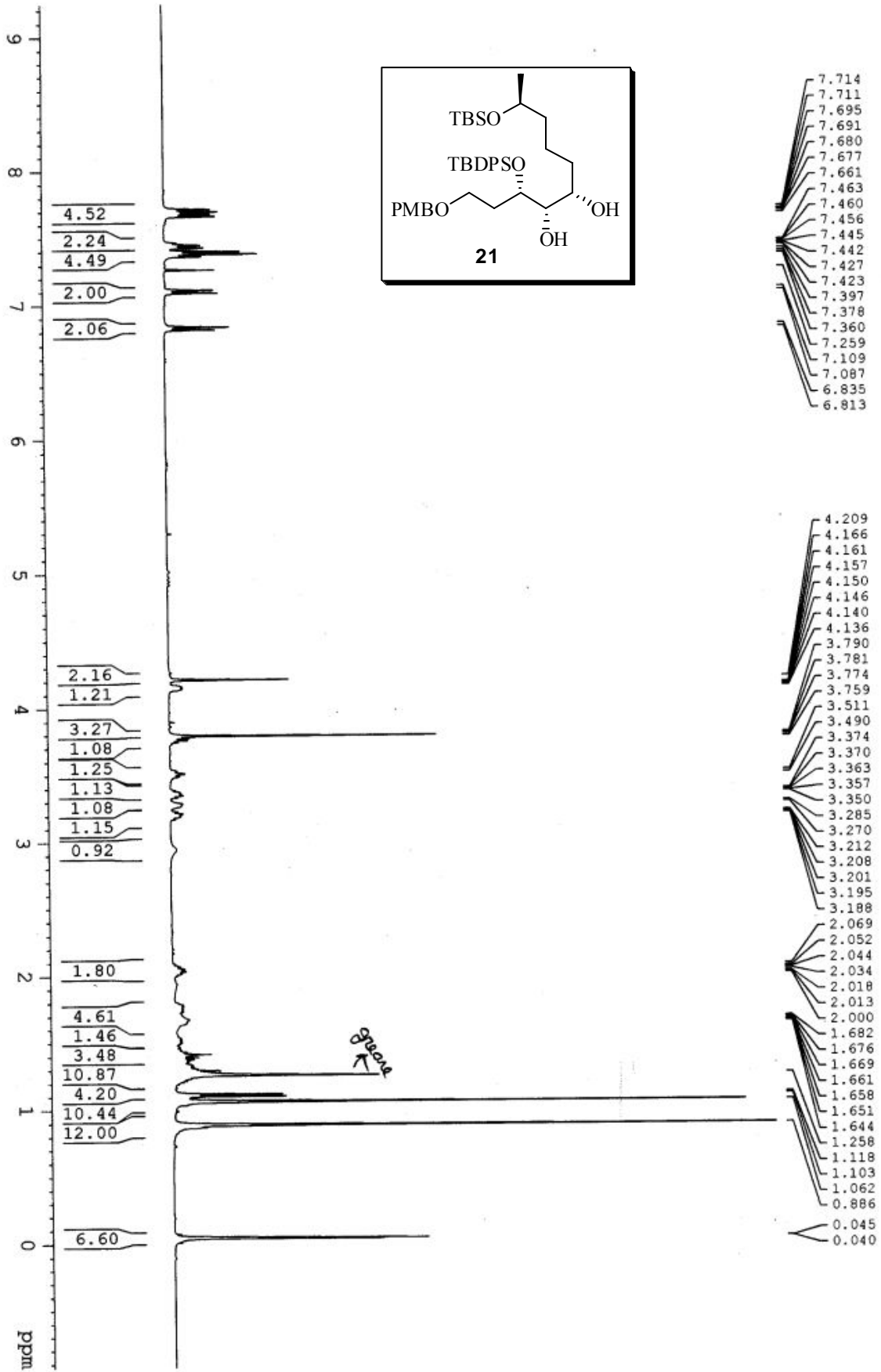
^{13}C -NMR of compound 22 (50MHz, CDCl_3)



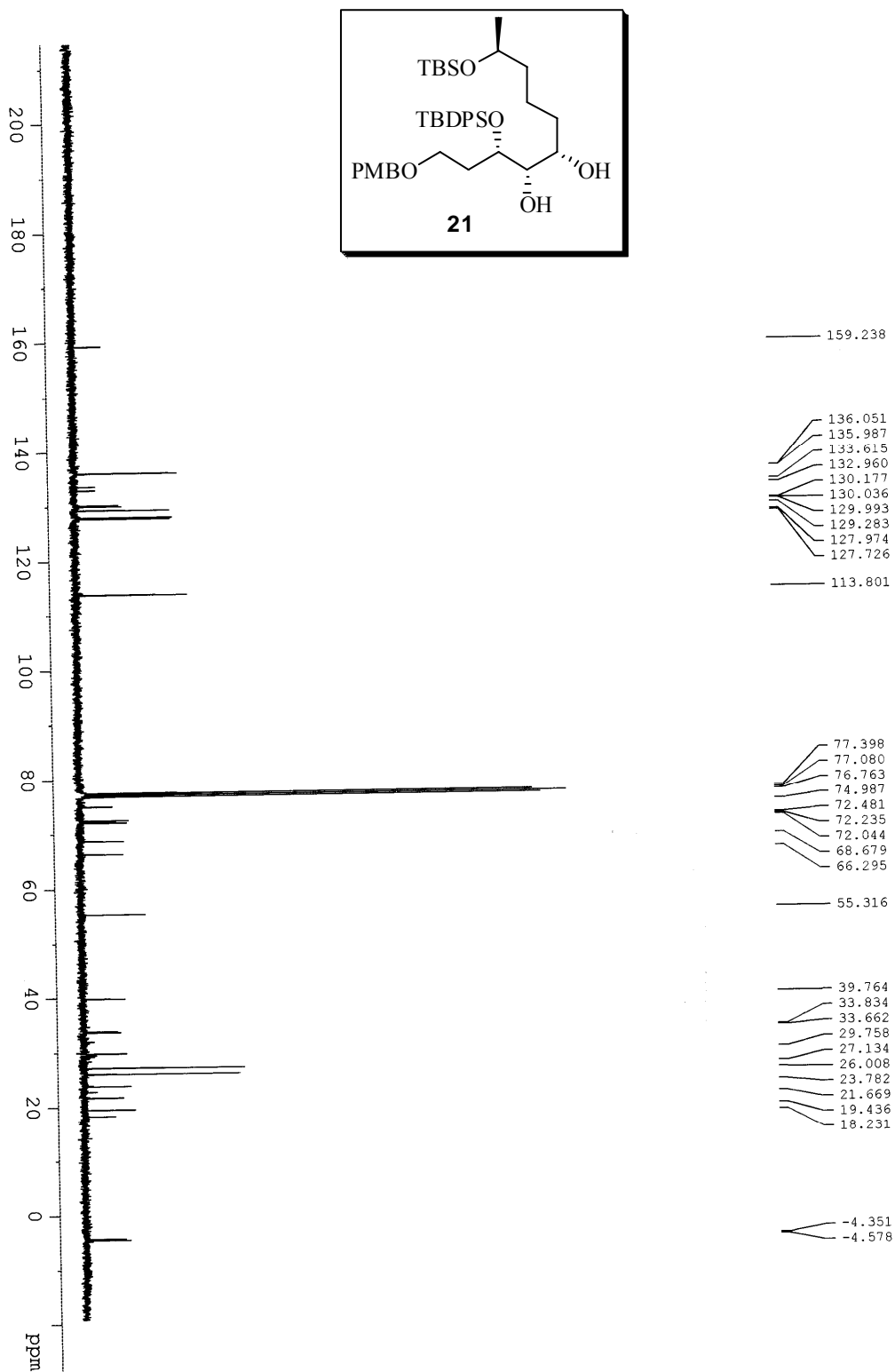
DEPT- NMR of compound 22 (50MHz, CDCl₃)



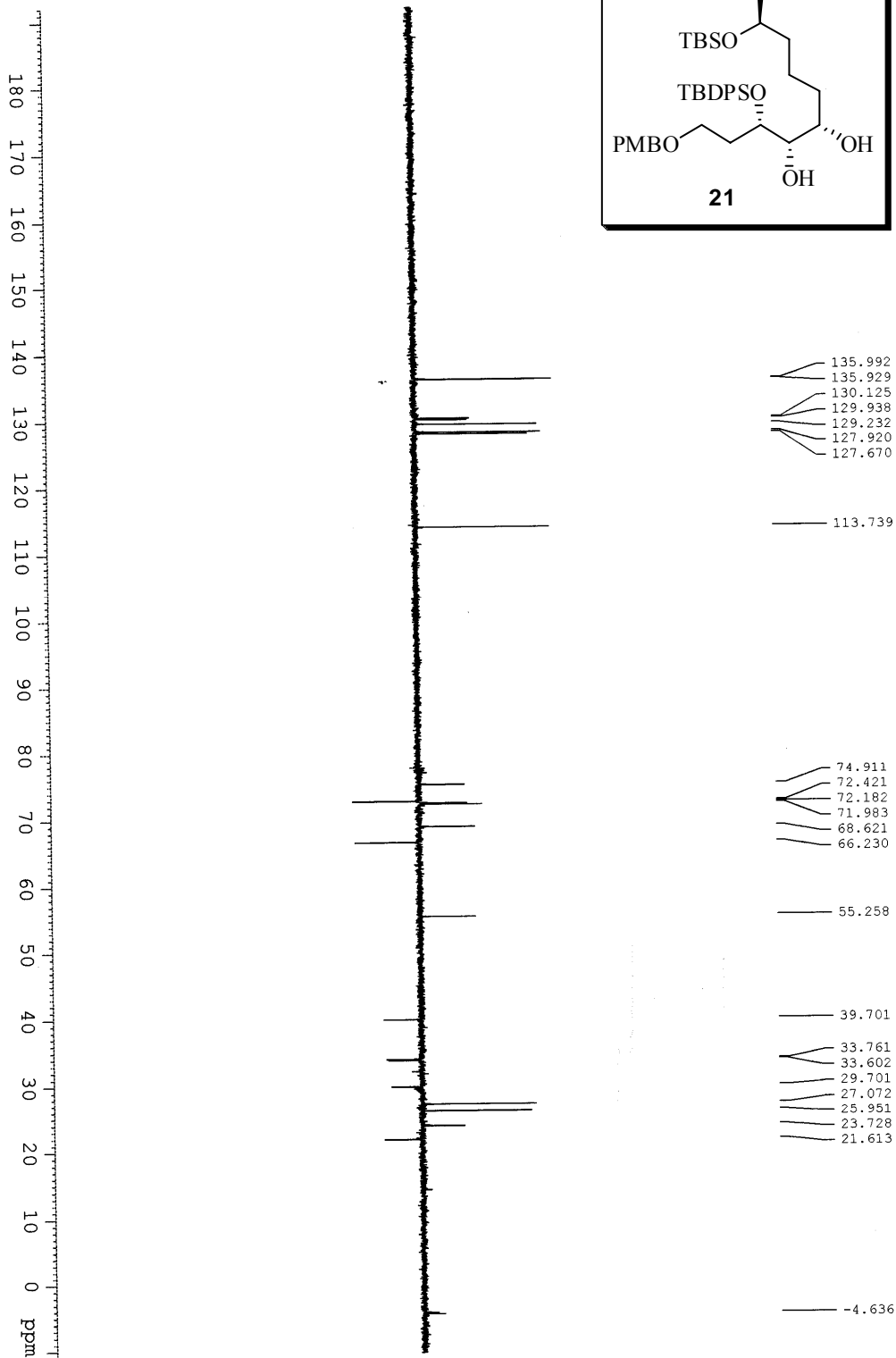
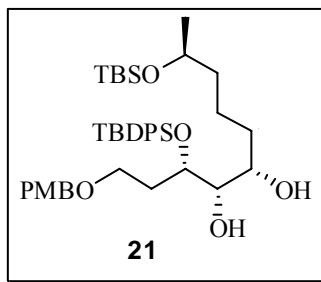
¹H-NMR of compound 21 (400MHz, CDCl₃)



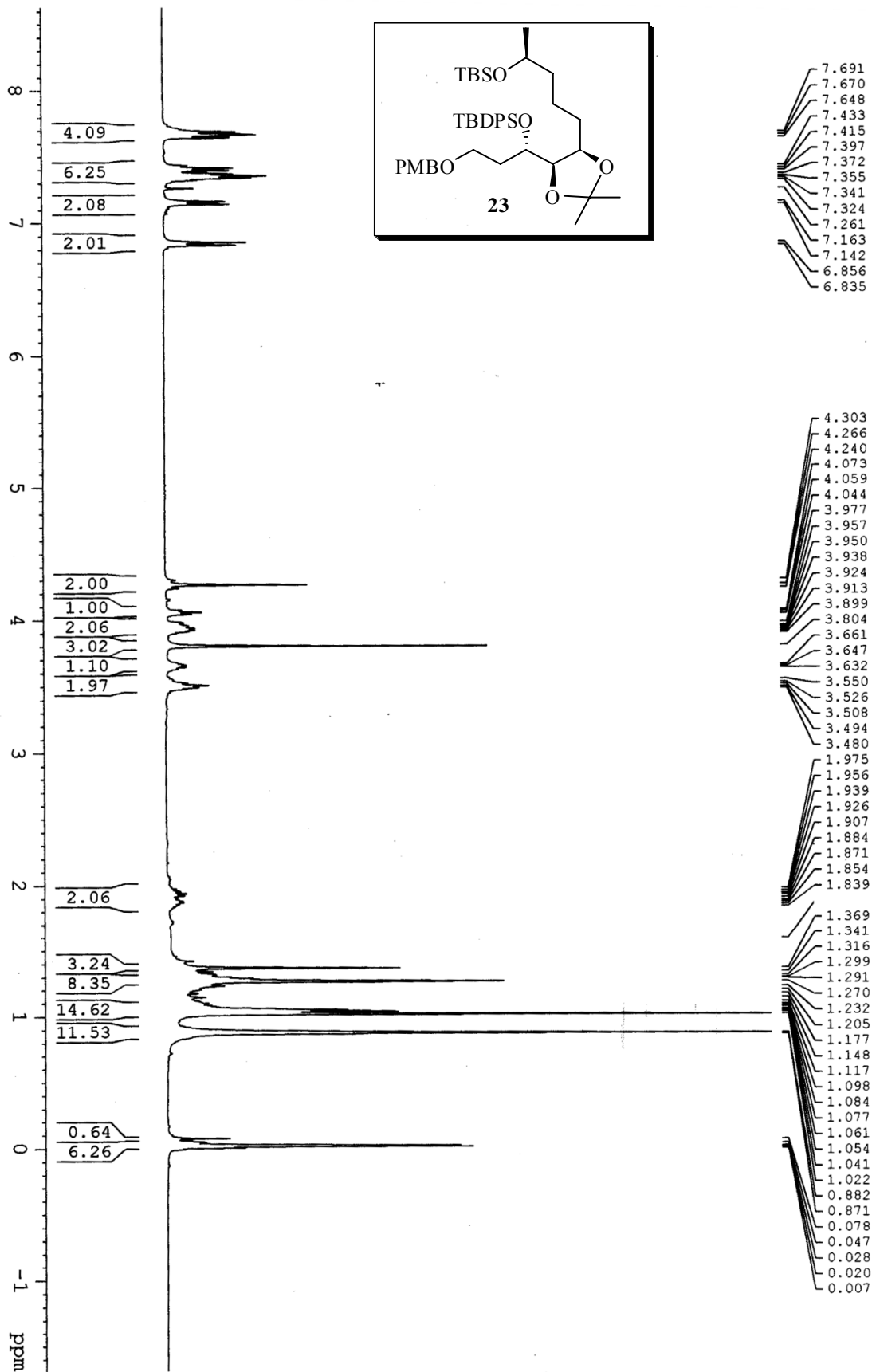
^{13}C -NMR of compound 21 (100MHz, CDCl_3)



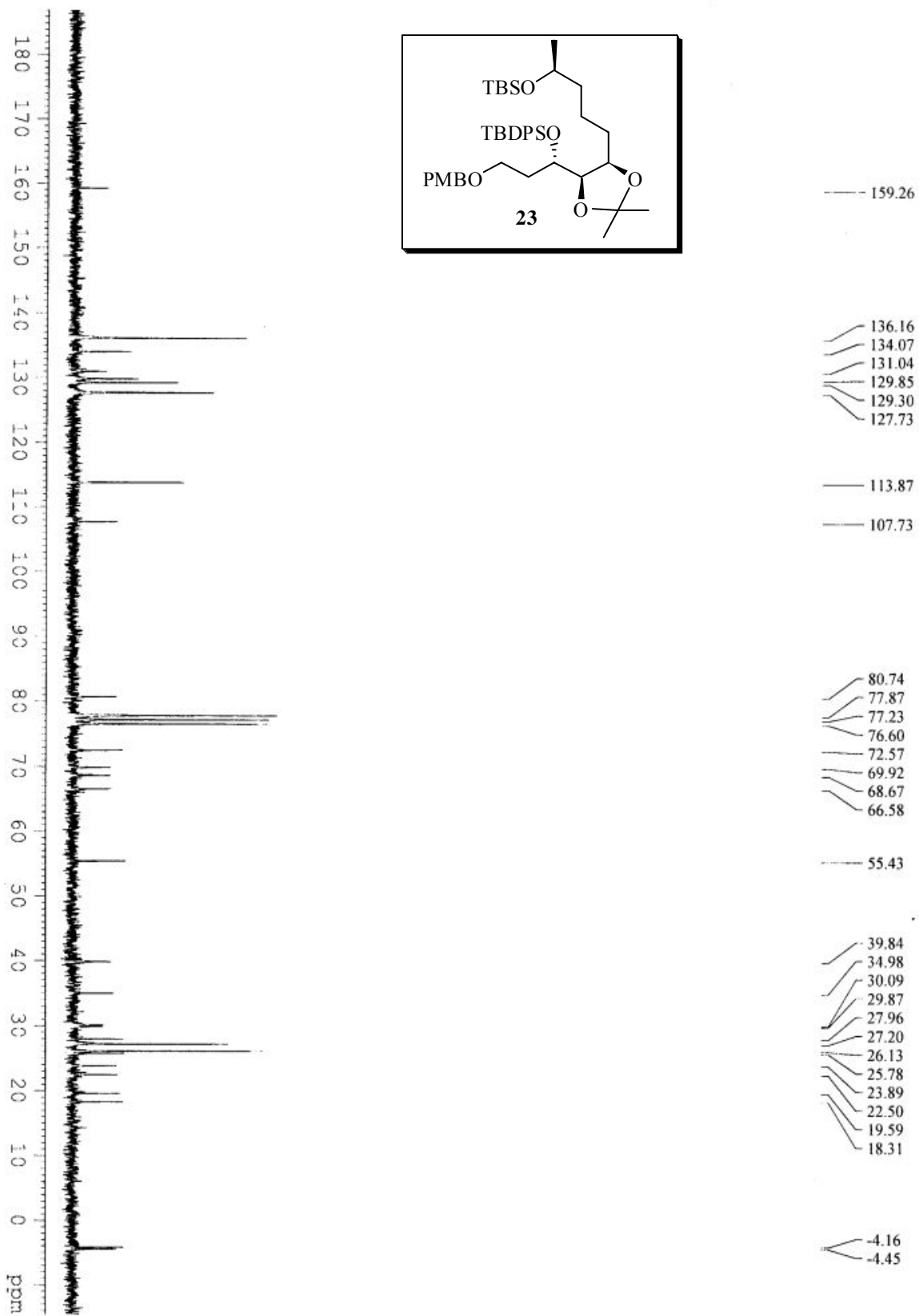
DEPT-NMR of compound 21 (100MHz, CDCl₃)



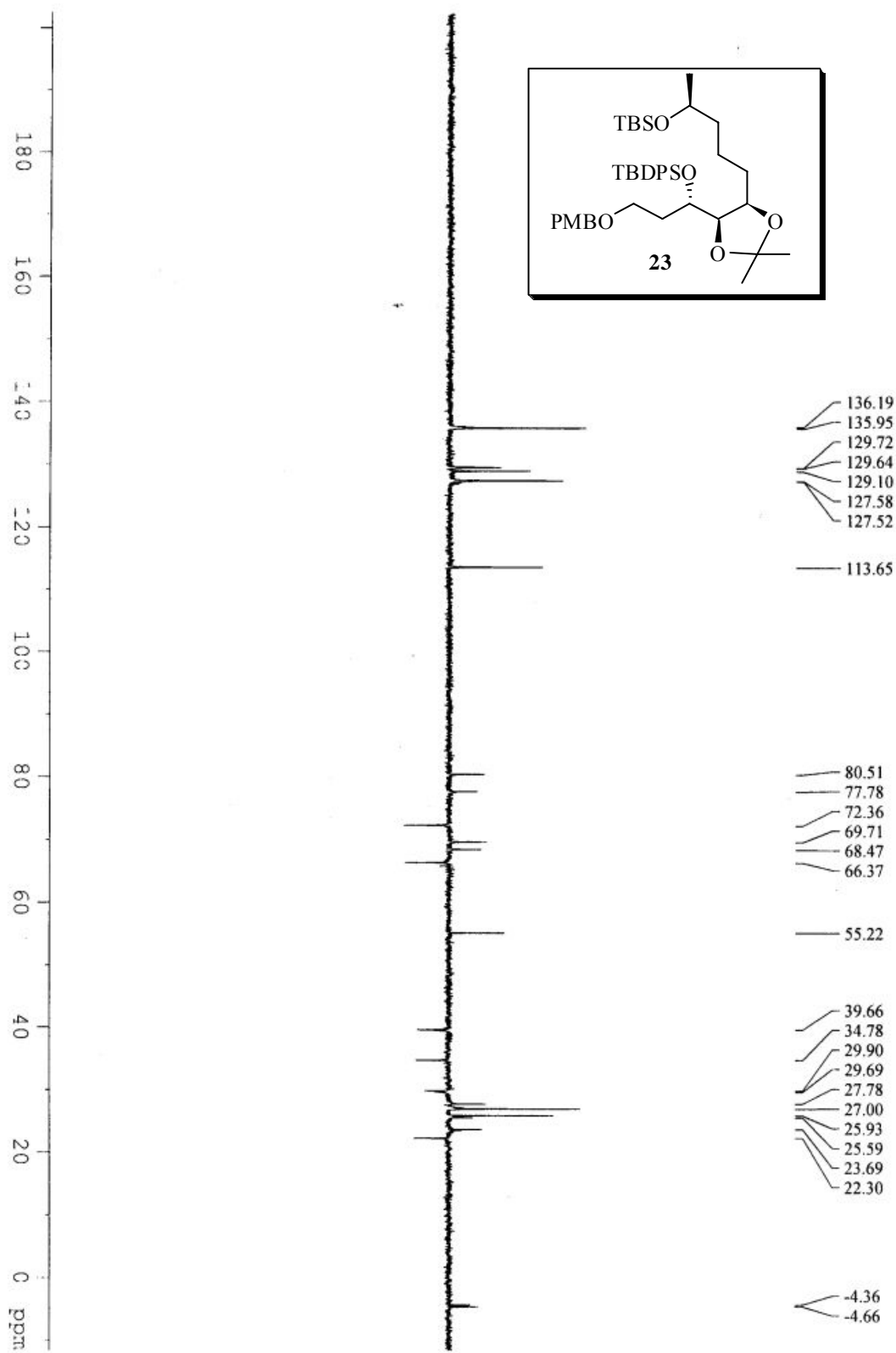
¹H-NMR of compound 23 (400MHz, CDCl₃)



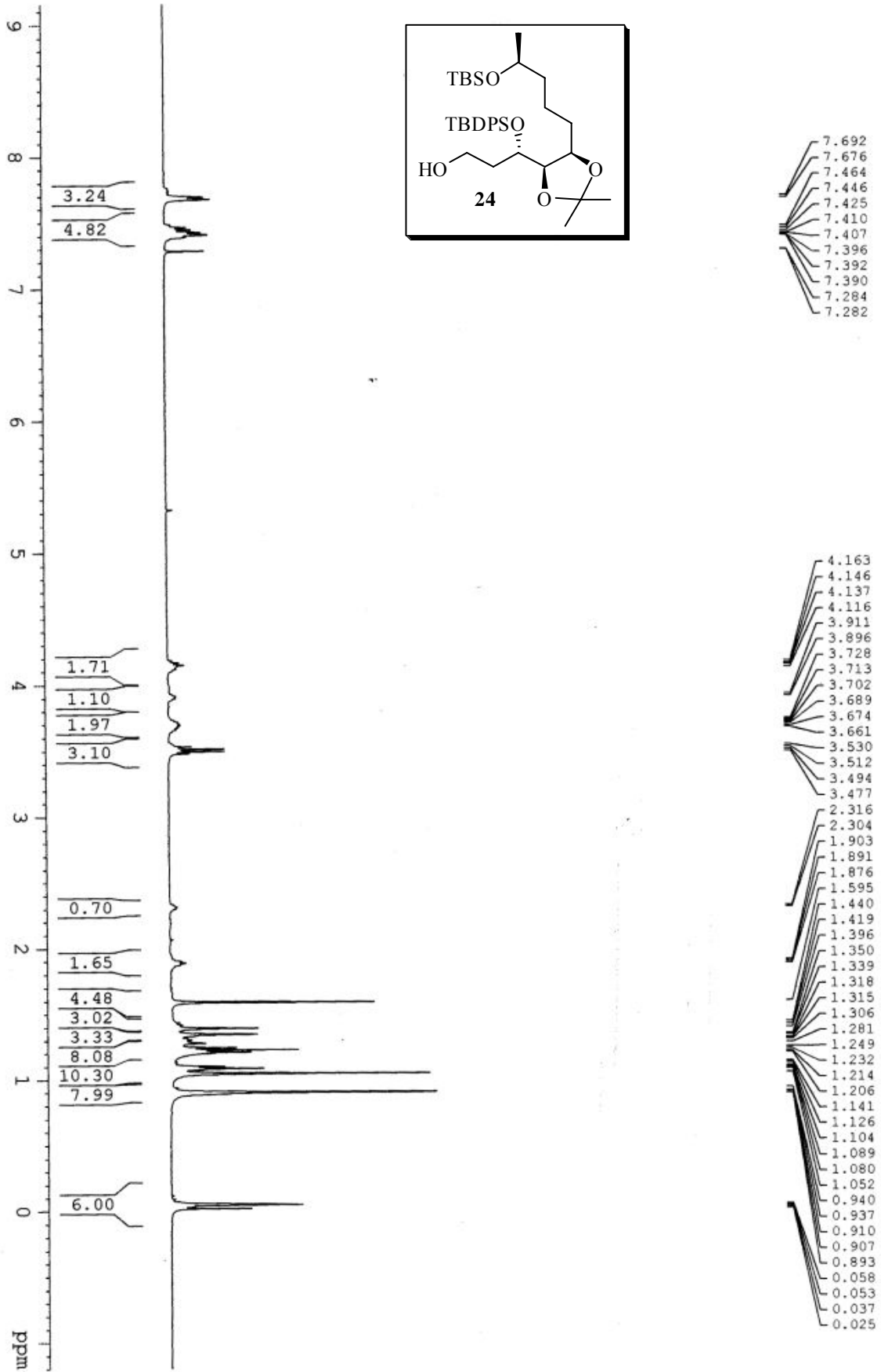
¹³C-NMR of compound 23 (50MHz, CDCl₃)



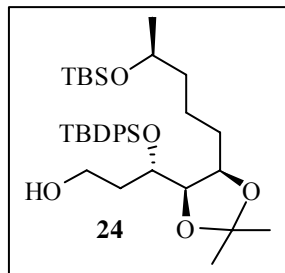
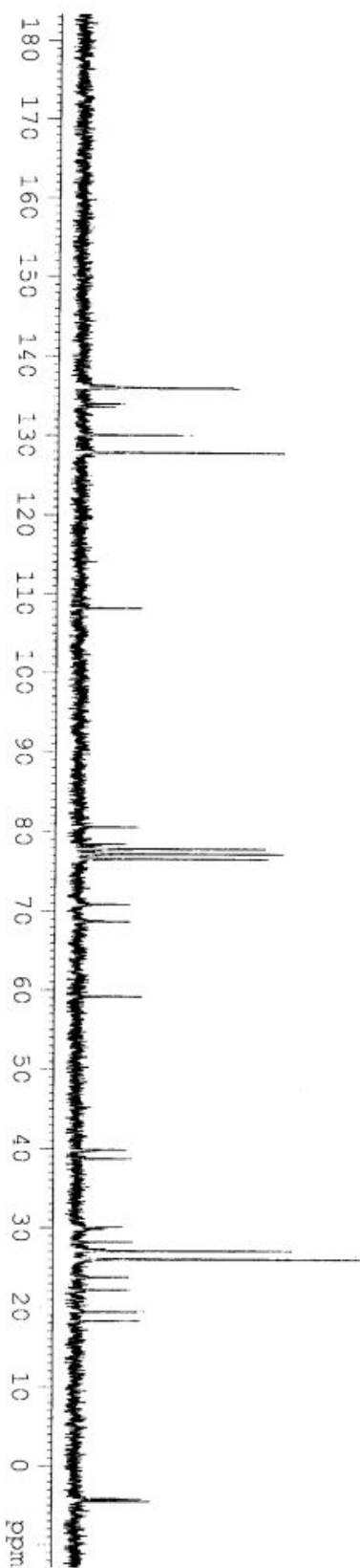
DEPT-NMR of compound 23 (50MHz, CDCl₃)



¹H-NMR of compound 24 (400MHz, CDCl₃)



¹³C-NMR of compound 24 (50MHz, CDCl₃)



136.08
136.00
134.01
133.61
130.07
127.85

108.19

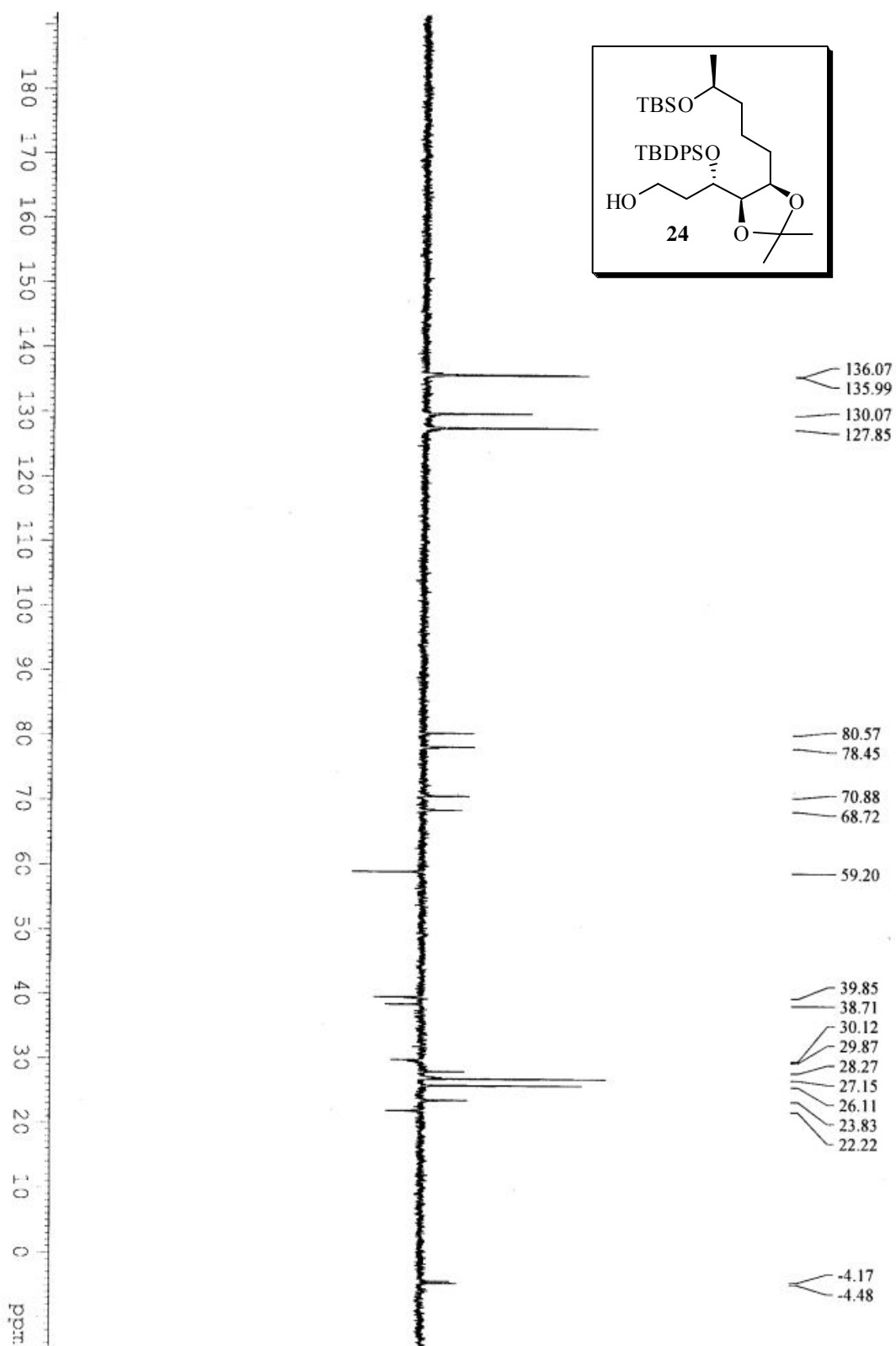
80.59
78.45
78.28
77.86
77.23
76.59
70.87
68.72

59.20

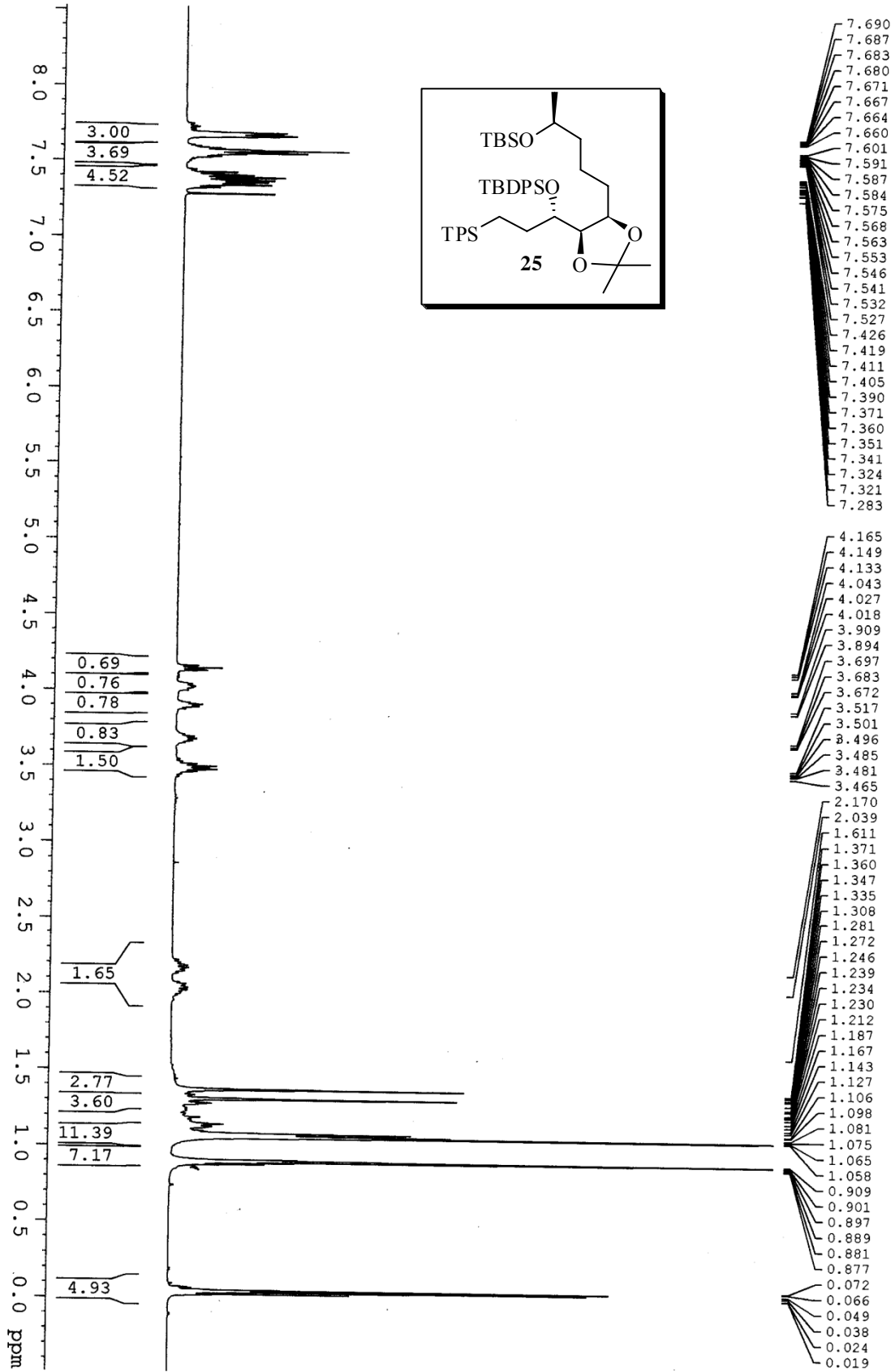
39.84
38.71
30.11
28.26
27.36
27.15
26.11
23.83
22.23
19.46
18.30

-4.17
-4.48

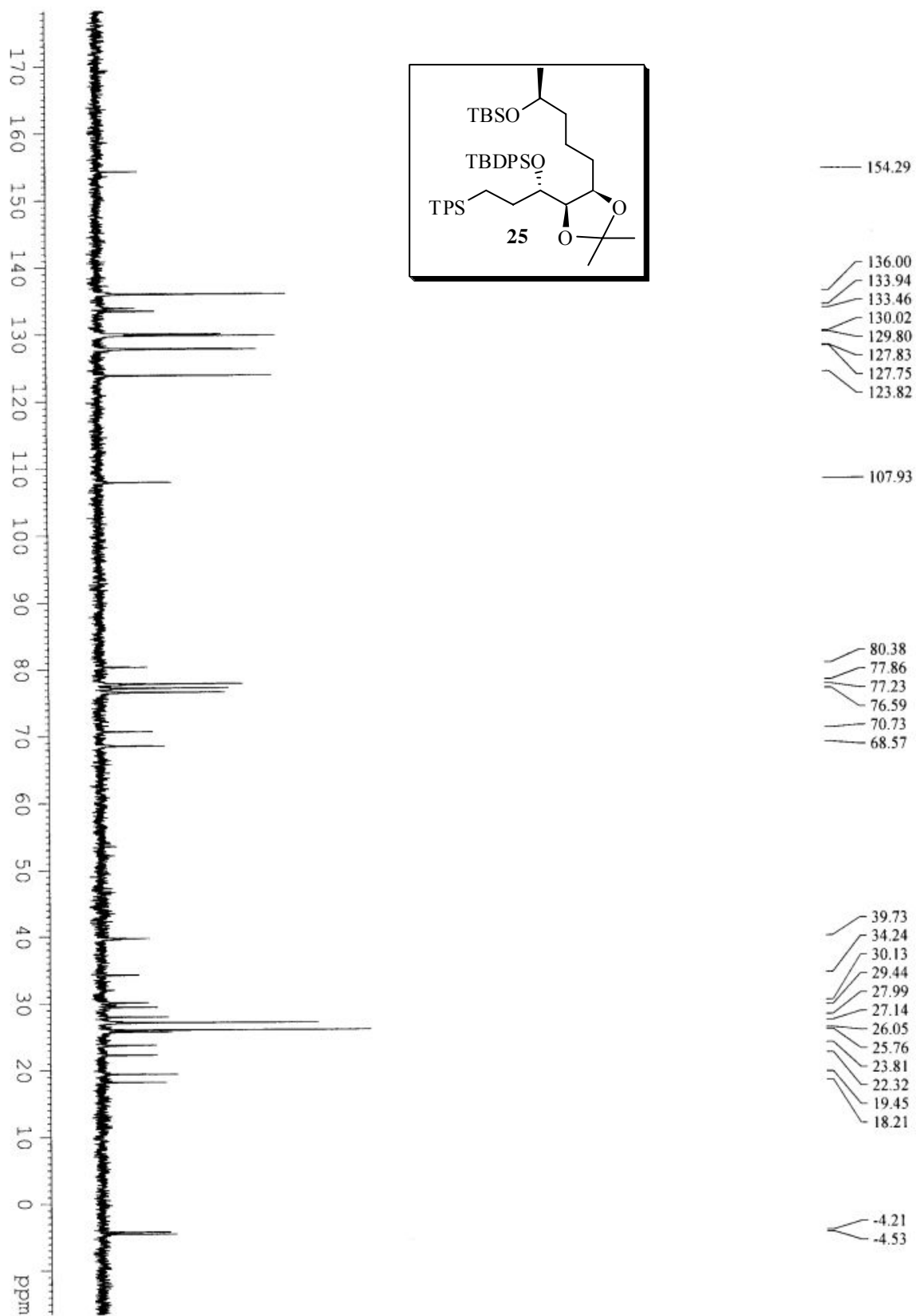
DEPT-NMR of compound 24 (50MHz, CDCl₃)



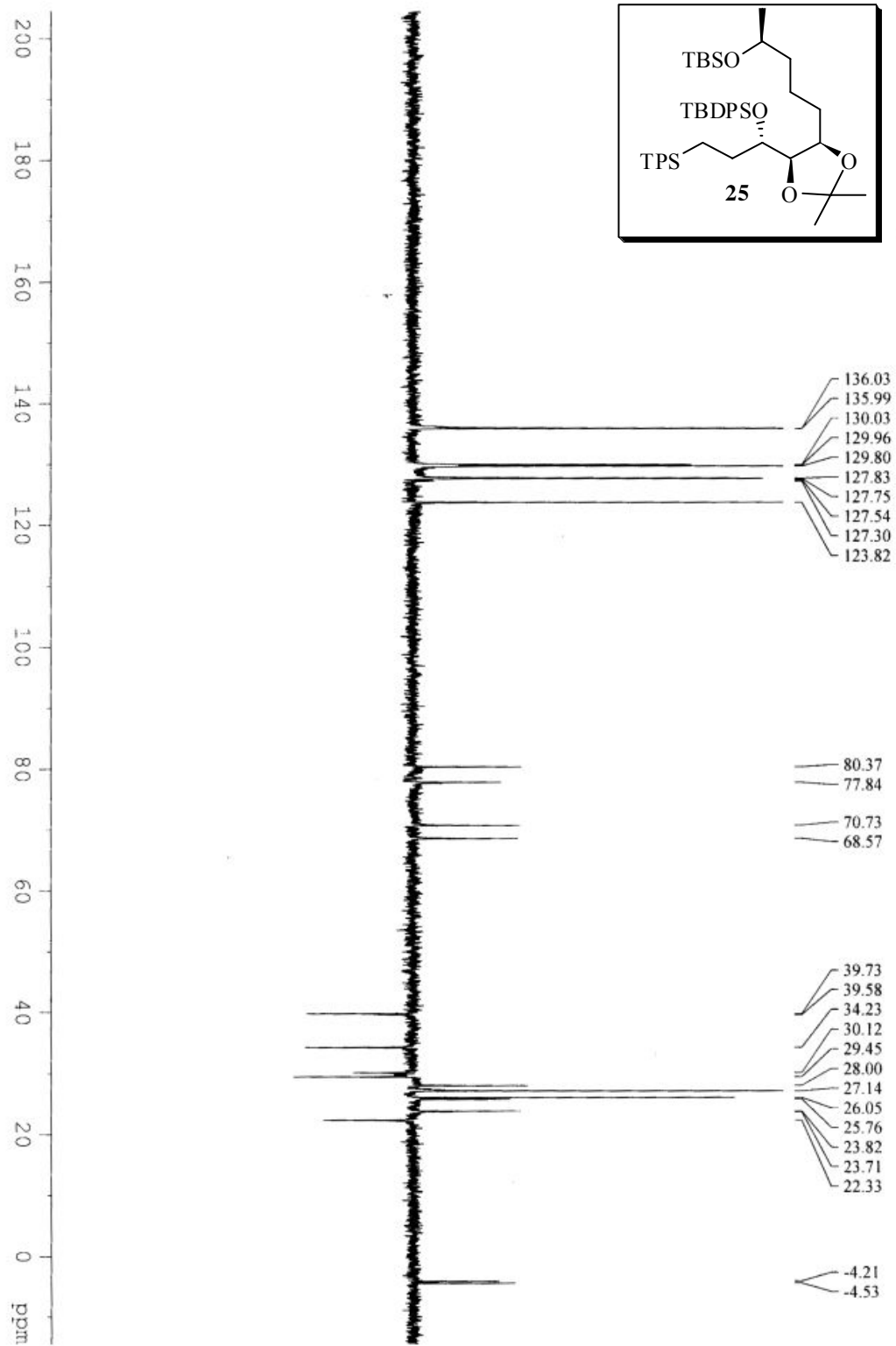
¹H-NMR of compound 25 (400MHz, CDCl₃)



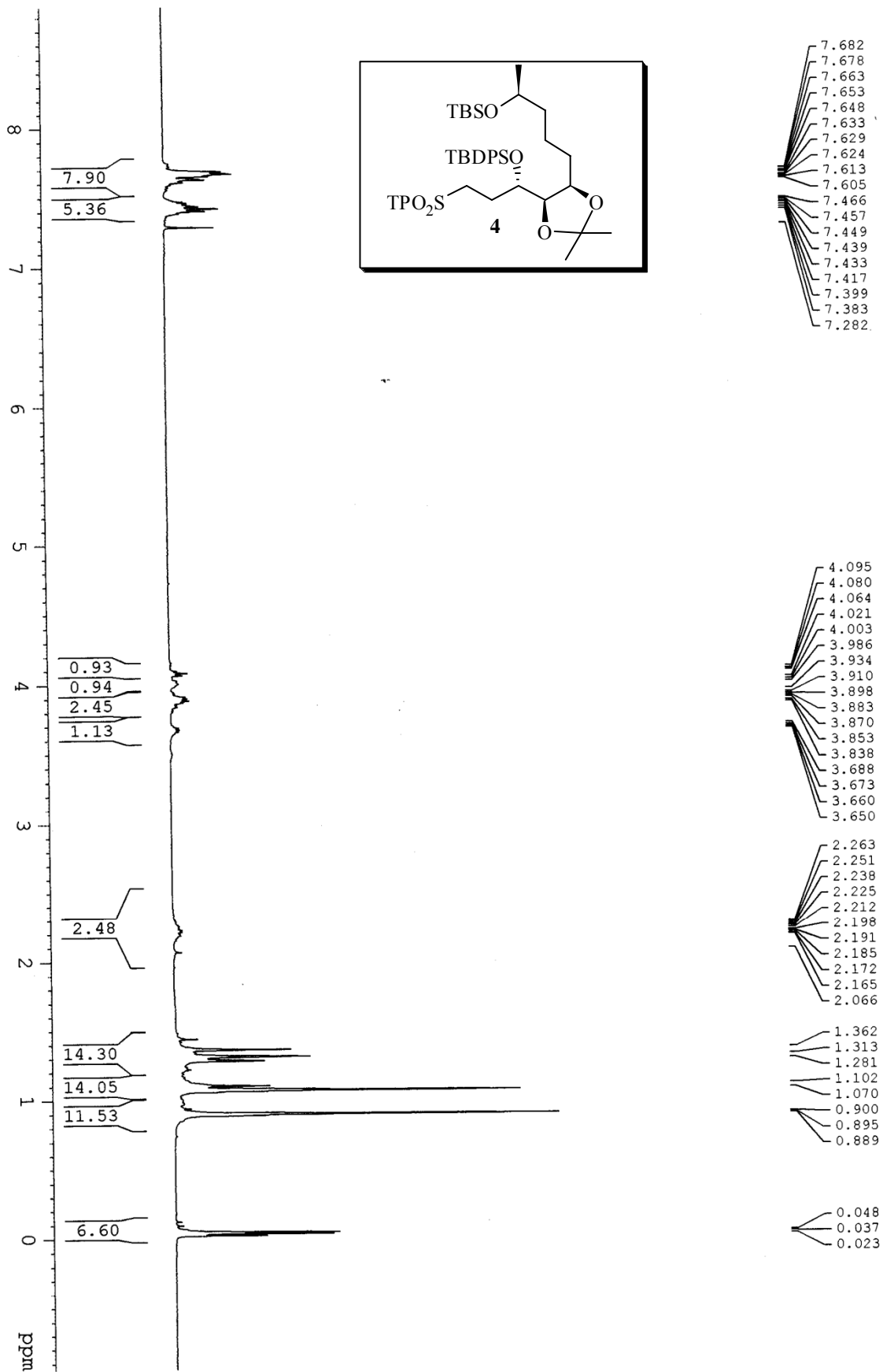
¹³C-NMR of compound 25 (50MHz, CDCl₃)



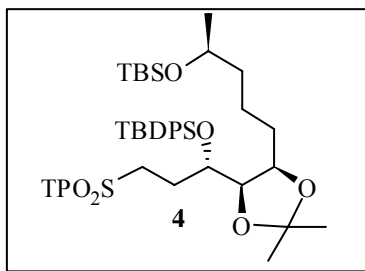
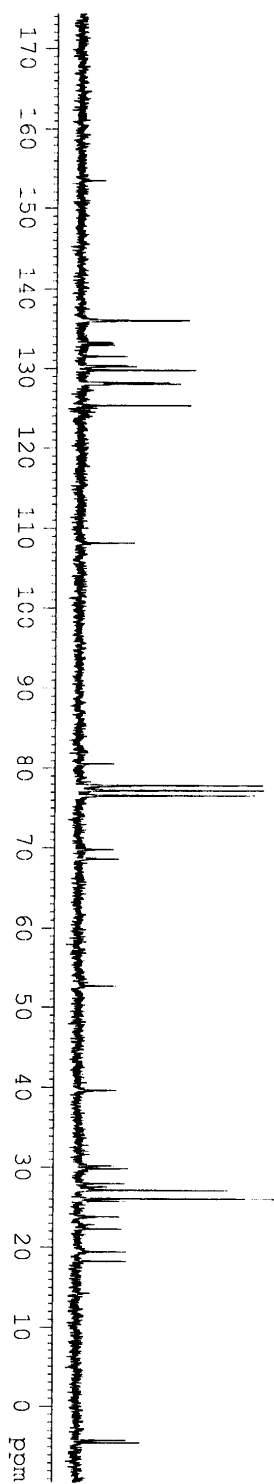
DEPT- NMR of compound 25 (50MHz, CDCl₃)



¹H- NMR of compound 4 (400MHz, CDCl₃)



¹³C-NMR of compound 4 (50MHz, CDCl₃)



- 153.57
- 136.06
- 135.99
- 133.28
- 133.15
- 132.92
- 131.51
- 130.35
- 130.24
- 129.79
- 128.10
- 127.95
- 125.30

- 108.19

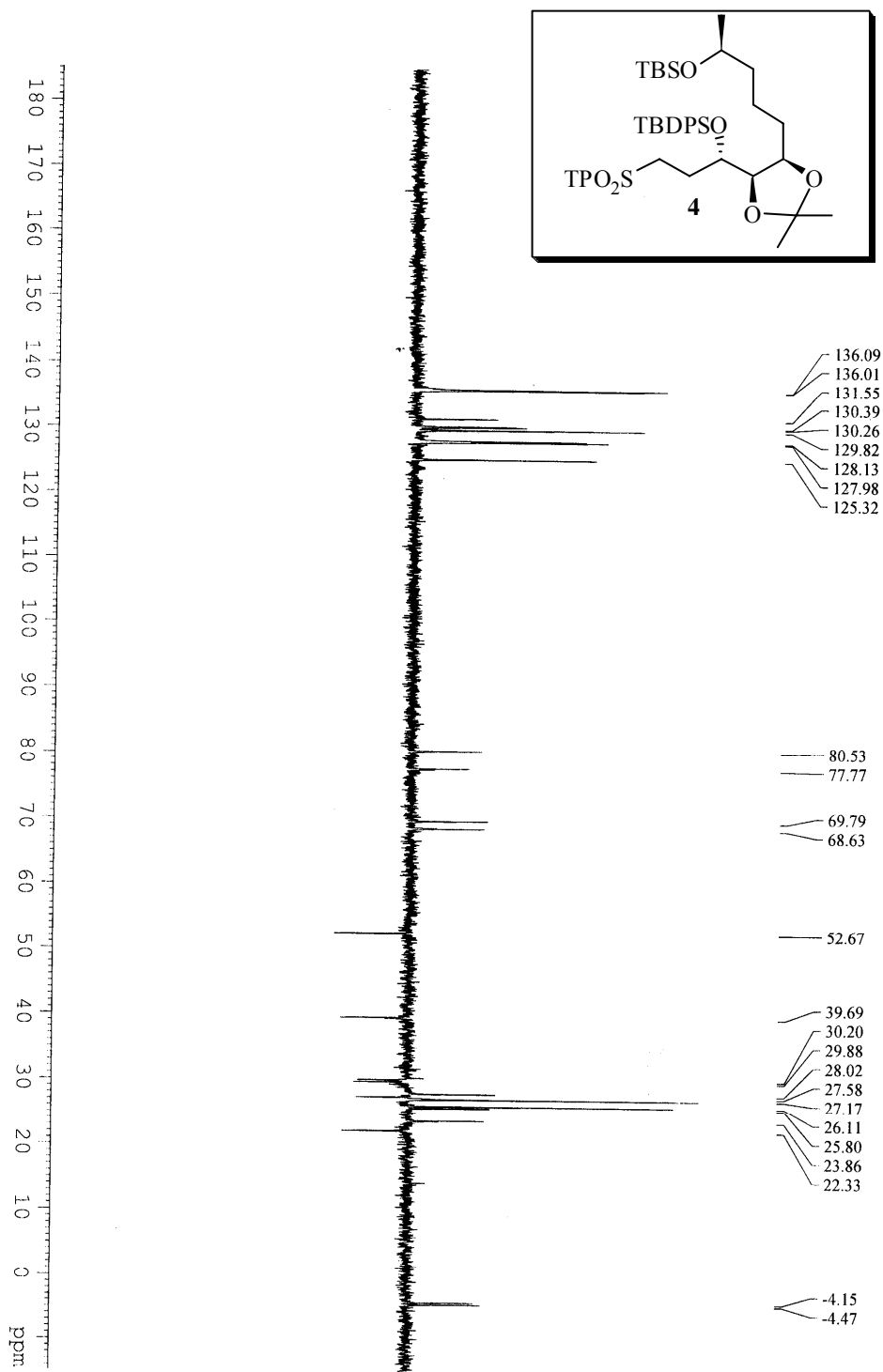
- 80.53
- 77.86
- 77.23
- 76.59
- 69.79
- 68.61

- 52.67

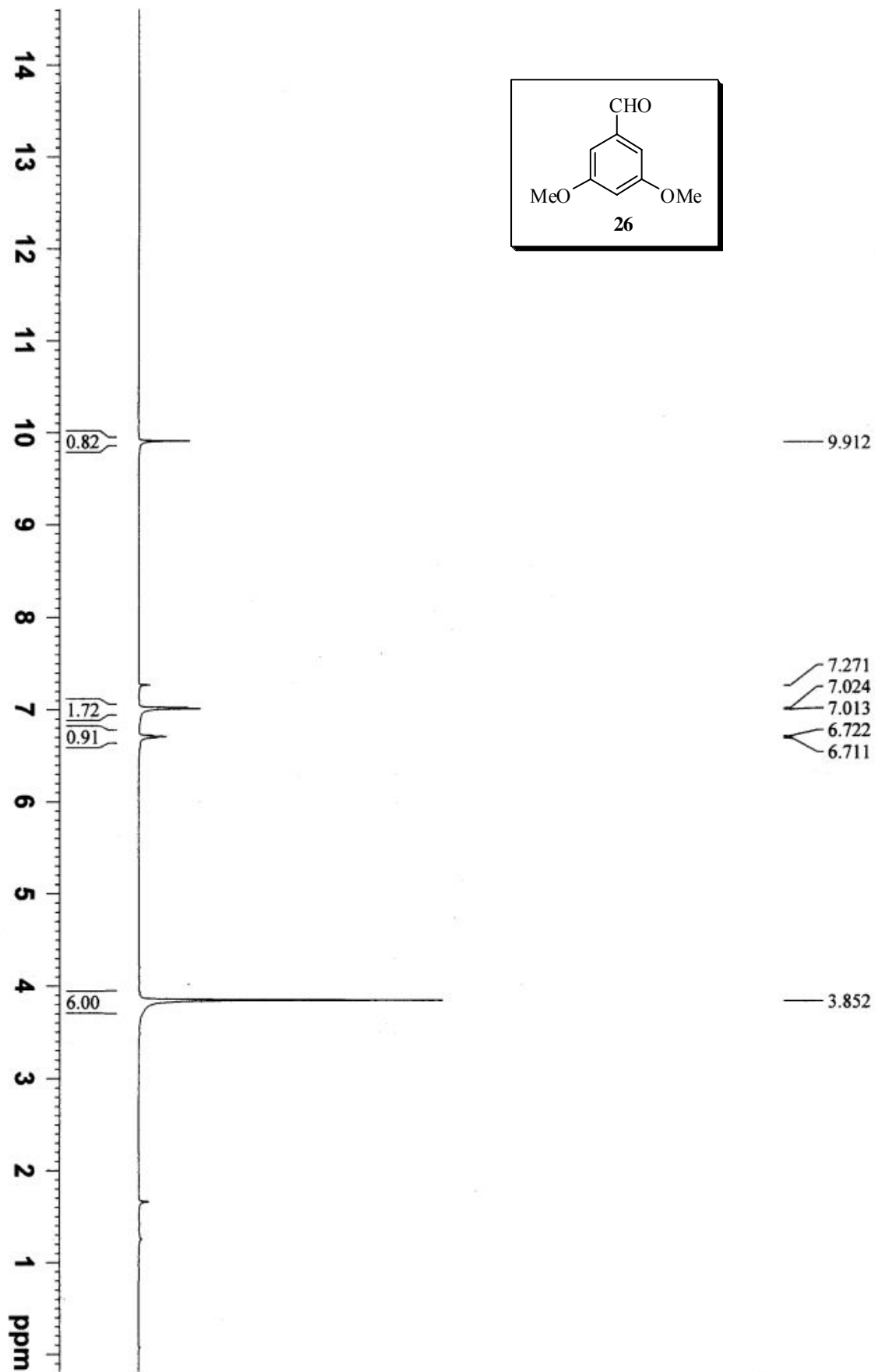
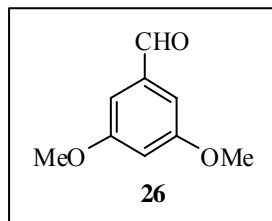
- 39.67
- 30.19
- 29.84
- 27.99
- 27.57
- 27.15
- 26.09
- 25.77
- 23.83
- 22.85
- 22.31
- 19.44
- 18.28

- -4.18
- -4.50

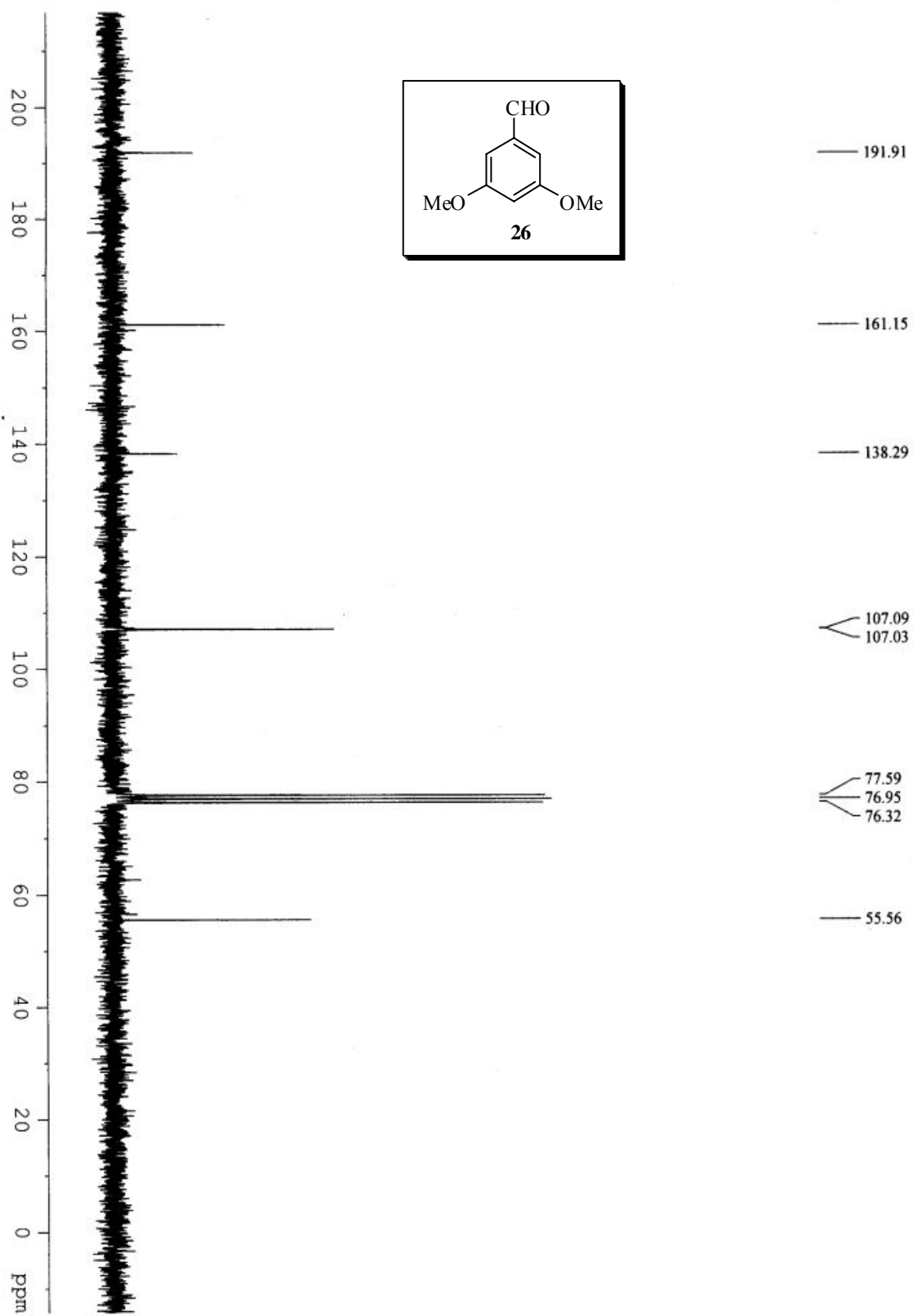
DEPT-NMR of compound 4 (50MHz, CDCl₃)



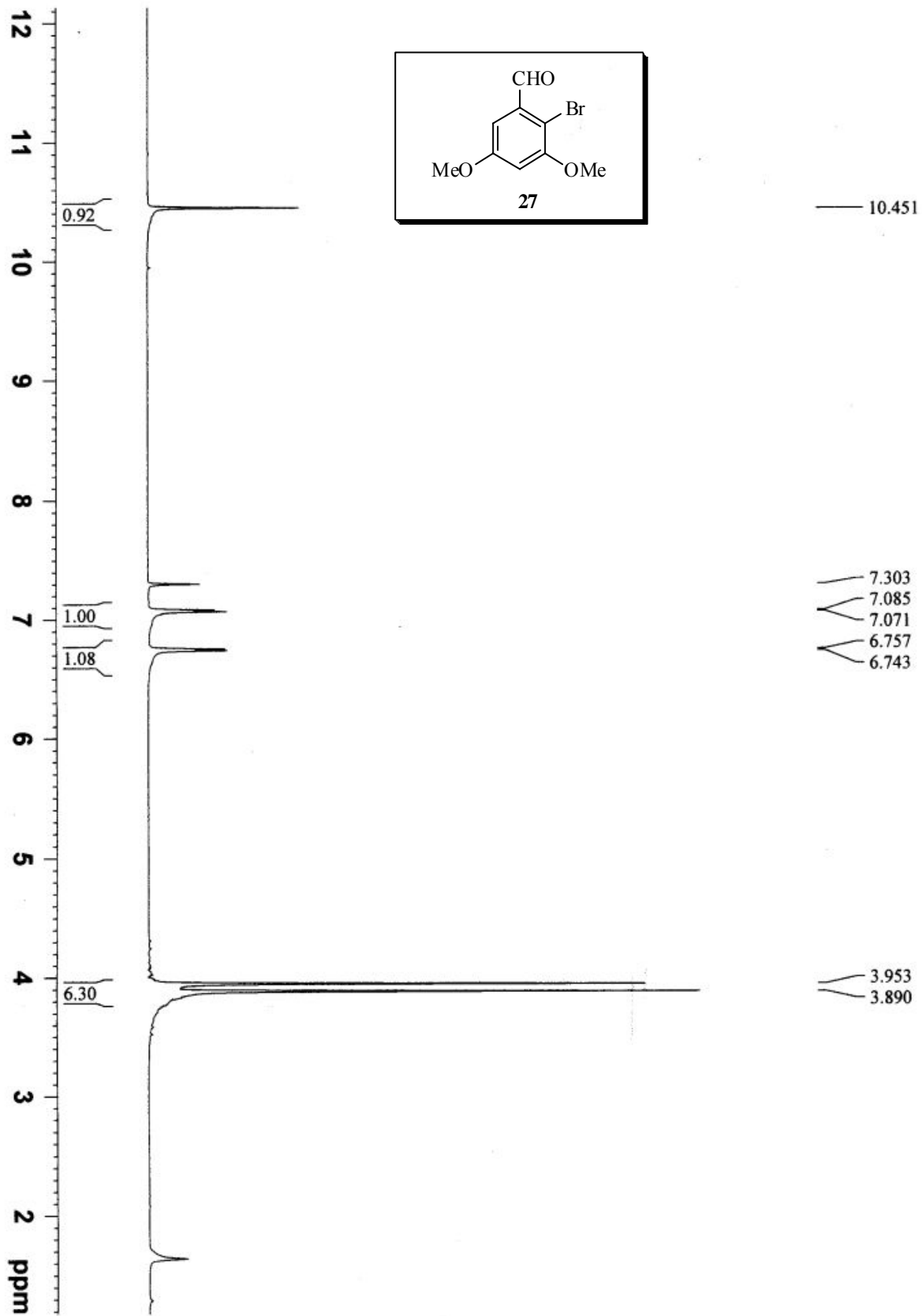
¹H- NMR of compound 26 (200MHz, CDCl₃)



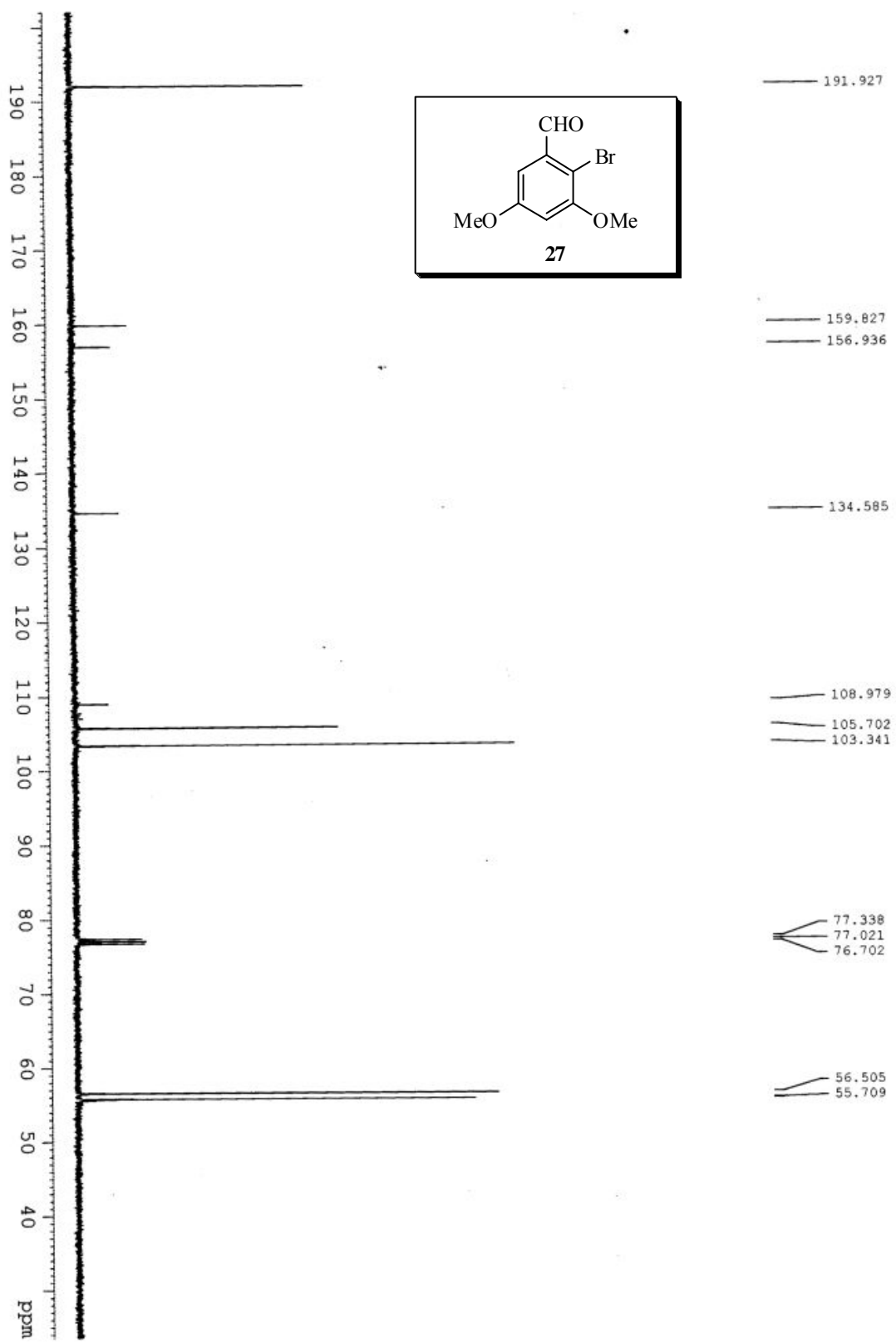
¹³C-NMR of compound 26 (50MHz, CDCl₃)



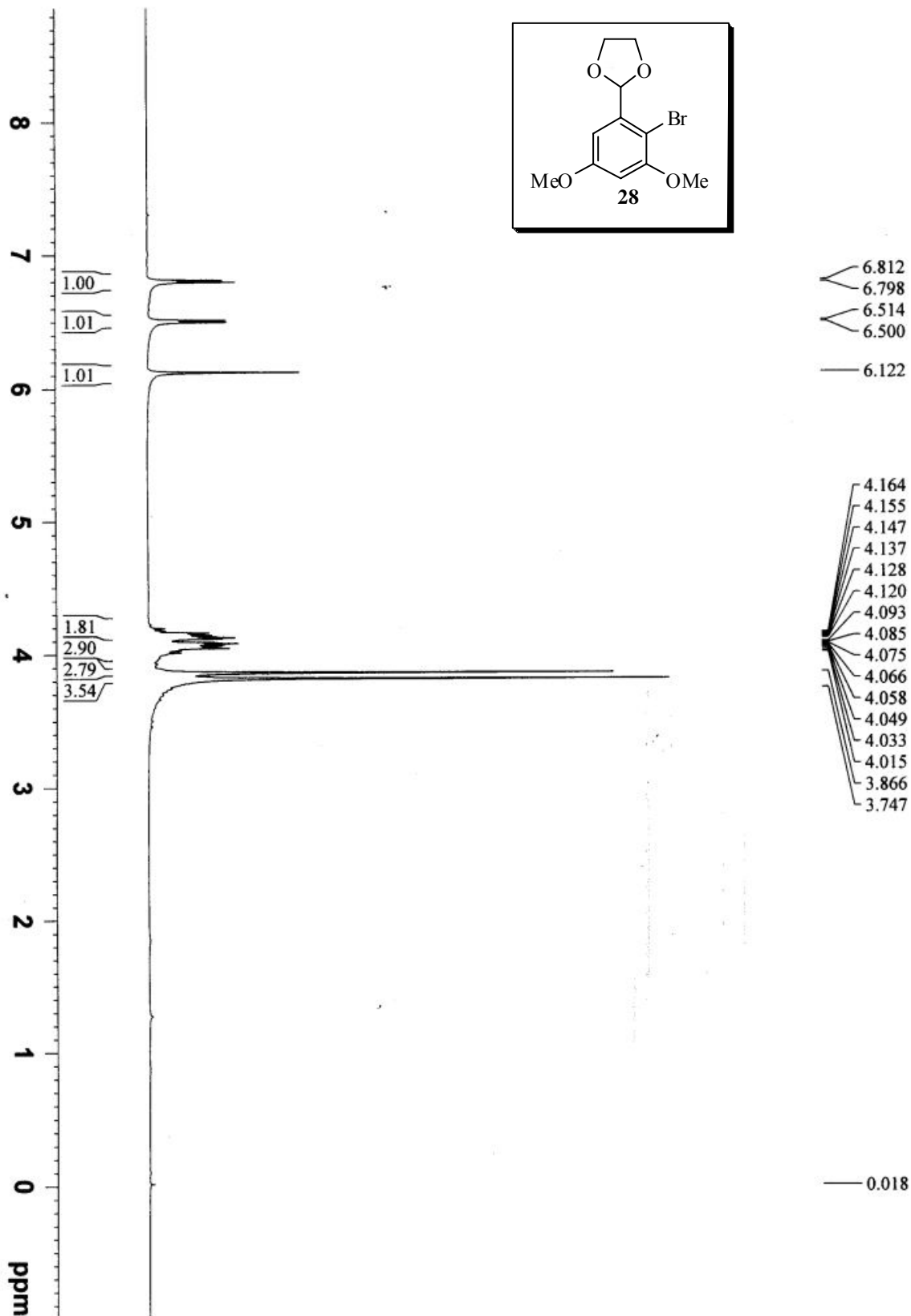
¹H- NMR of compound 27 (200MHz, CDCl₃)



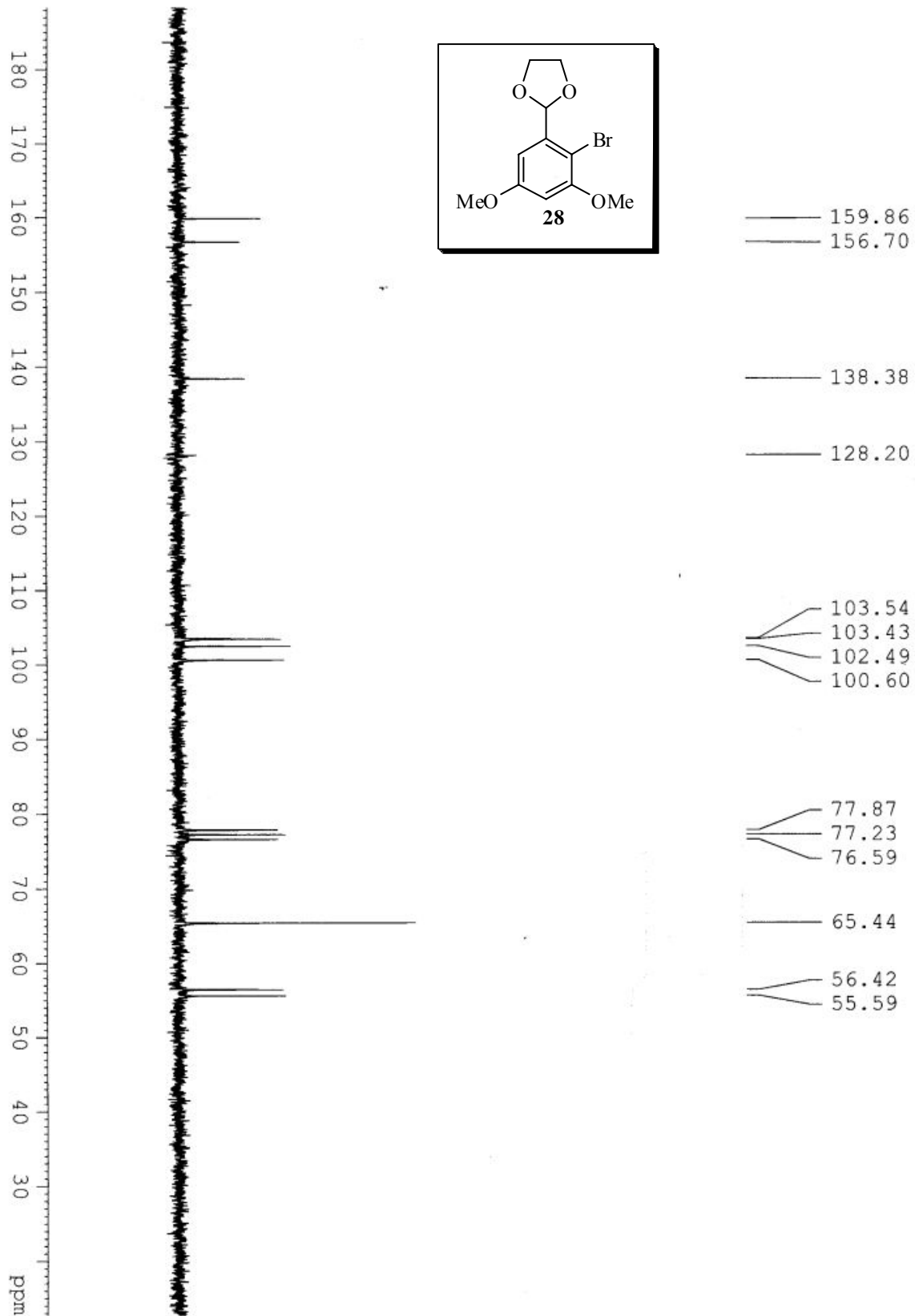
¹³C-NMR of compound 27 (100MHz, CDCl₃)



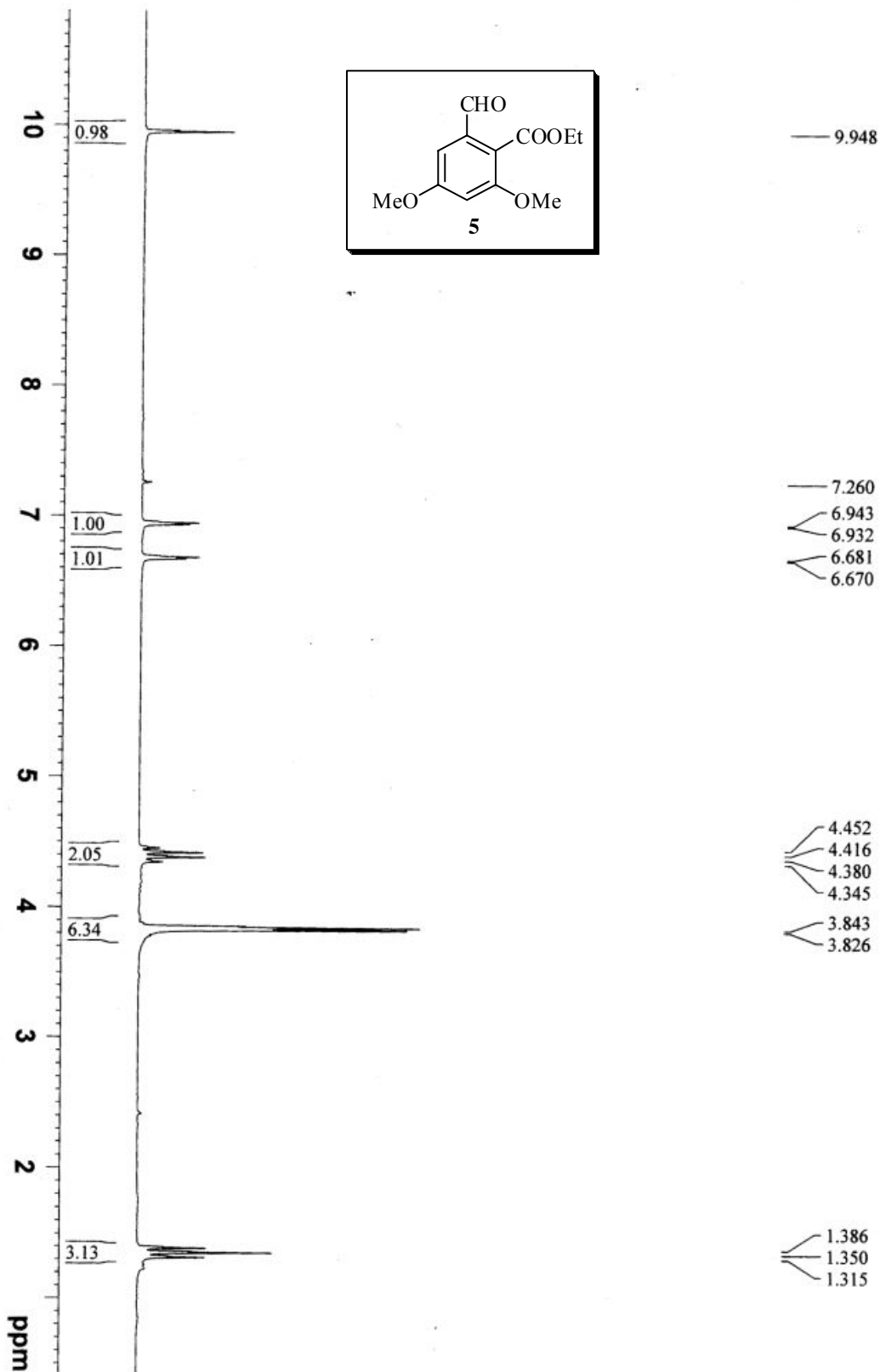
¹H-NMR of compound 28 (200MHz, CDCl₃)



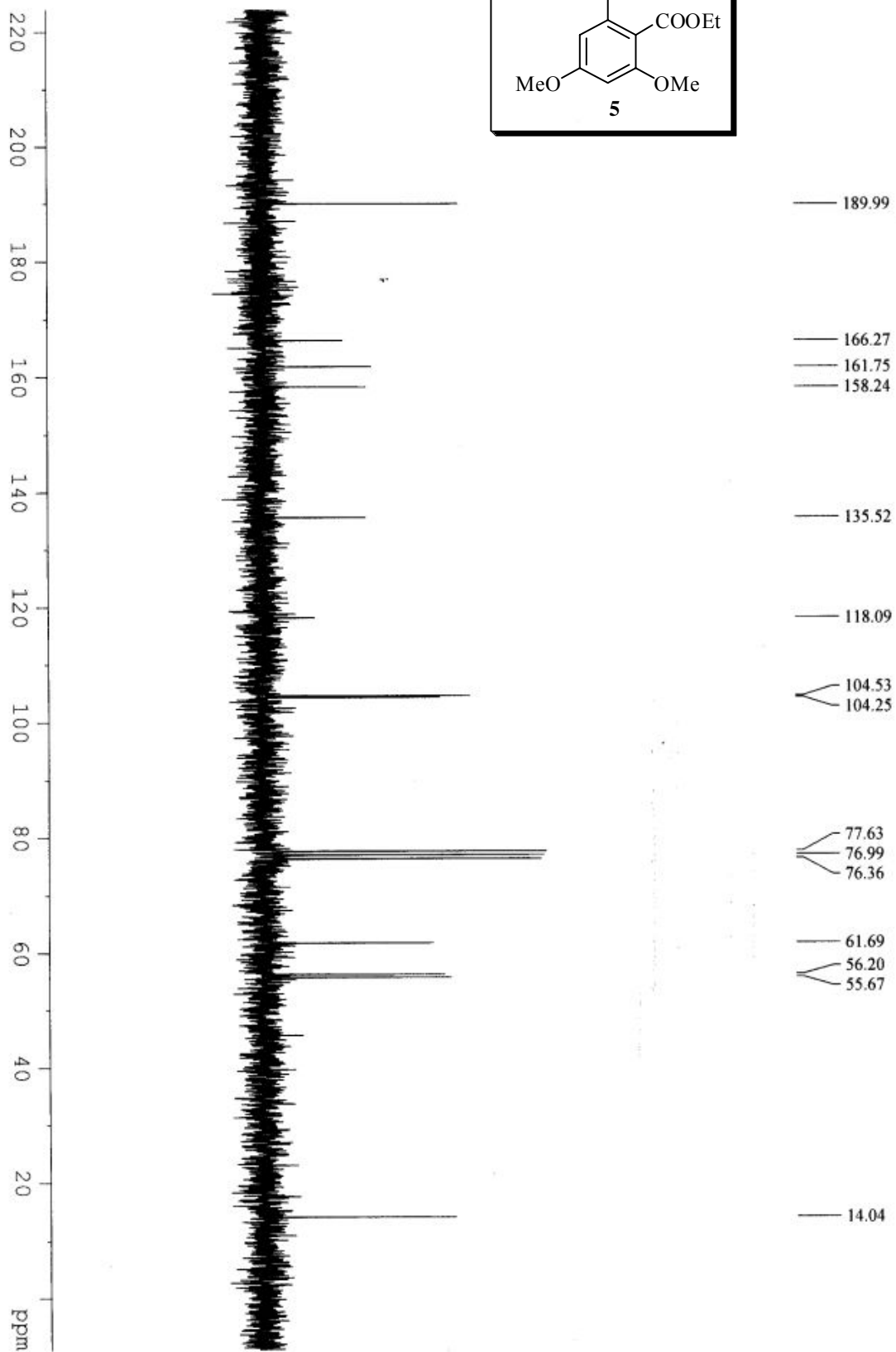
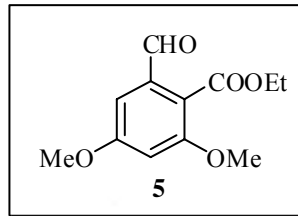
^{13}C -NMR of compound 28 (50MHz, CDCl_3)



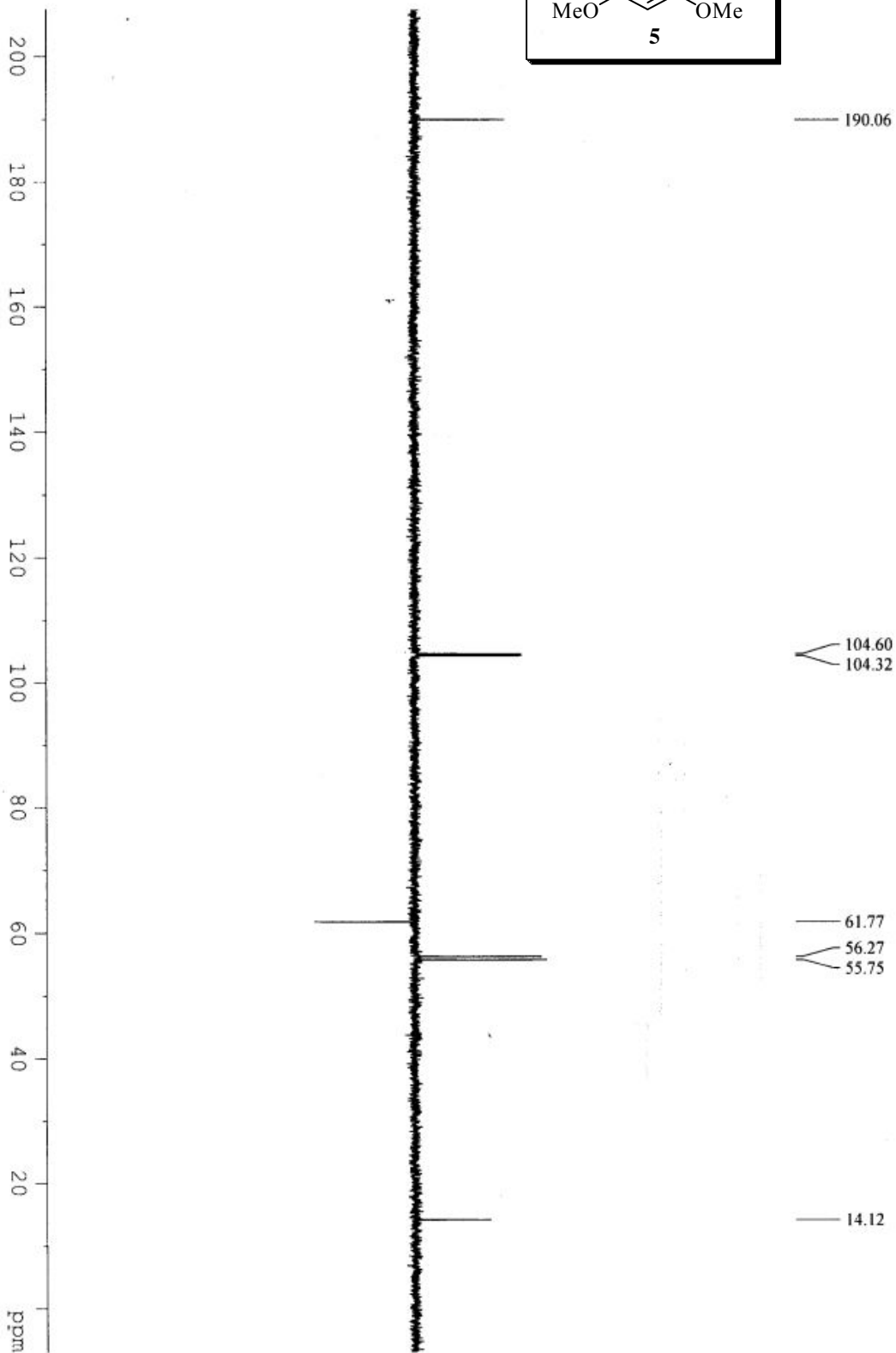
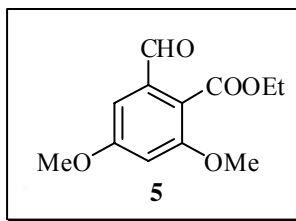
¹H- NMR of compound 5 (200MHz, CDCl₃)



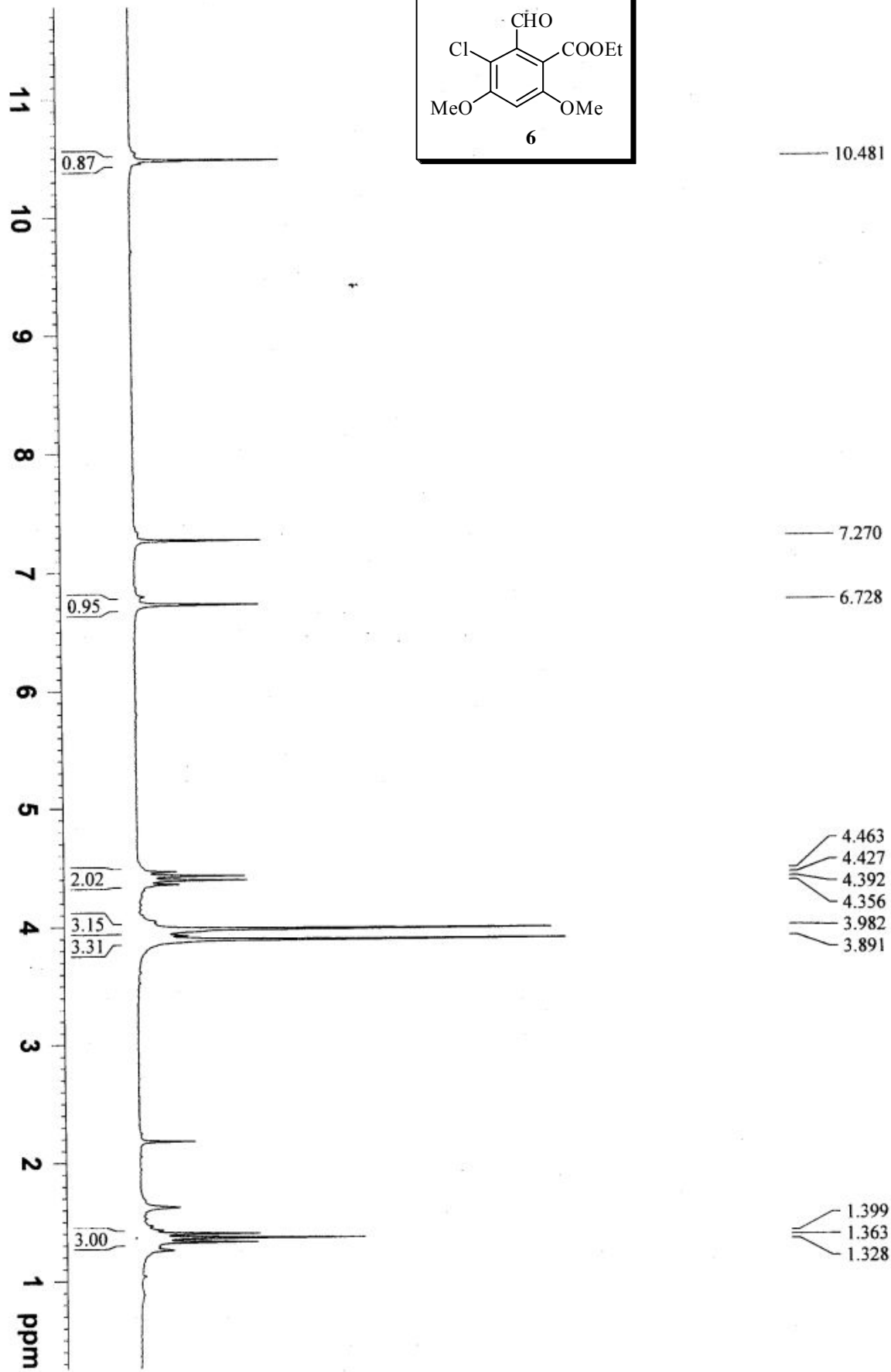
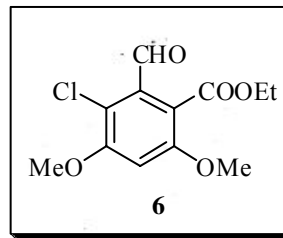
¹³C-NMR of compound 5 (50MHz, CDCl₃)



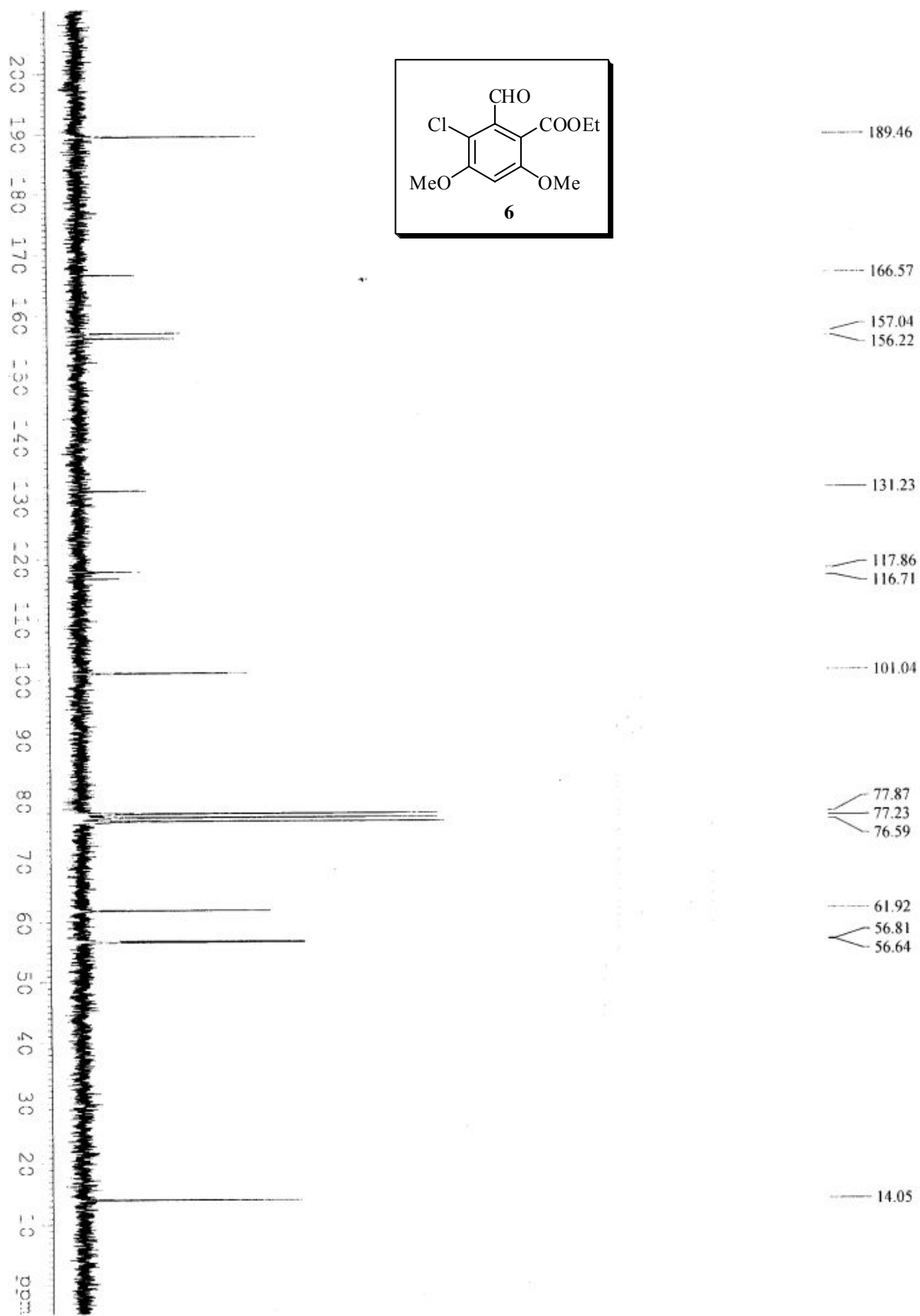
DEPT- NMR of compound 5 (50MHz, CDCl₃)



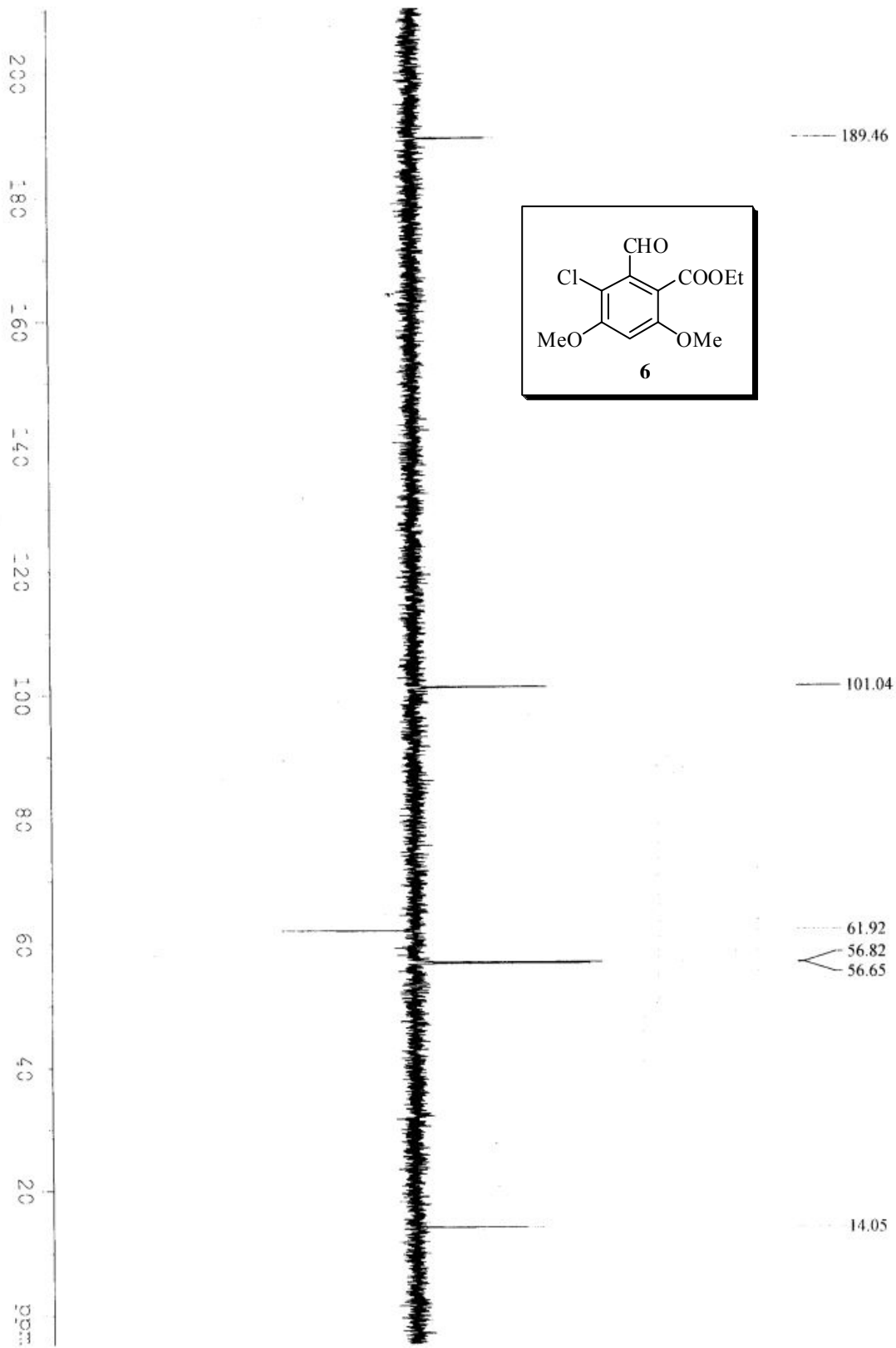
¹H-NMR of compound 6 (200MHz, CDCl₃)



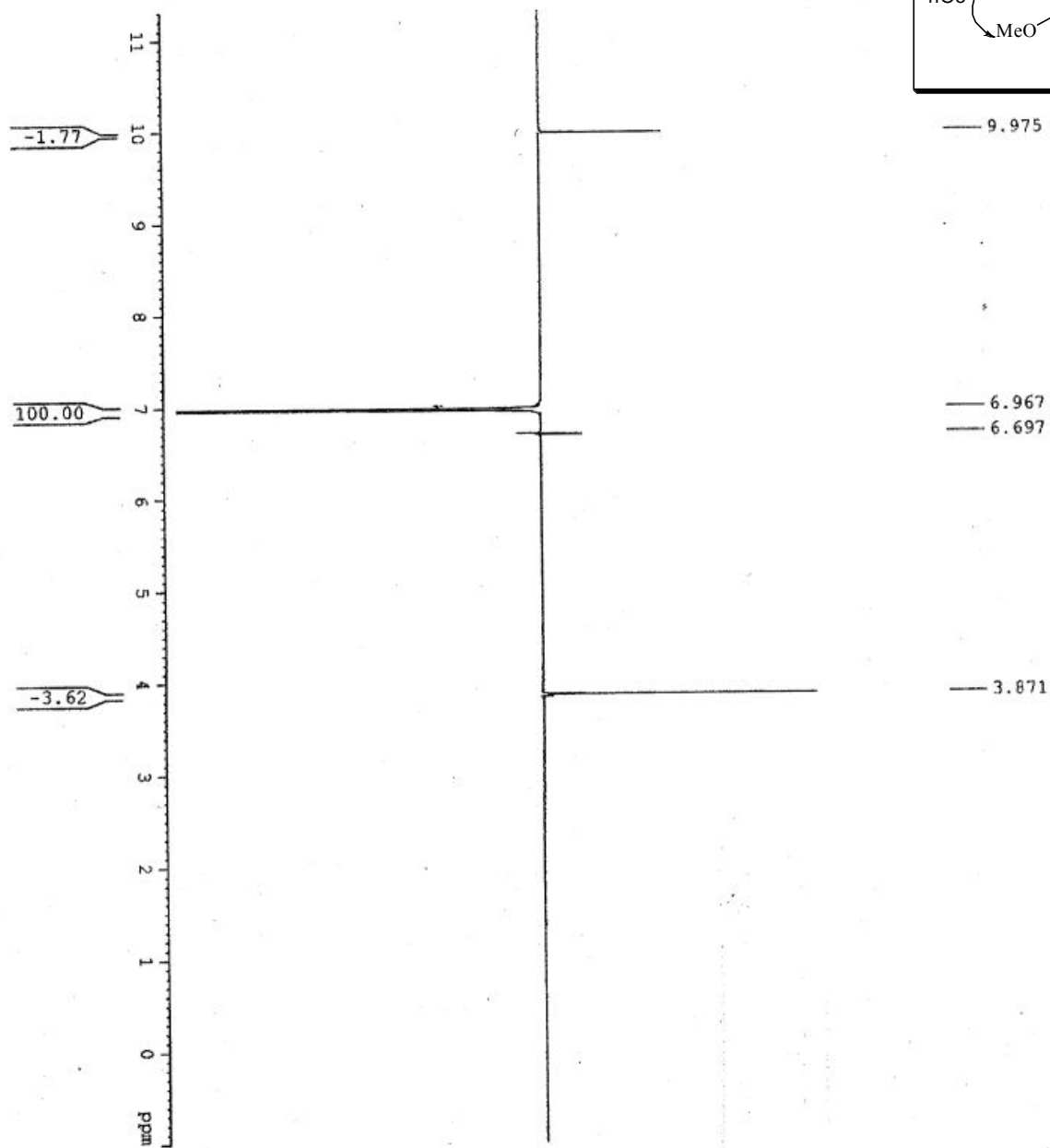
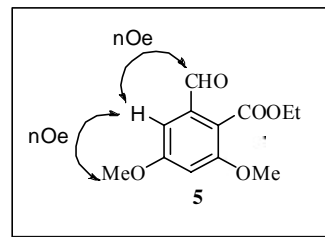
¹³C-NMR of compound 6 (50MHz, CDCl₃)



DEPT- NMR of compound 6 (50MHz, CDCl₃)

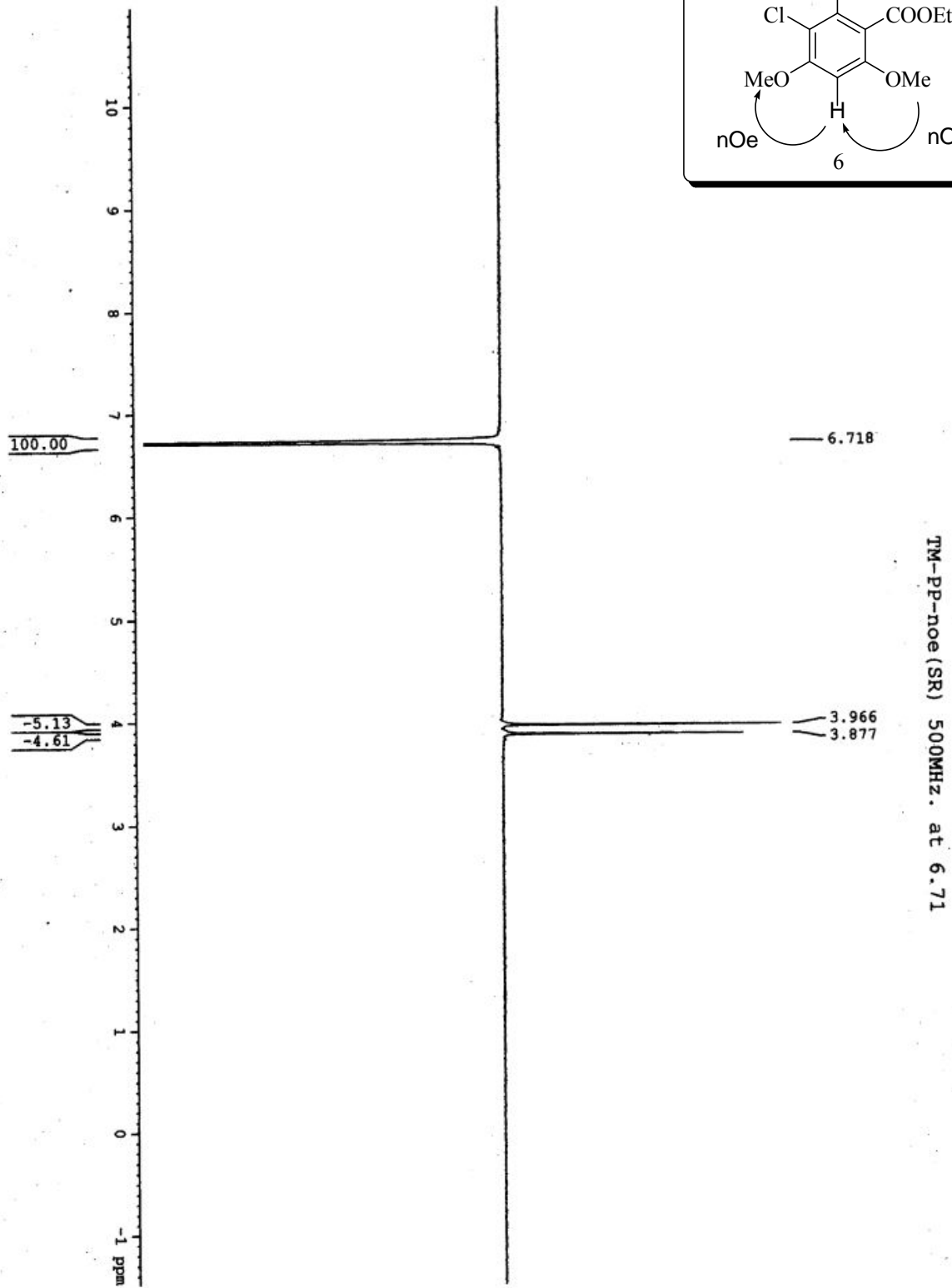
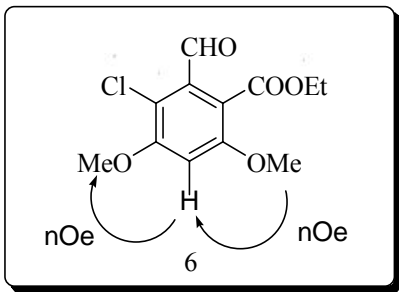


NOE spectra of compound 5 (500 MHz, CDCl₃)

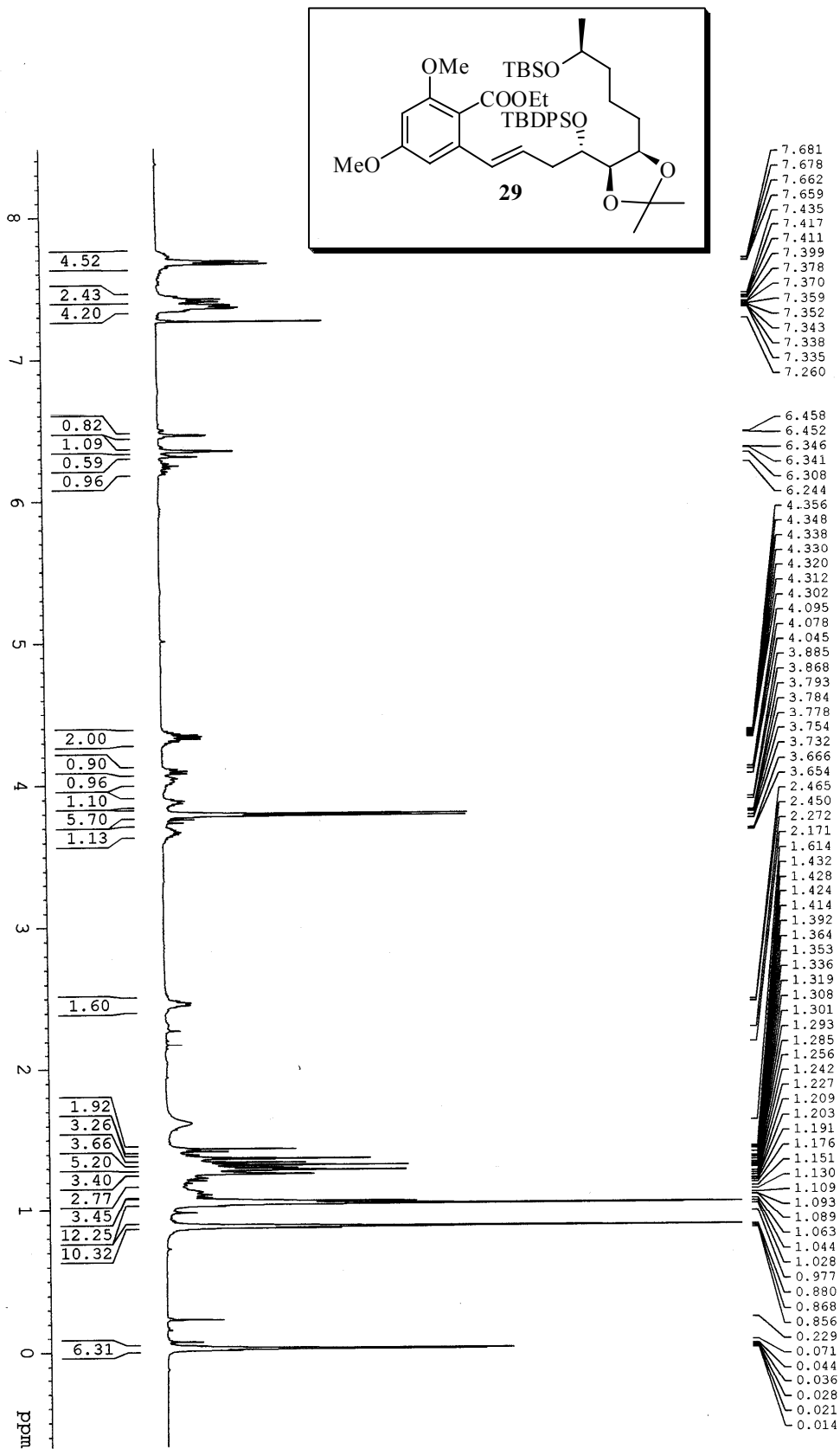


TMC-PP-1-noe-1H(SR) 500MHZ. at 6.9668

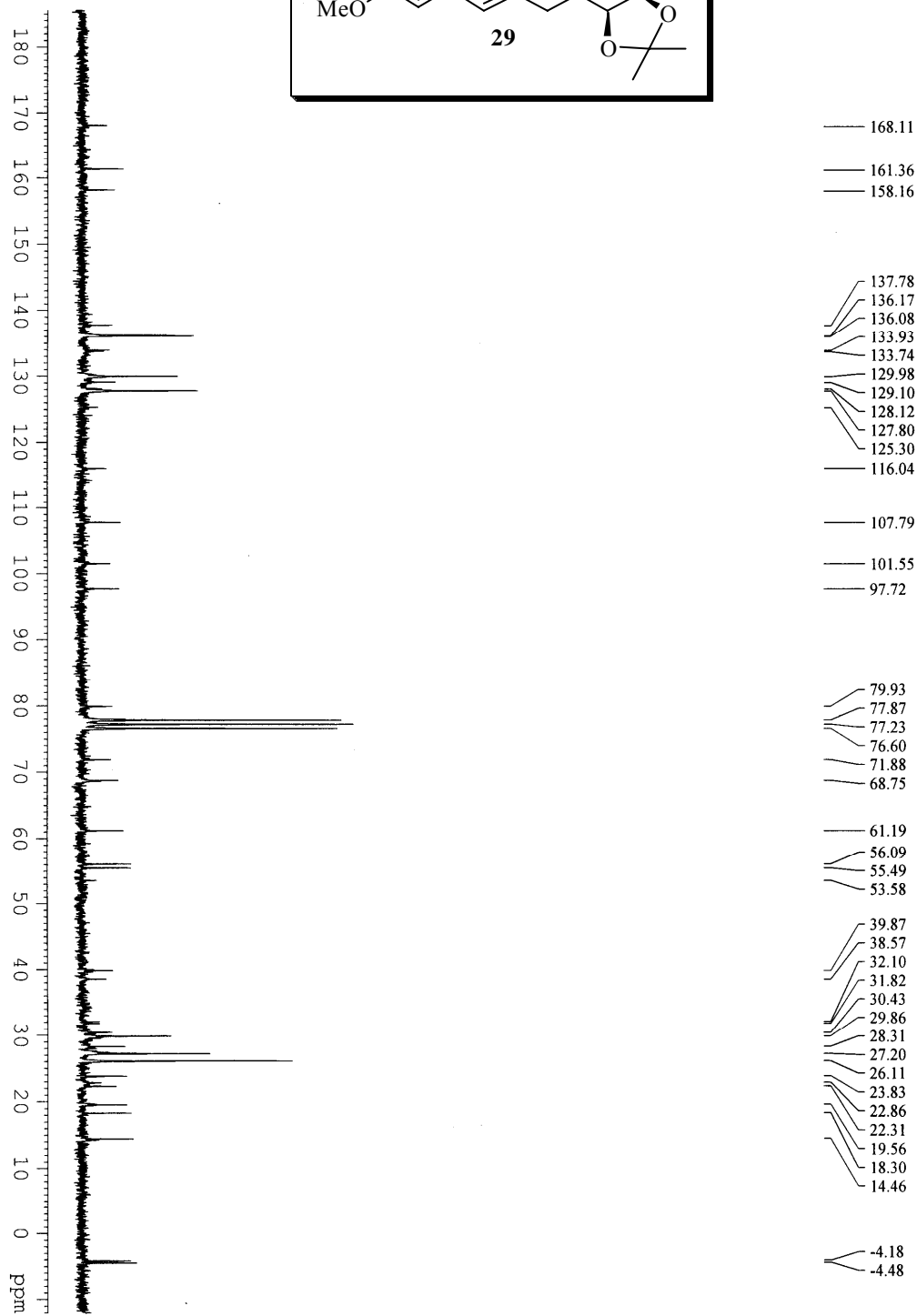
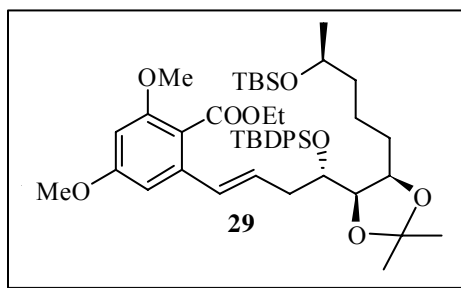
NOE spectra of compound 6 (500 MHz, CDCl₃)



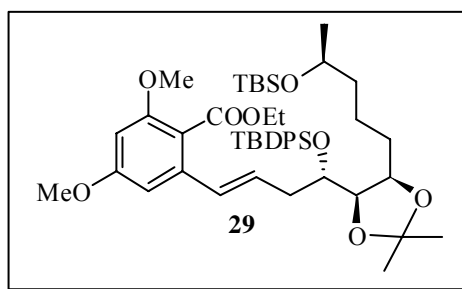
¹H-NMR of compound 29 (400MHz, CDCl₃)



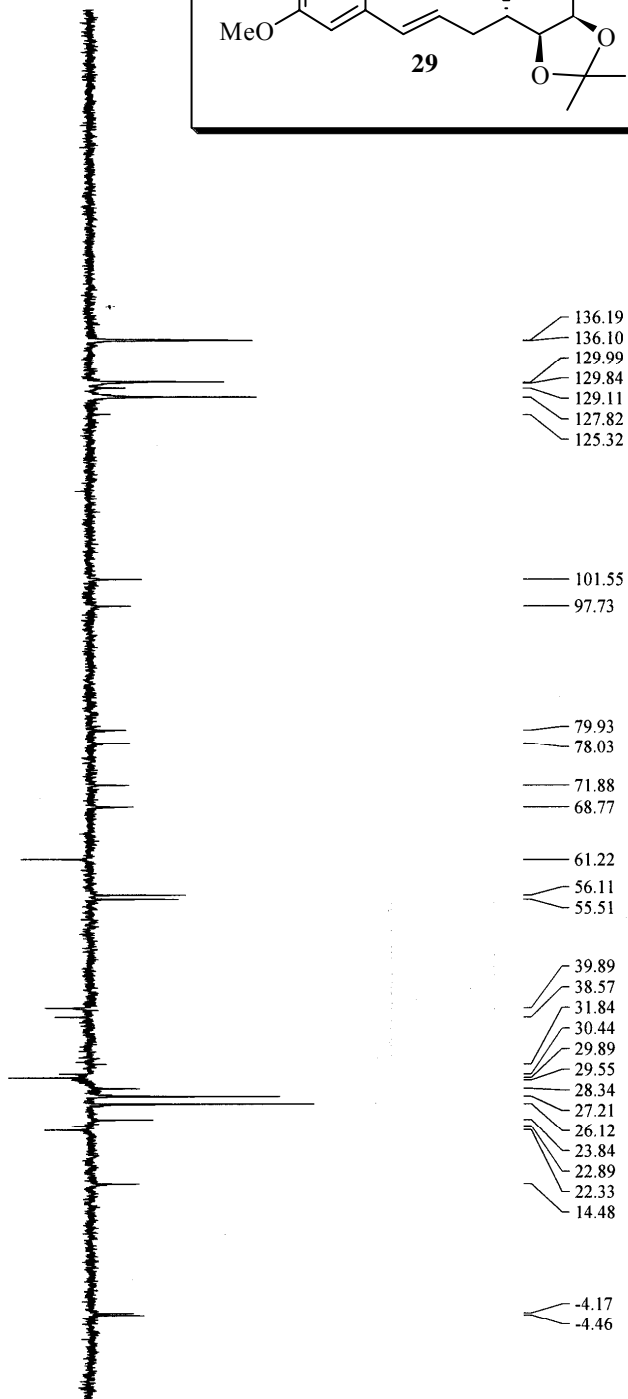
¹³C-NMR of compound 29 (50MHz, CDCl₃)



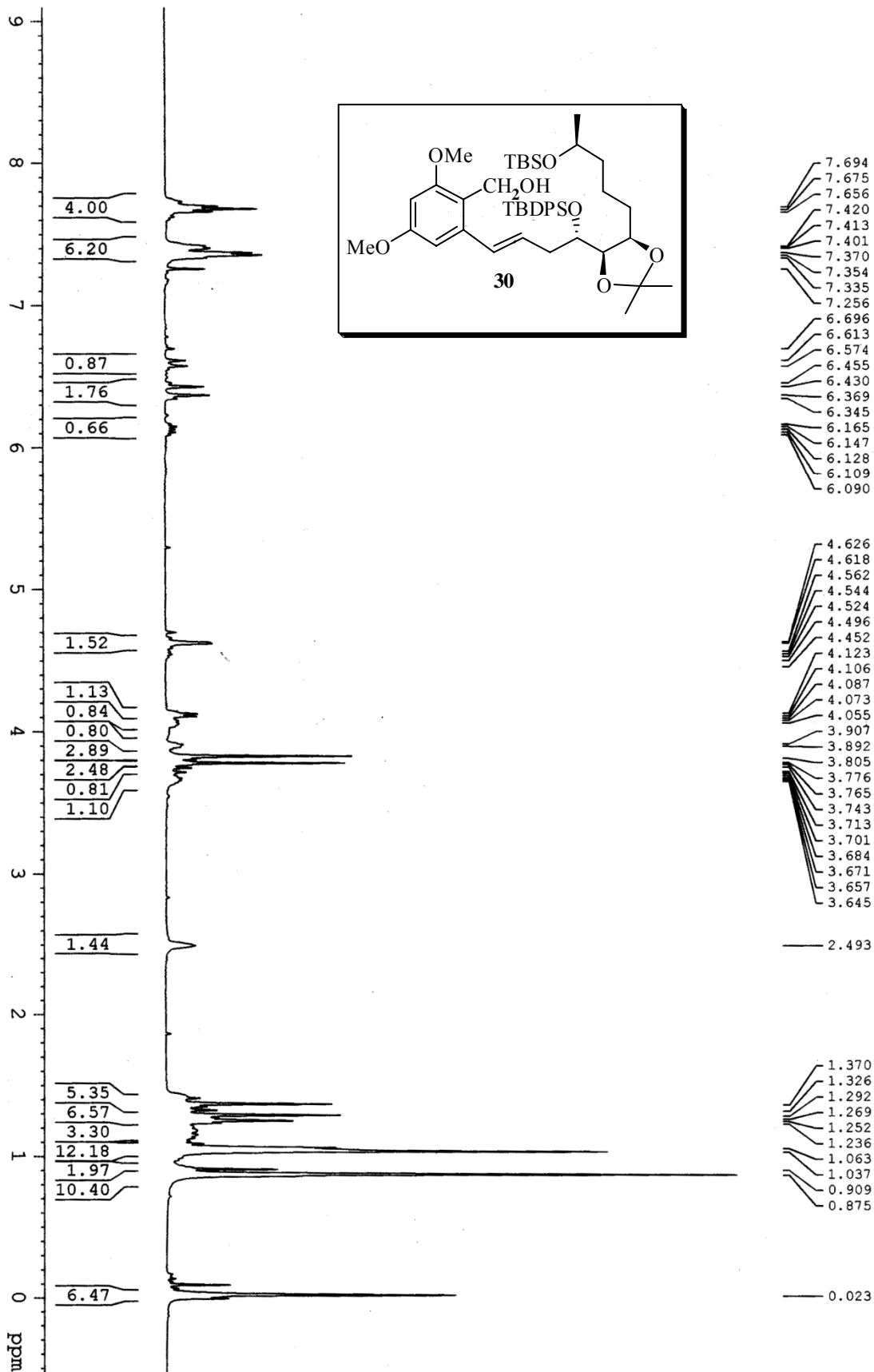
DEPT-NMR of compound 29 (50MHz, CDCl₃)



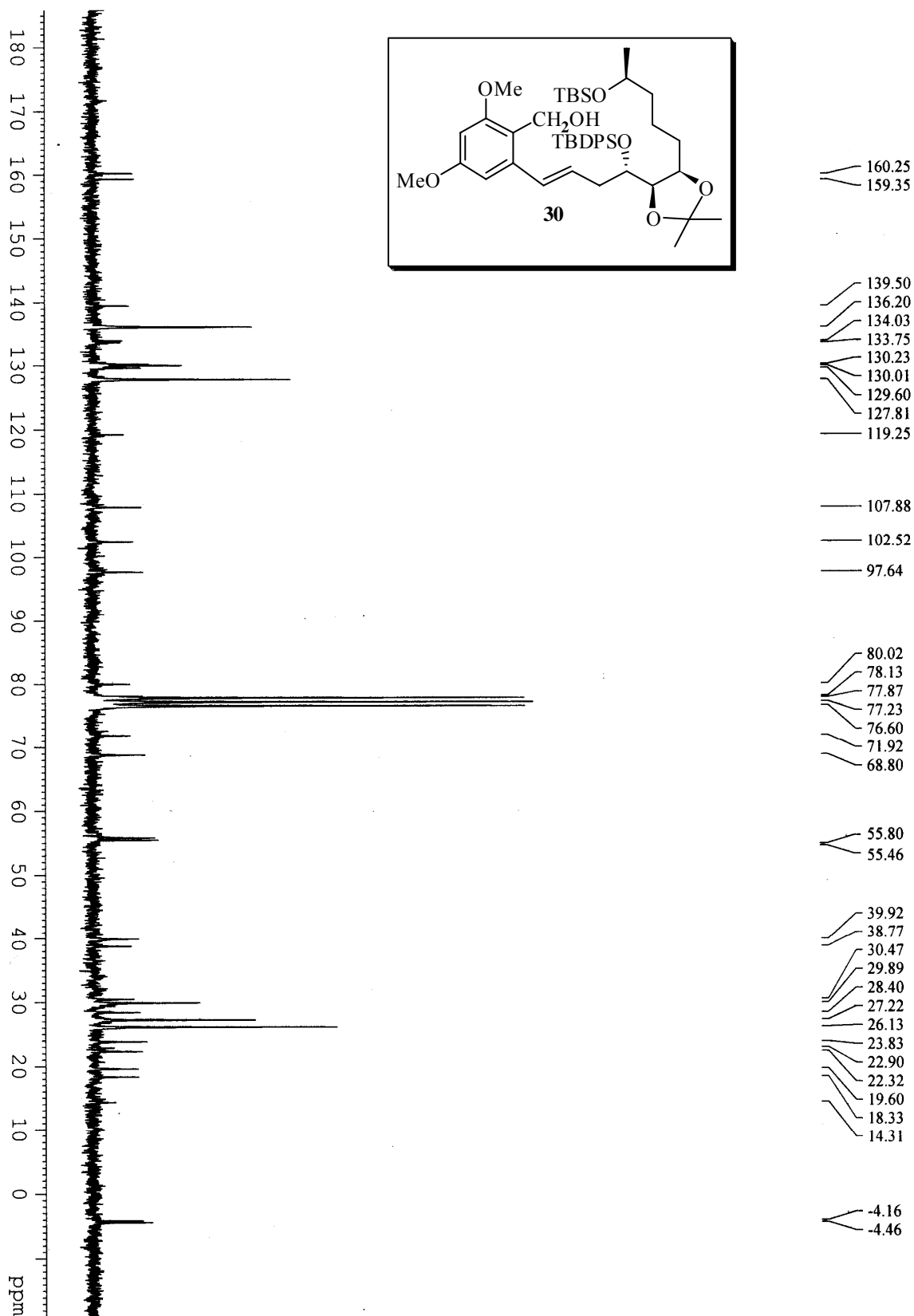
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



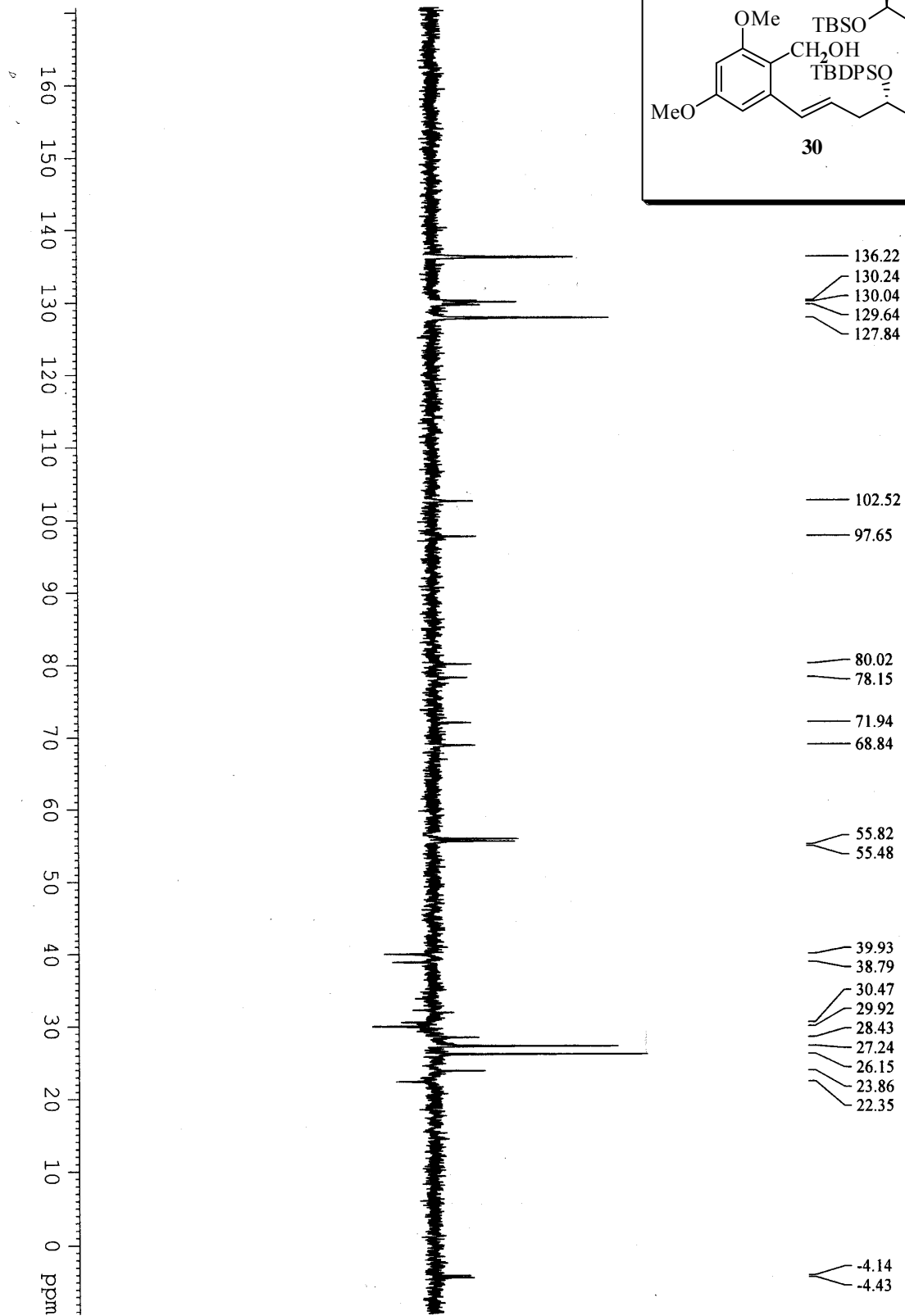
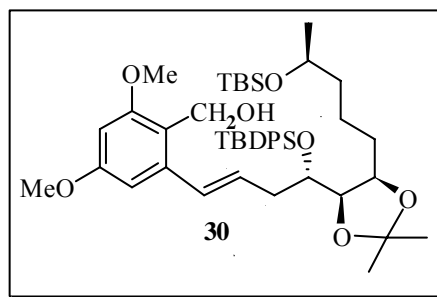
¹H-NMR of compound 30 (400MHz, CDCl₃)



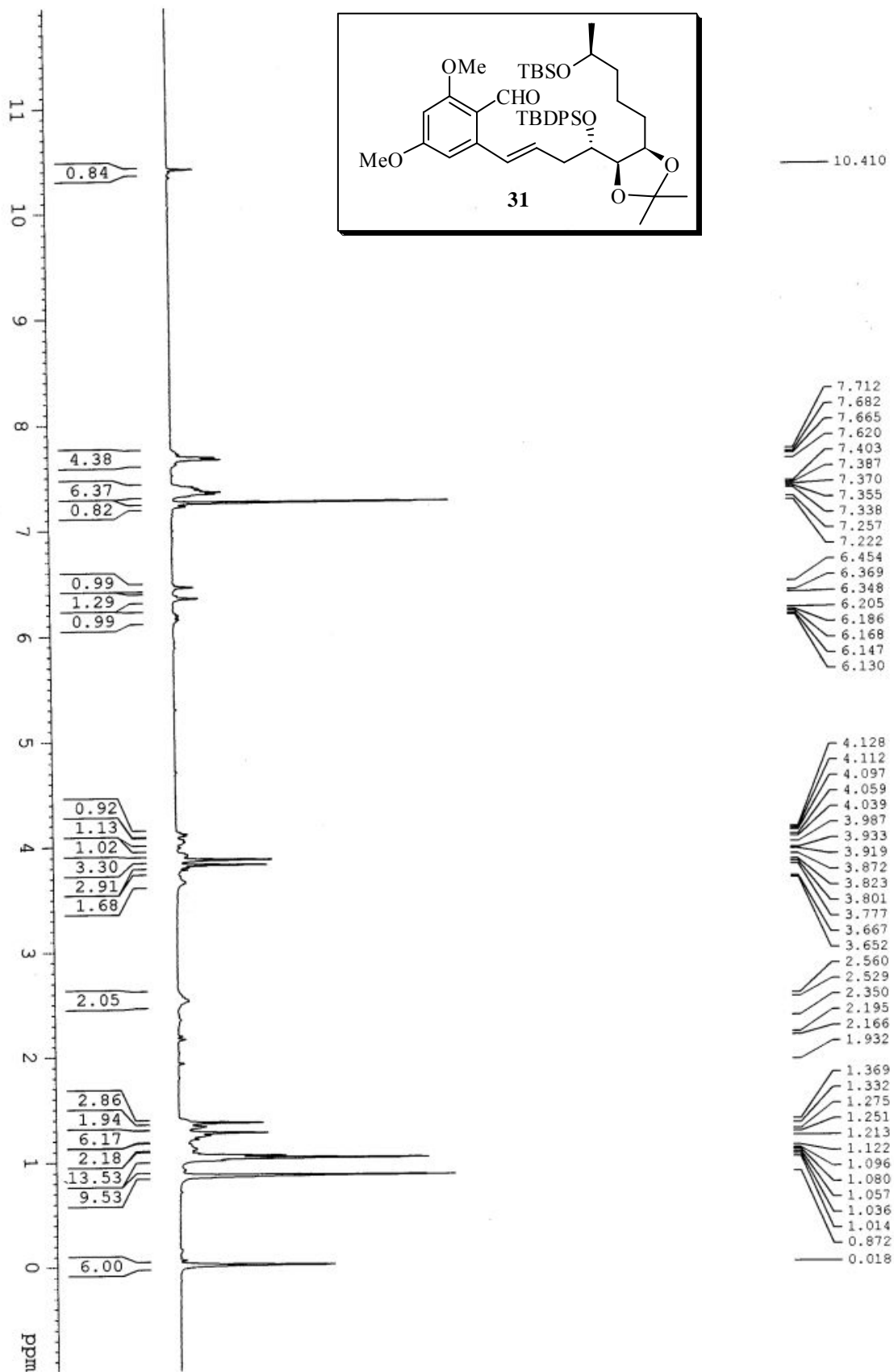
¹³C- NMR of compound 30 (50MHz, CDCl₃)



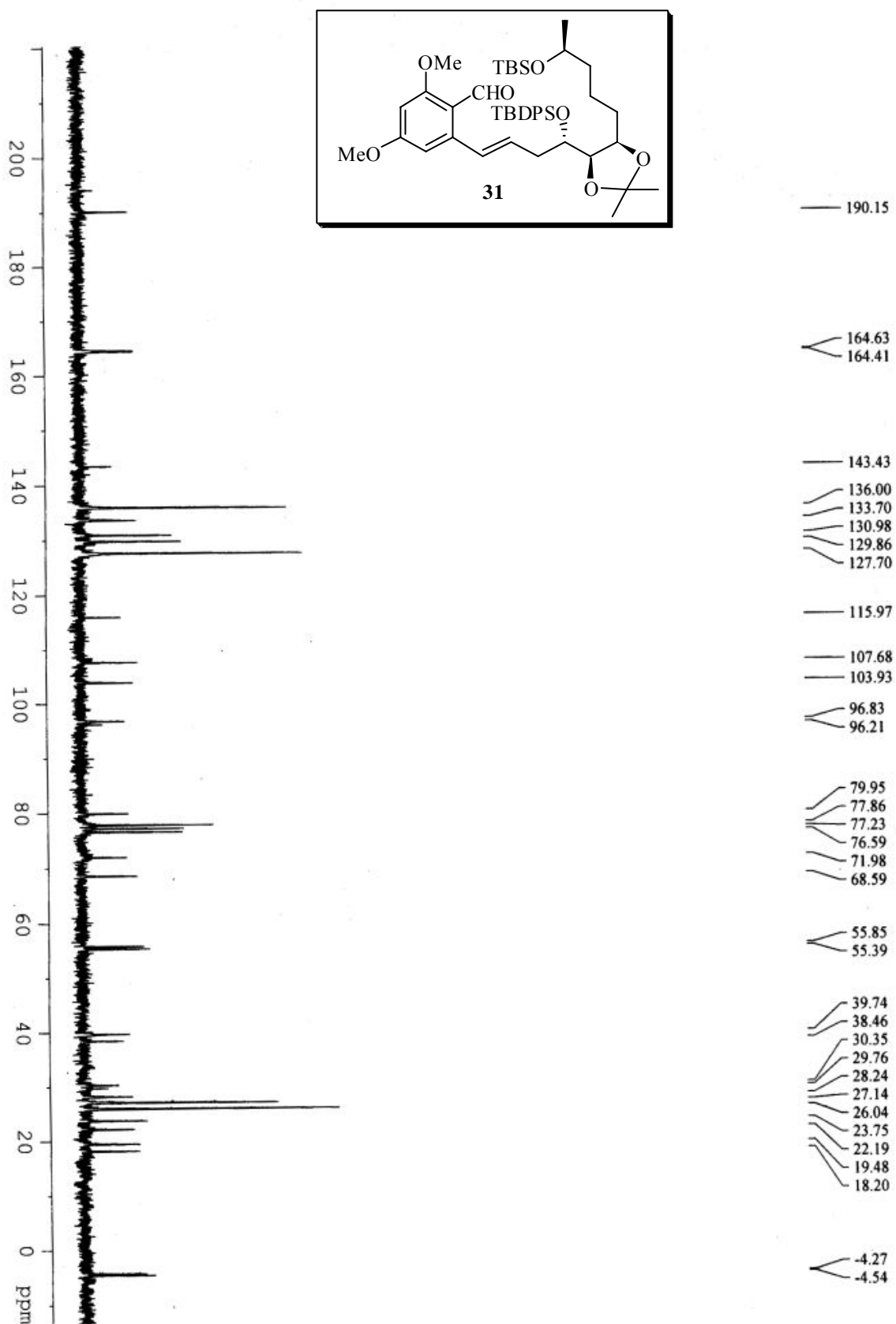
DEPT- NMR of compound 30 (50MHz, CDCl₃)



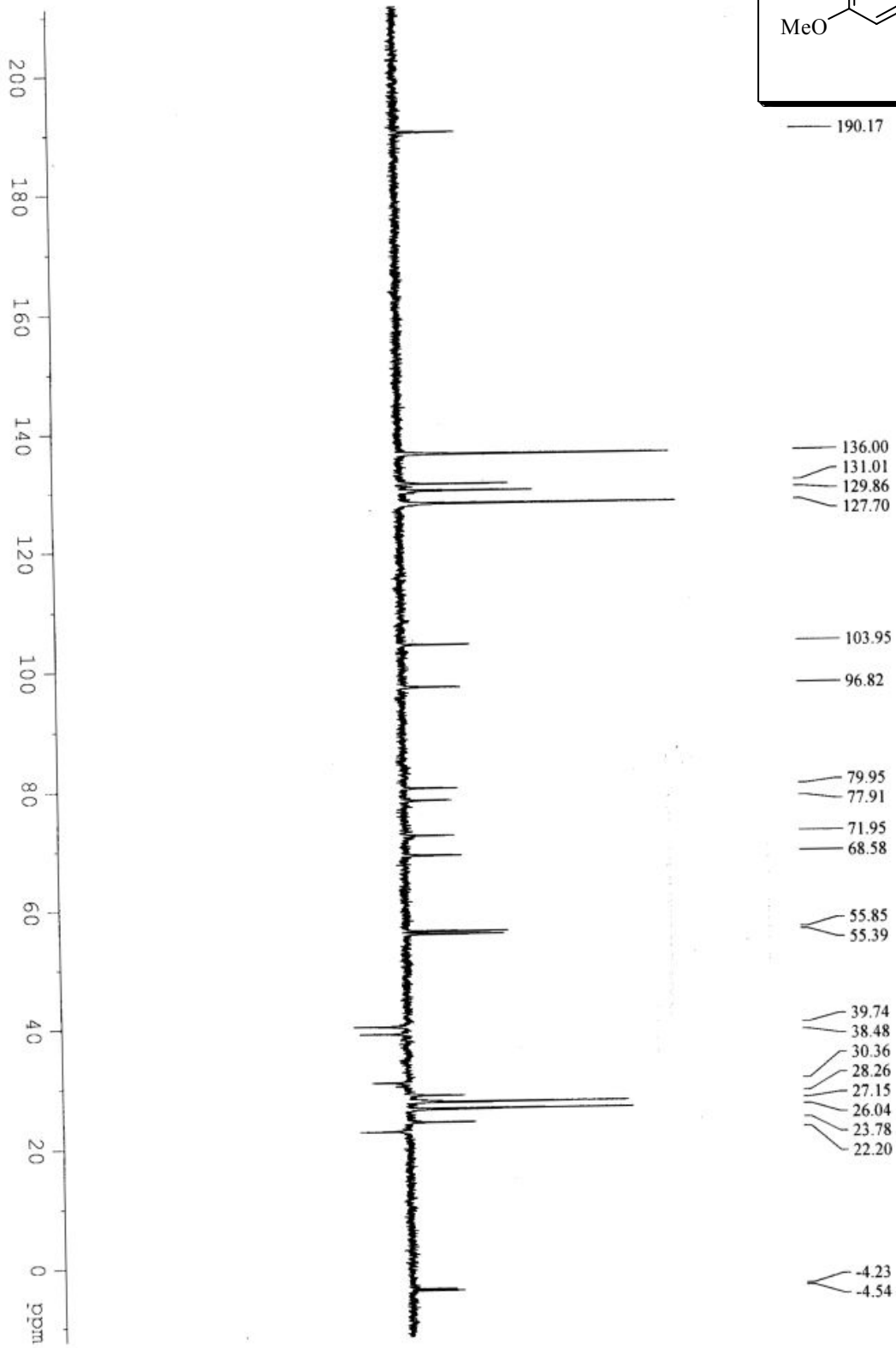
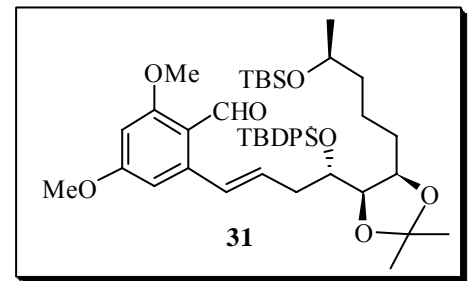
¹H-NMR of compound 31 (400MHz, CDCl₃)



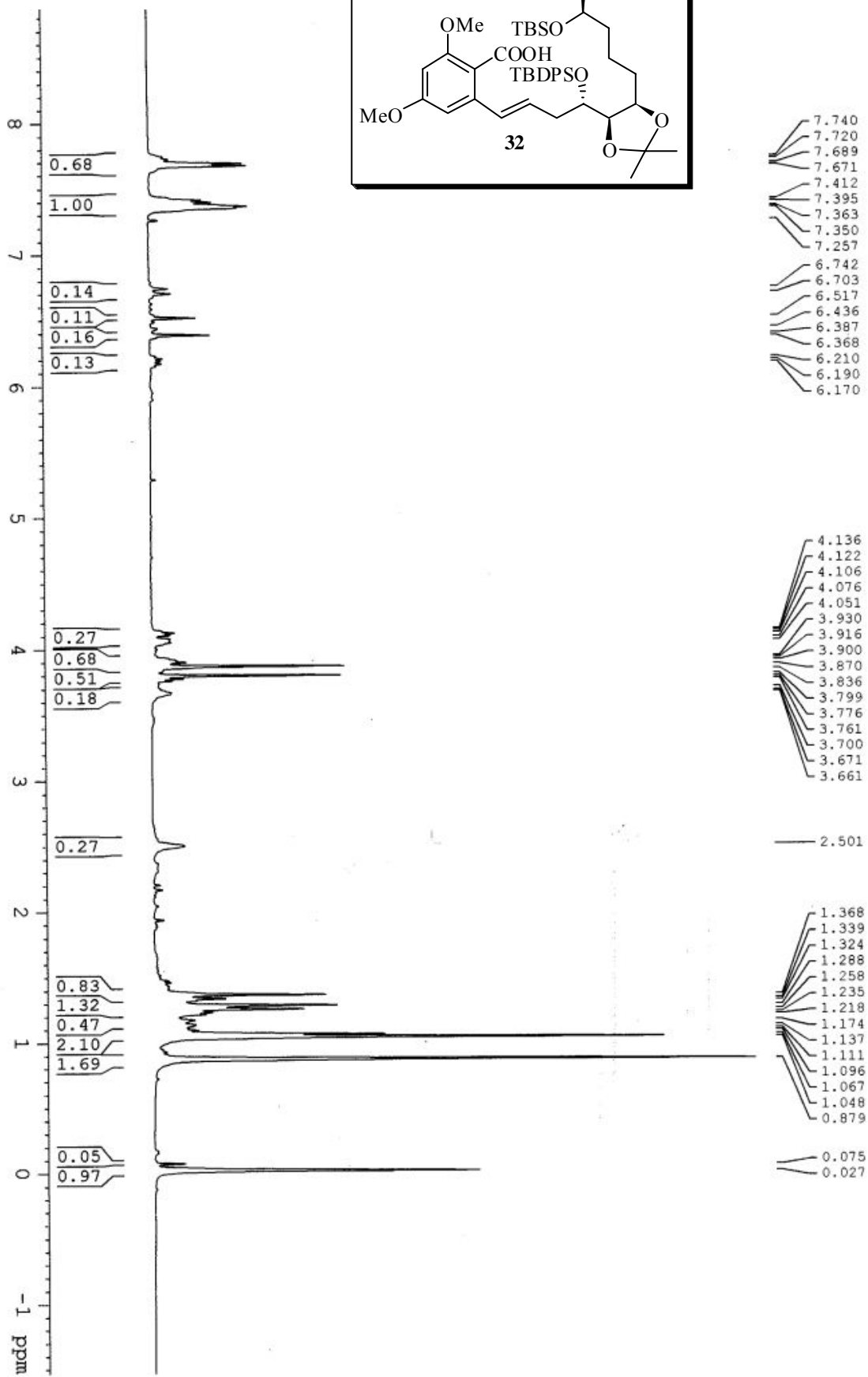
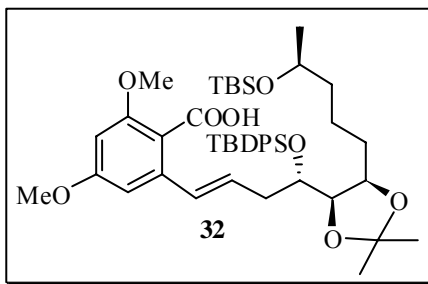
¹³C- NMR of compound 31 (50MHz, CDCl₃)



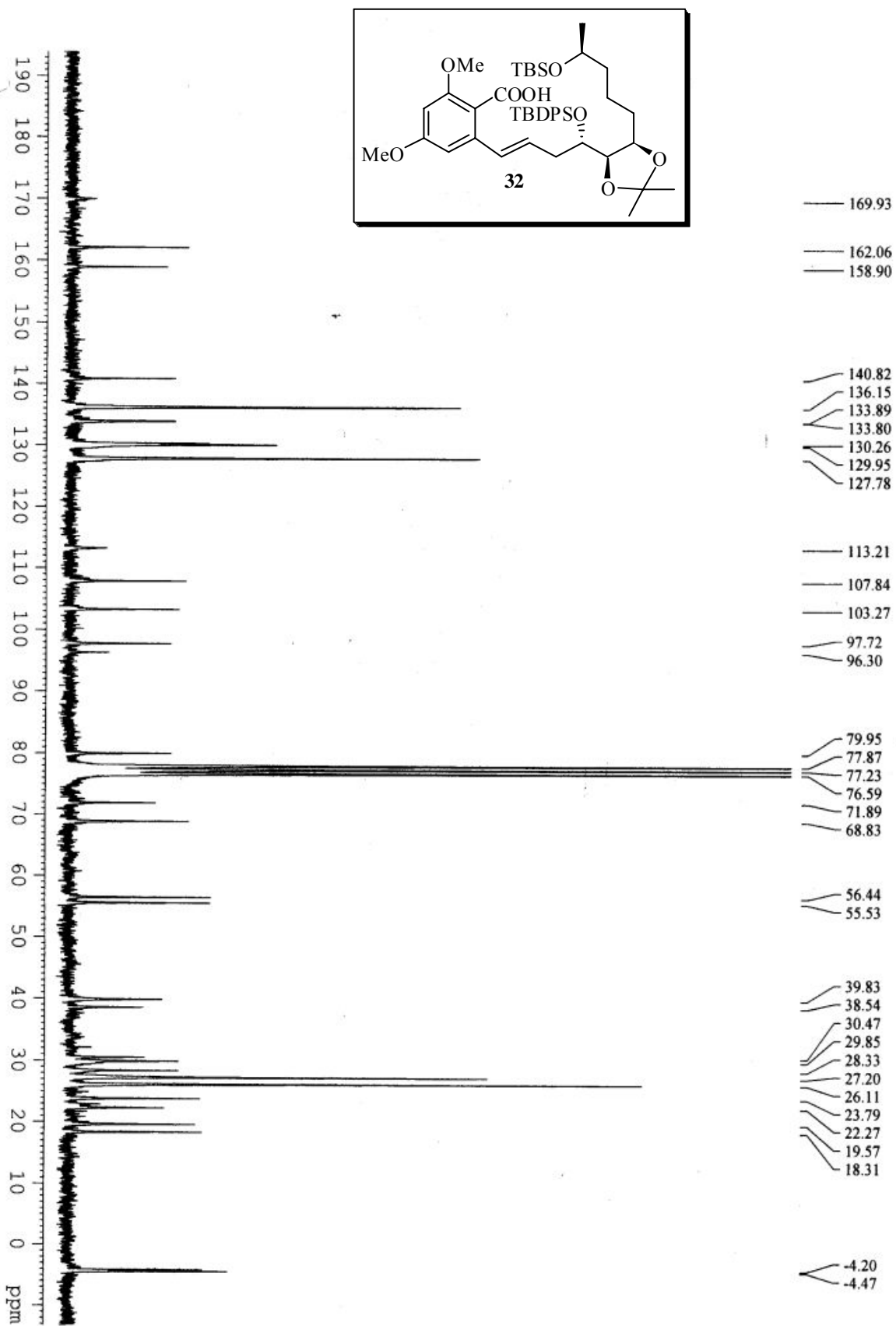
DEPT- NMR of compound 31 (50MHz, CDCl₃)



¹H- NMR of compound 32 (400MHz, CDCl₃)

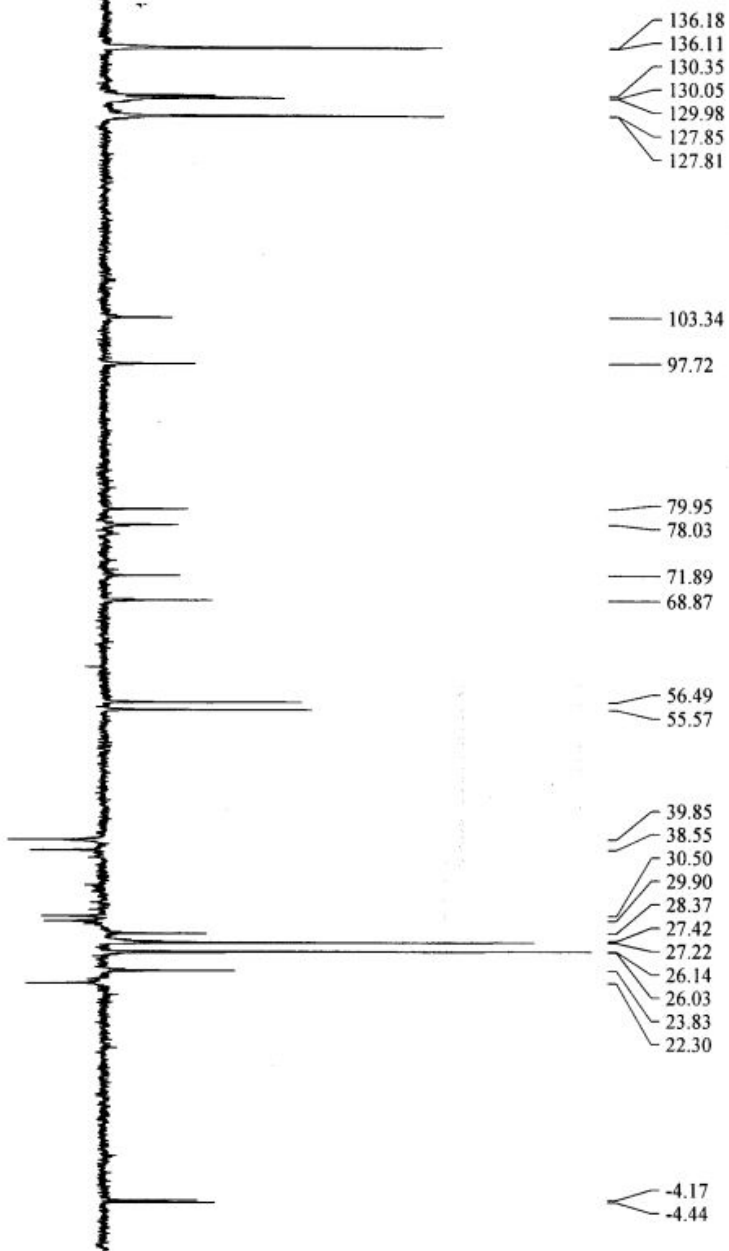
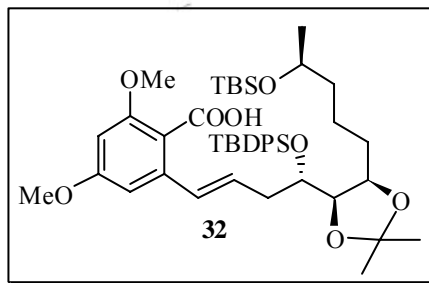


¹³C- NMR of compound 32 (50MHz, CDCl₃)

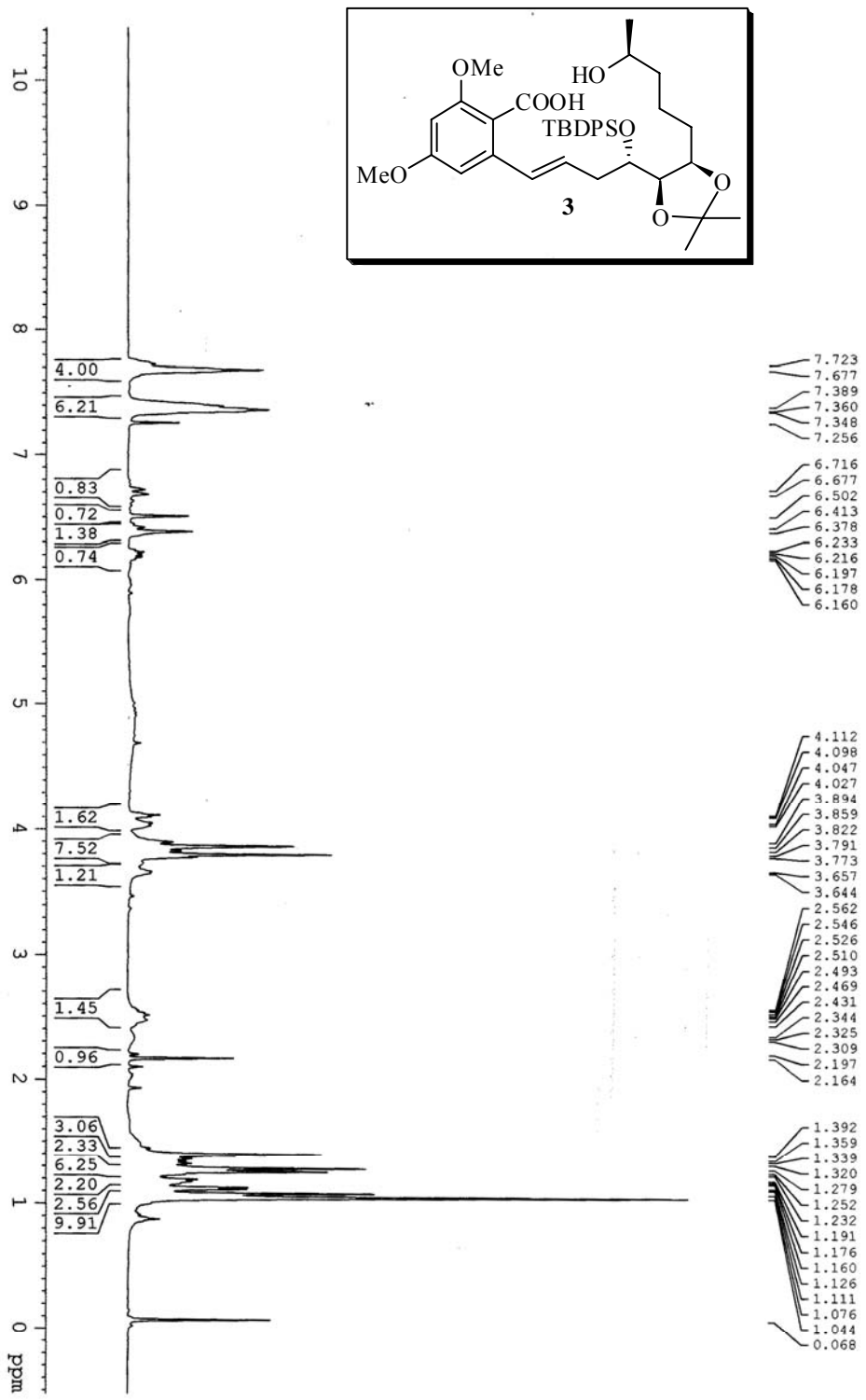


DEPT- NMR of compound 32 (50MHz, CDCl₃)

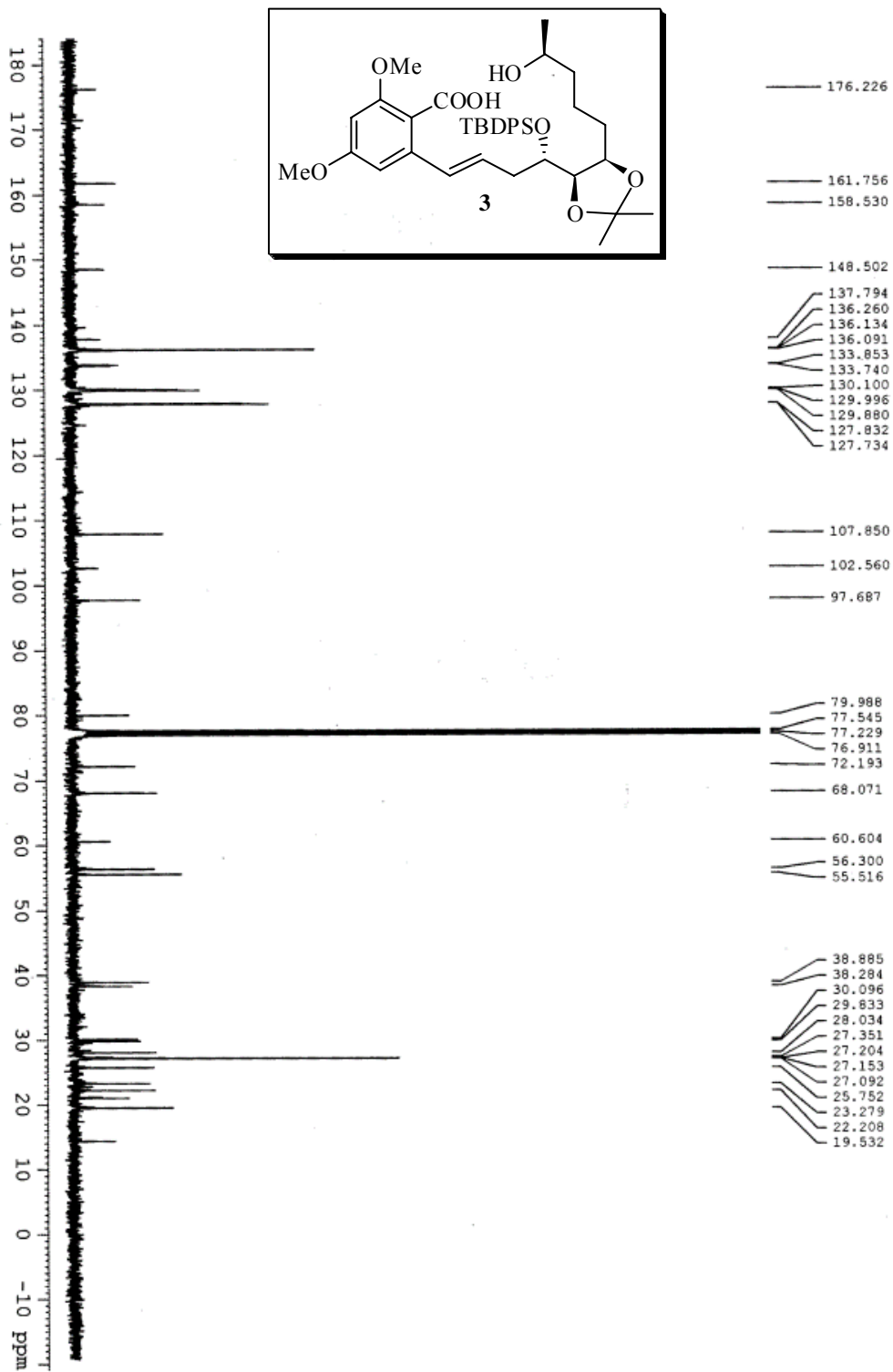
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



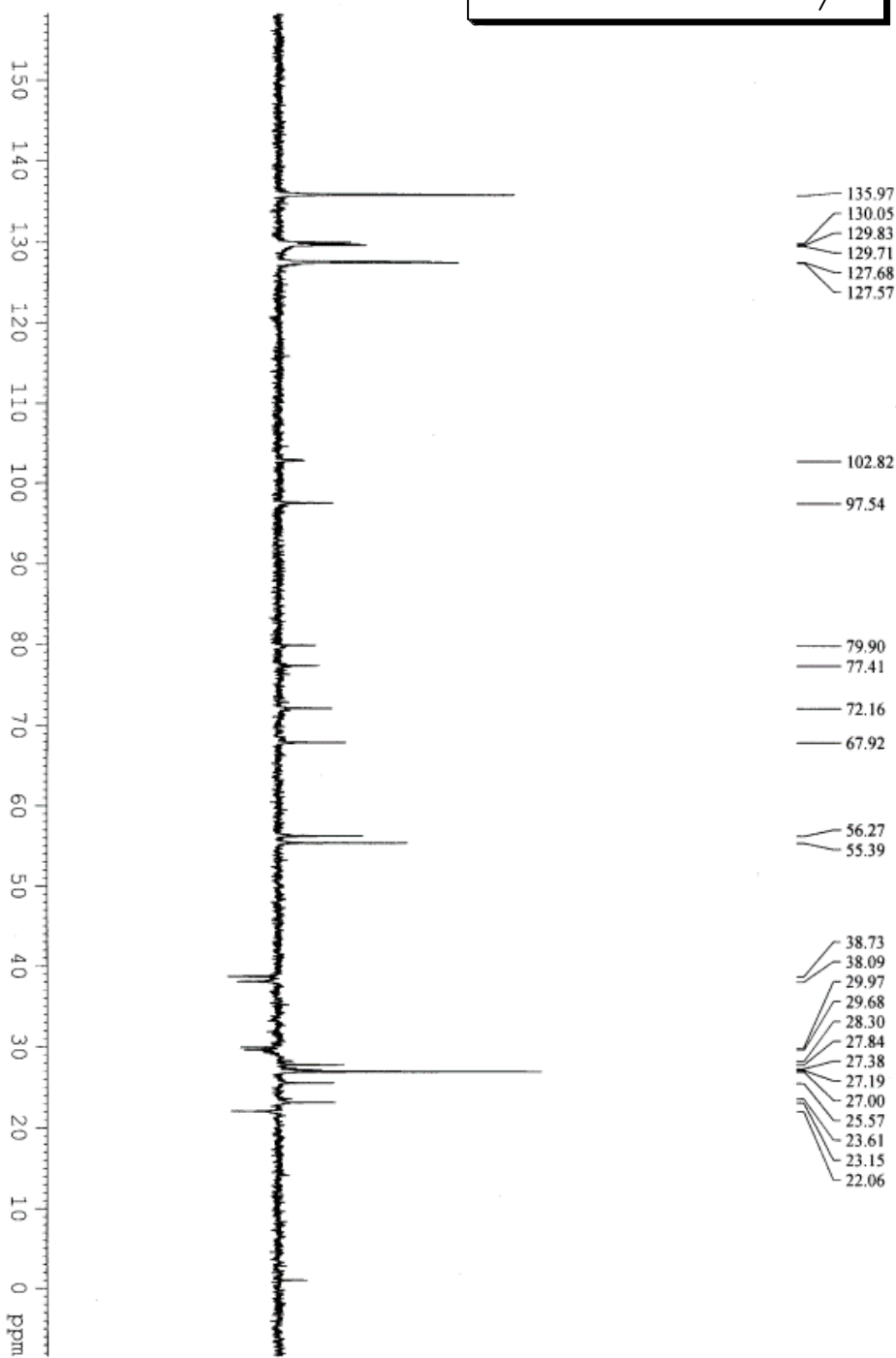
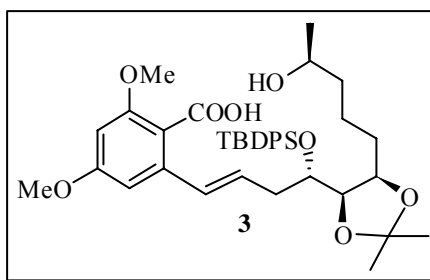
¹H-NMR of compound 3 (400MHz, CDCl₃)



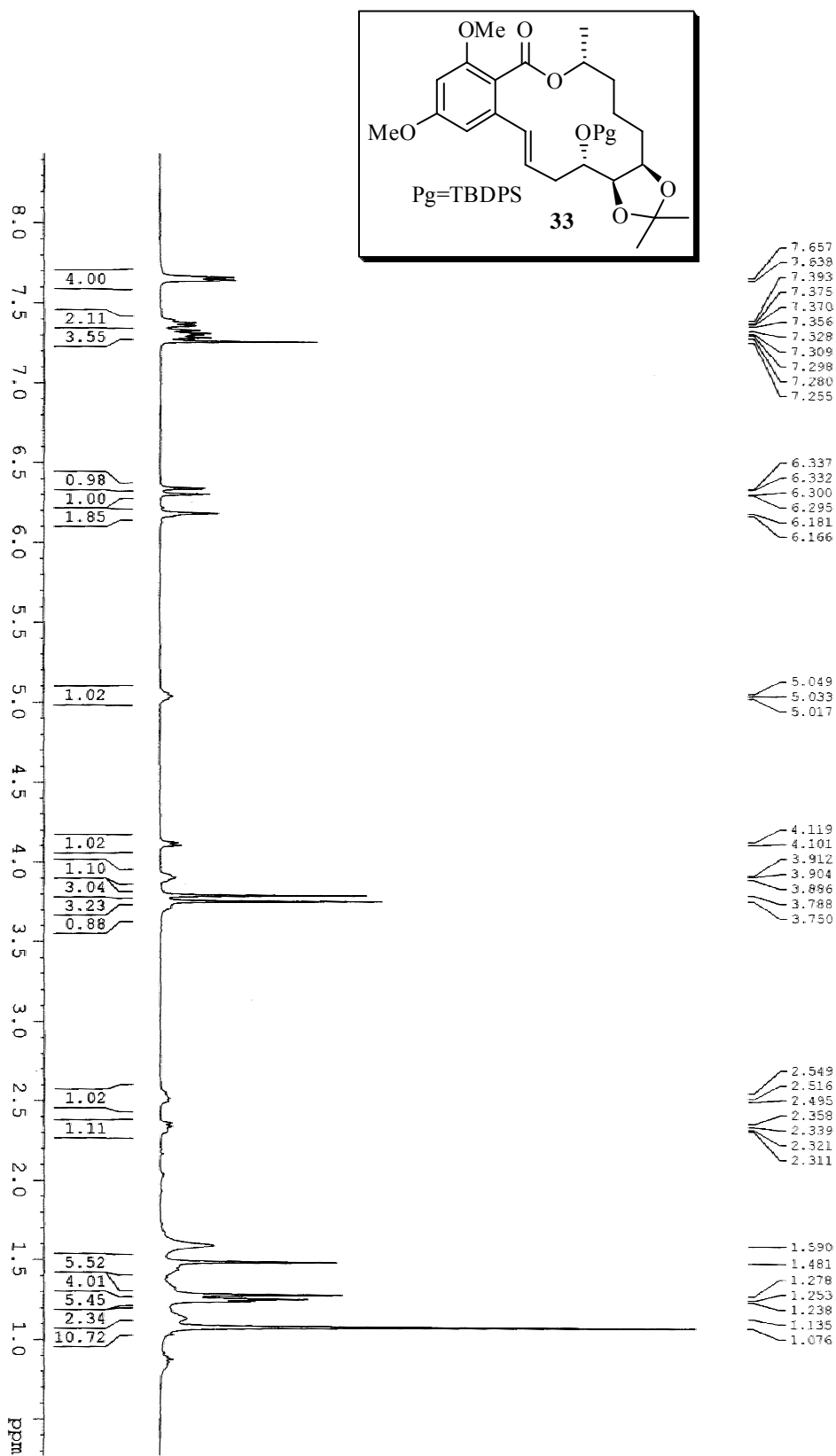
^{13}C -NMR of compound 3 (100MHz, CDCl_3)



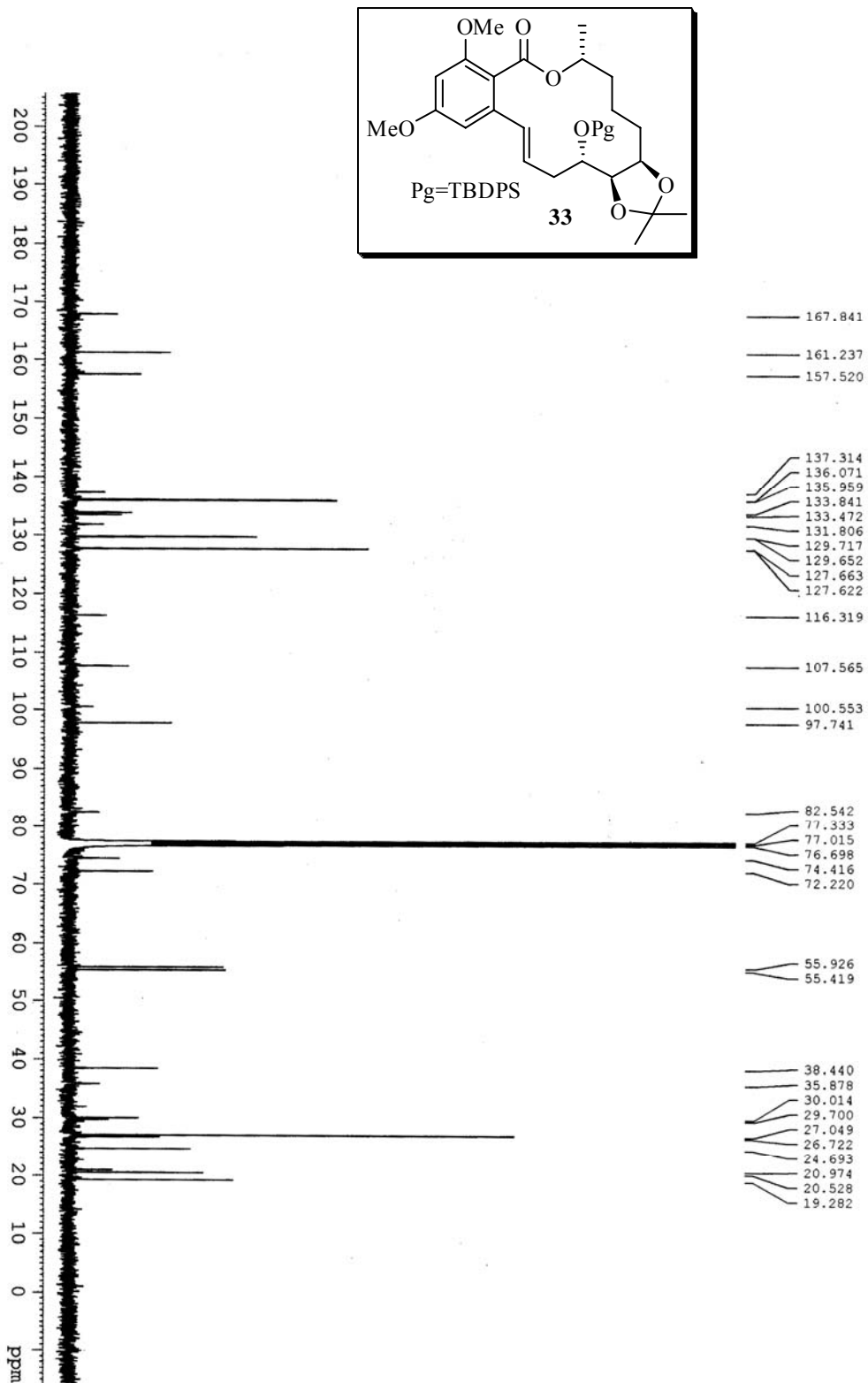
DEPT- NMR of compound 3 (50MHz, CDCl₃)



¹H-NMR of compound 33 (400MHz, CDCl₃)

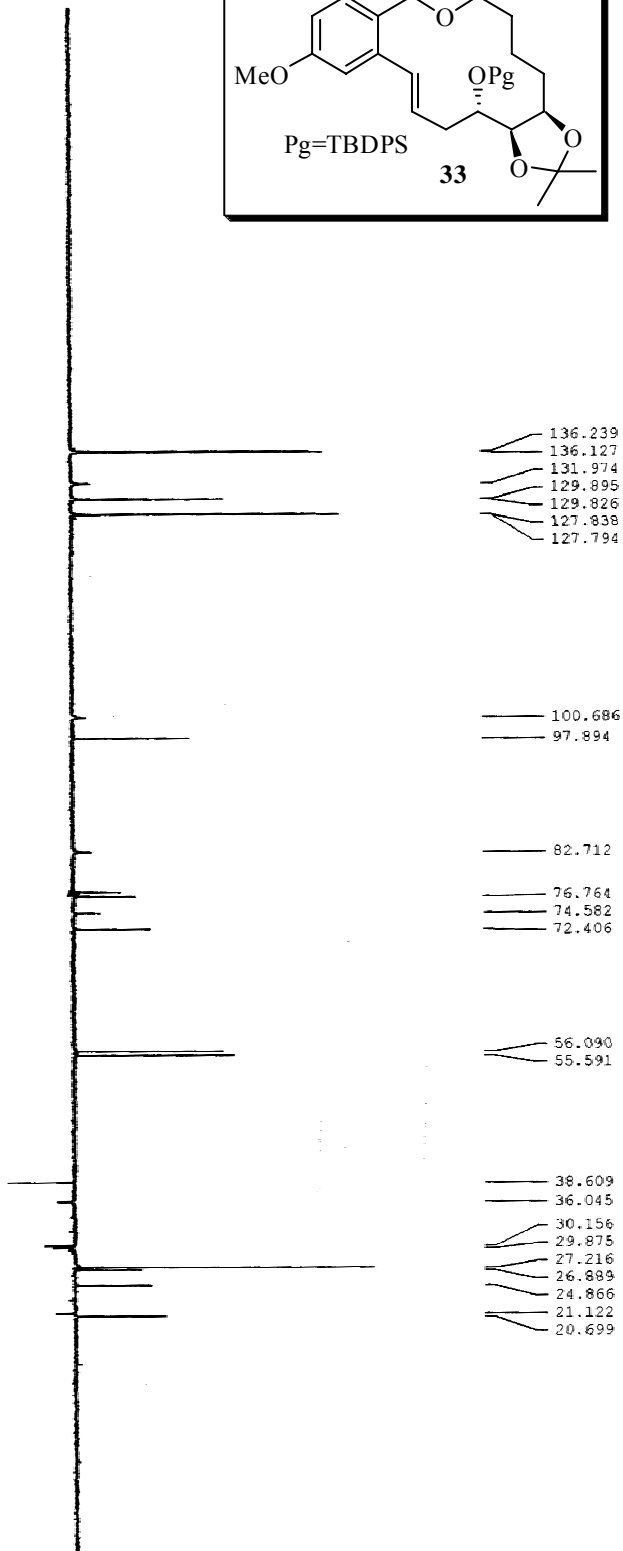
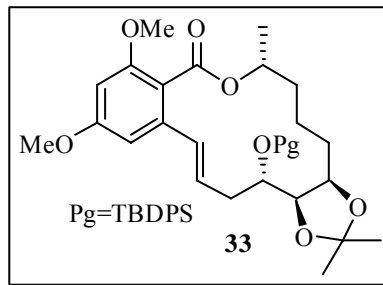


¹³C-NMR of compound 33 (100MHz, CDCl₃)

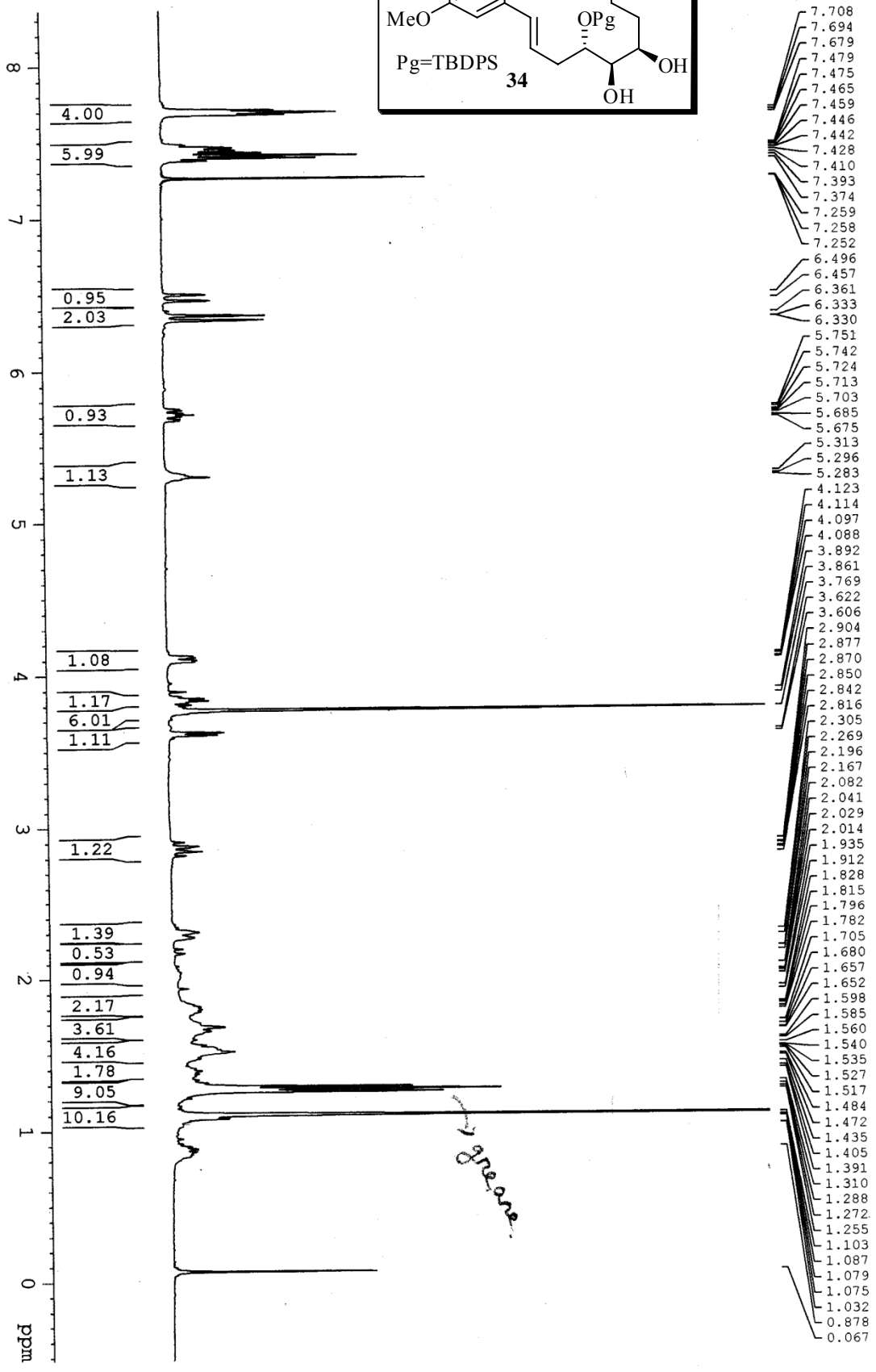
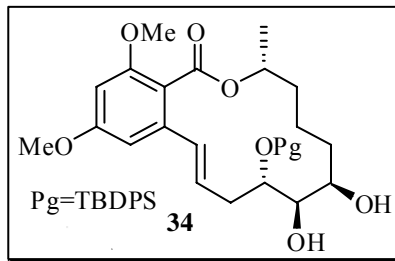


DEPT- NMR of compound 33 (100MHz, CDCl₃)

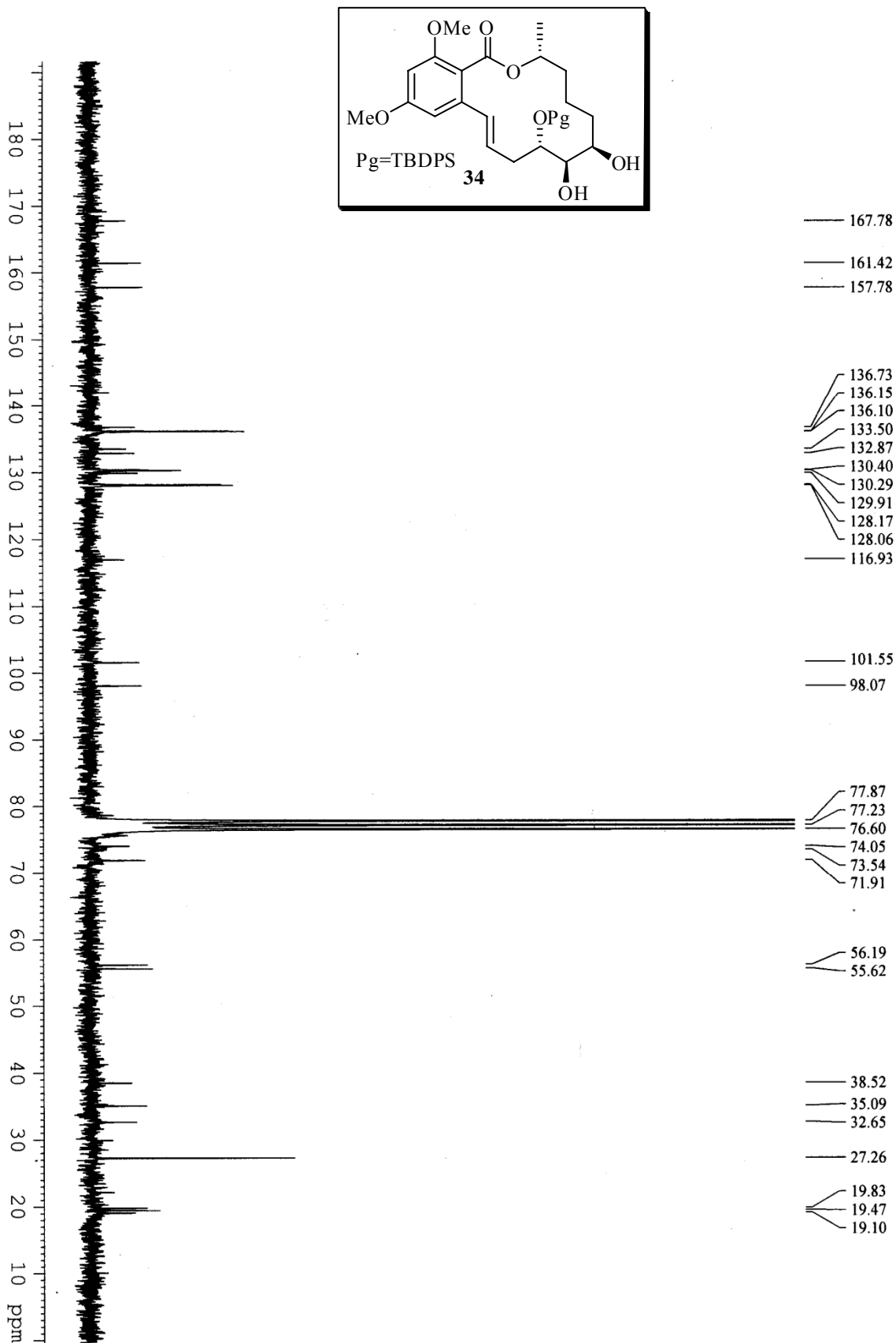
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



¹H-NMR of compound 34 (400MHz, CDCl₃)

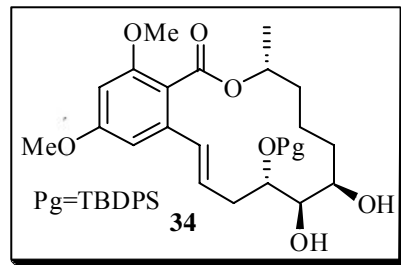
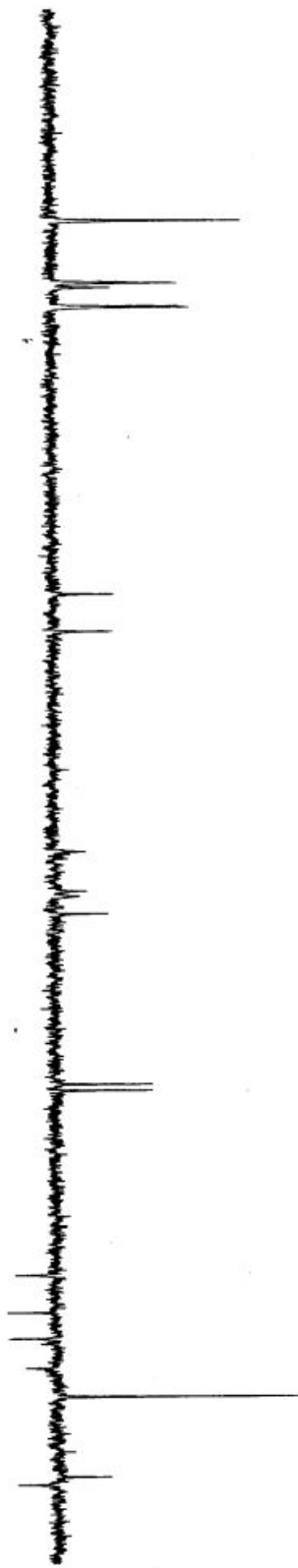


¹³C-NMR of compound 34 (50MHz, CDCl₃)



DEPT- NMR of compound 34 (50MHz, CDCl₃)

150
140
130
120
110
100
90
80
70
60
50
40
30
20 ppm



- 136.13
- 130.44
- 130.33
- 129.92
- 128.21
- 128.09

- 101.54
- 98.09

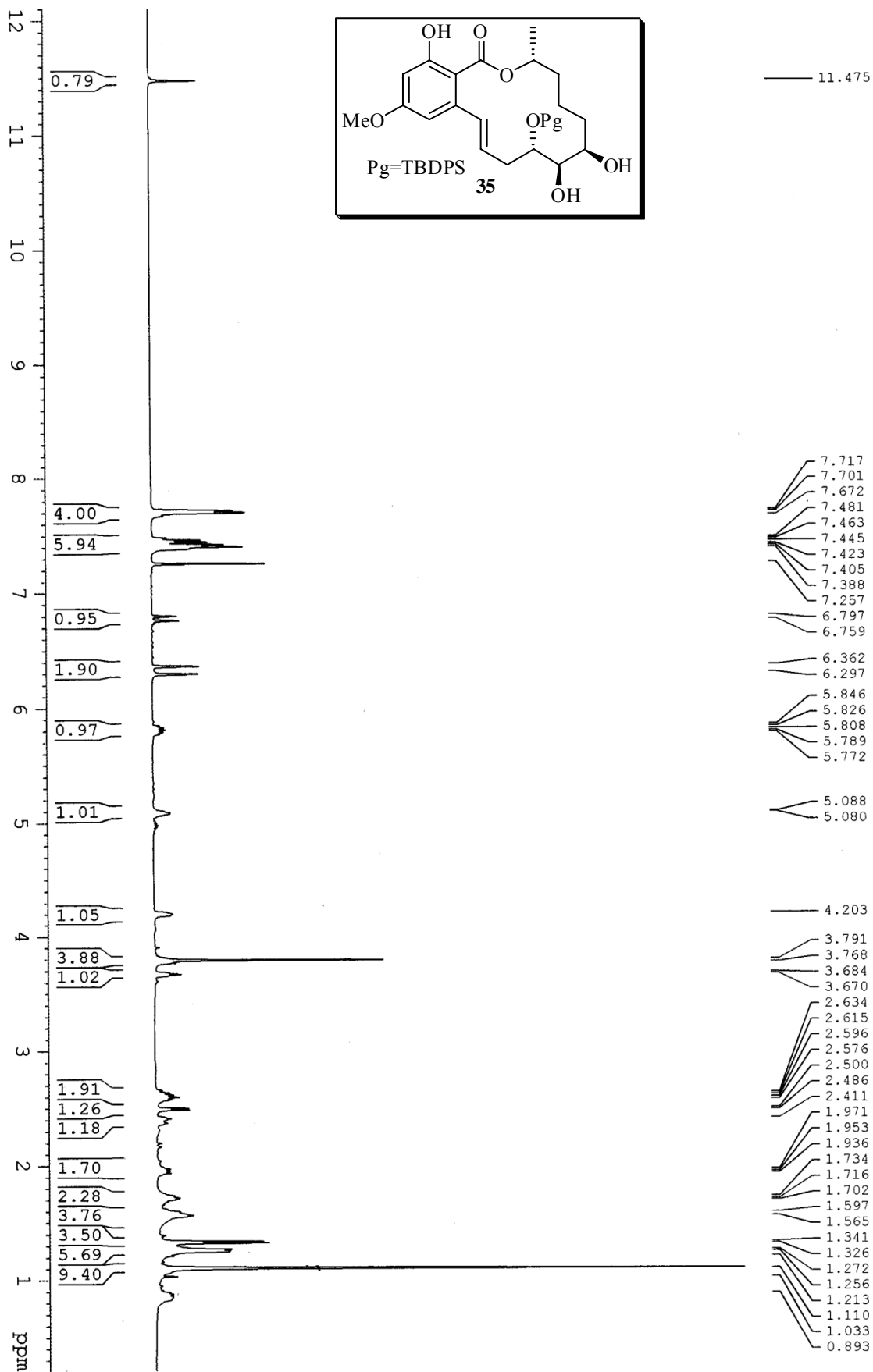
- 77.71
- 74.04
- 73.60
- 71.96

- 56.22
- 55.66

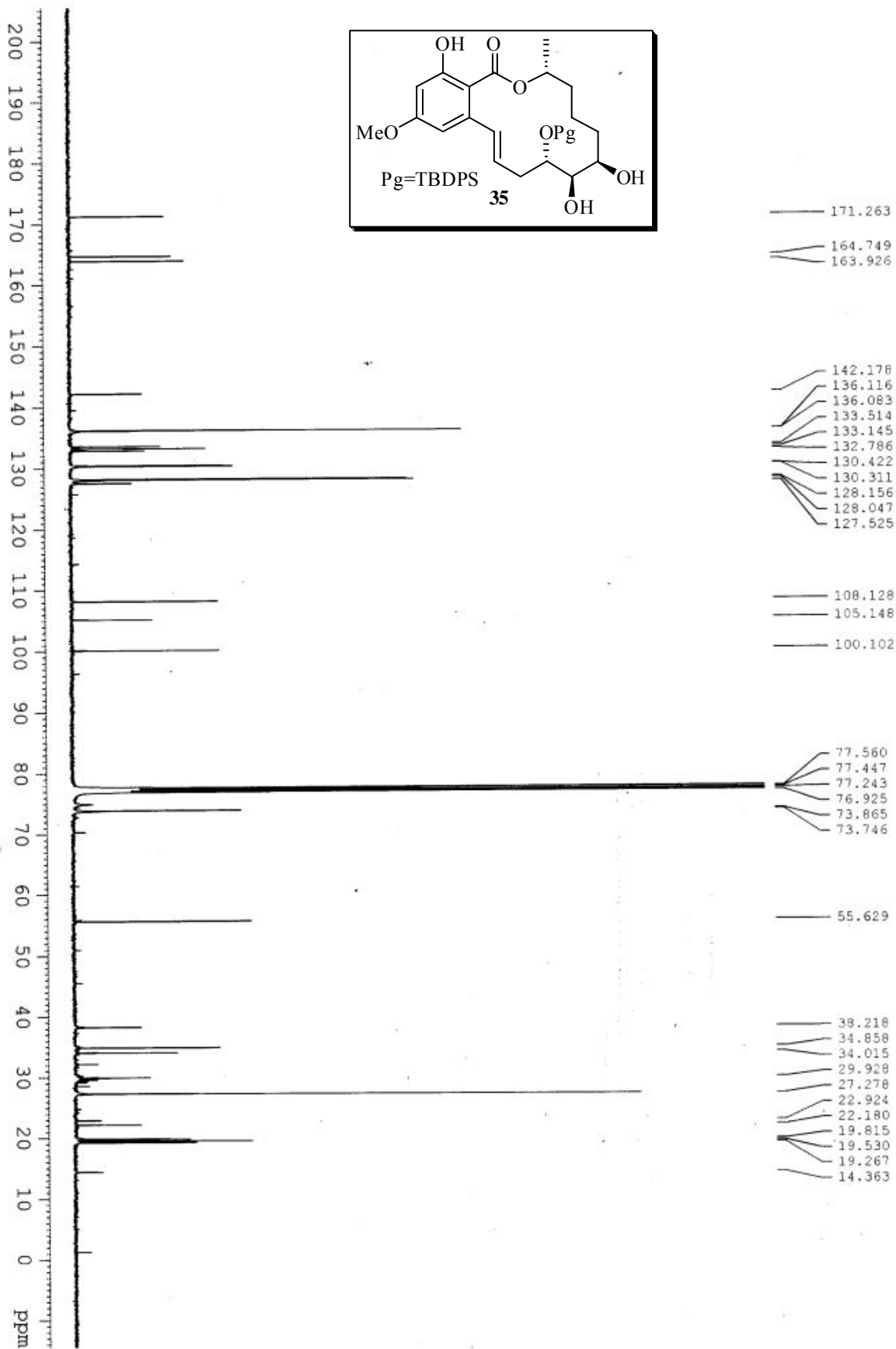
- 38.56
- 35.11
- 32.68
- 29.95
- 27.29

- 22.21
- 19.87
- 19.14

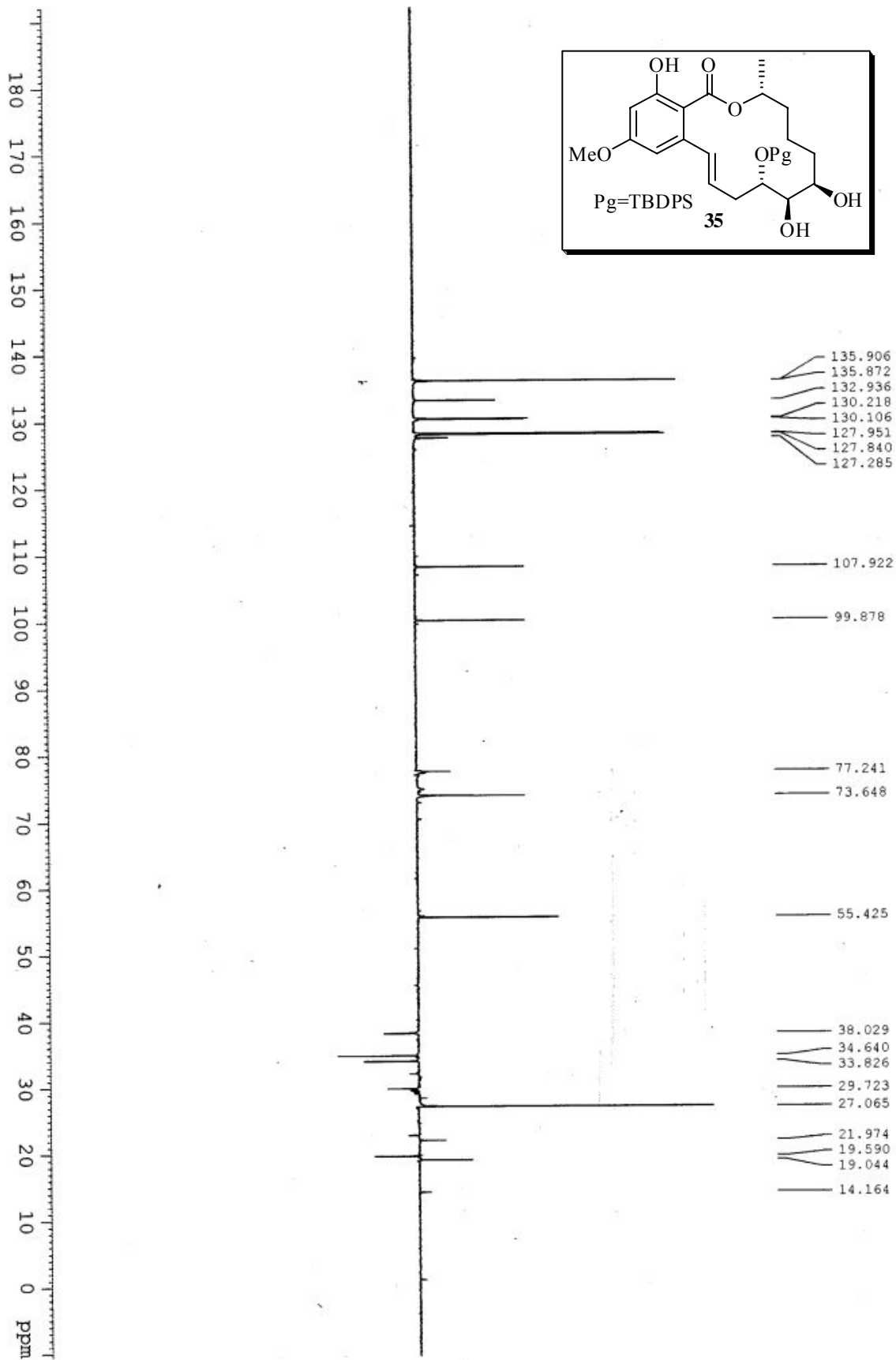
¹H- NMR of compound 35 (400MHz, CDCl₃)



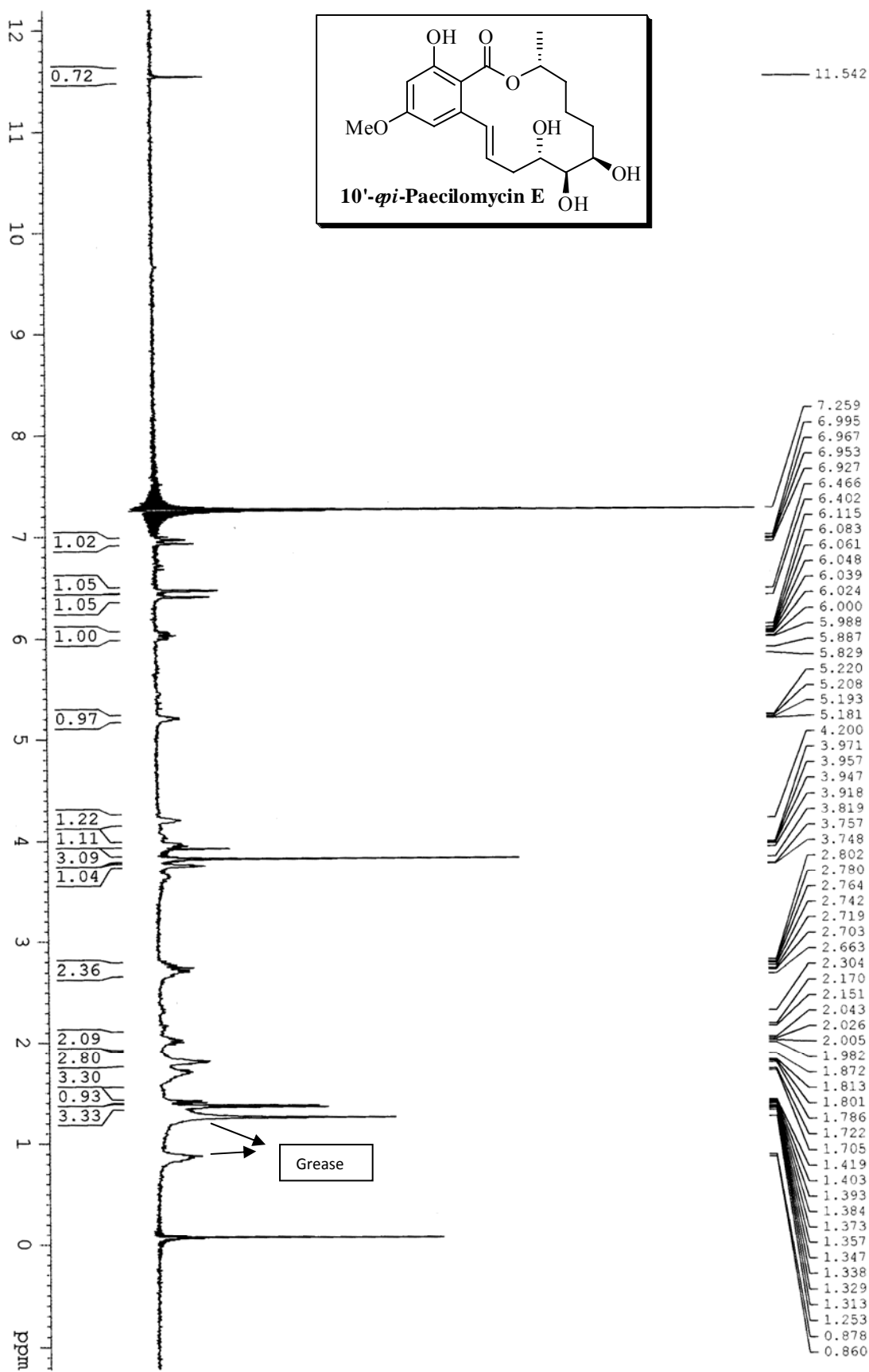
¹³C-NMR of compound 35 (100MHz, CDCl₃)



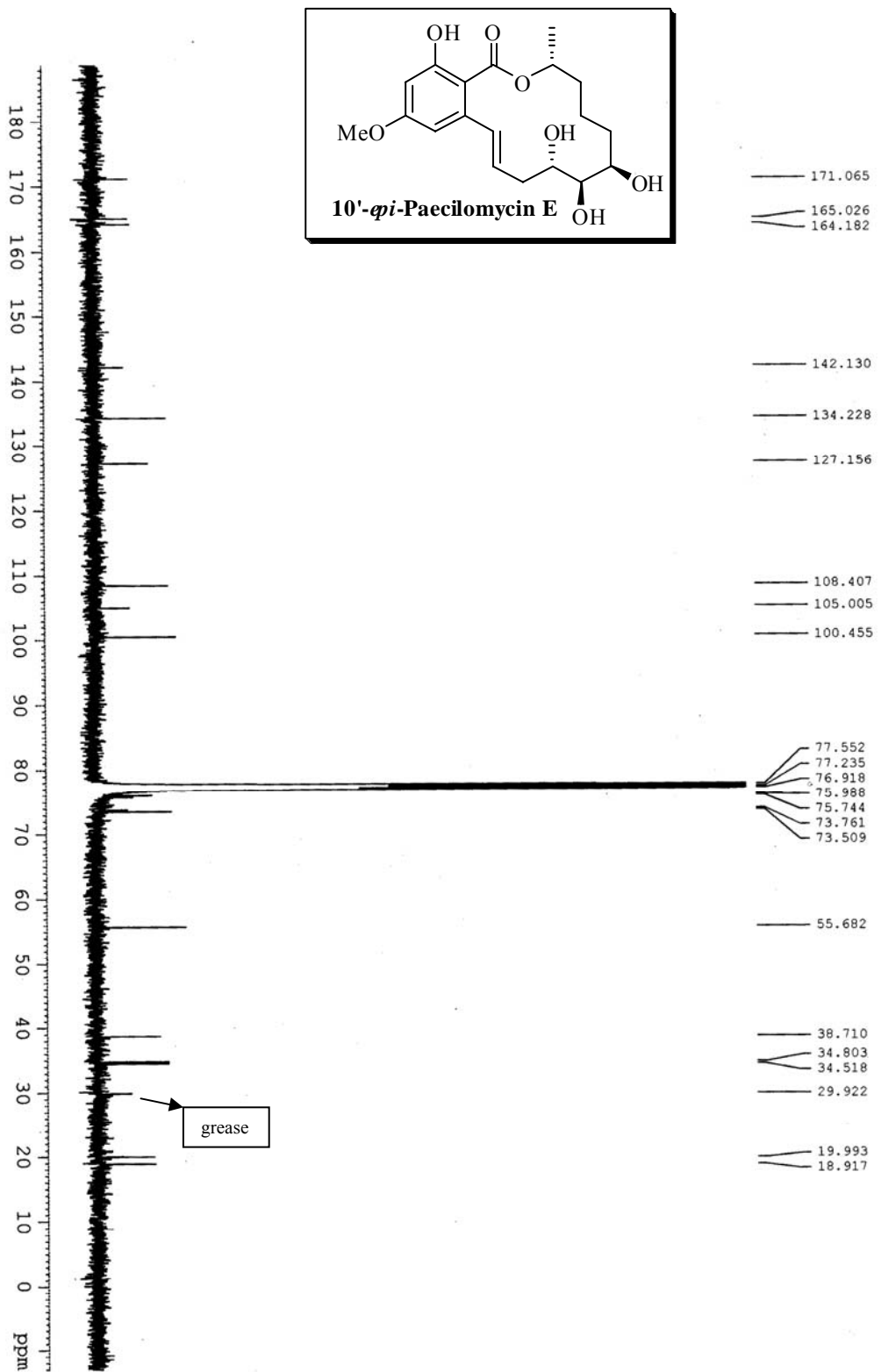
DEPT-NMR of compound 35 (100MHz, CDCl₃)



¹H- NMR of 10'-*phi*-Paecilomycin E (400MHz, CDCl₃)

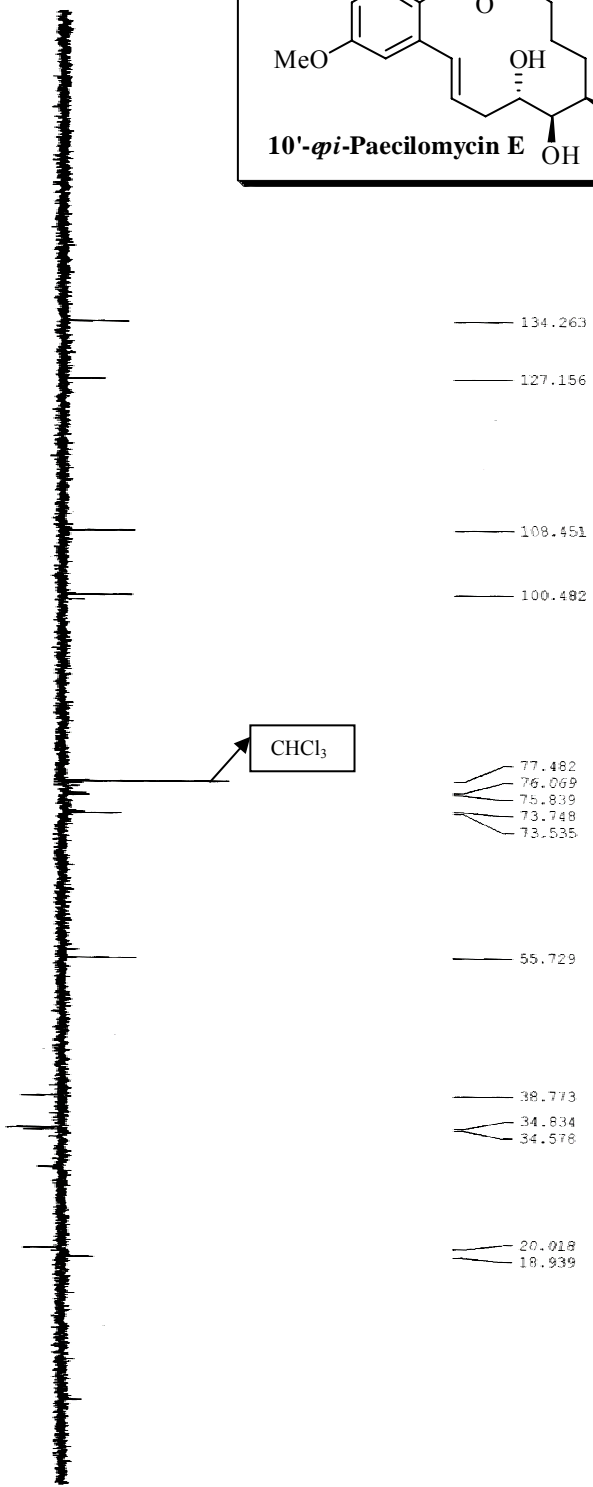
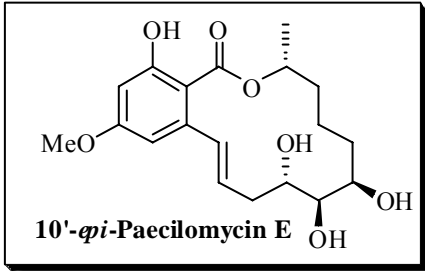


¹³C-NMR of 10'-*phi*-Paecilomycin E (100MHz, CDCl₃)

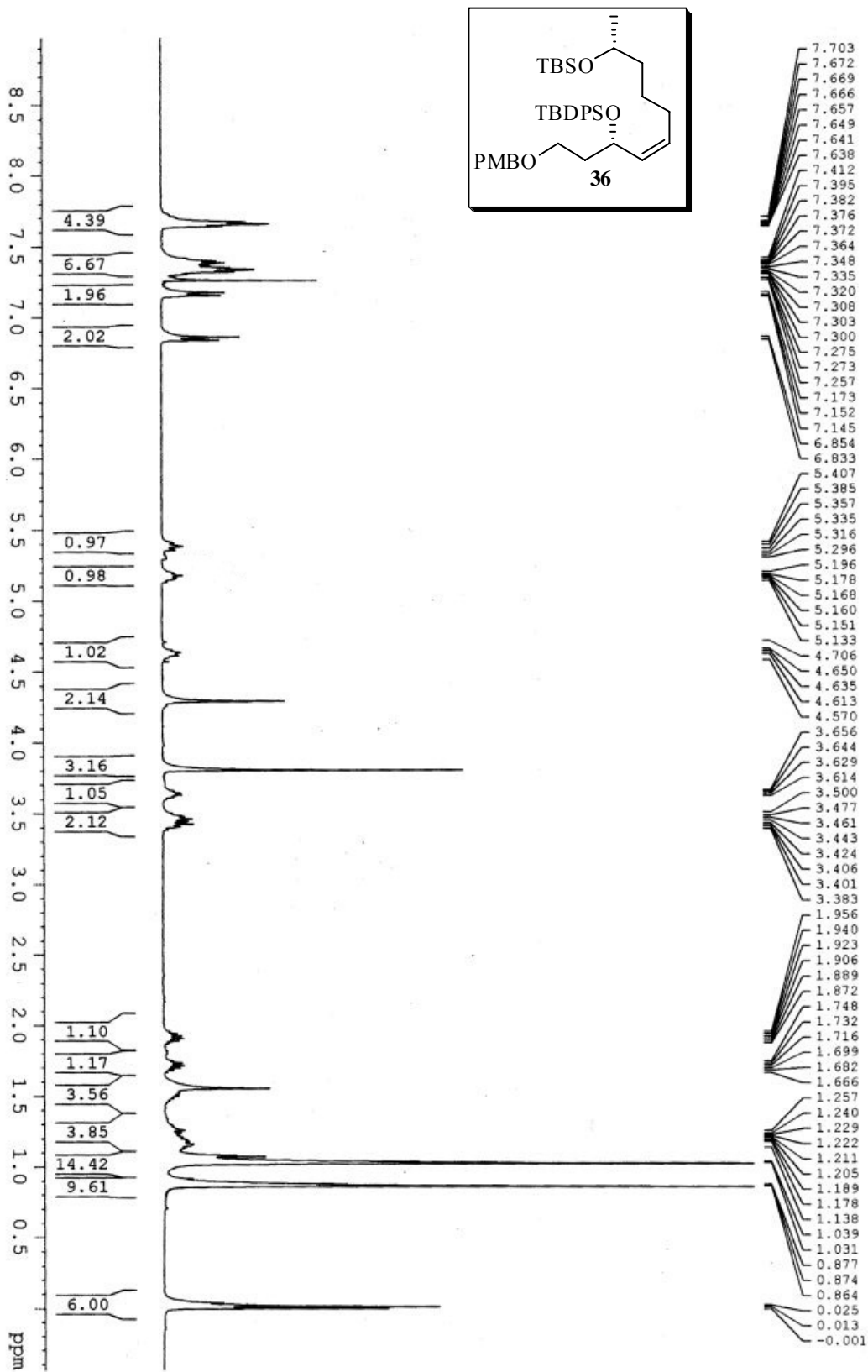


DEPT- NMR of 10'-*phi*-Paecilomycin E (100MHz, CDCl₃)

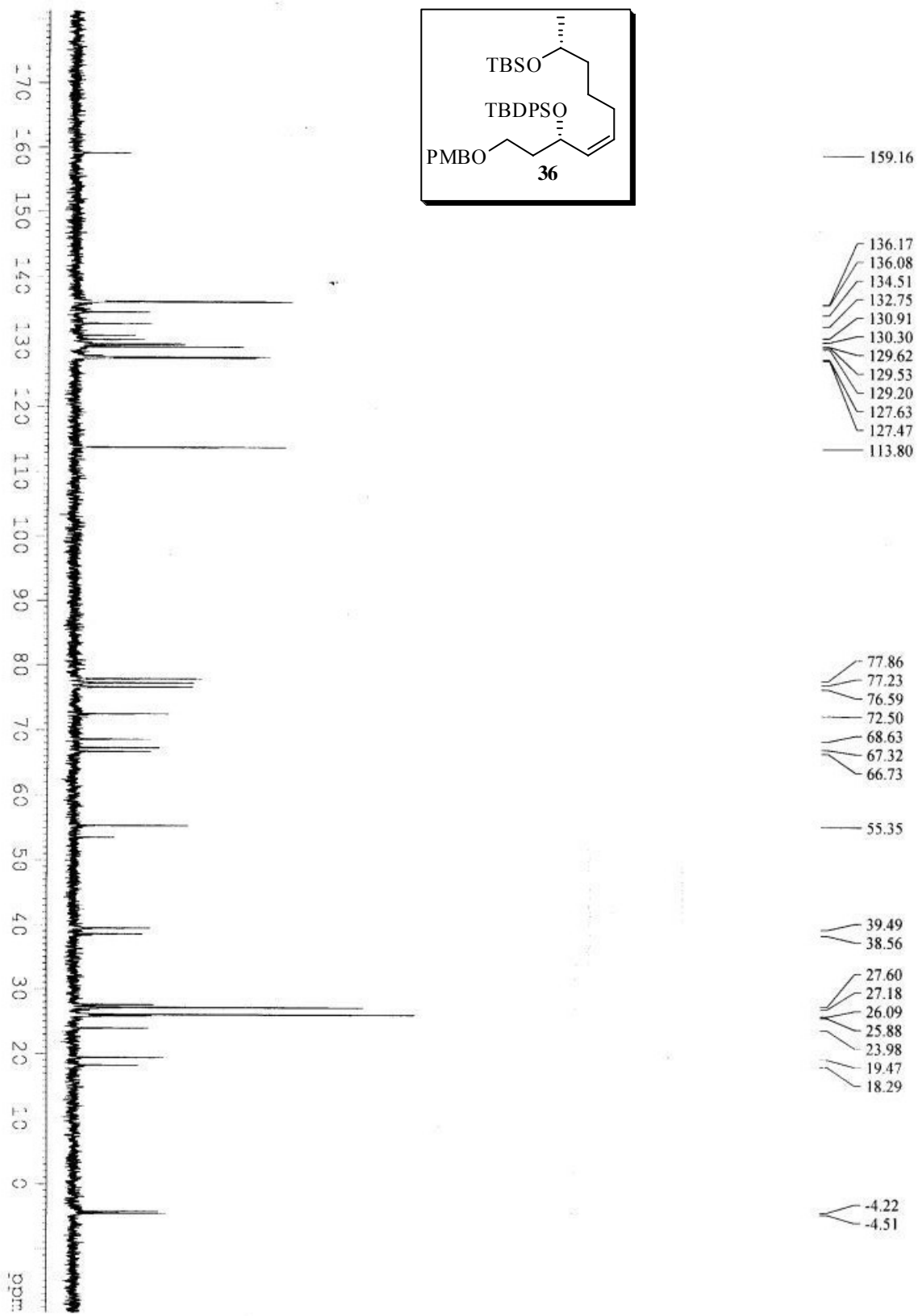
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



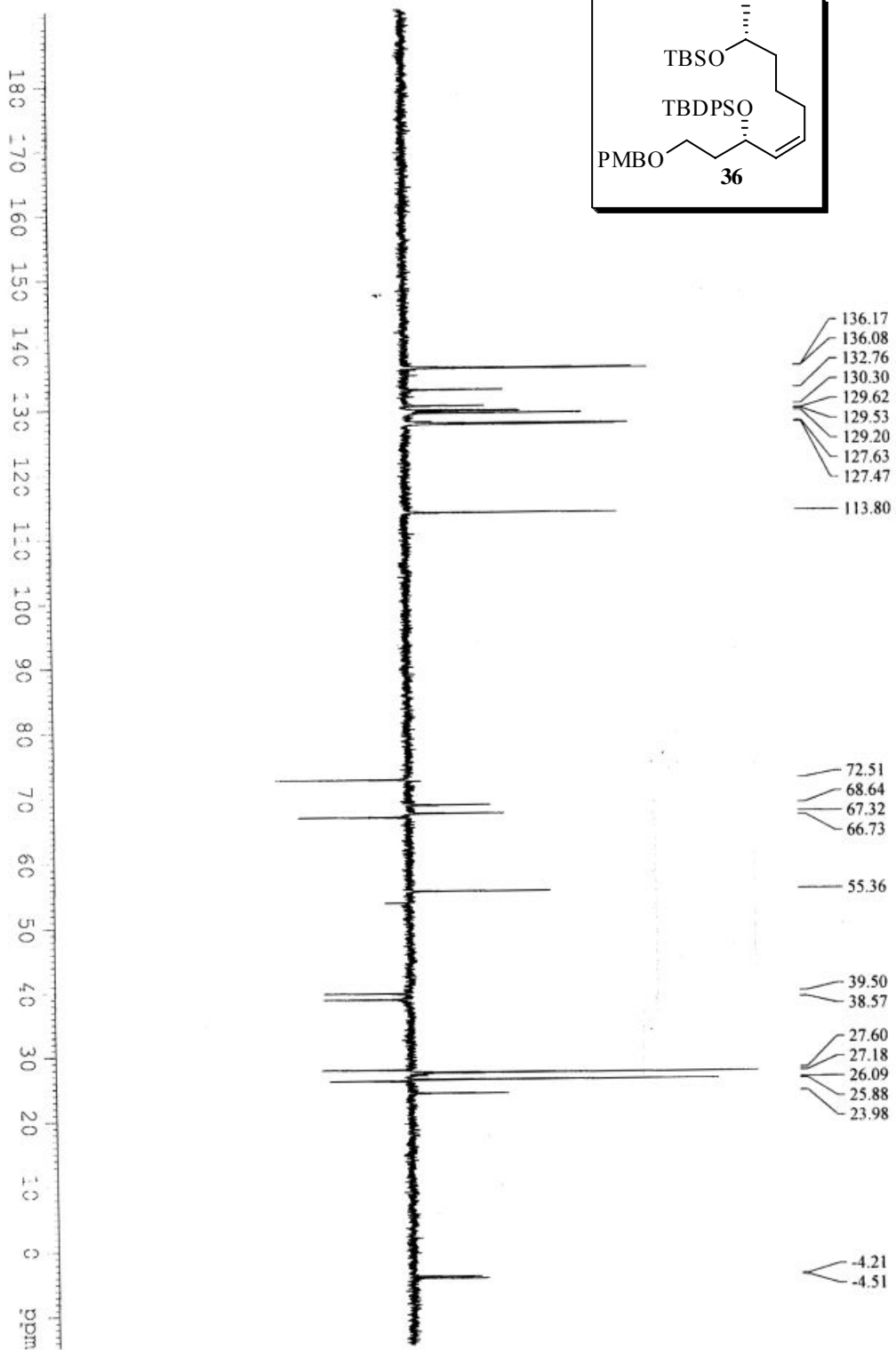
¹H- NMR of compound 36 (400MHz, CDCl₃)



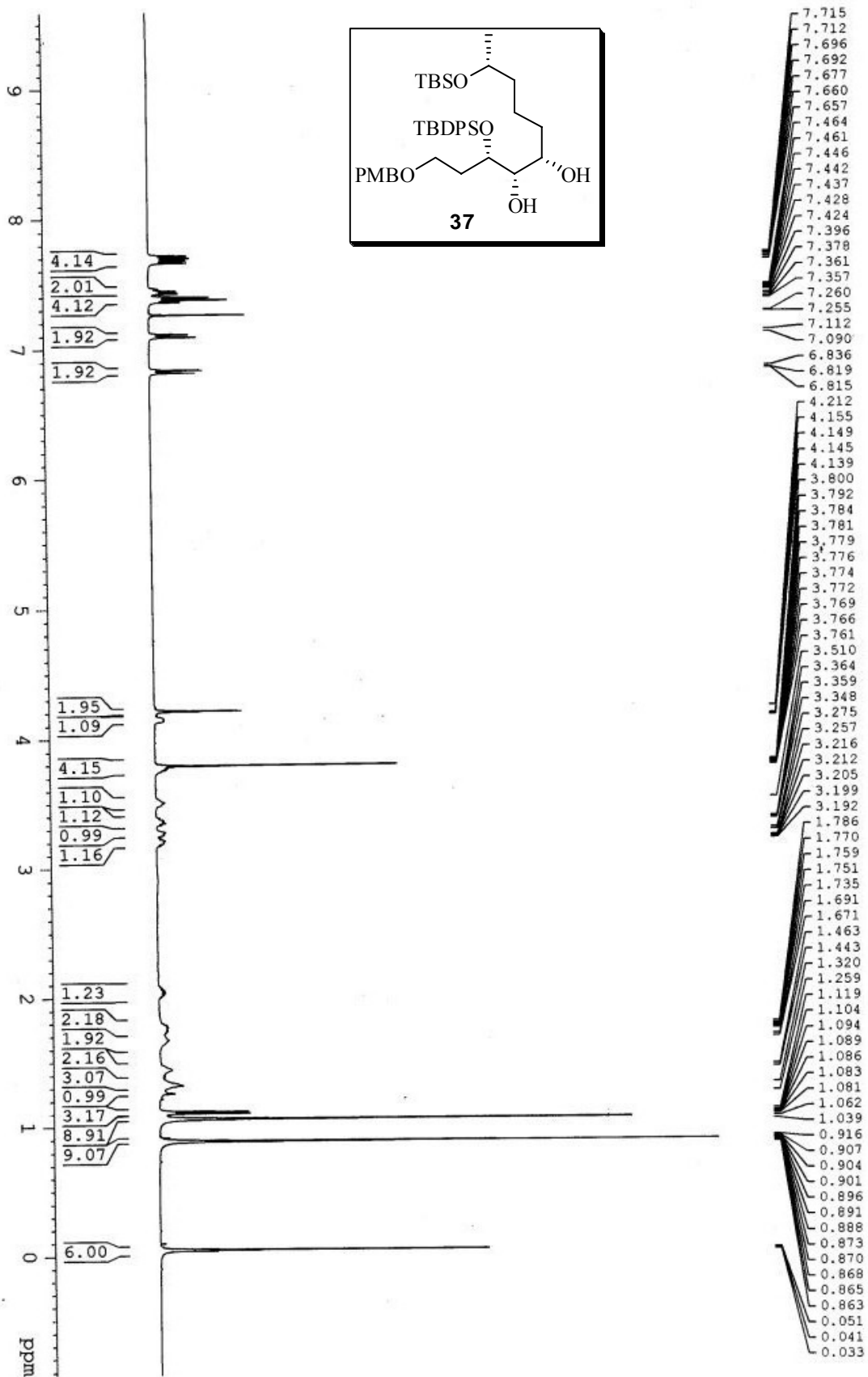
¹³C-NMR of compound 36 (50MHz, CDCl₃)



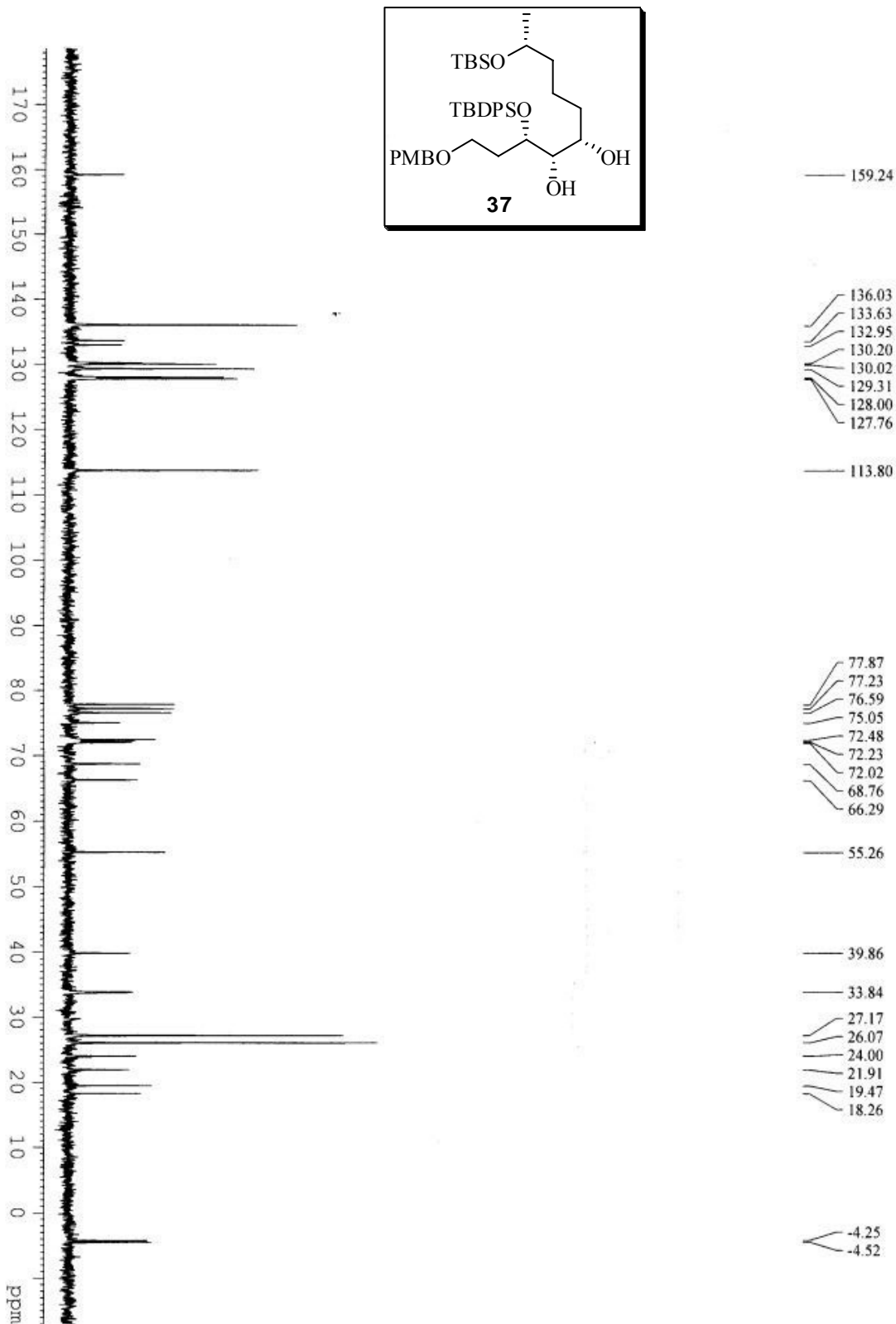
DEPT-NMR of compound 36 (50MHz, CDCl₃)



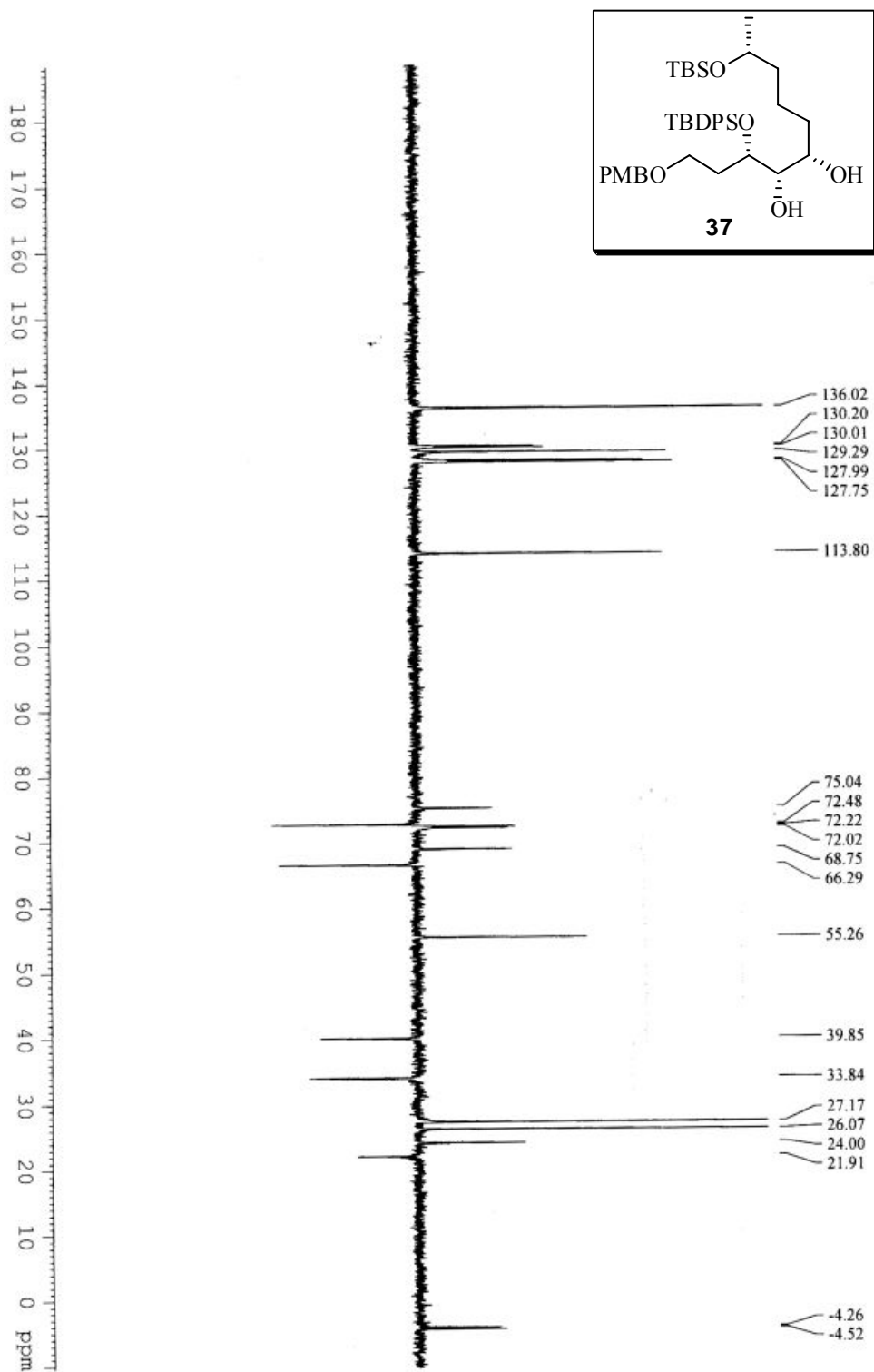
¹H- NMR of compound 37 (400MHz, CDCl₃)



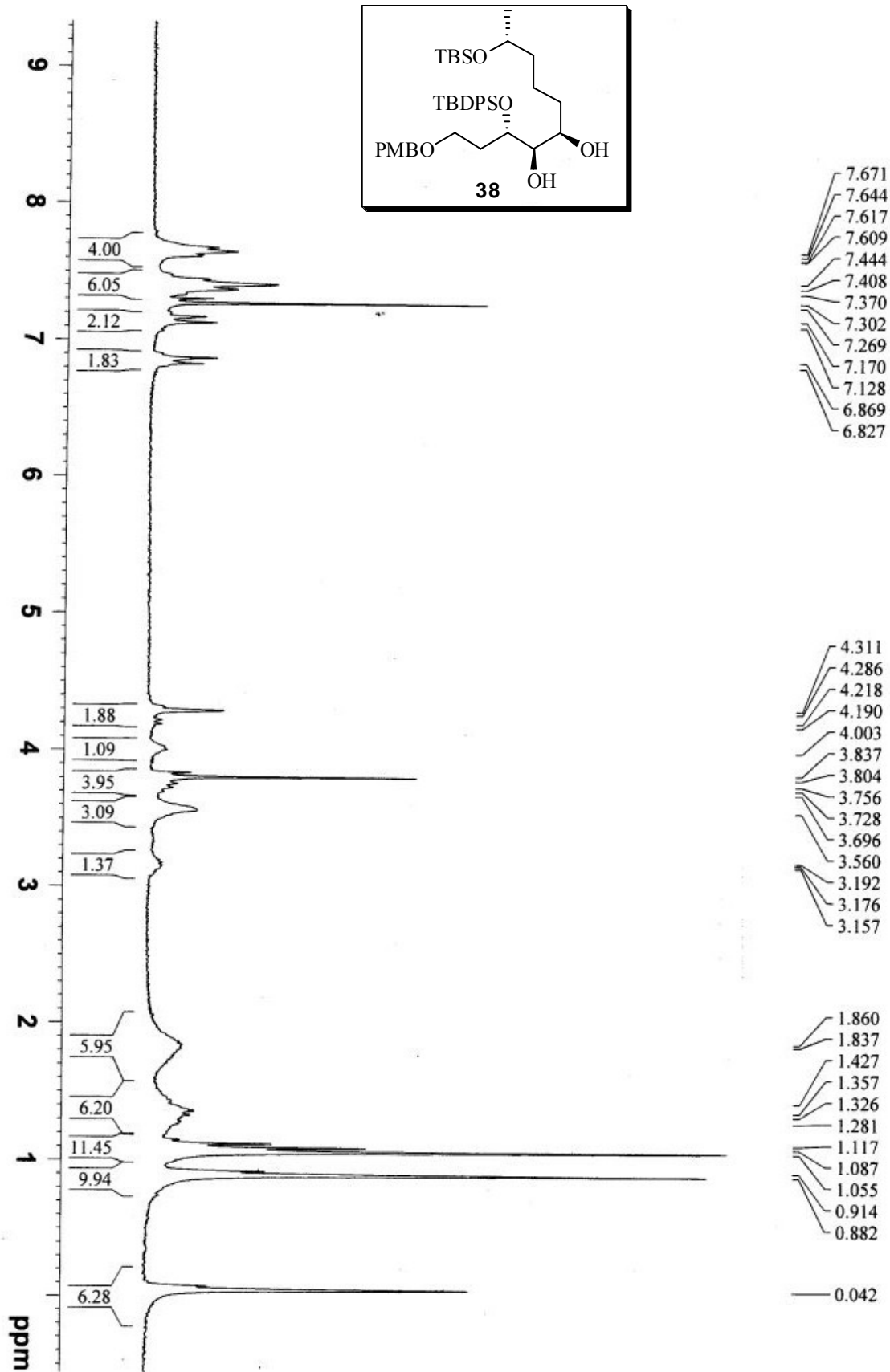
¹³C-NMR of compound 37 (50MHz, CDCl₃)



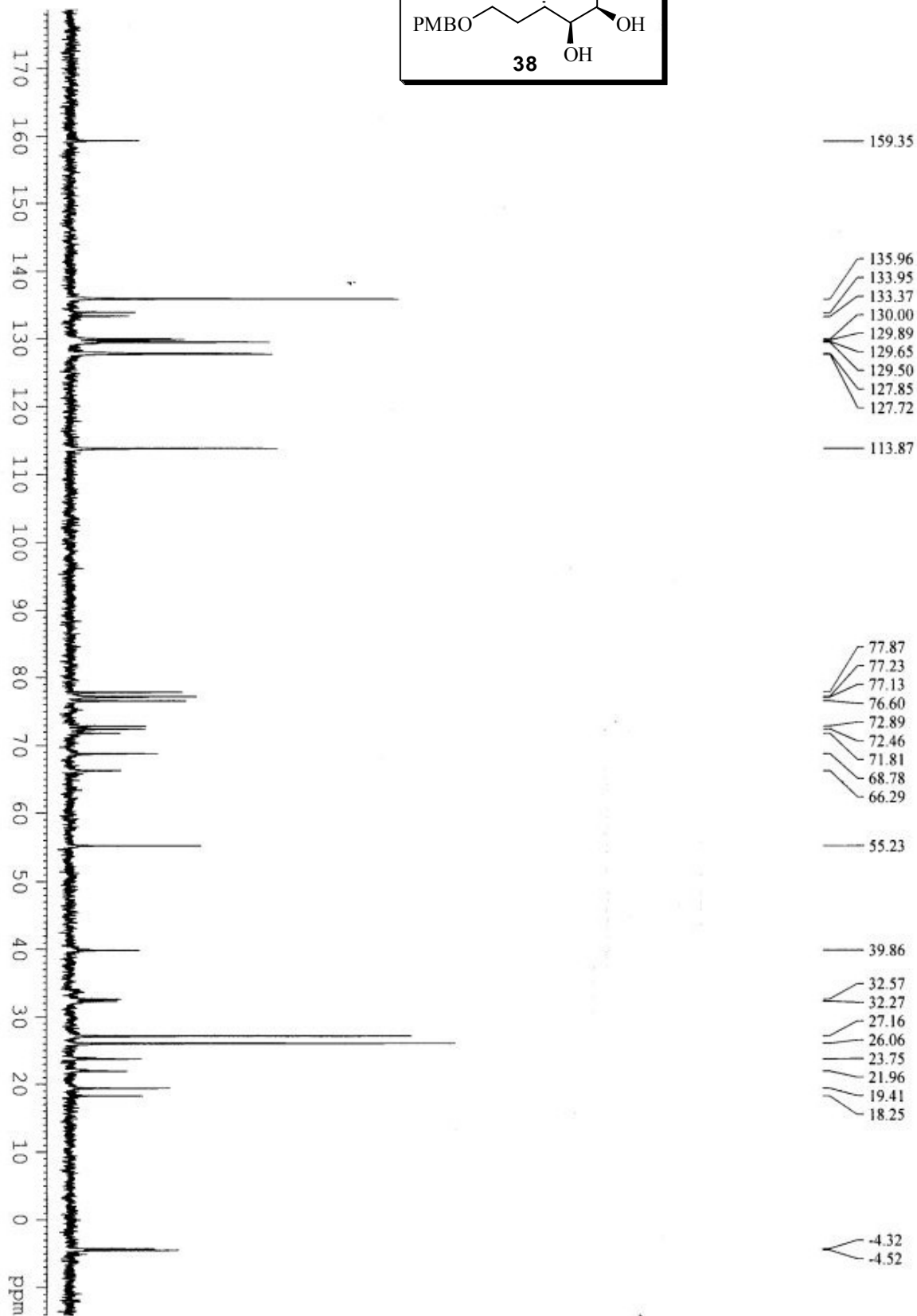
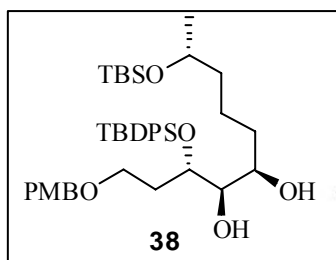
DEPT-NMR of compound 37 (50MHz, CDCl₃)



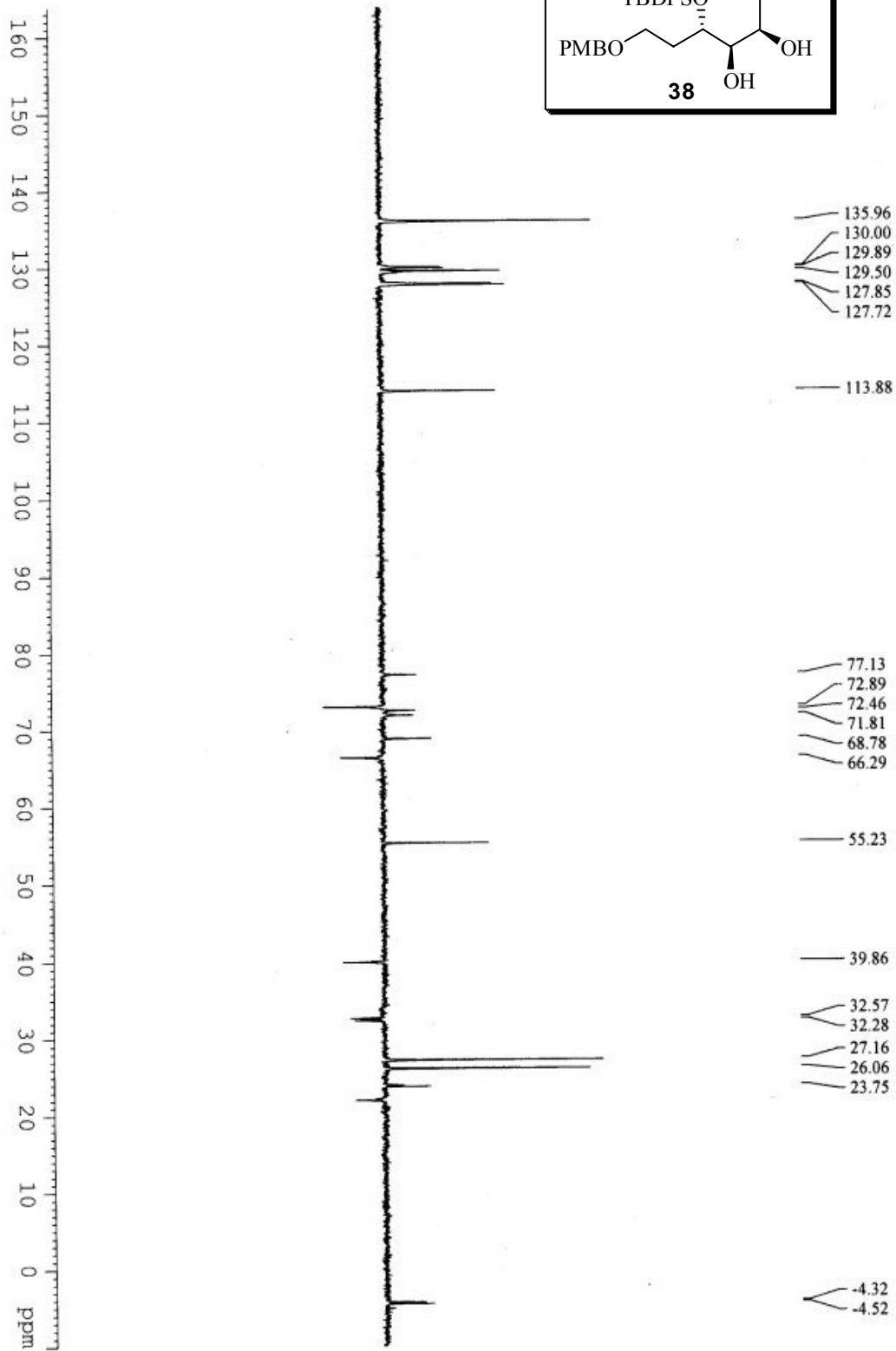
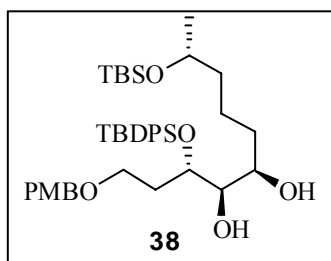
¹H- NMR of compound 38 (400MHz, CDCl₃)



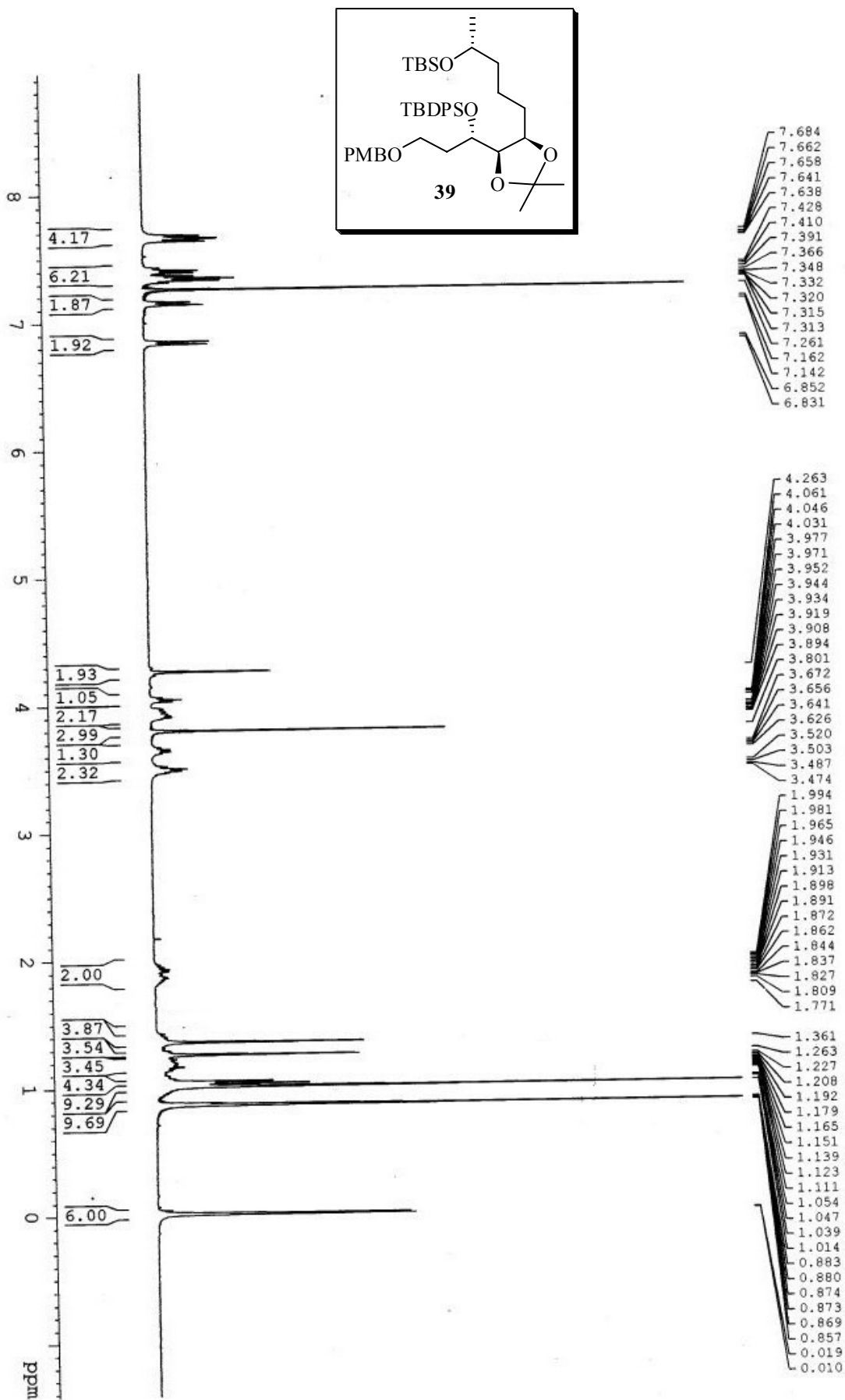
¹³C-NMR of compound 38 (50MHz, CDCl₃)



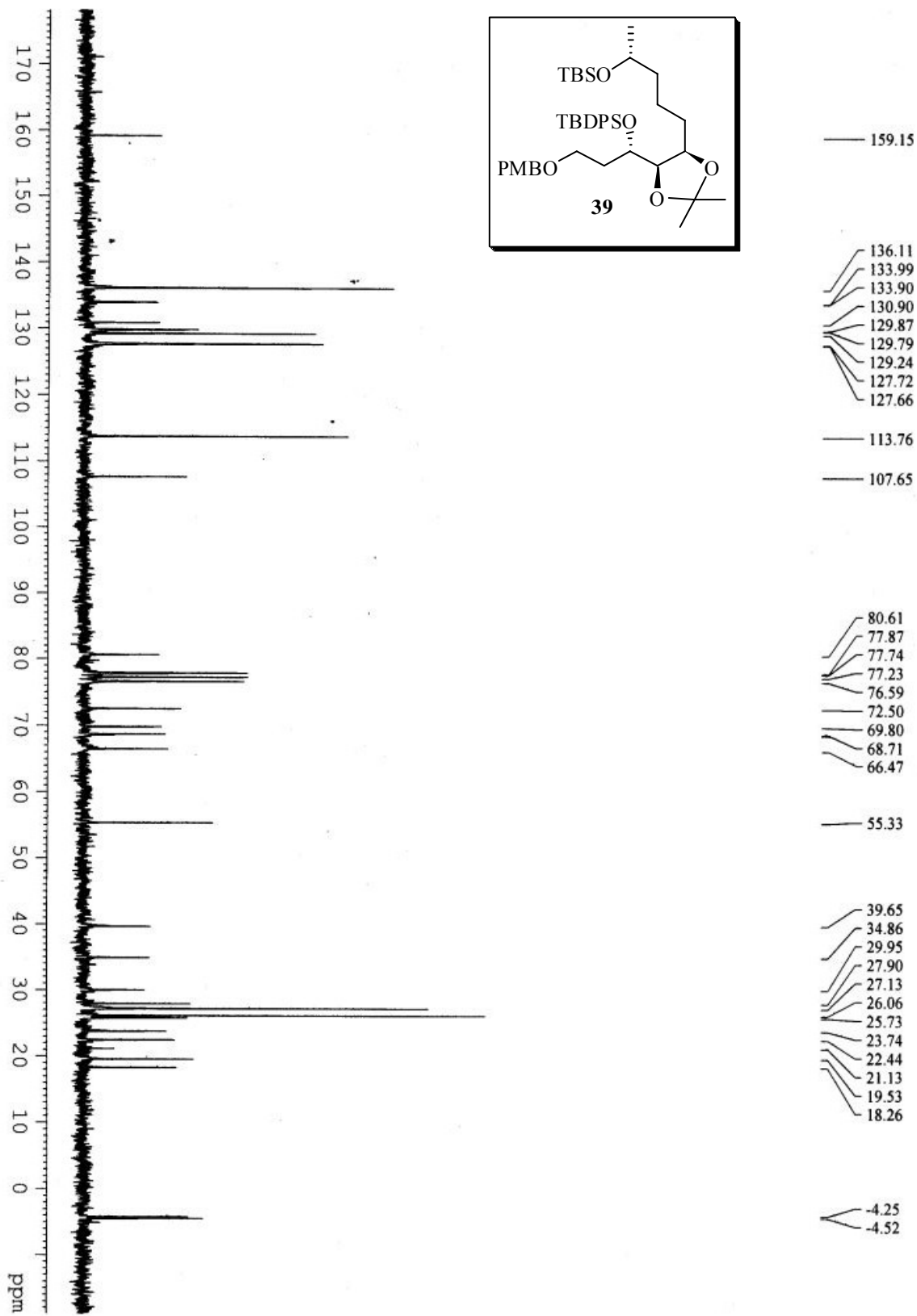
DEPT-NMR of compound 38 (50MHz, CDCl₃)



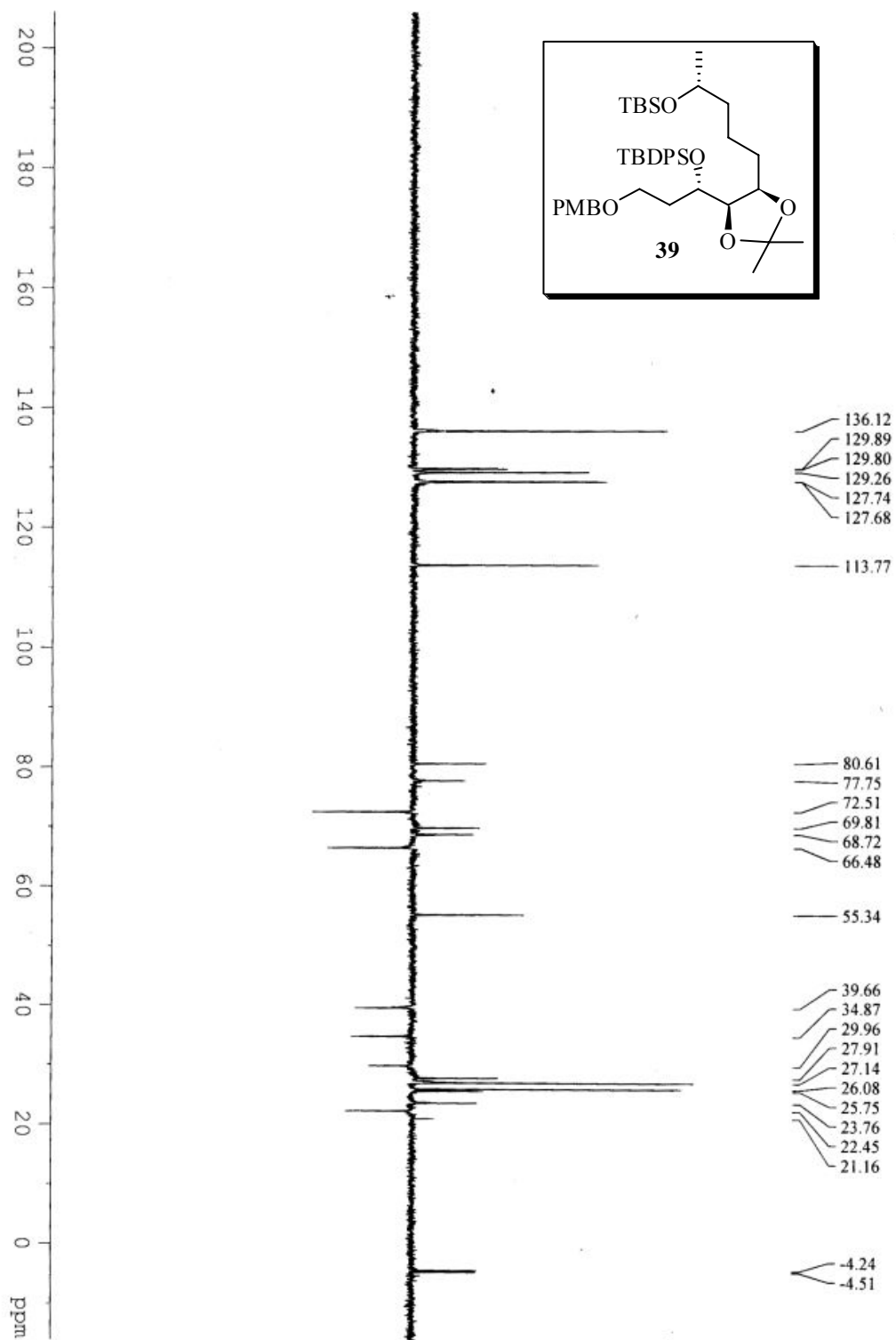
¹H-NMR of compound 39 (400MHz, CDCl₃)



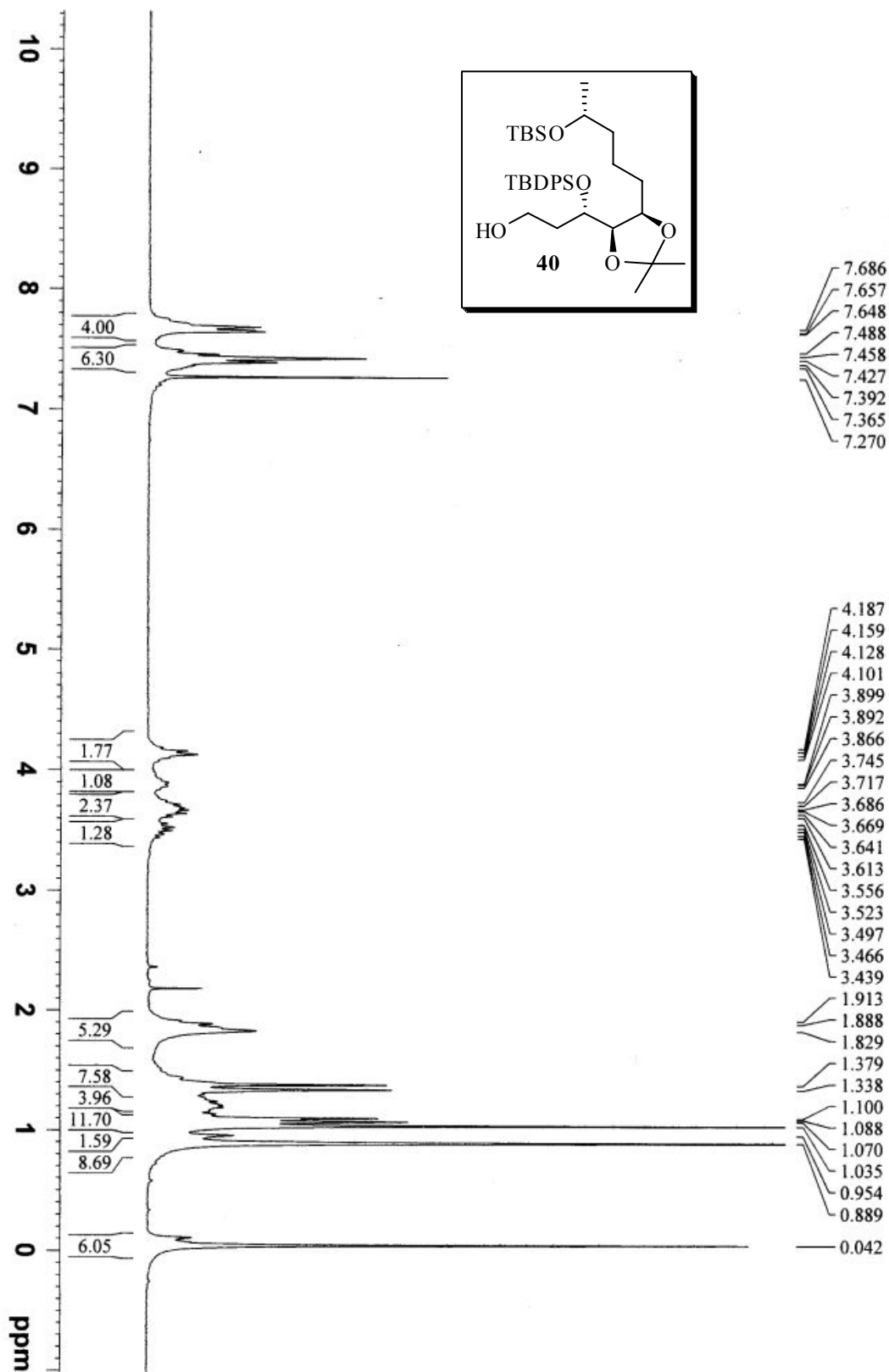
^{13}C -NMR of compound 39 (50MHz, CDCl_3)



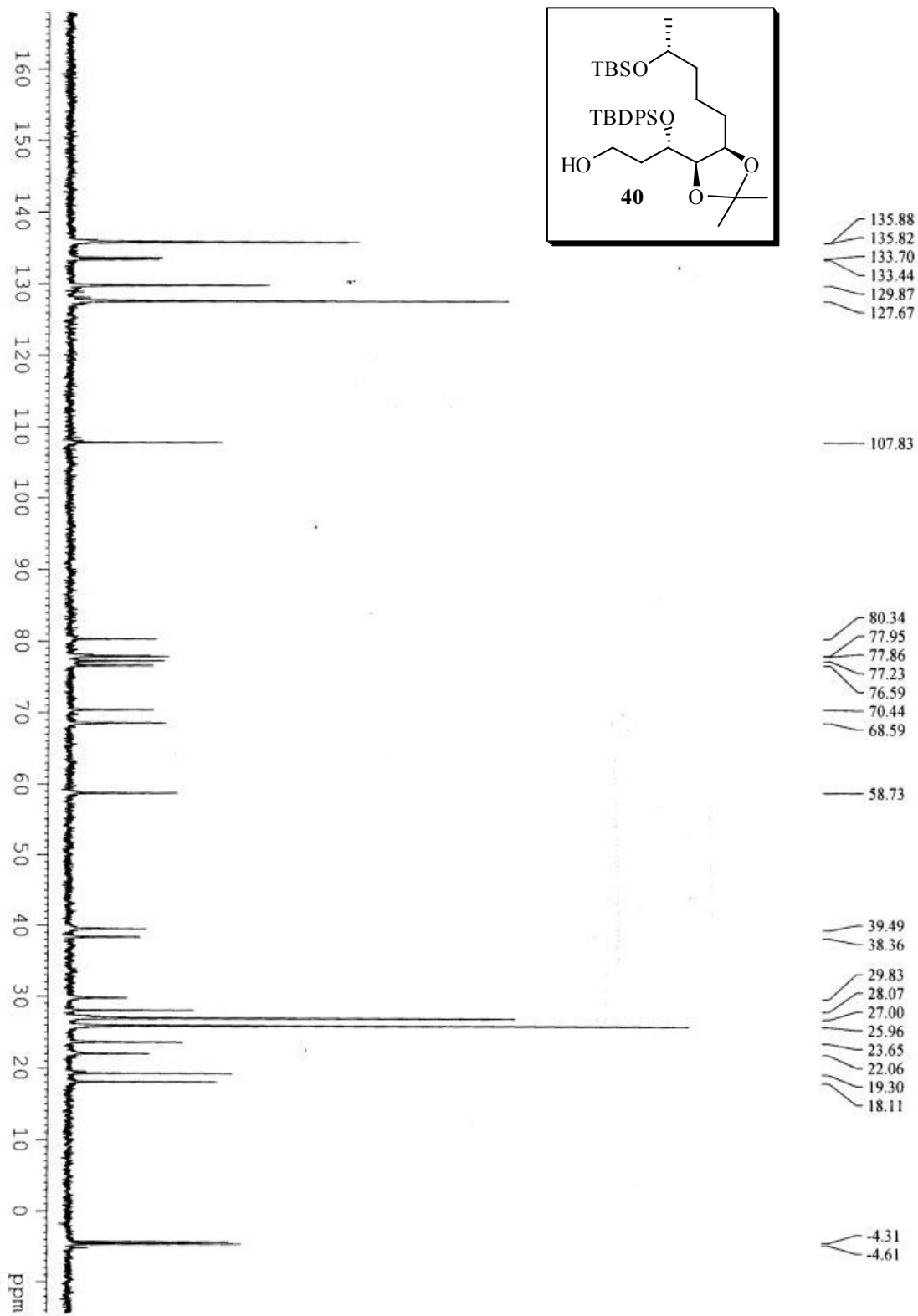
DEPT-NMR of compound 39 (50MHz, CDCl₃)



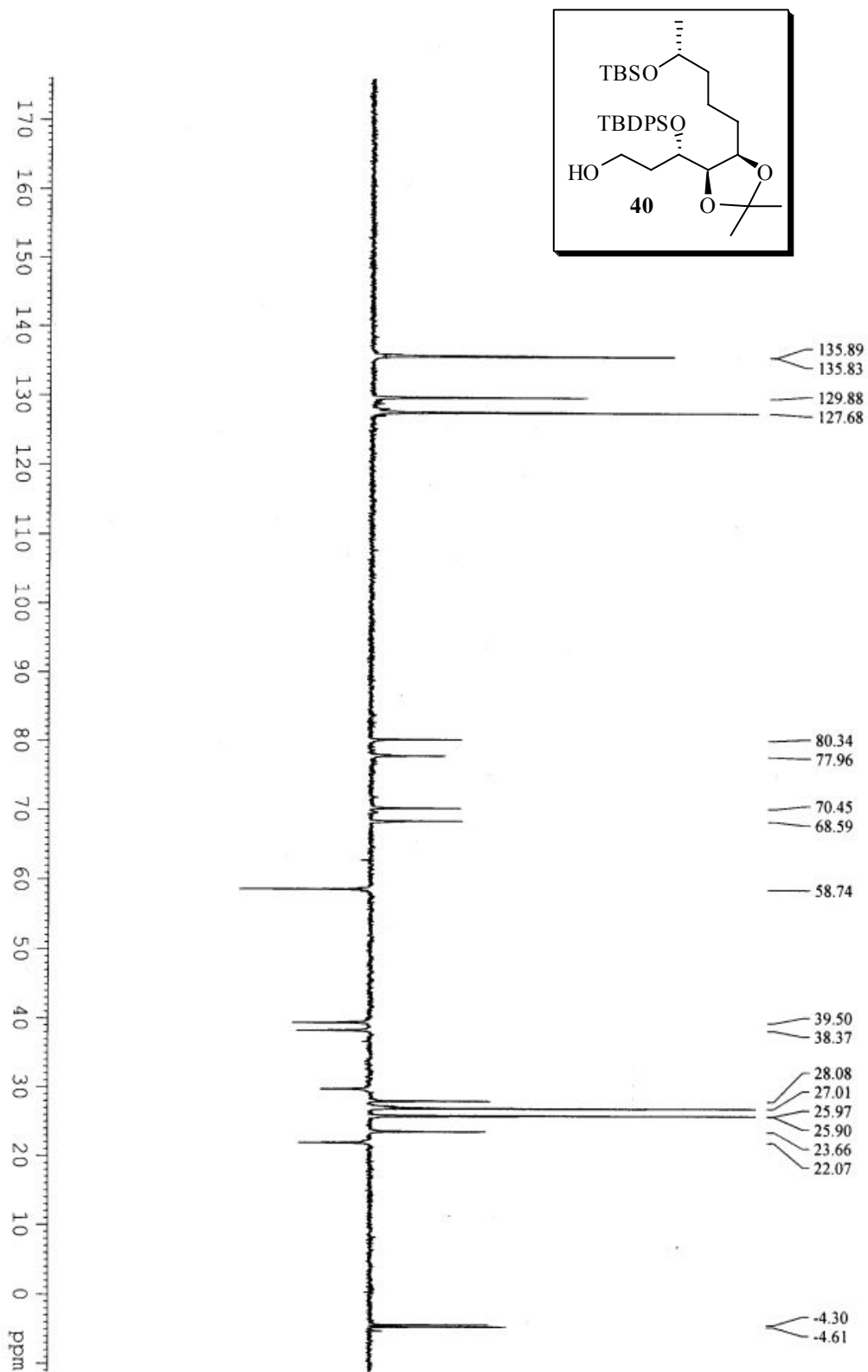
¹H- NMR of compound 40 (200MHz, CDCl₃)



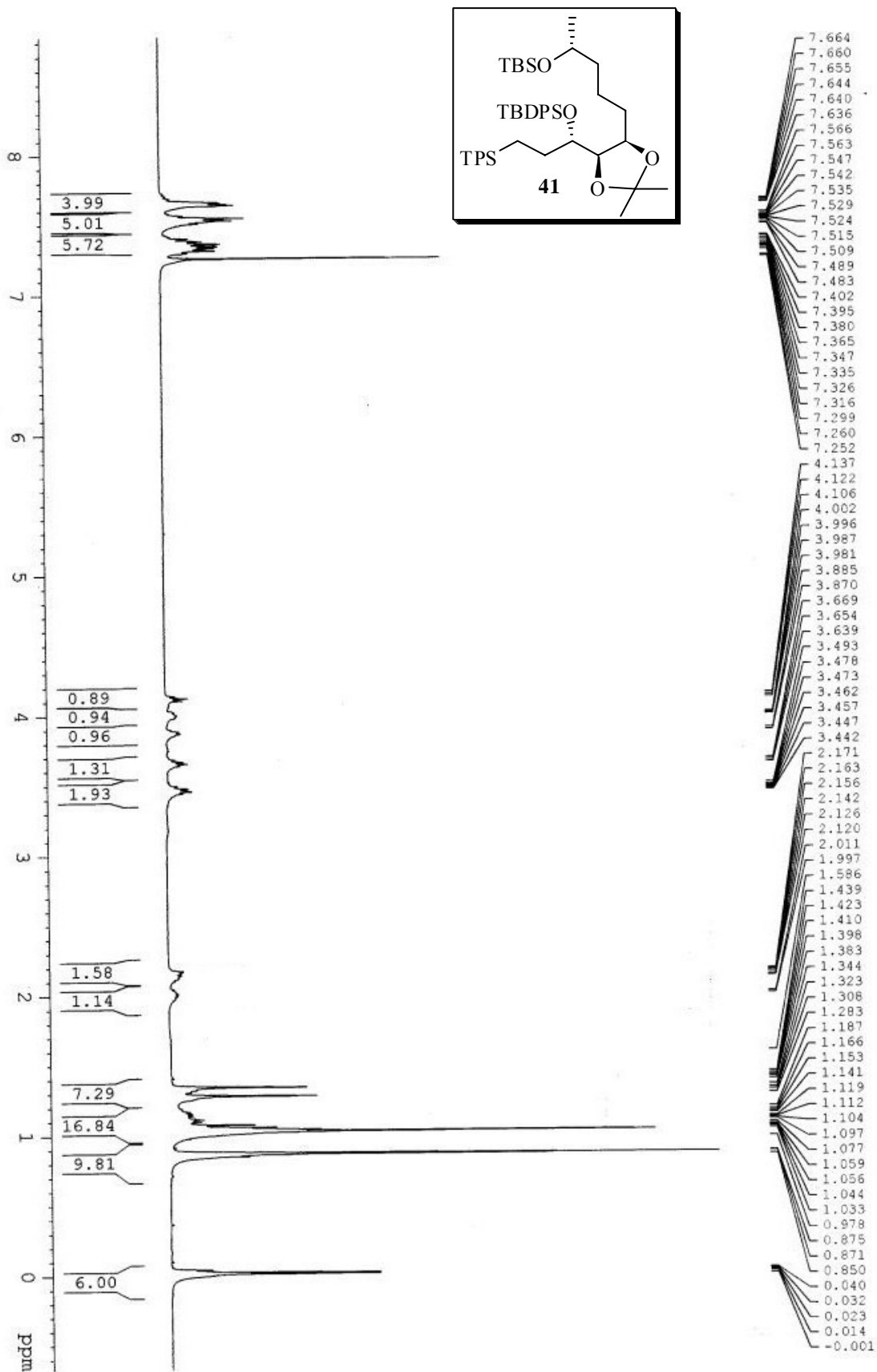
¹³C-NMR of compound 40 (50MHz, CDCl₃)



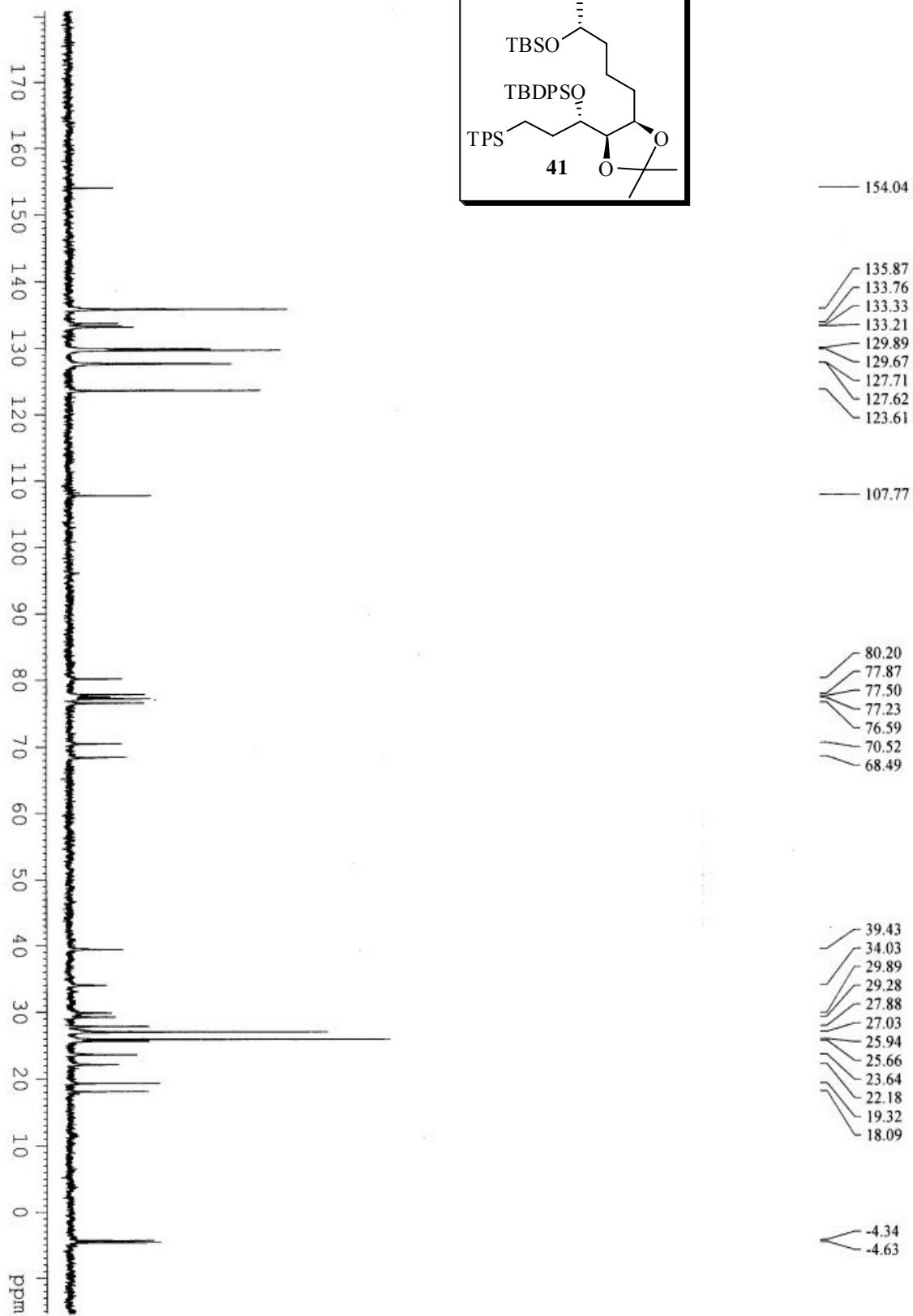
DEPT- NMR of compound 40 (50MHz, CDCl₃)



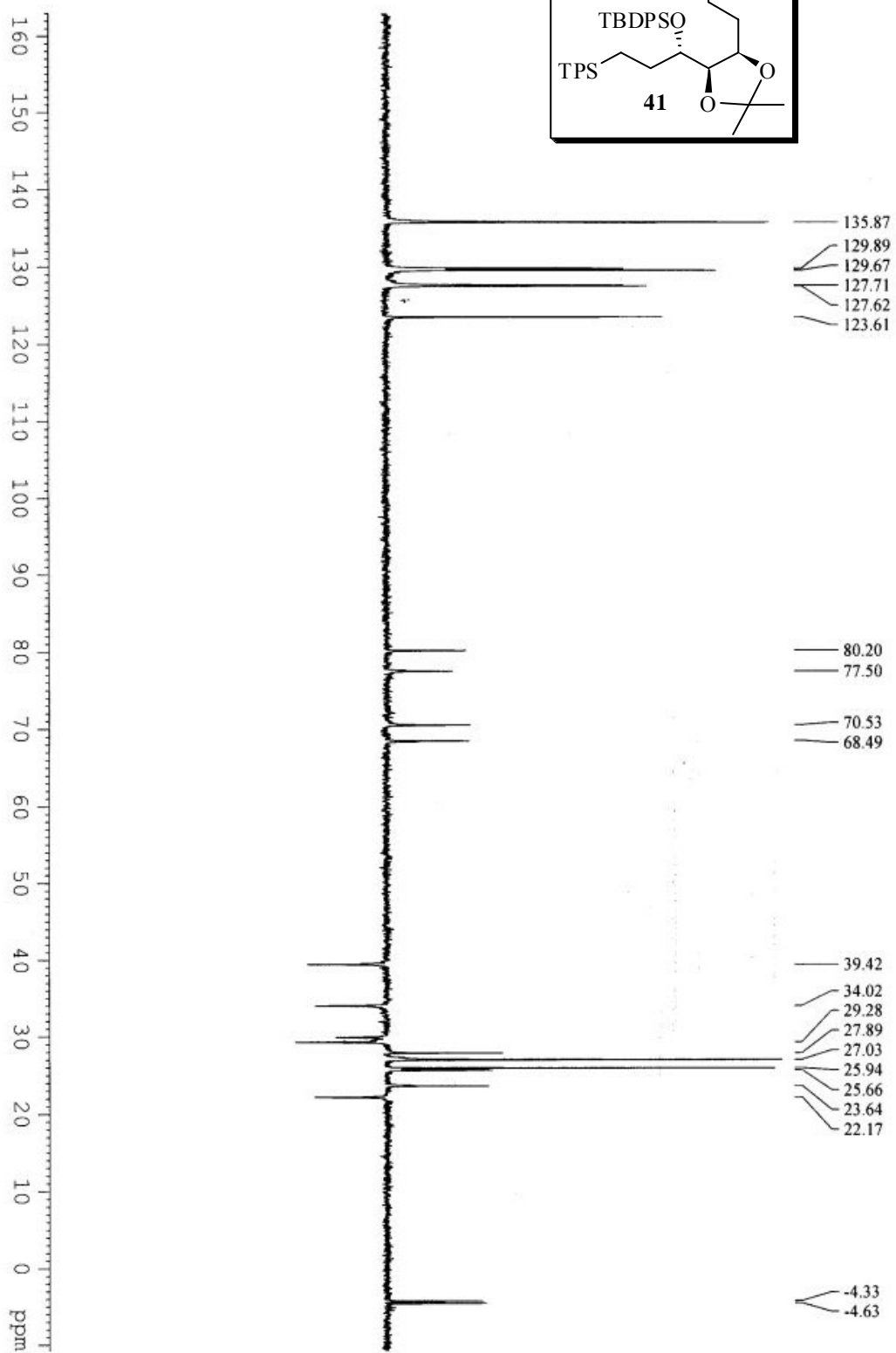
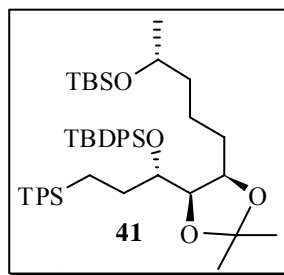
¹H-NMR of compound 41 (200MHz, CDCl₃)



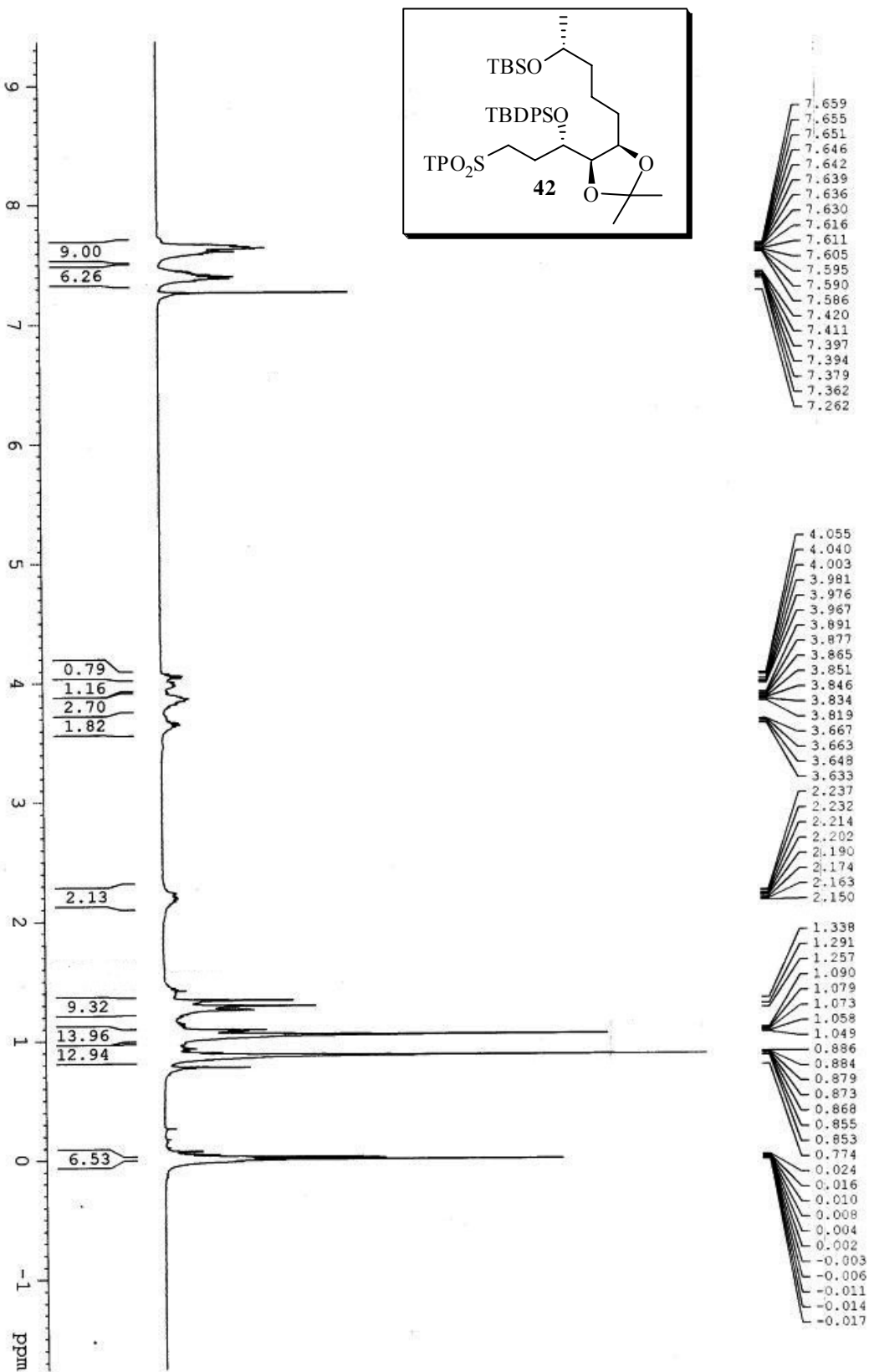
¹³C-NMR of compound 41 (50MHz, CDCl₃)



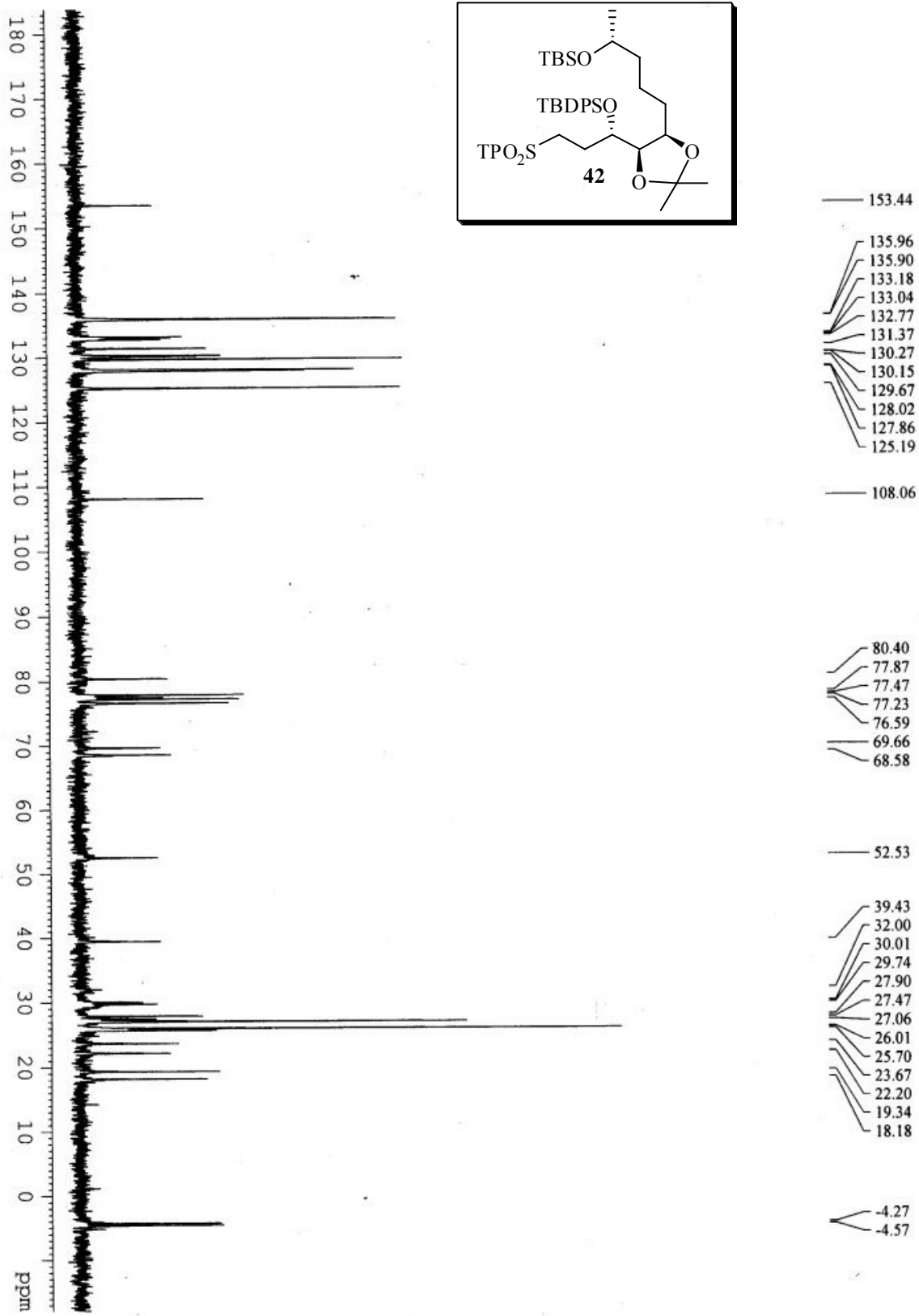
DEPT-NMR of compound 41 (50MHz, CDCl₃)



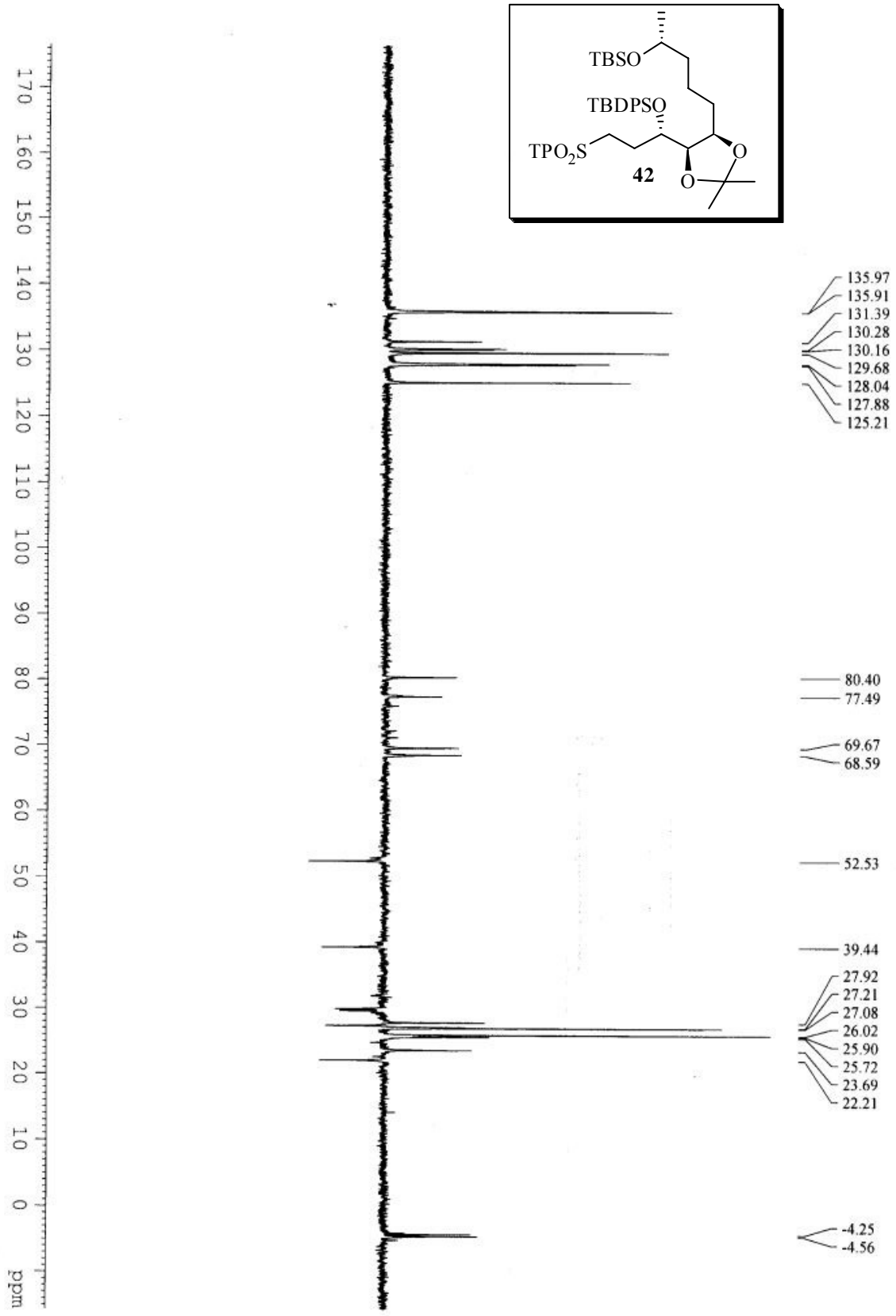
¹H-NMR of compound 42 (400MHz, CDCl₃)



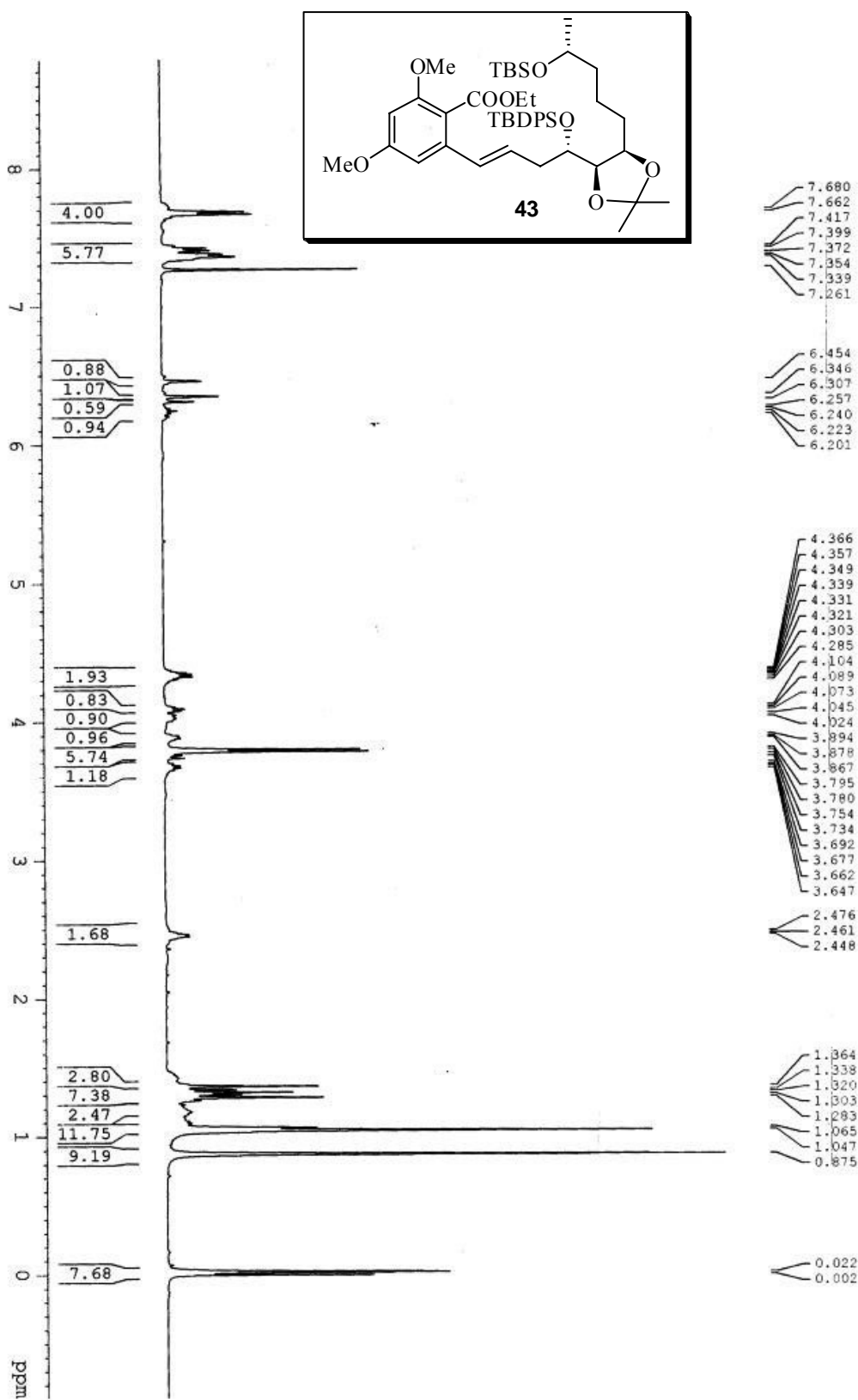
¹³C-NMR of compound 42 (50MHz, CDCl₃)



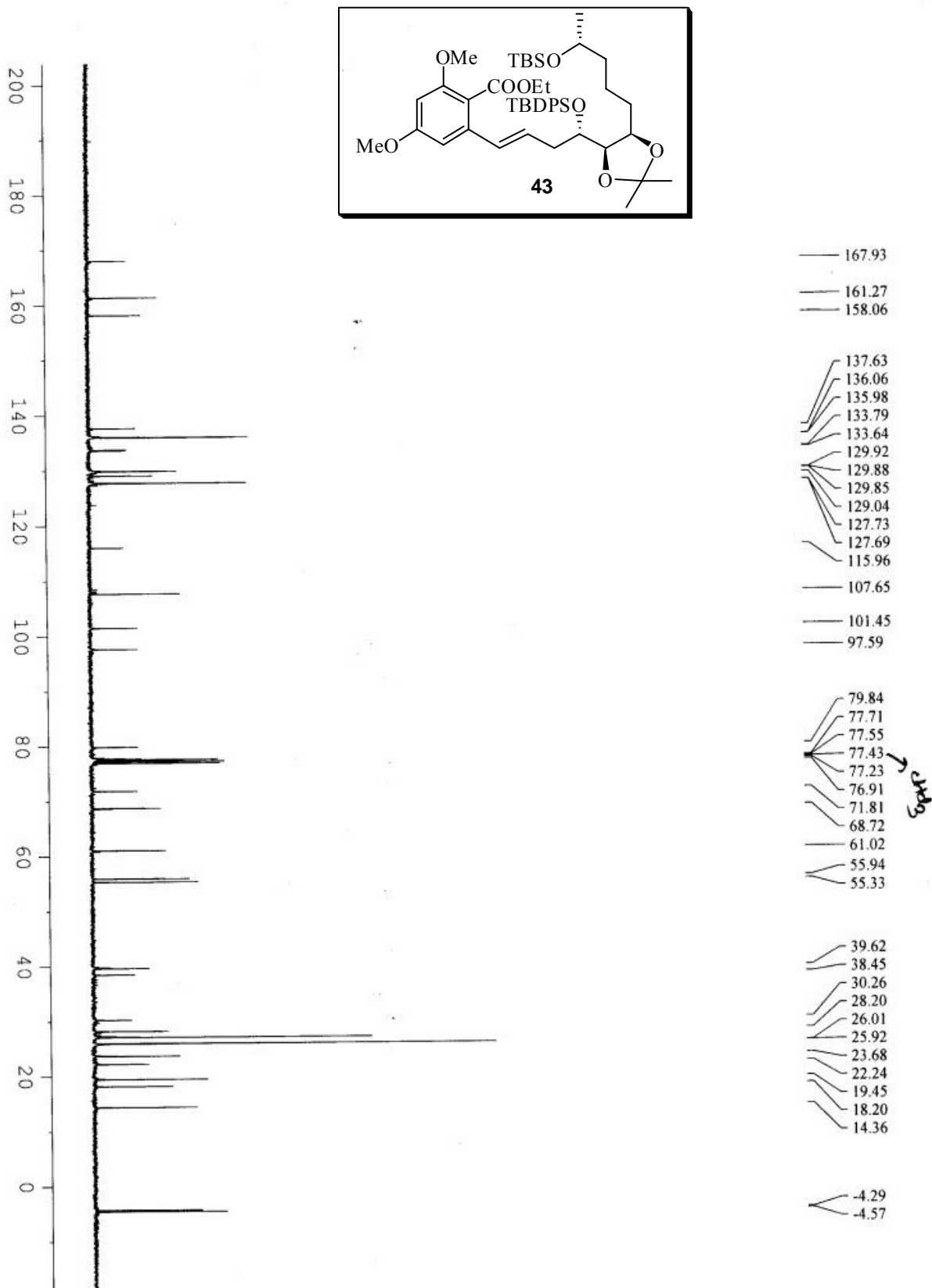
DEPT-NMR of compound 42 (50MHz, CDCl₃)



¹H-NMR of compound 43 (400MHz, CDCl₃)

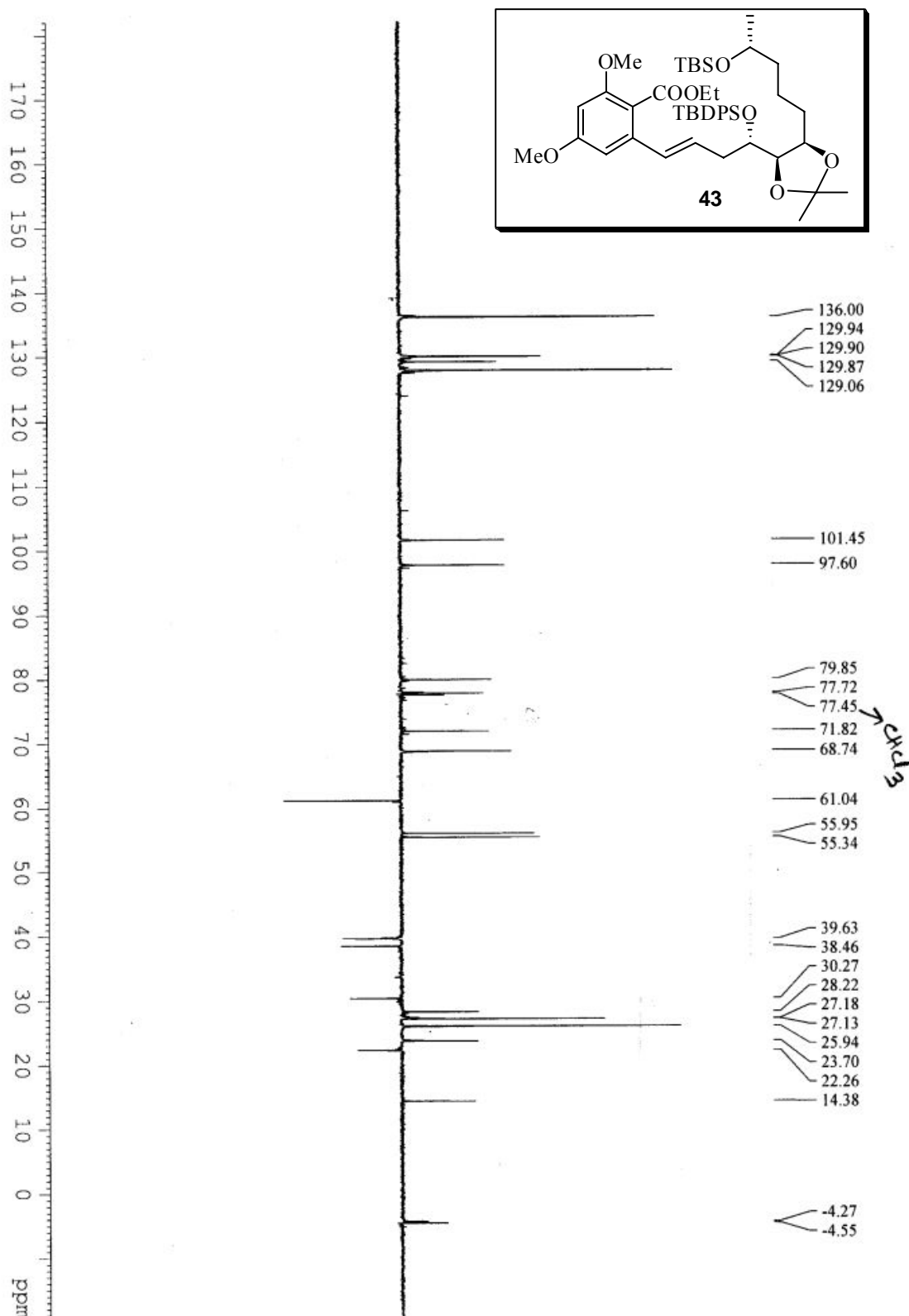


¹³C-NMR of compound 43 (100MHz, CDCl₃)

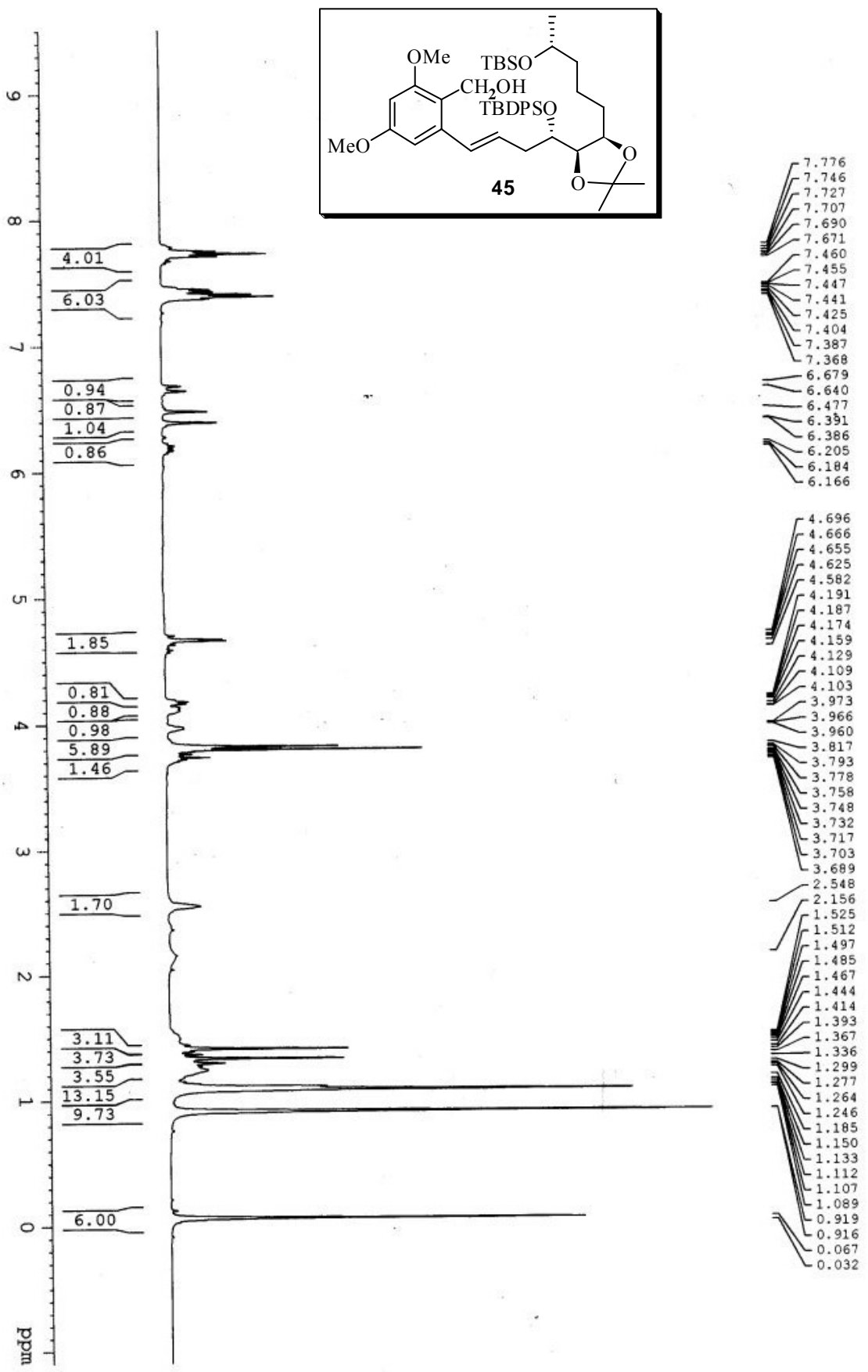


- 167.93
- 161.27
- 158.06
- 137.63
- 136.06
- 135.98
- 133.79
- 133.64
- 129.92
- 129.88
- 129.85
- 129.04
- 127.73
- 127.69
- 115.96
- 107.65
- 101.45
- 97.59
- 79.84
- 77.71
- 77.55
- 77.43
- 77.23
- 76.91
- 71.81
- 68.72
- 61.02
- 55.94
- 55.33
- 39.62
- 38.45
- 30.26
- 28.20
- 26.01
- 25.92
- 23.68
- 22.24
- 19.45
- 18.20
- 14.36
- 4.29
- 4.57

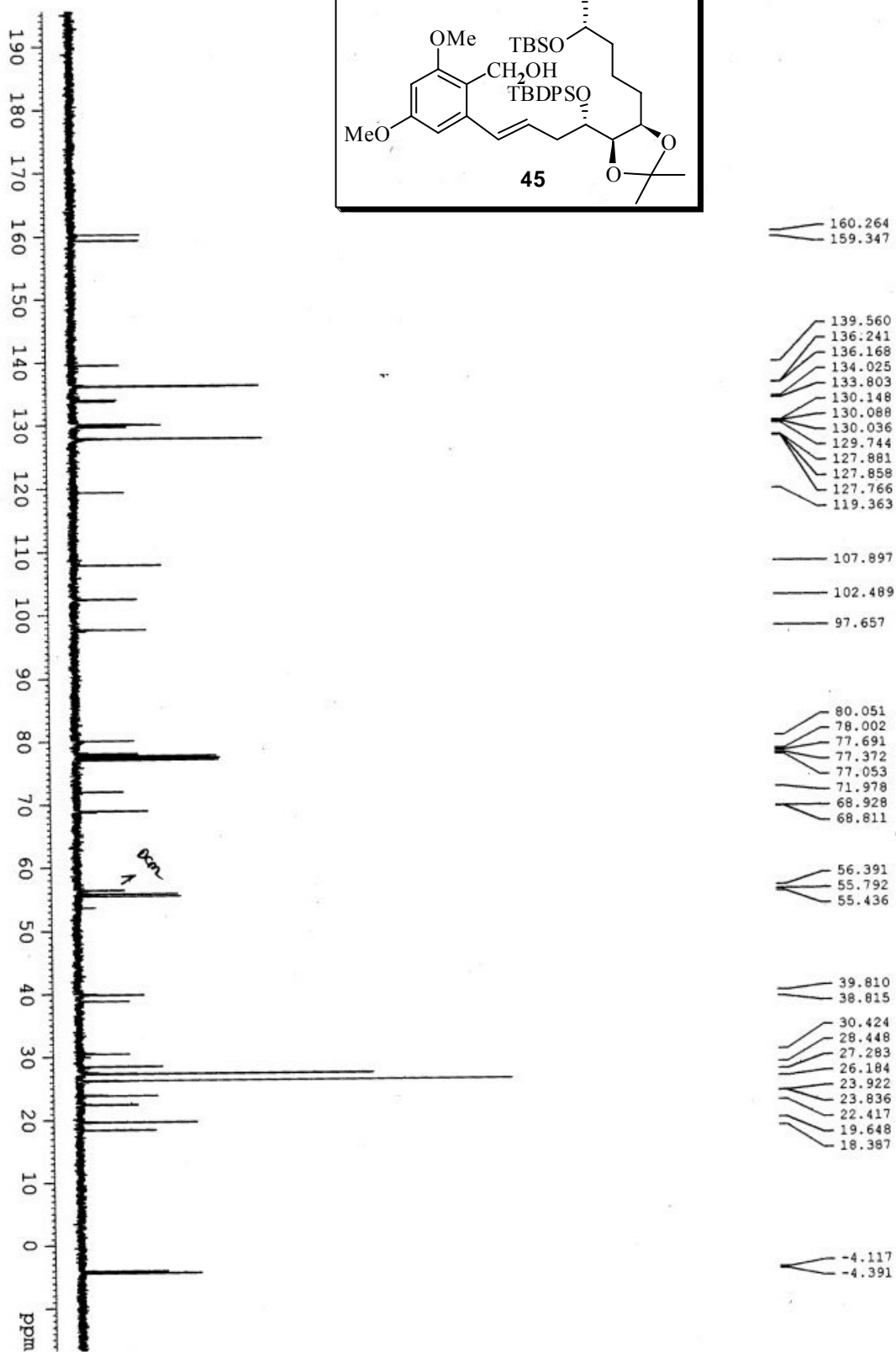
DEPT- NMR of compound 43 (100MHz, CDCl₃)



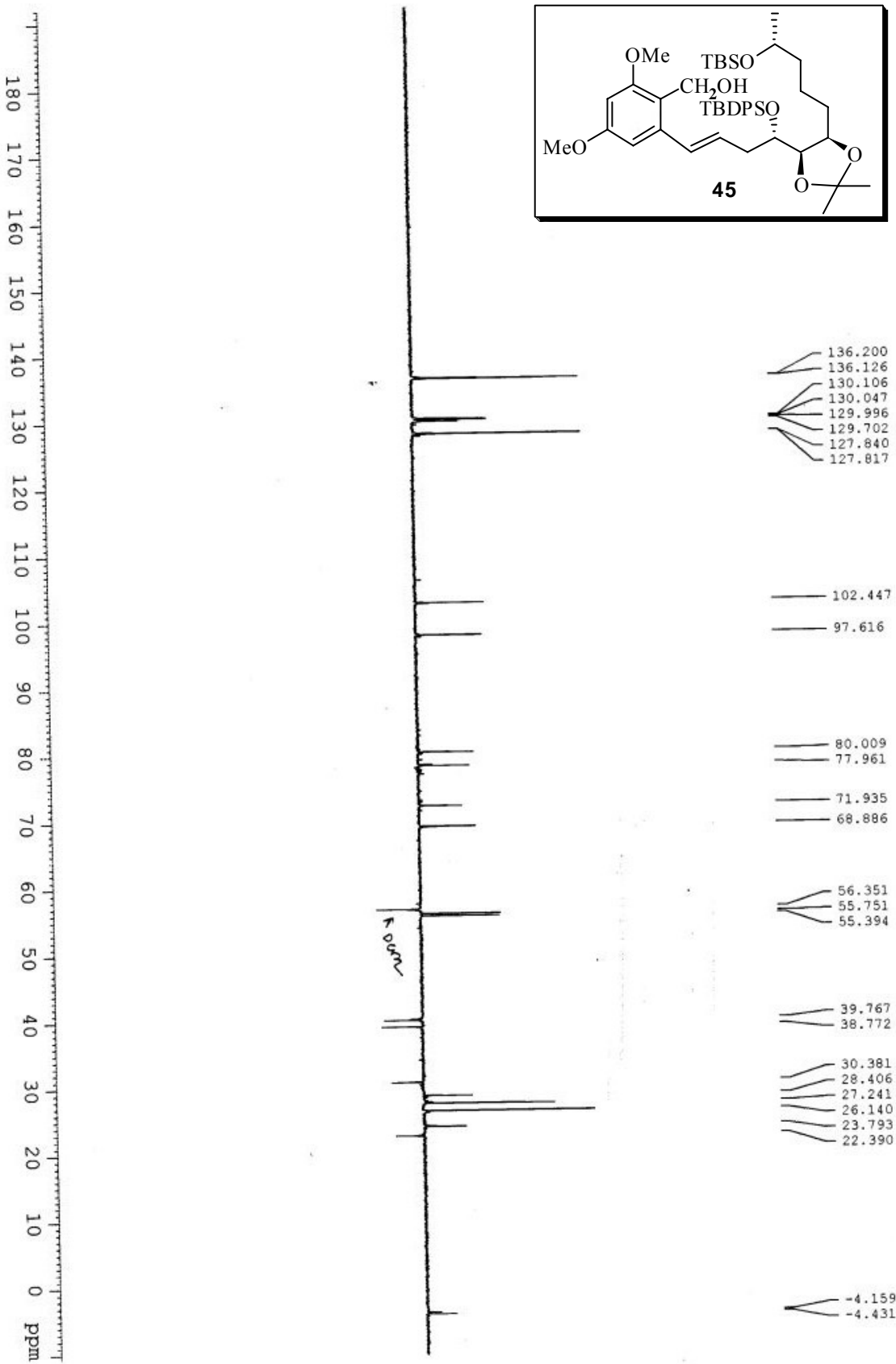
¹H-NMR of compound 45 (400MHz, CDCl₃)



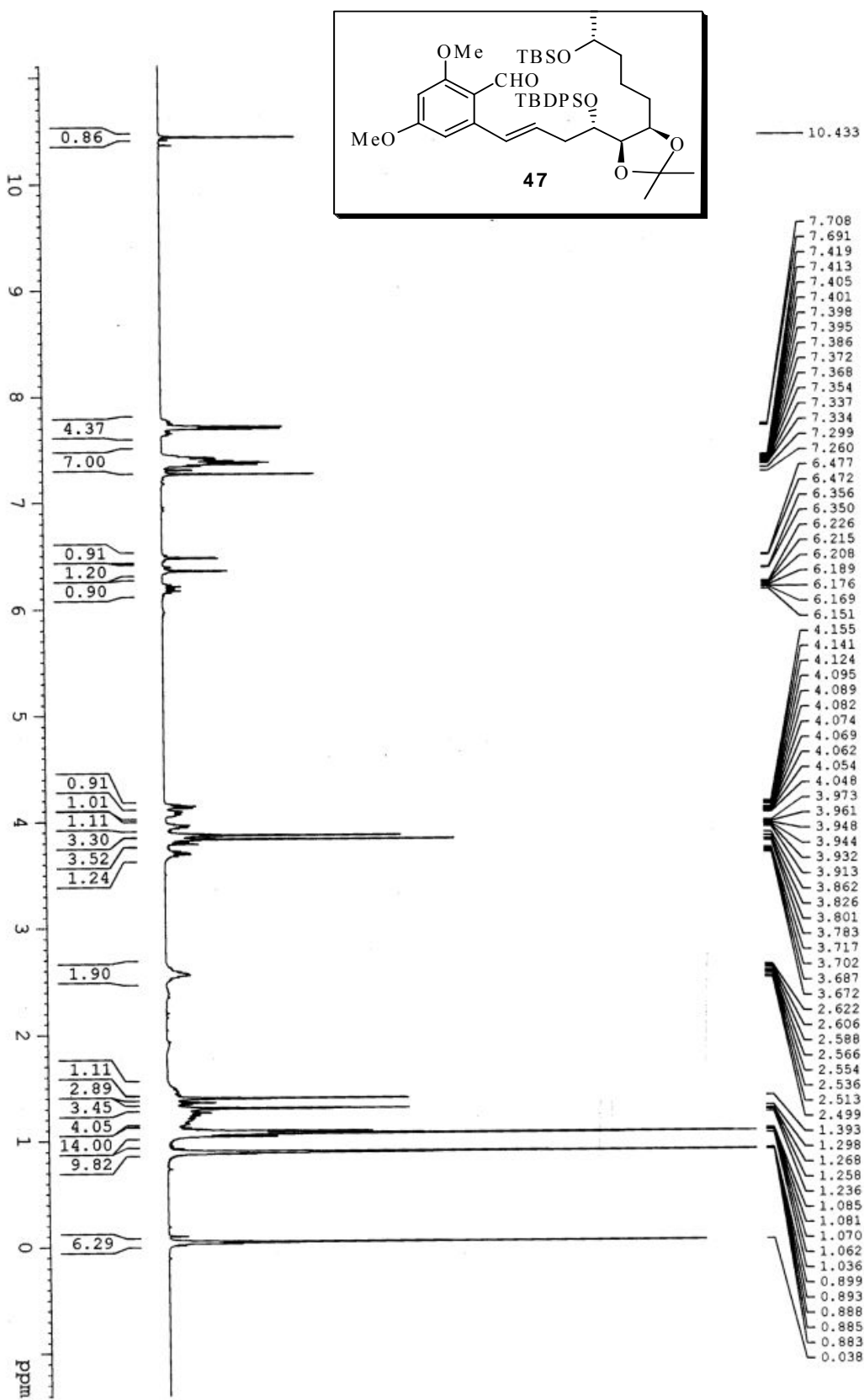
¹³C-NMR of compound 45 (100MHz, CDCl₃)



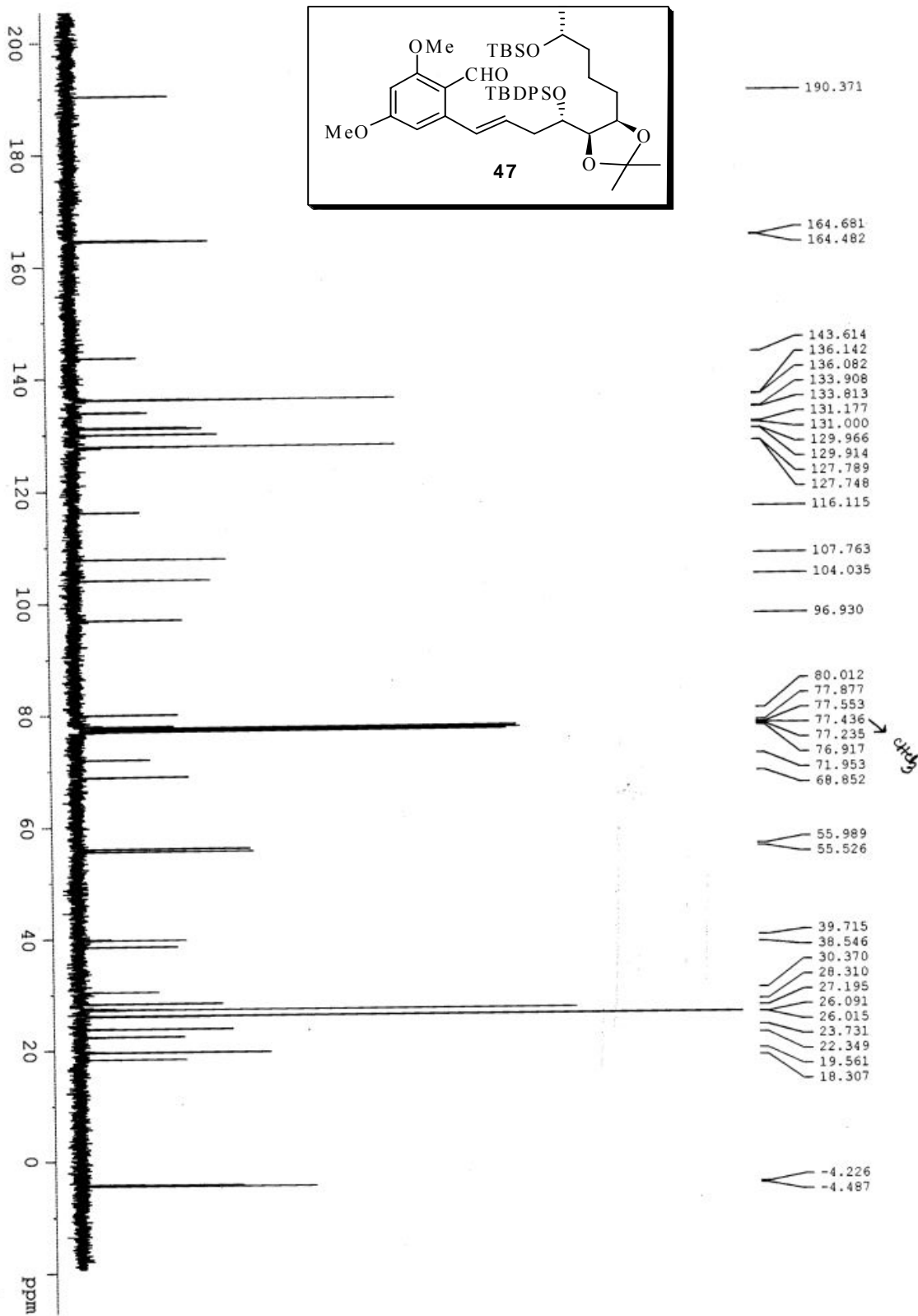
DEPT- NMR of compound 45 (100MHz, CDCl₃)



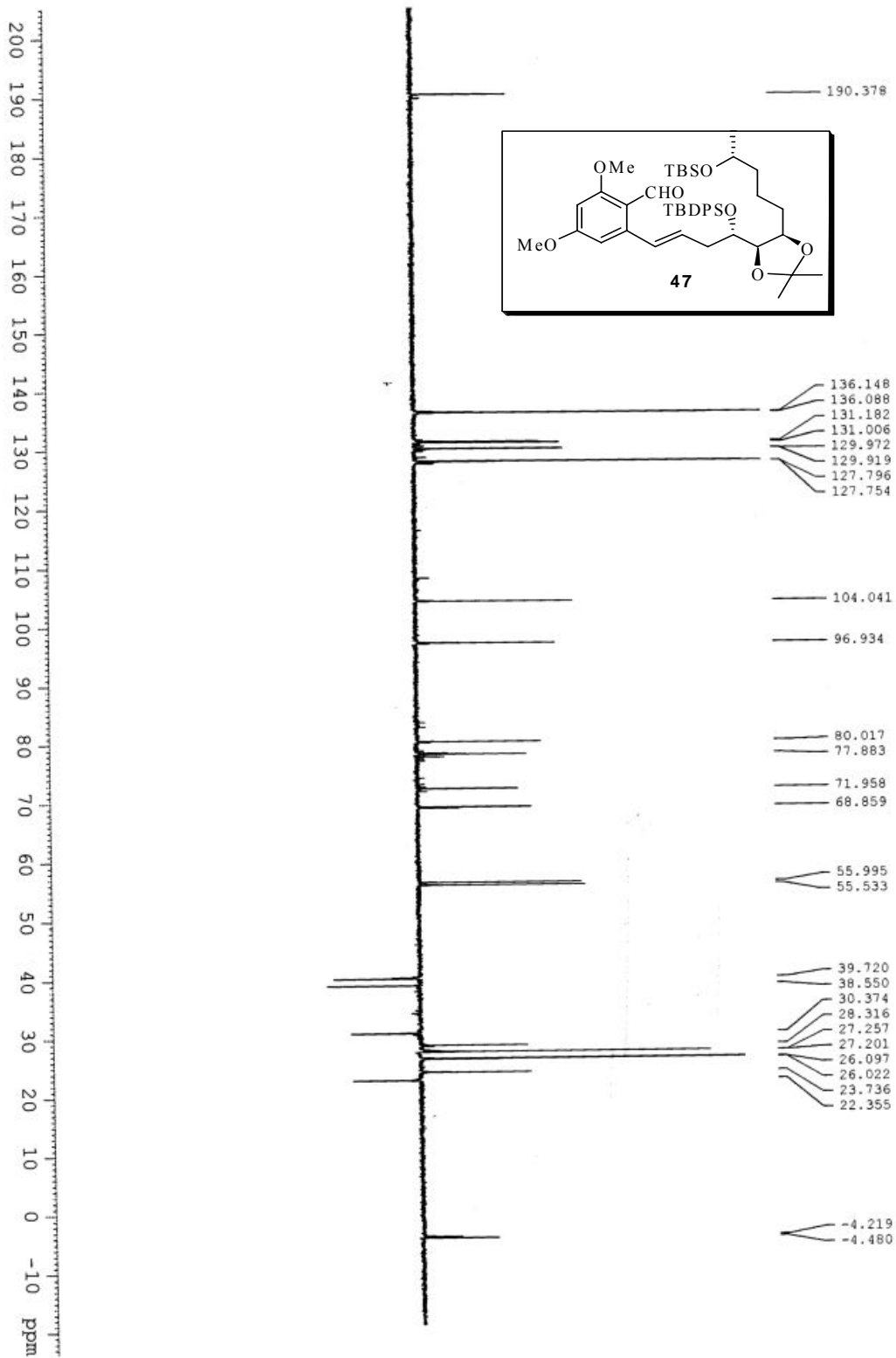
¹H-NMR of compound 47 (400MHz, CDCl₃)



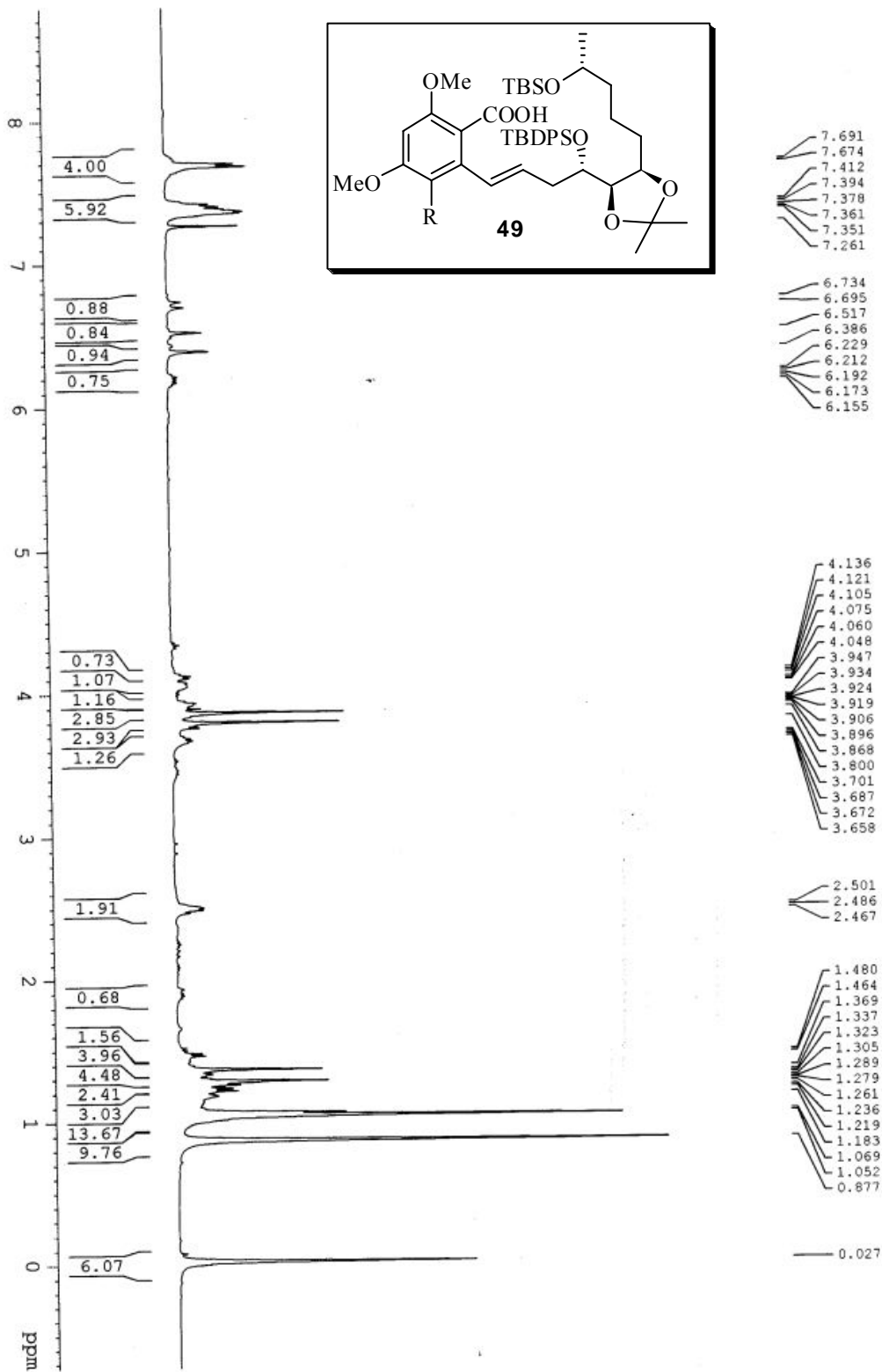
¹³C-NMR of compound 47 (100MHz, CDCl₃)



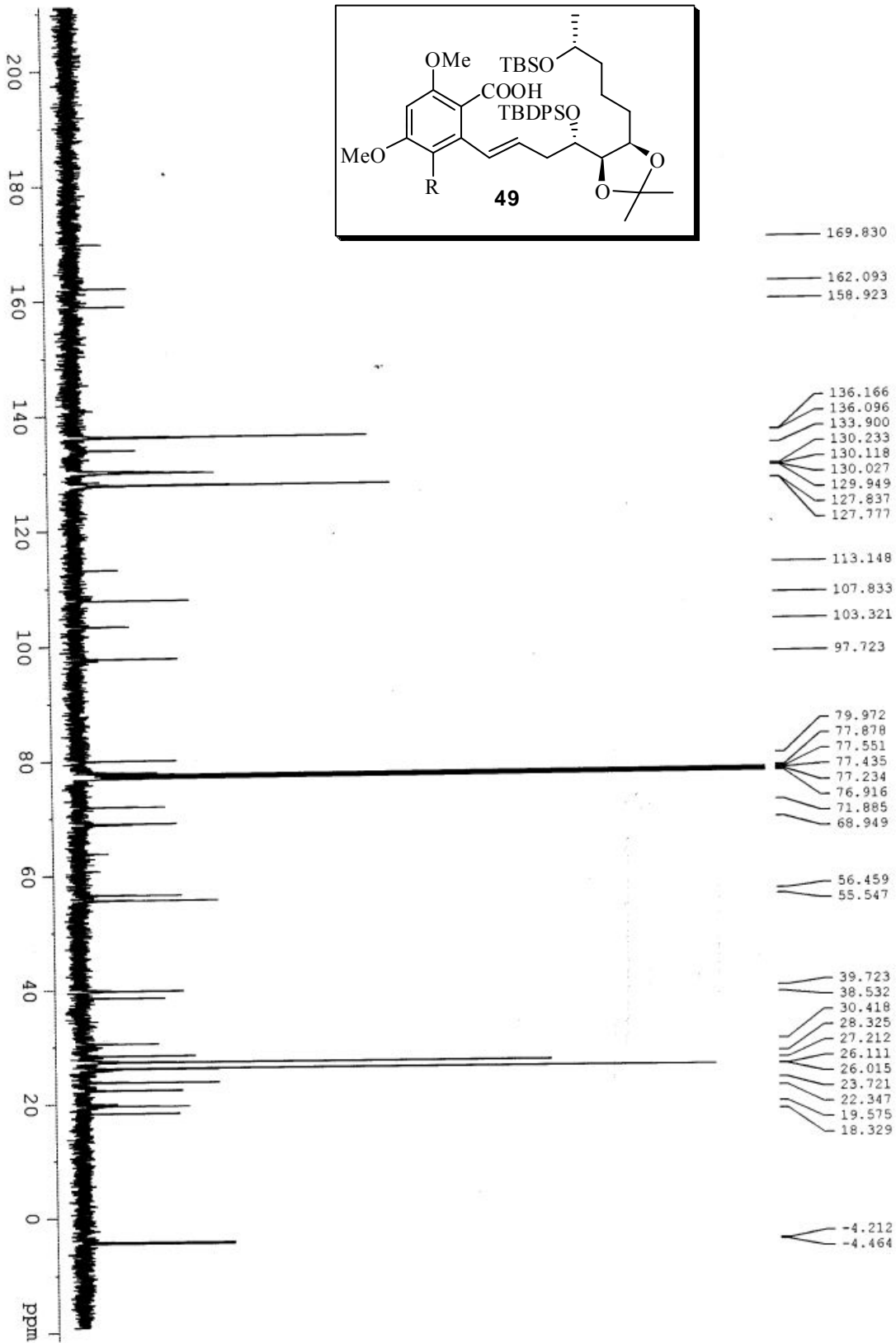
DEPT-NMR of compound 47 (100MHz, CDCl₃)



¹H- NMR of compound 49 (400MHz, CDCl₃)

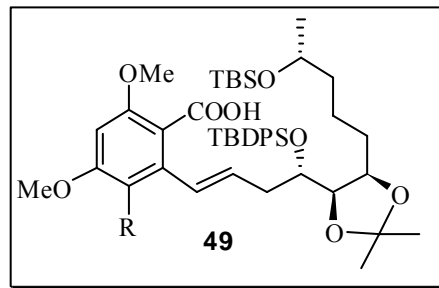


¹³C-NMR of compound 49 (100MHz, CDCl₃)



DEPT- NMR of compound 49 (100MHz, CDCl₃)

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



- 136.163
- 136.091
- 130.212
- 130.111
- 130.027
- 129.949
- 127.834
- 127.775

- 103.285
- 97.714

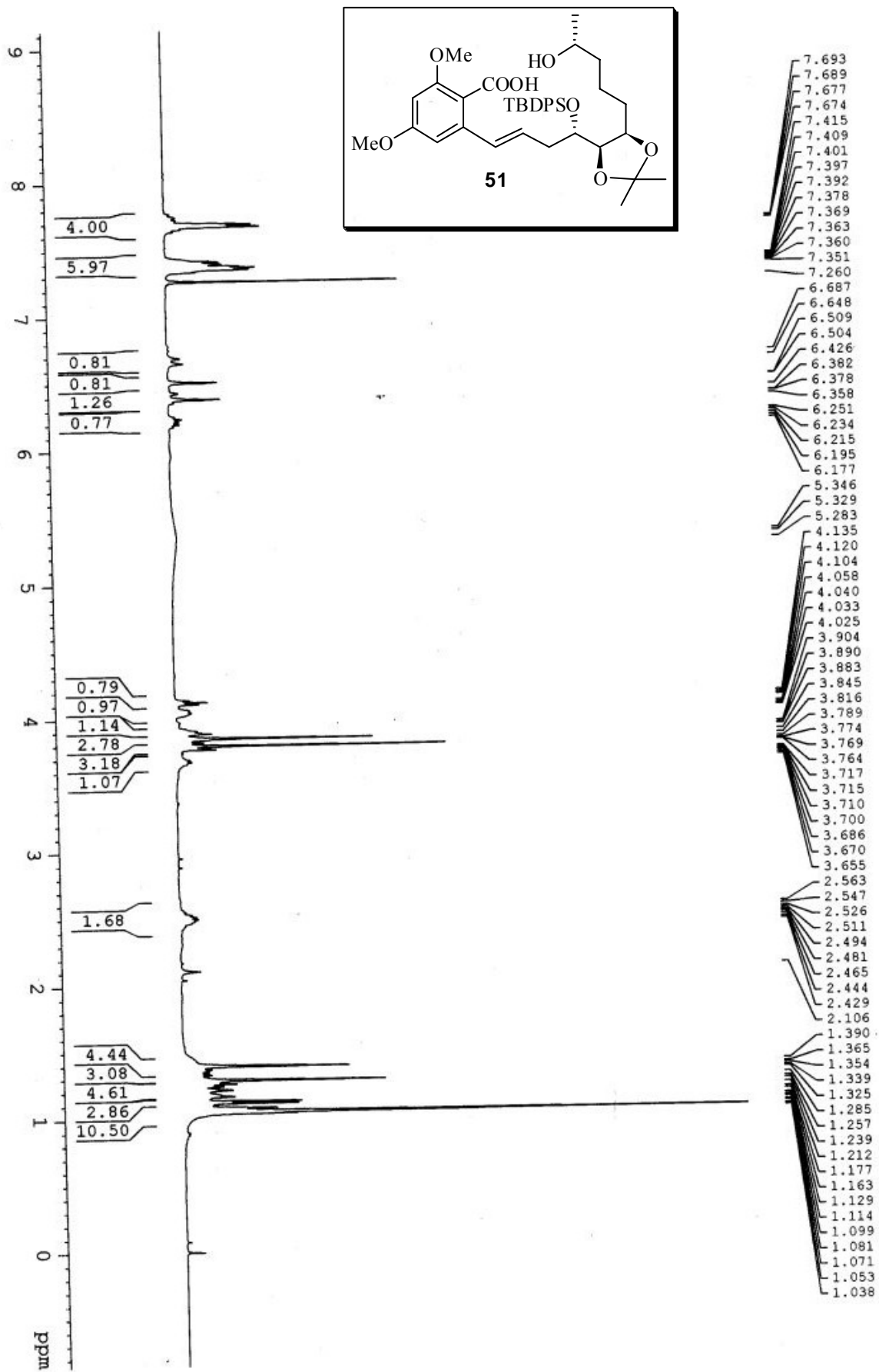
- 79.962
- 77.872
- 71.873
- 68.949

- 56.450
- 55.547

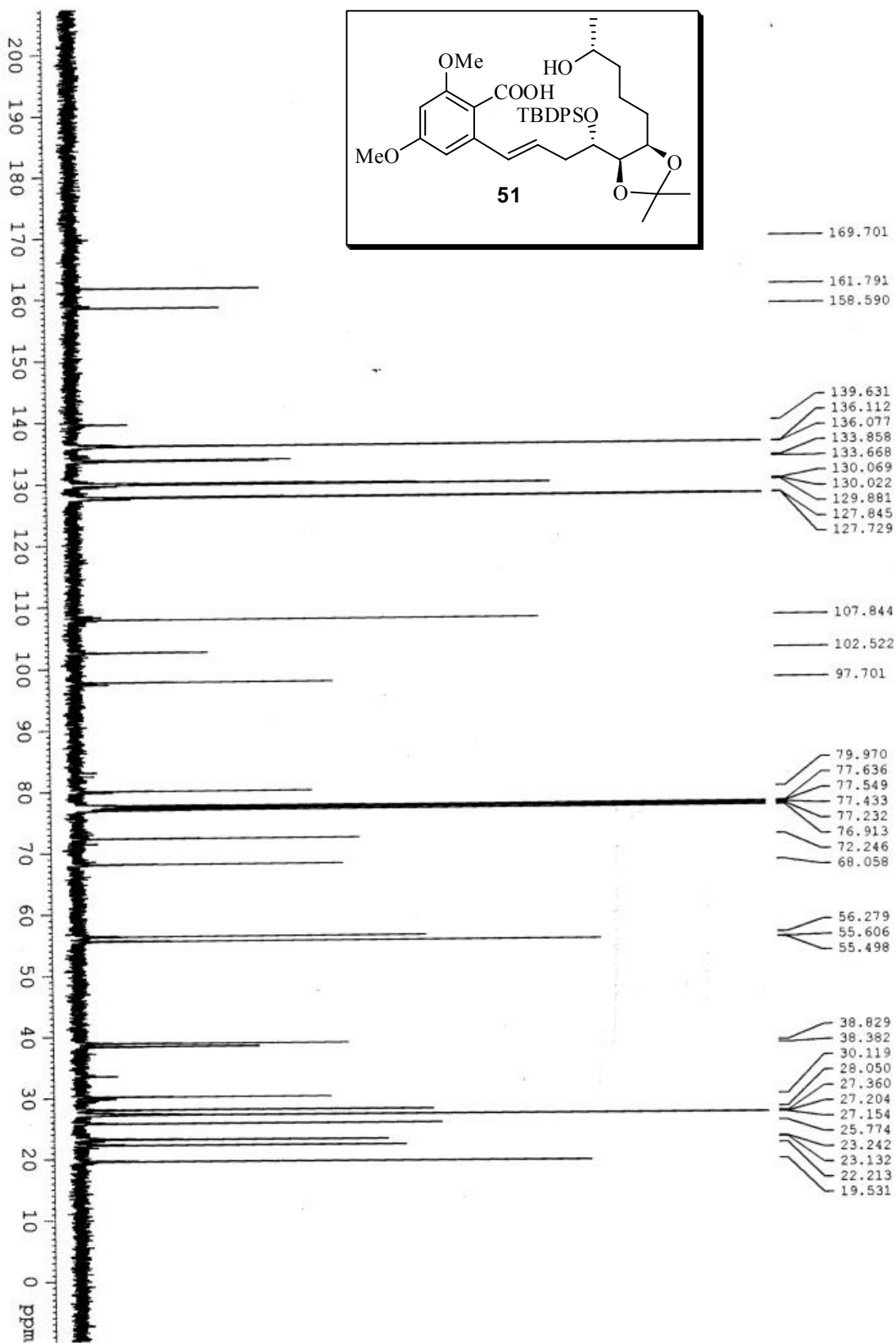
- 39.718
- 38.525
- 30.398
- 28.323
- 27.206
- 26.105
- 26.010
- 23.716
- 22.341

- 4.224
- 4.465

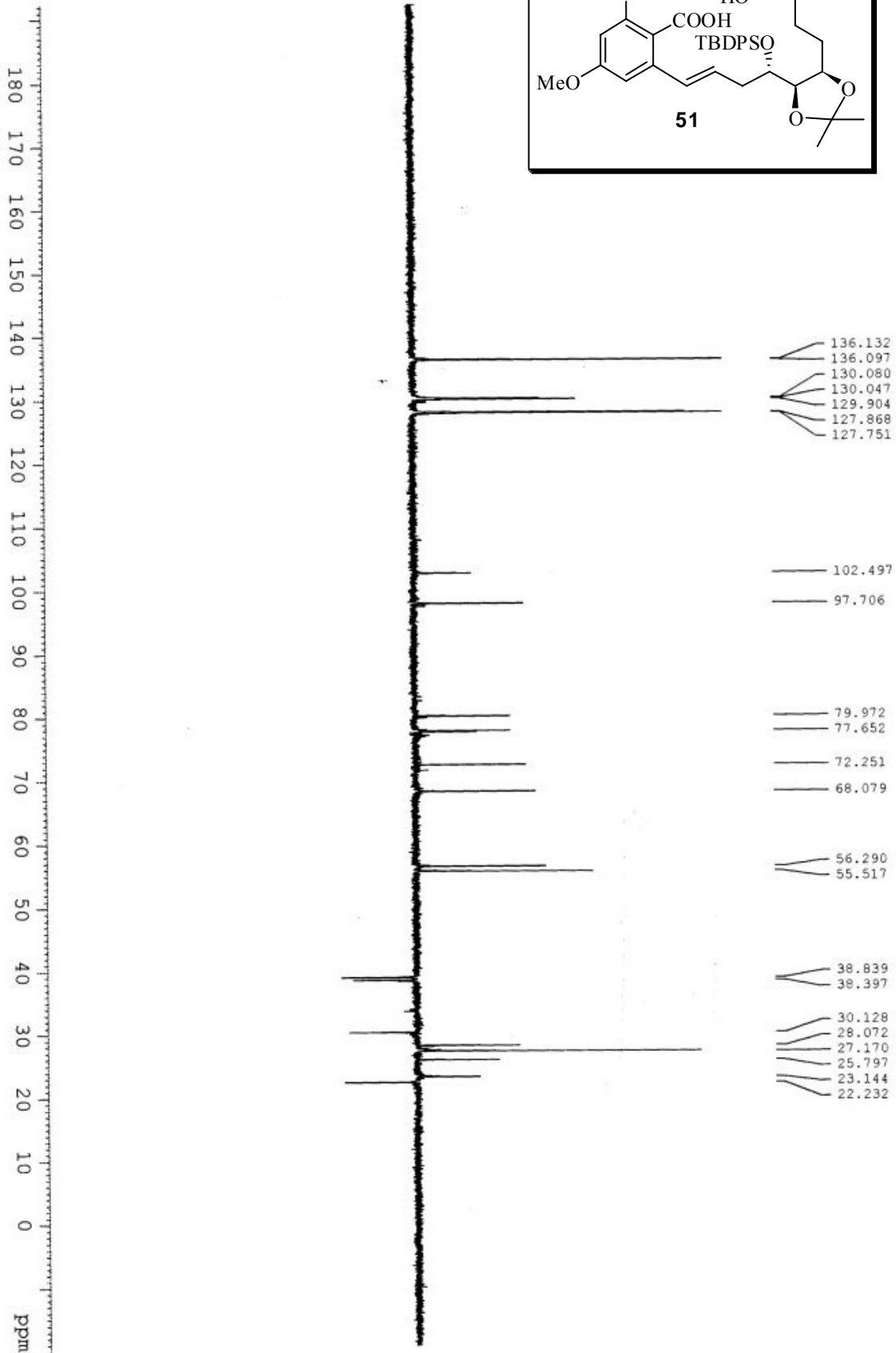
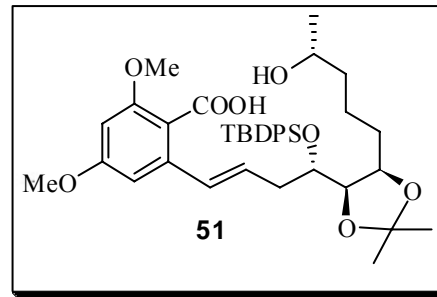
¹H-NMR of compound 51 (400MHz, CDCl₃)



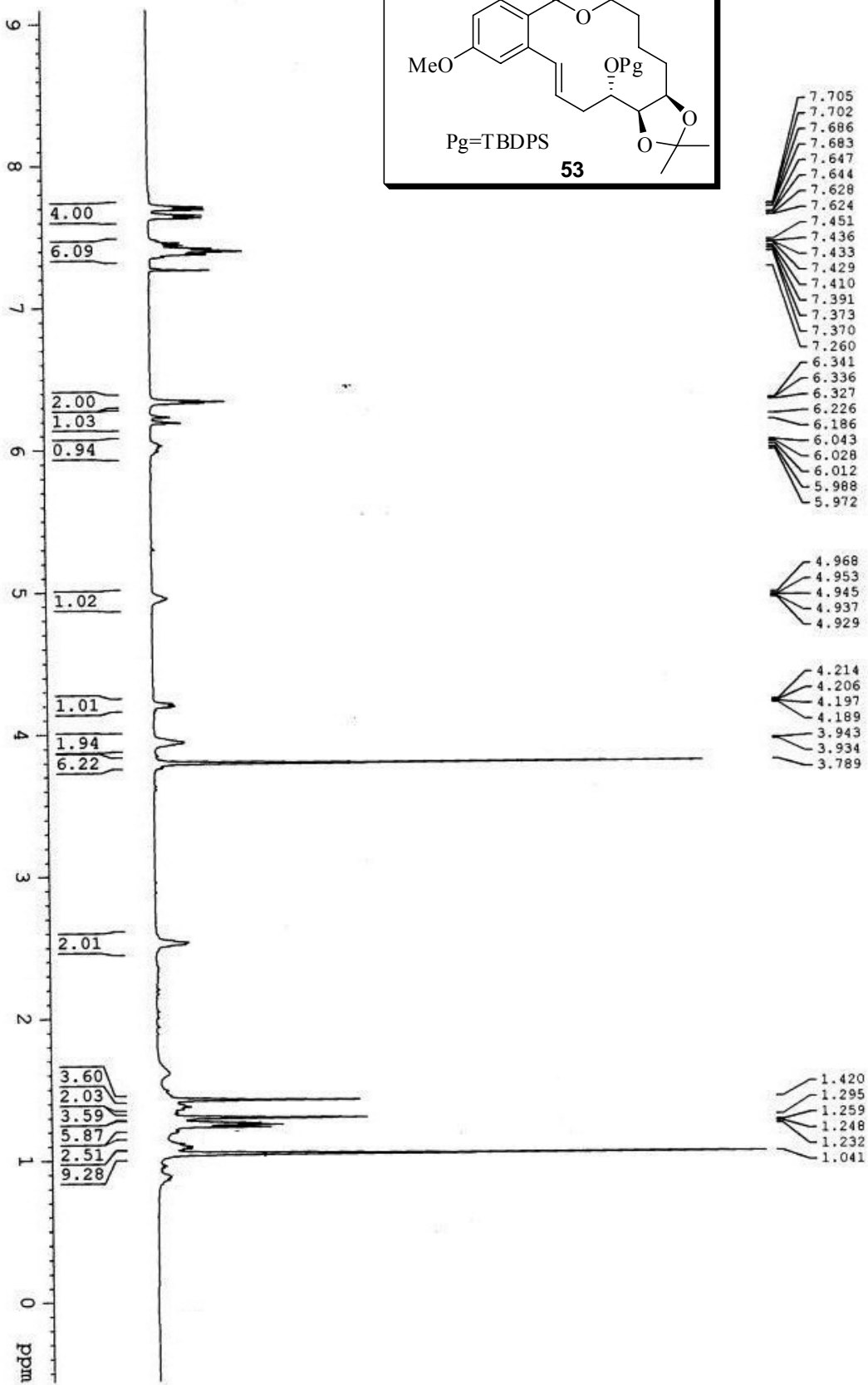
¹³C-NMR of compound 51 (100MHz, CDCl₃)



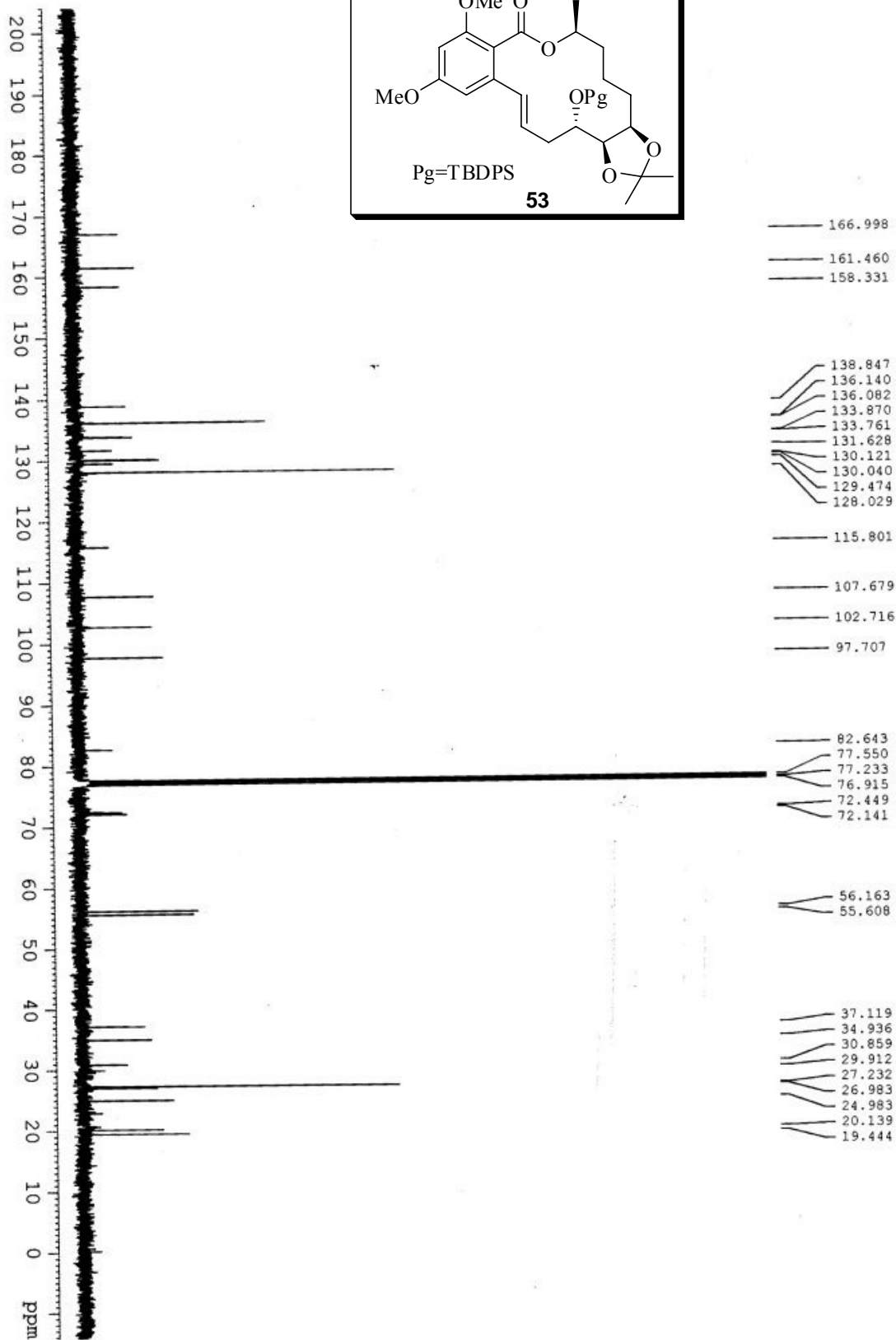
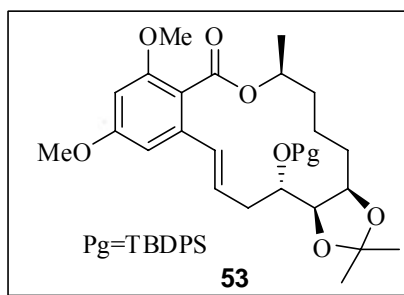
DEPT-NMR of compound 51 (100MHz, CDCl₃)



¹H-NMR of compound 53 (400MHz, CDCl₃)

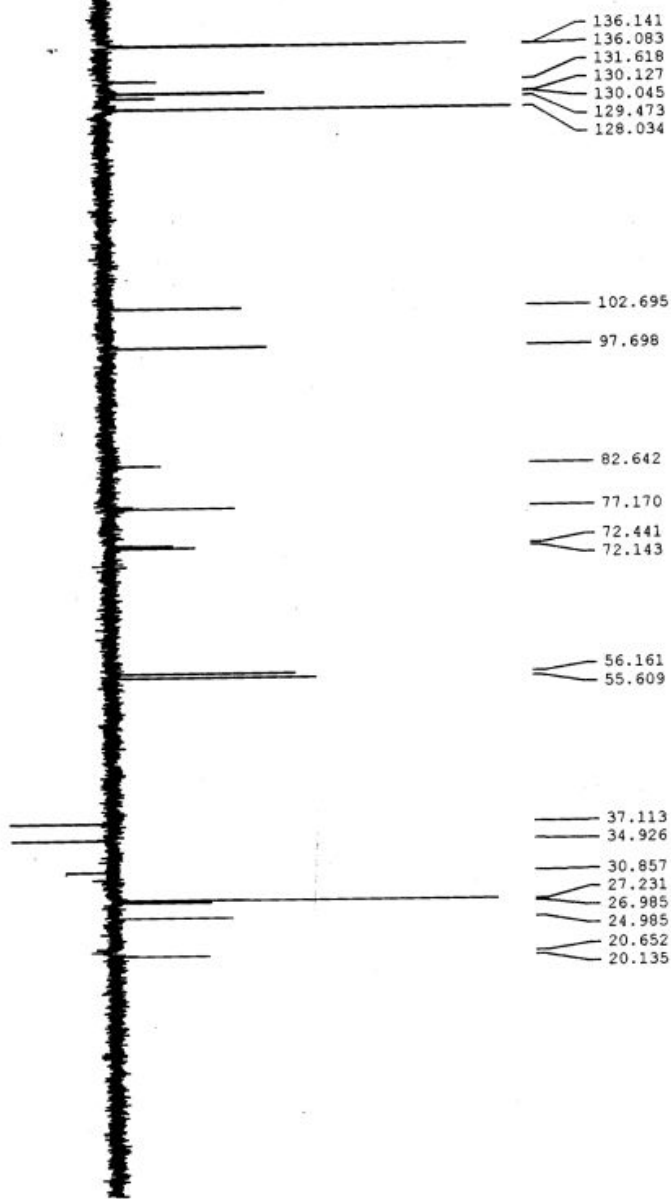
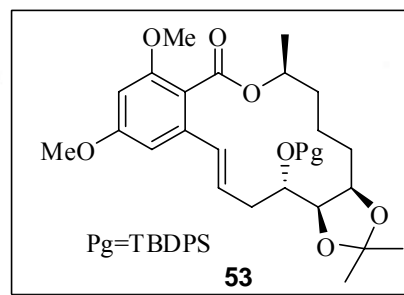


¹³C-NMR of compound 53 (100MHz, CDCl₃)

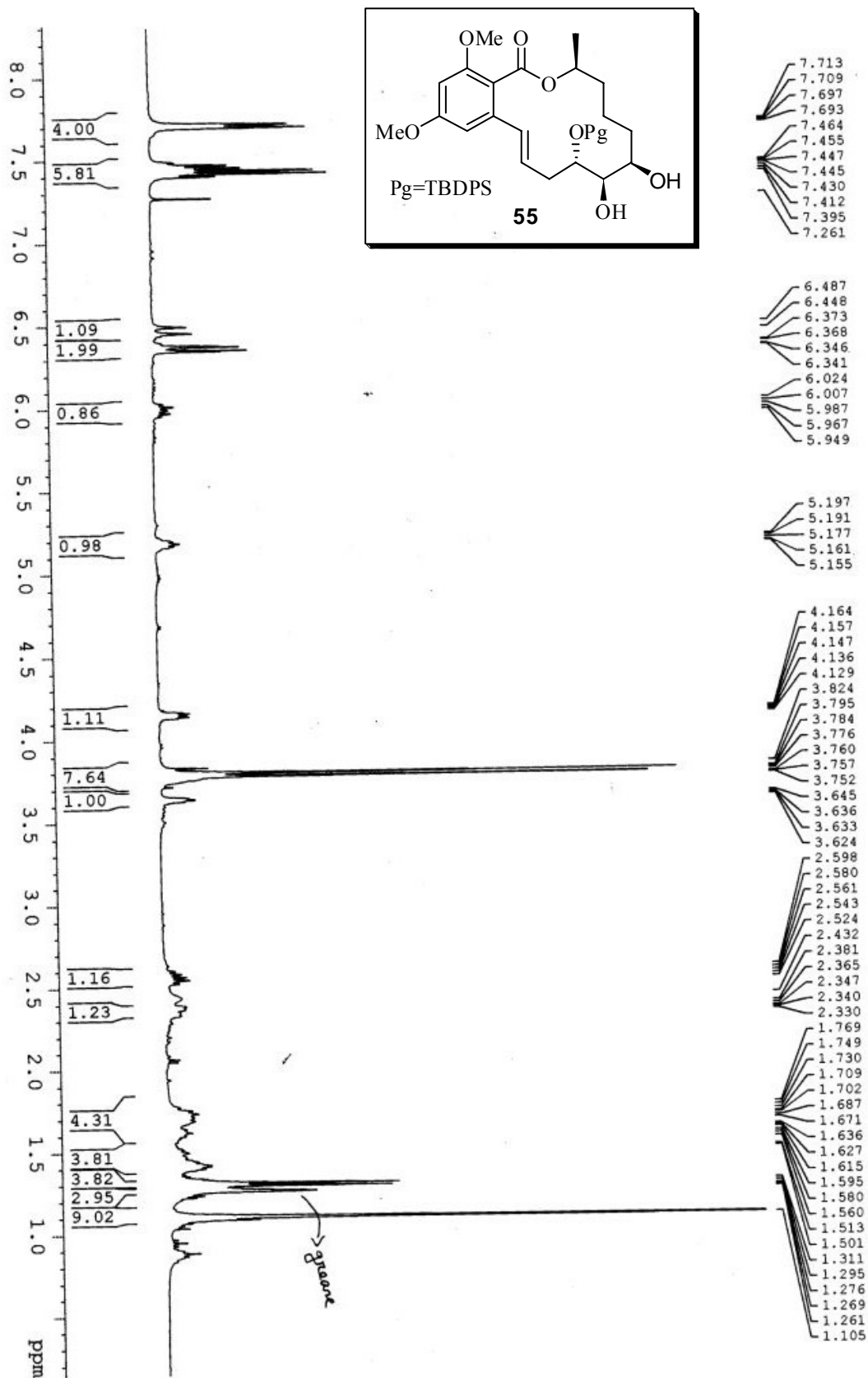


DEPT-NMR of compound 53 (100MHz, CDCl₃)

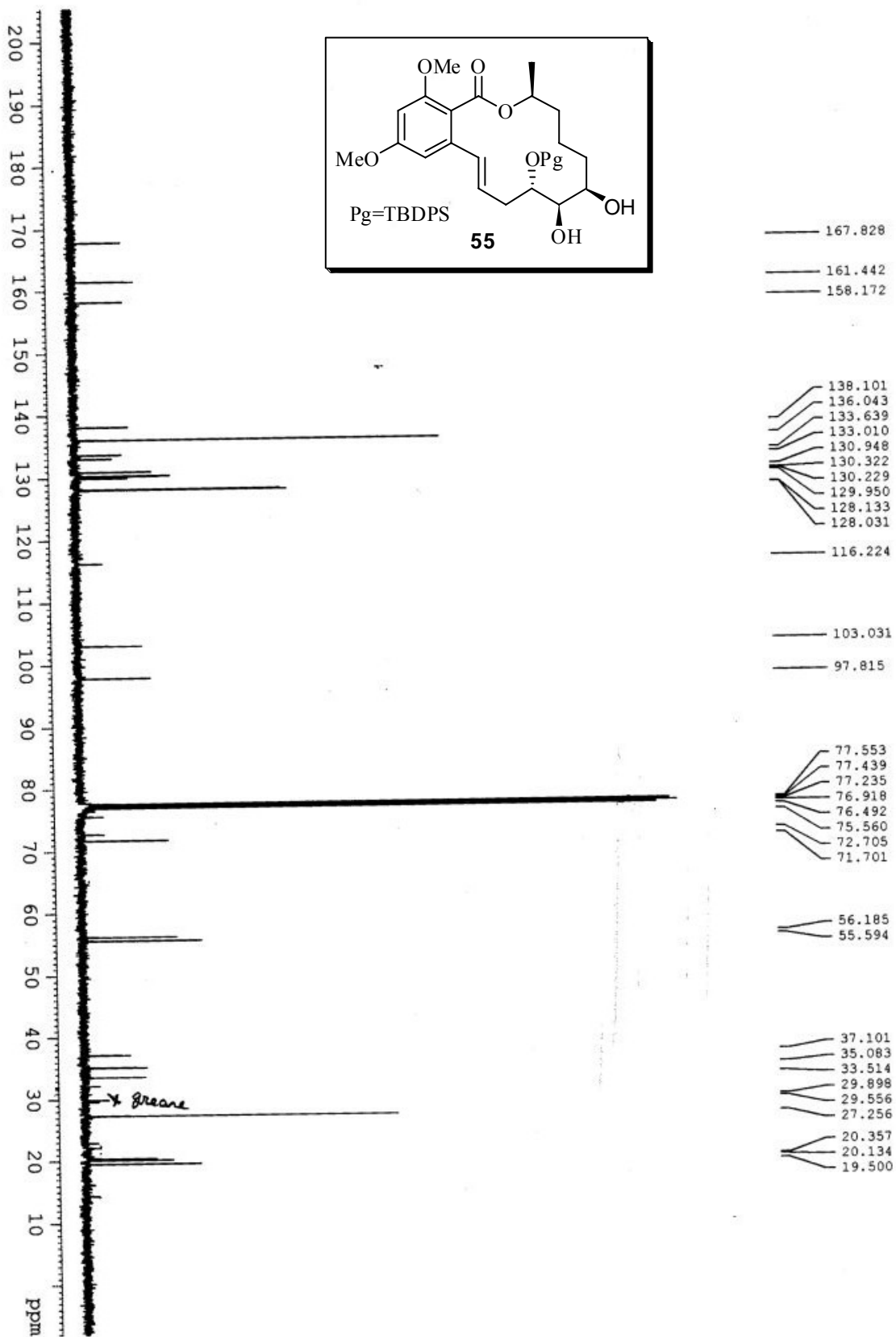
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



¹H-NMR of compound 55 (400MHz, CDCl₃)

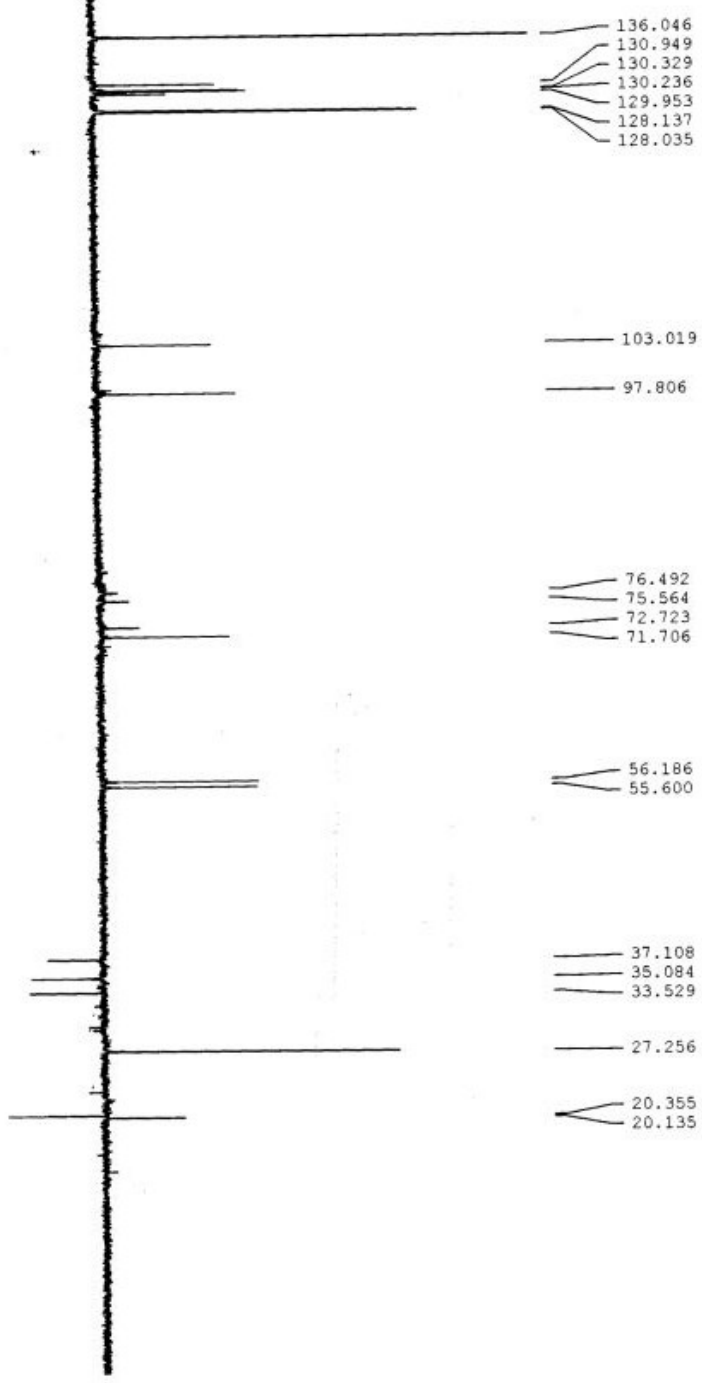
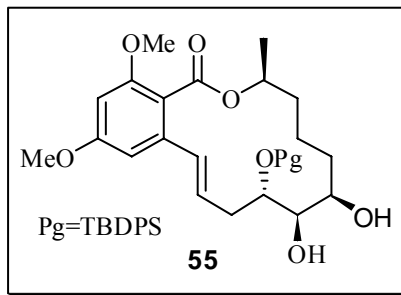


¹³C-NMR of compound 55 (100MHz, CDCl₃)

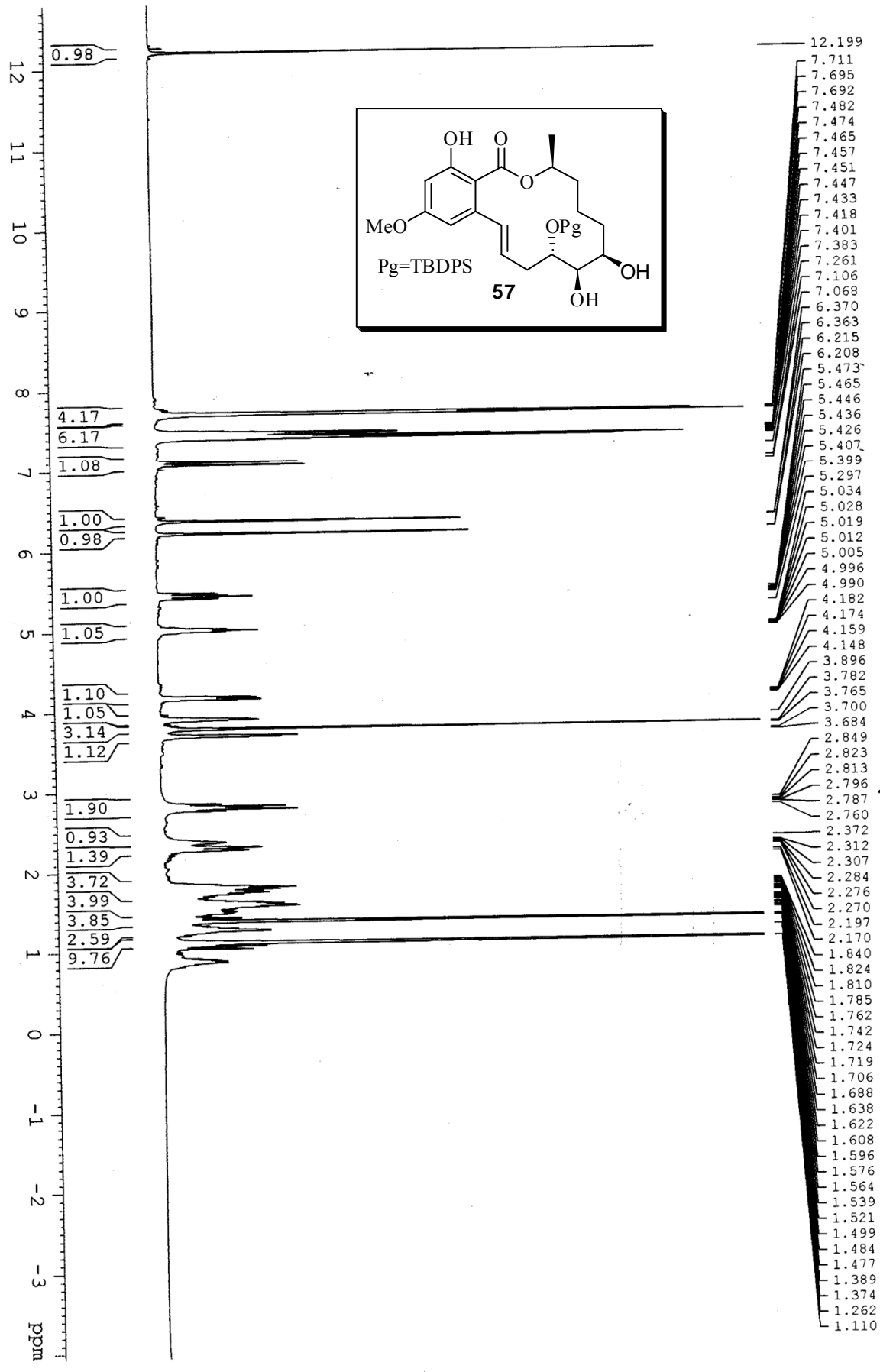


DEPT-NMR of compound 55 (100MHz, CDCl₃)

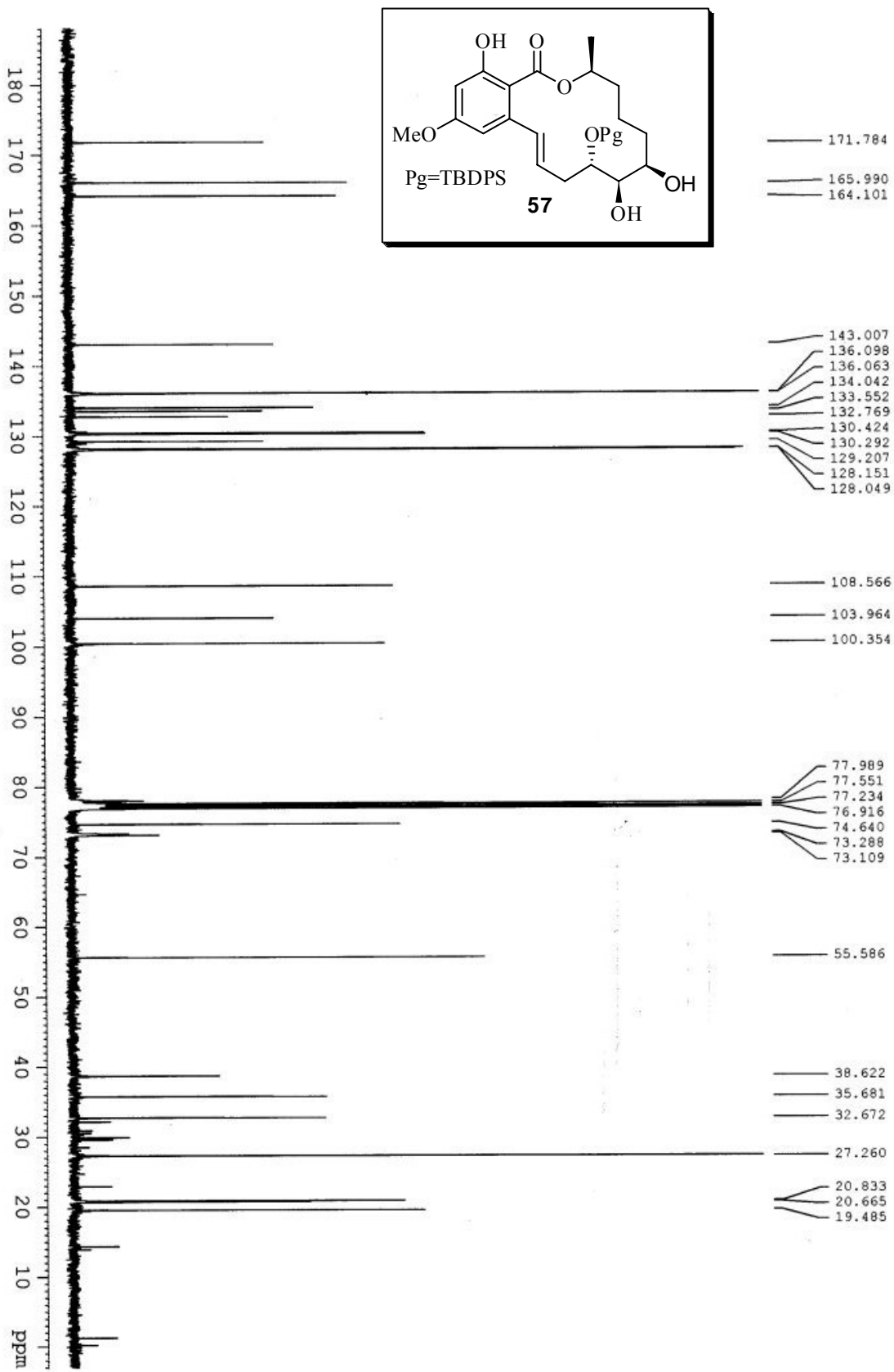
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



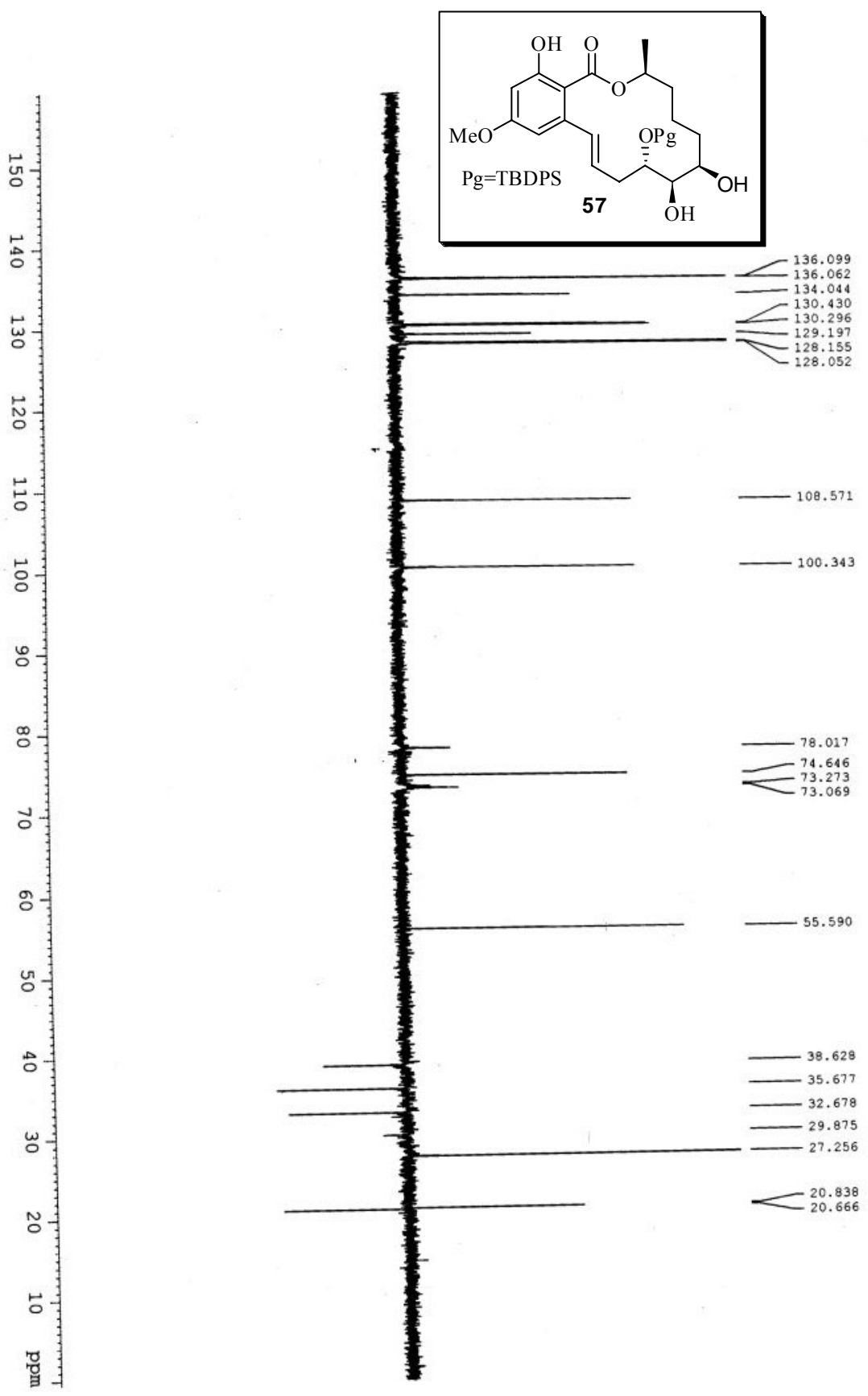
¹H-NMR of compound 57 (400MHz, CDCl₃)



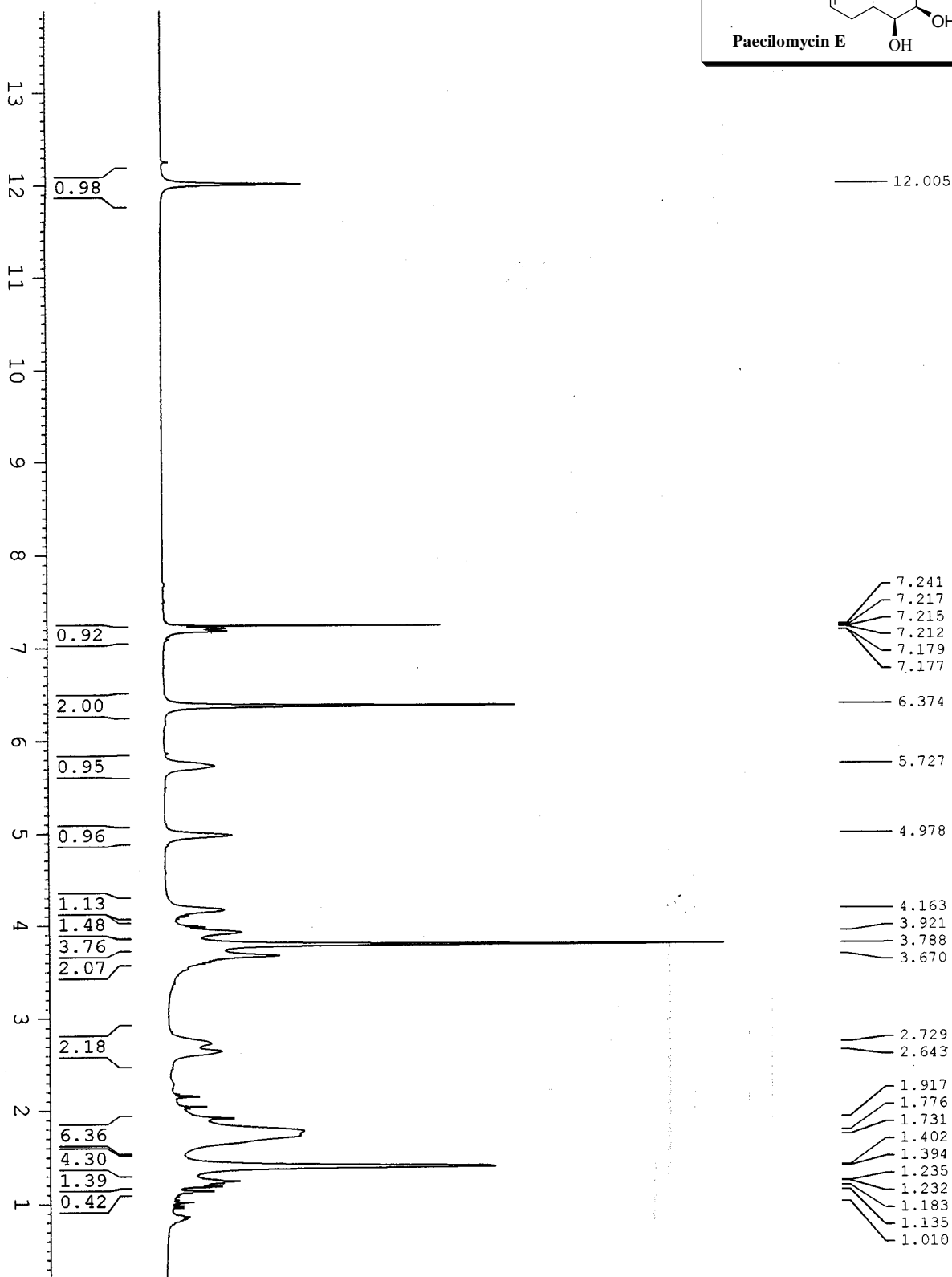
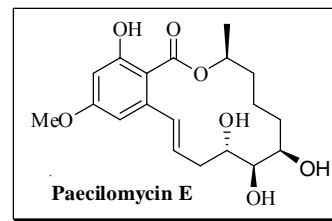
¹³C-NMR of compound 57 (100MHz, CDCl₃)



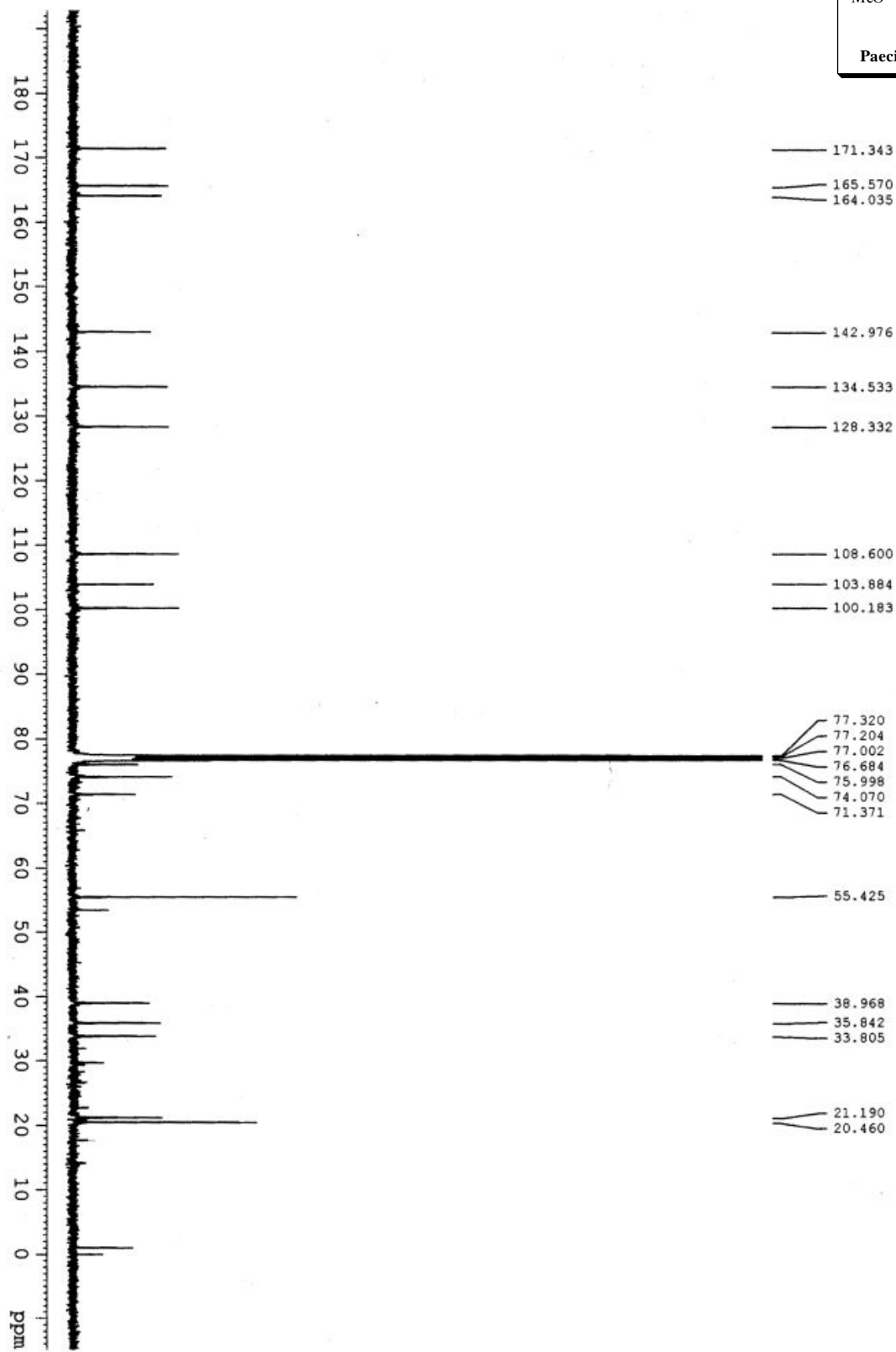
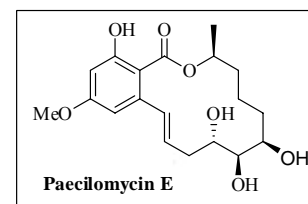
DEPT- NMR of compound 57 (100MHz, CDCl₃)



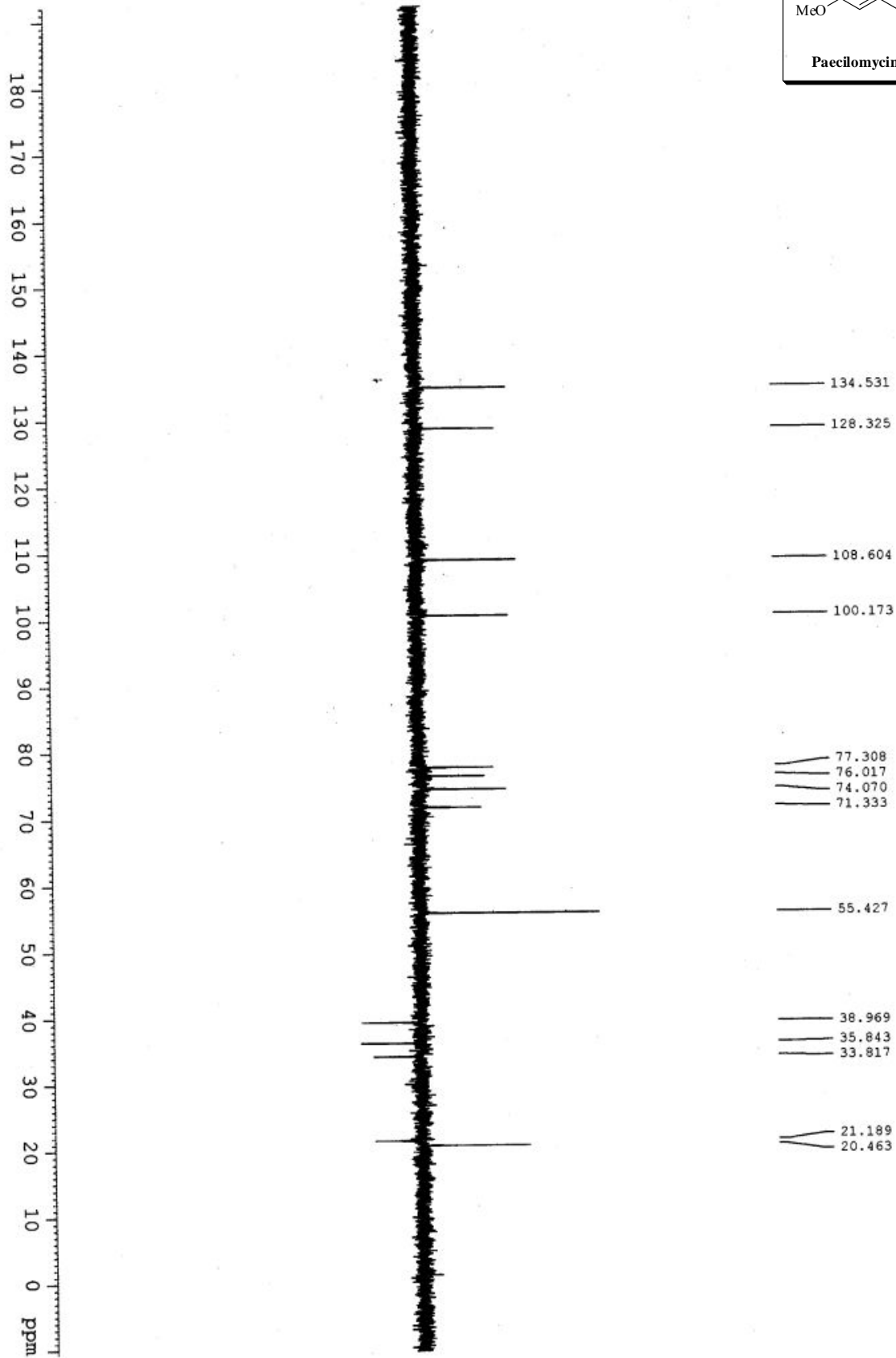
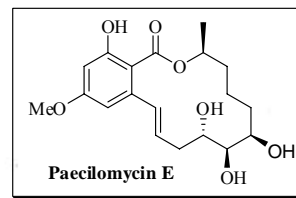
¹H-NMR of Paecilomycin E (100MHz, CDCl₃)



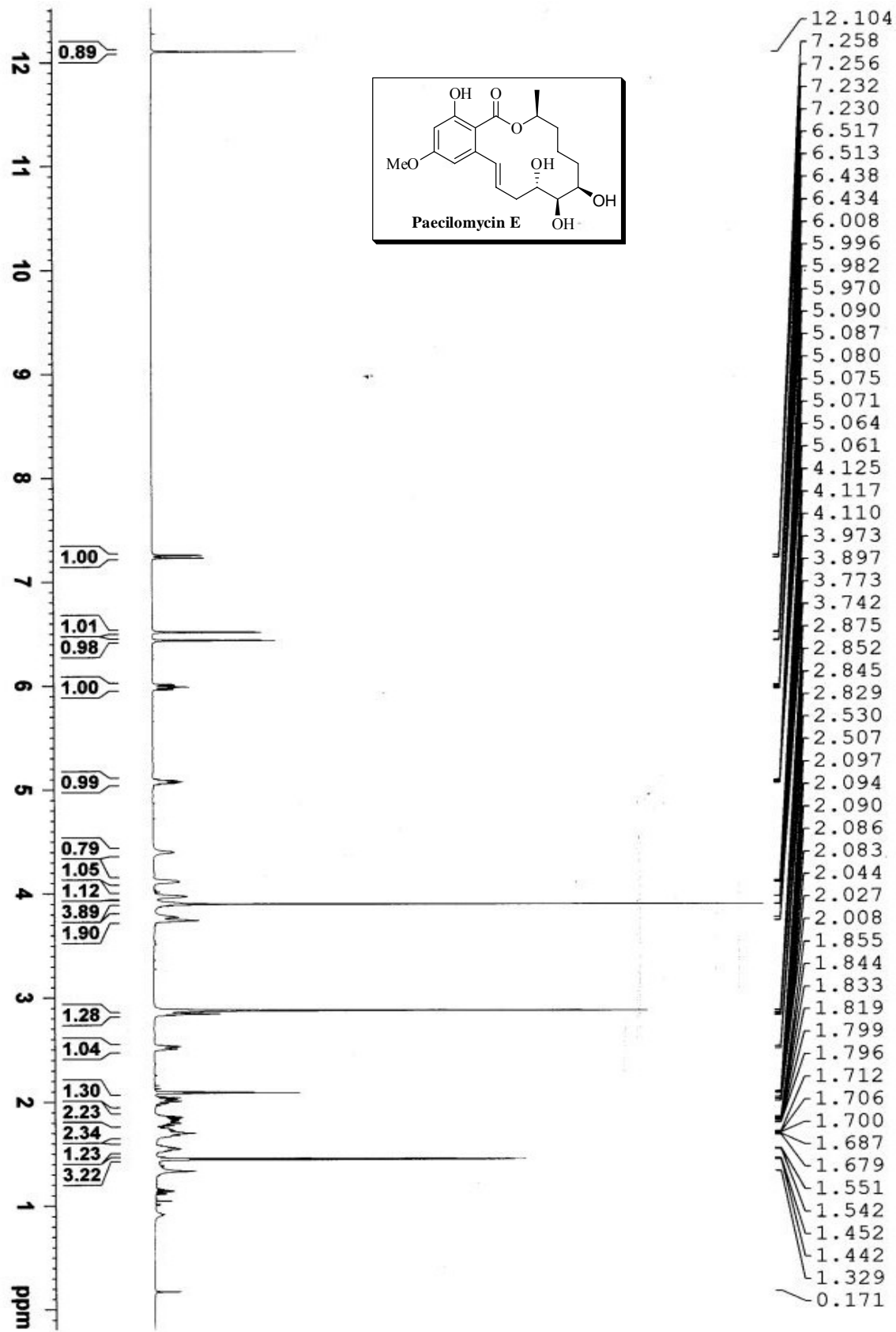
¹³C-NMR of Paecilomycin E (100MHz, CDCl₃)



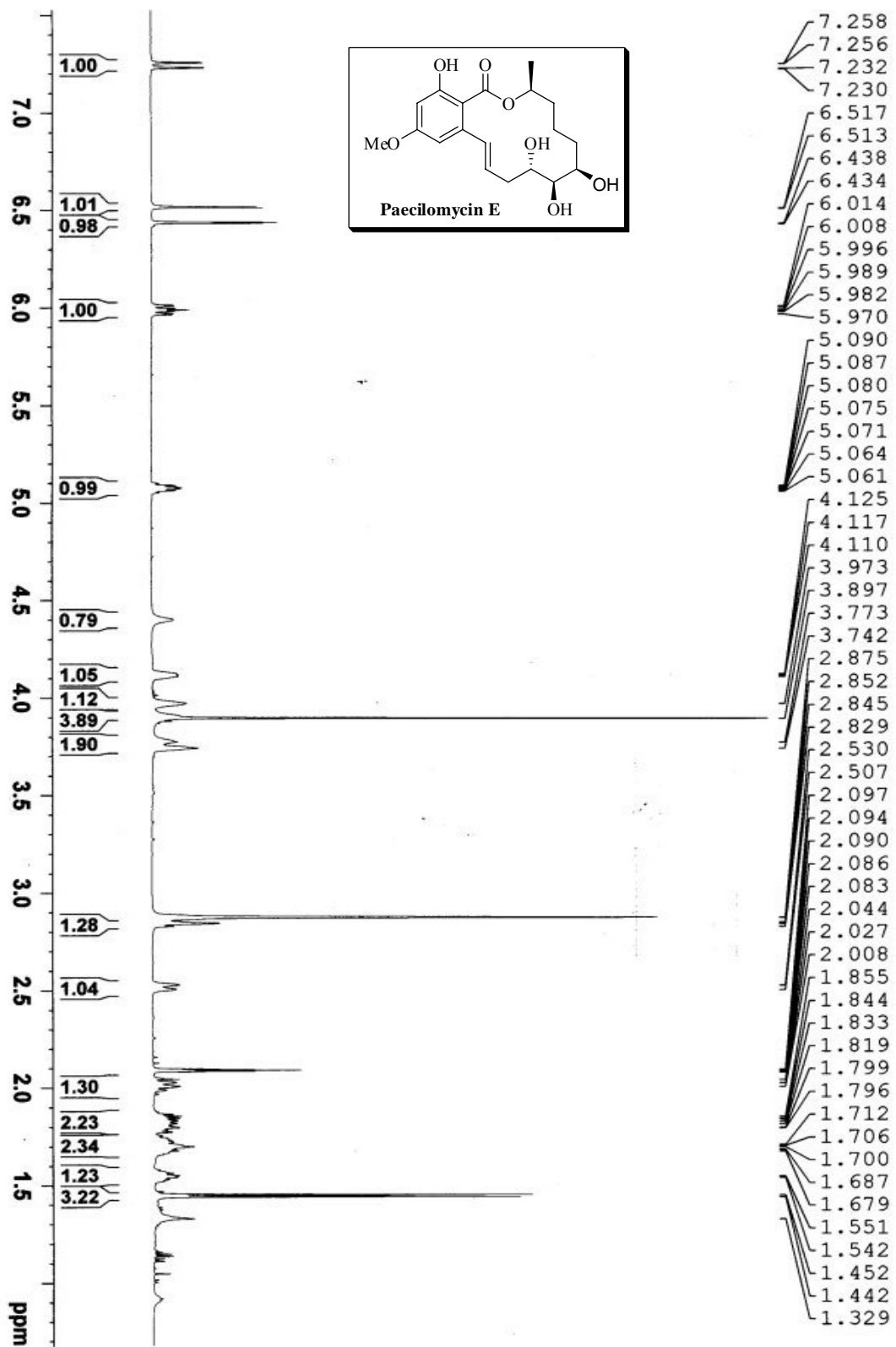
DEPT-NMR of Paecilomycin E (100MHz, CDCl₃)



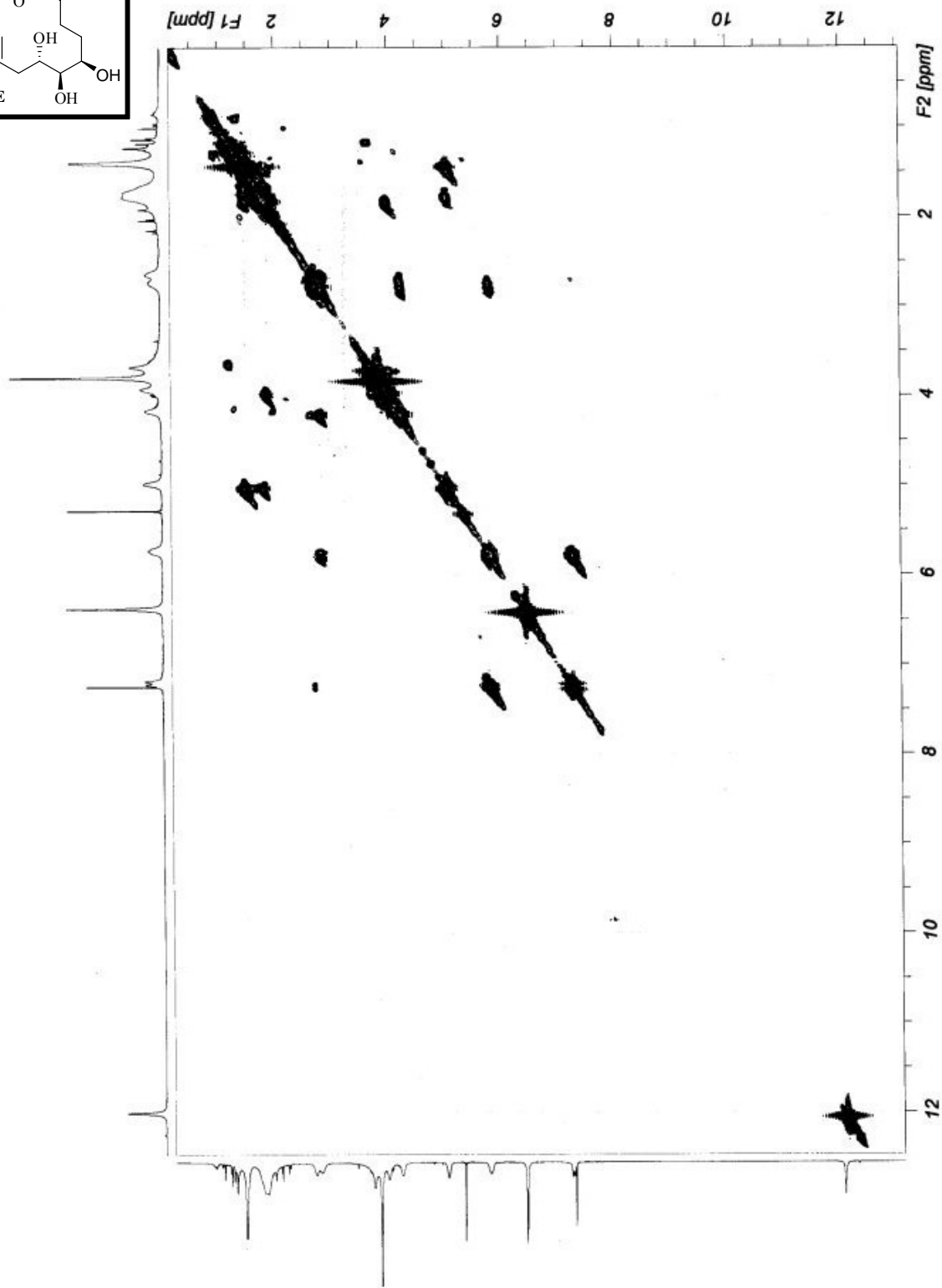
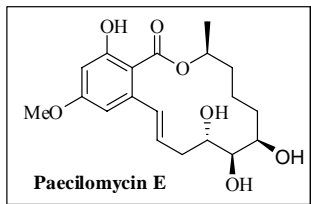
¹H- NMR of Paecilomycin E (600MHz, Acetone-d₆)



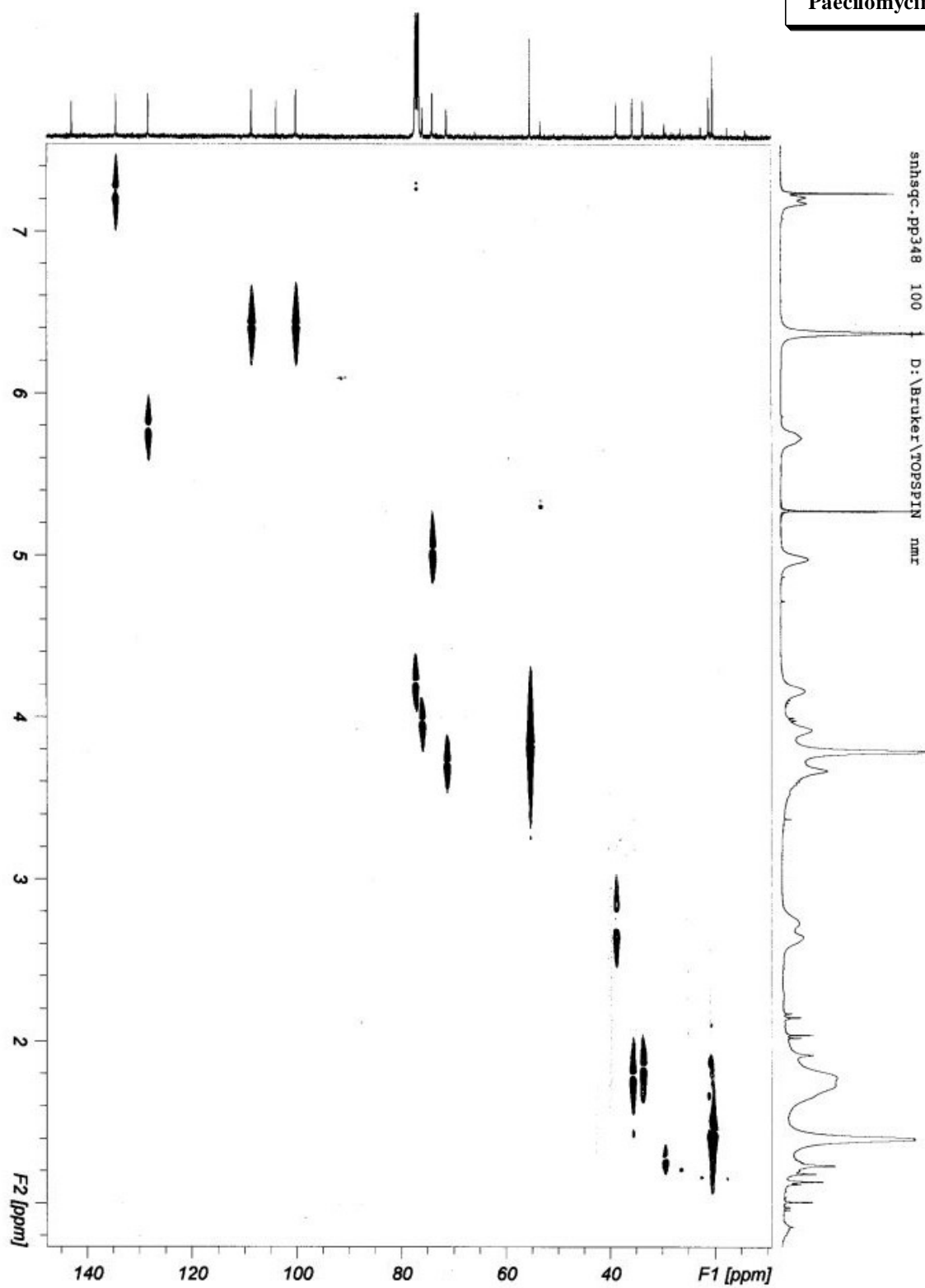
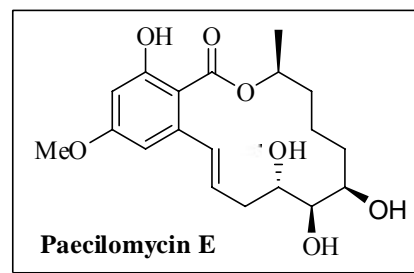
Expanded $^1\text{H-NMR}$ of Paecilomycin E (600 MHz, Acetone- d_6)



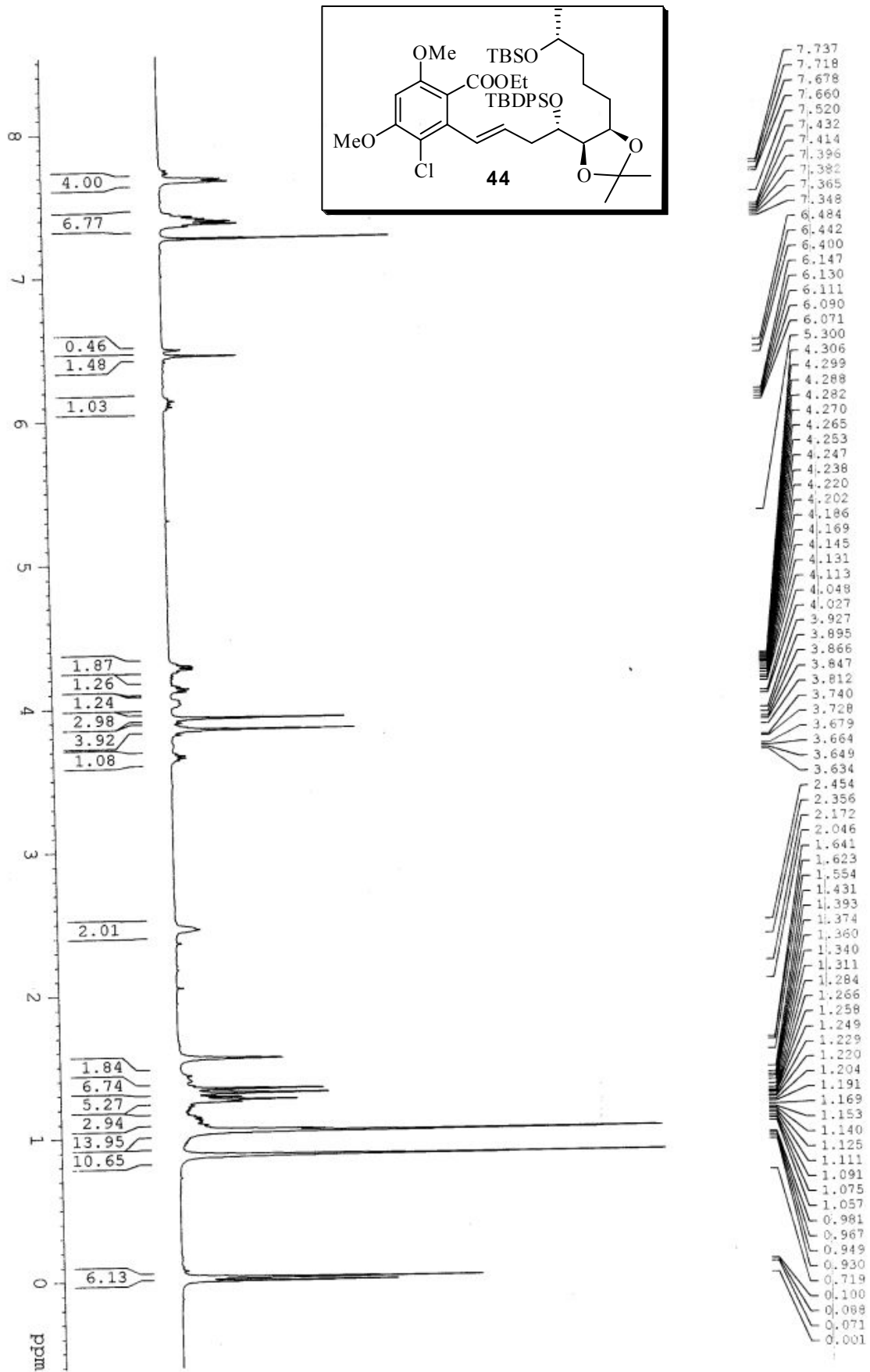
^1H - ^1H COSY of paecilomycin E (600 MHz, CDCl_3)



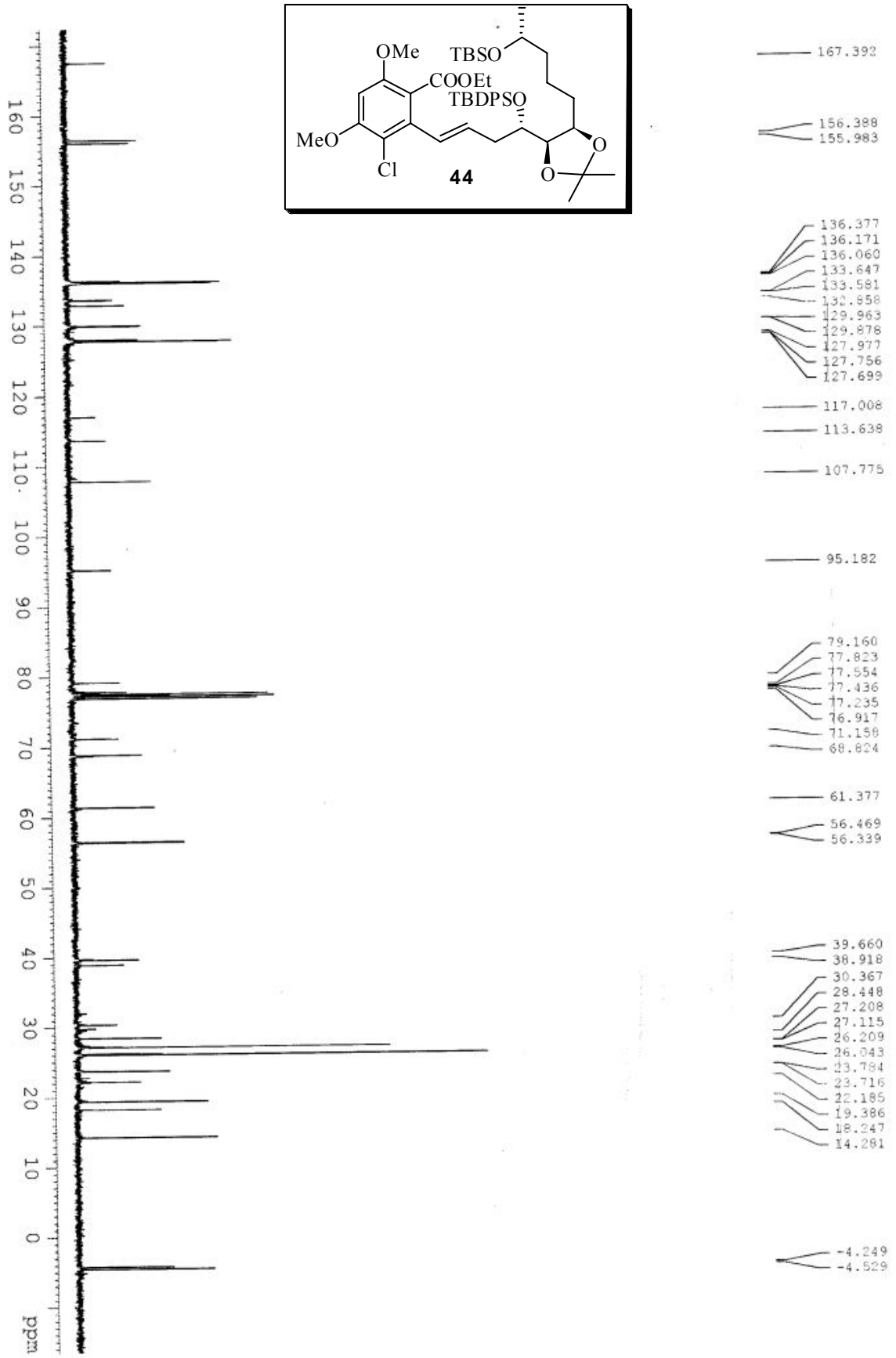
HSQC of paecilomycin E (600 MHz, CDCl₃)



¹H- NMR of compound 44 (400MHz, CDCl₃)

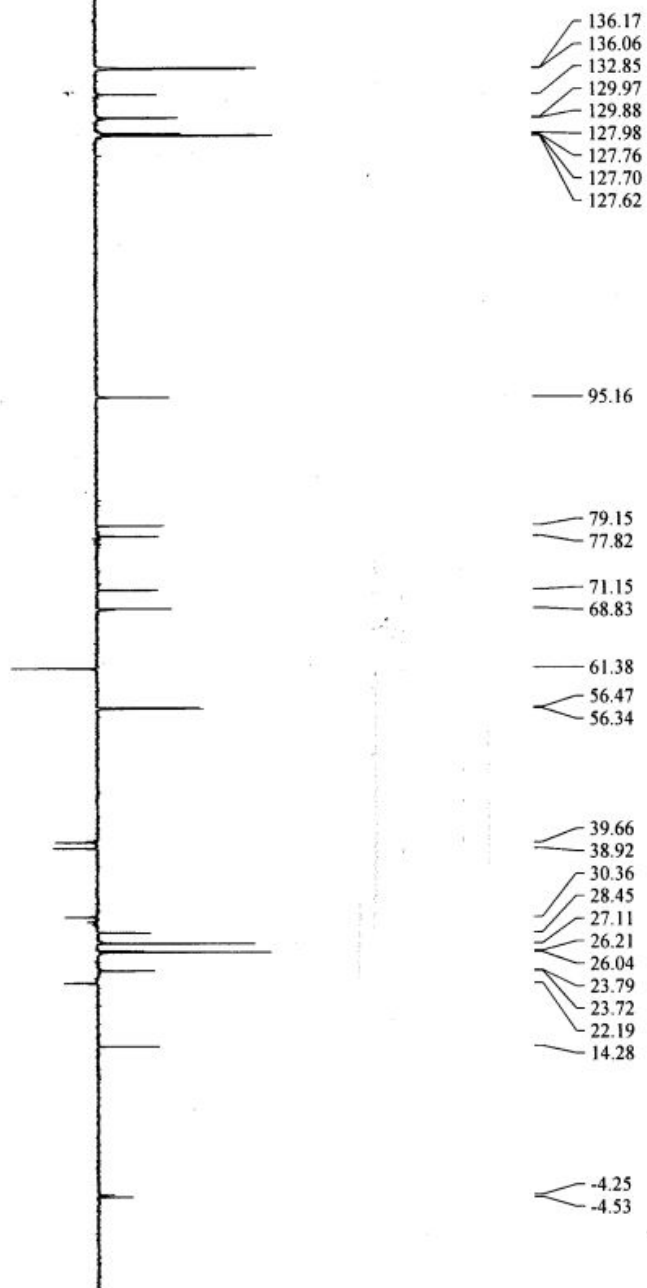
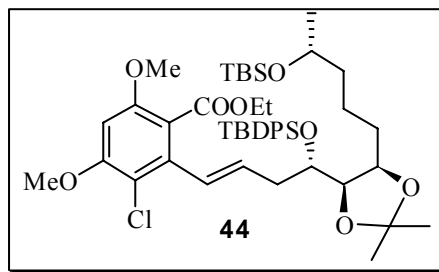


¹³C- NMR of compound 44 (100MHz, CDCl₃)

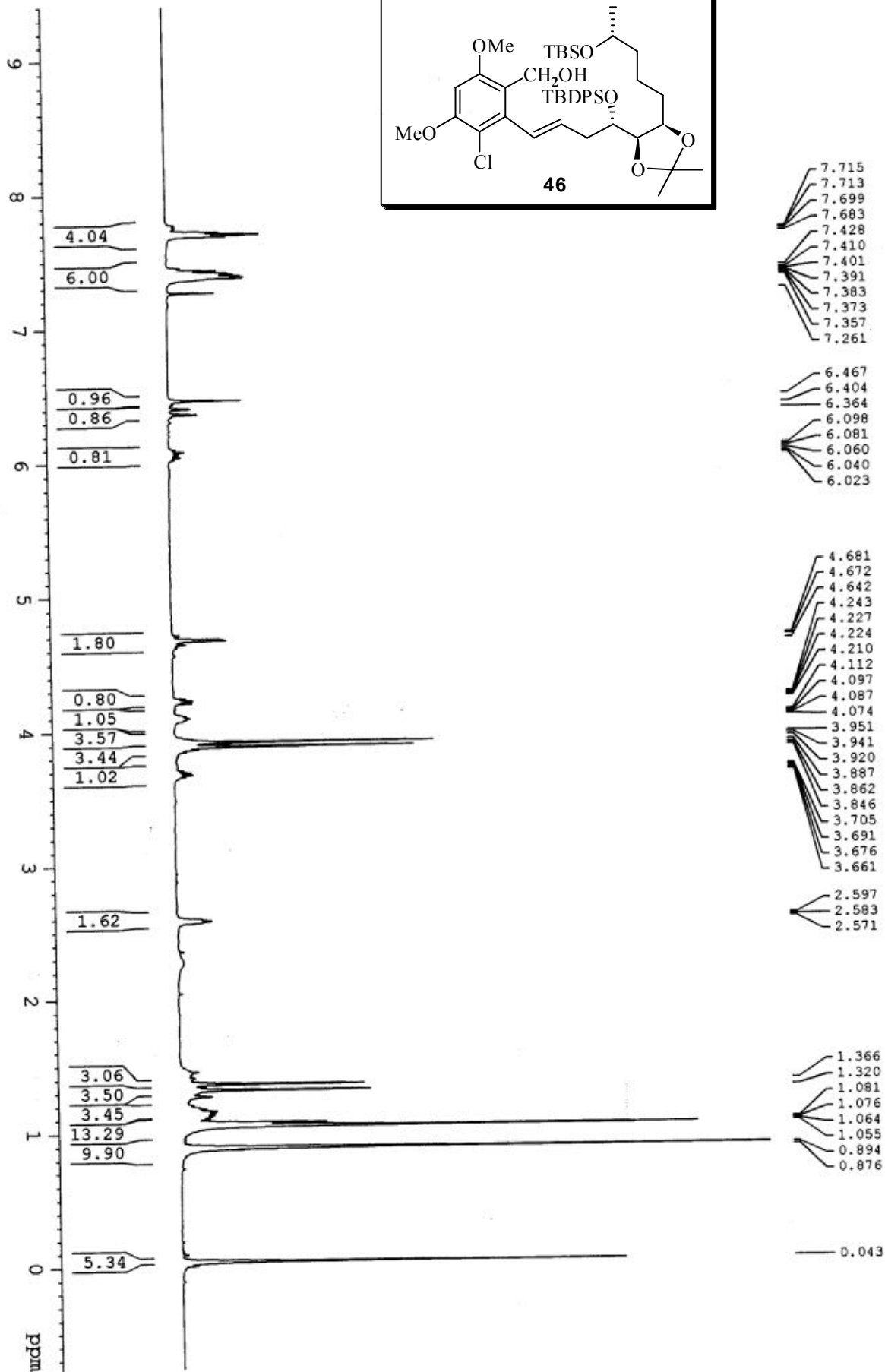


DEPT- NMR of compound 44 (100MHz, CDCl₃)

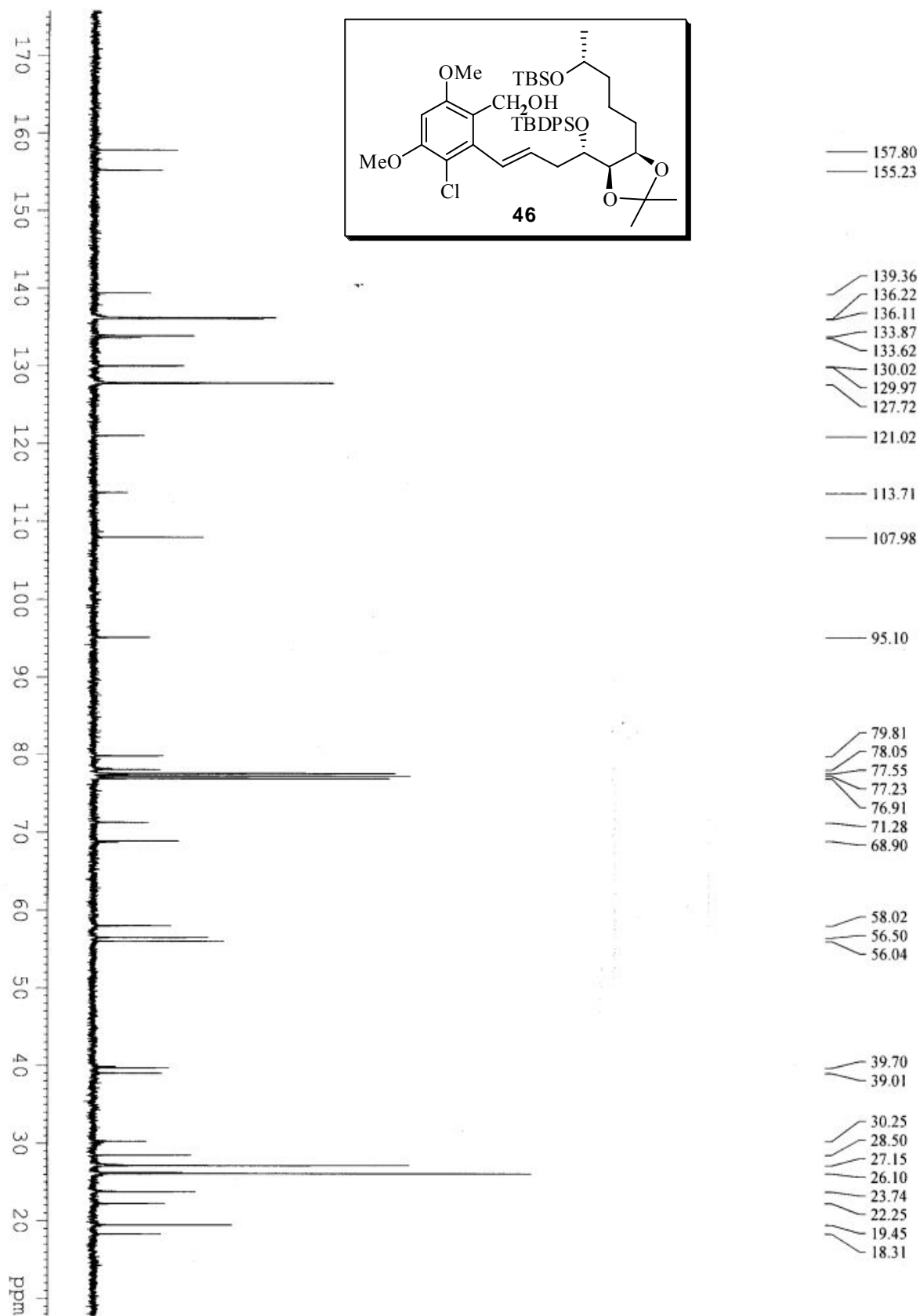
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



¹H-NMR of compound 46 (400MHz, CDCl₃)

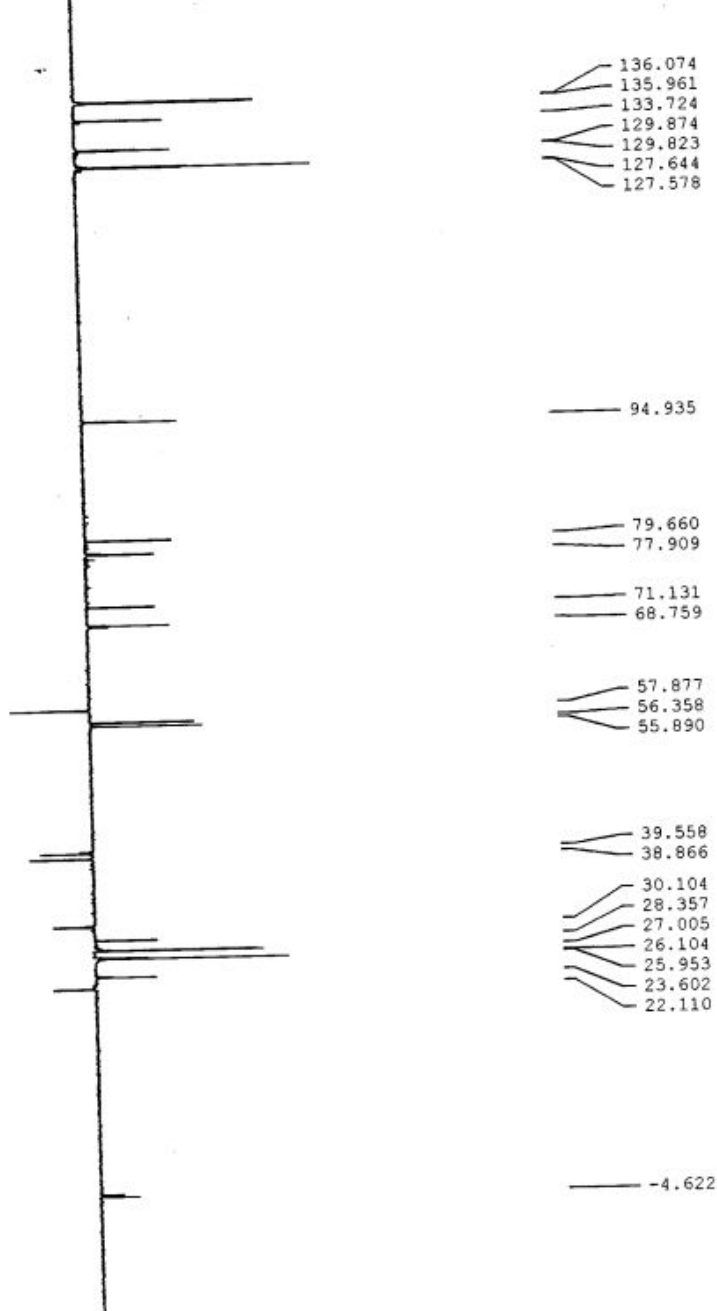
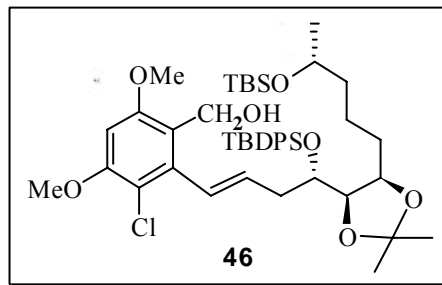


¹³C- NMR of compound 46 (100MHz, CDCl₃)

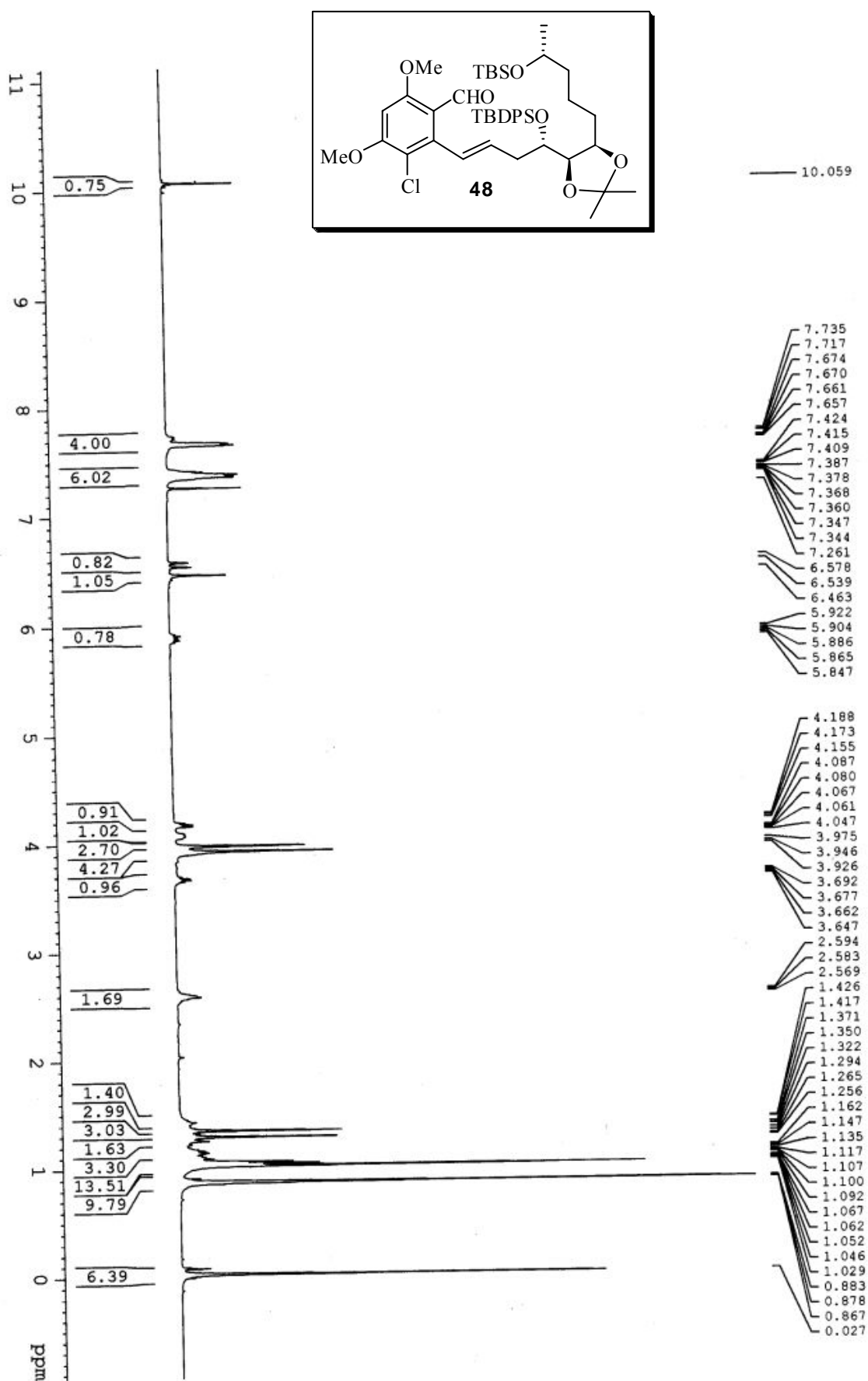


DEPT- NMR of compound 46 (100MHz, CDCl₃)

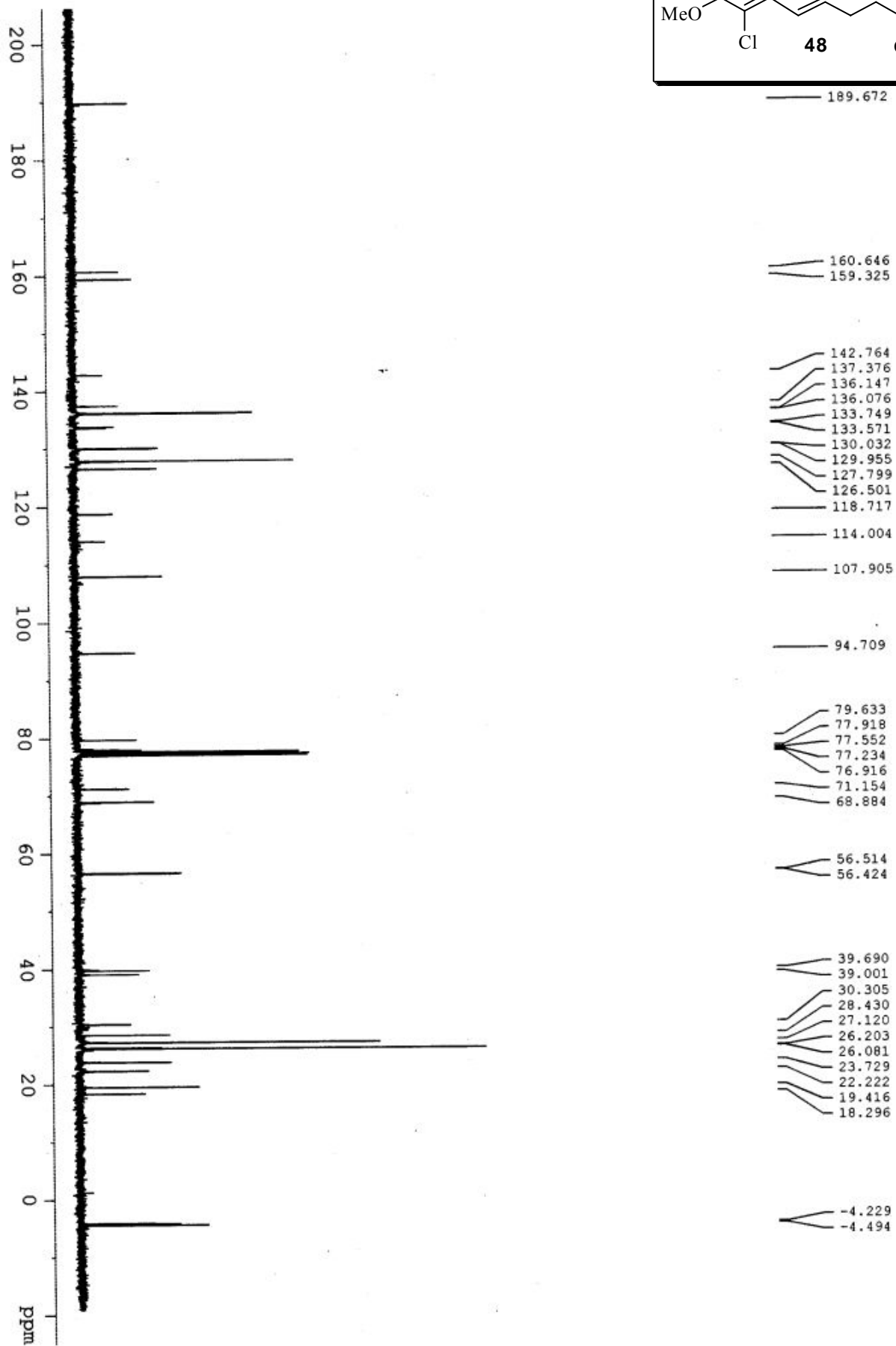
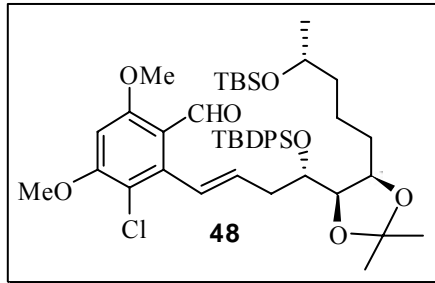
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



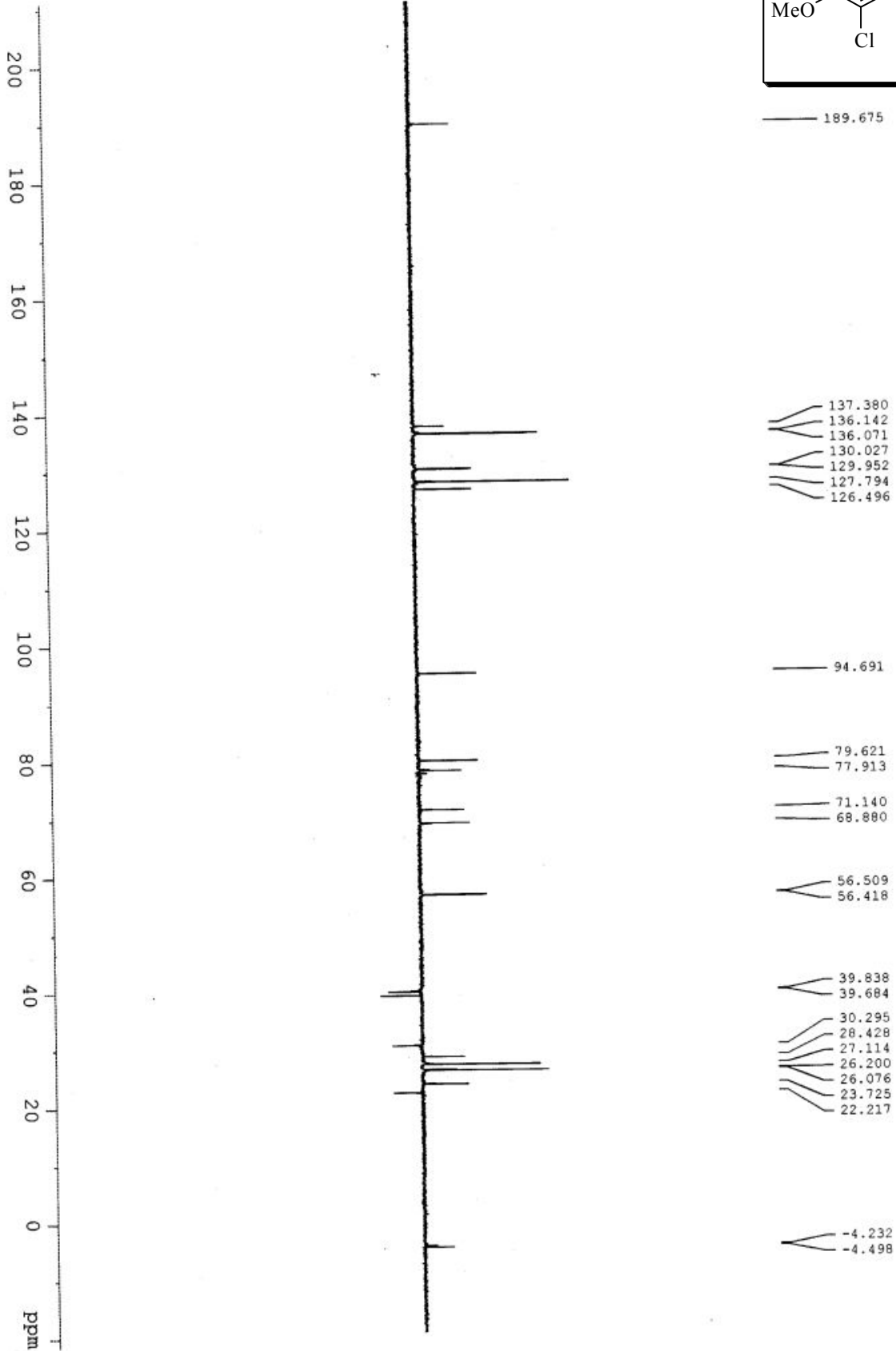
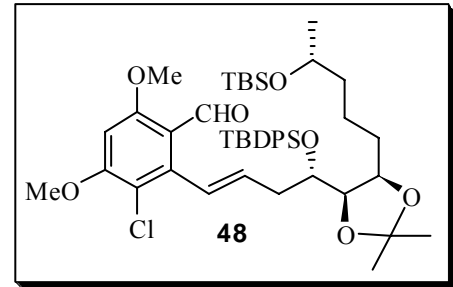
¹H-NMR of compound 48 (400MHz, CDCl₃)



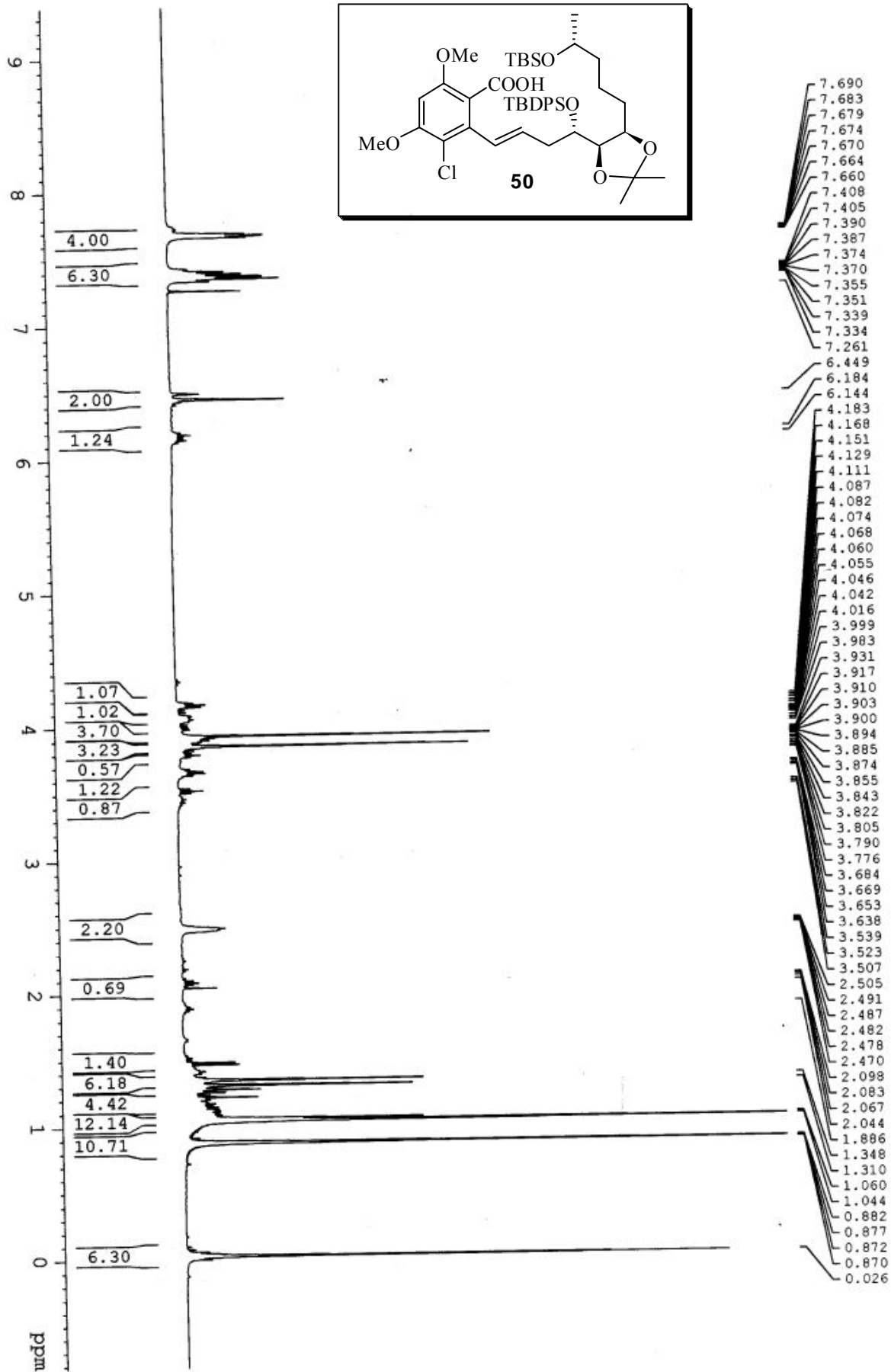
¹³C-NMR of compound 48 (100MHz, CDCl₃)



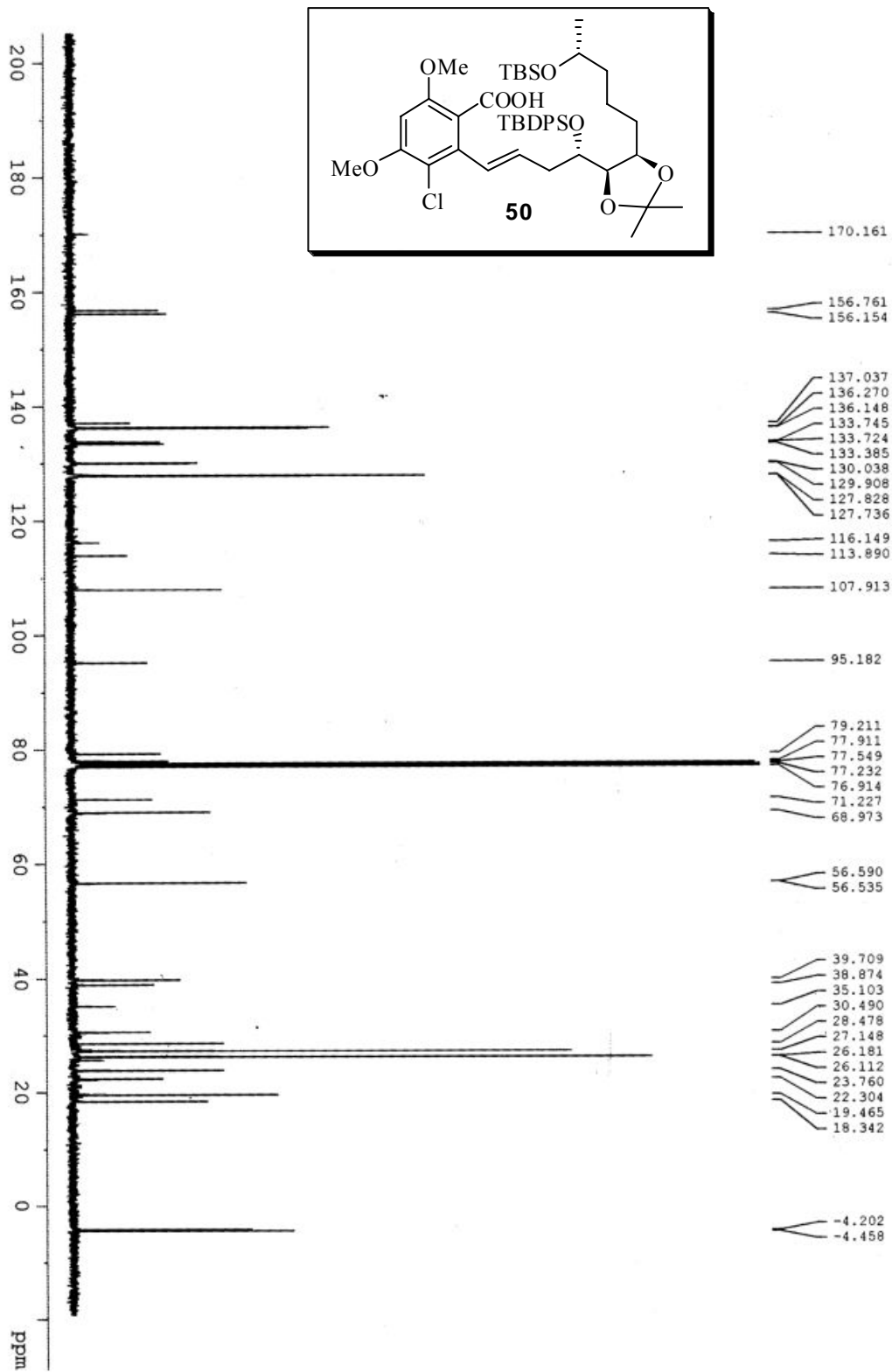
DEPT- NMR of compound 48 (100MHz, CDCl₃)



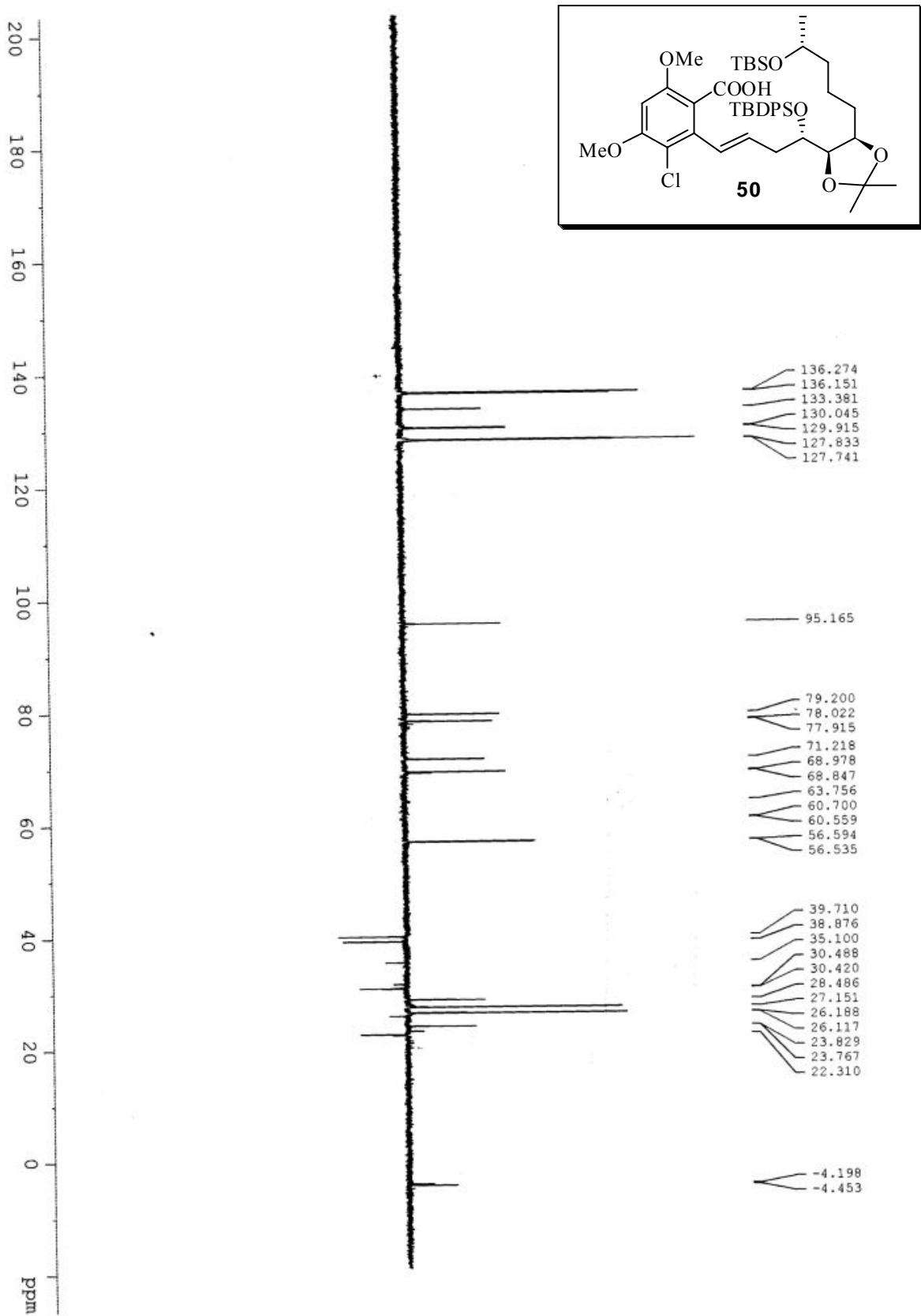
¹H-NMR of compound 50 (400MHz, CDCl₃)



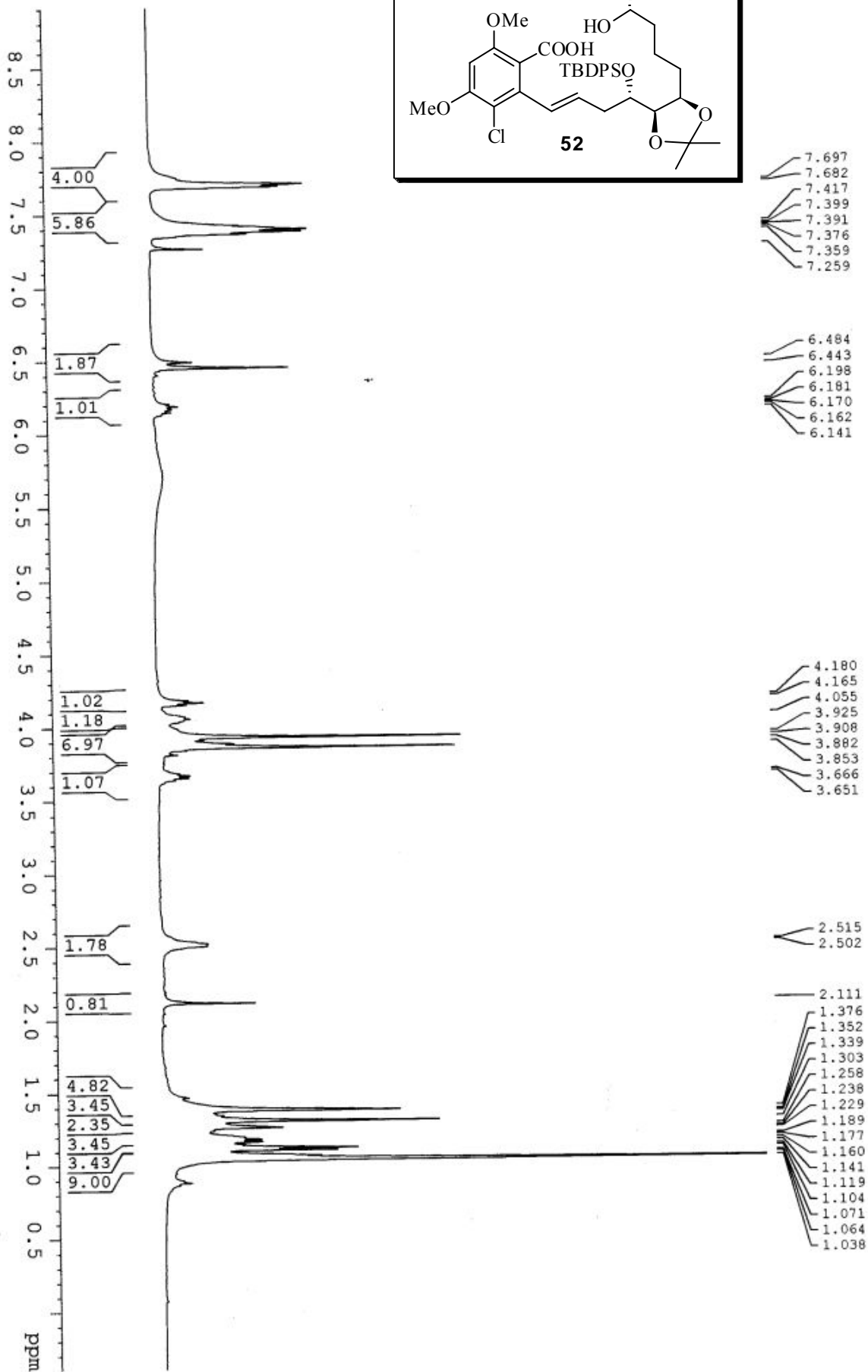
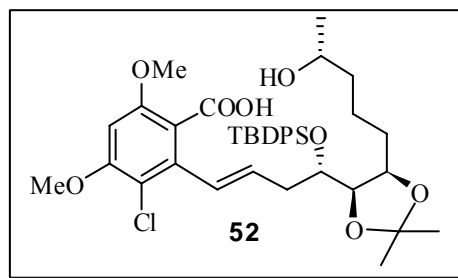
¹³C-NMR of compound 50 (100MHz, CDCl₃)



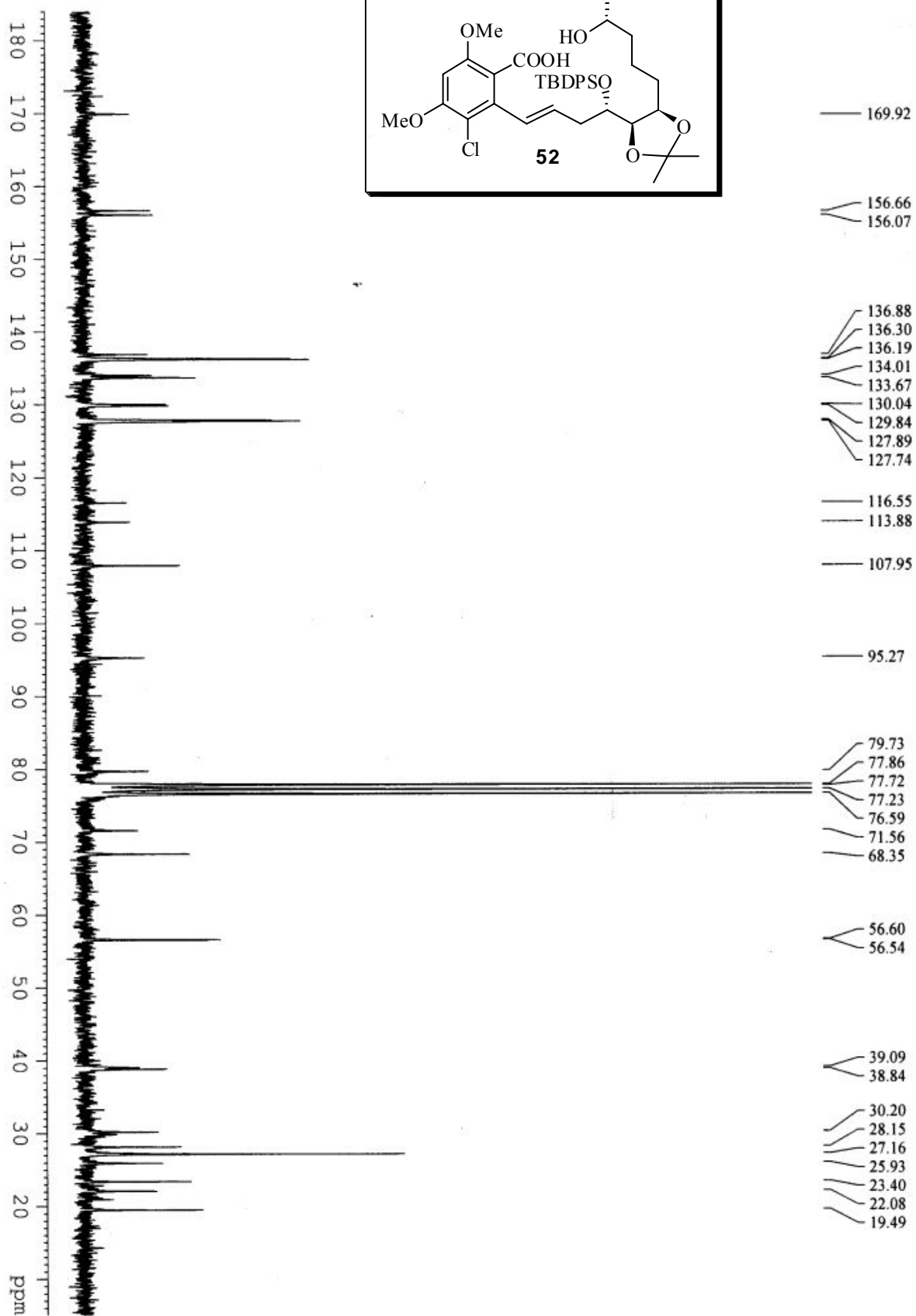
DEPT- NMR of compound 50 (100MHz, CDCl₃)



¹H-NMR of compound 52 (200MHz, CDCl₃)

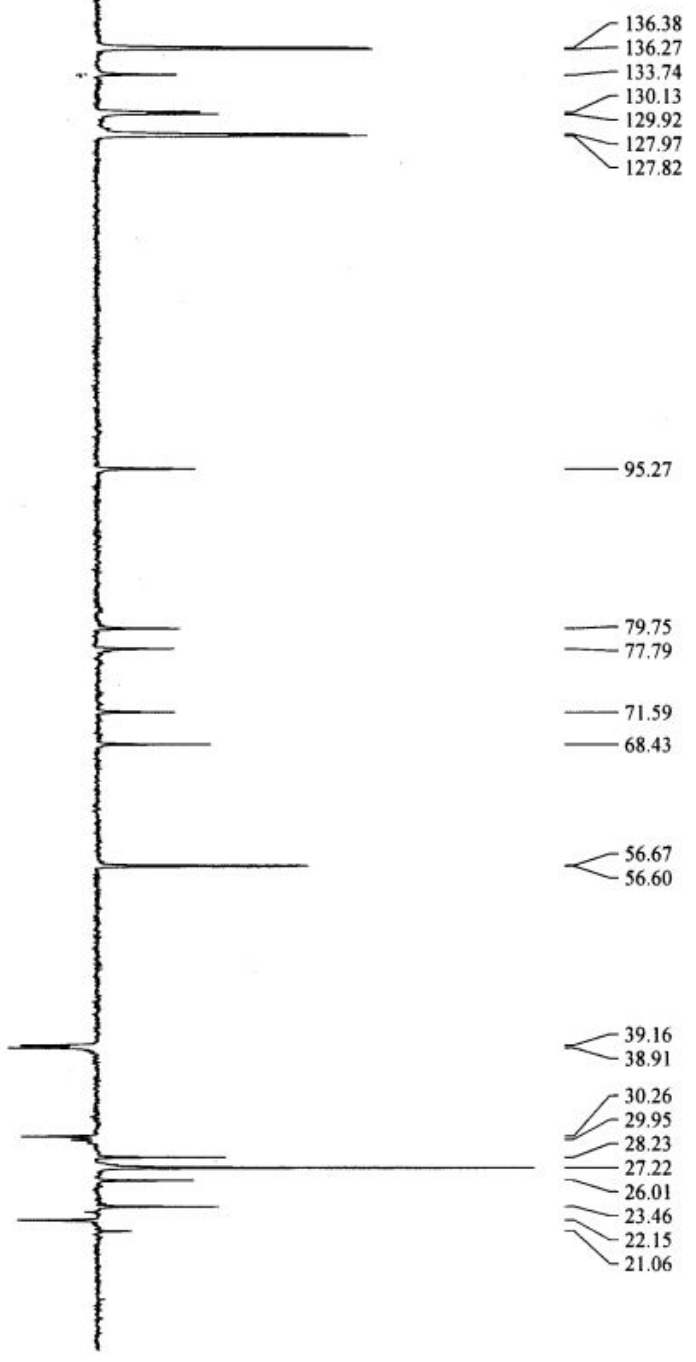
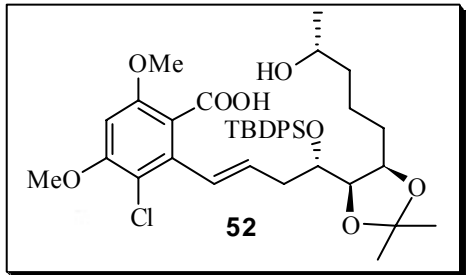


¹³C-NMR of compound 52 (50MHz, CDCl₃)

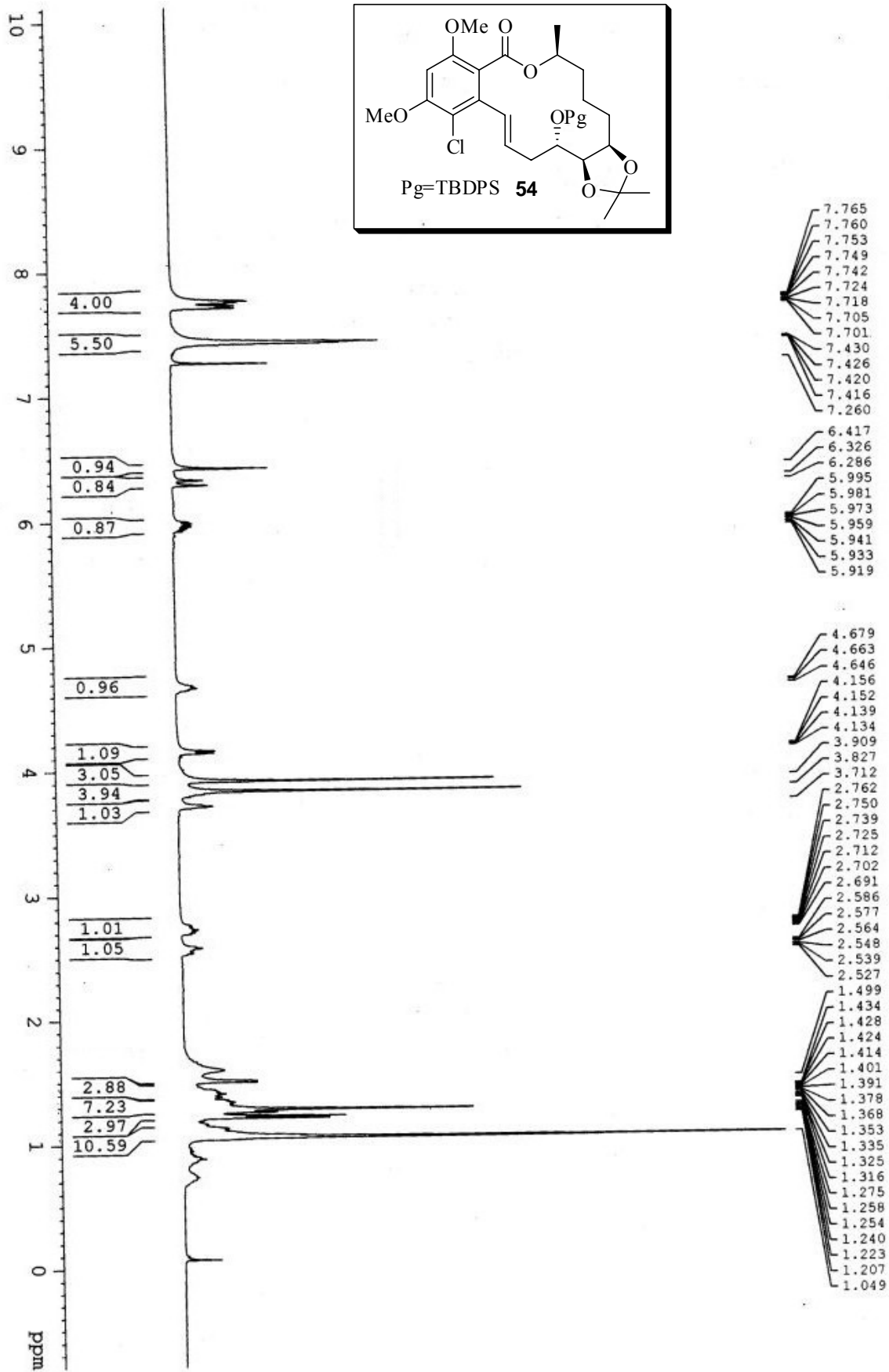


DEPT-NMR of compound 52 (50MHz, CDCl₃)

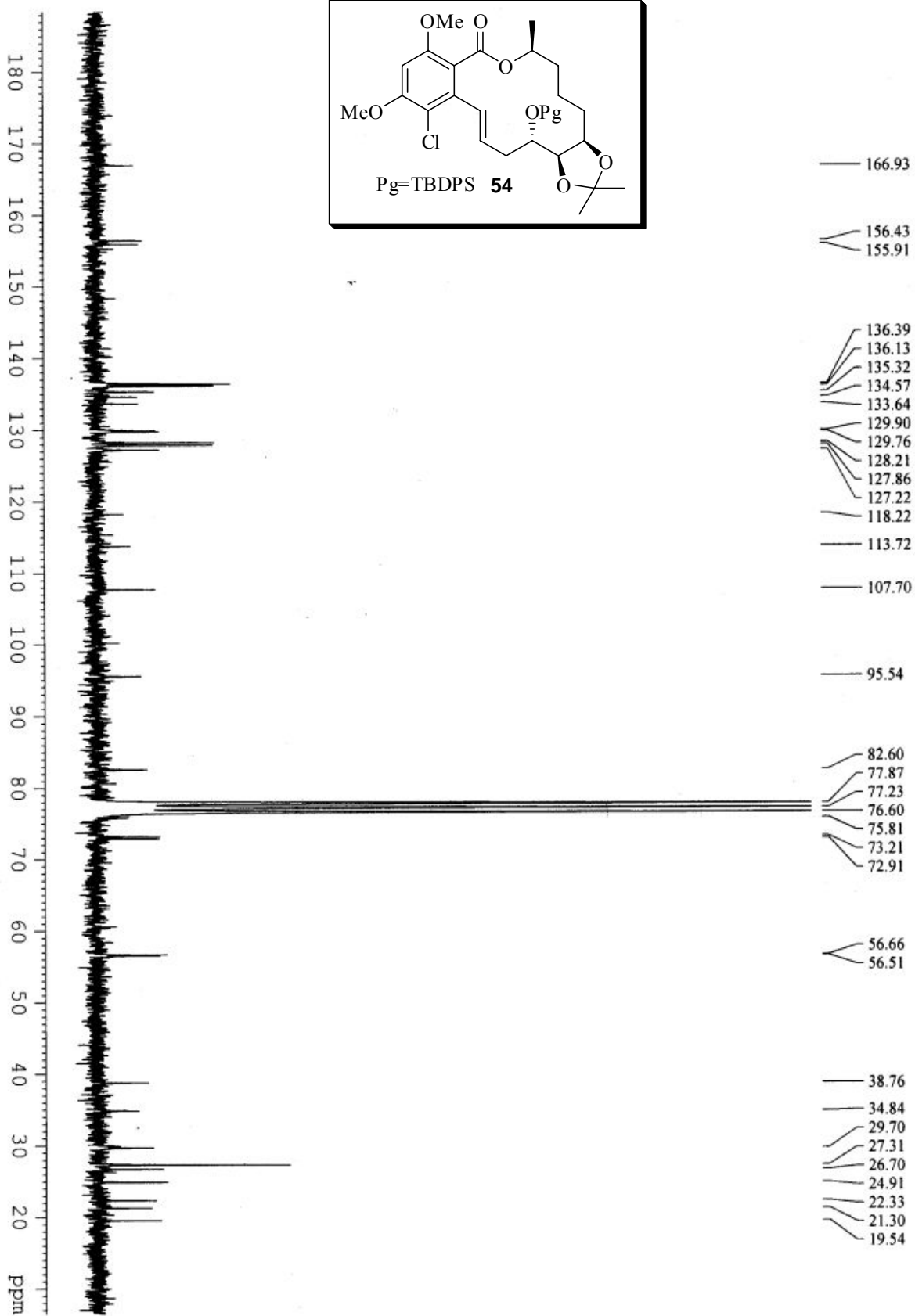
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



¹H- NMR of compound 54 (400MHz, CDCl₃)

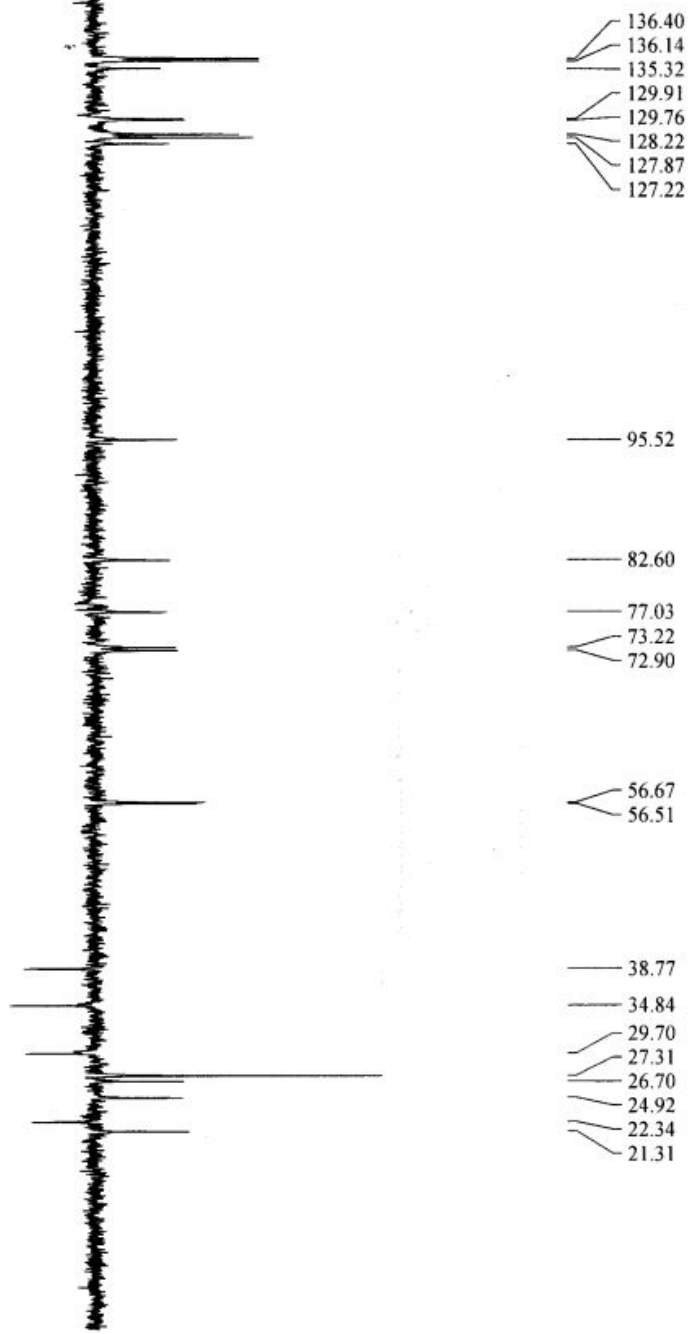
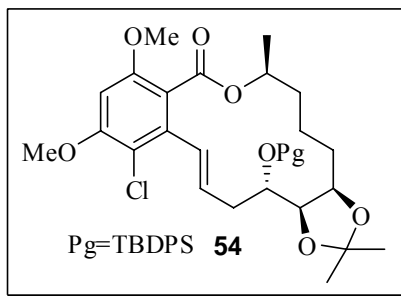


¹³C-NMR of compound 54 (50MHz, CDCl₃)

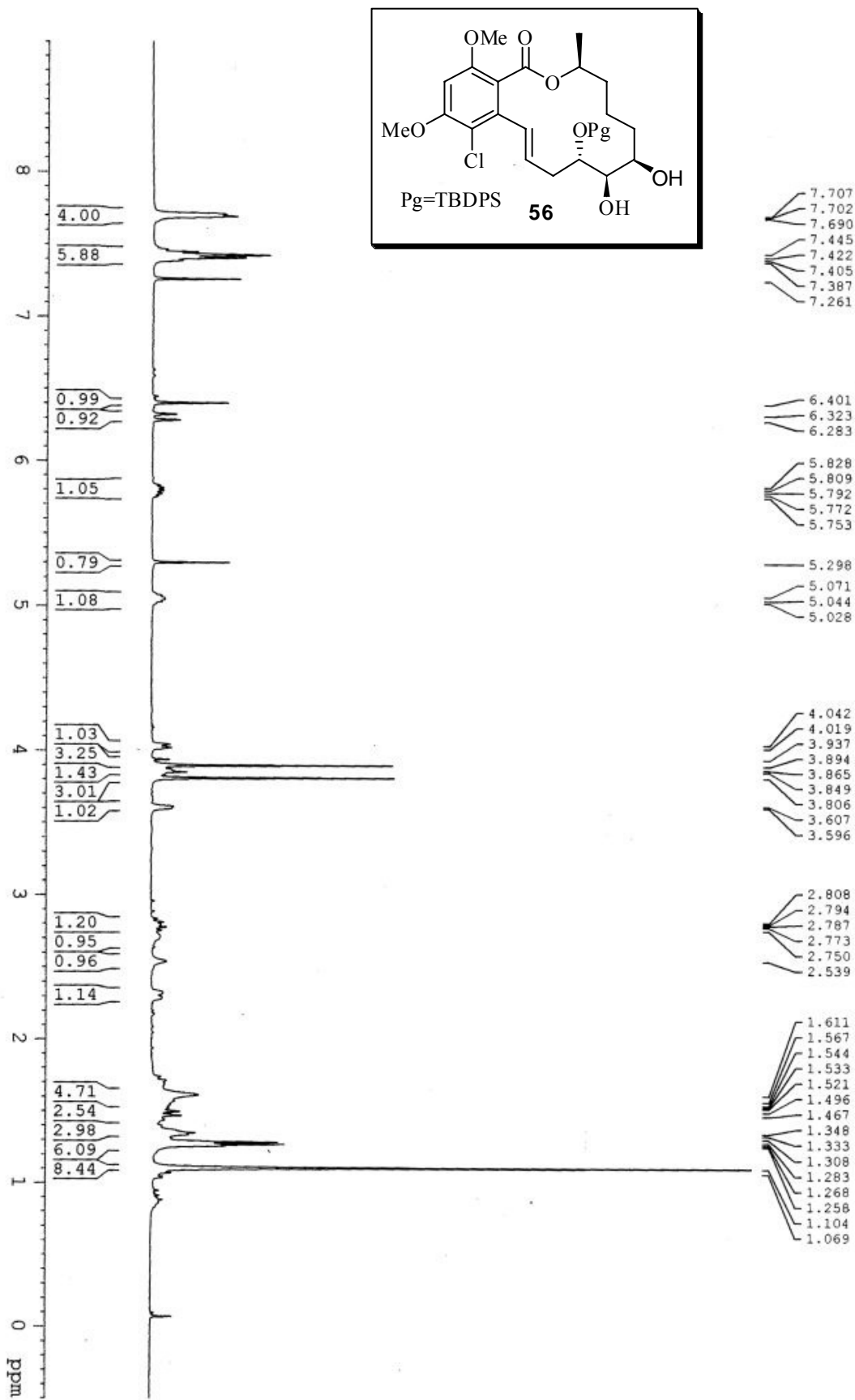


DEPT- NMR of compound 54 (50MHz, CDCl₃)

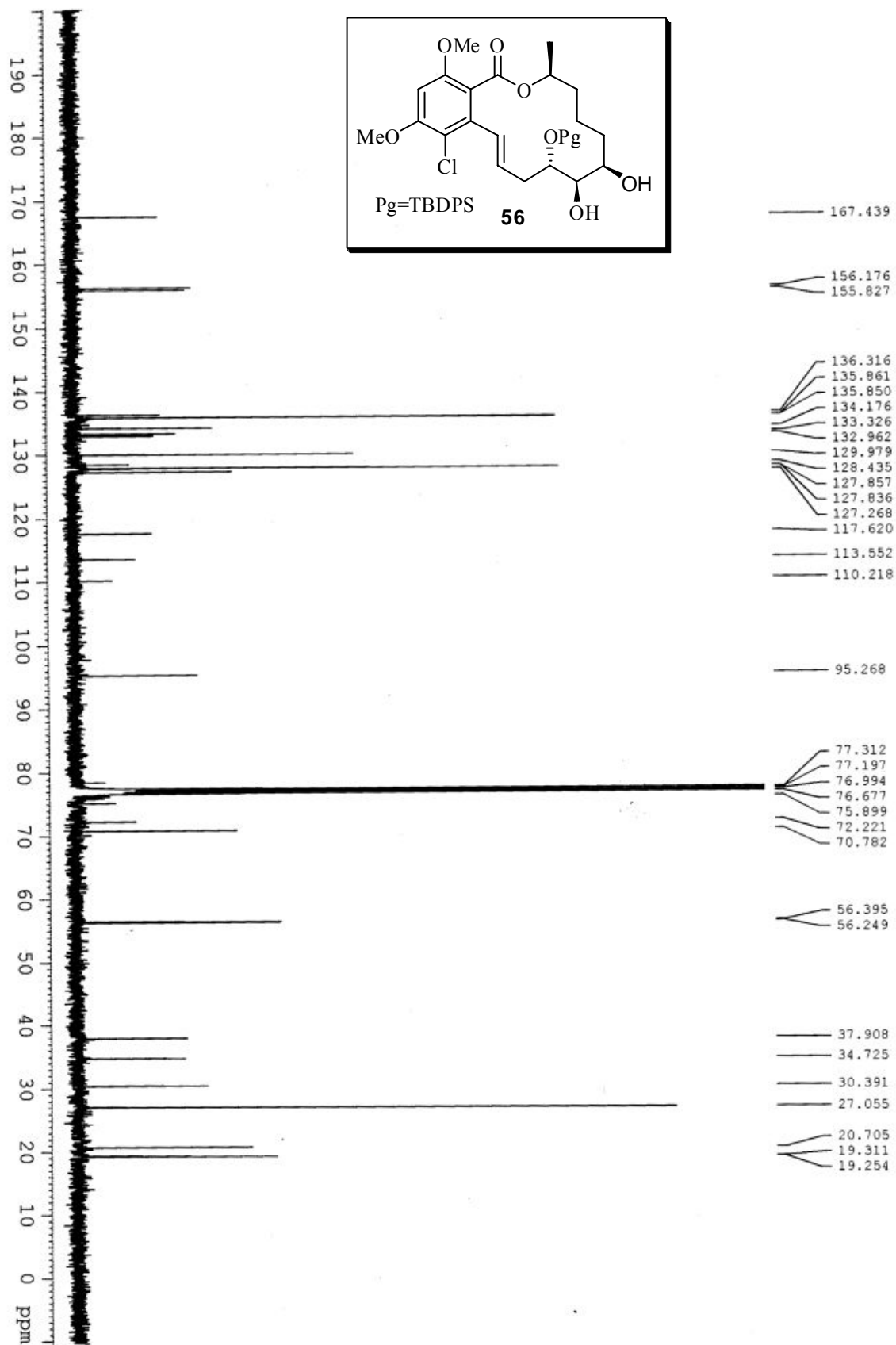
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



¹H-NMR of compound 56 (400MHz, CDCl₃)

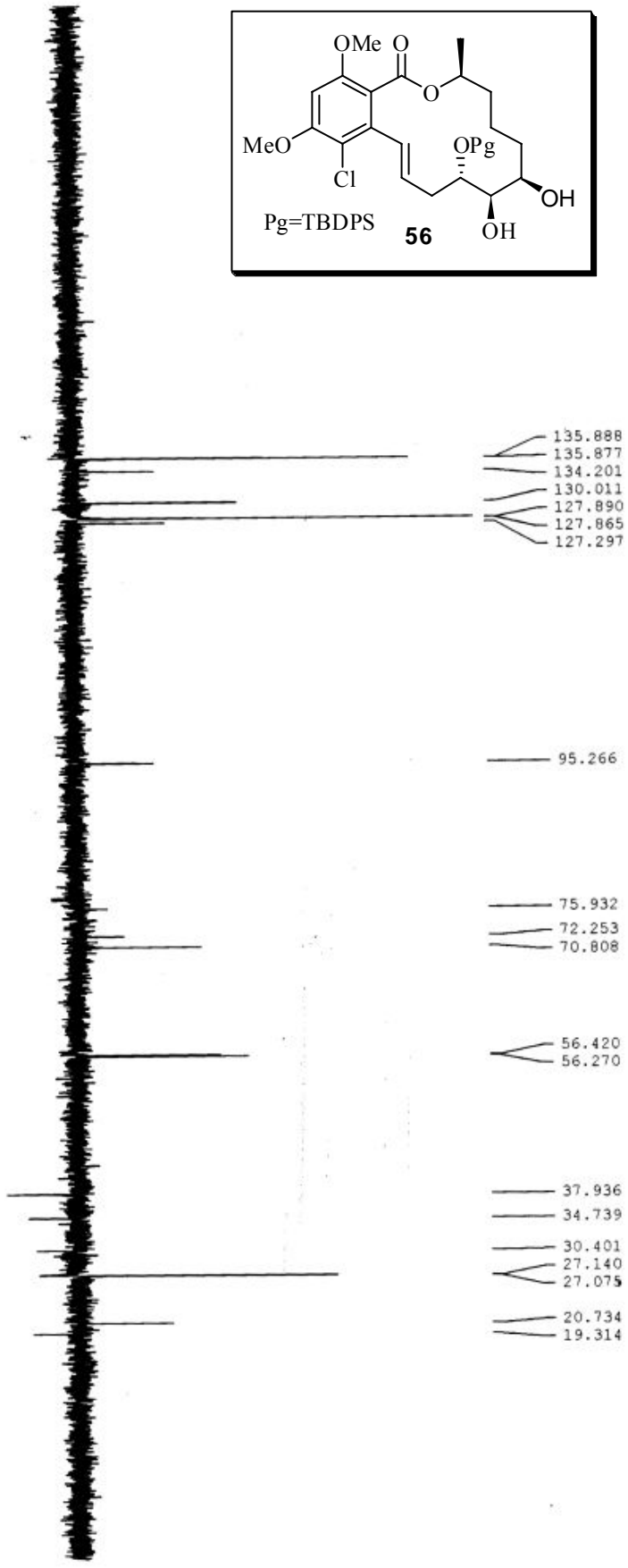
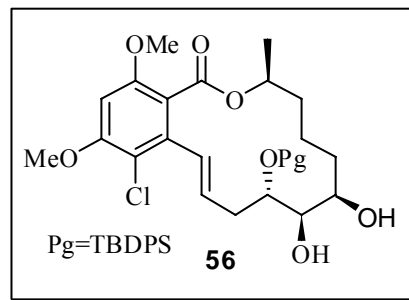


¹³C-NMR of compound 56 (100MHz, CDCl₃)

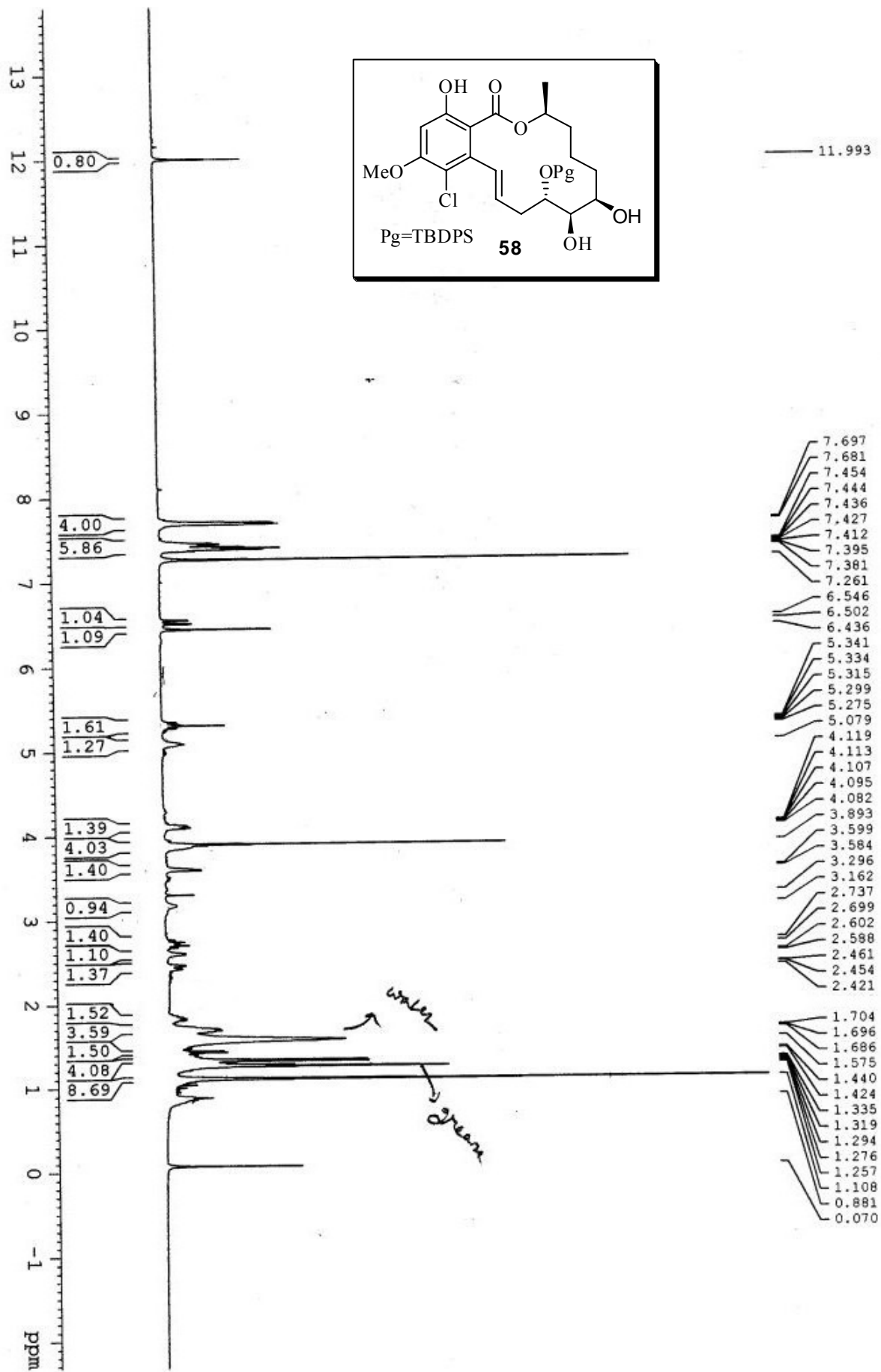


DEPT- NMR of compound 56 (100MHz, CDCl₃)

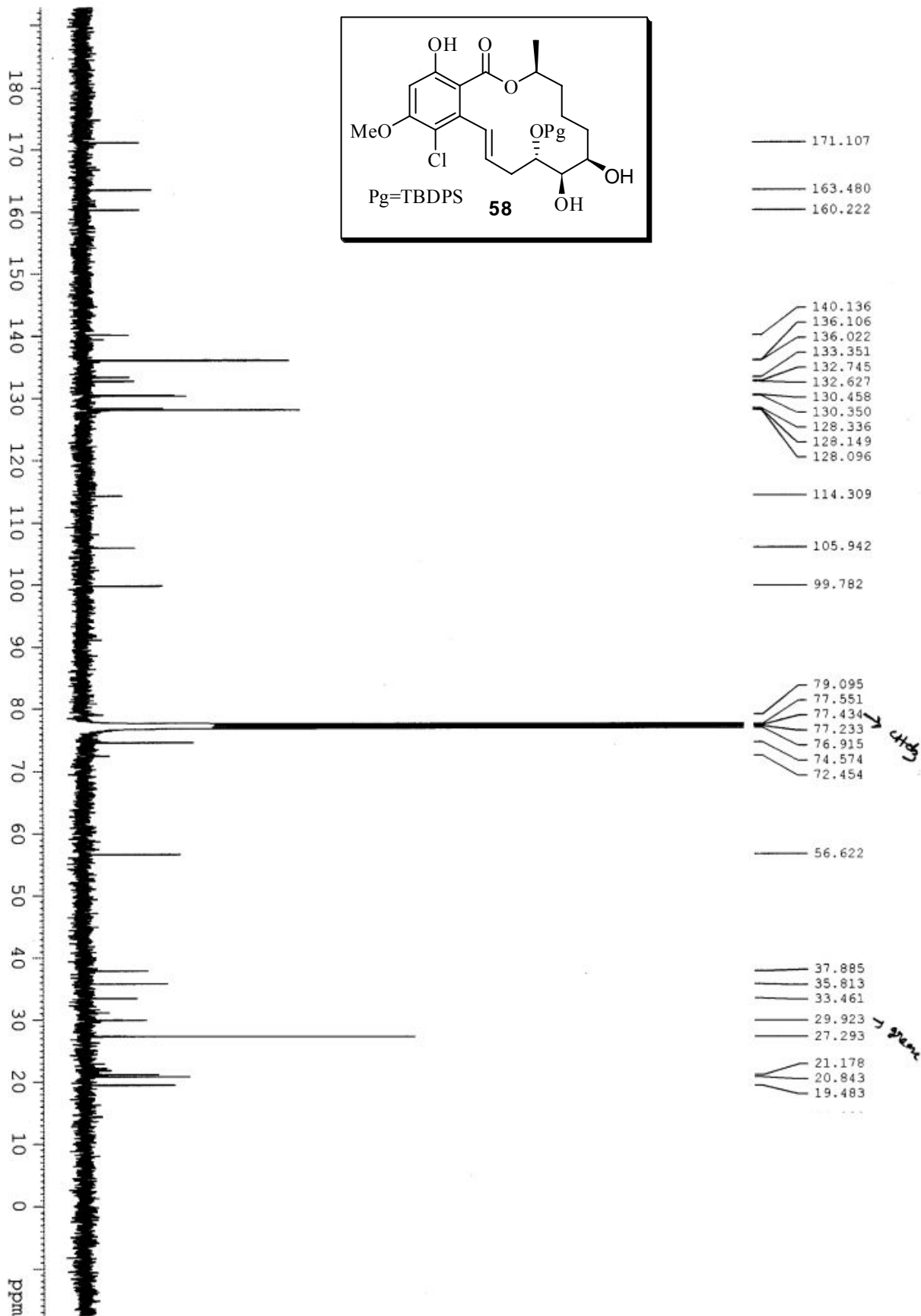
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



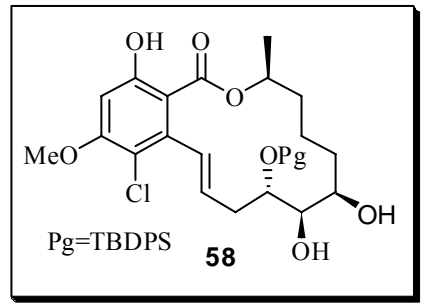
¹H-NMR of compound 58 (400MHz, CDCl₃)



¹³C-NMR of compound 58 (100MHz, CDCl₃)



DEPT- NMR of compound 58 (100MHz, CDCl₃)



- 136.196
- 136.102
- 136.014
- 132.709
- 130.464
- 130.352
- 128.335
- 128.151
- 128.095

99.771

- 79.103
- 77.437
- 74.578
- 72.358

56.626

- 37.881
- 35.806
- 33.493

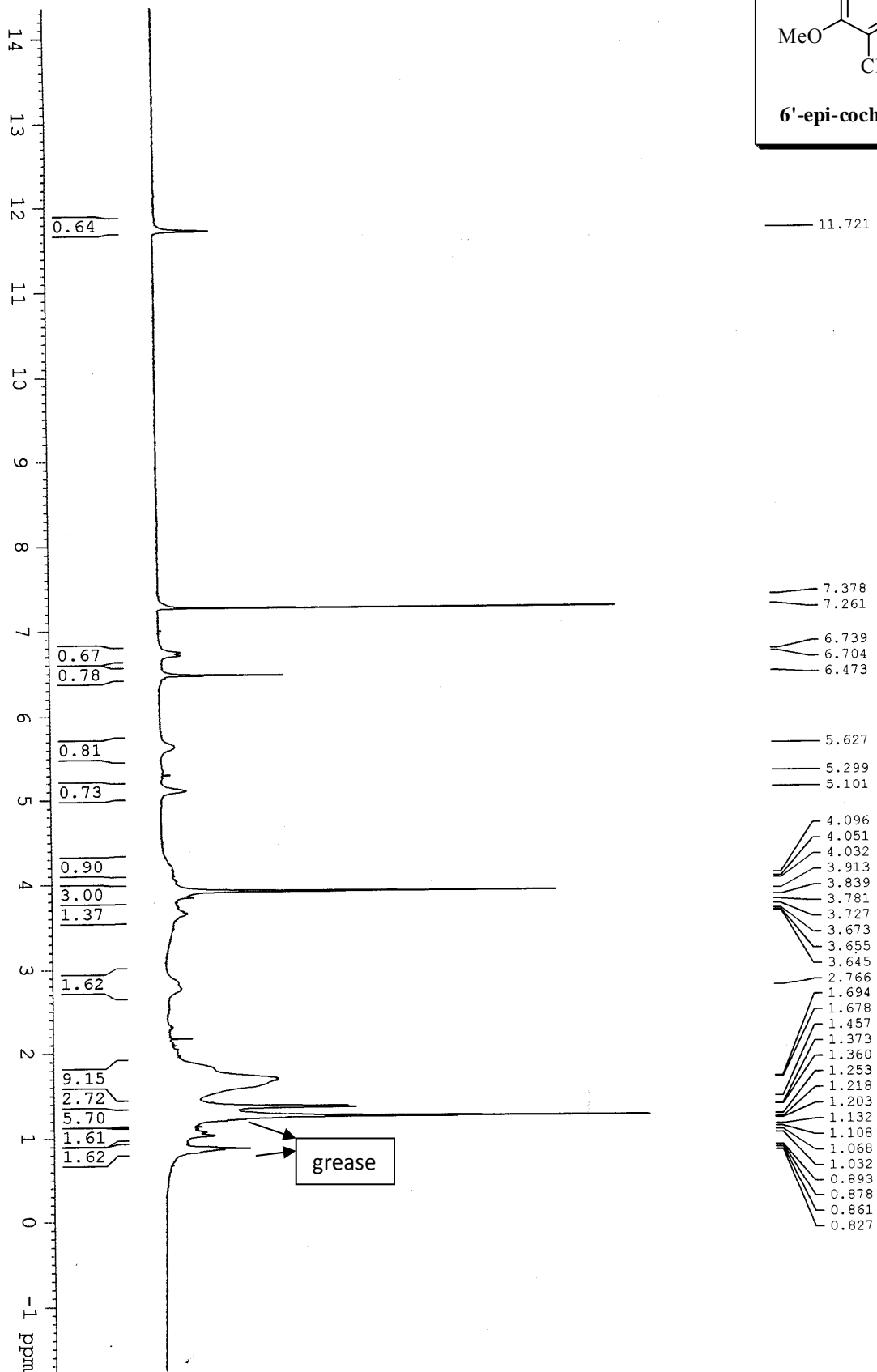
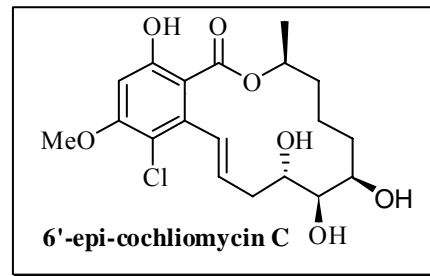
- 29.924
- 27.282

- 21.177
- 20.843

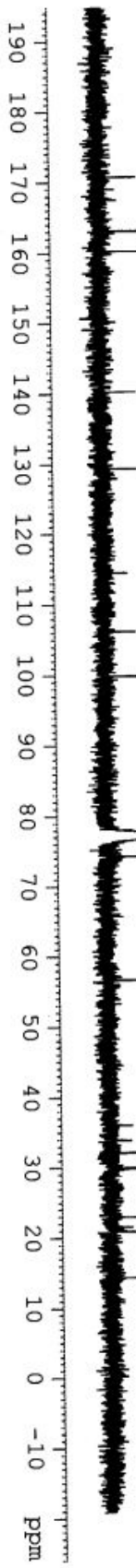
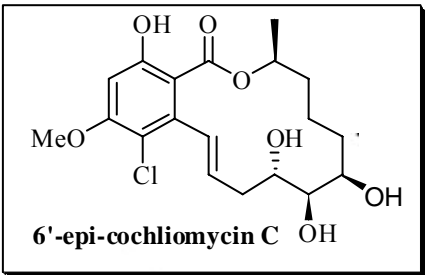
← CDCl₃

↓ grease

¹H-NMR of 6'-epi-cochliomycin C (400MHz, CDCl₃)



¹³C-NMR of 6'-epi-cochliomycin C (100MHz, CDCl₃)



- 170.763
- 163.129
- 160.268

- 140.293
- 129.321

- 114.483
- 106.222
- 99.862

- 77.553
- 77.235
- 76.918
- 74.261

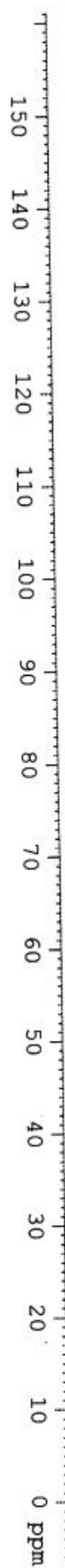
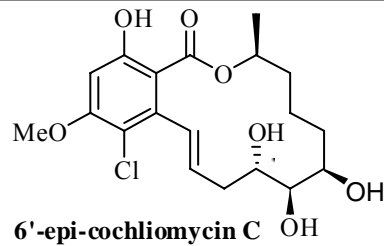
- 56.655

- 38.408
- 36.119
- 32.153
- 29.928
- 22.919
- 21.600
- 20.850
- 14.341

grease

→ grease
→ grease

DEPT- NMR 6'-epi-cochliomycin C (100MHz, CDCl₃)



136.184
131.734
129.325

99.859

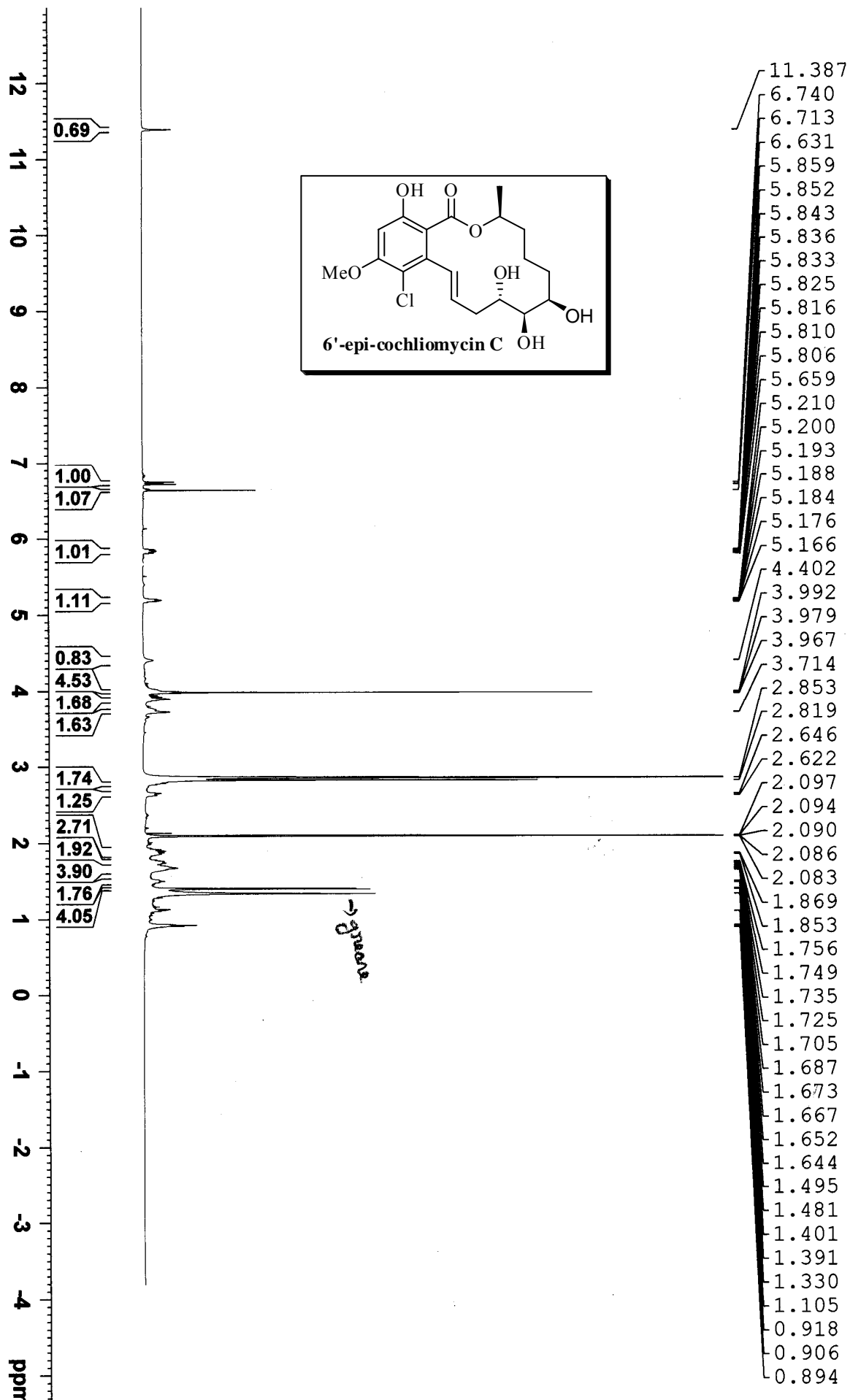
77.550
77.438
77.243
76.908
74.273
→ CDCl₃

56.653

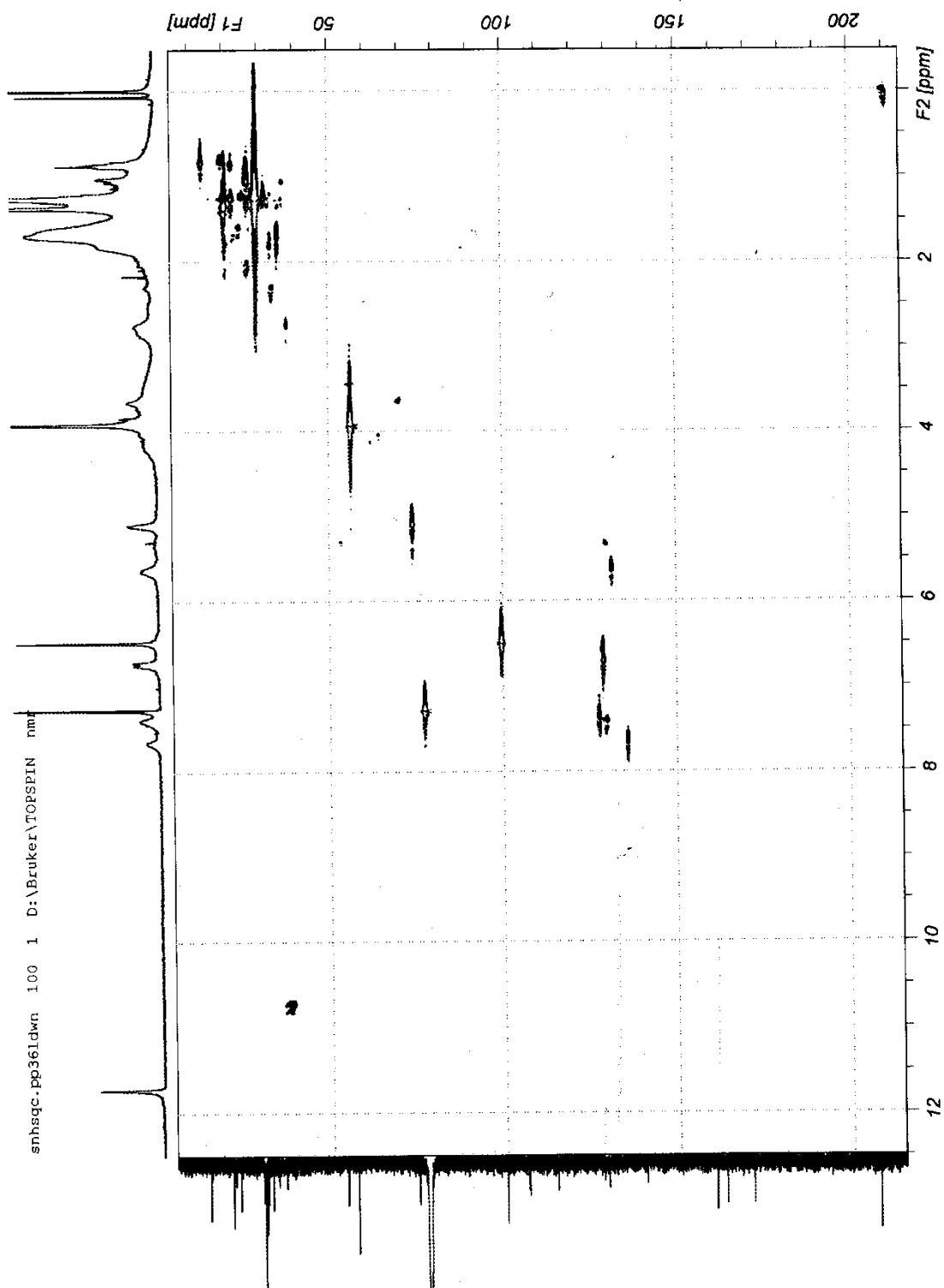
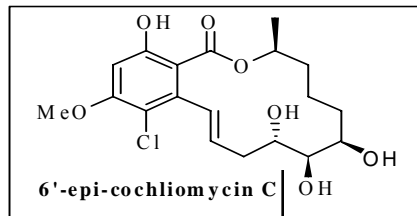
38.384
36.033
32.153
29.925
22.917
21.539
20.846
→ grease

grease

¹H-NMR of 6'-epi-cochliomycin C (600MHz, Acetone-d₆)



HSQC of 6'-epi-cochliomycin C (600 MHz, CDCl₃)

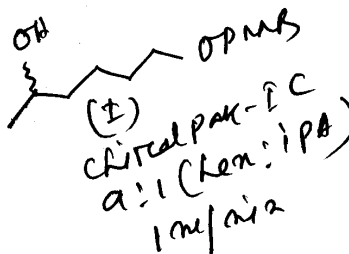


HPLC chromatogram of racemic 11

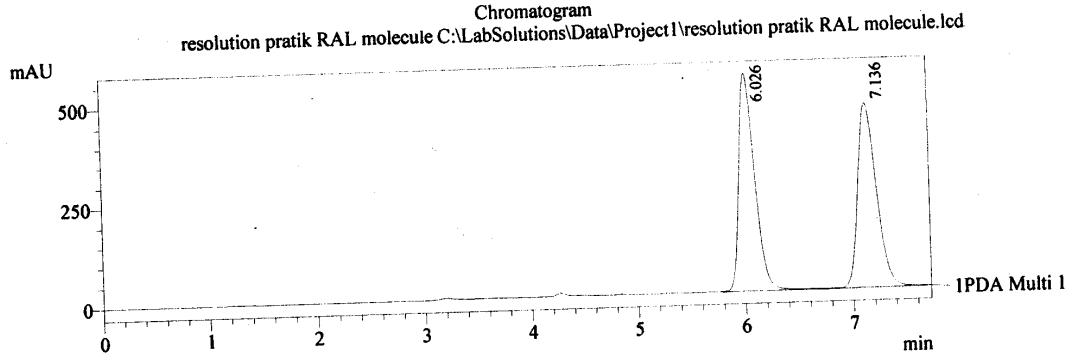
Department of Chemistry, IIT-Kharagpur

Sample Information

Acquired by : Admin
 Sample Name : resolution pratik RAL molecule
 Sample ID : transesterification
 Vail# :
 Injection Volume : 5 uL
 Data Filename : resolution pratik RAL molecule.lcd
 Method Filename : new.lcm
 Batch Filename :
 Report Filename : Default.lcr
 Date Acquired : 7/13/2012 9:04:00 AM
 Date Processed : 7/3/2014 9:22:30 AM



Chromatogram



1 PDA Multi 1 / 254nm 4nm

PeakTable

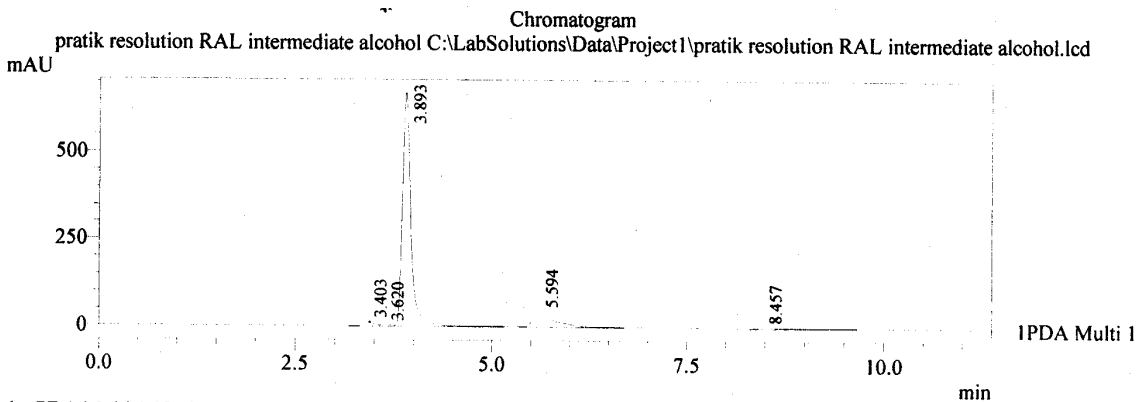
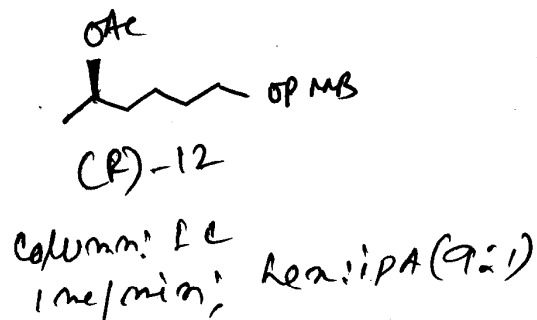
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.026	5518957	544895	49.936	54.166
2	7.136	5533124	461080	50.064	45.834
Total		11052081	1005975	100.000	100.000

HPLC chromatogram of (R)-12

Department of Chemistry, IIT-Kharagpur

Sample Information
 Acquired by : Admin
 Sample Name : pratik resolution RAL intermediate alcohol
 Sample ID : transterification
 Vail# :
 Injection Volume : 5 uL
 Data Filename : pratik resolution RAL intermediate alcohol.lcd
 Method Filename : pda.lcm
 Batch Filename :
 Report Filename : Default.lcr
 Date Acquired : 7/1/2014 4:32:14 PM
 Data Processed : 7/1/2014 4:47:11 PM



PDA Ch1 254nm 4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.403	107232	11007	1.805	1.510
2	3.620	30112	3356	0.507	0.460
3	3.893	4946640	669929	83.255	91.876
4	5.594	781458	42896	13.152	5.883
5	8.457	76131	1976	1.281	0.271
Total		5941574	729165	100.000	100.000


ee = 98%

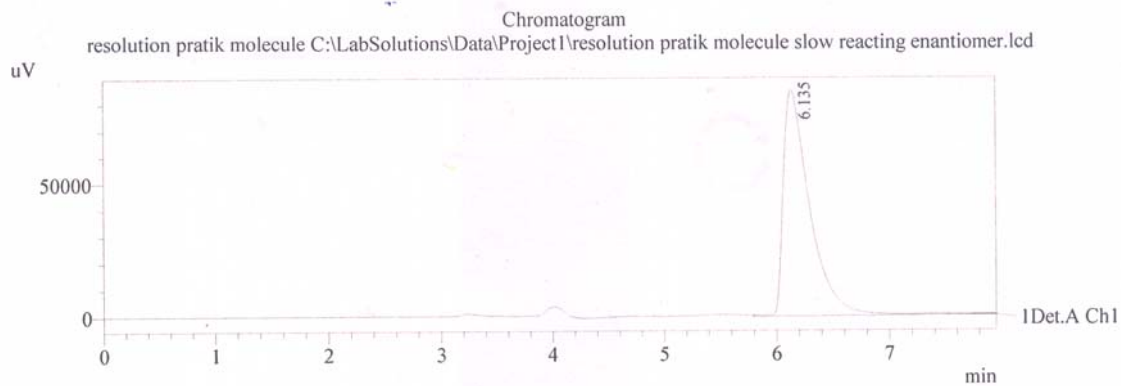
HPLC chromatogram of (S)-13

Department of Chemistry, IIT-Kharagpur

Sample Information

Acquired by : Admin
 Sample Name : resolution pratik molecule slow reacting enantiomer
 Sample ID : transesterification
 Vail# :
 Injection Volume : 5 uL
 Data Filename : resolution pratik molecule slow reacting enantiomer.lcd
 Method Filename : adduct1.lcm
 Batch Filename :
 Report Filename : Default.lcr
 Date Acquired : 1/11/2010 2:30:30 PM
 Data Processed : 1/11/2010 2:39:04 PM

OH

 chiral pak-IC
 9:1 (hex:IPA)
 1 ml/min



1 Det.A Ch1 / 254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.135	1378194	85153	100.000	100.000
Total		1378194	85153	100.000	100.000

ee > 99%