**Supporting Information**

# Total Synthesis of Methyl Sarcophytoate

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**General.**

The optical rotations were measured on a JASCO DIP-360 polarimeter. The IR spectra were recorded using a JASCO FT IR-200 spectrometer. The $^{1}H$ and $^{13}C$ NMR spectra were measured by a JEOL GSX-270, a JEOL Lambda 300, a Varian MERCURY plus 300, or a Bruker AVANCE 500 spectrometer at ambient temperature. Chemical shifts of the $^{1}H$ NMR spectra are expressed in ppm relative to the solvent residual signal 7.26 in $CDCl_3$ or to tetramethylsilane ($\delta$ = 0.00). Chemical shifts of the $^{13}C$ NMR spectra are expressed in ppm relative to the solvent signal 77.16 in $CDCl_3$ unless otherwise noted. The high and low resolution mass spectra were recorded using a JEOL GC mate (EI). Analytical thin layer chromatography (TLC) was performed using Merck TLC 60F-254 plates (0.25 mm), and visualization was accomplished with ethanolic phosphomolybudic acid. Column chromatography was performed on Fuji silysia PSQ 100 B silica gel. All reactions requiring anhydrous conditions were carried out in oven-dried glassware under an argon atmosphere. Organic solvents were distilled by appropriate procedures and stored under argon atmosphere.

**(3*S*,6*E*)-8-(4-Methoxybenzyloxy)-2,6-dimethylocta-1,6-dien-3-ol (5).**

$R_f$ = 0.27 (2:1 hexane–EtOAc).

$[\alpha]_D^{26}$ −7.54 (*c* 2.16, $CHCl_3$).

IR (neat) $cm^{-1}$ 3430, 2940, 2860, 1615, 1585, 1515, 1440, 1370, 1300, 1250, 1175, 1110, 1070, 1040, 900, 820, 760.

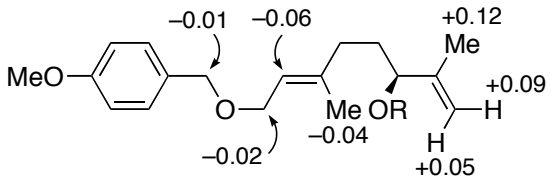
$^{1}H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.60–1.76 (2H, m), 1.65 (3H, br s), 1.72 (3H, br s), 1.95–2.20 (2H, m), 3.80 (3H, s), 3.96–4.09 (1H, m), 3.99 (2H, d, *J* = 7.0 Hz), 4.43 (2H, s), 4.84 (1H, br s), 4.94 (1H, br s), 5.42 (1H, tq, *J* = 7.0 Hz, 1.0 Hz), 6.87 (2H, d, *J* = 9.0 Hz), 7.27 (2H, d, *J* = 9.0 Hz).

$^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 16.68, 17.70, 32.98, 35.63, 55.38, 66.36, 71.85, 75.66, 111.26, 113.84, 121.26, 129.54, 130.69, 140.10, 147.50, 159.22.

MS (EI) *m*/*z* 290 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{18}H_{26}O_3$ ($M^+$) 290.1882, found 290.1874.

Enantiomeric excess was determined to be >98% by comparing the $^{1}H$ NMR of (*S*)-MTPA and (*R*)-MTPA esters of **5**. The absolute configuration of **5** was determined by the modified

Mosher ester analysis shown in SI-Figure 1.




***SI-Figure 1.*** Δδ ($\delta_S - \delta_R$) values of MTPA esters of **5**.

**(3*Z*,5*S*,8*E*)-10-(4-Methoxybenzyloxy)-4,8-dimethyldeca-3,8-dien-5-olide (8).**

$R_f$ = 0.25 (2:1 hexane–EtOAc).

$[\alpha]_D^{27}$ +36.9 (*c* 1.87, $CHCl_3$).

IR (neat) $cm^{-1}$ 2940, 2860, 1740, 1615, 1585, 1515, 1440, 1390, 1360, 1300, 1250, 1215, 1180, 1070, 1040, 930, 820, 755.

$^1H$ NMR (300 MHz, $CDCl_3$) δ 1.62 (3H, s), 1.65–1.79 (1H, m), 1.71 (3H, d, *J* = 2.0 Hz), 1.88–2.28 (3H, m), 2.95–3.04 (2H, m), 3.77 (3H, s), 3.97 (2H, d, *J* = 7.0 Hz), 4.41 (2H, s), 4.76 (1H, dd, *J* = 7.5 Hz, 3.0 Hz), 5.39 (1H, tq, *J* = 7.0 Hz, 1.0 Hz), 5.48 (1H, br s), 6.85 (2H, d, *J* = 9.0 Hz), 7.24 (2H, d, *J* = 9.0 Hz).

$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 16.65, 18.82, 29.93, 31.97, 33.84, 55.26, 66.23, 71.88, 82.56, 113.74, 116.58, 121.72, 129.42, 130.50, 132.69, 138.83, 159.14, 169.37.

MS (EI) *m*/*z* 330 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{20}H_{26}O_4$ ($M^+$) 330.1831, found 330.1845.

**(2*R*,3*S*,5*Z*,7*S*,10*E*)-2,3-Epoxy-12-(4-methoxybenzyloxy)-2,6,10-trimethyl-7-(triethylsiloxy)dodeca-5,10-dien-1-al (10).**

$R_f$ = 0.78 (2:1 hexane–EtOAc).

$[\alpha]_D^{27}$ +41.5 (*c* 2.27, $CHCl_3$).

IR (neat) $cm^{-1}$ 2950, 2910, 2880, 1730, 1615, 1585, 1515, 1460, 1380, 1300, 1250, 1175, 1080, 1040, 1010, 820, 740.

$^1H$ NMR (300 MHz, $CDCl_3$) δ 0.56 (6H, q, *J* = 8.0 Hz), 0.94 (9H, t, *J* = 8.0 Hz), 1.43 (3H, s), 1.46–1.61 (1H, m), 1.64 (3H, br s), 1.71 (3H, br s), 1.66–1.80 (1H, m), 1.82–1.98 (1H, m), 2.00–2.16 (1H, m), 2.20–2.40 (1H, m), 2.40–2.60 (1H, m), 3.01 (1H, t, *J* = 7.0 Hz), 3.80 (3H, s), 3.98 (2H, d, *J* = 7.0 Hz), 4.36–4.46 (1H, m), 4.43 (2H, s), 5.16 (1H, br t, *J* = 7.0 Hz), 5.39 (1H, br t, *J* = 7.0 Hz), 6.87 (2H, d, *J* = 9.0 Hz), 7.27 (2H, d, *J* = 9.0 Hz), 8.85 (1H, s).

$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 4.98, 7.00, 10.16, 16.82, 18.30, 26.76, 34.69, 35.96, 55.41, 59.47, 62.47, 66.42, 70.35, 71.97, 113.87, 118.40, 120.99, 129.53, 130.72, 140.12, 142.46, 159.26, 200.02.

MS (EI) *m*/*z* 502 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{29}H_{46}O_5Si$ ($M^+$) 502.3115, found 502.3136.

***tert*-Butyl (3*S*,4*S*,5*S*,7*Z*,9*S*,12*E*)-4,5-Epoxy-3-hydroxy-14-(4-methoxybenzyloxy)-4,8,12-trimethyl-9-(triethylsiloxy)tetradeca-7,12-dienoate (11a).**

$R_f$ = 0.53 (3:1 hexane–EtOAc).

$[\alpha]_D^{27}$ −15.3 (*c* 2.41, $CHCl_3$).

IR (neat) $cm^{-1}$ 3470, 2955, 2880, 1730, 1615, 1515, 1455, 1370, 1250, 1155, 1070, 1040, 1010, 820, 745.

$^1H$ NMR (300 MHz, $CDCl_3$) δ 0.56 (6H, q, *J* = 8.0 Hz), 0.93 (9H, t, *J* = 8.0 Hz), 1.29 (3H, s), 1.46 (9H, s), 1.63 (3H, br s), 1.70 (3H, br s), 1.40–1.78 (1H, m), 1.80–2.16 (2H, m), 2.16–2.46 (2H, m), 2.37 (1H, dd, *J* = 16.5 Hz, 9.5 Hz), 2.52 (1H, dd, *J* = 16.5 Hz, 3.0 Hz), 2.87 (1H, d, *J* = 2.0 Hz), 2.95 (1H, t, *J* = 6.5 Hz), 3.80 (3H, s), 3.85 (1H, dt, *J* = 9.0 Hz, 2.0 Hz), 3.98 (2H, d, *J* = 6.5 Hz), 4.42 (1H, t, *J* = 6.8 Hz), 4.43 (2H, s), 5.15 (1H, br t, *J* = 7.5 Hz), 5.39 (1H, tq, *J* = 6.5 Hz, 1.0 Hz), 6.87 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.5 Hz).

$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 4.96, 7.01, 13.29, 16.82, 18.10, 27.00, 28.20, 34.66, 36.00, 38.64, 55.40, 60.70, 61.87, 66.41, 70.35, 71.21, 71.88, 81.54, 113.85, 119.50, 120.84, 129.54, 130.76, 140.32, 141.27, 159.23, 171.59.

MS (EI) *m*/*z* 561 $[(M-tBu)^+]$; HRMS (EI) *m*/*z* calcd for $C_{31}H_{49}O_7Si$ $[(M-tBu)^+]$ 561.3248, found 561.3247.

***tert*-Butyl (3*R*,4*S*,5*S*,7*Z*,9*S*,12*E*)-4,5-Epoxy-3-hydroxy-14-(4-methoxybenzyloxy)-4,8,12-trimethyl-9-(triethylsiloxy)tetradeca-7,12-dienoate (11b).**

$R_f$ = 0.42 (3:1 hexane–EtOAc).

$[\alpha]_D^{27}$ −1.07 (*c* 2.43, $CHCl_3$).

IR (neat) $cm^{-1}$ 3450, 2950, 2910, 2880, 1730, 1615, 1585, 1515, 1460, 1415, 1370, 1300, 1250, 1170, 1150, 1070, 1040, 1010, 980, 955, 850, 820, 745.

$^1H$ NMR (300 MHz, $CDCl_3$) δ 0.56 (6H, q, *J* = 8.0 Hz), 0.93 (9H, t, *J* = 8.0 Hz), 1.29 (3H, s), 1.47 (9H, s), 1.48–1.78 (2H, m), 1.63 (3H, br s), 1.69 (3H, br s), 1.82–1.97 (1H, m), 1.98–2.28 (2H, m), 2.30–2.50 (3H, m), 2.86 (1H, d, *J* = 4.0 Hz), 2.94 (1H, t, *J* = 6.5 Hz), 3.72–3.82 (1H, m), 3.80 (3H, s), 3.98 (2H, d, *J* = 6.5 Hz), 4.38–4.46 (1H, m), 4.42 (2H, s), 5.13 (1H, br t, *J* = 6.5 Hz), 5.38 (1H, tq, *J* = 6.5 Hz, 1.0 Hz), 6.87 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.5 Hz).

$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 4.95, 7.01, 12.58, 16.83, 18.09, 26.92, 28.20, 34.66, 35.98, 38.88, 55.40, 60.46, 62.57, 66.40, 70.34, 71.88, 72.33, 81.58, 113.85, 119.50, 120.82, 129.54, 130.74, 140.32, 141.26, 159.22, 171.31.

MS (EI) *m*/*z* 561 $[(M-tBu)^+]$; HRMS (EI) *m*/*z* calcd for $C_{31}H_{49}O_7Si$ $[(M-tBu)^+]$ 561.3248, found 561.3257.

**Structure Determination of 11a (SI-Figure 2).** To a stirred solution of **11a** (26.6 mg, 0.0430

mmol) in dry THF (0.215 mL) was added 1.0 M THF solution of TBAF (0.0860 mL, 0.0860 mmol) at room temperature. After 1 h at room temperature, saturated aqueous solution of $NH_4Cl$ (0.5 mL) and water (1 mL) were added and the mixture was extracted with EtOAc (1 mL×3). The extracts were washed with brine (1 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (1.0 g of silica gel, 1:1 hexane–EtOAc) to afford **alcohol** (21.6 mg, 99%) as a colorless syrup. To a stirred solution of this **alcohol** (6.1 mg, 0.0121 mmol) in dry toluene (0.605 mL) was added ($i$-PrO)$_4$Ti (0.0036 mL, 0.0121 mmol) in dry toluene (0.806 mL) and the solution was heated at 50 °C for 3 h. After cooling to room temperature, water (2 mL) was added and the mixture was extracted with EtOAc (2 mL×3). The extracts were washed with brine (2 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (1.0 g of silica gel, 3:1 hexane–EtOAc) to afford **dihydropyran** (2.4 mg, 40%) as a colorless syrup. A solution of this **dihydropyran** (8.2 mg, 0.0162 mmol) in dry $CH_2Cl_2$ (0.0810 mL) were added 2,2-dimethoxypropane (0.0199 mL, 0.162 mmol) and PPTS (0.4 mg, 0.00162 mmol) at room temperature. After 22 h at room temperature, saturated aqueous solution of $NaHCO_3$ (0.5 mL) and water (1 mL) were added. The mixture was extracted with $CHCl_3$ (1 mL×3) and the extracts were washed with brine (1 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (1.0 g of silica gel, 3:1 hexane–EtOAc) to afford **acetonide S-1** (5.0 mg, 56%) as a colorless syrup.

$R_f$ = 0.71 (2:1 hexane–EtOAc).

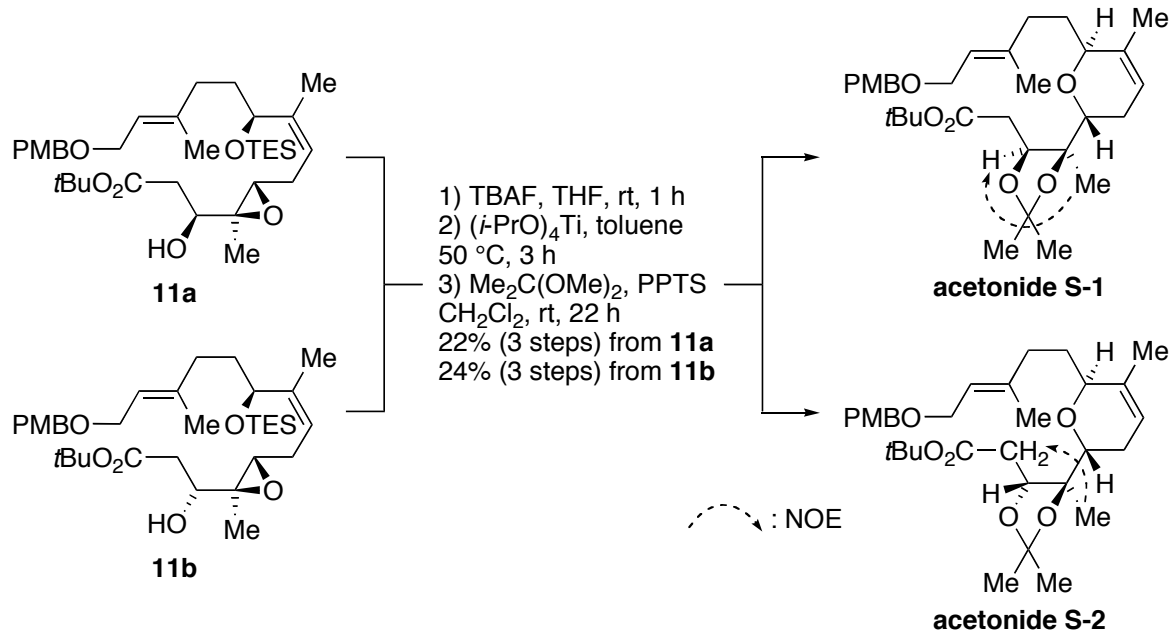
$[\alpha]_D^{27}$ +17.5 ($c$ 0.92, $CHCl_3$).

IR (neat) cm$^{-1}$ 2980, 2935, 2860, 1735, 1610, 1515, 1460, 1370, 1310, 1250, 1155, 1100, 1070, 1045, 1000, 935, 850, 820.

$^1$H NMR (300 MHz, $CDCl_3$) δ 1.26 (3H, s), 1.38 (6H, s), 1.46 (9H, s), 1.50–1.78 (2H, m), 1.62 (3H, br s), 1.68 (3H, br s), 1.90–2.24 (3H, m), 2.26–2.44 (1H, m), 2.52 (1H, dd, $J$ = 16.5 Hz, 9.0 Hz), 2.84 (1H, dd, $J$ = 16.5 Hz, 3.0 Hz), 3.70 (1H, dd, $J$ = 10.0 Hz, 3.5 Hz), 3.80 (3H, s), 3.91 (1H, br s), 4.00 (2H, d, $J$ = 6.5 Hz), 4.25 (1H, dd, $J$ = 9.5 Hz, 3.0 Hz), 4.44 (2H, s), 5.46 (1H, t, $J$ = 6.5 Hz), 5.54 (1H, m), 6.87 (2H, d, $J$ = 8.5 Hz), 7.27 (2H, d, $J$ = 8.5 Hz).

$^{13}$C NMR (75 MHz, $CDCl_3$) δ 16.79, 18.65, 20.22, 25.61, 26.67, 28.27, 28.41, 29.71, 35.69, 37.59, 55.42, 66.44, 67.22, 71.94, 79.88, 80.95, 82.65, 107.44, 113.86, 120.02, 121.42, 129.58, 130.74, 134.58, 140.02, 159.26, 170.75.

MS (EI) $m/z$ 544 ($M^+$); HRMS (EI) $m/z$ calcd for $C_{32}H_{48}O_7$ ($M^+$) 544.3400, found 544.3418.




***SI-Figure 2*.** Structure determination of **11**.

**Structure Determination of 11b (SI-Figure 2). Acetonide S-2** was synthesized from **11b** (24% in 3 steps) by the same procedure as described above.

$R_f$ = 0.63 (2:1 hexane–EtOAc).

$[\alpha]_D^{27}$ +16.4 (*c* 1.76, $CHCl_3$).

IR (neat) $cm^{-1}$ 2980, 2935, 2860, 1735, 1610, 1515, 1455, 1370, 1305, 1250, 1155, 1100, 950, 850.

$^1H$ NMR (300 MHz, $CDCl_3$) δ 1.11 (3H, s), 1.36 (3H, s), 1.44 (9H, s), 1.52–1.76 (2H, m), 1.61 (3H, br s), 1.66 (3H, br s), 1.88–2.34 (4H, m), 2.49 (1H, dd, *J* = 16.0 Hz, 9.5 Hz), 2.68 (1H, dd, *J* = 16.0 Hz, 2.5 Hz), 3.54 (1H, dd, *J* = 10.5 Hz, 3.0 Hz), 3.80 (3H, s), 3.92 (1H, d, *J* = 9.5 Hz), 4.00 (2H, d, *J* = 6.5 Hz), 4.32 (1H, dd, *J* = 9.5 Hz, 2.5 Hz), 4.42 (2H, s), 5.42 (1H, t, *J* = 6.5 Hz), 5.51 (1H, m), 6.87 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.5 Hz).

$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 16.70, 17.16, 20.09, 25.50, 26.87, 28.24, 28.76, 29.20, 36.24, 37.08, 55.40, 66.41, 71.78, 72.04, 76.49, 78.80, 80.88, 82.34, 107.93, 113.84, 119.26, 121.56, 129.53, 130.78, 135.32, 139.88, 159.23, 170.45.

MS (EI) *m*/*z* 544 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{32}H_{48}O_7$ ($M^+$) 544.3400, found 544.3425.

**(2*E*,5*S*,6*R*,7*R*,9*Z*,11*S*,14*E*)-7,11-Epoxy-5,6-(isopropylidenedioxy)-16-(4-methoxybenzyloxy)-2,6,10,14-tetramethylhexadeca-2,9,14-trien-1-ol (13).** To a −78 °C solution of **12** (343 mg, 0.487 mmol) in dry MeOH (9.7 mL) was added $BF_3$•$OEt_2$ (0.184 mL, 1.46 mmol) and the resulting solution was warmed up to 0 °C over 2 h. After 1 h at 0 °C, saturated aqueous solution of $NaHCO_3$ (3 mL) and water (6 mL) were added. This was extracted with 1:1 hexane–EtOAc (9 mL×3) and the extracts were washed with brine (9 mL), dried over $Na_2SO_4$,

and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (11.6 g of silica gel, 1:2 hexane–EtOAc) to afford **dihydropyran** (224 mg, 97%) as a colorless syrup [$R_f$ = 0.20 (1:1 hexane–EtOAc); $[\alpha]_D^{27}$ +16.7 (*c* 1.21, $CHCl_3$); IR (neat) $cm^{-1}$ 3420, 2935, 2860, 1735, 1610, 1515, 1455, 1440, 1375, 1300, 1250, 1175, 1070, 1040, 930, 820; $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.28 (3H, s), 1.58–1.78 (2H, m), 1.63 (3H, br s), 1.66 (3H, br s), 1.69 (3H, br s), 1.92–2.48 (6H, m), 3.63 (1H, dd, *J* = 10.5 Hz, 2.5 Hz), 3.67 (1H, dd, *J* = 11.0 Hz, 3.5 Hz), 3.80 (3H, s), 3.92–4.06 (5H, m), 4.44 (2H, s), 5.43 (1H, br t, *J* = 6.5 Hz), 5.47–5.64 (2H, m), 6.88 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.5 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.17, 16.72, 19.60, 20.01, 25.10, 29.53, 29.77, 36.59, 55.42, 66.45, 68.72, 70.97, 71.98, 74.91, 75.31, 77.05, 113.89, 119.68, 121.54, 122.52, 129.62, 130.62, 135.06, 138.21, 139.85, 159.28; MS (EI) *m*/*z* 456 [$(M-H_2O)^+$]; HRMS (EI) *m*/*z* calcd for $C_{28}H_{40}O_5$ [$(M-H_2O)^+$] 456.2876, found 456.2855]. To a solution of this **dihydropyran** (121 mg, 0.255 mmol) in dry $CH_2Cl_2$ (2.6 mL) were added 2,2-dimethoxypropane (0.313 mL, 2.55 mmol) and PPTS (6.4 mg, 0.0255 mmol) at room temperature. After 1 h at room temperature, dry MeOH (2.6 mL) was added and the solution was stirred for 5 min. This was cooled to 0 °C and saturated aqueous solution of $NaHCO_3$ (1 mL) and water (3 mL) were added. The mixture was extracted with 1:1 hexane–EtOAc (4 mL×3) and the extracts were washed with brine (4 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (7.3 g of silica gel, 2:1 hexane–EtOAc) to afford **13** (134 mg, 91%) as a colorless syrup.

$R_f$ = 0.55 (1:1 hexane–EtOAc).

$[\alpha]_D^{26}$ +9.58 (*c* 1.16, $CHCl_3$).

IR (neat) $cm^{-1}$ 3440, 2985, 2935, 2860, 1615, 1515, 1450, 1380, 1300, 1250, 1180, 1095, 1070, 1040, 930, 855, 820.

$^1H$ NMR (300 MHz, $CDCl_3$) δ 1.27 (3H, s), 1.34 (3H, s), 1.38 (3H, s), 1.56–1.76 (2H, m), 1.60 (3H, br s), 1.62 (3H, br s), 1.70 (3H, br s), 1.87–2.44 (6H, m), 2.57 (1H, ddd, *J* = 15.0 Hz, 8.0 Hz, 3.5 Hz), 3.70–3.82 (2H, m), 3.80 (3H, s), 3.90 (1H, br d, *J* = 8.0 Hz), 3.94–4.04 (4H, m), 4.42 (2H, s), 5.35 (1H, br t, *J* = 6.0 Hz), 5.56 (2H, br s), 6.87 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.5 Hz).

$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.09, 16.55, 19.16, 20.18, 25.93, 26.71, 27.89, 28.38, 29.43, 37.57, 55.38, 66.45, 67.18, 68.94, 71.88, 77.25, 82.89, 84.09, 107.12, 113.86, 120.19, 121.70, 122.84, 129.65, 130.41, 134.63, 136.99, 139.27, 159.28.

MS (EI) *m*/*z* 514 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{31}H_{46}O_6$ ($M^+$) 514.3294, found 514.3294.

**(2*E*,6*S*,7*Z*,10*R*,11*R*,12*S*,14*S*)-6,10:14,15-Diepoxy-11,12-(isopropylidenedioxy)-3,7,11,15-tetramethyl-1-(phenylthio)hexadeca-2,7-diene (14).** To a mixture of L-(+)-DET (2.35 mg, 0.0114 mmol) and MS4AP (78.4 mg) in dry $CH_2Cl_2$ (0.381 mL) was added (*i*-PrO)$_4$Ti (0.00227 mL, 0.00762 mmol) at 0 °C. After 0.5 h at 0 °C, the reaction mixture was cooled to

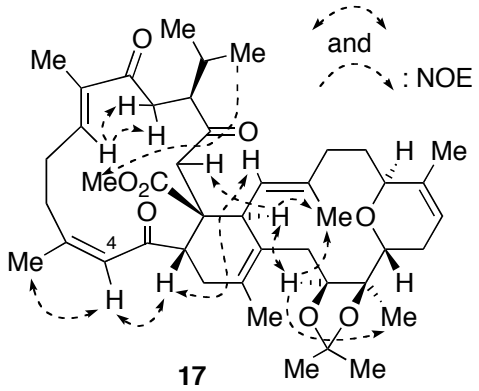
−40 °C and 3.98 M $CH_2Cl_2$ solution of TBHP (0.0382 mL, 0.152 mmol) was added. After 0.5 h at −40 °C, a solution of **13** (39.2 mg, 0.0762 mmol) in dry $CH_2Cl_2$ (0.254 mL) was added and the resulting mixture was stirred at −40 °C for 17 h. The reaction was quenched with water (1 mL) and the organic layer was separated. The aqueous layer was extracted with EtOAc (1 mL×3) and the combined organic layers were washed with brine (1 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (2.0 g of silica gel, 4:1 hexane–EtOAc to 3:1 hexane–EtOAc) to afford **epoxide** (38.2 mg, 95%) as a colorless syrup [$R_f$ = 0.44 (1:1 hexane–EtOAc); $[\alpha]_D^{27}$ +7.30 (*c* 1.89, $CHCl_3$); IR (neat) $cm^{-1}$ 3450, 2985, 2935, 2860, 1615, 1515, 1455, 1380, 1300, 1250, 1220, 1180, 1095, 1070, 1040, 930, 870, 850, 820; $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.24 (3H, s), 1.32 (3H, s), 1.37 (3H, s), 1.39 (3H, s), 1.54–1.74 (8H, m), 1.86–2.38 (6H, m), 3.24 (1H, dd, *J* = 7.5 Hz, 5.0 Hz), 3.54 (1H, d, *J* = 12.0 Hz), 3.59 (1H, d, *J* = 12.0 Hz), 3.74 (1H, dd, *J* = 10.0 Hz, 4.0 Hz), 3.80 (3H, s), 3.89 (1H, br), 3.96 (1H, dd, *J* = 9.0 Hz, 4.5 Hz), 4.00 (2H, d, *J* = 7.0 Hz), 4.43 (2H, s), 5.37 (1H, br t, *J* = 7.0 Hz), 5.55 (1H, m), 6.88 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.5 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.75, 16.83, 18.52, 20.18, 25.71, 26.76, 28.42, 28.56, 29.37, 37.47, 55.40, 58.70, 61.51, 65.99, 66.51, 67.02, 72.07, 81.22, 82.88, 107.42, 113.89, 120.12, 121.44, 129.68, 130.38, 134.56, 139.47, 159.33; MS (EI) *m*/*z* 530 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{31}H_{46}O_7$ ($M^+$) 530.3243, found 530.3253]. To a solution of this **epoxide** (212 mg, 0.399 mmol), $PPh_3$ (209 mg, 0.797 mmol), and imidazole (108 mg, 1.59 mmol) in dry $CH_2Cl_2$ (9.5 mL) was added $I_2$ (181 mg, 0.718 mmol) at 0 °C. The resulting mixture was shielded from light and stirred at 0 °C for 3 h. Saturated aqueous solution of $Na_2S_2O_3$ (2 mL) and saturated aqueous solution of $NaHCO_3$ (2.0 mL) were added and the organic layer was separated. The aqueous layer was extracted with hexane (4 mL×3) and the combined organic layers were washed with brine (4 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (12.8 g of silica gel, 4:1 hexane–EtOAc) to afford **iodide** (238 mg, 93%) as a colorless syrup [$R_f$ = 0.83 (2:1 hexane–EtOAc); $[\alpha]_D^{27}$ +8.61 (*c* 2.13, $CHCl_3$); IR (neat) $cm^{-1}$ 2985, 2935, 2860, 1735, 1615, 1585, 1515, 1455, 1380, 1300, 1250, 1220, 1185, 1170, 1095, 1070, 1045, 930, 870, 850, 820; $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.24 (3H, s), 1.36 (3H, s), 1.39 (3H, s), 1.47 (3H, s), 1.61 (3H, br s), 1.66 (3H, br s), 1.56–1.72 (2H, m), 1.82-2.36 (6H, m), 3.12 (1H, d, *J* = 10.0 Hz), 3.14 (1H, dd, *J* = 5.5 Hz, 2.5 Hz), 3.19 (1H, d, *J* = 10.0 Hz), 3.73 (1H, dd, *J* = 10.5 Hz, 4.0 Hz), 3.80 (3H, s), 3.85–3.93 (1H, m), 3.93 (1H, dd, *J* = 9.5 Hz, 4.5 Hz), 4.00 (2H, d, *J* = 6.5 Hz), 4.43 (2H, s), 5.39 (1H, tq, *J* = 6.5 Hz, 1.0 Hz), 5.55 (1H, m), 6.88 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.5 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.04, 16.65, 17.05, 18.56, 20.20, 25.68, 26.75, 28.42, 29.31, 29.54, 37.40, 55.41, 60.56, 64.67, 66.49, 66.99, 72.05, 80.96, 82.86, 107.45, 113.89, 120.04, 121.46, 129.61, 130.60, 134.55, 139.56, 159.26; MS (EI) *m*/*z* 640 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{31}H_{45}O_6I$ ($M^+$) 640.2261, found 640.2268]. To a solution of this **iodide** (65.6 mg, 0.102 mmol) in dry THF (1.0 mL) was

added $NaBH_3CN$ (96.5 mg, 1.54 mmol) and the resulting mixture was stirred at 50 °C for 18 h. After cooling to 0 °C, water (2 mL) was added and the mixture was extracted with EtOAc (2 mL×3). The extracts were washed with brine (2 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (2.95 g of silica gel, 7:1 hexane–EtOAc) to afford **the reduction product** (38.6 mg, 73%) as a colorless syrup [$R_f$ = 0.48 (4:1 hexane–EtOAc); $[\alpha]_D^{27}$ +9.55 (*c* 0.94, $CHCl_3$); IR (neat) $cm^{-1}$ 2985, 2930, 2855, 1735, 1610, 1515, 1460, 1380, 1300, 1250, 1220, 1185, 1170, 1095, 1070, 1040, 1010, 930, 870, 850, 815; $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.24 (3H, s), 1.29 (3H, s), 1.31 (3H, s), 1.37 (3H, s), 1.39 (3H, s), 1.54–1.72 (2H, m), 1.62 (3H, br s), 1.64 (3H, br s), 1.76-2.38 (6H, m), 2.99 (1H, dd, *J* = 8.5 Hz, 4.0 Hz), 3.73 (1H, dd, *J* = 10.5 Hz, 4.0 Hz), 3.80 (3H, s), 3.89 (1H, br s), 3.94–4.02 (1H, m), 3.99 (2H, d, *J* = 6.0 Hz), 4.43 (2H, s), 5.39 (1H, tq, *J* = 6.0 Hz, 1.0 Hz), 5.55 (1H, m), 6.88 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.5 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 16.82, 18.61, 19.19, 20.18, 24.86, 25.75, 26.73, 28.38, 29.20, 29.27, 37.35, 55.38, 58.86, 62.17, 66.38, 67.05, 71.92, 77.08, 81.34, 82.89, 107.31, 113.84, 120.07, 121.49, 129.54, 130.63, 134.59, 139.69, 159.24; MS (EI) *m*/*z* 514 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{31}H_{46}O_6$ ($M^+$) 514.3294, found 514.3276]. A mixture of **the reduction product** (78.2 mg, 0.152 mmol) in dry $CH_2Cl_2$ (2.1 mL) and water (0.210 mL) was cooled to 0 °C and DDQ (41.4 mg, 0.150 mmol) was added. The resulting dark brown mixture was stirred at this temperature for 0.5 h and saturated aqueous solution of $Na_2S_2O_3$ (0.5 mL), saturated aqueous solution of $NaHCO_3$ (0.5 mL), and water (2.0 mL) were added. The mixture was extracted with hexane (2 mL×3) and the extracts were washed with brine (2 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified with silica-gel column chromatography (2.7 g of silica gel, 2:1 hexane–EtOAc) to afford **allyl alcohol** (53.1 mg, 89%) as a colorless syrup [$R_f$ = 0.10 (4:1 hexane–EtOAc); $[\alpha]_D^{28}$ +11.5 (*c* 0.69, $CHCl_3$); IR (neat) $cm^{-1}$ 3450, 2985, 2935, 2870, 1450, 1380, 1260, 1190, 1095, 1060, 1045, 1010, 930, 915, 870, 845, 810; $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.26 (3H, s), 1.30 (3H, s), 1.34 (3H, s), 1.37 (3H, s), 1.39 (3H, s), 1.50–1.76 (2H, m), 1.62 (3H, br s), 1.68 (3H, br s), 1.80–2.40 (6H, m), 2.98 (1H, dd, *J* = 7.5 Hz, 5.5 Hz), 3.73 (1H, dd, *J* = 10.0 Hz, 3.5 Hz), 3.89 (1H, br), 3.97 (1H, dd, *J* = 9.5 Hz, 4.0 Hz), 4.16 (2H, d, *J* = 7.0 Hz), 5.43 (1H, tq, *J* = 7.0 Hz, 1.0 Hz), 5.56 (1H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 16.54, 18.73, 19.24, 20.16, 24.88, 25.79, 26.75, 28.40, 29.14, 29.22, 37.33, 59.03, 59.41, 62.45, 67.15, 77.11, 81.36, 82.90, 107.33, 120.16, 124.00, 134.53, 138.95; MS (EI) *m*/*z* 394 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{23}H_{38}O_5$ ($M^+$) 394.2719, found 394.2716]. To a stirred solution of this **allyl alcohol** (53.1 mg, 0.135 mmol) in 10:1 $CH_2Cl_2$–pyridine (2.69 mL) were added at 0 °C diphenyldisulfide (88.1 mg, 0.404 mmol) and tri-*n*-butylphosphine (0.129 mL, 0.404 mmol). After 2.5 h at room temperature, the mixture was diluted with hexane (10 mL) and water (10 mL). The organic layer was separated and the aqueous layer was extracted with hexane (10 mL×3). The combined organic layers were washed with brine (10 mL), and dried over $Na_2SO_4$, and concentrated under reduced pressure.

The residue was purified with silica-gel column chromatography (3.3 g of silica gel, 7:1 hexane–EtOAc) to afford **14** (58.1 mg, 89%) as a colorless syrup.
$R_f$ = 0.54 (4:1 hexane–EtOAc).
$[\alpha]_D^{29}$ +8.45 (*c* 1.18, $CHCl_3$).
IR (neat) $cm^{-1}$ 3060, 2985, 2935, 2870, 1585, 1480, 1450, 1440, 1380, 1260, 1220, 1190, 1095, 1050, 1010, 870, 845.
$^1H$ NMR (300 MHz, $CDCl_3$) δ 1.24 (3H, s), 1.28 (3H, s), 1.33 (3H, s), 1.37 (3H, s), 1.39 (3H, s), 1.51–1.65 (8H, m), 1.82 (1H, ddd, *J* = 15.0 Hz, 8.0 Hz, 3.0 Hz), 1.92 (1H, ddd, *J* = 15.0 Hz, 10.5 Hz, 4.0 Hz), 1.84–2.38 (4H, m), 2.99 (1H, dd, *J* = 8.0 Hz, 4.0 Hz), 3.55 (2H, d, *J* = 7.5 Hz), 3.72 (1H, dd, *J* = 10.5 Hz, 4.0 Hz), 3.84 (1H, br d, *J* = 7.0 Hz), 3.97 (1H, dd, *J* = 10.5 Hz, 3.0 Hz), 5.31 (1H, br t, *J* = 7.5 Hz), 5.54 (1H, m), 7.12–7.38 (5H, m).
$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 16.27, 18.61, 19.21, 20.17, 24.92, 25.75, 26.74, 28.41, 29.31, 32.33, 37.31, 58.86, 62.17, 67.03, 76.89, 81.36, 82.91, 107.32, 119.93, 120.07, 126.25, 128.86, 130.08, 134.58, 136.72, 139.46.
MS (EI) *m*/*z* 486 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{29}H_{42}O_4S$ ($M^+$) 486.2804, found 486.2796.

**Diels–Alder Reaction Between 2 and 15.** A solution of **2** (3.8 mg, 0.0105 mmol) and **15** (3.7 mg, 0.0103 mmol) in dry toluene (0.105 mL) was heated at 100 °C for 1.5 d under argon atmosphere. The resulting solution was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified with preparative TLC on silica gel (2:1 hexane–EtOAc) to afford the Diels–Alder adducts **17** (27%, 2.0 mg) and **16** (22%, 1.6 mg) along with the recovered starting materials **2** (1.5 mg, 39%) and **15** (1.1 mg, 30%).
**17**: $R_f$ = 0.67 (2:1 hexane–EtOAc).
$[\alpha]_D^{27}$ +45.7 (*c* 0.50, $CHCl_3$).
IR (neat) $cm^{-1}$ 2985, 2935, 2855, 1735, 1715, 1655, 1620, 1440, 1370, 1140, 1105, 1055, 1020, 855.
$^1H$ NMR (300 MHz, $CDCl_3$) δ 0.78 (3H, d, *J* = 6.5 Hz), 1.03 (3H, d, *J* = 6.5 Hz), 1.31 (3H, s), 1.44 (3H, s), 1.47 (3H, s), 1.63 (3H, br s), 1.72 (3H, br s), 1.79 (6H, br s), 1.94 (3H, s), 1.50–2.52 (13H, m), 2.35 (1H, dd, *J* = 14.0 Hz, 10.0 Hz), 2.61 (1H, d, *J* = 14.0 Hz), 2.52–2.75 (2H, m), 2.83 (1H, d, *J* = 18.0 Hz), 2.91 (1H, d, *J* = 18.0 Hz), 3.20 (1H, br d, *J* = 11.0 Hz), 3.36 (1H, dd, *J* = 13.5 Hz, 7.0 Hz), 3.53 (3H, s), 3.54 (1H, dd, *J* = 11.0 Hz, 3.0 Hz), 3.64 (1H, dd, *J* = 10.0 Hz, 3.5 Hz), 3.87 (1H, d, *J* = 10.0 Hz), 4.08 (1H, br d, *J* = 9.5 Hz), 4.74 (1H, d, *J* = 11.0 Hz), 5.59 (1H, m), 6.60 (1H, dd, *J* = 10.5 Hz, 5.0 Hz), 6.65 (1H, s).
$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 11.46, 18.02, 19.55, 20.47, 20.59, 21.20, 21.44, 25.36, 26.08, 27.30, 29.67, 30.08, 30.72, 31.68, 31.96, 32.02, 32.40, 33.98, 39.39, 44.56, 46.30, 47.37, 49.34, 51.19, 55.71, 68.47, 79.18, 84.15, 84.41, 109.39, 120.54, 126.08, 126.94, 127.10, 127.45, 134.27, 137.05, 140.92, 143.85, 156.73, 174.46, 201.64, 203.54, 210.06.
MS (EI) *m*/*z* 718 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{44}H_{62}O_8$ ($M^+$) 718.4444, found 718.4447.

Results of the NOE experiments are shown in SI-Figure 3.




***SI-Figure 3.*** NOEs of **17**.

**16**: $R_f$ = 0.54 (2:1 hexane–EtOAc).
$[\alpha]_D^{26}$ +73.5 (*c* 0.39, $CHCl_3$).
IR (neat) $cm^{-1}$ 2960, 2930, 2855, 1735, 1715, 1655, 1610, 1460, 1370, 1260, 1105, 1055, 1020, 895, 855, 805.
$^1H$ NMR (300 MHz, $CDCl_3$) δ 0.80 (3H, d, *J* = 7.0 Hz), 0.98 (3H, d, *J* = 7.0 Hz), 1.29 (3H, s), 1.42 (3H, s), 1.46 (3H, s), 1.64 (3H, br s), 1.73 (3H, s), 1.76 (3H, br s), 1.80 (3H, s), 2.08 (3H, s), 2.17 (1H, d, *J* = 19.0 Hz), 1.53–2.70 (16H, m), 2.86 (1H, dd, *J* = 18.0 Hz, 8.5 Hz), 3.27 (1H, d, *J* = 19.0 Hz), 3.46–3.55 (1H, m), 3.47 (1H, dd, *J* = 13.5 Hz, 5.5 Hz), 3.56 (3H, s), 3.68 (1H, dd, *J* = 10.0 Hz, 3.5 Hz), 3.88 (1H, d, *J* = 9.0 Hz), 3.90 (1H, d, *J* = 8.5 Hz), 4.07 (1H, d, *J* = 9.5 Hz), 4.64 (1H, d, *J* = 12.0 Hz), 5.59 (1H, m), 6.02 (1H, s), 6.24 (1H, br d, *J* = 8.0 Hz).
$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 11.90, 17.53, 18.45, 19.85, 20.52, 20.61, 20.85, 21.18, 25.46, 26.33, 29.77, 29.85, 30.29, 31.78, 32.37, 33.11, 33.63, 39.06, 39.84, 41.17, 46.83, 47.65, 48.29, 51.35, 56.20, 68.26, 79.36, 84.33, 85.19, 108.69, 120.59, 125.72, 126.82, 126.85, 127.00, 134.26, 137.86, 140.28, 141.36, 158.29, 173.64, 202.62, 203.64, 210.42.
MS (EI) *m*/*z* 718 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{44}H_{62}O_8$ ($M^+$) 718.4444, found 718.4430.

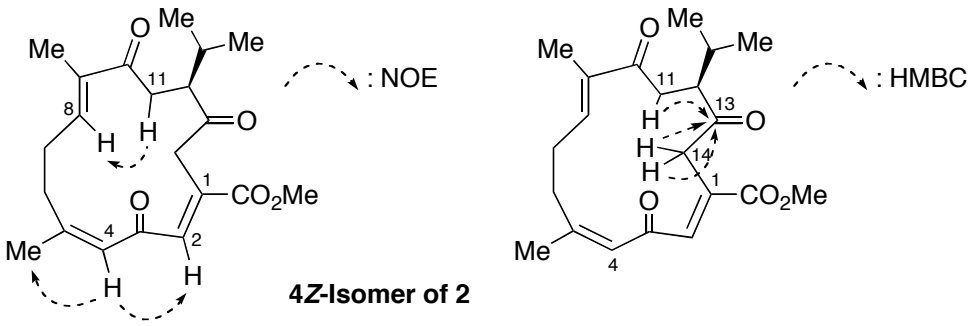
**Methyl Sarcophytoate (1).** A solution of **16** (2.1 mg, 0.00292 mmol) in 80% aqueous solution of AcOH (0.30 mL) was heated at 50 °C for 3 h. After cooling to room temperature, the solvents were removed under reduced pressure and the residue was purified with preparative TLC on silica gel (1:1 hexane–EtOAc) to afford **1** (1.0 mg, 50%) as a colorless syrup.
$R_f$ = 0.24 (2:1 hexane–EtOAc).
$[\alpha]_D^{26}$ +152 (*c* 0.10, $CHCl_3$) [lit.[3] $[\alpha]_D$ +157 (*c* 0.34, $CHCl_3$)].
IR (neat) $cm^{-1}$ 3520, 2925, 2855, 1730, 1710, 1665, 1610, 1435, 1370, 1275, 1100, 1075, 1055, 1020, 965, 940.

$^1$H NMR (300 MHz, $CDCl_3$) δ 0.82 (3H, d, *J* = 7.0 Hz), 0.98 (3H, d, *J* = 7.2 Hz), 1.31 (3H, s), 1.64 (3H, br s), 1.70 (3H, br s), 1.73 (3H, s), 1.83 (3H, d, *J* = 1.5 Hz), 1.96 (1H, d, *J* = 18.8 Hz), 2.09 (3H, d, *J* = 1.0 Hz), 1.60–2.25 (8H, m), 2.25–2.70 (8H, m), 2.97 (1H, dd, *J* = 18.0 Hz, 7.5 Hz), 3.19 (1H, d, *J* = 11.0 Hz), 3.28 (1H, d, *J* = 18.8 Hz), 3.44 (1H, dd, *J* = 14.0 Hz, 6.0 Hz), 3.57 (3H, s), 3.56–3.63 (1H, m), 3.65 (1H, dd, *J* = 10.2 Hz, 3.2 Hz), 3.98 (1H, d, *J* = 7.5 Hz), 4.01 (1H, d, *J* = 10.0 Hz), 4.69 (1H, d, *J* = 11.0 Hz), 5.58 (1H, m), 6.05 (1H, s), 6.25 (1H, dd, *J* = 8.6 Hz, 4.0 Hz).
$^{13}$C NMR (75 MHz, $CDCl_3$) δ 11.92, 17.66, 18.94, 19.52, 20.08, 20.26, 20.56, 20.93, 24.78, 25.56, 30.38, 31.31, 32.76, 33.26, 38.95, 39.85, 40.77, 46.86, 47.35, 48.59, 51.47, 56.24, 68.43, 70.76, 75.45, 79.63, 120.49, 124.22, 125.77, 126.82, 129.27, 134.52, 138.17, 140.84, 141.43, 159.41, 173.16, 203.26, 203.43, 210.52.
MS (EI) *m*/*z* 678 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{41}H_{58}O_8$ ($M^+$) 678.4131, found 678.4112.

**Isomerization of 17 to 16. 17** (1.1 mg, 0.00153 mmol) was dissolved in AcOH (0.220 mL) and the solution was stirred at room temperature for 6.5 d. This solution was concentrated under reduced pressure to afford a 52:48 mixture of **17** and **16** (determined by the $^1$H NMR analysis). This crude mixture was purified with silica-gel column chromatography (1 g of silica gel, 2:1 hexane–EtOAc) to afford the desired isomer **16** (0.5 mg, 45%) as a colorless syrup.

**4*Z*-Isomer of Methyl Sarcoate (2).** A solution of methyl sarcoate (**2**) (1.3 mg, 0.00361 mmol) in dry toluene (0.130 mL) was heated at 100 °C for 12 h. After cooling to room temperature, the solution was concentrated under reduced pressure to afford a 1:0.41 mixture of **2** and **4*Z*-isomer of 2** (contaminated with some unidentified products). This crude mixture was purified with preparative TLC on silica gel (2:1 hexane–EtOAc) to afford **4*Z*-isomer of 2** (contaminated with an unidentified product). This was further purified with preparative TLC on silica gel (5:1 toluene–EtOAc) to afford the pure **4*Z*-isomer of 2** (0.3 mg, 23%) as a pale yellow syrup.
$R_f$ = 0.36 (2:1 hexane–EtOAc), 0.43 (5:1 toluene–EtOAc).
$[\alpha]_D^{28}$ +78.4 (*c* 0.30, $CHCl_3$).
$^1$H NMR (300 MHz, $CDCl_3$) δ 0.94 (3H, d, *J* = 6.5 Hz), 0.97 (3H, d, *J* = 6.5 Hz), 1.76 (3H, s), 1.94–2.08 (1H, m), 2.19 (1H, dd, *J* = 13.5 Hz, 3.5 Hz), 2.28–2.42 (1H, m), 2.51–2.68 (2H, m), 2.82 (1H, ddd, *J* = 11.0 Hz, 8.5 Hz, 3.5 Hz), 3.20 (1H, dd, *J* = 13.5 Hz, 8.5 Hz), 3.36–3.50 (1H, m), 3.75 (1H, dd, *J* = 18.0 Hz, 1.5 Hz), 3.77 (3H, s), 3.95 (1H, d, *J* = 18.0 Hz), 6.22 (1H, d, *J* = 1.0 Hz), 6.40–6.52 (1H, m), 7.27 (1H, d, *J* = 1.5 Hz).
$^{13}$C NMR (75 MHz, $CDCl_3$) δ 11.54, 19.67, 20.89, 25.52, 27.27, 30.28, 31.50, 35.25, 41.14, 52.72, 56.68, 124.75, 132.69, 138.44, 140.44, 141.92, 160.53, 167.35, 191.72, 202.24, 208.33.
MS (EI) *m*/*z* 360 ($M^+$); HRMS (EI) *m*/*z* calcd for $C_{21}H_{28}O_5$ ($M^+$) 360.1937, found 360.1908.

Results of NOE and HMBC experiments are shown in SI-Figure 4.



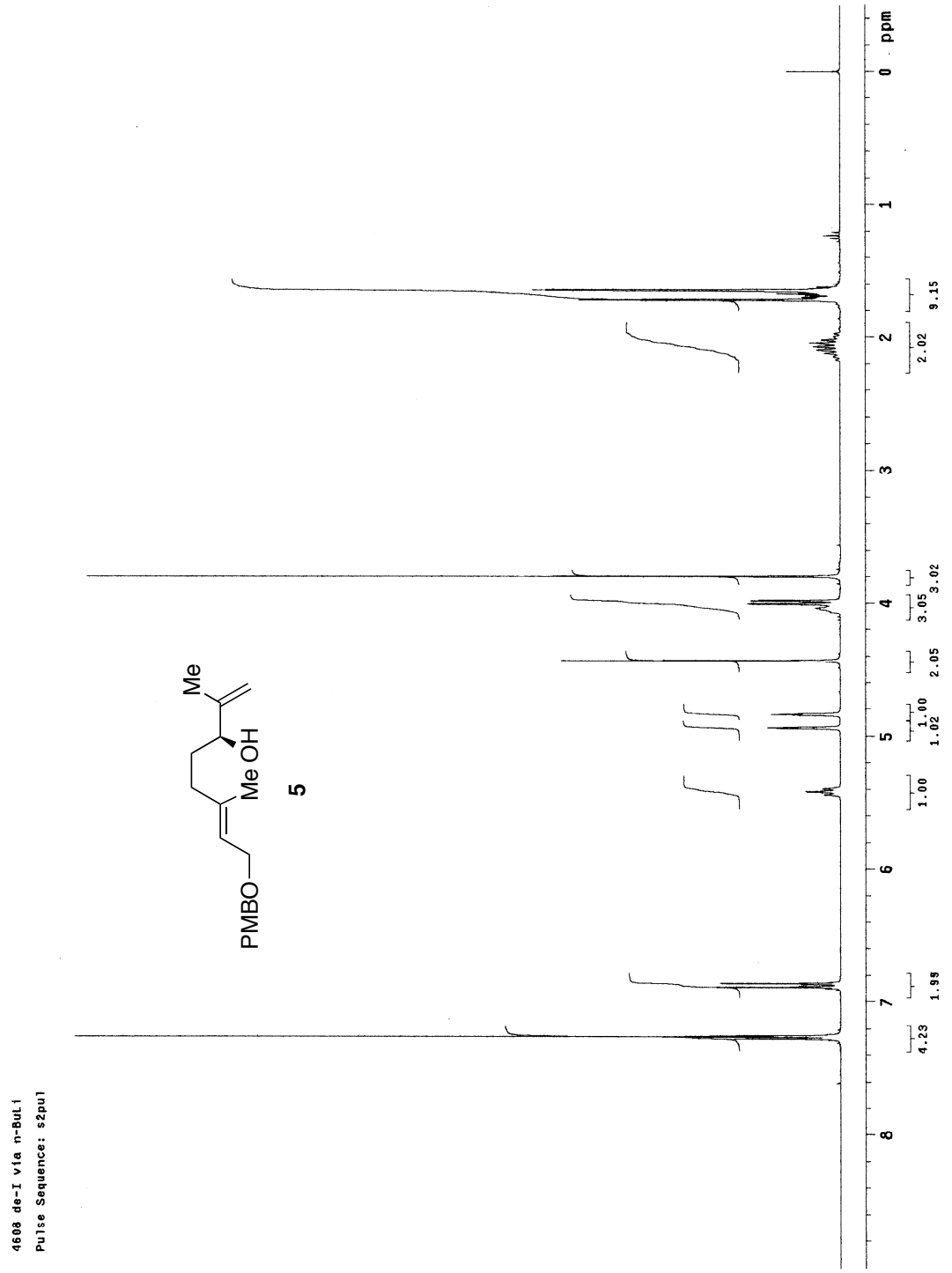

***SI-Figure 4.*** NOEs and HMBC of **4*Z*-isomer of 2**.

**$^1$H NMR Data of Methyl Sarcoate (2) and Diene 15 in Toluene-$d_8$.**

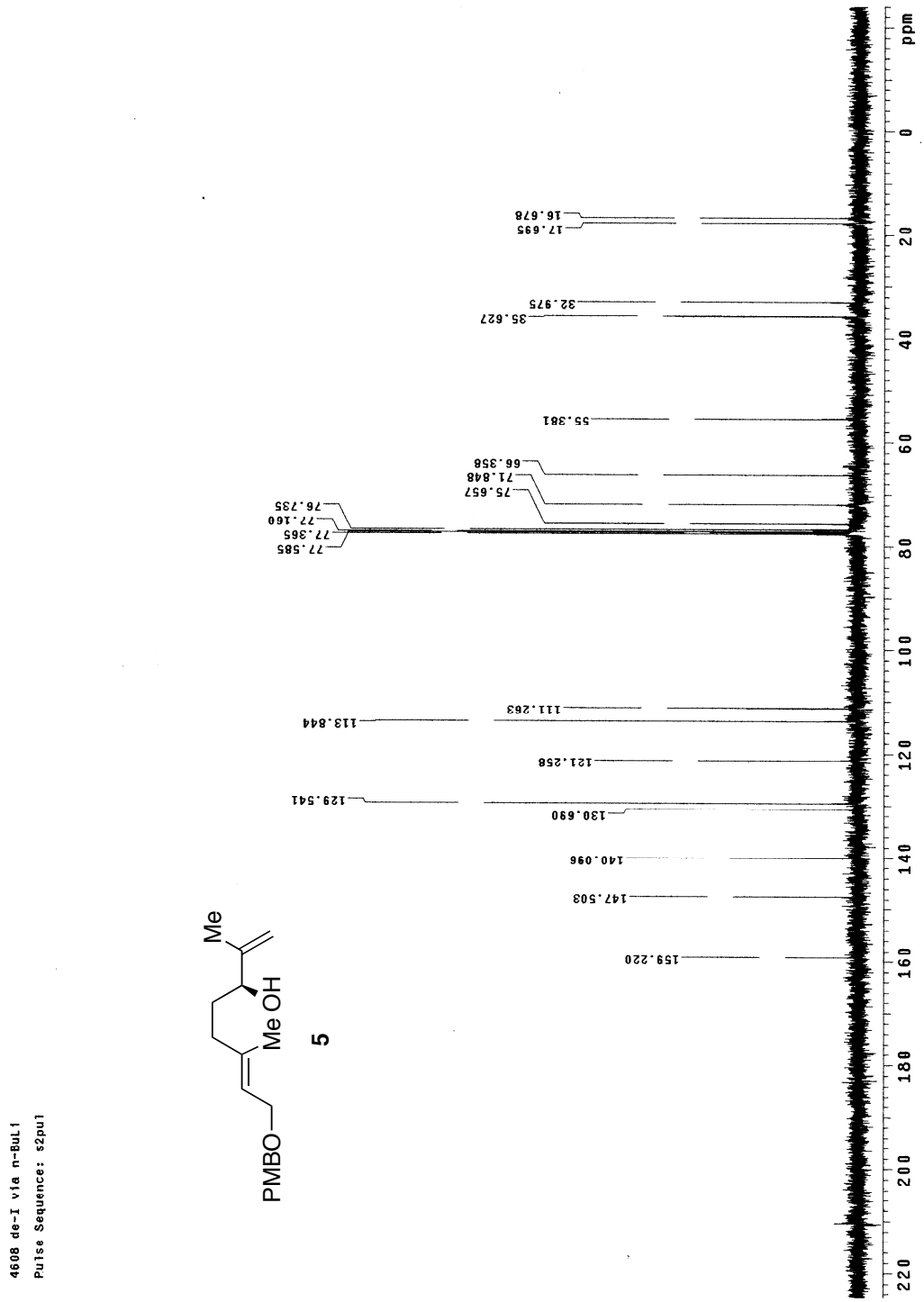
**Methyl Sarcoate (2)**: $^1$H NMR (300 MHz, toluene-$d_8$, 50 °C) δ 0.85 (3H, d, $J$ = 6.5 Hz), 0.99 (3H, d, $J$ = 6.5 Hz), 1.63 (3H, s), 1.70–2.15 (5H, m), 1.96 (3H, d, $J$ = 1.5 Hz), 1.98 (1H, dd, $J$ = 13.0 Hz, 3.0 Hz), 2.67 (1H, ddd, $J$ = 9.0 Hz, 6.0 Hz, 3.0 Hz), 2.77 (1H, d, $J$ = 17.0 Hz), 3.16 (1H, dd, $J$ = 13.0 Hz, 9.0 Hz), 3.26 (3H, s), 3.33 (1H, d, $J$ = 17.0 Hz), 5.96 (1H, br dd, $J$ = 9.0 Hz, 4.0 Hz), 5.98 (1H, br s), 7.15 (1H, s).

**Diene 15**: $^1$H NMR (300 MHz, toluene-$d_8$, 50 °C) δ 1.22 (3H, s), 1.30 (3H, s), 1.34 (3H, s), 1.49 (3H, br s), 1.58 (3H, s), 1.47–1.72 (2H, m), 1.91 (3H, s), 1.87–2.36 (4H, m), 2.68 (1H, dd, $J$ = 14.5 Hz, 1.5 Hz), 3.35 (1H, dd, $J$ = 14.5 Hz, 8.5 Hz), 3.90–3.99 (1H, br d), 3.99 (1H, dd, $J$ = 9.5 Hz, 4.5 Hz), 4.05 (1H, dd, $J$ = 8.5 Hz, 1.5 Hz), 5.05 (1H, s), 5.42 (1H, s), 5.52 (1H, m), 6.09 (1H, d, $J$ = 5.5 Hz), 6.28 (1H, d, $J$ = 5.5 Hz).

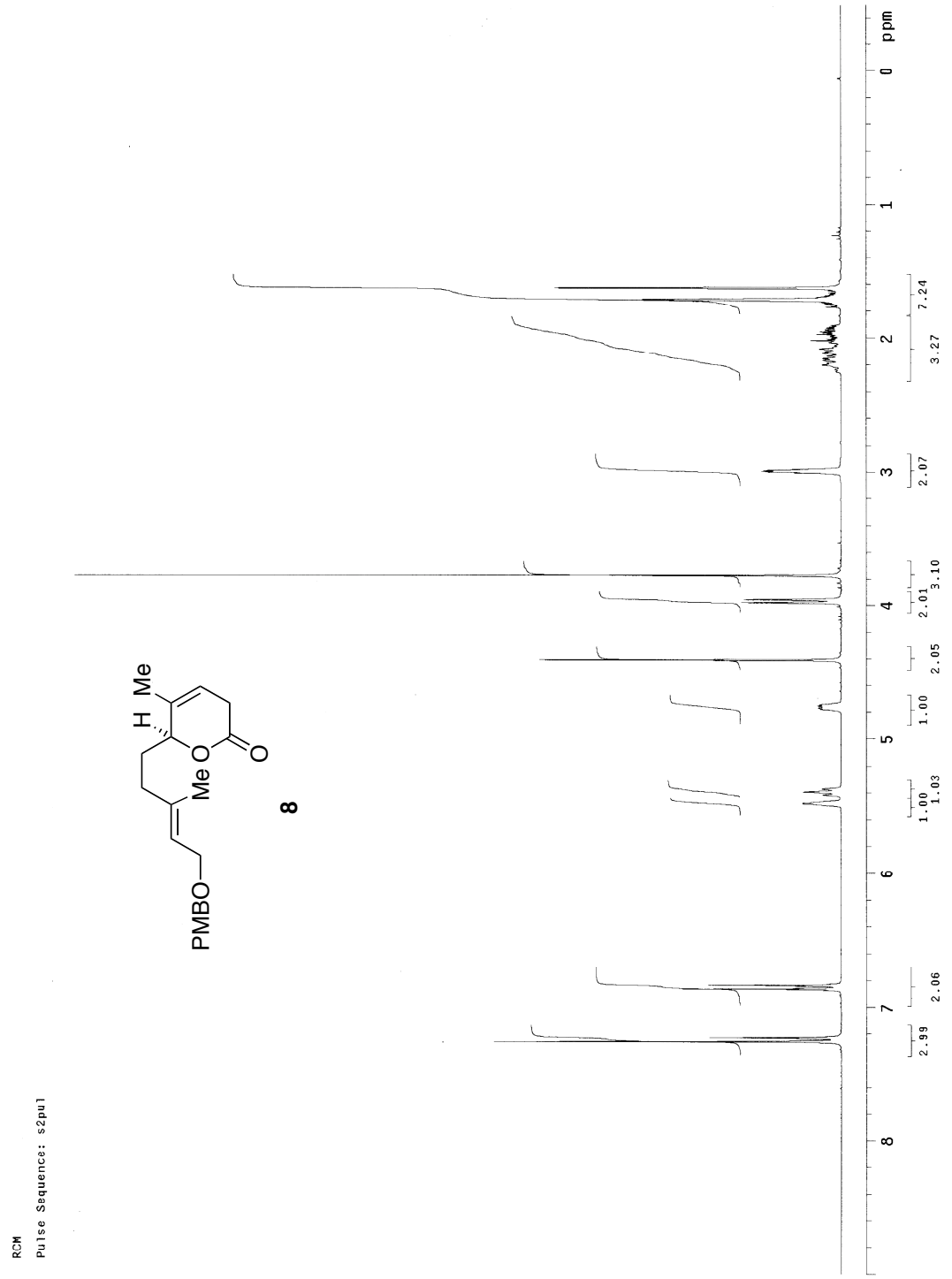
**$^1$H NMR Spectrum of 5 (300 MHz, $CDCl_3$)**



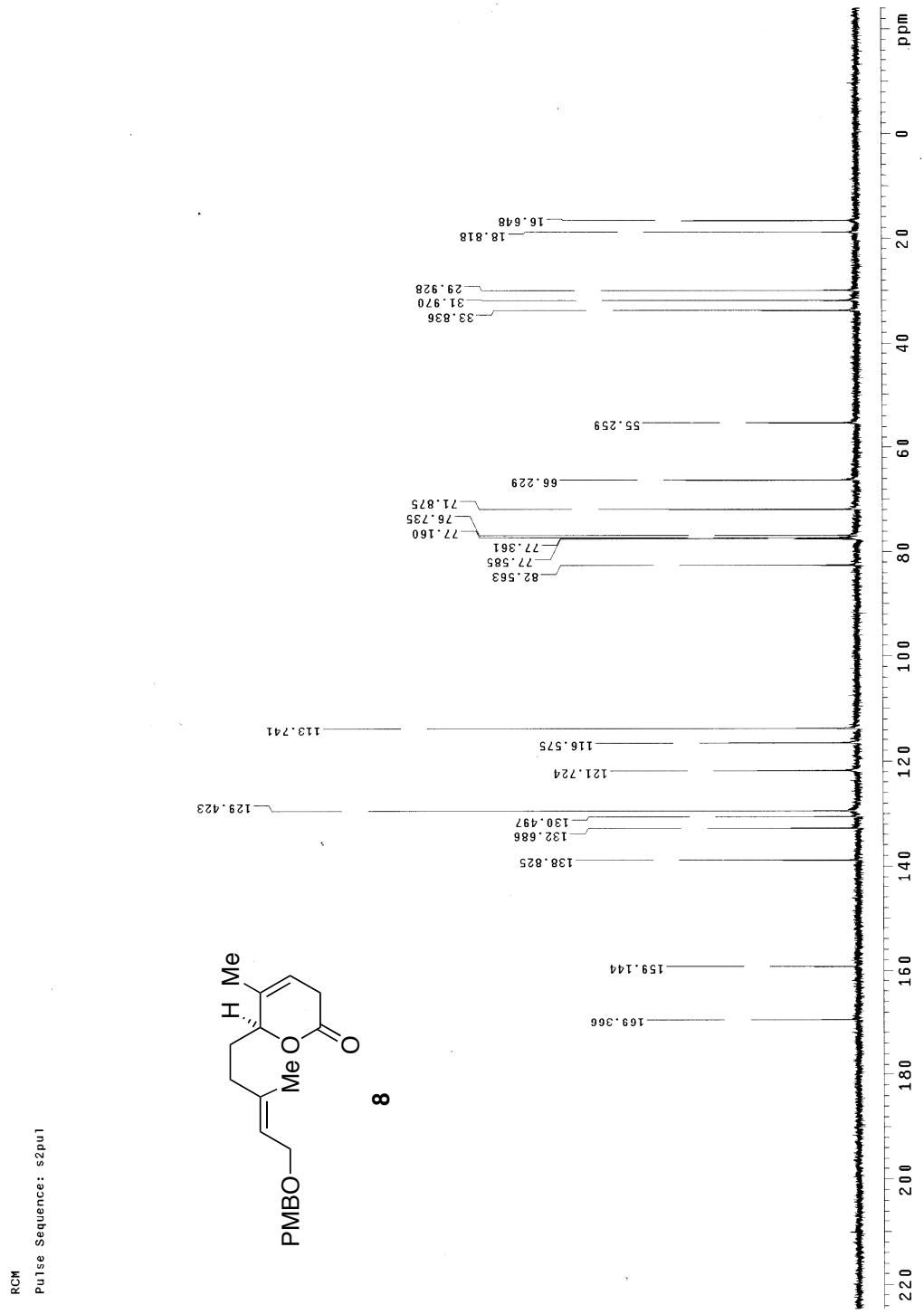
**$^{13}$C NMR Spectrum of 5 (75 MHz, $CDCl_3$)**



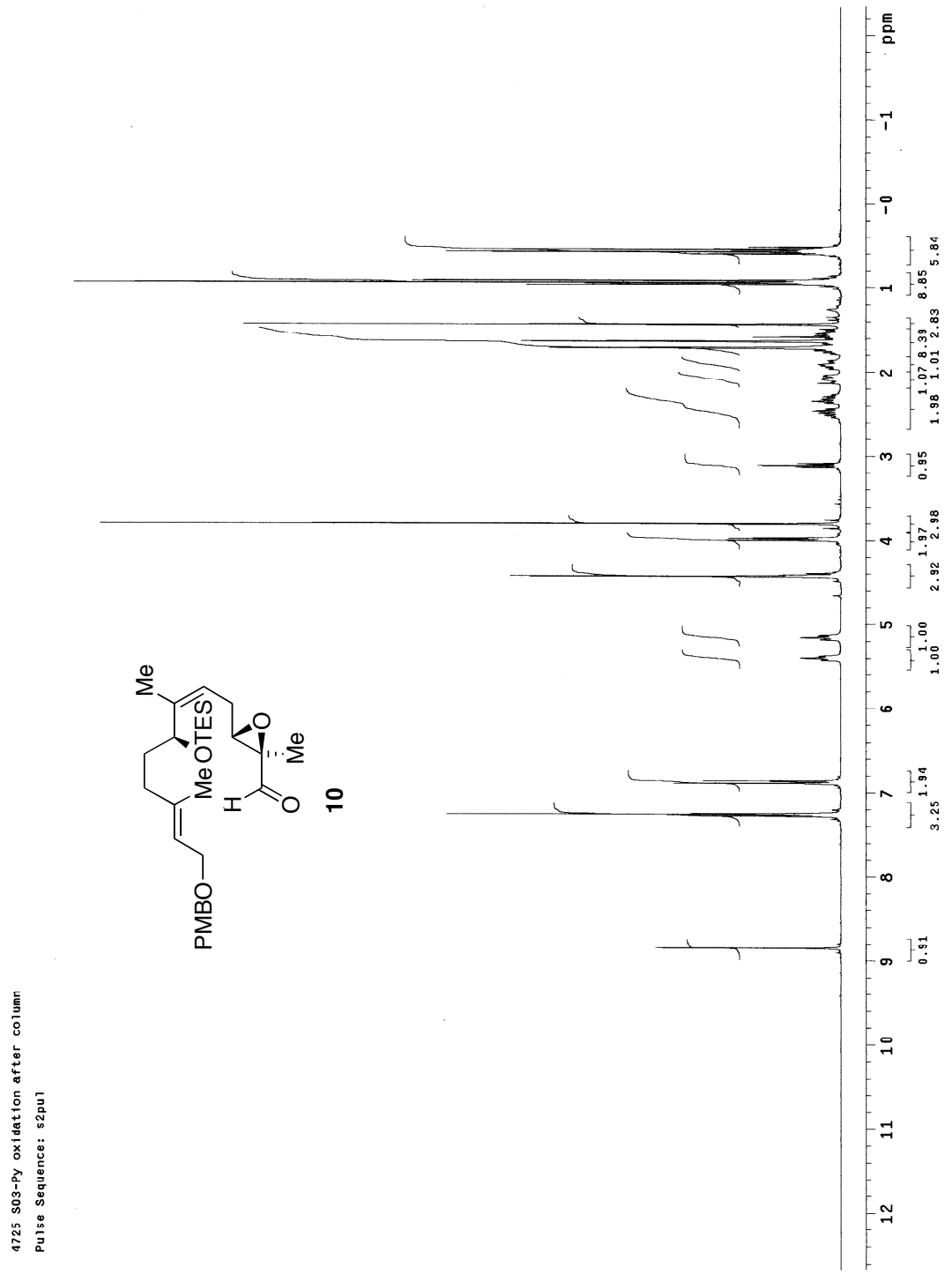
**$^1$H NMR Spectrum of 8 (300 MHz, $CDCl_3$)**



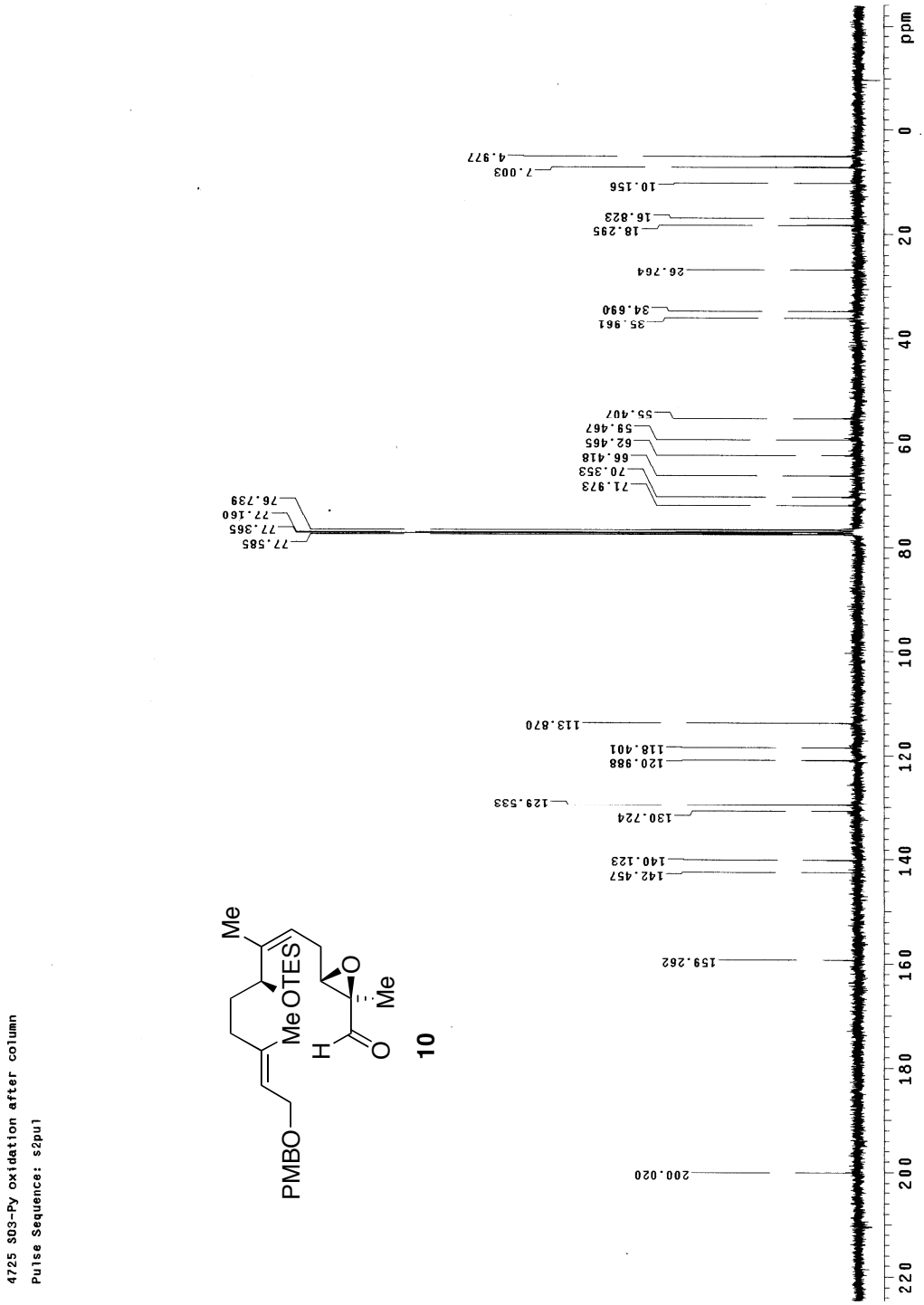
## $^{13}$C NMR Spectrum of 8 (75 MHz, $CDCl_3$)



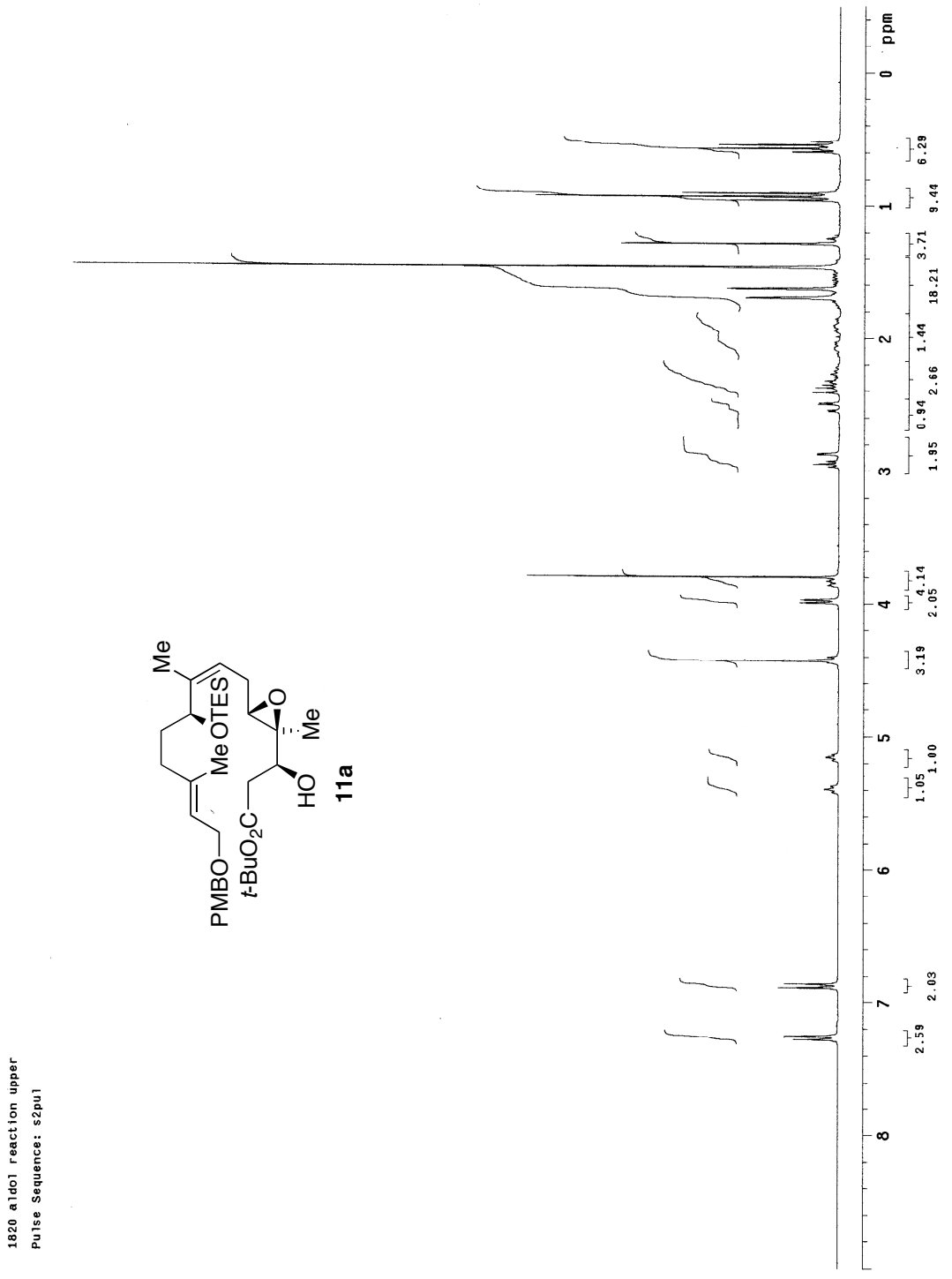
**$^1$H NMR Spectrum of 10 (300 MHz, $CDCl_3$)**



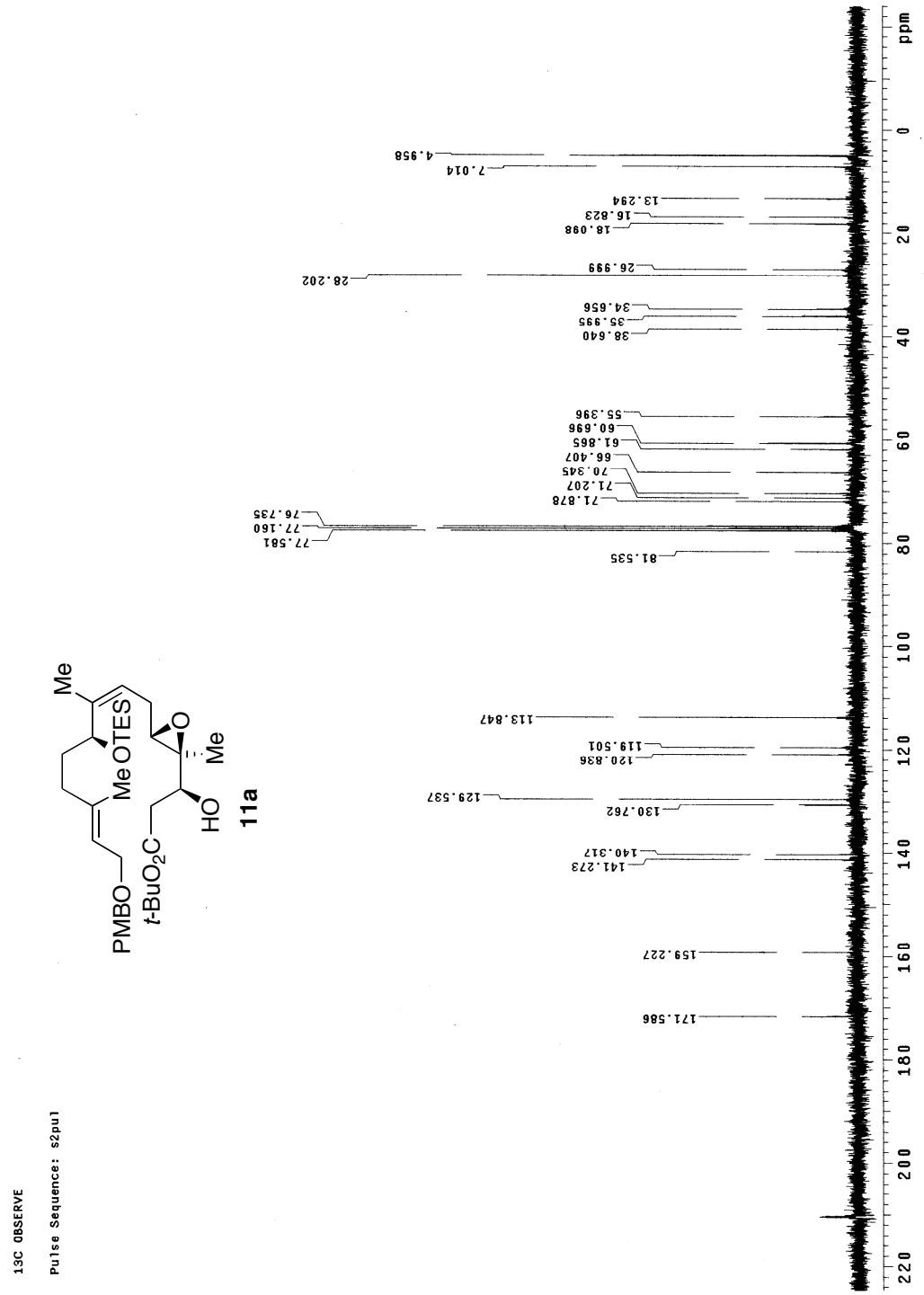
## $^{13}$C NMR Spectrum of 10 (75 MHz, $CDCl_3$)



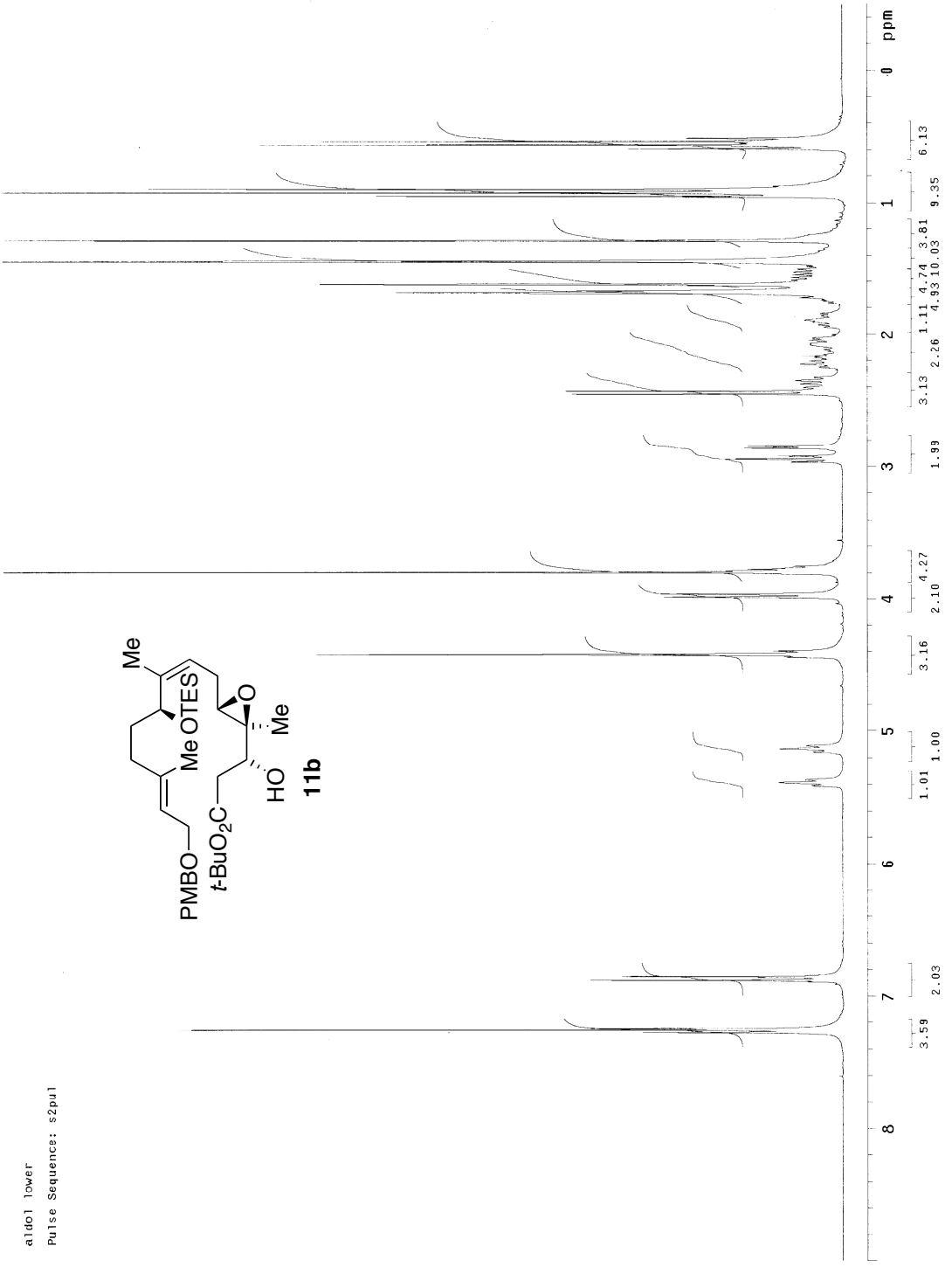
**$^1$H NMR Spectrum of 11a (300 MHz, $CDCl_3$)**



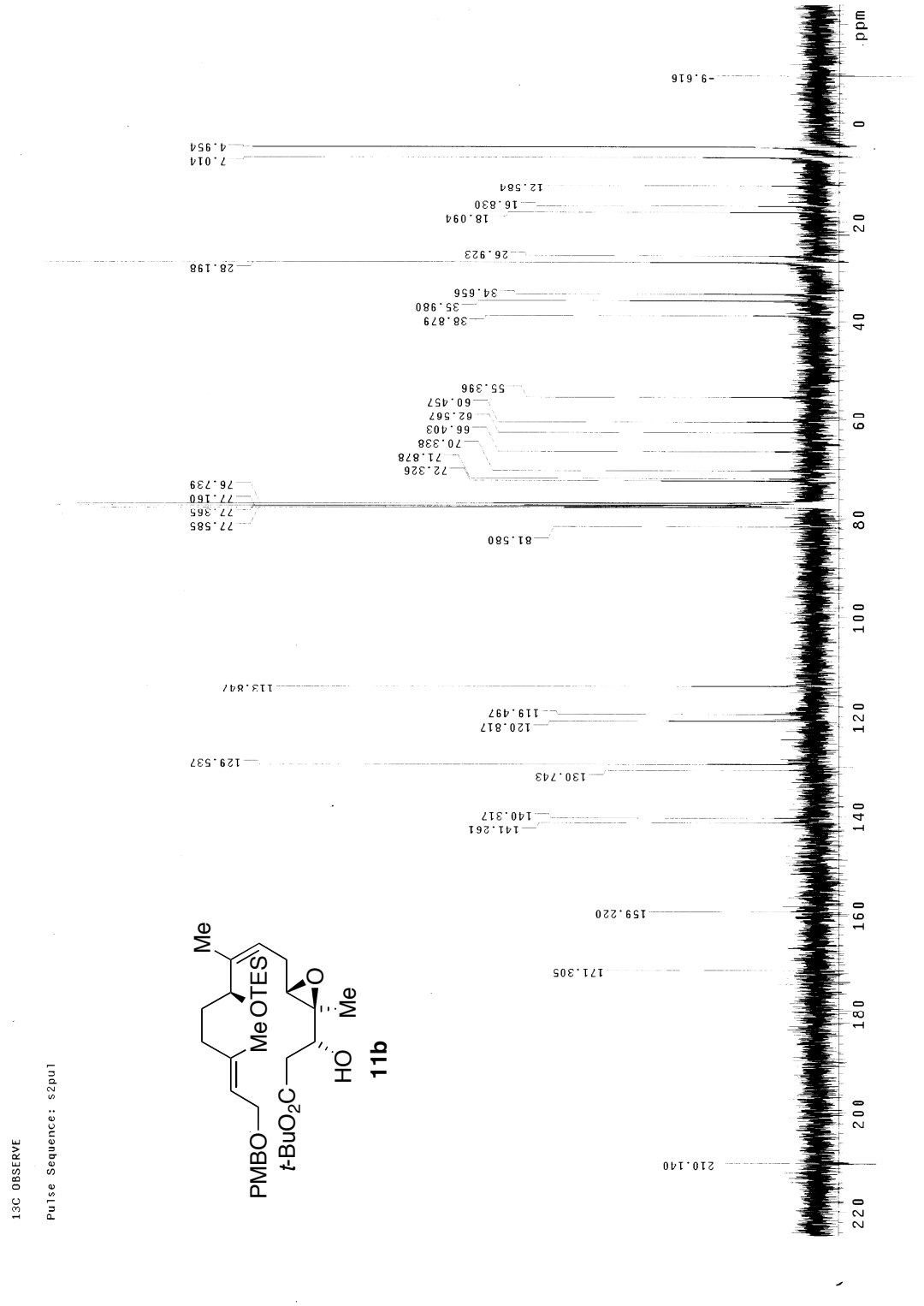
**$^{13}$C NMR Spectrum of 11a (75 MHz, $CDCl_3$)**



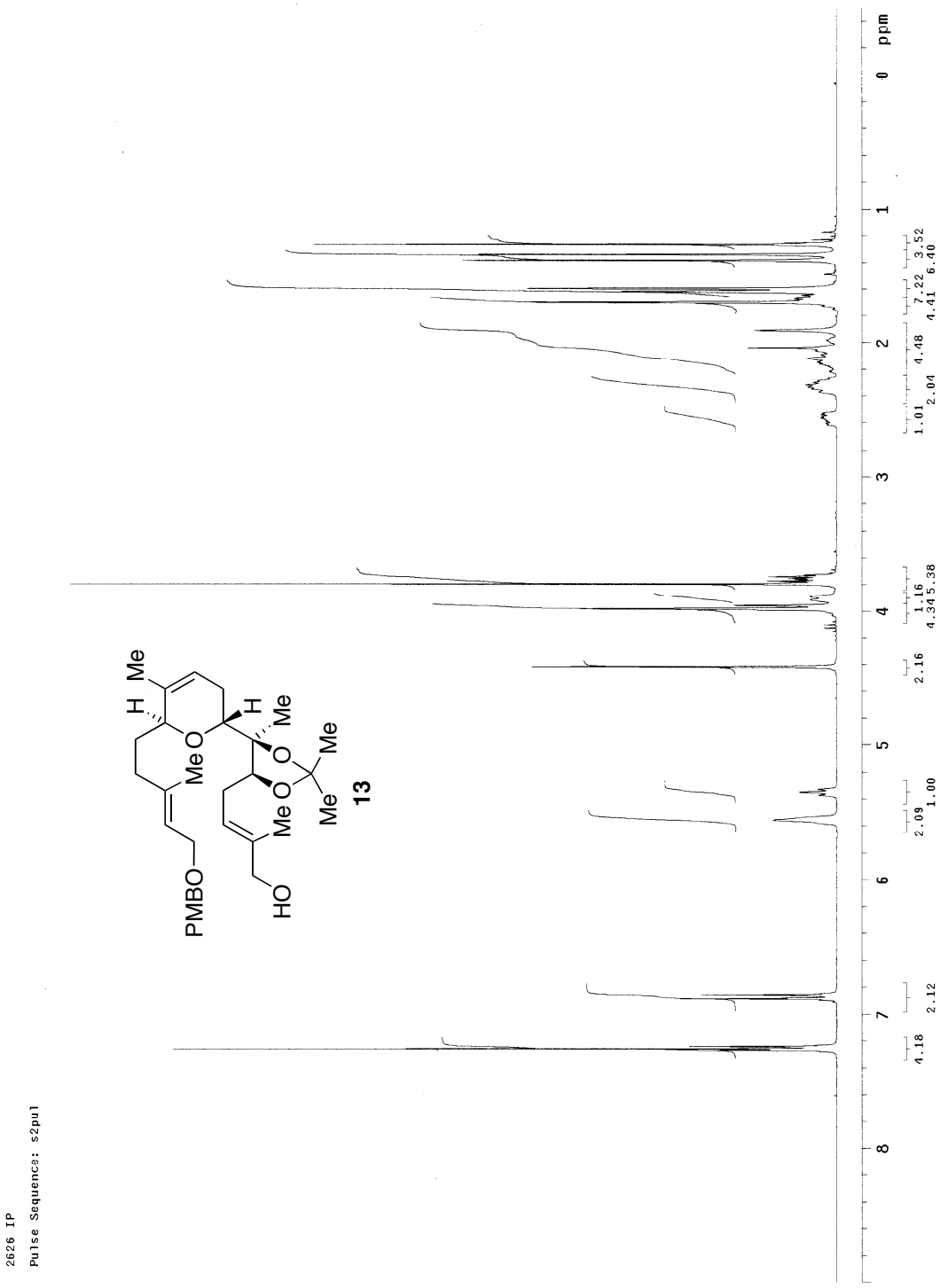
**$^1$H NMR Spectrum of 11b (300 MHz, $CDCl_3$)**



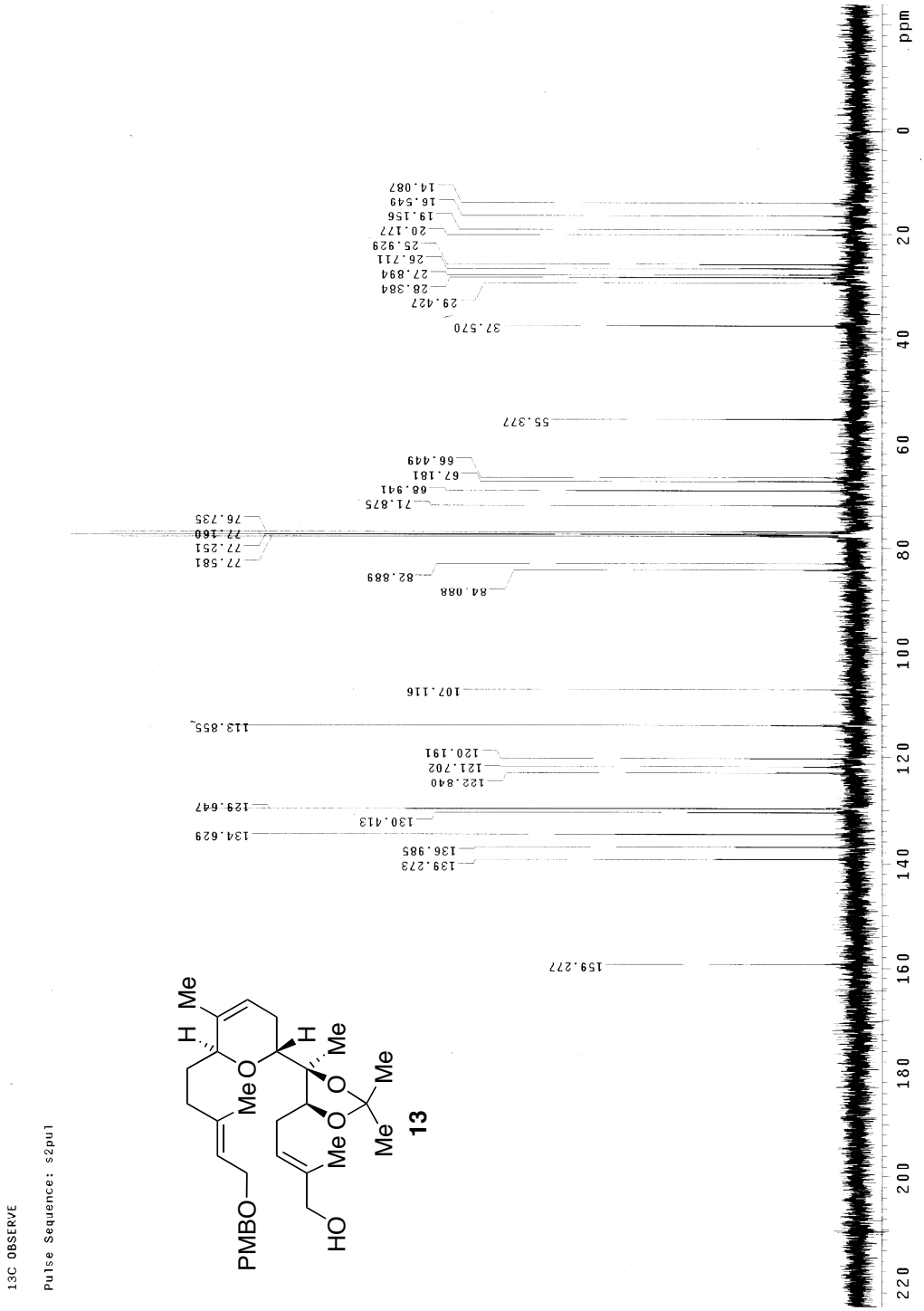
## $^{13}$C NMR Spectrum of 11b (75 MHz, $CDCl_3$)



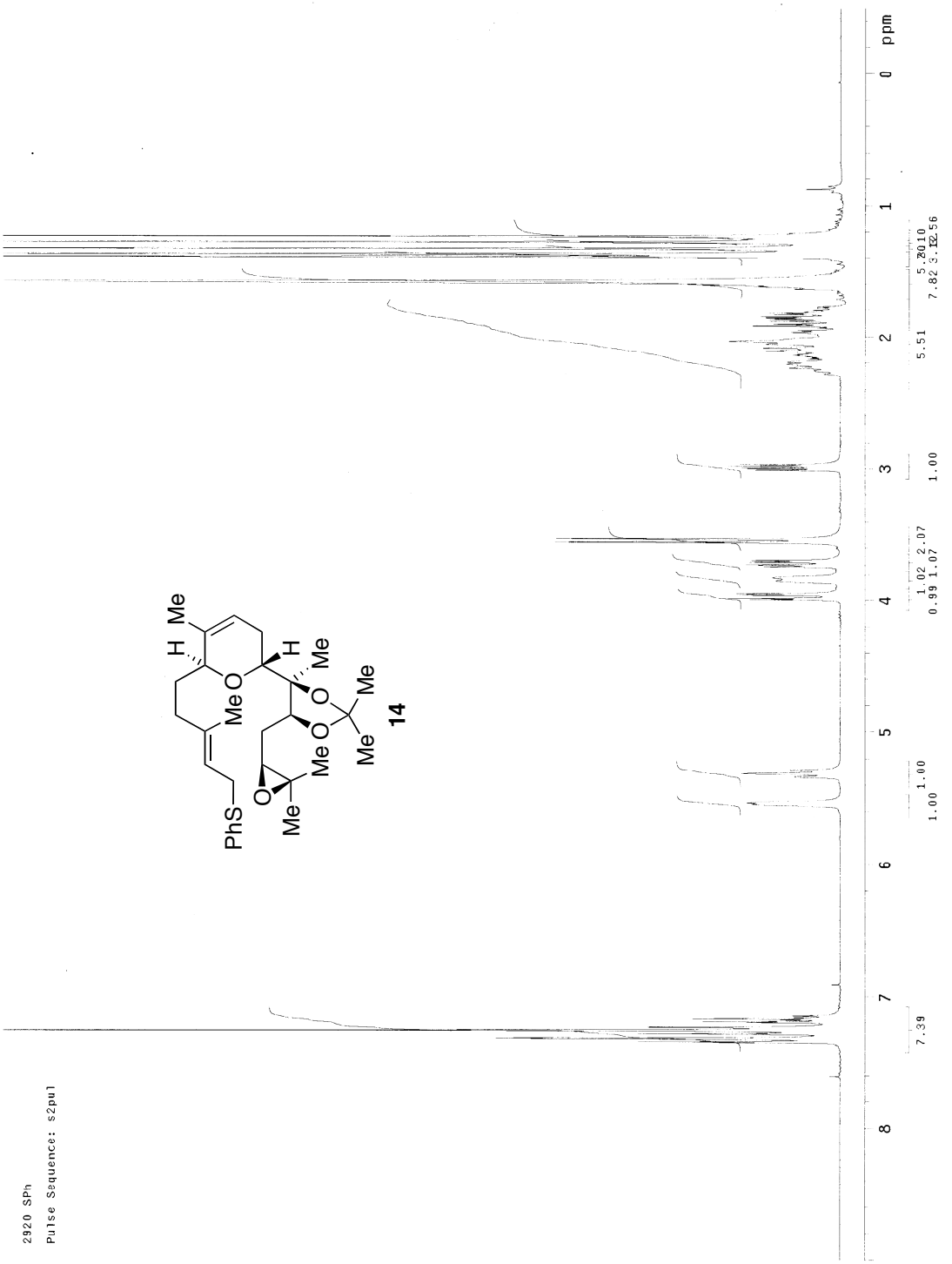
**$^1$H NMR Spectrum of 13 (300 MHz, $CDCl_3$)**



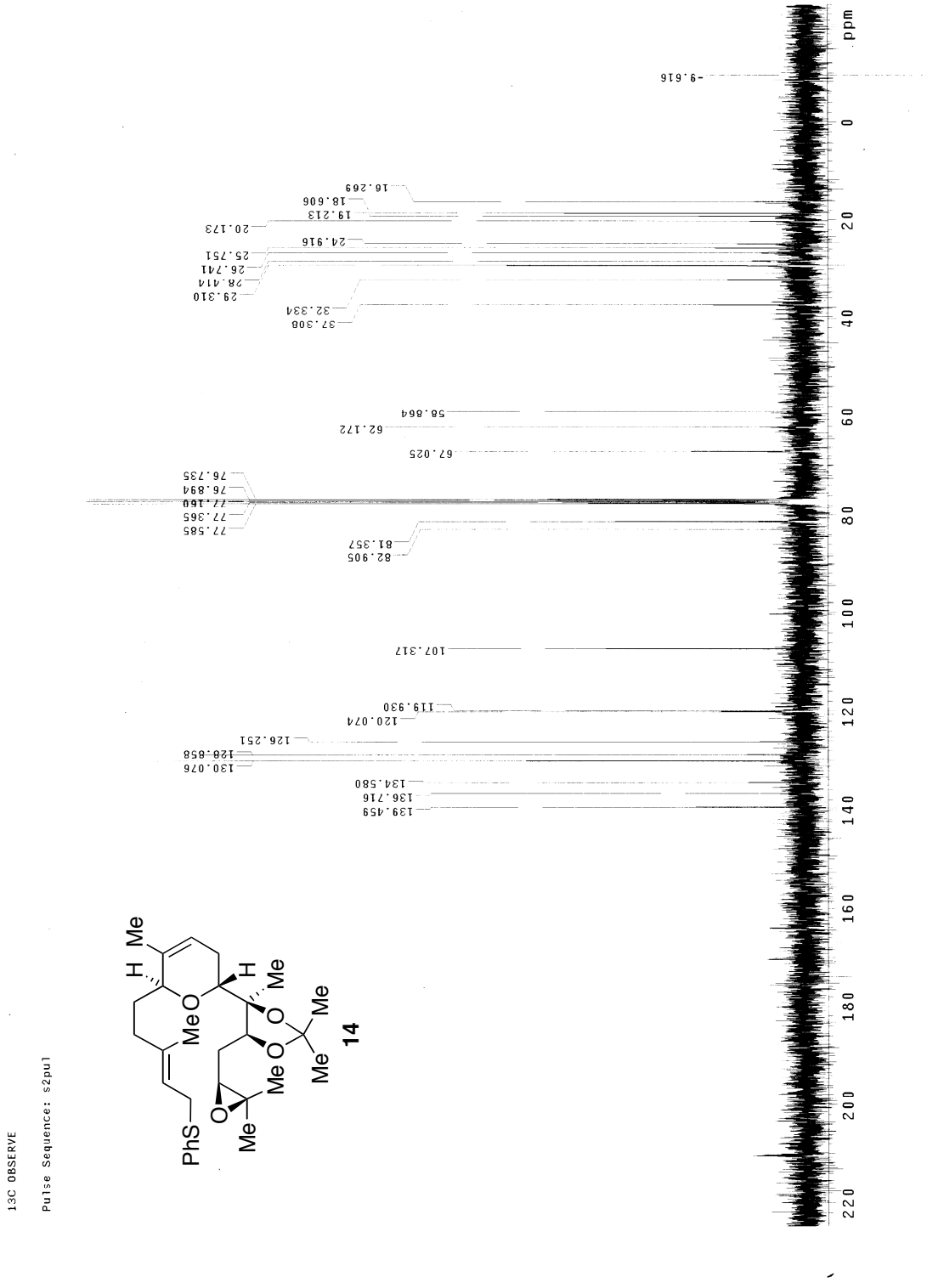
## $^{13}$C NMR Spectrum of 13 (75 MHz, $CDCl_3$)



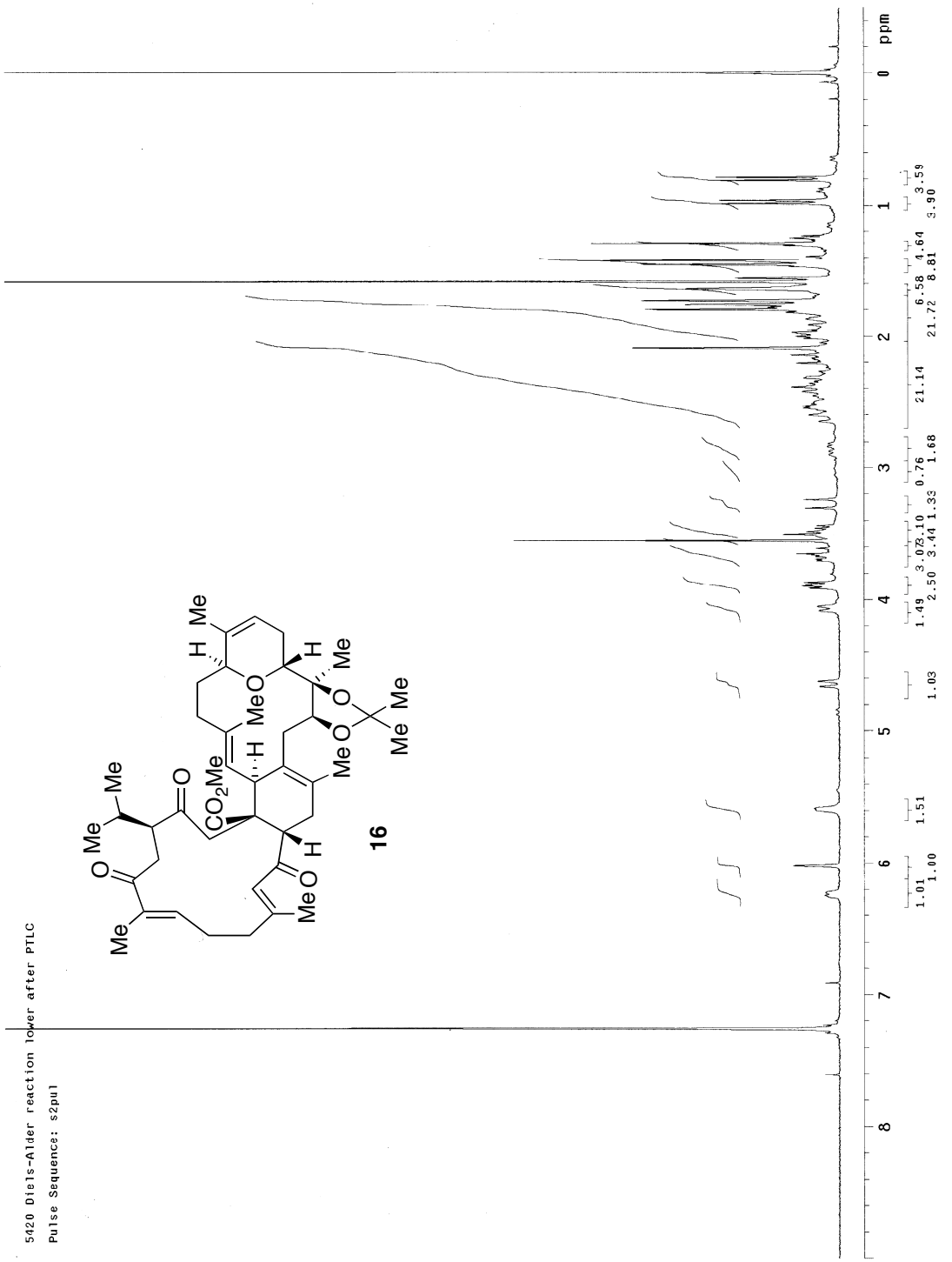
**$^1$H NMR Spectrum of 14 (300 MHz, $CDCl_3$)**



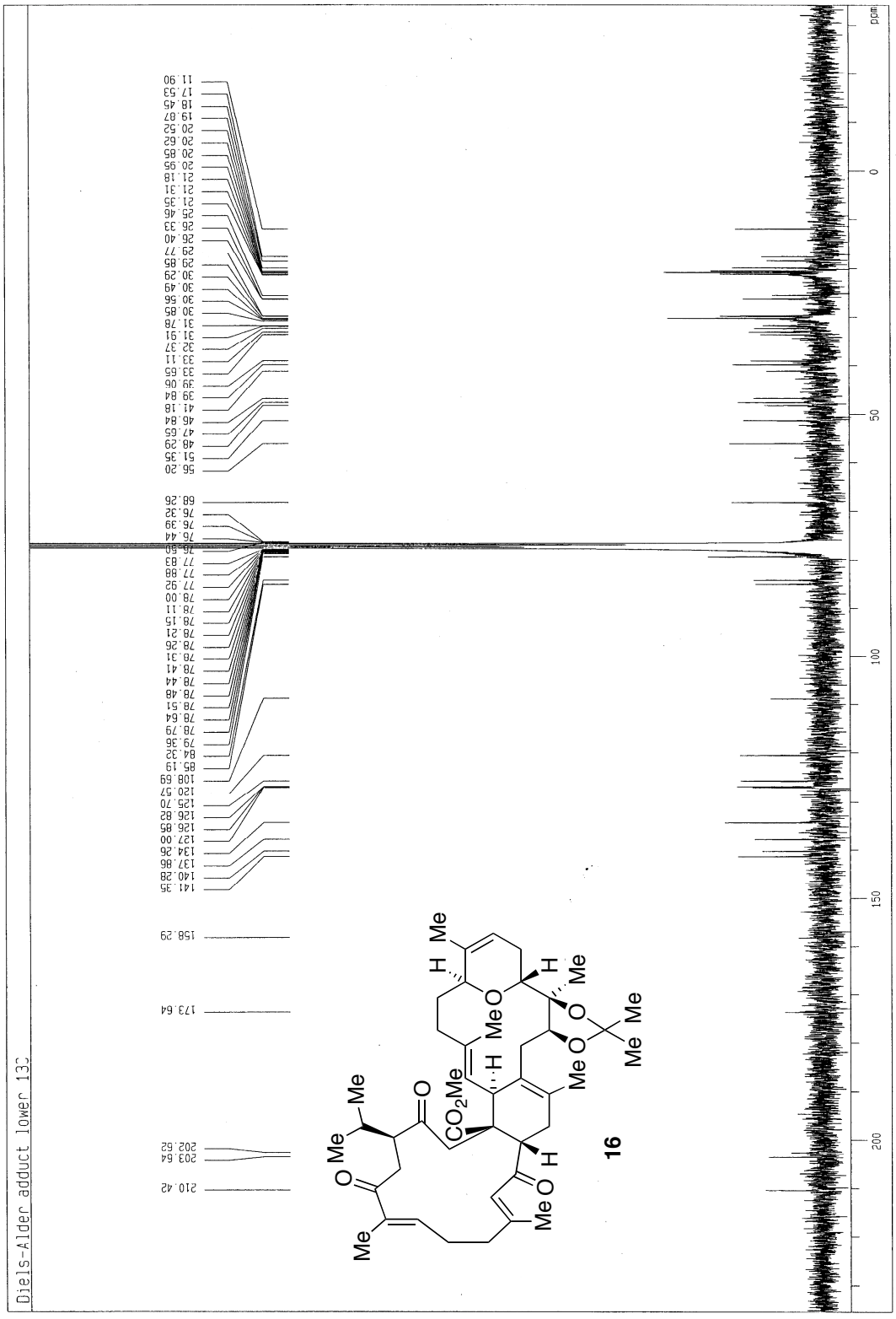
**$^{13}$C NMR Spectrum of 14 (75 MHz, $CDCl_3$)**



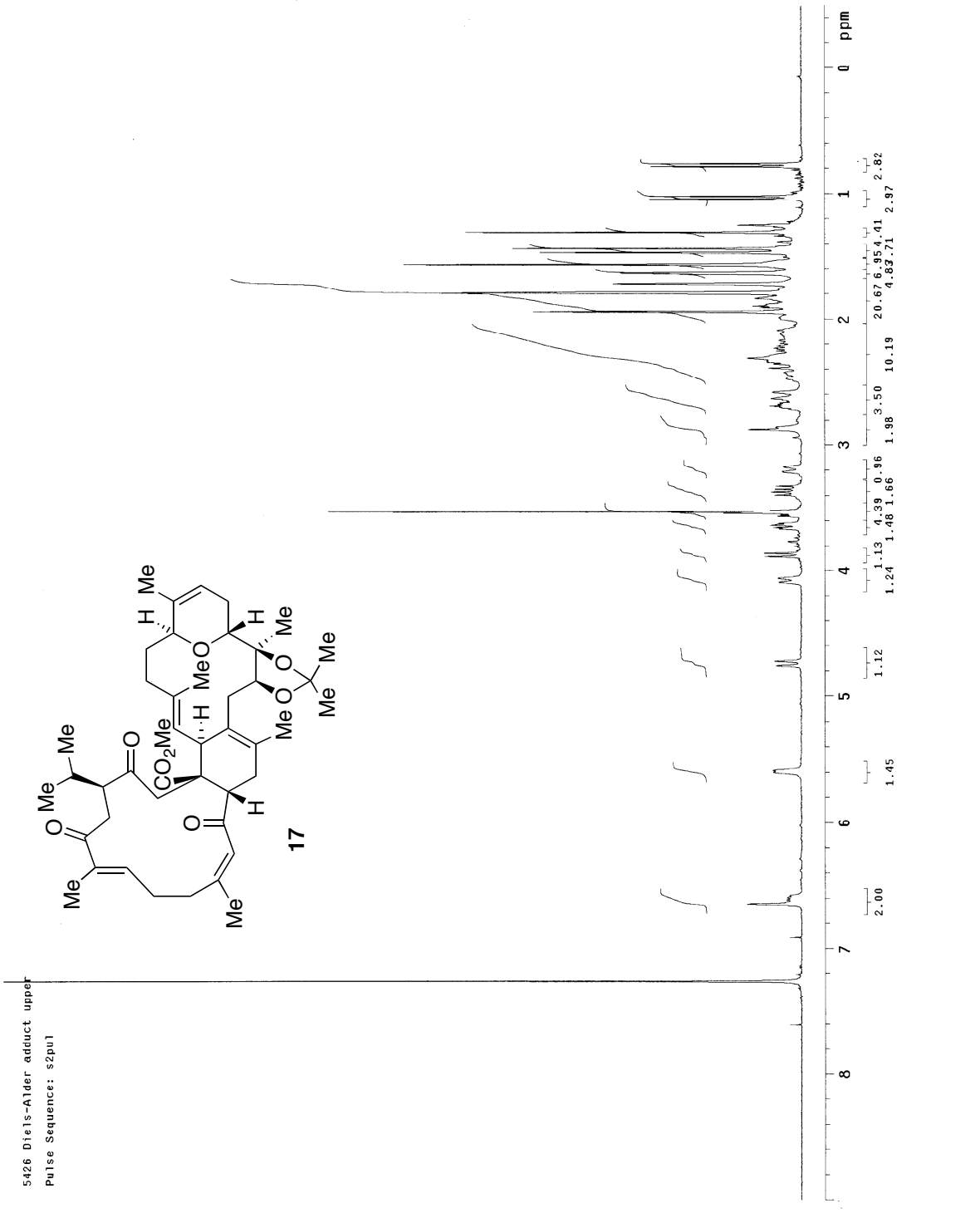
**$^1$H NMR Spectrum of 16 (300 MHz, $CDCl_3$)**



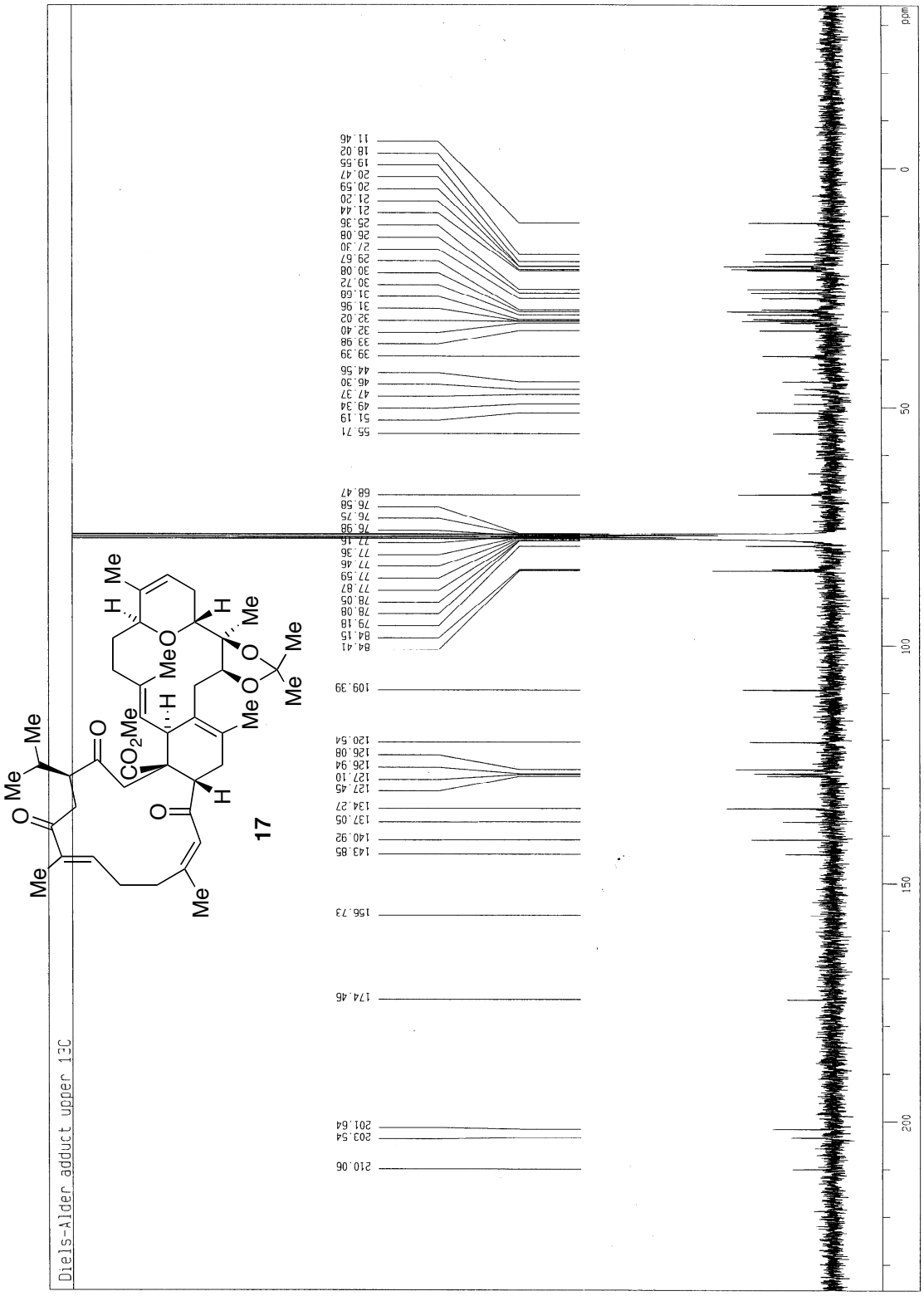
**$^{13}$C NMR Spectrum of 16 (75 MHz, $CDCl_3$)**



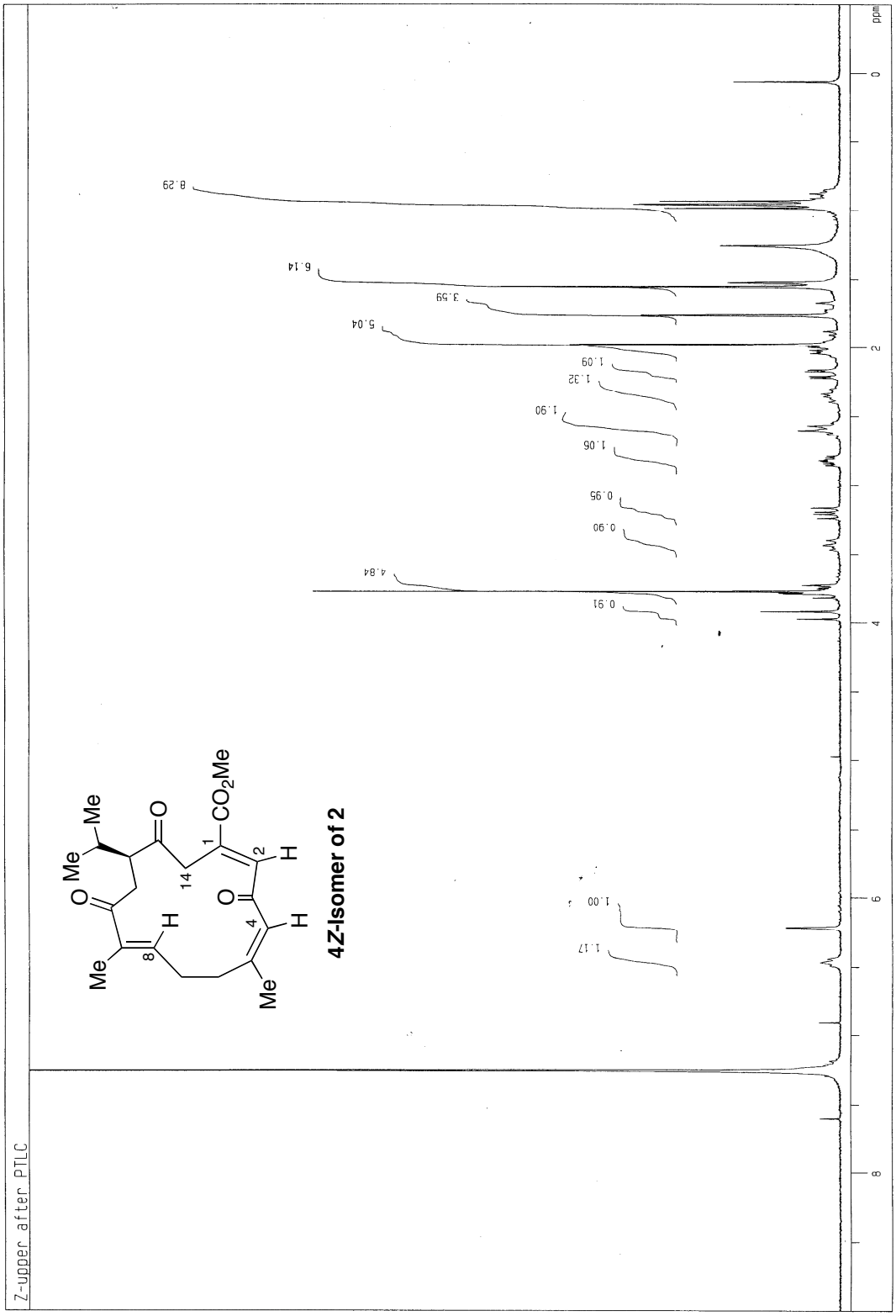
**$^1$H NMR Spectrum of 17 (300 MHz, $CDCl_3$)**



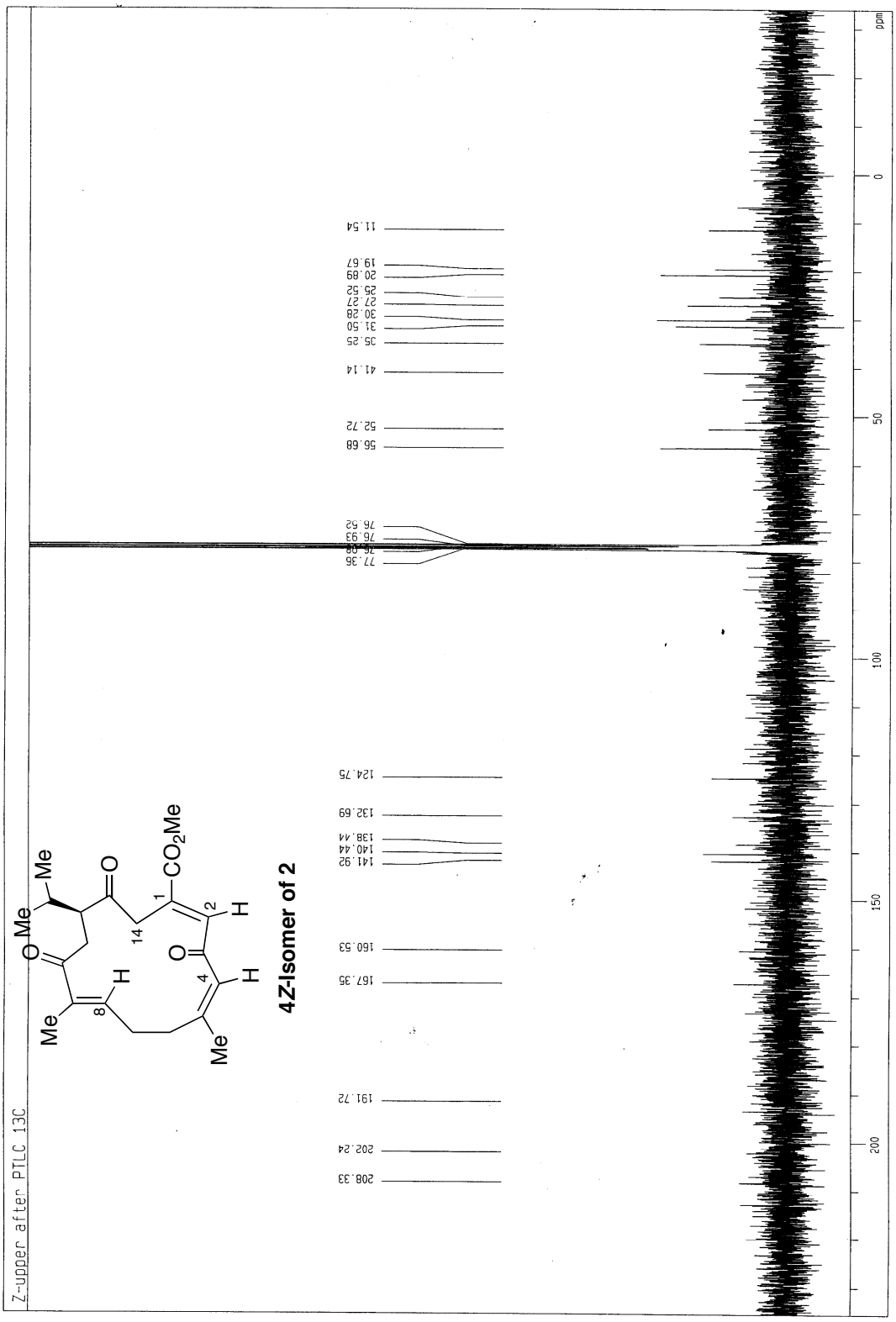
**$^{13}$C NMR Spectrum of 17 (75 MHz, $CDCl_3$)**



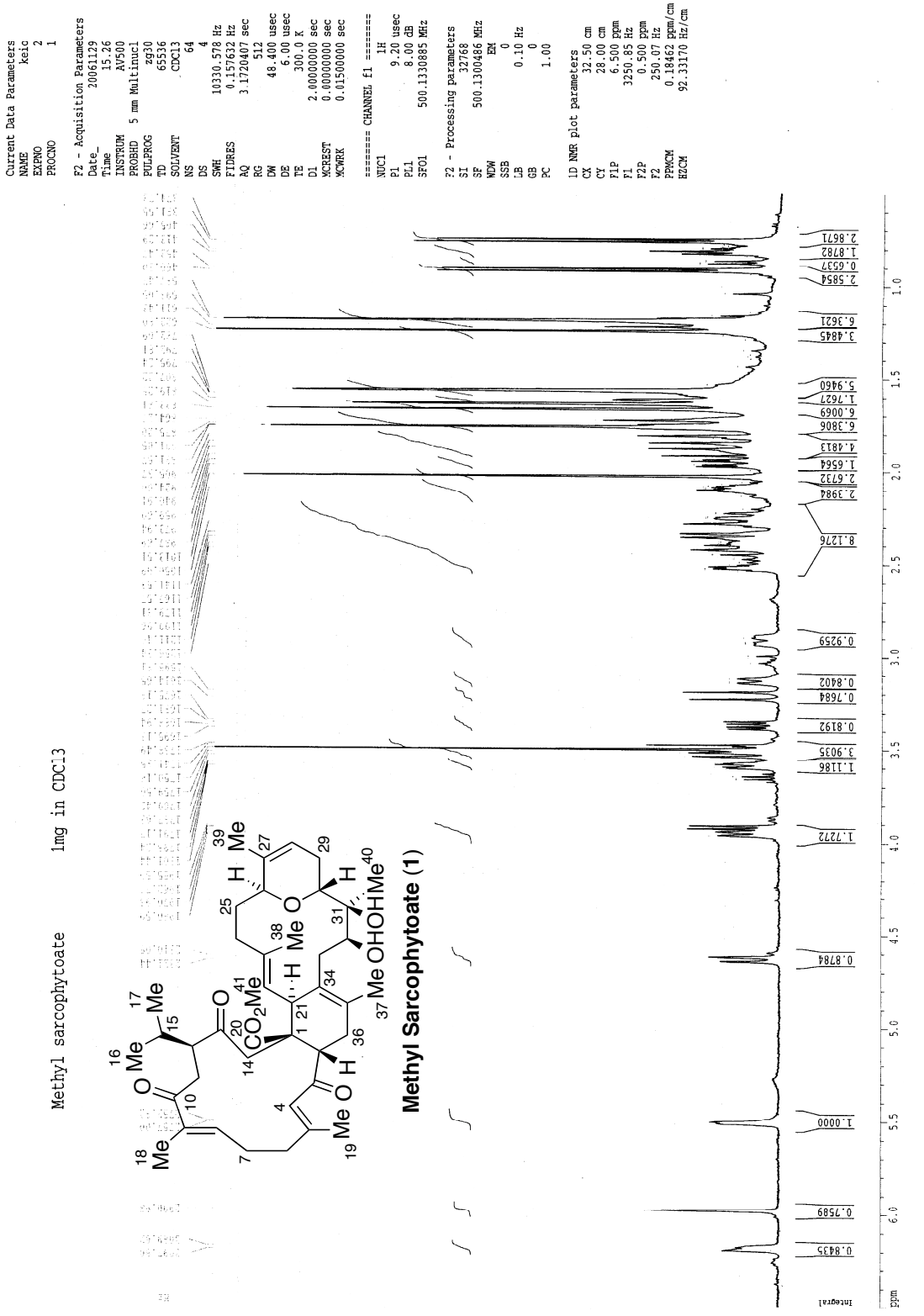
**$^1$H NMR Spectrum of 4*Z*-Isomer of 2 (300 MHz, $CDCl_3$)**



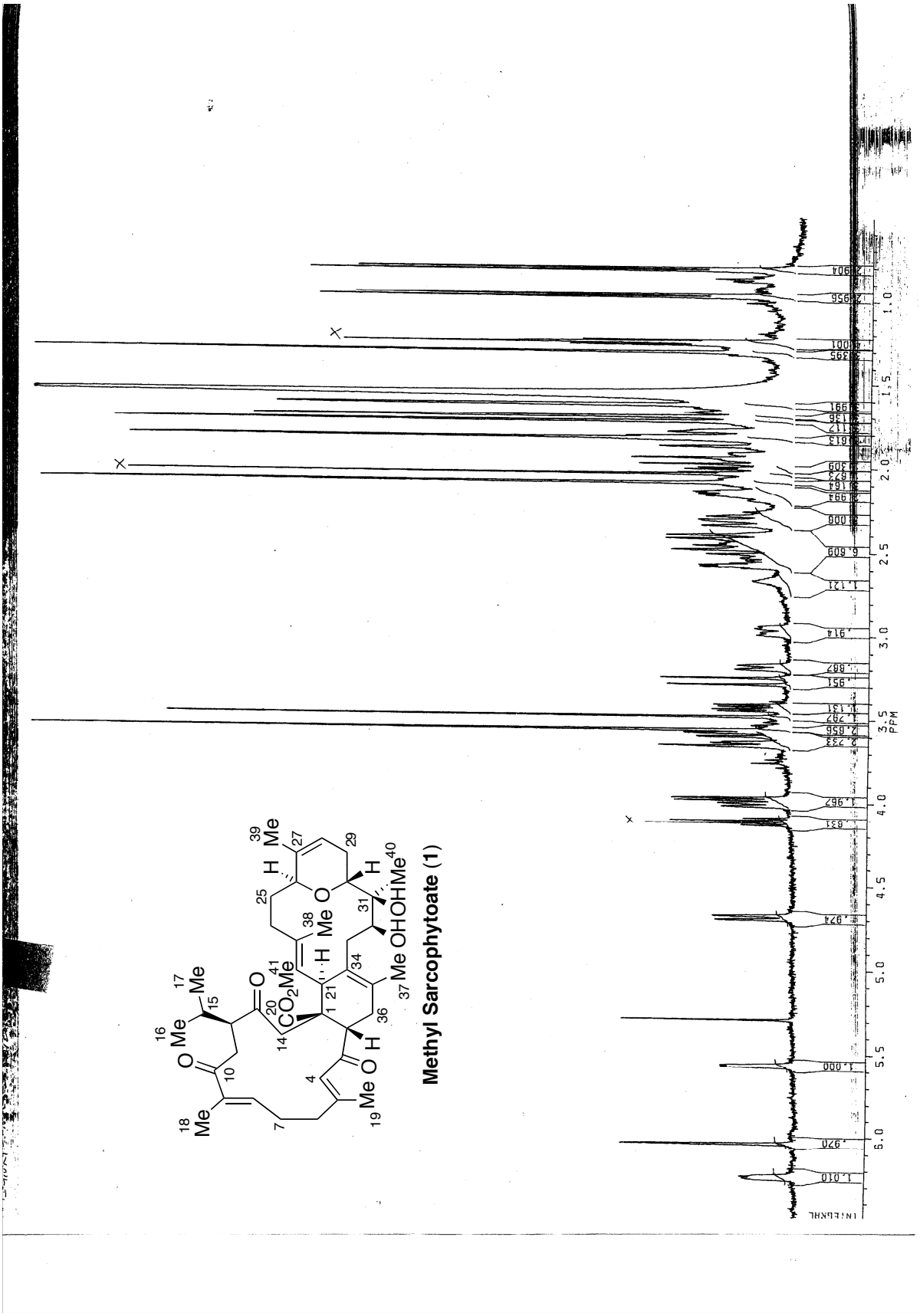
**$^{13}$C NMR Spectrum of 4*Z*-Isomer of 2 (75 MHz, $CDCl_3$)**



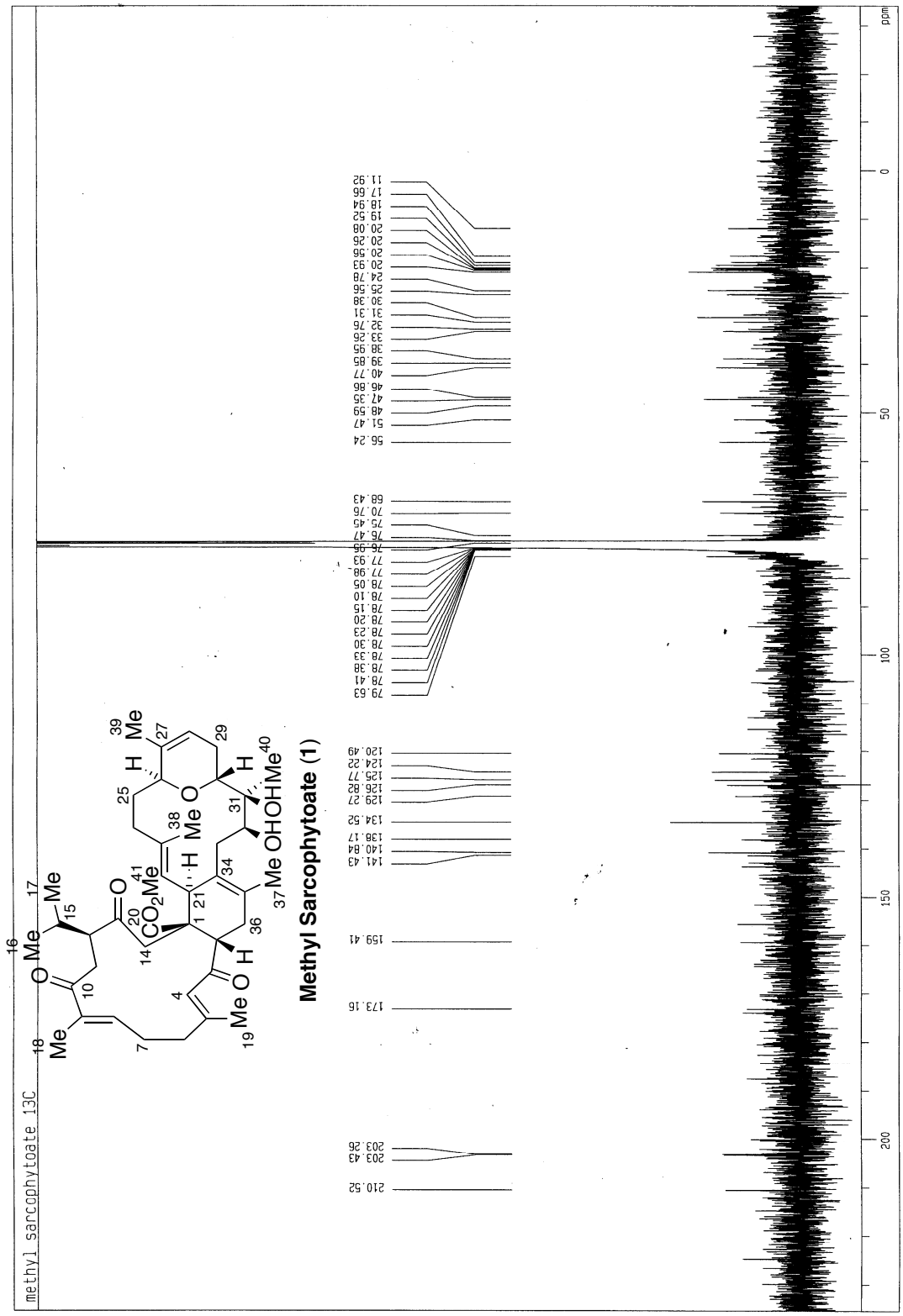
## $^{1}$H NMR Spectrum of Synthetic Methyl Sarcophytoate (1) (500 MHz, $CDCl_3$)



**$^1$H NMR Spectrum of Natural Methyl Sarcophytoate (1) (500 MHz, $CDCl_3$)**



**$^{13}$C NMR Spectrum of Synthetic Methyl Sarcophytoate (1) (75 MHz, $CDCl_3$)**



**$^{13}$C NMR Spectrum of Natural Methyl Sarcophytoate (1) (125 MHz, $CDCl_3$)**