



Supporting Information

© Wiley-VCH 2006

69451 Weinheim, Germany

Total Synthesis of (±)-Merrilactone A

Goverdhan Mehta* and S. Robindro Singh

¹H and ¹³C NMR SPECTRAL DATA

Diol 5

IR(Neat) 3408, 1686, 1649 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.76 (d, *J*=3.6Hz, 4H), 2.02 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 9.3, 57.8, 61.6, 157.3, 204.9; HRMS (ES) *m/z* Calcd for C₉H₁₂NaO₄, [M+Na]⁺: 207.0633, Found 207.0639

Acetonide 6

mp:134.9–135.8 °C; IR (Neat) 3456, 1678, 1649 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.42 (s, 3H), 1.57 (s, 3H), 1.68 (s, 3H), 2.13 (s, 3H), 3.26 (s, 1H), 3.38 (dd, *J*=2.7, 11.7 Hz, 1H), 3.87 (dd, *J*=3, 11.7 Hz, 1H), 4.13(d, *J*=11.7 Hz, 1H), 4.24(d, *J*=11.4 Hz, 1H), 4.77(s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 7.9, 14.1, 18.1, 29.6, 51.6, 62.3, 66.0, 79.1, 98.3, 136.7, 168.3, 204.4; HRMS (ES) *m/z* Calcd for C₁₂H₁₈NaO₄, [M+Na]⁺: 249.1103, Found 249.1103

Enone 7

IR (Neat) 1654, 1698, 3456 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.42 (s, 3H), 1.54 (s, 3H), 1.66 (s, 3H), 2.04 (s, 3H), 2.71 (dd, *J*=6, 14.4 Hz, 1H), 2.82 (dd, *J*=7.8, 14.7 Hz, 1H), 3.81 (dd, *J*=3, 11.4 Hz, 1H), 3.94 (d, *J*=11.7 Hz, 1H), 4.01 (dd, *J*=3 Hz, 12.9 Hz, 1H), 4.12 (s, 1H), 4.33 (d, *J*=12.9 Hz, 1H), 5.0 (d, *J*=9.9 Hz, 1H), 5.09 (dd, *J*=1.5, 17.1 Hz, 1H), 5.51-5.37(m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 7.7, 12.2, 17.9, 29.5, 43.0, 54.3, 61.5, 66.8, 82.7, 98.7, 118.2, 133.6, 134.7, 171.2, 203.1; HRMS (ES) *m/z* Calcd for C₁₅H₂₂NaO₄, [M+Na]⁺: 289.1416, Found: 289.1414

Triol 8

mp: 78–79.8 °C; IR (Neat) 1690, 1649, 3393 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.68 (s, 3H), 2.02 (s, 3H), 2.65-2.50 (m, 2H), 3.99-3.82 (m, 4H), 5.16–5.08 (m, 2H), 5.75-5.63 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 7.7, 12.2, 41.1, 60.0, 61.9, 65.6, 82.3, 118.9, 133.1, 136.0, 173.1, 208.3; HRMS (ES) *m/z* Calcd for C₁₂H₁₈NaO₄, [M+Na]⁺: 249.1113 Found 249.1113

Acetonide 9

mp: 84-85 °C; IR (Neat) 1651, 1697, 3075, 3483 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.26 (s, 3H), 1.35 (s, 3H), 1.75 (d, *J*=0.9 Hz, 3H), 2.01 (d, *J*= 0.9 Hz, 3H), 2.41 (ddt, *J*=1.5, 6.9, 14.7 Hz, 1H), 2.57 (ddt, *J*= 1.5, 3, 6.6, 15.3 Hz, 1H), 2.98 (dd, *J*=2.4, 9.3 Hz, 1H), 3.81 (dd, *J*=9, 11.4 Hz, 1H), 3.93-3.97 (m, 3H), 5.03-5.14 (m, 2H), 5.61-5.75

(m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 7.9, 13.1, 26.7, 27.1, 39.6, 53.6, 62.1, 63.4, 82.2, 100.7, 118.1, 132.9, 138.3, 172.0, 209.6; HRMS (ES) m/z Calcd for $\text{C}_{15}\text{H}_{22}\text{NaO}_4$, $[\text{M}+\text{Na}]^+$: 289.1416 Found 289.1400

Alcohols (mixture) 10

^{13}C NMR (75 MHz, CDCl_3) δ 7.6, 7.8, 12.6, 12.9, 18.3, 20.5, 23.4, 26.5, 26.9, 28.9, 39.7, 40.8, 52.4, 56.7, 59.5, 63.3, 66.4, 67.6, 81.7, 82.9, 98.9, 100.4, 117.3, 118.3, 132.1, 133.3, 136.0, 138.1, 170.8, 171.06, 208.3, 208.5; HRMS(ES) m/z Calcd for $\text{C}_{16}\text{H}_{24}\text{NaO}_4$, $[\text{M}+\text{Na}]^+$: 303.1572 Found 303.1573

Triene 11

IR (Neat) 1709, 1660, 1447 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.21 (s, 3H), 1.36 (s, 3H), 1.70 (s, 3H), 1.80 (s, 3H), 2.02 (s, 3H), 2.05 (dd, $J=1.8$, 6.9 Hz, 1H), 3.90 (d, $J=11.4$ Hz, 1H), 4.0 (d, $J=11.1$ Hz, 1H), 4.88 (s, 1H), 4.96-5.05 (m, 2H), 5.12 (s, 1H), 5.7-5.81 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 8.2, 13.4, 23.0, 26.8, 27.0, 40.4, 58.4, 64.3, 83.7, 100.6, 116.7, 117.4, 133.3, 139.0, 141.1, 169.9, 207.4; HRMS (ES) m/z Calcd for $\text{C}_{17}\text{H}_{24}\text{NaO}_3$, $[\text{M}+\text{Na}]^+$: 299.1623 Found 299.162

Tricyclic enone 12

IR (Neat) 1705, 1653, 1444 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.22 (s, 3H), 1.33 (s, 3H), 1.69 (dd, $J=2.1$, 3.9 Hz, 3H), 1.72 (d, $J=0.6$ Hz, 3H), 2.06 (d, $J=0.9$ Hz, 3H), 2.51 (ddt, $J=2.1$, 2.4, 17.7 Hz, 1H), 2.62 (ddt, $J=2.4$, 4.5, 18 Hz, 1H), 3.72 (d, $J=11.1$ Hz, 1H), 4.14 (d, $J=10.8$ Hz, 1H), 5.24 (d, $J=1.8$, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 8.1, 12.1, 13.2, 26.4, 27.7, 43.5, 62.1, 63.9, 88.0, 99.8, 123.6, 136.8, 137.4, 168.3, 205.7; HRMS (ES) m/z Calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_3$, $[\text{M}+\text{Na}]^+$: 271.1310 Found 271.1312

Tetracyclic ketone 16

mp: 73-74 $^{\circ}\text{C}$; IR (Neat) 1726, 1596, 1441 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.12 (s, 3H), 1.3 (s, 3H), 1.31 (s, 3H), 1.47 (s, 3H), 1.53 (m, 3H), 2.6 (ddt, $J=2.1$, 2.1, 17.1 Hz, 1H), 2.73 (ddt, $J=2.4$, 2.4, 17.4 Hz, 1H), 3.59 (d, $J=11.7$ Hz, 1H), 4.32 (d, $J=11.7$ Hz, 1H), 5.15 (m, 1H), 5.99 (d, $J=3$ Hz, 1H), 6.03 (d, $J=2.7$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.2, 13.4, 13.5, 23.4, 30.1, 38.9, 59.3, 60.6, 62.6, 64.2, 84.4, 98.1, 123.4, 137.6, 146.9, 148.5; 216.9
HRMS (ES) m/z Calcd for $\text{C}_{17}\text{H}_{22}\text{NaO}_3$, $[\text{M}+\text{Na}]^+$: 297.1467 Found 297.1467.

Tetracyclic ketone 15

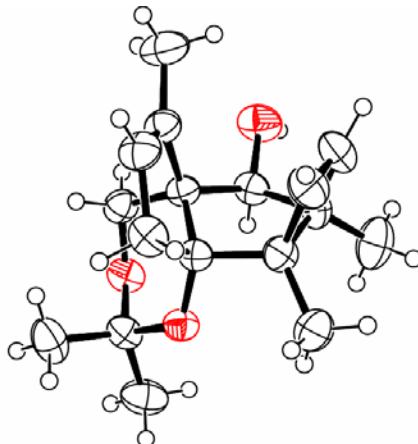
IR (Neat) 1728, cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.1 (s, 3H), 1.3 (s, 9H), 1.37 (s, 3H), 1.80 (m, 3H), 2.53 (ddt, $J=2.1$, 2.1, 18.3 Hz, 1H), 2.74 (ddt, $J=2.7$, 2.4, 18.3 Hz), 3.8 (d, 11.4 Hz, 1H), 3.97 (d, $J=11.4$ Hz, 1H), 5.45 (d, 1.2 Hz, 1H), 5.93 (d, $J=2.4$ Hz, 1H), 6.57 (d, $J=2.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.7, 13.2, 16.3, 27.6, 42.3 (2C), 58.1, 62.4, 62.7, 66.3, 85.7, 99.4, 125.6, 136.3, 138.2, 147.8, 212.1.

Tetracyclic alcohol 17

mp: 131-132.8 $^{\circ}\text{C}$; IR (Neat) 3483, 1624, 1440 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.06 (s, 3H), 1.1 (s, 3H), 1.36 (s, 3H), 1.47 (s, 3H), 1.68 (m, 3H), 2.23 (ddt, $J=2.1$,

2.4, 16.8 Hz, 1H), 2.53 (ddt, $J=2.1, 2.7, 16.8$ Hz, 1H), 3.6 (d, $J=11.7$ Hz, 1H), 3.98 (d, $J=11.7$ Hz, 1H), 4.16 (d, $J=5.7$ Hz, 1H), 5.14 (bs, 1H), 5.82 (d, $J=2.7$ Hz, 1H), 5.99 (d, $J=3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.7, 16.2, 18.3, 23.1, 31.1, 38.3, 54.4, 55.9, 60.9, 65.9, 77.3, 85.2, 98.1, 123.7, 134.2, 144.1, 144.2; HRMS (ES) m/z Calcd for $\text{C}_{17}\text{H}_{24}\text{NaO}_3$, $[\text{M}+\text{Na}]^+$: 299.1623 Found 299.1623.

Crystal data for compound 17: The single crystal X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer at 292 K. The X-ray generator was operated at 50 KV and 35 mA using MoK_α radiation. The data was collected with a ω scan width of 0.3° . A total of 606 frames per set were collected using SMART in four different settings of φ (0° , 90° , 180° and 270°) keeping the sample to detector distance of 6.062 cm and the 2θ value fixed at -25° . The data were reduced by SAINTPLUS; an empirical absorption correction was applied using the package SADABS, and XPREP was used to determine the space group. The structures were solved using SIR92 and refined using SHELXL97. Crystal data for compound **17**: $\text{C}_{17}\text{H}_{24}\text{O}_3$, $M = 276.4$, triclinic, space group P-1, $a = 9.084(2)$ Å, $b = 9.175(2)$ Å, $c = 9.517(3)$ Å, $\alpha = 96.840(5)^\circ$, $\beta = 100.169(4)^\circ$, $\gamma = 94.488(5)^\circ$, $V = 771.1(3)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.19$ gcm⁻³, $F(000) = 300$, $\mu = 0.080$ mm⁻¹, $T = 292$ K, number of l.s. parameters = 187, $R = 0.057$, $R_w = 0.135$, GOF = 1.024 for 2109 reflections with $I > 2\sigma(I)$. An ORTEP diagram of **17** has been shown below. Displacement ellipsoids for non-H atoms have been drawn at 50% probability level.



Tetracyclic compound 18

^1H NMR (300 MHz, CDCl_3) δ 0.12 (s, 3H), 0.14 (s, 3H), 0.92 (s, 9H), 1.04 (s, 3H), 1.06 (s, 3H), 1.36 (s, 3H), 1.46 (s, 3H), 1.65 (d, $J=1.5$ Hz, 3H), 2.20 (d, $J=16.8$ Hz, 1H), 2.51 (d, $J=16.8$ Hz, 1H), 3.54 (d, $J=11.7$ Hz, 1H), 3.87 (d, $J=11.7$ Hz, 1H), 4.2 (s, 1H), 5.1 (s, 1H), 5.7 (d, $J=2.7$ Hz, 1H), 5.94 (d, $J=3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.7, -3.4, 12.9, 16.9, 18.3, 18.7, 23.4, 26.1(3C), 31.3, 38.1, 54.7, 55.6, 60.6, 65.6, 77.6, 85.4, 98.1, 122.8, 135.5, 142.6, 145.2;

Diol 19

mp: 106.2-107.2°C; IR (Neat) 1461, 3448 cm⁻¹; ^1H NMR (300 MHz, CDCl_3) δ 0.10 (s, 3H), 0.11 (s, 3H), 0.91 (s, 9H), 1.09 (s, 3H), 1.1 (s, 3H), 1.69 (d, $J=0.9$ Hz, 3H), 2.20 (ddt, $J=2.4, 2.7, 16.2$ Hz, 1H), 2.32 (ddt, $J=1.8, 16.2$ Hz, 1H), 3.63 (d, $J=11.1$ Hz, 1H), 3.66 (d, $J=11.1$ Hz, 1H), 3.91 (s, 1H), 5.2 (s, 1H), 5.74 (d, $J=3$ Hz, 1H), 5.98

(d, $J=2.7$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.8, -3.7, 13.0, 16.7, 18.2, 18.9, 26.0(3C), 42.0, 56.7, 58.3, 63.9, 64.3, 77.0, 88.3, 124.1, 136.0, 142.2, 144.6; HRMS (ES) m/z Calcd for $\text{C}_{20}\text{H}_{34}\text{NaO}_3\text{Si}$, $[\text{M}+\text{Na}]^+$: 373.2175 Found 373.2175

Enolether 20

IR (Neat) 3364, 1650, 1454 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.09 (s, 3H), 0.10 (s, 3H), 0.90 (s, 9H), 1.1 (s, 3H), 1.15 (s, 3H), 1.68 (m, 3H), 2.25 (ddt, $J=1.5$, 15.6 Hz, 1H), 2.04 (ddt, $J=2.1$, 1.8, 15.9 Hz, 1H), 3.20 (s, 1H), 3.62 (s, 3H), 3.96 (s, 1H), 4.28 (d, $J=7.2$ Hz, 1H), 4.94 (bs, 1H), 5.77 (d, $J=2.7$ Hz, 1H), 5.89 (d, $J=3$ Hz, 1H), 5.90 (d, $J=8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ -3.2, -4.8, 13.8, 17.2, 18.3, 19.2, 26.1(3C), 40.9, 55.7, 58.8, 59.9, 65.7, 80.8, 86.9, 109.4, 121.6, 134.0, 143.7, 144.5, 146.3; HRMS (ES) m/z Calcd for $\text{C}_{22}\text{H}_{36}\text{NaO}_3\text{Si}$, $[\text{M}+\text{Na}]^+$: 399.2331 Found 399.2350

Lactone 22

mp:79-81.5°C; IR (Neat) 1780, 1455 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.11 (s, 6H), 0.91 (s, 9H), 1.1 (s, 3H), 1.2 (s, 3H), 1.8-1.76 (m, 3H), 2.4 (ddt, $J=2.1$, 2.7, 16.8 Hz, 1H), 2.45 (d, $J=17.7$ Hz, 1H), 2.54 (ddt, $J=1.8$, 2.1, 16.8 Hz, 1H), 2.8 (d, $J=17.7$, 1H), 5.12 (d, $J=1.8$ Hz, 1H), 5.9 (d, $J=3$ Hz, 1H), 6.04 (d, $J=3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ -3.1, -4.9, 13.5, 17.2, 18.1, 18.9, 25.9(3C), 39.6, 44.4, 57.7, 59.5, 65.2, 83.4, 100.2, 124.0, 138.7, 139.6, 145.5, 176.5; HRMS (ES) m/z Calcd for $\text{C}_{21}\text{H}_{32}\text{NaO}_3\text{Si}$, $[\text{M}+\text{Na}]^+$: 383.2018 Found 383.2014

Bis-lactone 24

mp:180-182°C; IR (Neat) 1778 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.10 (s, 3H), 0.13 (s, 3H), 0.89 (s, 9H), 1.20 (s, 3H), 1.22 (s, 3H), 1.78 (d, $J=1.5$ Hz, 1H), 2.5-2.43 (m, 2H), 2.70 (1/2ABq, $J=18.9$ Hz, 1H), 2.81 (1/2ABq, $J=19.2$ Hz, 1H), 3.85 (d, $J=8.4$ Hz, 1H), 4.1 (s, 1H), 4.21 (d, $J=8.4$ Hz, 1H), 5.39 (d, $J=1.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ -3.1, -3.2, 16.0, 16.3, 16.6, 17.7, 25.9(3C), 39.4, 42.3, 55.9, 62.2, 70.4, 72.2, 90.0, 104.7, 125.9, 141.7, 175.1, 176.5; HRMS (ES) m/z Calcd for $\text{C}_{21}\text{H}_{32}\text{NaO}_5\text{Si}$, $[\text{M}+\text{Na}]^+$: 415.1917 Found 415.1934

Hydroxy bis-lactone 25

IR(Neat) 3382, 2924, 1767, 1576, 1452 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.22 (s, 3H), 1.24 (s, 3H), 1.82 (d, $J=1.8$ Hz, 3H), 2.52 (m, 2H), 2.65 (d, $J=18.9$ Hz, 1H), 2.84 (d, $J=18.9$ Hz, 1H), 2.92 (d, $J=5.7$ Hz, 1H), 3.95 (d, $J=8.7$ Hz, 1H), 4.13 (d, $J=5.4$ Hz, 1H), 4.21 (d, $J=8.7$ Hz, 1H), 5.38 (m, $J=1.5$ Hz, 1H); ^{13}C NMR (75 MHz; CDCl_3) δ 15.1, 15.9, 16.7, 40.0, 41.1, 55.3, 62.0, 69.7, 73.6, 86.7, 104.5, 125.1, 141.1, 175.0, 178.4;

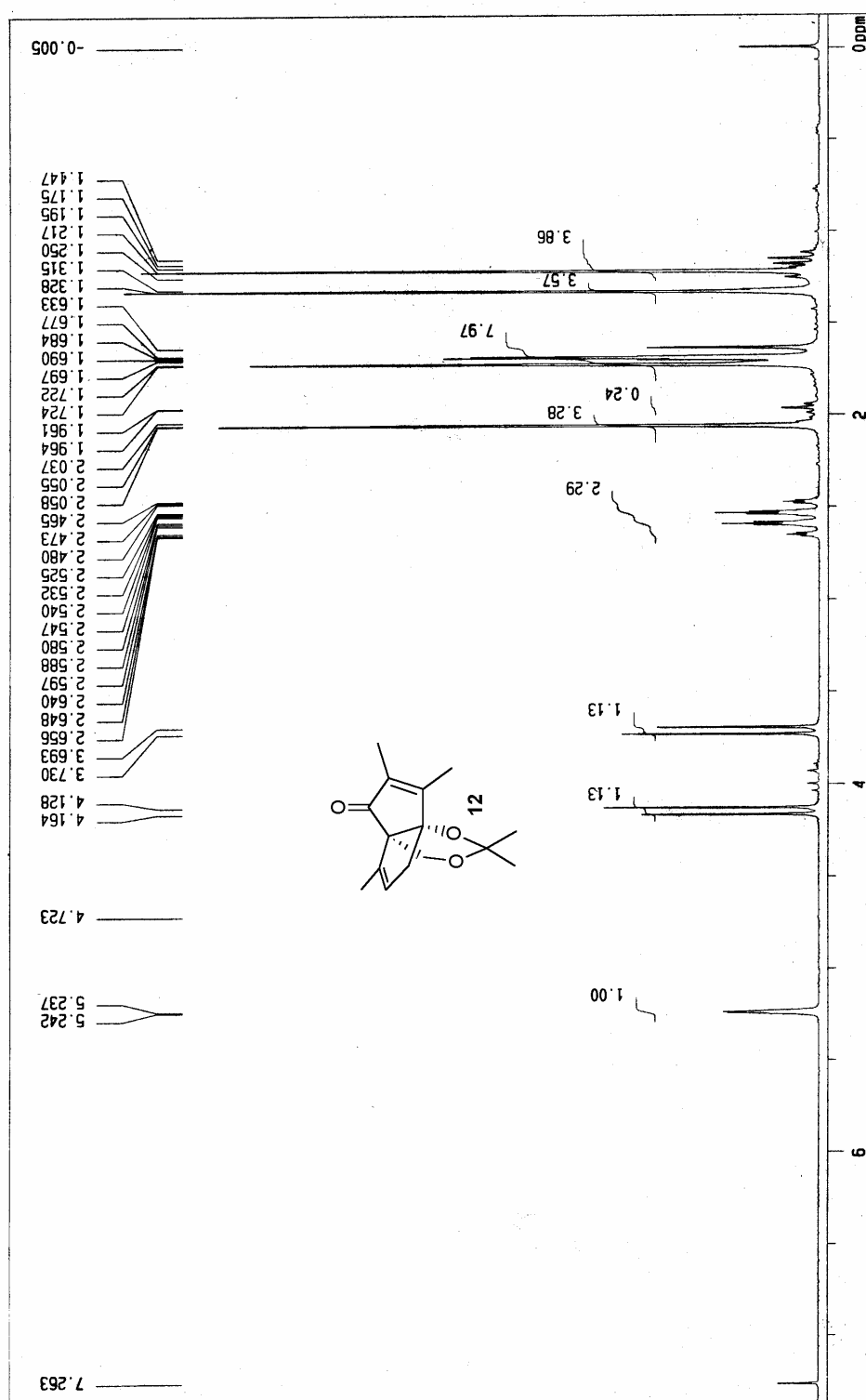
^1H NMR (300 MHz, CD_3OD) δ 1.18 (s, 3H), 1.22 (d, $J=0.9$ Hz, 3H), 1.82 (ddd, $J=1.5$, 2.1, 2.4 Hz, 3H), 2.35 (ddt, $J=2.4$, 2.4, 18.3, 1H), 2.57 (ddt, 1.8, 2.1, 18.8 Hz, 1H), 2.75 (d, $J=18.9$ Hz, 1H), 2.87 (d, $J=18.9$ Hz, 1H), 3.97 (d, $J=8.4$ Hz), 4.08 (s, 1H), 4.15 (d, $J=8.7$ Hz, 1H), 5.33 (bs, 1H); ^{13}C NMR (75 MHz; CD_3OD) δ 15.1, 16.1, 16.9, 40.6, 41.9, 57.0, 64.0, 71.5, 74.4, 87.1, 106.5, 125.1, 143.8, 177.9, 180.2; HRMS (ES) m/z Calcd for $\text{C}_{15}\text{H}_{18}\text{NaO}_5\text{Si}$, $[\text{M}+\text{Na}]^+$: 301.1052 Found 301.1053

Epoxide 26

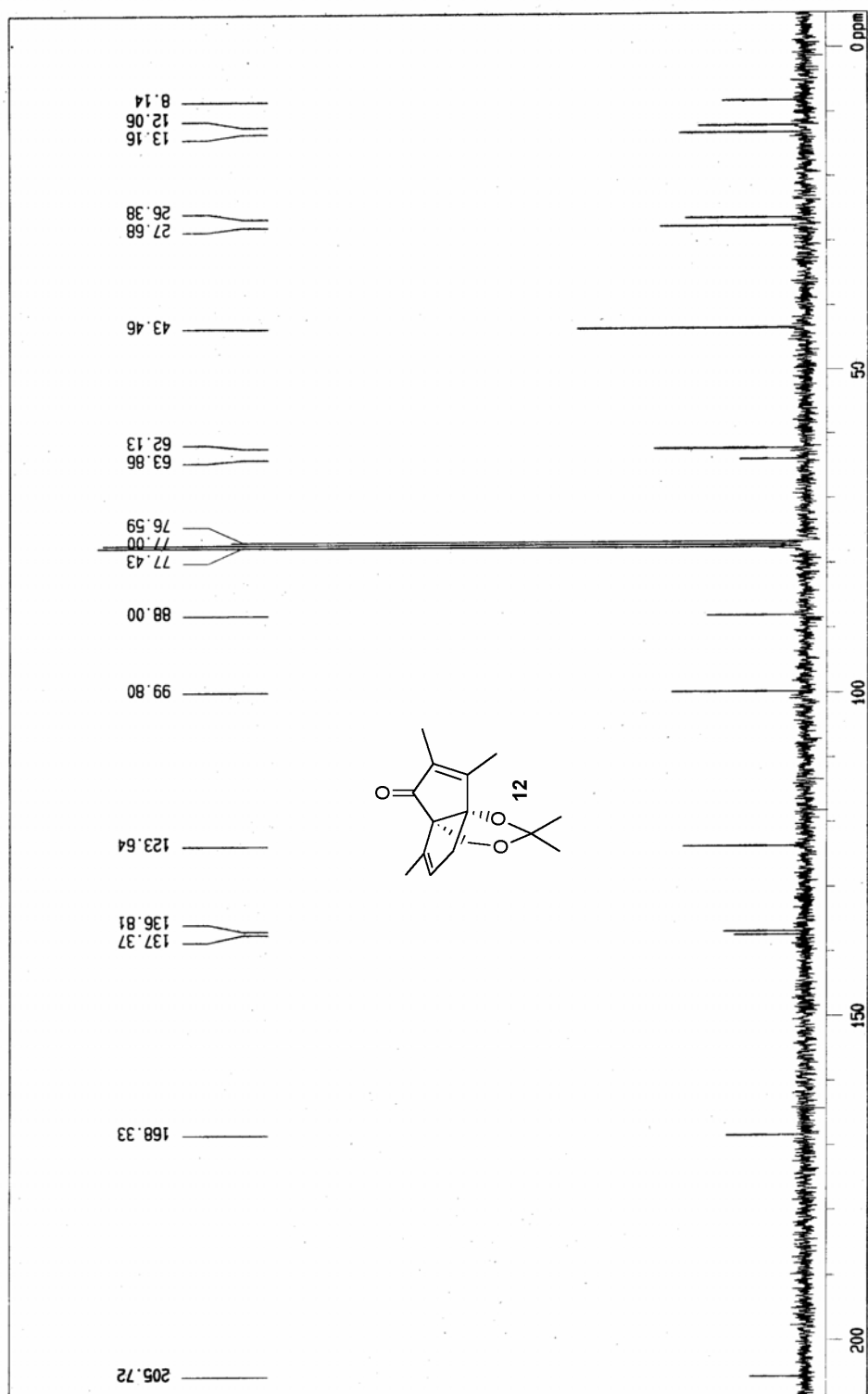
IR (Neat) : 1260, 1772, 3418(br) cm^{-1} ; ^1H NMR (400 MHz, CD_3OD) δ 1.11 (s, 3H), 1.17 (s, 3H), 1.55 (s, 3H), 2.08 (d, $J=16.2$ Hz, 1H), 2.26 (dd, $J=1.9, 16$ Hz, 1H), 2.59 (d, $J=19$ Hz, 1H), 3.02 (d, $J=19$ Hz, 1H), 3.66 (d, $J=1.7$ Hz, 1H), 3.94 (d, $J=8.4$ Hz, 1H), 4.13 (s, 1H), 4.48 (d, $J=8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 16.1, 16.6, 17.9, 37.3, 38.6, 57.3, 64.8, 67.4, 69.4, 71.7, 75.8, 83.9, 108.3, 177.4, 180.2; HRMS (ES) m/z Calcd for $\text{C}_{15}\text{H}_{18}\text{NaO}_6$, $[\text{M}+\text{Na}]^+$: 317.1001 Found 317.1000

Merrilactone A 1

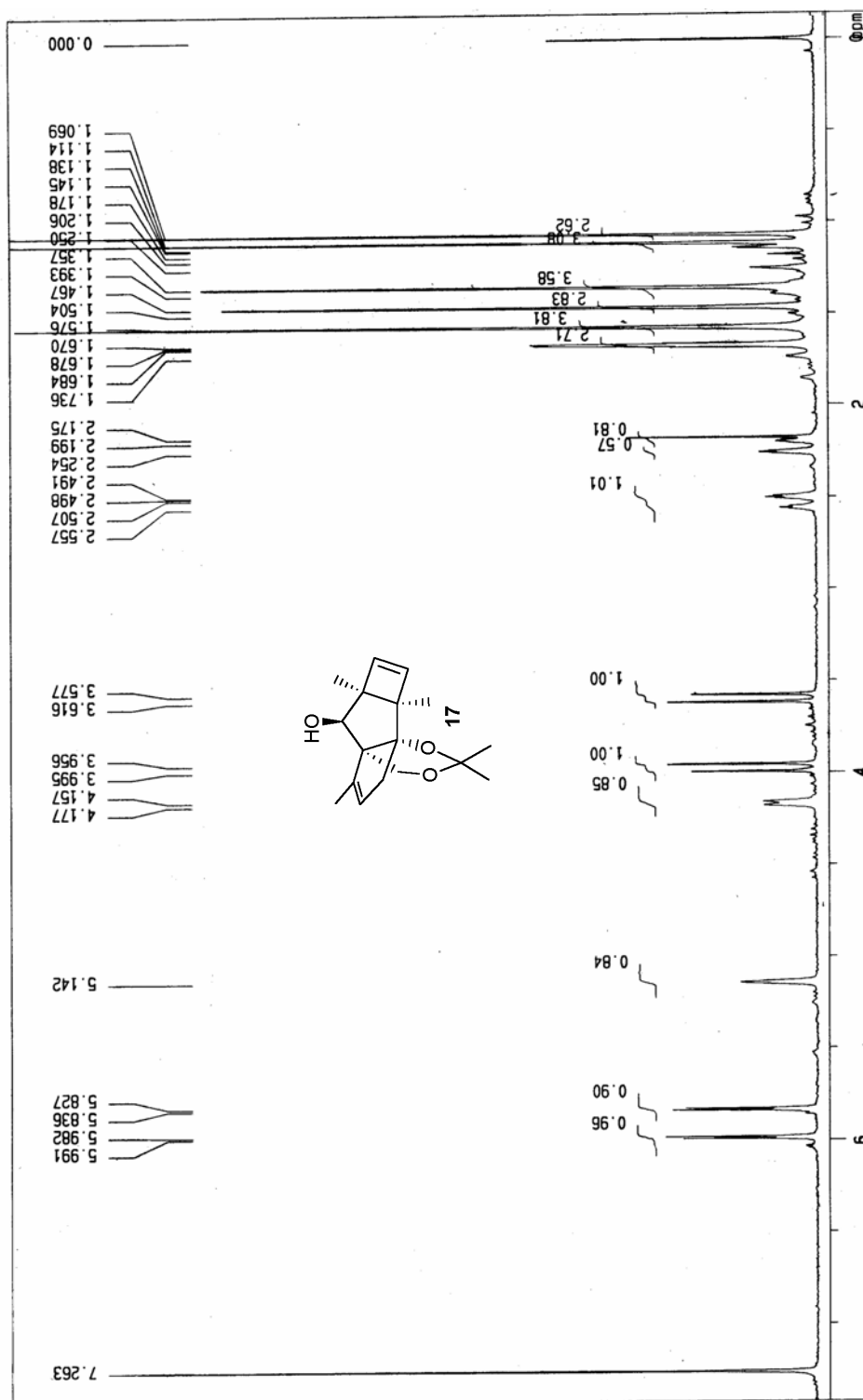
IR (Neat) : 1259, 1763, 1770, 2928, 3449(br) cm^{-1} ; ^1H NMR (400 MHz, CD_3OD) δ 1.08 (s, 3H), 1.24 (s, 3H), 1.49 (s, 3H), 2.28 (dd, $J=1.5, 15.3$ Hz, 1H), 2.68 (d, $J=19.5$ Hz, 1H), 2.72 (dd, $J=15.3, 5.2$ Hz, 1H), 2.91 (d, $J=19.4$ Hz, 1H), 3.95 (dd, $J=1.3, 5.1$ Hz, 1H), 4.02 (d, $J=10.0$ Hz, 1H), 4.61 (d, $J=10$ Hz, 1H), 4.74 (s, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 16.0, 17.3, 17.5, 32.2, 44.0, 58.5, 61.2, 66.1, 75.5, 80.0, 90.3, 96.2, 107.3, 177.6, 179.3; HRMS (ES) m/z Calcd for $\text{C}_{15}\text{H}_{18}\text{NaO}_6$, $[\text{M}+\text{Na}]^+$: 317.1001 Found 317.1025.



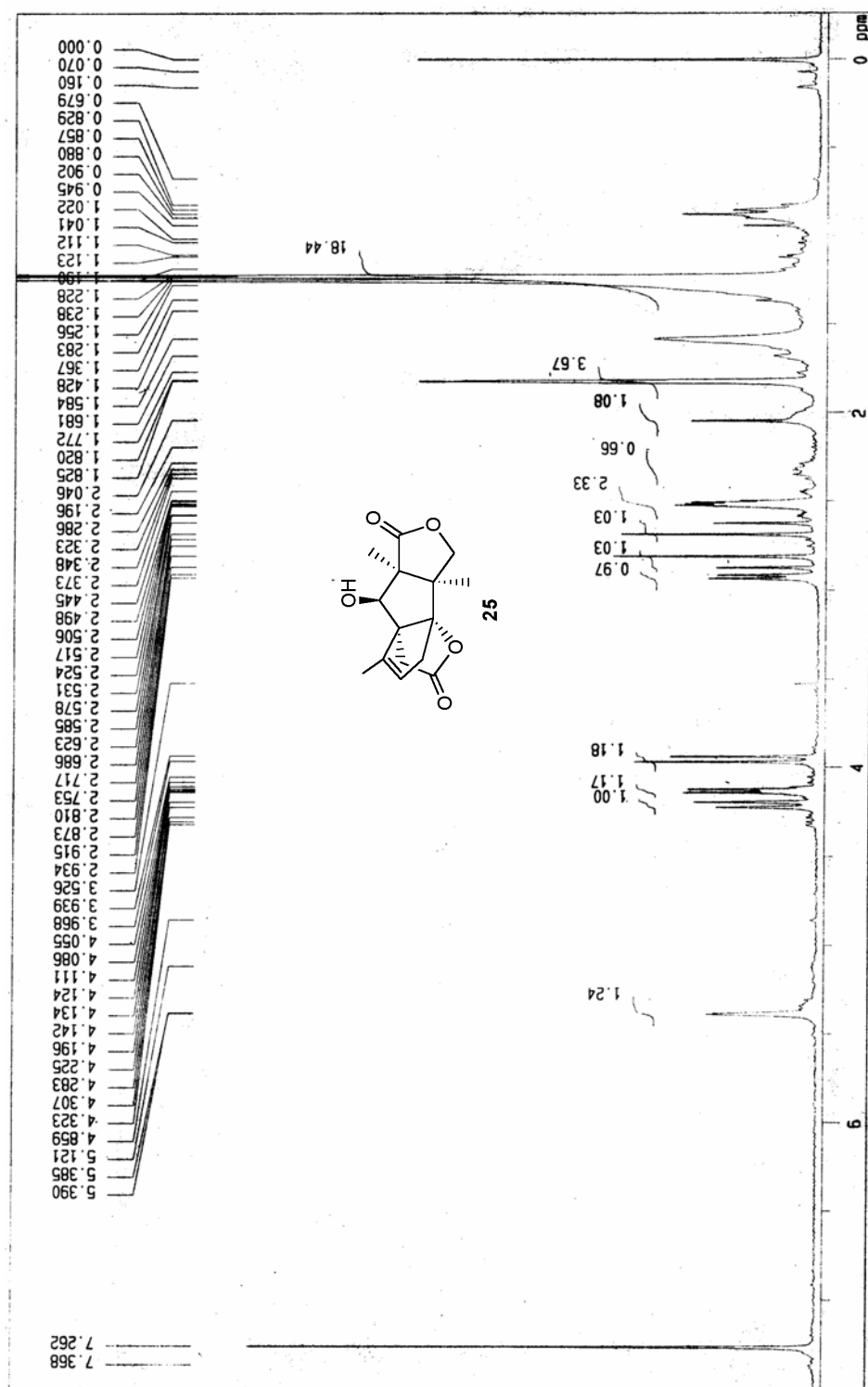
¹H NMR spectrum of compound 12



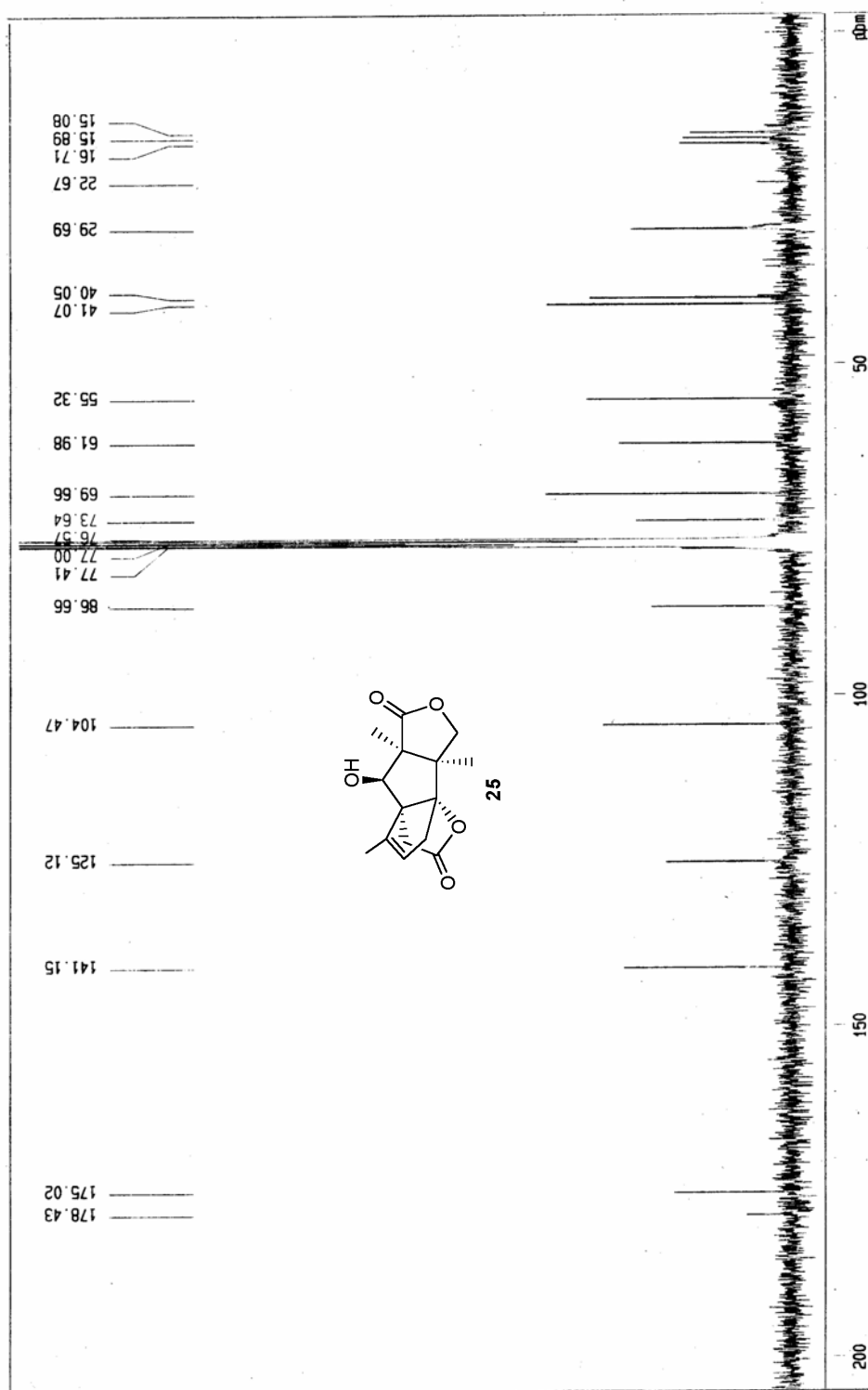
^{13}C NMR spectrum of compound **12**



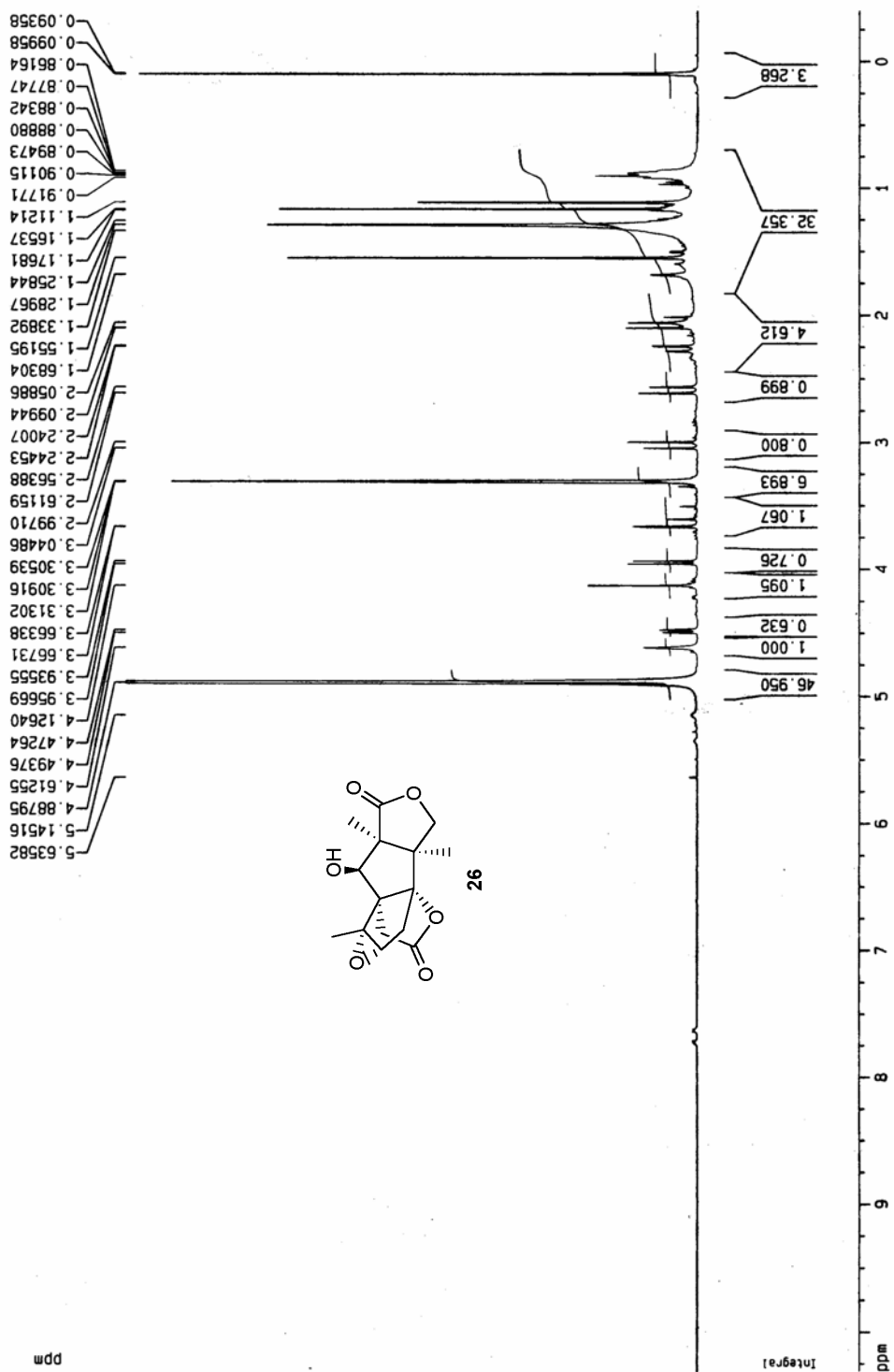
¹H NMR spectrum of compound 17



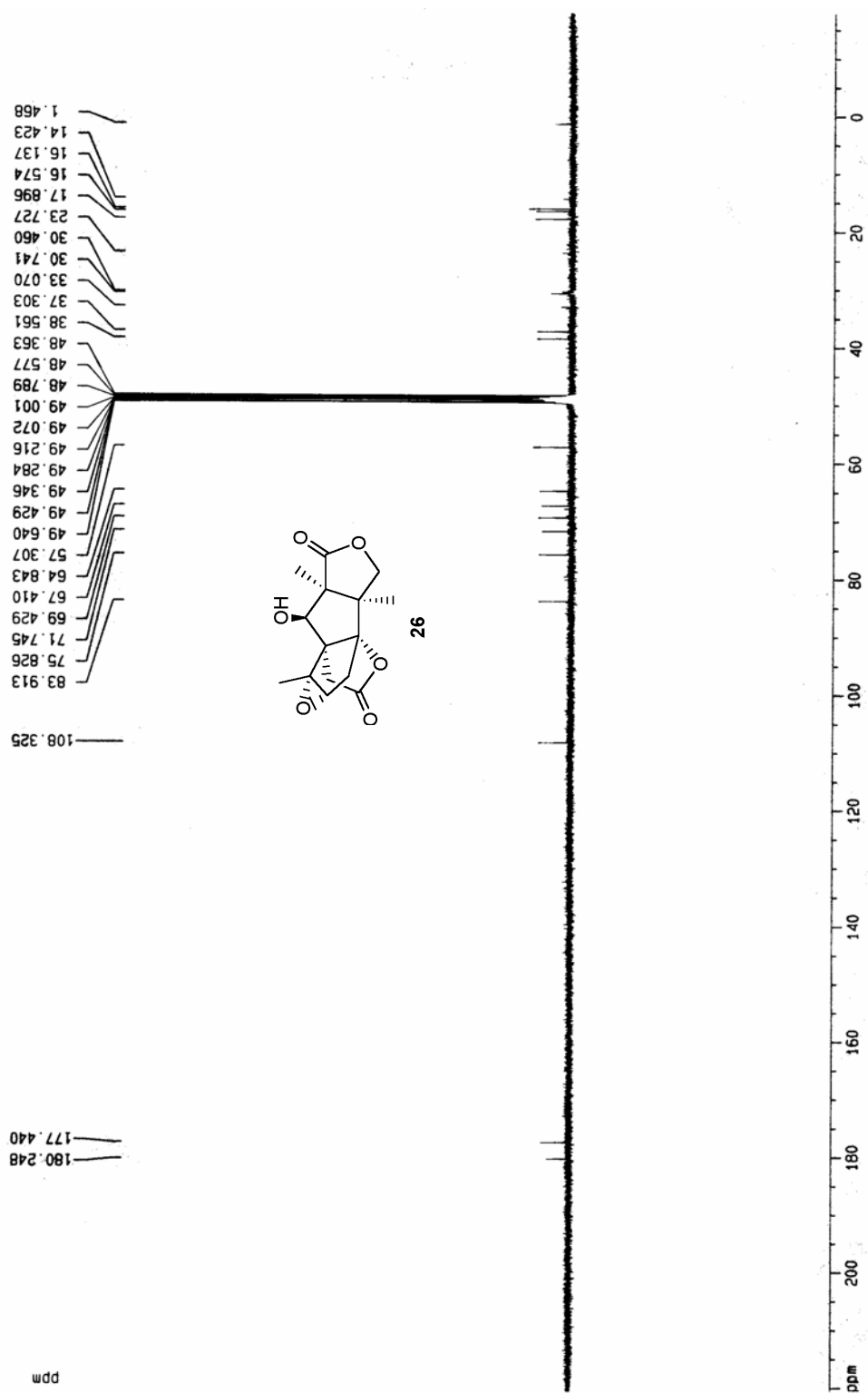
^1H NMR spectrum of compound **25**

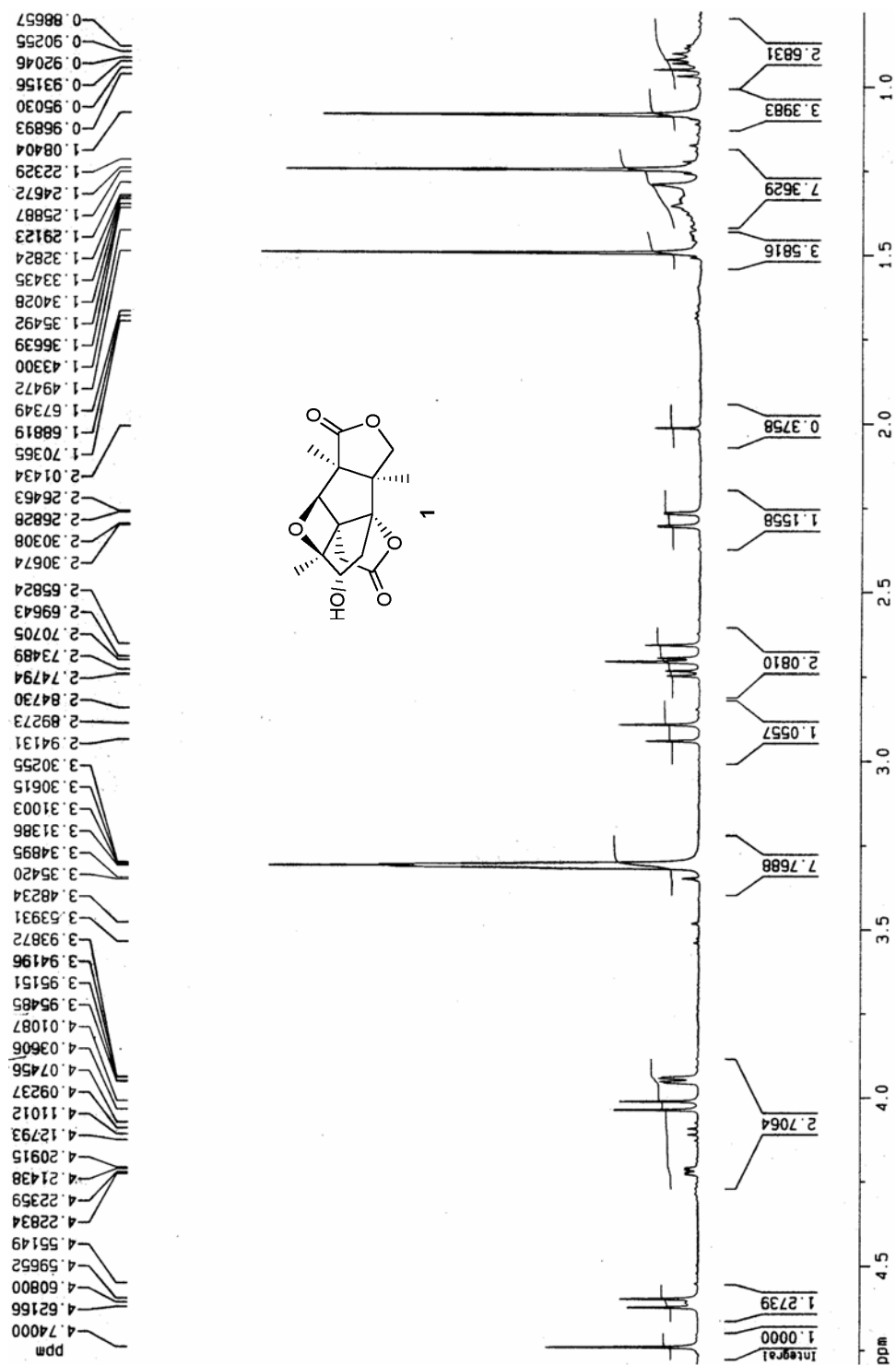


¹³C NMR spectrum of compound **25**

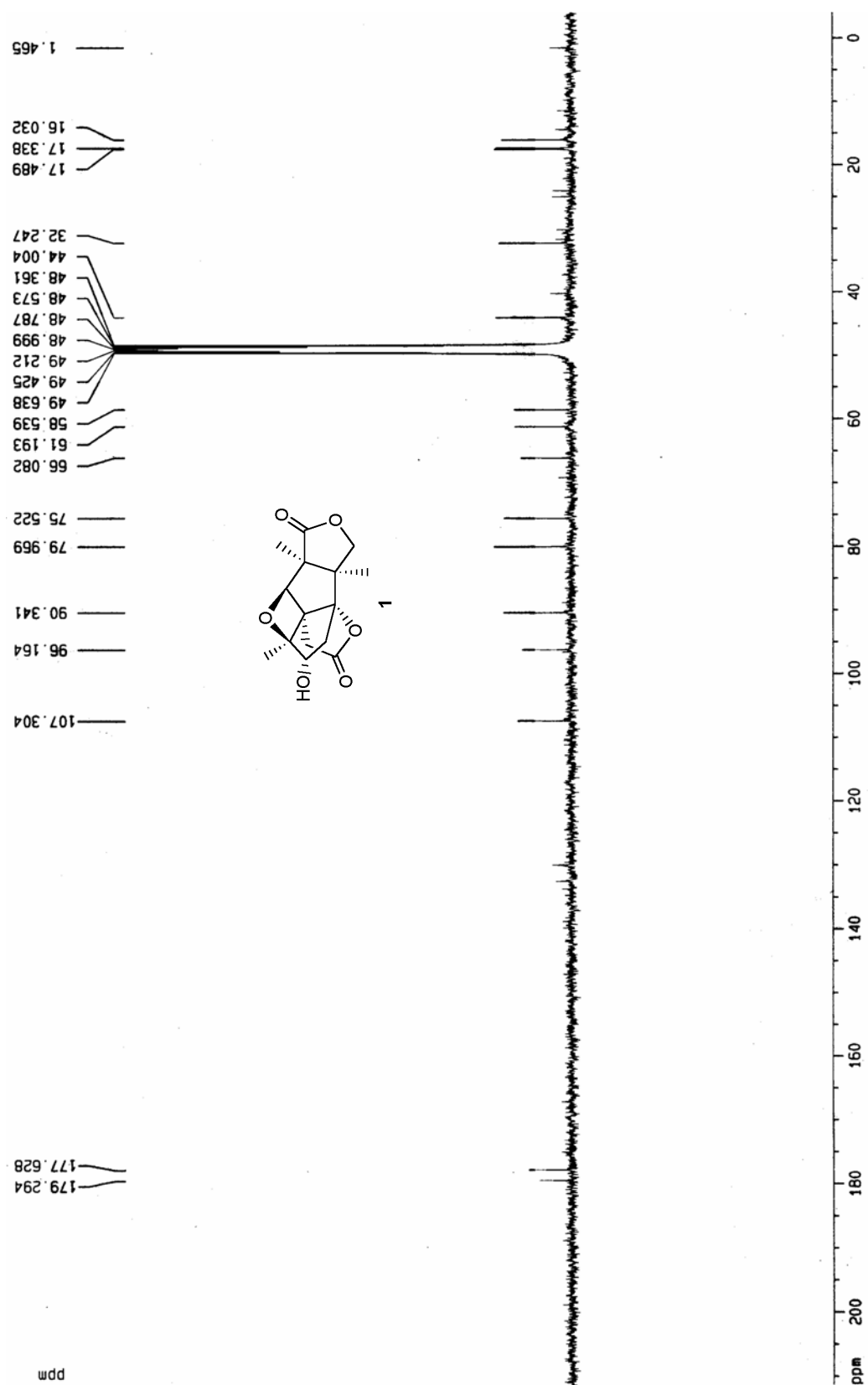


¹H NMR spectrum of compound **26**





¹H NMR spectrum of compound **1**



¹³C NMR spectrum of compound **1**