

Enantioselective Total Synthesis of (+)-Eupenoxide and (+)-Phomoxide: Revision of Structures and Assignment of Absolute Configuration

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Supporting Information

Compound 8:

$[\alpha]_D^{23}$ -13.9 (*c* 2.37, CH₃OH)

¹H NMR (300 MHz, CD₃OD) δ 4.83 (d, *J* = 12.6 Hz, 1H), 4.69 (d, *J* = 12.6 Hz, 1H), 4.53 (d, *J* = 1.5 Hz, 1H), 4.40 (d, *J* = 1.5 Hz, 1H), 4.32 (d, *J* = 12.9 Hz, 1H), 4.17 (d, *J* = 12.9 Hz, 1H), 3.32-3.29 (m, 2H), 2.04 (s, 3H)

¹³C NMR (75 MHz, CD₃OD) δ 172.8, 137.4, 130.1, 64.8, 64.2, 62.2, 59.7, 53.8, 53.8, 20.8

HRMS (ES) *m/z* calcd for C₁₀H₁₄NaO₆ [M + Na]⁺ 253.0688, found 253.0691

Compound 14:

$[\alpha]_D^{25}$ -177.71 (*c* 1.75, CHCl₃)

¹H NMR (300 MHz, CDCl₃) δ 6.43 (d, *J* = 15.9 Hz, 1H), 6.34 (s, 1H), 6.28-6.18 (m, 1H), 5.01 (d, *J* = 12 Hz, 1H), 4.84 (d, *J* = 12 Hz, 1H), 3.76-3.74 (m, 1H), 3.57 (d, *J* = 3.6 Hz, 1H), 2.21 (q, *J* = 6.9 Hz, 2H), 2.12 (s, 3H), 2.04 (s, 3H), 1.47-1.25 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H)

¹³C NMR (75 MHz, CDCl₃) δ 193.1, 170.7, 169.9, 145.7, 142.9, 128.2, 124.8, 63.3, 56.4, 53.0, 51.9, 33.9, 31.2, 28.3, 22.4, 20.8, 20.7, 14.0

HRMS (ES) *m/z* calcd for C₁₈H₂₄NaO₆ [M + Na]⁺ 359.1471, found 359.1496

Compound 15:

$[\alpha]_{\text{D}}^{23} -150.0$ (*c* 0.58, CHCl_3)

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.65-6.47 (m, 2H), 5.02 (br s, 1H), 4.34 (s, 2H), 3.88- 3.86 (m, 1H), 3.49 (d, $J = 3.6$ Hz, 1H), 2.30-2.22 (m, 2H), 1.52-1.28 (m, 6H), 0.90 (t, $J = 6.6$ Hz, 3H)

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.2, 149.1, 143.7, 129.4, 125.0, 63.0, 55.7, 55.5, 52.4, 34.0, 31.4, 28.4, 22.4, 14.0

HRMS (ES) m/z calcd for $\text{C}_{14}\text{H}_{20}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 275.1259, found 275.1244.

Compound 16:

$[\alpha]_{\text{D}}^{26} -167.02$ (*c* 0.94, CHCl_3)

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.69-6.56 (m, 1H), 6.48 (d, $J = 15.6$ Hz, 1H), 6.37 (s, 1H), 6.25-6.17 (m, 1H), 6.10-6.00 (m, 1H), 5.04 (1/2ABq, $J = 12.3$ Hz, 1H), 4.86 (1/2ABq, $J = 12.3$ Hz, 1H), 3.76-3.74 (m, 1H), 3.57 (d, $J = 3.6$ Hz, 1H), 2.19-2.10 (m, 2H), 2.13 (s, 3H), 2.05 (s, 3H), 1.52-1.40 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H)

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 192.8, 170.8 170.0, 145.9, 143.6, 139.2, 130.5, 128.4, 124.2, 63.1, 56.4, 52.8, 51.9, 35.1, 22.0, 20.8, 20.8, 13.7

HRMS (ES) m/z calcd for $\text{C}_{18}\text{H}_{22}\text{NaO}_6$ $[\text{M} + \text{Na}]^+$ 357.1314, found 357.1295

Compound 17:

$[\alpha]_{\text{D}}^{25} -143.2$ (*c* 1.14, CHCl_3)

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.0-6.92 (m, 1H), 6.55 (d, $J = 15.3$ Hz, 1H), 6.28-6.19 (m, 1H), 6.14-6.04 (m, 1H), 5.06 (s, 1H), 4.38 (s, 2H), 3.89-3.87 (m, 1H), 3.50 (d, $J = 3.6$ Hz, 1H), 2.16 (q, $J = 6.9$ Hz, 2H), 1.53-1.40 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H)

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 195.7, 149.6, 143.1, 140.1, 130.7, 129.6, 124.6, 62.7, 55.5, 55.3, 52.4, 35.2, 22.1, 13.7

HRMS (ES) m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 273.1103, found 273.1104

Compound 1:

$[\alpha]_{\text{D}}^{25} (+)20.0$ (*c* 1.95, CHCl_3)

IR (cm^{-1}): 3372

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.29 (d, $J = 15.9$ Hz, 1H), 6.15-6.05 (m, 1H), 4.75 (s, 1H), 4.59 (s, 1H), 4.57 (d, $J = 12.6$ Hz, 1H), 4.10 (d, $J = 12.6$ Hz, 1H), 3.46 (br s, 1H), 3.37 (br s, 1H), 2.24-2.07 (m, 2H), 1.44-1.28 (m, 6H), 0.89 (t, $J = 6.6$ Hz, 3H)

^{13}C NMR (75 MHz, CDCl_3) 135.8, 131.8, 129.9, 124.4, 66.9, 63.1, 62.1, 52.2, 51.3, 33.5, 31.4, 28.8, 22.5, 14.0

HRMS (ES) m/z calcd for $\text{C}_{14}\text{H}_{22}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 277.1416, found 277.1407

Compound 2:

$[\alpha]_{\text{D}}^{25} +161.2$ (c 1.16, CH_3OH)

IR (cm^{-1}): 3377

^1H NMR (300 MHz, CDCl_3) δ 6.64-6.55 (m, 1H), 6.35 (d, $J = 15.3$ Hz, 1H), 6.17-6.09 (m, 1H), 5.93-5.83 (m, 1H), 4.77 (br s, 1H), 4.58 (br s, 1H), 4.53 (d, $J = 12.6$ Hz, 1H), 4.09 (d, $J = 12.6$ Hz, 1H), 3.45 (br s, 1H), 3.35 (br s, 1H), 2.15-2.08 (m, 2H), 1.50-1.37 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H)

^{13}C NMR (75 MHz, CDCl_3) 138.5, 133.3, 132.1, 130.9, 130.5, 124.5, 66.5, 62.7, 61.7, 52.4, 51.5, 35.0, 22.3, 13.7

HRMS (ES) m/z calcd for $\text{C}_{14}\text{H}_{20}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 275.1259, found 275.1246

Compound 3:

$[\alpha]_{\text{D}}^{24} +1.8$ (c 1.15, CH_3OH)

IR (cm^{-1}): 3387

^1H NMR (300 MHz, CDCl_3) δ 6.28 (d, $J = 15.9$ Hz, 1H), 6.08-5.99 (m, 1H), 4.72 (br s, 2H), 4.40 (br s, 2H), 3.48 (s, 2H), 2.16-2.12 (m, 2H), 1.44-1.29 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H)

^{13}C NMR (75 MHz, CDCl_3) 135.2, 131.4, 131.3, 124.6, 66.6, 63.2, 58.9, 54.7, 53.6, 33.5, 31.4, 28.9, 22.5, 14.0

HRMS (ES) m/z calcd for $\text{C}_{14}\text{H}_{22}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 277.1416, found 277.1410

Compound 4:

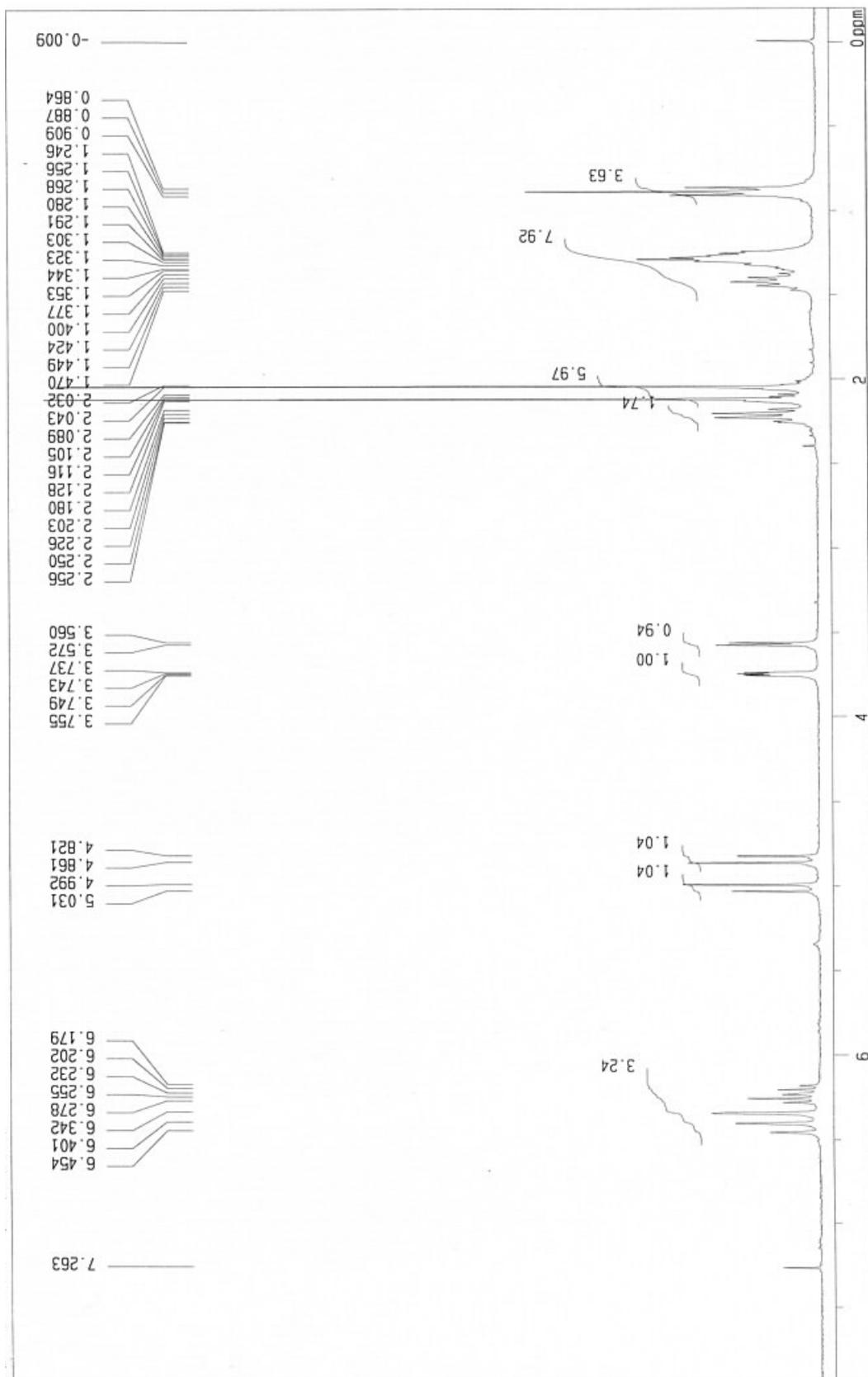
$[\alpha]_{\text{D}}^{24} +18.3$ (c 0.71, CH_3OH)

IR (cm^{-1}): 3392

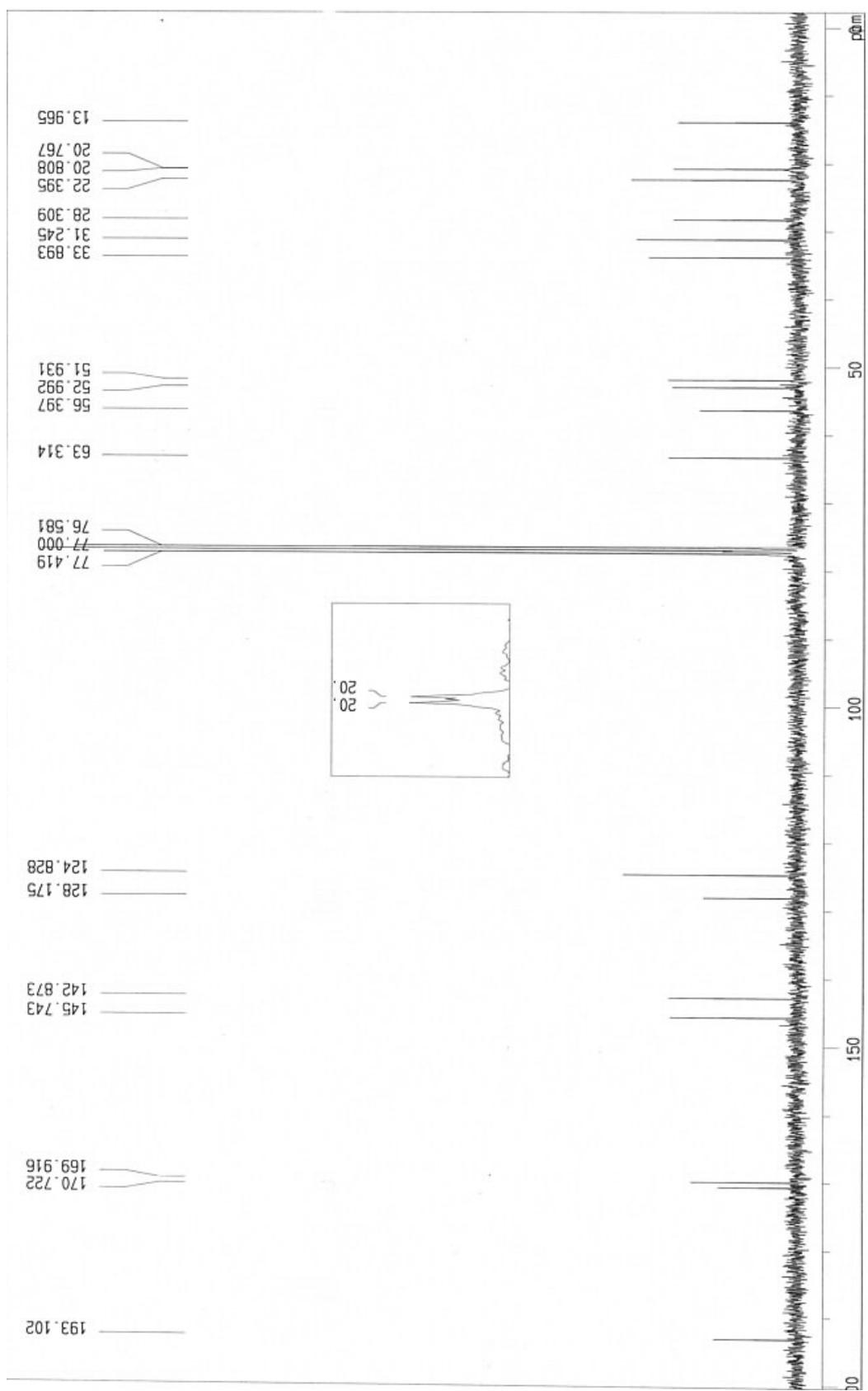
^1H NMR (300 MHz, $\text{CDCl}_3 + \text{CD}_3\text{OD}$) δ 6.56-6.48 (m, 1H), 6.36 (d, $J = 15.6$ Hz, 1H), 6.14-6.06 (m, 1H), 5.84-5.74 (m, 1H), 4.69 (br s, 1H), 4.66 (br s, 1H), 4.38 (br s, 2H), 3.50 (s, 2H), 2.10-2.03 (m, 2H), 1.45-1.33 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H)

^{13}C NMR (75 MHz, $\text{CDCl}_3 + \text{CD}_3\text{OD}$) 137.2, 132.5, 132.4, 131.6, 130.7, 124.9, 66.3, 62.6, 58.3, 54.4, 53.7, 34.8, 22.3, 13.6

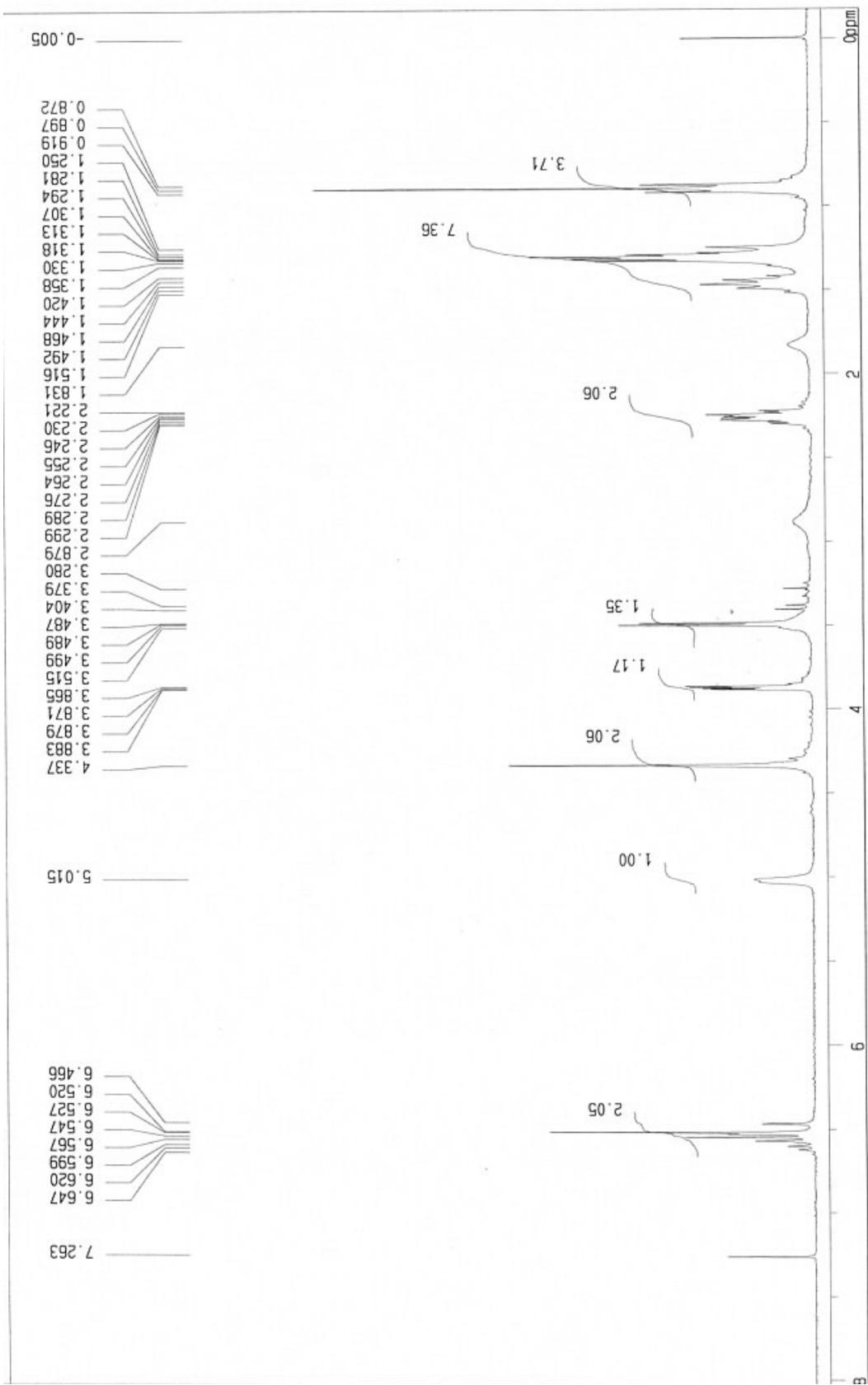
HRMS (ES) m/z calcd for $\text{C}_{14}\text{H}_{20}\text{KO}_4$ $[\text{M} + \text{K}]^+$ 291.0999, found 291.1001



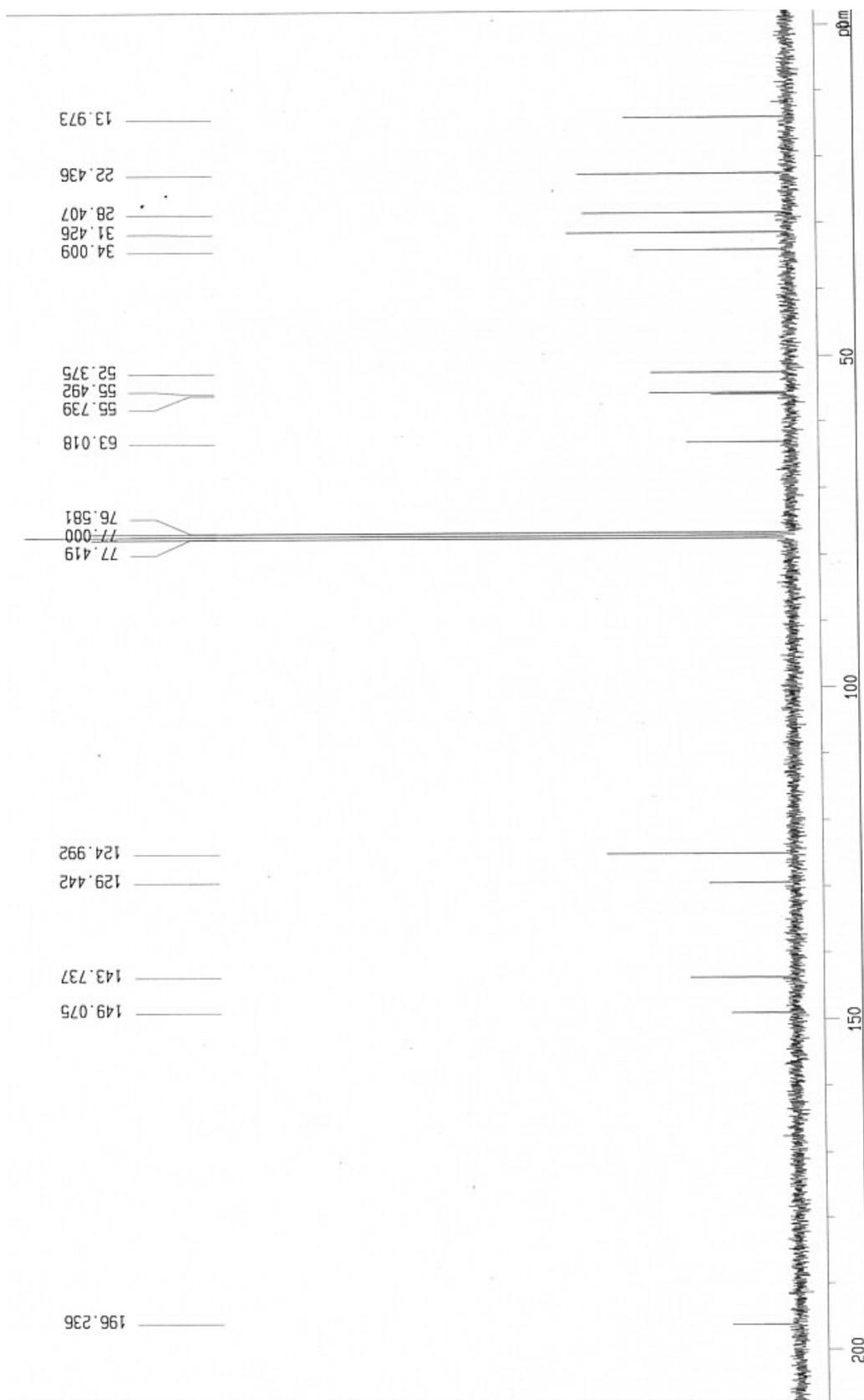
^1H NMR (300 MHz, CDCl_3) of 14



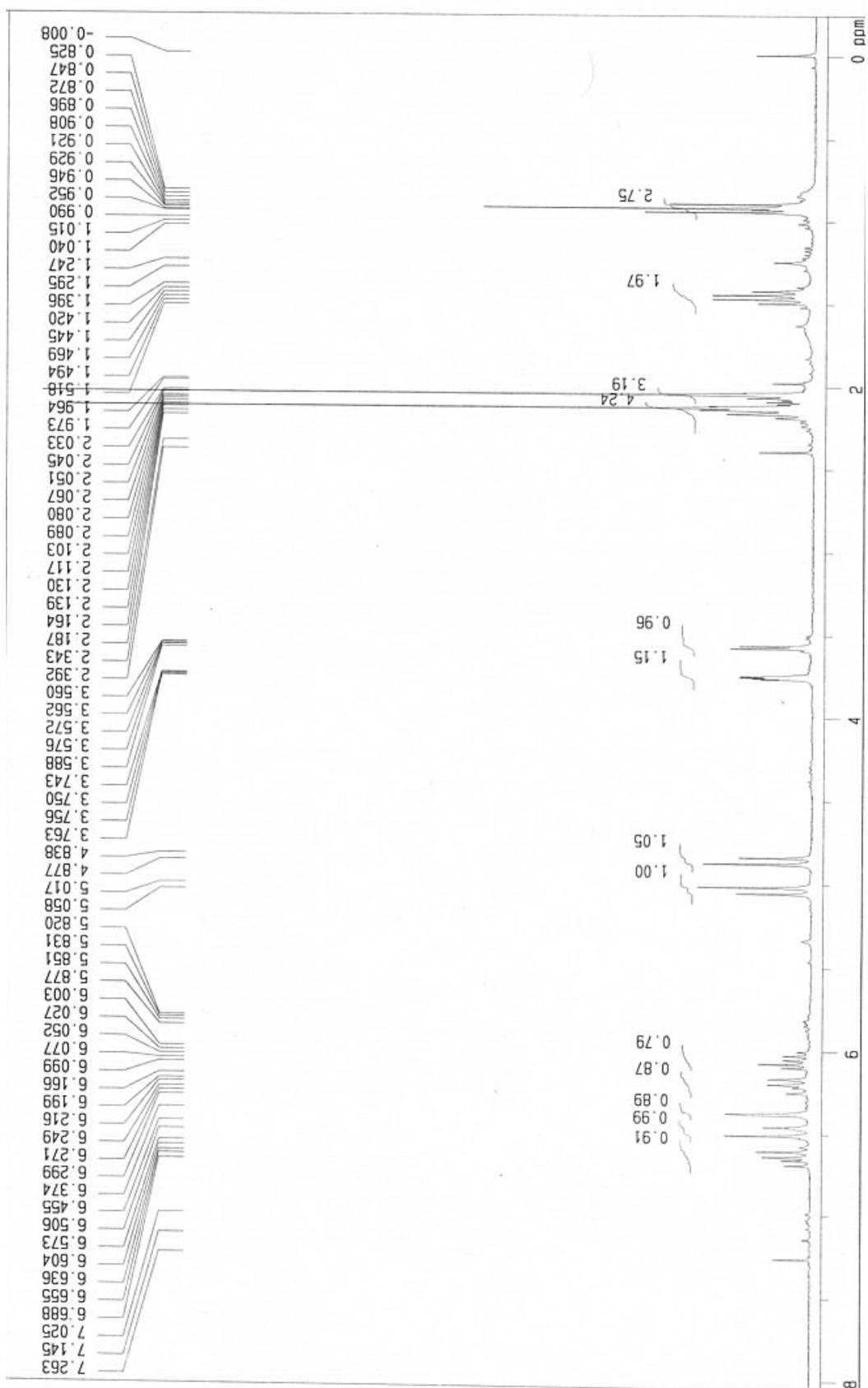
¹³C NMR (75 MHz, CDCl₃) of 14



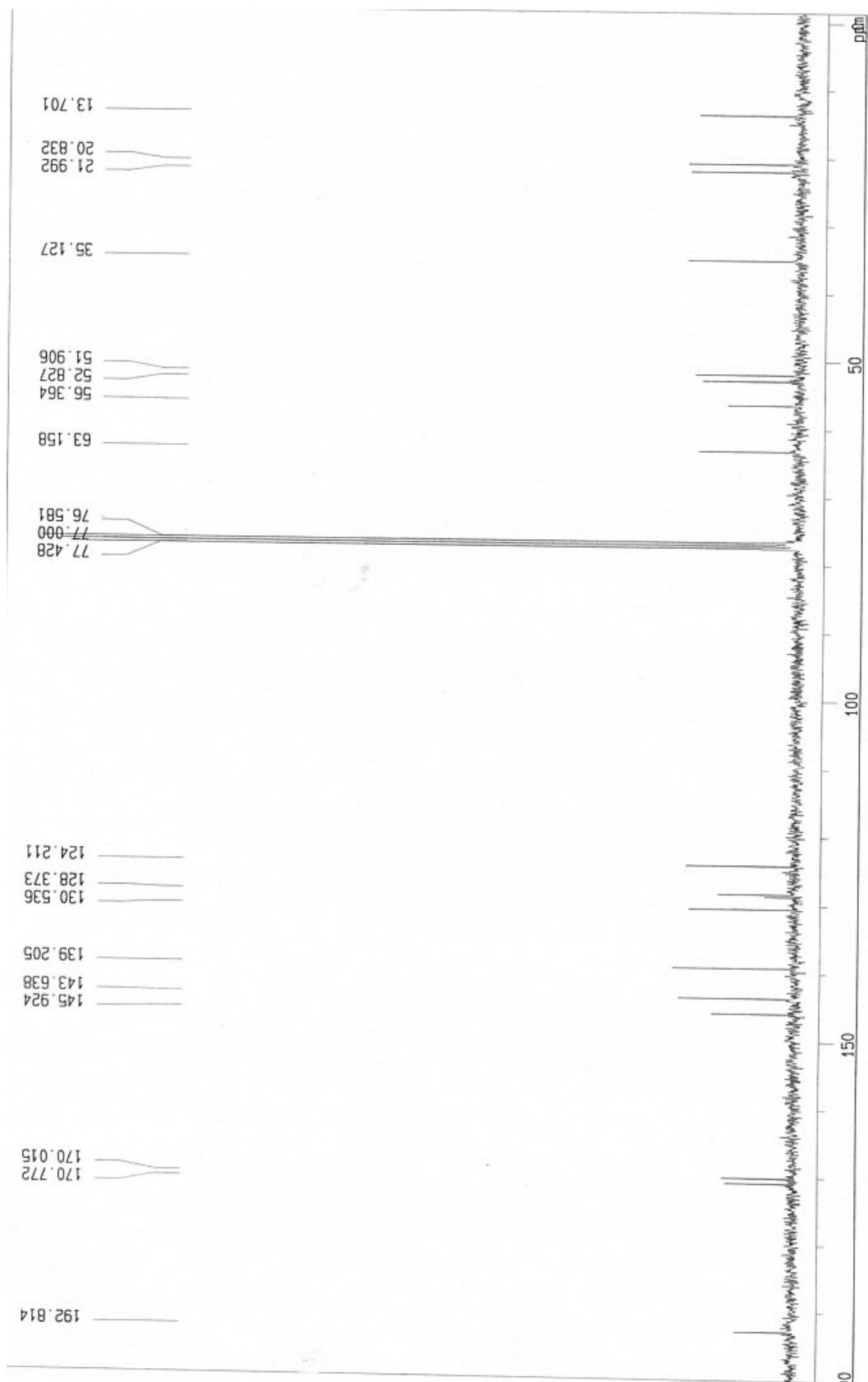
¹H NMR (300 MHz, CDCl₃) of 15



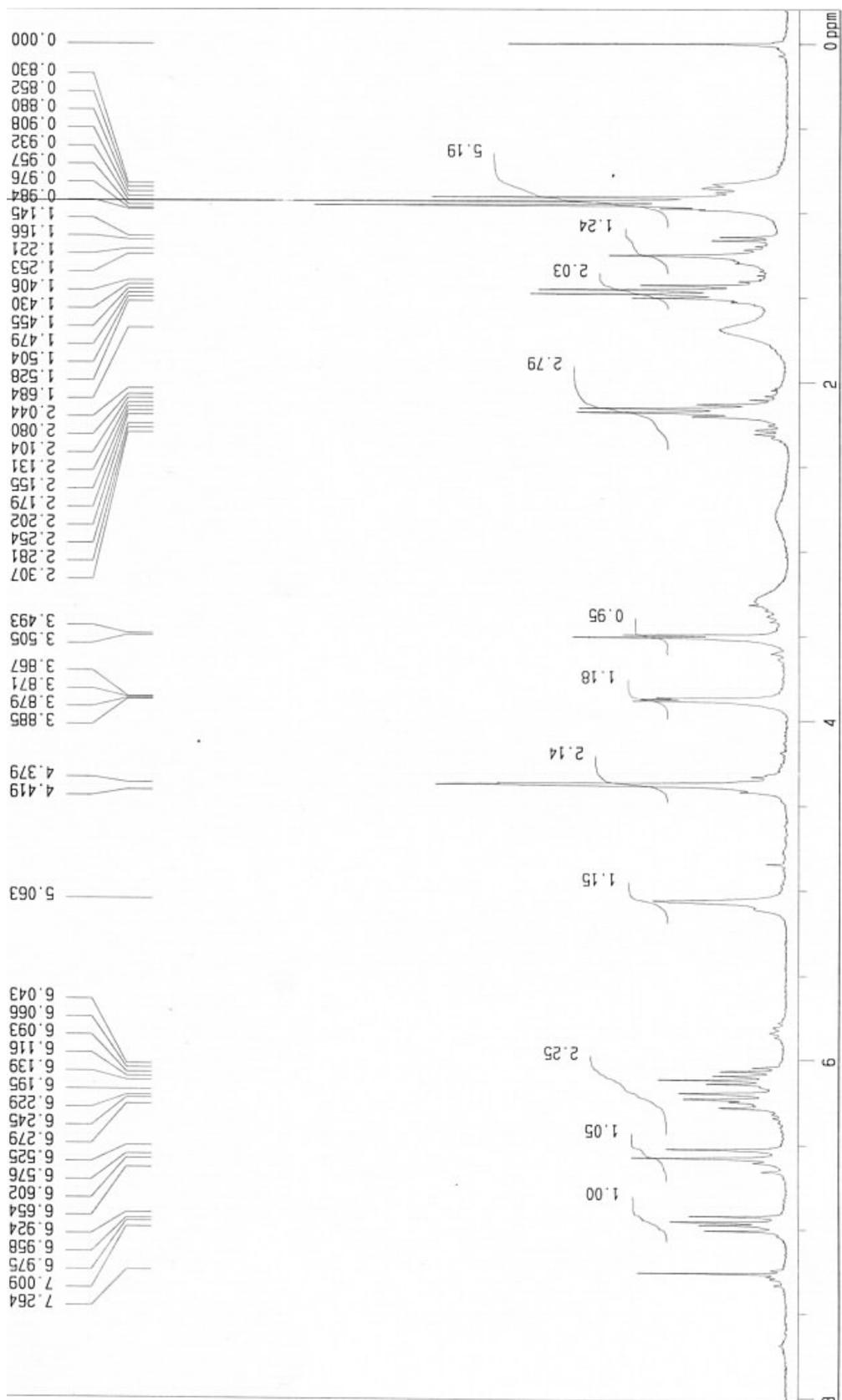
¹³C NMR (75 MHz, CDCl₃) of 15



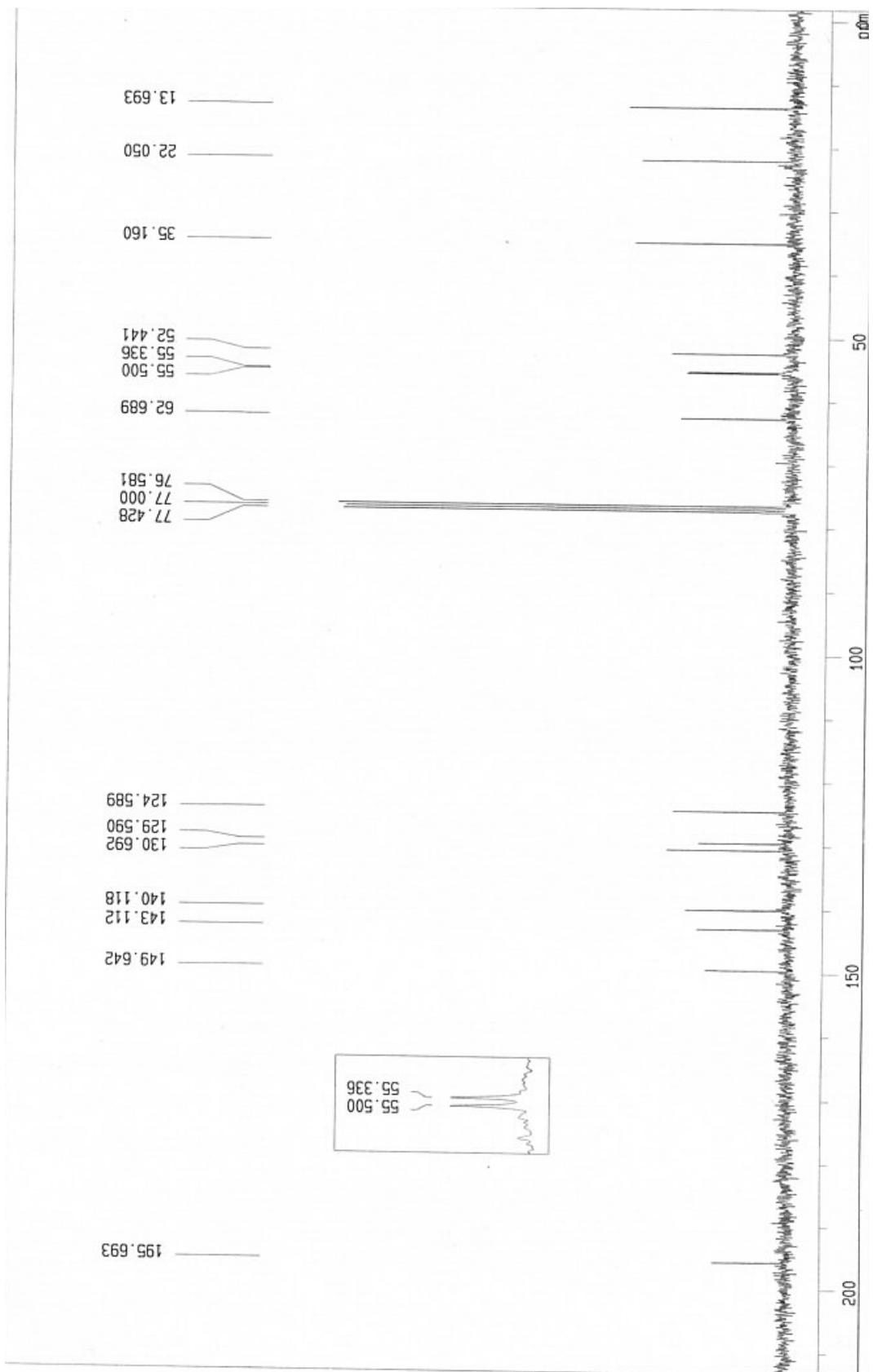
^1H NMR (300 MHz, CDCl_3) of 16



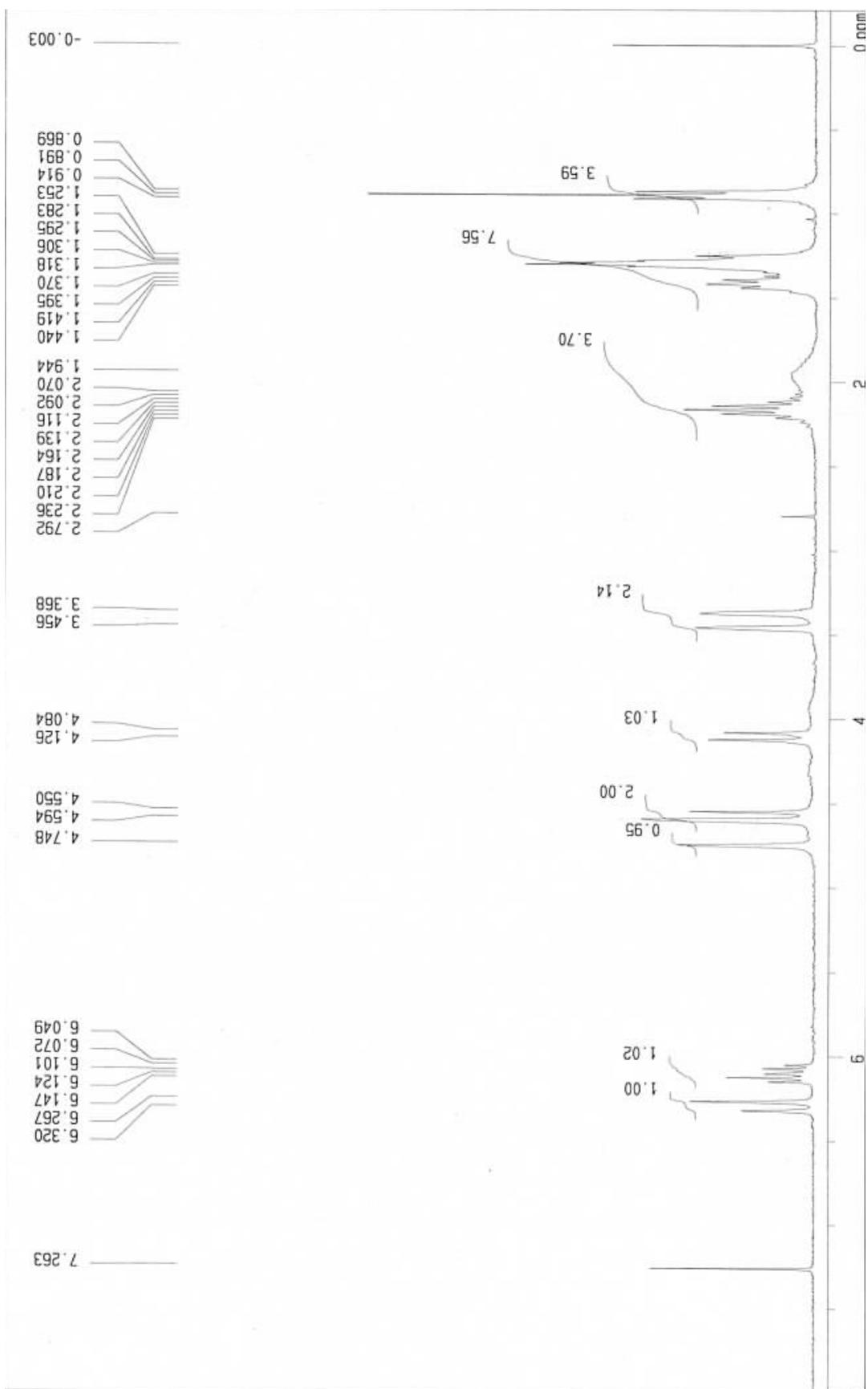
^{13}C NMR (75 MHz, CDCl_3) of 16



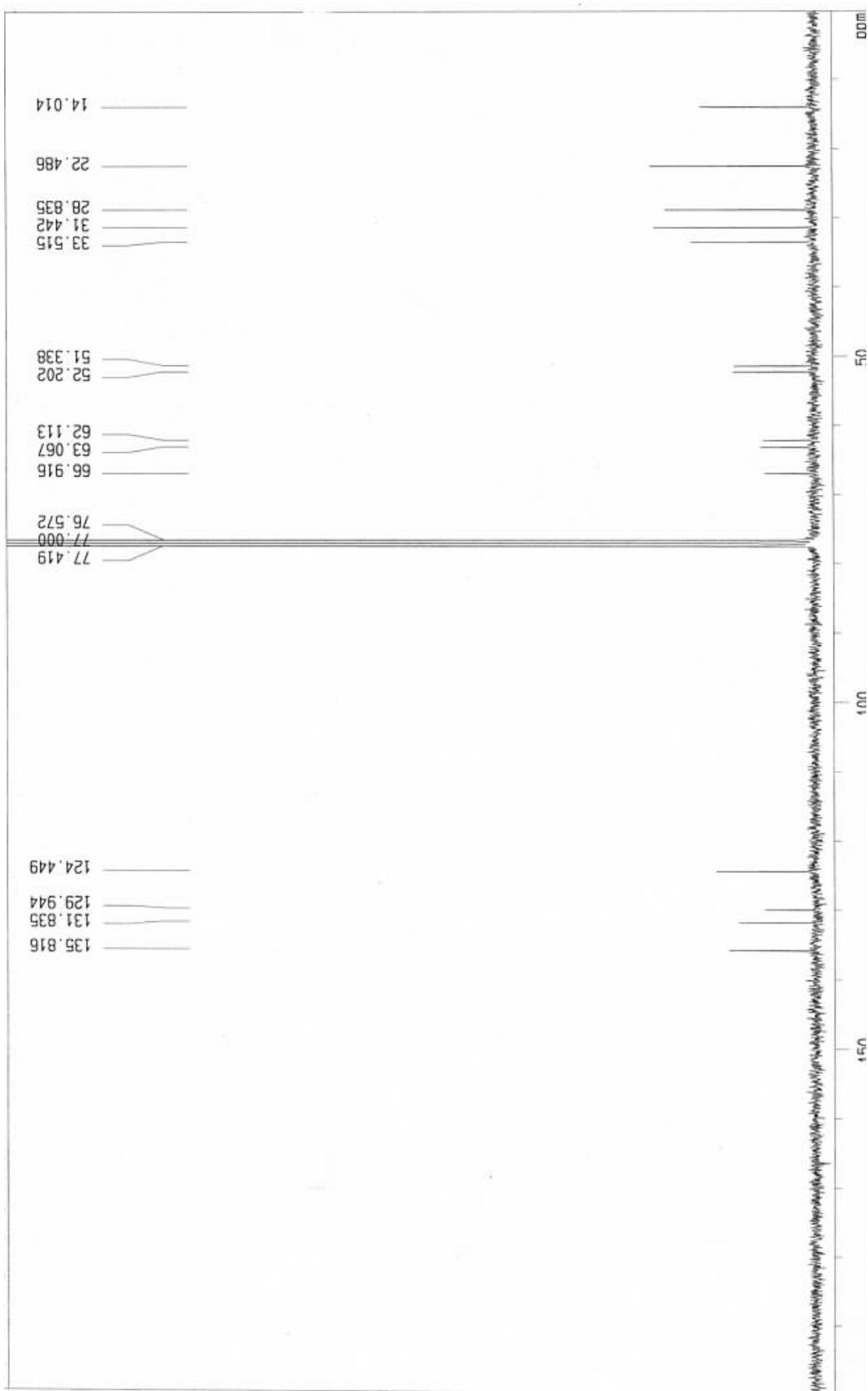
^1H NMR (300 MHz, CDCl_3) of 17



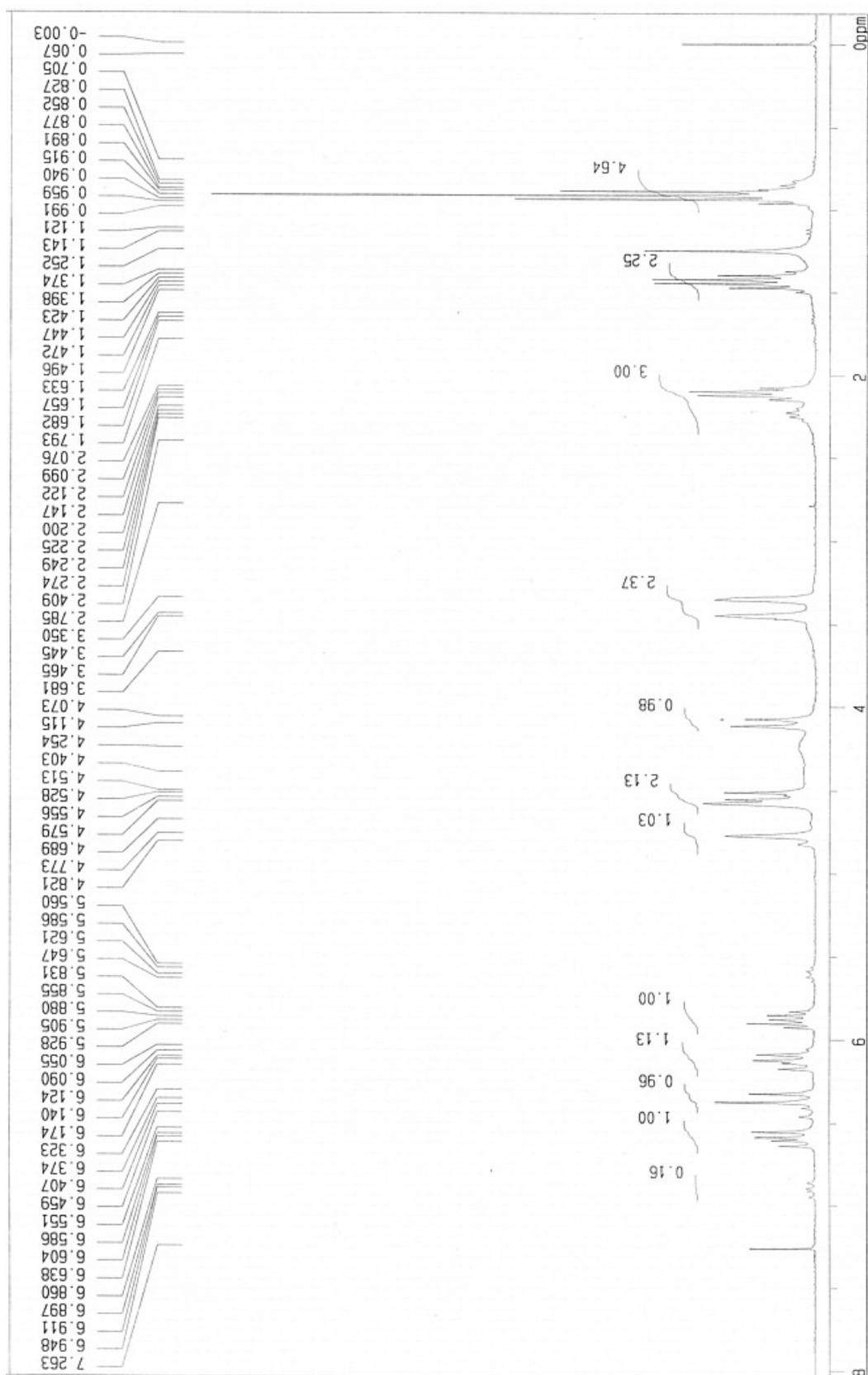
^{13}C NMR (75 MHz, CDCl_3) of 17



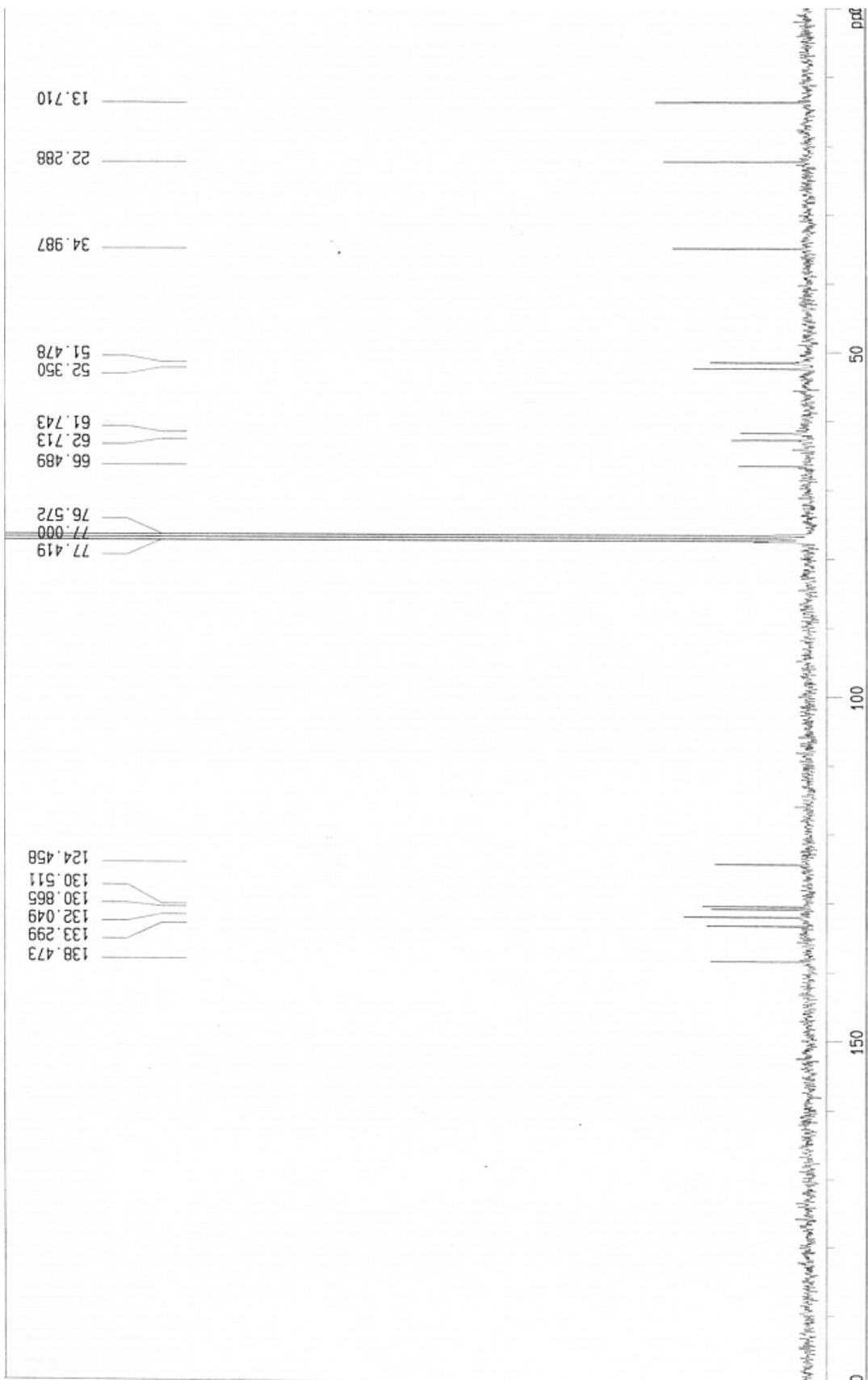
^1H NMR (300 MHz, CDCl_3) of 1



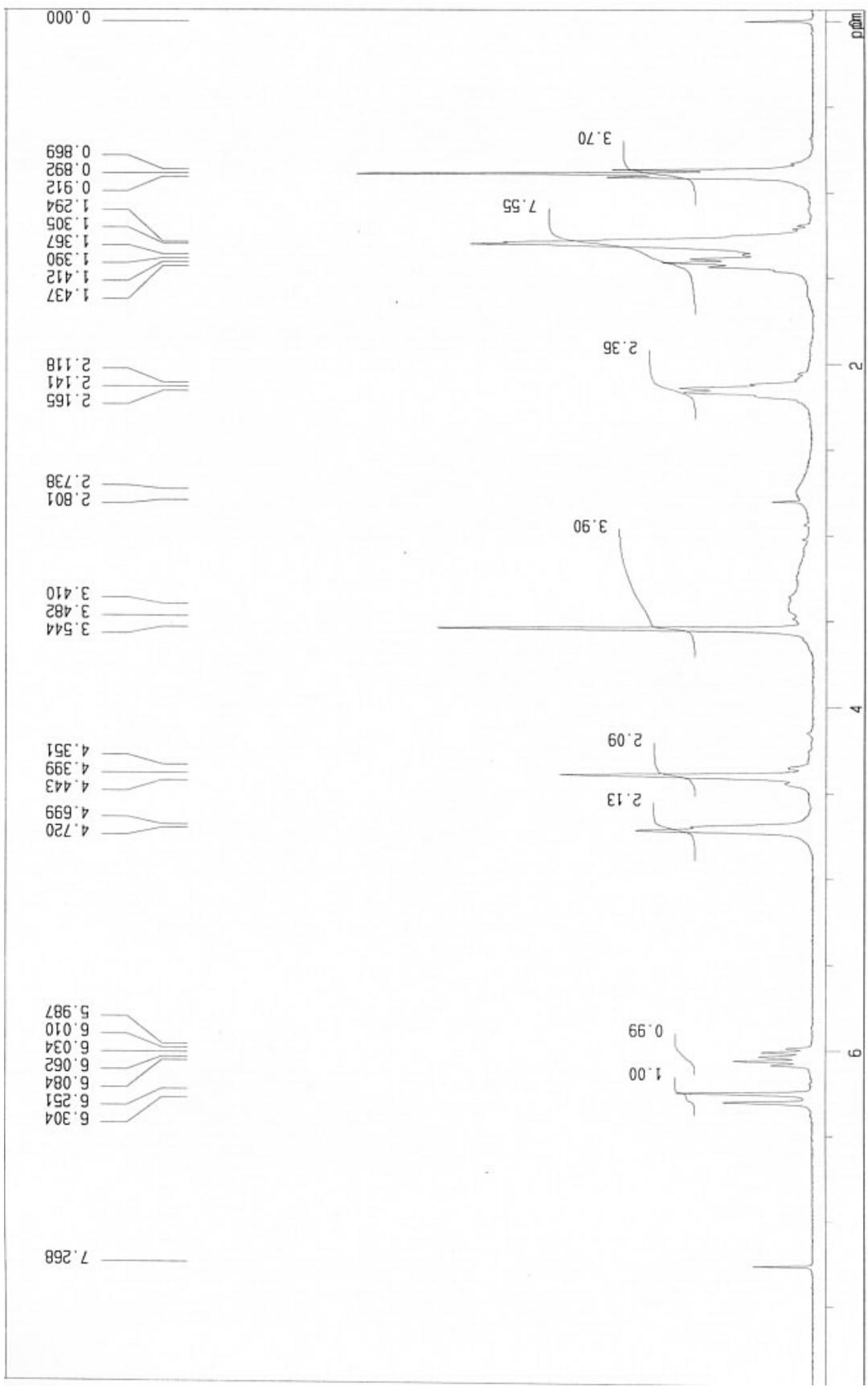
^{13}C NMR (75 MHz, CDCl₃) of 1



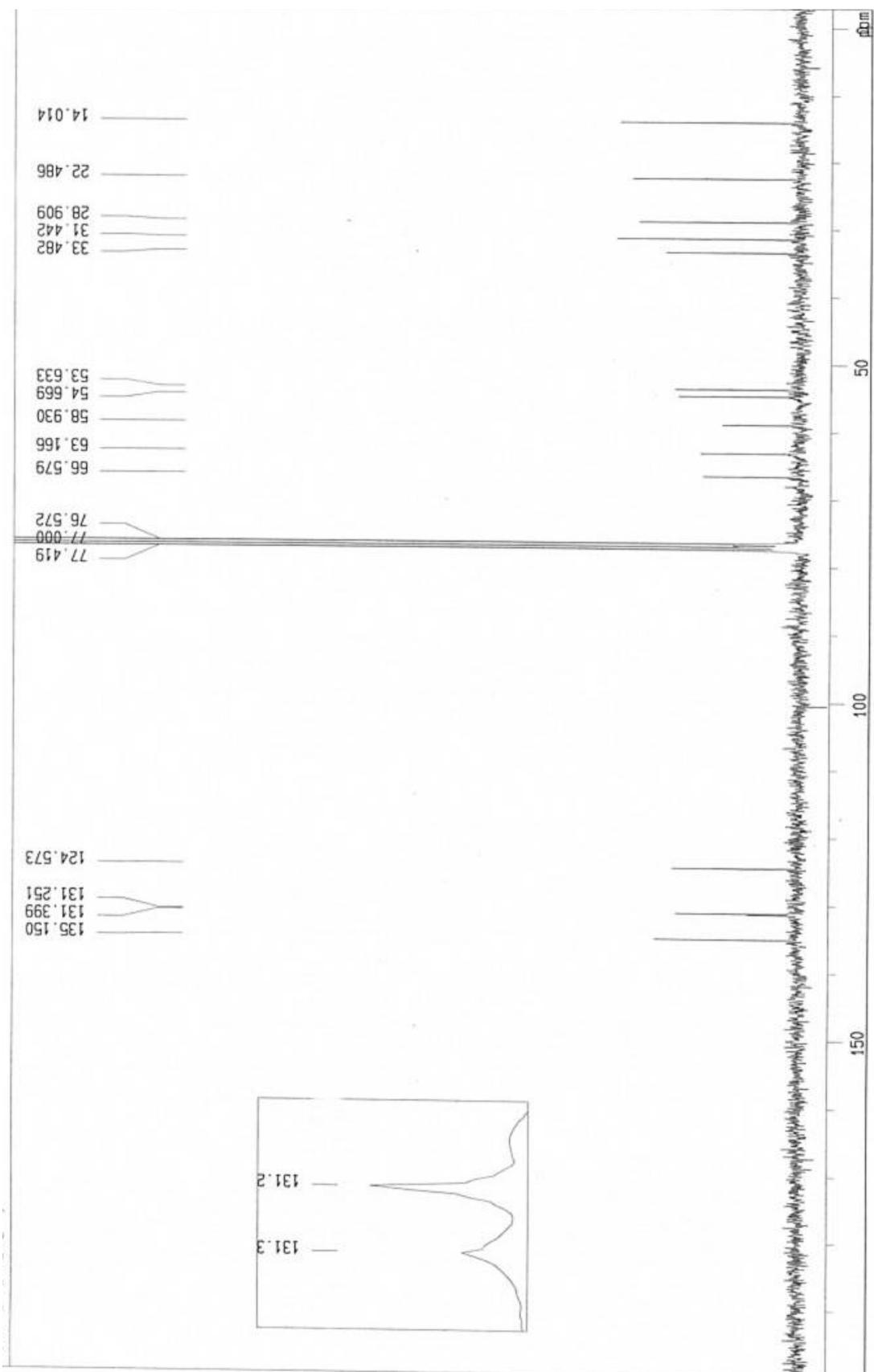
^1H NMR (300 MHz, CDCl_3) of 2



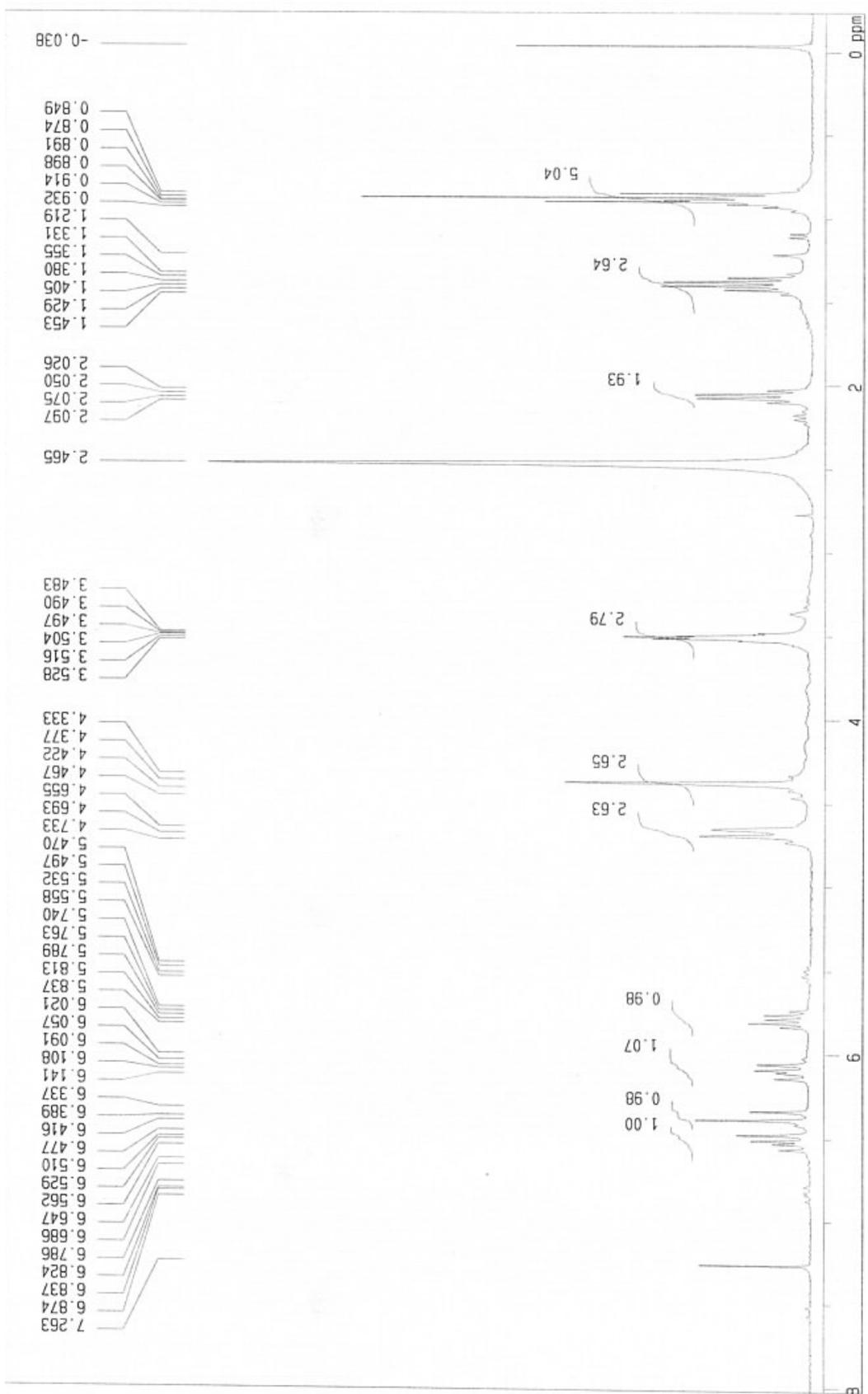
^{13}C NMR (75 MHz, CDCl_3) of 2



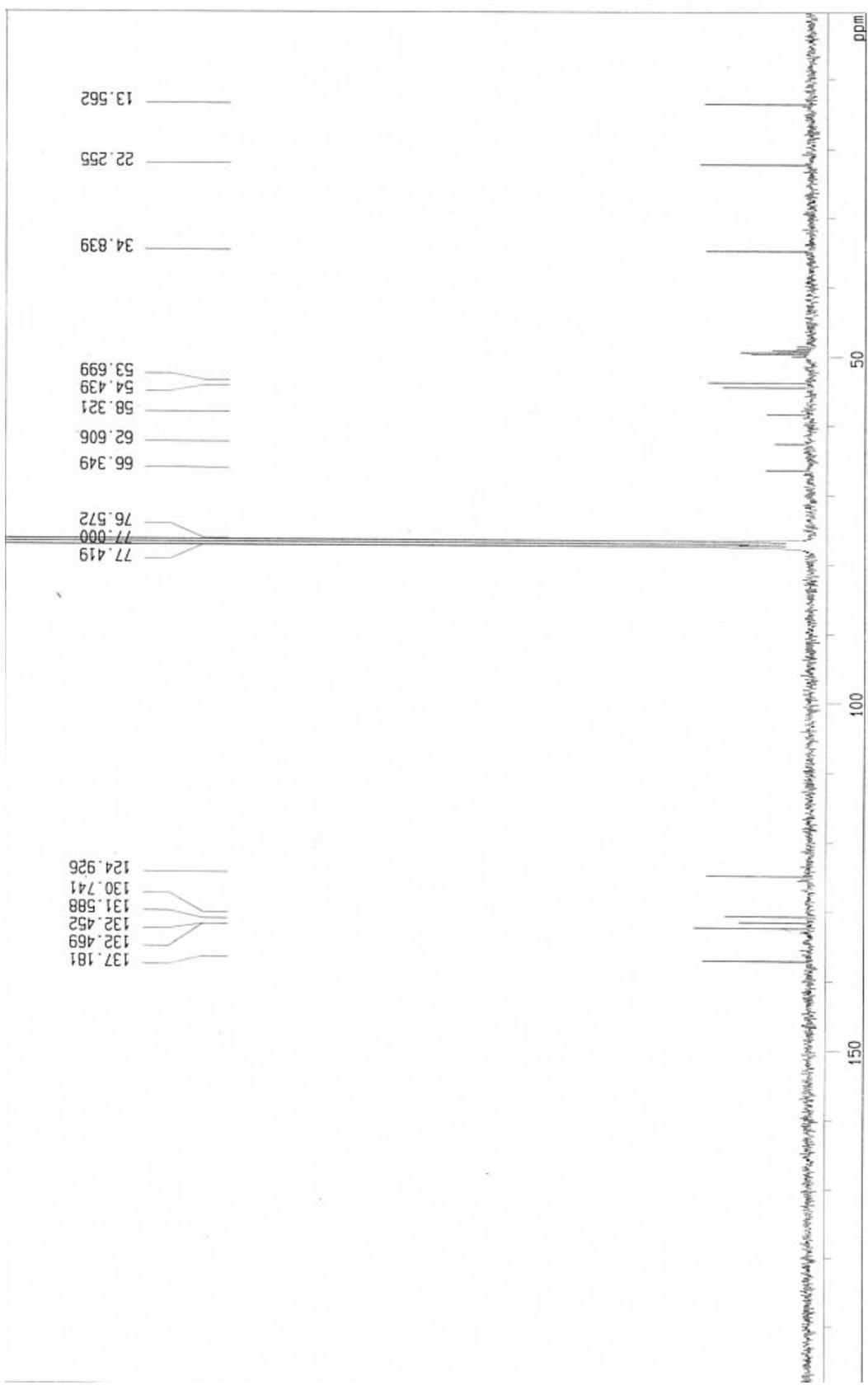
^1H NMR (300 MHz, CDCl_3) of 3



¹³C NMR (75 MHz, CDCl₃) of 3



¹H NMR (300 MHz, CDCl₃+CD₃OD) of 4



¹³C NMR (75 MHz, CDCl₃+CD₃OD) of 4