Electronic supplementary information

Water-promoted *ortho*-selective monohydroxymethylation of phenols in $NaBO_2$ system

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2. General Information

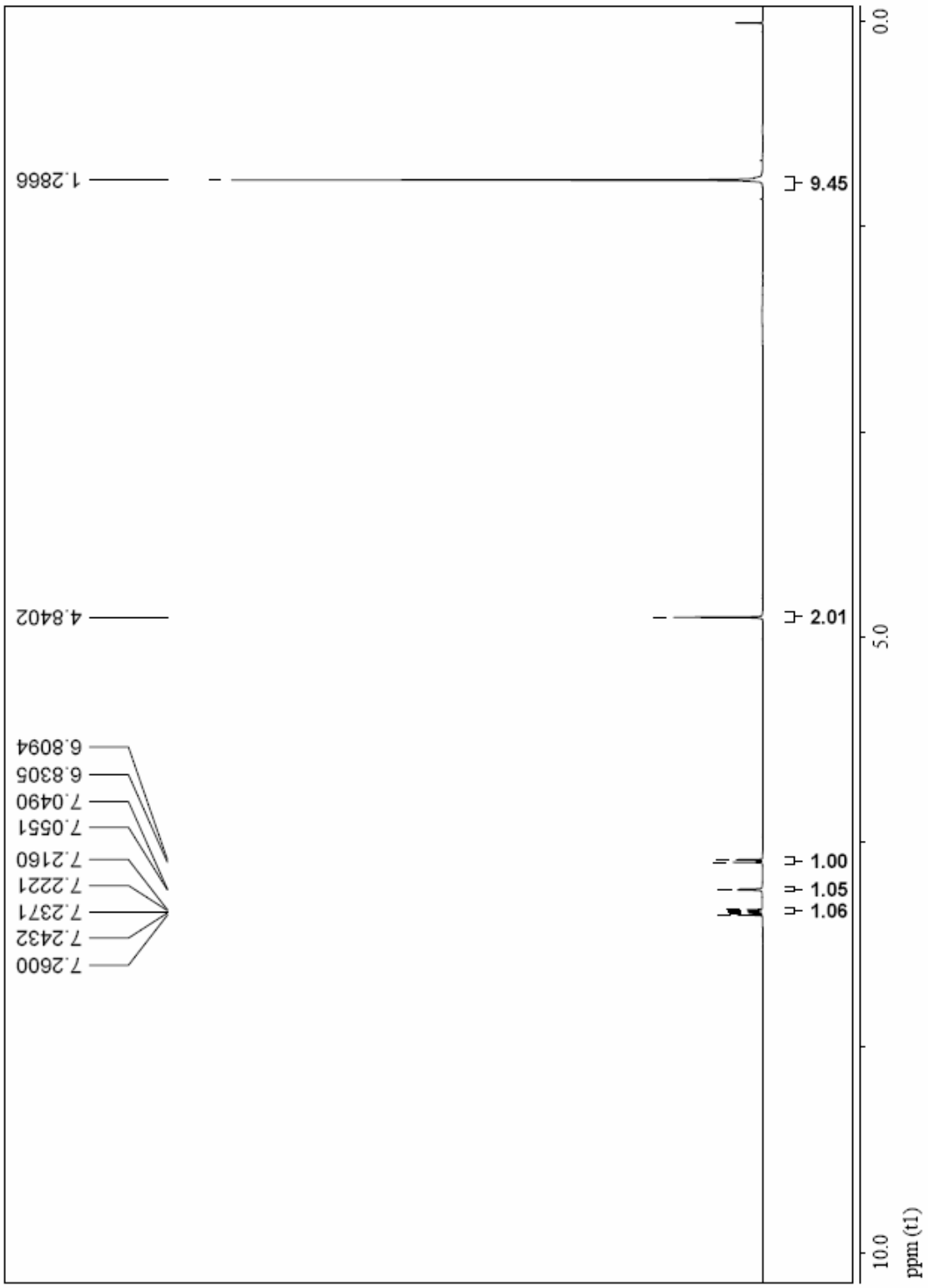
Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Where necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under argon. Organic extracts were, in general, dried over anhydrous sodium sulfate (Na_2SO_4). TLC plates were visualized by exposure to ultraviolet light (UV). Chemical shifts for protons are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents ($CHCl_3$: δ 7.26; DMSO-d_6: δ 2.50). Chemical shifts for carbon resonances are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0; DMSO-d_6: δ 39.43). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant in Hz. Coupling constants (*J*) are reported in Hertz (Hz).

3. NMR Spectra

3a. NMR spectra of salicyl alcohol **2a–t**

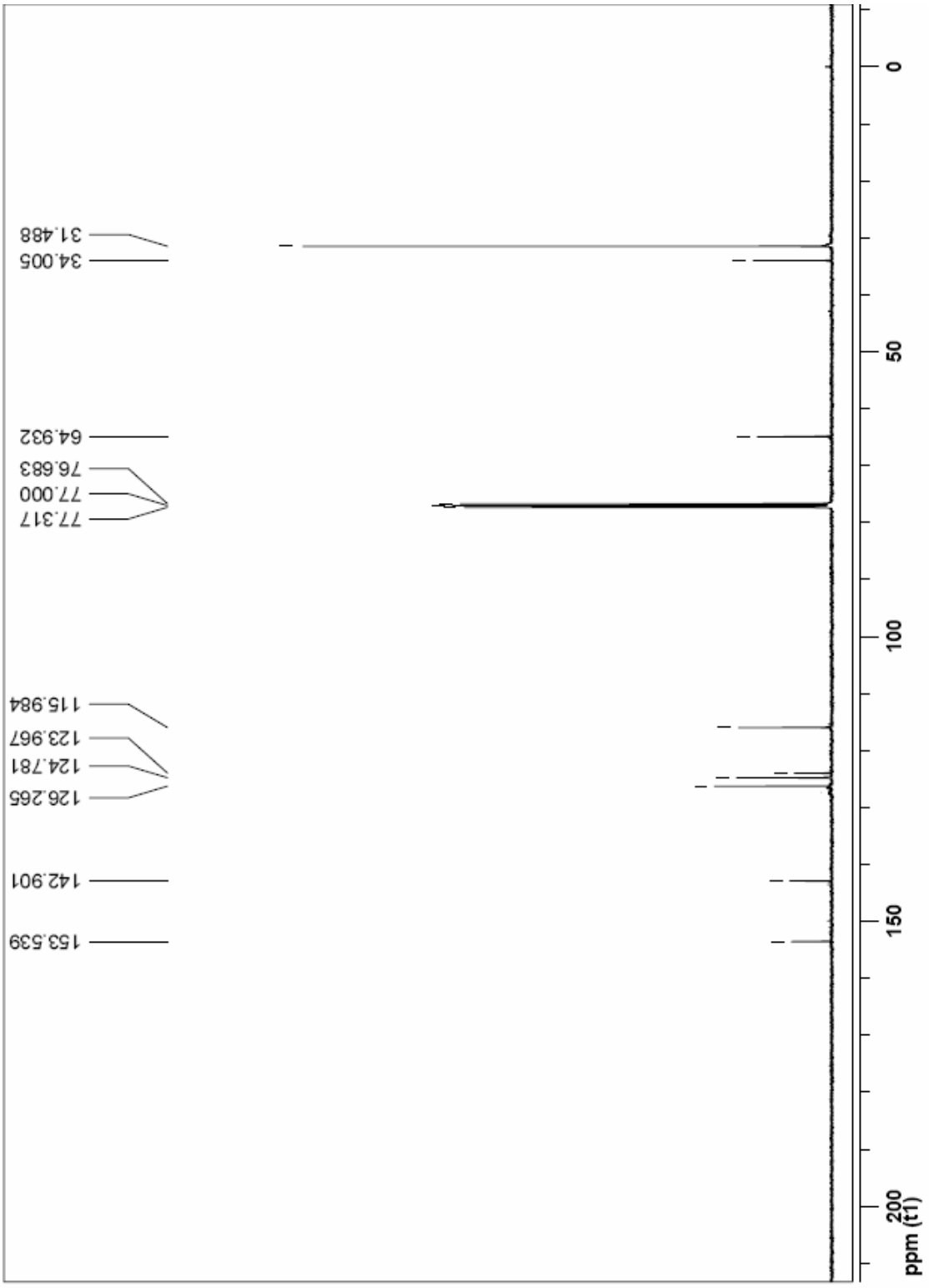
Salicyl alcohol **2a**

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



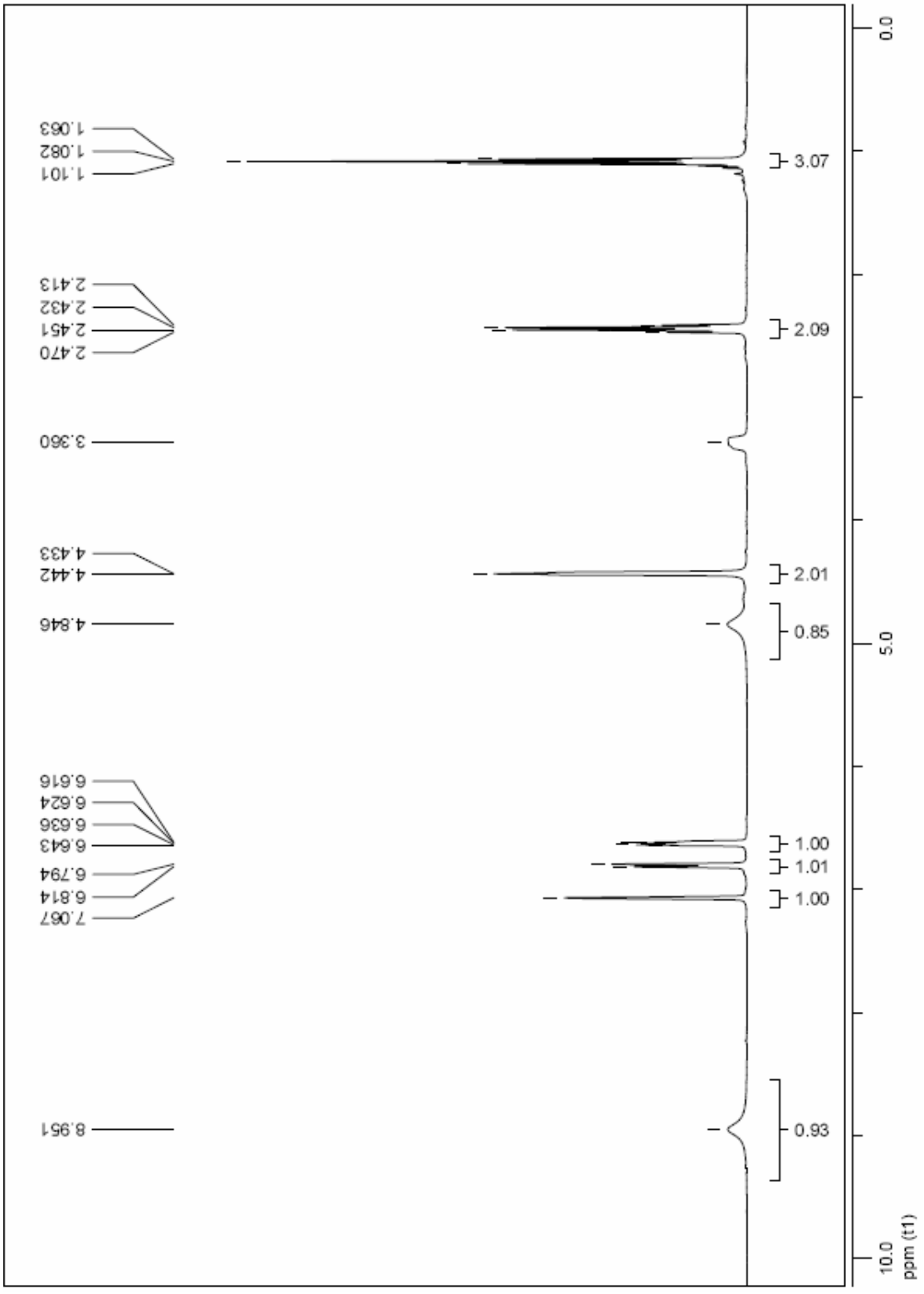
Salicyl alcohol **2a**

^{13}C NMR (100 MHz, $CDCl_3$)



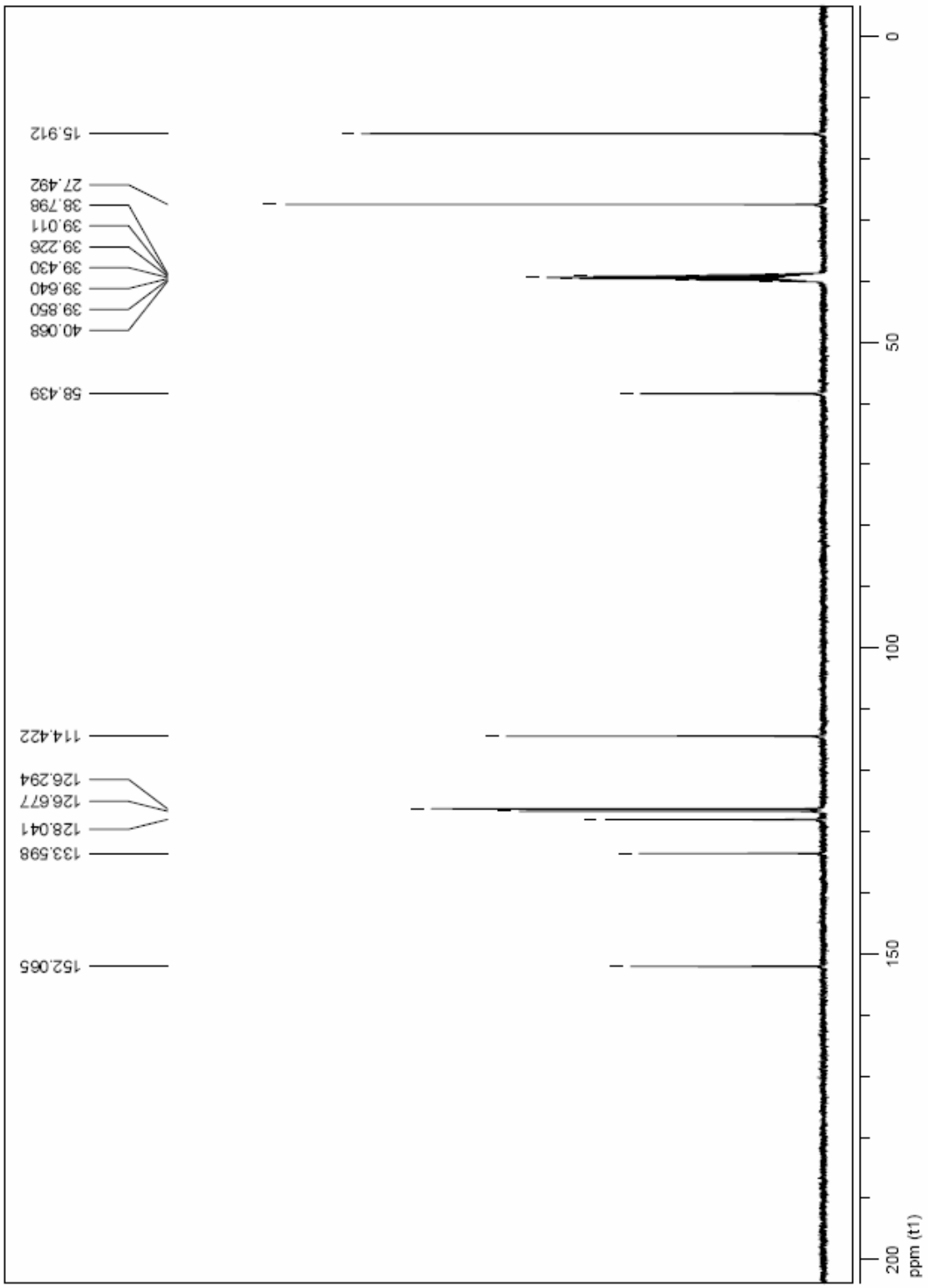
Salicyl alcohol **2b**

^{1}H NMR (400 MHz, DMSO-d_6)



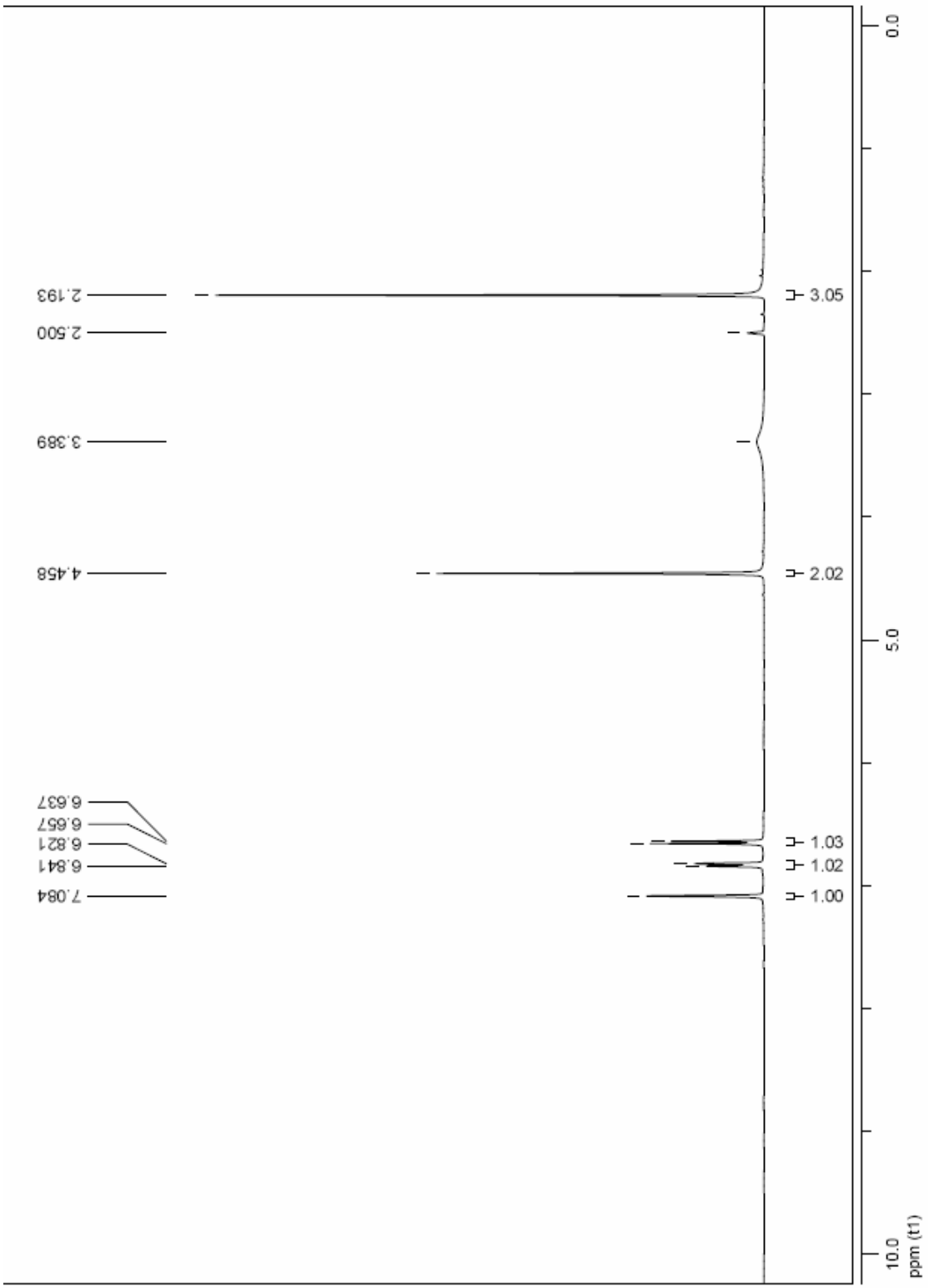
Salicyl alcohol **2b**

^{13}C NMR (100 MHz, DMSO-d_6)



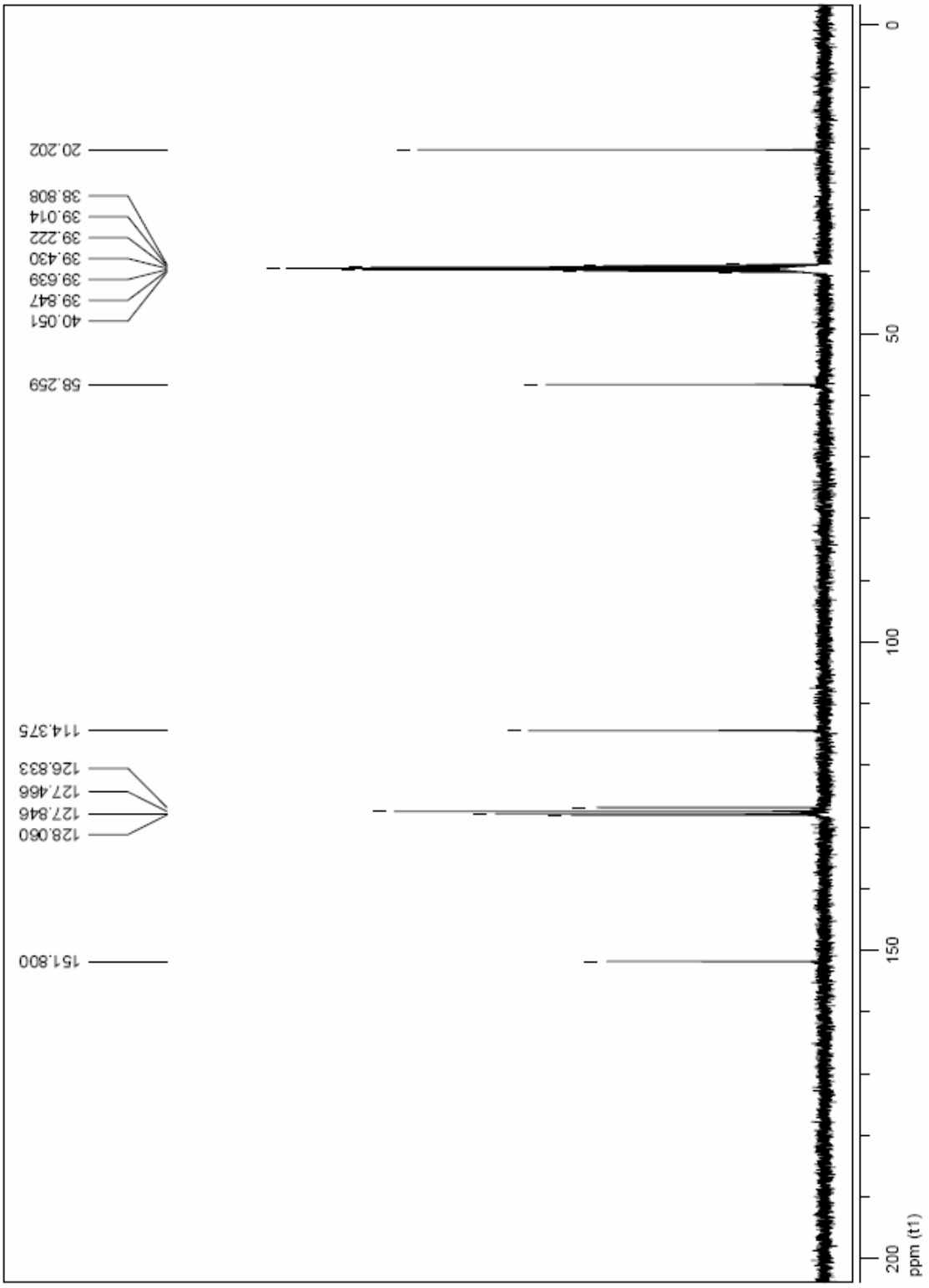
Salicyl alcohol **2c**

^{1}H NMR (400 MHz, DMSO-d_6)



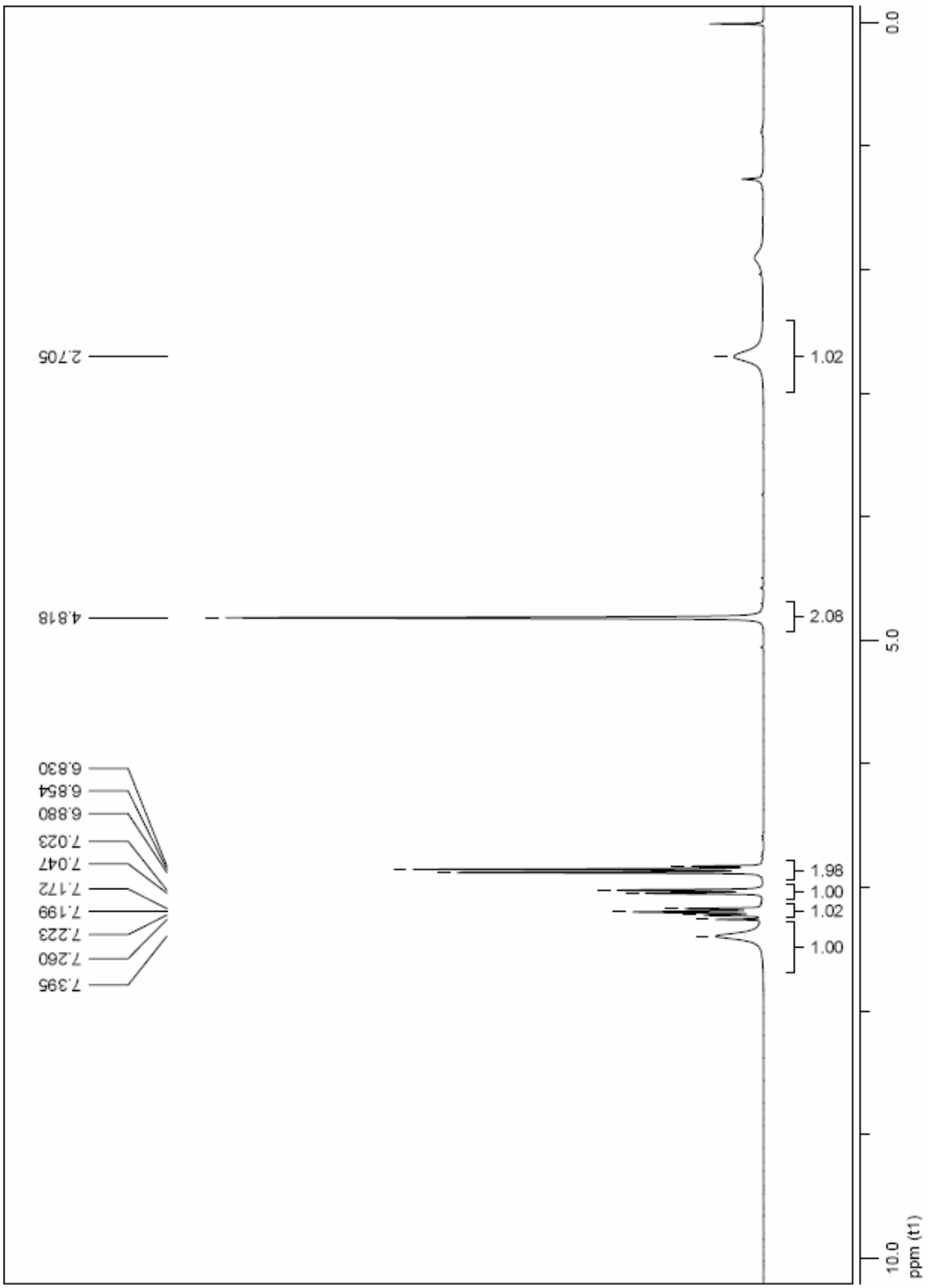
Salicyl alcohol **2c**

^{13}C NMR (100 MHz, DMSO-d_6)



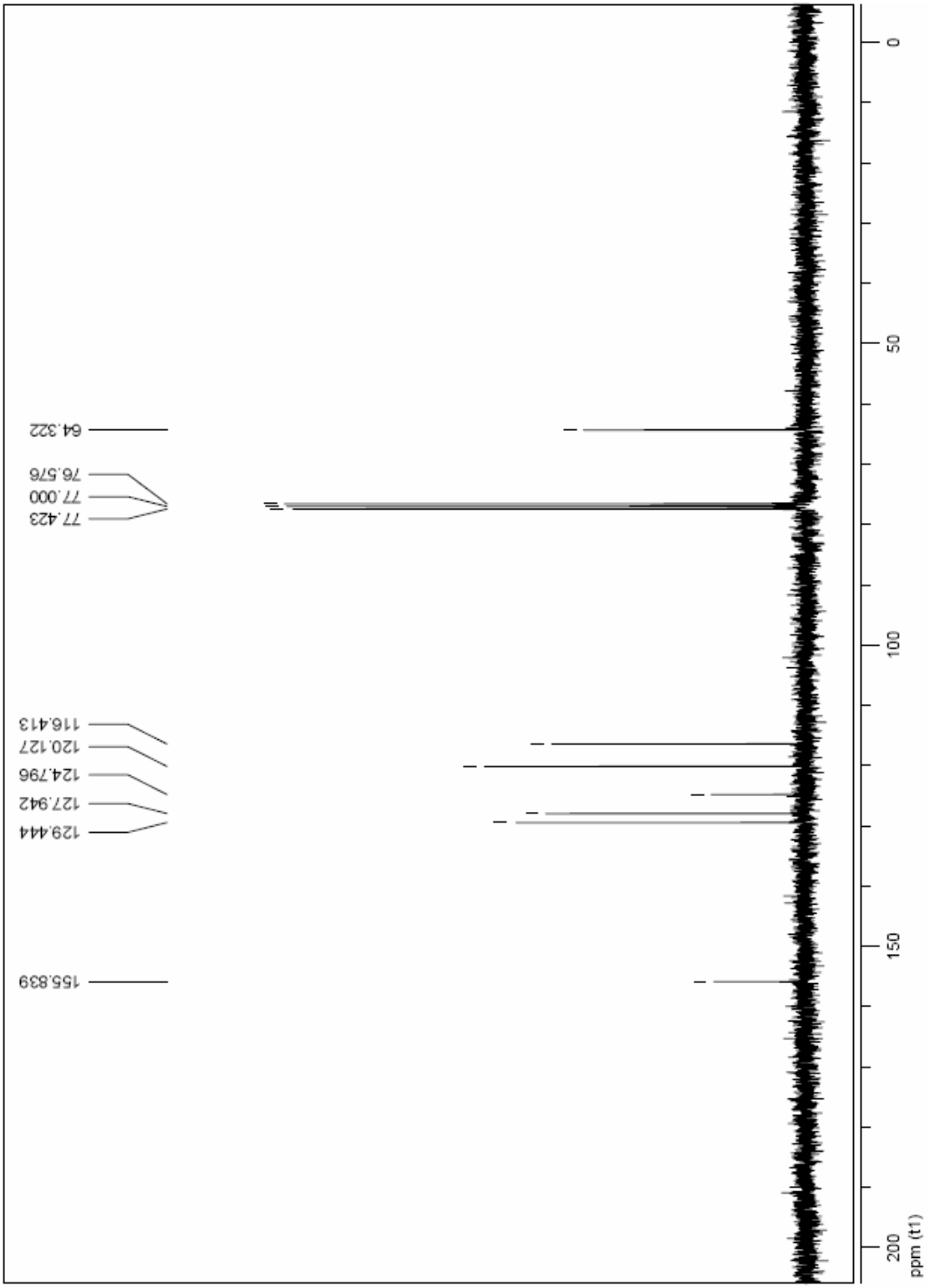
Salicyl alcohol **2d**

^{1}H NMR (300 MHz, $CDCl_3$)



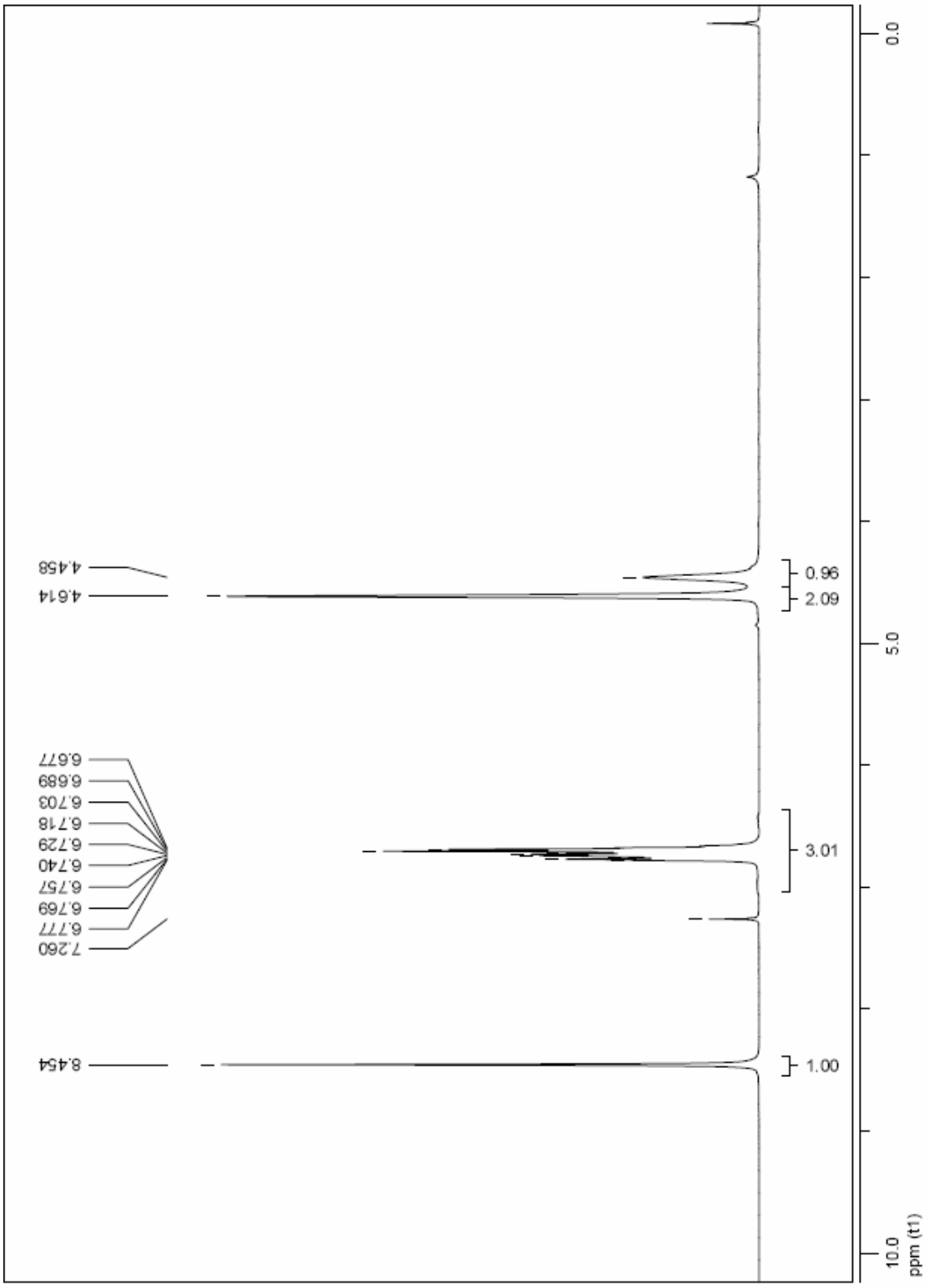
Salicyl alcohol **2d**

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



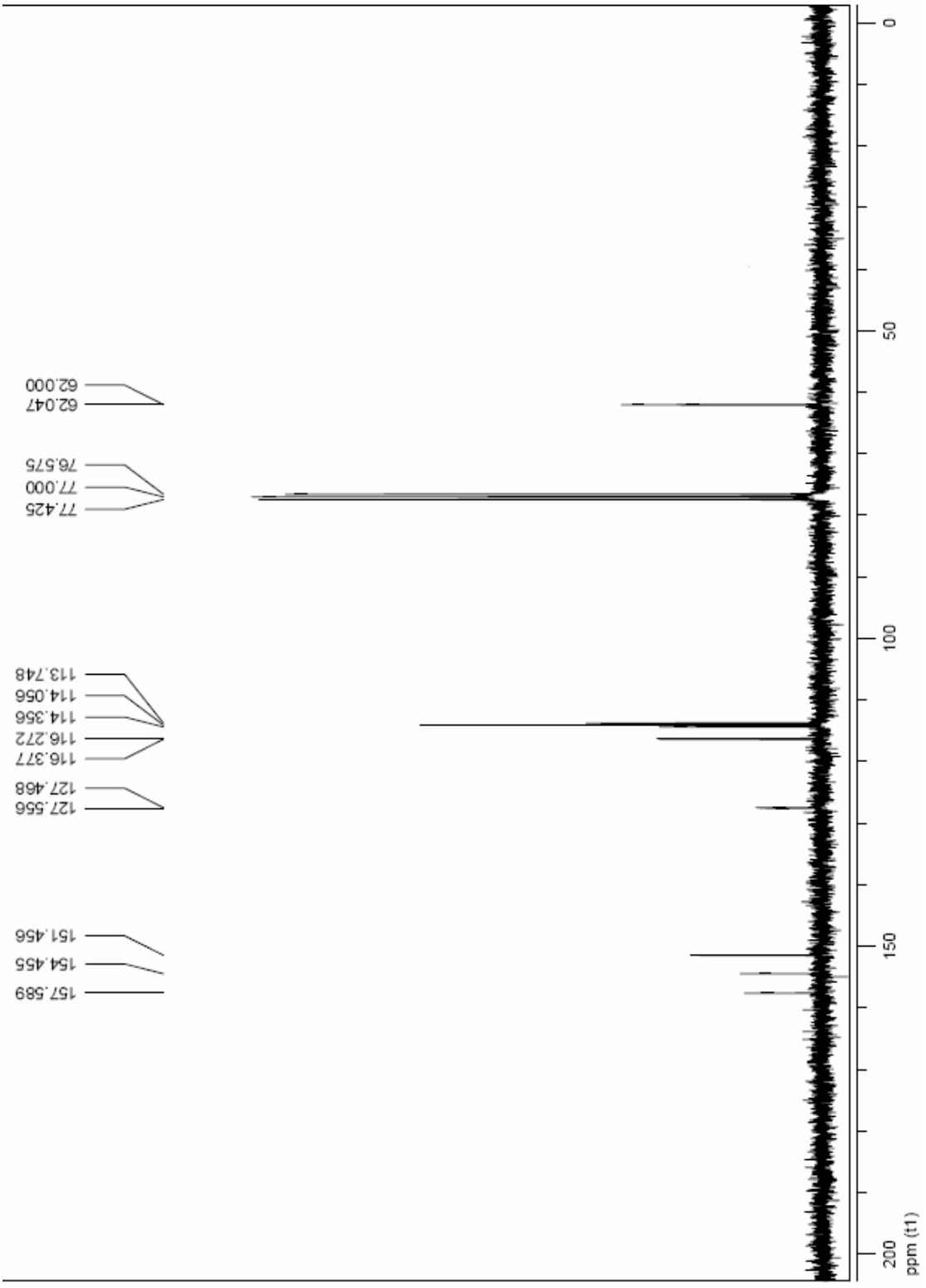
Salicyl alcohol **2e**

^{1}H NMR (300 MHz, $CDCl_3$)



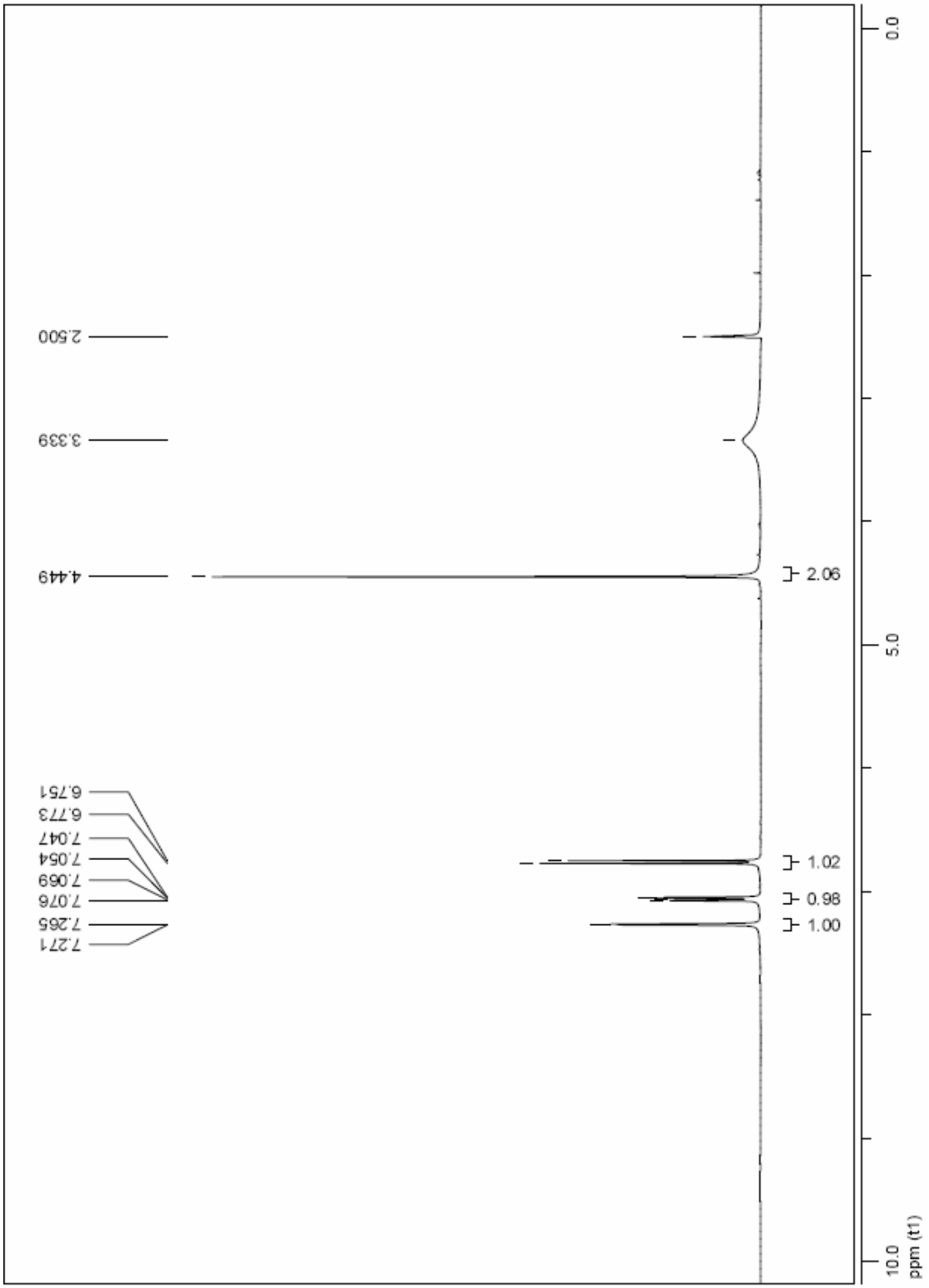
Salicyl alcohol **2e**

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



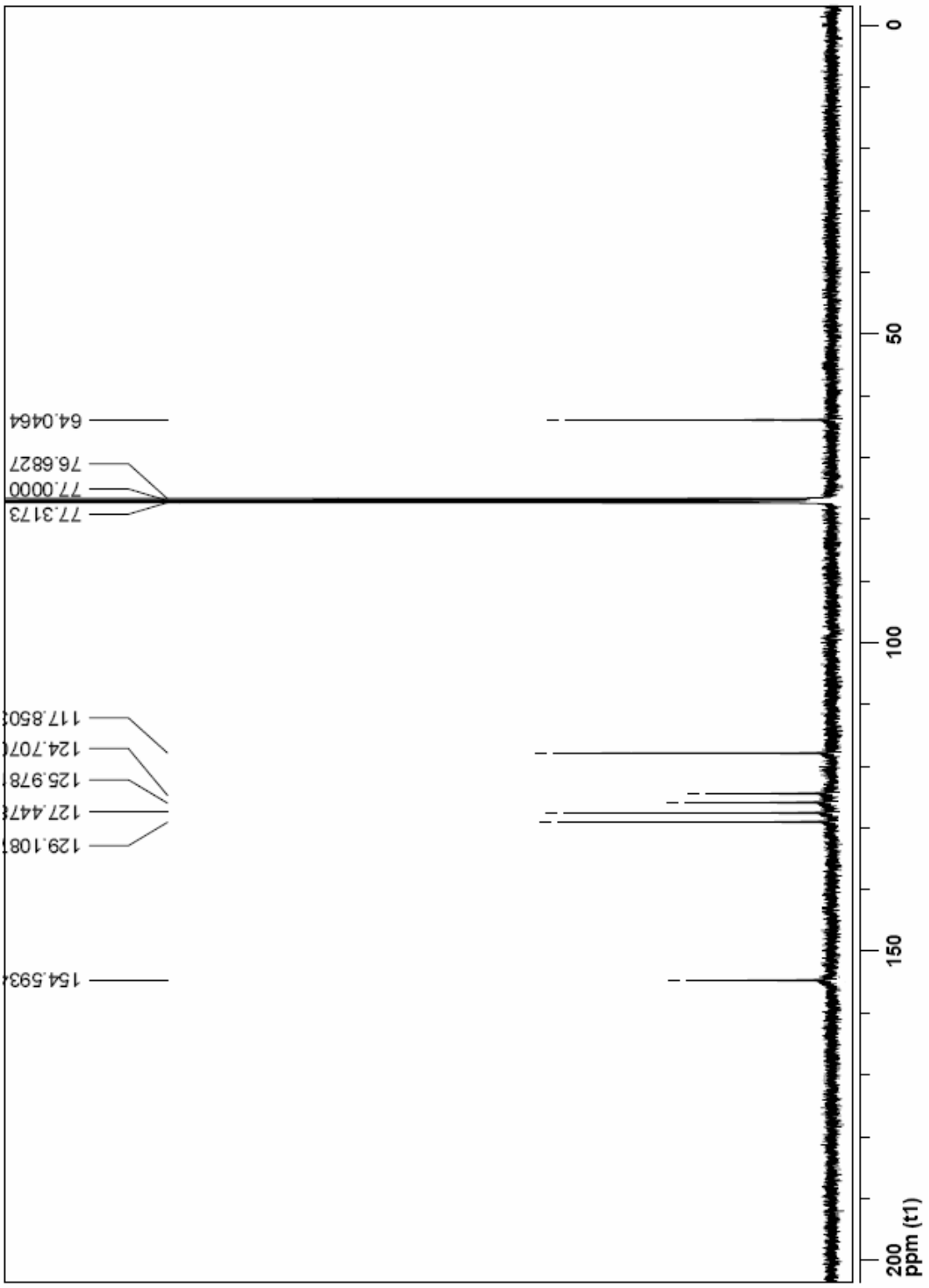
Salicyl alcohol **2f**

^{1}H NMR (400 MHz, DMSO-d_6)



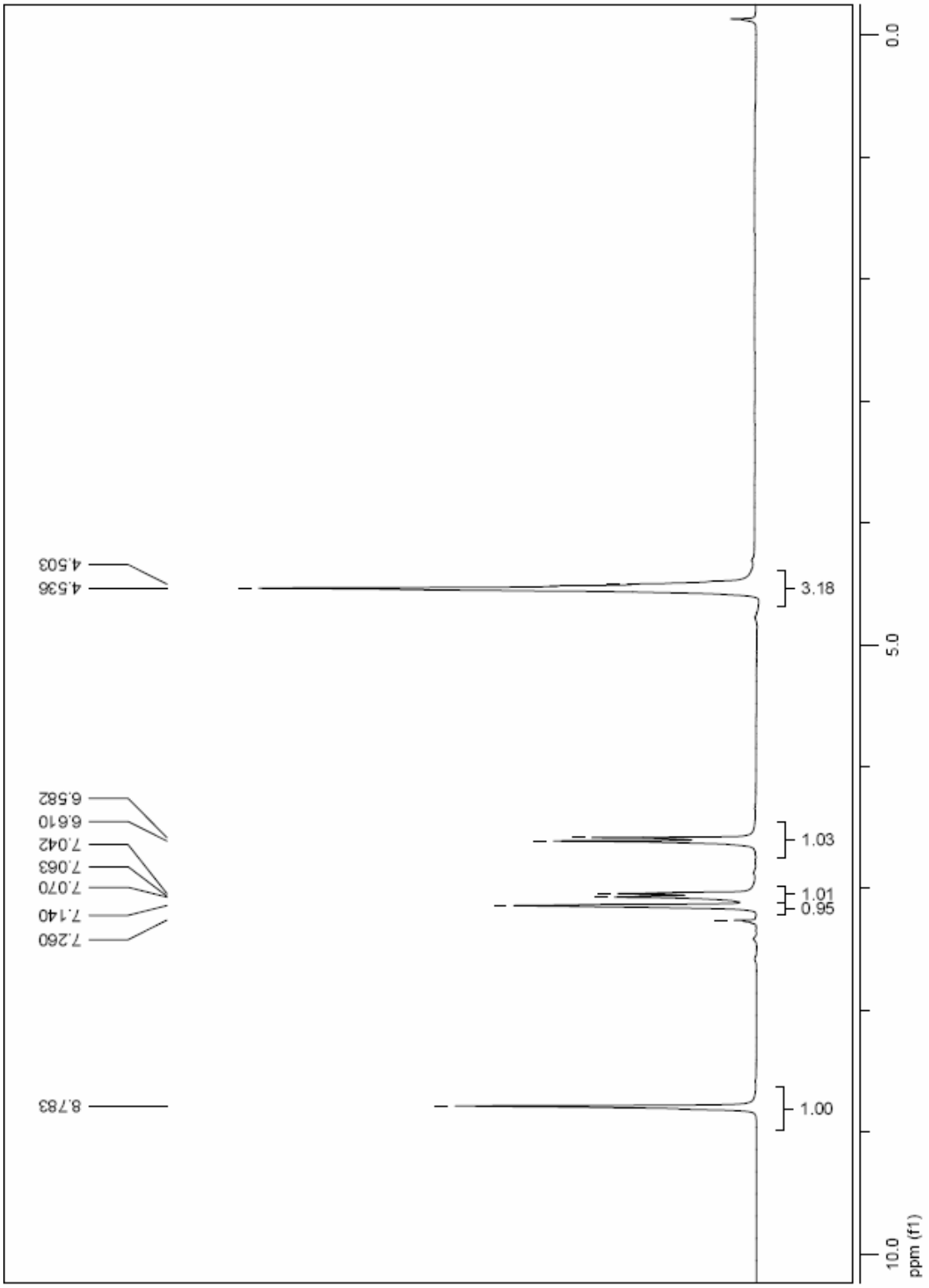
Salicyl alcohol **2f**

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



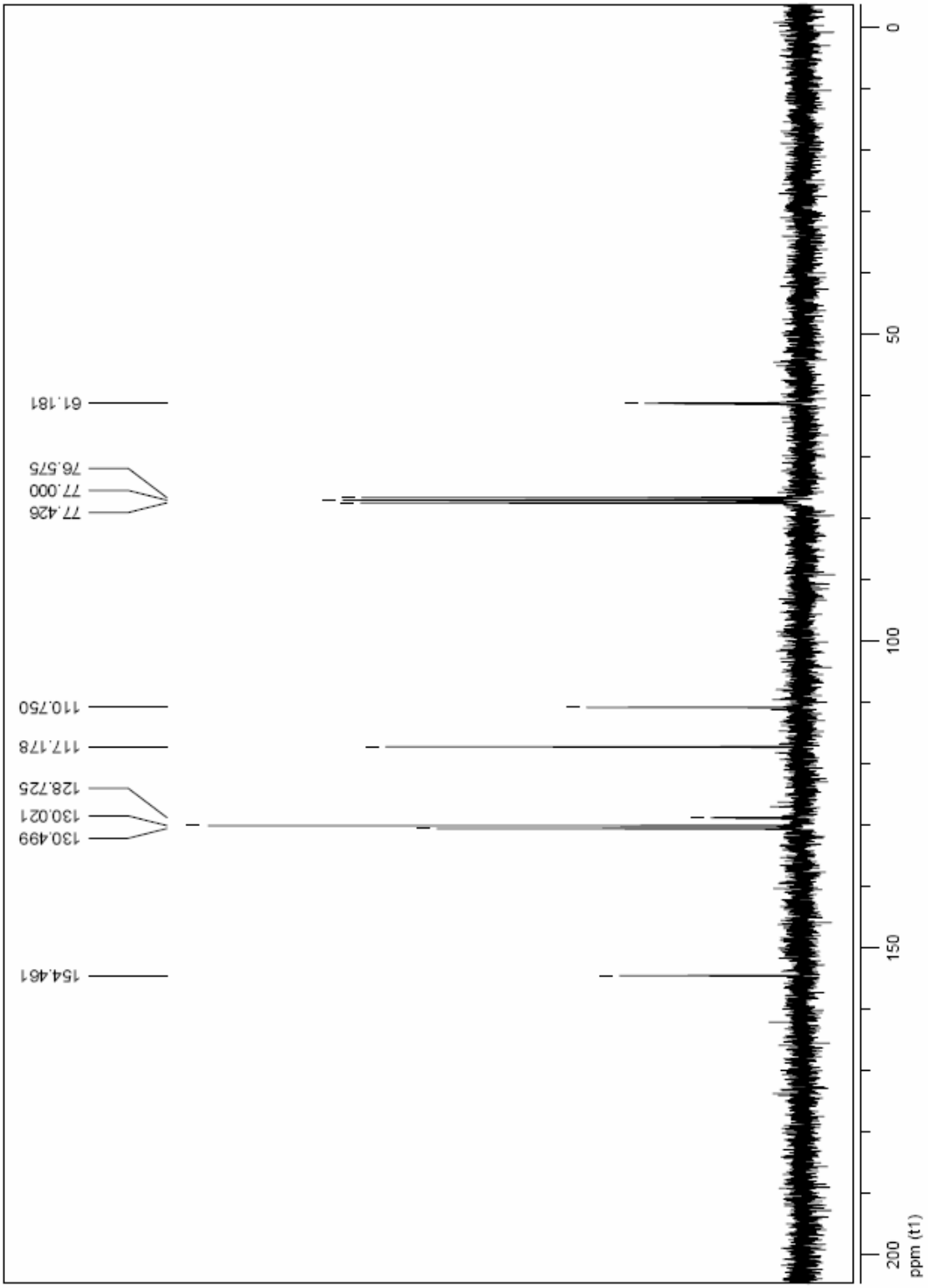
Salicyl alcohol **2g**

^{1}H NMR (300 MHz, $CDCl_3$)



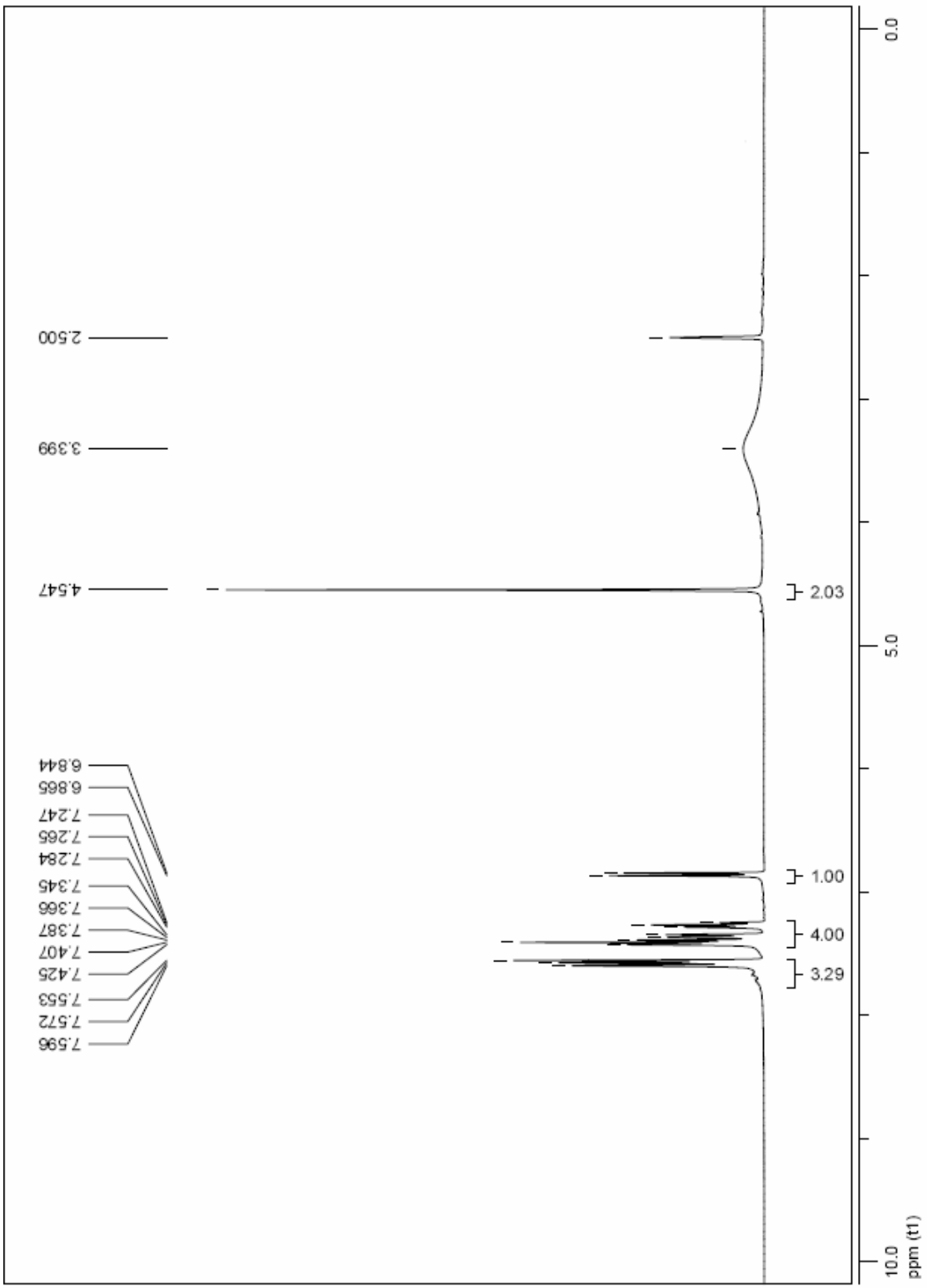
Salicyl alcohol **2g**

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



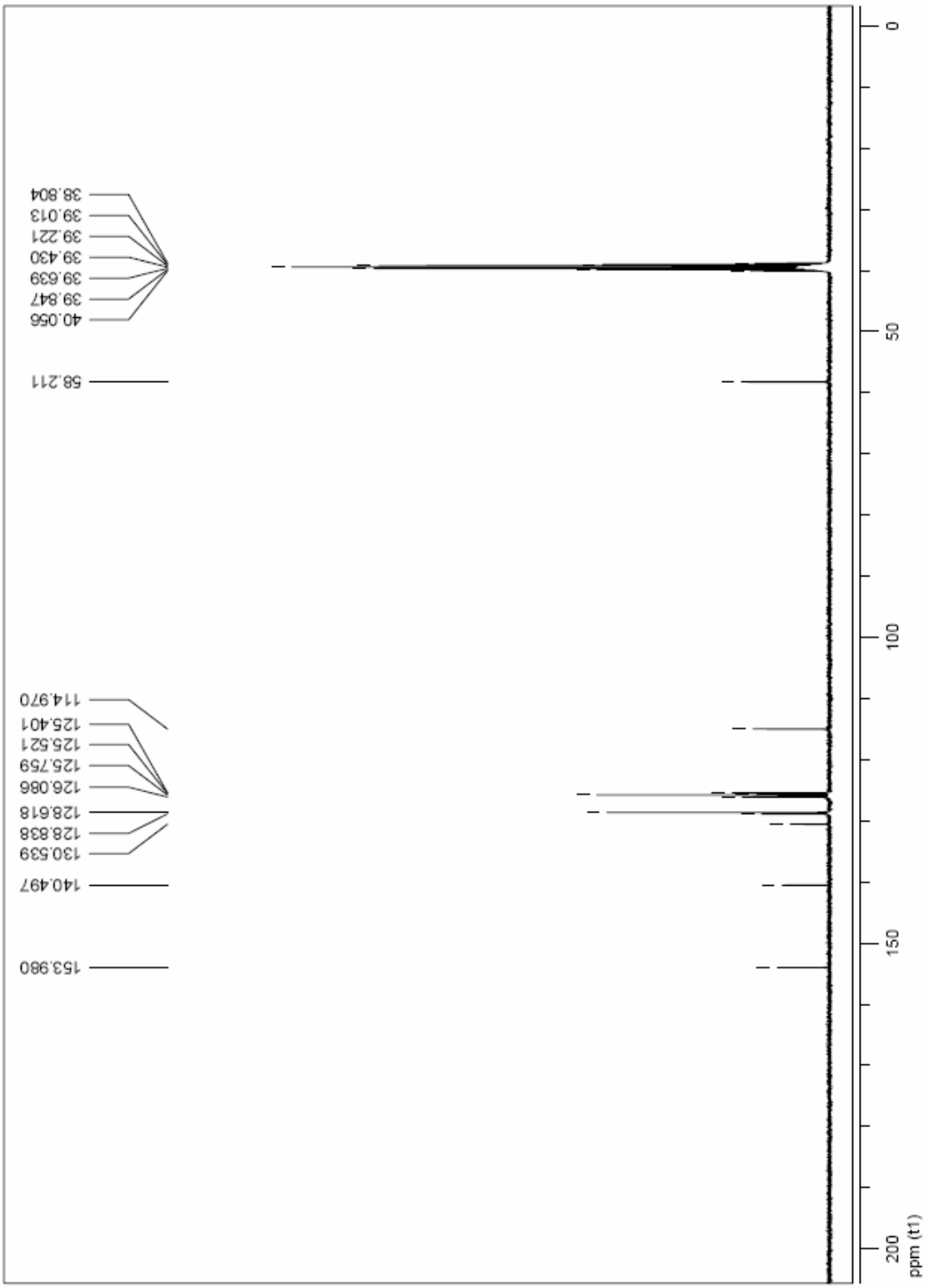
Salicyl alcohol **2h**

^{1}H NMR (400 MHz, DMSO-d_6)



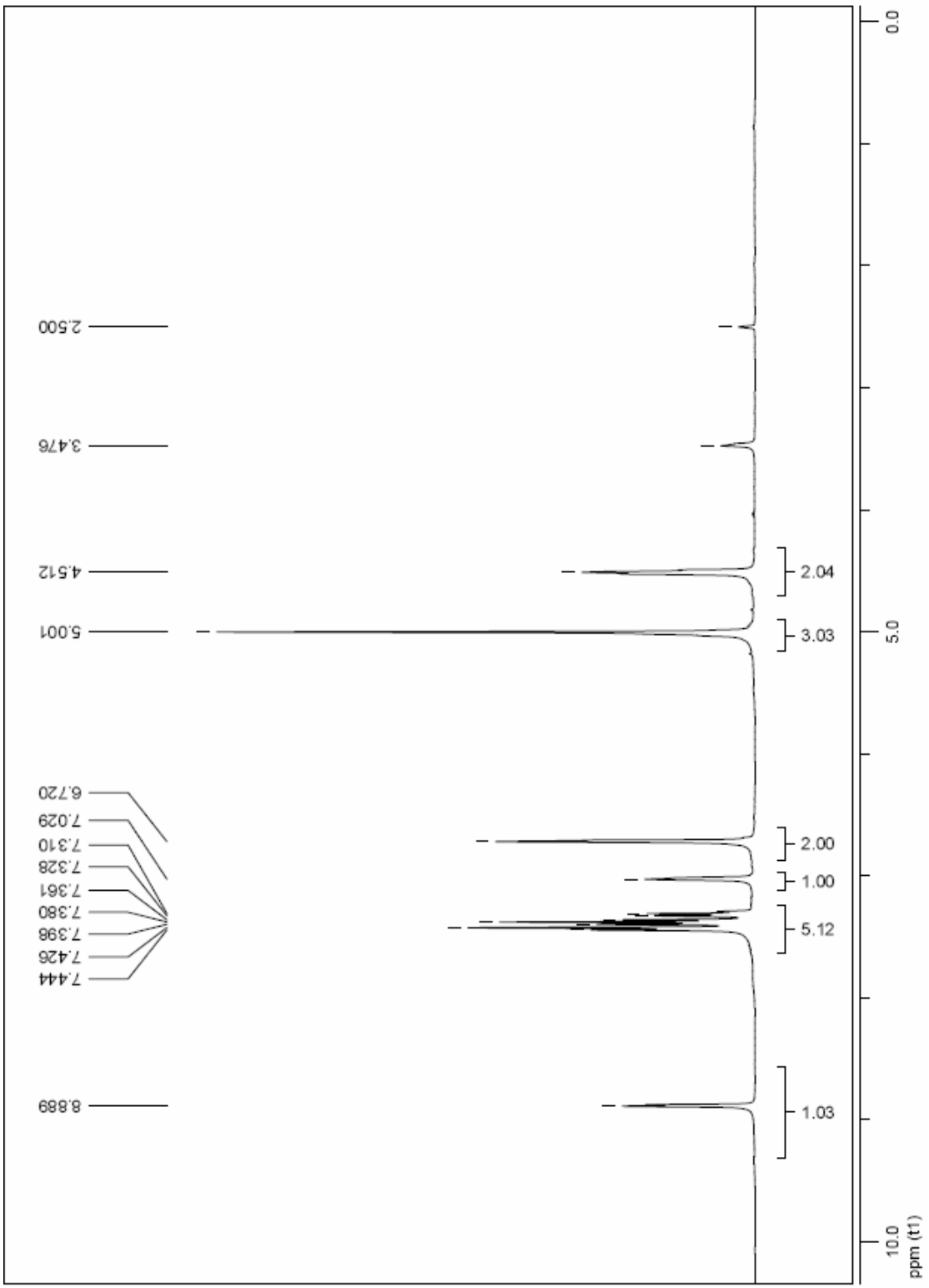
Salicyl alcohol **2h**

^{13}C NMR (100 MHz, DMSO-d_6)



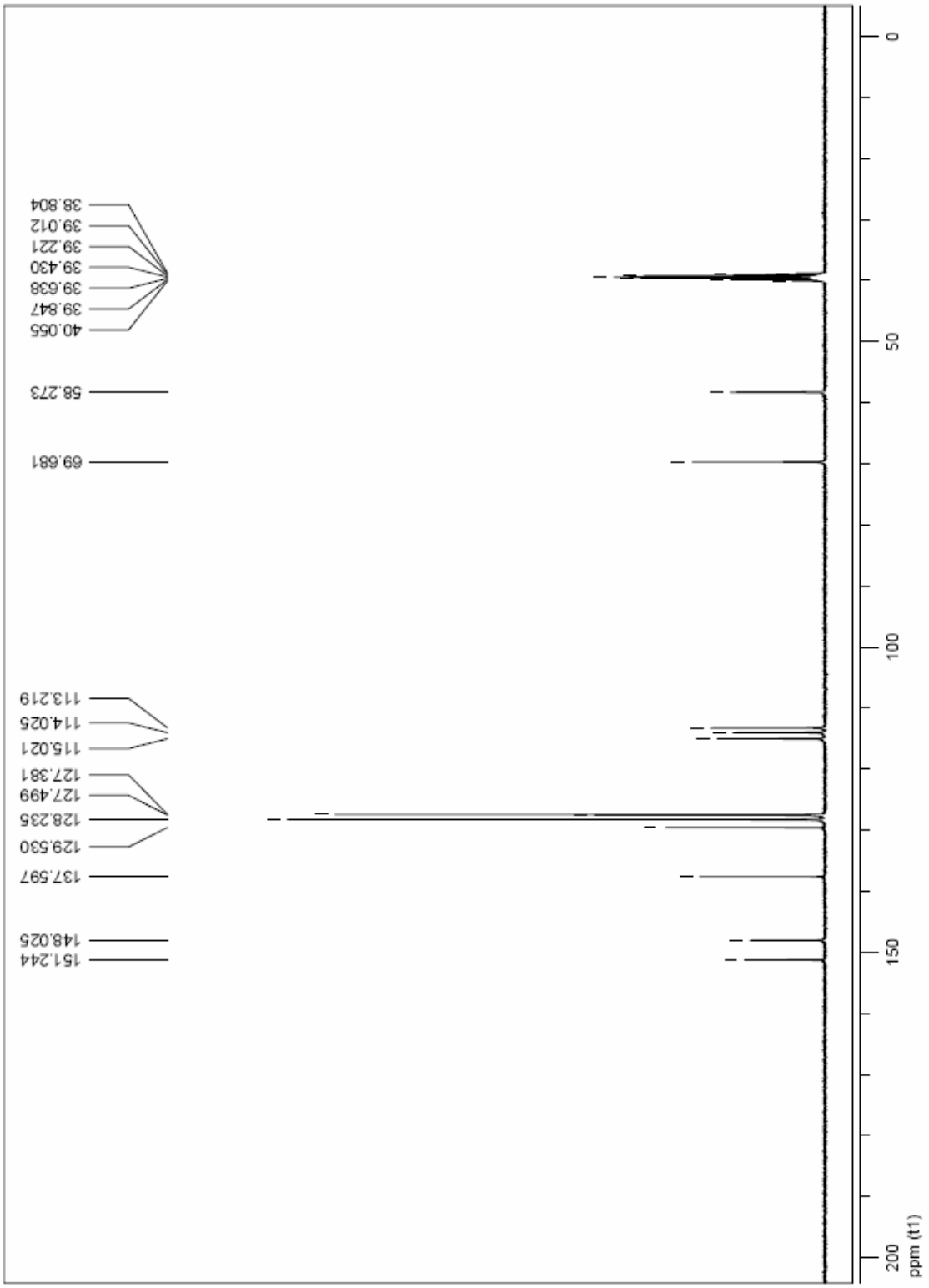
Salicyl alcohol **2i**

^{1}H NMR (400 MHz, DMSO-d_6)



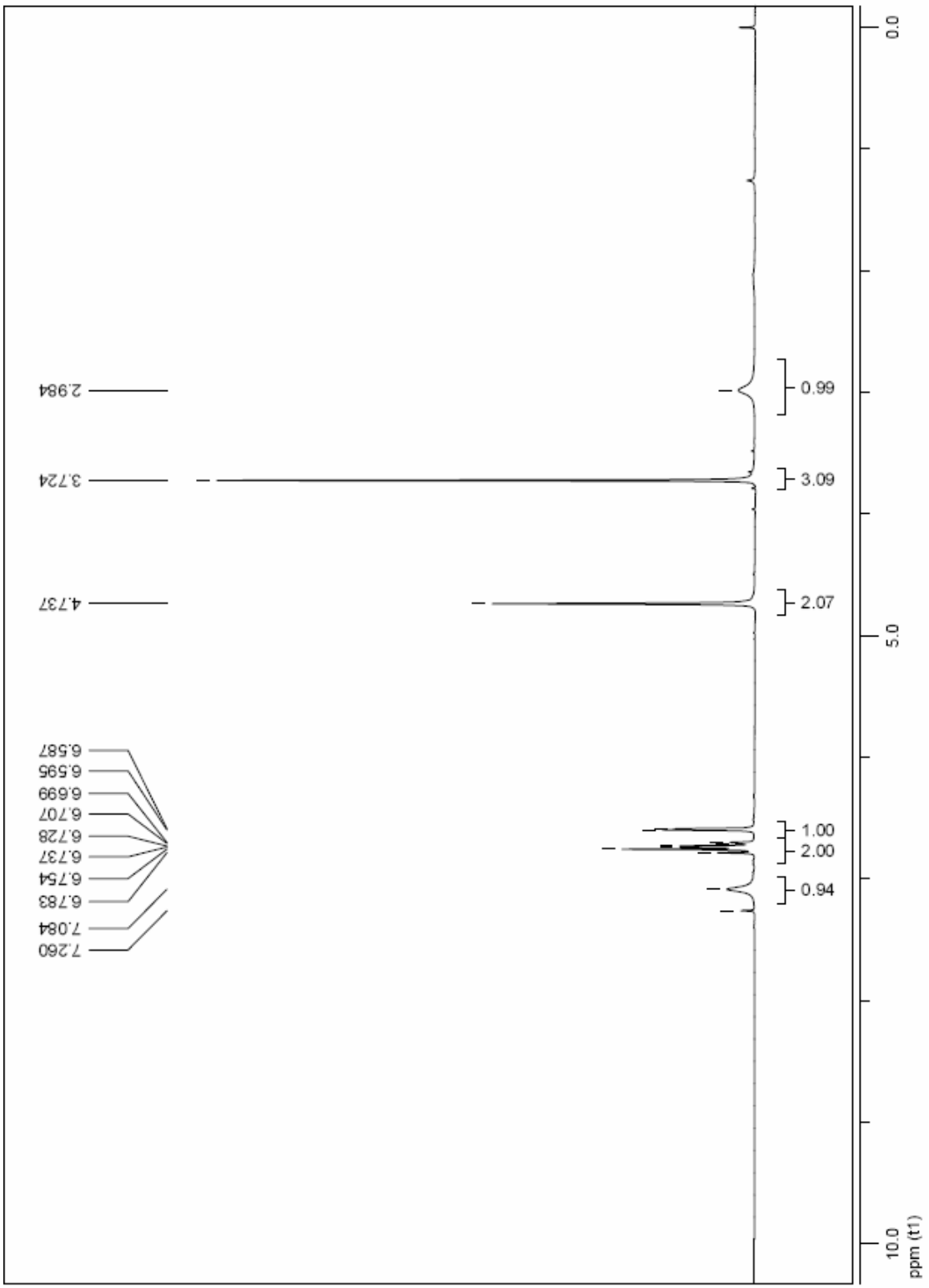
Salicyl alcohol **2i**

^{13}C NMR (100 MHz, DMSO-d_6)



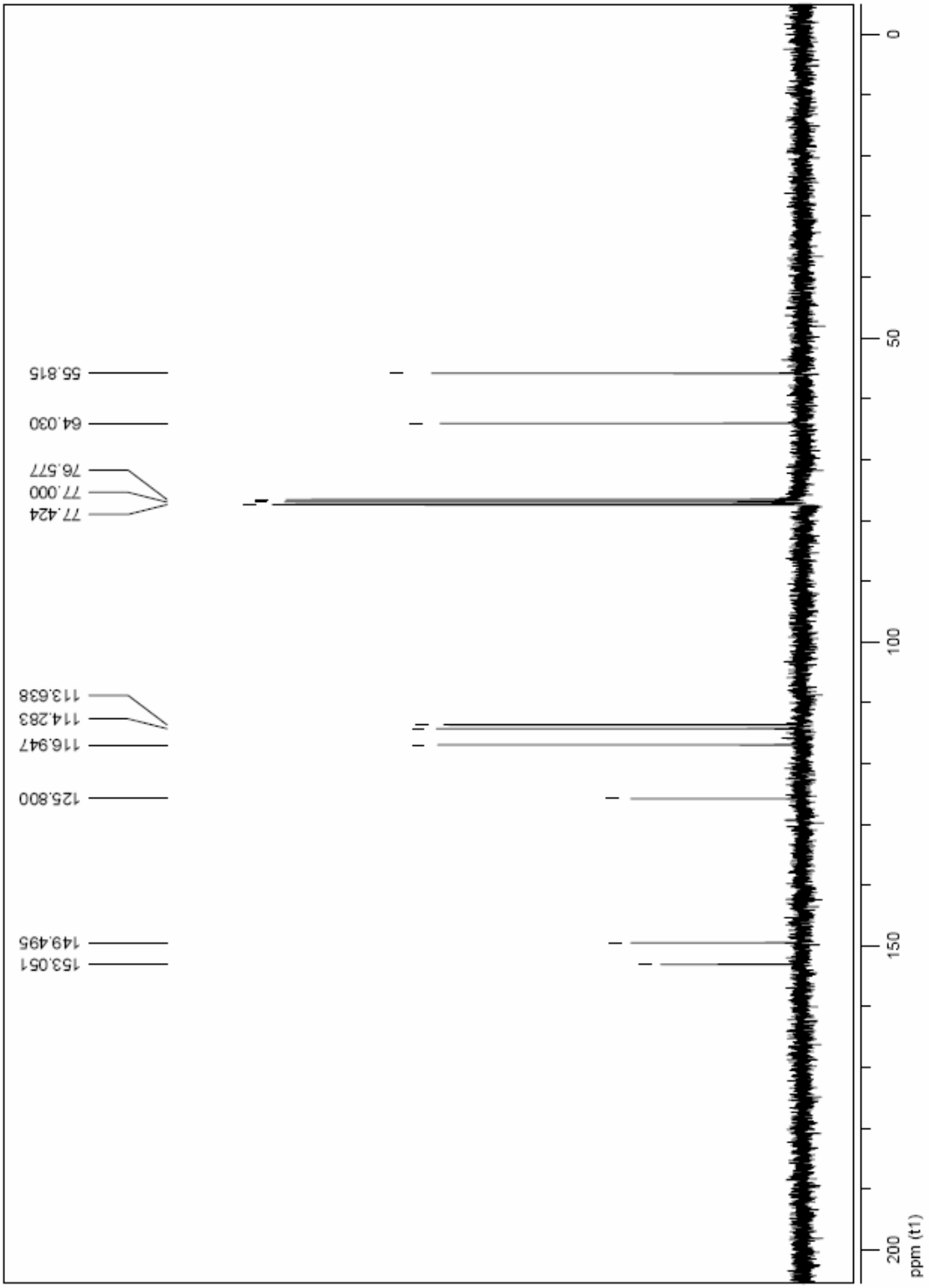
Salicyl alcohol **2j**

^{1}H NMR (300 MHz, $CDCl_3$)



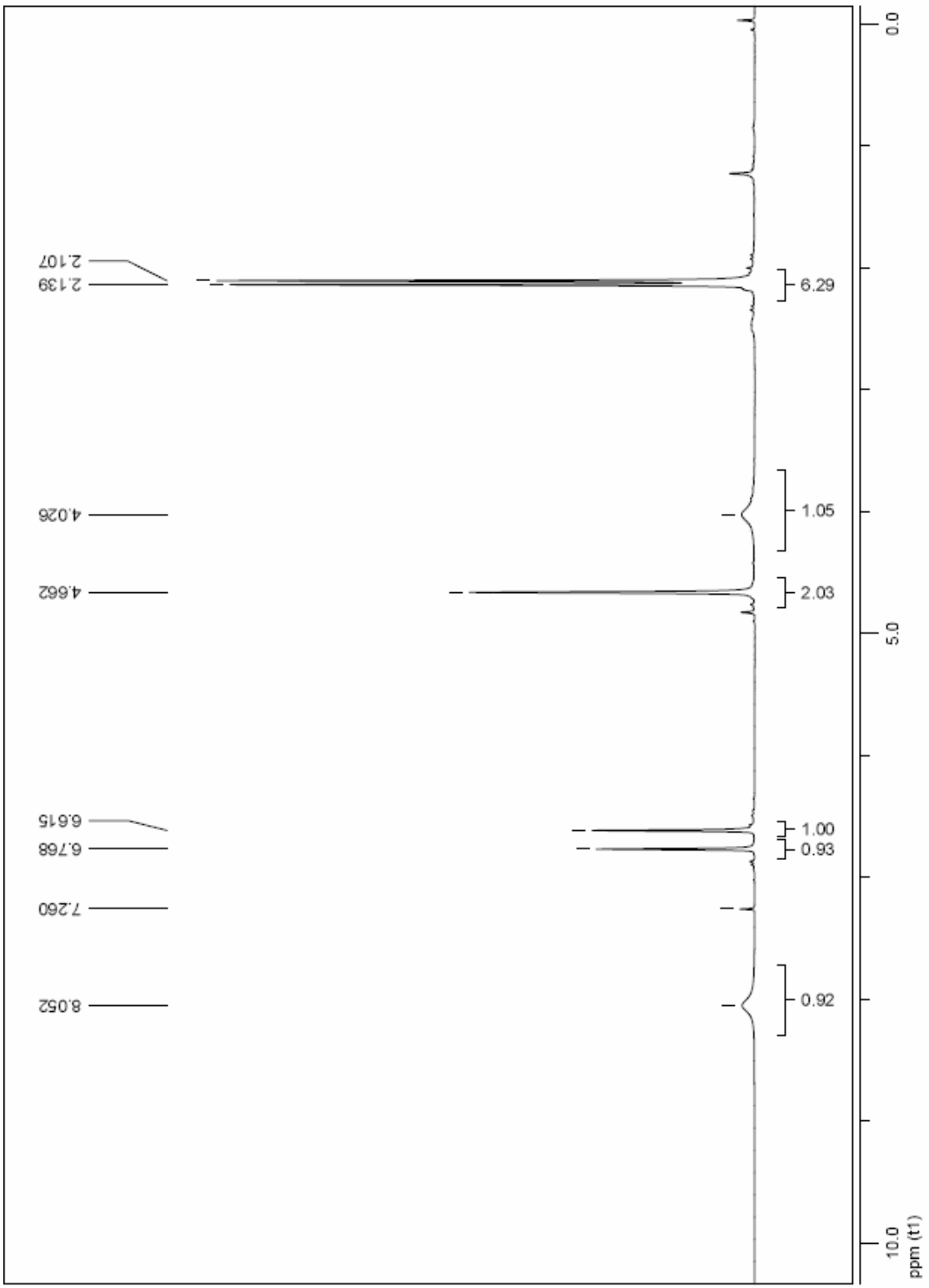
Salicyl alcohol **2j**

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



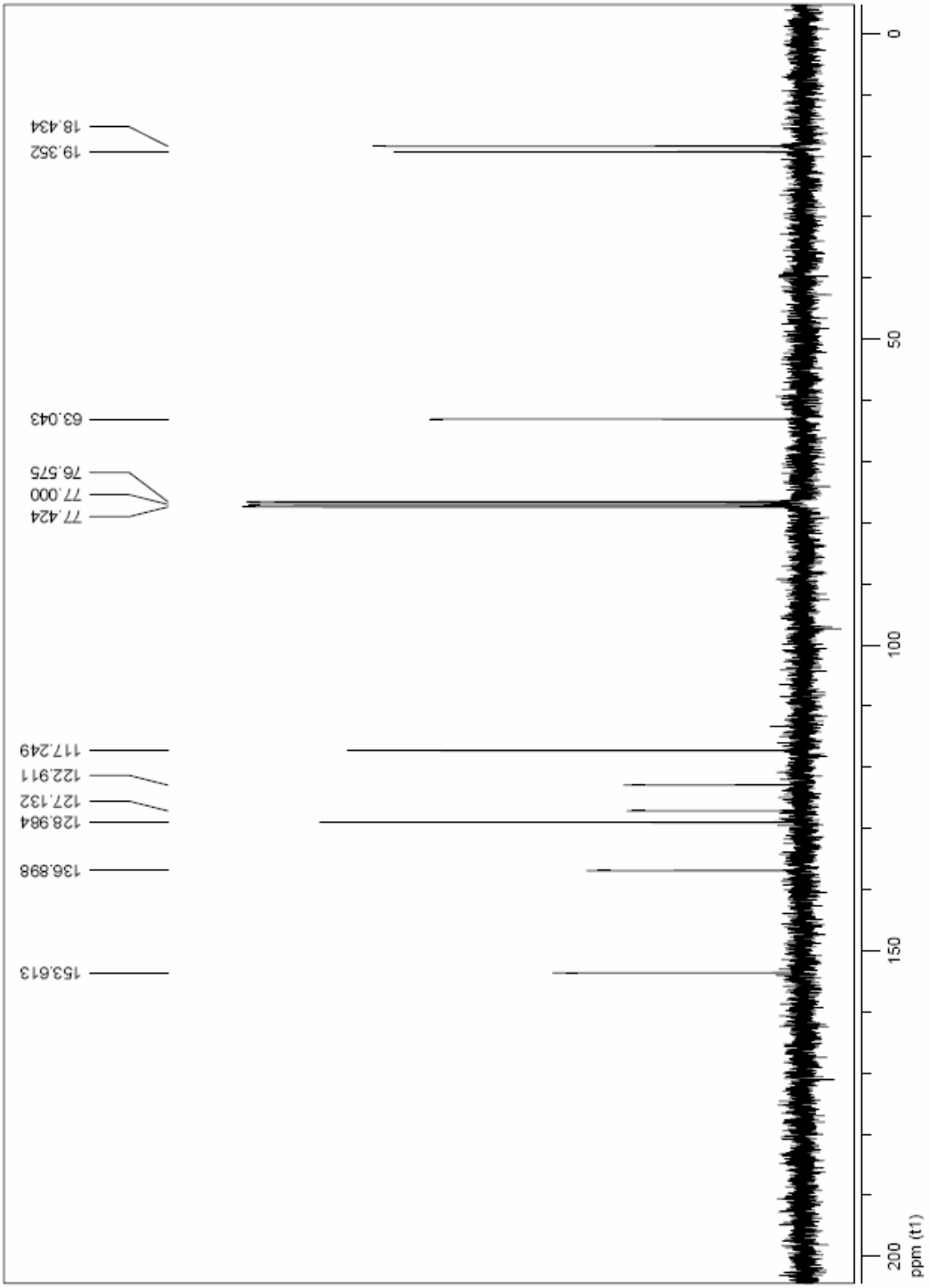
Salicyl alcohol **2k**

^{1}H NMR (300 MHz, $CDCl_3$)



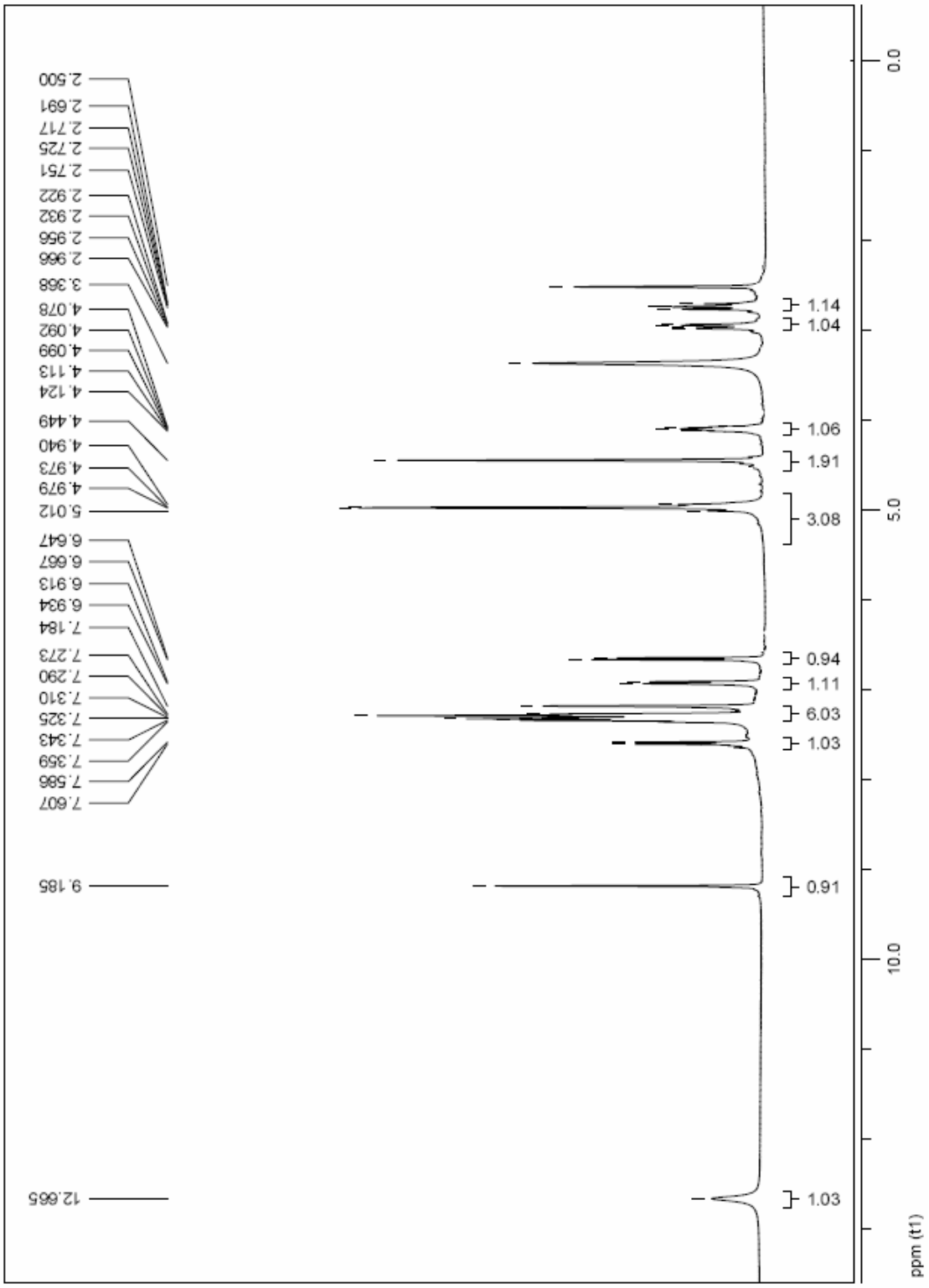
Salicyl alcohol **2k**

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



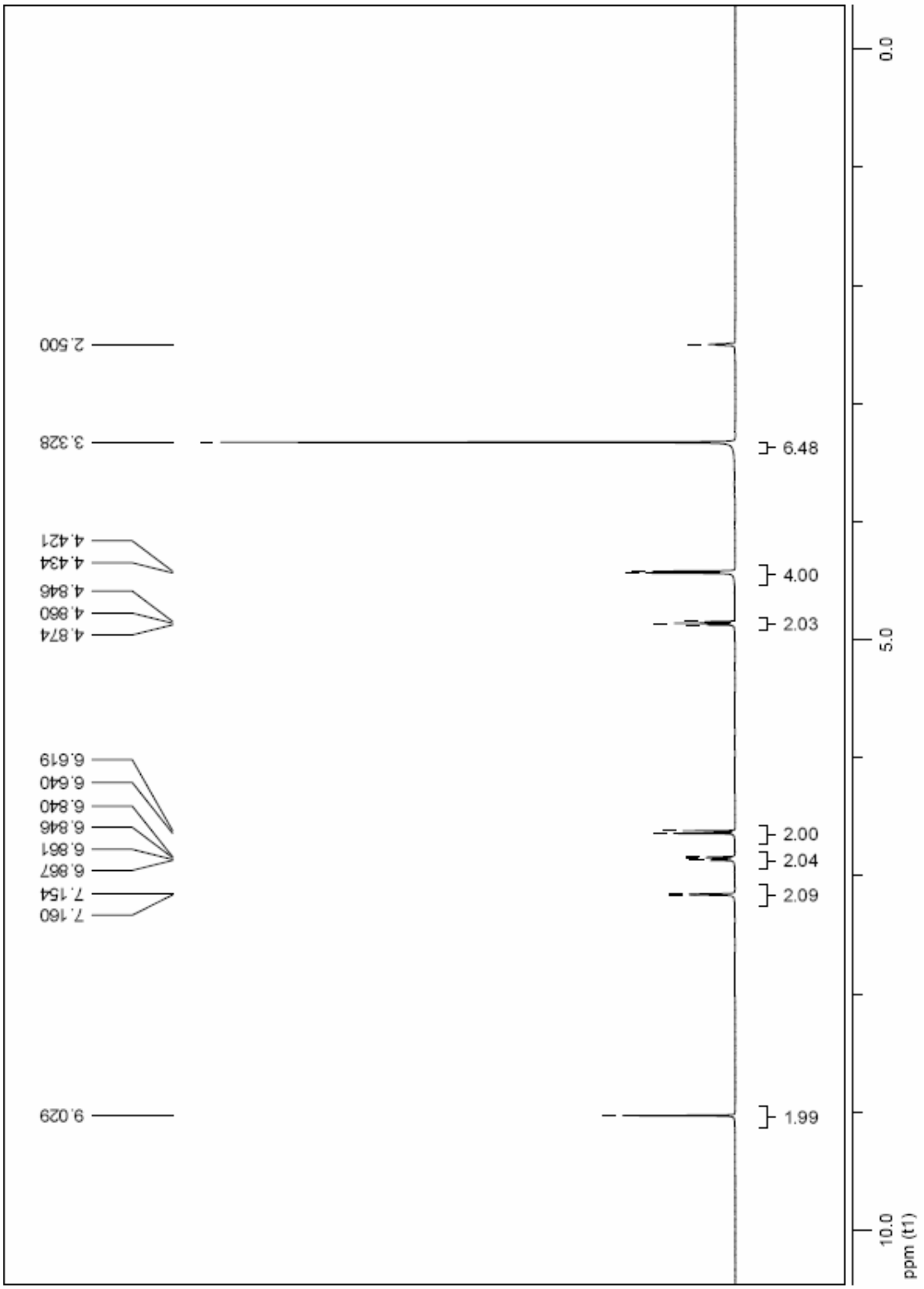
Salicyl alcohol **2l**

^{1}H NMR (400 MHz, DMSO-d_6)



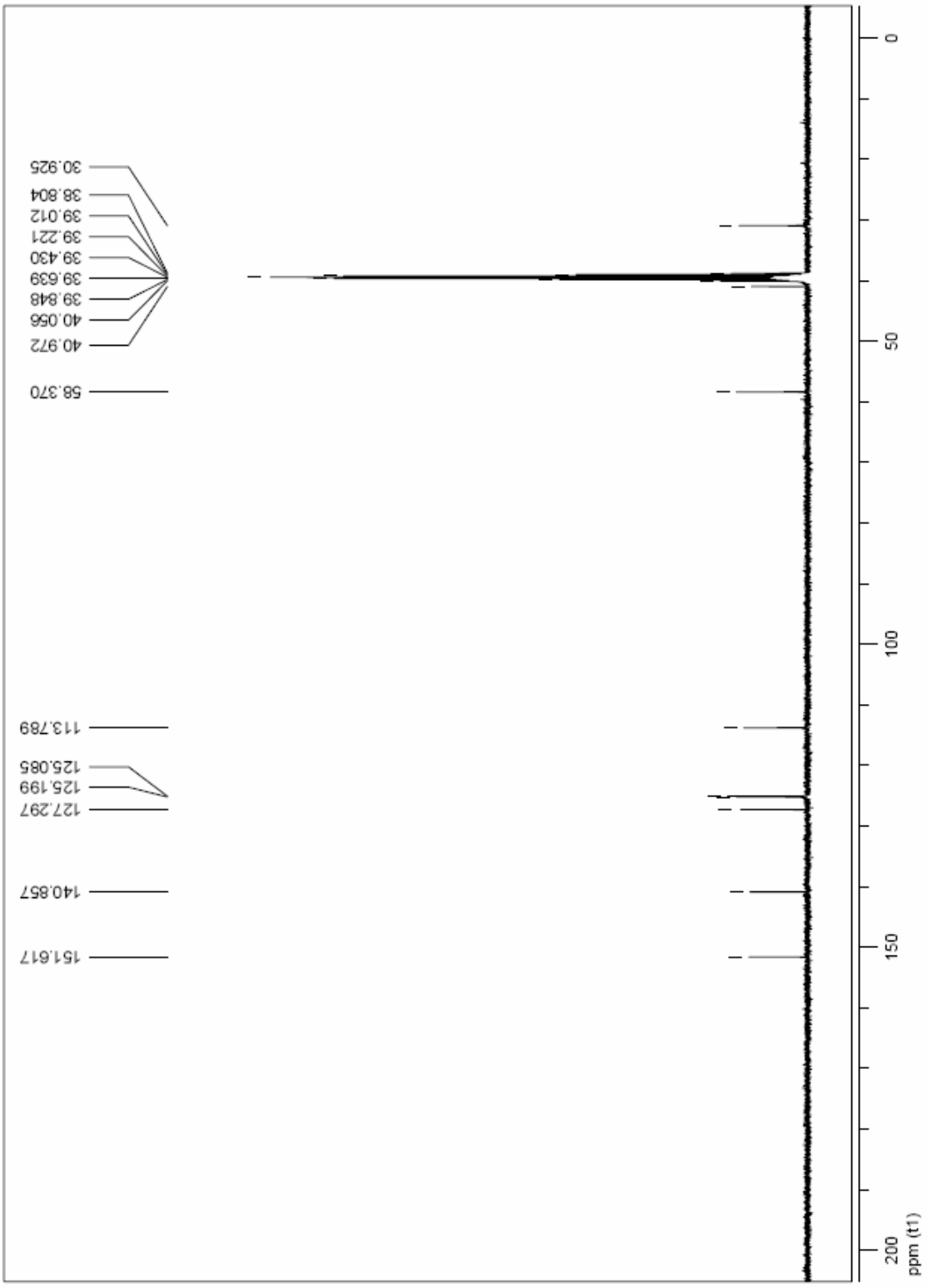
Salicyl alcohol **2m**

^{1}H NMR (400 MHz, DMSO-d_6)



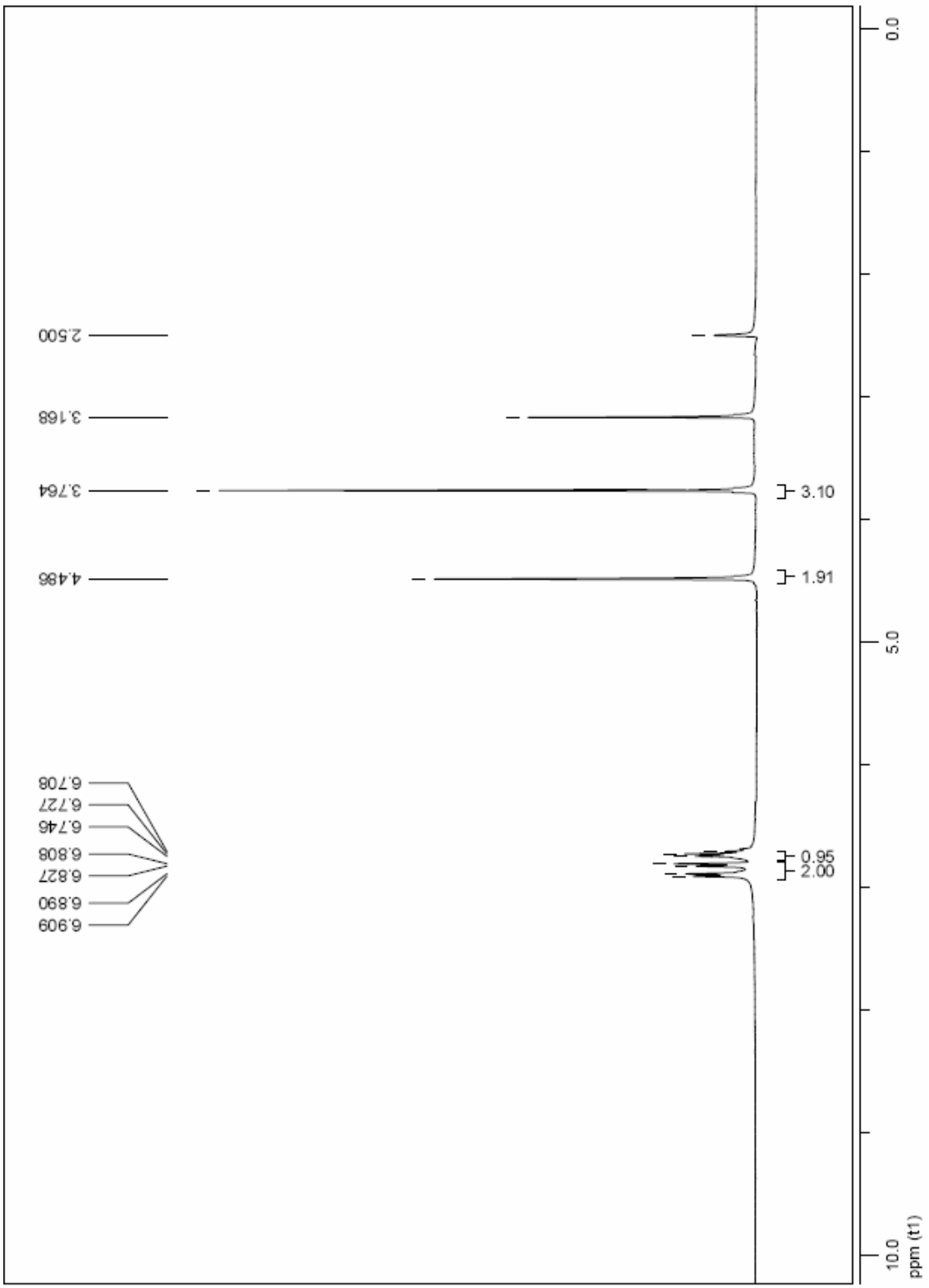
Salicyl alcohol **2m**

^{13}C NMR (100 MHz, DMSO-d_6)



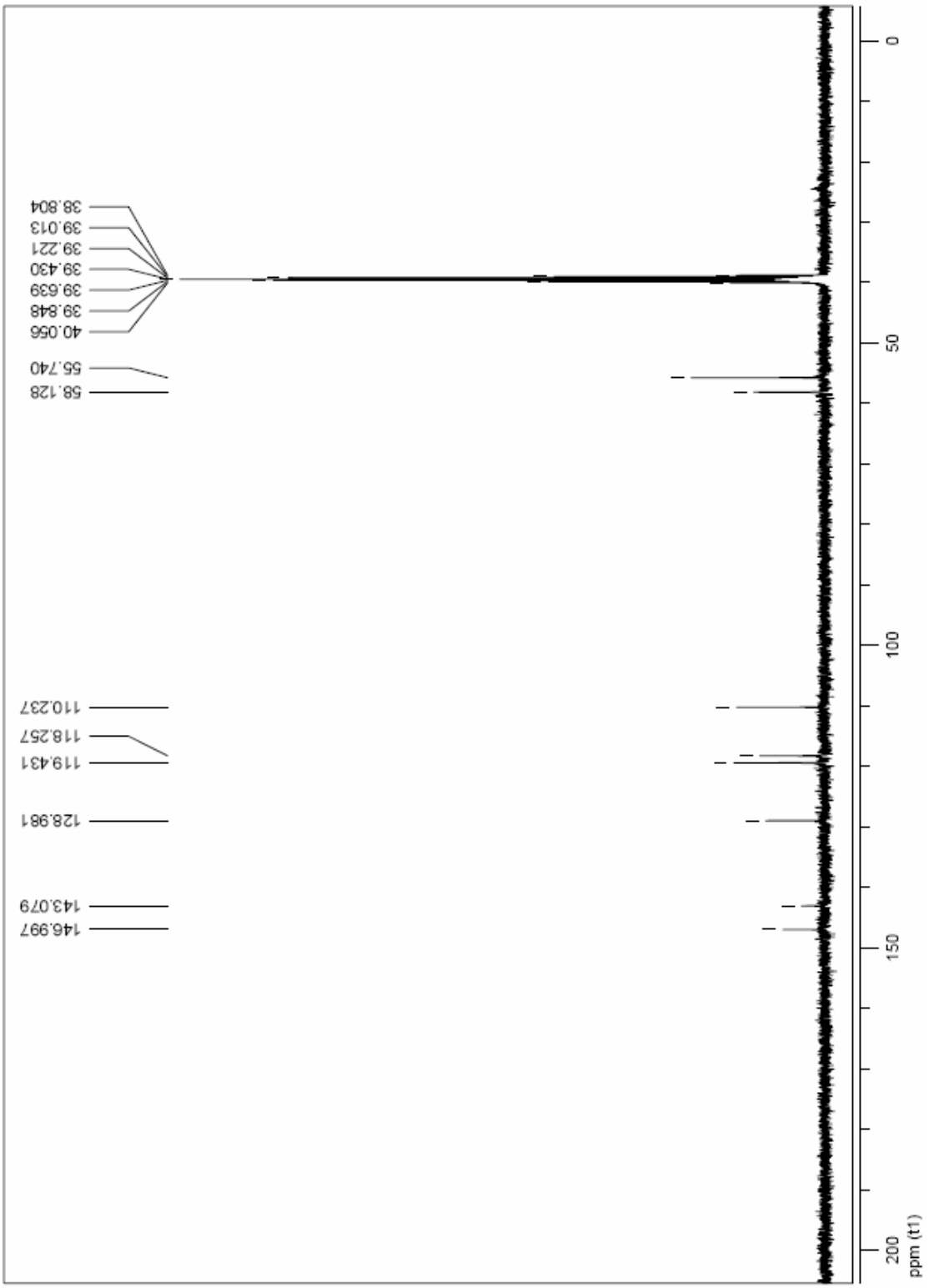
Salicyl alcohol **2n**

^{1}H NMR (400 MHz, DMSO-d_6)



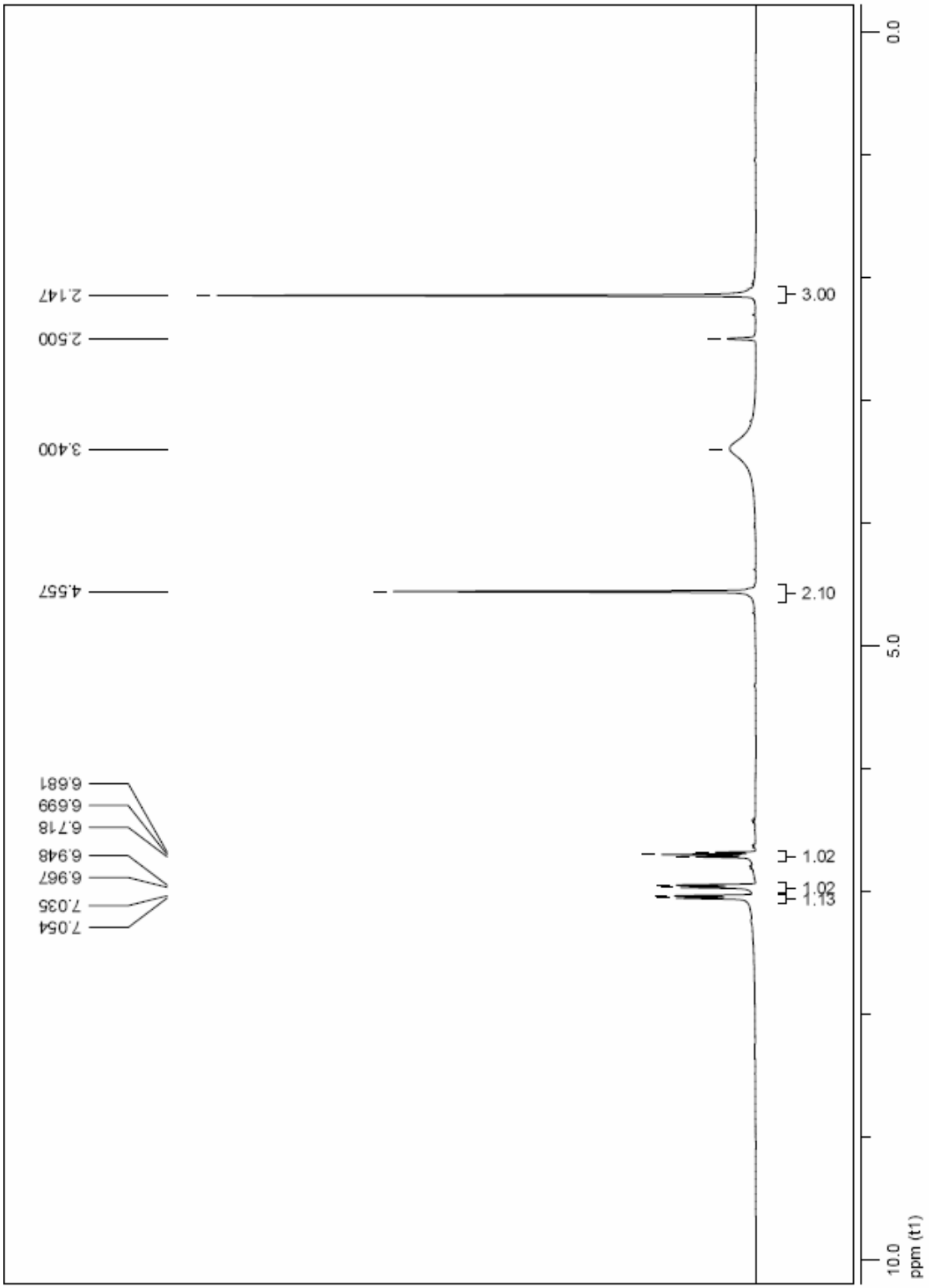
Salicyl alcohol **2n**

^{13}C NMR (100 MHz, DMSO-d_6)



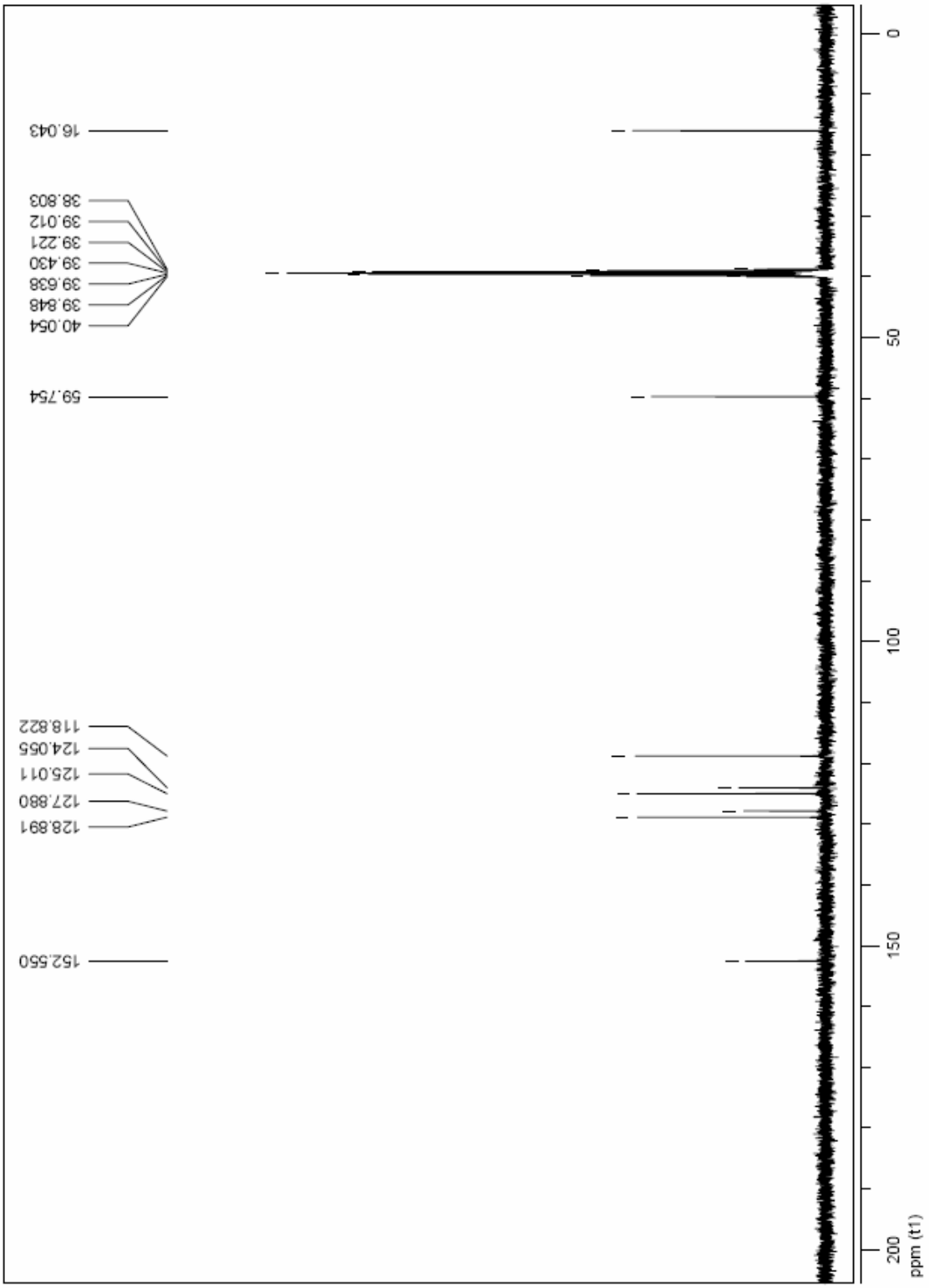
Salicyl alcohol **2o**

^{1}H NMR (400 MHz, DMSO-d_6)



Salicyl alcohol **2o**

^{13}C NMR (100 MHz, DMSO-d_6)

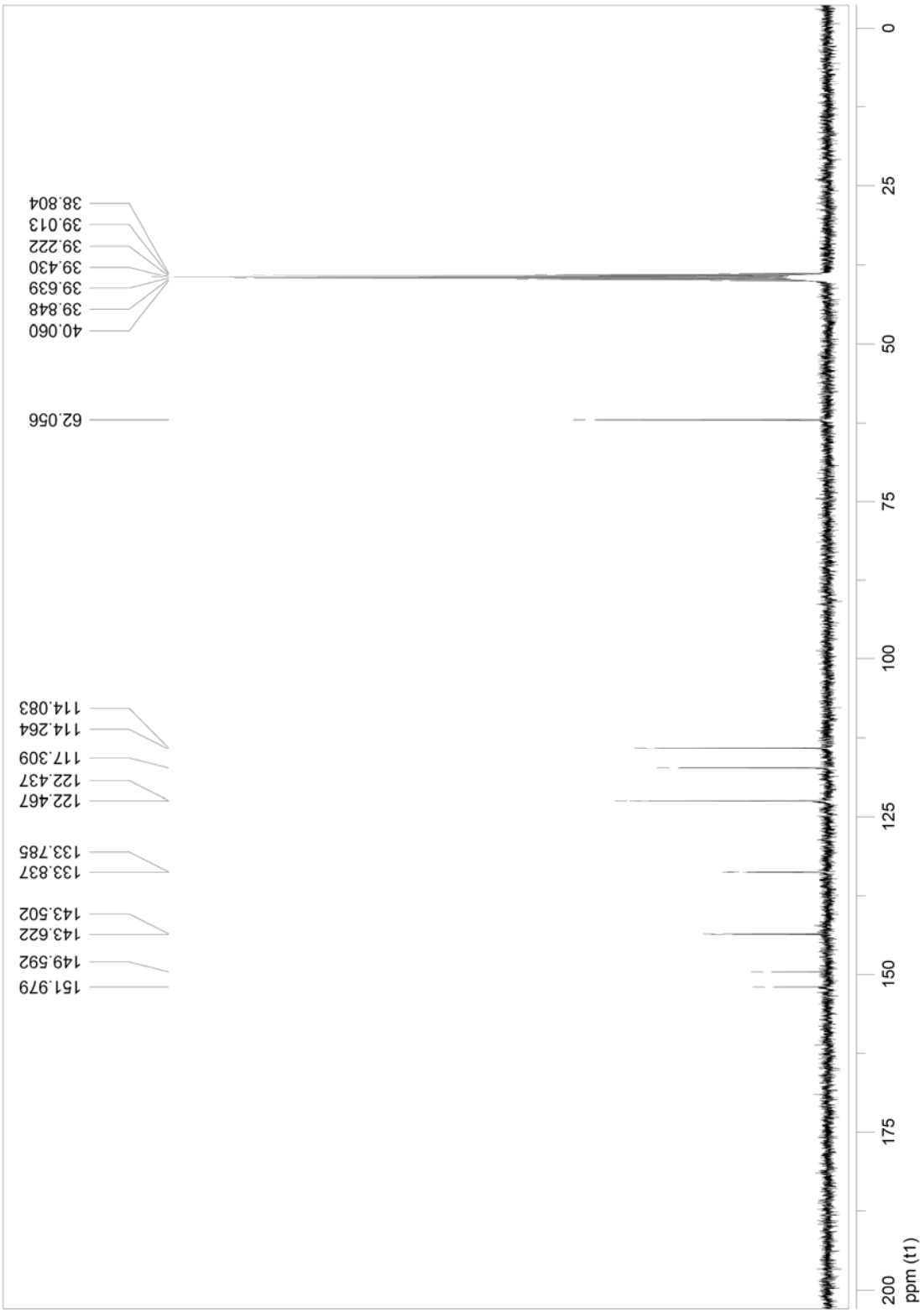


Salicyl alcohol **2p**

^{1}H NMR (400 MHz, DMSO-d_6)

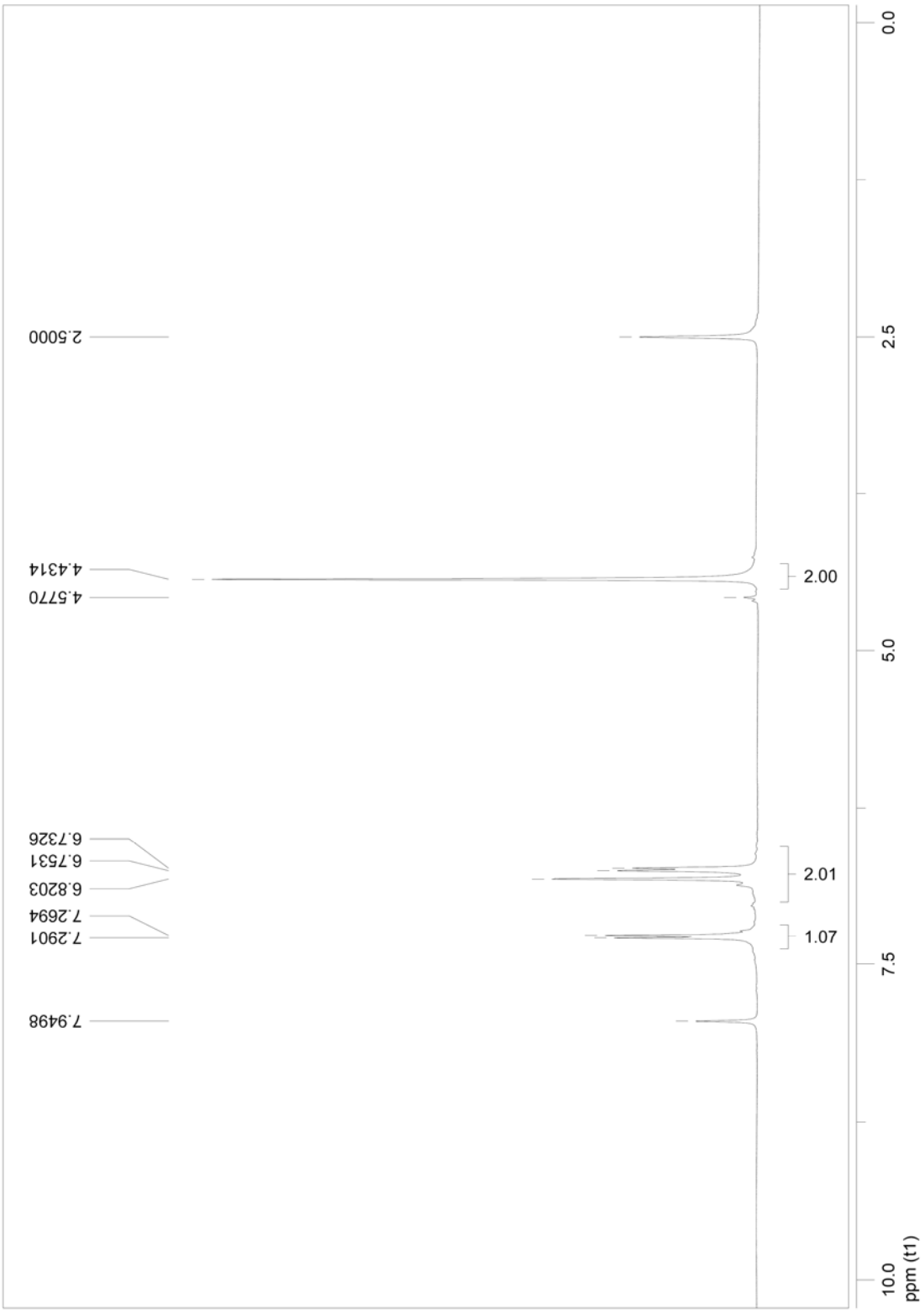
Salicyl alcohol **2p**

^{13}C NMR (100 MHz, DMSO-d_6)



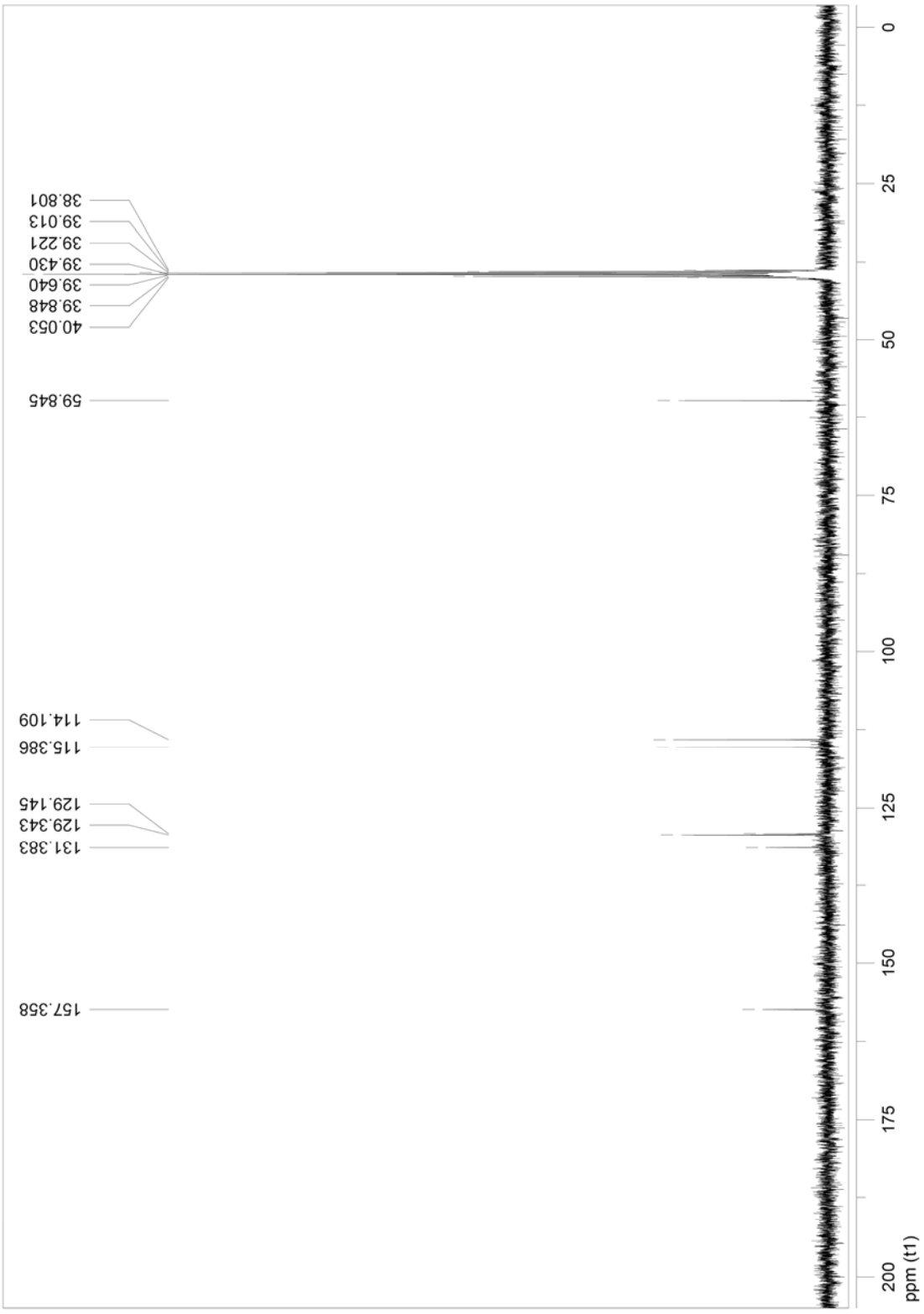
Salicyl alcohol **2q**

^{1}H NMR (400 MHz, DMSO-d_6)



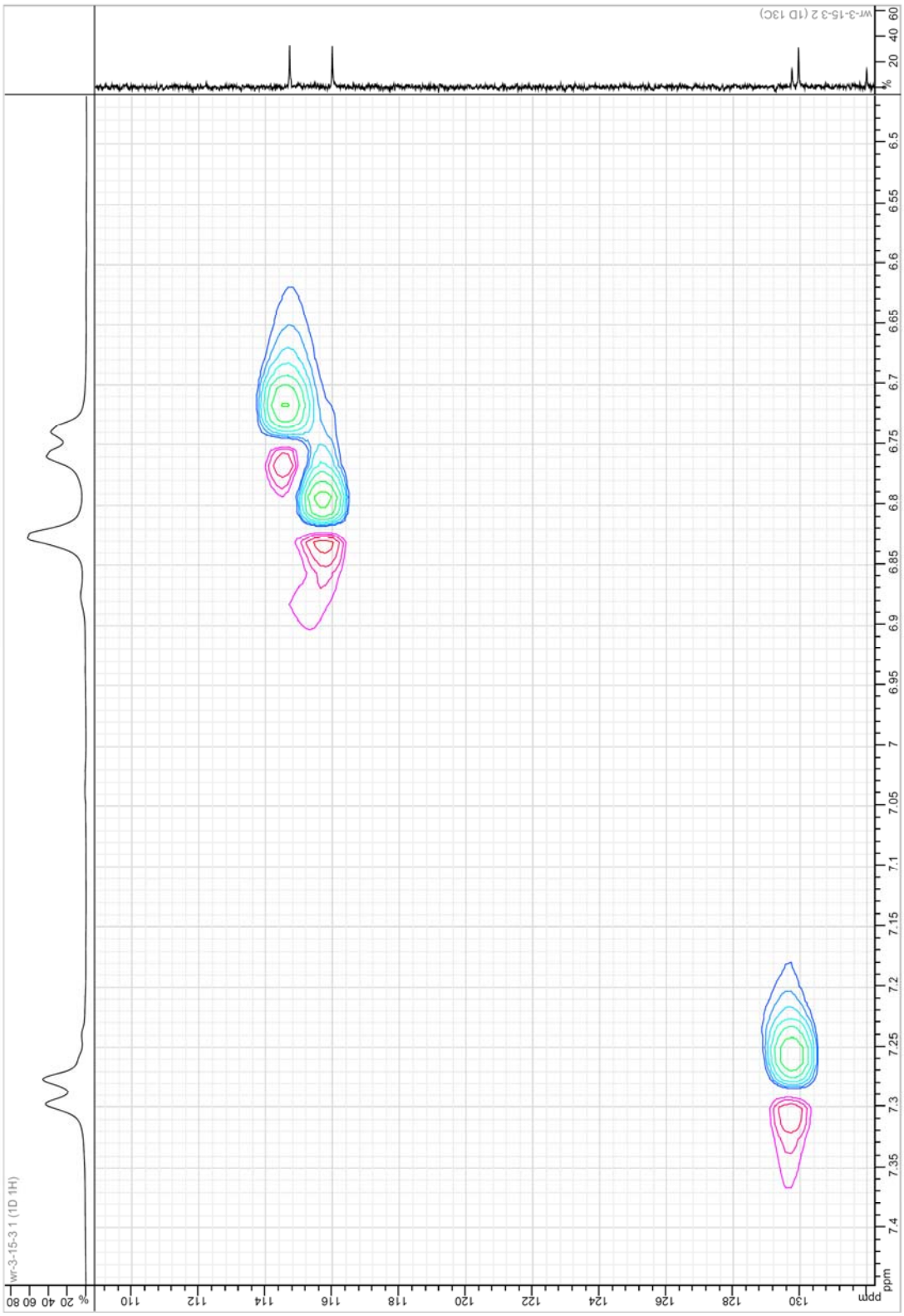
Salicyl alcohol **2q**

^{13}C NMR (100 MHz, DMSO-d_6)



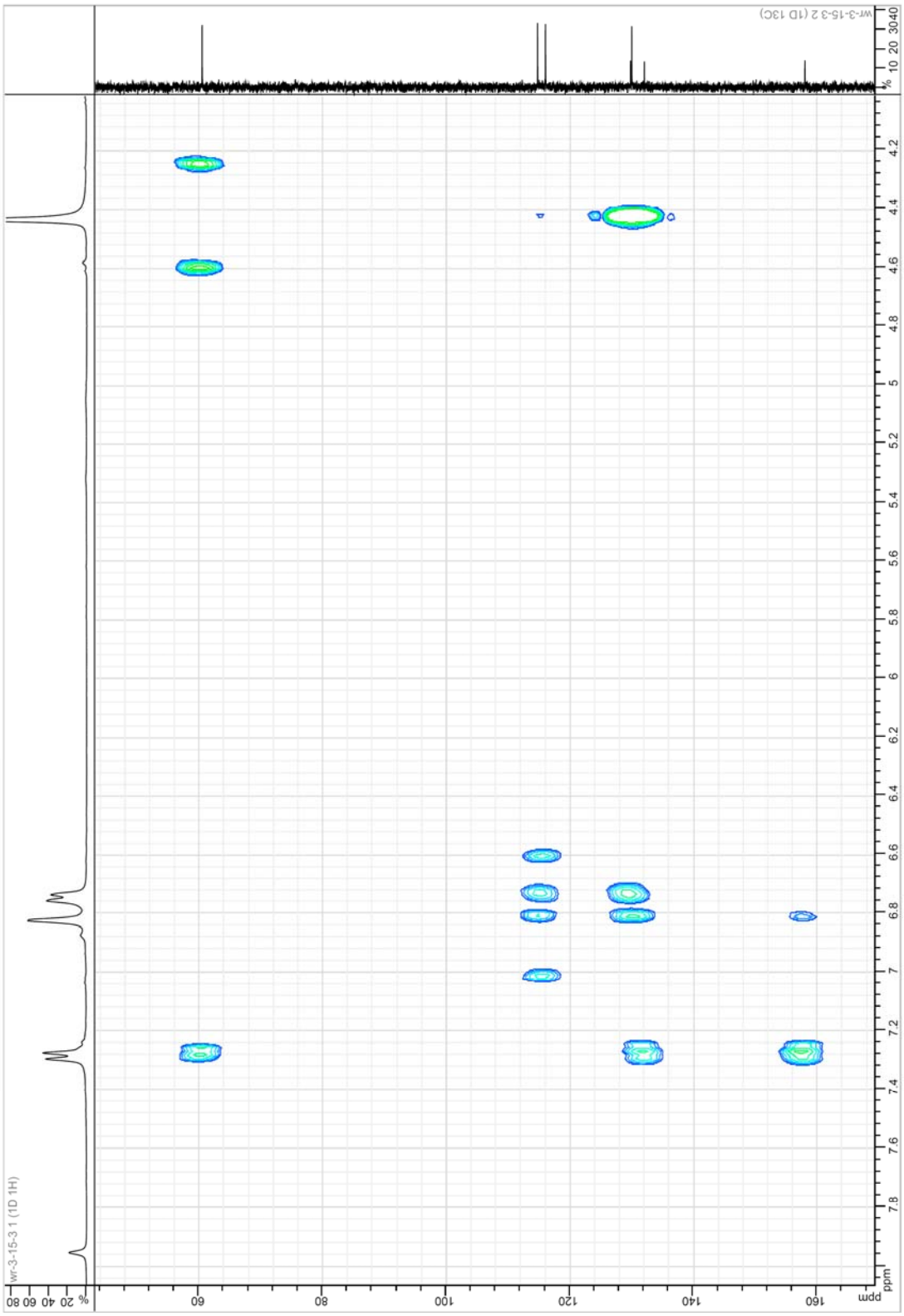
Salicyl alcohol **2q**

HSQC (100 MHz, DMSO-d_6)



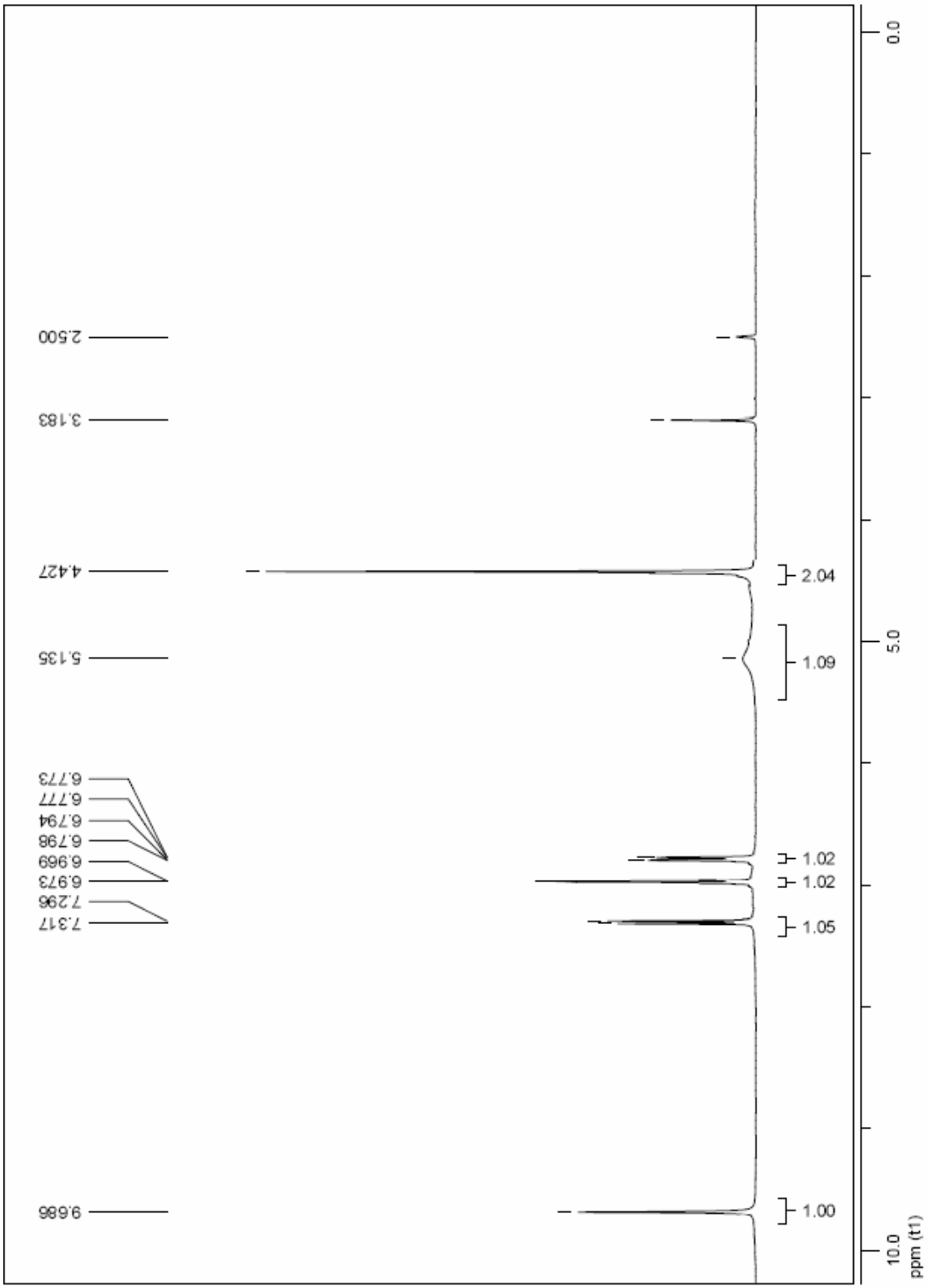
Salicyl alcohol **2q**

HMBC (100 MHz, DMSO-d_6)



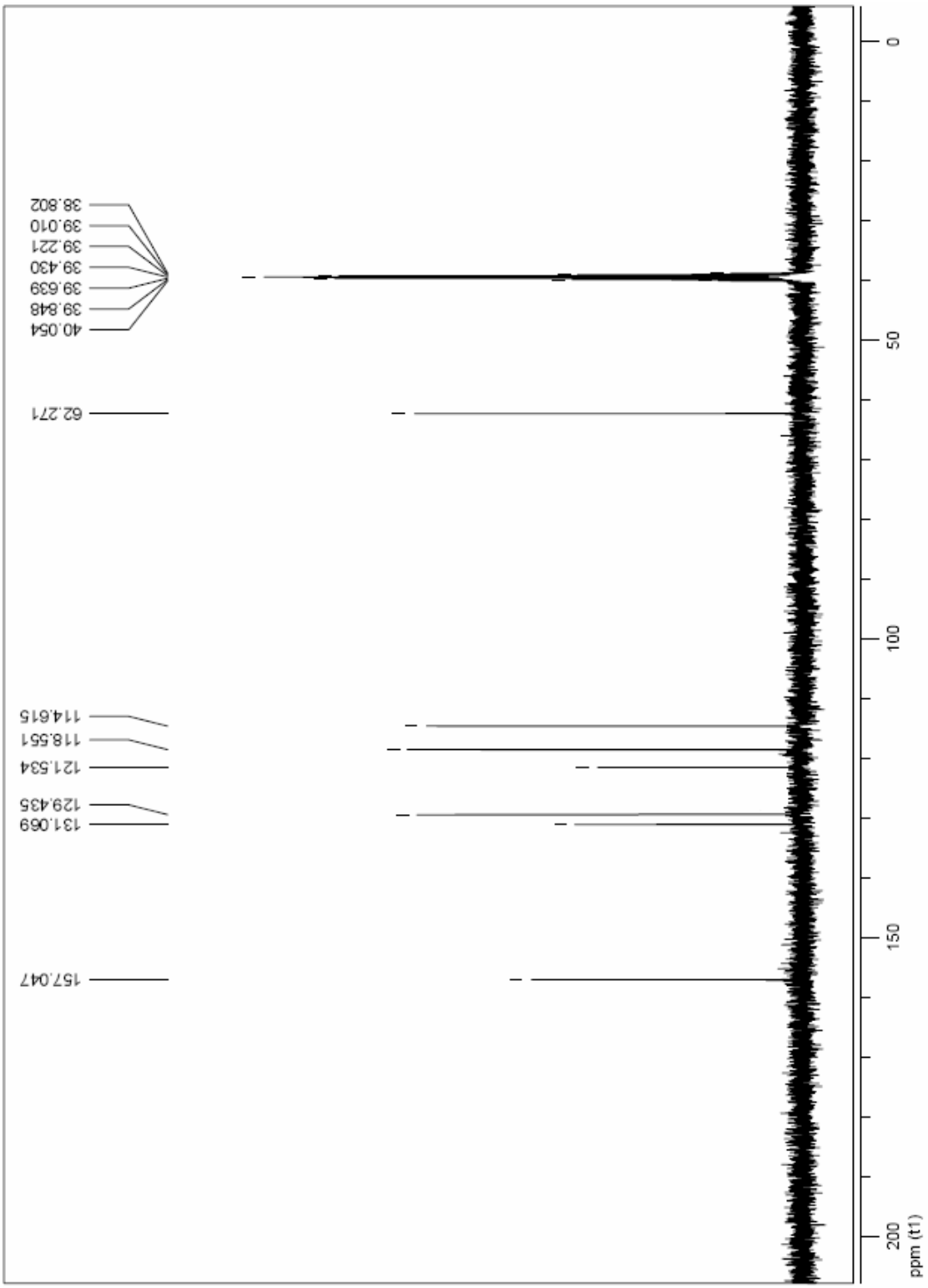
Salicyl alcohol **2r**

^{1}H NMR (400 MHz, DMSO-d_6)



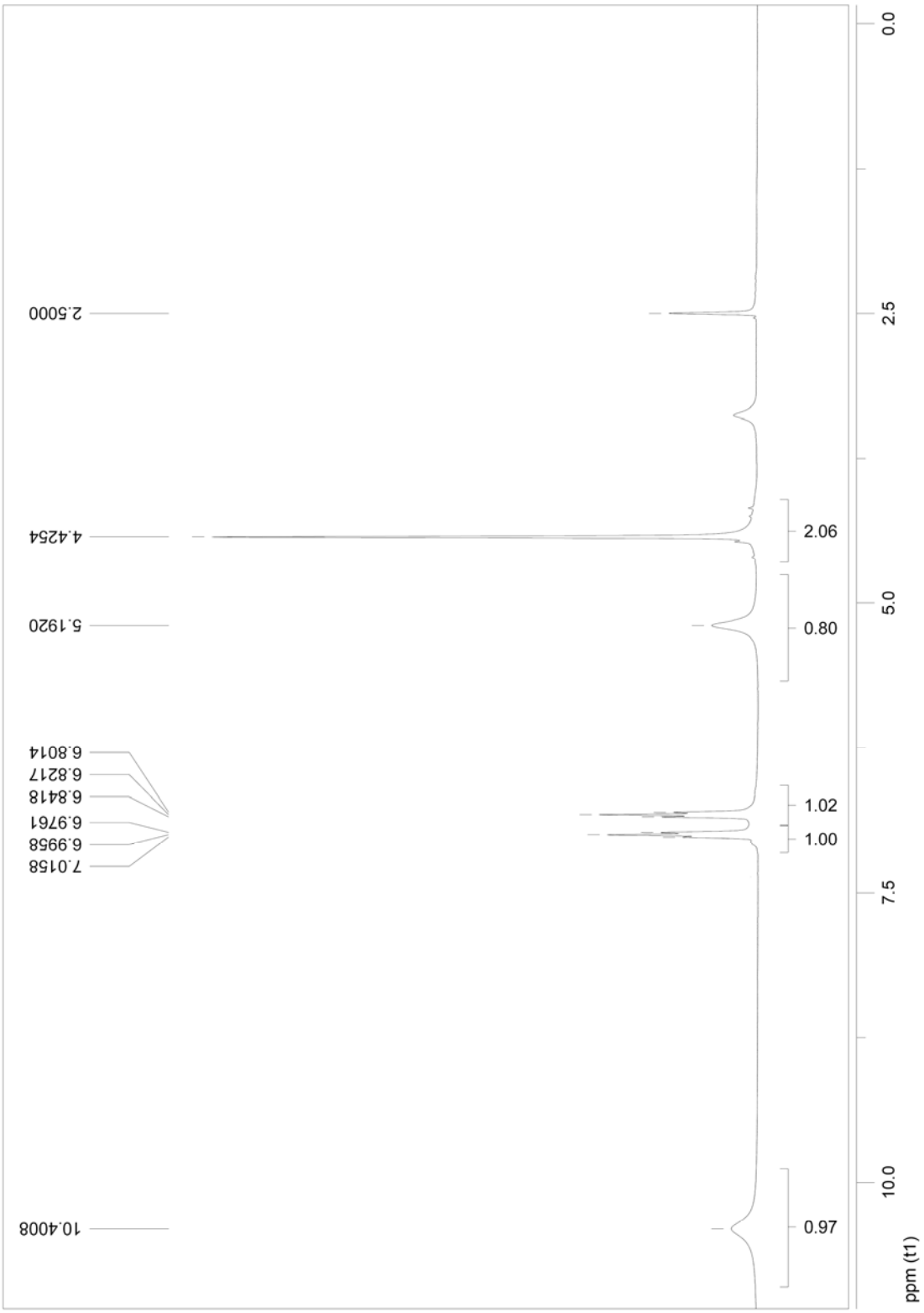
Salicyl alcohol **2r**

^{13}C NMR (100 MHz, DMSO-d_6)



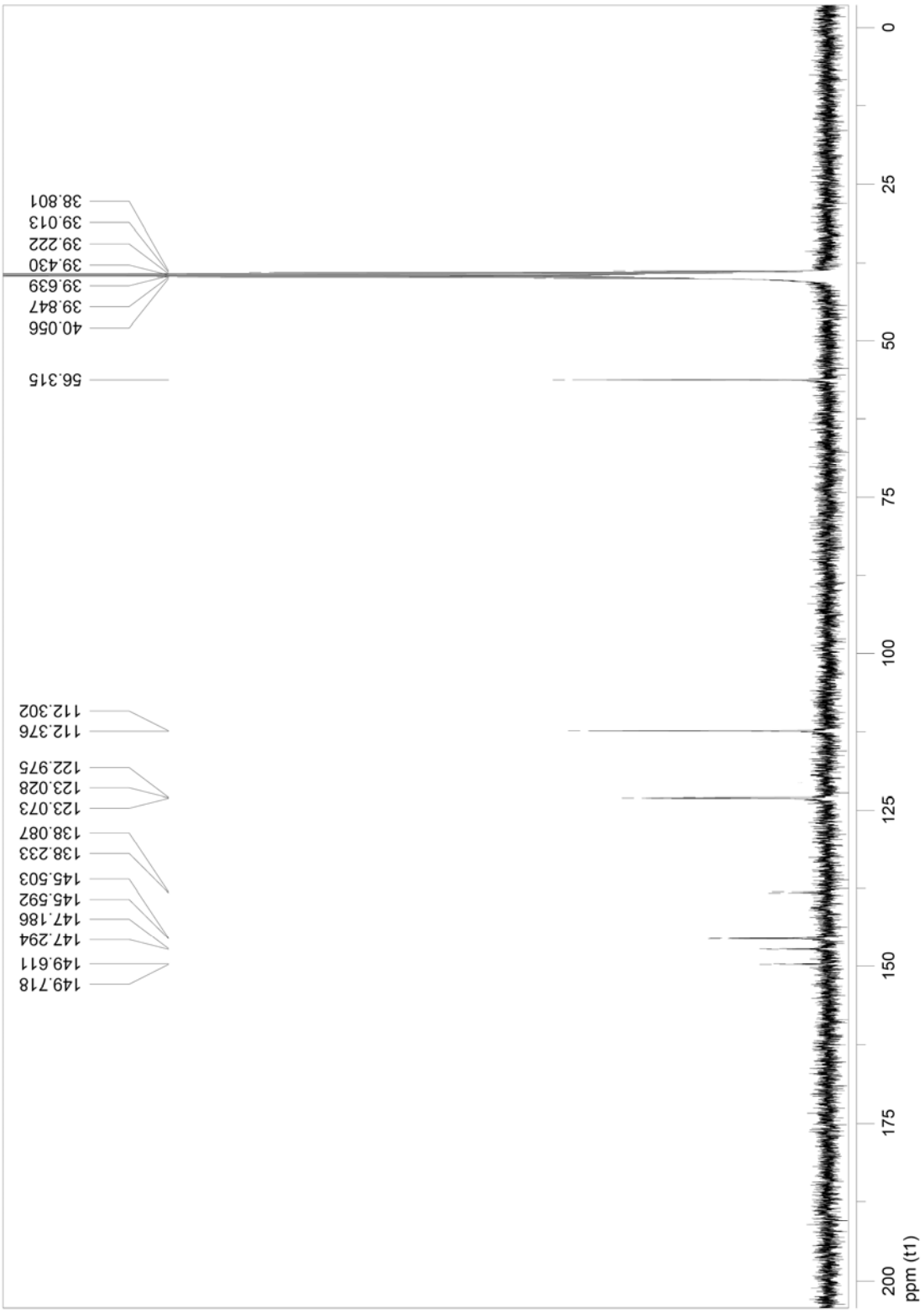
Salicyl alcohol **2s**

^{1}H NMR (400 MHz, DMSO-d_6)



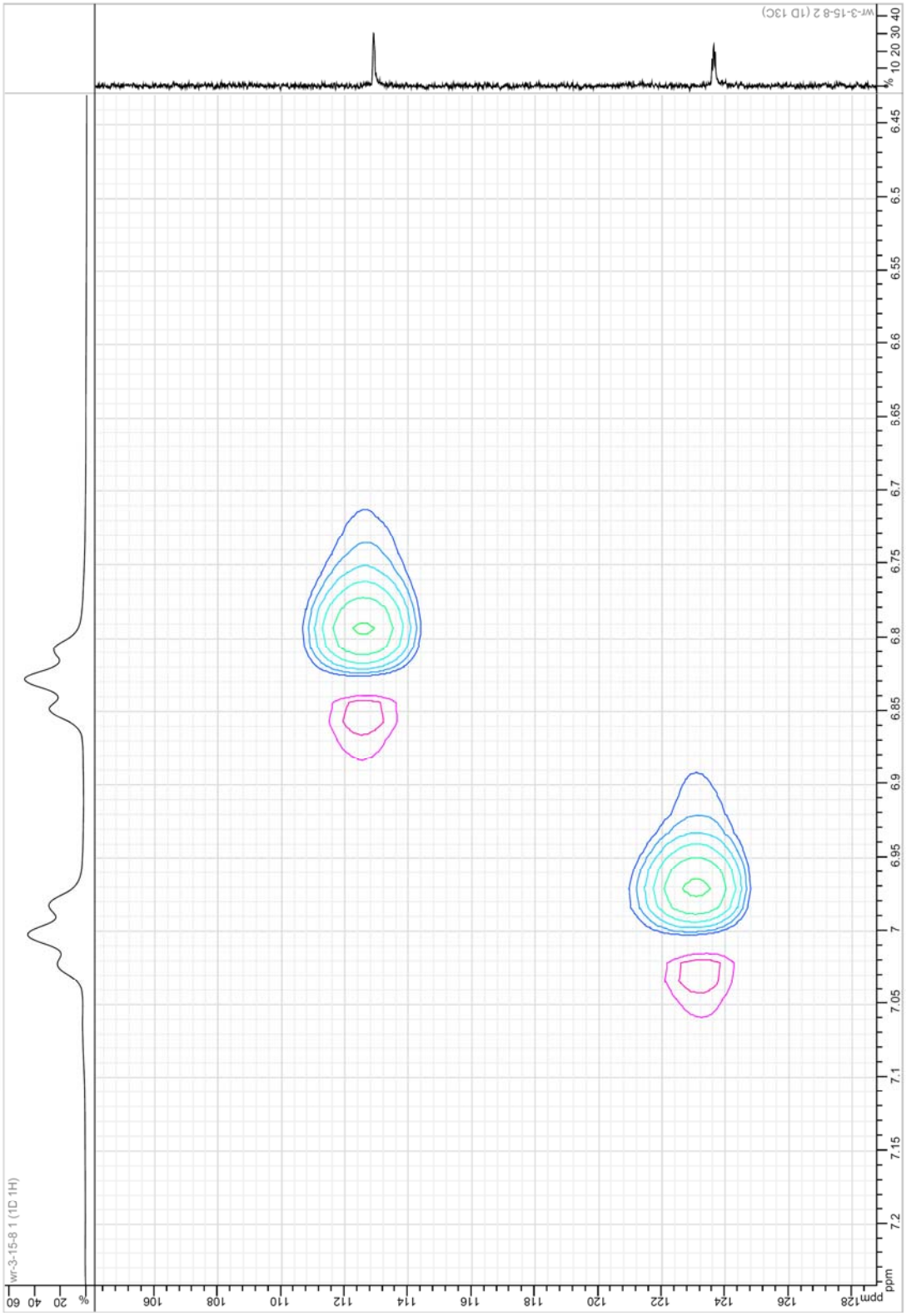
Salicyl alcohol **2s**

^{13}C NMR (100 MHz, DMSO-d_6)



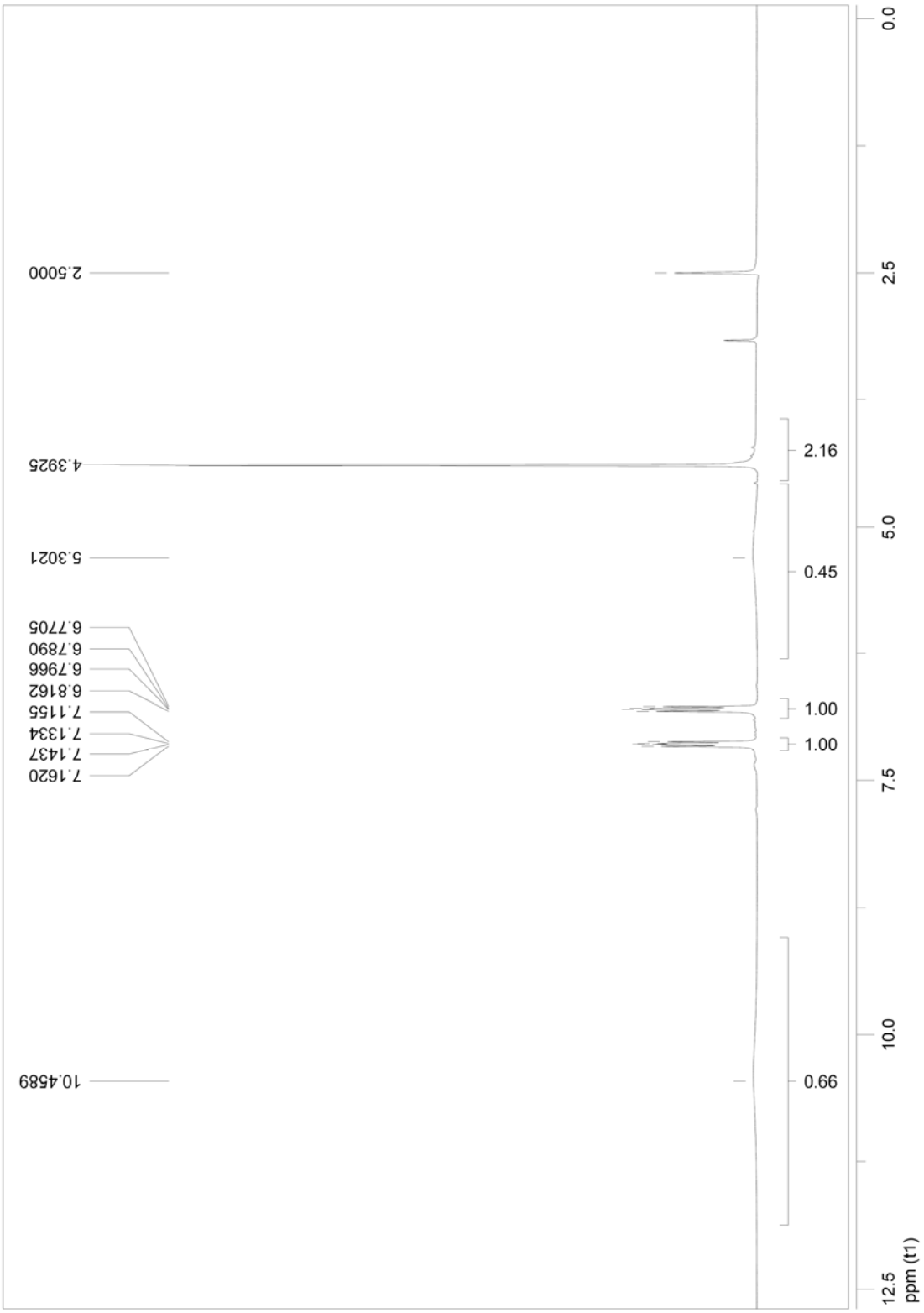
Salicyl alcohol **2s**

HSQC (100 MHz, DMSO-d_6)



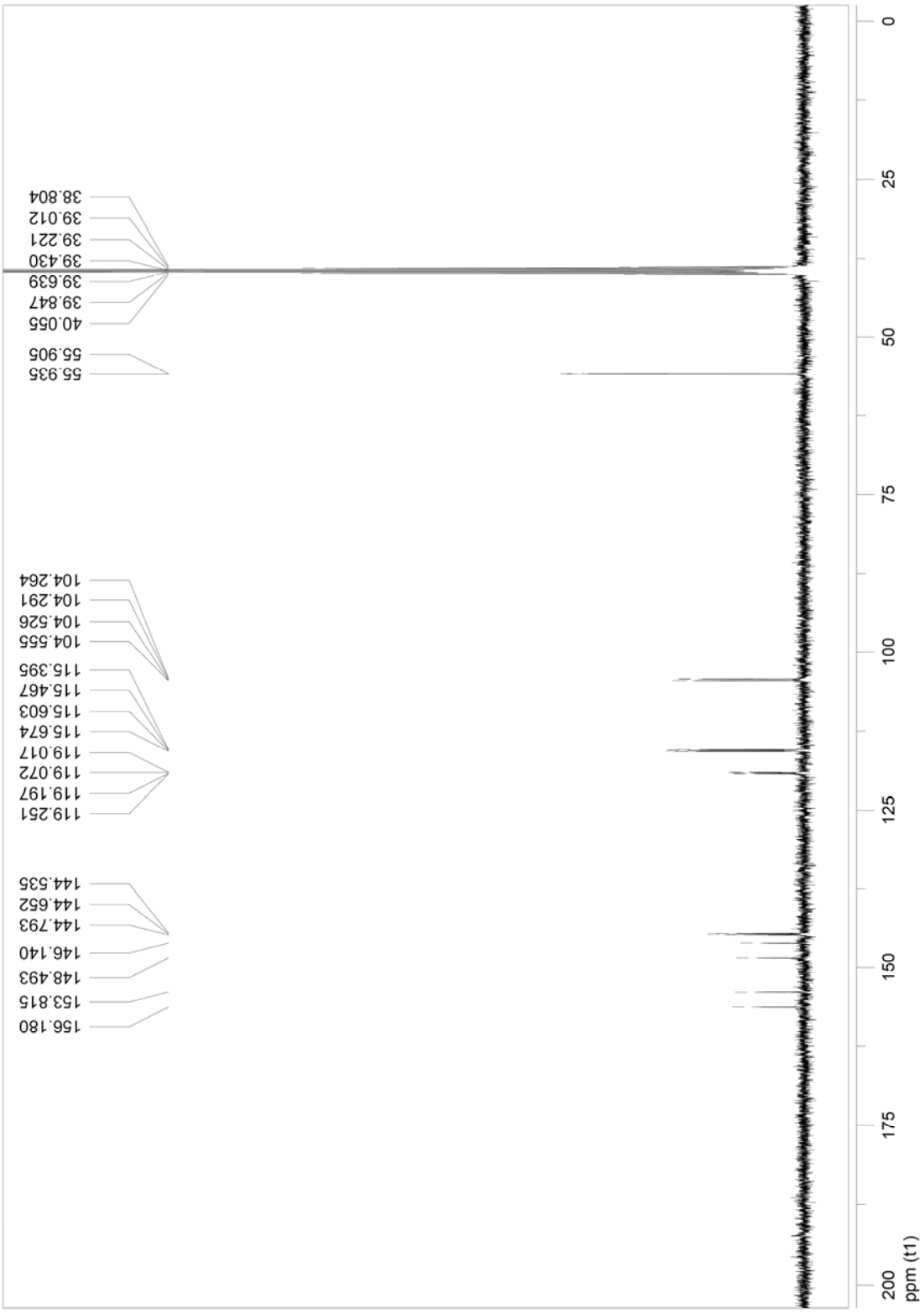
Salicyl alcohol **2t**

^{1}H NMR (400 MHz, DMSO-d_6)



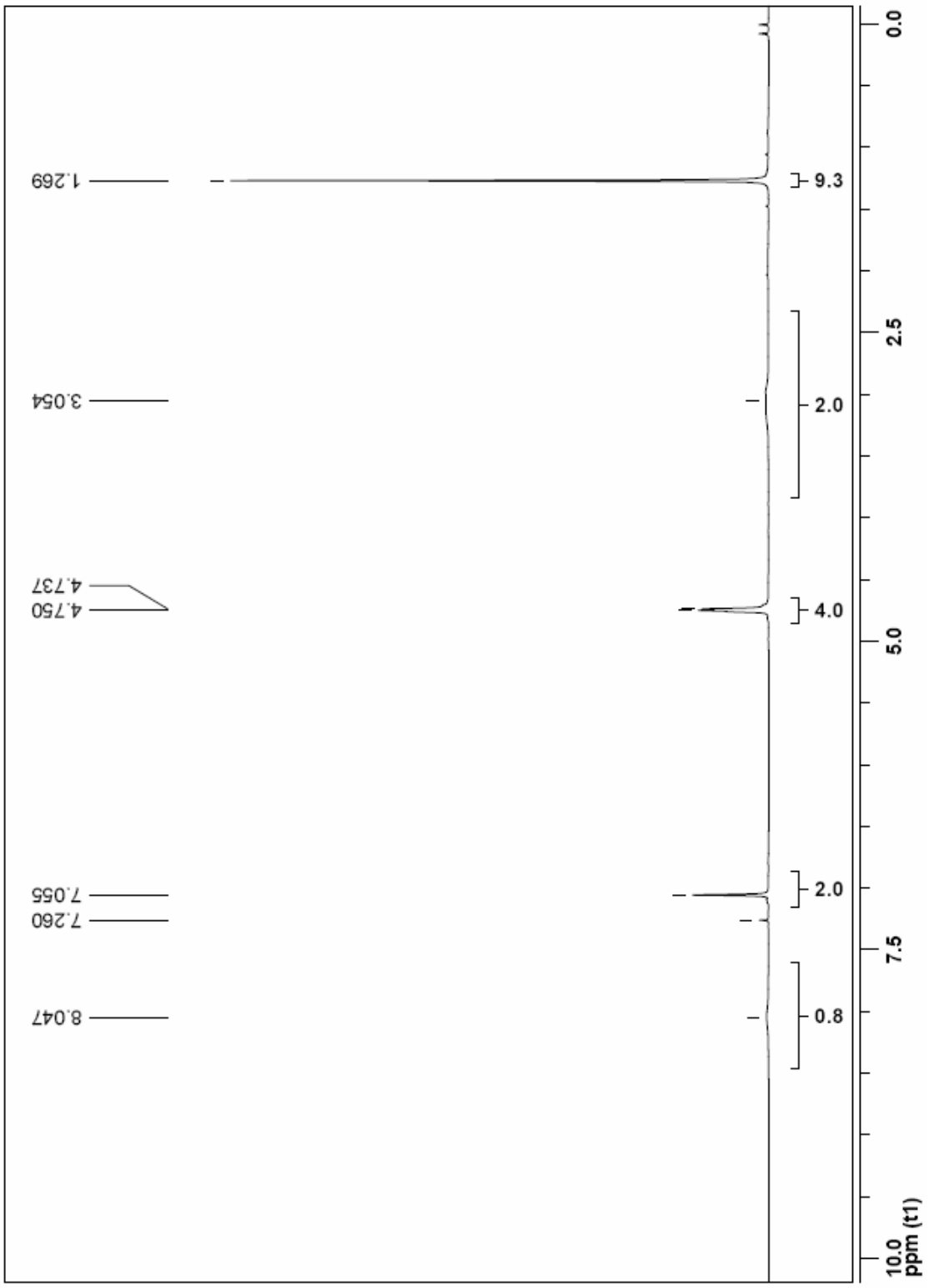
Salicyl alcohol **2t**

^{13}C NMR (100 MHz, DMSO-d_6)



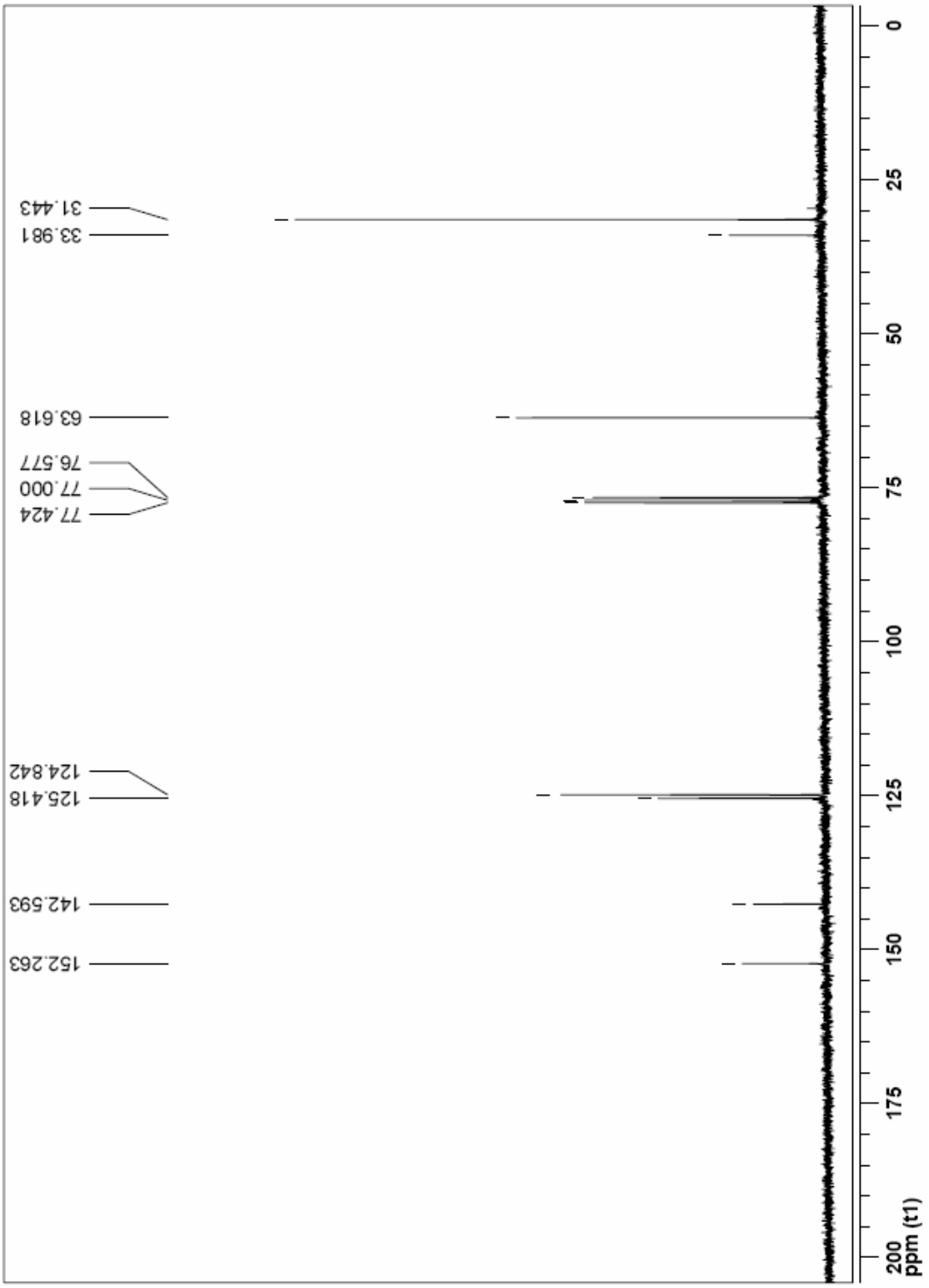
3b. NMR spectra of bishydroxymethyled product **3a**

^{1}H NMR (300 MHz, $CDCl_3$)



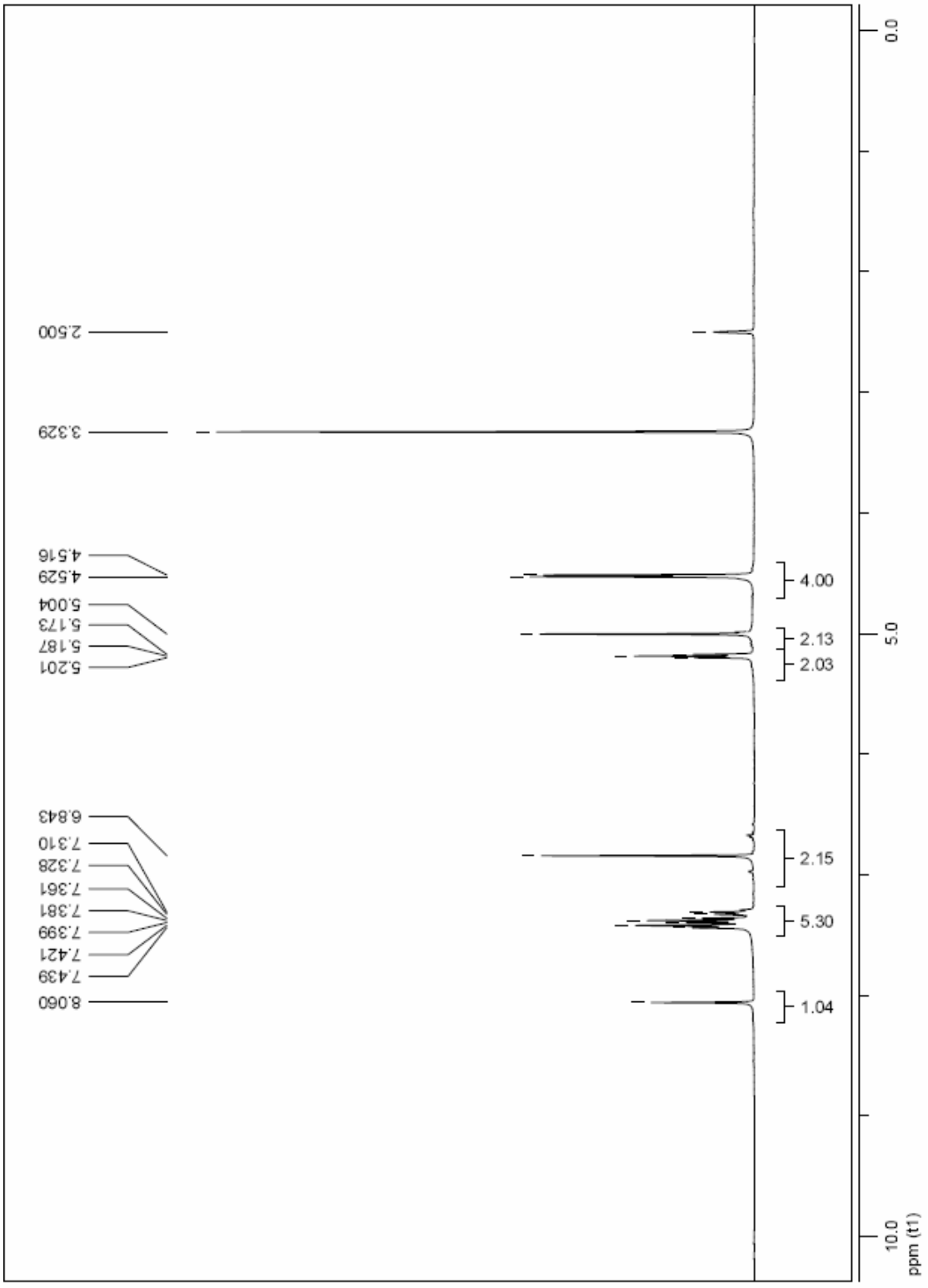
Bishydroxymethyled product **3a**

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



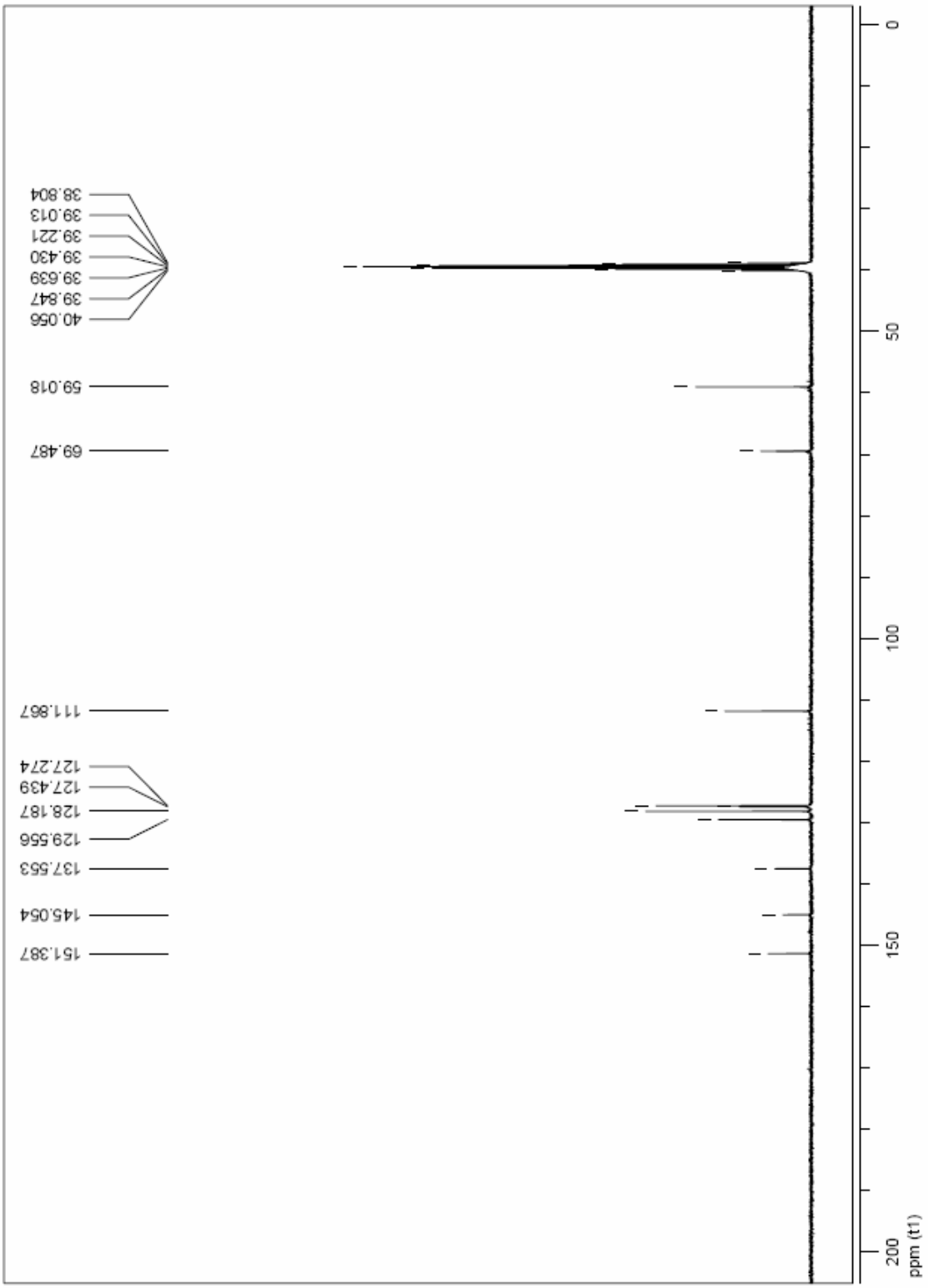
3c. NMR spectra of bishydroxymethyled product **3i**

^{1}H NMR (400 MHz, DMSO-d_6)



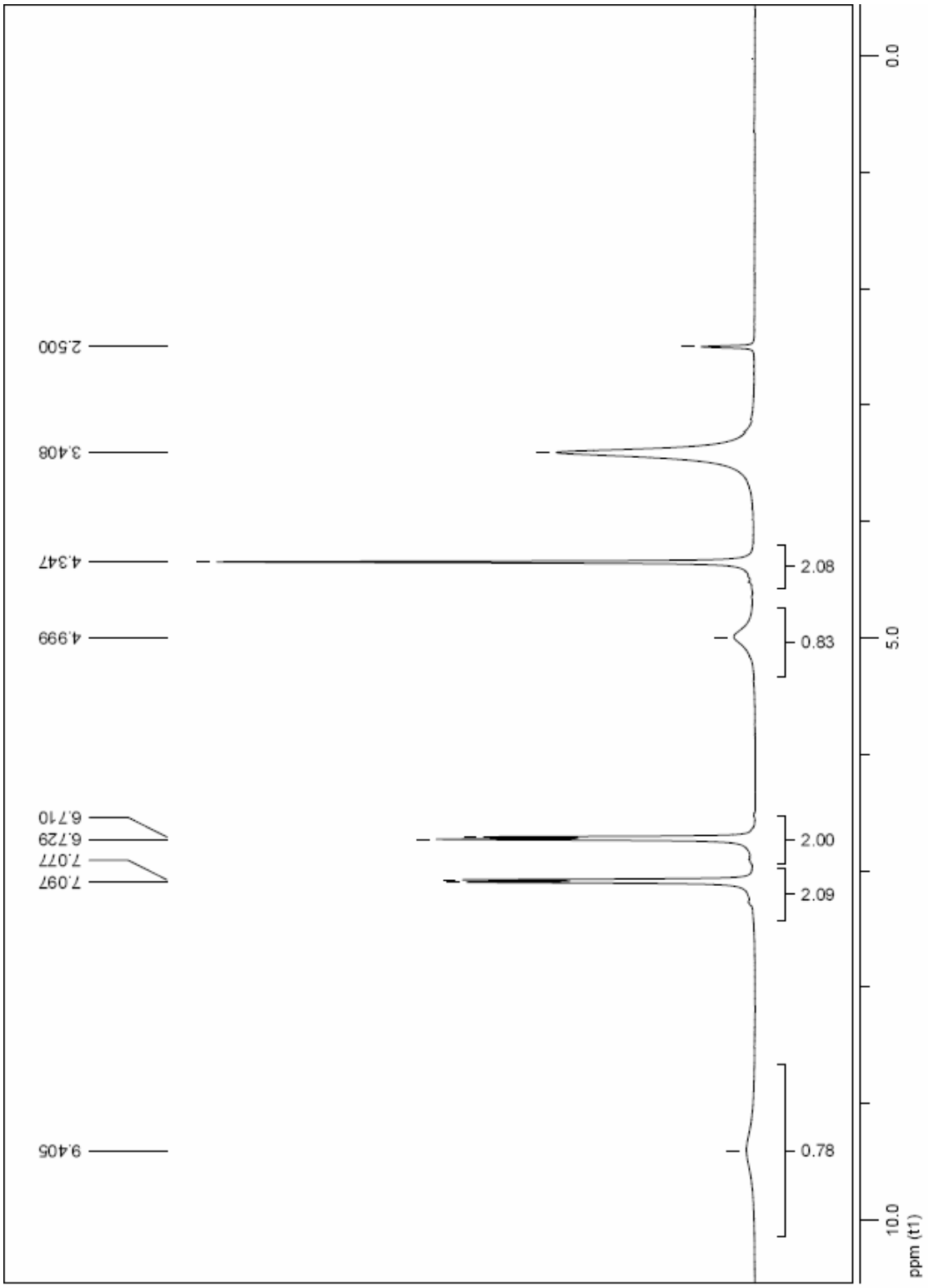
Bishydroxymethyled product **3i**

^{13}C NMR (100 MHz, DMSO-d_6)



3d. NMR spectra of *para*-hydroxymethyled product **4d**

^{1}H NMR (400 MHz, DMSO-d_6)



para-Hydroxymethyled product **4d**

^{13}C NMR (100 MHz, DMSO-d_6)