

Complete tetraglycosylation of a calix[4]arene by a chemo-enzymatic approach

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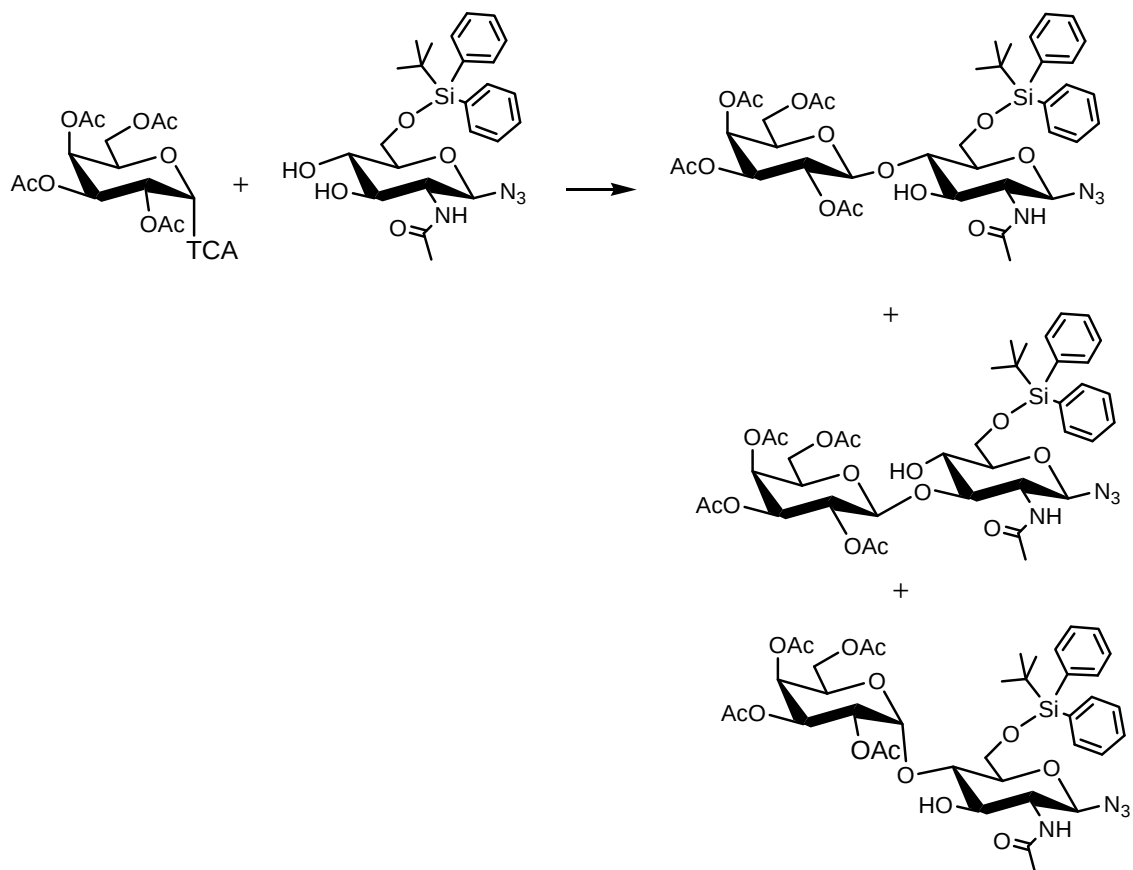
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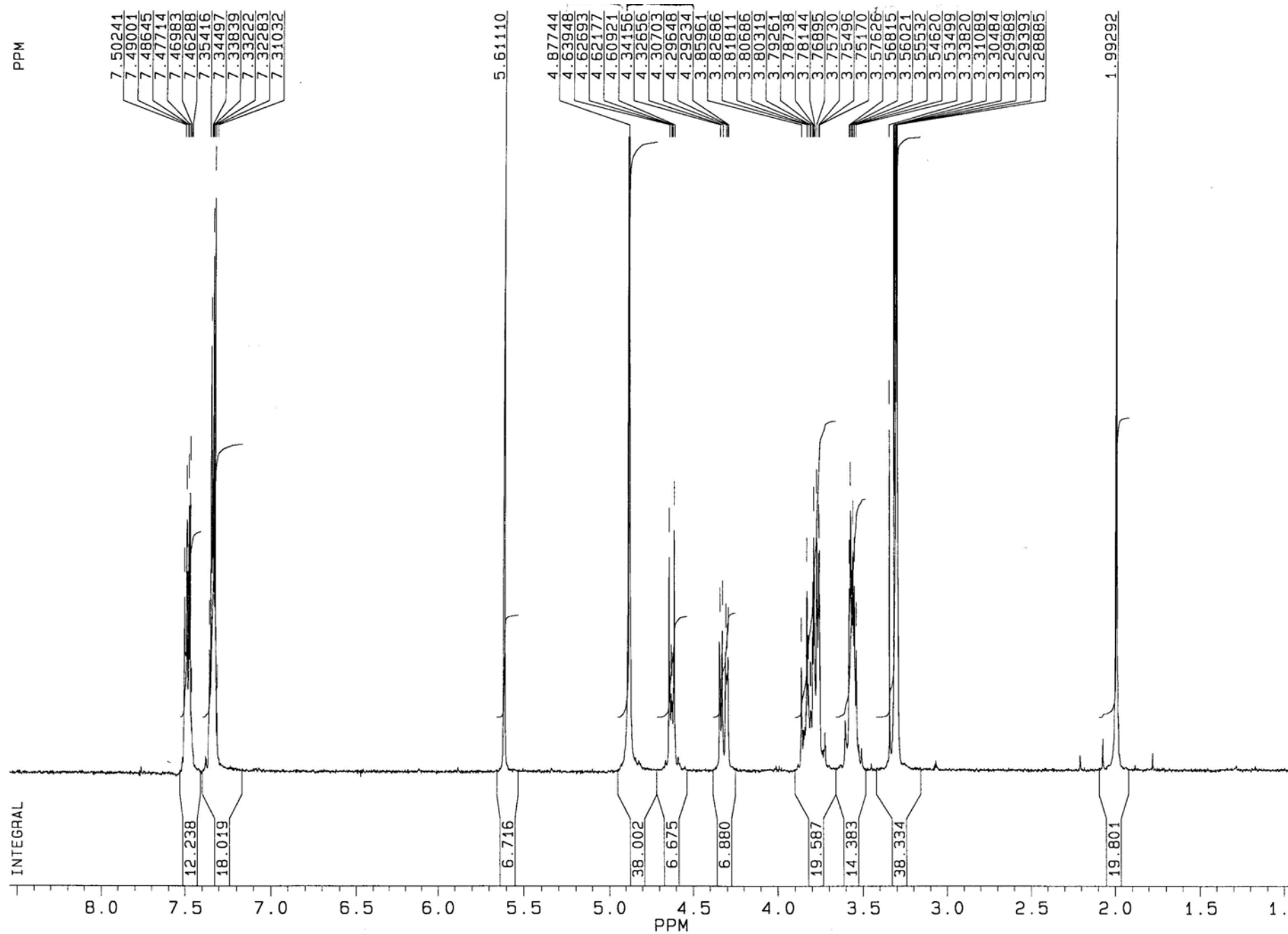
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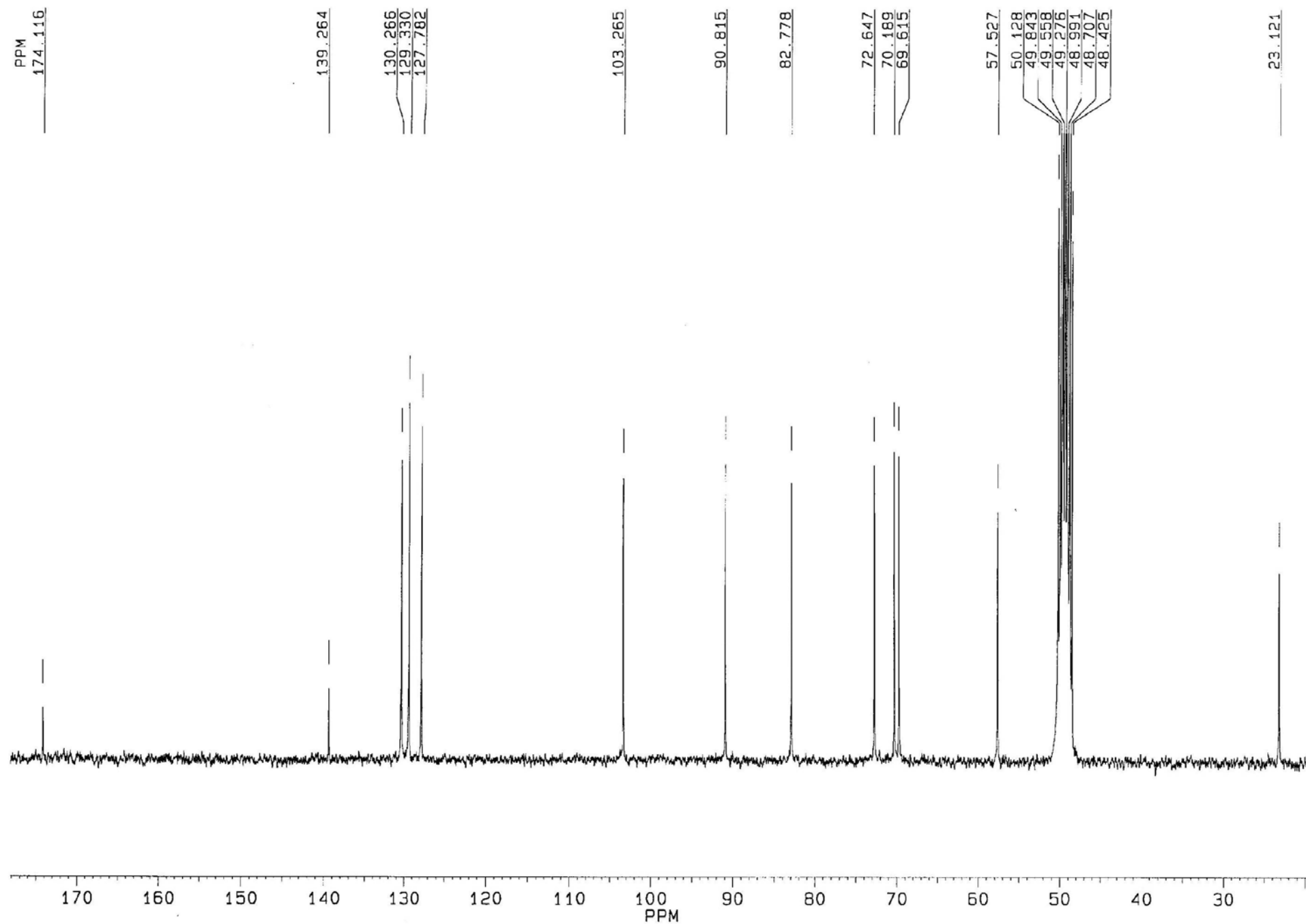
Scheme S1. Glycosylation reaction between 2-acetamido-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl- β -D-glucopyranosyl azide and 2,3,4,6-tetraacetyl- α -galactosyl trichloroacetimidate. Reagents and conditions: $\text{BF}_3 \cdot \text{Et}_2\text{O}$, dry CH_2Cl_2 , Ar atmosphere, -45°C , 2h.



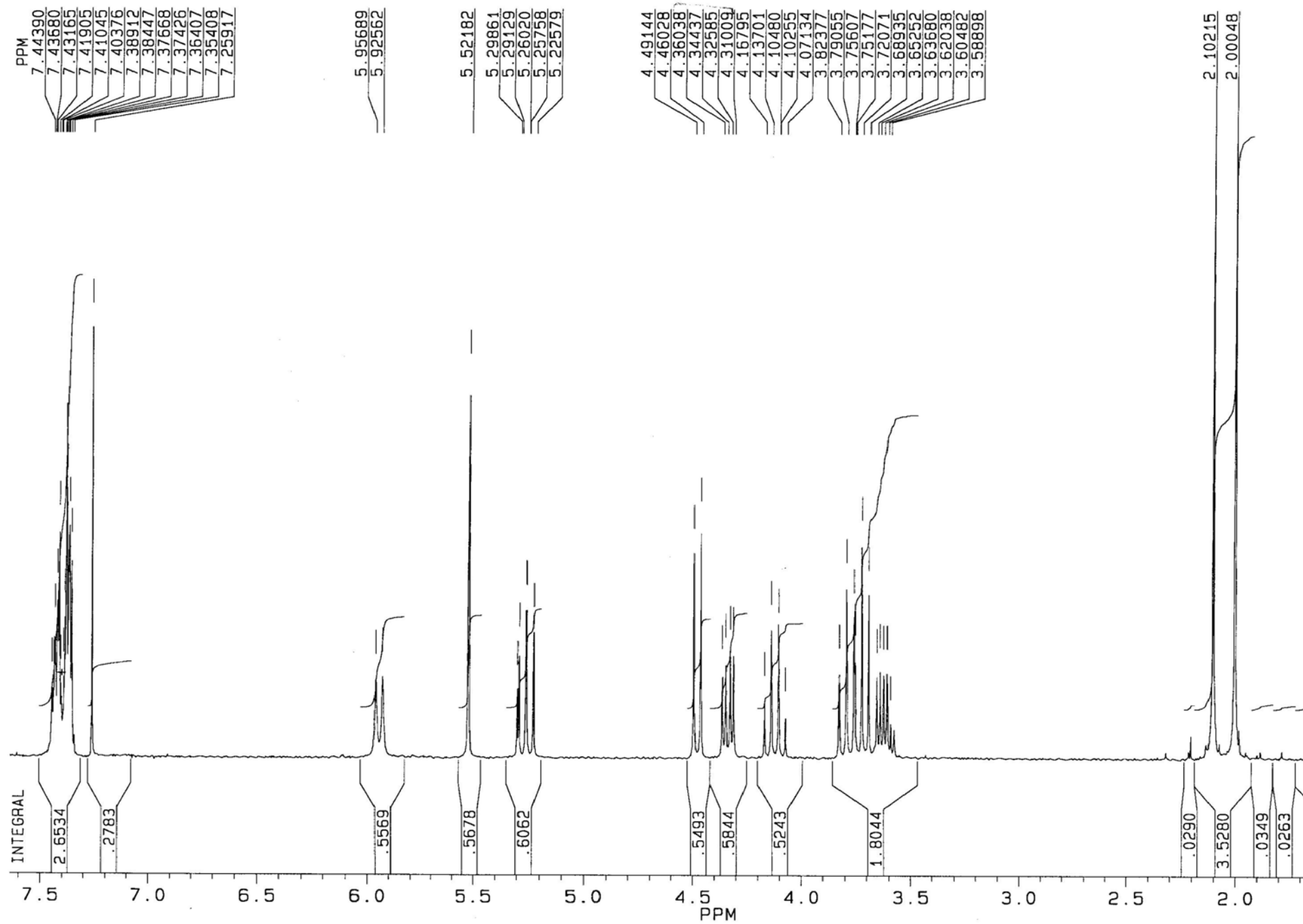
^1H NMR (300 MHz, CD_3OD) of compound **4**



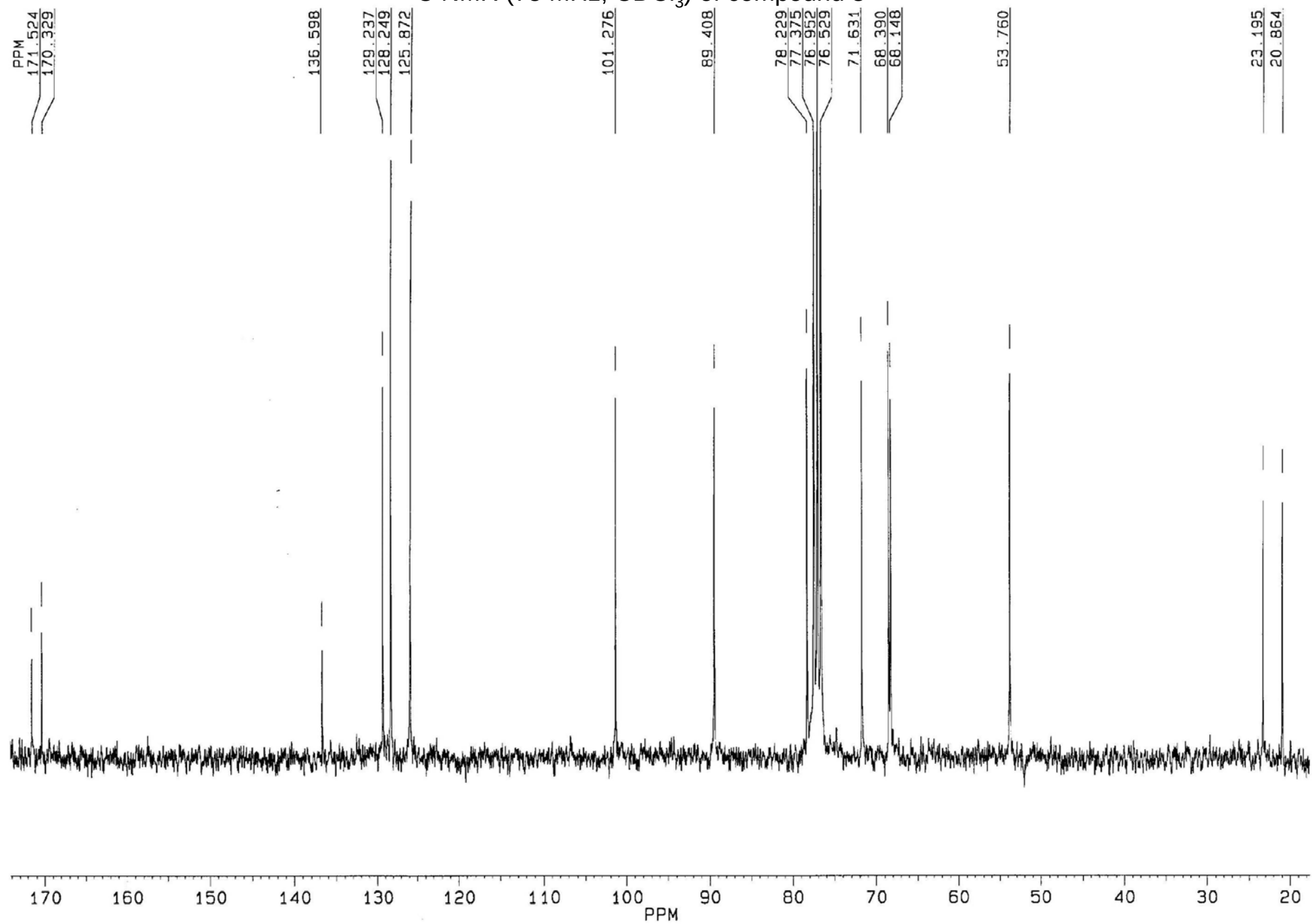
¹³C NMR (75 MHz, CD₃OD) of compound **4**



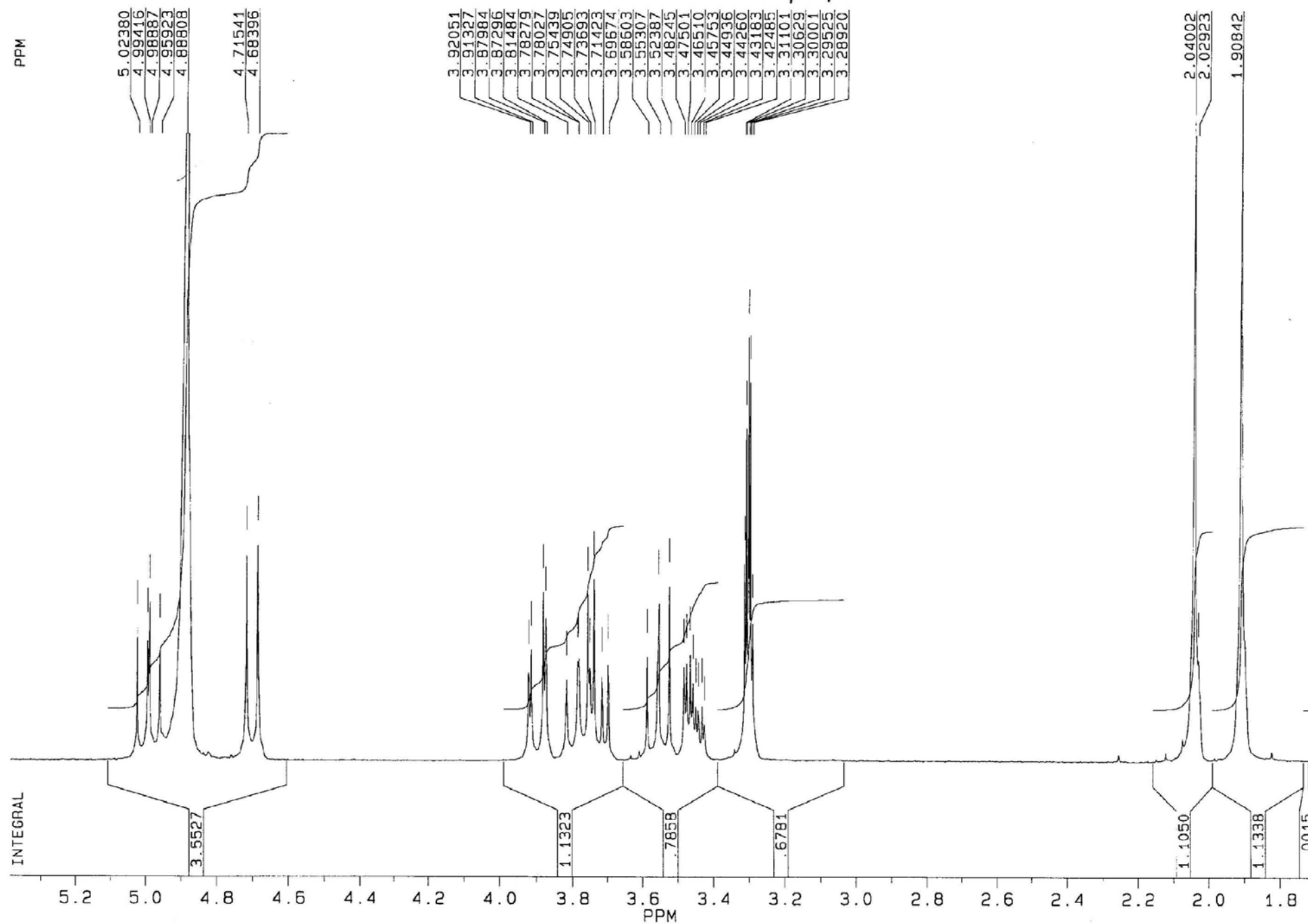
¹H NMR (300 MHz, CDCl₃) of compound **5**



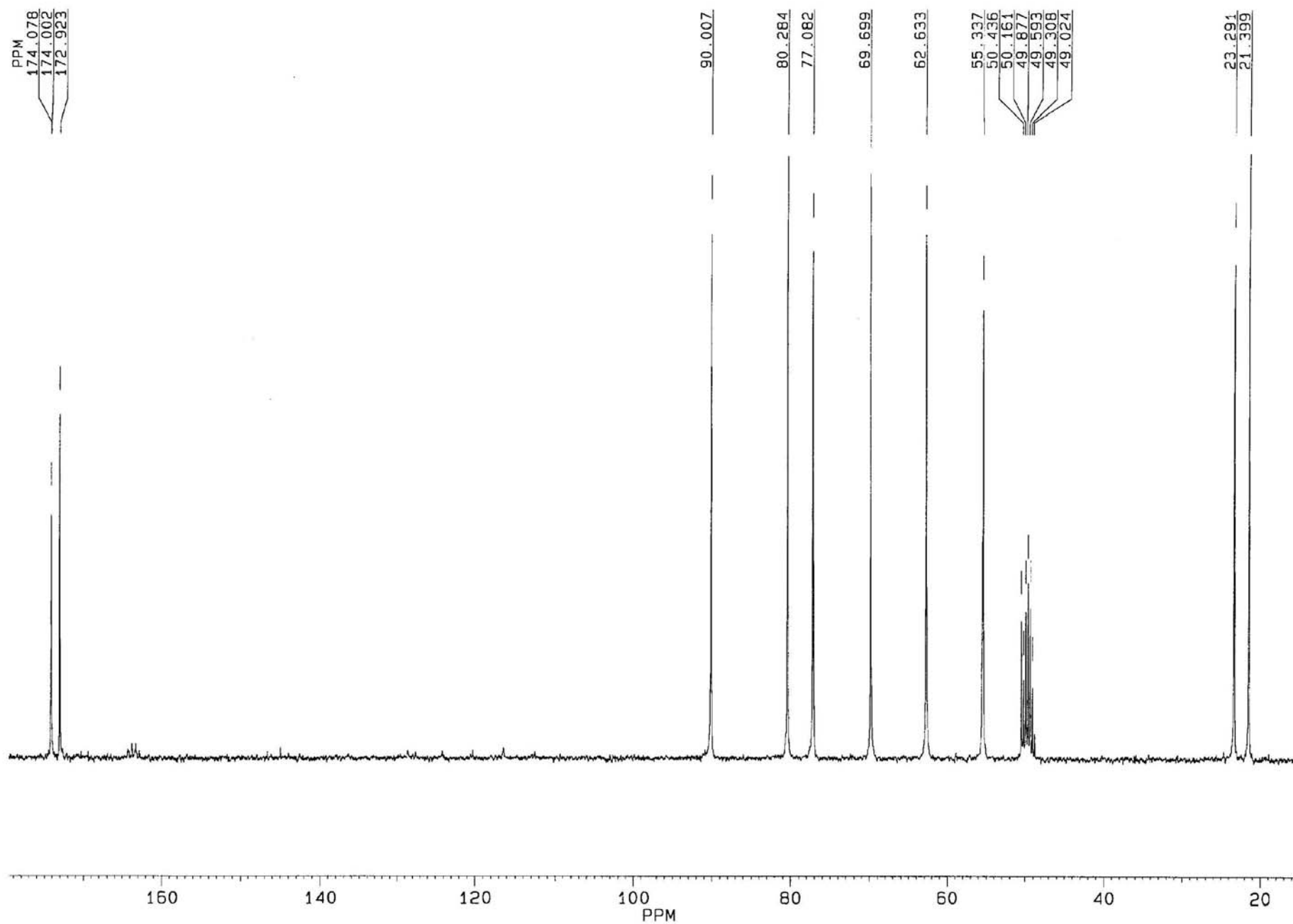
¹³C NMR (75 MHz, CDCl₃) of compound **5**



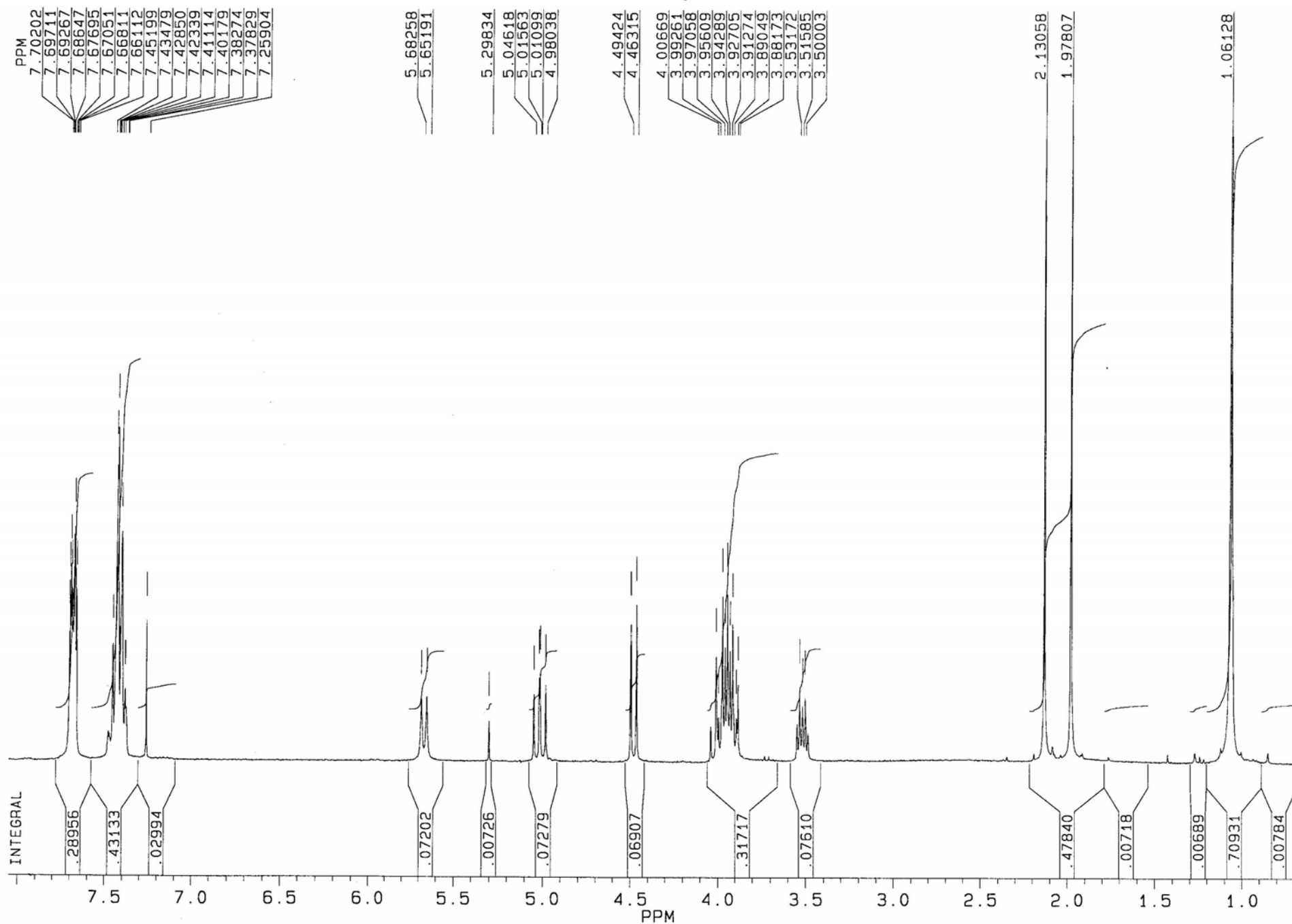
¹H NMR (300 MHz, CD₃OD) of compound 6



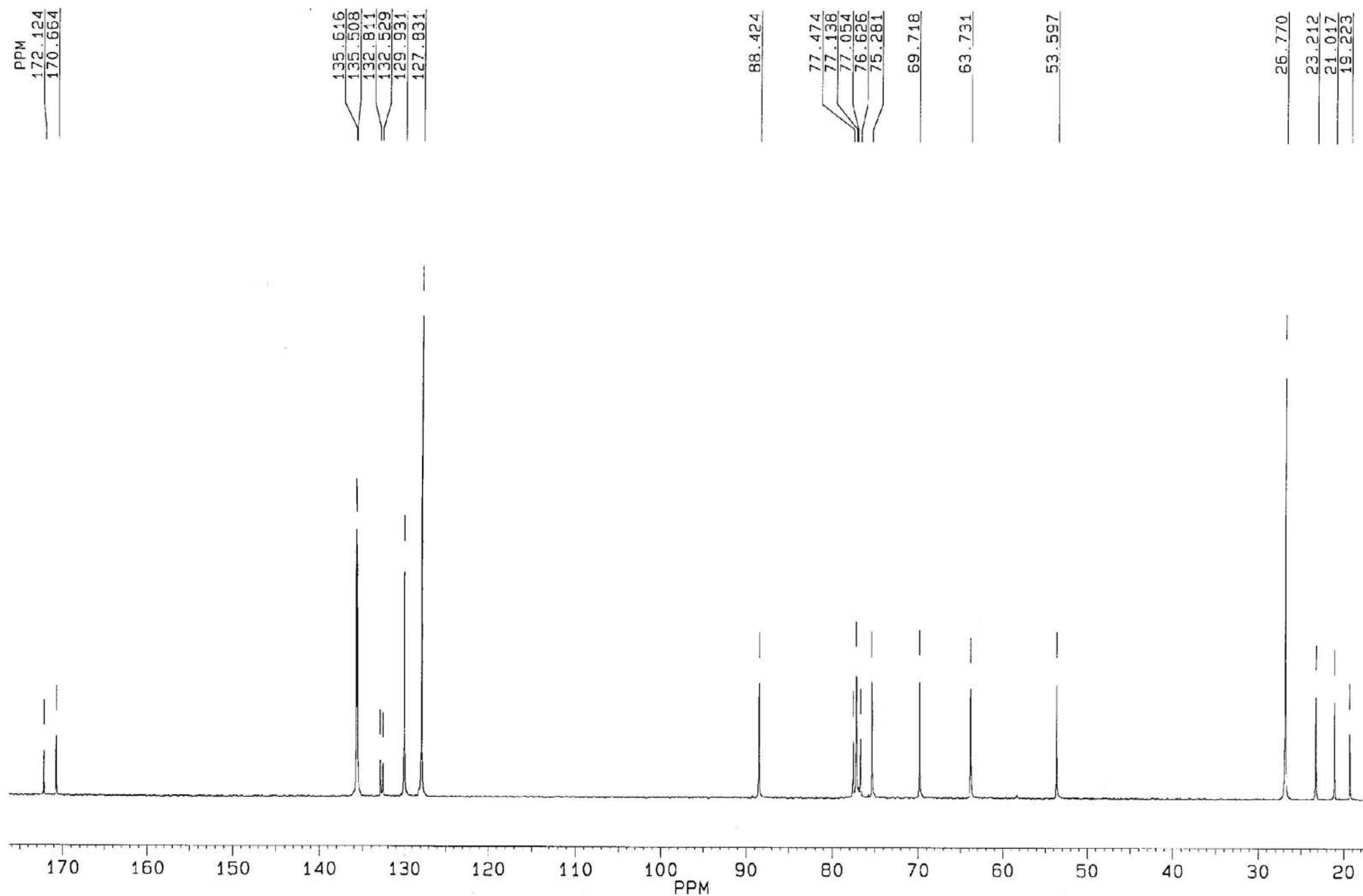
^{13}C NMR (75 MHz, CD_3OD) of compound **6**



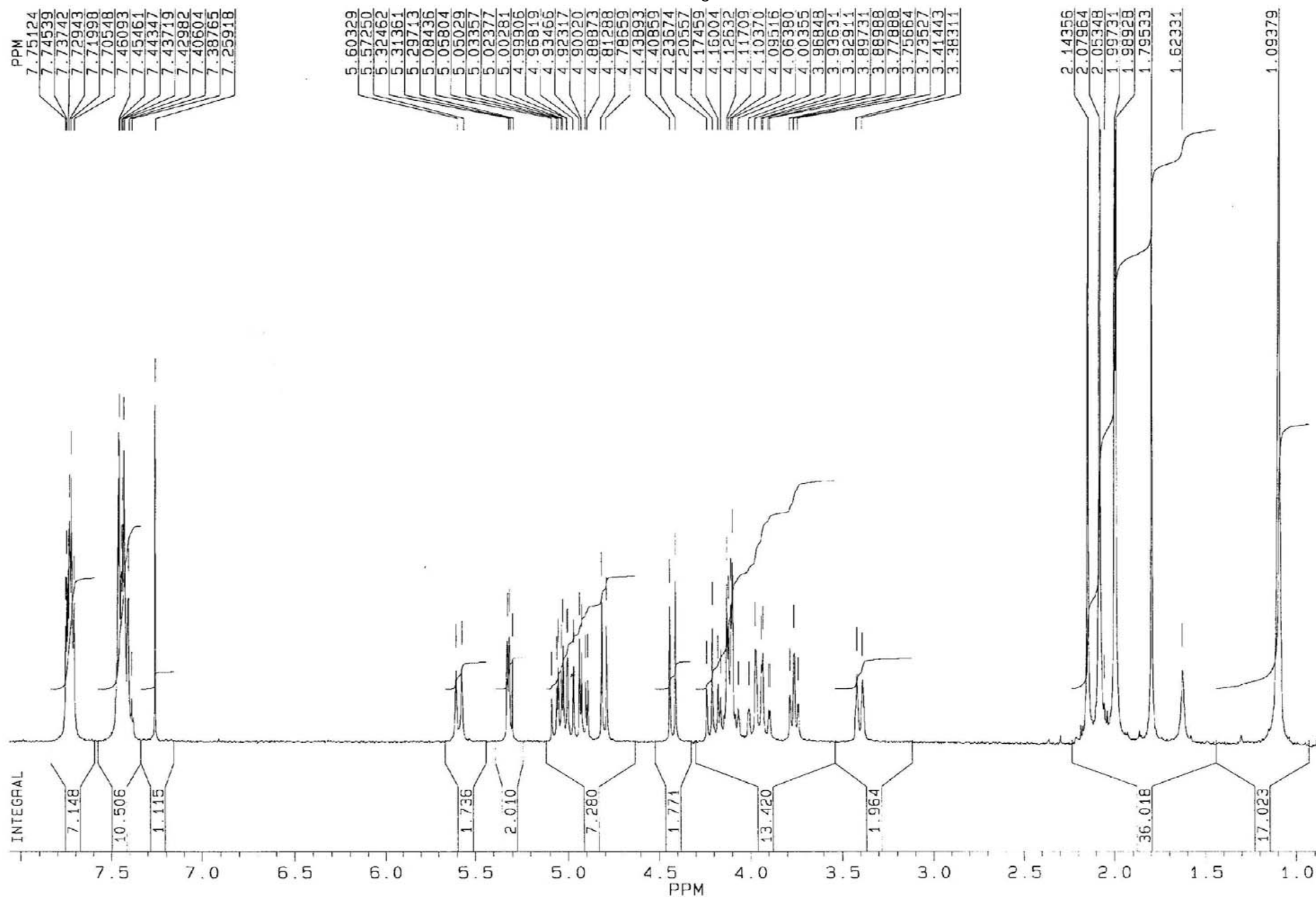
^1H NMR (300 MHz, CDCl_3) of compound 7



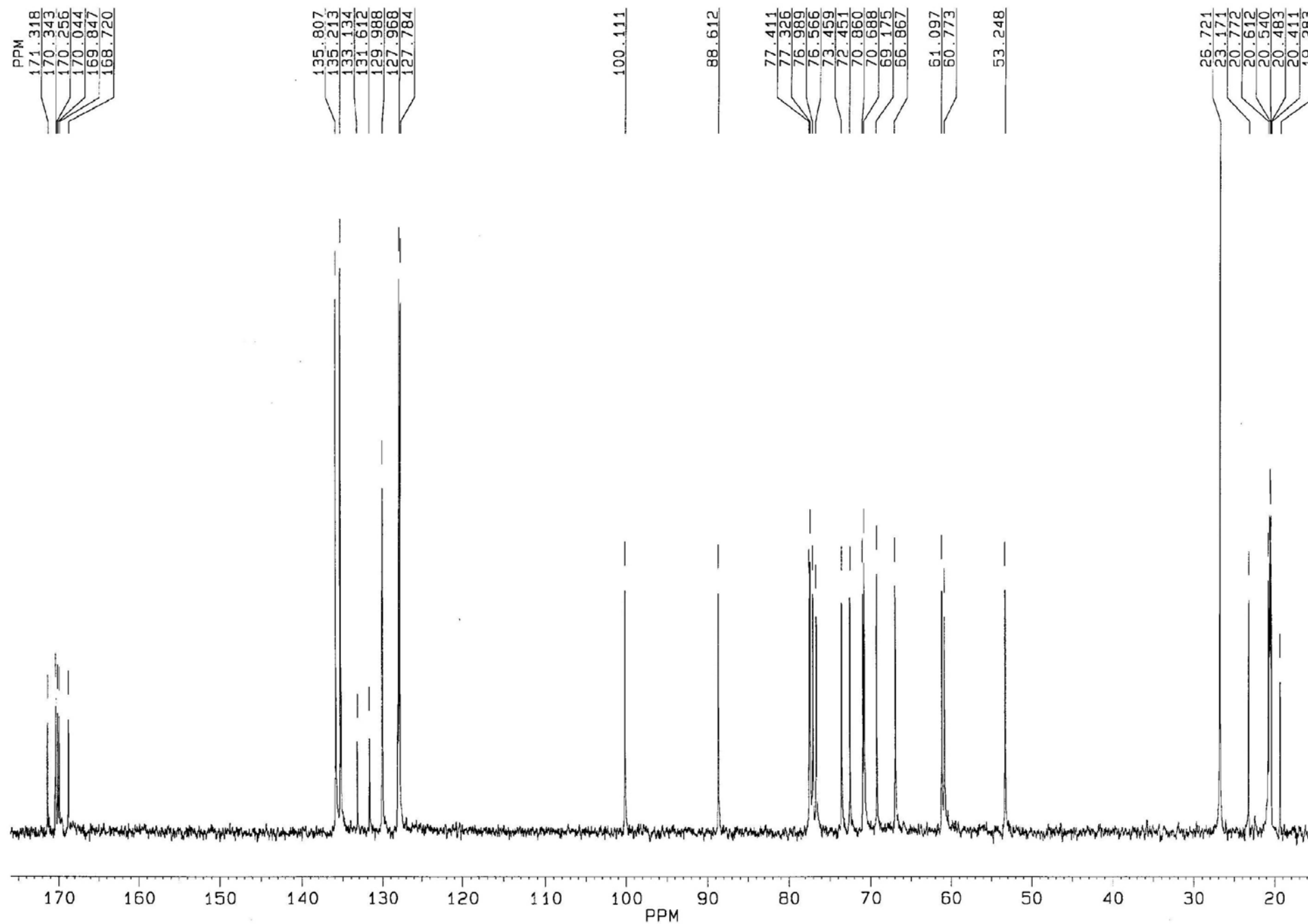
^{13}C NMR (75 MHz, CDCl_3) of compound **7**



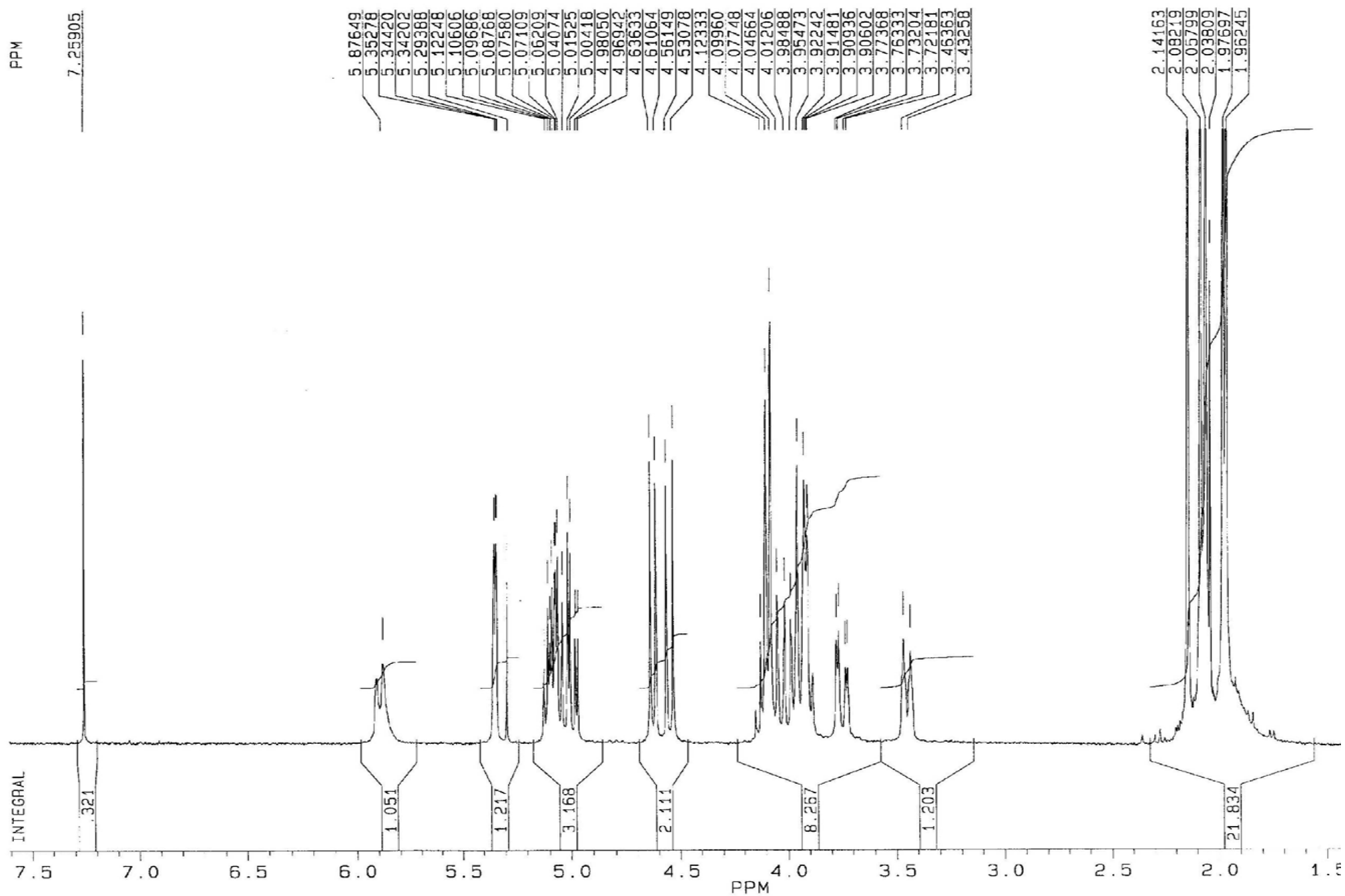
¹H NMR (300 MHz, CDCl₃) of compound **9**



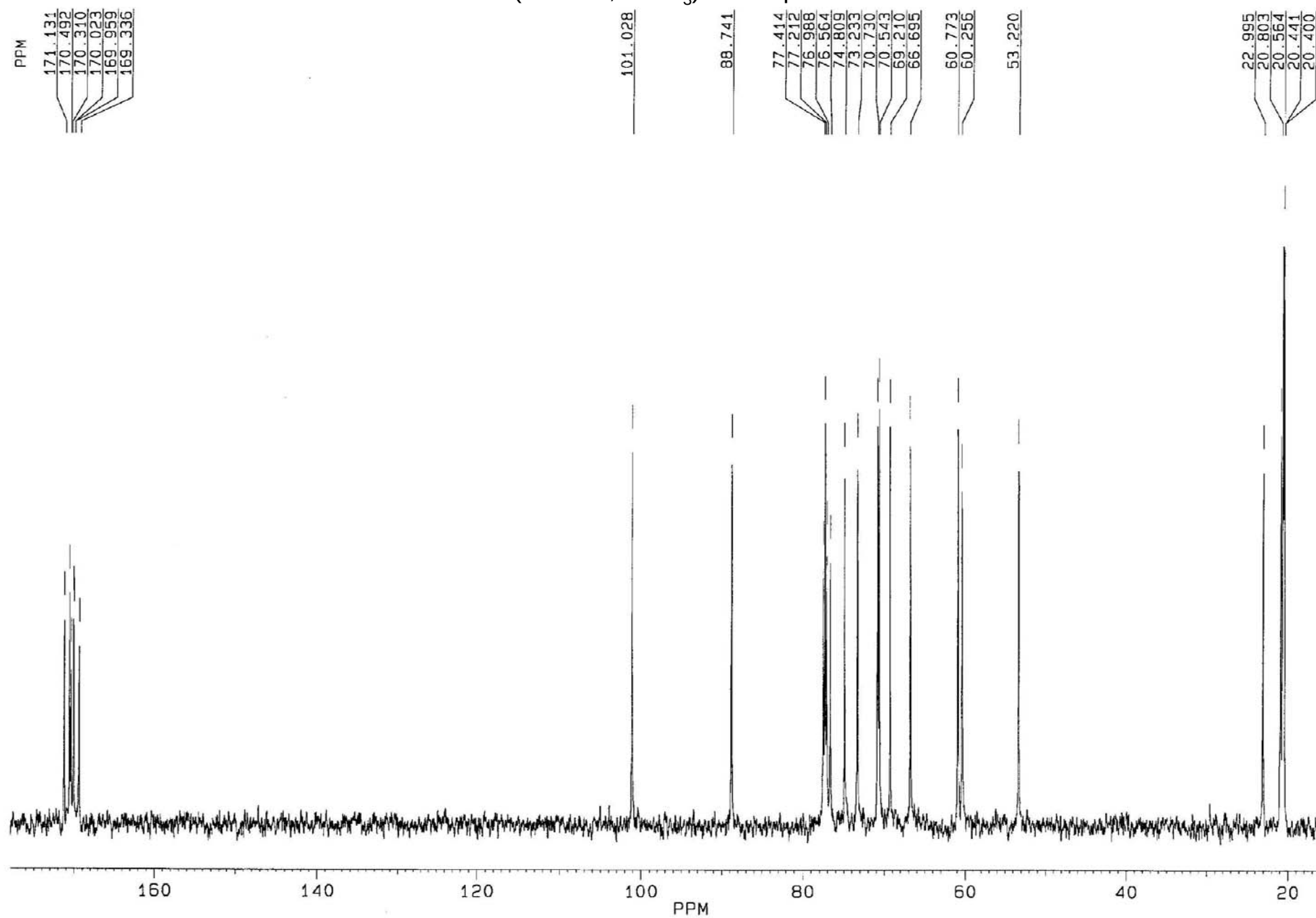
^{13}C NMR (75 MHz, CDCl_3) of compound **9**



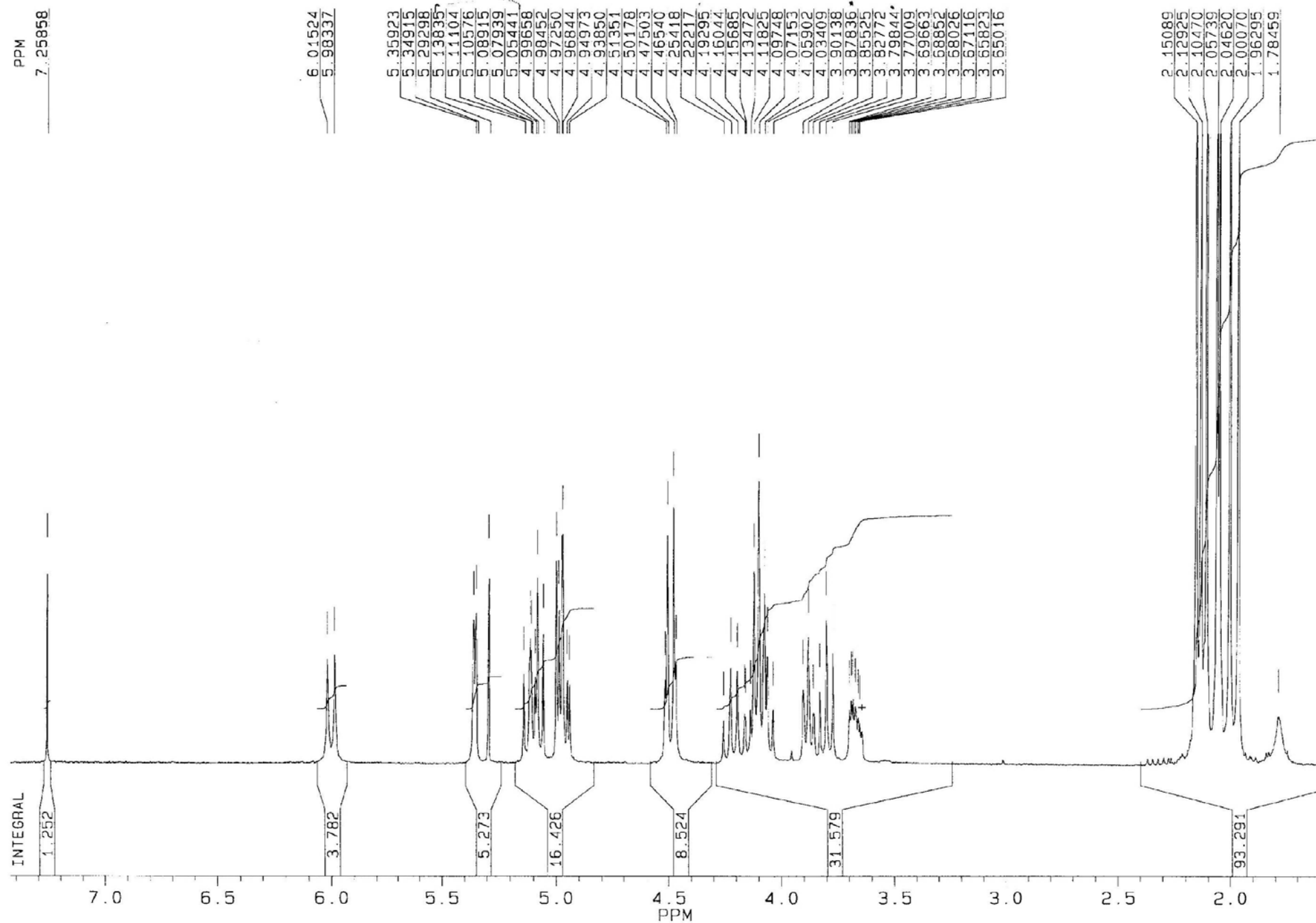
^1H NMR (300 MHz, CDCl_3) of compound **10**



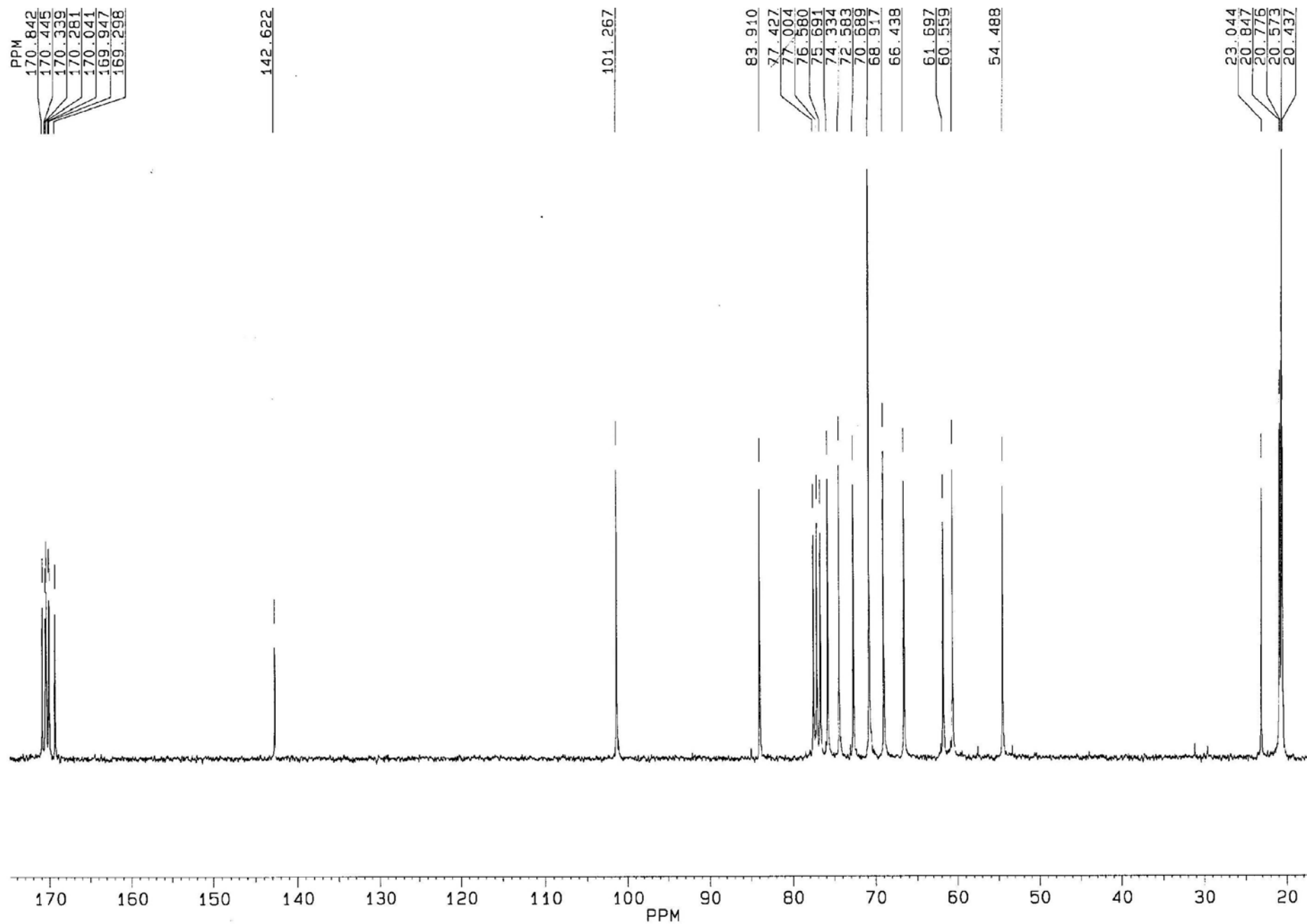
^{13}C NMR (75 MHz, CDCl_3) of compound **10**



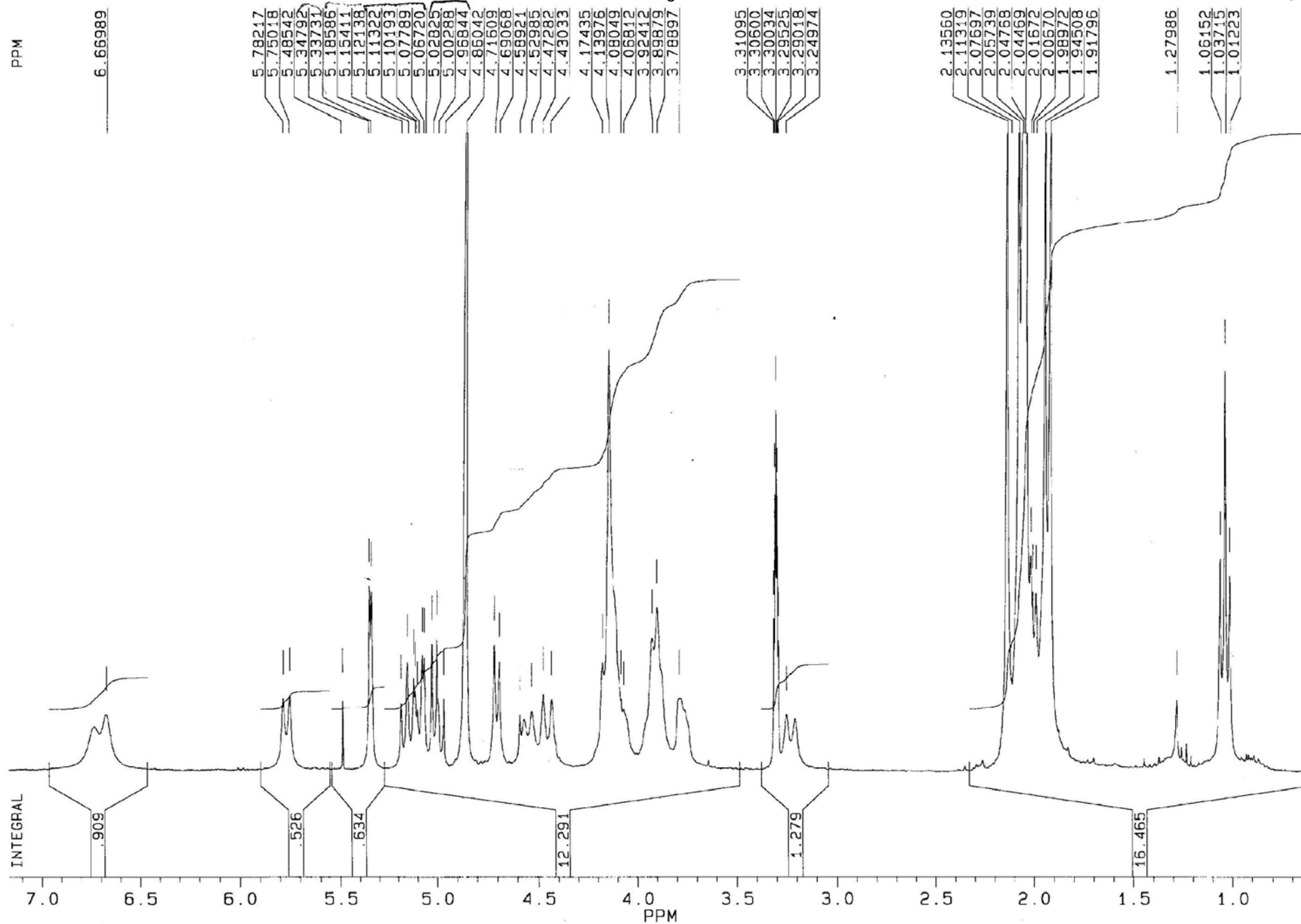
¹H NMR (300 MHz, CDCl₃) of compound **13**



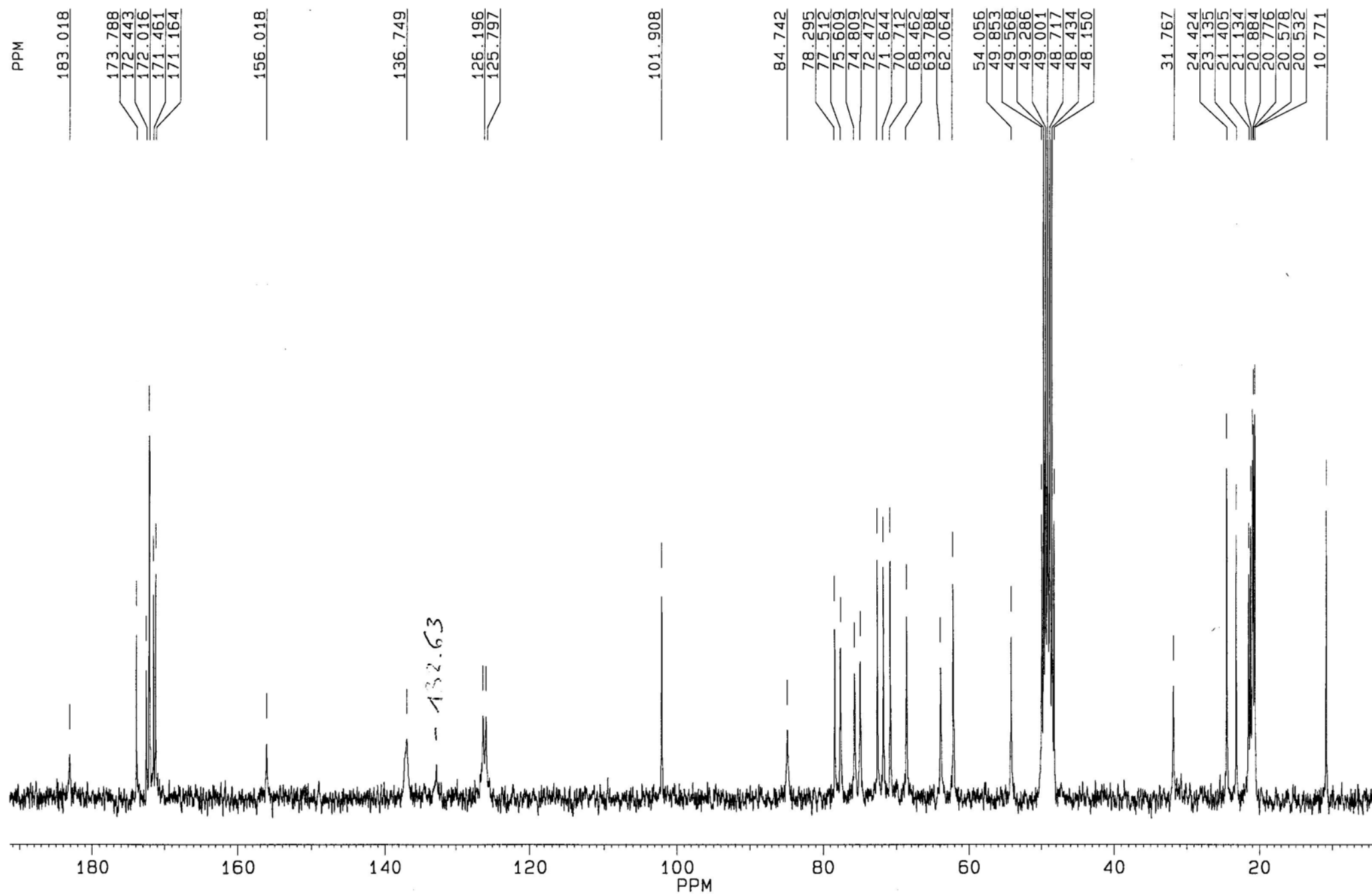
^{13}C NMR (75 MHz, CDCl_3) of compound **13**



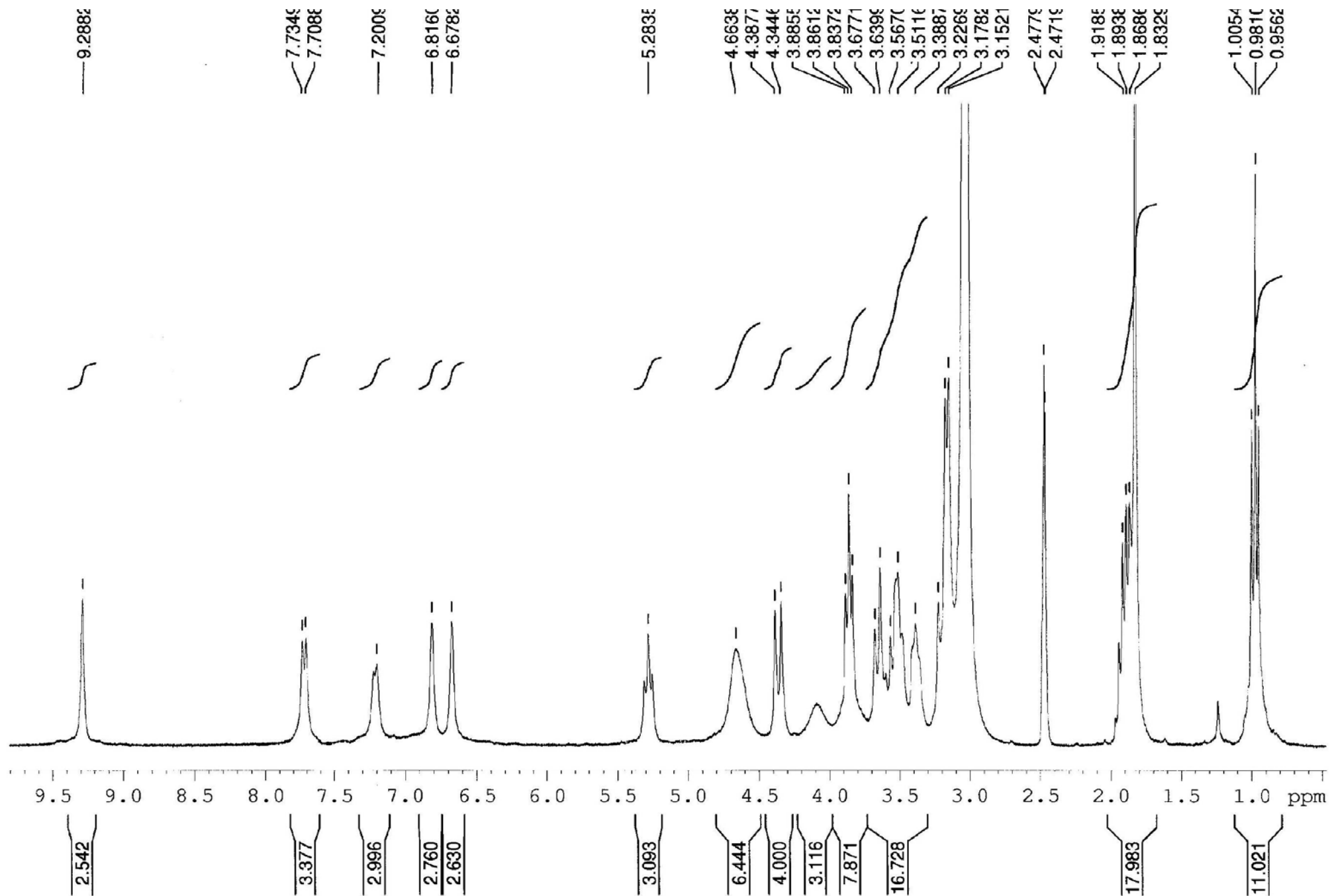
¹H NMR (300 MHz, CD₃OD) of compound **15**



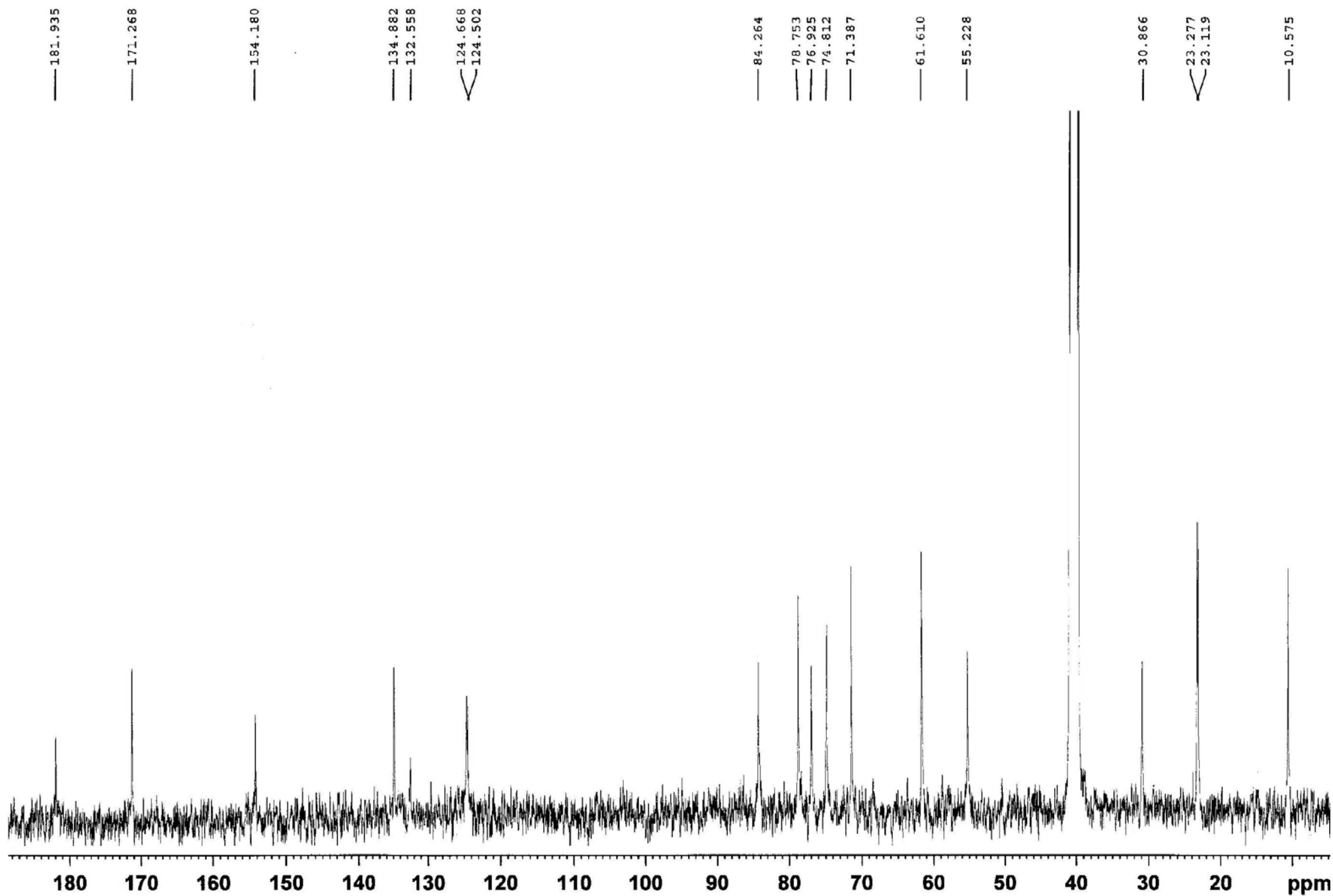
¹³C NMR (75 MHz, CD₃OD) of compound **15**



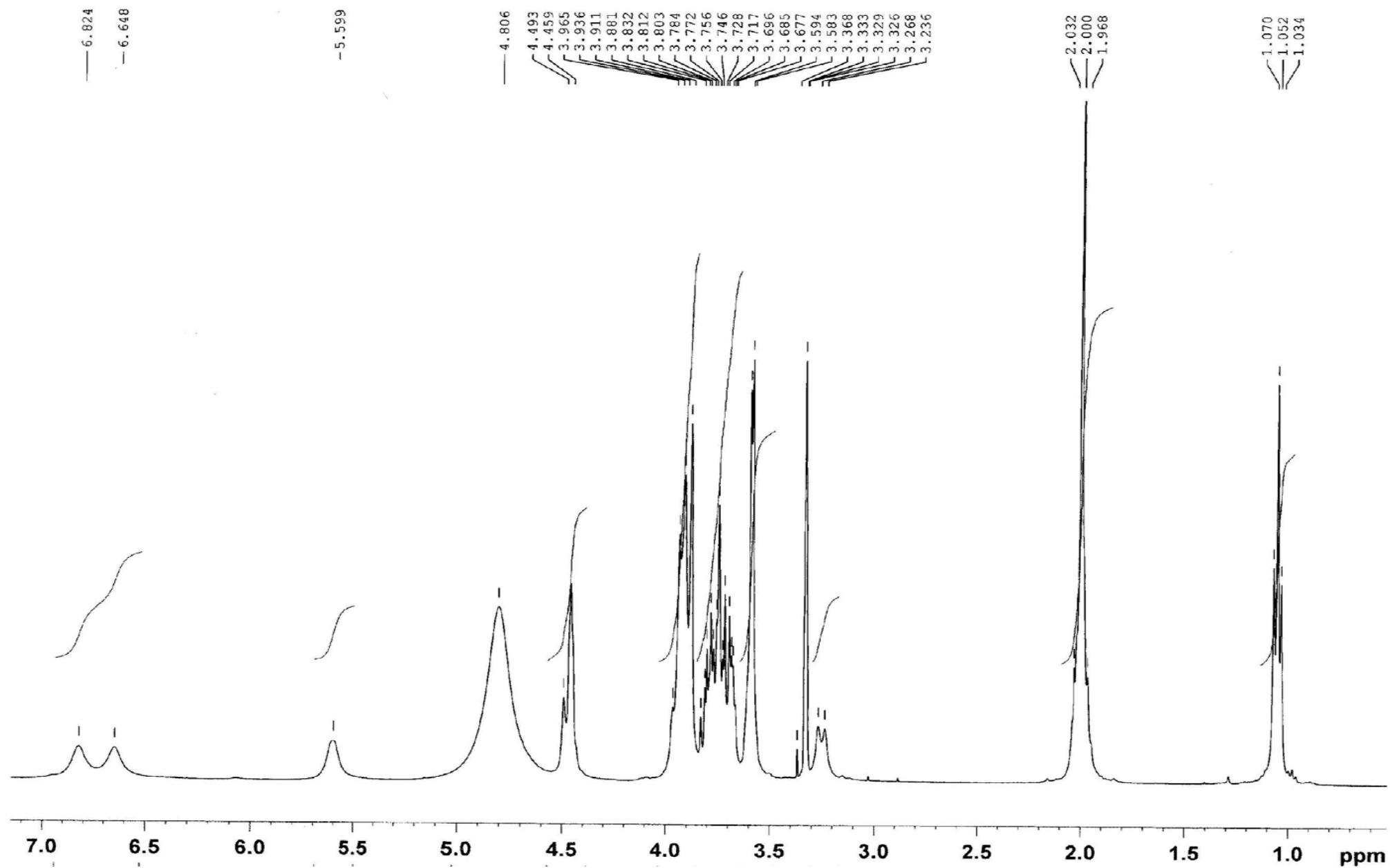
^1H NMR (300 MHz, DMSO- d_6 , 80 $^\circ\text{C}$) of compound **17**



^{13}C NMR (100 MHz, DMSO- d_6 , 80 $^{\circ}\text{C}$) of compound **17**



^1H NMR (400 MHz, $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 5/1 v/v) of compound **1**



¹³C NMR (100 MHz, CD₃OD/D₂O 5/1 v/v) of compound 1

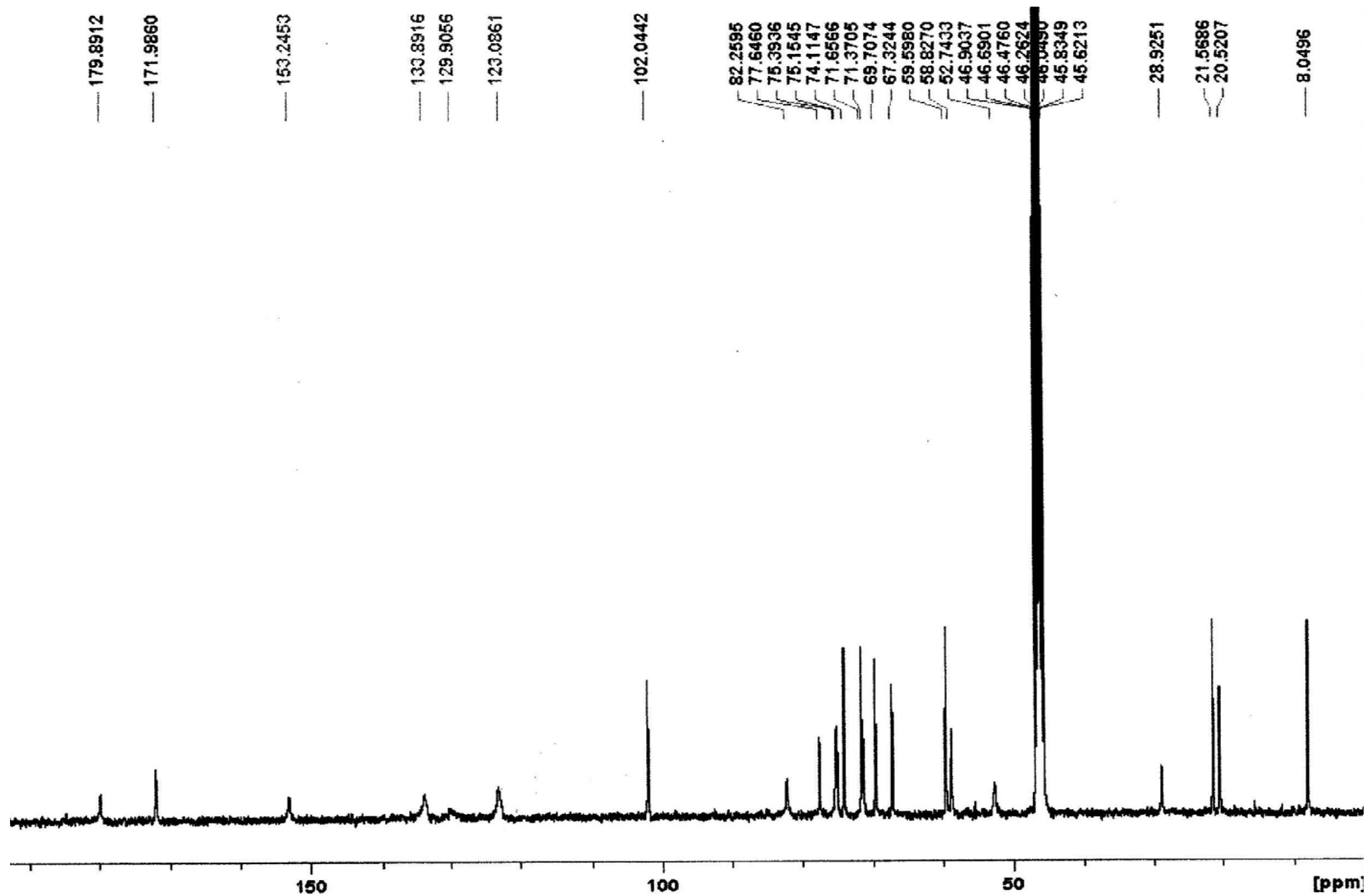


Figure S1. HPLC profile (PRONTOSIL 120-5-Phenyl 5.0 μm column and isopropanol/water with 0.1% formic acid as eluent (gradient from 30% to 60% of isopropanol in 20 minutes)) of the enzymatic galactosylation reaction (a) after 1 hour and (b) after 48 h and after removal of proteins and addition of the starting calixarene **17** (rt 15.842 min) as internal standard. c) Overlap of the two profiles.

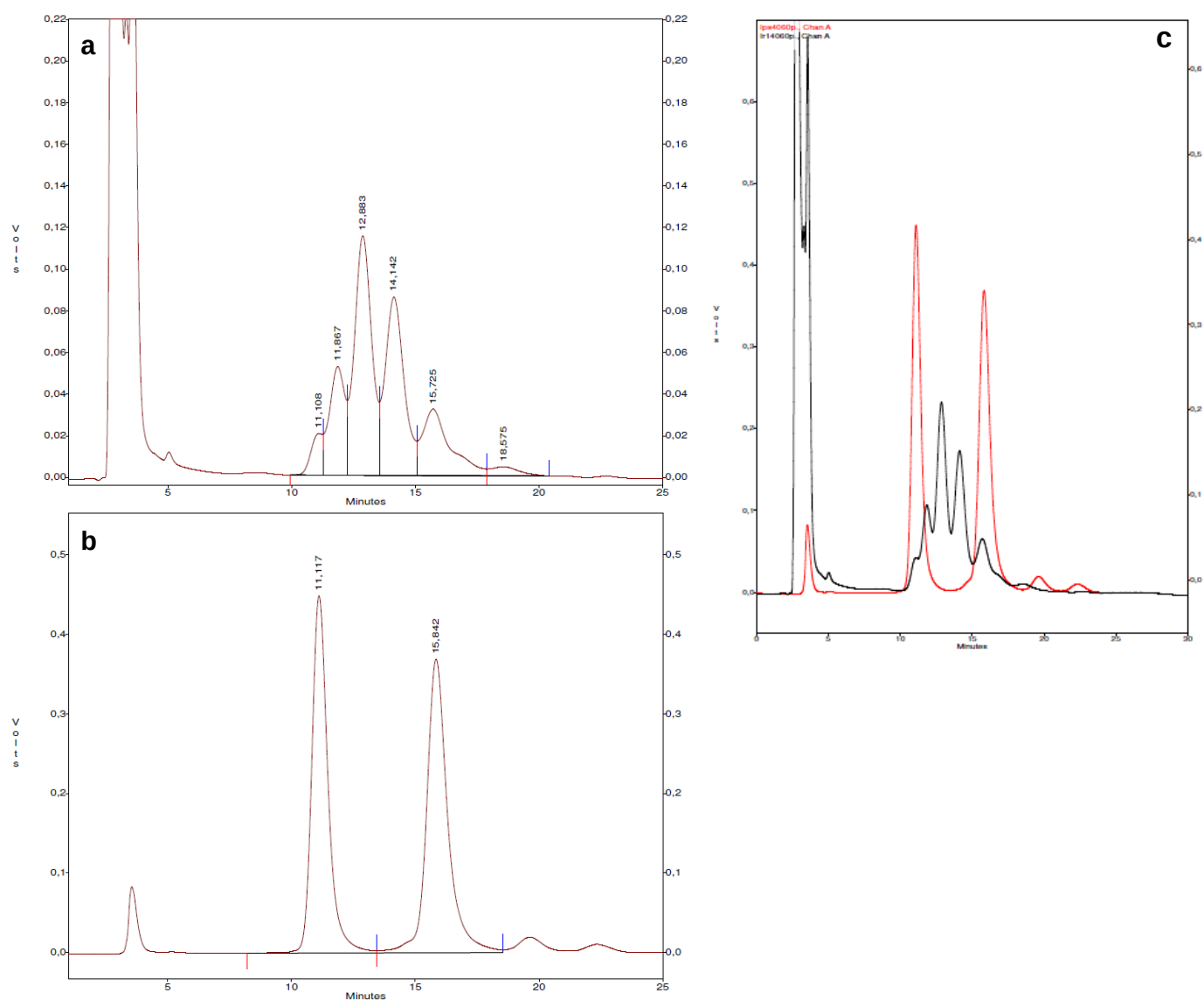


Figure S2. ^1H -NMR in $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 5:1 (400 MHz) of glycolalixarene **1** at room temperature (black) and at 70 °C (red).

