Supplementary Information

Prenylated phenylpropanoids with unprecedented skeletons from *Illicium burmanicum*

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Figure S1 HRESIMS spectrum of compound **1**

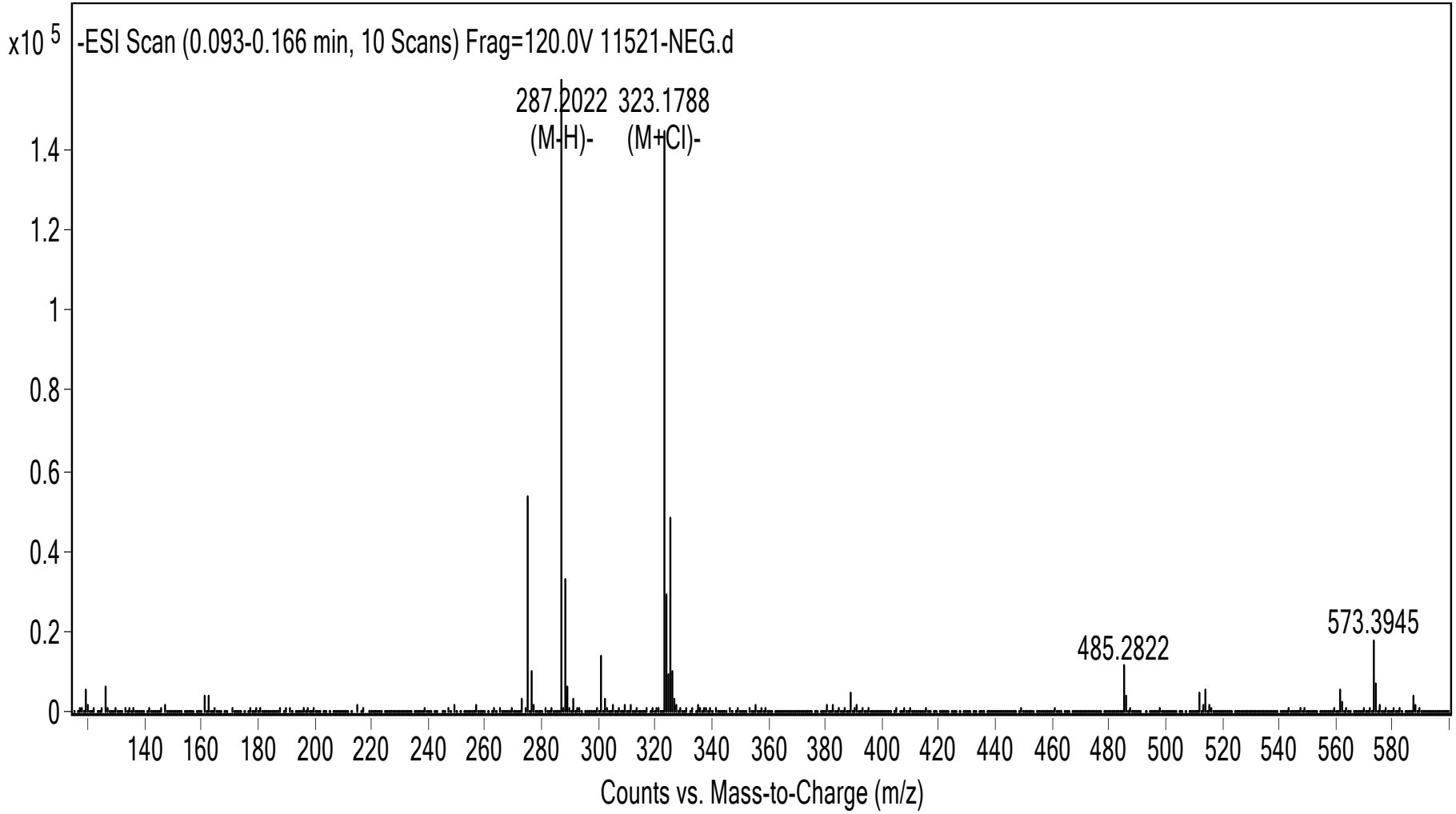


Figure S2 CD spectrum of compound **1**

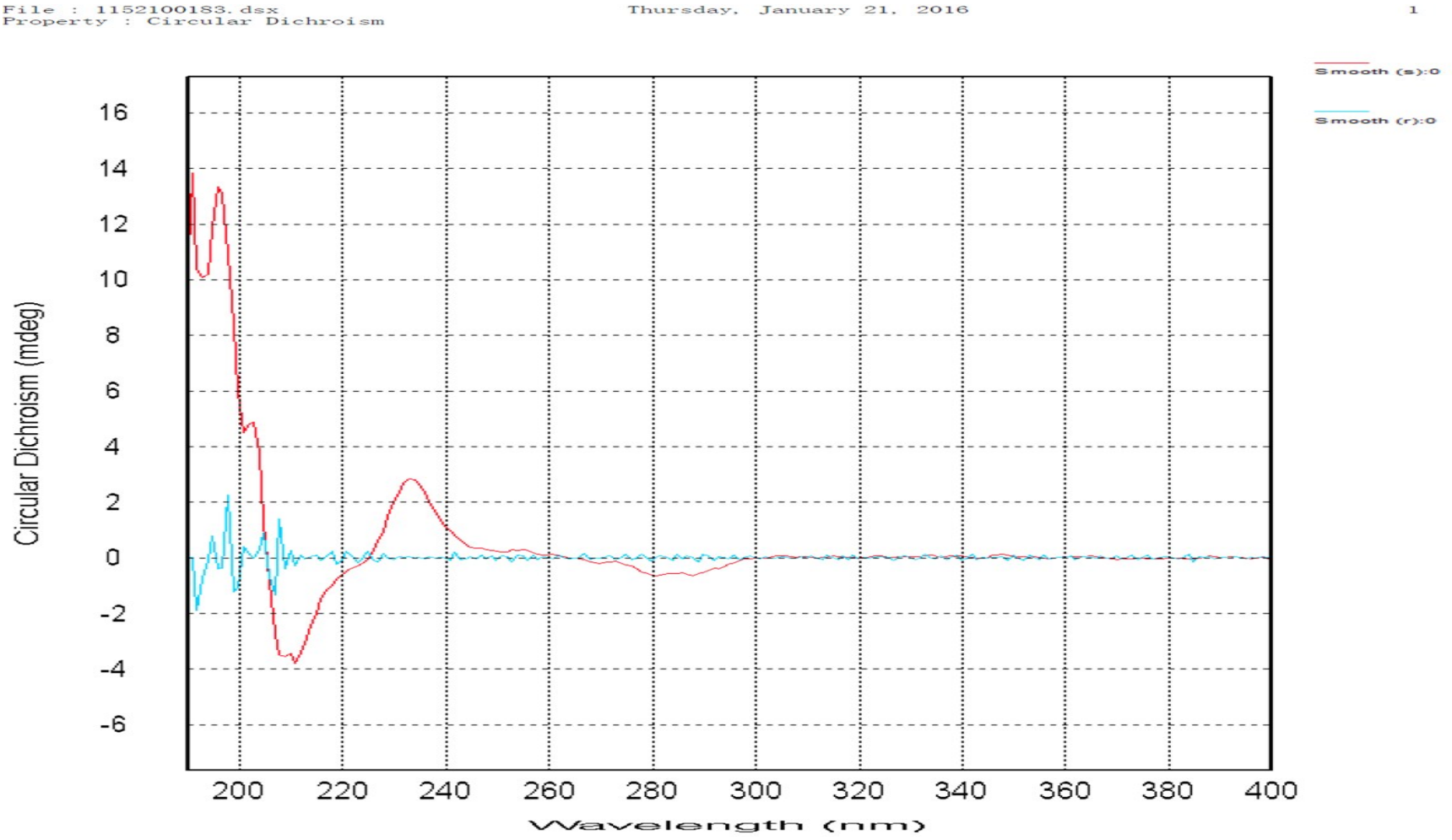


Figure S3 ^{1}H NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

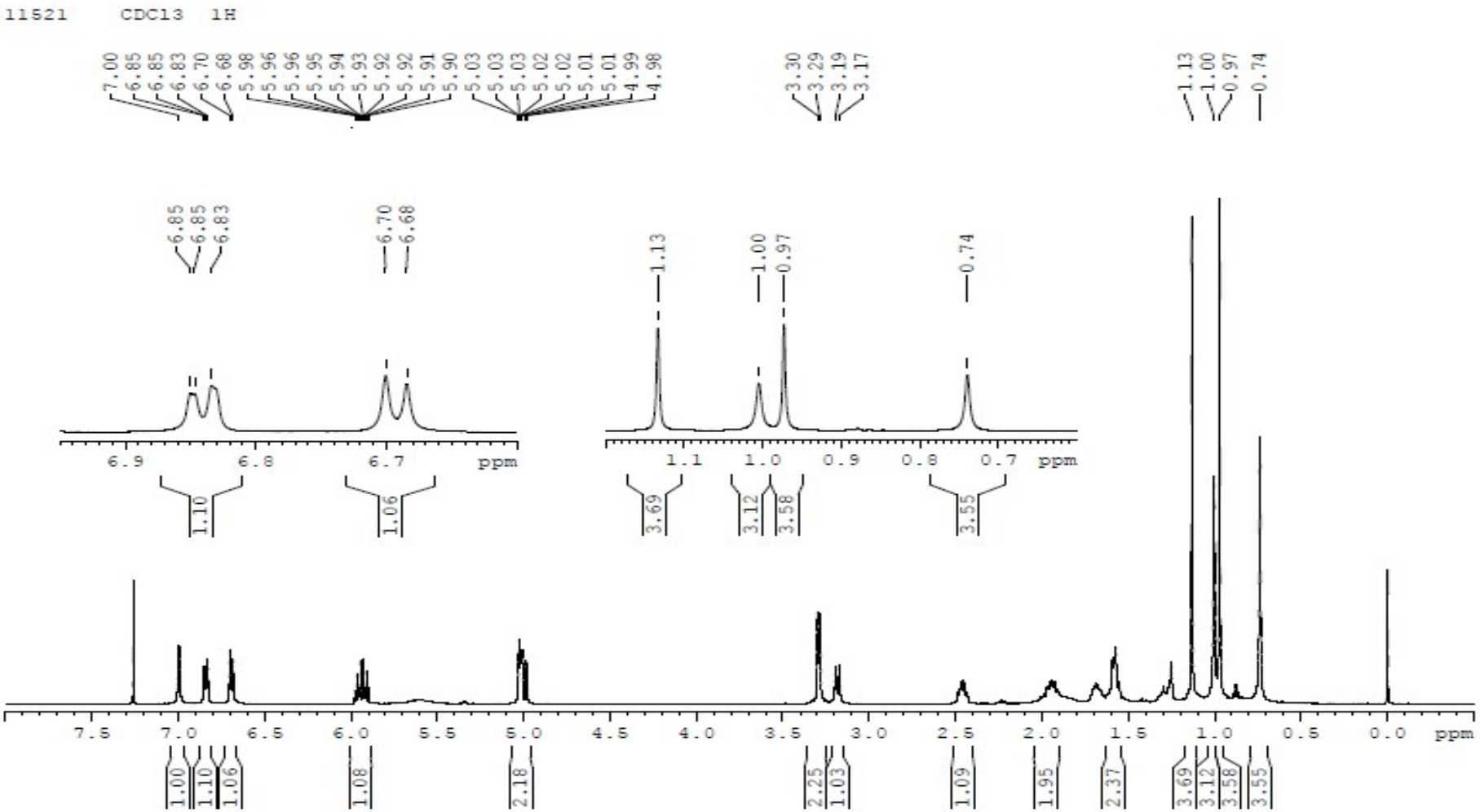


Figure S4 ^{13}C NMR spectrum of compound **1** (125 MHz, $CDCl_3$)

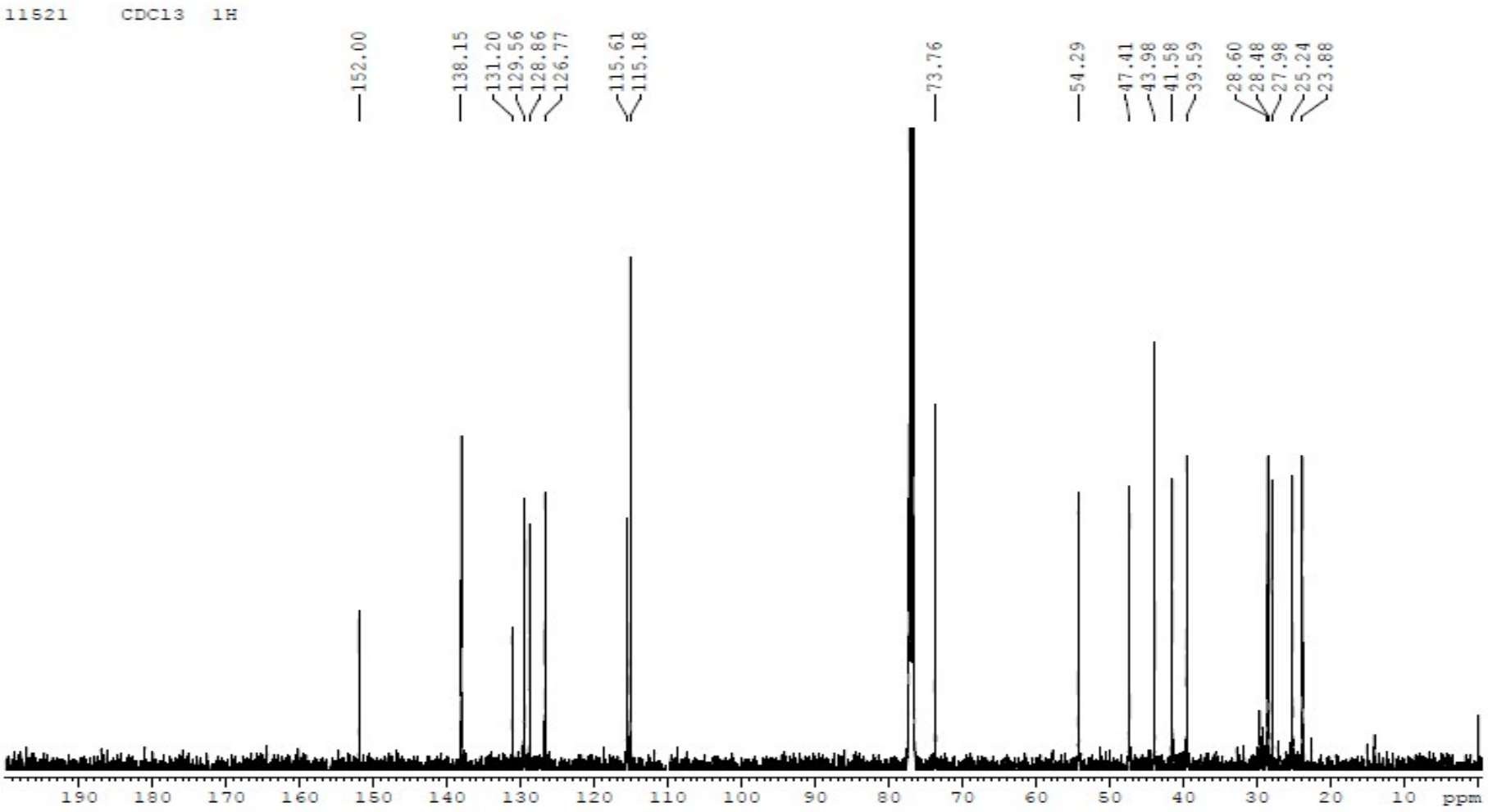


Figure S5 DEPT NMR spectrum of compound **1** (125 MHz, $CDCl_3$)

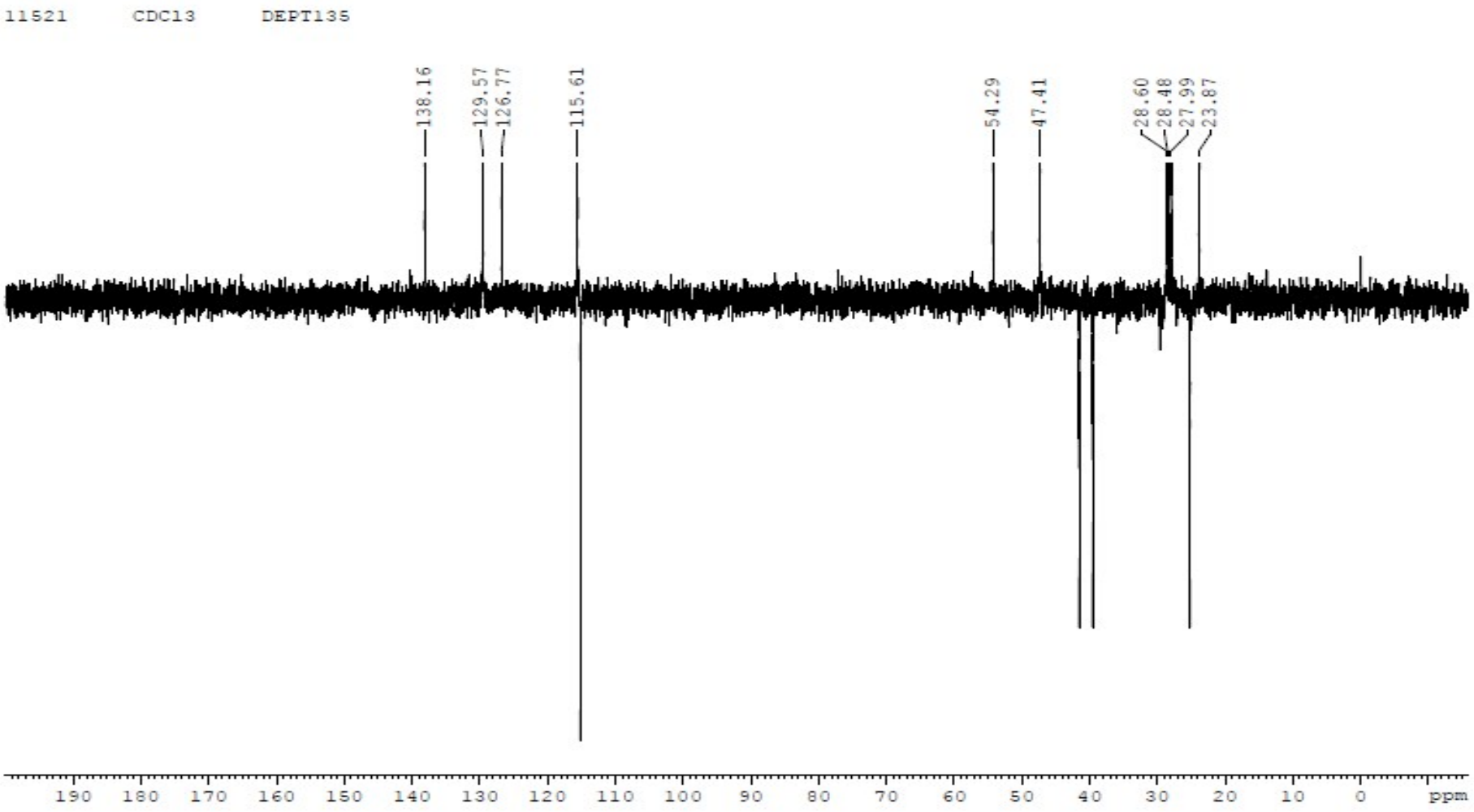


Figure S6 ^{1}H-^{1}H COSY NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

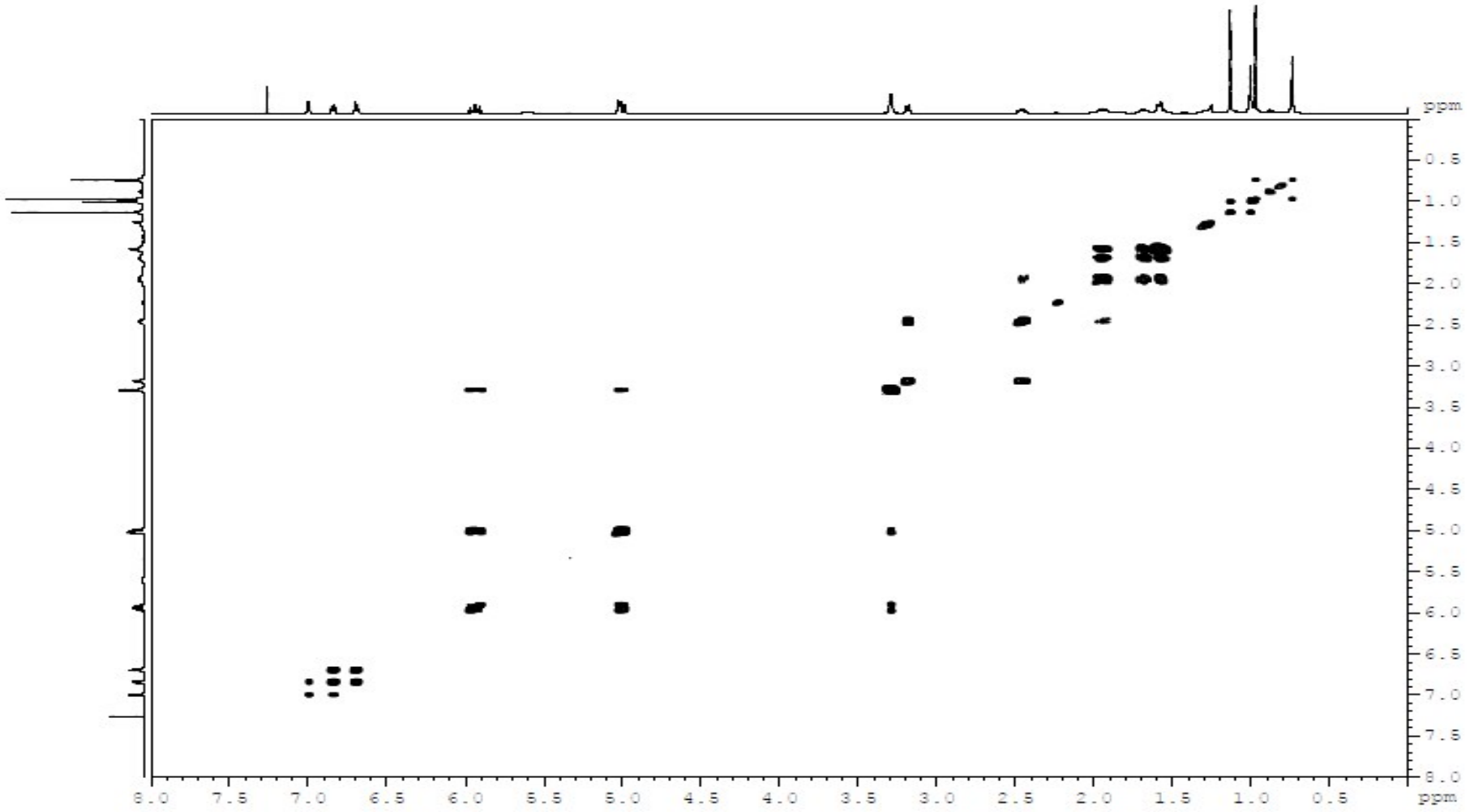


Figure S7 HSQC NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

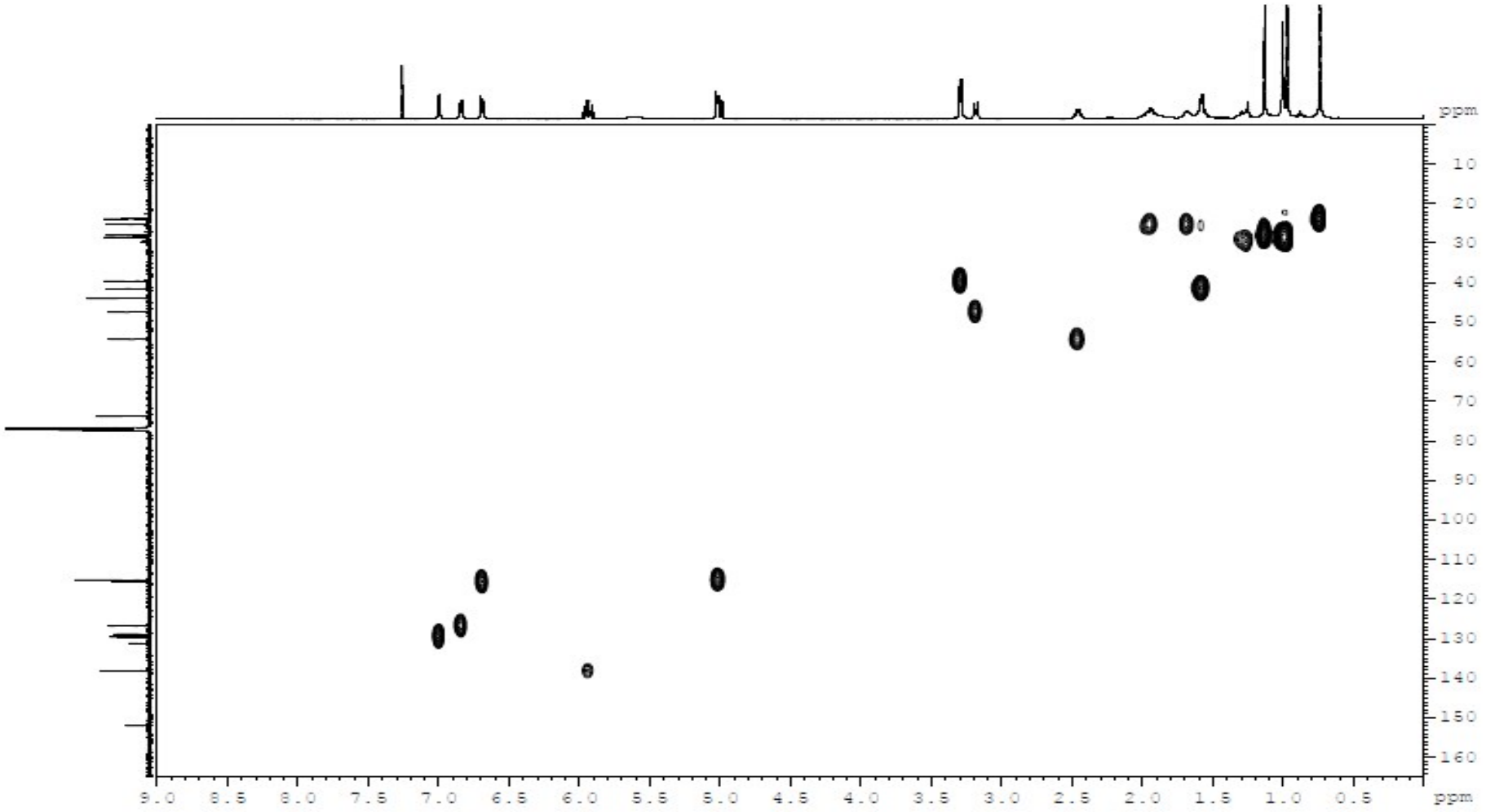


Figure S8 HMBC NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

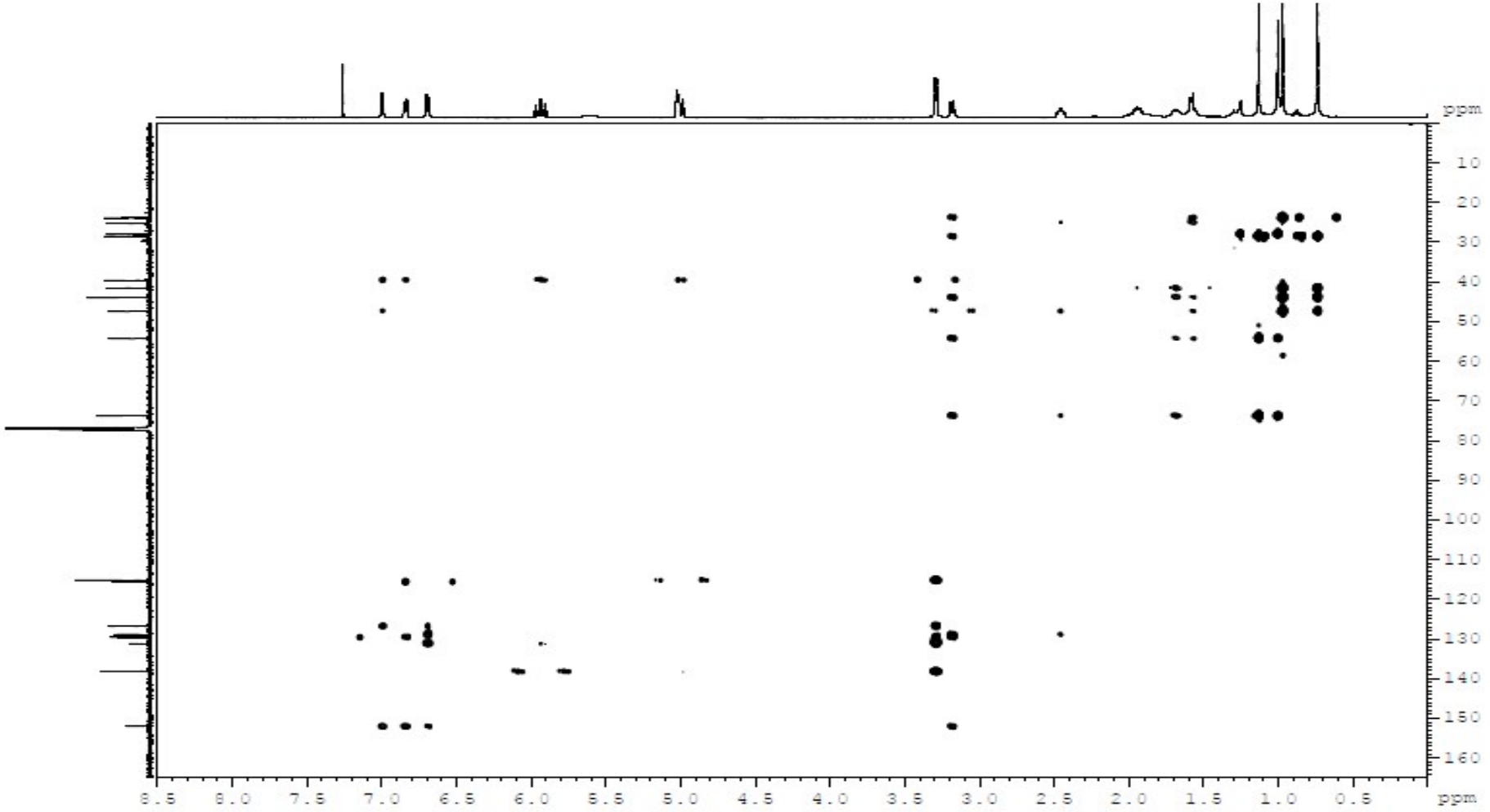


Figure S9 Expanded HMBC NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

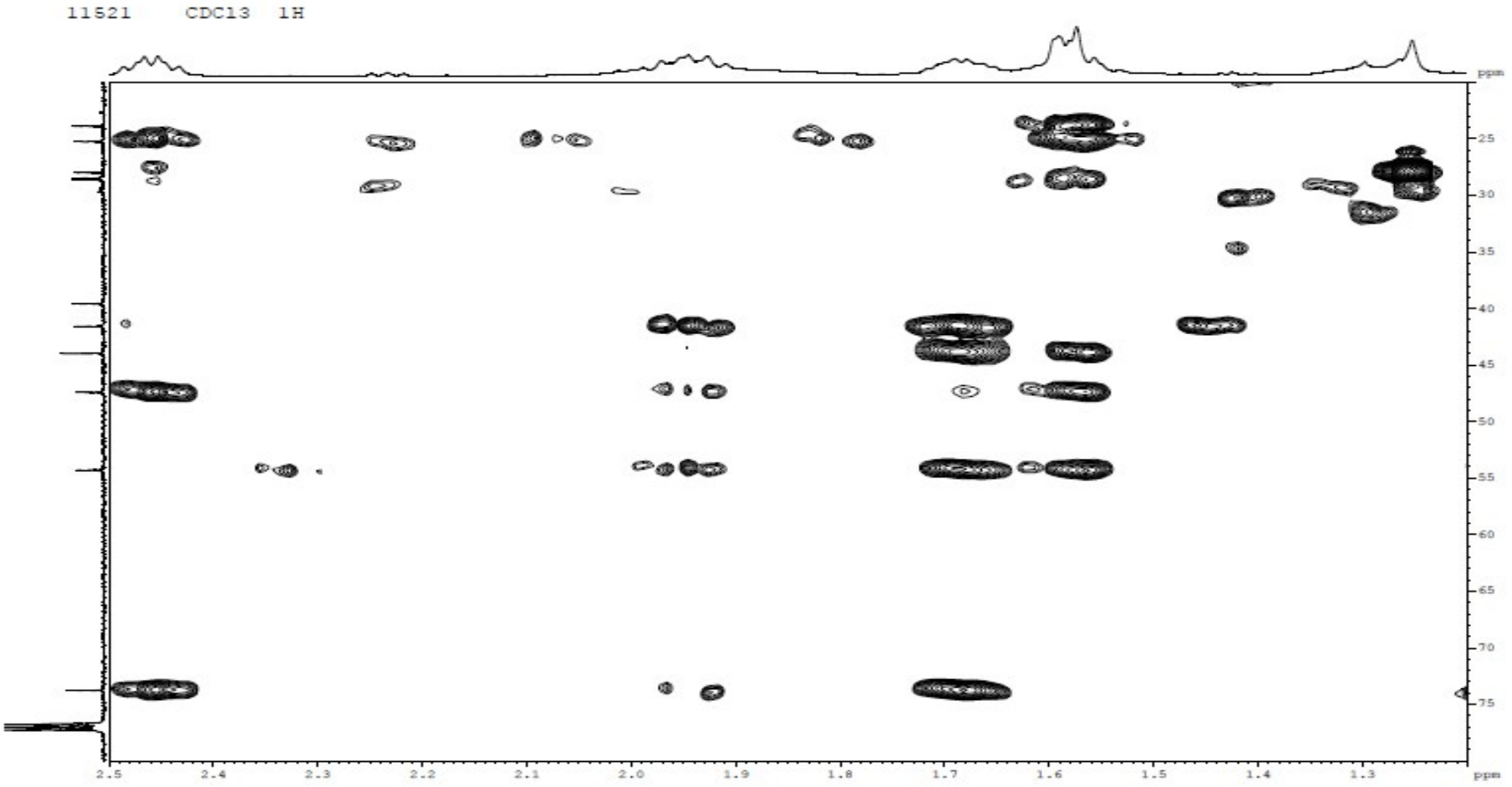


Figure S10 NOESY NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

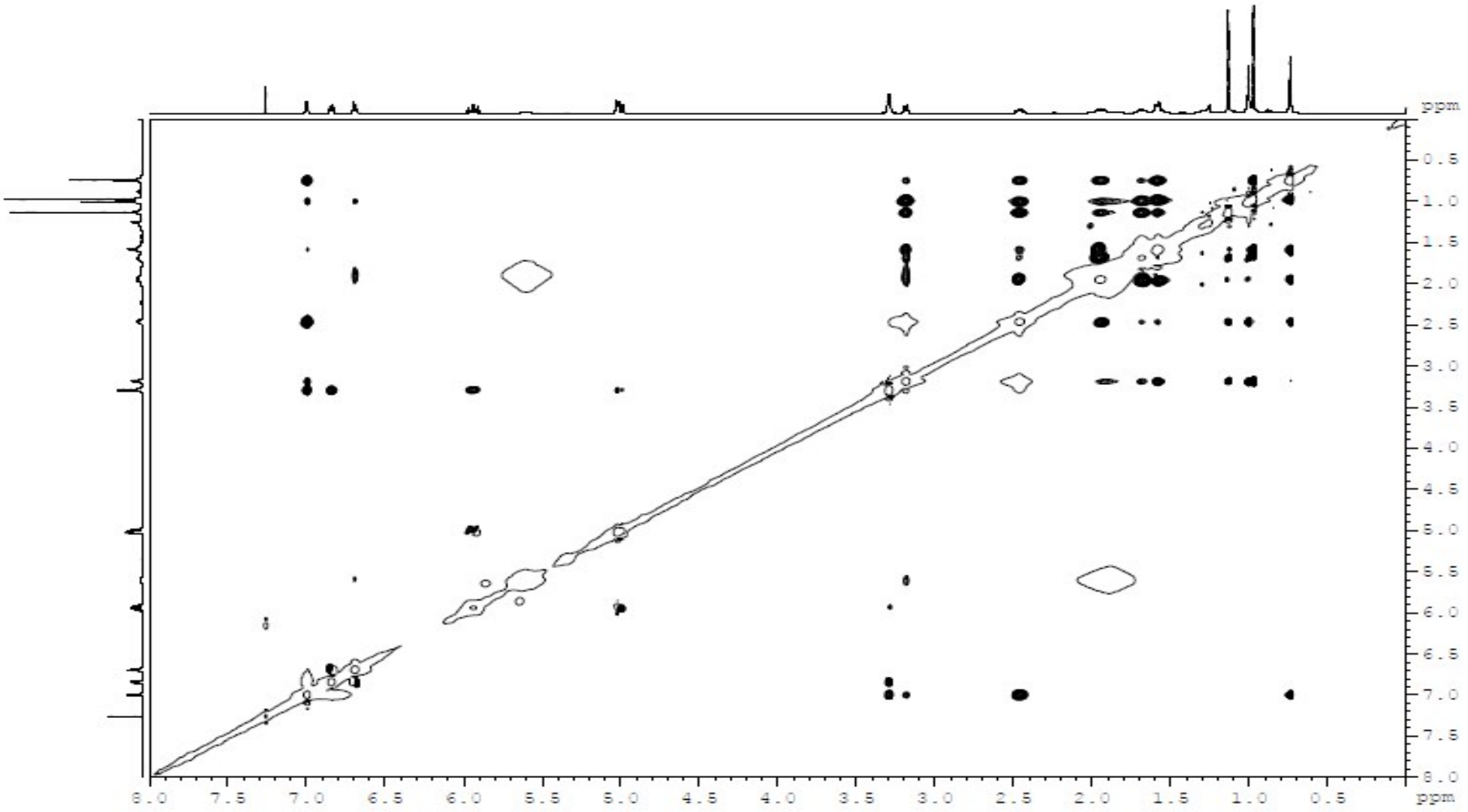


Figure S11 Expanded NOESY NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

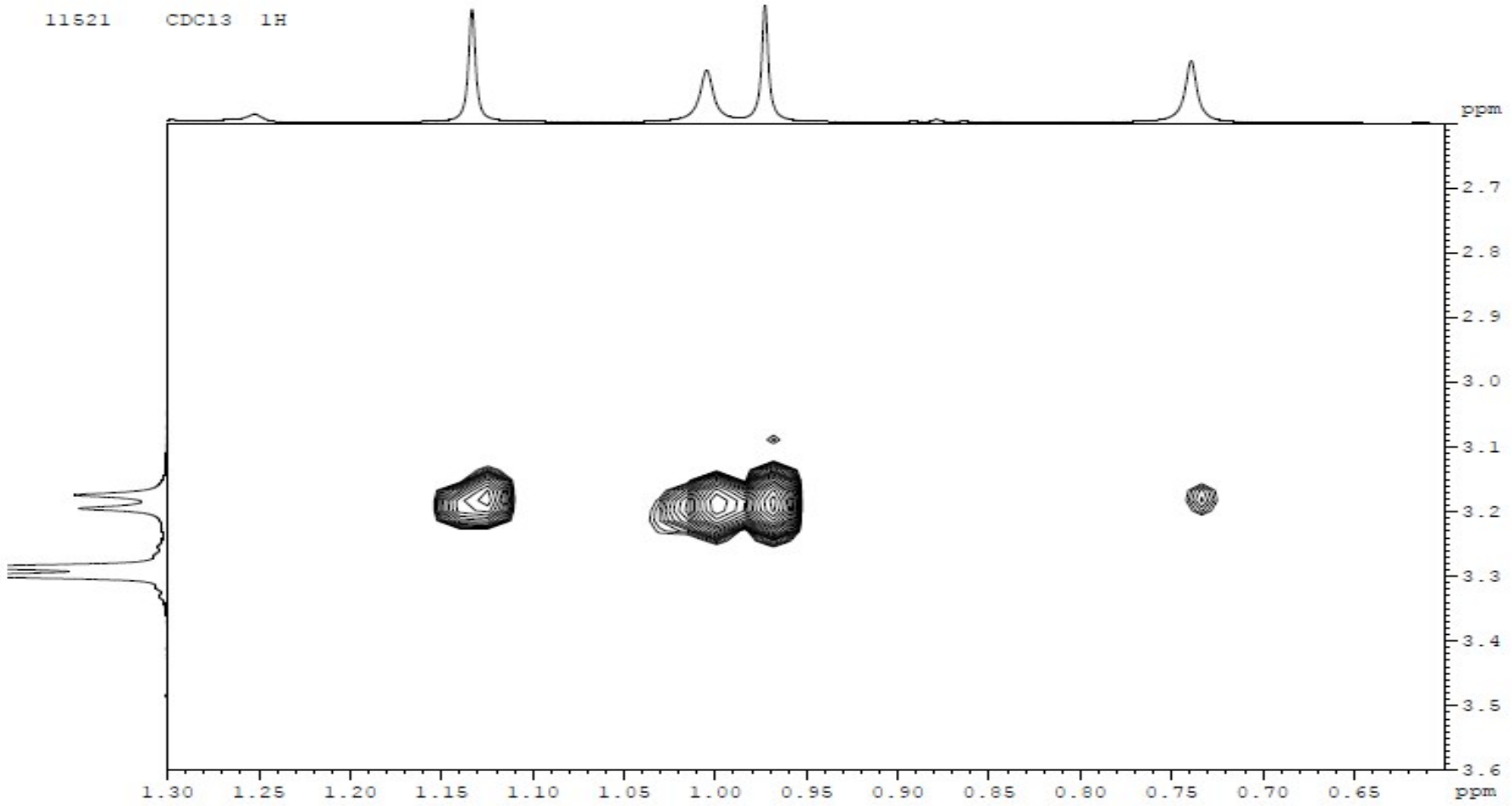


Figure S12 Expanded NOESY NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

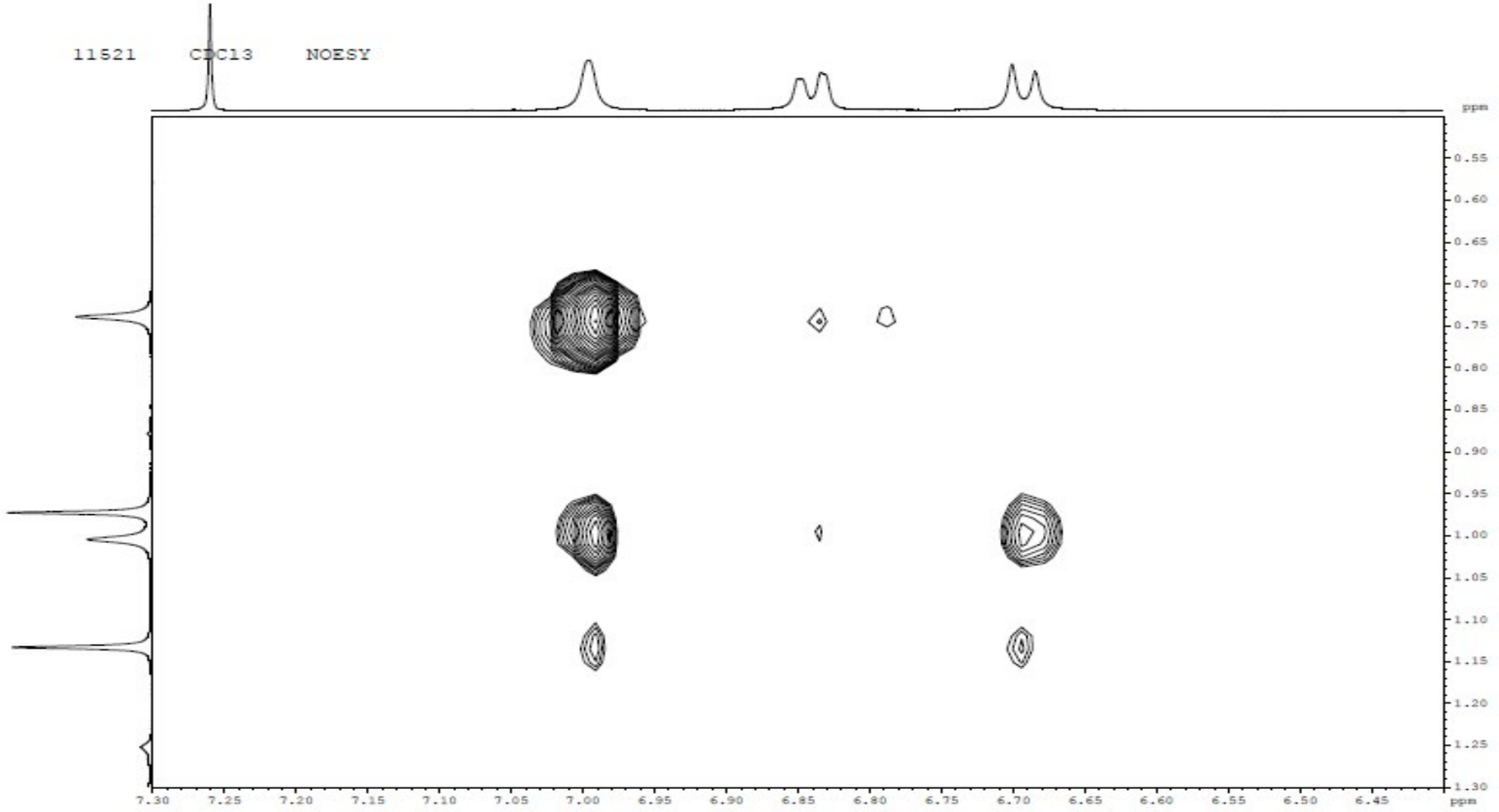
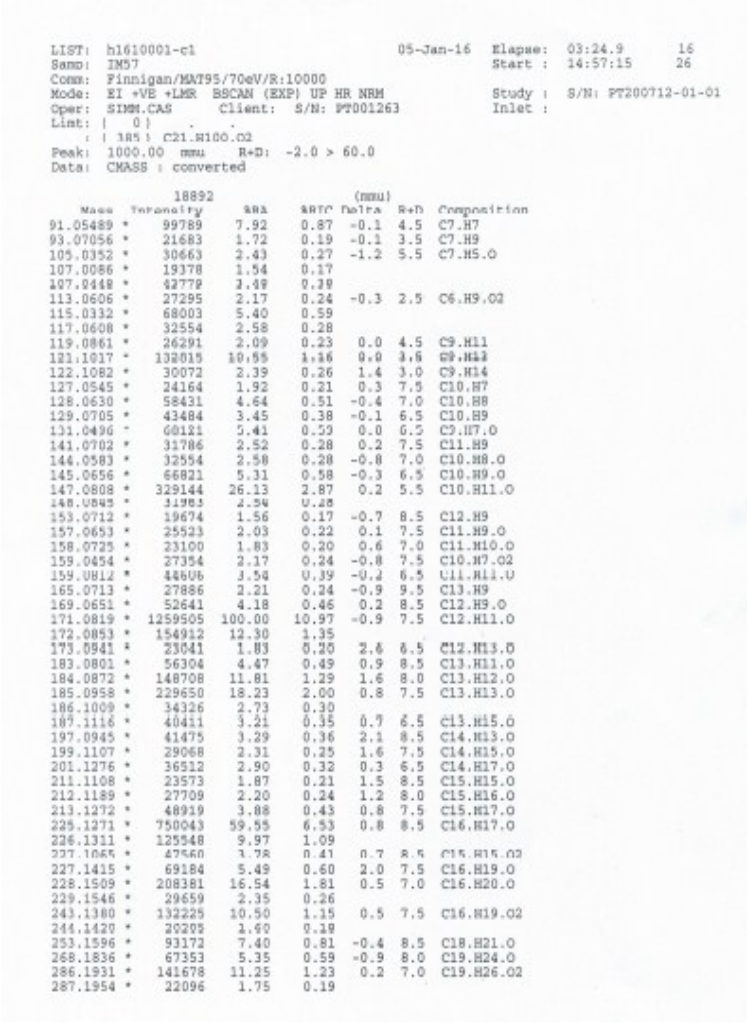


Figure S13 HREIMS spectrum of compound **2**



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Oper:  SIMM.CAS      Client:  S/N: PT001263            Inlet :
Limt:  |    0 |      .      .
       : | 185 | C21.H100.O2
Peak:  1000.00  mmu     R+D:  -2.0 > 60.0
Data:  CMASS : converted

                18892                          (mmu)
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107.0448 *     42779    3.40    0.39
113.0606 *     27295    2.17    0.24   -0.3   2.5  C6.H9.O2
115.0332 *     68003    5.40    0.59
117.0608 *     32554    2.58    0.28
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122.1082 *     30072    2.39    0.26    1.4   3.0  C9.H14
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159.0812 *     44606    3.54    0.39   -0.2   6.5  C11.H11.O
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183.0801 *     56304    4.47    0.49    0.9   8.5  C13.H11.O
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185.0958 *    229650   18.23    2.00    0.8   7.5  C13.H13.O
186.1009 *     34326    2.73    0.30
187.1116 *     40411    3.21    0.35    0.7   6.5  C13.H15.O
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211.1108 *     23573    1.87    0.21    1.5   8.5  C15.H15.O
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225.1271 *    750043   59.55    6.53    0.8   8.5  C16.H17.O
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227.1065 *     47560    3.78    0.41    0.7   8.5  C15.H15.O2
227.1415 *     69184    5.49    0.60    2.0   7.5  C16.H19.O
228.1509 *    208381   16.54    1.81    0.5   7.0  C16.H20.O
229.1546 *     29659    2.35    0.26
243.1380 *    132225   10.50    1.15    0.5   7.5  C16.H19.O2
244.1420 *     20203    1.60    0.18
253.1596 *     93172    7.40    0.81   -0.4   8.5  C18.H21.O
268.1836 *     67353    5.35    0.59   -0.9   8.0  C19.H24.O
286.1931 *    141678   11.25    1.23    0.2   7.0  C19.H26.O2
287.1954 *     22096    1.75    0.19
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Figure S14 CD spectrum of compound **2**

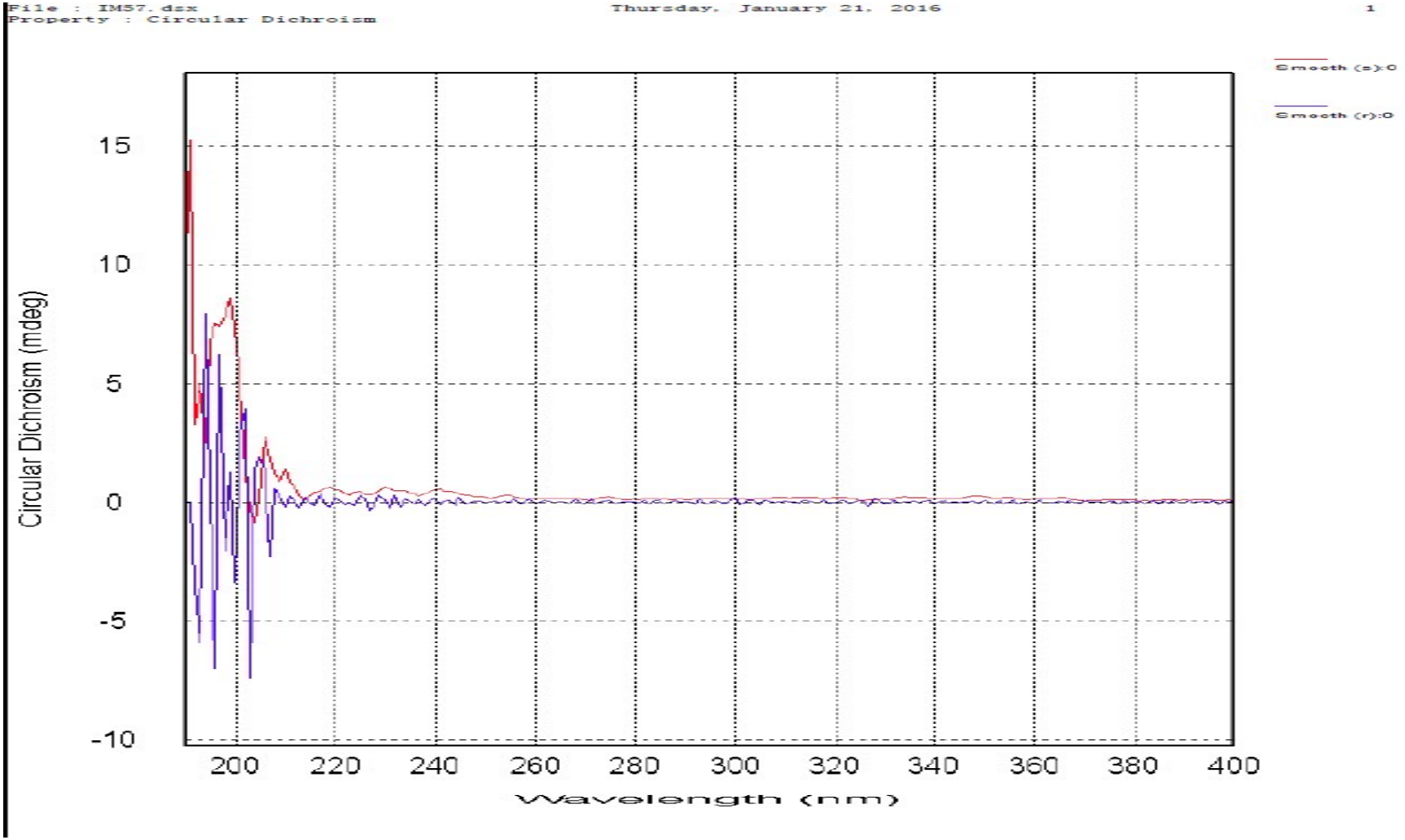


Figure S15 ^{1}H NMR spectrum of compound **2** (500 MHz, $CDCl_3$)

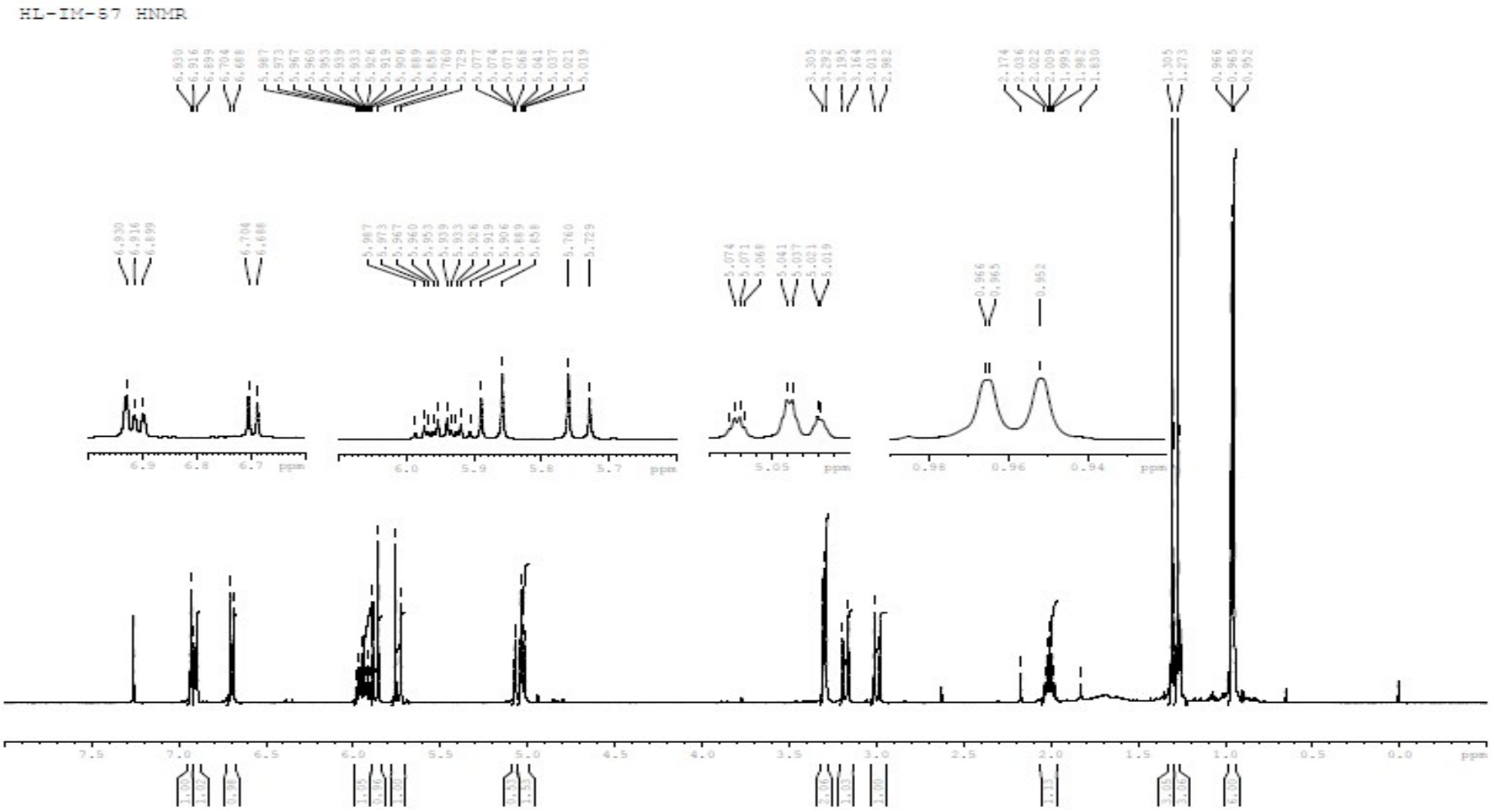


Figure S16 ^{13}C NMR spectrum of compound **2** (125 MHz, $CDCl_3$)

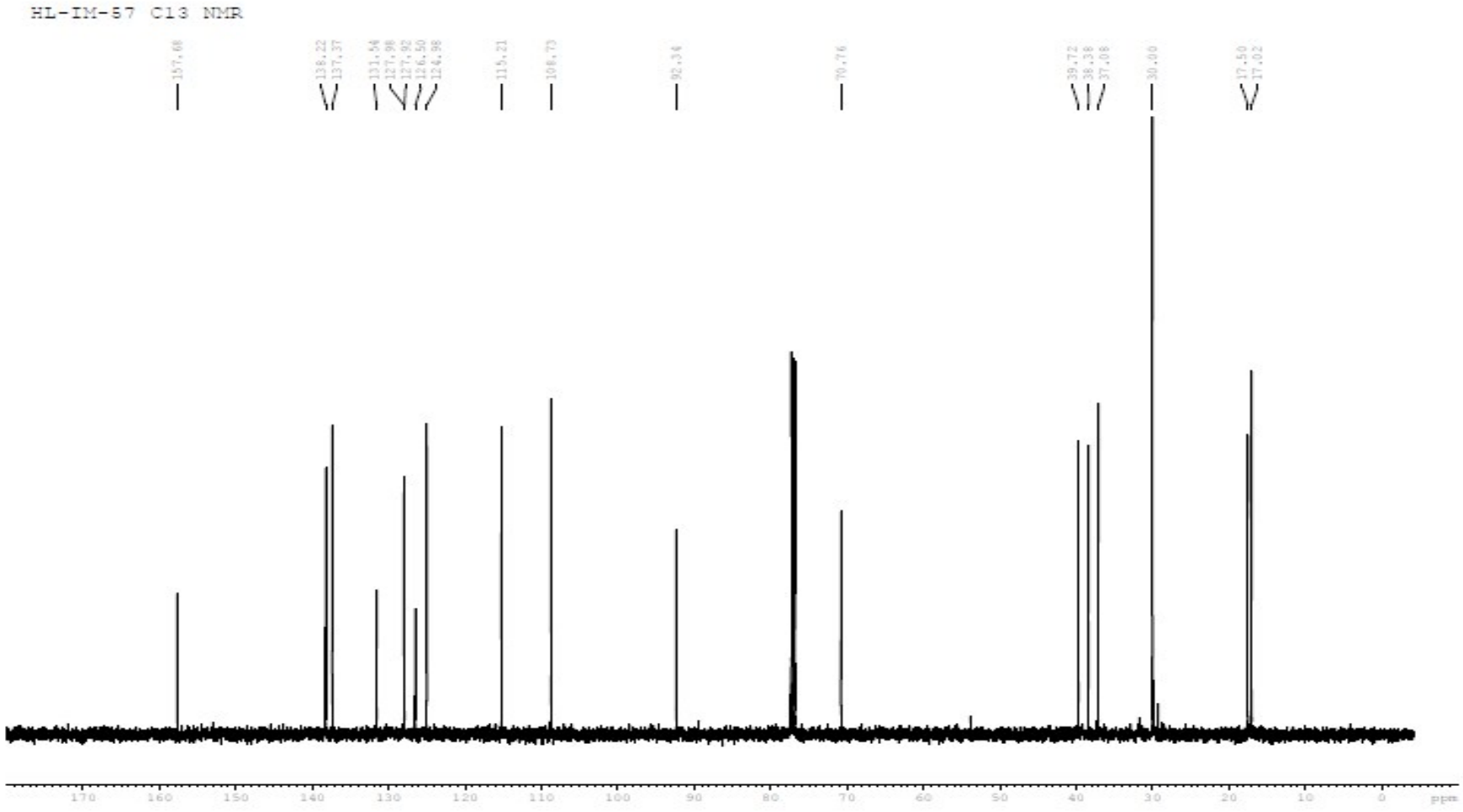


Figure S17 DEPT NMR spectrum of compound **2** (125 MHz, $CDCl_3$)

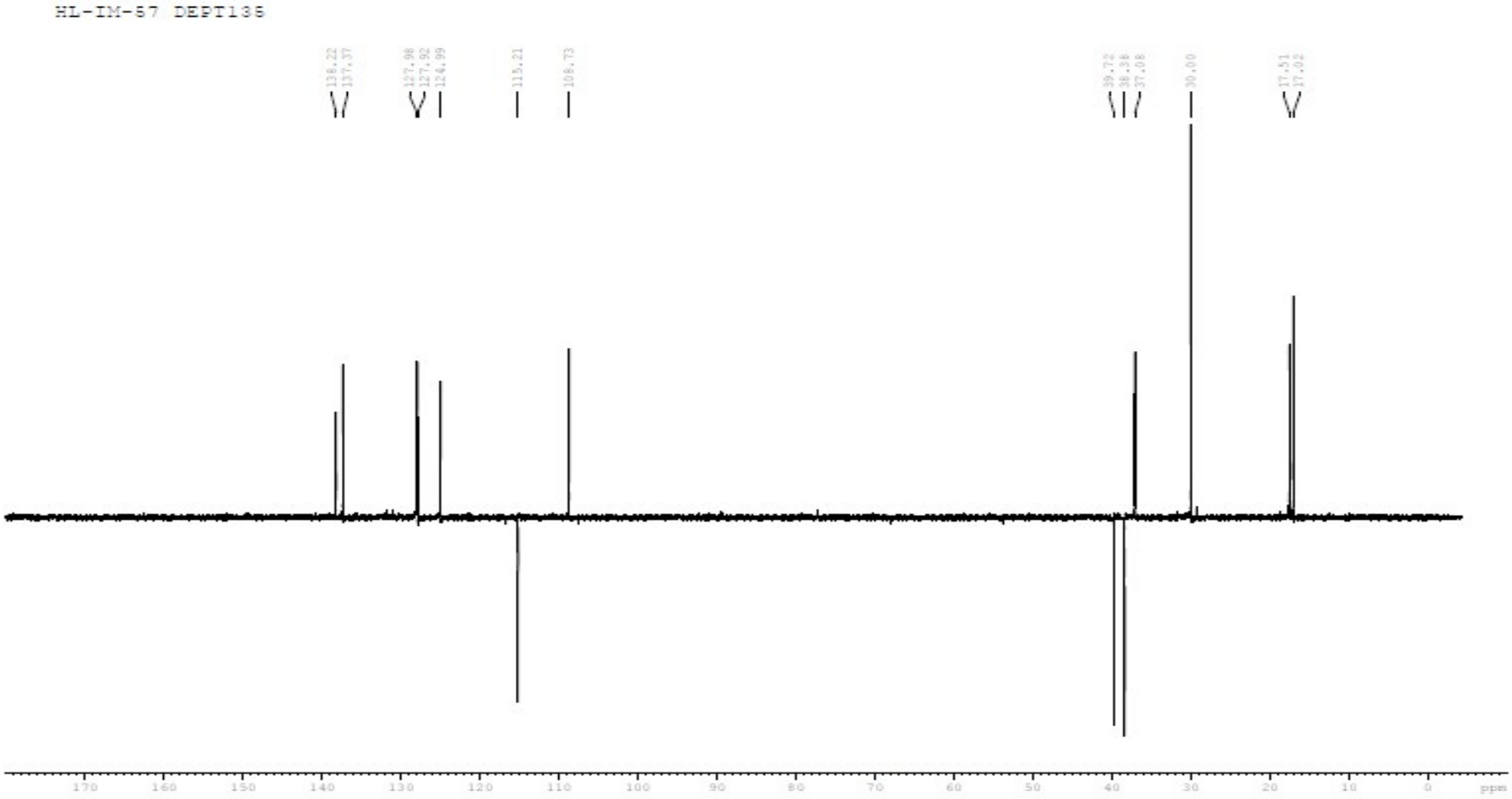


Figure S18 ^{1}H-^{1}H COSY NMR spectrum of compound **2** (500 MHz, $CDCl_3$)

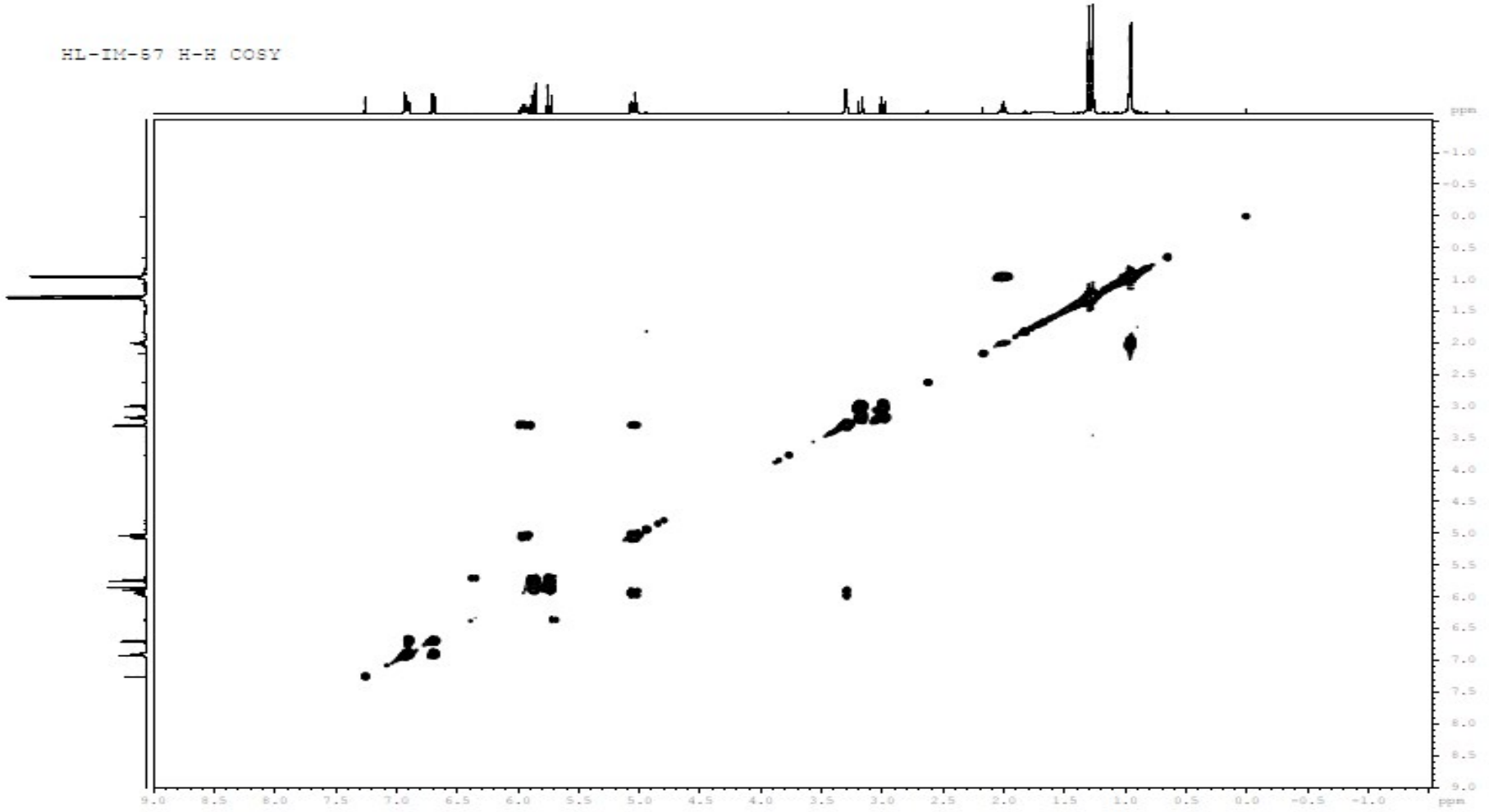


Figure S19 HSQC NMR spectrum of compound **2** (500 MHz, $CDCl_3$)

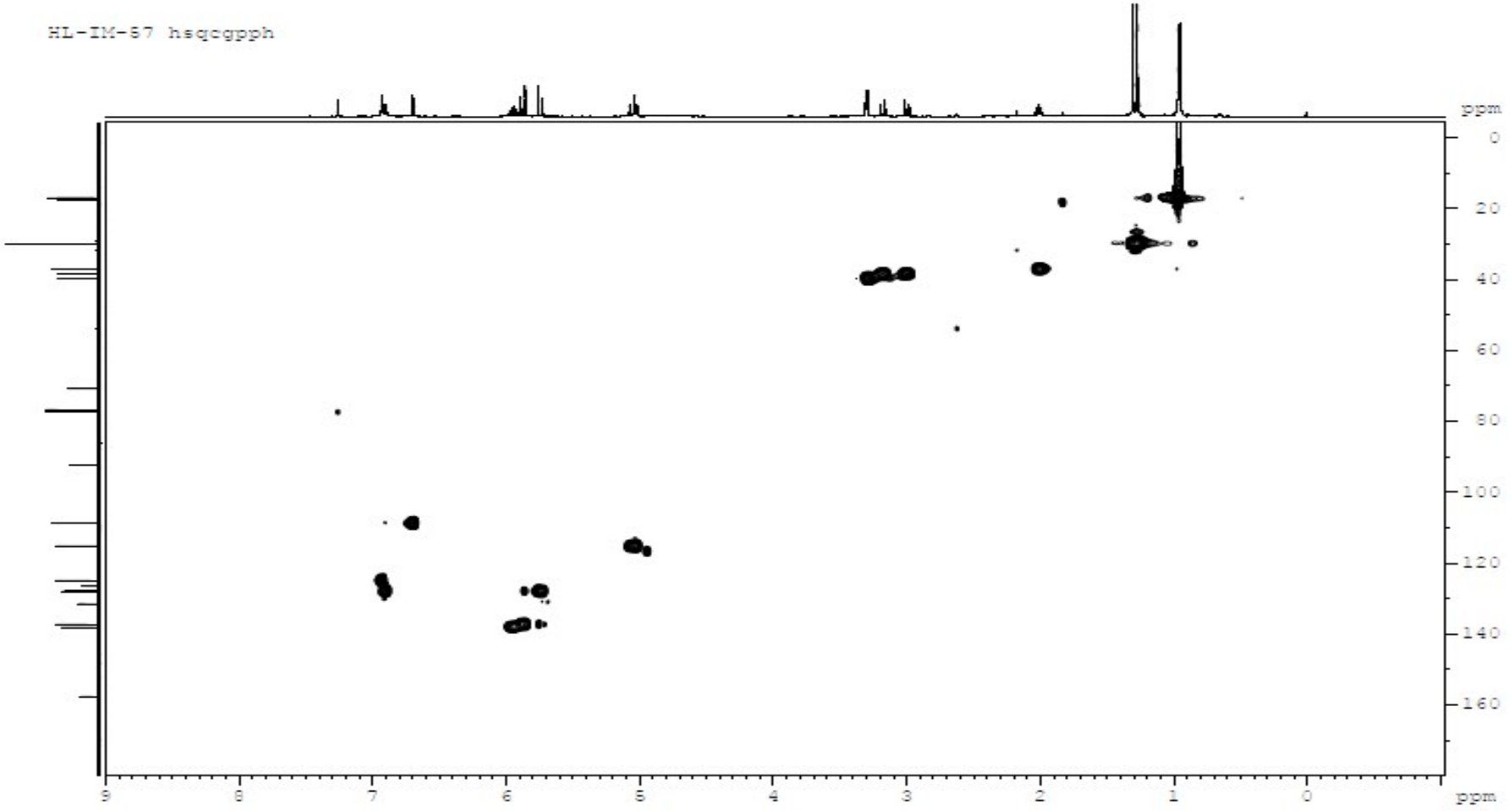


Figure S20 HMBC NMR spectrum of compound **2** (500 MHz, $CDCl_3$)

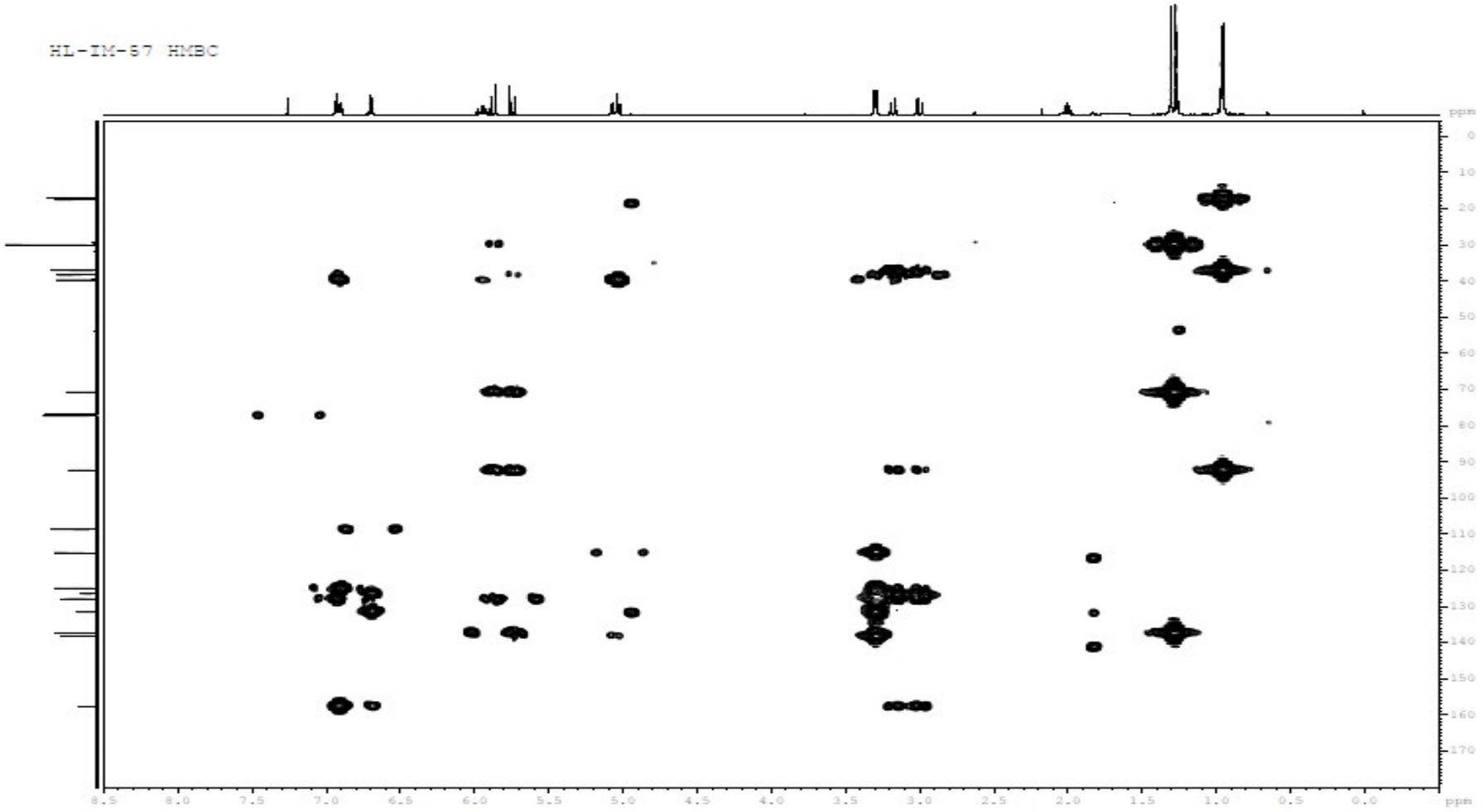


Figure S21 NOESY NMR spectrum of compound **2** (500 MHz, $CDCl_3$)

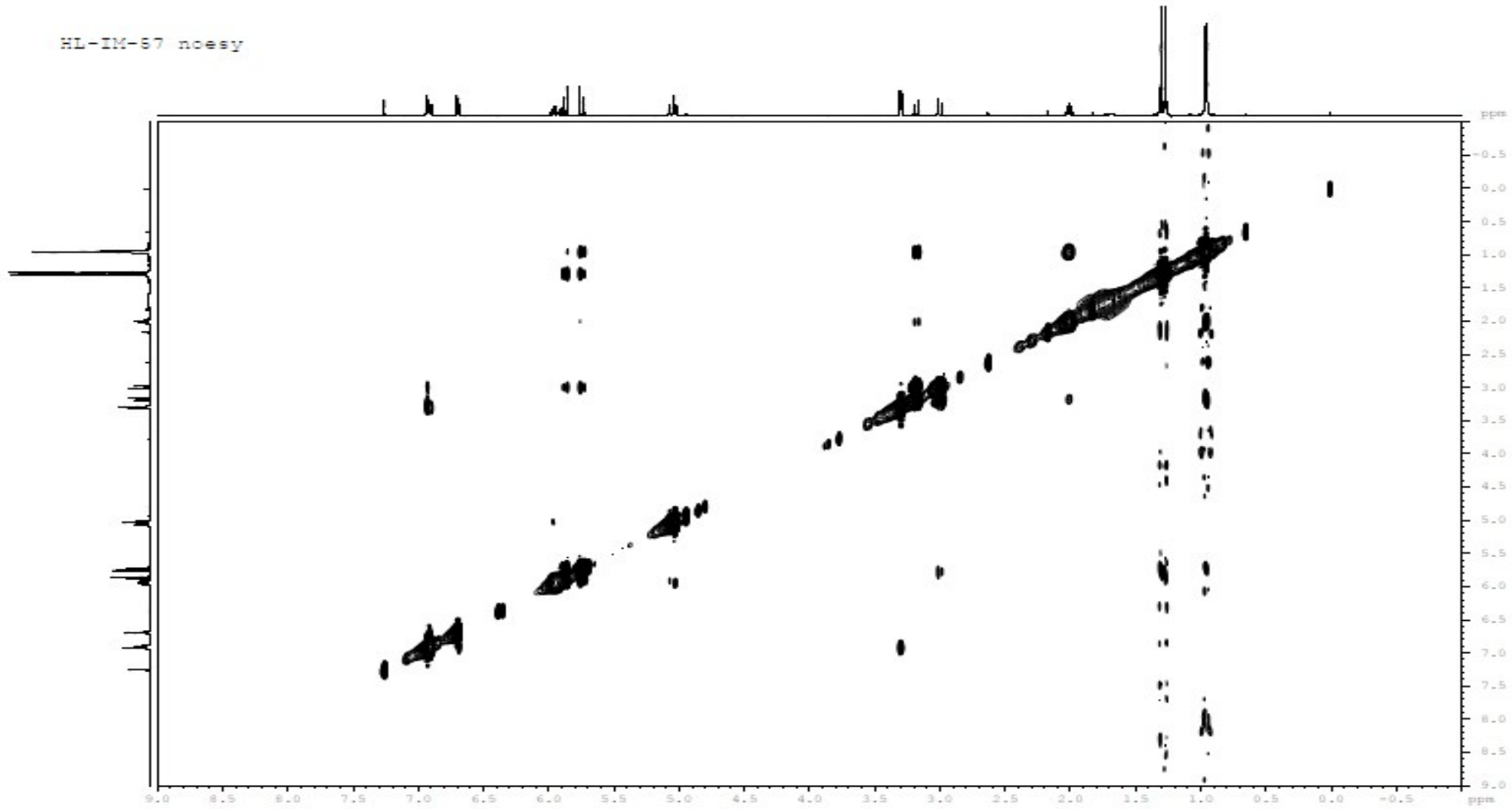


Figure S22 HRESIMS spectrum of compound **3**

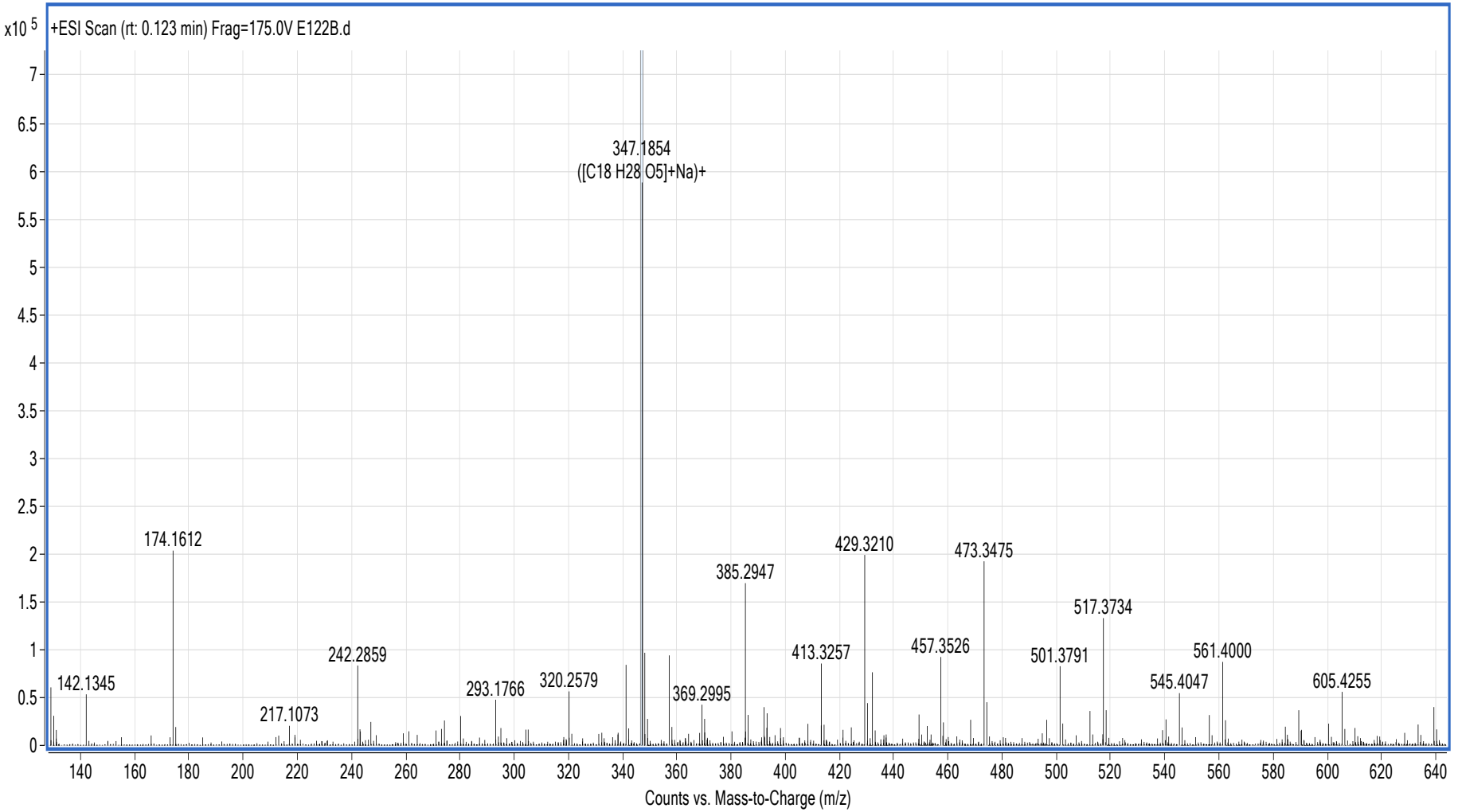


Figure S23 CD spectrum of compound **3** (500 MHz, $CDCl_3$)

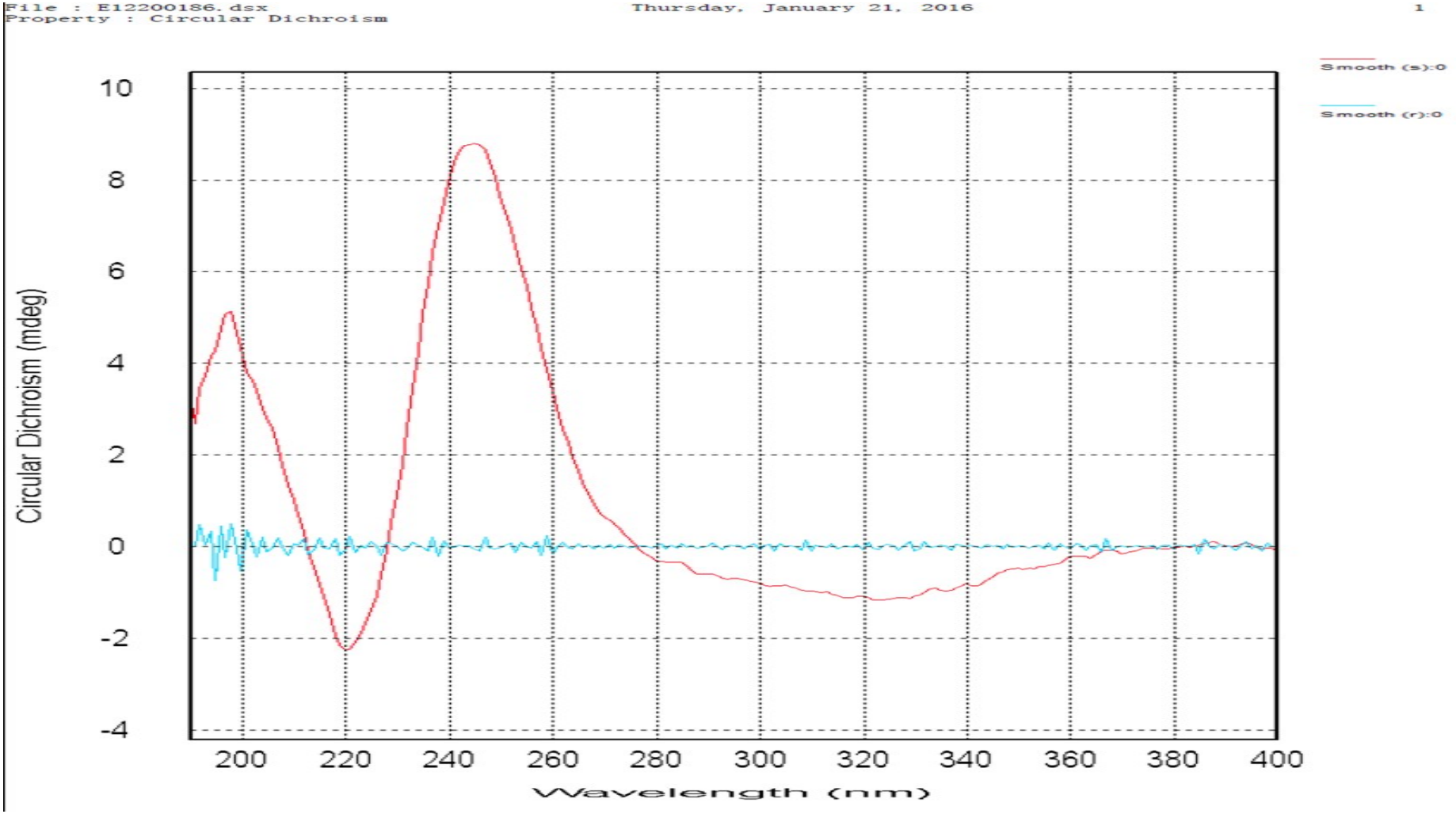


Figure S24 ^{1}H NMR spectrum of compound **3** (500 MHz, $CDCl_3$)

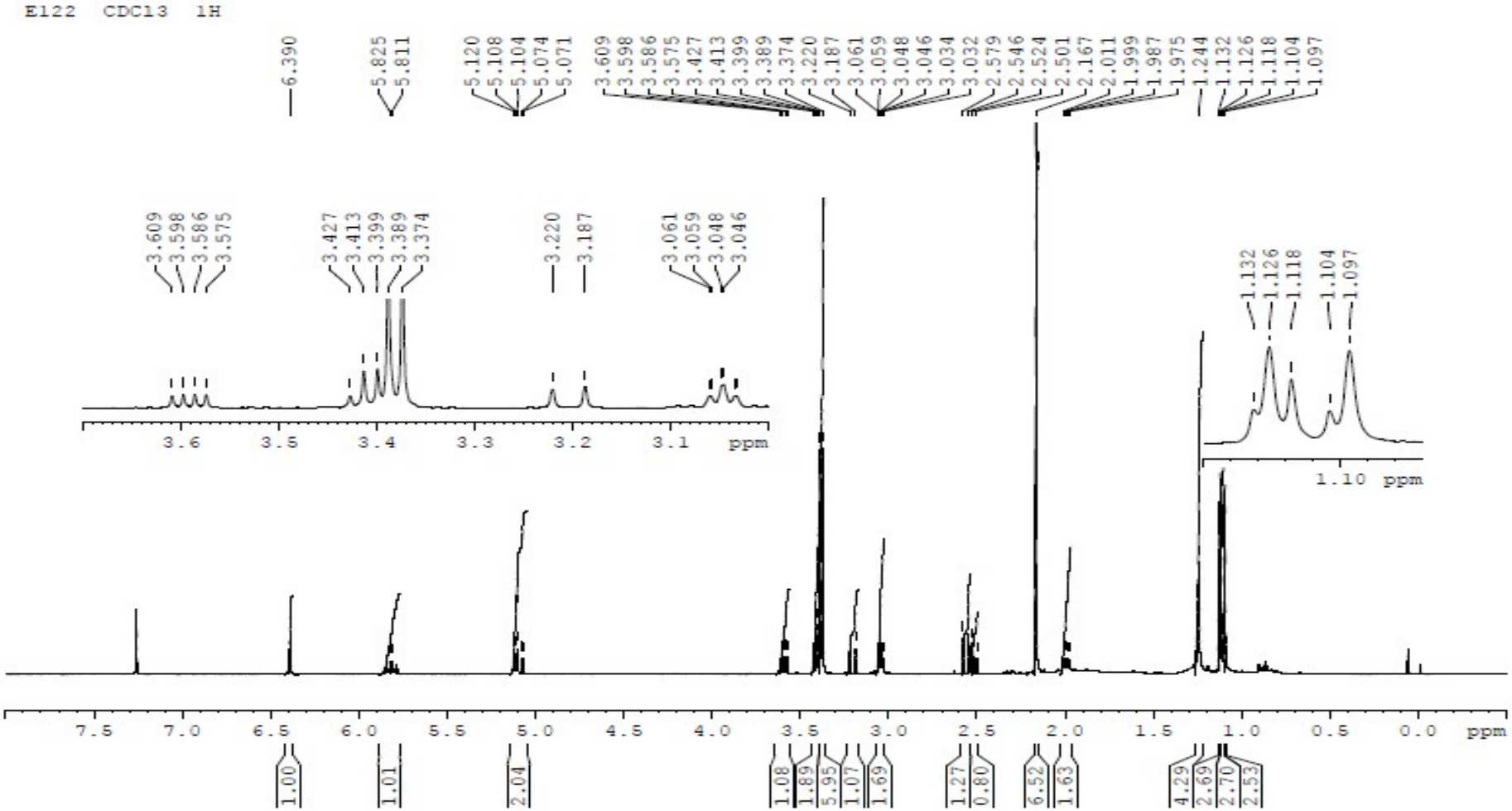


Figure S25 ^{13}C NMR spectrum of compound **3** (125 MHz, $CDCl_3$)

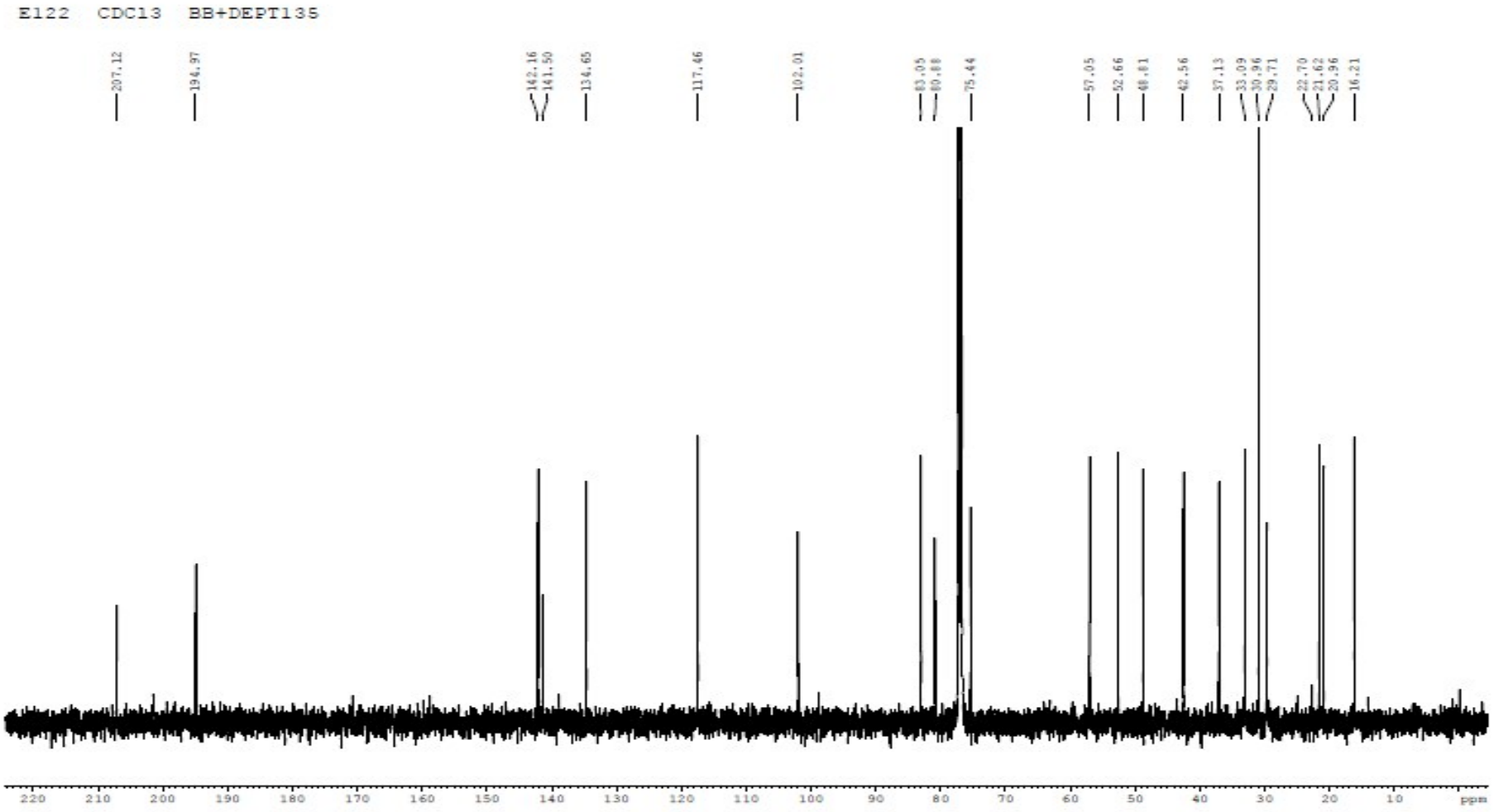


Figure S26 DEPT NMR spectrum of compound **3** (125 MHz, $CDCl_3$)

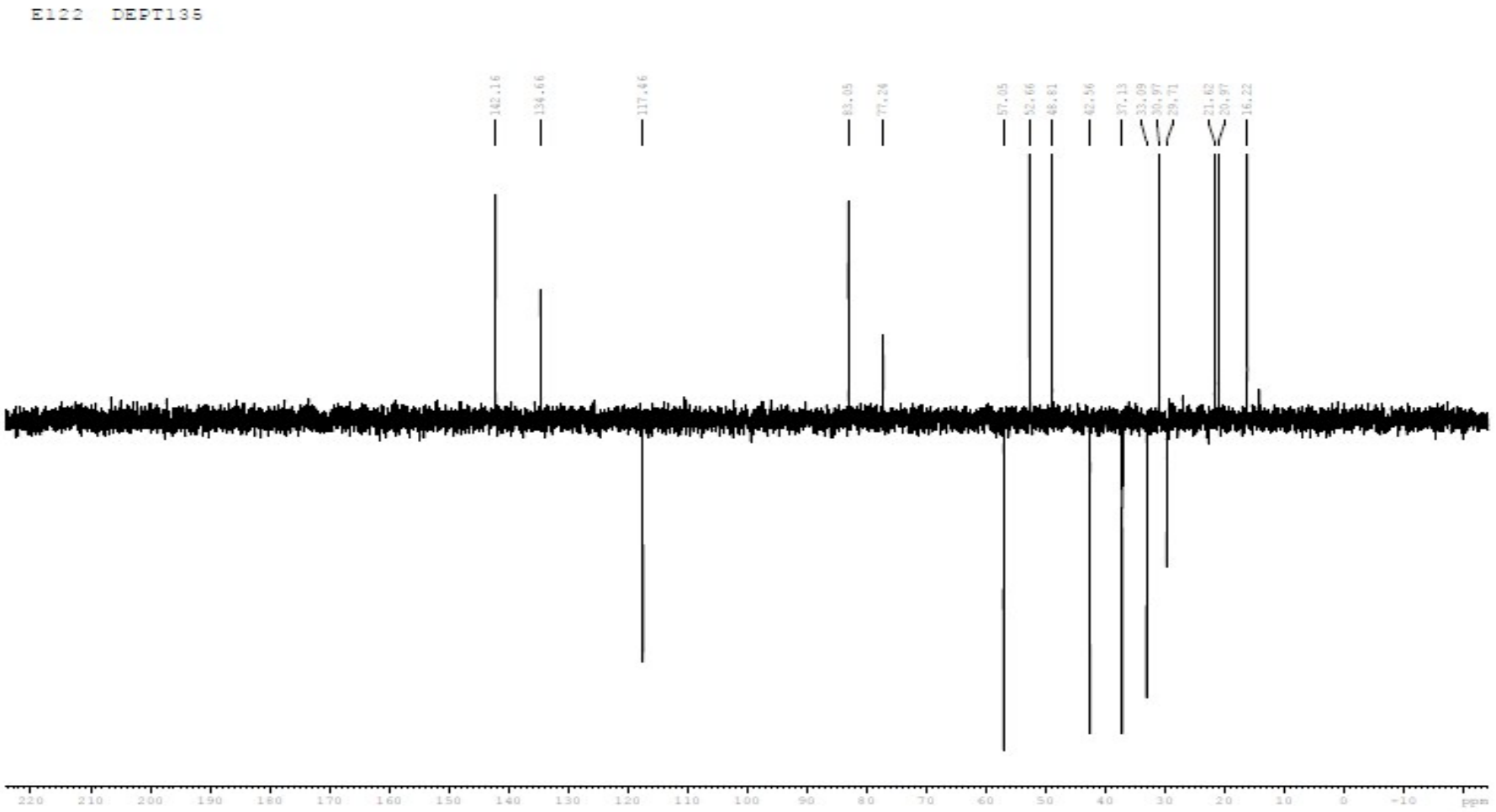


Figure S27 ^{1}H-^{1}H COSY NMR spectrum of compound **3** (500 MHz, $CDCl_3$)

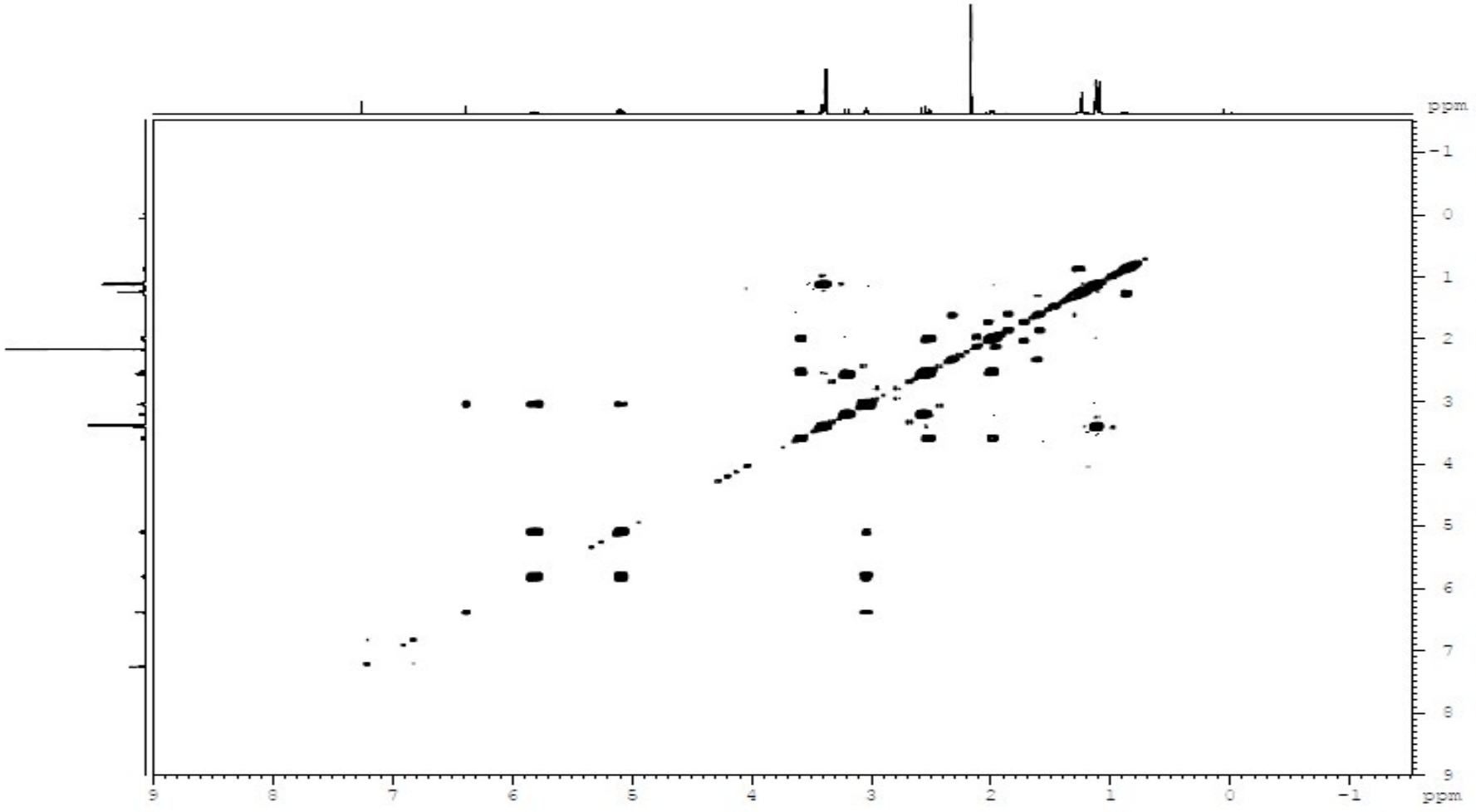


Figure S28 HSQC NMR spectrum of compound **3** (500 MHz, $CDCl_3$)

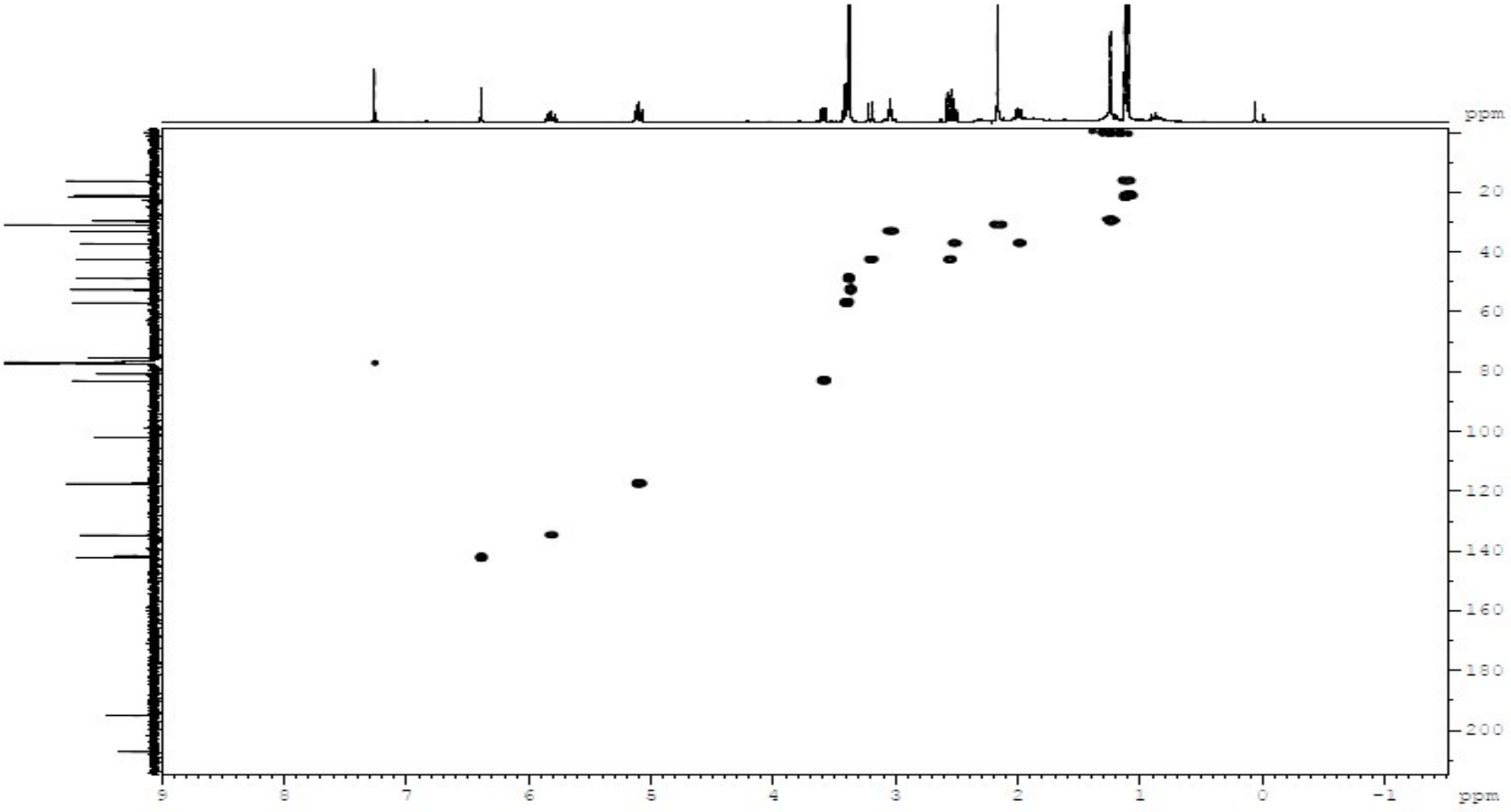


Figure S29 HMBC NMR spectrum of compound **3** (500 MHz, $CDCl_3$)

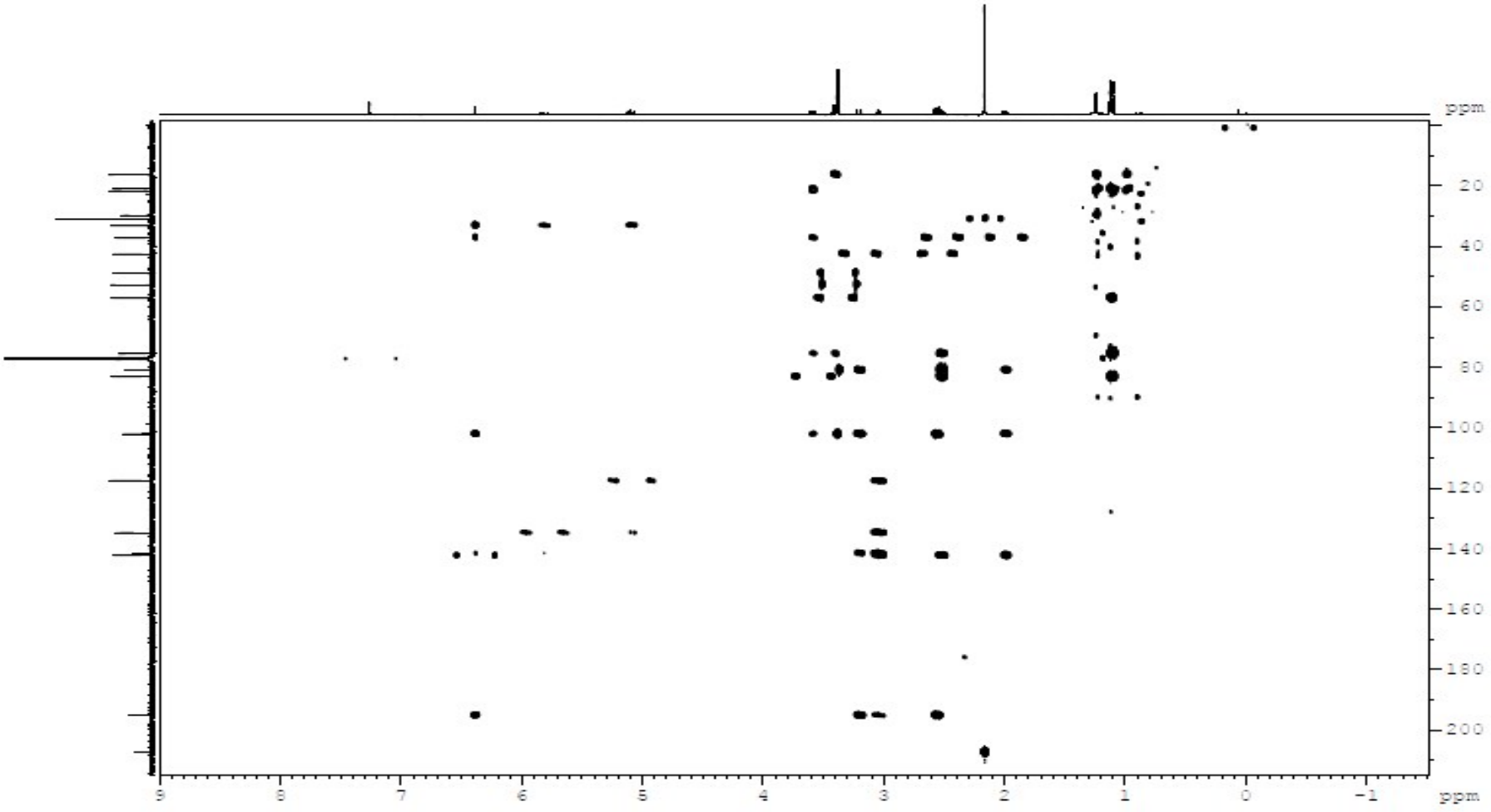


Figure S30 NOESY NMR spectrum of compound **3** (500 MHz, $CDCl_3$)

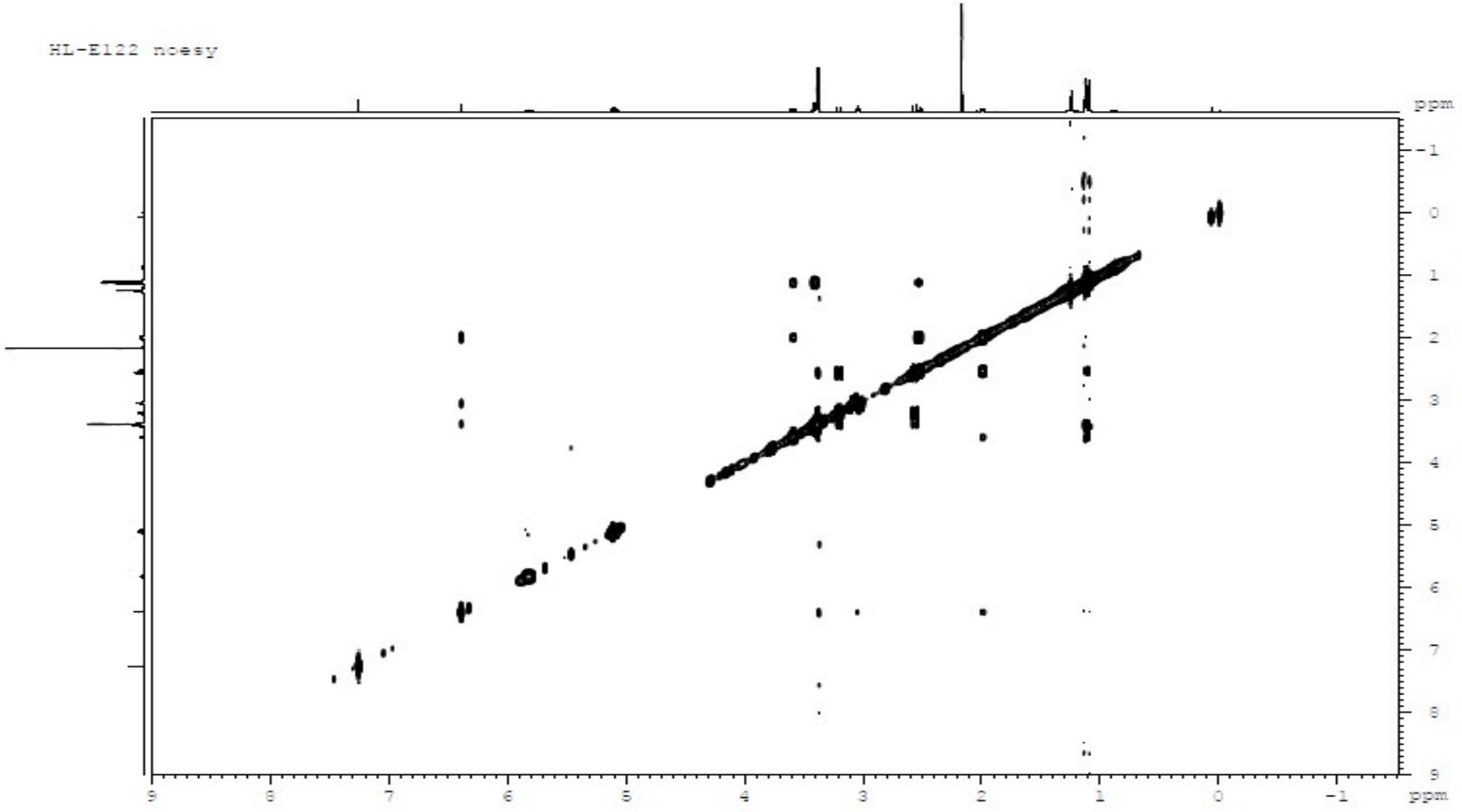


Figure S31 HRESIMS spectrum of compound **4**

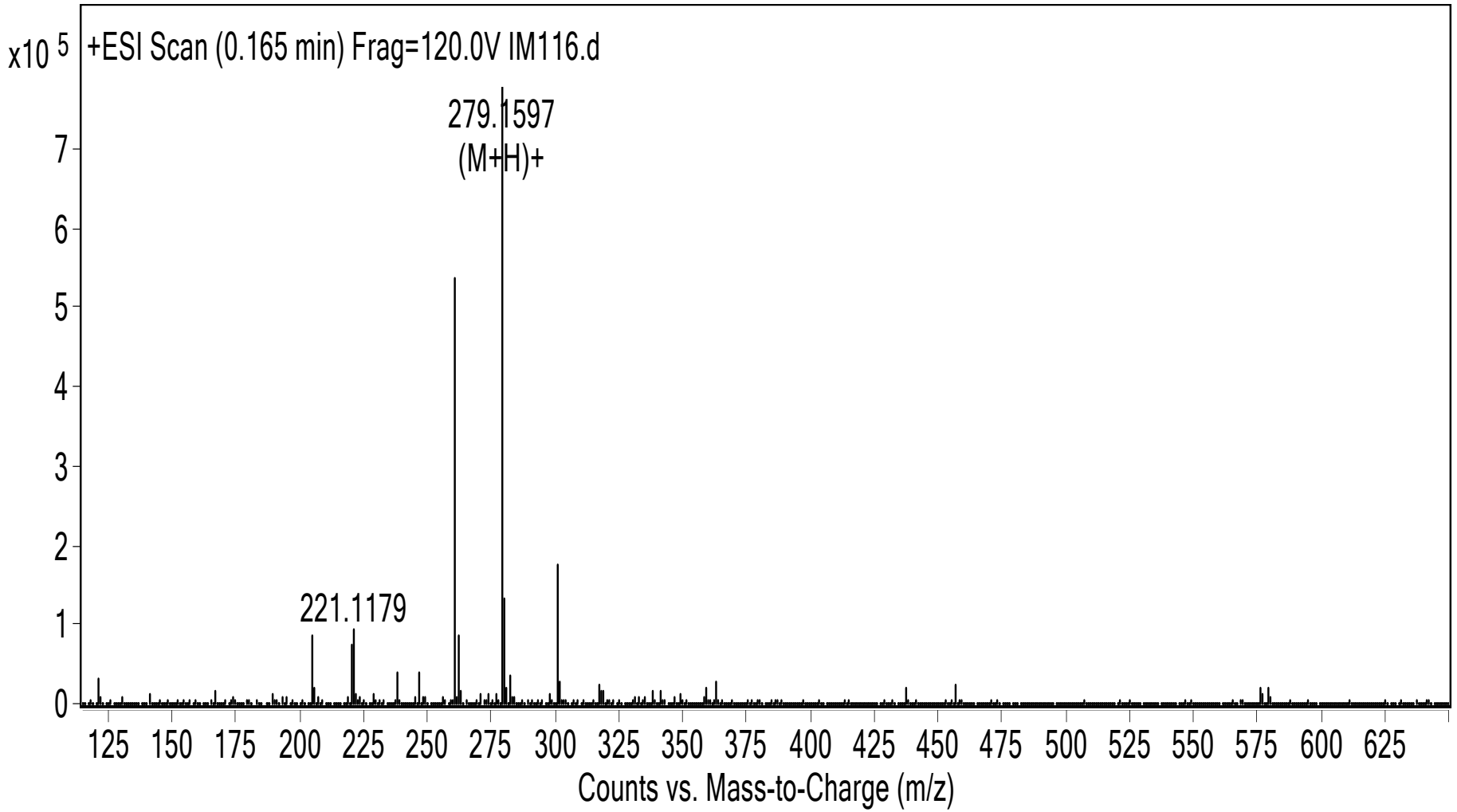


Figure S32 CD spectrum of compound **4**

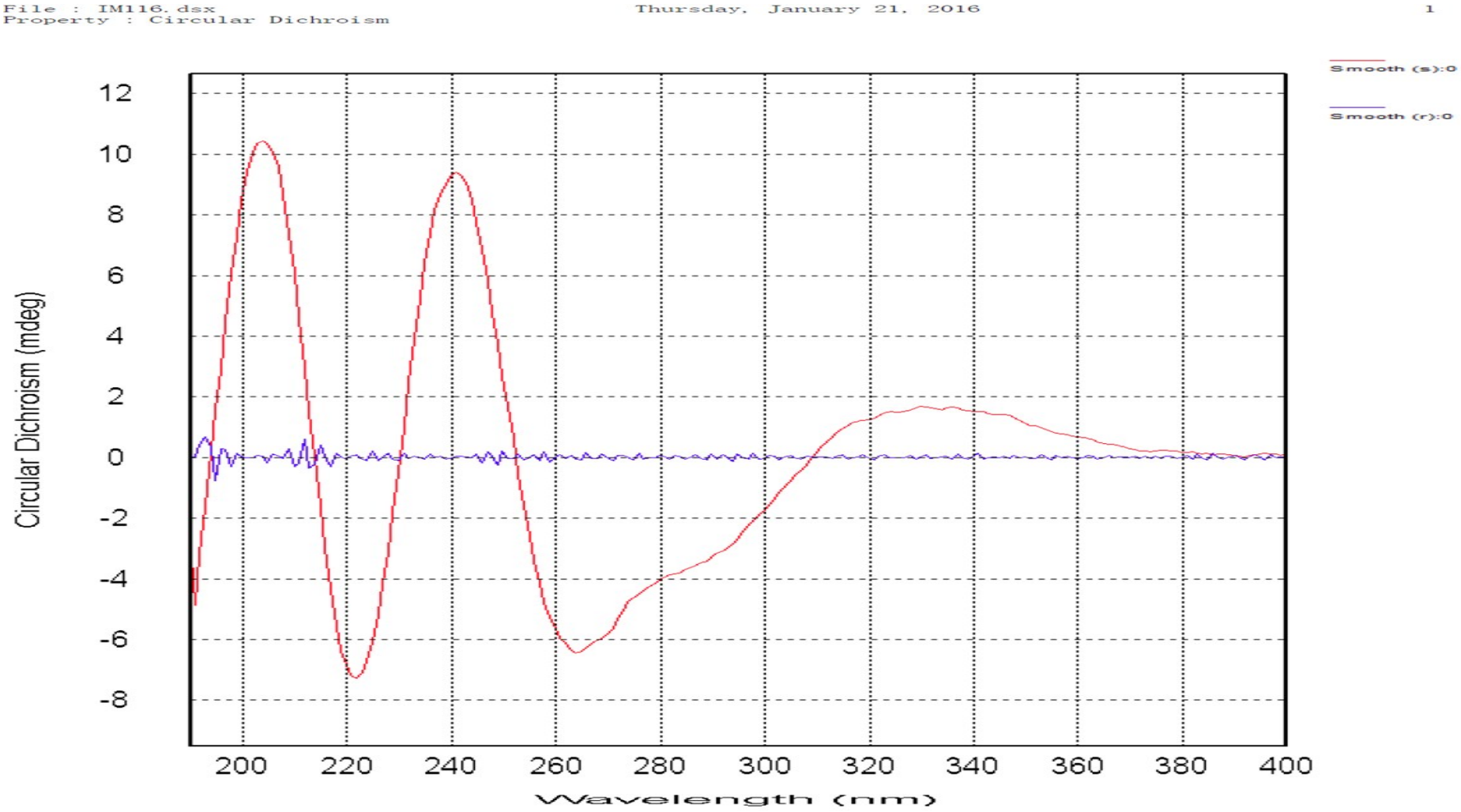


Figure S33 ^{1}H NMR spectrum of compound **4** (500 MHz, $CDCl_3$)

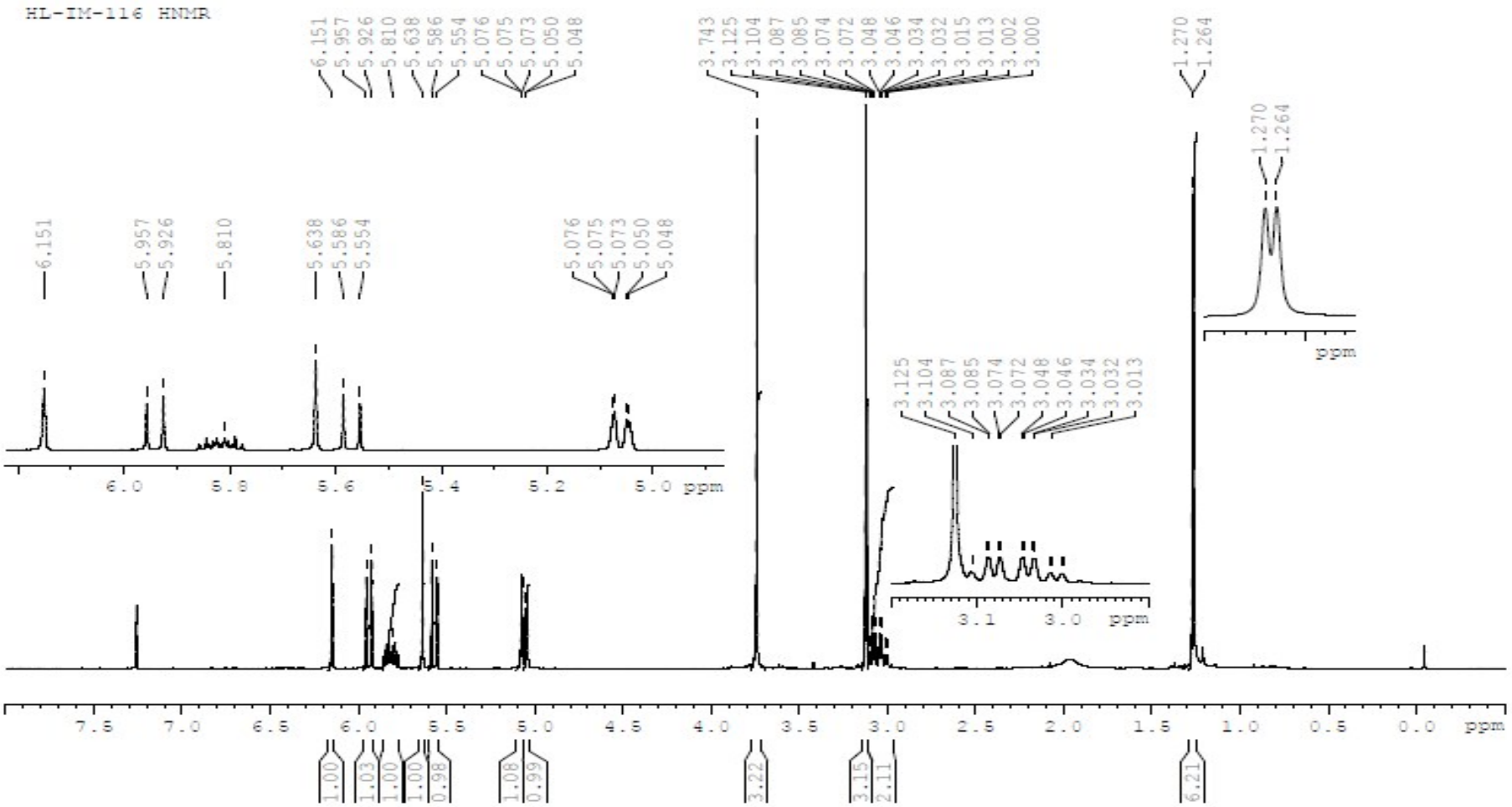


Figure S34 ^{13}C NMR spectrum of compound **4** (125 MHz, $CDCl_3$)

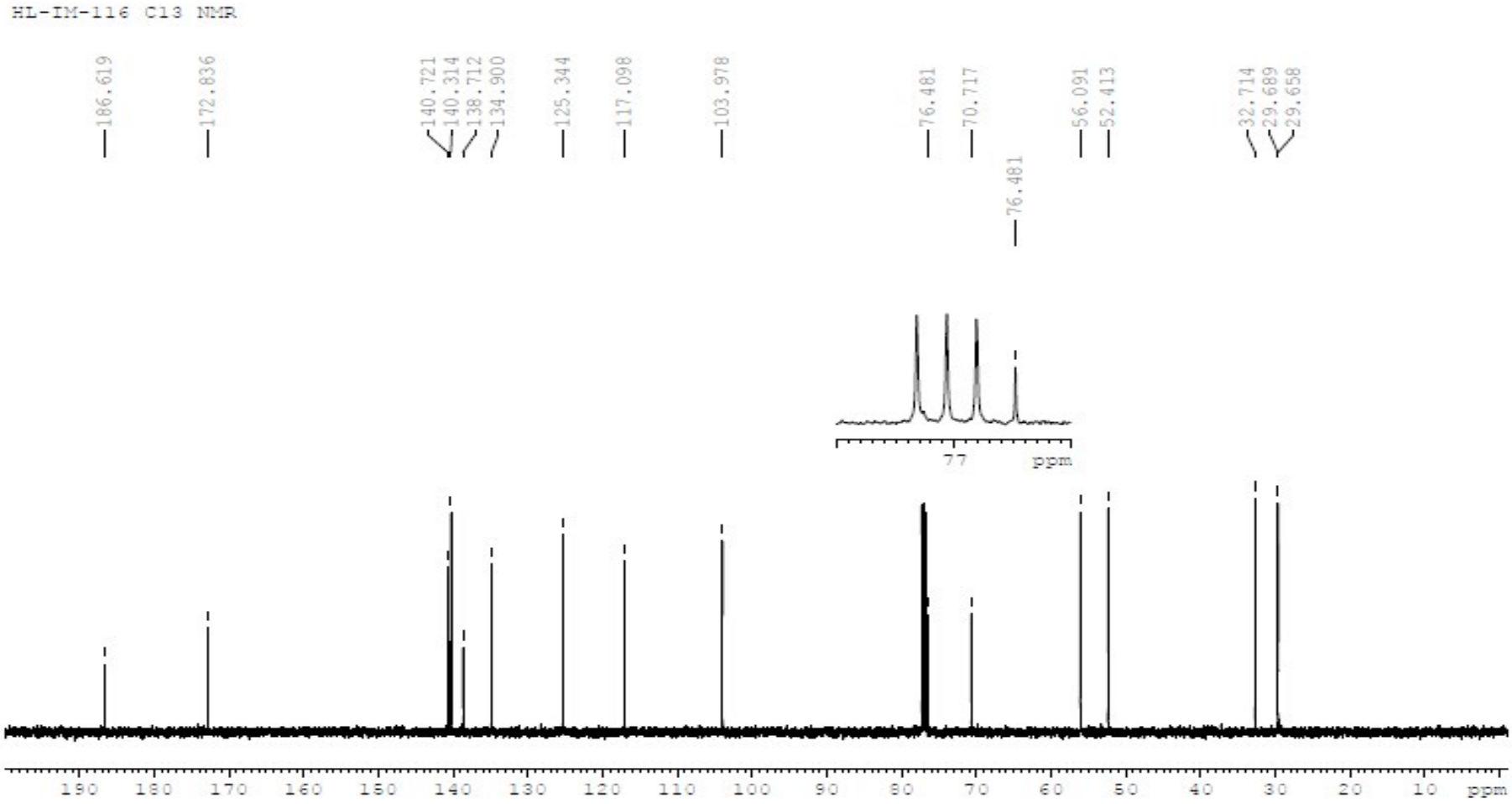


Figure S35 DEPT NMR spectrum of compound **4** (125 MHz, $CDCl_3$)

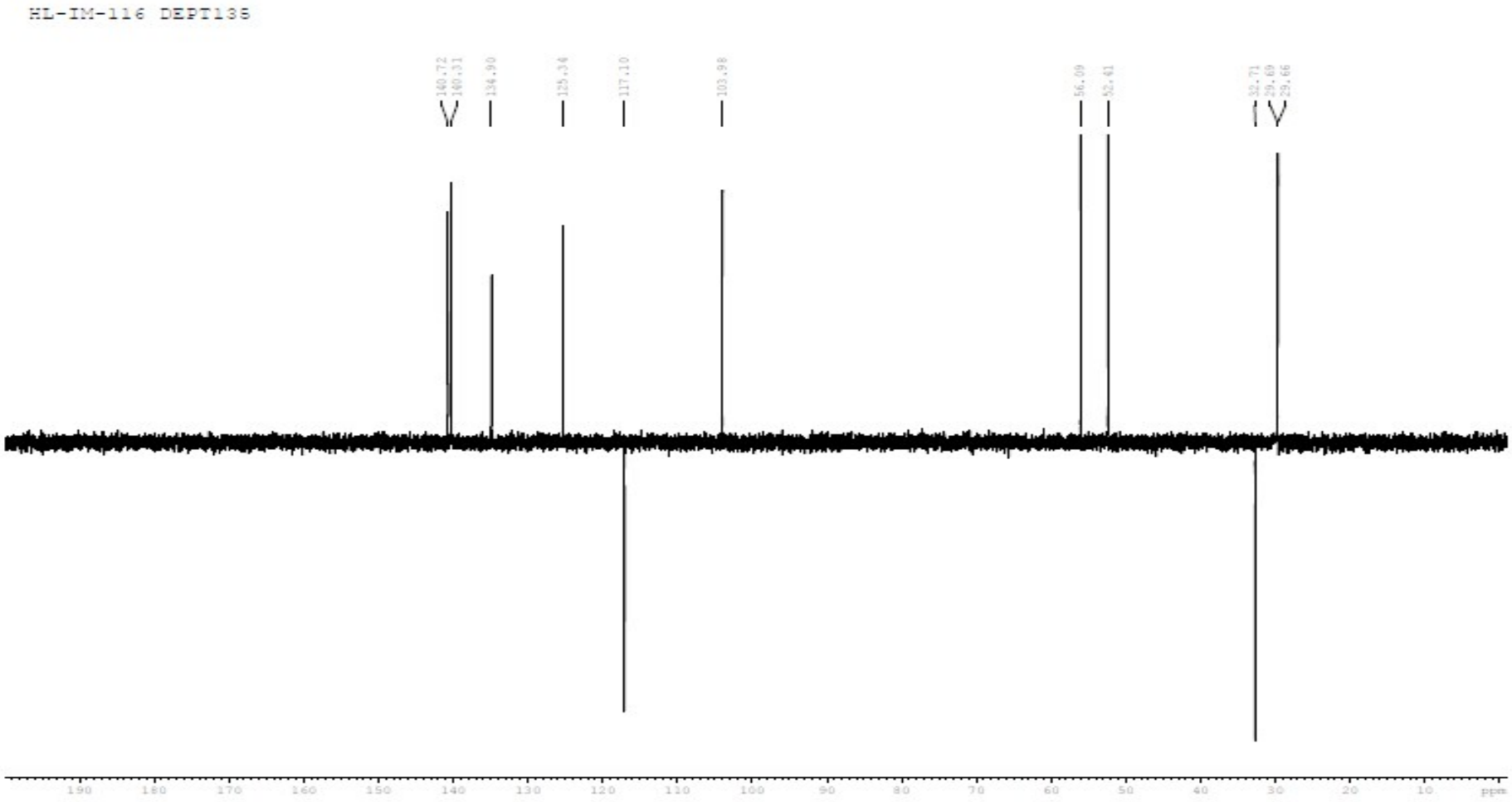


Figure S36 ^{1}H-^{1}H COSY NMR spectrum of compound **4** (500 MHz, $CDCl_3$)

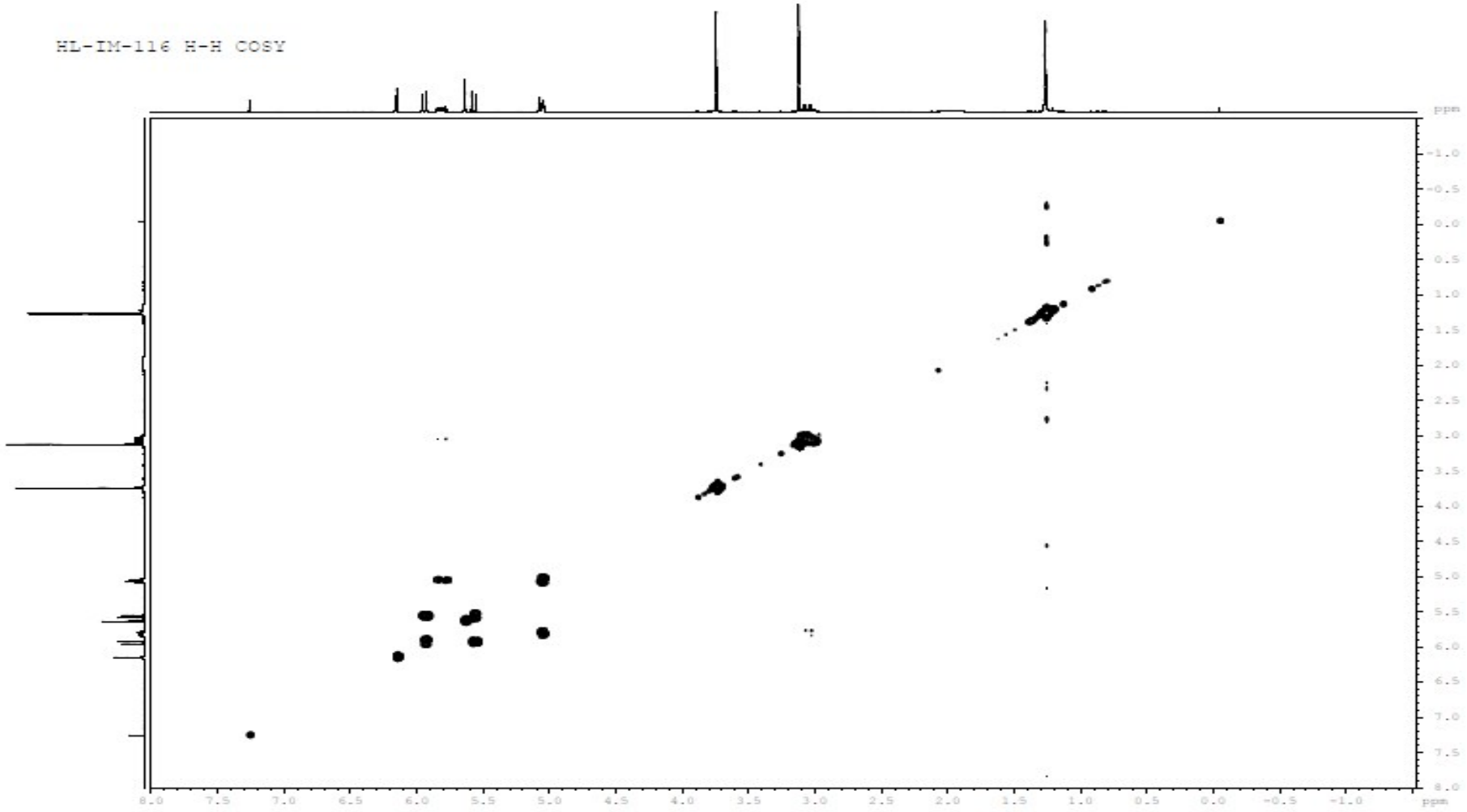


Figure S37 HSQC NMR spectrum of compound **4** (500 MHz, $CDCl_3$)

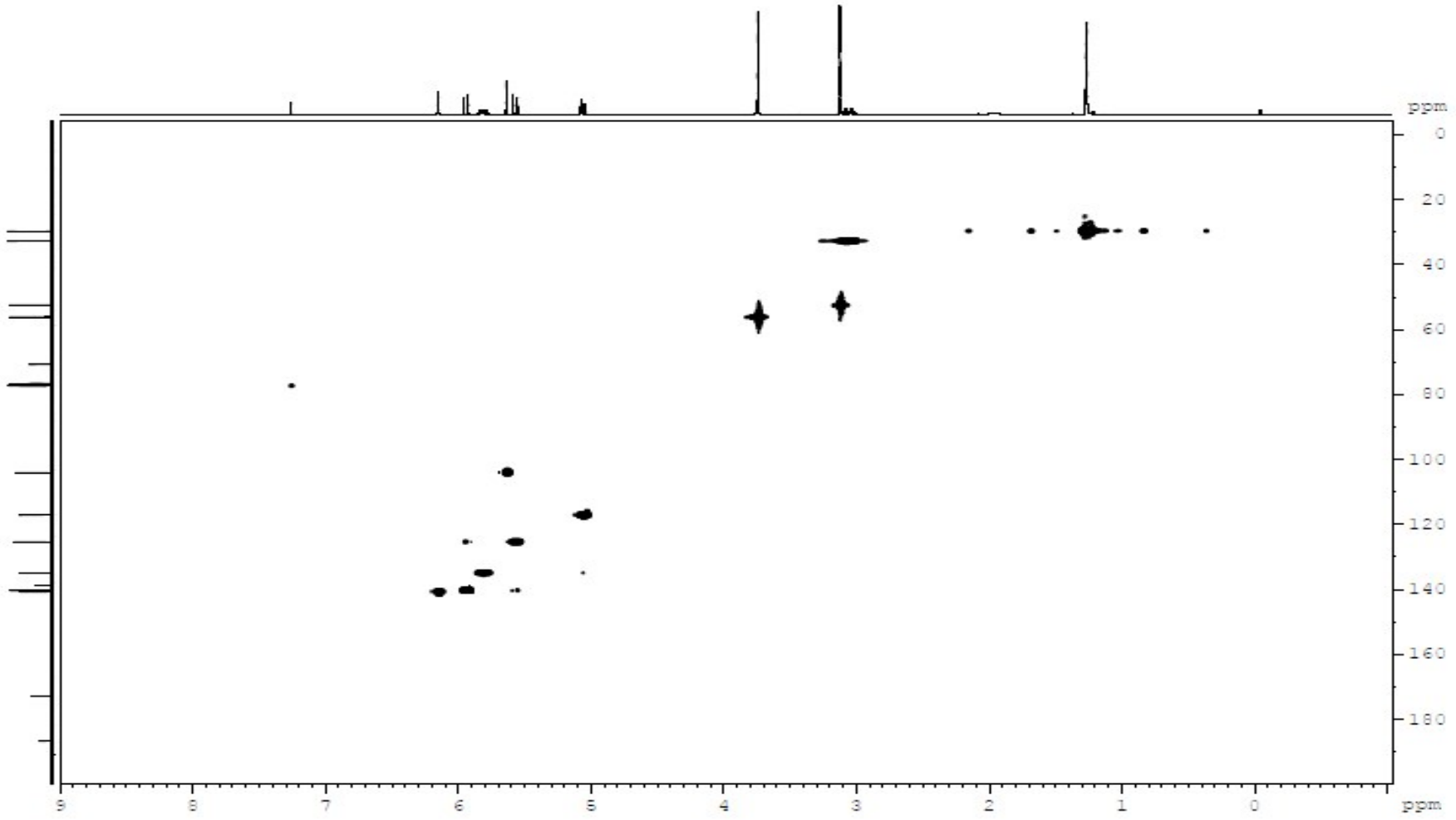


Figure S38 HMBC NMR spectrum of compound **4** (500 MHz, $CDCl_3$)

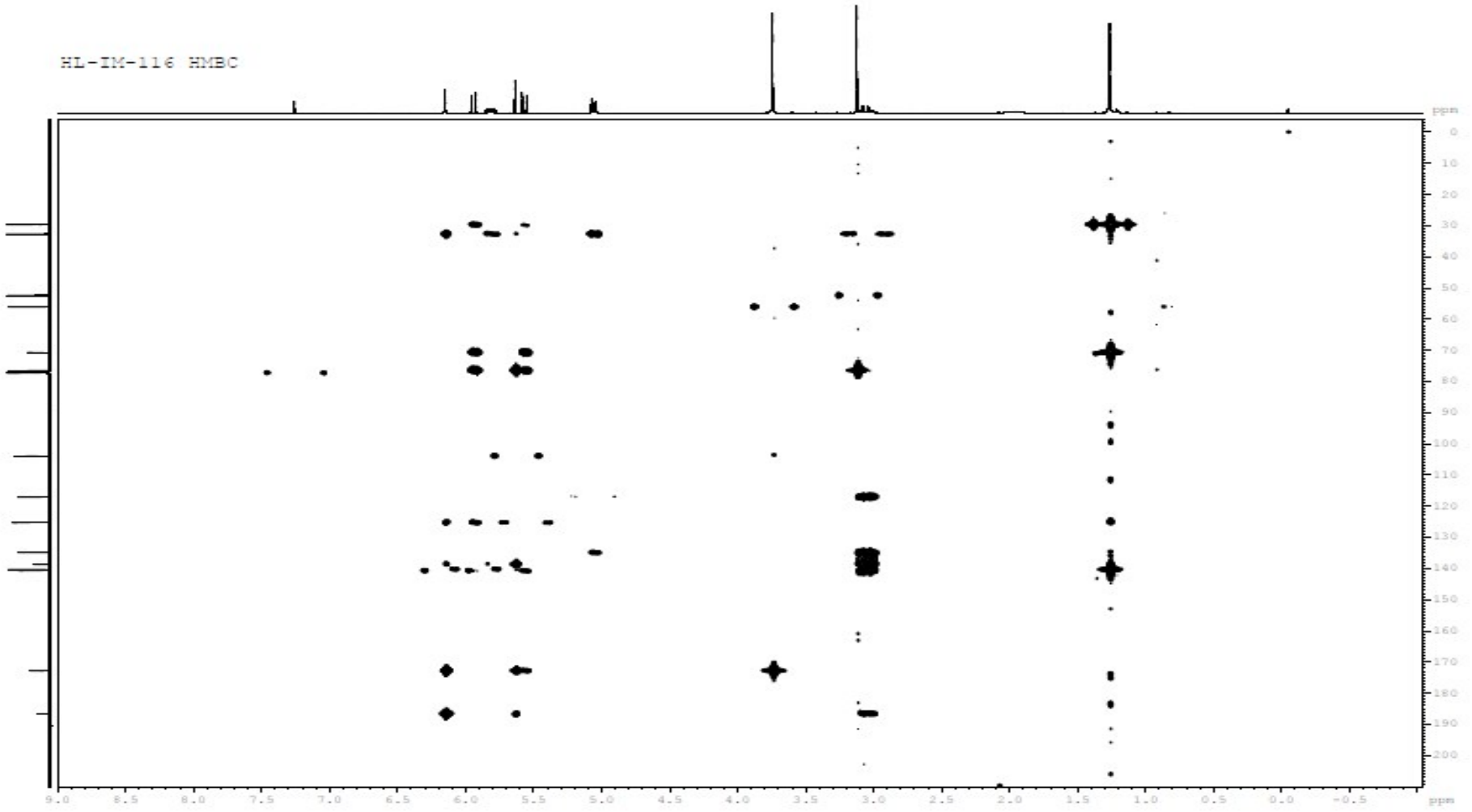


Figure S39 NOESY NMR spectrum of compound **4** (500 MHz, $CDCl_3$)

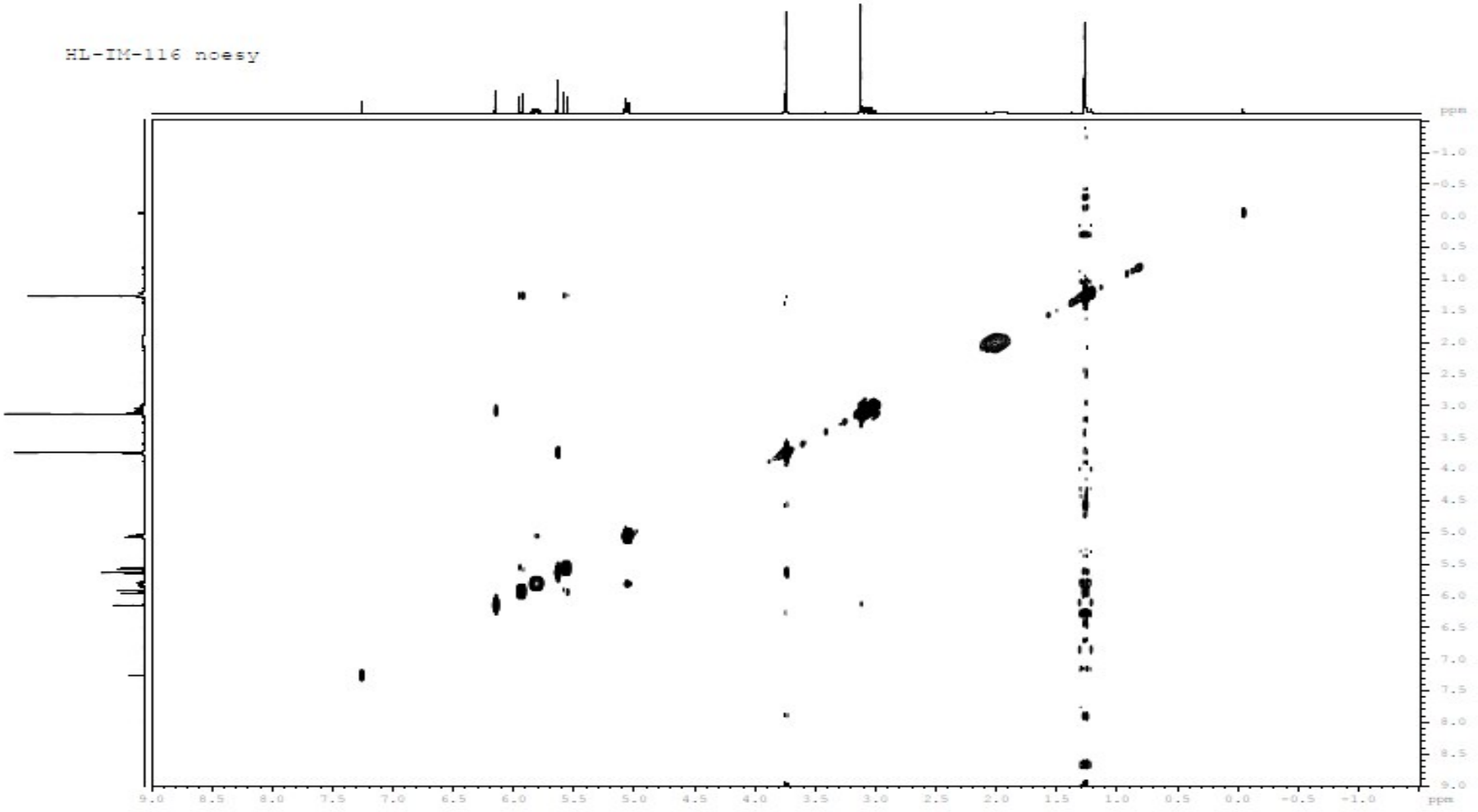


Figure S40 HRESIMS spectrum of compound **5**

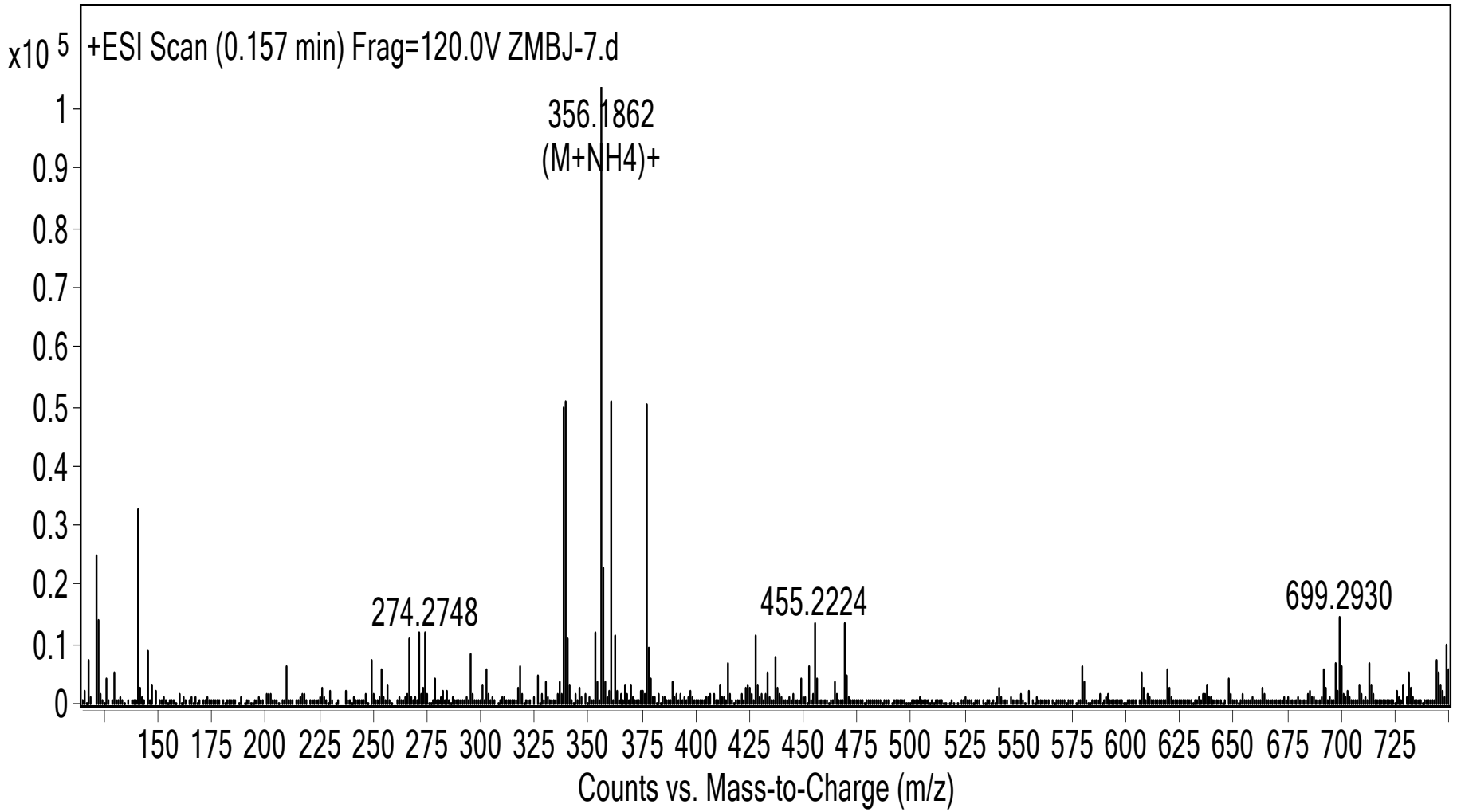


Figure S41 ^{1}H NMR spectrum of compound **5** (500 MHz, $CDCl_3$)

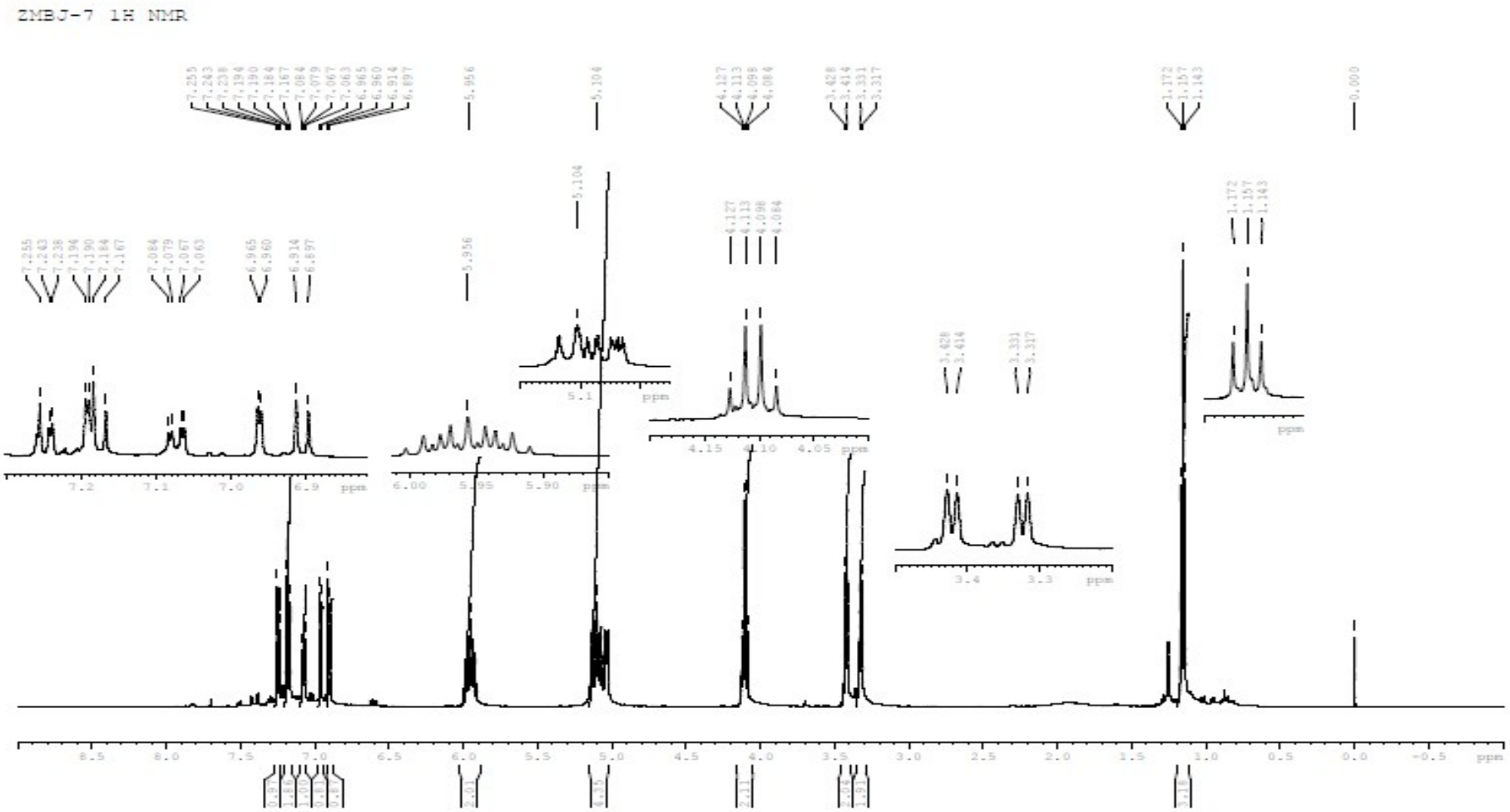


Figure S42 ^{13}C NMR spectrum of compound **5** (125 MHz, $CDCl_3$)

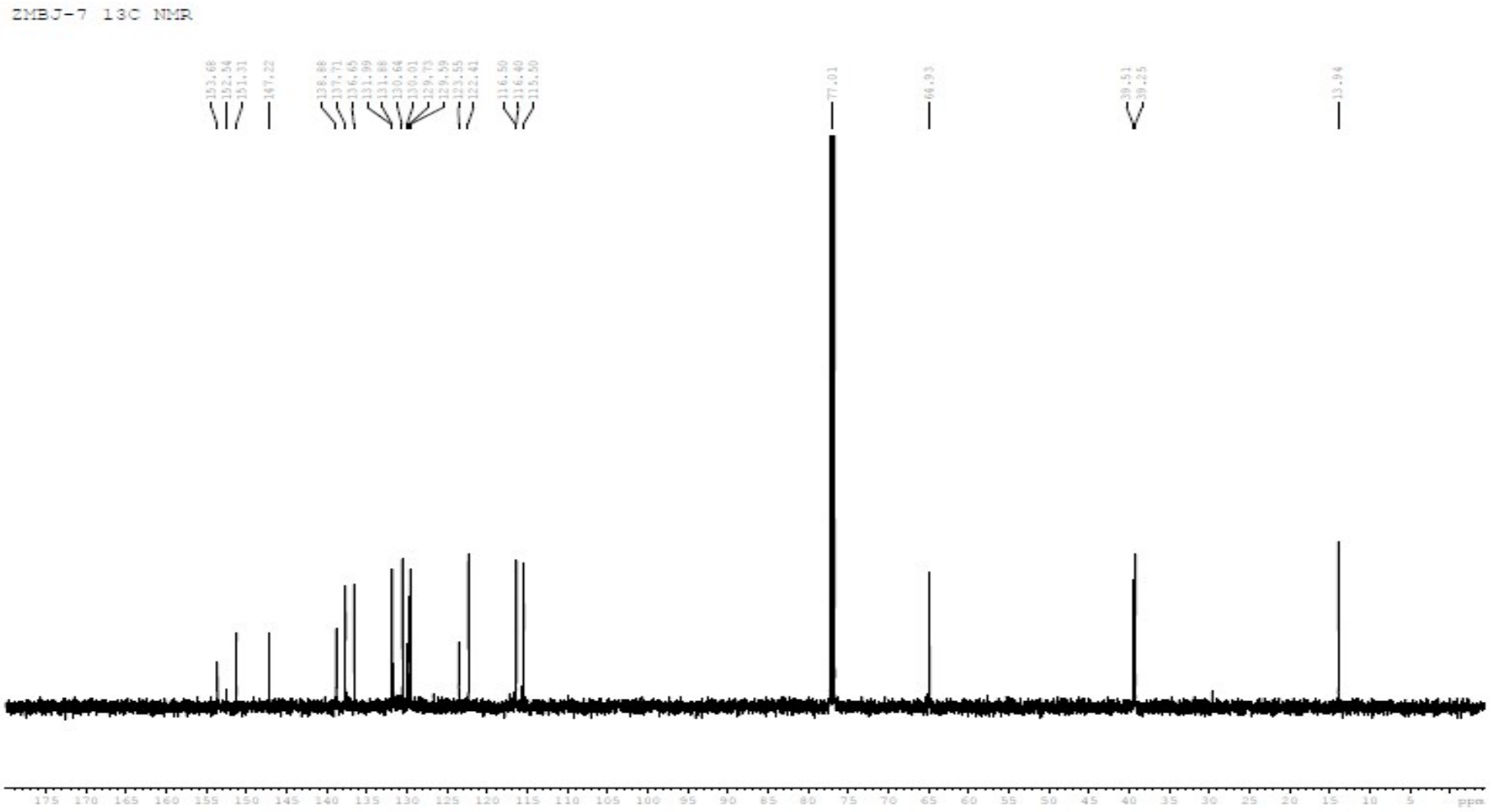


Figure S43 DEPT NMR spectrum of compound **5** (125 MHz, $CDCl_3$)

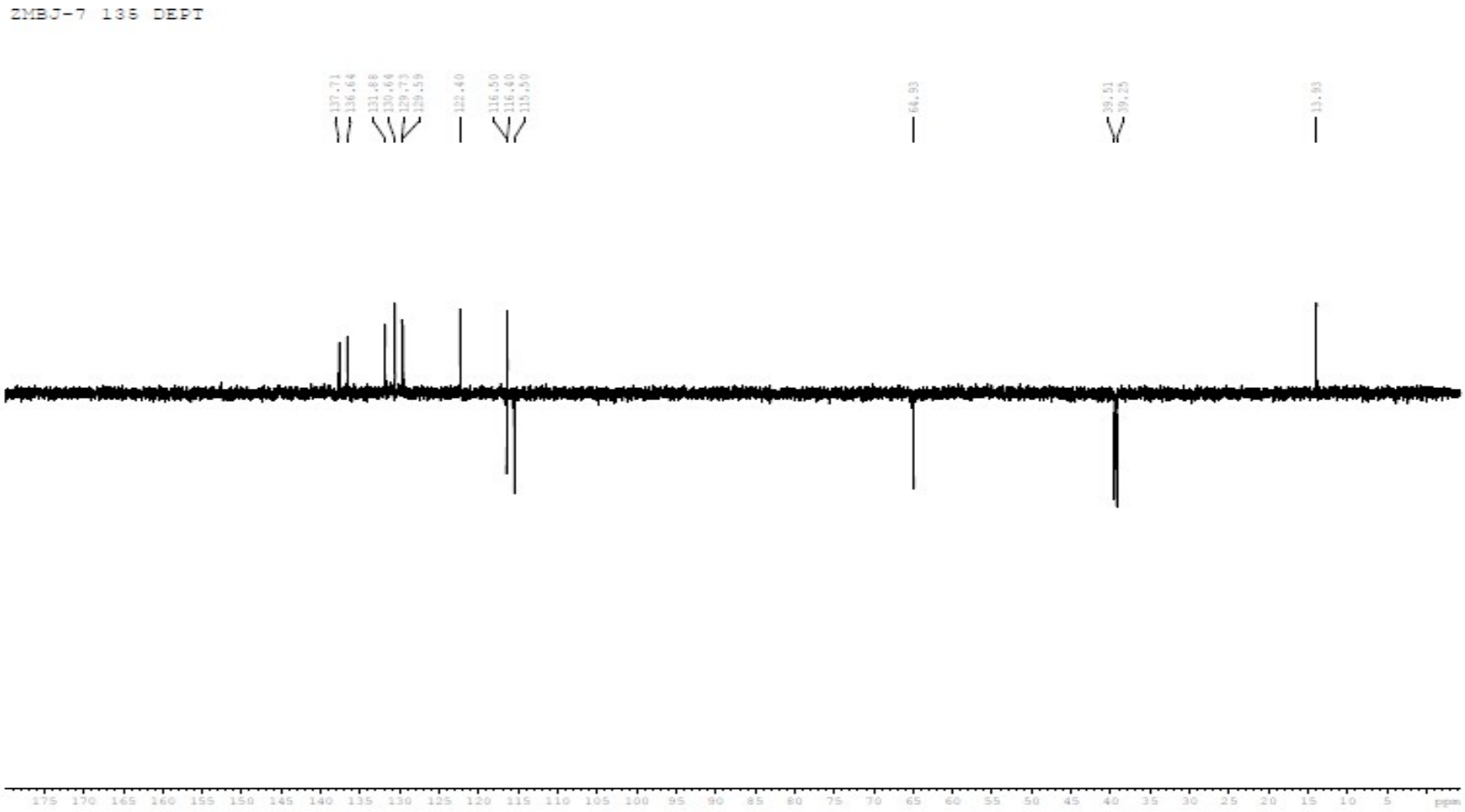


Figure S44 ^{1}H-^{1}H COSY NMR spectrum of compound **5** (500 MHz, $CDCl_3$)

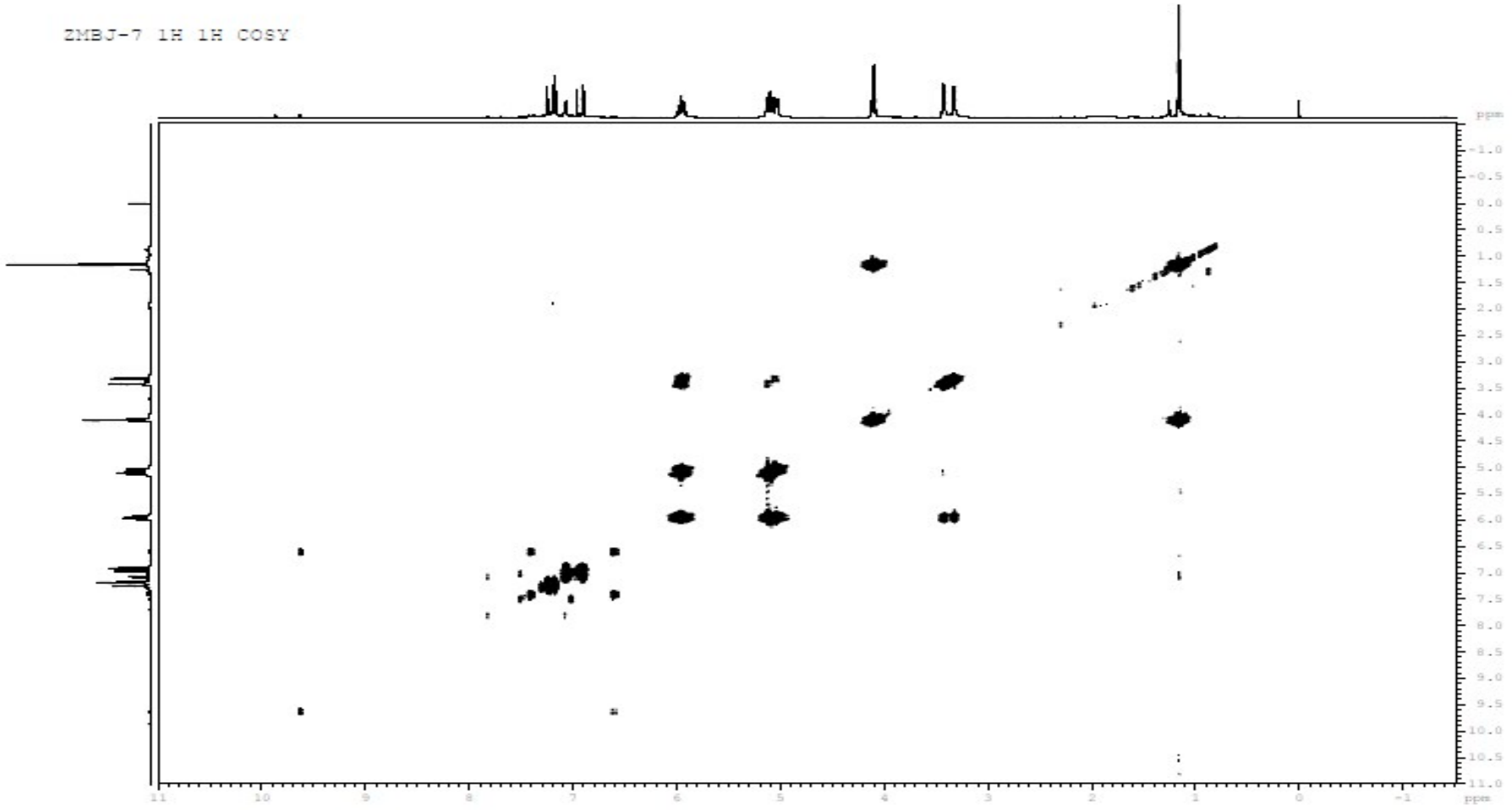


Figure S45 HSQC NMR spectrum of compound **5** (500 MHz, $CDCl_3$)

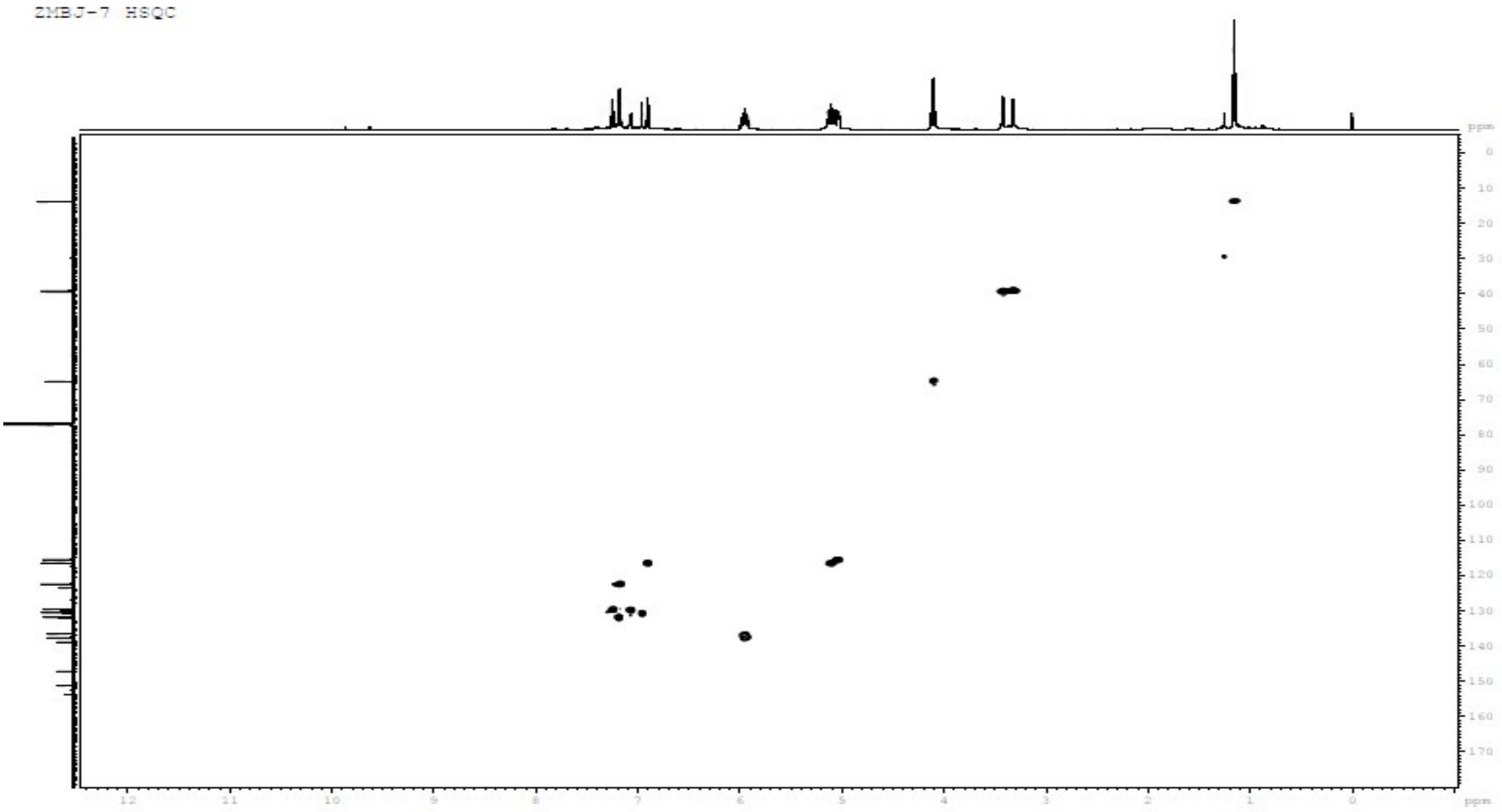


Figure S46 HMBC NMR spectrum of compound **5** (500 MHz, $CDCl_3$)

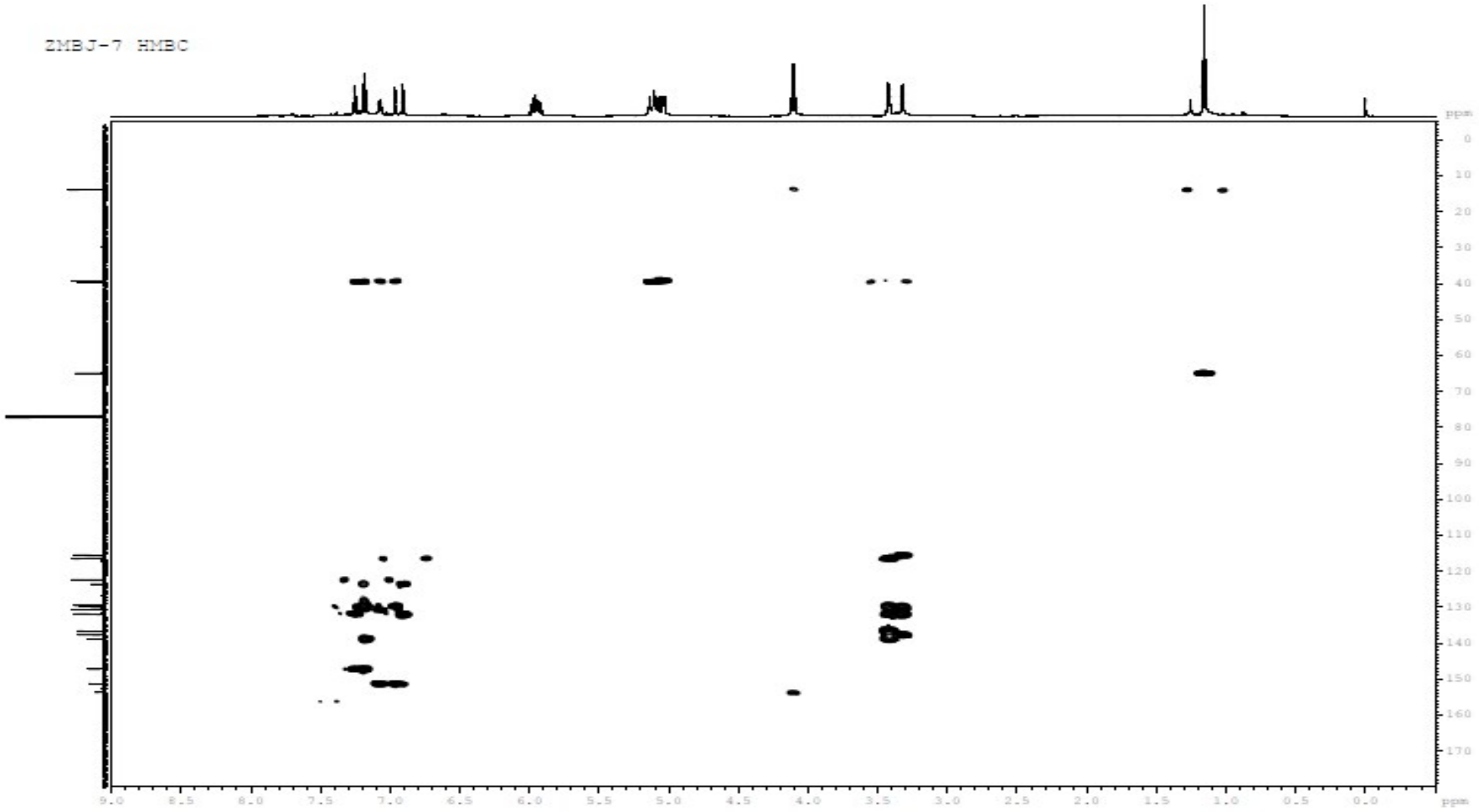


Figure S47 NOESY NMR spectrum of compound **5** (500 MHz, $CDCl_3$)

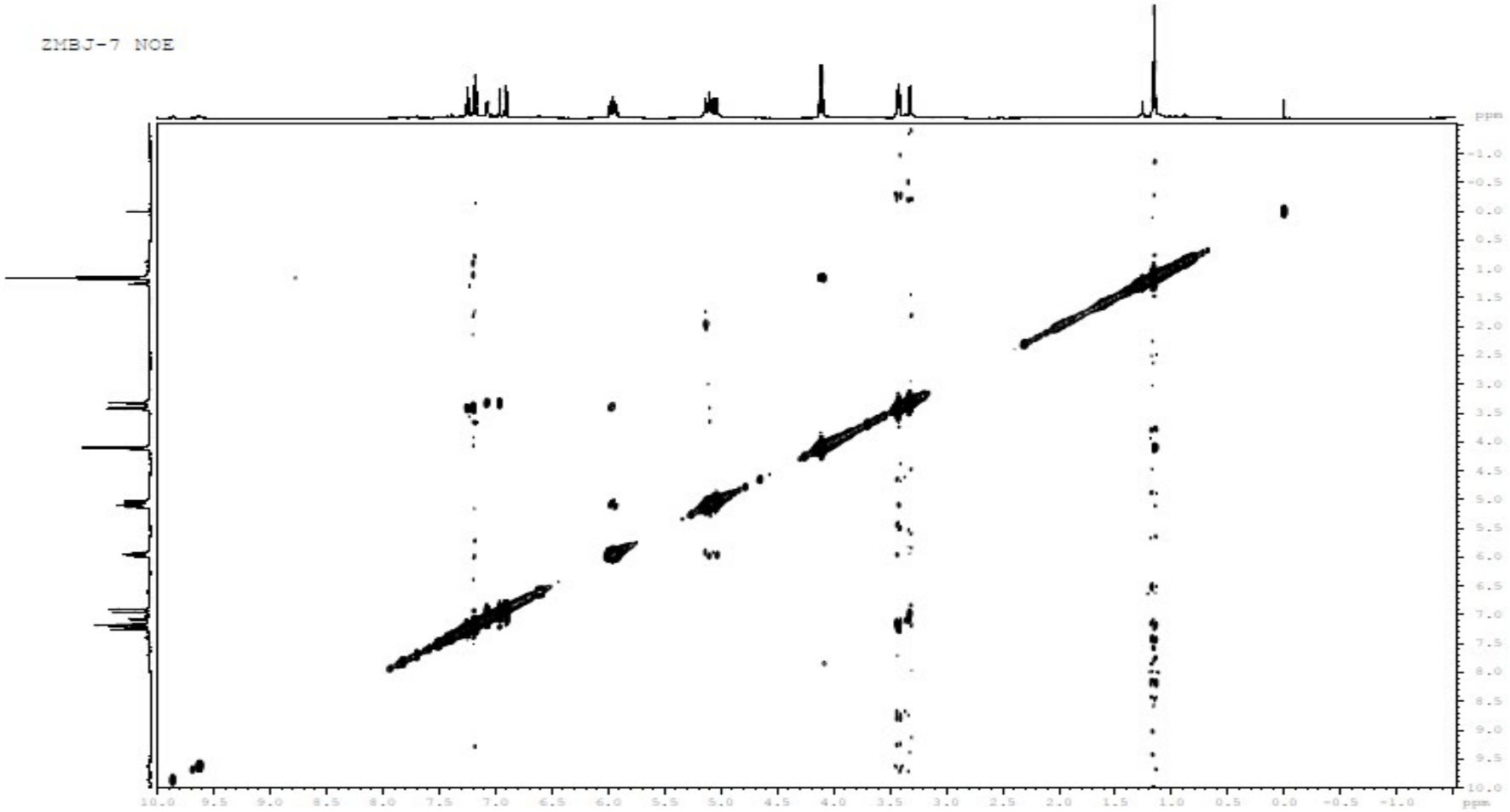


Figure S48 ESIMS spectrum of compound **7**

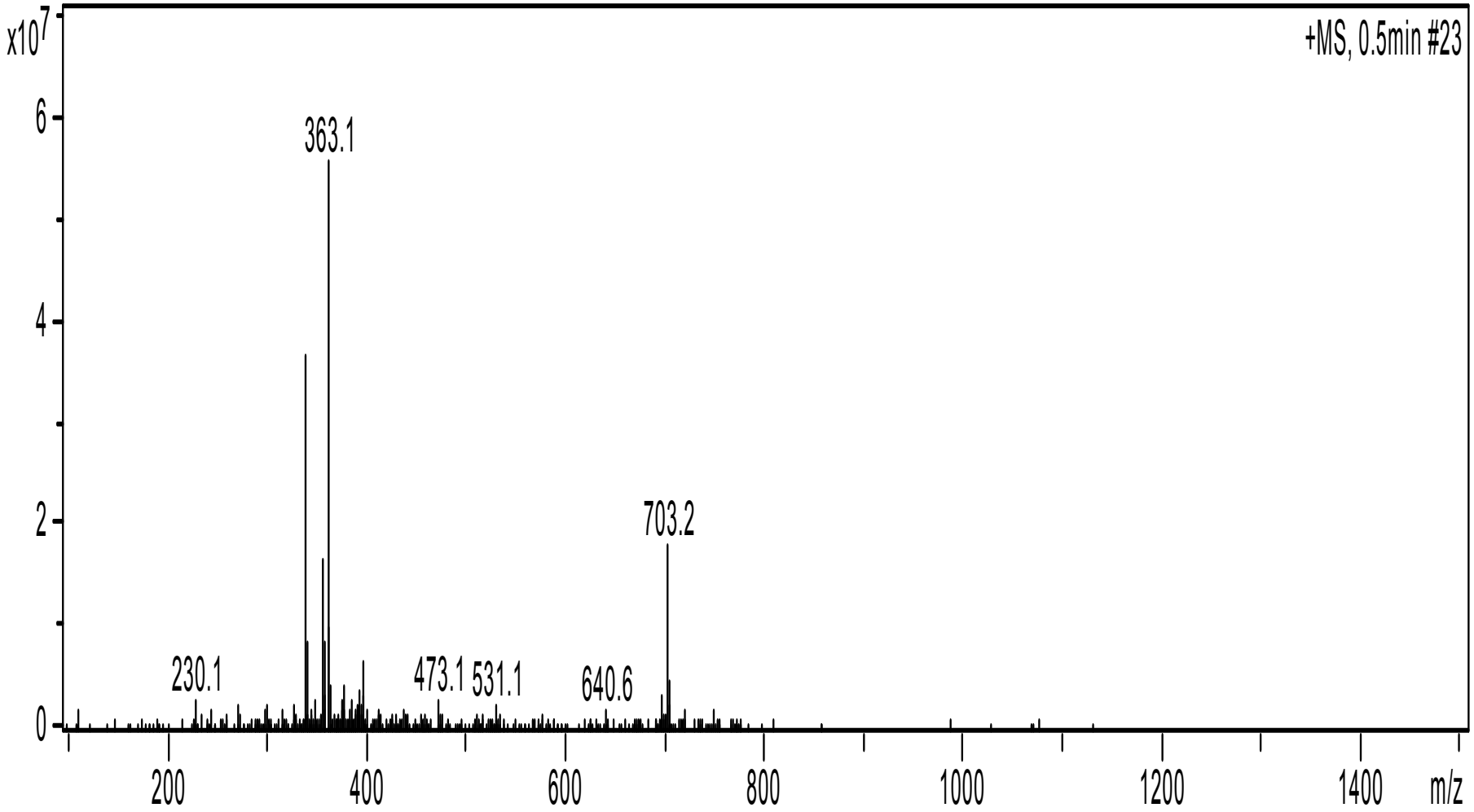


Figure S49 ^{1}H NMR spectrum of compound **7**

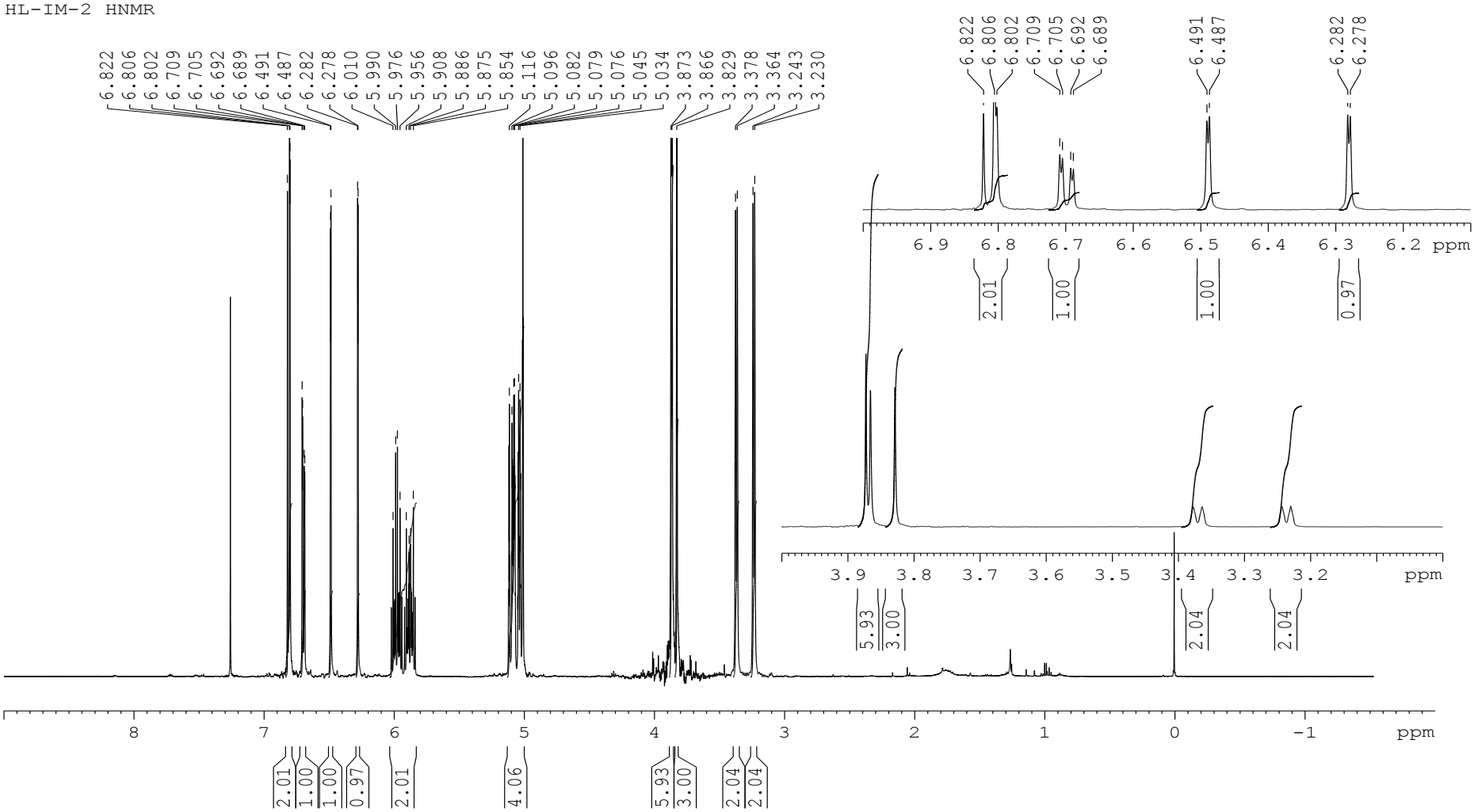


Figure S50 ^{13}C NMR spectrum of compound **7**

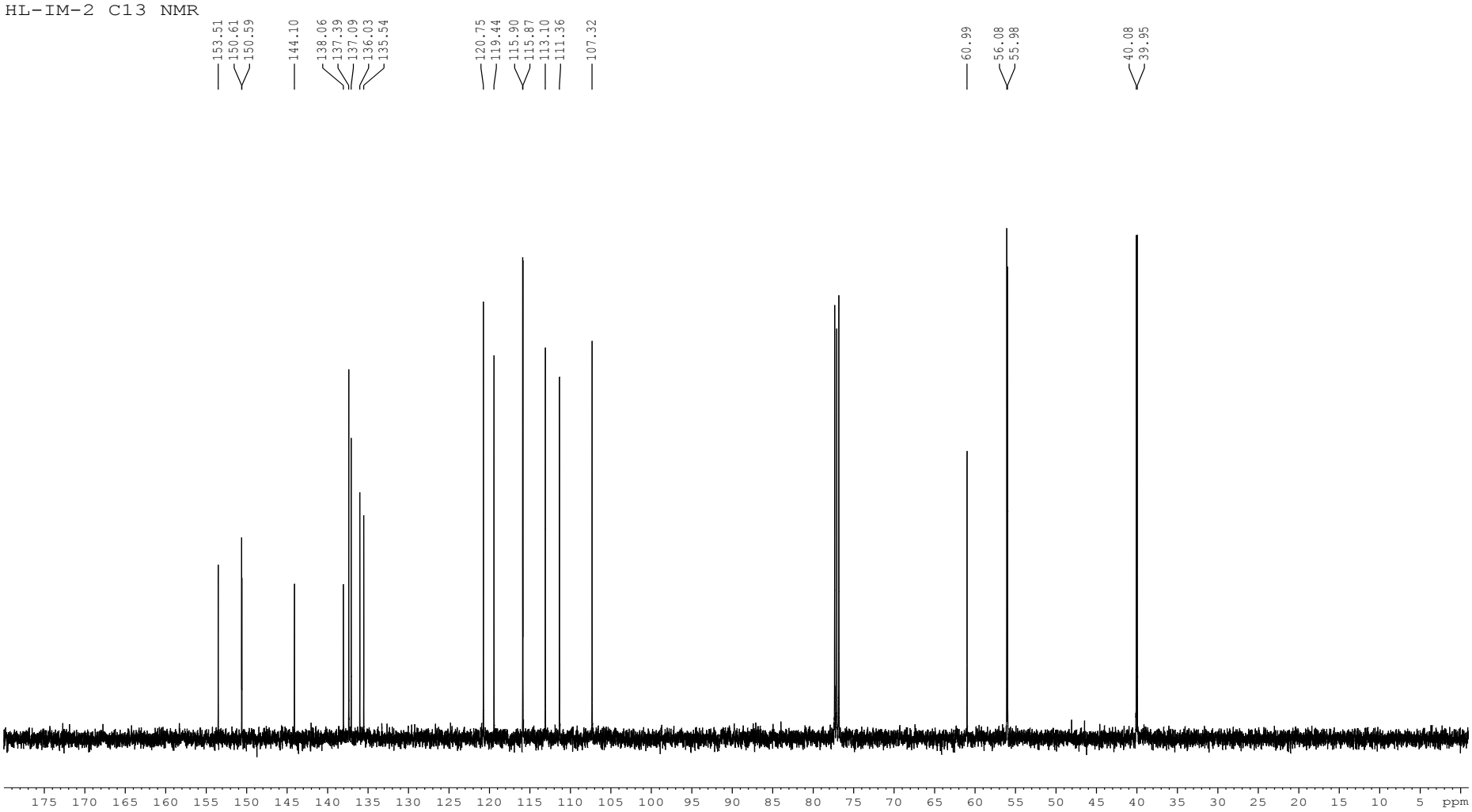


Figure S51 DEPT spectrum of compound **7**

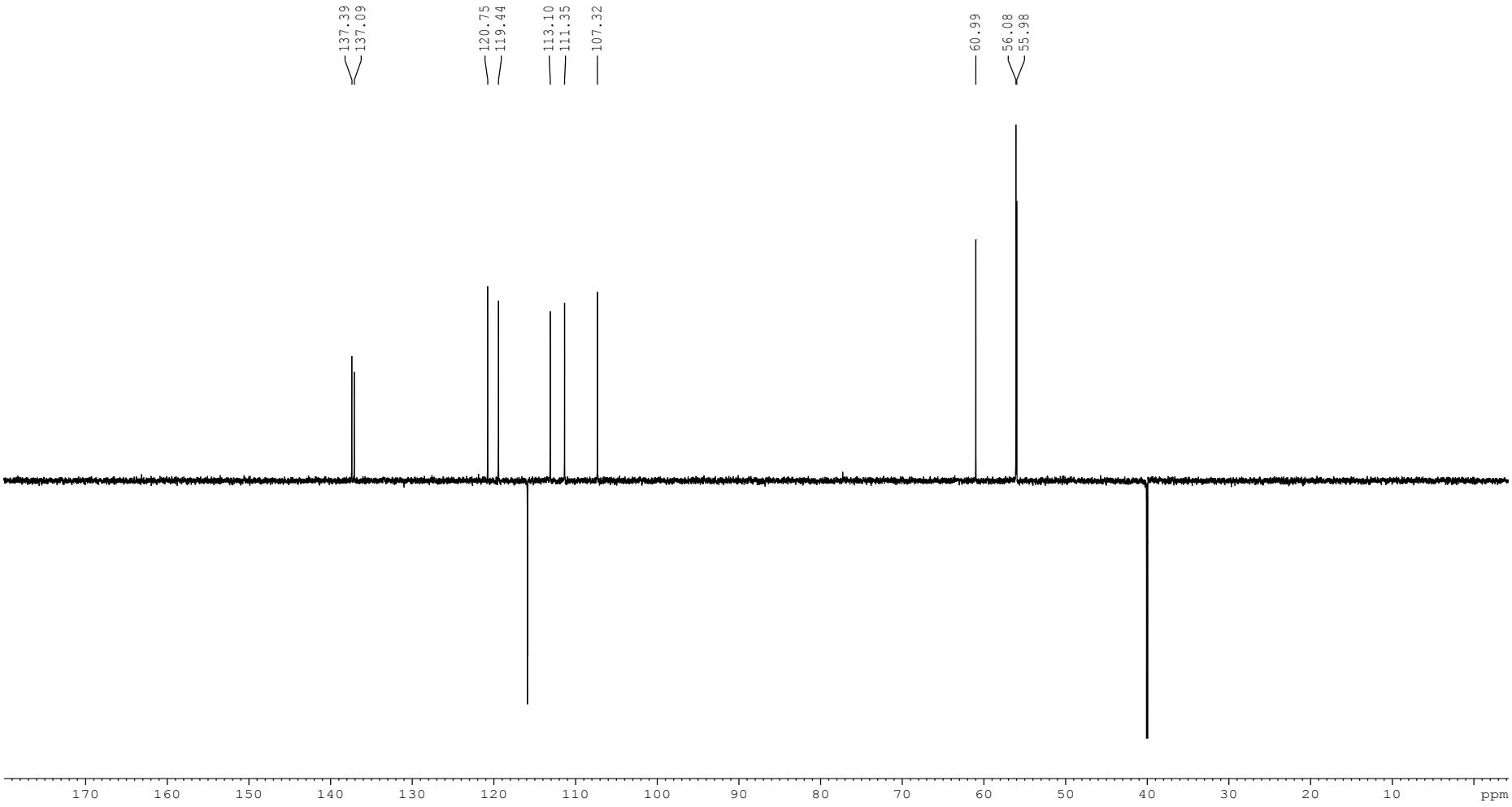


Figure S52 HSQC spectrum of compound **7**

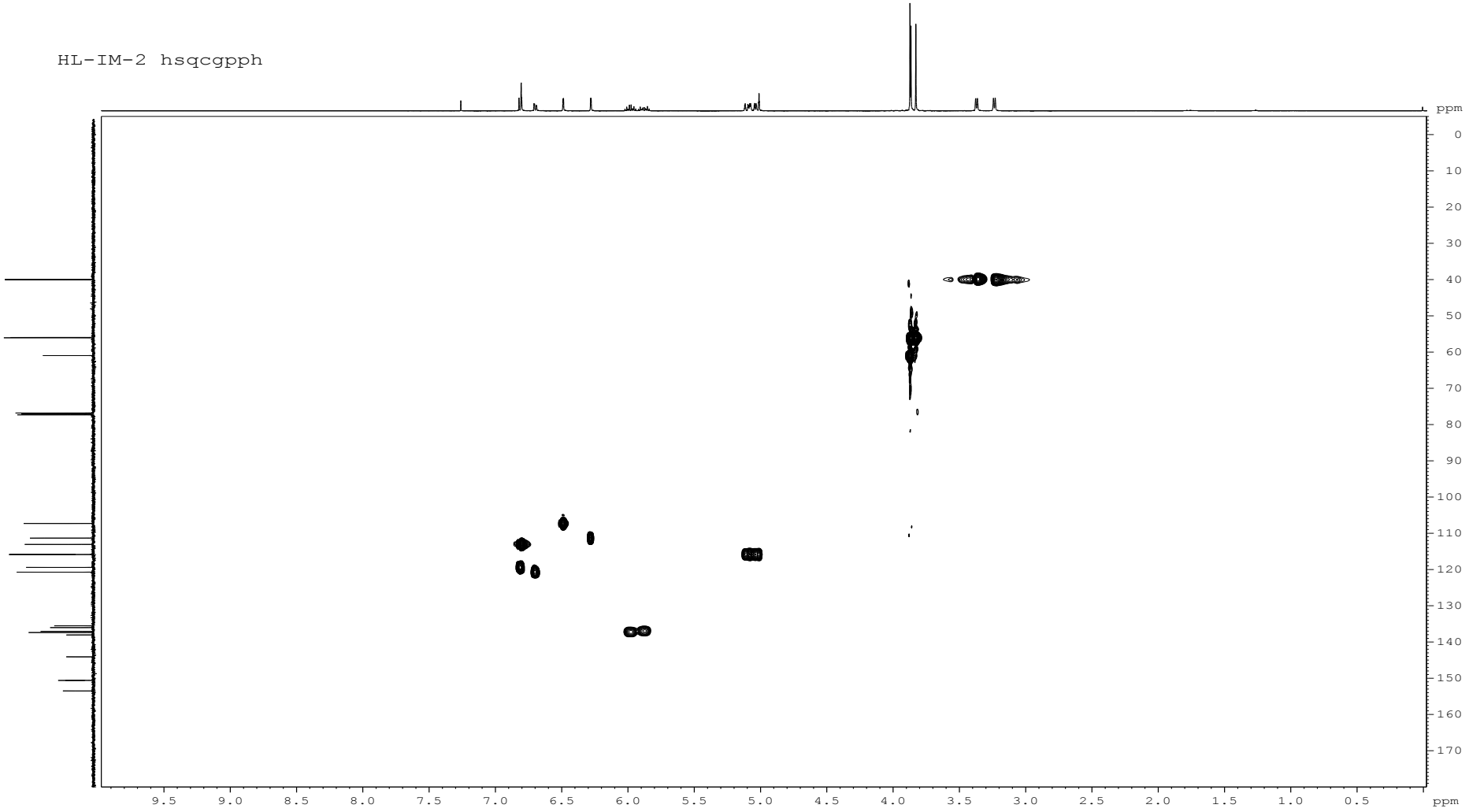


Figure S53 HMBC spectrum of compound **7**

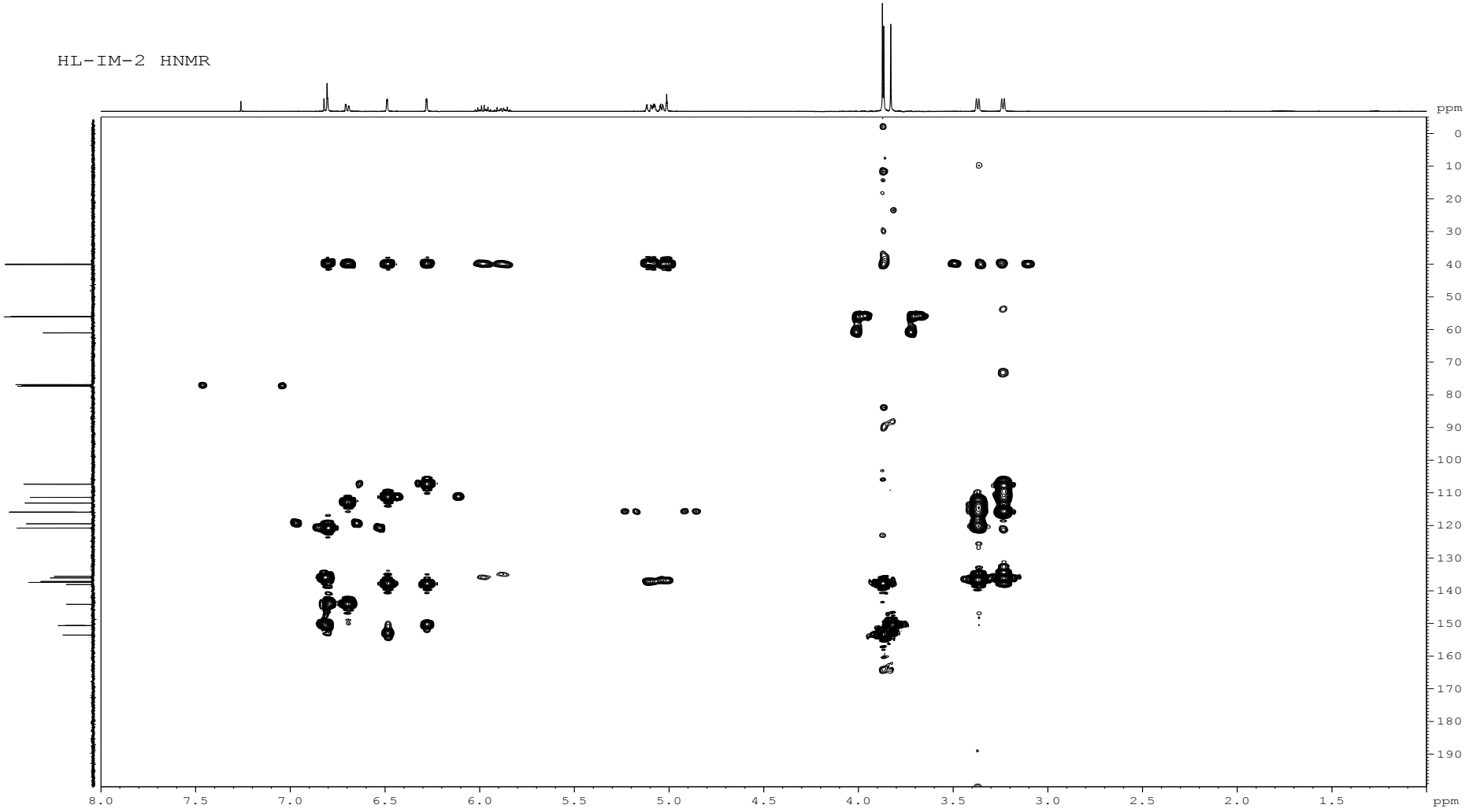
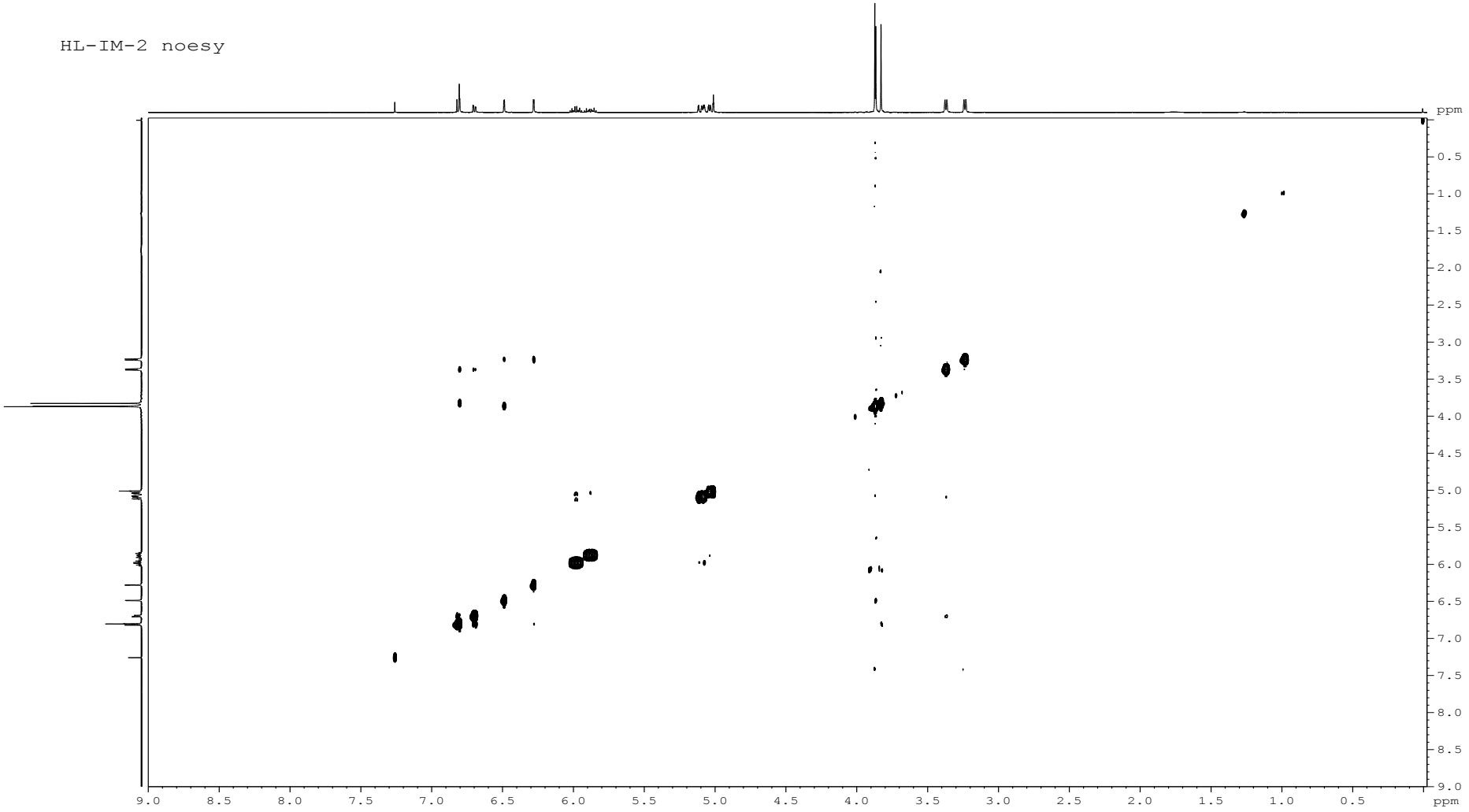


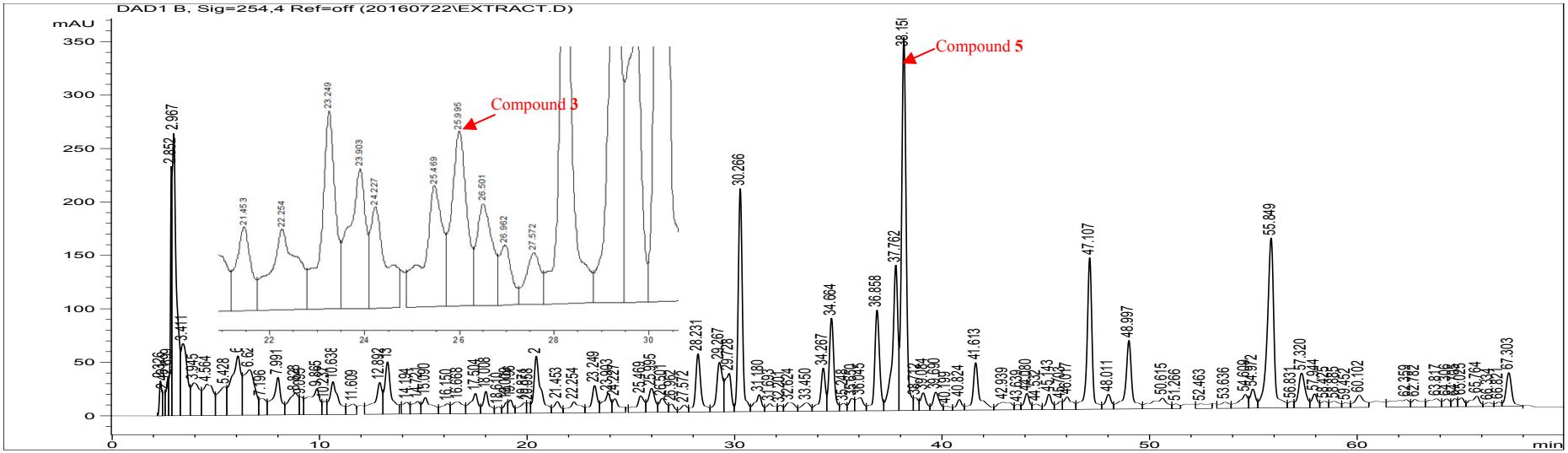
Figure S54 NOESY spectrum of compound **7**

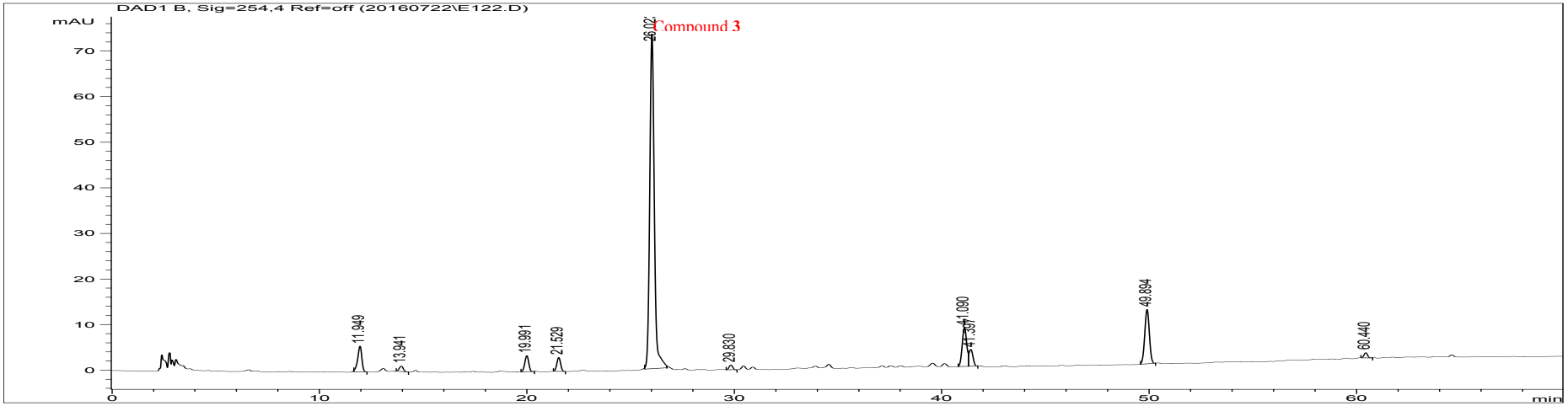


Experimental Section

To prove whether compounds **3** and **5** were ethoxy artifacts or not, we ran the HPLC, and LC-MS of the methanol extract of *Illicium burmanicum* and compounds **3** and **5**. The results indicated that compounds **3** and **5** could be detected from the HPLC spectrum (**Fig. S55**), and from the extracted ion chromatogram of the extract (**Fig. S56** and **S57**), indicating that compounds **3** and **5** should be natural products, rather than artifacts.

The experimental details are as follows: Chromatographically pure reagents acetonitrile and methanol were obtained from Fisher Scientific Co. (Nepean, Ont., Canada); Water was purified by a Milli-Q system (Millipore, MA, USA). Air-dried branches and leaves of *I. burmanicum* (10 g) were powdered and extracted with methanol (100 mL) three times (0.5 h) under condition of reflux. The solvent was removed under low pressure to afford a crude extract (680 mg), which was then dissolved in acetonitrile and filtered through a syringe filter (0.22 μm). A total of 5 μL filtrate was subject to LC/MS system for analysis. Compounds **3** and **5** were also dissolved in acetonitrile for analysis. LC-MS was run on an Agilent 1100 Series LC/MSD Trap XCT with an ESI ion source (Agilent Technologies, Santa Clara, CA, USA). Samples were separated on an XTerra-MS-C_{18} (4.6 × 250 mm, 5 μm, Waters, Milford, USA) at 25 °C. Water (A) and acetonitrile (B) were used as the mobile phase: 0–60 min, 20–100 % B at a flow rate of 0.8 mL/min. ESI-MS conditions: carrier gas N_2, capillary temperature 350 °C, gas flow 12 L/min, capillary voltage 3500 V, nebulizer pressure 45 psi, positive scan mode (*m/z* 100–1000).


DAD1 B, Sig=254,4 Ref=off (20160722\EXTRACT.D)
mAU
Compound 3
Compound 5
min


DAD1 B, Sig=254,4 Ref=off (20160722\E122.D)
mAU
Compound 3
min

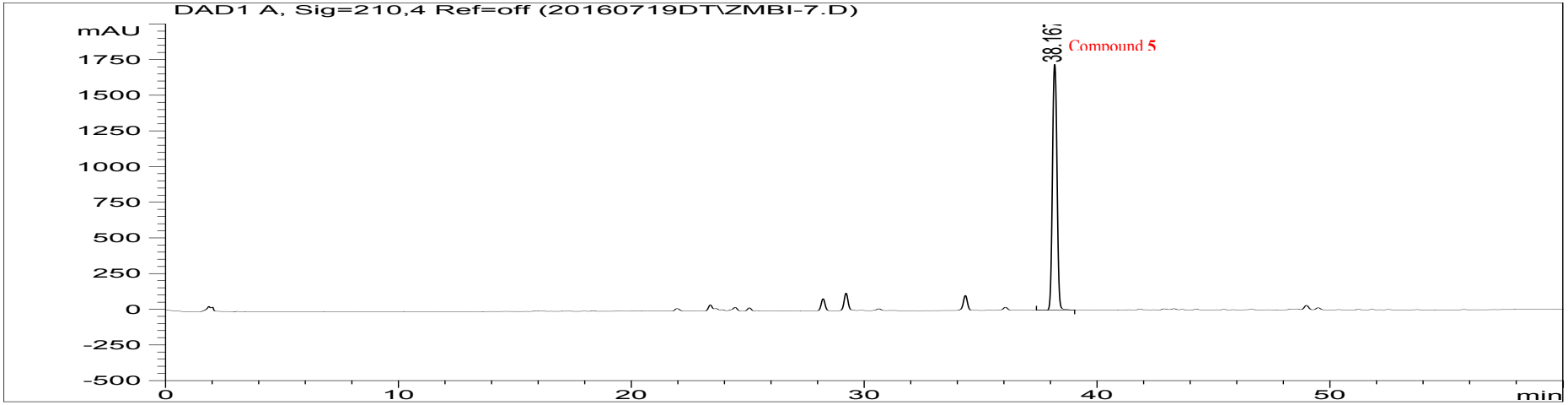


Figure S55 HPLC spectrum of the extract, compounds **3** (t_R = 26.0 min) and **5** (t_R = 38.2 min).

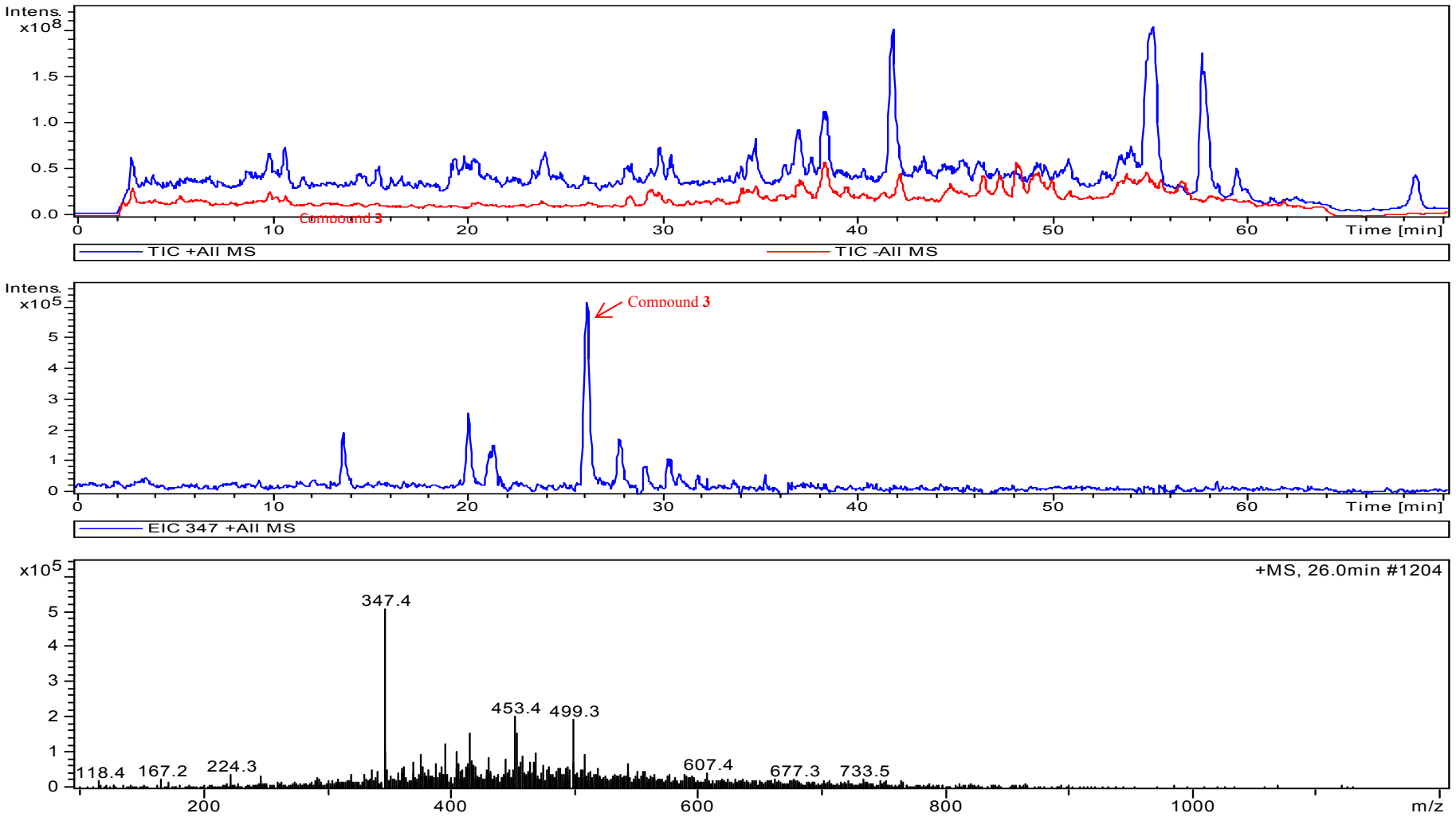


Figure S56 Base peak and extracted ion chromatogram of the methanol extract at 26.0 min (Compound **3**: *m/z* = 347 $[M + Na]^+$).

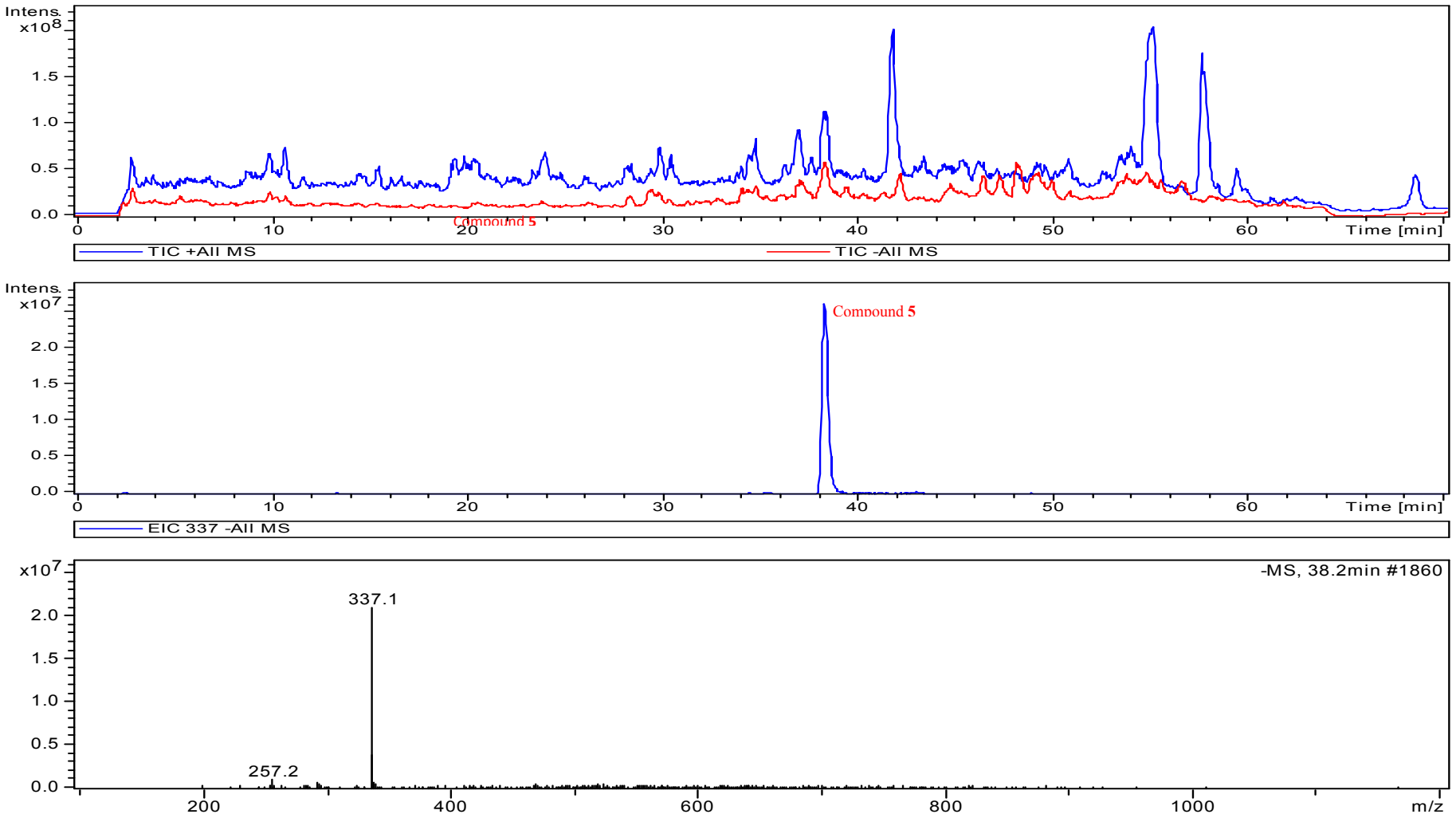


Figure S57 Base peak and extracted ion chromatogram of the methanol extract at 38.2 min (Compound **5**: *m/z* = 337 $[M - H]^-$).