

## Supporting Information for

### **Pierreiones A – D, Solid Tumor Selective Pyranoisoflavones and Other Cytotoxic Constituents**

#### ***from *Antheroporum pierrei****

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**Figure S1.**  $^1\text{H}$  NMR Spectrum (500 MHz) of Pierreione A (**1**) in  $\text{CDCl}_3$

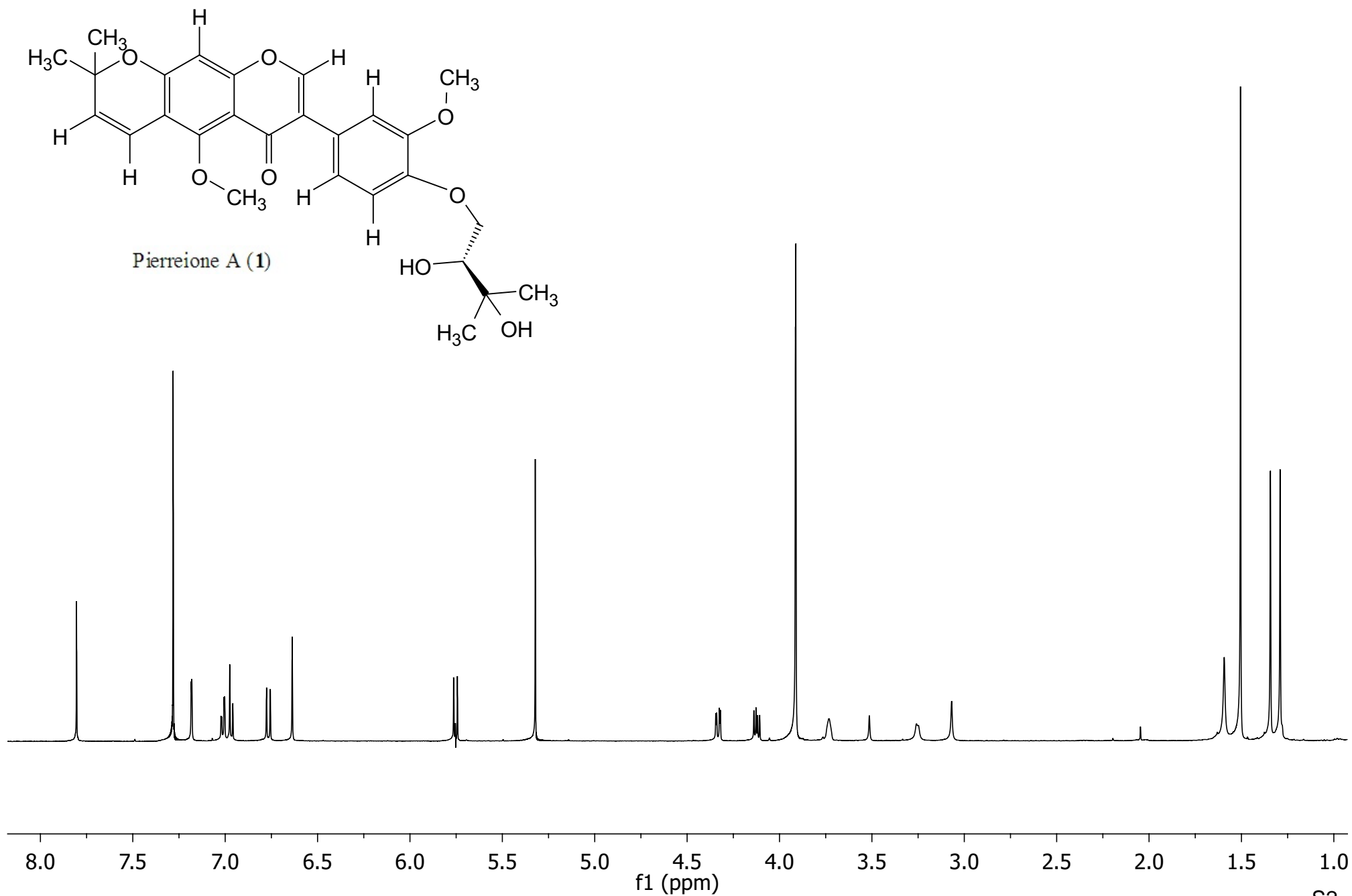


Figure S2.  $^{13}\text{C}$  NMR Spectrum (125 MHz) of Pierreione A (1) in  $\text{CDCl}_3$

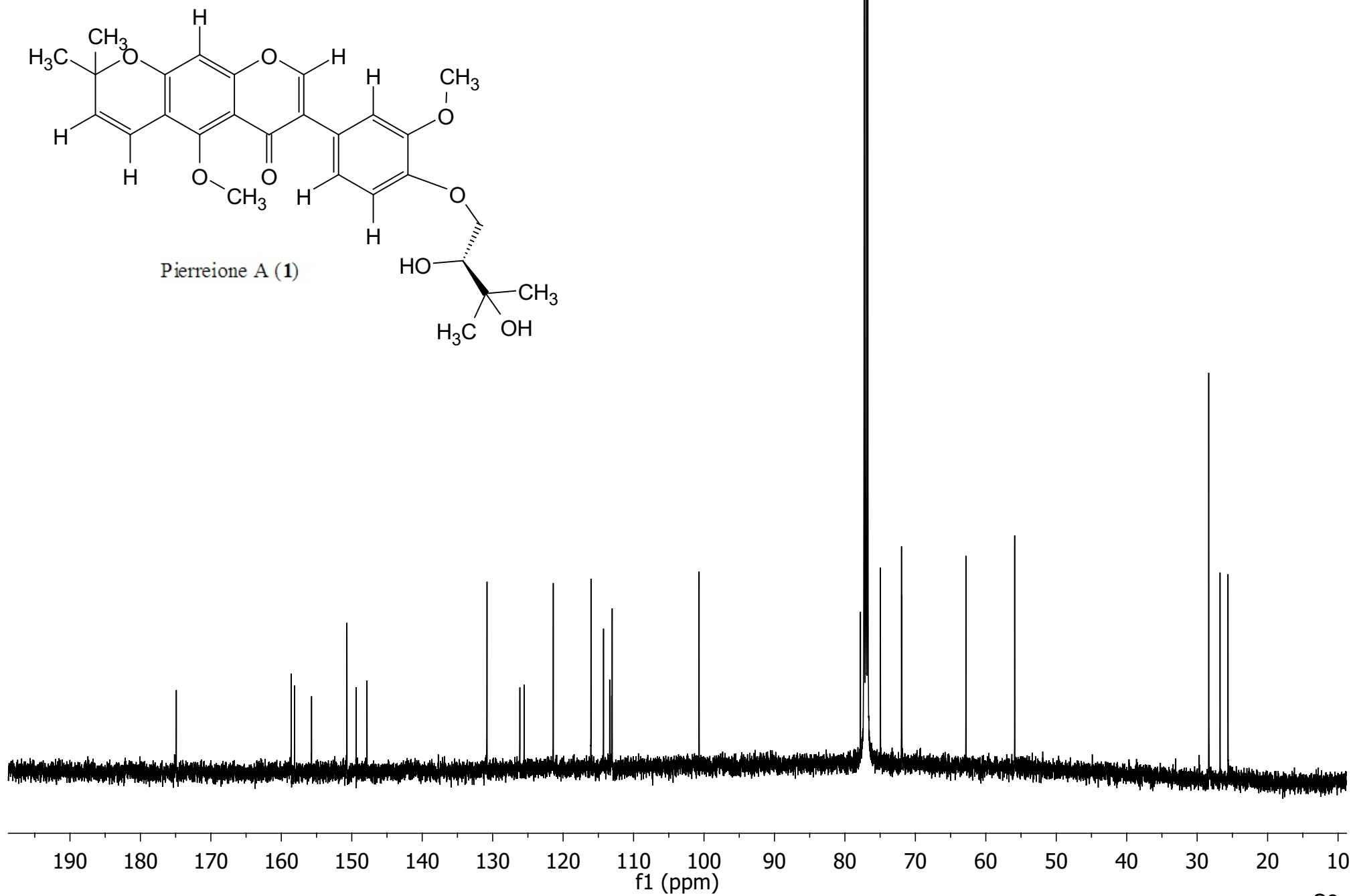


Figure S3. COSY Spectra (500 MHz) of Pierreione A (1) in CDCl<sub>3</sub>

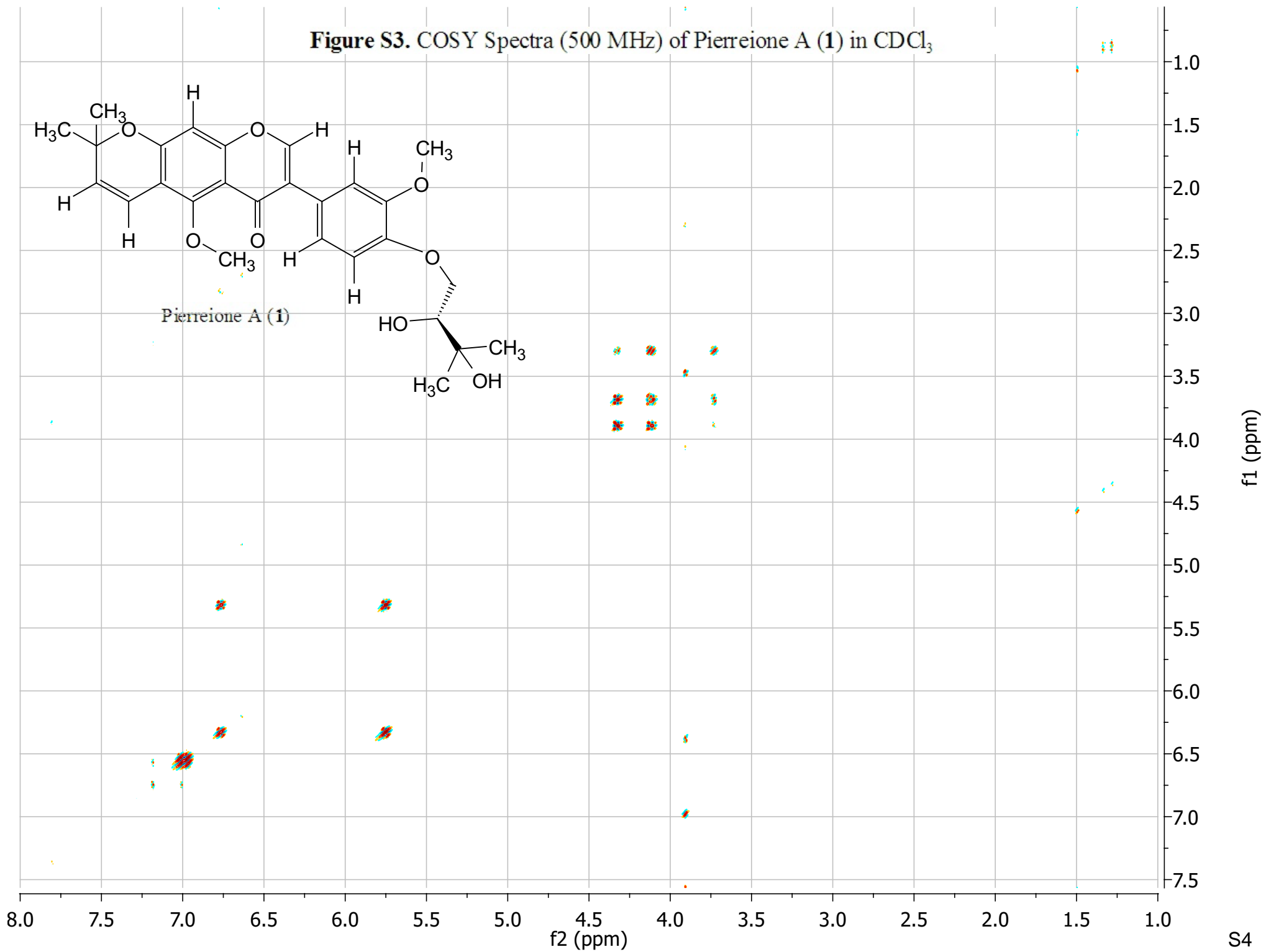


Figure S4. HSQC Spectra (500 MHz) of Pierreione A (1) in CDCl<sub>3</sub>

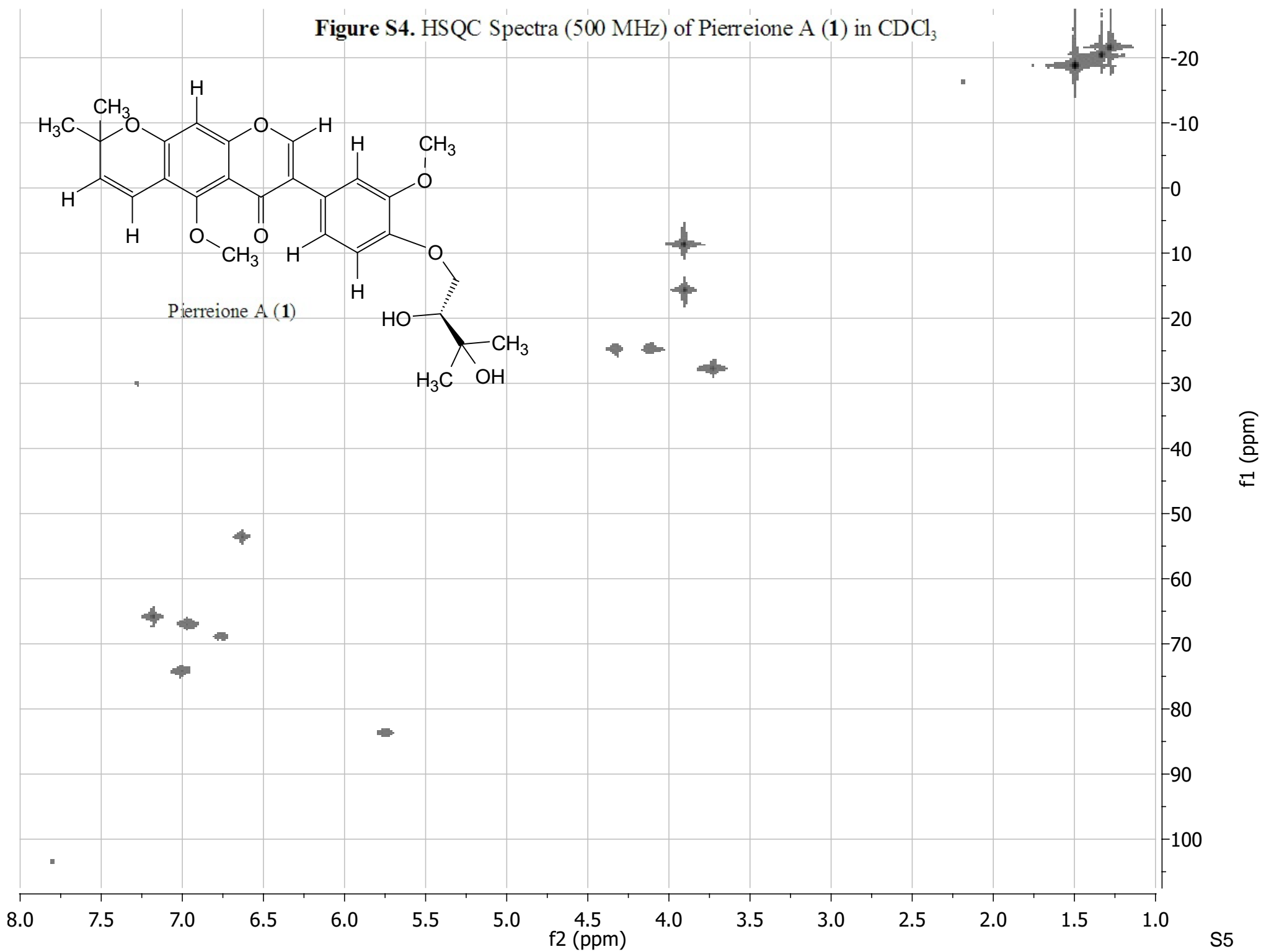
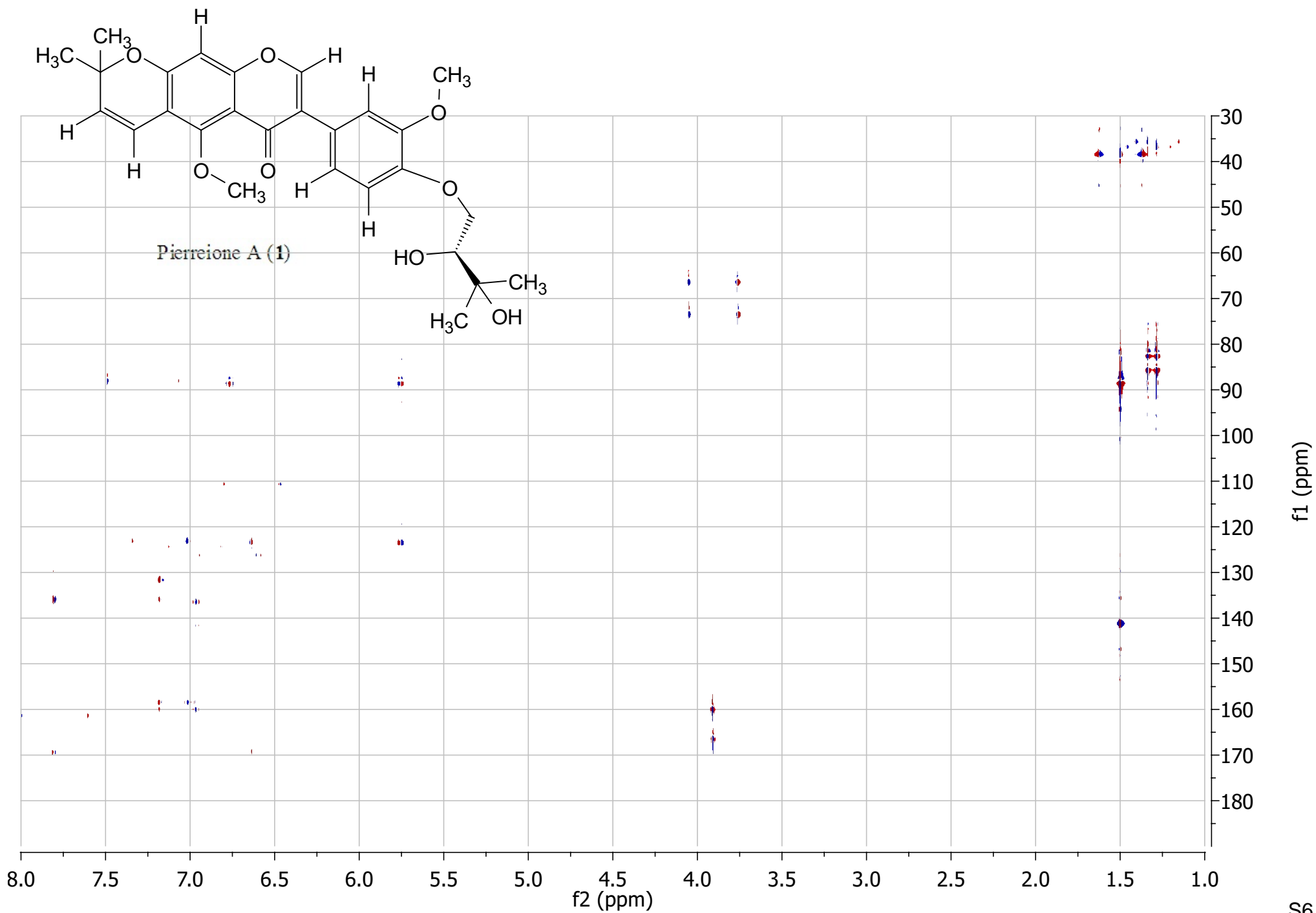
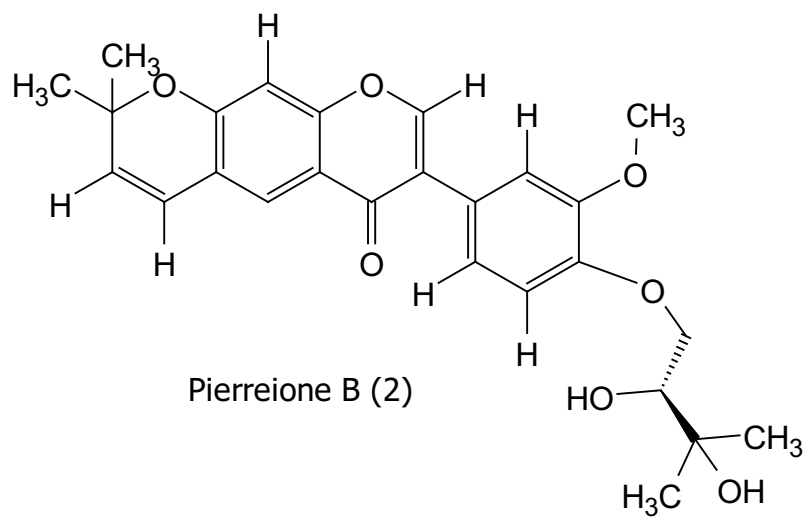


Figure S5. HMBC Spectra (500 MHz) of Pierreione A (1) in CDCl<sub>3</sub>



**Figure S6.**  $^1\text{H}$  NMR Spectrum (500 MHz) of Pierreione B (2) in  $\text{CDCl}_3$



Pierreione B (2)

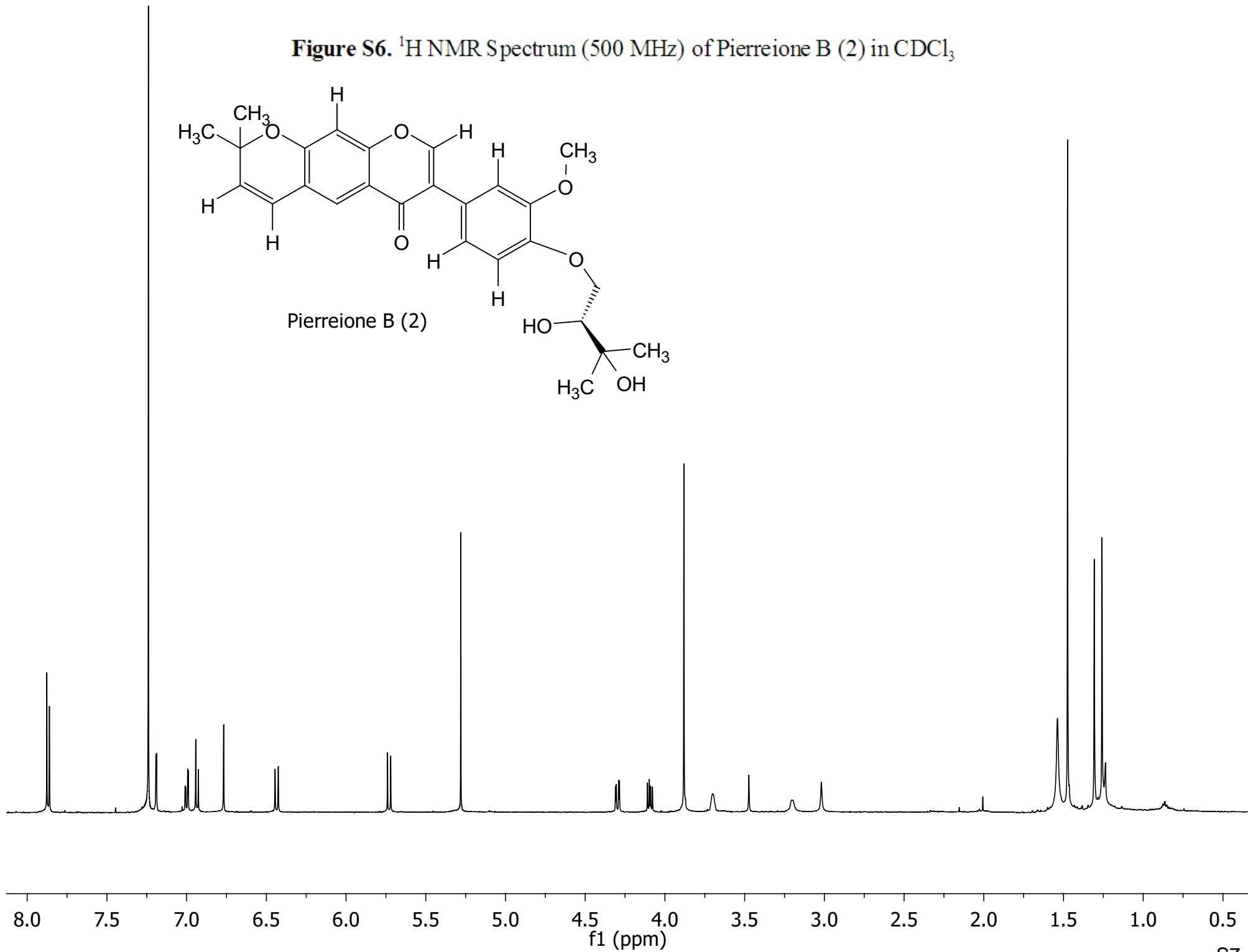




Figure S7.  $^{13}\text{C}$  NMR Spectrum (125 MHz) of Pierreione B (2) in  $\text{CDCl}_3$

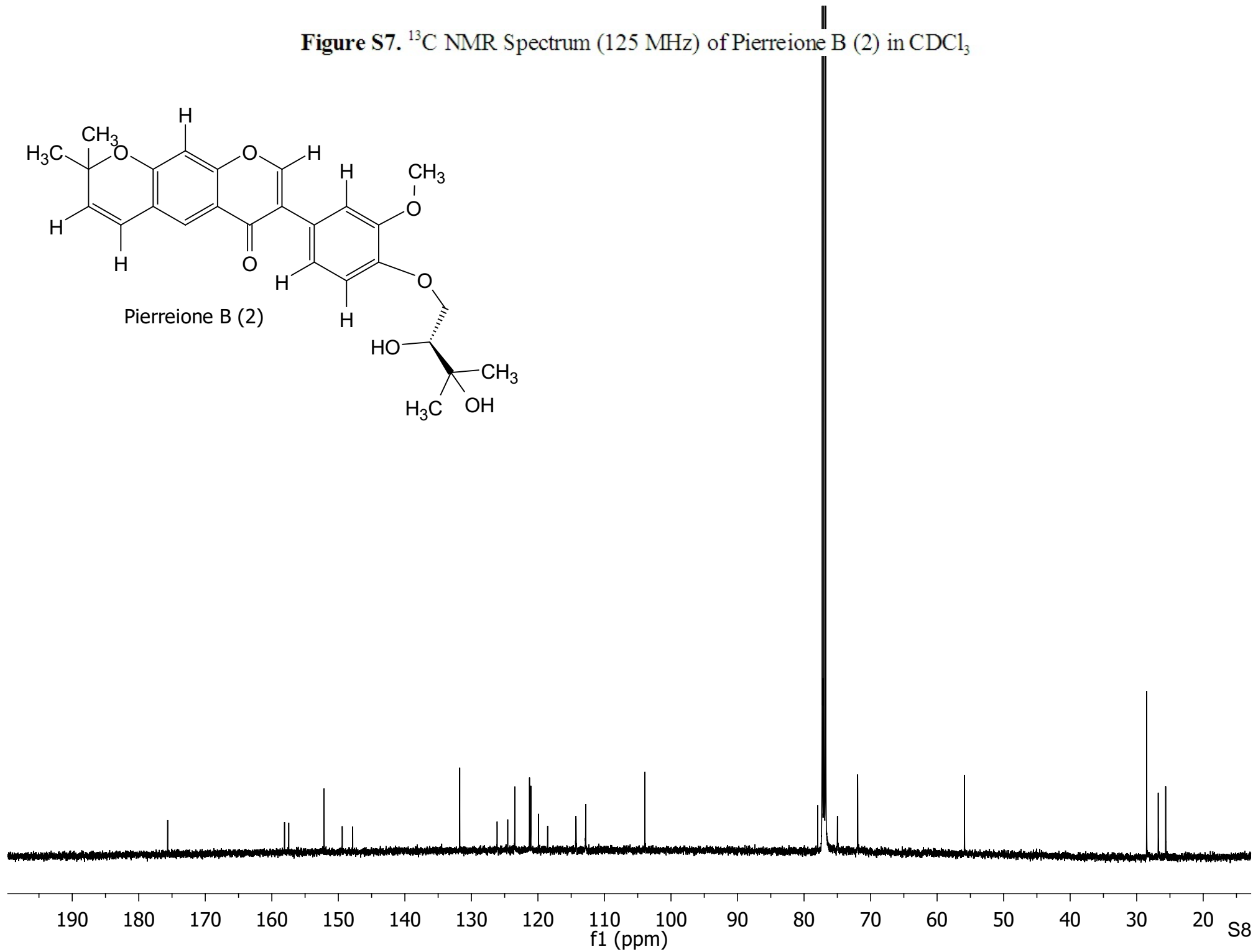
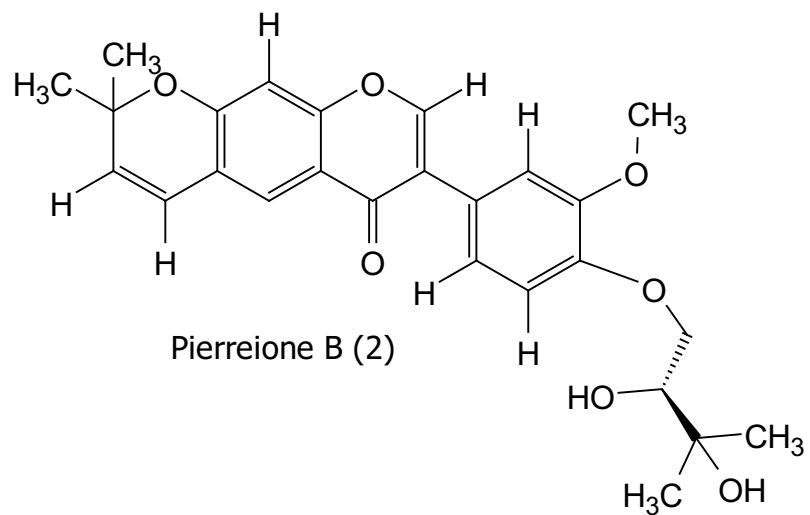
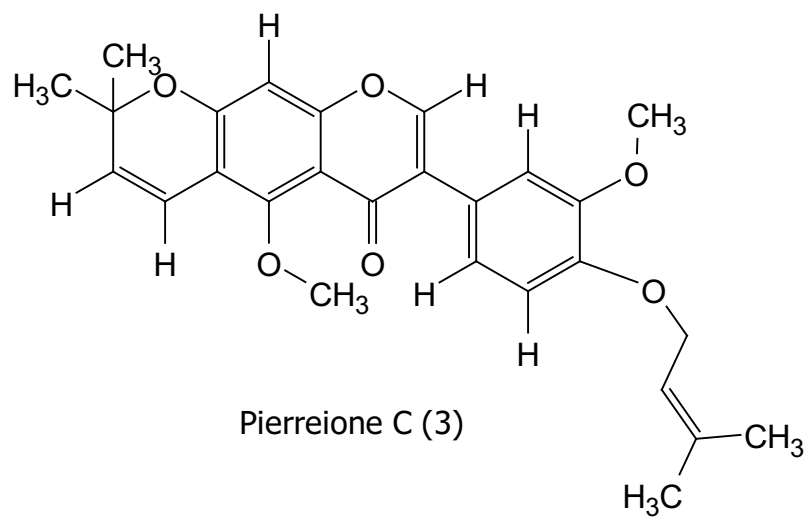


Figure S8.  $^1\text{H}$  NMR Spectrum (400 MHz) of Pierreione C (3) in  $\text{CDCl}_3$



Pierreione C (3)

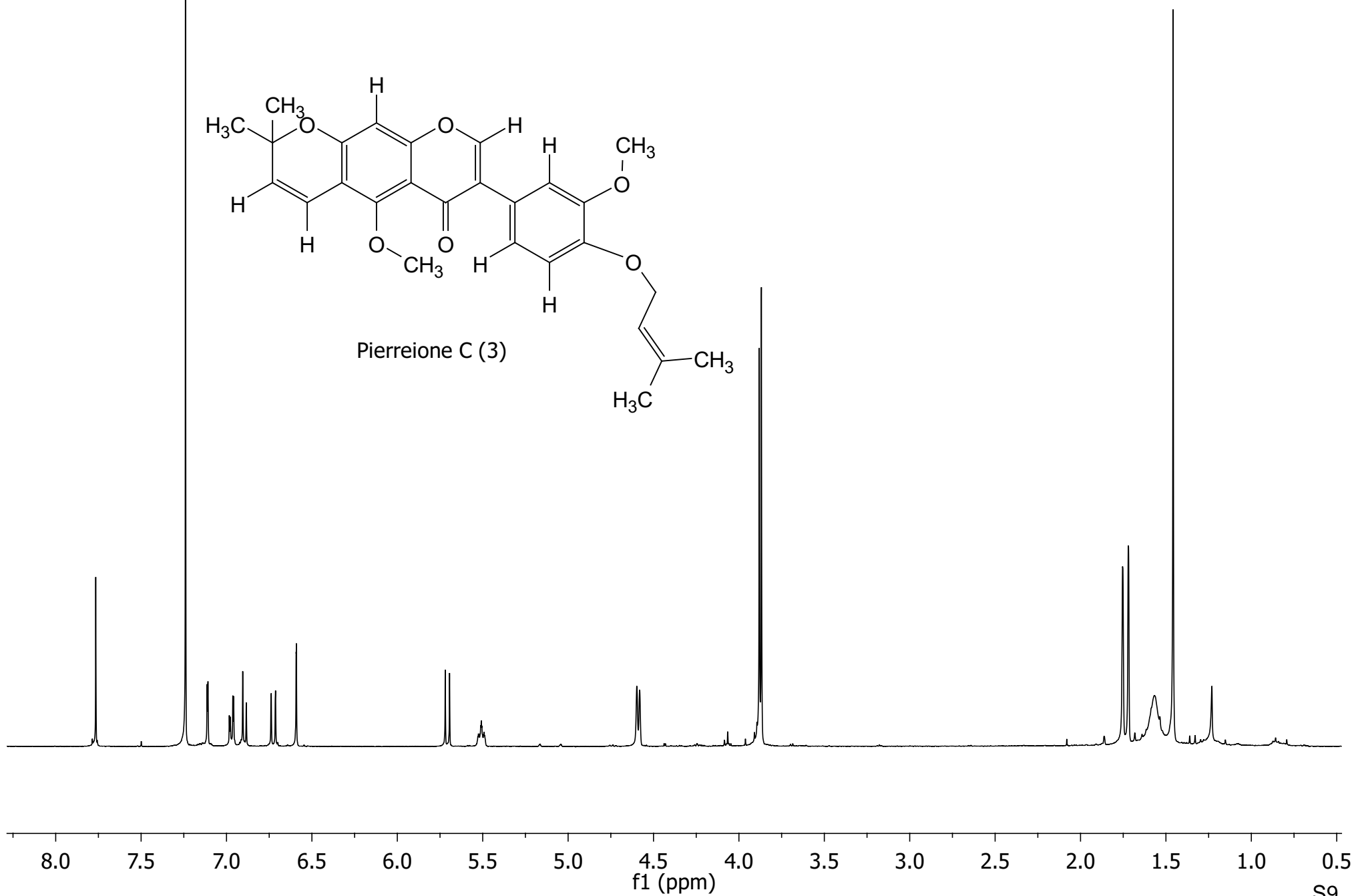


Figure S9.  $^{13}\text{C}$  NMR Spectrum (100 MHz) of Pierreione C (3) in  $\text{CDCl}_3$

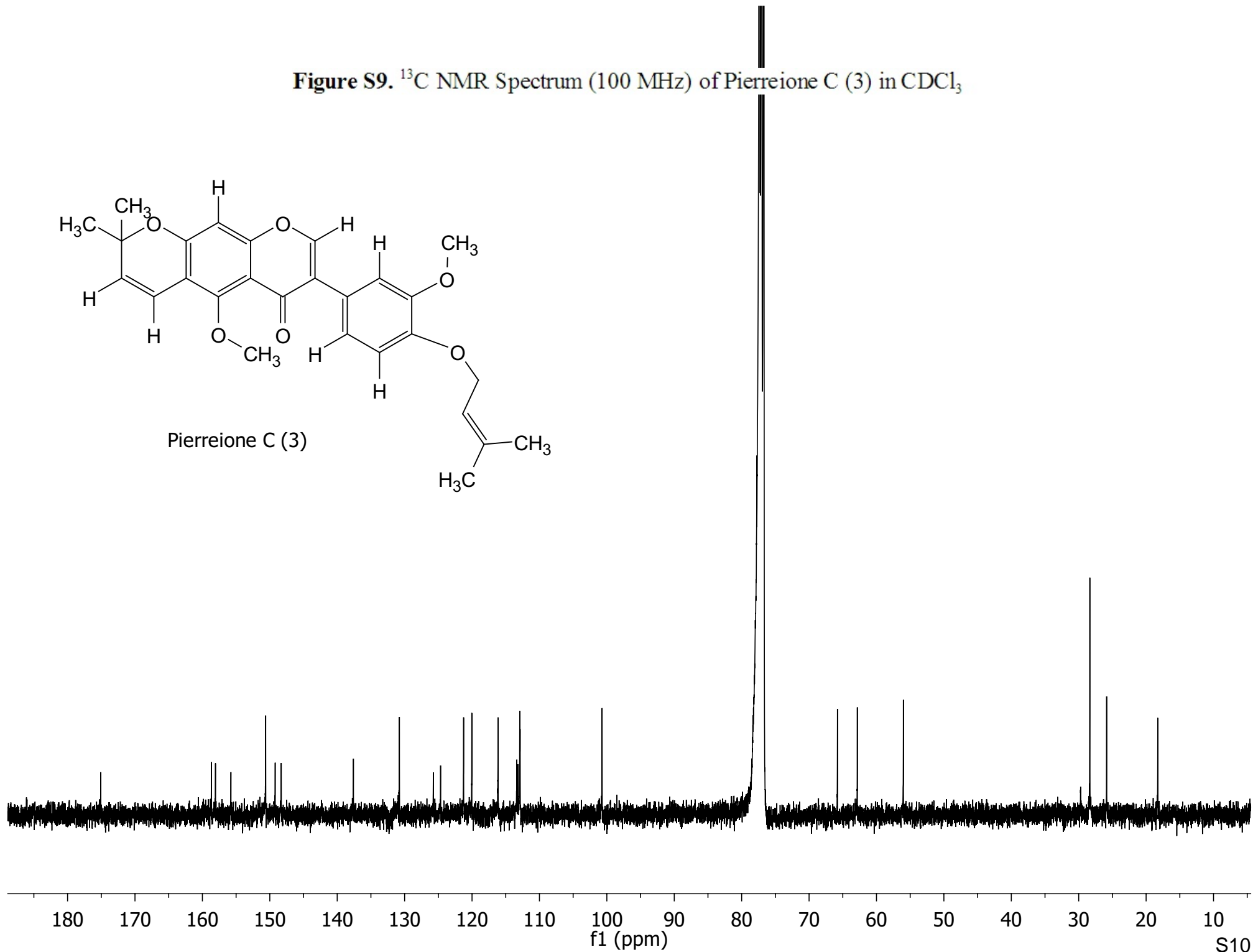
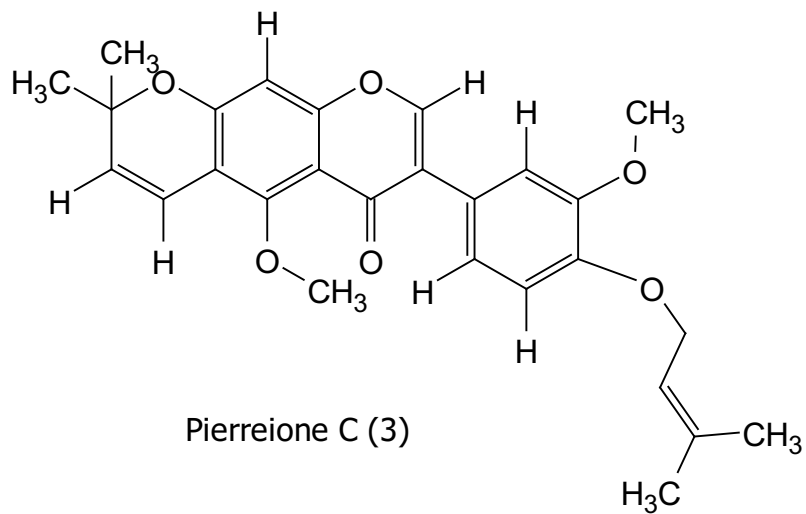
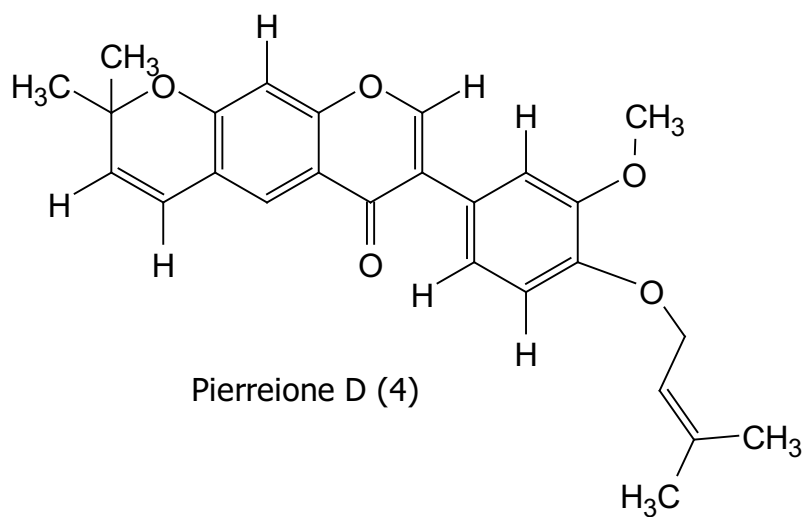
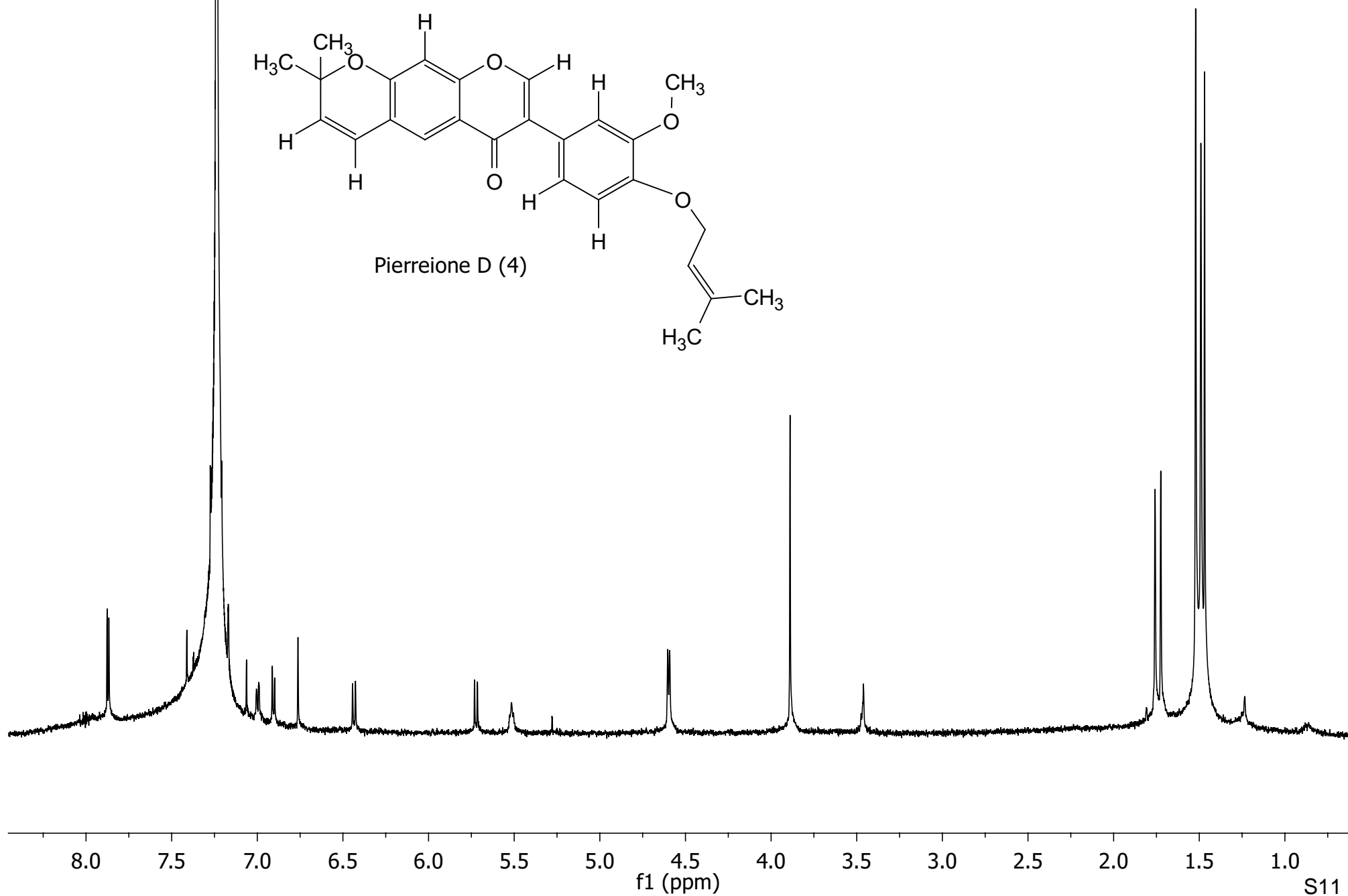


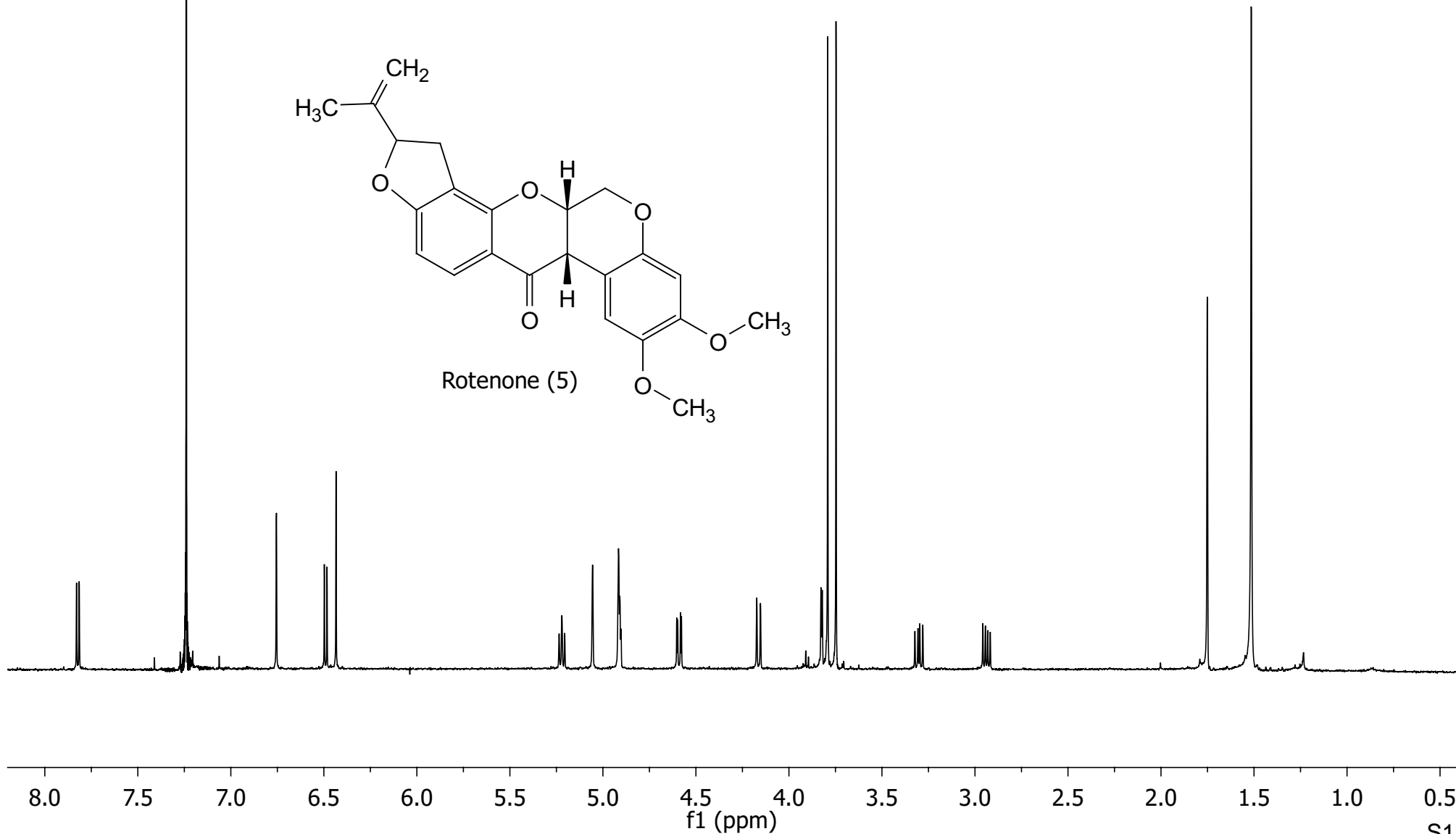
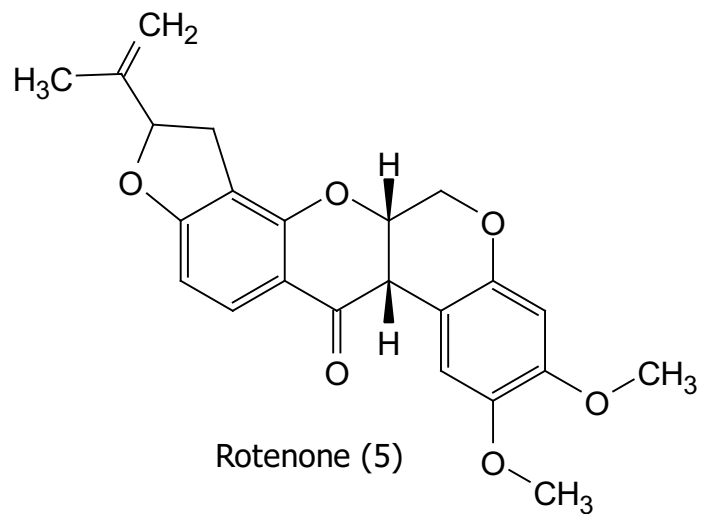
Figure S10.  $^1\text{H}$  NMR Spectrum (400 MHz) of Pierreione D (4) in  $\text{CDCl}_3$



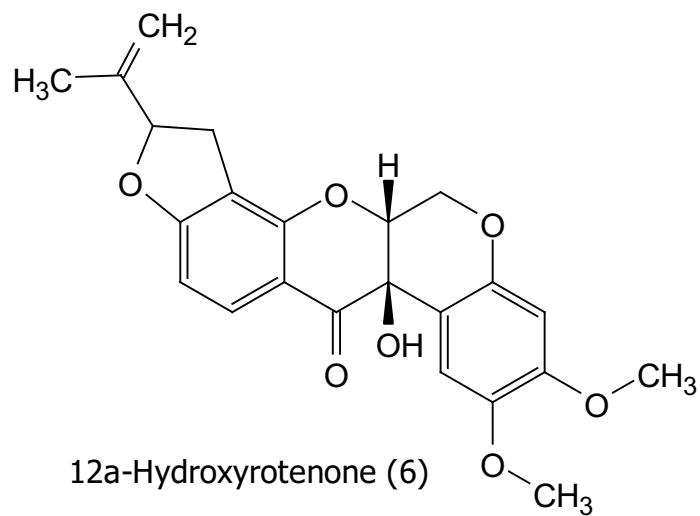
Pierreione D (4)



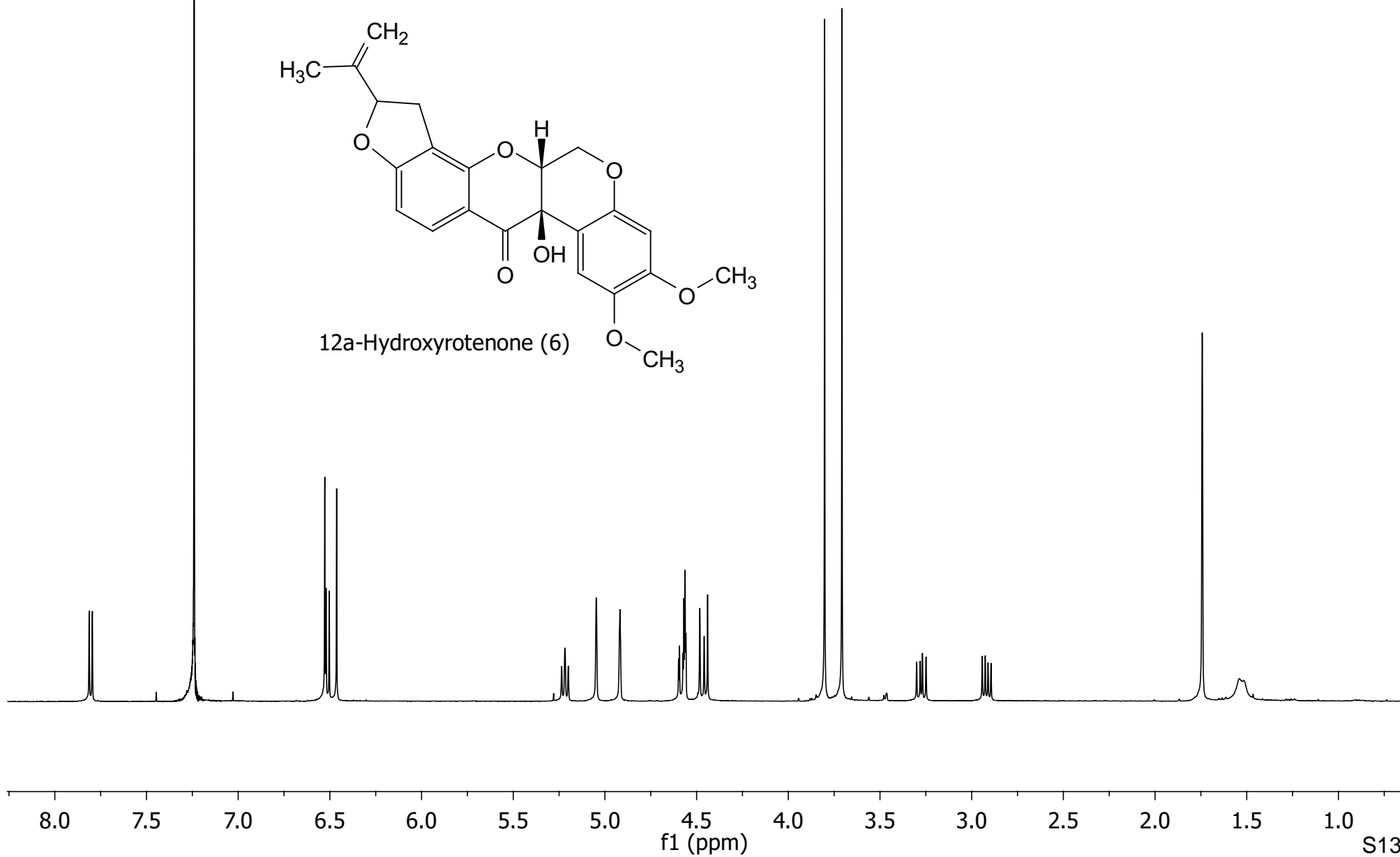
**Figure S11.**  $^1\text{H}$  NMR Spectrum (600 MHz) of Rotenone (5) in  $\text{CDCl}_3$



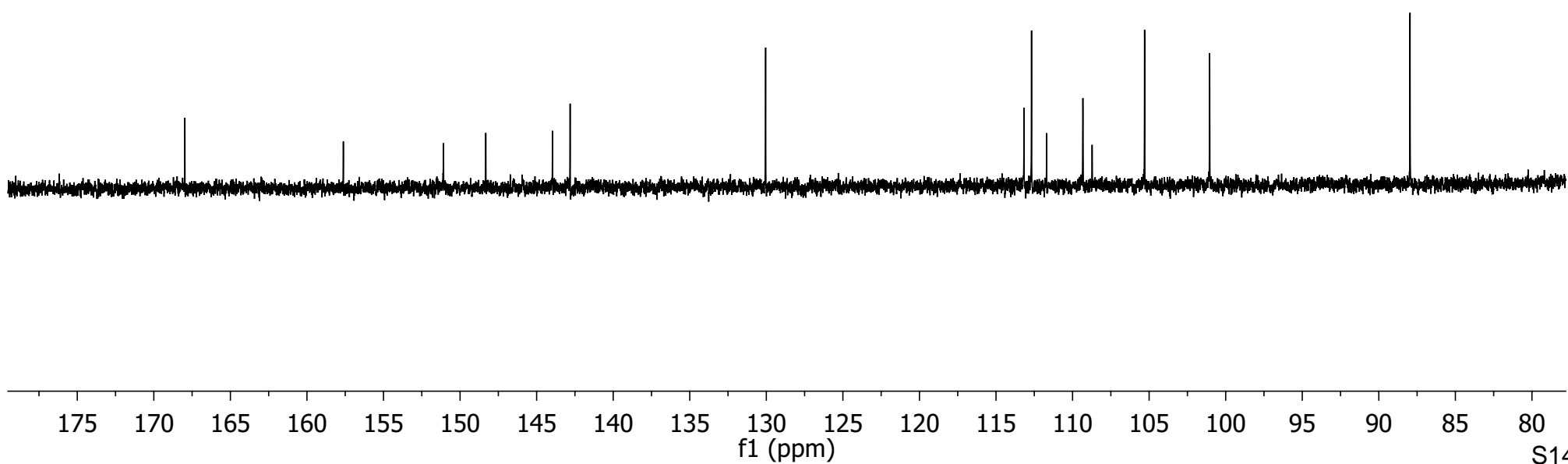
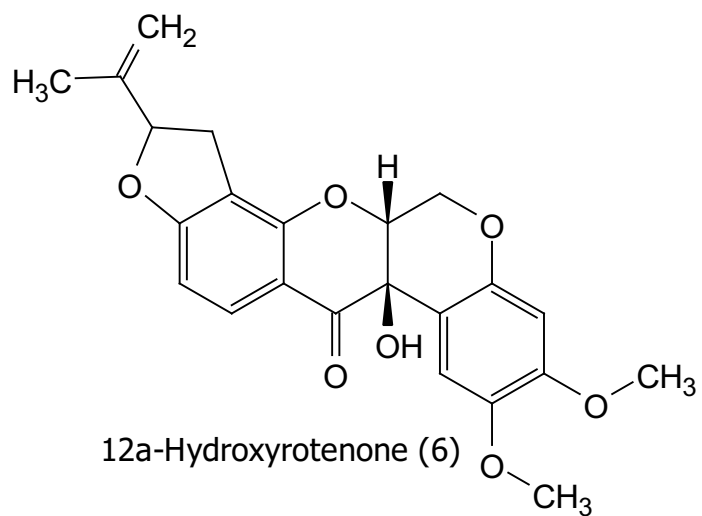
**Figure S12.**  $^1\text{H}$  NMR Spectrum (500 MHz) of 12a-Hydroxyrotenone (6) in  $\text{CDCl}_3$



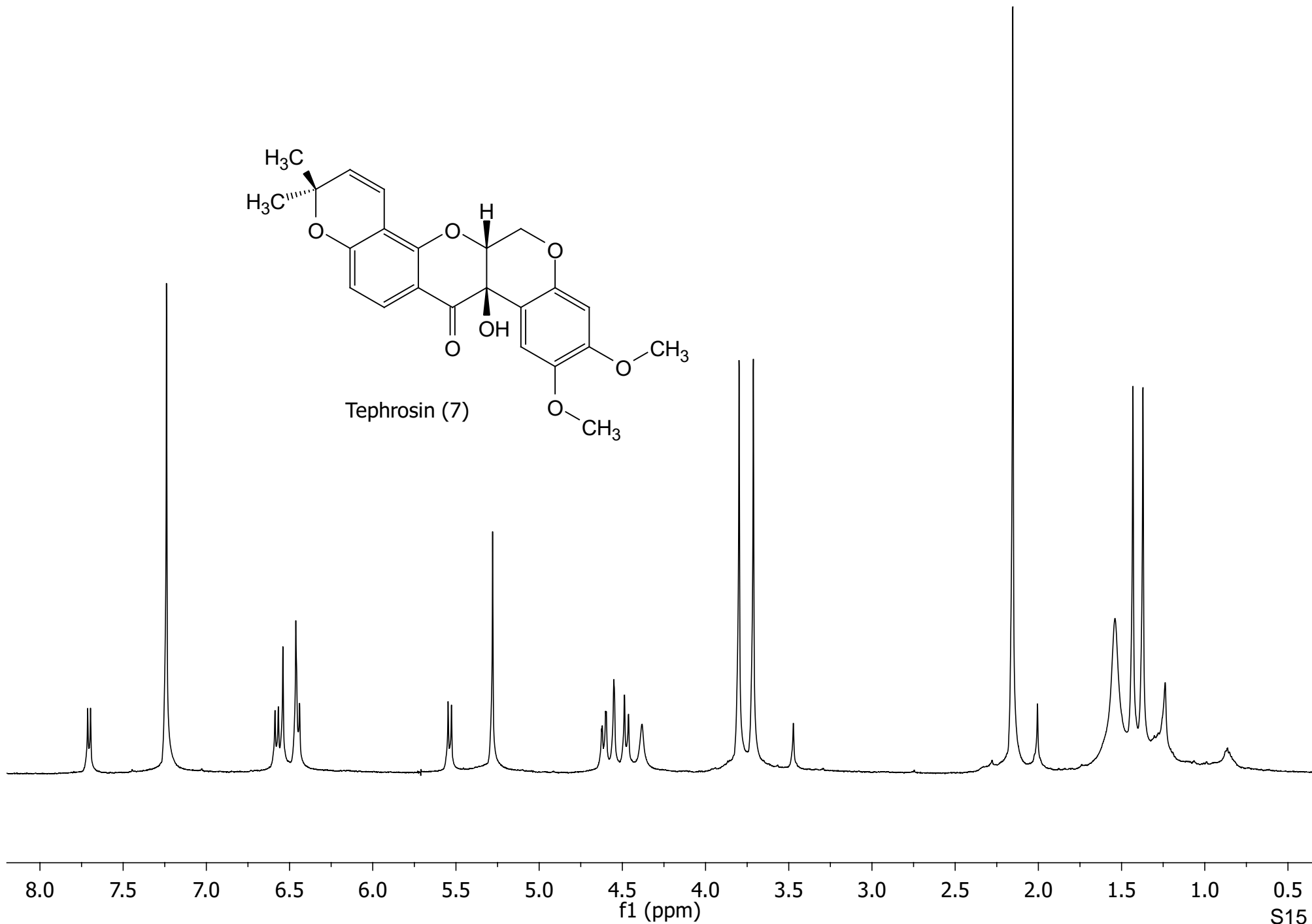
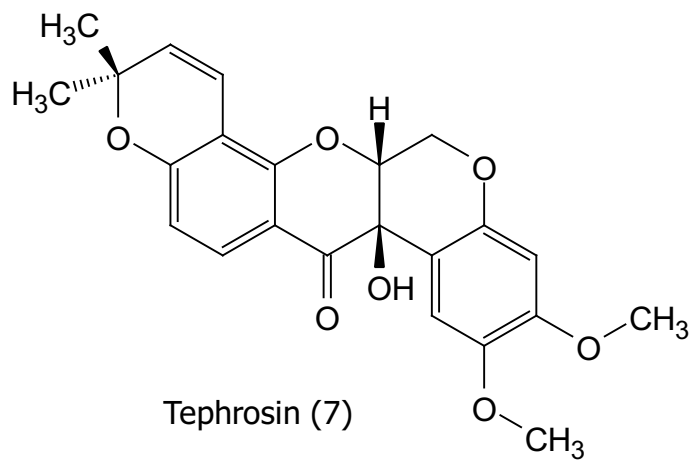
12a-Hydroxyrotenone (6)



**Figure S13.**  $^{13}\text{C}$  NMR Spectrum (125 MHz) of 12a-Hydroxyrotenone (6) in  $\text{CDCl}_3$

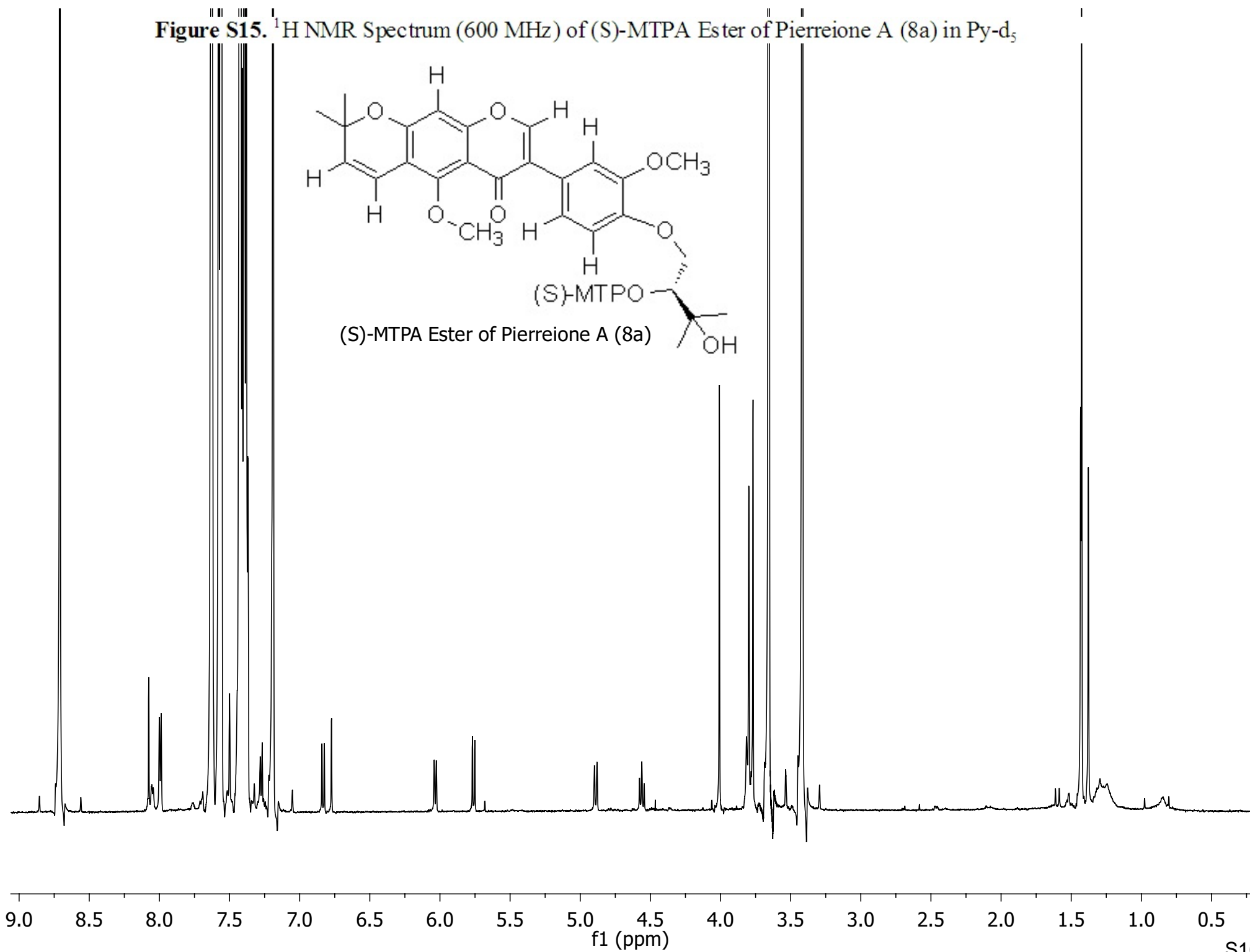
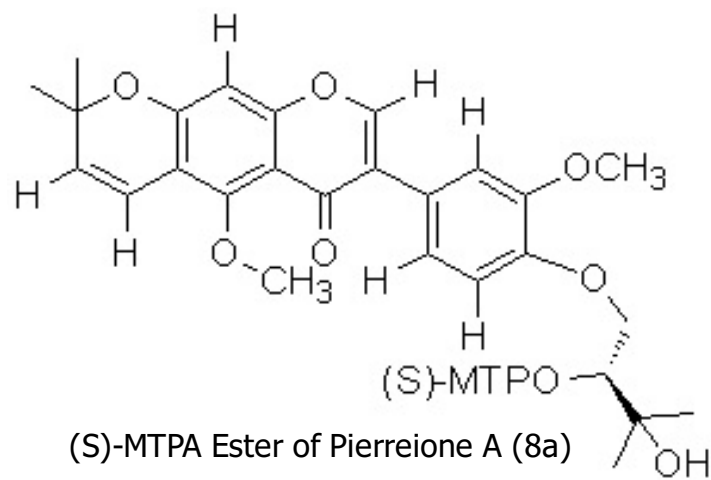


**Figure S14.**  $^1\text{H}$  NMR Spectrum (500 MHz) of Tephrosin (7) in  $\text{CDCl}_3$

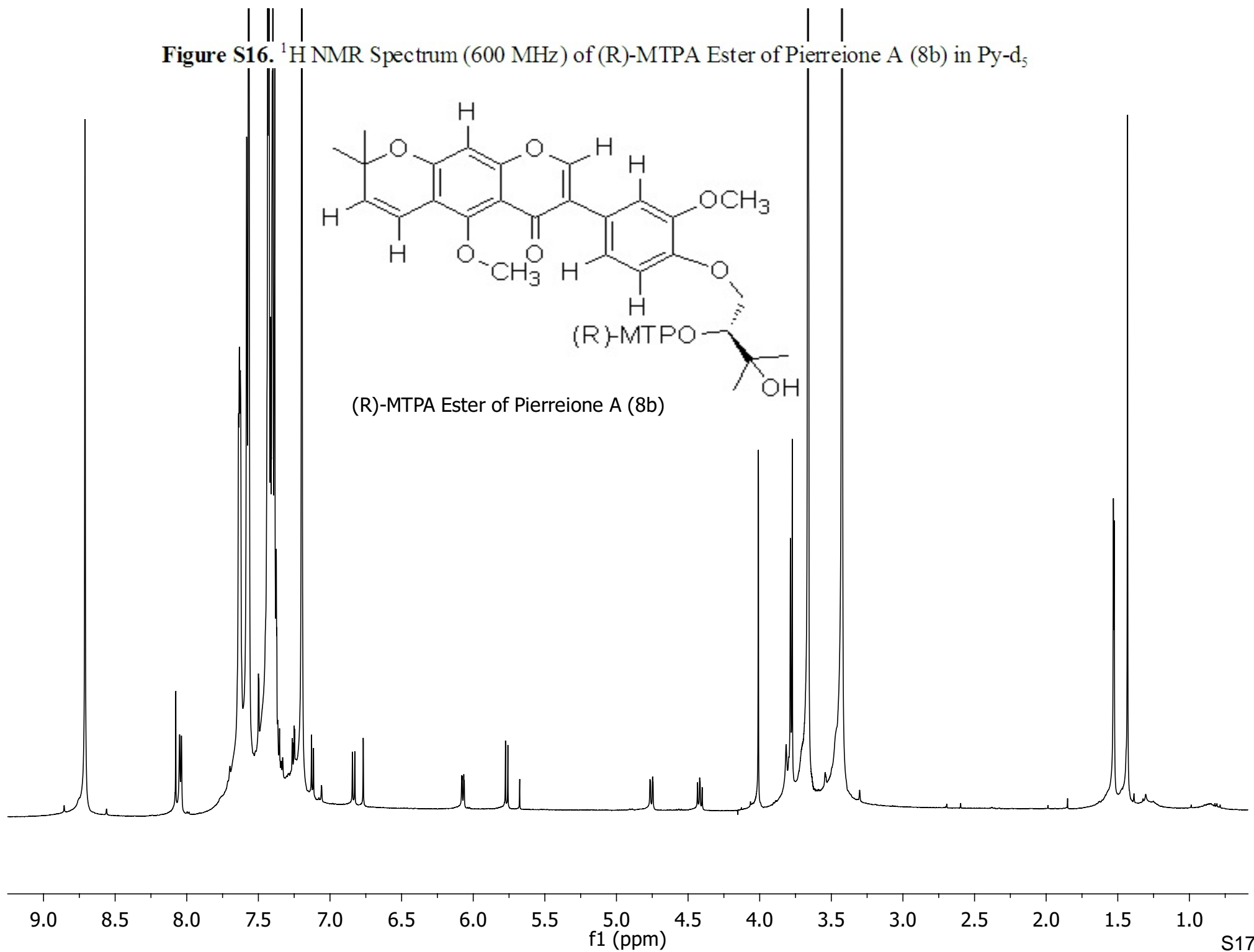


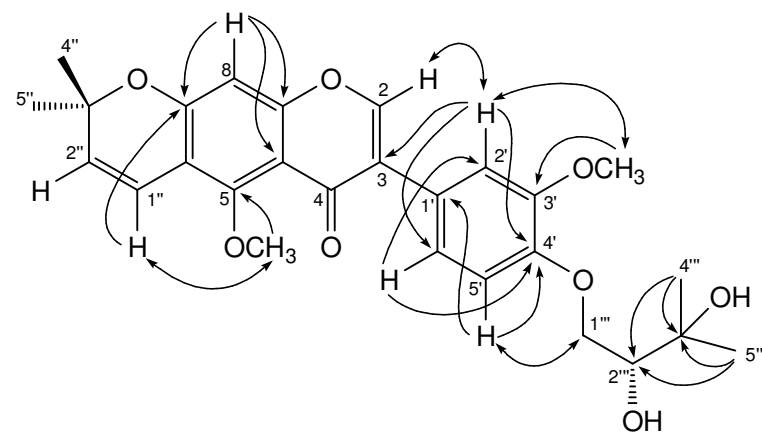


**Figure S15.**  $^1\text{H}$  NMR Spectrum (600 MHz) of (S)-MTPA Ester of Pierreione A (8a) in  $\text{Py-d}_5$

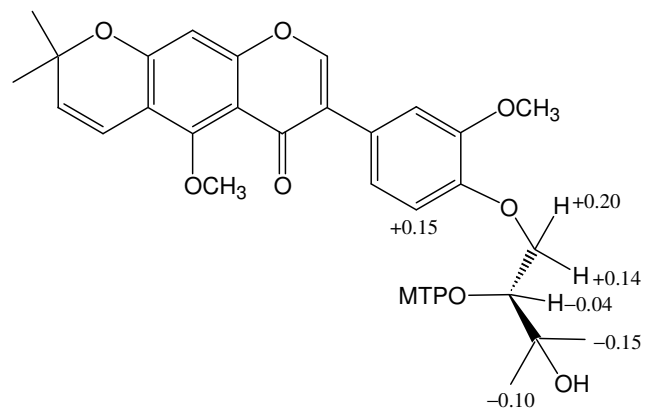


**Figure S16.**  $^1\text{H}$  NMR Spectrum (600 MHz) of (R)-MTPA Ester of Pierreione A (8b) in  $\text{Py-d}_5$





**Figure S17.** Key HMBC (H→C) and NOE (H↔H) correlations for **1**.



**Figure S18.**  $\Delta\delta$  values [ $\Delta\delta$  (in ppm) =  $\delta_S - \delta_R$ ] obtained for (*S*)- and (*R*)-MTPA esters (**8a** and **8b**, respectively) of **1**.