

# Supporting Information

## Bioactive Polyketides from the Natural Complex of the Sea Urchin-associated Fungi *Penicillium sajarovii* KMM 4718 and *Aspergillus protuberus* KMM 4747

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Figure S1. HRESIMS for 1

Figure S2. <sup>1</sup>H NMR spectrum of 1 measured at 500 MHz in acetone-d<sub>6</sub>

Figure S3. <sup>13</sup>C NMR spectrum of 1 measured at 125 MHz in acetone-d<sub>6</sub>

Figure S4. DEPT-135 spectrum of 1 measured at 125 MHz in acetone-d<sub>6</sub>

Figure S5. HSQC spectrum of 1 measured in acetone-d<sub>6</sub>

Figure S6. COSY spectrum of 1 measured in acetone-d<sub>6</sub>

Figure S7. HMBC spectrum of 1 measured in acetone-d<sub>6</sub>

Figure S8. HRESIMS for 2

Figure S9. <sup>1</sup>H NMR spectrum of 2 measured at 500 MHz in acetone-d<sub>6</sub>

Figure S10. <sup>13</sup>C NMR spectrum of 2 measured at 125 MHz in acetone-d<sub>6</sub>

Figure S11. DEPT-135 spectrum of 2 measured at 125 MHz in acetone-d<sub>6</sub>

Figure S12. HSQC spectrum of 2 measured in acetone-d<sub>6</sub>

Figure S13. COSY spectrum of 2 measured in acetone-d<sub>6</sub>

Figure S14. HMBC spectrum of 2 measured in acetone-d<sub>6</sub>

Figure S15. HRESIMS for 3

Figure S16. <sup>1</sup>H NMR spectrum of 3 measured at 500 MHz in acetone-d<sub>6</sub>

Figure S17. <sup>13</sup>C NMR spectrum of 3 measured at 125 MHz in acetone-d<sub>6</sub>

Figure S18. HRESIMS for 4

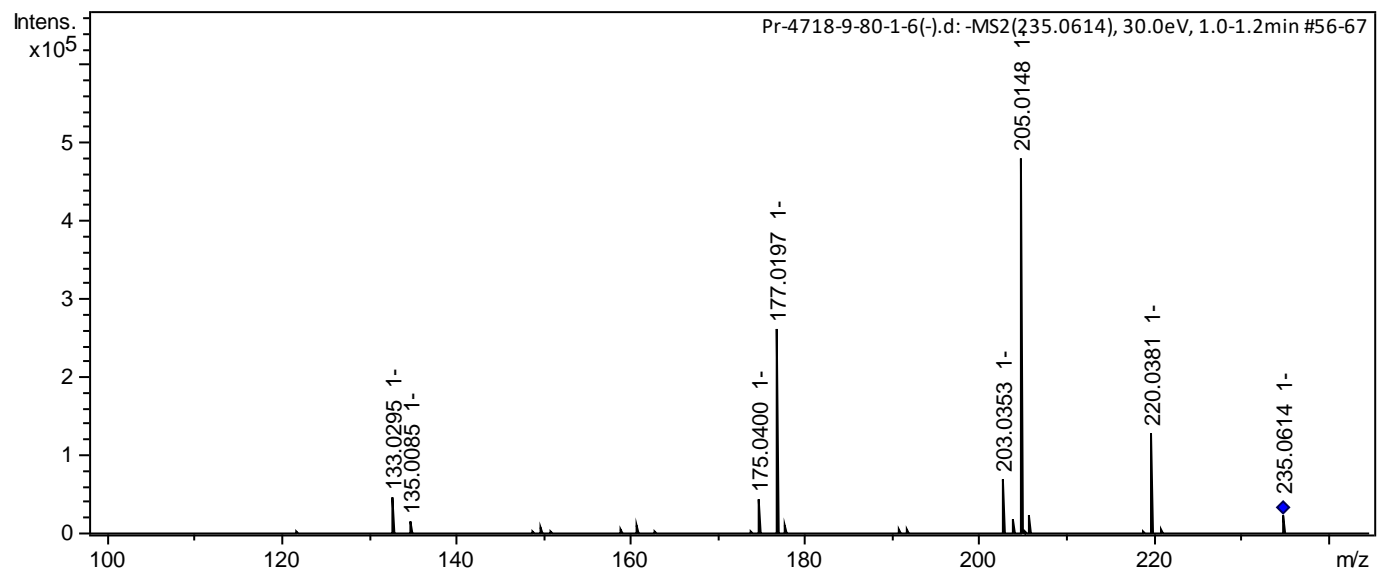
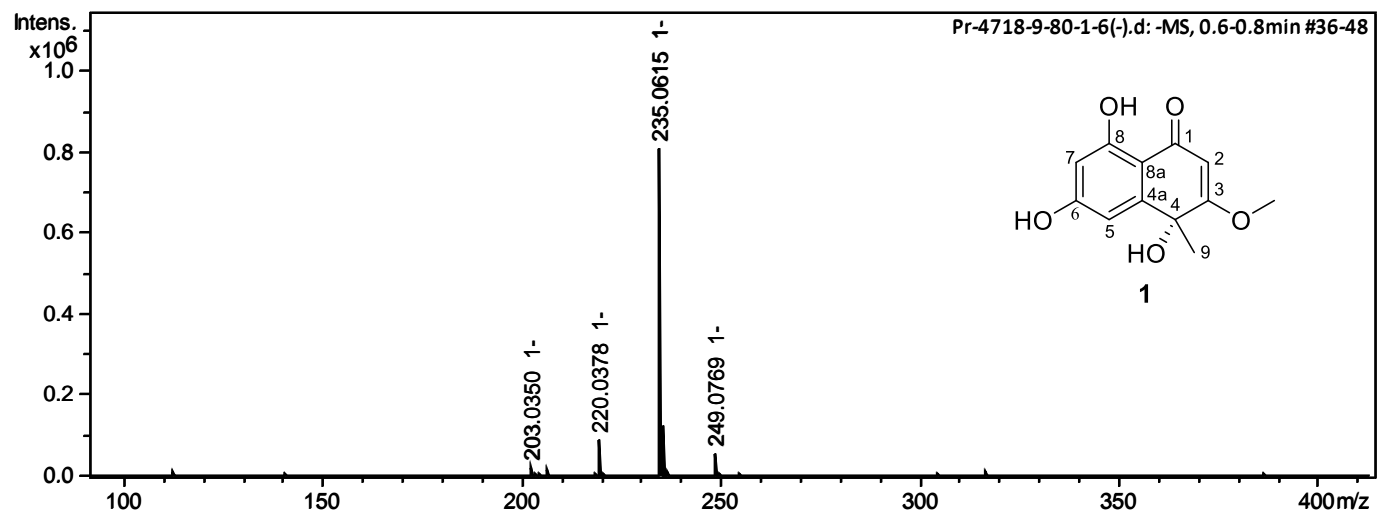
Figure S19. <sup>1</sup>H NMR spectrum of 4 measured at 500 MHz in acetone-d<sub>6</sub>

Figure S20. <sup>13</sup>C NMR spectrum of 4 measured at 125 MHz in acetone-d<sub>6</sub>

Figure S21. HRESIMS for 5

Figure S22.  $^1\text{H}$  NMR spectrum of 5 measured at 500 MHz in acetone- $\text{d}_6$   
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Figure S42. Two most stable conformations of *R*-1 calculated with B3LYP/cc-pvTz\_PCM method.  
Figure S43. The optimized structures of 4*R*-1 & (CH<sub>3</sub>OH)×2.

Figure S1. HRESIMS for 1



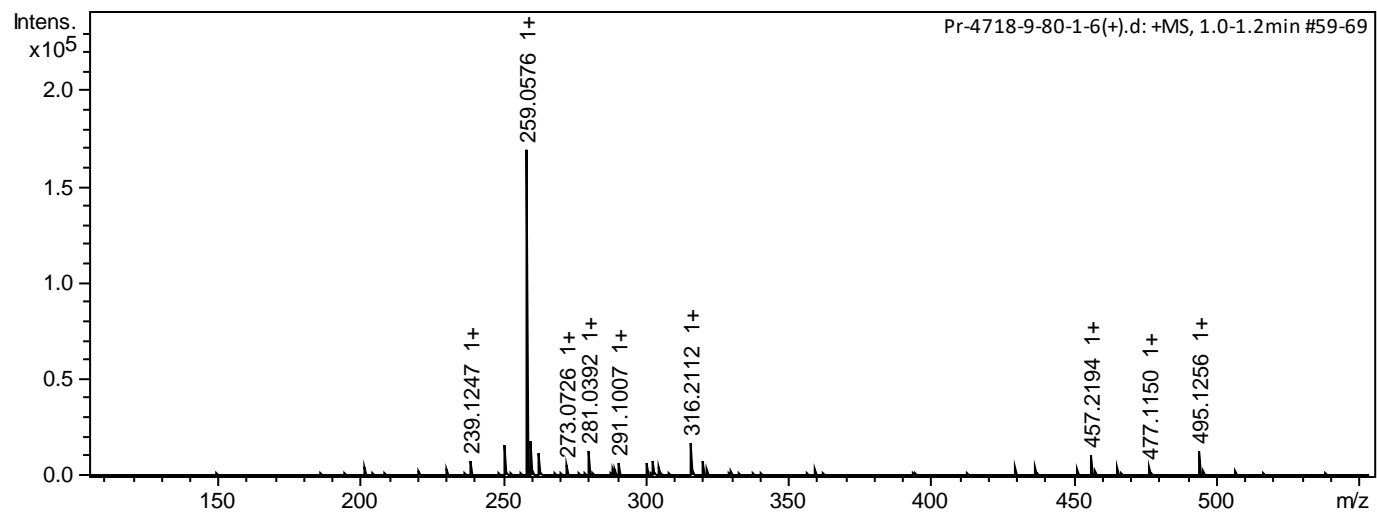


Figure S2.  $^1\text{H}$  NMR spectrum of **1** measured at 500 MHz in acetone- $d_6$

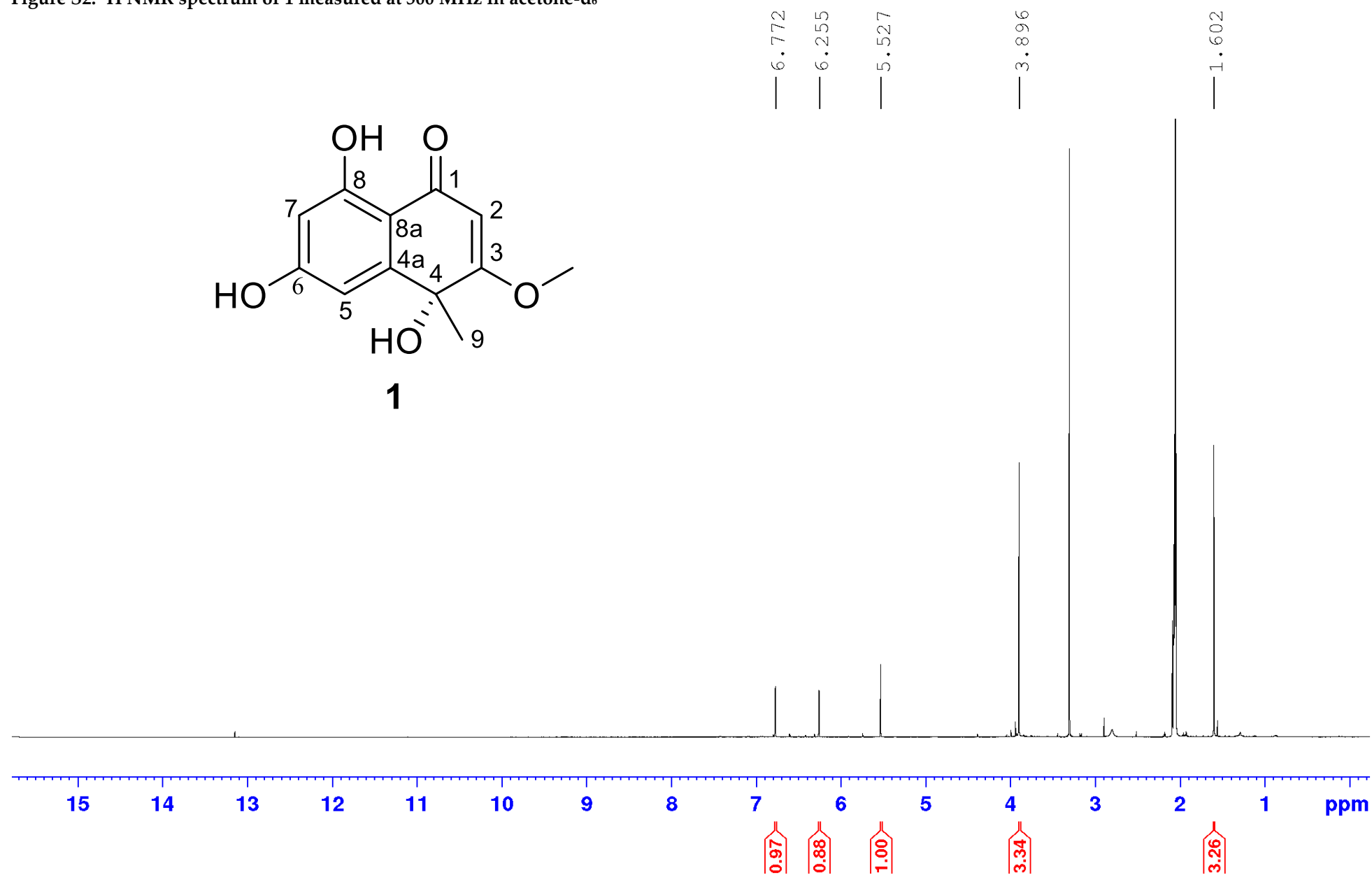


Figure S3.  $^{13}\text{C}$  NMR spectrum of **1** measured at 125 MHz in acetone- $d_6$

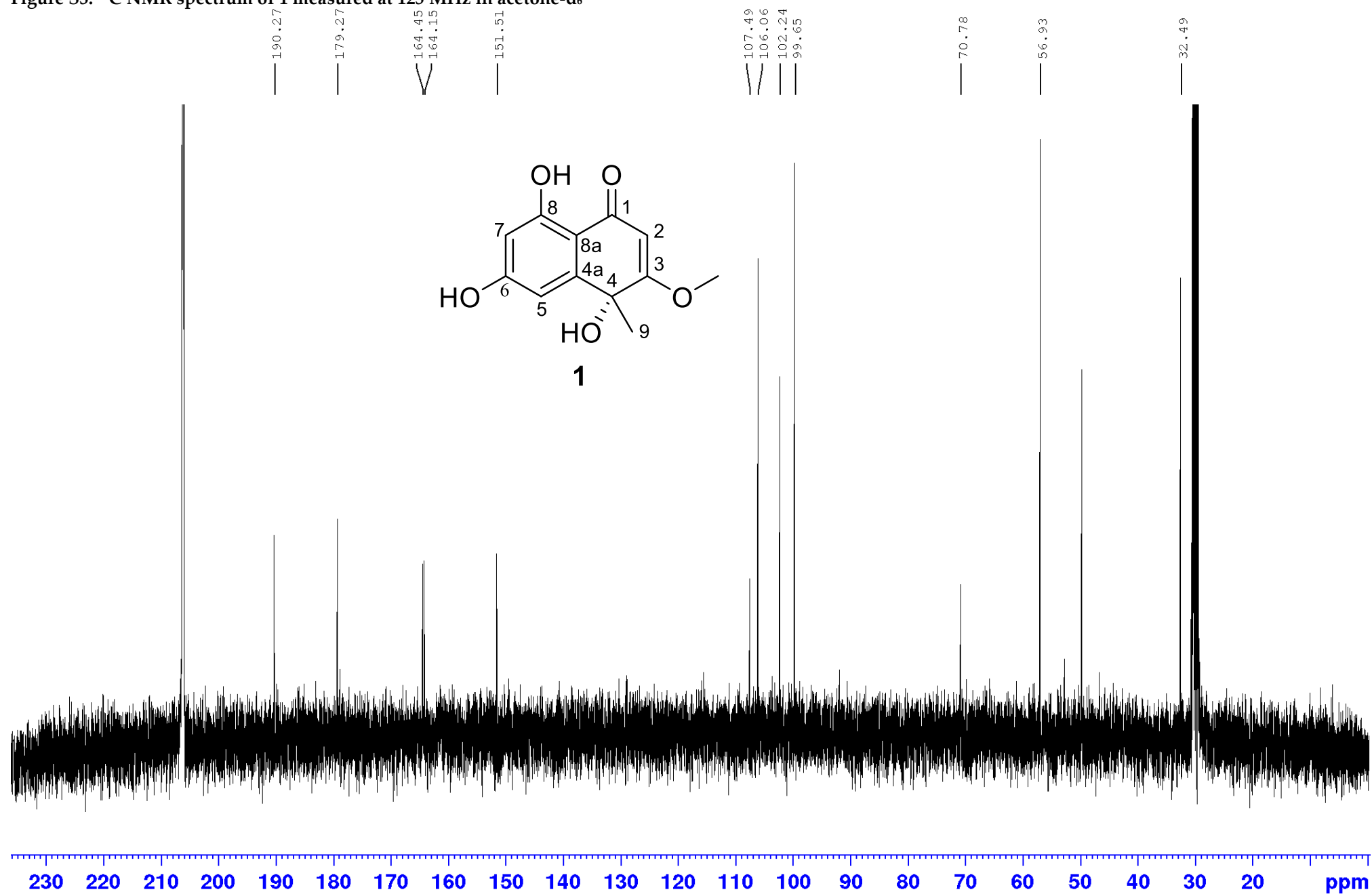


Figure S4. DEPT-135 spectrum of **1** measured at 125 MHz in acetone- $d_6$

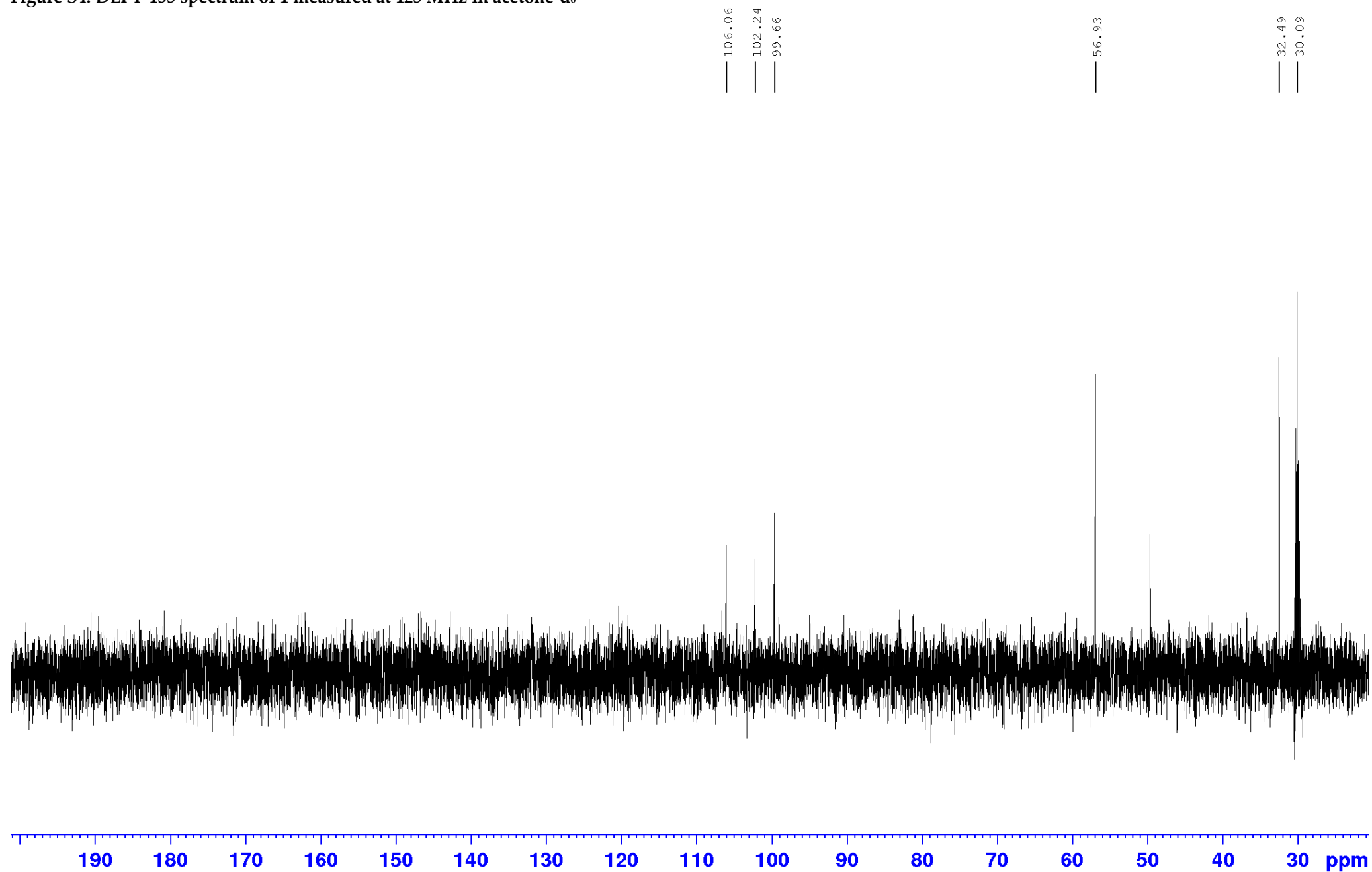


Figure S5. HSQC spectrum of 1 measured in acetone-d<sub>6</sub>

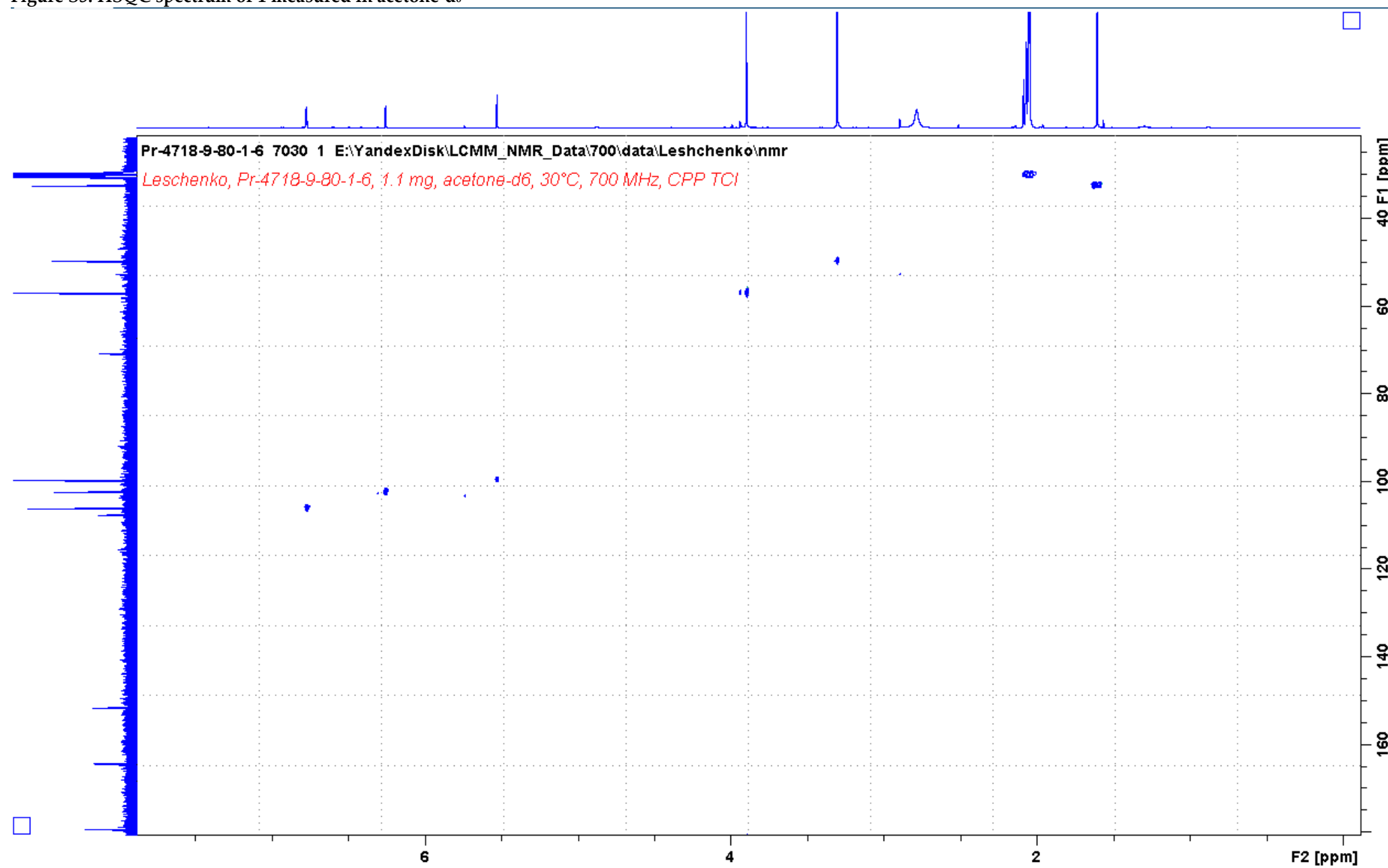




Figure S6. COSY spectrum of 1 measured in acetone-d<sub>6</sub>

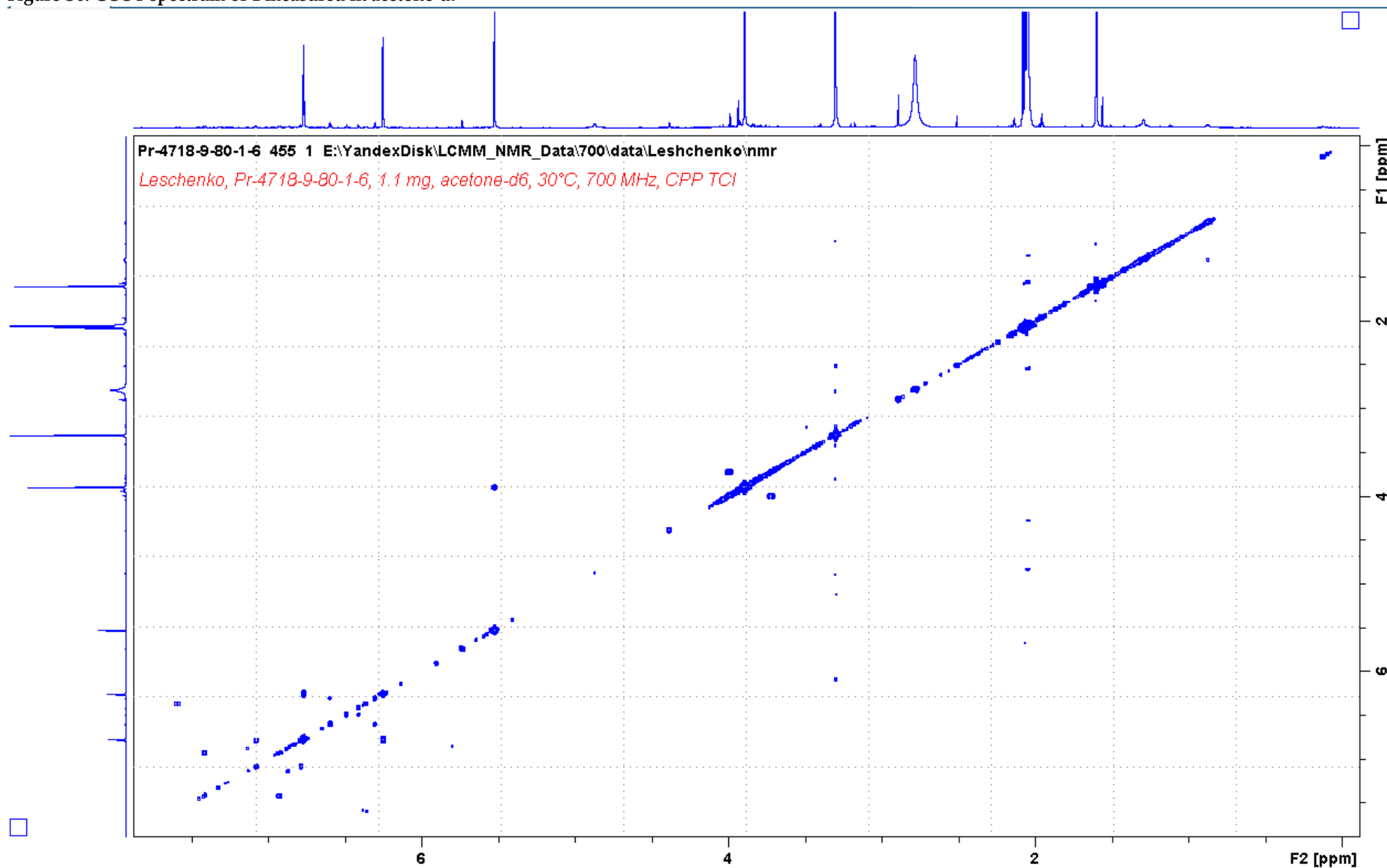


Figure S7. HMBC spectrum of 1 measured in acetone-d<sub>6</sub>

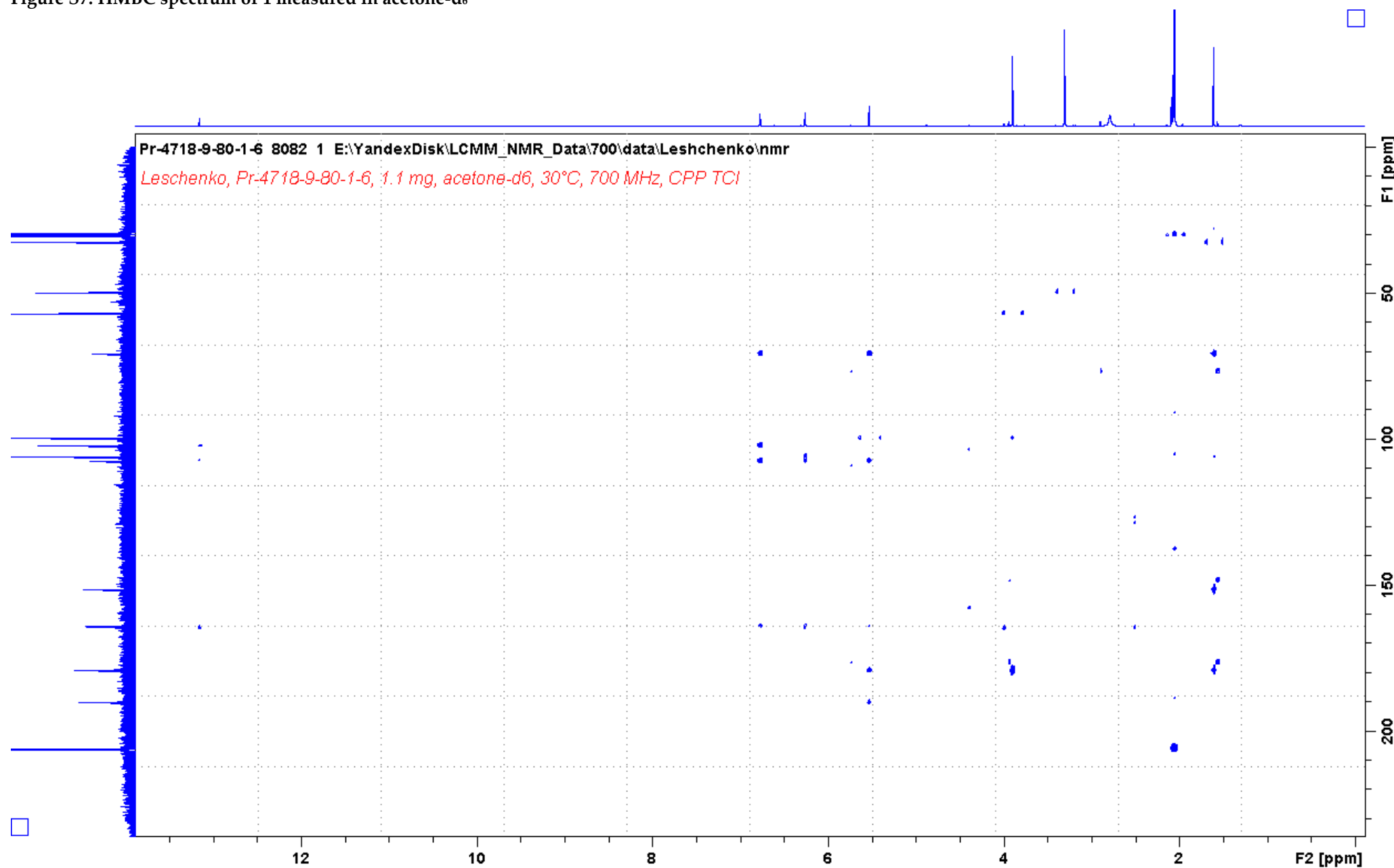
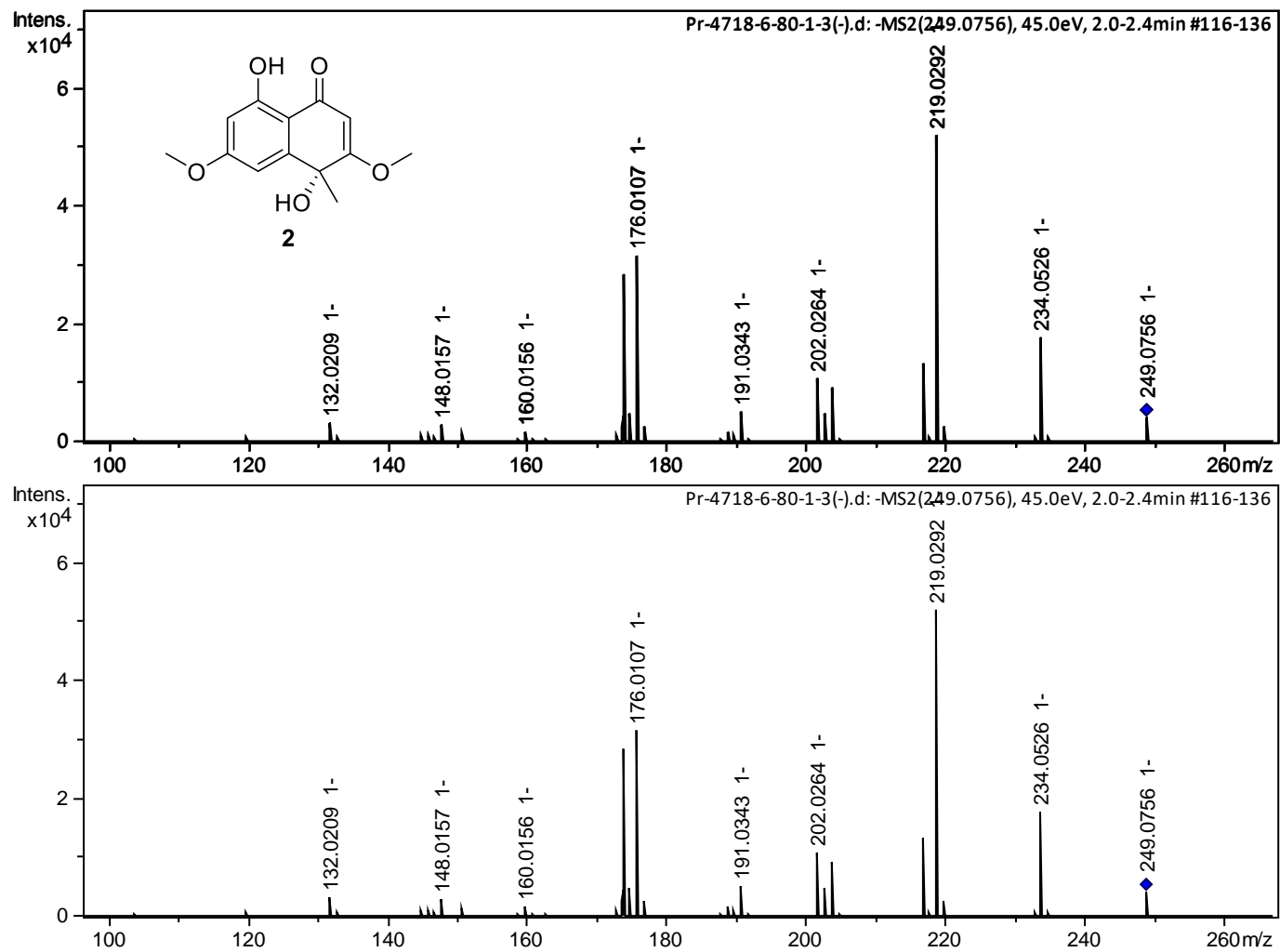


Figure S8. HRESIMS for 2



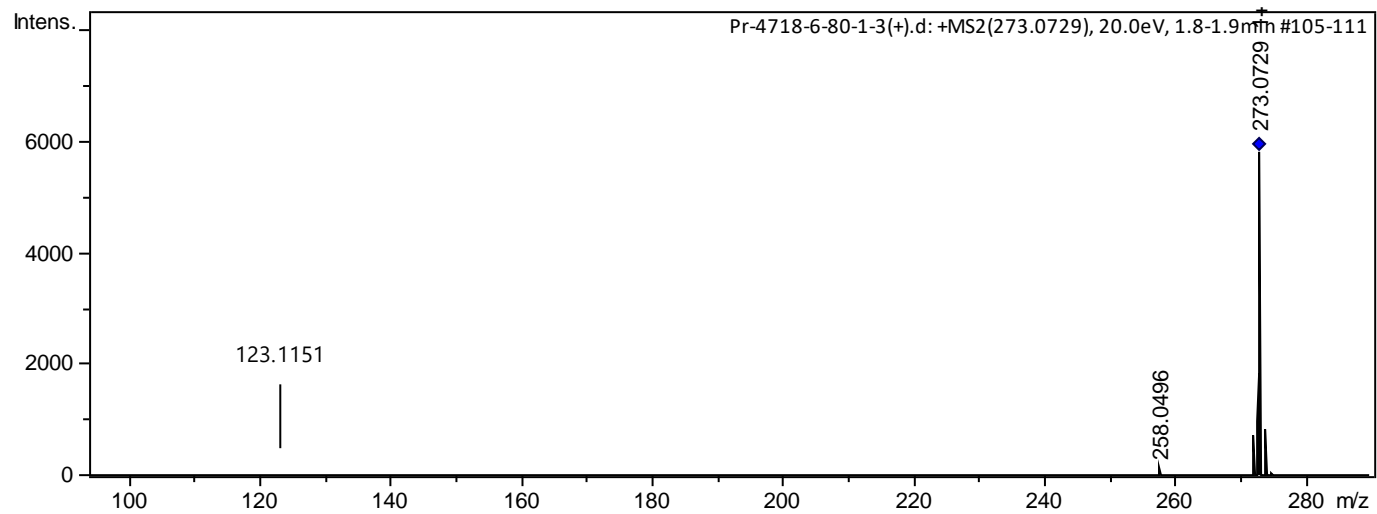
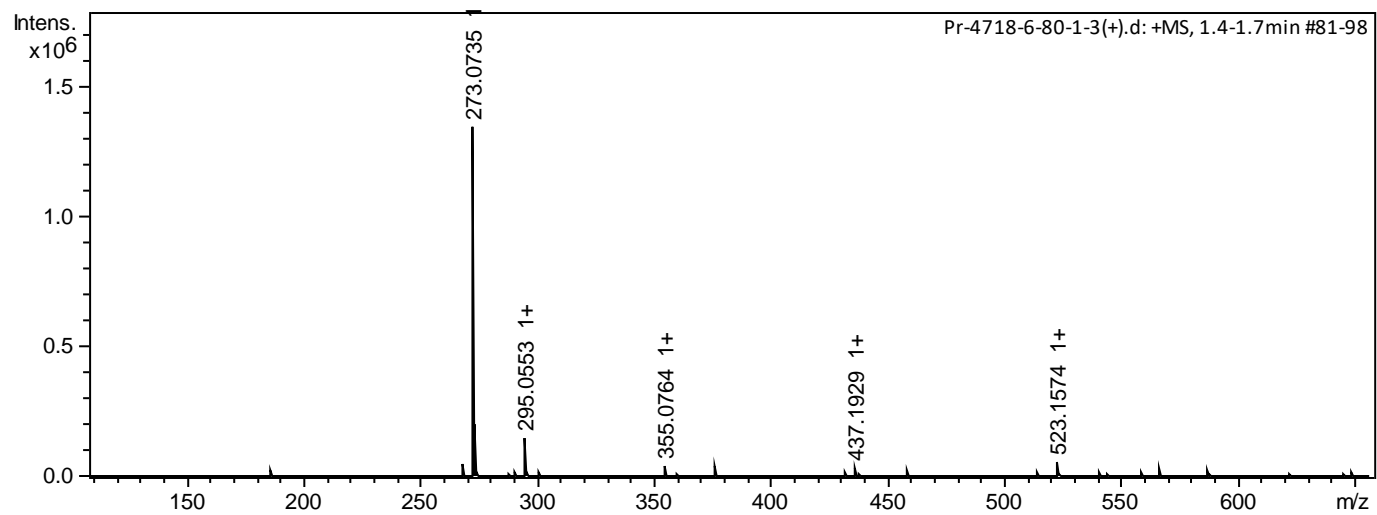


Figure S9.  $^1\text{H}$  NMR spectrum of **2** measured at 500 MHz in acetone- $\text{d}_6$

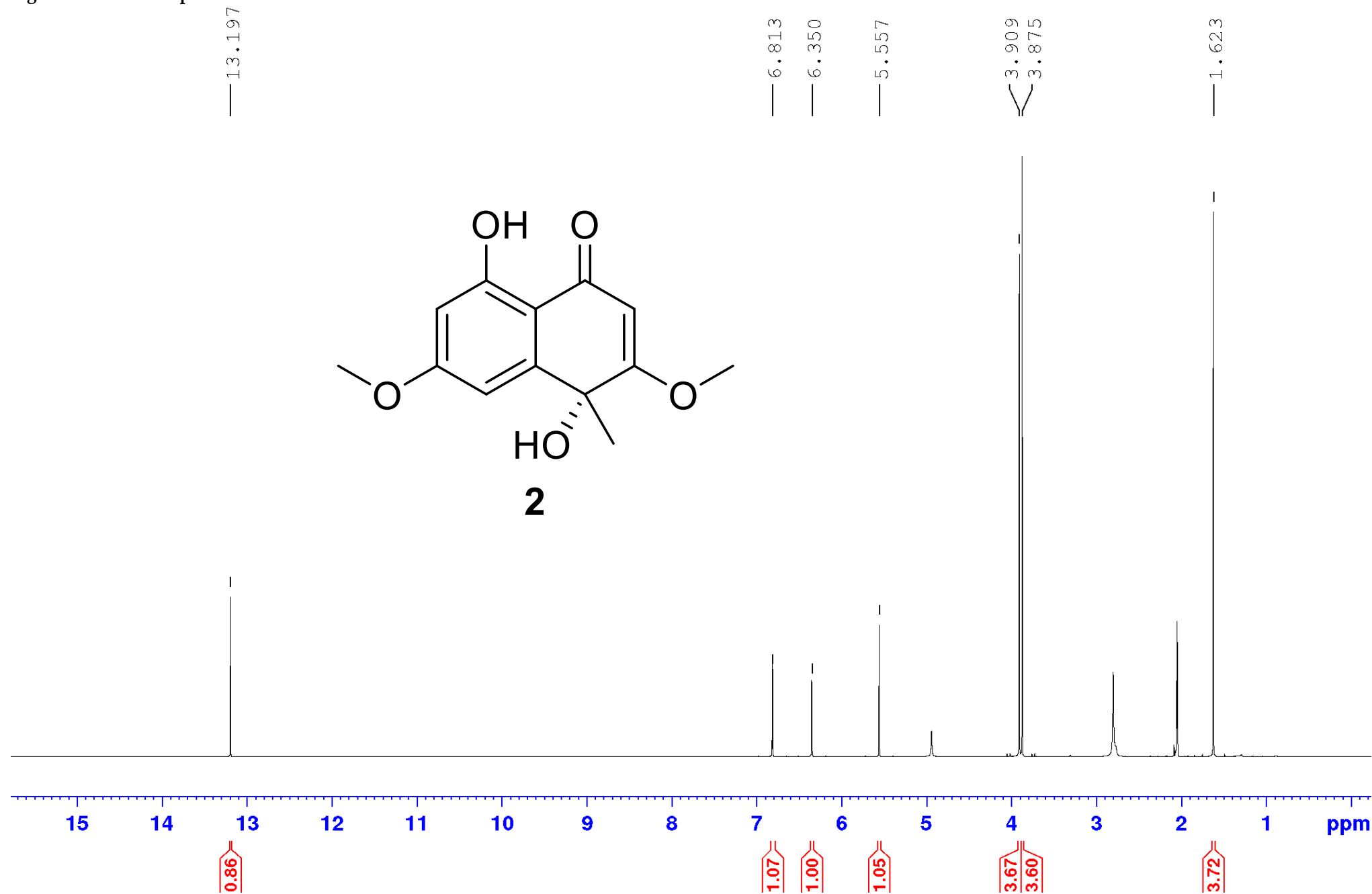


Figure S10.  $^{13}\text{C}$  NMR spectrum of **2** measured at 125 MHz in acetone- $\text{d}_6$

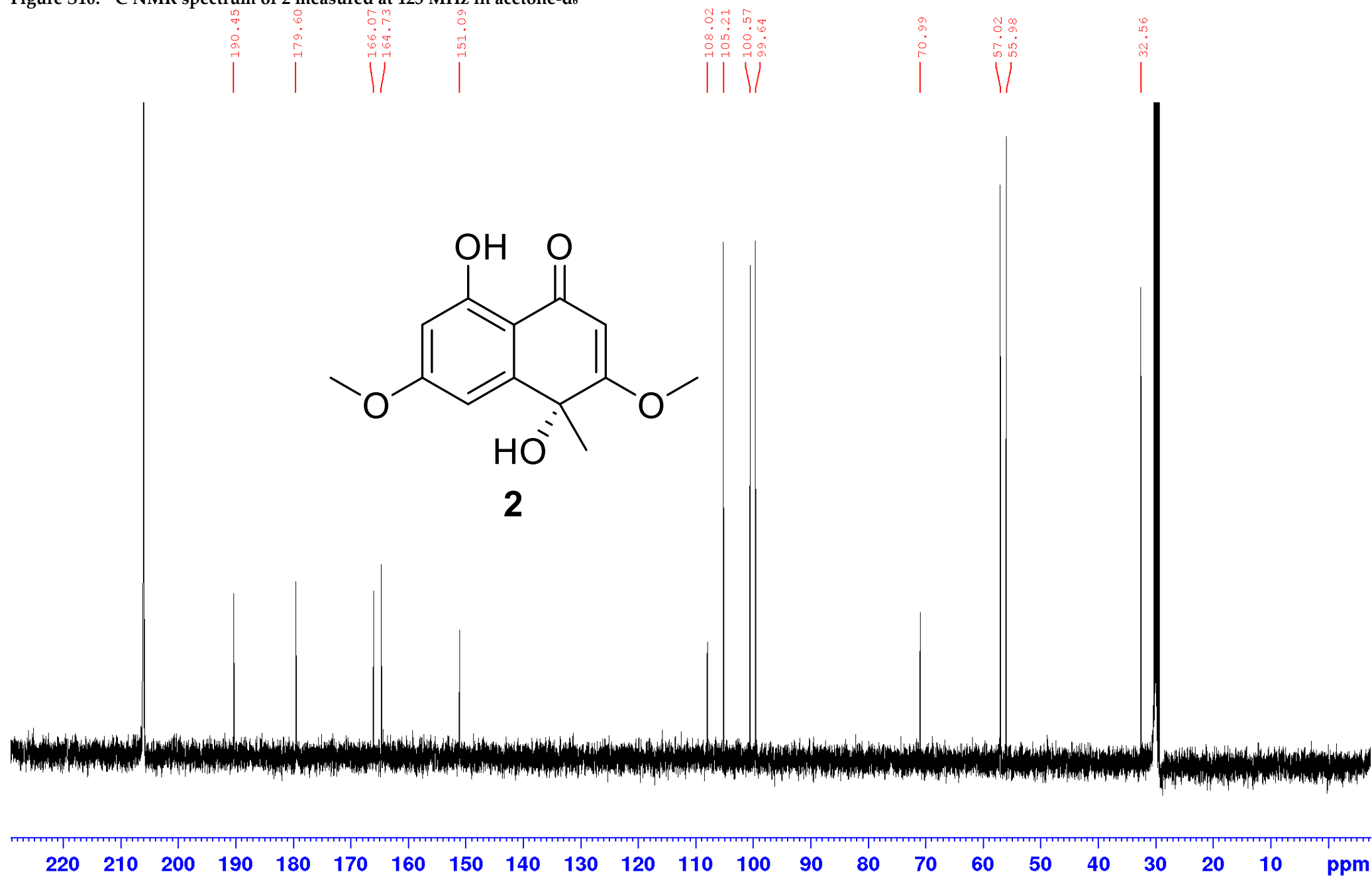


Figure S11. DEPT-135 spectrum of **2** measured at 125 MHz in acetone- $d_6$

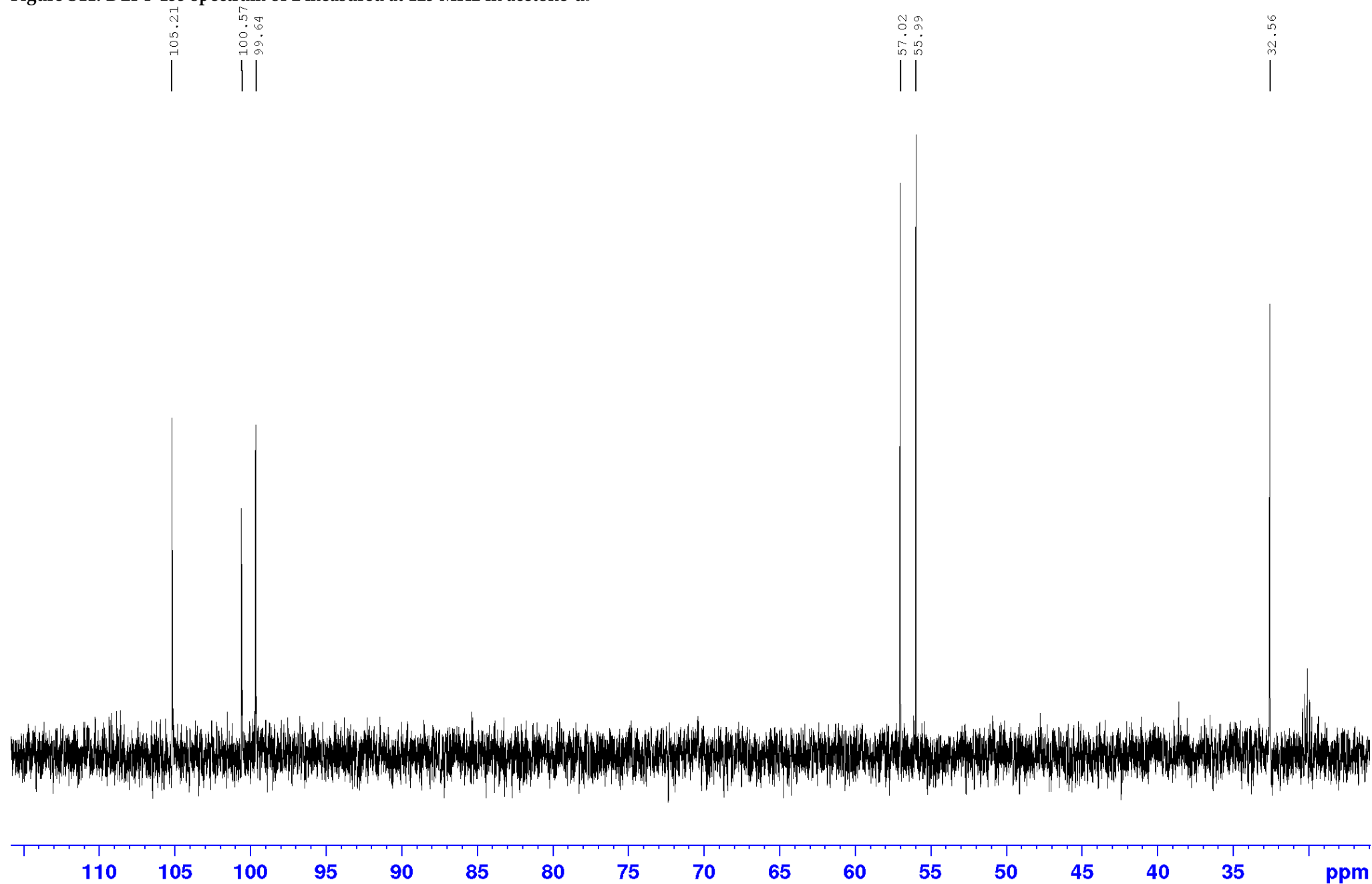


Figure S12. HSQC spectrum of 2 measured in acetone-d<sub>6</sub>

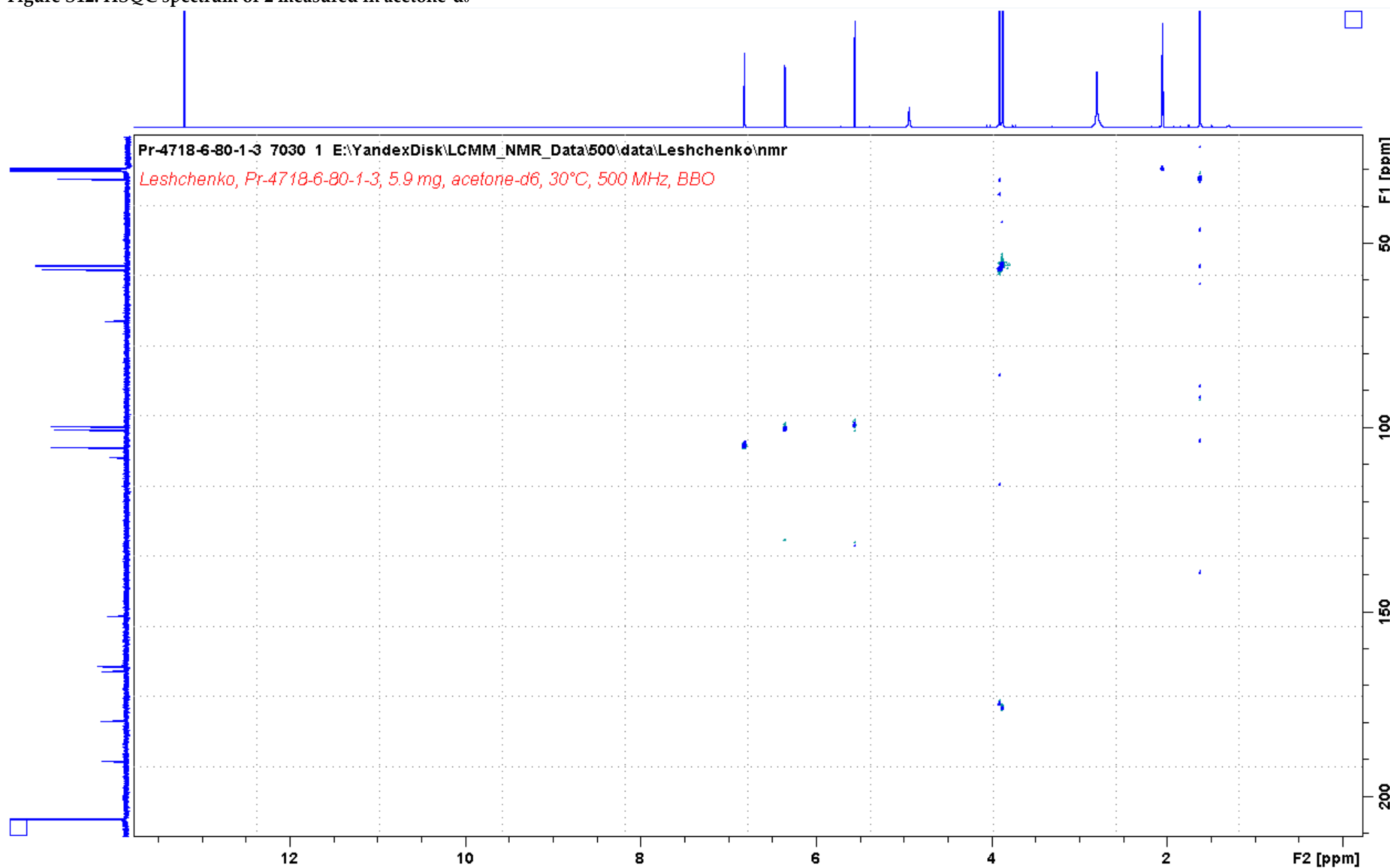




Figure S13. COSY spectrum of 2 measured in acetone-d<sub>6</sub>

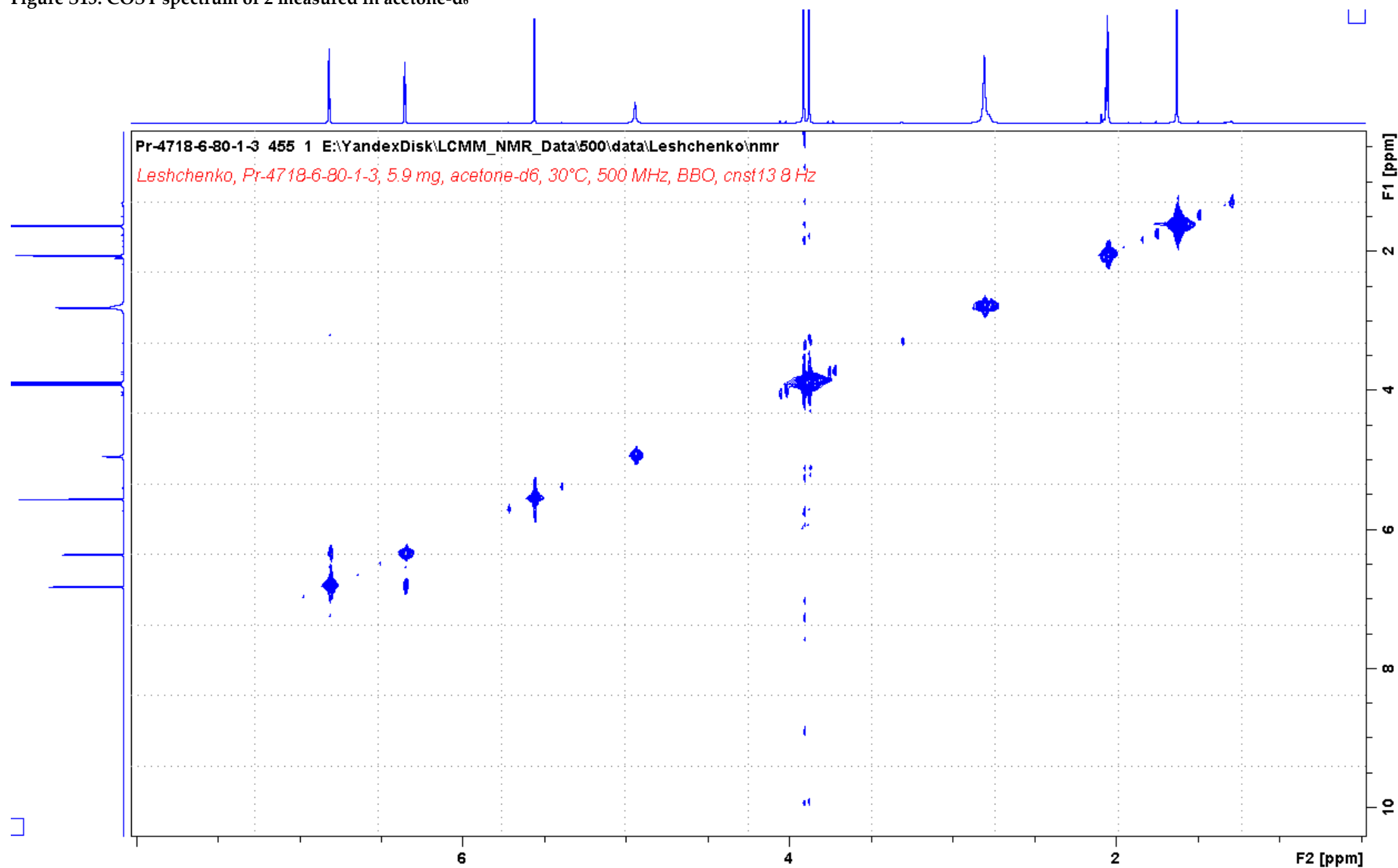


Figure S14. HMBC spectrum of 2 measured in acetone-d<sub>6</sub>

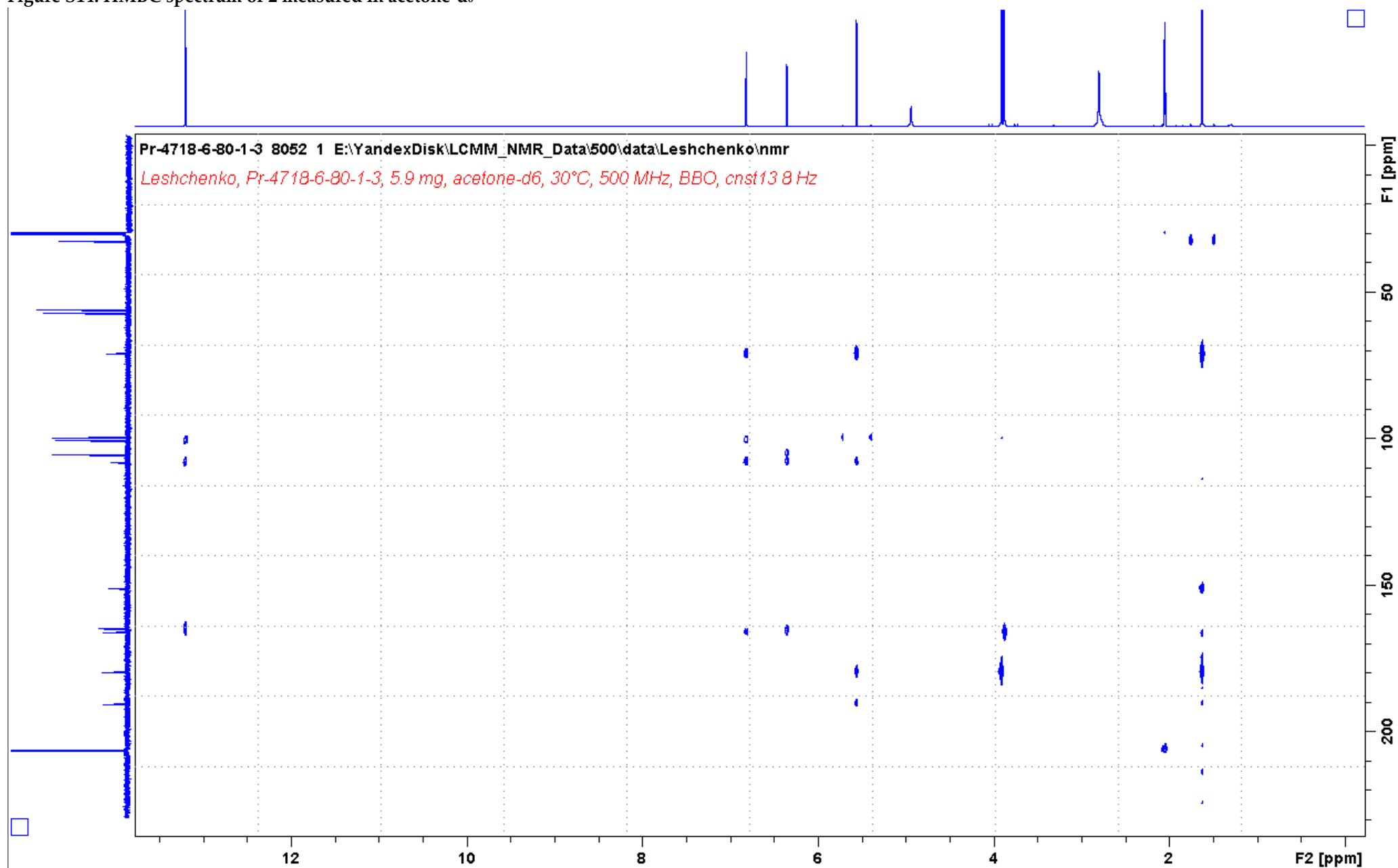
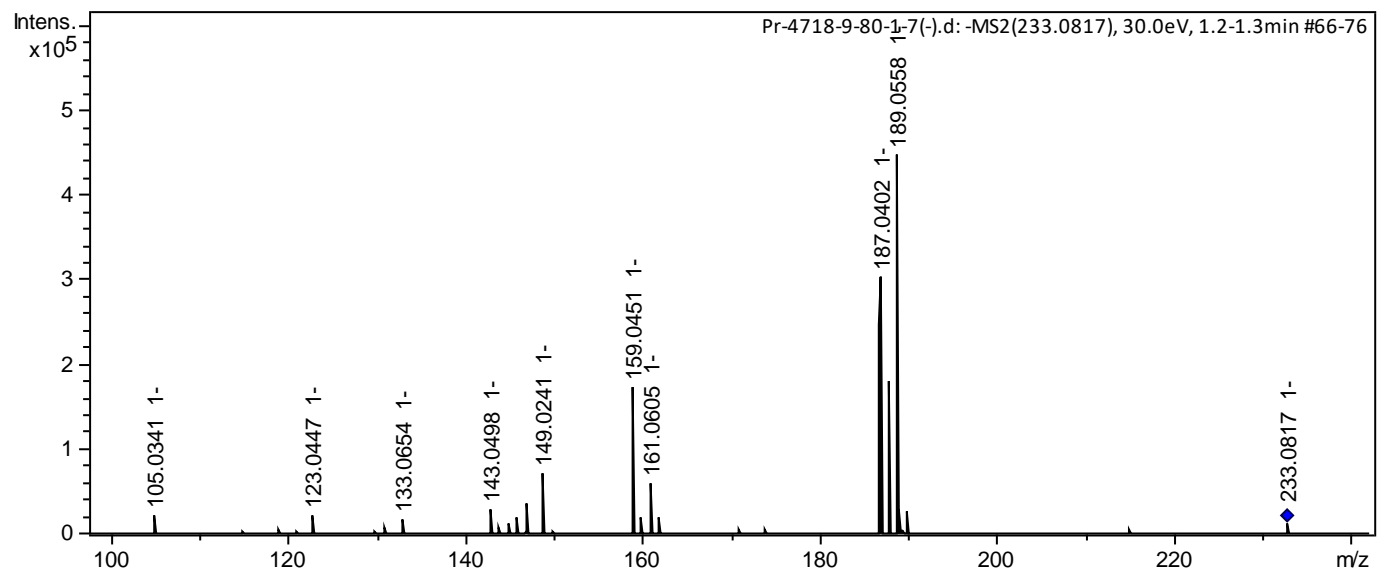
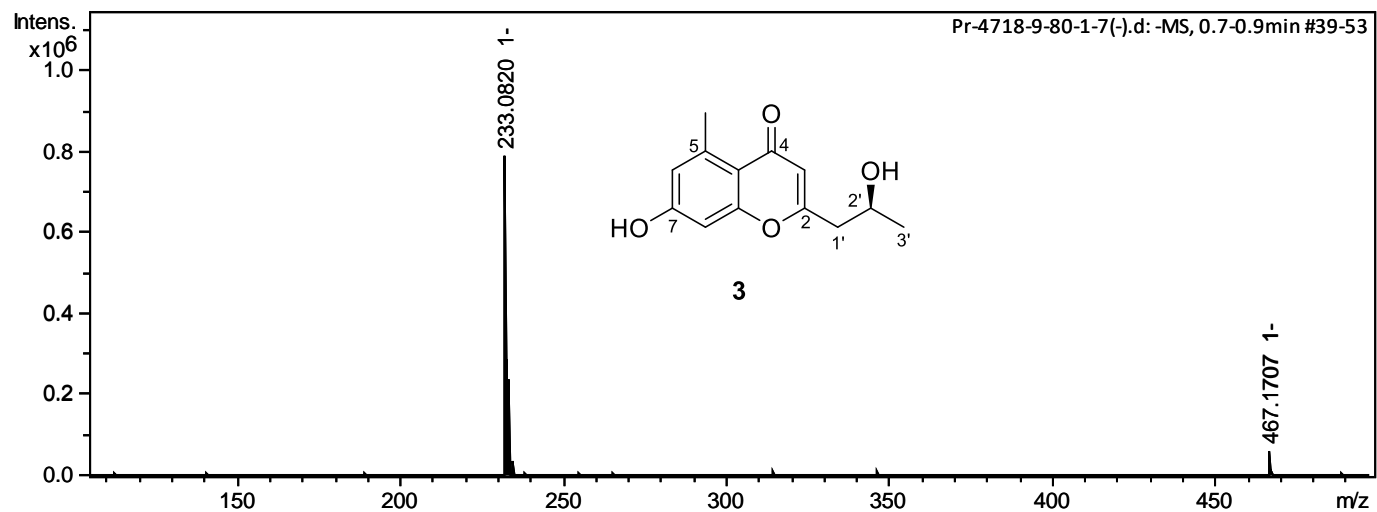


Figure S15. HRESIMS for **3**



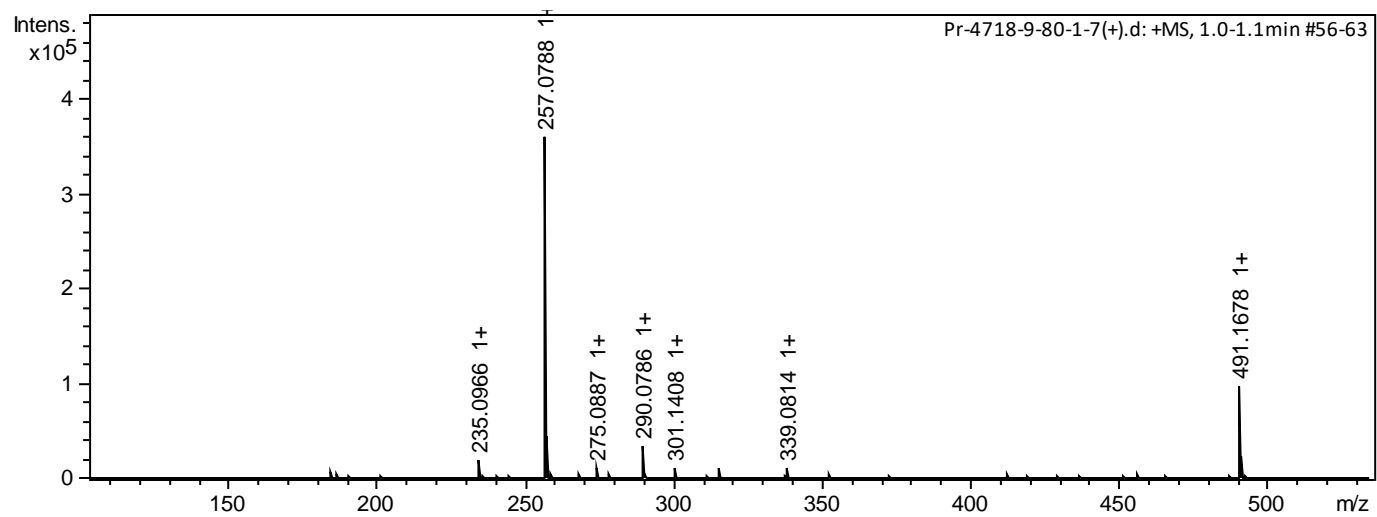


Figure S16.  $^1\text{H}$  NMR spectrum of **3** measured at 500 MHz in acetone- $\text{d}_6$

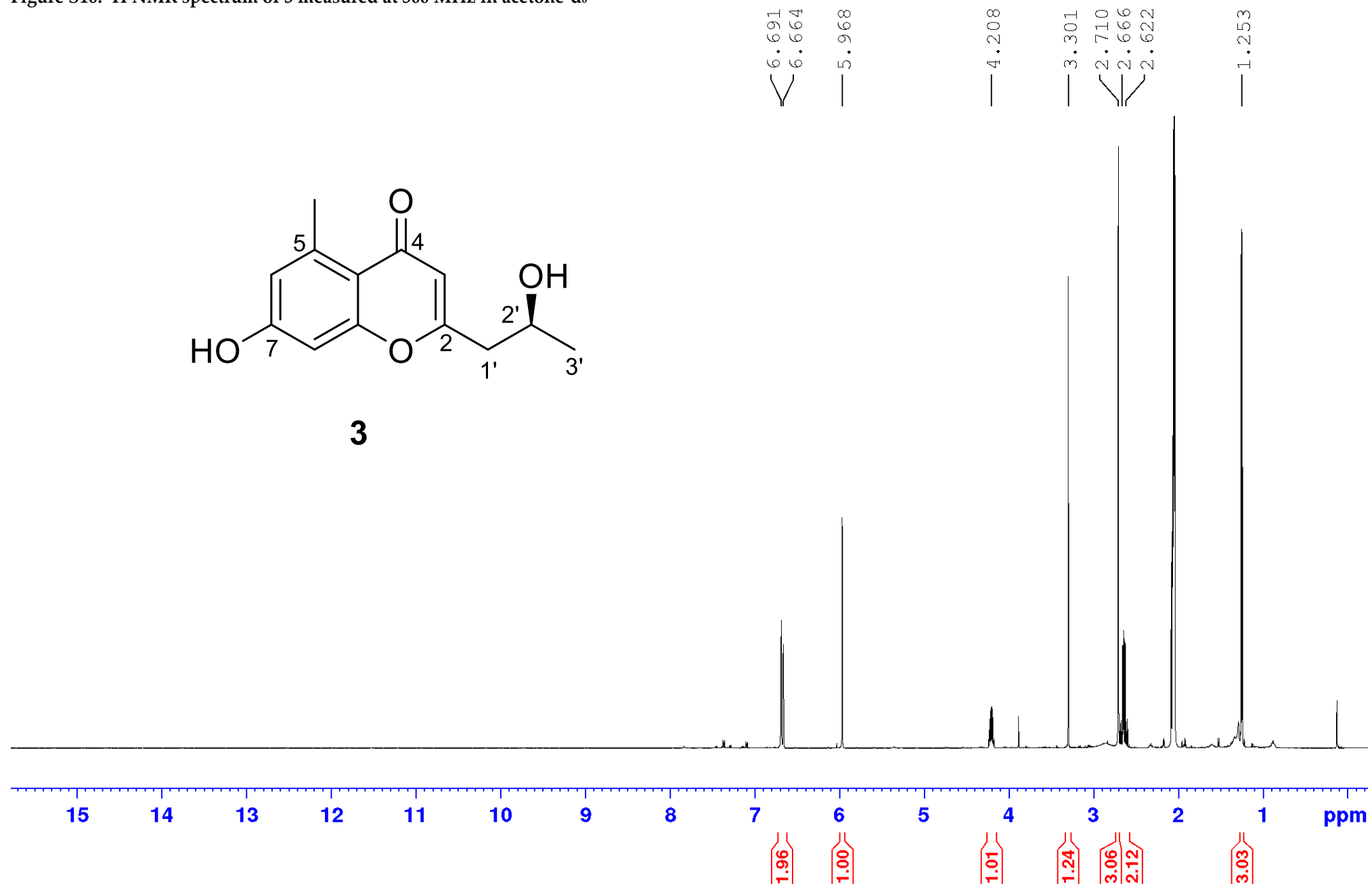


Figure S17.  $^{13}\text{C}$  NMR spectrum of **3** measured at 125 MHz in acetone- $\text{d}_6$

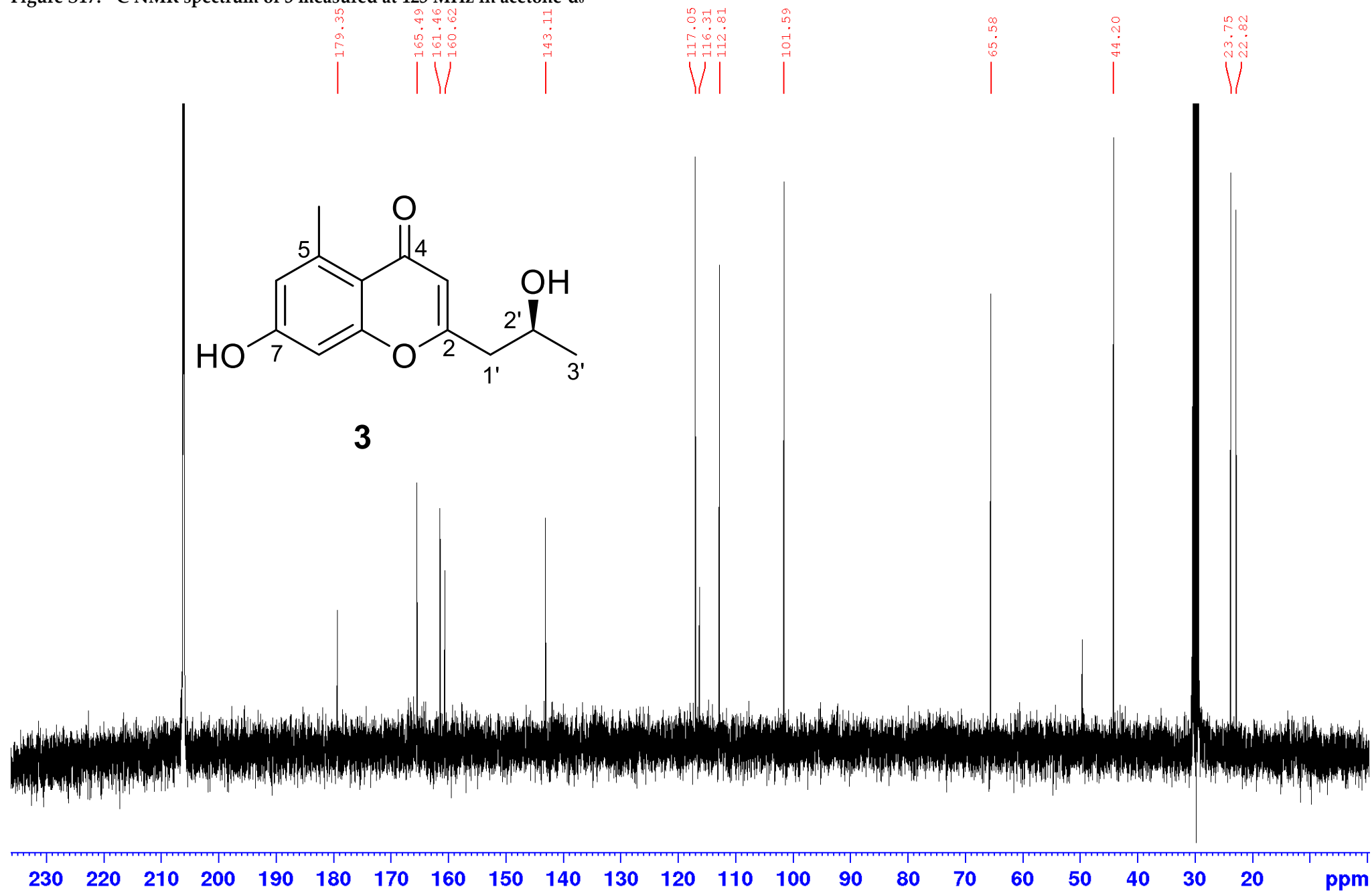
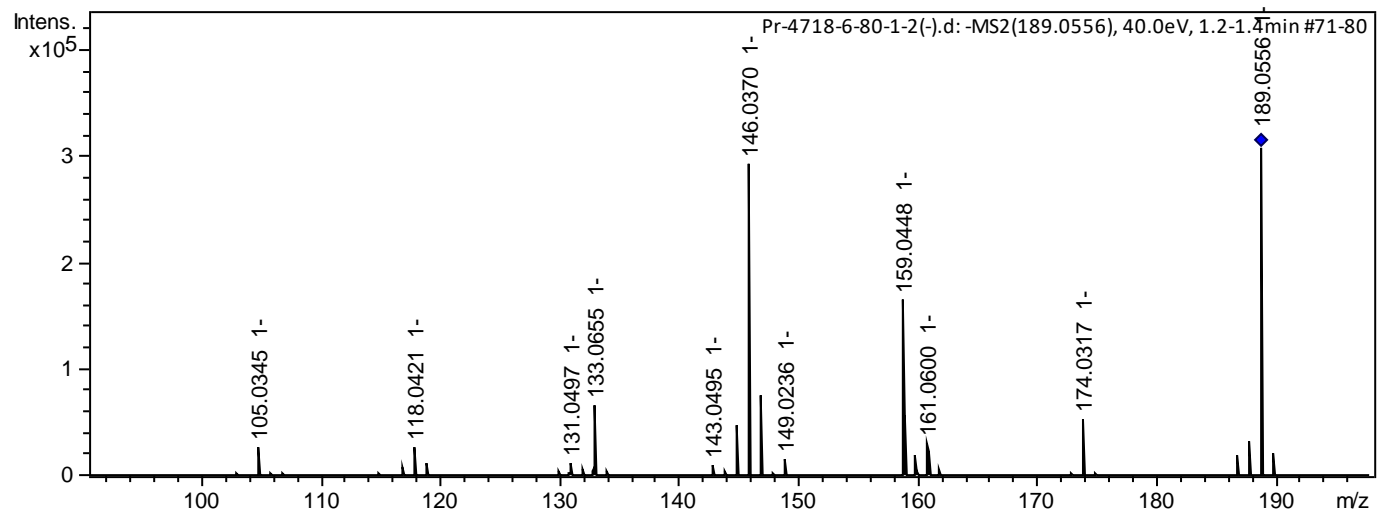
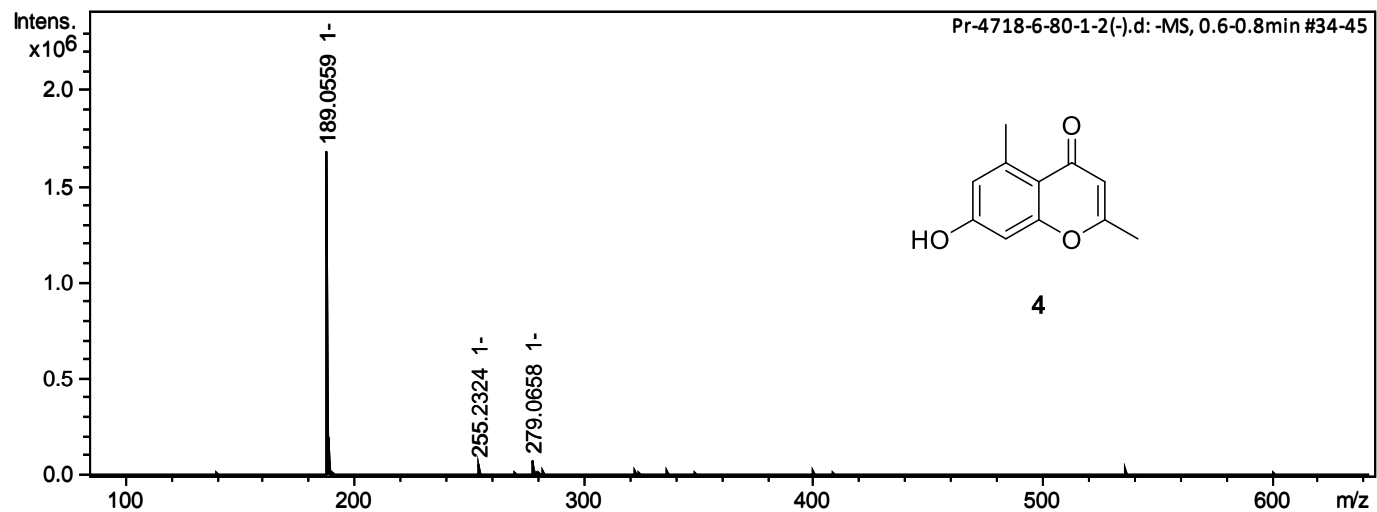


Figure S18. HRESIMS for 4



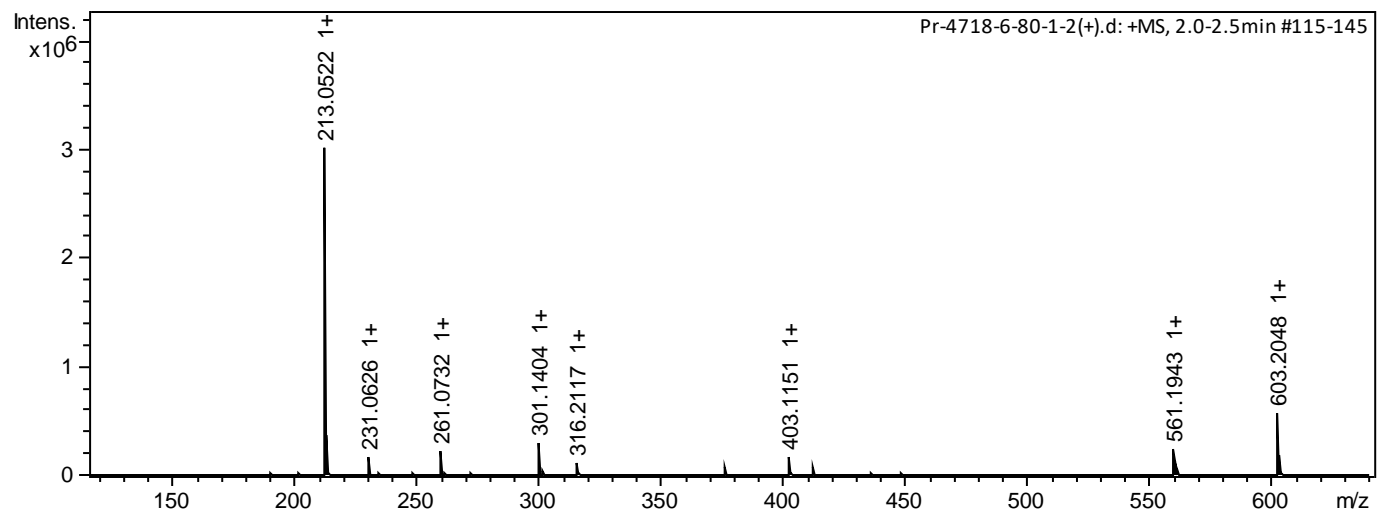




Figure S19.  $^1\text{H}$  NMR spectrum of **4** measured at 500 MHz in acetone- $\text{d}_6$

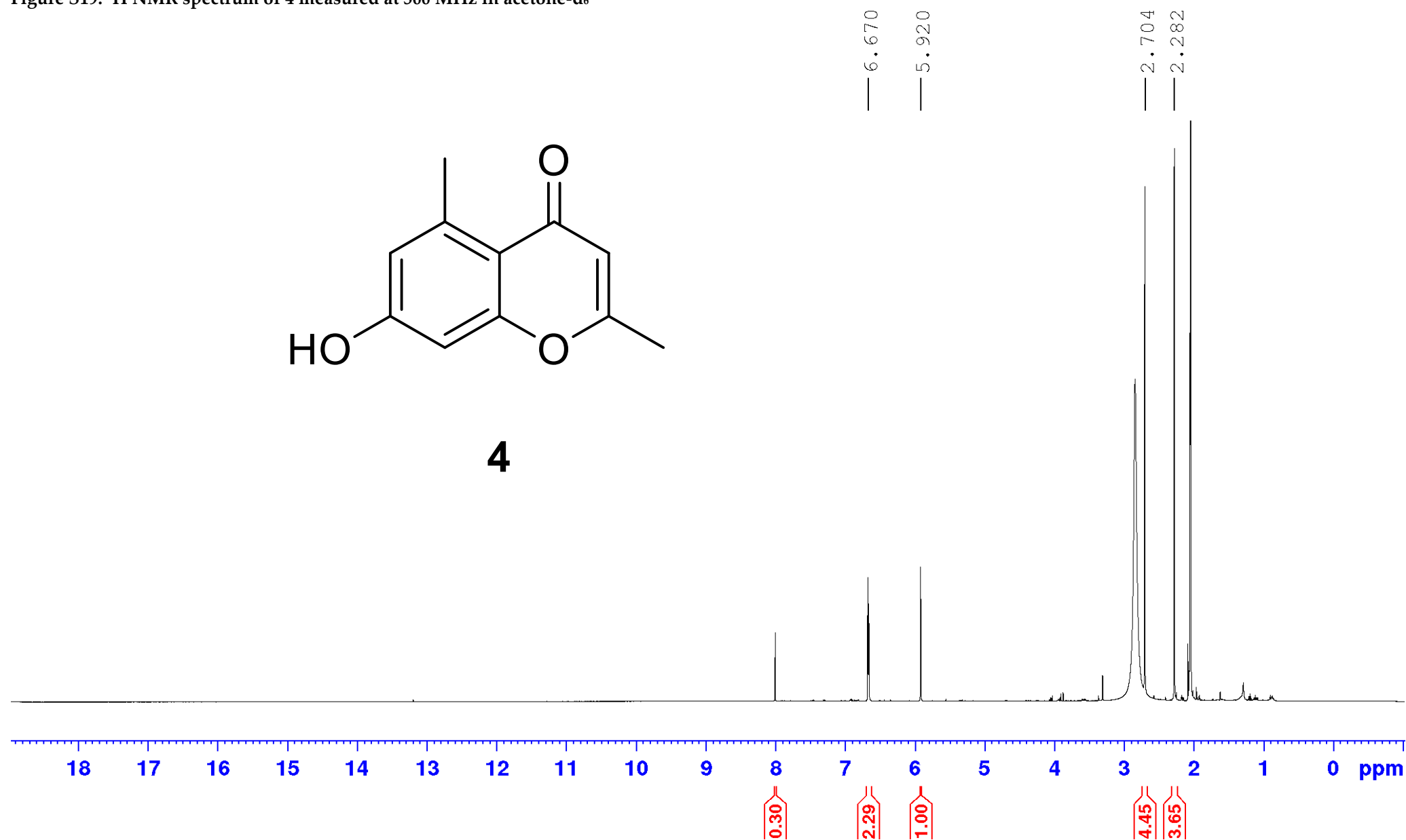


Figure S20.  $^{13}\text{C}$  NMR spectrum of **4** measured at 125 MHz in acetone- $\text{d}_6$

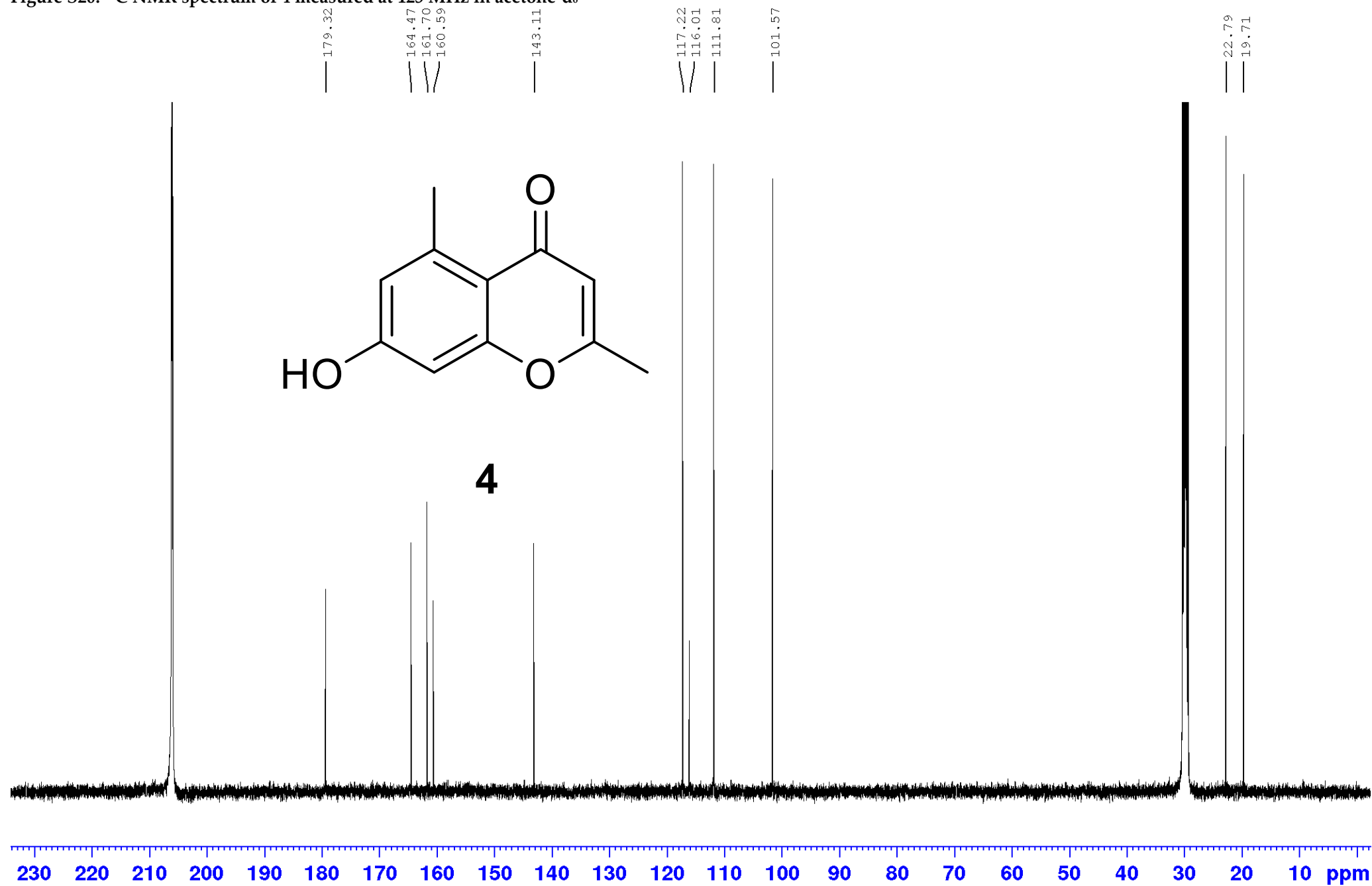
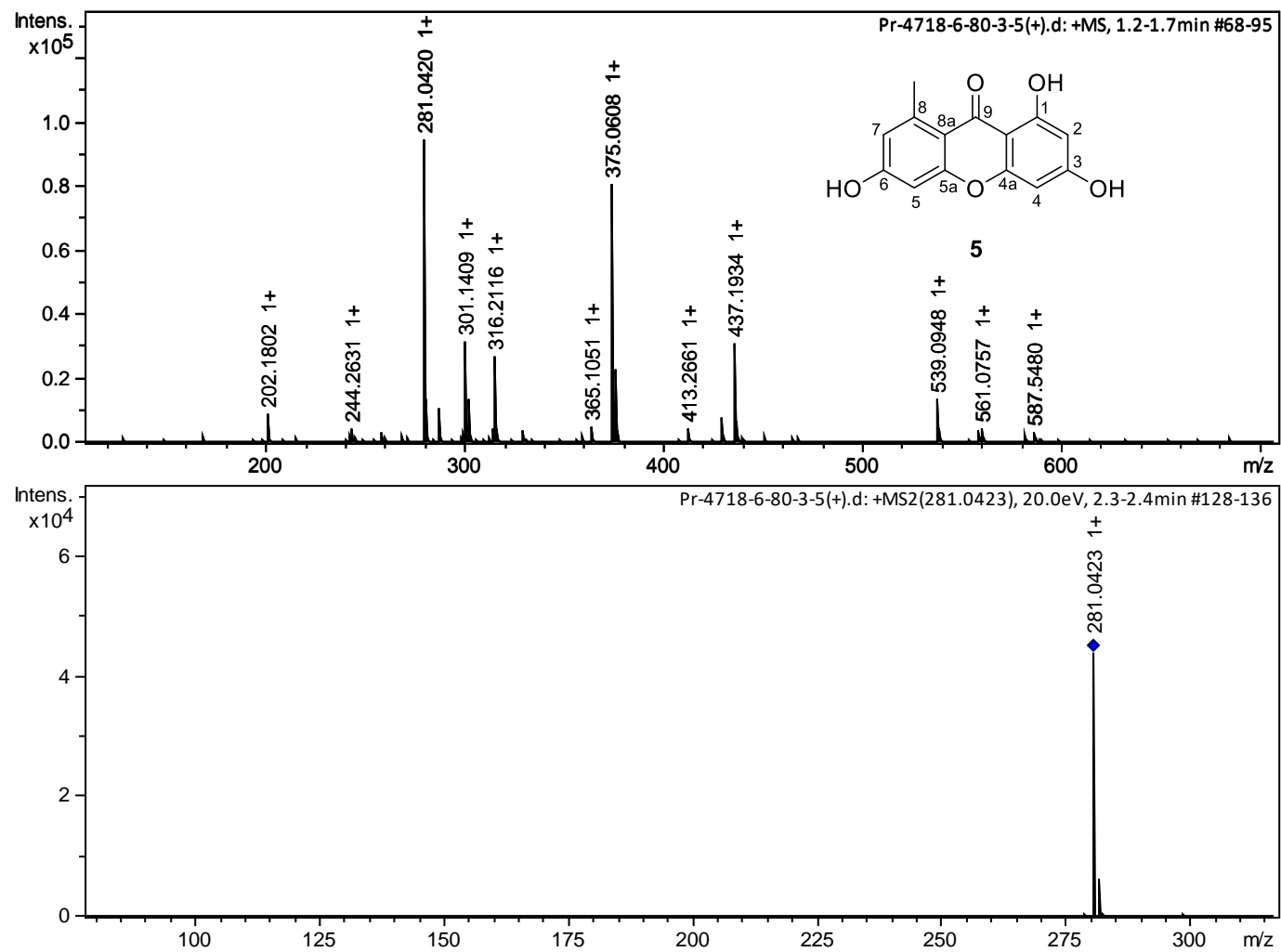


Figure S21. HRESIMS for 5



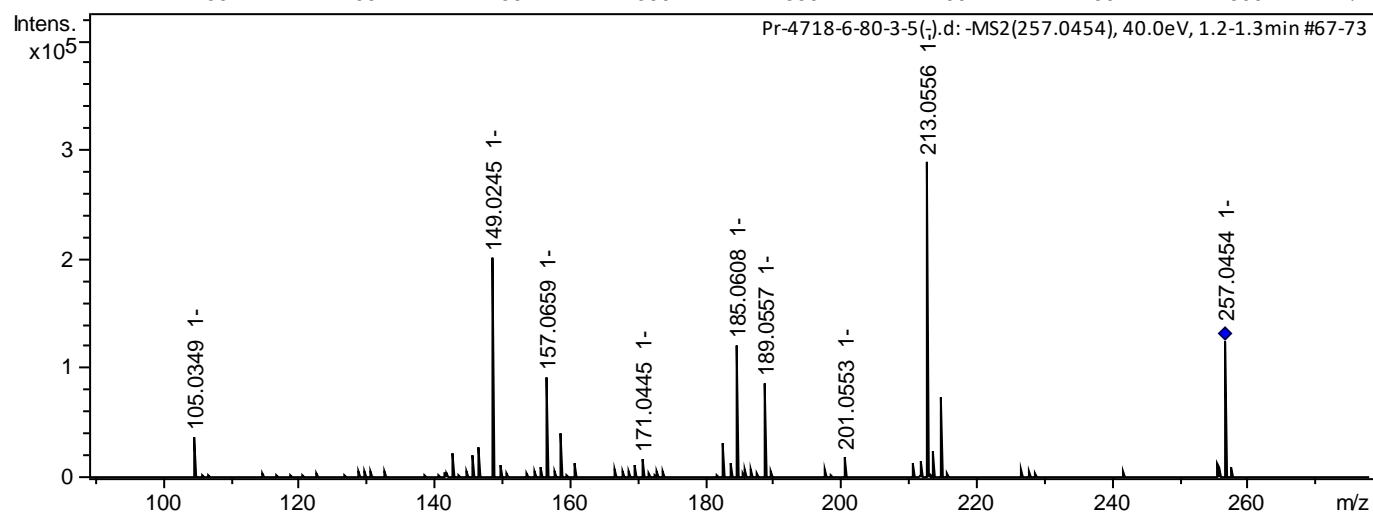
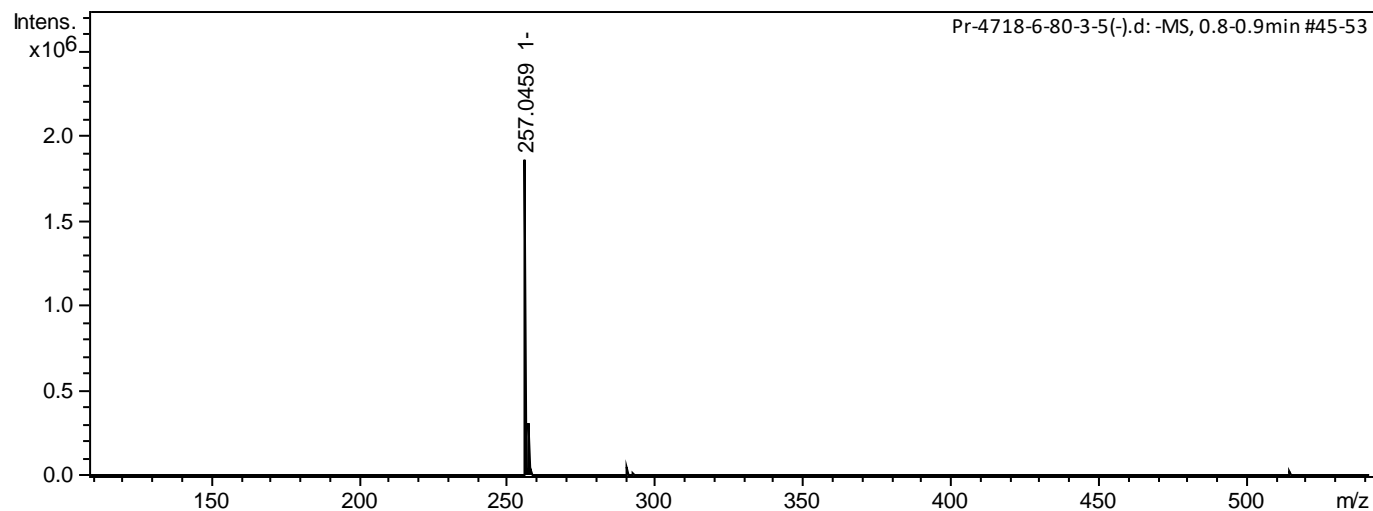


Figure S22.  $^1\text{H}$  NMR spectrum of **5** measured at 500 MHz in acetone- $\text{d}_6$

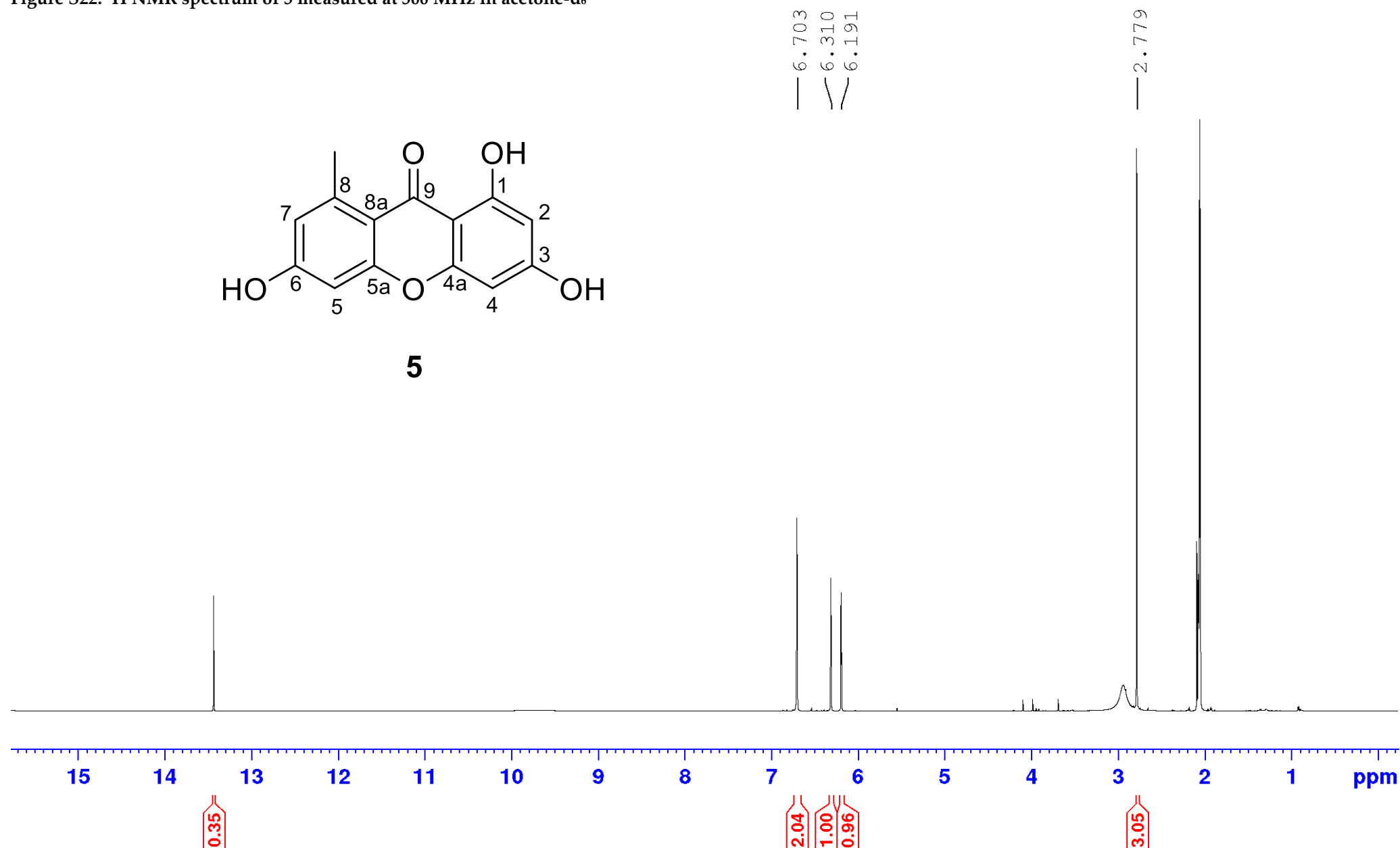


Figure S23.  $^{13}\text{C}$  NMR spectrum of **5** measured at 125 MHz in acetone- $\text{d}_6$

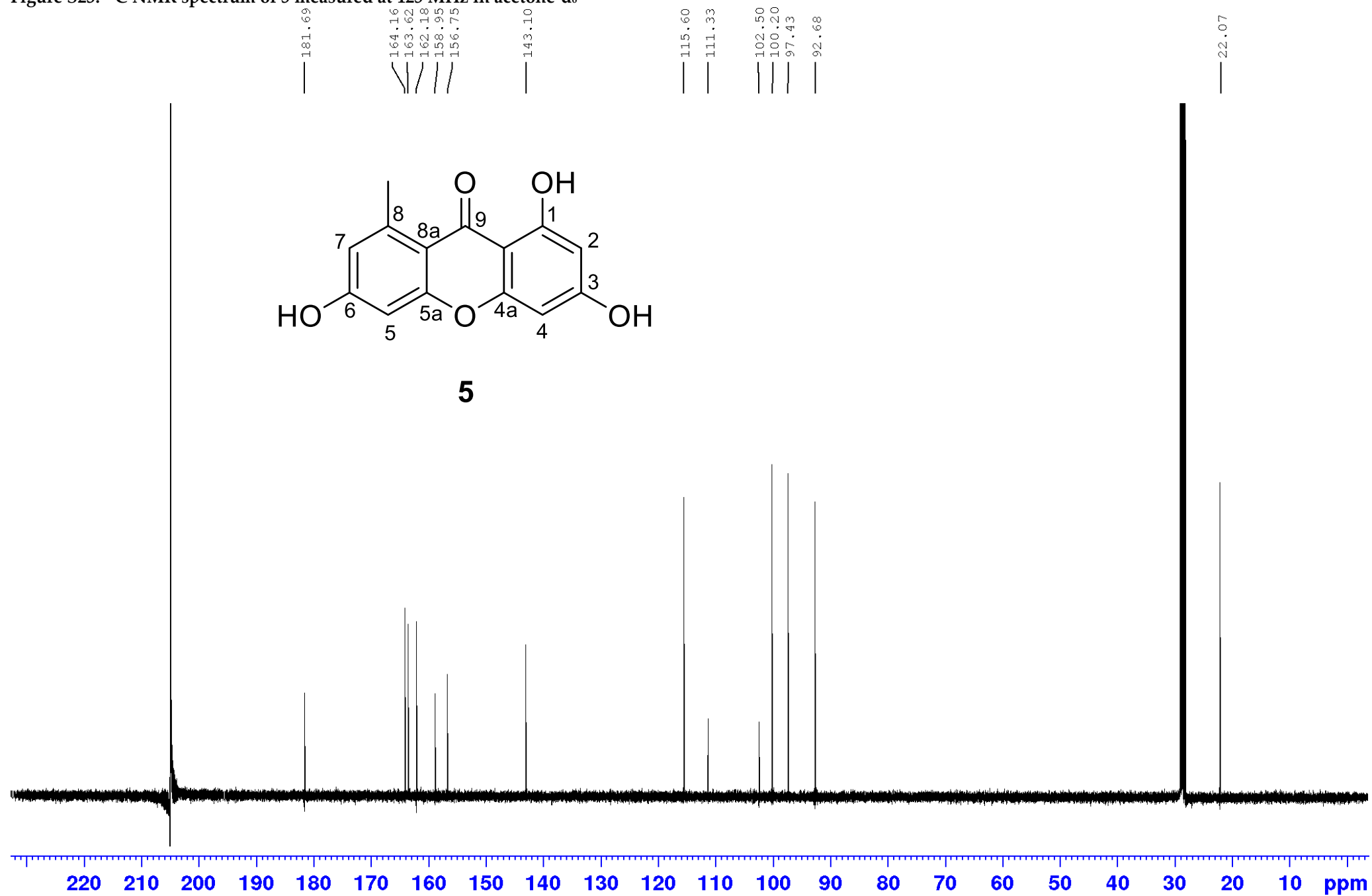
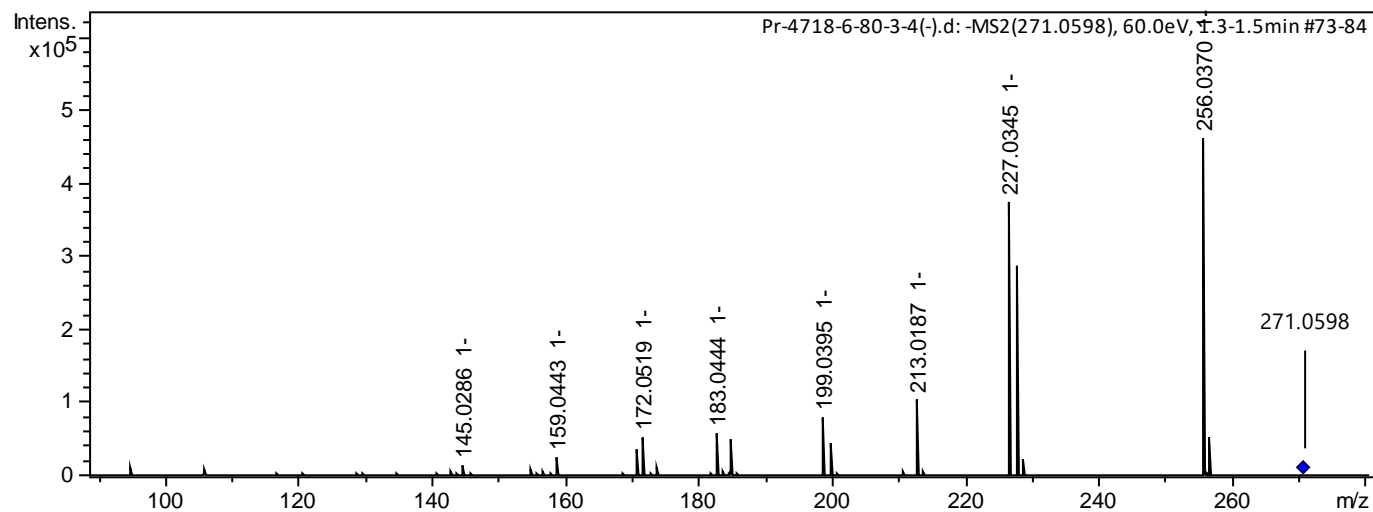
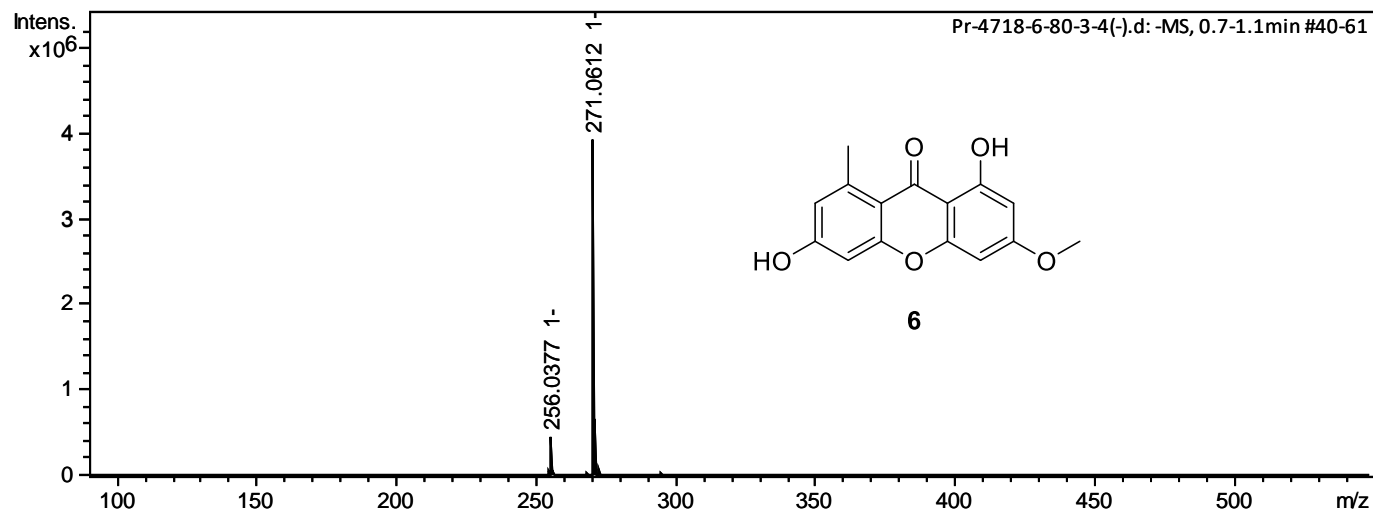


Figure S24. HRESIMS for 6



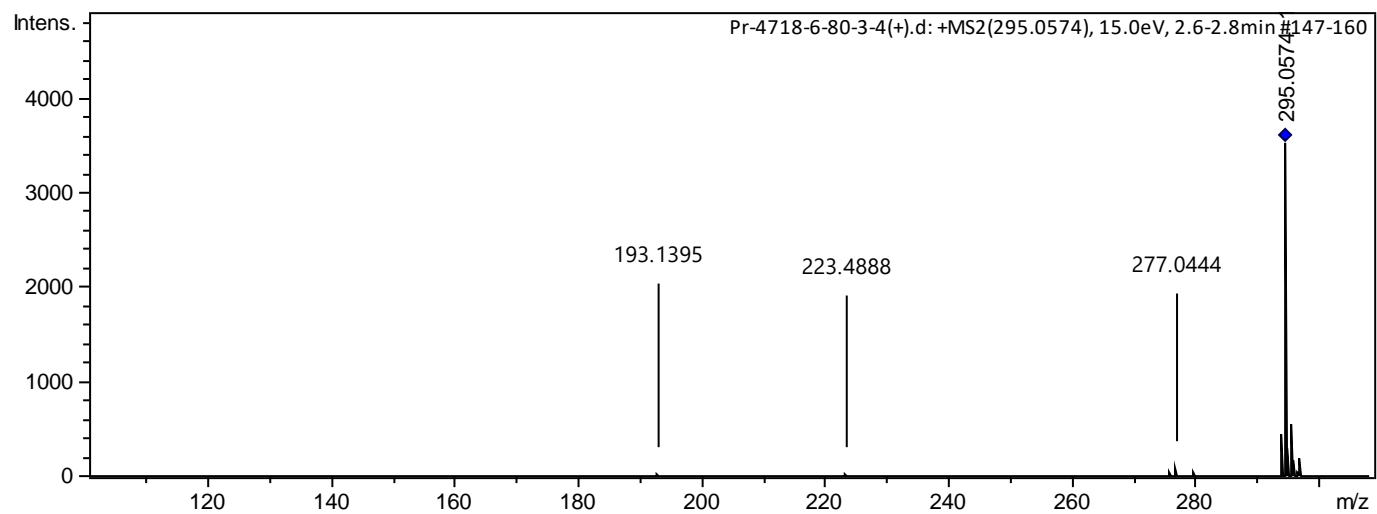
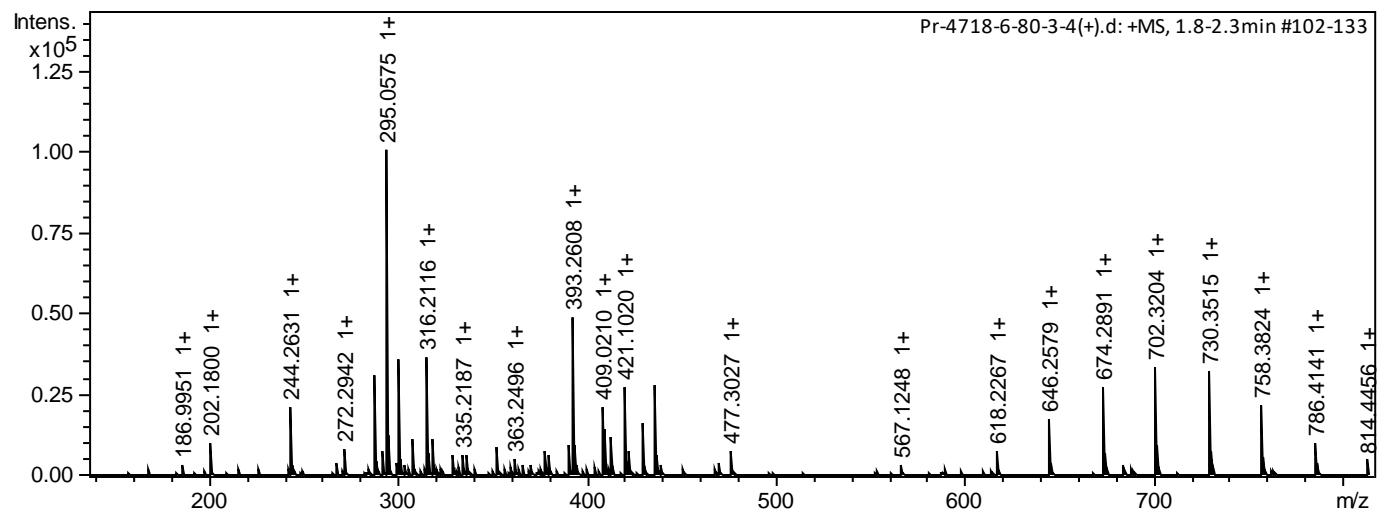




Figure S25.  $^1\text{H}$  NMR spectrum of **6** measured at 300 MHz in acetone- $\text{d}_6$

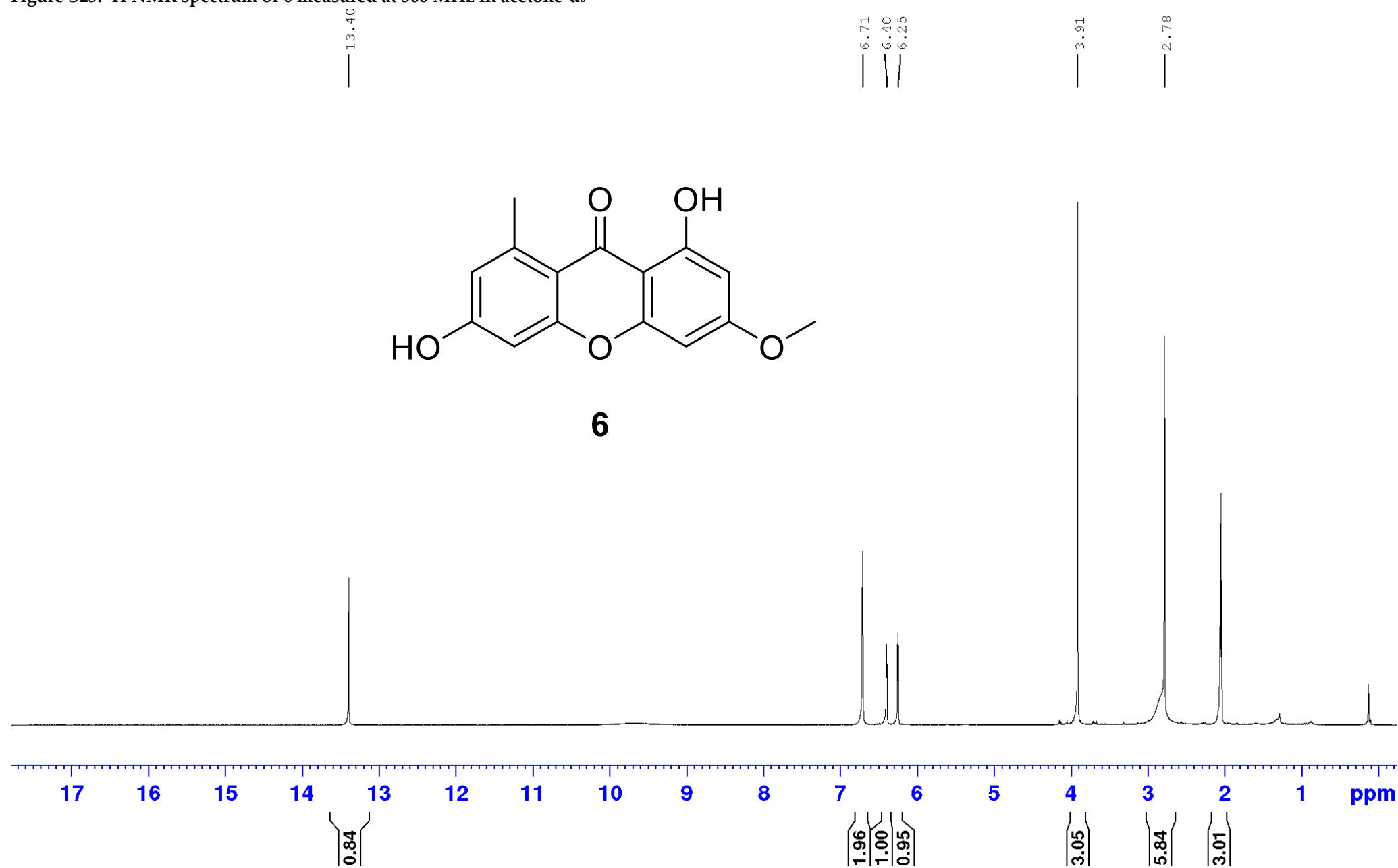


Figure S26.  $^{13}\text{C}$  NMR spectrum of **6** measured at 75 MHz in acetone- $\text{d}_6$

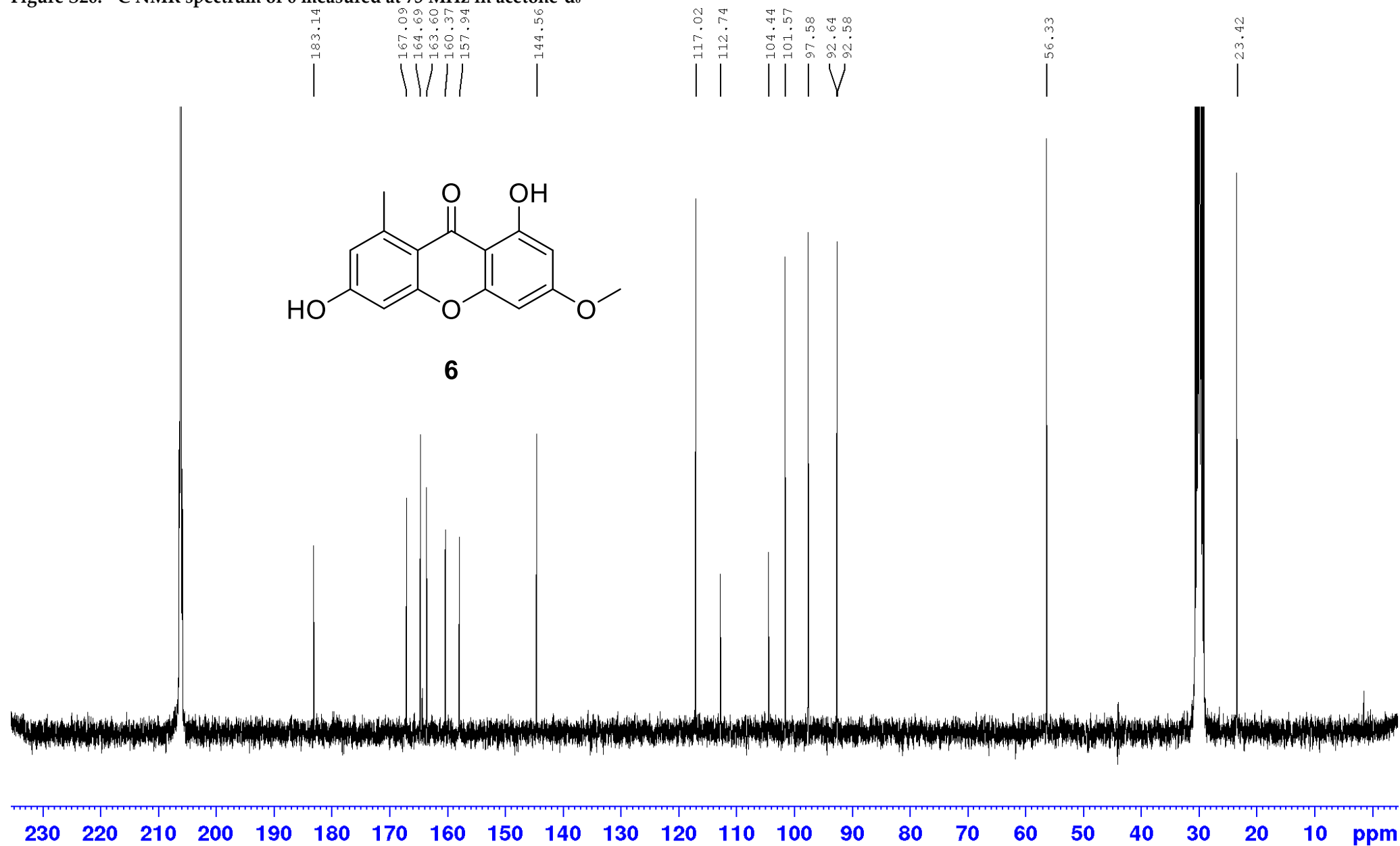
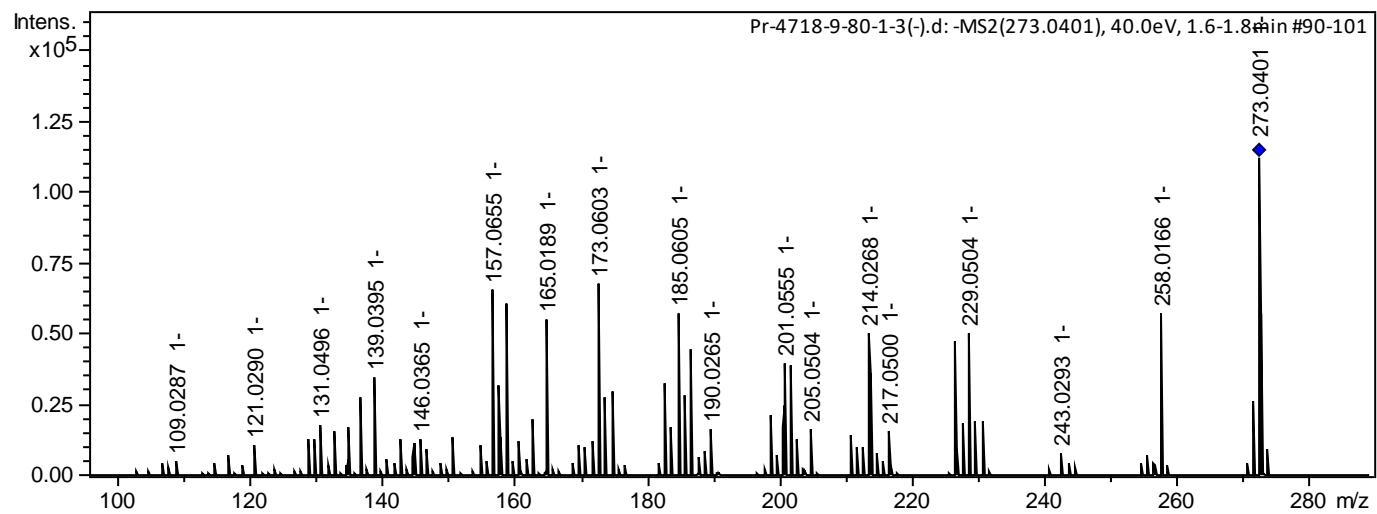
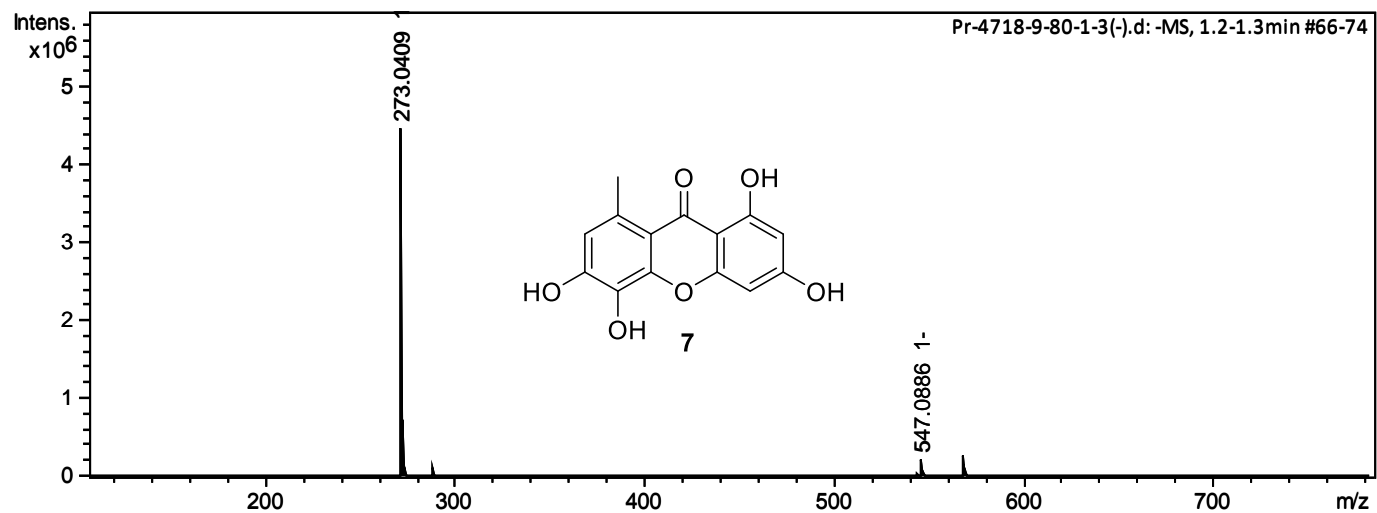


Figure S27. HRESIMS for 7



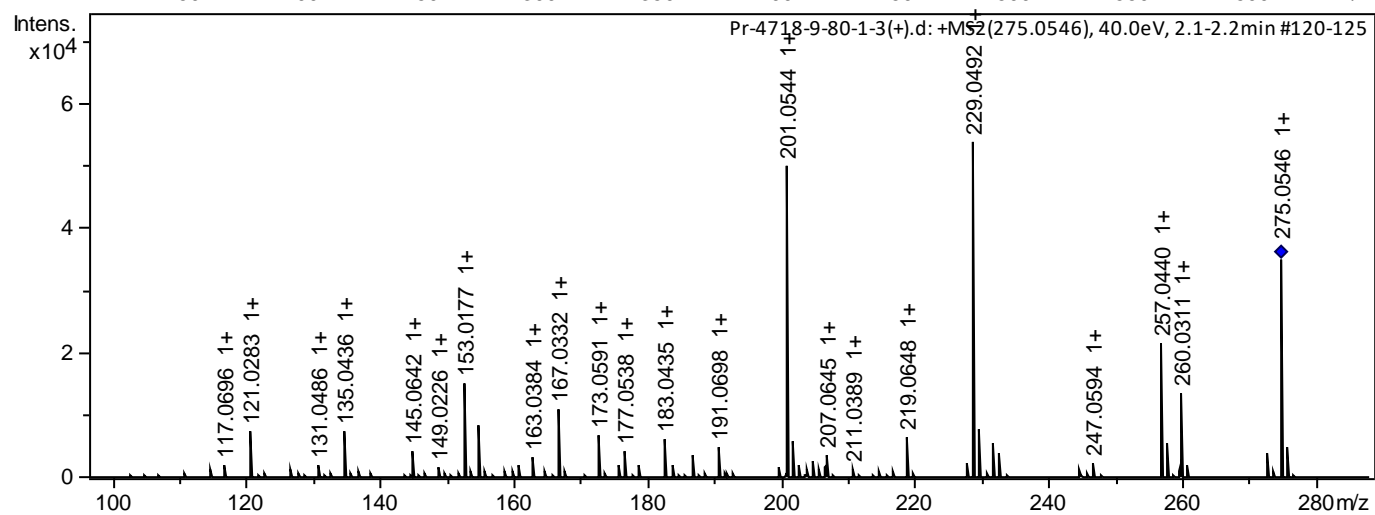
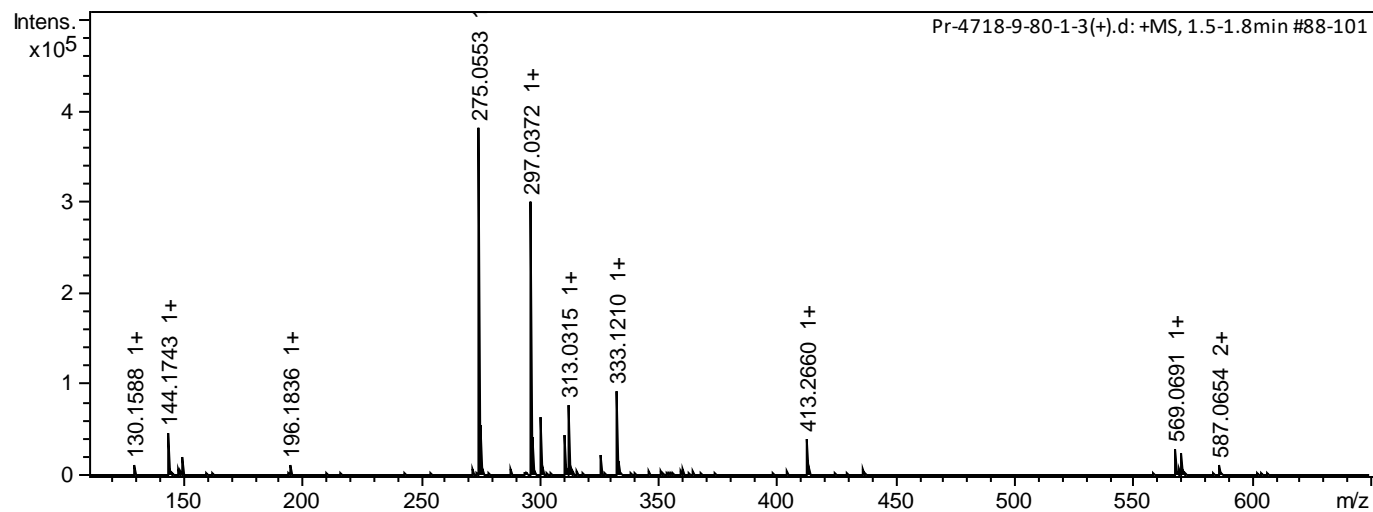


Figure S28.  $^1\text{H}$  NMR spectrum of **7** measured at 700 MHz in acetone- $\text{d}_6$

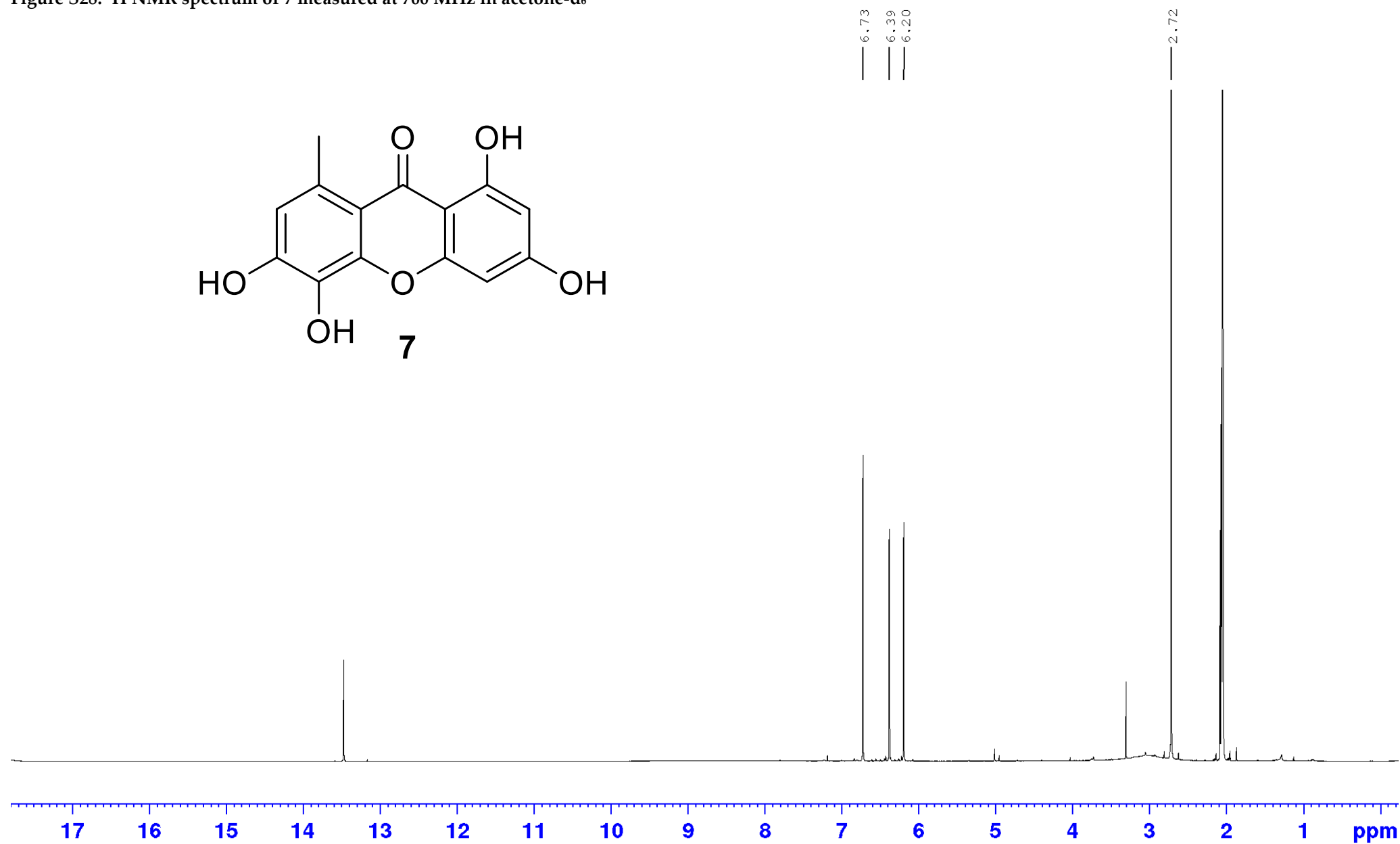


Figure S29.  $^{13}\text{C}$  NMR spectrum of **7** measured at 175 MHz in acetone- $\text{d}_6$

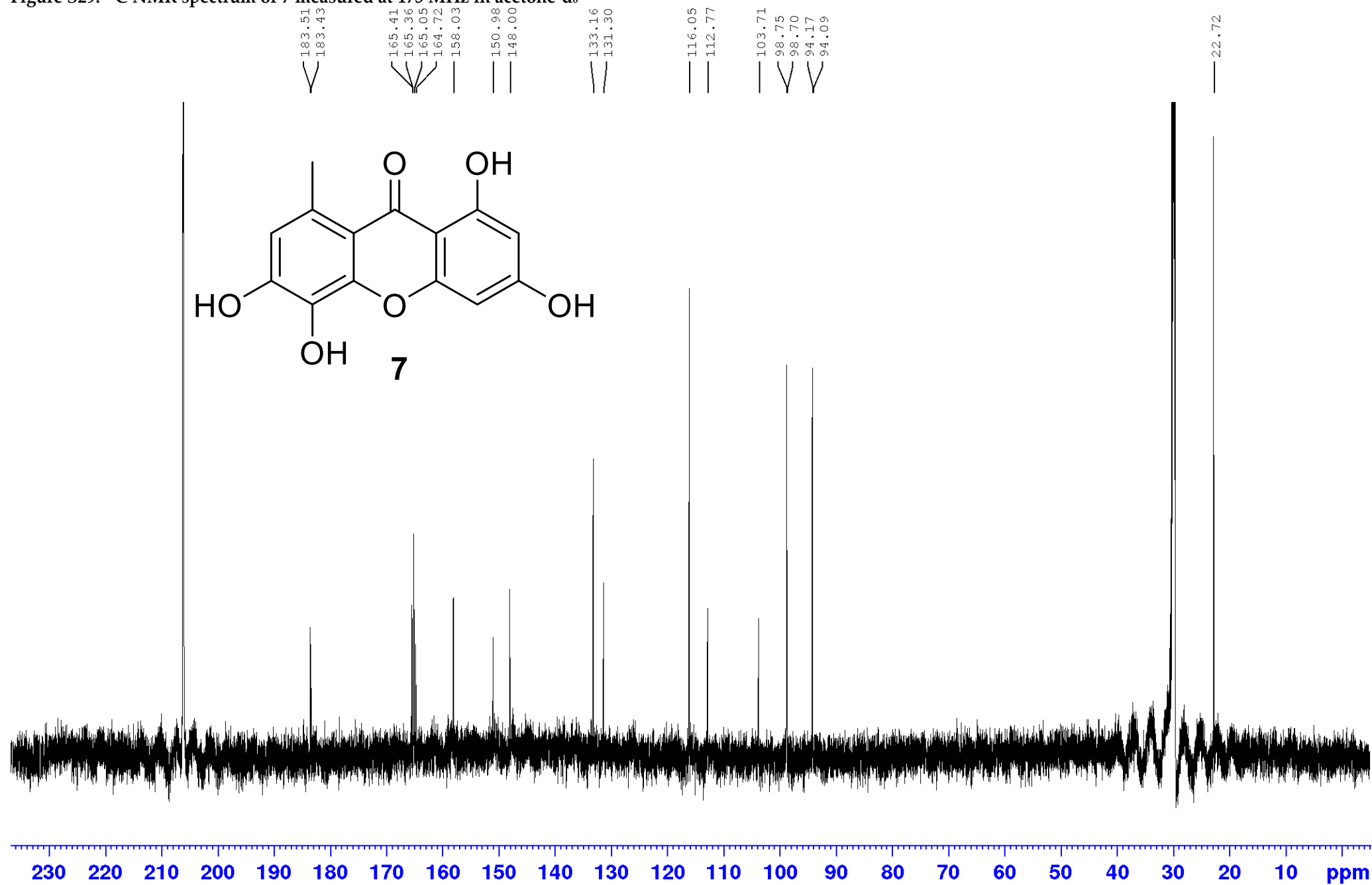
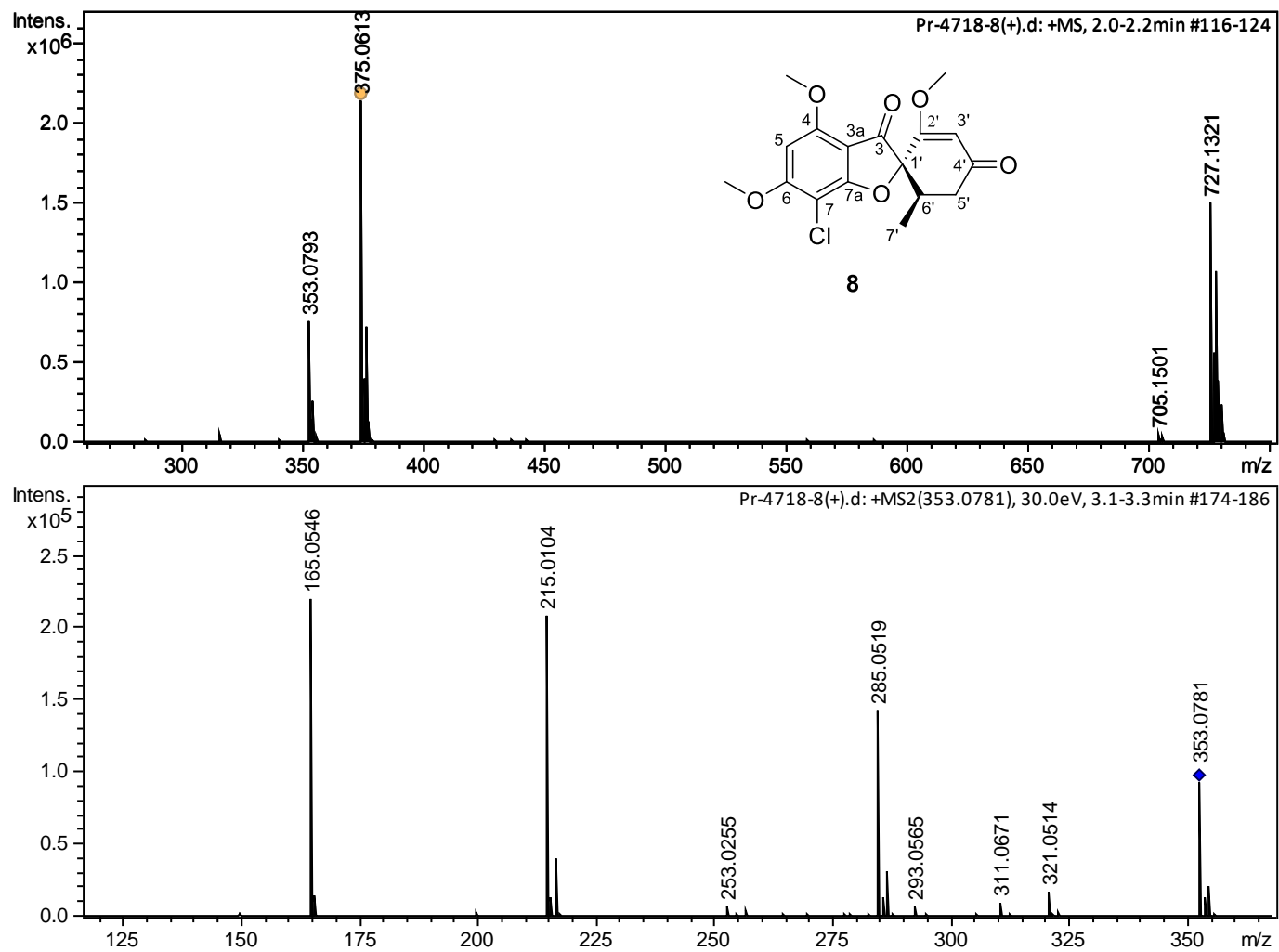


Figure S30. HRESIMS for 8



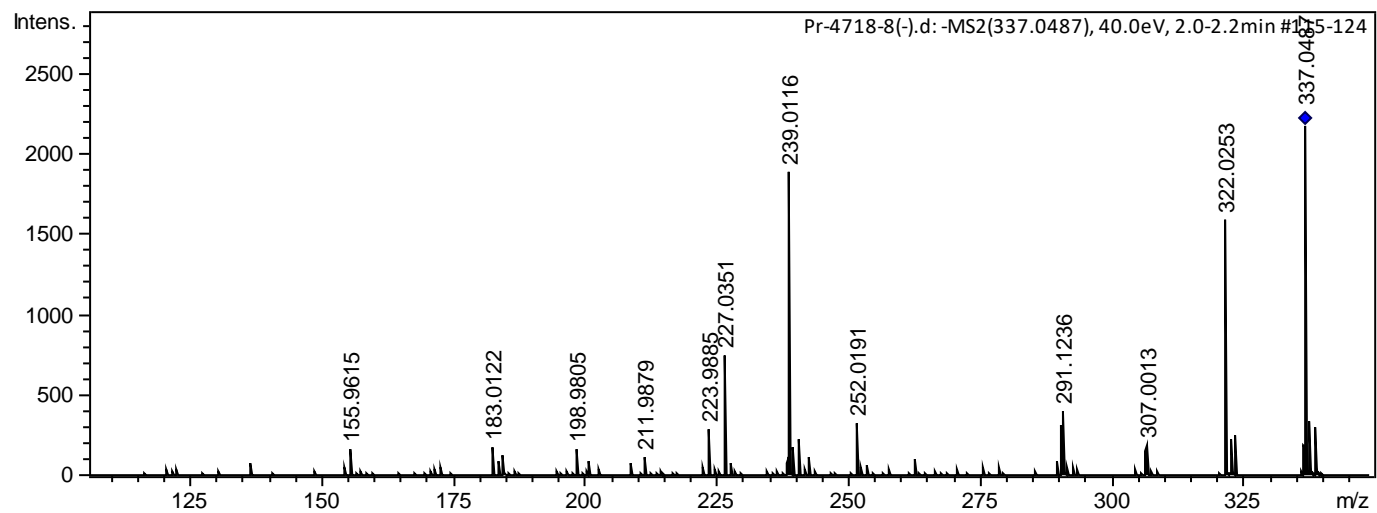
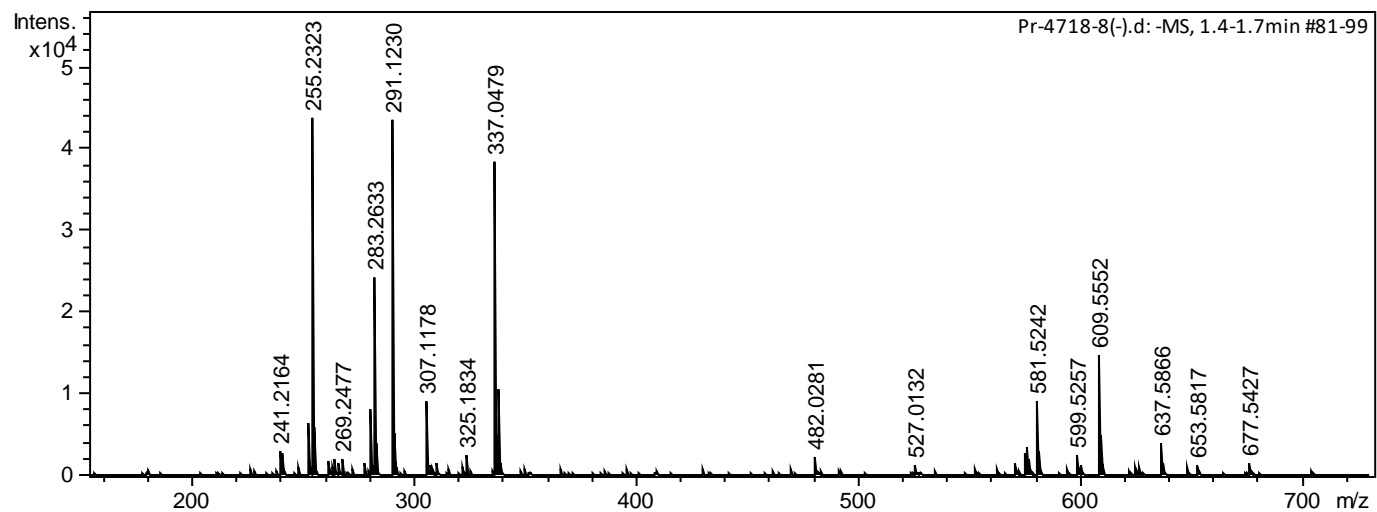




Figure S31.  $^1\text{H}$  NMR spectrum of **8** measured at 700 MHz in acetone- $\text{d}_6$

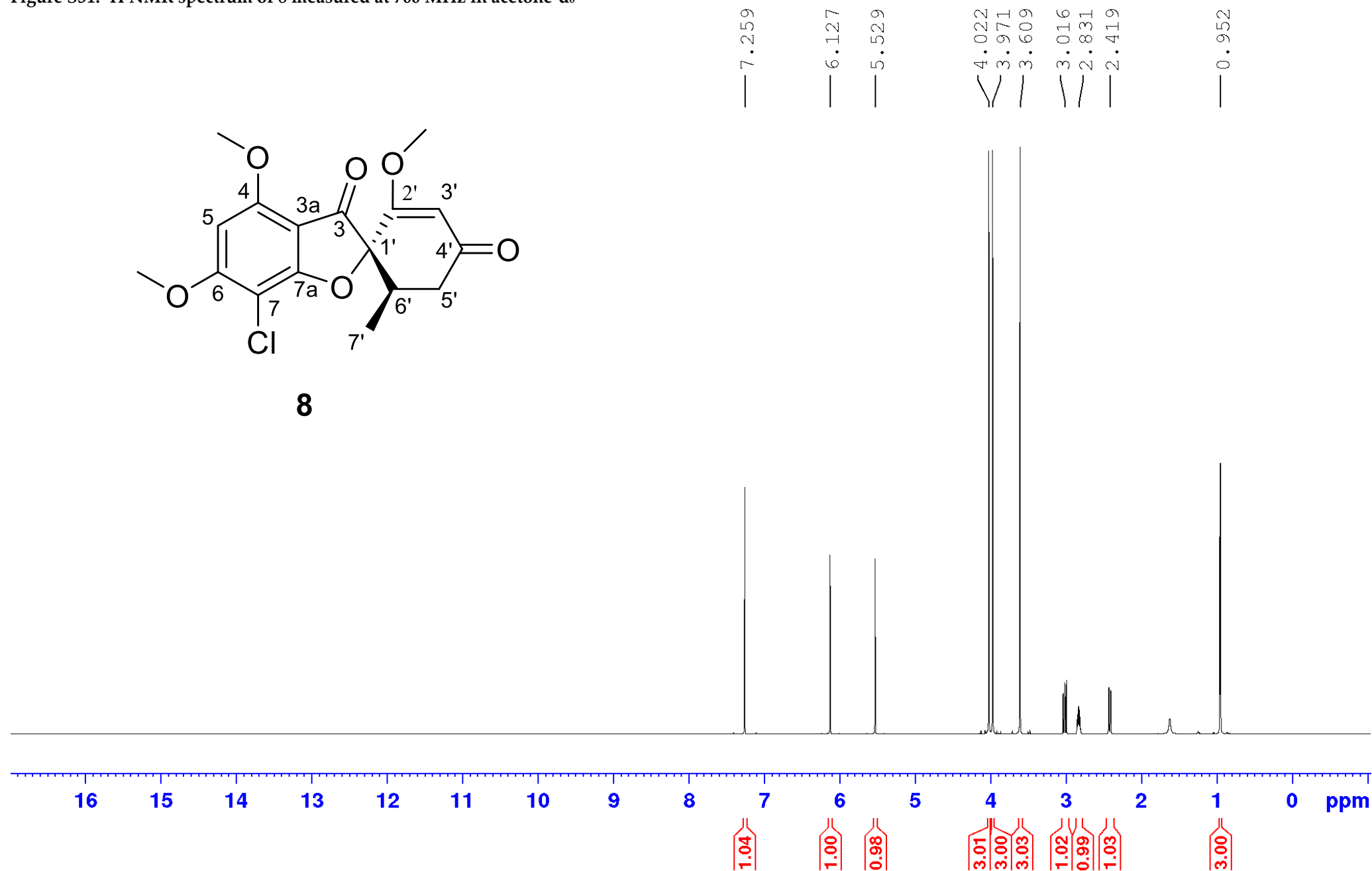


Figure S32.  $^{13}\text{C}$  NMR spectrum of **8** measured at 175 MHz in acetone- $\text{d}_6$

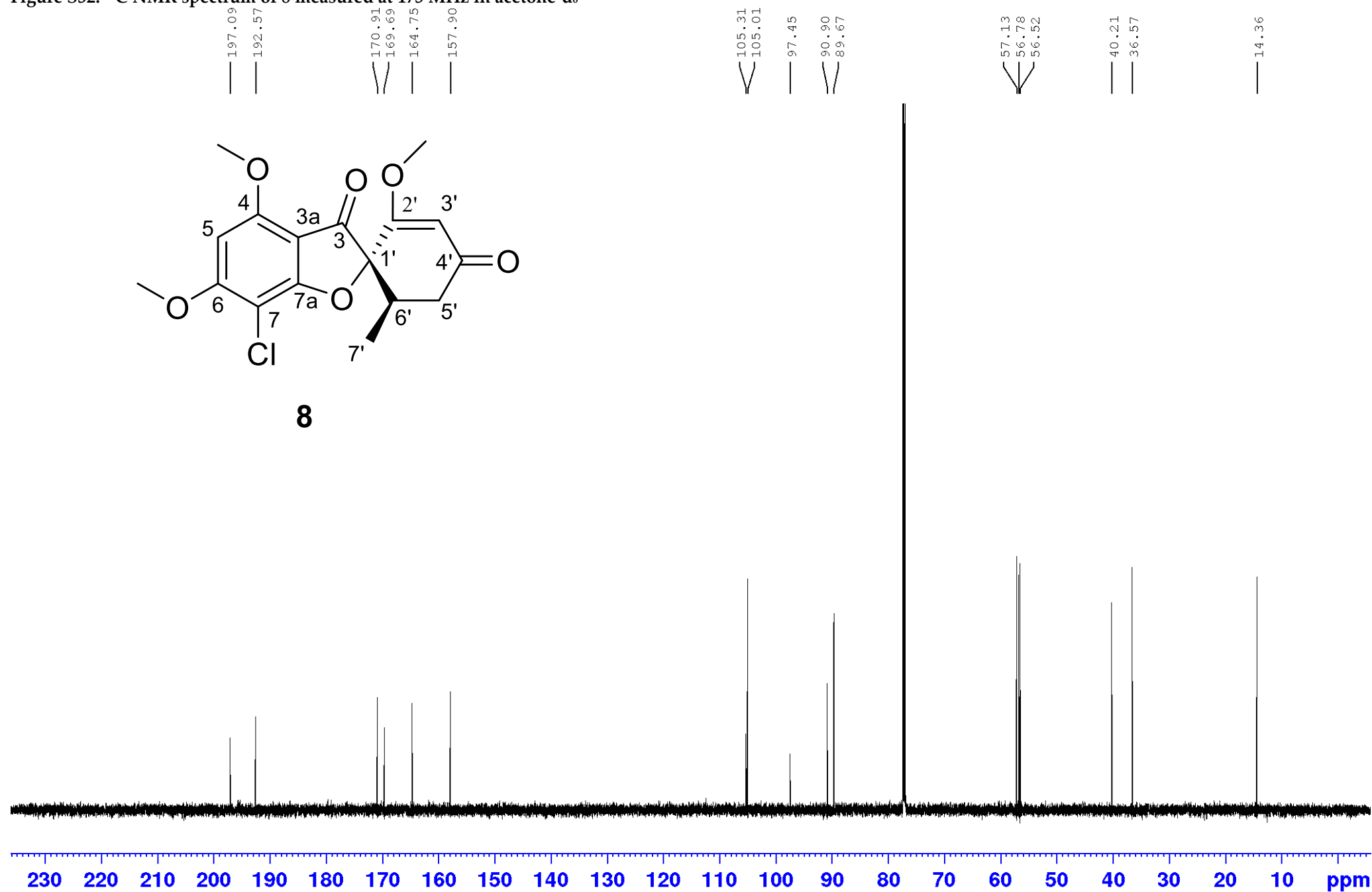
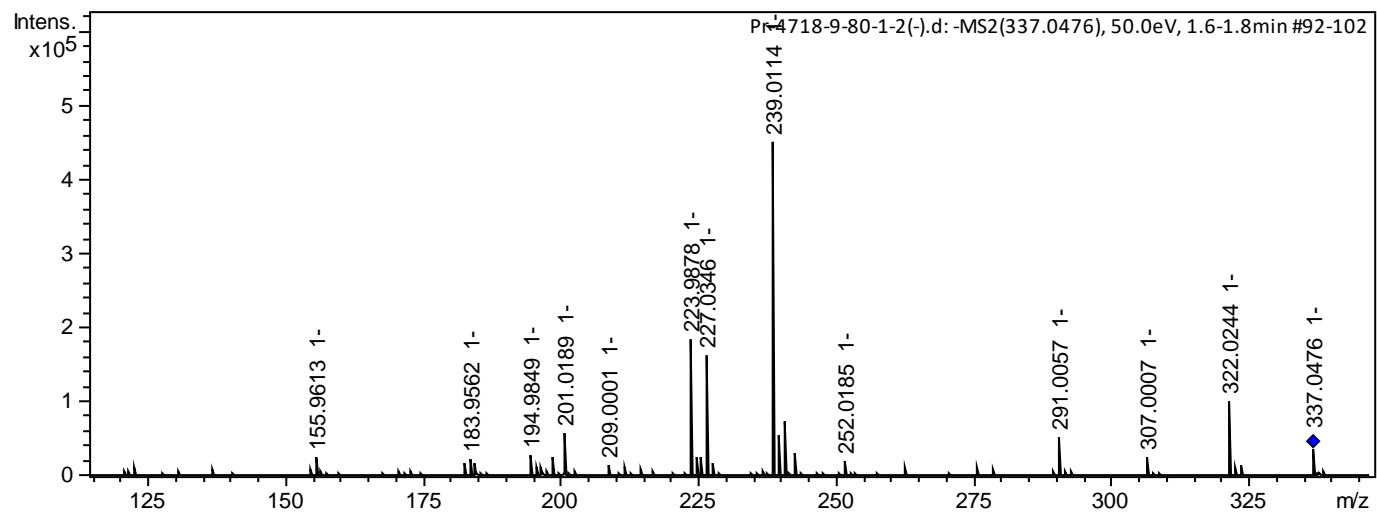
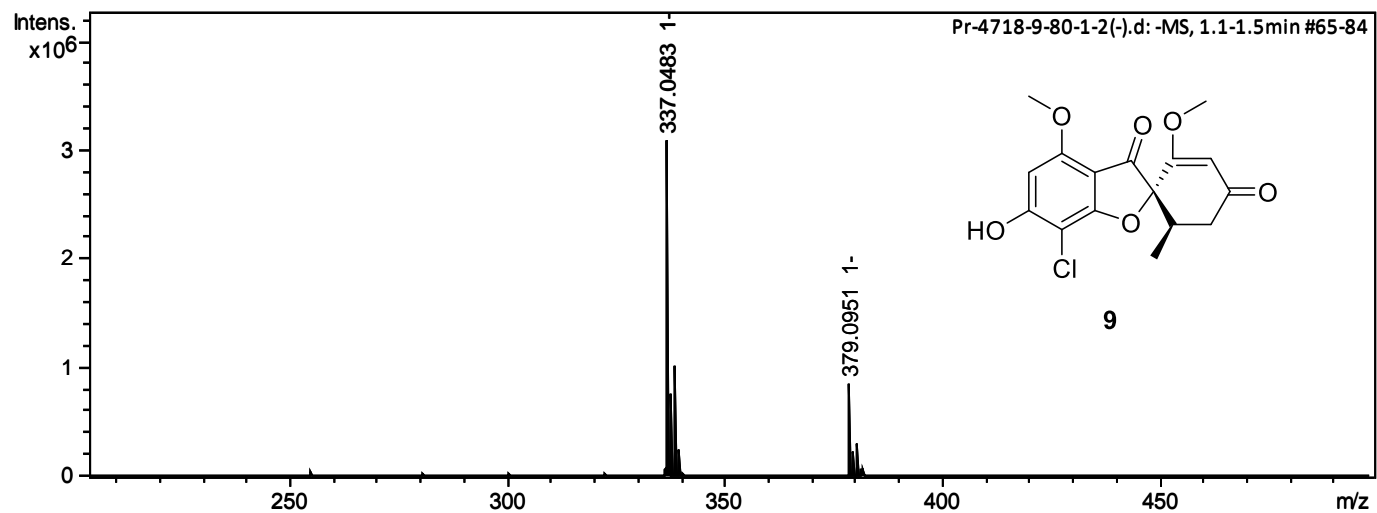


Figure S33. HRESIMS for 9



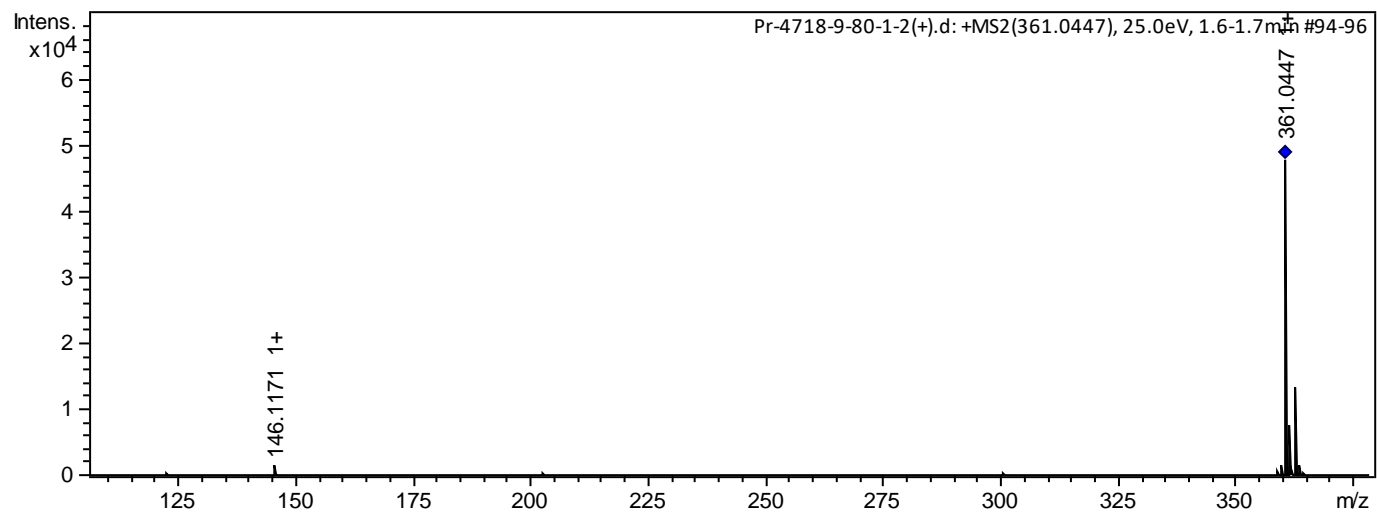
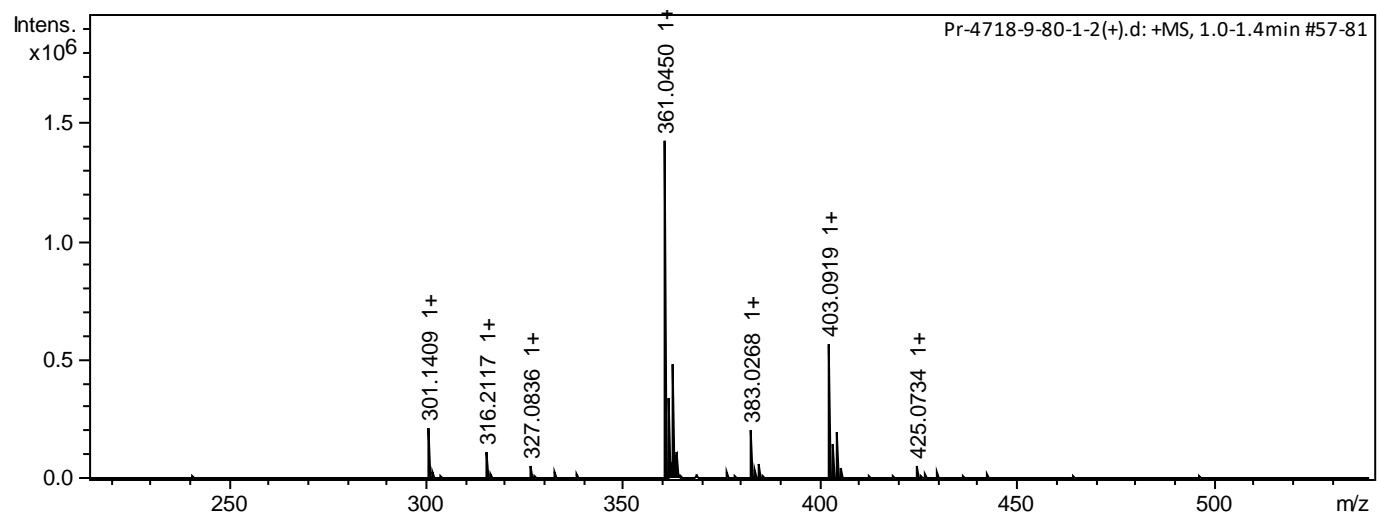


Figure S34.  $^1\text{H}$  NMR spectrum of **9** measured at 700 MHz in acetone- $\text{d}_6$

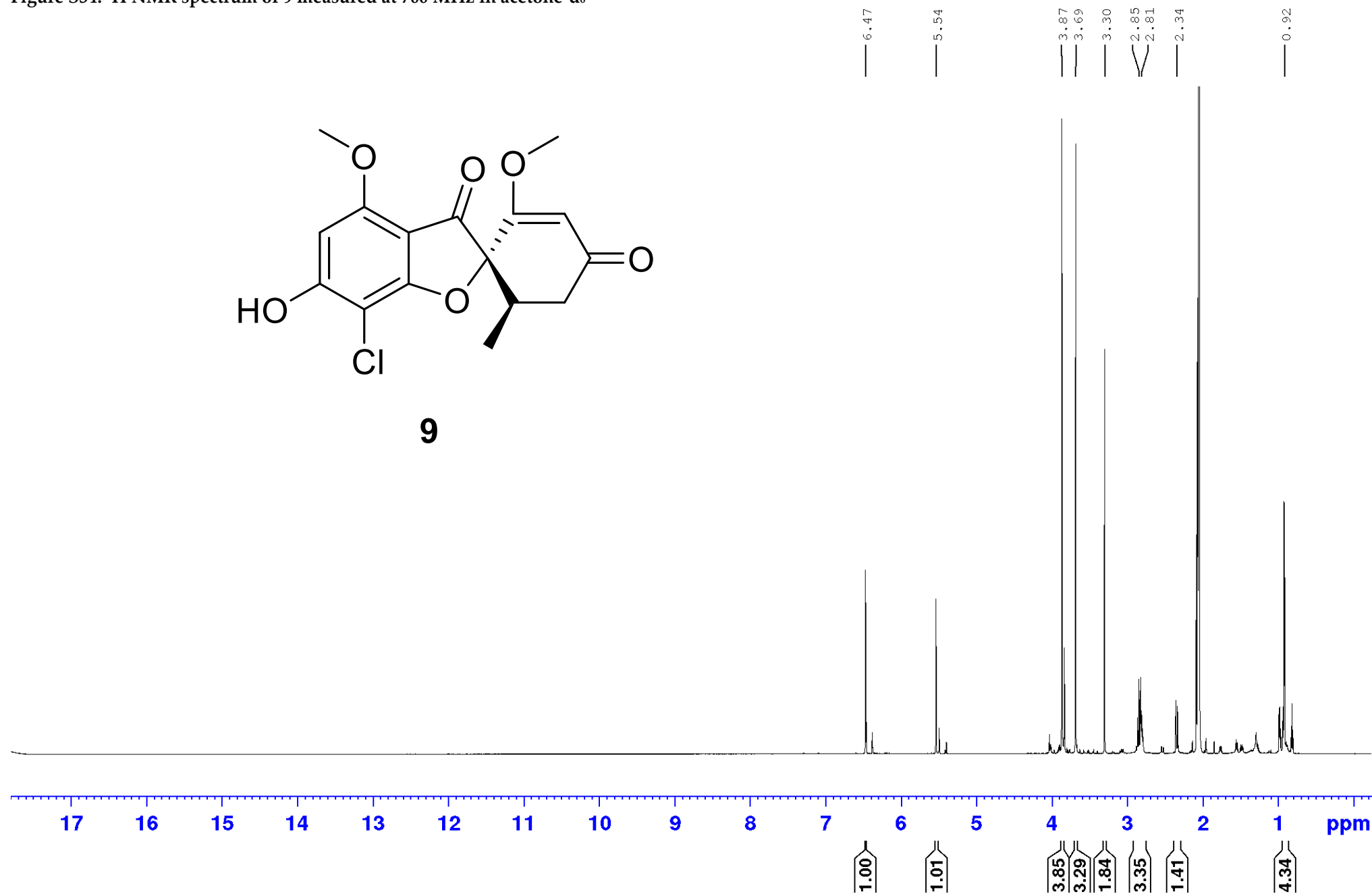


Figure S35.  $^{13}\text{C}$  NMR spectrum of **9** measured at 175 MHz in acetone- $\text{d}_6$

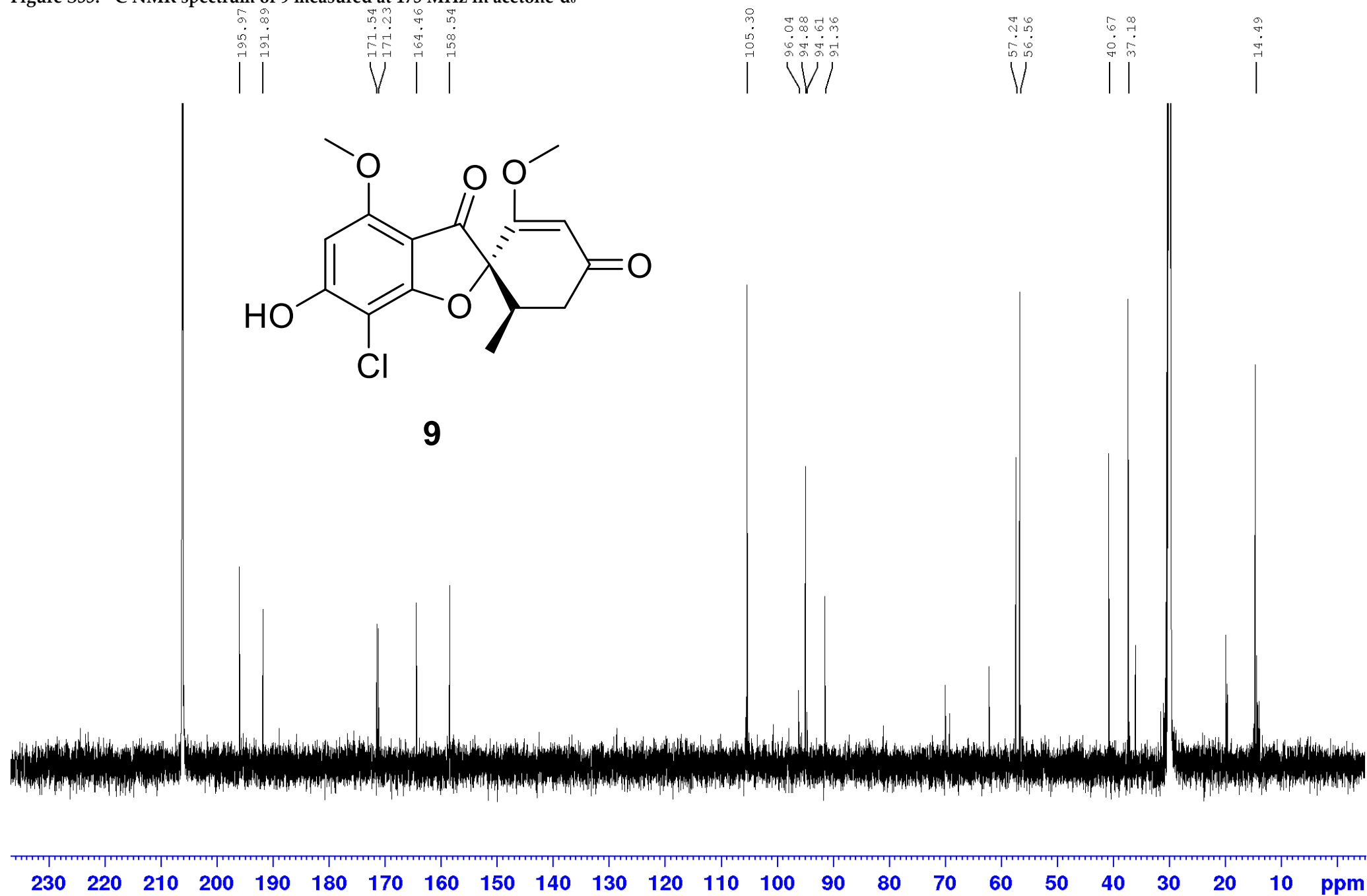
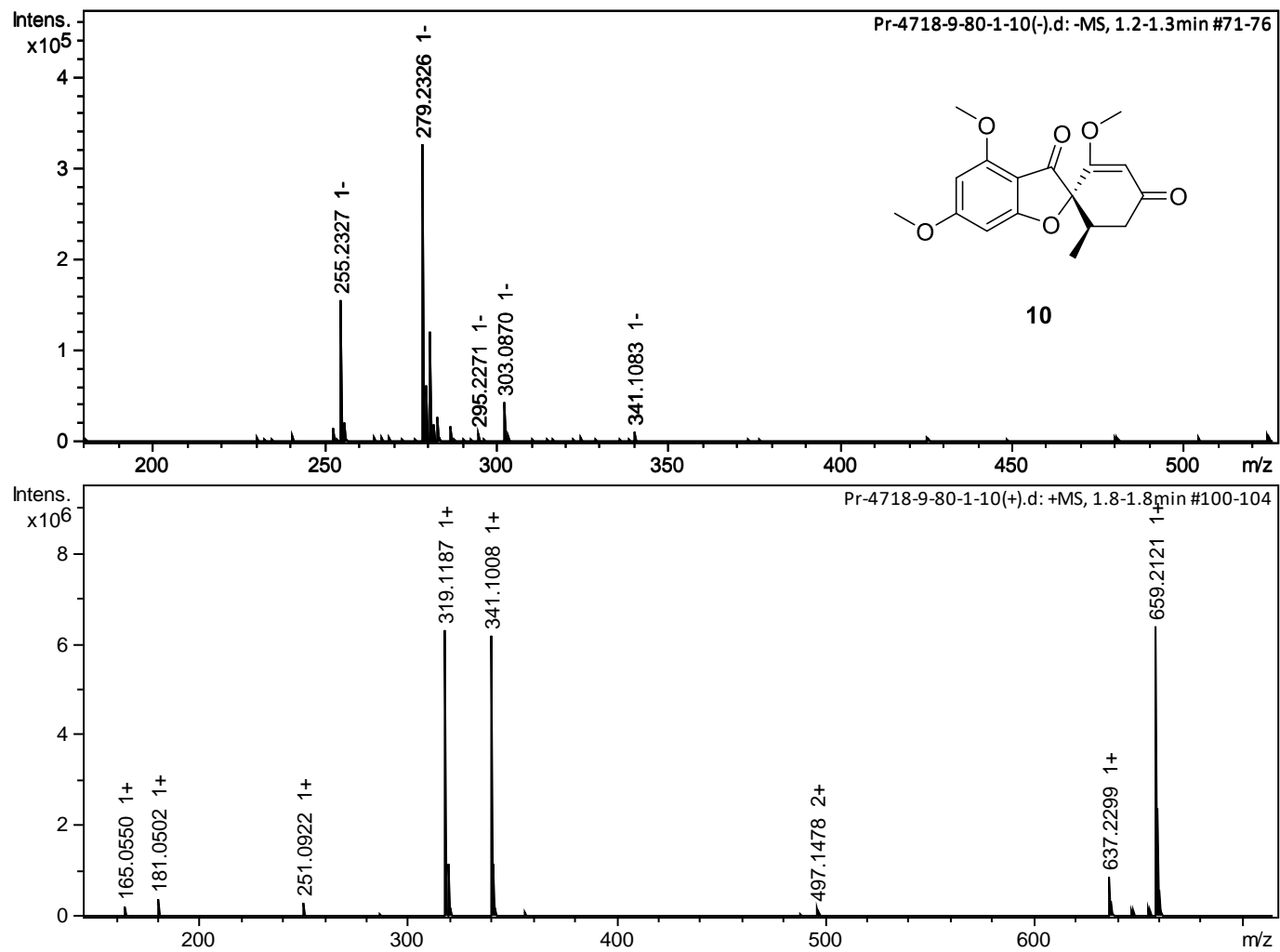


Figure S36. HRESIMS for 10



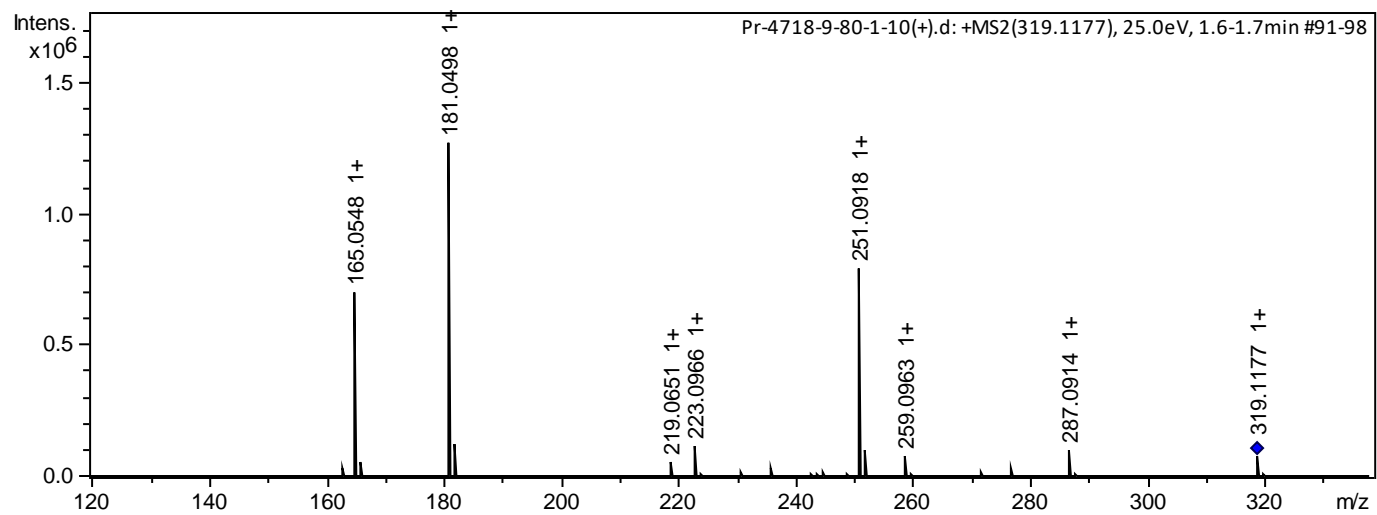




Figure S37.  $^1\text{H}$  NMR spectrum of **10** measured at 500 MHz in acetone- $\text{d}_6$

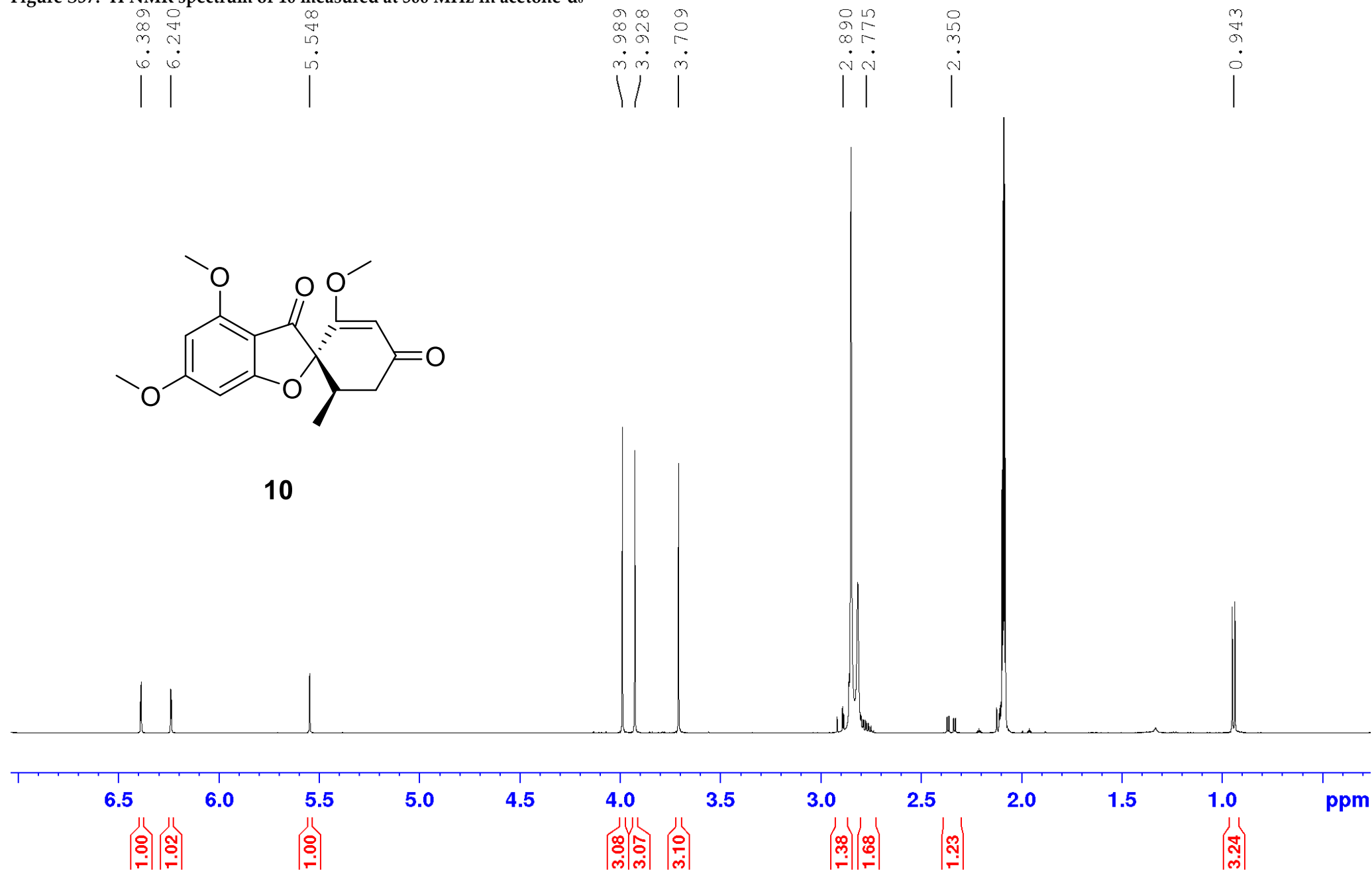


Figure S38.  $^{13}\text{C}$  NMR spectrum of **10** measured at 125 MHz in acetone- $\text{d}_6$

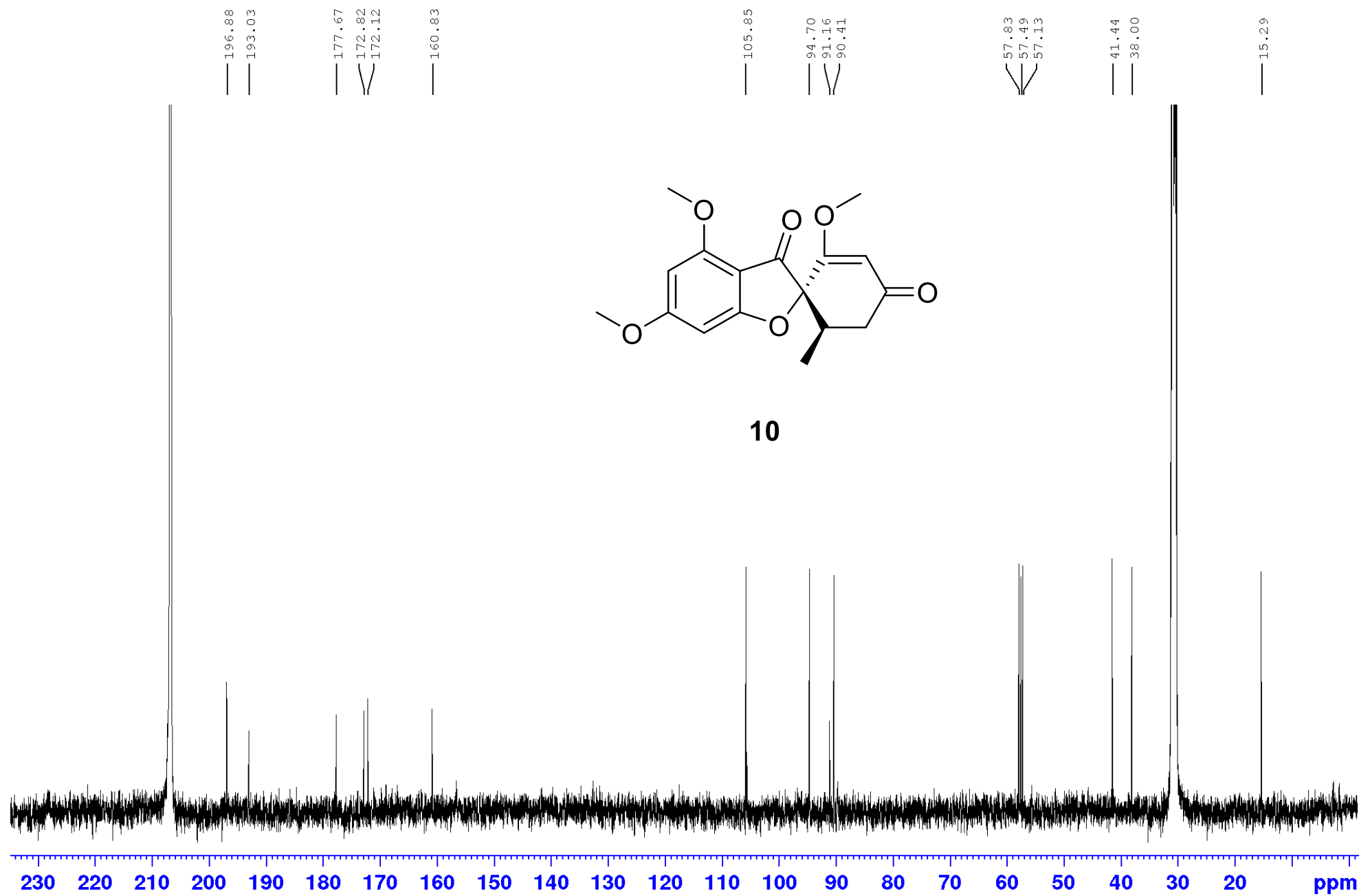
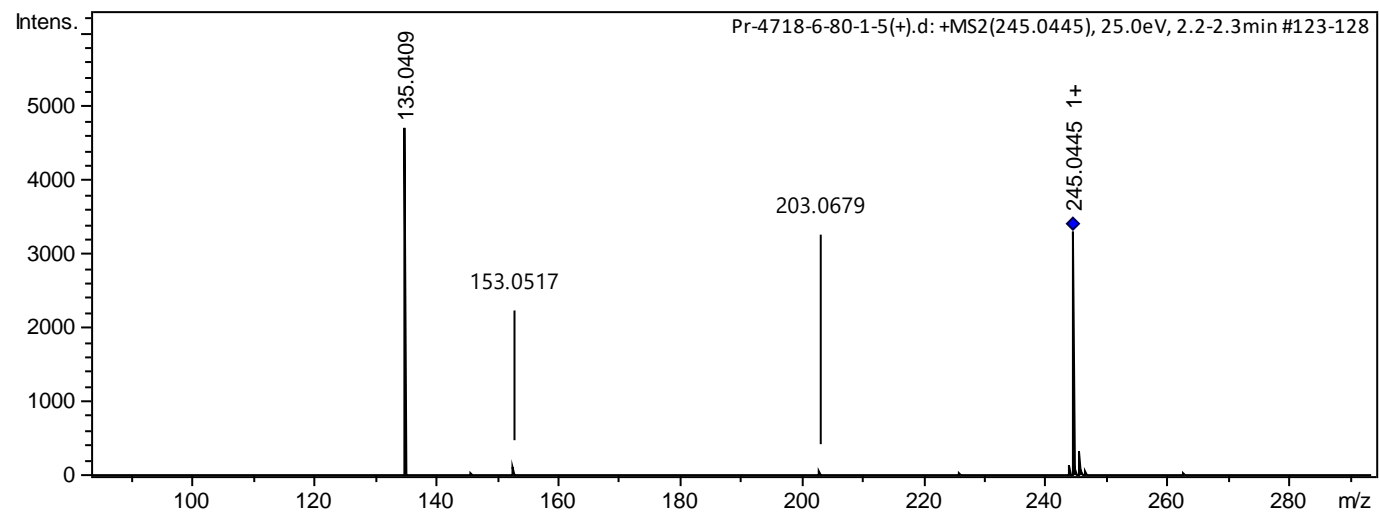
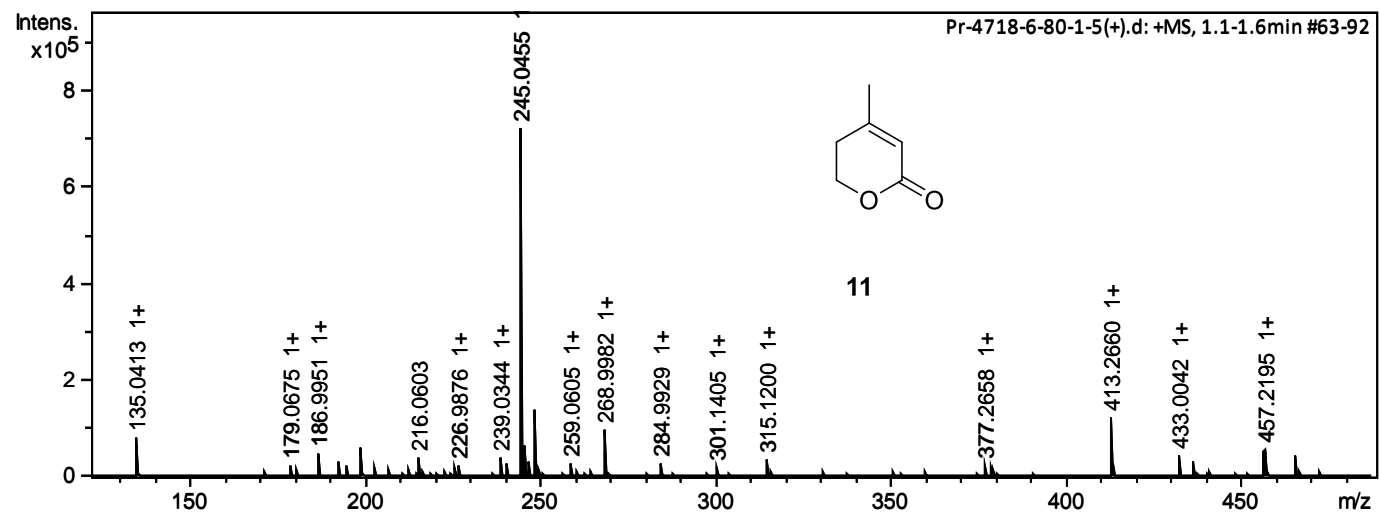


Figure S39. HRESIMS for 11



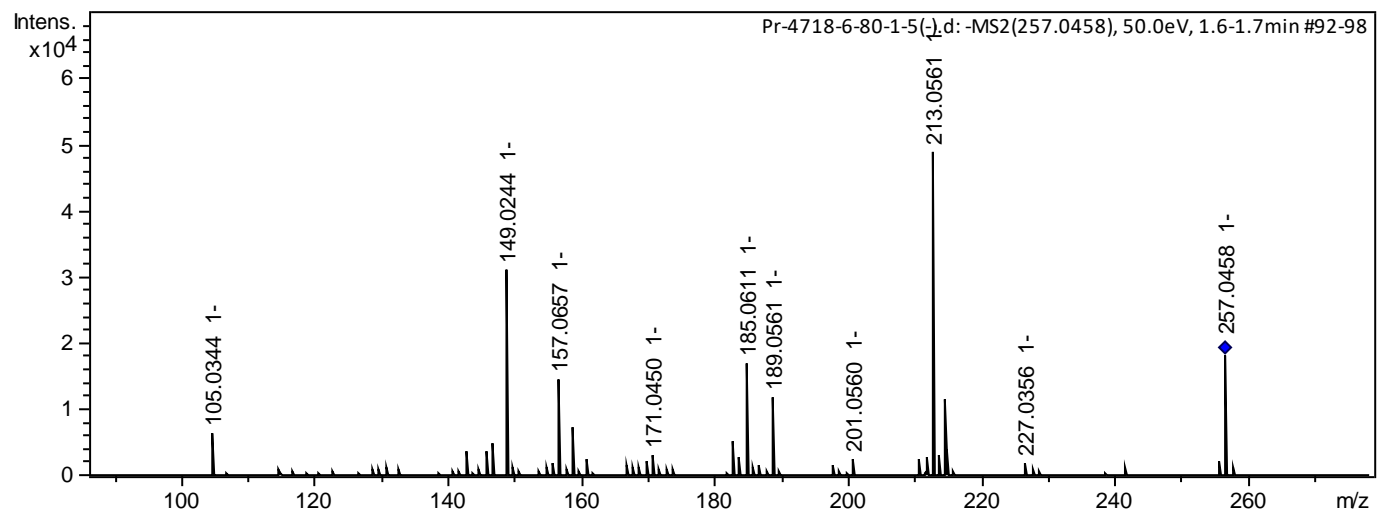
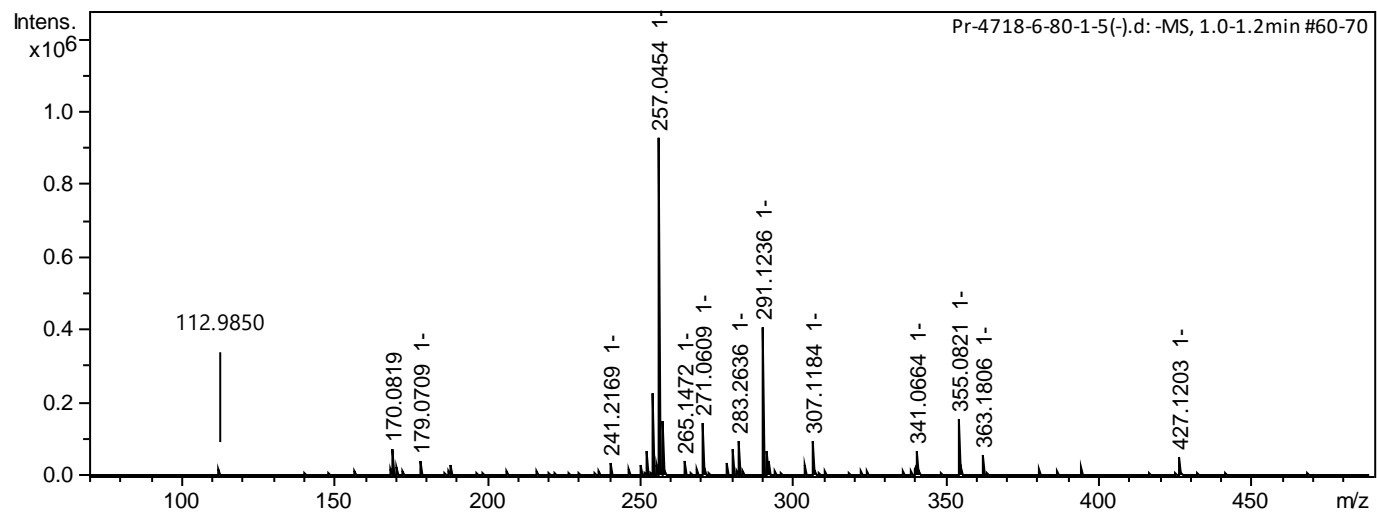
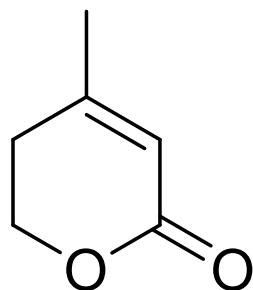


Figure S40.  $^1\text{H}$  NMR spectrum of 11 measured at 500 MHz in acetone- $\text{d}_6$



11

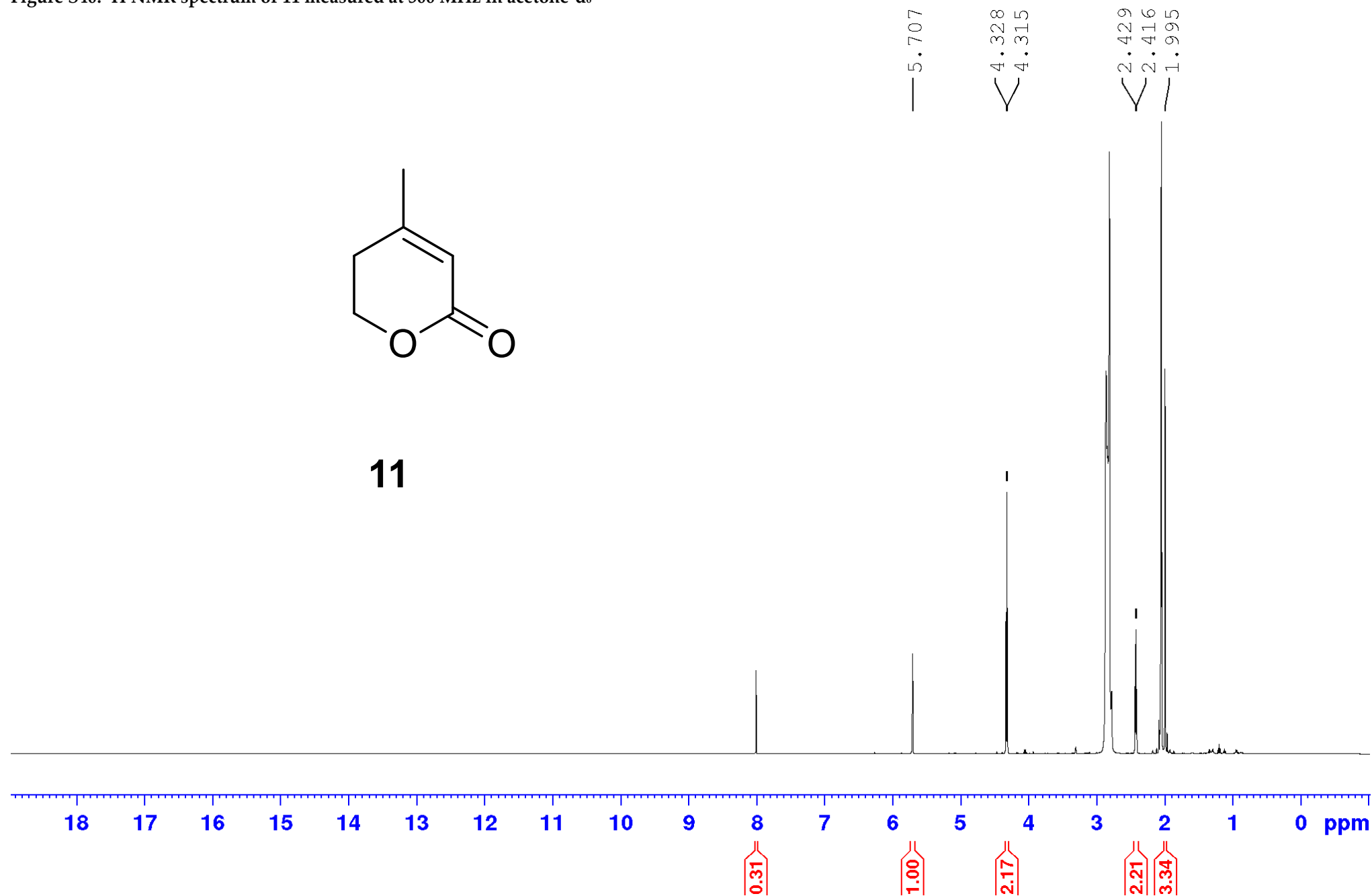
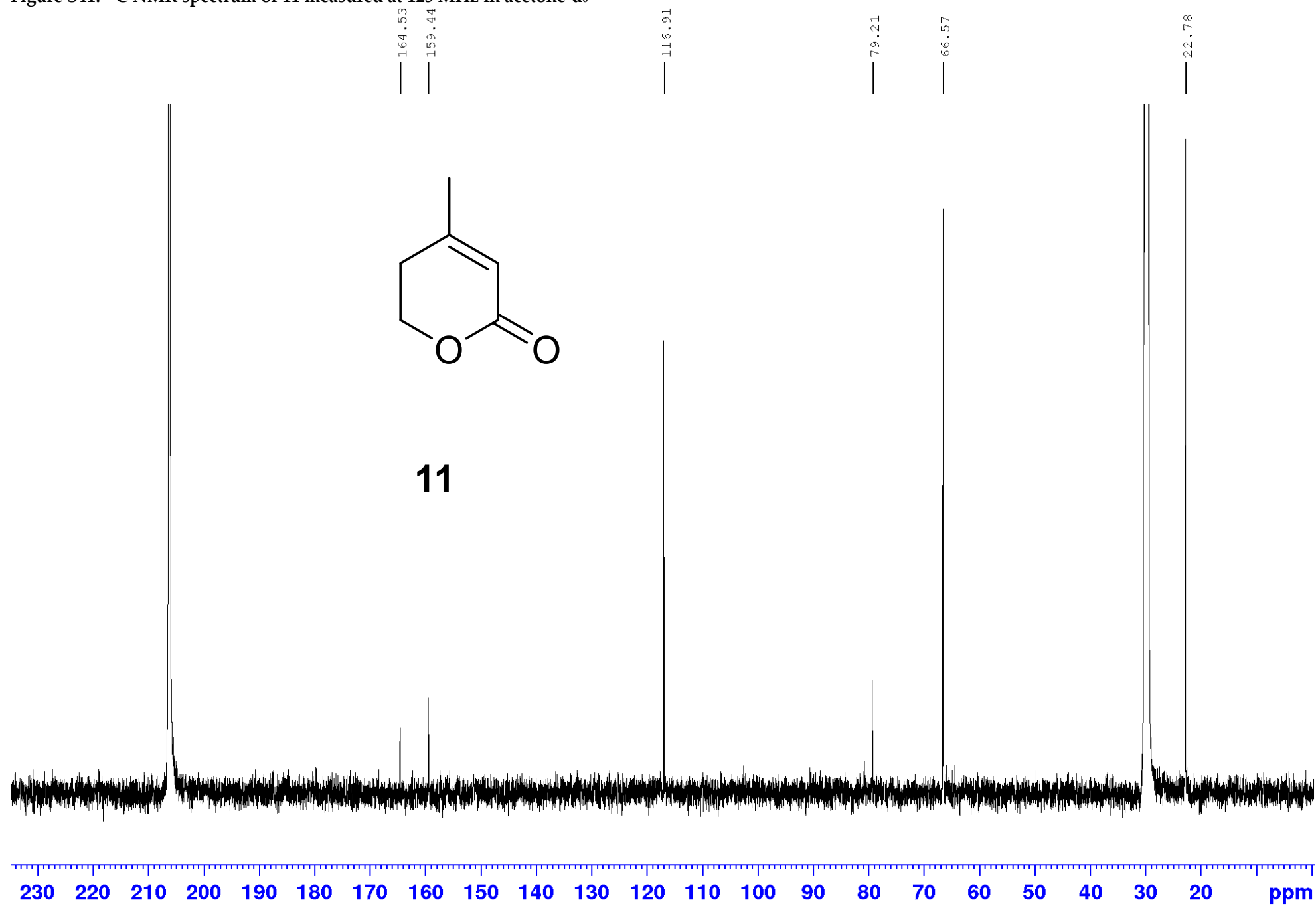
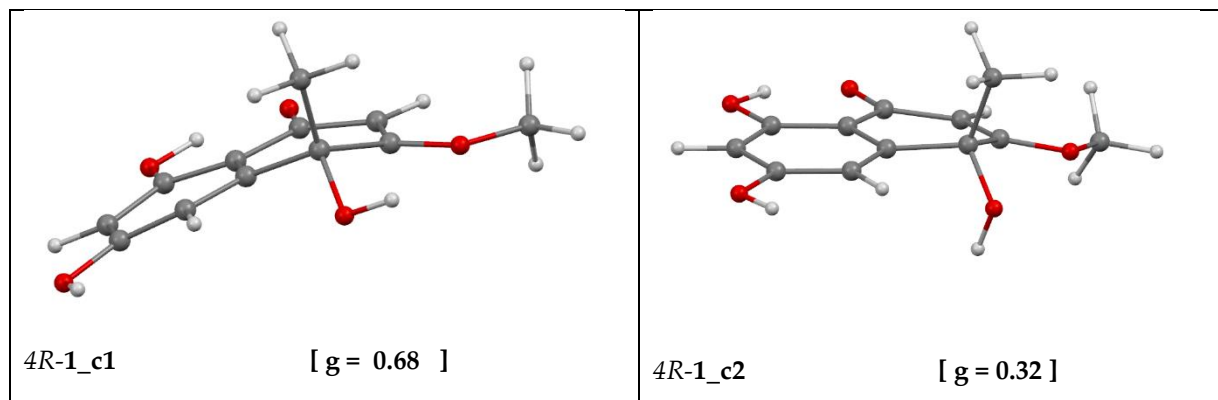


Figure S41.  $^{13}\text{C}$  NMR spectrum of 11 measured at 125 MHz in acetone- $\text{d}_6$

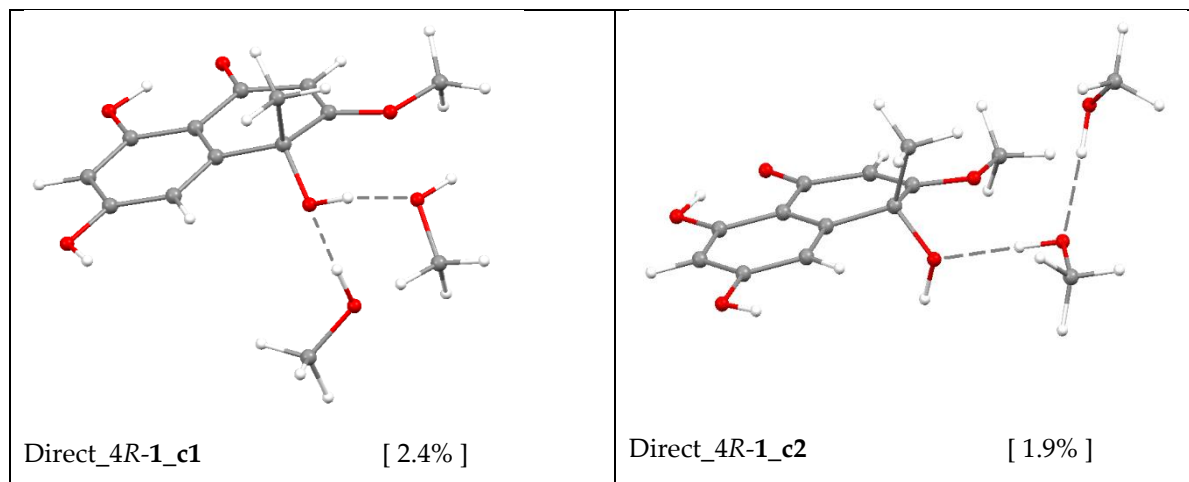


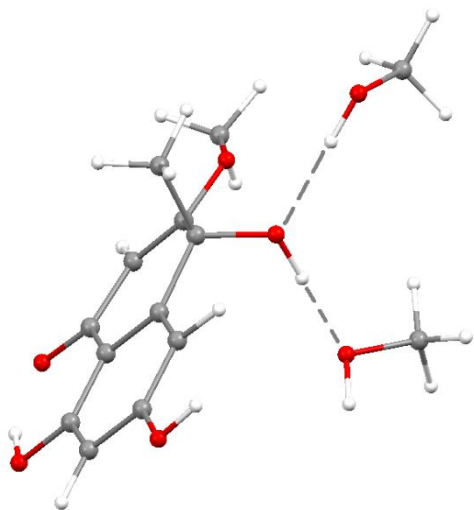
**Figure S42. Two most stable conformations of *R*-1 calculated with B3LYP/cc-pvTz\_PCM method.**

Interaction between compounds under study with the solvent was accounted for at two levels of theory: first, using polarizable continuum model (PCM; “PCM level”), and second, via direct introduction to theoretical model of two methanol molecules (Direct; “Direct level”). At the “Direct level” the PCM approach was also used for modeling interaction of the clusters  $1\&(\text{CH}_3\text{OH})\times 2$  and  $2\&(\text{CH}_3\text{OH})\times 2$  with the solvent.



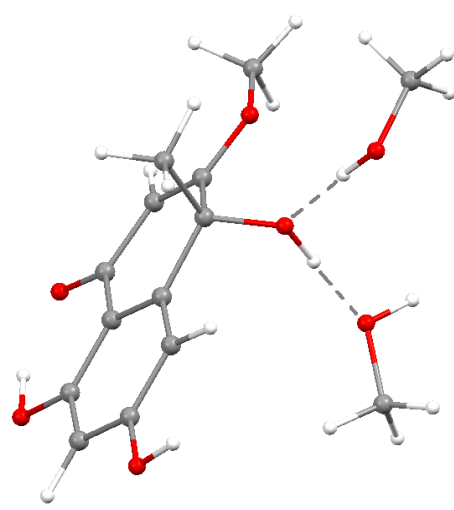
**Figure S43. The optimized structures of  $4R-1\&(\text{CH}_3\text{OH})\times 2$ .**





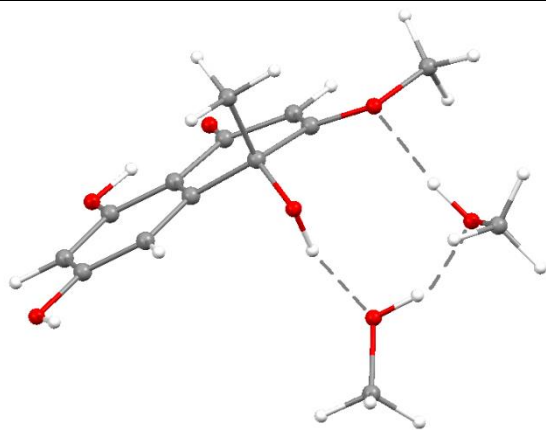
Direct\_4R-1\_c3

[ 2.6% ]



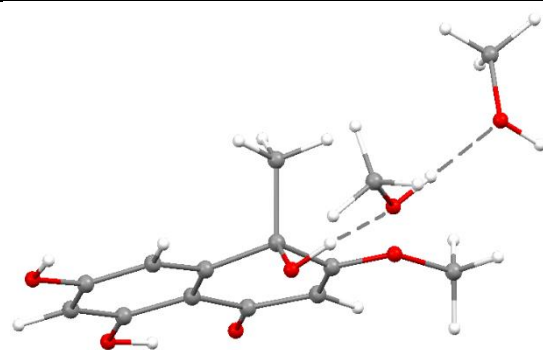
Direct\_4R-1\_c4

[ 2.6% ]



Direct\_4R-1\_c5

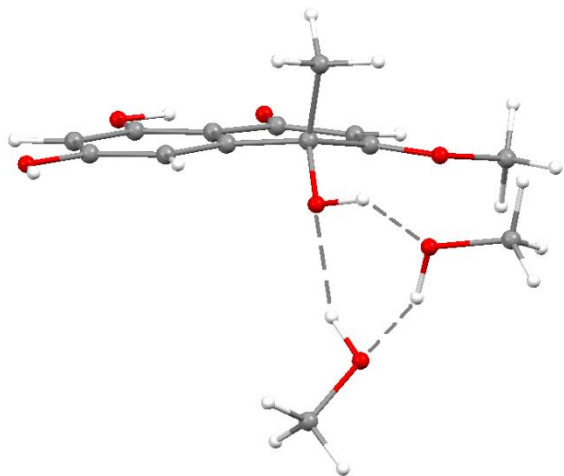
[ 60.4% ]



Direct\_4R-1\_c6

[ 18.8% ]





Direct\_4R-1\_c7

[ 11.3% ]