

## Supplementary Material

### Straightforward synthesis of unnatural poly-oxygenated steroid sapogenins

Anielka Rosado Abón and Martin A. Iglesias-Arteaga\*

Facultad de Química, Universidad Nacional Autónoma de México, CDMX 04510, México

Email: [martin.iglesias@unam.mx](mailto:martin.iglesias@unam.mx)

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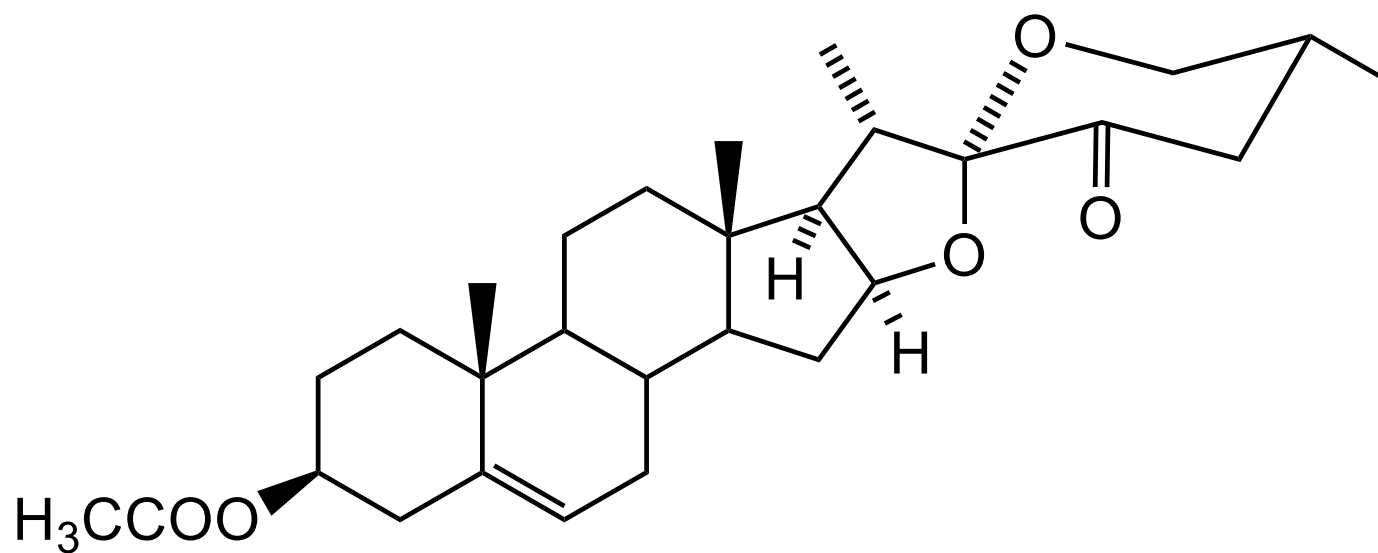
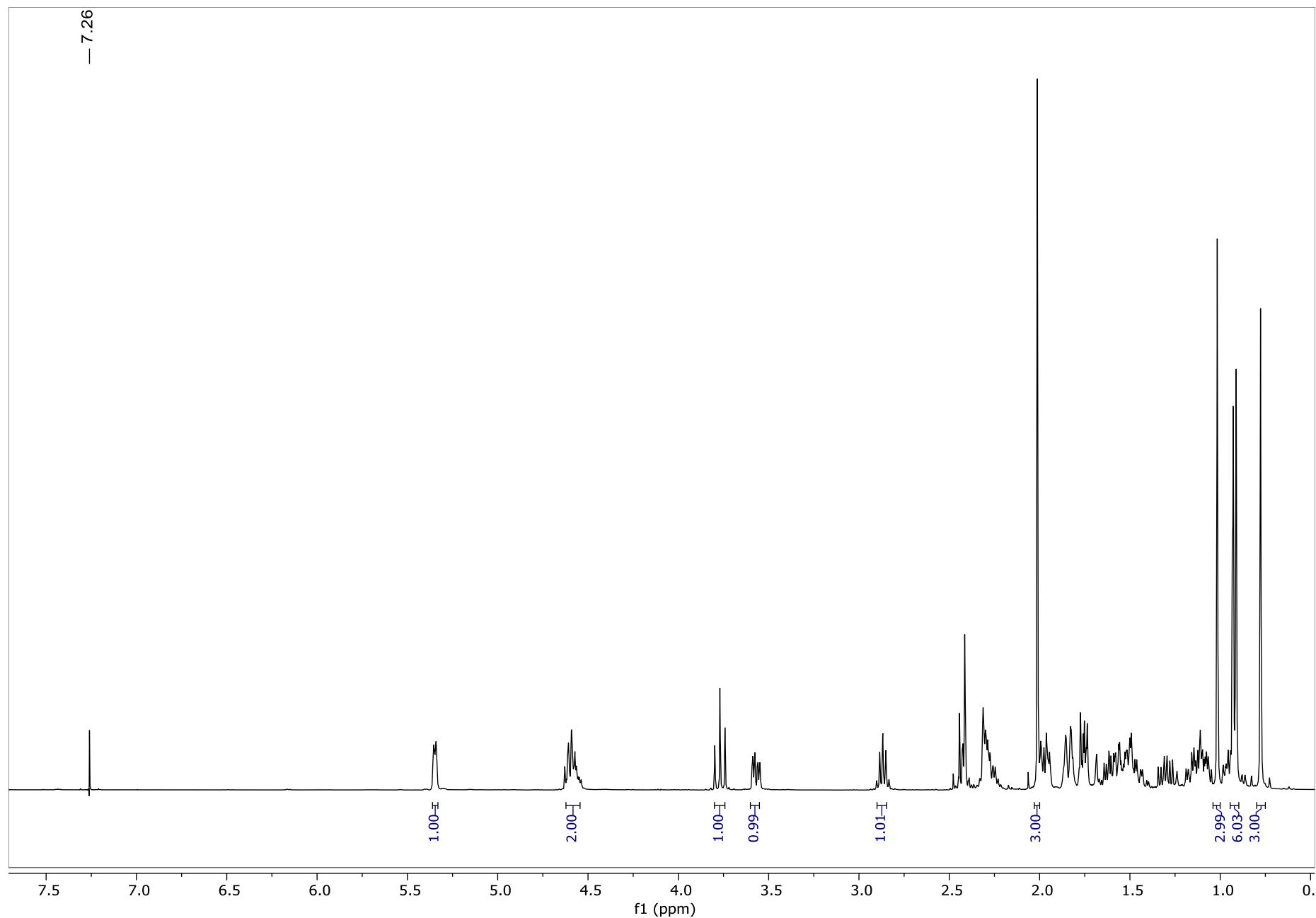
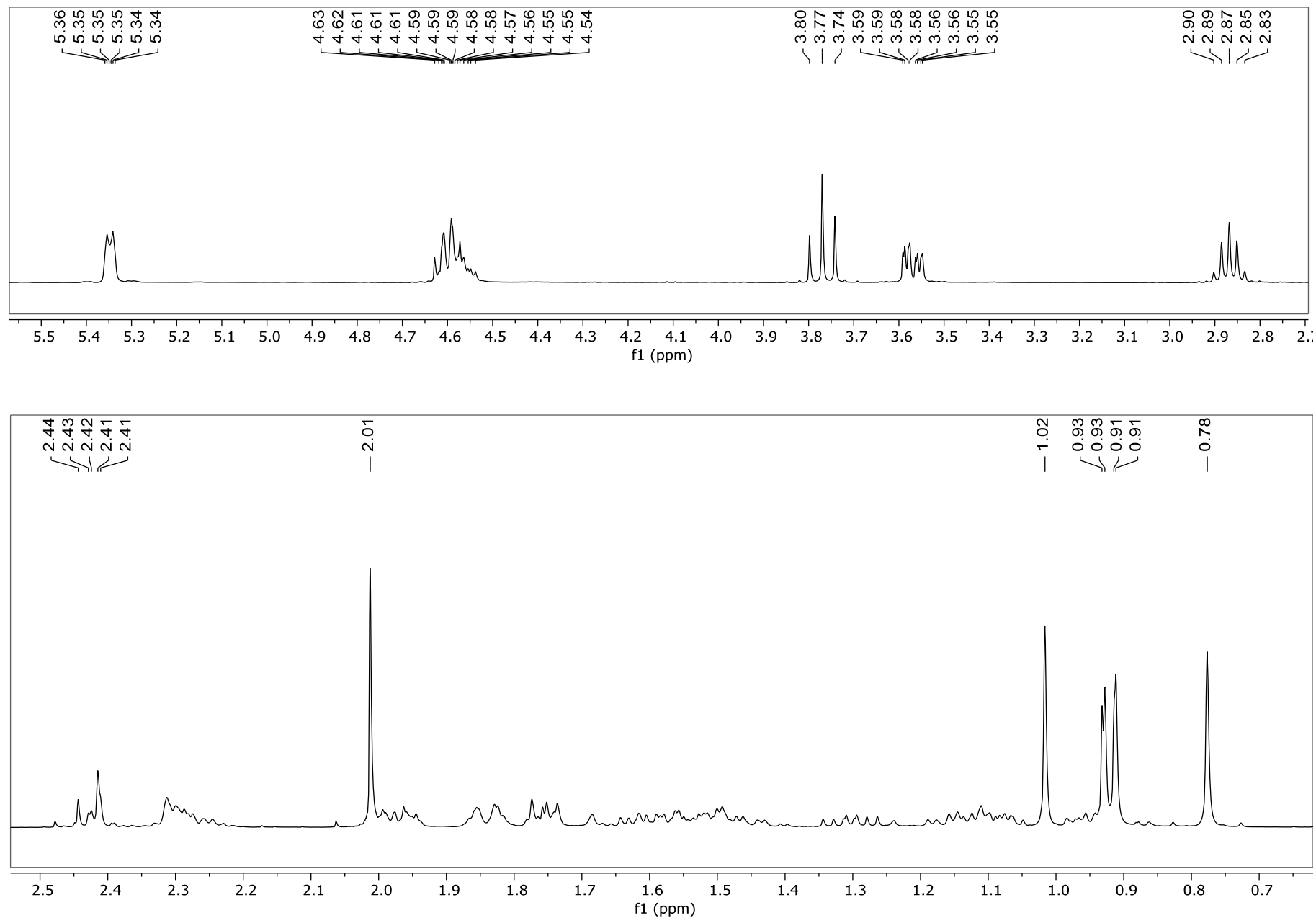


Figure S1. (25R)-3β-Acetoxy Spirost-5-en-23-one (2)

Figure S2.  $^1\text{H}$  NMR spectrum of compound 2

Figure S3. Sections of the  $^1\text{H}$  NMR spectrum of compound 2

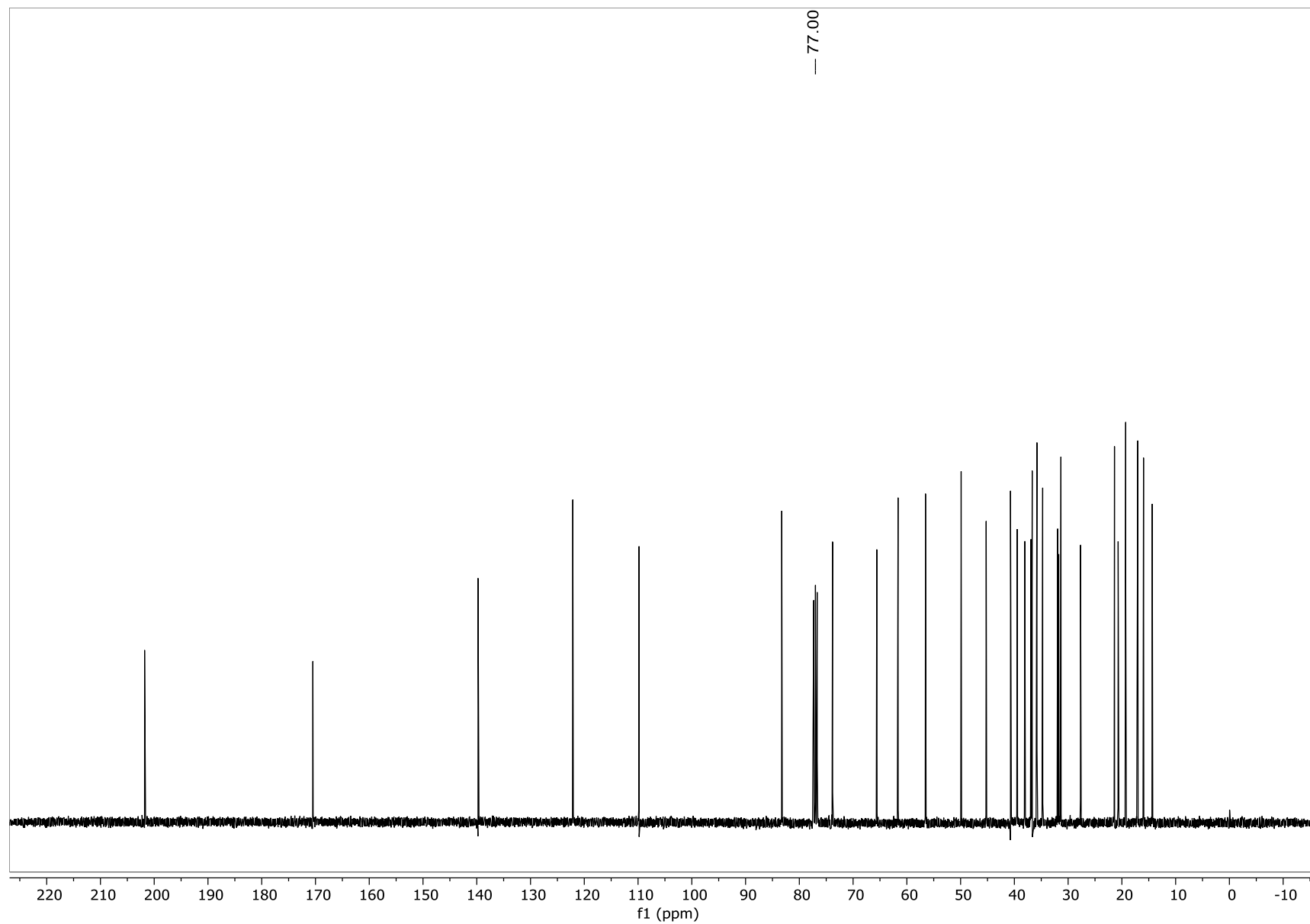
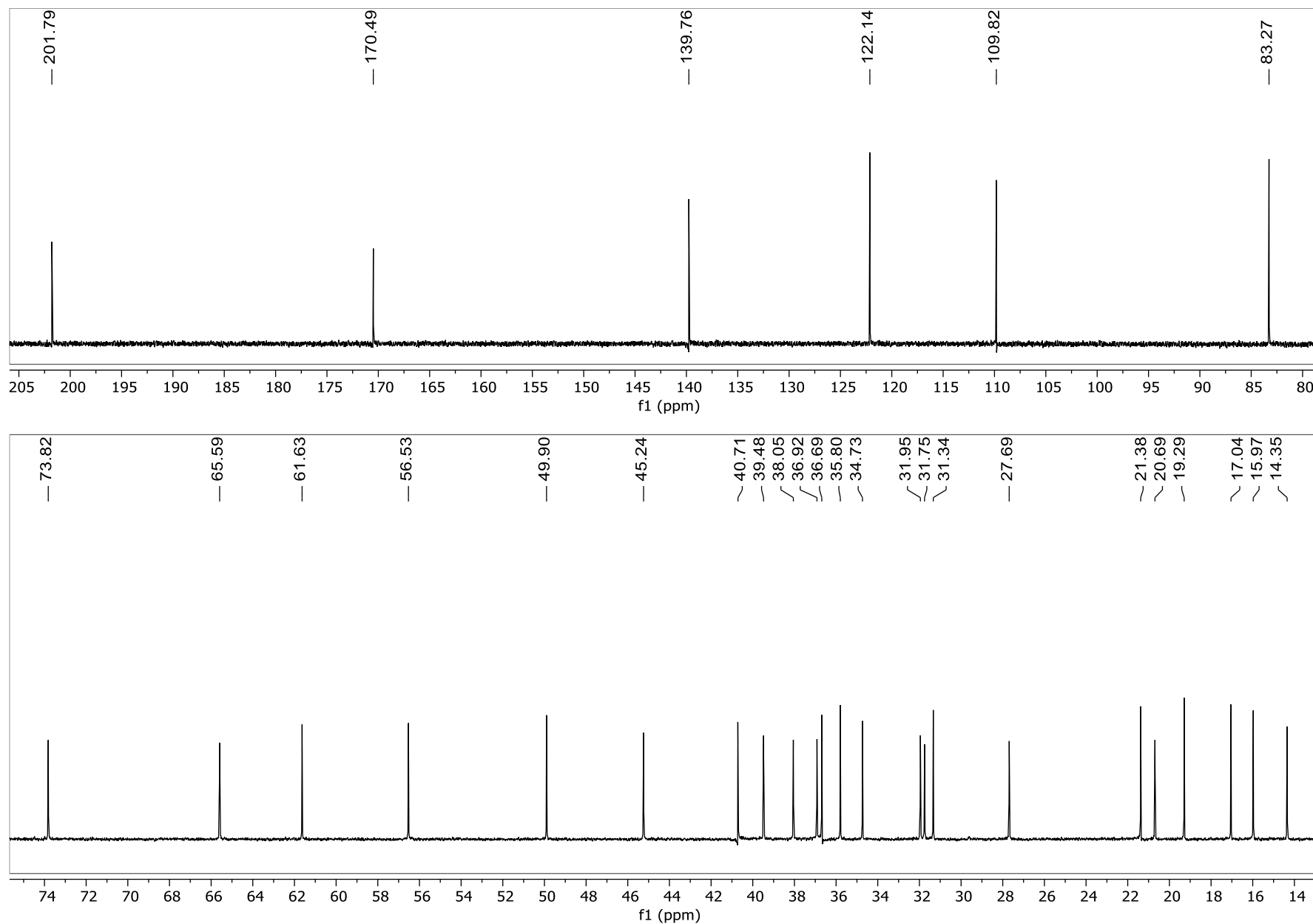
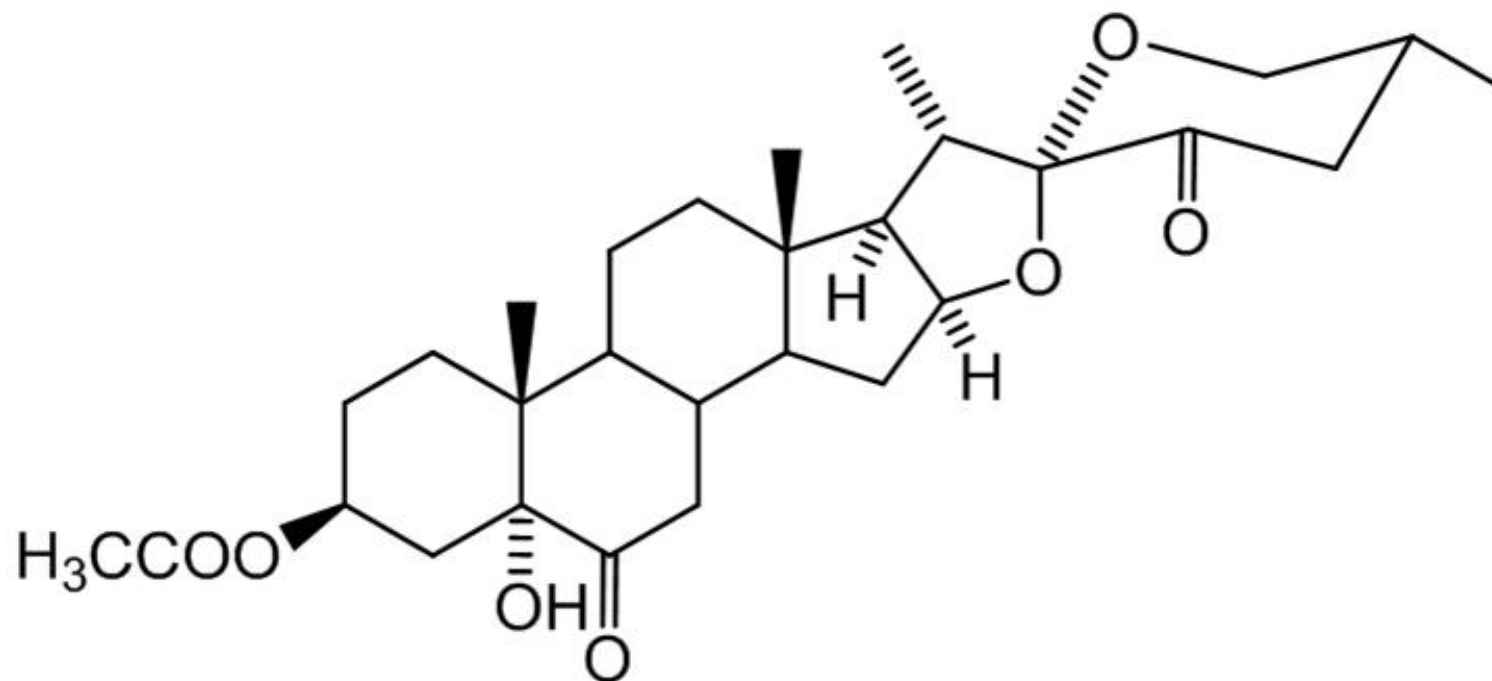


Figure S4.  $^{13}\text{C}$  NMR spectrum of compound 2

Figure S5. Sections of the  $^{13}\text{C}$  NMR spectrum of compound 2



**Figure S6. (25R)-3β-Acetoxy-5-hydroxy-5α-spirostan-6,23-dione (3)**

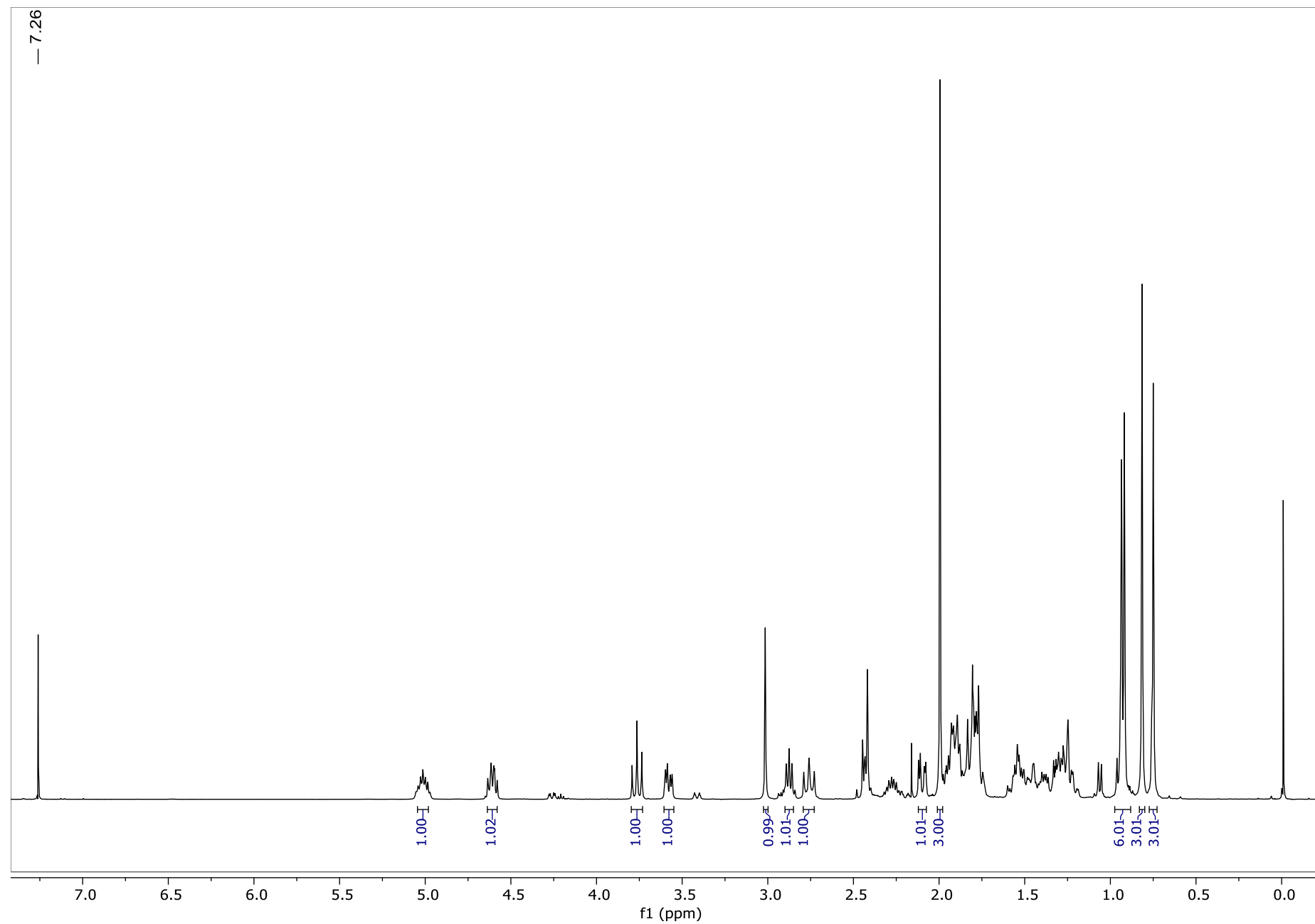
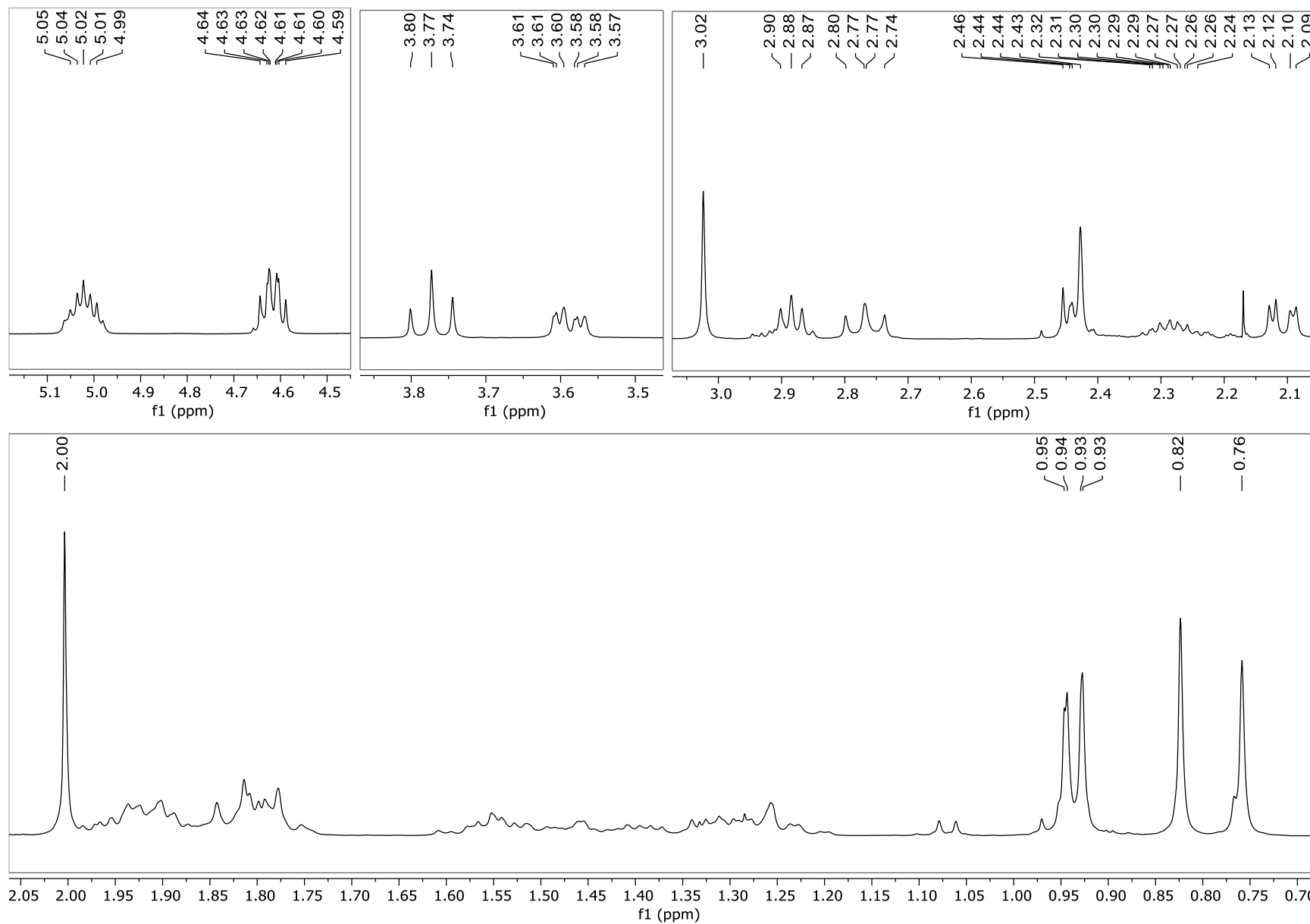


Figure S7.  $^1\text{H}$  NMR spectrum of compound 3



Figure S8. Sections of the  $^1\text{H}$  NMR spectrum of compound 3

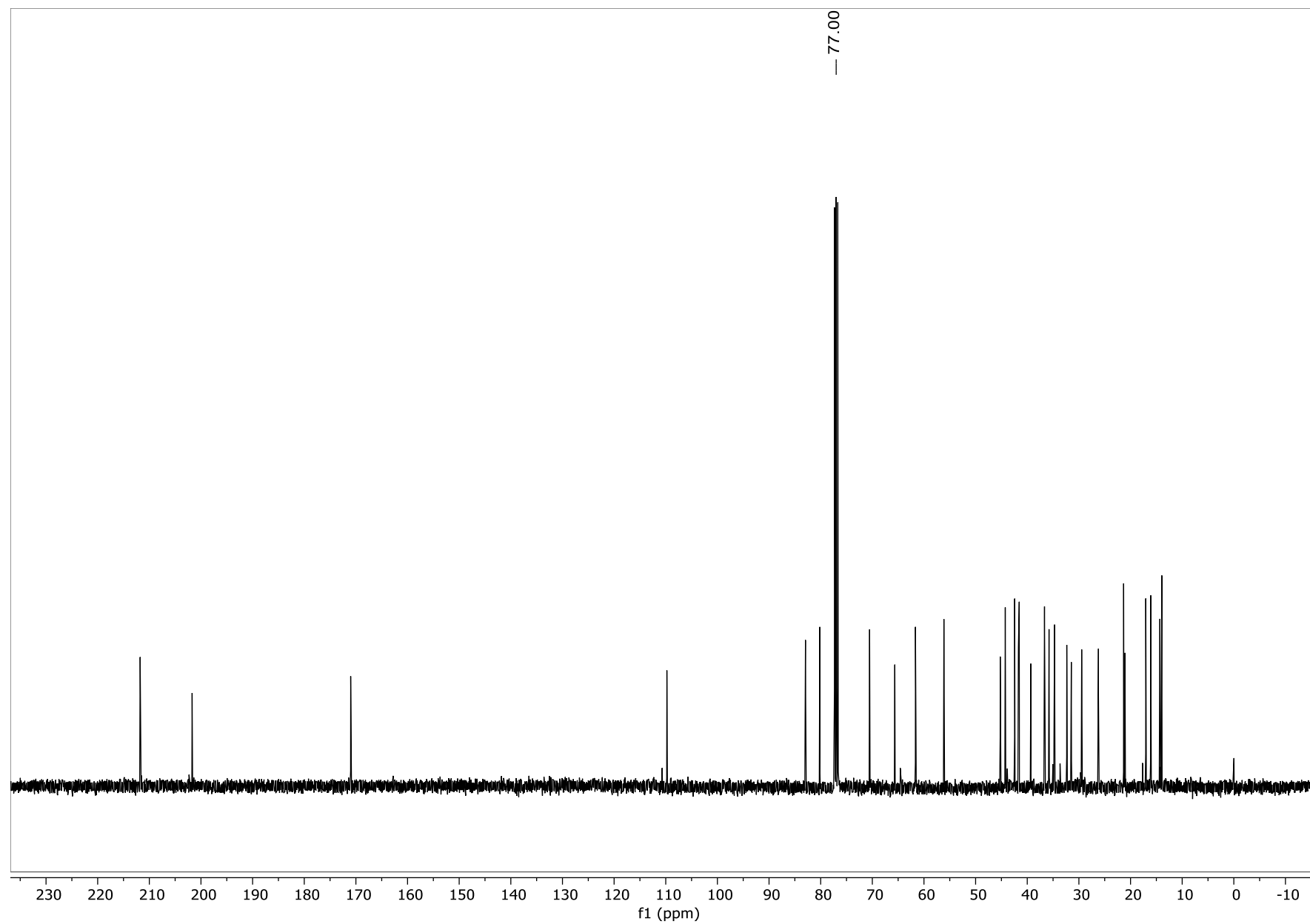
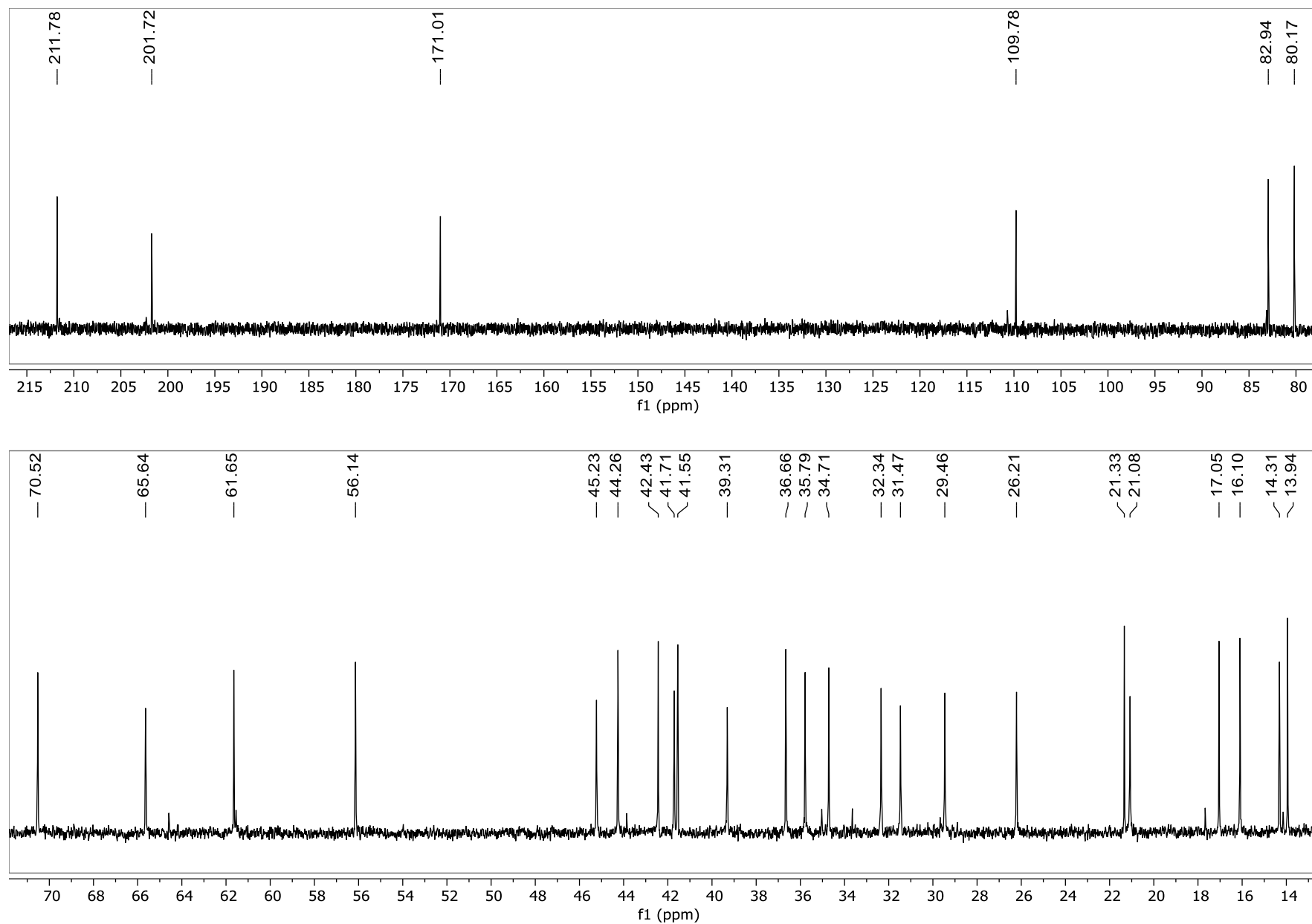
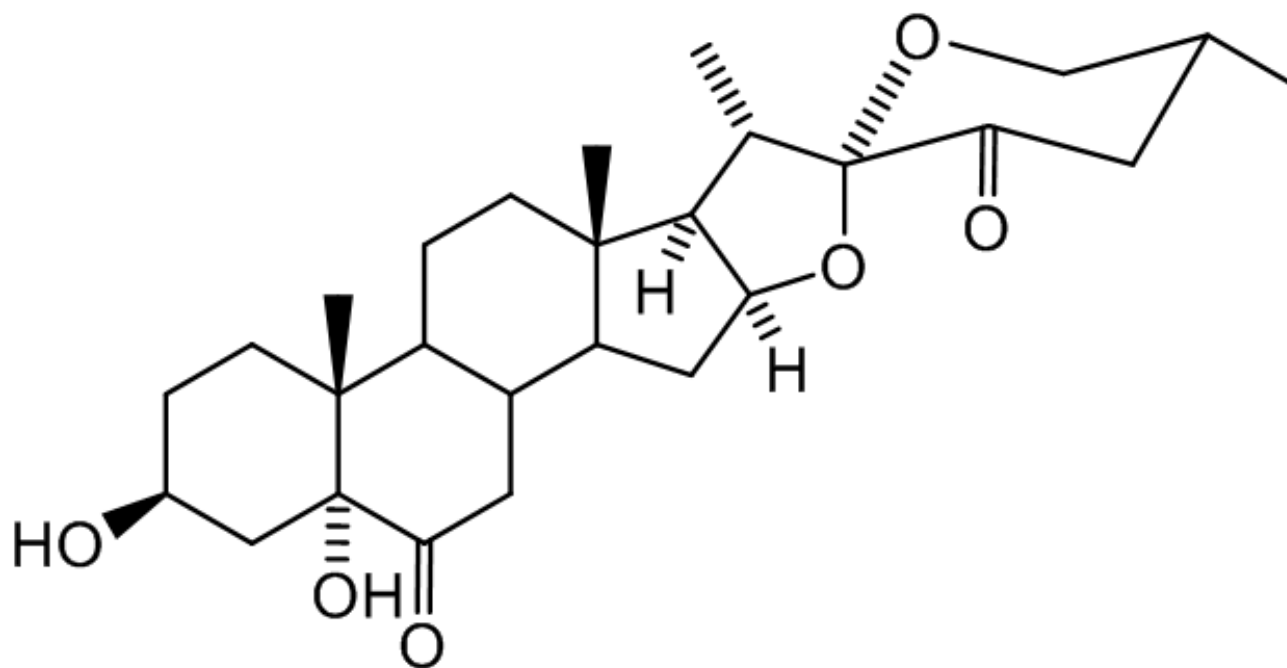
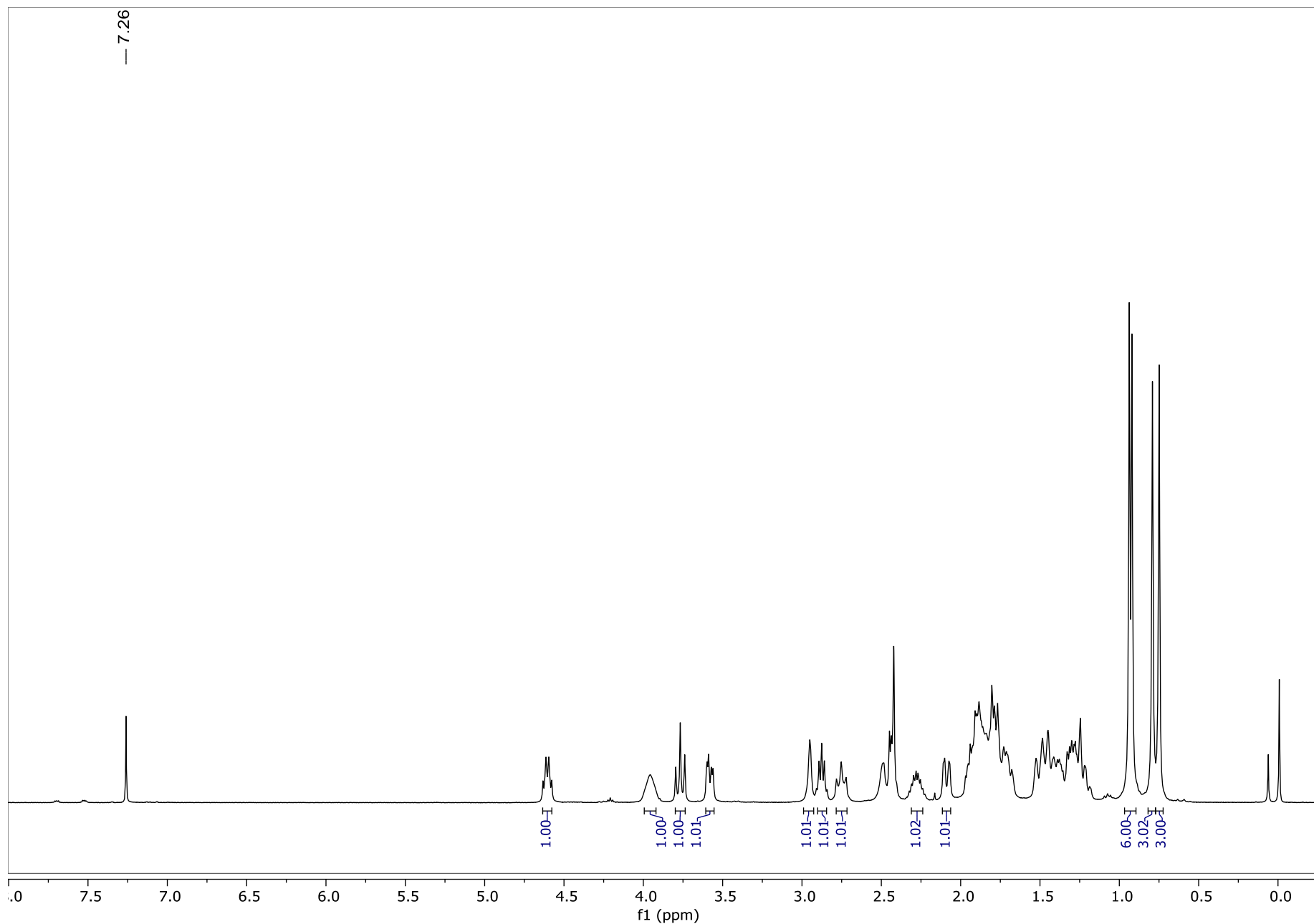


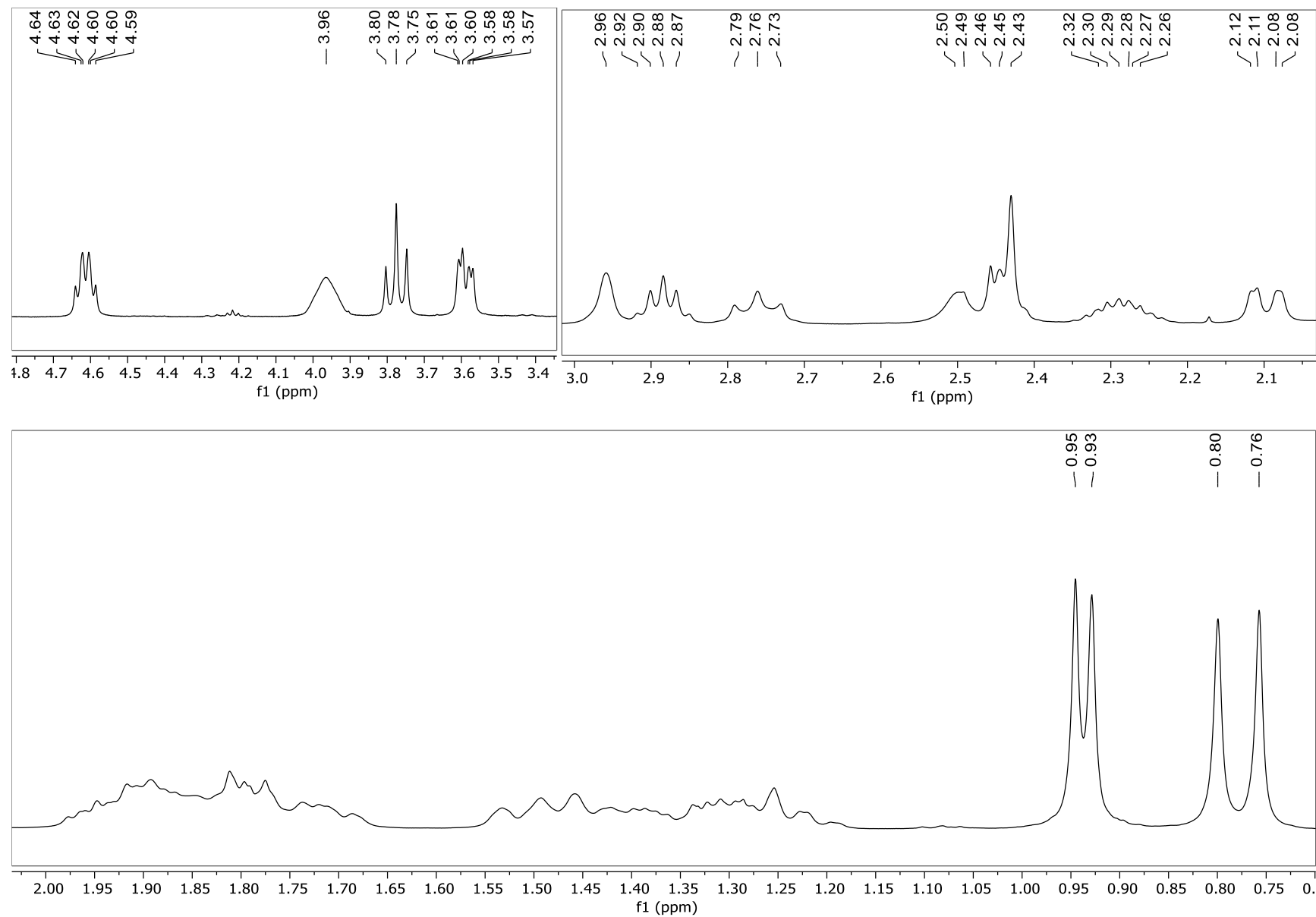
Figure S9.  $^{13}\text{C}$  NMR spectrum of compound 3

Figure S10. Sections of the  $^{13}\text{C}$  NMR spectrum of compound 3



**Figure S11. (25*R*)-3 $\beta$ ,5-Dihydroxy-5 $\alpha$ -spirostan-6,23-dione (4)**

Figure S12.  $^1\text{H}$  NMR spectrum of compound 4

Figure S13. Sections of the  $^1\text{H}$  NMR spectrum of compound 4

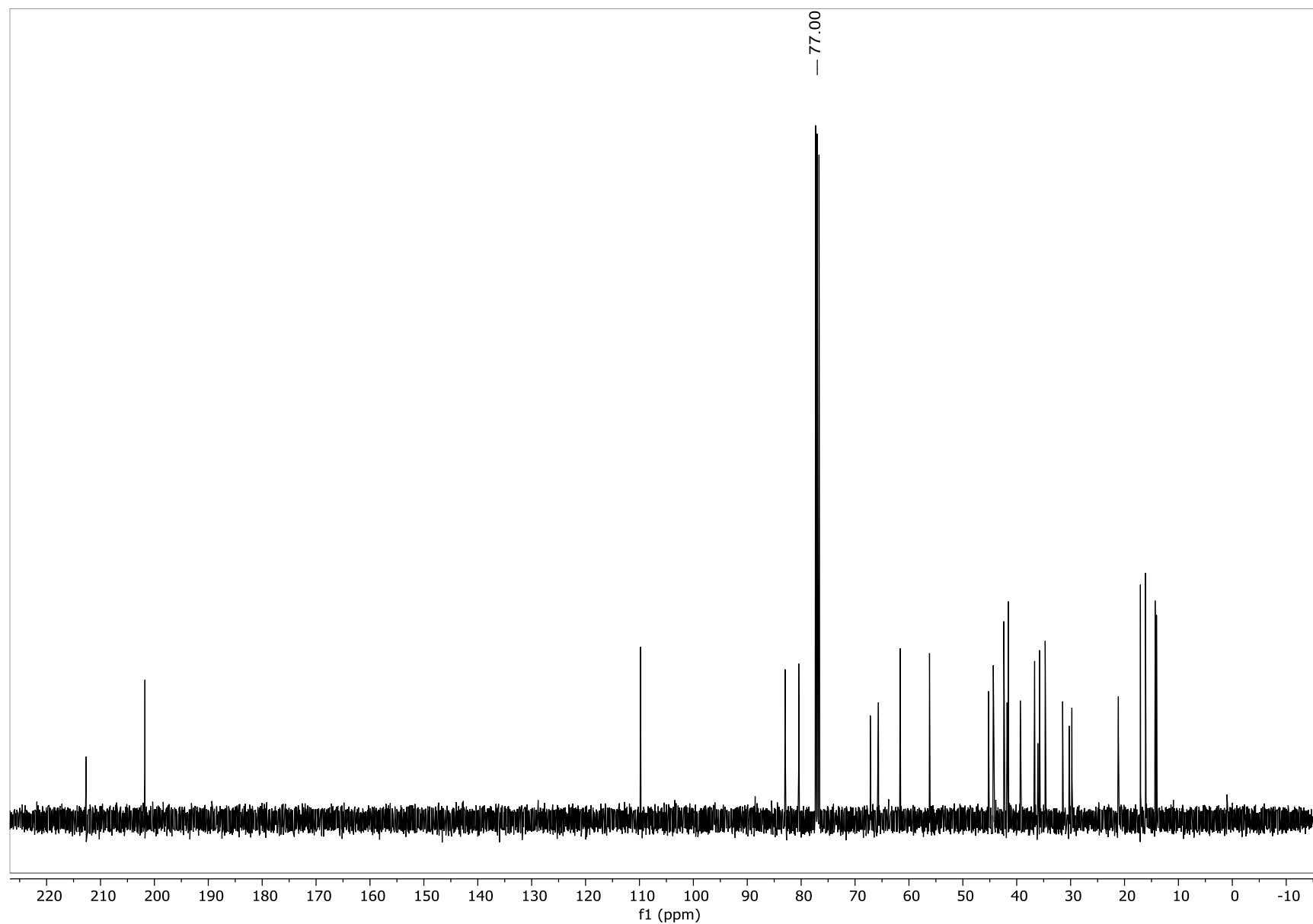
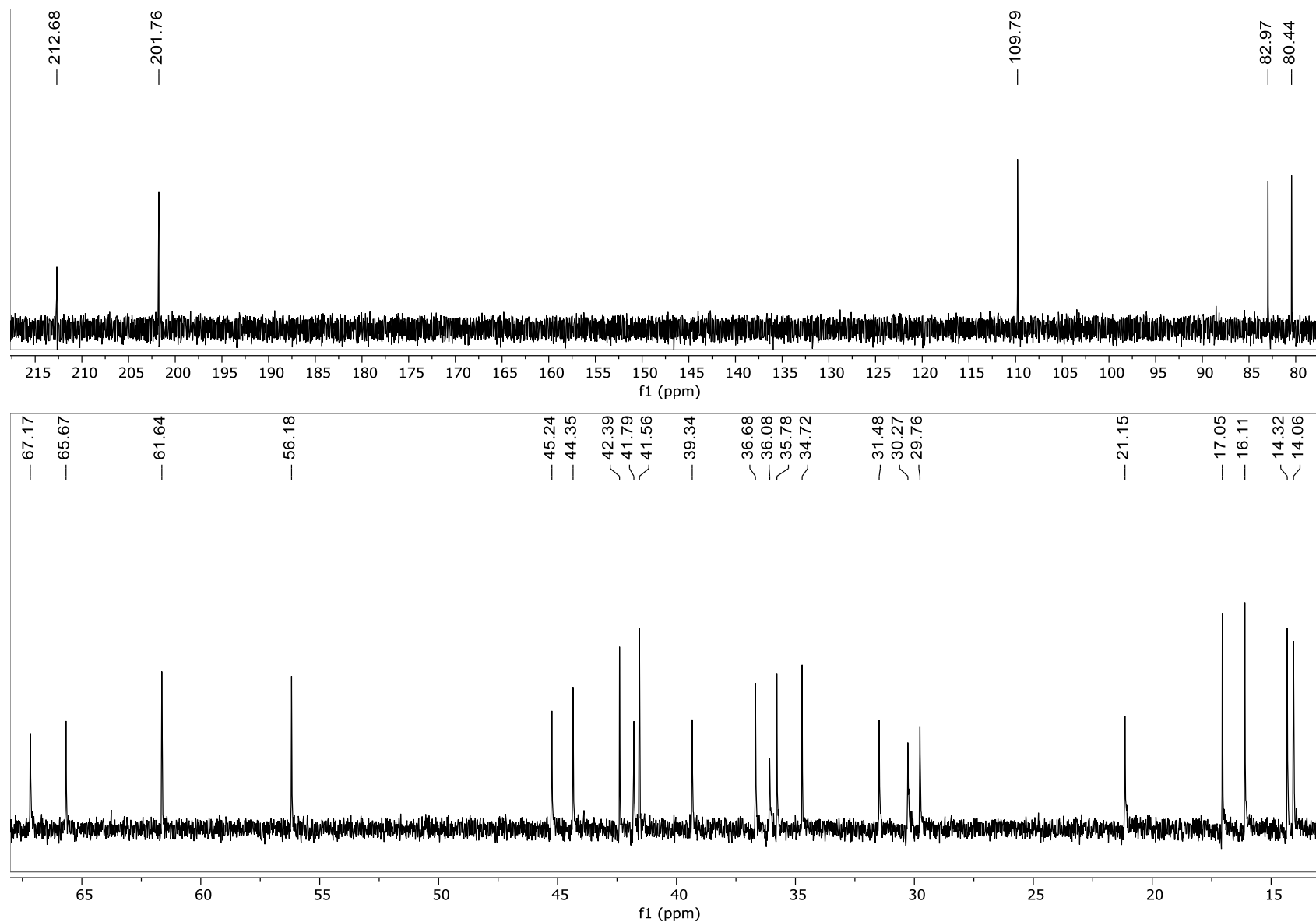


Figure S14.  $^{13}\text{C}$  NMR spectrum of compound 4

Figure S15. Sections of the  $^{13}\text{C}$  NMR spectrum of compound 4



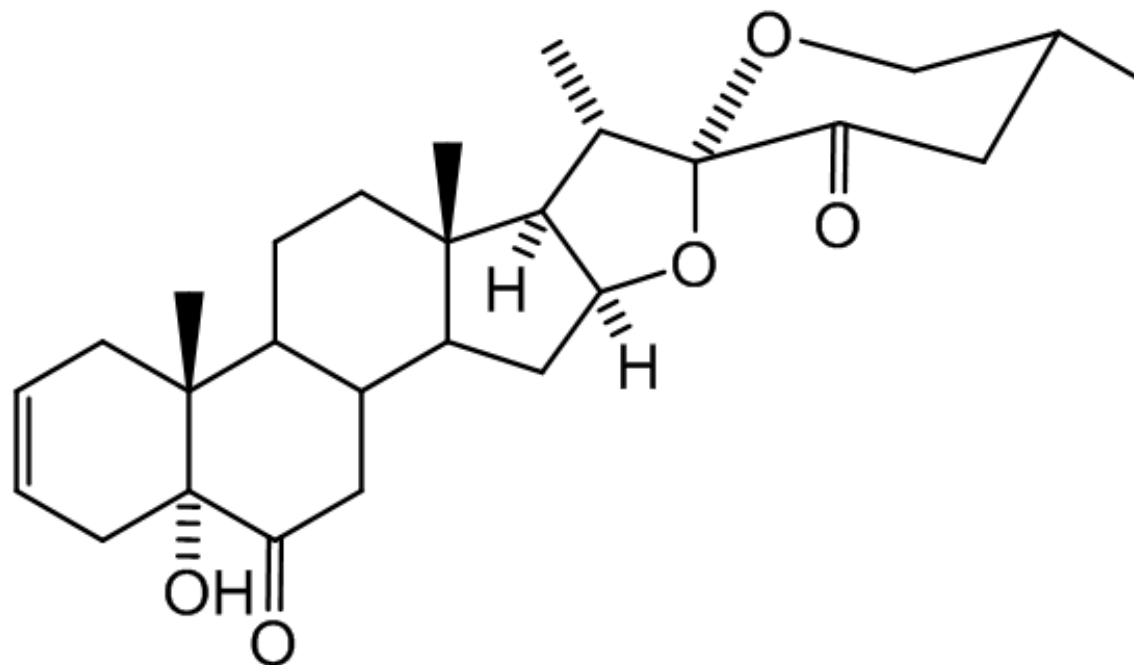
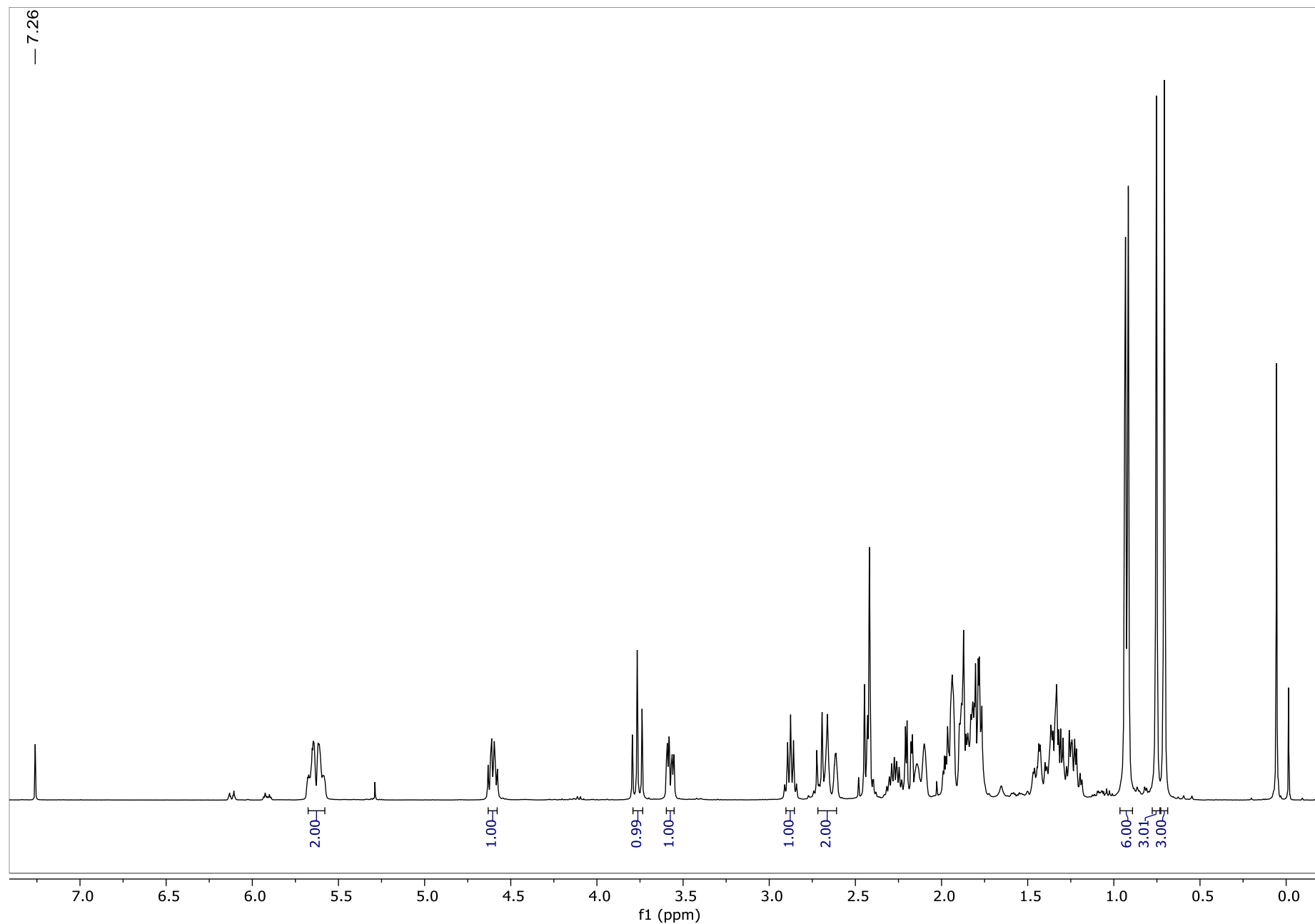


Figure S16. (25*R*)-5-Hydroxy-5 $\alpha$ -spirost-2-en-6,23-dione (5)

Figure S17.  $^1\text{H}$  NMR spectrum of compound 5

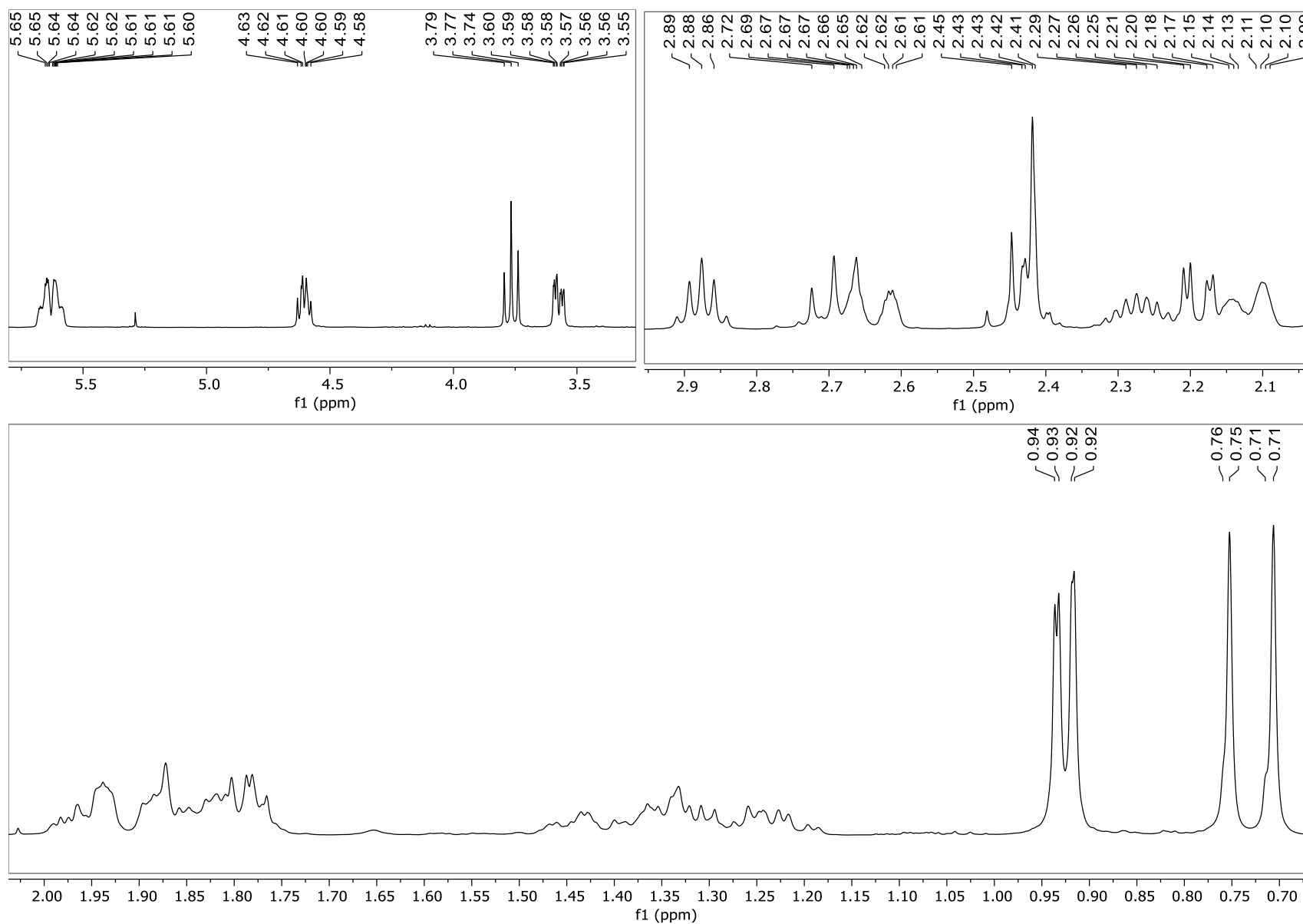


Figure S18. Sections of the  $^1\text{H}$  NMR spectrum of compound 5

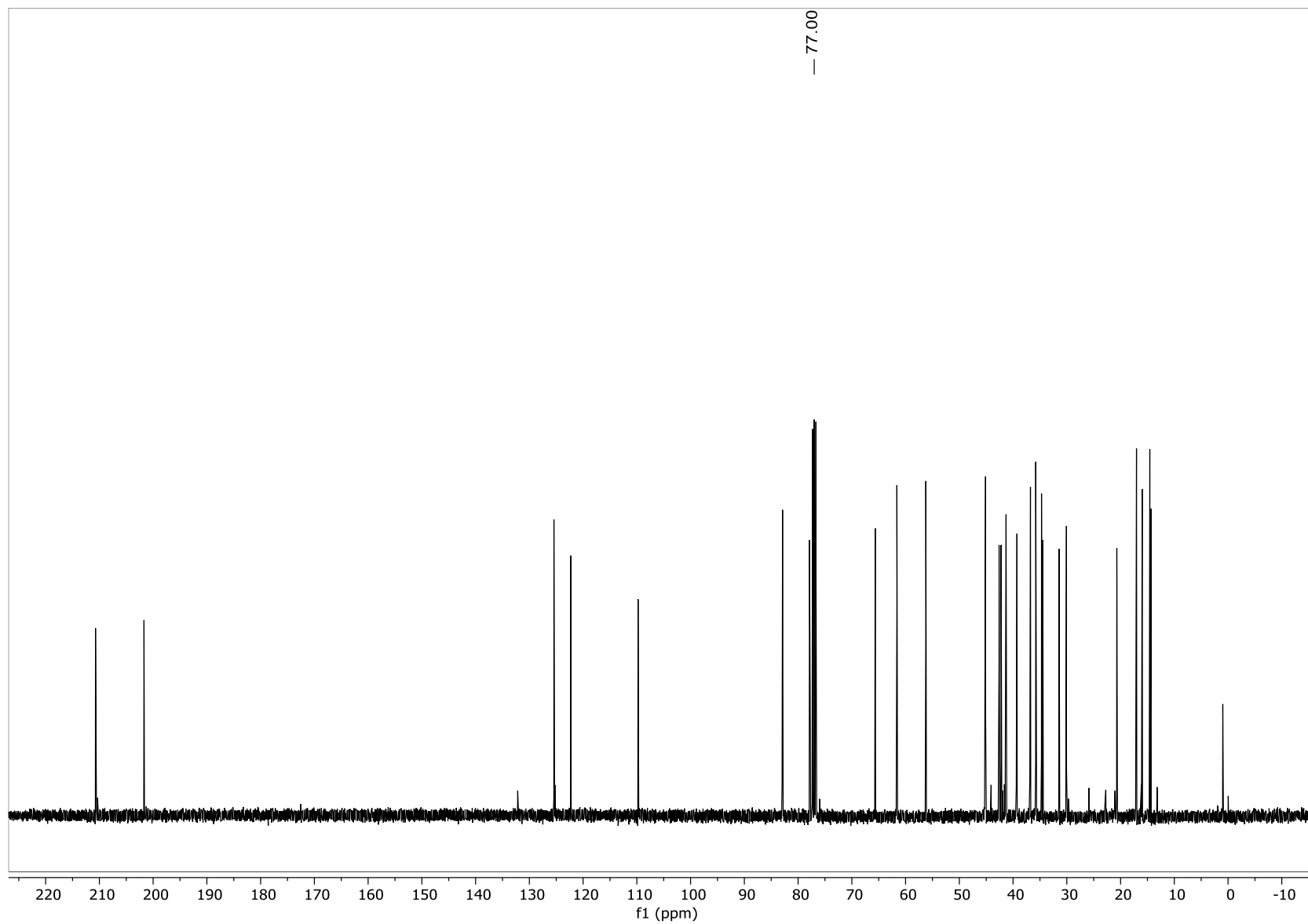
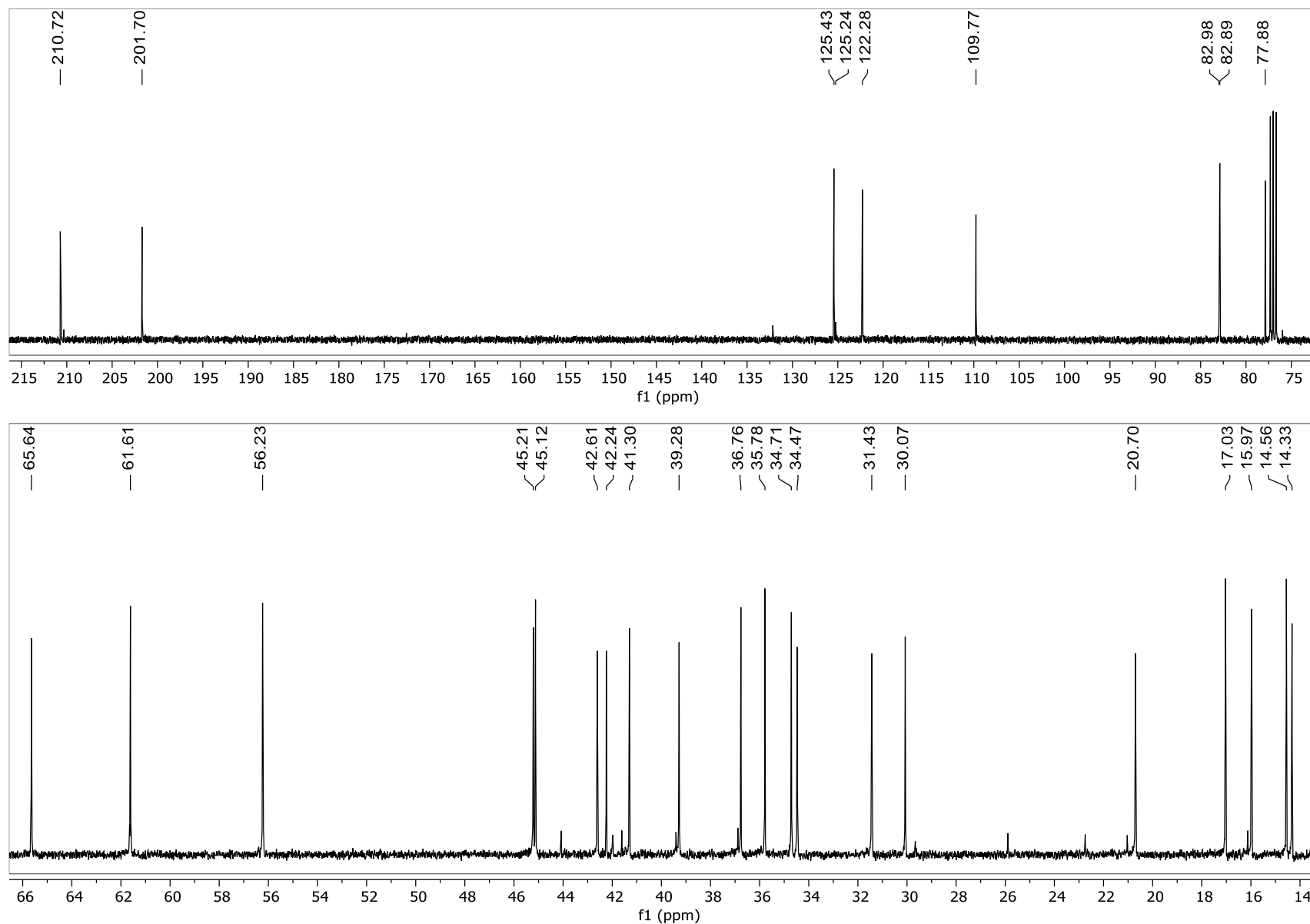


Figure S19.  $^{13}\text{C}$  NMR spectrum of compound 6

Figure S20. Sections of the  $^{13}\text{C}$  NMR spectrum of compound 5

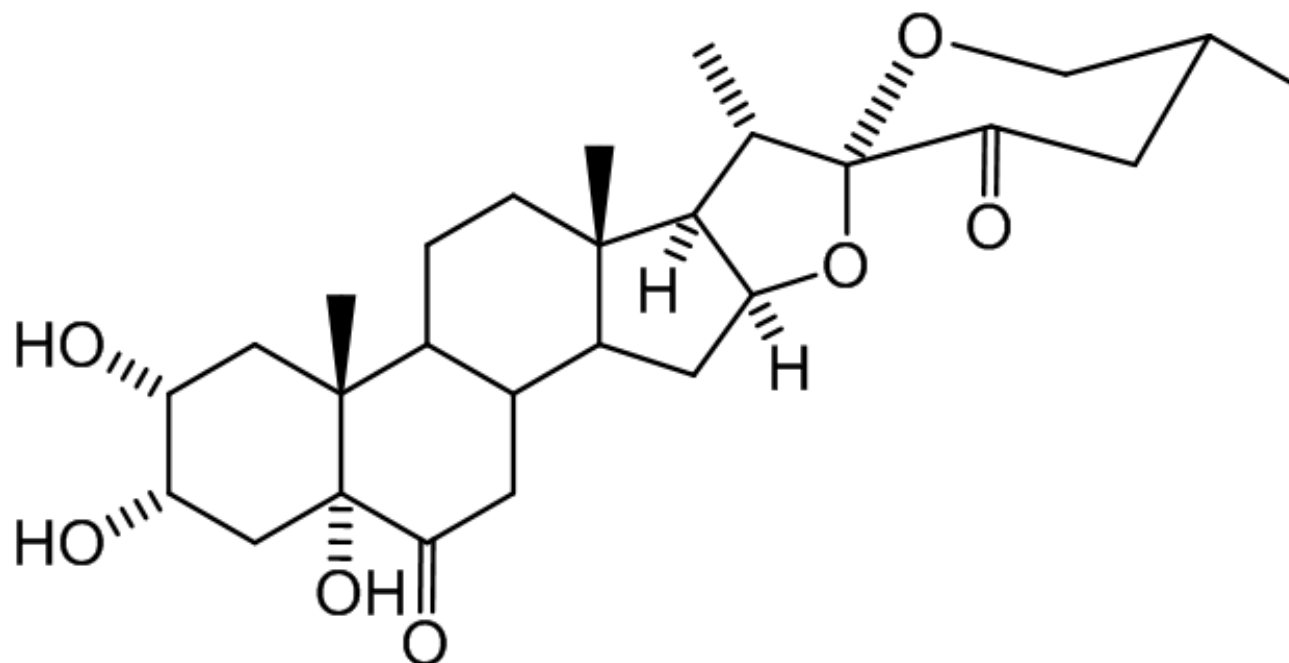
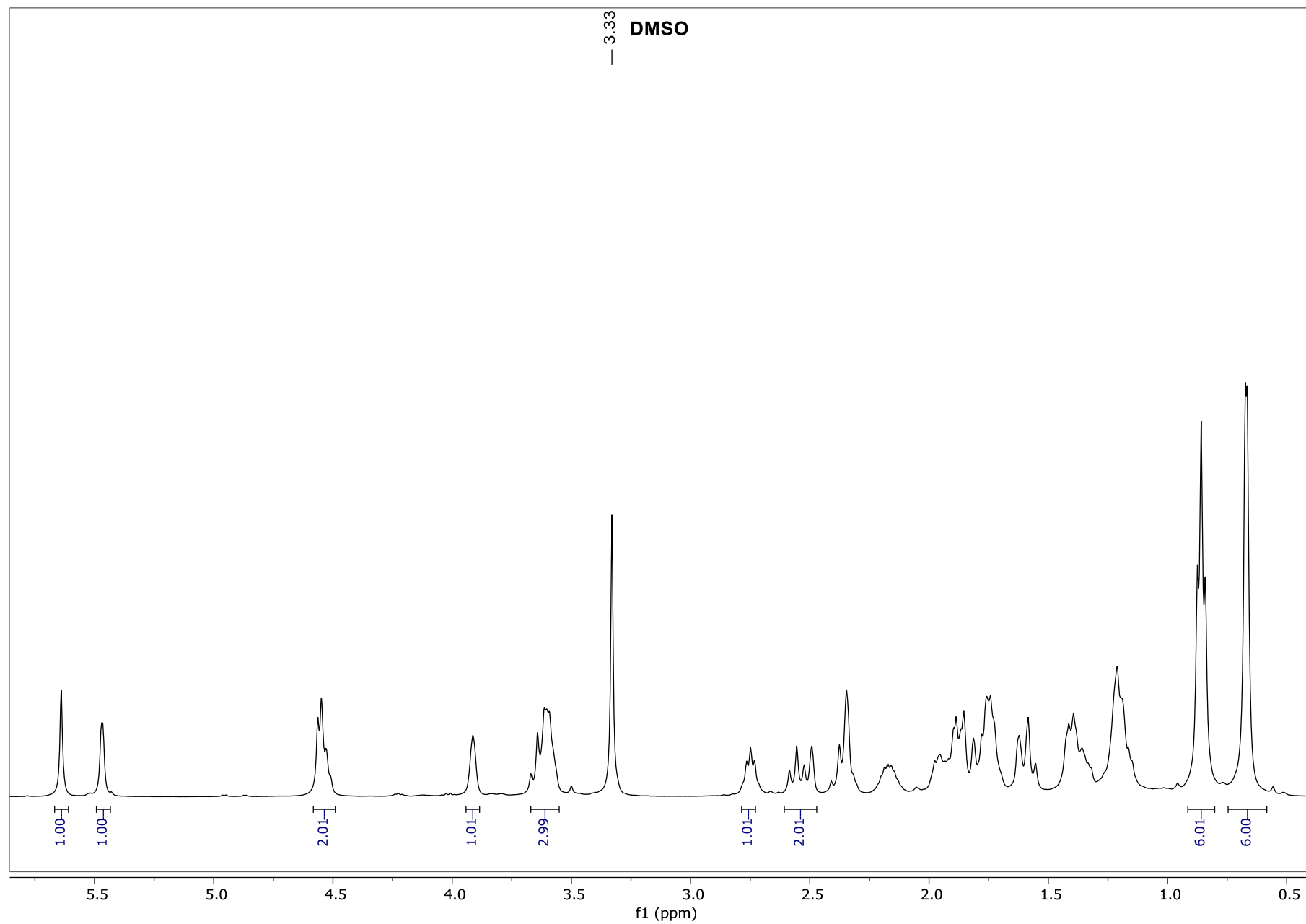


Figure S21. (25*R*)-2 $\alpha$ ,3 $\alpha$ ,5-Trihydroxy-5 $\alpha$ -spirostan-6,23-dione (6)

Figure S22. <sup>1</sup>H NMR spectrum of compound 6

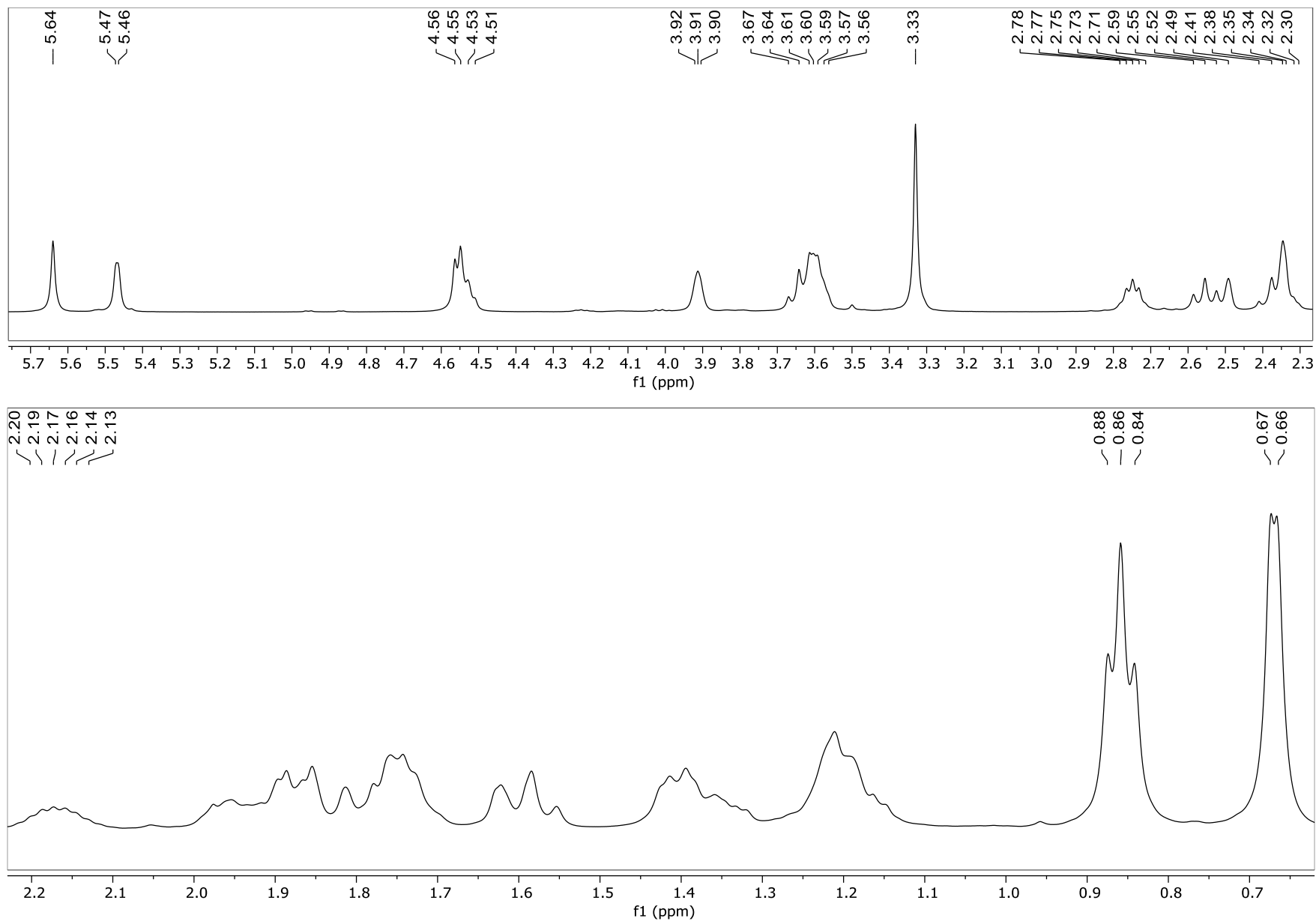


Figure S23. Sections of the  $^1\text{H}$  NMR spectrum of compound 6



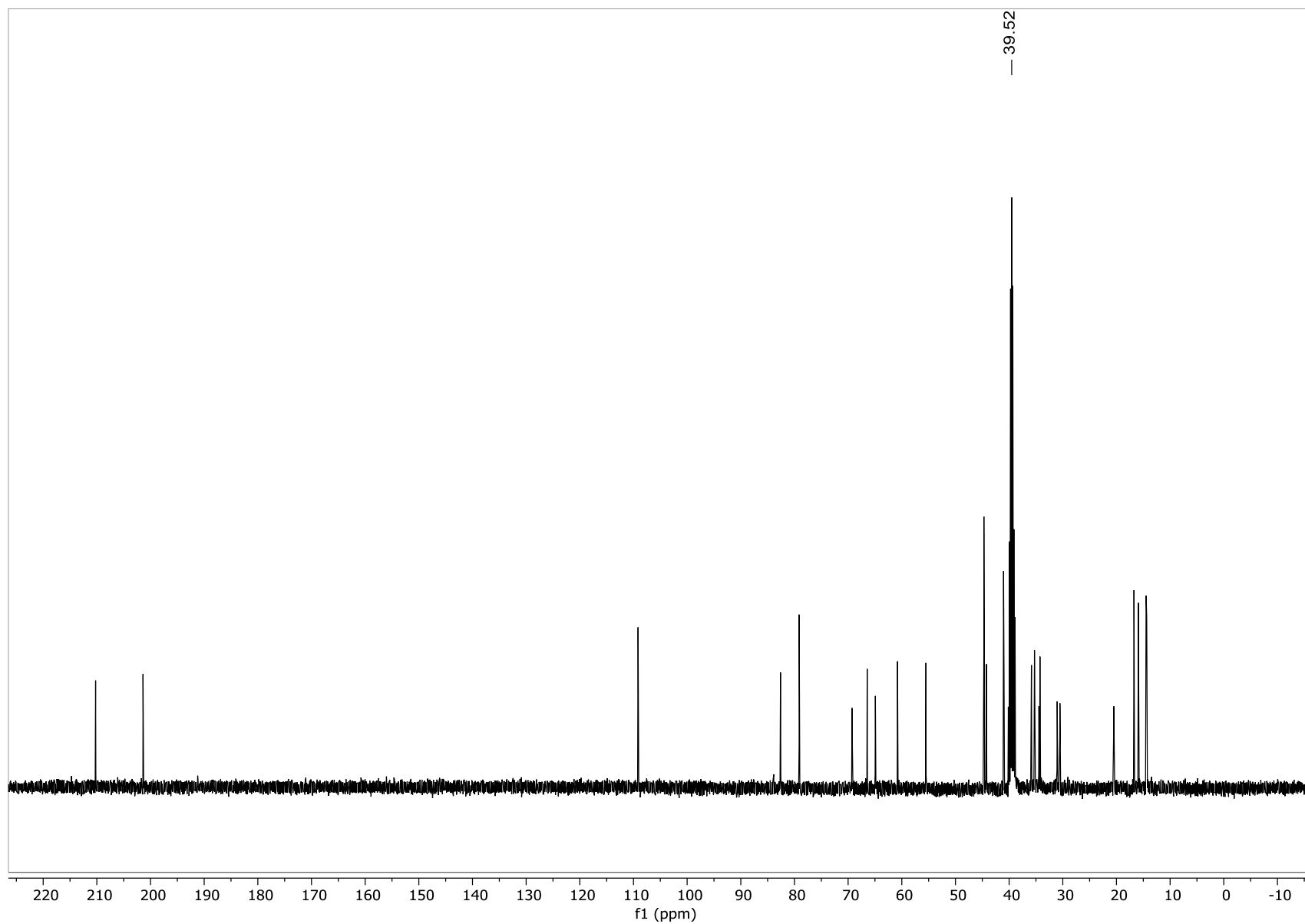
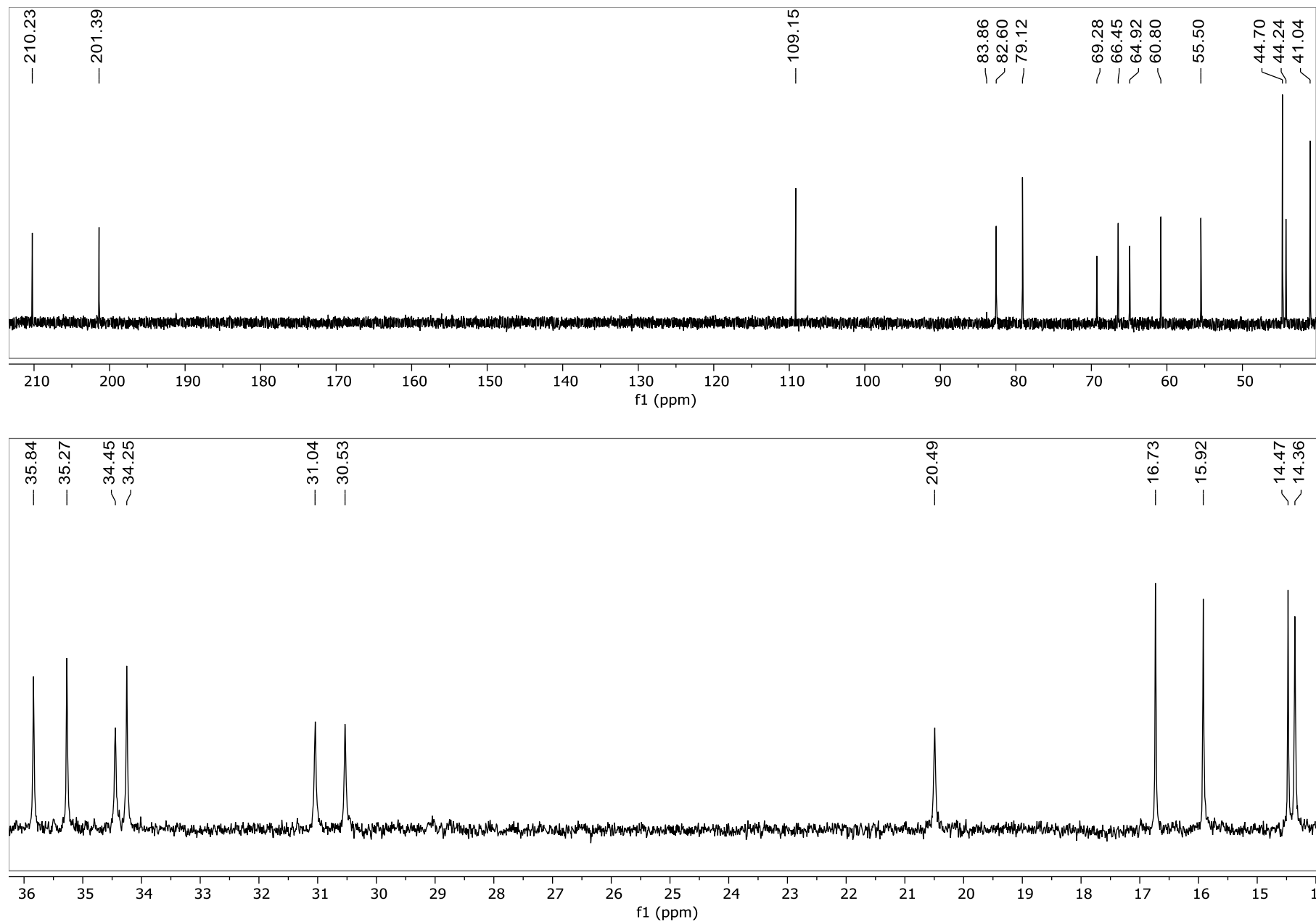


Figure S24.  $^{13}\text{C}$  NMR spectrum of compound 6

Figure S25. Sections of the  $^{13}\text{C}$  NMR spectrum of compound 6

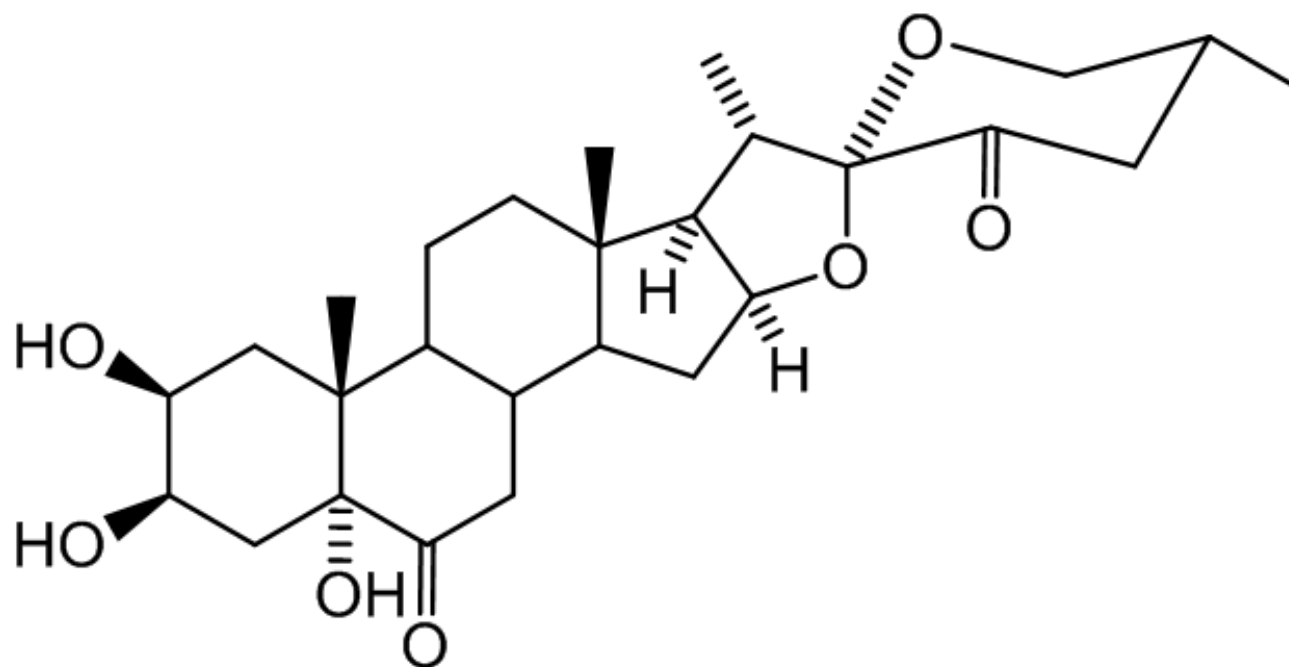
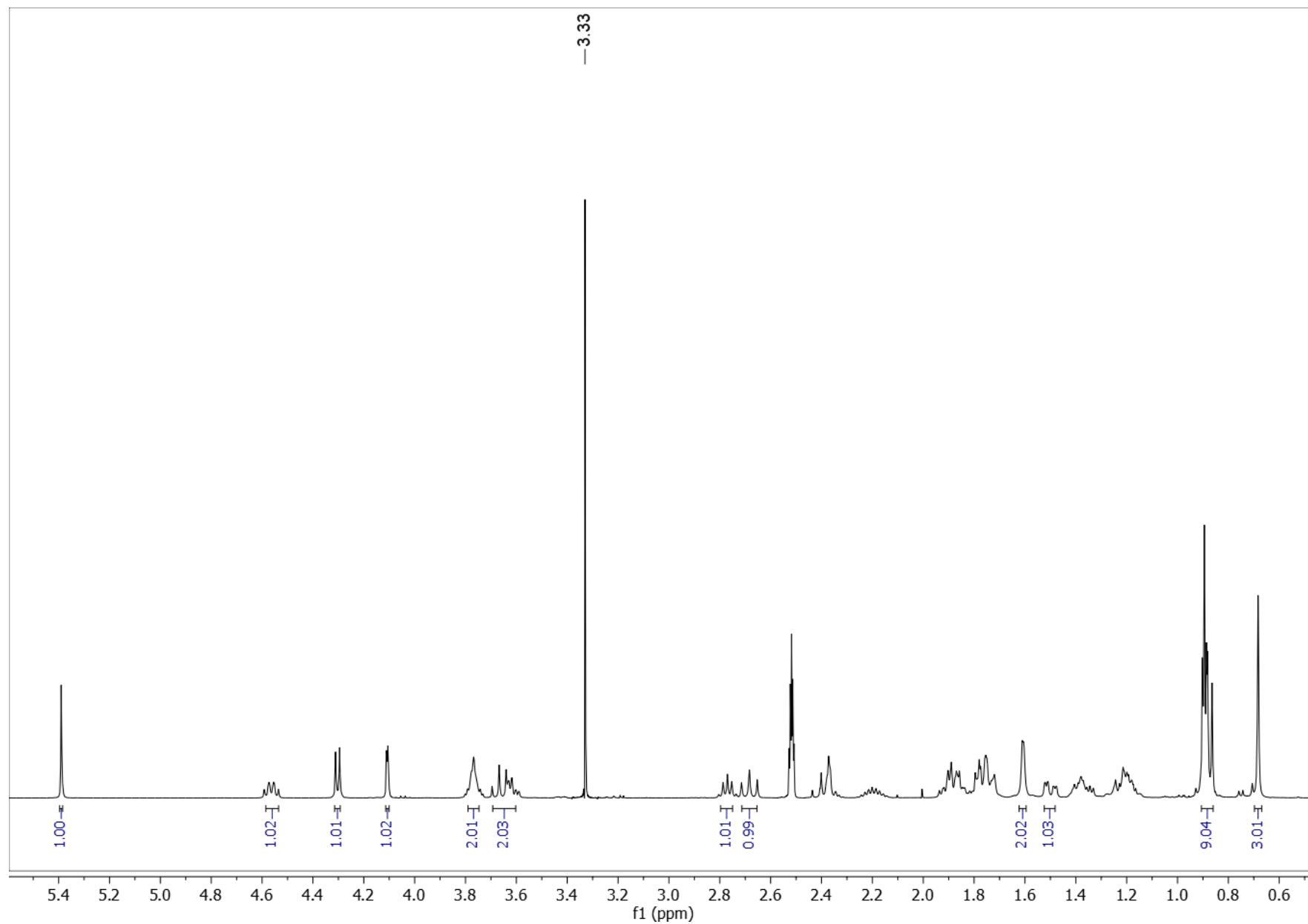
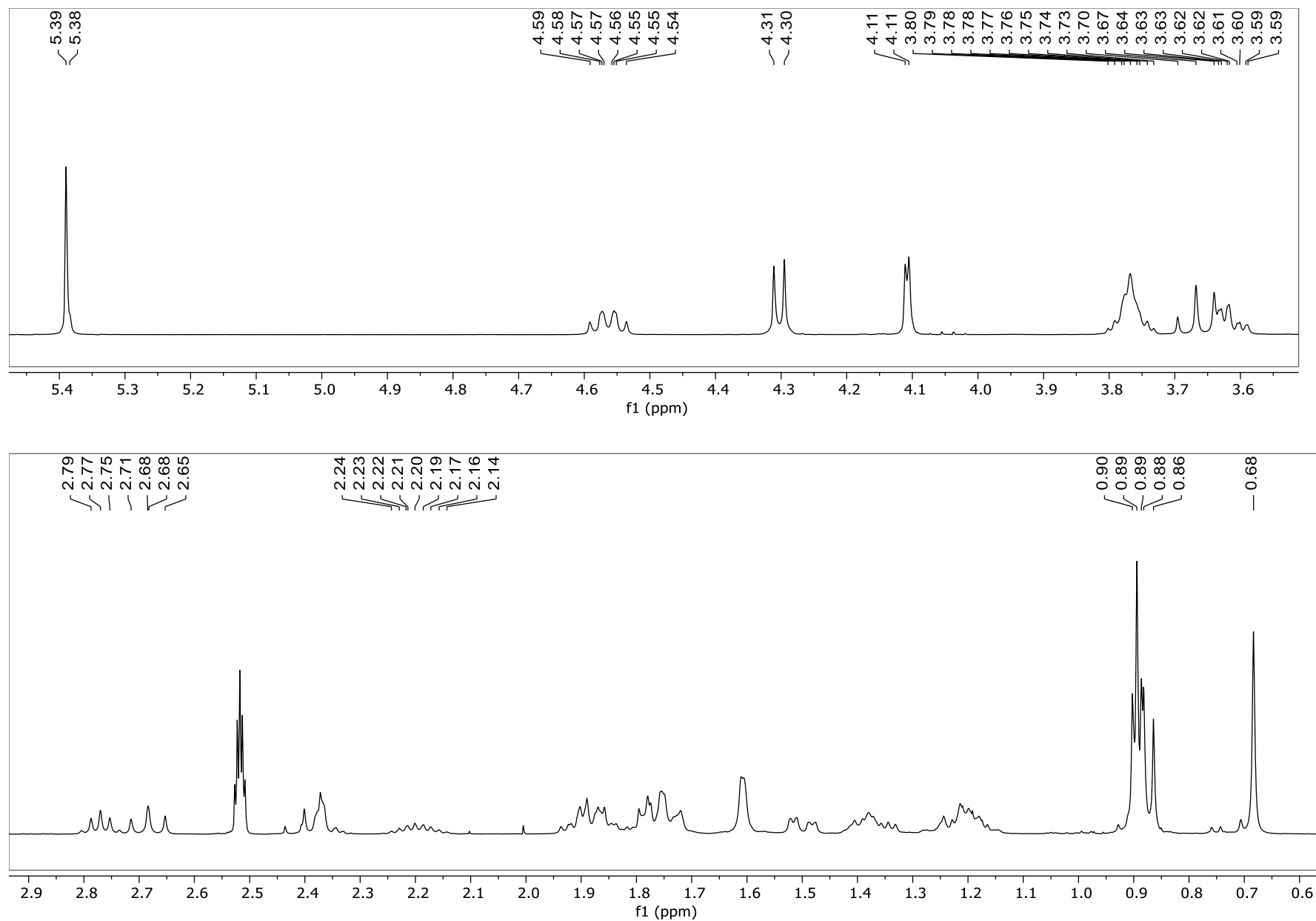
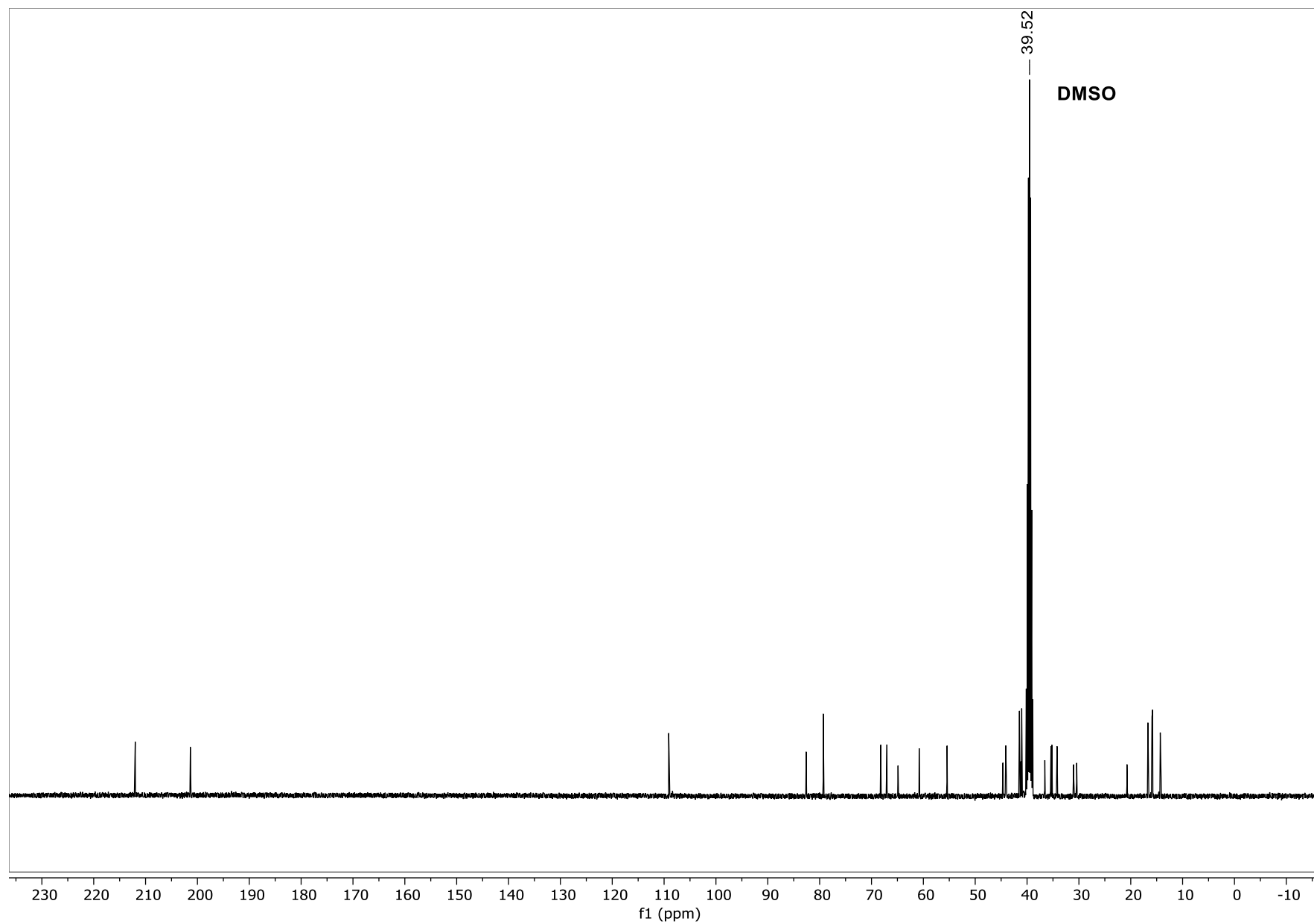
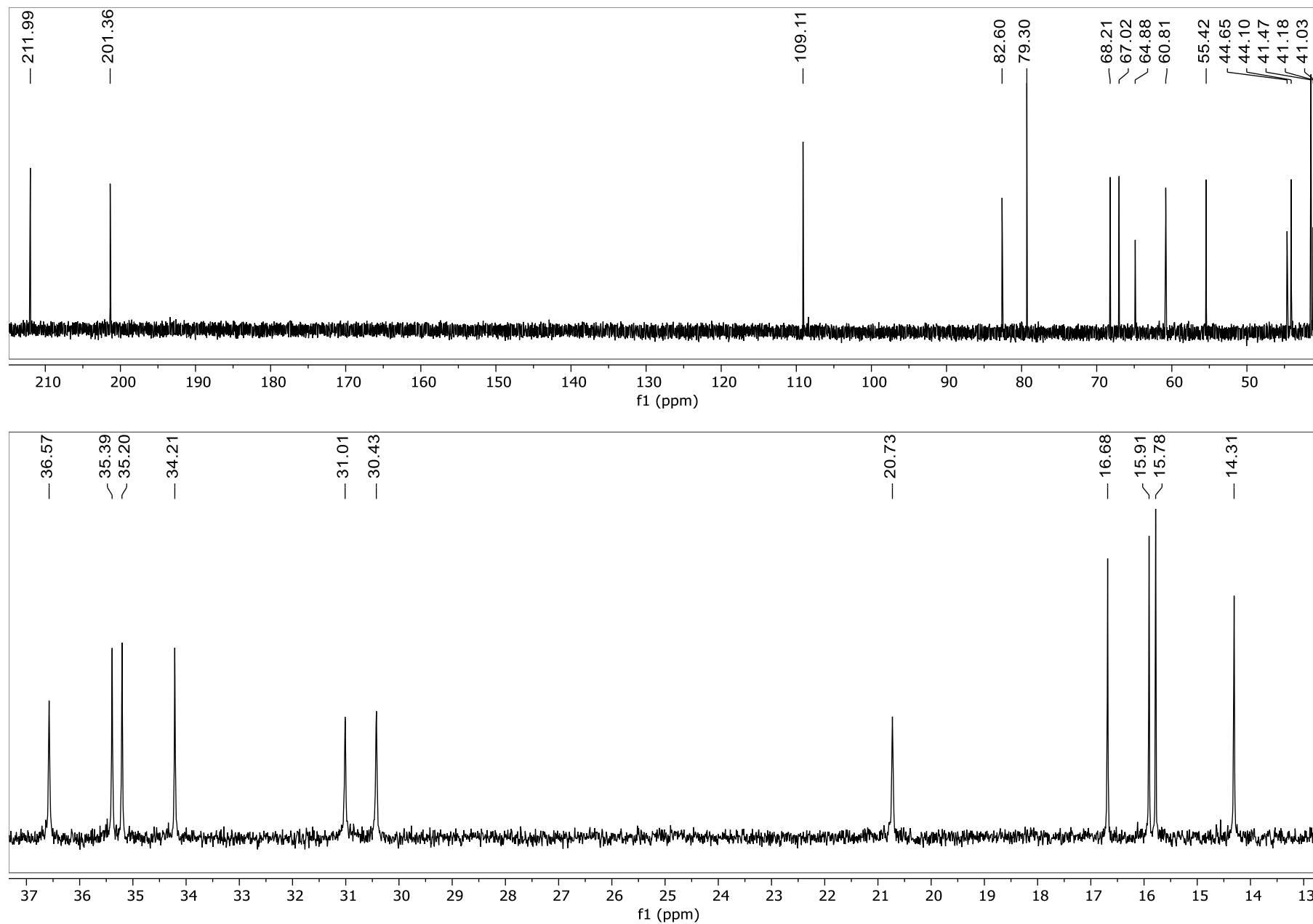


Figure S26. (25*R*)-2β,3β,5-Trihydroxy-5α-spirostan-6,23-dione (7)

Figure S27. <sup>1</sup>H NMR spectrum of compound 7

Figure S28. Sections of the  $^1\text{H}$  NMR spectrum of compound 7

Figure S29.  $^{13}\text{C}$  NMR spectrum of compound 7

Figure S30. Sections of the  $^{13}\text{C}$  NMR spectrum of compound 7