SUPPLEMENTARY INFORMATION

Tetra-glucopyranosyl diterpene *ent*-kaur-16-en-19-oic acid and ent-13(*S*)-hydroxyatisenoic acid derivatives from a commercial extract of *Stevia rebaudiana* (Bertoni) Bertoni

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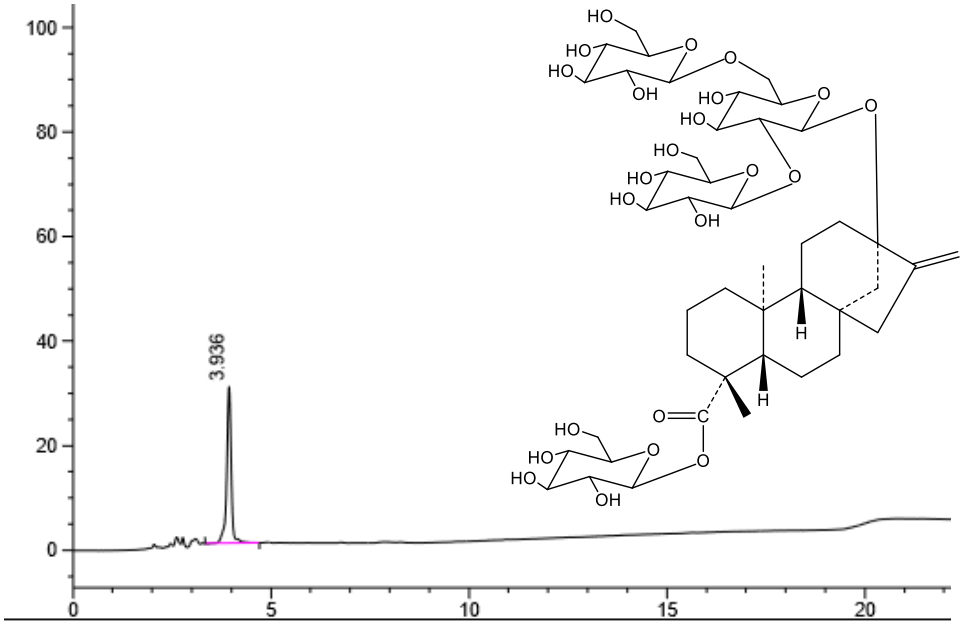
† Charles D. Hufford deceased on May 15th, 2017.

Rebaudioside Z
(compound 1)



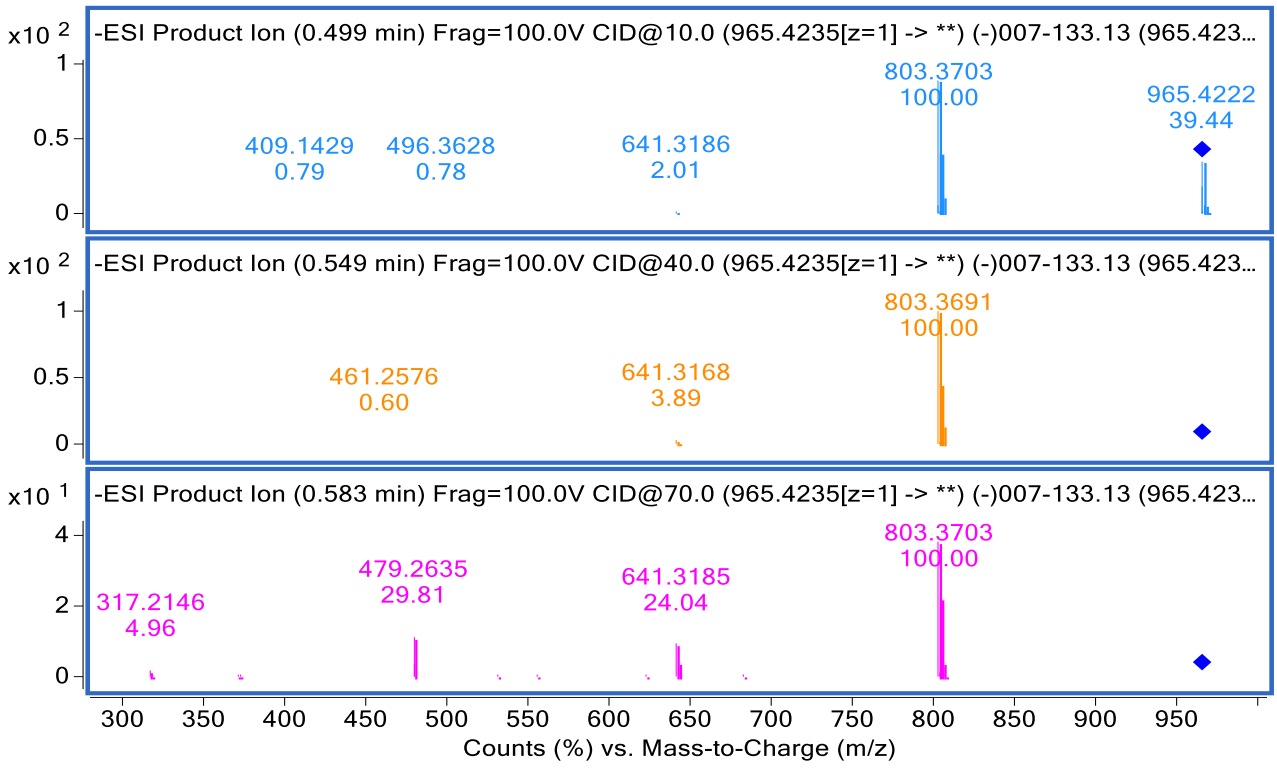


Figure 1. RP-C18 HPLC chromatogram**,** chemical structure and MS/MS spectrum of compound **1**.

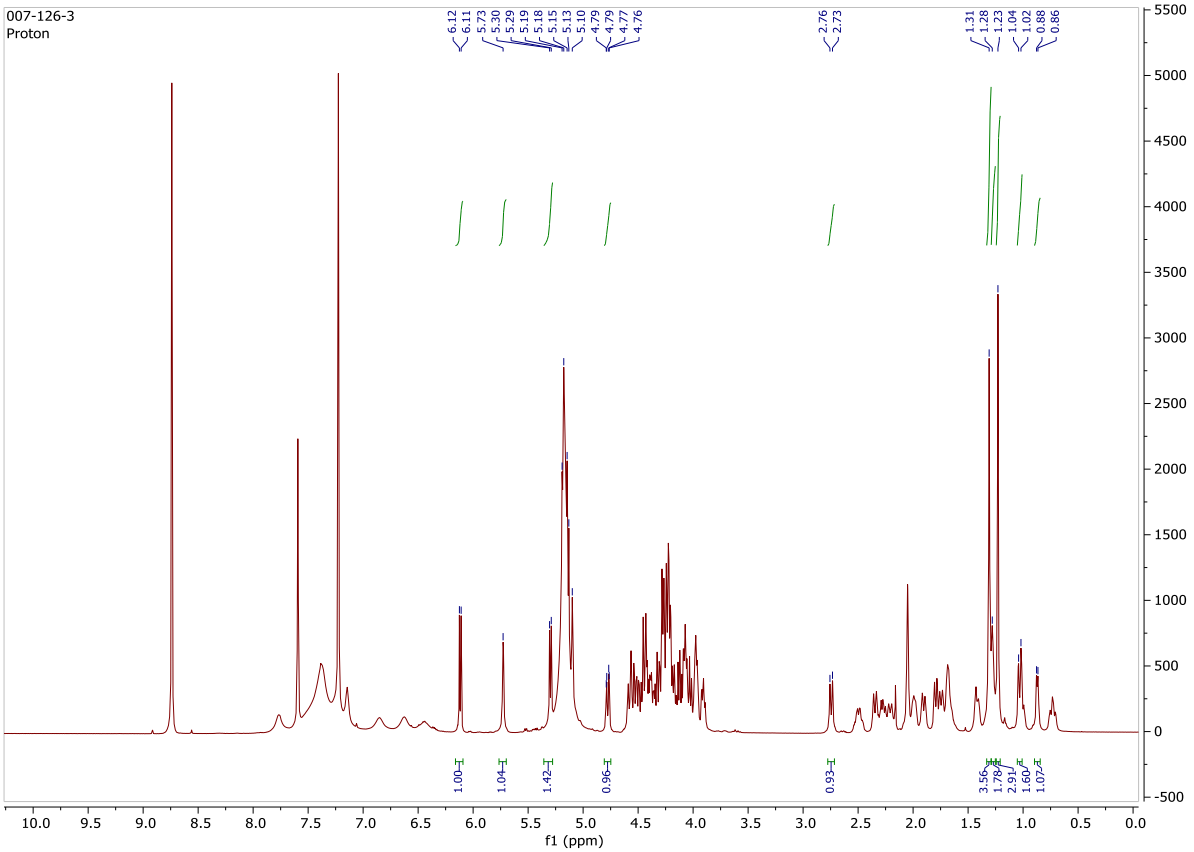


Figure 2. ^{1}H NMR spectrum of compound **1**.

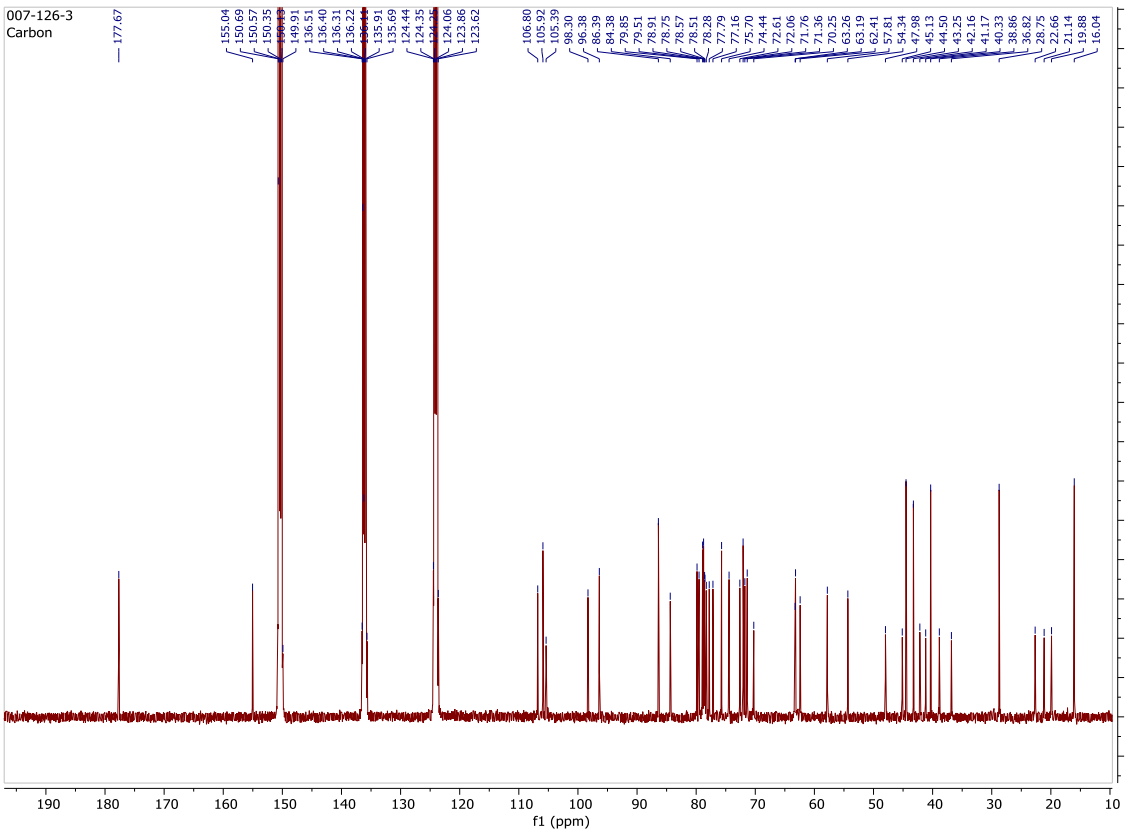


Figure 3. ^{13} C NMR spectrum of compound **1**.

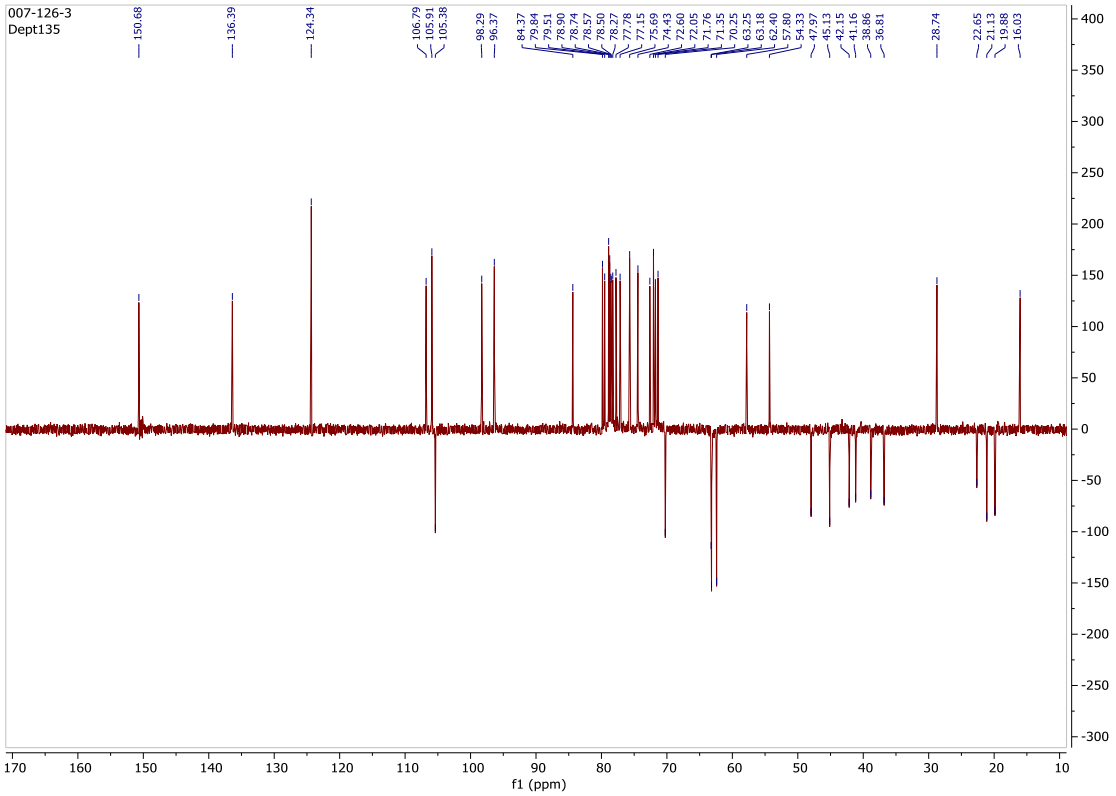


Figure 4. DEPT 135 spectrum of compound **1**.

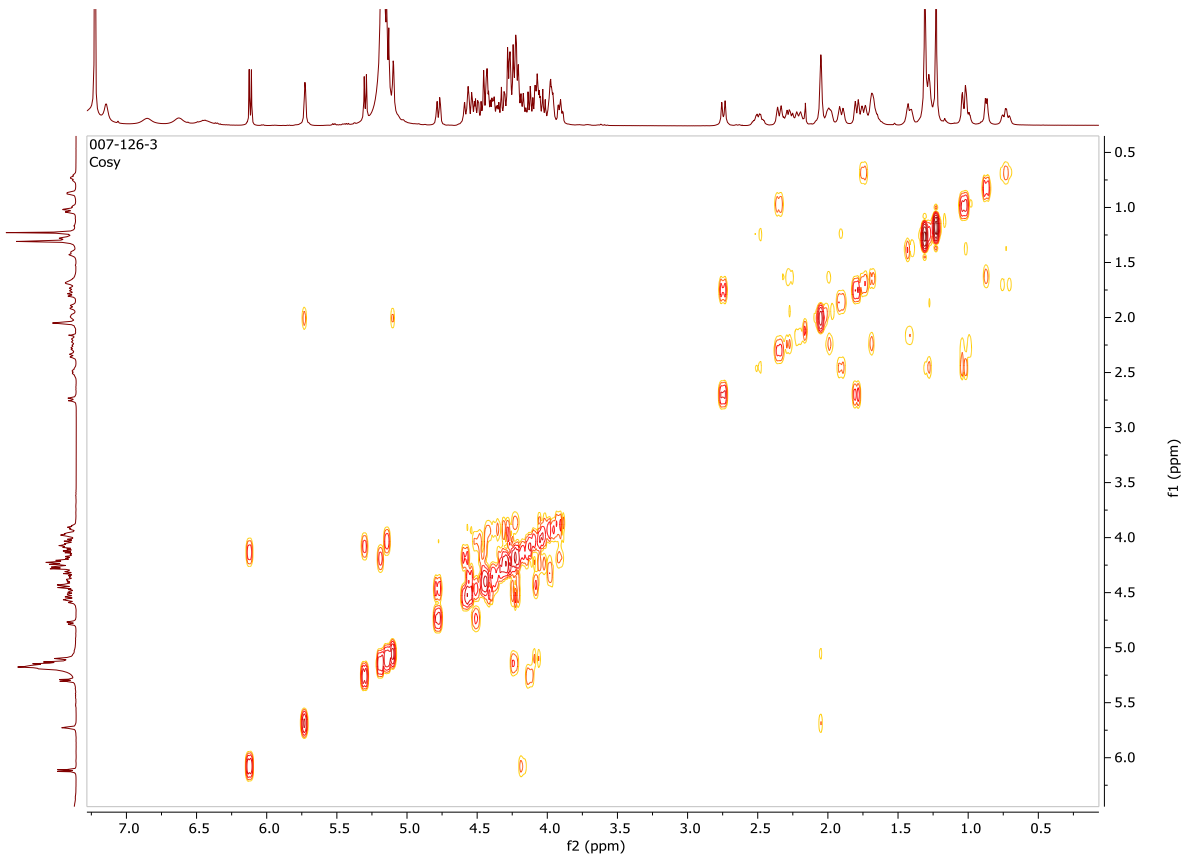


Figure 5. DQCOSY spectrum of compound **1**.

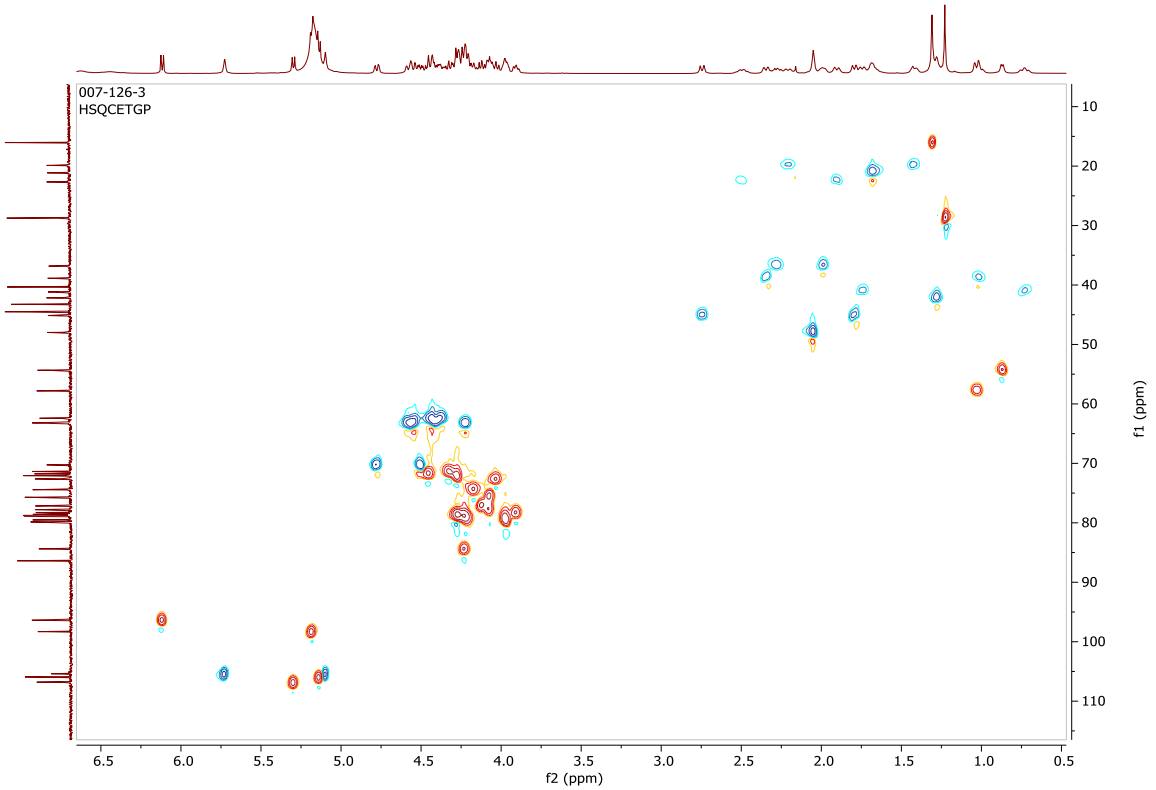


Figure 6. HSQC spectrum of compound **1**.

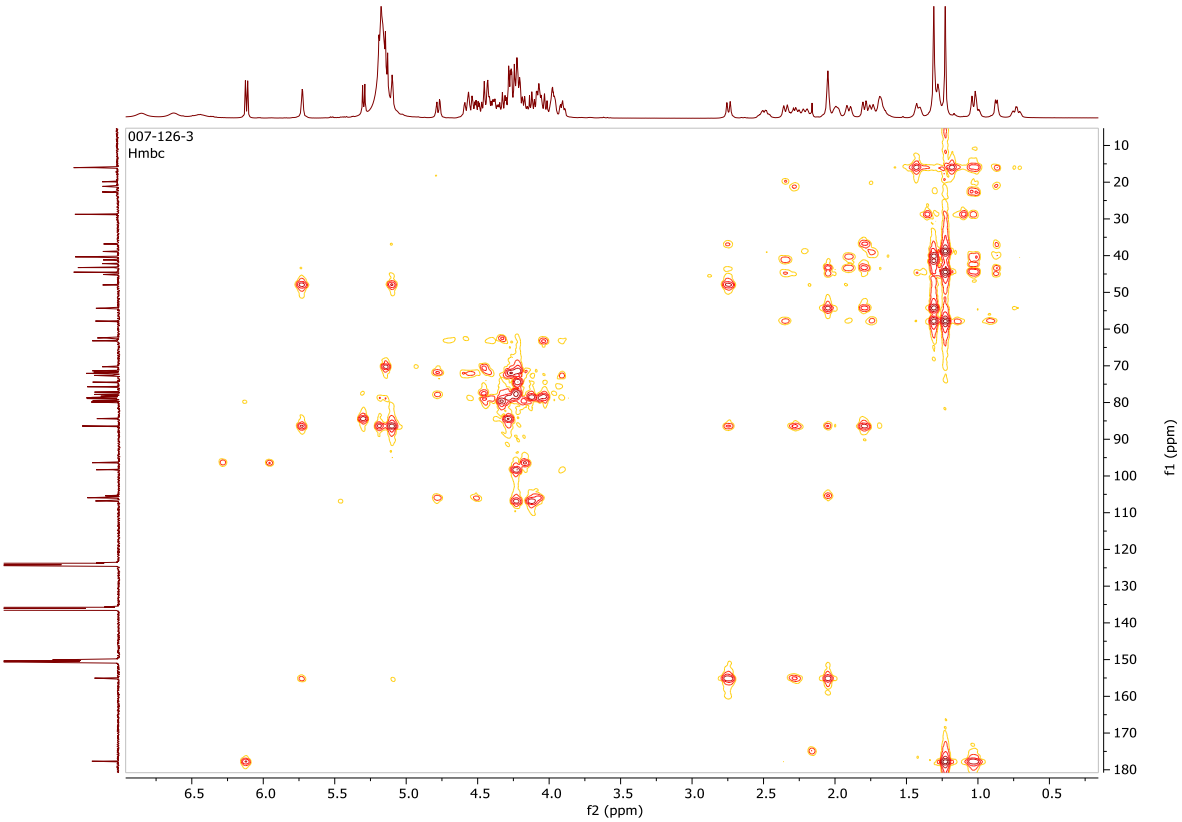


Figure 7. HMBC spectrum of compound **1**.

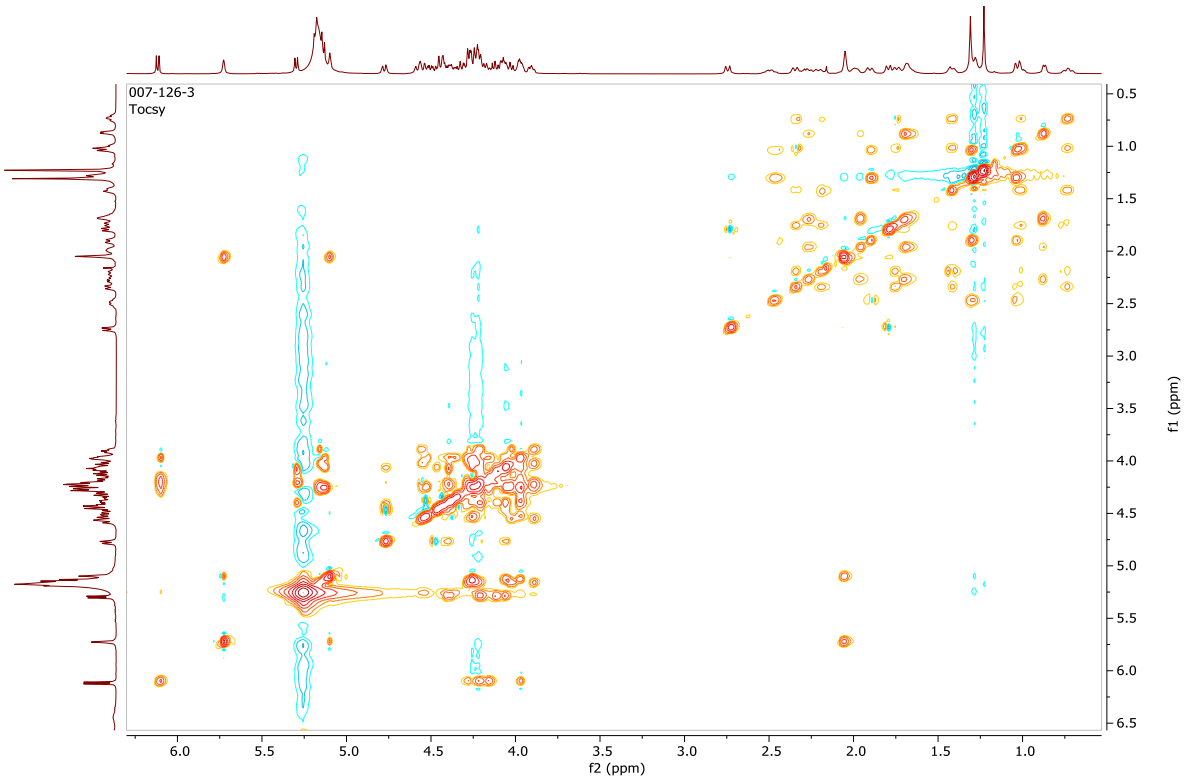
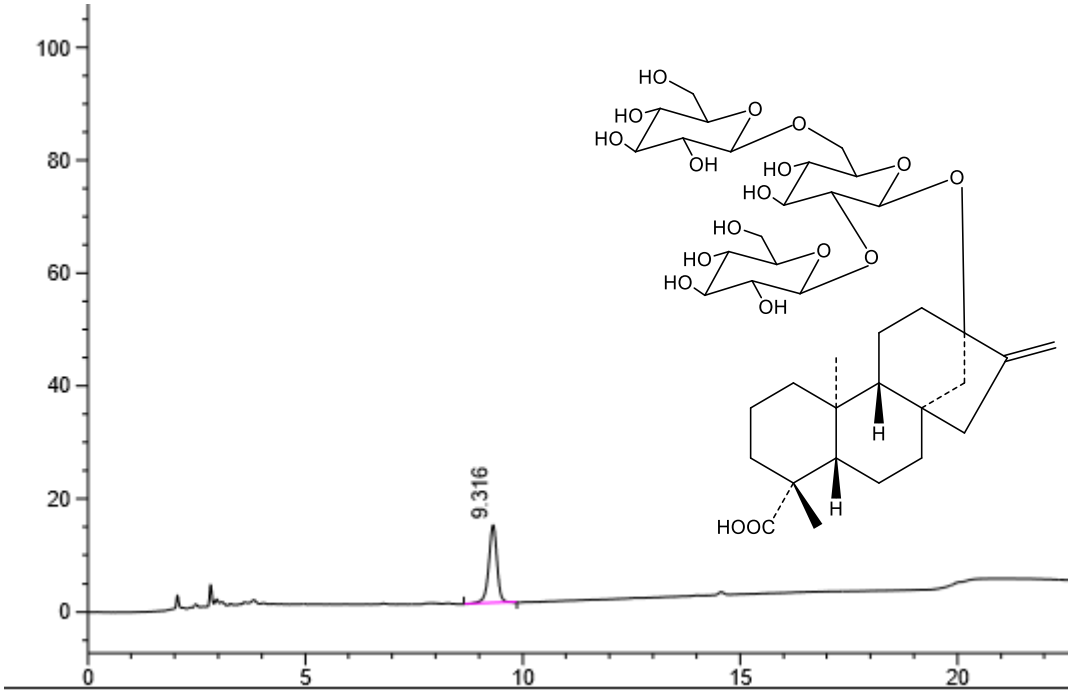


Figure 8. TOCSY spectrum of compound **1**.

Rebaudioside Z_1
(compound 2)



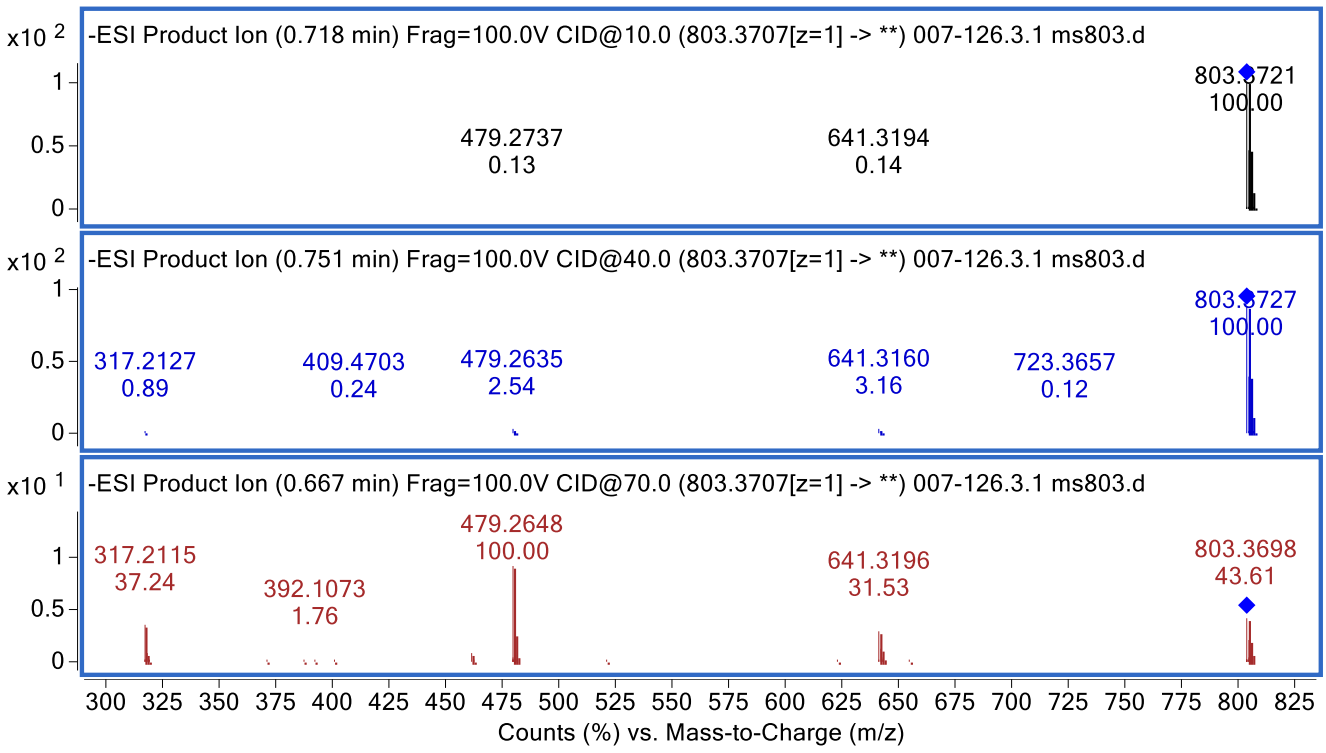


Figure 9. RP-C18 HPLC chromatogram**,** chemical structure and MS/MS spectrum of compound **2**.

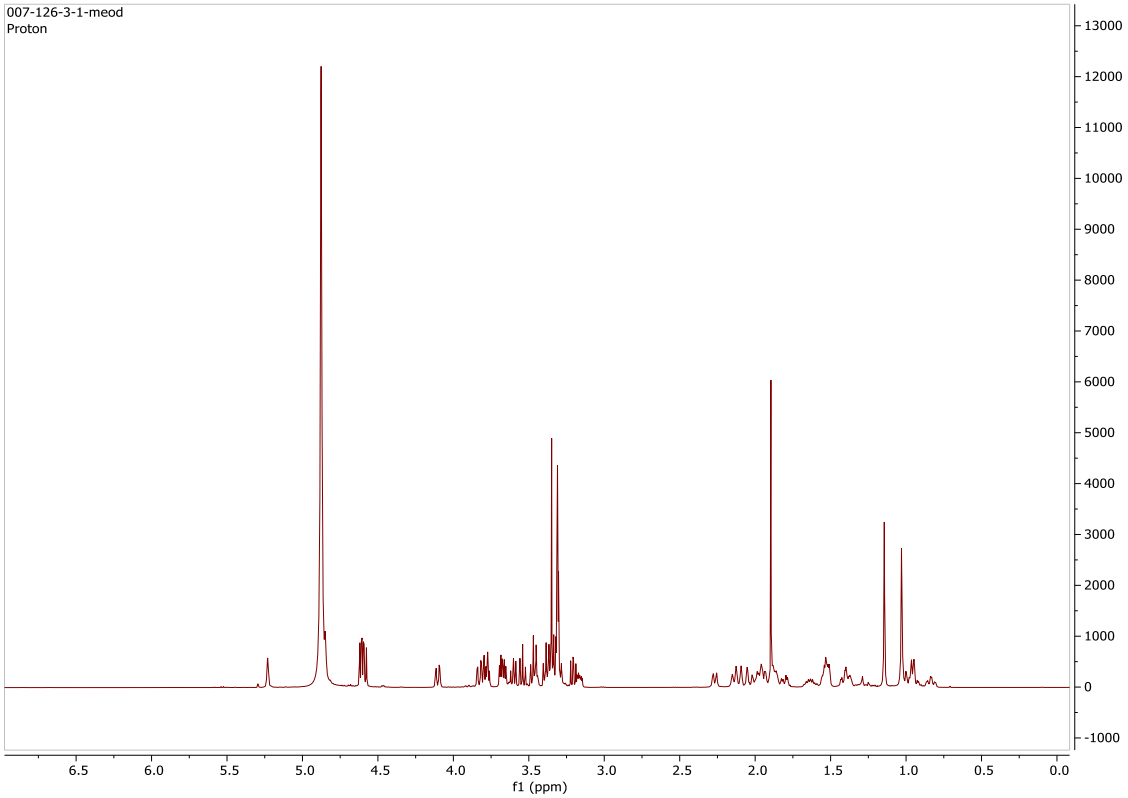


Figure 10. ^{1}H NMR spectrum of compound **2**.

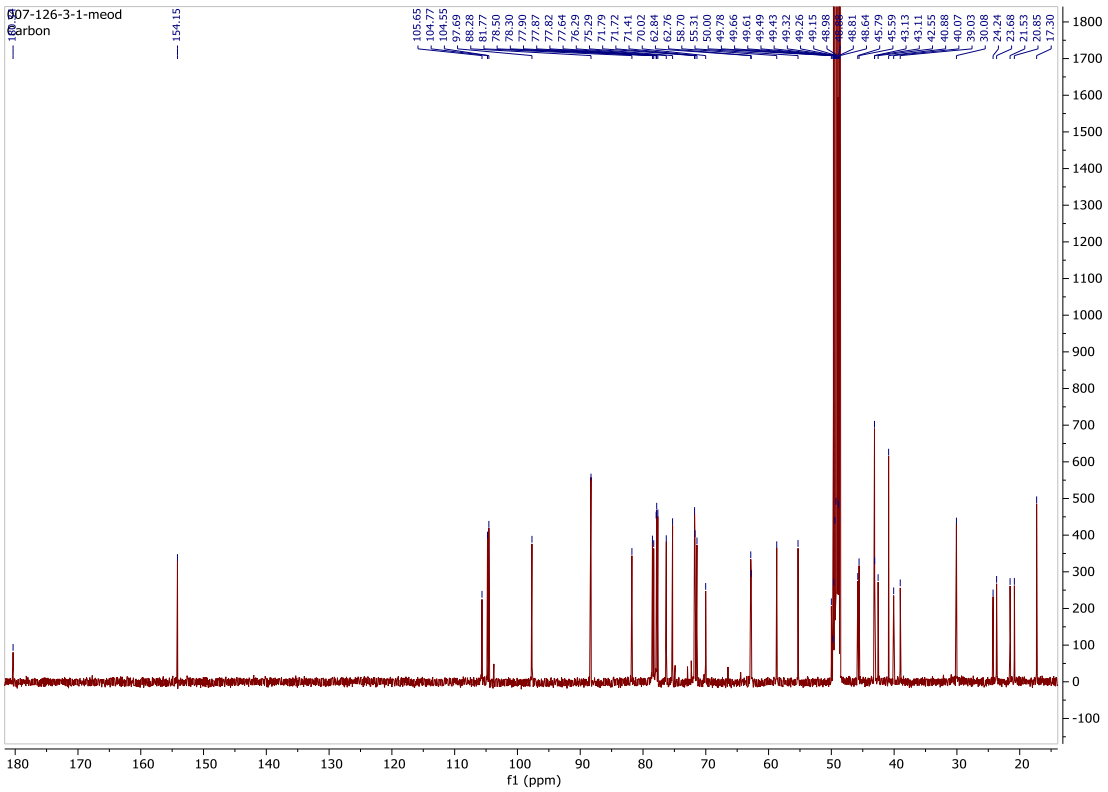


Figure 11. ^{13} C NMR spectrum of compound **2**.

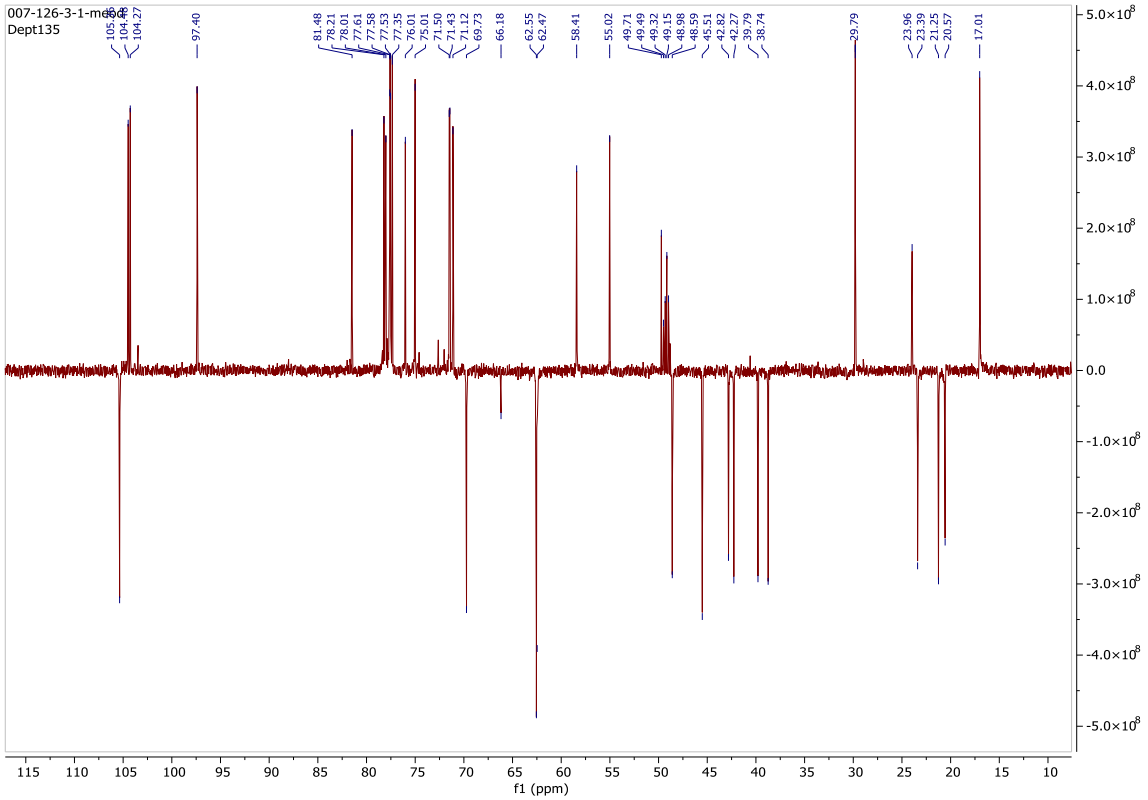


Figure 12. DEPT 135 spectrum of compound **2**.

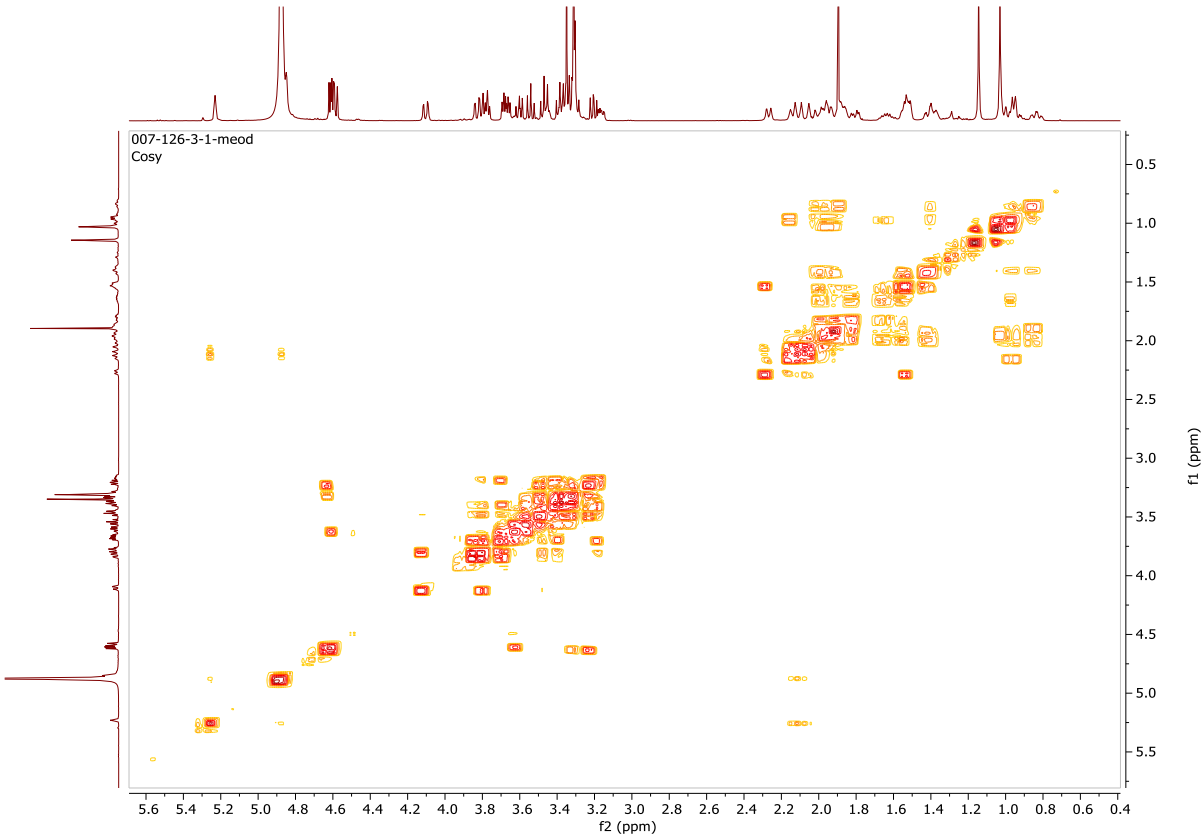


Figure 13. DQCOSY spectrum of compound **2**.

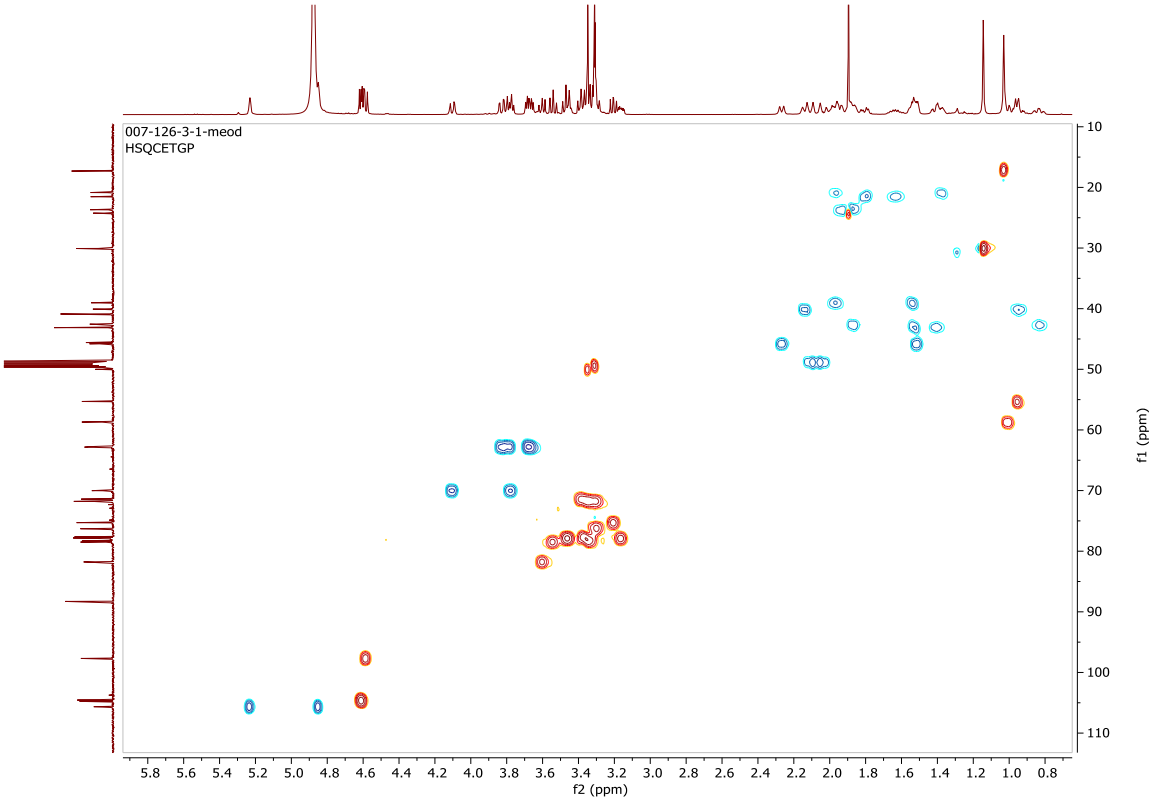


Figure 14. HSQC spectrum of compound **2**.

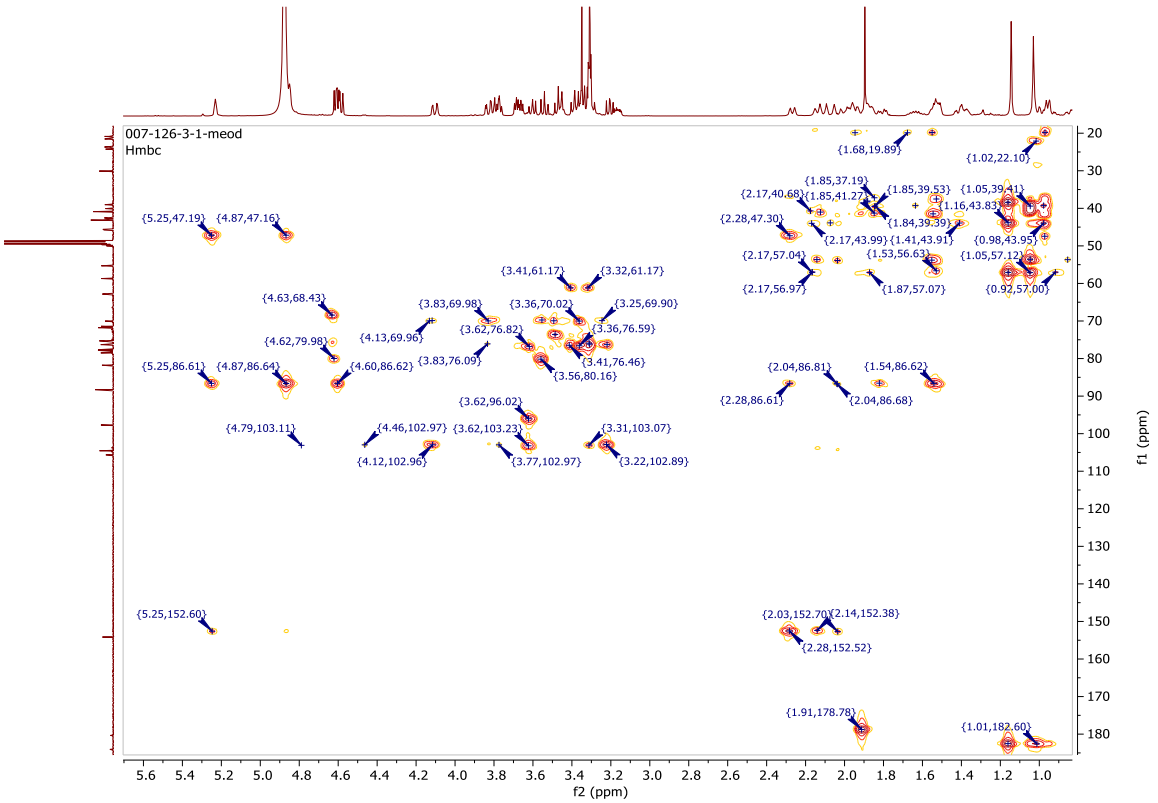
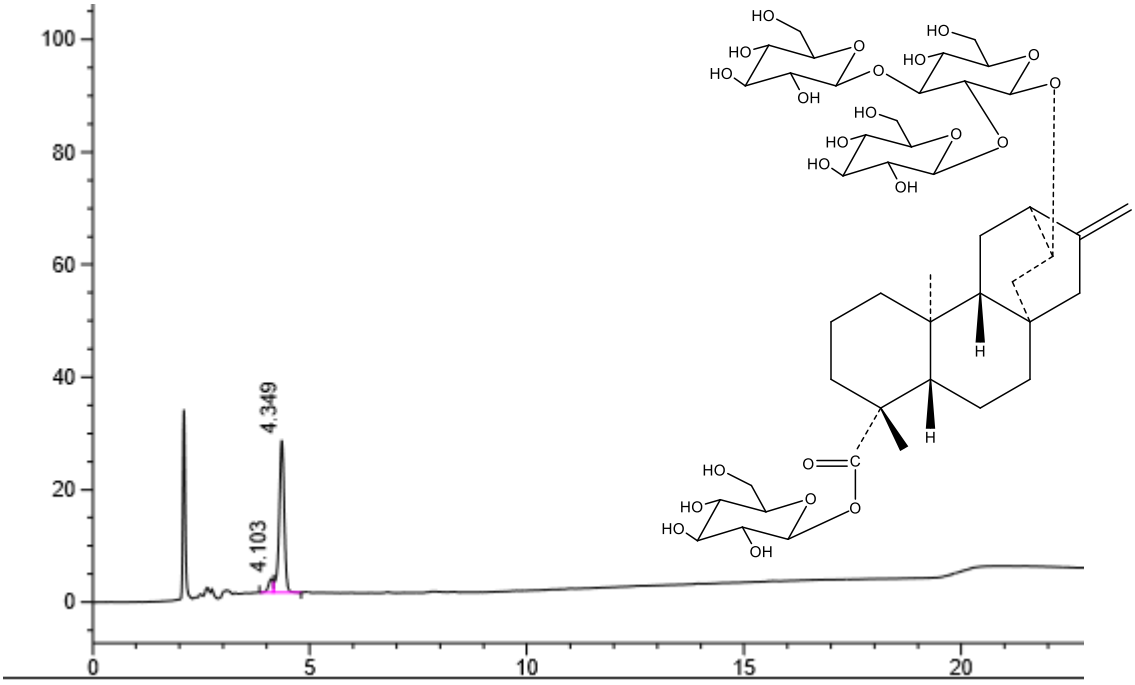


Figure 15. HMBC spectrum of compound **2**.

13-[(2-*O*-β-D-glucopyranosyl-3-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl) oxy]*ent*-hydroxyatis-16-en-19-oic acid -β-D-glucopyranosy ester (compound 3)



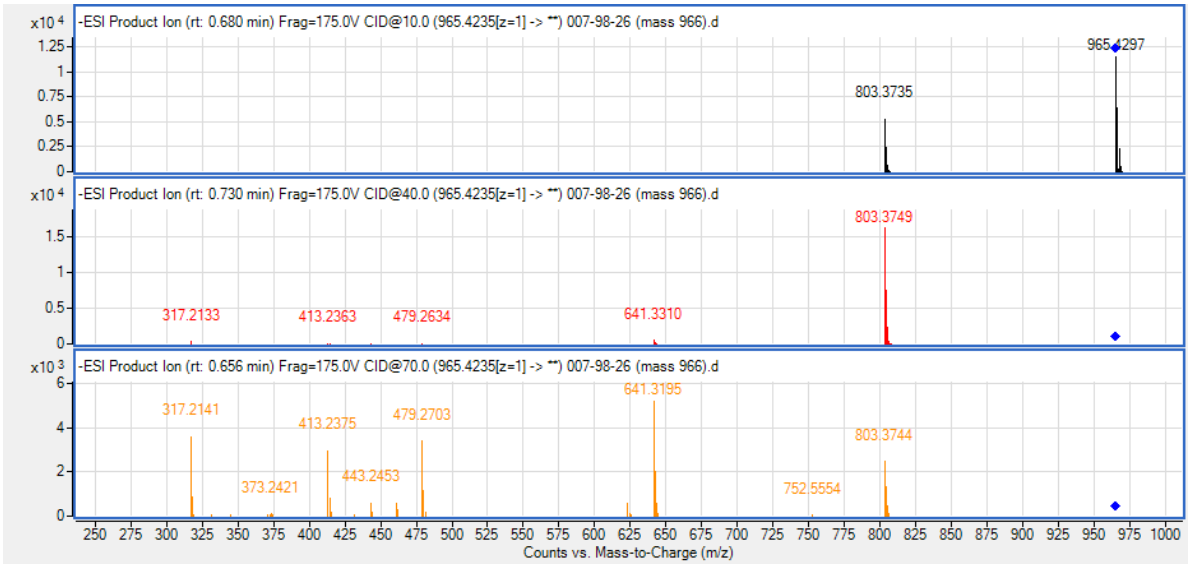


Figure 16. RP-C18 HPLC chromatogram**,** chemical structure and MS/MS spectrum of compound **3**.

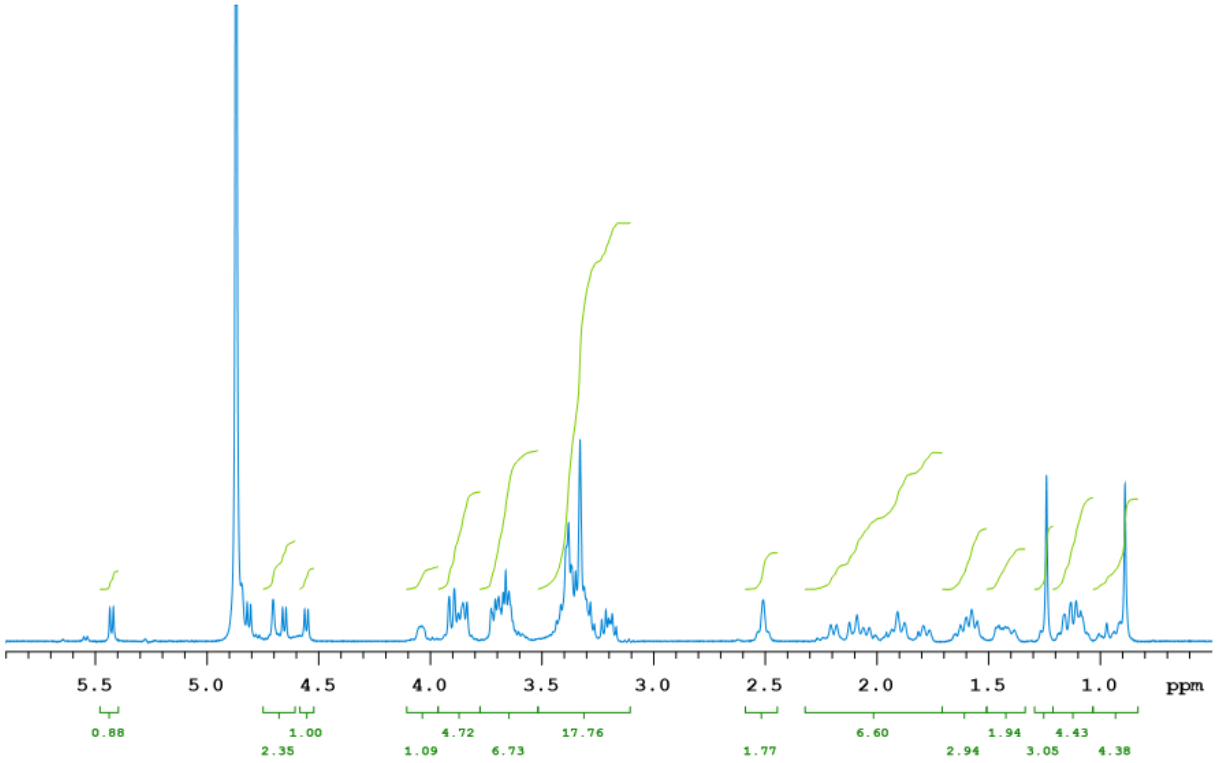


Figure 17. ^{1}H NMR spectrum of compound **3**.

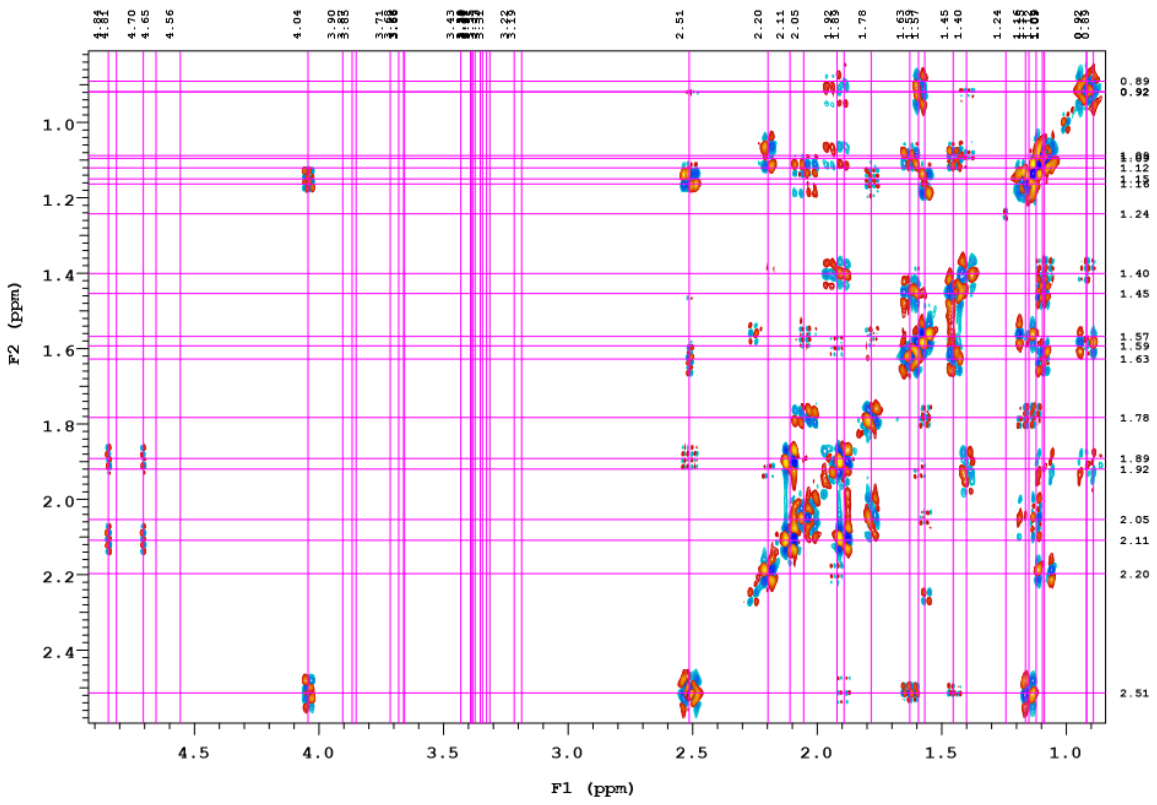


Figure 18. DQCOSY spectrum of compound 3.

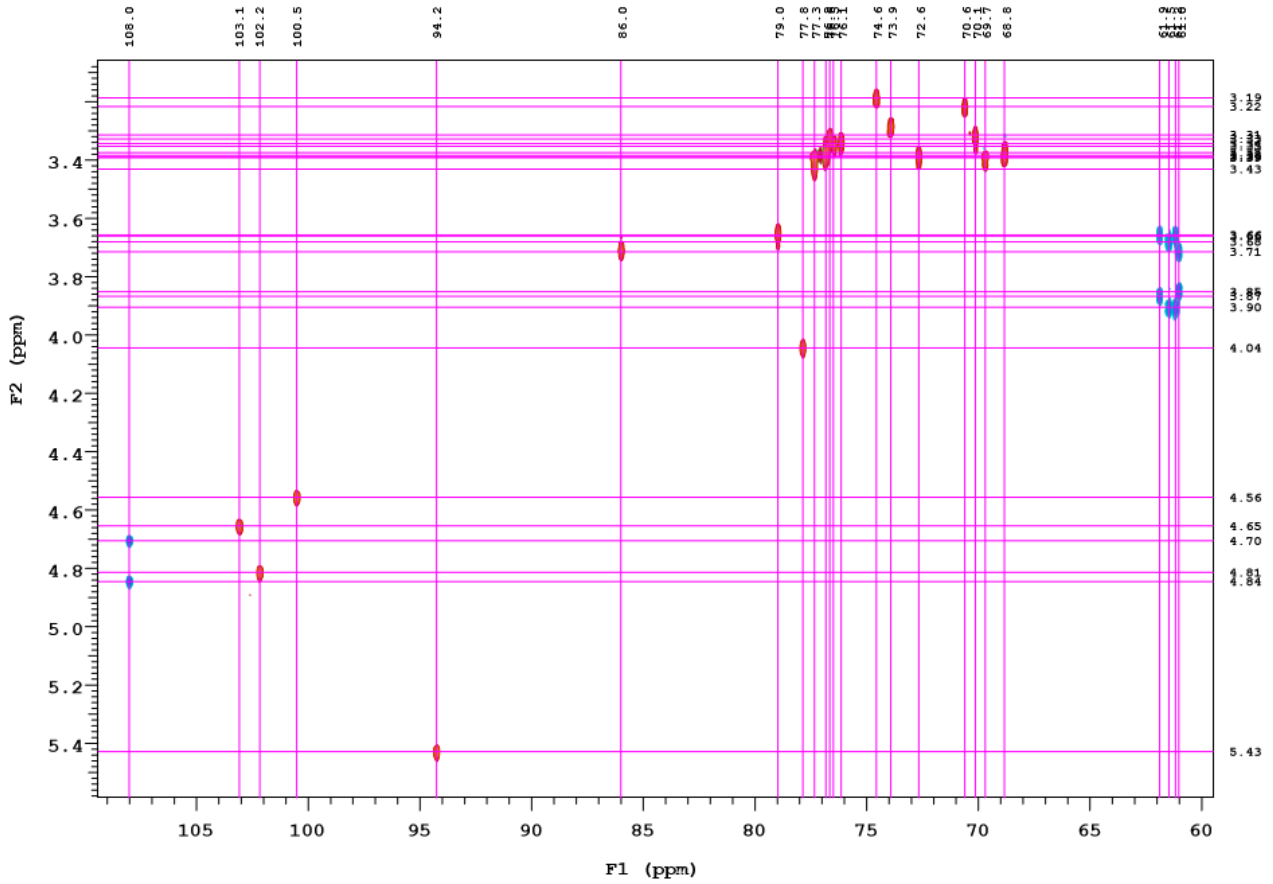


Figure 19. HSQC spectrum of compound 3 from 60 - 110 ppm.

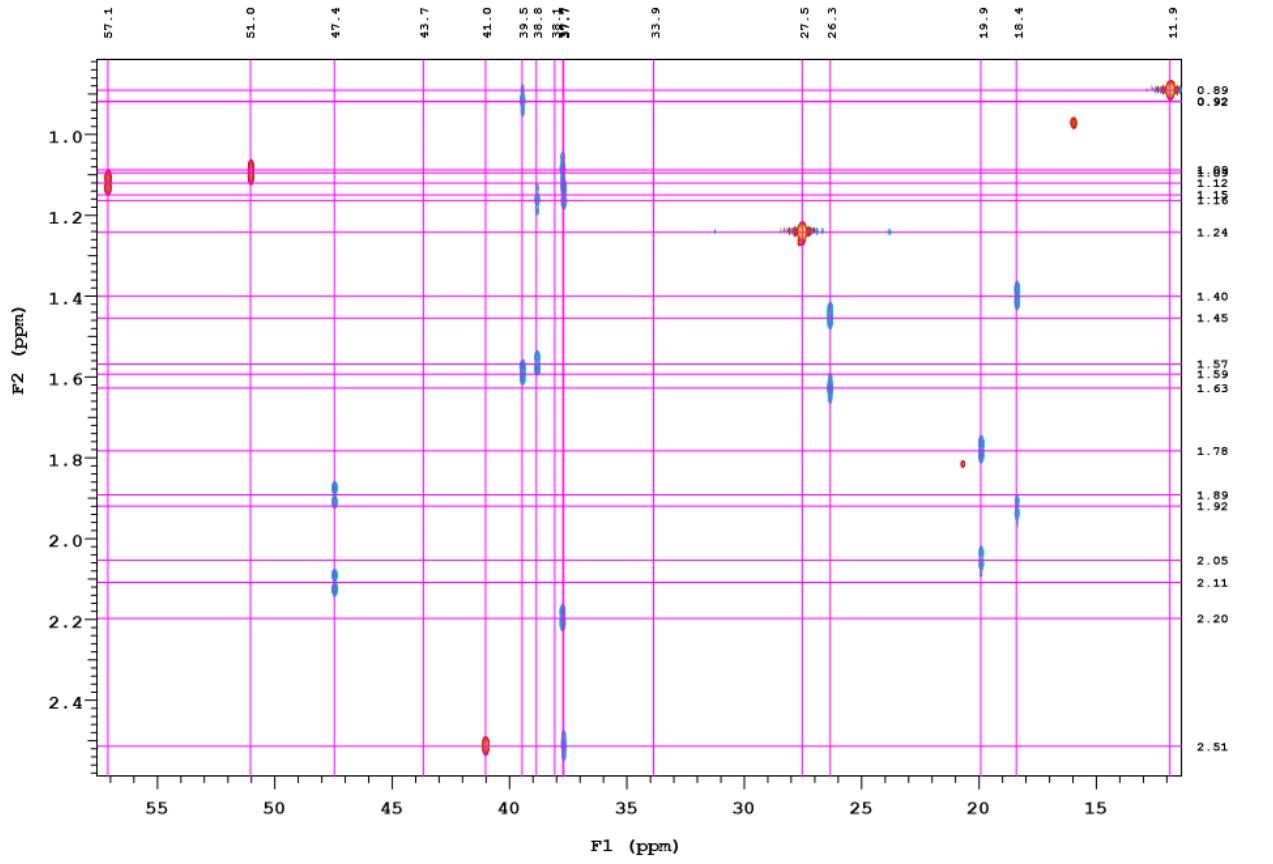


Figure 20. HSQC spectrum of compound 3 from 10 – 60 ppm.

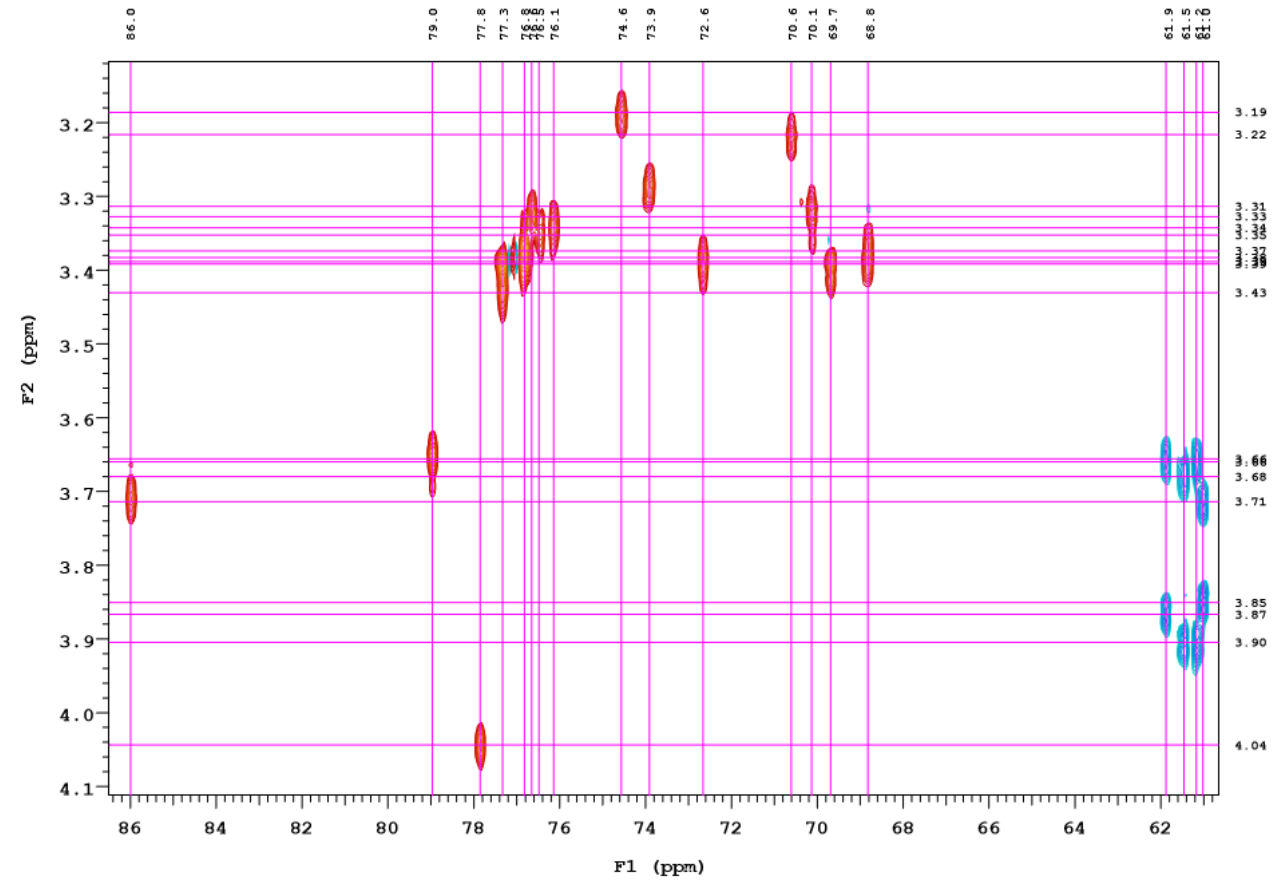


Figure 21. HSQC spectrum of compound 3 from 60 – 88 ppm.

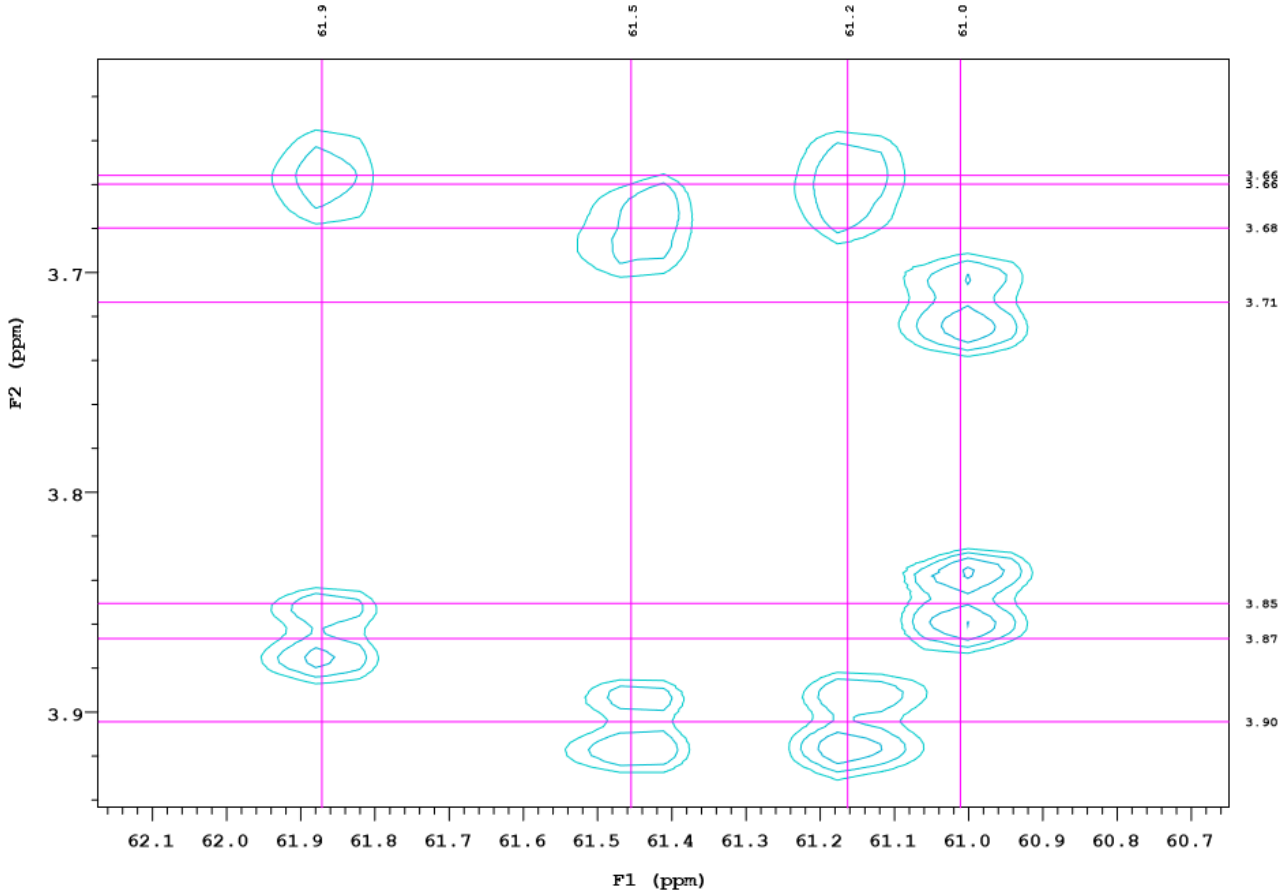


Figure 22. HSQC spectrum of compound 3 from 60 – 63 ppm.

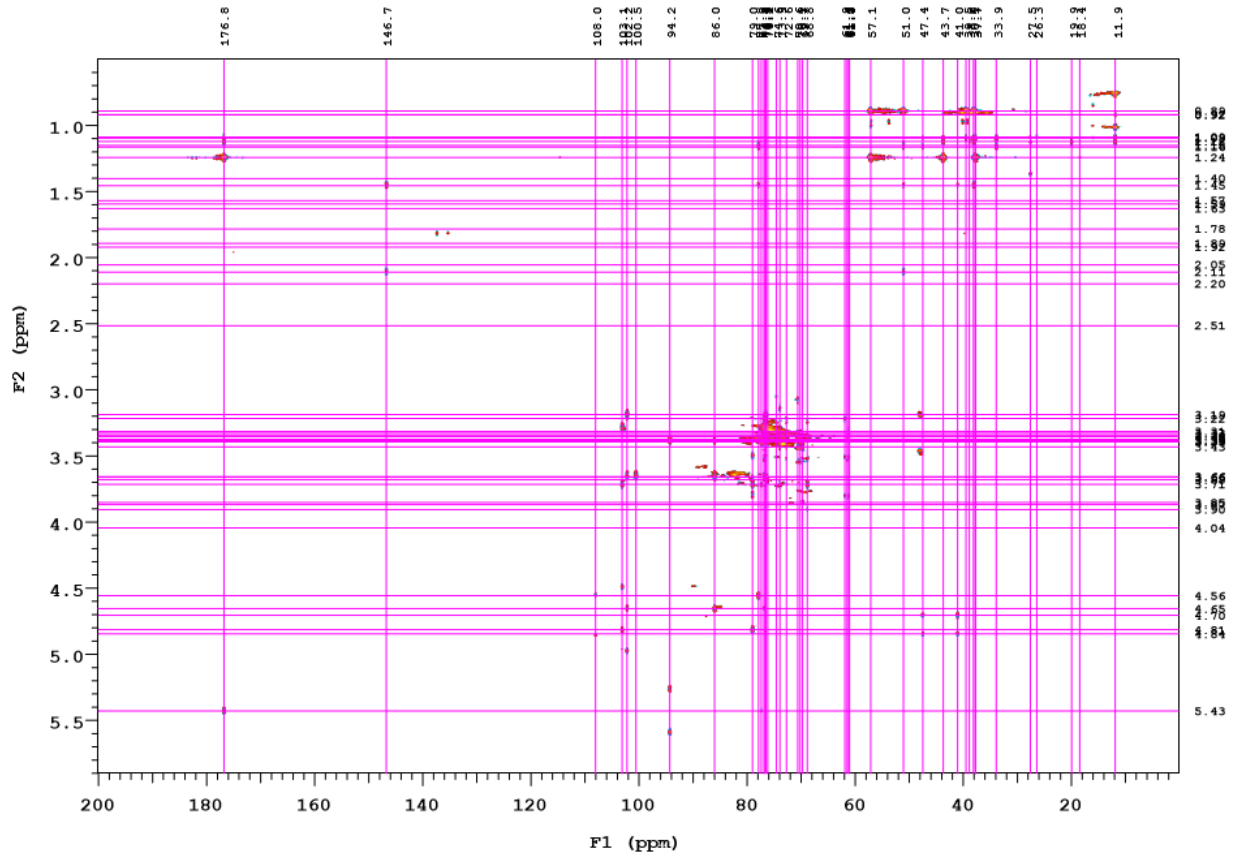


Figure 23. HMBC spectrum of compound 3.

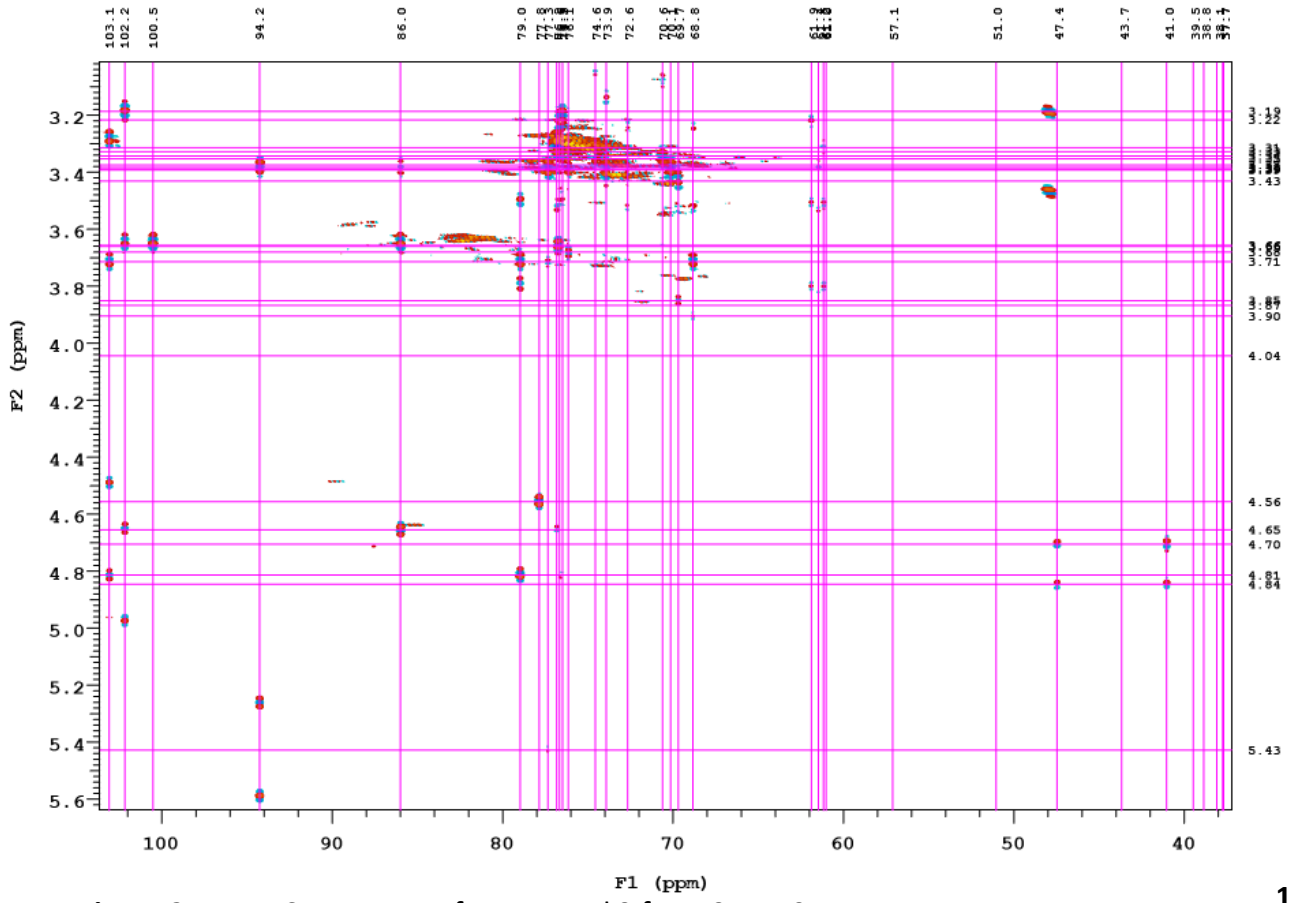


Figure 24. HMBC spectrum of compound 3 from 35 – 105 ppm.

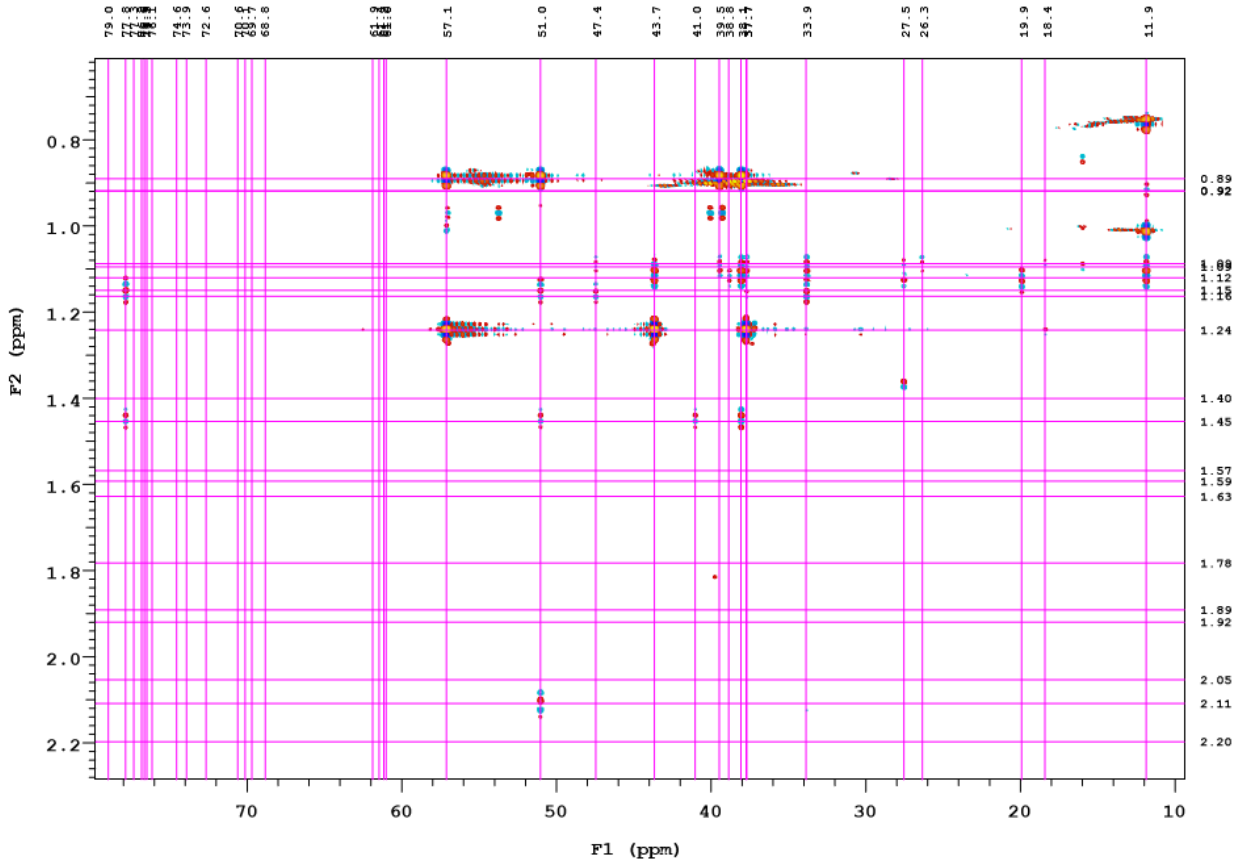


Figure 25. HMBC spectrum of compound 3 from 10 – 80 ppm.

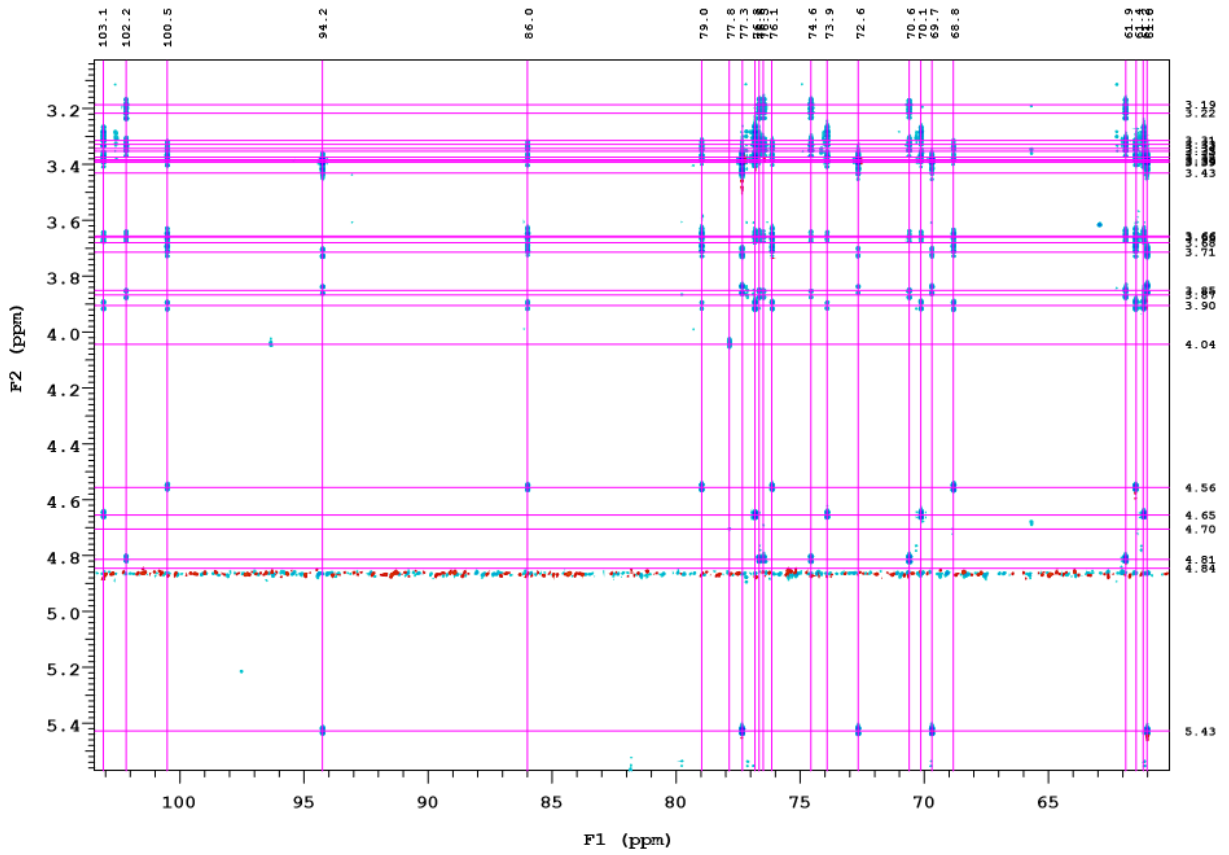


Figure 26. HMBC spectrum of compound 3 from 60 – 105 ppm.

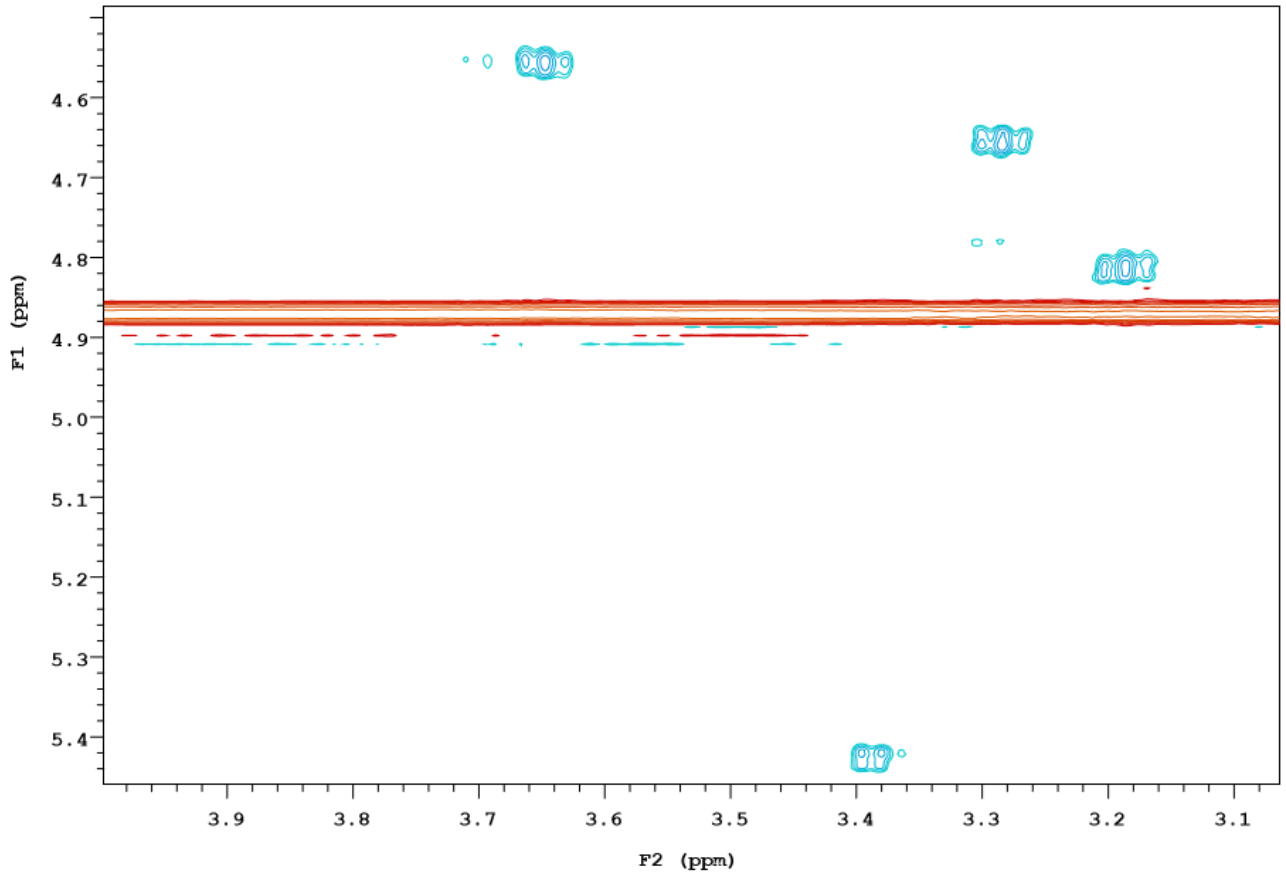


Figure 27. ^{1}H-^{1}H band-selective TOCSY spectrum of compound 3 with a mixing time of 50 ms.

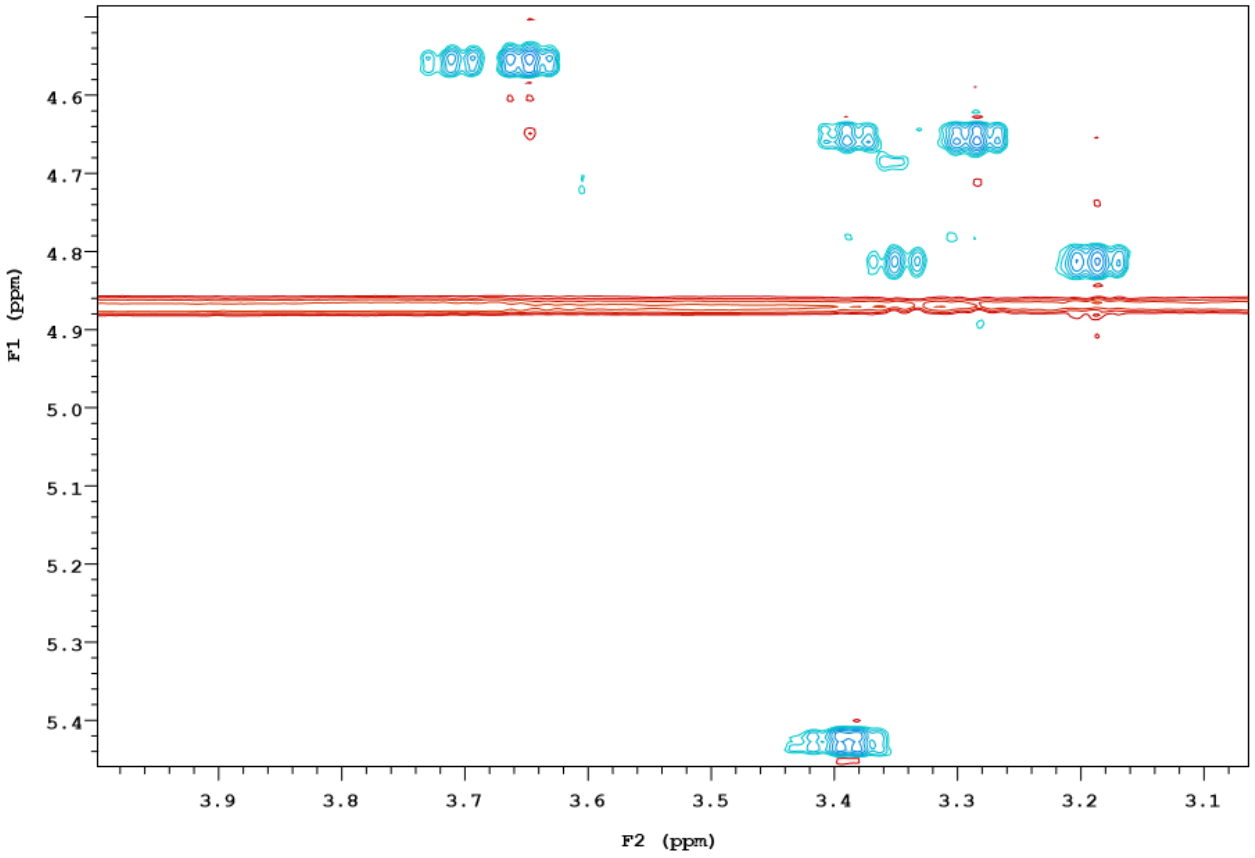


Figure 28. ^{1}H-^{1}H band-selective TOCSY spectrum of compound 3 with a mixing time of 70 ms.

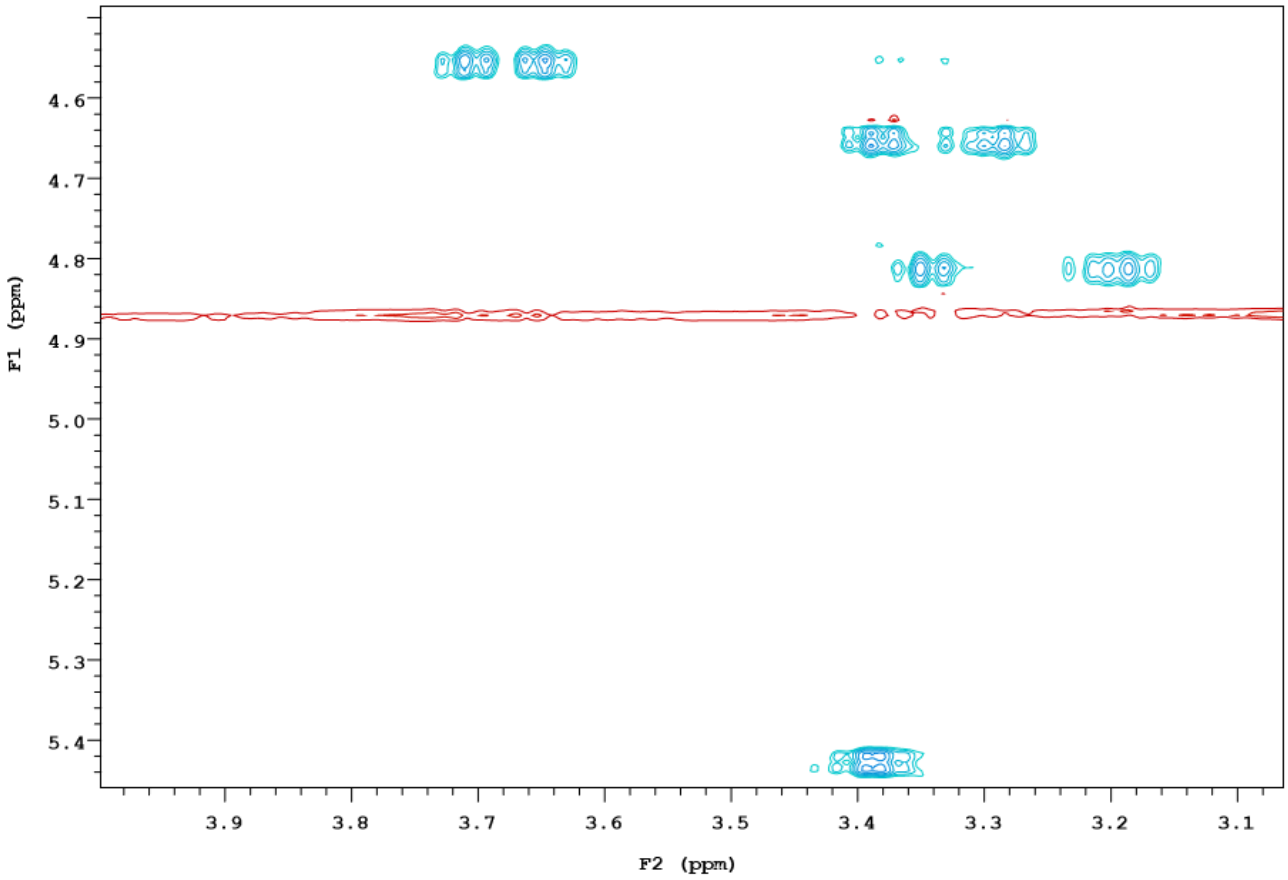


Figure 29. ^{1}H-^{1}H band-selective TOCSY spectrum of compound 3 with a mixing time of 100 ms.

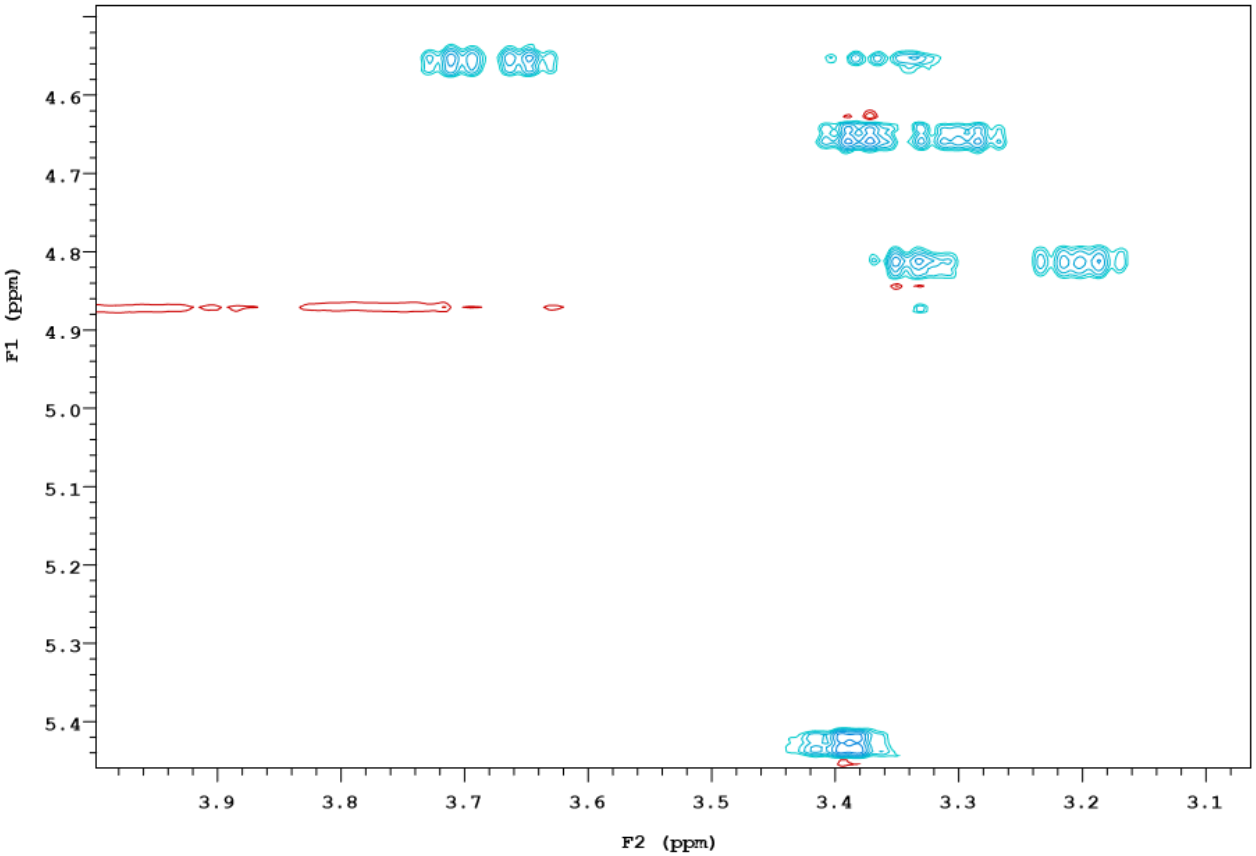
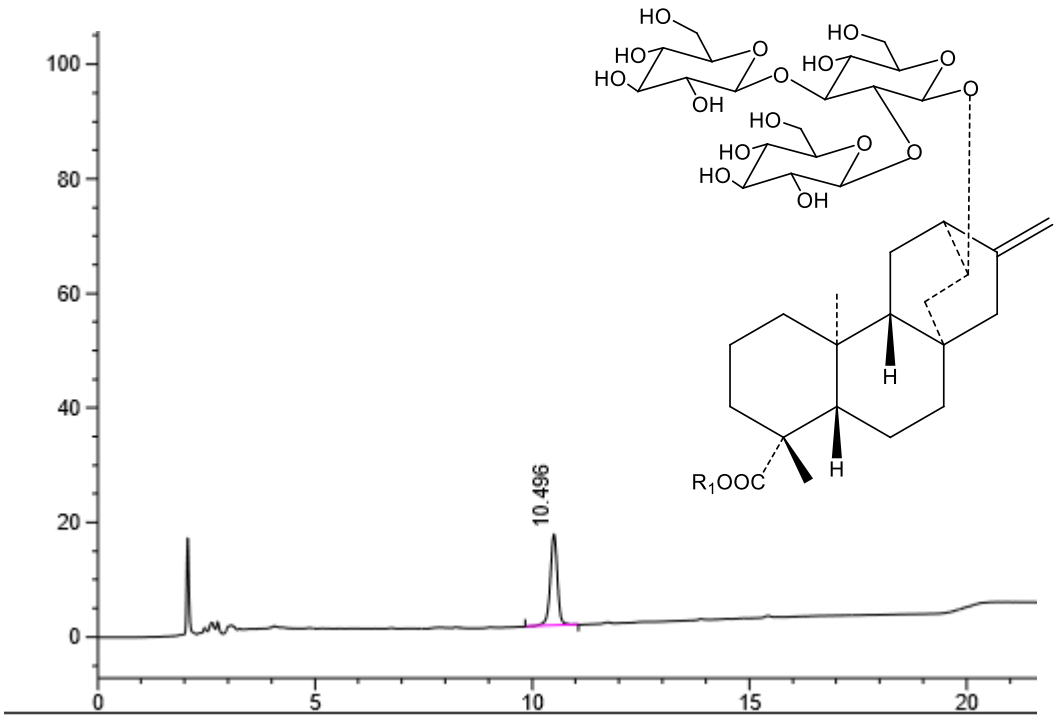


Figure 30. ^{1}H-^{1}H band-selective TOCSY spectrum of compound 3 with a mixing time of 150 ms.

13-[(2-*O*-β-D-glucopyranosyl-3-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl) oxy]*ent*-hydroxyatis-16-en-19-oic acid (compound 4)



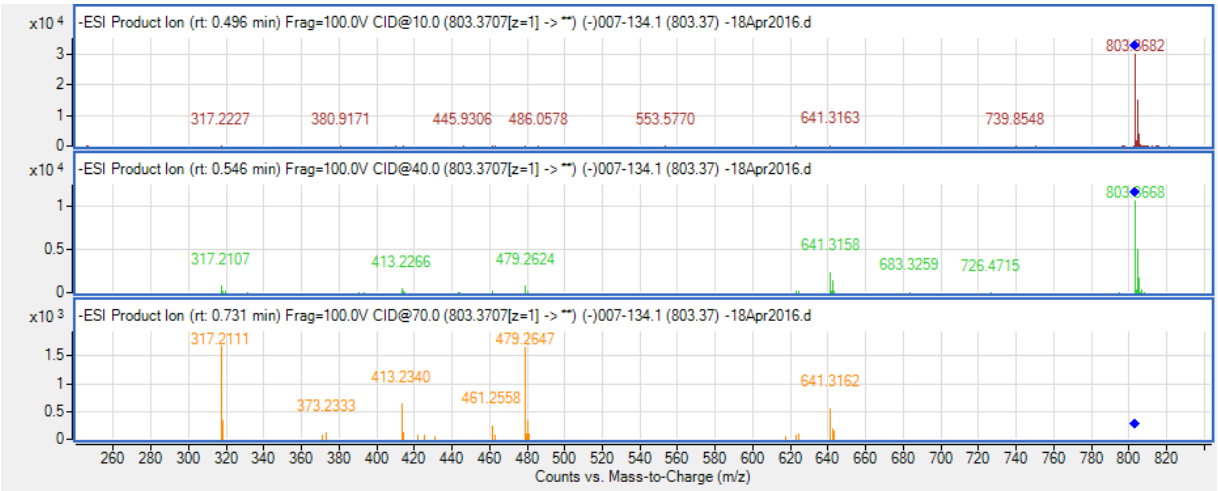


Figure 31. RP-C18 HPLC chromatogram**,** chemical structure and MS/MS spectrum of compound **4**.

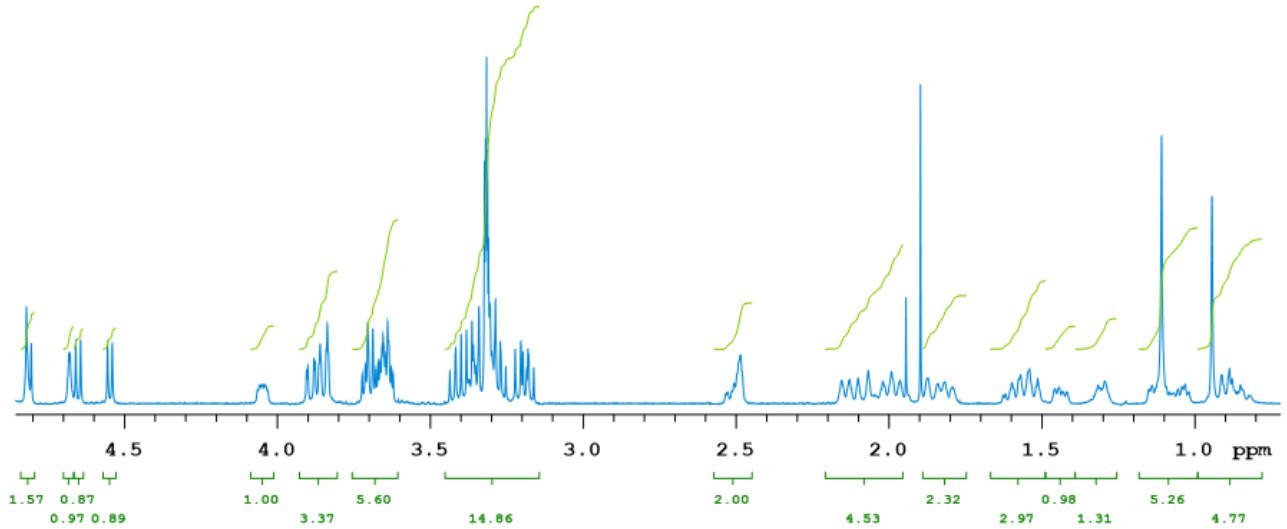


Figure 32. ^{1}H NMR spectrum of compound **4**.

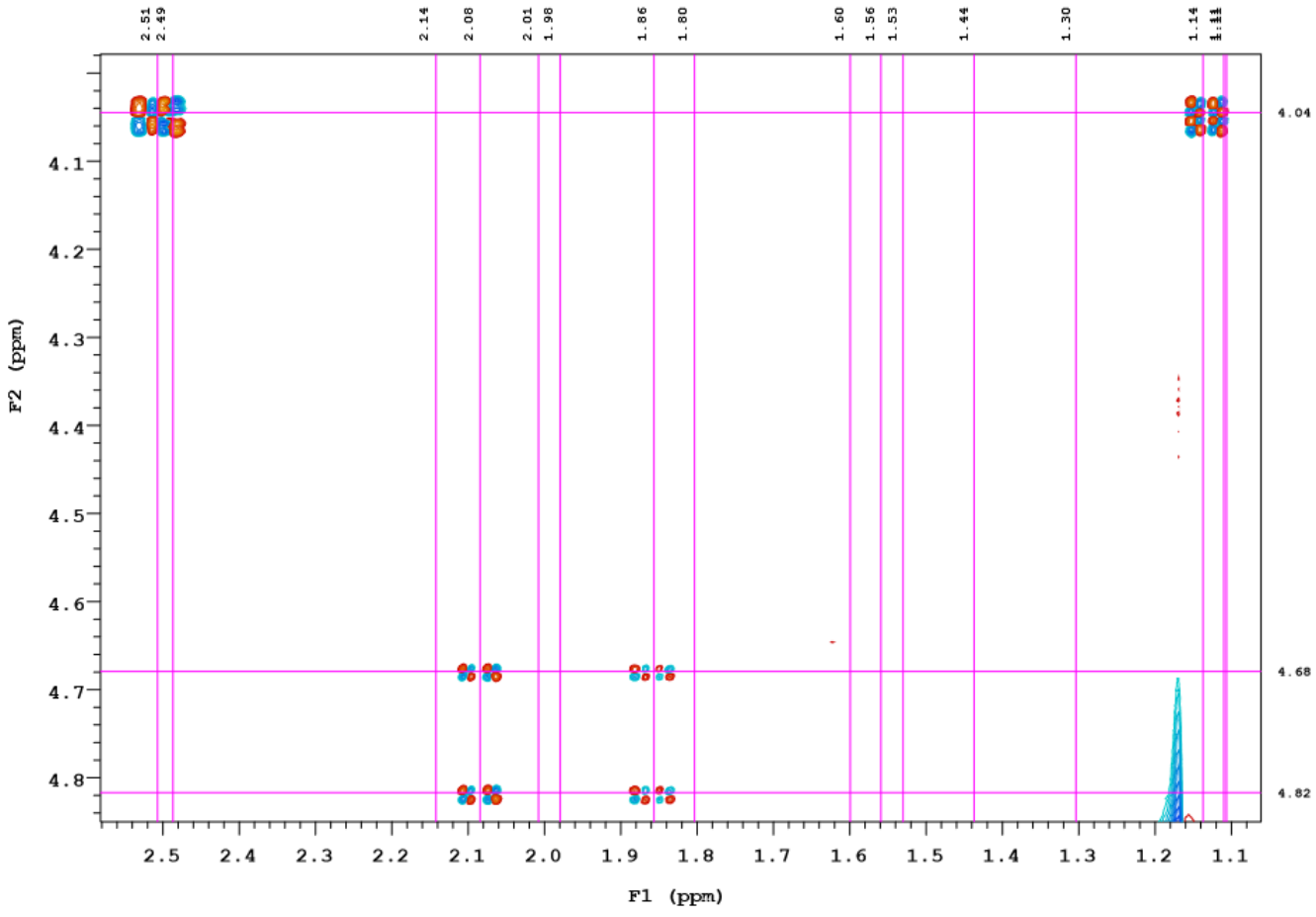


Figure 33. DQCOSY spectrum of compound 4.

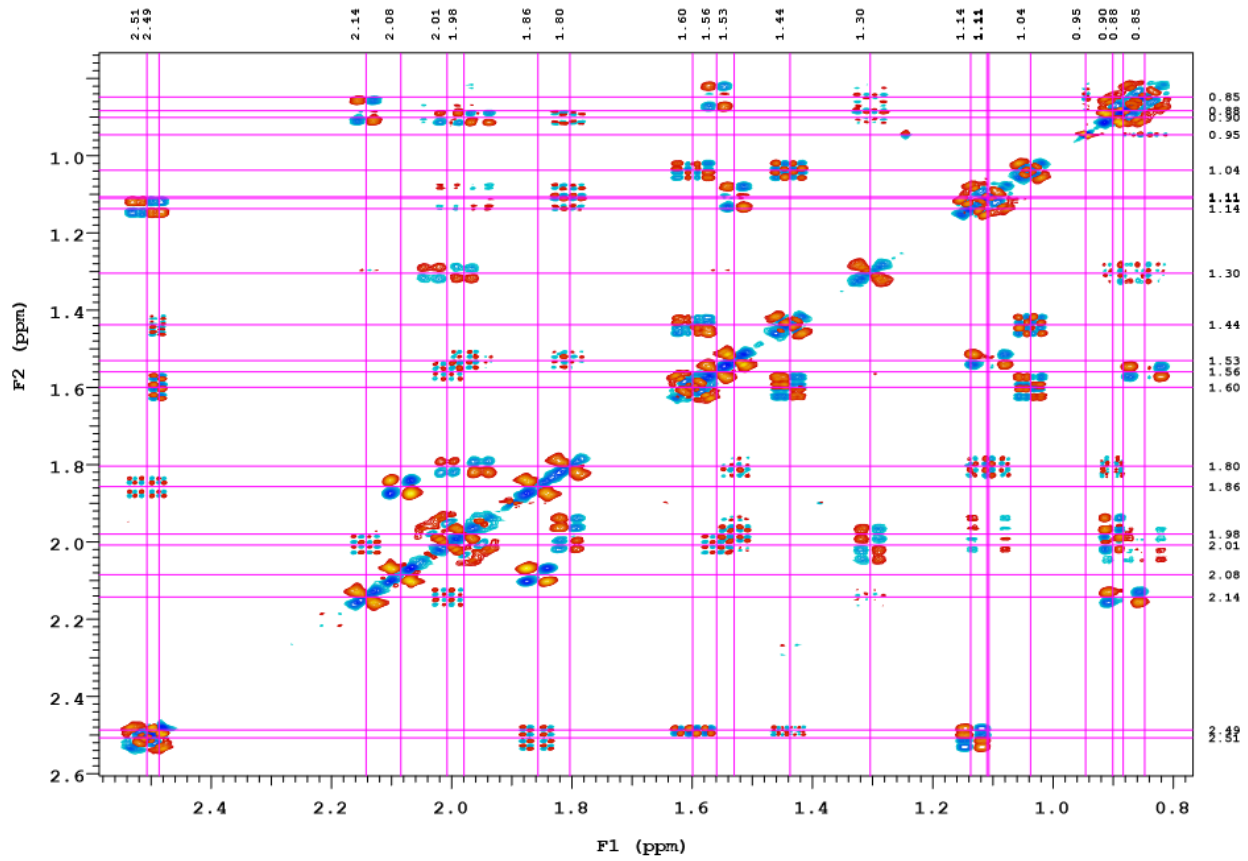


Figure 34. DQCOSY spectrum of compound 4.

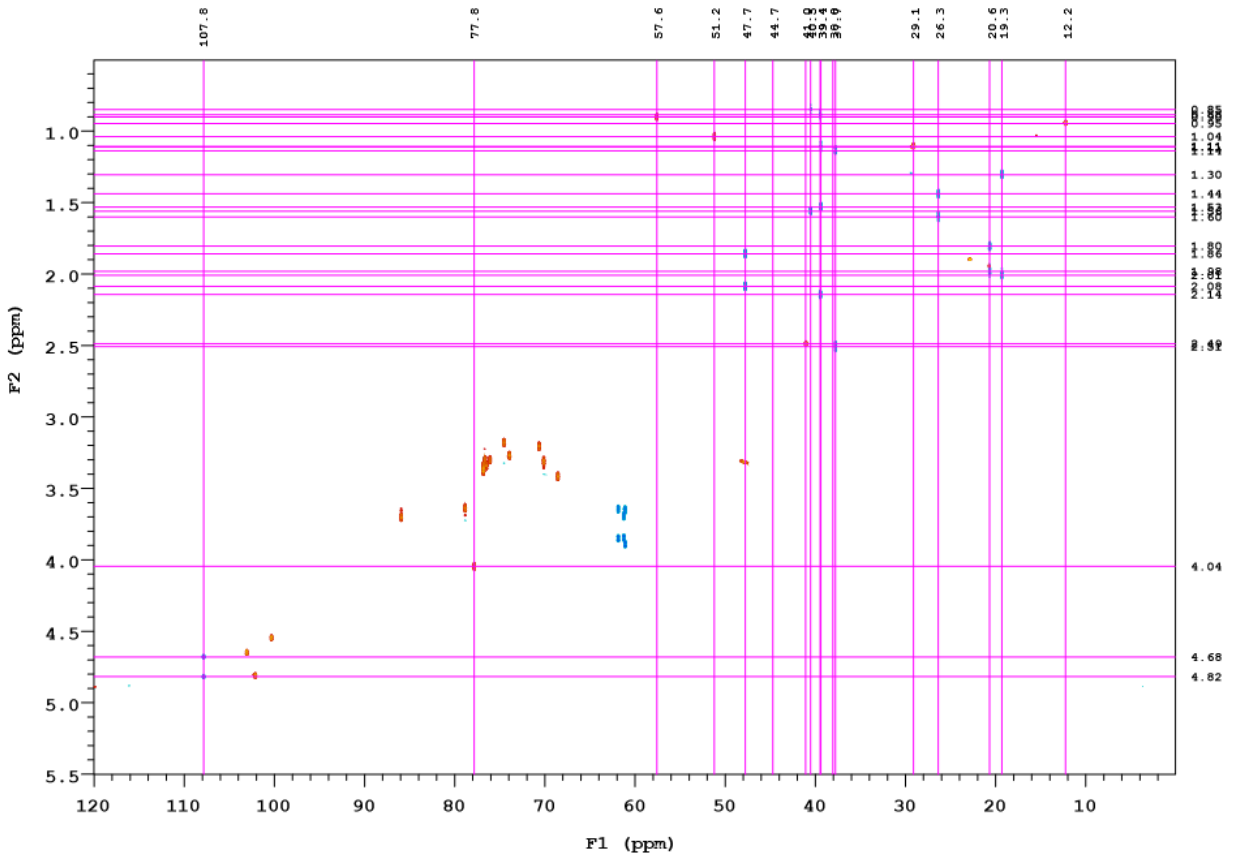


Figure 35. HSQC spectrum of compound 4 from 0 - 120 ppm.

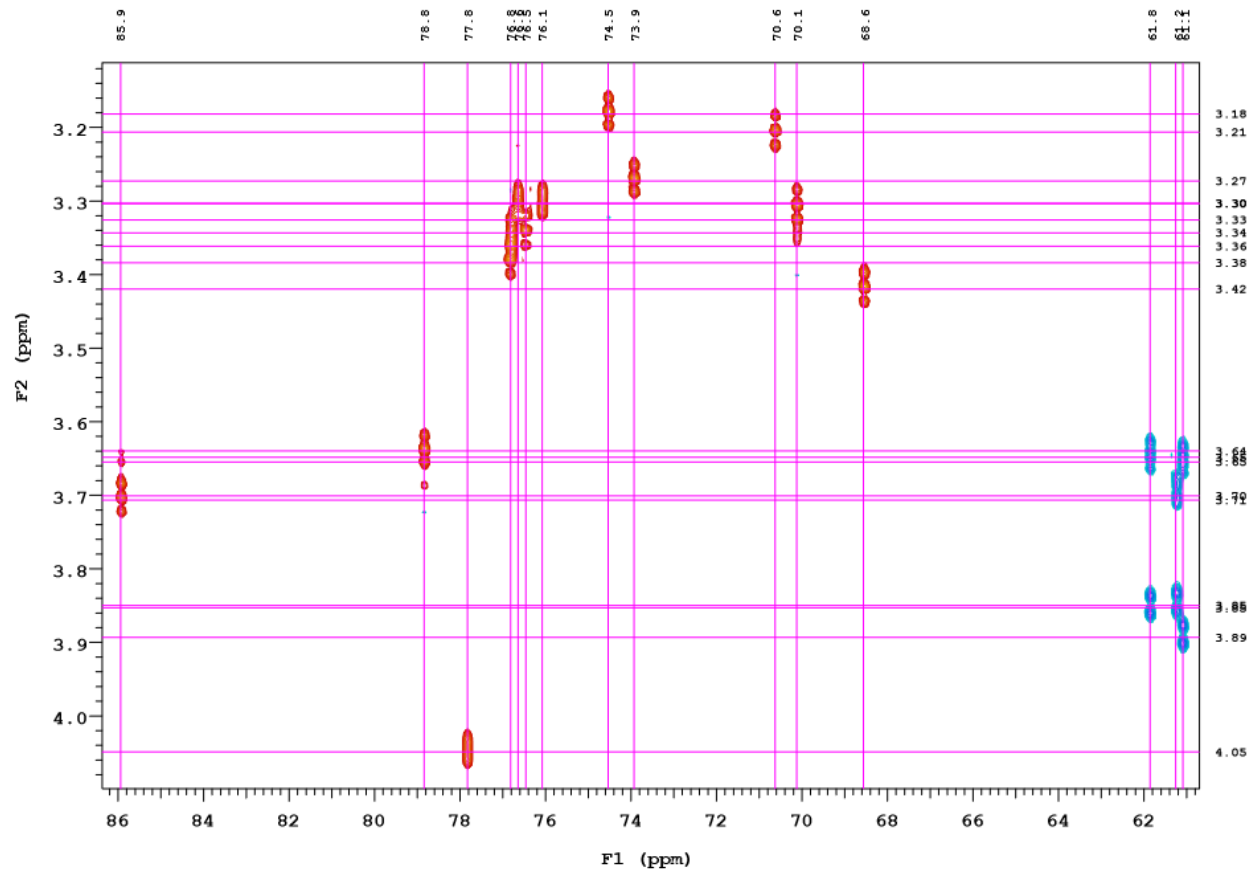


Figure 36. HSQC spectrum of compound 4 from 60 - 86 ppm.

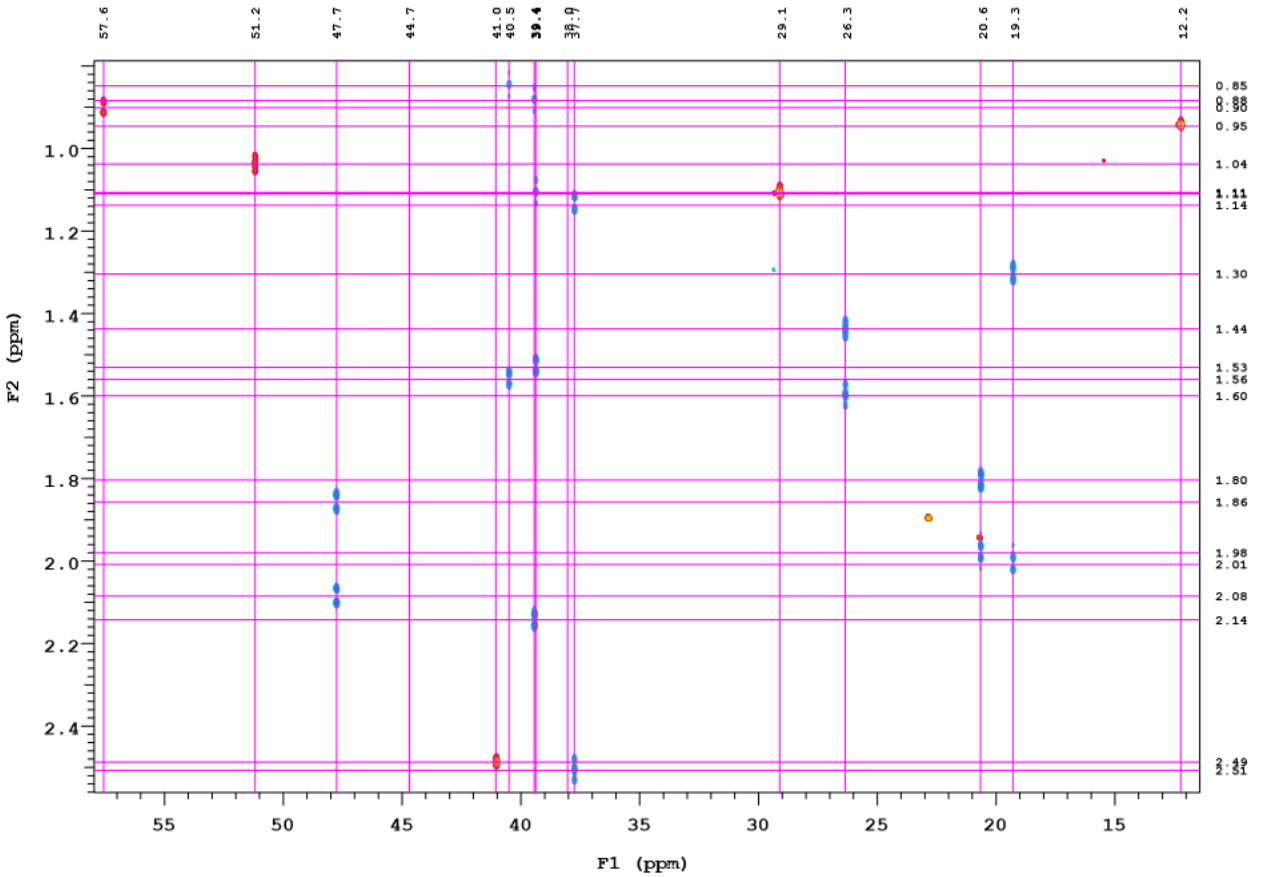


Figure 37. HSQC spectrum of compound 4 from 10 - 60 ppm.

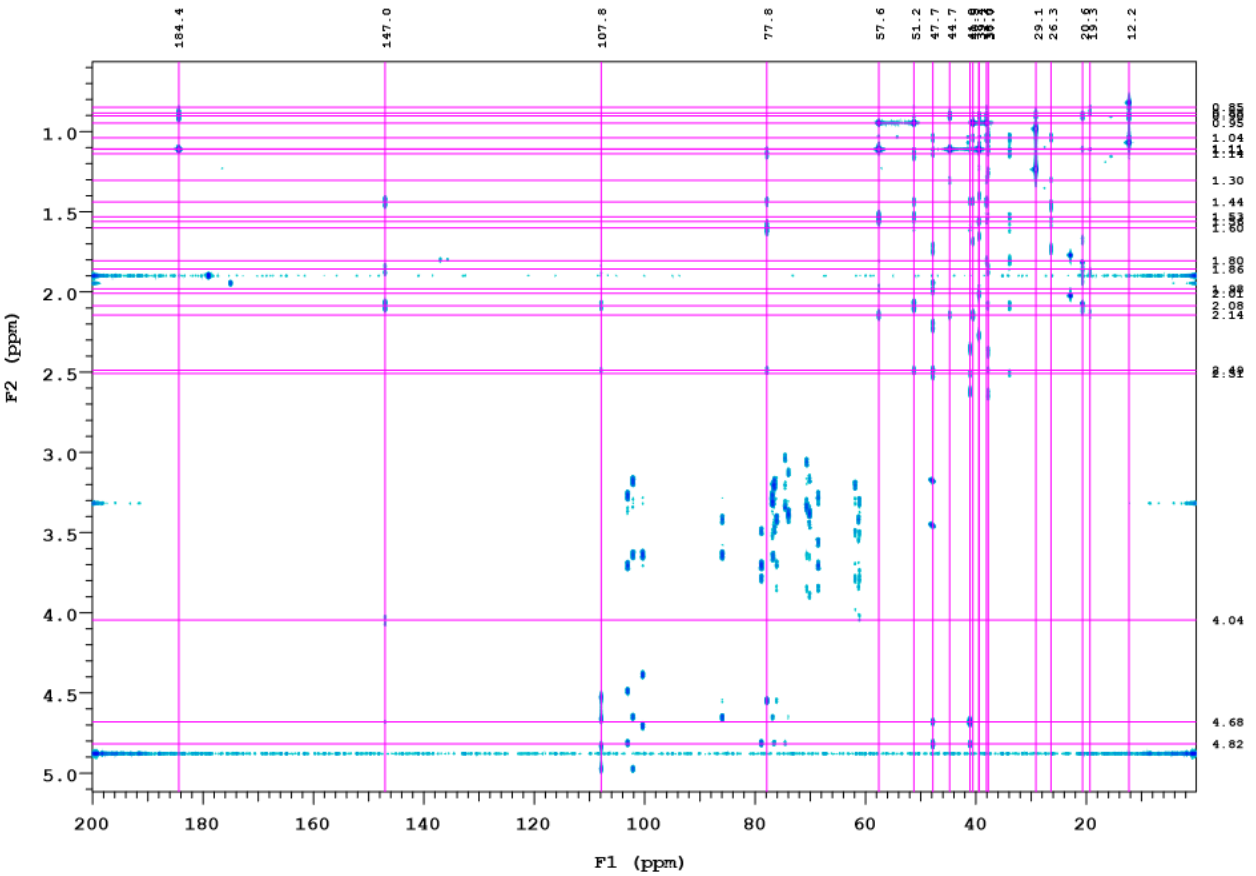


Figure 38. HMBC spectrum of compound 4 from 10 - 200 ppm.

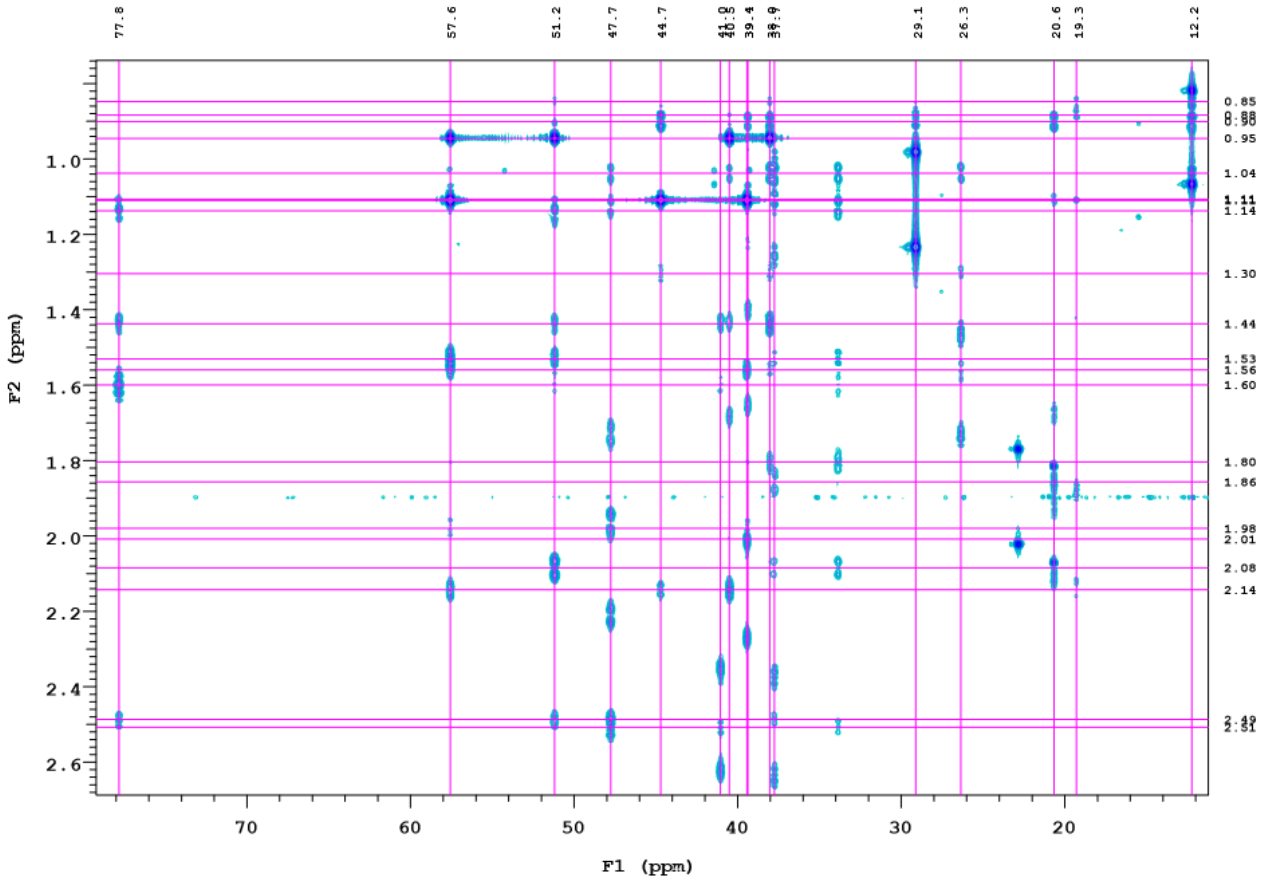


Figure 39. HMBC spectrum of compound 4 from 10 - 80 ppm.

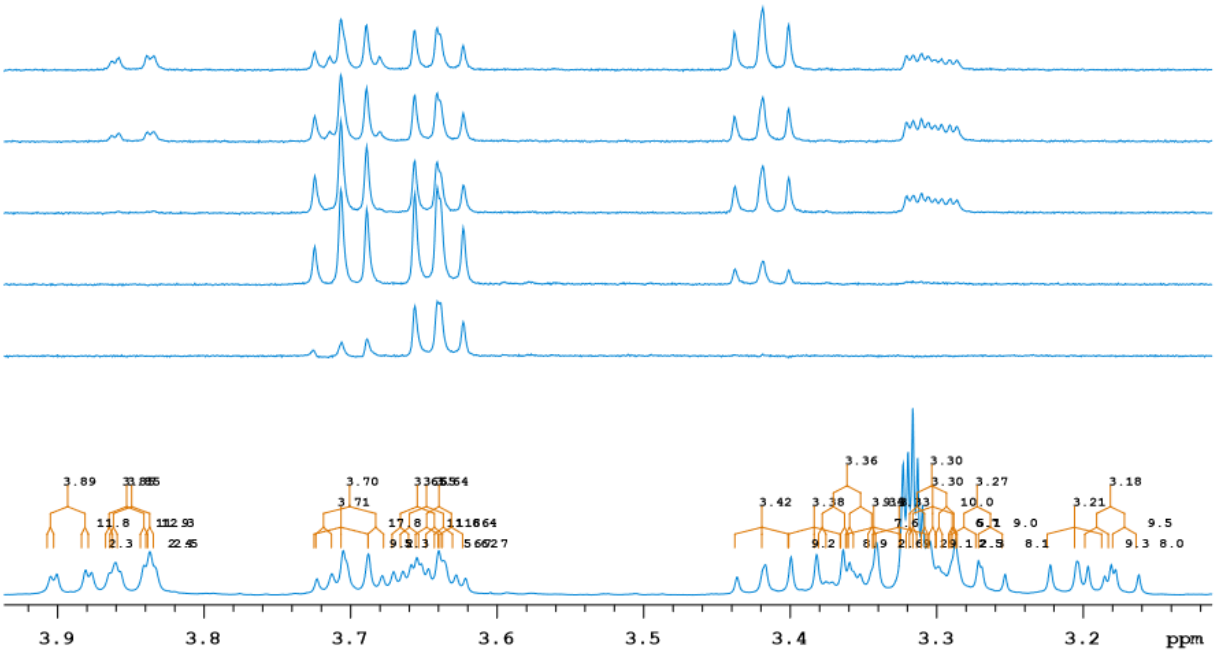


Figure 40: 1H spectrum, bottom, and TOCSY1D spectra with selective excitation at 4.55 ppm, and mixing times from lower to upper, 30, 60, 90, 120 and 150 ms.

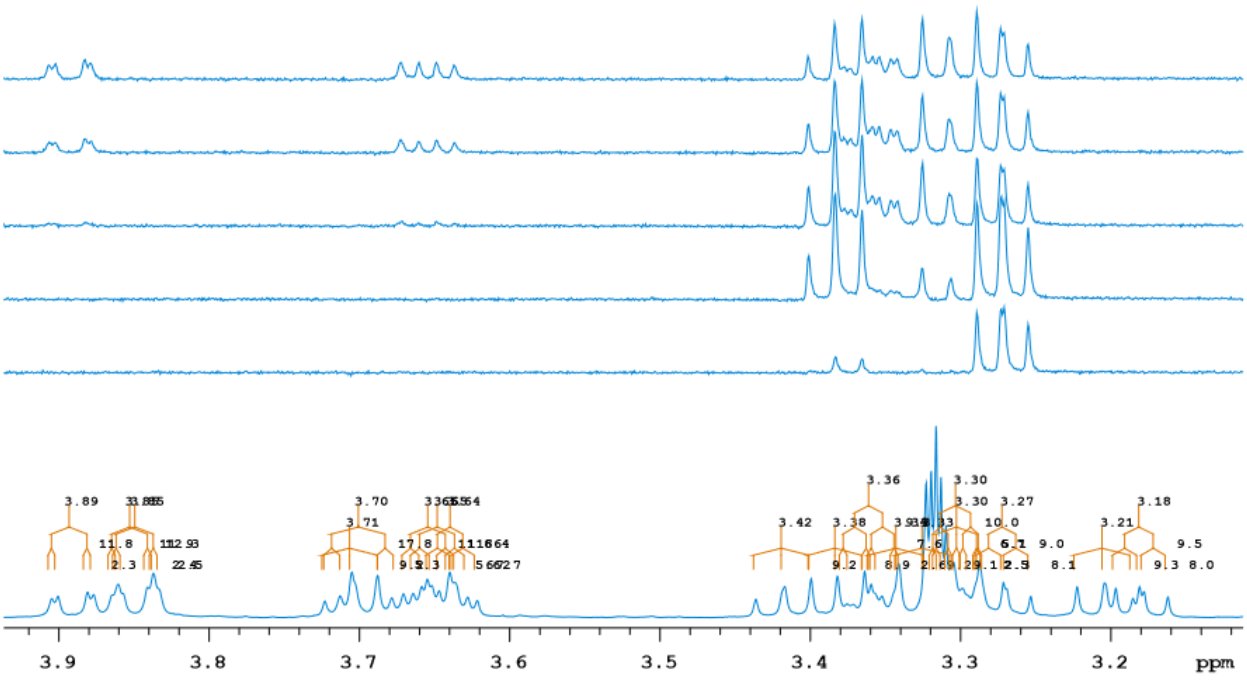


Figure 41: 1H spectrum, bottom, and TOCSY1D spectra with selective excitation at 4.65 ppm, and mixing times from lower to upper, 30, 60, 90, 120 and 150 ms.

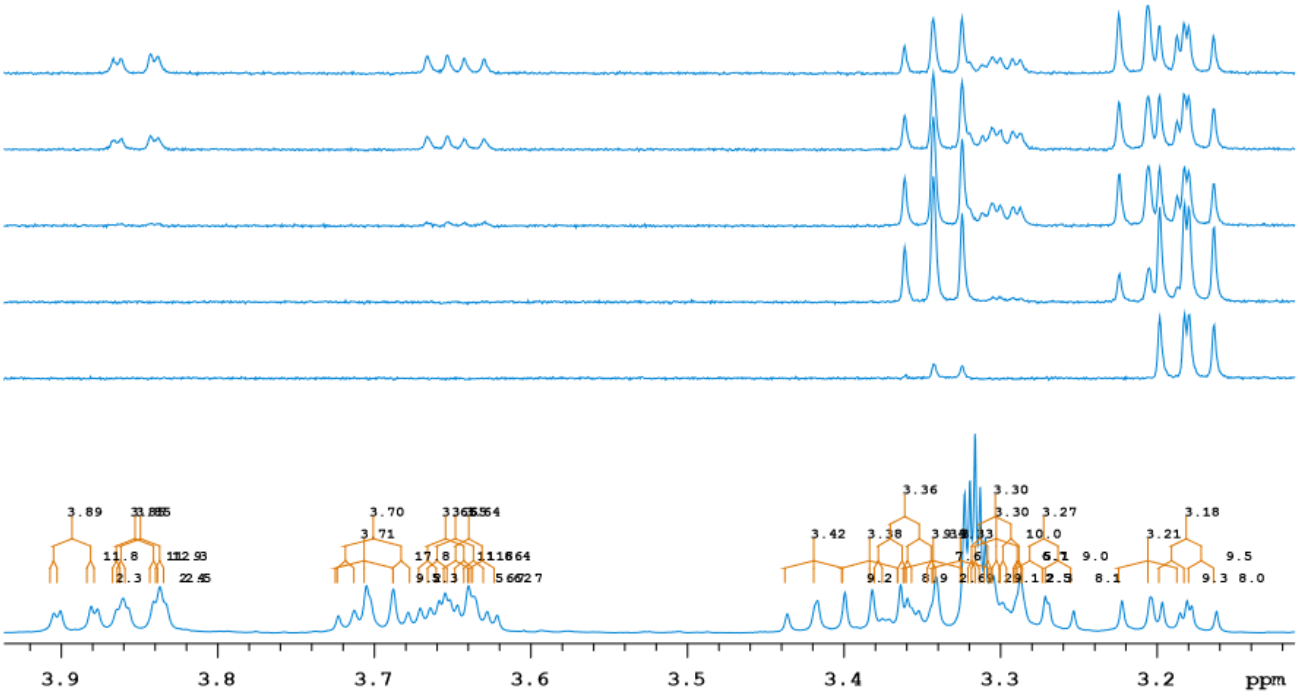


Figure 42: 1H spectrum, bottom, and TOCSY1D spectra with selective excitation at 4.81 ppm, and mixing times from lower to upper, 30, 60, 90, 120 and 150 ms.