Supporting Materials

Steroidal Constituents from Roots and Rhizomes of *Smilacina japonica*

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Physical and spectroscopic data of compounds 5–6

Compound **5**: White amorphous powder; was positive to Liebermann-Burchard and Molisch chemical reactions. ESI-MS m/z 1047.5 ([M_H]—), 1H-NMR (400MHz, pyridin-d5), 5.43（1H, *d*, *J* = 4.3Hz, H-11), 0.83（3H, *s*, CH_3-18), 0.91（3H, *s*, CH_3-19, 25S), 0.93（3H, *s*, CH_3-19, 25R), 0.92 (3H, *d*, *J* = 7.0 Hz), 1.07（3H, *d*, *J* = 7.1Hz, CH_3-27), 4.98（1H, d , *J* = 7.6Hz, H-Gal-1), 5.19（1H, d , J = 7.9Hz, H-Glc′-1), 5.26（1H, d , J = 7.7Hz, H-Xyl-1), 5.59（1H, d , J = 7.3Hz, H-Glc″-1); 13C-NMR (100MHz, pyridin-d5), 35.5（C-1), 29.3（C-2), 78.2（C-3), 34.1（C-4), 43.8（C-5), 29.3 (C-6), 33.8（C-7), 36.9（C-8), 146.6（C-9), 38.5（C-10), 117.5（C-11), 34.1（C-12), 43.8（C-13), 51.7（C-14), 31.3（C-15), 25S: 91.4 (C-16), 90.2（C-17), 16.7（C-18), 18.5（C-19), 45.8（C-20), 9.5（C-21), 110.9（C-22), 26.5（C-23), 25.7（C-24), 27.4（C-25), 65.1（C-26), 17.2（C-27）; 25R: 89.9 (C-16), 89.8（C-17), 16.7（C-18), 18.5（C-19), 45.7（C-20), 9.1（C-21), 109.9（C-22), 31.7（C-23), 29.1（C-24), 30.5（C-25), 66.8（C-26), 17.2（C-27）;103.0（Gal-1), 75.6（Gal-2), 73.7（Gal-3), 79.2（Gal-4), 76.7（Gal-5), 61.1（Gal-6); 105.3（Glc-1′), 81.8（Glc-2′), 87.3（Glc-3′), 71.5（Glc-4′), 77.9（Glc-5′), 63.4（Glc-6′); 105.4（Glc-1″), 75.5（Glc-1″), 78.2（Glc-1″), 71.2（Glc-4″), 78.1（Glc-5″), 62.9（Glc-6″); 105.7（Xyl-1), 75.5（Xyl-1), 79.1（Xyl-3), 70.9（Xyl-4), 67.8（Xyl-5）.Compared to the physical and spectroscopic data with literature values, compound **5** was identified as (25*S*)-5*α*-spirostan-9(11)-en-3*β*, 17*α*-diol 3-O-*β*-*D*-glucopyranosyl-(1→2)-[*β*-*D*- xylopyranosyl --(1→3)]-*β*-*D*-glucopyranosyl(1→4)-*β*-*D*-galactopyranoside(japonicoside B).

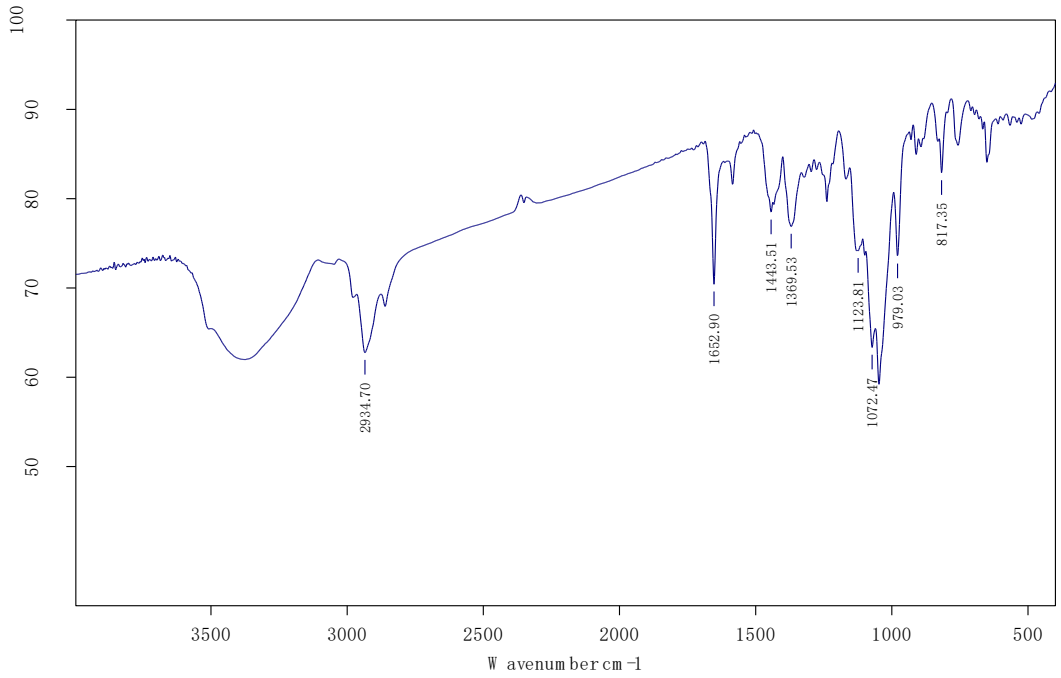
Compound **6**: White amorphous powder; was positive to Liebermann-Burchard and Molisch chemical reactions. ESI-MS *m/z* 1063.5 ([M-H]$^-$), ^{1}H-NMR (400MHz, pyridin-d_5) , 5.43（1H, d, *J* = 4.3Hz, H-11), 0.83（3H, s, CH_3-18), 1.22（3H, s, CH_3-19), 0.92 (3H, d, *J* = 7.0 Hz), 1.07（3H, d, *J* = 7.1Hz, CH_3-27), 4.98（1H,

d ，*J* = 7.6Hz，H-Gal-1），5.19（1H，d ，*J* = 7.9Hz，H-Glc′-1），5.26（1H，d ，*J* = 7.7Hz，H-Xyl-1），5.59（1H，d ，*J* = 7.3Hz，H-Glc″-1）；^{13}C-NMR (100MHz，pyridin-d_5), 35.5（C-1），29.3（C-2），78.2（C-3），34.1（C-4），43.8（C-5），29.3 (C-6)，33.3（C-7），36.4（C-8），146.6（C-9），37.3（C-10），117.5（C-11），32.5（C-12），43.8（C-13），51.7（C-14），31.3（C-15），91.4 (C-16)，90.2（C-17），16.7（C-18），18.5（C-19），45.3（C-20），9.5（C-21），110.9（C-22），36.4（C-23），65.5（C-24），34.1（C-25），63.5（C-26），9.8（C-27），103.0（Gal-1），75.6（Gal-2），73.7（Gal-3），79.2（Gal-4），76.7（Gal-5），61.1（Gal-6）；105.3（Glc-1′），81.8（Glc-2′），87.3（Glc-3′），71.5（Glc-4′），77.9（Glc-5′），63.4（Glc-6′）；105.4（Glc-1″），75.5（Glc-1″），78.2（Glc-1″），71.2（Glc-4″），78.1（Glc-5″），62.9（Glc-6″）；105.7（Xyl-1），75.5（Xyl-1），79.1（Xyl-3），70.9（Xyl-4），67.8（Xyl-5）。Compared to the physical and spectroscopic data with literature values, compound **6** was identified as (25*S*)-5*α*-spirostan-9(11)-en-3*β*, 17*α*, ,24*α*-diol 3-O-*β*-*D*-glucopyranosyl-(1→2)-[*β*-*D*- xylopyranosyl -(1→3)]-*β*-*D*-glucopyranosyl(1→4)-*β*-*D*-galactopyranoside(japonicoside C).

Reference

1.Liu X, Zhang H, Niu X F, et al. Steroidal saponins from Smilacina japonica. Fitoterapia, 2012, 83(4):812-816.

S1. The IR spectrum of compound 1 (in KBr)



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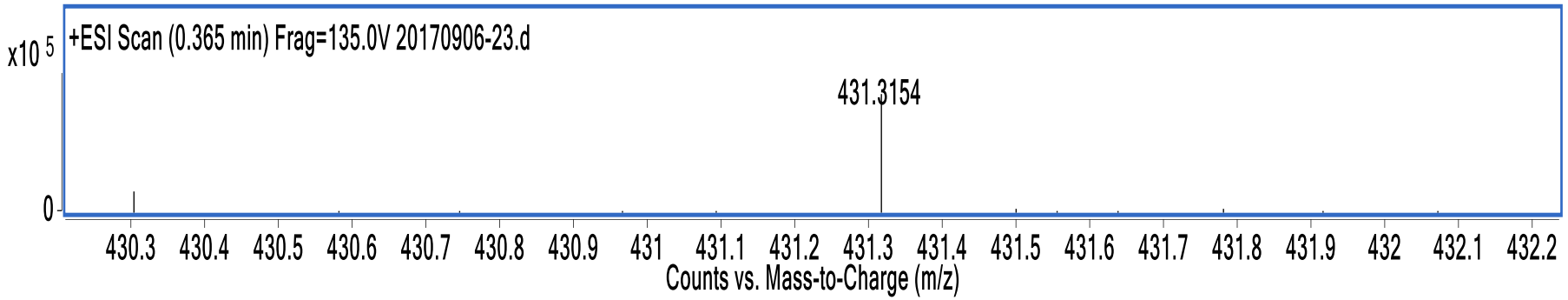
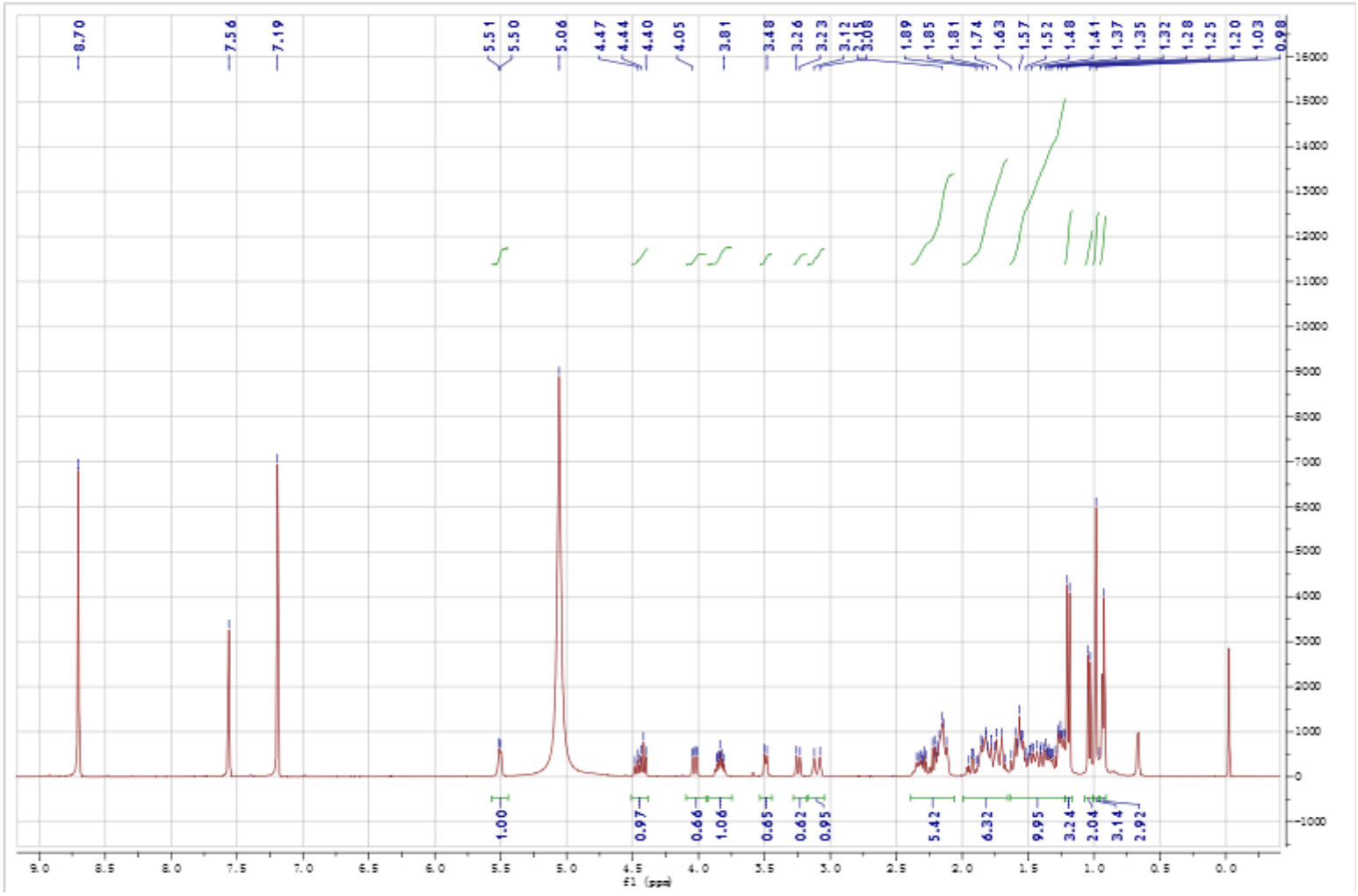
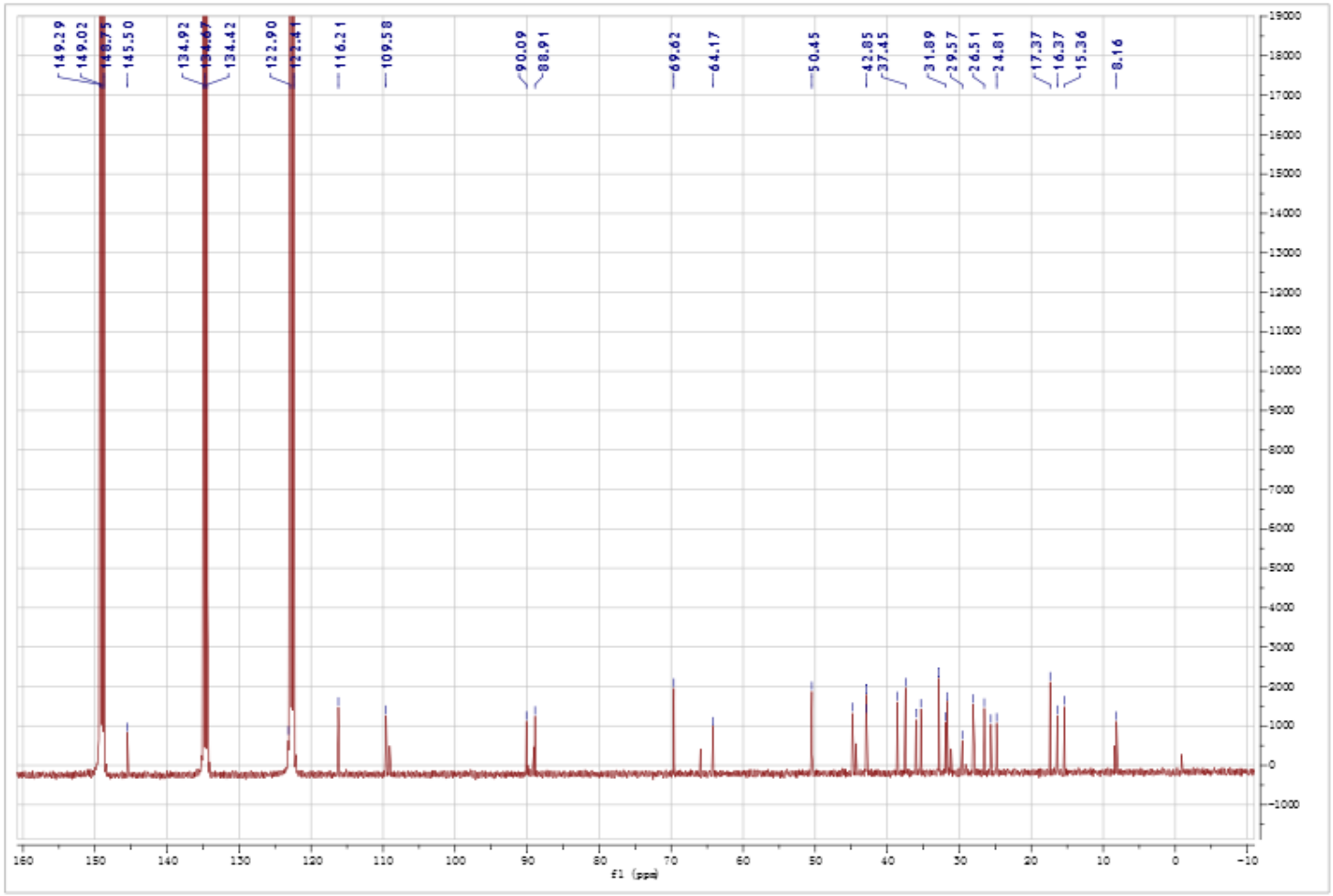
S2. The HR-ESI-MS spectrum of compound 1 (in MeOH)



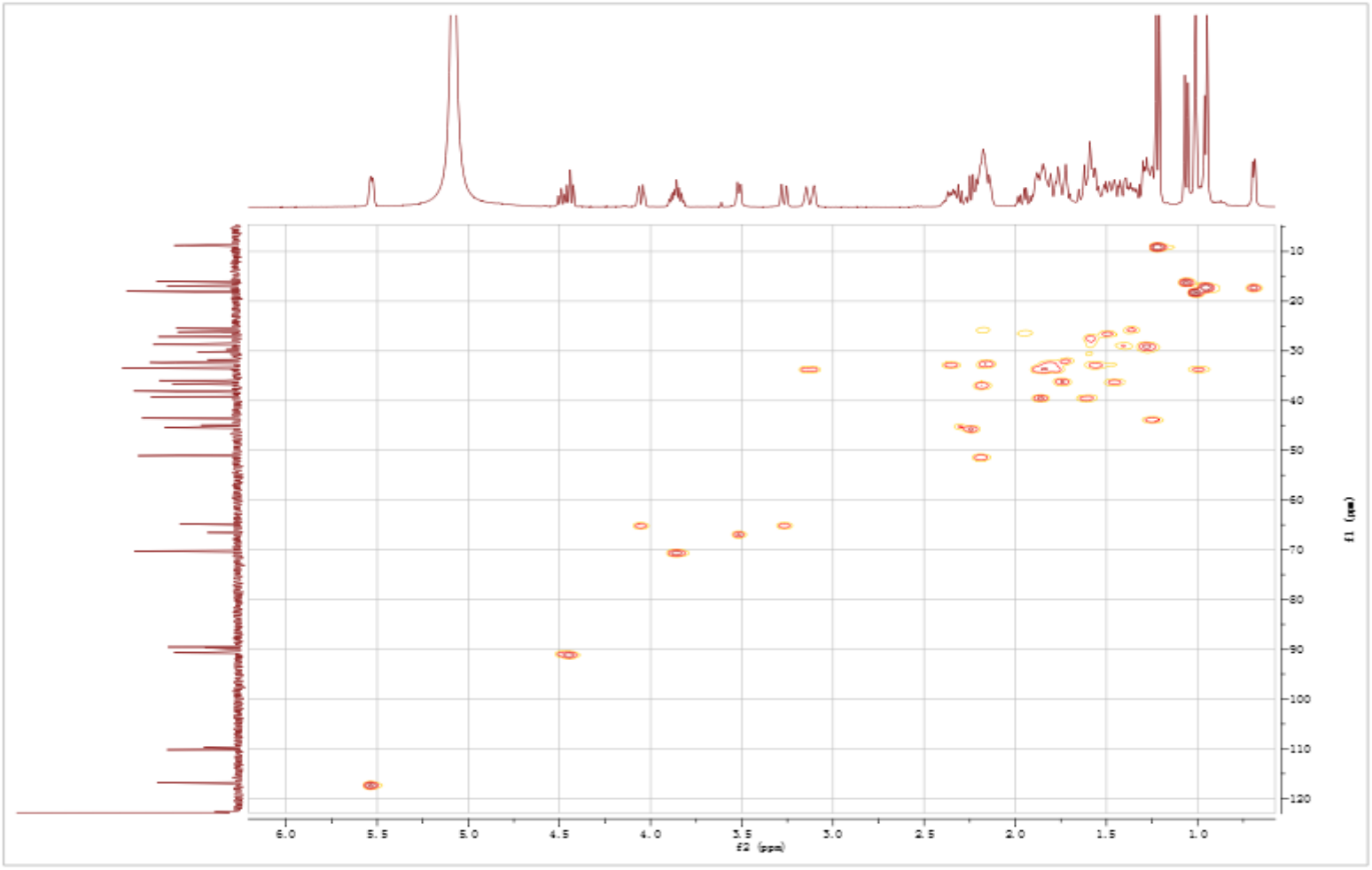
S3. The ^{1}H NMR spectrum of compound 1 (in pyridine-d5)



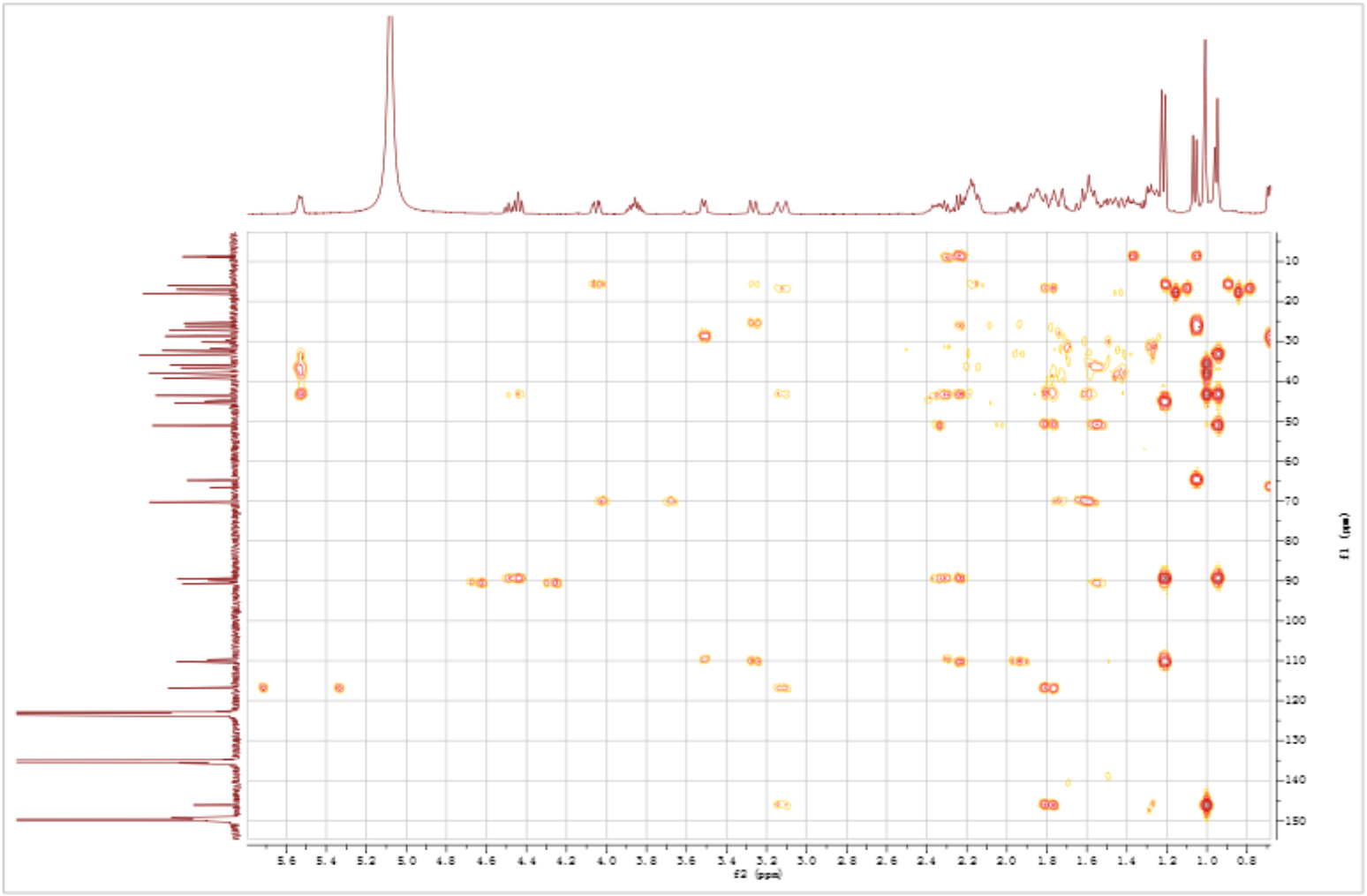
S4. The ^{13}C NMR spectrum of compound 1 (in pyridine-d5)



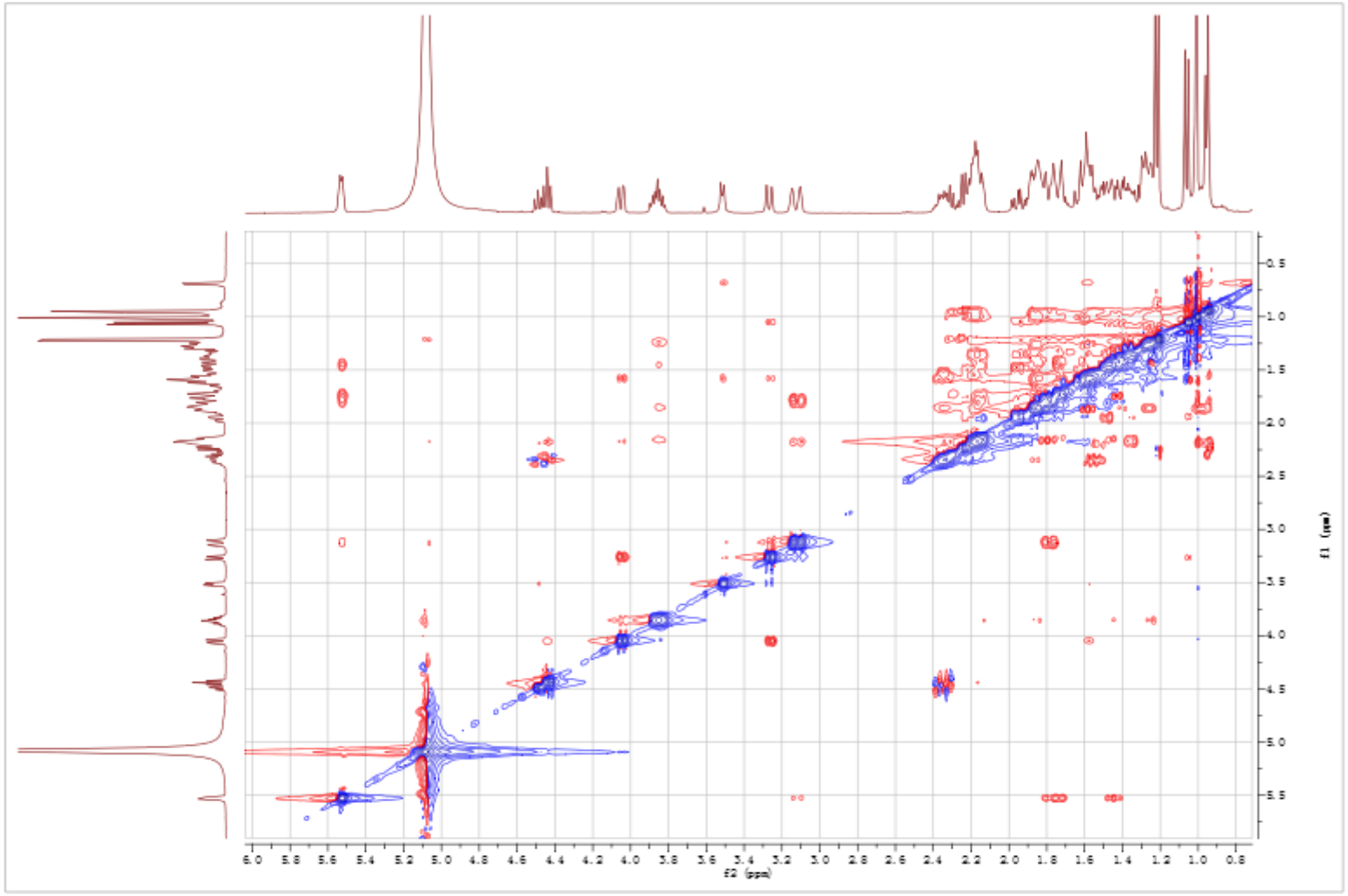
S5. The HSQC spectrum of compound 1 (in pyridine-d5)



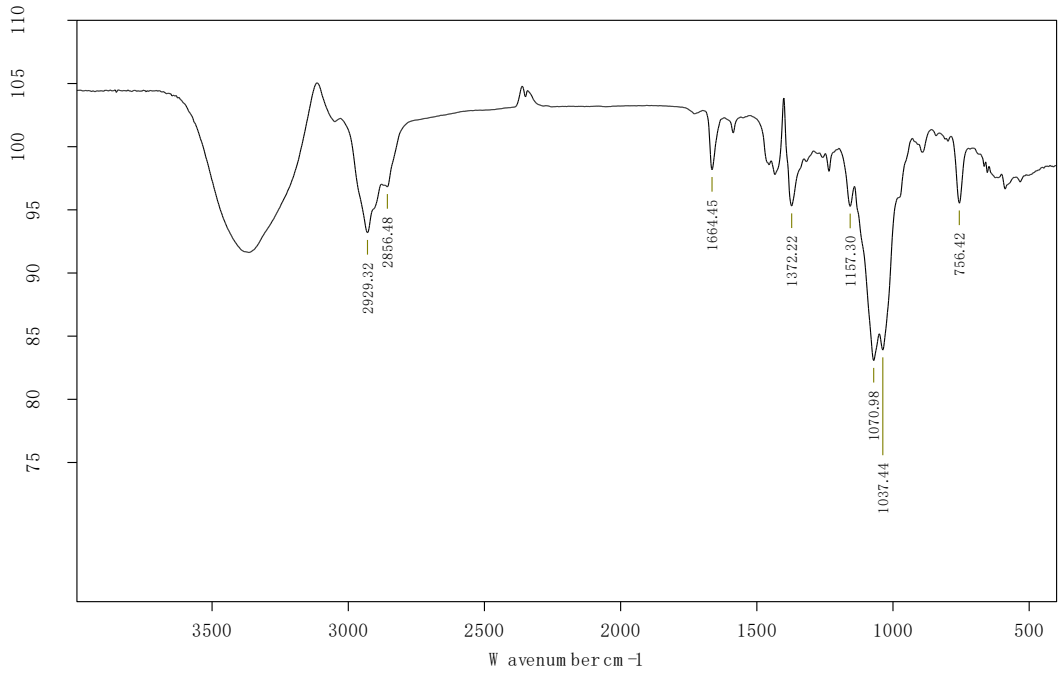
S6. The HMBC spectrum of compound 1 (in pyridine-d5)



S7. The NOESY spectrum of compound 1(in pyridine-d5)



S8. The IR spectrum of compound 2 (in KBr)



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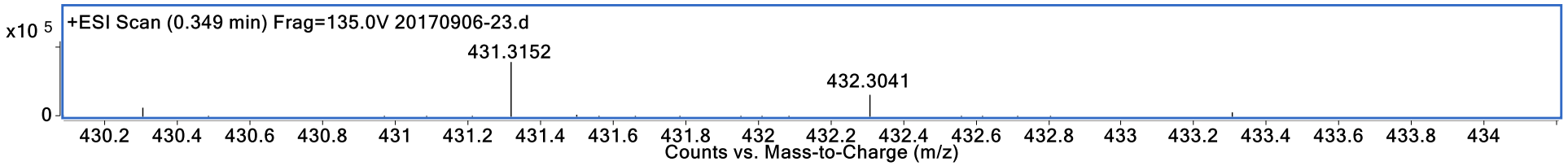
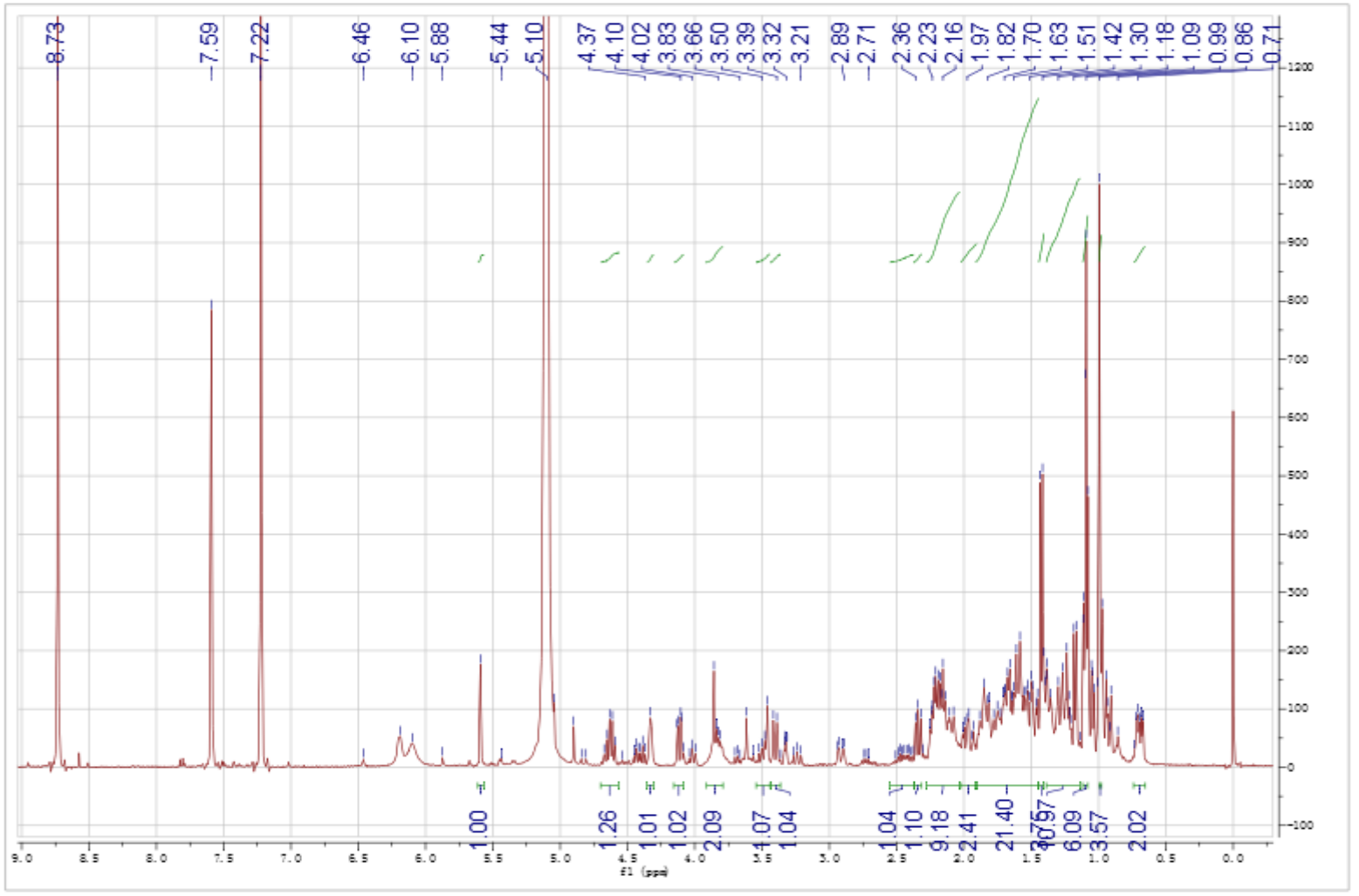
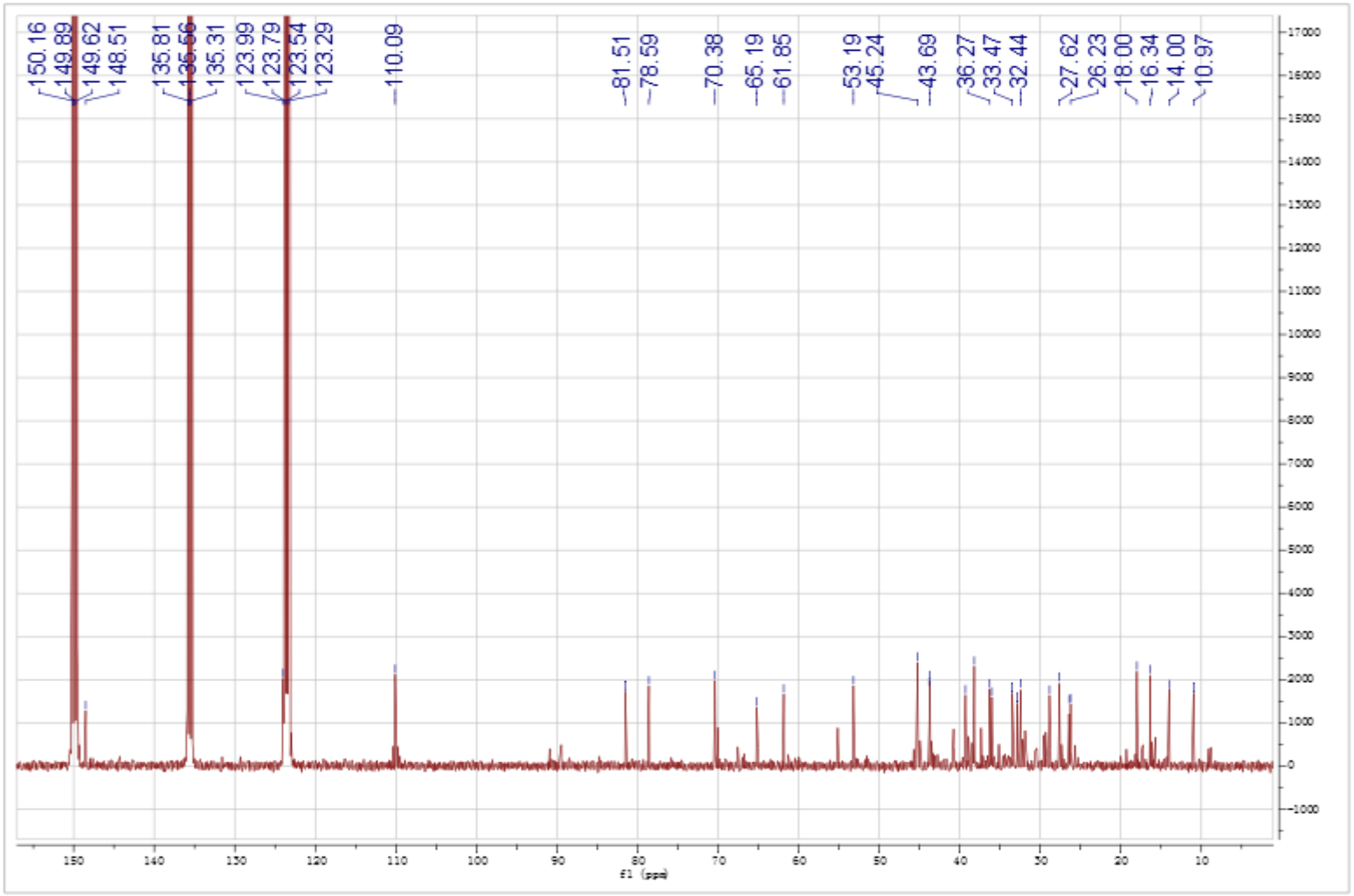
S9. The HR-ESI-MS spectrum of compound 2 (in MeOH)



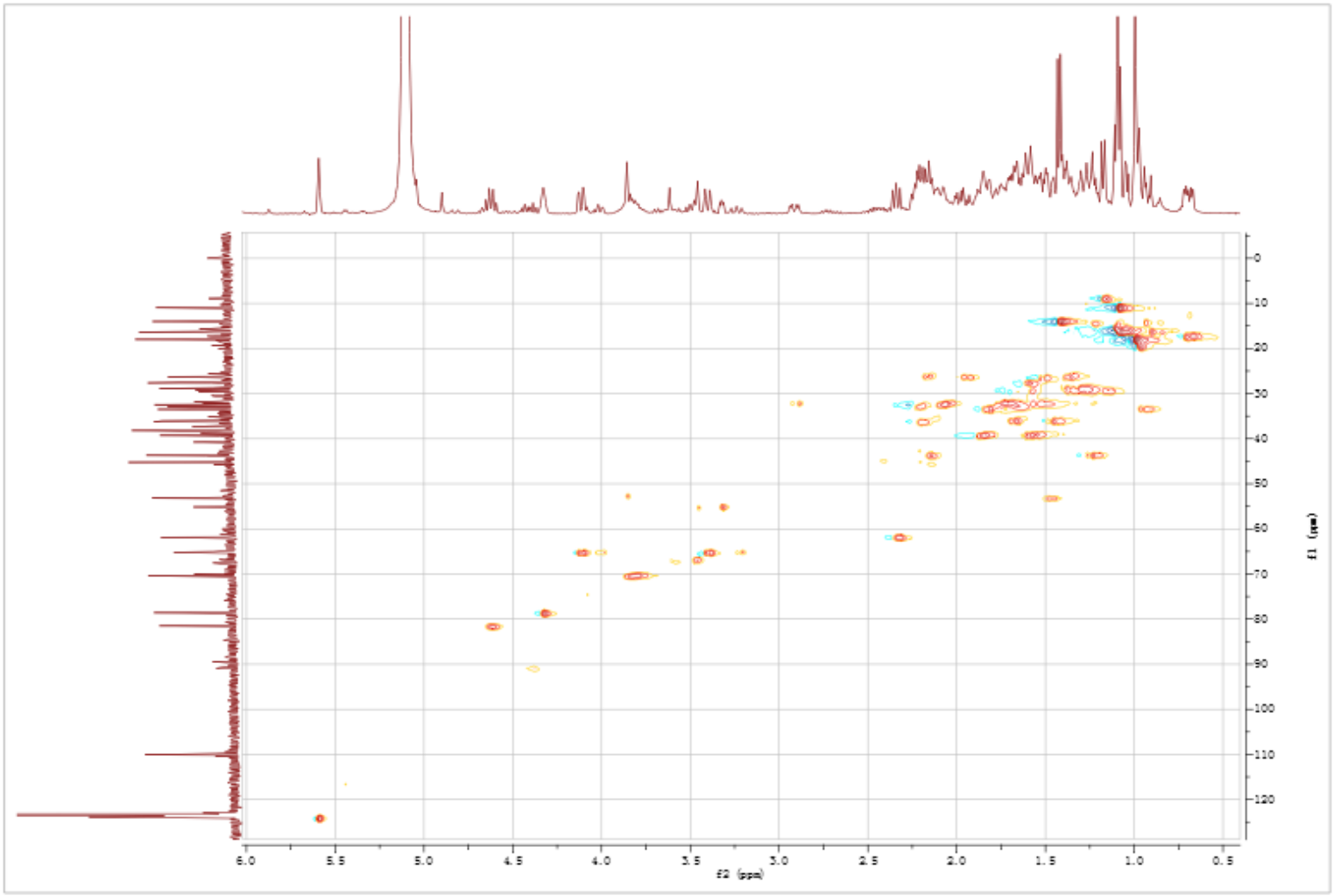
S10. The ^{1}H NMR spectrum of compound 2 (in pyridine-d



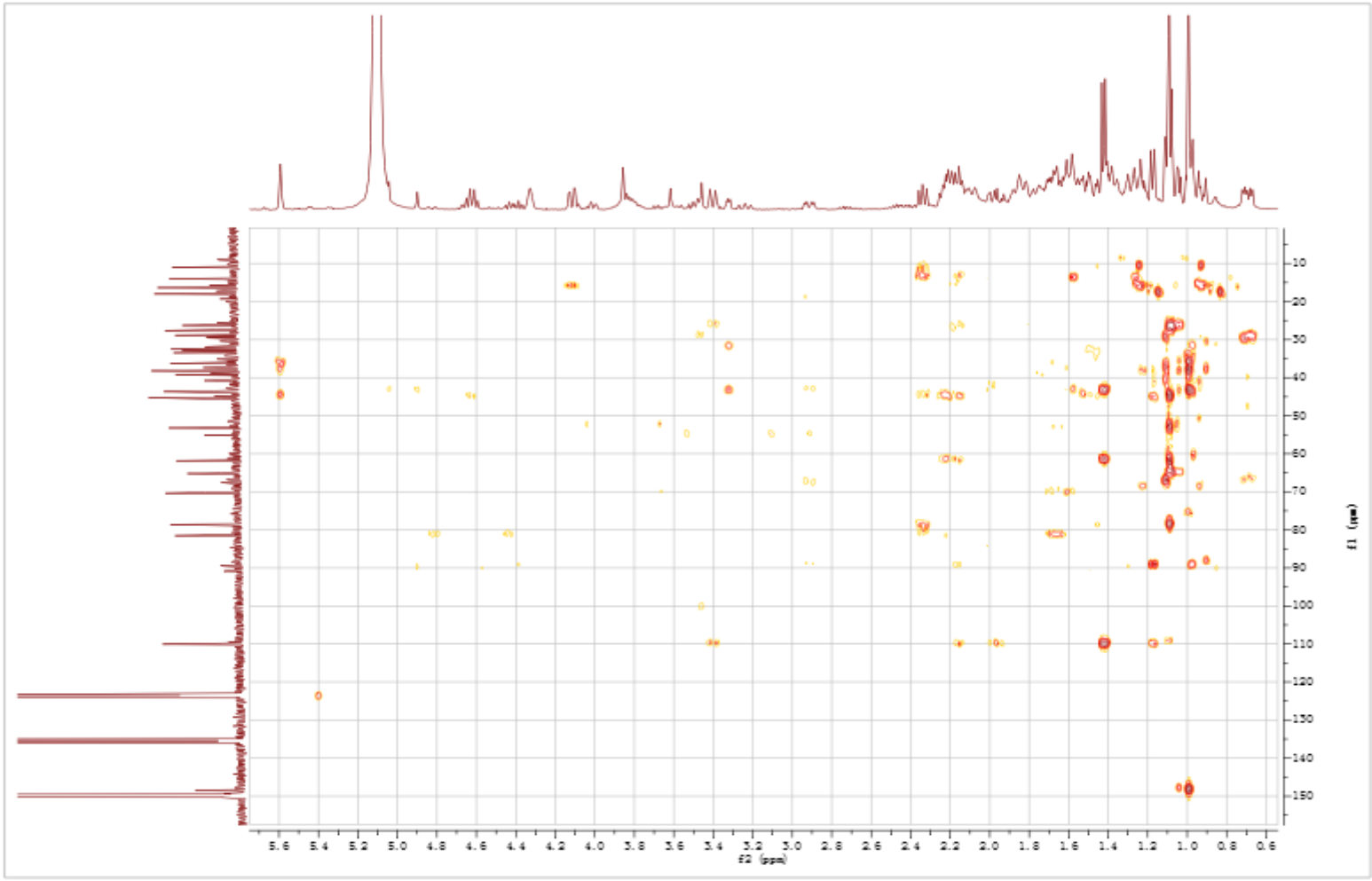
S11. The ^{13}C NMR spectrum of compound 2 (in pyridine-d5)



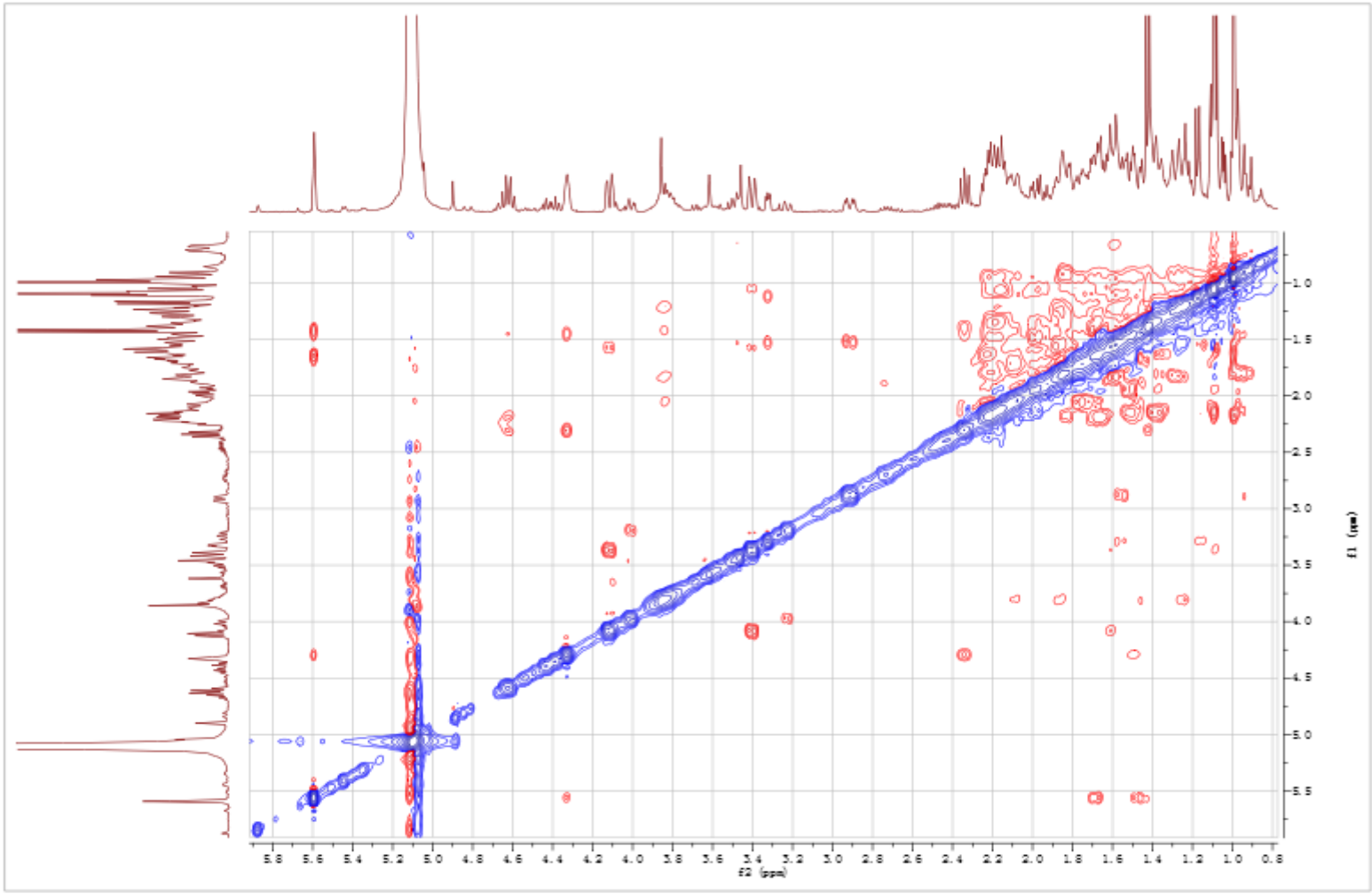
S12. The HSQC spectrum of compound 2 (in pyridine-d5)



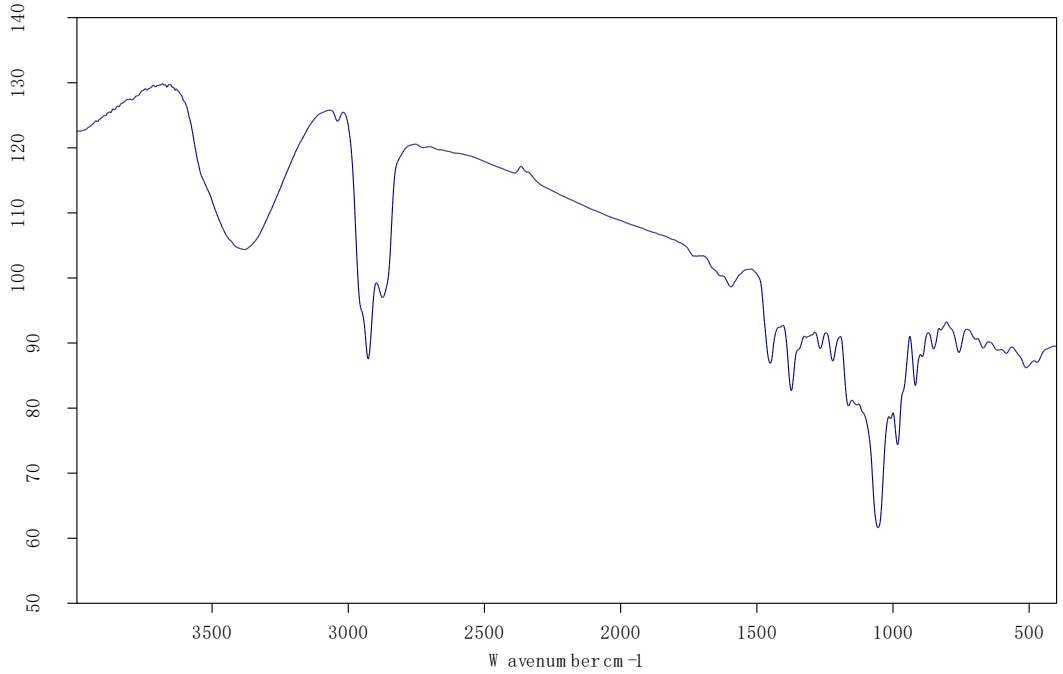
S13. The HMBC spectrum of compound 2 (in pyridine-d5)



S14. The NOESY spectrum of compound 2 (in pyridine-d5)



S15. The IR spectrum of compound 3 (in KBr)



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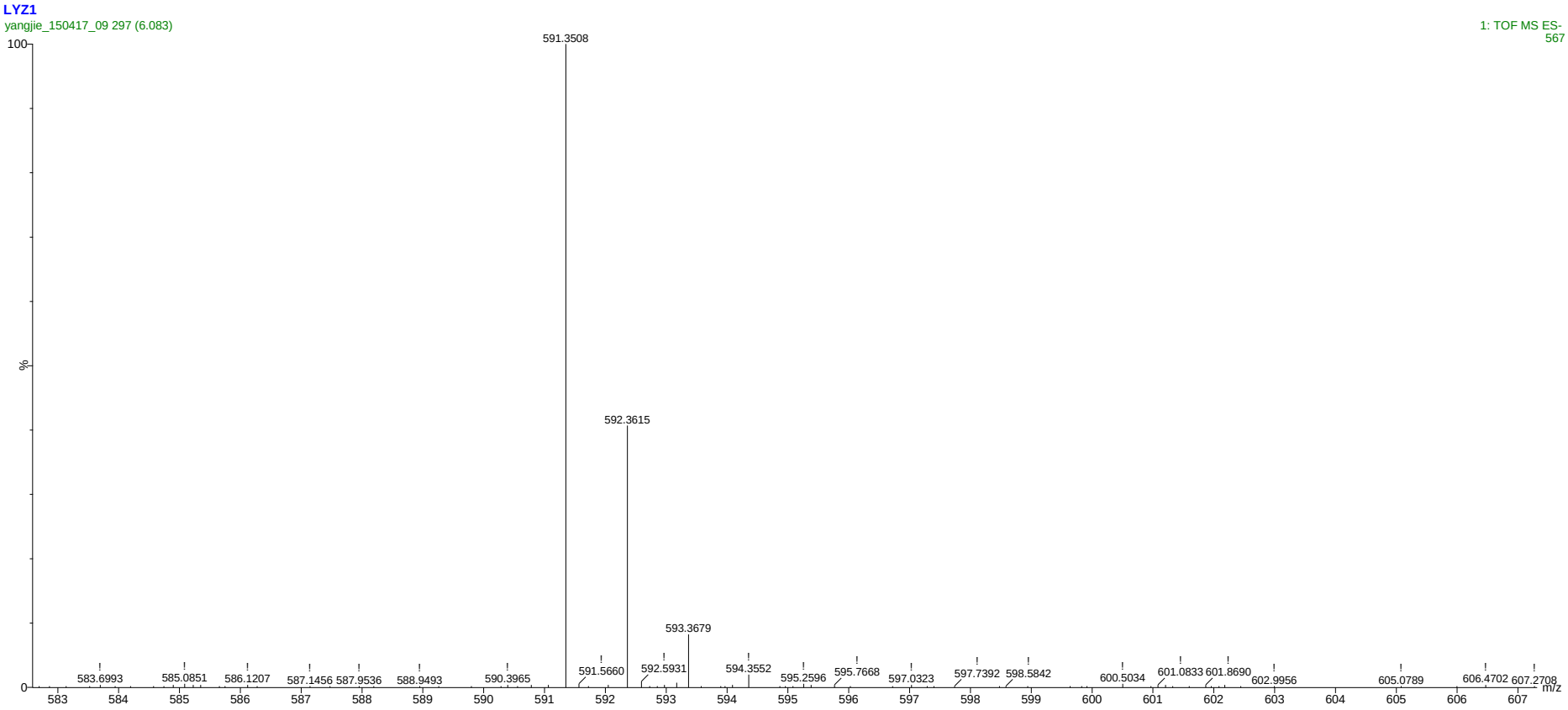
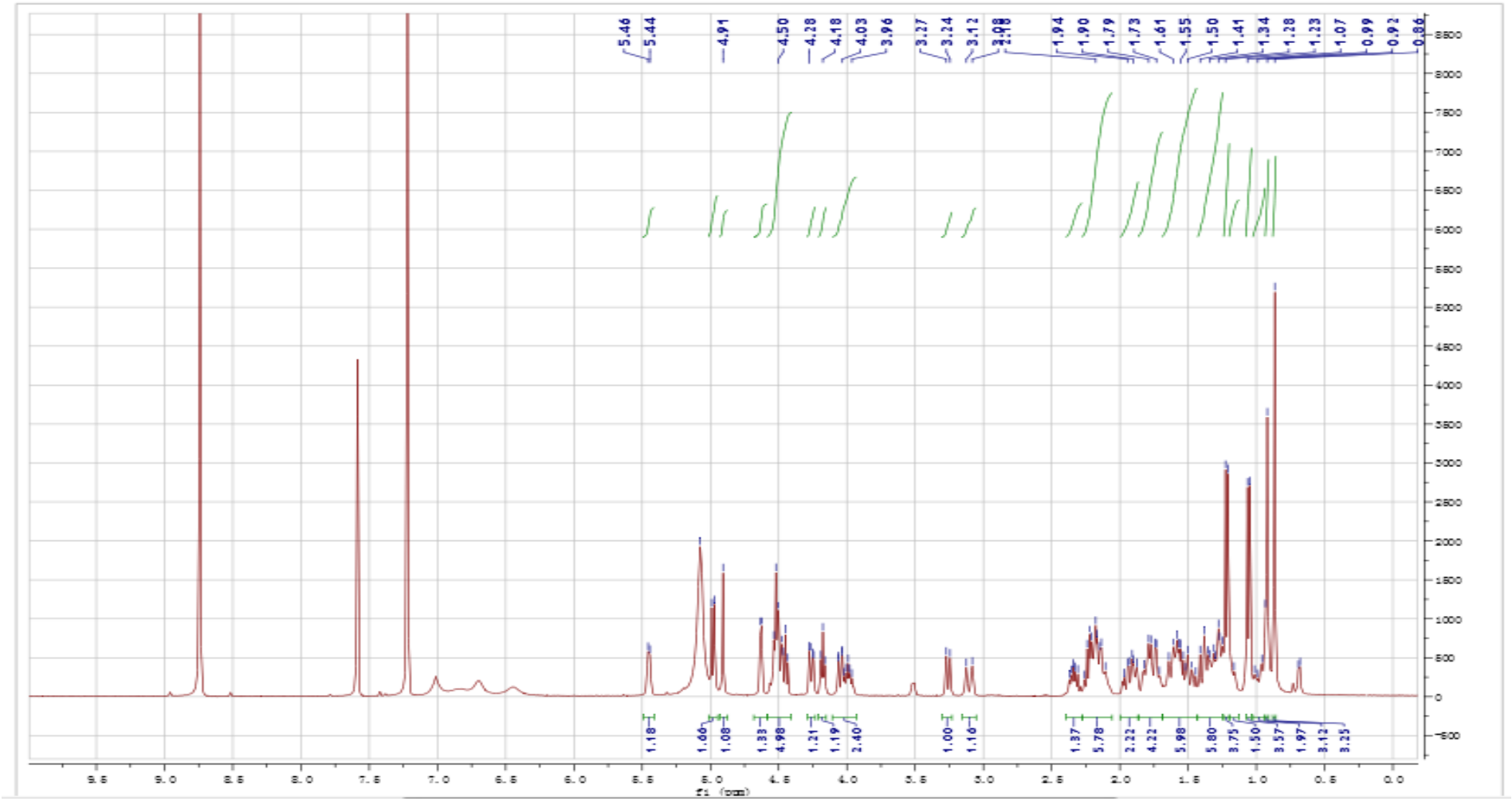
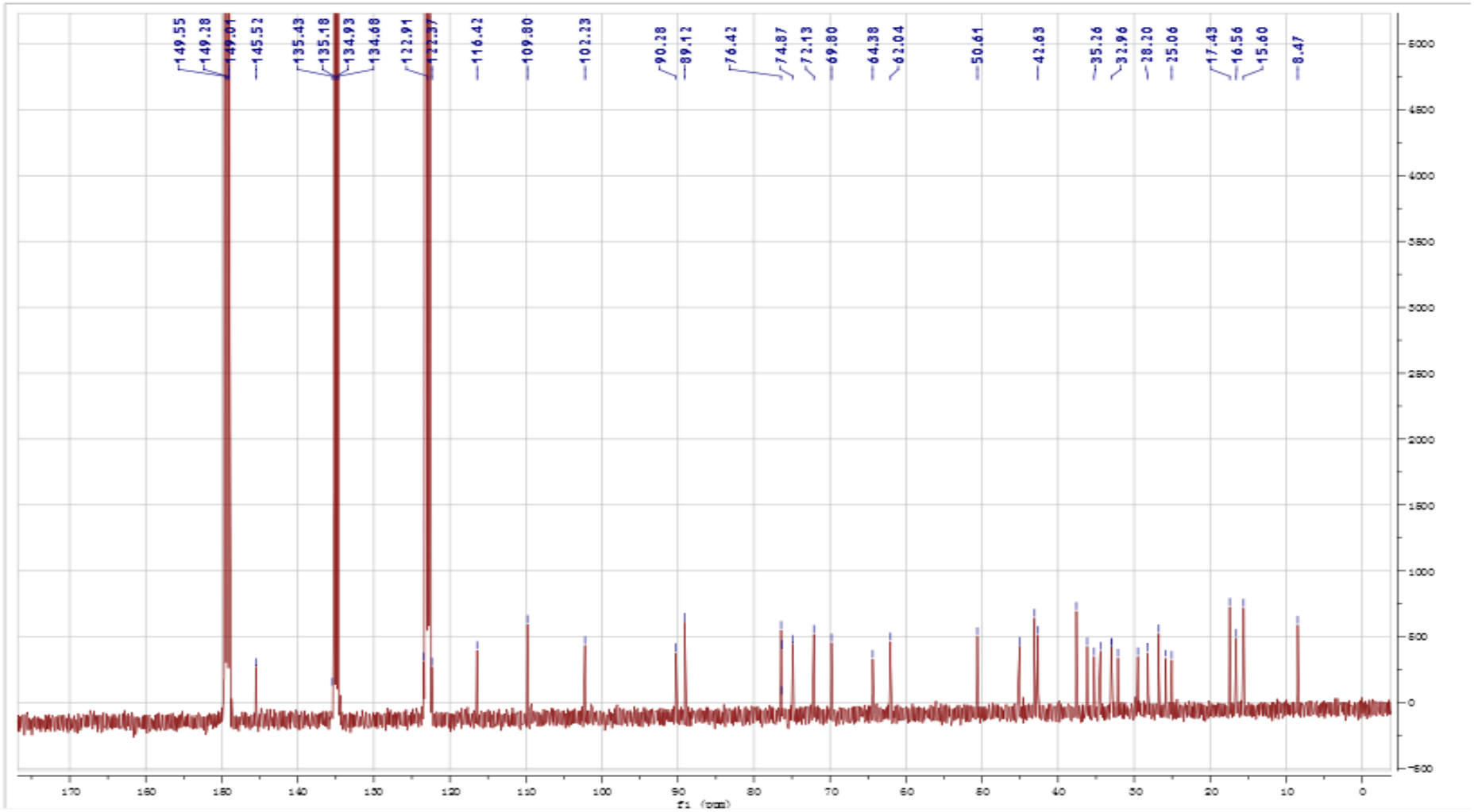
S16. The HR-ESI-MS spectrum of compound 3 (in MeOH)



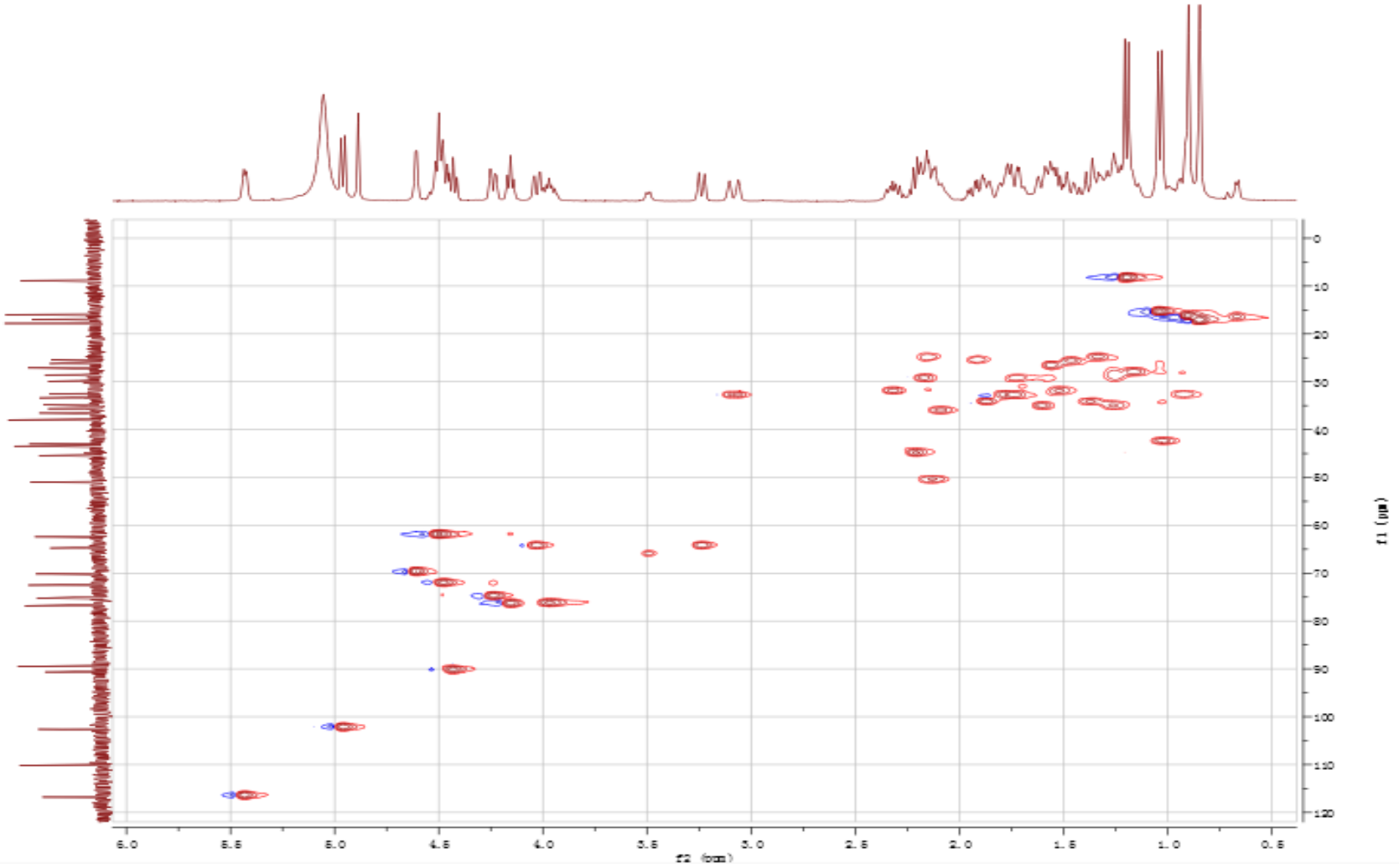
S17. The ^{1}H NMR spectrum of compound 3 (in pyridine-d5)



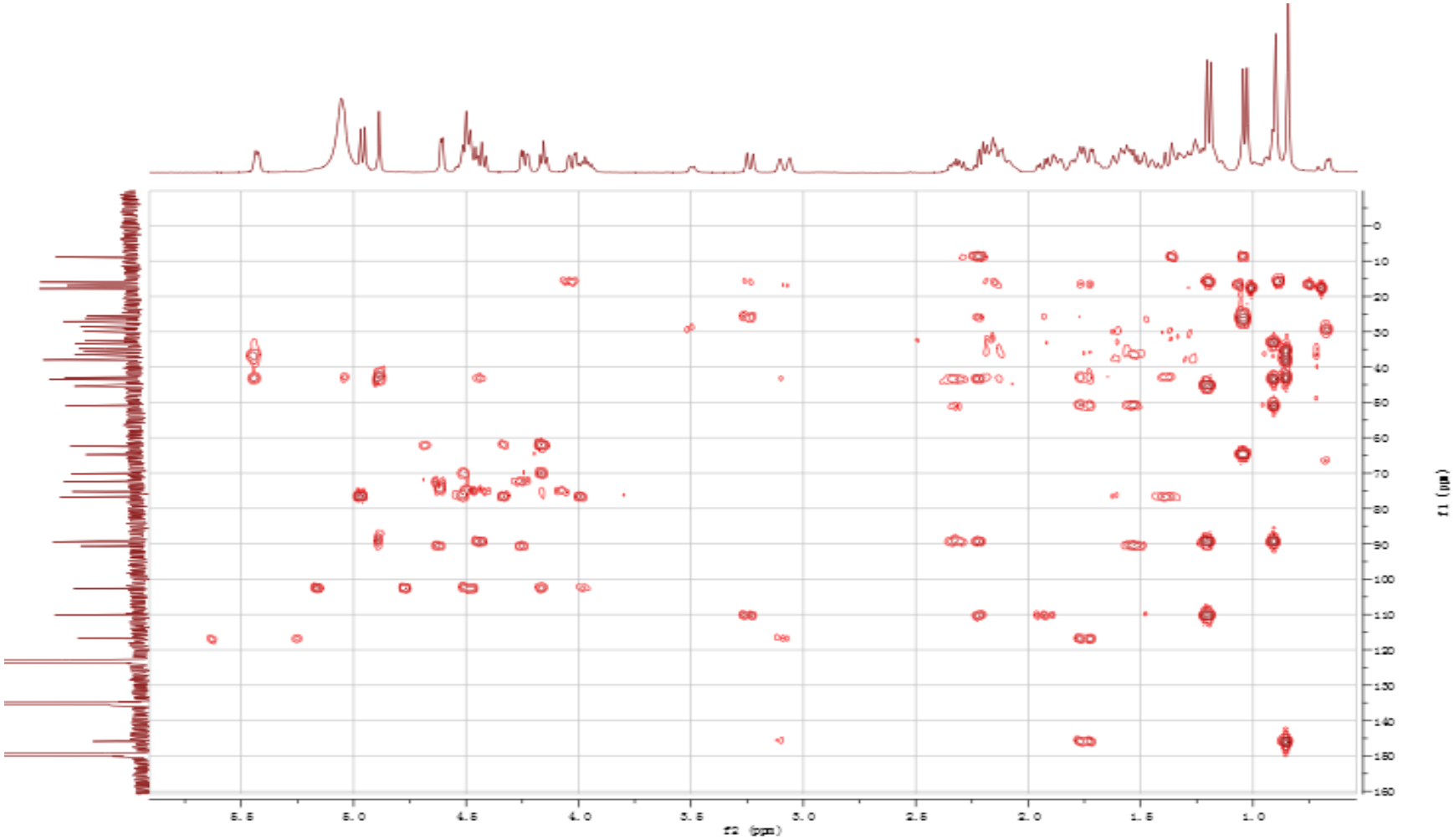
S18. The ^{13}C NMR spectrum of compound 3 (in pyridine-d5)



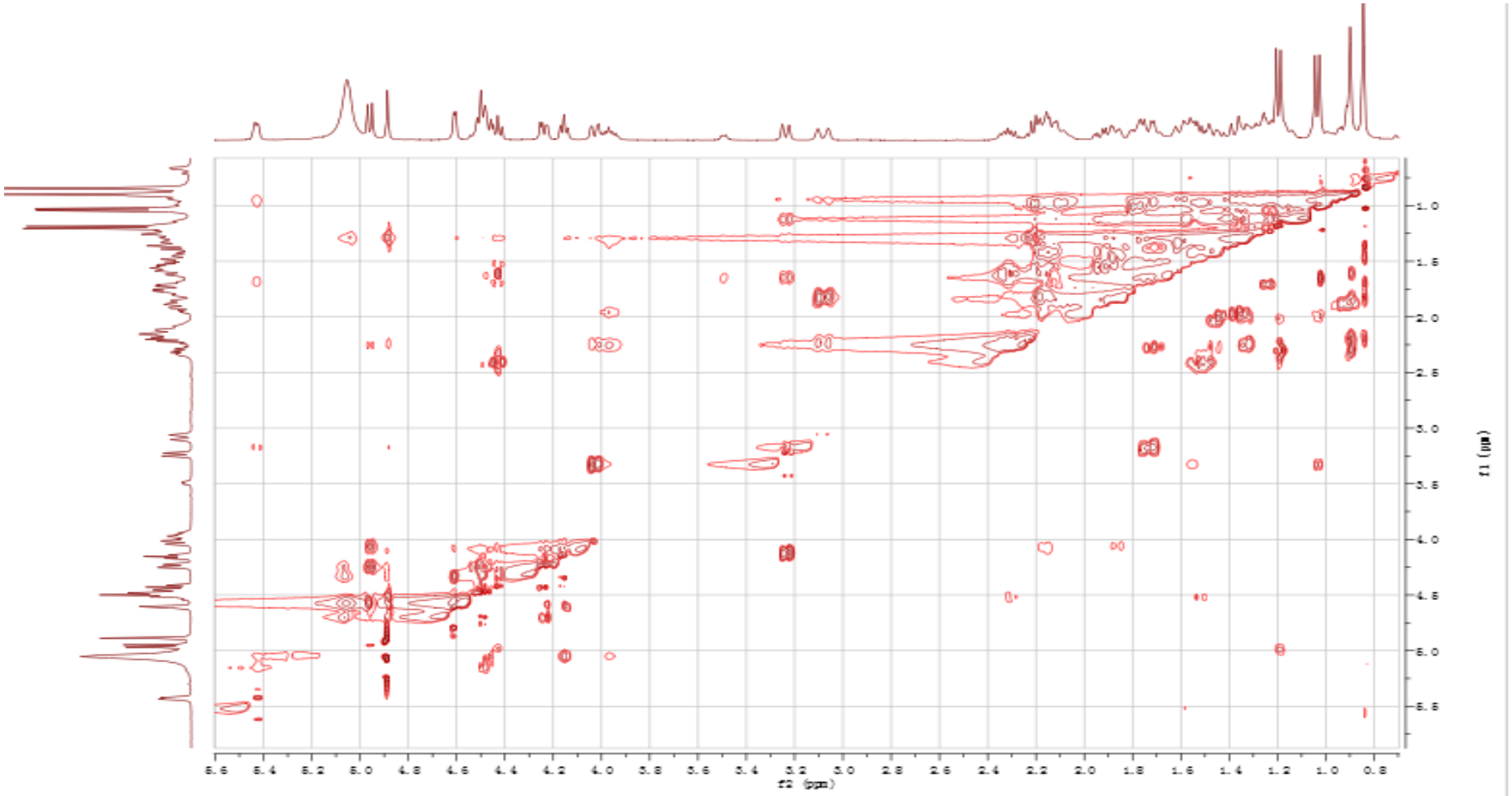
S19. The HSQC spectrum of compound 3 (in pyridine-d5)



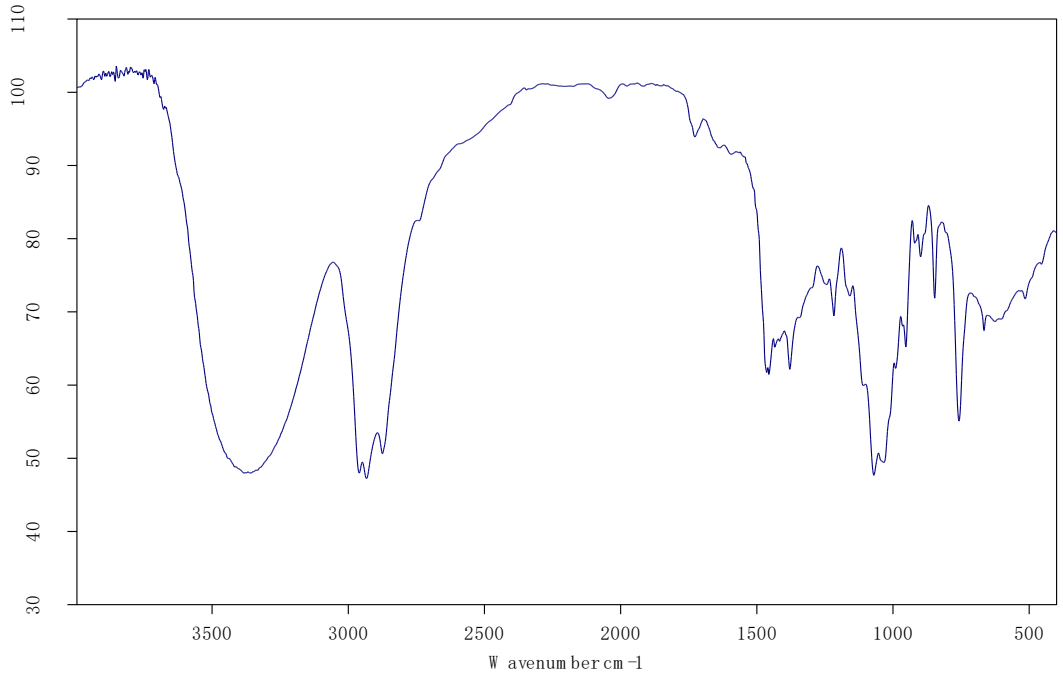
S20. The HMBC spectrum of compound 3 (in pyridine-d5)



S21. The NOESY spectrum of compound 3 (in pyridine-d5)



S22. The IR spectrum of compound 4 (in KBr)



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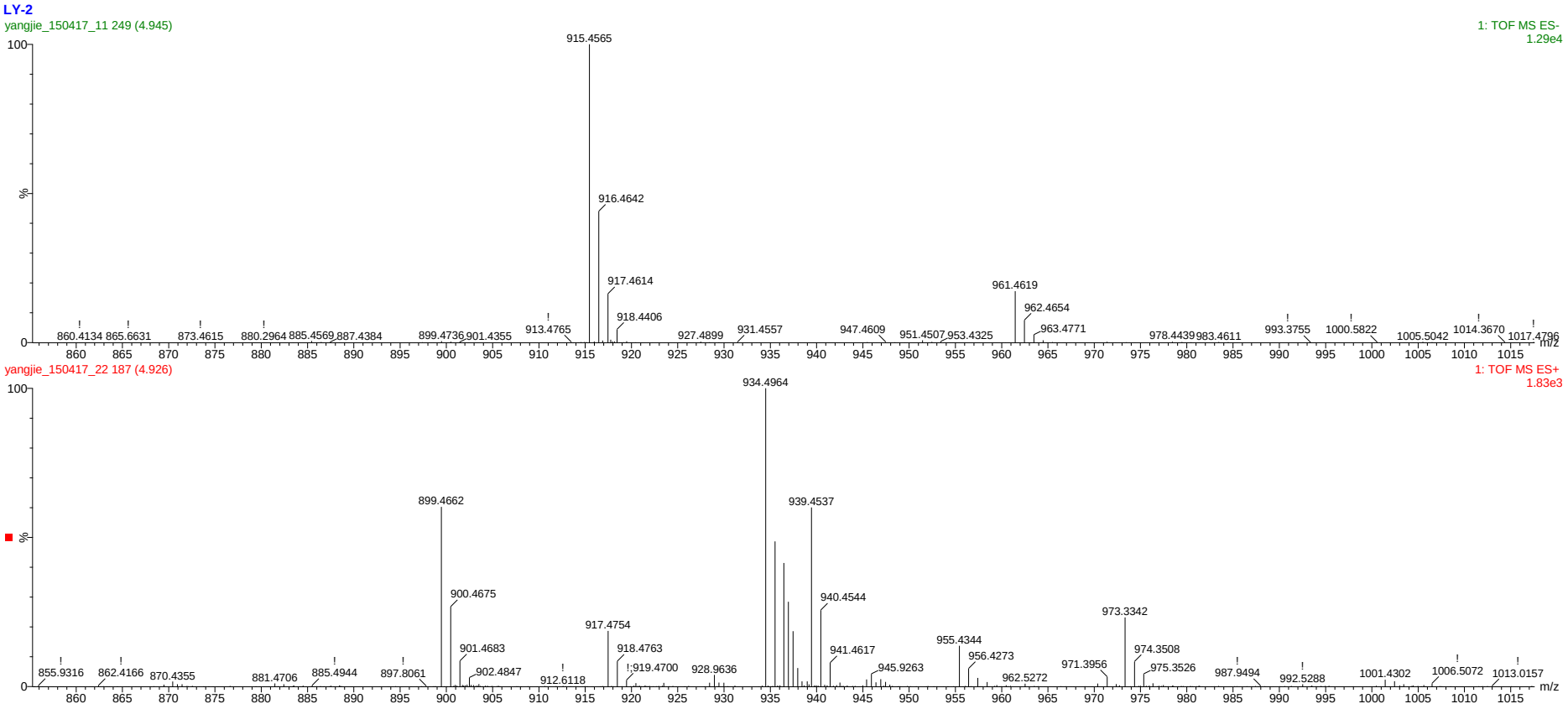
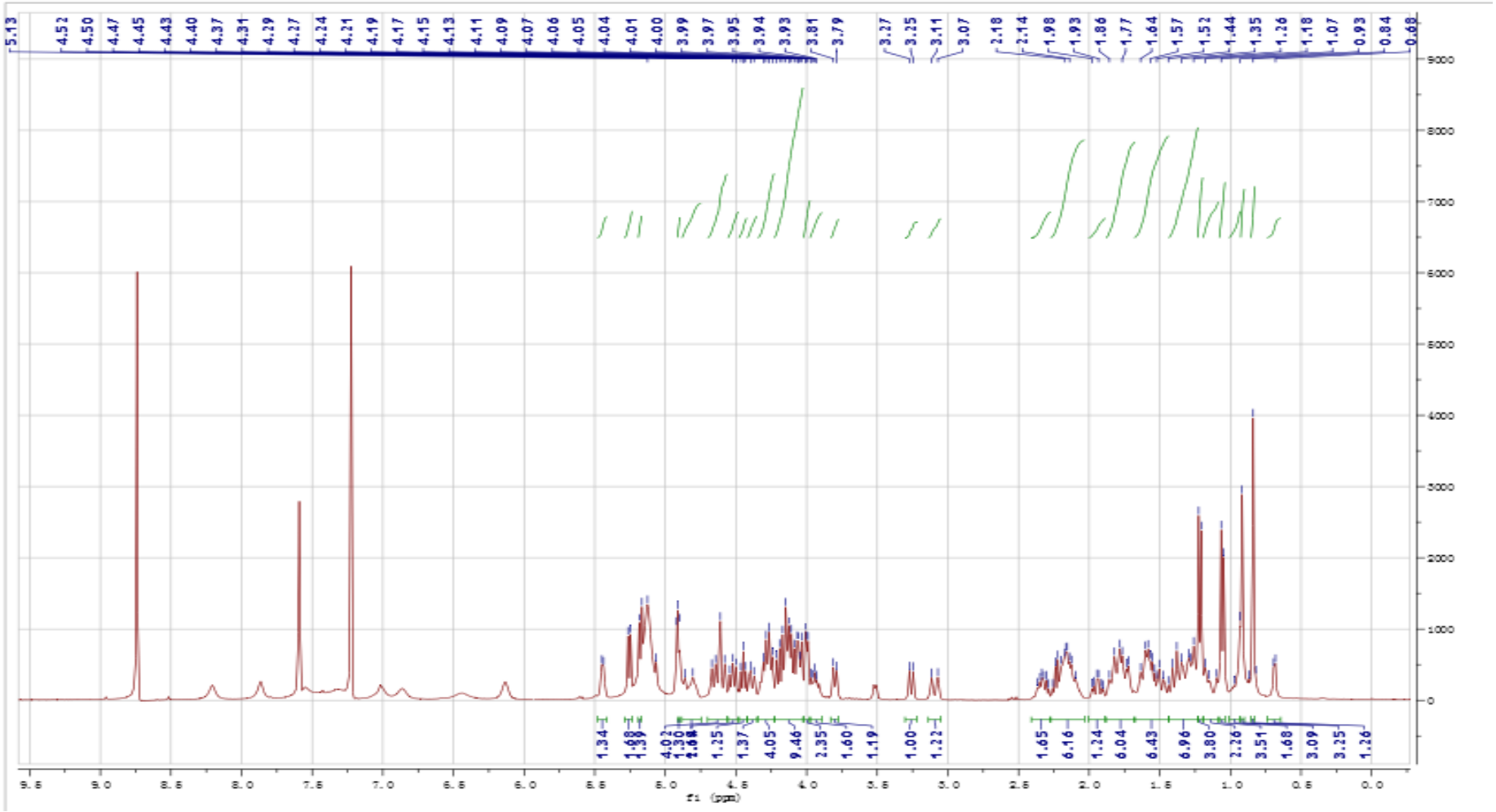
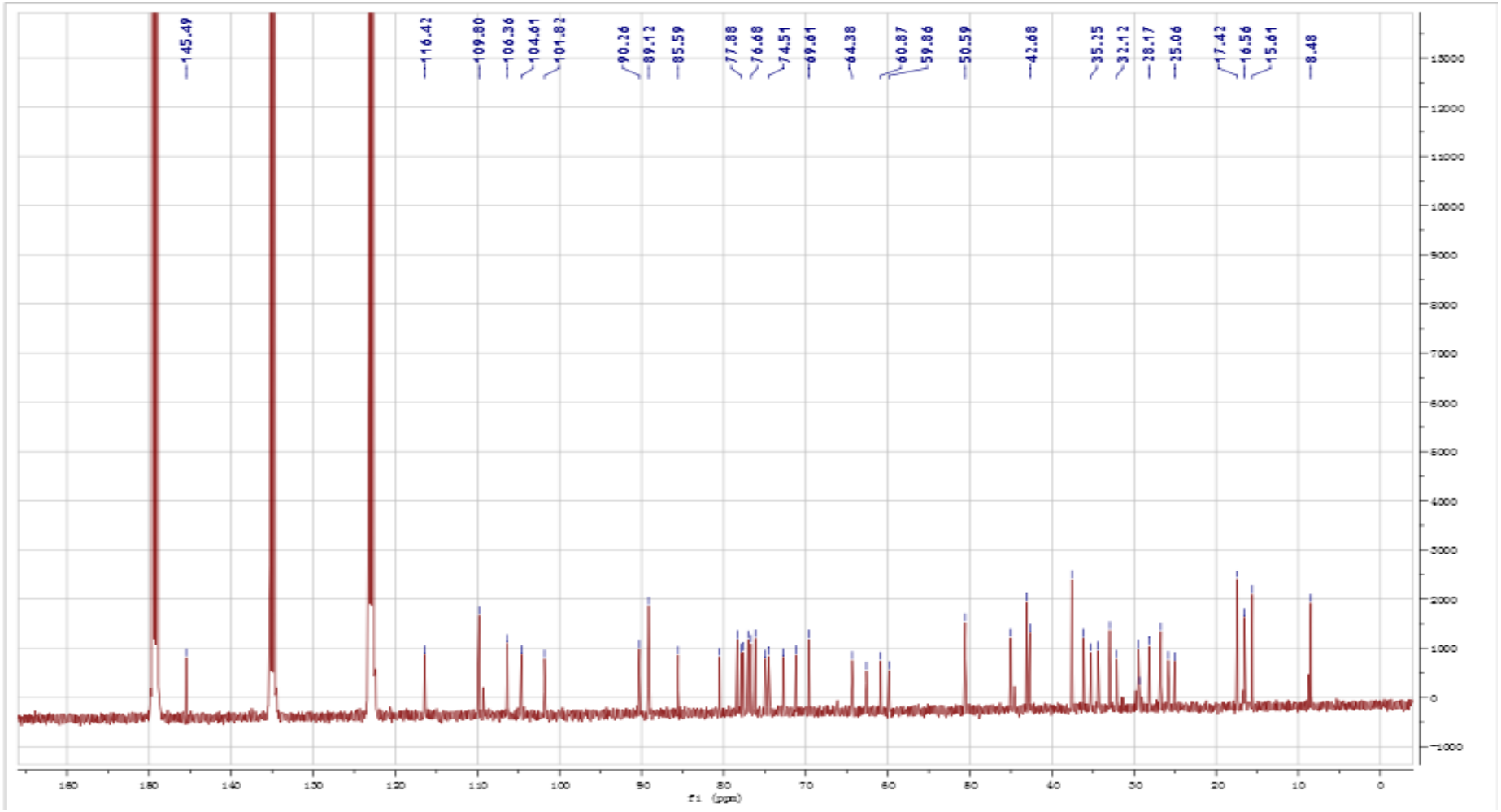
S23. The HR-ESI-MS spectrum of compound 4 (in MeOH)



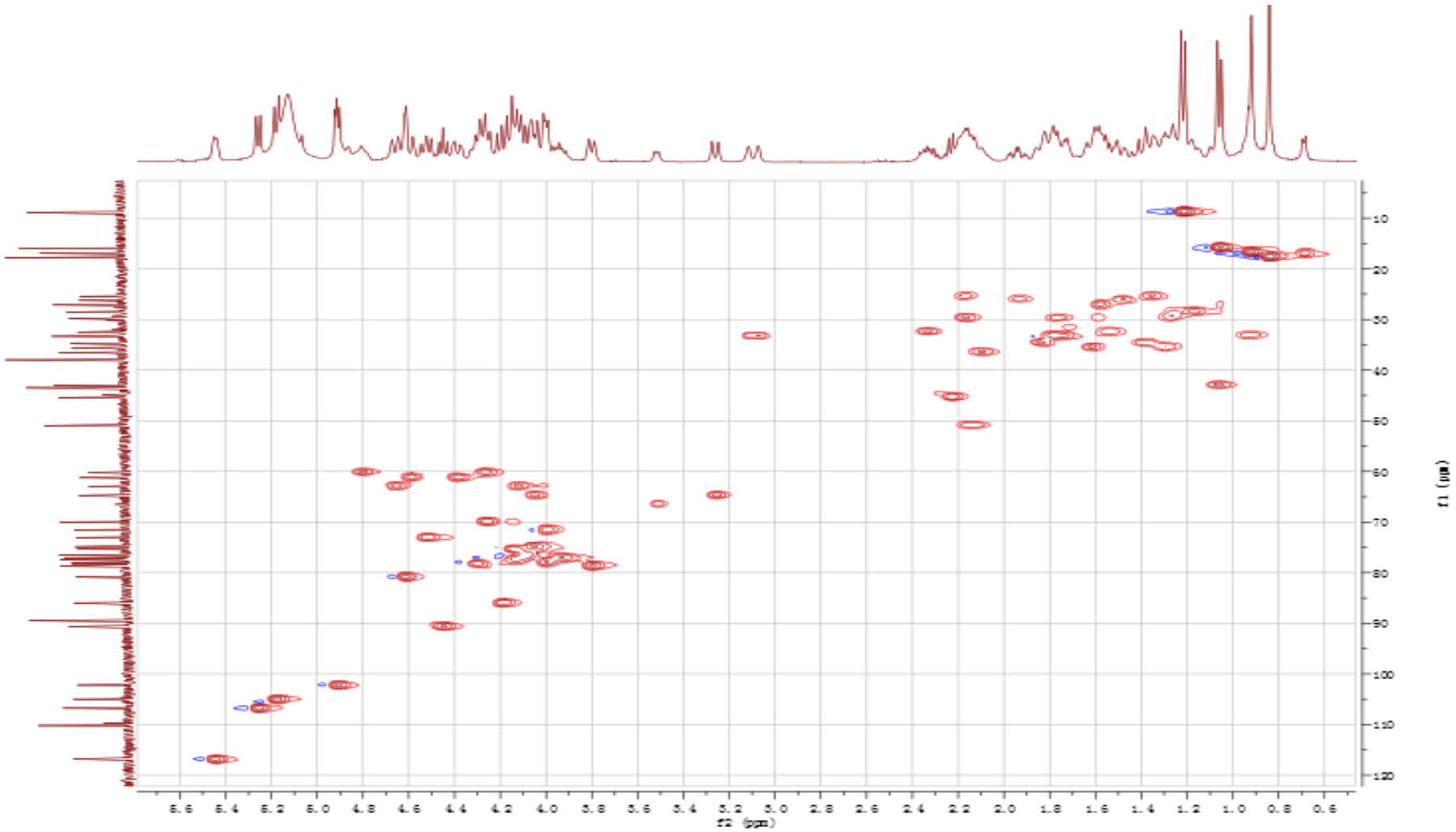
S24. The ^{1}H NMR spectrum of compound 4(in pyridine-d5)



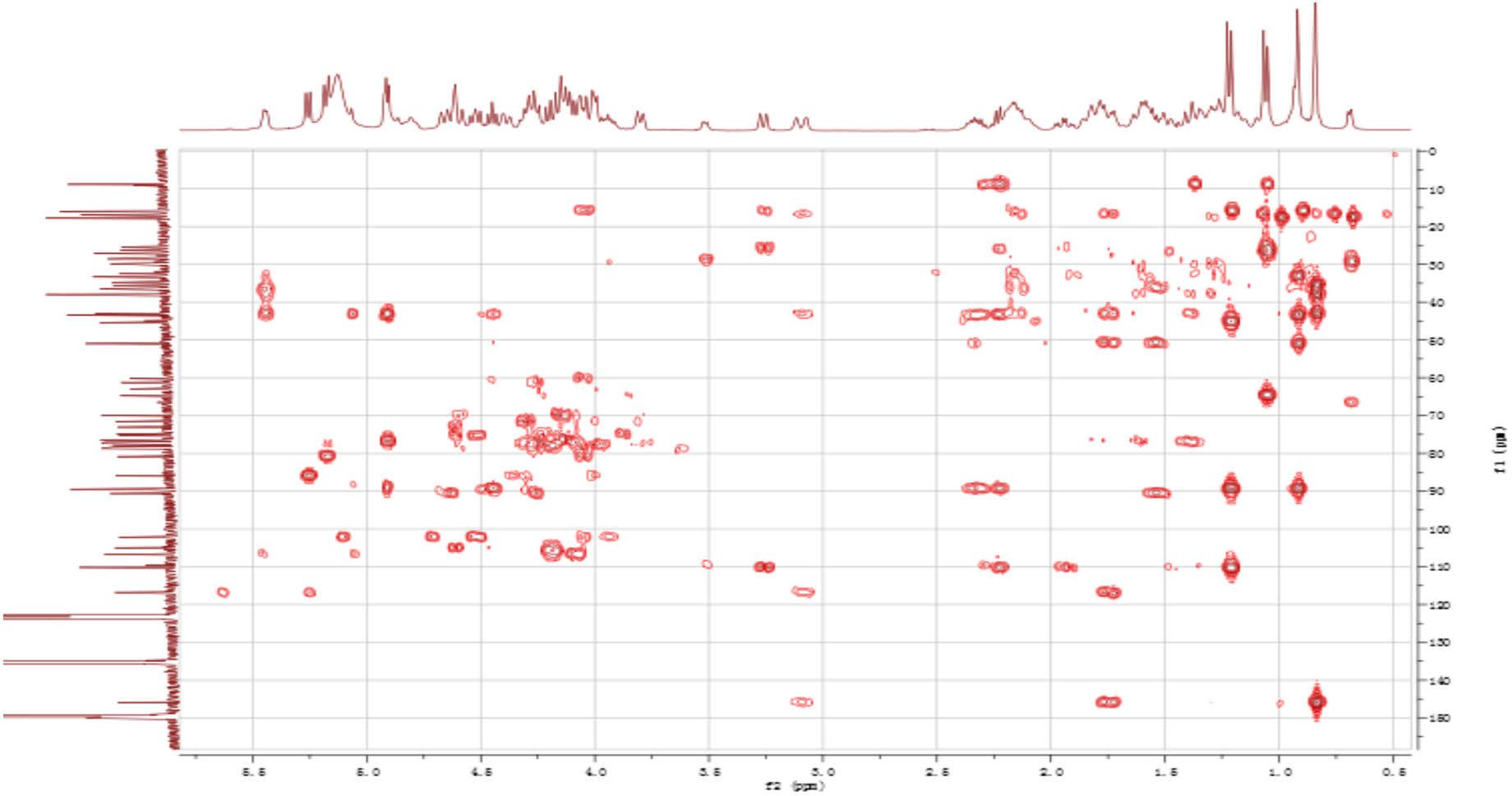
S25. The ^{13}C NMR spectrum of compound 4 (in pyridine-d5)



S26. The HSQC spectrum of compound 4 (in pyridine-d5)



S27. The HMBC spectrum of compound 4 (in pyridine-d5)



S28. The NOESY spectrum of compound 4 (in pyridine-d5)