**Supporting information**

**for**

# Synthesis and transformation of sphingosine analogue pinane-based 2-amino-1,3-diols

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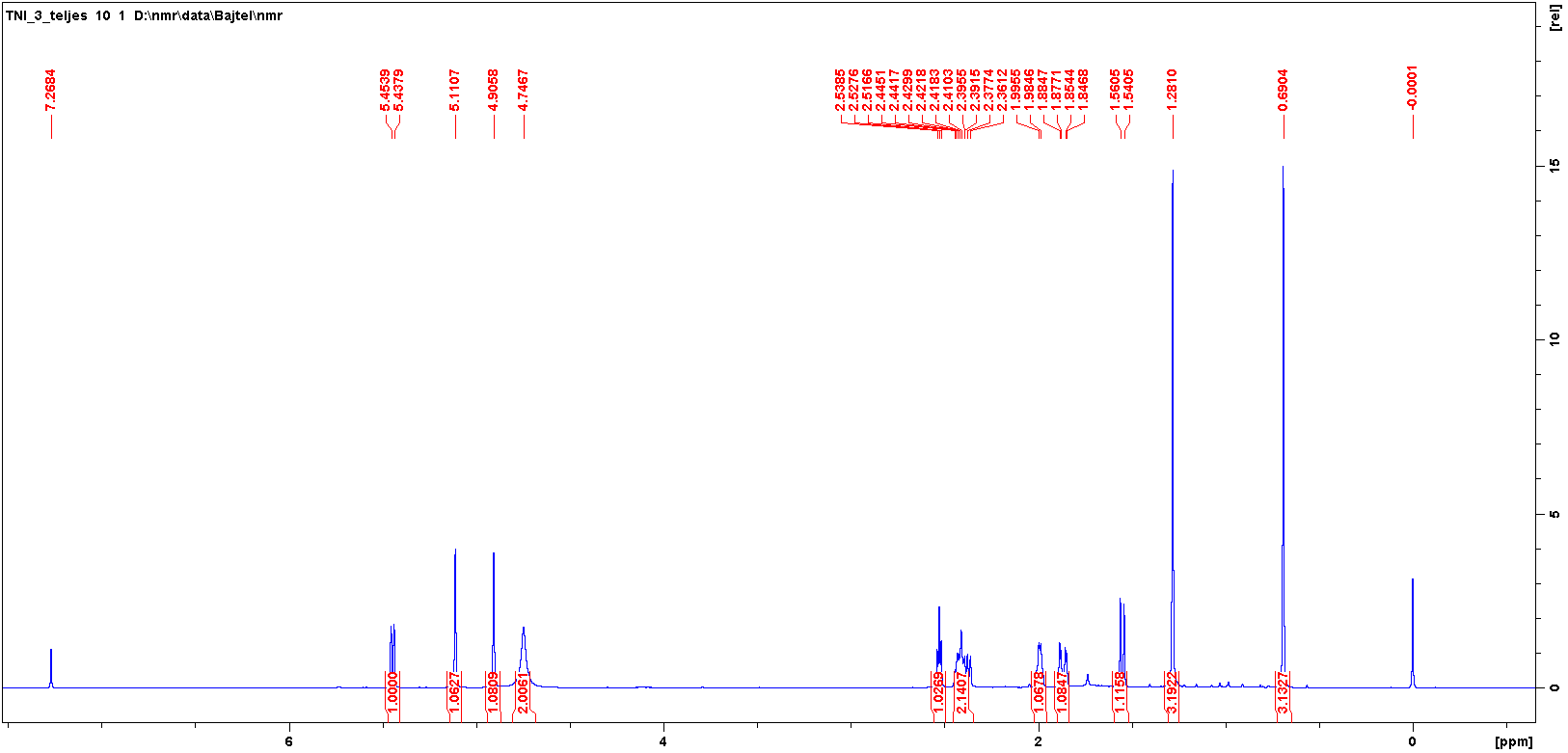
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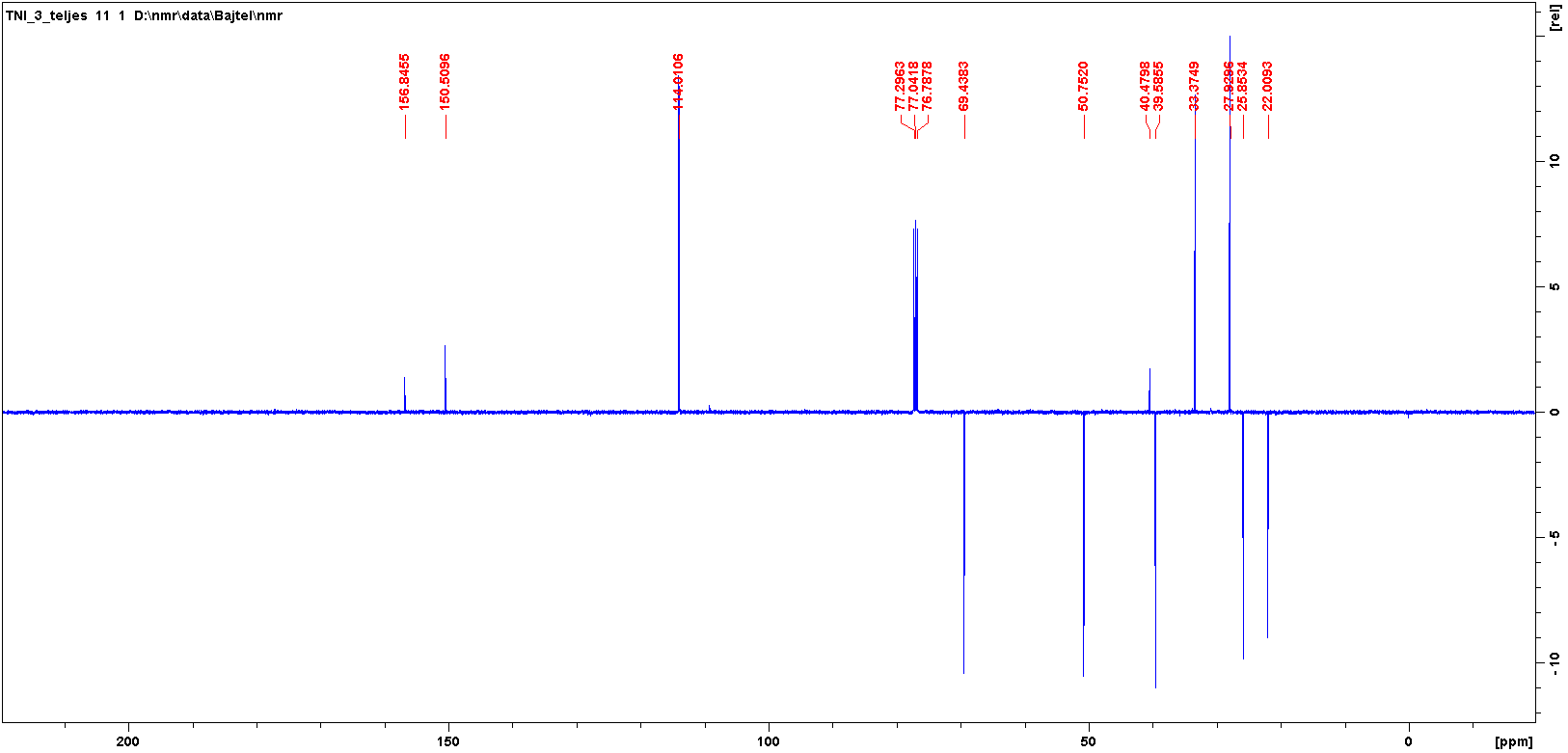
1H, 13C NMR, COSY, NOESY, HSQC and HMBC spectra of new compounds S3-S30

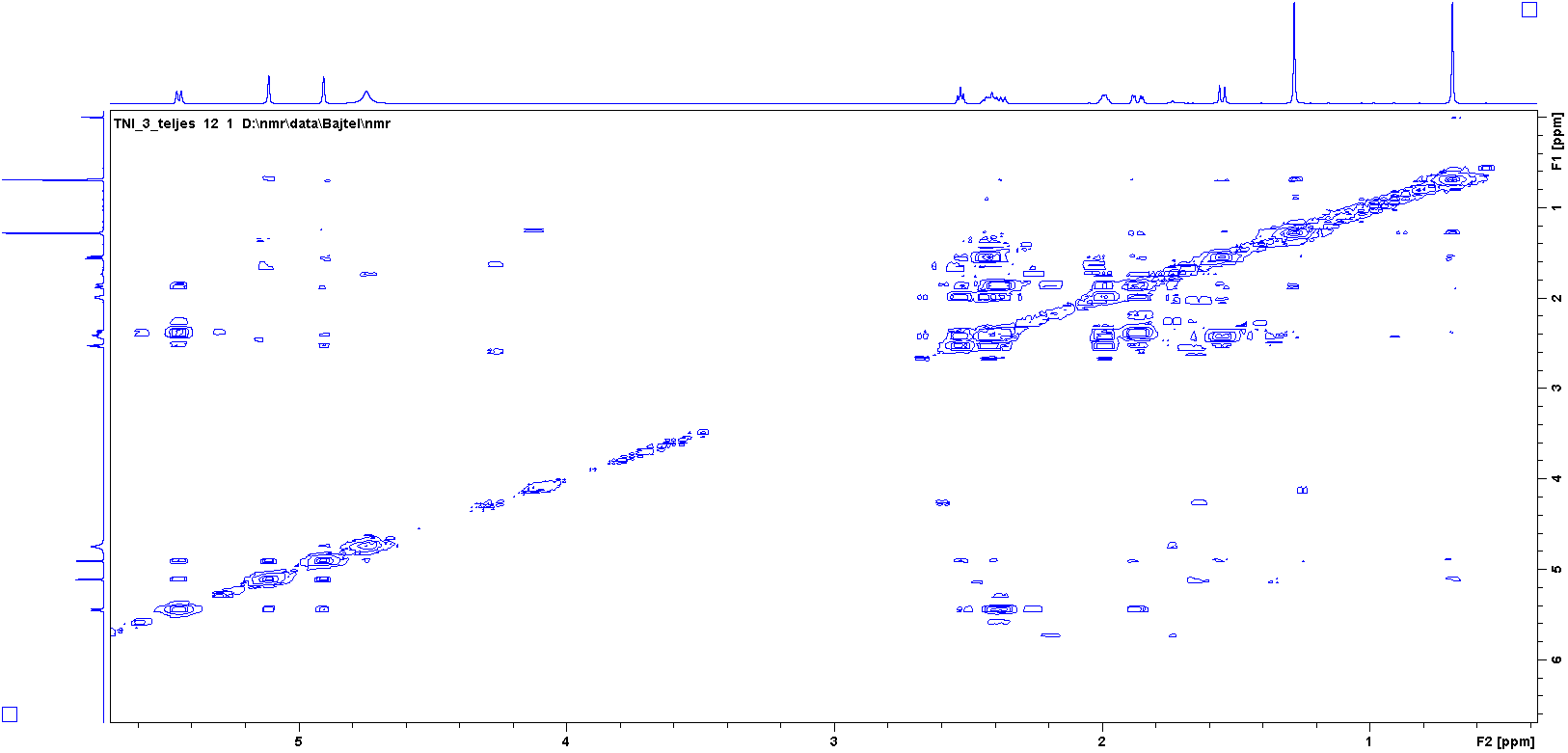
Time-dependent tautomerisation of **19A** to **19B** in CDCl3 solution S31

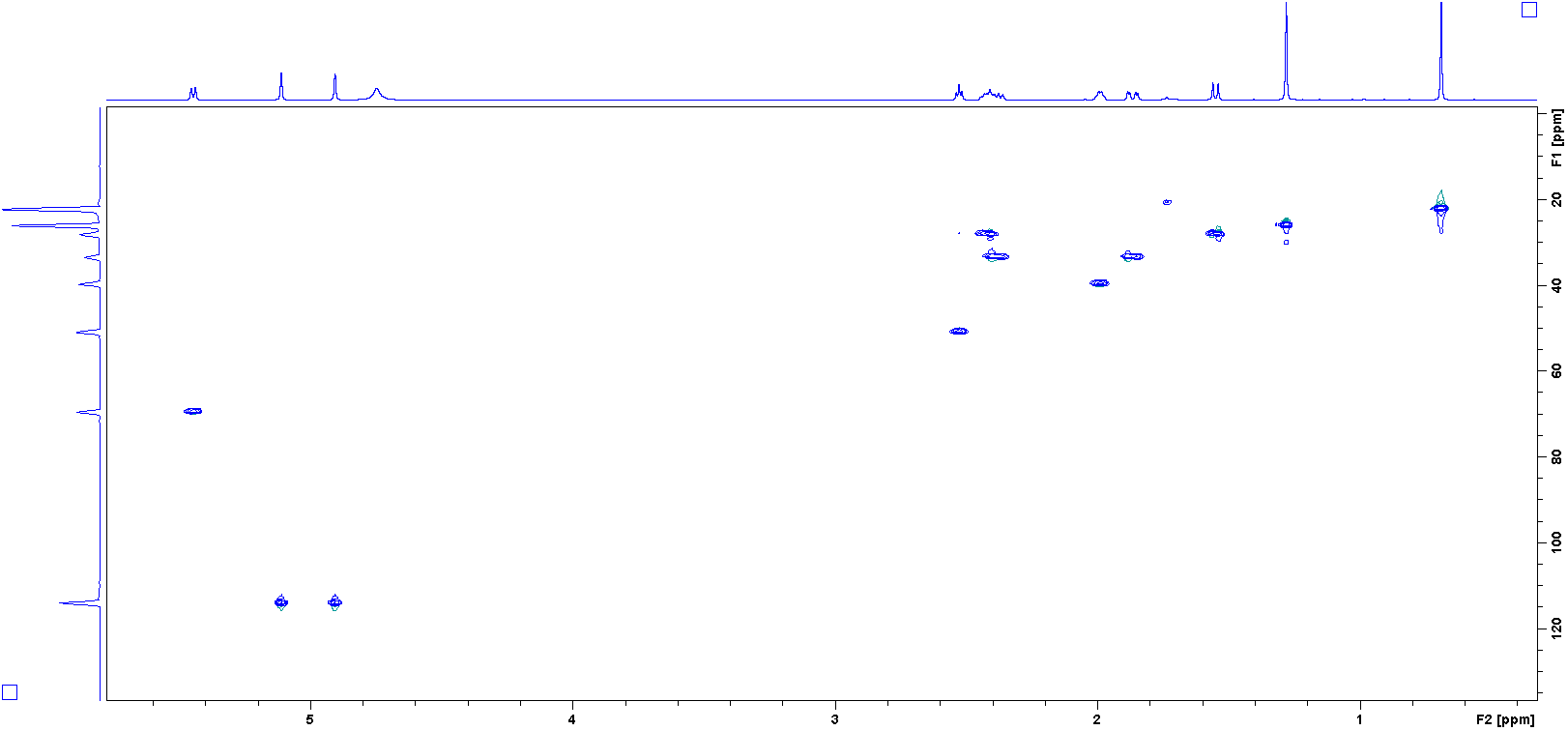
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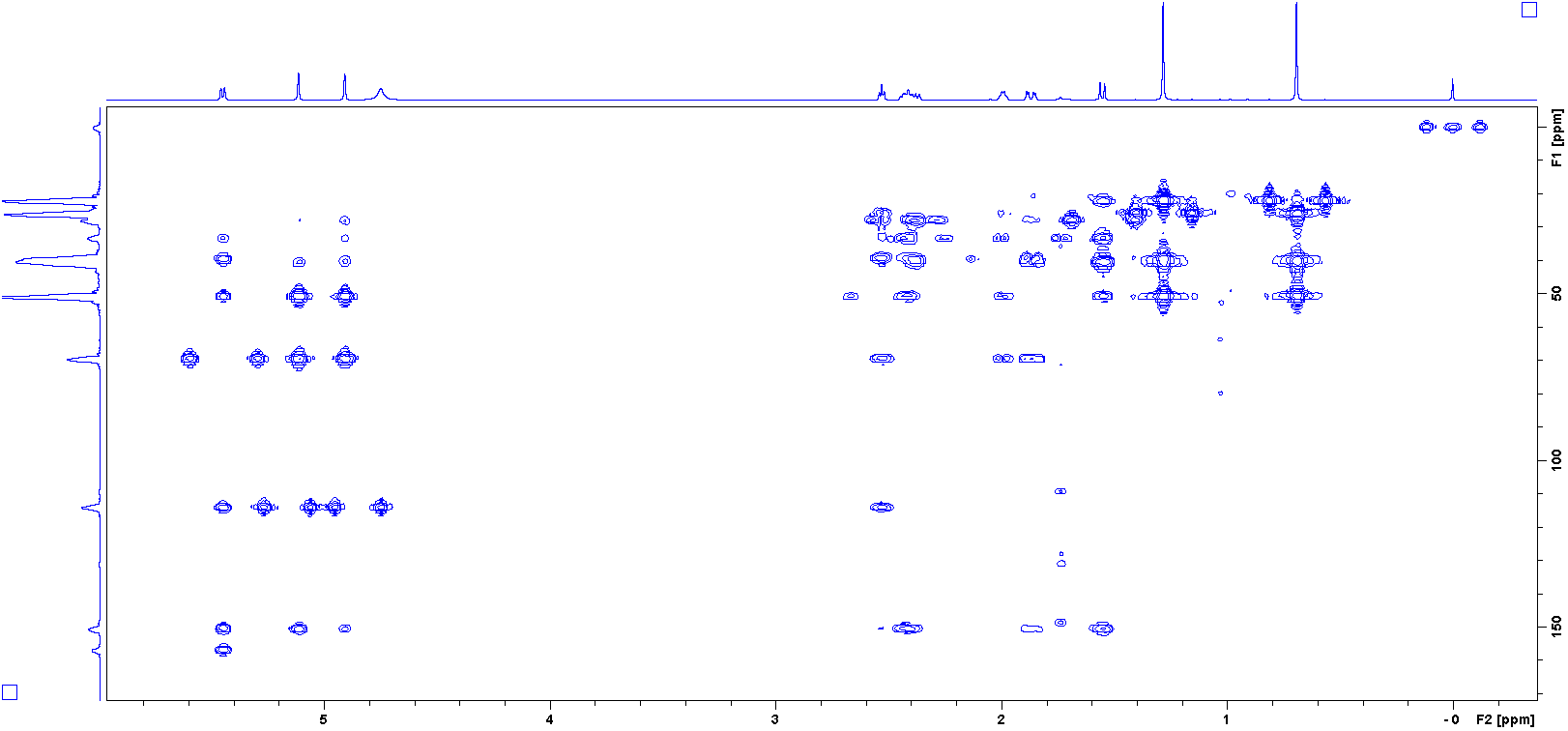
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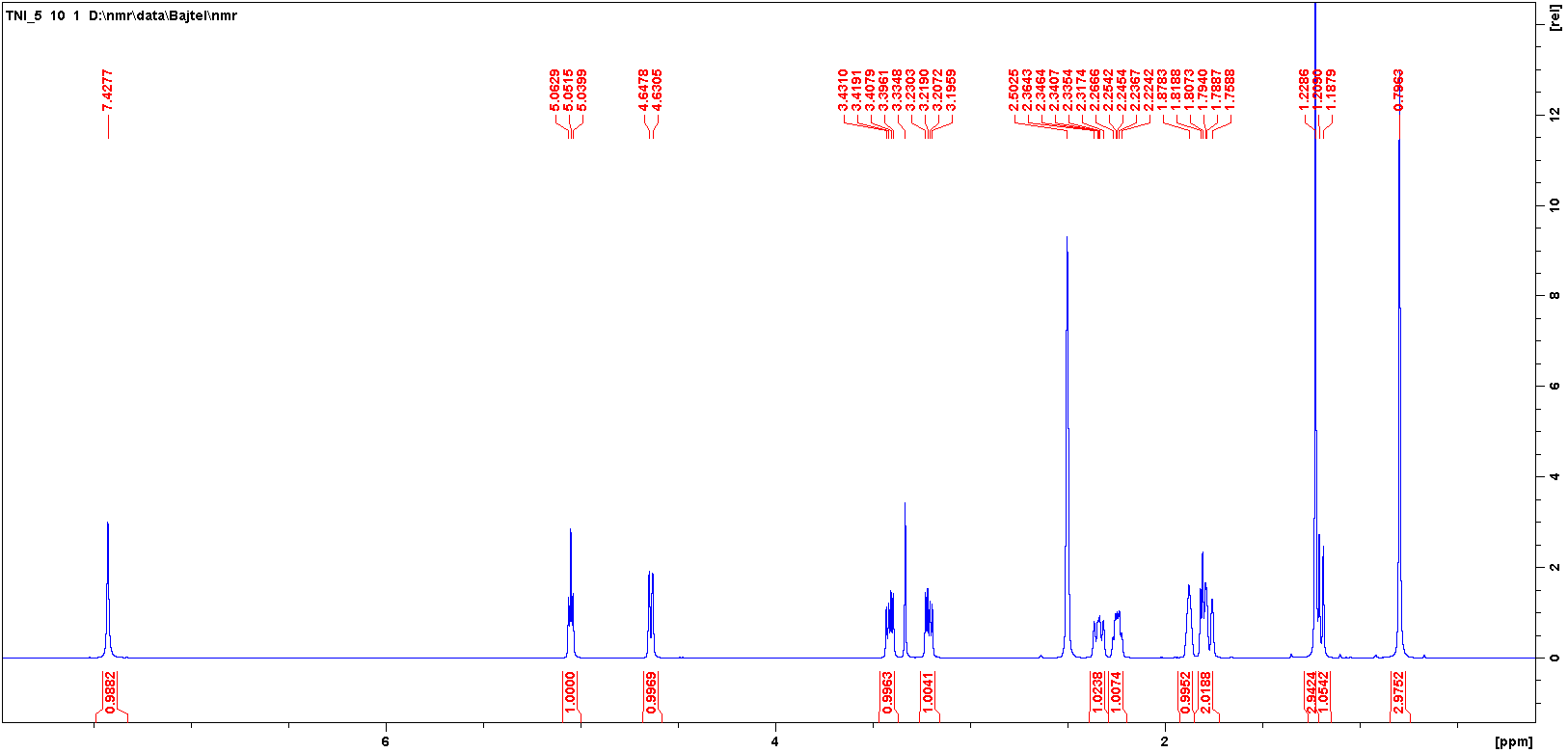




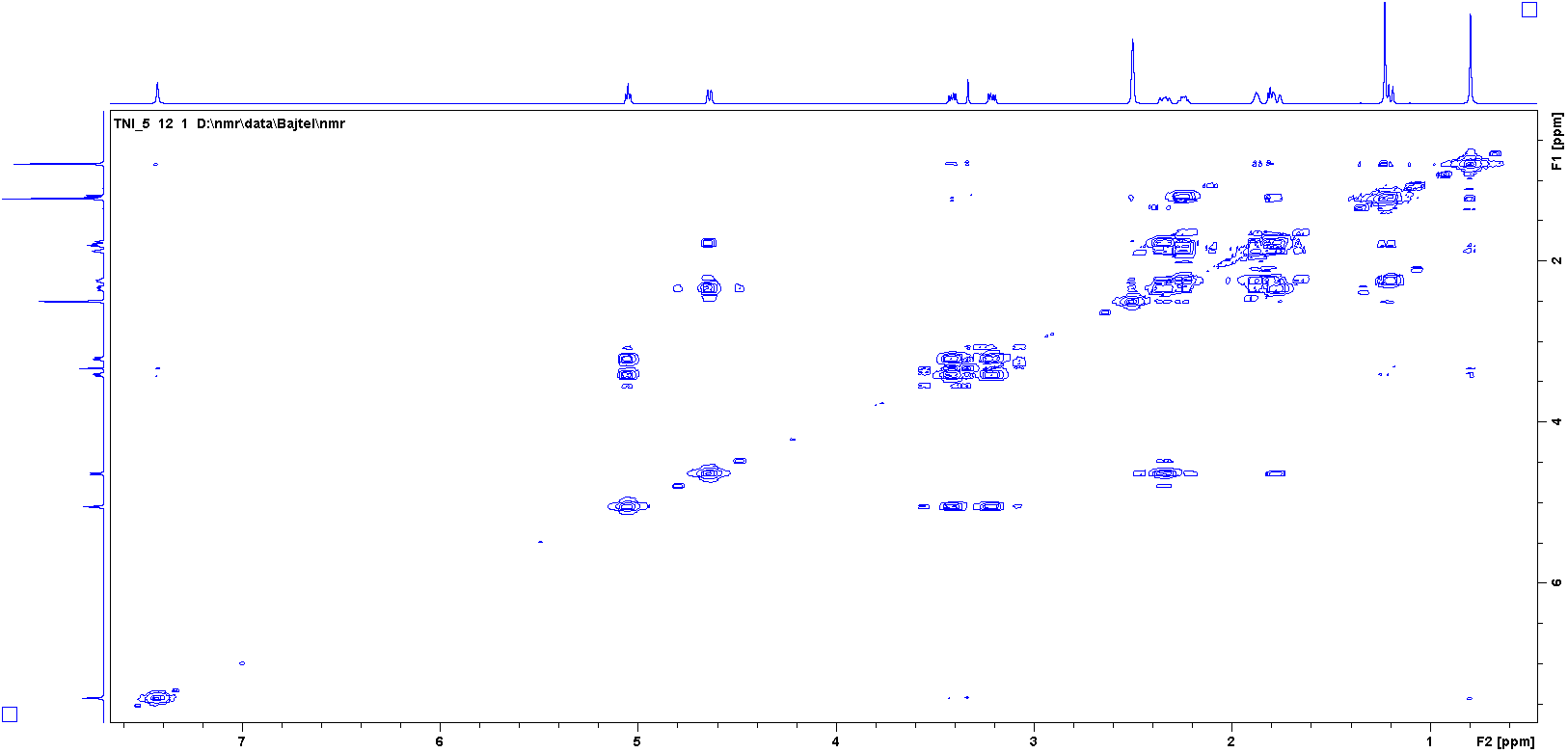


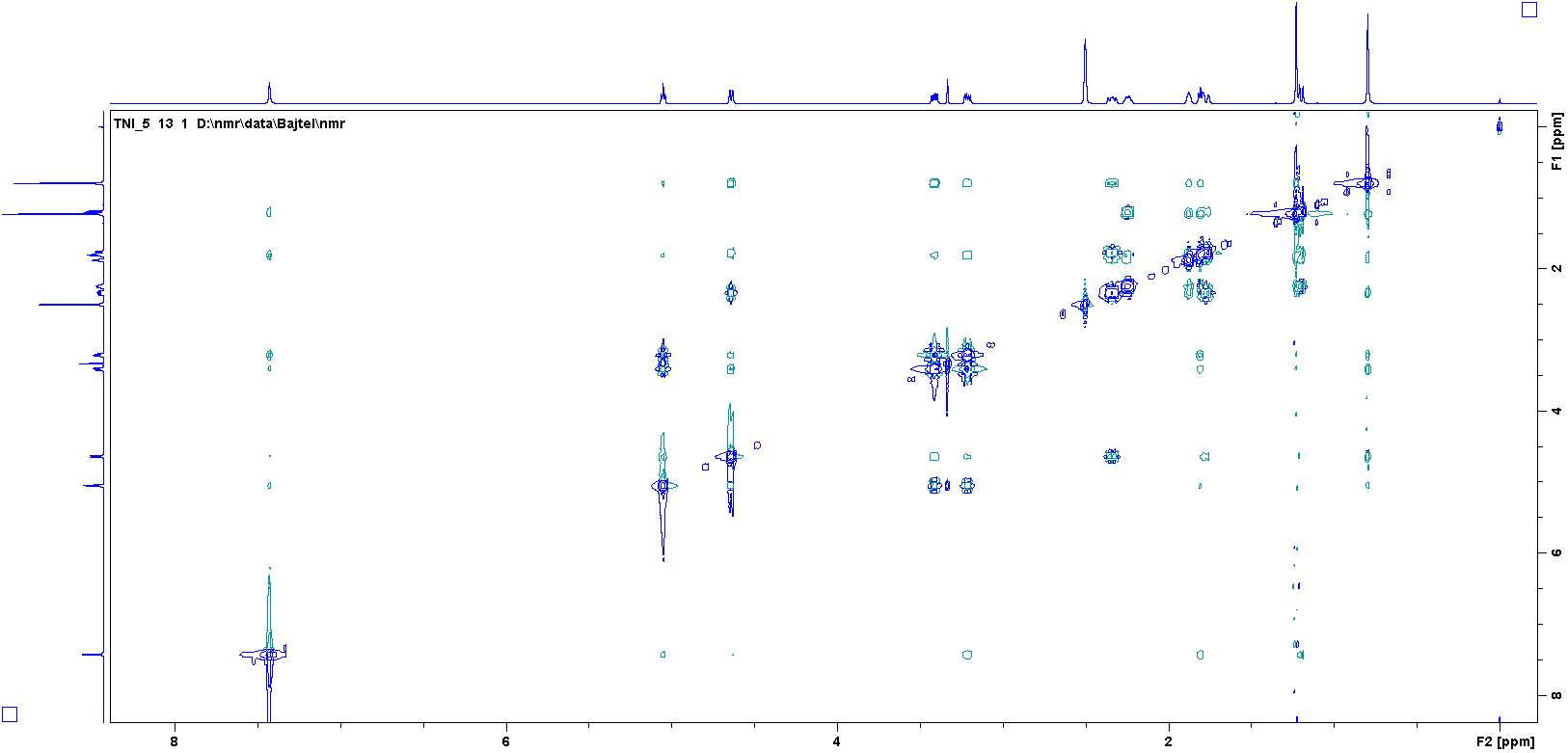


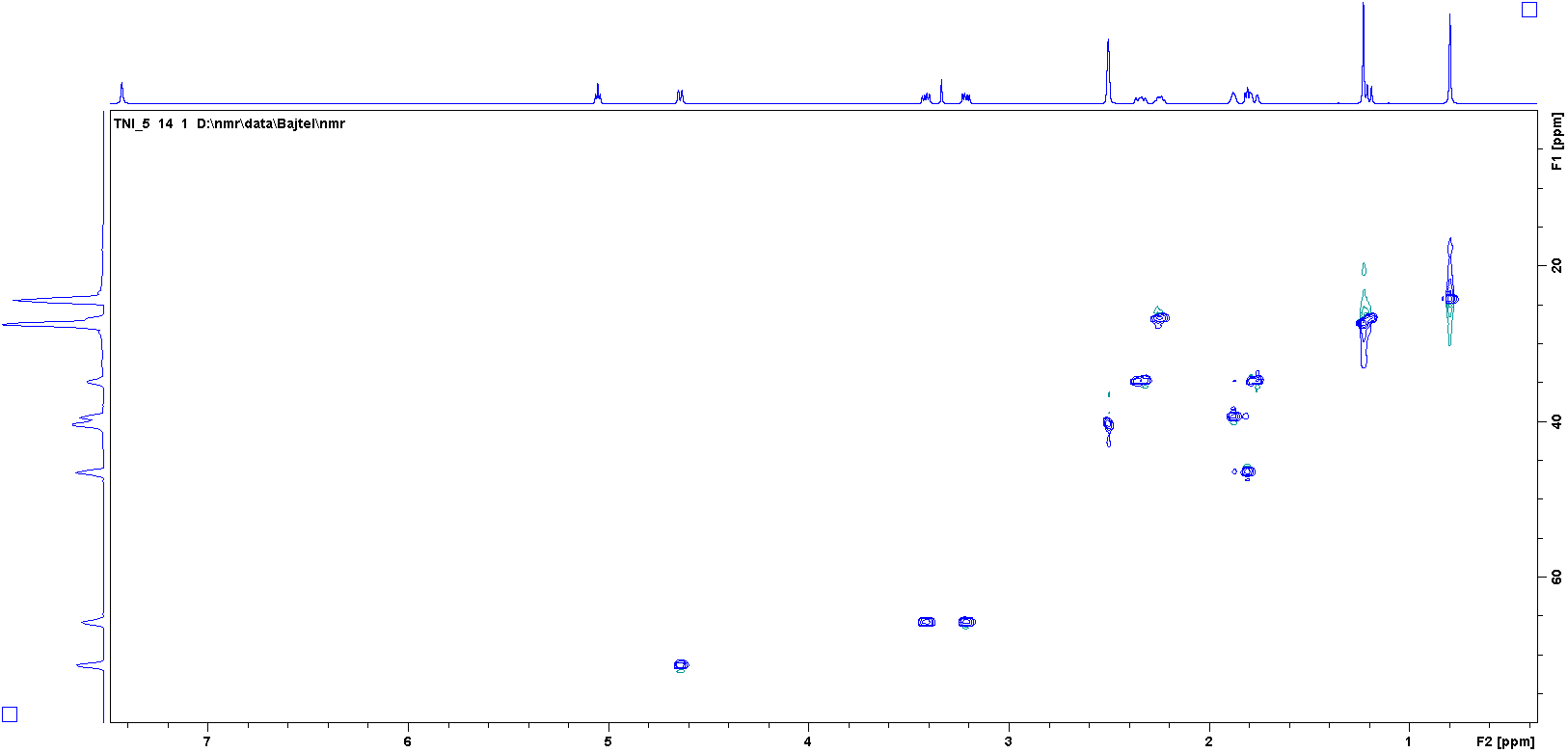
1H, 13C NMR, COSY, NOESY, HSQC and HMBC of **7** (DMSO-d6)

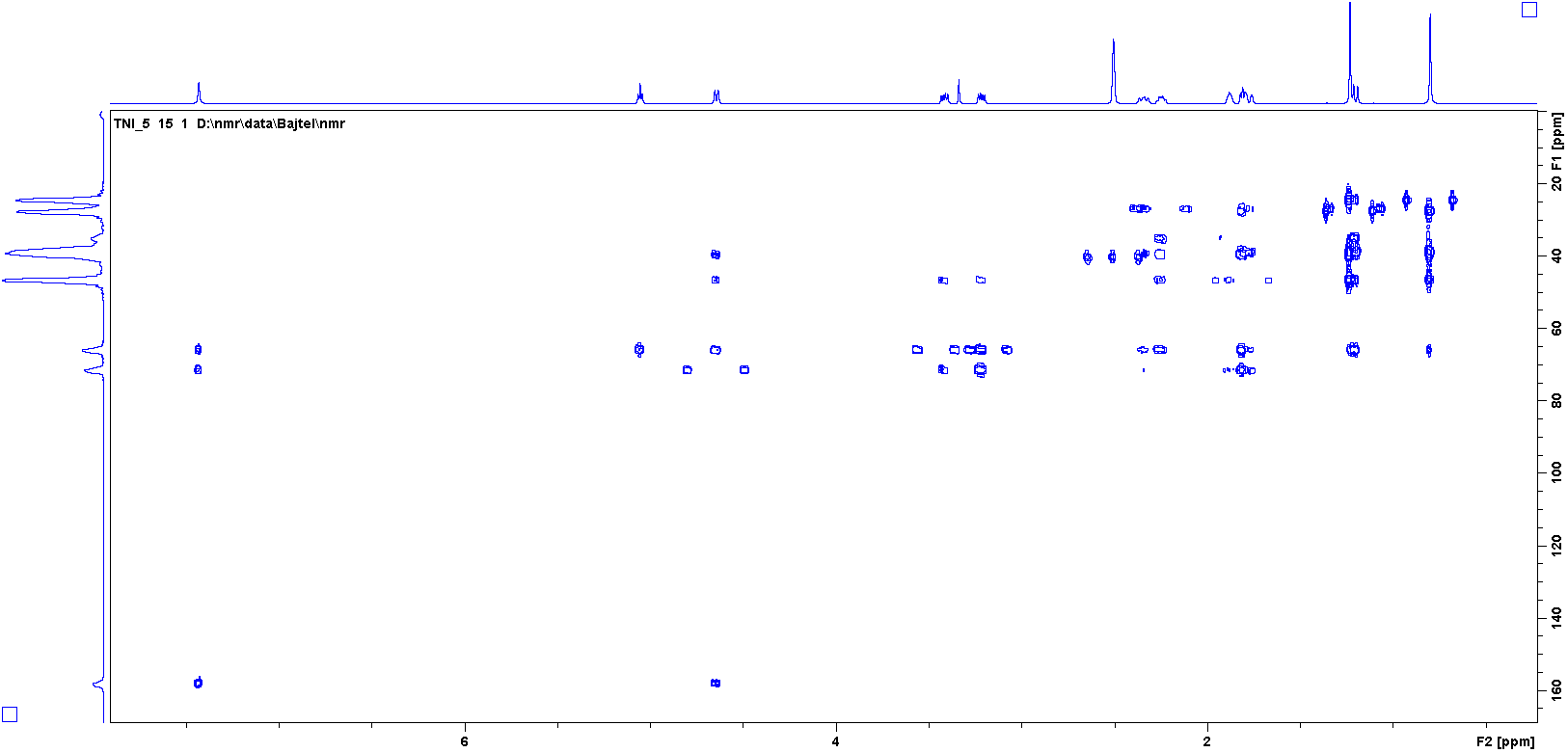




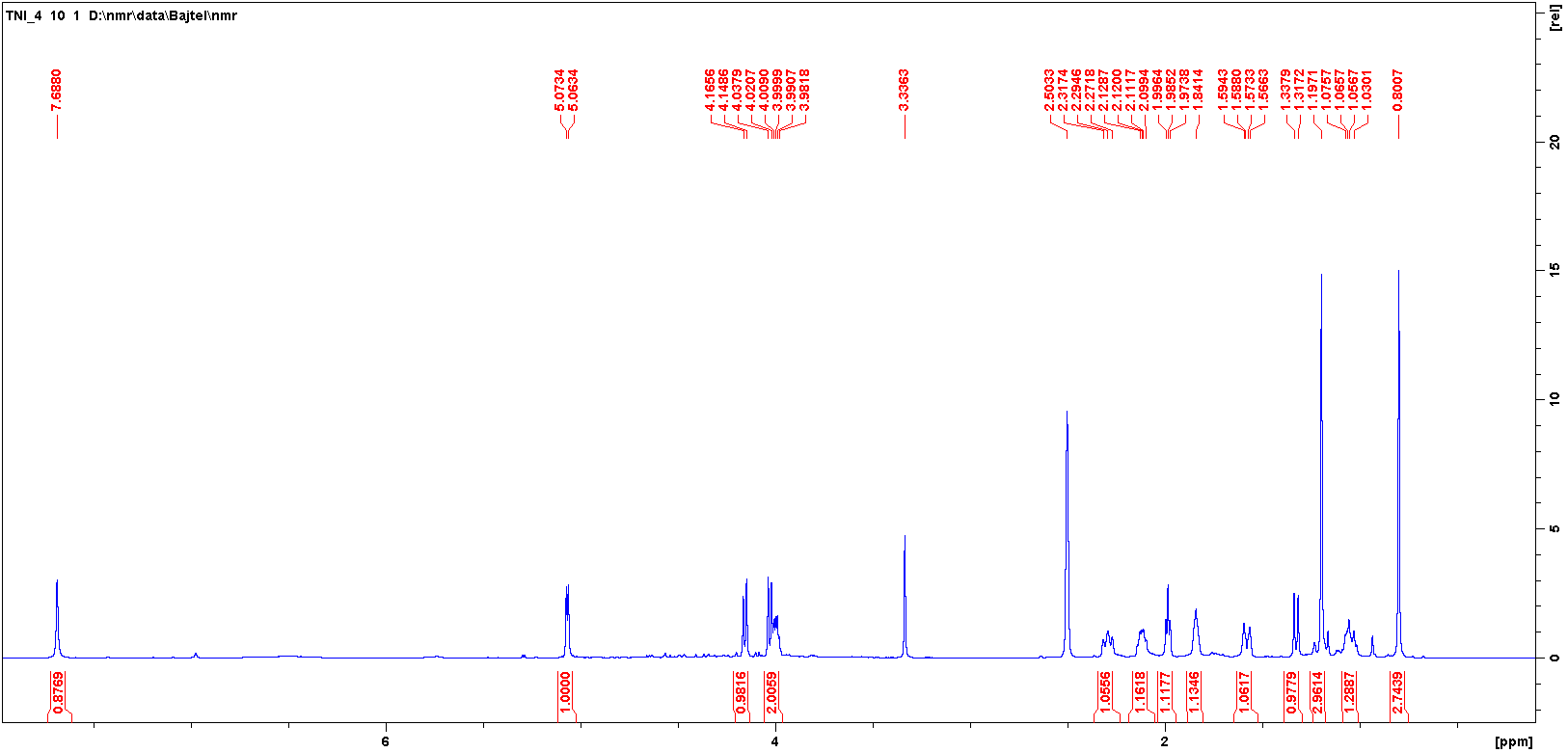


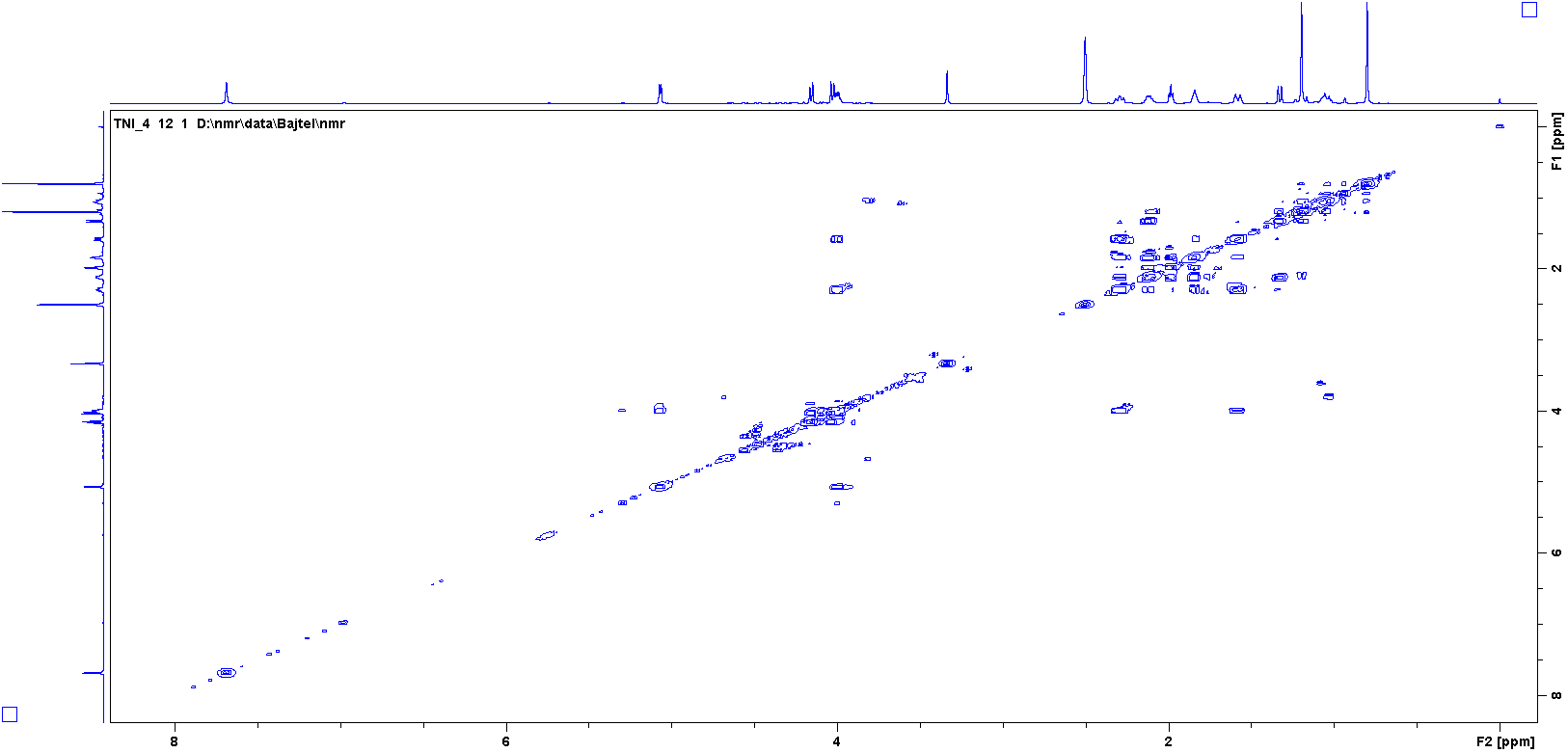
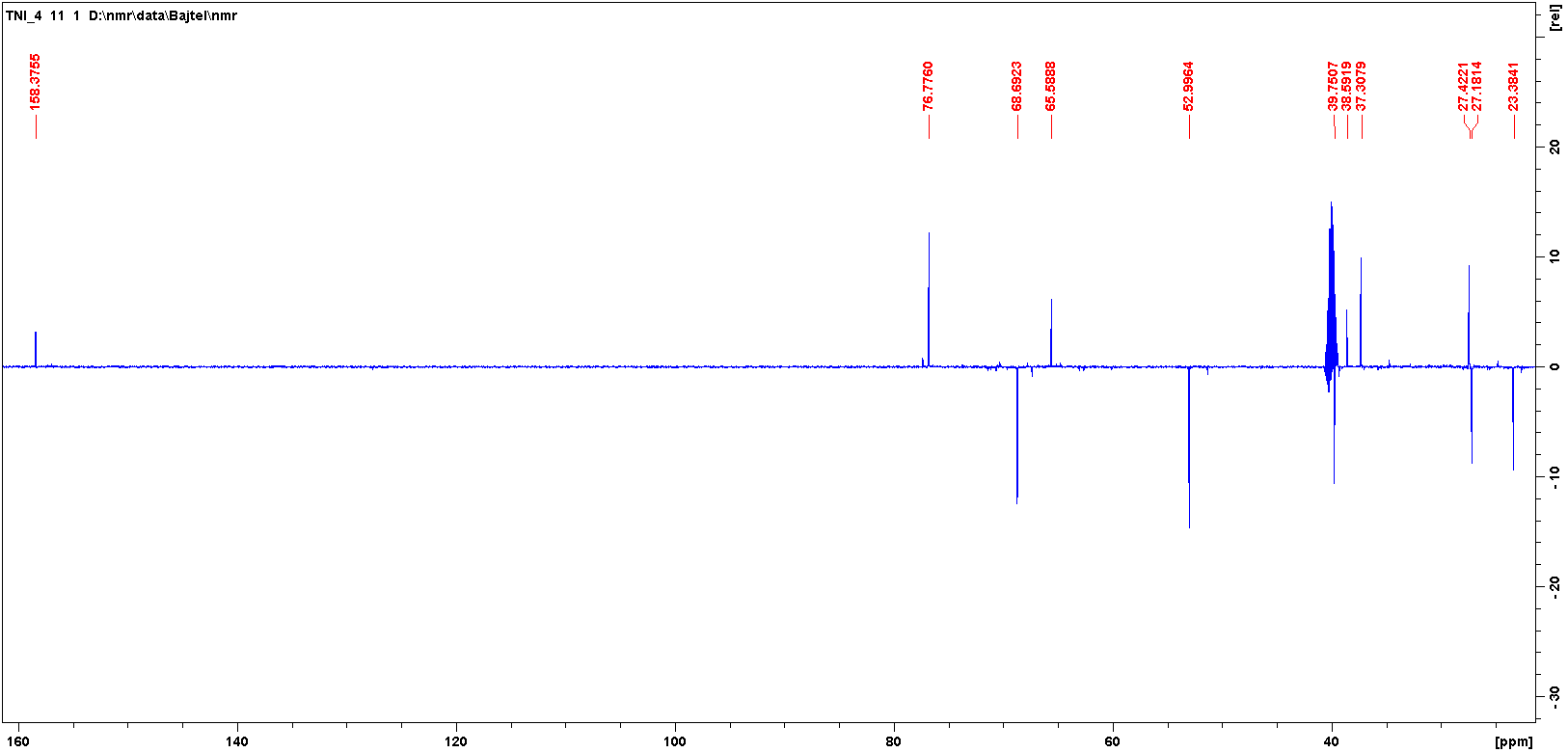


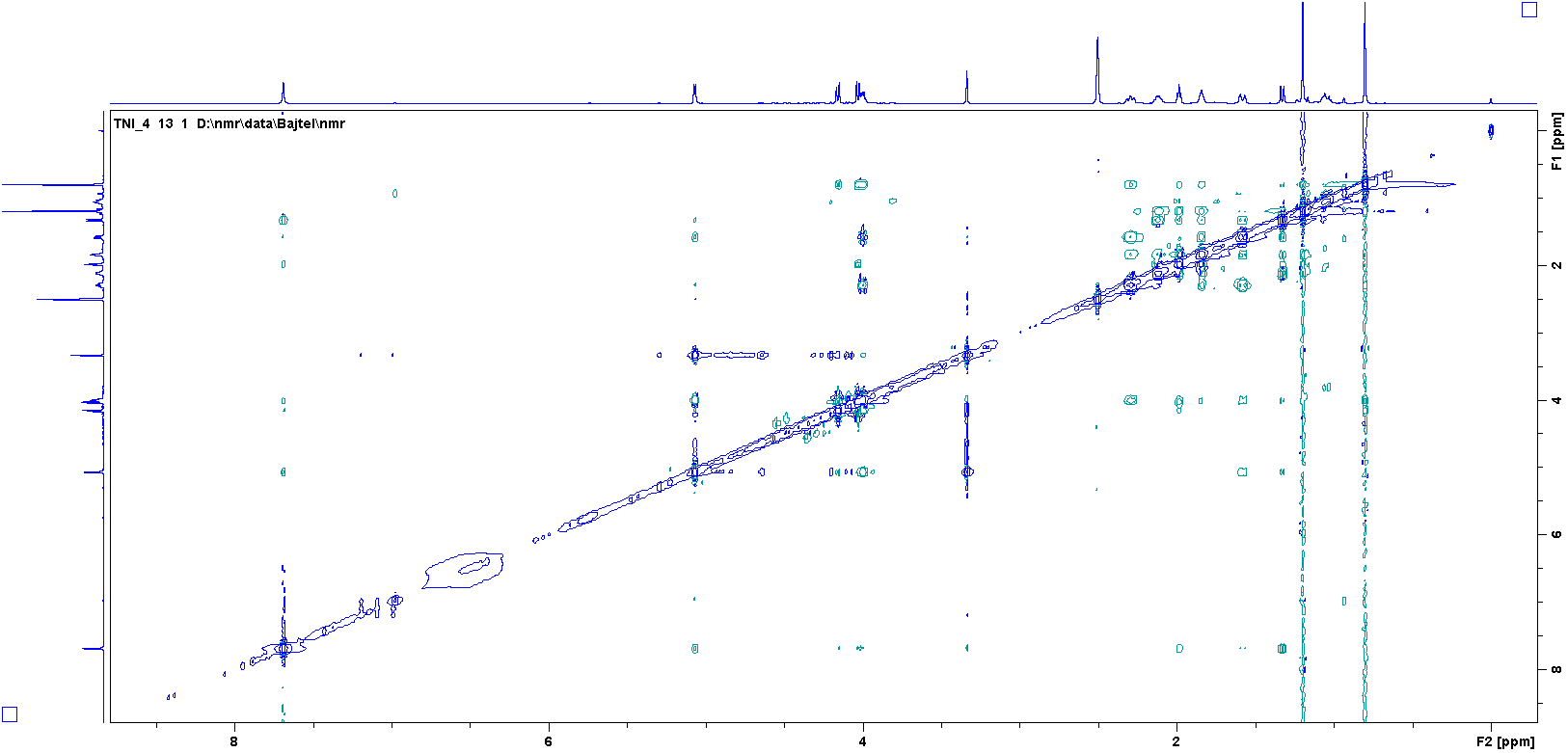


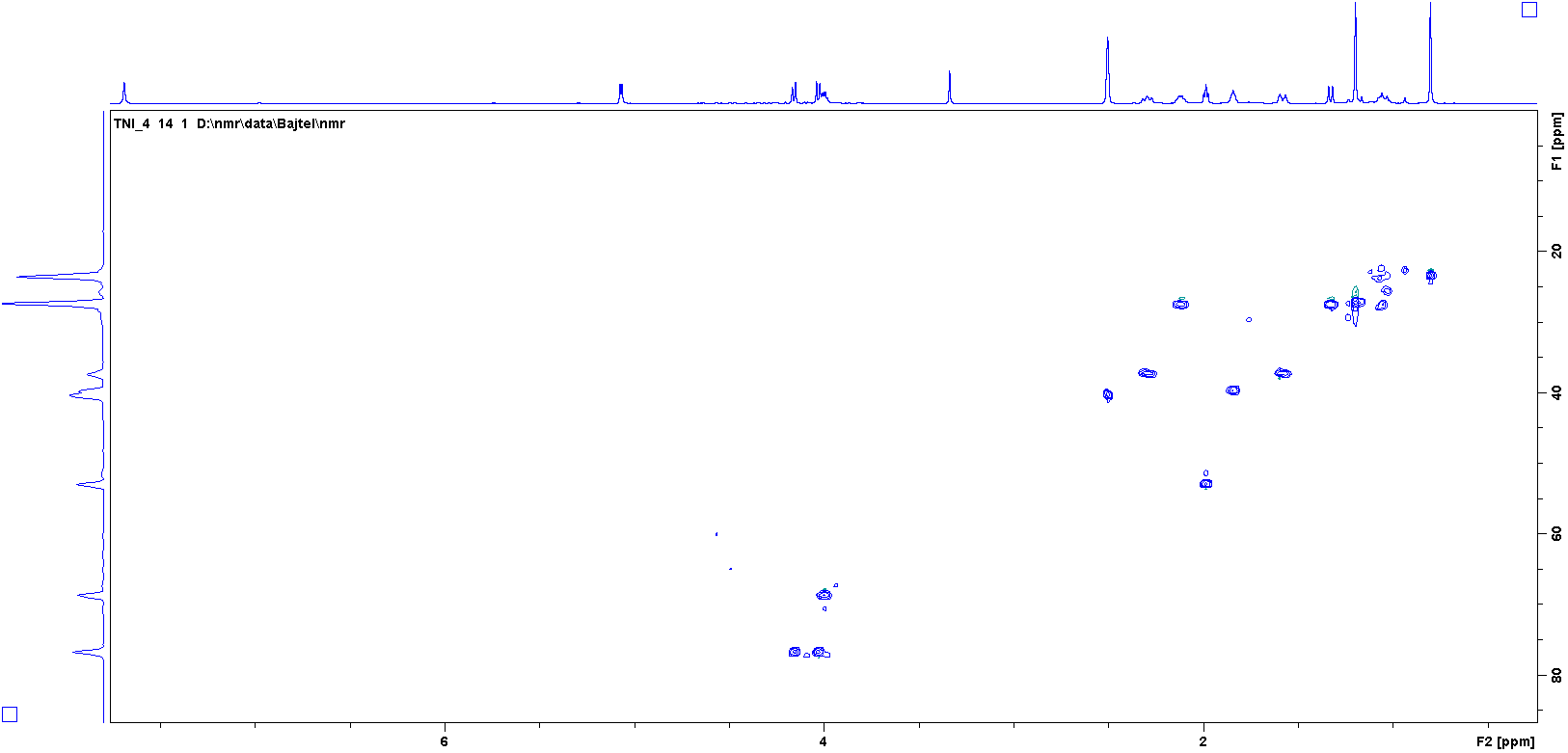


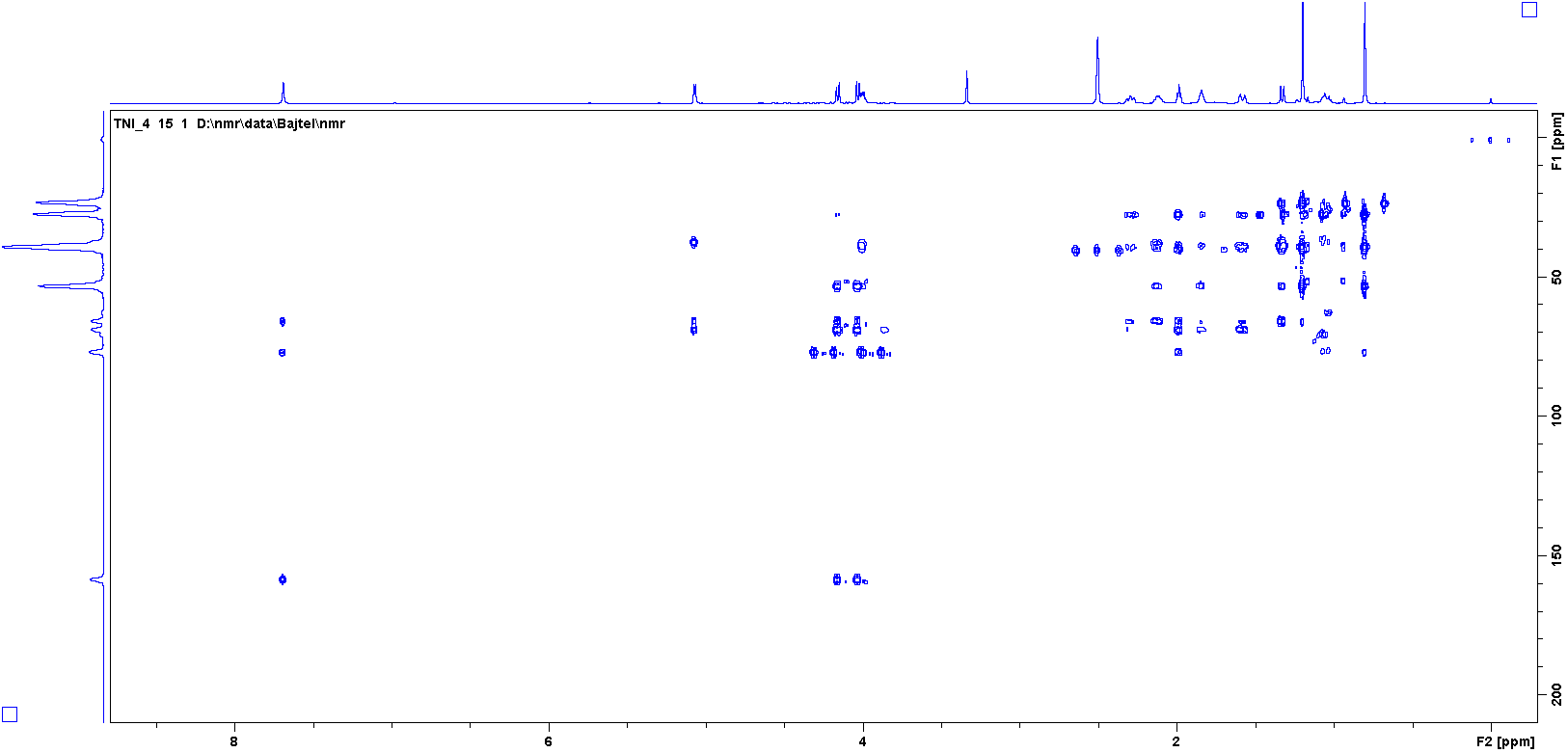
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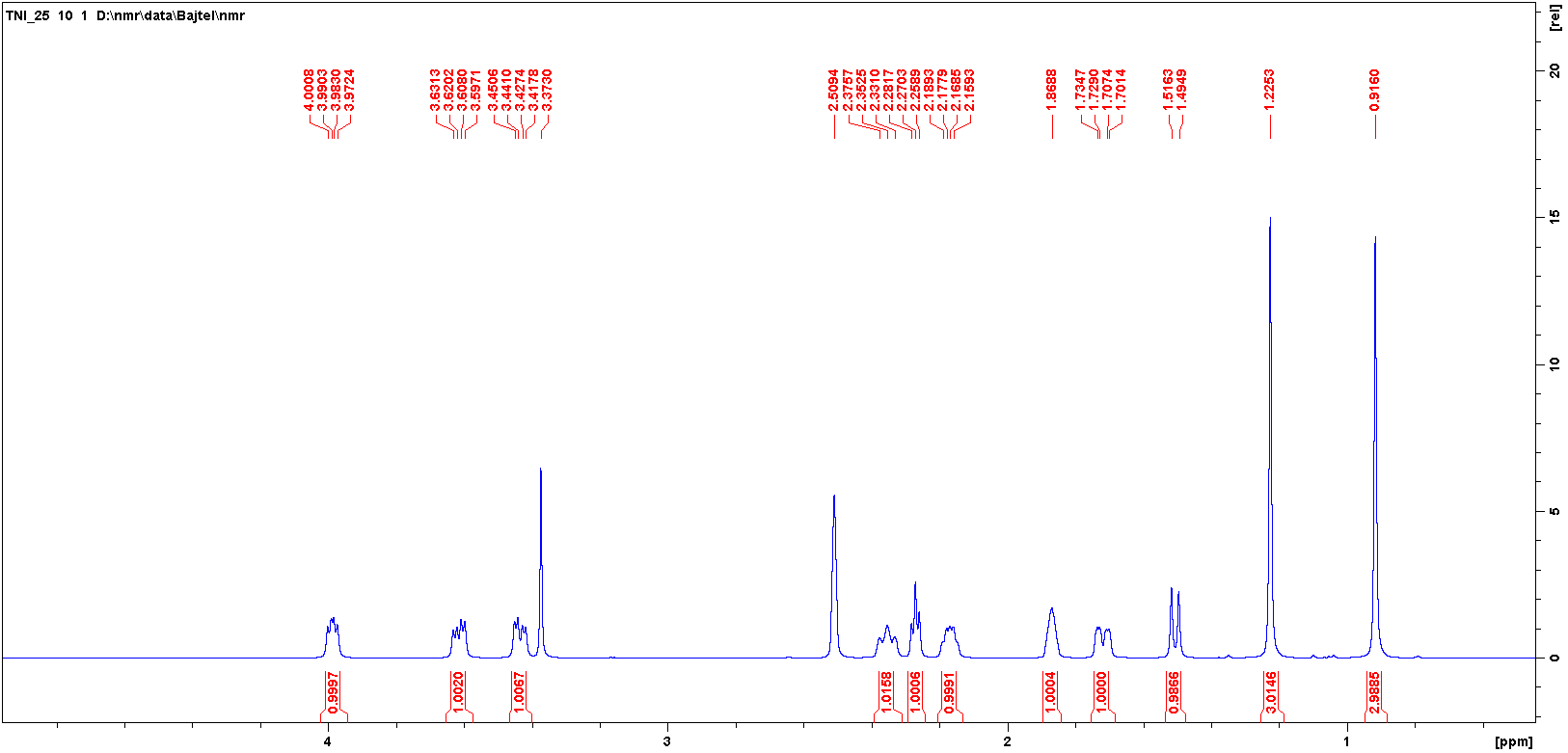


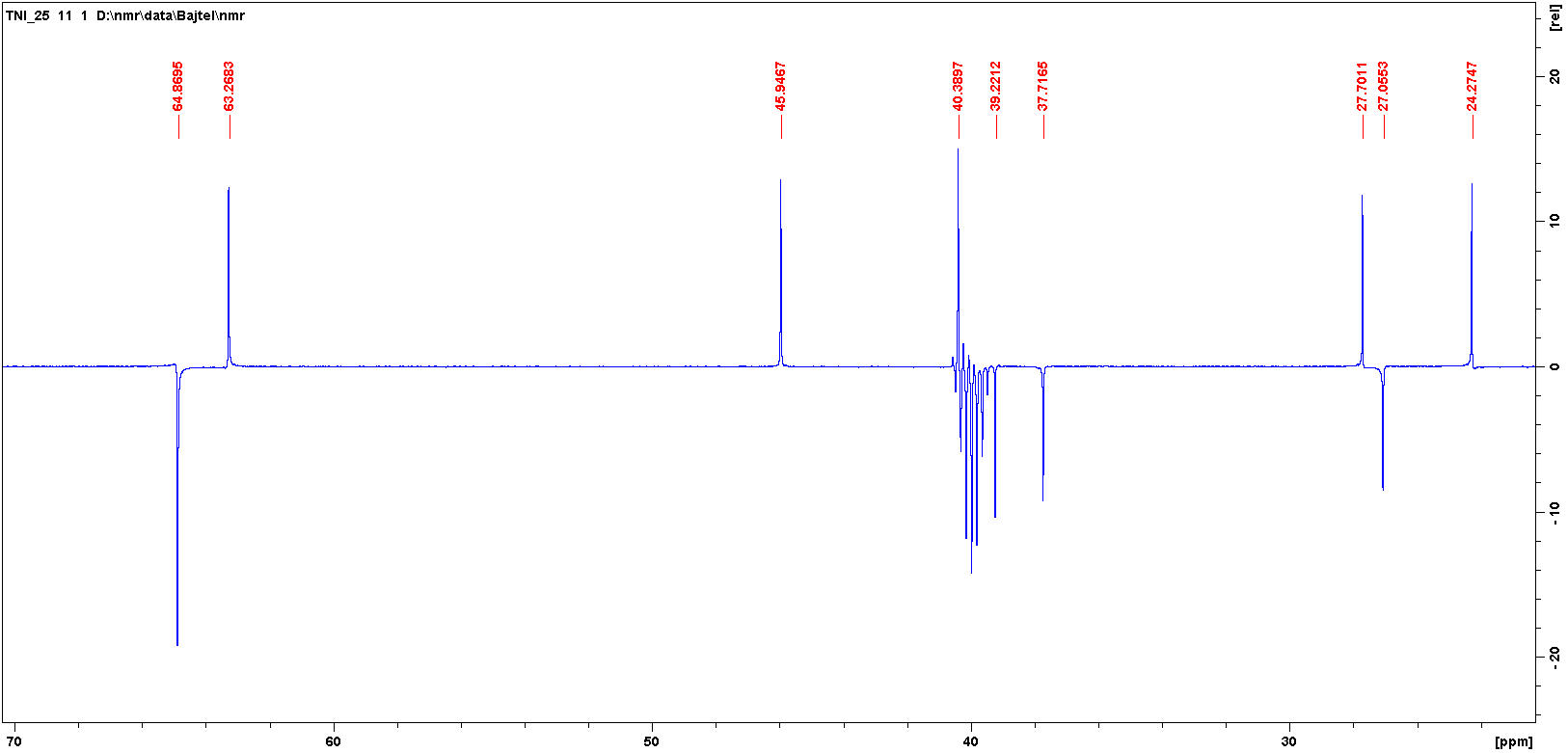


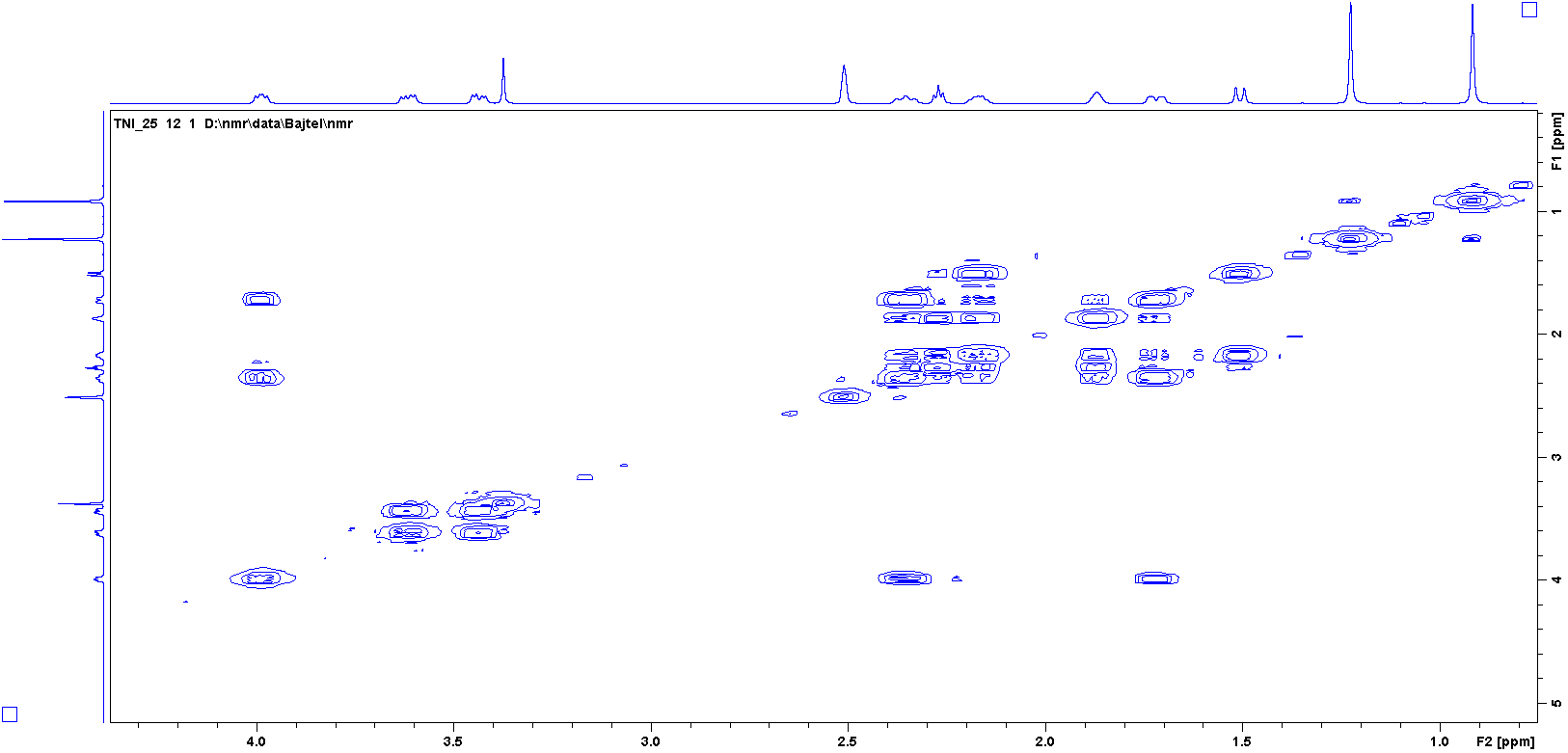


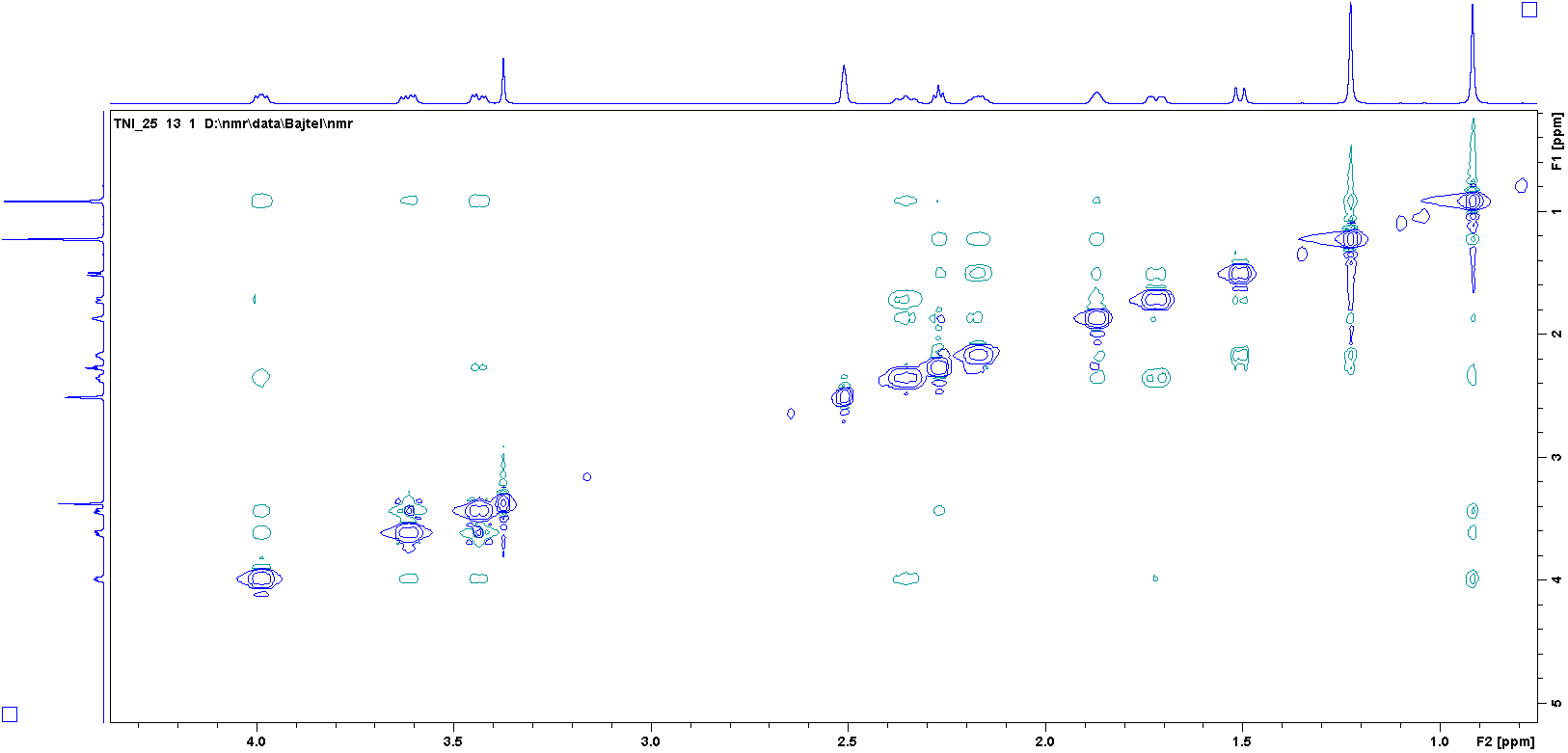


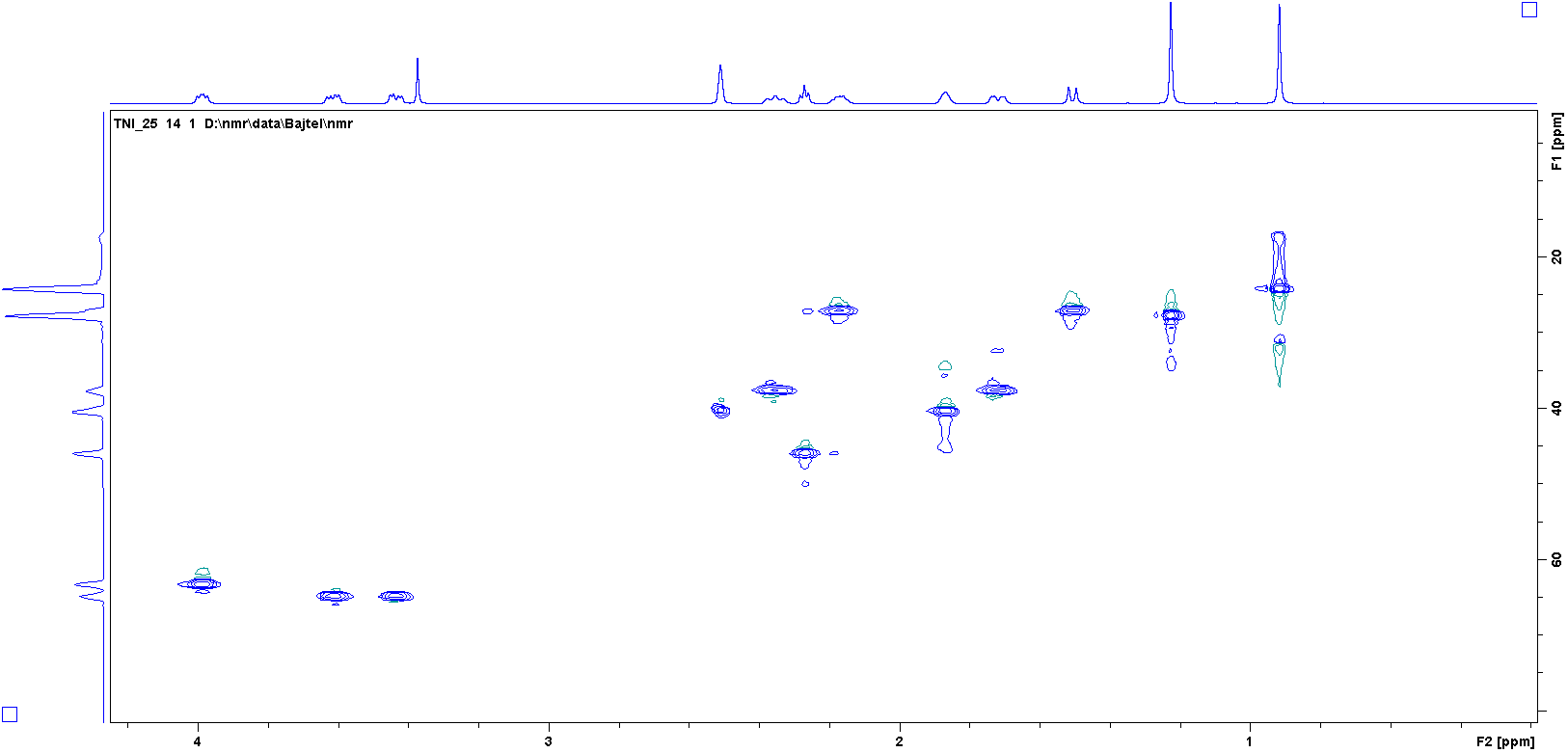
1H, 13C NMR, COSY, NOESY, HSQC and HMBC of **11** (DMSO-d6)

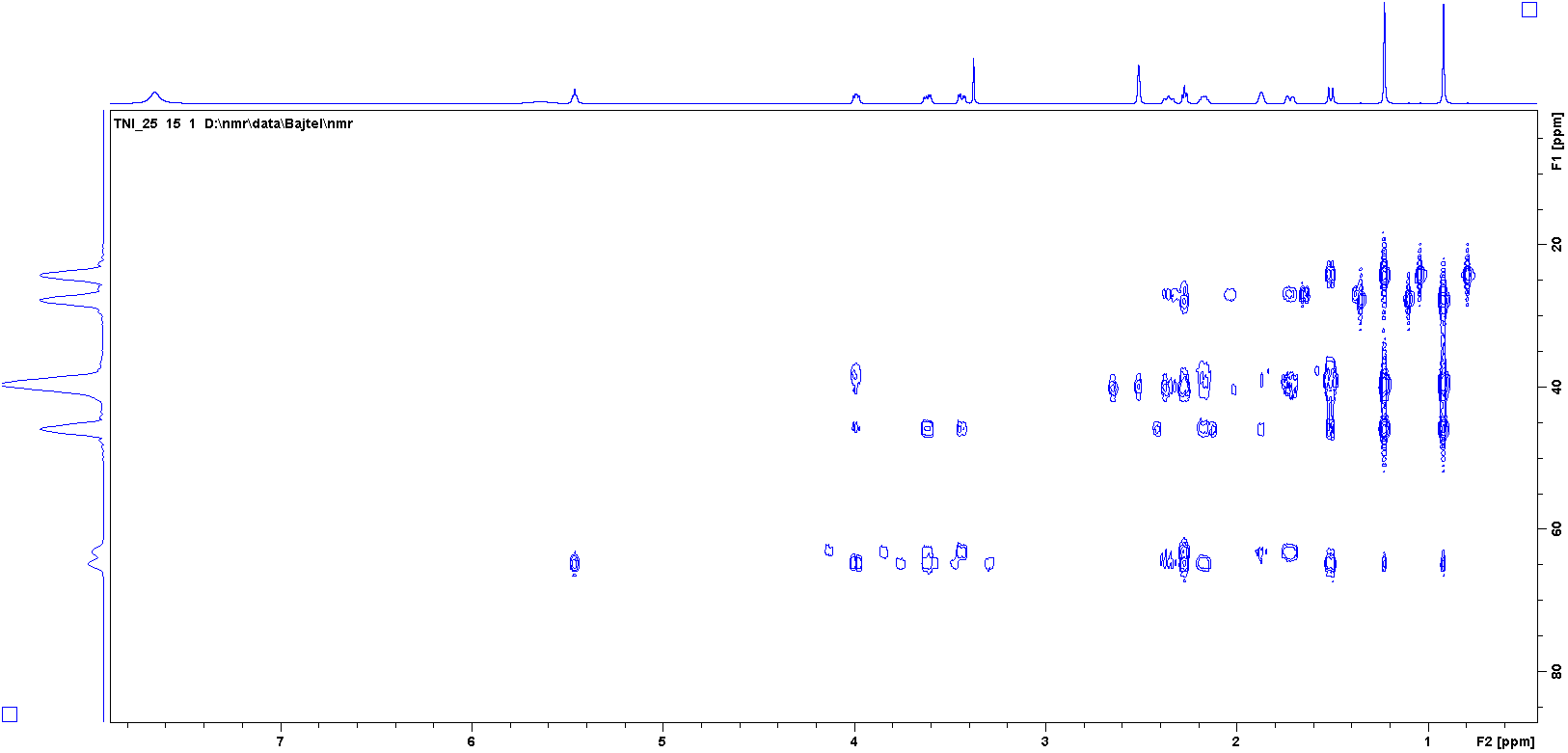




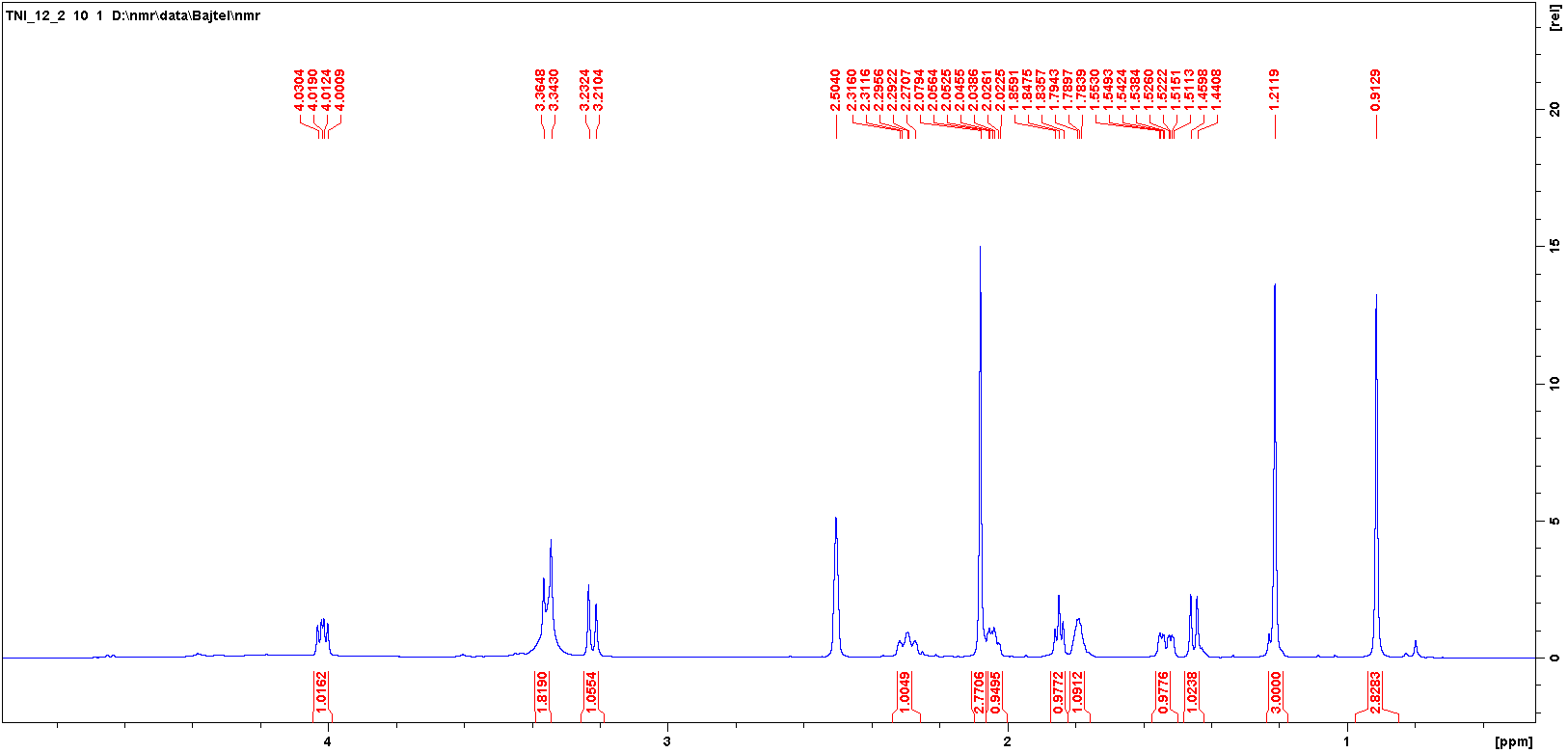


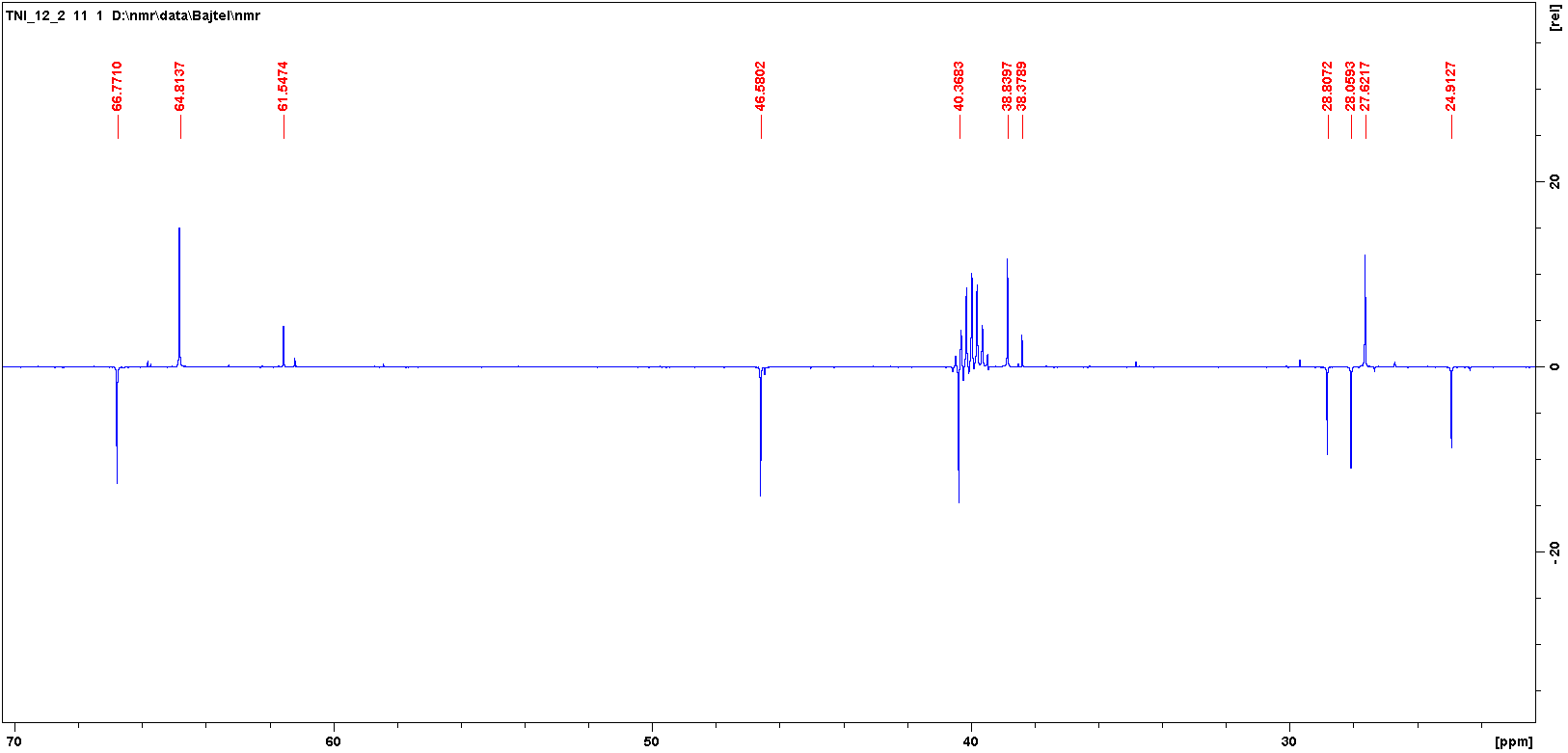


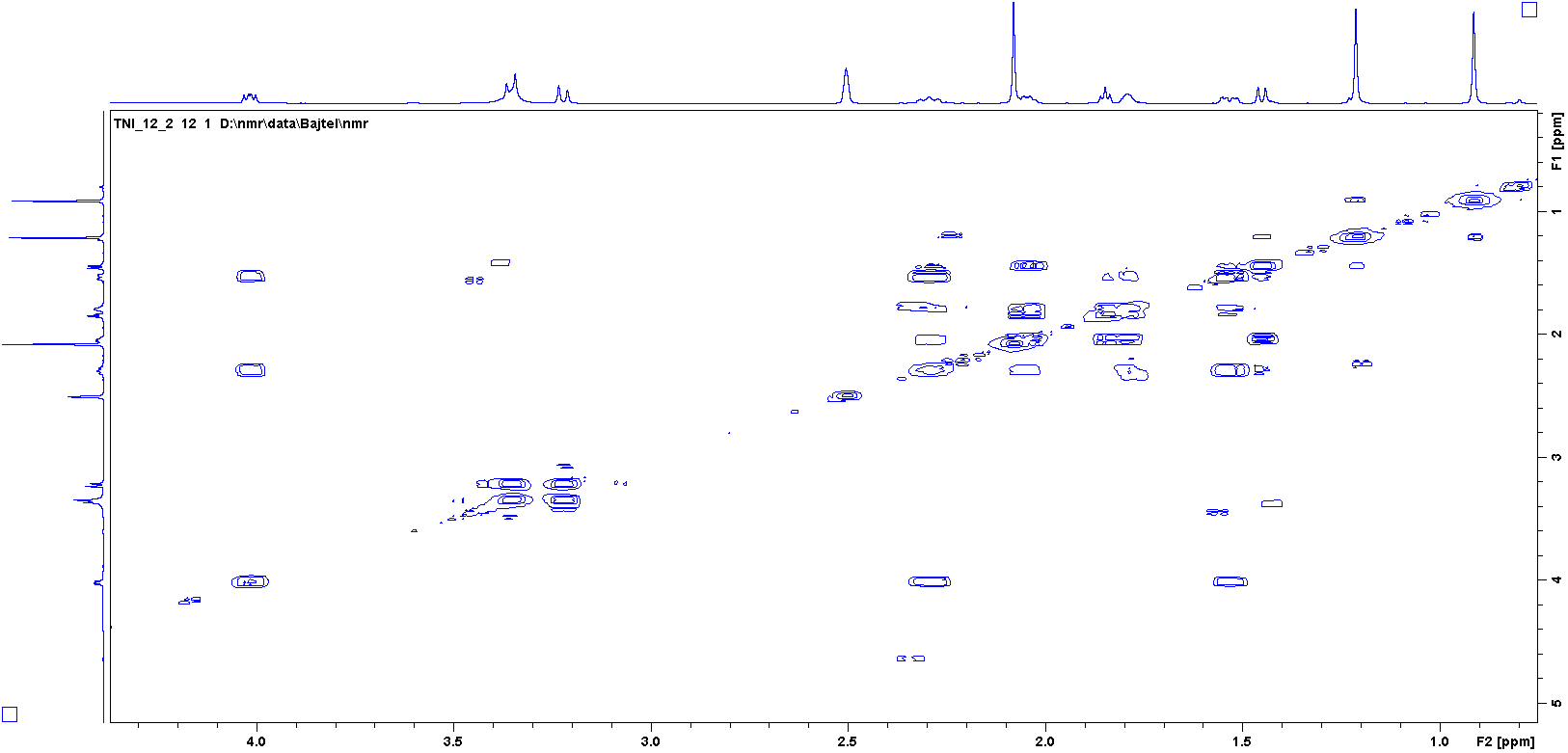


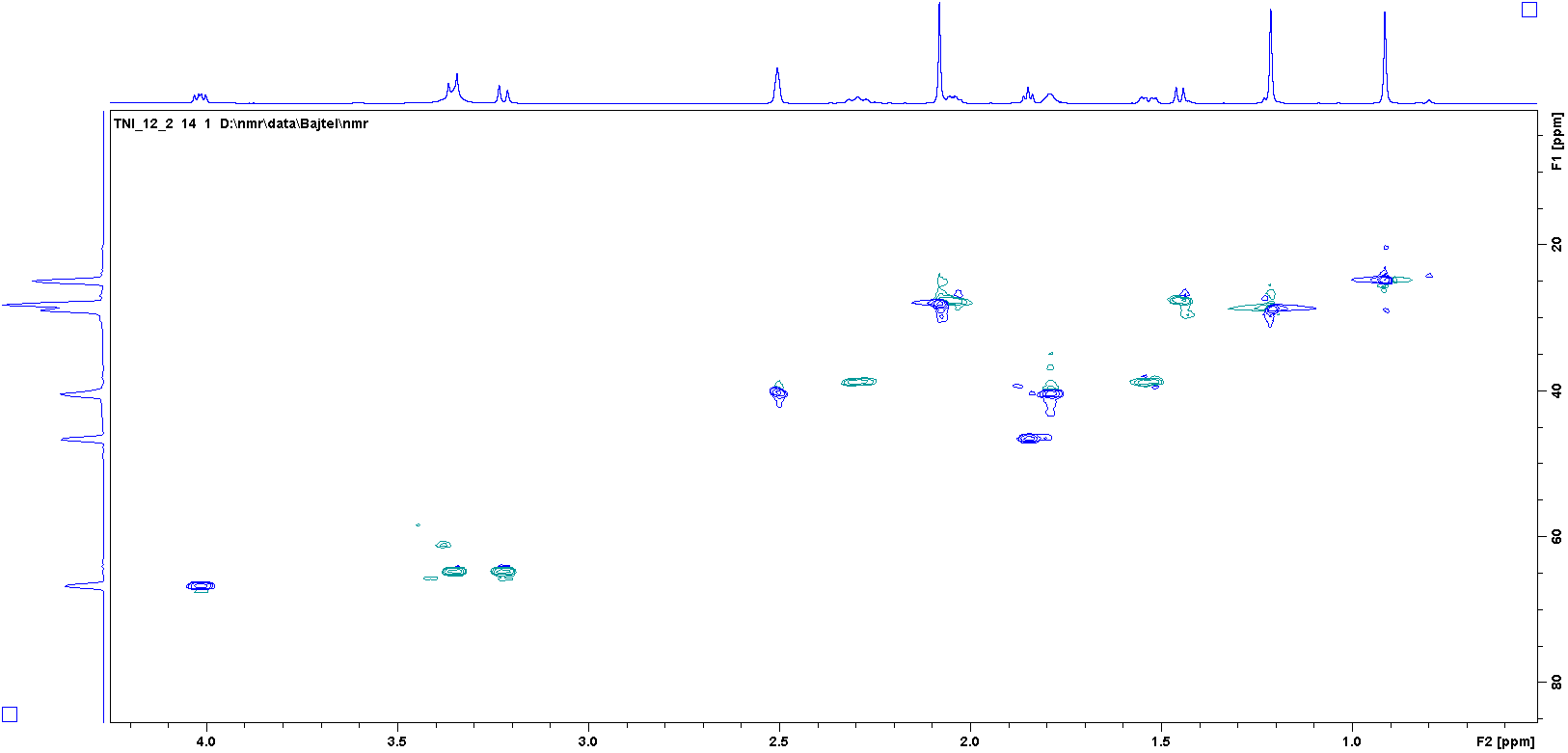


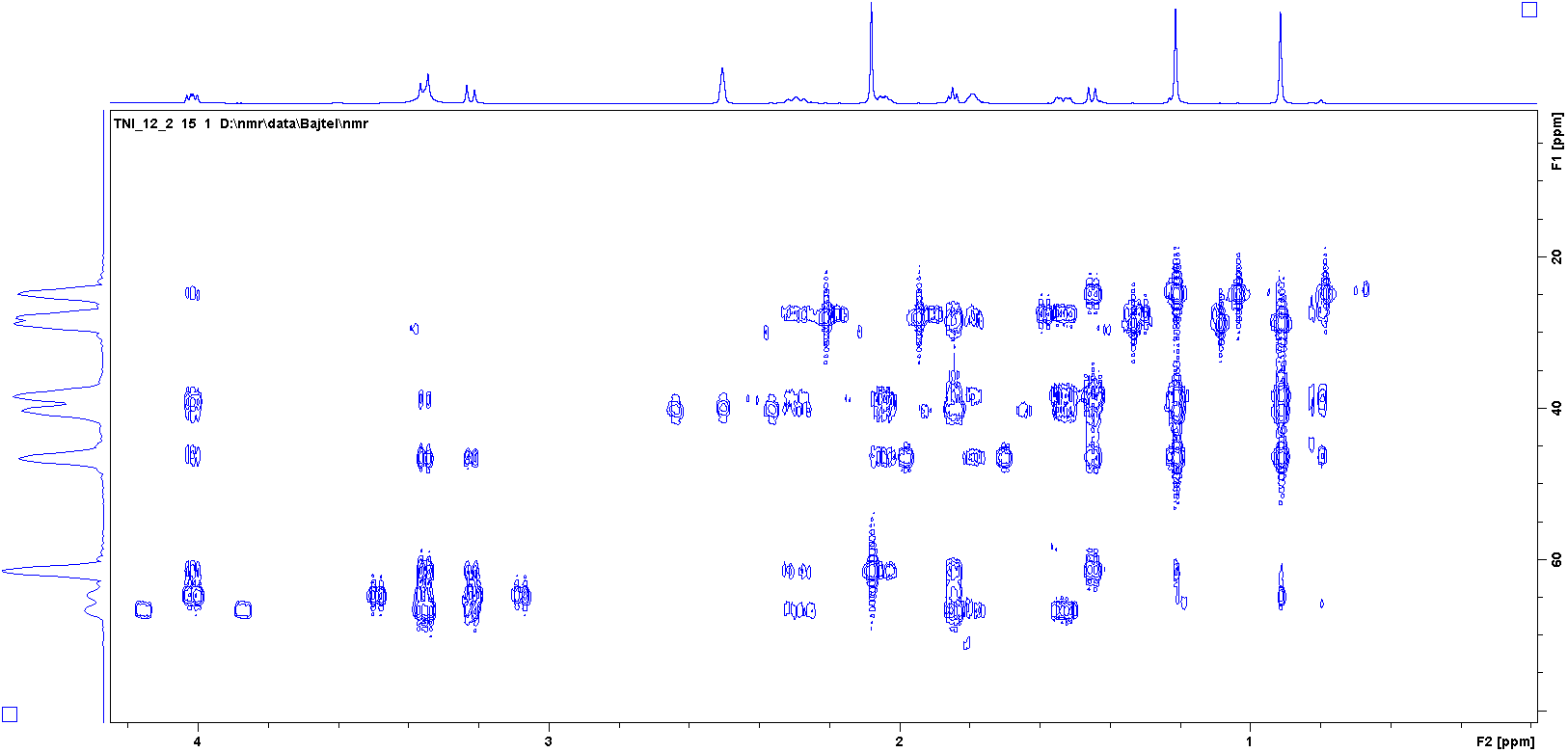
1H, 13C NMR, COSY, HSQC and HMBC of **12** (DMSO-d6)



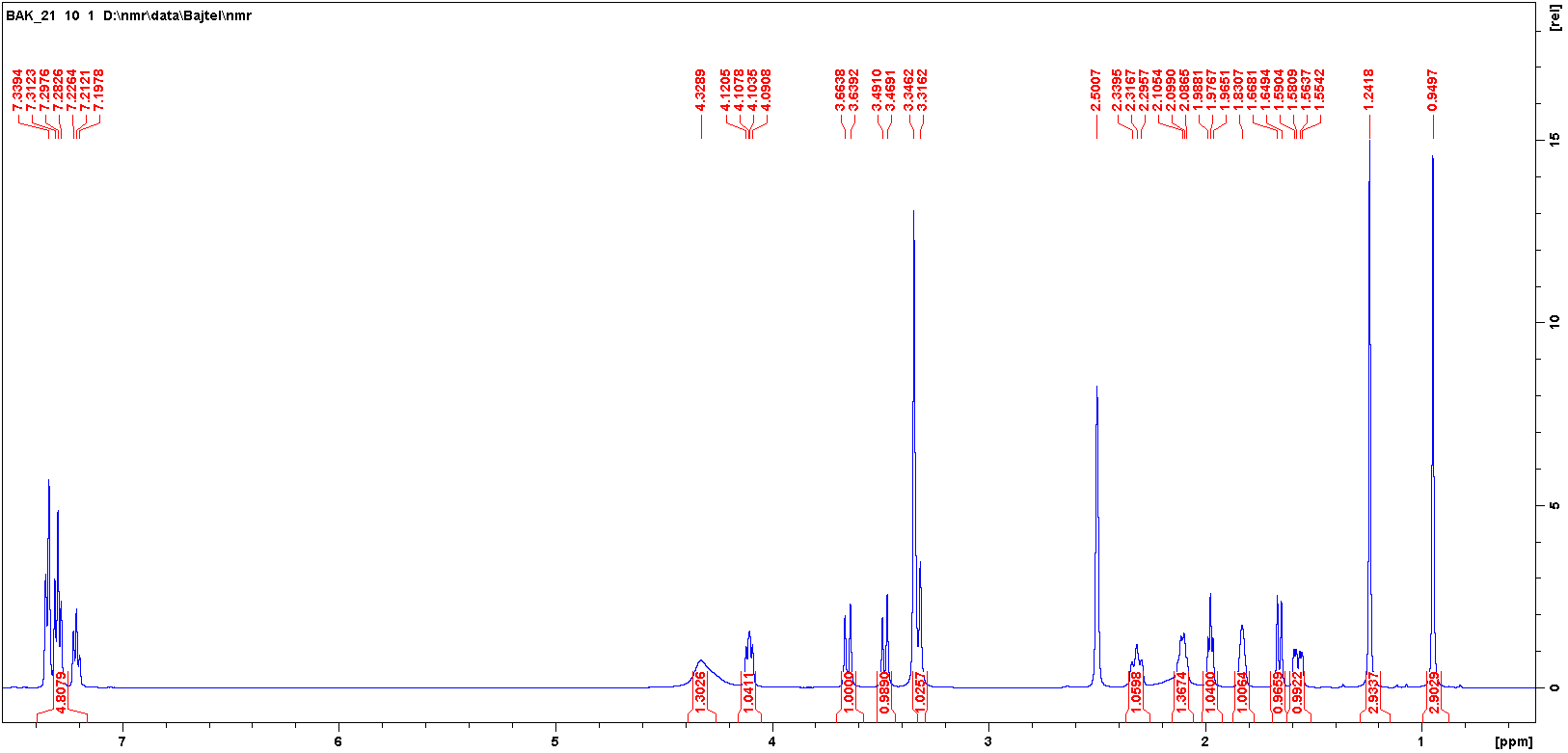


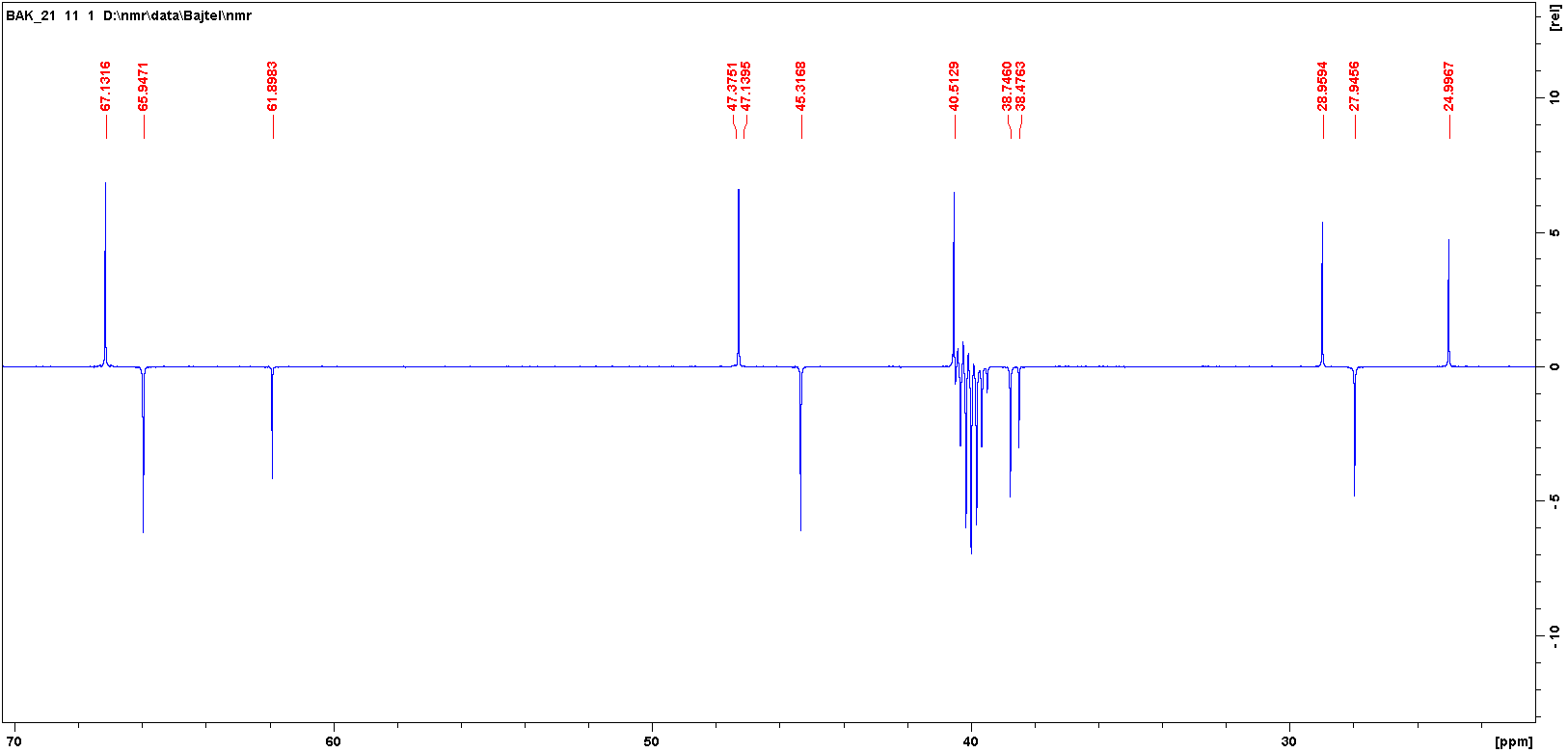


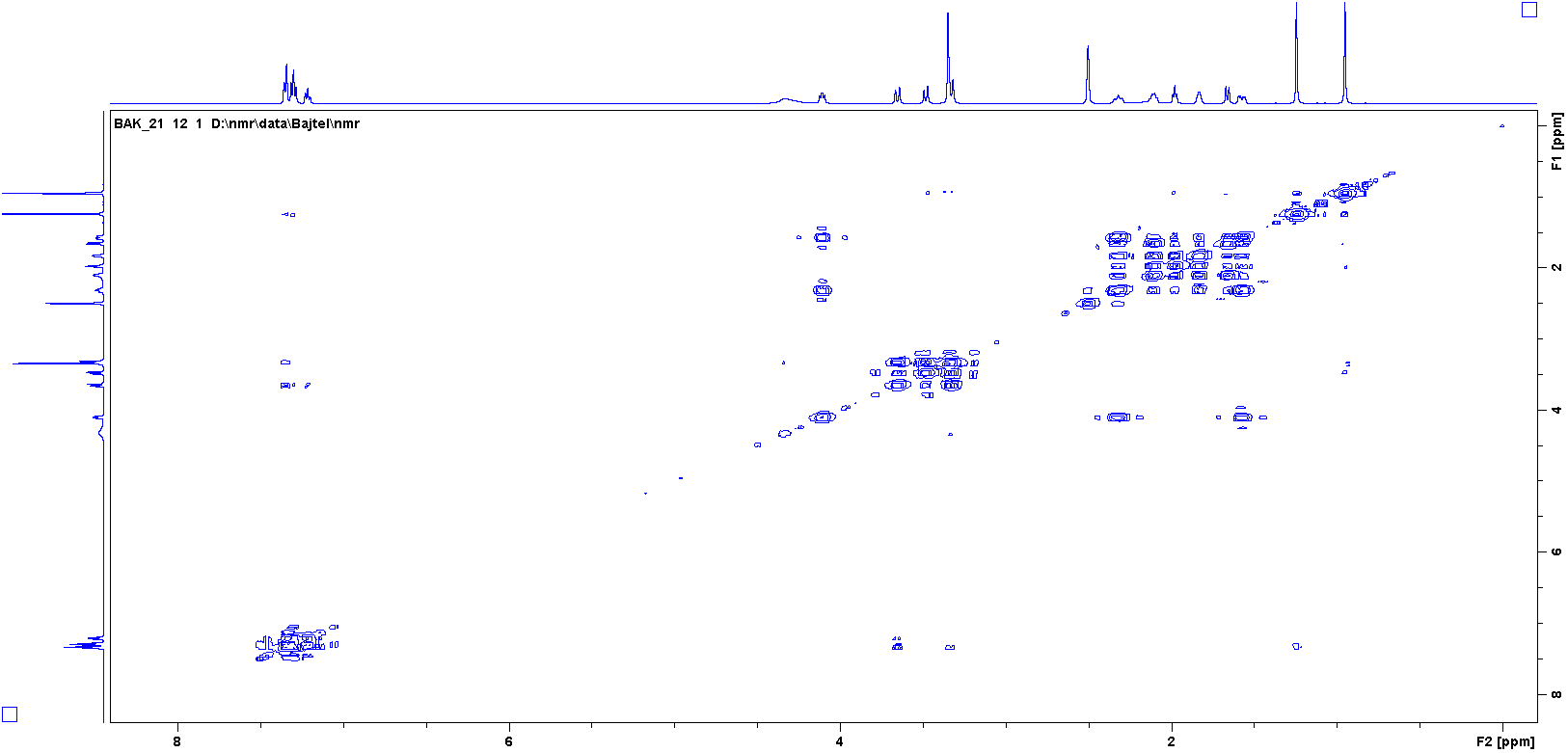


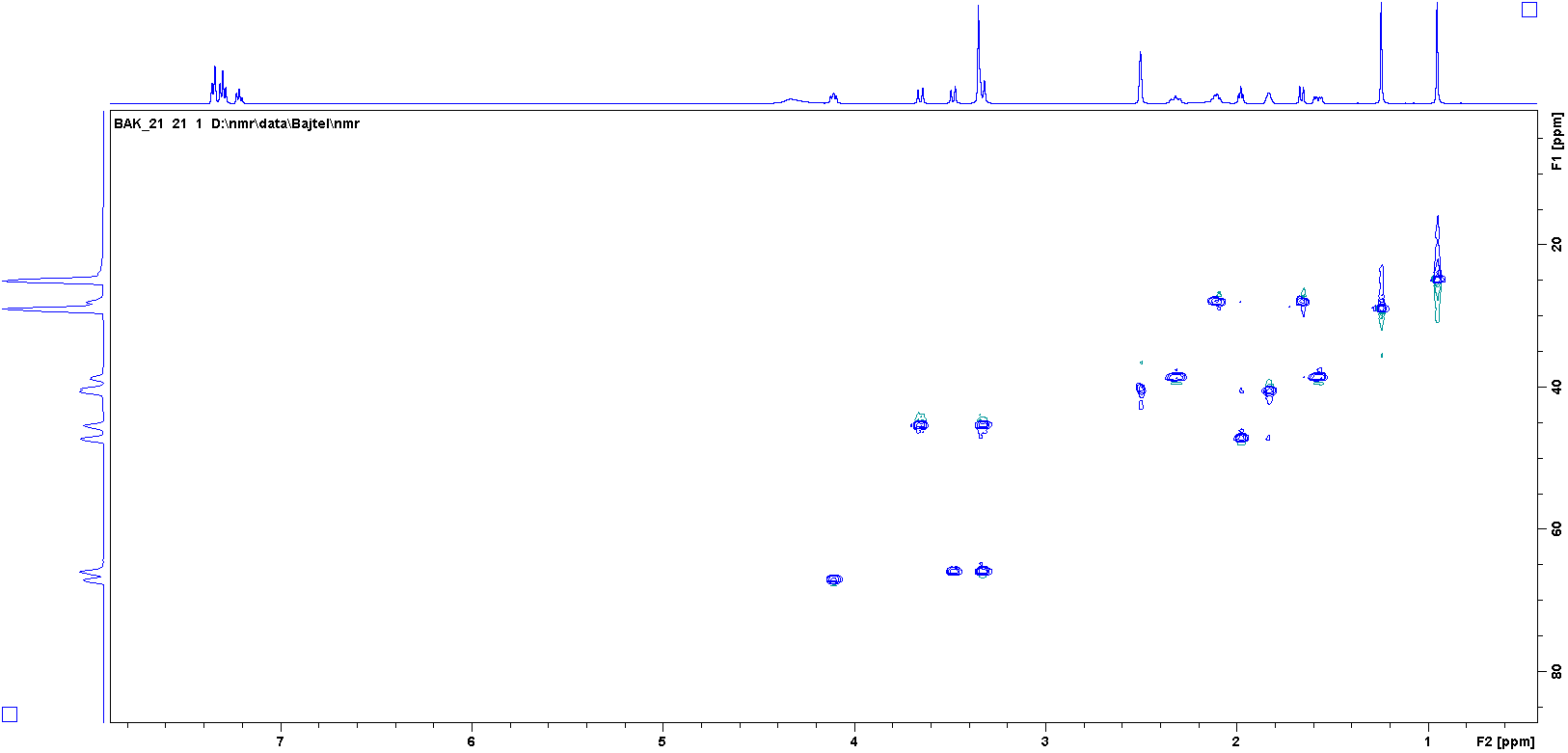


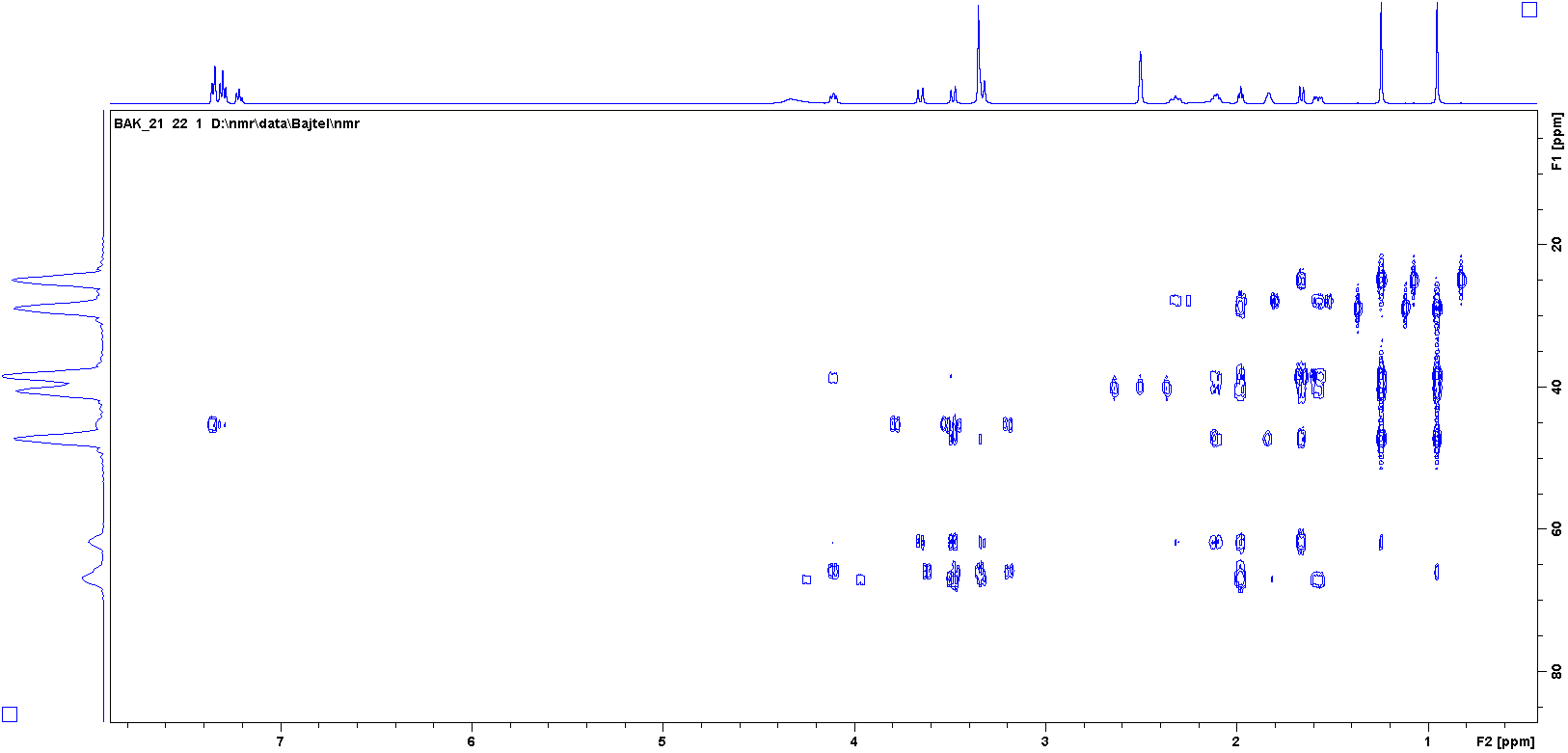
1H, 13C NMR, COSY, HSQC and HMBC of **14** (DMSO-d6)



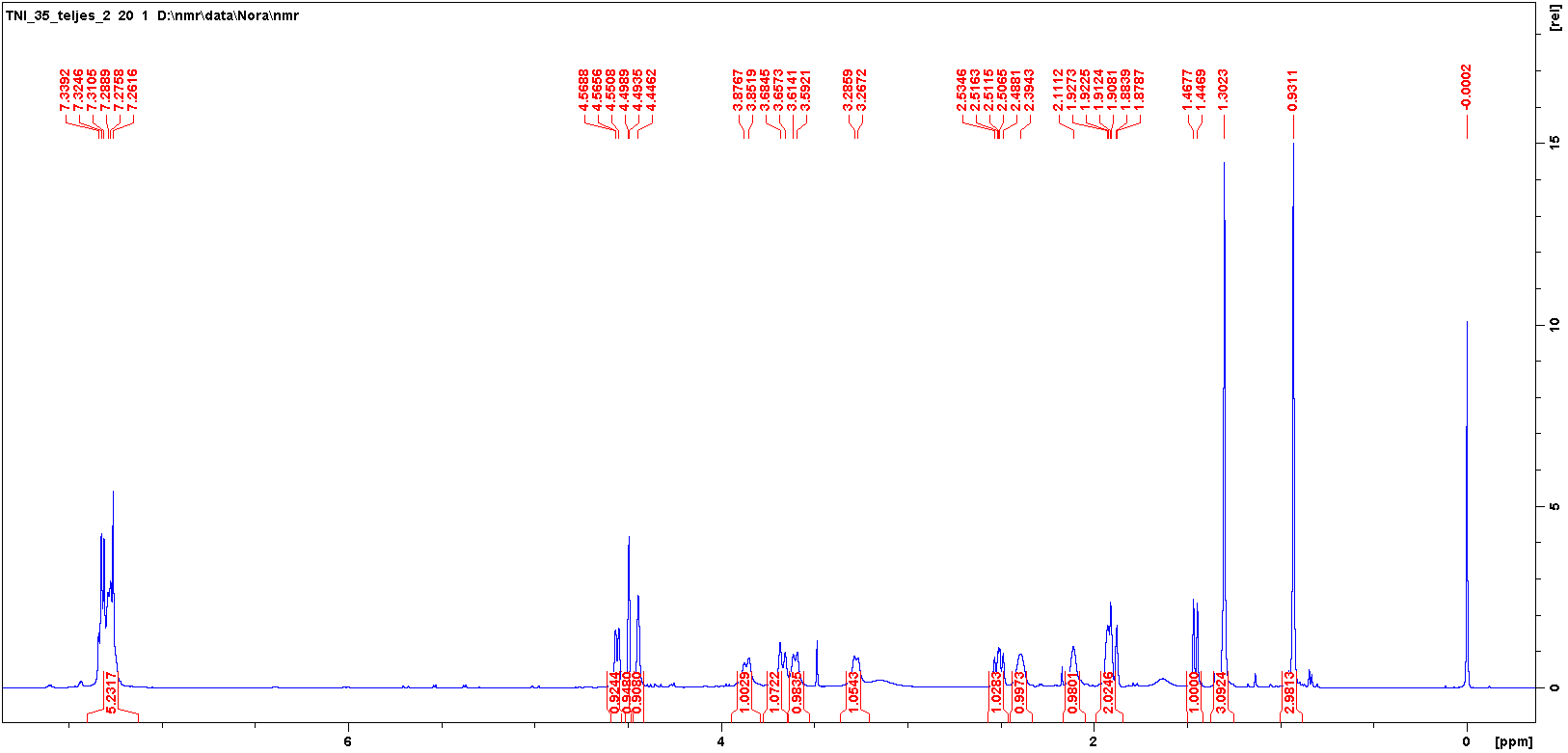


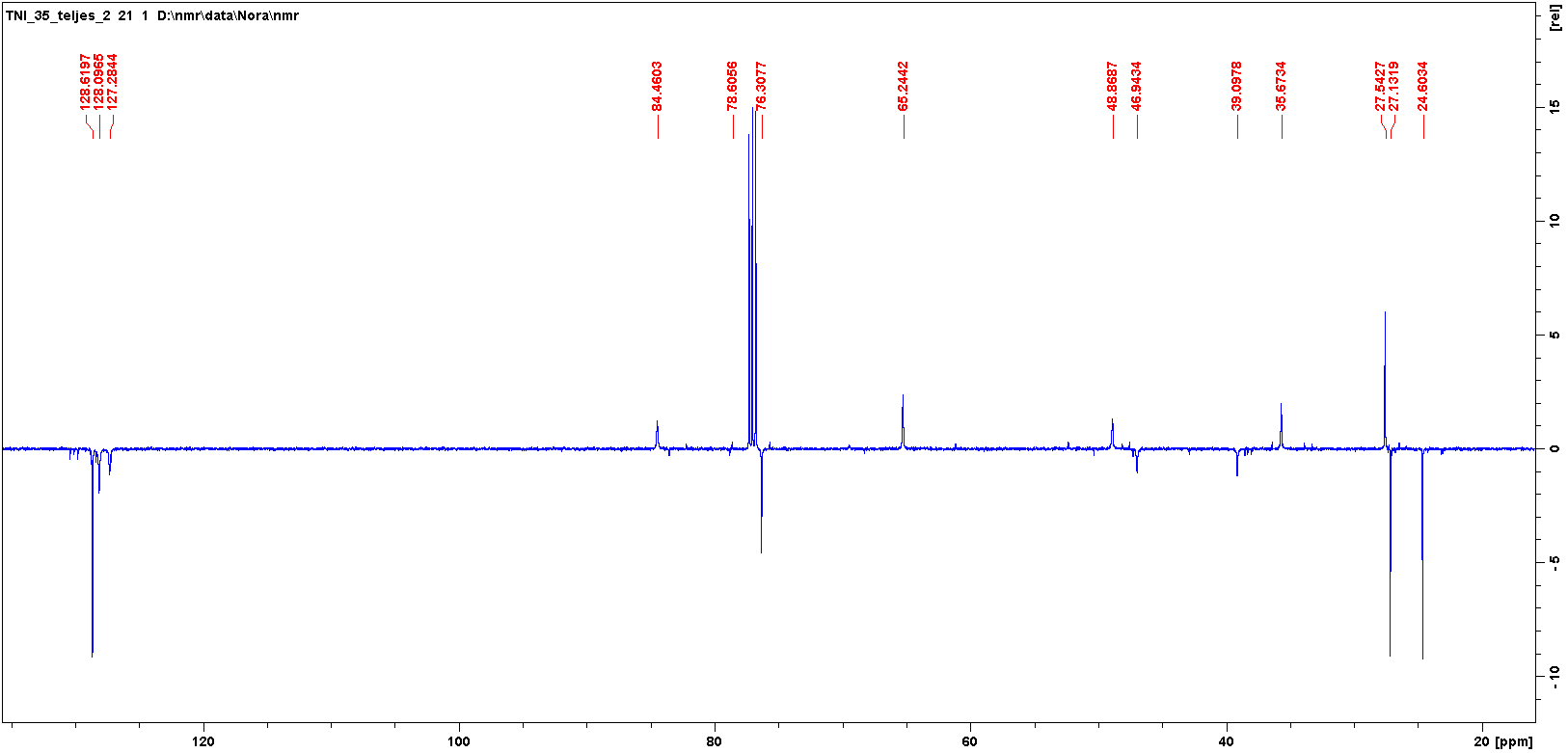


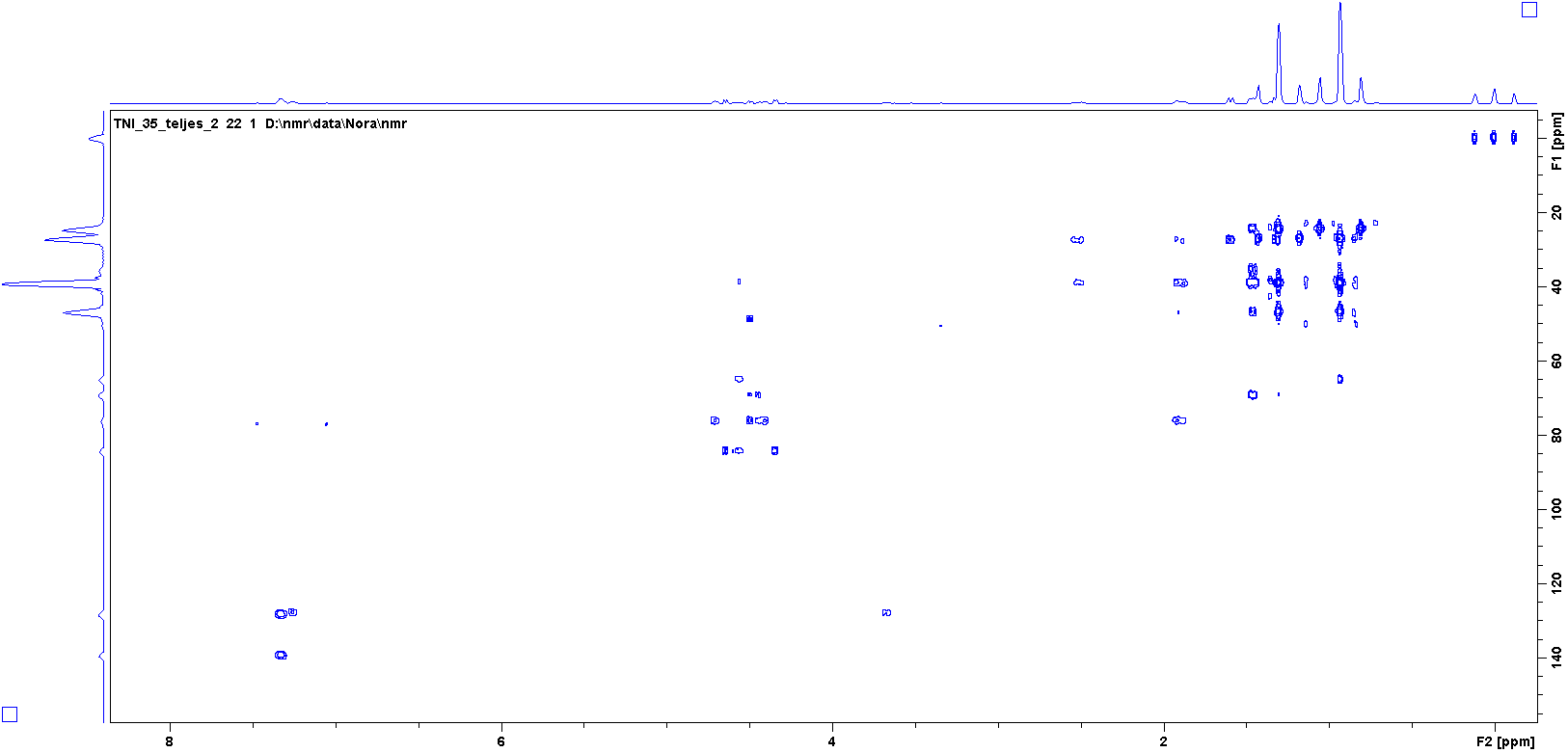




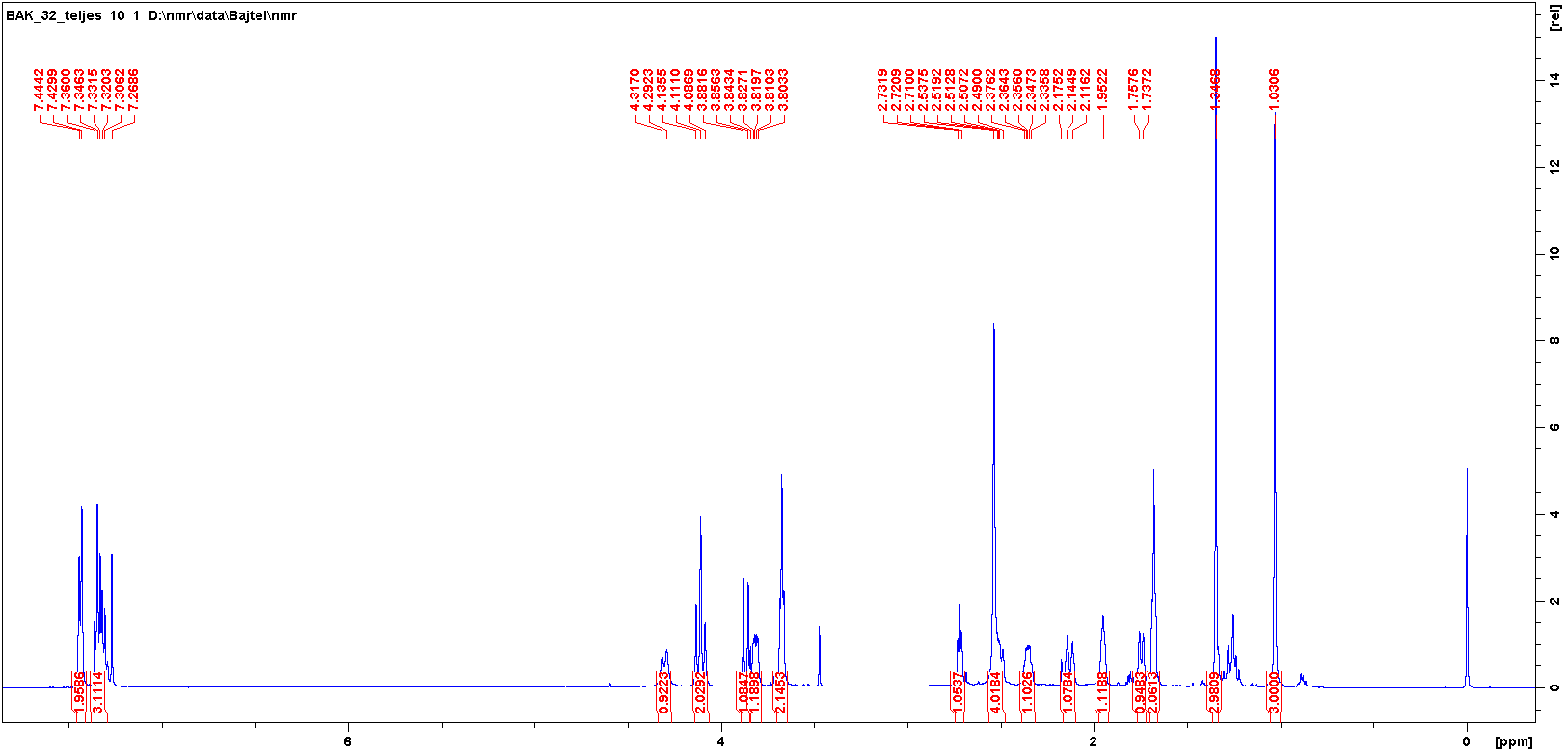
1H, 13C NMR and HMBC of **15** (CDCl3)

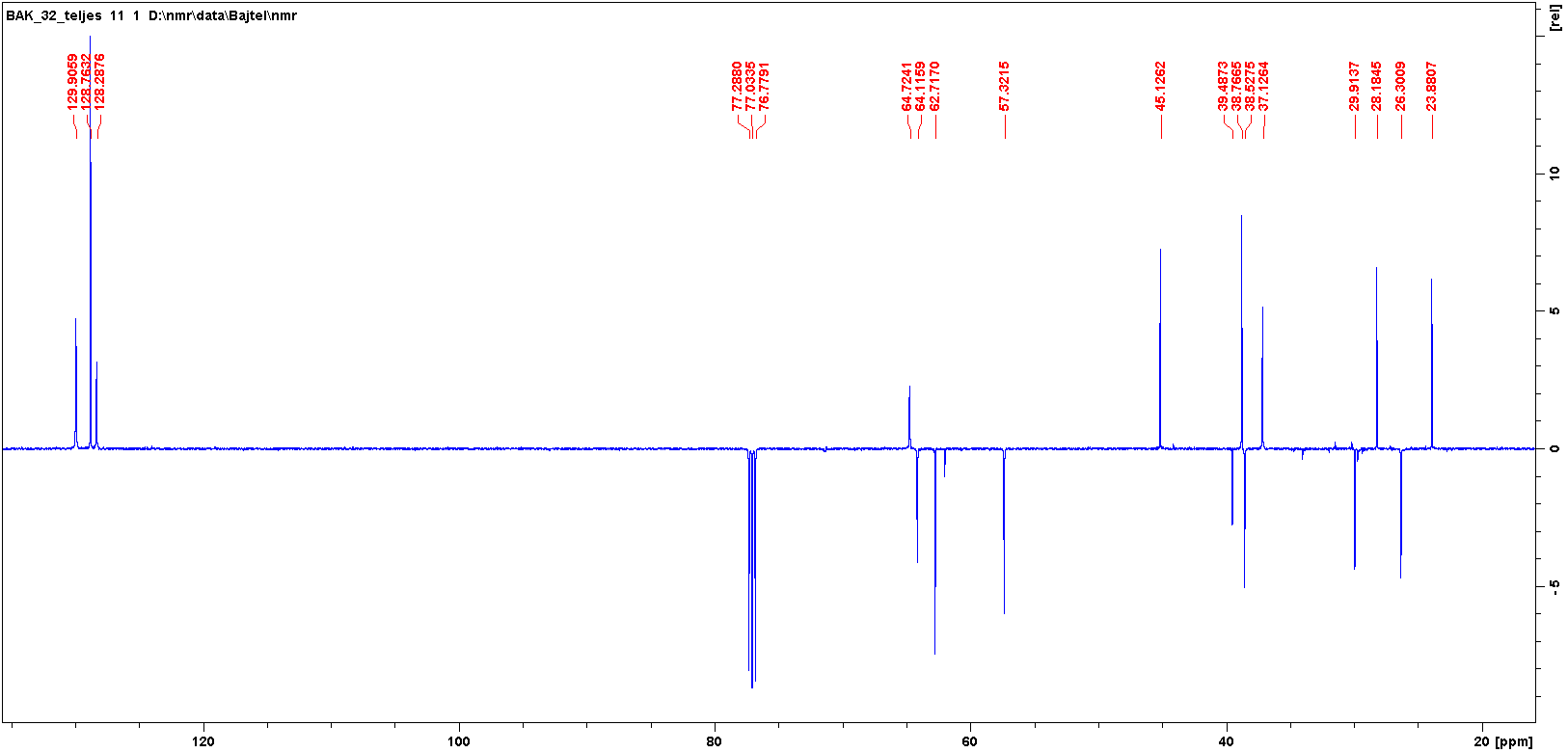


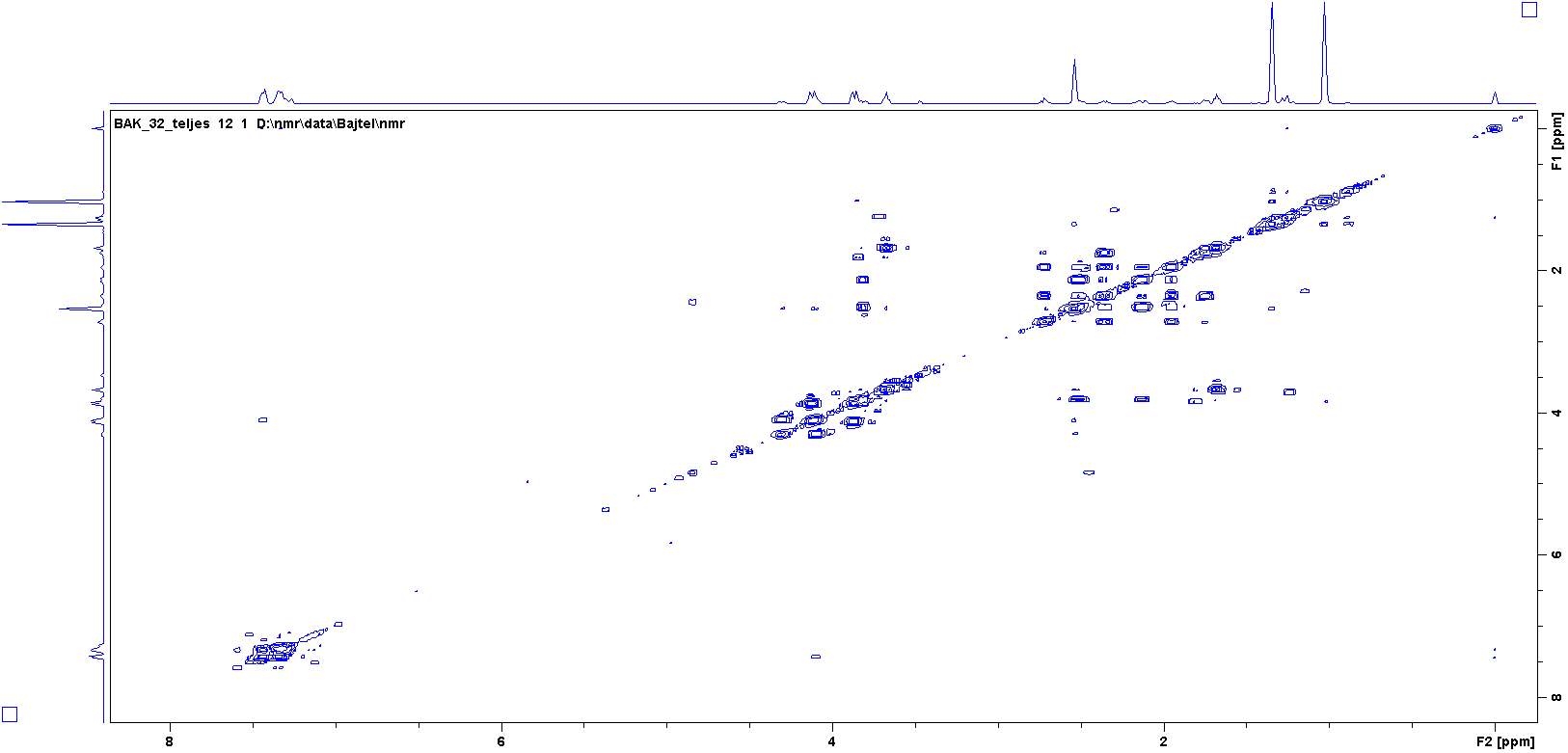


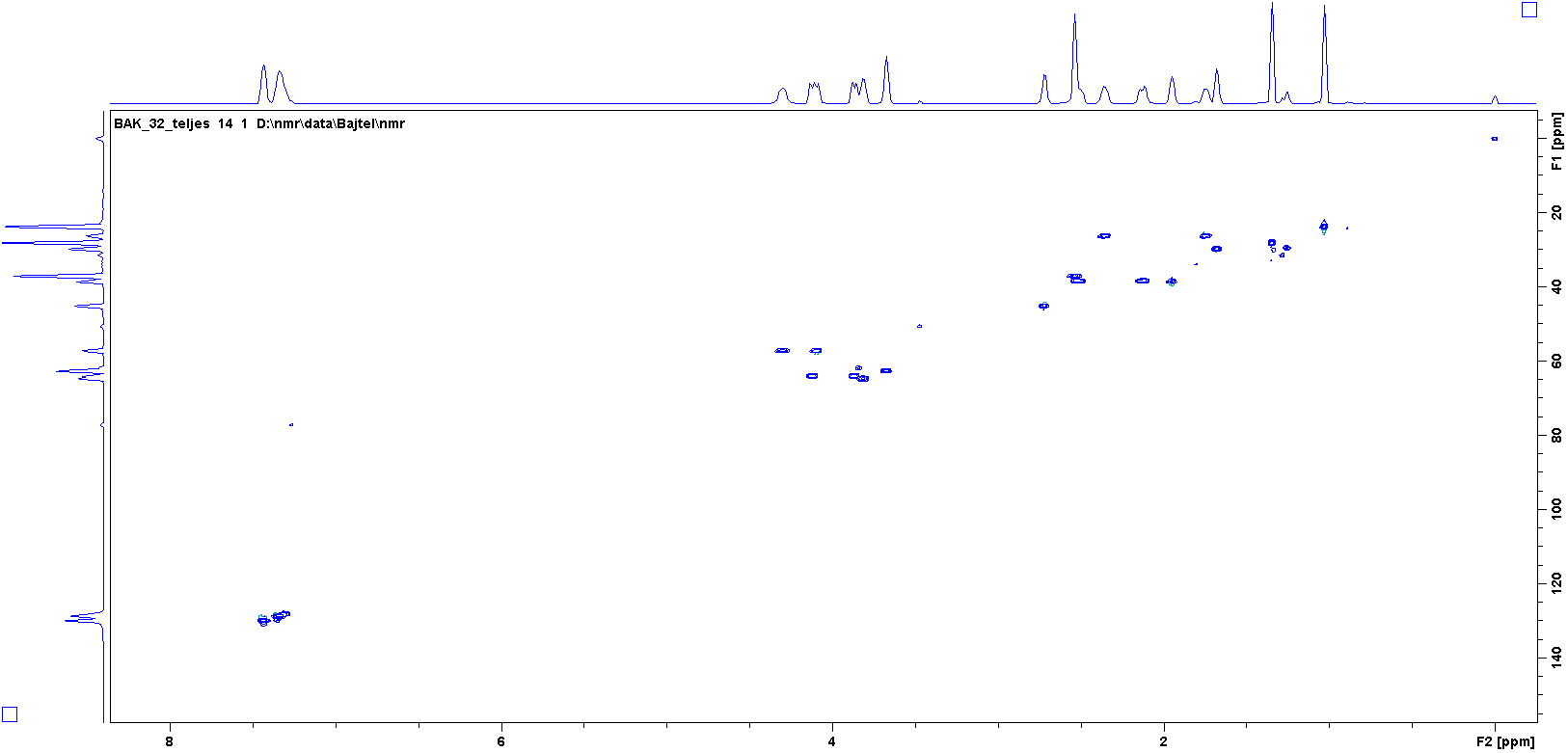


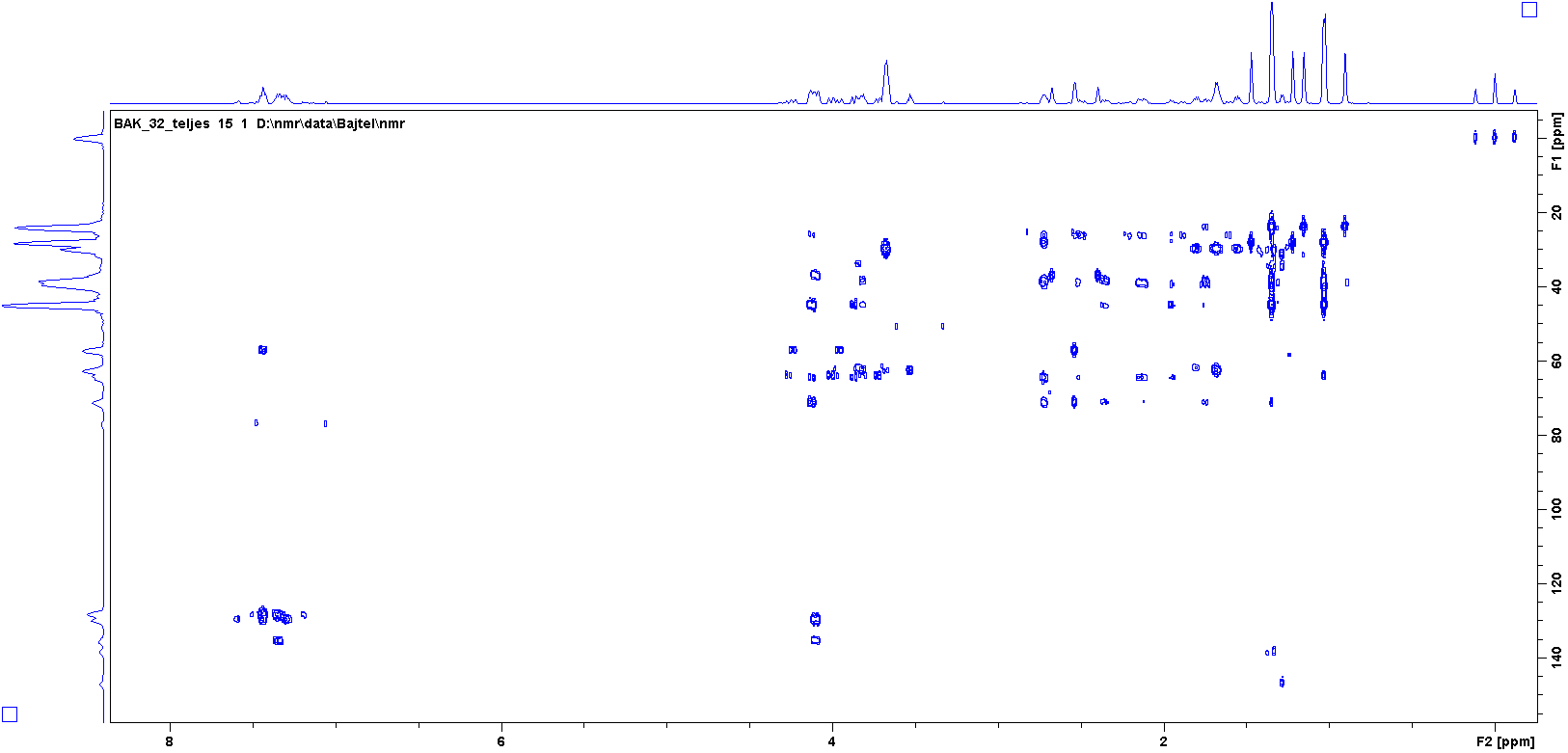
1H, 13C NMR, COSY, HSQC and HMBC of **16** (CDCl3)



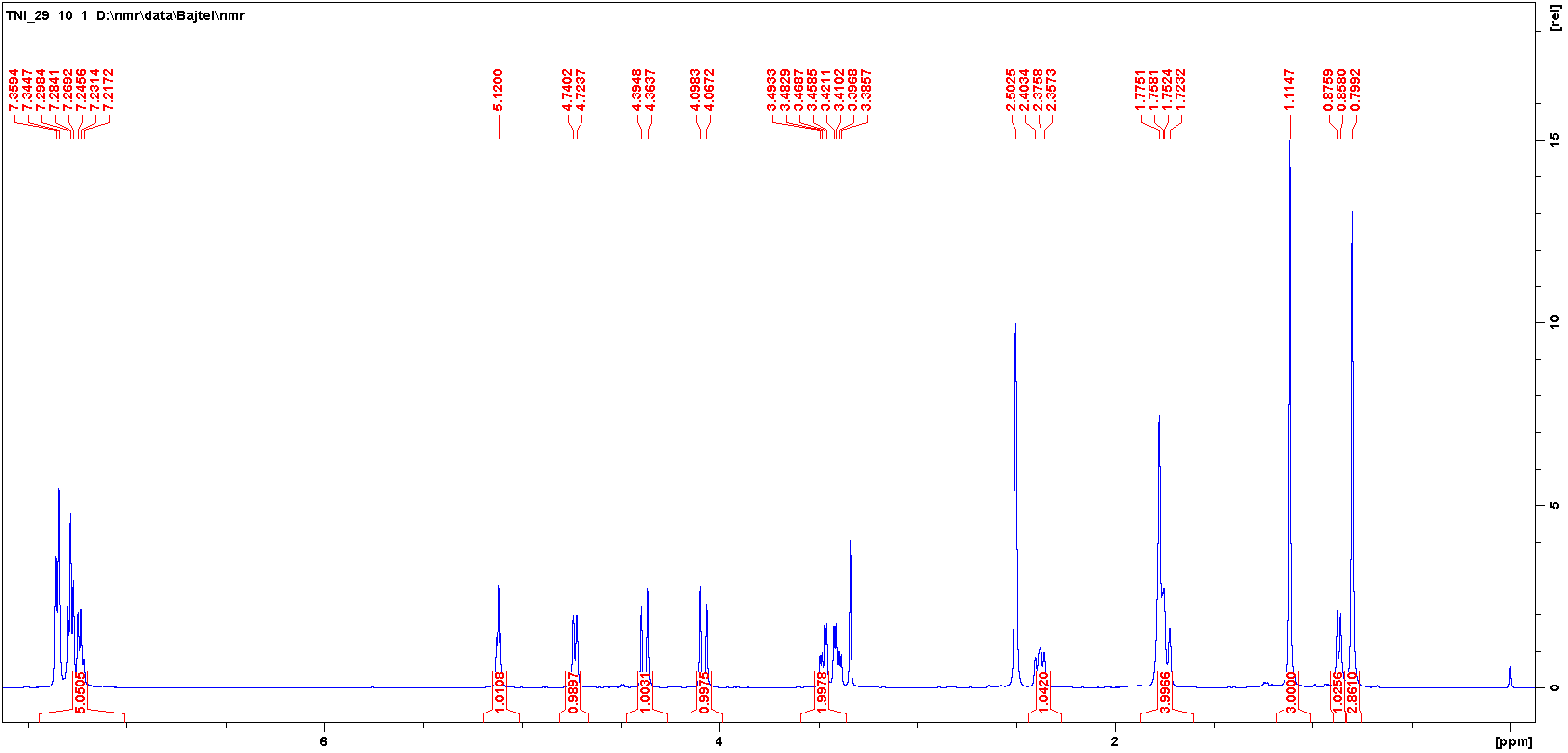


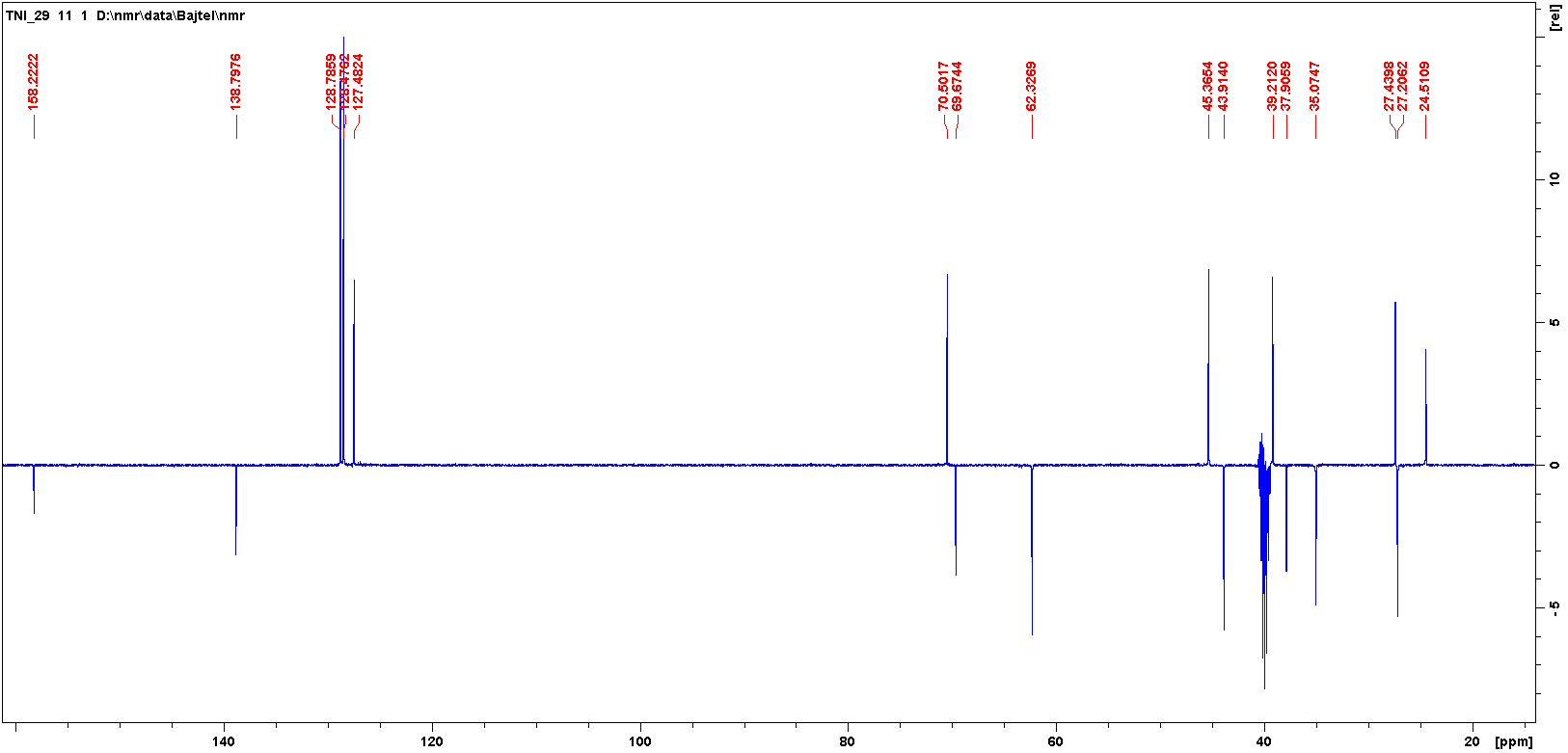


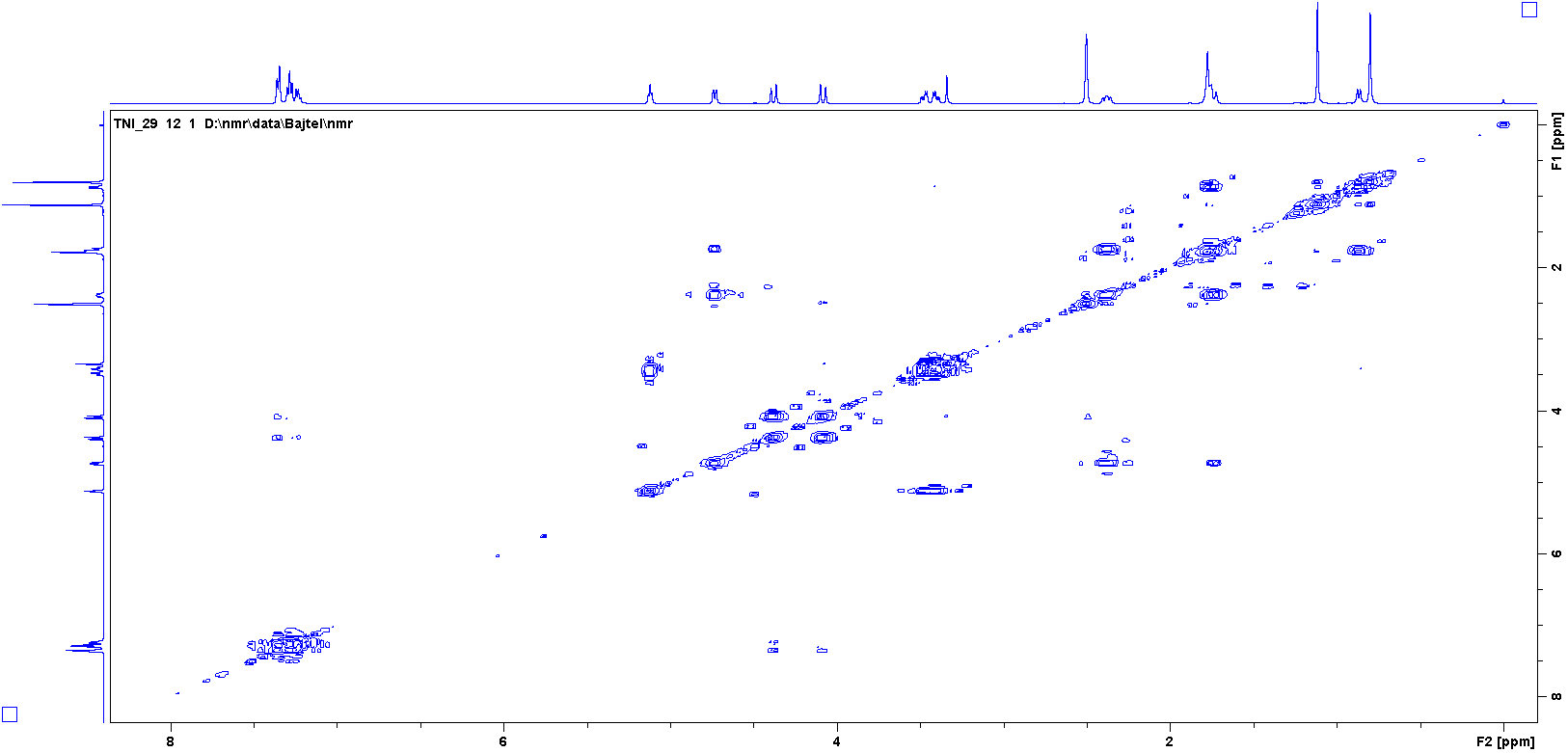


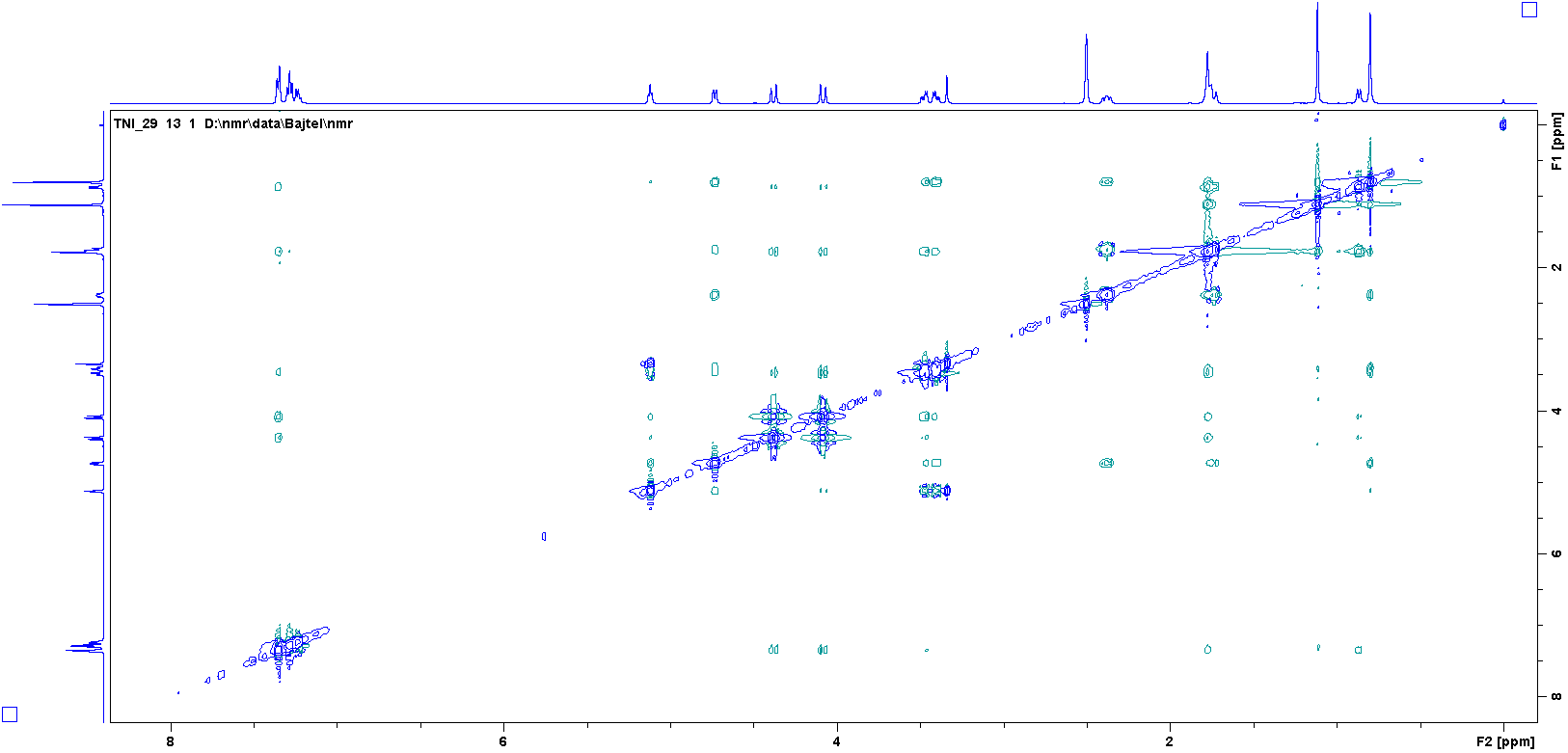


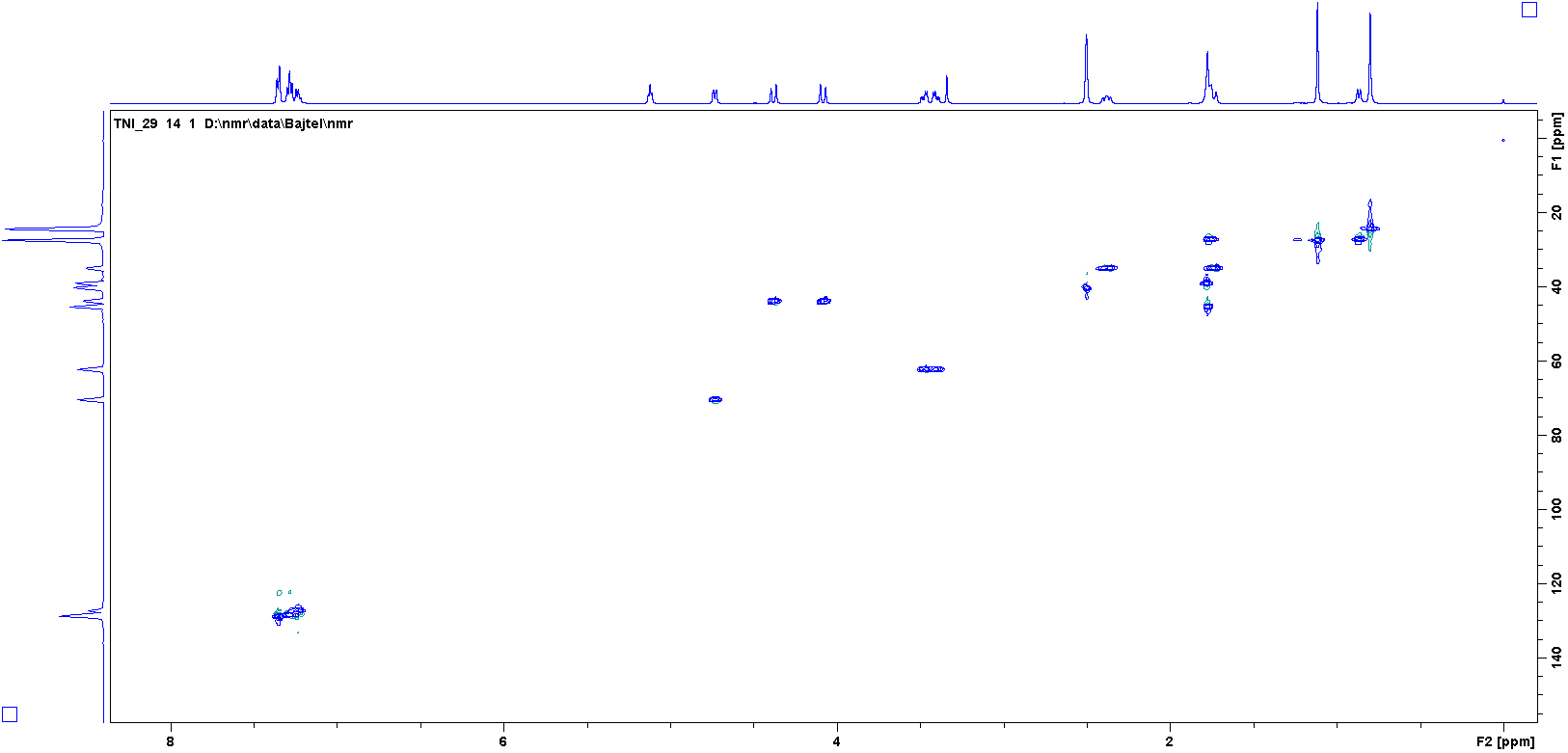
1H, 13C NMR, COSY, NOESY, HSQC and HMBC of **17** (DMSO-d6)

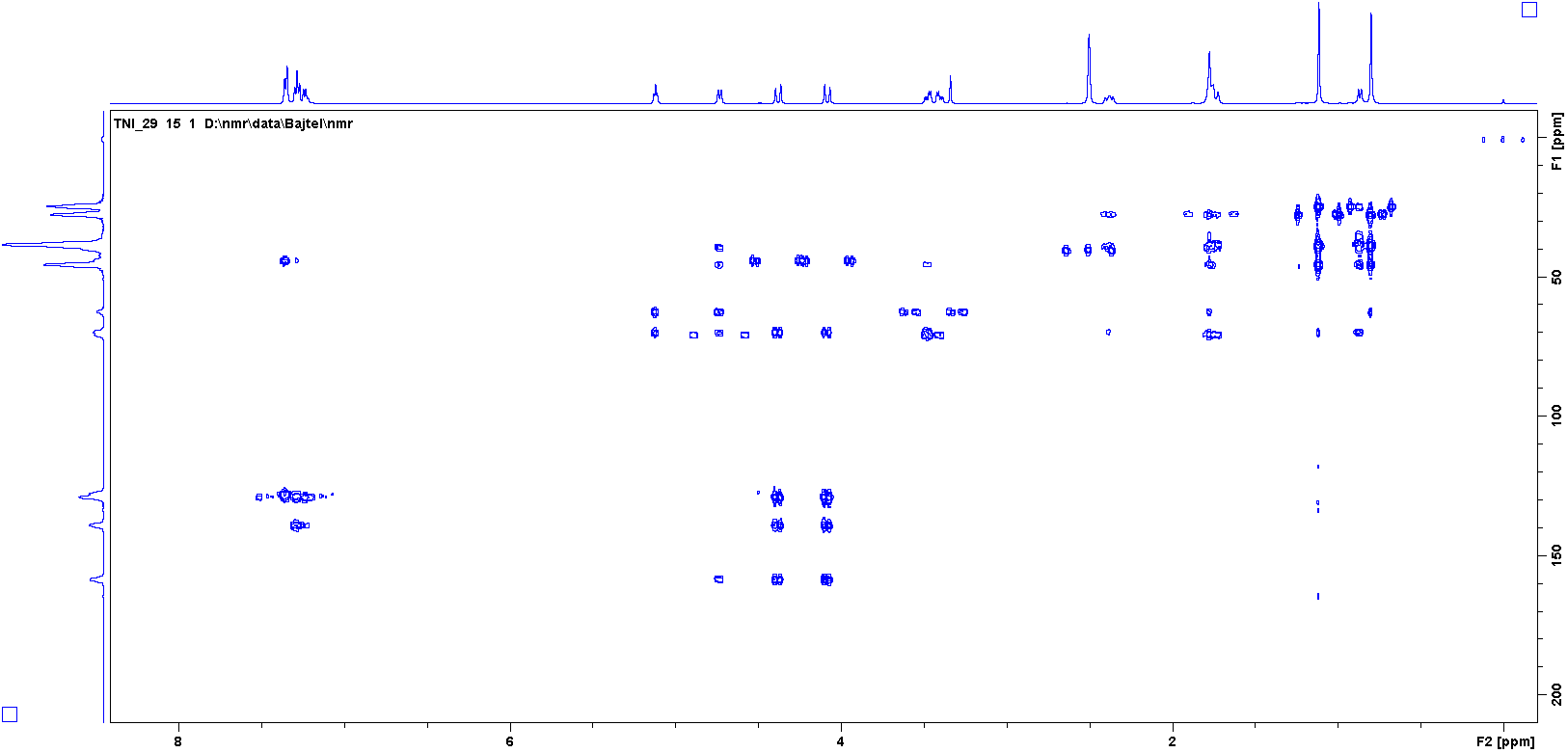




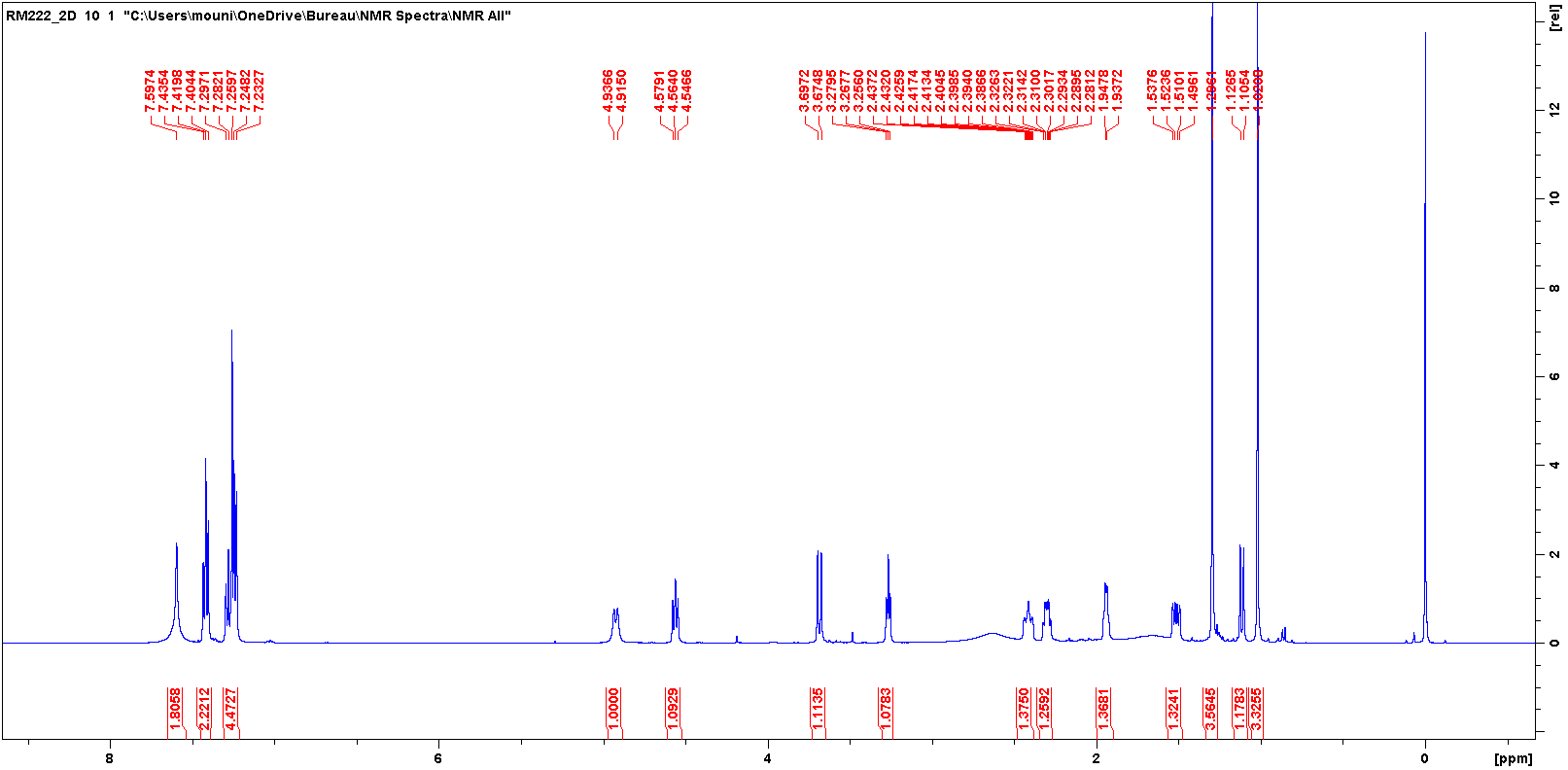


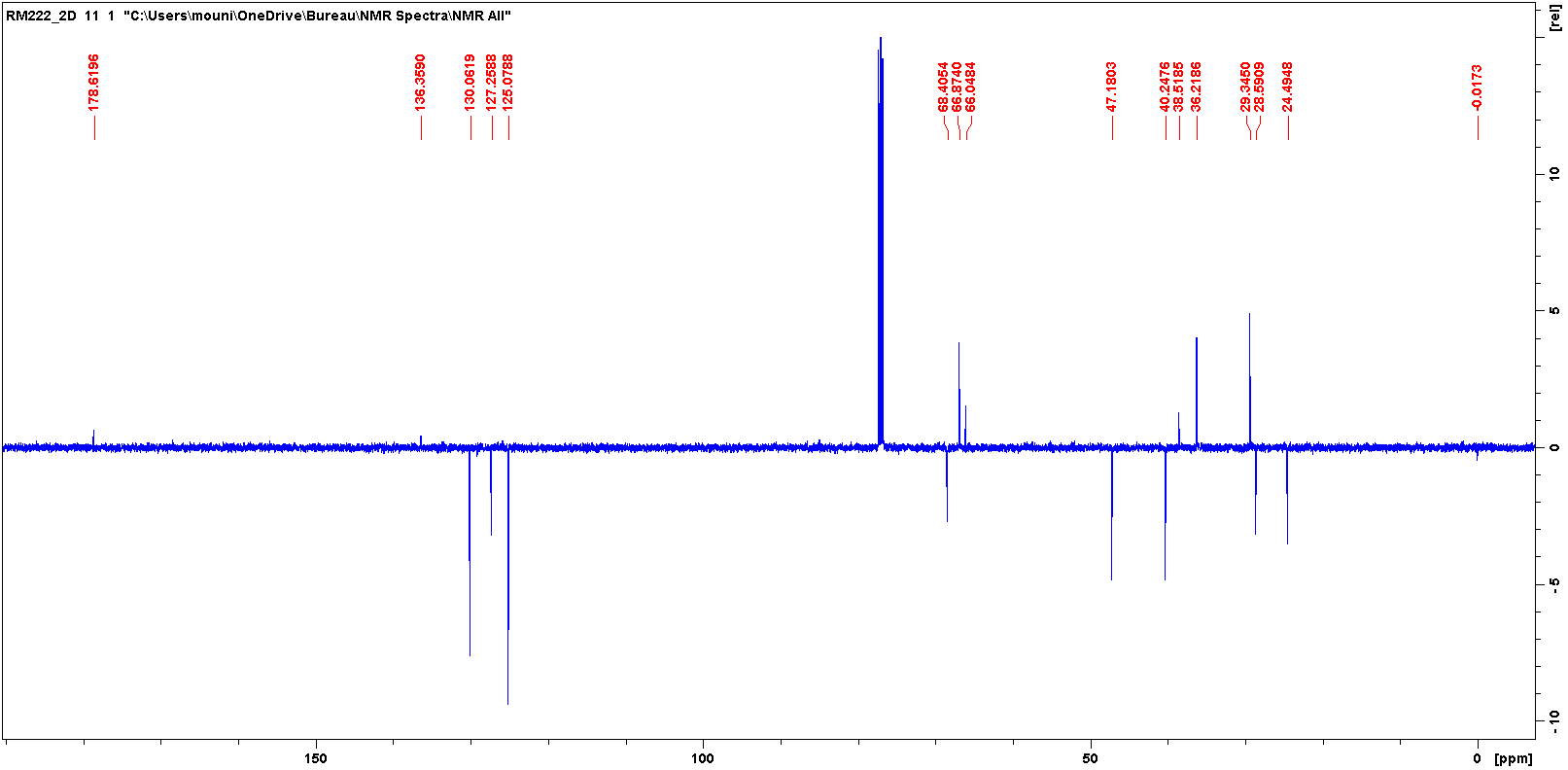


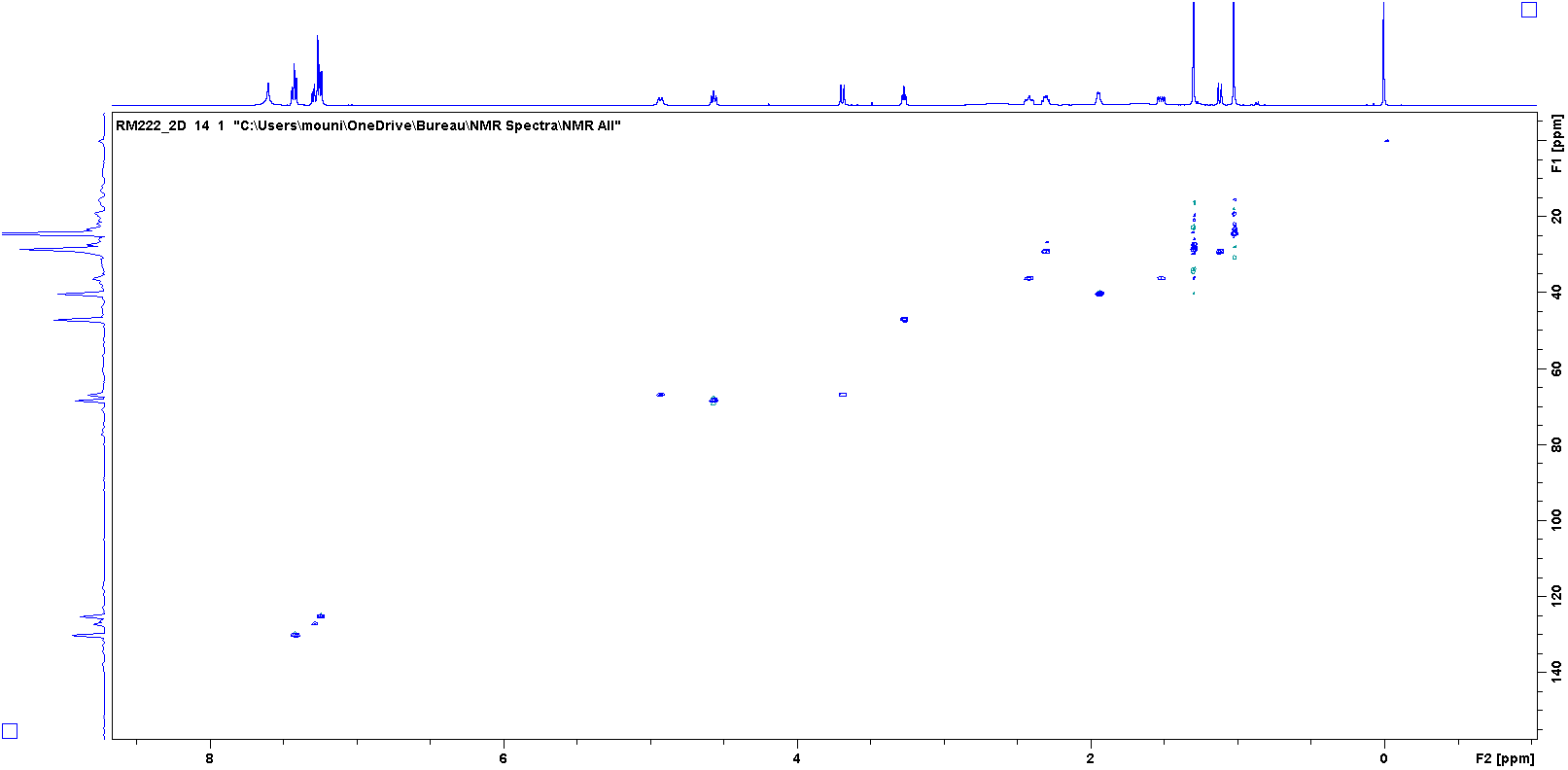


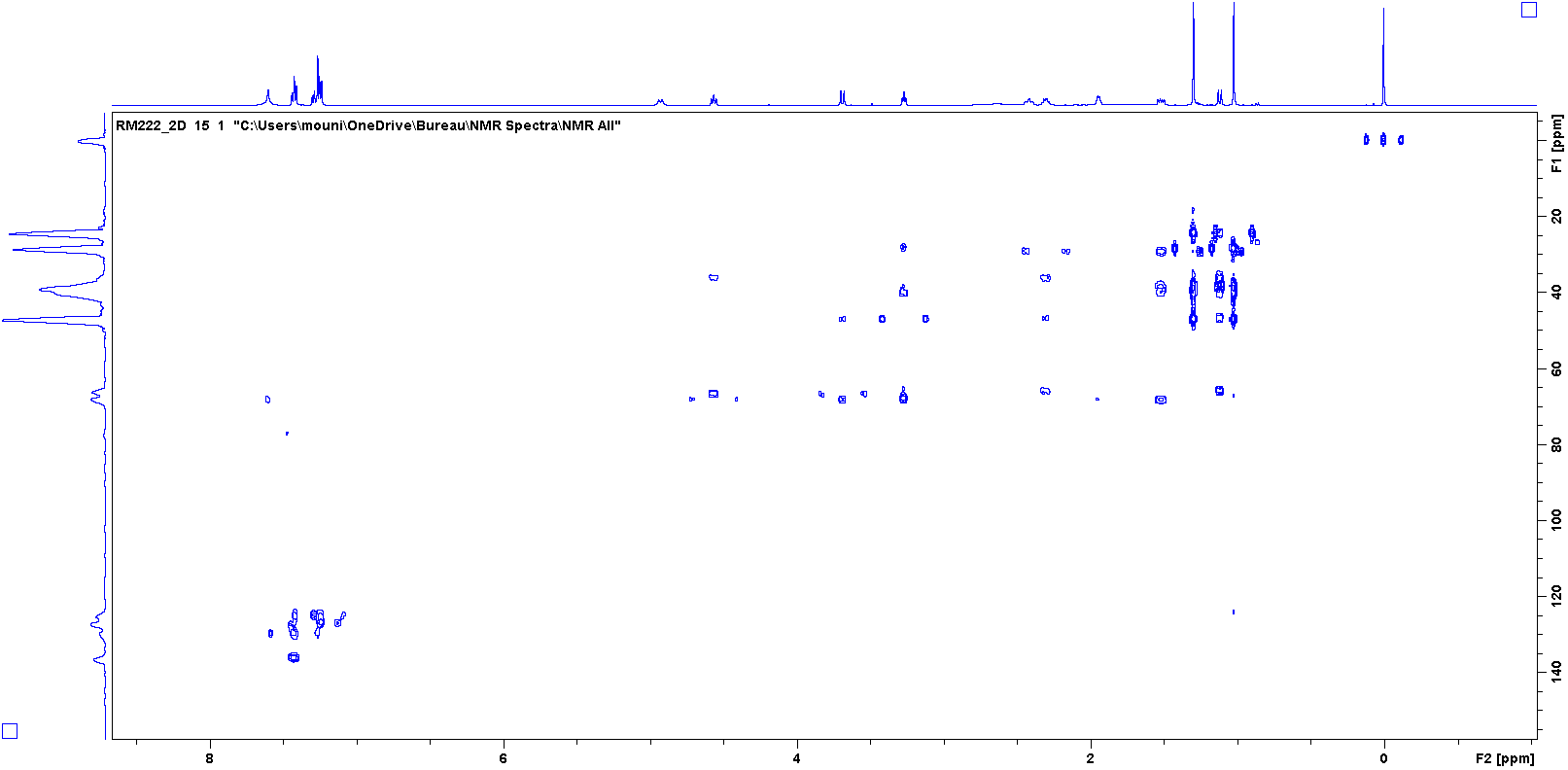


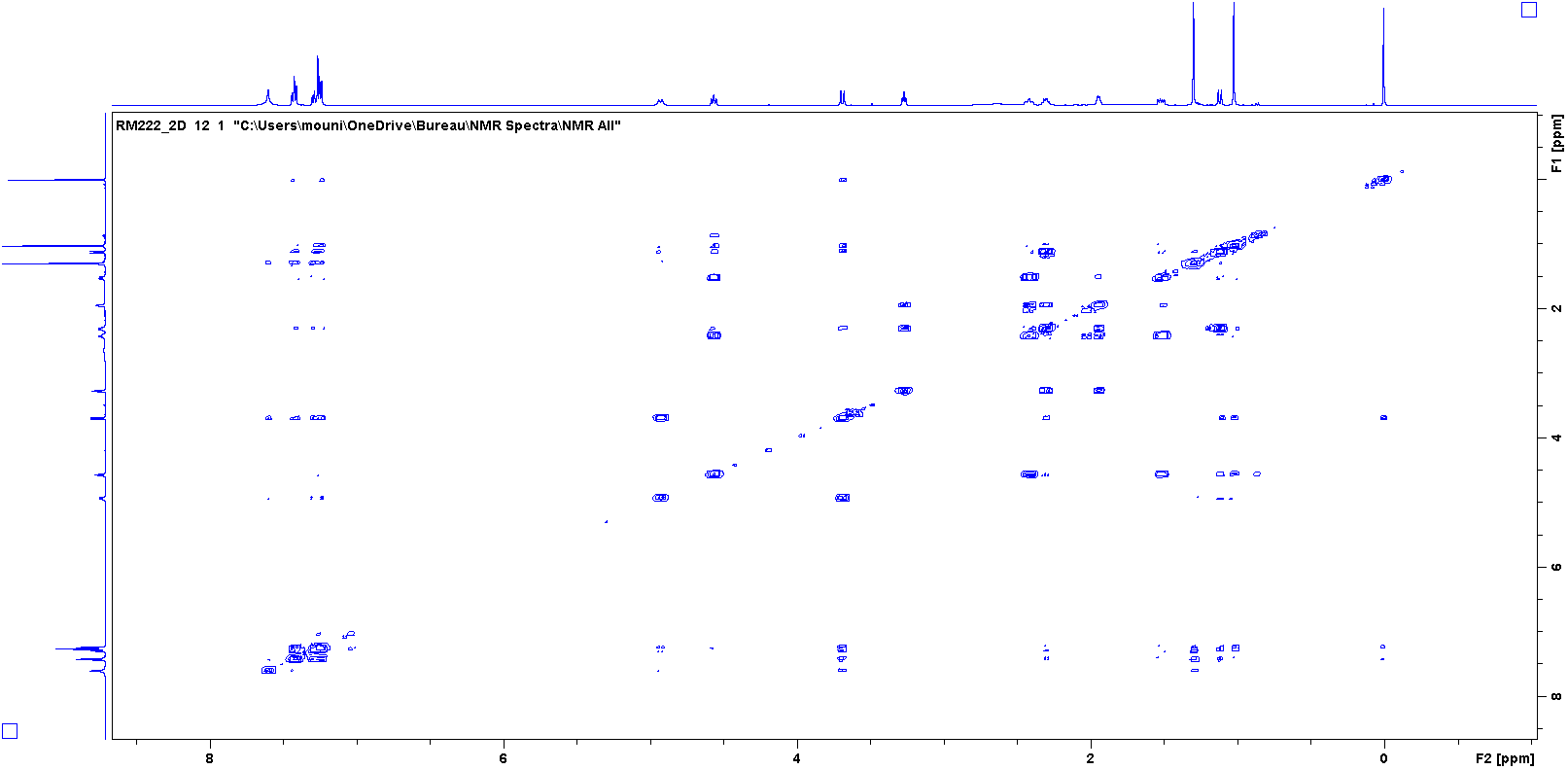
1H, 13C NMR, COSY, HSQC and HMBC of **18** (CDCl3)



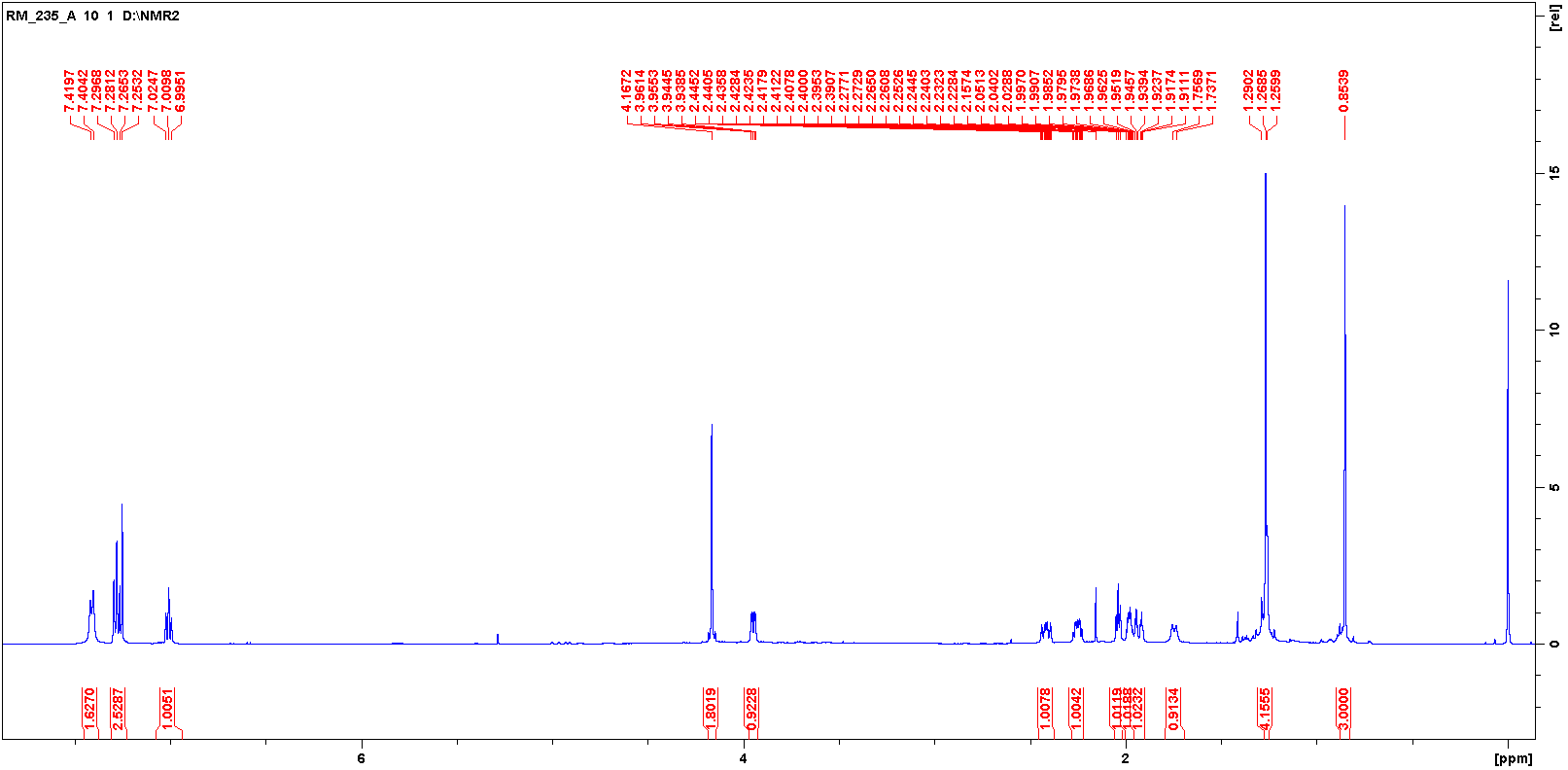


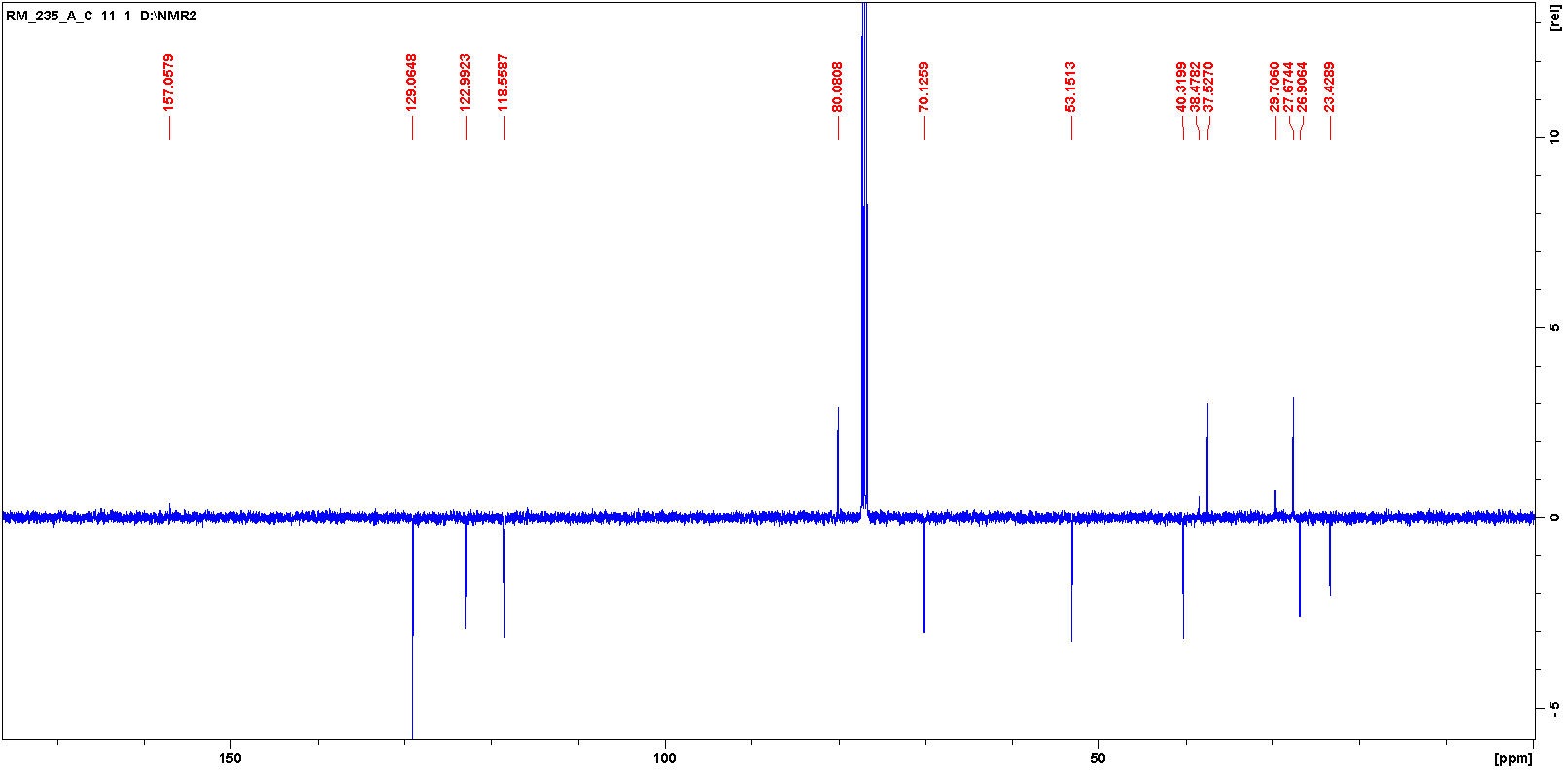


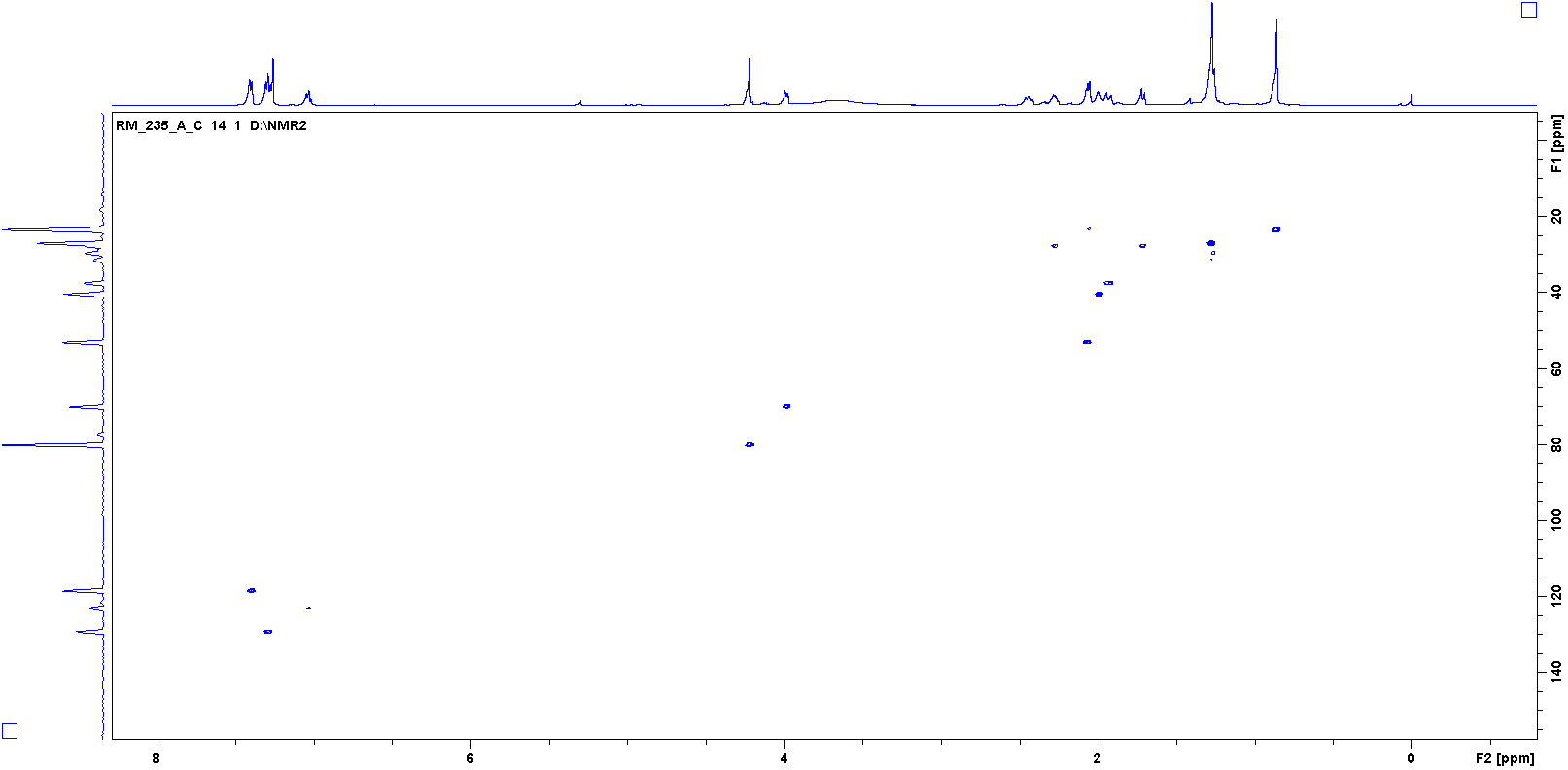


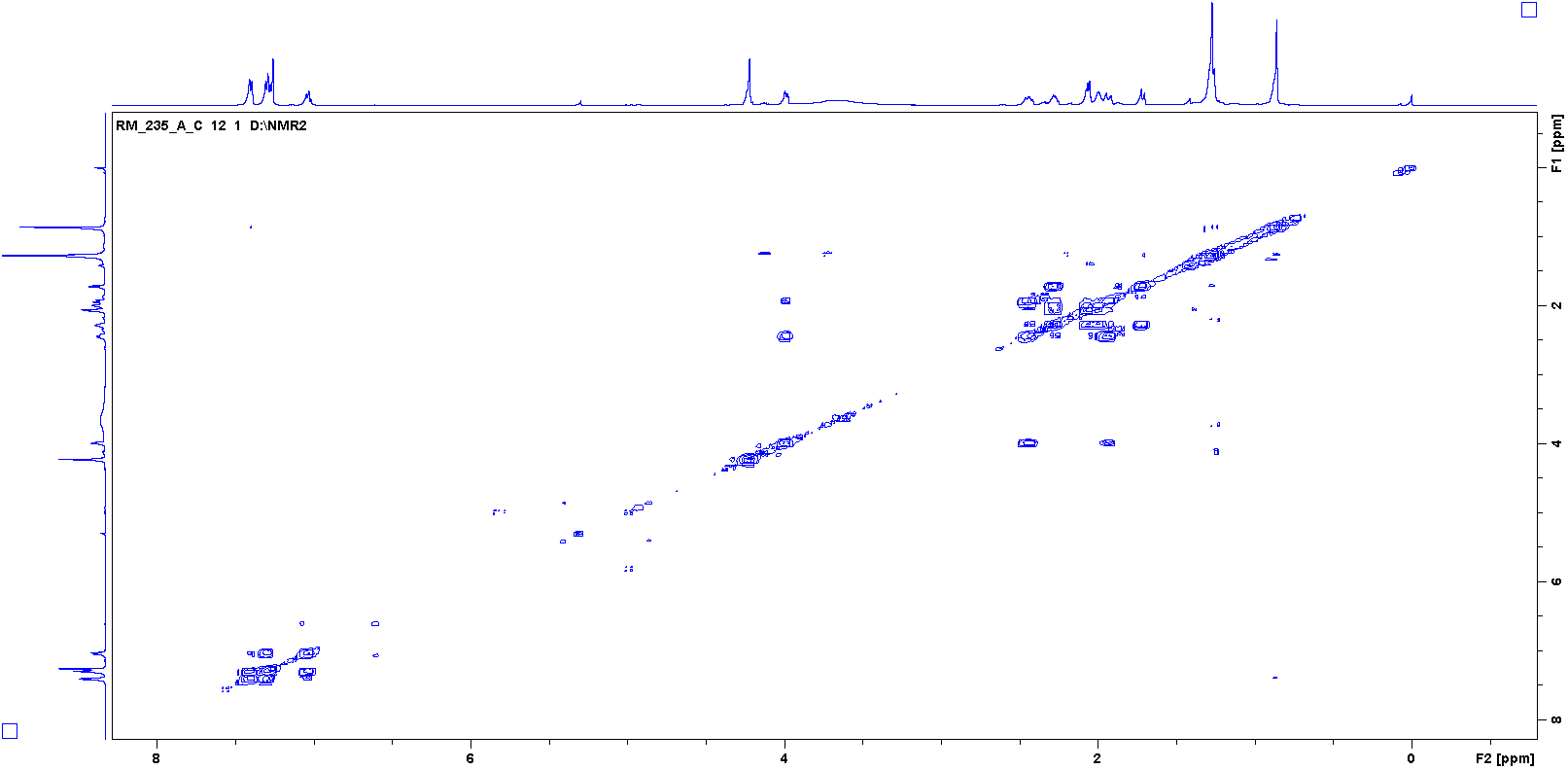


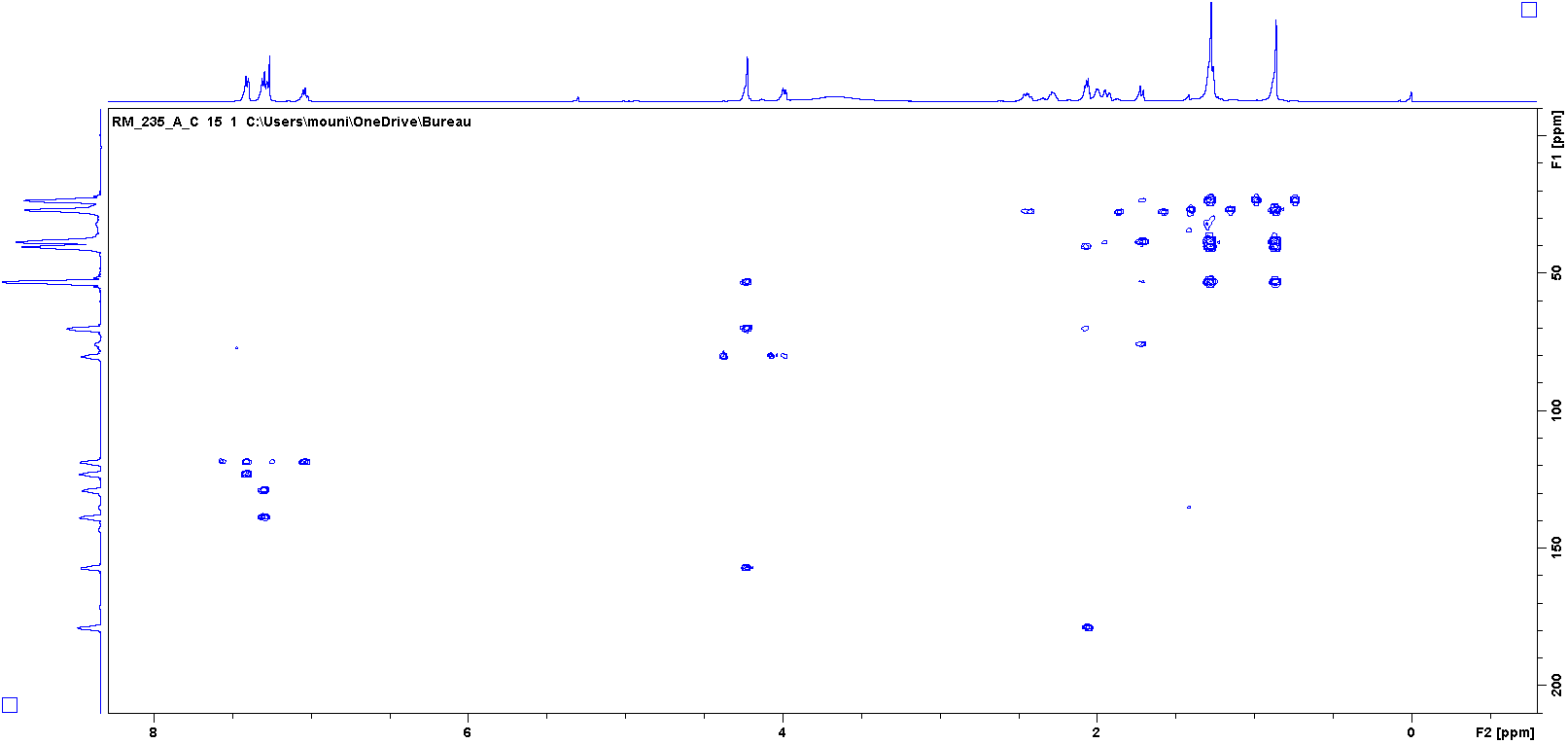
1H, 13C NMR, COSY, NOESY, HSQC and HMBC of **19A** (CDCl3)

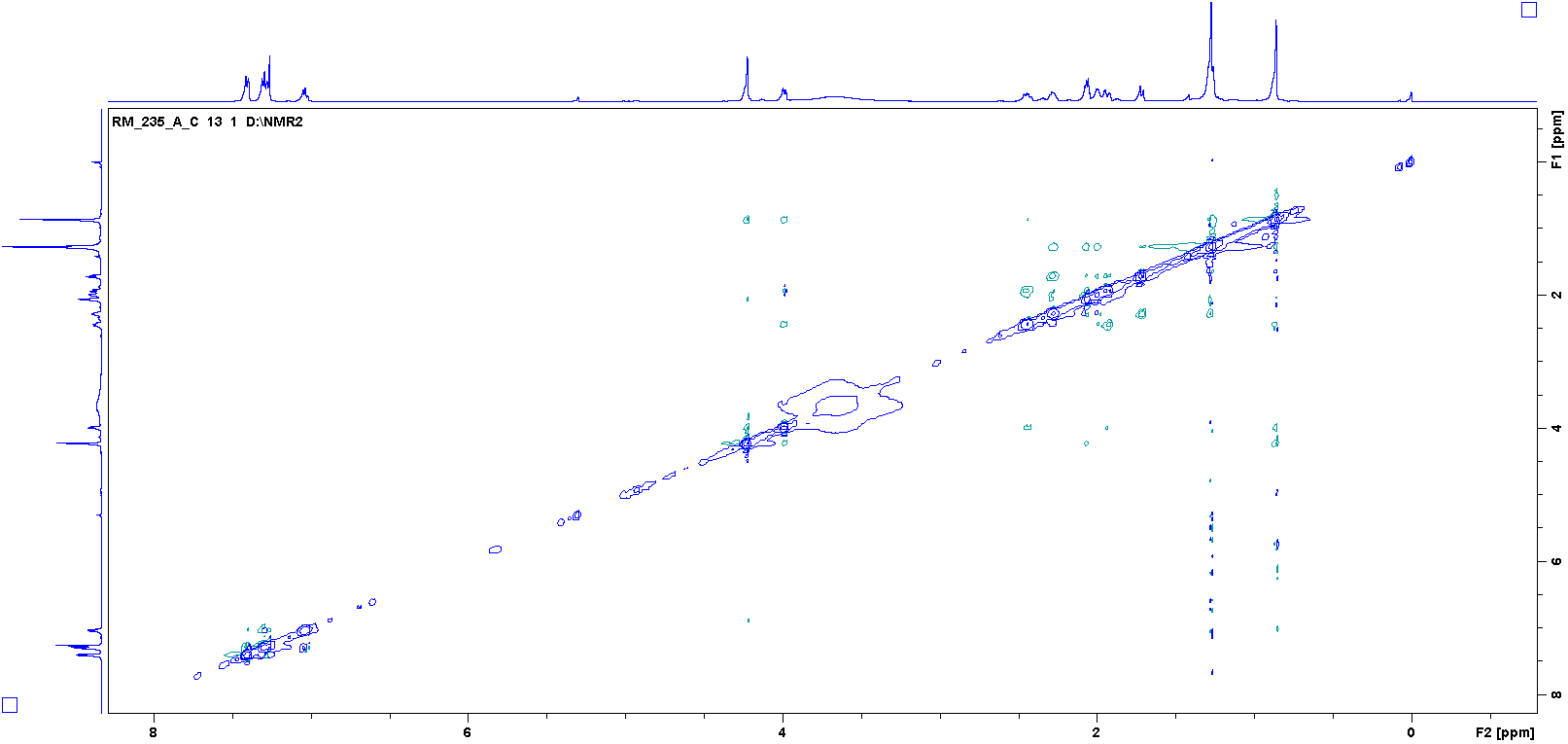






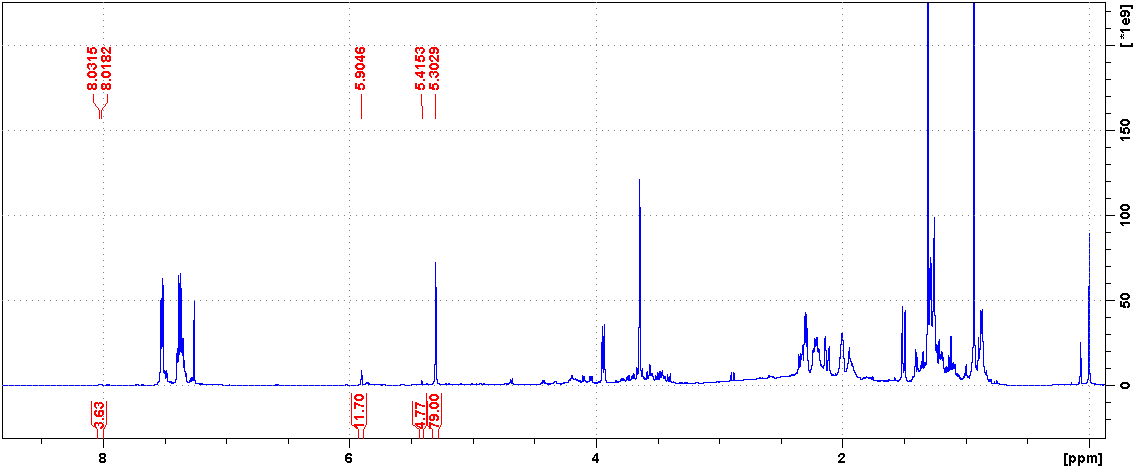


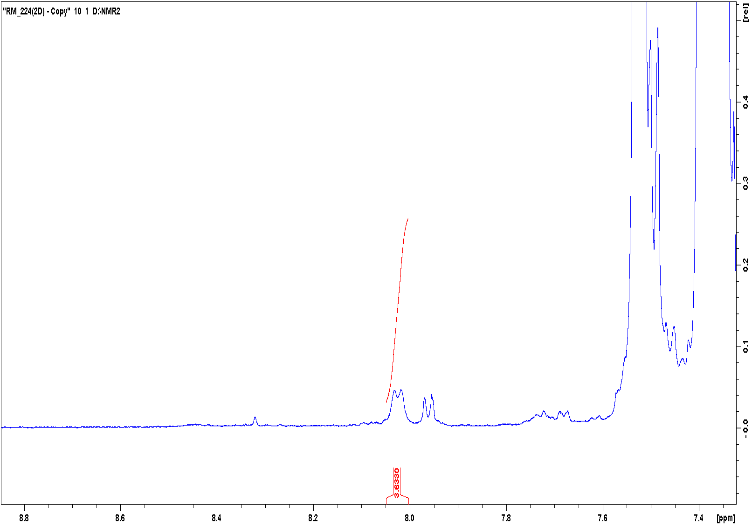


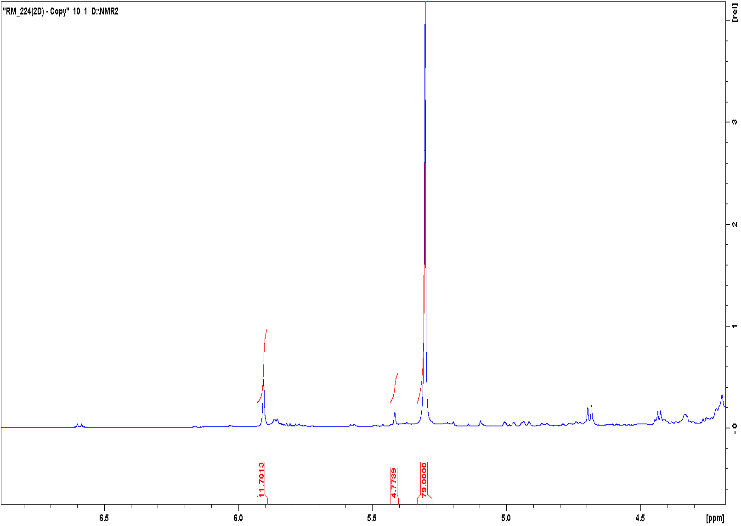


1H, 13C NMR, COSY,NOESY, HSQC and HMBC of **13A-E** (CDCl3)





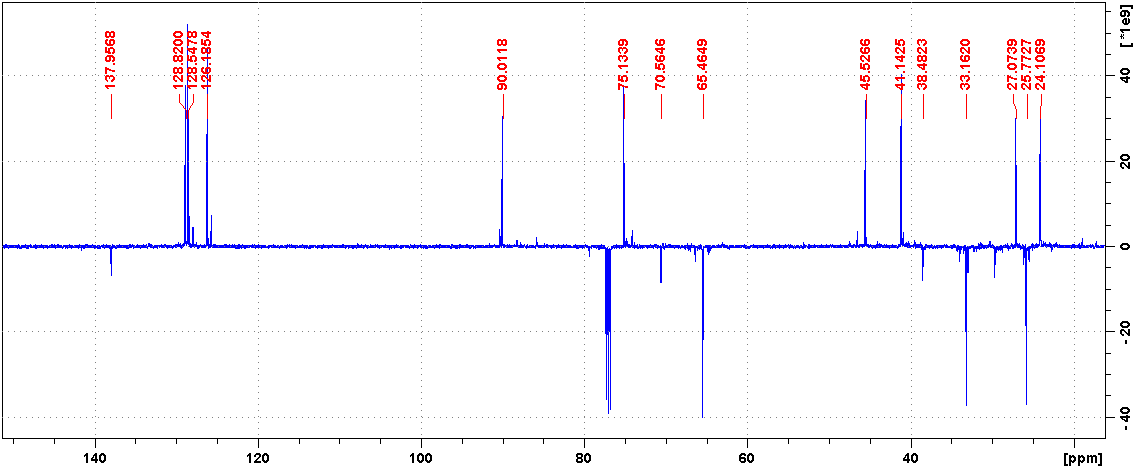




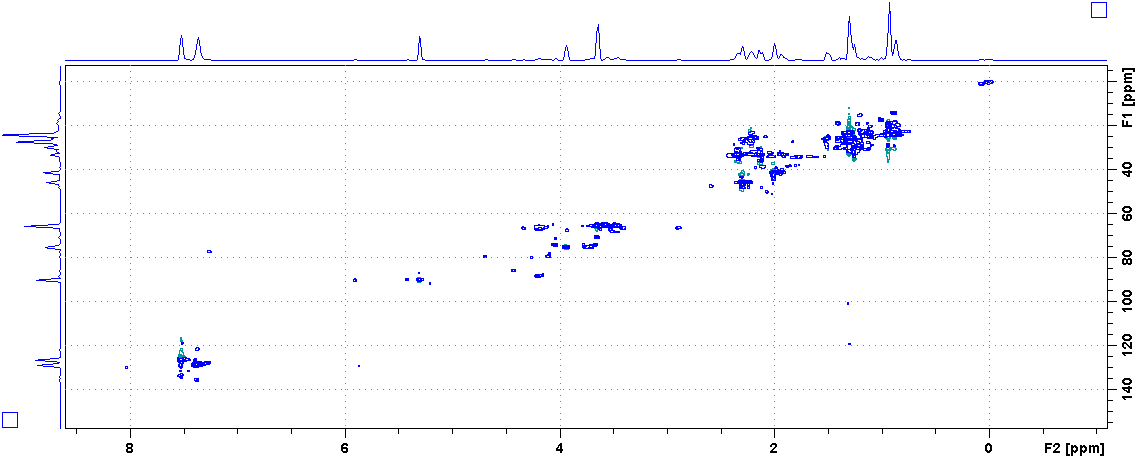




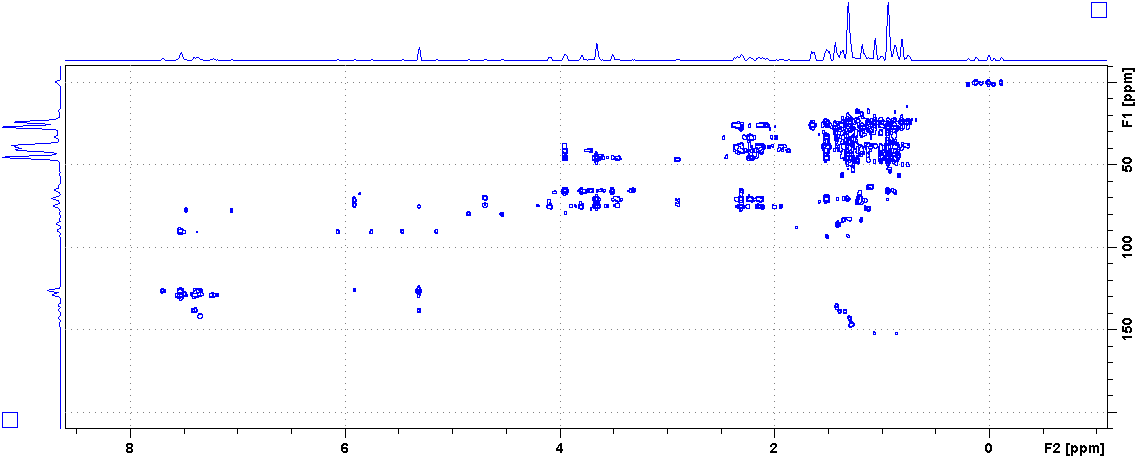




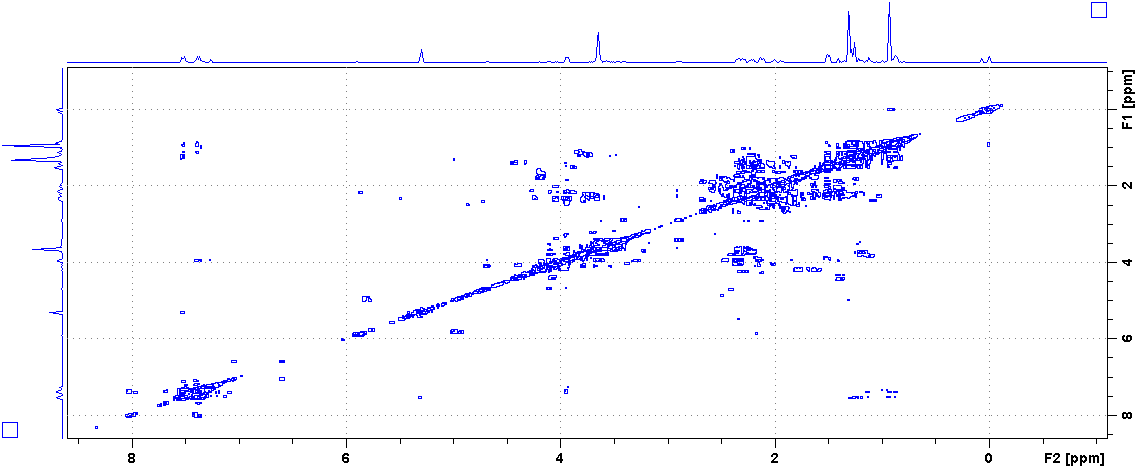
**13A-E**



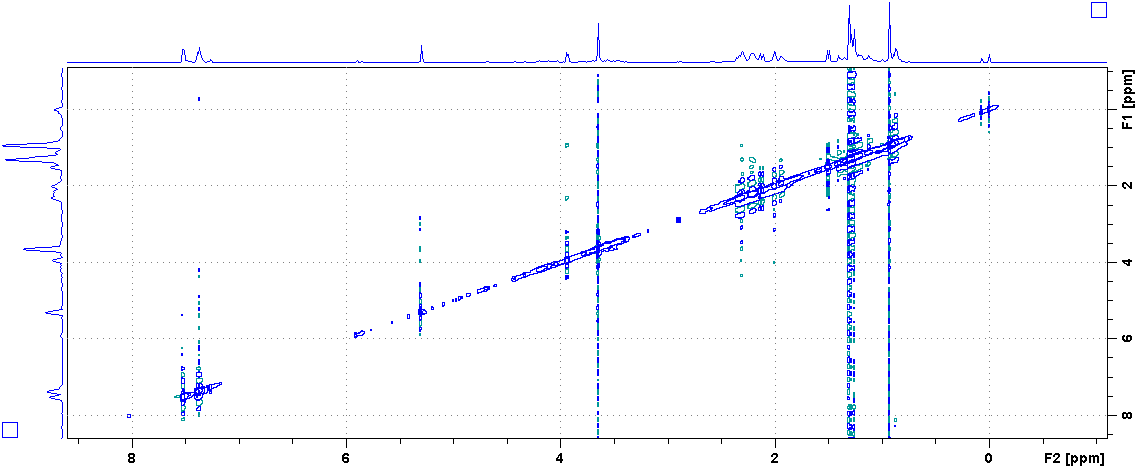
**13A-E**



**13A-E**

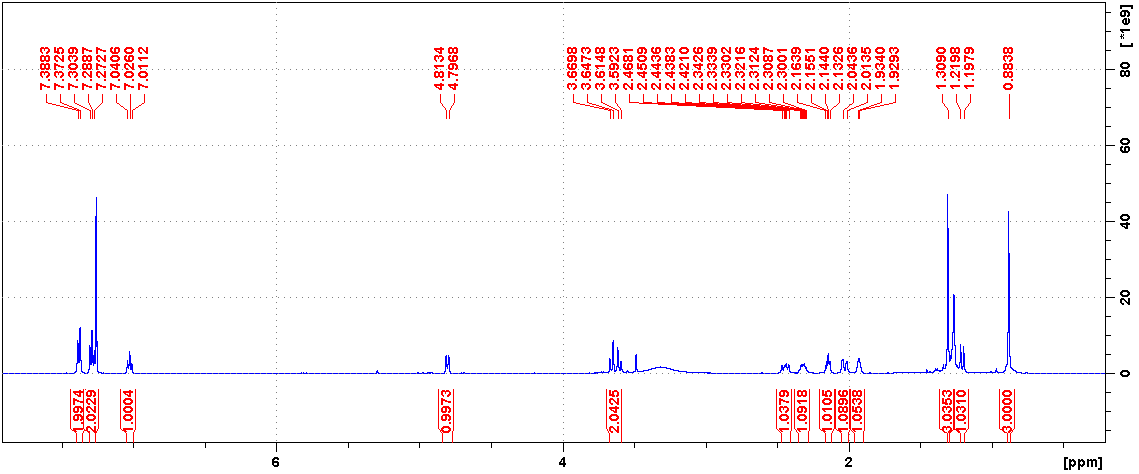


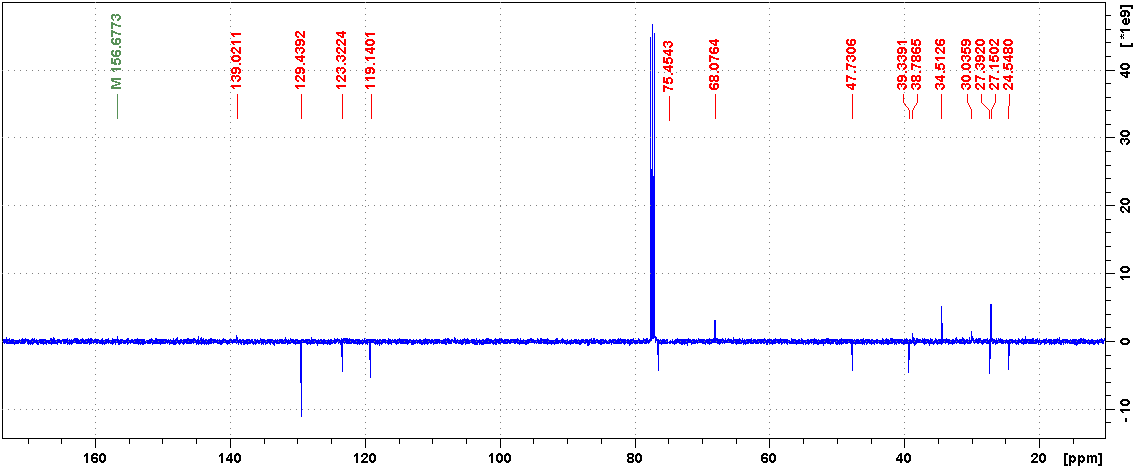
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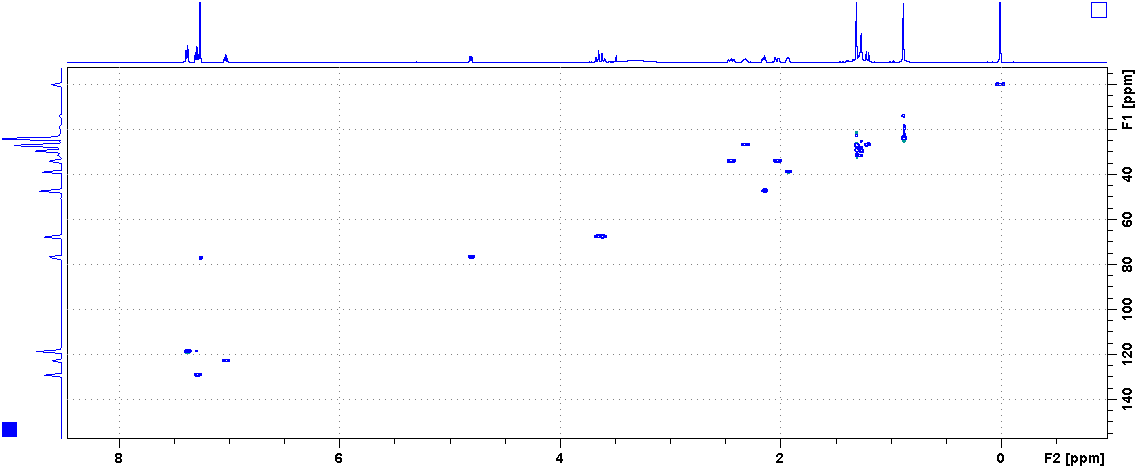


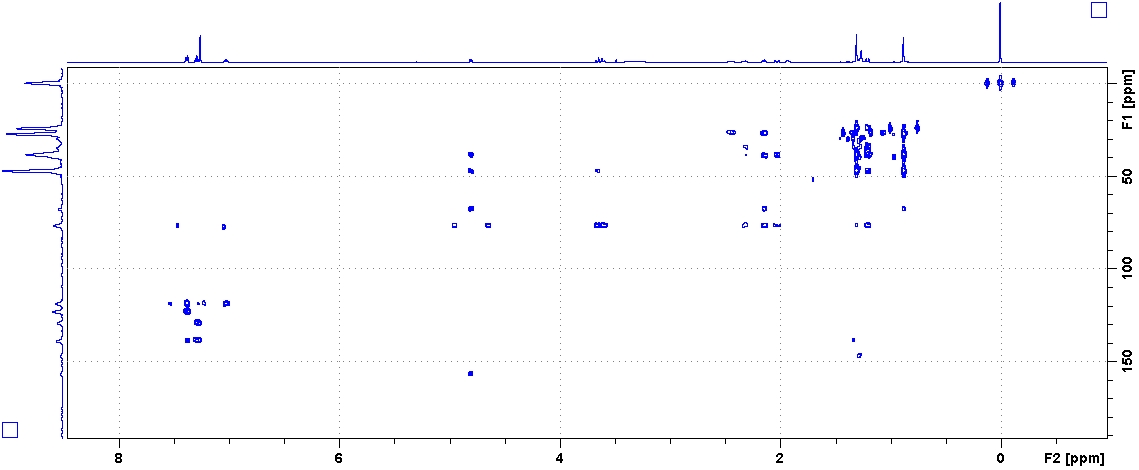
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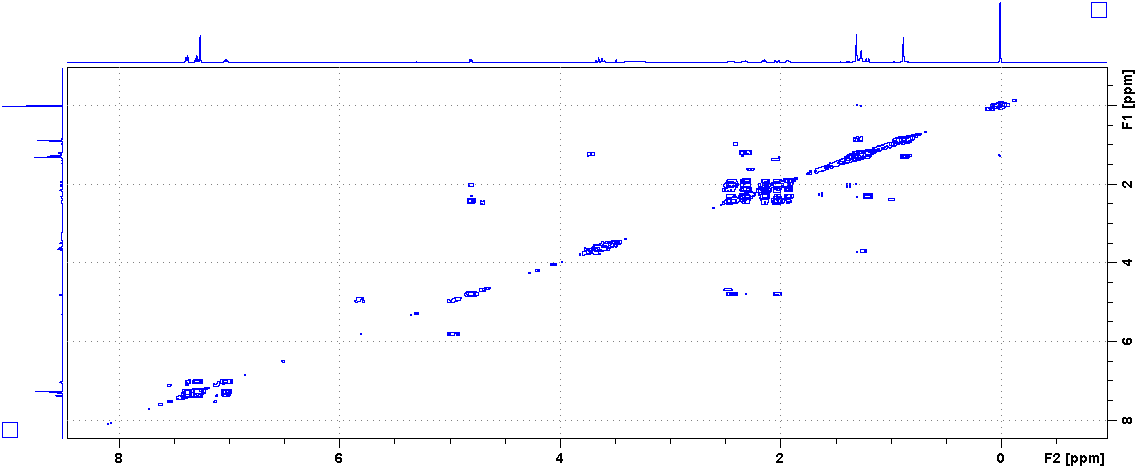
1H, 13C NMR, HSQC, HMBC, COSY and NOESY of **19B** (CDCl3)

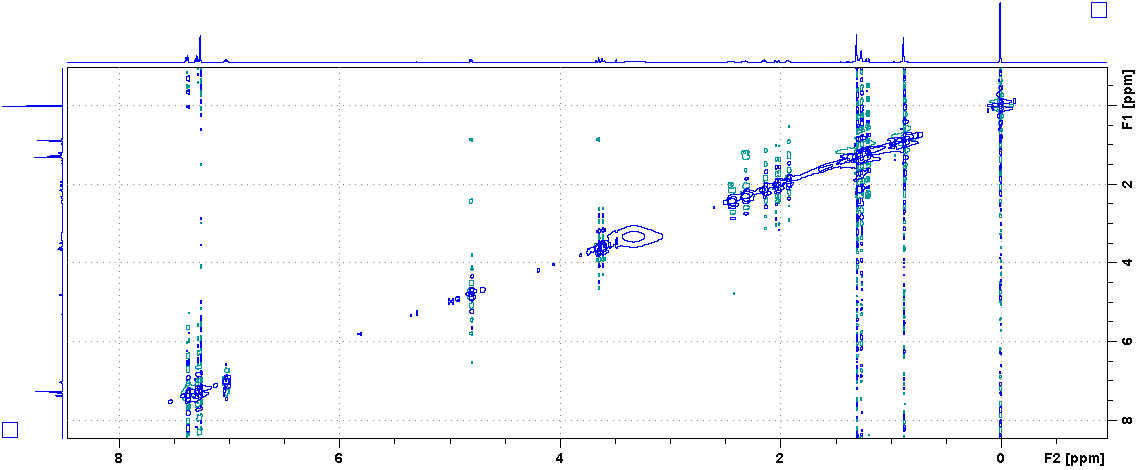




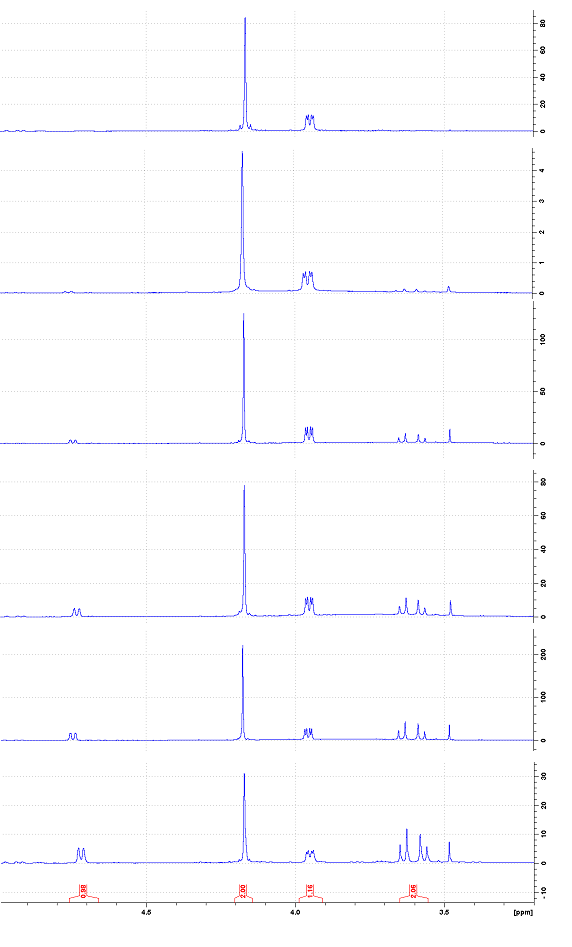








Time-dependent tautomerisation of **19A** to **19B** in CDCl3 solution



**10 days**

**5 days**

**17 days**

**24 days**

**30 days**

**X-Ray structure determinations**

The crystals of **7** and **15** were immersed in cryo-oil, mounted in a loop, and measured at a temperature of 120 K. The X-ray diffraction data were collected on a Rigaku Oxford Diffraction Supernova diffractometer using Cu Kα radiation. The *CrysAlisPro*software package was used for cell refinements and data reductions. A multi-scan (**7**) or an analytical absorption correction (**15**) was applied to the intensities before structure solutions by using *CrysAlisPro* software. The structures were solved by intrinsic phasing (*SHELXT*) method. Structural refinements were carried out using *SHELXL* software with *SHELXLE* graphical user interface. The NH and OH hydrogen atoms were located from the difference Fourier map and refined isotropically. All other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.95-1.00 Å and Uiso = 1.2-1.5 Ueq(parent atom). The crystallographic details are summarized in Table **S1**. The deposition number CCDC 2063842 (**7**) and CCDC 2063843 (**15**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://[www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk))

**Table S1.** Crystal Data.

|  |  |  |
| --- | --- | --- |
|  | **7** | **15** |
| empirical formula | C11H17NO3 | C18H25NO2 |
| fw | 211.25 | 287.39 |
| temp (K) | 120(2) | 120(2) |
| *λ*(Å) | 1.54184 | 1.54184 Å |
| cryst syst | Monoclinic | Monoclinic |
| space group | P2**1** | P2**1** |
| *a* (Å) | 7.93530(6) | a = 8.41050(10) |
| *b* (Å) | 10.89885(6) | b = 7.23460(10) |
| *c* (Å) | 12.63719(8) | c = 13.4036(2) |
| β (deg) |  |  |
| *V* (Å3) | 1082.498(12) | 794.79(2) |
| Z | 4 | 2 |
| *ρ*calc (Mg/m3) | 1.296 | 1.201 |
| *μ*(Mo K*α*) (mm-1) | 0.770 | 0.608 |
| No. reflns. | 24009 | 16590 |
| Unique reflns. | 4528 | 3329 |
| GOOF (F2) | 1.042 | 1.038 |
| Rint | 0.0194 | 0.0310 |
| R1a (*I* ≥ 2σ) | 0.0249 | 0.0305 |
| wR2b (*I* ≥ 2σ) | 0.0664 | 0.0766 |

*a* *R1* = Σ||*F*o| – |*F*c||/Σ|*F*o|. *b* wR2 = [Σ[*w*(*F*o2 – *F*c2)2]/ Σ[*w*(*F*o2)2]]1/2.