

Electronic Supporting Information to:

Ergot alkaloid biosynthesis in *Aspergillus fumigatus*: Conversion of chanoclavine-I aldehyde to festuclavine by the festuclavine synthase FgaFS in the presence of the old yellow enzyme FgaOx3

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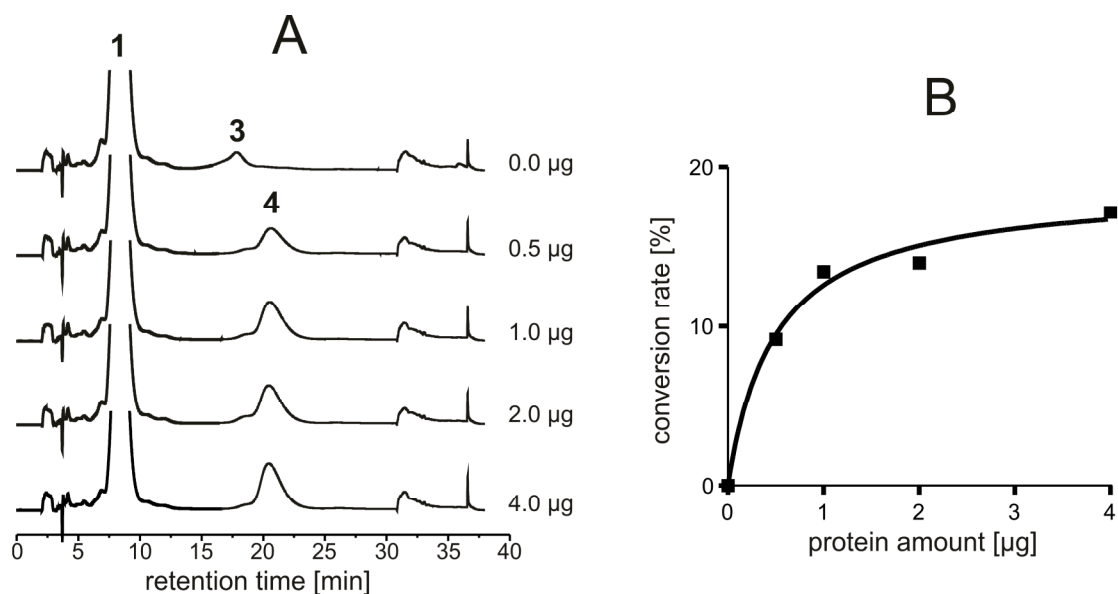


Figure S1 Protein dependence of the product formation of the FgaFS reaction. The assays (100 µl) contained 1 mM chanoclavine-I, 5 mM NAD^+ , 5 µg (0.42 µM) of FgaDH, 5 mM FMN, 5 mM NADH, 5 µg (1.2 µM) of FgaOx3 and different amounts of FgaFS. The incubation time was 3 hours.

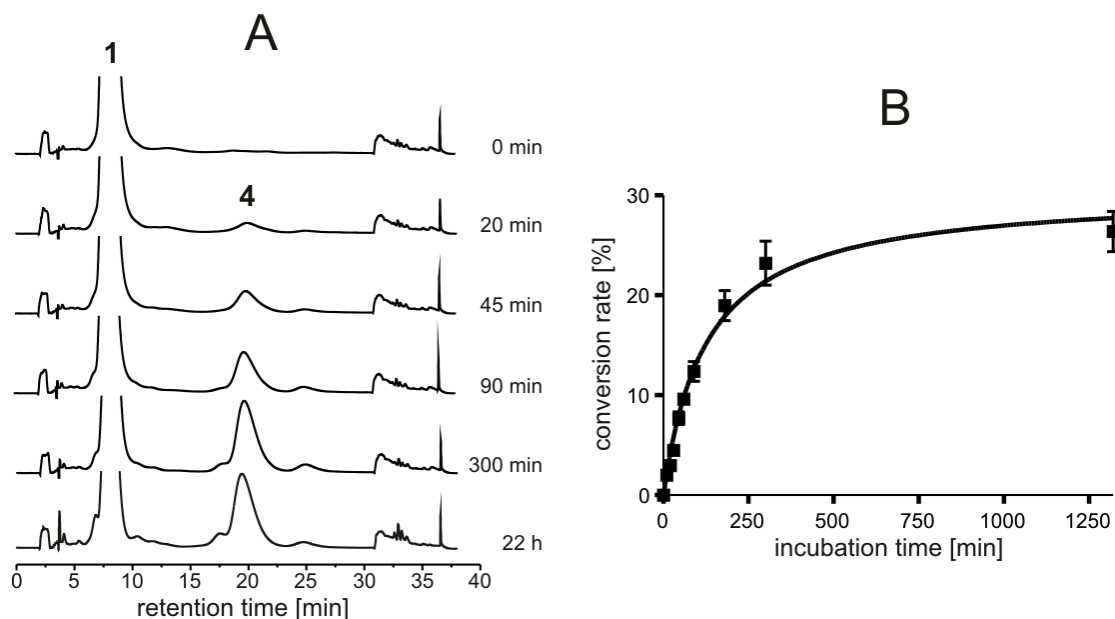


Figure S2 Time dependence of the product formation of the FgaFS reaction. The assays (100 µl) contained 1 mM chanoclavine-I, 5 mM NAD^+ , 5 µg (0.42 µM) of FgaDH, 5 mM FMN, 5 mM NADH, 5 µg (1.2 µM) of FgaOx3 and 1.5 µg (450 nM) of FgaFS.

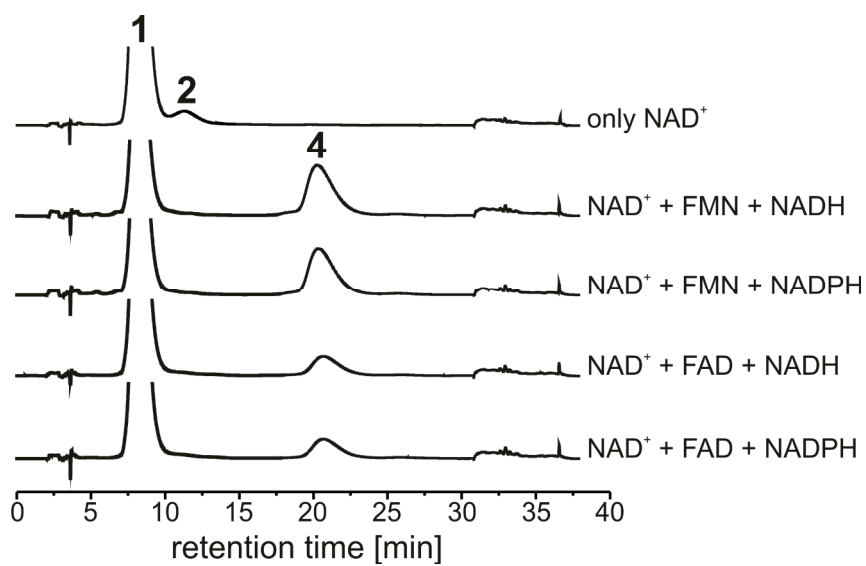


Figure S3 Dependence of the product formation of the FgaFS reaction on cofactors. The assays (100 μl) contained 1 mM chanoclavine-I, 5 μg (0.42 μM) of FgaDH, 5 μg (1.2 μM) of FgaOx3, 5 μg (1.5 μM) of FgaFS and 5 mM of each cofactor. The incubation time was 1 hour.

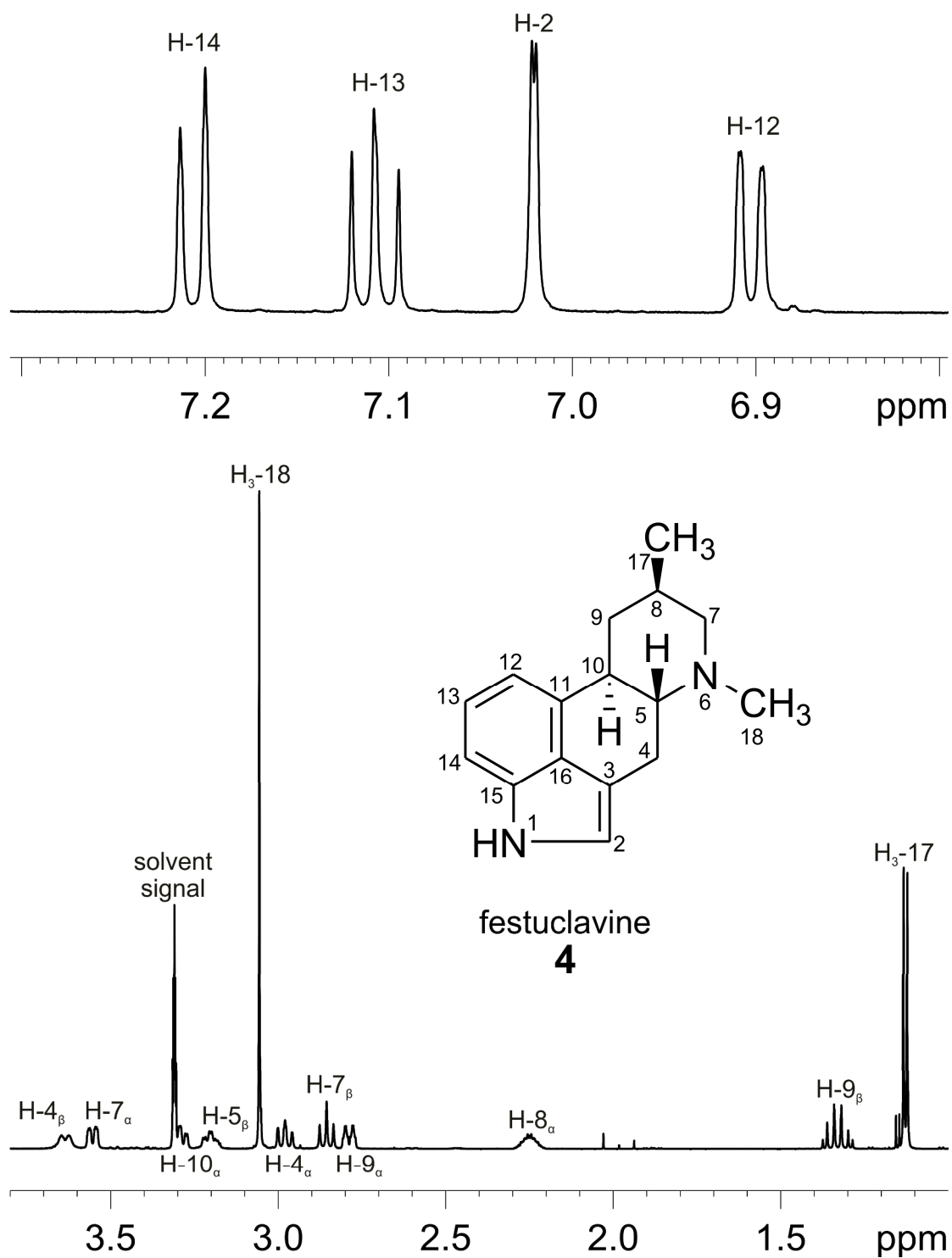


Figure S4 $^1\text{H-NMR}$ spectrum of **4** in protonated form in CD_3OD

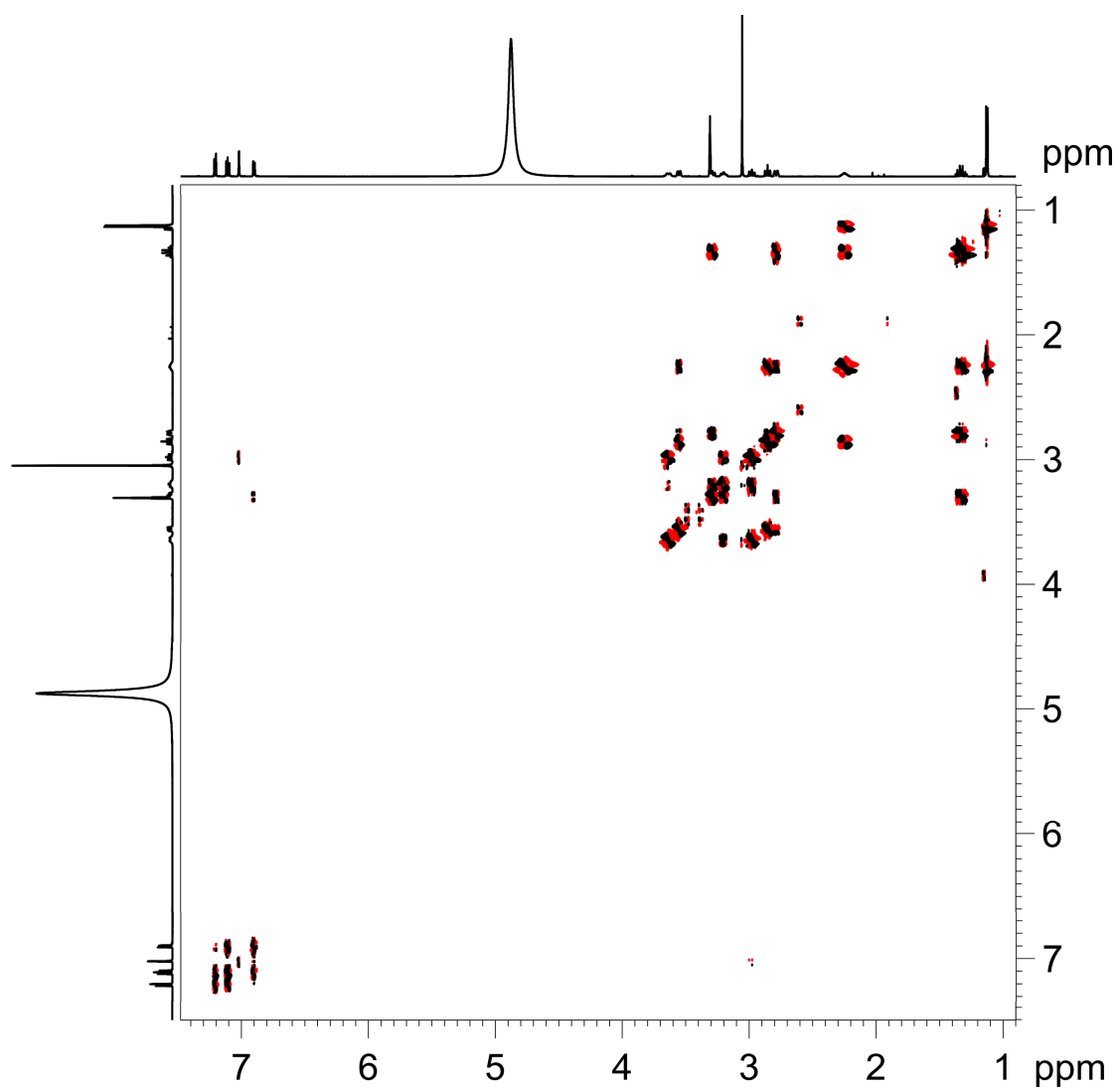


Figure S5 DQF-COSY spectrum of **4** in protonated form in CD₃OD

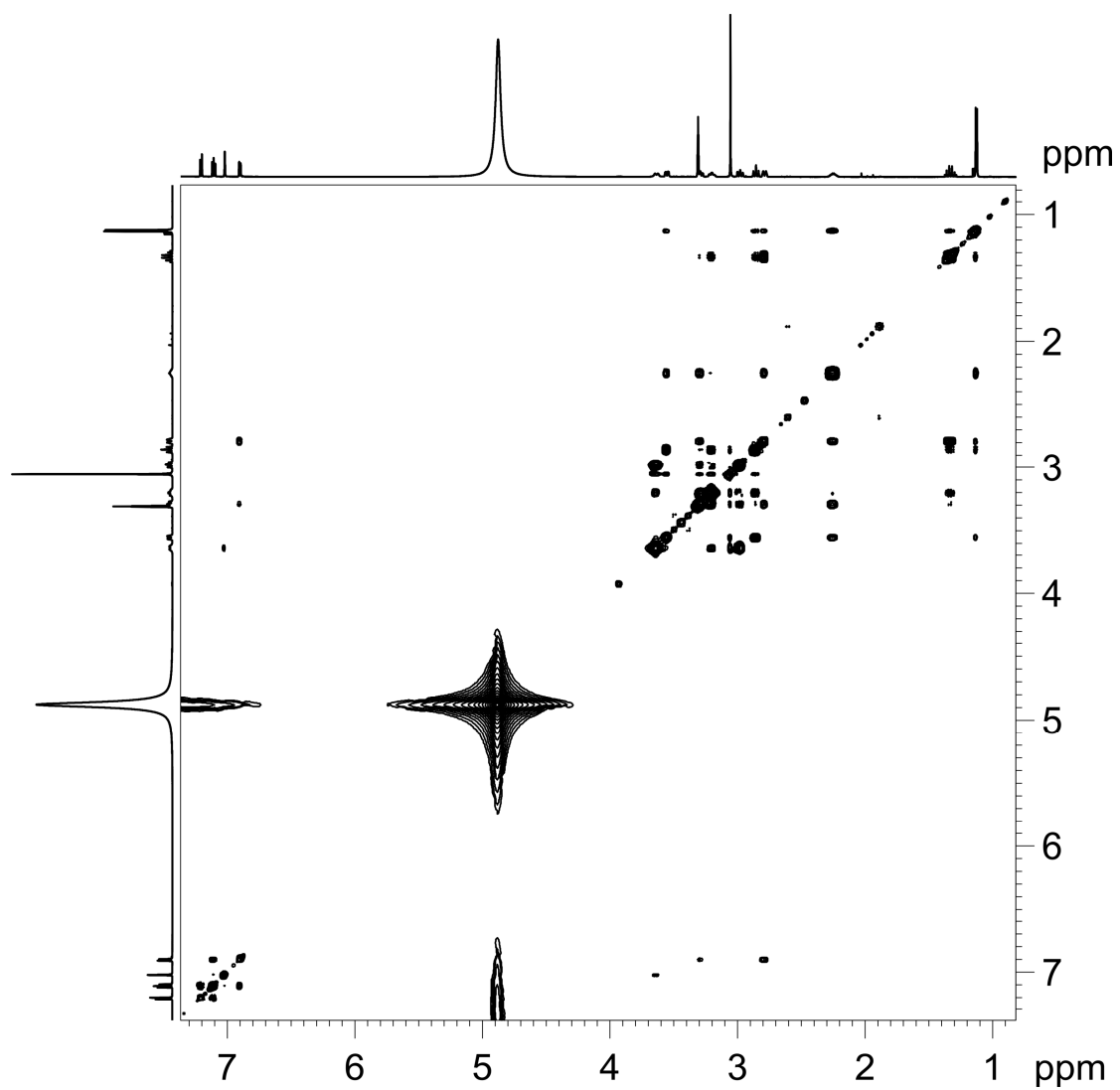


Figure S6 NOESY spectrum of **4** in protonated form in CD₃OD

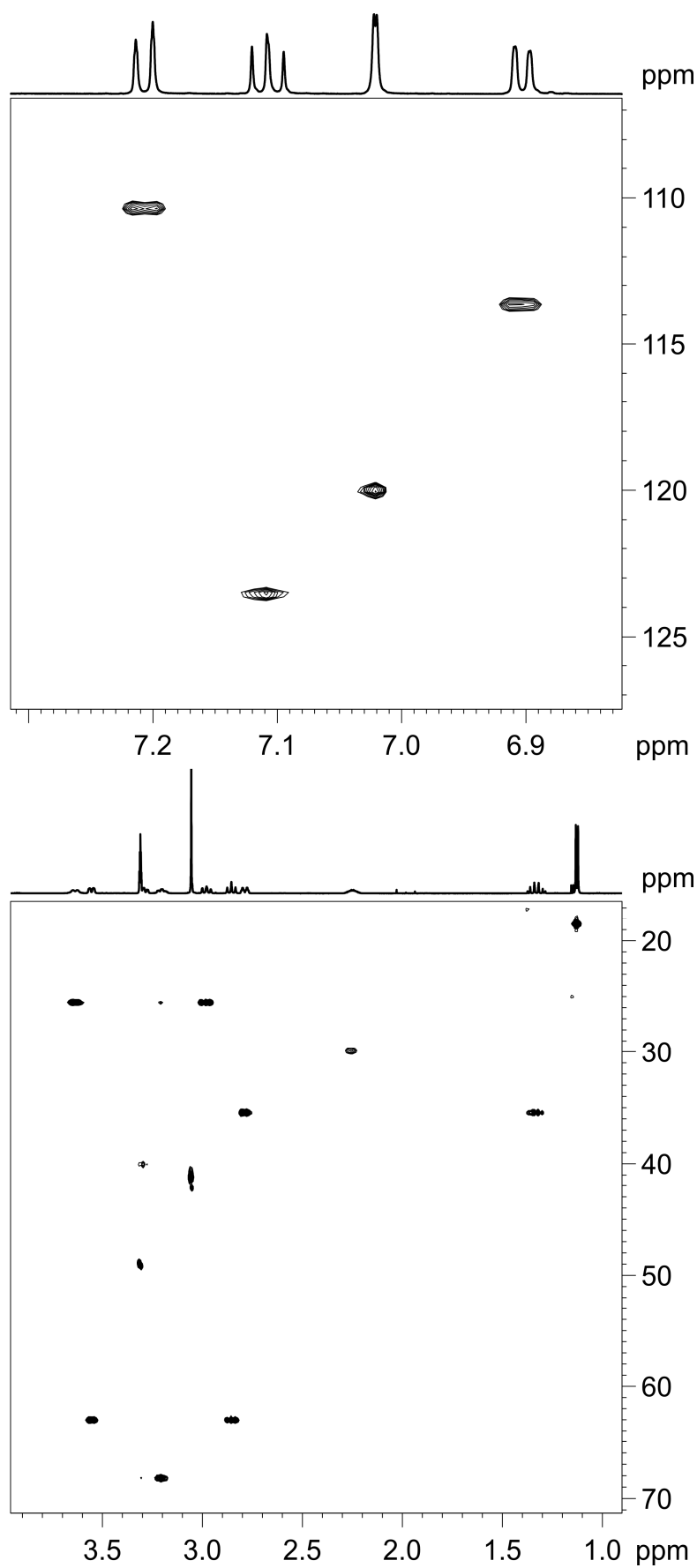


Figure S7 Enhanced parts of the HSQC spectrum of **4** in protonated form in CD₃OD

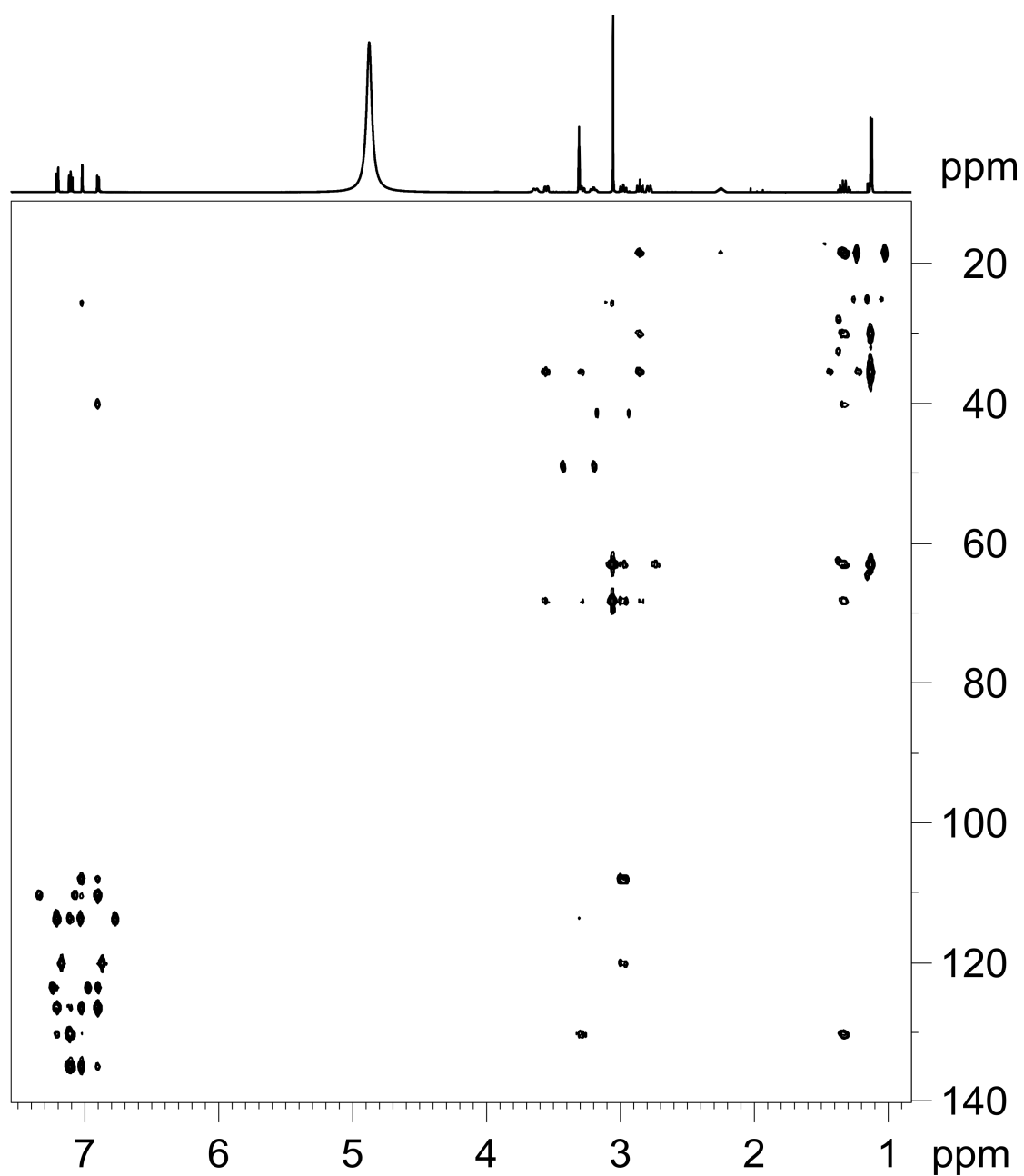


Figure S8 HMBC spectrum of 4 in protonated form in CD₃OD

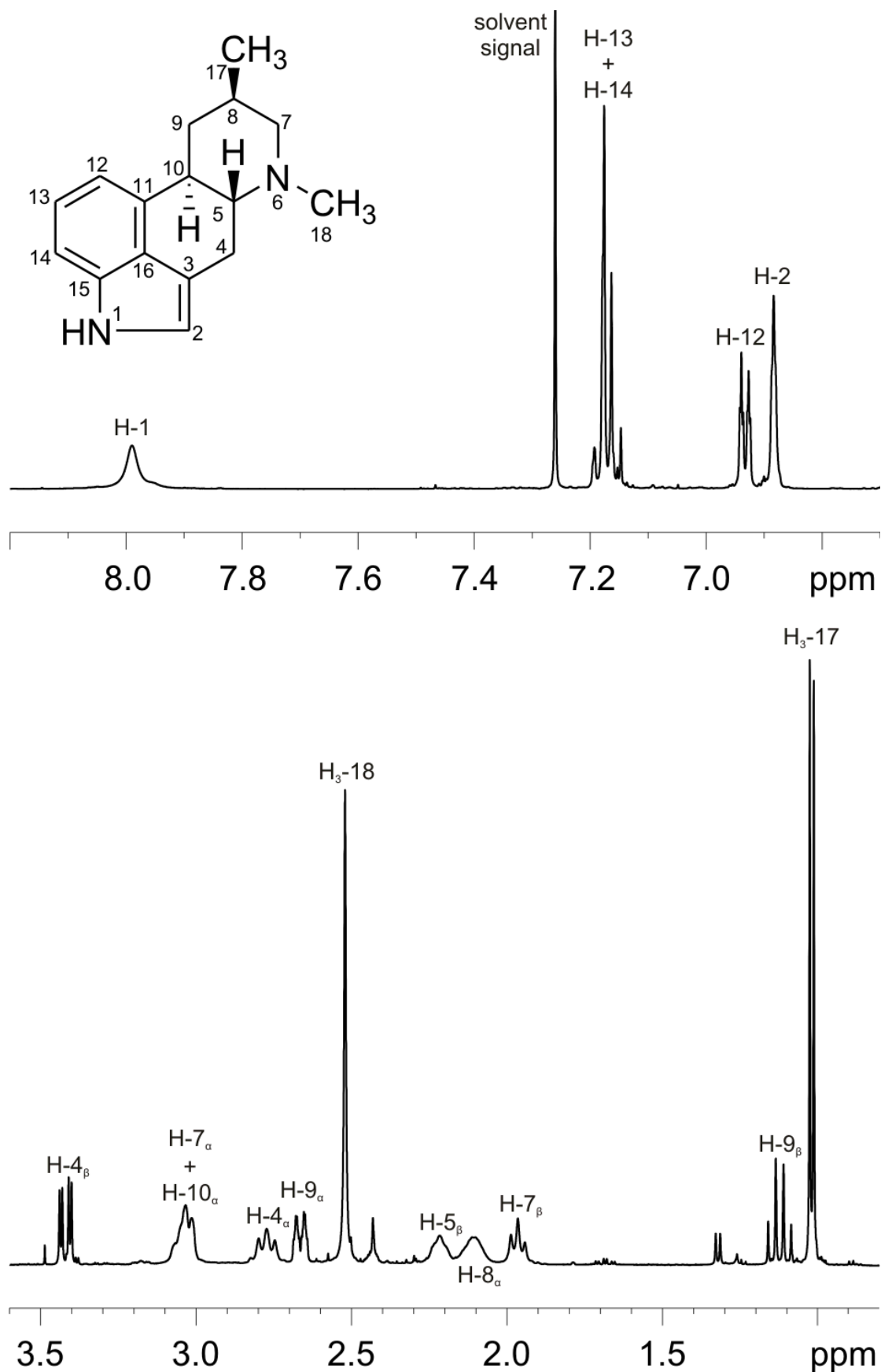


Figure S9 $^1\text{H-NMR}$ spectrum of authentic festuclavine as free base in CDCl_3

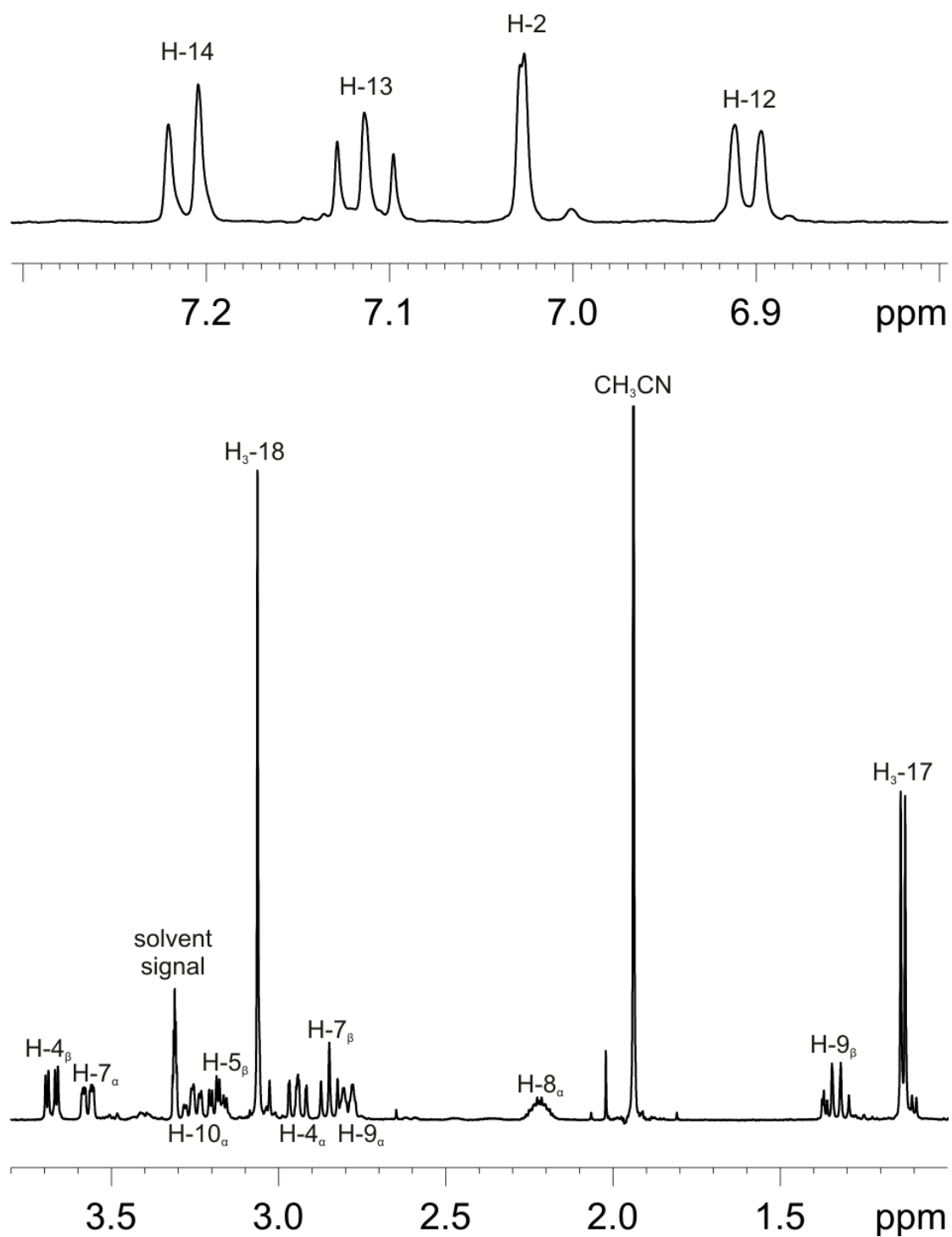


Figure S10 ¹H-NMR spectrum of authentic festuclavine in protonated form in CD₃OD
The sample of authentic festuclavine as free base was treated after NMR measurement in CDCl₃ with HPLC solvents containing CH₃CN and 0.5 % trifluoroacetic acid and evaporated to dryness.