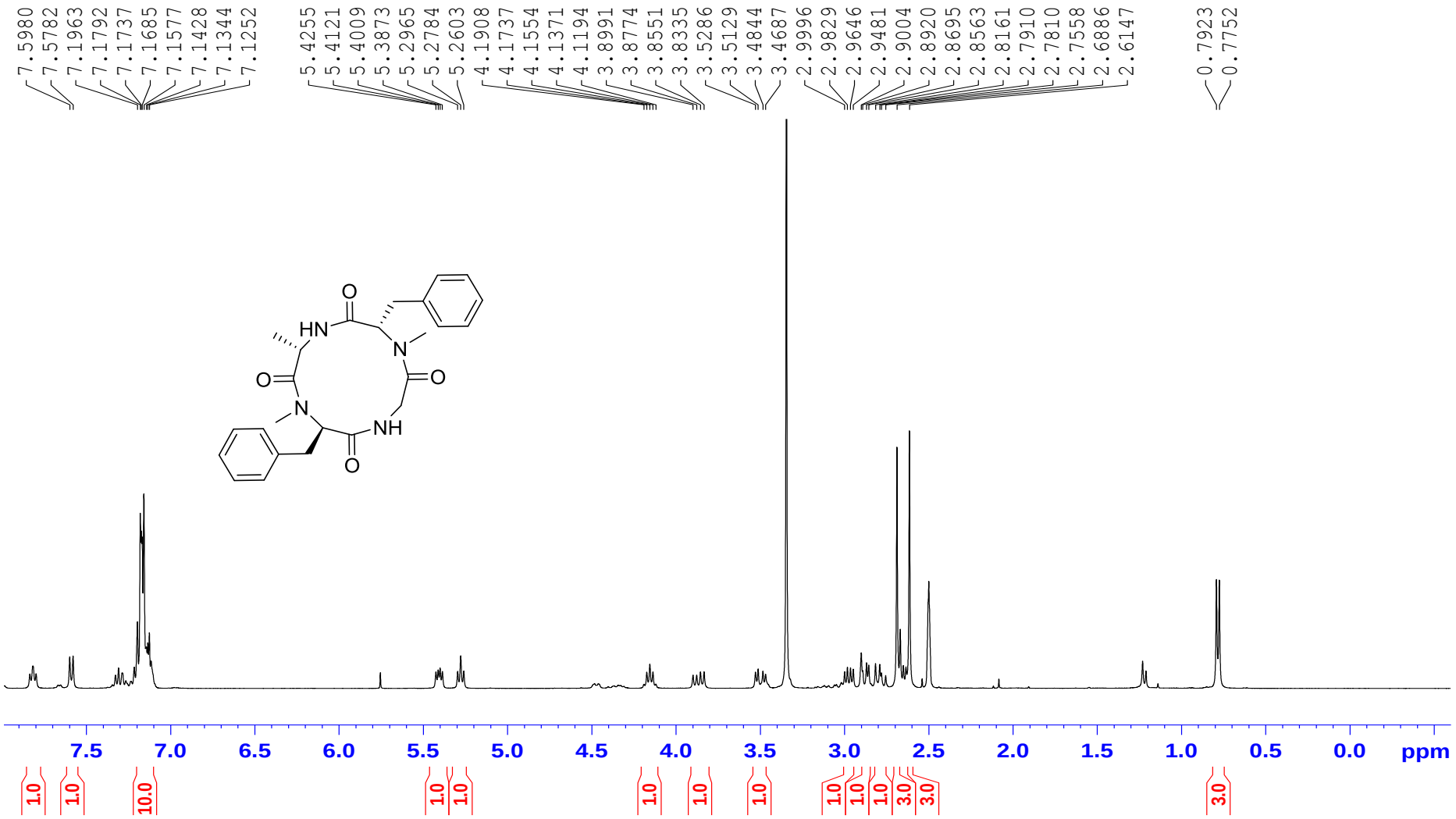
Electronic Supplementary Material (ESI) for RSC Advances.

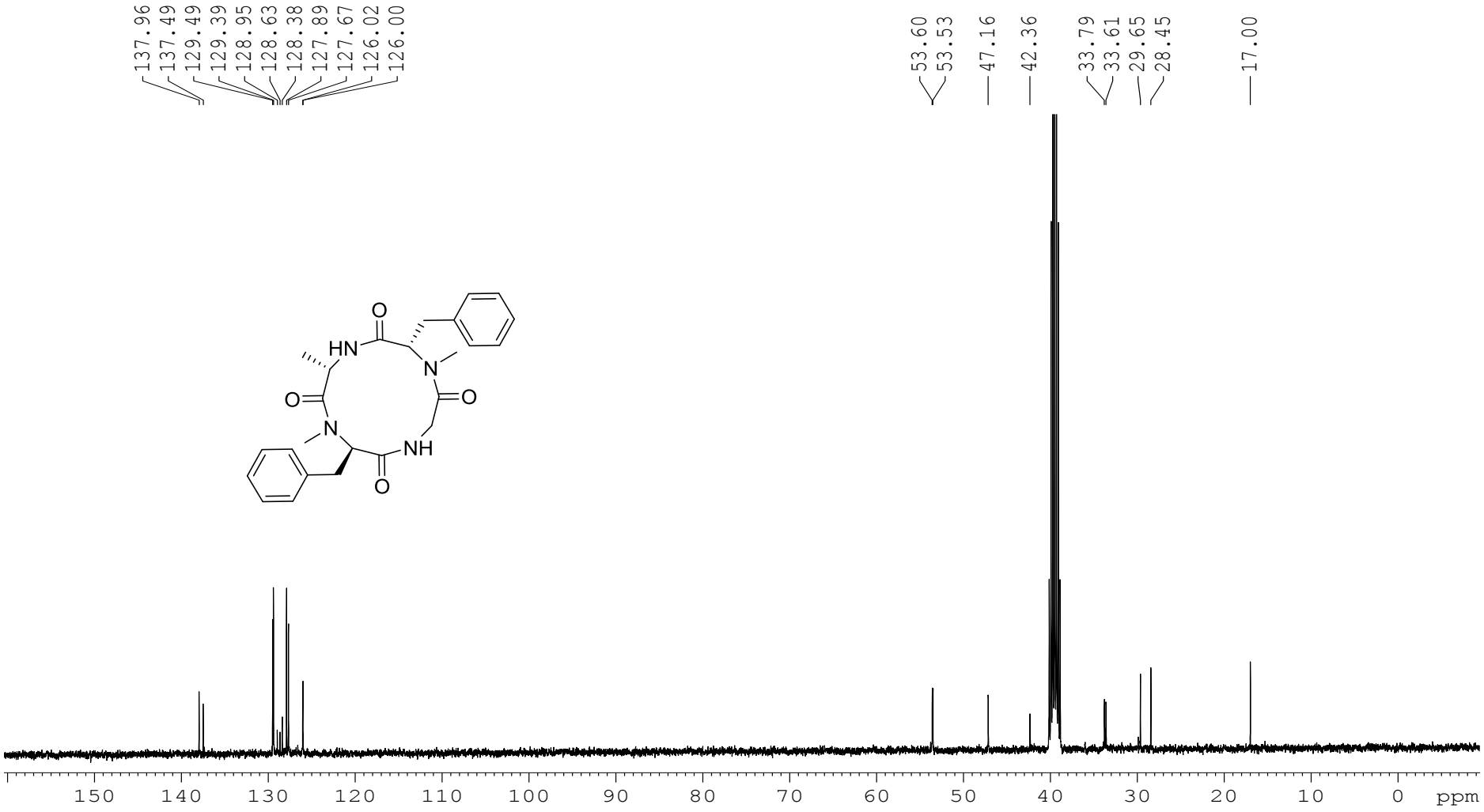
Versicotides D-F, new cyclopeptides with lipid-lowering activities

Supporting Information

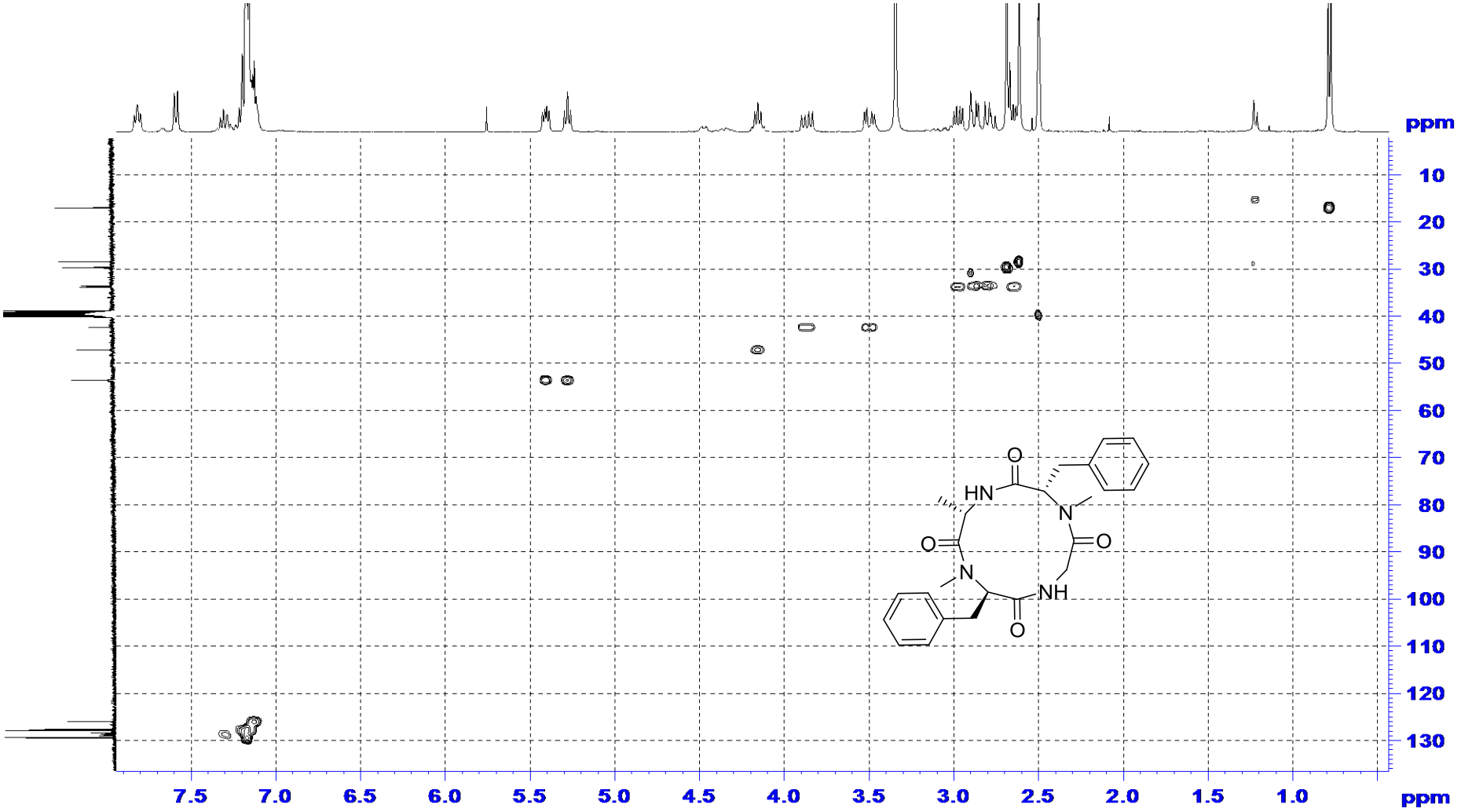
S1 ^{1}H NMR Spectrum of **1** in DMSO-d_6



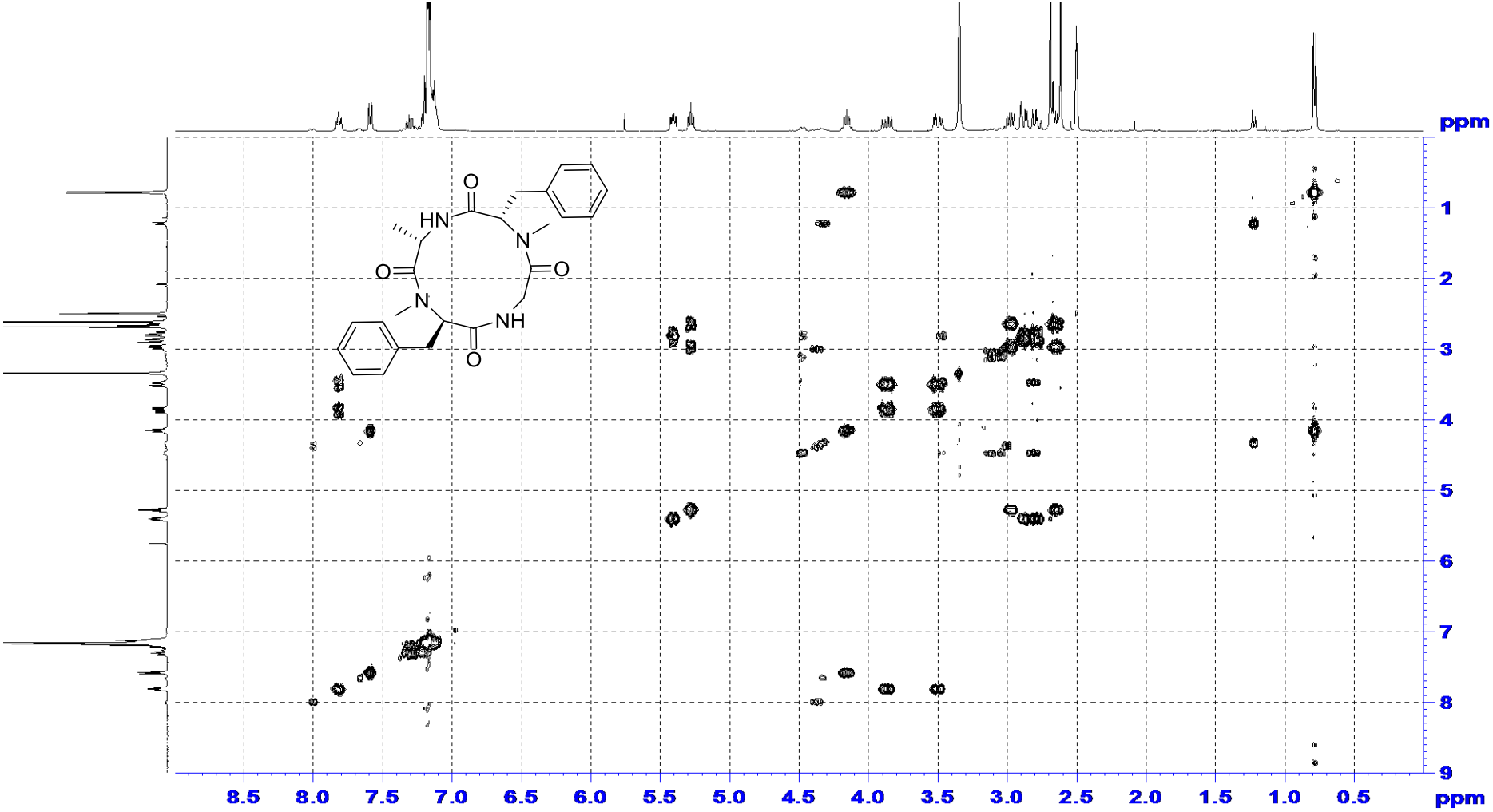
S2 ^{13}C NMR Spectrum of **1** in DMSO-d_6



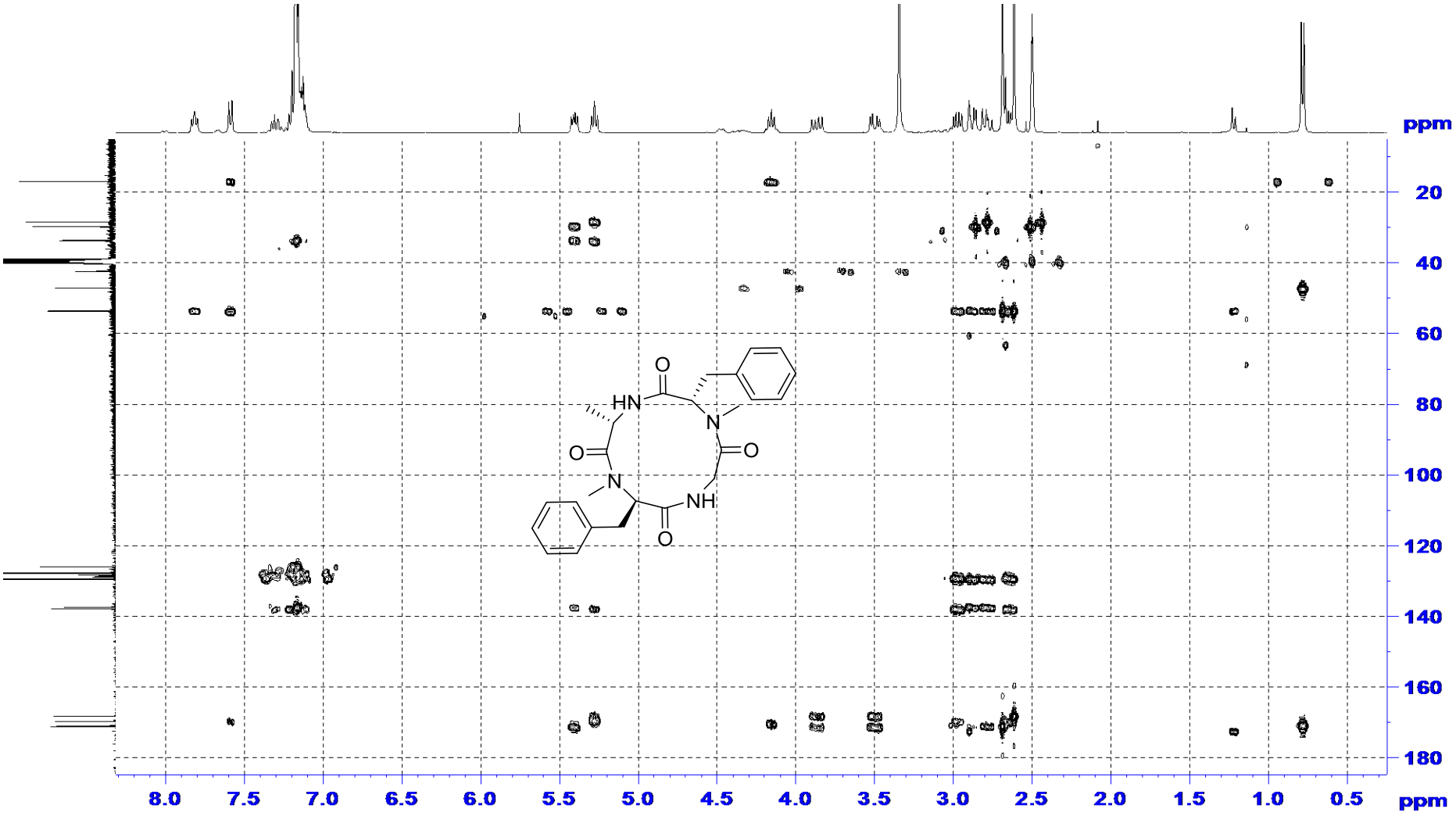
S3 HSQC Spectrum of **1** in DMSO-d_6



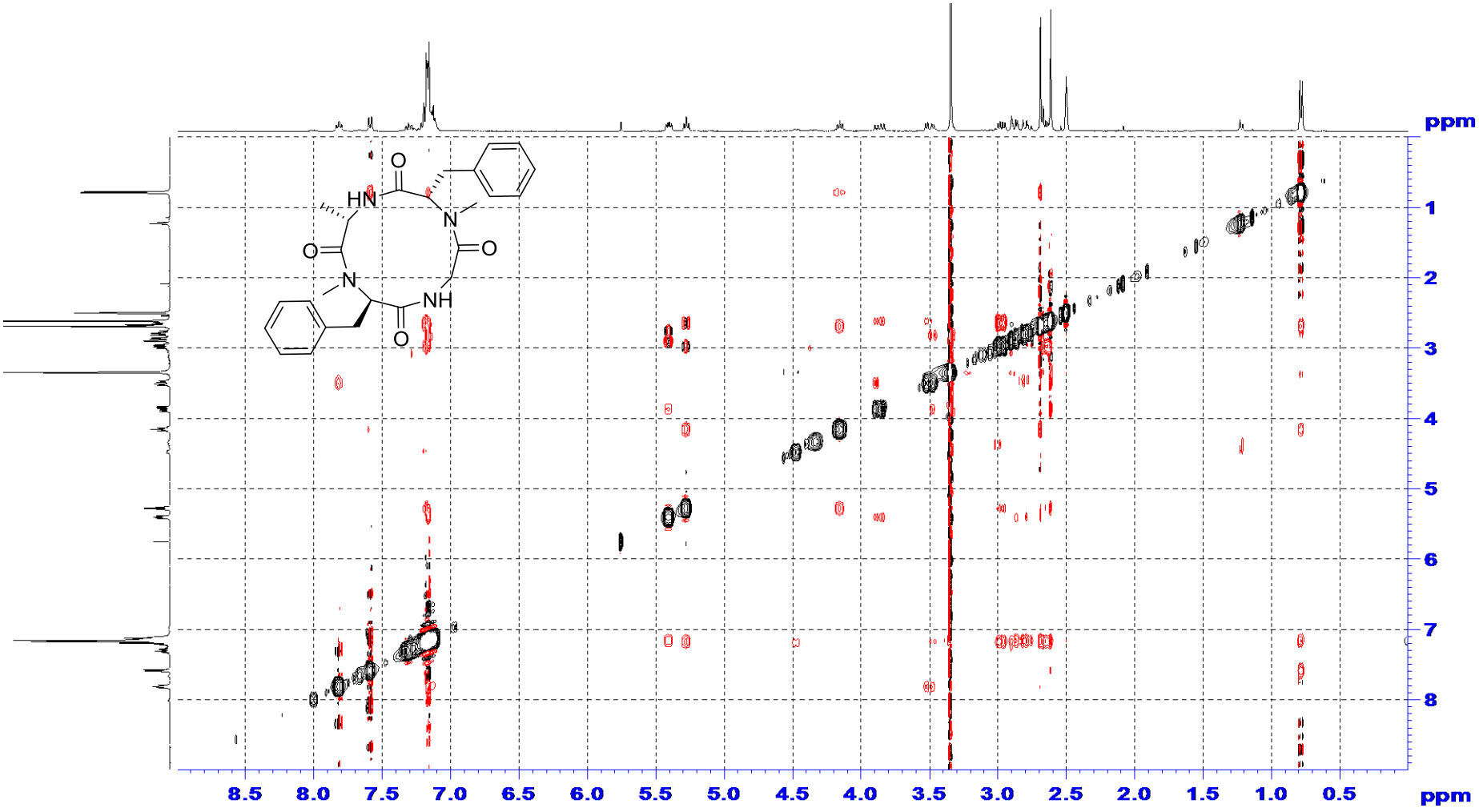
S4 ^{1}H-^{1}H COSY Spectrum of **1** in DMSO-d_6



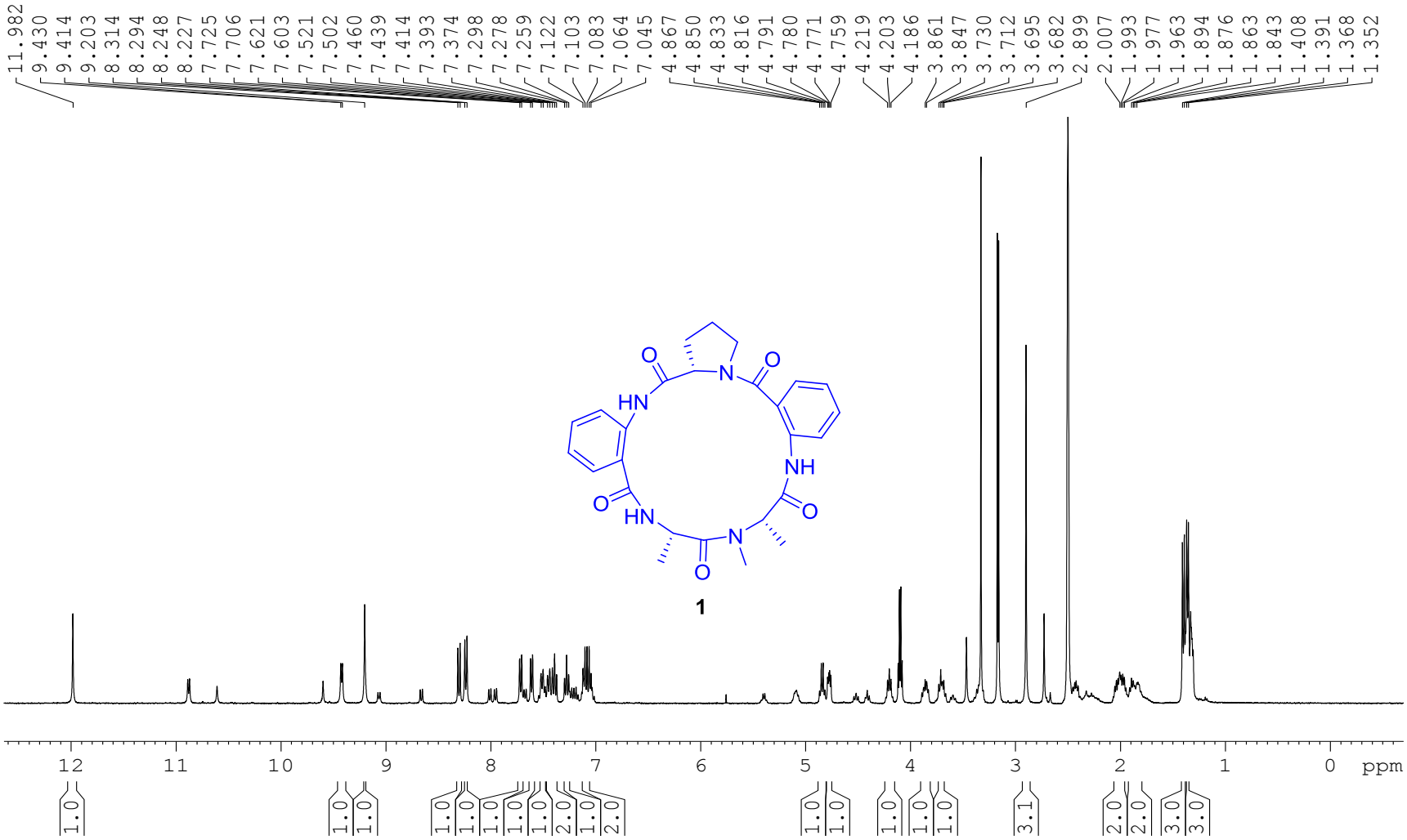
S5 HMBC Spectrum of **1** in DMSO-d_6



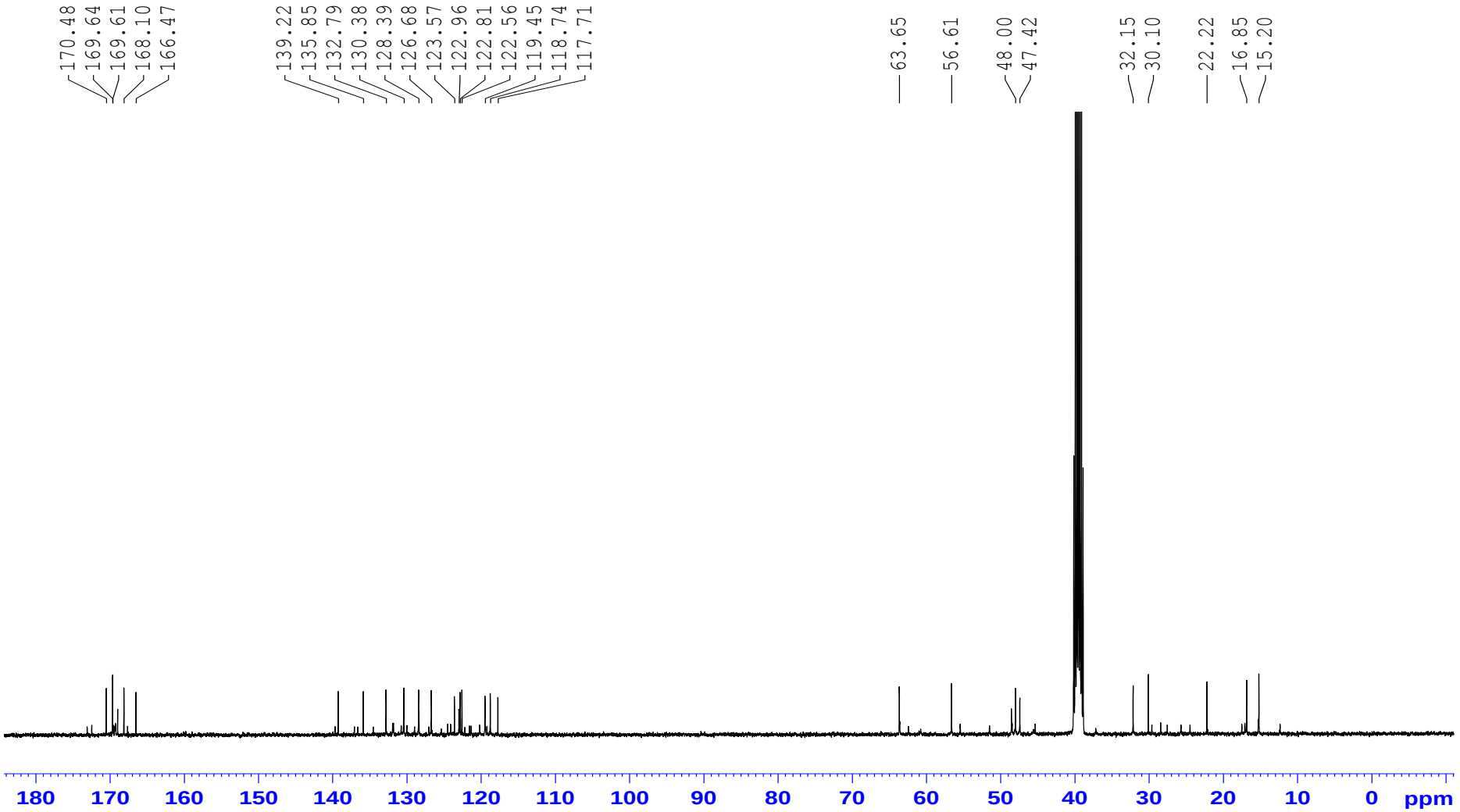
S6 NOESY Spectrum of **1** in DMSO-d_6



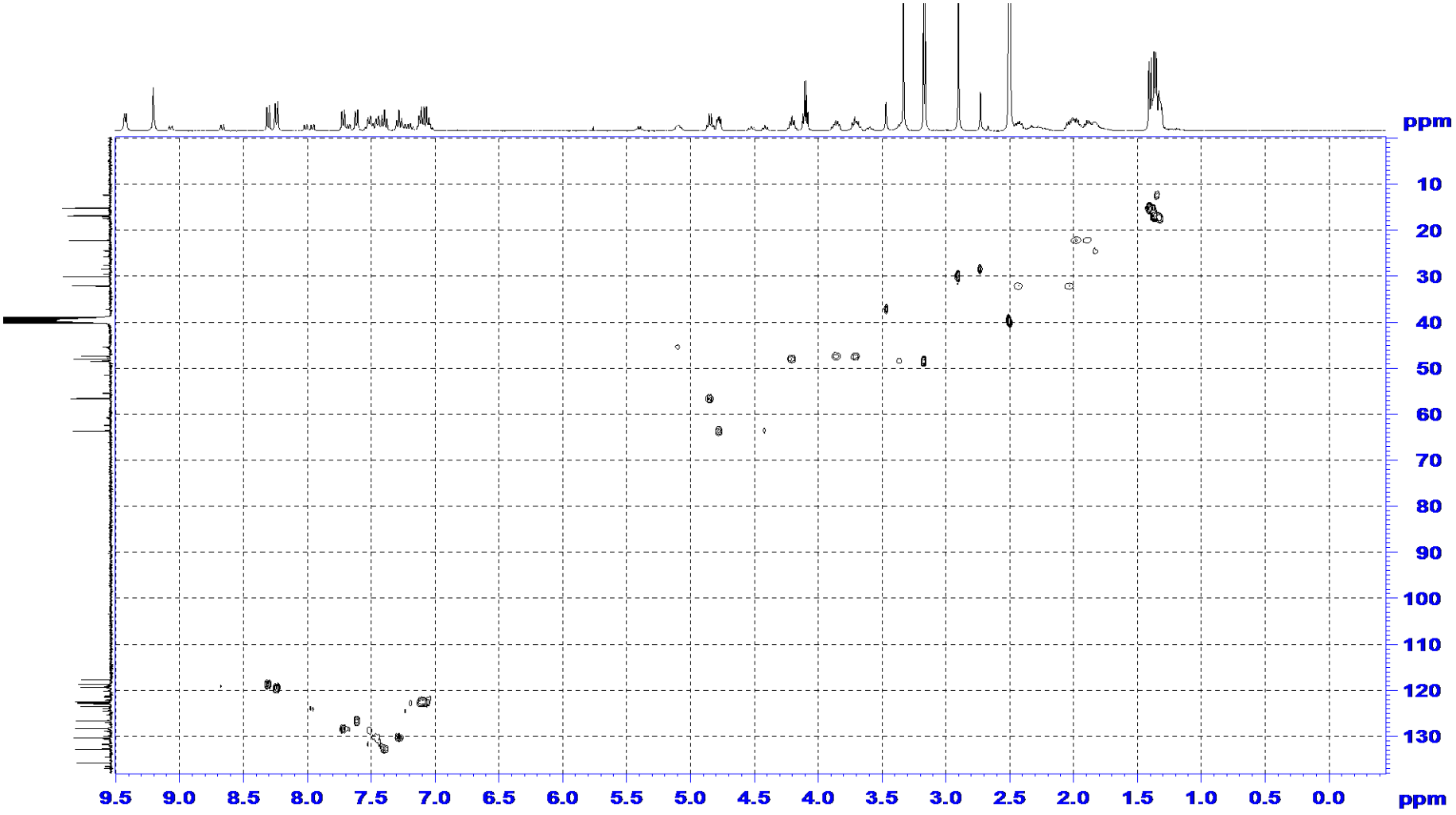
S7 ^{1}H NMR Spectrum of **2** in DMSO-d_6



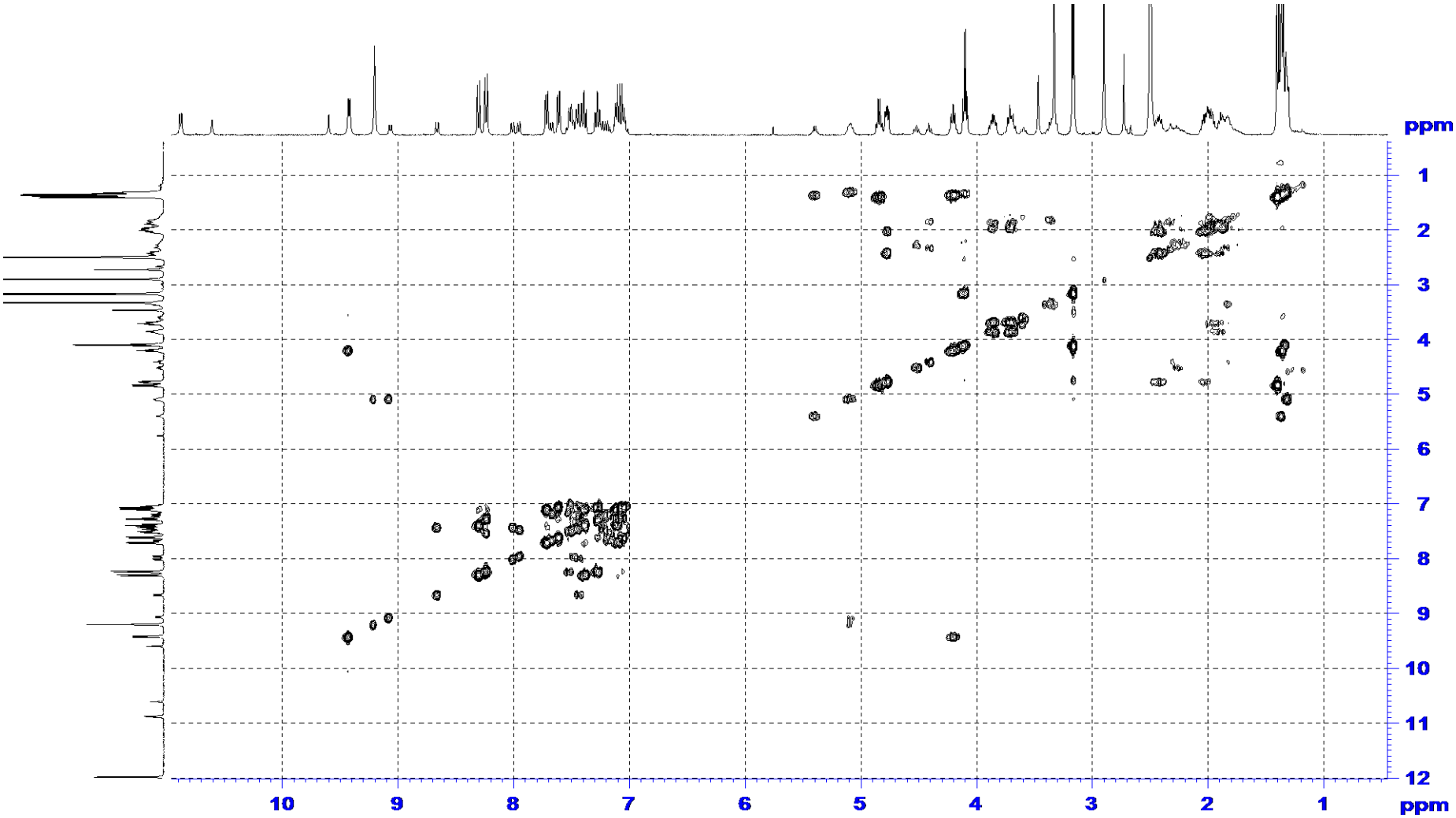
S8 ^{13}C NMR Spectrum of **2** in DMSO-d_6



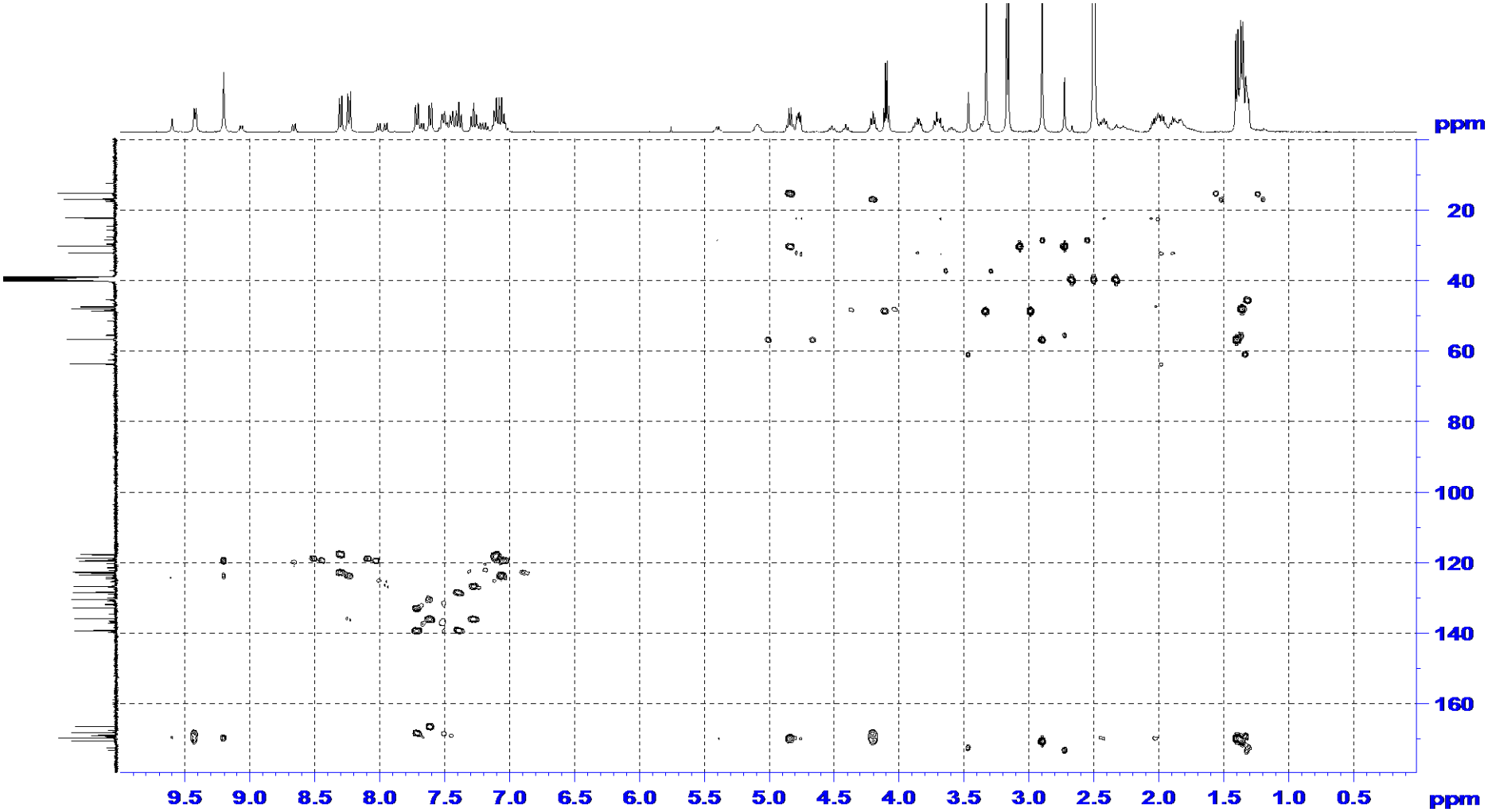
S9 HSQC Spectrum of **2** in DMSO-d_6



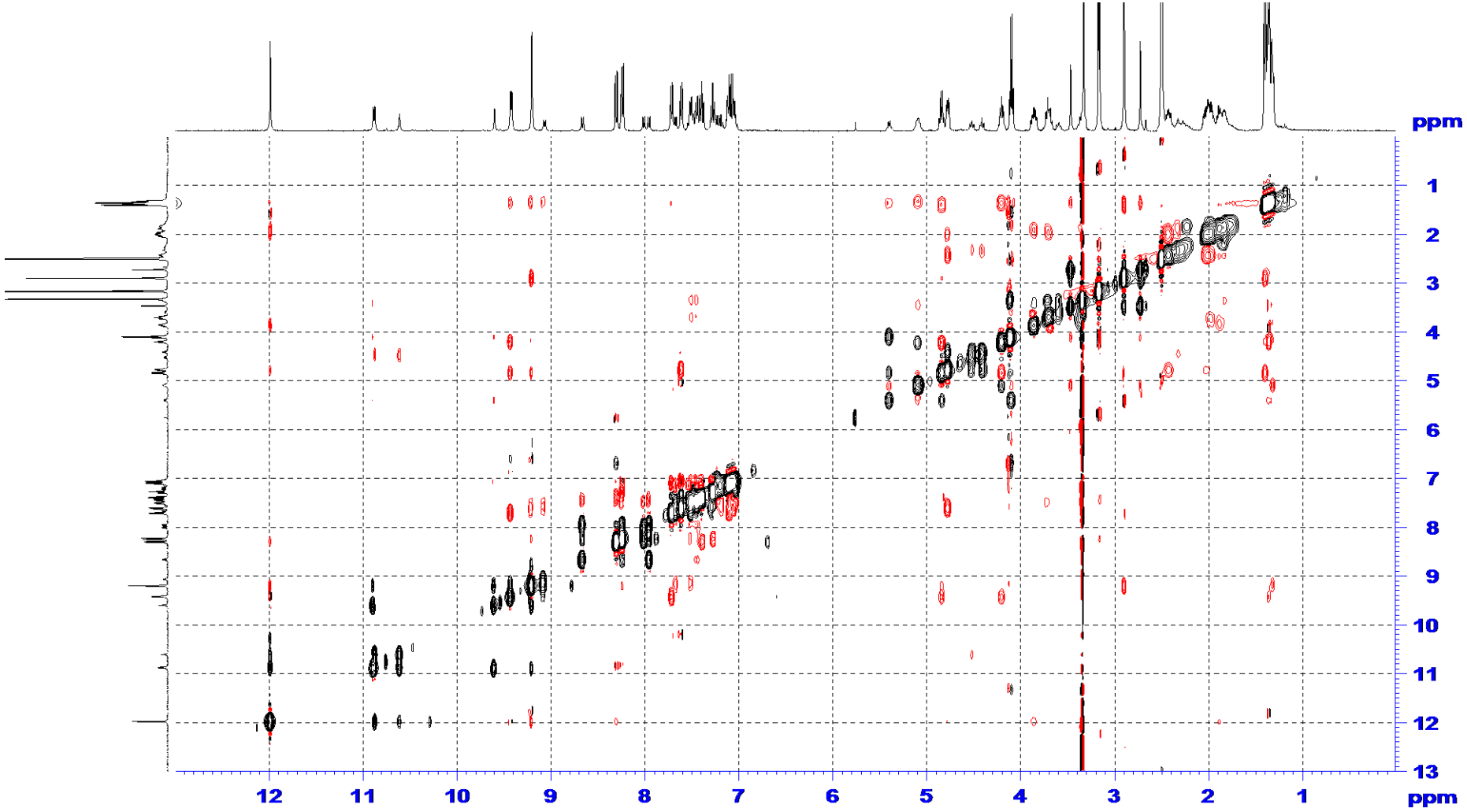
S10 ^{1}H-^{1}H COSY Spectrum of **2** in DMSO-d_6



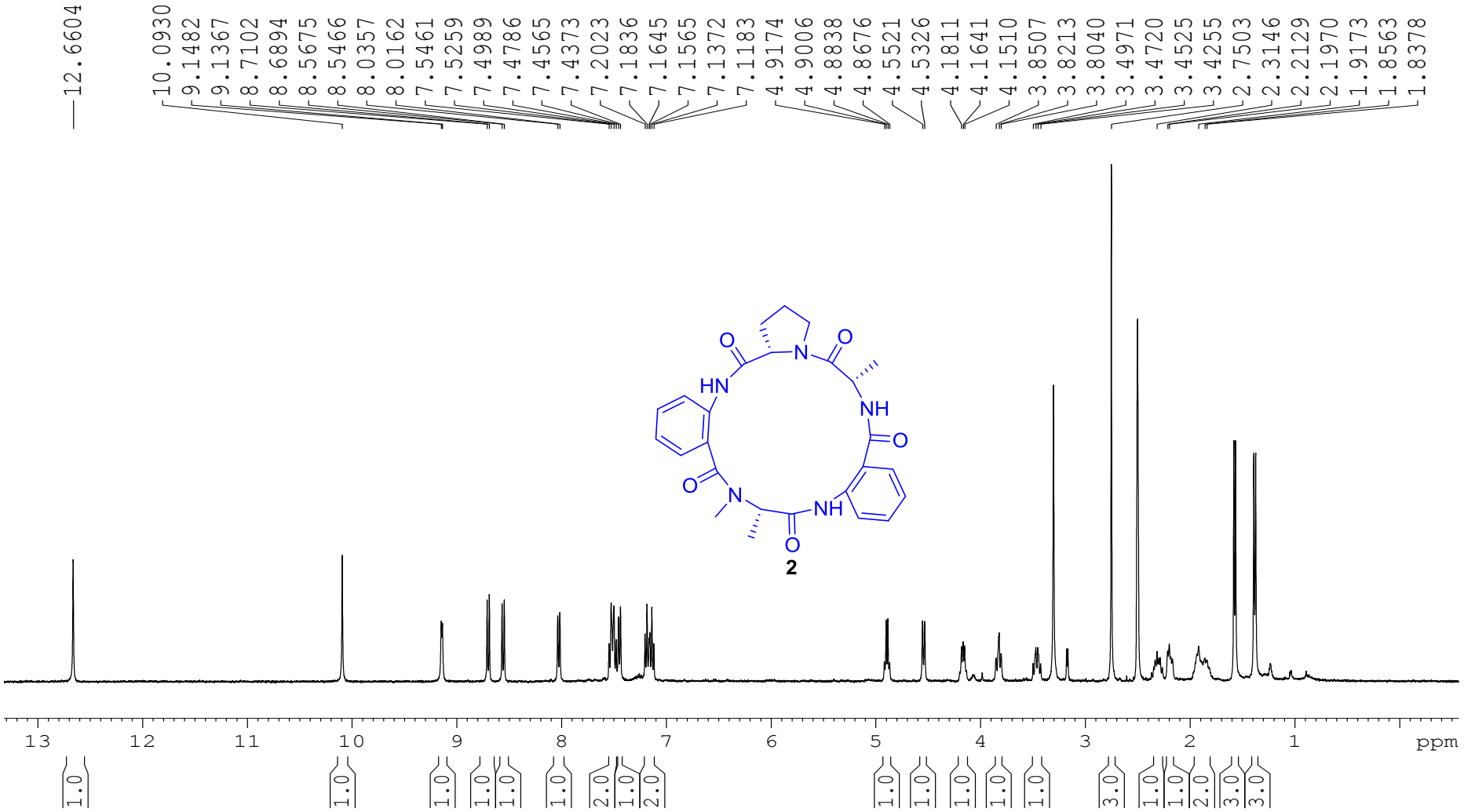
S11 HMBC Spectrum of **2** in DMSO-d_6



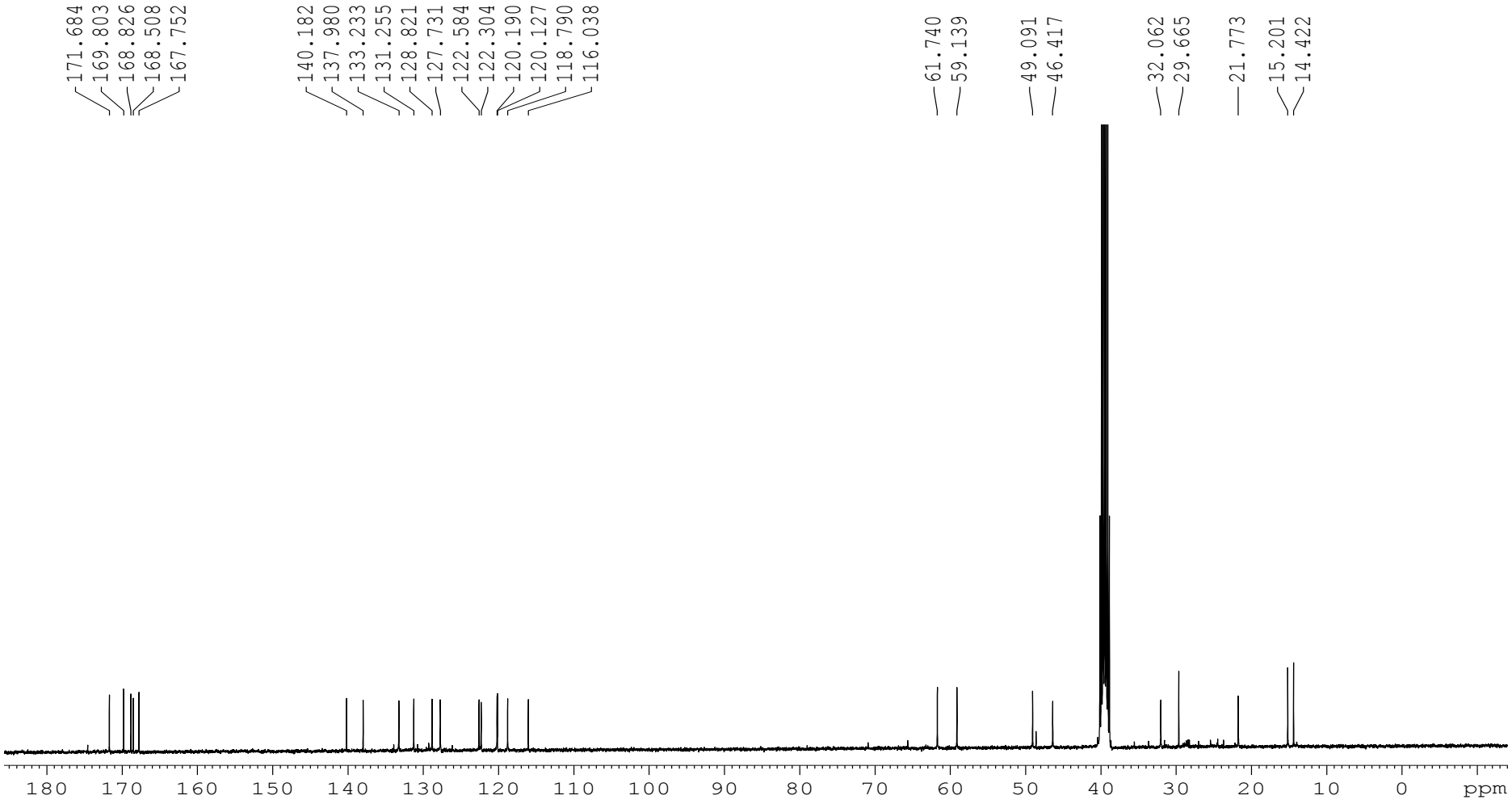
S12 NOESY Spectrum of **2** in DMSO-d_6



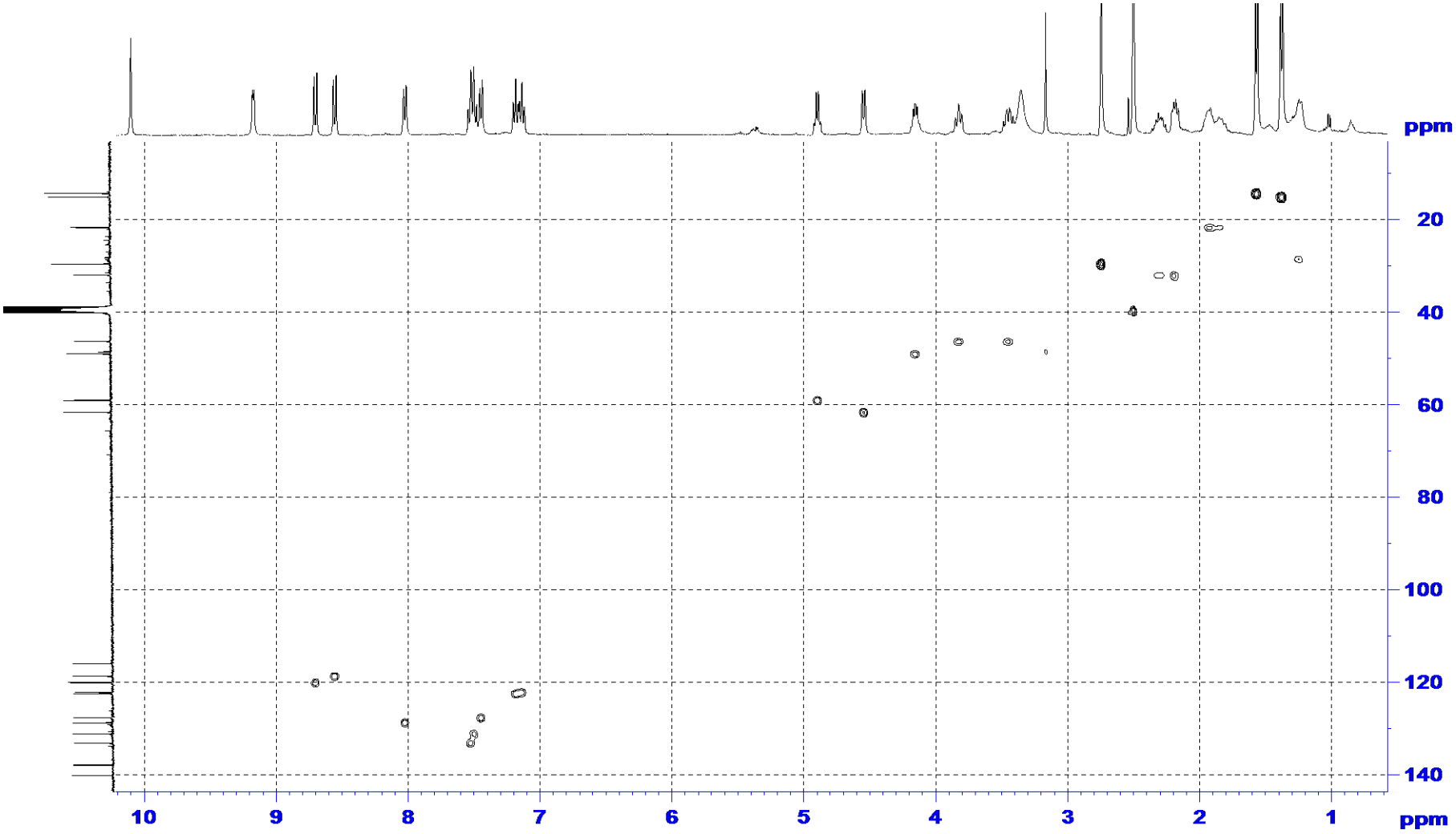
S13 ^{1}H NMR Spectrum of **3** in DMSO-d_6



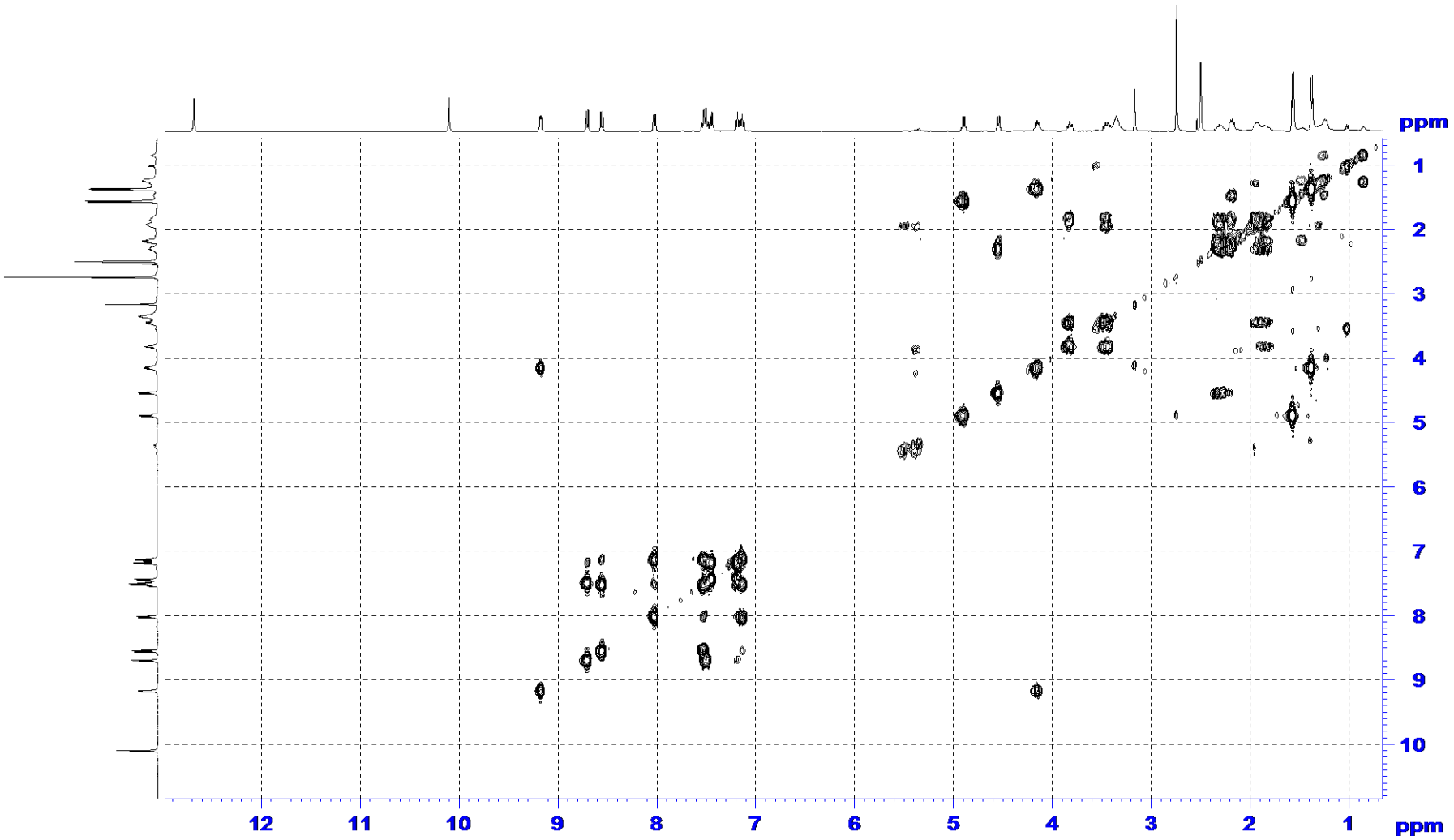
S14 ^{13}C NMR Spectrum of **3** in DMSO-d_6



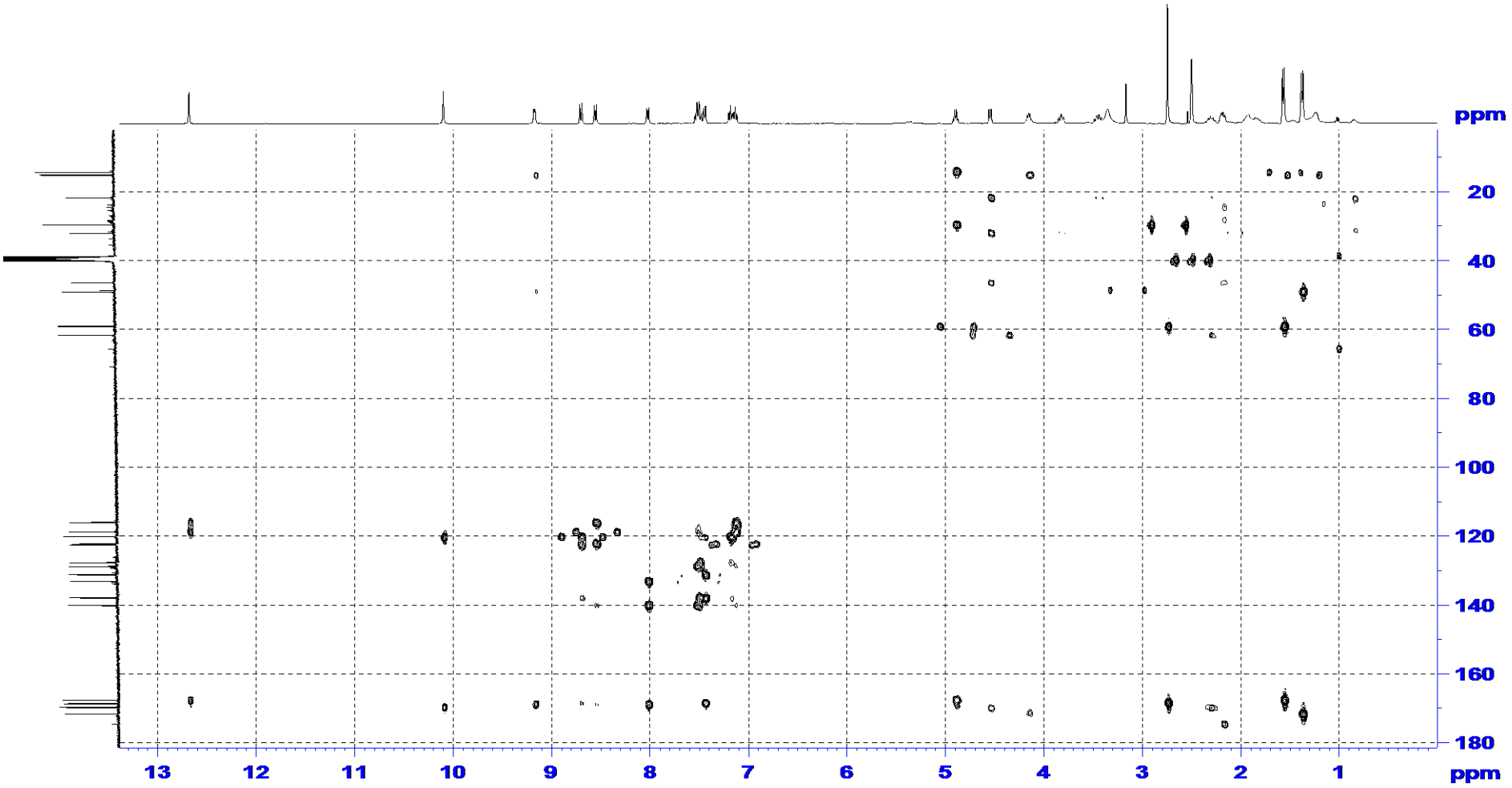
S15 HSQC Spectrum of **3** in DMSO-d_6



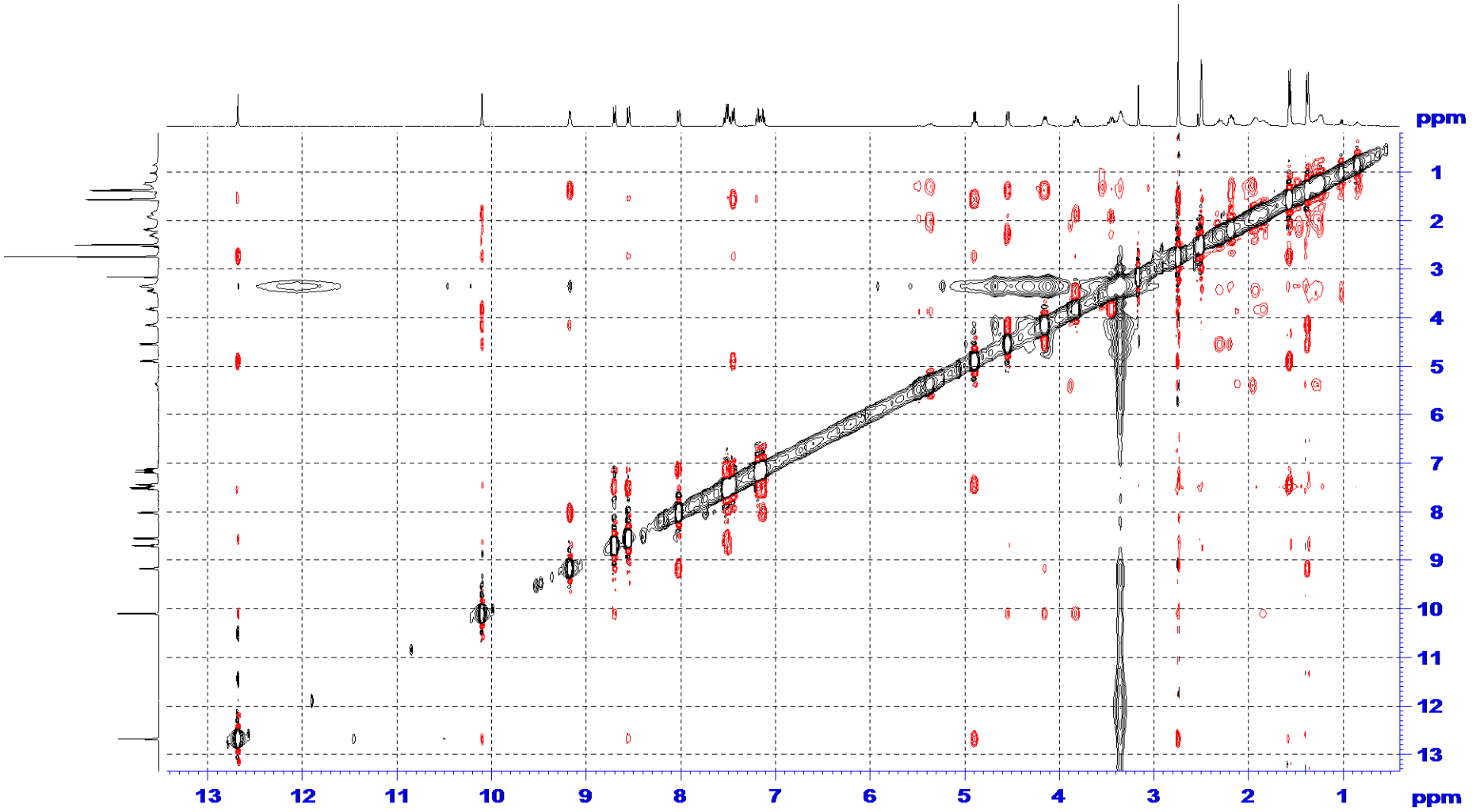
S16 ^{1}H-^{1}H COSY Spectrum of **3** in DMSO-d_6



S17 HMBC Spectrum of **3** in DMSO-d_6



S18 NOESY Spectrum of **3** in DMSO-d_6



S19 Acid Hydrolysis of **3** and determination of the absolute configuration of amino acids by advanced Marfey method

1. Acid Hydrolysis of **2**.

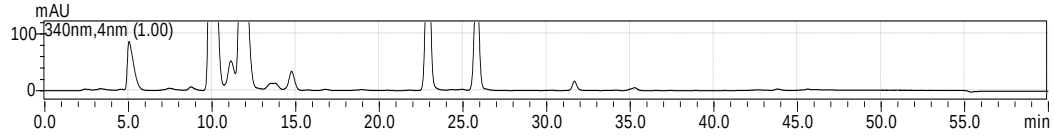
Compound **3** (1 mg each) was dissolved in degassed 6 N HCl (1 mL) and heated at 110 ℃ for 14 h. After cooling, the solvent was removed *in vacuo*.

2. Determination of the absolute configuration of amino acids by advanced Marfey method.

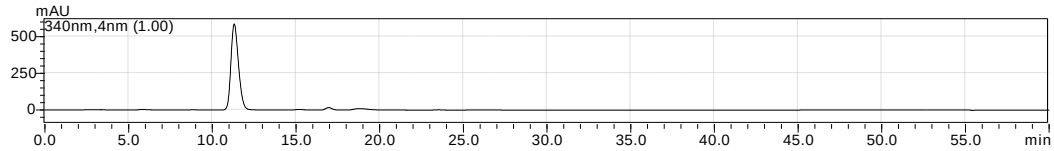
The acid hydrolysate of **3** was dissolved in H_2O (50 μL) separately, and then 0.25 μM L-FDAA in 100 μL of acetone was added, followed by 1 N $NaHCO_3$ (50 μL). The mixtures were heated for 1 h at 43 ℃. After cooling to room temperature, the reaction was quenched by the addition 2 N HCl (25 μL). Finally the resulting solution was concentrated and was dissolved in methanol for HPLC analysis. Amino acid standards were derivatized with *L*-FDAA in a similar manner. The resulting *L*-FDAA derivatives of compound **3**, *L*- and *D*-alanine, *L*- and *D*-Me-alanine, *L*- and *D*- proline were separately analyzed by reversed-phase HPLC (4.6 × 150 mm, BDS HYPERSIL C18 column, 5 μm, with a linear gradient of methanol (A) and 0.05% aqueous H_3PO (B) from 30% to 70% A for *L*(*D*)-alanine and *L*(*D*)-proline, from 5% to 100 % A for *L*(*D*)-Me-alanine in 40 min at a flow rate of 1 mL/min, UV detection at 340 nm). Each chromatographic peak was identified by comparing its retention times for the *L*-FDAA derivatives of the *L*- and *D*-amino acid standards. The standards gave the following retention times (in min): 11.31 for L-Ala, 16.93 for D-Ala, 12.06 for L-Pro, 13.74 for D-Pro, 22.59 for L-Me-Ala (5% to 100% A), 22.41 for D-Me-Ala (5% to 100% A),. The analysis of acid hydrolysate of **3** gave retention times (in min) of 11.19, 12.00, and 22.61 (30% to 70% A) for L-Ala, L-Pro, and L-Me-Ala, respepectively.

S20 HPLC spectra of *L*-FDAA derivatives.

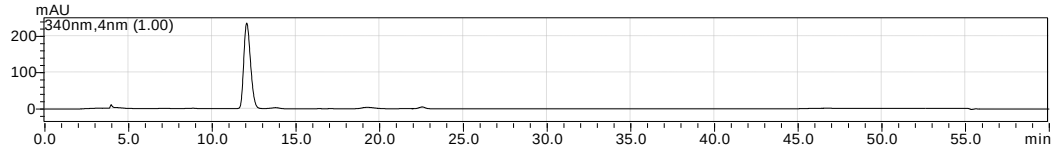
HPLC spectrum of *L*-FDAA derivatives of acid hydrolysate of **3** (MeOH:H_2O: from 3:7 to 7:3)



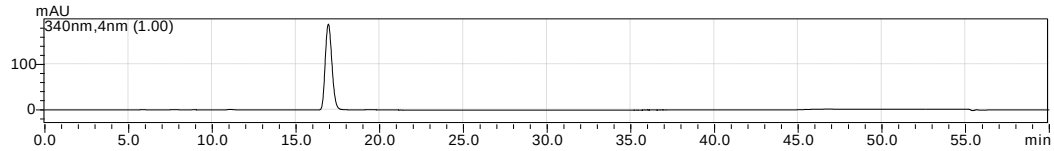
L-Ala



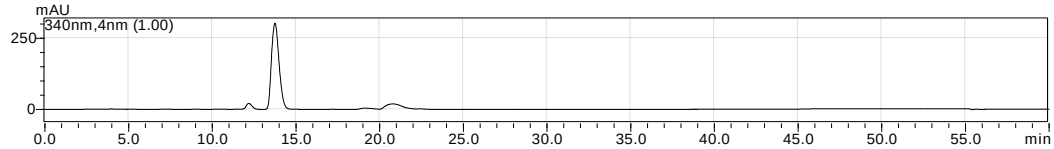
L-Pro



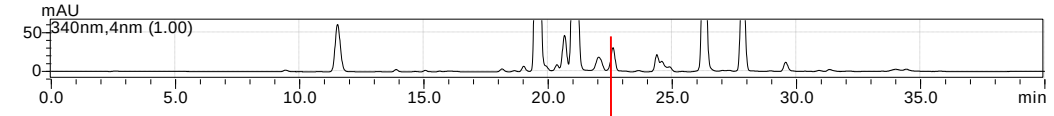
D-Ala



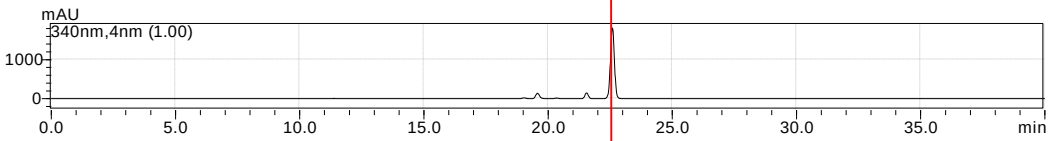
D-pro



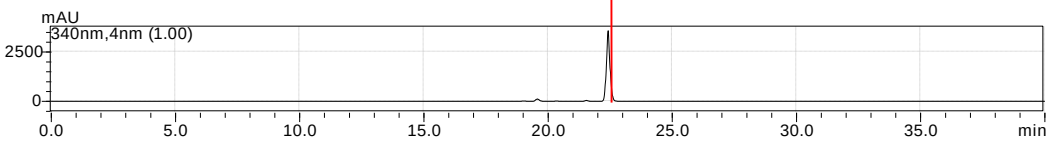
HPLC spectrum of L-FDAA derivatives of acid hydrolysate of **3** (MeOH:H_2O: from 5:95 to 100:0 in 40 min)



N-methyl -*L*-Ala



N-methyl-*D*-Ala



S21 Crystal data for compounds **1**, **2**, and **4**

Crystal data for compounds **1**: mp 274–275 ℃, $C_{25}H_{30}N_4O_4$•CH_3OH, M = 482.57 g/mol, orthorhombic, space group $P2_12_12$ (no. 18), a = 29.9420(3) Å, b = 12.19640(13) Å, c = 6.85035(8) Å, V = 2501.64(5) Å^3, Z = 4, T = 100 K, μ(CuKα) = 0.731 mm^{-1}, *Dcalc* = 1.281 g/cm^3, 22121 reflections measured (5.904° ≤ 2Θ ≤ 137.338°), 4506 unique (R_{int} = 0.0297, R_{sigma} = 0.0165) which were used in all calculations. The final R_1 was 0.0327 (I > 2σ(I)) and wR_2 was 0.0895 (all data). Flack parameter = –0.02(6)

Crystal data for compounds **2**: mp 220–221 ℃, $C_{27}H_{33}N_5O_6$, M = 523.58 g/mol, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.58993(7) Å, b = 10.68072(7) Å, c = 28.6559(2) Å, V = 2629.09(3) Å^3, Z = 4, T = 293(2) K, μ(CuKα) = 0.782 mm^{-1}, *Dcalc* = 1.323 g/cm^3, 24101 reflections measured (6.168° ≤ 2Θ ≤ 137.368°), 4759 unique (R_{int} = 0.0281, R_{sigma} = 0.0138) which were used in all calculations. The final R_1 was 0.0354 (I > 2σ(I)) and wR_2 was 0.0997. Flack parameter = 0.03 (5)

Crystal data for compounds **4**: mp 270–271 ℃, $C_{26}H_{33}N_5O_6$, M =511.57 g/mol, monoclinic, space group $P2_1$ (no. 4), a = 9.91935(9) Å, b = 8.16154(7) Å, c = 15.73111(16) Å, β = 92.8934(9) °, V = 1271.92(2) Å^3, Z = 2, T = 293(2) K, μ(CuKα) = 0.794 mm^{-1}, *Dcalc* = 1.336 g/cm^3, 25191 reflections measured (5.626° ≤ 2Θ ≤ 136.356 °), 4472 unique (R_{int} = 0.0352, R_{sigma} = 0.0149) which were used in all calculations. The final R_1 was 0.0276 (I > 2σ(I)) and wR_2 was 0.0697 (all data). Flack parameter = 0.04(5).