Supporting Information

Effective self-assembly of 21- and 14-membered azamacrocycles via condition-controlled cyclotrimerization or cyclodimerization of different thiosemicarbazide-based precursors

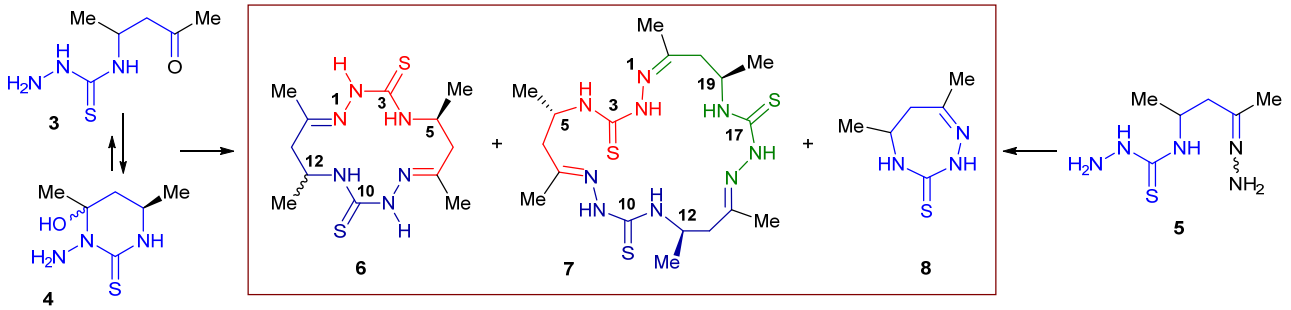
Anastasia A. Fesenko,[a] Mikhail S. Grigoriev[a] and Anatoly D. Shutalev*[b]

[a] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Leninsky Ave., Bldg 4, 119071 Moscow, Russian Federation*

[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Ave., 119991 Moscow, Russian Federation*

Contents

Table 1 Synthesis of cyclic thiosemicarbazones **6**, **7**, and **8**[a]



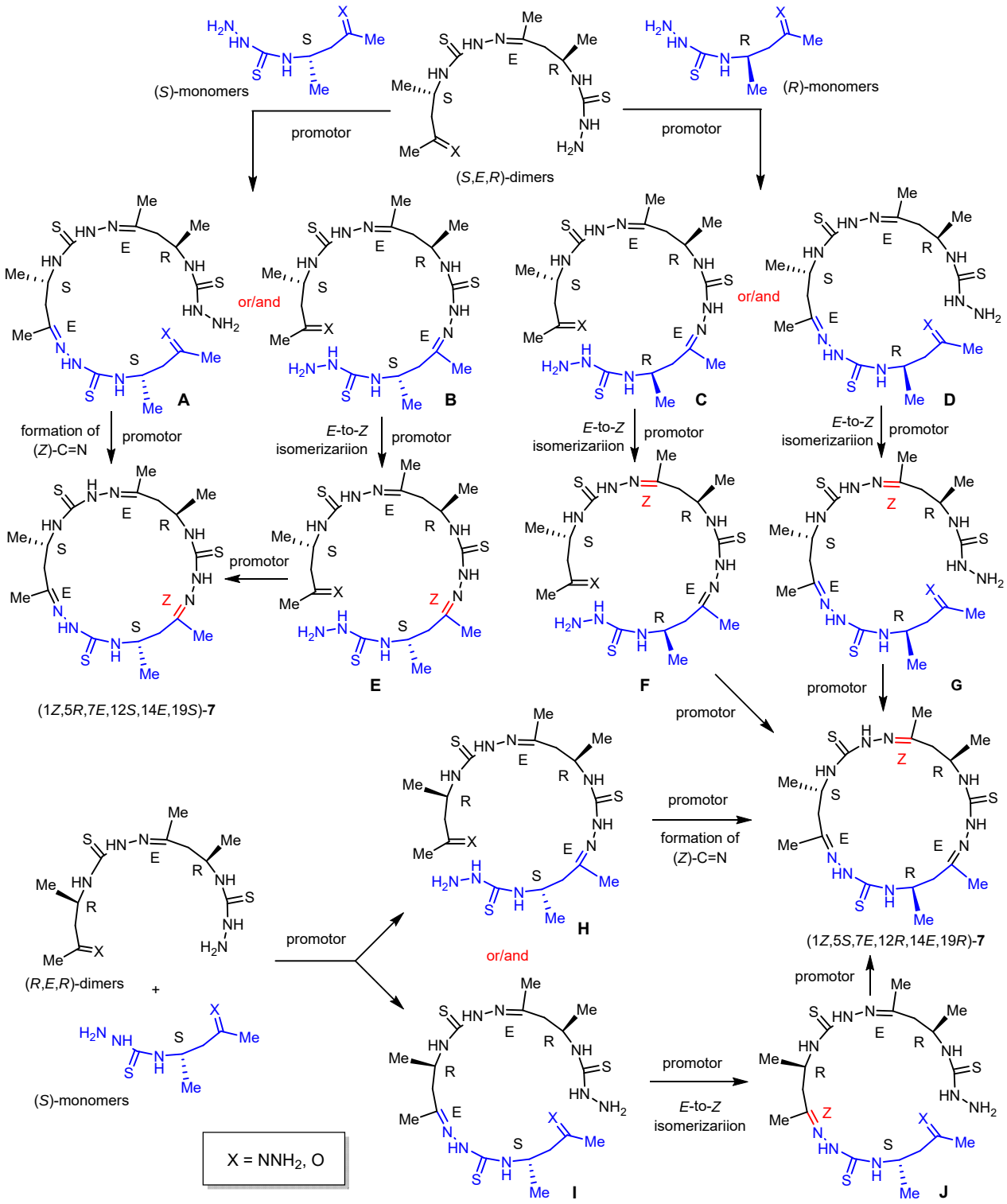
Entry	Substrate[b]	Promotor (equiv)	Solvent	Conc. of substrate, mmol/mL	Reaction conditions	Products distribution (%)[c]			Isolated yield[d,e] (%)
						6 (*cis*/*trans*)	**7**	**8**	
1	**3** + **4**	$TsOH·H_2O$ (0.09)	MeCN	0.22	reflux, 1.25 h	53 (73:27)	26	21	77
2	**3** + **4**	$TsOH·H_2O$ (0.10)	EtOH	0.24	reflux, 1.25 h	44 (72:28)	46	10	79
3	**3** + **4**	$TsOH·H_2O$ (0.30)	EtOH	0.21	reflux, 1.25 h	40 (74:26)	60	0	76
4	**3** + **4**	$TsOH·H_2O$ (0.10)	EtOH	0.066	reflux, 1.25 h	27 (64:36)	14	59	74
5	**3** + **4**	$TsOH·H_2O$ (0.10)	EtOH	0.21	rt, 1.25 h	12 (73:27)	25	63	-[f,g]
6	**3** + **4**	$TsOH·H_2O$ (0.10)	MeOH	0.21	reflux, 1.25 h	32 (73:27)	57	11	-[h,g]
7	**3** + **4**	AcOH (0.09)	EtOH	0.20	reflux, 1.25 h	22 (53:47)	12	66	-[i,g]
8	**3** + **4**	$NH_2OH·HCl$ (1.24)	EtOH	0.25	reflux, 2 h	10 (73:27)	88	2	84
9	**3** + **4**	$NH_2OH·HCl$ (1.75)	EtOH	0.25	reflux, 2 h	7 (77:23)	89	4	73
10	**3** + **4**	$NH_2OH·HCl$ (1.26)	EtOH	1.00	reflux, 2 h	1 (76:24)	96	3	74
11	**3** + **4**	$N_2H_4·H_2O$ (1.03) + $TsOH·H_2O$ (1.15)	MeCN	0.50	reflux, 2 h	99 (83:17)	1	0	84
12	**5**	$TsOH·H_2O$ (1.10)	MeCN	0.51	reflux, 2 h	99 (80:20)	1	0	91
13	**5**	$TsOH·H_2O$ (1.10)	MeCN	0.25	reflux, 6 h	96 (81:19)	4	0	84
14	**5**	$TsOH·H_2O$ (1.11)	MeCN	0.50	reflux, 0.5 h	86 (75:25)	14	0	83
15	**5**	$TsOH·H_2O$ (1.11)	MeCN	0.50	reflux, 0.25 h	79 (70:30)	21	0	85
16	**5**	$TsOH·H_2O$ (1.11)	MeCN	0.46	rt, 24 h	48 (87:13)	52	0	91
17	**5**	$TsOH·H_2O$ (1.11)	EtOH	0.47	reflux, 2 h	30 (81:19)	70	0	81
18	**5**	$TsOH·H_2O$ (1.11)	EtOH	0.50	reflux, 0.5 h	30 (83:17)	70	0	81
19	**5**	$TsOH·H_2O$ (1.10)	EtOH	0.50	rt, 24 h	18 (88:12)	81	1	87
20	**5**	$N_2H_4·H_2O$ (1.00) + $TsOH·H_2O$ (2.11)	EtOH	0.42	rt, 24 h	8 (89:11)	92	0	84

21	**5**	$TsOH·H_2O$ (1.11)	MeOH	1.00	reflux, 2 h	3 (79:21)	97	0	83
22	**5**	$TsOH·H_2O$ (1.11)	MeOH	0.20	reflux, 2 h	71 (78:22)	29	0	78
23	**5**	$N_2H_4·H_2O$ (1.00) + $TsOH·H_2O$ (2.11)	MeOH	1.00	reflux, 2 h	1 (74:26)	99	0	78
24	**5**	$N_2H_4·H_2O$ (1.00) + $TsOH·H_2O$ (2.12)	MeOH	0.20	reflux, 2 h	17 (80:20)	83	0	80
25	**5**	$TsOH·H_2O$ (1.10)	MeOH	0.95	rt, 24 h	18 (100:0)	82	0	87
26	**5**	$N_2H_4·H_2O$ (1.01) + $TsOH·H_2O$ (2.14)	MeOH	1.02	rt, 24 h	0	100	0	87
27	**5**	$N_2H_4·H_2O$ (1.01) + $TsOH·H_2O$ (2.11)	MeOH	0.57	rt, 24 h	0	99	1	84
28	**5**	$N_2H_4·H_2O$ (1.00) + $TsOH·H_2O$ (2.10)	MeOH	0.41	rt, 24 h	0	100	0	91
29	**5**	$N_2H_4·H_2O$ (1.01) + $TsOH·H_2O$ (2.12)	MeOH	0.33	rt, 24 h	1 (84:16)	99	0	80
30	**5**	$NH_2OH·HCl$ (1.01) + $TsOH·H_2O$ (1.12)	MeOH	0.50	rt, 24 h	3 (98:2)	90	7	73
31	**5**	$CH_3NH_2·HCl$ (1.00) + $TsOH·H_2O$ (1.13)	MeOH	0.50	rt, 24 h	9 (100:0)	90	1	77

[a] In all cases, the conversion of the starting material was complete, with the exception of entry 7, where the conversion was 98%. After completion of the reaction, solvent was removed under reduced pressure, solid residue was triturated with a saturated aqueous $NaHCO_3$ (entries 1-7, 11-31) or with water (entry 8-10), suspension was cooled to 0°C, precipitate was filtered, washed with cold water, and dried. [b] Substrate **5** was the 85:15 mixture of (*E*)- and (*Z*)-izomers, substrate **3** + **4** was the 90:10 mixture of pyrimidine **4** (two diastereomers, 75:25) and thiosemicarbazide **3**. Substrate **5** or **3** + **4** loading was 0.099–0.269 g, with the exception of entry 13 (0.489 g) and entry 26 (1.395 g). [c] According to ^{1}H NMR spectroscopic data for the crude products. [d] Total yield of the heterocyclization product(s). [e] Reactions in EtOH or MeOH gave products containing a significant amount (up to 49 mol%) of the corresponding alcohol (very strong solvates). In these cases, the product yields shown in the table were corrected based on ^{1}H NMR analysis of the crude products. [f] Significant amount of unidentified by-products was also formed; ^{1}H NMR estimated purity of heterocycles was about 27%. [g] Purity was estimated using ^{1}H NMR spectra of the crude products comparing the expected and observed integral intensities of proton signals at intervals of 9.6–10.6 ppm (NH–N proton) and 7.5–8.6 ppm (N*H*-CH proton). [h] Some amount of unidentified by-products was also formed; ^{1}H NMR estimated purity of heterocycles was about 80%. [i] Significant amount of unidentified by-products was also formed; ^{1}H NMR estimated purity of heterocycles was about 42%.

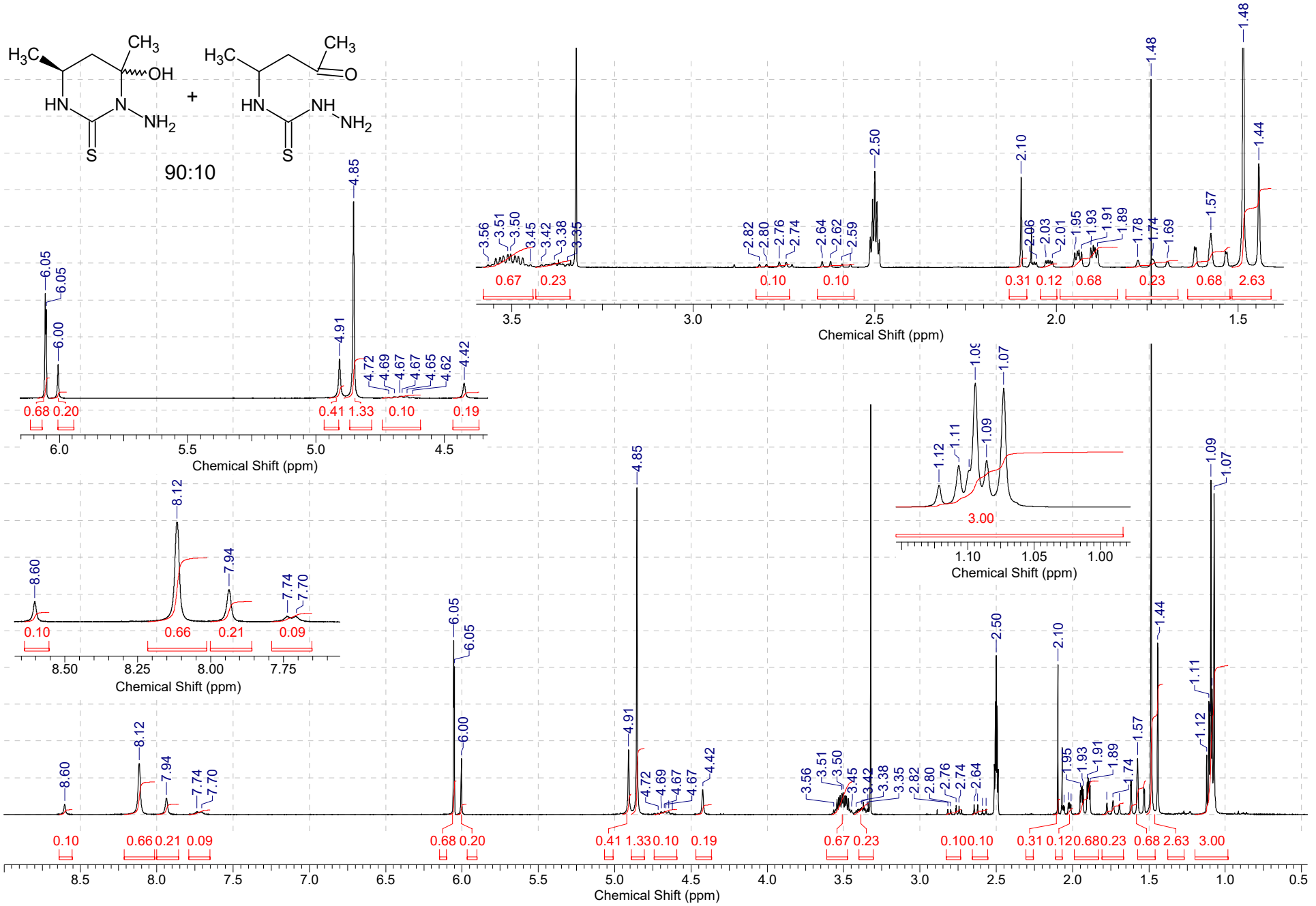
Discussion of the stereoselectivity of the formation of macrocycle 7

As an example, Scheme 1 demonstrates plausible pathways for the stereoselective formation of (1*Z*,5*R*,7*E*,12*S*,14*E*,19*S*)- and (1*Z*,5*S*,7*E*,12*R*,14*E*,19*R*)-enantiomers of macrocycle **7** by the reaction of (*S*,*E*,*R*)- and (*R*,*E*,*R*)-diastereomers of the dimers **9** or **11** with enantiomers of the corresponding monomers **5** and **3** in the presence of a promotor. Clearly, each the reaction can proceed with the participation of the thiosemicarbazide NH_2 group of both the reactants to give two possible trimers with (*Z*)-configuration or, preferably, with (*E*)-configuration of the new C=N bond. Thus, the reaction of the (*S*,*E*,*R*)-dimers **9** or **11** with the corresponding (*S*)-monomers **5** and **3** gives the trimers **A** or/and **B**. For simplicity, only (*E*)-configuration of the new C=N bond is shown. Next, trimer **A** cyclizes with the formation of the C=N bond with (*Z*)-configuration to afford (1*Z*,5*R*,7*E*,12*S*,14*E*,19*S*)-**7**. The latter is also obtained from trimer **B** through its preliminary *E*-to-*Z* izomerization to trimer **E**. Similarly, the reaction of the (*S*,*E*,*R*)-dimers **9** or **11** with the corresponding (*R*)-monomers **5** and **3** gives the trimers **C** or/and **D**, which after *E*-to-*Z* izomerization to the corresponding trimers **F** and **G** followed by cyclization transform into (1*Z*,5*S*,7*E*,12*R*,14*E*,19*R*)-enantiomer of macrocycle **7**. The latter is also formed by the reaction of the (*R*,*E*,*R*)-dimers **9** or **11** with the corresponding (*S*)-monomers **5** and **3** through the intermediate trimers **H**, **I**, and **J** as shown in Scheme 10. Clearly, the reaction of the (*R*,*E*,*R*)-dimers **9** or **11** with the corresponding (*R*)-monomers **5** and **3**, which is not presented in Scheme 10, cannot lead in a simple way to the target stereoisomer of macrocycle **7**. Apparently, this reaction does not occur due to its very low rate.

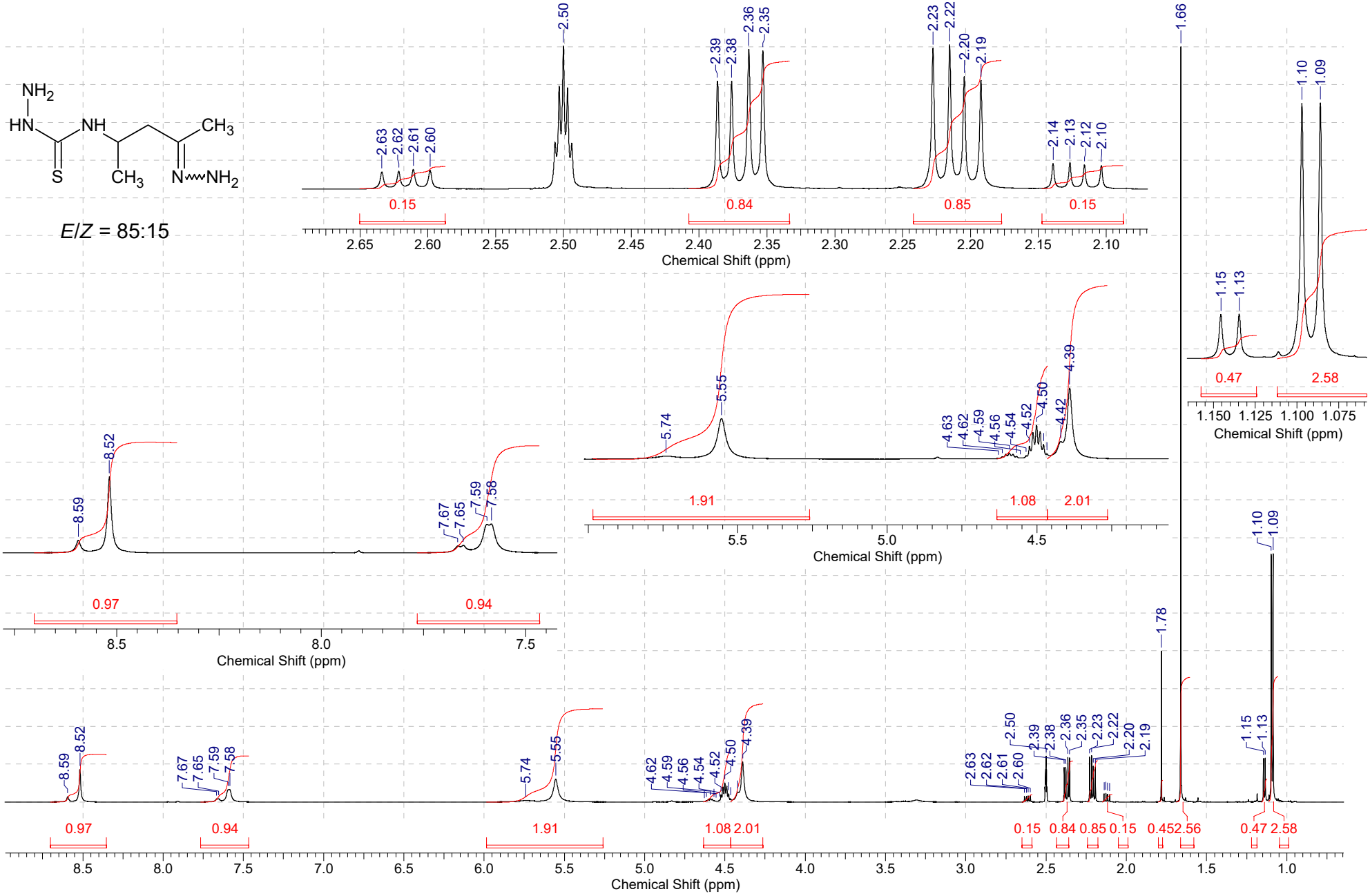


Scheme 1 Plausible pathways for the stereoselective formation of (1*Z*,5*R**,7*E*,12*S**,14*E*,19*S**)-**7** via the reaction of dimers **9** or **11** with the corresponding monomers **5** and **3** in the presence of promotor.

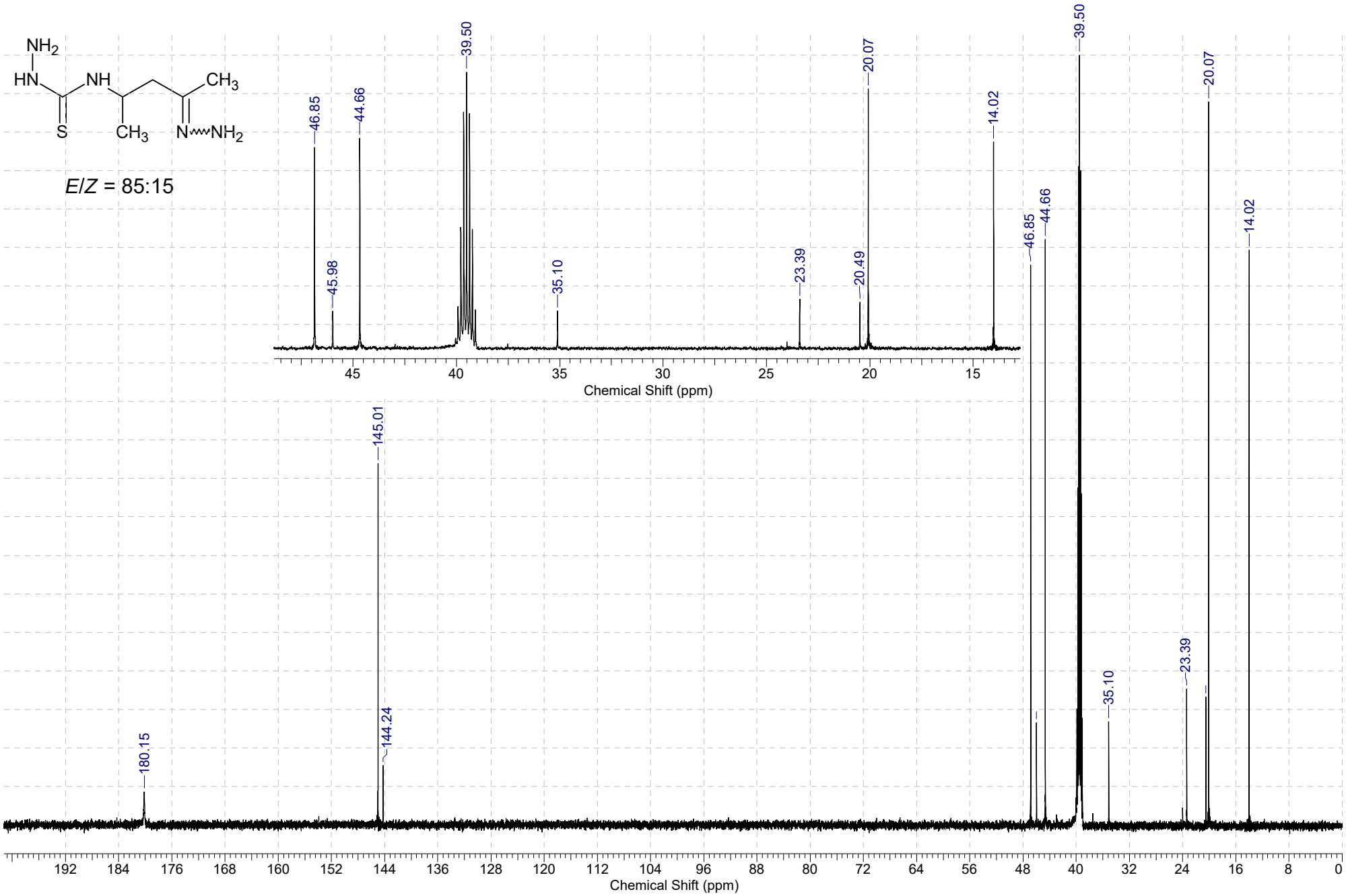
^{1}H NMR spectrum of a 90:10 mixture of pyrimidine **4** (two diastereomers, 75:25) and its acyclic isomer, thiosemicarbazide **3** (300.13 MHz, DMSO-d_6)



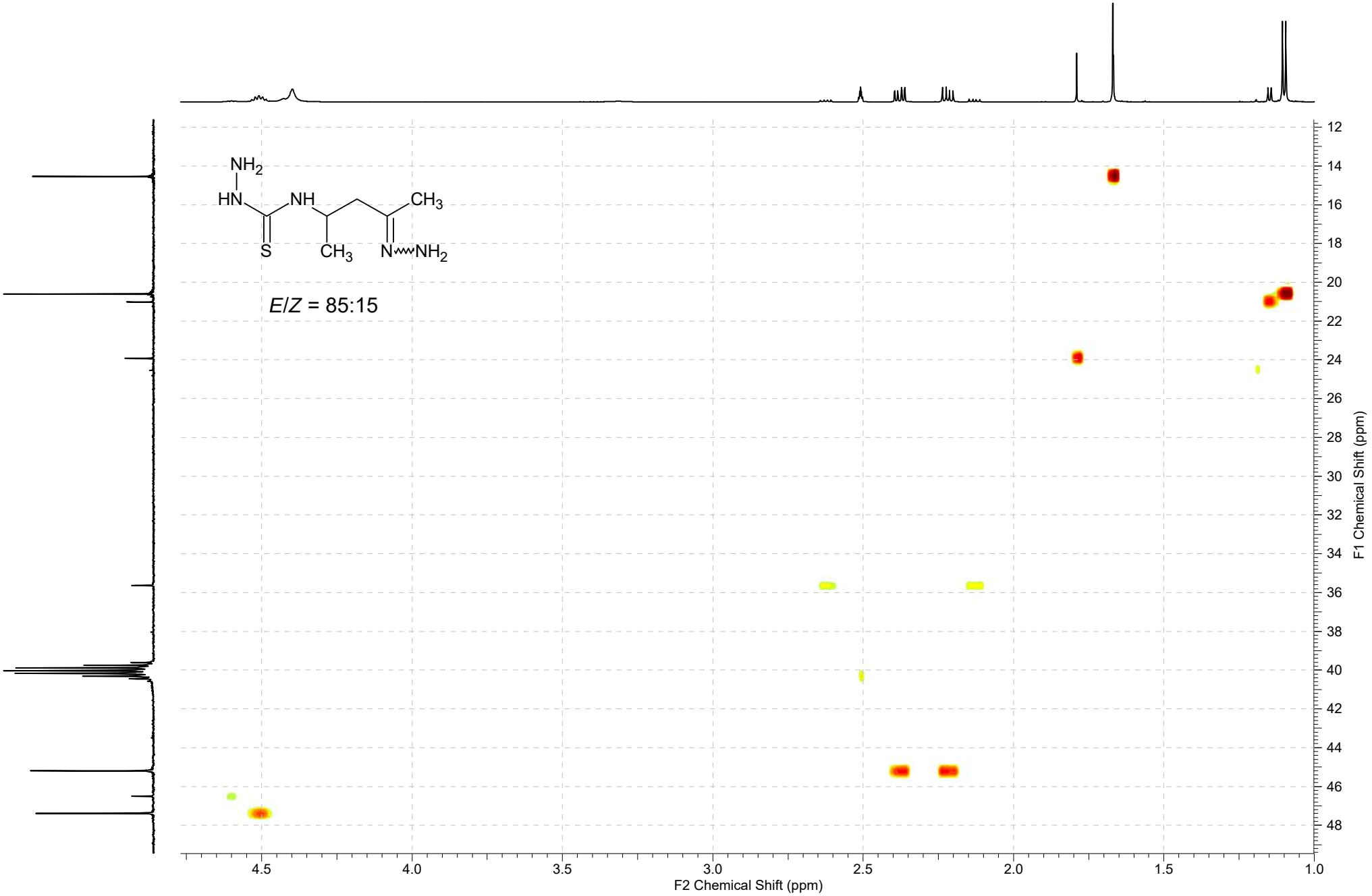
[1]H NMR spectrum of crude hydrazone **5** (mixture of *E*- and *Z*-isomers in a ratio of 85:15) (600.13 MHz, DMSO-d_6)



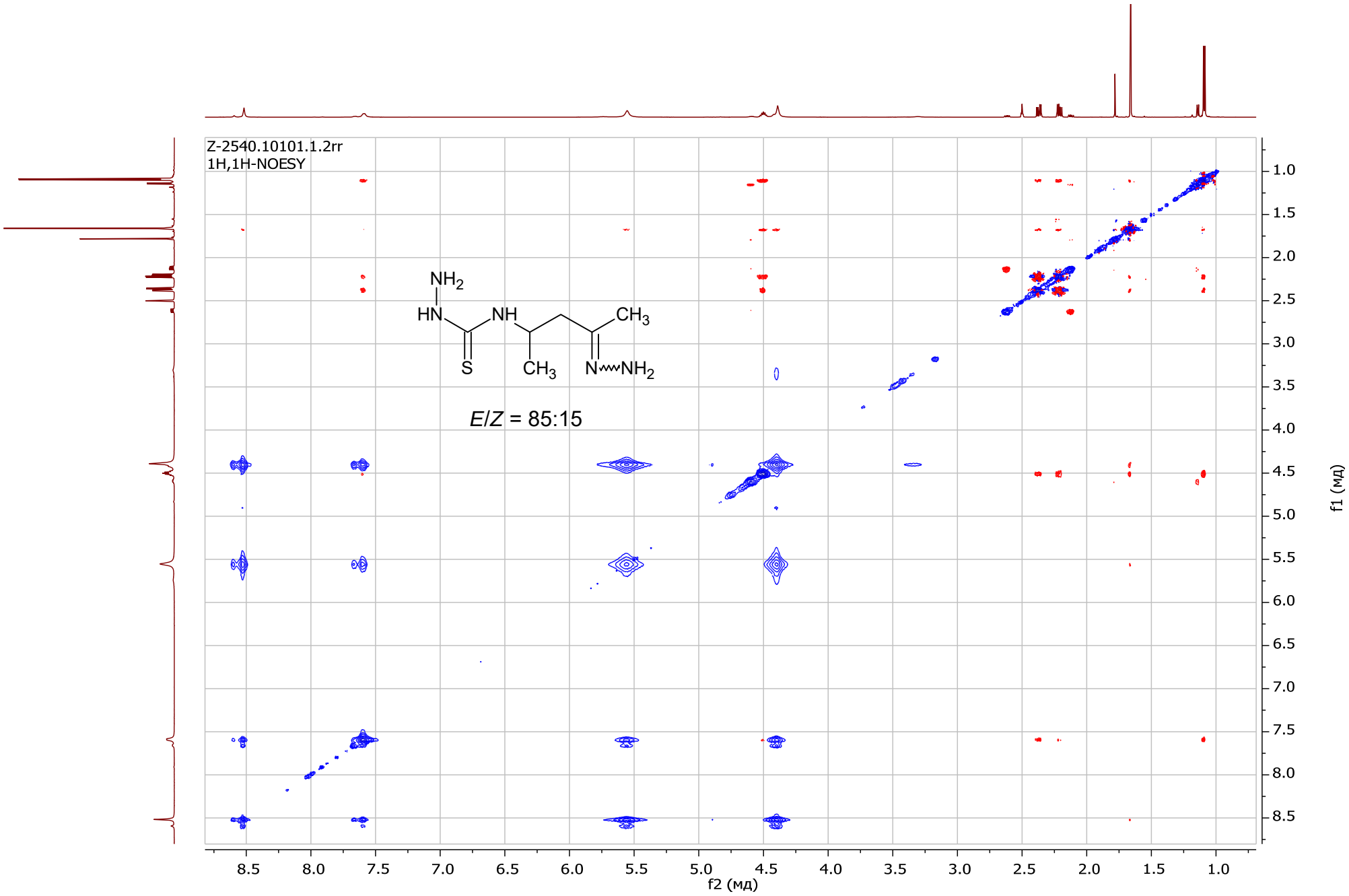
^{13}C NMR spectrum of crude hydrazone **5** (mixture of *E*- and *Z*-isomers in a ratio of 85:15) (150.90 MHz, DMSO-d_6)



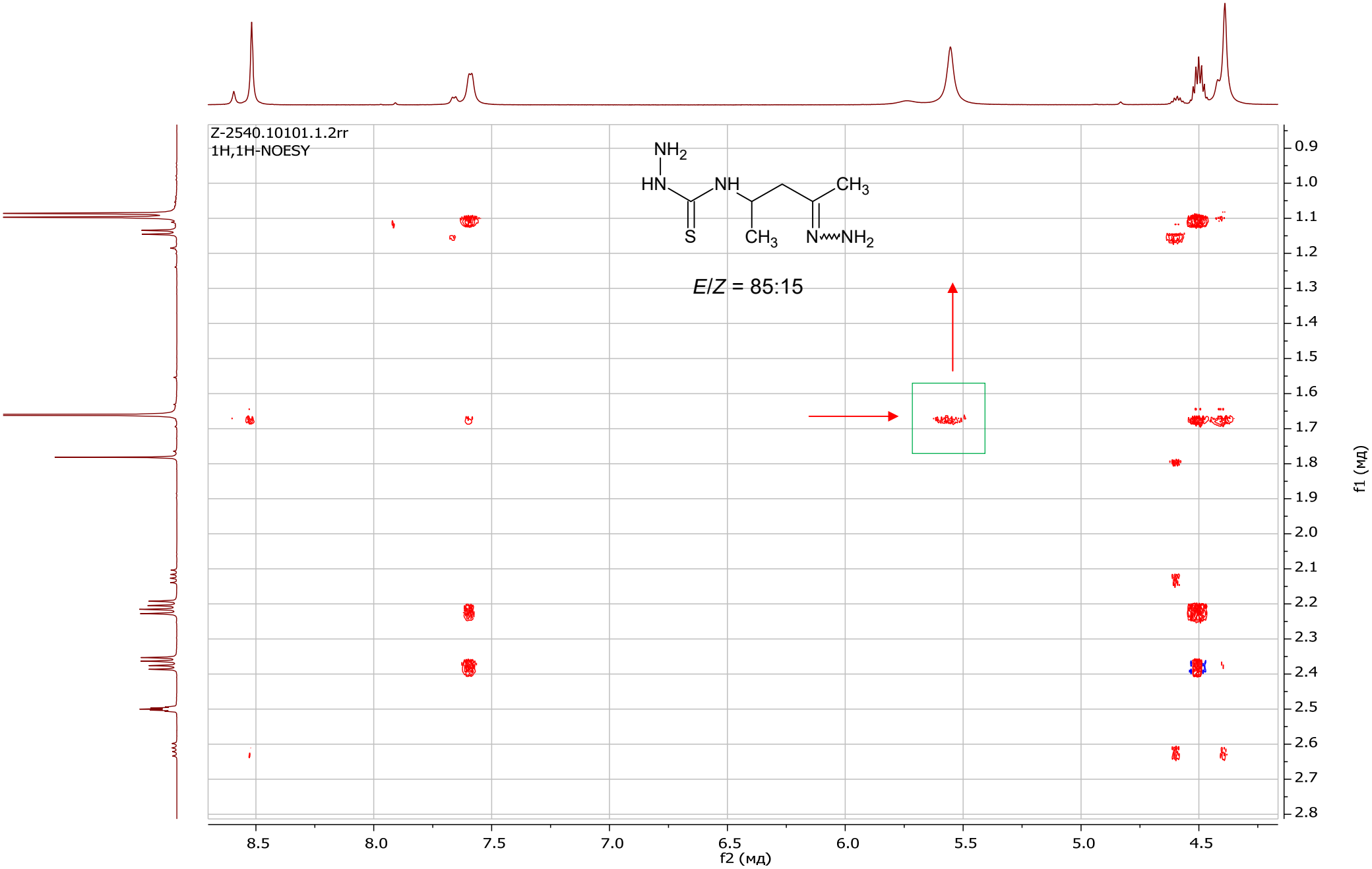
$^{1}H,^{13}C$ HSQC spectrum of crude hydrazone **5** (mixture of *E*- and *Z*-isomers in a ratio of 85:15) (Bruker Avance III, DMSO-d_6)



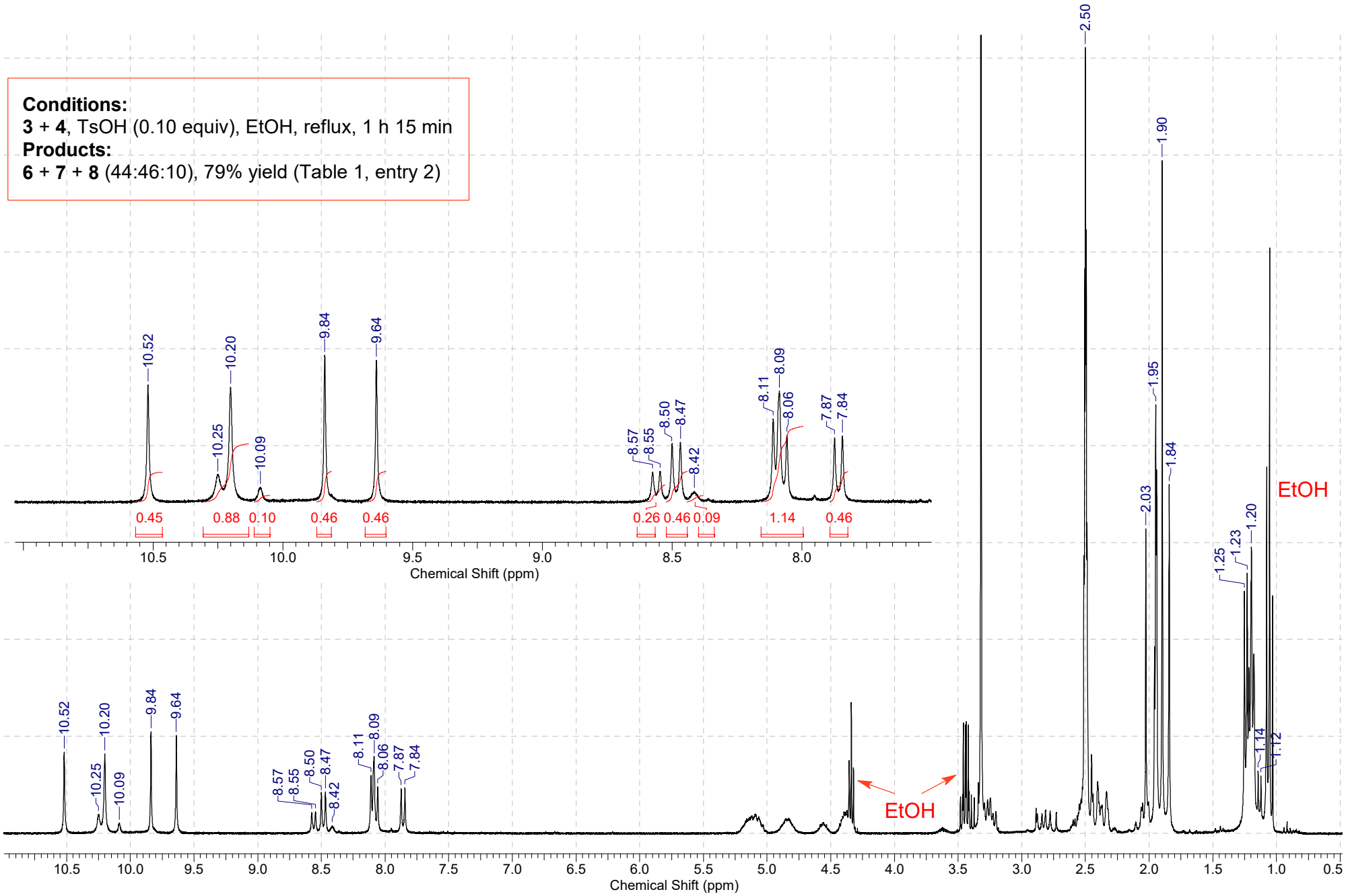
^{1}H,^{1}H NOESY spectrum of crude hydrazone **5** (mixture of *E*- and *Z*-isomers in a ratio of 85:15) (600.13 MHz, DMSO-d_6)



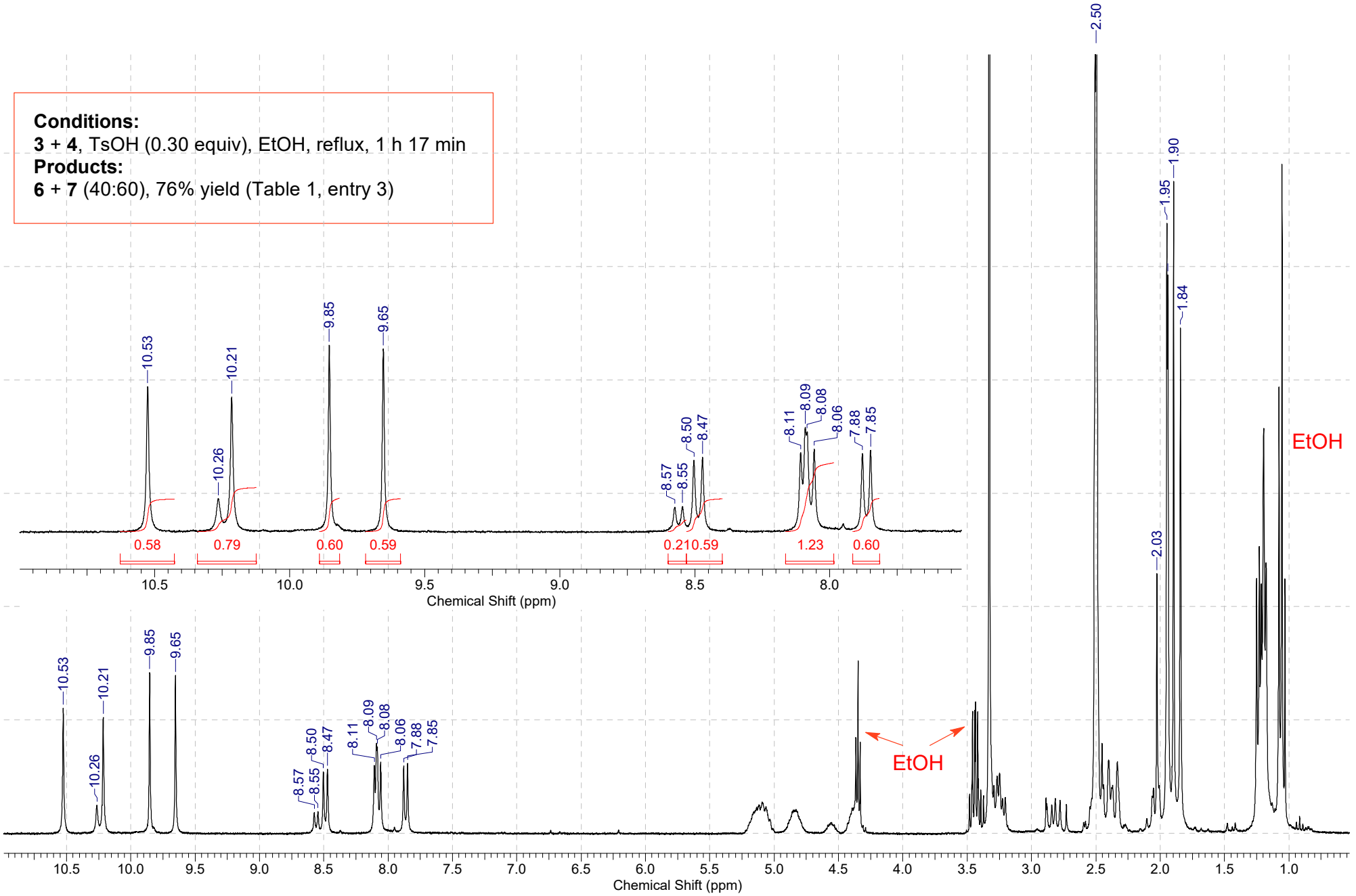
Fragment of ^{1}H,^{1}H NOESY spectrum of crude hydrazone **5** (mixture of *E*- and *Z*-isomers in a ratio of 85:15) (600.13 MHz, DMSO-d_6)



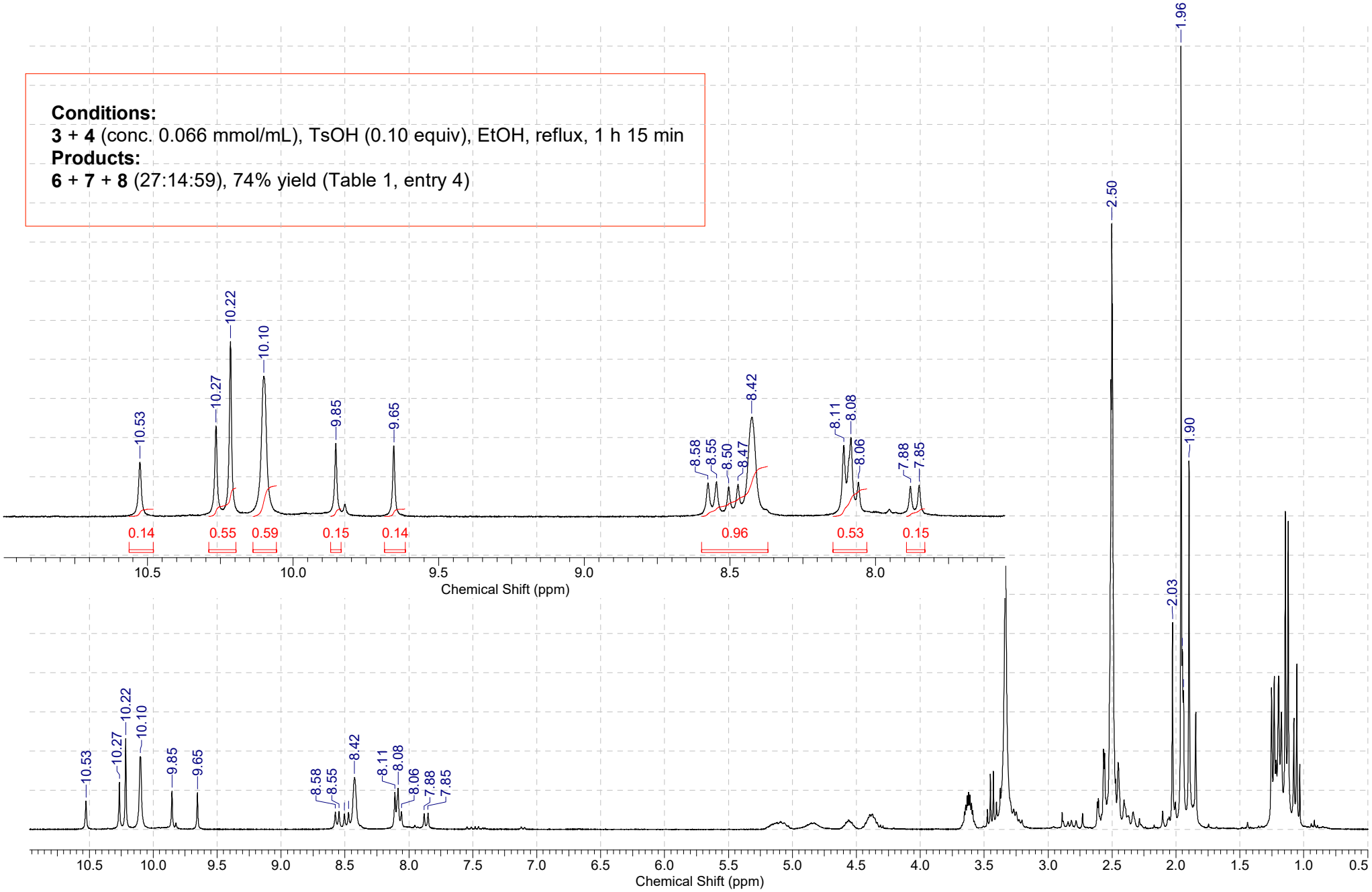
^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of the **3**+**4** mixture (Table 1, entry 2) (300.13 MHz, DMSO-d_6)



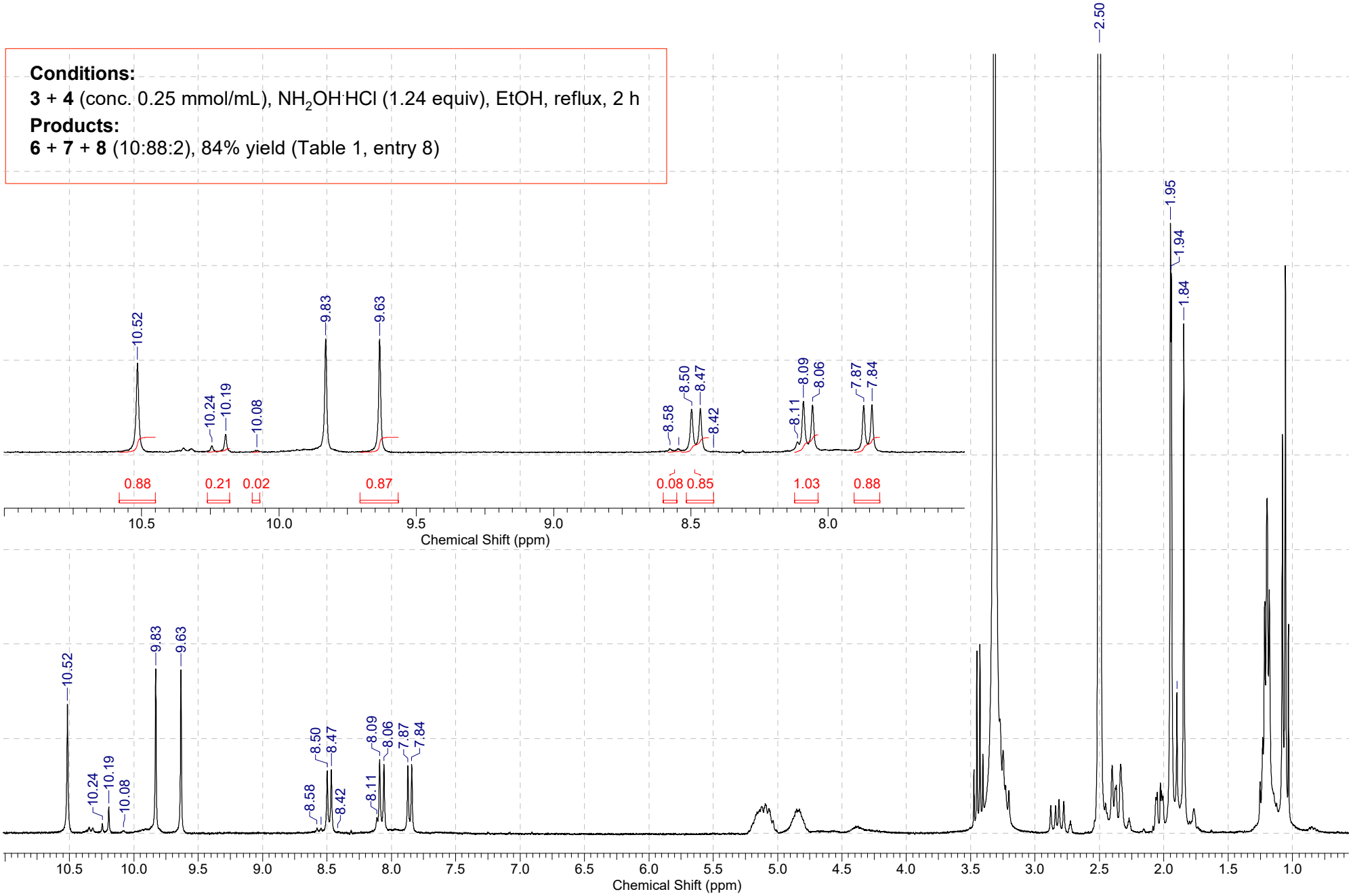
^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of the **3**+**4** mixture (Table 1, entry 3) (300.13 MHz, DMSO-d_6)



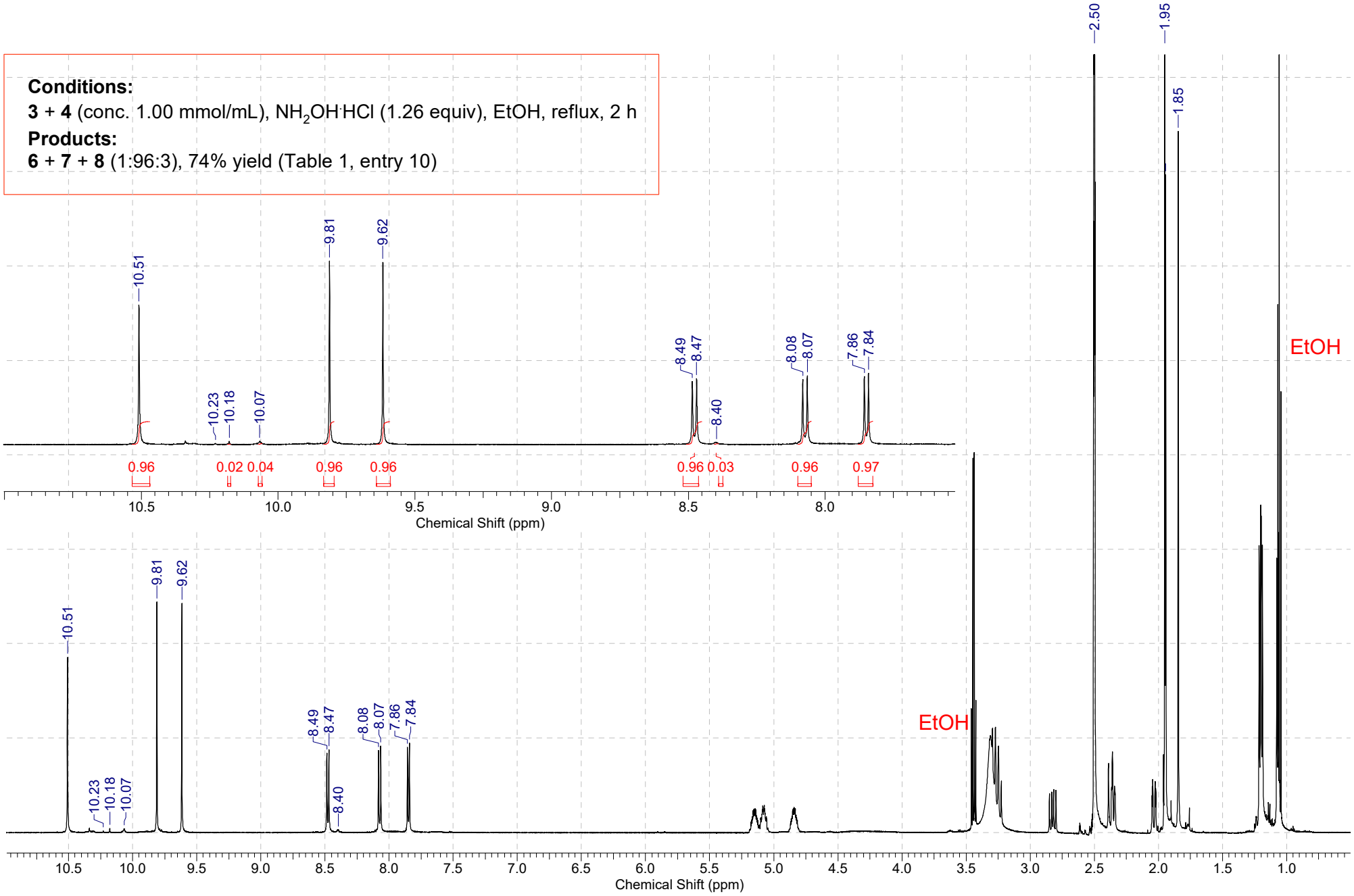
^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of the **3**+**4** mixture (Table 1, entry 4) (300.13 MHz, DMSO-d_6)



[1]H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of the **3**+**4** mixture (Table 1, entry 8) (300.13 MHz, DMSO-d_6)

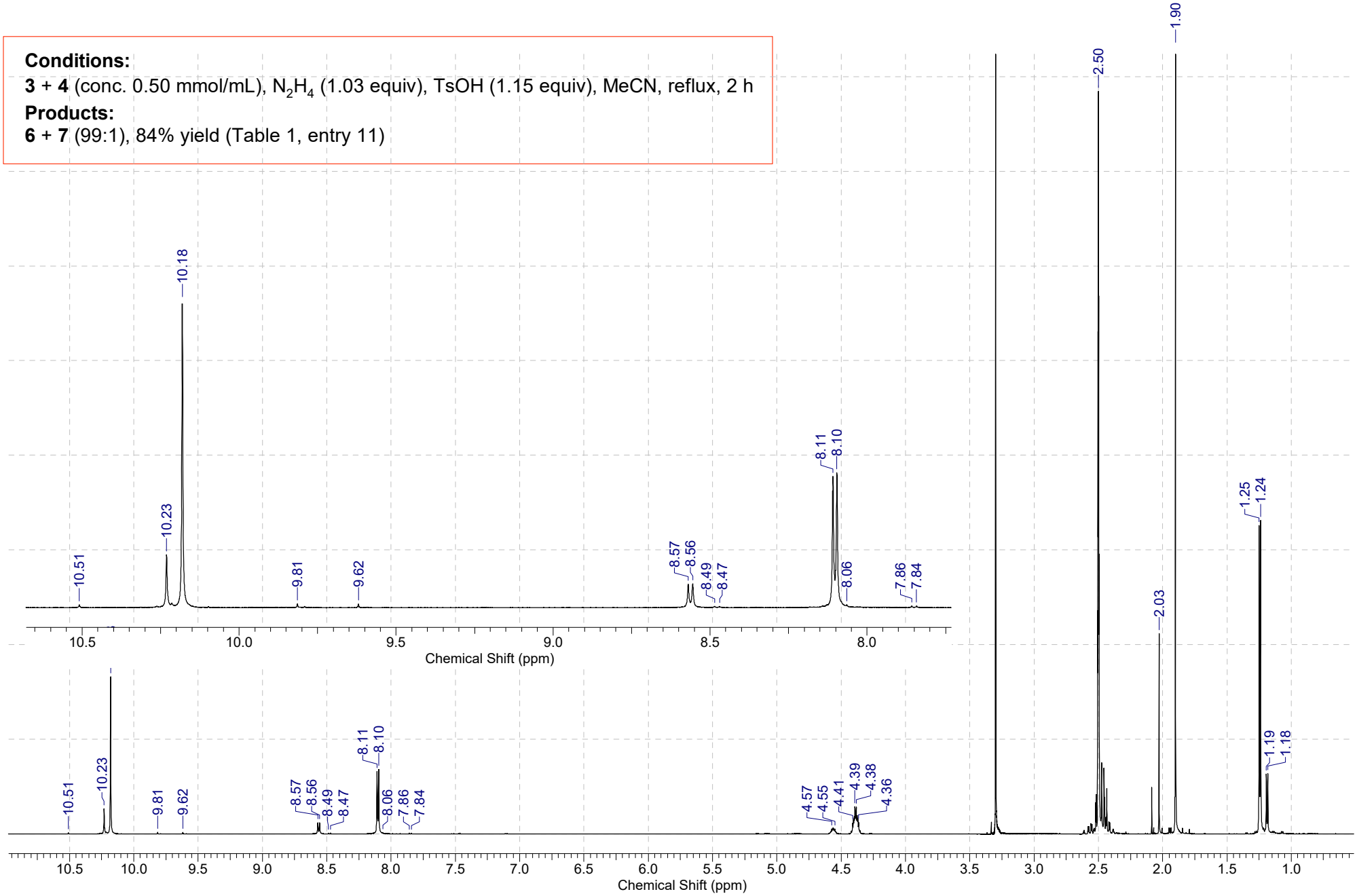


^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of the **3**+**4** mixture (Table 1, entry 10) (600.13 MHz, DMSO-d_6)

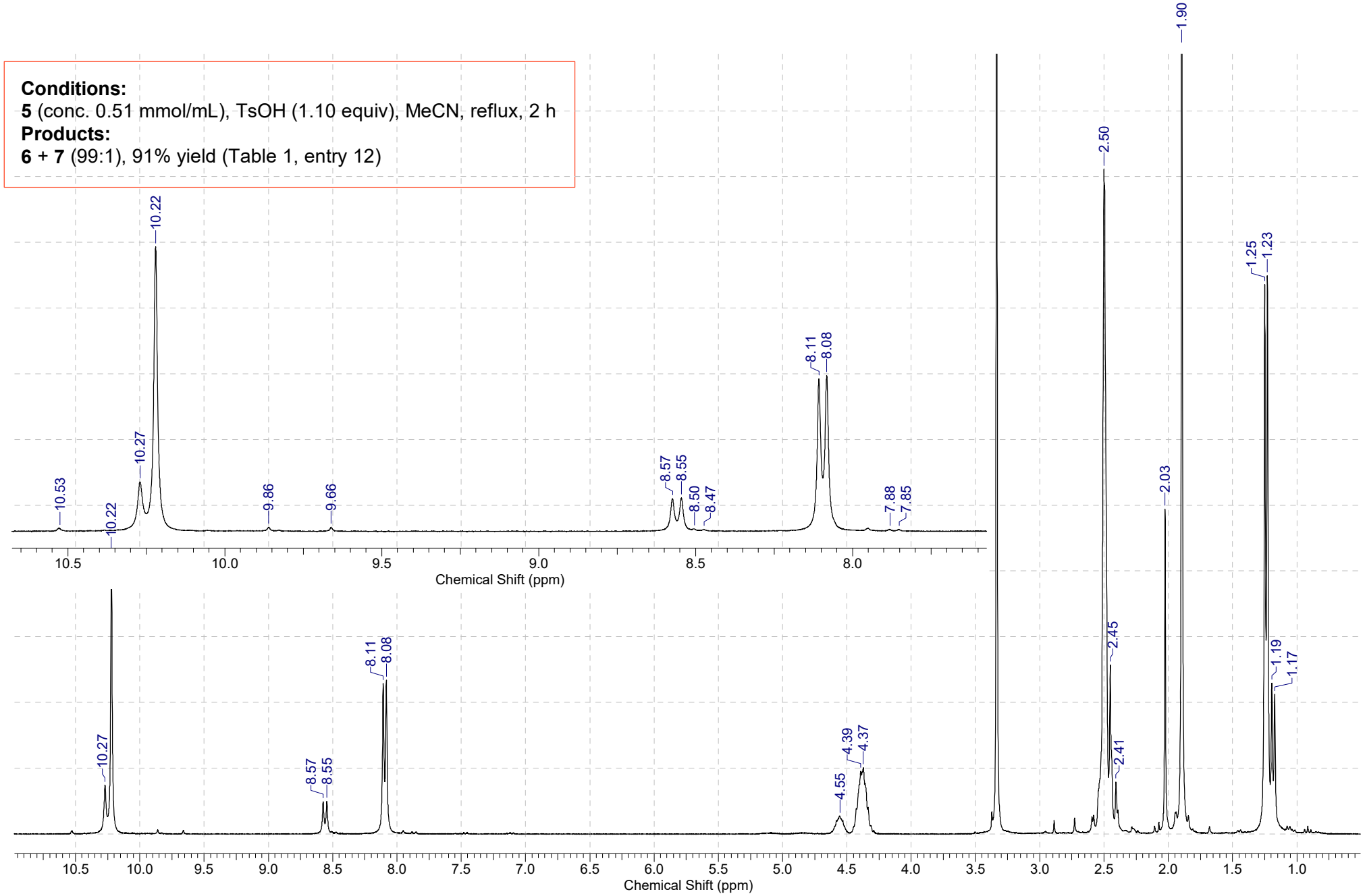


[1]H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of the **3**+**4** mixture (Table 1, entry 11) (600.13 MHz, DMSO-d_6)

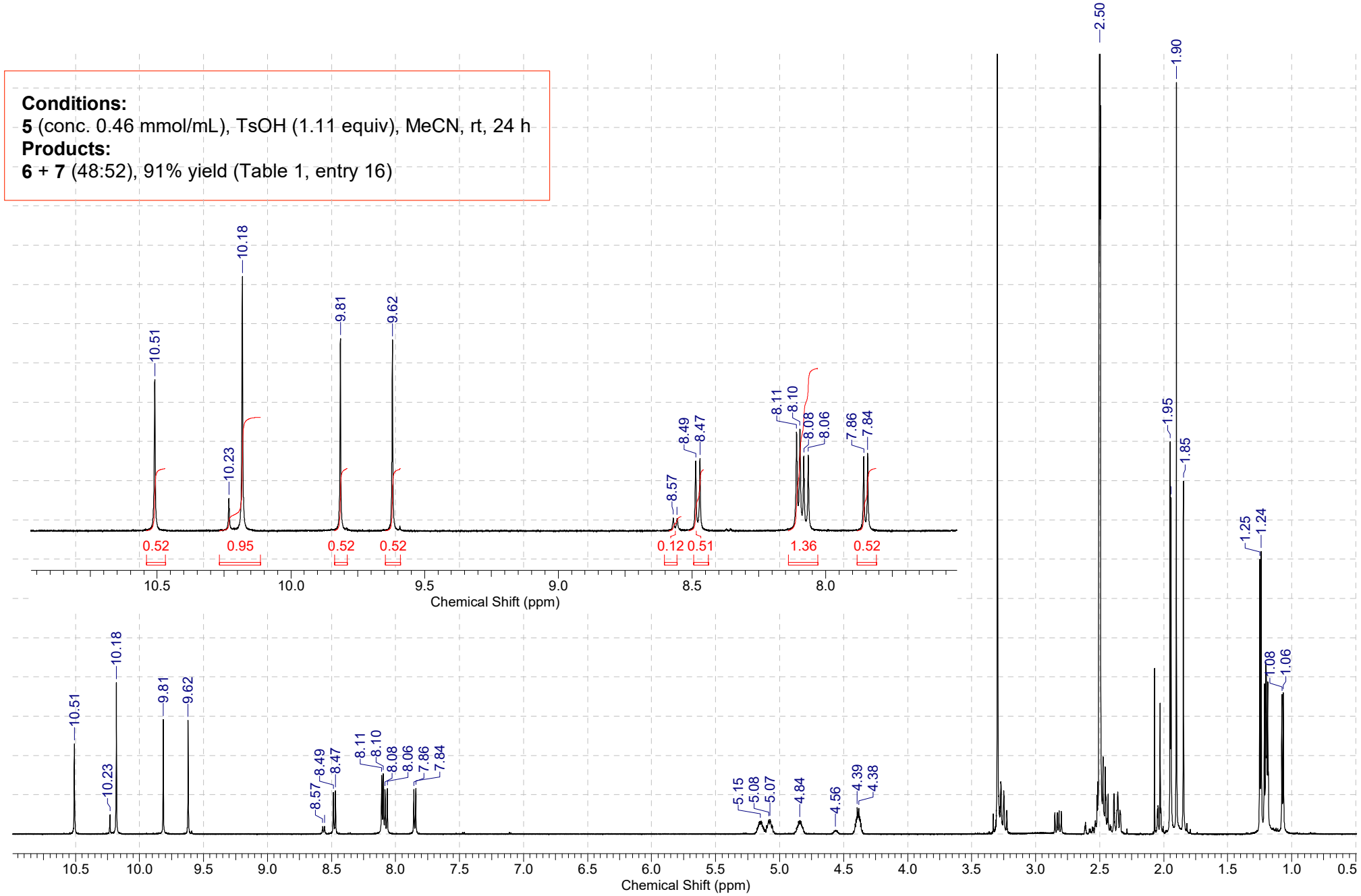
Conditions:
3 + **4** (conc. 0.50 mmol/mL), N_2H_4 (1.03 equiv), TsOH (1.15 equiv), MeCN, reflux, 2 h
Products:
6 + **7** (99:1), 84% yield (Table 1, entry 11)



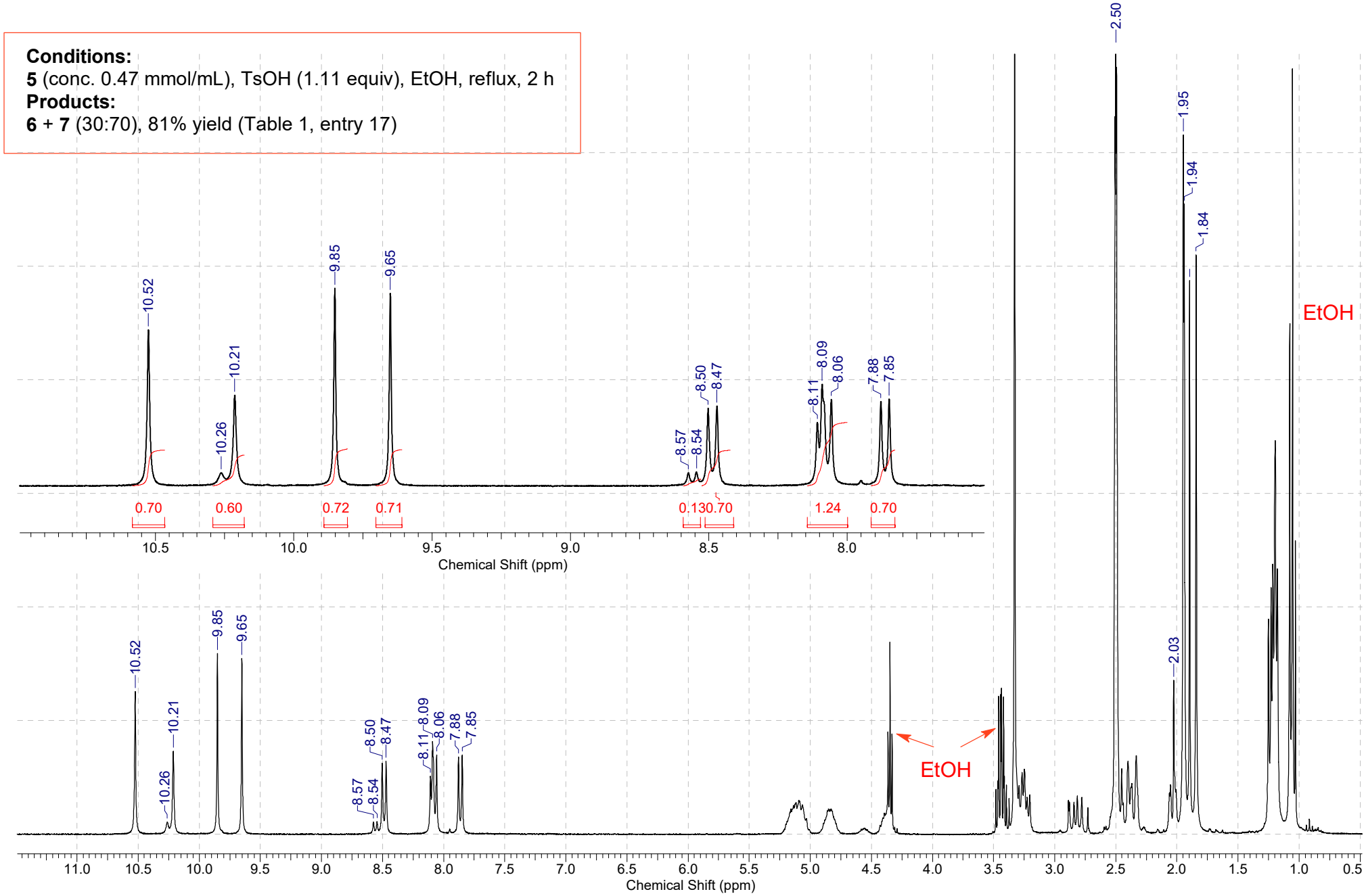
^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of hydrazone **5** (Table 1, entry 12) (300.13 MHz, DMSO-d_6)



^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of hydrazone **5** (Table 1, entry 16) (600.13 MHz, DMSO-d_6)

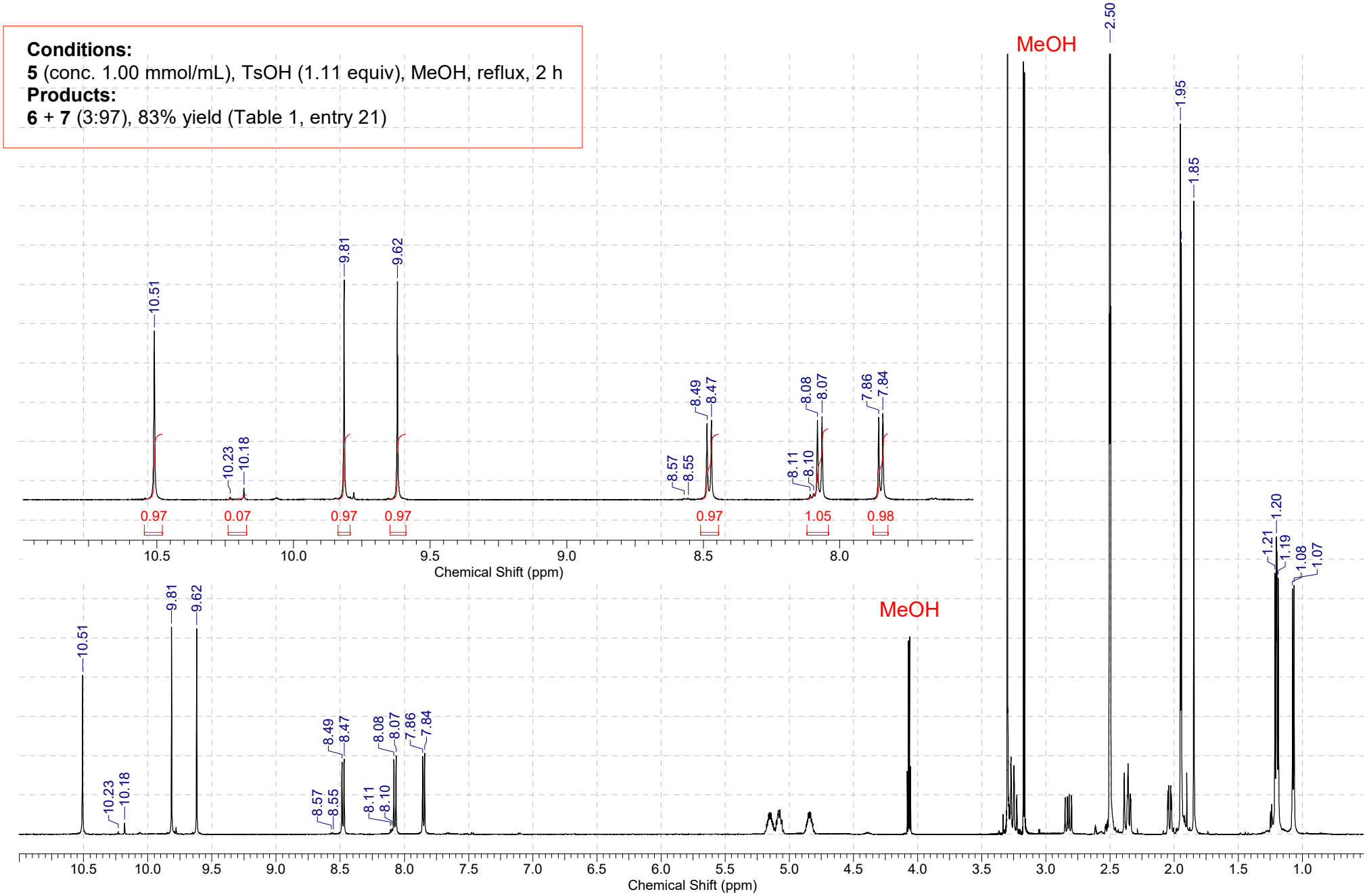


[1]H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of hydrazone **5** (Table 1, entry 17) (600.13 MHz, DMSO-d_6)

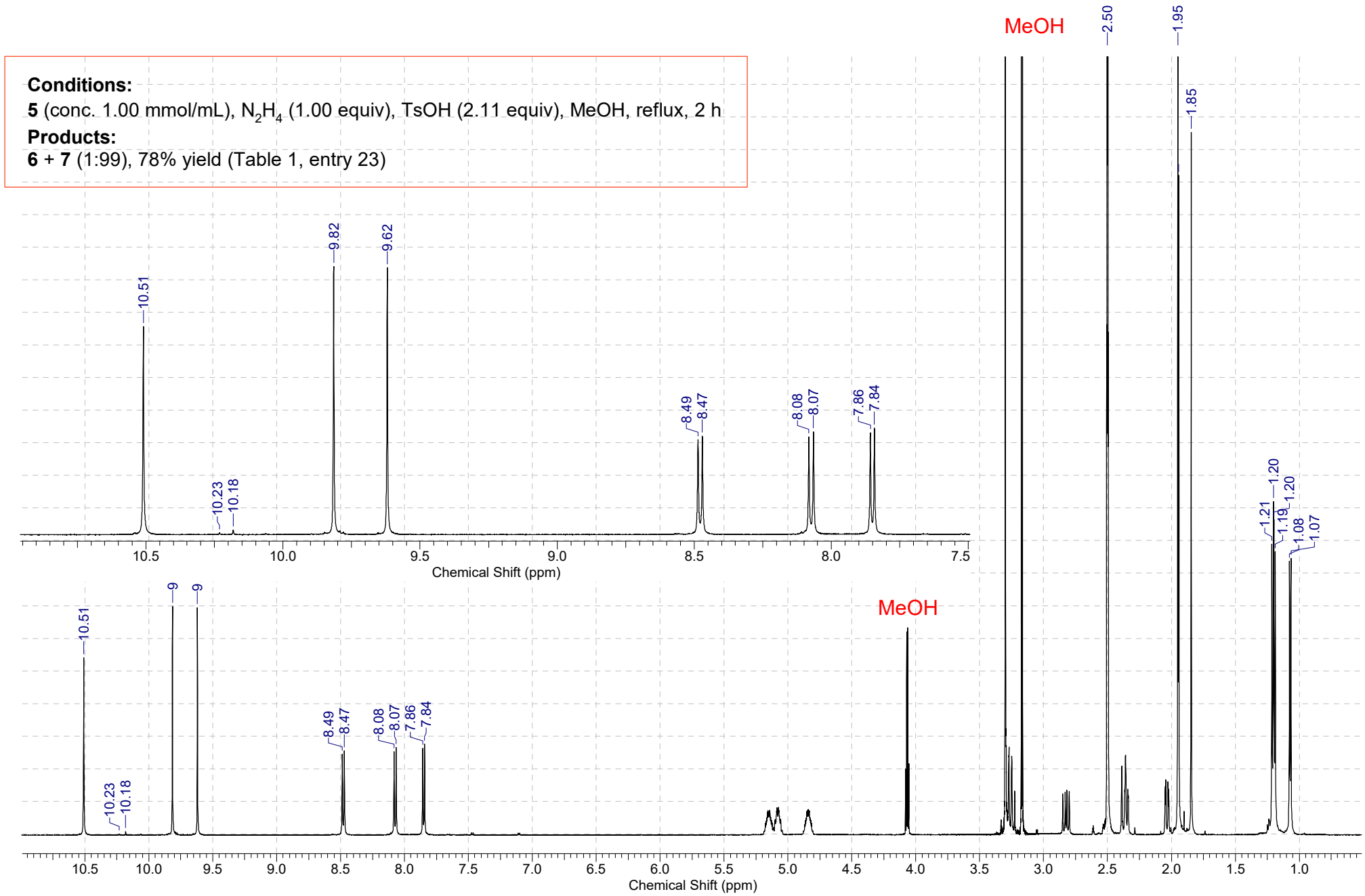


^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of hydrazone **5** (Table 1, entry 21) (600.13 MHz, DMSO-d_6)

Conditions:
5 (conc. 1.00 mmol/mL), TsOH (1.11 equiv), MeOH, reflux, 2 h
Products:
6 + **7** (3:97), 83% yield (Table 1, entry 21)

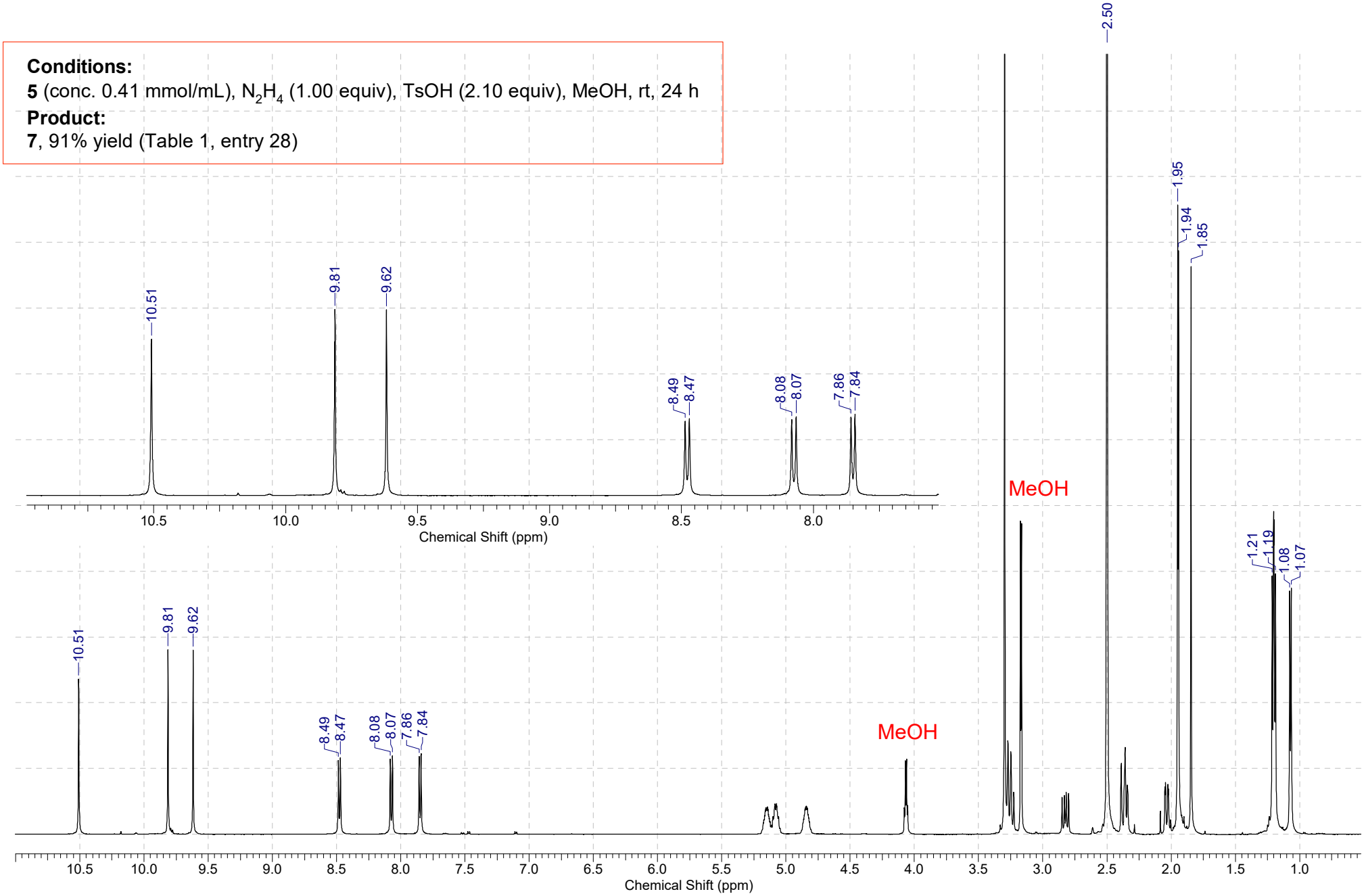


^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of hydrazone **5** (Table 1, entry 23) (600.13 MHz, DMSO-d_6)

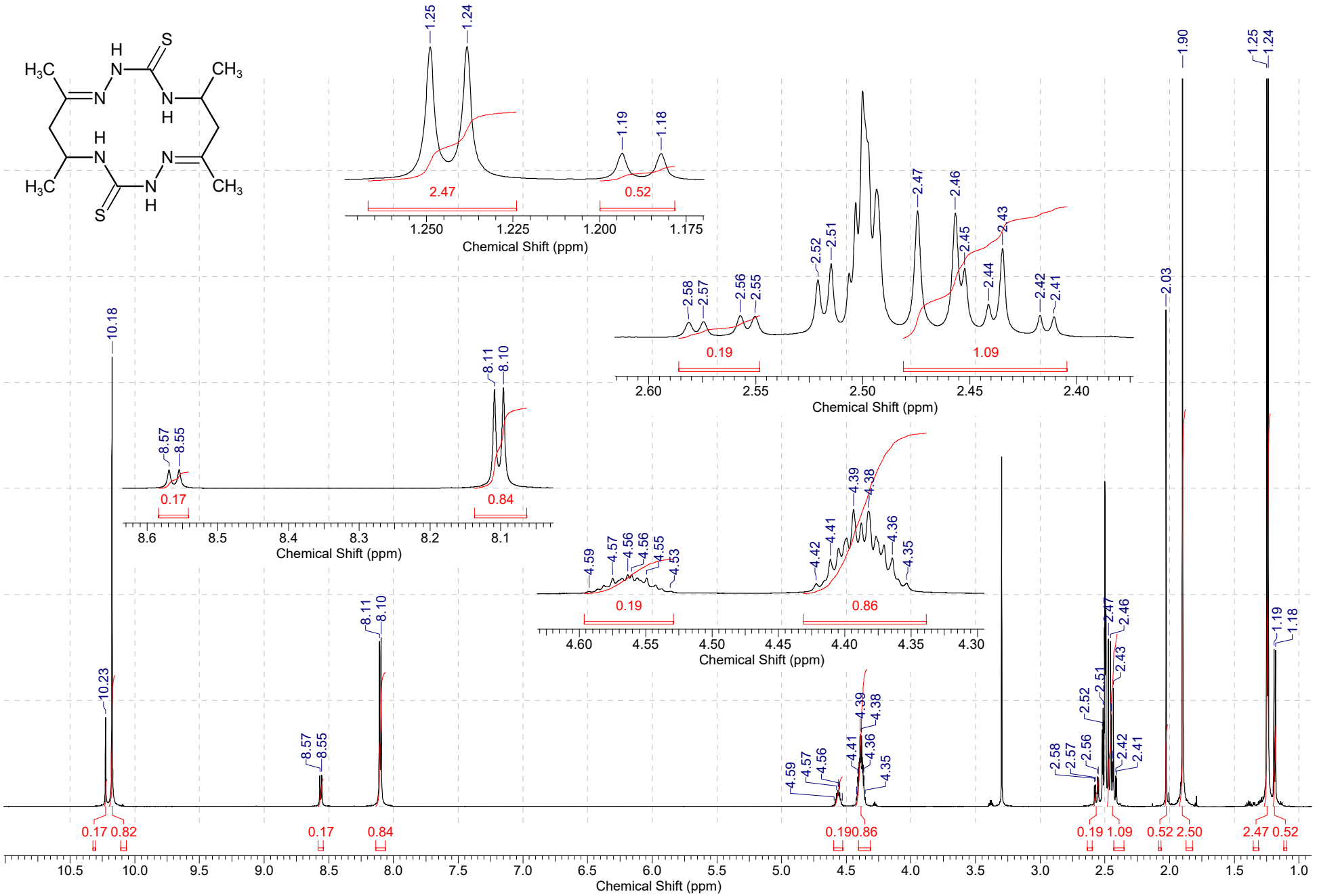


^{1}H NMR spectrum of the crude product formed by the acid-catalyzed cyclization of hydrazone **5** (Table 1, entry 28) (600.13 MHz, DMSO-d_6)

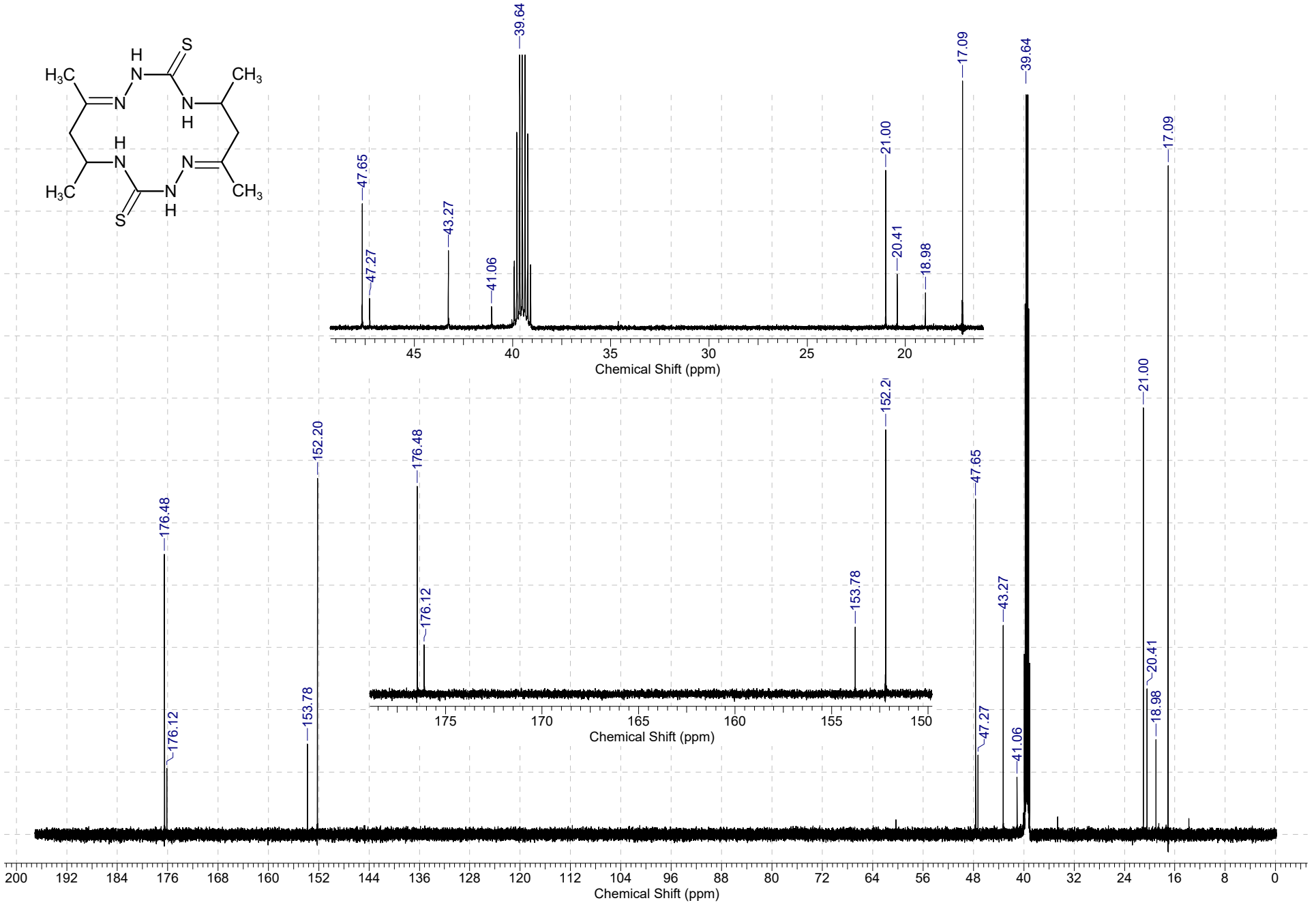
Conditions:
5 (conc. 0.41 mmol/mL), N_2H_4 (1.00 equiv), TsOH (2.10 equiv), MeOH, rt, 24 h
Product:
7, 91% yield (Table 1, entry 28)



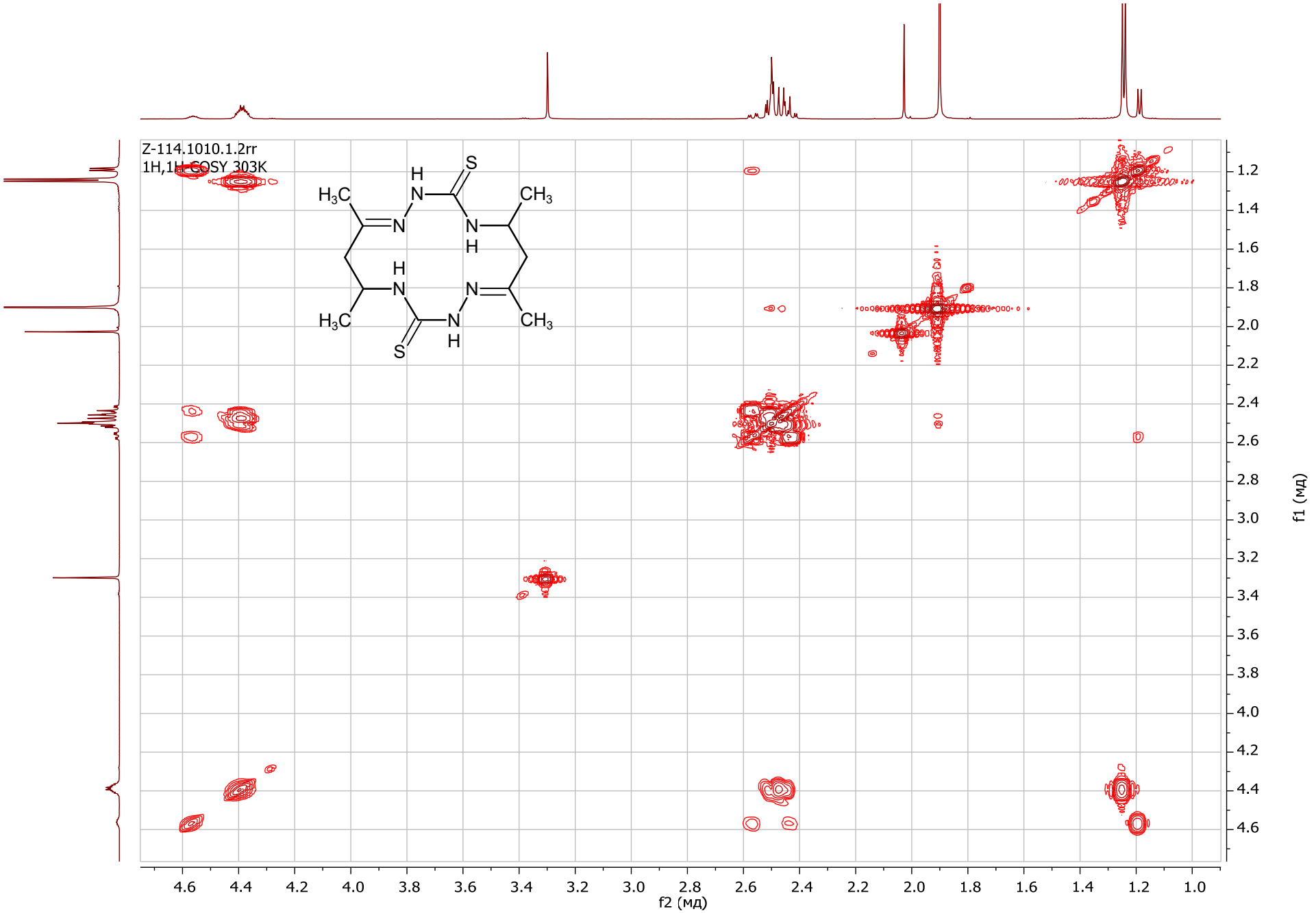
[1]H NMR spectrum of 14-membered cyclic bis-thiosemicarbazone **6** (600.13 MHz, DMSO-d_6)



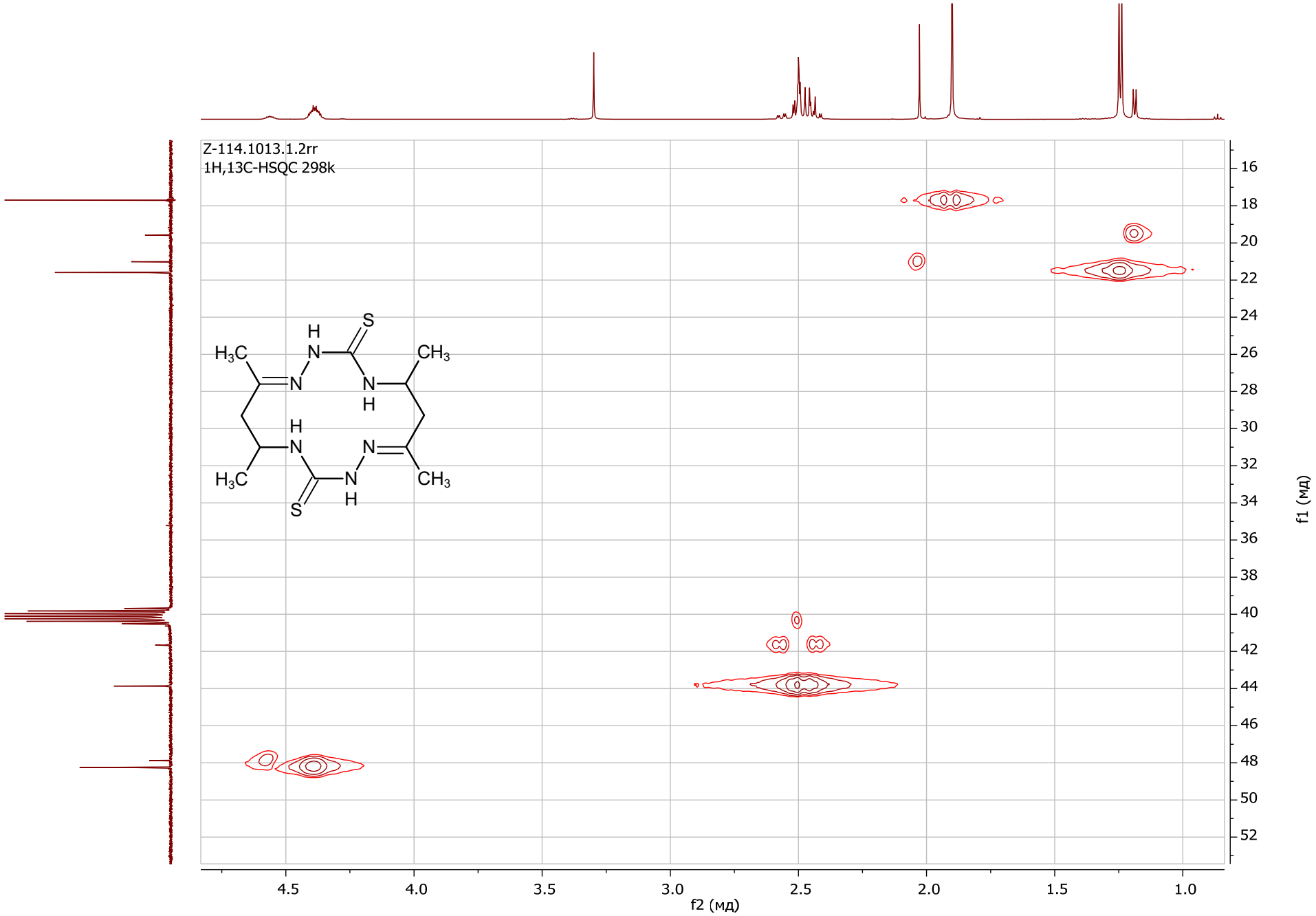
^{13}C NMR spectrum of 14-membered cyclic bis-thiosemicarbazone **6** (150.90 MHz, DMSO-d_6)



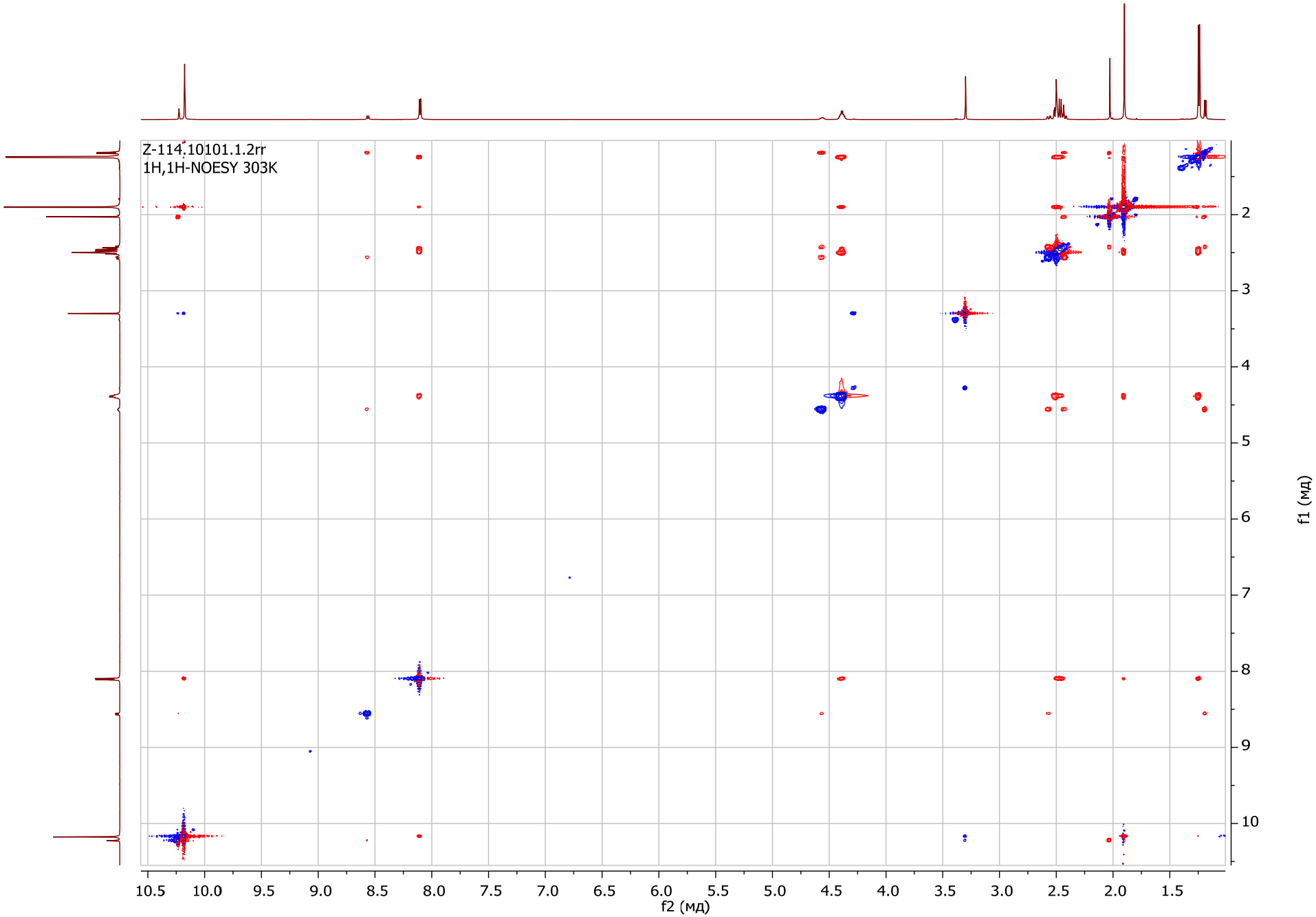
^{1}H,^{1}H COSY spectrum of 14-membered cyclic bis-thiosemicarbazone **6** (600.13 MHz, DMSO-d_6)



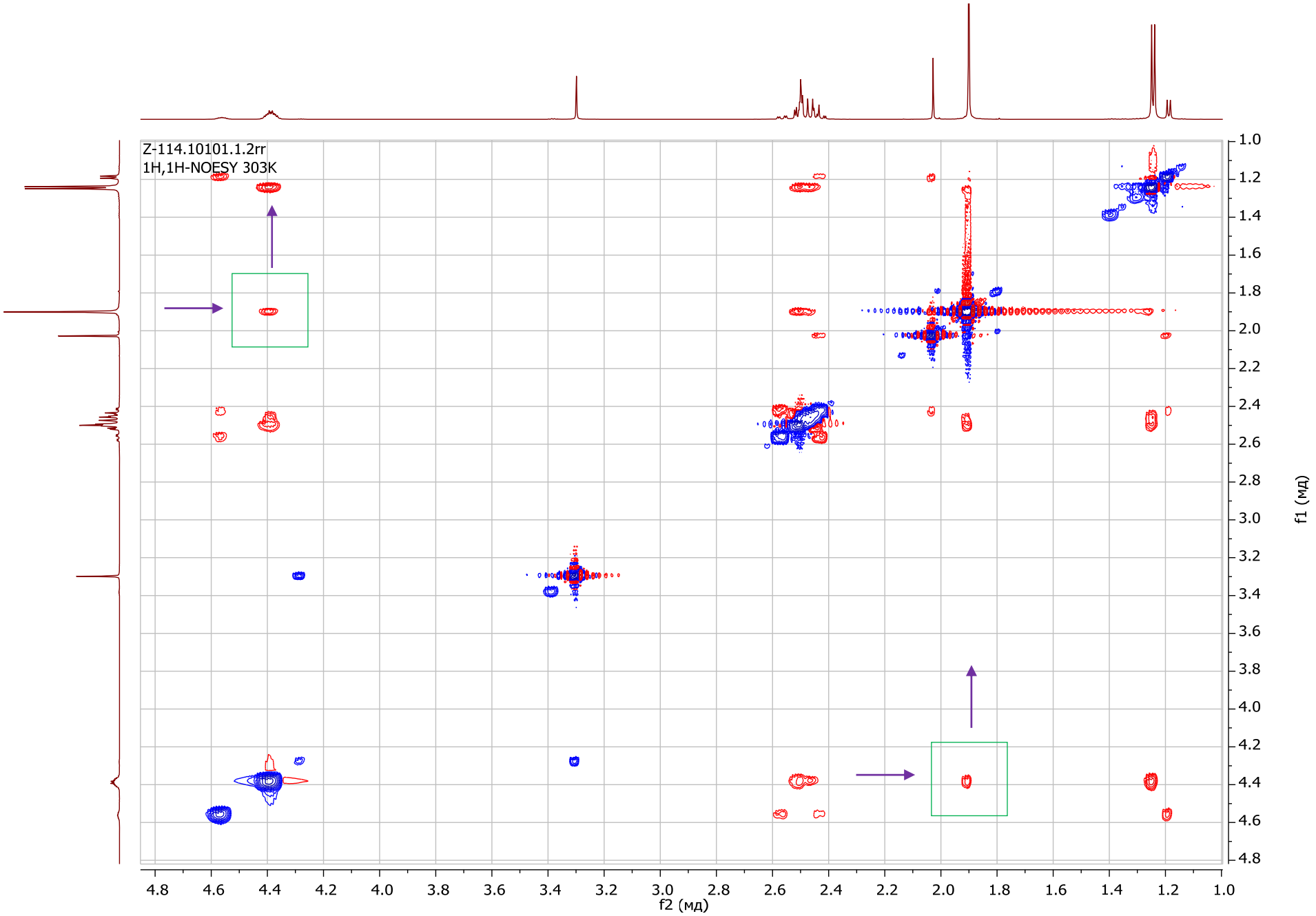
$^{1}H,^{13}C$ HSQC spectrum of 14-membered cyclic bis-thiosemicarbazone **6** (Bruker Avance III, DMSO-d_6)



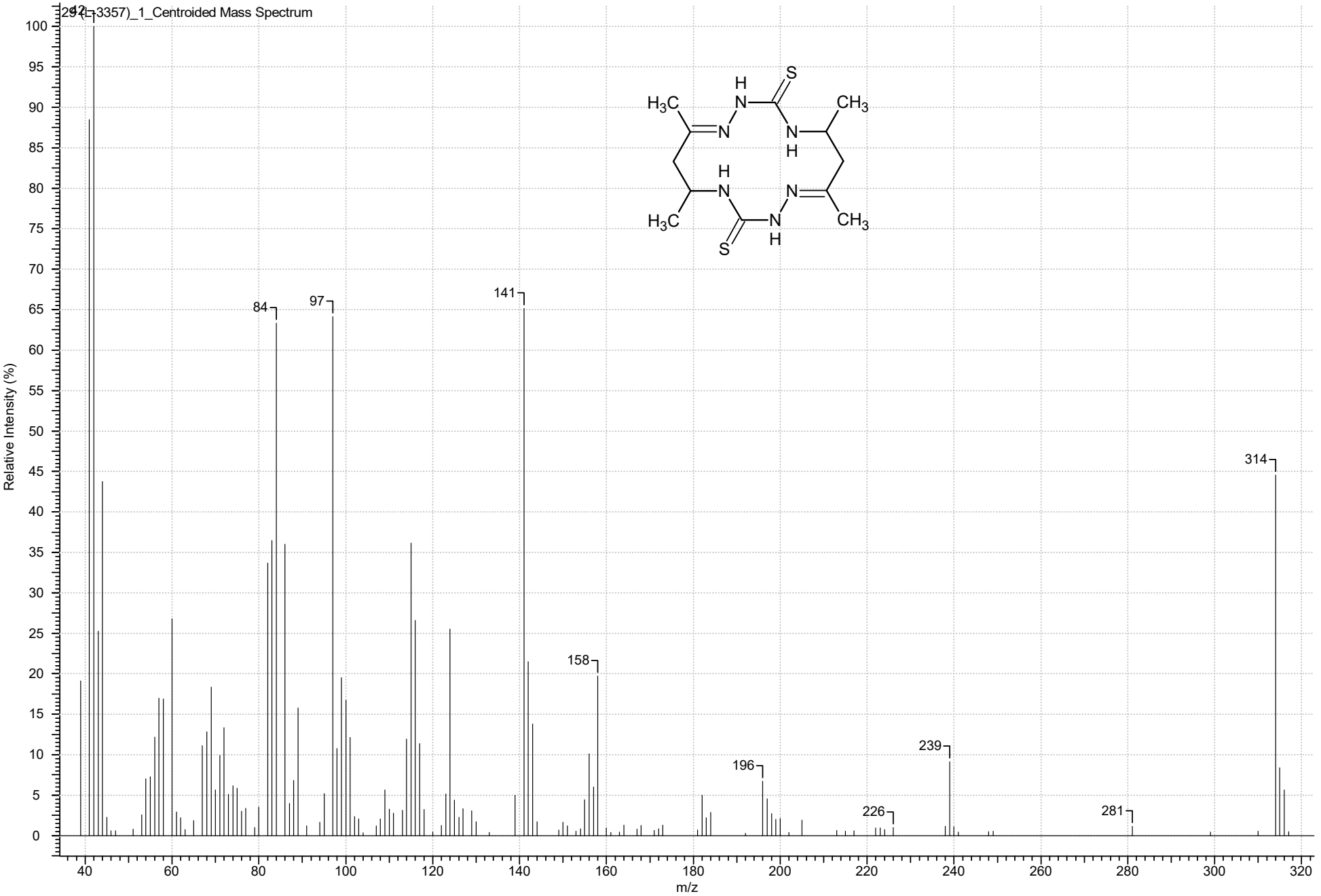
^{1}H,^{1}H NOESY spectrum of 14-membered cyclic bis-thiosemicarbazone **6** (600.13 MHz, DMSO-d_6)



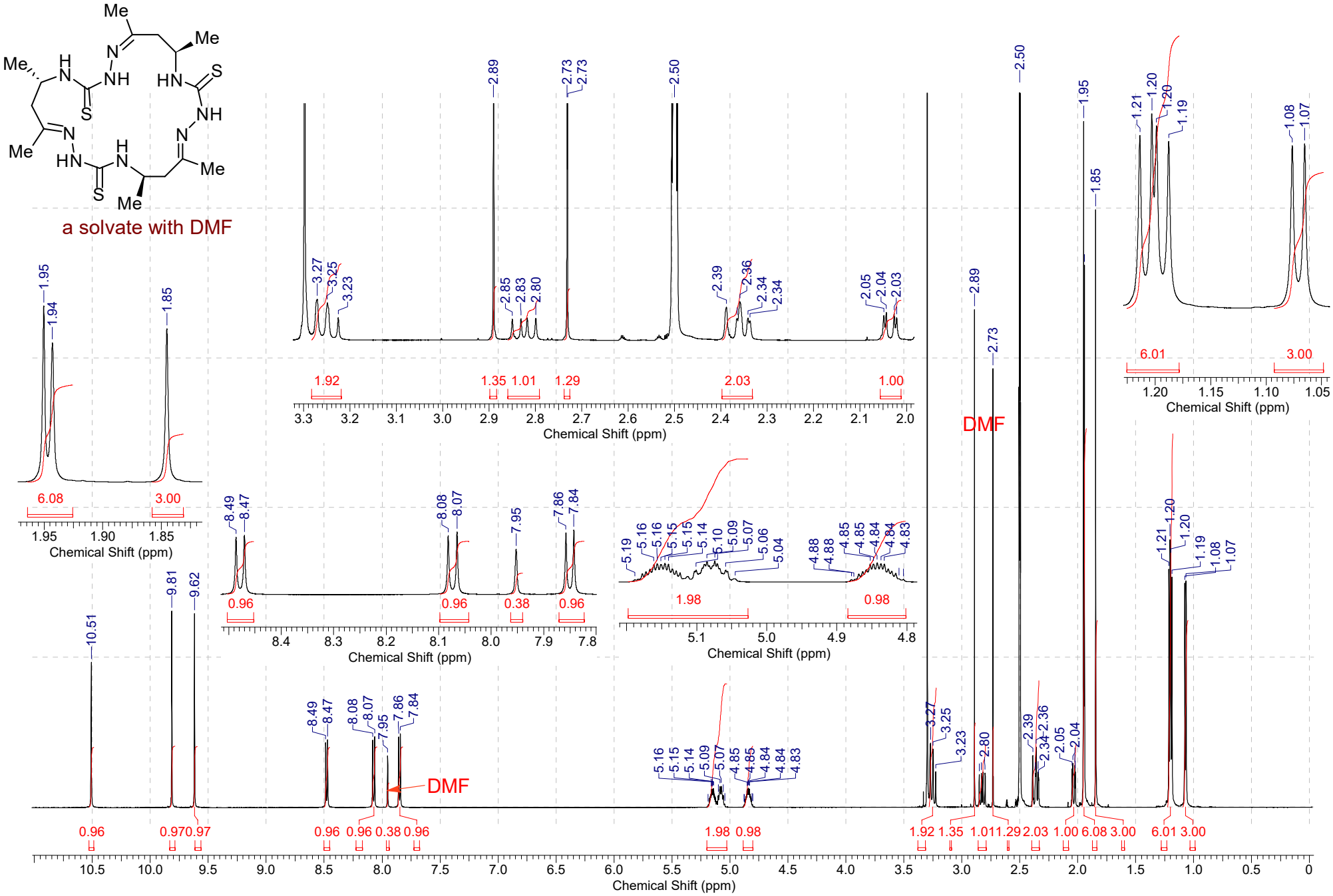
Fragment of ^{1}H,^{1}H NOESY spectrum of 14-membered cyclic bis-thiosemicarbazone **6** (600.13 MHz, DMSO-d_6)



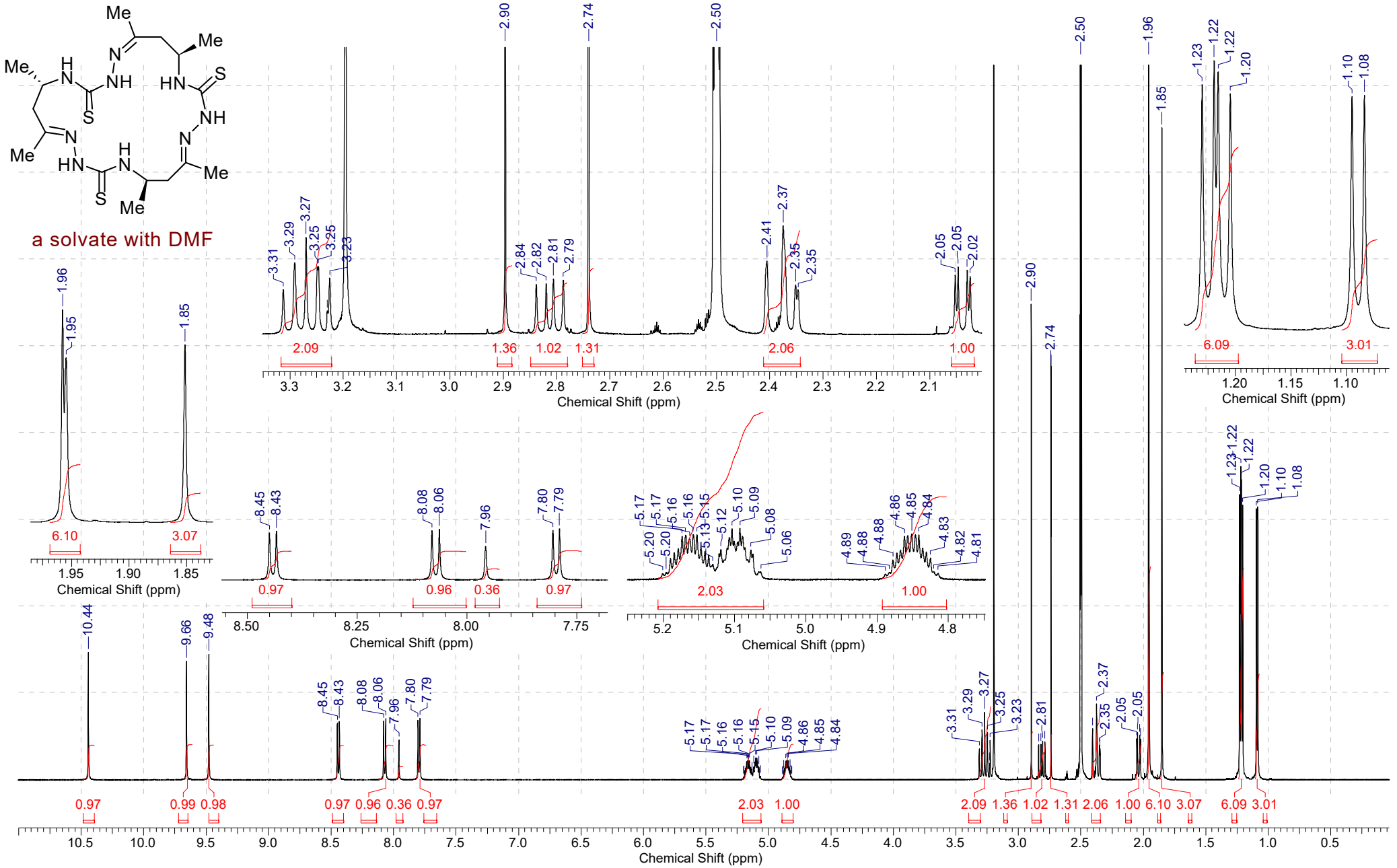
Mass-spectrum of 14-membered cyclic bis-thiosemicarbazone **6** (electron impact, 70 eV)



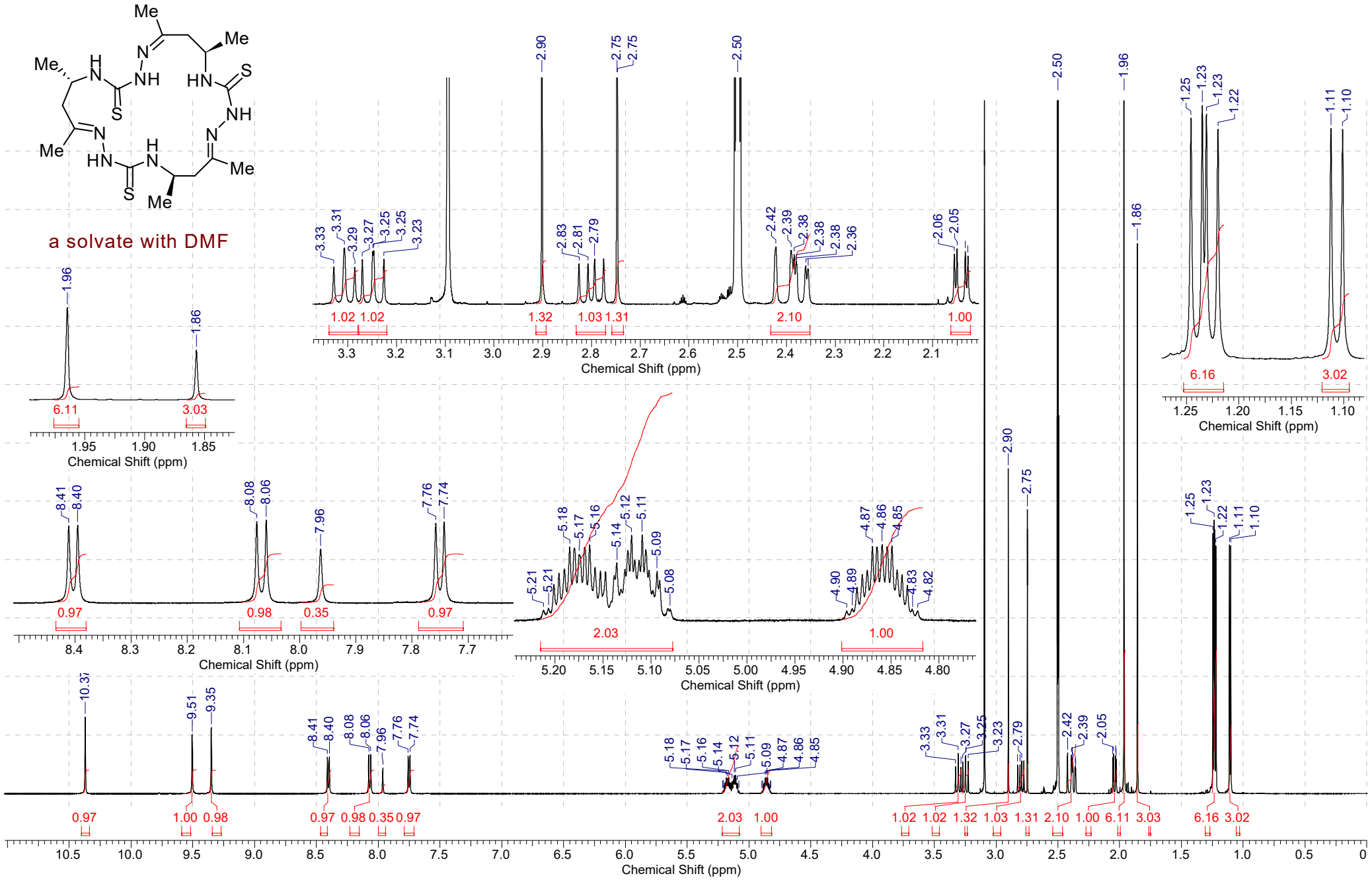
^{1}H NMR spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



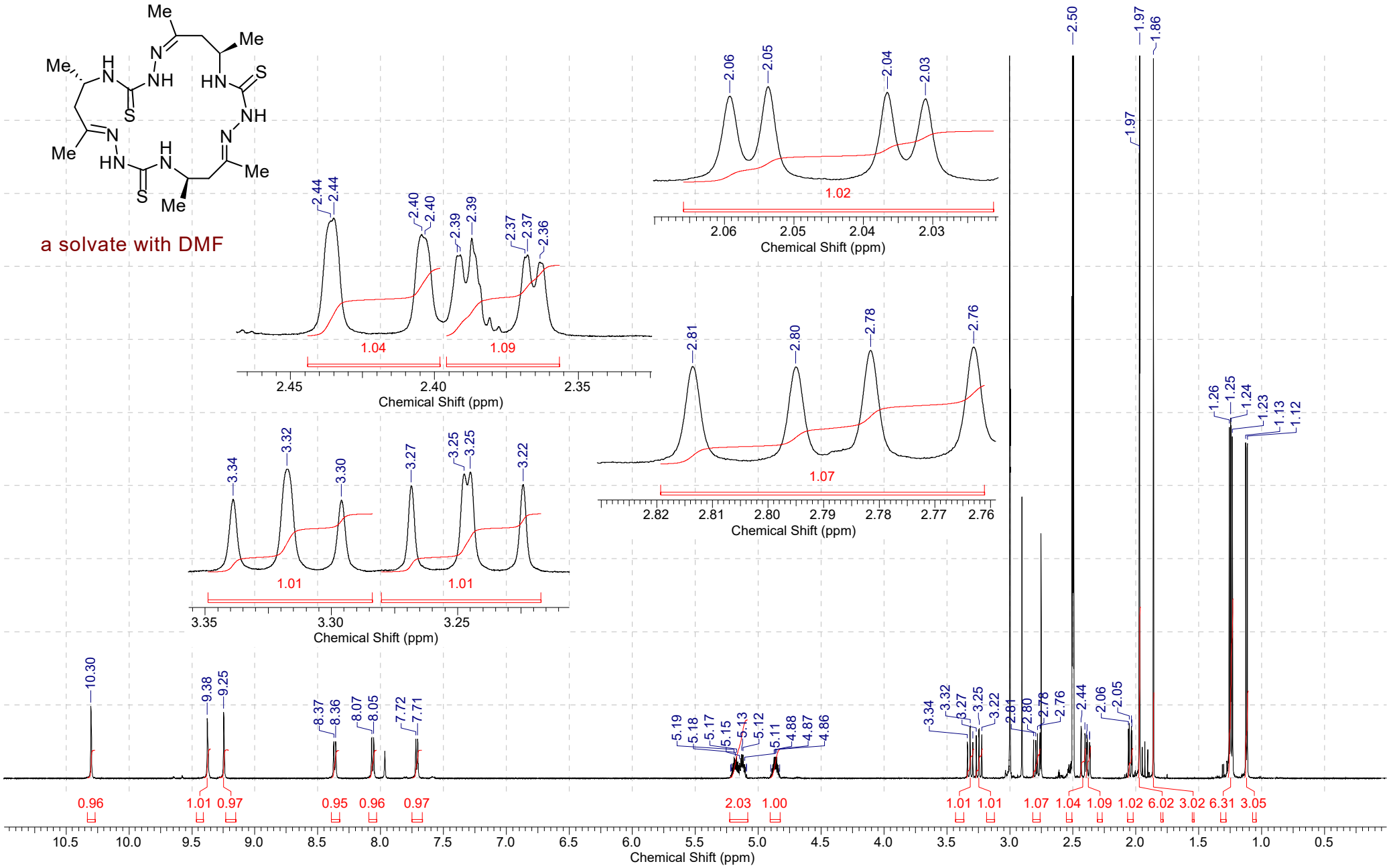
[1]H NMR spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 50 °C, DMSO-d_6)



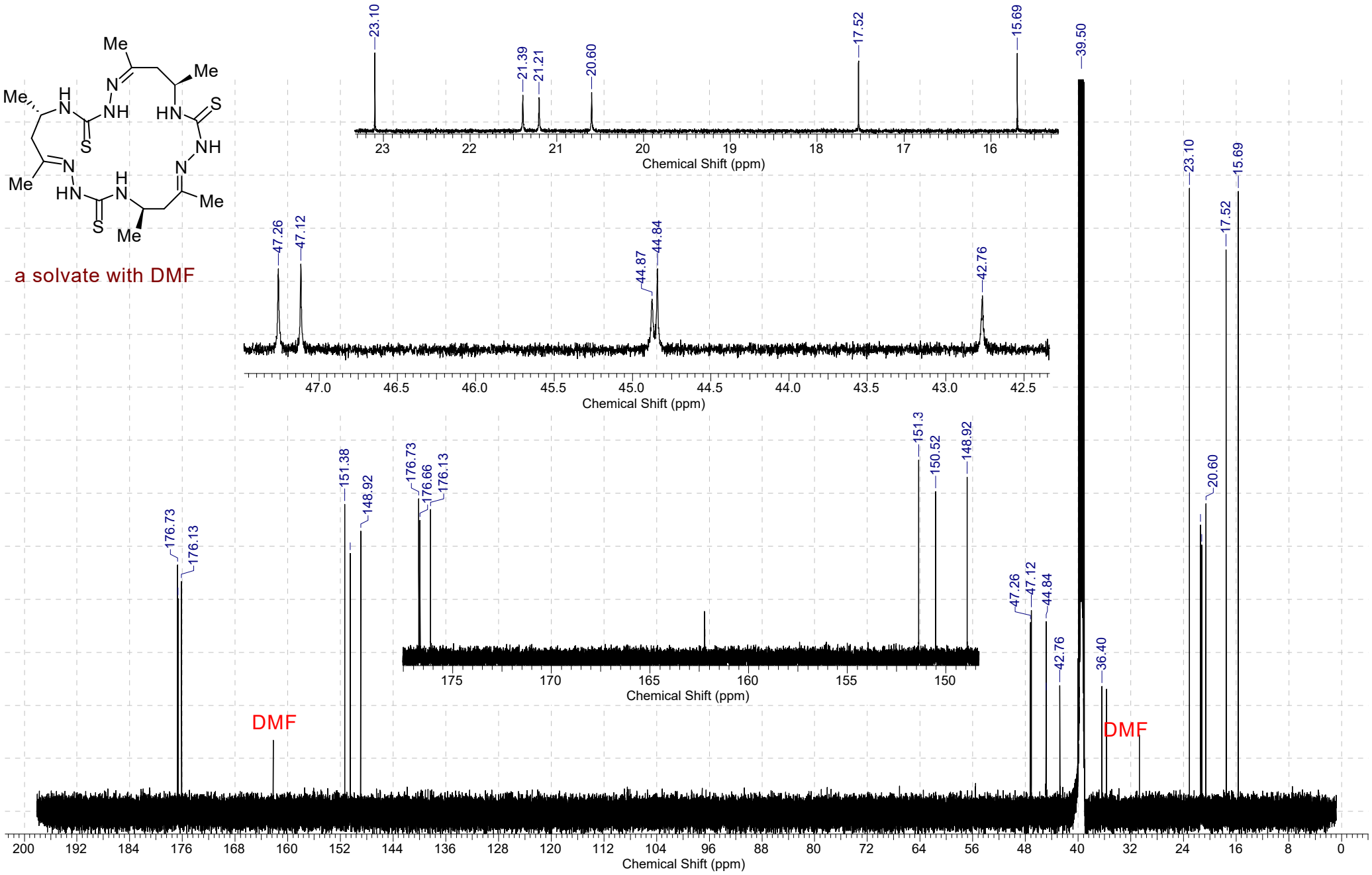
[1]H NMR spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 70 °C, DMSO-d_6)



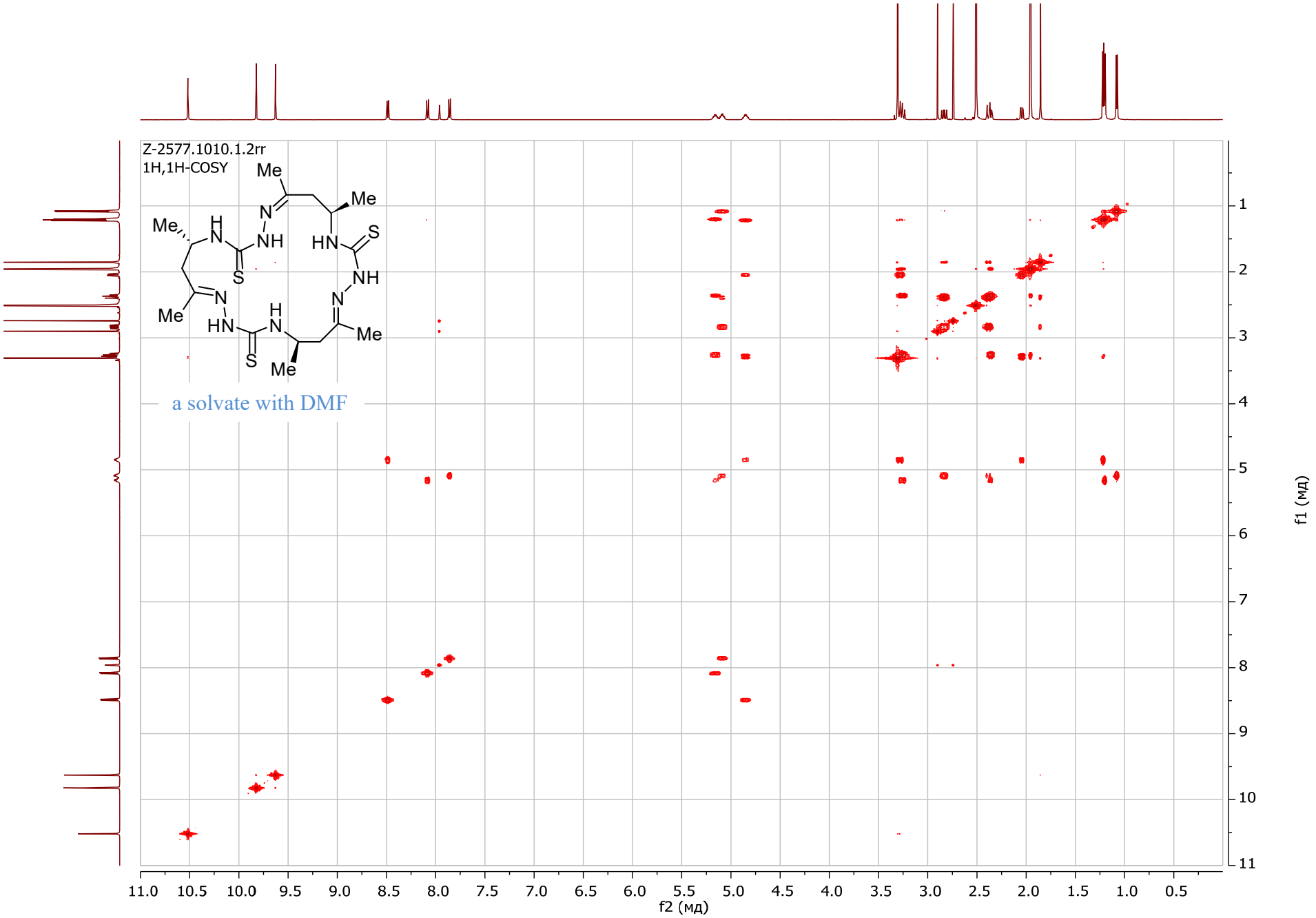
[1]H NMR spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 90 °C, DMSO-d_6)



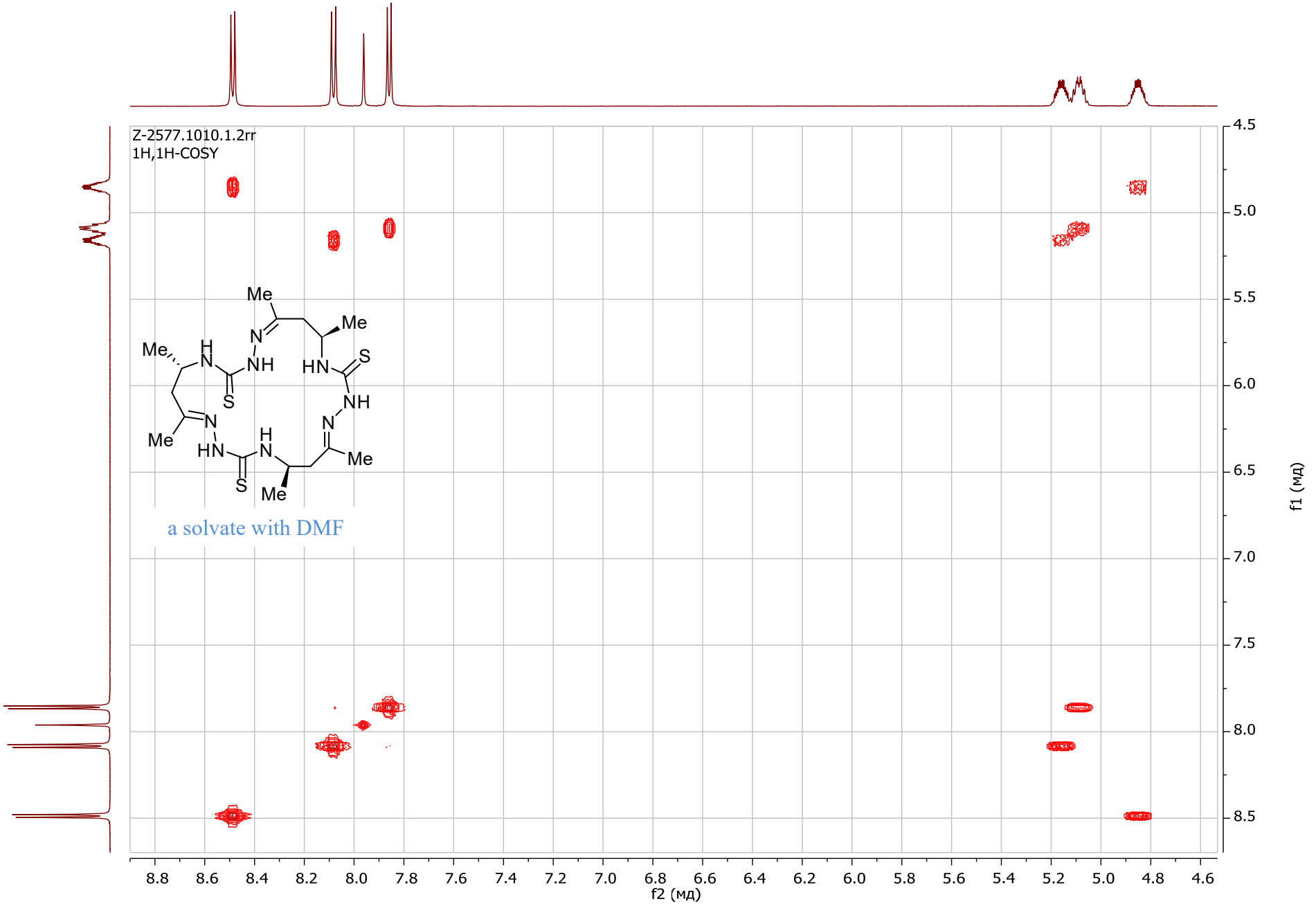
^{13}C NMR spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (150.90 MHz, 30 °C, DMSO-d_6)



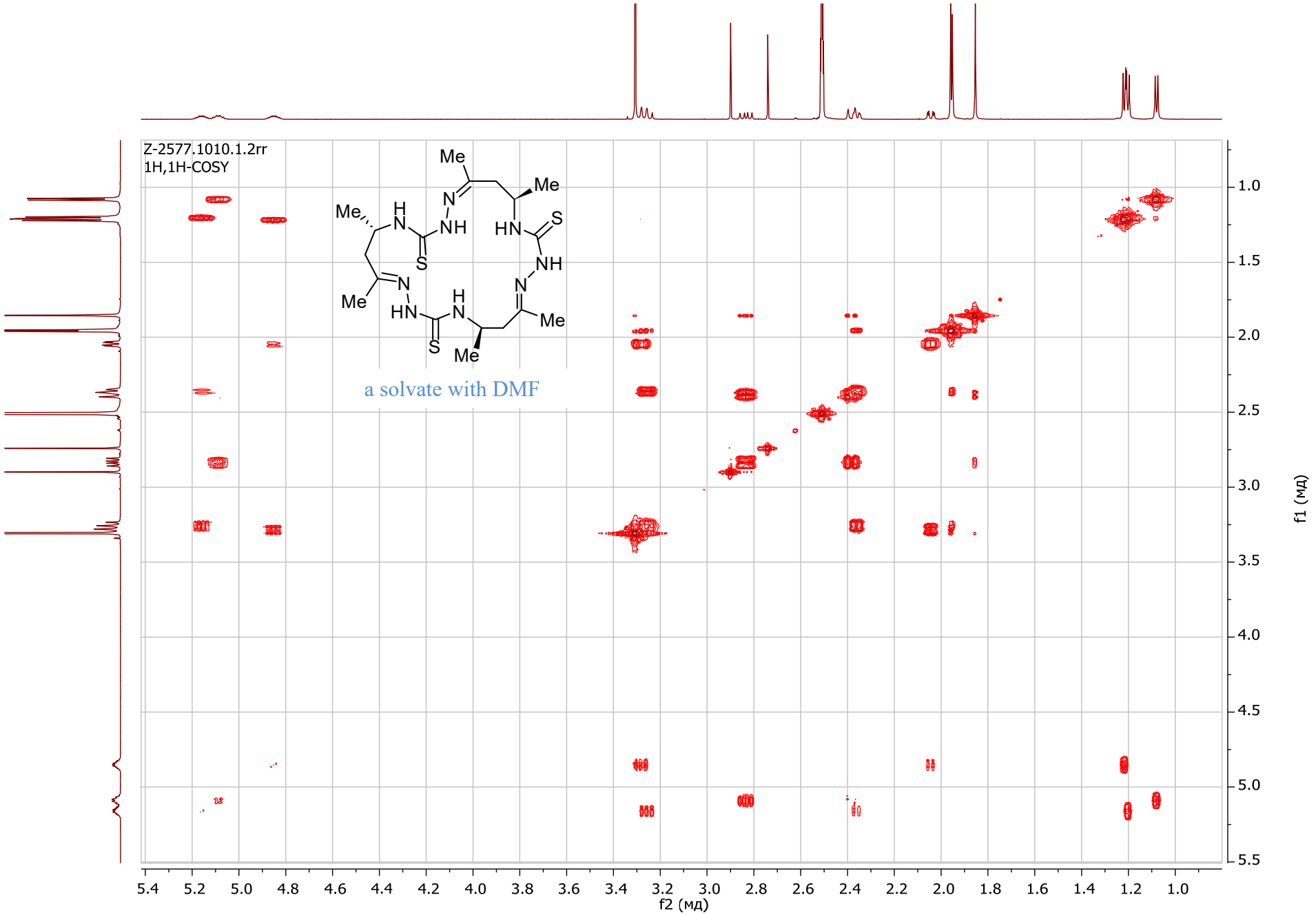
^{1}H,^{1}H COSY spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



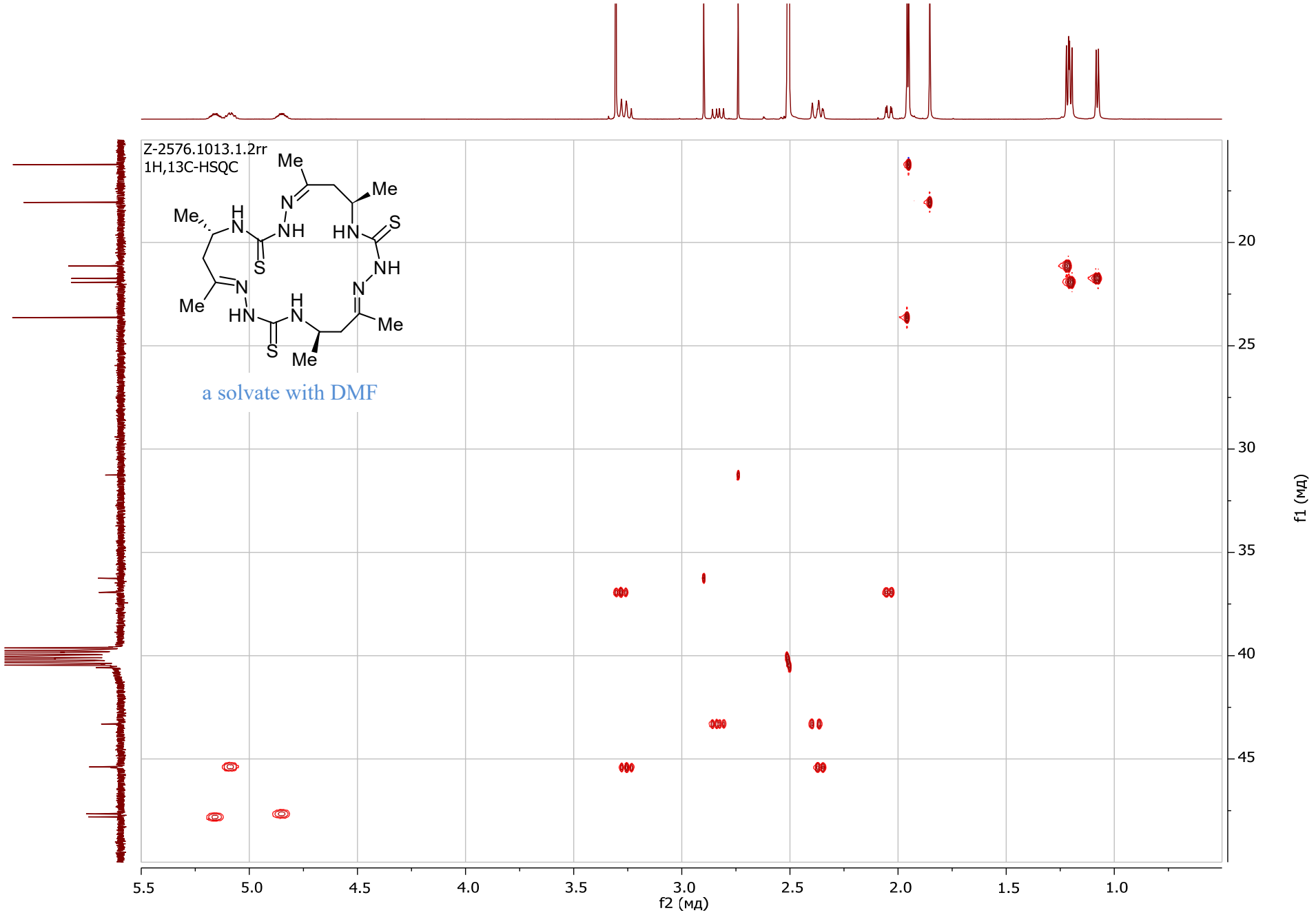
Fragment of ^{1}H,^{1}H COSY spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



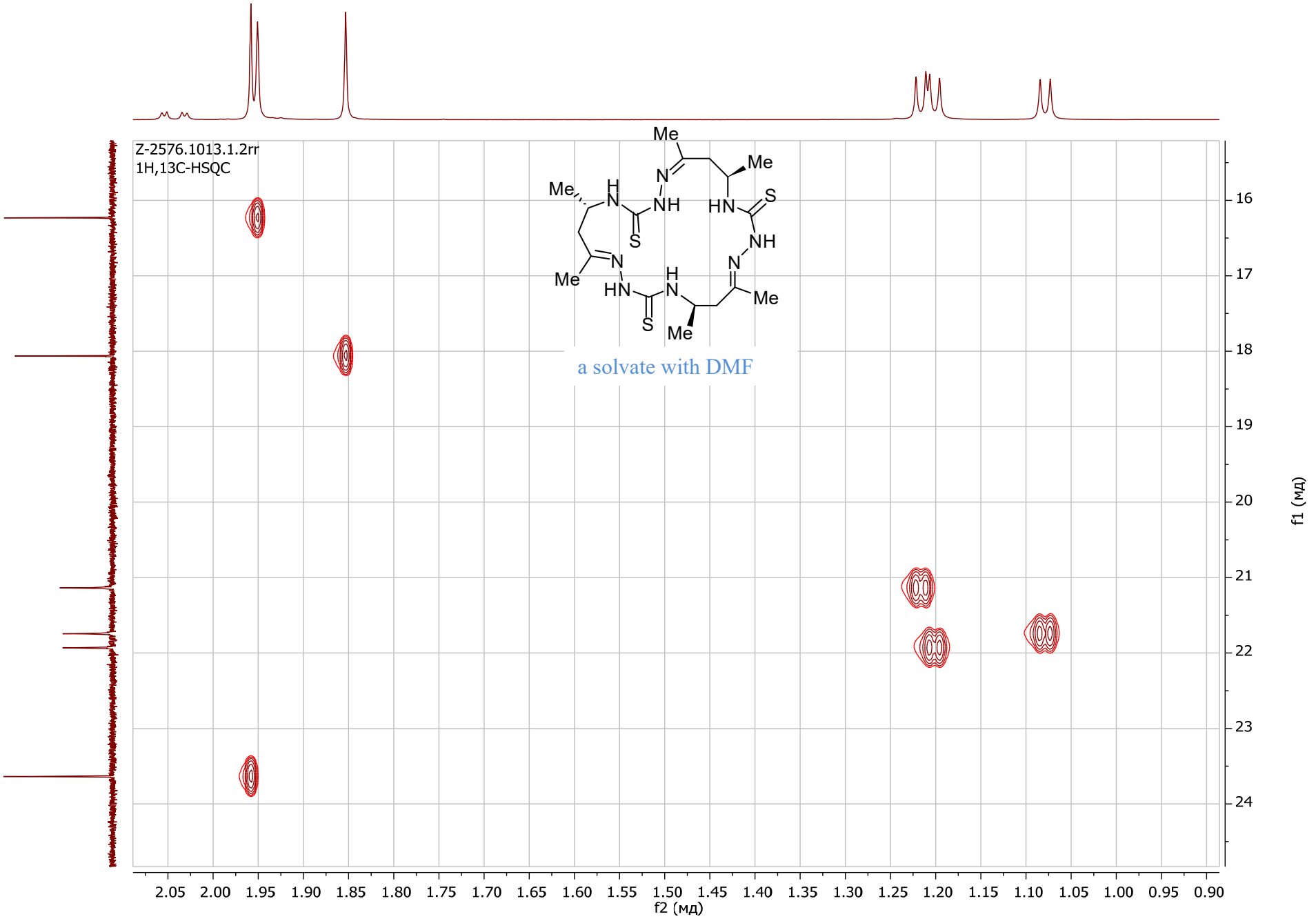
Fragment of ^{1}H,^{1}H COSY spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



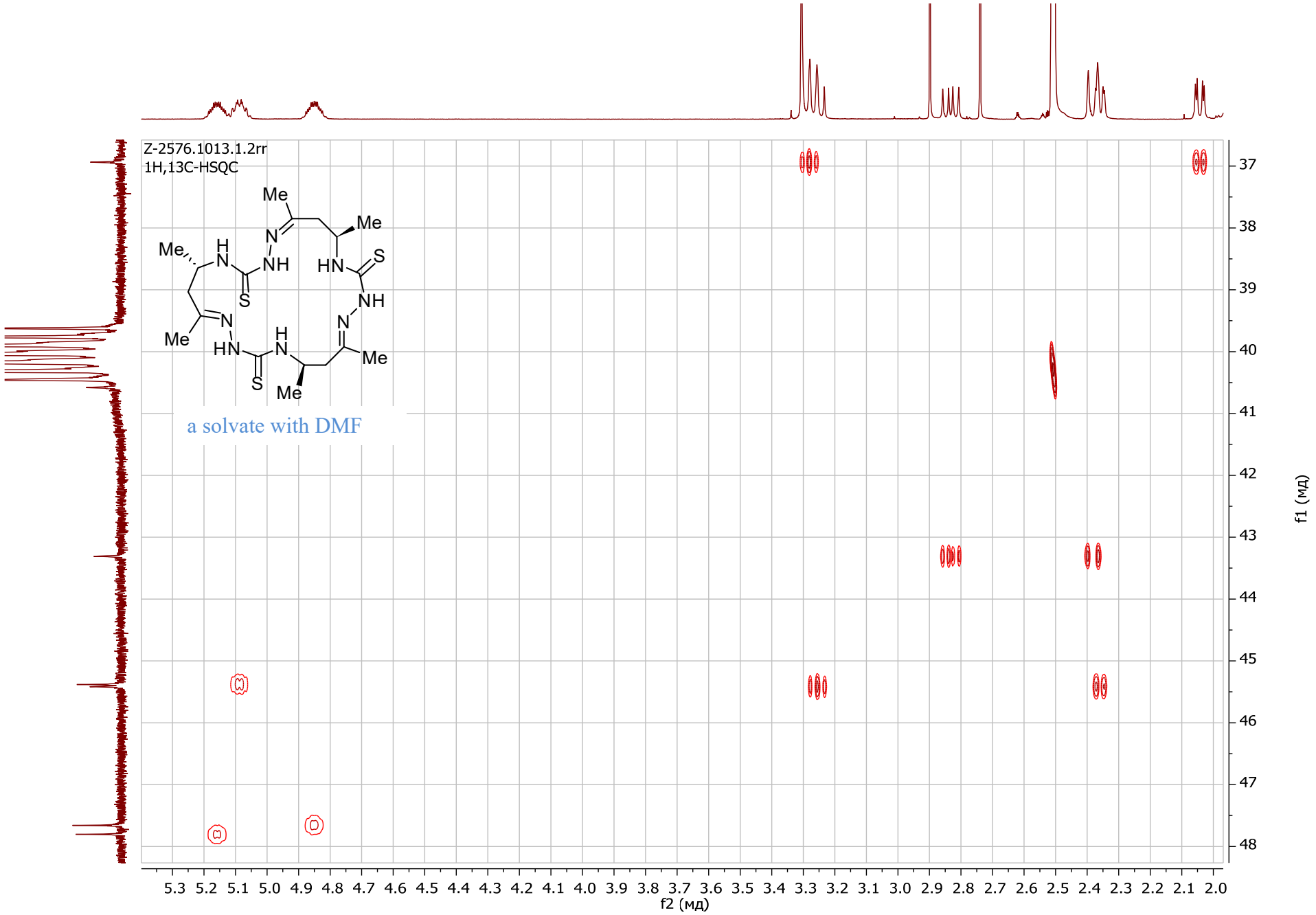
$^{1}H,^{13}C$ HSQC spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (Bruker Avance III, 30 °C, DMSO-d_6)



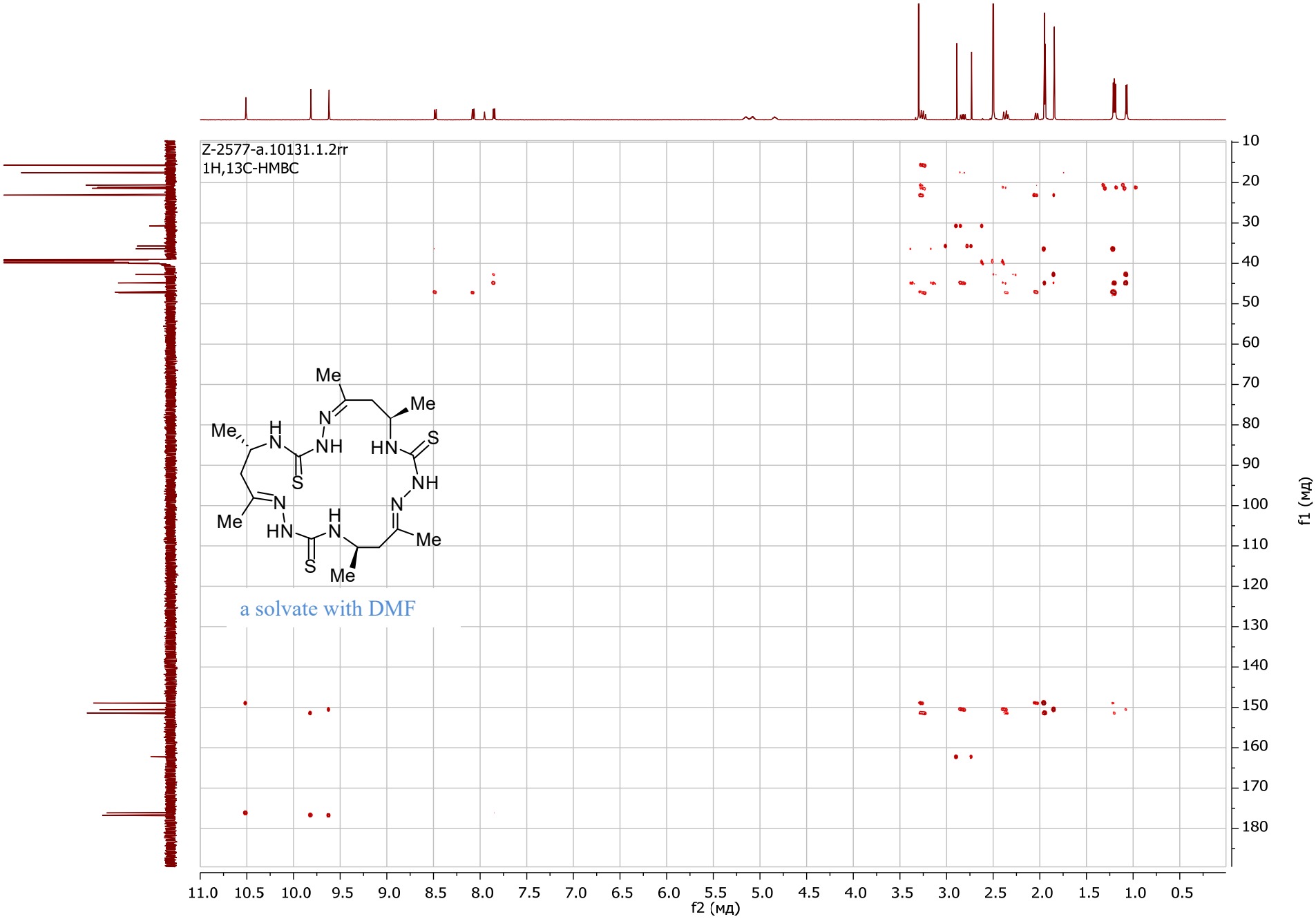
Fragment of $^{1}H,^{13}C$ HSQC spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (Bruker Avance III, 30 °C, DMSO-d_6)



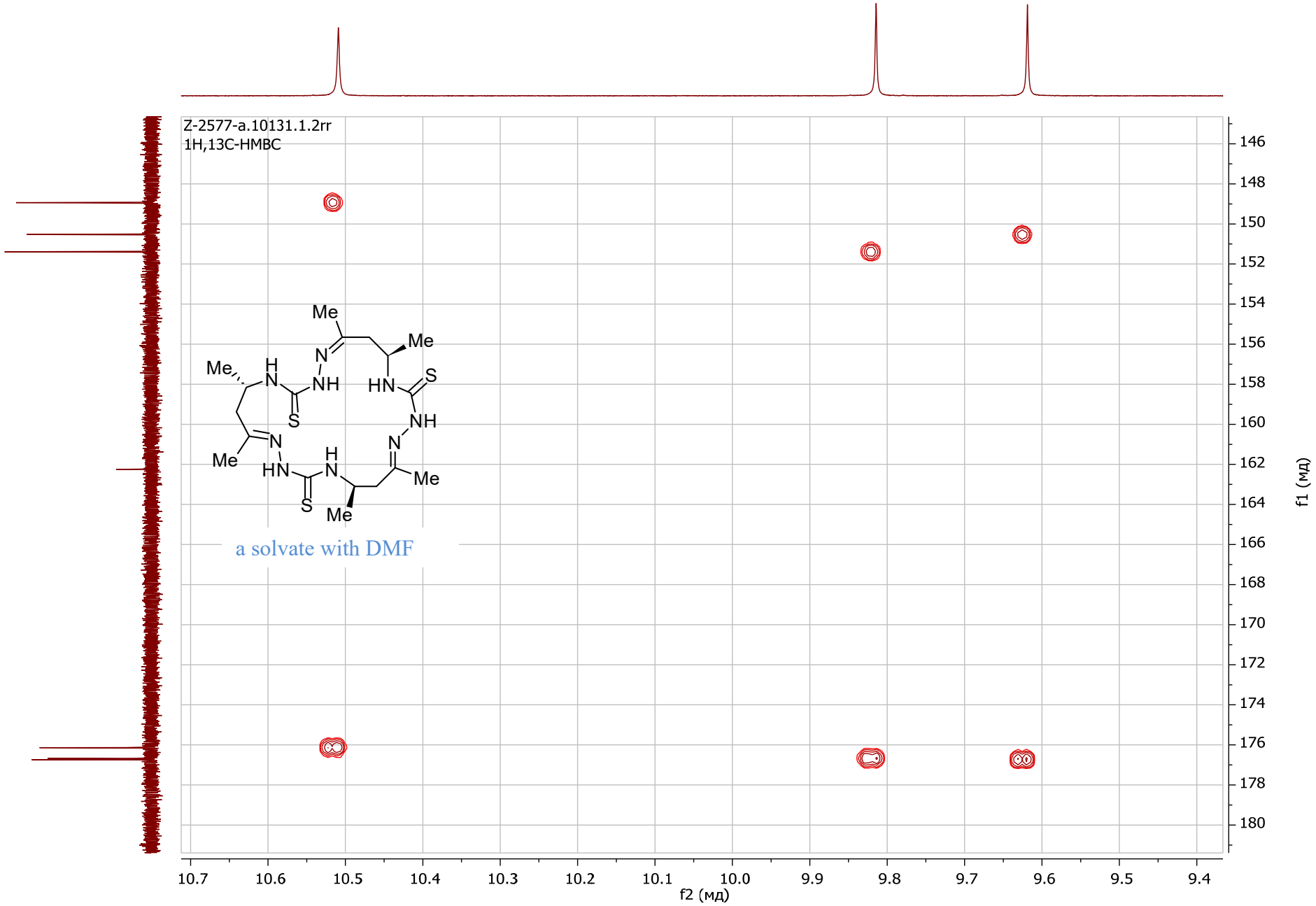
Fragment of $^{1}H,^{13}C$ HSQC spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (Bruker Avance III, 30 °C, DMSO-d_6)



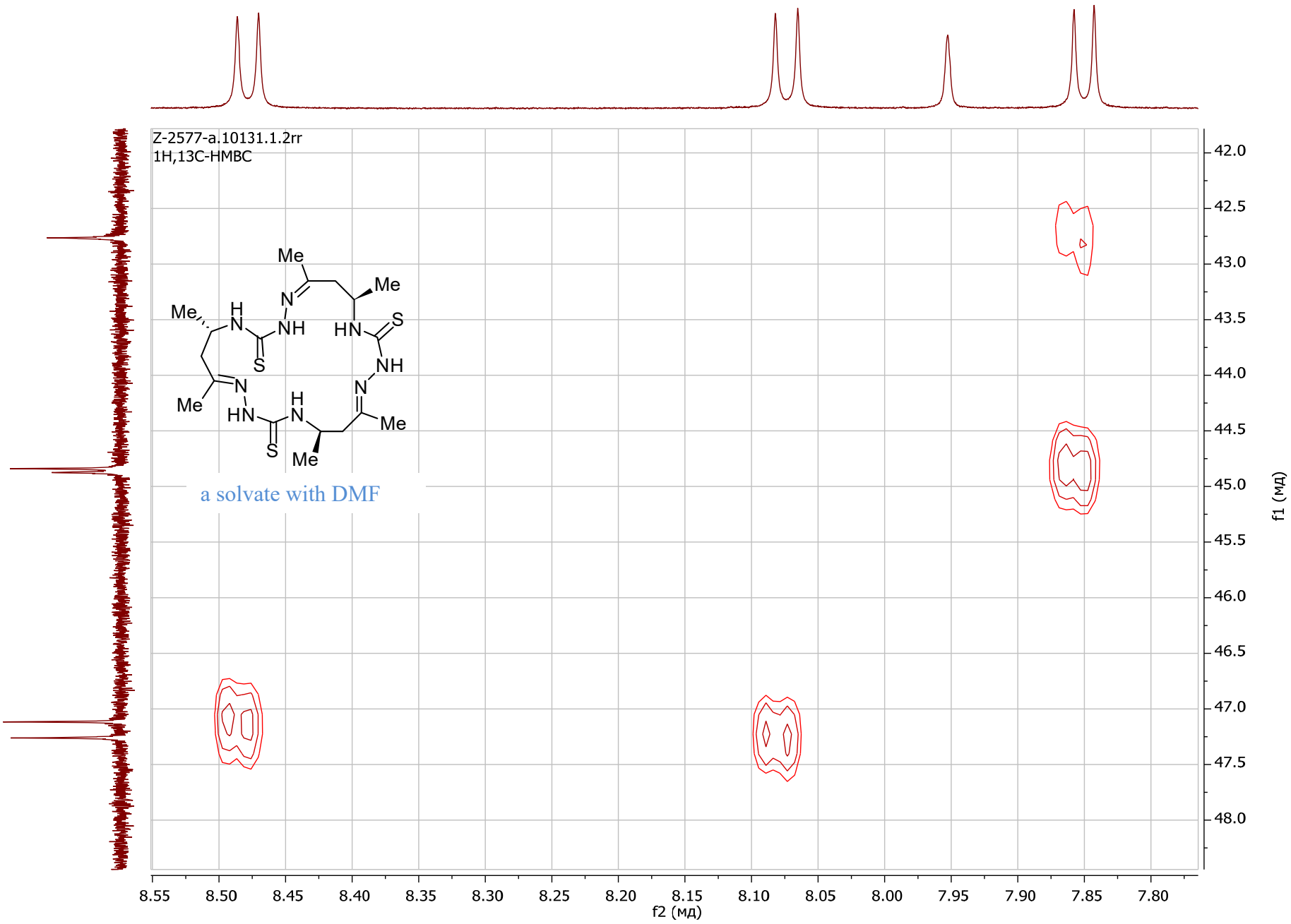
$^{1}H,^{13}C$ HMBC spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (Bruker Avance III, 30 °C, DMSO-d_6)



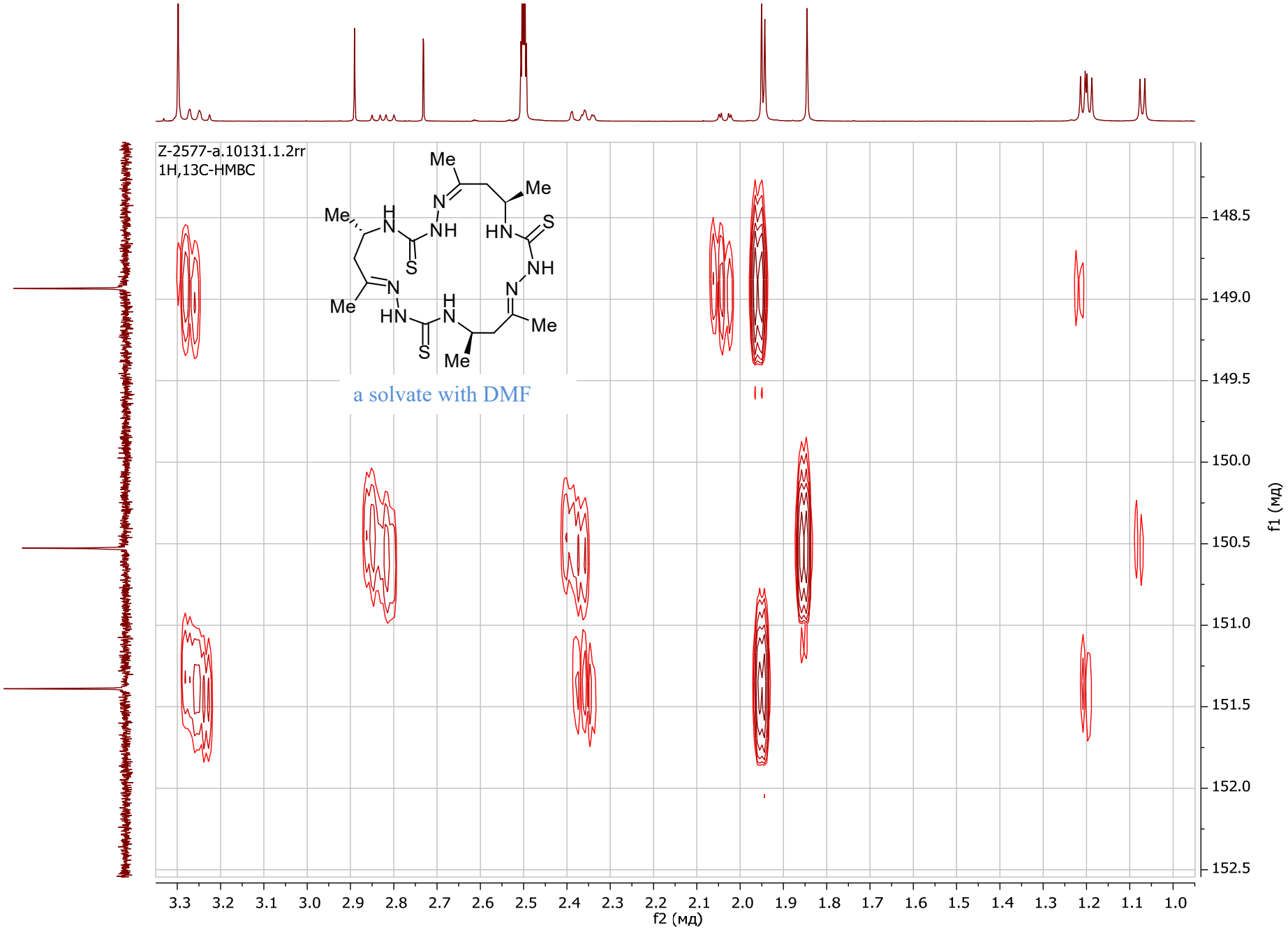
Fragment of $^{1}H,^{13}C$ HMBC spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (Bruker Avance III, 30 °C, DMSO-d_6)



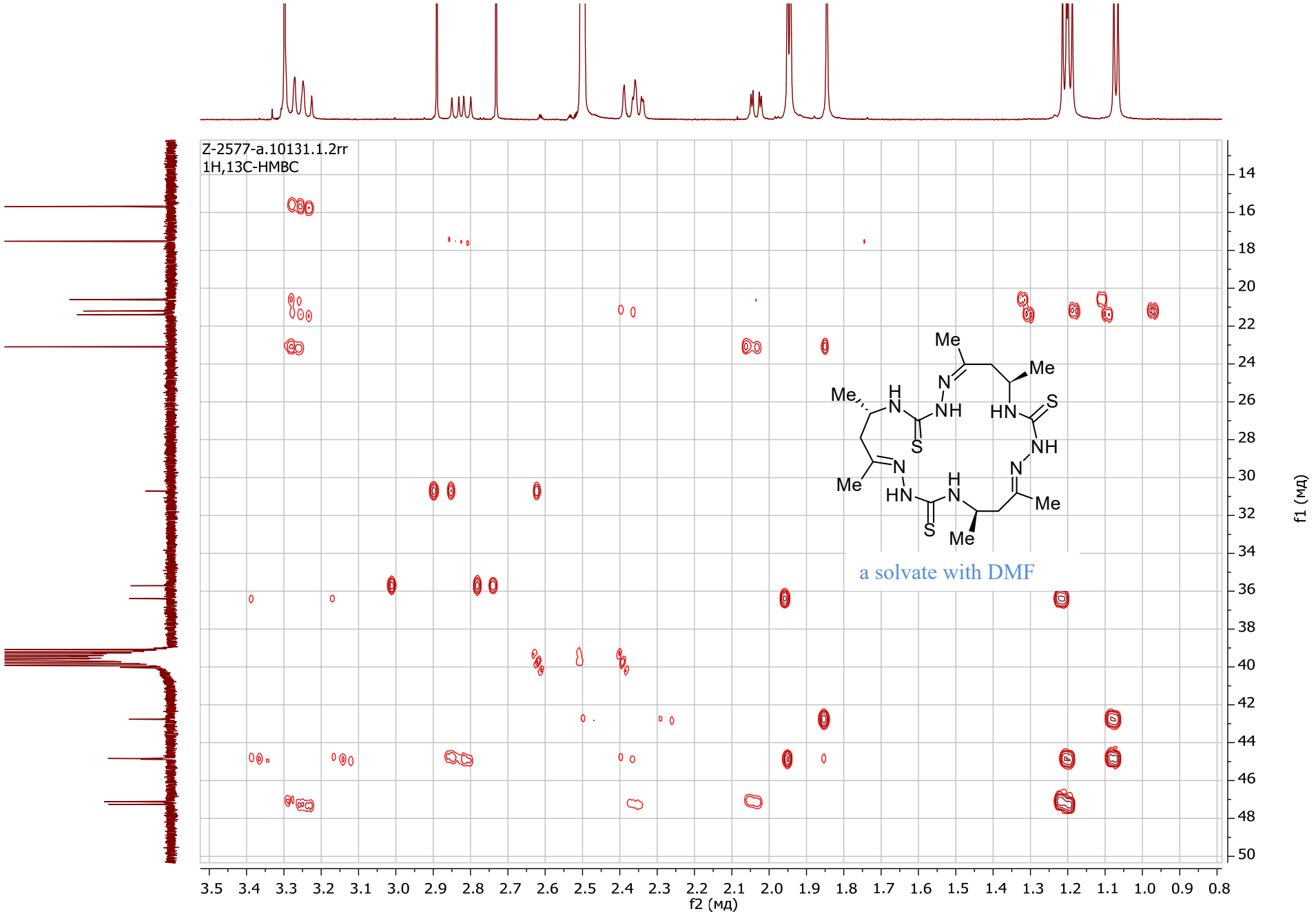
Fragment of $^{1}H,^{13}C$ HMBC spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (Bruker Avance III, 30 °C, DMSO-d_6)



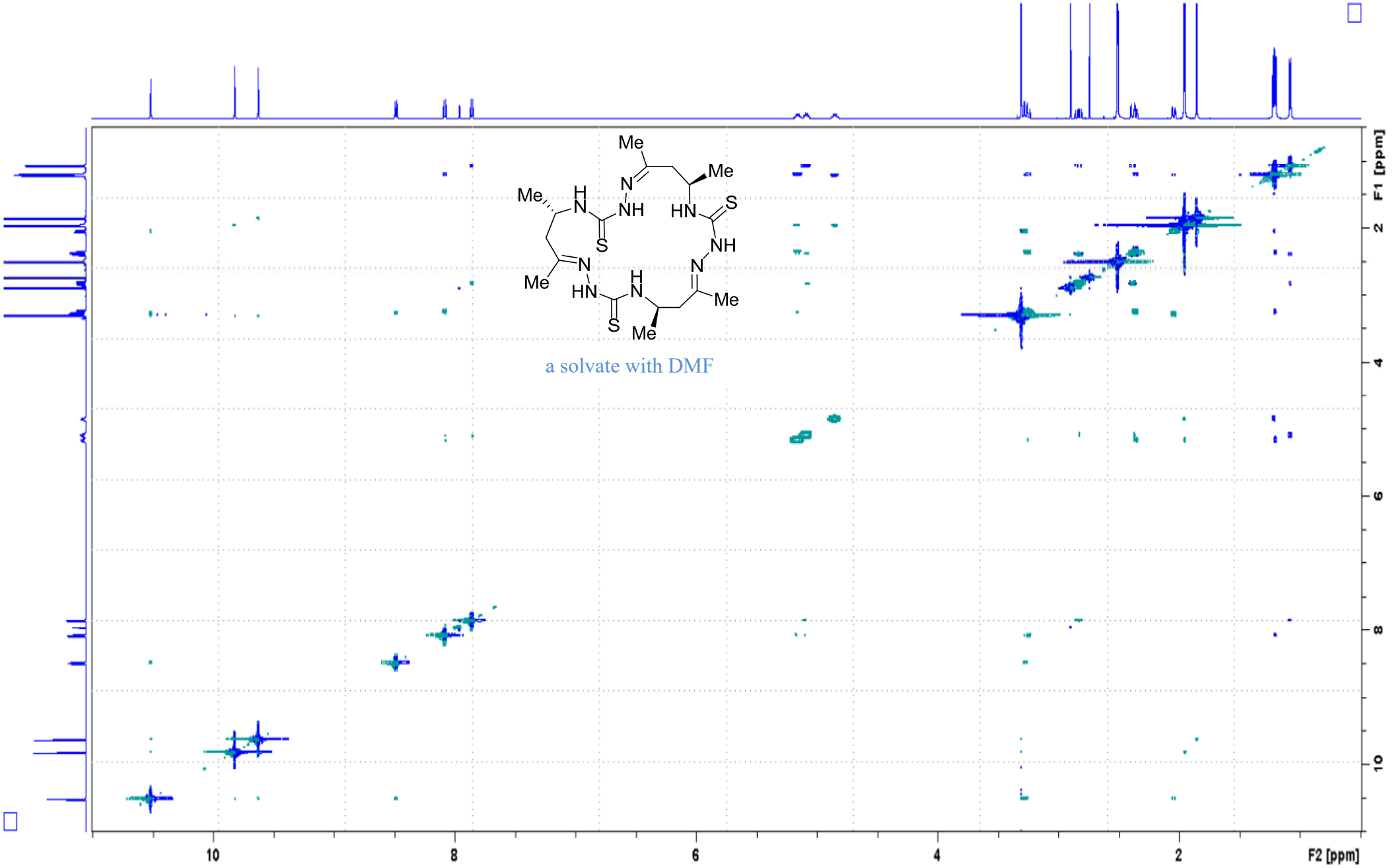
Fragment of $^{1}H,^{13}C$ HMBC spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (Bruker Avance III, 30 °C, DMSO-d_6)



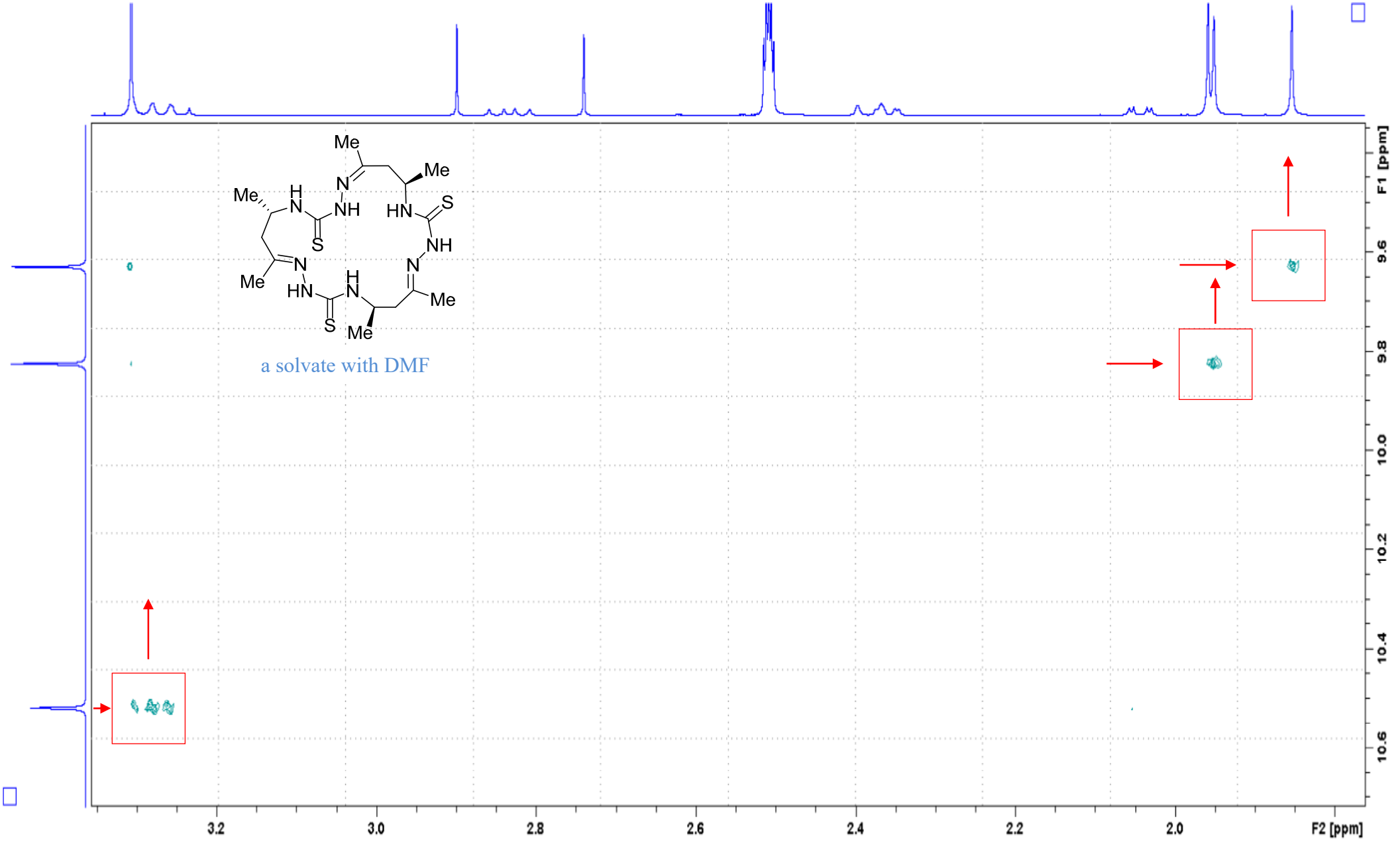
Fragment of $^{1}H,^{13}C$ HMBC spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (Bruker Avance III, 30 °C, DMSO-d_6)



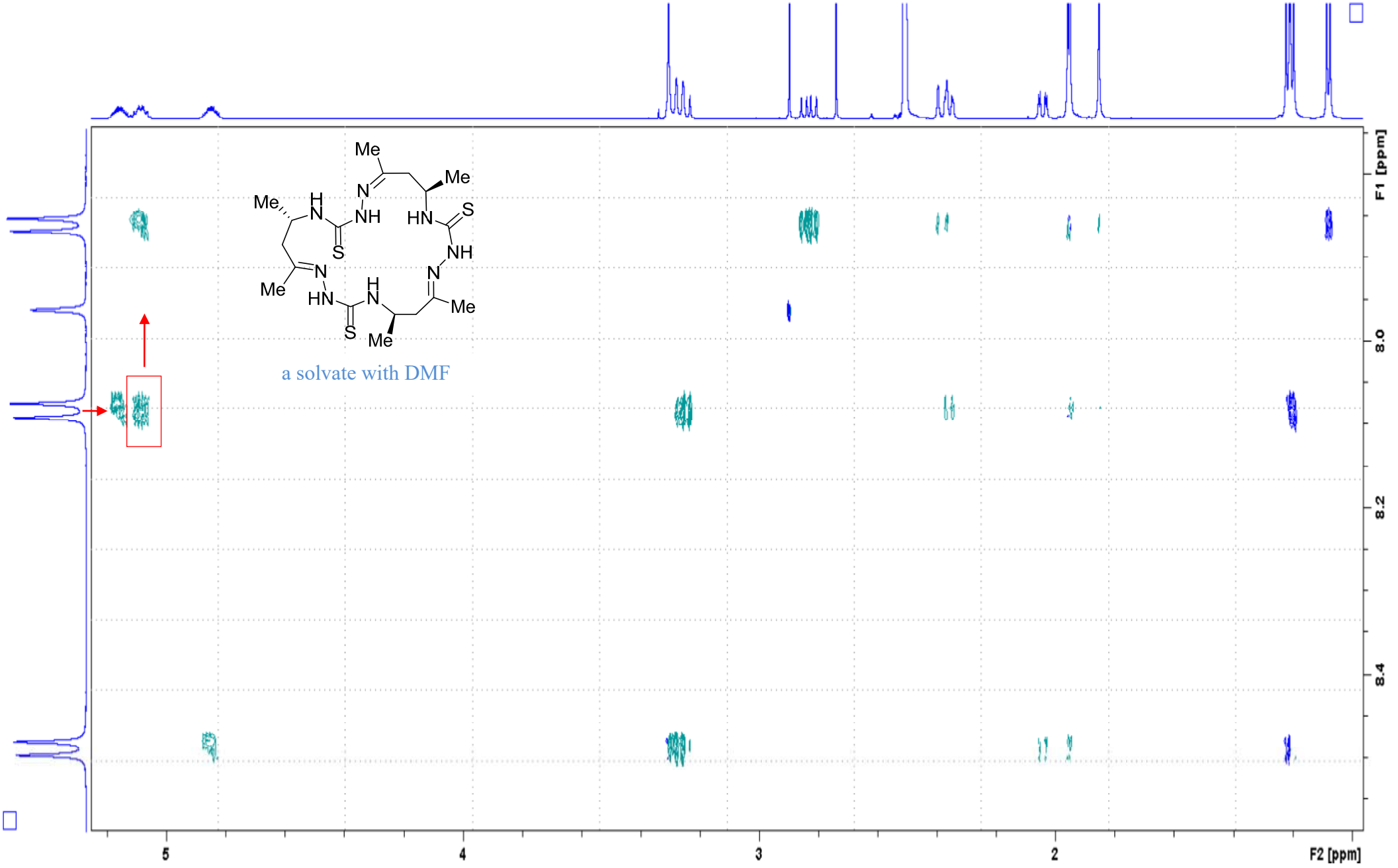
^{1}H,^{1}H NOESY spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



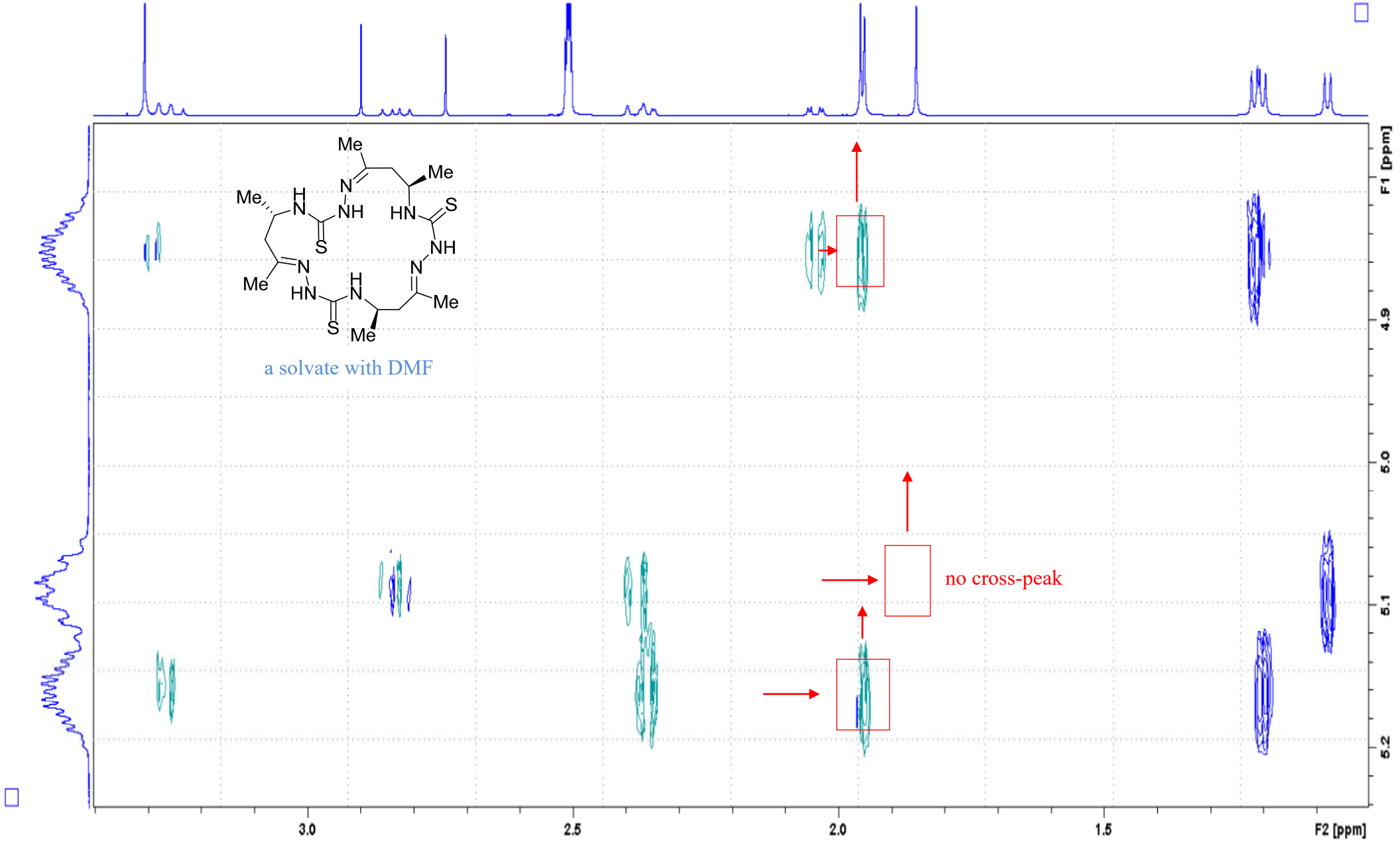
Fragment of ^{1}H,^{1}H NOESY spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



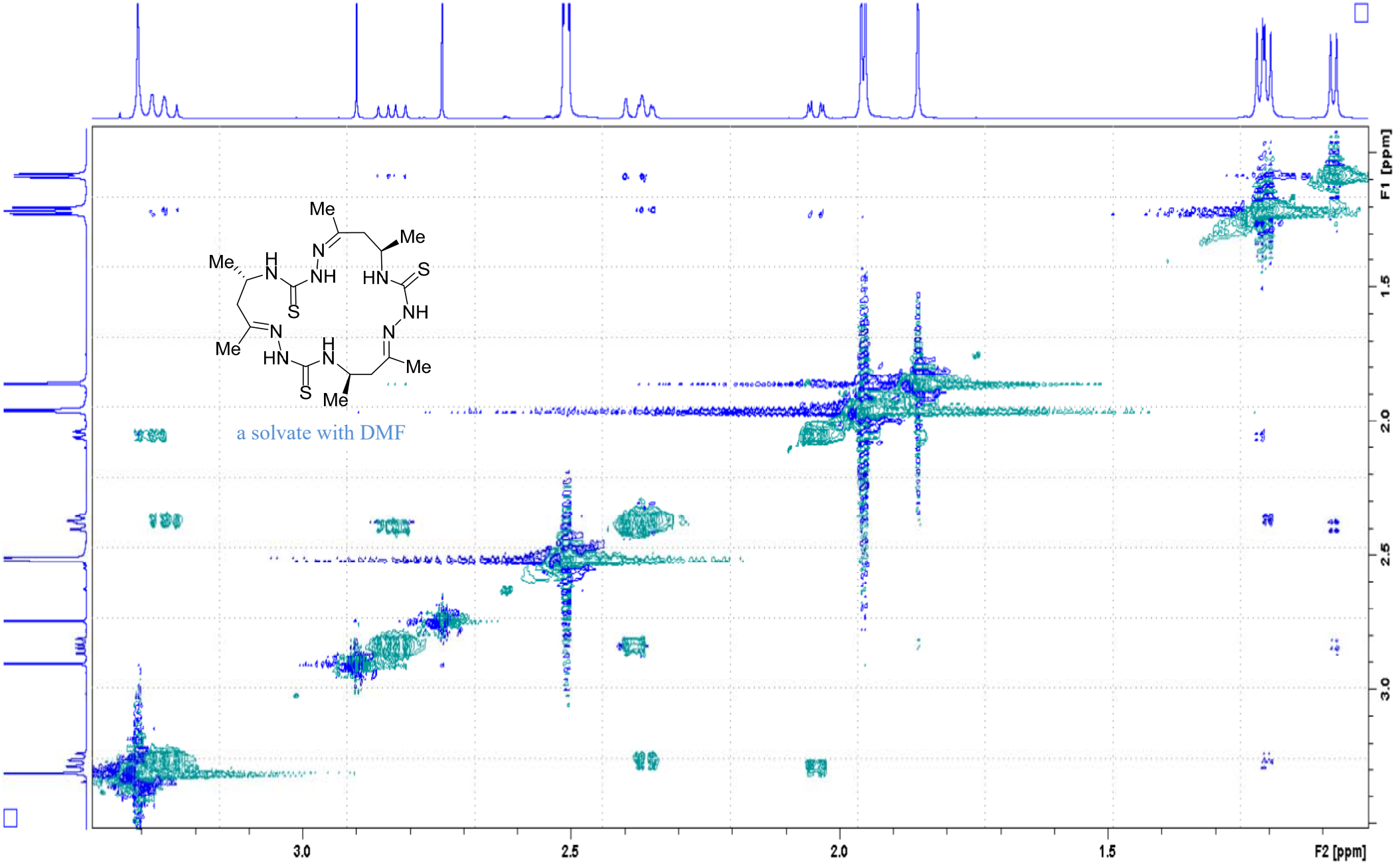
Fragment of ^{1}H,^{1}H NOESY spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



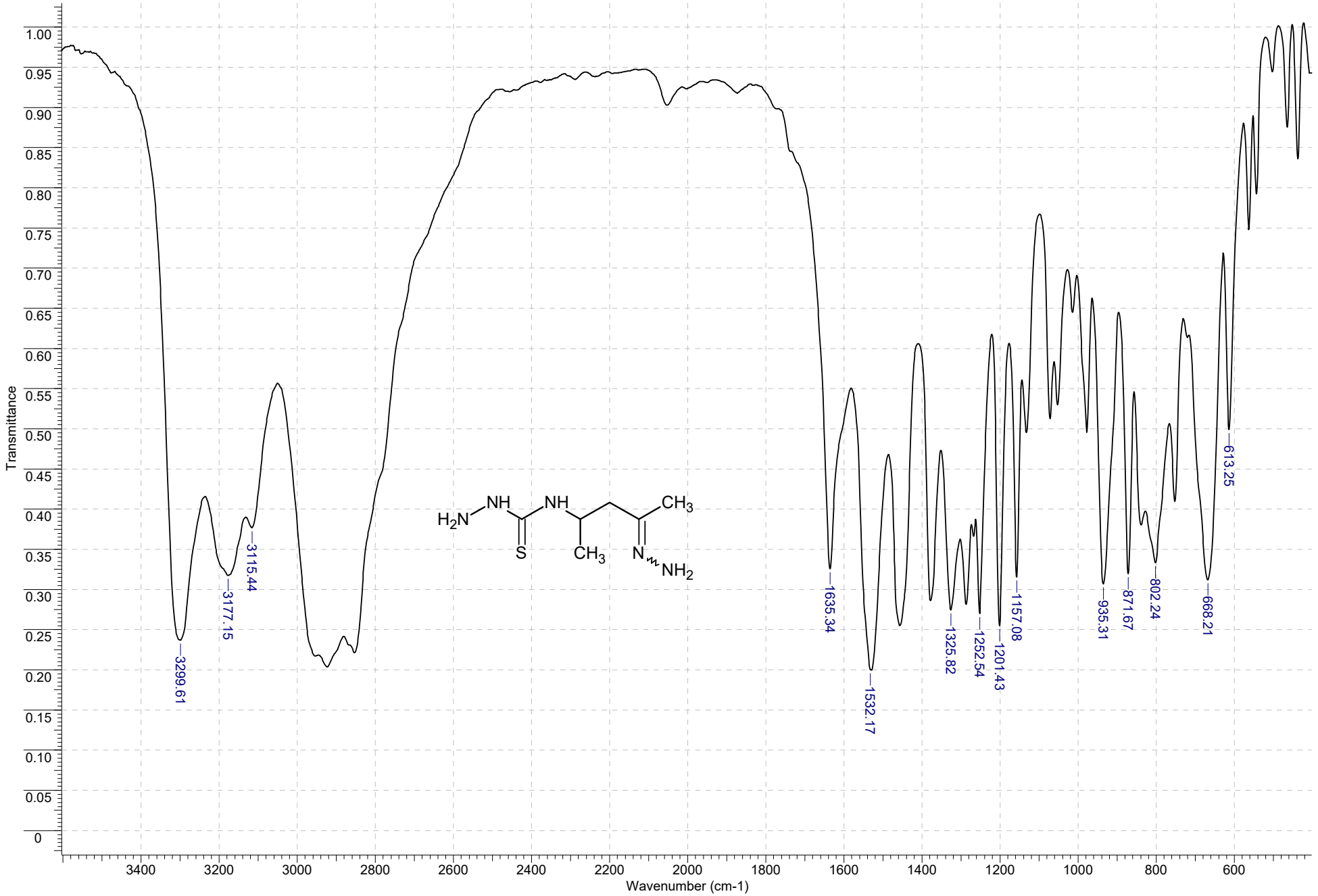
Fragment of ^{1}H,^{1}H NOESY spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



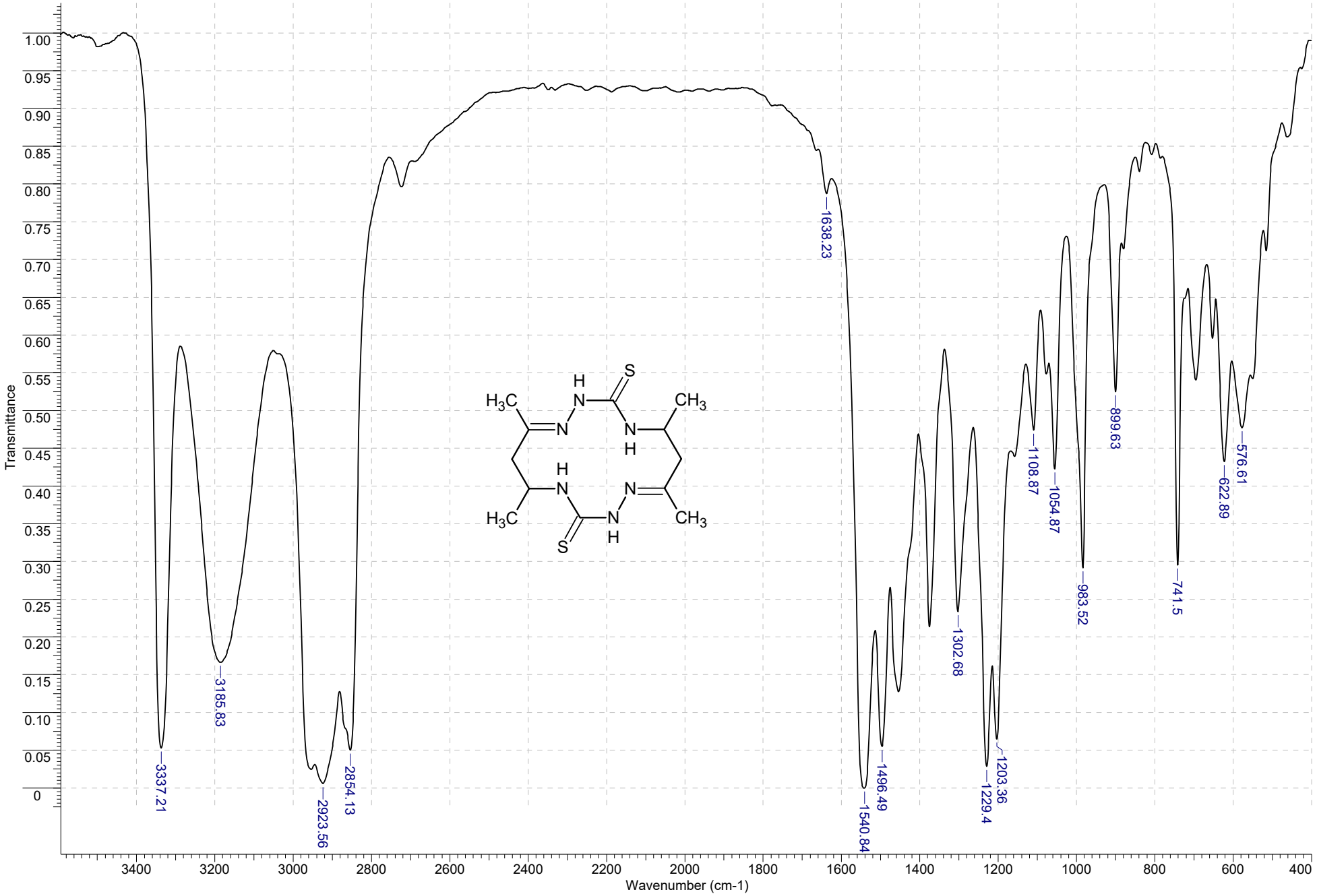
Fragment of ^{1}H,^{1}H NOESY spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallyzation from DMF (600.13 MHz, 30 °C, DMSO-d_6)



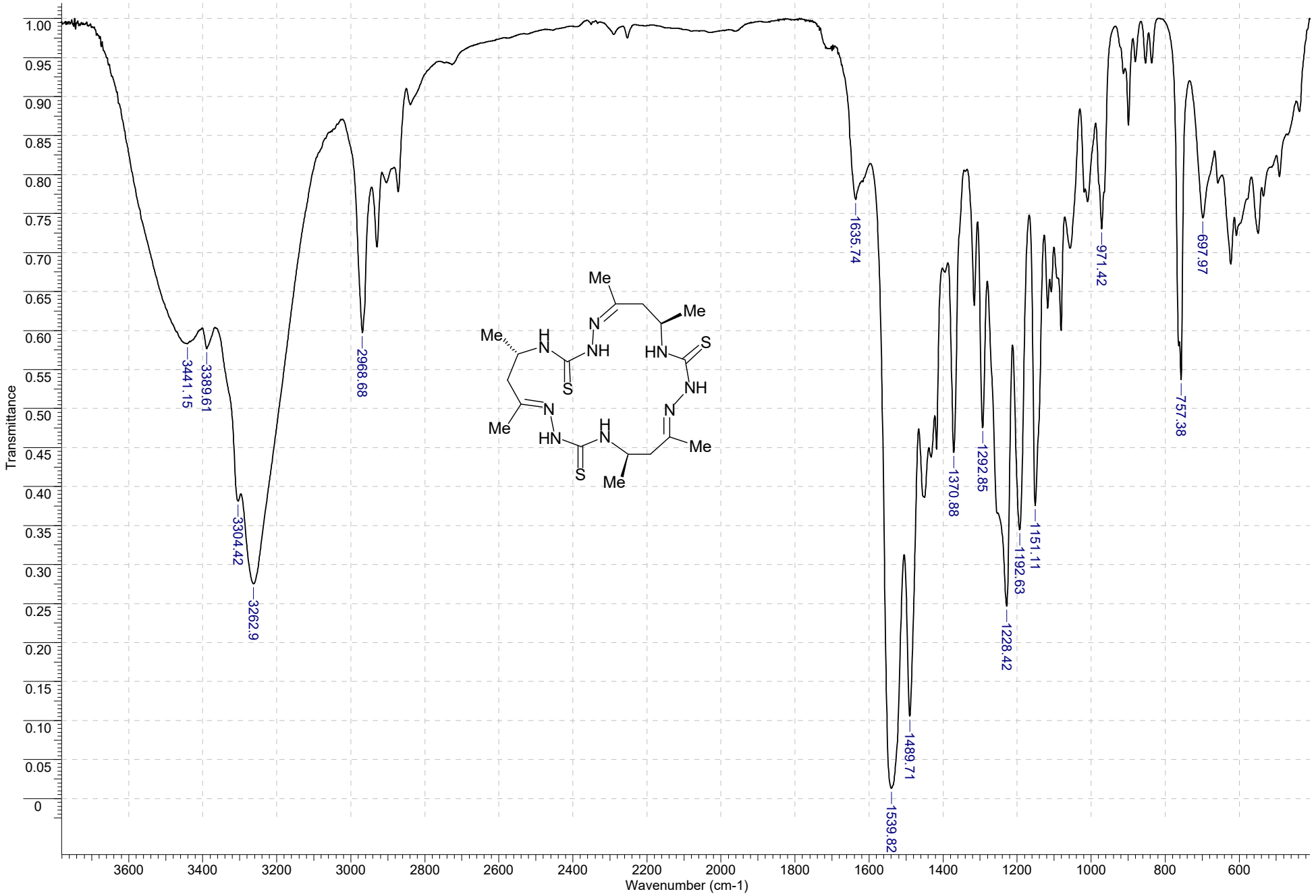
IR spectrum of hydrazone **5** (Nujol).



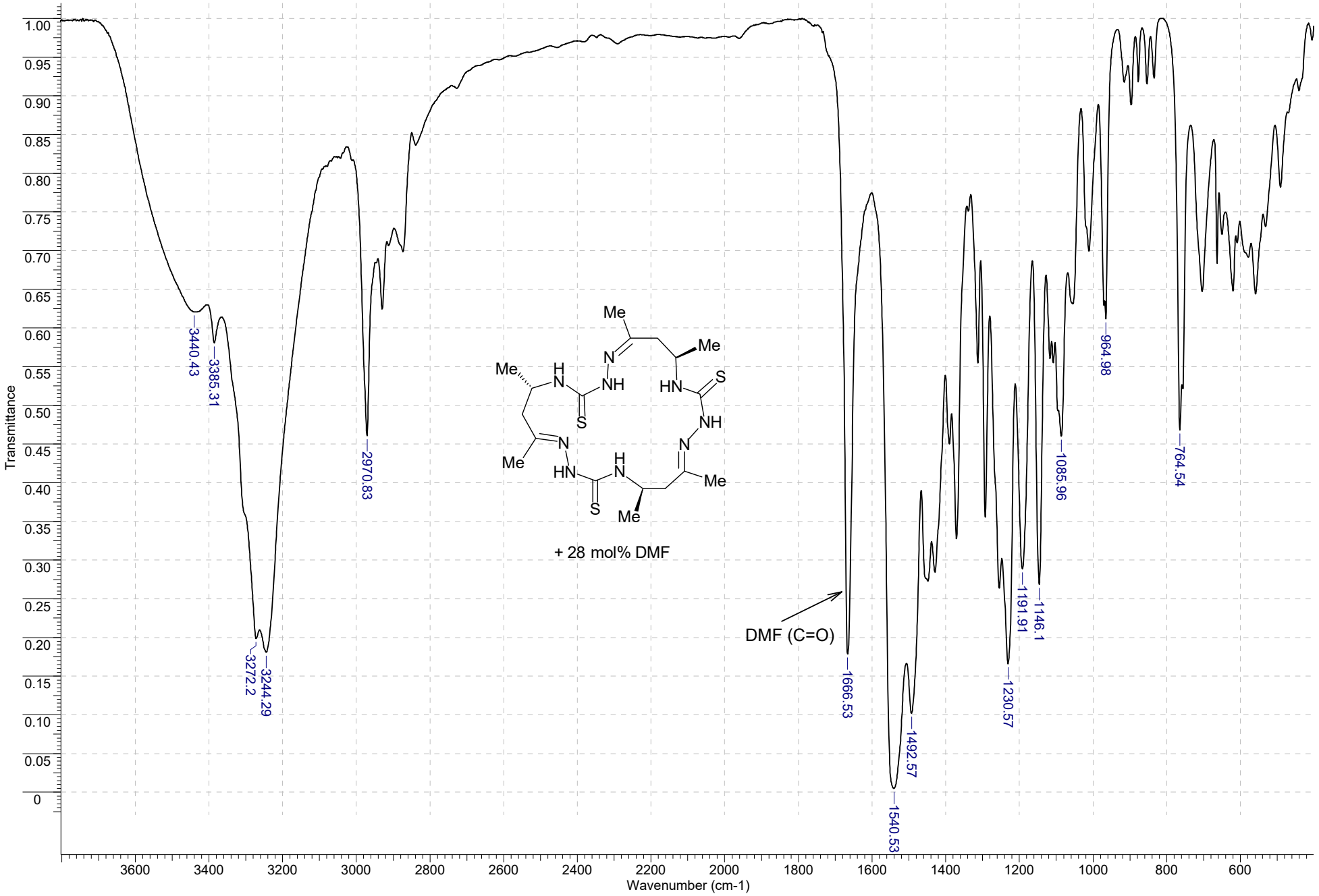
IR spectrum of 14-membered cyclic bis-thiosemicarbazone **6** (Nujol).



IR spectrum of crude 21-membered cyclic tris-thiosemicarbazone **7** (KBr).



IR spectrum of 21-membered cyclic tris-thiosemicarbazone **7** after crystallization from DMF (KBr).



X-ray diffraction data

Single crystals of macrocycle *cis*-**6** suitable for X-ray crystallographic analysis were obtained by recrystallyzation of a 80:20 mixture of *cis*- and *trans*-isomers of **6** from BuOH. Single crystals of DMF solvate of macrocycle **7**·(**7**·DMF) were formed by slow crystallyzation from a saturated solution in DMF (8.2 mg of **7** and 1.0 mL of DMF) at room temperature.

X-ray diffraction experiments were carried out on a Bruker KAPPA APEX II area-detector diffractometer.[1] Unit cell parameters were refined over the whole dataset together with data reduction.[2] Absorption corrections were introduced using the SADABS program.[3] The structures were solved by an intrinsic phasing method using the SHELXT program[4] and refined by full-matrix least-squares on F^2 in the anisotropic approximation for all non-hydrogen atoms (except disordered C atoms of solvate DMF molecule in **7**) (SHELXL-2018[5]). The H atoms of CH, CH_2 and CH_3 groups were placed in geometrically calculated positions with isotropic temperature factors equal to $1.2U_{eq}$(C) for CH and CH_2 and $1.5U_{eq}$(C) for CH_3 groups, the orientation of CH_3 groups was refined. The H atoms of NH groups were objectively located from the difference Fourier synthesis and refined with isotropic temperature factors equal to $1.2U_{eq}$(N). Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2 Crystallographic data and details of data collection and structure refinement

Compound	**6**	**7**·DMF
CCDC deposition number	2361716	2361717
Empirical formula	$C_{12}H_{22}N_6S_2$	$C_{21}H_{40}N_{10}S_3O$
M	314.47	544.81
T, K	296(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a, Å	9.7250(3)	12.8167(4)
b, Å	9.1469(2)	11.8970(4)
c, Å	18.4748(5)	18.1261(6)
α, °	90	90
β, °	97.306(1)	90.928(1)
γ, °	90	90
V, Å^3; *Z*	1630.06(8), 4	2763.51(16), 4
$\rho_{calc.}$, g/cm^3	1.281	1.309

μ(MoK_α), mm^{-1}	0.327	0.303
Crystal size, mm^3	0.4 × 0.38 × 0.34	0.18 × 0.16 × 0.14
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
$2\theta_{max}$, ^{o}	60	60
Reflections collected	31725	100195
Independent reflections	4733 [R_{int} = 0.0307, R_{sigma} = 0.0236]	8049 [R_{int} = 0.1133, R_{sigma} = 0.0616]
Data/restraints/parameters	4733/4/197	8049/7/357
Final *R* indexes [*I*>=2σ(*I*)]	R_1 = 0.0604, wR_2 = 0.1587	R_1 = 0.0490, wR_2 = 0.0867
Final *R* indexes [all data]	R_1 = 0.0764, wR_2 = 0.1714	R_1 = 0.0866, wR_2 = 0.0980
GOOF	1.057	1.041
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, $e\cdot$Å^{-3}	0.63, -0.39	0.53, -0.43

Structure 6

Bond lengths and bond angles in the structure **6** are given in Tables 3 and 4. The structure contains intramolecular H-bonds N-H…N (Fig. 1, Table 5). Intermolecular H-bonds N-H...S (Fig. 2, Table 5) link the molecules into the chains along the [100] direction.

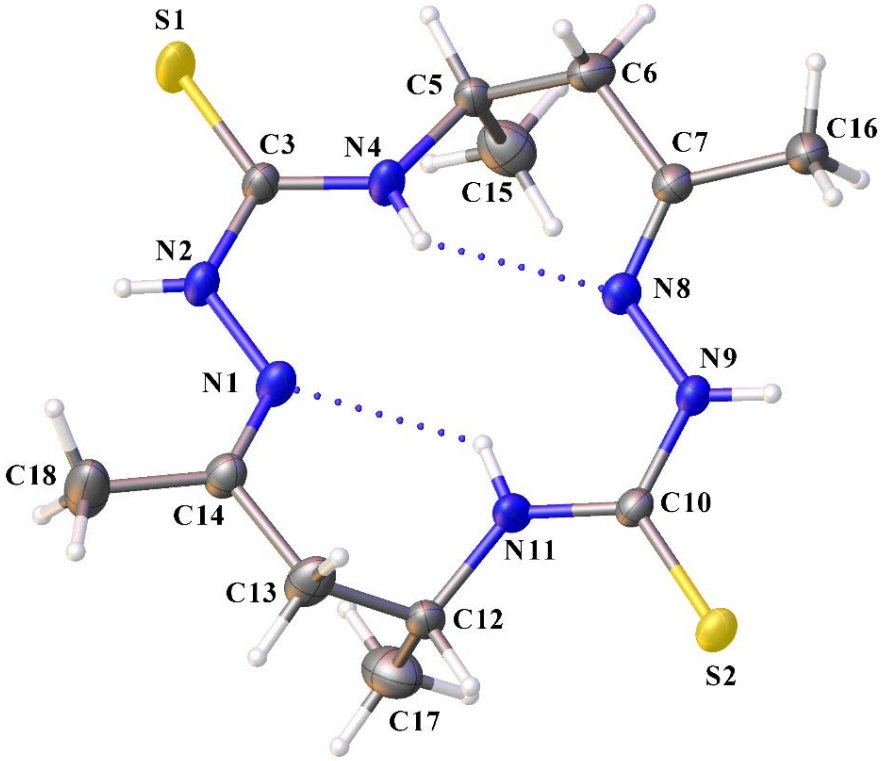


Figure 1. A view of **6**. Displacement ellipsoids are shown at 30% probability level. Dotted lines indicate H-bonds.

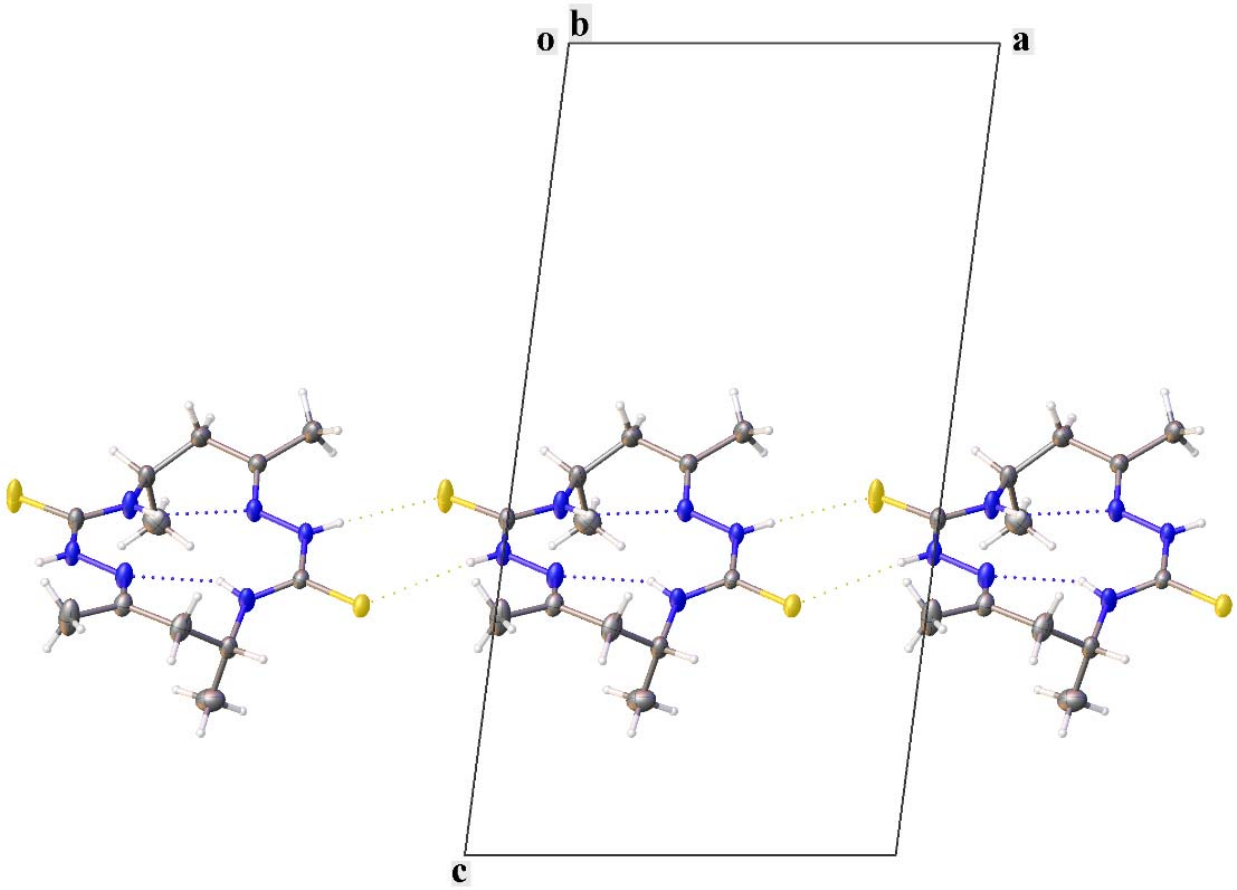


Figure 2. Chain formed by N-H..S bonds in the structure **6**. Dotted lines indicate H-bonds.

Table 3 Bond lengths for **6**

Atom	Atom	Length/Å
S1	C3	1.672(2)
S2	C10	1.684(2)
N1	N2	1.388(2)
N1	C14	1.264(3)
N2	C3	1.357(3)
N4	C3	1.318(3)
N4	C5	1.455(3)
N8	N9	1.389(2)
N8	C7	1.277(3)
N9	C10	1.350(3)

Atom	Atom	Length/Å
N11	C10	1.317(3)
N11	C12	1.452(3)
C5	C6	1.531(3)
C5	C15	1.497(4)
C6	C7	1.510(3)
C7	C16	1.473(3)
C12	C13	1.501(4)
C12	C17	1.514(4)
C13	C14	1.512(3)
C14	C18	1.490(4)

Table 4 Bond angles for **6**

Atom	Atom	Atom	Angle/°
C14	N1	N2	120.43(19)
C3	N2	N1	118.28(18)
C3	N4	C5	127.17(19)
C7	N8	N9	120.02(18)
C10	N9	N8	118.98(17)
C10	N11	C12	128.19(18)
N2	C3	S1	120.12(16)
N4	C3	S1	123.59(17)
N4	C3	N2	116.26(18)
N4	C5	C6	109.6(2)
N4	C5	C15	110.8(2)
C15	C5	C6	112.5(2)
C7	C6	C5	119.55(19)
N8	C7	C6	119.1(2)
N8	C7	C16	125.2(2)
C16	C7	C6	115.6(2)
N9	C10	S2	120.27(15)
N11	C10	S2	123.53(16)
N11	C10	N9	116.20(18)
N11	C12	C13	111.3(2)
N11	C12	C17	108.7(2)
C13	C12	C17	113.0(2)
C12	C13	C14	119.0(2)
N1	C14	C13	118.8(2)
N1	C14	C18	125.5(2)
C18	C14	C13	115.6(2)
N8	C7	C6	119.1(2)

Table 5 Hydrogen bonds for **6**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2	S2[1]	0.819(17)	2.732(18)	3.5413(19)	170(3)
N4	H4	N8	0.845(18)	2.19(3)	2.823(2)	132(3)
N9	H9	S1[2]	0.825(17)	2.655(18)	3.4738(18)	172(3)
N11	H11	N1	0.836(18)	2.26(3)	2.827(3)	125(3)

Symmetry transformations: 1 – (-1+*x*, *y*, *z*); 2 – (1+*x*, *y*, *z*).

Structure 7

The structure **7** contains one solvate DMF molecule (Fig. 3). The CH and CH_3 groups of the DMF molecule are disordered by two positions with occupancies 0.87 and 0.13. Bond lengths and bond angles in the structure **7** are given in Tables 6 and 7. The structure contains one rather weak intramolecular H-bonds N-H…S (Fig. 3, Table 8). Solvate DMF molecules are linked with the molecule of **7** by H-bonds of N-H...O and CH…O types. The H-bonds of the C-H…N type link

molecules into the centrosymmetric dimers (Fig. 4, Table 8). Three NH groups do not participate in H-bonding.

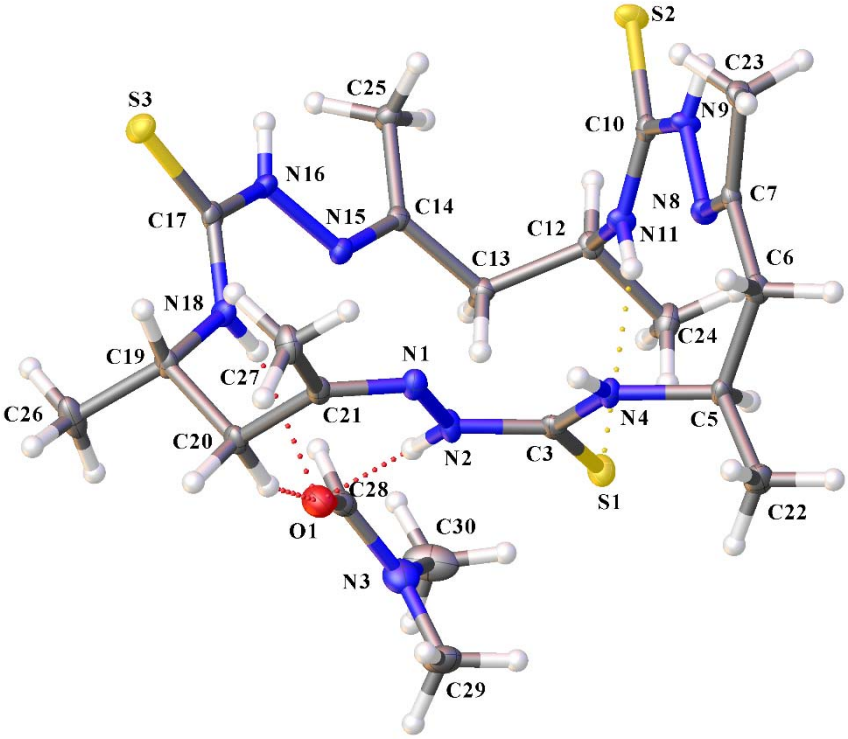


Figure 3. A view of **7**. Displacement ellipsoids are shown at 50% probability level. Dotted lines indicate H-bonds. Only the main orientation of the solvate DMF molecule is shown.

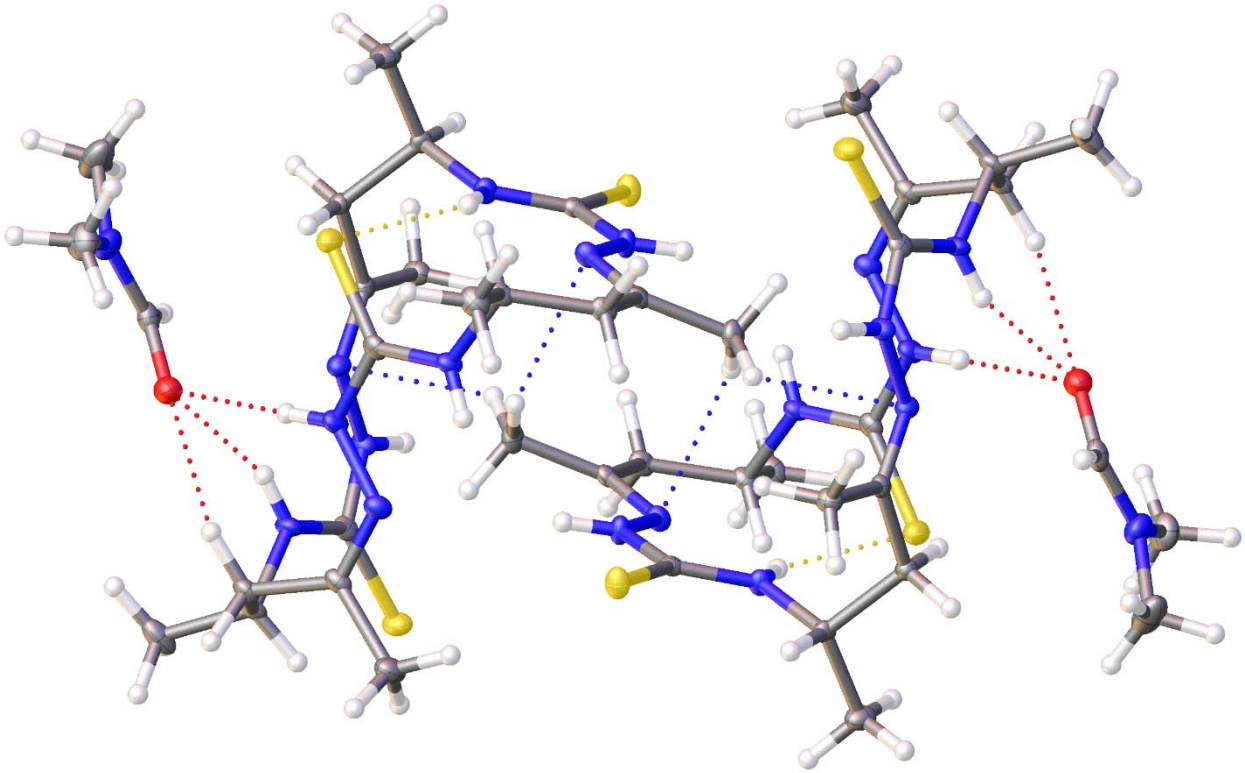


Figure 4. Centrosymmetric dimer formed by C-H..N bonds in the structure **7**. Dotted lines indicate H-bonds.

Table 6 Bond lengths for **7**·DMF

Atom	Atom	Length/Å
S2	C10	1.6901(18)
S1	C3	1.6952(19)
S3	C17	1.6854(19)
O1	C28	1.237(3)
O1	C28A	1.221(8)
N1	N2	1.382(2)
N1	C21	1.282(2)
N2	C3	1.358(2)
N3	C28	1.347(3)
N3	C29	1.410(3)
N3	C30	1.482(3)
N3	C28A	1.406(8)
N3	C29A	1.324(8)
N3	C30A	1.557(8)
N4	C3	1.328(2)
N4	C5	1.462(2)
N8	N9	1.387(2)
N8	C7	1.280(2)
N9	C10	1.358(2)

Atom	Atom	Length/Å
N11	C10	1.332(2)
N11	C12	1.463(2)
N15	N16	1.388(2)
N15	C14	1.283(2)
N16	C17	1.373(2)
N18	C17	1.328(2)
N18	C19	1.469(2)
C5	C6	1.523(3)
C5	C22	1.526(3)
C6	C7	1.501(2)
C7	C23	1.496(2)
C12	C13	1.532(2)
C12	C24	1.524(3)
C13	C14	1.504(2)
C14	C25	1.500(2)
C19	C20	1.542(3)
C19	C26	1.523(3)
C20	C21	1.499(3)
C21	C27	1.502(3)

Table 7 Bond angles for **7**·DMF

Atom	Atom	Atom	Angle/°
C21	N1	N2	119.85(16)
C3	N2	N1	117.57(16)
C28	N3	C29	123.63(19)
C28	N3	C30	117.72(19)
C29	N3	C30	118.4(2)
C28A	N3	C30A	106.5(6)

Atom	Atom	Atom	Angle/°
C23	C7	C6	116.97(15)
N9	C10	S2	117.33(13)
N11	C10	S2	125.92(14)
N11	C10	N9	116.73(16)
N11	C12	C13	111.87(14)
N11	C12	C24	108.67(15)

Atom	Atom	Atom	Angle/°
C29A	N3	C28A	127.9(7)
C29A	N3	C30A	119.8(7)
C3	N4	C5	125.80(16)
C7	N8	N9	115.39(15)
C10	N9	N8	120.45(15)
C10	N11	C12	125.40(15)
C14	N15	N16	117.72(15)
C17	N16	N15	117.46(15)
C17	N18	C19	124.78(16)
N2	C3	S1	119.51(14)
N4	C3	S1	124.44(14)
N4	C3	N2	116.04(16)
N4	C5	C6	108.87(15)
N4	C5	C22	109.34(15)
C6	C5	C22	110.79(15)
C7	C6	C5	115.76(15)
N8	C7	C6	118.82(16)
N8	C7	C23	124.20(16)

Atom	Atom	Atom	Angle/°
C24	C12	C13	109.68(15)
C14	C13	C12	115.06(15)
N15	C14	C13	115.52(16)
N15	C14	C25	125.67(16)
C25	C14	C13	118.81(15)
N16	C17	S3	118.51(14)
N18	C17	S3	125.54(14)
N18	C17	N16	115.95(16)
N18	C19	C20	109.86(15)
N18	C19	C26	110.41(15)
C26	C19	C20	110.57(15)
C21	C20	C19	114.08(15)
N1	C21	C20	127.51(18)
N1	C21	C27	115.28(17)
C20	C21	C27	117.19(16)
O1	C28	N3	124.3(2)
O1	C28A	N3	120.7(8)

Table 8 Hydrogen bonds for **7**·DMF

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2	O1	0.86(2)	2.15(2)	3.009(2)	178(2)
N11	H11	S1	0.84(2)	2.80(2)	3.5602(16)	151.5(18)
N18	H18	O1	0.84(2)	2.20(2)	2.965(2)	151.4(19)
C20	H20B	O1	0.99	2.35	3.208(2)	144
C23	H23A	N8[1]	0.98	2.63	3.441(2)	141
C23	H23C	N15[1]	0.98	2.50	3.249(2)	133

Symmetry transformation: 1 – (-*x*, 1-*y*, 1-*z*).

Computational details

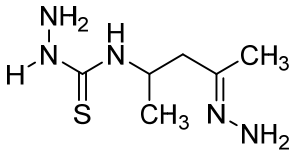
The geometry optimizations were carried out at the B3LYP level of theory using Gaussian 16 suite[6] of quantum chemical programs. Pople's basis sets, 6-311++G(d,p), was employed for geometry optimization. The effect of continuum solvation was incorporated by using the polarizable continuum model (PCM). Enthalpies and Gibbs free energies were obtained by adding unscaled zero-point vibrational energy corrections (ZPVE) and thermal contributions to the energies (temperature 298.150 Kelvin, pressure 1.000 atm). The calculations of carbon chemical shifts were performed by the GIAO method at the WC04/6-311+G(2d,p) level of theory (DMSO solution; PCM) using the DFT B3LYP/6-311++G(d,p) optimized geometries (DMSO solution; PCM).

Computational data for the starting materials

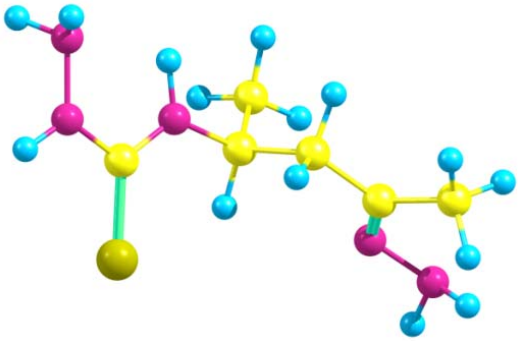
Hydrazone 5

DMSO solution

*Computational data for various conformers of hydrazone (E)-**5***



Data 1: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of *(E)*-**5** in DMSO solution.

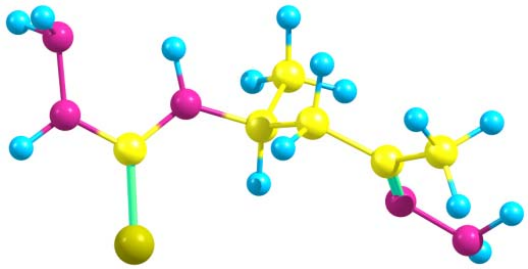


Electronic Energy =	-909.774389855 a.u.
Zero-point correction=	0.228960 (Hartree/Particle)
Thermal correction to Energy=	0.243947
Thermal correction to Enthalpy=	0.244891
Thermal correction to Gibbs Free Energy=	0.185498
Sum of electronic and zero-point Energies=	-909.545430
Sum of electronic and thermal Energies=	-909.530443
Sum of electronic and thermal Enthalpies=	-909.529499
Sum of electronic and thermal Free Energies=	-909.588892

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.801359	-1.280779	0.512571
2	7	0	3.409616	0.061015	0.377026
3	6	0	2.147279	0.392353	-0.002928
4	16	0	1.746377	2.046872	-0.177450
5	7	0	1.312114	-0.629331	-0.214585
6	6	0	-0.106535	-0.546589	-0.581969
7	6	0	-0.977496	-0.581713	0.686364
8	6	0	-2.421243	-0.161147	0.525790
9	7	0	-2.812857	0.312515	-0.597287
10	6	0	-3.316072	-0.309467	1.732065
11	7	0	-4.154269	0.665222	-0.730532
12	1	0	4.138116	-1.445089	1.456765
13	1	0	4.548425	-1.490945	-0.143507
14	1	0	4.072758	0.812447	0.508223
15	1	0	1.715720	-1.546703	-0.047828
16	1	0	-4.240784	1.322209	-1.495411
17	1	0	-4.574859	1.060755	0.108481
18	1	0	-0.247881	0.412861	-1.076739
19	1	0	-0.951864	-1.590599	1.119258
20	1	0	-0.524453	0.073150	1.441219
21	1	0	-4.197157	-0.913385	1.489524
22	1	0	-2.788325	-0.784187	2.559051
23	1	0	-3.677834	0.664354	2.083778
24	6	0	-0.423920	-1.681437	-1.557715
25	1	0	0.186338	-1.597719	-2.460143
26	1	0	-0.229291	-2.656927	-1.099540
27	1	0	-1.474763	-1.642671	-1.843915

Data 2: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of *(E)*-**5** in DMSO solution.



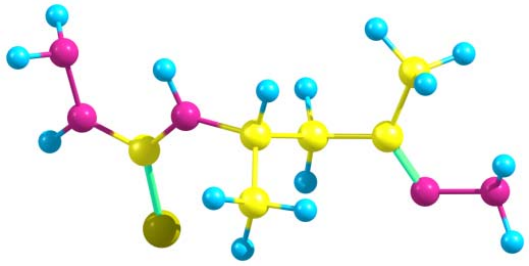
Electronic Energy =	-909.774321348 a.u.
Zero-point correction=	0.229015 (Hartree/Particle)
Thermal correction to Energy=	0.243985
Thermal correction to Enthalpy=	0.244929
Thermal correction to Gibbs Free Energy=	0.185557
Sum of electronic and zero-point Energies=	-909.545307
Sum of electronic and thermal Energies=	-909.530336
Sum of electronic and thermal Enthalpies=	-909.529392
Sum of electronic and thermal Free Energies=	-909.588764

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.788349	1.322209	-0.479348
2	7	0	3.412497	-0.027375	-0.381065
3	6	0	2.154709	-0.384153	-0.009075
4	16	0	1.775051	-2.047567	0.122628
5	7	0	1.306940	0.621220	0.229124

6	6	0	-0.110278	0.511243	0.594349
7	6	0	-0.982616	0.597015	-0.670606
8	6	0	-2.426011	0.169392	-0.524821
9	7	0	-2.806578	-0.380166	0.566933
10	6	0	-3.327541	0.385402	-1.715905
11	7	0	-4.116401	-0.847725	0.647801
12	1	0	4.124218	1.516269	-1.418181
13	1	0	4.532098	1.523319	0.183323
14	1	0	4.085303	-0.766968	-0.529230
15	1	0	1.699028	1.547648	0.086181
16	1	0	-4.378772	-0.908005	1.623392
17	1	0	-4.800438	-0.286467	0.143707
18	1	0	-0.243043	-0.470939	1.044568
19	1	0	-0.957930	1.622179	-1.062925
20	1	0	-0.530241	-0.027527	-1.451566
21	1	0	-4.134711	1.090742	-1.483325
22	1	0	-2.771683	0.787321	-2.562896
23	1	0	-3.797152	-0.554873	-2.023889
24	6	0	-0.435474	1.597844	1.621291
25	1	0	0.175564	1.476734	2.518892
26	1	0	-0.247442	2.594637	1.208642
27	1	0	-1.485990	1.539394	1.905752

Data 3: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of *(E)*-**5** in DMSO solution.



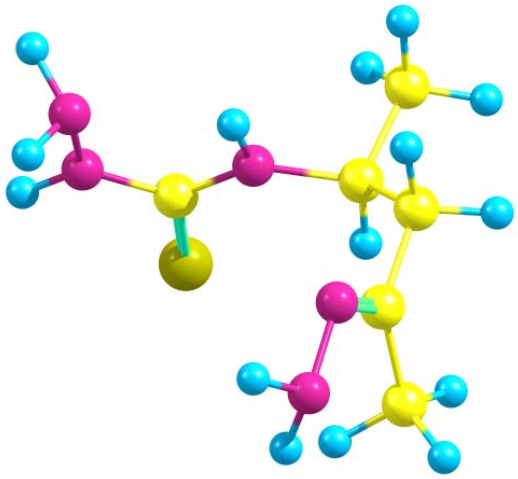
Electronic Energy =	-909.768992727 a.u.
Zero-point correction=	0.229272 (Hartree/Particle)
Thermal correction to Energy=	0.244166
Thermal correction to Enthalpy=	0.245110
Thermal correction to Gibbs Free Energy=	0.186273
Sum of electronic and zero-point Energies=	-909.539721
Sum of electronic and thermal Energies=	-909.524827
Sum of electronic and thermal Enthalpies=	-909.523883
Sum of electronic and thermal Free Energies=	-909.582719

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.757262	-1.612015	-0.226539
2	7	0	3.453295	-0.245597	-0.331330
3	6	0	2.198927	0.225823	-0.087623
4	16	0	1.928575	1.905905	-0.258366
5	7	0	1.301462	-0.701567	0.266874
6	6	0	-0.126690	-0.566257	0.611573
7	6	0	-0.968493	-0.088315	-0.597100
8	6	0	-2.453119	-0.276807	-0.404452
9	7	0	-3.178778	0.779892	-0.341915
10	6	0	-3.012769	-1.676342	-0.326375
11	7	0	-4.556405	0.623454	-0.233563
12	1	0	4.489567	-1.750313	0.463977
13	1	0	4.079875	-1.964318	-1.123381
14	1	0	4.155236	0.424091	-0.615399

15	1	0	1.691039	-1.638974	0.297757
16	1	0	-4.954078	1.476333	0.138140
17	1	0	-4.855598	-0.171490	0.327738
18	1	0	-0.421998	-1.595120	0.832083
19	1	0	-0.762844	0.962941	-0.794513
20	1	0	-0.649506	-0.665166	-1.473530
21	1	0	-3.817090	-1.807551	-1.058420
22	1	0	-2.245315	-2.424682	-0.523748
23	1	0	-3.439462	-1.889581	0.661486
24	6	0	-0.355981	0.259415	1.881571
25	1	0	-1.409638	0.212232	2.165963
26	1	0	0.238057	-0.141128	2.706521
27	1	0	-0.084547	1.303970	1.728927

Data 4: Cartesian coordinates and energies of the optimized geometry for the conformer **D** of *(E)*-**5** in DMSO solution.



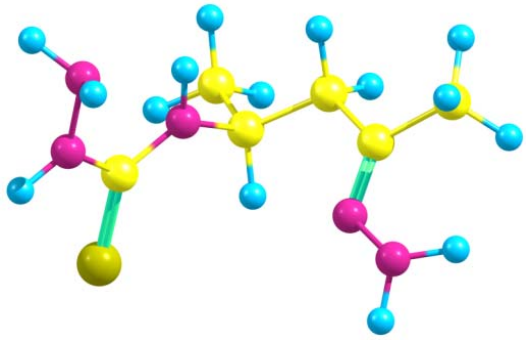
Electronic Energy =	-909.776381173 a.u.
Zero-point correction=	0.229267 (Hartree/Particle)
Thermal correction to Energy=	0.244127
Thermal correction to Enthalpy=	0.245071
Thermal correction to Gibbs Free Energy=	0.185923
Sum of electronic and zero-point Energies=	-909.547114
Sum of electronic and thermal Energies=	-909.532255
Sum of electronic and thermal Enthalpies=	-909.531310
Sum of electronic and thermal Free Energies=	-909.590458

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.940987	-2.146246	-1.314572
2	7	0	2.296498	-1.478268	-0.131565
3	6	0	1.700488	-0.310877	0.226271
4	16	0	2.176976	0.442689	1.687436
5	7	0	0.771751	0.153253	-0.615483
6	6	0	0.022322	1.406290	-0.496205
7	6	0	-1.448368	1.163640	-0.895720
8	6	0	-2.184080	0.196581	-0.002512
9	7	0	-2.552674	-0.918407	-0.518956
10	6	0	-2.461243	0.588897	1.427405
11	7	0	-3.281343	-1.798976	0.273929
12	1	0	1.574227	-3.067789	-1.093804
13	1	0	2.758907	-2.251448	-1.907897
14	1	0	2.990040	-1.862416	0.495317
15	1	0	0.628391	-0.418334	-1.443578
16	1	0	-3.208468	-2.728541	-0.118924

17	1	0	-3.010198	-1.816617	1.255194
18	1	0	0.075996	1.695362	0.554022
19	1	0	-1.956166	2.134563	-0.872418
20	1	0	-1.491818	0.798727	-1.926170
21	1	0	-1.920843	-0.050889	2.135419
22	1	0	-2.164830	1.619419	1.622225
23	1	0	-3.528804	0.488090	1.651298
24	6	0	0.660544	2.510449	-1.347081
25	1	0	1.699788	2.668559	-1.051288
26	1	0	0.638800	2.248191	-2.408938
27	1	0	0.118854	3.450733	-1.215858

Data 5: Cartesian coordinates and energies of the optimized geometry for the conformer **E** of *(E)*-**5** in DMSO solution.



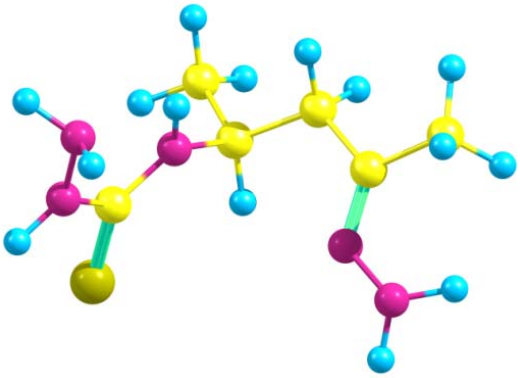
Electronic Energy =	-909.774093233 a.u.
Zero-point correction=	0.228990 (Hartree/Particle)
Thermal correction to Energy=	0.243930
Thermal correction to Enthalpy=	0.244874
Thermal correction to Gibbs Free Energy=	0.185809
Sum of electronic and zero-point Energies=	-909.545103
Sum of electronic and thermal Energies=	-909.530163
Sum of electronic and thermal Enthalpies=	-909.529219
Sum of electronic and thermal Free Energies=	-909.588284

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.103182	-1.357175	2.083109
2	7	0	-2.484797	-1.135143	0.750083
3	6	0	-1.800715	-0.268436	-0.044399
4	16	0	-2.303505	-0.070660	-1.668664
5	7	0	-0.775650	0.365010	0.528940
6	6	0	0.096405	1.369388	-0.089778
7	6	0	1.505678	1.251798	0.501120
8	6	0	2.320048	0.035153	0.118231
9	7	0	1.879961	-0.748054	-0.793078
10	6	0	3.632642	-0.164692	0.835658
11	7	0	2.628744	-1.879788	-1.104642
12	1	0	-1.841223	-2.330678	2.210583
13	1	0	-2.879107	-1.142080	2.702376
14	1	0	-3.249921	-1.648552	0.334882
15	1	0	-0.633236	0.135425	1.508338
16	1	0	2.371013	-2.193731	-2.031501
17	1	0	3.637801	-1.751759	-1.053567
18	1	0	0.128444	1.140565	-1.154191
19	1	0	2.074790	2.143048	0.208565
20	1	0	1.447899	1.304974	1.596974
21	1	0	4.480218	-0.116101	0.141332
22	1	0	3.786899	0.598205	1.598619
23	1	0	3.665737	-1.148150	1.317207
24	6	0	-0.472145	2.780412	0.111175
25	1	0	-1.488029	2.841449	-0.283836

26	1	0	-0.496209	3.046072	1.172413
27	1	0	0.143997	3.516194	-0.412491

Data 6: Cartesian coordinates and energies of the optimized geometry for the conformer **F** of *(E)*-**5** in DMSO solution.

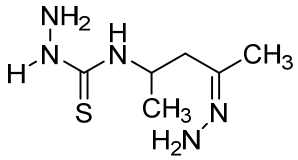


Electronic Energy =	-909.775823758 a.u.
Zero-point correction=	0.229322 (Hartree/Particle)
Thermal correction to Energy=	0.244186
Thermal correction to Enthalpy=	0.245130
Thermal correction to Gibbs Free Energy=	0.186146
Sum of electronic and zero-point Energies=	-909.546502
Sum of electronic and thermal Energies=	-909.531638
Sum of electronic and thermal Enthalpies=	-909.530694
Sum of electronic and thermal Free Energies=	-909.589678

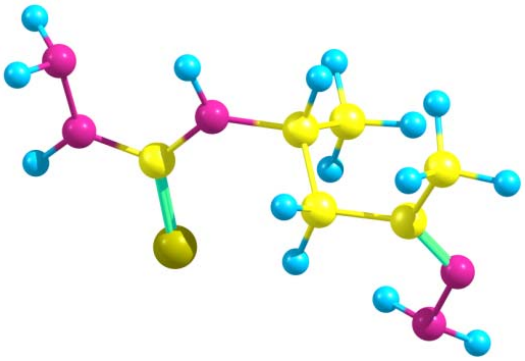
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.620096	-1.623648	-0.616801
2	7	0	-3.431098	-0.243156	-0.441602
3	6	0	-2.240410	0.256825	-0.019324
4	16	0	-2.086168	1.946350	0.202304
5	7	0	-1.272676	-0.640938	0.195817
6	6	0	0.110619	-0.363931	0.588899
7	6	0	1.015287	-0.327488	-0.668341
8	6	0	2.428296	0.123597	-0.395749
9	7	0	3.368247	-0.730963	-0.577470
10	6	0	2.666932	1.546642	0.045454
11	7	0	4.680905	-0.309693	-0.395885
12	1	0	-3.905877	-1.811173	-1.573375
13	1	0	-4.344475	-1.956080	0.013609
14	1	0	-4.192457	0.407925	-0.576247
15	1	0	-1.534795	-1.601839	-0.006431
16	1	0	5.265188	-1.119708	-0.234126
17	1	0	4.815147	0.369578	0.350622
18	1	0	0.102509	0.623834	1.050910
19	1	0	1.041589	-1.321100	-1.123559
20	1	0	0.555133	0.360567	-1.387002
21	1	0	3.392334	2.035066	-0.614330
22	1	0	1.744701	2.127046	0.031967
23	1	0	3.075028	1.592712	1.062590
24	6	0	0.561192	-1.404200	1.615424
25	1	0	-0.081291	-1.377363	2.498262
26	1	0	0.529808	-2.413829	1.193686
27	1	0	1.587683	-1.207115	1.929964

*Computational data for various conformers of hydrazone (Z)-**5***



Data 7: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of *(Z)*-**5** in DMSO solution.



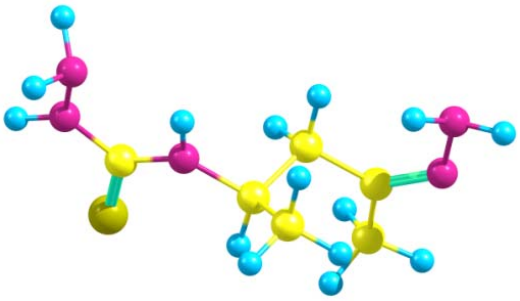
Electronic Energy =	-909.767048550 a.u.
Zero-point correction=	0.229417 (Hartree/Particle)
Thermal correction to Energy=	0.244318
Thermal correction to Enthalpy=	0.245262
Thermal correction to Gibbs Free Energy=	0.186072
Sum of electronic and zero-point Energies=	-909.537632
Sum of electronic and thermal Energies=	-909.522731
Sum of electronic and thermal Enthalpies=	-909.521787
Sum of electronic and thermal Free Energies=	-909.580976

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.738815	-1.451804	-0.244865
2	7	0	-3.308706	-0.117876	-0.323515
3	6	0	-2.015615	0.227151	-0.076582
4	16	0	-1.584320	1.877067	-0.214460
5	7	0	-1.207691	-0.788056	0.254325
6	6	0	0.226242	-0.784817	0.596508
7	6	0	0.525184	-0.005394	1.881829
8	6	0	1.091730	-0.370749	-0.621888
9	6	0	2.582071	-0.523253	-0.395654
10	7	0	3.410399	0.439730	-0.217192
11	6	0	3.146501	-1.920025	-0.423692
12	7	0	2.960381	1.756357	-0.245603
13	1	0	-4.096316	-1.753195	-1.146992
14	1	0	-4.478345	-1.535075	0.446790
15	1	0	-3.945408	0.620303	-0.591594
16	1	0	-1.680090	-1.686960	0.266779
17	1	0	0.434578	-1.837388	0.799834
18	1	0	1.578280	-0.121423	2.149044
19	1	0	-0.076871	-0.396220	2.705425
20	1	0	0.303630	1.055640	1.768138
21	1	0	0.811380	-1.021756	-1.456510
22	1	0	0.835700	0.646569	-0.916499
23	1	0	4.224432	-1.899995	-0.261798
24	1	0	2.691296	-2.550888	0.347246
25	1	0	2.940932	-2.399623	-1.387228

26	1	0	3.629819	2.335022	0.244812
27	1	0	2.030455	1.905975	0.138728

Data 8: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of *(Z)*-**5** in DMSO solution.

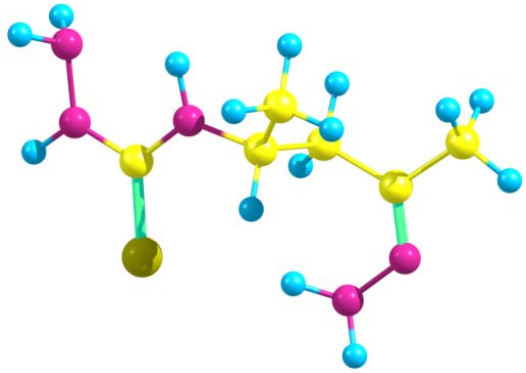


Electronic Energy =	-909.773001499 a.u.
Zero-point correction=	0.229416 (Hartree/Particle)
Thermal correction to Energy=	0.244282
Thermal correction to Enthalpy=	0.245226
Thermal correction to Gibbs Free Energy=	0.186126
Sum of electronic and zero-point Energies=	-909.543585
Sum of electronic and thermal Energies=	-909.528720
Sum of electronic and thermal Enthalpies=	-909.527775
Sum of electronic and thermal Free Energies=	-909.586875

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.335761	-1.845396	-0.540122
2	7	0	3.278707	-0.446045	-0.435546
3	6	0	2.147864	0.184255	-0.025246
4	16	0	2.151763	1.888668	0.110464
5	7	0	1.104208	-0.608030	0.248369
6	6	0	-0.237686	-0.180872	0.645717
7	6	0	-0.779012	-1.144821	1.702661
8	6	0	-1.147068	-0.070896	-0.606666
9	6	0	-2.517354	0.515172	-0.332696
10	7	0	-3.625186	-0.131206	-0.327611
11	6	0	-2.588369	2.000218	-0.087535
12	7	0	-3.638151	-1.494625	-0.610182
13	1	0	4.037222	-2.210933	0.097896
14	1	0	3.587020	-2.107238	-1.488934
15	1	0	4.094885	0.123038	-0.614129
16	1	0	1.271931	-1.598307	0.093346
17	1	0	-4.496001	-1.887284	-0.244535
18	1	0	-2.845651	-2.017988	-0.247172
19	1	0	-0.124714	0.811053	1.083326
20	1	0	-0.823974	-2.169835	1.320308
21	1	0	-1.785373	-0.849799	2.007412
22	1	0	-0.140586	-1.141443	2.588616
23	1	0	-0.641162	0.588424	-1.318982
24	1	0	-1.221465	-1.051226	-1.084754
25	1	0	-1.987871	2.291319	0.780502
26	1	0	-2.190356	2.551664	-0.946485
27	1	0	-3.619720	2.308655	0.084397

Data 9: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of *(Z)*-**5** in DMSO solution.

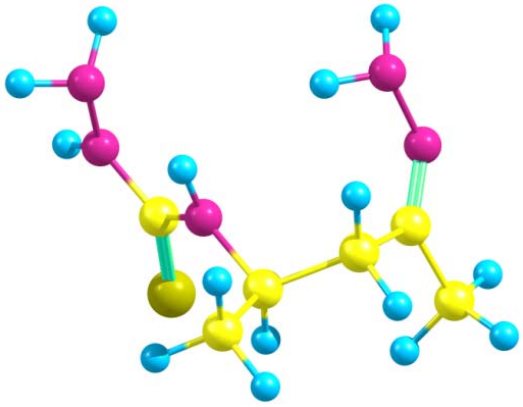


Electronic Energy =	-909.774378891 a.u.
Zero-point correction=	0.229715 (Hartree/Particle)
Thermal correction to Energy=	0.244276
Thermal correction to Enthalpy=	0.245220
Thermal correction to Gibbs Free Energy=	0.187873
Sum of electronic and zero-point Energies=	-909.544664
Sum of electronic and thermal Energies=	-909.530103
Sum of electronic and thermal Enthalpies=	-909.529159
Sum of electronic and thermal Free Energies=	-909.586506

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.614707	-1.328684	-0.671635
2	7	0	3.219892	-0.011263	-0.387962
3	6	0	1.960674	0.268977	0.031760
4	16	0	1.545057	1.890806	0.388730
5	7	0	1.128932	-0.772871	0.139793
6	6	0	-0.279107	-0.715909	0.538089
7	6	0	-0.622783	-1.981154	1.325000
8	6	0	-1.180630	-0.504631	-0.710361
9	6	0	-2.617417	-0.146311	-0.387793
10	7	0	-3.017487	1.039591	-0.100669
11	6	0	-3.661200	-1.229310	-0.465277
12	7	0	-2.119978	2.096486	-0.140925
13	1	0	4.370365	-1.603113	-0.050067
14	1	0	3.941561	-1.388041	-1.631667
15	1	0	3.875524	0.755220	-0.456240
16	1	0	1.525947	-1.668091	-0.130697
17	1	0	-2.478428	2.856690	0.421369
18	1	0	-1.149663	1.896062	0.104515
19	1	0	-0.375131	0.146246	1.198929
20	1	0	-0.529358	-2.874687	0.699960
21	1	0	-1.647585	-1.932831	1.695961
22	1	0	0.042442	-2.087915	2.184638
23	1	0	-0.739160	0.291843	-1.317993
24	1	0	-1.158529	-1.417886	-1.312028
25	1	0	-3.729463	-1.617872	-1.488283
26	1	0	-3.411443	-2.079576	0.176422
27	1	0	-4.637664	-0.841731	-0.173217

Data 10: Cartesian coordinates and energies of the optimized geometry for the conformer **D** of *(Z)*-**5** in DMSO solution.

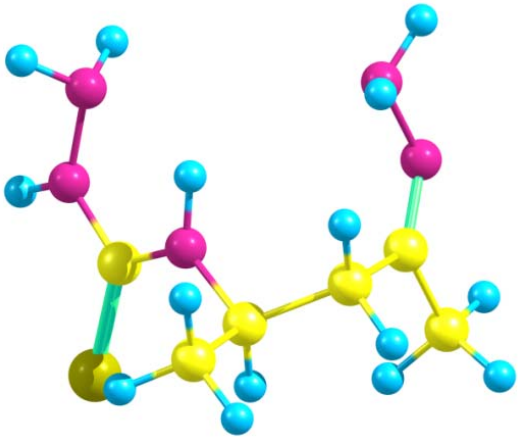


Electronic Energy =	-909.773076039 a.u.
Zero-point correction=	0.229370 (Hartree/Particle)
Thermal correction to Energy=	0.244254
Thermal correction to Enthalpy=	0.245199
Thermal correction to Gibbs Free Energy=	0.185881
Sum of electronic and zero-point Energies=	-909.543706
Sum of electronic and thermal Energies=	-909.528822
Sum of electronic and thermal Enthalpies=	-909.527877
Sum of electronic and thermal Free Energies=	-909.587195

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.771248	1.563945	-0.811871
2	7	0	2.597449	0.722350	0.299124
3	6	0	1.566887	-0.159255	0.362023
4	16	0	1.436990	-1.180771	1.725472
5	7	0	0.722052	-0.138385	-0.680262
6	6	0	-0.382034	-1.068301	-0.937336
7	6	0	-0.110811	-1.854869	-2.224150
8	6	0	-1.733277	-0.317205	-1.007568
9	6	0	-2.205921	0.268444	0.308251
10	7	0	-2.129318	1.500552	0.653630
11	6	0	-2.871799	-0.677572	1.272755
12	7	0	-1.578883	2.429487	-0.231313
13	1	0	3.675331	1.385151	-1.239717
14	1	0	2.734113	2.535492	-0.516712
15	1	0	3.245194	0.744174	1.074872
16	1	0	1.016679	0.475611	-1.435815
17	1	0	-1.327178	3.254419	0.298312
18	1	0	-0.757769	2.093474	-0.727612
19	1	0	-0.398357	-1.756279	-0.092370
20	1	0	-0.062271	-1.189160	-3.091508
21	1	0	-0.908106	-2.580684	-2.399266
22	1	0	0.836127	-2.394115	-2.150358
23	1	0	-1.684019	0.452022	-1.784187
24	1	0	-2.485911	-1.040963	-1.335669
25	1	0	-2.210018	-1.510929	1.529430
26	1	0	-3.149060	-0.157417	2.189772
27	1	0	-3.772680	-1.111561	0.824273

Data 11: Cartesian coordinates and energies of the optimized geometry for the conformer **E** of *(Z)*-**5** in DMSO solution.



Electronic Energy =	-909.773214303 a.u.
Thermal correction to Energy=	0.244179
Thermal correction to Enthalpy=	0.245123
Thermal correction to Gibbs Free Energy=	0.185869
Sum of electronic and zero-point Energies=	-909.543919
Sum of electronic and thermal Energies=	-909.529036
Sum of electronic and thermal Enthalpies=	-909.528091
Sum of electronic and thermal Free Energies=	-909.587346

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.771334	2.454479	0.429451
2	7	0	-2.300077	1.340675	-0.242286
3	6	0	-1.686983	0.129934	-0.192857
4	16	0	-2.387397	-1.183122	-1.037903
5	7	0	-0.560938	0.071954	0.527398
6	6	0	0.234285	-1.128819	0.798037
7	6	0	-0.174230	-1.777662	2.125389
8	6	0	1.738927	-0.777653	0.787520
9	6	0	2.218838	-0.165714	-0.513026
10	7	0	2.494487	1.071400	-0.706217
11	6	0	2.386564	-1.098974	-1.683460
12	7	0	2.307265	1.997620	0.317806
13	1	0	-2.462747	2.823517	1.075649
14	1	0	-1.527485	3.178687	-0.240313
15	1	0	-3.135912	1.420371	-0.805147
16	1	0	-0.294588	0.947376	0.970526
17	1	0	2.518368	1.652123	1.252059
18	1	0	2.885632	2.805094	0.122990
19	1	0	0.020706	-1.824096	-0.013936
20	1	0	0.006579	-1.098654	2.963656
21	1	0	0.400600	-2.691974	2.293947
22	1	0	-1.234824	-2.036777	2.111712
23	1	0	1.957500	-0.140184	1.648695
24	1	0	2.287015	-1.709535	0.954974
25	1	0	1.446735	-1.606936	-1.924110
26	1	0	2.720364	-0.549383	-2.563739
27	1	0	3.120181	-1.879250	-1.453203

Table 9 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of various conformers of (*E*)- and *(Z)*-**5** in DMSO solution

Conformer	(*E*)-**5**		*(Z)*-**5**	
	ΔE	ΔG	ΔE	ΔG
A	1.25	0.98	5.86	5.95
B	1.29	1.06	2.12	2.25
C	4.64	4.86	1.26	2.48
D	0.00	0.00	2.07	2.05
E	1.44	1.36	1.99	1.95
F	0.35	0.49	-	-

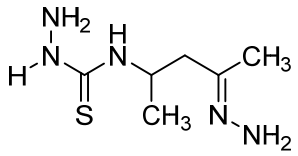
Table 10 Experimental ^{13}C chemical shifts of (*E*)- and *(Z)*-**5** (DMSO-d_6) and calculated ^{13}C chemical shifts for some conformers of (*E*)- and *(Z)*-**5** in DMSO solution[a]

^{13}C assign-ment	Calculated shift of (*E*)-**5**, ppm		Calculated shift of *(Z)*-**5**, ppm		Observed shift, ppm	
	Conformer **D**	Conformer **F**	Conformer **B**	Conformer **E**	Major isomer	Minor isomer
CH-N	43.69	43.33	43.51	44.08	46.90	46.03
$CH_2C{=}N$	45.31	46.56	33.11	30.79	44.76	35.15
CH_3-C=N	13.51	12.95	24.08	24.10	14.12	23.49

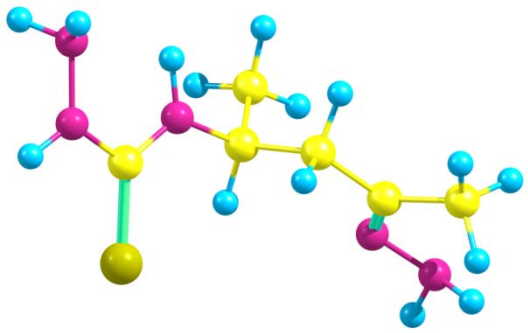
[a] Calculations were performed by the GIAO method at the WC04/6-311+G(2d,p) level of theory using the DFT B3LYP/6-311++G(d,p) optimized geometries.

MeCN solution

*Computational data for various conformers of hydrazone (E)-**5***



Data 12: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of *(E)*-**5** in MeCN solution.



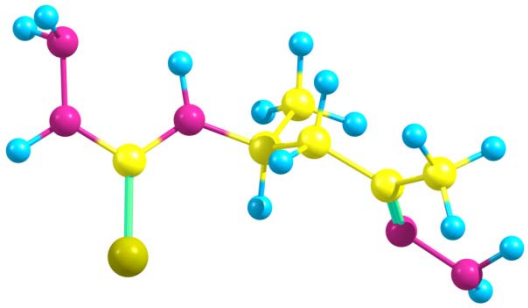
Electronic Energy =	-909.774120308 a.u.
Zero-point correction=	0.228941 (Hartree/Particle)
Thermal correction to Energy=	0.243939
Thermal correction to Enthalpy=	0.244883
Thermal correction to Gibbs Free Energy=	0.185436
Sum of electronic and zero-point Energies=	-909.545179
Sum of electronic and thermal Energies=	-909.530182
Sum of electronic and thermal Enthalpies=	-909.529238
Sum of electronic and thermal Free Energies=	-909.588684

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.804355	-1.274223	0.516419
2	7	0	3.409538	0.066104	0.375469
3	6	0	2.146210	0.393200	-0.005608
4	16	0	1.742203	2.045642	-0.188883
5	7	0	1.312825	-0.631348	-0.210894
6	6	0	-0.106189	-0.553124	-0.578000
7	6	0	-0.976397	-0.574882	0.691135
8	6	0	-2.420256	-0.156182	0.526799
9	7	0	-2.812727	0.304200	-0.601456
10	6	0	-3.314151	-0.290230	1.735459
11	7	0	-4.154087	0.655674	-0.737711
12	1	0	4.143524	-1.433508	1.460591
13	1	0	4.550142	-1.486313	-0.140504
14	1	0	4.071658	0.819512	0.500321
15	1	0	1.718337	-1.546998	-0.039634
16	1	0	-4.241106	1.303119	-1.510614
17	1	0	-4.573738	1.061665	0.096761
18	1	0	-0.248491	0.400845	-1.083044
19	1	0	-0.950385	-1.579102	1.134769
20	1	0	-0.523029	0.088189	1.438556
21	1	0	-4.195759	-0.896401	1.500553
22	1	0	-2.785965	-0.755719	2.567416
23	1	0	-3.675064	0.687739	2.076366
24	6	0	-0.423747	-1.698652	-1.541098
25	1	0	0.186063	-1.624729	-2.444687

26	1	0	-0.228867	-2.669125	-1.072386
27	1	0	-1.474709	-1.663085	-1.827240

Data 13: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of *(E)*-**5** in MeCN solution.

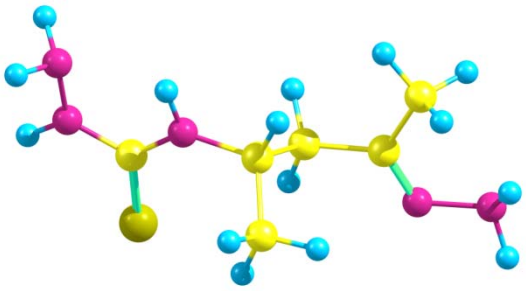


Electronic Energy =	-909.774023944 a.u.
Zero-point correction=	0.229026 (Hartree/Particle)
Thermal correction to Energy=	0.243988
Thermal correction to Enthalpy=	0.244933
Thermal correction to Gibbs Free Energy=	0.185615
Sum of electronic and zero-point Energies=	-909.544998
Sum of electronic and thermal Energies=	-909.530036
Sum of electronic and thermal Enthalpies=	-909.529091
Sum of electronic and thermal Free Energies=	-909.588409

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.788741	-1.321216	0.481540
2	7	0	3.412622	0.028129	0.381161
3	6	0	2.154778	0.384320	0.008037
4	16	0	1.775435	2.047077	-0.127842
5	7	0	1.306950	-0.621751	-0.227530
6	6	0	-0.110285	-0.512536	-0.593005
7	6	0	-0.982354	-0.593355	0.672453
8	6	0	-2.426038	-0.167181	0.525436
9	7	0	-2.808063	0.375161	-0.569378
10	6	0	-3.326173	-0.375709	1.718949
11	7	0	-4.117873	0.842033	-0.651719
12	1	0	4.125679	-1.513602	1.420318
13	1	0	4.531506	-1.523849	-0.181779
14	1	0	4.085738	0.768110	0.525910
15	1	0	1.699037	-1.547825	-0.082547
16	1	0	-4.381463	0.896429	-1.627301
17	1	0	-4.801429	0.284537	-0.142848
18	1	0	-0.242789	0.468098	-1.046720
19	1	0	-0.956894	-1.616817	1.069255
20	1	0	-0.530051	0.034945	1.450421
21	1	0	-4.134218	-1.081763	1.491522
22	1	0	-2.769530	-0.773146	2.567547
23	1	0	-3.794610	0.566713	2.022151
24	6	0	-0.435830	-1.602768	-1.615966
25	1	0	0.175687	-1.485426	-2.513742
26	1	0	-0.248692	-2.598195	-1.199545
27	1	0	-1.486150	-1.544550	-1.901107

Data 14: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of *(E)*-**5** in MeCN solution.

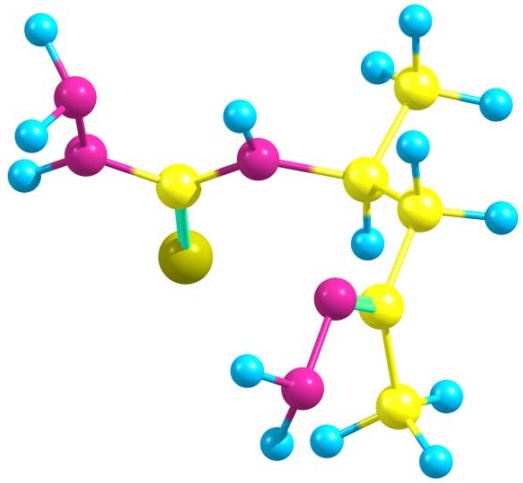


Electronic Energy =	-909.768687437 a.u.
Zero-point correction=	0.229272 (Hartree/Particle)
Thermal correction to Energy=	0.244166
Thermal correction to Enthalpy=	0.245110
Thermal correction to Gibbs Free Energy=	0.186268
Sum of electronic and zero-point Energies=	-909.539415
Sum of electronic and thermal Energies=	-909.524522
Sum of electronic and thermal Enthalpies=	-909.523578
Sum of electronic and thermal Free Energies=	-909.582420

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.756248	-1.613689	-0.225030
2	7	0	3.453193	-0.247186	-0.331151
3	6	0	2.199062	0.225592	-0.087884
4	16	0	1.929905	1.905296	-0.260447
5	7	0	1.301012	-0.700965	0.267737
6	6	0	-0.126972	-0.564048	0.612410
7	6	0	-0.968794	-0.086369	-0.596366
8	6	0	-2.453261	-0.276618	-0.404163
9	7	0	-3.180183	0.779154	-0.341292
10	6	0	-3.011400	-1.676859	-0.327033
11	7	0	-4.557543	0.621094	-0.233391
12	1	0	4.488368	-1.751998	0.465674
13	1	0	4.078389	-1.967321	-1.121515
14	1	0	4.155417	0.421829	-0.616079
15	1	0	1.689912	-1.638579	0.299714
16	1	0	-4.956445	1.473551	0.137914
17	1	0	-4.856215	-0.174319	0.327507
18	1	0	-0.423156	-1.592482	0.833919
19	1	0	-0.764222	0.965196	-0.793199
20	1	0	-0.648972	-0.662410	-1.473036
21	1	0	-3.815225	-1.808552	-1.059540
22	1	0	-2.243037	-2.424270	-0.524470
23	1	0	-3.438337	-1.891196	0.660506
24	6	0	-0.355367	0.263167	1.881565
25	1	0	-1.409213	0.218048	2.165599
26	1	0	0.237813	-0.137382	2.707140
27	1	0	-0.082251	1.307098	1.727753

Data 15: Cartesian coordinates and energies of the optimized geometry for the conformer **D** of *(E)*-**5** in MeCN solution.

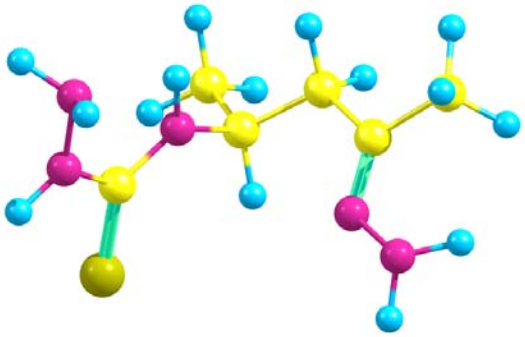


Electronic Energy =	-909.776131750 a.u.
Zero-point correction=	0.229269 (Hartree/Particle)
Thermal correction to Energy=	0.244129
Thermal correction to Enthalpy=	0.245073
Thermal correction to Gibbs Free Energy=	0.185924
Sum of electronic and zero-point Energies=	-909.546862
Sum of electronic and thermal Energies=	-909.532003
Sum of electronic and thermal Enthalpies=	-909.531059
Sum of electronic and thermal Free Energies=	-909.590207

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.940550	-2.146629	-1.314286
2	7	0	2.296075	-1.478637	-0.131334
3	6	0	1.700440	-0.310836	0.226419
4	16	0	2.177431	0.442838	1.687019
5	7	0	0.771566	0.153133	-0.615383
6	6	0	0.022385	1.406291	-0.496149
7	6	0	-1.448366	1.163861	-0.895572
8	6	0	-2.184098	0.196748	-0.002452
9	7	0	-2.552602	-0.918201	-0.519005
10	6	0	-2.461376	0.588943	1.427479
11	7	0	-3.281194	-1.798808	0.273792
12	1	0	1.573250	-3.067990	-1.093711
13	1	0	2.758304	-2.251936	-1.907805
14	1	0	2.989889	-1.862418	0.495458
15	1	0	0.627504	-0.418903	-1.443020
16	1	0	-3.208781	-2.728259	-0.119371
17	1	0	-3.010025	-1.816665	1.255039
18	1	0	0.076224	1.695419	0.554065
19	1	0	-1.956086	2.134834	-0.872177
20	1	0	-1.492026	0.799010	-1.926042
21	1	0	-1.921015	-0.050858	2.135514
22	1	0	-2.164871	1.619406	1.622479
23	1	0	-3.528979	0.488174	1.651206
24	6	0	0.660786	2.510298	-1.347098
25	1	0	1.700014	2.668282	-1.051217
26	1	0	0.639049	2.247958	-2.408950
27	1	0	0.119255	3.450703	-1.216019

Data 16: Cartesian coordinates and energies of the optimized geometry for the conformer **E** of *(E)*-**5** in MeCN solution.

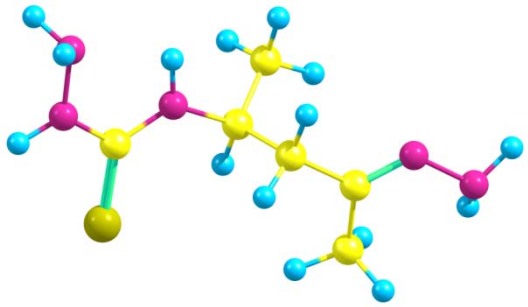


Electronic Energy =	-909.773782543 a.u.
Zero-point correction=	0.228986 (Hartree/Particle)
Thermal correction to Energy=	0.243934
Thermal correction to Enthalpy=	0.244878
Thermal correction to Gibbs Free Energy=	0.185746
Sum of electronic and zero-point Energies=	-909.544797
Sum of electronic and thermal Energies=	-909.529849
Sum of electronic and thermal Enthalpies=	-909.528905
Sum of electronic and thermal Free Energies=	-909.588037

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.094877	-1.378308	2.073259
2	7	0	-2.481758	-1.143105	0.744034
3	6	0	-1.801160	-0.268158	-0.044704
4	16	0	-2.310510	-0.054647	-1.664558
5	7	0	-0.774420	0.360364	0.531194
6	6	0	0.096017	1.369648	-0.081681
7	6	0	1.505956	1.249359	0.507141
8	6	0	2.320594	0.035374	0.116439
9	7	0	1.879404	-0.743113	-0.798310
10	6	0	3.634492	-0.167607	0.830651
11	7	0	2.628281	-1.872472	-1.117527
12	1	0	-1.831223	-2.352695	2.190040
13	1	0	-2.868496	-1.170080	2.697725
14	1	0	-3.247708	-1.653193	0.326294
15	1	0	-0.627523	0.120506	1.507414
16	1	0	2.367958	-2.182338	-2.045019
17	1	0	3.637374	-1.743906	-1.068666
18	1	0	0.127222	1.147997	-1.147682
19	1	0	2.074233	2.142642	0.219168
20	1	0	1.449189	1.296257	1.603366
21	1	0	4.481073	-0.113303	0.135515
22	1	0	3.788948	0.590363	1.598489
23	1	0	3.669483	-1.154241	1.305526
24	6	0	-0.473313	2.778882	0.129435
25	1	0	-1.489546	2.841940	-0.264282
26	1	0	-0.496581	3.037154	1.192532
27	1	0	0.141831	3.518699	-0.389723

Data 17: Cartesian coordinates and energies of the optimized geometry for the conformer **F** of *(E)*-**5** in MeCN solution.



Electronic Energy =	-909.775570199 a.u.
Zero-point correction=	0.229328 (Hartree/Particle)
Thermal correction to Energy=	0.244189
Thermal correction to Enthalpy=	0.245133
Thermal correction to Gibbs Free Energy=	0.186169
Sum of electronic and zero-point Energies=	-909.546243
Sum of electronic and thermal Energies=	-909.531382
Sum of electronic and thermal Enthalpies=	-909.530437
Sum of electronic and thermal Free Energies=	-909.589401

Standard orientation:

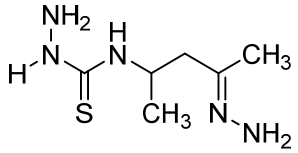
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.621582	-1.621431	-0.617717
2	7	0	-3.431023	-0.241276	-0.441754
3	6	0	-2.239777	0.257362	-0.018967
4	16	0	-2.083888	1.946292	0.203691
5	7	0	-1.273000	-0.641667	0.195717
6	6	0	0.110521	-0.365909	0.588827
7	6	0	1.014972	-0.327786	-0.668508
8	6	0	2.427767	0.123764	-0.395629
9	7	0	3.368095	-0.730320	-0.577526
10	6	0	2.665697	1.546831	0.045940
11	7	0	4.680485	-0.308546	-0.395815
12	1	0	-3.907332	-1.808315	-1.574419
13	1	0	-4.346179	-1.953622	0.012563
14	1	0	-4.191564	0.410851	-0.575899
15	1	0	-1.535882	-1.602169	-0.007281
16	1	0	5.265255	-1.118295	-0.234593
17	1	0	4.814588	0.370778	0.350659
18	1	0	0.102881	0.621148	1.052380
19	1	0	1.041792	-1.320912	-1.124767
20	1	0	0.554362	0.360837	-1.386320
21	1	0	3.390329	2.035955	-0.614184
22	1	0	1.743045	2.126583	0.033262
23	1	0	3.074432	1.592905	1.062837
24	6	0	0.560886	-1.408011	1.613573
25	1	0	-0.081144	-1.382105	2.496773
26	1	0	0.528719	-2.416983	1.190310
27	1	0	1.587686	-1.212153	1.927866

Table 11 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of various conformers of (*E*)-**5** in MeCN solution

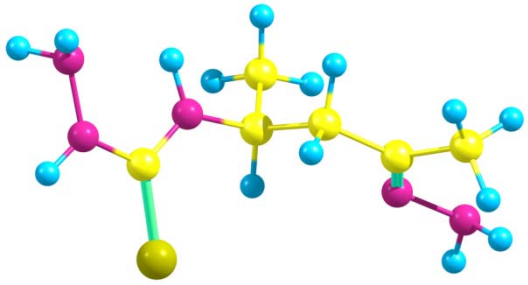
Conformer	(*E*)-**5**	
	ΔE	ΔG
A	1.26	0.96
B	1.32	1.13
C	4.67	4.89
D	0.00	0.00
E	1.47	1.36
F	0.35	0.51

EtOH solution

*Computational data for various conformers of hydrazone (E)-**5***



Data 18: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of *(E)*-**5** in EtOH solution.



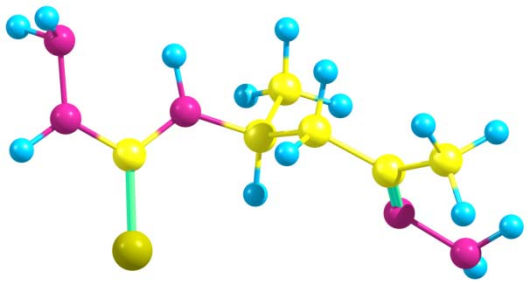
Electronic Energy =	-909.773636657 a.u.
Zero-point correction=	0.228944 (Hartree/Particle)
Thermal correction to Energy=	0.243941
Thermal correction to Enthalpy=	0.244885
Thermal correction to Gibbs Free Energy=	0.185465
Sum of electronic and zero-point Energies=	-909.544692
Sum of electronic and thermal Energies=	-909.529695
Sum of electronic and thermal Enthalpies=	-909.528751

Sum of electronic and thermal Free Energies= -909.588171

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.810303	-1.261857	0.522307
2	7	0	3.409351	0.075675	0.372533
3	6	0	2.144108	0.394754	-0.010364
4	16	0	1.733984	2.043200	-0.209207
5	7	0	1.314213	-0.635081	-0.204040
6	6	0	-0.105499	-0.565281	-0.570409
7	6	0	-0.974293	-0.562114	0.699839
8	6	0	-2.418362	-0.147090	0.528357
9	7	0	-2.811936	0.289694	-0.608809
10	6	0	-3.311087	-0.256043	1.740446
11	7	0	-4.153212	0.638700	-0.750873
12	1	0	4.154436	-1.412398	1.466075
13	1	0	4.553449	-1.476884	-0.136677
14	1	0	4.069496	0.832700	0.485378
15	1	0	1.723387	-1.547458	-0.024689
16	1	0	-4.240944	1.269026	-1.537699
17	1	0	-4.571611	1.062961	0.075083
18	1	0	-0.249652	0.378148	-1.094464
19	1	0	-0.947557	-1.557327	1.163325
20	1	0	-0.520377	0.116056	1.433183
21	1	0	-4.194184	-0.864822	1.518236
22	1	0	-2.782829	-0.706460	2.580646
23	1	0	-3.669521	0.729035	2.063029
24	6	0	-0.423458	-1.730380	-1.509554
25	1	0	0.184876	-1.674372	-2.415431
26	1	0	-0.227331	-2.691169	-1.021614
27	1	0	-1.474863	-1.701235	-1.794791

Data 19: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of *(E)*-**5** in EtOH solution.



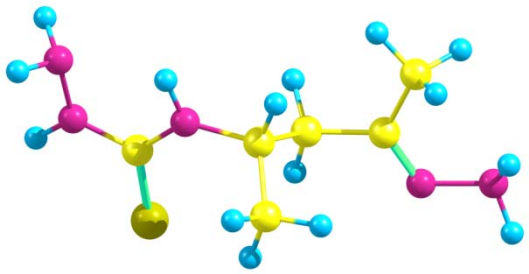
Electronic Energy =	-909.773491417 a.u.
Zero-point correction=	0.229038 (Hartree/Particle)
Thermal correction to Energy=	0.243989
Thermal correction to Enthalpy=	0.244934
Thermal correction to Gibbs Free Energy=	0.185706
Sum of electronic and zero-point Energies=	-909.544453
Sum of electronic and thermal Energies=	-909.529502
Sum of electronic and thermal Enthalpies=	-909.528558
Sum of electronic and thermal Free Energies=	-909.587786

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.789795	-1.318858	0.485513

2	7	0	3.412858	0.029949	0.381203
3	6	0	2.154788	0.384696	0.006088
4	16	0	1.775672	2.046128	-0.137797
5	7	0	1.307023	-0.622857	-0.224286
6	6	0	-0.110257	-0.515434	-0.590257
7	6	0	-0.981856	-0.586414	0.676102
8	6	0	-2.426042	-0.162915	0.526527
9	7	0	-2.810477	0.366093	-0.573894
10	6	0	-3.323925	-0.357617	1.724137
11	7	0	-4.120259	0.831655	-0.659271
12	1	0	4.128919	-1.507956	1.424143
13	1	0	4.530681	-1.524187	-0.179091
14	1	0	4.086423	0.770776	0.519329
15	1	0	1.699314	-1.548159	-0.075411
16	1	0	-4.385820	0.875237	-1.634817
17	1	0	-4.803034	0.281101	-0.141920
18	1	0	-0.242408	0.461990	-1.051043
19	1	0	-0.955029	-1.606470	1.081683
20	1	0	-0.529695	0.049165	1.448189
21	1	0	-4.133282	-1.065194	1.506084
22	1	0	-2.765996	-0.746442	2.575895
23	1	0	-3.790590	0.588608	2.018130
24	6	0	-0.436340	-1.613006	-1.605142
25	1	0	0.175994	-1.503106	-2.503304
26	1	0	-0.250706	-2.605584	-1.181162
27	1	0	-1.486320	-1.555558	-1.891536

Data 20: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of *(E)*-**5** in EtOH solution.



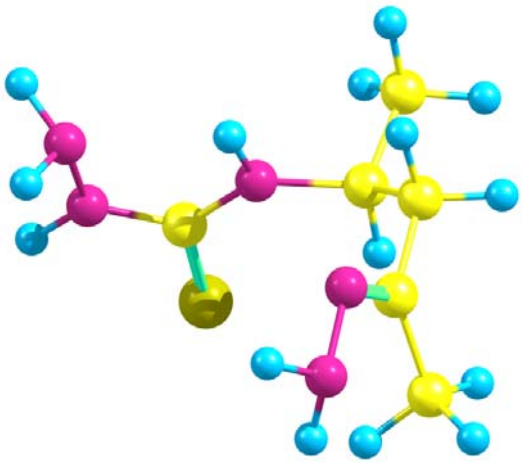
Electronic Energy =	-909.768140071 a.u.
Zero-point correction=	0.229273 (Hartree/Particle)
Thermal correction to Energy=	0.244166
Thermal correction to Enthalpy=	0.245111
Thermal correction to Gibbs Free Energy=	0.186259
Sum of electronic and zero-point Energies=	-909.538867
Sum of electronic and thermal Energies=	-909.523974
Sum of electronic and thermal Enthalpies=	-909.523030
Sum of electronic and thermal Free Energies=	-909.581881

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.754603	-1.616437	-0.222624
2	7	0	3.453127	-0.249749	-0.330535
3	6	0	2.199290	0.225243	-0.088276
4	16	0	1.932109	1.904259	-0.263893
5	7	0	1.300258	-0.699999	0.269036
6	6	0	-0.127434	-0.560433	0.613726
7	6	0	-0.969333	-0.083165	-0.595176
8	6	0	-2.453533	-0.276291	-0.403662
9	7	0	-3.182527	0.777948	-0.340247
10	6	0	-3.009197	-1.677688	-0.328074

11	7	0	-4.559441	0.617205	-0.233065
12	1	0	4.486508	-1.754996	0.468244
13	1	0	4.075761	-1.972106	-1.118652
14	1	0	4.155663	0.418120	-0.617328
15	1	0	1.688068	-1.637934	0.302855
16	1	0	-4.960372	1.469018	0.137451
17	1	0	-4.857244	-0.178906	0.327281
18	1	0	-0.425052	-1.588164	0.836885
19	1	0	-0.766546	0.968910	-0.791046
20	1	0	-0.648176	-0.657845	-1.472268
21	1	0	-3.812252	-1.810152	-1.061294
22	1	0	-2.239365	-2.423577	-0.525666
23	1	0	-3.436477	-1.893851	0.658957
24	6	0	-0.354301	0.269324	1.881488
25	1	0	-1.408453	0.227654	2.164936
26	1	0	0.237467	-0.131231	2.708092
27	1	0	-0.078385	1.312205	1.725730

Data 21: Cartesian coordinates and energies of the optimized geometry for the conformer **D** of *(E)*-**5** in EtOH solution.



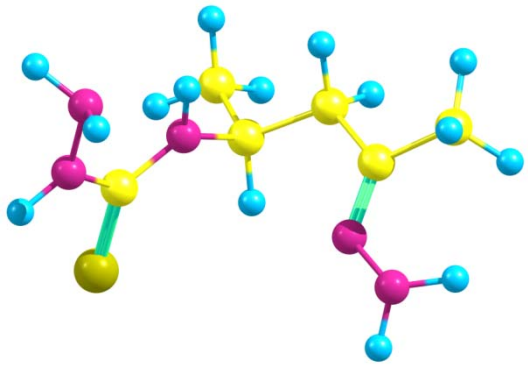
Electronic Energy =	-909.775682032 a.u.
Zero-point correction=	0.229273 (Hartree/Particle)
Thermal correction to Energy=	0.244133
Thermal correction to Enthalpy=	0.245077
Thermal correction to Gibbs Free Energy=	0.185926
Sum of electronic and zero-point Energies=	-909.546409
Sum of electronic and thermal Energies=	-909.531549
Sum of electronic and thermal Enthalpies=	-909.530605
Sum of electronic and thermal Free Energies=	-909.589756

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.939934	-2.147192	-1.313831
2	7	0	2.295329	-1.479246	-0.130897
3	6	0	1.700314	-0.310735	0.226703
4	16	0	2.178048	0.443063	1.686376
5	7	0	0.771278	0.152977	-0.615261
6	6	0	0.022486	1.406312	-0.496097
7	6	0	-1.448366	1.164216	-0.895343
8	6	0	-2.184092	0.196995	-0.002359
9	7	0	-2.552411	-0.917899	-0.519088
10	6	0	-2.461550	0.588979	1.427602
11	7	0	-3.280832	-1.798585	0.273570
12	1	0	1.571650	-3.068244	-1.093716
13	1	0	2.757457	-2.252631	-1.907619

14	1	0	2.989604	-1.862365	0.495764
15	1	0	0.626071	-0.419816	-1.442128
16	1	0	-3.209212	-2.727838	-0.120129
17	1	0	-3.009623	-1.816796	1.254787
18	1	0	0.076626	1.695535	0.554095
19	1	0	-1.955990	2.135260	-0.871795
20	1	0	-1.492392	0.799457	-1.925840
21	1	0	-1.921192	-0.050805	2.135663
22	1	0	-2.164943	1.619360	1.622892
23	1	0	-3.529214	0.488216	1.651074
24	6	0	0.661152	2.510084	-1.347173
25	1	0	1.700355	2.667872	-1.051158
26	1	0	0.639417	2.247619	-2.409021
27	1	0	0.119876	3.450683	-1.216321

Data 22: Cartesian coordinates and energies of the optimized geometry for the conformer **E** of *(E)*-**5** in EtOH solution.



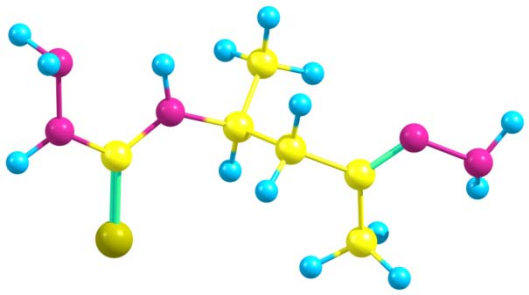
Electronic Energy =	-909.773226647 a.u.
Zero-point correction=	0.228968 (Hartree/Particle)
Thermal correction to Energy=	0.243933
Thermal correction to Enthalpy=	0.244877
Thermal correction to Gibbs Free Energy=	0.185601
Sum of electronic and zero-point Energies=	-909.544259
Sum of electronic and thermal Energies=	909.529294
Sum of electronic and thermal Enthalpies=	-909.528350
Sum of electronic and thermal Free Energies=	-909.587625

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.078809	-1.419608	2.053263
2	7	0	-2.477429	-1.157163	0.732646
3	6	0	-1.802588	-0.267481	-0.045087
4	16	0	-2.323650	-0.024555	-1.656354
5	7	0	-0.772579	0.351461	0.535600
6	6	0	0.095028	1.369757	-0.066120
7	6	0	1.505987	1.244337	0.519263
8	6	0	2.321569	0.035903	0.113518
9	7	0	1.879498	-0.732656	-0.809064
10	6	0	3.637134	-0.173539	0.822884
11	7	0	2.629328	-1.856770	-1.143208
12	1	0	-1.810100	-2.395106	2.147246
13	1	0	-2.847887	-1.227538	2.688373
14	1	0	-3.242714	-1.663301	0.308936
15	1	0	-0.617473	0.092471	1.505557
16	1	0	2.365141	-2.157940	-2.072445
17	1	0	3.638358	-1.726581	-1.097568
18	1	0	0.124969	1.161487	-1.134934
19	1	0	2.072695	2.141622	0.240722

20	1	0	1.450630	1.278775	1.616071
21	1	0	4.482647	-0.107319	0.127463
22	1	0	3.790872	0.574045	1.601020
23	1	0	3.675360	-1.166654	1.283793
24	6	0	-0.475732	2.775510	0.163546
25	1	0	-1.492492	2.842296	-0.228039
26	1	0	-0.497802	3.020212	1.229890
27	1	0	0.137739	3.522630	-0.347109

Data 23: Cartesian coordinates and energies of the optimized geometry for the conformer **F** of *(E)*-**5** in EtOH solution.



Electronic Energy =	-909.775113574 a.u.
Zero-point correction=	0.229338 (Hartree/Particle)
Thermal correction to Energy=	0.244194
Thermal correction to Enthalpy=	0.245138
Thermal correction to Gibbs Free Energy=	0.186205
Sum of electronic and zero-point Energies=	-909.545776
Sum of electronic and thermal Energies=	-909.530920
Sum of electronic and thermal Enthalpies=	-909.529975
Sum of electronic and thermal Free Energies=	-909.588908

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.624206	-1.617607	-0.619054
2	7	0	-3.430793	-0.237985	-0.442363
3	6	0	-2.238657	0.258324	-0.018425
4	16	0	-2.079983	1.946182	0.206135
5	7	0	-1.273555	-0.642913	0.195482
6	6	0	0.110354	-0.369344	0.588658
7	6	0	1.014430	-0.328191	-0.668835
8	6	0	2.426864	0.124098	-0.395408
9	7	0	3.367814	-0.729188	-0.577645
10	6	0	2.663624	1.547163	0.046904
11	7	0	4.679746	-0.306599	-0.395654
12	1	0	-3.910298	-1.803702	-1.575791
13	1	0	-4.348911	-1.949170	0.011426
14	1	0	-4.190127	0.415864	-0.574869
15	1	0	-1.537772	-1.602716	-0.008829
16	1	0	5.265334	-1.115915	-0.235426
17	1	0	4.813619	0.372764	0.350810
18	1	0	0.103521	0.616441	1.054967
19	1	0	1.042128	-1.320425	-1.126998
20	1	0	0.553043	0.361492	-1.385103
21	1	0	3.386989	2.037497	-0.613732
22	1	0	1.740280	2.125839	0.035612
23	1	0	3.073406	1.593152	1.063413
24	6	0	0.560357	-1.414710	1.610214
25	1	0	-0.080877	-1.390494	2.494047
26	1	0	0.526811	-2.422502	1.184221
27	1	0	1.587697	-1.221031	1.924075

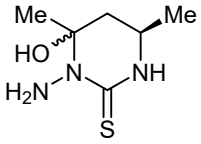
Table 12 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of various conformers of (*E*)-**5** in EtOH solution

Conformer	(*E*)-**5**	
	ΔE	ΔG
A	1.28	0.99
B	1.37	1.24
C	4.73	4.94
D	0.00	0.00
E	1.54	1.34
F	0.36	0.45

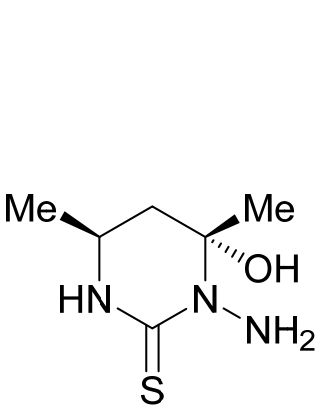
Hydroxypyrimidine-2-thione 4 and its acyclic isomer, thiosemicarbazide 3

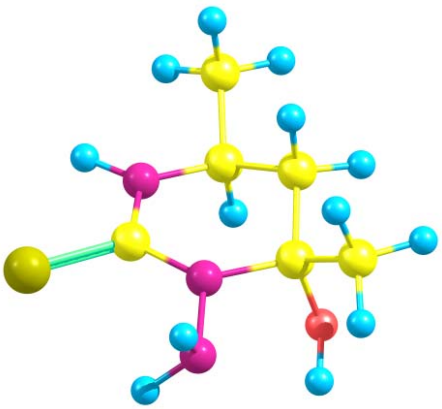
DMSO solution

Computational data for various stereoisomer of hydroxypyrimidine-2-thione ***4***



Data 24: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of (4*R**,6*R**)-**4** in DMSO solution.





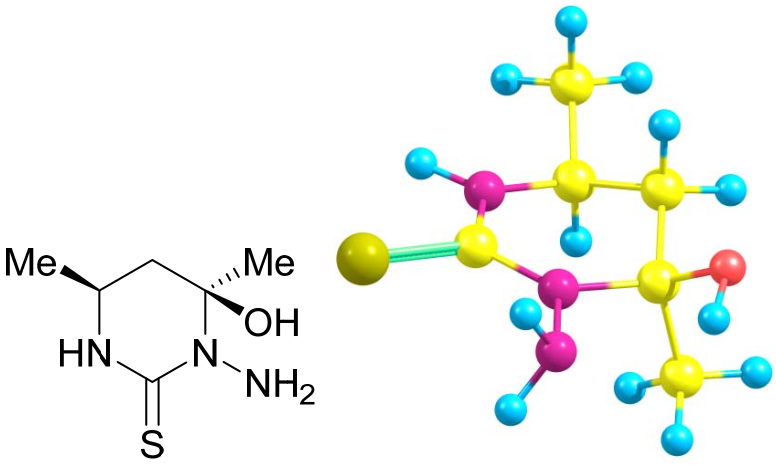
Electronic Energy = -874.313547221 a.u.

Zero-point correction=	0.202256 (Hartree/Particle)
Thermal correction to Energy=	0.214347
Thermal correction to Enthalpy=	0.215291
Thermal correction to Gibbs Free Energy=	0.164655
Sum of electronic and zero-point Energies=	-874.111291
Sum of electronic and thermal Energies=	-874.099200
Sum of electronic and thermal Enthalpies=	-874.098256
Sum of electronic and thermal Free Energies=	-874.148892

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.234239	-2.434266	-0.148359
2	6	0	1.378088	-1.257817	0.309290
3	7	0	-0.036951	-1.528598	0.025381
4	6	0	-0.999644	-0.589315	-0.044975
5	16	0	-2.648089	-1.053078	-0.079080
6	7	0	-0.612899	0.716062	-0.090940
7	6	0	0.793031	1.181889	-0.003327
8	6	0	1.733619	0.043484	-0.394117
9	8	0	1.087883	1.526754	1.349978
10	6	0	0.998752	2.389919	-0.920429
11	7	0	-1.556708	1.748161	0.123213
12	1	0	-0.373922	-2.476978	0.103146
13	1	0	0.483206	2.236610	1.605482
14	1	0	-2.268644	1.387536	0.754939
15	1	0	-2.031540	1.945282	-0.755528
16	1	0	3.281879	-2.247216	0.096818
17	1	0	1.932951	-3.356948	0.354818
18	1	0	2.149992	-2.582891	-1.228145
19	1	0	1.499215	-1.125252	1.390997
20	1	0	2.749933	0.347325	-0.139719
21	1	0	1.684122	-0.103160	-1.476563
22	1	0	0.730224	2.145135	-1.950372
23	1	0	0.395084	3.235734	-0.591992
24	1	0	2.051252	2.677294	-0.890501

Data 25: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of (4*R**,6*S**)-**4** in DMSO solution.



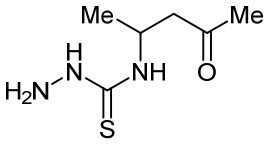
Electronic Energy =	-874.313895860 a.u.
Zero-point correction=	0.202570 (Hartree/Particle)
Thermal correction to Energy=	0.214453
Thermal correction to Enthalpy=	0.215397

Thermal correction to Gibbs Free Energy= 0.165302
Sum of electronic and zero-point Energies= -874.111326
Sum of electronic and thermal Energies= -874.099443
Sum of electronic and thermal Enthalpies= -874.098499
Sum of electronic and thermal Free Energies= -874.148594

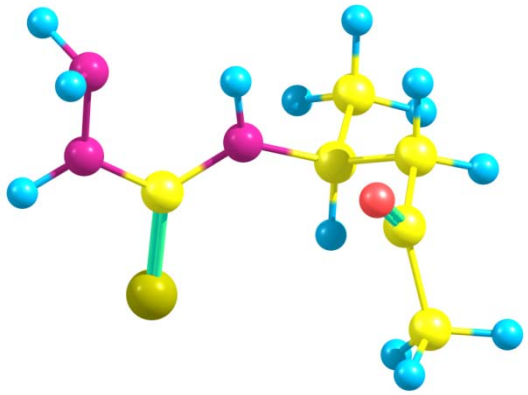
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.299124	-2.355586	-0.222648
2	6	0	1.451771	-1.196622	0.295981
3	7	0	0.026155	-1.518569	0.143634
4	6	0	-0.974836	-0.623429	0.032293
5	16	0	-2.603967	-1.149116	0.005146
6	7	0	-0.636226	0.687723	-0.064394
7	6	0	0.761767	1.218293	-0.038792
8	6	0	1.719392	0.102821	-0.453027
9	8	0	0.859299	2.224171	-1.029819
10	6	0	1.061060	1.804302	1.344585
11	7	0	-1.607363	1.705027	-0.128174
12	1	0	-0.267900	-2.476437	0.264462
13	1	0	0.109483	2.821445	-0.879581
14	1	0	-2.181352	1.671970	0.711565
15	1	0	-2.225596	1.514442	-0.913206
16	1	0	3.358230	-2.139312	-0.067494
17	1	0	2.064139	-3.279702	0.312061
18	1	0	2.127541	-2.516966	-1.289936
19	1	0	1.667055	-1.059677	1.362725
20	1	0	2.743936	0.433856	-0.276589
21	1	0	1.596402	-0.063815	-1.526695
22	1	0	1.006824	1.040070	2.122510
23	1	0	2.062388	2.239519	1.344887
24	1	0	0.340309	2.589162	1.583696

Computational data for various conformers of thiosemicarbazide ***3***



Data 26: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of thiosemicarbazide **3** in DMSO solution.



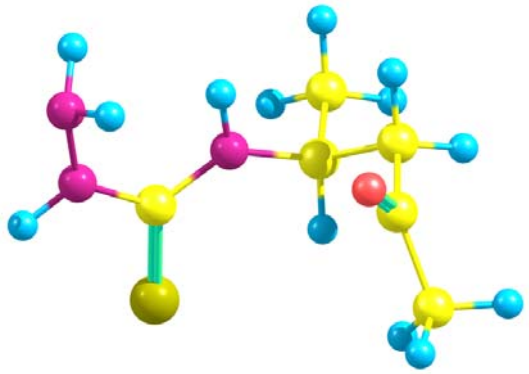
Electronic Energy = -874.316325536 a.u.
Zero-point correction= 0.199768 (Hartree/Particle)

Thermal correction to Energy=	0.213405
Thermal correction to Enthalpy=	0.214349
Thermal correction to Gibbs Free Energy=	0.157250
Sum of electronic and zero-point Energies=	-874.116558
Sum of electronic and thermal Energies=	-874.102920
Sum of electronic and thermal Enthalpies=	-874.101976
Sum of electronic and thermal Free Energies=	-874.159075

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.440040	1.995011	-1.825634
2	6	0	-0.648533	0.972264	-0.702851
3	7	0	0.470356	0.031451	-0.637710
4	6	0	1.477223	0.047227	0.245491
5	16	0	1.618797	1.126631	1.564437
6	7	0	2.446000	-0.883649	0.052088
7	6	0	-2.278191	-0.768616	0.240112
8	6	0	-1.973620	0.199256	-0.892203
9	8	0	-2.128727	-1.969648	0.094532
10	6	0	-2.787343	-0.184021	1.535503
11	7	0	2.376742	-1.797540	-1.012014
12	1	0	0.567538	-0.661444	-1.375522
13	1	0	2.333570	-2.746027	-0.649880
14	1	0	3.203577	-1.706009	-1.595052
15	1	0	3.205370	-0.916621	0.718450
16	1	0	-1.260521	2.716533	-1.839559
17	1	0	0.494670	2.538408	-1.671910
18	1	0	-0.398761	1.503301	-2.801650
19	1	0	-0.660359	1.495326	0.253150
20	1	0	-2.779981	0.935006	-0.962713
21	1	0	-1.942237	-0.365485	-1.827616
22	1	0	-2.826818	-0.948672	2.310148
23	1	0	-3.792812	0.218133	1.370627
24	1	0	-2.162828	0.650072	1.865236

Data 27: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of thiosemicarbazide **3** in DMSO solution.



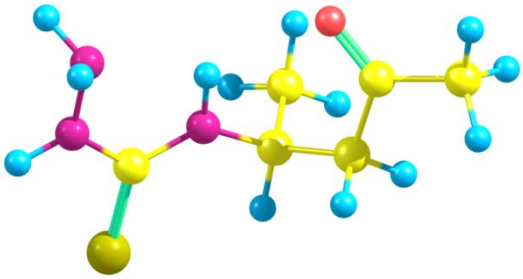
Electronic Energy =	-874.311519510 a.u.
Zero-point correction=	0.199790 (Hartree/Particle)
Thermal correction to Energy=	0.213395
Thermal correction to Enthalpy=	0.214339
Thermal correction to Gibbs Free Energy=	0.157782
Sum of electronic and zero-point Energies=	-874.111730
Sum of electronic and thermal Energies=	-874.098125
Sum of electronic and thermal Enthalpies=	-874.097180

Sum of electronic and thermal Free Energies= -874.153737

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.403126	2.014277	-1.780985
2	6	0	-0.637639	0.983284	-0.671885
3	7	0	0.451737	0.000419	-0.626238
4	6	0	1.500700	0.018597	0.211272
5	16	0	1.732604	1.170222	1.452204
6	7	0	2.432438	-0.957879	0.046114
7	6	0	-2.304257	-0.725688	0.260604
8	6	0	-1.985420	0.252562	-0.859688
9	8	0	-2.180544	-1.926868	0.094751
10	6	0	-2.790543	-0.149980	1.568150
11	7	0	2.394398	-2.010461	-0.875101
12	1	0	0.449299	-0.703959	-1.353908
13	1	0	2.449926	-1.675286	-1.832303
14	1	0	1.575471	-2.597374	-0.744061
15	1	0	3.204779	-0.963836	0.694198
16	1	0	-1.197095	2.764907	-1.773176
17	1	0	0.551894	2.521192	-1.628723
18	1	0	-0.390828	1.537441	-2.764997
19	1	0	-0.623351	1.491713	0.291652
20	1	0	-2.769417	1.013377	-0.909306
21	1	0	-1.982483	-0.296962	-1.804880
22	1	0	-2.843007	-0.925566	2.330995
23	1	0	-3.786959	0.279090	1.416864
24	1	0	-2.143856	0.663800	1.906137

Data 28: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of thiosemicarbazide **3** in DMSO solution.



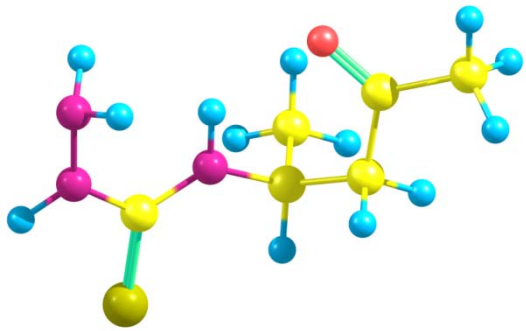
Electronic Energy = -874.317731124 a.u.
Zero-point correction= 0.199632 (Hartree/Particle)
Thermal correction to Energy= 0.213211
Thermal correction to Enthalpy= 0.214156
Thermal correction to Gibbs Free Energy= 0.157920
Sum of electronic and zero-point Energies= -874.118099
Sum of electronic and thermal Energies= -874.104520
Sum of electronic and thermal Enthalpies= -874.103576
Sum of electronic and thermal Free Energies= -874.159811

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.730439	-1.472972	1.686792
2	6	0	-0.422949	-1.085872	0.234159
3	7	0	0.458090	0.081660	0.172901
4	6	0	1.759644	0.081357	-0.127188

5	16	0	2.674030	-1.295726	-0.578816
6	7	0	2.386654	1.284681	-0.063452
7	6	0	-2.563507	0.327221	-0.224860
8	6	0	-1.686548	-0.853123	-0.609759
9	8	0	-2.164412	1.222142	0.502877
10	6	0	-3.955398	0.342011	-0.806611
11	7	0	1.691744	2.454465	0.284175
12	1	0	0.059141	0.977252	0.440154
13	1	0	1.729385	3.118372	-0.484182
14	1	0	2.120961	2.876427	1.102506
15	1	0	3.365967	1.315882	-0.311499
16	1	0	-1.361875	-2.365097	1.711979
17	1	0	0.196384	-1.696540	2.219603
18	1	0	-1.247382	-0.669110	2.214648
19	1	0	0.129716	-1.902386	-0.230830
20	1	0	-1.406878	-0.696489	-1.659778
21	1	0	-2.299079	-1.760438	-0.604344
22	1	0	-4.413857	1.321378	-0.674857
23	1	0	-4.561259	-0.411102	-0.291054
24	1	0	-3.940650	0.068956	-1.864872

Data 29: Cartesian coordinates and energies of the optimized geometry for the conformer **D** of thiosemicarbazide **3** in DMSO solution.



Electronic Energy =	-874.313910319 a.u.
Zero-point correction=	0.199767 (Hartree/Particle)
Thermal correction to Energy=	0.213234
Thermal correction to Enthalpy=	0.214179
Thermal correction to Gibbs Free Energy=	0.158525
Sum of electronic and zero-point Energies=	-874.114143
Sum of electronic and thermal Energies=	-874.100676
Sum of electronic and thermal Enthalpies=	-874.099732
Sum of electronic and thermal Free Energies=	-874.155385

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.691732	-1.562212	1.578955
2	6	0	-0.413474	-1.098173	0.143598
3	7	0	0.449719	0.088856	0.127961
4	6	0	1.765719	0.106012	-0.113019
5	16	0	2.704421	-1.267564	-0.518063
6	7	0	2.388121	1.313089	-0.028083
7	6	0	-2.563292	0.328171	-0.205577
8	6	0	-1.694903	-0.833074	-0.663277
9	8	0	-2.120143	1.230502	0.488745
10	6	0	-3.996519	0.319707	-0.670550
11	7	0	1.786589	2.548904	0.238986
12	1	0	-0.016200	0.947371	0.402044
13	1	0	1.389937	2.573816	1.174000
14	1	0	1.075816	2.774177	-0.451825

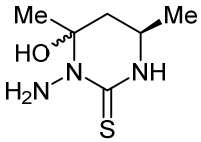
15	1	0	3.373117	1.336022	-0.240923
16	1	0	-1.303466	-2.468087	1.567959
17	1	0	0.246935	-1.790865	2.087919
18	1	0	-1.218563	-0.796790	2.152952
19	1	0	0.142389	-1.880644	-0.372440
20	1	0	-1.437345	-0.624696	-1.710155
21	1	0	-2.301984	-1.742796	-0.686047
22	1	0	-4.463578	1.287072	-0.490207
23	1	0	-4.540866	-0.453468	-0.117292
24	1	0	-4.061577	0.057375	-1.729748

Table 13 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of stereoisomers of hydroxypyrimidine-2-thione **4** and its acyclic isomer **3** in DMSO solution

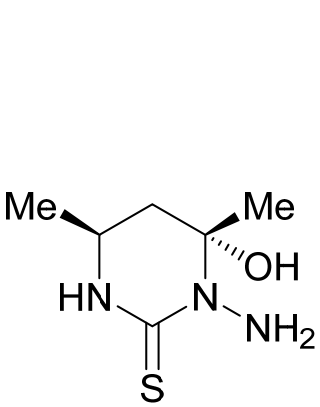
	Stereoisomers of pyrimidine **4**		Conformers of thiosemicarbazide **3**			
	(4*R**,6*R**)	(4*R**,6*S**)	**A**	**B**	**C**	**D**
ΔE	2.63	2.41	0.88	3.90	0.00	2.40
ΔG	6.85	7.04	0.46	3.81	0.00	2.78

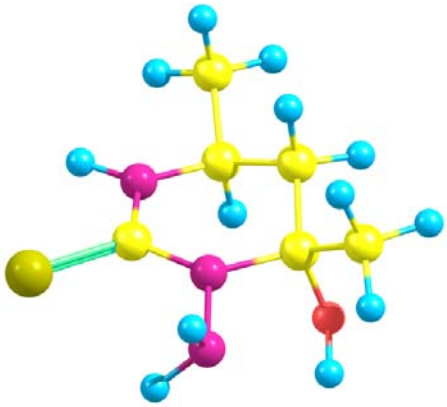
EtOH solution

Computational data for various stereoisomer of hydroxypyrimidine-2-thione ***4***



Data 30: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of (4*R**,6*R**)-**4** in EtOH solution.





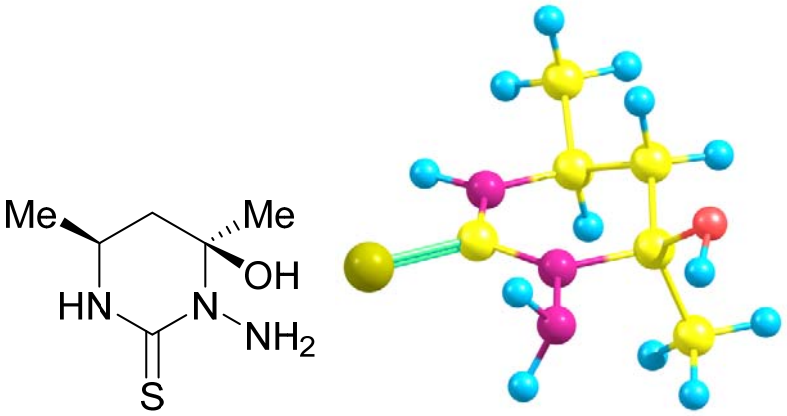
Electronic Energy = -874.313098579 a.u.
Zero-point correction= 0.202275 (Hartree/Particle)
Thermal correction to Energy= 0.214359

Thermal correction to Enthalpy=	0.215303
Thermal correction to Gibbs Free Energy=	0.164684
Sum of electronic and zero-point Energies=	-874.110823
Sum of electronic and thermal Energies=	-874.098739
Sum of electronic and thermal Enthalpies=	-874.097795
Sum of electronic and thermal Free Energies=	-874.148415

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.236124	-2.432871	-0.146499
2	6	0	1.378101	-1.257075	0.309321
3	7	0	-0.036031	-1.528931	0.022511
4	6	0	-0.999779	-0.590101	-0.046072
5	16	0	-2.647362	-1.054105	-0.078907
6	7	0	-0.613148	0.715646	-0.091725
7	6	0	0.792288	1.182270	-0.003607
8	6	0	1.733935	0.044427	-0.393592
9	8	0	1.086640	1.527800	1.349550
10	6	0	0.997514	2.390260	-0.920996
11	7	0	-1.557309	1.746976	0.125093
12	1	0	-0.372946	-2.477245	0.101342
13	1	0	0.479093	2.235070	1.605406
14	1	0	-2.268506	1.384324	0.756616
15	1	0	-2.033497	1.944556	-0.752821
16	1	0	3.283156	-2.245244	0.100903
17	1	0	1.934486	-3.355829	0.355996
18	1	0	2.154250	-2.581694	-1.226448
19	1	0	1.497231	-1.123964	1.391214
20	1	0	2.749751	0.348901	-0.137882
21	1	0	1.685694	-0.102272	-1.476112
22	1	0	0.730297	2.144875	-1.951163
23	1	0	0.392411	3.235371	-0.593362
24	1	0	2.049583	2.679142	-0.890069

Data 31: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of (4*R**,6*S**)-**4** in EtOH solution.



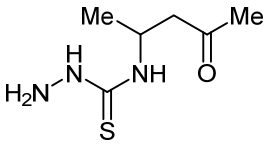
Electronic Energy =	-874.313414457 a.u.
Zero-point correction=	0.202574 (Hartree/Particle)
Thermal correction to Energy=	0.214459
Thermal correction to Enthalpy=	0.215403
Thermal correction to Gibbs Free Energy=	0.165291
Sum of electronic and zero-point Energies=	-874.110840
Sum of electronic and thermal Energies=	-874.098956

Sum of electronic and thermal Enthalpies= -874.098011
Sum of electronic and thermal Free Energies= -874.148123

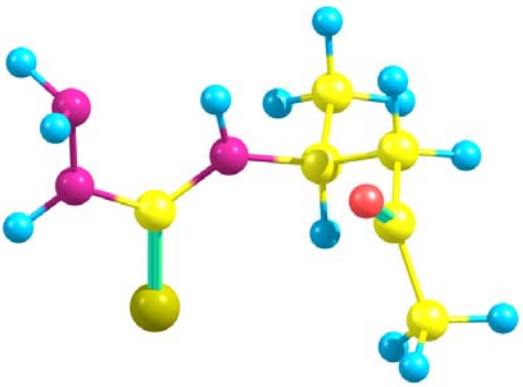
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.300103	-2.354732	-0.222557
2	6	0	1.451993	-1.196181	0.295825
3	7	0	0.026782	-1.518731	0.142980
4	6	0	-0.975008	-0.623926	0.032017
5	16	0	-2.603360	-1.149642	0.005543
6	7	0	-0.636348	0.687463	-0.064453
7	6	0	0.761219	1.218612	-0.038675
8	6	0	1.719370	0.103528	-0.452876
9	8	0	0.858902	2.224669	-1.029290
10	6	0	1.060140	1.804485	1.344935
11	7	0	-1.608083	1.704194	-0.128823
12	1	0	-0.267201	-2.476659	0.263290
13	1	0	0.108124	2.820927	-0.879979
14	1	0	-2.183450	1.669304	0.709934
15	1	0	-2.225304	1.512938	-0.914554
16	1	0	3.359114	-2.138436	-0.066627
17	1	0	2.064940	-3.279165	0.311595
18	1	0	2.129284	-2.515850	-1.289997
19	1	0	1.667146	-1.059142	1.362688
20	1	0	2.743773	0.435055	-0.276356
21	1	0	1.596544	-0.062774	-1.526594
22	1	0	1.006411	1.040091	2.122783
23	1	0	2.061046	2.240686	1.345371
24	1	0	0.338756	2.588746	1.584138

Computational data for various conformers of thiosemicarbazide ***3***



Data 32: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of thiosemicarbazide **3** in EtOH solution.



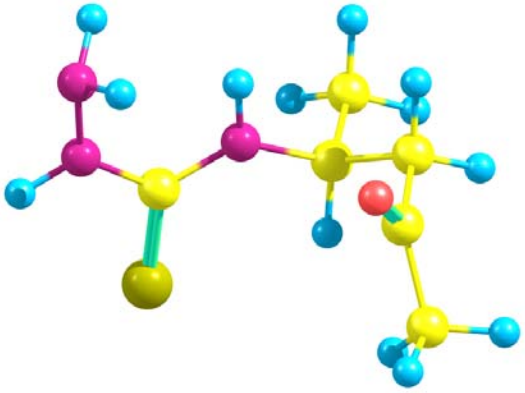
Electronic Energy = -874.315655846 a.u.
Zero-point correction= 0.199687 (Hartree/Particle)
Thermal correction to Energy= 0.213366
Thermal correction to Enthalpy= 0.214310
Thermal correction to Gibbs Free Energy= 0.156943

Sum of electronic and zero-point Energies= -874.115969
Sum of electronic and thermal Energies= -874.102290
Sum of electronic and thermal Enthalpies= -874.101346
Sum of electronic and thermal Free Energies= -874.158713

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.419164	-1.955426	-1.857218
2	6	0	0.643528	-0.962437	-0.710933
3	7	0	-0.455628	0.000091	-0.625652
4	6	0	-1.485565	-0.039395	0.230259
5	16	0	-1.682671	-1.180891	1.487019
6	7	0	-2.430773	0.920410	0.059489
7	6	0	2.298424	0.736216	0.269212
8	6	0	1.982390	-0.209833	-0.878922
9	8	0	2.200990	1.943102	0.129693
10	6	0	2.751976	0.122293	1.571788
11	7	0	-2.308354	1.892596	-0.946493
12	1	0	-0.519512	0.731239	-1.329310
13	1	0	-2.242965	2.816727	-0.528899
14	1	0	-3.122999	1.861934	-1.552432
15	1	0	-3.199730	0.942857	0.715240
16	1	0	1.224867	-2.693190	-1.884086
17	1	0	-0.526818	-2.483153	-1.718987
18	1	0	0.392048	-1.441411	-2.822170
19	1	0	0.642171	-1.508187	0.232415
20	1	0	2.777021	-0.957780	-0.955718
21	1	0	1.968181	0.370106	-1.805501
22	1	0	2.837058	0.886060	2.343557
23	1	0	3.726243	-0.354840	1.421333
24	1	0	2.063025	-0.661110	1.898181

Data 33: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of thiosemicarbazide **3** in EtOH solution.

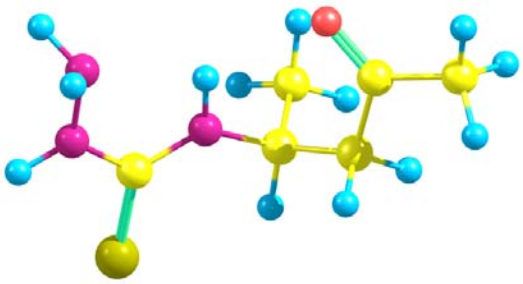


Electronic Energy = -874.310827803 a.u.
Zero-point correction= 0.199844 (Hartree/Particle)
Thermal correction to Energy= 0.213420
Thermal correction to Enthalpy= 0.214364
Thermal correction to Gibbs Free Energy= 0.158054
Sum of electronic and zero-point Energies= -874.110984
Sum of electronic and thermal Energies= -874.097408
Sum of electronic and thermal Enthalpies= -874.096464
Sum of electronic and thermal Free Energies= -874.152774

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.400379	-2.022745	-1.772196
2	6	0	0.636874	-0.989680	-0.665443
3	7	0	-0.447528	-0.001286	-0.624903
4	6	0	-1.500838	-0.015217	0.207884
5	16	0	-1.746042	-1.168516	1.443481
6	7	0	-2.425327	0.968113	0.040488
7	6	0	2.304933	0.721424	0.261363
8	6	0	1.988475	-0.265857	-0.851926
9	8	0	2.189098	1.921372	0.082581
10	6	0	2.777816	0.155822	1.578253
11	7	0	-2.374918	2.023755	-0.876424
12	1	0	-0.435820	0.706082	-1.349472
13	1	0	-2.429444	1.693077	-1.835191
14	1	0	-1.552755	2.604684	-0.739270
15	1	0	-3.200155	0.977892	0.685549
16	1	0	1.190796	-2.777120	-1.760547
17	1	0	-0.557245	-2.524887	-1.620717
18	1	0	0.392724	-1.548576	-2.757601
19	1	0	0.617617	-1.495453	0.299459
20	1	0	2.769858	-1.030026	-0.891076
21	1	0	1.992958	0.275810	-1.801689
22	1	0	2.834543	0.939906	2.332015
23	1	0	3.769990	-0.286646	1.438213
24	1	0	2.119395	-0.646013	1.922252

Data 34: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of thiosemicarbazide **3** in EtOH solution.



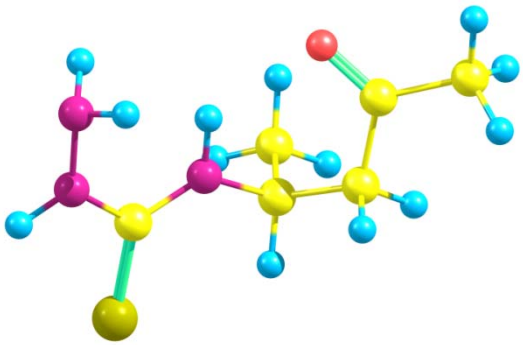
Electronic Energy =	-874.317088567 a.u.
Zero-point correction=	0.199636 (Hartree/Particle)
Thermal correction to Energy=	0.213219
Thermal correction to Enthalpy=	0.214163
Thermal correction to Gibbs Free Energy=	0.157875
Sum of electronic and zero-point Energies=	-874.117453
Sum of electronic and thermal Energies=	-874.103869
Sum of electronic and thermal Enthalpies=	-874.102925
Sum of electronic and thermal Free Energies=	-874.159213

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.734389	-1.464270	1.697232
2	6	0	-0.423262	-1.084606	0.243428
3	7	0	0.458710	0.081849	0.178757
4	6	0	1.758934	0.079405	-0.128152
5	16	0	2.668941	-1.297946	-0.584857
6	7	0	2.387689	1.282423	-0.067488
7	6	0	-2.561797	0.327337	-0.227883

8	6	0	-1.684709	-0.855589	-0.604788
9	8	0	-2.165574	1.223245	0.499857
10	6	0	-3.950577	0.343006	-0.817608
11	7	0	1.696902	2.452454	0.286886
12	1	0	0.062163	0.978077	0.447313
13	1	0	1.732069	3.119070	-0.479160
14	1	0	2.128829	2.870661	1.105701
15	1	0	3.366567	1.311328	-0.317438
16	1	0	-1.366928	-2.355564	1.725480
17	1	0	0.191064	-1.686520	2.232924
18	1	0	-1.251405	-0.657230	2.220145
19	1	0	0.130394	-1.903532	-0.216129
20	1	0	-1.402252	-0.704839	-1.654928
21	1	0	-2.297994	-1.762483	-0.596155
22	1	0	-4.407594	1.323772	-0.691382
23	1	0	-4.561089	-0.407023	-0.303038
24	1	0	-3.930588	0.066673	-1.874936

Data 35: Cartesian coordinates and energies of the optimized geometry for the conformer **D** of thiosemicarbazide **3** in EtOH solution.



Electronic Energy =	-874.313299361 a.u.
Zero-point correction=	0.199784 (Hartree/Particle)
Thermal correction to Energy=	0.213246
Thermal correction to Enthalpy=	0.214190
Thermal correction to Gibbs Free Energy=	0.158570
Sum of electronic and zero-point Energies=	-874.113515
Sum of electronic and thermal Energies=	-874.100054
Sum of electronic and thermal Enthalpies=	-874.099109
Sum of electronic and thermal Free Energies=	-874.154730

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.691038	-1.560497	1.580508
2	6	0	-0.413291	-1.097865	0.144579
3	7	0	0.449501	0.089203	0.127277
4	6	0	1.765979	0.105361	-0.113576
5	16	0	2.703482	-1.267959	-0.518595
6	7	0	2.388358	1.312721	-0.028283
7	6	0	-2.563095	0.328324	-0.206224
8	6	0	-1.695190	-0.834146	-0.662071
9	8	0	-2.119315	1.232442	0.485160
10	6	0	-3.997014	0.318744	-0.669511
11	7	0	1.787033	2.548348	0.239709
12	1	0	-0.015962	0.947794	0.401617
13	1	0	1.390423	2.572993	1.174737
14	1	0	1.076692	2.774801	-0.451121
15	1	0	3.373462	1.335486	-0.240637
16	1	0	-1.302219	-2.466800	1.570825
17	1	0	0.247944	-1.788208	2.089256

18	1	0	-1.218053	-0.794703	2.153908
19	1	0	0.142865	-1.880692	-0.370663
20	1	0	-1.438093	-0.627953	-1.709526
21	1	0	-2.302526	-1.743803	-0.682746
22	1	0	-4.463715	1.286594	-0.490922
23	1	0	-4.540876	-0.452916	-0.113659
24	1	0	-4.063490	0.053796	-1.727991

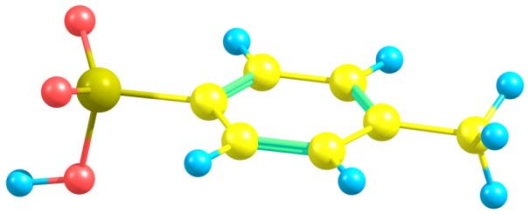
Table 14 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of stereoisomers of hydroxypyrimidine-2-thione **4** and its acyclic isomer **3** in EtOH solution

	Stereoisomers of pyrimidine **4**		Conformers of thiosemicarbazide **3**			
	(4*R**,6*R**)	(4*R**,6*S**)	**A**	**B**	**C**	**D**
ΔE	2.50	2.31	0.90	3.93	0.00	2.38
ΔG	6.78	6.96	0.31	4.04	0.00	2.81

p-Toluenesulfonic acid (TsOH)

MeCN solution

Data 36: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of TsOH in MeCN solution.



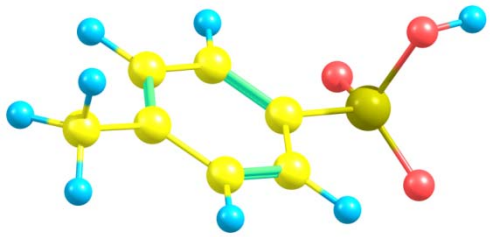
Electronic Energy =	-895.543591140 a.u.
Zero-point correction=	0.140670 (Hartree/Particle)
Thermal correction to Energy=	0.151746
Thermal correction to Enthalpy=	0.152690
Thermal correction to Gibbs Free Energy=	0.099908
Sum of electronic and zero-point Energies=	-895.402922
Sum of electronic and thermal Energies=	-895.391846
Sum of electronic and thermal Enthalpies=	-895.390901
Sum of electronic and thermal Free Energies=	-895.443683

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.560926	-1.216873	-0.066988
2	6	0	-0.118436	0.000266	-0.086807
3	6	0	0.561060	1.217217	-0.066235
4	6	0	1.950912	1.205007	-0.026641
5	6	0	2.666228	0.000044	-0.000742
6	6	0	1.950688	-1.204882	-0.027367
7	6	0	4.170863	-0.000323	0.073861
8	16	0	-1.894979	0.000440	-0.118263
9	8	0	-2.398395	1.258481	-0.664566
10	8	0	-2.398841	-1.254518	-0.671293
11	8	0	-2.165710	-0.004074	1.502256
12	1	0	-3.122489	-0.007449	1.677410
13	1	0	0.016700	-2.152090	-0.093406
14	1	0	0.016921	2.152494	-0.092004
15	1	0	2.487026	2.147287	-0.018868
16	1	0	2.486685	-2.147244	-0.020148
17	1	0	4.592642	-0.883396	-0.409537
18	1	0	4.499795	-0.008805	1.118553
19	1	0	4.592504	0.890325	-0.395439

EtOH solution

Data 37: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of TsOH in EtOH solution.



Electronic Energy =	-895.543331919 a.u.
Zero-point correction=	0.140676 (Hartree/Particle)
Thermal correction to Energy=	0.151755
Thermal correction to Enthalpy=	0.152699
Thermal correction to Gibbs Free Energy=	0.099691
Sum of electronic and zero-point Energies=	-895.402656
Sum of electronic and thermal Energies=	-895.391577
Sum of electronic and thermal Enthalpies=	-895.390633
Sum of electronic and thermal Free Energies=	-895.443641

Standard orientation:

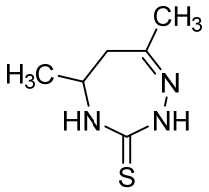
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.560919	1.216835	-0.066965
2	6	0	0.118438	-0.000263	-0.086731
3	6	0	-0.561049	-1.217175	-0.066216
4	6	0	-1.950901	-1.204981	-0.026657
5	6	0	-2.666213	-0.000045	-0.000754
6	6	0	-1.950679	1.204857	-0.027379
7	6	0	-4.170880	0.000322	0.073829
8	16	0	1.895060	-0.000437	-0.118431

9	8	0	2.398230	-1.258580	-0.664428
10	8	0	2.398681	1.254655	-0.671079
11	8	0	2.165819	0.004029	1.502352
12	1	0	3.122650	0.007434	1.676963
13	1	0	-0.016543	2.151962	-0.093542
14	1	0	-0.016760	-2.152362	-0.092147
15	1	0	-2.487030	-2.147266	-0.018954
16	1	0	-2.486693	2.147222	-0.020226
17	1	0	-4.592705	0.883300	-0.409724
18	1	0	-4.499935	0.008888	1.118483
19	1	0	-4.592561	-0.890311	-0.395483

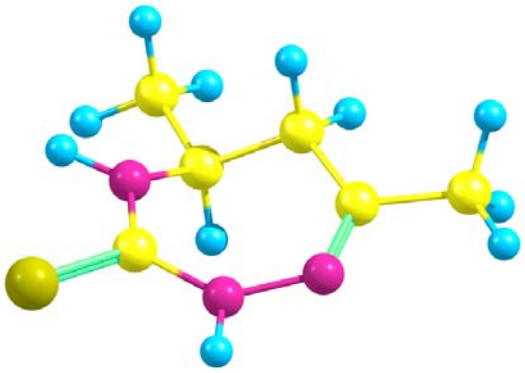
Computational data for the reaction products

Triazepine-3-thione 8

DMSO solution



Data 38: Cartesian coordinates and energies of the optimized geometry for the 1st conformer of triazepine **8** in DMSO solution.

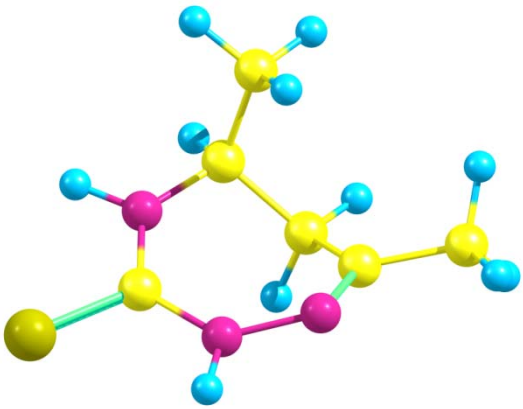


Electronic Energy =	-797.841513284 a.u.
Zero-point correction=	0.174778 (Hartree/Particle)
Thermal correction to Energy=	0.185145
Thermal correction to Enthalpy=	0.186089
Thermal correction to Gibbs Free Energy=	0.138525
Sum of electronic and zero-point Energies=	-797.666736
Sum of electronic and thermal Energies=	-797.656368
Sum of electronic and thermal Enthalpies=	-797.655424
Sum of electronic and thermal Free Energies=	-797.702989

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.795405	-1.637450	-0.257068
2	6	0	1.730211	-0.820534	0.062136
3	6	0	1.651132	0.658068	0.342893
4	7	0	-0.794756	0.946453	0.163480
5	6	0	-1.337368	-0.263817	-0.018370
6	16	0	-3.014820	-0.531093	0.169729
7	7	0	-0.549013	-1.318232	-0.387464
8	1	0	-1.456112	1.658345	0.439211
9	1	0	-1.082224	-2.156587	-0.563026
10	6	0	0.505922	1.401170	-0.346530
11	1	0	2.599733	1.104511	0.030818
12	1	0	1.582108	0.812816	1.426042
13	1	0	0.542210	1.188408	-1.420818
14	6	0	3.106837	-1.423602	0.166868
15	1	0	3.541784	-1.207633	1.148217
16	1	0	3.071982	-2.502325	0.020678
17	1	0	3.772141	-0.979570	-0.581360
18	6	0	0.607944	2.910864	-0.137507
19	1	0	0.572816	3.160193	0.926844
20	1	0	1.550073	3.280052	-0.545272
21	1	0	-0.206934	3.430979	-0.646583

Data 39: Cartesian coordinates and energies of the optimized geometry for the 2nd conformer of triazepine **8** in DMSO solution.



Electronic Energy =	-797.841021309 a.u.
Zero-point correction=	0.175088 (Hartree/Particle)
Thermal correction to Energy=	0.185347
Thermal correction to Enthalpy=	0.186291
Thermal correction to Gibbs Free Energy=	0.139121
Sum of electronic and zero-point Energies=	-797.665933
Sum of electronic and thermal Energies=	-797.655674
Sum of electronic and thermal Enthalpies=	-797.654730
Sum of electronic and thermal Free Energies=	-797.701901

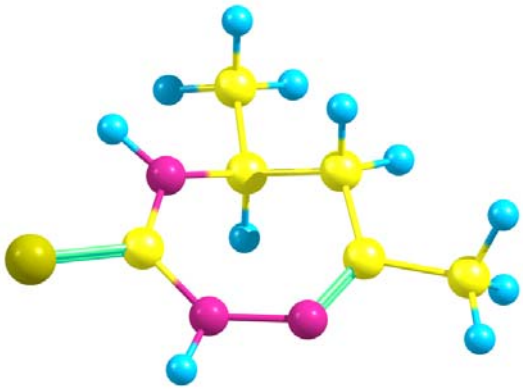
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.720080	-1.527114	-0.364226
2	6	0	-1.641142	-0.791035	0.137170
3	6	0	-1.394113	0.386075	1.042599
4	6	0	-0.574805	1.505035	0.383713
5	7	0	0.822882	1.083848	0.196154

6	6	0	1.366754	-0.127035	0.022700
7	16	0	3.075937	-0.297435	-0.053990
8	7	0	0.623173	-1.266086	-0.095226
9	1	0	-0.866593	0.038635	1.938104
10	1	0	-2.347267	0.803057	1.369646
11	1	0	-0.523090	2.333368	1.095024
12	1	0	1.512995	1.819375	0.252237
13	1	0	1.191514	-2.065915	-0.331718
14	6	0	-3.059118	-1.161428	-0.186104
15	1	0	-3.561913	-0.335737	-0.699681
16	1	0	-3.097183	-2.050481	-0.814458
17	1	0	-3.616280	-1.346170	0.738271
18	6	0	-1.190143	2.027400	-0.918759
19	1	0	-0.579843	2.834034	-1.330252
20	1	0	-1.262622	1.237704	-1.670467
21	1	0	-2.191141	2.422480	-0.727682

MeCN solution

Data 40: Cartesian coordinates and energies of the optimized geometry for the 1st conformer of triazepine **8** in MeCN solution.



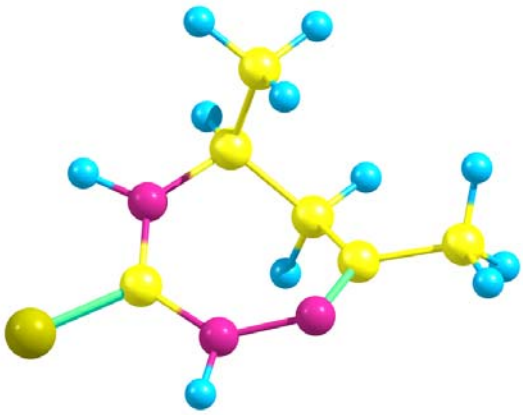
Electronic Energy =	-797.841337316 a.u.
Zero-point correction=	0.174783 (Hartree/Particle)
Thermal correction to Energy=	0.185148
Thermal correction to Enthalpy=	0.186092
Thermal correction to Gibbs Free Energy=	0.138547
Sum of electronic and zero-point Energies=	-797.666554
Sum of electronic and thermal Energies=	-797.656190
Sum of electronic and thermal Enthalpies=	-797.655245
Sum of electronic and thermal Free Energies=	-797.702791

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.795321	-1.637033	-0.257522
2	6	0	1.730174	-0.820299	0.061909
3	6	0	1.651914	0.658704	0.341044
4	7	0	-0.794240	0.945882	0.165884
5	6	0	-1.337452	-0.264009	-0.018142
6	16	0	-3.014421	-0.531501	0.170129
7	7	0	-0.548796	-1.317492	-0.389813
8	1	0	-1.455486	1.657421	0.442771
9	1	0	-1.081902	-2.155758	-0.566168

10	6	0	0.505260	1.401195	-0.346501
11	1	0	2.599967	1.104549	0.026309
12	1	0	1.585452	0.814743	1.424179
13	1	0	0.539780	1.188251	-1.420837
14	6	0	3.106391	-1.424041	0.168638
15	1	0	3.540449	-1.207595	1.150285
16	1	0	3.070973	-2.502856	0.023313
17	1	0	3.772813	-0.981108	-0.579259
18	6	0	0.607012	2.910969	-0.137938
19	1	0	0.573413	3.160503	0.926426
20	1	0	1.548352	3.280561	-0.547182
21	1	0	-0.208867	3.430680	-0.645822

Data 41: Cartesian coordinates and energies of the optimized geometry for the 2nd conformer of triazepine **8** in MeCN solution.



Electronic Energy =	-797.840823028 a.u.
Zero-point correction=	0.175081 (Hartree/Particle)
Thermal correction to Energy=	0.185342
Thermal correction to Enthalpy=	0.186286
Thermal correction to Gibbs Free Energy=	0.139098
Sum of electronic and zero-point Energies=	-797.665742
Sum of electronic and thermal Energies=	-797.655481
Sum of electronic and thermal Enthalpies=	-797.654537
Sum of electronic and thermal Free Energies=	-797.701725

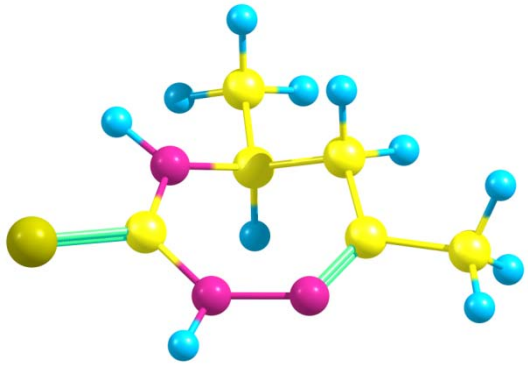
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.720240	-1.526953	-0.364122
2	6	0	-1.641247	-0.790825	0.137233
3	6	0	-1.394257	0.386447	1.042517
4	6	0	-0.574600	1.505153	0.383603
5	7	0	0.823014	1.083807	0.196659
6	6	0	1.366929	-0.127173	0.022789
7	16	0	3.075757	-0.297656	-0.053924
8	7	0	0.622996	-1.266102	-0.095505
9	1	0	-0.866973	0.039127	1.938214
10	1	0	-2.347476	0.803568	1.369264
11	1	0	-0.523097	2.333728	1.094692
12	1	0	1.513308	1.819129	0.252941
13	1	0	1.191270	-2.065826	-0.332524
14	6	0	-3.059272	-1.161309	-0.185869
15	1	0	-3.562089	-0.335830	-0.699796
16	1	0	-3.097273	-2.050571	-0.813917
17	1	0	-3.616491	-1.345796	0.738533
18	6	0	-1.189579	2.027140	-0.919214
19	1	0	-0.578939	2.833352	-1.331021

20	1	0	-1.262081	1.237118	-1.670571
21	1	0	-2.190518	2.422635	-0.728593

EtOH solution

Data 42: Cartesian coordinates and energies of the optimized geometry for the 1st conformer of triazepine **8** in EtOH solution.

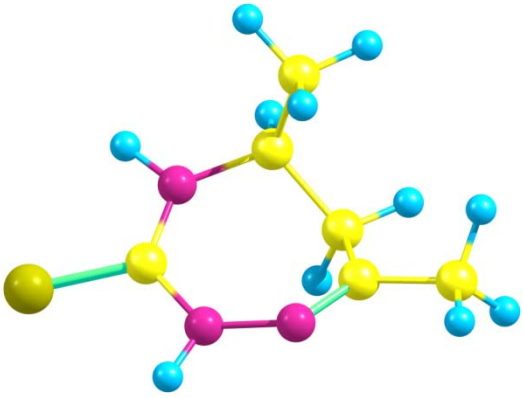


Electronic Energy =	-797.841020039 a.u.
Zero-point correction=	0.174793 (Hartree/Particle)
Thermal correction to Energy=	0.185153
Thermal correction to Enthalpy=	0.186097
Thermal correction to Gibbs Free Energy=	0.138587
Sum of electronic and zero-point Energies=	-797.666227
Sum of electronic and thermal Energies=	-797.655868
Sum of electronic and thermal Enthalpies=	-797.654923
Sum of electronic and thermal Free Energies=	-797.702433

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.795181	-1.636325	-0.258256
2	6	0	1.730113	-0.819896	0.061540
3	6	0	1.653206	0.659777	0.337972
4	7	0	-0.793362	0.944907	0.169935
5	6	0	-1.337611	-0.264351	-0.017744
6	16	0	-3.013732	-0.532184	0.170770
7	7	0	-0.548416	-1.316263	-0.393706
8	1	0	-1.454470	1.655849	0.448649
9	1	0	-1.081344	-2.154386	-0.571358
10	6	0	0.504135	1.401228	-0.346440
11	1	0	2.600330	1.104635	0.018820
12	1	0	1.590988	0.817969	1.421065
13	1	0	0.535714	1.187966	-1.420851
14	6	0	3.105655	-1.424746	0.171550
15	1	0	3.538272	-1.207501	1.153673
16	1	0	3.069286	-2.503710	0.027671
17	1	0	3.773914	-0.983655	-0.575821
18	6	0	0.605422	2.911143	-0.138668
19	1	0	0.574377	3.161036	0.925707
20	1	0	1.545433	3.281421	-0.550384
21	1	0	-0.212132	3.430163	-0.644565

Data 43: Cartesian coordinates and energies of the optimized geometry for the 2nd conformer of triazepine **8** in EtOH solution.

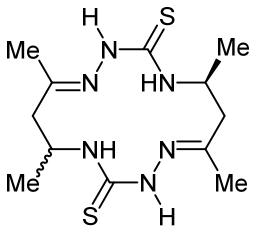


Electronic Energy =	-797.840465591 a.u.
Zero-point correction=	0.175068 (Hartree/Particle)
Thermal correction to Energy=	0.185334
Thermal correction to Enthalpy=	0.186278
Thermal correction to Gibbs Free Energy=	0.139059
Sum of electronic and zero-point Energies=	-797.665398
Sum of electronic and thermal Energies=	-797.655132
Sum of electronic and thermal Enthalpies=	-797.654188
Sum of electronic and thermal Free Energies=	-797.701407

Standard orientation:

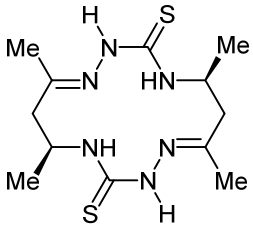
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.720518	-1.526678	0.363901
2	6	0	1.641435	-0.790452	-0.137344
3	6	0	1.394528	0.387112	-1.042372
4	6	0	0.574241	1.505361	-0.383419
5	7	0	-0.823248	1.083729	-0.197603
6	6	0	-1.367244	-0.127423	-0.022967
7	16	0	-3.075429	-0.298040	0.053856
8	7	0	-0.622682	-1.266150	0.095904
9	1	0	0.867678	0.040004	-1.938418
10	1	0	2.347870	0.804482	-1.368572
11	1	0	0.523125	2.334367	-1.094113
12	1	0	-1.513867	1.818688	-0.254158
13	1	0	-1.190839	-2.065679	0.333872
14	6	0	3.059537	-1.161080	0.185520
15	1	0	3.562347	-0.336000	0.700151
16	1	0	3.097398	-2.050747	0.812980
17	1	0	3.616926	-1.345057	-0.738903
18	6	0	1.188556	2.026675	0.920026
19	1	0	0.577337	2.832170	1.332362
20	1	0	1.261039	1.236082	1.670770
21	1	0	2.189412	2.422862	0.730251

14-Membered cyclic bis-thiosemicarbazone 6



DMSO solution

Data 44: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of macrocycle *cis*-**6** in DMSO solution.



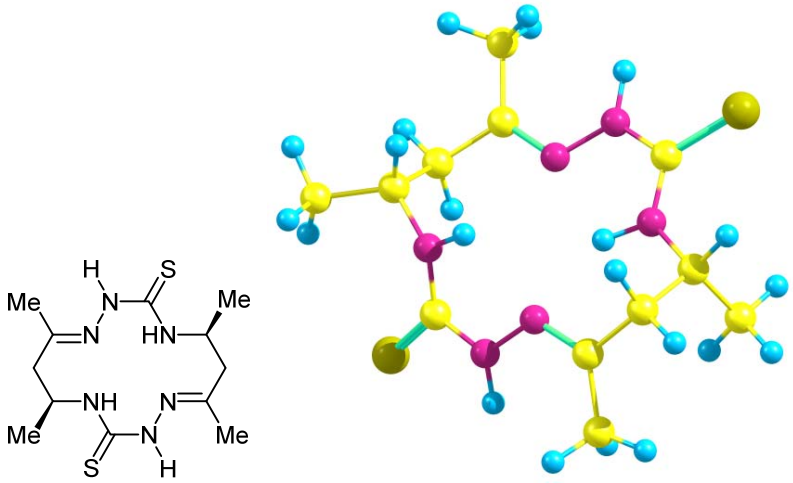
Electronic Energy =	-1595.69807706 a.u.
Zero-point correction=	0.349577 (Hartree/Particle)
Thermal correction to Energy=	0.372302
Thermal correction to Enthalpy=	0.373246
Thermal correction to Gibbs Free Energy=	0.296263
Sum of electronic and zero-point Energies=	-1595.348500
Sum of electronic and thermal Energies=	-1595.325775
Sum of electronic and thermal Enthalpies=	-1595.324831
Sum of electronic and thermal Free Energies=	-1595.401814

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-4.345222	0.668939	0.127934
2	16	0	4.345222	-0.668941	0.127940
3	7	0	-1.962126	1.780545	-0.226050
4	1	0	-2.508959	2.632172	-0.248952
5	7	0	-0.590706	1.792991	-0.265602
6	7	0	1.903837	0.495390	-0.013760
7	1	0	0.901253	0.378259	-0.096683
8	7	0	1.962125	-1.780546	-0.226048
9	1	0	2.508959	-2.632173	-0.248953
10	7	0	0.590705	-1.792991	-0.265596
11	7	0	-1.903835	-0.495389	-0.013753
12	1	0	-0.901251	-0.378258	-0.096669
13	6	0	-2.649473	0.608451	-0.034263
14	6	0	0.029604	2.883398	-0.544406
15	6	0	-0.651114	4.184751	-0.877046
16	1	0	-1.515415	4.037092	-1.530048
17	1	0	0.040168	4.862484	-1.377243

18	1	0	-0.998081	4.682667	0.035861
19	6	0	1.548852	2.863264	-0.596220
20	1	0	1.903721	3.864867	-0.338838
21	1	0	1.835469	2.709986	-1.644894
22	6	0	2.320467	1.865158	0.291724
23	1	0	3.374672	1.942781	0.021831
24	6	0	2.172907	2.165947	1.789851
25	1	0	2.767565	1.462210	2.375766
26	1	0	1.131165	2.088771	2.109200
27	1	0	2.527682	3.176784	2.006987
28	6	0	2.649474	-0.608451	-0.034263
29	6	0	-0.029605	-2.883396	-0.544407
30	6	0	0.651112	-4.184747	-0.877061
31	1	0	1.515412	-4.037081	-1.530064
32	1	0	-0.040171	-4.862475	-1.377261
33	1	0	0.998082	-4.682670	0.035840
34	6	0	-1.548853	-2.863265	-0.596213
35	1	0	-1.835474	-2.709994	-1.644887
36	1	0	-1.903718	-3.864868	-0.338825
37	6	0	-2.320466	-1.865158	0.291730
38	1	0	-3.374672	-1.942779	0.021838
39	6	0	-2.172906	-2.165948	1.789857
40	1	0	-2.767548	-1.462199	2.375774
41	1	0	-1.131161	-2.088793	2.109202
42	1	0	-2.527701	-3.176777	2.006995

Data 45: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of macrocycle *cis*-**6** in DMSO solution.



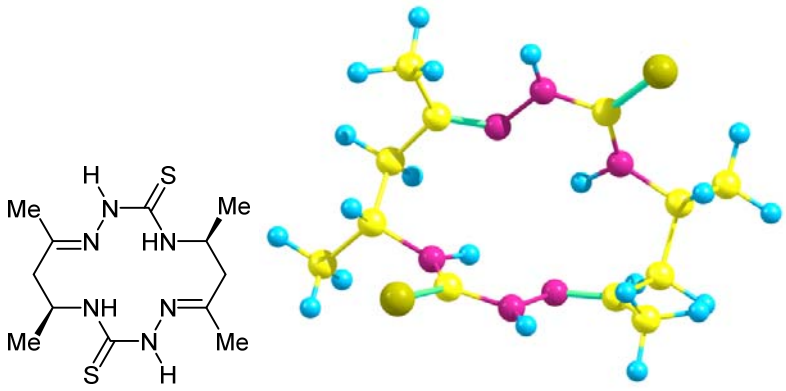
Electronic Energy =	-1595.68983017 a.u.
Zero-point correction=	0.350376 (Hartree/Particle)
Thermal correction to Energy=	0.372687
Thermal correction to Enthalpy=	0.373631
Thermal correction to Gibbs Free Energy=	0.298595
Sum of electronic and zero-point Energies=	-1595.339454
Sum of electronic and thermal Energies=	-1595.317144
Sum of electronic and thermal Enthalpies=	-1595.316199
Sum of electronic and thermal Free Energies=	-1595.391235

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.913820	2.068807	-0.064978
2	7	0	-0.019474	1.725596	0.423821
3	7	0	-1.285628	2.234853	0.267036
4	1	0	-1.475500	3.229232	0.261042

5	7	0	-2.058782	0.096002	0.062844
6	1	0	-1.069578	-0.126599	0.136615
7	6	0	-2.355158	1.396504	0.097718
8	6	0	-2.972276	-1.020058	-0.187754
9	1	0	-3.830220	-0.613078	-0.724850
10	6	0	-2.271490	-2.031460	-1.138781
11	1	0	-2.976184	-2.836622	-1.353913
12	1	0	-2.055248	-1.516327	-2.077079
13	6	0	-0.983192	-2.604306	-0.583696
14	6	0	-0.963085	-3.950716	0.089781
15	1	0	-0.752427	-3.857540	1.161594
16	1	0	-0.185721	-4.589345	-0.342845
17	1	0	-1.919388	-4.458944	-0.017965
18	16	0	3.522364	-1.637053	1.058129
19	7	0	0.044274	-1.836447	-0.687966
20	7	0	1.231790	-2.207977	-0.115440
21	1	0	1.290544	-2.994305	0.522232
22	7	0	2.121913	-0.214714	-0.808190
23	1	0	1.235246	-0.197580	-1.301522
24	6	0	2.253767	-1.287990	-0.015544
25	6	0	2.815499	1.087481	-0.745399
26	1	0	2.450135	1.606634	-1.634617
27	6	0	2.362341	1.900120	0.502479
28	1	0	3.088111	2.696398	0.677203
29	1	0	2.385354	1.243440	1.374465
30	6	0	0.988646	2.518490	0.335873
31	6	0	0.890933	3.994713	0.048307
32	1	0	0.127757	4.216787	-0.702637
33	1	0	0.635952	4.549788	0.958857
34	1	0	1.843859	4.380357	-0.312745
35	6	0	4.338440	1.005264	-0.877024
36	1	0	4.723496	2.006550	-1.086347
37	1	0	4.809334	0.628525	0.028599
38	1	0	4.614313	0.352737	-1.708516
39	6	0	-3.461770	-1.644178	1.123691
40	1	0	-2.630449	-2.022517	1.724029
41	1	0	-3.994928	-0.898146	1.716391
42	1	0	-4.145731	-2.471882	0.918955

Data 46: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of macrocycle *cis*-**6** in DMSO solution.

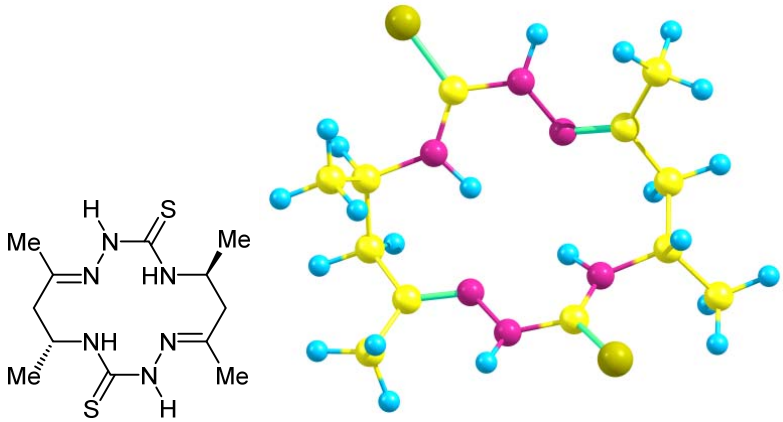


Electronic Energy =	-1595.70034522 a.u.
Zero-point correction=	0.350313 (Hartree/Particle)
Thermal correction to Energy=	0.372552
Thermal correction to Enthalpy=	0.373496
Thermal correction to Gibbs Free Energy=	0.299029
Sum of electronic and zero-point Energies=	-1595.350032
Sum of electronic and thermal Energies=	-1595.327793
Sum of electronic and thermal Enthalpies=	-1595.326849
Sum of electronic and thermal Free Energies=	-1595.401316

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	3.215073	-1.677838	-1.582953
2	16	0	-3.215096	1.677877	-1.582919
3	7	0	-0.133685	-1.845723	0.464632
4	7	0	0.887194	-2.150277	-0.399701
5	1	0	0.761744	-2.771725	-1.190010
6	7	0	2.127958	-0.510138	0.605501
7	1	0	1.308248	-0.462166	1.202422
8	7	0	0.133691	1.845710	0.464625
9	7	0	-0.887188	2.150264	-0.399706
10	1	0	-0.761764	2.771773	-1.189970
11	7	0	-2.127952	0.510126	0.605494
12	1	0	-1.308240	0.462148	1.202411
13	6	0	2.039459	-1.405897	-0.382961
14	6	0	3.117943	0.564228	0.731590
15	1	0	3.541778	0.719736	-0.262443
16	6	0	2.386167	1.849438	1.197519
17	1	0	1.939090	1.664090	2.178130
18	1	0	3.133727	2.636625	1.320190
19	6	0	1.313252	2.300888	0.235482
20	6	0	-2.039461	1.405902	-0.382955
21	6	0	-3.117938	-0.564238	0.731577
22	1	0	-3.541768	-0.719744	-0.262459
23	6	0	-2.386168	-1.849451	1.197507
24	1	0	-1.939103	-1.664107	2.178124
25	1	0	-3.133732	-2.636637	1.320166
26	6	0	-1.313244	-2.300901	0.235482
27	6	0	1.683844	3.173153	-0.934775
28	1	0	1.331910	2.748889	-1.880589
29	1	0	2.763954	3.296339	-1.001927
30	1	0	1.240877	4.170274	-0.832504
31	6	0	-1.683823	-3.173165	-0.934782
32	1	0	-1.331951	-2.748852	-1.880598
33	1	0	-2.763927	-3.296421	-1.001899
34	1	0	-1.240783	-4.170258	-0.832554
35	6	0	4.242072	0.185237	1.699951
36	1	0	4.742055	-0.724858	1.363173
37	1	0	4.983464	0.986699	1.751273
38	1	0	3.848206	0.014011	2.705630
39	6	0	-4.242072	-0.185245	1.699936
40	1	0	-3.848206	-0.014016	2.705613
41	1	0	-4.742054	0.724850	1.363158
42	1	0	-4.983468	-0.986704	1.751263

Data 47: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of macrocycle *trans*-**6** in DMSO solution.



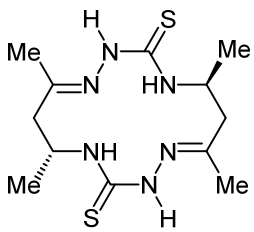
Electronic Energy = -1595.69547977 a.u.
Zero-point correction= 0.350254 (Hartree/Particle)
Thermal correction to Energy= 0.372498
Thermal correction to Enthalpy= 0.373442

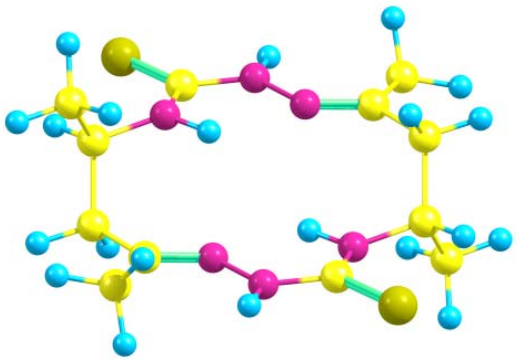
Thermal correction to Gibbs Free Energy=	0.299192
Sum of electronic and zero-point Energies=	-1595.345225
Sum of electronic and thermal Energies=	-1595.322982
Sum of electronic and thermal Enthalpies=	-1595.322038
Sum of electronic and thermal Free Energies=	-1595.396288

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	3.458694	-1.651808	1.386868
2	16	0	-3.947234	1.953117	0.389401
3	7	0	1.218283	-2.192444	0.077475
4	1	0	1.242974	-3.015054	0.669062
5	7	0	0.077794	-1.819760	-0.584122
6	7	0	-2.044475	0.131425	-0.247899
7	1	0	-1.052831	-0.049257	-0.381214
8	7	0	-1.314022	2.249531	0.178849
9	1	0	-1.542148	3.213640	0.389036
10	7	0	-0.100174	1.916405	-0.386918
11	7	0	2.120645	-0.143214	-0.419156
12	1	0	1.281313	-0.056374	-0.981935
13	6	0	2.220696	-1.273101	0.285628
14	6	0	-0.925331	-2.624834	-0.624829
15	6	0	-0.915562	-4.006755	-0.027835
16	1	0	-0.083925	-4.596581	-0.427692
17	1	0	-1.841918	-4.535441	-0.243342
18	1	0	-0.797155	-3.968979	1.061429
19	6	0	-2.179818	-2.072397	-1.279005
20	1	0	-2.870887	-2.887459	-1.496363
21	1	0	-1.914558	-1.603122	-2.229680
22	6	0	-2.929346	-1.027134	-0.409682
23	1	0	-3.806747	-0.699742	-0.972648
24	6	0	-3.387450	-1.593169	0.939592
25	1	0	-3.939058	-0.836388	1.497990
26	1	0	-2.535986	-1.914266	1.544993
27	1	0	-4.045516	-2.451715	0.781768
28	6	0	-2.373147	1.381654	0.077804
29	6	0	0.931499	2.633173	-0.116952
30	6	0	0.950913	3.803344	0.826435
31	1	0	0.692916	4.728867	0.297912
32	1	0	1.950404	3.937761	1.241958
33	1	0	0.244167	3.675083	1.649054
34	6	0	2.204283	2.264110	-0.854147
35	1	0	1.964301	2.073019	-1.904454
36	1	0	2.884613	3.117304	-0.835233
37	6	0	2.978970	1.043966	-0.305362
38	1	0	3.200765	1.188130	0.755669
39	6	0	4.293687	0.868056	-1.073994
40	1	0	4.933671	1.741539	-0.925683
41	1	0	4.828188	-0.013575	-0.719771
42	1	0	4.101338	0.756574	-2.144688

Data 48: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of macrocycle *trans*-**6** in DMSO solution.



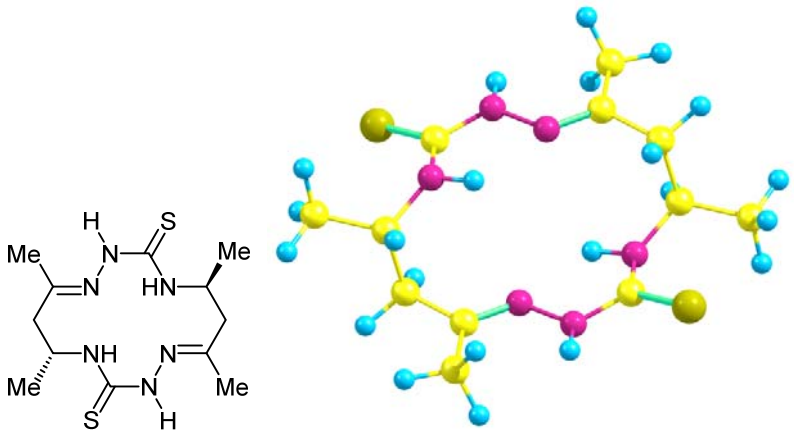


Electronic Energy =	-1595.69814555 a.u.
Zero-point correction=	0.350356 (Hartree/Particle)
Thermal correction to Energy=	0.372654
Thermal correction to Enthalpy=	0.373598
Thermal correction to Gibbs Free Energy=	0.298471
Sum of electronic and zero-point Energies=	-1595.347789
Sum of electronic and thermal Energies=	-1595.325492
Sum of electronic and thermal Enthalpies=	-1595.324548
Sum of electronic and thermal Free Energies=	-1595.399674

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.952317	-1.743878	0.500516
2	7	0	-0.175152	-1.767873	-0.579589
3	7	0	-1.433575	-2.160372	-0.210366
4	1	0	-1.651827	-3.112313	0.058178
5	7	0	-2.094130	0.022336	-0.392508
6	1	0	-1.119927	0.145881	-0.652143
7	6	0	-2.429309	-1.229200	-0.062204
8	6	0	-2.864482	1.238179	-0.126511
9	1	0	-3.814479	0.911710	0.296127
10	6	0	-2.148867	2.087715	0.961731
11	1	0	-2.803672	2.921934	1.221566
12	1	0	-2.040041	1.465390	1.852747
13	6	0	-0.787416	2.621298	0.559658
14	6	0	-0.622623	4.064428	0.159529
15	1	0	-0.165890	4.154766	-0.832059
16	1	0	0.024982	4.591551	0.869573
17	1	0	-1.580882	4.579734	0.137386
18	16	0	3.952310	1.743870	-0.500548
19	7	0	0.175156	1.767878	0.579594
20	7	0	1.433577	2.160373	0.210360
21	1	0	1.651825	3.112309	-0.058204
22	7	0	2.094136	-0.022332	0.392528
23	1	0	1.119936	-0.145874	0.652176
24	6	0	2.429310	1.229200	0.062200
25	6	0	2.864484	-1.238178	0.126532
26	1	0	3.814485	-0.911712	-0.296098
27	6	0	2.148873	-2.087707	-0.961719
28	1	0	2.803679	-2.921926	-1.221555
29	1	0	2.040051	-1.465378	-1.852732
30	6	0	0.787420	-2.621293	-0.559654
31	6	0	0.622626	-4.064426	-0.159535
32	1	0	0.165880	-4.154771	0.832046
33	1	0	-0.024967	-4.591548	-0.869592
34	1	0	1.580887	-4.579728	-0.137382
35	6	0	3.127822	-2.000968	1.427568
36	1	0	2.196457	-2.293707	1.920371
37	1	0	3.706743	-2.905547	1.225732
38	1	0	3.695657	-1.377658	2.121454
39	6	0	-3.127834	2.000963	-1.427548
40	1	0	-2.196475	2.293706	-1.920359
41	1	0	-3.695670	1.377647	-2.121428
42	1	0	-3.706759	2.905539	-1.225711

Data 49: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of macrocycle *trans*-**6** in DMSO solution.



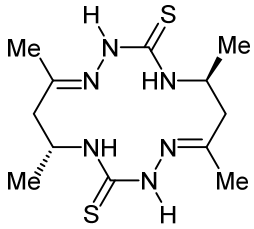
Electronic Energy =	-1595.67959839 a.u.
Zero-point correction=	0.351025 (Hartree/Particle)
Thermal correction to Energy=	0.373036
Thermal correction to Enthalpy=	0.373981
Thermal correction to Gibbs Free Energy=	0.299833
Sum of electronic and zero-point Energies=	-1595.328573
Sum of electronic and thermal Energies=	-1595.306562
Sum of electronic and thermal Enthalpies=	-1595.305618
Sum of electronic and thermal Free Energies=	-1595.379765

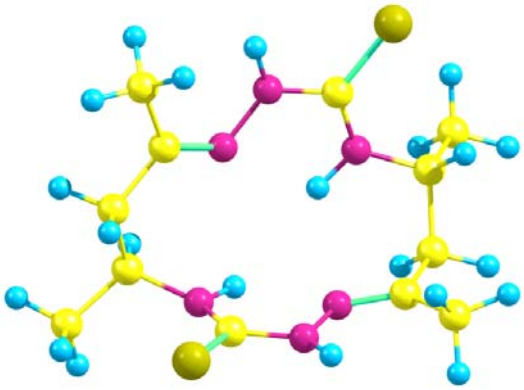
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.652517	1.876042	-0.673922
2	7	0	-0.010591	1.687262	0.712375
3	7	0	-1.248034	2.168896	0.352106
4	1	0	-1.340763	3.044080	-0.151197
5	7	0	-2.160205	0.115079	0.797860
6	1	0	-1.229375	-0.005273	1.186790
7	6	0	-2.310765	1.307943	0.201907
8	6	0	-2.882396	-1.152796	0.567830
9	1	0	-2.565927	-1.773908	1.409594
10	6	0	-2.371468	-1.829350	-0.742914
11	1	0	-3.080542	-2.606759	-1.035613
12	1	0	-2.338605	-1.083304	-1.538750
13	6	0	-1.011626	-2.442623	-0.517602
14	6	0	-0.934072	-3.842937	0.039696
15	1	0	-0.486059	-3.855956	1.039826
16	1	0	-0.322544	-4.484873	-0.603210
17	1	0	-1.924397	-4.289064	0.114557
18	16	0	3.652519	-1.876034	0.673927
19	7	0	0.010594	-1.687269	-0.712376
20	7	0	1.248037	-2.168900	-0.352104
21	1	0	1.340769	-3.044084	0.151200
22	7	0	2.160203	-0.115084	-0.797867
23	1	0	1.229374	0.005263	-1.186799
24	6	0	2.310766	-1.307944	-0.201906
25	6	0	2.882390	1.152795	-0.567840
26	1	0	2.565909	1.773906	-1.409600
27	6	0	2.371472	1.829343	0.742910
28	1	0	3.080549	2.606749	1.035608
29	1	0	2.338615	1.083294	1.538743
30	6	0	1.011629	2.442620	0.517612
31	6	0	0.934072	3.842941	-0.039666
32	1	0	0.486101	3.855966	-1.039815
33	1	0	0.322503	4.484856	0.603222
34	1	0	1.924391	4.289088	-0.114479
35	6	0	-4.407825	-1.070663	0.640213
36	1	0	-4.798091	-2.087096	0.737968
37	1	0	-4.721659	-0.498664	1.515845
38	1	0	-4.840801	-0.610256	-0.244805

39	6	0	4.407819	1.070670	-0.640242
40	1	0	4.798079	2.087106	-0.737997
41	1	0	4.840808	0.610262	0.244770
42	1	0	4.721645	0.498677	-1.515879

Data 50: Cartesian coordinates and energies of the optimized geometry for the conformer **D** of macrocycle *trans*-**6** in DMSO solution.





Electronic Energy =	-1595.69180287 a.u.
Zero-point correction=	0.350015 (Hartree/Particle)
Thermal correction to Energy=	0.372390
Thermal correction to Enthalpy=	0.373334
Thermal correction to Gibbs Free Energy=	0.298779
Sum of electronic and zero-point Energies=	-1595.341788
Sum of electronic and thermal Energies=	-1595.319413
Sum of electronic and thermal Enthalpies=	-1595.318469
Sum of electronic and thermal Free Energies=	-1595.393024

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.087124	-1.349258	0.247575
2	16	0	-3.361464	-1.341543	1.372144
3	7	0	-0.992559	-2.147127	0.502291
4	7	0	0.119008	-2.013606	-0.284431
5	6	0	1.257835	-2.464381	0.102159
6	7	0	-2.009653	-0.662096	-0.897063
7	6	0	-2.754408	0.530702	-1.341156
8	6	0	2.079102	1.426457	0.142652
9	16	0	3.454898	2.044365	0.936218
10	7	0	0.920578	2.155121	0.184566
11	7	0	-0.273553	1.634640	-0.265338
12	6	0	-1.354182	2.236628	0.084217
13	6	0	-2.698584	1.700282	-0.347404
14	7	0	2.028347	0.271013	-0.528679
15	6	0	3.069399	-0.768005	-0.544515
16	1	0	-0.971084	-2.615339	1.401102
17	1	0	-1.124439	-0.800617	-1.369850
18	1	0	0.953215	2.993562	0.751835
19	1	0	1.107722	0.011015	-0.866953
20	6	0	2.403441	-2.140288	-0.827884
21	1	0	-2.215047	0.837589	-2.240129
22	1	0	-3.251360	1.438402	0.562507
23	1	0	-3.255413	2.532651	-0.793931
24	1	0	3.527051	-0.780165	0.448216
25	1	0	2.031767	-2.139193	-1.855943
26	1	0	3.179656	-2.904698	-0.757590
27	6	0	-1.389450	3.470084	0.954266
28	1	0	-0.888398	3.295110	1.912138
29	1	0	-0.891450	4.313868	0.464347

30	1	0	-2.416085	3.766744	1.163866
31	6	0	1.499975	-3.186304	1.399143
32	1	0	0.991123	-4.156574	1.404837
33	1	0	2.562942	-3.364922	1.554595
34	1	0	1.123536	-2.611248	2.251865
35	6	0	4.151412	-0.479635	-1.589472
36	1	0	4.621823	0.484729	-1.395114
37	1	0	4.923050	-1.253195	-1.553051
38	1	0	3.721896	-0.465917	-2.594944
39	6	0	-4.196152	0.208837	-1.749948
40	1	0	-4.208994	-0.607838	-2.475027
41	1	0	-4.797491	-0.081808	-0.888170
42	1	0	-4.651710	1.086370	-2.215613

Table 15 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of various conformers of *cis*- and *trans*-**6** in DMSO solution

Conformer	*cis*-**6**		*trans*-**6**	
	ΔE	ΔG	ΔE	ΔG
A	1.42	0.00	3.05	3.47
B	6.60	6.64	1.38	1.34
C	0.00	0.31	13.02	13.83
D			5.36	5.51

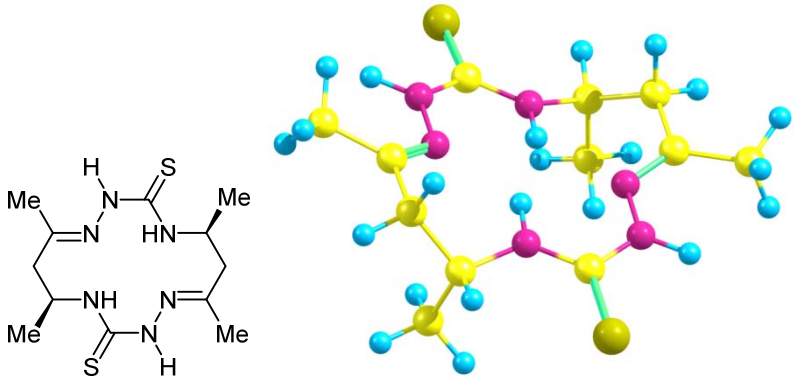
Table 16 Experimental ^{13}C chemical shifts of *cis*- and *trans*-**6** (DMSO-d_6) and calculated ^{13}C chemical shifts for the most stable conformers of *cis*- and *trans*-**6** in DMSO solution[a]

^{13}C assignment	Calculated shift, ppm		Observed shift, ppm	
	cis-**6** Conformer **C**	*trans*-**6** Conformer **B**	Major isomer	Minor isomer
CH-N	44.92	44.99	47.65	47.27
$CH_2C{=}N$	43.49	40.84	43.27	41.06
CH_3-C=N	14.68	17.69	17.09	20.41

[a] Calculations were performed by the GIAO method at the WC04/6-311+G(2d,p) level of theory using the DFT B3LYP/6-311++G(d,p) optimized geometries.

MeCN solution

Data 51: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of macrocycle *cis*-**6** in MeCN solution.



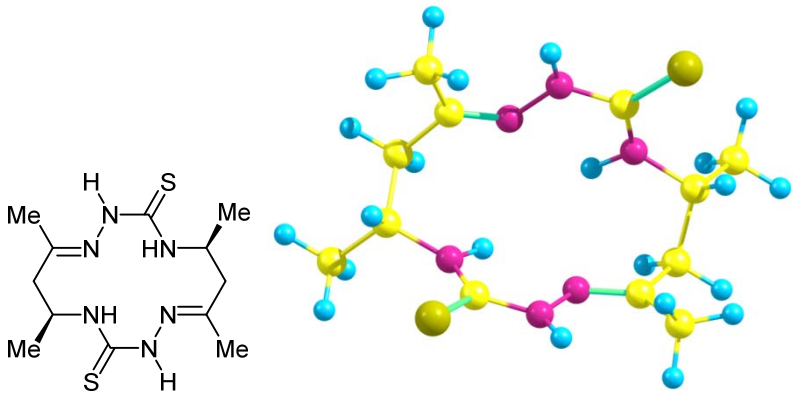
Electronic Energy =	-1595.69779870 a.u.
Zero-point correction=	0.349575 (Hartree/Particle)
Thermal correction to Energy=	0.372306
Thermal correction to Enthalpy=	0.373250
Thermal correction to Gibbs Free Energy=	0.296213
Sum of electronic and zero-point Energies=	-1595.348224
Sum of electronic and thermal Energies=	-1595.325492
Sum of electronic and thermal Enthalpies=	-1595.324548
Sum of electronic and thermal Free Energies=	-1595.401585

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-4.345237	0.668227	0.127328
2	16	0	4.345237	-0.668227	0.127319
3	7	0	-1.962392	1.780227	-0.226358
4	1	0	-2.509529	2.631645	-0.249595
5	7	0	-0.591077	1.792988	-0.265746
6	7	0	1.903736	0.495739	-0.014113
7	1	0	0.901188	0.378394	-0.096887
8	7	0	1.962391	-1.780226	-0.226363
9	1	0	2.509529	-2.631645	-0.249602
10	7	0	0.591077	-1.792988	-0.265748
11	7	0	-1.903736	-0.495739	-0.014109
12	1	0	-0.901188	-0.378394	-0.096885
13	6	0	-2.649756	0.607943	-0.034645
14	6	0	0.029111	2.883632	-0.543874
15	6	0	-0.652107	4.184964	-0.875804
16	1	0	-1.515025	4.037418	-1.530707
17	1	0	0.039409	4.864150	-1.373688
18	1	0	-1.001472	4.681205	0.037111
19	6	0	1.548378	2.863742	-0.595839
20	1	0	1.903167	3.865308	-0.338161
21	1	0	1.834985	2.710806	-1.644576
22	6	0	2.320235	1.865427	0.291694
23	1	0	3.374406	1.943180	0.021682
24	6	0	2.172949	2.165760	1.789944
25	1	0	2.768004	1.462014	2.375427
26	1	0	1.131309	2.088177	2.109551
27	1	0	2.527540	3.176610	2.007373
28	6	0	2.649756	-0.607943	-0.034650
29	6	0	-0.029112	-2.883631	-0.543877
30	6	0	0.652105	-4.184963	-0.875811
31	1	0	1.515022	-4.037416	-1.530715

32	1	0	-0.039412	-4.864148	-1.373694
33	1	0	1.001472	-4.681206	0.037103
34	6	0	-1.548380	-2.863742	-0.595838
35	1	0	-1.834989	-2.710806	-1.644575
36	1	0	-1.903167	-3.865308	-0.338160
37	6	0	-2.320234	-1.865427	0.291697
38	1	0	-3.374406	-1.943180	0.021687
39	6	0	-2.172946	-2.165761	1.789947
40	1	0	-2.767999	-1.462016	2.375431
41	1	0	-1.131305	-2.088178	2.109551
42	1	0	-2.527536	-3.176612	2.007375

Data 52: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of macrocycle *cis*-**6** in MeCN solution.



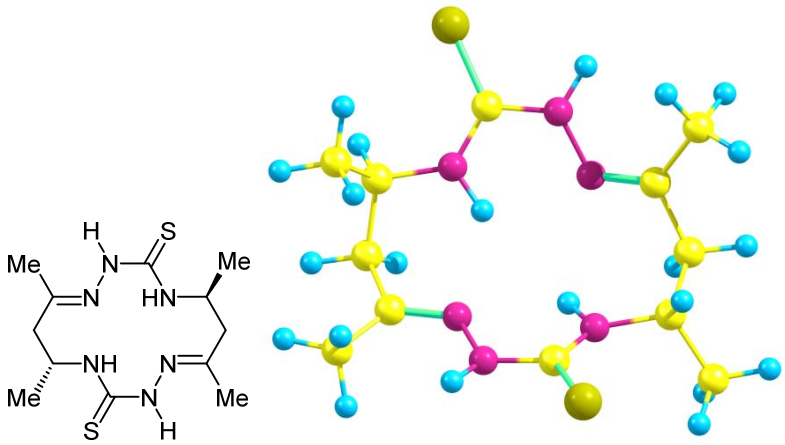
Electronic Energy =	-1595.70006762 a.u.
Zero-point correction=	0.350315 (Hartree/Particle)
Thermal correction to Energy=	0.372557
Thermal correction to Enthalpy=	0.373501
Thermal correction to Gibbs Free Energy=	0.299010
Sum of electronic and zero-point Energies=	-1595.349753
Sum of electronic and thermal Energies=	-1595.327511
Sum of electronic and thermal Enthalpies=	-1595.326567
Sum of electronic and thermal Free Energies=	-1595.401057

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.214417	1.677823	-1.583108
2	16	0	3.214415	-1.677830	-1.583104
3	7	0	0.133938	1.845659	0.464816
4	7	0	-0.886911	2.150385	-0.399382
5	1	0	-0.761163	2.771125	-1.190195
6	7	0	-2.128061	0.510439	0.605784
7	1	0	-1.308277	0.462206	1.202542
8	7	0	-0.133938	-1.845657	0.464825
9	7	0	0.886911	-2.150387	-0.399372
10	1	0	0.761162	-2.771130	-1.190183
11	7	0	2.128062	-0.510436	0.605784
12	1	0	1.308279	-0.462200	1.202543
13	6	0	-2.039382	1.406057	-0.382921
14	6	0	-3.118120	-0.563825	0.731560
15	1	0	-3.541716	-0.719185	-0.262612
16	6	0	-2.386528	-1.849117	1.197555
17	1	0	-1.939485	-1.663826	2.178207
18	1	0	-3.134166	-2.636244	1.320254
19	6	0	-1.313544	-2.300701	0.235652
20	6	0	2.039382	-1.406059	-0.382917
21	6	0	3.118121	0.563828	0.731553
22	1	0	3.541717	0.719183	-0.262619

23	6	0	2.386530	1.849123	1.197543
24	1	0	1.939488	1.663837	2.178197
25	1	0	3.134168	2.636251	1.320237
26	6	0	1.313544	2.300702	0.235639
27	6	0	-1.684063	-3.172857	-0.934750
28	1	0	-1.332921	-2.747927	-1.880575
29	1	0	-2.764115	-3.296778	-1.001530
30	1	0	-1.240317	-4.169708	-0.833146
31	6	0	1.684062	3.172851	-0.934768
32	1	0	1.332918	2.747916	-1.880591
33	1	0	2.764114	3.296772	-1.001550
34	1	0	1.240317	4.169703	-0.833170
35	6	0	-4.242569	-0.184798	1.699542
36	1	0	-4.742297	0.725353	1.362572
37	1	0	-4.984111	-0.986156	1.750554
38	1	0	-3.849116	-0.013645	2.705407
39	6	0	4.242570	0.184806	1.699537
40	1	0	3.849118	0.013658	2.705403
41	1	0	4.742298	-0.725347	1.362571
42	1	0	4.984113	0.986164	1.750544

Data 53: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of macrocycle *trans*-**6** in MeCN solution.



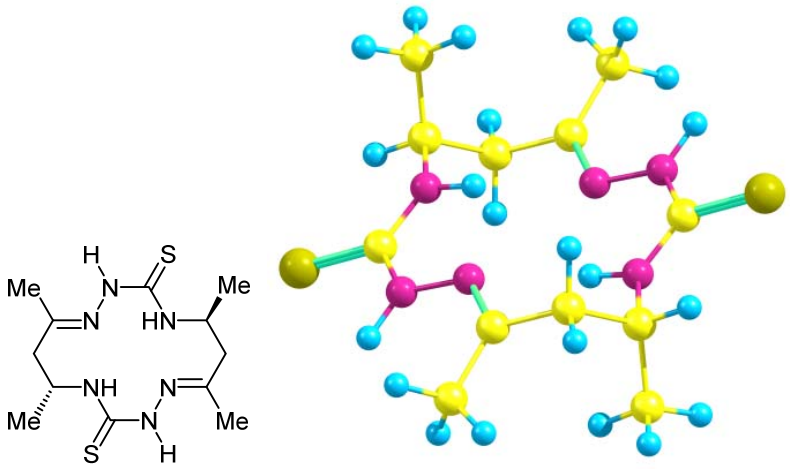
Electronic Energy =	-1595.69520431 a.u.
Zero-point correction=	0.350262 (Hartree/Particle)
Thermal correction to Energy=	0.372504
Thermal correction to Enthalpy=	0.373448
Thermal correction to Gibbs Free Energy=	0.299197
Sum of electronic and zero-point Energies=	-1595.344943
Sum of electronic and thermal Energies=	-1595.322700
Sum of electronic and thermal Enthalpies=	-1595.321756
Sum of electronic and thermal Free Energies=	-1595.396007

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.459083	1.651833	1.386058
2	16	0	3.947341	-1.952774	0.389219
3	7	0	-1.218625	2.192503	0.076944
4	1	0	-1.243662	3.015166	0.668438
5	7	0	-0.077973	1.819897	-0.584257
6	7	0	2.044534	-0.131217	-0.247911
7	1	0	1.052899	0.049352	-0.381216
8	7	0	1.314185	-2.249328	0.179095
9	1	0	1.542487	-3.213342	0.389511

10	7	0	0.100355	-1.916425	-0.386592
11	7	0	-2.120626	0.142962	-0.419330
12	1	0	-1.280944	0.055894	-0.981525
13	6	0	-2.221086	1.273036	0.285262
14	6	0	0.925193	2.624928	-0.624685
15	6	0	0.915228	4.006789	-0.027482
16	1	0	0.083570	4.596625	-0.427301
17	1	0	1.841539	4.535633	-0.242833
18	1	0	0.796762	3.968883	1.061778
19	6	0	2.179835	2.072665	-1.278724
20	1	0	2.870843	2.887843	-1.495914
21	1	0	1.914737	1.603500	-2.229504
22	6	0	2.929373	1.027312	-0.409509
23	1	0	3.806828	0.699957	-0.972427
24	6	0	3.387487	1.593137	0.939859
25	1	0	3.939092	0.836222	1.498073
26	1	0	2.536017	1.914101	1.545336
27	1	0	4.045607	2.451704	0.782255
28	6	0	2.373477	-1.381452	0.077821
29	6	0	-0.931223	-2.633387	-0.116819
30	6	0	-0.950392	-3.803693	0.826460
31	1	0	-0.692332	-4.729215	0.297949
32	1	0	-1.949800	-3.938265	1.242150
33	1	0	-0.243621	-3.675353	1.649053
34	6	0	-2.204103	-2.264396	-0.853909
35	1	0	-1.964211	-2.073354	-1.904256
36	1	0	-2.884410	-3.117630	-0.834964
37	6	0	-2.978811	-1.044237	-0.305163
38	1	0	-3.200434	-1.188222	0.755944
39	6	0	-4.293735	-0.868545	-1.073491
40	1	0	-4.933708	-1.741986	-0.924814
41	1	0	-4.828120	0.013146	-0.719269
42	1	0	-4.101690	-0.757279	-2.144270

Data 54: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of macrocycle *trans*-**6** in MeCN solution.



Electronic Energy =	-1595.69787303 a.u.
Zero-point correction=	0.350368 (Hartree/Particle)
Thermal correction to Energy=	0.372660
Thermal correction to Enthalpy=	0.373605
Thermal correction to Gibbs Free Energy=	0.298506
Sum of electronic and zero-point Energies=	-1595.347505
Sum of electronic and thermal Energies=	-1595.325213
Sum of electronic and thermal Enthalpies=	-1595.324268
Sum of electronic and thermal Free Energies=	-1595.399367

Standard orientation:

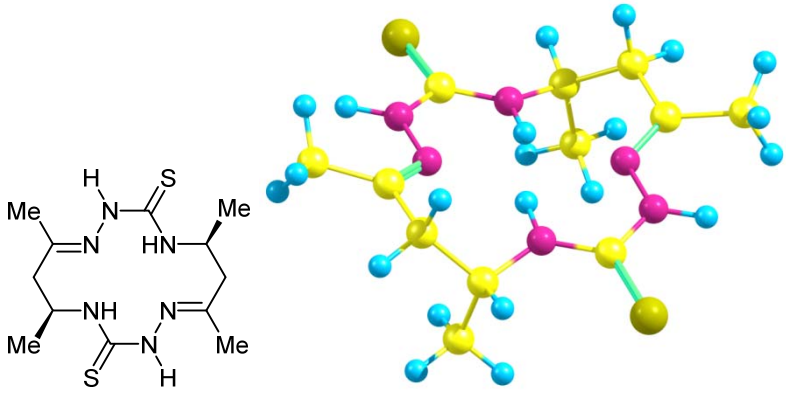
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.951678	-1.744206	0.501525
2	7	0	-0.174793	-1.767978	-0.578951
3	7	0	-1.433120	-2.160570	-0.209810
4	1	0	-1.651356	-3.112467	0.058885
5	7	0	-2.094069	0.022002	-0.392499
6	1	0	-1.119896	0.145604	-0.652145
7	6	0	-2.429166	-1.229503	-0.061671
8	6	0	-2.864616	1.237689	-0.126674
9	1	0	-3.814591	0.911011	0.295871
10	6	0	-2.149268	2.087526	0.961523
11	1	0	-2.804265	2.921655	1.221225
12	1	0	-2.040465	1.465336	1.852639
13	6	0	-0.787851	2.621324	0.559567
14	6	0	-0.623022	4.064686	0.160178
15	1	0	-0.166181	4.155583	-0.831322
16	1	0	0.024526	4.591469	0.870540
17	1	0	-1.581264	4.580047	0.138178
18	16	0	3.951674	1.744201	-0.501543
19	7	0	0.174796	1.767980	0.578954
20	7	0	1.433121	2.160570	0.209807
21	1	0	1.651355	3.112465	-0.058900
22	7	0	2.094072	-0.022000	0.392512
23	1	0	1.119902	-0.145599	0.652165
24	6	0	2.429167	1.229502	0.061669
25	6	0	2.864617	-1.237689	0.126687
26	1	0	3.814595	-0.911013	-0.295853
27	6	0	2.149272	-2.087521	-0.961516
28	1	0	2.804270	-2.921650	-1.221219
29	1	0	2.040472	-1.465328	-1.852630
30	6	0	0.787854	-2.621321	-0.559566
31	6	0	0.623024	-4.064685	-0.160184
32	1	0	0.166173	-4.155587	0.831311
33	1	0	-0.024515	-4.591466	-0.870554
34	1	0	1.581267	-4.580043	-0.138176
35	6	0	3.127962	-2.000317	1.427820
36	1	0	2.196588	-2.293289	1.920496
37	1	0	3.707184	-2.904766	1.226216
38	1	0	3.695490	-1.376788	2.121746
39	6	0	-3.127970	2.000314	-1.427808
40	1	0	-2.196600	2.293288	-1.920489
41	1	0	-3.695499	1.376781	-2.121730
42	1	0	-3.707195	2.904761	-1.226203

Table 17 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of various conformers of *cis*- and *trans*-**6** in MeCN solution

Conformer	*cis*-**6**		*trans*-**6**	
	ΔE	ΔG	ΔE	ΔG
A	1.42	0.00	3.05	3.50
B	0.00	0.33	1.38	1.39

EtOH solution

Data 55: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of macrocycle *cis*-**6** in EtOH solution.



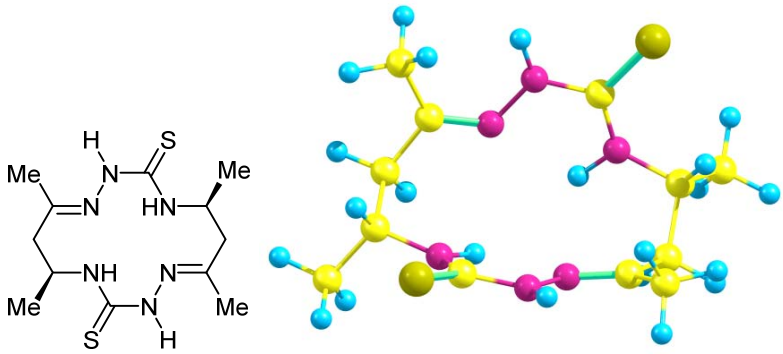
Electronic Energy =	-1595.69729706 a.u.
Zero-point correction=	0.349570 (Hartree/Particle)
Thermal correction to Energy=	0.372313
Thermal correction to Enthalpy=	0.373258
Thermal correction to Gibbs Free Energy=	0.296116
Sum of electronic and zero-point Energies=	-1595.347727
Sum of electronic and thermal Energies=	-1595.324984
Sum of electronic and thermal Enthalpies=	-1595.324039
Sum of electronic and thermal Free Energies=	-1595.401181

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-4.345263	0.666892	0.126278
2	16	0	4.345263	-0.666893	0.126269
3	7	0	-1.962889	1.779628	-0.226956
4	1	0	-2.510583	2.630669	-0.250739
5	7	0	-0.591765	1.792980	-0.266002
6	7	0	1.903539	0.496386	-0.014719
7	1	0	0.901060	0.378637	-0.097249
8	7	0	1.962889	-1.779628	-0.226962
9	1	0	2.510582	-2.630669	-0.250747
10	7	0	0.591765	-1.792979	-0.266005
11	7	0	-1.903539	-0.496386	-0.014715
12	1	0	-0.901060	-0.378637	-0.097248
13	6	0	-2.650264	0.606998	-0.035317
14	6	0	0.028199	2.884038	-0.542963
15	6	0	-0.653927	4.185292	-0.873745
16	1	0	-1.514309	4.037888	-1.532094
17	1	0	0.038011	4.867059	-1.367478
18	1	0	-1.007660	4.678577	0.039111
19	6	0	1.547503	2.864610	-0.595142
20	1	0	1.902119	3.866117	-0.336920
21	1	0	1.834139	2.712285	-1.643977
22	6	0	2.319770	1.865933	0.291690
23	1	0	3.373891	1.943933	0.021511
24	6	0	2.172903	2.165444	1.790154
25	1	0	2.768633	1.461677	2.374890
26	1	0	1.131429	2.087132	2.110168
27	1	0	2.527153	3.176318	2.008126
28	6	0	2.650264	-0.606998	-0.035323
29	6	0	-0.028201	-2.884037	-0.542966
30	6	0	0.653925	-4.185291	-0.873751
31	1	0	1.514306	-4.037886	-1.532102

32	1	0	-0.038014	-4.867057	-1.367484
33	1	0	1.007660	-4.678577	0.039103
34	6	0	-1.547504	-2.864609	-0.595142
35	1	0	-1.834143	-2.712284	-1.643976
36	1	0	-1.902120	-3.866117	-0.336919
37	6	0	-2.319769	-1.865933	0.291693
38	1	0	-3.373891	-1.943933	0.021516
39	6	0	-2.172899	-2.165445	1.790157
40	1	0	-2.768629	-1.461679	2.374894
41	1	0	-1.131425	-2.087134	2.110168
42	1	0	-2.527149	-3.176320	2.008128

Data 56: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of macrocycle *cis*-**6** in EtOH solution.



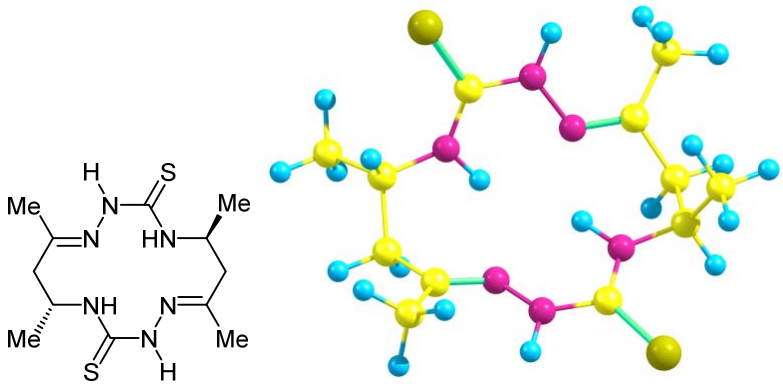
Electronic Energy =	-1595.69956812 a.u.
Zero-point correction=	0.350316 (Hartree/Particle)
Thermal correction to Energy=	0.372563
Thermal correction to Enthalpy=	0.373508
Thermal correction to Gibbs Free Energy=	0.298971
Sum of electronic and zero-point Energies=	-1595.349252
Sum of electronic and thermal Energies=	-1595.327005
Sum of electronic and thermal Enthalpies=	-1595.326060
Sum of electronic and thermal Free Energies=	-1595.400598

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.213198	1.677731	-1.583426
2	16	0	3.213196	-1.677738	-1.583422
3	7	0	0.134420	1.845518	0.465132
4	7	0	-0.886345	2.150498	-0.398879
5	1	0	-0.760067	2.769974	-1.190591
6	7	0	-2.128275	0.511043	0.606359
7	1	0	-1.308354	0.462337	1.202818
8	7	0	-0.134419	-1.845516	0.465141
9	7	0	0.886345	-2.150500	-0.398869
10	1	0	0.760066	-2.769980	-1.190578
11	7	0	2.128276	-0.511040	0.606359
12	1	0	1.308355	-0.462331	1.202819
13	6	0	-2.039221	1.406325	-0.382861
14	6	0	-3.118466	-0.563036	0.731582
15	1	0	-3.541685	-0.718099	-0.262819
16	6	0	-2.387198	-1.848504	1.197623
17	1	0	-1.940189	-1.663364	2.178346
18	1	0	-3.134982	-2.635524	1.320350
19	6	0	-1.314122	-2.300281	0.235906
20	6	0	2.039221	-1.406327	-0.382857
21	6	0	3.118467	0.563040	0.731576
22	1	0	3.541684	0.718098	-0.262826
23	6	0	2.387199	1.848510	1.197611
24	1	0	1.940192	1.663376	2.178336
25	1	0	3.134983	2.635530	1.320333

26	6	0	1.314122	2.300282	0.235893
27	6	0	-1.684551	-3.172130	-0.934820
28	1	0	-1.334885	-2.745894	-1.880633
29	1	0	-2.764499	-3.297389	-1.000888
30	1	0	-1.239385	-4.168498	-0.834549
31	6	0	1.684550	3.172125	-0.934838
32	1	0	1.334882	2.745884	-1.880649
33	1	0	2.764498	3.297383	-1.000908
34	1	0	1.239385	4.168494	-0.834572
35	6	0	-4.243431	-0.183965	1.698959
36	1	0	-4.742724	0.726292	1.361685
37	1	0	-4.985232	-0.985141	1.749451
38	1	0	-3.850651	-0.012952	2.705132
39	6	0	4.243433	0.183973	1.698954
40	1	0	3.850654	0.012965	2.705127
41	1	0	4.742725	-0.726285	1.361684
42	1	0	4.985234	0.985149	1.749441

Data 57: Cartesian coordinates and energies of the optimized geometry for the conformer **A** of macrocycle *trans*-**6** in EtOH solution.



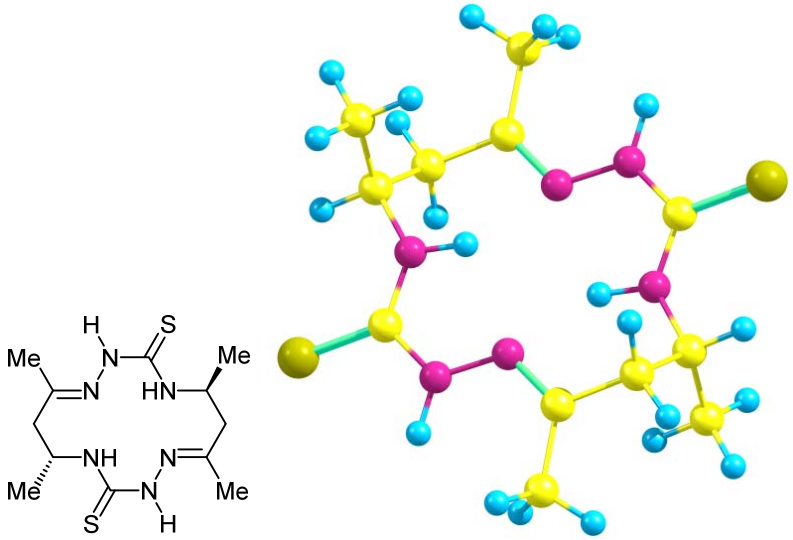
Electronic Energy =	-1595.69470823 a.u.
Zero-point correction=	0.350274 (Hartree/Particle)
Thermal correction to Energy=	0.372515
Thermal correction to Enthalpy=	0.373459
Thermal correction to Gibbs Free Energy=	0.299203
Sum of electronic and zero-point Energies=	-1595.344434
Sum of electronic and thermal Energies=	-1595.322193
Sum of electronic and thermal Enthalpies=	-1595.321249
Sum of electronic and thermal Free Energies=	-1595.395505

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.459769	1.651915	1.384565
2	16	0	3.947502	-1.952178	0.388947
3	7	0	-1.219244	2.192640	0.075928
4	1	0	-1.244895	3.015387	0.667272
5	7	0	-0.078291	1.820166	-0.584547
6	7	0	2.044635	-0.130850	-0.247932
7	1	0	1.053020	0.049529	-0.381228
8	7	0	1.314452	-2.248960	0.179571
9	1	0	1.543061	-3.212795	0.390445
10	7	0	0.100651	-1.916444	-0.385938
11	7	0	-2.120602	0.142530	-0.419684
12	1	0	-1.280278	0.055016	-0.980805
13	6	0	-2.221789	1.272950	0.284554
14	6	0	0.924972	2.625094	-0.624427
15	6	0	0.914677	4.006824	-0.026796
16	1	0	0.083042	4.596736	-0.426588
17	1	0	1.840954	4.535915	-0.241768

18	1	0	0.796017	3.968647	1.062446
19	6	0	2.179884	2.073141	-1.278233
20	1	0	2.870791	2.888524	-1.495114
21	1	0	1.915067	1.604186	-2.229205
22	6	0	2.929434	1.027611	-0.409221
23	1	0	3.806967	0.700302	-0.972072
24	6	0	3.387609	1.593057	0.940303
25	1	0	3.939208	0.835895	1.498178
26	1	0	2.536150	1.913803	1.545935
27	1	0	4.045836	2.451646	0.783069
28	6	0	2.374050	-1.381092	0.077885
29	6	0	-0.930749	-2.633777	-0.116542
30	6	0	-0.949445	-3.804386	0.826473
31	1	0	-0.691158	-4.729858	0.297956
32	1	0	-1.948719	-3.939343	1.242392
33	1	0	-0.242691	-3.675887	1.649072
34	6	0	-2.203807	-2.264911	-0.853432
35	1	0	-1.964088	-2.074003	-1.903862
36	1	0	-2.884084	-3.118204	-0.834395
37	6	0	-2.978535	-1.044695	-0.304802
38	1	0	-3.199851	-1.188317	0.756450
39	6	0	-4.293828	-0.869415	-1.072592
40	1	0	-4.933764	-1.742794	-0.923266
41	1	0	-4.828029	0.012369	-0.718369
42	1	0	-4.102326	-0.758530	-2.143523

Data 58: Cartesian coordinates and energies of the optimized geometry for the conformer **B** of macrocycle *trans*-**6** in EtOH solution.



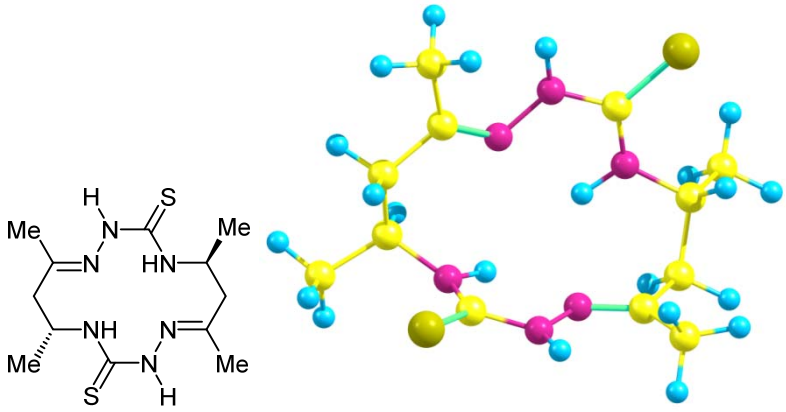
Electronic Energy =	-1595.69738185 a.u.
Zero-point correction=	0.350387 (Hartree/Particle)
Thermal correction to Energy=	0.372672
Thermal correction to Enthalpy=	0.373616
Thermal correction to Gibbs Free Energy=	0.298559
Sum of electronic and zero-point Energies=	-1595.346995
Sum of electronic and thermal Energies=	-1595.324710
Sum of electronic and thermal Enthalpies=	-1595.323765
Sum of electronic and thermal Free Energies=	-1595.398823

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.950659	-1.745024	0.501454
2	7	0	-0.173892	-1.767981	-0.578301

3	7	0	-1.432173	-2.160892	-0.209922
4	1	0	-1.650409	-3.112747	0.058903
5	7	0	-2.093872	0.021430	-0.393445
6	1	0	-1.119641	0.145232	-0.652651
7	6	0	-2.428866	-1.230092	-0.061985
8	6	0	-2.864860	1.236761	-0.127809
9	1	0	-3.814953	0.909576	0.294113
10	6	0	-2.150394	2.086803	0.960829
11	1	0	-2.805848	2.920674	1.220326
12	1	0	-2.041923	1.464578	1.851967
13	6	0	-0.788919	2.621144	0.559710
14	6	0	-0.623960	4.065012	0.161994
15	1	0	-0.166581	4.157143	-0.829167
16	1	0	0.023207	4.591075	0.873261
17	1	0	-1.582194	4.580420	0.140006
18	16	0	3.950656	1.745020	-0.501465
19	7	0	0.173894	1.767983	0.578303
20	7	0	1.432174	2.160892	0.209919
21	1	0	1.650409	3.112746	-0.058913
22	7	0	2.093875	-0.021429	0.393453
23	1	0	1.119645	-0.145229	0.652663
24	6	0	2.428866	1.230091	0.061983
25	6	0	2.864860	-1.236761	0.127817
26	1	0	3.814956	-0.909577	-0.294102
27	6	0	2.150396	-2.086800	-0.960825
28	1	0	2.805850	-2.920670	-1.220322
29	1	0	2.041927	-1.464573	-1.851961
30	6	0	0.788921	-2.621142	-0.559709
31	6	0	0.623962	-4.065011	-0.161998
32	1	0	0.166576	-4.157145	0.829160
33	1	0	-0.023199	-4.591074	-0.873270
34	1	0	1.582196	-4.580418	-0.140004
35	6	0	3.127735	-1.999524	1.428975
36	1	0	2.196163	-2.293075	1.920976
37	1	0	3.707582	-2.903667	1.227702
38	1	0	3.694449	-1.375822	2.123384
39	6	0	-3.127741	1.999522	-1.428967
40	1	0	-2.196171	2.293075	-1.920971
41	1	0	-3.694455	1.375818	-2.123374
42	1	0	-3.707589	2.903664	-1.227693

Data 59: Cartesian coordinates and energies of the optimized geometry for the conformer **C** of macrocycle *trans*-**6** in EtOH solution.



Electronic Energy =	-1595.69107158 a.u.
Zero-point correction=	0.350089 (Hartree/Particle)
Thermal correction to Energy=	0.372426
Thermal correction to Enthalpy=	0.373370
Thermal correction to Gibbs Free Energy=	0.299001
Sum of electronic and zero-point Energies=	-1595.340983
Sum of electronic and thermal Energies=	-1595.318645
Sum of electronic and thermal Enthalpies=	-1595.317701

Sum of electronic and thermal Free Energies= -1595.392070

Standard orientation:

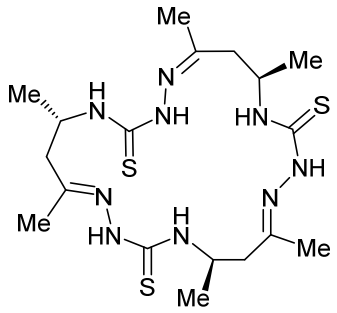
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.087016	-1.349100	-0.247336
2	16	0	3.359812	-1.340562	-1.372503
3	7	0	0.991998	-2.147254	-0.501476
4	7	0	-0.119633	-2.013321	0.284751
5	6	0	-1.258270	-2.464550	-0.101900
6	7	0	2.009831	-0.662472	0.897901
7	6	0	2.755183	0.530061	1.341248
8	6	0	-2.079136	1.426962	-0.142073
9	16	0	-3.453870	2.044692	-0.935971
10	7	0	-0.920112	2.155536	-0.183080
11	7	0	0.273894	1.634707	0.266345
12	6	0	1.354681	2.235991	-0.083910
13	6	0	2.699183	1.699444	0.347190
14	7	0	-2.028319	0.271198	0.529299
15	6	0	-3.069694	-0.767304	0.543975
16	1	0	0.969886	-2.613163	-1.401464
17	1	0	1.124401	-0.800243	1.370344
18	1	0	-0.952516	2.993067	-0.751691
19	1	0	-1.107388	0.010164	0.865807
20	6	0	-2.404501	-2.140018	0.827267
21	1	0	2.216610	0.837461	2.240595
22	1	0	3.251374	1.436742	-0.562842
23	1	0	3.256611	2.531812	0.793071
24	1	0	-3.526829	-0.778737	-0.449053
25	1	0	-2.033528	-2.139502	1.855620
26	1	0	-3.181037	-2.904097	0.756408
27	6	0	1.389833	3.468954	-0.954775
28	1	0	0.889309	3.293053	-1.912776
29	1	0	0.891220	4.312972	-0.465831
30	1	0	2.416430	3.765866	-1.164277
31	6	0	-1.499070	-3.186897	-1.399017
32	1	0	-0.982592	-4.153113	-1.408000
33	1	0	-2.561069	-3.373484	-1.551631
34	1	0	-1.129865	-2.607572	-2.252104
35	6	0	-4.152466	-0.478709	1.588104
36	1	0	-4.621921	0.486060	1.393573
37	1	0	-4.924757	-1.251609	1.550718
38	1	0	-3.723917	-0.465619	2.594021
39	6	0	4.197158	0.207438	1.748731
40	1	0	4.210188	-0.608738	2.474361
41	1	0	4.796979	-0.084679	0.886413
42	1	0	4.654229	1.084898	2.213121

Table 18 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of various conformers of *cis*- and *trans*-**6** in EtOH solution

Conformer	*cis*-**6**		*trans*-**6**	
	ΔE	ΔG	ΔE	ΔG
A	1.43	0.00	3.05	3.56
B	0.00	0.37	1.37	1.50
C			5.33	5.72

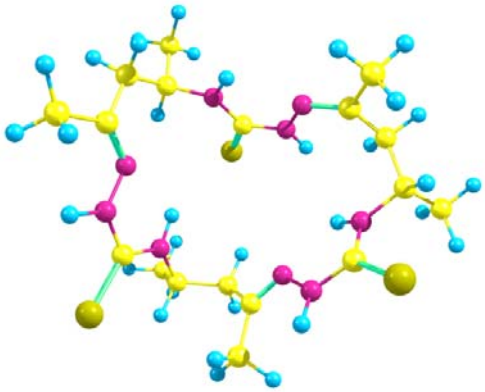
21-Membered cyclic tris-thiosemicarbazone 7

(1Z,5R,7E,12S*,14E,19S*)-diastereomer*



DMSO solution

Data 60: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of macrocycle **7** in DMSO solution.



Electronic Energy =	-2393.55546623 a.u.
Zero-point correction=	0.525444 (Hartree/Particle)
Thermal correction to Energy=	0.560070
Thermal correction to Enthalpy=	0.561014
Thermal correction to Gibbs Free Energy=	0.457342
Sum of electronic and zero-point Energies=	-2393.030023
Sum of electronic and thermal Energies=	-2392.995396
Sum of electronic and thermal Enthalpies=	-2392.994452
Sum of electronic and thermal Free Energies=	-2393.098124

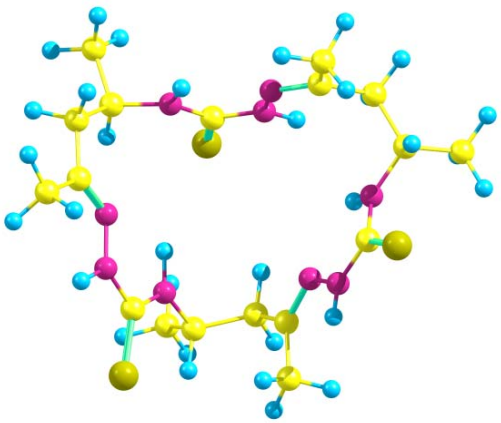
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	3.411846	3.236078	1.298787
2	16	0	0.894297	-1.701801	-2.666908
3	16	0	-4.136468	1.845960	2.080085
4	7	0	-1.650520	-2.533893	0.210967
5	7	0	-1.090197	-2.107529	-0.963101
6	1	0	-1.630343	-1.715489	-1.723762
7	7	0	0.945357	-2.840694	-0.209573
8	1	0	0.395449	-3.142045	0.589110
9	7	0	2.906373	-0.644232	0.923410
10	7	0	3.140383	0.614693	1.417015
11	1	0	3.601856	0.764569	2.305929
12	7	0	2.338047	1.535797	-0.528573
13	1	0	2.142835	0.568218	-0.775365
14	7	0	-1.233628	2.095607	-0.562215

15	7	0	-2.110070	2.375733	0.458187
16	1	0	-1.948173	3.125000	1.120082
17	7	0	-3.321890	0.533344	-0.149770
18	1	0	-2.684078	0.552384	-0.939427
19	6	0	0.250148	-2.262393	-1.190663
20	6	0	2.370629	-3.185161	-0.247039
21	1	0	2.843918	-2.472589	-0.921245
22	6	0	2.970929	-3.039279	1.153787
23	1	0	2.378194	-3.613958	1.877688
24	1	0	3.956879	-3.520295	1.158055
25	6	0	3.157725	-1.641781	1.690981
26	6	0	2.925633	1.729541	0.658290
27	6	0	2.106683	2.563374	-1.549591
28	1	0	2.383424	3.509289	-1.085144
29	6	0	0.618054	2.605882	-1.961381
30	1	0	0.526163	3.359024	-2.752810
31	1	0	0.323171	1.642587	-2.384476
32	6	0	-0.331666	2.965990	-0.848794
33	6	0	-3.157613	1.539236	0.721098
34	6	0	-4.436091	-0.417549	-0.169981
35	1	0	-4.835558	-0.438001	0.843581
36	6	0	-3.924219	-1.826492	-0.548737
37	1	0	-4.792636	-2.491407	-0.556762
38	1	0	-3.556240	-1.811980	-1.578393
39	6	0	-2.912722	-2.405426	0.415932
40	6	0	2.569919	-4.606306	-0.790166
41	1	0	2.114577	-4.701816	-1.777694
42	1	0	2.116991	-5.348284	-0.126008
43	1	0	3.635763	-4.831175	-0.880577
44	6	0	3.675002	-1.519850	3.102229
45	1	0	2.997363	-0.922521	3.721167
46	1	0	4.658985	-1.038340	3.123905
47	1	0	3.777122	-2.500753	3.564493
48	6	0	3.009466	2.321089	-2.764347
49	1	0	4.059322	2.316777	-2.463617
50	1	0	2.866503	3.111833	-3.504795
51	1	0	2.781325	1.362835	-3.239553
52	6	0	-0.195519	4.301087	-0.165566
53	1	0	-1.164217	4.806452	-0.101375
54	1	0	0.488773	4.949792	-0.710838
55	1	0	0.197161	4.190765	0.850868
56	6	0	-5.538777	0.044233	-1.129609
57	1	0	-5.900010	1.033387	-0.841633
58	1	0	-6.381272	-0.651164	-1.102247
59	1	0	-5.168211	0.095513	-2.157461
60	6	0	-3.431579	-2.899499	1.737585
61	1	0	-2.617139	-3.283747	2.350719
62	1	0	-4.169580	-3.693475	1.582919
63	1	0	-3.936113	-2.097136	2.284643

MeCN solution

Data 61: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of macrocycle **7** in MeCN solution.



Electronic Energy =	-2393.55507849 a.u.
Zero-point correction=	0.525467 (Hartree/Particle)
Thermal correction to Energy=	0.560087
Thermal correction to Enthalpy=	0.561032
Thermal correction to Gibbs Free Energy=	0.457384
Sum of electronic and zero-point Energies=	-2393.029612
Sum of electronic and thermal Energies=	-2392.994991
Sum of electronic and thermal Enthalpies=	-2392.994047
Sum of electronic and thermal Free Energies=	-2393.097695

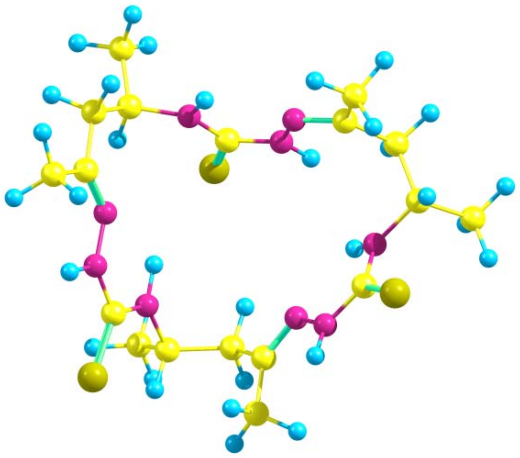
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	3.401808	-3.241757	-1.300453
2	16	0	0.898000	1.702240	2.667150
3	16	0	-4.140543	-1.842452	-2.077626
4	7	0	-1.645156	2.537636	-0.211105
5	7	0	-1.085726	2.111582	0.963398
6	1	0	-1.626290	1.719298	1.723610
7	7	0	0.951300	2.840184	0.209500
8	1	0	0.402051	3.141668	-0.589558
9	7	0	2.906409	0.639584	-0.924863
10	7	0	3.136507	-0.619824	-1.418653
11	1	0	3.596003	-0.771123	-2.308349
12	7	0	2.335002	-1.538667	0.528345
13	1	0	2.142066	-0.570610	0.775029
14	7	0	-1.237123	-2.094383	0.563634
15	7	0	-2.114340	-2.374167	-0.456116
16	1	0	-1.953764	-3.124117	-1.117553
17	7	0	-3.321665	-0.528095	0.149502
18	1	0	-2.682822	-0.546980	0.938323
19	6	0	0.255027	2.263520	1.190880
20	6	0	2.377380	3.181159	0.246581
21	1	0	2.849228	2.467065	0.920205
22	6	0	2.976619	3.034464	-1.154635
23	1	0	2.384842	3.610944	-1.877933
24	1	0	3.963737	3.513099	-1.159232
25	6	0	3.159529	1.636637	-1.692435
26	6	0	2.920235	-1.734211	-0.659410
27	6	0	2.102834	-2.565386	1.549957
28	1	0	2.378064	-3.511895	1.085788
29	6	0	0.614364	-2.605702	1.962658
30	1	0	0.522014	-3.357928	2.754920
31	1	0	0.320903	-1.641595	2.384901
32	6	0	-0.336358	-2.965752	0.850903
33	6	0	-3.160250	-1.535780	-0.719980
34	6	0	-4.434162	0.424679	0.169208
35	1	0	-4.833274	0.445682	-0.844498
36	6	0	-3.919811	1.832687	0.548023
37	1	0	-4.787064	2.499155	0.556241
38	1	0	-3.551801	1.817358	1.577693
39	6	0	-2.907351	2.410074	-0.416605
40	6	0	2.580456	4.601482	0.790460
41	1	0	2.125674	4.697432	1.778193
42	1	0	2.129201	5.345066	0.126931
43	1	0	3.646891	4.823629	0.880749
44	6	0	3.675204	1.513666	-3.104201
45	1	0	2.995011	0.918956	-3.722879
46	1	0	4.657508	1.028781	-3.127013
47	1	0	3.780277	2.494428	-3.566131
48	6	0	3.006646	-2.323630	2.764060
49	1	0	4.056323	-2.320960	2.462704
50	1	0	2.863054	-3.113736	3.505084
51	1	0	2.780111	-1.364775	3.238823
52	6	0	-0.202307	-4.301838	0.169159
53	1	0	-1.172029	-4.805098	0.103892
54	1	0	0.479664	-4.951566	0.716160
55	1	0	0.192467	-4.193423	-0.846668
56	6	0	-5.538100	-0.034961	1.128447
57	1	0	-5.900906	-1.023514	0.840432
58	1	0	-6.379431	0.661844	1.100620

59	1	0	-5.168100	-0.086736	2.156489
60	6	0	-3.425213	2.903578	-1.738868
61	1	0	-2.610266	3.287617	-2.351455
62	1	0	-4.163433	3.697564	-1.585249
63	1	0	-3.929068	2.100900	-2.286089

EtOH solution

Data 62: Cartesian coordinates and energies of the optimized geometry for the most stable conformer of macrocycle **7** in EtOH solution.



Electronic Energy =	-2393.55438359 a.u.
Zero-point correction=	0.525503 (Hartree/Particle)
Thermal correction to Energy=	0.560116
Thermal correction to Enthalpy=	0.561061
Thermal correction to Gibbs Free Energy=	0.457418
Sum of electronic and zero-point Energies=	-2393.028880
Sum of electronic and thermal Energies=	-2392.994267
Sum of electronic and thermal Enthalpies=	-2392.993323
Sum of electronic and thermal Free Energies=	-2393.096966

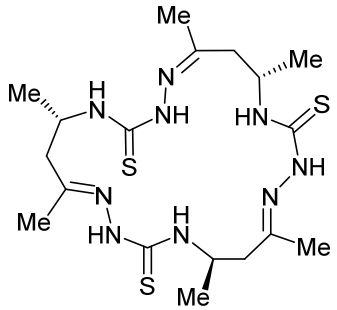
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	3.382033	-3.252194	-1.304299
2	16	0	0.905118	1.702013	2.667391
3	16	0	-4.147588	-1.835349	-2.073359
4	7	0	-1.635055	2.544489	-0.211196
5	7	0	-1.077231	2.118635	0.963960
6	1	0	-1.618549	1.725673	1.723237
7	7	0	0.962447	2.839199	0.209624
8	1	0	0.414390	3.141280	-0.589974
9	7	0	2.906332	0.631046	-0.927553
10	7	0	3.128856	-0.629199	-1.421905
11	1	0	3.584355	-0.783083	-2.313210
12	7	0	2.329349	-1.543976	0.527833
13	1	0	2.140986	-0.575035	0.774553
14	7	0	-1.243425	-2.091969	0.566294
15	7	0	-2.122092	-2.371064	-0.452269
16	1	0	-1.963871	-3.122151	-1.112968
17	7	0	-3.321110	-0.518259	0.149110
18	1	0	-2.680570	-0.537059	0.936544
19	6	0	0.264258	2.265148	1.191319

20	6	0	2.390013	3.173649	0.246063
21	1	0	2.859124	2.456643	0.918535
22	6	0	2.987317	3.025600	-1.155870
23	1	0	2.397478	3.605659	-1.877973
24	1	0	3.976688	3.499600	-1.160950
25	6	0	3.162730	1.627249	-1.695031
26	6	0	2.909725	-1.742784	-0.661810
27	6	0	2.095758	-2.569198	1.550471
28	1	0	2.368043	-3.516780	1.086694
29	6	0	0.607644	-2.605367	1.965072
30	1	0	0.514506	-3.355851	2.758915
31	1	0	0.316949	-1.639719	2.385721
32	6	0	-0.345060	-2.965303	0.854979
33	6	0	-3.164877	-1.529092	-0.717939
34	6	0	-4.430432	0.438012	0.167868
35	1	0	-4.828799	0.460122	-0.846134
36	6	0	-3.911502	1.844239	0.546935
37	1	0	-4.776584	2.513580	0.555577
38	1	0	-3.543421	1.827305	1.576620
39	6	0	-2.897278	2.418839	-0.417582
40	6	0	2.600113	4.592342	0.791521
41	1	0	2.146384	4.688972	1.779654
42	1	0	2.151955	5.338976	0.129272
43	1	0	3.667624	4.809427	0.881583
44	6	0	3.675139	1.502507	-3.107867
45	1	0	2.989912	0.913070	-3.726072
46	1	0	4.654115	1.011039	-3.133067
47	1	0	3.785959	2.483051	-3.568970
48	6	0	3.001663	-2.328601	2.763254
49	1	0	4.050959	-2.328971	2.460592
50	1	0	2.856981	-3.117601	3.505269
51	1	0	2.778206	-1.368688	3.237339
52	6	0	-0.215105	-4.303336	0.176205
53	1	0	-1.186878	-4.802273	0.108360
54	1	0	0.461907	-4.955164	0.726943
55	1	0	0.184274	-4.198750	-0.838219
56	6	0	-5.536740	-0.017739	1.126274
57	1	0	-5.902437	-1.005148	0.838085
58	1	0	-6.375899	0.681677	1.097597
59	1	0	-5.167840	-0.070516	2.154681
60	6	0	-3.413362	2.911683	-1.740799
61	1	0	-2.597480	3.295305	-2.352394
62	1	0	-4.151793	3.705810	-1.588832
63	1	0	-3.916223	2.108658	-2.288424

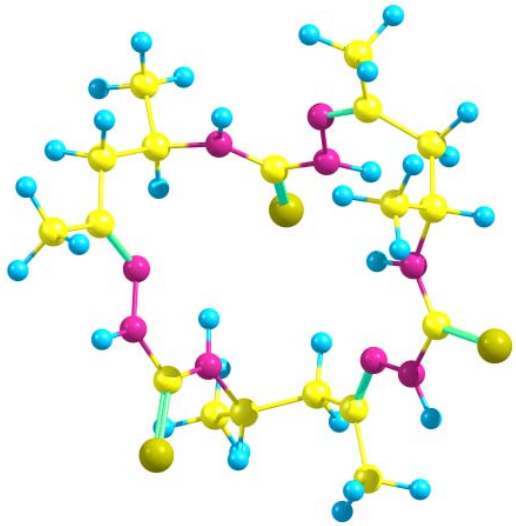
Other diastereomers of 21-membered cyclic tris-thiosemicarbazone 7

(1Z,5R,7E,12S*,14E,19R*)-diastereomer*



DMSO solution

Data 63: Cartesian coordinates and energies of the optimized geometry for the (1*Z*,5*R**,7*E*,12*S**,14*E*,19*R**)-diastereomer of macrocycle **7** in DMSO solution.



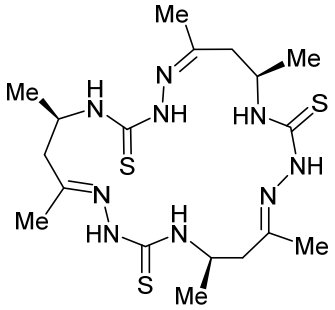
Electronic Energy =	-2393.54784461 a.u.
Zero-point correction=	0.526115 (Hartree/Particle)
Thermal correction to Energy=	0.560352
Thermal correction to Enthalpy=	0.561296
Thermal correction to Gibbs Free Energy=	0.458841
Sum of electronic and zero-point Energies=	-2393.021730
Sum of electronic and thermal Energies=	-2392.987492
Sum of electronic and thermal Enthalpies=	-2392.986548
Sum of electronic and thermal Free Energies=	-2393.089004

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.254306	-3.431171	-2.087750
2	16	0	1.163208	0.942922	2.666367
3	16	0	-5.118650	-1.659400	-0.739335
4	7	0	-1.094115	3.125895	0.321767
5	7	0	-0.687900	2.090139	1.140930
6	1	0	-1.298700	1.743723	1.873442
7	7	0	1.463993	2.631851	0.574641
8	1	0	0.987003	3.247812	-0.077649
9	7	0	2.814997	0.319705	-1.051529
10	7	0	2.655300	-0.836307	-1.770963
11	1	0	2.882981	-0.897321	-2.755902
12	7	0	2.022150	-1.912545	0.150975
13	1	0	2.108078	-0.983376	0.558242
14	7	0	-1.505329	-2.025907	0.753904
15	7	0	-2.690317	-2.261497	0.097778
16	1	0	-3.076376	-3.195442	0.026106
17	7	0	-3.084258	0.002282	-0.072901
18	1	0	-2.110334	0.089355	0.198570
19	6	0	0.661166	1.954791	1.394128
20	6	0	2.930412	2.632904	0.583563
21	1	0	3.235948	1.713952	1.081169
22	6	0	3.442895	2.629440	-0.861283
23	1	0	3.006368	3.472082	-1.412746
24	1	0	4.521429	2.830661	-0.848963
25	6	0	3.227020	1.368591	-1.664418
26	6	0	2.304403	-2.003968	-1.152255
27	6	0	1.790138	-3.027831	1.072775
28	1	0	1.718933	-3.923435	0.455814
29	6	0	0.469790	-2.808825	1.845919
30	1	0	0.462030	-3.507884	2.689511
31	1	0	0.453539	-1.796474	2.254377
32	6	0	-0.779402	-3.048808	1.041784
33	6	0	-3.551211	-1.247015	-0.208677
34	6	0	-3.858124	1.206281	-0.416035
35	6	0	-3.488342	2.402423	0.509157
36	1	0	-4.373639	3.039670	0.560478

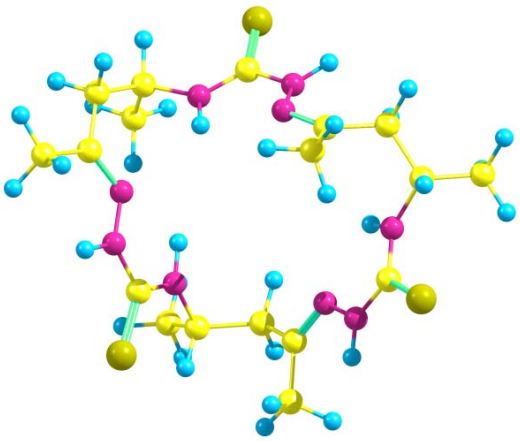
37	1	0	-3.333940	2.024504	1.523550
38	6	0	-2.338563	3.282923	0.051337
39	6	0	3.468236	3.837656	1.365381
40	1	0	3.077721	3.833084	2.384864
41	1	0	3.179240	4.778689	0.888195
42	1	0	4.559365	3.799713	1.415295
43	6	0	3.549882	1.424336	-3.135954
44	1	0	2.662253	1.212886	-3.742160
45	1	0	4.318140	0.690667	-3.402634
46	1	0	3.919141	2.410065	-3.416009
47	6	0	2.978712	-3.172081	2.031259
48	1	0	3.906196	-3.309752	1.471241
49	1	0	2.835983	-4.038629	2.681321
50	1	0	3.084139	-2.285002	2.662663
51	6	0	-1.131938	-4.467412	0.671160
52	1	0	-2.025254	-4.802691	1.211514
53	1	0	-0.322744	-5.150003	0.926757
54	1	0	-1.333676	-4.564587	-0.399908
55	6	0	-2.681628	4.500151	-0.763828
56	1	0	-1.777142	5.000412	-1.108498
57	1	0	-3.259747	5.199606	-0.149718
58	1	0	-3.304646	4.245299	-1.623649
59	6	0	-3.762118	1.511627	-1.914794
60	1	0	-4.424594	2.338436	-2.181069
61	1	0	-2.741539	1.770833	-2.207552
62	1	0	-4.074038	0.636050	-2.485364
63	1	0	-4.893555	0.953044	-0.187317

(1Z,5R,7E,12R*,14E,19R*)-diastereomer*



DMSO solution

Data 64: Cartesian coordinates and energies of the optimized geometry for the (1*Z*,5*R**,7*E*,12*R**,14*E*,19*R**)-diastereomer of macrocycle **7** in DMSO solution.



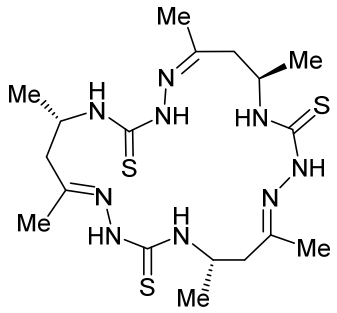
Electronic Energy =	-2393.54996199 a.u.
Zero-point correction=	0.525723 (Hartree/Particle)
Thermal correction to Energy=	0.560203
Thermal correction to Enthalpy=	0.561148
Thermal correction to Gibbs Free Energy=	0.458788
Sum of electronic and zero-point Energies=	-2393.024239
Sum of electronic and thermal Energies=	-2392.989759
Sum of electronic and thermal Enthalpies=	-2392.988814
Sum of electronic and thermal Free Energies=	-2393.091174

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.507845	4.173831	-1.312232
2	16	0	-1.942941	-4.264785	1.865234
3	16	0	5.191730	0.725224	-1.321093
4	7	0	0.301284	-2.486682	-0.806538
5	7	0	-0.080882	-3.119613	0.360445
6	1	0	0.472933	-3.872828	0.749445
7	7	0	-2.157778	-2.180294	0.150837
8	1	0	-1.677104	-1.548489	-0.479193
9	7	0	-2.893806	0.514599	-0.921444
10	7	0	-2.496472	1.726051	-1.432734
11	1	0	-2.817986	2.058852	-2.333516
12	7	0	-1.449929	2.204828	0.554693
13	1	0	-1.755108	1.264935	0.787807
14	7	0	2.128470	1.549851	1.003036
15	7	0	3.249509	1.657489	0.219152
16	1	0	3.575190	2.546293	-0.141092
17	7	0	3.423198	-0.625956	0.221920
18	1	0	2.656064	-0.553601	0.883377
19	6	0	-1.403449	-3.119146	0.725091
20	6	0	-3.612365	-2.030394	0.281816
21	6	0	-4.187446	-1.522434	-1.050717
22	1	0	-3.994340	-2.272082	-1.828282
23	1	0	-5.279320	-1.483193	-0.956842
24	6	0	-3.734418	-0.185591	-1.594860
25	6	0	-1.818737	2.629967	-0.661794
26	6	0	-0.971699	3.047631	1.657297
27	1	0	-0.781934	4.028756	1.222987
28	6	0	0.333842	2.482759	2.260445
29	1	0	0.519703	3.026358	3.193854
30	1	0	0.200086	1.429199	2.517762
31	6	0	1.550523	2.632285	1.386301
32	6	0	3.891627	0.541018	-0.237371
33	6	0	3.892589	-1.959267	-0.171627
34	1	0	4.334478	-1.850249	-1.161983
35	6	0	2.683756	-2.915094	-0.239125
36	1	0	3.039025	-3.877482	-0.624778
37	1	0	2.335862	-3.095879	0.781213
38	6	0	1.548848	-2.418625	-1.109058
39	6	0	-4.314871	0.232361	-2.921988
40	1	0	-3.532942	0.316491	-3.684663
41	1	0	-4.814796	1.203642	-2.846376
42	1	0	-5.045471	-0.495120	-3.272720
43	6	0	-2.063768	3.176250	2.726226
44	1	0	-2.981778	3.574002	2.288606
45	1	0	-1.737943	3.853494	3.519098
46	1	0	-2.288288	2.205720	3.178652
47	6	0	2.039154	4.016731	1.045798
48	1	0	3.082168	4.147066	1.353409
49	1	0	1.446087	4.778188	1.549960
50	1	0	1.981306	4.208213	-0.030880
51	6	0	4.961595	-2.487134	0.790009
52	1	0	5.813677	-1.805703	0.818679
53	1	0	5.315864	-3.467245	0.460614
54	1	0	4.561503	-2.587375	1.802745
55	6	0	1.872519	-1.828440	-2.453557
56	1	0	0.955726	-1.548088	-2.970852
57	1	0	2.411670	-2.561218	-3.063773
58	1	0	2.515837	-0.949453	-2.366567

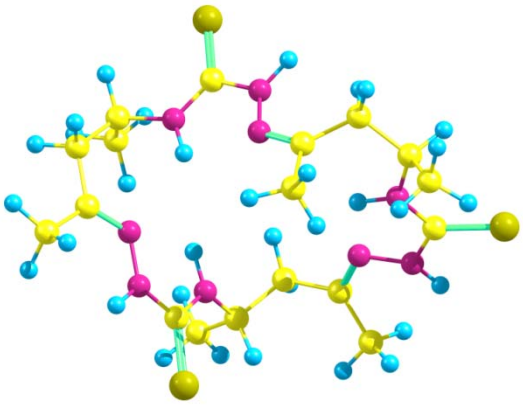
59	6	0	-4.021606	-1.201021	1.506096
60	1	0	-5.111926	-1.188821	1.590110
61	1	0	-3.618019	-1.654018	2.413073
62	1	0	-3.670357	-0.172743	1.436129
63	1	0	-4.006709	-3.038983	0.423987

(1Z,5R,7E,12R*,14E,19S*)-diastereomer*



DMSO solution

Data 65: Cartesian coordinates and energies of the optimized geometry for the (1*Z*,5*R**,7*E*,12*R**,14*E*,19*S**)-diastereomer of macrocycle **7** in DMSO solution.



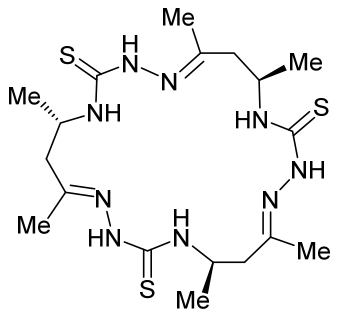
Electronic Energy =	-2393.53832030 a.u.
Zero-point correction=	0.525919 (Hartree/Particle)
Thermal correction to Energy=	0.560398
Thermal correction to Enthalpy=	0.561342
Thermal correction to Gibbs Free Energy=	0.458386
Sum of electronic and zero-point Energies=	-2393.012401
Sum of electronic and thermal Energies=	-2392.977922
Sum of electronic and thermal Enthalpies=	-2392.976978
Sum of electronic and thermal Free Energies=	-2393.079934

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.528037	3.858431	1.991642
2	16	0	1.698225	-3.944226	-2.380664
3	16	0	-5.898397	0.087106	-0.247571
4	7	0	-0.018676	-2.318475	0.736615
5	7	0	0.144667	-2.926399	-0.481025

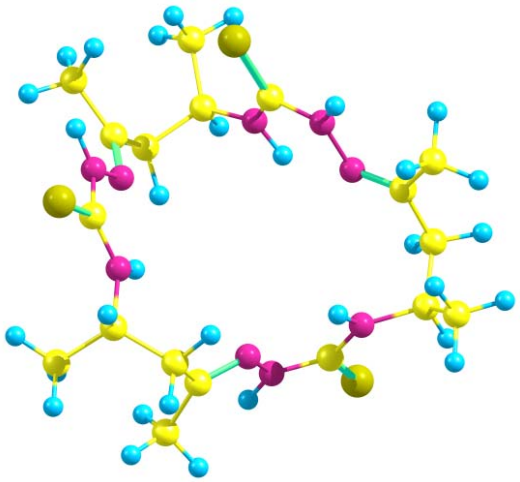
6	1	0	-0.495847	-3.631001	-0.825952
7	7	0	2.238189	-2.013117	-0.559699
8	1	0	1.873760	-1.437748	0.191643
9	7	0	3.087318	0.456346	0.776133
10	7	0	2.729479	1.543379	1.535240
11	1	0	3.151869	1.736847	2.435085
12	7	0	1.336480	2.217542	-0.157333
13	1	0	1.697051	1.375048	-0.593946
14	7	0	-2.275864	1.363962	-1.030354
15	7	0	-3.619033	1.354756	-0.713713
16	1	0	-4.253864	2.028258	-1.126252
17	7	0	-3.355280	-0.688685	0.280230
18	1	0	-2.374188	-0.457305	0.160590
19	6	0	1.384724	-2.898015	-1.075216
20	6	0	3.646115	-1.825440	-0.923863
21	6	0	4.451718	-1.488014	0.344028
22	1	0	4.427572	-2.352644	1.019152
23	1	0	5.504954	-1.375305	0.060786
24	6	0	4.068710	-0.275477	1.165043
25	6	0	1.861738	2.482119	1.048373
26	6	0	0.681508	3.189375	-1.043744
27	1	0	0.174914	3.905499	-0.396429
28	6	0	-0.347553	2.449019	-1.938662
29	1	0	-0.344656	2.926605	-2.923645
30	1	0	-0.032961	1.414595	-2.090498
31	6	0	-1.771737	2.471478	-1.444943
32	6	0	-4.203691	0.221214	-0.213068
33	6	0	-3.701214	-1.999899	0.850081
34	6	0	-2.440343	-2.902427	0.797905
35	1	0	-2.666366	-3.814659	1.359916
36	1	0	-2.305985	-3.202508	-0.242198
37	6	0	-1.154000	-2.307100	1.340688
38	6	0	4.873614	-0.020713	2.413170
39	1	0	4.251657	-0.117114	3.309988
40	1	0	5.298565	0.988308	2.407630
41	1	0	5.693588	-0.732346	2.498843
42	6	0	1.728649	3.932858	-1.884064
43	1	0	2.470506	4.408477	-1.239320
44	1	0	1.246945	4.708130	-2.485190
45	1	0	2.244199	3.245310	-2.561200
46	6	0	-2.534222	3.767009	-1.542678
47	1	0	-3.218724	3.750329	-2.399367
48	1	0	-1.857150	4.608187	-1.688870
49	1	0	-3.127853	3.951552	-0.643350
50	6	0	-1.130338	-1.675871	2.709499
51	1	0	-0.102922	-1.443976	2.987091
52	1	0	-1.555594	-2.354503	3.454340
53	1	0	-1.713601	-0.751998	2.740186
54	6	0	3.834094	-0.826575	-2.073395
55	1	0	4.890243	-0.785252	-2.353790
56	1	0	3.264880	-1.151374	-2.946260
57	1	0	3.513003	0.176706	-1.795429
58	1	0	4.002460	-2.797707	-1.270420
59	6	0	-4.365832	-1.901421	2.230180
60	1	0	-4.584502	-2.907342	2.597965
61	1	0	-3.742834	-1.393205	2.964214
62	1	0	-5.306870	-1.358550	2.144745
63	1	0	-4.430685	-2.458153	0.176767

(1E,5R,7E,12S*,14E,19S*)-diastereomer*



DMSO solution

Data 66: Cartesian coordinates and energies of the optimized geometry for the (1*E*,5*R**,7*E*,12*R**,14*E*,19*S**)-diastereomer of macrocycle **7** in DMSO solution.



Electronic Energy =	-2393.54061102 a.u.
Zero-point correction=	0.526851 (Hartree/Particle)
Thermal correction to Energy=	0.560893
Thermal correction to Enthalpy=	0.561837
Thermal correction to Gibbs Free Energy=	0.460727
Sum of electronic and zero-point Energies=	-2393.013760
Sum of electronic and thermal Energies=	-2392.979718
Sum of electronic and thermal Enthalpies=	-2392.978774
Sum of electronic and thermal Free Energies=	-2393.079884

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.691734	-2.716796	-1.151031
2	6	0	-0.433965	-2.997471	-0.416410
3	16	0	-1.828006	-3.463578	-1.274188
4	7	0	-0.275628	-2.878850	0.907775
5	6	0	-2.004295	-1.773754	2.362880
6	6	0	-2.977113	-1.262810	1.333930
7	6	0	-4.310507	-1.939075	1.146782
8	7	0	-2.612034	-0.204810	0.697530
9	7	0	-3.458313	0.293500	-0.260861
10	6	0	-3.221289	1.503828	-0.846081
11	7	0	-2.151163	2.172956	-0.395456
12	16	0	-4.287679	2.044395	-2.061846
13	6	0	-1.835929	3.571252	-0.705322
14	6	0	-2.503756	4.511690	0.306653
15	6	0	0.585587	3.456493	0.297038
16	7	0	1.371750	2.445342	0.160909
17	6	0	-0.309420	3.757800	-0.881965
18	7	0	2.227531	2.141844	1.188482
19	6	0	3.269322	1.274455	1.002116
20	7	0	3.380771	0.754515	-0.225085
21	16	0	4.314951	0.960750	2.309469
22	6	0	2.955876	-2.414168	-2.737389
23	6	0	2.893335	-2.114580	-1.261057
24	6	0	4.113982	-1.618184	-0.529263
25	1	0	-4.242521	-0.238451	-0.618261
26	1	0	-1.643034	1.715364	0.355257
27	1	0	2.156628	2.575347	2.100910
28	1	0	2.665756	1.046266	-0.883721
29	6	0	-1.208359	-3.069901	2.033434
30	6	0	-2.035471	-4.356022	1.968523

31	7	0	1.837760	-2.281240	-0.543926
32	1	0	0.650026	-2.549416	1.165177
33	6	0	4.459701	-0.113661	-0.703256
34	6	0	4.842099	0.302248	-2.125664
35	1	0	0.600712	-2.791183	-2.157104
36	6	0	0.589307	4.359594	1.504321
37	1	0	-1.278518	-0.982626	2.561698
38	1	0	-2.545124	-1.967568	3.295921
39	1	0	-4.365576	-2.443350	0.177066
40	1	0	-5.122757	-1.206159	1.196585
41	1	0	-4.482412	-2.684677	1.920735
42	1	0	-2.275307	3.765414	-1.684125
43	1	0	-2.256625	5.552931	0.084259
44	1	0	-3.588445	4.400465	0.246133
45	1	0	-2.200101	4.293428	1.332266
46	1	0	-0.151753	4.803099	-1.170411
47	1	0	0.013822	3.132329	-1.716061
48	1	0	3.975601	-2.346247	-3.110696
49	1	0	2.589881	-3.426256	-2.941137
50	1	0	2.338912	-1.718584	-3.317464
51	1	0	4.987957	-2.192350	-0.854529
52	1	0	3.972942	-1.801448	0.537168
53	1	0	-0.534895	-3.187519	2.886156
54	1	0	-2.771021	-4.349854	1.168822
55	1	0	-1.376294	-5.213958	1.816904
56	1	0	-2.548198	-4.488669	2.924797
57	1	0	5.310190	0.070647	-0.045408
58	1	0	4.000629	0.228666	-2.819260
59	1	0	5.194118	1.336116	-2.131234
60	1	0	5.646749	-0.333762	-2.500501
61	1	0	0.156546	3.865590	2.381478
62	1	0	0.019846	5.267217	1.318215
63	1	0	1.612535	4.652512	1.761438

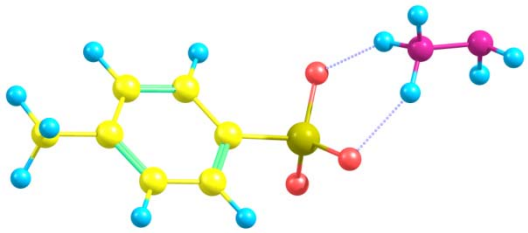
Table 19 Relative electronic (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) of macrocycle **7** and some its diastereomers in DMSO solution

Compound	ΔE	ΔG
Macrocycle **7** (1*Z*,5*R**,7*E*,12*S**,14*E*,19*S**)-configuration	0.00	0.00
(1*Z*,5*R**,7*E*,12*S**,14*E*,19*R**)-diastereomer of **7**	4.78	5.72
(1*Z*,5*R**,7*E*,12*R**,14*E*,19*R**)-diastereomer of **7**	3.45	4.36
(1*Z*,5*R**,7*E*,12*R**,14*E*,19*S**)-diastereomer of **7**	10.76	11.41
(1*E*,5*R**,7*E*,12*S**,14*E*,19*S**)-diastereomer of **7**	9.32	11.45

Hydrazinium tosylate

MeCN solution

Data 67: Cartesian coordinates and energies of the optimized geometry for the 1st conformer of hydrazonium tosylate in MeCN solution.

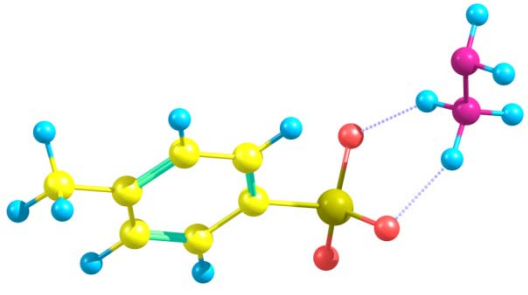


Electronic Energy =	-1007.49312906 a.u.
Zero-point correction=	0.199156 (Hartree/Particle)
Thermal correction to Energy=	0.213992
Thermal correction to Enthalpy=	0.214936
Thermal correction to Gibbs Free Energy=	0.153117
Sum of electronic and zero-point Energies=	-1007.293973
Sum of electronic and thermal Energies=	-1007.279137
Sum of electronic and thermal Enthalpies=	-1007.278193
Sum of electronic and thermal Free Energies=	-1007.340012

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.000221	0.775909	-0.258047
2	8	0	-1.609751	0.660423	1.107633
3	8	0	-1.636750	-0.199353	-1.211499
4	8	0	-0.987918	2.164320	-0.776092
5	6	0	0.717215	0.257764	-0.089994
6	6	0	1.441684	0.644699	1.038710
7	6	0	2.783686	0.295536	1.142387
8	6	0	3.424856	-0.435953	0.131749
9	6	0	2.676906	-0.809865	-0.989173
10	6	0	1.329991	-0.466635	-1.108031
11	6	0	4.880191	-0.810751	0.262880
12	7	0	-3.454147	-1.344357	0.481697
13	7	0	-4.856215	-1.077567	0.261341
14	1	0	-3.337745	-2.323258	0.745118
15	1	0	-2.987048	-0.727921	1.172215
16	1	0	-2.909514	-1.160313	-0.391152
17	1	0	-5.314095	-1.116859	1.169244
18	1	0	-4.919921	-0.115890	-0.065004
19	1	0	0.959451	1.203224	1.831577
20	1	0	3.341974	0.593886	2.023709
21	1	0	3.149429	-1.379102	-1.782460
22	1	0	0.760789	-0.767832	-1.978270
23	1	0	5.235552	-1.341943	-0.621559
24	1	0	5.503458	0.077690	0.399873
25	1	0	5.041913	-1.454646	1.132691

Data 68: Cartesian coordinates and energies of the optimized geometry for the 2nd conformer of hydrazonium tosylate in MeCN solution.



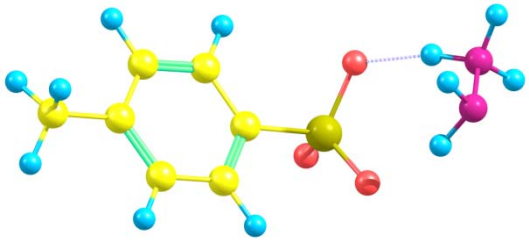
Electronic Energy =	-1007.49383351 a.u.
Zero-point correction=	0.199042 (Hartree/Particle)

Thermal correction to Energy=	0.213814
Thermal correction to Enthalpy=	0.214758
Thermal correction to Gibbs Free Energy=	0.153361
Sum of electronic and zero-point Energies=	-1007.294791
Sum of electronic and thermal Energies=	-1007.280020
Sum of electronic and thermal Enthalpies=	-1007.279075
Sum of electronic and thermal Free Energies=	-1007.340472

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.822599	0.972347	0.047892
2	6	0	-0.648265	-0.412857	0.007367
3	6	0	-1.749054	-1.260946	-0.043883
4	6	0	-3.034254	-0.716485	-0.052634
5	6	0	-3.236055	0.665782	-0.009561
6	6	0	-2.108184	1.499775	0.038906
7	6	0	-4.624854	1.254329	-0.001839
8	16	0	1.018255	-1.097648	0.014671
9	8	0	0.878529	-2.569574	0.015704
10	8	0	1.698152	-0.564163	-1.218680
11	8	0	1.690710	-0.556552	1.245968
12	1	0	0.034878	1.633604	0.085890
13	1	0	-1.602873	-2.332803	-0.076553
14	1	0	-3.889921	-1.381825	-0.094157
15	1	0	-2.239696	2.576364	0.069595
16	1	0	-4.854955	1.695563	0.973294
17	1	0	-5.380041	0.495233	-0.212205
18	1	0	-4.720752	2.049543	-0.745966
19	7	0	3.639896	0.943200	-0.004915
20	7	0	3.587394	2.381778	-0.048510
21	1	0	3.111619	0.582511	0.814145
22	1	0	4.583465	0.545131	-0.006875
23	1	0	3.083437	0.531892	-0.785385
24	1	0	4.117360	2.727778	0.747378
25	1	0	4.074831	2.675176	-0.891356

Data 69: Cartesian coordinates and energies of the optimized geometry for the 3rd conformer of hydrazonium tosylate in MeCN solution.



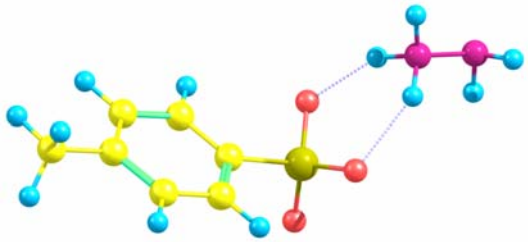
Electronic Energy =	-1007.49501299 a.u.
Zero-point correction=	0.199071 (Hartree/Particle)
Thermal correction to Energy=	0.212846
Thermal correction to Enthalpy=	0.213791
Thermal correction to Gibbs Free Energy=	0.155592
Sum of electronic and zero-point Energies=	-1007.295942
Sum of electronic and thermal Energies=	-1007.282167
Sum of electronic and thermal Enthalpies=	-1007.281222
Sum of electronic and thermal Free Energies=	-1007.339421

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.086579	0.914941	-0.175317
2	8	0	1.702543	0.197453	-1.331016
3	8	0	1.743343	0.511861	1.123847
4	8	0	1.036762	2.386757	-0.343865
5	6	0	-0.615388	0.335318	-0.058153
6	6	0	-1.262516	-0.135991	-1.198211
7	6	0	-2.598290	-0.523991	-1.115944
8	6	0	-3.302984	-0.449270	0.091337
9	6	0	-2.630092	0.032554	1.222127
10	6	0	-1.296310	0.425809	1.155450
11	6	0	-4.739048	-0.902201	0.179875
12	1	0	-0.727112	-0.205031	-2.136695
13	1	0	-3.098332	-0.890999	-2.006023
14	1	0	-3.155610	0.101686	2.168733
15	1	0	-0.789887	0.790988	2.040373
16	1	0	-5.287108	-0.340727	0.939379
17	1	0	-5.252869	-0.783681	-0.776241
18	1	0	-4.794128	-1.961619	0.452774
19	7	0	3.846044	-1.129886	0.739012
20	7	0	3.437248	-2.007849	-0.345510
21	1	0	4.157055	-1.688593	1.534709
22	1	0	3.069619	-0.466838	1.030753
23	1	0	4.649801	-0.583266	0.425866
24	1	0	2.854314	-1.414455	-0.946368
25	1	0	2.812535	-2.694313	0.072688

EtOH solution

Data 70: Cartesian coordinates and energies of the optimized geometry for the 1st conformer of hydrazonium tosylate in EtOH solution.



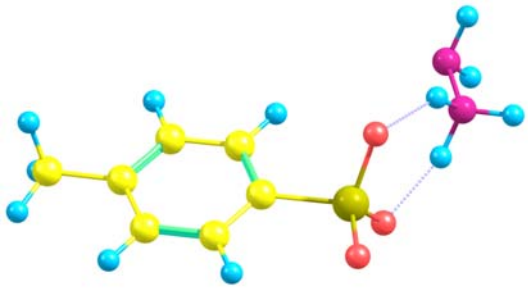
Electronic Energy =	-1007.49235355 a.u.
Zero-point correction=	0.199088 (Hartree/Particle)
Thermal correction to Energy=	0.213953
Thermal correction to Enthalpy=	0.214897
Thermal correction to Gibbs Free Energy=	0.153086
Sum of electronic and zero-point Energies=	-1007.293266
Sum of electronic and thermal Energies=	-1007.278401
Sum of electronic and thermal Enthalpies=	-1007.277457
Sum of electronic and thermal Free Energies=	-1007.339267

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.000755	-0.770209	0.266494
2	8	0	-1.610627	-0.662741	-1.100402

3	8	0	-1.635170	0.213900	1.212154
4	8	0	-0.991265	-2.154702	0.793533
5	6	0	0.717444	-0.256255	0.093269
6	6	0	1.442981	-0.661163	-1.028436
7	6	0	2.785192	-0.314266	-1.136119
8	6	0	3.425592	0.432717	-0.136375
9	6	0	2.676669	0.824285	0.977769
10	6	0	1.329450	0.483491	1.100582
11	6	0	4.881255	0.804773	-0.271833
12	7	0	-3.454367	1.336764	-0.491831
13	7	0	-4.857081	1.068163	-0.277563
14	1	0	-3.339348	2.312204	-0.768227
15	1	0	-2.979076	0.710951	-1.169336
16	1	0	-2.914836	1.166860	0.386857
17	1	0	-5.308273	1.090992	-1.189348
18	1	0	-4.919645	0.111699	0.064024
19	1	0	0.961416	-1.232082	-1.812841
20	1	0	3.344376	-0.626849	-2.011934
21	1	0	3.148697	1.405429	1.762692
22	1	0	0.759387	0.797921	1.965541
23	1	0	5.236177	1.348853	0.604929
24	1	0	5.504209	-0.085913	-0.394990
25	1	0	5.044134	1.435648	-1.150939

Data 71: Cartesian coordinates and energies of the optimized geometry for the 2nd conformer of hydrazonium tosylate in EtOH solution.



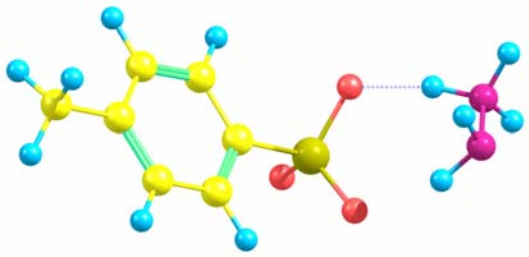
Electronic Energy =	-1007.49297865 a.u.
Zero-point correction=	0.199020 (Hartree/Particle)
Thermal correction to Energy=	0.213785
Thermal correction to Enthalpy=	0.214729
Thermal correction to Gibbs Free Energy=	0.153355
Sum of electronic and zero-point Energies=	-1007.293959
Sum of electronic and thermal Energies=	-1007.279194
Sum of electronic and thermal Enthalpies=	-1007.278250
Sum of electronic and thermal Free Energies=	-1007.339624

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.823333	-0.972808	0.046781
2	6	0	0.648074	0.412260	0.007134
3	6	0	1.748232	1.261148	-0.043033
4	6	0	3.033799	0.717589	-0.051627
5	6	0	3.236541	-0.664534	-0.009445
6	6	0	2.109263	-1.499344	0.037977
7	6	0	4.625774	-1.252120	-0.001571
8	16	0	-1.018761	1.096188	0.014378
9	8	0	-0.880182	2.567835	0.014855
10	8	0	-1.698628	0.561046	-1.218573
11	8	0	-1.690940	0.554306	1.245755
12	1	0	-0.033780	-1.634591	0.083923
13	1	0	1.601098	2.332893	-0.075028
14	1	0	3.889041	1.383540	-0.092344
15	1	0	2.241540	-2.575877	0.067975

16	1	0	4.855869	-1.693935	0.973308
17	1	0	5.380520	-0.492320	-0.211029
18	1	0	4.722656	-2.046608	-0.746364
19	7	0	-3.638098	-0.940895	-0.004165
20	7	0	-3.588461	-2.379419	-0.047933
21	1	0	-3.107925	-0.580574	0.814366
22	1	0	-4.580734	-0.540635	-0.005776
23	1	0	-3.080190	-0.530001	-0.784524
24	1	0	-4.118775	-2.725090	0.747815
25	1	0	-4.075339	-2.672245	-0.891258

Data 72: Cartesian coordinates and energies of the optimized geometry for the 3rd conformer of hydrazonium tosylate in EtOH solution.



Electronic Energy =	-1007.49428651 a.u.
Zero-point correction=	0.199444 (Hartree/Particle)
Thermal correction to Energy=	0.213913
Thermal correction to Enthalpy=	0.214858
Thermal correction to Gibbs Free Energy=	0.155458
Sum of electronic and zero-point Energies=	-1007.294843
Sum of electronic and thermal Energies=	-1007.280373
Sum of electronic and thermal Enthalpies=	-1007.279429
Sum of electronic and thermal Free Energies=	-1007.338829

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.082831	0.894636	-0.232139
2	8	0	1.699168	0.101775	-1.337396
3	8	0	1.736630	0.572537	1.091504
4	8	0	1.037442	2.352340	-0.492387
5	6	0	-0.620781	0.327941	-0.080551
6	6	0	-1.248663	-0.272830	-1.168990
7	6	0	-2.585041	-0.653921	-1.063692
8	6	0	-3.309065	-0.443802	0.115579
9	6	0	-2.655175	0.167108	1.194147
10	6	0	-1.321395	0.554626	1.103887
11	6	0	-4.745869	-0.887943	0.232776
12	1	0	-0.697821	-0.444822	-2.084979
13	1	0	-3.070178	-1.121856	-1.913814
14	1	0	-3.196401	0.343211	2.117796
15	1	0	-0.830479	1.021782	1.948815
16	1	0	-5.304820	-0.248833	0.919497
17	1	0	-5.246561	-0.874080	-0.737489
18	1	0	-4.804259	-1.911903	0.617416
19	7	0	3.858238	-1.056082	0.814942
20	7	0	3.472901	-2.005439	-0.216892
21	1	0	4.173339	-1.559352	1.645011
22	1	0	3.067810	-0.389549	1.060864
23	1	0	4.654423	-0.515296	0.473828
24	1	0	2.877429	-1.461745	-0.851878
25	1	0	2.864261	-2.681375	0.240093

Water (H_2O)

EtOH solution

Data 73: Cartesian coordinates and energies of the optimized geometry for water in EtOH solution.

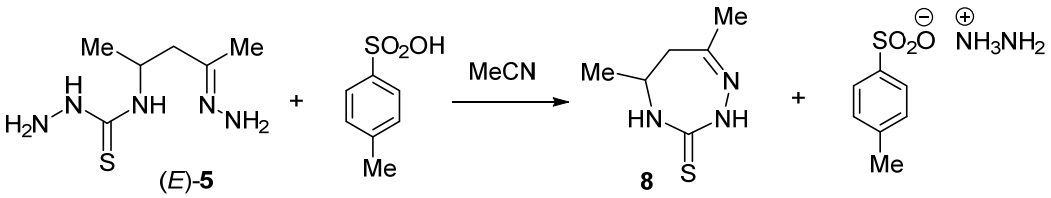
Electronic Energy =	-76.4661333306 a.u.
Zero-point correction=	0.021197 (Hartree/Particle)
Thermal correction to Energy=	0.024032
Thermal correction to Enthalpy=	0.024977
Thermal correction to Gibbs Free Energy=	0.003547
Sum of electronic and zero-point Energies=	-76.444937
Sum of electronic and thermal Energies=	-76.442101
Sum of electronic and thermal Enthalpies=	-76.441157
Sum of electronic and thermal Free Energies=	-76.462586

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.117942
2	1	0	-0.000000	0.762250	-0.471769
3	1	0	-0.000000	-0.762250	-0.471769

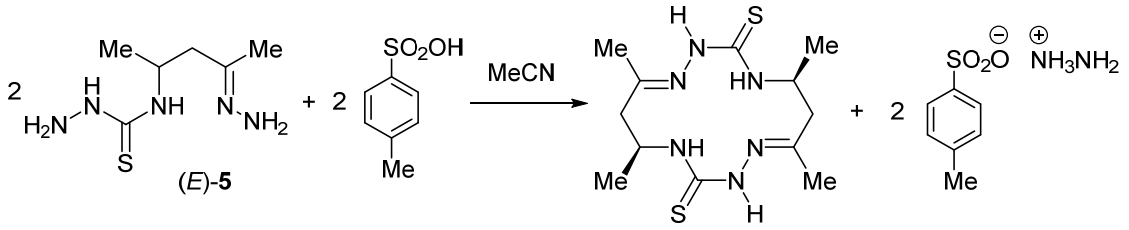
Thermodynamic parameters for the TsOH-promoted transformation of hydrazone 5 to azaheterocycles 8, 6, and 7 in MeCN solution

Formation of triazepine **8**



	Starting compounds: (*E*)-**5** + TsOH	Products: **8** + $TsO^-N_2H_5^+$
Electronic energy (E), a.u.	(-909.776131750) + (-1805.31972289) = -1805.31972289	(-797.841337316) + (-1007.49501299) = -1805.336350306
ΔE, a.u.	0.00	-0.016627416
ΔE, kcal/mol	0.00	-10.43
Free Energy (G), a.u.	(-909.590207) + (-895.443683) = -1805.03389	(-797.702791) + (-1007.340472) = -1805.043263
ΔG, a.u.	0.00	-0.009373
ΔG, kcal/mol	0.00	-5.88

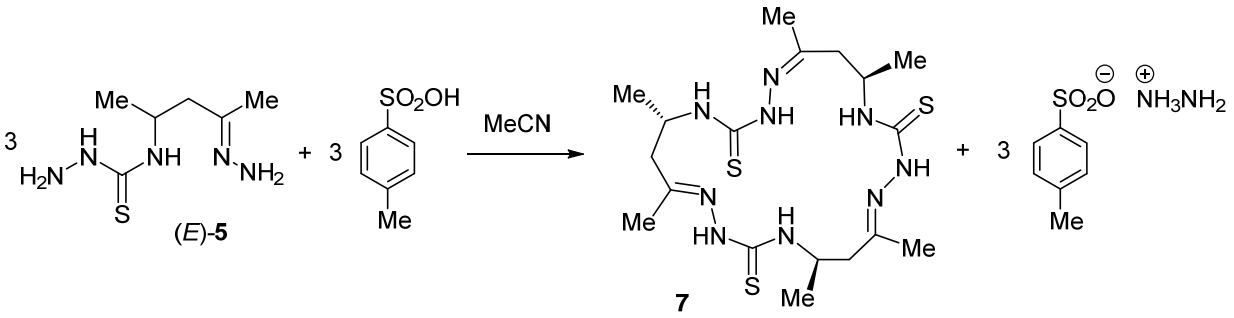
Formation of 14-membered macrocycle *cis*-**6**



cis-**6**

	Starting compounds: 2 (*E*)-**5** + 2 TsOH	Products: *cis*-**6** + 2 $TsO^-N_2H_5^+$
Electronic energy (E), a.u.	2×(-909.776131750) + 2×(-895.543591140) = -3610.63944578	(-1595.70006762) + 2×(-1007.49501299) = -3610.6900936
ΔE, a.u.	0.00	-0.05064782
ΔE, kcal/mol	0.00	-31.78
Free Energy (G), a.u.	2×(-909.590207) + 2×(-895.443683) = -3610.06778	(-1595.401585) + 2×(-1007.340472) = -3610.082529
ΔG, a.u.	0.00	-0.014749
ΔG, kcal/mol	0.00	-9.26

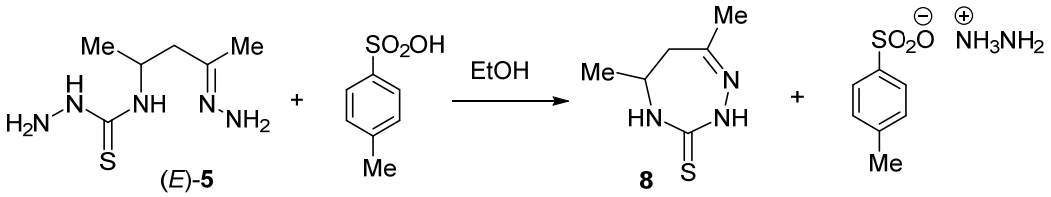
Formation of 21-membered macrocycle **7**



	Starting compounds: 3 (*E*)-**5** + 3 TsOH	Products: **7** + 3 $TsO^-N_2H_5^+$
Electronic energy (E), a.u.	3×(-909.776131750) + 3×(-895.543591140) = -5415.95916867	(-2393.55507849) + 3×(-1007.49501299) = -5416.04011746
ΔE, a.u.	0.00	-0.08094879
ΔE, kcal/mol	0.00	-50.80
Free Energy (G), a.u.	3 ×(-909.590207) + 3 ×(-895.443683) = -5415.10167	(-2393.097695) + 3×(-1007.340472) = -5415.119111
ΔG, a.u.	0.00	-0.017441
ΔG, kcal/mol	0.00	-10.94

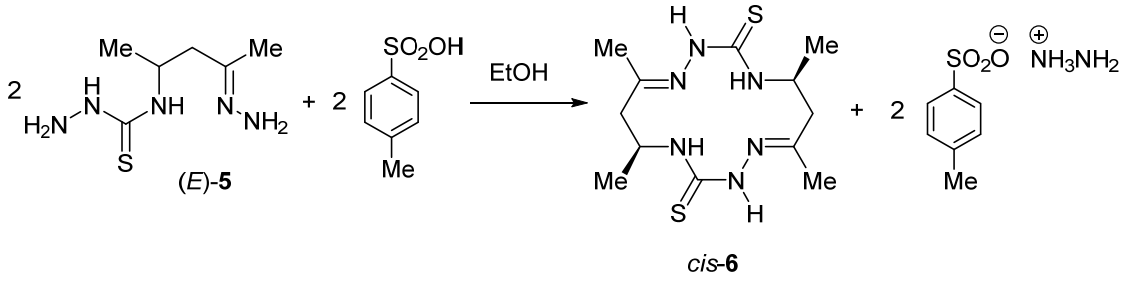
Thermodynamic parameters for the TsOH-promoted transformation of hydrazone 5 to azaheterocycles 8, 6, and 7 in EtOH solution

Formation of triazepine **8**



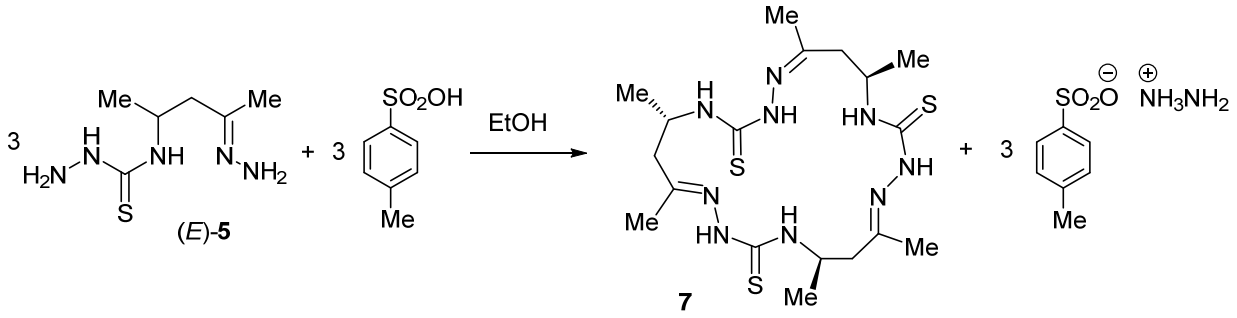
	Starting compounds: (*E*)-**5** + TsOH	Products: **8** + $TsO^-N_2H_5^+$
Electronic energy (E), a.u.	(-909.775682032) + (-895.543331919) = -1805.319013951	(-797.841020039) + (-1007.49428651) = -1805.335306549
ΔE, a.u.	0.00	-0.016292598
ΔE, kcal/mol	0.00	-10.22
Free Energy (G), a.u.	(-909.589756) + (-895.443641) = -1805.033397	(-797.702433) + (-1007.339624) = -1805.042057
ΔG, a.u.	0.00	-0.00866
ΔG, kcal/mol	0.00	-5.43

Formation of 14-membered macrocycle *cis*-**6**



	Starting compounds: 2 (*E*)-**5** + 2 TsOH	Products: *cis*-**6** + 2 $TsO^-N_2H_5^+$
Electronic energy (E), a.u.	2×(-909.775682032) + 2×(-895.543331919) = -3610.638027902	(-1595.69956812) + 2×(-1007.49428651) = -3610.68814114
ΔE, a.u.	0.00	-0.050113238
ΔE, kcal/mol	0.00	-31.45
Free Energy (G), a.u.	2×(-909.589756) + 2×(-895.443641) = -3610.066794	(-1595.401181) + 2×(-1007.339624) = -3610.080429
ΔG, a.u.	0.00	-0.013635
ΔG, kcal/mol	0.00	-8.56

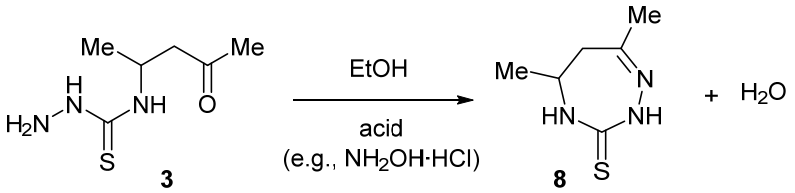
Formation of 21-membered macrocycle **7**



	Starting compounds: 3 (*E*)-**5** + 3 TsOH	Products: **7** + 3 $TsO^-N_2H_5^+$
Electronic energy (E), a.u.	3×(-909.775682032) + 3×(-895.543331919) = -5415.957041853	(-2393.55438359) + 3×(-1007.49428651) = -5416.03724312
ΔE, a.u.	0.00	-0.080201267
ΔE, kcal/mol	0.00	-50.33
Free Energy (G), a.u.	3 ×(-909.589756) + 3 ×(-895.443641) = -5415.100191	(-2393.096966) + 3×(-1007.339624) = -5415.115838
ΔG, a.u.	0.00	-0.015647
ΔG, kcal/mol	0.00	-9.82

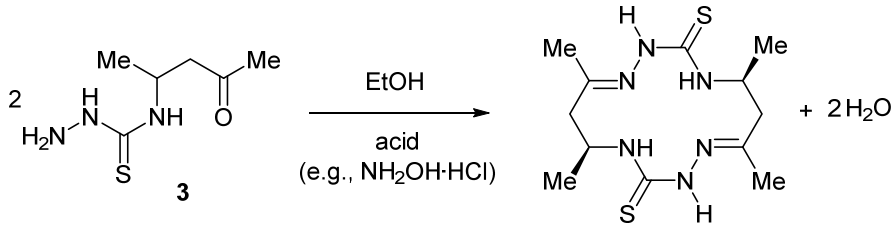
Thermodynamic parameters for the acid-catalized transformation of thiosemicarbazone 3 to azaheterocycles 8, 6, and 7 in EtOH solution

Formation of triazepine **8**



	Starting compound: **3**	Products: **8** + H_2O
Electronic energy (E), a.u.	-874.313414457	(-797.841020039) + (-76.4661333306) = -874.3071533696
ΔE, a.u.	0.00	0.0062610874
ΔE, kcal/mol	0.00	6.23
Free Energy (G), a.u.	-874.159213	(-797.702433) + (-76.462586) = -874.165019
ΔG, a.u.	0.00	0.005806
ΔG, kcal/mol	0.00	-3.64

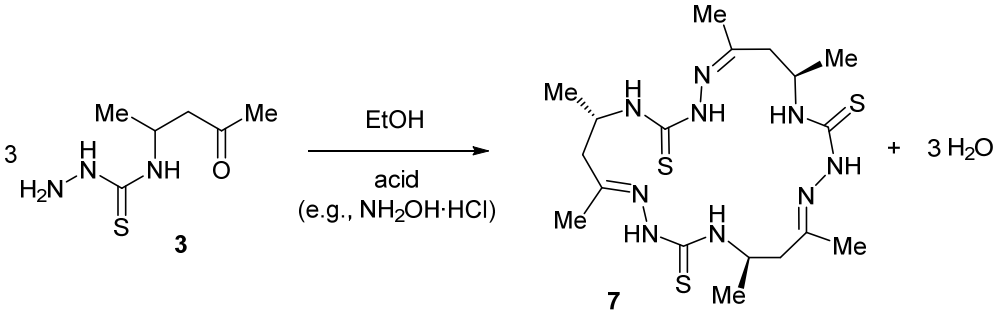
Formation of 14-membered macrocycle *cis*-**6**



cis-**6**

	Starting compound: 2 (**3**)	Products: *cis*-**6** + 2 H_2O
Electronic energy (E), a.u.	2×(-874.317088567) = -1748.634177134	(-1595.69956812) + 2×(-76.4661333306) = -1748.6318347812
ΔE, a.u.	0.00	0.0023423528
ΔE, kcal/mol	0.00	1.47
Free Energy (G), a.u.	2 × (-874.159213) = -1748.318426	(-1595.401181) + 2×(-76.462586) = -1748.326353
ΔG, a.u.	0.00	0.007927
ΔG, kcal/mol	0.00	-4.97

Formation of 14-membered macrocycle **7**



	Starting compound: 3 (**3**)	Products: **7** + 3H_2O
Electronic energy (E), a.u.	3×(-874.317088567) = -2622.951265701	(-2393.55438359) + 3×(-76.4661333306) = -2622.9527835818
ΔE, a.u.	0.00	0.0015178808
ΔE, kcal/mol	0.00	-0.95
Free Energy (G), a.u.	3×(-874.159213) = -2622.477639	(-2393.096966) + 3×(-76.462586) = -2622.484724
ΔG, a.u.	0.00	0.007085
ΔG, kcal/mol	0.00	-4.45

References and notes

1. X-ray diffraction experiments were performed at the Center for Shared Use of Physical Methods of Investigation at Frumkin Institute of Physical Chemistry and Electrochemistry, RAS.
2. No Title. *SAINT, V8.40B,* 2020, Bruker AXS Inc., Madison, WI, USA.
3. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, Comparison of Silver and Molybdenum Microfocus X-Ray Sources for Single-Crystal Structure Determination. *J. Appl. Crystallogr.,* 2015, **48**, 3–10. https://doi.org/10.1107/S1600576714022985.
4. G. M. Sheldrick. SHELXT - Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A Found. Crystallogr.* 2015, **71**, 3–8. https://doi.org/10.1107/S2053273314026370.
5. G. M. Sheldrick. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71**, 3–8. https://doi.org/10.1107/S2053229614024218.
6. *Gaussian 16, Revision A.03*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.