SUPPLEMENTARY INFORMATION

for

Competing Hydrogen Bonding and Acyclic π–Stacking Between Hydrogen-Bridged Quasi-Rings in *Z*- and *E*-Methyl Pyruvate Semicarbazone: A Quantitative Interaction Energy Analysis

by

Vidak Raičević[a], Niko S. Radulović[b], Nemanja Banić[c], Vukadin M. Leovac[c], Marko V. Rodić[c*]

[a] University of Novi Sad, Faculty of Medicine, Hajduk Veljkova 3, 21000 Novi Sad, Serbia
[b] University of Niš, Faculty of Sciences and Mathematics, Višegradska 33, 18106 Niš, Serbia
[c] University of Novi Sad, Faculty of Sciences, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

Table of Contents

Table S1. Selected crystallographic and refinement details of **1-*E*** and **1-*Z***.

	1-*E*	**1-*Z***
Crystal data		
Chemical formula	$C_5H_9N_3O_3$	$C_5H_9N_3O_3$
M_r	159.15	159.15
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Fdd*2
Temperature, K	295	295
a / Å	4.1764(4)	36.4109(10)
b / Å	7.4068(10)	23.9057(9)
c / Å	12.2230(13)	7.0463(2)
α / °	90.144(10)	90
β / °	97.506(9)	90
γ / °	91.316(10)	90
V / Å^3	374.76(7)	6133.3(3)
Z	2	32
Radiation type	Cu $K\alpha$	Mo $K\alpha$
μ / mm^{-1}	1.01	0.11
Crystal size, mm	0.63 × 0.32 × 0.21	0.29 × 0.61 × 0.77
Data collection		
Diffractometer	Gemini S	Gemini S
Absorption correction	Multi-scan	Multi-scan
T_{min}	0.894	0.955
T_{max}	1.000	1.000
No. of measured reflections	2123	12757
No. of independent reflections	1393	3654
No. of observed reflections [$I > 2\sigma(I)$]	1238	2871
R_{int}	0.018	0.019
$(\sin\theta/\lambda)_{max}$ / Å^{-1}	0.614	0.688
Refinement		
$R[F^2 > 2\sigma(F^2)]$	0.038	0.038
$wR(F^2)$	0.116	0.093
S	1.09	1.04
No. of reflections	1393	3654
No. of parameters	114	223
No. of restraints	1	1
H-atom treatment	Mixed	Mixed
$\Delta\rho_{max}$ / e Å^{-3}	0.17	0.11
$\Delta\rho_{min}$ / e Å^{-3}	−0.18	−0.17
Absolute structure parameter	–	Meaningless

Table S2. Pairwise intermolecular interaction energies and atom–atom contacts within the first coordination spheres in the crystal structure of **1-*E***.

No.	Symmetry operation	E / kJ mol^{-1}	100 E / ΣE	Interaction
Monomeric building unit				
1	−*x*, 1−*y*, 2−*z*	−70.4	28	N2–H2···O3′ O3···H2′–N2′
2	−1+*x*, *y*, *z*	−27.7	11	C5–H5B···O2′ SBHB/SBHB stacking non-specific
3	1+*x*, *y*, *z*	−27.7	11	O2···H5B′–C5′ SBHB/SBHB stacking non-specific
4	−1+*x*, 1+*y*, *z*	−25.5	10	N3–H3B···O1′
5	1+*x*, −1+*y*, *z*	−25.5	10	O1···H3B′–N3′
6	1−*x*, 1−*y*, 2−*z*	−19.8	8	C4–H4C···O3′
7	1−*x*, −*y*, 1−*z*	−11.2	4	C5–H5A···O1
8	*x*, −1+*y*, *z*	−9.4	4	non-specific
9	*x*, 1+*y*, *z*	−9.4	4	non-specific
10	1−*x*, 1−*y*, 1−*z*	−8.4	3	N3–H3A···C5 H3A···H5C C5–H5C···O2 H5C···H3A
11	−*x*, 1−*y*, 1−*z*	−7.4	3	non-specific
12	2−*x*,1−*y*, 1−*z*	−3.7	1	non-specific
Dimeric building unit				
1	−1+*x*, *y*, *z*	−70.5	20	C5–H5B···O2′ O2···H5B′–C5′
2	1+*x*, *y*, *z*	−70.5	20	C5–H5B···O2′ O2···H5B′–C5′
3	−1+*x*, 1+*y*, *z*	−51.6	15	N3–H3B···O1′ O1···H3B′–N3′
4	1+*x*, −1+*y*, *z*	−51.6	15	N3–H3B···O1′ O1···H3B′–N3′
5	*x*, −1+*y*, *z*	−17.0	5	non-specific
6	*x*, 1+*y*, *z*	−17.0	5	non-specific
7	−1+*x*, 1+*y*, 1+*z*	−11.9	3	C5–H5A···O1 O1···H5A–C5
8	1+*x*, −1+*y*, −1+*z*	−11.9	3	C5–H5A···O1 O1···H5A–C5
9	−1+*x*, *y*, 1+*z*	−10.2	3	C5–H5C···O2 O2···H5C–C5 N3–H3A···C5 C5··· H3A–N3 H5C···H3A
10	1+*x*, *y*, −1+*z*	−10.2	3	C5–H5C···O2 O2···H5C–C5 N3–H3A···C5 C5··· H3A–N3 H5C···H3A
11	*x*, *y*, −1+*z*	−7.9	2	non-specific
12	*x*, *y*, 1+*z*	−7.9	2	non-specific
13	−2+*x*, *y*, 1+*z*	−4.7	1	non-specific
14	2+*x*, *y*, −1+*z*	−4.7	1	non-specific

Notes: Geometrical parameters of *D*–H···*A* interactions are calculated with positions of hydrogen atoms normalized to standard neutron *D*–H distances. When the BU is the dimer, the symmetry operation transforms coordinates of the centroid of the molecular complex.

Table S3. Pairwise intermolecular interaction energies and atom–atom contacts within the first coordination spheres in the crystal structure of **1-*Z***.

No.	Type	Symmetry operation	E / kJ mol^{-1}	100 E / ΣE	Interaction
mol. A					
1	A···B	x, y, z	−61.7	36	N3A–H31A···O3B′ N3B′–H31B′···O3A
2	A···B	1/4+x, 5/4−y, −3/4+z	−47.4	27	C5A–H52A···O3B′ O3B′···H52A′–C5A stacking
3	A···B	1/4+x, 5/4−y, 1/4+z	−38.1	22	C5A–H53A···O3B′ C4B′–H42B′···N3A stacking
4	A···B	3/2−x, 3/2−y, z	−25.1	15	N3A–H32A···O3B′
5	A···A	5/4−x, −1/4+y, −1/4+z	−12.0	7	non-specific
6	A···A	7/4−x, −1/4+y, 1/4+z	−8.9	5	C4A–H41A···O1A′
7	A···A	7/4−x, 1/4+y, −1/4+z	−8.9	5	O1A···H41A′–C4A′
8	A···B	1/2+x, y, −1/2+z	−7.5	4	C5A–H51A···O2B′ C5B′–H51B′···O2A
9	A···A	−1/4+x, 5/4−y, −1/4+z	−7.0	4	non-specific
10	A···A	1/4+x, 5/4−y, 1/4+z	−7.0	4	non-specific
11	A···B	3/2−x, 1−y, −1/2+z	−6.2	4	non-specific
12	A···B	3/2−x, 3/2−y, −1+z	−3.1	2	non-specific
13	A···A	2−x, 1−y, z	−1.8	1	non-specific
14	A···A	3/2−x, 3/2−y, z	0.4	0	non-specific
mol. B					
1	B···A	x, y, z	−61.7	35	N3B–H31B···O3A′ N3A′–H31A′···O3B
2	B···A	−1/4+x, 5/4−y, 3/4+z	−47.4	27	C4B–H43B···N1A′ C5A′–H52A′···O3B stacking
3	B···A	−1/4+x, 5/4−y, −1/4+z	−38.1	22	C4B–H42B···N3A′ C5A′–H53A′···O3B stacking
4	B···A	3/2−x, 3/2−y, z	−25.1	14	N3A′–H32A′···O3B
5	B···B	5/4−x, 1/4+y, 1/4+z	−15.9	9	N3B′–H32B′···O1B
6	B···B	5/4−x, −1/4+y, −1/4+z	−15.9	9	N3B–H32B···O1B′
7	B···A	5/4−x, 1/4+y, 1/4+z	−12.0	7	non-specific
8	B···A	−1/2+x, y, 1/2+z	−7.5	4	C5B–H51B···O2A′ C5A′–H51A′···O2B
9	B···A	3/2−x, 1−y, 1/2+z	−6.2	4	non-specific
10	B···A	3/2−x, 3/2−y, 1+z	−3.1	2	non-specific
11	B···B	1−x, 3/2−y, 1/2+z	−2.3	1	non-specific
12	B···B	1−x, 3/2−y, −1/2+z	−2.3	1	non-specific

Note: Geometrical parameters of *D*–H···*A* interactions are calculated with positions of hydrogen atoms normalized to standard neutron *D*–H distances.

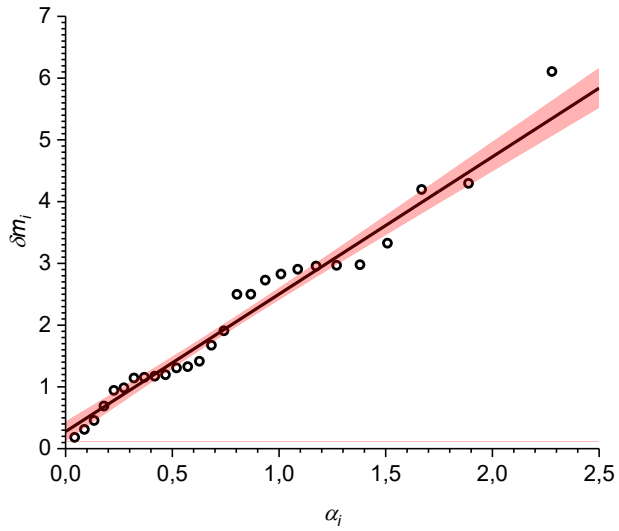

Figure S1. Half-normal probability plot of differences between pairs of independent distances in molecules A and B of **1-*Z***.

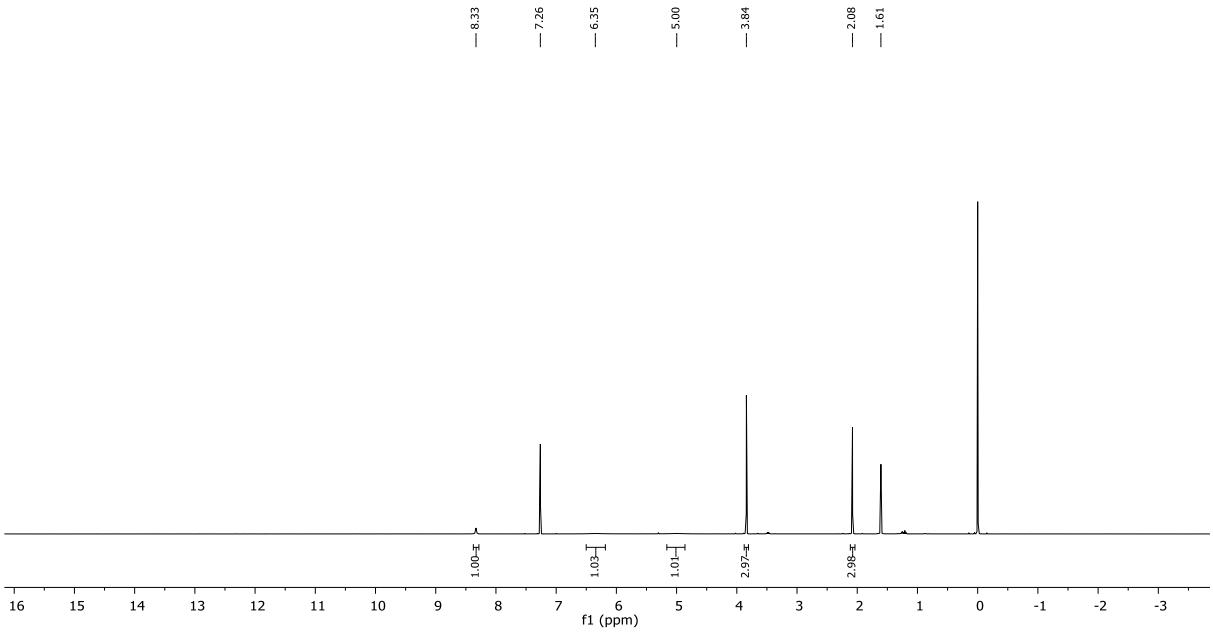

Figure S2. ^{1}H NMR spectrum of **1-*E*** (400 MHz, $CDCl_3$).

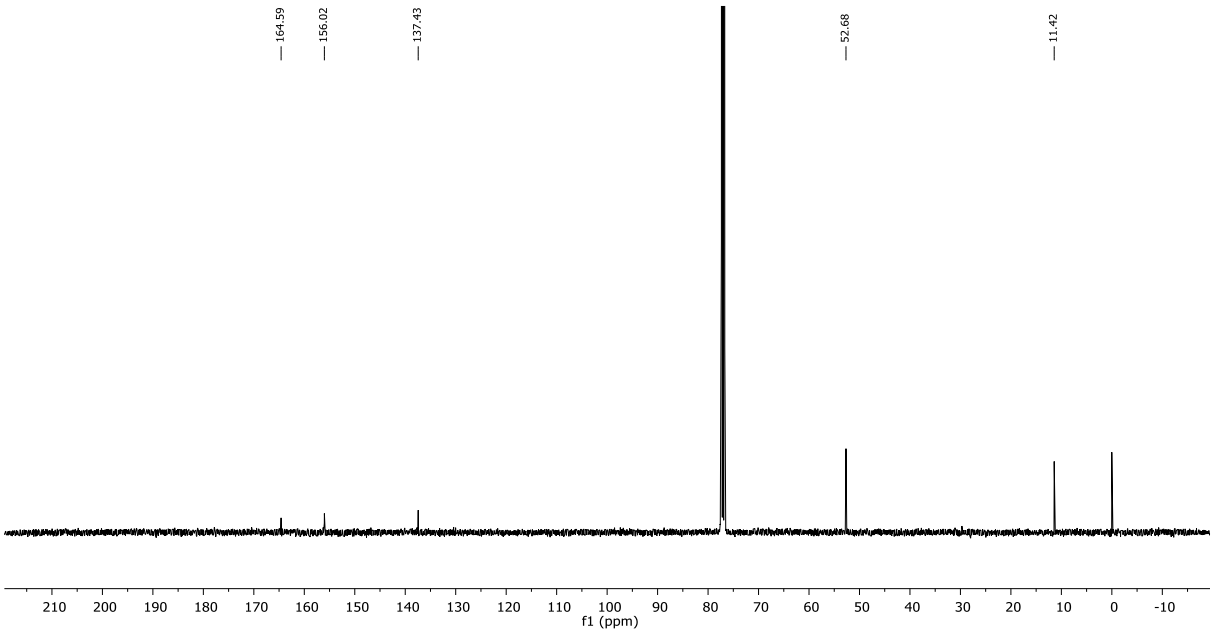

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1-*E*** (101 MHz, $CDCl_3$).

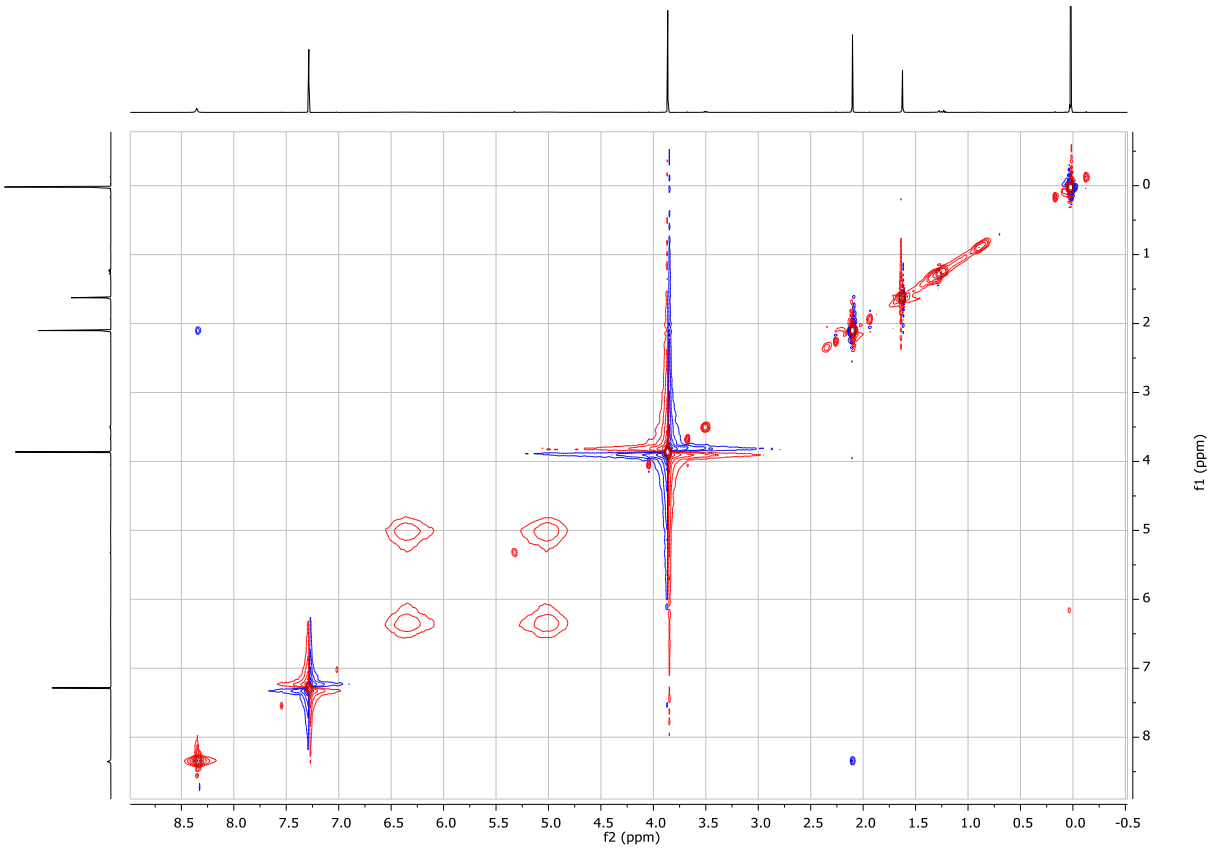

Figure S4. 2D NOESY spectrum of **1-*E*** (400 MHz, $CDCl_3$).

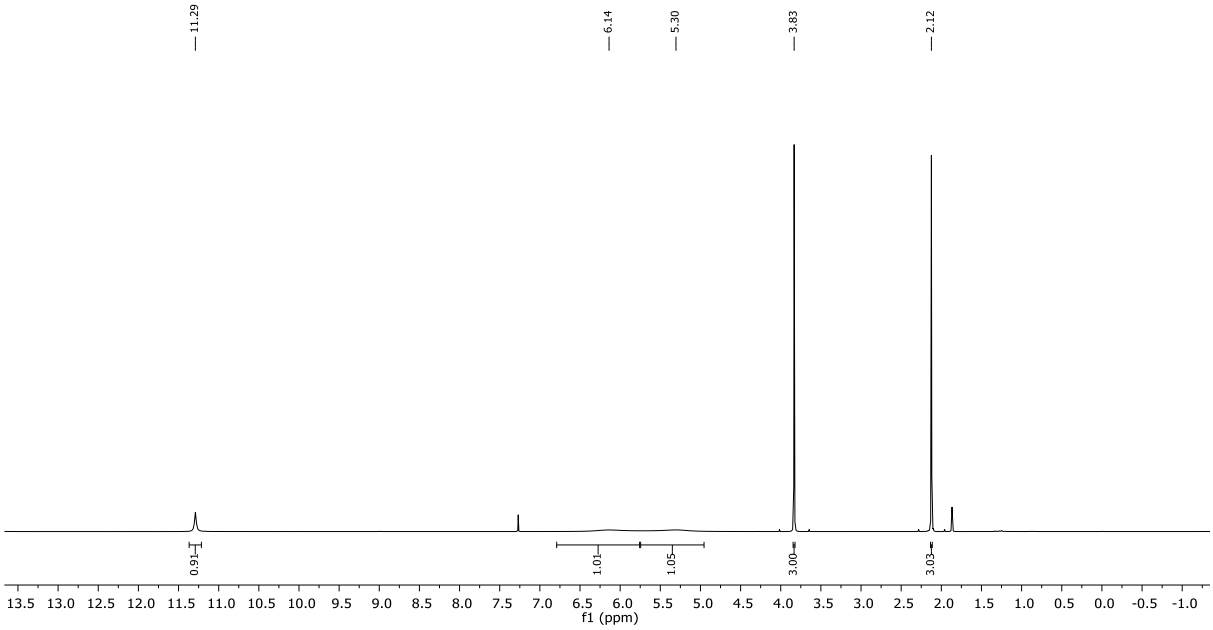

Figure S5. ^{1}H NMR spectrum of **1-*Z*** (400 MHz, $CDCl_3$).

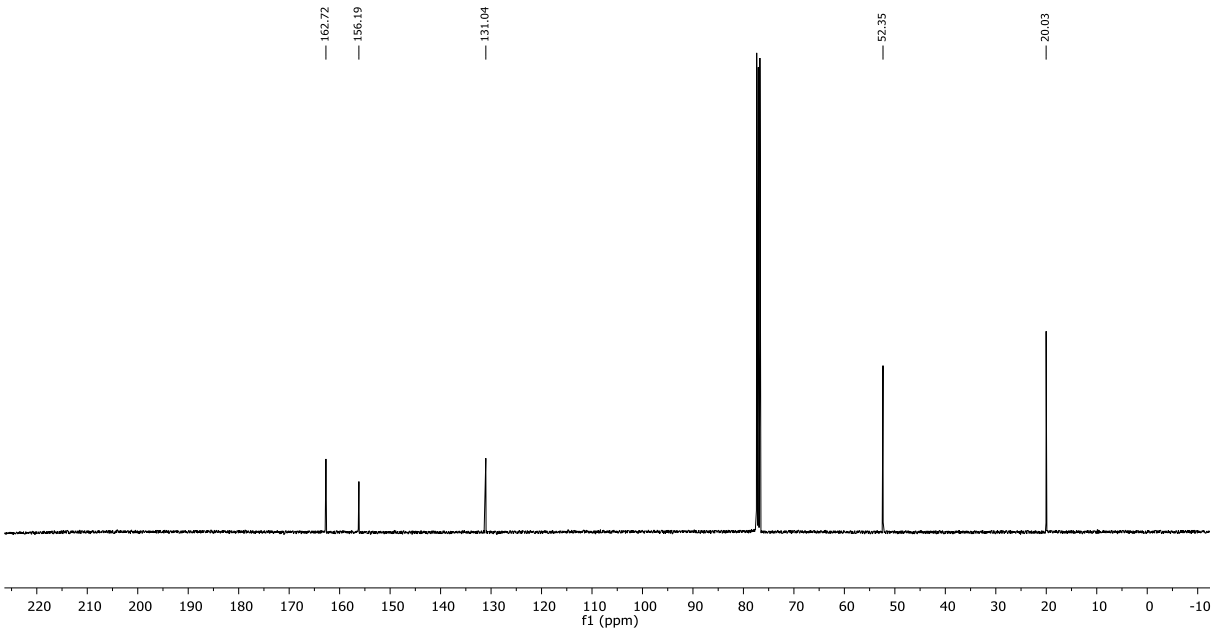

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **1-*Z*** (101 MHz, $CDCl_3$).

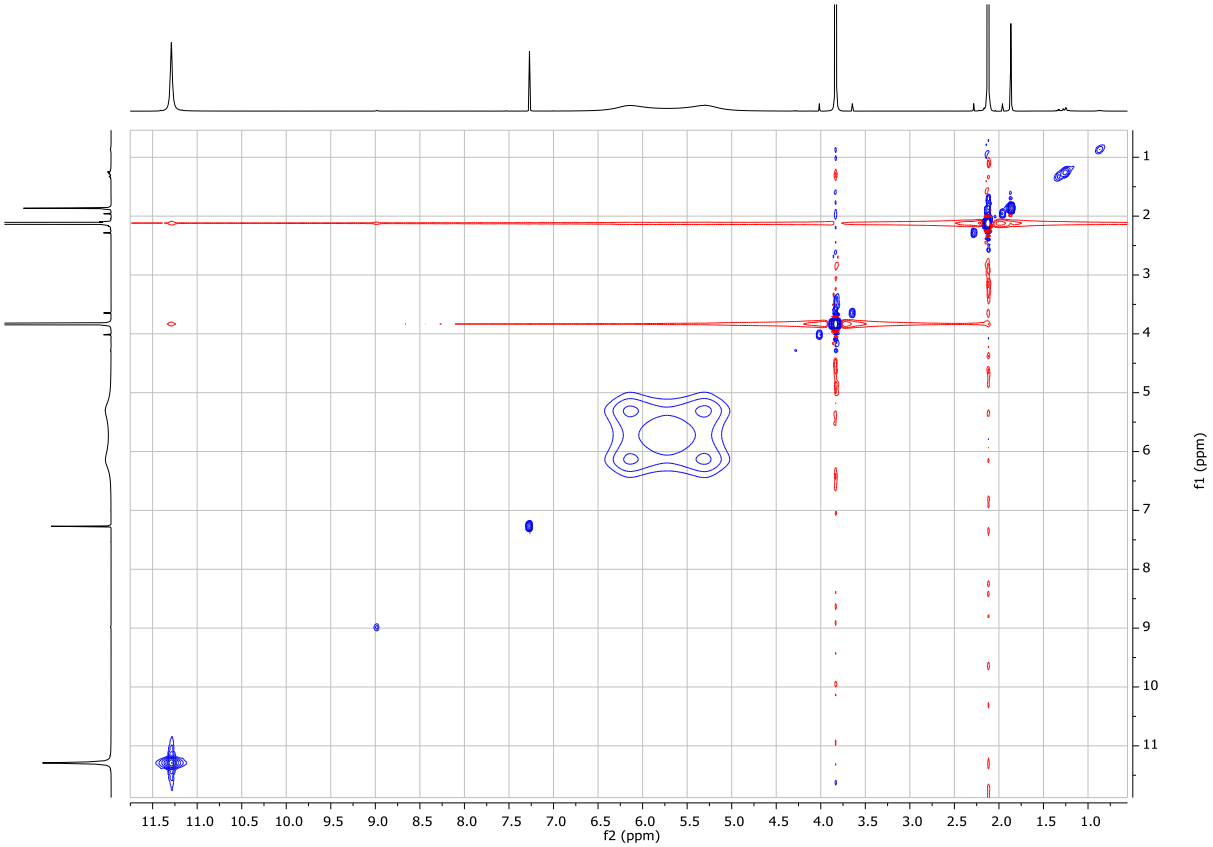

Figure S7. 2D NOESY spectrum of **1-*Z*** (400 MHz, $CDCl_3$).

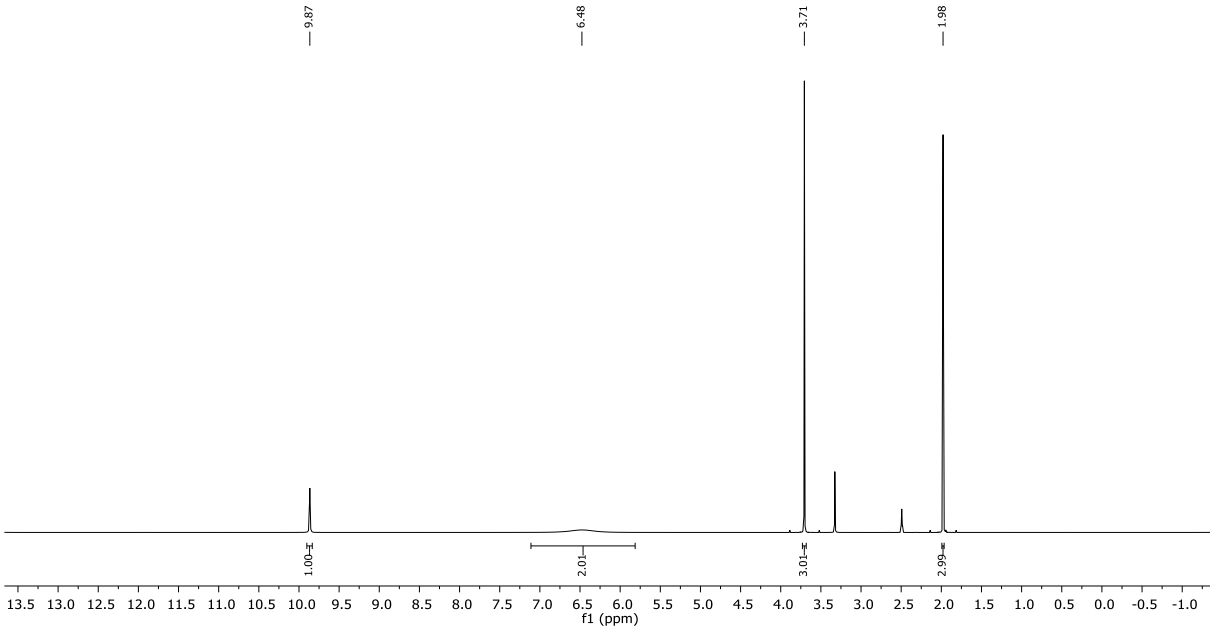

Figure S8. ^{1}H NMR spectrum of **1-*E*** (400 MHz, DMSO-d_6).

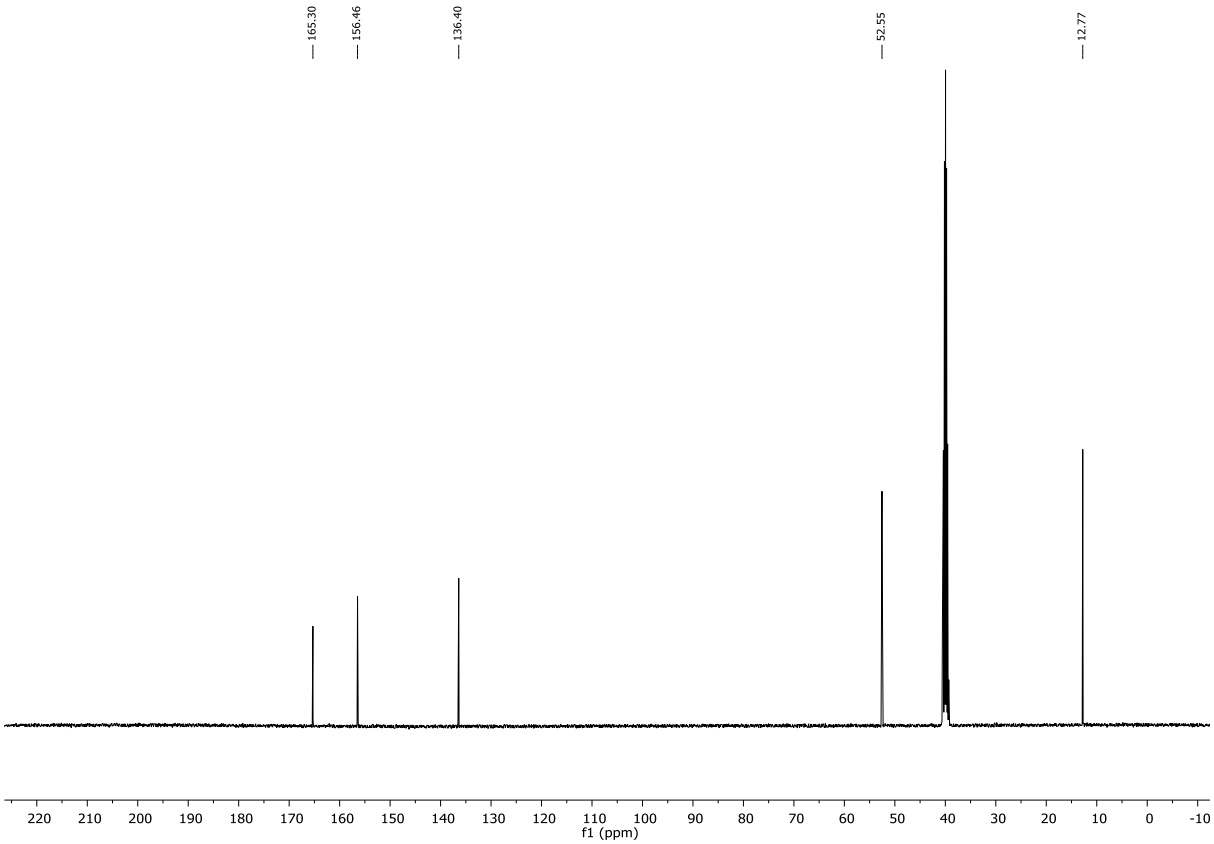

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **1-*E*** (101 MHz, DMSO-d_6).

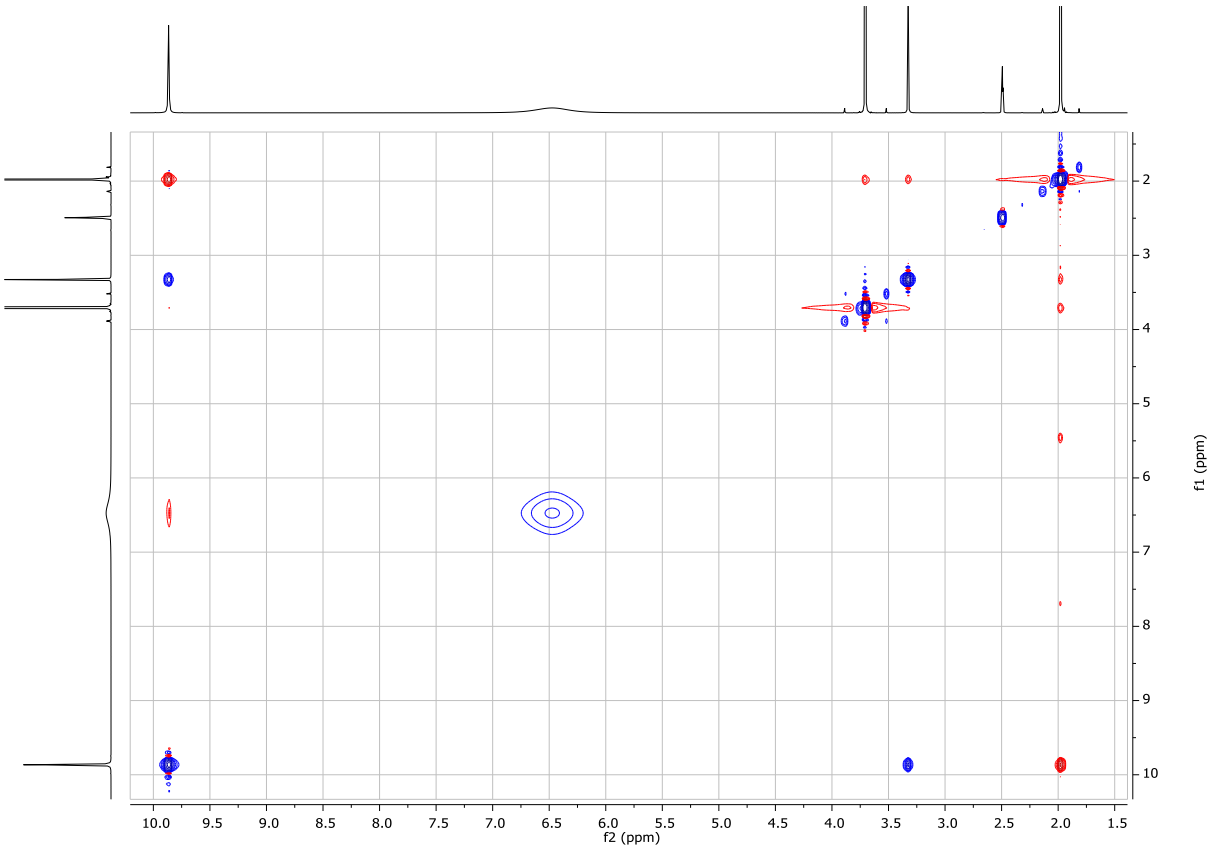

Figure S10. 2D NOESY spectrum of **1-*E*** (400 MHz, DMSO-d_6).

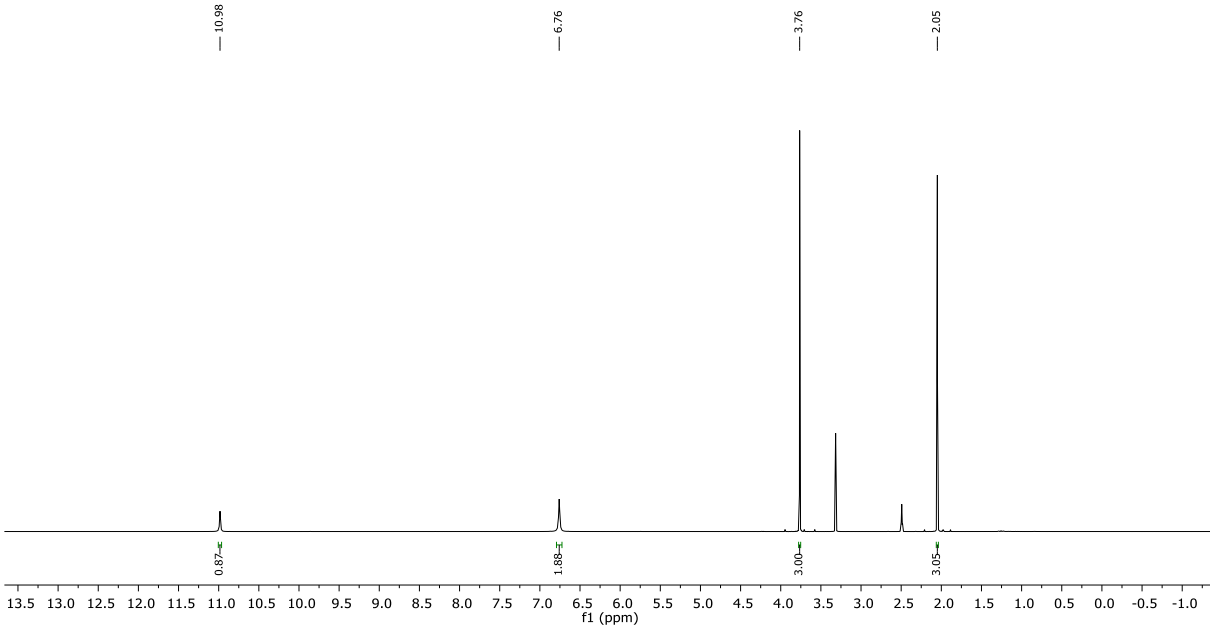

Figure S11. ^{1}H NMR spectrum of **1-*Z*** (400 MHz, DMSO-d_6).

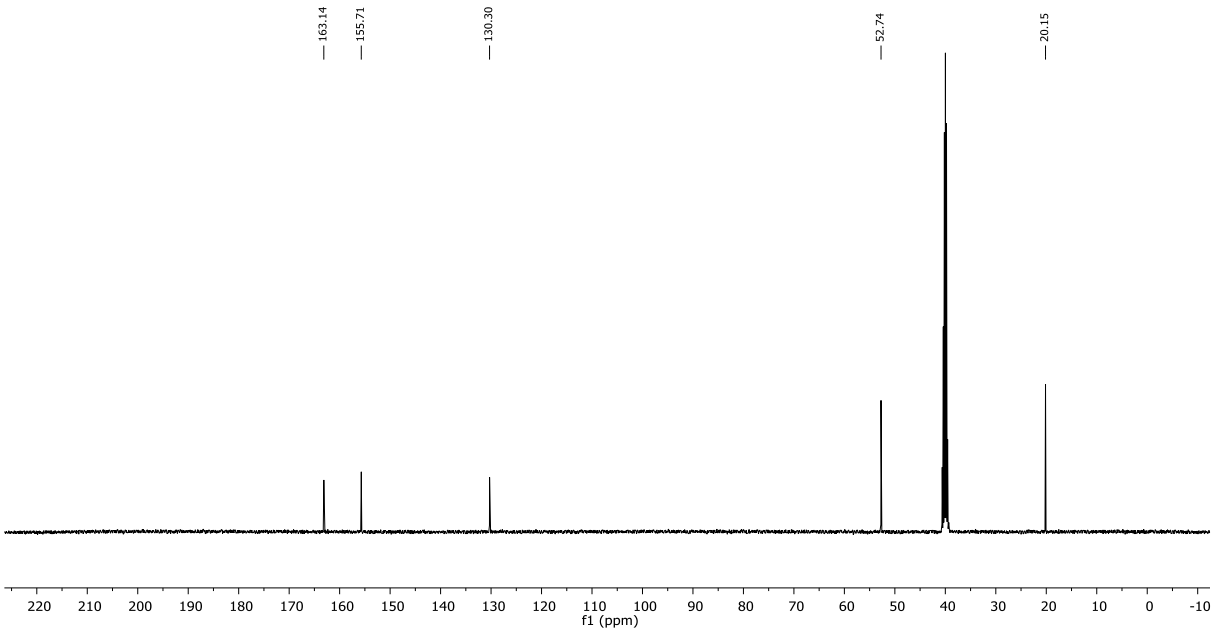

Figure S12. ^{13}C{^{1}H} NMR spectrum of **1-*Z*** (101 MHz, DMSO-d_6).

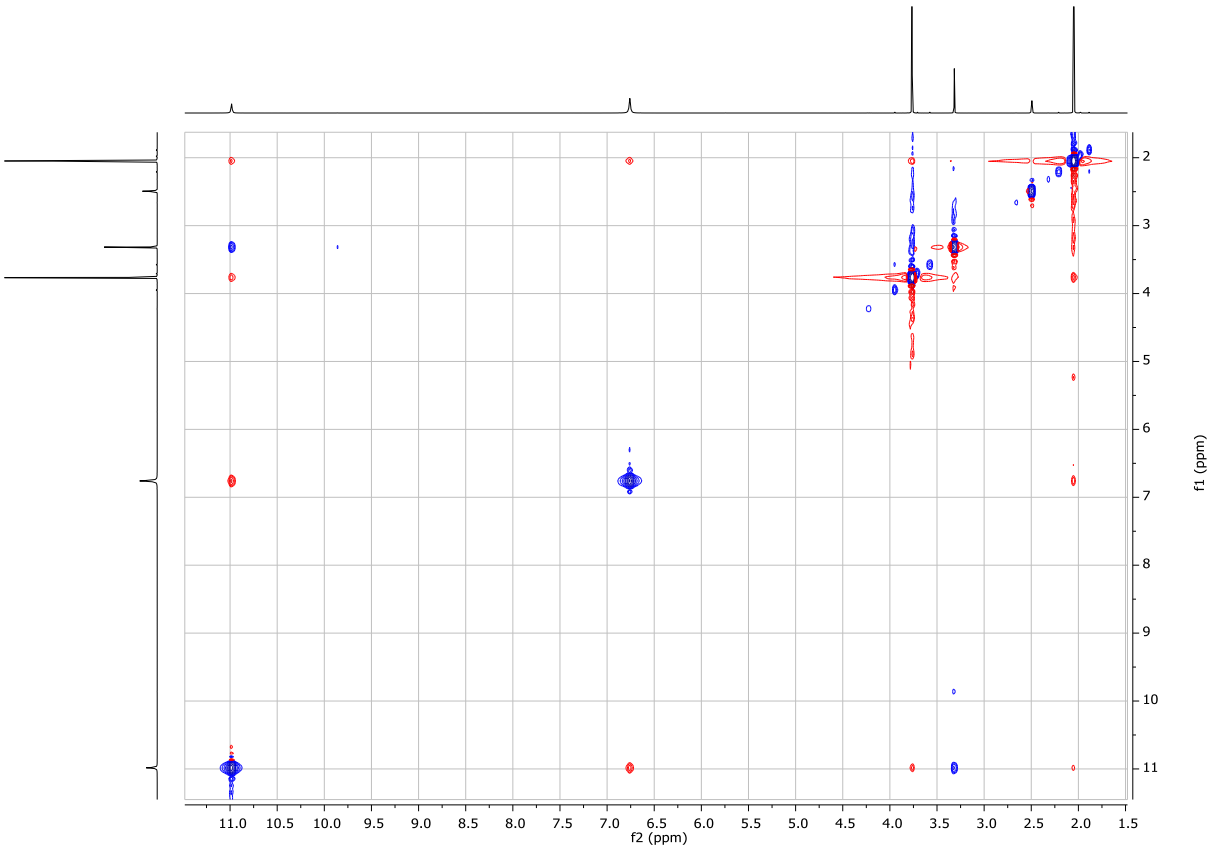

Figure S13. 2D NOESY spectrum of **1-*Z*** (400 MHz, DMSO-d_6).

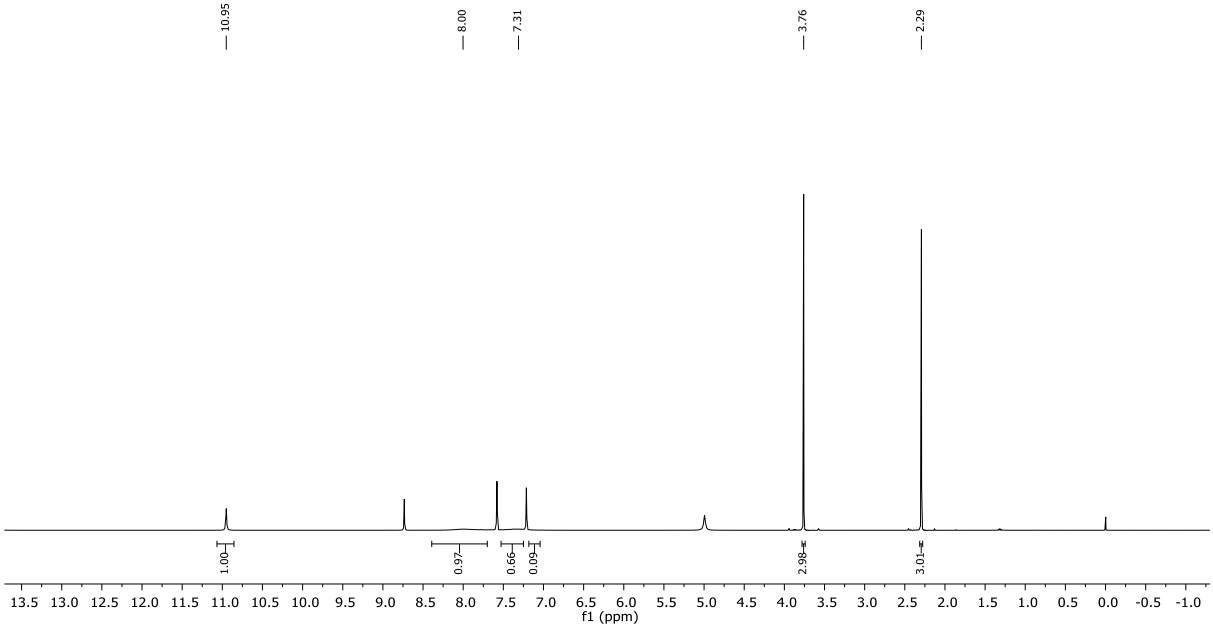

Figure S14. ^{1}H NMR spectrum of **1-*E*** (400 MHz, pyridine-d_5).

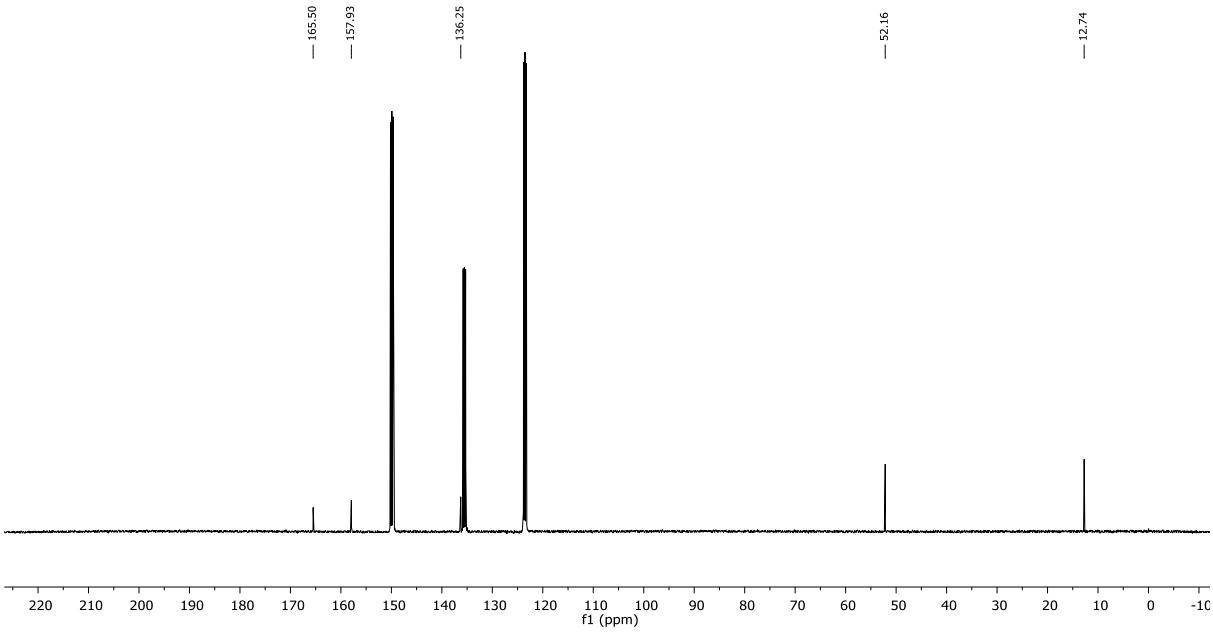

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **1-*E*** (101 MHz, pyridine-d_5).

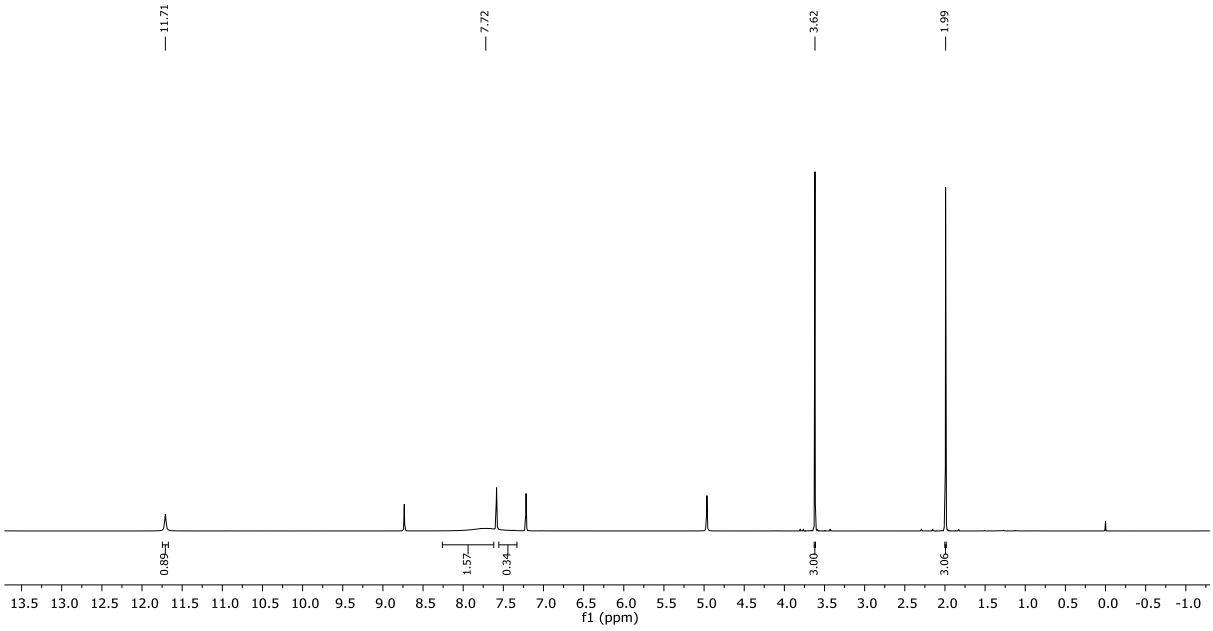

Figure S16. ^{1}H NMR spectrum of **1-*Z*** (400 MHz, pyridine-d_5).

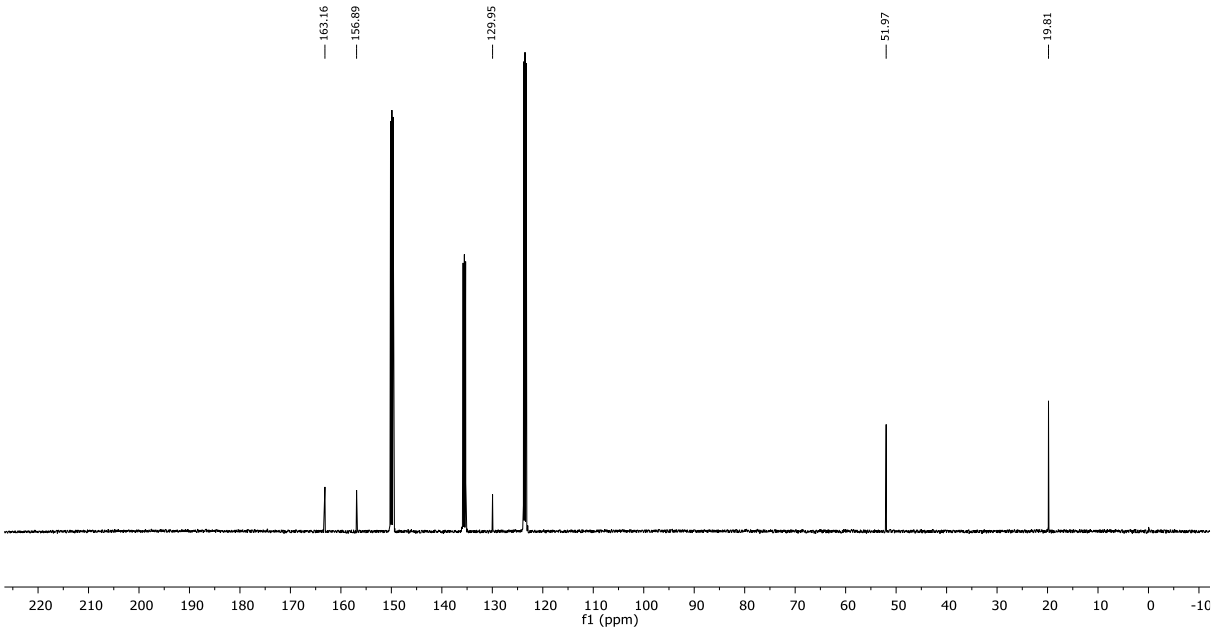

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **1-*Z*** (101 MHz, pyridine-d_5).

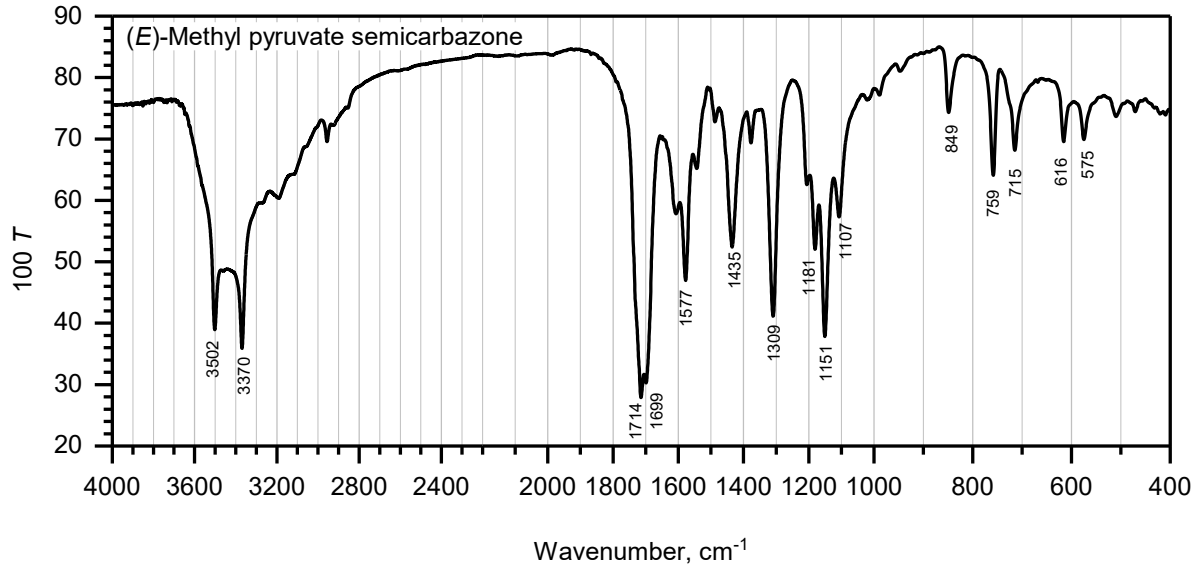

Figure S18. IR spectrum (KBr) of **1-*E***.

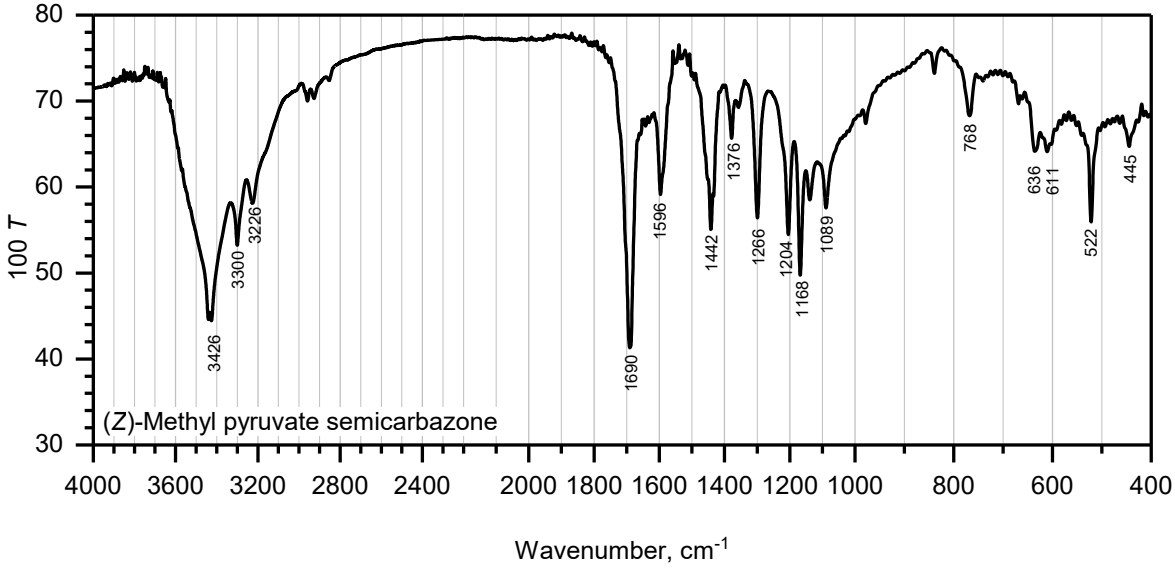

Figure S19. IR spectrum (KBr) of **1-*Z***.

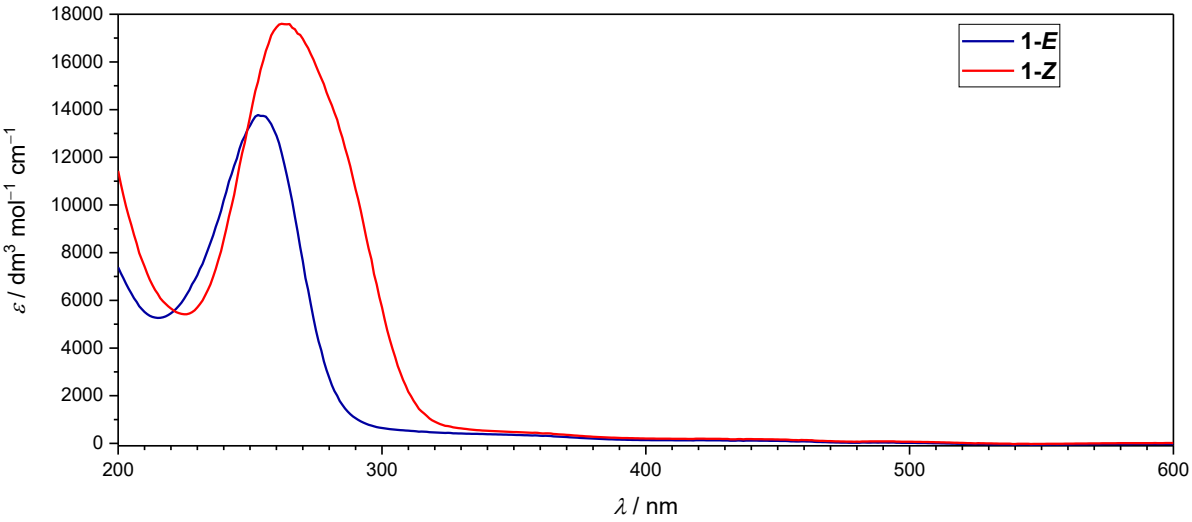

Figure S20. UV–Vis spectra of **1-*E*** (0.19 mM) and **1-*Z*** (0.16 mM) in acetonitrile.

Instrumental setup for the synthesis of 1-*Z*

The experimental setup used for the synthesis of **1-*Z*** under UVC irradiation consisted of a foldable housing, (1165 × 100 × 72) mm. The interior of the housing was lined with reflective mirrors to enable multiple reflections of the applied radiation. A quartz tube (length: 65 cm; diameter: 1 cm) was placed inside the housing, into which 50 mL of a solution of compound **1-*E*** (10 g/L) was added. A UVC fluorescent lamp (Philips, Netherlands; model: TUV 36W G13 germicidal) was mounted parallel to the quartz tube. The lamp had an emission maximum at 254 nm, and the measured radiation intensity was 1.0 mW/cm². During the experiment, fans were employed to continuously remove harmful gaseous species from the irradiated chamber. The solution was irradiated for 12 h.

The radiation energy flux was measured using a Delta Ohm HD 2102.2 radiometer (Padova, Italy), equipped with an LP 471 UVC probe (spectral range: 220–280 nm).

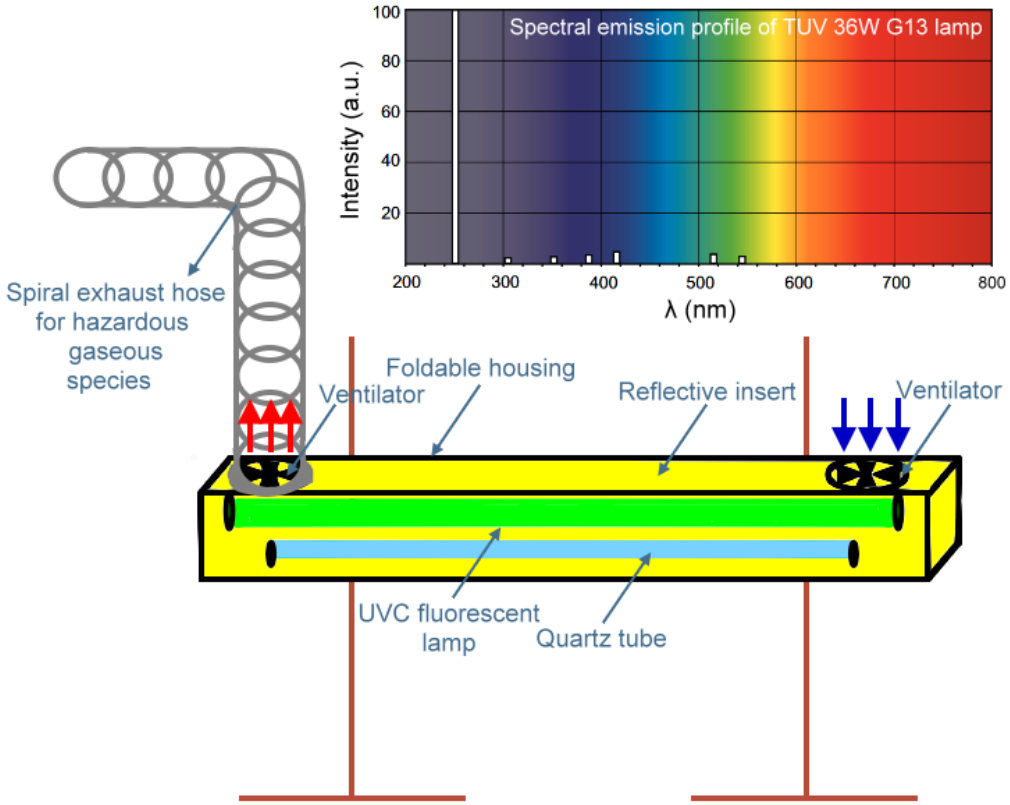

Figure S21. Instrumental setup for the UVC-induced isomerization and the corresponding lamp emission spectrum.