

Supplementary data

Characterization of compound 4 [5-(4-chlorobenzylidene)-2-[[6-(trifluoromethoxy)-1,3-benzothiazol-2-yl]imino]-1,3-thiazolidin-4-one]

Physical appearance: Yellow powder

Yield: 36%

TLC %Rf: 75

Melting point: 287-289°C

Calculated combustion elemental analysis: C, 46.42; H, 2.054; N, 8.961; S, 12.60

Molecular formula: $C_{18}H_9ClF_3N_3O_2S_2 \cdot 3 H_2O$

IR spectrum

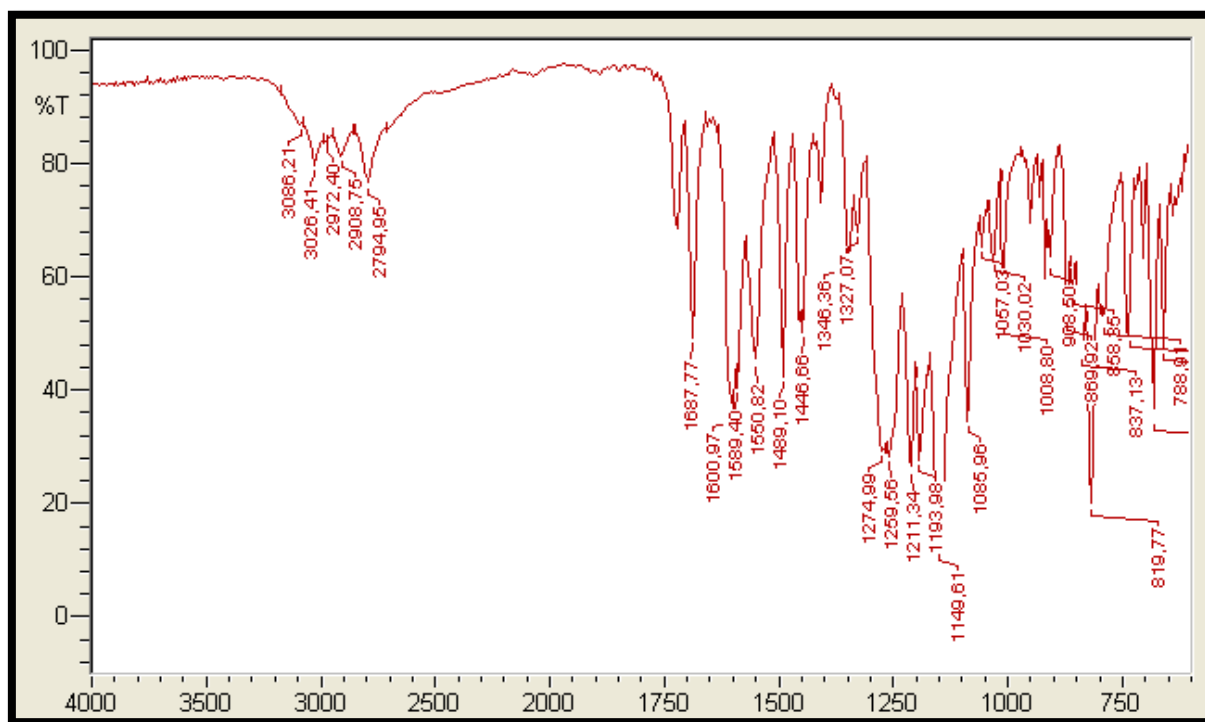
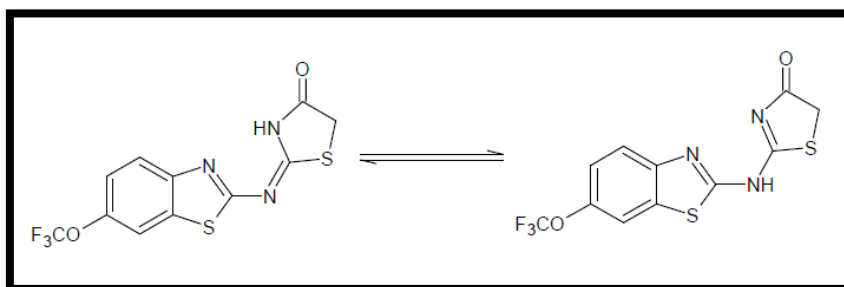


Figure 1: IR spectrum

Table I			
FTIR findings			
Functional group	Number of related C	Frequency (cm ⁻¹)	Comment
N-H	-	3086	Stretching
Ar C-H and =C-H	C2, C3, C5-7, C11, C12, C14	3026, 2972	Stretching
C=O	C9	1699, 1688	Stretching
N-H	-	1601, 1589	Bending
C=N	C16, C17	1551	Stretching
Ar C=C	C1-8, C10-15	1489, 1447	Stretching
C-N	C9, C10, C17	1275, 1260	Stretching
C-O-C	C13, C18	1211	Stretching
C-F	C18	1150	Stretching
Ar C-H and =C-H	C2, C3, C5-7, C11, C12, C14	870, 837, 820, 788	Bending
C-S-C	C8, C15-17	734, 681	Stretching
C-Cl	C4	660	Stretching

The presence of two strong carbonyl bands in the IR spectrum of compound **4** can be explained by the presence of two tautomeric forms which 2-amino-4-thiazolinone and the 2-imino-4-thiazolidinone structure.



¹H NMR spectra obtained from fid file of HMBC spectrum

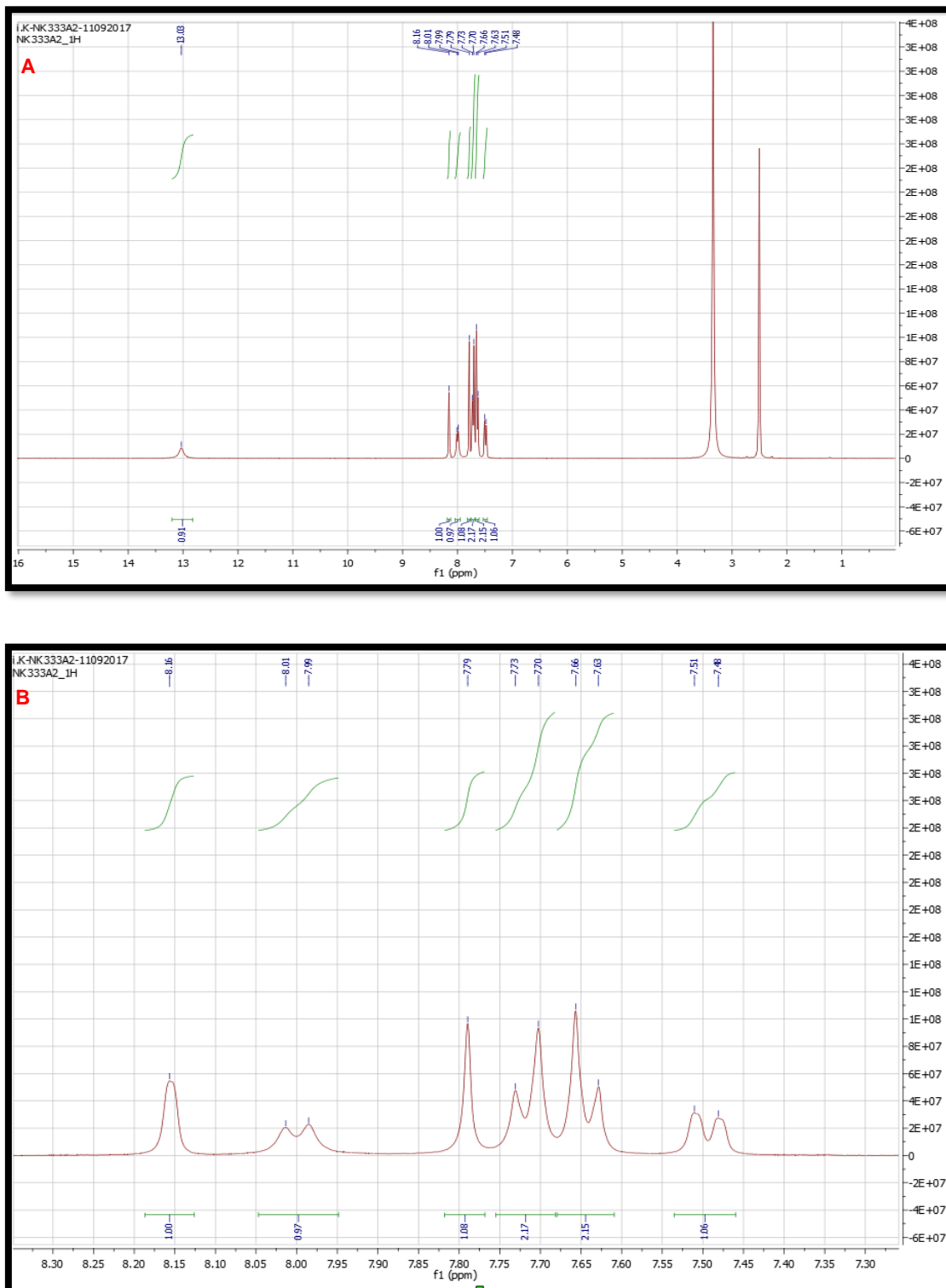


Figure 2: ¹H NMR spectrum. Full spectrum (A); 7.3-8.3 ppm (B)

^1H NMR (300 MHz, DMSO- d_6 /TMS) δ ppm: 7.50 (1H, d, $J=8.7$ Hz, ArH); 7.65 (2H, d, $J=8.7$ Hz, ArH); 7.72 (2H, d, $J=8.7$ Hz, ArH); 7.79 (1H, s, =CH-Ar); 8.00 (1H, d, $J=8.4$ Hz, ArH); 8.16 (1H, s, ArH); 13.03 (1H, s, NH).

Significant findings indicating that the target compounds were obtained:

- ✓ Detection of additional four aromatic protons belonging to 4-chlorobenzylidene structures between 7.50-8.16 ppm,
- ✓ $-\text{CH}_2-$ protons which belong to the thiazolidinone ring of compound **2**, at 4.09 ppm are not observed in the spectrum of compound **4**.
- ✓ Detection of methine proton (=CH-Ar) at 7.79 ppm

It is known that the NH proton of the 2-amino-4-thiazolinone ring is detected around 9 ppm, while the lactam proton of the 2-imino-4-thiazolidinone ring is detected in the range of 12-13 ppm (Haider and Hamada, 2012; Kulabaş et al., 2017; Vicini et al., 2008). In the ^1H NMR spectrum of compound **4**, the NH proton was detected at 13.03 ppm. Although the presence of both 2-amino-4-thiazolinone and the 2-imino-4-thiazolidinone tautomeric forms in solid form is detected in the IR spectrum, it is observed that only the 2-imino-4-thiazolidinone form is in solution.

When the *E* and *Z* geometric isomers of the C=C exocyclic double bond in the 5th position of benzylidene derivatives were examined, the =CH-Ar proton of compound **4** was detected at 7.79 ppm. In many previously reported studies, the =CH-Ar proton detected in the range of 6.90-7.97 ppm was reported as the *Z* isomer, while the related proton for *E* isomer was reported to be detected in the higher energy area (about 6 ppm) (Havrylyuk et al., 2010; Mushtaque et al., 2012; Ottanà et al., 2005; Vicini et al., 2008, 2006). This finding confirms that compound **4** was obtained as the *Z* isomer.

^{13}C NMR spectra obtained from fid file of HMBC spectrum

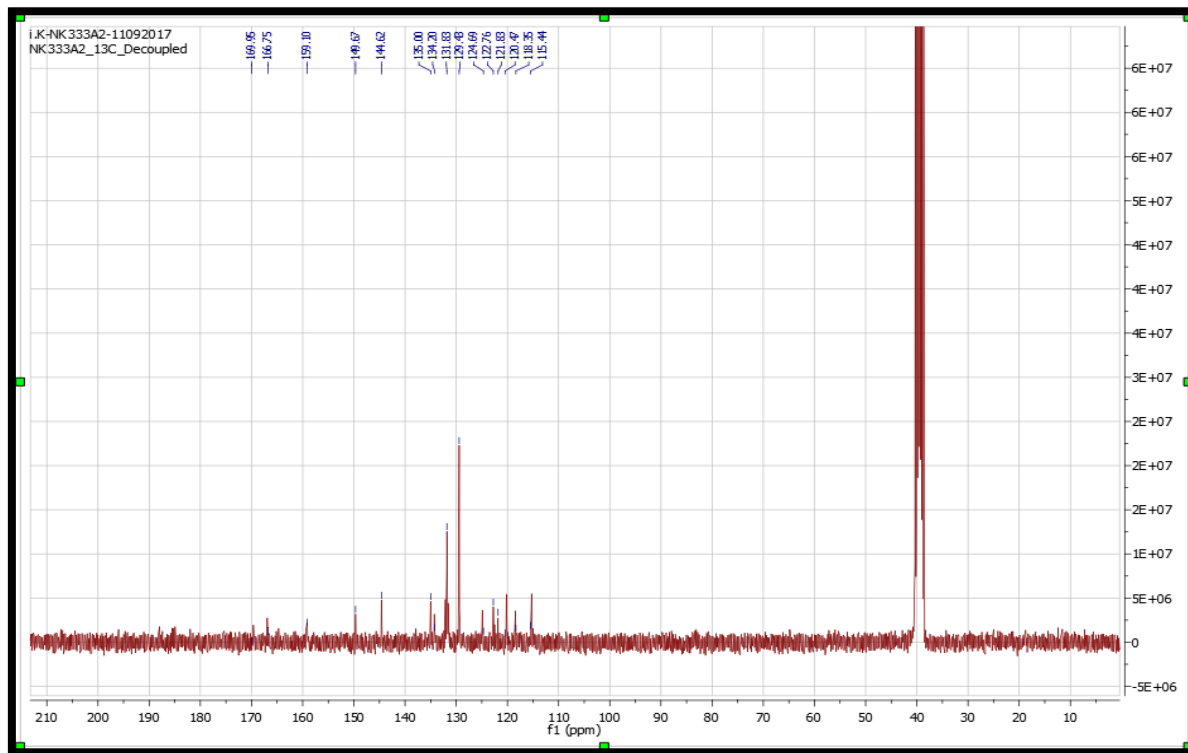


Figure 3: ^{13}C NMR spectrum

^{13}C NMR (150 MHz, $\text{DMSO-d}_6/\text{TMS}$) δ ppm: 115.44 (ArC), 118.35 (C5, thiazolidinone), 120.47 (ArC), 121.83 (=CH-Ar), 122.76, 124.69, 129.43 (ArC), 131.83 (-OCF₃), 134.20, 135.00, 144.62, 149.67, 159.10 (ArC), 166.75 (C2, thiazolidinone), 169.95 (C=O, thiazolidinone).

HRMS (DART⁺)

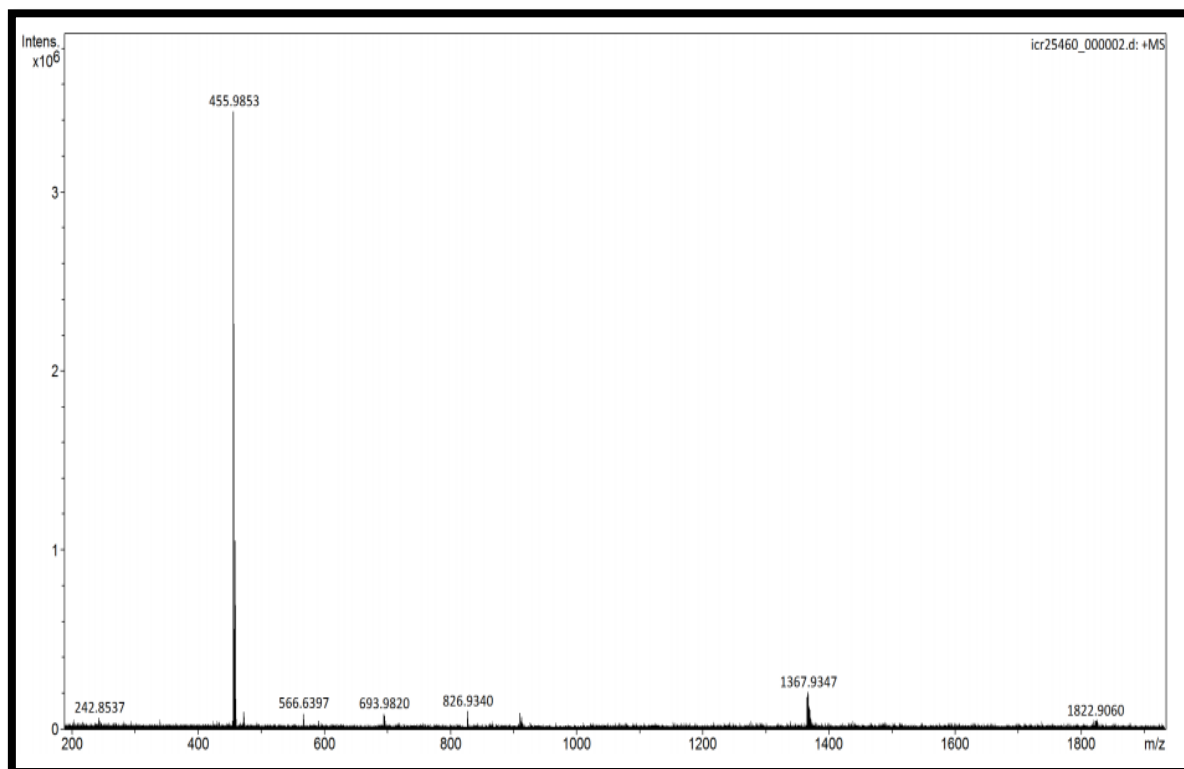


Figure 4: DART(+)-MS spectrum

It was observed that the molecular ion peak $[M+H]^+$ of compound **4** in the DART-MS spectrum was compatible with the calculated m/z value.

m/z , calculated/found): 455.9777/455.9853 $[M+H]^+$

HMBC analysis was applied to elucidate the structure of compound 4, and thus the structure was elucidated by evaluating ^{13}C - ^1H interactions at two, three or more bond distances.

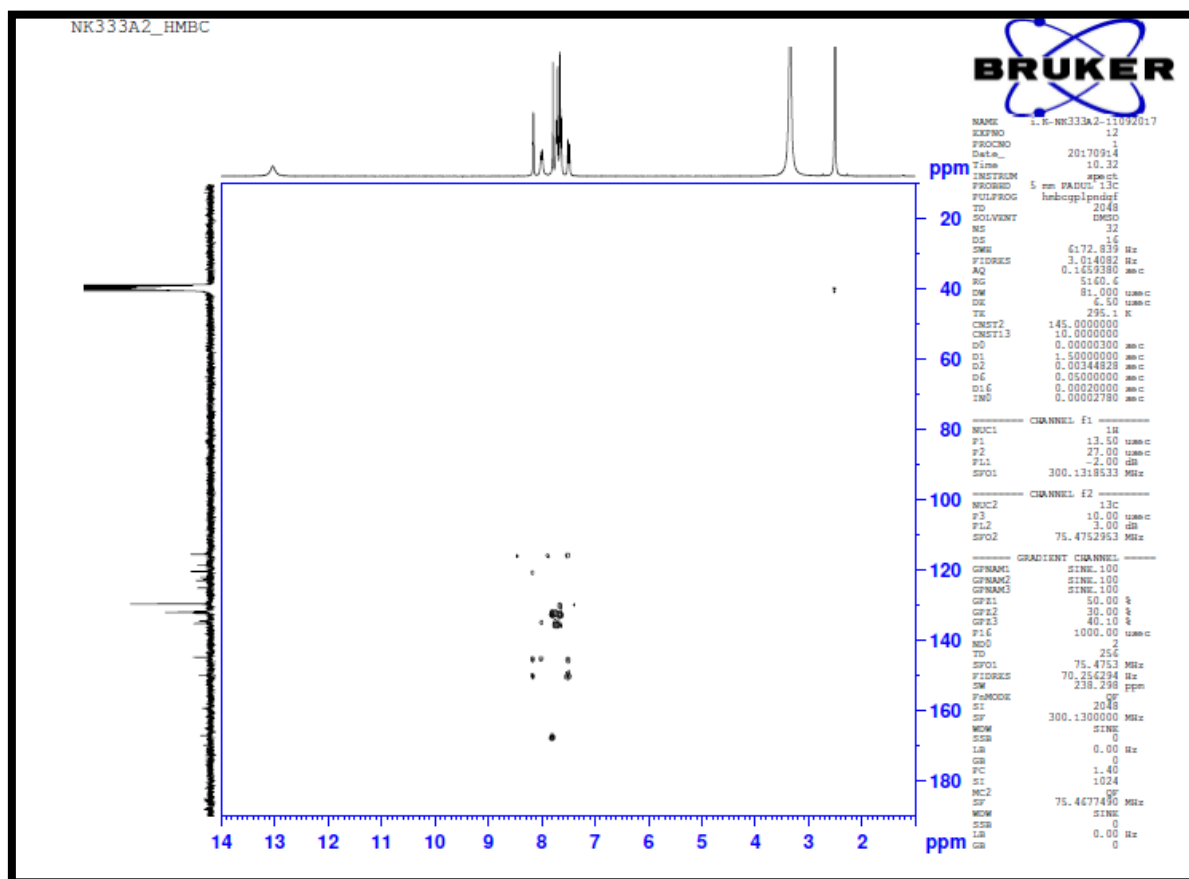


Figure 5: HMBC spectrum

When the 107-128 ppm range of the HMBC spectrum was examined, the chemical shift value of the carbons of the benzothiazole ring (C11, C14 and C15), the carbons of the thiazolidin-4-one ring (C8), and the C1 and C7 carbon of the benzene ring were determined. The C14 carbon of the benzothiazole ring was detected at 115.44 ppm, with two symmetrical contours with the H14 proton attached to it.

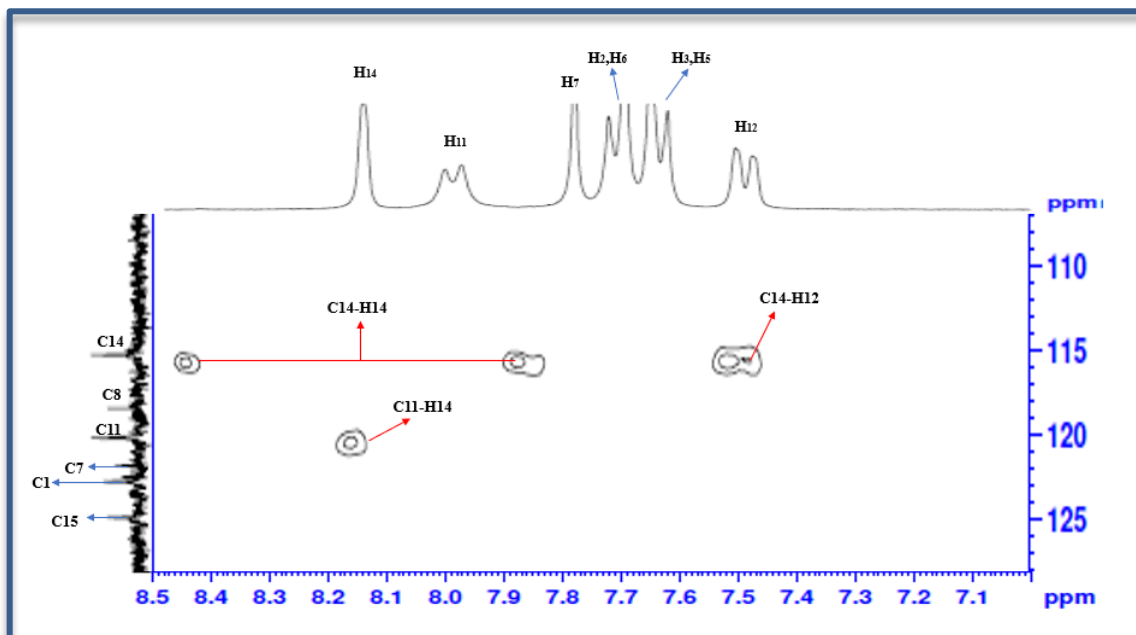


Figure 6: Sections from the HMBC spectrum (107-128 ppm)

In the 129-154 ppm range of the spectrum, the chemical shift values of the carbon atoms of the 1,4 disubstituted benzene ring (C2-6) and the carbon atoms of the benzothiazole ring (C10, C12, C13 and C18) were observed and were identified as a result of their coupling with the surrounding hydrogen atoms. The peak observed at 131.83 ppm was attributed to the C18 carbon of the benzothiazole ring due to its contour with the H12 proton around 7.5 ppm, whereas the peak at 144.62 ppm was attributed to the C10 carbon due to its interactions with H14, H11 and H12 hydrogens. The interactions of the C4 carbon with the H2, H3, H5, H6 protons on the 1,4 disubstituted benzene ring confirmed that this carbon resonated at 135.00 ppm.

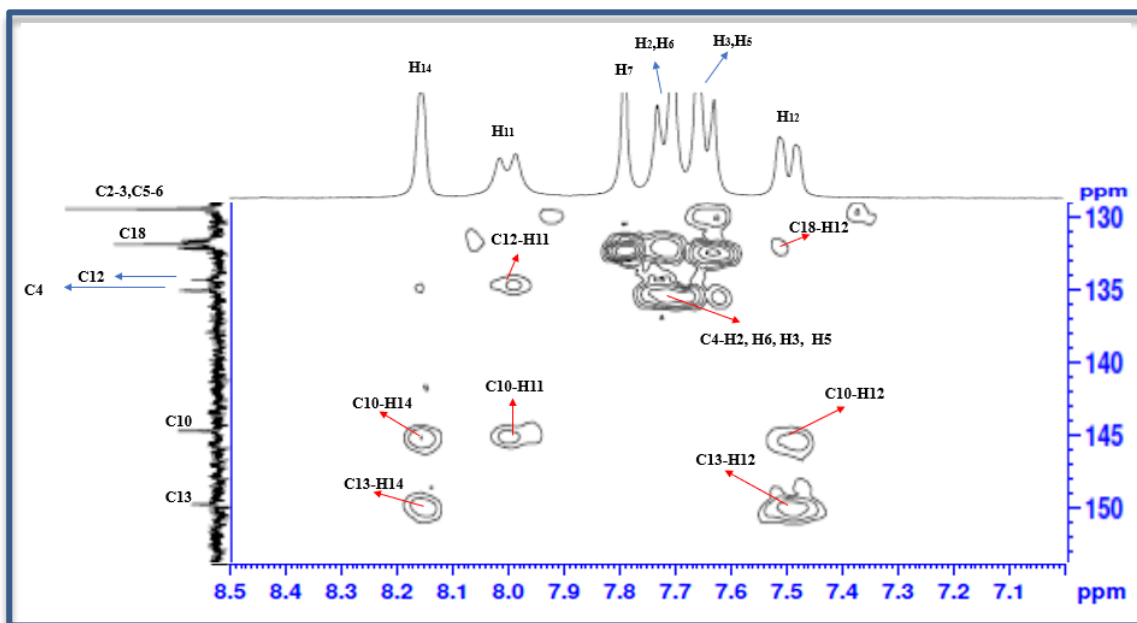


Figure 7: Sections from the HMBC spectrum (129-154 ppm)

The C17 carbon atom of the thiazolidin-4-one ring was detected at 166.75 ppm due to its interaction with the methine proton (Figure 8). All the obtained results are given in Table II.

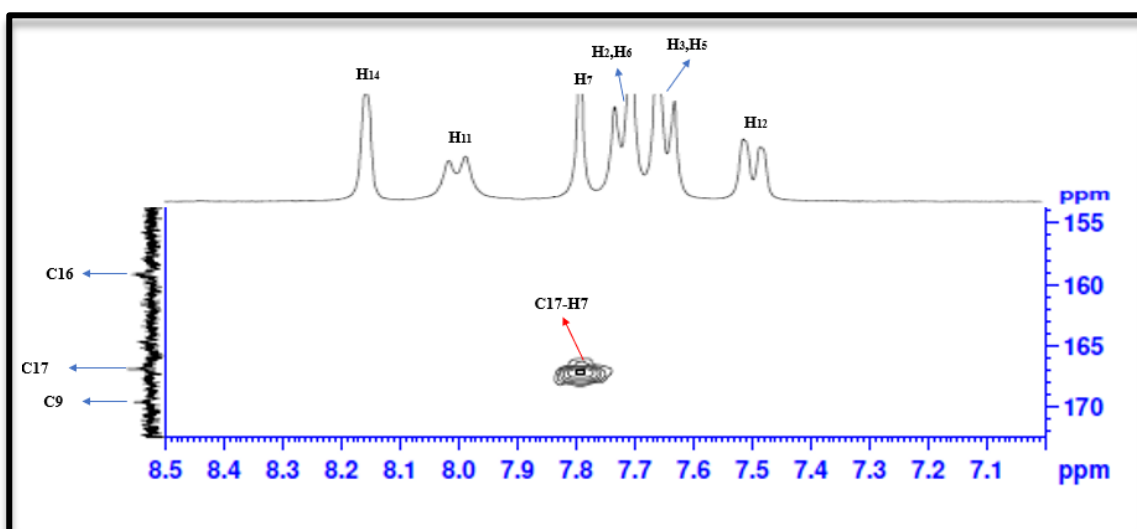


Figure 8: Sections from the HMBC spectrum (155-173 ppm)

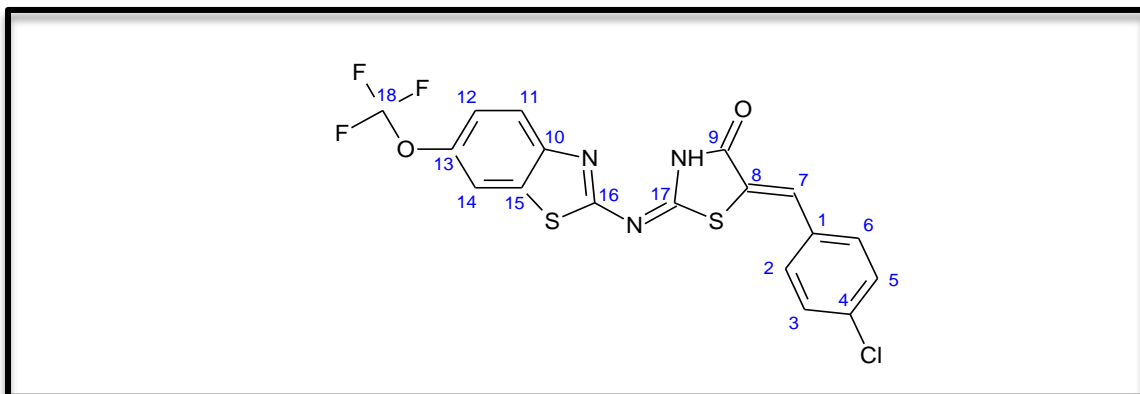


Table II

HMBC findings

Carbon No.	¹ H NMR (ppm)	¹³ C NMR (ppm)	¹ H- ¹³ C couplings	¹³ C - ¹ H couplings
1	-	122.76	-	-
2, 3, 5, 6	7.63-7.73	129.43	2*,3*, 4, 5*,6*	2*, 3*, 5*, 6*
4	-	135.00	-	2, 3, 5, 6
7	7.79	121.83	17	-
8	-	118.35	-	-
9	-	169.95	-	-
10	-	144.62	-	11, 12, 14
11	7.99-8.01	120.47	12, 10	14
12	7.48-7.51	134.20	10, 13, 14, 18	11
13	-	149.67	-	12, 14
14	8.16	115.44	12, 14*	10, 11, 13, 14*
15	-	124.69	-	-
16	-	159.10	-	-
17	-	166.75	-	7
18	-	131.83	-	12

*The carbon atom interacting with its own proton

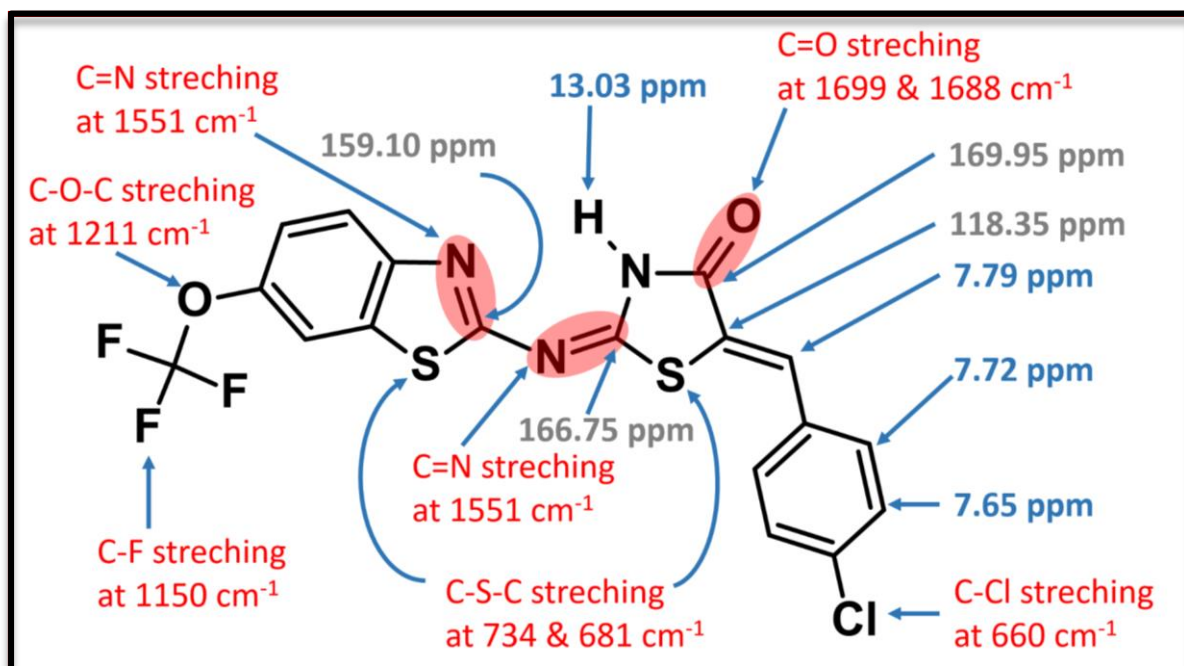


Figure 9: Visual summary of the characterization of compound 4 in the light of FTIR, ¹H NMR and ¹³C NMR findings. Remaining benzene signals observed in FTIR and NMR spectra are not shown for clarity (Please see Tables I and II). Colour chart for signals: FTIR (red), ¹H NMR (blue), ¹³C NMR (grey).

References

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