Supplementary Material

Synthesis and some reactions of 5-carbmethoxymethylidene-4-oxo-1,3-thiazol-2-ylguanidine

Nadezhda V. Stolpovskaya,[a] Do Van Quy,[a] Alexey A. Kruzhilin,[a] Evgeniya S. Shvetsova,[a] Khidmet S. Shikhaliev,*[a] and Fedor I. Zubkov[b]

[a] Department of Organic Chemistry, Voronezh State University, Universitetskaya pl. 1, Voronezh, 394006, Russia

[b] Department of Organic Chemistry, Peoples' Friendship University of Russia, 6 Miklukho-Maklaya St., Moscow, 117198, Russian Federation

Email: chocd261@chem.vsu.ru

Table of Contents

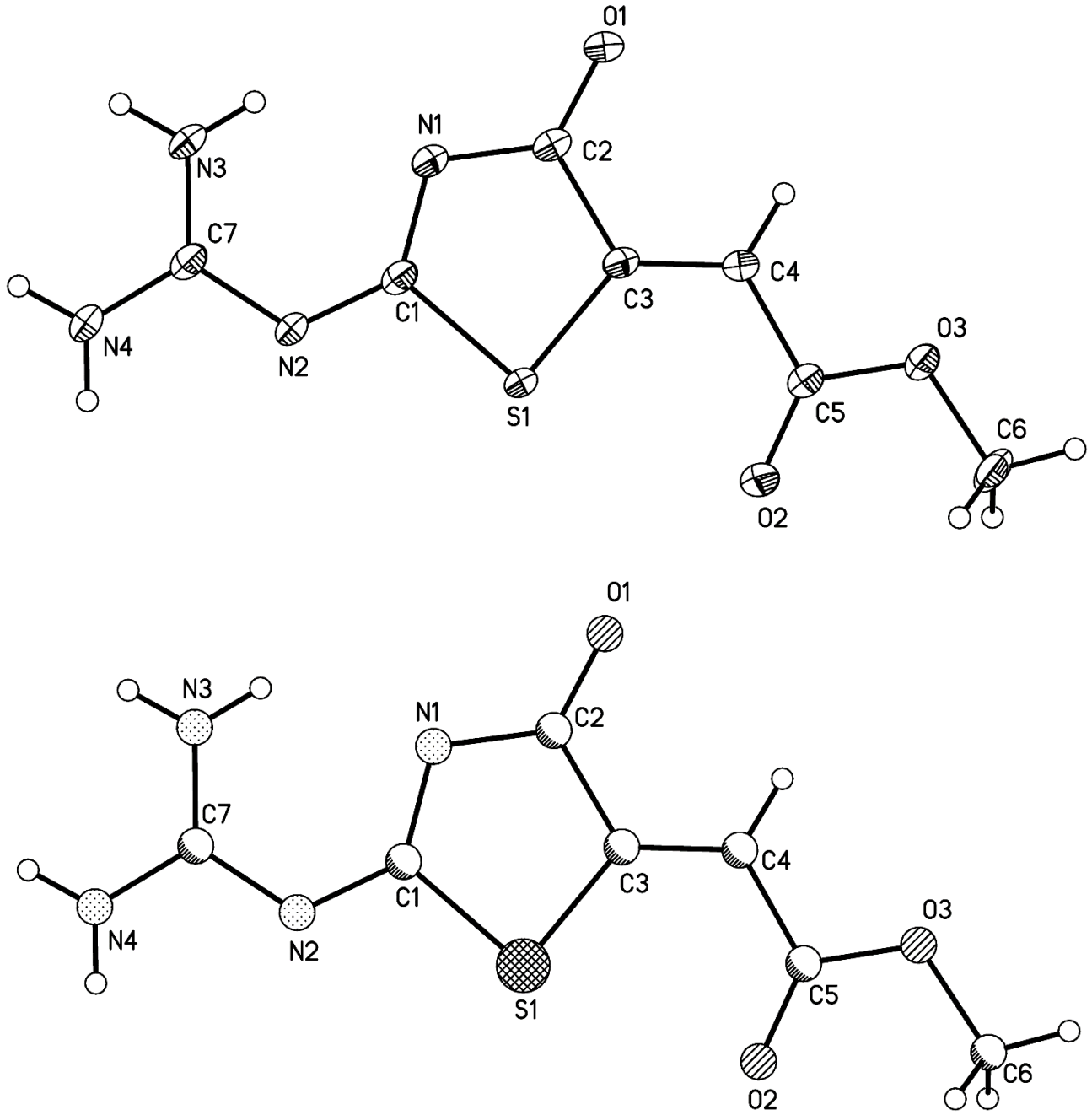


Figure S1. General view of the structure without the DMF solvate molecule (two versions of the image, ellipsoids of atomic displacements are given with a probability of 50%). There are two crystallographically independent molecules of the same structure in the structure; the second molecule is numbered atoms with the index A (not shown in the figure). Structural data deposited as CDCC: 2131042.

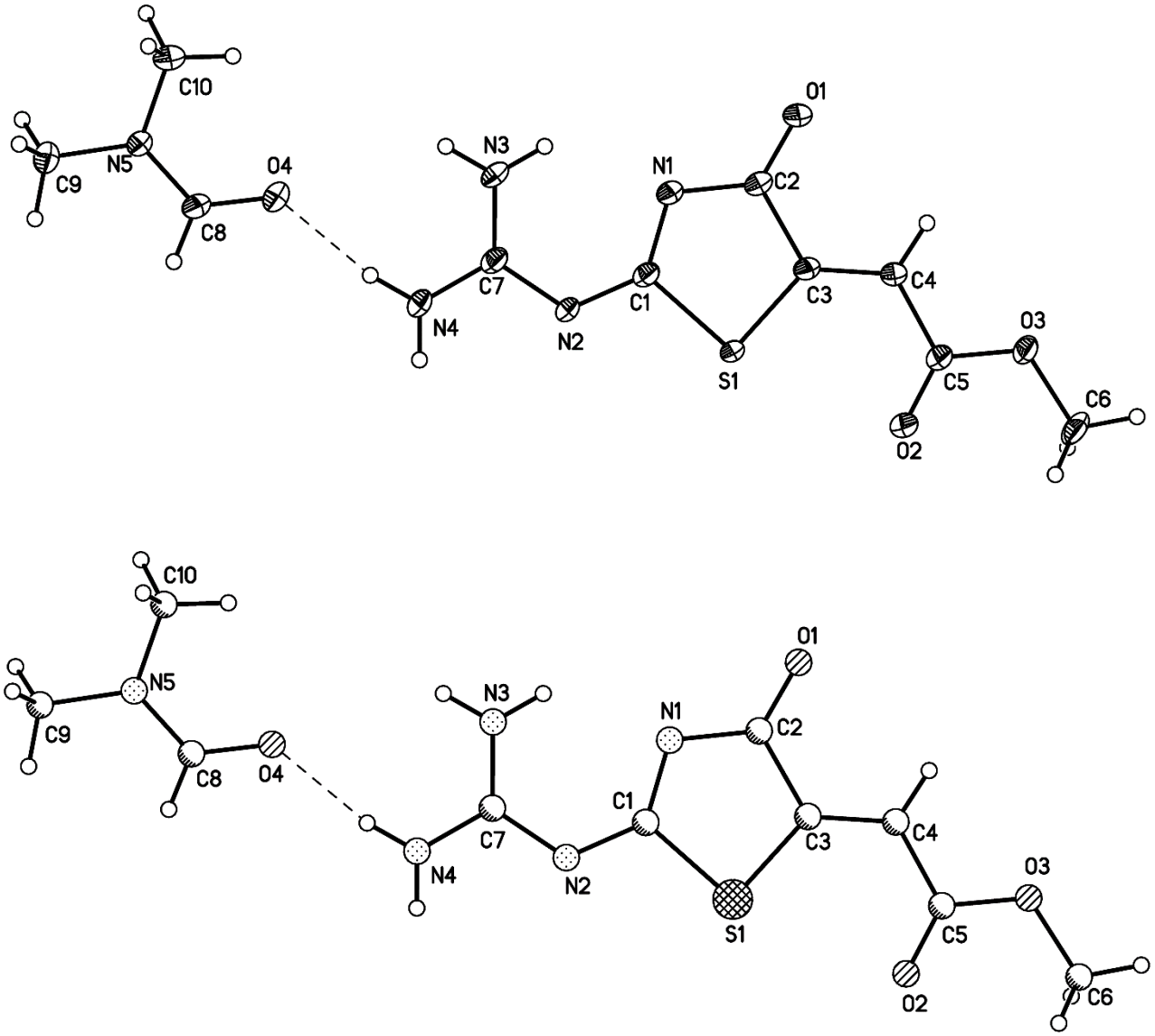


Figure S2. General view of structure 1 with a solvate DMF molecule (two versions of the image, ellipsoids of atomic displacements are given with a probability of 50%). Structural data deposited as CDCC: 2131042.

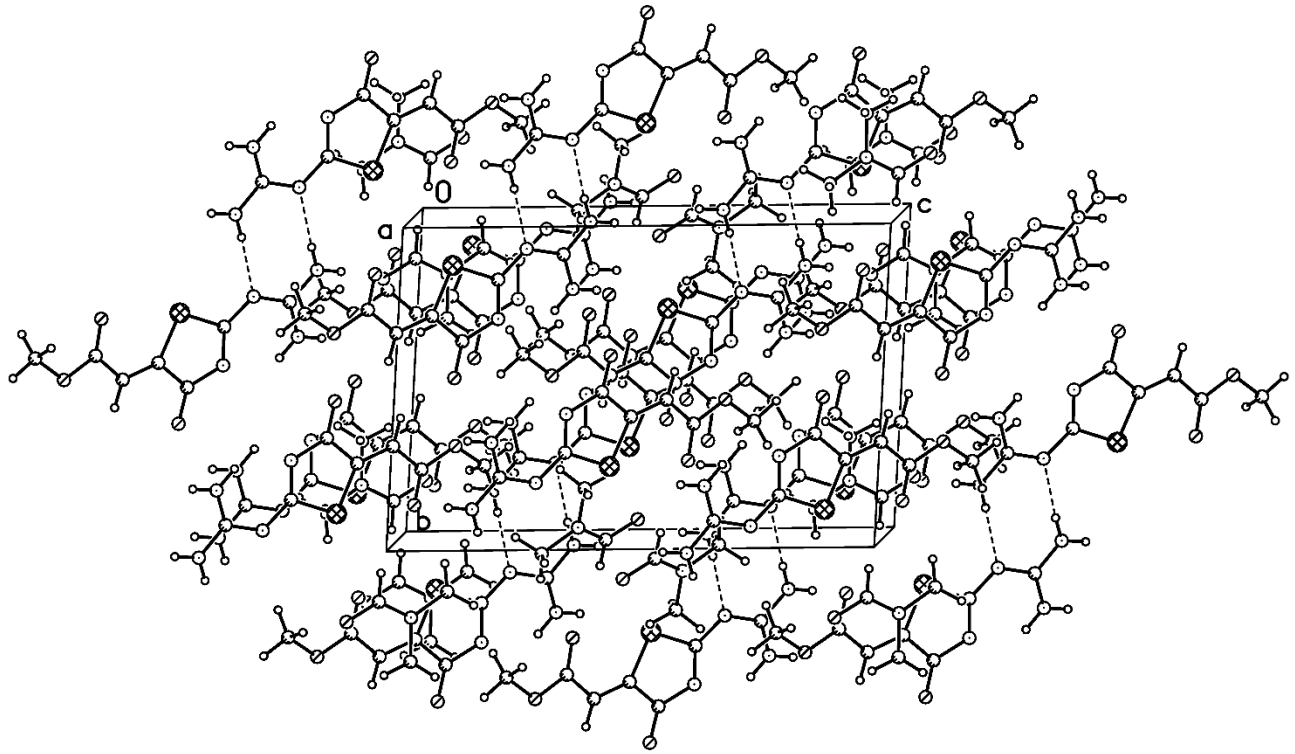


Figure S3. General view of the crystal packing **9**.

Table S1. Crystal data and structure refinement for **9**

Identification code	1
Empirical formula	$C_{10}H_{15}N_5O_4S$
Formula weight	301.33
Temperature/K	120
Crystal system	triclinic
Space group	P-1
a/Å	8.5470(8)
b/Å	11.0867(10)
c/Å	15.3765(14)
α/°	91.309(2)
β/°	98.926(2)
γ/°	108.968(2)
Volume/Å^3	1357.0(2)
Z	4
ρ_{calc}g/cm^3	1.475
μ/mm^{-1}	0.261
F(000)	632.0
Crystal size/mm^3	0.28 × 0.24 × 0.17

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.896 to 61.006
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	18774
Independent reflections	8275 [R_{int} = 0.0320, R_{sigma} = 0.0459]
Data/restraints/parameters	8275/0/367
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1086
Final R indexes [all data]	R_1 = 0.0655, wR_2 = 0.1227
Largest diff. peak/hole / e Å^{-3}	0.61/-0.35

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
S1	6926.4(5)	2750.9(3)	5396.1(2)	17.60(9)
O1	6840.9(14)	6184.4(10)	5482.6(7)	23.9(2)
O2	8471.2(14)	2819(1)	3851.4(7)	23.9(2)
O3	9521.7(14)	4636.9(9)	3189.5(7)	22.7(2)
N1	6059.4(16)	4438.3(11)	6304.1(8)	17.9(2)
N2	5610.3(15)	2345.8(11)	6838.6(8)	17.5(2)
N3	4690.2(17)	3654.2(12)	7754.9(8)	24.3(3)
N4	4567.0(17)	1607.9(12)	8075.2(8)	23.2(3)
C1	6088.7(17)	3243.4(13)	6286.2(9)	16.4(3)
C2	6706.7(18)	5071.7(13)	5617.3(9)	18.0(3)
C3	7320.4(17)	4266.8(13)	5024.1(9)	16.4(3)
C4	8064.4(18)	4733.3(13)	4338.4(9)	18.8(3)
C5	8682.1(18)	3947.1(13)	3782.7(9)	18.0(3)
C6	10134(2)	3926.7(15)	2600.7(10)	25.1(3)
C7	4953.2(18)	2566.0(13)	7560.3(9)	18.1(3)
S1A	6418.5(5)	1393.9(3)	919.9(2)	17.77(9)
O1A	6501.8(16)	4870.5(10)	1076.5(8)	29.0(3)
O2A	8114.7(14)	1538.3(10)	-598.0(7)	23.6(2)
O3A	8815.7(14)	3311.8(10)	-1352.1(7)	24.1(2)
N1A	5671.0(16)	3104.0(11)	1879.1(8)	19.2(2)
N2A	5127.7(15)	977.9(11)	2370.3(8)	17.4(2)
N3A	4264.5(16)	2283.0(12)	3322.6(8)	20.4(3)

N4A	4108.8(16)	215.6(12)	3609.9(8)	22.1(3)
C1A	5636.2(17)	1891.5(13)	1837.2(9)	16.6(3)
C2A	6318.9(19)	3745.7(14)	1193.5(9)	20.0(3)
C3A	6852.3(18)	2923.5(13)	568.8(9)	17.6(3)
C4A	7571.7(19)	3397.9(14)	-121.9(9)	20.3(3)
C5A	8170.5(19)	2634.7(14)	-703.9(9)	19.1(3)
C6A	9512(2)	2658.1(16)	-1940(1)	27.7(3)
C7A	4510.3(17)	1194.8(13)	3110.0(9)	17.2(3)
O4	7136.3(16)	8002.6(11)	10629.1(8)	31.1(3)
N5	8180.9(16)	8054.6(12)	9352.2(8)	19.5(2)
C8	7708.2(19)	8583.4(14)	10010.2(10)	21.3(3)
C9	8917(2)	8807.2(15)	8664.9(10)	23.3(3)
C10	8009(2)	6703.2(14)	9309.0(11)	25.8(3)
O4A	2692.7(15)	757(1)	4982.5(7)	26.4(2)
N5A	1291.8(16)	606.2(11)	6143.2(8)	19.7(2)
C8A	2098.9(19)	172.4(14)	5597.9(9)	20.9(3)
C9A	576(2)	-154.1(16)	6833.4(11)	27.3(3)
C10A	1045(2)	1829.1(15)	6039.1(11)	28.2(3)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	25.91(19)	15.42(16)	16.42(16)	1.59(12)	9.54(13)	10.82(14)
O1	37.7(6)	17.0(5)	23.9(5)	2.5(4)	12.7(5)	14.8(5)
O2	33.3(6)	18.3(5)	26.5(5)	3.4(4)	15.0(5)	12.6(4)
O3	31.8(6)	18.5(5)	20.8(5)	0.7(4)	14.7(4)	8.0(4)
N1	23.3(6)	17.5(6)	16.2(5)	-0.1(4)	6.0(5)	10.0(5)
N2	23.7(6)	17.4(5)	15.0(5)	0.7(4)	8.8(5)	9.4(5)
N3	36.3(7)	23.8(6)	20.6(6)	0.8(5)	14.7(5)	16.4(6)
N4	34.6(7)	22.4(6)	18.2(6)	2.1(5)	14.1(5)	12.8(5)
C1	17.5(6)	18.9(6)	14.6(6)	-1.2(5)	3.6(5)	8.4(5)
C2	21.2(7)	17.5(6)	17.7(6)	-1.6(5)	5.5(5)	8.7(5)
C3	20.0(7)	15.1(6)	16.1(6)	-0.6(5)	4.3(5)	8.3(5)
C4	26.3(7)	14.3(6)	18.9(6)	1.0(5)	8.1(6)	8.9(5)
C5	21.4(7)	17.4(6)	17.1(6)	-0.2(5)	6.4(5)	7.7(5)
C6	29.0(8)	28.1(8)	20.0(7)	-3.9(6)	13.0(6)	8.3(7)
C7	20.4(7)	21.0(7)	15.2(6)	-1.6(5)	5.0(5)	9.1(6)

S1A	26.01(19)	15.84(16)	15.98(16)	0.92(12)	8.69(13)	10.75(14)
O1A	47.1(7)	18.3(5)	31.0(6)	4.4(4)	19.7(5)	17.6(5)
O2A	35.8(6)	20.0(5)	22.1(5)	3.3(4)	12.0(5)	15.4(5)
O3A	37.6(6)	23.3(5)	21.1(5)	7.0(4)	16.8(5)	17.7(5)
N1A	24.9(6)	17.7(6)	18.6(6)	-0.1(4)	8.2(5)	10.2(5)
N2A	21.6(6)	19.0(6)	14.8(5)	0.0(4)	7.0(5)	9.2(5)
N3A	26.9(6)	21.3(6)	17.2(5)	-1.8(4)	8.1(5)	11.8(5)
N4A	31.6(7)	22.3(6)	18.6(6)	2.3(5)	13.4(5)	12.9(5)
C1A	17.9(6)	19.2(6)	14.8(6)	-1.2(5)	4.9(5)	8.2(5)
C2A	26.0(7)	18.9(7)	19.6(7)	0.5(5)	8.0(6)	11.7(6)
C3A	23.5(7)	16.1(6)	16.8(6)	0.8(5)	5.5(5)	10.8(5)
C4A	28.7(8)	17.0(6)	20.3(7)	2.2(5)	9.1(6)	12.2(6)
C5A	24.6(7)	19.8(7)	16.6(6)	2.0(5)	6.7(5)	10.9(6)
C6A	40.1(9)	33.9(8)	21.3(7)	6.2(6)	18.5(7)	22.5(7)
C7A	18.8(7)	19.3(7)	14.9(6)	-1.8(5)	4.5(5)	8.0(5)
O4	46.1(7)	33.8(6)	26.6(6)	9.7(5)	22.2(5)	23.6(6)
N5	26.6(6)	19.7(6)	16.9(6)	2.6(4)	8.6(5)	11.8(5)
C8	27.5(8)	21.9(7)	20.2(7)	1.4(5)	8.2(6)	13.9(6)
C9	28.1(8)	27.2(8)	18.0(7)	4.6(6)	8.7(6)	11.4(6)
C10	36.0(9)	20.3(7)	27.3(8)	1.3(6)	11.3(7)	15.0(7)
O4A	36.6(6)	26.5(6)	22.4(5)	2.9(4)	16.4(5)	14.0(5)
N5A	25.9(6)	18.8(6)	20.3(6)	4.4(4)	11.9(5)	11.4(5)
C8A	25.4(7)	19.2(7)	21.3(7)	0.2(5)	8.5(6)	9.7(6)
C9A	32.3(9)	28.9(8)	25.7(8)	9.2(6)	16.0(7)	11.5(7)
C10A	41.5(10)	22.6(7)	28.7(8)	2.8(6)	13.5(7)	18.5(7)

Table S4. Bond Lengths for **9**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.7912(14)	O3A	C5A	1.3403(17)
S1	C3	1.7324(14)	O3A	C6A	1.4540(17)
O1	C2	1.2268(17)	N1A	C1A	1.3347(17)
O2	C5	1.2139(17)	N1A	C2A	1.3724(18)
O3	C5	1.3454(16)	N2A	C1A	1.3225(17)
O3	C6	1.4475(17)	N2A	C7A	1.3735(17)
N1	C1	1.3328(17)	N3A	C7A	1.3321(17)
N1	C2	1.3700(17)	N4A	C7A	1.3286(18)
N2	C1	1.3271(18)	C2A	C3A	1.5255(18)

N2	C7	1.3698(17)	C3A	C4A	1.3419(19)
N3	C7	1.3329(18)	C4A	C5A	1.4724(19)
N4	C7	1.3250(18)	O4	C8	1.2357(17)
C2	C3	1.5228(18)	N5	C8	1.3359(17)
C3	C4	1.3426(19)	N5	C9	1.4542(18)
C4	C5	1.4743(18)	N5	C10	1.4559(18)
S1A	C1A	1.7995(13)	O4A	C8A	1.2394(17)
S1A	C3A	1.7320(14)	N5A	C8A	1.3367(17)
O1A	C2A	1.2264(17)	N5A	C9A	1.4555(18)
O2A	C5A	1.2167(17)	N5A	C10A	1.4469(19)

Table S5. Bond Angles for **9**

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C3	S1	C1	89.18(6)	N1A	C1A	S1A	116.07(10)
C5	O3	C6	115.13(11)	N2A	C1A	S1A	113.48(10)
C1	N1	C2	111.86(11)	N2A	C1A	N1A	130.45(12)
C1	N2	C7	121.32(12)	O1A	C2A	N1A	125.47(13)
N1	C1	S1	116.32(10)	O1A	C2A	C3A	121.29(13)
N2	C1	S1	113.68(10)	N1A	C2A	C3A	113.23(12)
N2	C1	N1	130.00(12)	C2A	C3A	S1A	109.46(10)
O1	C2	N1	125.25(12)	C4A	C3A	S1A	128.64(11)
O1	C2	C3	121.43(12)	C4A	C3A	C2A	121.88(12)
N1	C2	C3	113.30(11)	C3A	C4A	C5A	122.51(13)
C2	C3	S1	109.31(9)	O2A	C5A	O3A	124.49(13)
C4	C3	S1	128.29(11)	O2A	C5A	C4A	124.17(13)
C4	C3	C2	122.39(12)	O3A	C5A	C4A	111.33(12)
C3	C4	C5	121.59(13)	N3A	C7A	N2A	124.14(13)
O2	C5	O3	123.90(12)	N4A	C7A	N2A	115.39(12)
O2	C5	C4	124.50(13)	N4A	C7A	N3A	120.44(12)
O3	C5	C4	111.61(12)	C8	N5	C9	121.50(12)
N3	C7	N2	124.10(13)	C8	N5	C10	120.95(12)
N4	C7	N2	115.64(12)	C9	N5	C10	117.54(12)
N4	C7	N3	120.27(13)	O4	C8	N5	124.29(14)
C3A	S1A	C1A	89.20(6)	C8A	N5A	C9A	121.30(12)
C5A	O3A	C6A	115.47(11)	C8A	N5A	C10A	120.66(12)
C1A	N1A	C2A	112.02(11)	C10A	N5A	C9A	117.99(12)
C1A	N2A	C7A	121.31(12)	O4A	C8A	N5A	124.36(14)

Table S6. Hydrogen Bonds for **9**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N3	H3A	O1A[1]	0.88	2.18	2.9085(16)	140.3
N3	H3B	N1	0.88	2.06	2.7091(17)	129.9
N4	H4A	O4[2]	0.88	1.88	2.7467(16)	166.4
N3A	H3AA	O1[1]	0.88	2.21	2.9317(15)	138.6
N3A	H3AB	N1A	0.88	2.07	2.7220(17)	129.7
N4A	H4AA	O4A	0.88	1.87	2.7362(16)	167.0

[1]1-X,1-Y,1-Z; [2]1-X,1-Y,2-Z

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **9**

Atom	*x*	*y*	*z*	U(eq)
H3A	4258	3739	8227	29
H3B	4948	4288	7411	29
H4A	4135	1689	8548	28
H4B	4742	891	7945	28
H4	8196	5591	4208	23
H6A	10717	4501	2191	38
H6B	9185	3233	2267	38
H6C	10914	3566	2947	38
H3AA	3834	2357	3797	25
H3AB	4533	2928	2989	25
H4AA	3677	283	4085	27
H4AB	4274	-501	3466	27
H4AC	7699	4259	-240	24
H6AA	10458	2460	-1603	42
H6AB	9903	3211	-2405	42
H6AC	8645	1863	-2208	42
H8	7819	9464	10002	26
H9A	10085	8837	8703	35
H9B	8886	9678	8744	35
H9C	8278	8413	8085	35
H10A	7255	6272	8764	39
H10B	7541	6316	9819	39
H10C	9113	6613	9315	39
H8A	2226	-638	5688	25

H9AA	855	-944	6839	41
H9AB	-647	-366	6719	41
H9AC	1039	336	7407	41
H10D	-160	1702	5920	42
H10E	1563	2227	5545	42
H10F	1566	2387	6582	42

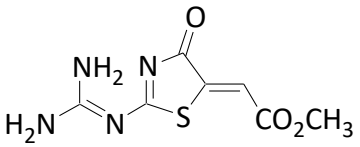
Experimental

Single crystals of $C_{10}H_{15}N_5O_4S$ were prism. A suitable crystal was selected, and X-ray dataset was collected on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341], the structure was solved with the ShelXT [Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8] structure solution program using Intrinsic Phasing and refined with the ShelXL [Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8] refinement package using Least Squares minimisation.

Crystal structure determination of [Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341]

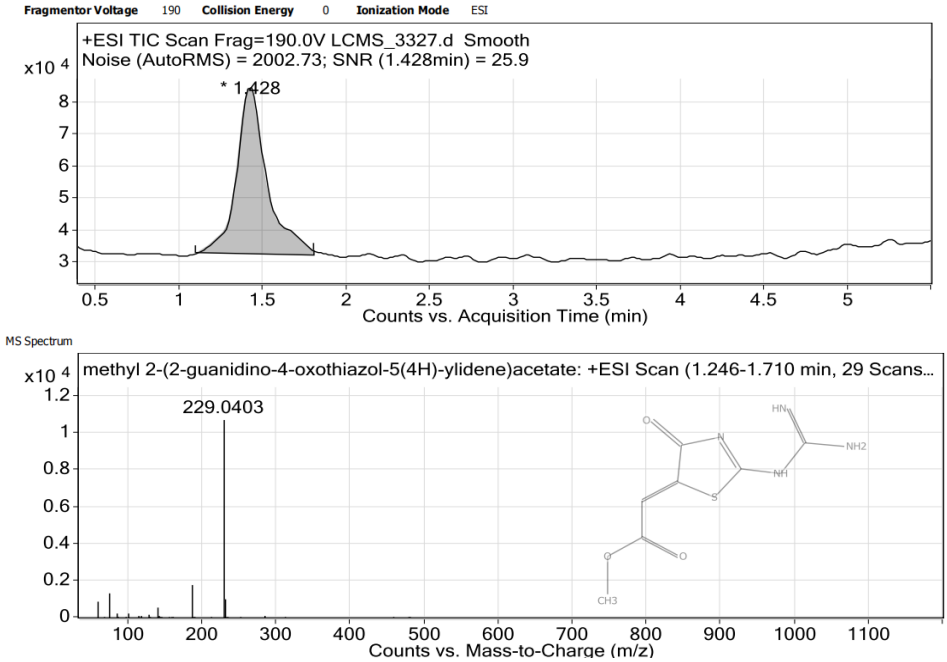
Crystal Data for $C_{10}H_{15}N_5O_4S$ (*M* =301.33 g/mol): triclinic, space group P-1 (no. 2), a = 8.5470(8) Å, b = 11.0867(10) Å, c = 15.3765(14) Å, α = 91.309(2)°, β = 98.926(2)°, γ = 108.968(2)°, V = 1357.0(2) Å^3, Z = 4, T = 120 K, μ(MoKα) = 0.261 mm^{-1}, *Dcalc* = 1.475 g/cm^3, 18774 reflections measured (3.896° ≤ 2Θ ≤ 61.006°), 8275 unique (R_{int} = 0.0320, R_{sigma} = 0.0459) which were used in all calculations. The final R_1 was 0.0424 (I > 2σ(I)) and wR_2 was 0.1227 (all data). Structural data deposited as CDCC: 2131042.

IR, ^{1}H and ^{13}C NMR spectra and data LCMS for compounds 9, 17 a-f

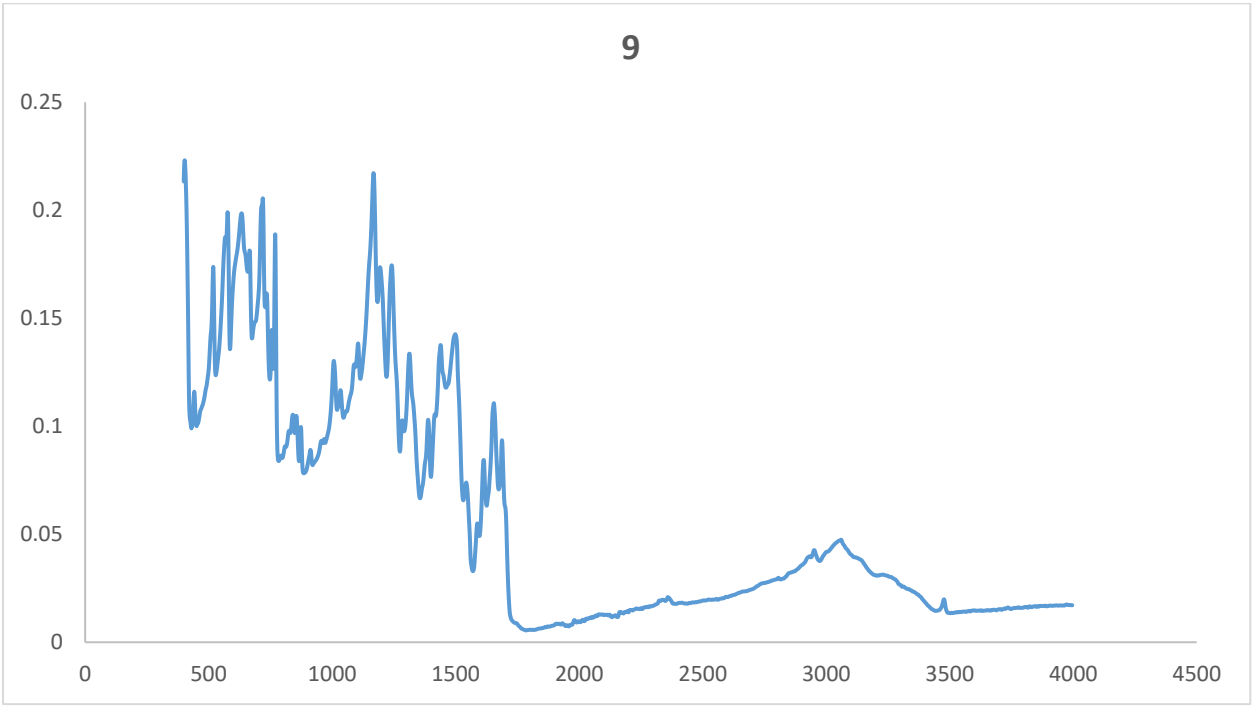


9

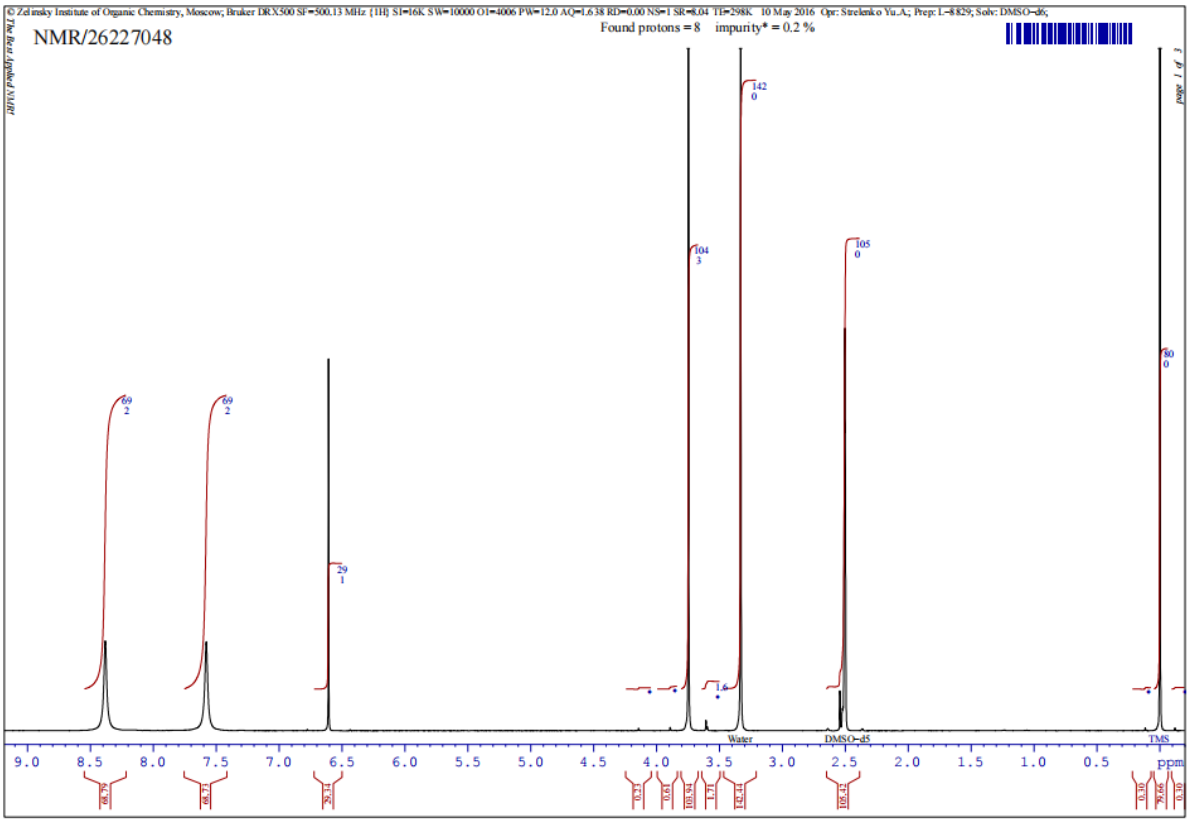
Data LCMS for compound **9**



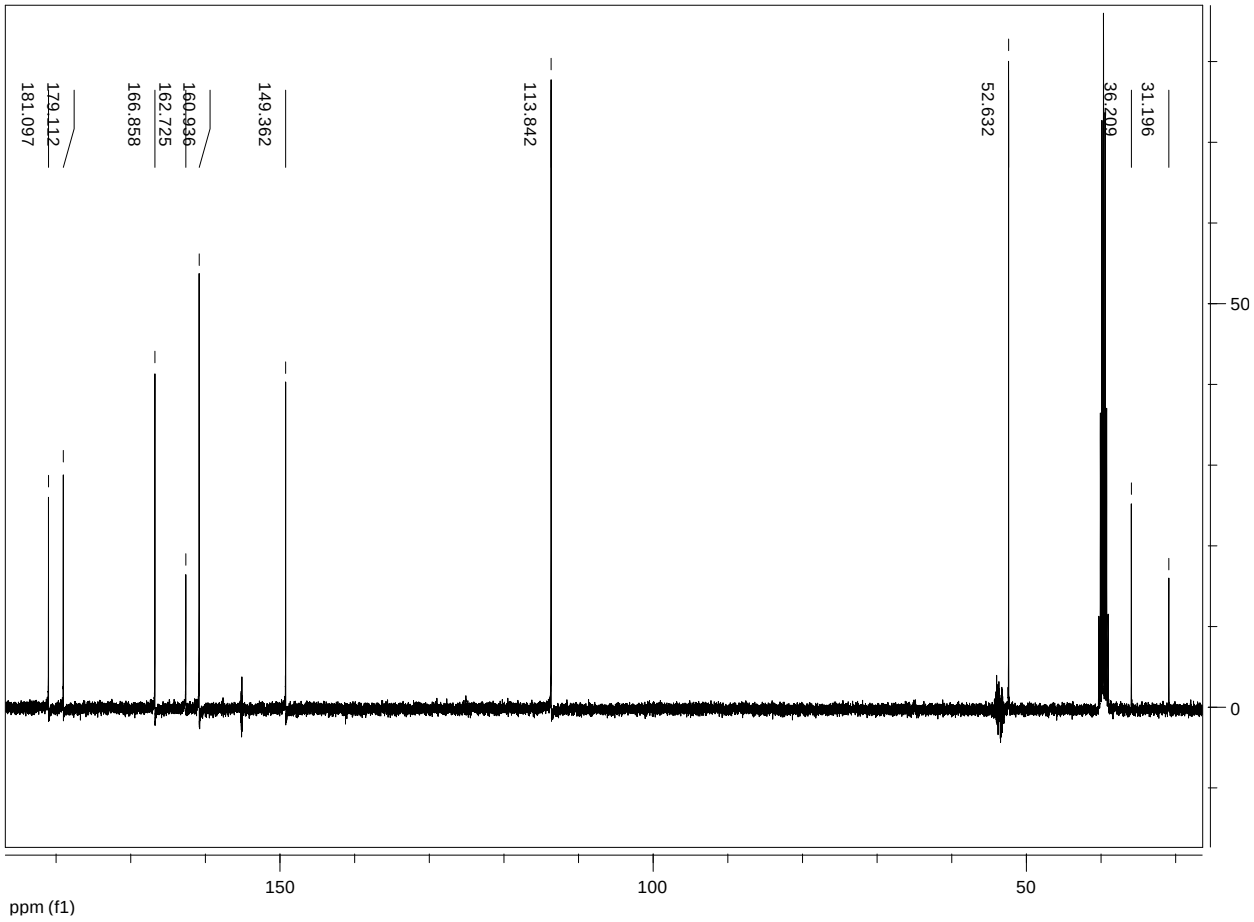
IR spectra for compound **9**

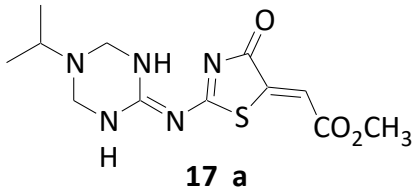


^{1}H NMR spectra for compound **9**



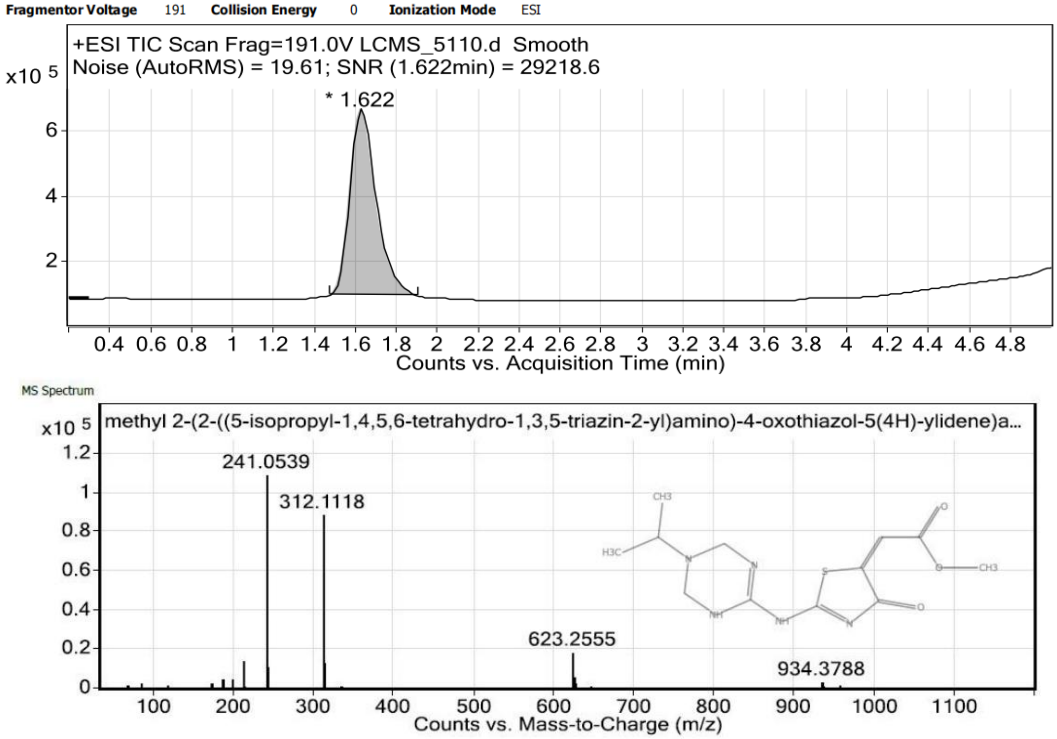
^{13}C NMR spectra for compound **9**



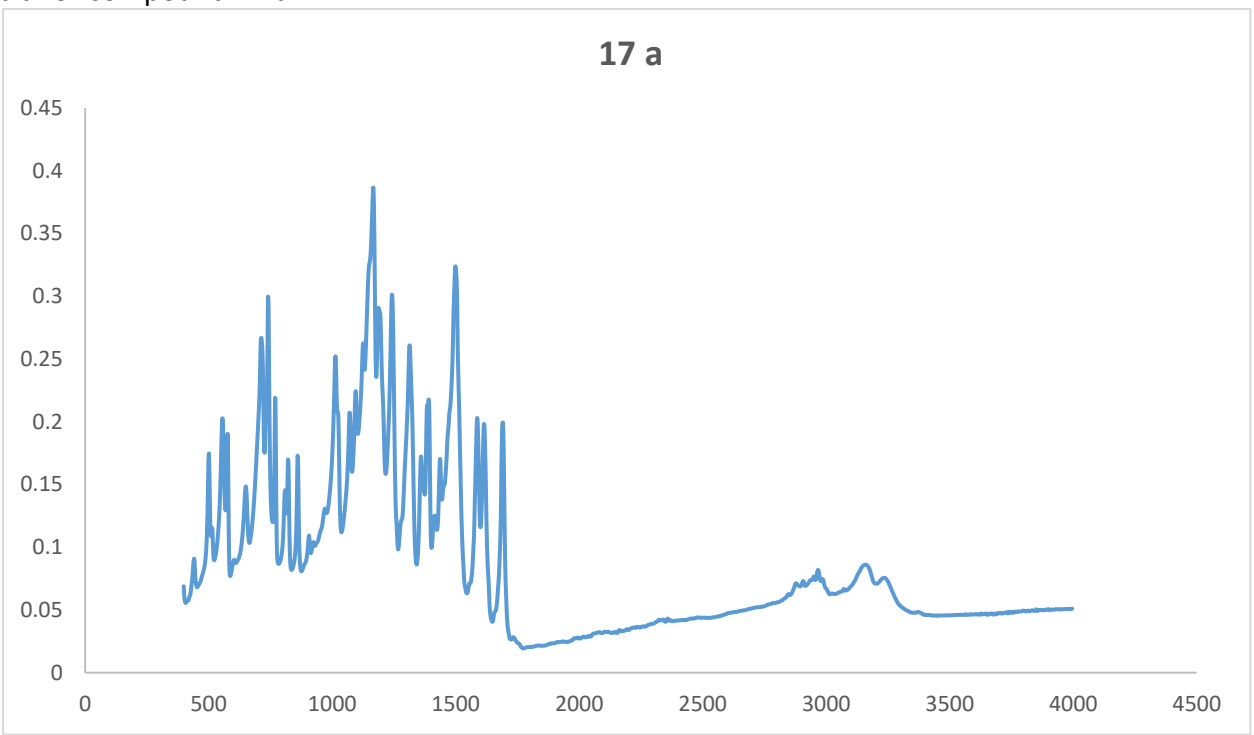


17 a

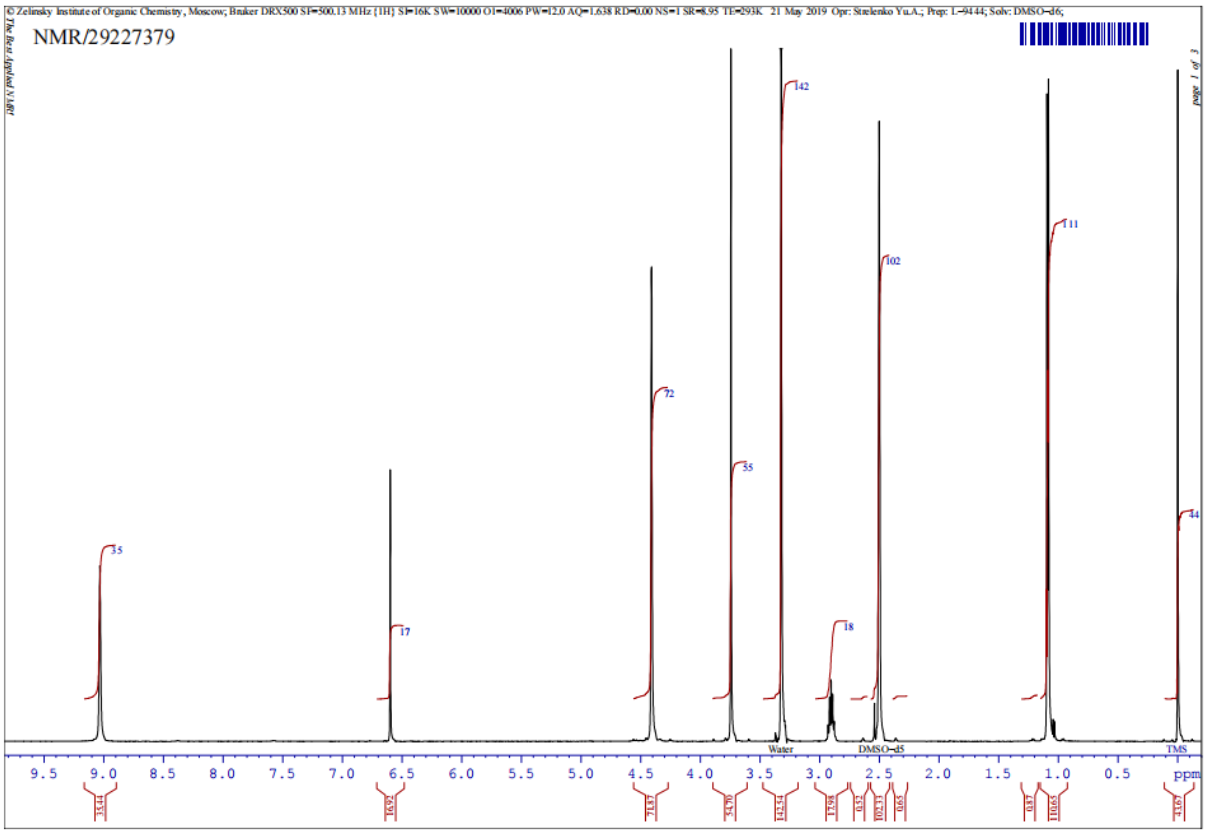
Data LCMS for compound **17 a**



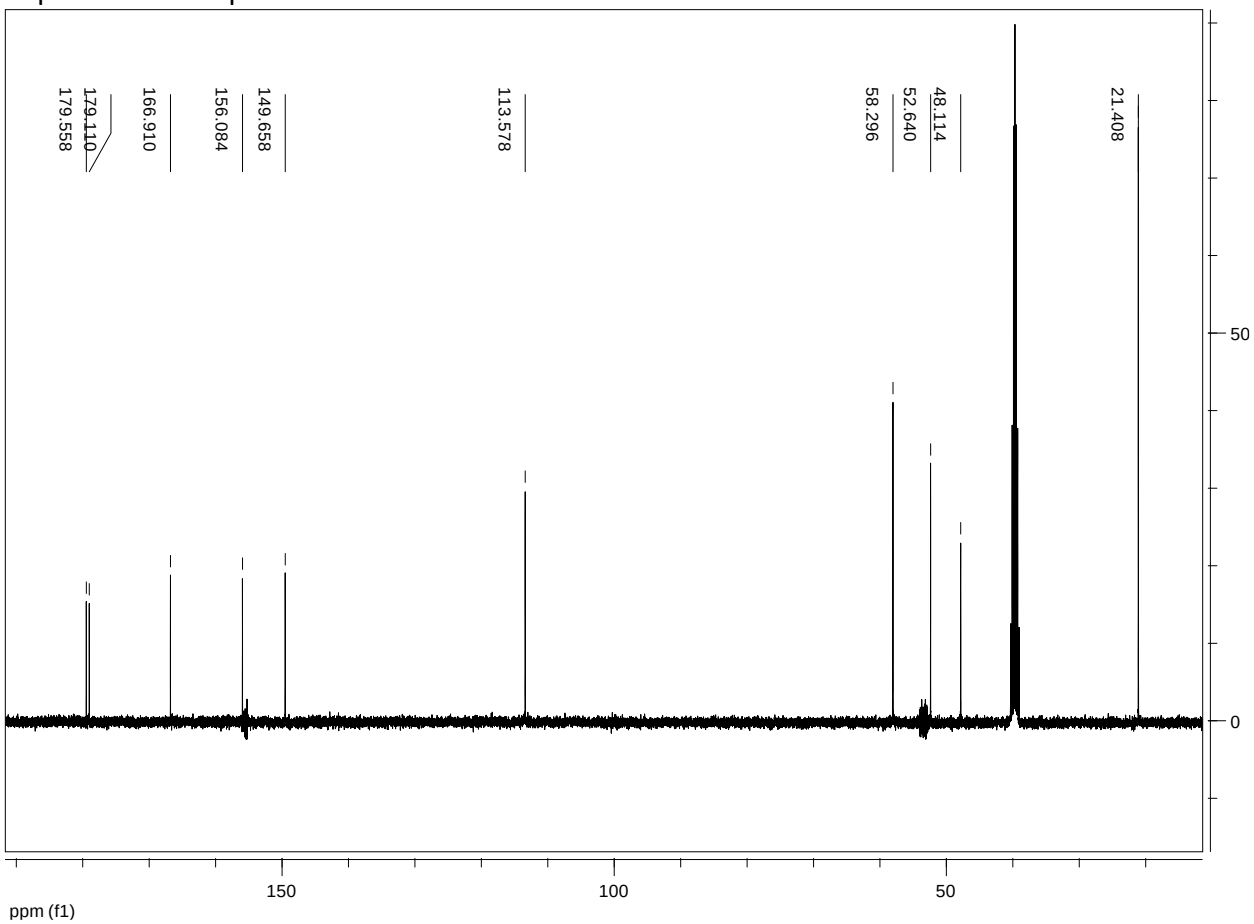
IR spectra for compound **17 a**

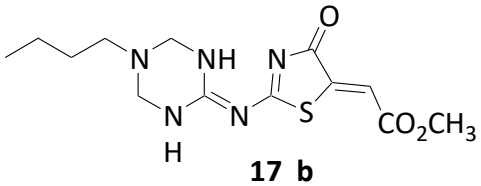


^{1}H NMR spectra for compound **17 a**



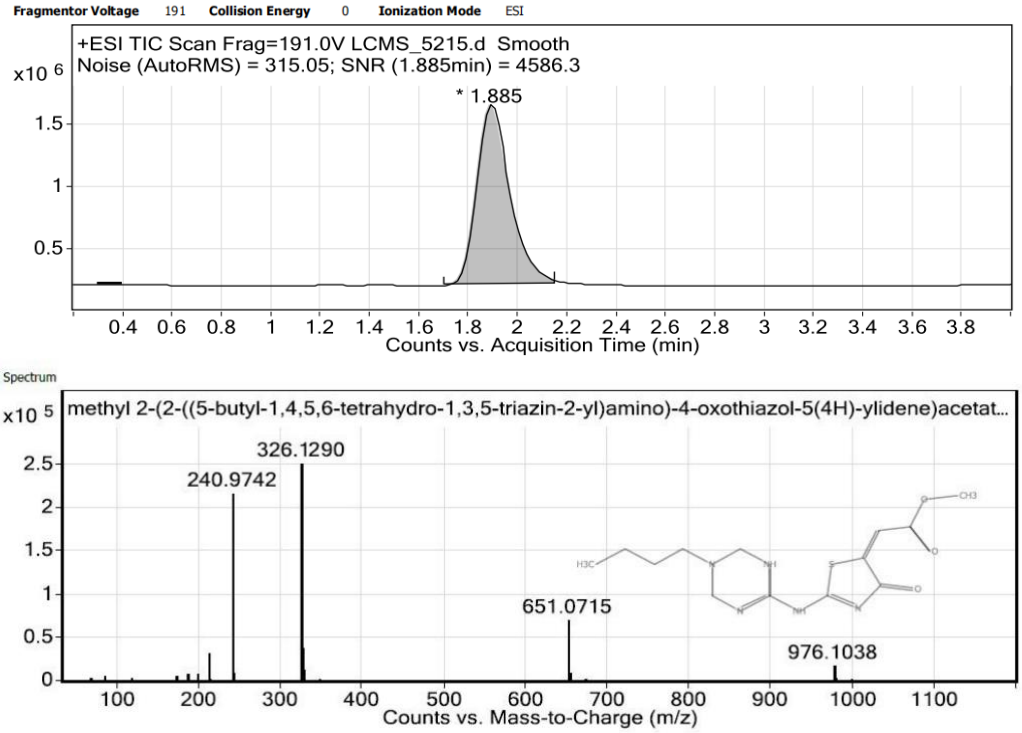
^{13}C NMR spectra for compound **17 a**



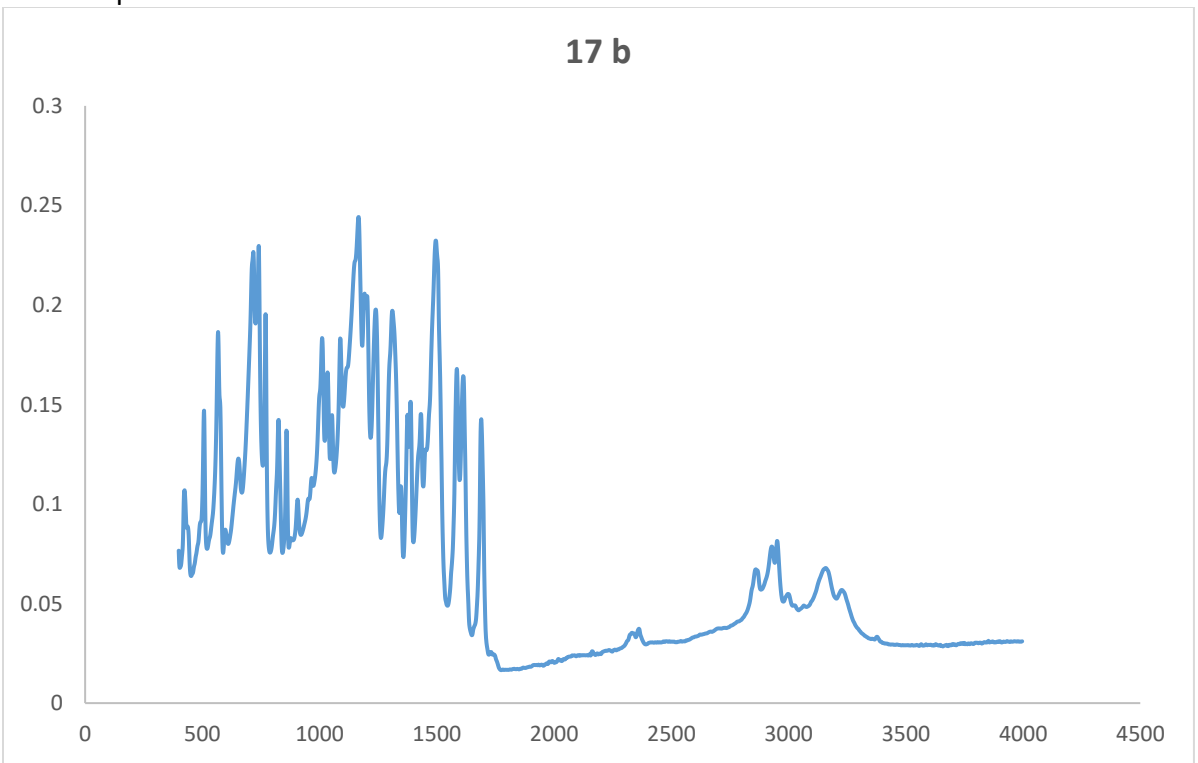


17 b

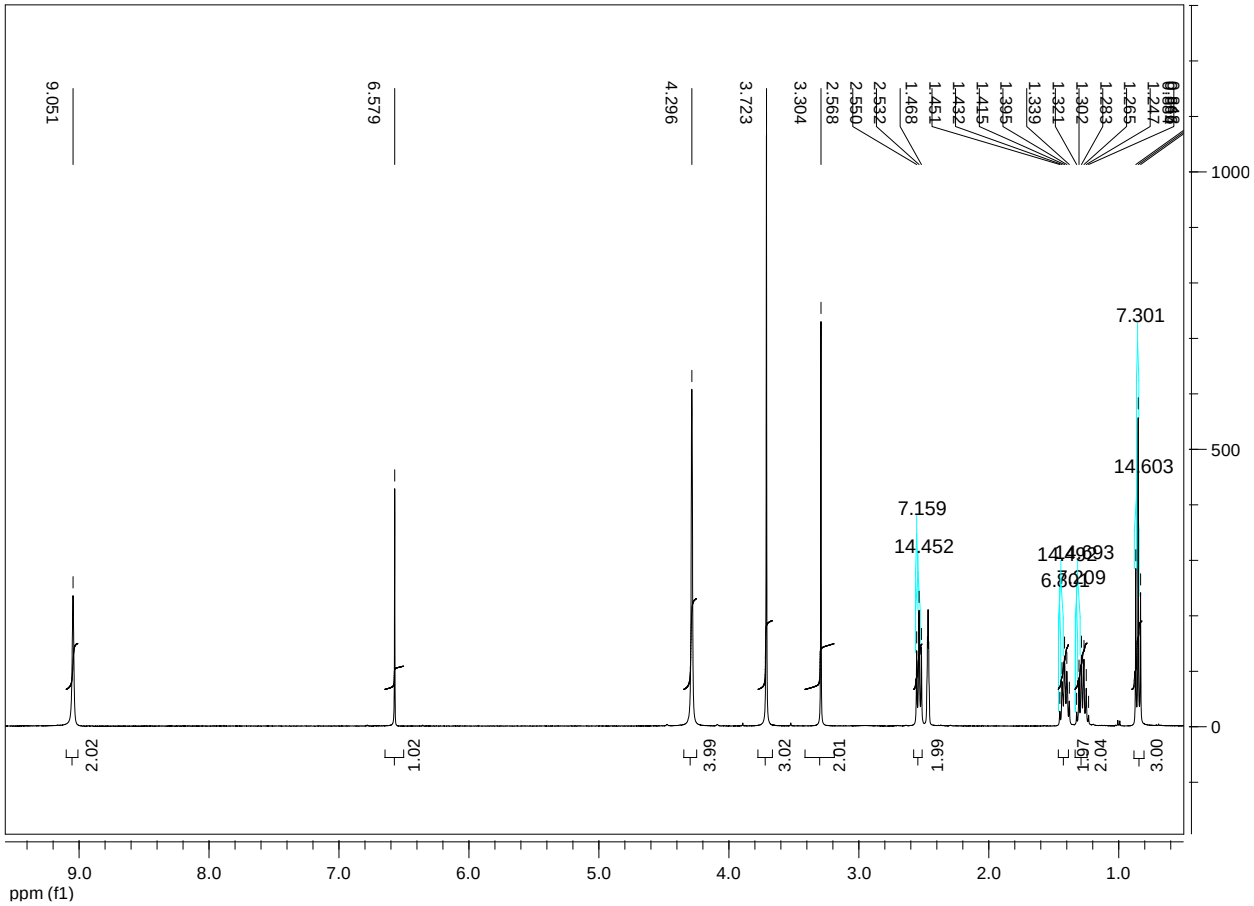
Data LCMS for compound **17 b**



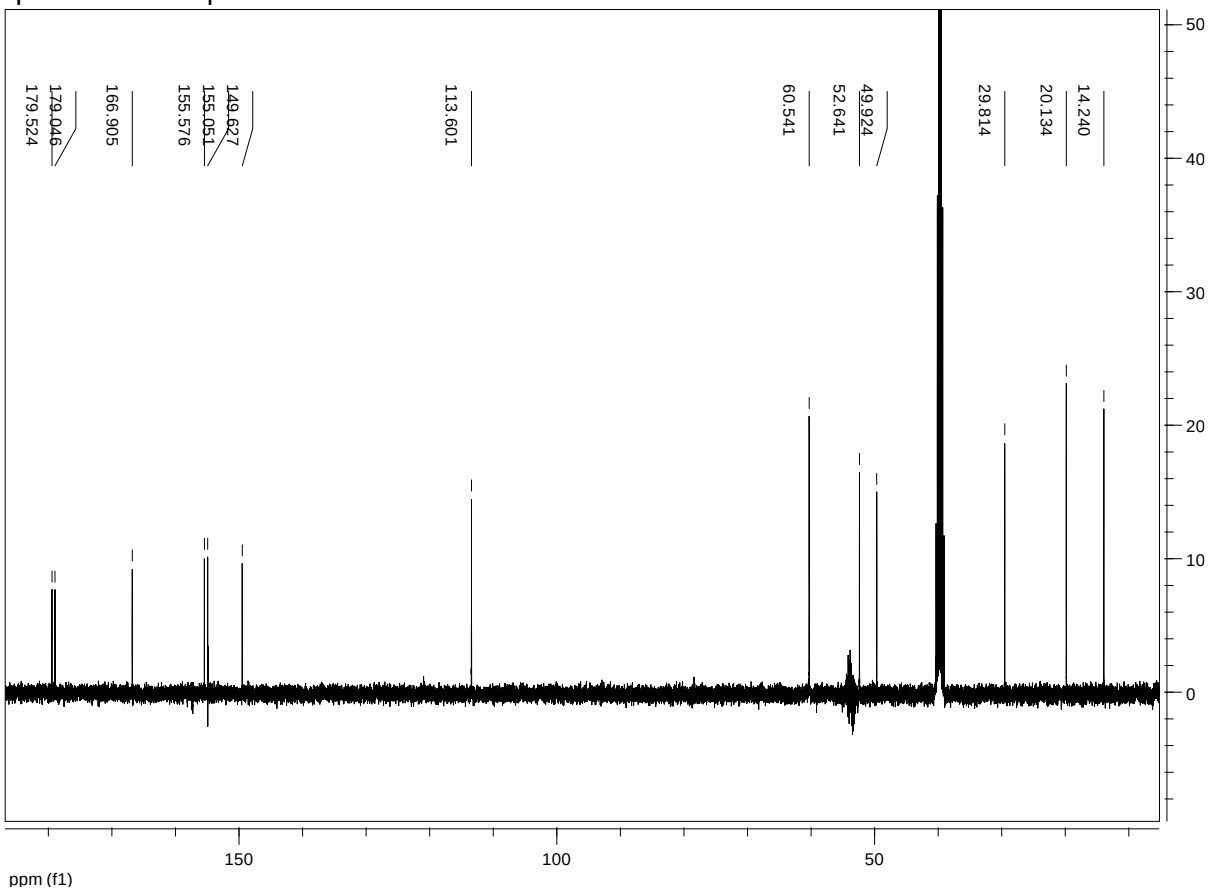
IR spectra for compound **17 b**

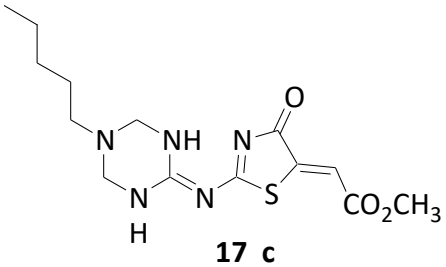


^{1}H NMR spectra for compound **17 b**



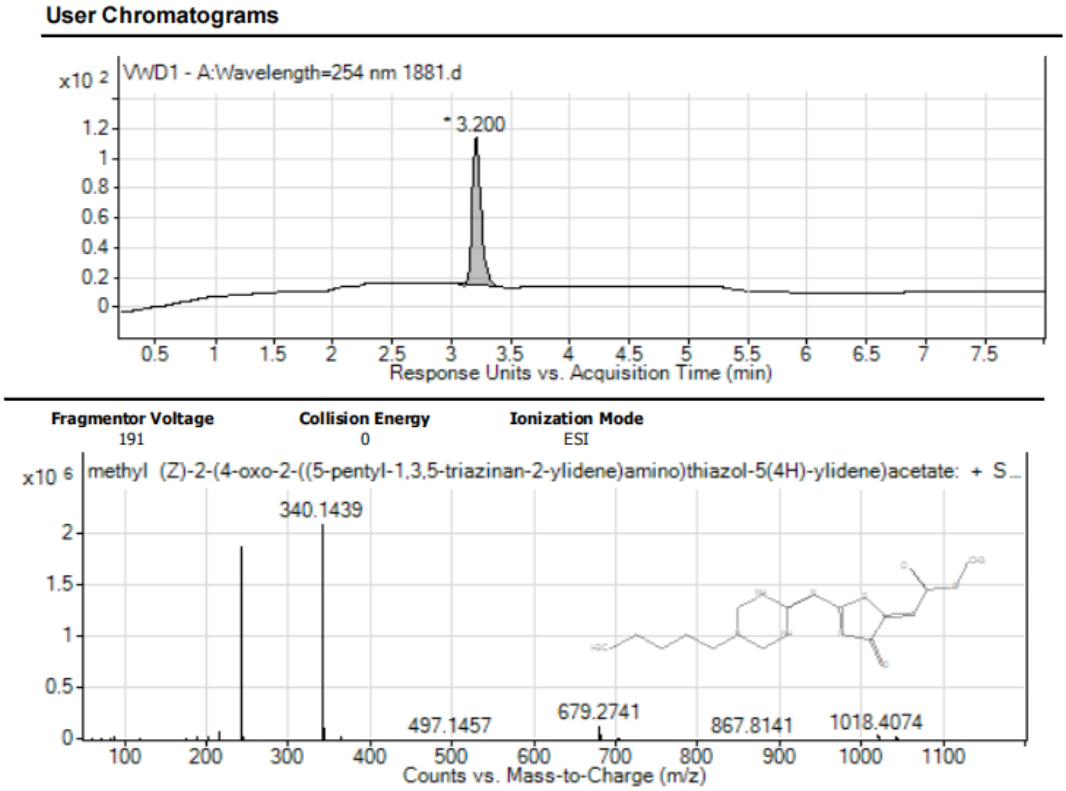
^{13}C NMR spectra for compound **17 b**



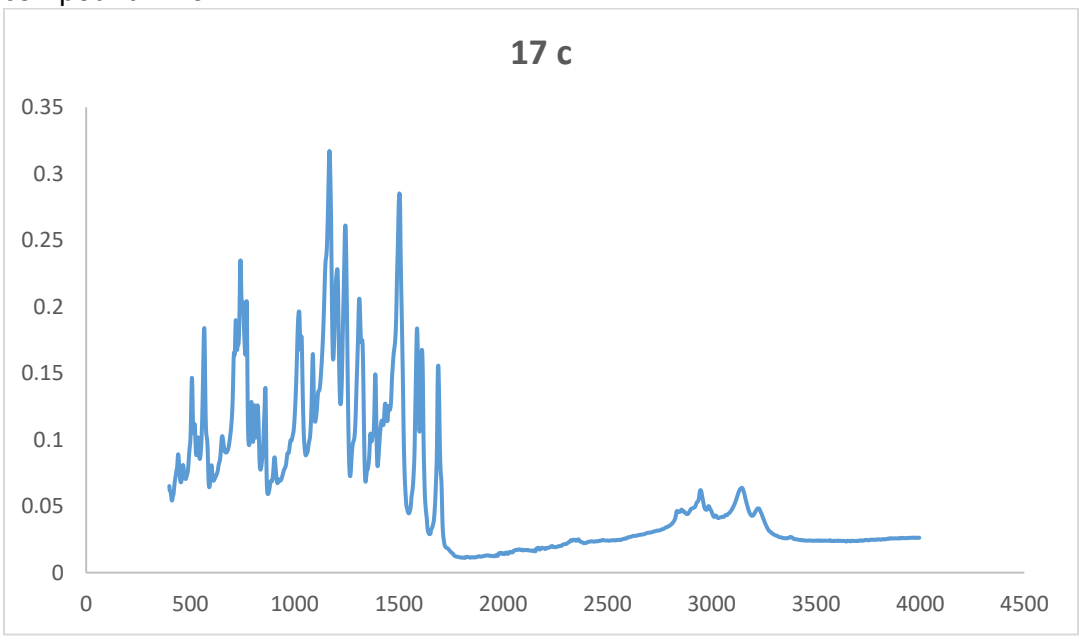


17 c

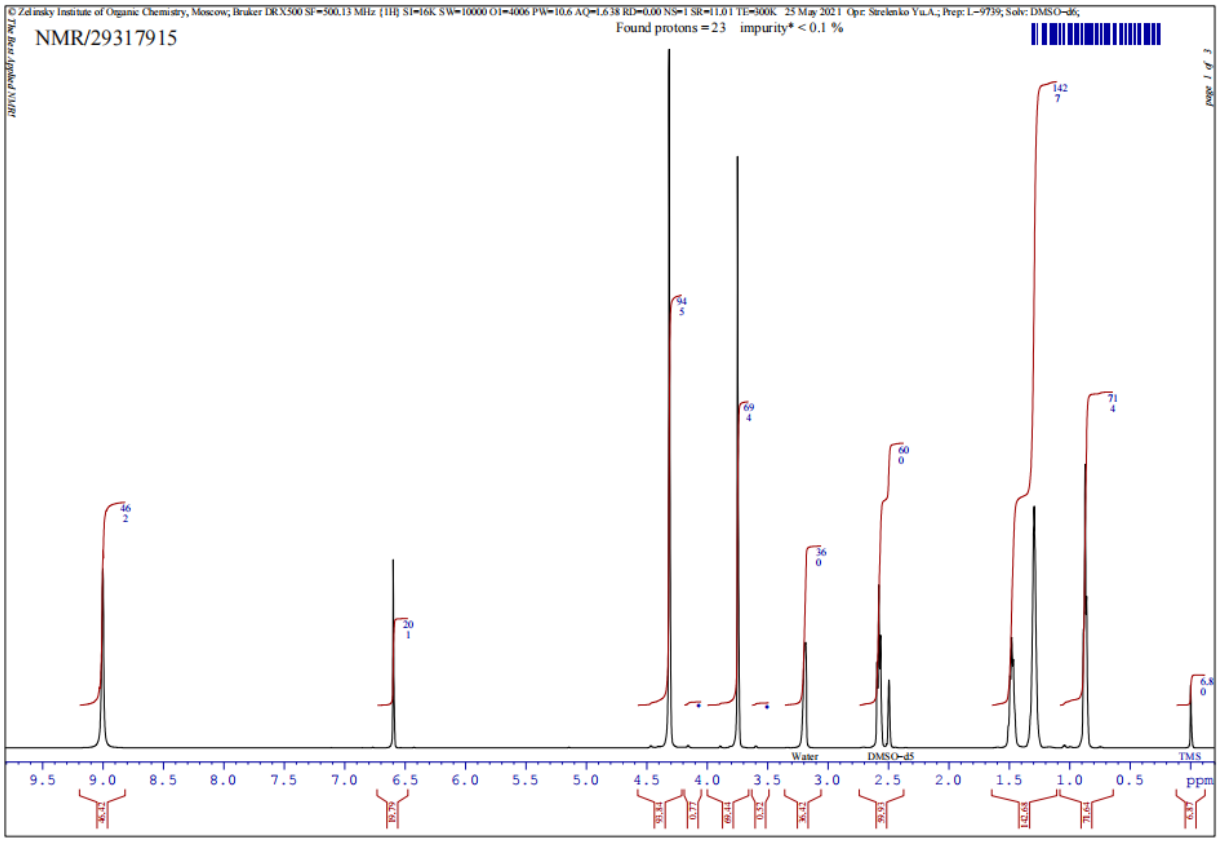
Data LCMS for compound **17 c**



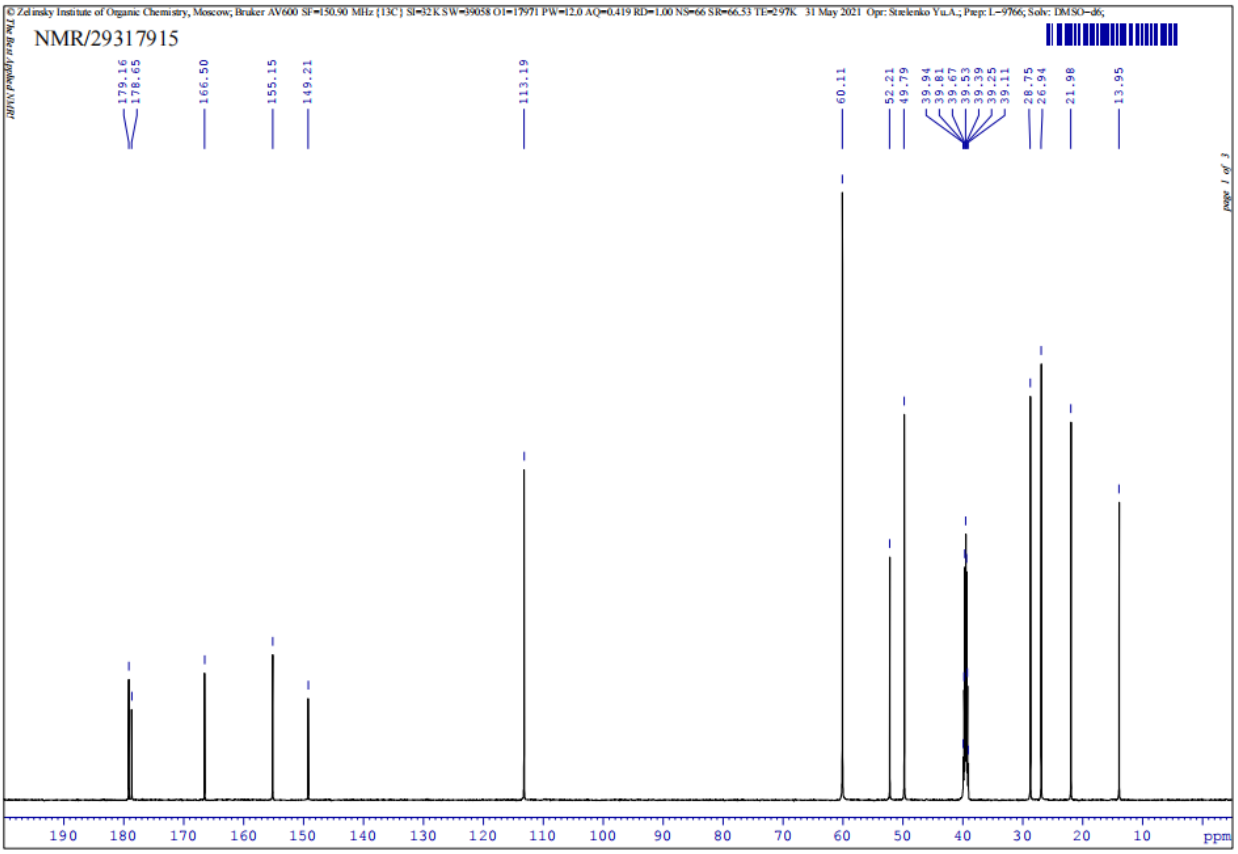
IR spectra for compound **17 c**

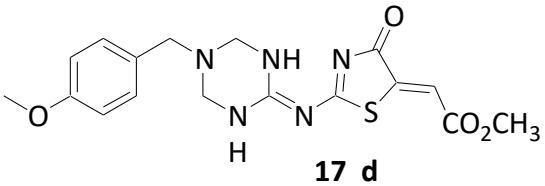


^{1}H NMR spectra for compound **17 c**



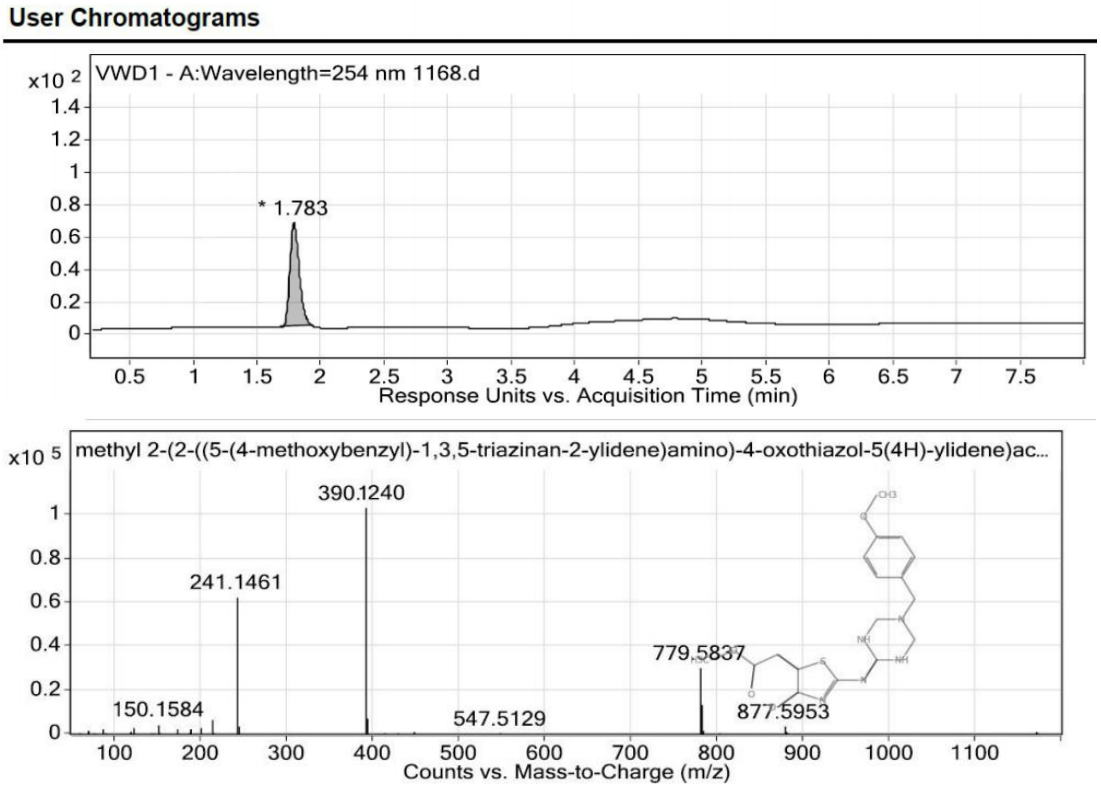
^{13}C NMR spectra for compound **17 c**



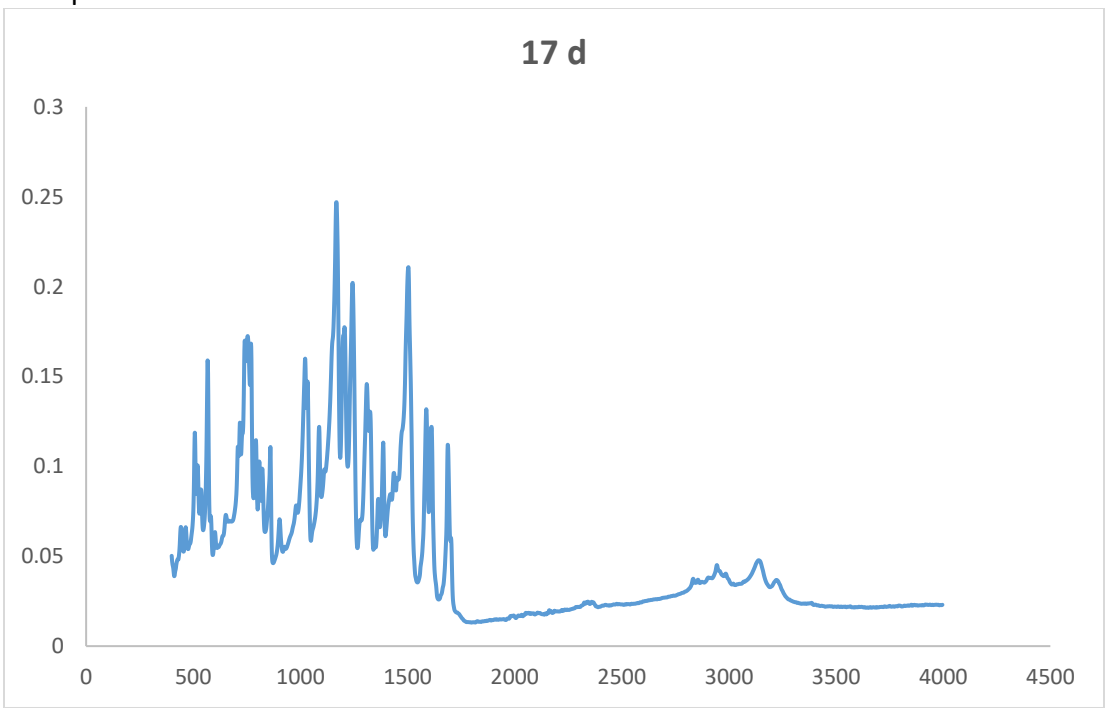


17 d

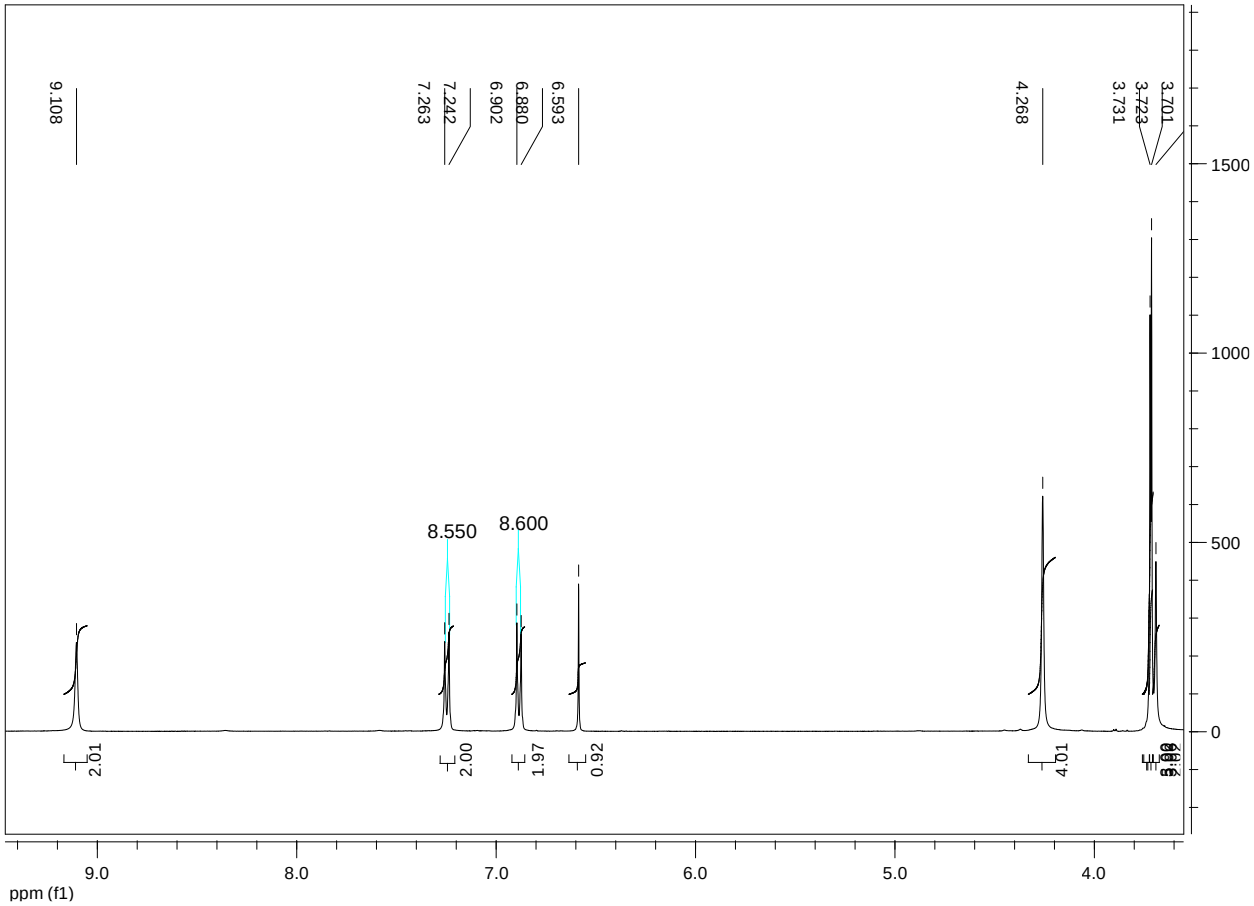
Data LCMS for compound **17 d**



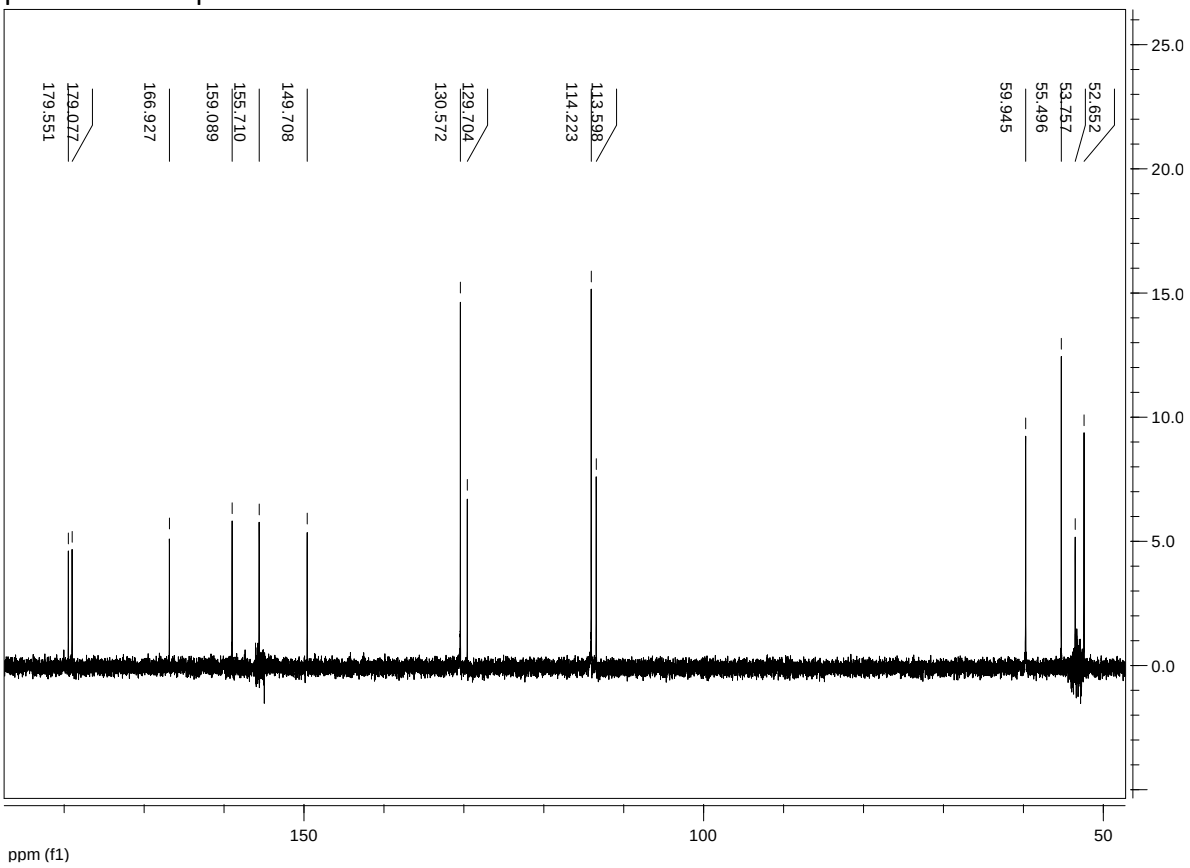
IR spectra for compound **17d**

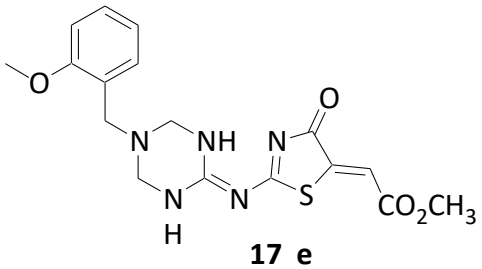


^{1}H NMR spectra for compound **17 d**



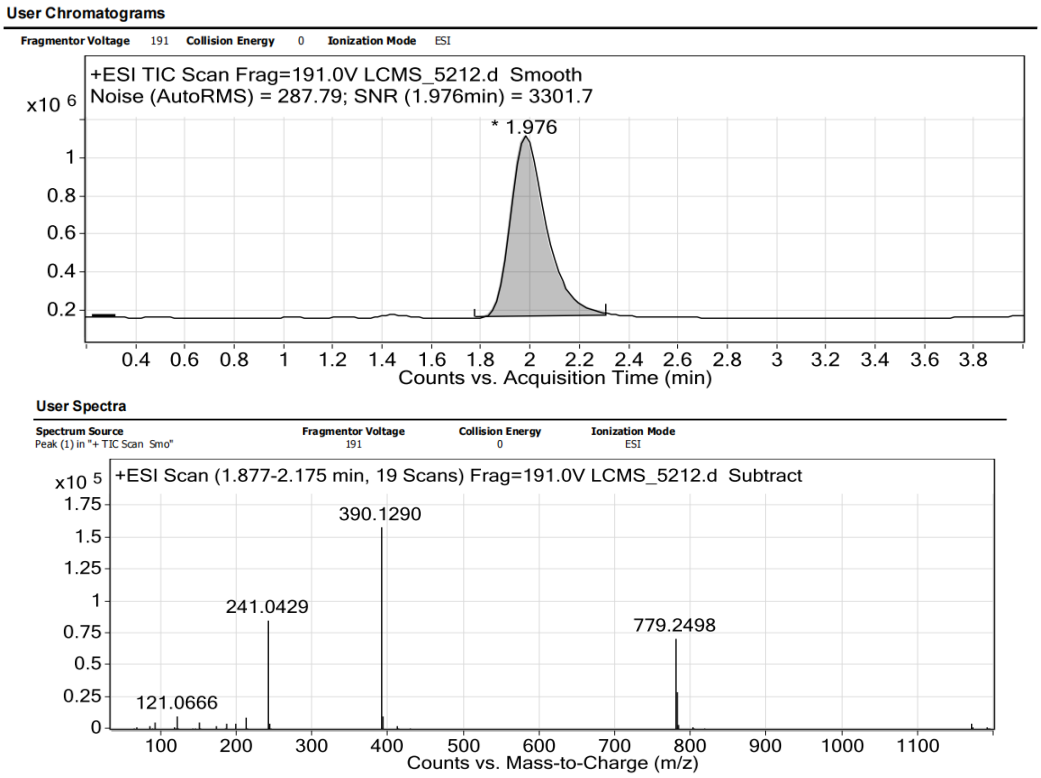
^{13}C NMR spectra for compound **17 d**



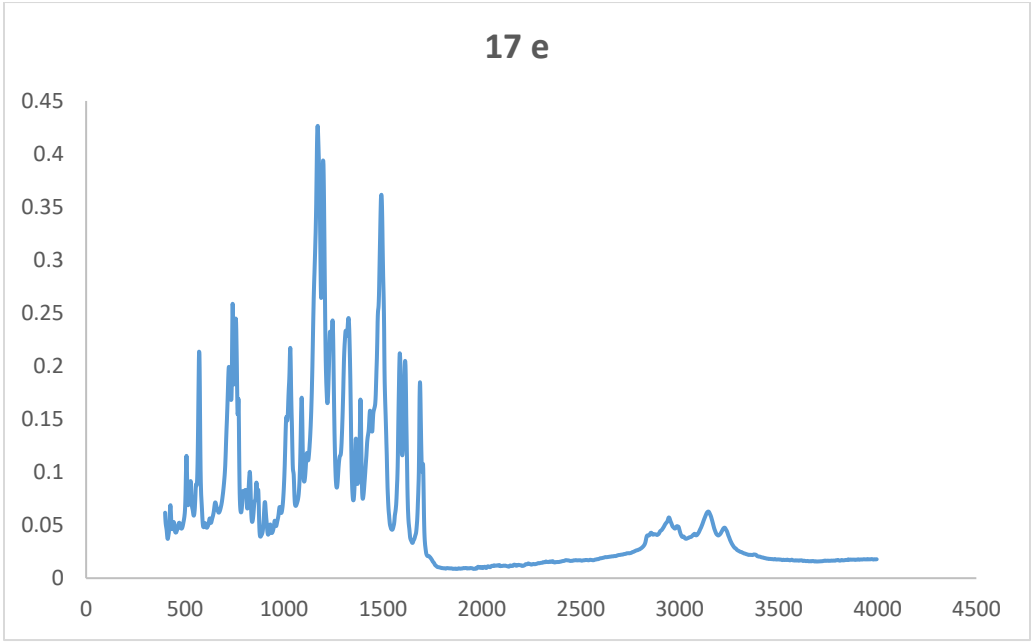


17 e

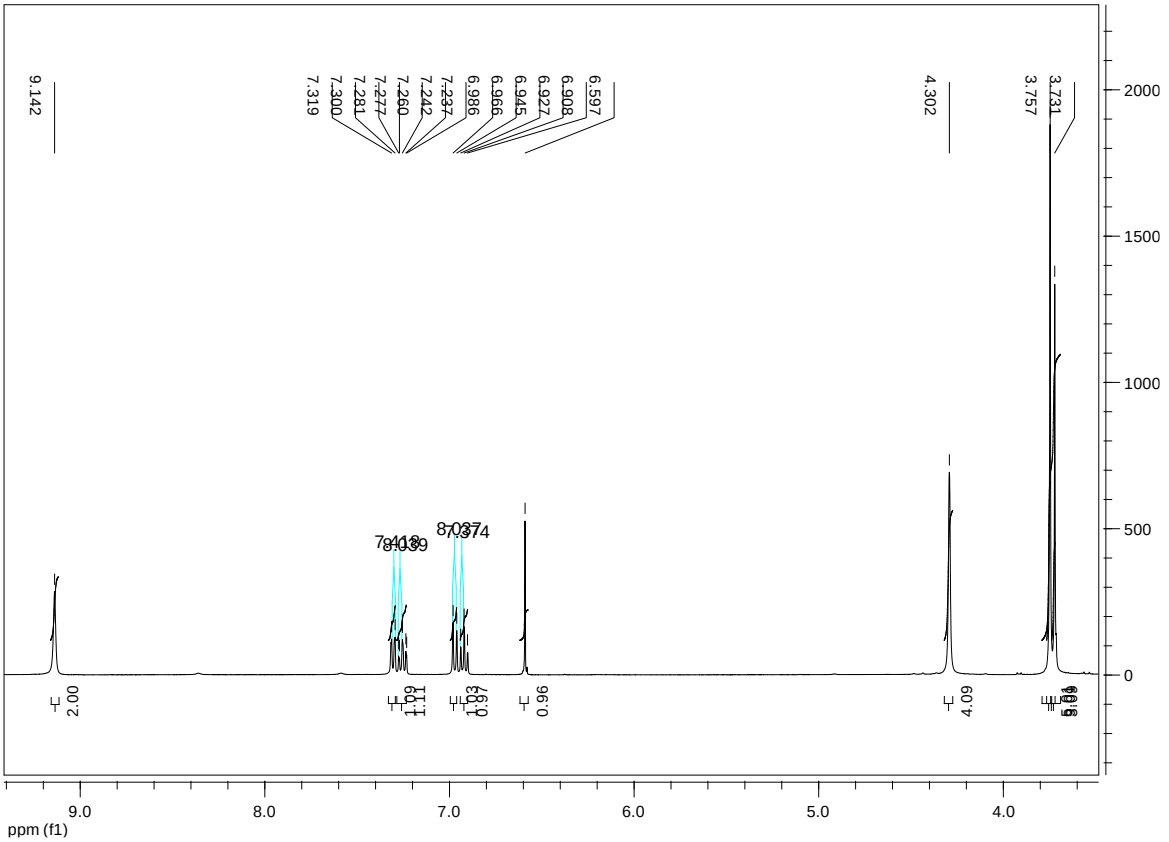
Data LCMS for compound **17 e**



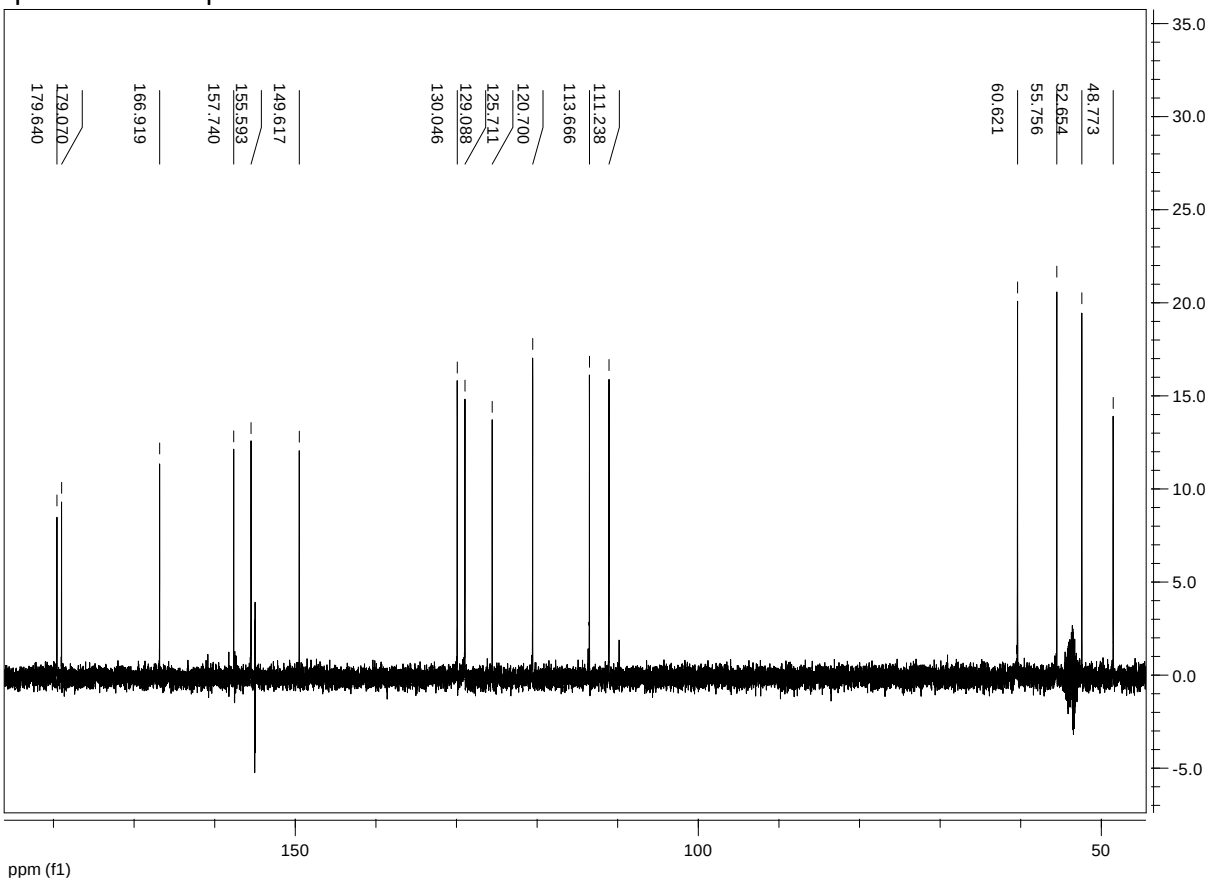
IR spectra for compound **17 e**

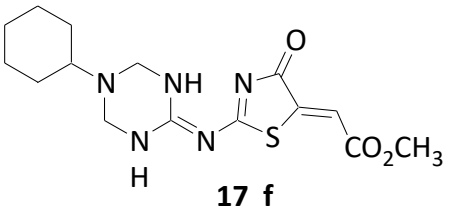


^{1}H NMR spectra for compound **17 e**



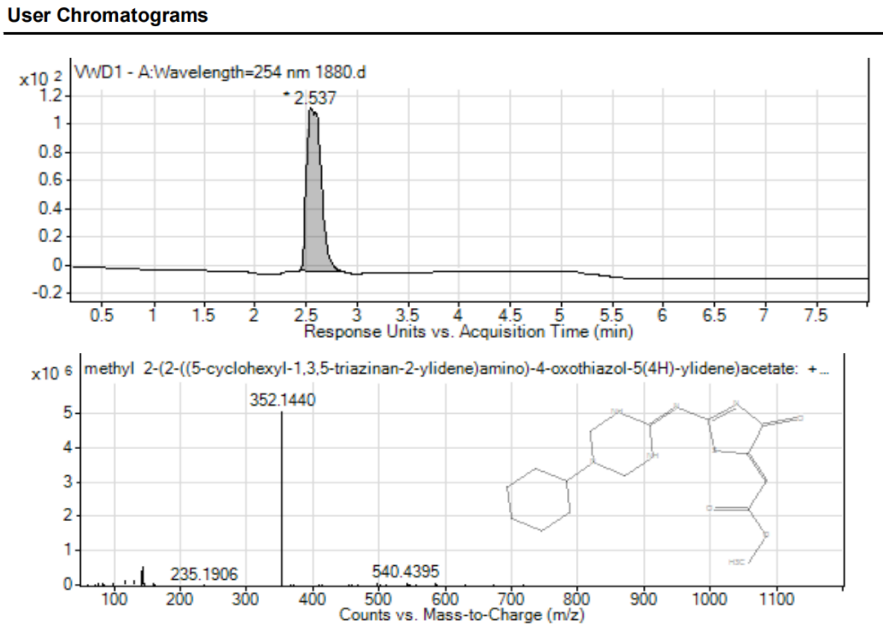
^{13}C NMR spectra for compound **17 e**



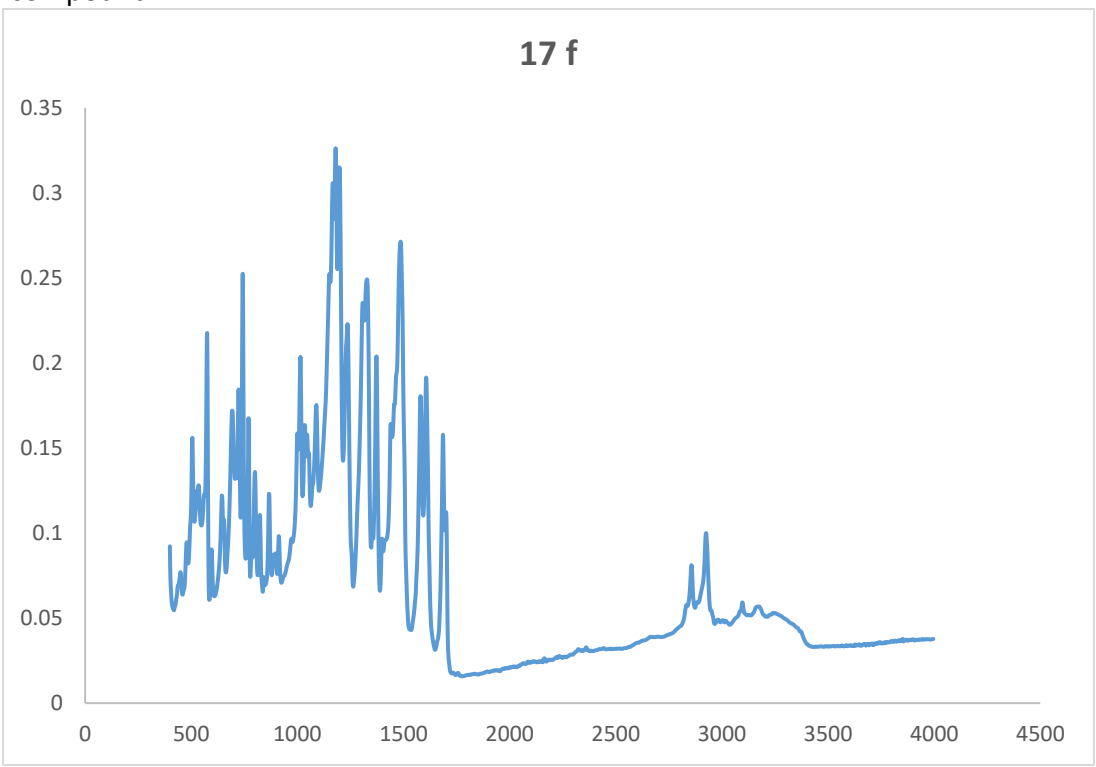


17 f

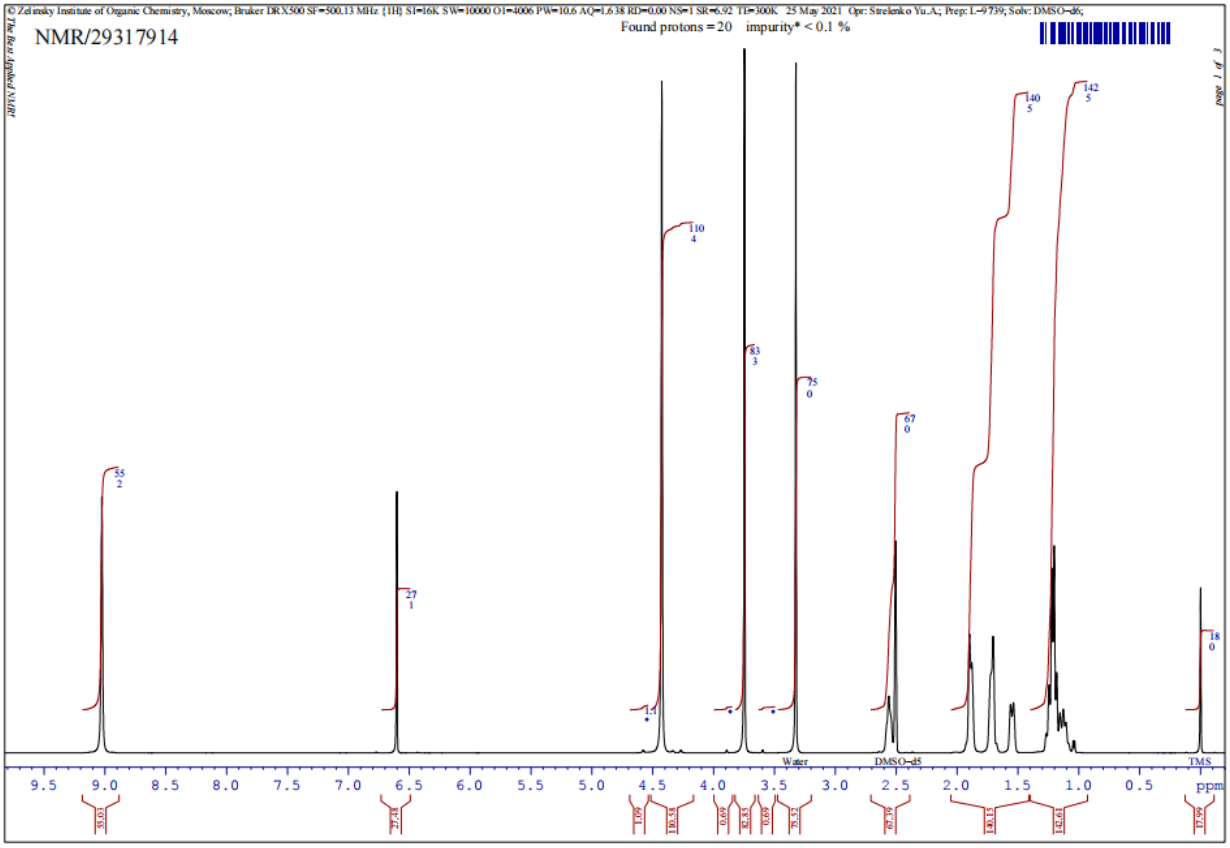
Data LCMS for compound **17 f**



IR spectra for compound **17 f**



^{1}H NMR spectra for compound **17 f**



^{13}C NMR spectra for compound **17 f**