

Electronic supporting information

Non-aromatic Azolo[5,1-c][1,2,4]triazines: A Pot, Atom and Step Economic (PASE) Synthesis, Mechanistic Insight and Fluorescent Properties

Elena V. Sadchikova,* Nikolai A. Beliaev, Daria L. Alexeeva, Nikita E. Safronov, Nataliya P. Belskaya*

Department of Technology for Organic Chemistry, Ural Federal University, Ekaterinburg, 620002, Russia

Corresponding Authors

Dr. Sadchikova Elena, E-mail: e.v.sadchikova@urfu.ru

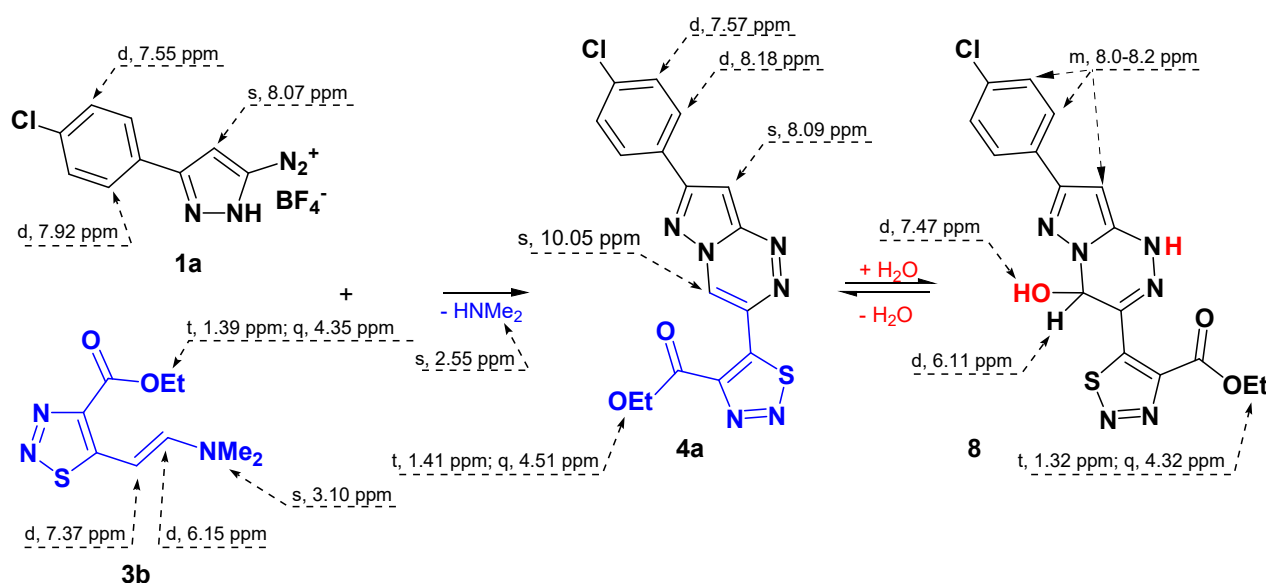
Prof. Belskaya Nataliya, E-mail: n.p.belskaya@urfu.ru

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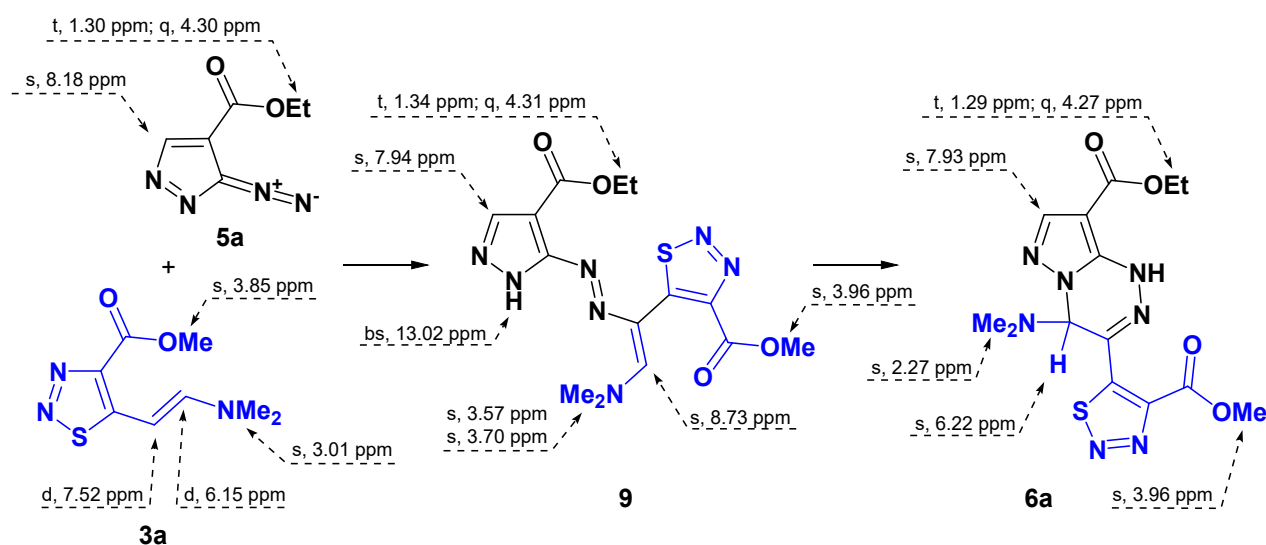
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1. Investigation of the reaction mechanism of pyrazole-5-diazonium salt or 5-diazopyrazole with thiadiazol-5-yl enamine by NMR spectroscopy

The NMR tubes (5 mm) were used for monitoring the reactions (**1a** + **3b** → **4a**, Scheme S1; **5a** + **3a** → **6a**, Scheme S2). The amounts of each substance were determined by integration of the corresponding proton signals. Solutions of pyrazole-5-diazonium salt **1a** (0.05 mmol) with enamine **3b** (0.05 mmol) and 5-diazopyrazole **5a** (0.05 mmol) with enamines **3a** (0.05 mmol) in DMSO-*d*₆ were prepared and added to NMR tubes. The ¹H NMR spectra were detected immediately after mixing. The time of each experiment depended on the reaction rate. The spectra obtained were analyzed in comparison with the spectra of pure compounds.



Scheme S1. Monitoring the reaction of pyrazole-5-diazonium salt **1a** with thiadiazol-5-yl enamine **3b** by ¹H NMR spectroscopy (in DMSO-*d*₆)



Scheme S2. Monitoring the reaction of 5-diazopyrazole **5a** with thiadiazol-5-yl enamine **3a** by ¹H NMR spectroscopy (in DMSO-*d*₆)

2. Photophysical study

UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer (Kyoto, Japan). The fluorescence of the sample solutions was measured using a Hitachi F-7000 spectrophotometer (Tokyo, Japan). The absorption and emission spectra were recorded in toluene, dioxane, CH₂Cl₂, CHCl₃, THF, EtOH, EtOAc, acetone, MeCN, DMF and DMSO using 10.00 mm quartz cells. The excitation wavelength was at the absorption maxima. The atmospheric oxygen contained in the solutions was not removed. The concentration of the compounds in the solution was 5.0×10^{-5} M and 5.0×10^{-6} M for the absorption and fluorescence measurements, respectively. The relative fluorescence quantum yields (Φ_F) were determined using quinine sulfate (5×10^{-5} M) in 0.1 M H₂SO₄ as a standard ($\Phi_F = 0.546$).

The absolute quantum yield for the solid-state and time-resolution study was recorded on Horiba FluoroMax 4 Spectrofluorometer (Kyoto, Japan) with a Quanta- ϕ integrating sphere using FluorEssence 3.5 Software.

Lippert-Mataga plot:^{1, 2}

$$\tilde{\nu}_a - \tilde{\nu}_f = m_{L-M} f(\varepsilon, n) + constant \quad (\text{Eq. S1})$$

m_{L-M} – the slope of the linear plot of the Stokes shift versus the orientation polarizability

$f(\varepsilon, n)$ – orientation polarizability of the solvents

$\tilde{\nu}_a - \tilde{\nu}_f$ – Stokes shift

$$f(\varepsilon, n) = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \quad (\text{Eq. S2})$$

ε dielectric constant

n refractive index

Reichardt plot:¹⁴⁻¹⁶

$$\tilde{\nu}_a - \tilde{\nu}_f = m_{E_T^N} E_T^N + constant \quad (\text{Eq. S3})$$

E_T^N – the normalized solvent polarity of Reichardt

$m_{E_T^N}$ – the slope of the linear plot of the Stokes shift versus the microscopic solvent polarity

$$E_T^N = \frac{E_T(30)_{\text{solvent}} - E_T(30)_{\text{TMS}}}{E_T(30)_{\text{water}} - E_T(30)_{\text{TMS}}} = \frac{E_T(30)_{\text{solvent}} - 30.7}{32.4} \quad (\text{Eq. S4})$$

$E_T(30)_i$ – the empirical solvent polarity parameter

TMS represent tetramethylsilane (non-polar solvent)

Dimrot-Reichert plot:³⁻⁵

$$\tilde{\nu}_a - \tilde{\nu}_f = m_{E_T(30)} E_T(30) + constant \quad (\text{Eq. S5})$$

$$E_T(30)_i = hcN\tilde{\nu}_{ai} = 2.8591 \times 10^{-3} \tilde{\nu}_{ai} \quad (\text{in } kcal \text{ mol}^{-1}) \quad (\text{Eq. S6})$$

$m_{E_{T(30)}}$ – the slope of the linear plot of the Stokes shift versus the empirical solvent polarity parameter

3. X-ray structural analysis of compound 7g

Single crystals of $C_{13}H_{15}N_7O_4S$ **7g** were grown from EtOH. The experiments were accomplished on the automated X-ray diffractometer «Xcalibur 3» with CCD detector on standard procedure (MoK α -irradiation, graphite monochromator, ω -scans with 1° step at T= 295(2) K). Empirical absorption correction was applied. The crystal was kept at 295(2) K during data collection. Using Olex2⁶, the structure was solved with the ShelXS⁷ structure solution program using Direct Methods and refined with the ShelXL⁷ refinement package using Least Squares minimisation.

Crystal Data. $C_{13}H_{15}N_7O_4S$, $M=365.38$, monoclinic, $a = 18.226(3)$ Å, $b = 12.3104(11)$ Å, $c = 7.2437(11)$ Å, $\beta = 98.275(16)^\circ$, $V = 1608.3(4)$ Å³, $T = 295(2)$, space group $P2_1/c$ (no. 14), $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.238$, 5855 reflections measured, 3198 unique ($R_{\text{int}} = 0.0340$) which were used in all calculations. The final wR_2 was 0.1483 (all data) and R_1 was 0.0531 ($>2\sigma(I)$).

CCDC 2177562 for **7g** can be obtained free of charge from the Cambridge Crystallographic Data Centre via link www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Details of the Structure Determination for compound **7g**

Crystal Data	
Formula	$C_{13}H_{15}N_7O_4S$
Formula Weight	365.38
Crystal System	Monoclinic
Space group	$P2_1/c$ (№ 14)
$a/\text{Å}$	18.226(3)
$b/\text{Å}$	12.3104(11)
$c/\text{Å}$	7.2437(11)
$\alpha/^\circ$	90.00
$\beta/^\circ$	98.275(16)
$\gamma/^\circ$	90.00
Volume/Å ³	1608.3(4)
Z	4
ρ_{calc} , g/cm ³	1.509
μ/mm^{-1}	0.238
F(000)	760.0
Crystal size, mm	0.25 × 0.11 × 0.01
Data Collection and refinement	
Temperature, K	295(2)
Radiation, Å	Mo K α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	4.52 to 52.72
Index ranges	$-7 \leq h \leq 22$, $-8 \leq k \leq 15$, $-9 \leq l \leq 8$
Reflections collected	5855
Independent reflections	3198 [$R_{\text{int}} = 0.0340$]
Data / restraints / parameters	3198 / 26 / 260
Goodness-of-fit on F^2	1.006
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0531$, $wR_2 = 0.1198$
Final R indexes [all data]	$R_1 = 0.1045$, $wR_2 = 0.1483$
Largest diff. peak / hole, e/Å ³	0.22 / -0.22

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **7g**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
N7	1387.7(13)	1878.1(17)	-942(3)	38.6(6)
N1	1056.0(13)	-284.9(16)	-1201(3)	39.6(6)
O3	2275.8(12)	-248.2(15)	-2031(3)	48.9(6)
N6	737.2(15)	1530.8(19)	-1868(4)	41.7(7)
N12	3790.4(15)	2029(2)	2004(4)	59.1(8)
N3	25.4(14)	-1205.2(18)	-2163(4)	44.9(7)
O1	3137.4(14)	-615(2)	2084(4)	73.7(8)
C4	-98.6(16)	-107(2)	-2544(4)	38.7(7)
N13	3544.1(16)	3009(2)	1792(4)	63.1(8)
C9	1832.7(17)	-28(2)	-608(5)	39.0(7)
C5	538.4(16)	458(2)	-1933(4)	36.1(7)
O4	-878.3(14)	1320.6(16)	-3664(4)	71.2(8)
C8	1891.8(16)	1173(2)	-285(4)	37.7(7)
N15	-1349.8(17)	-369(2)	-3949(5)	57.8(9)
C11	3273.7(18)	1248(2)	1374(5)	46.2(8)
C2	712.8(18)	-1276(2)	-1373(4)	46.2(8)
O2	4232.1(15)	6(2)	1509(5)	93.6(10)
C21	-797.6(18)	338(2)	-3429(4)	45.9(8)
C10	2588.8(17)	1658(2)	610(4)	39.8(7)
C14	3525(2)	110(3)	1689(5)	58.7(10)
C22	2448(2)	-1378(3)	-2263(6)	67.5(11)
C23	3093(3)	-1420(4)	-3305(7)	107.9(18)
C17	4599(15)	-1050(20)	1740(20)	86(3)
S1	2657.9(5)	3029.1(6)	769.2(13)	53.5(3)
C20	4604(8)	-1639(13)	770(20)	161(6)
C19	4840(20)	-910(20)	3910(30)	108(7)
C18	4596(15)	-1010(20)	2360(20)	86(3)
C12	4720(20)	-1410(20)	3790(30)	108(7)

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **7g**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*U_{11} + \dots + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N7	29.7(14)	31.7(12)	52.6(16)	-1.3(11)	-0.5(11)	-0.2(11)
N1	34.2(15)	26.0(11)	56.8(17)	2.2(10)	0.3(12)	-1.3(11)
O3	46.3(14)	34.9(11)	66.0(15)	-2(1)	10.2(11)	7.4(10)
N6	32.8(15)	25.7(12)	62.9(18)	0.2(12)	-5.7(13)	0.2(12)
N12	38.6(17)	51.4(16)	82(2)	-4.1(15)	-7.5(14)	-1.1(14)
N3	39.3(16)	30.3(12)	63.2(18)	0.8(11)	0.6(13)	-5.1(11)
O1	50.4(16)	58.2(15)	106(2)	27.5(14)	-9.0(14)	-2.1(13)
C4	36.1(18)	29.3(13)	49.3(18)	-0.7(12)	1.3(14)	-2.5(13)
N13	42.3(18)	50.4(16)	91(2)	-9.6(15)	-10.5(16)	-5.5(14)
C9	33.2(18)	32.2(14)	50.1(19)	3.6(14)	1.2(15)	0.4(13)
C5	33.5(17)	28.9(14)	44.9(18)	1.3(12)	1.9(13)	0.4(13)
O4	57.9(17)	31.7(12)	114(2)	6.9(12)	-20.2(15)	-3.2(11)
C8	32.5(17)	31.8(14)	48.4(18)	-1.0(13)	4.0(14)	-1.1(13)
N15	41.3(19)	34.3(16)	90(2)	3.8(15)	-17.4(17)	-4.6(14)
C11	36.3(19)	40.9(16)	59(2)	-2.7(14)	0.5(15)	-1.3(14)
C2	45(2)	27.2(14)	64(2)	1.4(13)	-2.1(16)	-3.5(14)
O2	46.1(18)	59.2(16)	176(3)	22.1(17)	18.6(18)	18.4(14)
C21	44(2)	34.0(15)	58(2)	0.8(14)	1.0(15)	-4.1(15)
C10	34.7(18)	37.7(15)	46.2(18)	-3.2(13)	2.8(14)	1.7(13)
C14	43(2)	50(2)	79(3)	5.0(18)	-6.3(19)	3.1(18)
C22	74(3)	39.7(18)	87(3)	-8.7(17)	5(2)	19.8(18)
C23	111(4)	89(3)	129(4)	-27(3)	39(4)	37(3)
C17	75(3)	74(3)	108(8)	4(6)	8(6)	21(3)
S1	42.3(5)	36.7(4)	77.3(6)	-9.7(4)	-5.7(4)	-0.1(4)
C20	114(12)	148(13)	213(19)	32(11)	-8(12)	20(10)
C19	96(10)	115(15)	114(9)	48(9)	19(7)	21(12)
C18	75(3)	74(3)	108(8)	4(6)	8(6)	21(3)
C12	96(10)	115(15)	114(9)	48(9)	19(7)	21(12)

Table S4. Bond Lengths for **7g**

Atom–Atom	Length/ \AA	Atom–Atom	Length/ \AA	Atom–Atom	Length/ \AA
N7–N6	1.345(3)	N3–C4	1.391(3)	C11–C10	1.385(4)
N7–C8	1.303(3)	N3–C2	1.303(4)	C11–C14	1.481(4)
N1–C9	1.454(4)	O1–C14	1.198(4)	O2–C14	1.321(4)
N1–C5	1.365(3)	C4–C5	1.372(4)	O2–C17	1.46(2)
N1–C2	1.369(3)	C4–C21	1.449(4)	O2–C18	1.51(2)
O3–C9	1.423(4)	N13–S1	1.678(3)	C10–S1	1.695(3)
O3–C22	1.441(3)	C9–C8	1.499(4)	C22–C23	1.485(6)
N6–C5	1.368(3)	O4–C21	1.228(3)	C17–C12	1.539(18)
N12–N13	1.289(3)	C8–C10	1.467(4)	C20–C18	1.38(2)
N12–C11	1.377(4)	N15–C21	1.342(4)		

Table S5. Bond Angles for **7g**

Atom–Atom– Atom	Angle/°	Atom–Atom– Atom	Angle/°	Atom–Atom– Atom	Angle/°
C8–N7–N6	119.7(2)	O3–C9–C8	105.4(2)	O4–C21–C4	120.9(3)
C5–N1–C9	123.9(2)	N1–C5–N6	118.0(3)	O4–C21–N15	122.0(3)
C5–N1–C2	106.3(2)	N1–C5–C4	106.9(2)	N15–C21–C4	117.1(3)
C2–N1–C9	129.3(2)	N6–C5–C4	135.1(3)	C8–C10–S1	119.1(2)
C9–O3–C22	115.1(2)	N7–C8–C9	124.7(3)	C11–C10–C8	134.6(3)
N7–N6–C5	122.3(2)	N7–C8–C10	114.3(2)	C11–C10–S1	106.3(2)
N13–N12–C11	113.8(3)	C10–C8–C9	120.5(2)	O1–C14–C11	124.2(3)
C2–N3–C4	105.7(2)	N12–C11–C10	114.4(3)	O1–C14–O2	124.6(3)
N3–C4–C21	124.2(2)	N12–C11–C14	115.3(3)	O2–C14–C11	111.1(3)
C5–C4–N3	108.9(2)	C10–C11–C14	130.3(3)	O3–C22–C23	107.2(3)
C5–C4–C21	126.9(2)	N3–C2–N1	112.2(2)	O2–C17–C12	111.7(17)
N12–N13–S1	111.3(2)	C14–O2–C17	120.9(11)	N13–S1–C10	94.19(14)
N1–C9–C8	107.8(2)	C14–O2–C18	114.7(10)	C20–C18–O2	100.4(12)
O3–C9–N1	112.0(2)	C17–O2–C18	17.5(11)		

Table S6. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **7g**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H2	944	-1926	-972	55
H22A	2027	-1751	-2955	81
H22B	2571	-1726	-1057	81
H23A	2951	-1136	-4538	162
H23B	3253	-2159	-3385	162
H23C	3491	-993	-2665	162
H17A	5075	-1002	1289	103
H17B	4301	-1582	990	103
H20A	4858	-1254	-96	242
H20B	4104	-1785	213	242
H20C	4855	-2312	1106	242
H19A	5137	-267	4160	162
H19B	4391	-833	4447	162
H19C	5112	-1527	4440	162
H18A	5094	-873	2990	103
H18B	4305	-1350	3225	103
H9	1987(16)	-440(20)	460(40)	41(8)
H12A	4272	-1735	4091	162
H12B	4847	-795	4581	162
H12C	5114	-1935	3978	162
H6	470(20)	2020(30)	-2190(50)	64(12)
H15A	-1281(18)	-990(30)	-3870(40)	48(10)
H15B	-1730(20)	-160(30)	-4780(50)	78(13)

4. NMR spectra of compounds 6a–i, 7b–d, 9

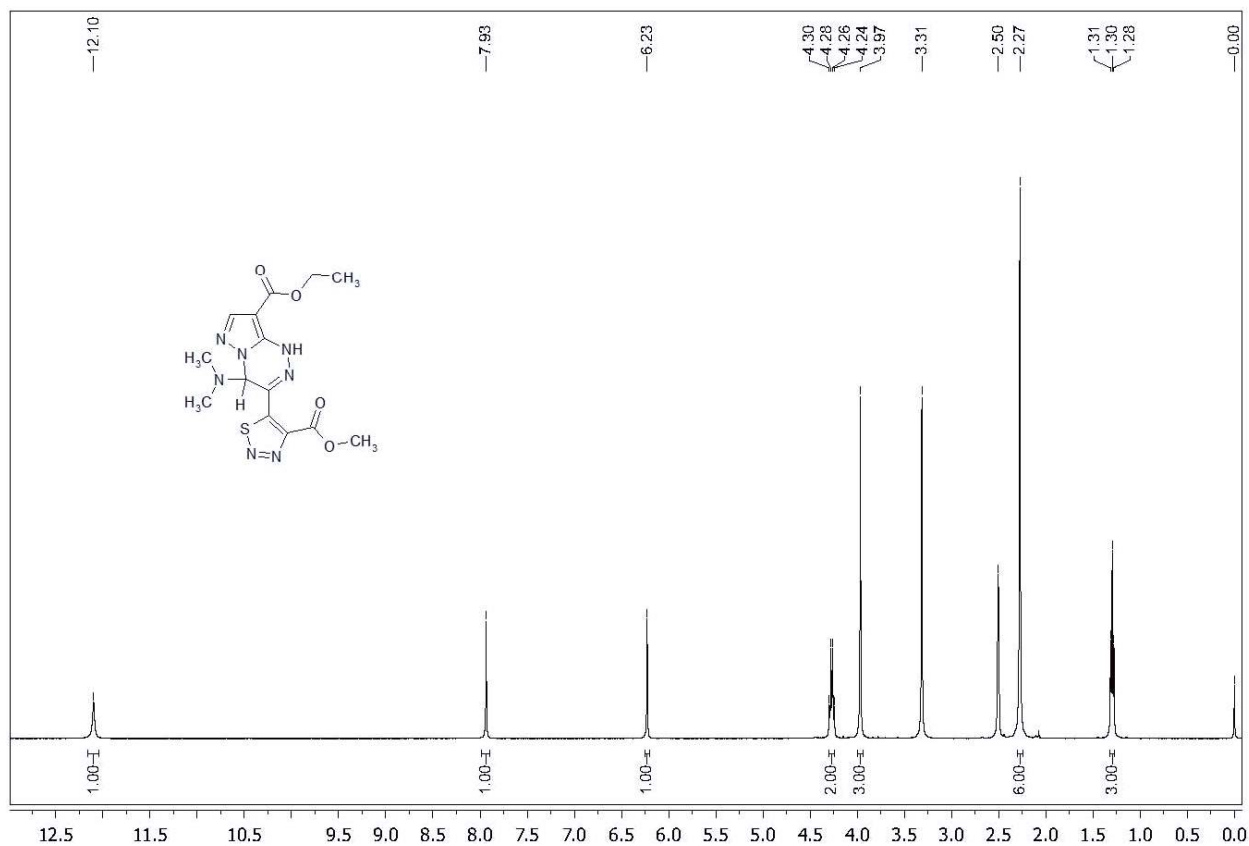


Fig. S1. ¹H NMR spectrum of ethyl 4-(*N,N*-dimethylamino)-3-[4-(methoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6a**)

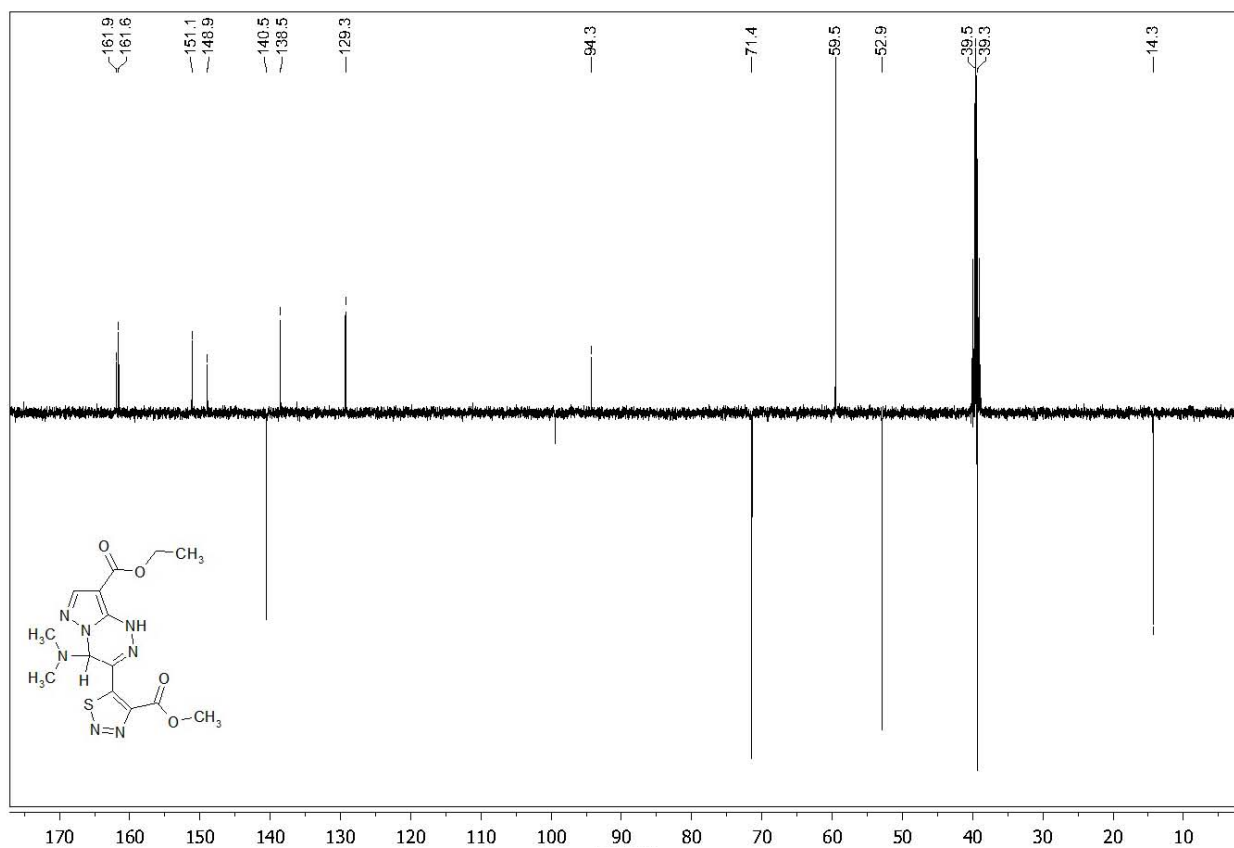


Fig. S2. ¹³C(Apt) NMR spectrum of ethyl 4-(*N,N*-dimethylamino)-3-[4-(methoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6a**)

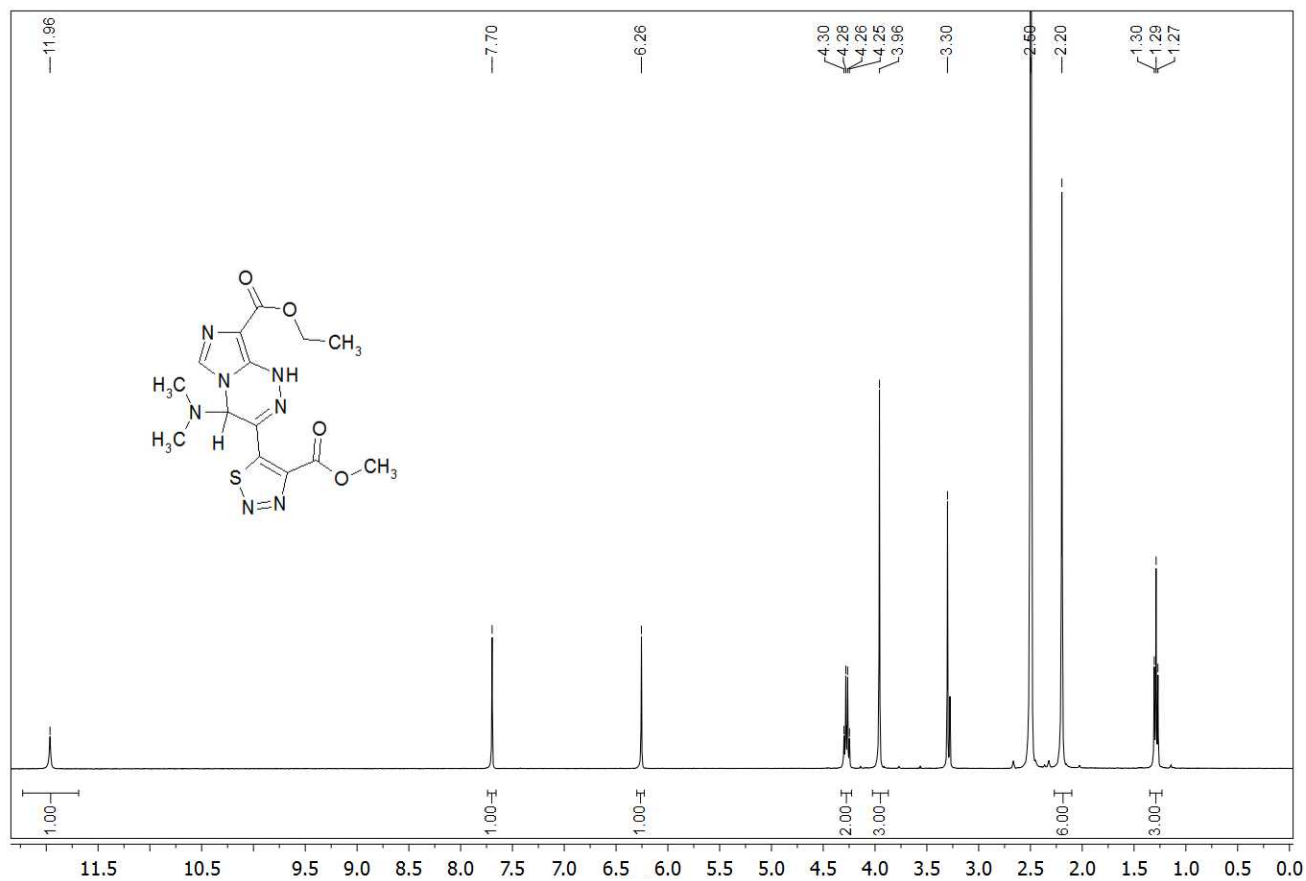


Fig. S3. ¹H NMR spectrum of ethyl 4-(*N,N*-dimethylamino)-3-[4-(methoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6b**)

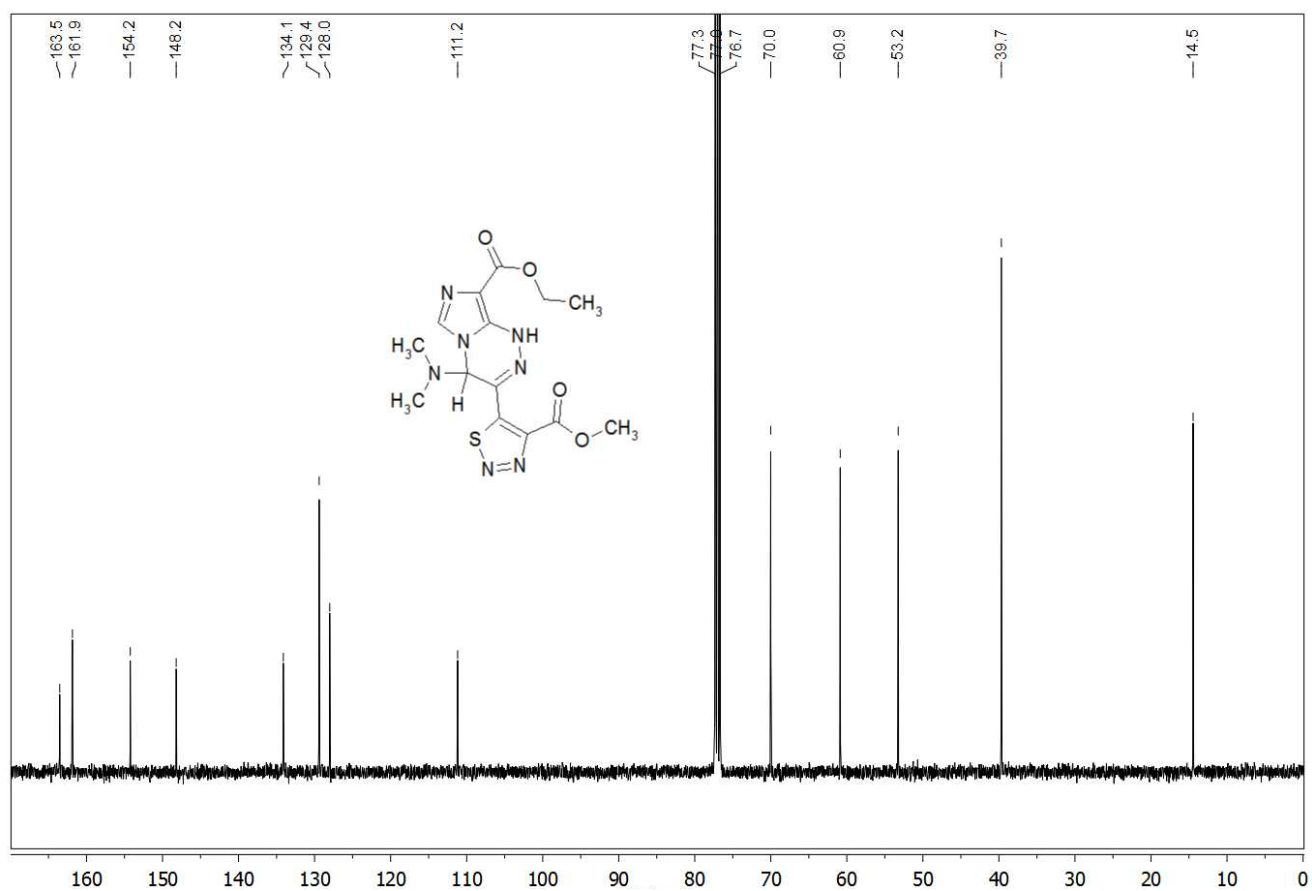


Fig. S4. ¹³C NMR spectrum of ethyl 4-(*N,N*-dimethylamino)-3-[4-(methoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6b**)

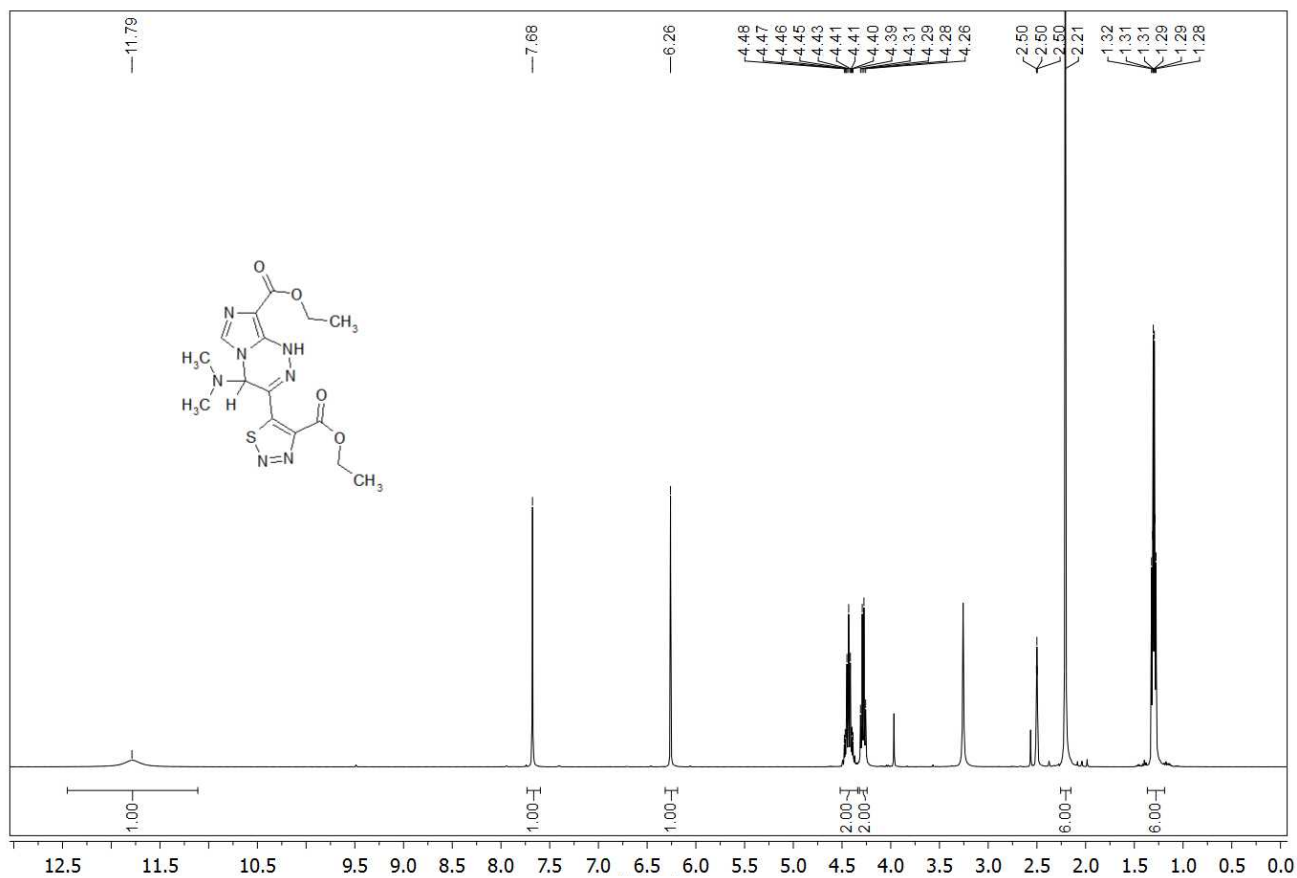


Fig. S5. ¹H NMR spectrum of ethyl 4-(*N,N*-dimethylamino)-3-[4-(ethoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6c**)

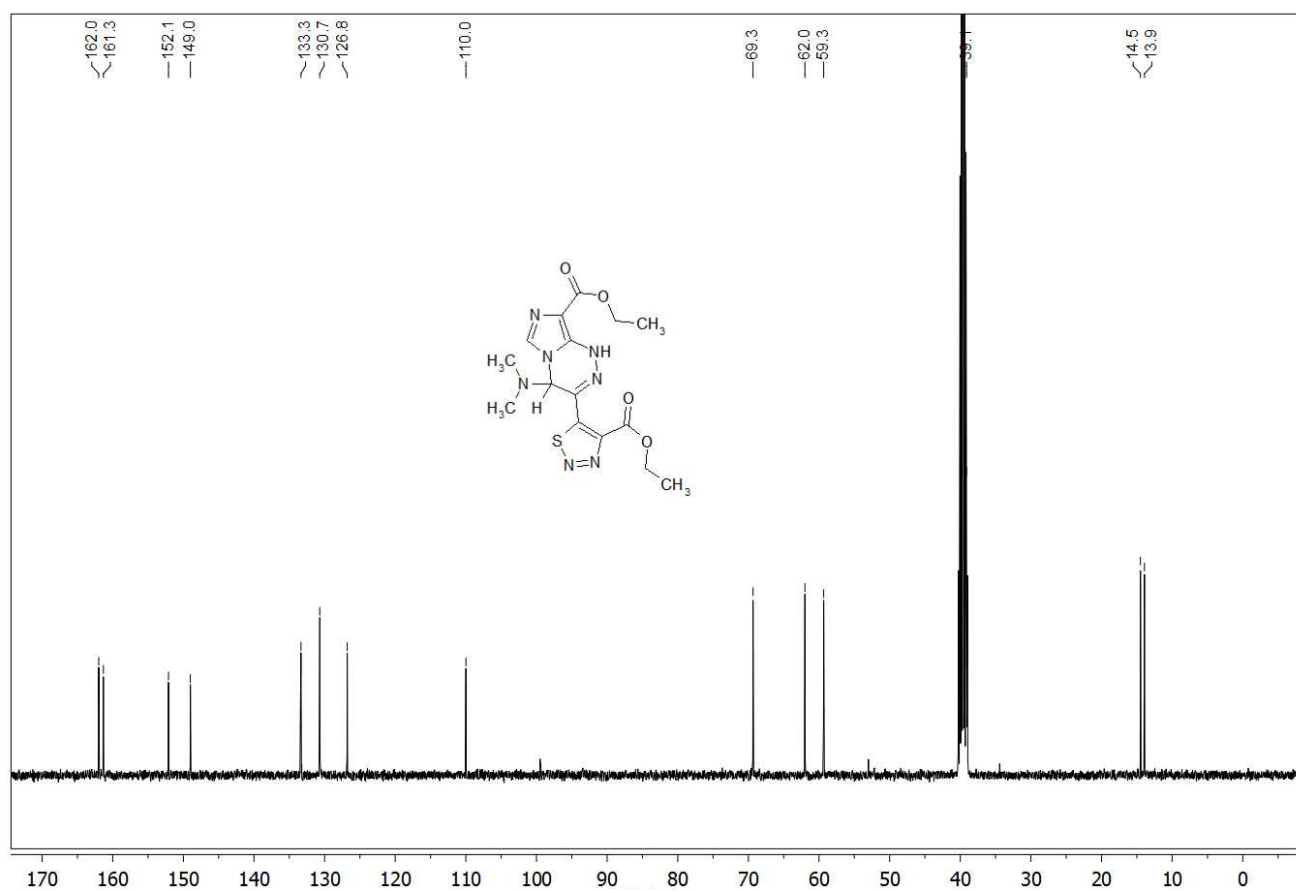


Fig. S6. ¹³C NMR spectrum of ethyl 4-(*N,N*-dimethylamino)-3-[4-(ethoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6c**)

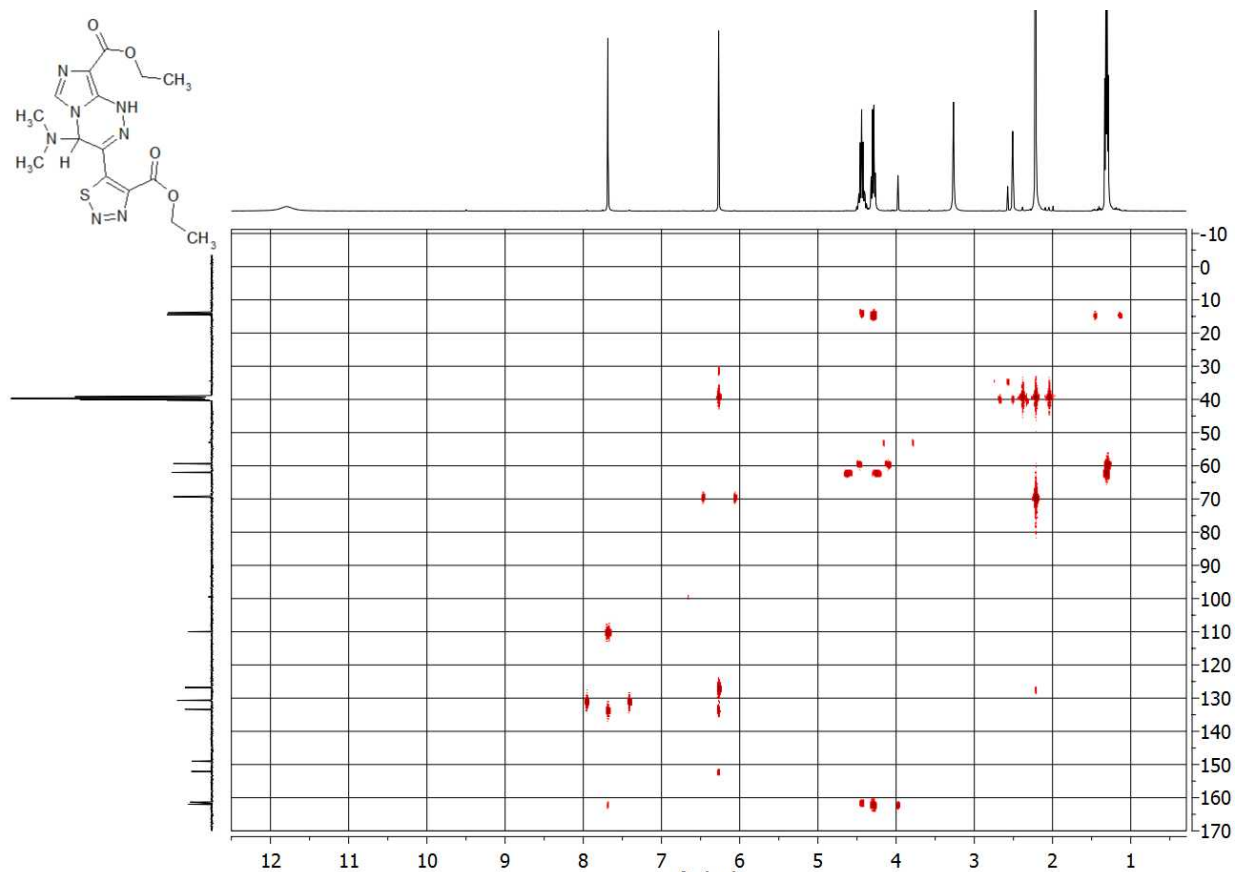


Fig. S7. HMBC spectrum of ethyl 4-(*N,N*-dimethylamino)-3-[4-(ethoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6c**)

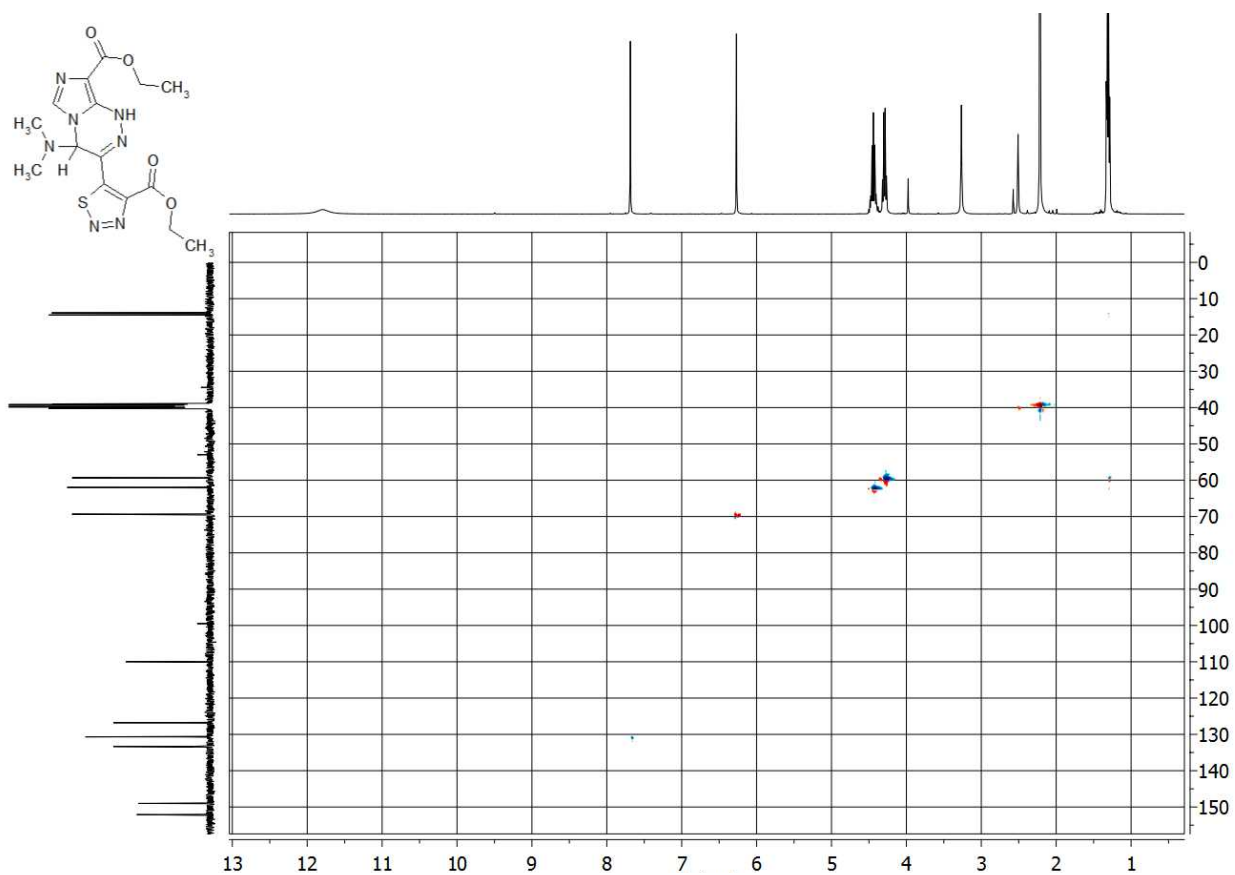


Fig. S8. HSQC spectrum of ethyl 4-(*N,N*-dimethylamino)-3-[4-(ethoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6c**)

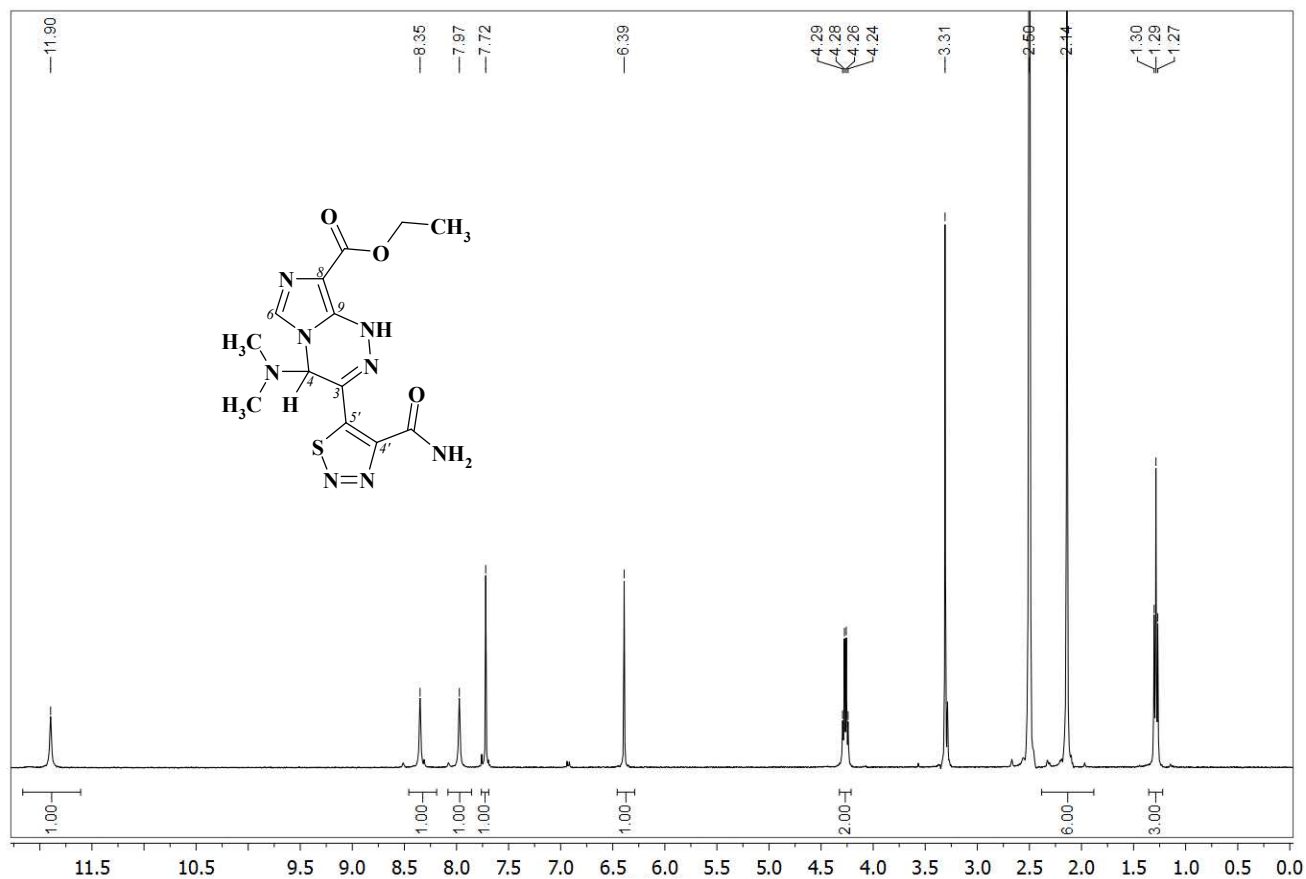


Fig. S9. ¹H NMR spectrum of ethyl 3-(4-carbamoyl-1,2,3-thiadiazol-5-yl)-4-(*N,N*-dimethylamino)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6d**)

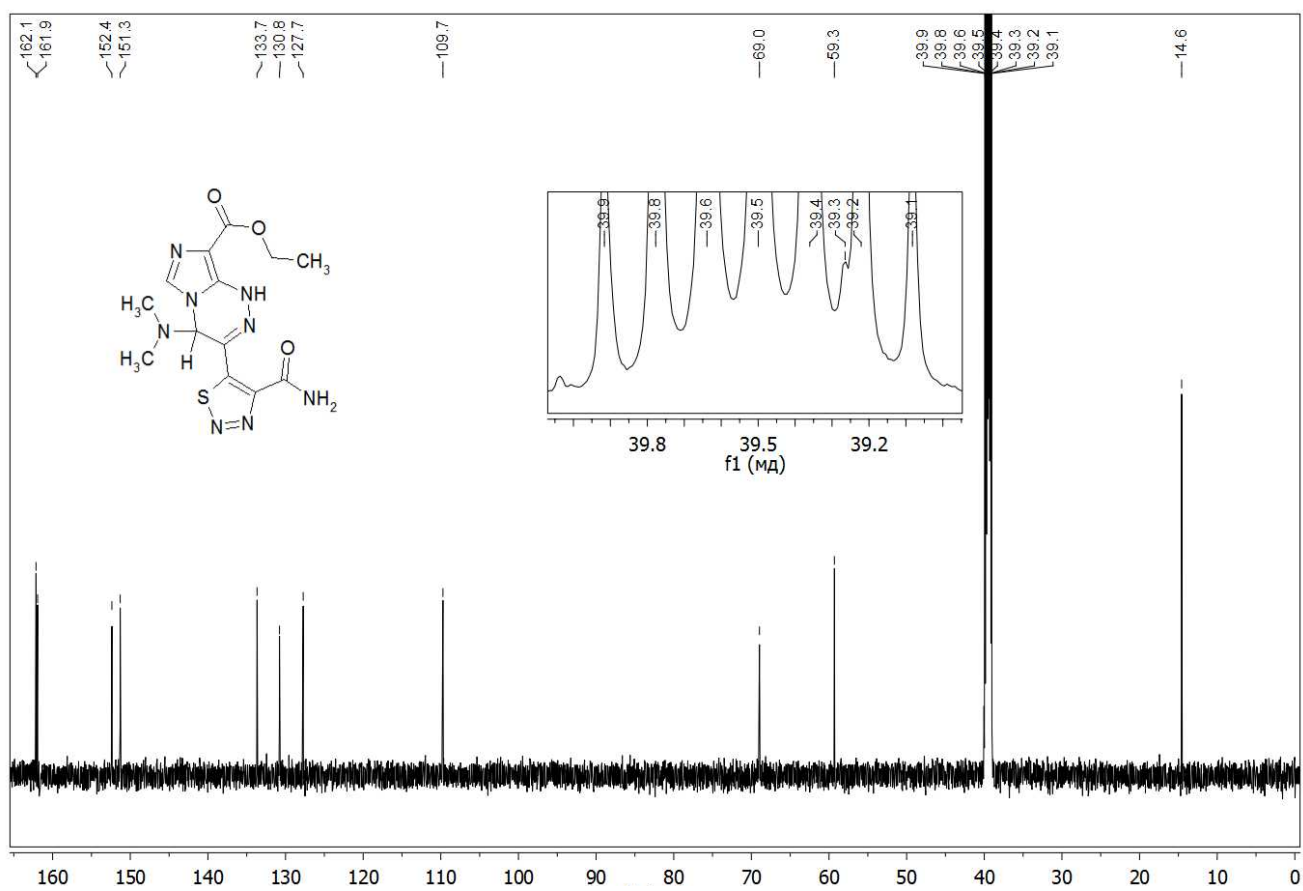


Fig. S10. ¹³C NMR spectrum of ethyl 3-(4-carbamoyl-1,2,3-thiadiazol-5-yl)-4-(*N,N*-dimethylamino)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6d**)

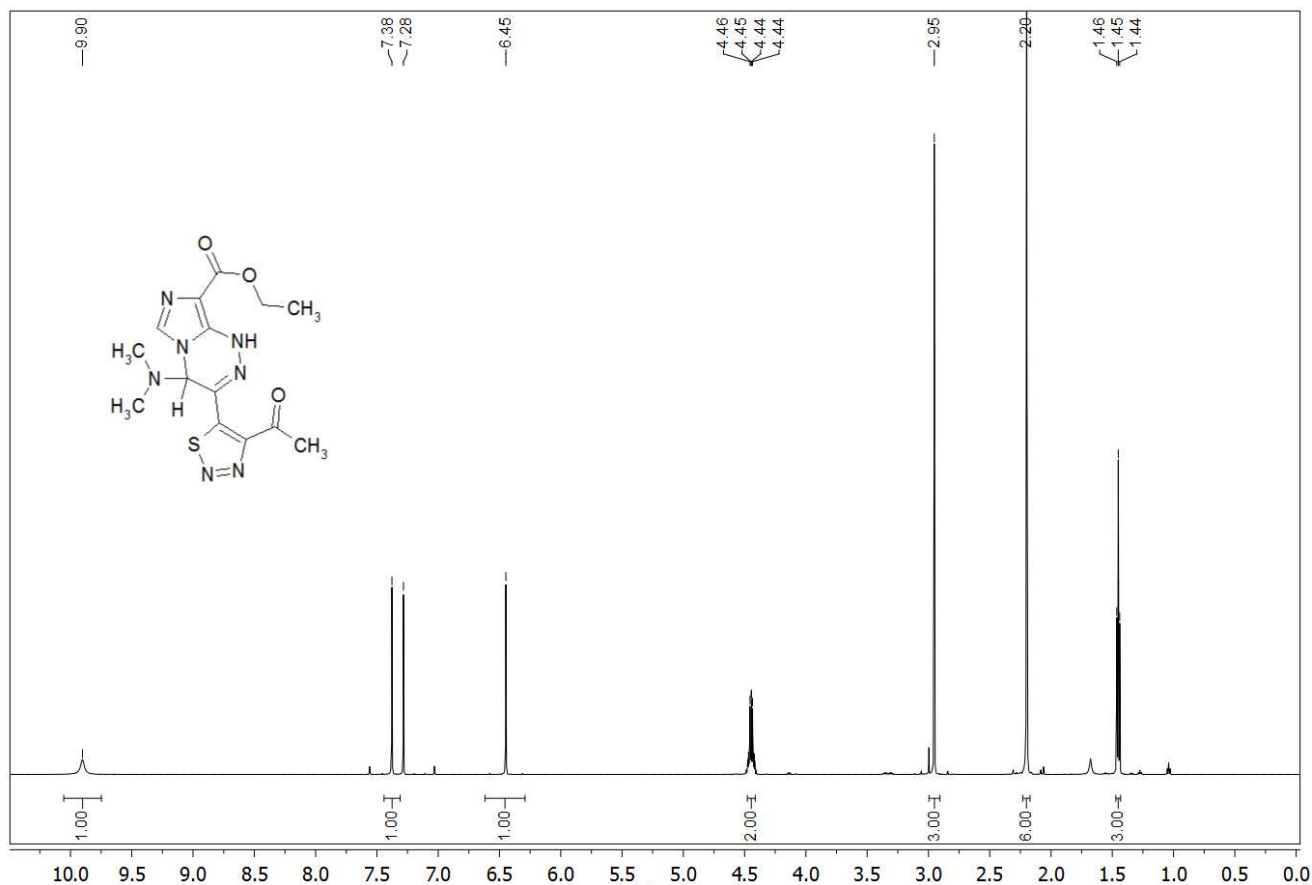


Fig. S11. ¹H NMR spectrum of ethyl 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-(*N,N*-dimethylamino)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6e**)

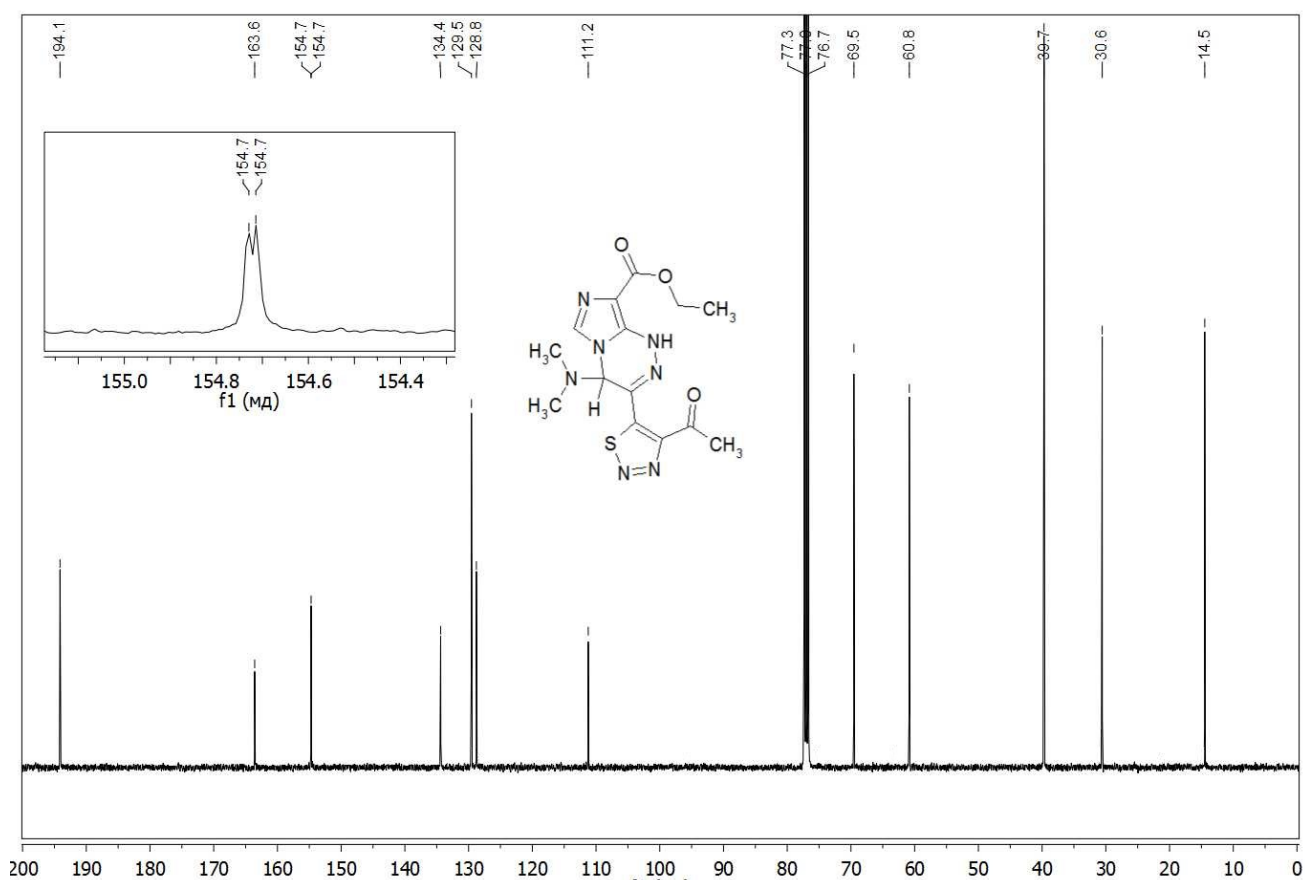


Fig. S12. ¹³C NMR spectrum of ethyl 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-(*N,N*-dimethylamino)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6e**)

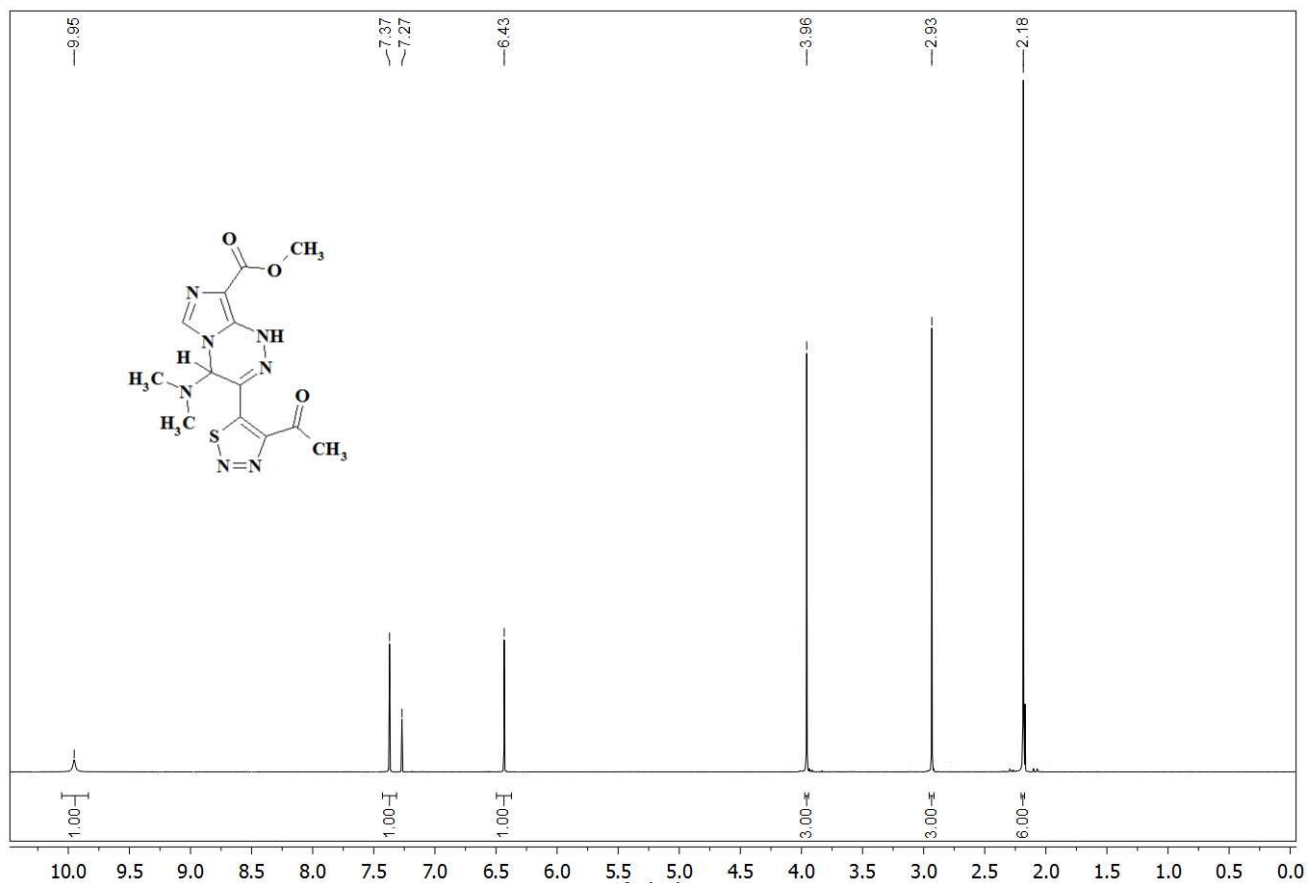


Fig. S13. ¹H NMR spectrum of methyl 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-(*N,N*-dimethylamino)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6f**)

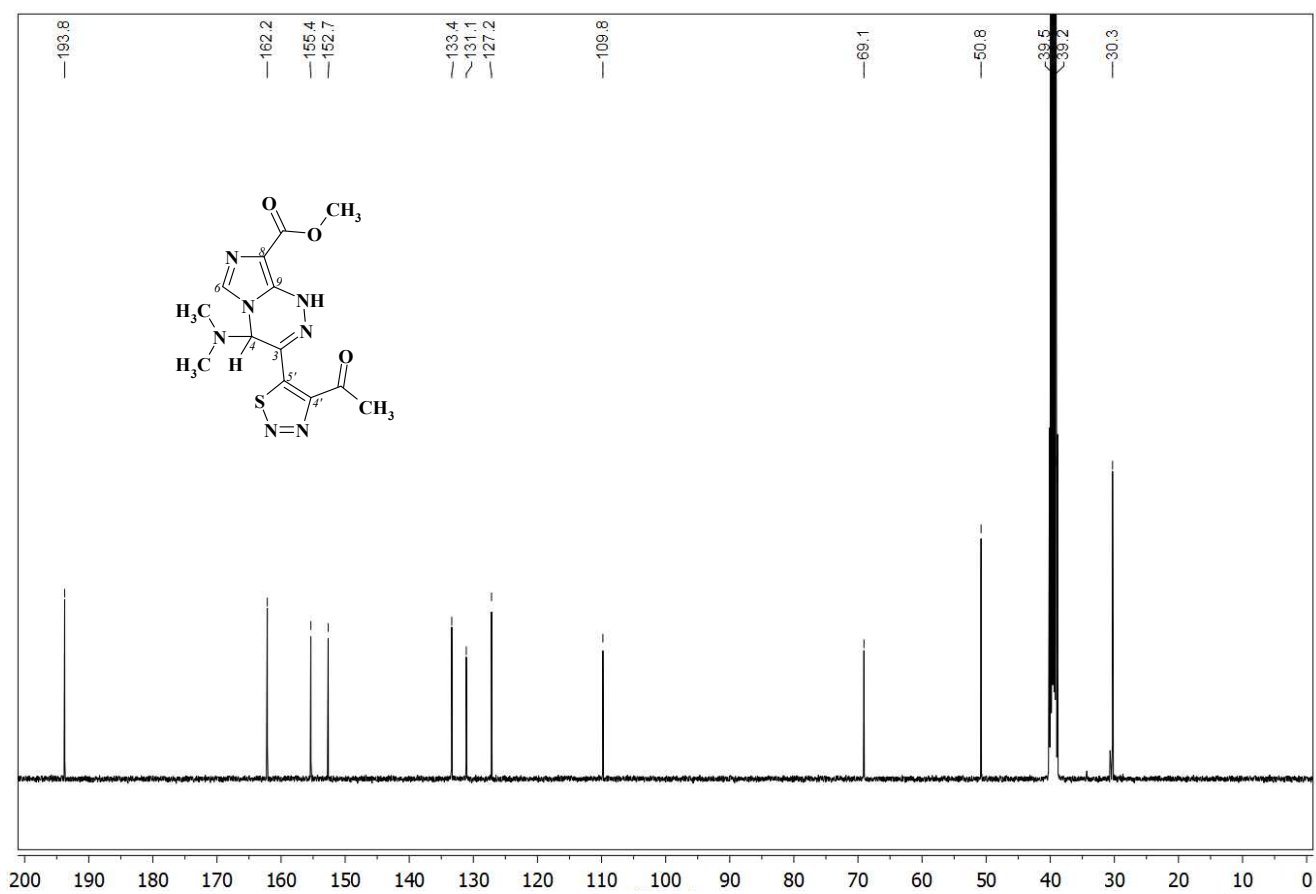


Fig. S14. ¹³C NMR spectrum of methyl 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-(*N,N*-dimethylamino)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**6f**)

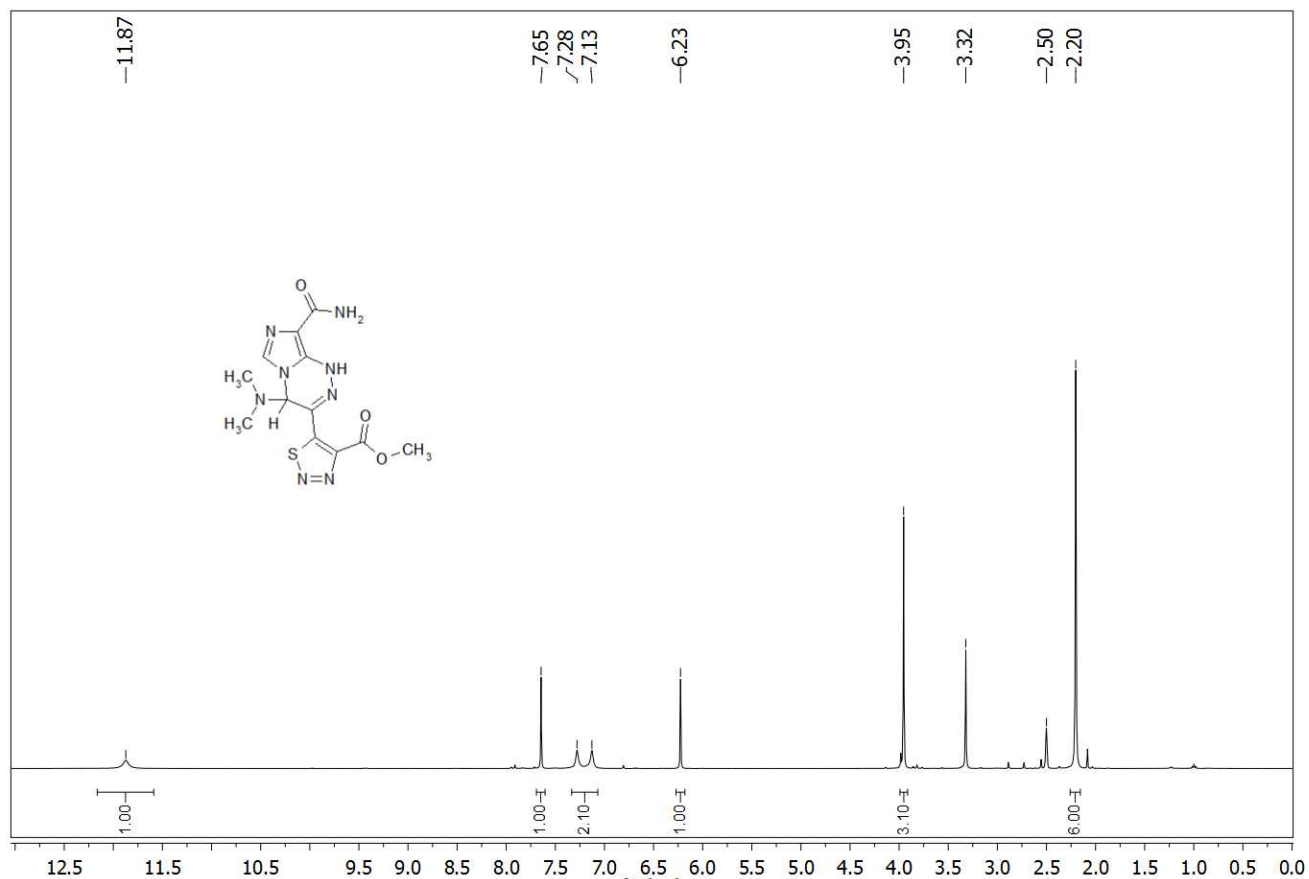


Fig. S15. ¹H NMR spectrum of 4-(*N,N*-dimethylamino)-3-[4-(methoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxamide (**6h**)

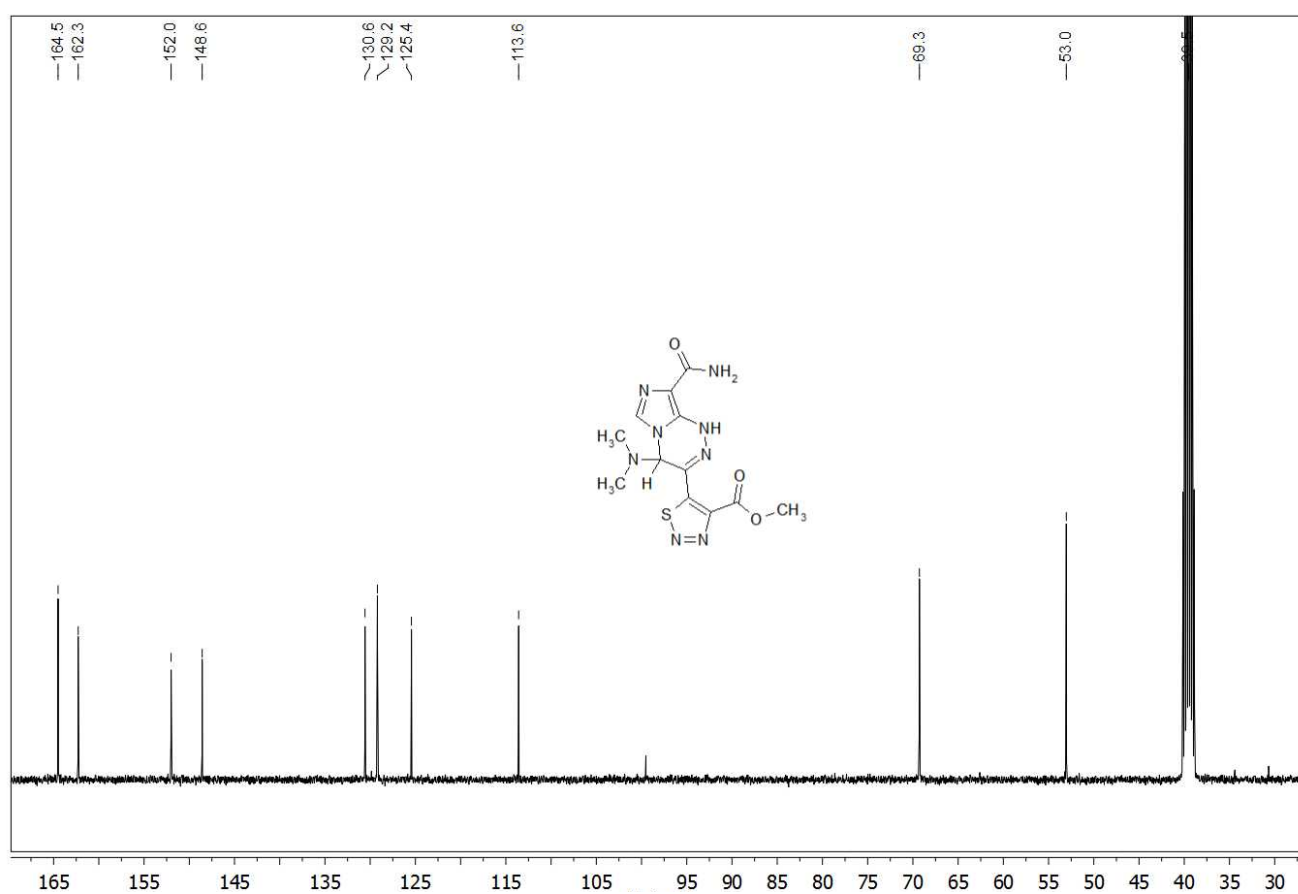


Fig. S16. ¹³C NMR spectrum of 4-(*N,N*-dimethylamino)-3-[4-(methoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxamide (**6h**)

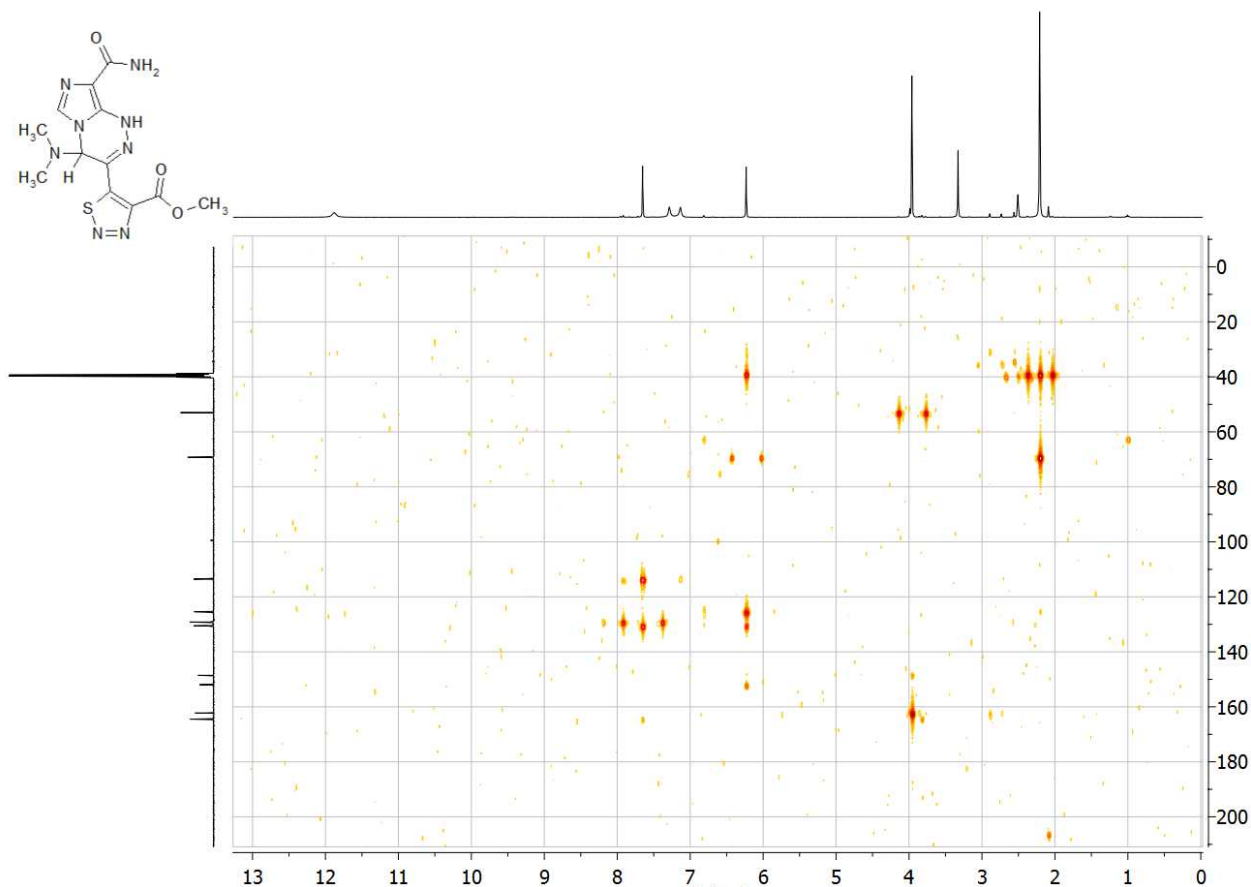


Fig. S17. HMBC spectrum of 4-(*N,N*-dimethylamino)-3-[4-(methoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxamide (**6h**)

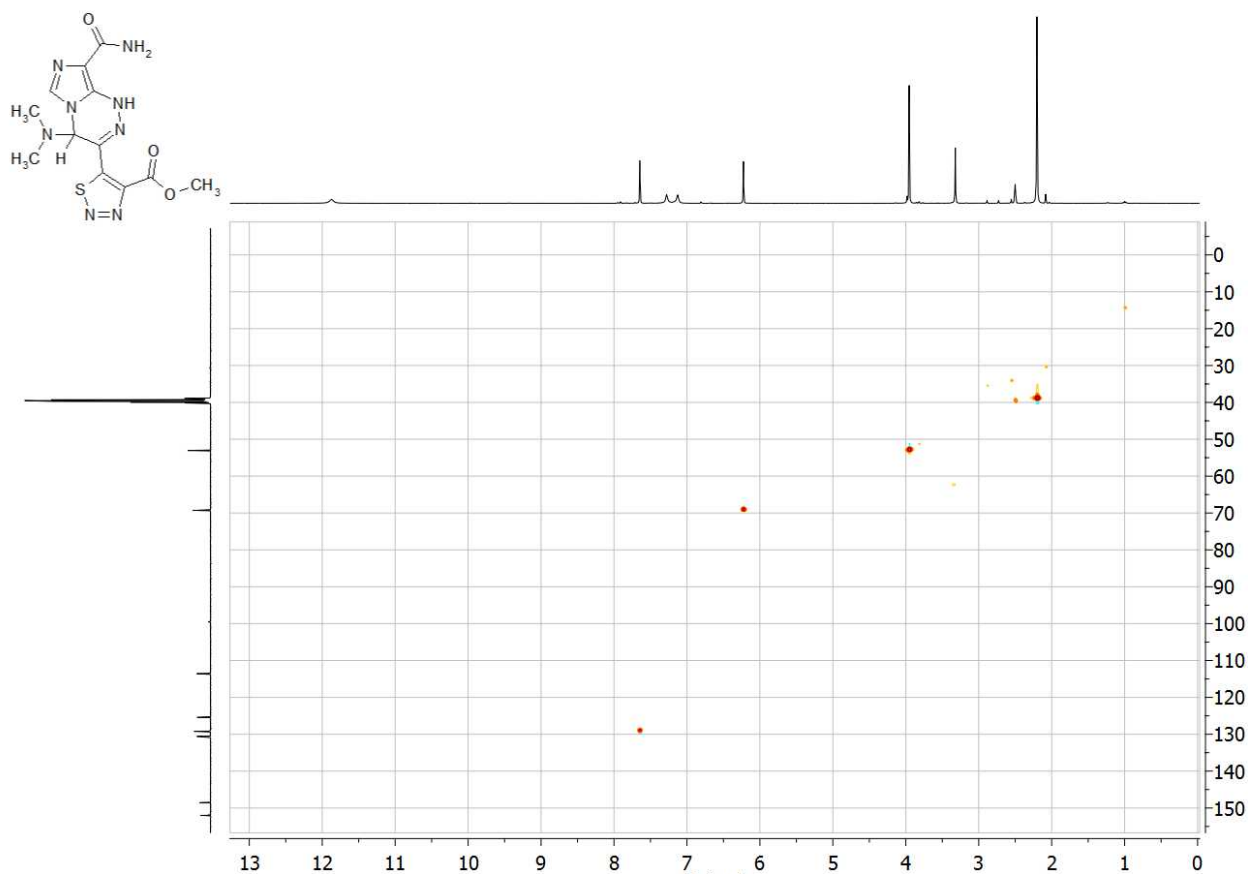


Fig. S18. HSQC spectrum of 4-(*N,N*-dimethylamino)-3-[4-(methoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxamide (**6h**)

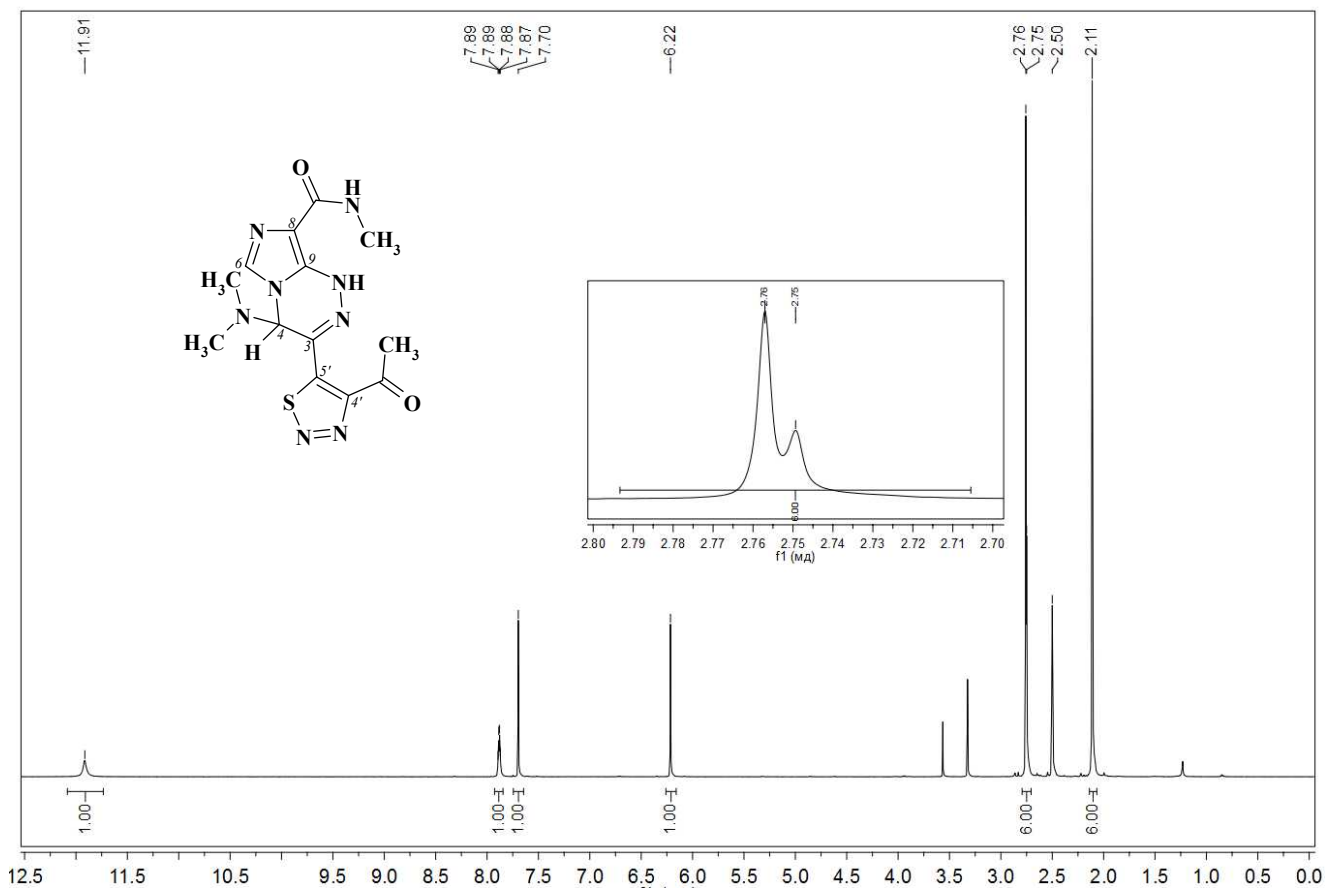


Fig. S19. ¹H NMR spectrum of 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-(*N,N*-dimethylamino)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-*N*-methylcarboxamide (**6i**)

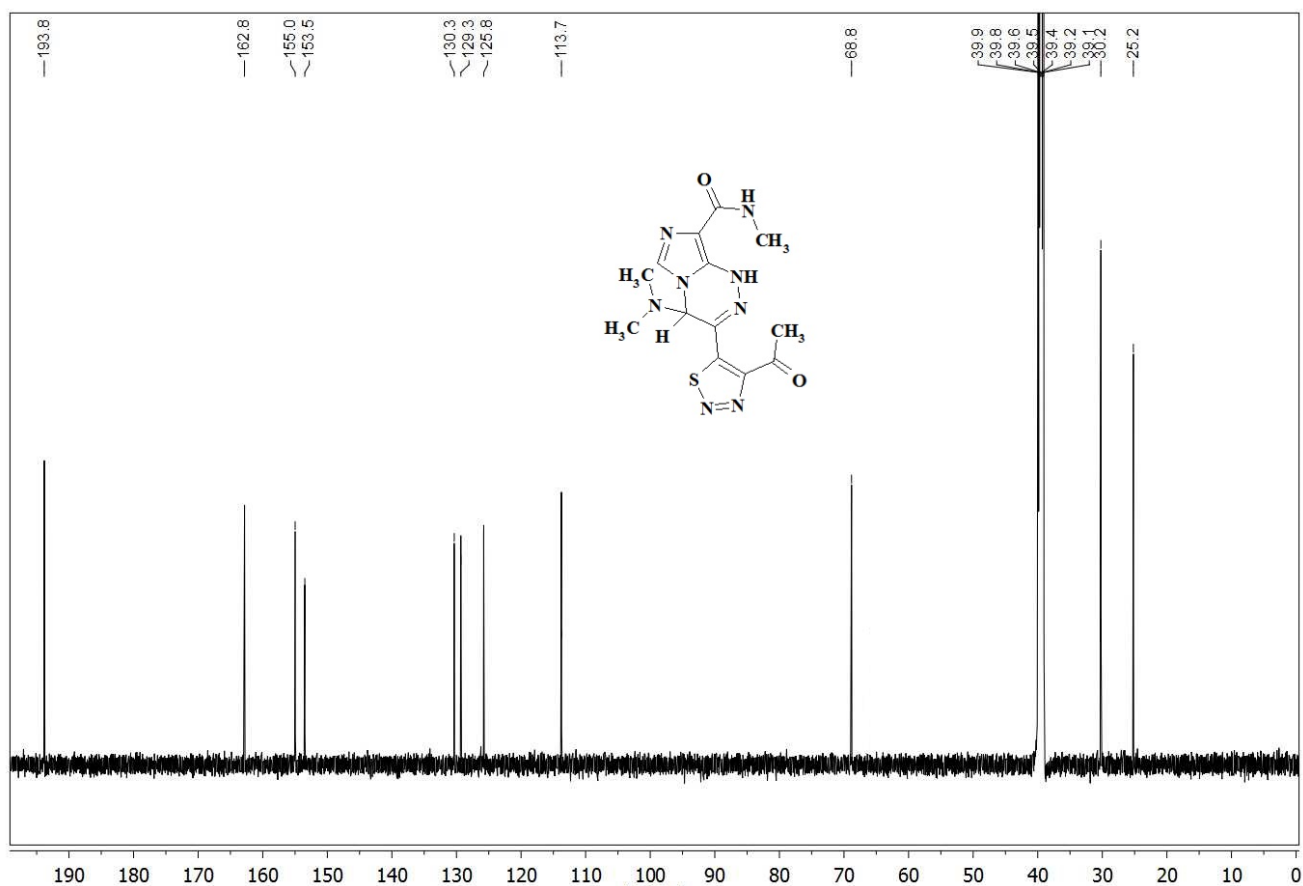
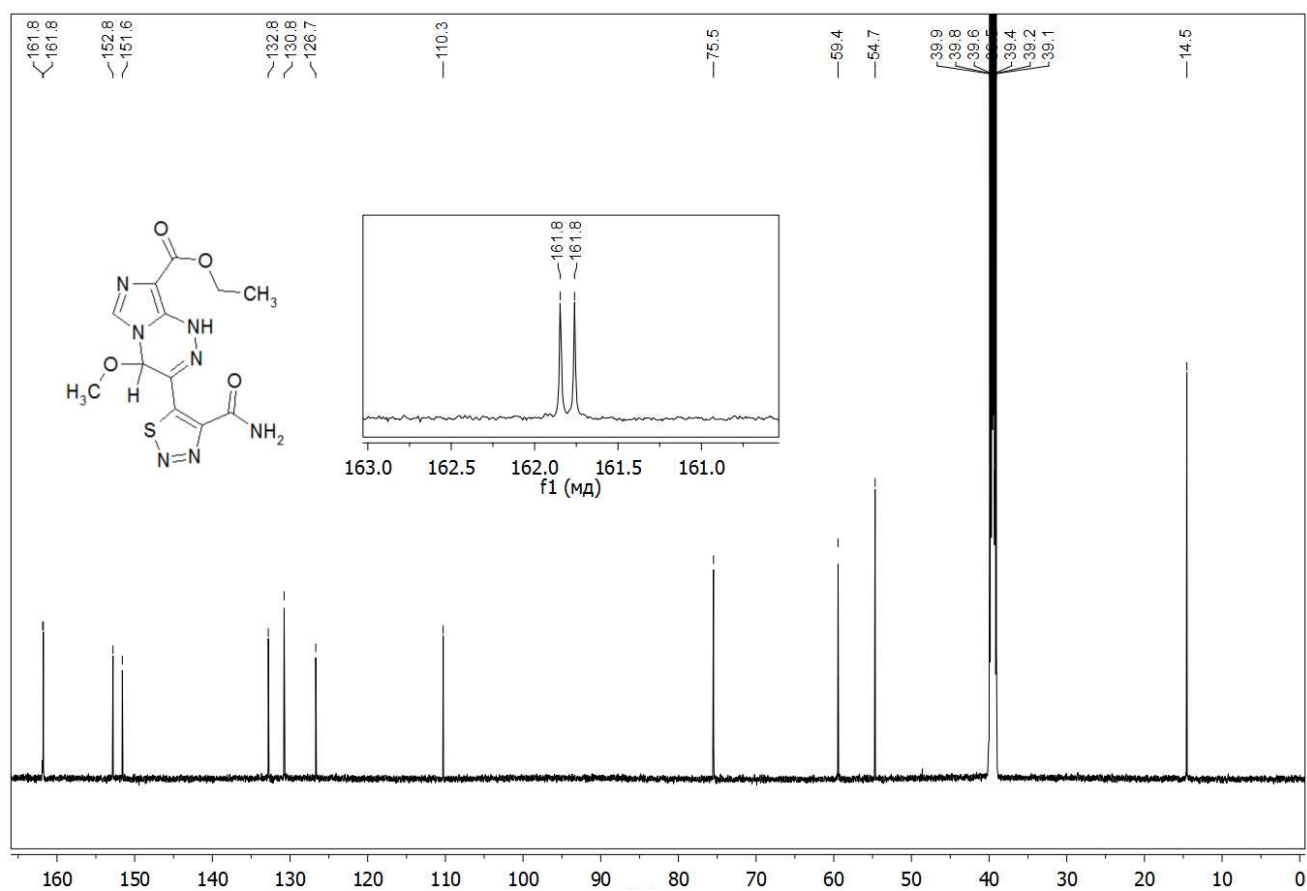
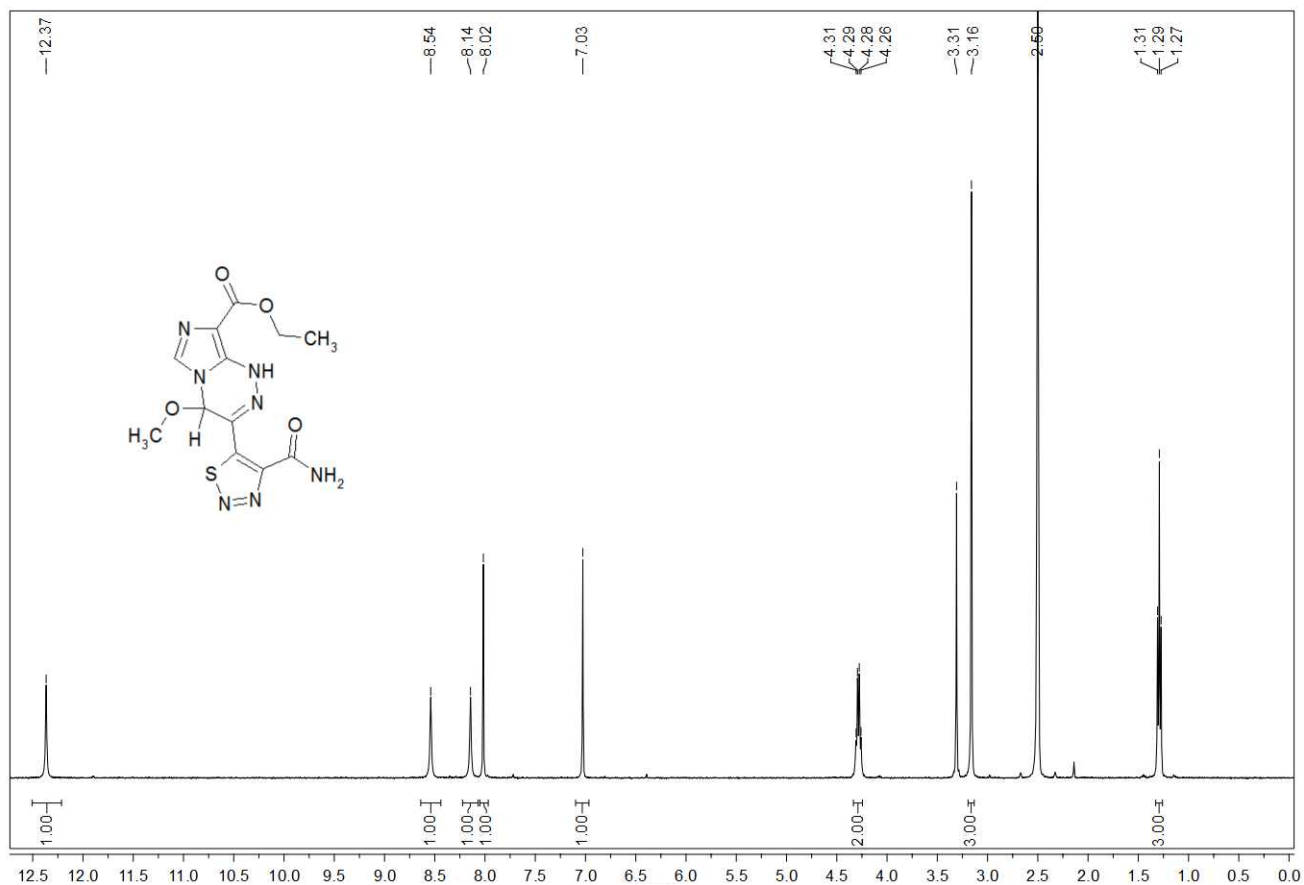


Fig. S20. ¹³C NMR spectrum of 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-(*N,N*-dimethylamino)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-*N*-methylcarboxamide (**6i**)



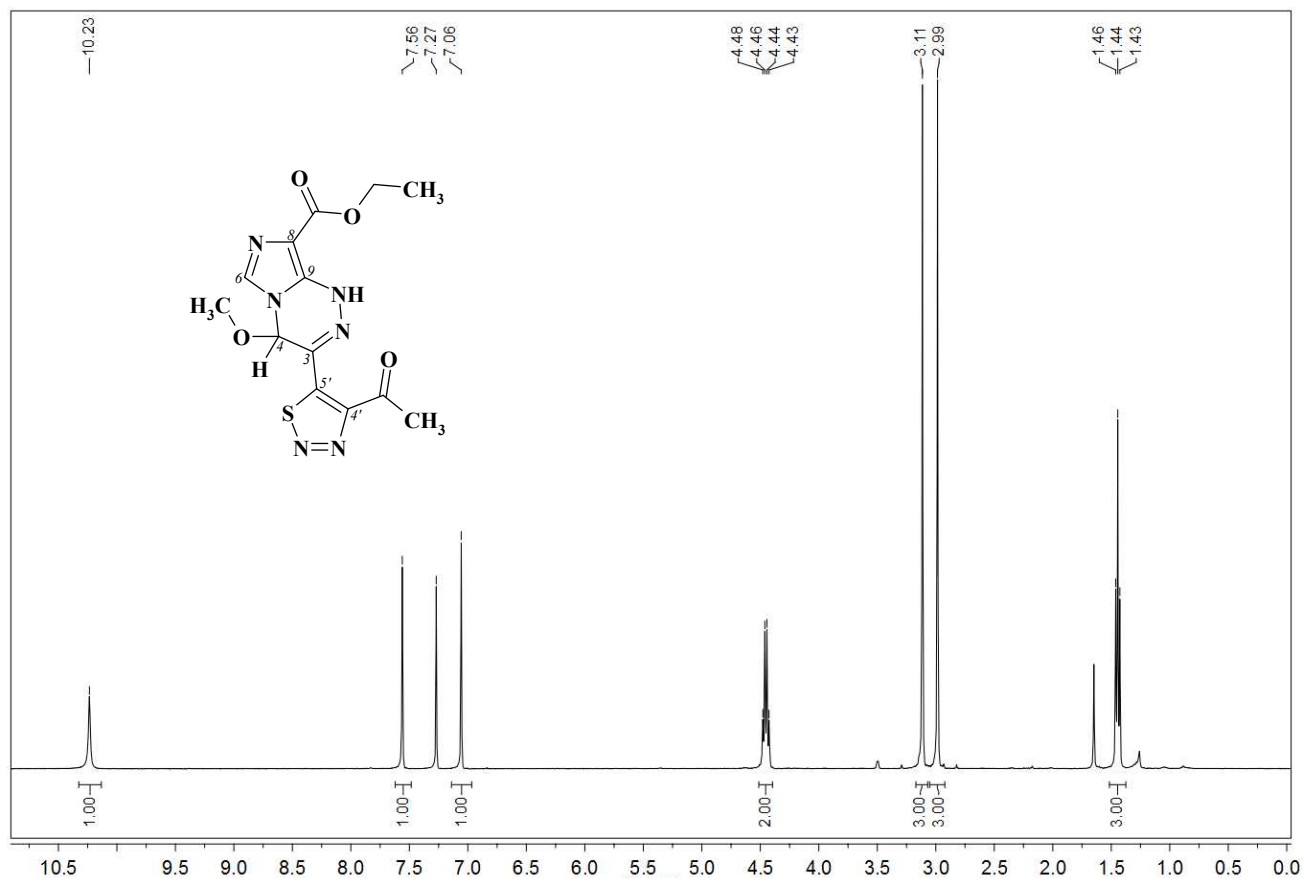


Fig. S23. ¹H NMR spectrum of ethyl 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-methoxy-1,4-dihydroimidazo[5,1-c][1,2,4]triazine-8-carboxylate (7e)

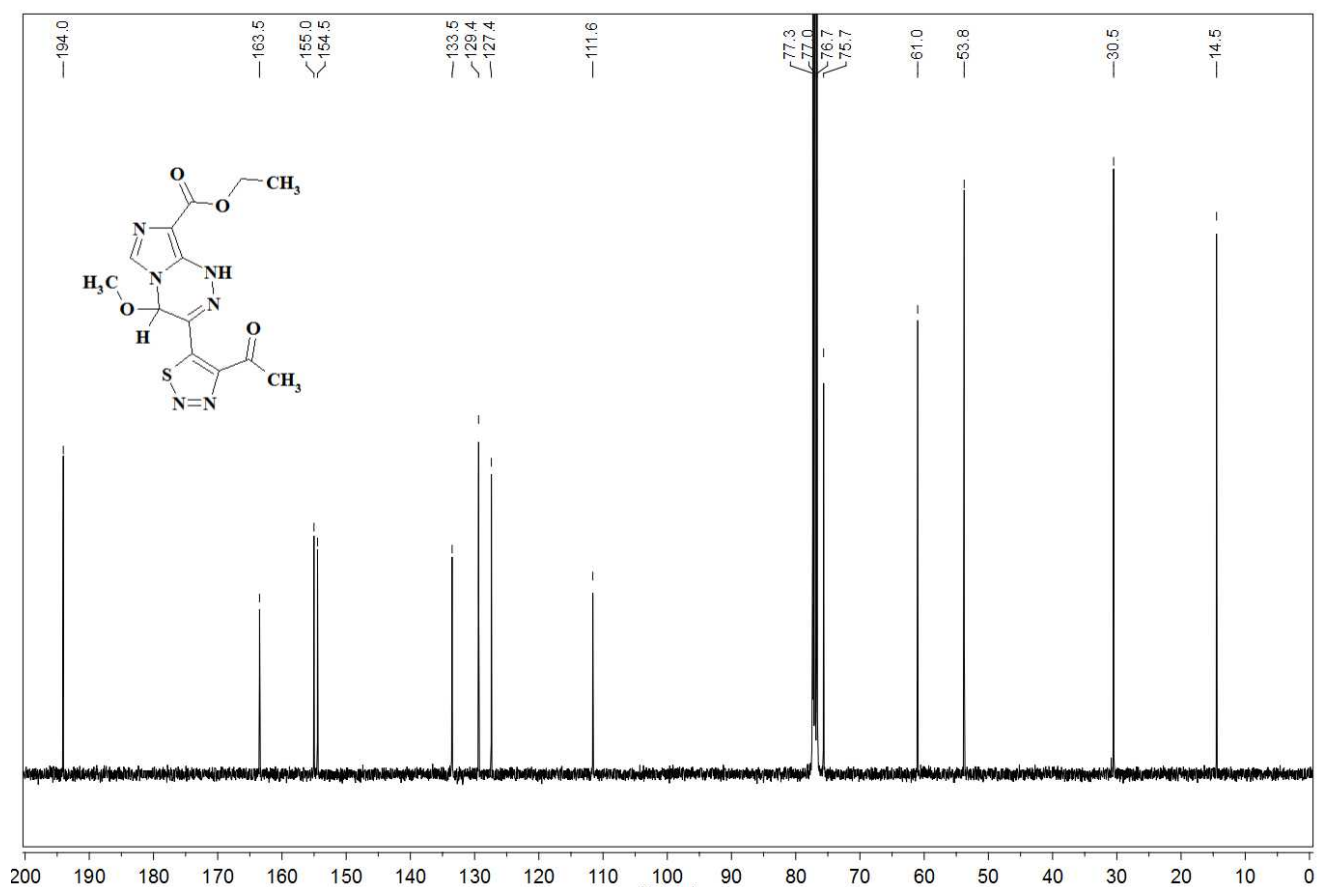


Fig. S24. ¹³C NMR spectrum of ethyl 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-methoxy-1,4-dihydroimidazo[5,1-c][1,2,4]triazine-8-carboxylate (7e)

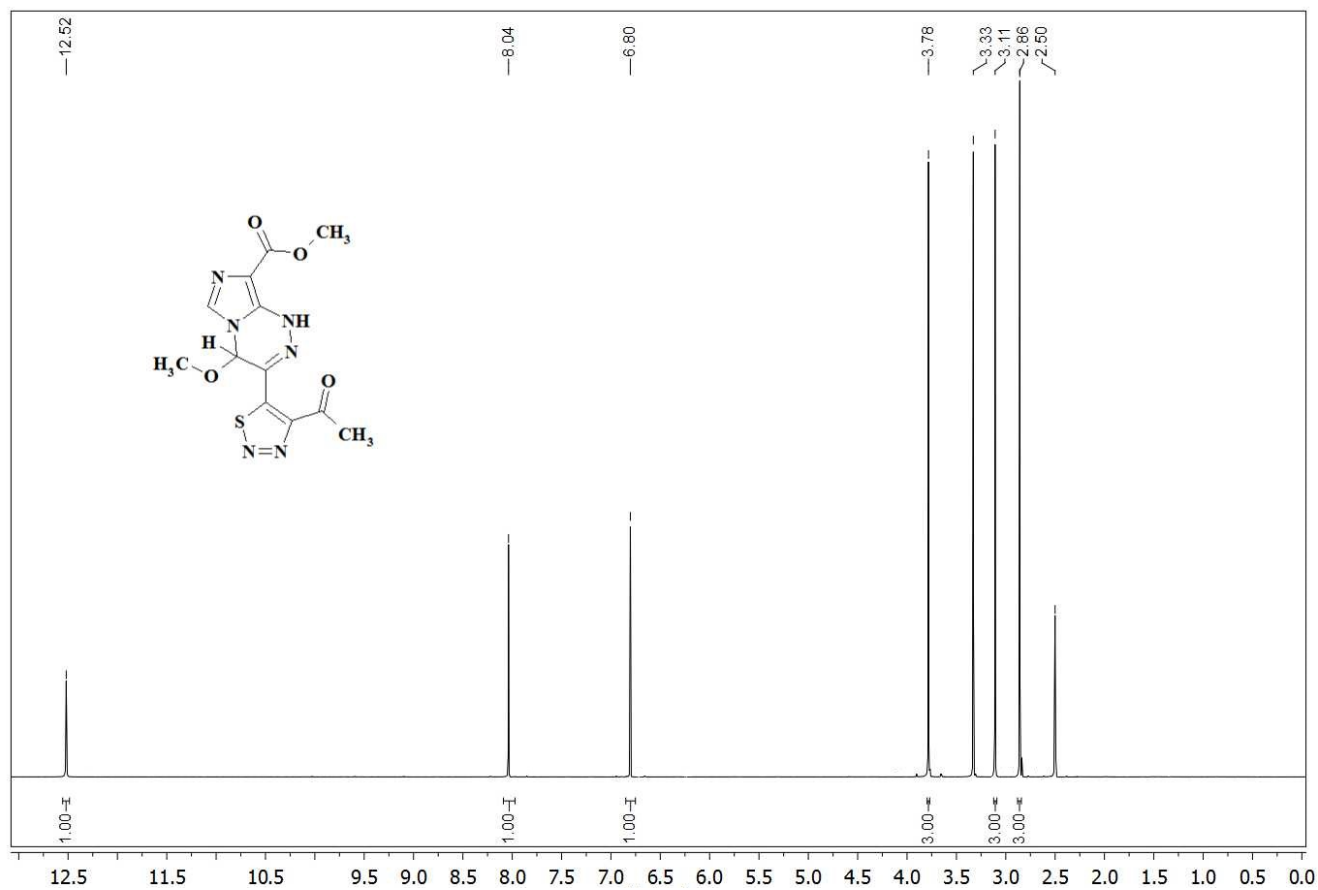


Fig. S25. ¹H NMR spectrum of methyl 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-methoxy-1,4-dihydroimidazo[5,1-c][1,2,4]triazine-8-carboxylate (**7f**)

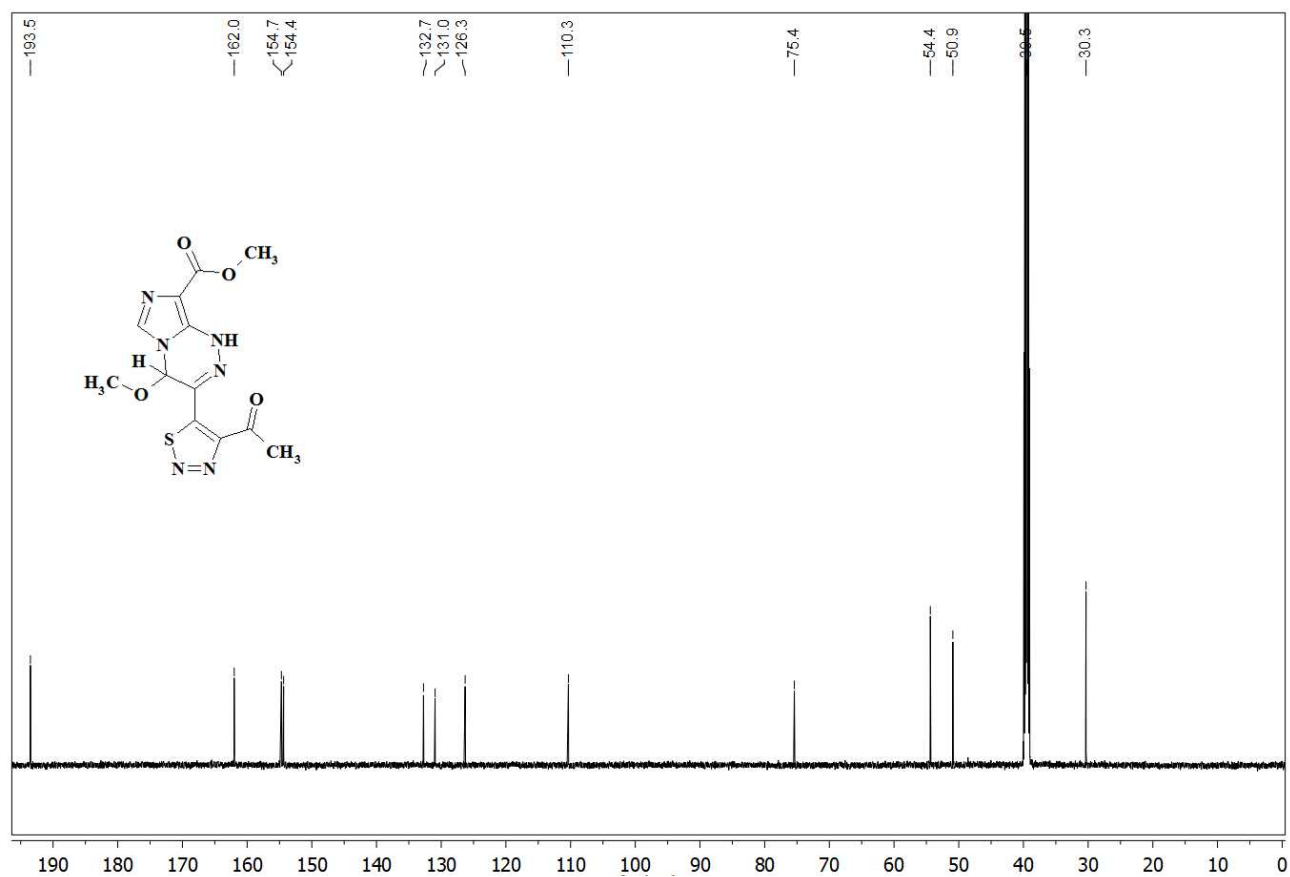


Fig. S26. ¹³C NMR spectrum of methyl 3-(4-acetyl-1,2,3-thiadiazol-5-yl)-4-methoxy-1,4-dihydroimidazo[5,1-c][1,2,4]triazine-8-carboxylate (**7f**)

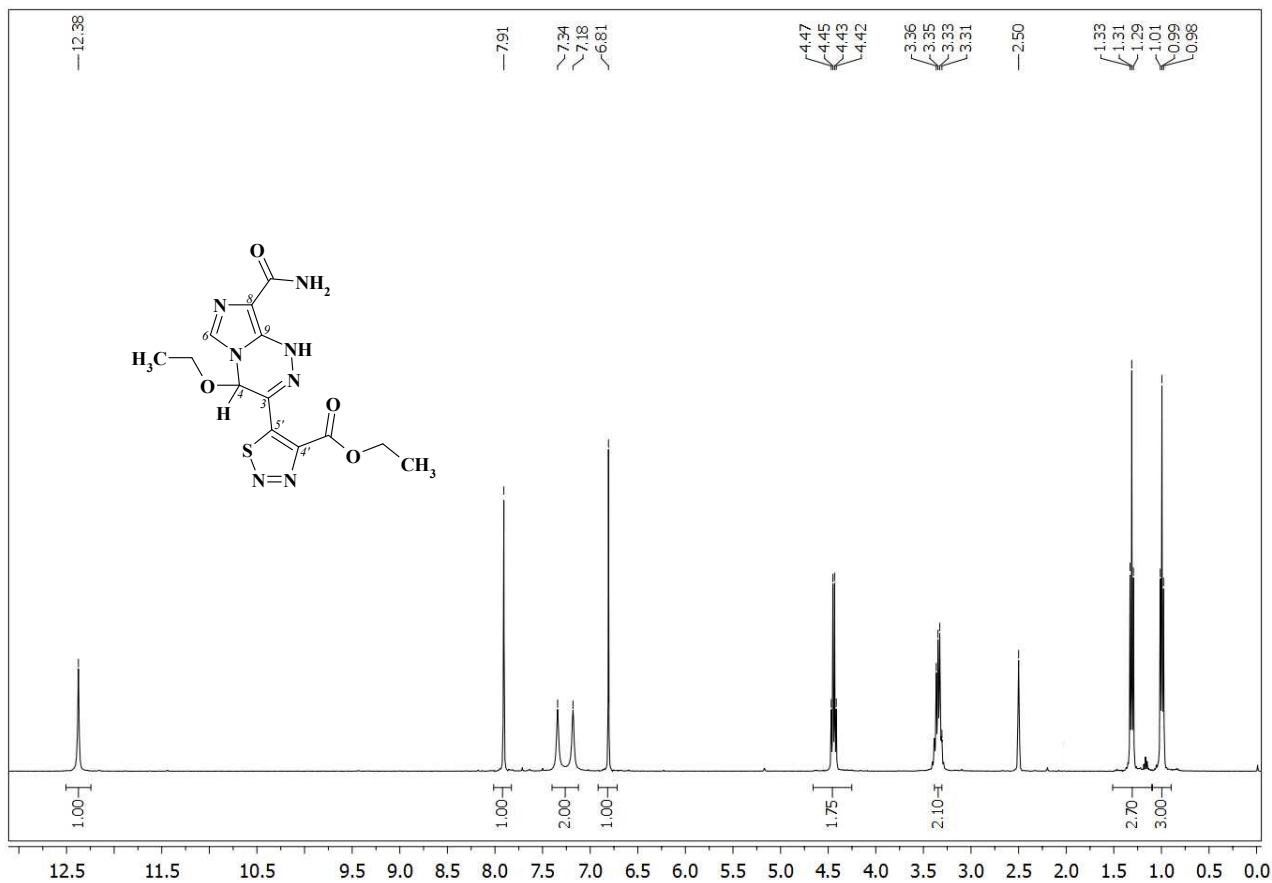


Fig. S27. ^1H NMR spectrum of 4-ethoxy-3-[4-(ethoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-c][1,2,4]-triazine-8-carboxamide (**7g**)

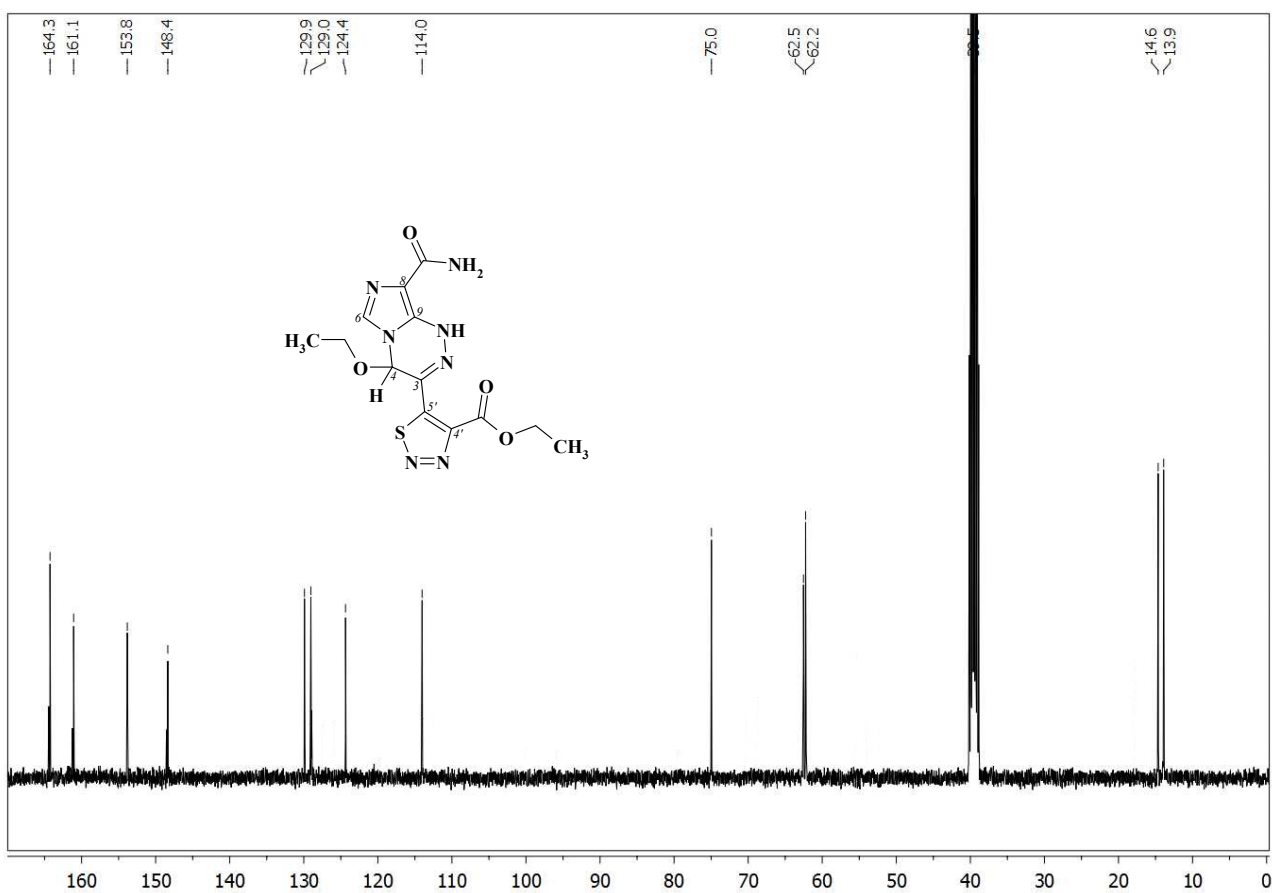


Fig. S28. ^{13}C NMR spectrum of 4-ethoxy-3-[4-(ethoxycarbonyl)-1,2,3-thiadiazol-5-yl]-1,4-dihydroimidazo[5,1-c][1,2,4]-triazine-8-carboxamide (**7g**)

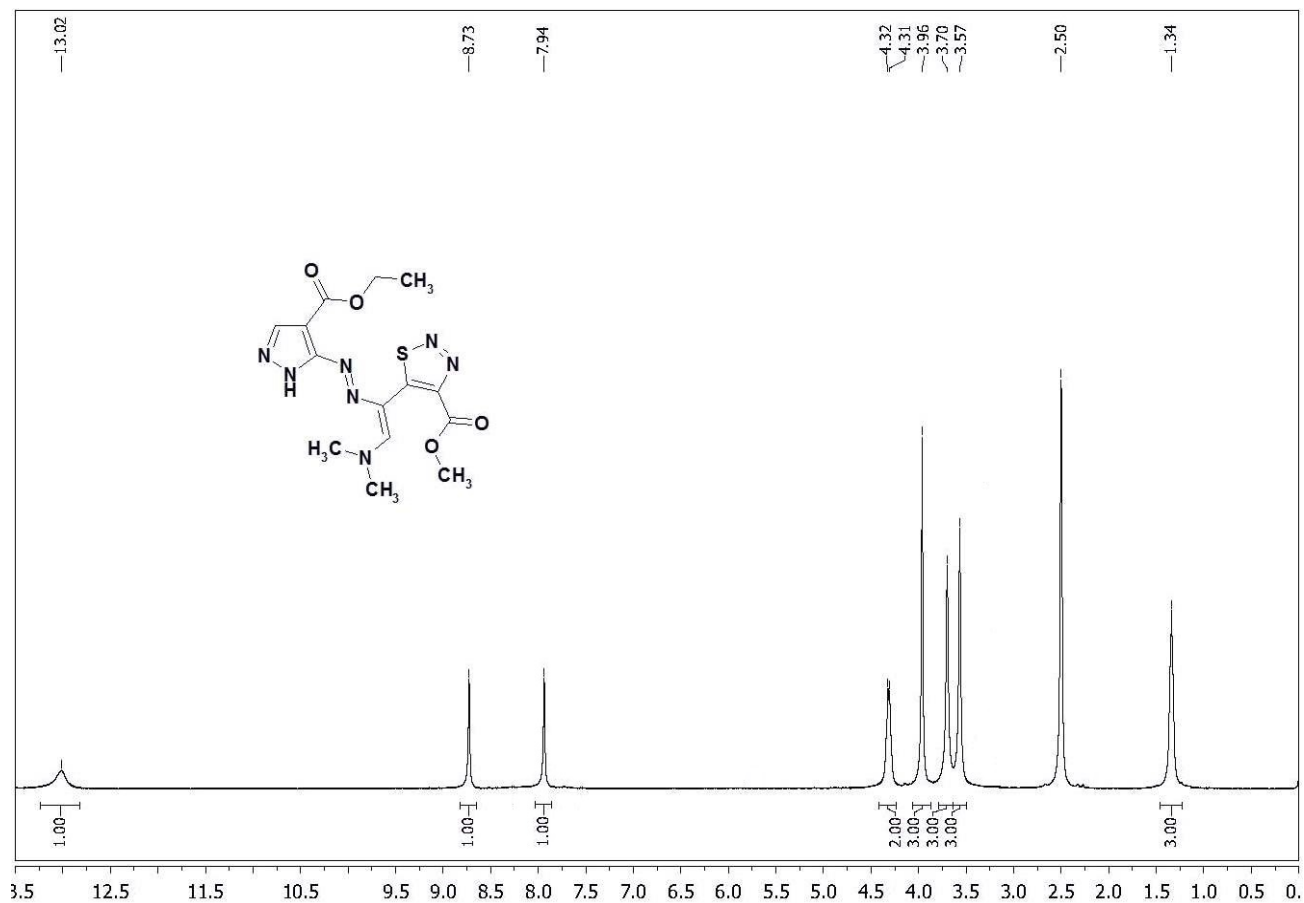


Fig. S29. ^1H NMR spectrum of 4-(*N,N*-dimethylamino)-3-(4-methoxycarbonylthiadiazol-5-yl)-1-(4-ethoxycarbonylpyrazol-5-yl)-1,2-diazabuta-1,3-diene (**9**)

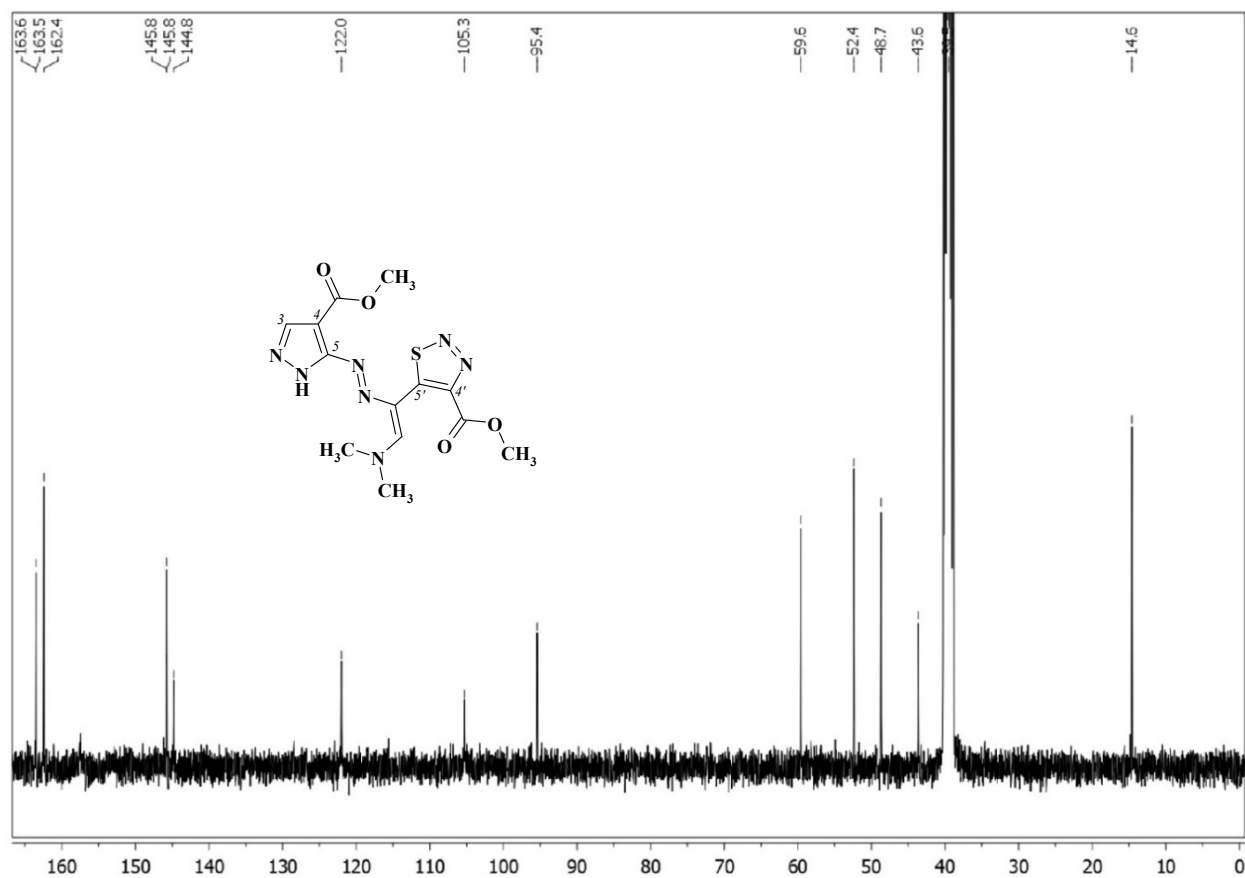


Fig. S30. ^{13}C NMR spectrum of 4-(*N,N*-dimethylamino)-3-(4-methoxycarbonylthiadiazol-5-yl)-1-(4-ethoxycarbonylpyrazol-5-yl)-1,2-diazabuta-1,3-diene (**9**)

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