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Supporting Information

for

Synthesis of functionalized imidazo[4,5-*e*]thiazolo[3,2-*b*]triazines by condensation of imidazo[4,5-*e*]triazinethiones with DMAD or DEAD and rearrangement to imidazo[4,5-*e*]thiazolo[2,3-*c*]triazines

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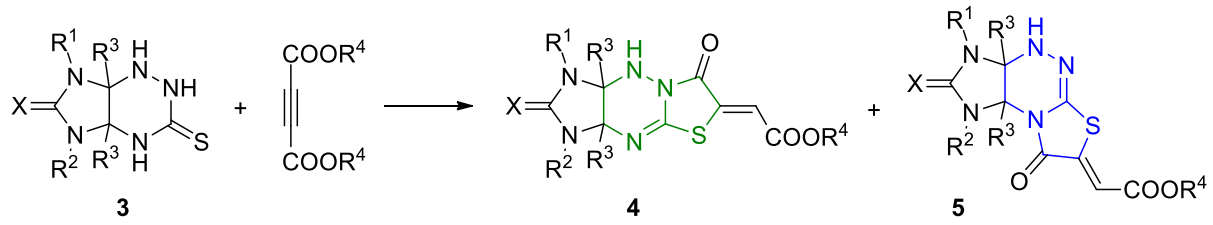
Experimental and analytical data

Table of contents

Table S1 Results for the screening of the reaction conditions[a]



Entry	Compound **3**	X	R^1, R^2, R^3	R^4	Conditions	Ratio of **4** and **5**	Total yield of **4**+**5**, %
1	**3a**	O	R^1=R^2=Me, R^3=H	Et	MeOH, reflux, 2h	38/62	80
2					95% EtOH, reflux, 2 h	30/70	72
3					Anh. EtOH, reflux, 2 h	32/68	71
4					MeOH + HCl, reflux, 2 h	—	0, decomp.
5					AcOH, 50 °C, 2 h	83/17	72
6					AcOH, 40 °C, 2 h	84/16	79
7					AcOH, 20 °C, 2 h	91/9	80
8				Me	AcOH, 20 °C, 2 h	89/11	88
9	**3b**	O	R^1=R^2=Et, R^3=H	Et	MeOH, reflux, 2 h	54/46	68
10					AcOH, 45 °C, 2 h	74/26	47
11					AcOH, 20 °C, 2 h	66/34	71
12				Me	AcOH, 20 °C, 2 h	94/6	63
13	**3c**	O	R^1=R^2=Me, R^3=Ph	Et	MeOH, reflux, 2 h	97/3	81
14					95% EtOH, reflux, 2 h	100/0	68
15					Anh. EtOH, reflux, 2 h	100/0	51
16				Me	MeOH, reflux, 2 h	100/0	81
17	**3d**	O	R^1=Me, R^2=Ph, R^3=H	Et	MeOH, reflux, 2 h	77/23	48[c]
18					AcOH, 20 °C, 2 h	100/0	64[b]
19					AcOH, 20 °C, 4 h	100/0	86
20					AcOH, 20 °C, 6 h	100/0	85
21				Me	AcOH, 20 °C, 4 h	100/0	87
22	**3e**	O	R^1=Et, R^2=Ph, R^3=H	Et	AcOH, 20 °C, 4 h	100/0	79
23				Me	AcOH, 20 °C, 4 h	100/0	92
24	**3f**	S	R^1=Me, R^2=Ph, R^3=H	Et	MeOH, reflux, 4 h	100/0	52
25					AcOH, 20 °C, 4 h	—	0
26					AcOH, 20 °C, 72 h	—	0
27				Me	MeOH, reflux, 4 h	100/0	65
28	**3g**	S	R^1=Et, R^2=Ph, R^3=H	Et	MeOH, reflux, 4 h	100/0	50
29				Me	MeOH, reflux, 4 h	100/0	54

[a]Reaction conditions: stirring the mixture of imidazo[4,5-*e*][1,2,4]triazin-3-thione **3** (2.0 mmol), and DMAD or DEAD (2.1 mmol) in solvent (4 ml). [b]Product **4k** was isolated in the mixture with **3d**. [c]The pure product **4** has not been isolated.

Experimental

IR spectra were recorded on a Bruker Alpha instrument in KBr pellets. ^{1}H NMR spectra were recorded on Bruker AM300 (300 MHz) and Bruker AV 600 (600 MHz) spectrometers in DMSO-d_6, using TMS as internal standard. ^{13}C NMR spectra were recorded on Bruker AM300 (75 MHz), Bruker DRX-500 (126 MHz), and Bruker AV 600 (151 MHz) spectrometers in DMSO-d_6, using TMS as internal standard. High-resolution mass spectra were obtained on a Bruker micrOTOF II instrument using electrospray ionization. Melting points were determined in open glass capillaries on a Gallenkamp (Sanyo) melting point apparatus.

All the reagents were purchased from Acros Organics and used without further purification. Compounds **3** were prepared according to known procedures for **3a**, **b** [1,2], **3c** [2], and **3d–g** [3].

Introductory experimental paragraph: Give a brief description of apparatus, instrumentation (makes and models), and methods used. Include the sources of any unusual reagents. All known compounds should be indicated by a reference or a CAS registry number.

General procedure for the synthesis of compounds 4a–n

Dimethyl or diethyl acetylenedicarboxylate (DMAD or DEAD, 4.2 mmol) were added to a suspension of imidazotriazine **3a**, **b**, **d**, **e** (4 mmol) in glacial AcOH (8 mL), and the mixture was stirred at room temperature for 2 h (for **4a**, **b**, **h**, **i**) or 4 h (for **4d**, **e**, **k**, **l**). The precipitate of compounds **4a**, **b**, **h**, **i** was filtered off, washed with MeOH and recrystallized from MeOH if necessary.

Dimethyl or diethyl acetylenedicarboxylate (DMAD or DEAD) (4.2 mmol) were added to a refluxing suspension of imidazotriazine **3c**, **f**, **g** (4 mmol) in MeOH (8 mL), and the mixture was refluxed with stirring for 2 h (for **4c**, **j**) or 4 h (for **4f**, **g**, **m**, **n**). The precipitate of compounds **4c**, **f**, **g**, **j**, **m**, **n** was filtered off and washed with MeOH.

Methyl (*Z*)-2-(1,3-dimethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4a)

Yield 722 mg (58%) as a pale yellow solid. Mp: 221–222 °C. IR (KBr), ν 3466, 3434, 3190 (NH), 2951 (Alk), 1724, 1697, 1639, 1616 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.58 (s, 3 H, NCH_3), 2.77 (s, 3 H, NCH_3), 3.79 (s, 3 H, OCH_3), 4.76 (dd, J = 5.9, 2.5 Hz, 1 H, 9a-H), 4.91 (d, J = 6.0 Hz, 1 H 3a-H), 6.86 (s, 1 H, =CH), 6.93 (d, J = 2.5 Hz, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 27.34, 28.28 ($2NCH_3$), 53.12 (OCH_3), 65.79, 66.42 (C-3a, C-9a), 116.51 (=CH), 139.79 (C-6), 149.28 (4a-C=N), 159.08, 159.69 (2-C=O, 7-C=O), 166.32 (COOMe). HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{11}H_{13}N_5O_4S$: 312.0761; found: 312.0756.

Methyl (*Z*)-2-(1,3-diethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4b)

Yield 719 mg (59%) as a pale yellow solid. Mp: 202–204 °C. IR (KBr), ν 3249 (NH), 2974, 2960, 2936, 2875 (Alk), 1738, 1700, 1646, 1614 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.94 (t, J = 7.2 Hz, 3 H, CH_3), 1.14 (t, J = 7.2 Hz, 3 H, CH_3), 3.01–3.19 (m, 3 H, NCH_2), 3.31–3.41 (m, 1 H, NCH_2), 3.78 (s, 3 H, OCH_3), 4.89 (dd, J = 6.0, 2.4 Hz, 1 H, 9a-H), 4.96 (d, J = 5.9 Hz, 1H 3a-H), 6.86 (s, 1 H, =CH), 6.89 (d, J = 2.4 Hz, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 13.25, 13.88 ($2CH_3$), 34.91, 35.61 ($2NCH_2$), 53.12 (OCH_3), 63.77, 64.73

(C-3a, C-9a), 116.62 (=CH), 139.70 (C-6), 149.27 (4a-C=N), 158.12, 159.68 (2-C=O, 7-C=O), 166.31 (COOMe). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{13}H_{17}N_5O_4S$: 340.1074; found: 340.1074.

Methyl (*Z*)-2-(1,3-dimethyl-2,7-dioxo-3a,9a-diphenyl-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4c)

Yield 1502 mg (81%) as a white solid. Mp: 268–270 °C. IR (KBr), ν 3233 (NH), 3054 (Ar), 2945 (Alk), 1719, 1641, 1616 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 2.61 (s, 6 H, 2NCH$_3$), 3.83 (s, 3 H, OCH$_3$), 6.72 (d, *J* = 7.4 Hz, 2 H, Ph-2,6), 6.80 (d, *J* = 7.5 Hz, 2 H, Ph-2,6), 6.97 (s, 1 H, =CH), 7.03–7.21 (m, 6 H, 2Ph-3-5), 7.77 (s, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 25.78, 26.48 (2NCH$_3$), 53.22 (OCH$_3$), 80.21, 82.44 (C-3a, C-9a), 116.98 (=CH), 126.67, 127.87, 128.12, 128.46, 128.51, 128.77 (2Ph-2-6), 134.27, 134.98 (2Ph-1), 140.20 (C-6), 148.39 (4a-C=N), 158.92, 159.51 (2-C=O, 7-C=O), 166.41 (COOMe). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{23}H_{21}N_5O_4S$: 464.1387; found: 464.1385.

Methyl (*Z*)-2-(1-methyl-2,7-dioxo-3-phenyl-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4d)

Yield 1298 mg (87%) as a pale yellow solid. Mp: 257–259 °C. IR (KBr), ν 3216, 3187 (NH), 3061, 3009 (Ar), 2955, 2913 (Alk), 1736, 1680, 1648, 1615 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 2.69 (s, 3 H, NCH$_3$), 3.78 (s, 3 H, OCH$_3$), 5.00 (dd, *J* = 5.9, 2.5 Hz, 1 H, 9a-H), 5.65 (d, *J* = 6.1 Hz, 1 H, 3a-H), 6.87 (s, 1 H, =CH), 7.02–7.20 (m, 2 H, Ph-4, NH), 7.34 (t, *J* = 8.0 Hz, 2 H, Ph-3,5), 7.71 (d, *J* = 7.8 Hz, 2 H, Ph-2,6). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 27.53 (NCH$_3$), 52.60 (OCH$_3$), 64.27, 65.02 (C-3a, C-9a), 116.24 (=CH), 119.21 (Ph-2,6), 122.83 (Ph-4), 128.58 (Ph-3,5), 138.45, 139.11 (Ph-1, C-6), 149.58 (4a-C=N), 155.60, 159.10 (2-C=O, 7-C=O), 165.77 (COOMe). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{16}H_{15}N_5O_4S$: 374.0918; found: 374.0912.

Methyl (*Z*)-2-(1-ethyl-2,7-dioxo-3-phenyl-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4e)

Yield 1424 mg (92%) as a white solid. Mp: 230–232 °C. IR (KBr), ν 3222 (NH), 3067, 3013 (Ar), 2980, 2960, 2876, 2839 (Alk), 1732, 1690, 1650, 1611 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.01 (t, *J* = 7.1 Hz, 3 H, CH$_3$), 3.21 (q, *J* = 7.0 Hz, 2 H, NCH$_2$), 3.77 (s, 3 H, OCH$_3$), 5.13 (d, *J* = 6.1 Hz, 1 H, 9a-H), 5.62 (d, *J* = 6.1 Hz, 1 H, 3a-H), 6.88 (s, 1 H, =CH), 7.06 (t, *J* = 7.2 Hz, 1 H, Ph-4), 7.34 (t, *J* = 7.9 Hz, 2 H, Ph-3,5), 7.70 (d, *J* = 8.1 Hz, 2 H, Ph-2,6). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 13.11 (CH$_3$), 35.67 (NCH$_2$), 53.16 (OCH$_3$), 63.74, 64.61 (C-3a, C-9a), 116.95 (=CH), 119.70 (Ph-2,6), 123.37 (Ph-4), 129.12 (Ph-3,5), 138.93, 139,44 (Ph-1, C-6), 150.22 (4a-C=N), 155.54, 159.71 (2-C=O, 7-C=O), 166.31 (COOMe). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{17}H_{17}N_5O_4S$: 388.1074; found: 388.1068.

Methyl (*Z*)-2-(1-methyl-7-oxo-3-phenyl-2-thioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4f)

Yield 1012 mg (65%) as a pale yellow powder. Mp: 236–237 °C. IR (KBr), ν 3203, 3167 (NH), 3064, (Ar), 2949, 2918, 2846, (Alk), 1736, 1652, 1616 (C=N, C=O,), 1327 (C=S) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 3.01 (s, 1 H, NCH$_3$), 3.79 (s, 1 H, OCH$_3$), 5.34 (dd, *J* = 6.7, 2.9 Hz, 1 H, 9a-H), 5.55 (d, *J* = 6.6 Hz, 1 H, 3a-H), 6.88 (s, 1 H, =CH), 7.23 (d, *J* = 2.9 Hz, 1 H, NH), 7.28 (t, *J* = 7.3 Hz, 1 H, Ph-4), 7.41 (t, *J* = 7.7 Hz, 2 H, Ph-3,5), 7.57 (d, *J* = 7.9 Hz, 2 H, Ph-2,6). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 31.25 (NCH$_3$), 53.18 (OCH$_3$), 68.65, 68.78 (C-3a, C-9a),

116.88 (=CH), 127.00 (Ph-4), 127.73 (Ph-2,6), 128.83 (Ph-3,5), 139.21, 139.44 (Ph-1, C-6), 150.83 (4a-C=N), 159.59 (7-C=O), 166.32 (COOMe), 181.43 (2-C=S). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{16}H_{15}N_5O_3S_2$: 390.0689; found: 390.0688.

Methyl (*Z*)-2-(1-ethyl-7-oxo-3-phenyl-2-thioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4g)

Yield 871 mg (54%) as a pale yellow powder. Mp: 225–227 °C. IR (KBr), ν 3216 (NH), 3063, 3002 (Ar), 2977, 2954, 2933, 2843 (Alk), 1733, 1655, 1607, (C=N, C=O), 1325 (C=S) cm^{-1}.

^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.06 (t, *J* = 7.0 Hz, 3 H, CH_3), 3.46–3.71 (m, 2 H, NCH_2), 3.78 (s, 3 H, OCH_3), 5.44 (d, *J* = 6.8 Hz, 1 H, 9a-H), 5.51 (d, *J* = 6.7 Hz, 1 H, 3a-H), 6.90 (s, 1 H, =CH), 7.28 (t, *J* = 7.4 Hz, 1 H, Ph-4), 7.40 (t, *J* = 7.7 Hz, 2 H, Ph-3,5), 7.55 (d, *J* = 7.7 Hz, 2 H, Ph-2,6). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 12.23 (CH_3), 38.75 (NCH_2), 53.20 (OCH_3), 67.16, 68.55 (C-3a, C-9a), 117.12 (=CH), 127.05 (Ph-4), 127.88 (Ph-2,6), 128.82 (Ph-3,5), 139.10, 139.19 (Ph-1, C-6), 150.90 (4a-C=N), 159.69 (7-C=O), 166.31 (COOMe), 180.59 (2-C=S). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{17}H_{17}N_5O_3S_2$: 404.0846; found: 404.0842.

Ethyl (*Z*)-2-(1,3-dimethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4h)

Yield 689 mg (53%) as a pale yellow solid. Mp: 221–222 °C. IR (KBr), ν 3187 (NH), 2971, 2939, 2902 (Alk), 1723, 1697, 1641 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.26 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.60 (s, 3 H, NCH_3), 2.77 (s, 3 H, NCH_3), 4.24 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.75 (dd, *J* = 5.9, 2.3 Hz, 1 H, 9a-H), 4.90 (d, *J* = 5.9 Hz, 1 H, 3a-H), 6.81 (s, 1 H, =CH), 6.92 (d, *J* = 2.2 Hz, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 13.92 (CH_3), 26.86, 27.74 ($2NCH_3$), 61.52 (OCH_2), 65.32, 65.93 (C-3a, C-9a), 116.29 (=CH), 139.11 (C-6), 148.78 (4a-C=N), 158.55, 159.18 (2-C=O, 7-C=O), 165.24 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{12}H_{15}N_5O_4S$: 326.0918; found: 326.0913.

Ethyl (*Z*)-2-(1,3-diethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4i)

Yield 664 mg (47%) as a pale yellow solid. Mp: 216–217 °C. IR (KBr), ν 3254 (NH), 3048, 2976, 2936, 2900, 2878 (Alk), 1738, 1697, 1644, 1613 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 0.94 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.13 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.00–3.20 (m, 3 H, NCH_2), 3.32–3.43 (m, 1 H, NCH_2), 4.24 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.89 (dd, *J* = 6.0, 2.4 Hz, 1 H, 9a-H), 4.96 (d, *J* = 5.9 Hz, 1 H, 3a-H), 6.82 (s, 1 H, =CH), 6.89 (d, *J* = 2.4 Hz, 1 H, NH). ^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ 12.78, 13.41, 13.97 ($3CH_3$), 34.45, 35.16 ($2NCH_2$), 61.59, 63.33, 64.30 (OCH_2, C-3a, C-9a), 116.42 (=CH), 139.13 (C-6), 148.85 (4a-C=N), 157.67, 159.24 (2-C=O, 7-C=O), 165.31 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{14}H_{19}N_5O_4S$: 354.1231; found: 354.1225.

Ethyl (*Z*)-2-(1,3-dimethyl-2,7-dioxo-3a,9a-diphenyl-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4j)

Yield 1546 mg (81%) as a pale yellow powder. Mp: 235–237 °C. IR (KBr), ν 3234 (NH), 3062 (Ar), 2981, 2938, 2904 (Alk), 1735, 1697, 1648, 1619 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.29 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.61 (s, 6 H, $2NCH_3$), 4.29 (q, *J* = 7.1 Hz, 2 H, OCH_2), 6.72 (d, *J* = 7.4 Hz, 2 H, Ph-2,6), 6.81 (d, *J* = 7.6 Hz, 2 H, Ph-2,6), 6.93 (s, 1 H, =CH), 7.01–7.25 (m, 6 H, 2Ph-3-5), 7.76 (s, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 13.96 (CH_3), 25.25, 25.96 ($2NCH_3$), 61.64 (OCH_2), 79.72, 81.95 (C-3a, C-9a), 116.75 (=CH), 126.17,

127.33, 127.61, 127.92, 127.97, 128.24 (2Ph-2-6), 133.78, 134.48 (2Ph-1), 139.53 (C-6), 147.89 (4a-C=N), 158.41, 159.00 (2-C=O, 7-C=O), 165.32 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{24}H_{23}N_5O_4S$: 478.1544; found: 478.1530.

Ethyl (*Z*)-2-(1-methyl-2,7-dioxo-3-phenyl-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4k)

Yield 1331 mg (86%) as a pale yellow solid. Mp: 221–222 °C. IR (KBr), ν 3278, 3257 (NH), 3106, 3080, 3069, 3012 (Ar), 2978, 2959, 2935, 2913 (Alk), 1737, 1690, 1643, 1624 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.69 (s, 3 H, NCH_3), 4.23 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.00 (dd, *J* = 6.1, 2.5 Hz, 1 H, 9a-H), 5.65 (d, *J* = 6.1 Hz, 1 H, 3a-H), 6.84 (s, 1 H, =CH), 7.06 (t, *J* = 7.3 Hz, 1 H, Ph-4), 7.12 (d, *J* = 2.5 Hz, 1 H, NH), 7.34 (t, *J* = 7.4 Hz, 2 H, Ph-3,5), 7.71 (d, *J* = 7.9 Hz, 2 H, Ph-2,6). ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.00 (CH_3), 27.62 (NCH_3), 61.66 (OCH_2), 64.33, 65.10 (C-3a, C-9a), 116.63 (=CH), 119.25 (Ph-2,6), 122.91 (Ph-4), 128.69 (Ph-3,5), 138.55, 139.04 (C-6, Ph-1), 149.72 (4a-C=N), 155.69, 159.23 (2-C=O, 7-C=O), 165.33 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{17}H_{17}N_5O_4S$: 388.1074; found: 388.1084.

Ethyl (*Z*)-2-(1-ethyl-2,7-dioxo-3-phenyl-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4l)

Yield 1267 mg (79%) as a pale yellow solid. Mp: 134–136 °C. IR (KBr), ν 3251, 3232, 3205 (NH), 3065, 3029 (Ar), 2980, 2936, 2903, 2875 (Alk), 1741, 1698, 1647, 1617 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.01 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.21 (q, *J* = 7.2 Hz, 2 H, NCH_2), 4.23 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.13 (d, *J* = 6.1 Hz, 1 H, 9a-H), 5.62 (d, *J* = 6.1 Hz, 1 H, 3a-H), 6.85 (s, 1 H, =CH), 7.04–7.09 (m, 2 H, Ph-4, NH), 7.34 (t, *J* = 7.9 Hz, 2 H, Ph-3,5), 7.71 (d, *J* = 7.9 Hz, 2 H, Ph-2,6). ^{13}C NMR (75 MHz, DMSO-d_6): δ 13.13, 14.42 ($2CH_3$), 35.67 (NCH_2), 62.11 (OCH_2), 63.75, 64.61 (C-3a, C-9a), 117.24 (=CH), 119.69 (Ph-2,6), 123.34 (Ph-4), 129.11 (Ph-3,5), 138.95, 139.28 (Ph-1, C-6), 150.24 (4a-C=N), 155.53, 159.72 (2-C=O, 7-C=O), 165.74 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{18}H_{19}N_5O_4S$: 402.1231; found: 402.1229.

Ethyl (*Z*)-2-(1-methyl-7-oxo-3-phenyl-2-thioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4m)

Yield 838 mg (52%) as a yellow solid. Mp: 244–246 °C. IR (KBr), ν 3220 (NH), 3057, (Ar), 2979, 2935, 2914 (Alk), 1741, 1695, 1651, 1618 (C=N, C=O), 1323 (C=S) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.26 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.01 (s, 3 H, NCH_3), 4.25 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.34 (dd, *J* = 6.7, 2.8 Hz, 1 H, 9a-H), 5.55 (d, *J* = 6.6 Hz, 1 H, 3a-H), 6.85 (s, 1 H, =CH), 7.24 (d, *J* = 2.8 Hz, 1 H, NH), 7.28 (t, *J* = 7.3 Hz, 1 H, Ph-4), 7.41 (t, *J* = 7.7 Hz, 2 H, Ph-3,5), 7.57 (d, *J* = 7.7 Hz, 2 H, Ph-2,6). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.45 (CH_3), 31.24 (NCH_3), 62.13 (OCH_2), 68.66, 68.78 (C-3a, C-9a), 117.18 (=CH), 126.99 (Ph-4), 127.71 (Ph-2,6), 128.83 (Ph-3,5), 139.21, 139.28, (C-6, Ph-1), 150.86 (4a-C=N), 159.61 (7-C=O), 165.78 (COOEt), 181.41 (2-C=S). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{17}H_{17}N_5O_3S_2$: 404.0846; found: 404.0846.

Ethyl (*Z*)-2-(1-ethyl-7-oxo-3-phenyl-2-thioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*][1,2,4]triazin-6(7*H*)-ylidene)acetate (4n)

Yield 834 mg (50%) as a yellow powder. Mp: 223–225 °C. IR (KBr), ν 3189 (NH), 3057 (Ar), 2977, 2934, 2872 (Alk), 1735, 1693, 1647, 1617 (C=N, C=O), 1317 (C=S) cm^{-1}. ^{1}H NMR (300

MHz, DMSO-d_6): δ 1.07 (t, J = 7.0 Hz, CH_3), 1.26 (t, J = 7.1 Hz, CH_3), 3.53–3.76 (m, 2 H, NCH_2), 4.25 (q, J = 7.1 Hz, OCH_2), 5.46 (dd, J = 6.7, 2.7 Hz, 1 H, 9a-H), 5.52 (d, J = 6.7 Hz, 1 H, 3a-H), 6.87 (s, 1 H, =CH), 7.19 (d, J = 2.7 Hz, 1 H, NH), 7.29 (t, J = 7.3 Hz, 1 H, Ph-4), 7.42 (t, J = 7.7 Hz, 2 H, Ph-3,5), 7.57 (t, J = 7.2 Hz, 2 H, Ph-2,6). ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.34, 14.44 ($2CH_3$), 38.75 (NCH_2), 62.15 (OCH2), 67.17, 68.55 (C-3a, C-9a), 117.40 (=CH), 127.02 (Ph-4), 127.85 (Ph-2,6), 128.81 (Ph-3,5), 139.04, 139.12 (Ph-1, C-6), 150.92 (4a-C=N), 159.69 (7-C=O), 165.76 (COOEt), 180.57 (2-C=S). HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{18}H_{19}N_5O_3S_2$: 418.1002; found: 418.0988.

General procedure for the synthesis of compounds 5a–n

Method A. Triethylamine (0.28 mL, 2 mmol, for **4a**, **b**, **h**, **i**), MeONa as 30% in methanol (0.093 mL, 0.5 mmol, for **4c–g**) or EtONa as 21% in ethanol (0.187 ml, 0.5 mmol, for **4j–n**) were added to a refluxing suspension of ester **4** (2 mmol) in corresponding alcohol (10 mL) (MeOH for **4a–g** or EtOH for **4h–n**), and the mixture was refluxed for 4 h (for **4a**, **b**, **h**, **i**) or 1 h (for **4d–g**, **k–n**). After cooling, the precipitate of compounds **5a–n** was filtered off and washed with MeOH or EtOH.

Method B (one-pot method for the synthesis of **5a**, **b**, **h**, **i**). Dimethyl or diethyl acetylenedicarboxylate (DMAD or DEAD, 2.1 mmol) were added to a refluxing suspension of imidazotriazine **3a**, **b** (2 mmol) in MeOH or EtOH (4 mL), and the mixture was refluxed for 2 h. Then, triethylamine (0.275 mL, 2 mmol) was added to the suspension, and the mixture was refluxed for additional 4 h. After cooling, the precipitate of compounds **5a**, **b**, **h**, **i** was filtered off and washed with MeOH or EtOH.

Methyl (*Z*)-2-(1,3-dimethyl-2,8-dioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5a)

Yield Method A: 566 mg (91%); Method B: 516 mg (83%) as a bright yellow solid. Mp: 214–216 °C. IR (KBr), ν 3303 (NH), 3009, 2958, (Alk), 1707, 1649, 1602 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.63 (s, 3 H, NCH_3), 2.86 (s, 3 H, NCH_3), 3.78 (OCH_3), 4.80 (dd, J = 6.0, 2.1 Hz, 1 H, 3a-H), 5.64 (d, J = 6.0 Hz, 1 H, 9a-H), 6.74 (s, 1 H, =CH), 8.05 (d, J = 2.1 Hz, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 27.94, 31.34 ($2NCH_3$), 52.51 (OCH_3), 64.02, 66.06 (C-3a, C-9a), 113.14 (=CH), 135.19 (C-7), 142.08 (5a-C=N), 158.97, 162.73 (2-C=O, 8-C=O), 166.23 (COOMe). HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{11}H_{23}N_5O_4S$: 312.0761; found: 312.0761.

Methyl (*Z*)-2-(1,3-diethyl-2,8-dioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5b)

Yield Method A: 603 mg (89%); Method B: 515 mg (76%) as a orange solid. Mp: 202–204 °C. IR (KBr), ν 3357, 3272 (NH), 2973, 2952, 2934, 2875 (Alk), 1719, 1696, 1637, 1603 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.02 (t, J = 7.1 Hz, 3 H, CH_3), 1.08 (t, J = 7.0 Hz, 3 H, CH_3), 3.01–3.12 (m, 1 H, NCH_2), 3.13–3.30 (m, 2 H, NCH_2), 3.38–3.57 (m, 1 H, NCH_2), 4.88 (dd, J = 6.1, 3.0 Hz, 1 H, 3a-H), 5.71 (d, J = 5.8 Hz, 1 H, 9a-H), 6.76 (s, 1 H, =CH), 8.03 (d, J = 2.1 Hz, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): 12.65, 12.89 ($2CH_3$), 34.84, 37.73 ($2CH_2$), 52.42 (OCH_3), 61.48, 63.68 (C-3a, C-9a), 113.18 (=CH), 134.83, 141.91 (5a-C=N, C-7), 157.79, 162.66 (2-C=O, 8-C=O), 166.12 (COOMe). HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{17}N_5O_4S$: 340.1074; found: 340.1076.

Methyl (*Z*)-2-(1,3-dimethyl-2,8-dioxo-3a,9a-diphenyl-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5c)

Yield 843 mg (91%) as a bright yellow powder. Mp: 252–254 °C.

IR (KBr), ν 3359, 3310 (NH), 3105, 3056 (Ar), 2954, 2908 (Alk), 1725, 1706, 1686, 1649 (C=N, C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ 2.59 (s, 3 H, NCH_3), 2.85 (s, 3 H, NCH_3), 3.78 (s, 3 H, OCH_3), 6.64 (s, 1 H, =CH), 6.67 (br.s, 3 H, Ph), 7.10 (br.s, 3 H, Ph), 7.15–7.30 (m, 4 H, Ph), 8.41 (s, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 25.58, 30.76 ($2NCH_3$), 52.49 (OCH_3), 81.31, 86.89 (C-3a, C-9a), 113.49 (=CH), 127.20, 127.73, 128.03, 128.56, 128.98 (2Ph-2-6), 131.50, 132.66 (2Ph-1), 136.98, 142.33 (5a-C=N, C-7), 158.12, 161.86 (2-C=O, 8-C=O), 166.25 (COOMe). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{23}H_{21}N_5O_4S$: 464.1387; found: 464.1383.

Methyl (*Z*)-2-(3-methyl-2,8-dioxo-1-phenyl-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5d)

Yield 552 mg (74%) as a bright yellow solid. Mp: 250–251 °C. IR (KBr), ν 3299 (NH), 3070, 3058 (Ar), 2992, 2978, 2948 (Alk), 1711, 1694, 1651, 1604 (C=N, C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ 2.68 (s, 3 H, NCH_3), 3.74 (s, 3 H, OCH_3), 5.15 (dd, *J* = 5.9, 1.7 Hz, 1 H, 3a-H), 6.48 (d, *J* = 6.0 Hz, 1 H, 9a-H), 6.55 (s, 1 H, =CH), 7.15 (t, *J* = 7.2 Hz, 1 H, Ph-4), 7.31 (t, *J* = 7.8 Hz, 2 H, Ph-3,5), 7.40 (d, *J* = 7.7 Hz, 2 H, Ph-2,6), 8.25 (d, *J* = 1.7 Hz, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): 28.12 (NCH_3), 52.92 (OCH_3), 65.31, 65.31 (C-3a, C-9a), 113.72 (=CH), 124.62 (Ph-2,6), 125.52 (Ph-4), 128.63 (Ph-3,5), 136.13 (Ph-1), 139.11, 142.08 (5a-C=N, C-7), 157.25, 161.98 (2-C=O, 8-C=O), 166.62 (COOMe).

HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{16}H_{15}N_5O_4S$: 374.0918; found: 374.0915.

Methyl (*Z*)-2-(3-ethyl-2,8-dioxo-1-phenyl-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5e)

Yield 573 mg (74%) as a bright yellow solid. Mp: 230–232 °C. IR (KBr), ν 3306, 3258 (NH), 3153, 3072 (Ar), 2992, 2973, 2948, 2849 (Alk), 1714, 1692, 1650, 1600 (C=N, C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 1.04 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.03–3.19 (m, 1 H, NCH_2), 3.20–3.32 (m, 1 H, NCH_2), 3.73 (s, 3 H, OCH_3), 5.26 (d, *J* = 6.0 Hz, 1 H, 3a-H), 6.44 (d, *J* = 5.9 Hz, 1 H, 9a-H), 6.54 (s, 1 H, =CH), 7.15 (t, *J* = 7.3 Hz, 1 H, Ph-4), 7.30 (t, *J* = 7.8 Hz, 2 H, Ph-3,5), 7.40 (d, *J* = 8.0 Hz, 2 H, Ph-2,6), 8.23 (d, *J* = 2.1 Hz, 1 H, NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ 12.45 (CH_3), 34.88 (NCH_2), 52.50 (OCH_3), 62.65, 65.00 (C-3a, C-9a), 113.36 (=CH), 124.11 (Ph-2,6), 125.04 (Ph-4), 128.22 (Ph-3,5), 135.65 (Ph-1), 138.65, 141.62 (C-7, 5a-C=N), 156.10, 161.54 (2-C=O, 8-C=O), 166.19 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{17}H_{17}N_5O_4S$: 388.1074; found: 388.1062.

Methyl (*Z*)-2-(3-methyl-8-oxo-1-phenyl-2-thioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5f)

Yield 451 mg (58%) as a bright yellow solid. Mp: 210–212 °C. IR (KBr), ν 3234 (NH), 3219, 3074, 3055 (Ar), 2955, 2949, 2845 (Alk), 1726, 1694, 1646, 1604 (C=N, C=O), 1318 (C=S) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 3.06 (s, 3 H, NCH_3), 3.75 (s, 3 H, OCH_3), 5.42 (dd, *J* = 6.6, 2.9 Hz, 1 H, 3a-H), 6.38 (d, *J* = 6.5 Hz, 1 H, 9a-H), 6.53 (s, 1 H, =CH), 7.23–7.42 (m, 5 H, Ph), 8.36 (d, *J* = 2.2 Hz, 1 H, NH). ^{13}C NMR (150 MHz, DMSO-d_6): δ 31.56 (NCH_3), 52.55 (OCH_3), 67.33, 67.56 (C-3a, C-9a), 113.60 (=CH), 127.42 (Ph-4), 128.43, 128.64 (Ph-2,3,5,6),

135.76 (Ph-1), 139.43, 141.43 (5a-C=N, C-7), 161.09 (8-C=O), 166.12 (COOMe), 182.87 (2-C=S). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{16}H_{15}N_5O_3S_2$: 390.0689; found: 390.0678.

Methyl (*Z*)-2-(3-ethyl-8-oxo-1-phenyl-2-thioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5g)

Yield 524 mg (65%) as a yellow solid. Mp: 208–210 °C. IR (KBr), ν 3236 (NH), 3131, 3067 (Ar), 2993, 2970, 2952, 2935, 2907, 2874, 2848 (Alk), 1732, 1684, 1652, 1604 (C=N, C=O), 1333 (C=S) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.13 (t, *J* = 7.0 Hz, 3 H, CH_3), 3.41–3.58 (m, 1 H, NCH_2), 3.74 (s, 3 H, OCH_3), 3.74–3.89 (m, 1 H, NCH_2), 5.52 (d, *J* = 7.0 Hz, 1 H, 3a-H), 6.34 (d, *J* = 6.6 Hz, 1 H, 9a-H), 6.52 (s, 1 H, =CH), 7.21–7.4 (m, 5 H, Ph), 8.36 (d, *J* = 2.2 Hz, 1 H, NH). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ 11.86 (CH_3), 38.60 (NCH_2), 52.55 (OCH_3), 65.70, 67.64 (C-3a,C-9a), 113.71 (=CH), 127.36 (Ph-4), 128.38, 128.67 (Ph-2,3,5,6), 135.90 (Ph-1), 139.39, 141.39 (C-7, 5a-C=N), 161.02 (8-C=O), 166.11 (COOMe), 181.85 (2-C=S). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{17}H_{17}N_5O_3S_2$: 404.0846; found: 404.0842.

Ethyl (*Z*)-2-(1,3-dimethyl-2,8-dioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5h)

Yield Method A: 520 mg (80%); Method B: 403 mg (62%) as a bright orange solid. Mp: 201–202 °C. IR (KBr), ν 3337 (NH), 2977, 2938, (Alk), 1734, 1707, 1678, 1640 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.63 (s, 3 H, NCH_3), 2.68 (s, 3 H, NCH_3), 4.24 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.80 (dd, *J* = 6.0, 2.0 Hz, 1 H, 3a-H), 5.64 (d, *J* = 6.0 Hz, 1 H, 9a-H), 6.70 (s, 1 H, =CH), 8.04 (d, *J* = 2.0 Hz, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 13.98 (CH_3), 27.86, 31.26 ($2NCH_3$), 61.30 (OCH_2), 63.95, 63.98 (C-3a,C-9a), 113.39 (=CH), 135.17, 141.84 (C-7, 5a-C=N), 158.87, 162.86 (2-C=O, 8-C=O), 165.64 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{12}H_{15}N_5O_4S$: 326.0918; found: 326.0914.

Ethyl (*Z*)-2-(1,3-diethyl-2,8-dioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5i)

Yield Method A: 537 mg (76%); Method B: 395 mg (56%) as a bright yellow solid. Mp: 150–152 °C. IR (KBr), ν 3281 (NH), 2982, 2941, 2879, (Alk), 1737, 1714, 1642, 1616 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 0.90–1.16 (m, 6 H, $2CH_3$), 1.26 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.90–3.10 (m, 1 H, NCH_2), 3.11–3.30 (m, 2 H, NCH_2), 3.35–3.53 (m, 1 H, NCH_2), 4.24 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.87 (dd, *J* = 5.9, 2.1 Hz, 1 H, 3a-H), 5.70 (d, *J* = 5.9 Hz, 1 H, 9a-H), 6.72 (s, 1 H, =CH), 8.02 (s, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 12.67, 12.92, 13.99 ($3CH_3$), 34.85, 37.76 ($2NCH_2$), 61.32, 61.60 (C-3a, C-9a), 63.69 (OCH_2), 113.50 (=CH), 134.94 (C-7), 141.78 (5a-C=N), 157.81, 162.69 (2-C=O, 8-C=O), 165.64 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{14}H_{19}N_5O_4S$: 354.1231; found: 354.1222.

Ethyl (*Z*)-2-(1,3-dimethyl-2,8-dioxo-3a,9a-diphenyl-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5j)

Yield 801 mg (84%) as a bright yellow solid. Mp: 236–238 °C. IR (KBr), ν 3296 (NH), 3144, 3056 (Ar), 2973, 2908, (Alk), 1726, 1703, 1651, 1602 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.59 (s, 3 H, NCH_3), 2.85 (s, 3 H, NCH_3), 4.25 (q, *J* = 7.1 Hz, 2 H, OCH_2), 6.61 (s, 1 H, =CH), 6.68 (br.s, 3 H, Ph), 7.10 (br.s, 3 H, Ph), 7.18–7.24 (m, 4 H, Ph), 8.40 (s, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 14.02 (CH_3), 25.52, 30.73 ($2NCH_3$), 61.28 (OCH_2), 81.31, 86.81 (C-3a, C-9a), 113.70 (=CH), 127.16, 127.68, 127.97, 128.49, 128.90 (2Ph-2-6), 131.50, 132.69, (2Ph-1), 136.91, 142.18 (C-7, 5a-C=N), 158.04,

161.82 (2-C=O, 8-C=O), 165.68 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{24}H_{23}N_5O_4S$: 478.1544; found: 478.1550.

Ethyl (*Z*)-2-(3-methyl-2,8-dioxo-1-phenyl-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5k)

Yield 627 mg (81%) as a bright yellow solid. Mp: 240–242 °C. IR (KBr), ν 3295 (NH), 3077, (Ar), 2982, 2941, 2913 (Alk), 1716, 1690, 1650, 1604 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.22 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.68 (s, 3 H, NCH_3), 4.20 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.15 (dd, *J* = 5.9, 2.0 Hz, 1 H, 3a-H), 6.47 (d, *J* = 6.0 Hz, 1 H, 9a-H), 6.51 (s, 1 H, =CH), 7.15 (t, *J* = 7.2 Hz, 1 H, Ph-4), 7.31 (t, *J* = 7.7 Hz, 2 H, Ph-3,5), 7.39 (d, *J* = 7.9 Hz, 2 H, Ph-2,6), 8.23 (d, *J* = 1.8 Hz, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 14.47 (CH_3), 28.12 (NCH_3), 61.78 (OCH_2), 65.21, 65.34 (C-3a, C-9a), 114.00 (=CH), 124.67 (Ph-2,6), 125.52 (Ph-4), 128.63 (Ph-3,5), 136.20 (Ph-1), 139.10, 141.94 (5a-C=N, C-7), 157.24, 161.99 (2-C=O, 8-C=O), 166.10 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{17}H_{17}N_5O_4S$: 388.1074; found: 388.1073.

Ethyl (*Z*)-2-(3-ethyl-2,8-dioxo-1-phenyl-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5l)

Yield 513 mg (64%) as a bright yellow solid. Mp: 220–222 °C. IR (KBr), ν 3256 (NH), 3141, 3077 (Ar), 2979, 2934, 2873 (Alk), 1721, 1689, 1650, 1603 (C=N, C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.04 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.22 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.03–3.19 (m, 1 H, NCH_2), 3.20–3.28 (m, 1 H, NCH_2), 4.20 (q, *J* = 7.0 Hz, 2 H, OCH_2), 5.27 (d, *J* = 6.2 Hz, 1 H, 3a-H), 6.44 (d, *J* = 5.9 Hz, 1 H, 9a-H), 6.51 (s, 1 H, =CH), 7.15 (t, *J* = 7.1 Hz, 1 H, Ph-4), 7.31 (t, *J* = 7.7 Hz, 2 H, Ph-3,5), 7.40 (d, *J* = 7.6 Hz, 2 H, Ph-2,6). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 12.36, 13.93 ($2CH_3$), 34.76 (NCH_2), 61.23, 62.62, 64.92 (OCH_2, C-3a, C-9a), 113.50 (=CH), 124.04 (Ph-2,6), 124.91 (Ph-4), 128.07 (Ph-3,5), 135.54 (Ph-1), 138.55, 141.36 (5a-C=N, C-7), 155.97, 161.41 (2-C=O, 8-C=O), 165.52 (COOEt). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{18}H_{19}N_5O_4S$: 402.1231; found: 402.1223.

Ethyl (*Z*)-2-(3-methyl-8-oxo-1-phenyl-2-thioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5m)

Yield 532 mg (66%) as a bright yellow powder. Mp: 219–221 °C. IR (KBr), ν 3315 (NH), 3077 (Ar), 2980, 2933, 2915, 2900 (Alk), 1729, 1681, 1647, 1604 (C=N, C=O), 1315 (C=S) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.23 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.05 (s, 3 H, NCH_3), 4.21 (q, *J* = 7.0 Hz, 2 H, OCH_2), 5.41 (dd, *J* = 6.4, 2.1 Hz, 1 H, 3a-H), 6.37 (d, *J* = 6.5 Hz, 1 H, 9a-H), 6.48 (s, 1 H, =CH), 7.23–7.40 (m, 5 H, Ph), 8.34 (s, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 14.47 (CH_3), 31.99 (NCH_3), 61.86 (OCH_2), 67.76, 68.00 (C-3a, C-9a), 114.32 (=CH), 127.84 (Ph-4), 128.86 (Ph-2,6), 129.09 (Ph-3,5), 136.21 (Ph-1), 139.87, 141.71 (5a-C=N, C-7), 161.53 (8-C=O), 166.04 (COOEt), 183.30 (2-C=S). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{17}H_{17}N_5O_3S_2$: 404.0846; found: 404.0840.

Ethyl (*Z*)-2-(3-ethyl-8-oxo-1-phenyl-2-thioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*][1,2,4]triazin-7(8*H*)-ylidene)acetate (5n)

Yield 500 mg (60%) as a bright yellow solid. Mp: 192–194 °C. IR (KBr), ν 3346 (NH), 3084, 3062 (Ar), 2984, 2940, 2904, 2874 (Alk), 1727, 1672, 1655, 1602 (C=N, C=O), 1319 (C=S) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.13 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.22 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.41–3.53 (m, 1 H, CH_2), 3.66–3.88 (m, 1 H, CH_2), 4.20 (q, *J* = 7.0 Hz, 2 H, OCH_2), 5.52 (d, *J* = 6.6 Hz, 1 H, 3a-H), 6.34 (d, *J* = 6.6 Hz, 1 H, 9a-H), 6.48 (s, 1 H, =CH), 7.20–7.42 (m, 5 H,

Ph), 8.36 (s, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.27, 14.46 ($2CH_3$), 39.01 (NCH_2), 61.89 (OCH_2), 66.12, 68.05 (C-3a, C-9a), 114.42 (=CH), 127.79 (Ph-4), 128.81 (Ph-2,6), 129.09 (Ph-3,5), 136.48, 139.80, 141.65 (Ph-1, C-7, 5a-C=N), 161.45 (8-C=O), 166.03 (COOEt), 182.24 (2-C=S). HRMS (ESI): *m/z* [*M* + H]$^+$ calcd for $C_{18}H_{19}N_5O_3S_2$: 418.1002; found: 418.1000.

X-ray diffraction data of compound 5i were collected at 100 K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using MoK_α-radiation. The intensity data were integrated by the SAINT program [4] and corrected for absorption and decay using SADABS [5]. The structure was solved by direct methods using SHELXT [6] and refined on F^2 using SHELXL-2018 [7]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions as riding atoms with relative isotropic displacement parameters; bond distances to H-atoms were refined. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 2069601).

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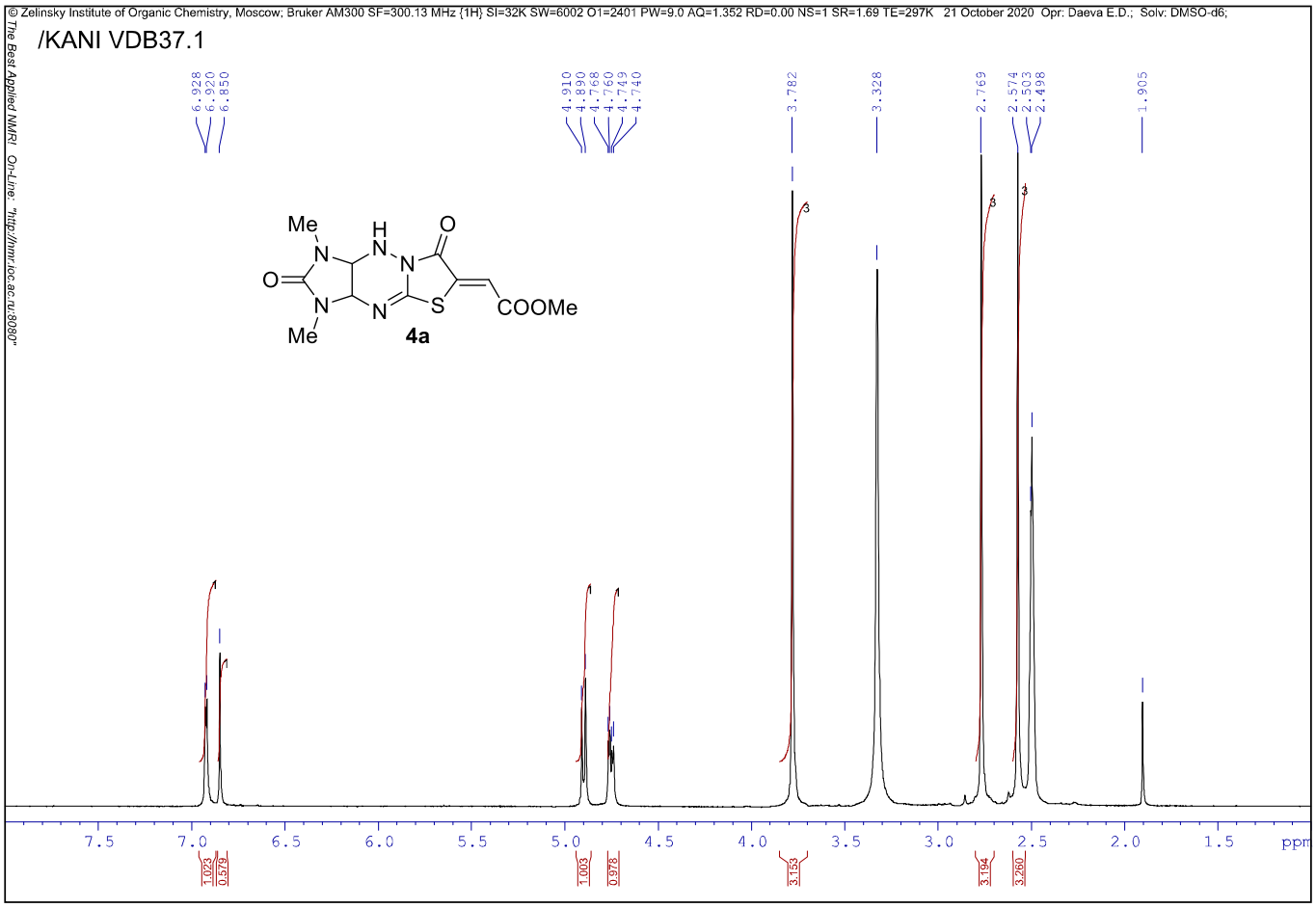
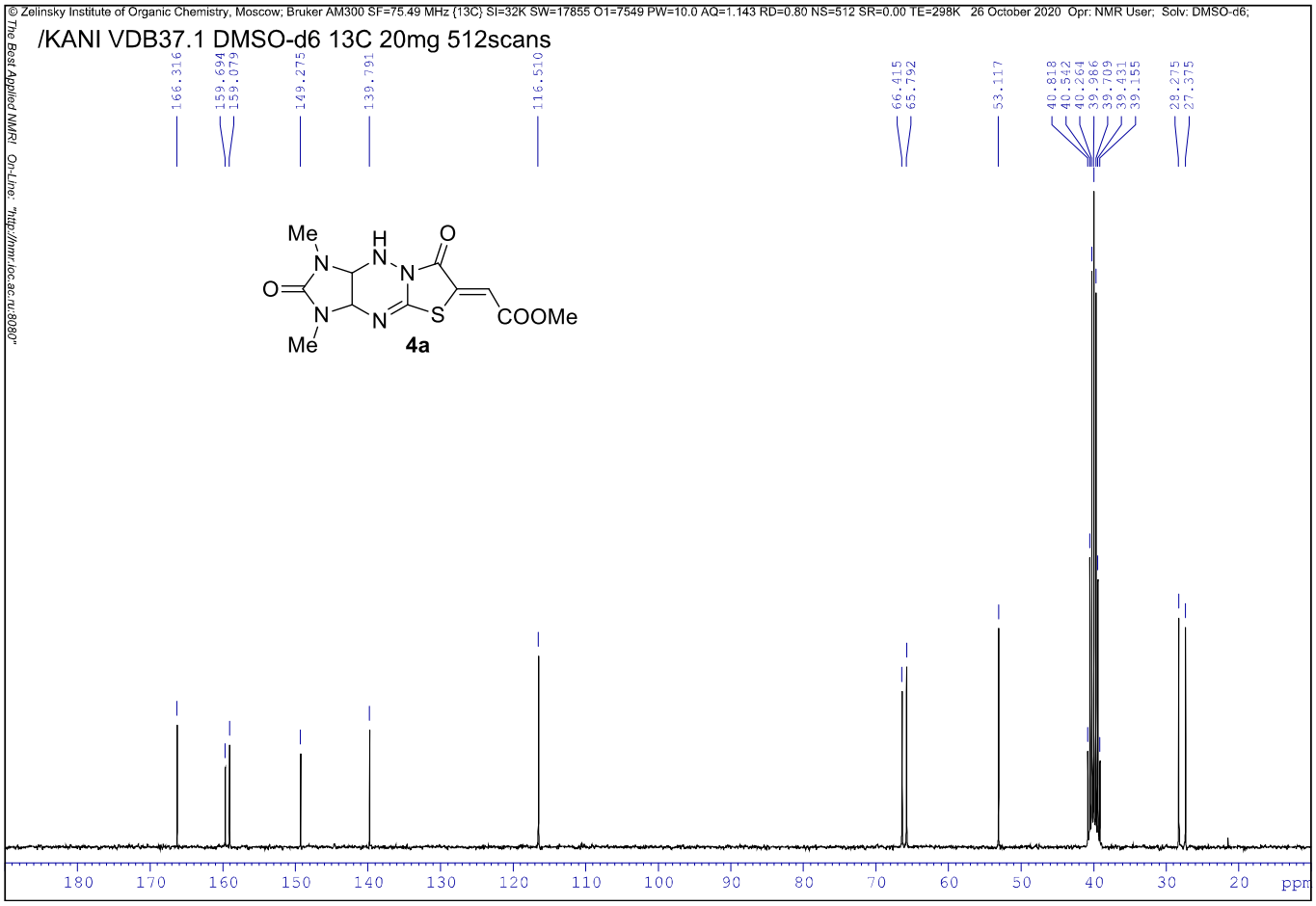
7. Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3.

^{1}H NMR spectrum of **4a**



^{13}C NMR spectrum of **4a**



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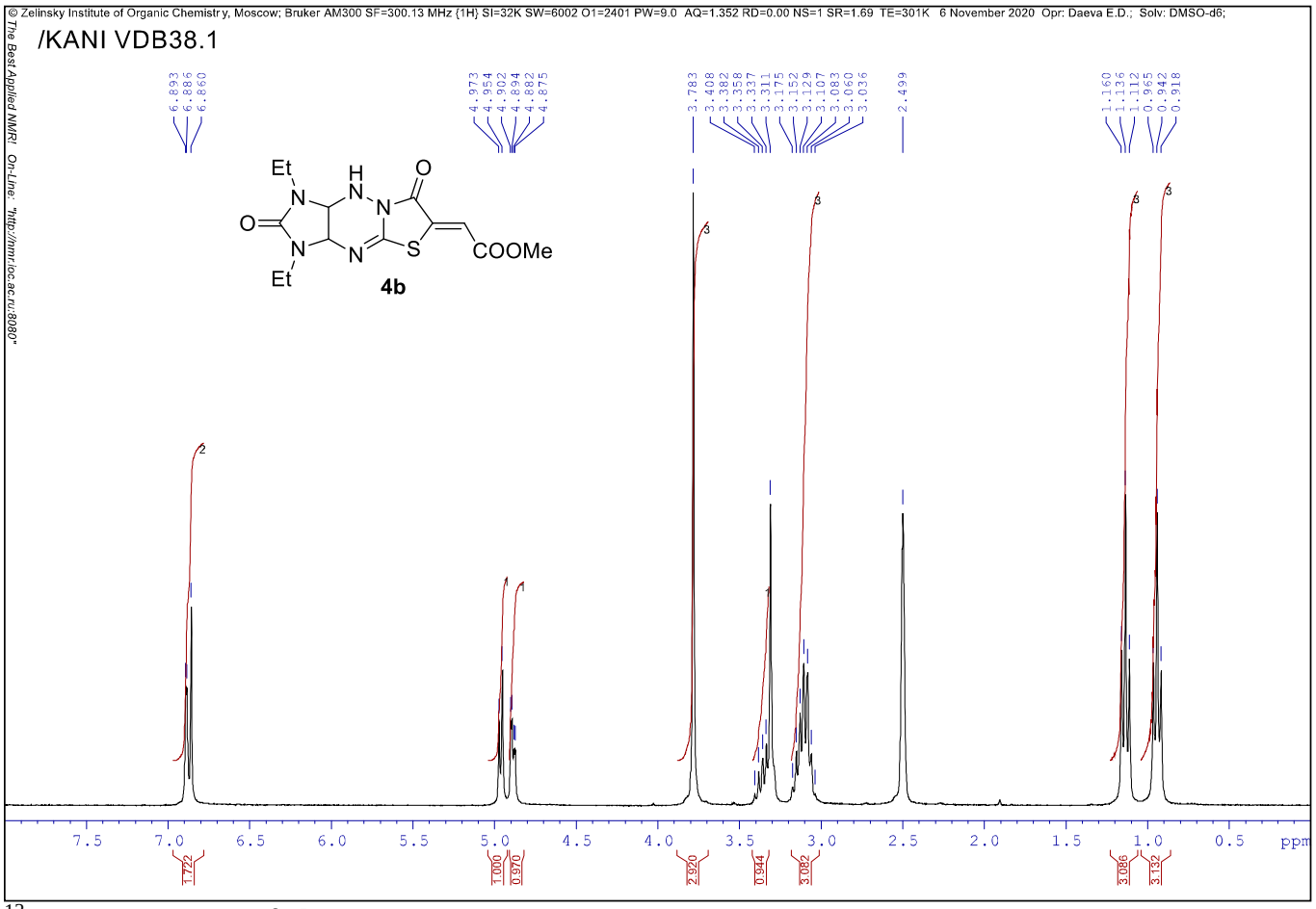
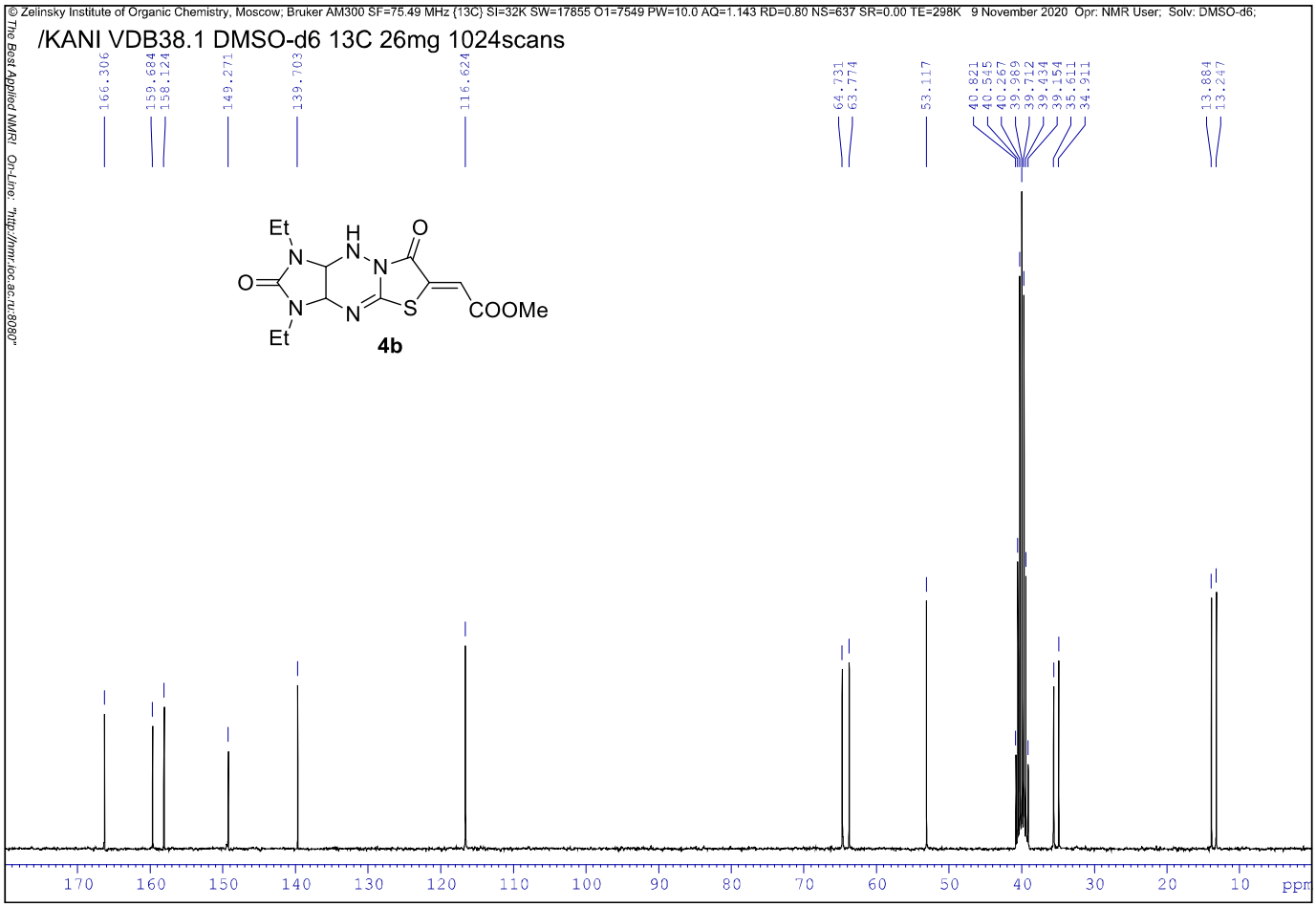
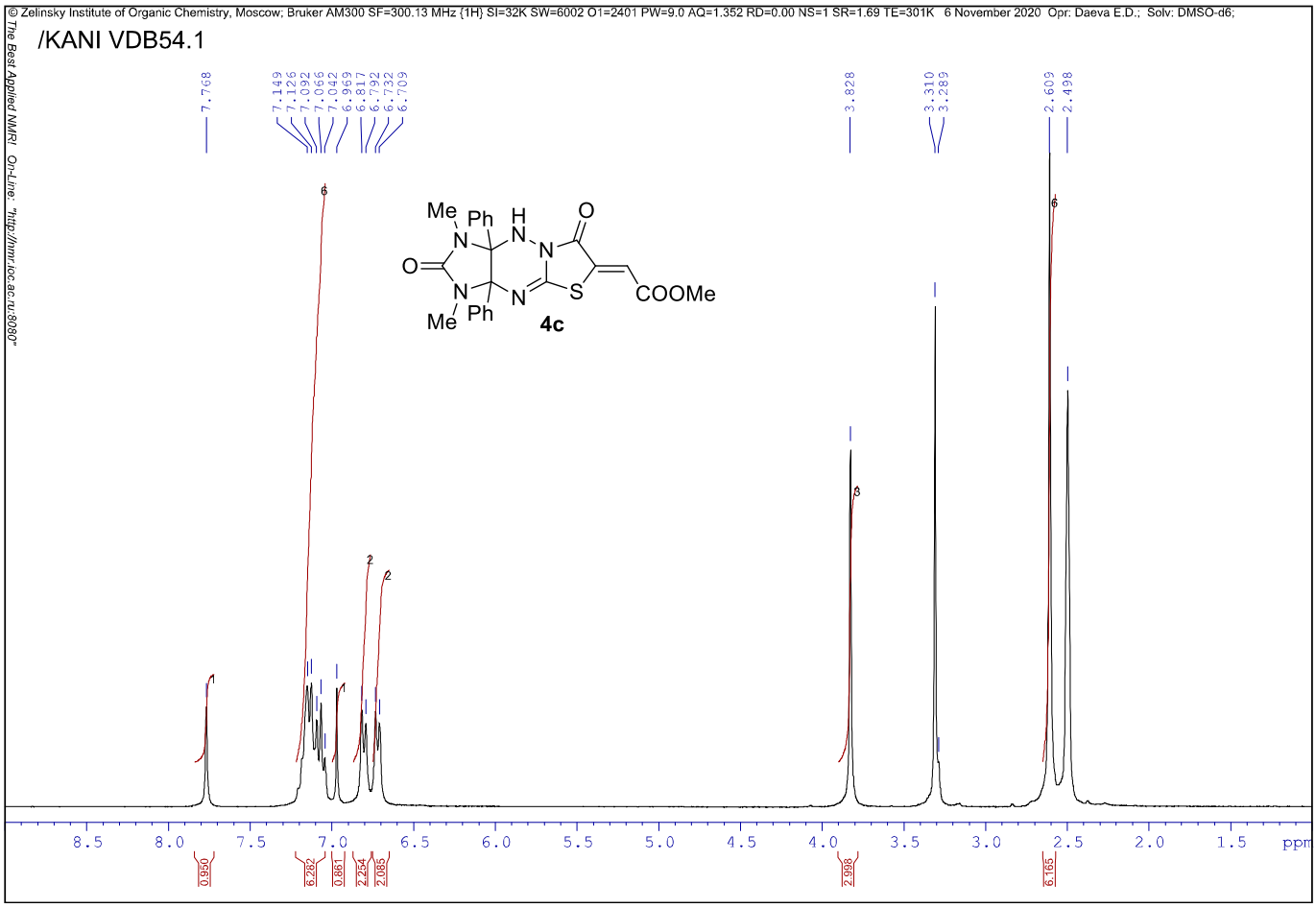


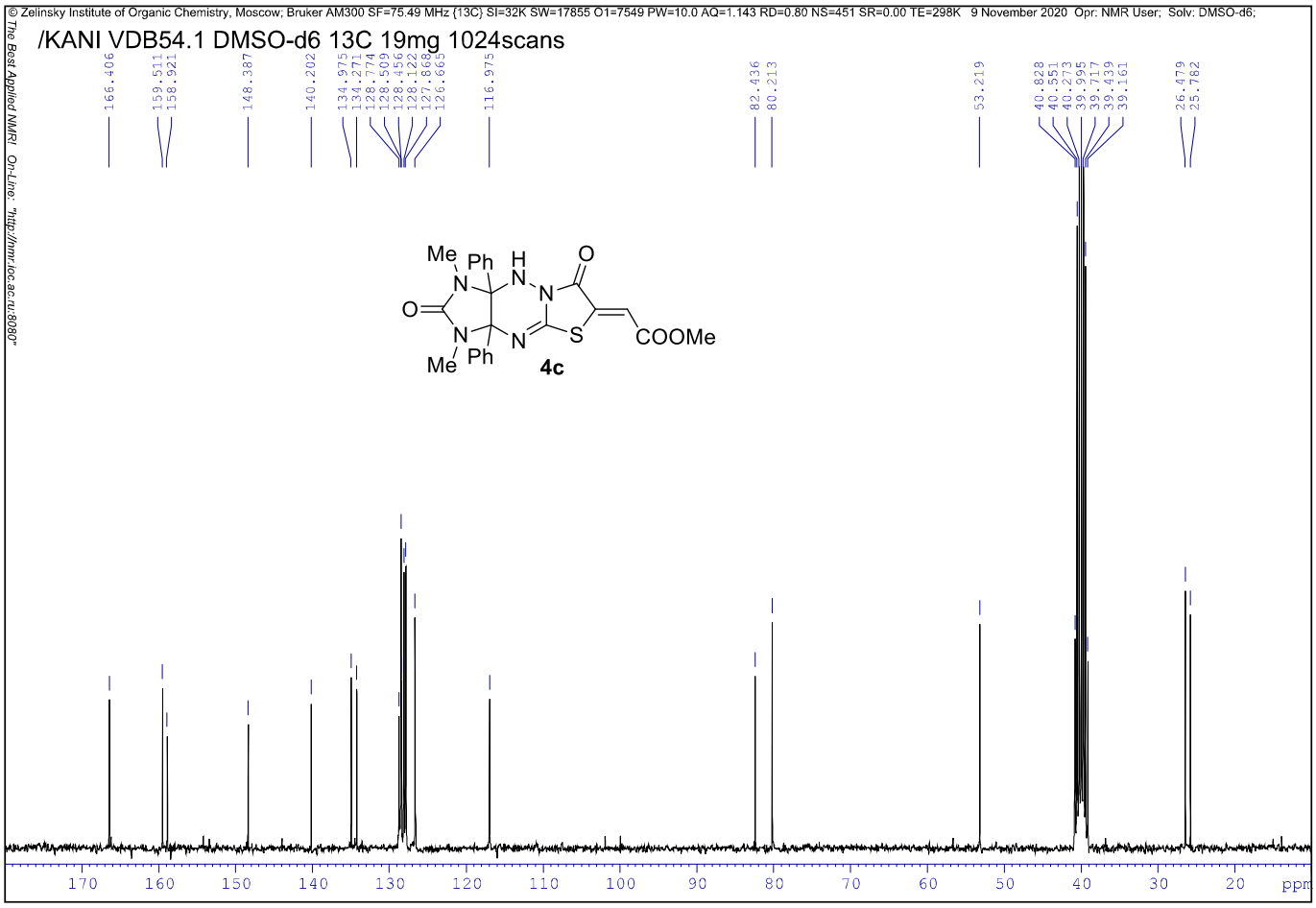
^{13}C NMR spectrum of **4b**



^{1}H NMR spectrum of **4c**



^{13}C NMR spectrum of **4c**



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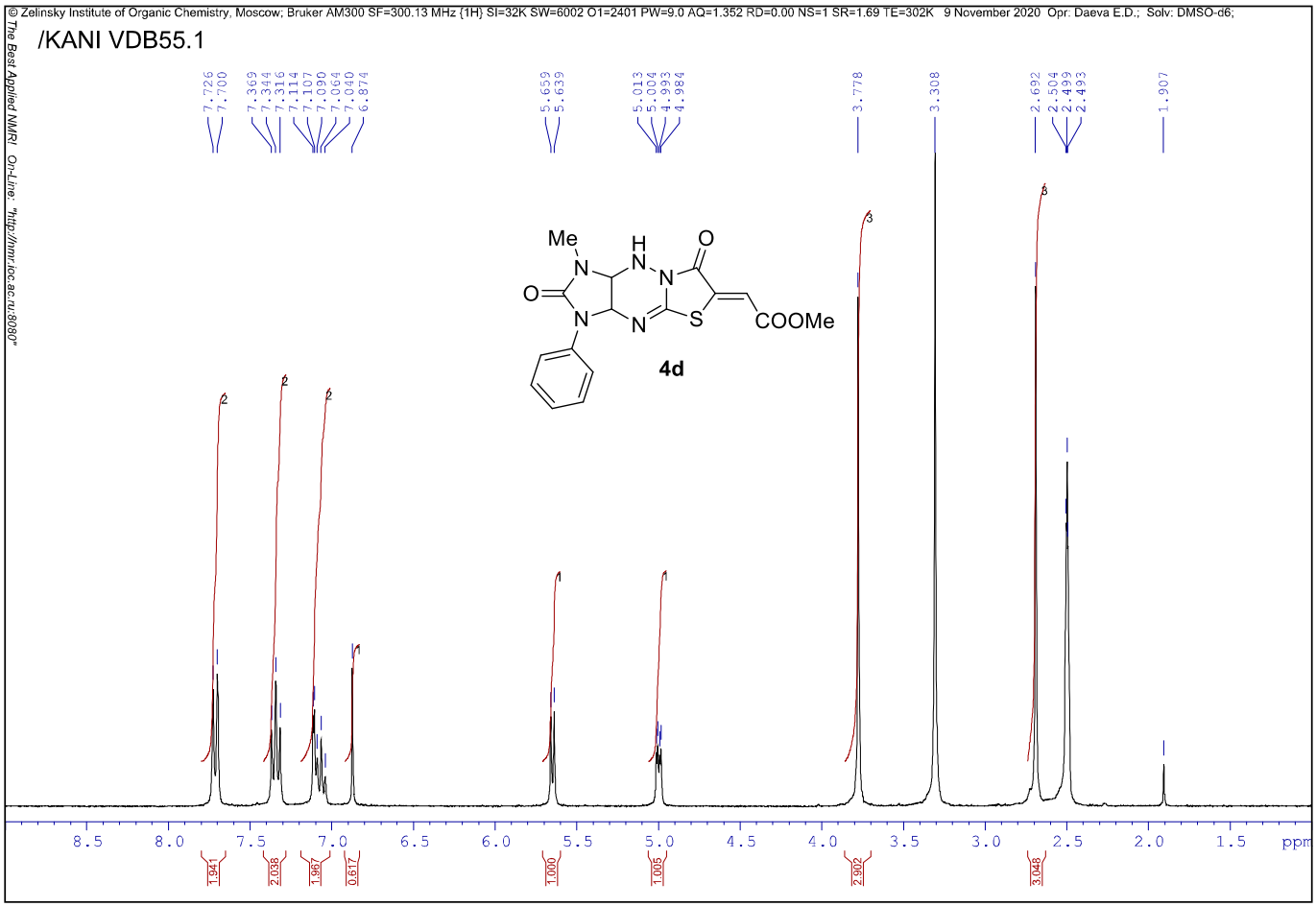

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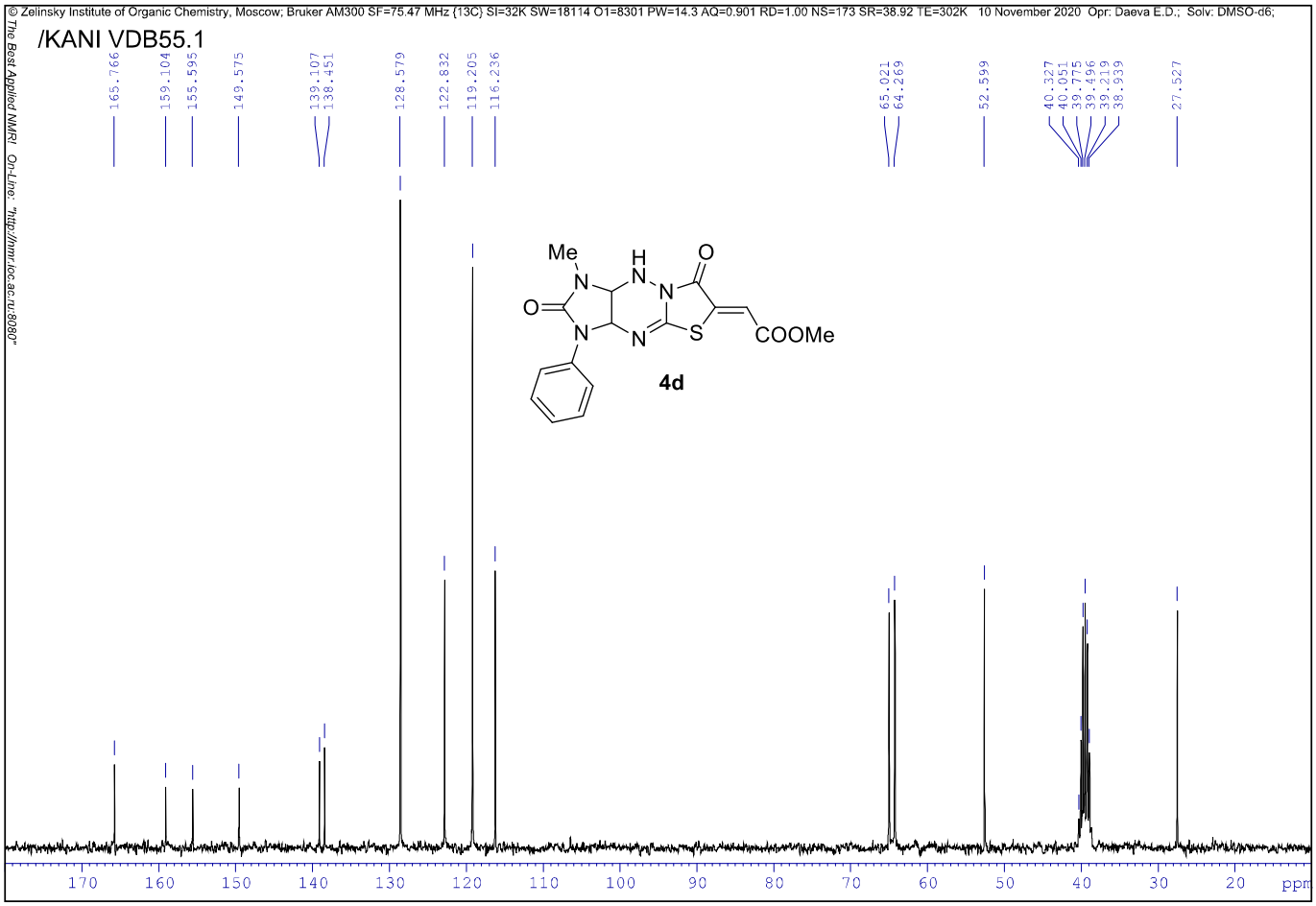
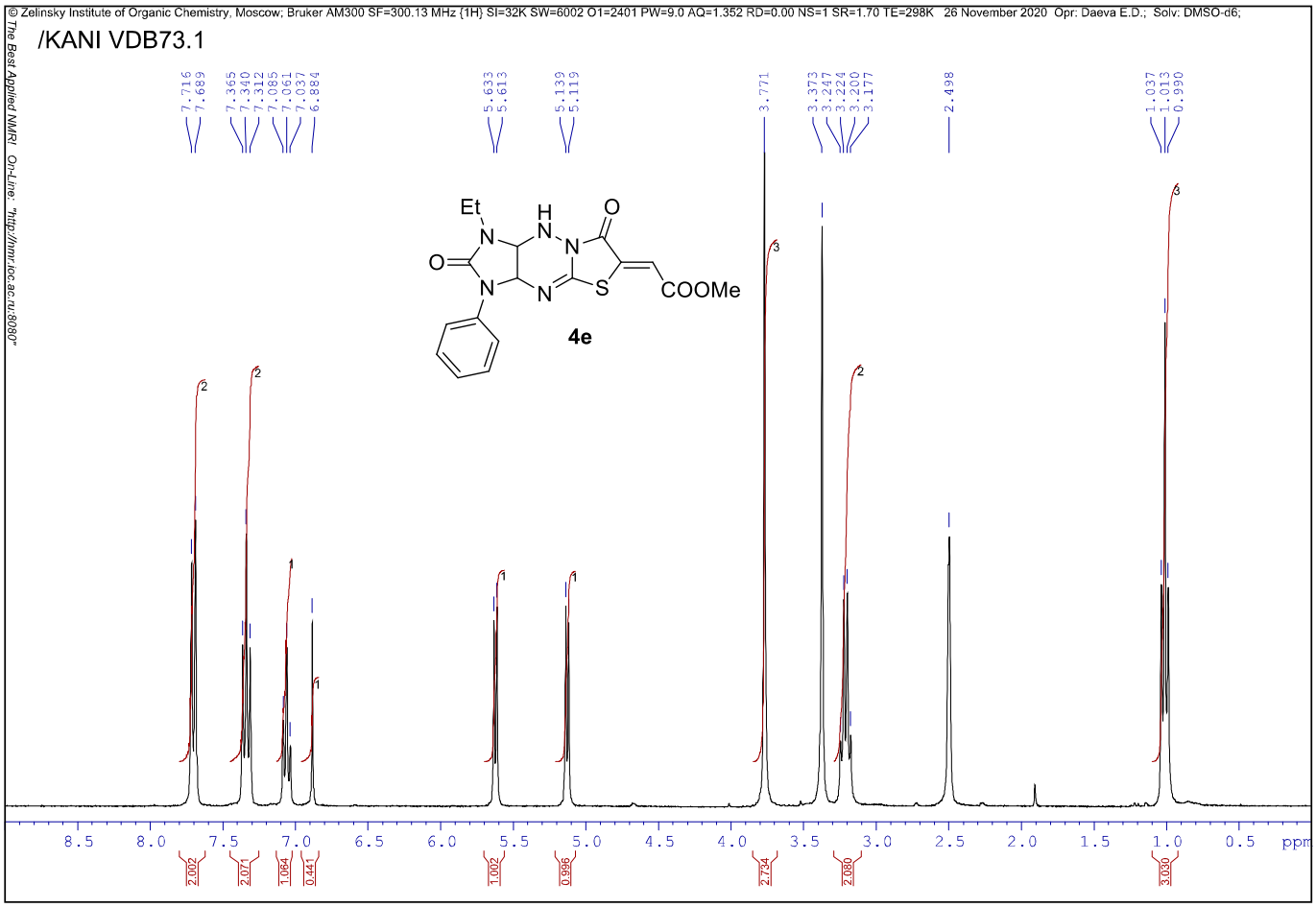
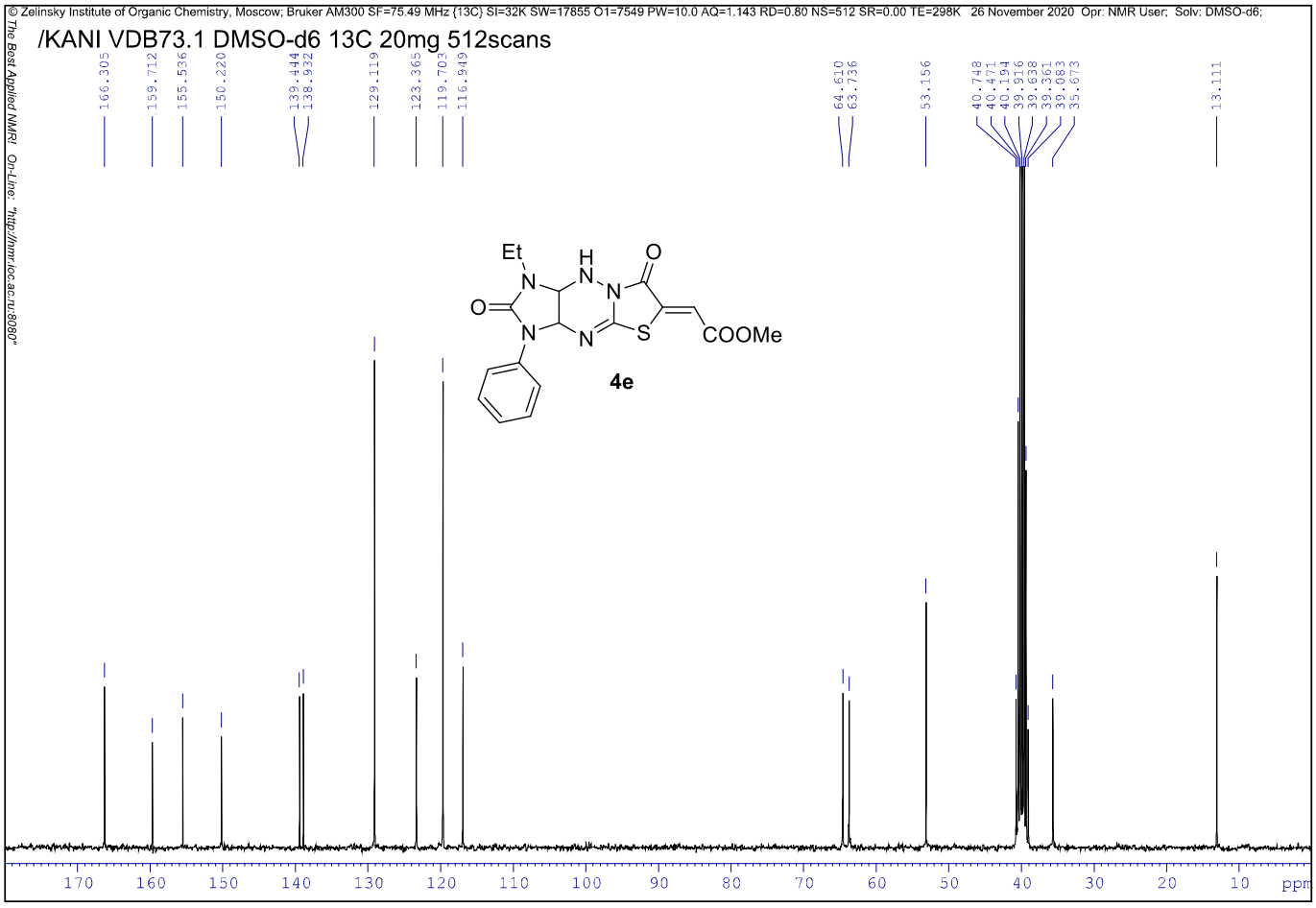


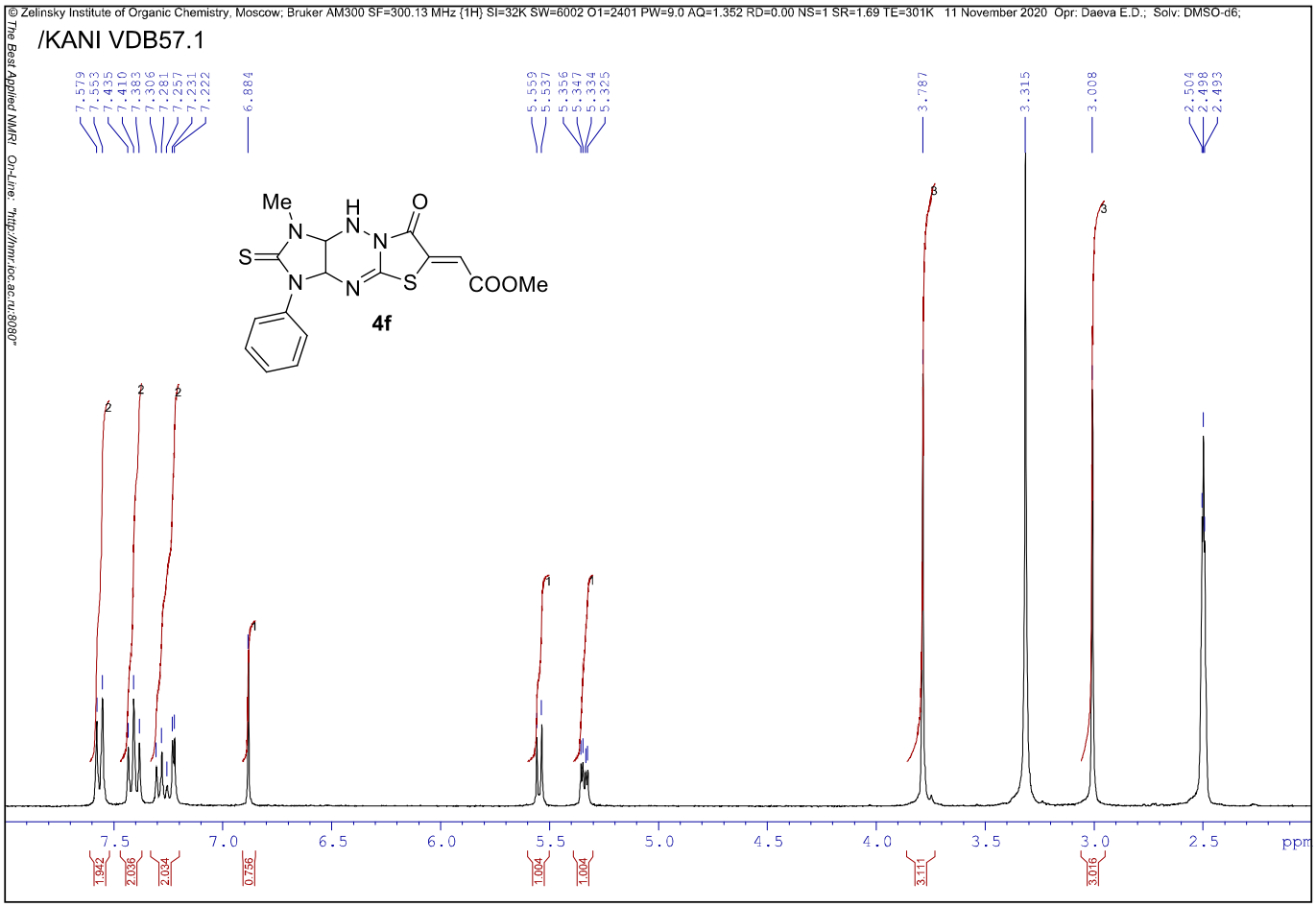
^{1}H NMR spectrum of **4e**



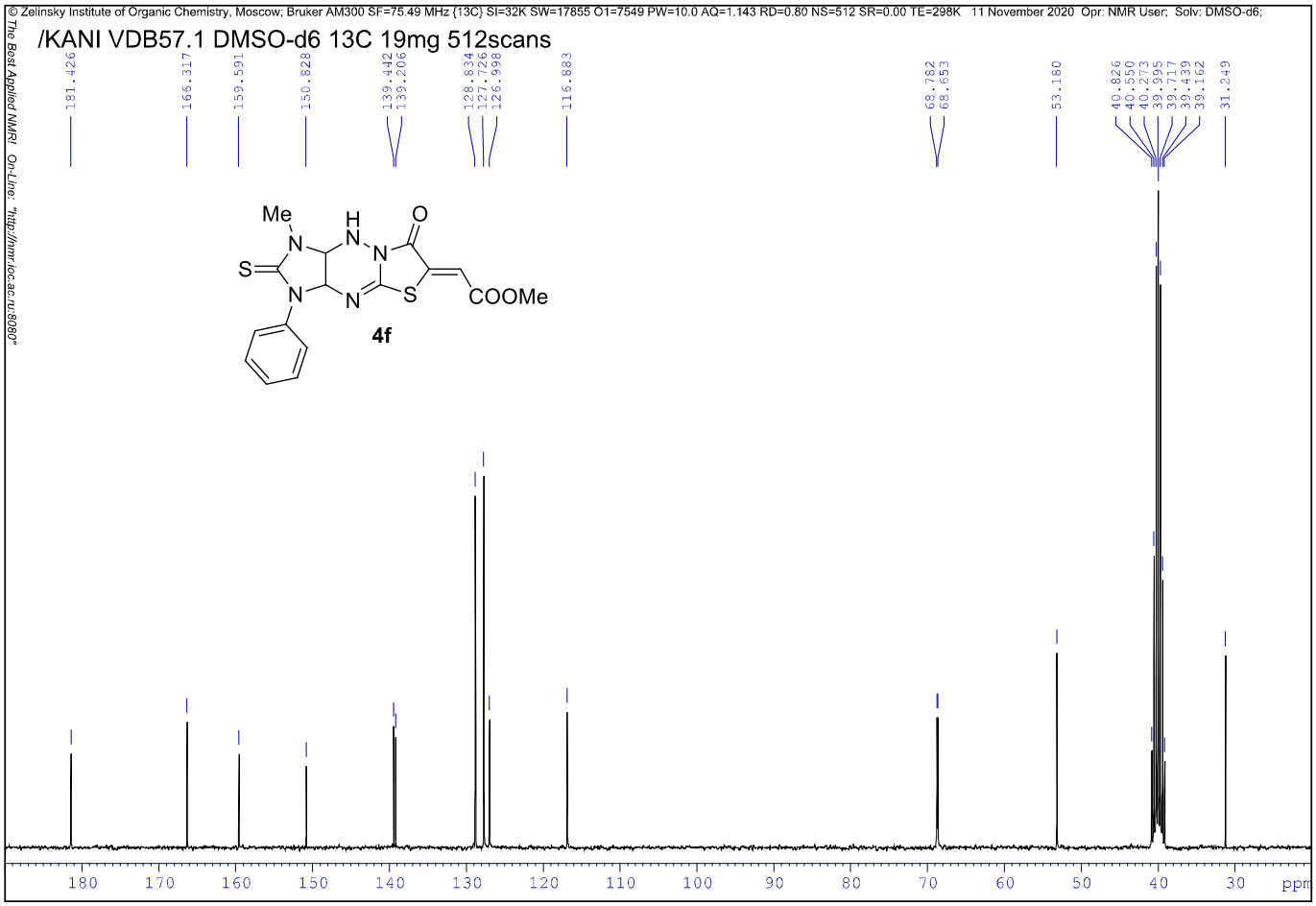
^{13}C NMR spectrum of **4e**



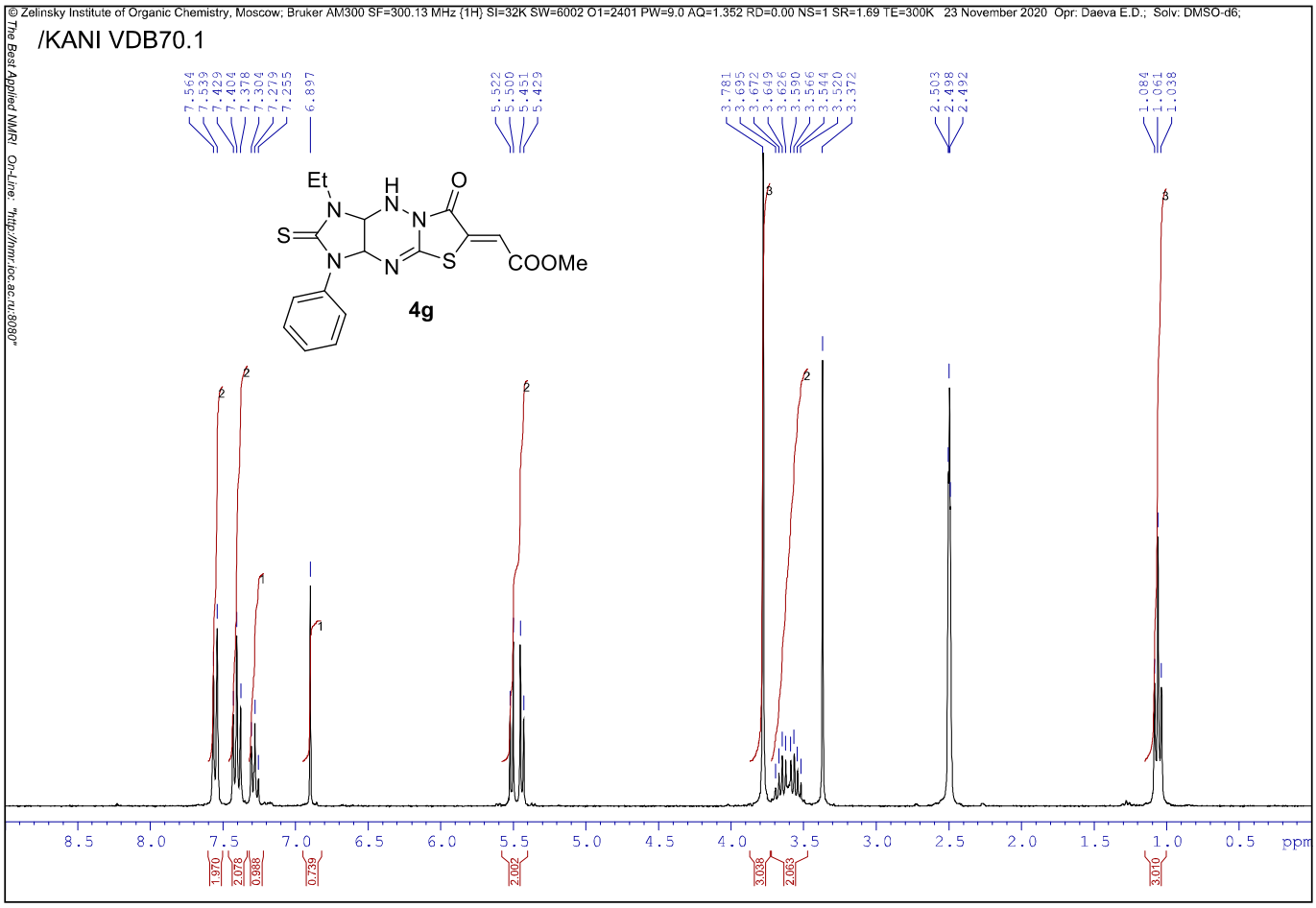
^{1}H NMR spectrum of **4f**



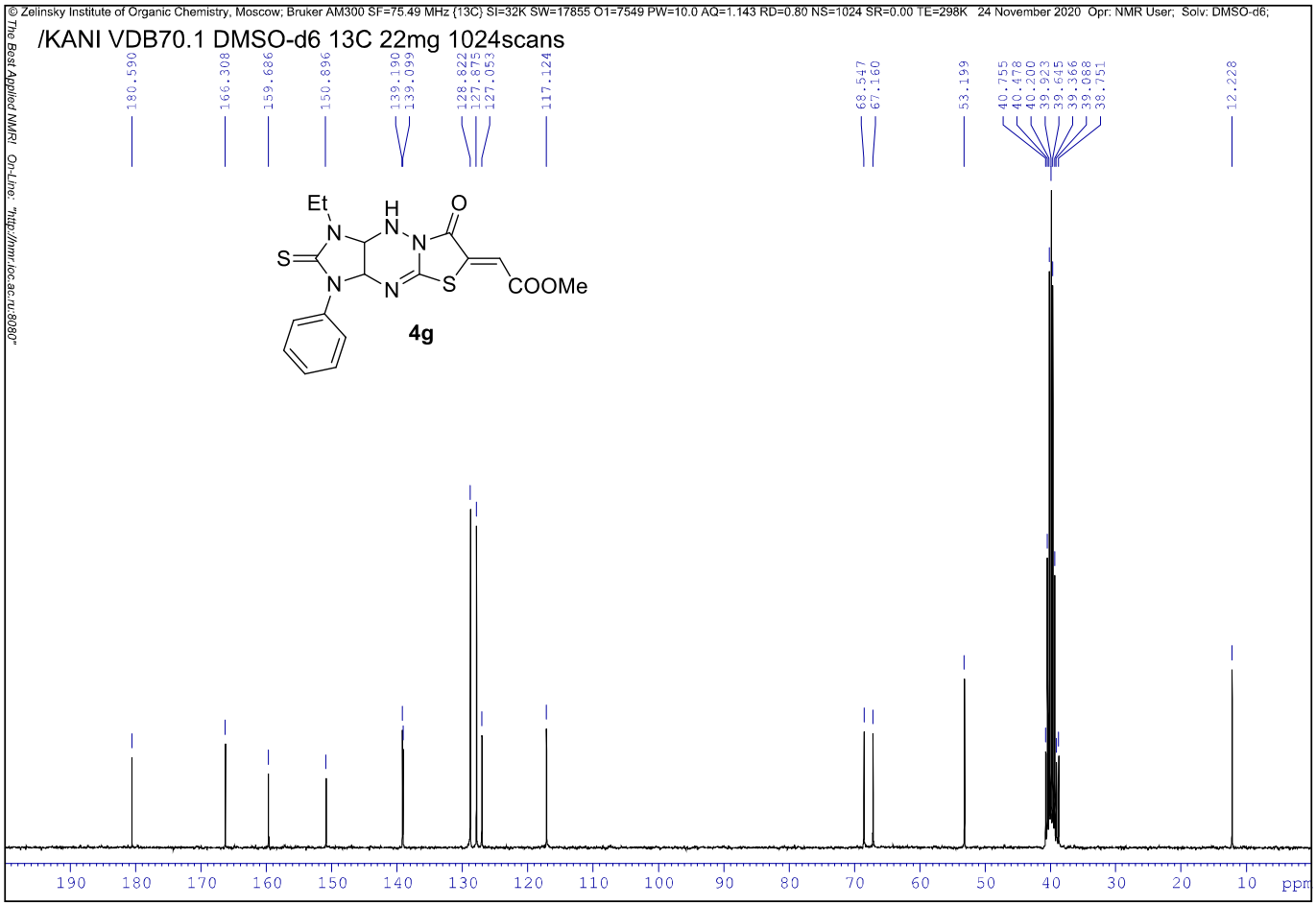
^{13}C NMR spectrum of **4f**



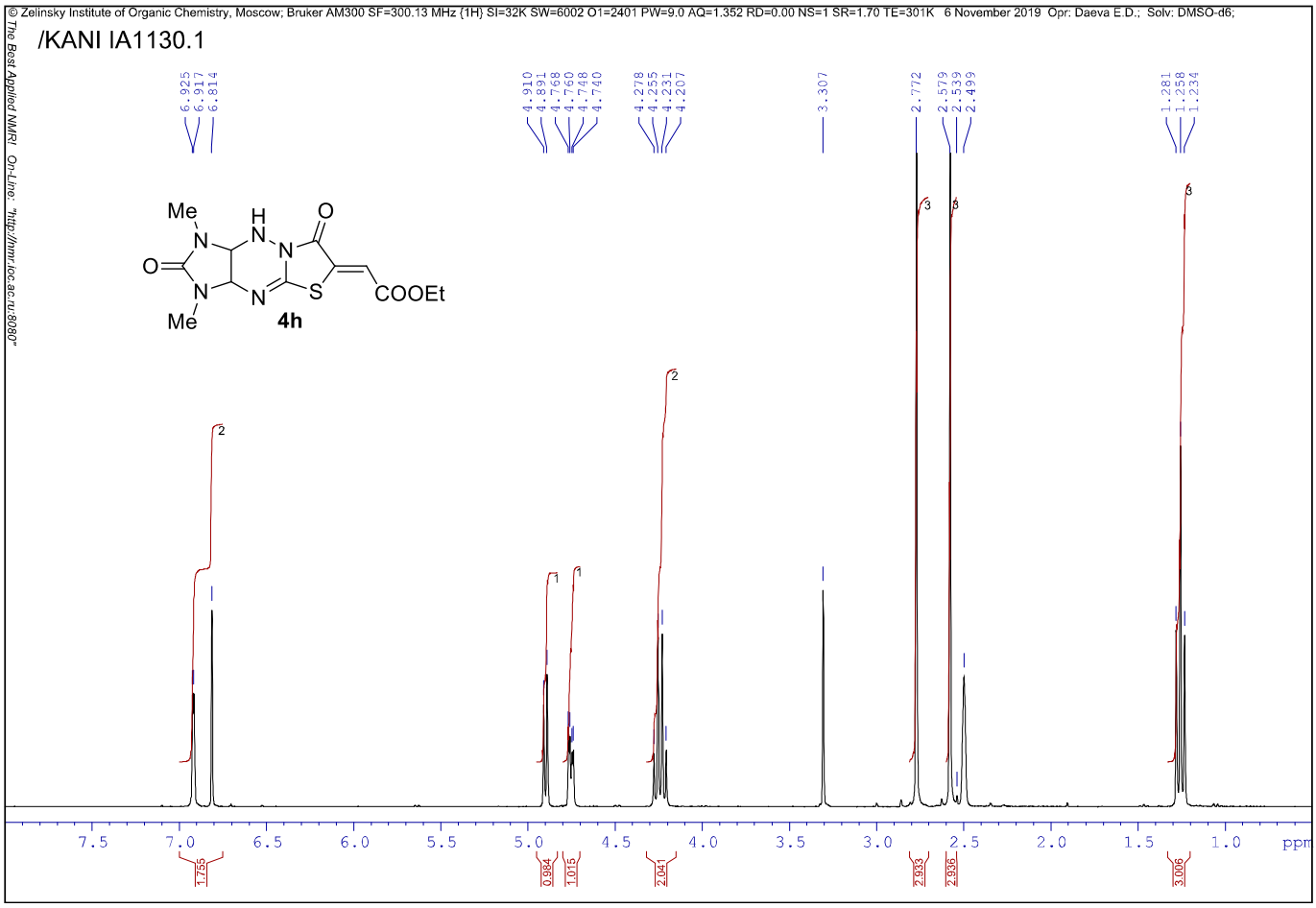
^{1}H NMR spectrum of **4g**



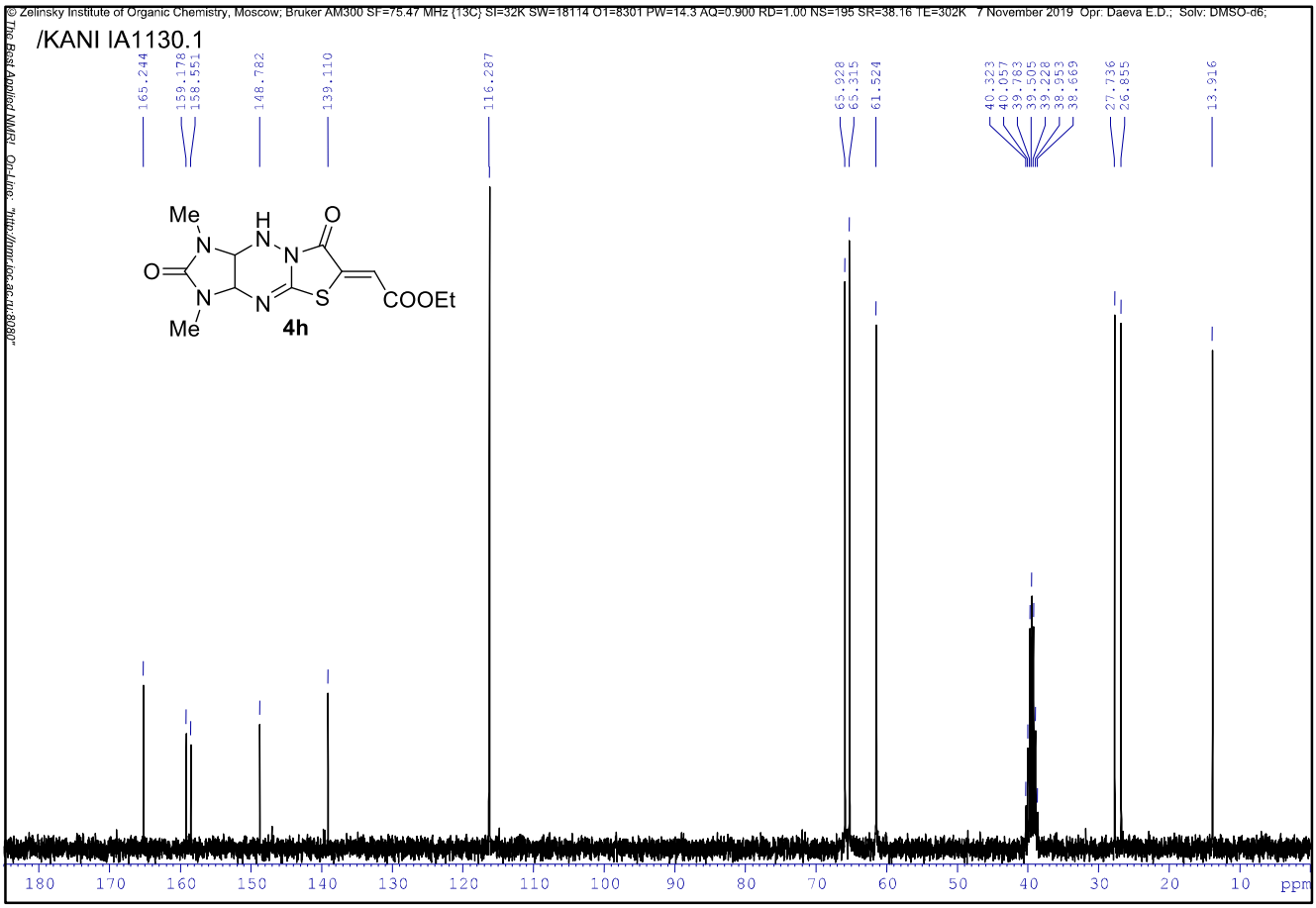
^{13}C NMR spectrum of **4g**



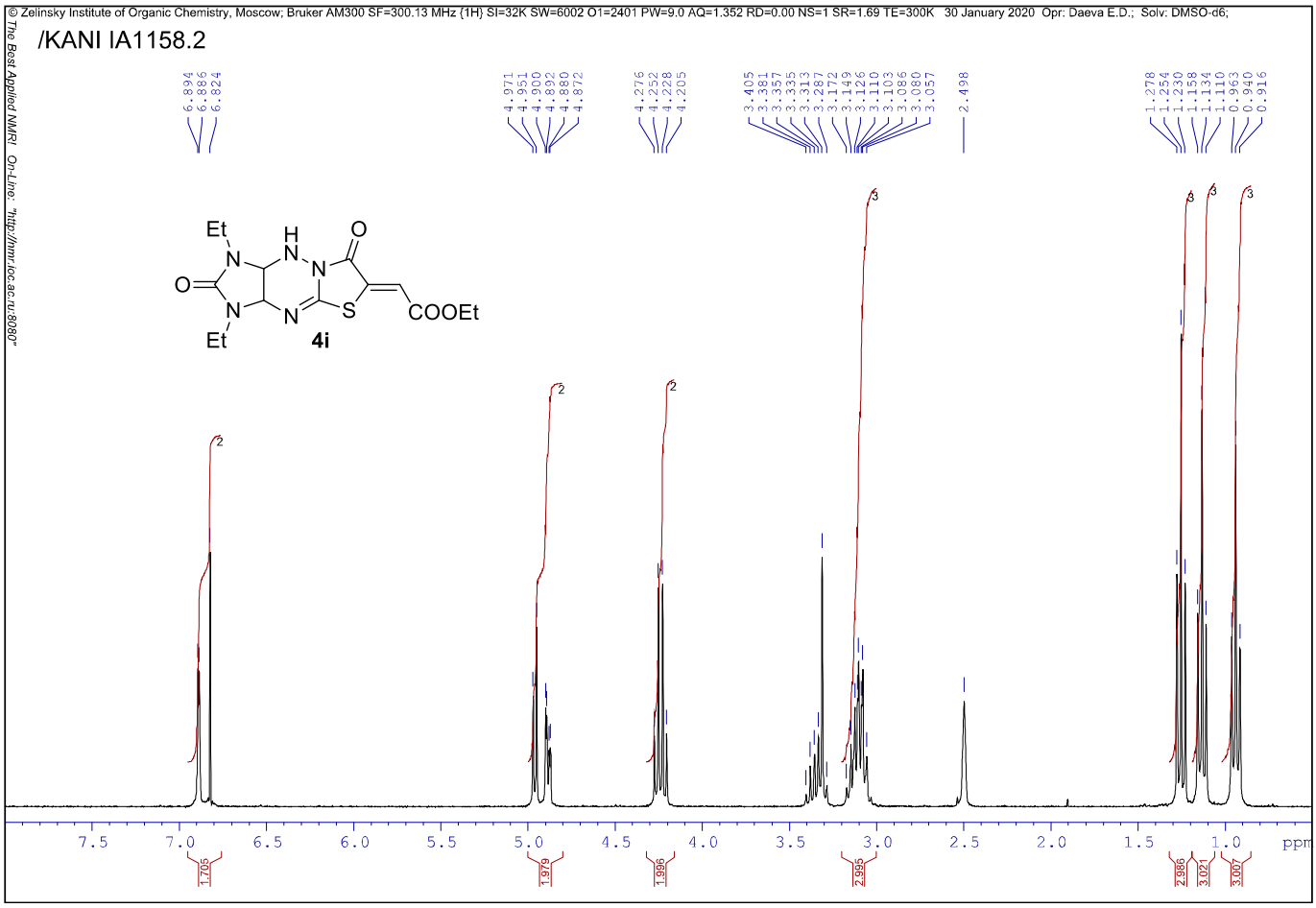
^{1}H NMR spectrum of **4h**



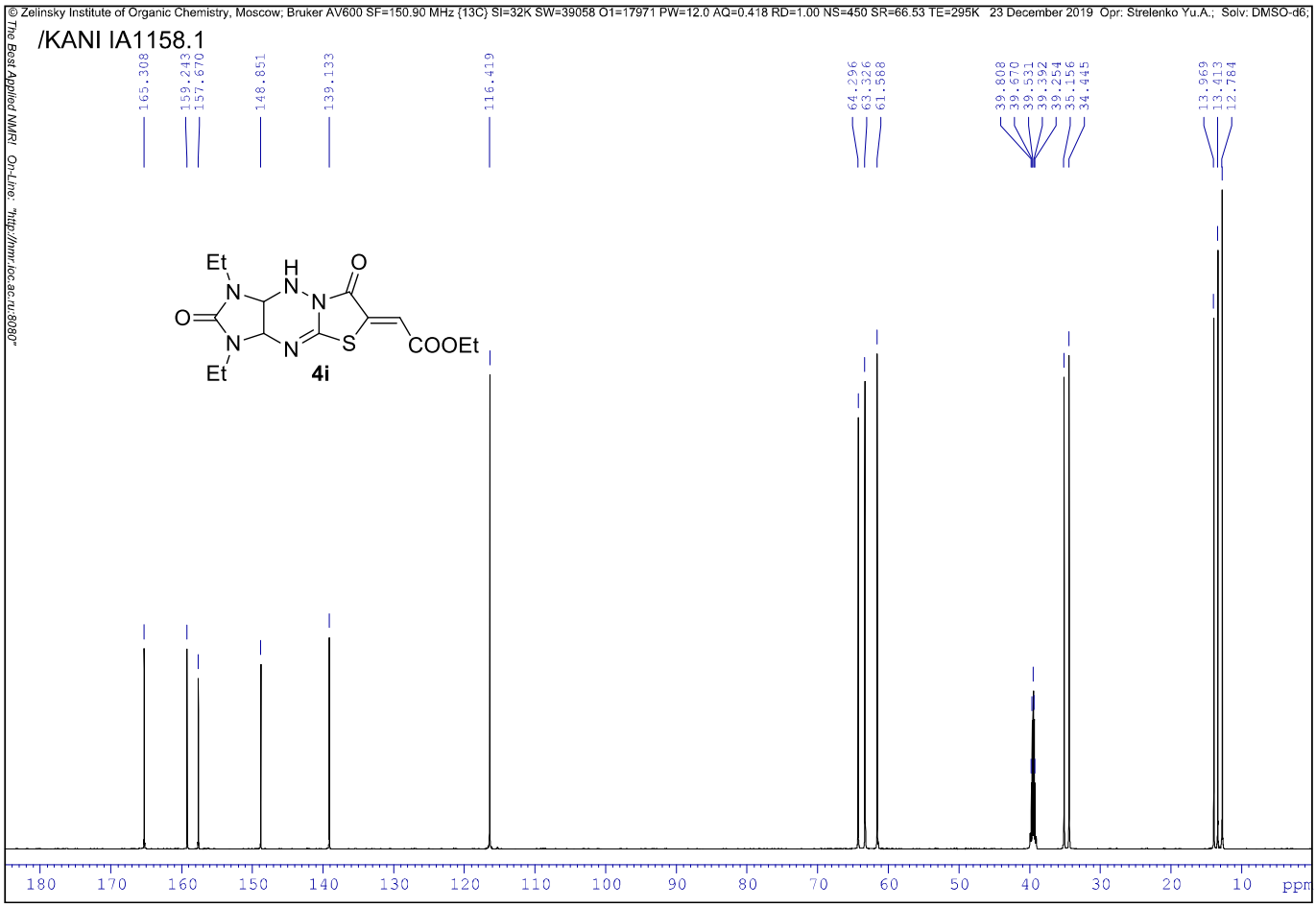
^{13}C NMR spectrum of **4h**



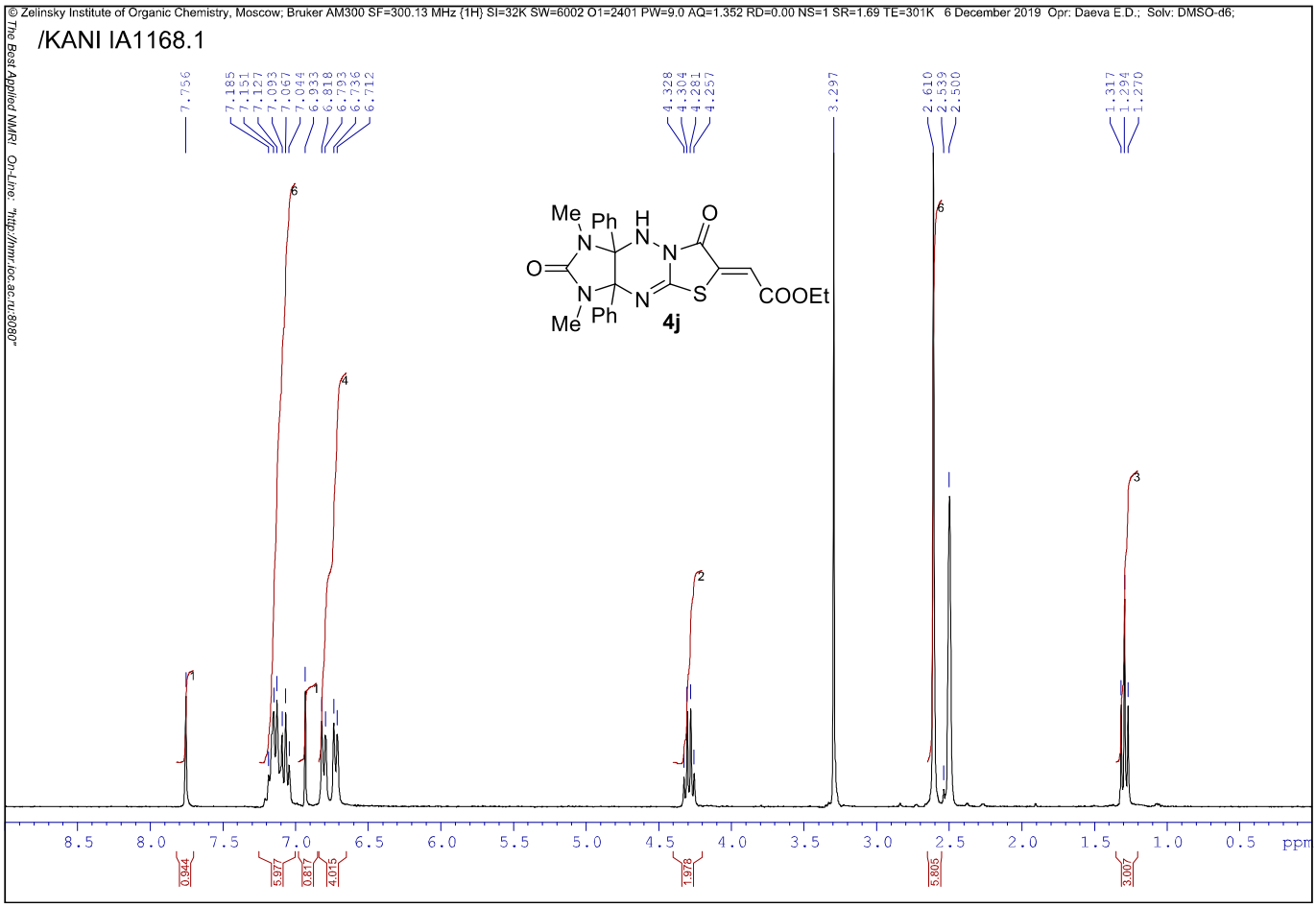
^{1}H NMR spectrum of **4i**



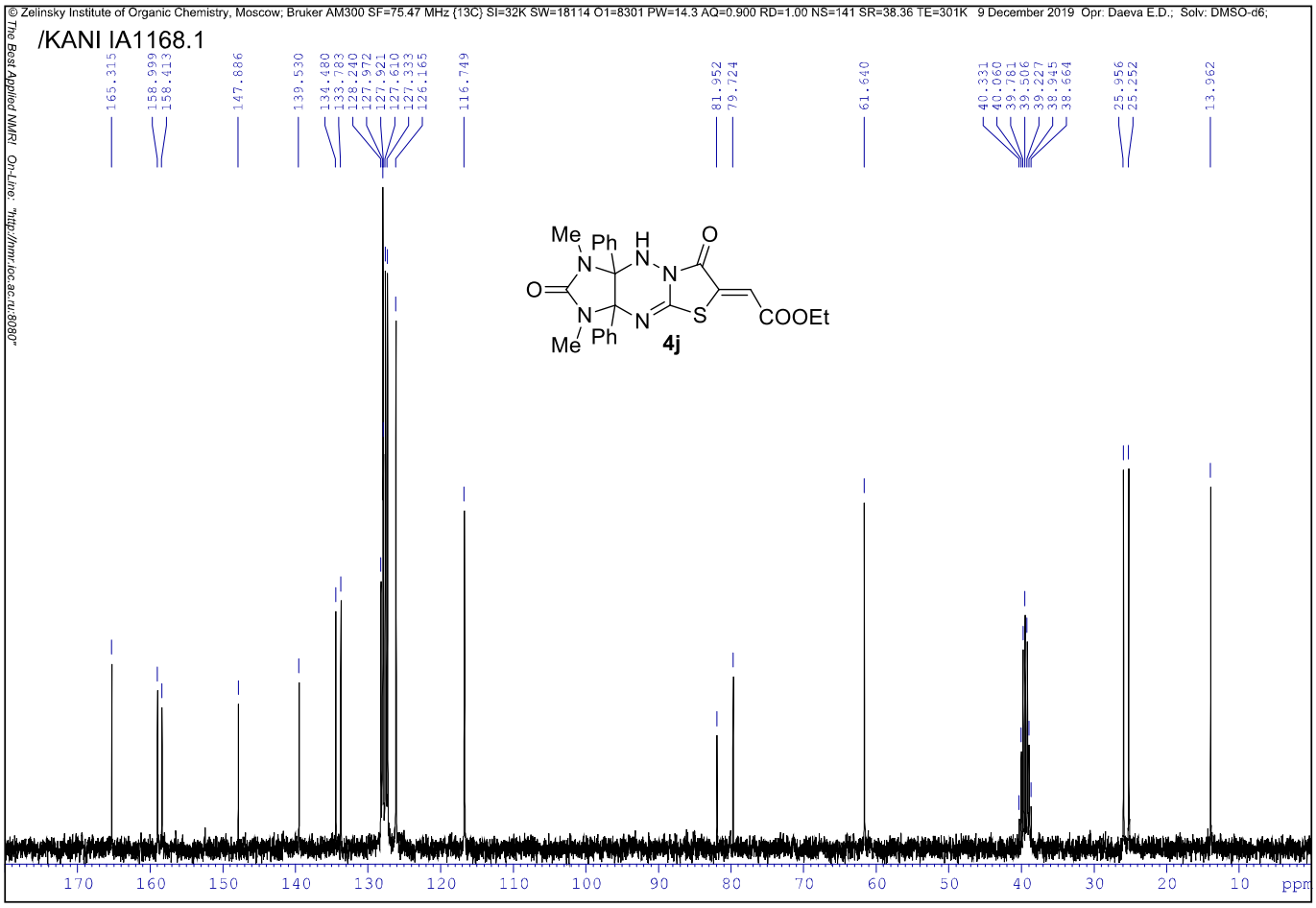
^{13}C NMR spectrum of **4i**



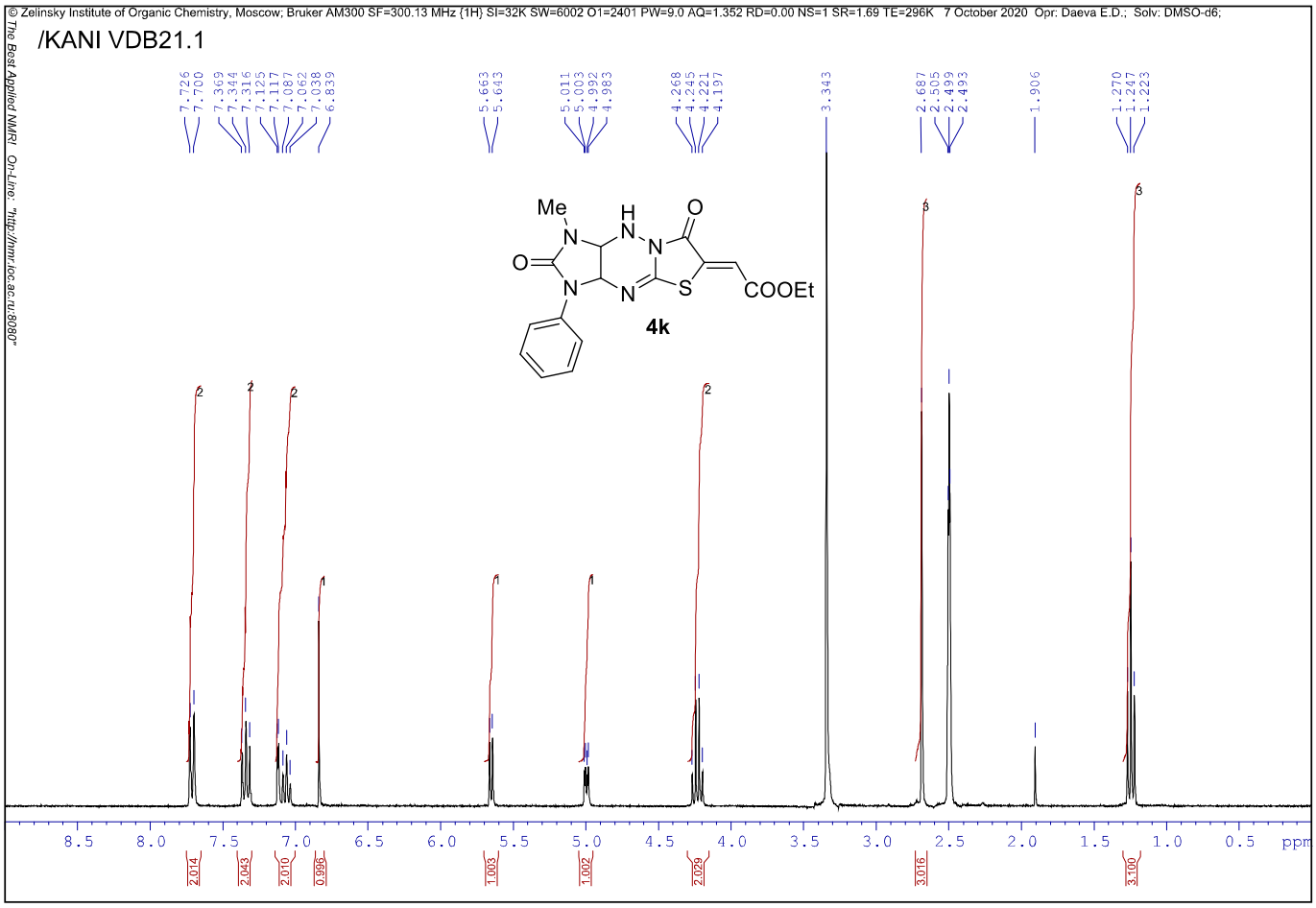
^{1}H NMR spectrum of **4j**



^{13}C NMR spectrum of **4j**



^{1}H NMR spectrum of **4k**



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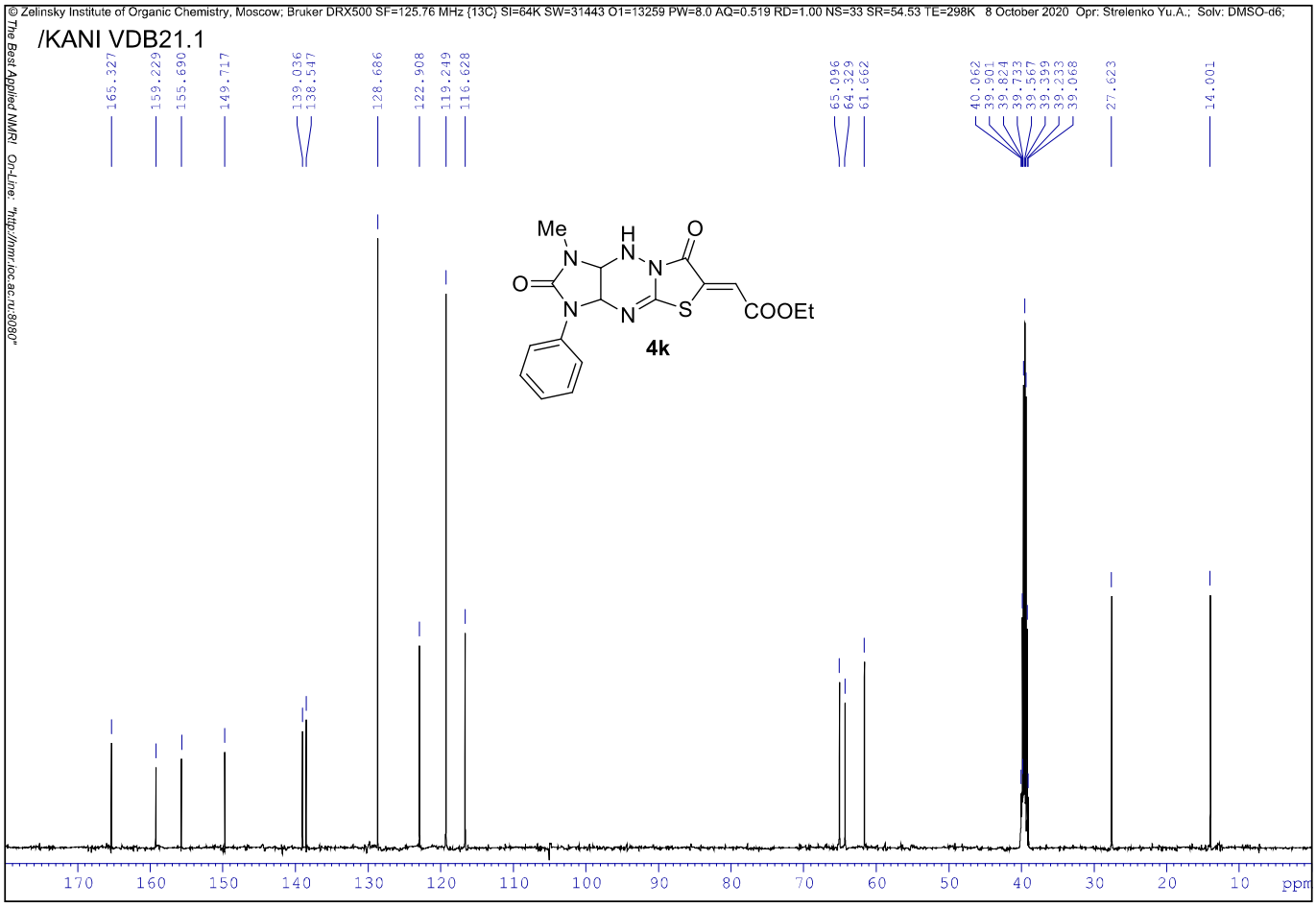
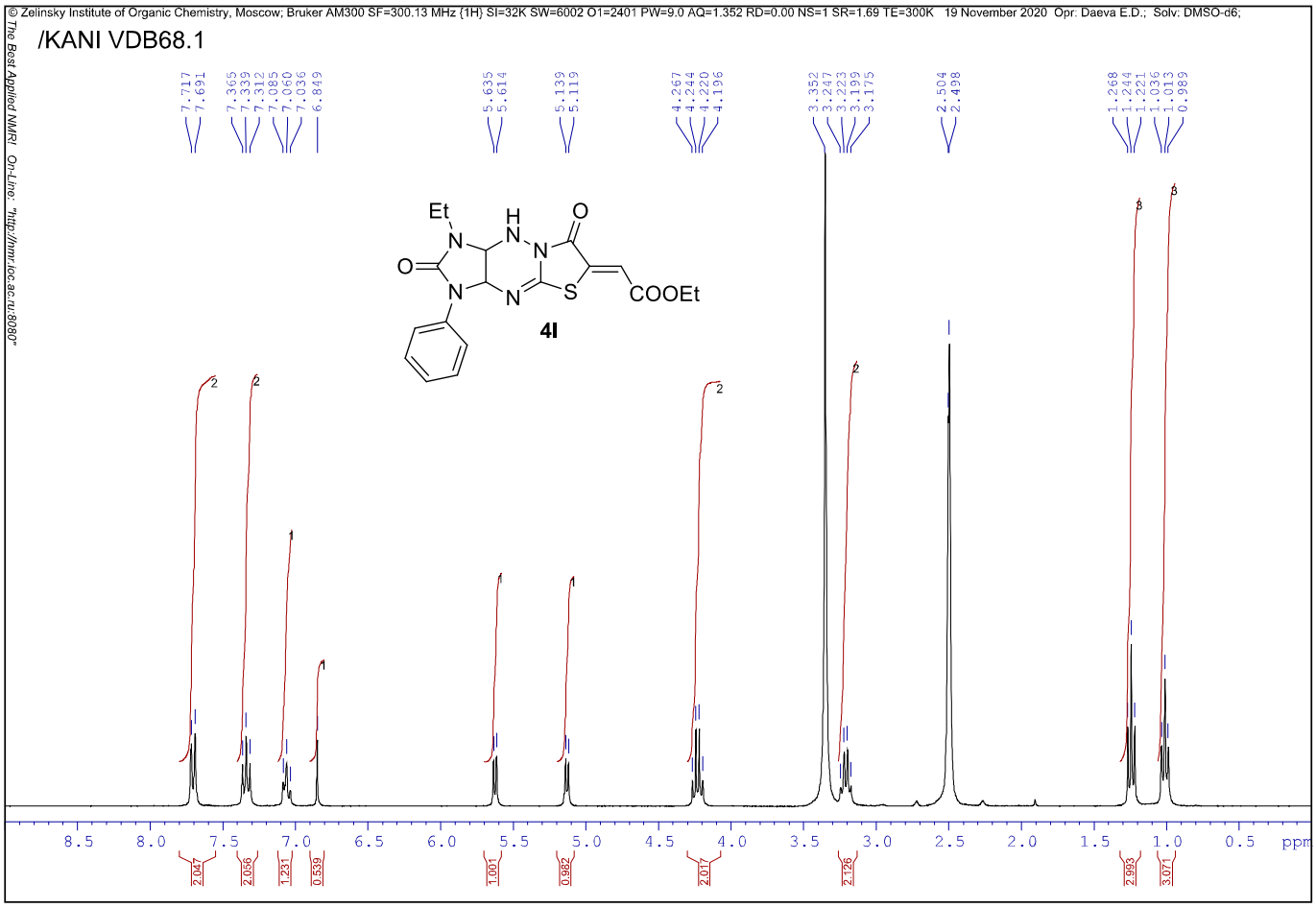
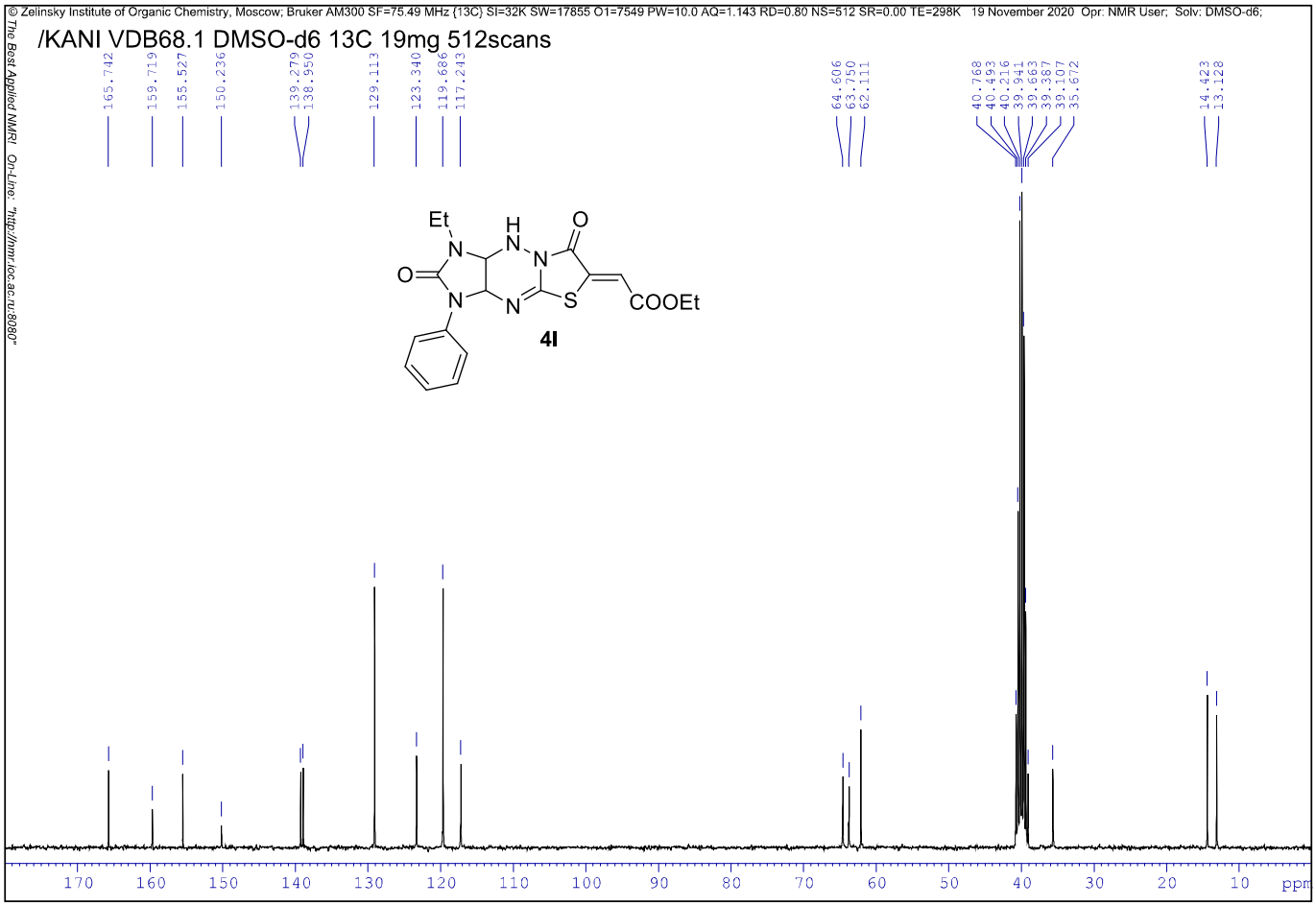


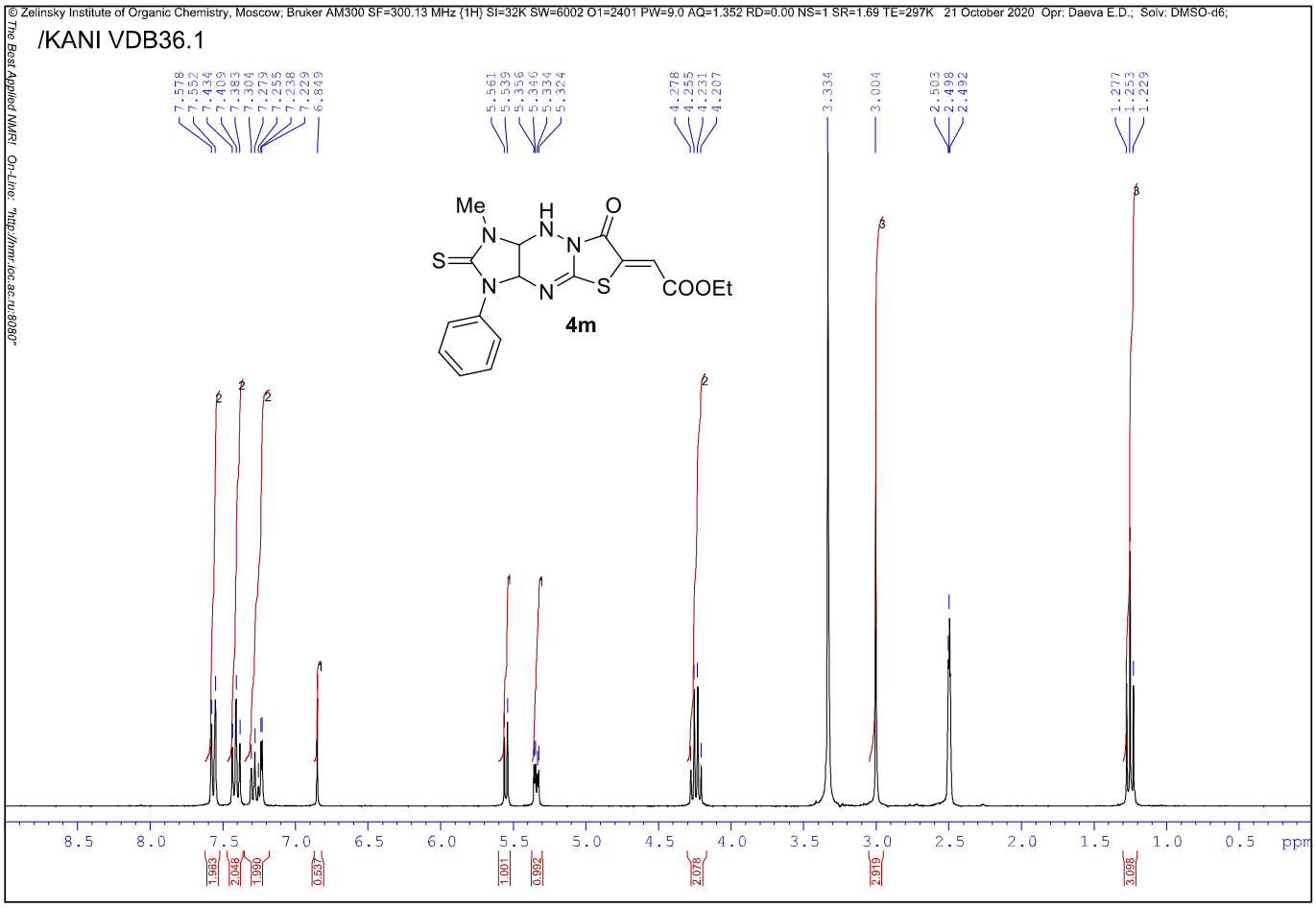
^{1}H NMR spectrum of **4l**



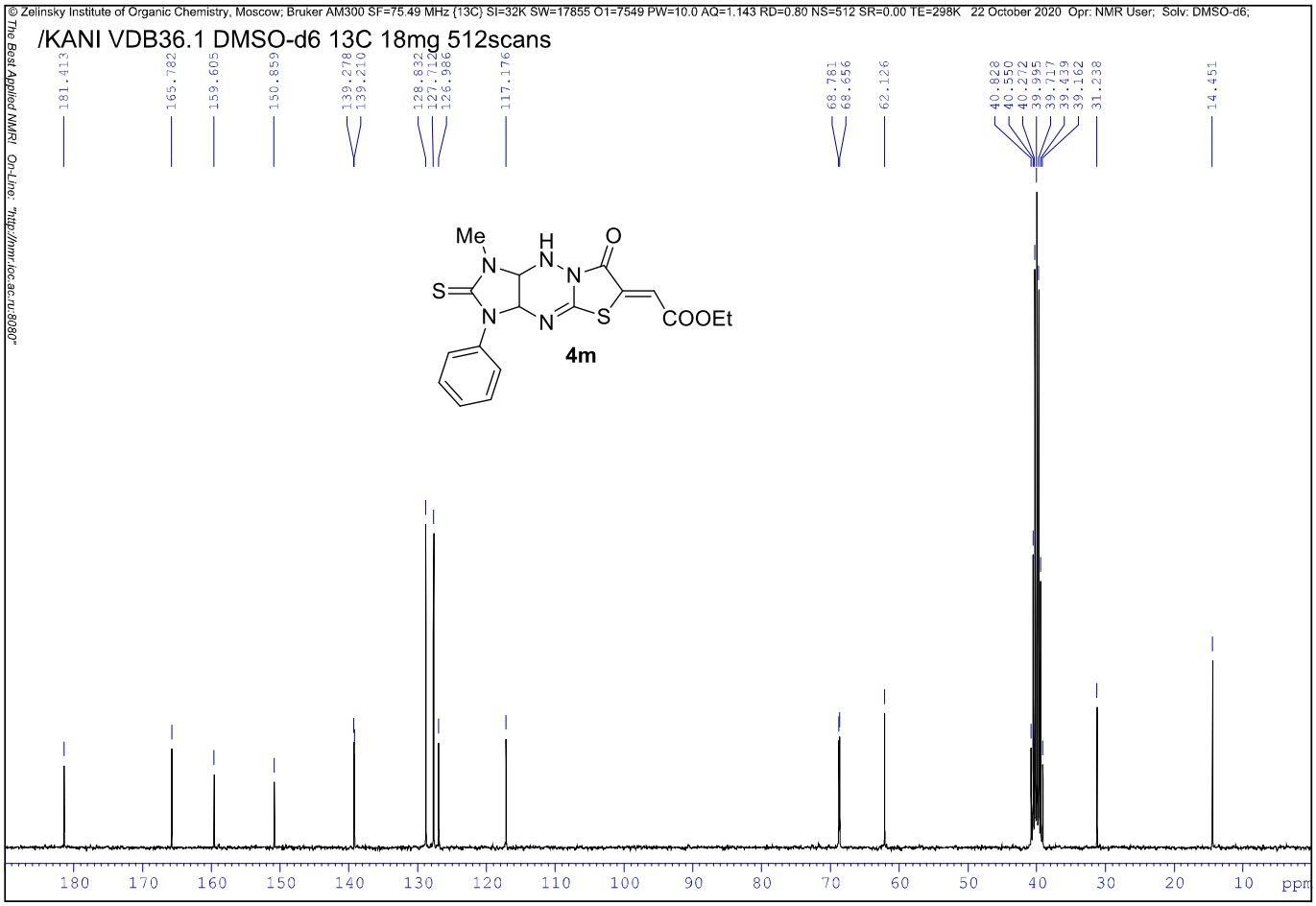
^{13}C NMR spectrum of **4l**



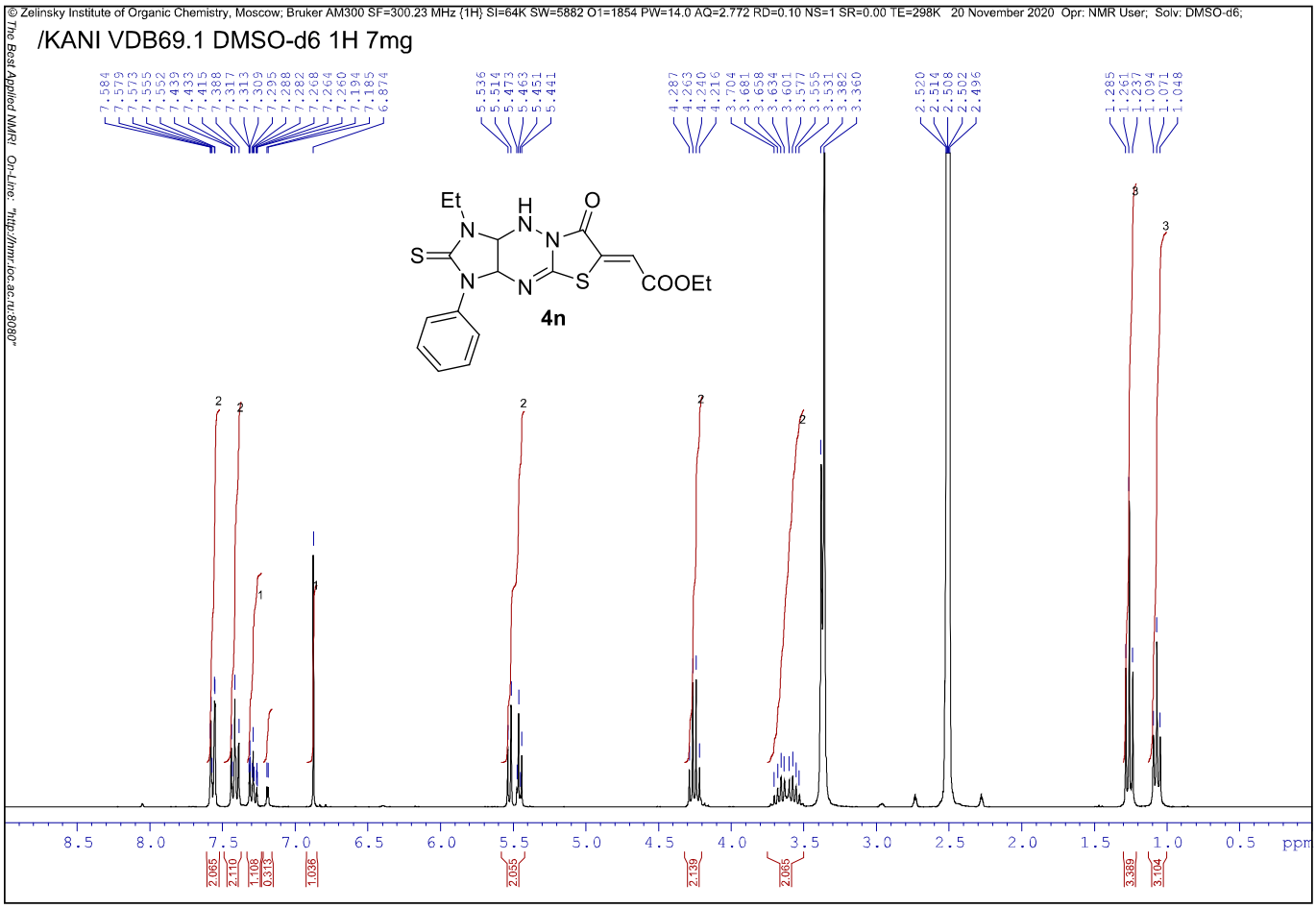
^{1}H NMR spectrum of **4m**



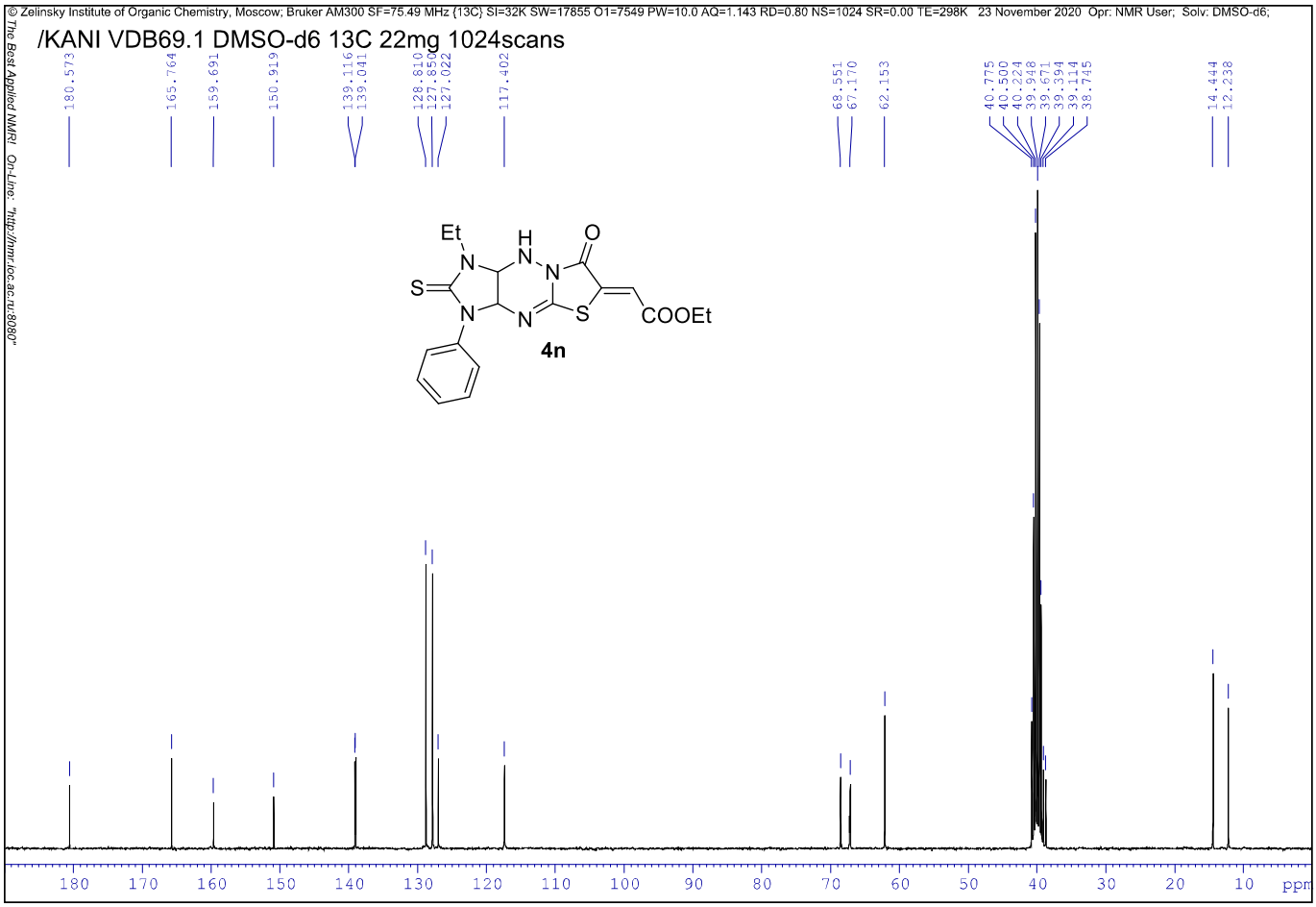
^{13}C NMR spectrum of **4m**



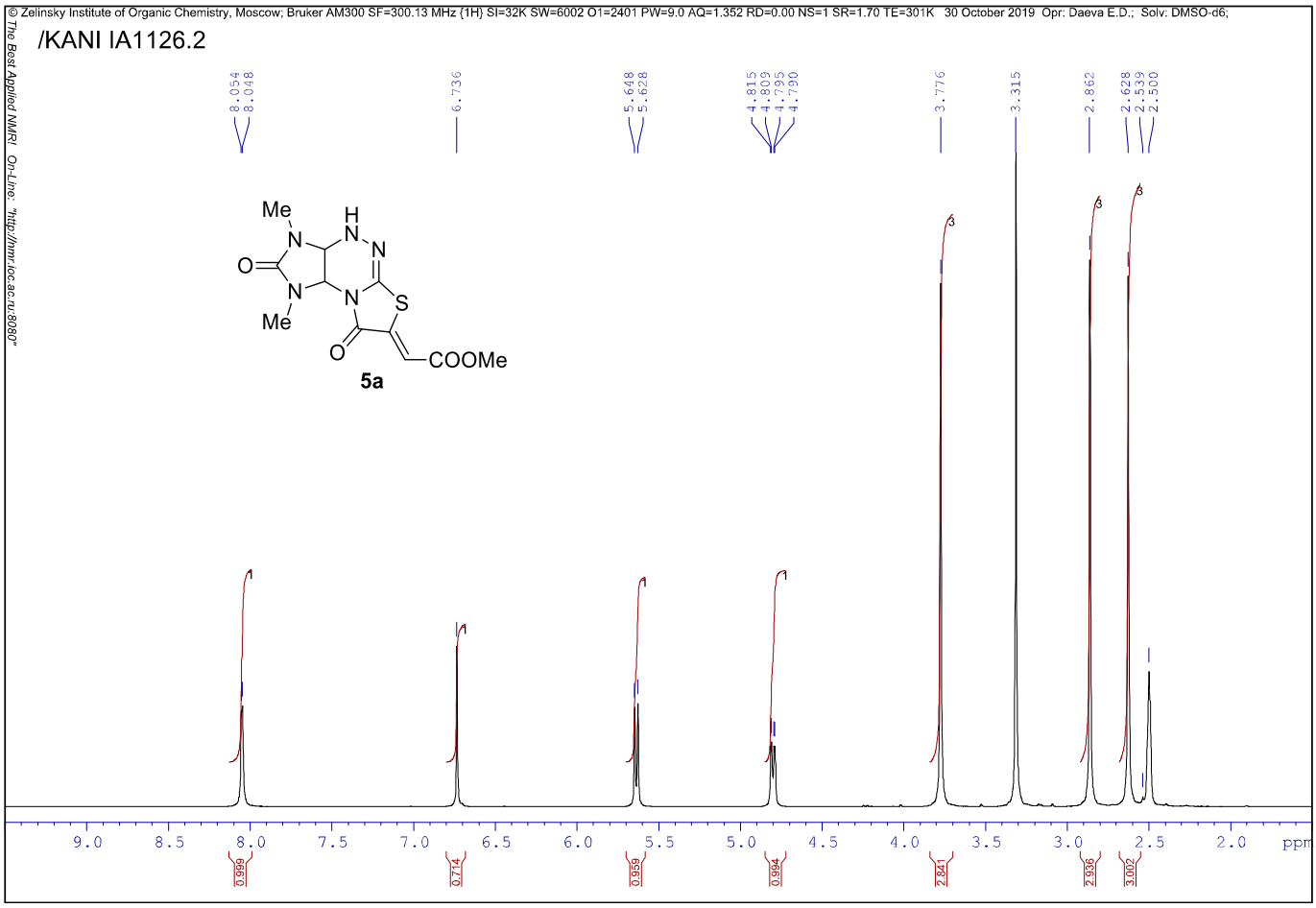
^{1}H NMR spectrum of **4n**



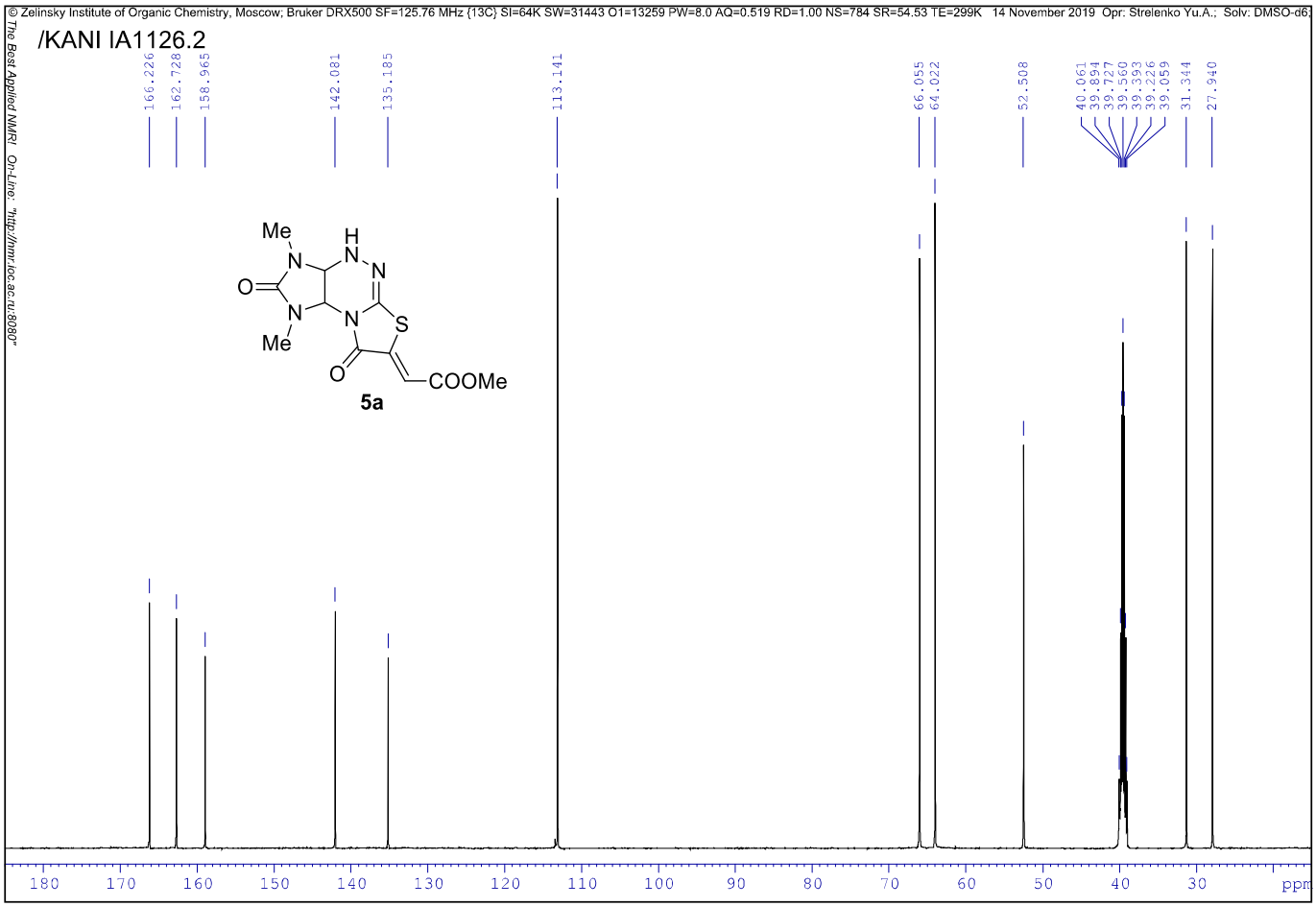
^{13}C NMR spectrum of **4n**



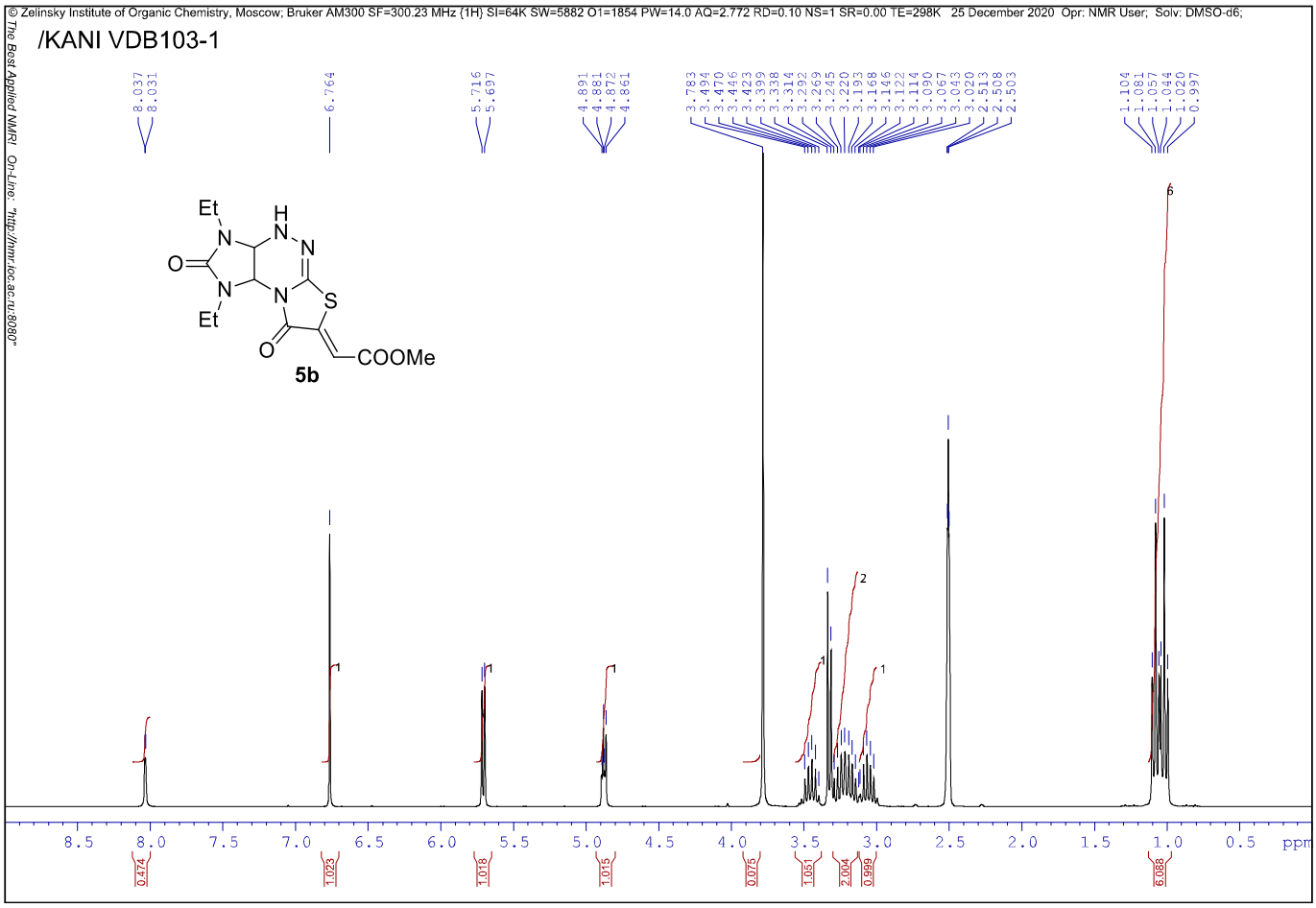
^{1}H NMR spectrum of **5a**



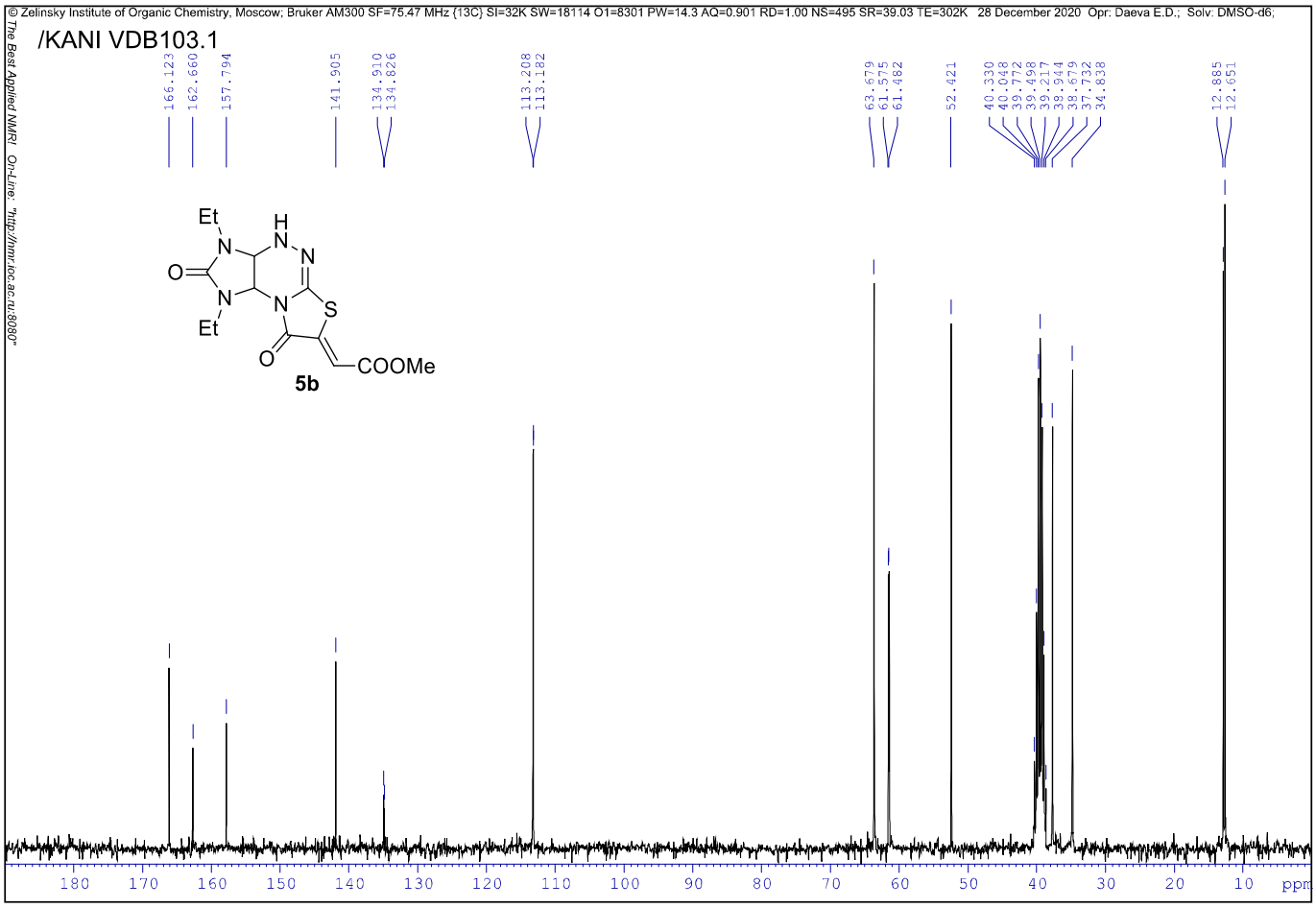
^{13}C NMR spectrum of **5a**



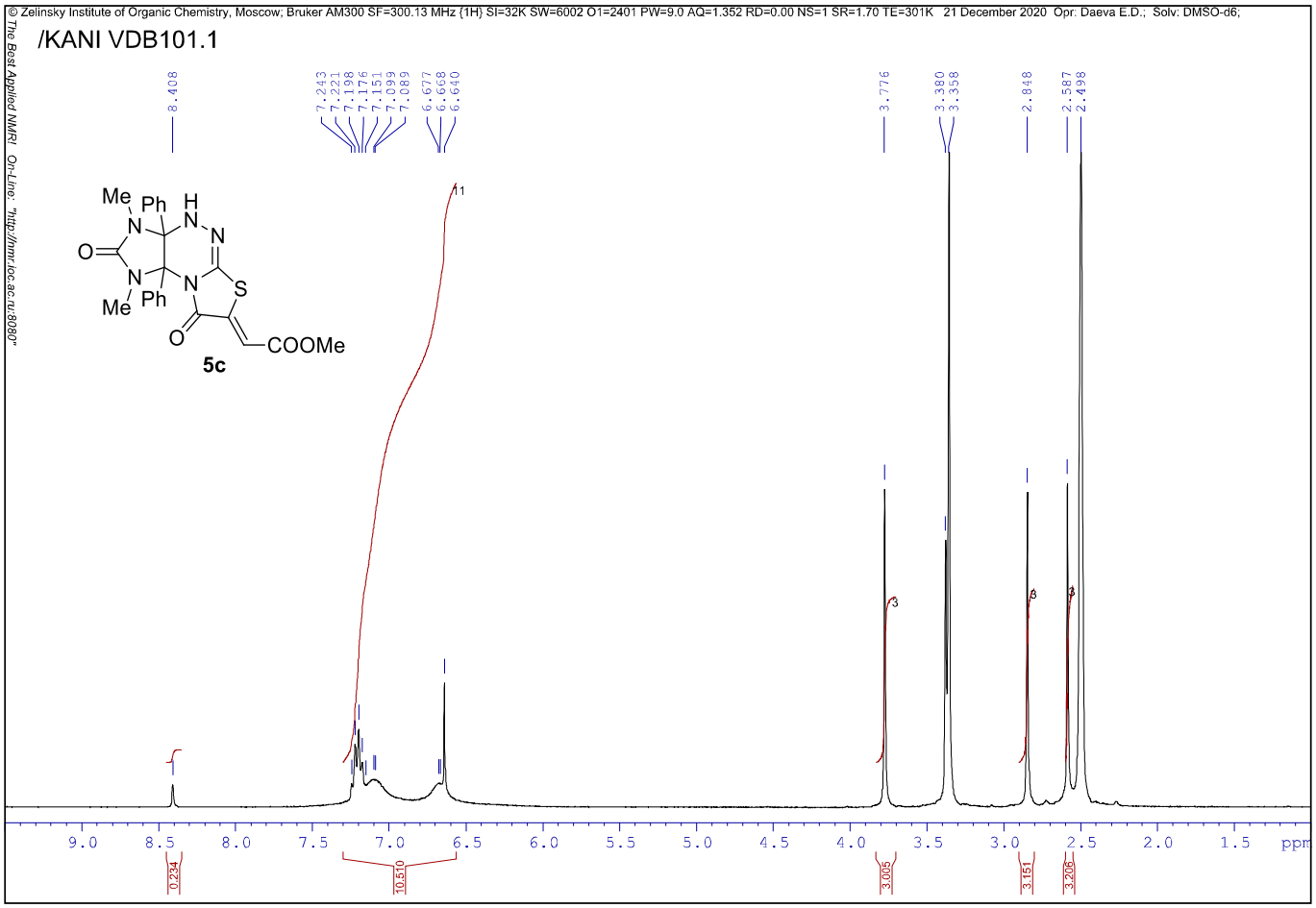
^{1}H NMR spectrum of **5b**



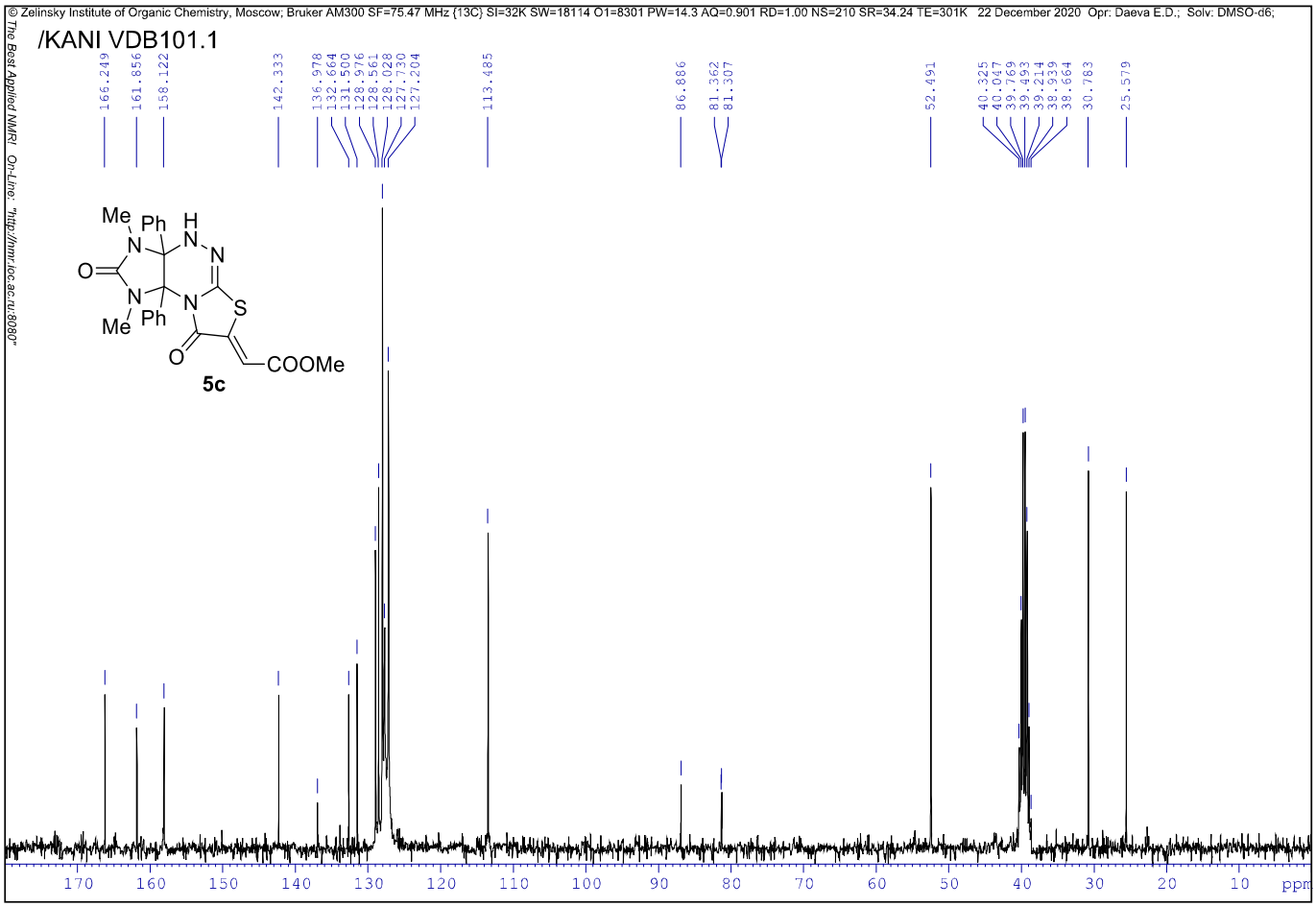
^{13}C NMR spectrum of **5b**



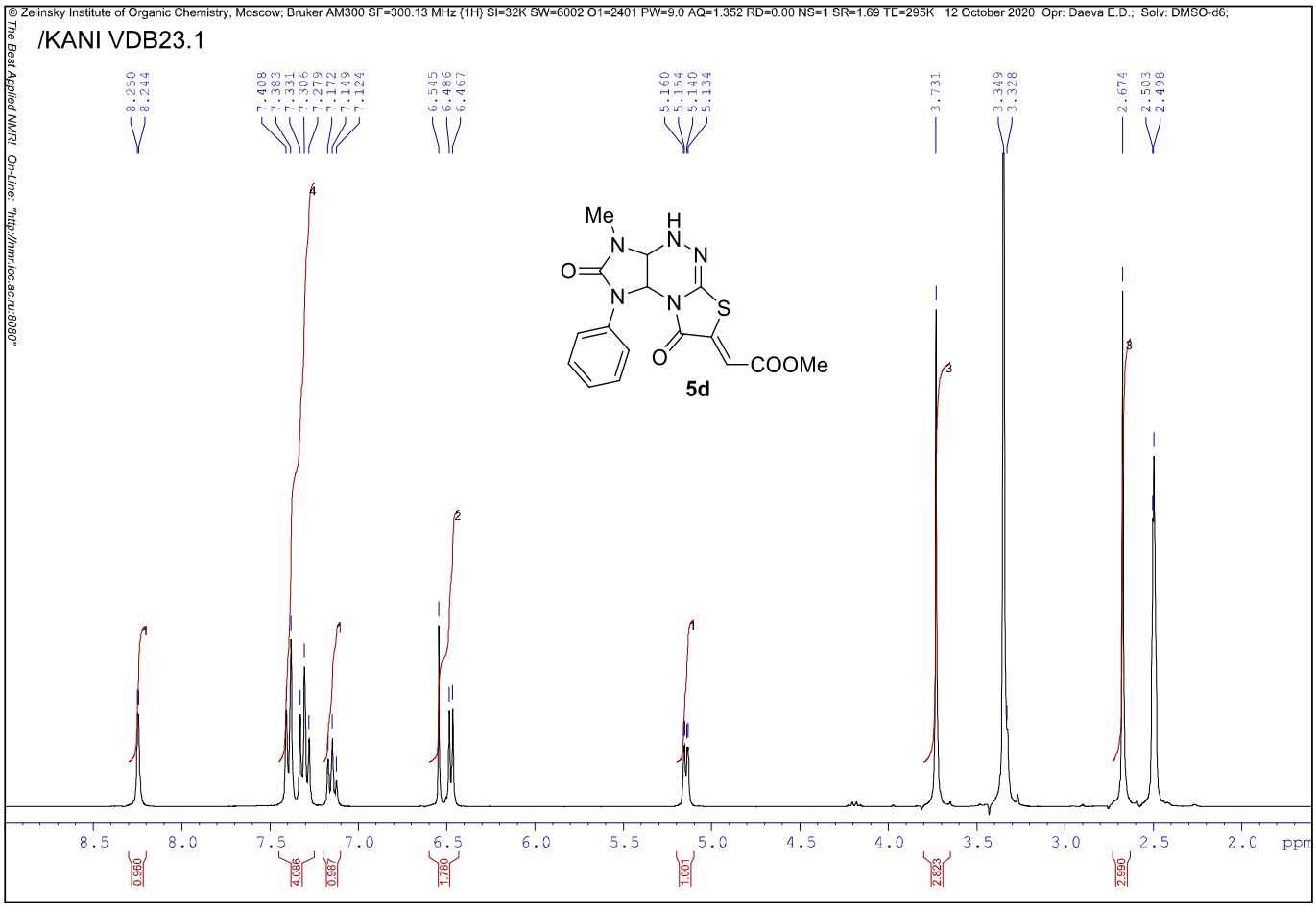
^{1}H NMR spectrum of **5c**



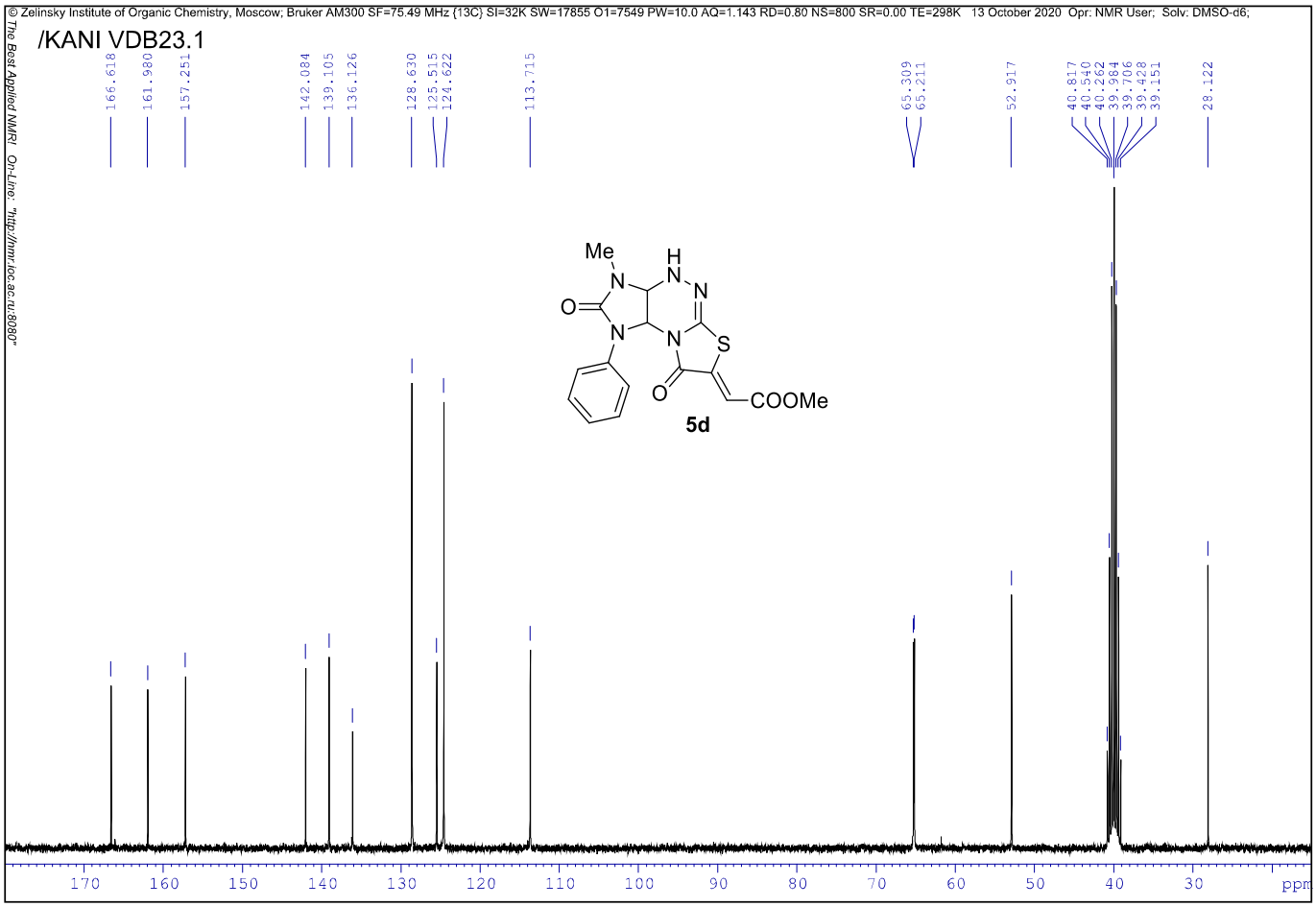
^{13}C NMR spectrum of **5c**



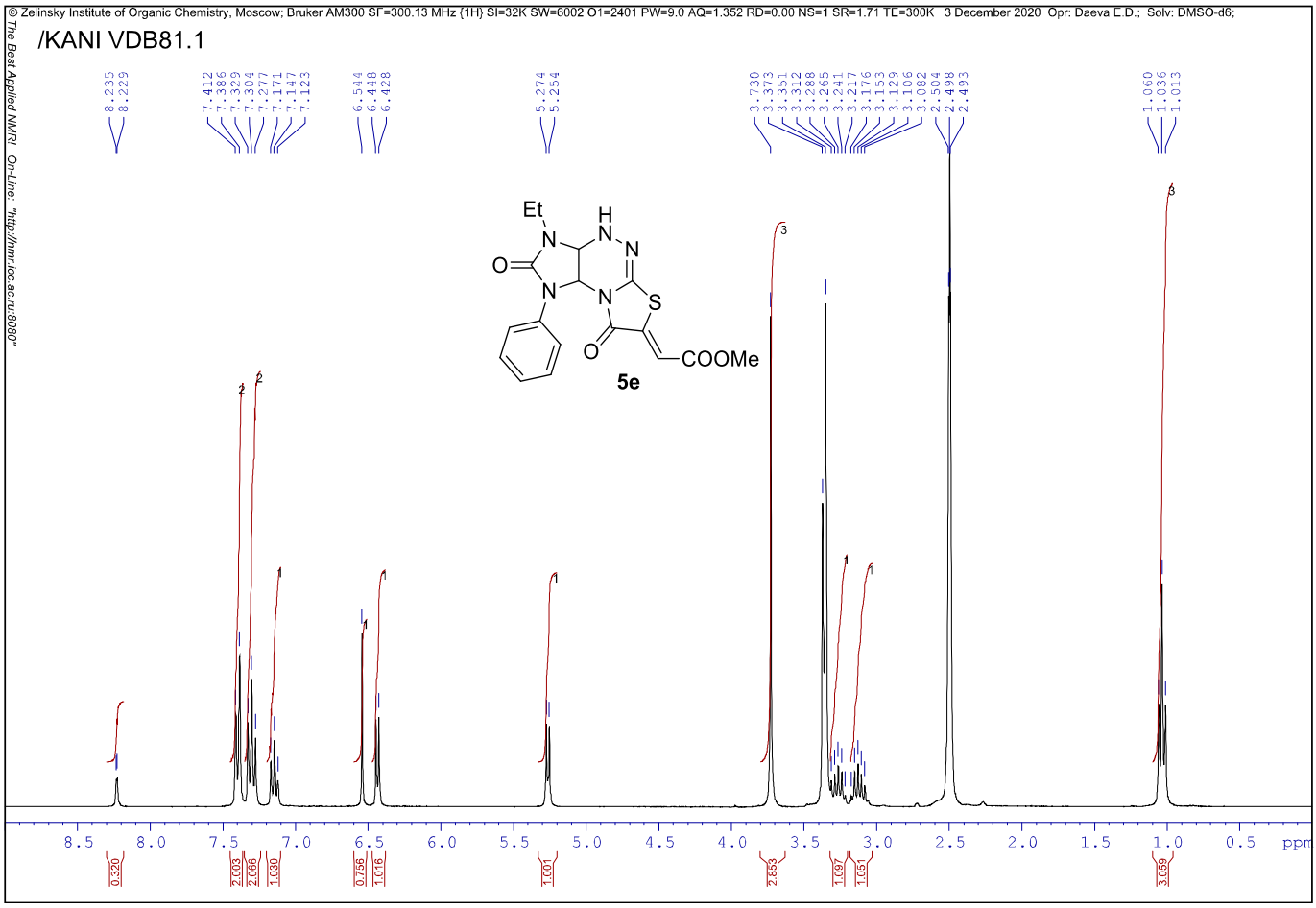
^{1}H NMR spectrum of **5d**



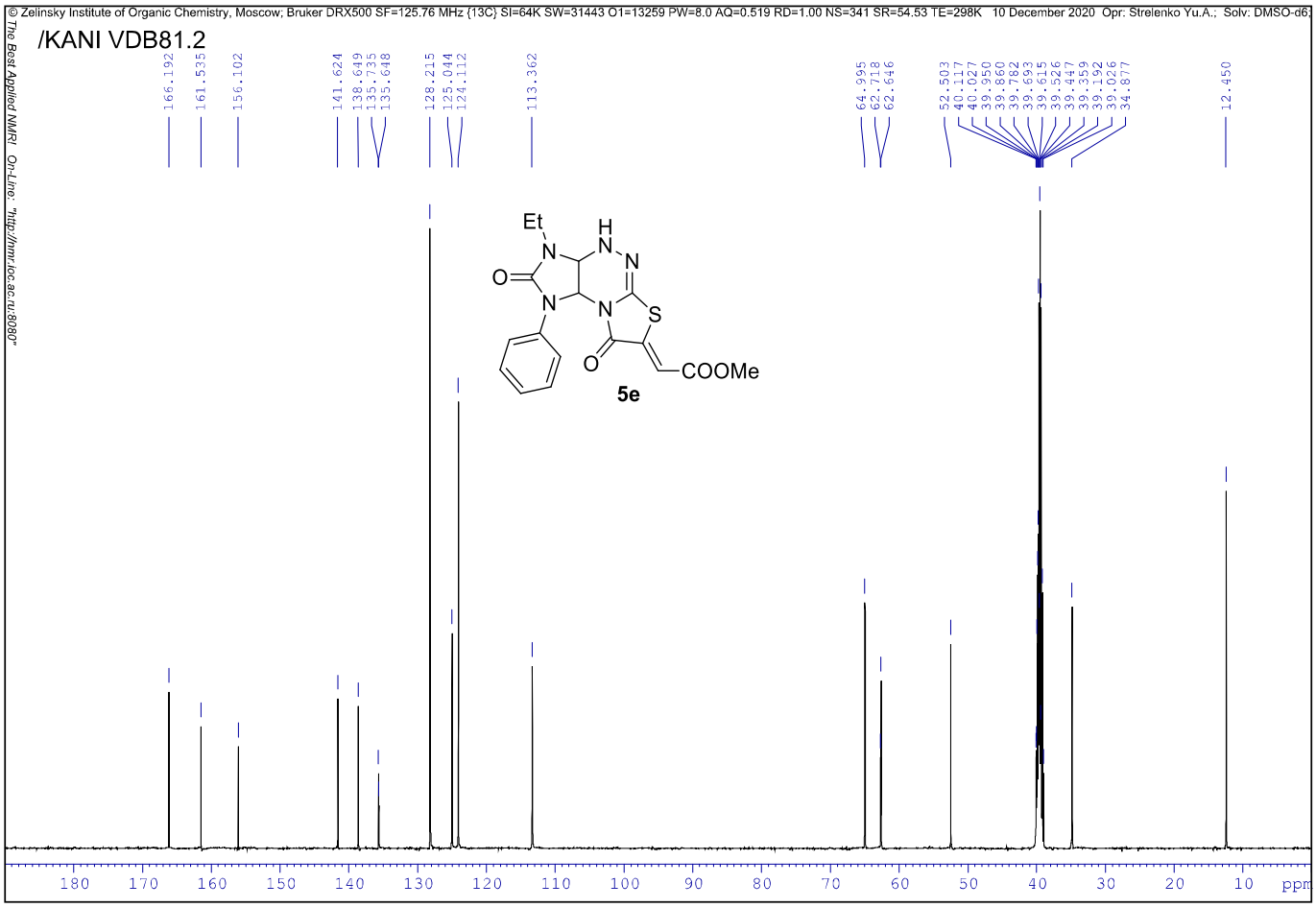
^{13}C NMR spectrum of **5d**



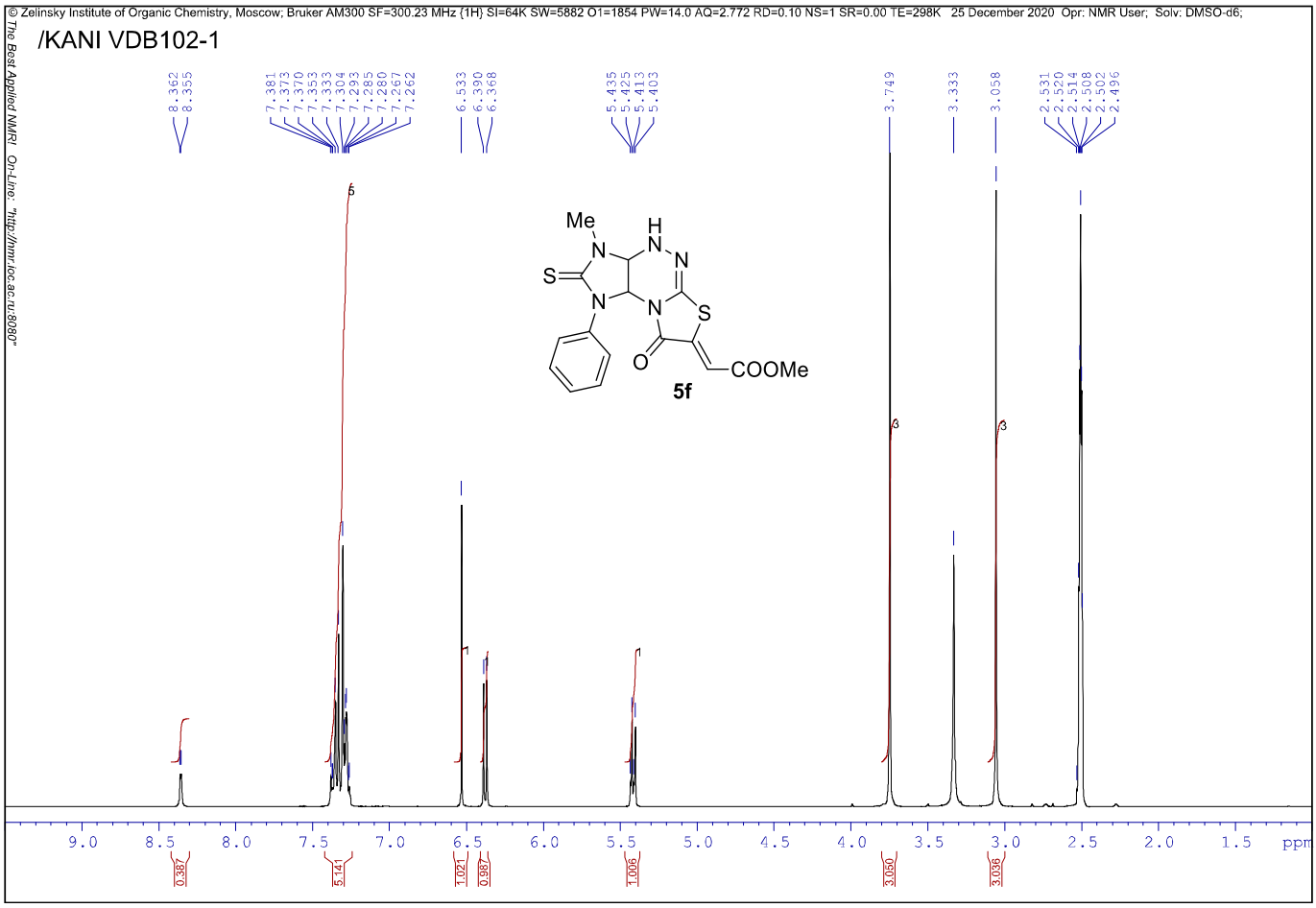
^{1}H NMR spectrum of **5e**



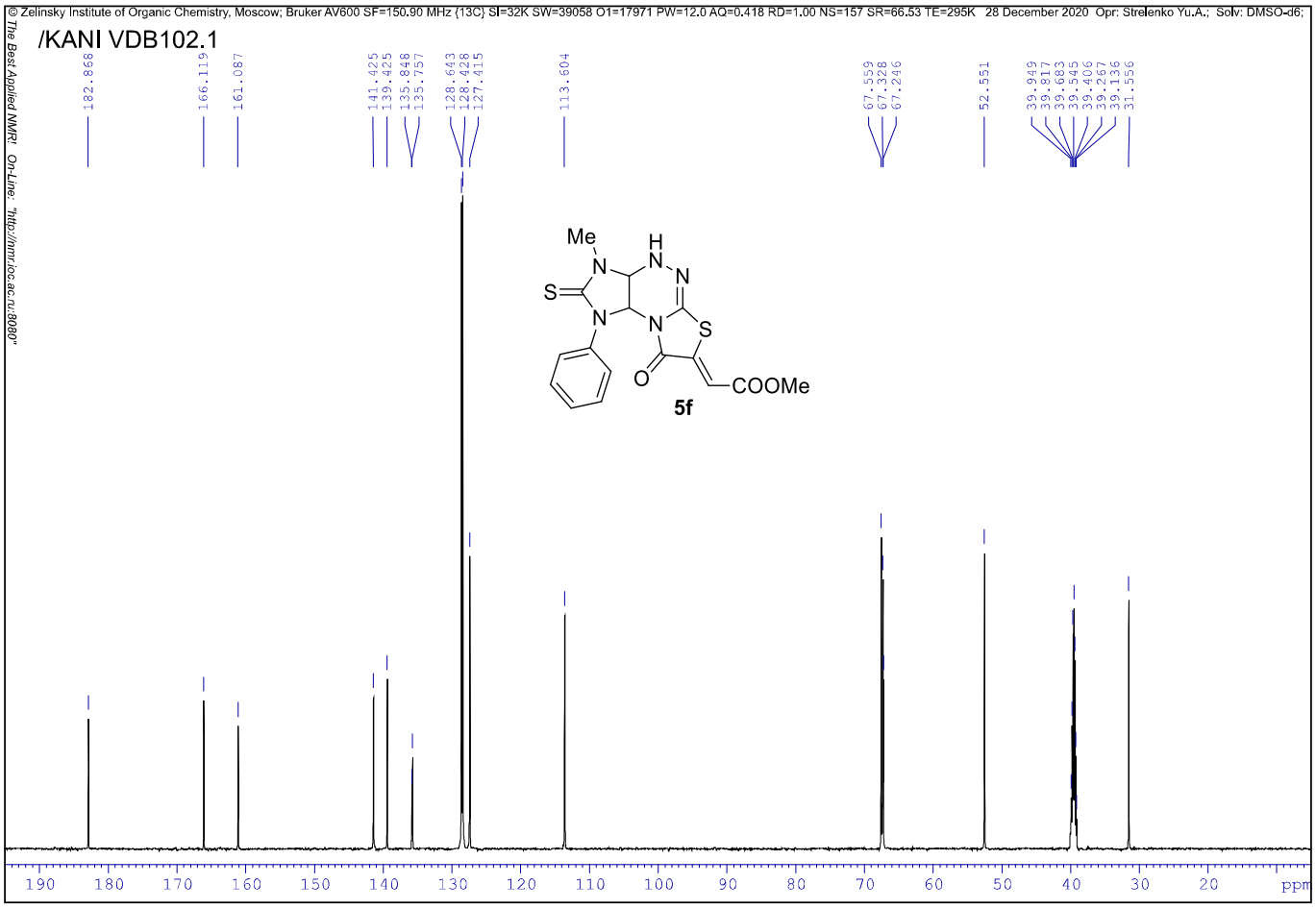
^{13}C NMR spectrum of **5e**



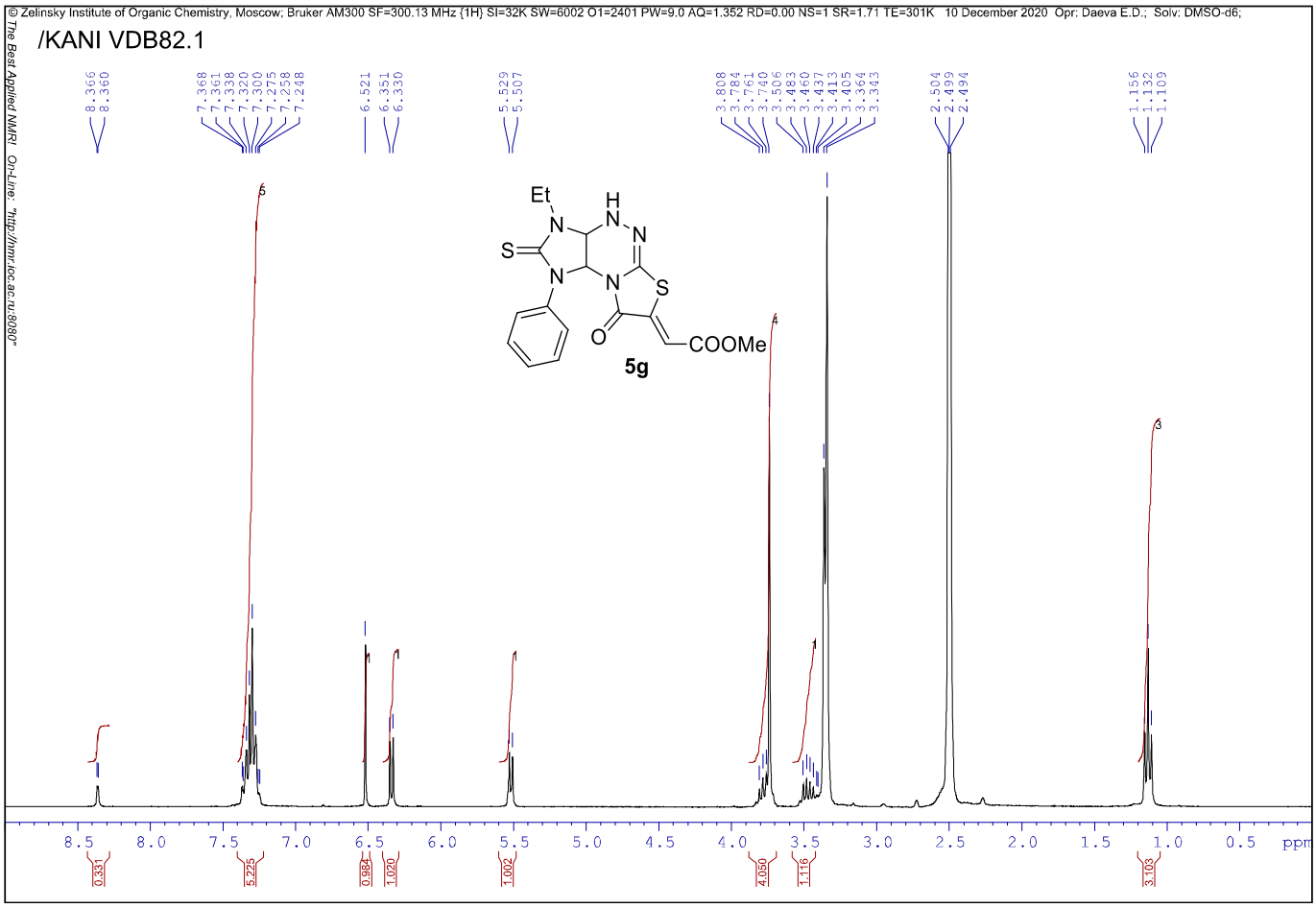
^{1}H NMR spectrum of **5f**



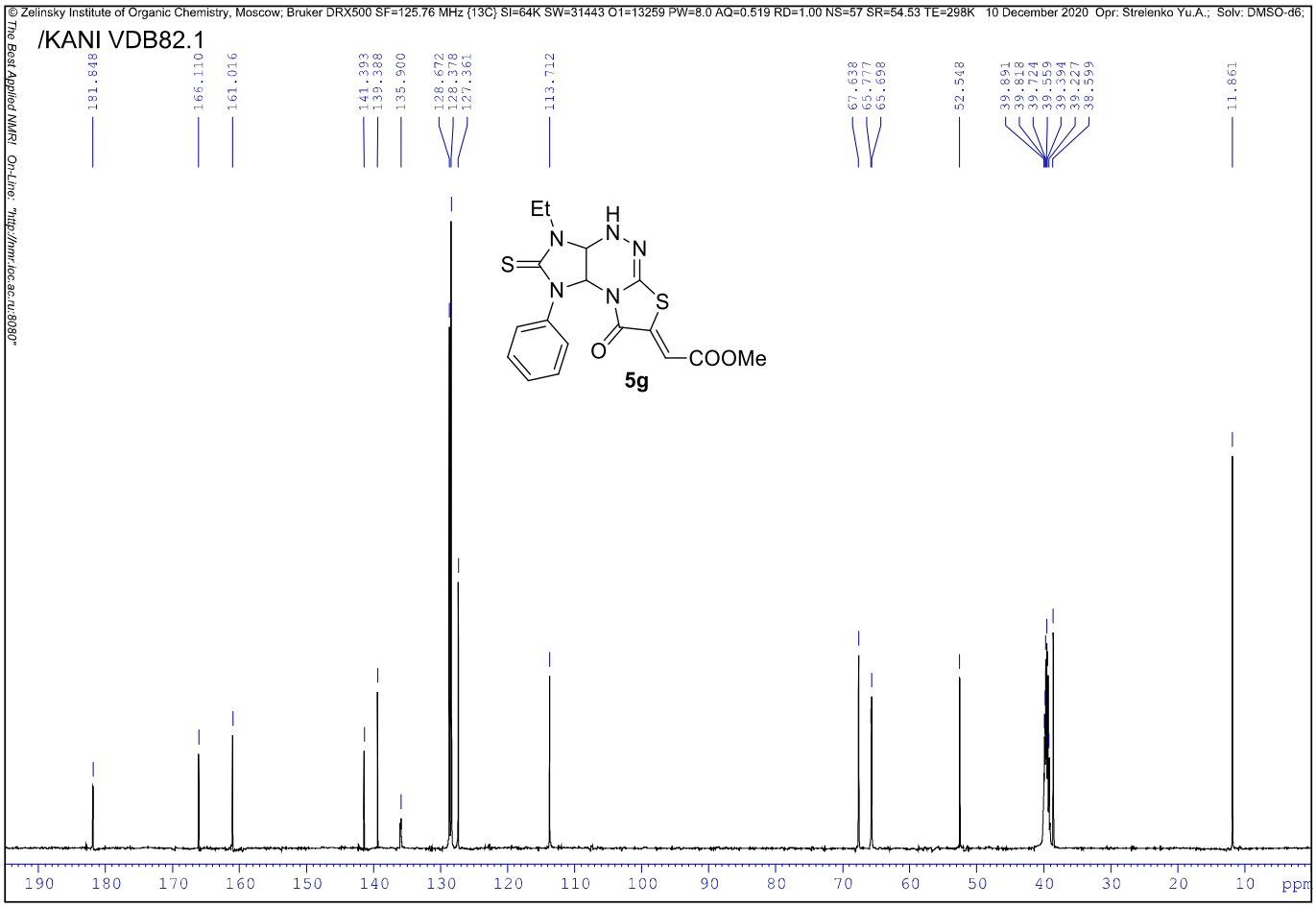
^{13}C NMR spectrum of **5f**



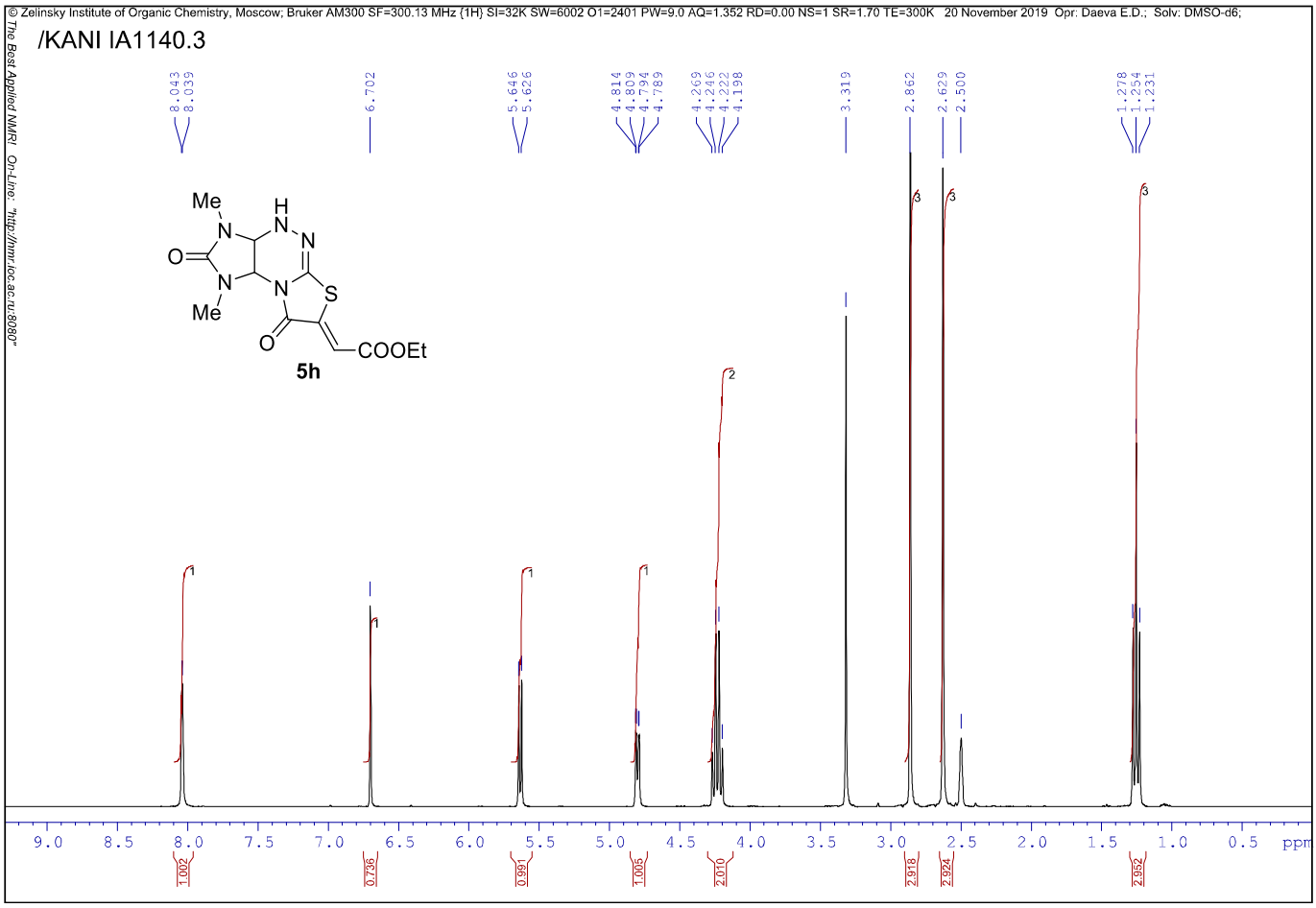
^{1}H NMR spectrum of **5g**



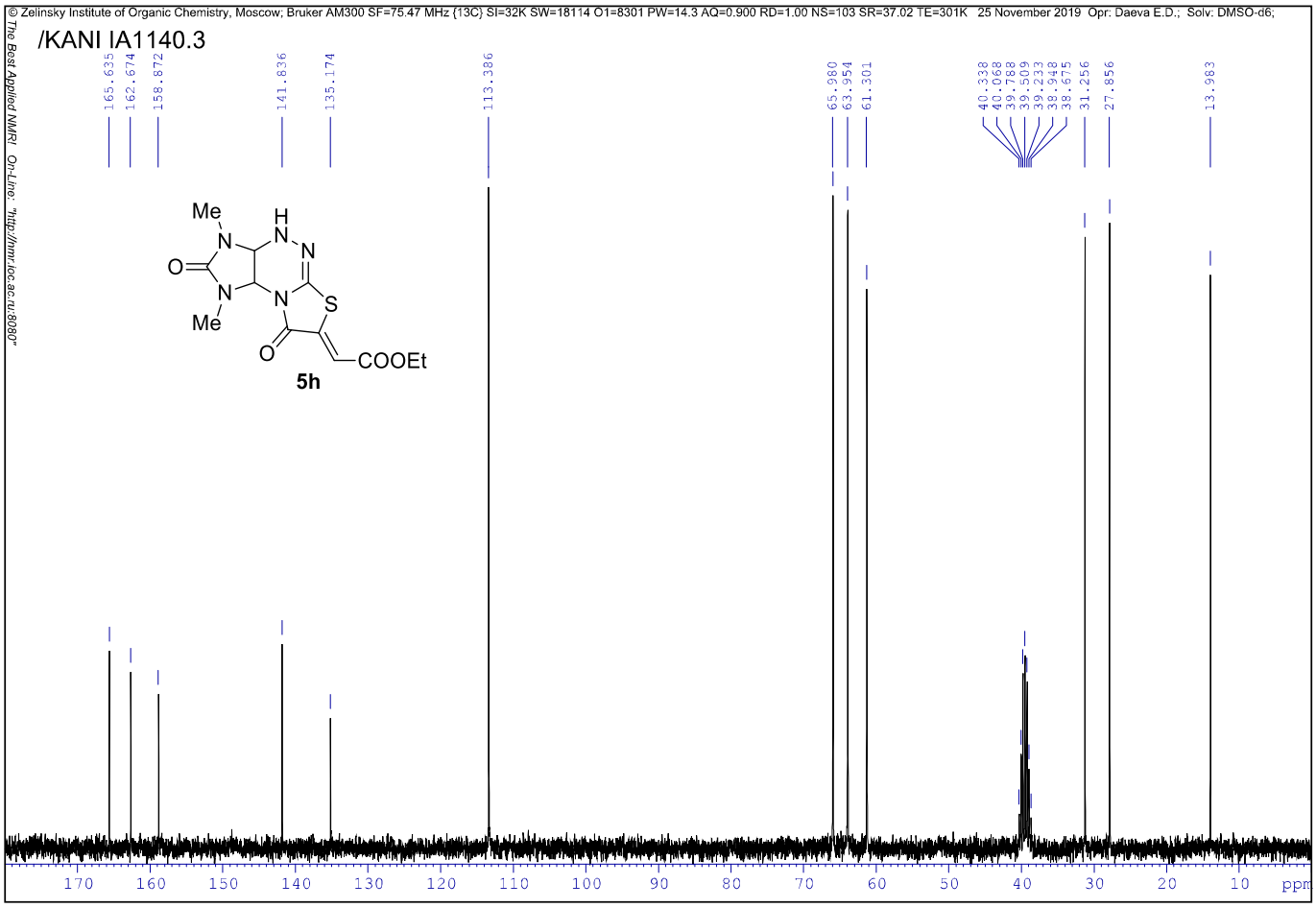
^{13}C NMR spectrum of **5g**



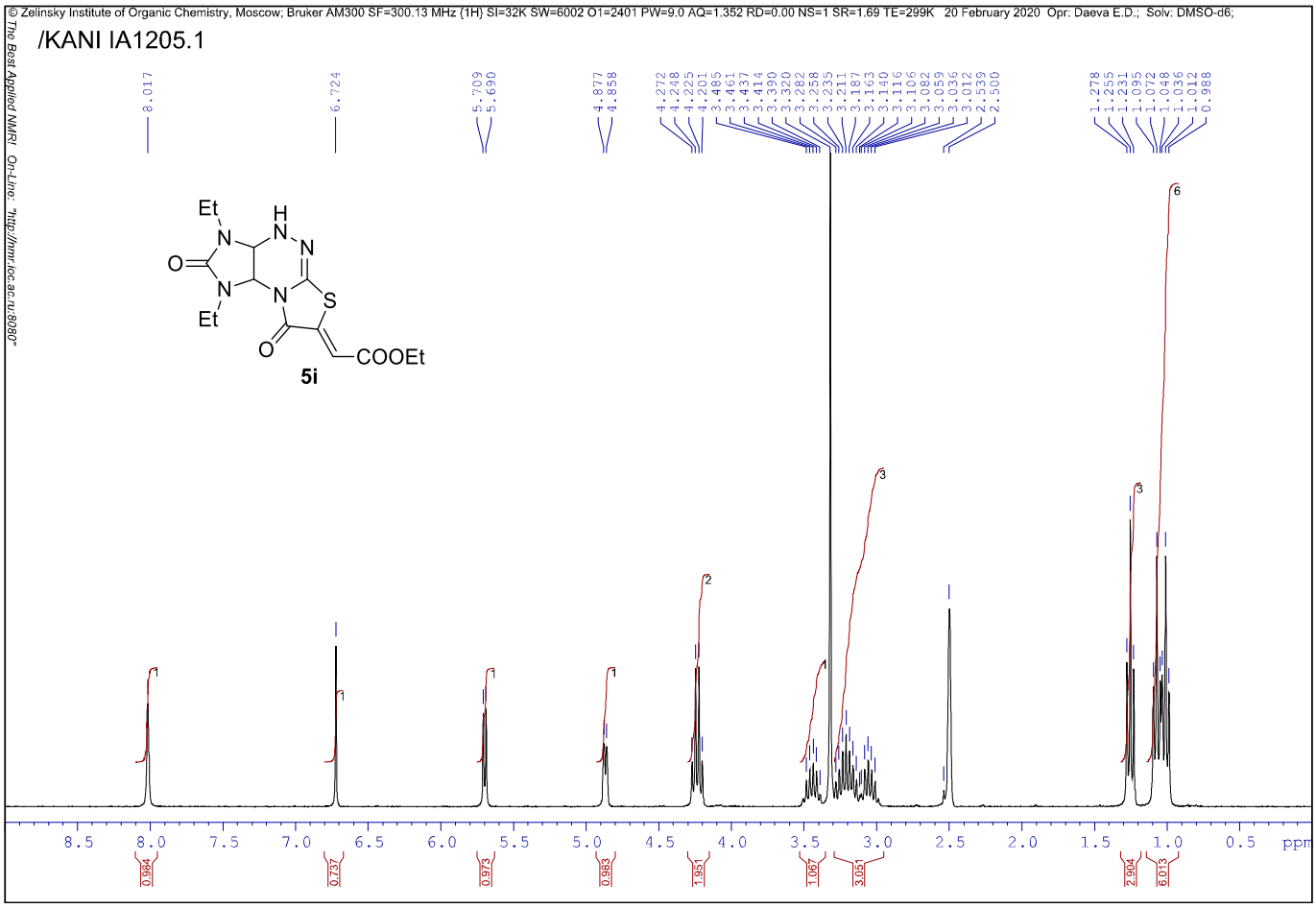
^{1}H NMR spectrum of **5h**



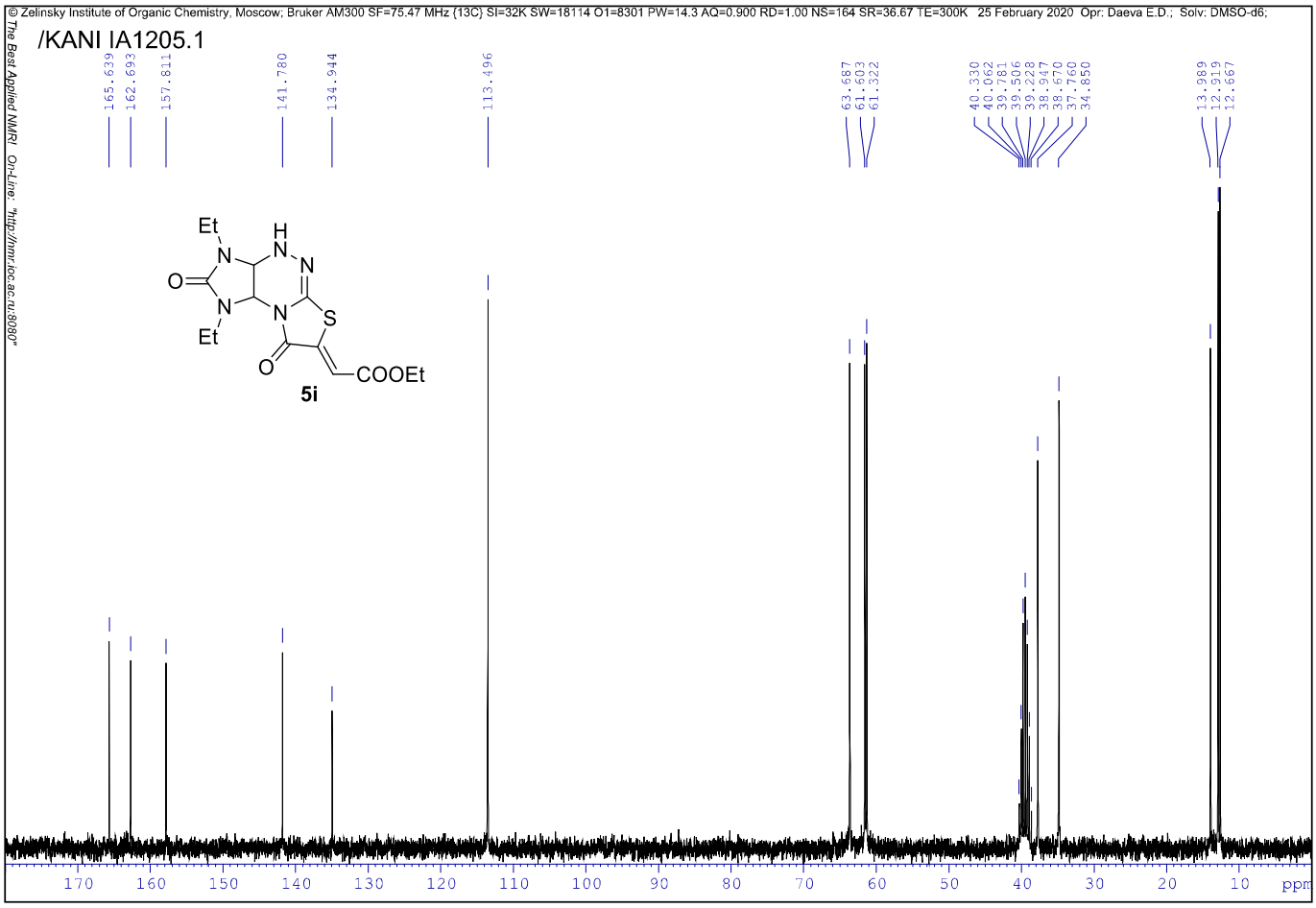
^{13}C NMR spectrum of **5h**



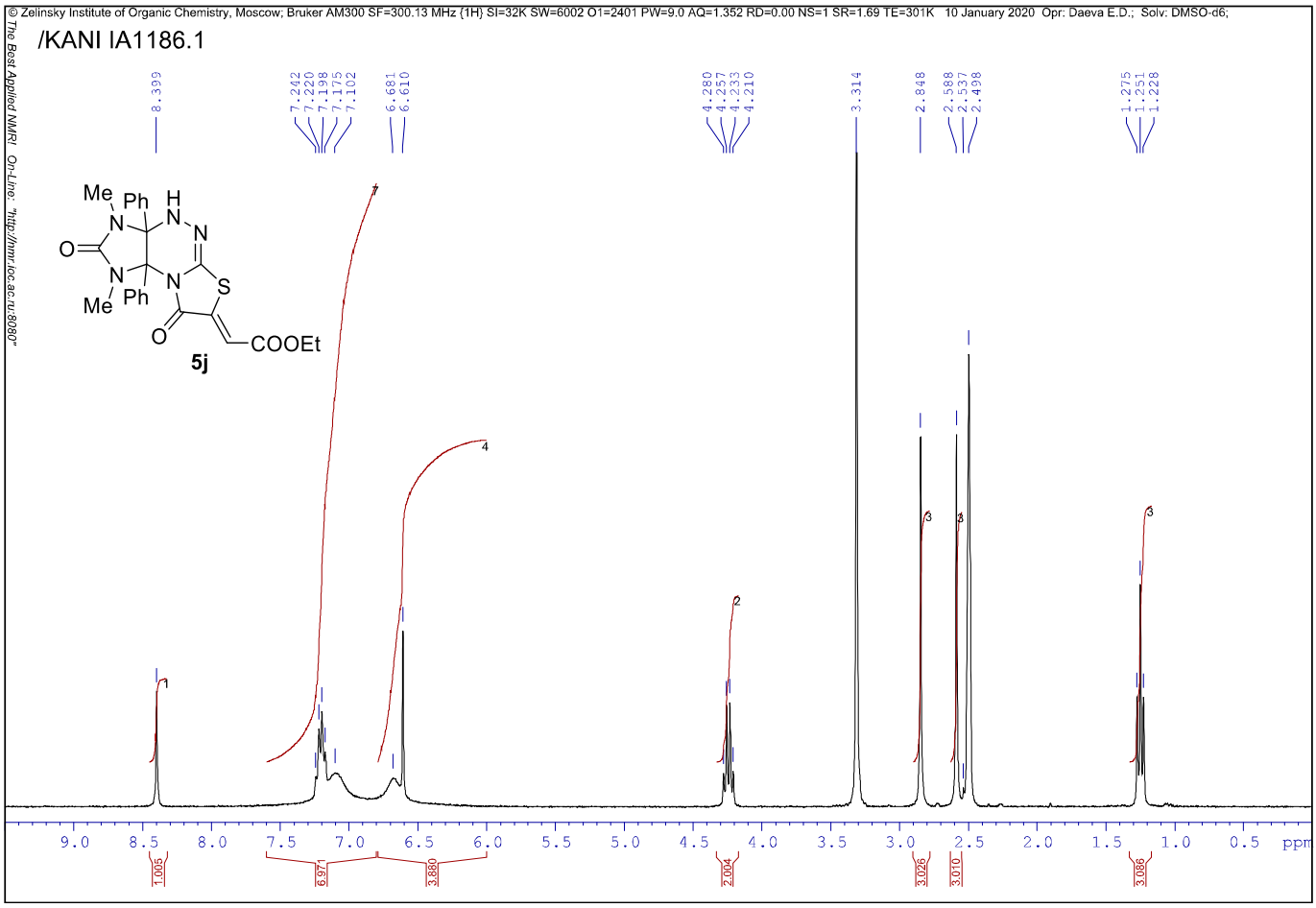
^{1}H NMR spectrum of **5i**



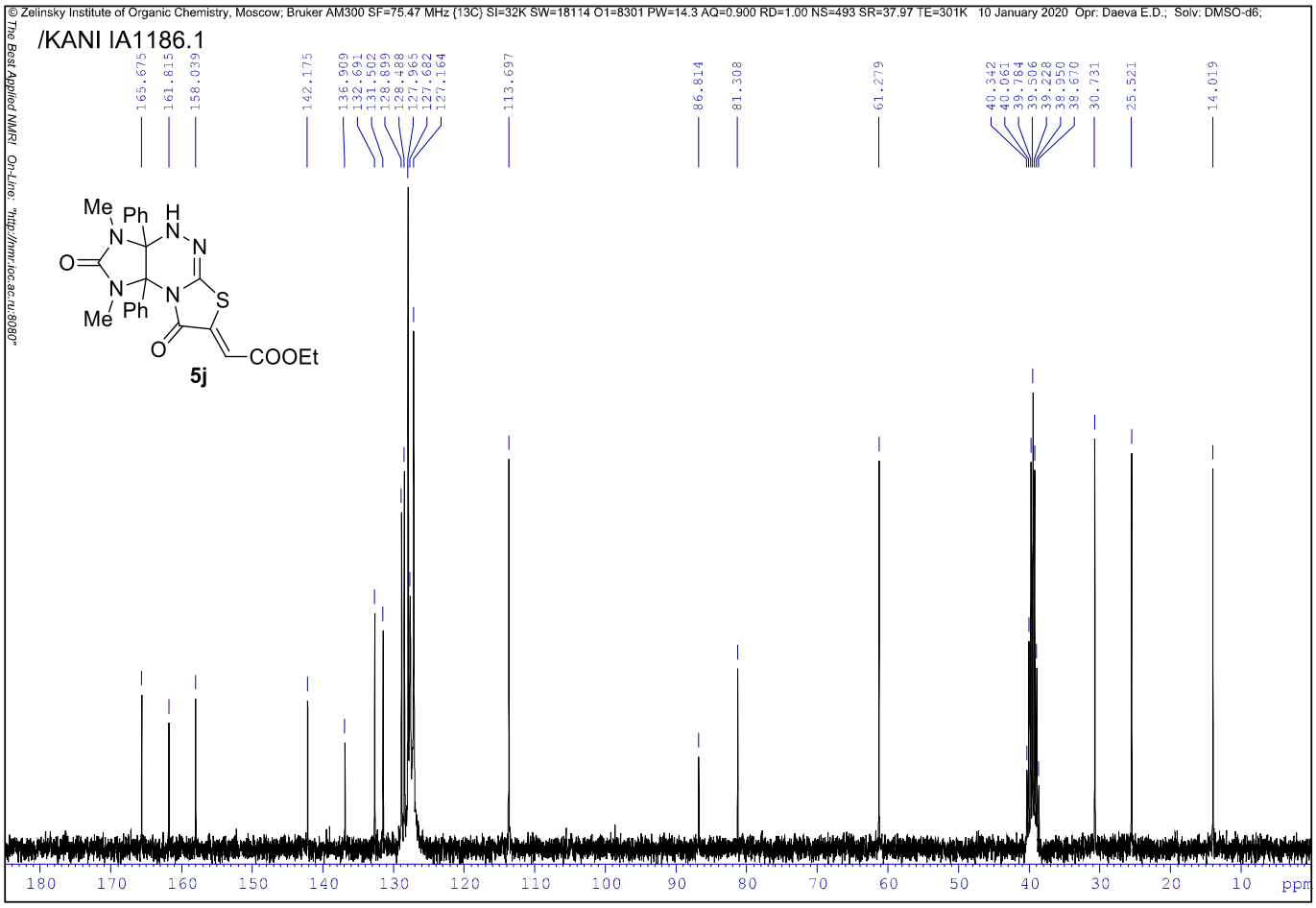
^{13}C NMR spectrum of **5i**



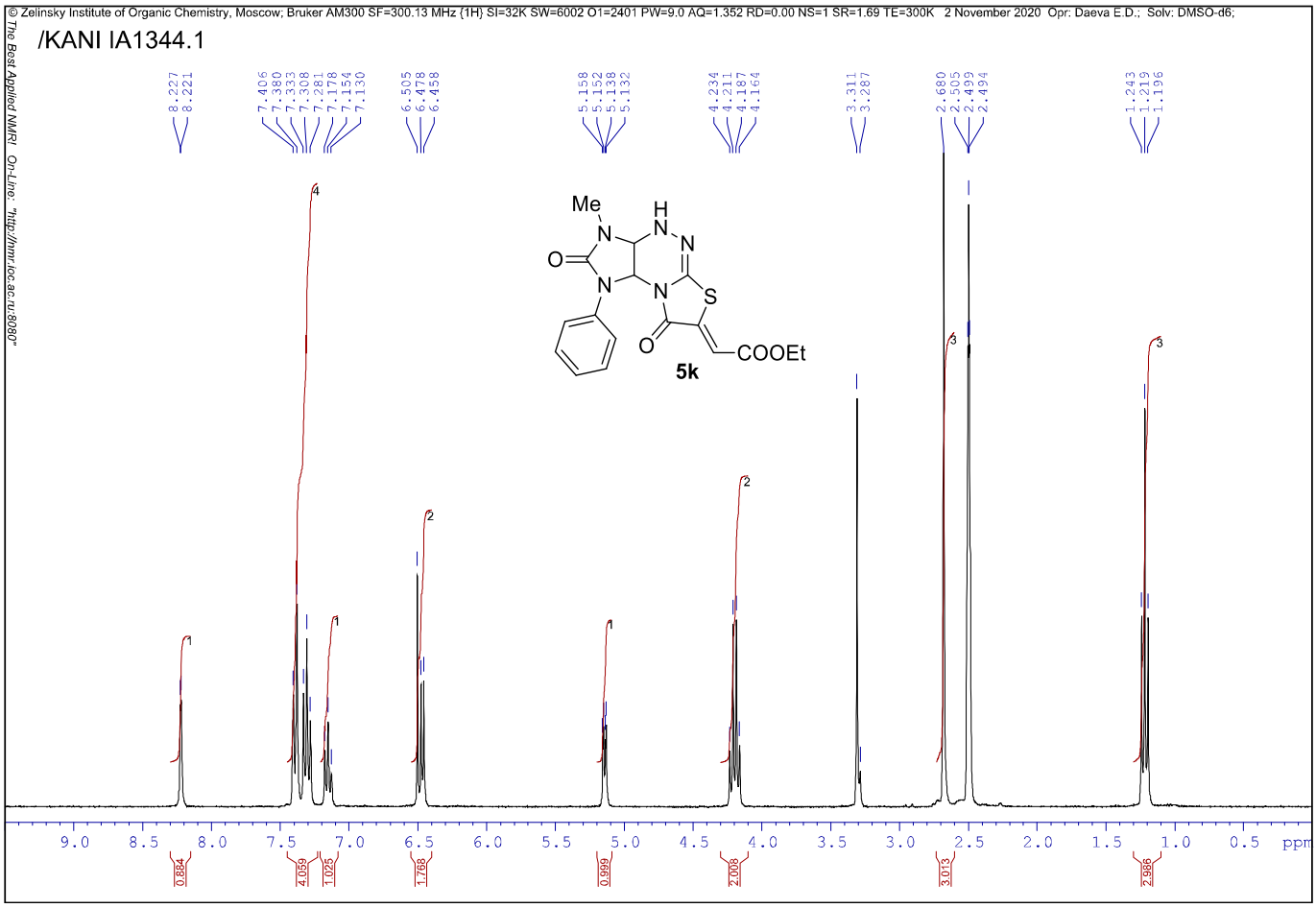
^{1}H NMR spectrum of **5j**



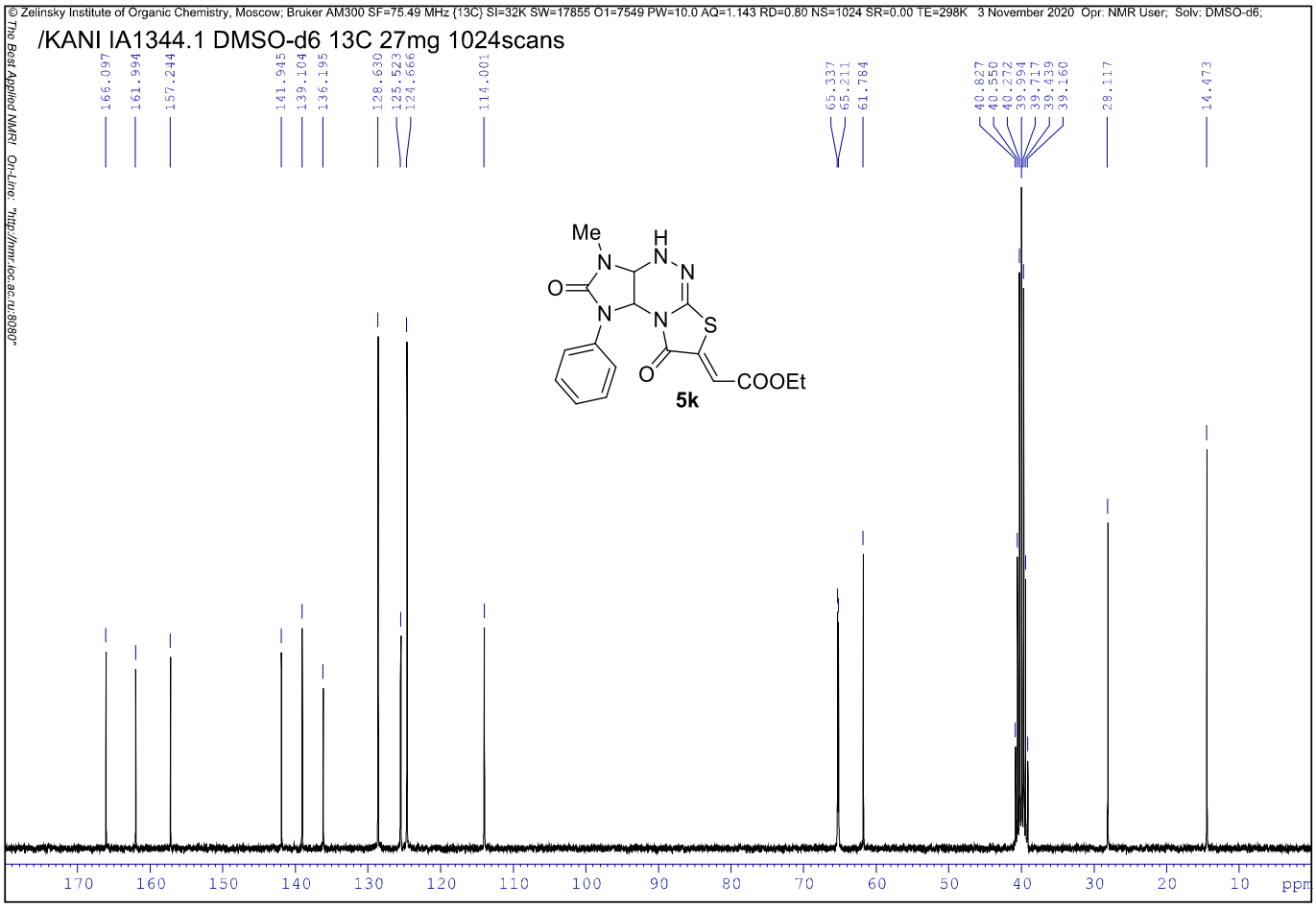
^{13}C NMR spectrum of **5j**



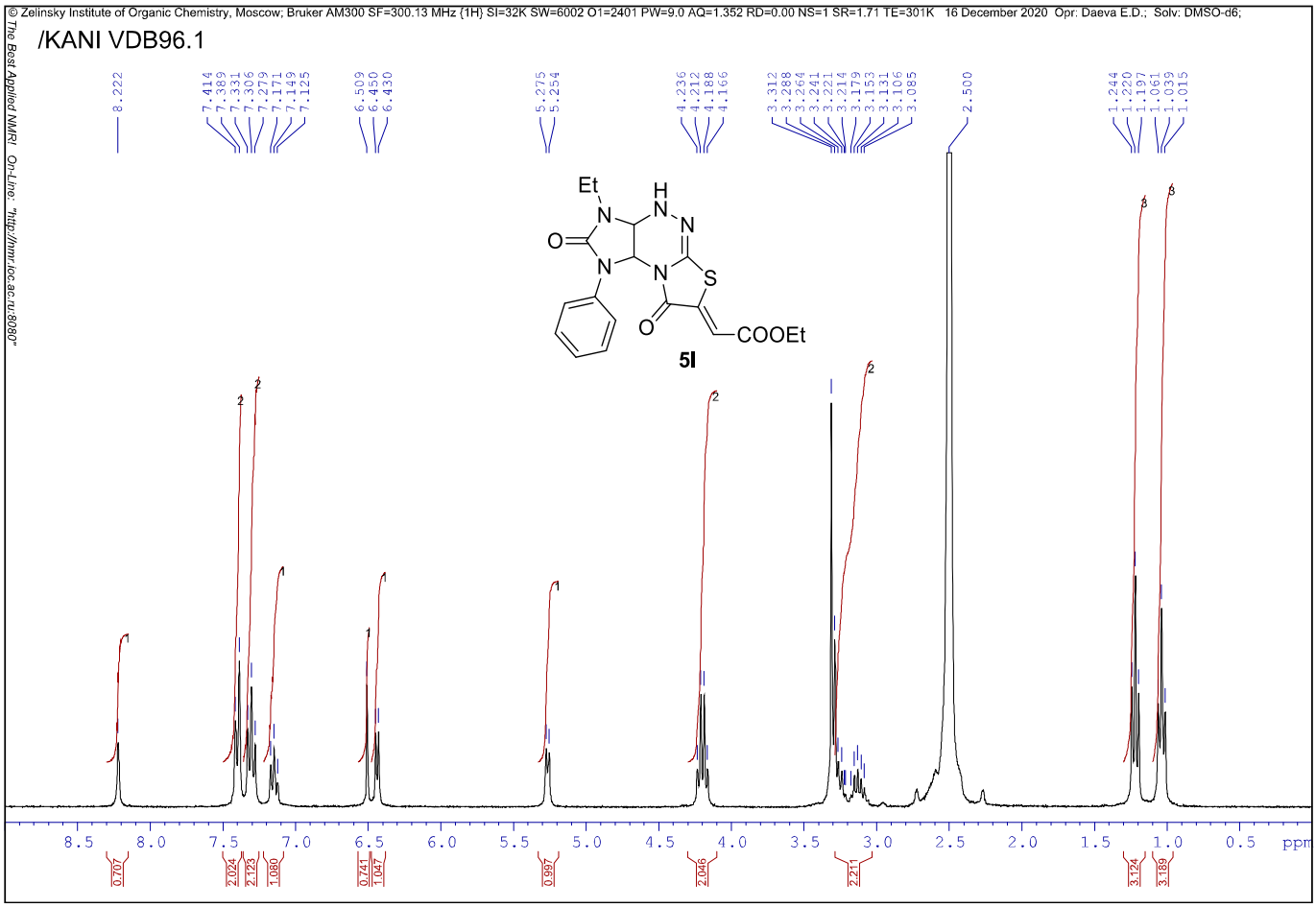
^{1}H NMR spectrum of **5k**



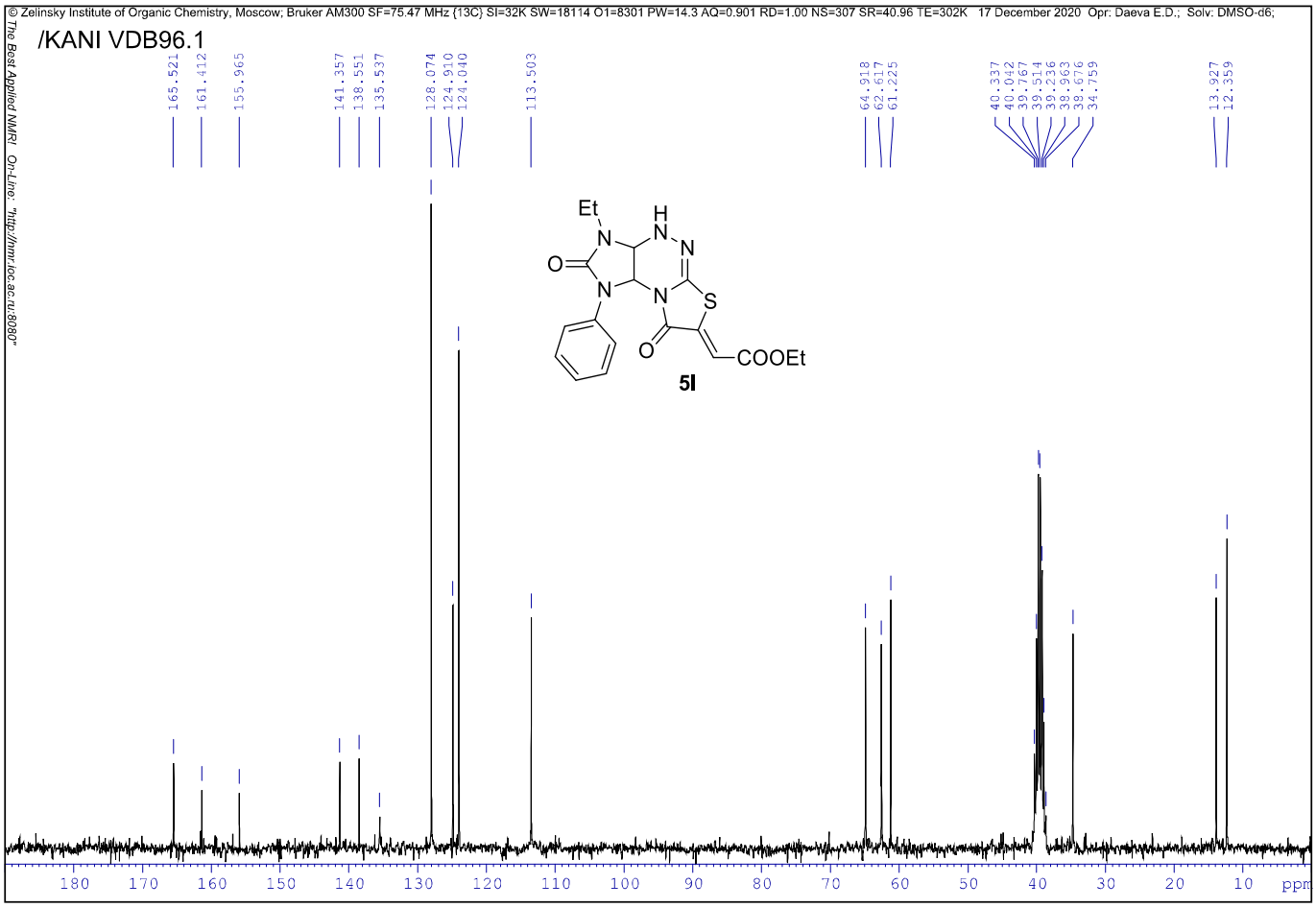
^{13}C NMR spectrum of **5k**



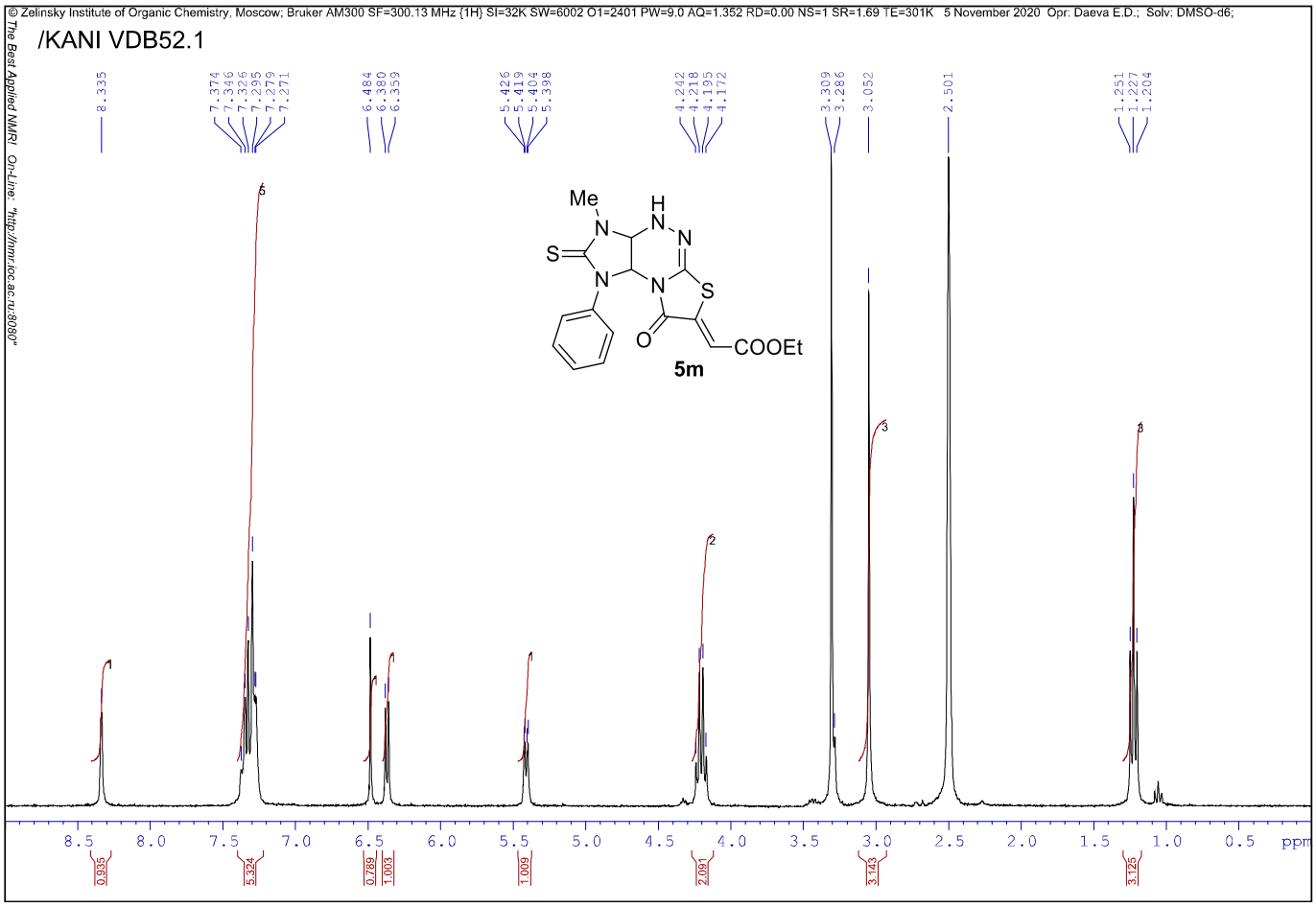
^{1}H NMR spectrum of **5l**



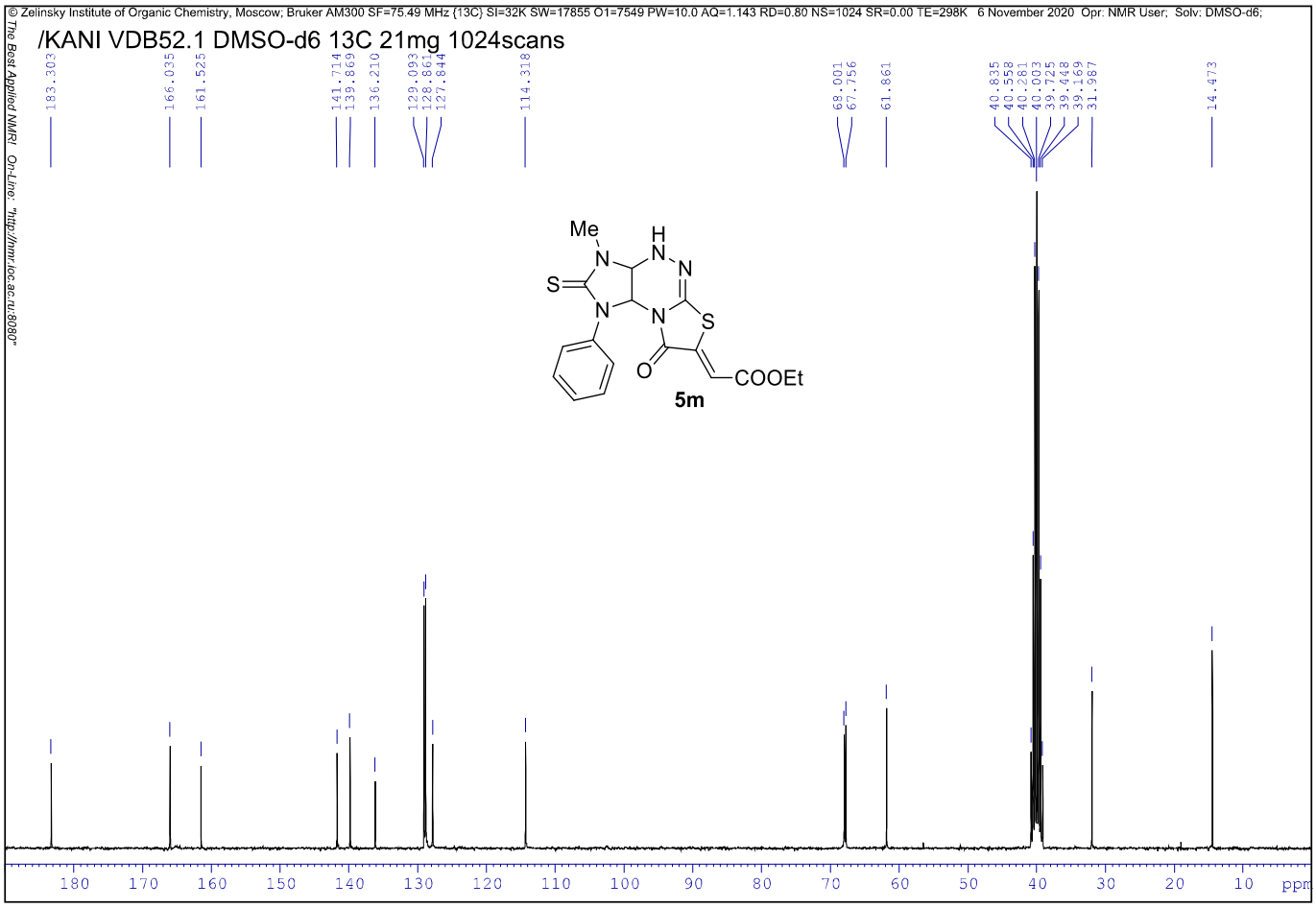
^{13}C NMR spectrum of **5l**



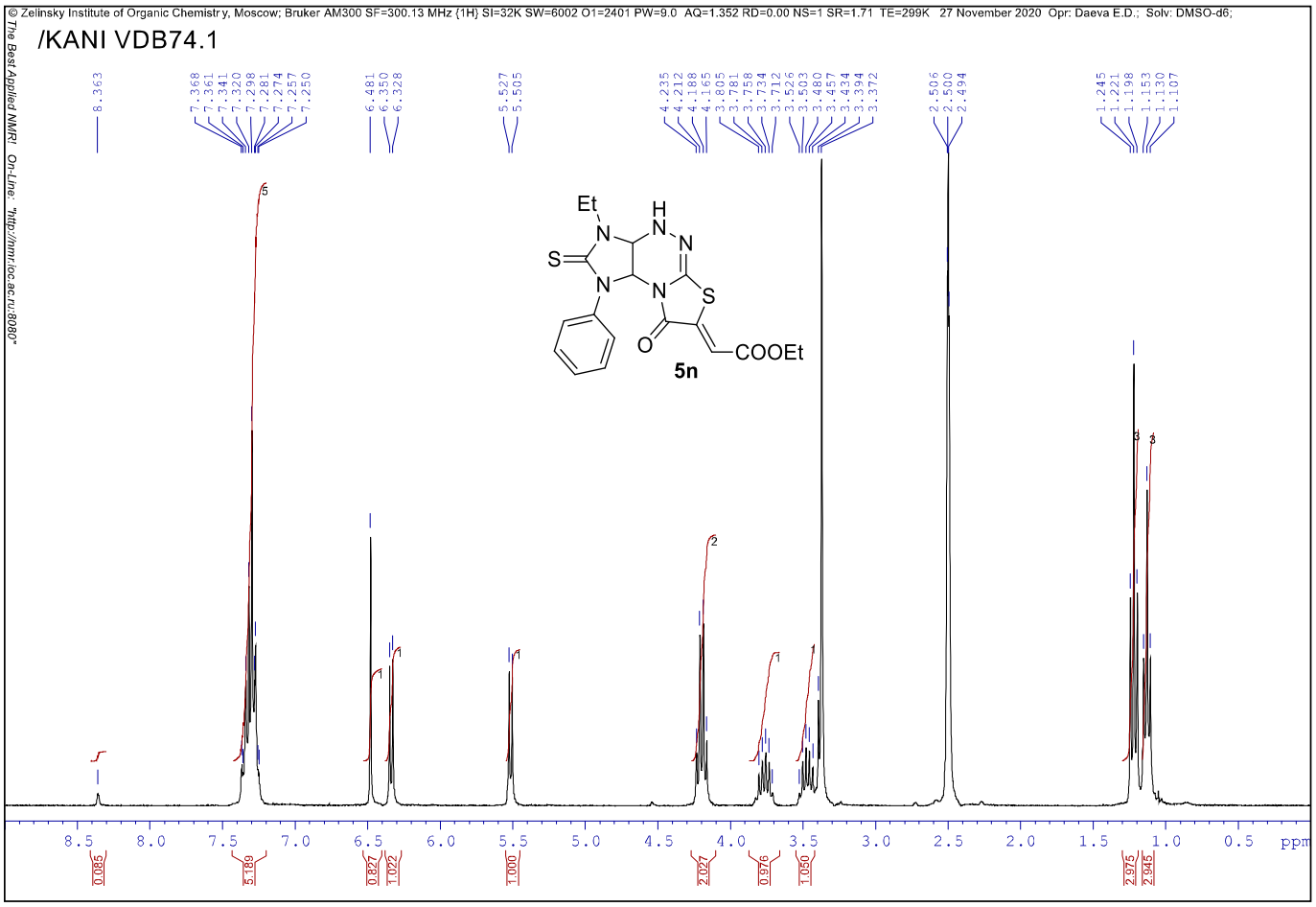
^{1}H NMR spectrum of **5m**



^{13}C NMR spectrum of **5m**



^{1}H NMR spectrum of **5n**



^{13}C NMR spectrum of **5n**