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Supplementary Information

Dimroth-type N/S-interchange of N-aminothioglycolurils in the synthesis of 2-hydrazonoimidazo[4,5-*d*]thiazolones

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Table of Contents

General Methods

Commercially available solvents and reagents were used as purchased.

NMR spectroscopy was performed at 298 K using a Bruker AM300 (300.13 MHz, ^{1}H; 75.47 MHz, ^{13}C; 282.40 MHz, ^{19}F), a Bruker DRX500 (125.76 MHz, ^{13}C) and a Bruker AV600 (150.9 MHz, ^{13}C). Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane or $CFCl_3$ as the internal standard and is reported as position (δ in ppm), multiplicity (s = singlet, br.s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), coupling constant (*J* in Hz) and integration (number of protons). ^{13}C NMR spectra were recorded with complete proton decoupling.

Infrared spectra were obtained on a BrukerALPHA spectrometer using KBr pellets and are reported in wavenumbers (cm^{-1}).

HRMS were performed at the Bruker micrOTOF II using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage: 4500 V); mass range from m/z 50 to 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in MeCN or MeOH (flow rate 3 μL/min). N_2 was applied as a dry gas.

Starting imidazo[4,5-*e*]-1,2,4-triazin-6-ones **9a-c** were prepared by cyclisation of corresponding 1,3-disubstituted 4,5-dihydroxyimidazolidine-2-ones with thiosemicarbazide.[1,2] Thioglycolurils **8a-j,l-o** were prepared according to known method.[3]

General procedure for the synthesis of thioglycolurils 8a-o.[3] To a stirring suspension of 5,7-dialkyl-3-thioxoperhydroimidazo[4,5-*e*]-1,2,4-triazine-6-one (**9a-c**, 2 mmol) in methanole (30 mL), 2 drops of concentrated HCl (0.06 mL, 0.66 mmol) and corresponding aromatic aldehyde (2.1 mmol) were added. The resulting mixture was refluxed with stirring for 1-1.5 h. After cooling for 4-48 h the solid product was filtered and dried. Recrystallization from EtOH or MeOH : H_2O (10 : 1) gave thioglycoluril (**8a-o**).

General procedure for the synthesis of hydrazonoimidazo[4,5-*d*]thiazolones 10a-o. Procedure A. Suspension of corresponding thioglycoluril **8a-o** (1 mmol) in a mixture of MeOH (10 ml) and concentrated HCl (d = 1.170, 10 ml) was stirred at room temperature for 2 h. The suspension gradually dissolved. The resulting solution was poured into 100 ml of water and pH value of the mixture was adjusted to 5-7 by adding sodium bicarbonate (until an abundant precipitate was formed). The precipitate of compound **10** was filtered of, washed with water, and dried in air. Compound **10d** was recrystallized from MeOH.

Procedure B. To a stirring suspension of compound **9a-c** (1 mmol) in methanol (10 mL), 2 drops of concentrated HCl (d = 1.170, 0.03 mL, 0.33 mmol) and corresponding aromatic aldehyde (1.05 mmol) were added. The resulting mixture was refluxed with stirring for 1.5 h.

[1] G. A. Gazieva, A. N. Kravchenko, *J. Heterocycl. Chem.,* 2015, **52**, 1858.

[2] G. A. Gazieva, T. B. Karpova, T. V. Nechaeva, Yu. V. Nelyubina, I.E. Zanin, and A. N. Kravchenko, *Synlett*, 2017, **28**, 858.

[3] (a) G. A. Gazieva, P. A. Poluboyarov, L. D. Popov, N. G. Kolotyrkina, A. N. Kravchenko, N. N. Makhova, *Synthesis*, 2012, **44**, 3366; (b) G. A. Gazieva, T. V. Nechaeva, N. N. Kostikova, N. V. Sigay, S. A. Serkov, and S. V. Popkov, *Russ. Chem. Bull*., 2018, **67**, 1059; (c) G. A. Gazieva, L. V. Anikina, S. A. Pukhov, T. B. Karpova, Yu. V. Nelyubina, and A. N. Kravchenko, *Mol. Diversity*, 2016, **20**, 837; (d) G. A. Gazieva, T. B. Karpova, L. D. Popov, Yu. V. Nelyubina, and A. N. Kravchenko, *J. Heterocycl. Chem*., 2015, **52**, 1390; (e) G. A. Gazieva, L. V. Anikina, T. V. Nechaeva, S. A. Pukhov, T. B. Karpova, S. V. Popkov, Yu. V. Nelyubina, N. G. Kolotyrkina, A. N. Kravchenko, *Eur. J. Med. Chem*., 2017, **140**, 141.

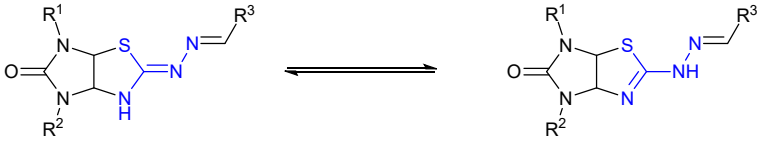
The suspension gradually dissolved. Then it was allowed to cool to room temperature. Concentrated HCl (10 mL) was added to the reaction mixture which was additionally stirred at room temperature for 2 h. The isolation of compounds **10** was carried out as indicated in Procedure A.

Characterization data of products 8k and 10a-o

All compounds gave satisfactory elemental analysis results.

(*E*)-4-(Benzylideneamino)-3-methyl-1-phenyl-5-thioxohexahydroimidazo[4,5-*d*]imidazol-2(1*H*)-one (8k). Yield 246 mg (35%) as a white powder. Mp: 199-201 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.96 (s, 3H, NCH_3), 6.11, 6.18 (AB, J = 8.4 Hz, 2H, 2CH), 7.13 (dd, J = 7.4, 7.3 Hz, 1H, Ph), 7.38 (dd, J = 7.7, 7.7 Hz, 2H, Ph), 7.48-7.51 (m, 3H, Ph), 7.60 (d, J = 8.1 Hz, 2H, Ph), 7.80 (br.s, 2H, Ph), 9.26 (s, 1H, N=CH), 10.23 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 29.93 (NCH_3), 66.60 (CH), 74.92 (CH), 119.45 (2 C), 123.62, 127.48 (2 C), 128.81 (2 C), 128.92 (2 C), 130.82, 133.75, 137.71 (Ph), 153.36 (N=CH), 155.08 (C=O), 179.36 (C=S); IR (KBr), ν 3433, 3163 (NH), 3040 (CH_{Ar}), 2971, 2956 (CH_{Alk}), 1721, 1594 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{18}H_{17}N_5NaOS$ [M + Na]$^+$: 374.1046, Found: 374.1030.

In the ^{1}H and ^{13}C NMR spectra of compounds **10**, the broadening of some signals are observed due to proton exchange between *endo*- and *exo*-cyclic nitrogen atoms.



(*Z*)-2-((*E*)-Benzylidenehydrazono)-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10a). Yield 231 mg (80%) as a white powder. Mp: 190-192 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.72 (s, 6H, $2NCH_3$), 5.45, 5.75 (AB, J = 7.0 Hz, 2H, 2CH), 7.39-7.41 (m, 3H, Ph), 7.65-7.67 (m, 2H, Ph), 8.21 (s, 1H, N=CH), 9.05 (br.s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 28.13 (NCH_3), 29.27 (NCH_3), 65.78 (CH), 72.16 (br., CH), 126.98 (2 C), 128.68 (2 C), 129.64, 134.90 (Ph), 151.38 (N=CH), 156.92 (C=O), 168.19 (N=CS); IR (KBr), ν 3187, 3153, 3131 (NH), 3061, 3023, 2997 (CH_{Ar}), 2916, 2891 (CH_{Alk}), 1710, 1688, 1617 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{13}H_{16}N_5OS$ [M + H]$^+$: 290.1070, Found: 290.1072.

(*Z*)-2-[(*E*)-(2-Fluorobenzylidene)hydrazono]-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10b). Yield 264 mg (86%) as a white powder. Mp: 185-187 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.72 (s, 6H, $2NCH_3$), 5.48, 5.77 (AB, J = 7.2 Hz, 2H, 2CH), 7.25 (m, 2H, Ar), 7.41-7.47 (m, 1H, Ar), 7.84 (t, J = 7.5 Hz, 1H, Ar), 8.33 (s, 1H, N=CH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 28.12 (NCH_3), 29.23 (NCH_3), 65.87 (CH), 72.64 (br, CH), 115.92 (d, J = 20.8 Hz), 122.30 (d, J = 10.1 Hz), 124.71 (d, J = 3.2 Hz), 126.57 (d, J = 2.6 Hz), 131.48 (d, J = 8.4 Hz) (all Ar), 143.70 (N=CH), 156.80 (C=O), 160.46 (d, J = 250.1 Hz, Ar), 169.08 (N=CS); ^{19}F NMR (282 MHz, DMSO-d_6): δ -121.52; IR (KBr), ν 3276 (NH), 3063, 2992

(CH_{Ar}), 2946, 2880 (CH_{Alk}), 1704, 1682, 1630 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{13}H_{15}FN_5OS$ [*M* + H]$^+$: 308.0976, Found: 308.0973.

(*Z*)-2-[((*E*)-4-Fluorobenzylidene)hydrazono]-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10c). Yield 209 mg (68%) as a white powder. Mp: 198-200 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.72 (s, 6H, $2NCH_3$), 5.45, 5.75 (AB, *J* = 7.0 Hz, 2H, 2CH), 7.22-7.28 (m, 2H, Ar), 7.70-7.74 (m, 2H, Ar), 8.22 (s, 1H, N=CH), 9.05 (br.s, 1H, NH); ^{13}C NMR (125.76 MHz, DMSO-d_6): δ 28.12 (NCH_3), 29.25 (NCH_3), 65.78 (CH), 72.52 (br, CH), 115.71 (d, *J* = 21.7 Hz, 2 C), 129.01 (d, *J* = 8.0 Hz, 2 C), 131.56 (all Ar), 150.05 (N=CH), 156.91 (C=O), 162.88 (d, *J* = 247.2 Hz, Ar), 168.21 (N=CS); ^{19}F NMR (282 MHz, DMSO-d_6): δ -111.54; IR (KBr), ν 3480 (NH), 3098 (CH_{Ar}), 2997, 2898 (CH_{Alk}), 1723, 1636, 1604 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{13}H_{15}N_5FOS$ [*M* + H]$^+$: 308.0976, Found: 308.0976.

(*Z*)-2-[((*E*)-4-Methoxybenzylidene)hydrazono]-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10d). Yield 192 mg (60%) as a light beige powder. Mp: 183-185 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.72 (s, 6H, $2NCH_3$), 3.78 (s, 3H, OCH_3), 5.43, 5.73 (AB, *J* = 7.1 Hz, 2H, 2CH), 6.97 (d, *J* = 8.3 Hz, 2H, Ar), 7.61 (d, *J* = 8.2 Hz, 2H, Ar), 8.16 (s, 1H, N=CH), 8.90 (br.s, 1H, NH); ^{13}C NMR (125.76 MHz, DMSO- d_6): δ 28.14 (NCH_3), 29.32 (NCH_3), 55.30 (OCH_3), 65.81 (CH), 72.20 (br, CH), 114.23 (2 C), 127.58, 128.60 (2 C) (all Ar), 151.31 (br, N=CH), 157.00 (C=O), 160.60 (Ar), 167.11 (N=CS); IR (KBr), ν 3184, 3156, 3137 (NH), 3074, 3009 (CH_{Ar}), 2958, 2933, 2908, 2836 (CH_{Alk}), 1710, 1689, 1615 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{14}H_{18}N_5O_2S$ [*M* + H]$^+$: 320.1176, Found: 320.1169.

(*Z*)-4,6-Dimethyl-2-[(*E*)-(thiophen-2-ylmethylidene)hydrazono]tetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10e). Yield 224 mg (76%) as a white powder. Mp: 175-177 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.72 (s, 6H, $2NCH_3$), 5.44, 5.74 (AB, *J* = 7.2 Hz, 2H, 2CH), 7.10 (br.s, 1H, Th), 7.36 (br.s, 1H, Th), 7.56 (br.s, 1H, Th), 8.37 (s, 1H, N=CH), 9.00 (br.s, 1H, NH); ^{13}C NMR (150.9 MHz, DMSO-d_6): δ 28.23 (NCH_3), 29.41 (NCH_3), 65.98 (CH), 72.42 (CH), 127.92, 128.34, 130.27, 139.82 (Th), 146.34 (N=CH), 157.13 (C=O), 167.60 (N=CS); IR (KBr), ν 3231, 3196 (NH), 3187, 3125, 3100 (CH_{Ar}), 2938, 2876 (CH_{Alk}), 1711, 1688, 1609 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{11}H_{14}N_5OS_2$ [*M* + H]$^+$: 296.0634, Found: 296.0642.

(*Z*)-2-[((*E*)-Benzylidene)hydrazono]-4,6-diethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10f). Yield 216 mg (68%) as a white powder. Mp: 150-152 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.02-1.11 (m, 6H, $2CH_3$), 2.93-3.00 (m, 1H, NCH_2), 3.09-3.15 (m, 1H, NCH_2), 3.26-3.45 (m, 2H, NCH_2), 5.58, 5.84 (AB, *J* = 7.2 Hz, 2H, 2CH), 7.39-7.44 (m, 3H, Ph), 7.64-7.67 (m, 2H, Ph), 8.21 (s, 1H, N=CH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.77 (CH_3), 12.91 (CH_3), 35.46 (NCH_2), 37.15 (NCH_2), 64.08 (CH), 70.42 (br, CH), 127.04 (2 C), 128.75 (2 C), 129.71, 134.94 (Ph), 151.41 (N=CH), 156.24 (C=O), 168.25 (N=CS); IR (KBr), ν 3190, 3127 (NH), 3090, 2974 (CH_{Ar}), 2933, 2898, 2875, 2838 (CH_{Alk}), 1687, 1627, 1607 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{15}H_{19}N_5OS$ [*M* + H]$^+$: 318.1383, Found: 318.1387.

(*Z*)-4,6-Diethyl-2-[(*E*)-(2-fluorobenzylidene)hydrazono]tetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10g). Yield 225 mg (67%) as a white powder. Mp: 167-169 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.03-1.11 (m, 6H, 2CH_3), 2.94-3.03 (m, 1H, NCH_2), 3.09-3.18 (m, 1H, NCH_2), 3.24-3.47 (m, 2H, NCH_2), 5.61, 5.86 (AB, J = 7.2 Hz, 2H, 2CH), 7.22-7.28 (m, 2H, Ar), 7.41-7.45 (m, 1H, Ar), 7.84 (t, J = 7.4 Hz, 1H, Ar), 8.32 (s, 1H, N=CH), 9.16 (br.s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.74 (CH_3), 12.86 (CH_3), 35.46 (NCH_2), 37.11 (NCH_2), 64.14 (CH), 70.47 (br, CH), 115.97 (d, J = 20.5 Hz), 122.35 (d, J = 9.9 Hz), 124.77, 126.59, 131.51 (d, J = 8.1 Hz) (all Ar), 143.73 (br, N=CH), 156.15 (C=O), 160.49 (d, J = 250.0 Hz, Ar), 169.24 (N=CS); ^{19}F NMR (282 MHz, DMSO-d_6): δ -121.61; IR (KBr), ν 3183 (NH), 3084 (CH_{Ar}), 2976, 2932, 2874 (CH_{Alk}), 1727, 1692, 1625 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{15}H_{18}N_5FOS$ [M + H]$^+$: 336.1289, Found: 336.1288.

(*Z*)-4,6-Diethyl-2-[(*E*)-(4-fluorobenzylidene)hydrazono]tetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10h). Yield 188 mg (56%) as a white powder. Mp: 198-200 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.02-1.10 (m, 6H, 2CH_3), 2.91-3.02 (m, 1H, NCH_2), 3.04-3.15 (m, 1H, NCH_2), 3.23-3.45 (m, 2H, NCH_2), 5.57, 5.84 (AB, J = 7.1 Hz, 2H, 2CH), 7.22-7.30 (m, 2H, Ar), 7.68-7.73 (m, 2H, Ar), 8.22 (s, 1H, N=CH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.78 12.91 (CH_3), 35.45 (NCH_2), 37.16 (NCH_2), 64.09 (CH), 70.44 (br, CH), 115.80 (d, J = 22.0 Hz), 129.11 (d, J = 8.2 Hz), 131.58 (Ar), 150.22 (N=CH), 156.25 (C=O), 162.96 (d, J = 245.9 Hz, Ar), 168.23 (N=CS); ^{19}F NMR (282 MHz, DMSO-d_6): δ -111.95; IR (KBr), ν 3232 (NH), 3073 (CH_{Ar}), 2978, 2933, 2874 (CH_{Alk}), 1682, 1623, 1599 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{15}H_{18}N_5OSF$ [M + H]$^+$: 336.1289, Found: 336.1298.

(*Z*)-4,6-Diethyl-2-[(*E*)-(4-methoxybenzylidene)hydrazono]tetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10i). Yield 174 mg (50%) as a light beige powder. Mp: 108-110 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.02-1.11 (m, 6H, 2CH_3), 2.93-3.03 (m, 1H, NCH_2), 3.08-3.18 (m, 1H, NCH_2), 3.26-3.49 (m, 2H, NCH_2), 3.78 (s, 3H, OCH_3), 5.56, 5.82 (AB, J = 7.2 Hz, 2H, 2CH), 6.98 (d, J = 8.6 Hz, 2H, Ar), 7.61 (d, J = 8.5 Hz, 2H, Ar), 8.16 (s, 1H, N=CH), 8.80 (br.s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.70 (CH_3), 12.84 (CH_3), 35.34 (NCH_2), 37.07 (NCH_2), 55.23 (OCH_3), 64.00 (CH), 70.51 (br, CH), 114.16, 127.47, 128.54 (Ar), 151.10 (N=CH), 156.13 (C=O), 160.55 (Ar), 167.14 (N=CS); IR (KBr), ν 3175 (NH), 3088, 2974 (CH_{Ar}), 2933, 2898, 2838 (CH_{Alk}), 1687, 1627, 1606 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{16}H_{22}N_5FO_2S$ [M + H]$^+$: 348.1489, Found: 348.1489.

(*Z*)-4,6-Diethyl-2-[(*E*)-(thiophen-2-ylmethylidene)hydrazono]tetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10j). Yield 272 mg (84%) as a beige powder. Mp: 144-146 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.02-1.10 (m, 6H, 2CH_3), 2.92-3.01 (m, 1H, NCH_2), 3.07-3.16 (m, 1H, NCH_2), 3.25-3.45 (m, 2H, NCH_2), 5.56, 5.83 (AB, J = 6.7 Hz, 2H, 2CH), 7.08-7.11 (m, 1H, Th), 7.35 (br.s, 1H, Th), 7.56 (d, J = 4.5 Hz, 1H, Th), 8.37 (s, 1H, N=CH), 8.90 (br.s, 1H, NH); ^{13}C NMR (150.9 MHz, DMSO-d_6): δ 12.67, 12.80 (CH_3), 35.33 (NCH_2), 37.04 (NCH_2), 64.06 (CH), 69.97 (br, CH), 127.69, 128.13, 129.97, 139.71 (Th), 146.17 (br, N=CH), 156.09 (C=O), 167.41 (br, N=CS); IR (KBr), ν 3196 (NH), 3101, 2975 (CH_{Ar}), 2930, 2871

(CH_{Alk}), 1687, 1611, 1565 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{13}H_{17}N_5OS_2$ [*M* + H]$^+$: 324.0947, Found: 324.0940.

(*Z*)-2-((*E*)-Benzylidenehydrazono)-6-methyl-4-phenyltetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10k). Yield 228 mg (65%) as a white powder. Mp: 113-115 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.84 (s, 3H, NCH_3), 5.91, 6.34 (AB, *J* = 7.2 Hz, 2H, 2CH), 7.13 (dd, *J* = 7.3, 7.4 Hz, 1H, Ph), 7.34-7.43 (m, 5H, Ph), 7.54 (d, *J* = 8.4 Hz, 2H, Ph), 7.64-7.68 (m, 2H, Ph), 8.16 (s, 1H, N=CH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 29.38 (NCH_3), 65.93 (CH), 73.13 (br, CH), 120.54 (2 C), 123.66, 126.96 (2 C), 127.27, 128.67 (4 C), 129.74, 134.63, 137.88 (Ph), 150.41 (br, N=CH), 154.51 (C=O), 166.91 (br, N=CS); IR (KBr), ν 3213 (NH), 3061 (CH_{Ar}), 2915 (CH_{Alk}), 1714, 1625, 1585 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{18}H_{17}N_5OS$ [*M* + H]$^+$: 352.1227, Found: 352.1221.

(*Z*)-4,6-Dimethyl-2-[(*E*)-((*E*)-3-phenylallylidene)hydrazono]tetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10l). Yield 173 mg (55%) as a beige powder. Mp: 174-176 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.72 (s, 6H, $2CH_3$), 5.44, 5.74 (AB, *J* = 6.8 Hz, 2H, 2CH), 6.96-7.03 (m, 2H, =CH, Ph), 7.29-7.39 (m, 3H, =CH, Ph), 7.57 (m, 2H, Ph), 8.02 (d, *J* = 7.2 Hz, 1H, N=CH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 28.12 (NCH_3), 29.21 (NCH_3), 65.86 (CH), 72.57 (br, CH), 125.80, 126.92 (2 C), 128.59, 128.78 (2 C) (Ph, =CH), 136.06, 138.54 (Ph-1, =CH), 153.97 (br, N=CH), 156.87 (C=O), 167.16 (N=CS); IR (KBr), ν 3234 (NH), 3081, 3030, 2997 (CH_{Ar}), 2931, 2876 (CH_{Alk}), 1704, 1686, 1628, 1601 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{15}H_{17}N_5OS$ [*M* + H]$^+$: 316.1227, Found: 316.1230.

(*Z*)-2-{(*E*)-[(*E*)-3-(2-Methoxyphenyl)allylidene]hydrazono}-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10m). Yield 183 mg (53%) as a yellow powder. Mp: 133-135 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.71 (s, 6H, $2CH_3$), 3.84 (s, 3H, OCH_3), 5.43, 5.74 (AB, *J* = 6.8 Hz, 2H, 2CH), 6.92-7.05 (m, 3H, =CH, Ar), 7.18 (d, *J* = 16.1 Hz, 1H, =CH), 7.30 (t, *J* = 7.1 Hz, 1H, Ar), 7.62 (d, *J* = 7.1 Hz, 1H, Ar), 8.02 (d, *J* = 9.5 Hz, 1H, N=CH), 8.92 (br.s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 28.17 (NCH_3), 29.30 (NCH_3), 55.58 (OCH_3), 65.94 (CH), 72.59 (br, CH), 111.58, 120.80, 124.46, 126.39, 127.29, 130.11, 133.44 (Ar, 2=CH), 154.81 (br, N=CH), 156.83, 157.01 (Ar, C=O), 167.05 (N=CS); IR (KBr), ν 3232 (NH), 3074, 3041, 2998 (CH_{Ar}), 2932, 2836 (CH_{Alk}), 1710, 1622, 1601 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{16}H_{19}N_5O_2S$ [*M* + H]$^+$: 346.1332, Found: 346.1328.

(*Z*)-4,6-Diethyl-2-{(*E*)-[(*E*)-3-(2-methoxyphenyl)allylidene]hydrazono}tetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10n). Yield 299 mg (80%) as a yellow powder. Mp: 138-140 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.03-1.10 (m, 6H, $2CH_3$), 2.92-3.04 (m, 1H, NCH_2), 3.08-3.17 (m, 1H, NCH_2), 3.23-3.45 (m, 2H, NCH_2), 3.84 (s, 3H, OCH_3), 5.56, 5.82 (AB, *J* = 7.0 Hz, 2H, 2CH), 6.92-7.05 (m, 3H, =CH, Ar), 7.18 (d, *J* = 16.1 Hz, 1H, =CH), 7.30 (t, *J* = 7.6 Hz, 1H, Ar), 7.62 (d, *J* = 7.4 Hz, 1H, Ar), 8.02 (d, *J* = 9.5 Hz, 1H, N=CH), 8.91 (br.s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 12.75 (CH_3), 12.92 (CH_3), 35.46 (NCH_2), 37.16 (NCH_2), 55.58 (OCH_3), 64.25 (CH), 70.51 (br, CH), 111.58, 120.79, 124.44, 126.34, 127.30, 130.14, 133.47 (Ar, 2 =CH), 154.76 (br, N=CH), 156.22, 156.83 (Ar, C=O), 167.23 (N=CS); IR

(KBr), ν 3180, 3120 (NH), 3073, 2974 (CH_{Ar}), 2932, 2875, 2838 (CH_{Alk}), 1721, 1626, 1560 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{18}H_{23}N_5O_2S$ [*M* + H]$^+$: 374.1645, Found: 374.1640.

(Z)-2-{(E)-[(E)-3-(2-methoxyphenyl)allylidene]hydrazono}-6-methyl-4-phenyltetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-one (10o). Yield 245 mg (60%) as a yellow powder. Mp: 192-194 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.83 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 5.89, 6.32 (AB, *J* = 7.2 Hz, 2H, 2CH), 6.95-7.18 (m, 5H, Ar, Ph, 2 =CH), 7.30-7.39 (m, 3H, Ar, Ph), 7.53-7.61 (m, 3H, Ar, Ph), 7.98 (d, *J* = 9.2 Hz, 1H, N=CH), 9.02 (br.s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 29.30, 55.50, 66.00, 71.32 (br), 111.50, 120.38, 120.69 (2 C), 123.53, 124.36, 126.08, 127.23, 128.61 (2 C), 130.02, 133.38, 137.96, 153.90 (br), 154.48, 156.76, 165.94 (br); IR (KBr), ν 3154 (NH), 3042 (CH_{Ar}), 2940, 2837 (CH_{Alk}), 1720, 1620, 1599 (C=O, C=N); HRMS (ESI): Exact mass calcd for $C_{21}H_{21}N_5O_2S$ [*M* + H]$^+$: 408.1489, Found: 408.1481.

X-ray Crystallography: Single crystals of **10a** and **10d** were grown from MeOH (Fig. S1). Data collection for samples **10a** and **10d** were performed on a Bruker D8 Quest diffractometer equipped with a Photon-III area-detector and a graphite monochromator for MoKα radiation (λ = 0.71073 Å, phi and omega scans). Frames were integrated using the Bruker SAINT software package[4] by a narrow-frame algorithm. A semiempirical absorption correction was applied with the SADABS[5] program using the intensity data of equivalent reflections. The structures were solved with a dual-space method with SHELXT program[6] and refined by the full-matrix least-squares technique against F^2_{hkl} in anisotropic approximation for non-hydrogen atoms with SHELXL[7] program. Hydrogen atoms connected to nitrogen atoms were found from difference Fourier synthesis and refined isotropically. Other H atoms were placed in calculated positions and refined in the riding model with $U_{iso}(H) = 1.5U_{eq}(C_m)$ for methyl groups and $1.2U_{eq}(C_i)$ for other carbon atoms to which corresponding H atoms are bonded.

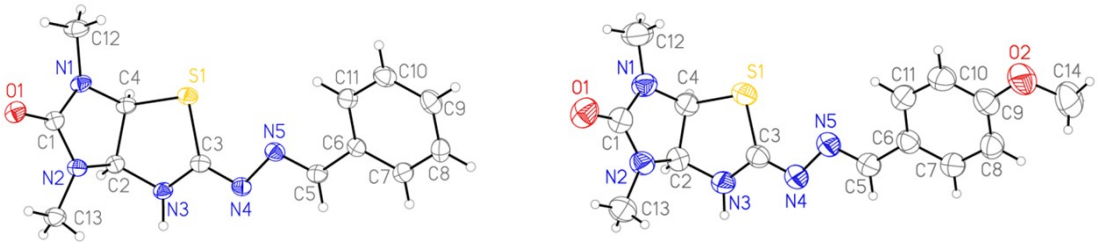


Fig. S1. General view of crystal structures of **10a** and **10d** in thermal ellipsoid representation for non-hydrogen atoms (p=50%).

[4] Bruker, SAINT v8.40B, 2019.

[5] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.,* 2015, **48**, 3–10. DOI: 10.1107/S1600576714022985.

[6] G. M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.,* 2015, **A71**, 3-8. DOI: 10.1107/S2053273314026370.

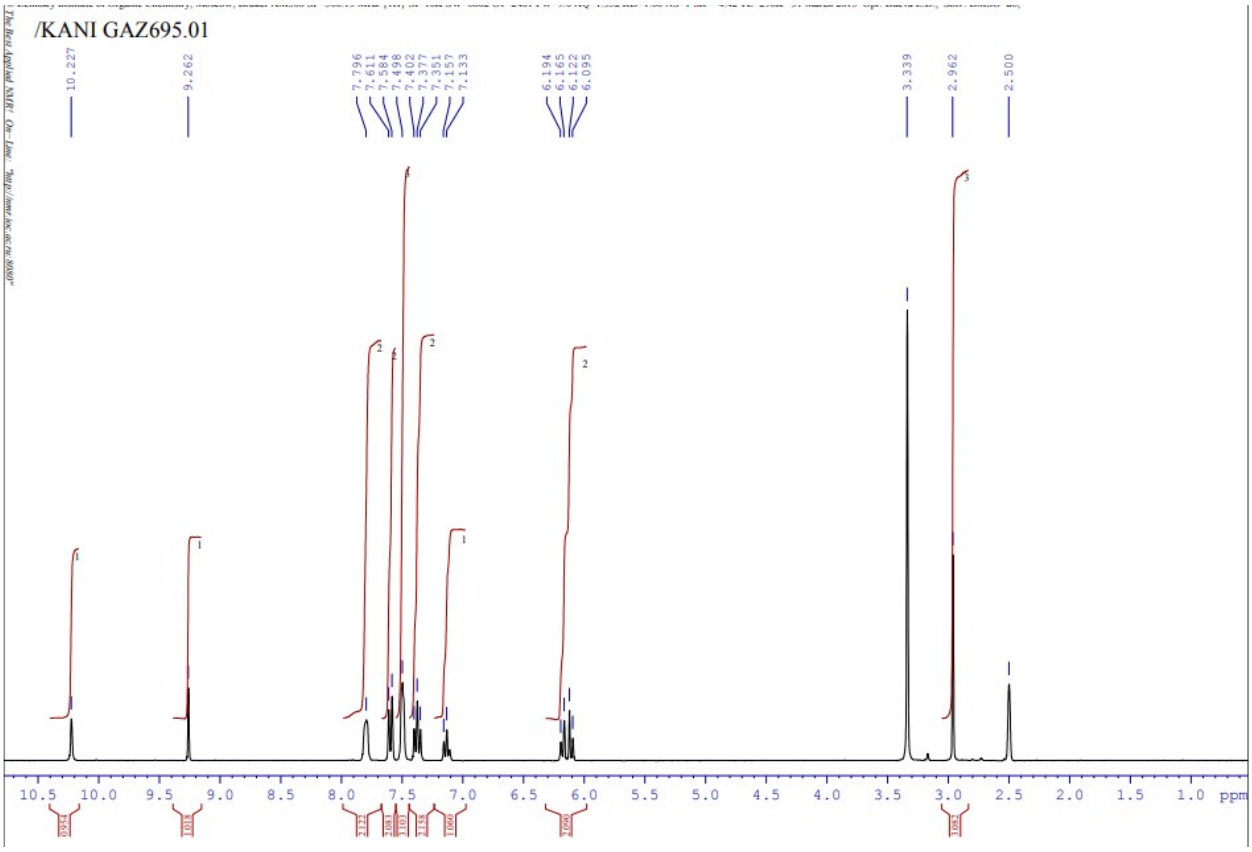
[7] G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Cryst.,* 2015, **C71**, 3-8. DOI: 10.1107/S2053229614024218.

Detailed crystallographic information is given in Table S1. CCDC 2095496-2095497 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

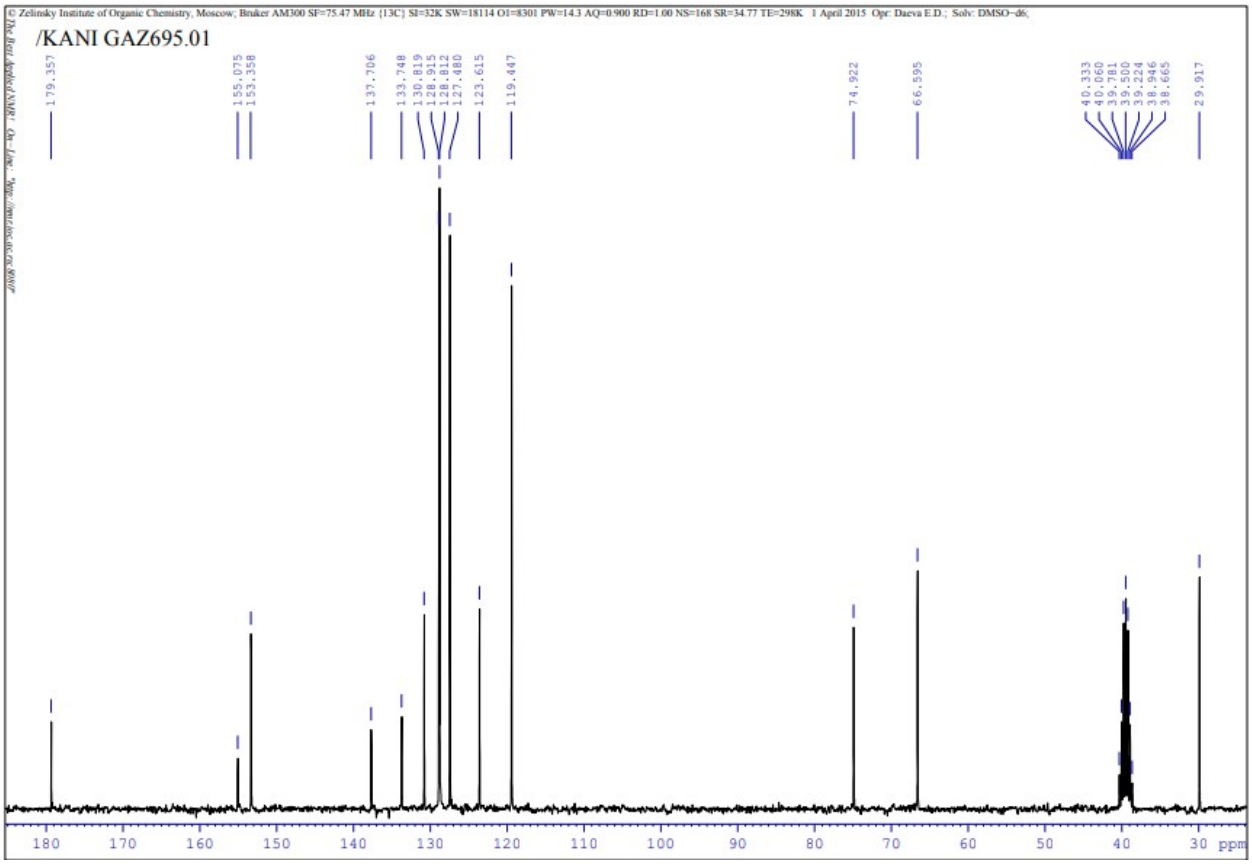
Table S1. Crystal data and structure refinement for **10a** and **10d**.

	10a	**10d**
CCDC number	2095497	2095496
Empirical formula	$C_{13}H_{15}N_5OS$	$C_{14}H_{17}N_5O_2S$
Formula weight	289.36	319.38
T, K	100	296
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	$P2_1/c$
Z / Z'	8 / 1	4 / 1
a, Å	9.7481(5)	16.2034(5)
b, Å	9.6628(4)	9.9224(3)
c, Å	30.3545(14)	10.1872(3)
β, °		102.899(2)
V, Å^3	2859.2(2)	1596.53(8)
d_{calc},g cm^{-3}	1.344	1.329
μ, cm^{-1}	2.3	2.17
$2\theta_{max}$, °	53	60
Refls collected	41443	22399
Independent refls [R_{int}]	2955 [0.0982]	4640 [0.0311]
Observed reflections [$I > 2\sigma(I)$]	2120	3533
Parameters	187	206
*R*1	0.0418	0.0417
w*R*2	0.1106	0.1167
GOF	1.040	1.035
Residual density, $\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e A^{-3})	0.222/-0.401	0.237/-0.194

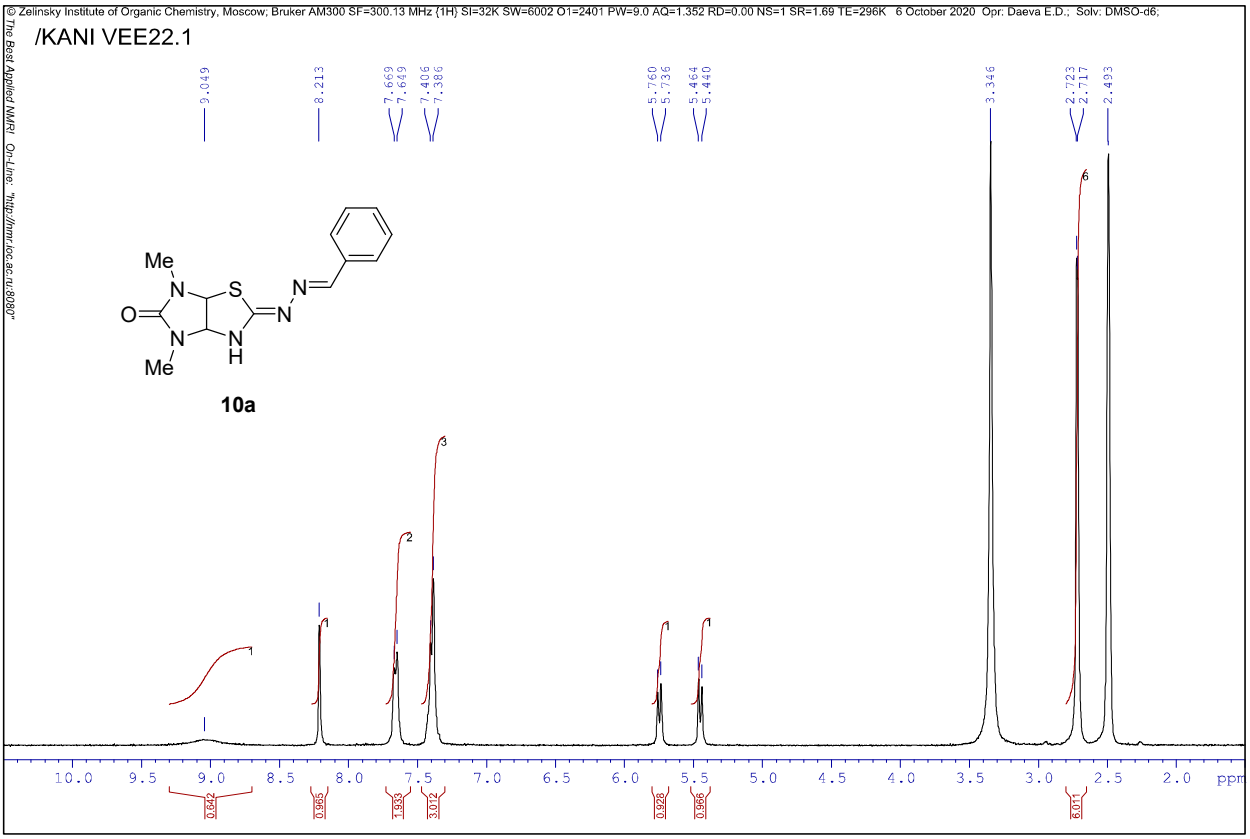
^{1}H NMR spectrum of **8k**

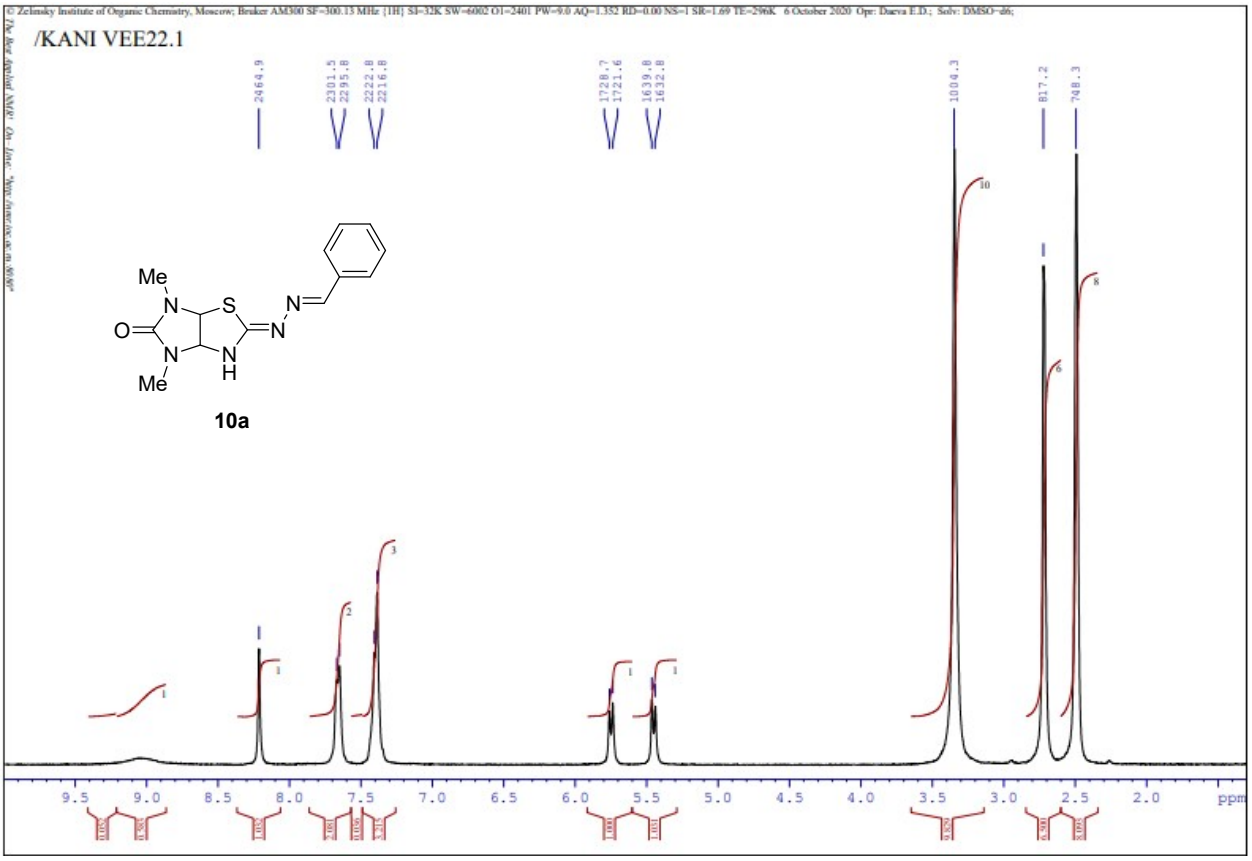


^{13}C NMR spectrum of **8k**

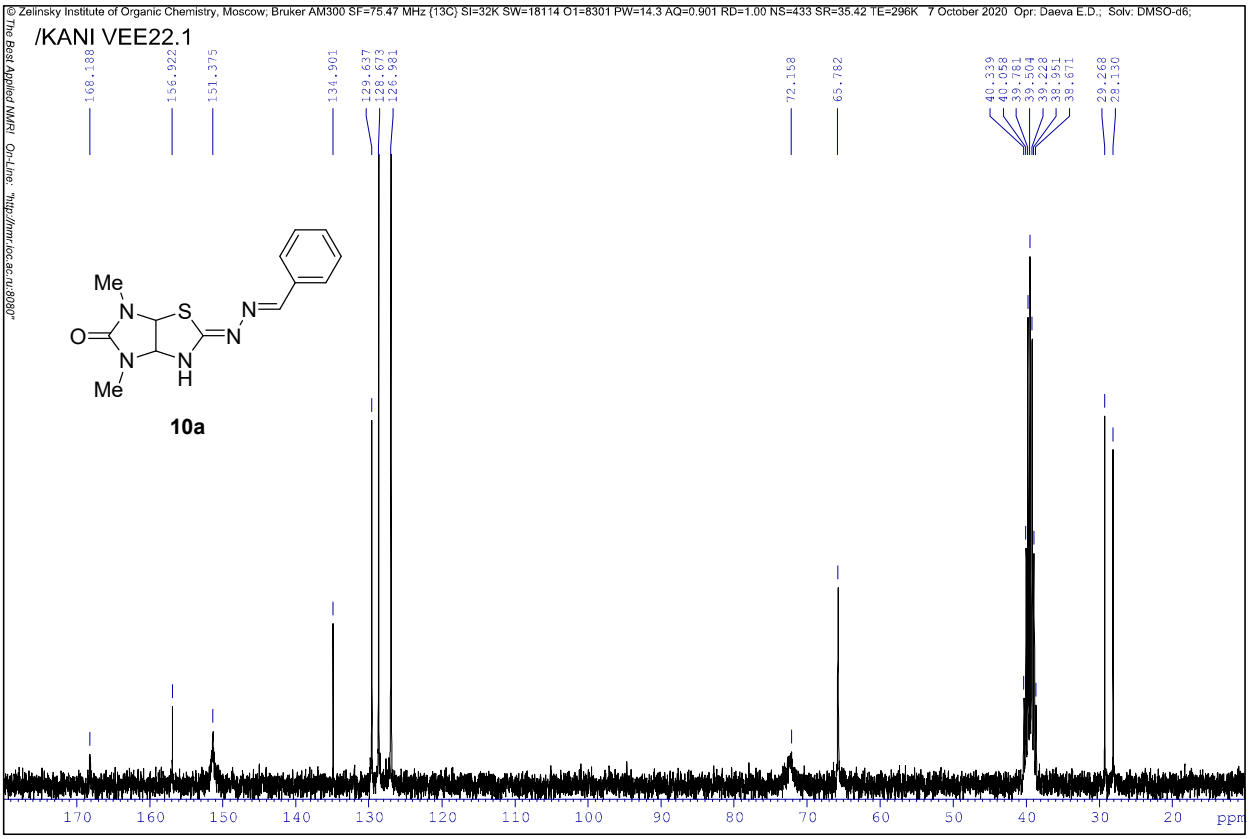


^{1}H NMR spectra of **10a** (in ppm and in Hz)

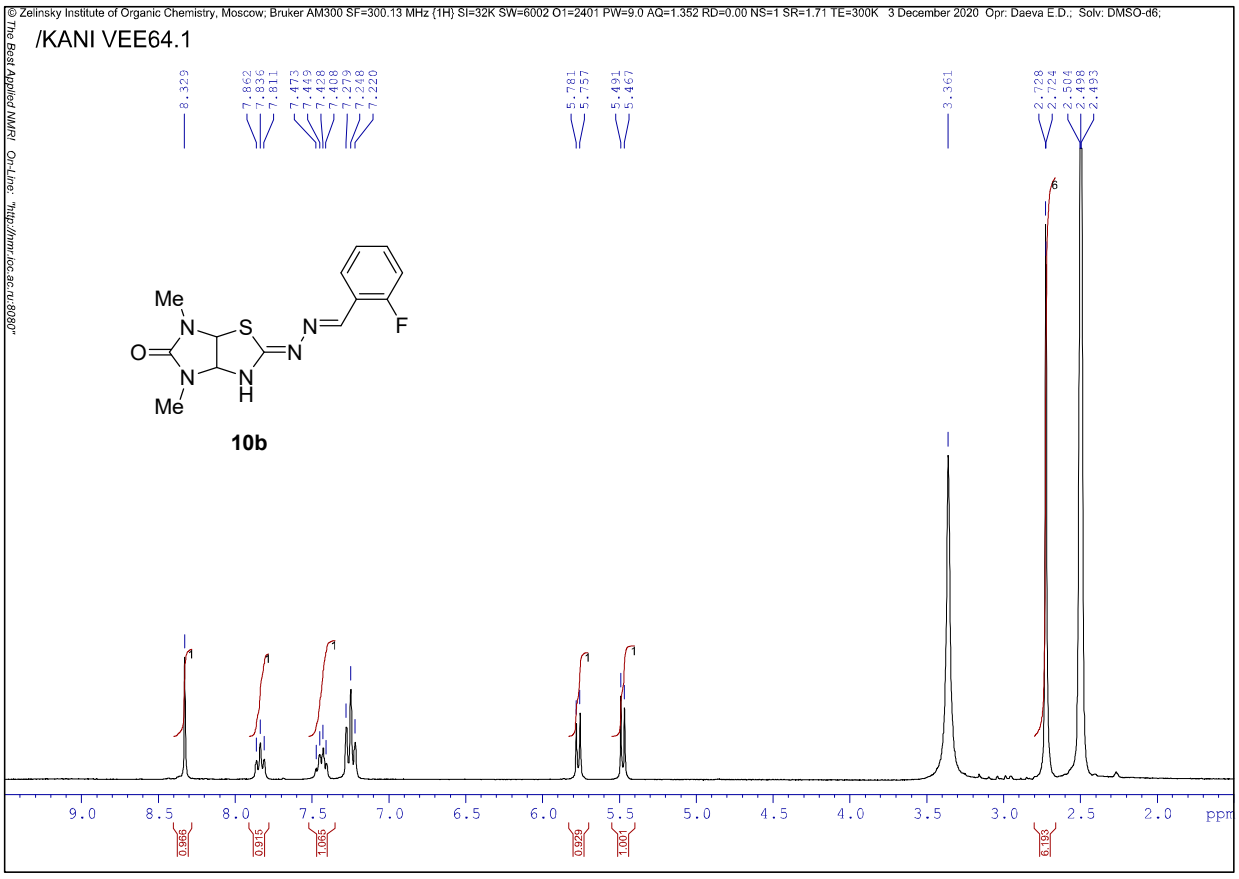


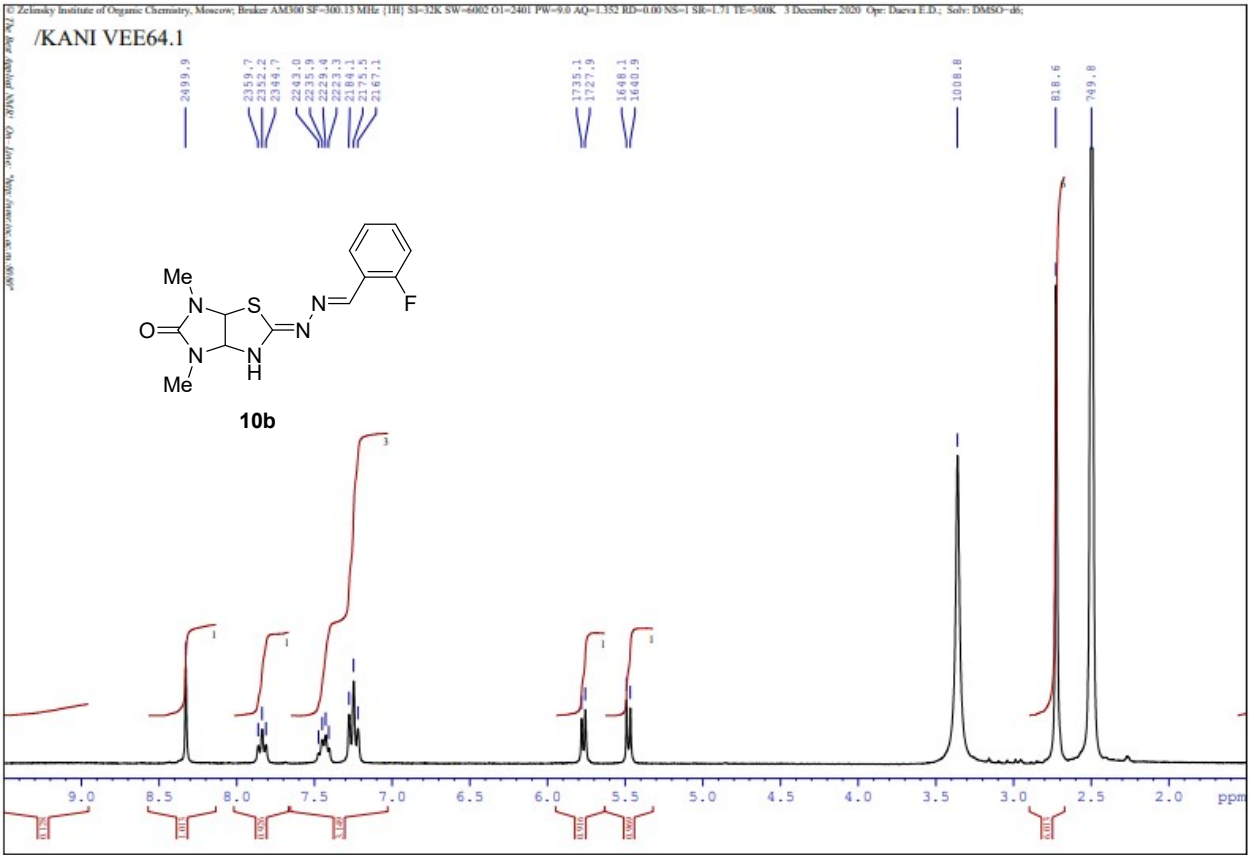


^{13}C NMR spectrum of **10a**

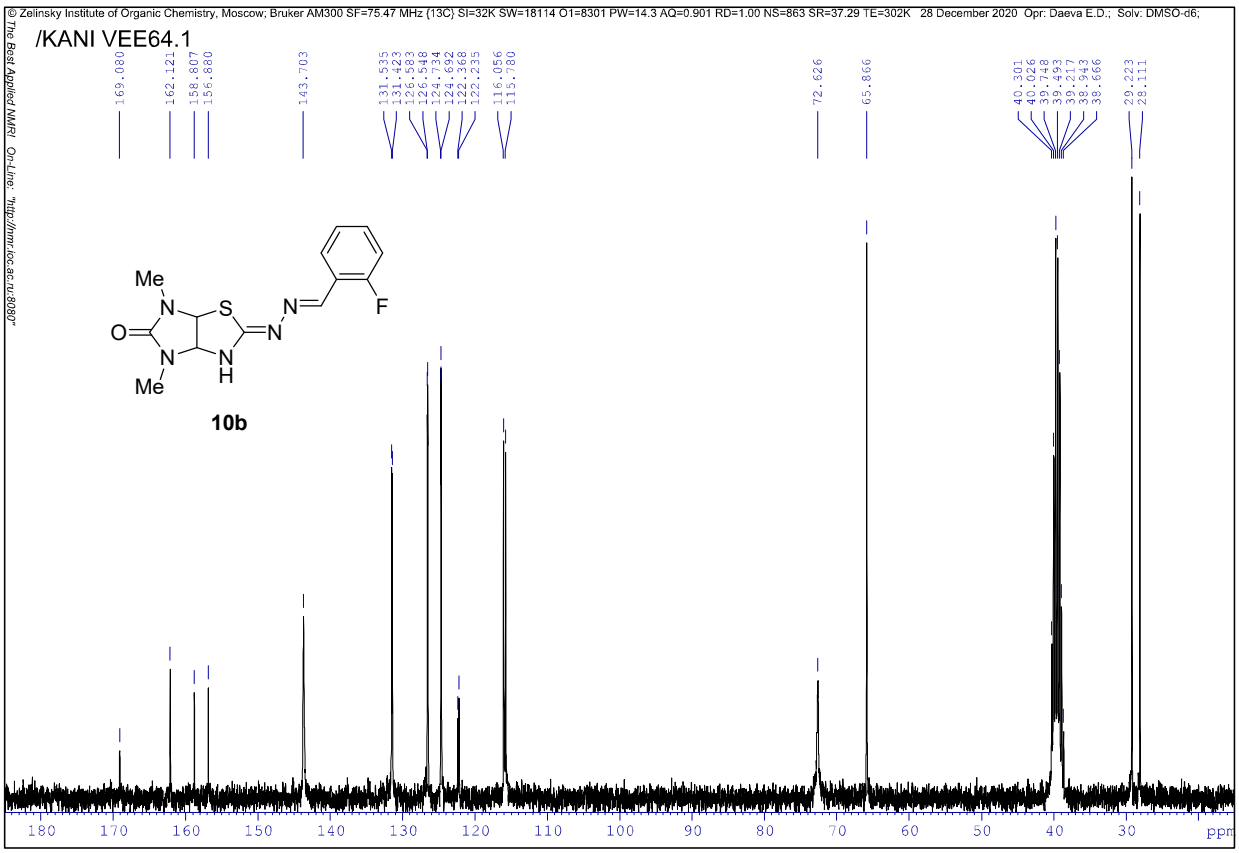


^{1}H NMR spectra of **10b** (in ppm and in Hz)

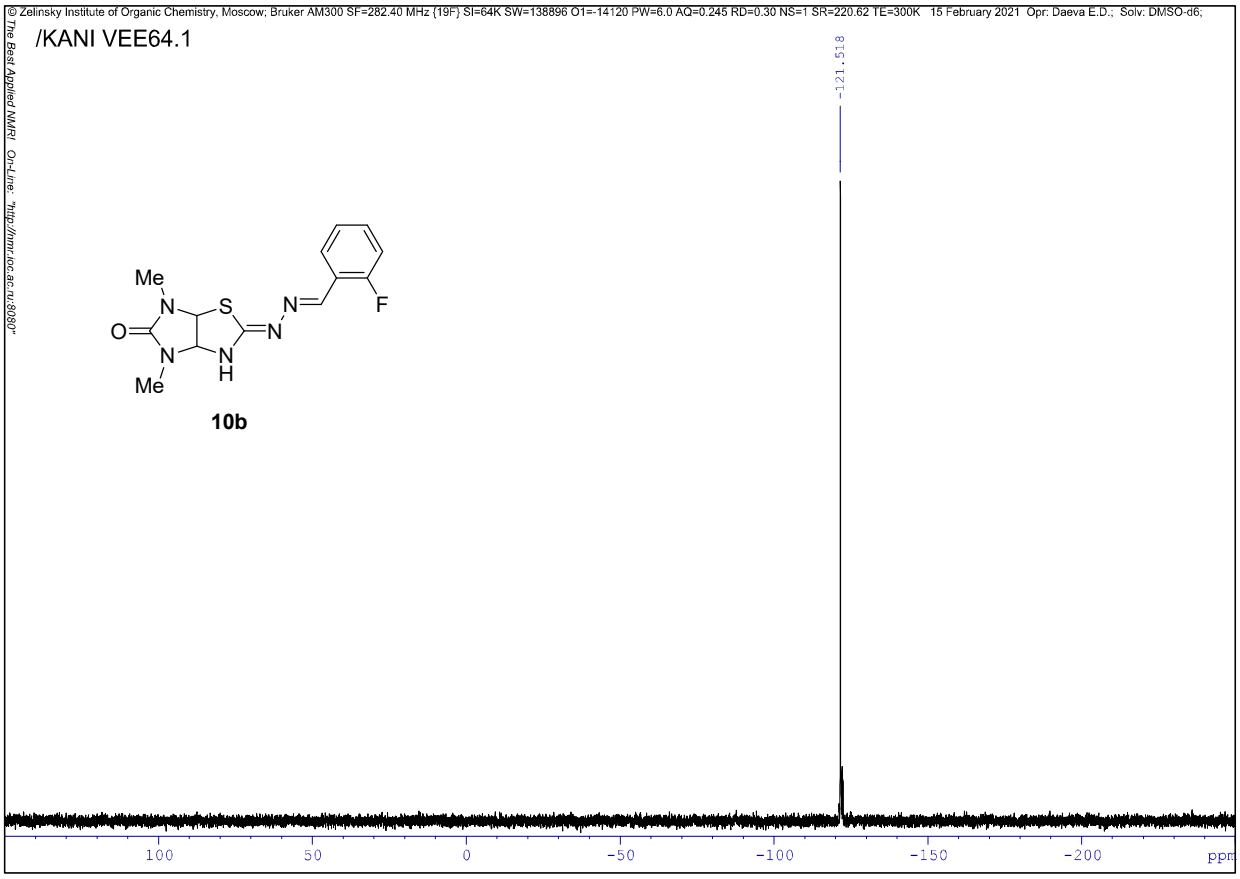




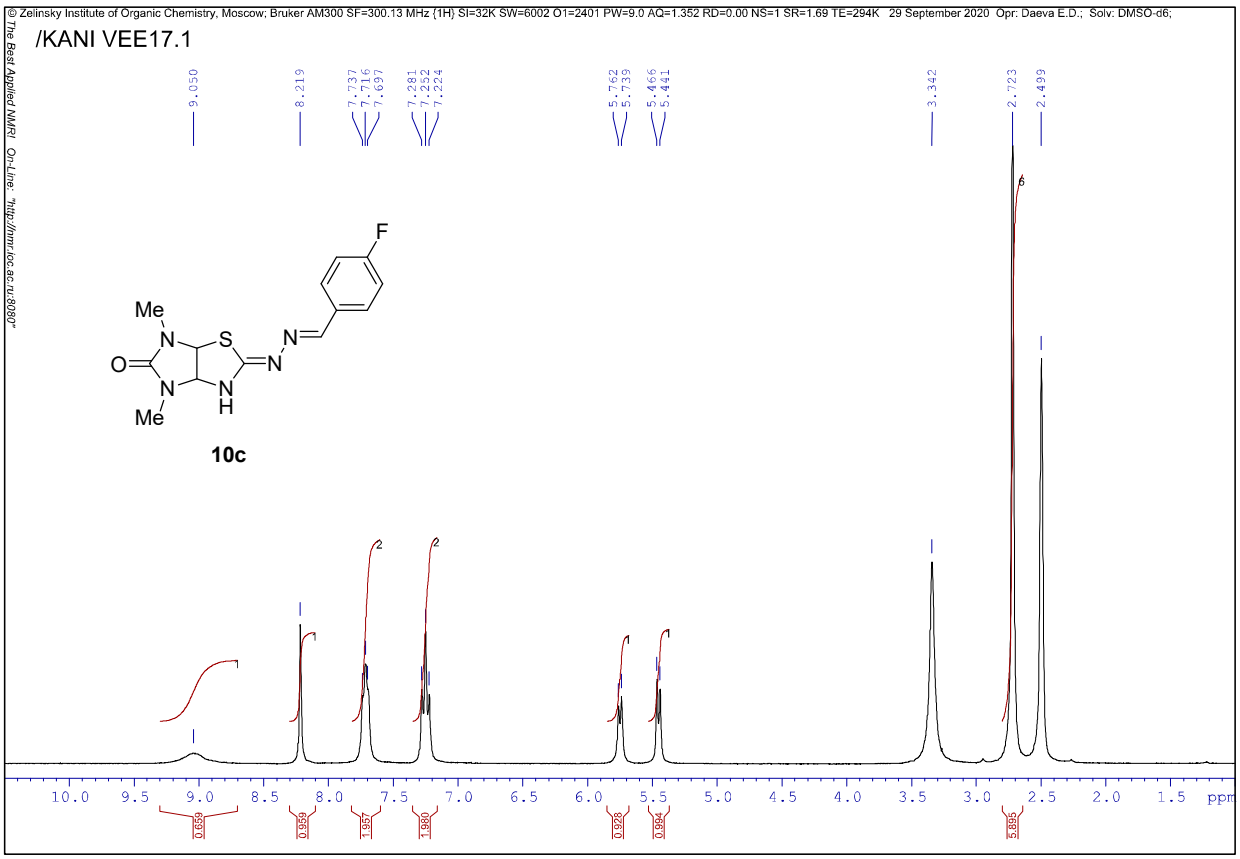
^{13}C NMR spectrum of **10b**



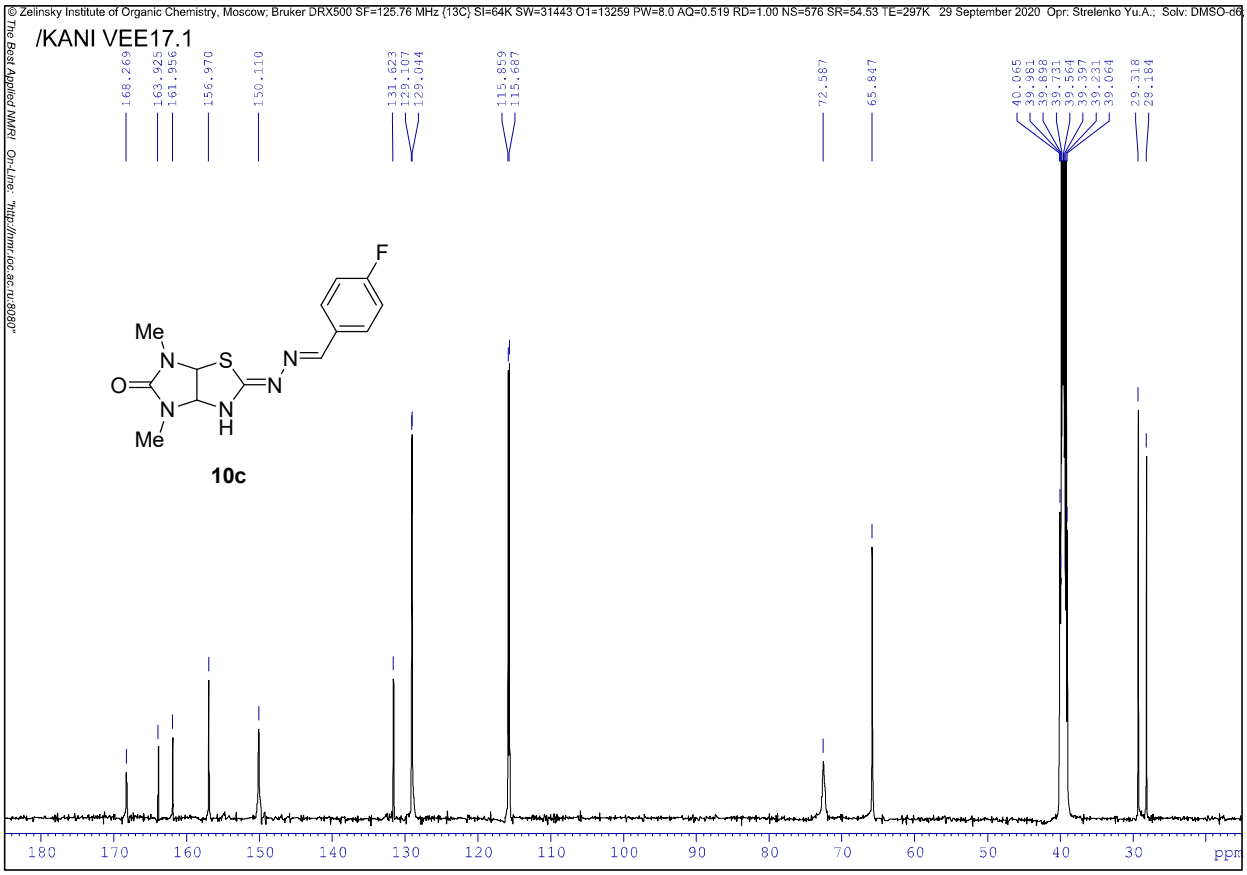
^{19}F NMR spectrum of **10b**



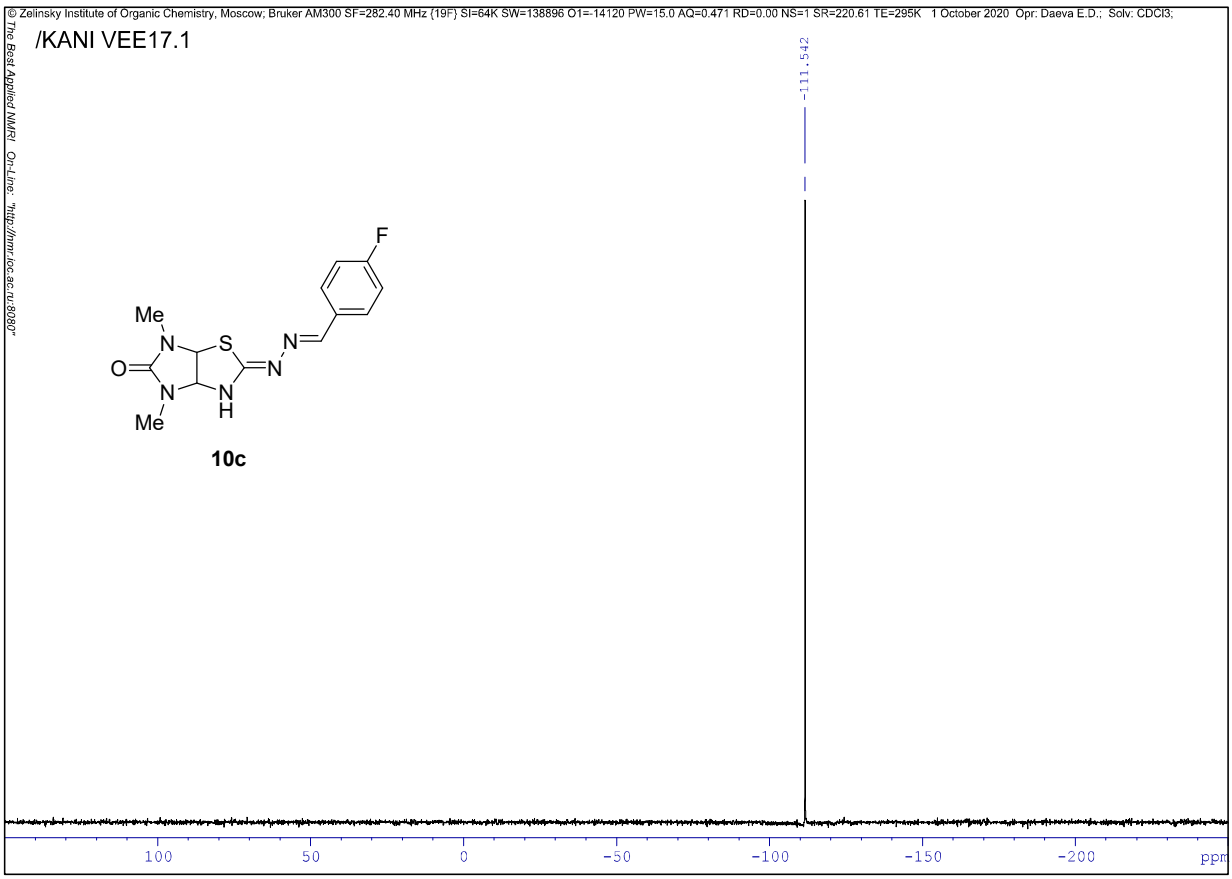
^{1}H NMR spectrum of **10c**



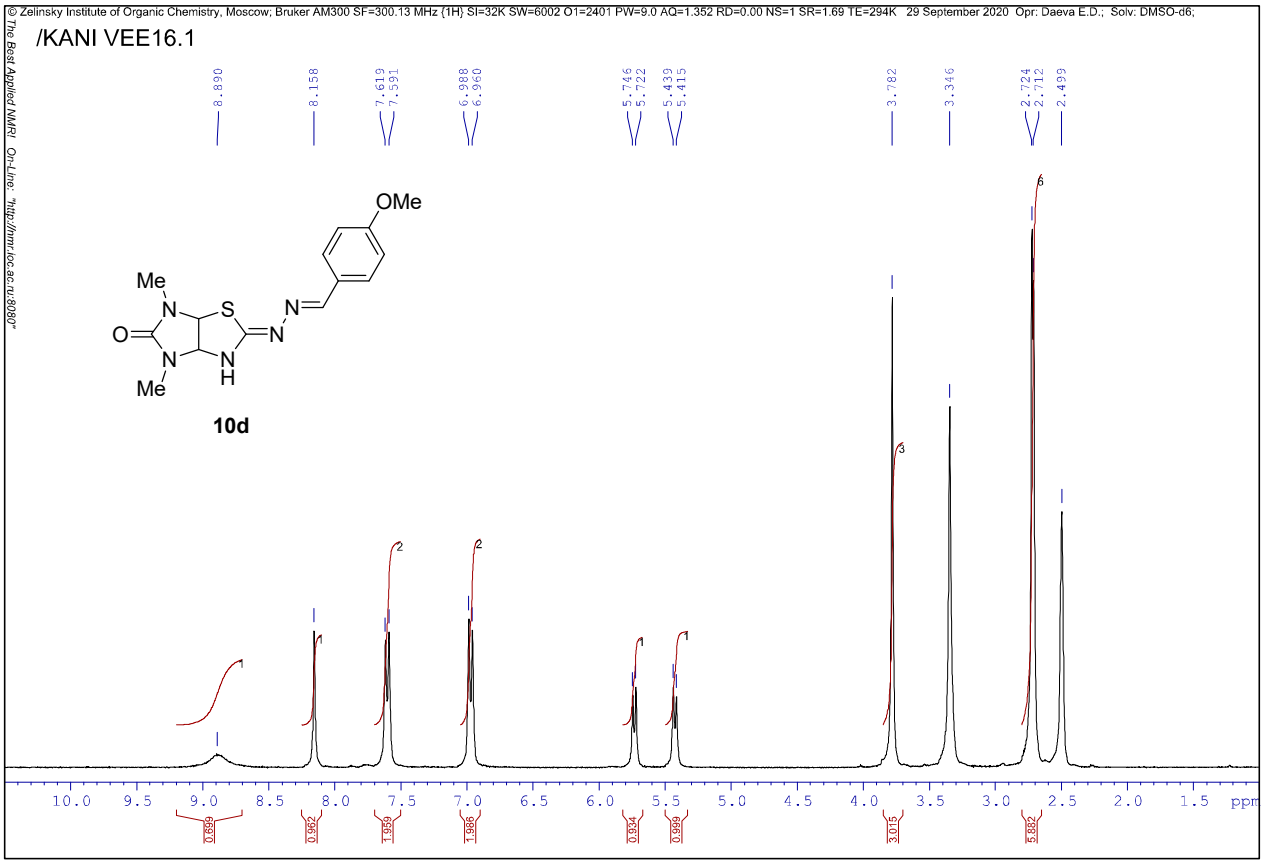
^{13}C NMR spectrum of **10c**

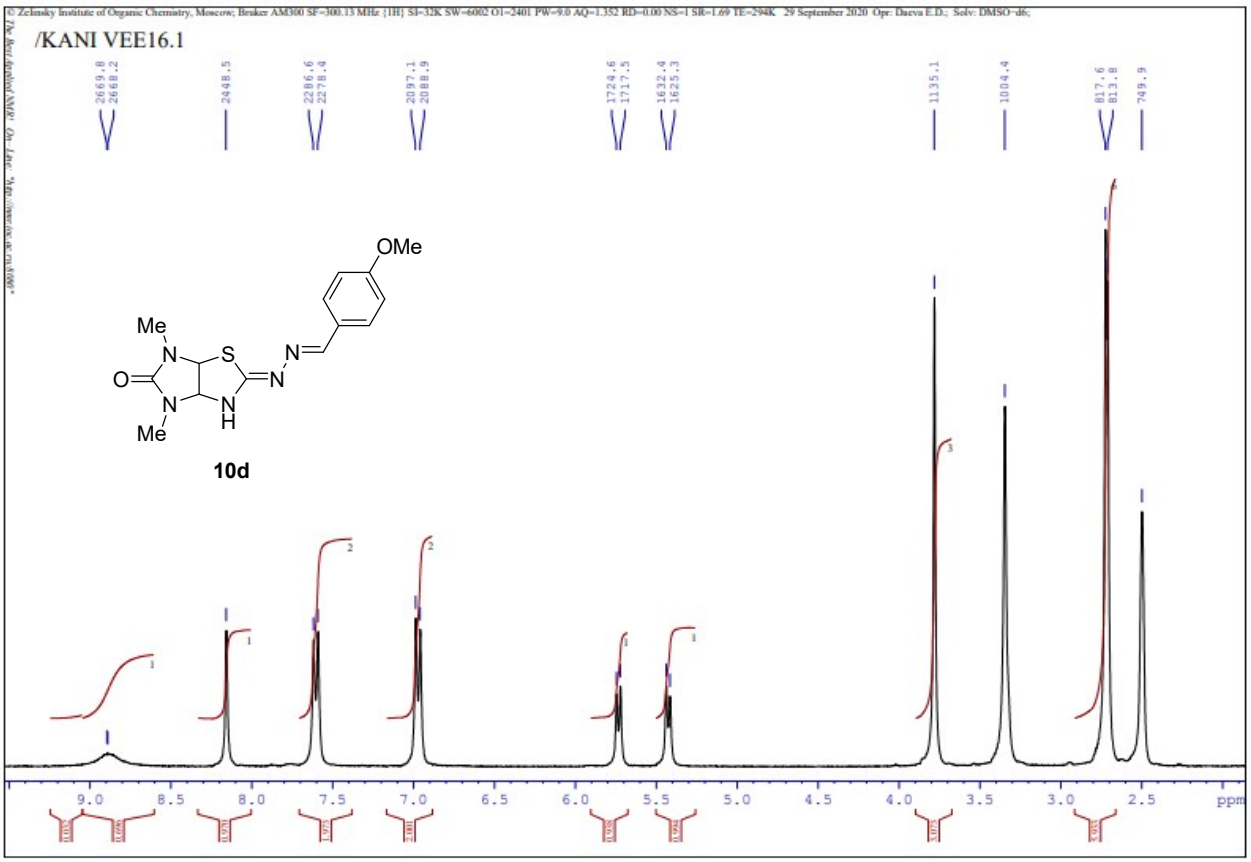


^{19}F NMR spectrum of **10c**

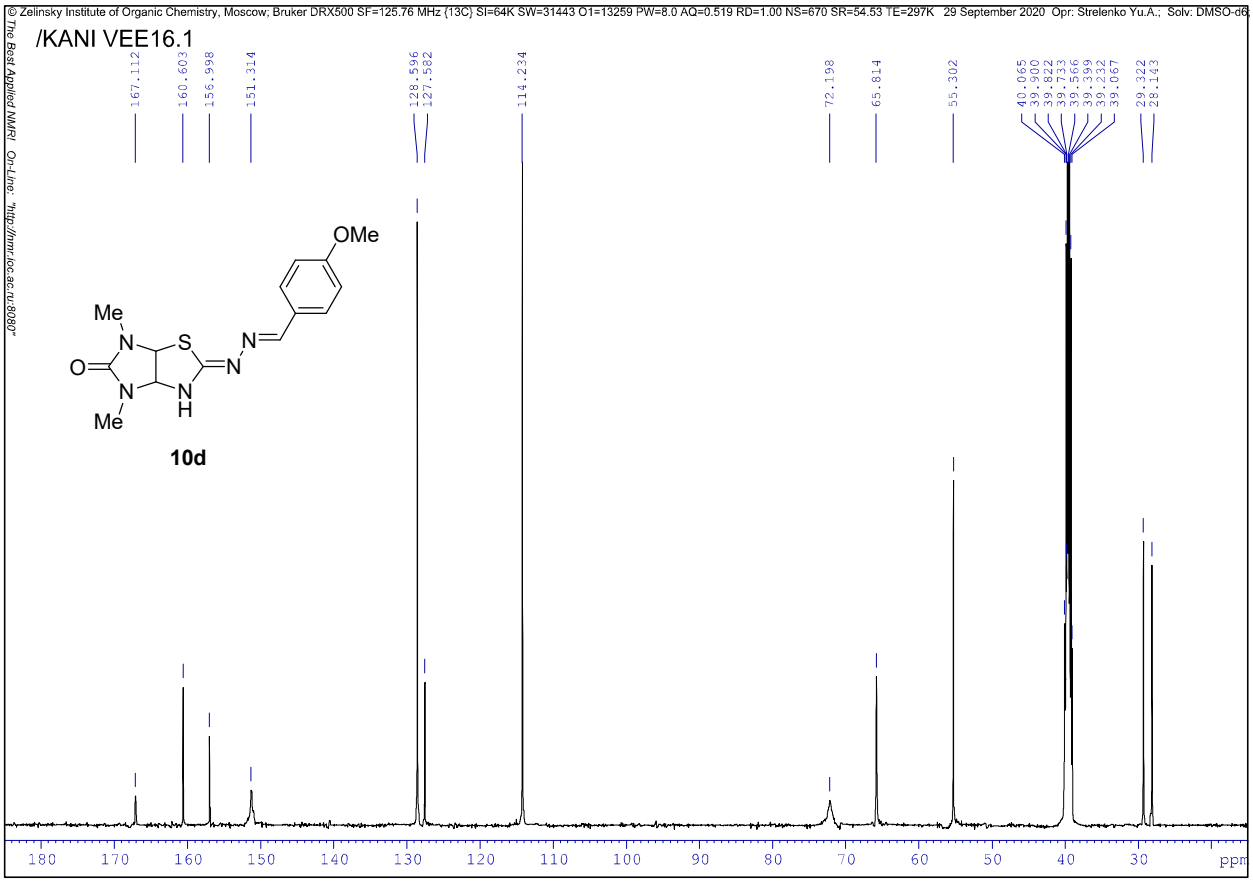


^{1}H NMR spectra of **10d** (in ppm and in Hz)

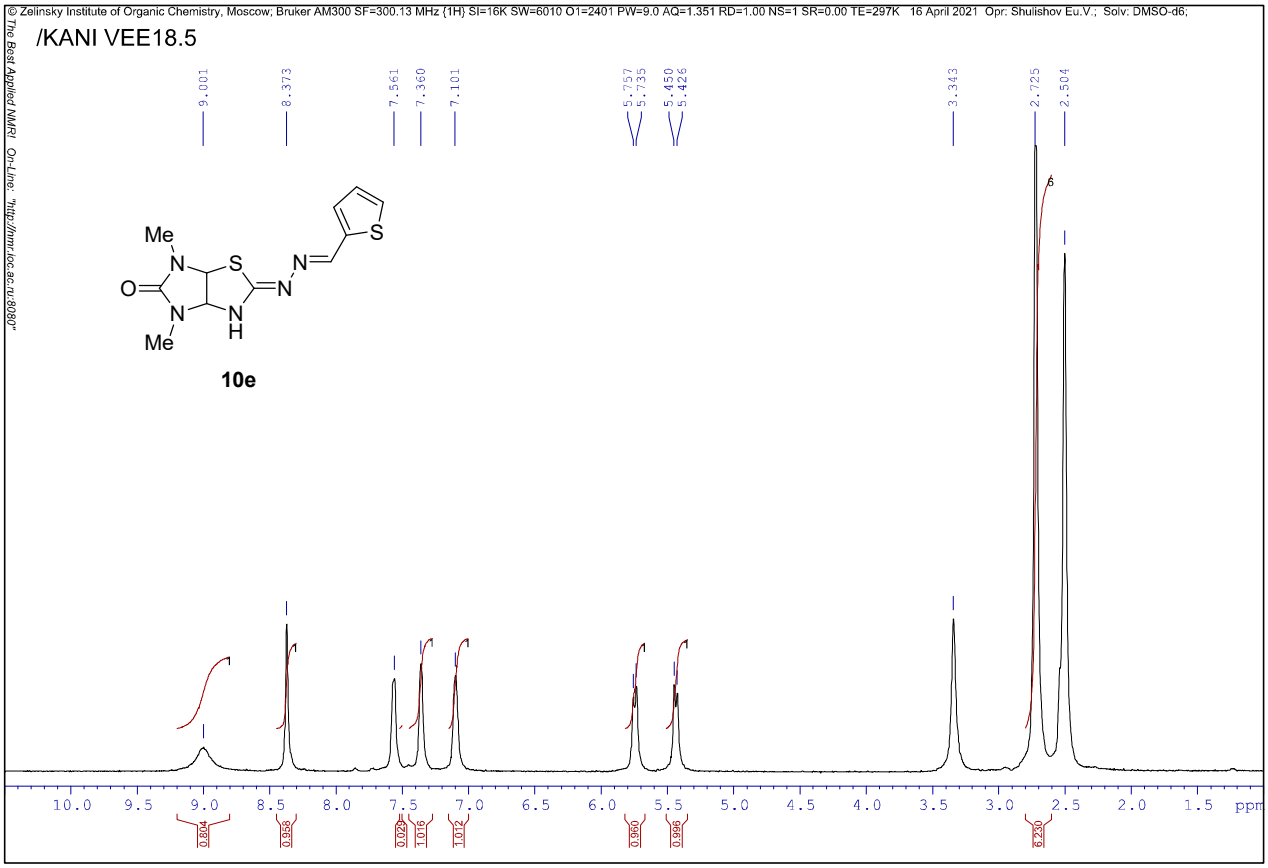




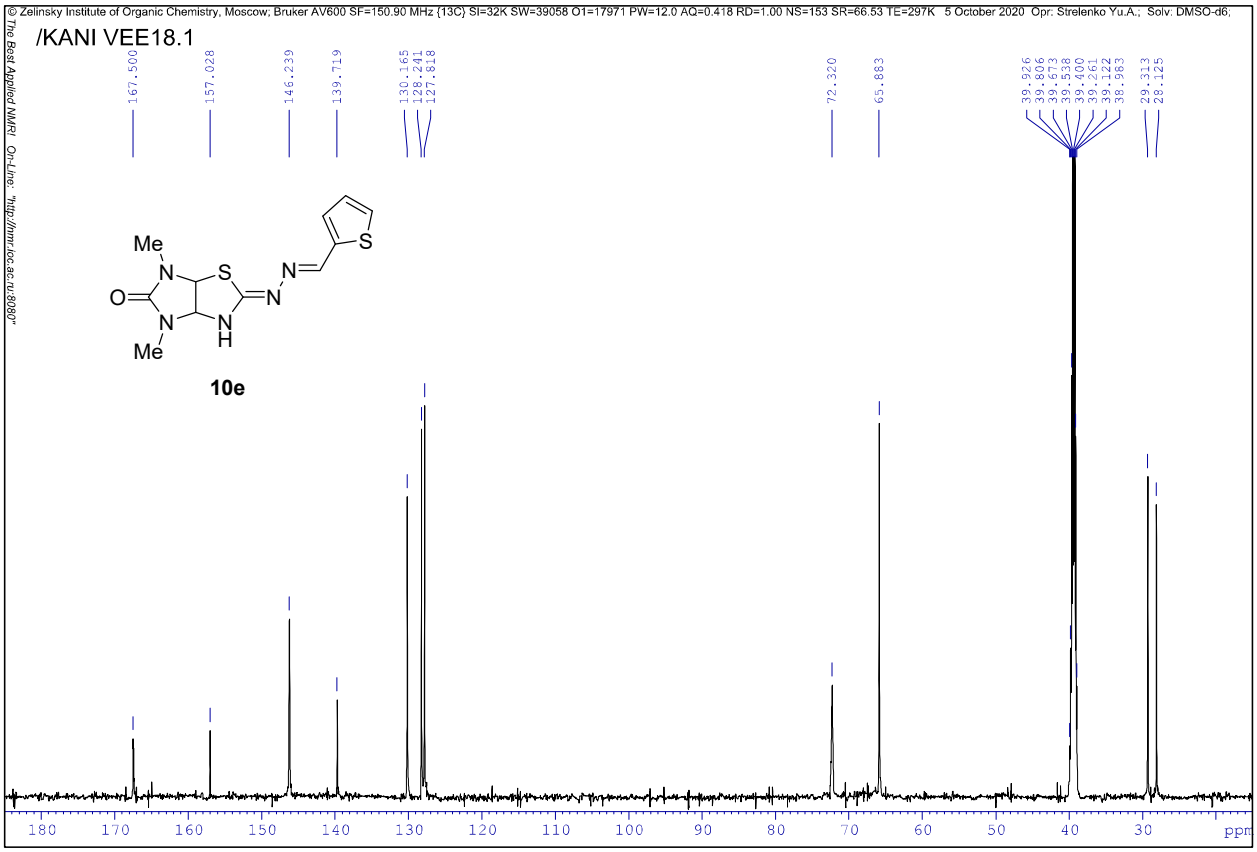
^{13}C NMR spectrum of **10d**



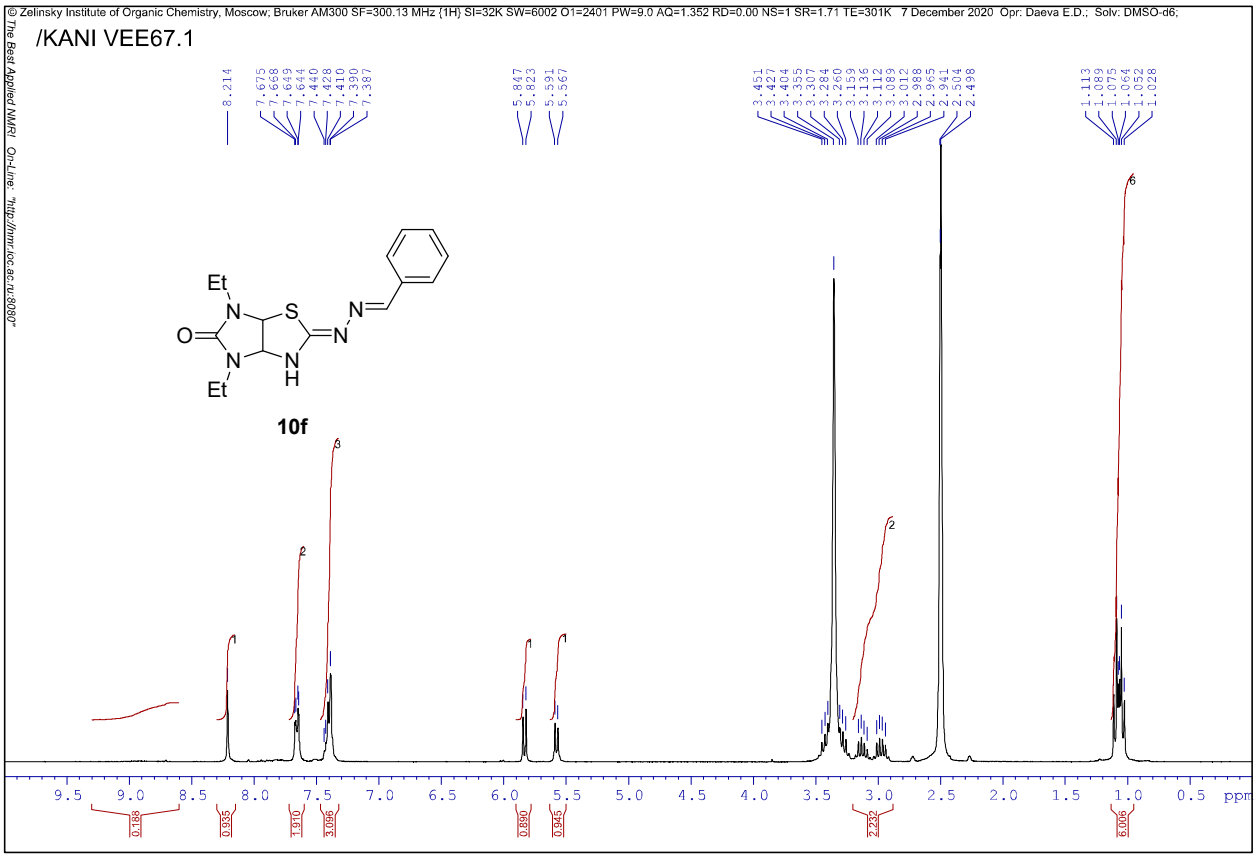
^{1}H NMR spectrum of **10e**

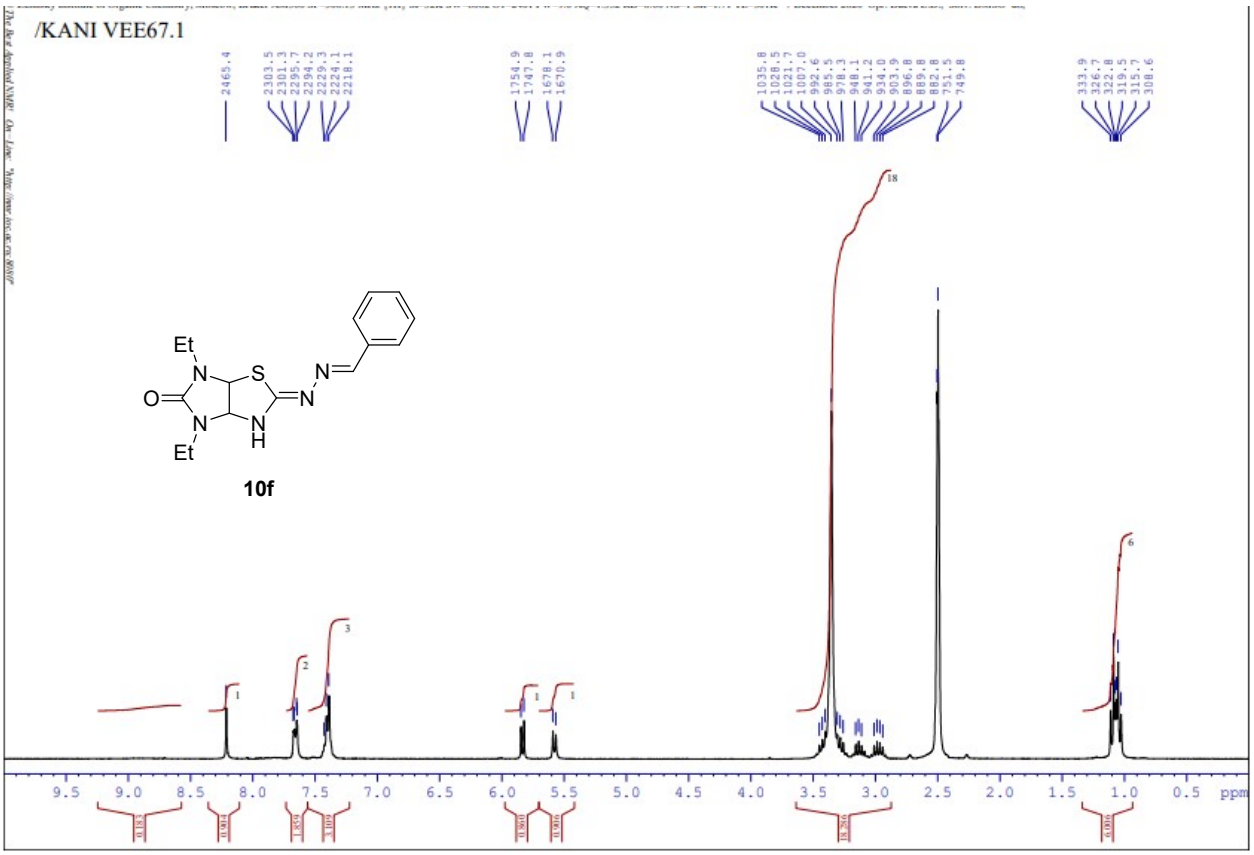


^{13}C NMR spectrum of **10e**

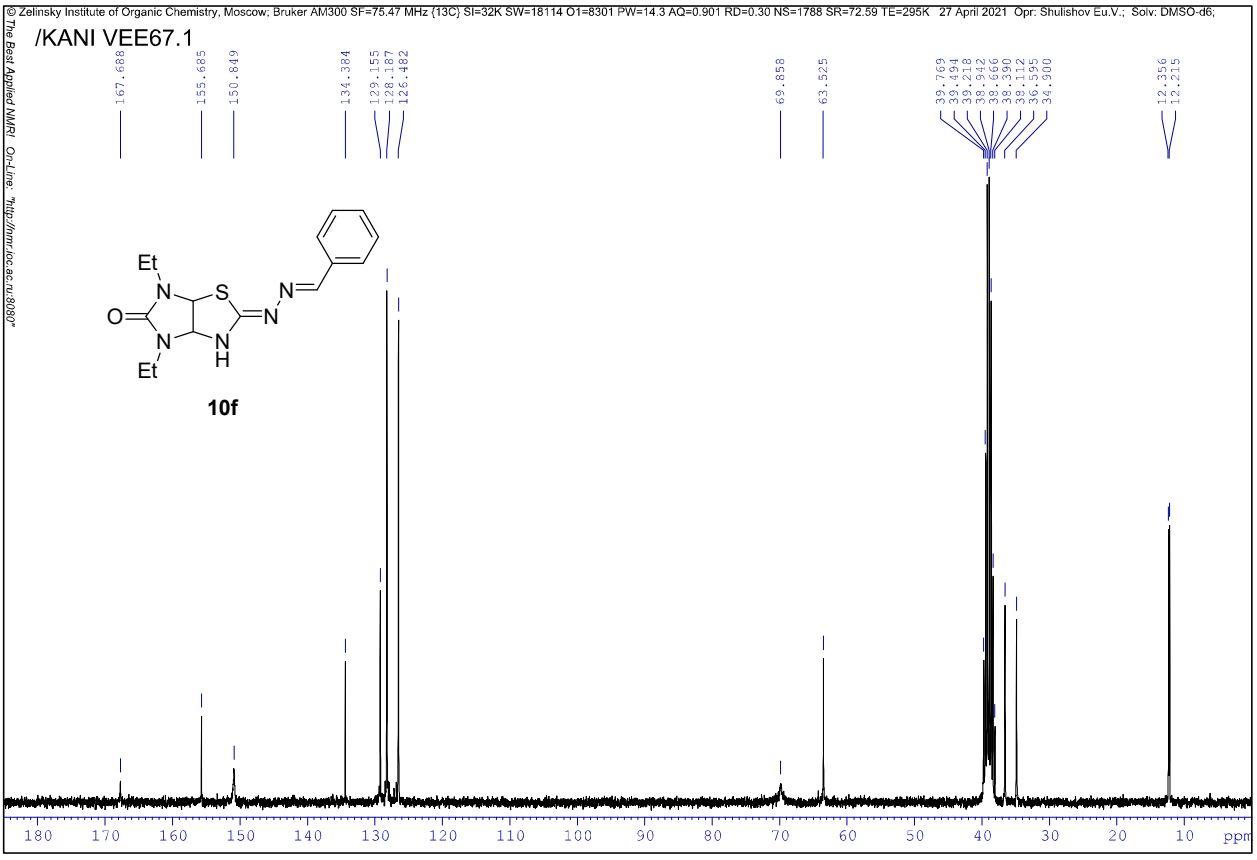


^{1}H NMR spectra of **10f (**in ppm and in Hz)

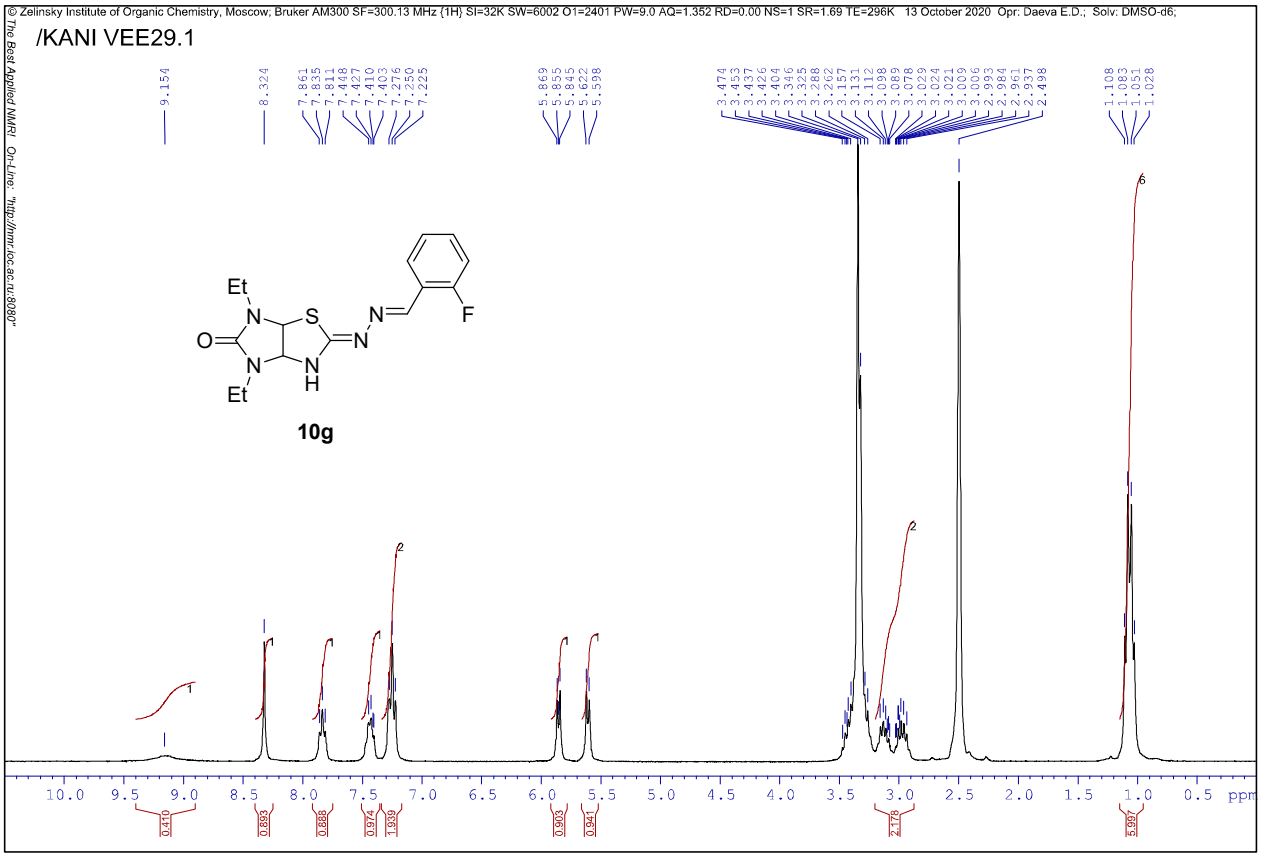




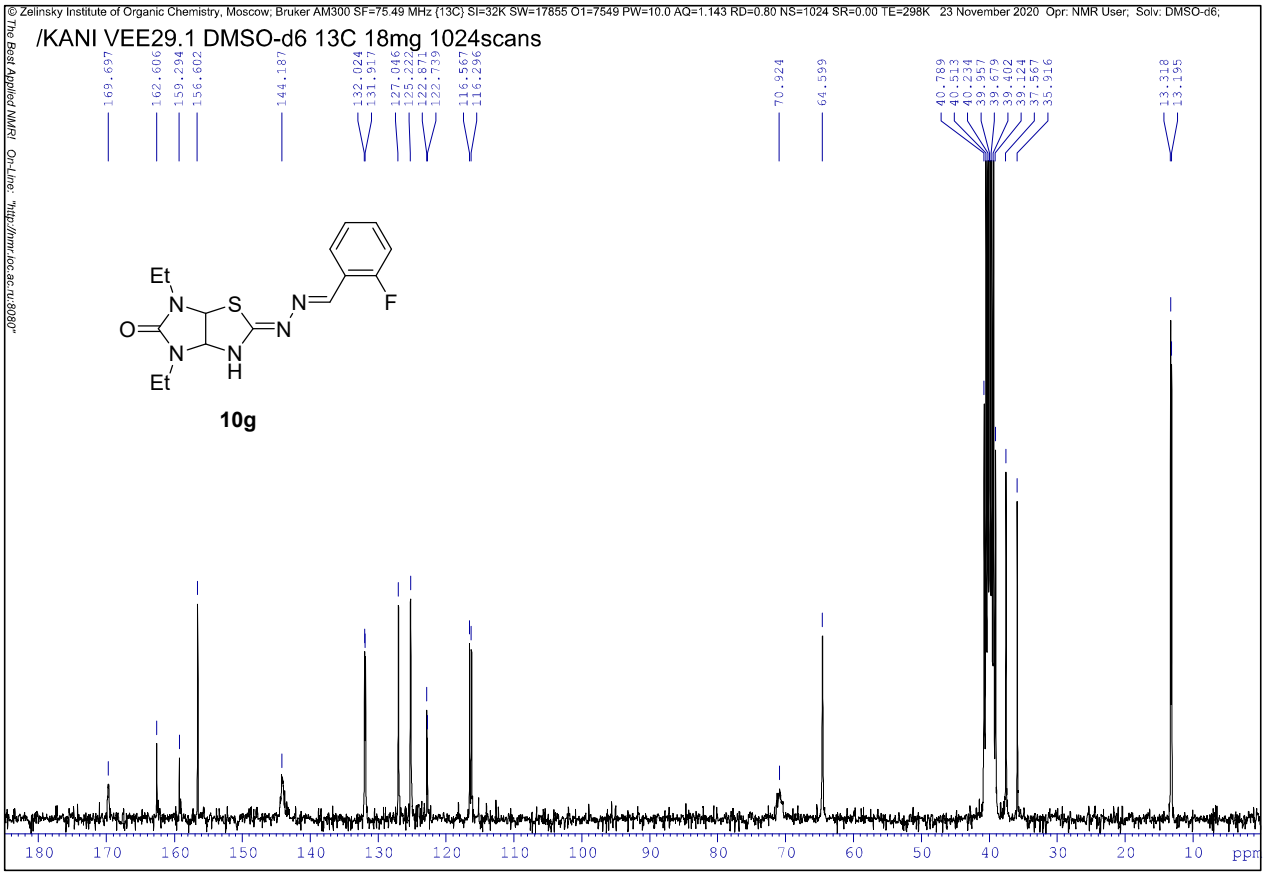
^{13}C NMR spectrum of **10f**



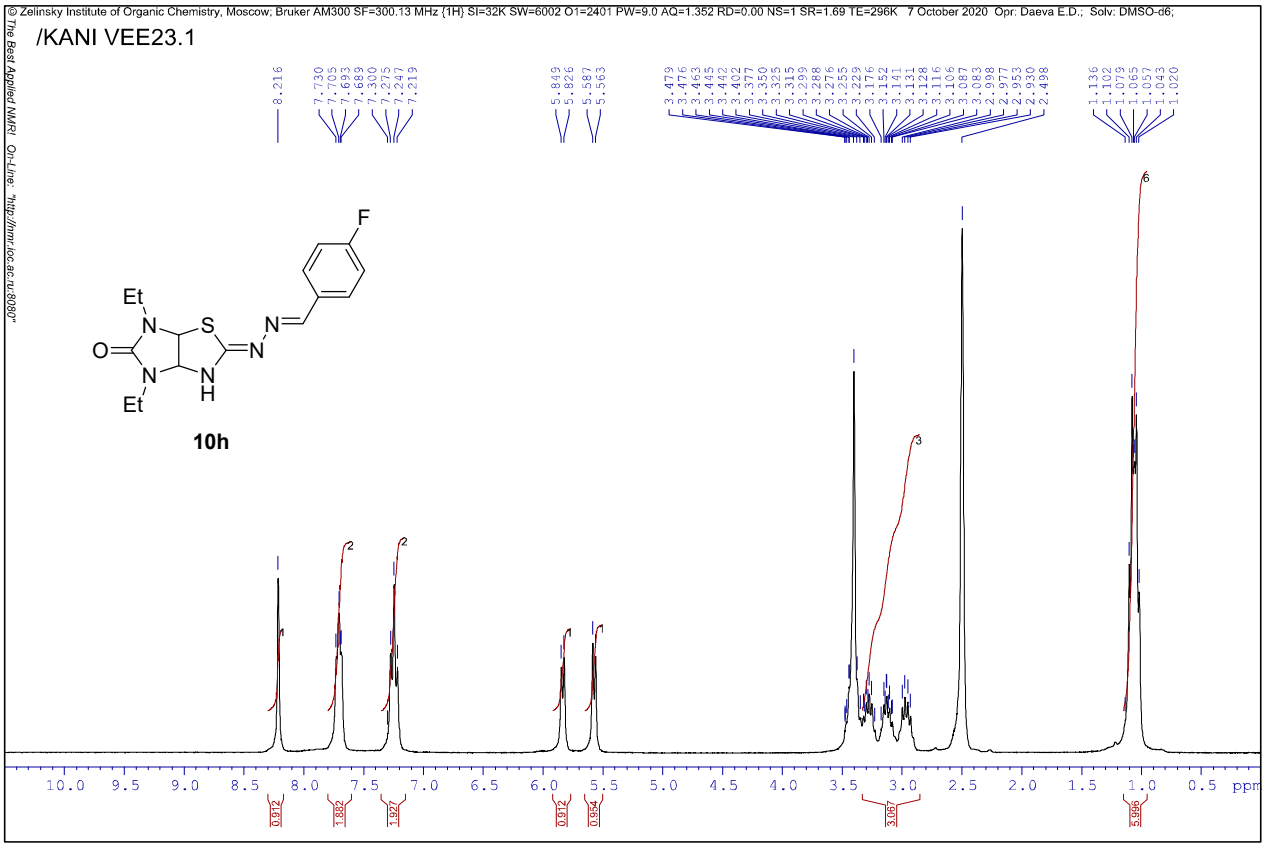
^{1}H NMR spectrum of **10g**



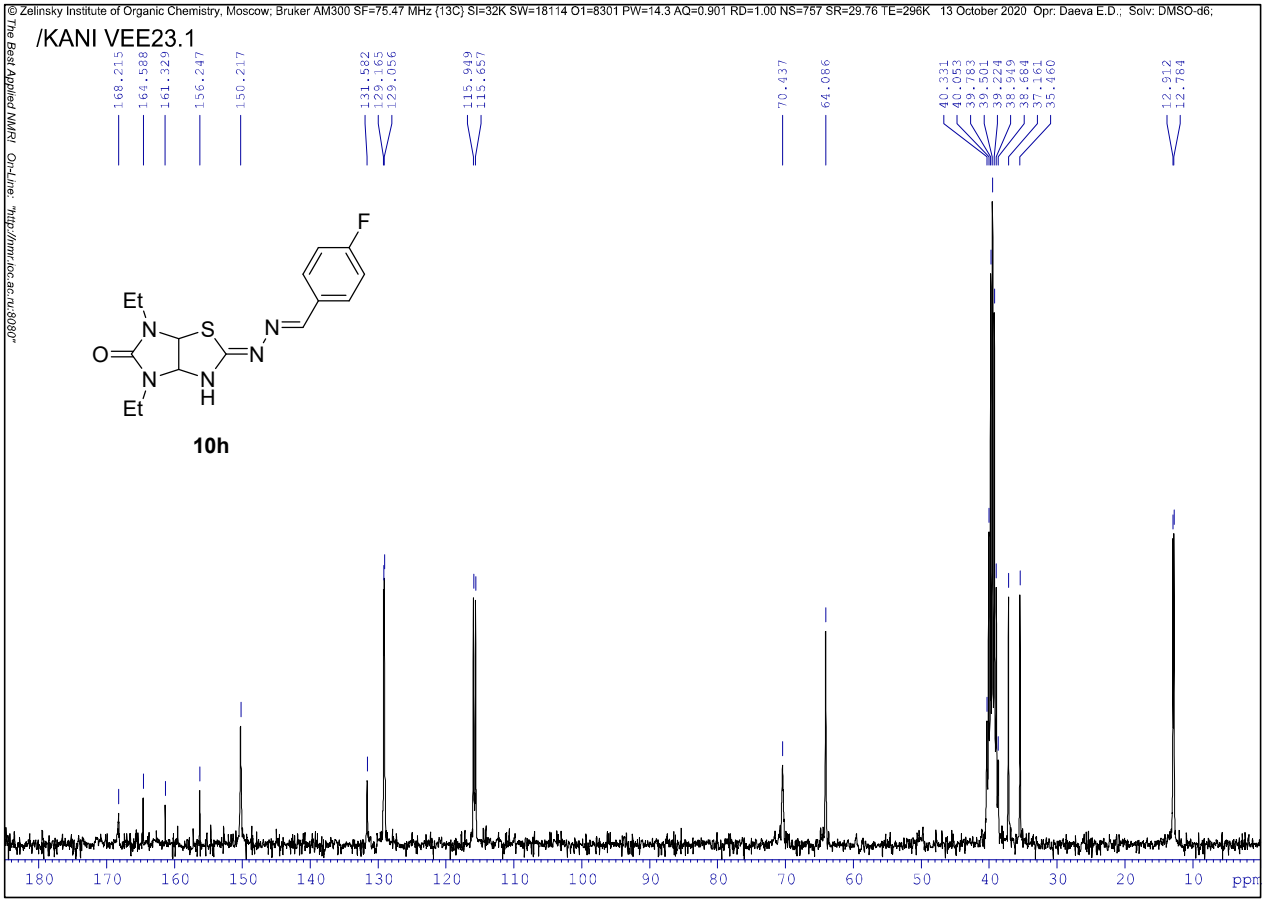
^{13}C NMR spectrum of **10g**



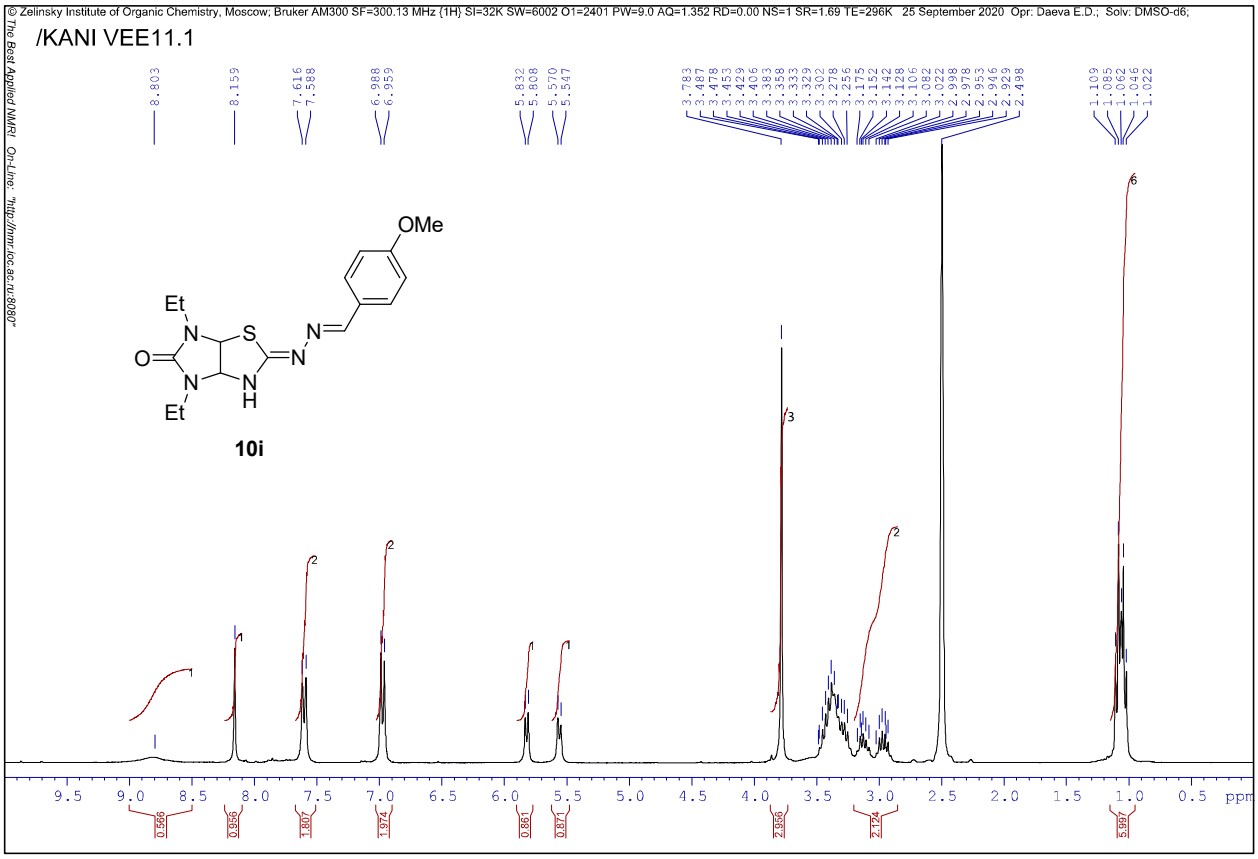
^{1}H NMR spectrum of **10h**



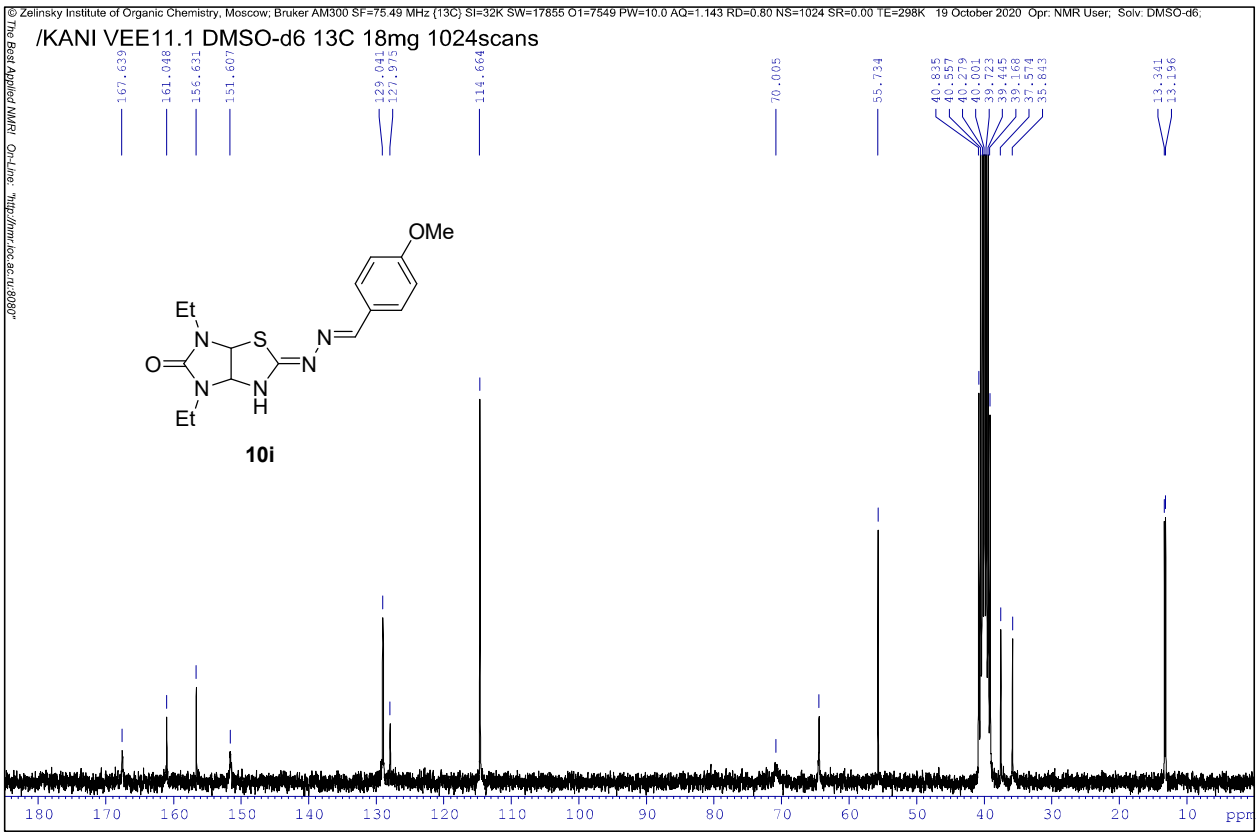
^{13}C NMR spectrum of **10h**



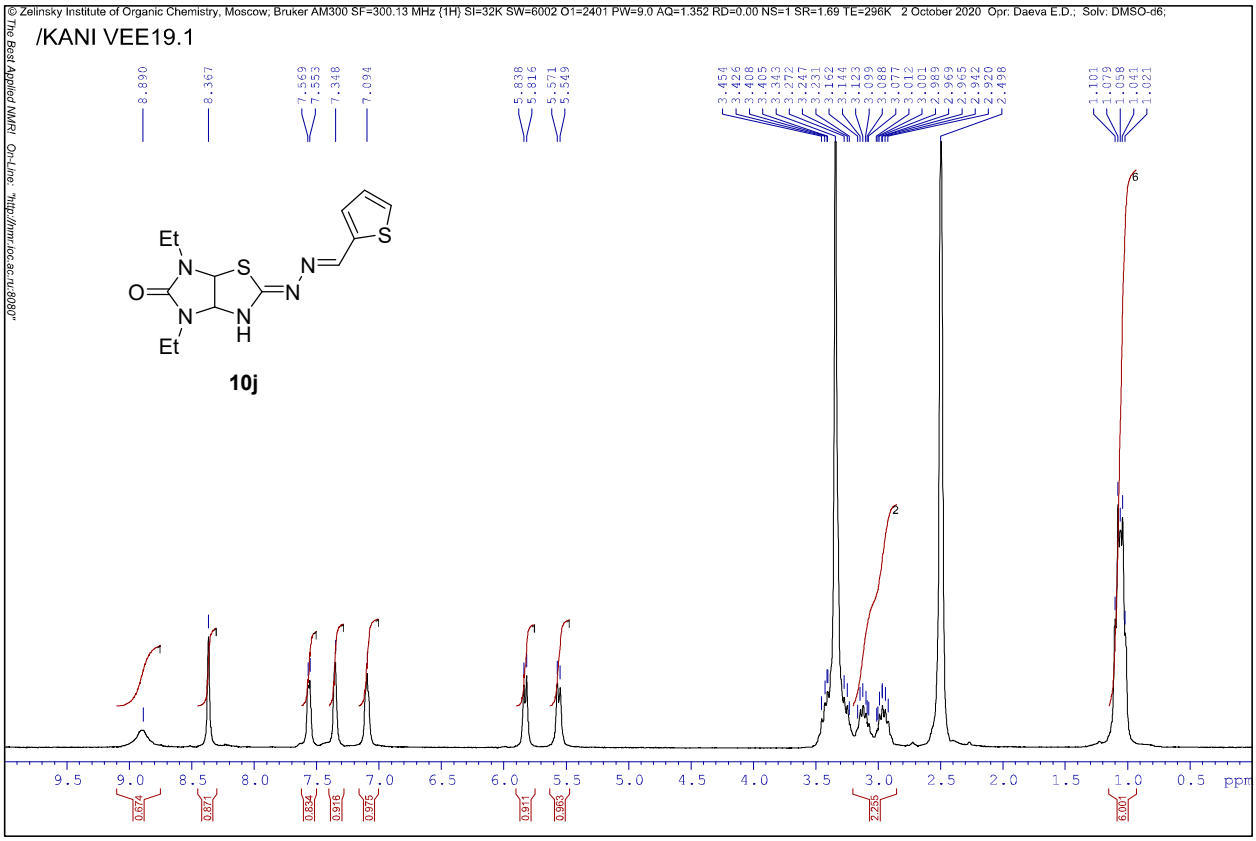
^{1}H NMR spectrum of **10i**



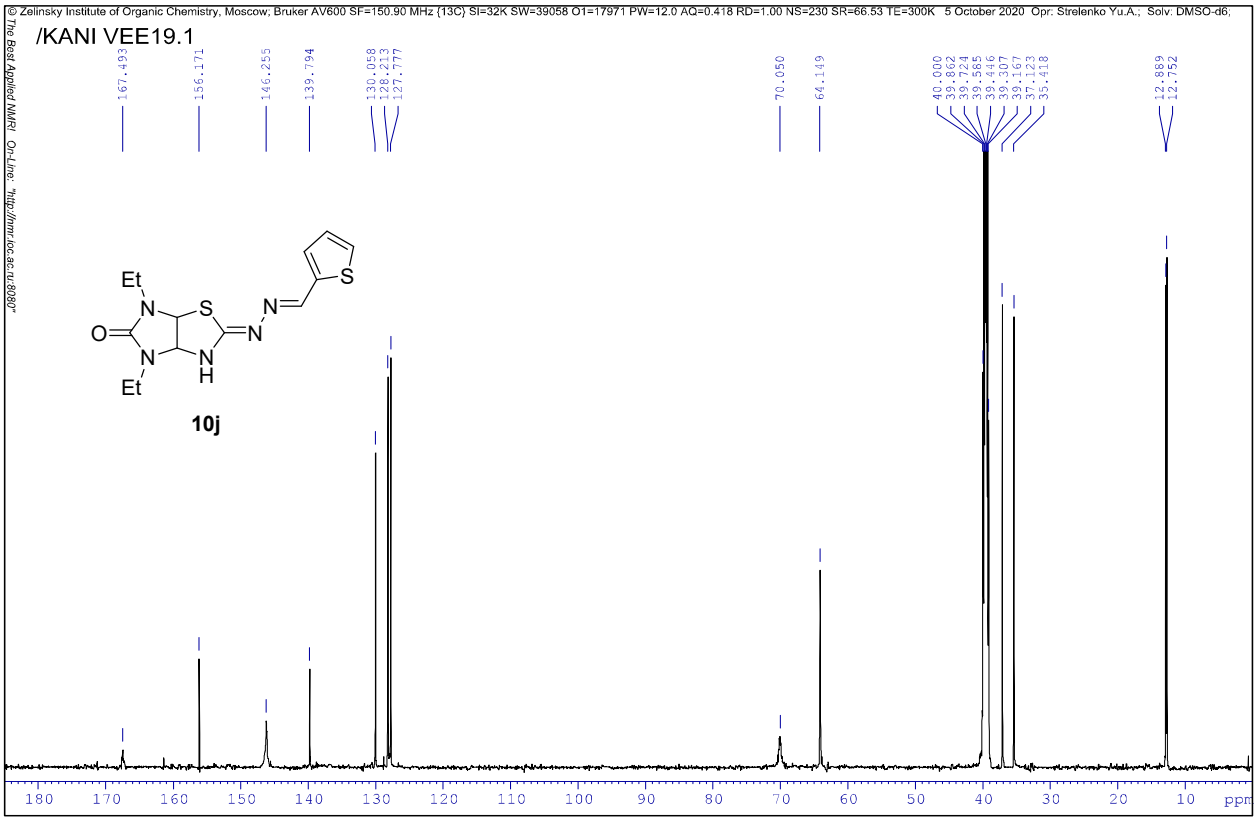
^{13}C NMR spectrum of **10i**



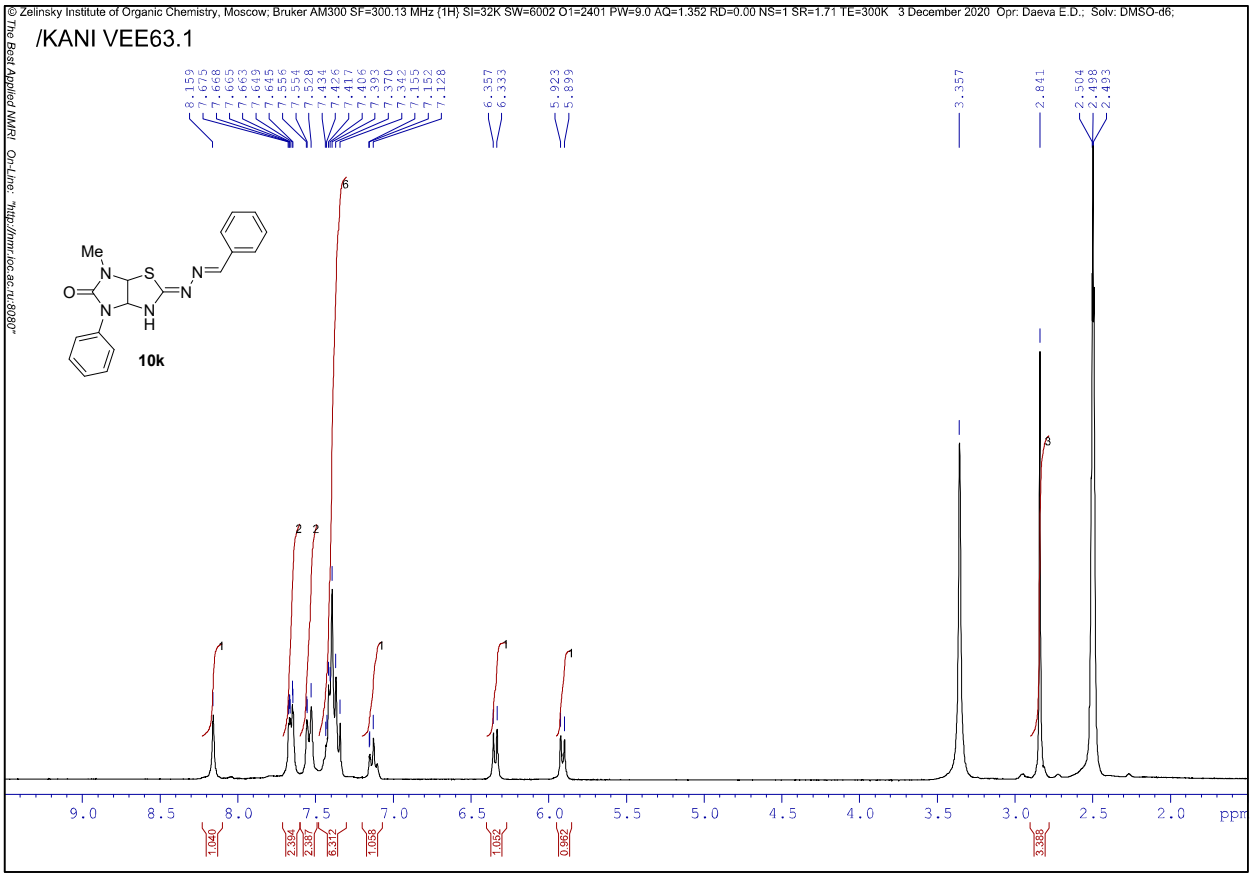
^{1}H NMR spectrum of **10j**



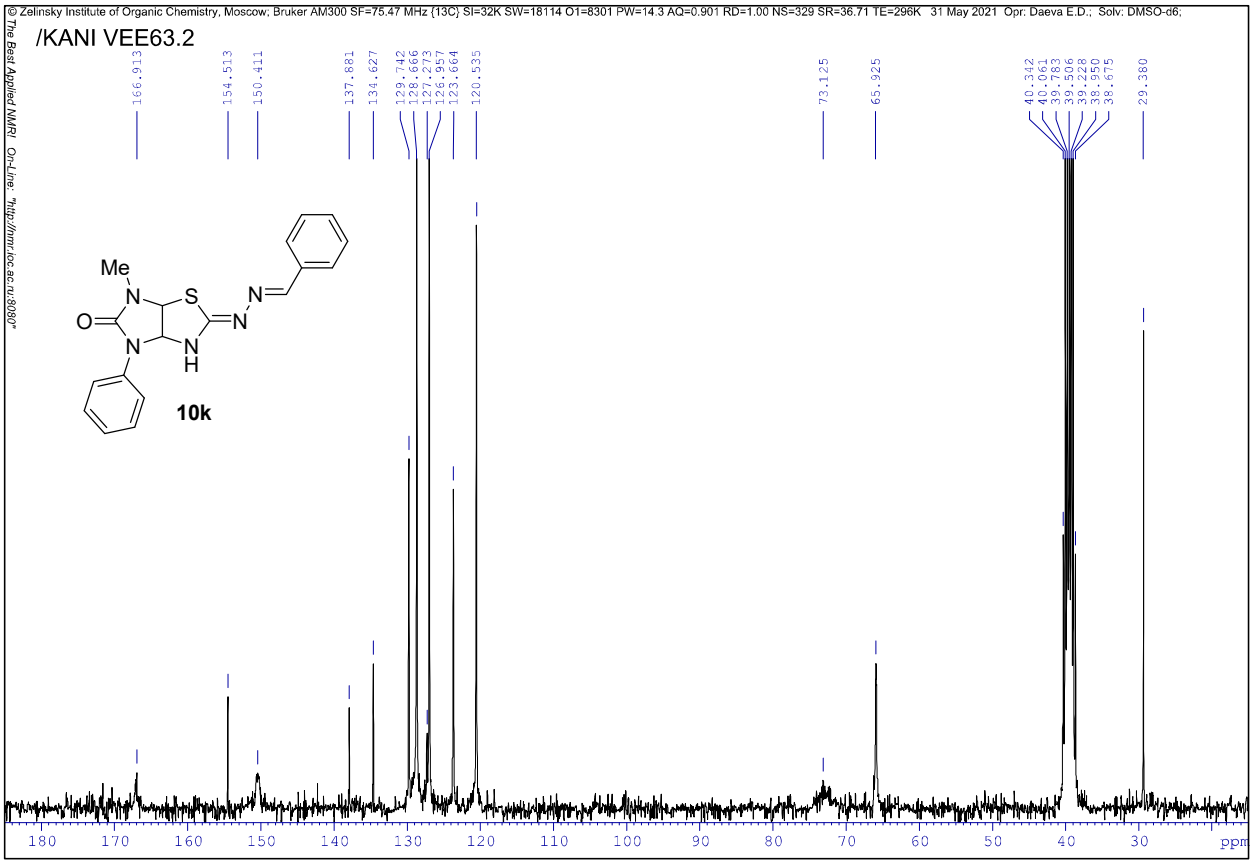
^{13}C NMR spectrum of **10j**



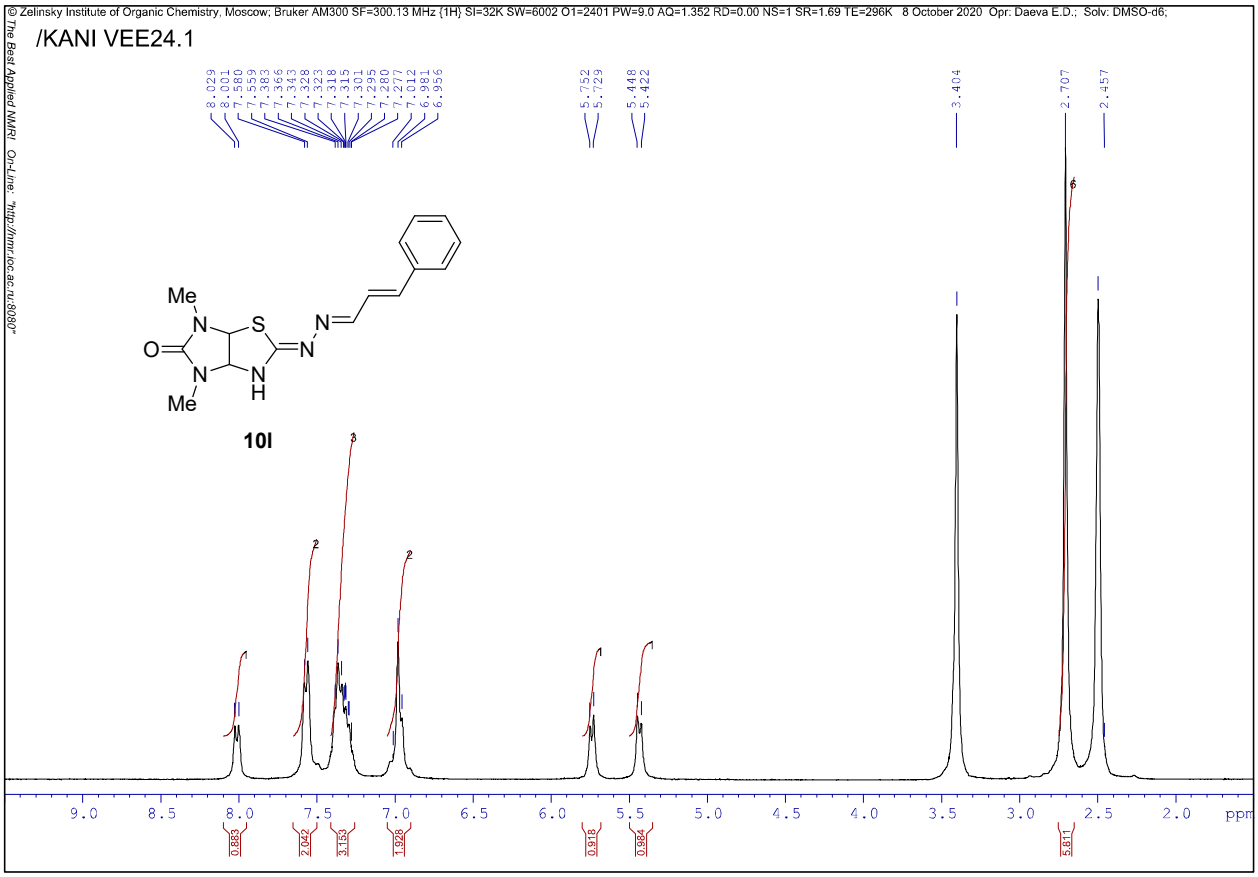
^{1}H NMR spectrum of **10k**

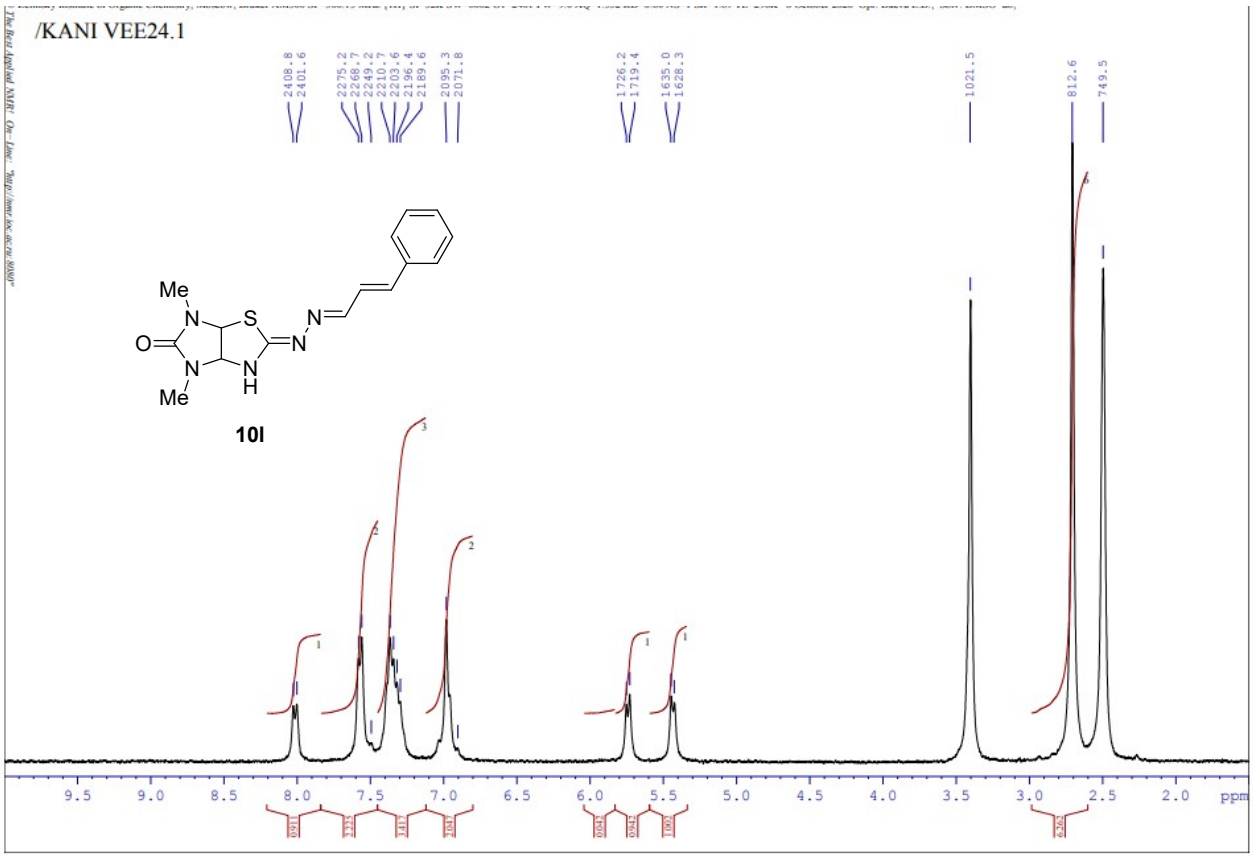


^{13}C NMR spectrum of **10k**

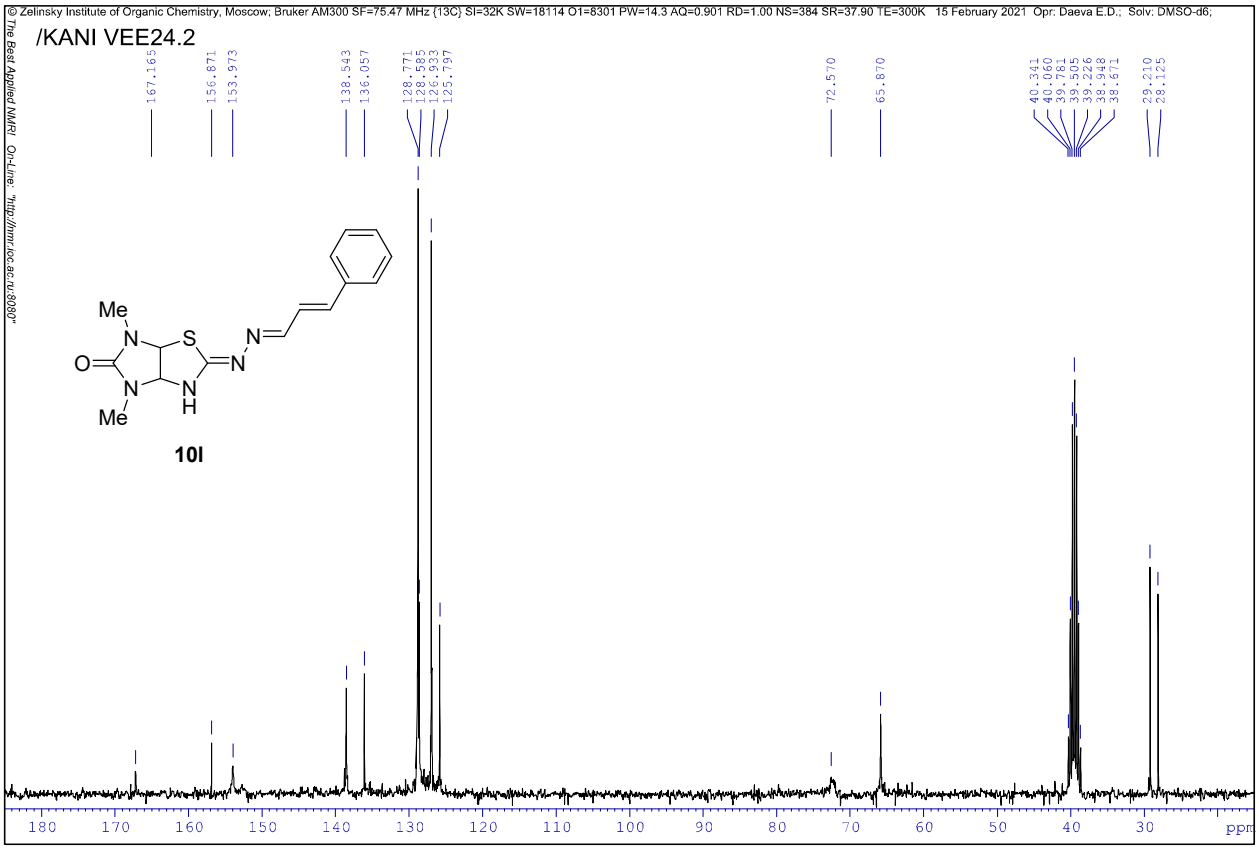


^{1}H NMR spectra of **10l** (in ppm and in Hz)

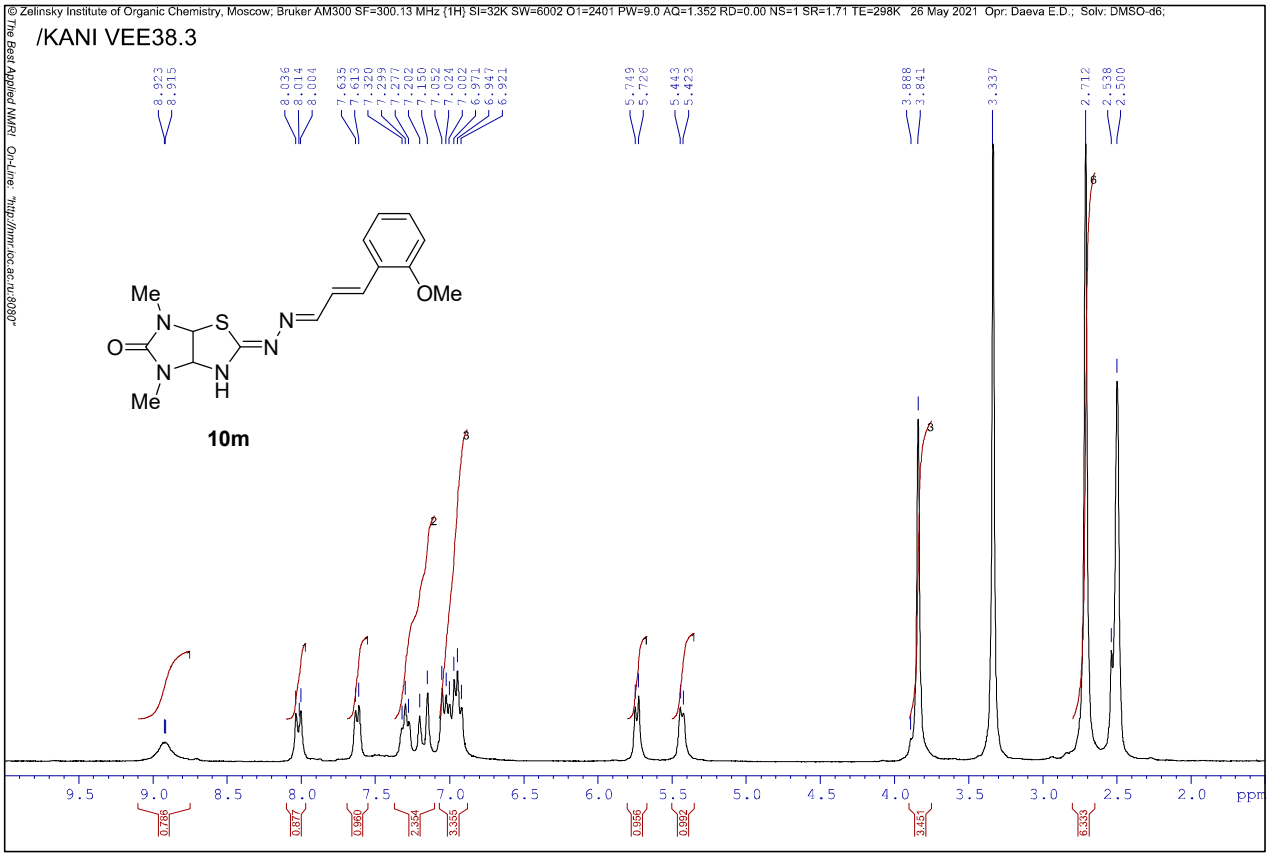




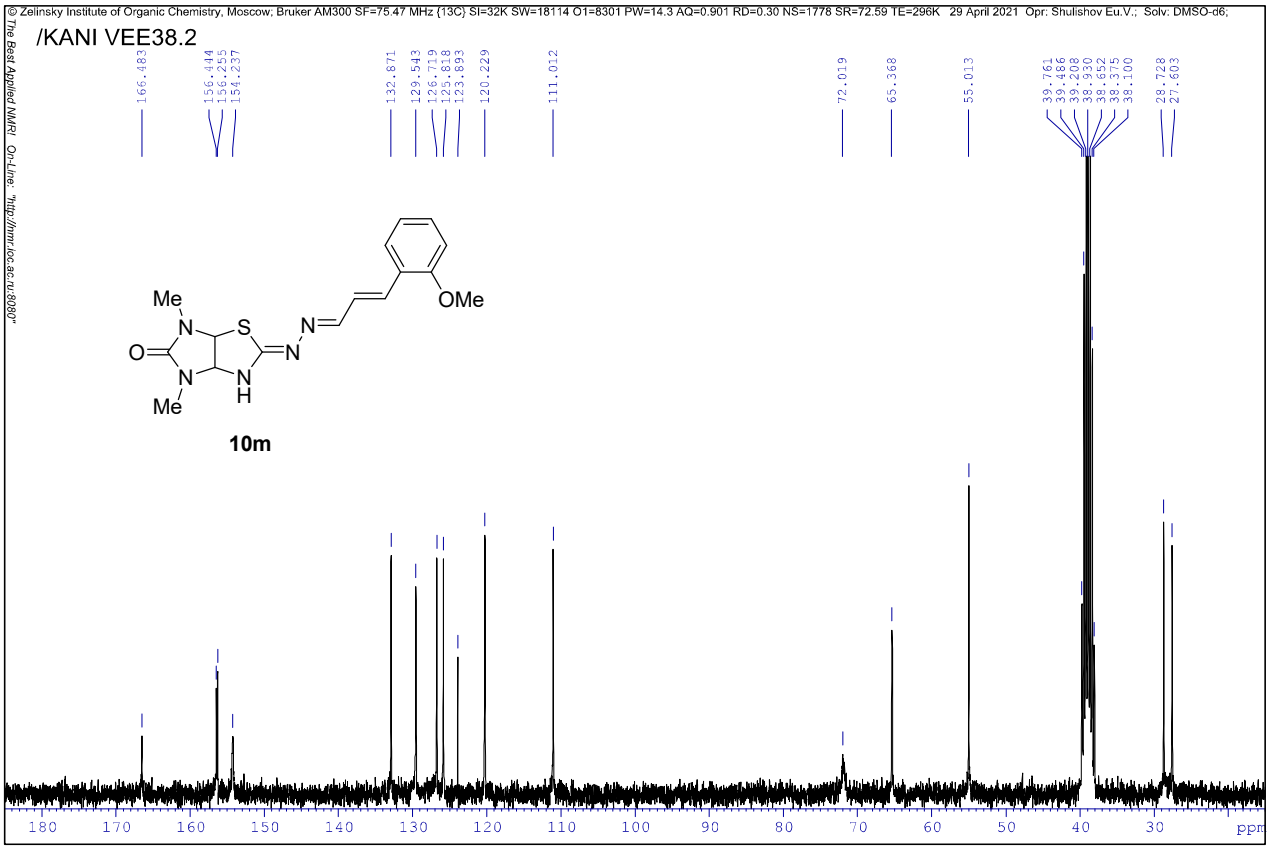
^{13}C NMR spectrum of **10l**



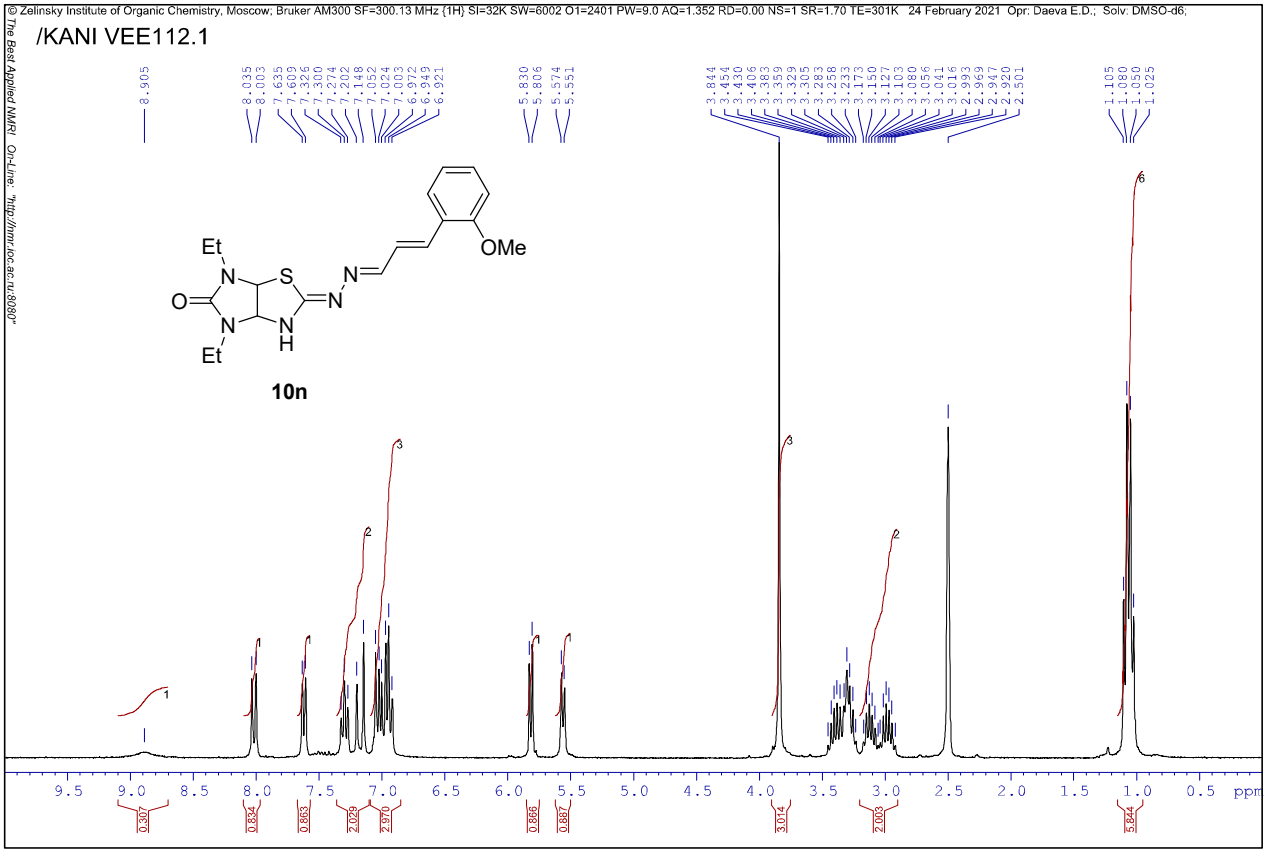
^{1}H NMR spectrum of **10m**

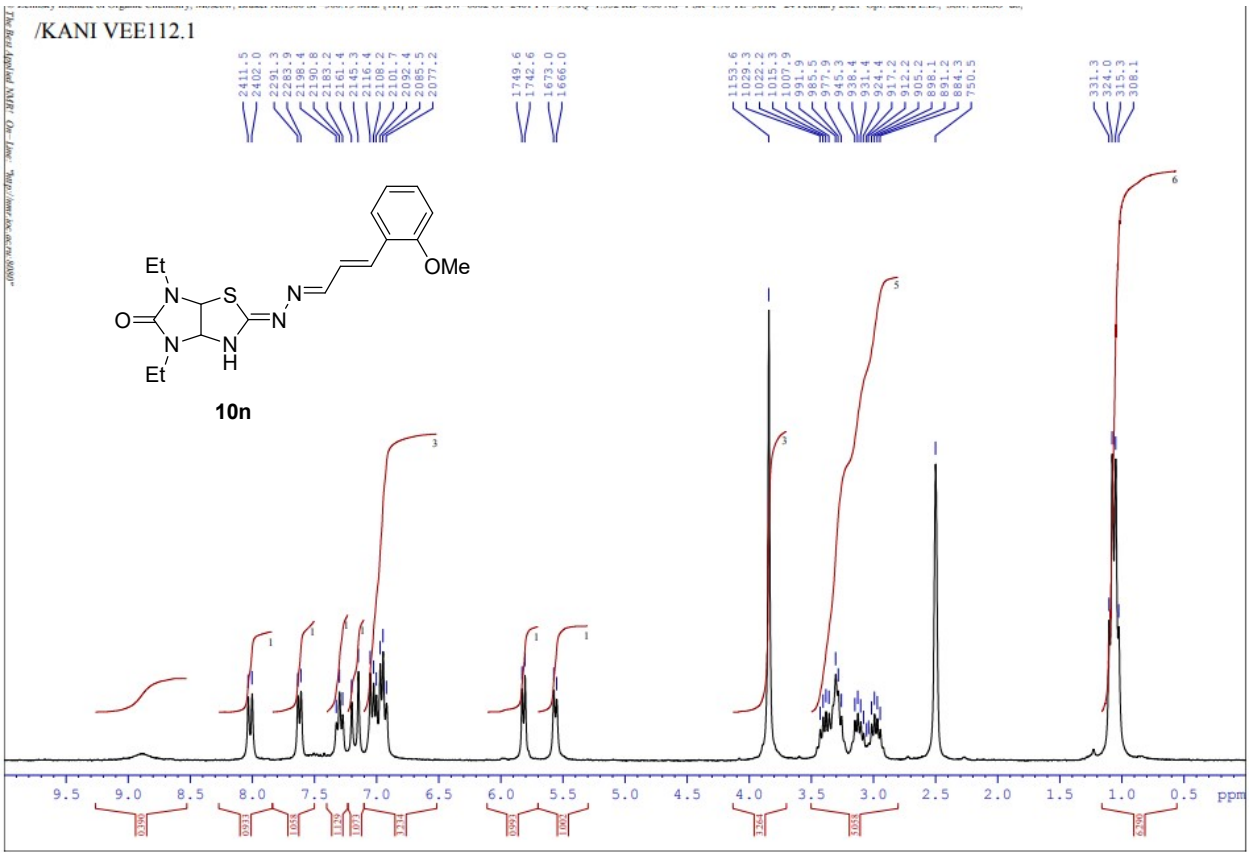


^{13}C NMR spectrum of **10m**

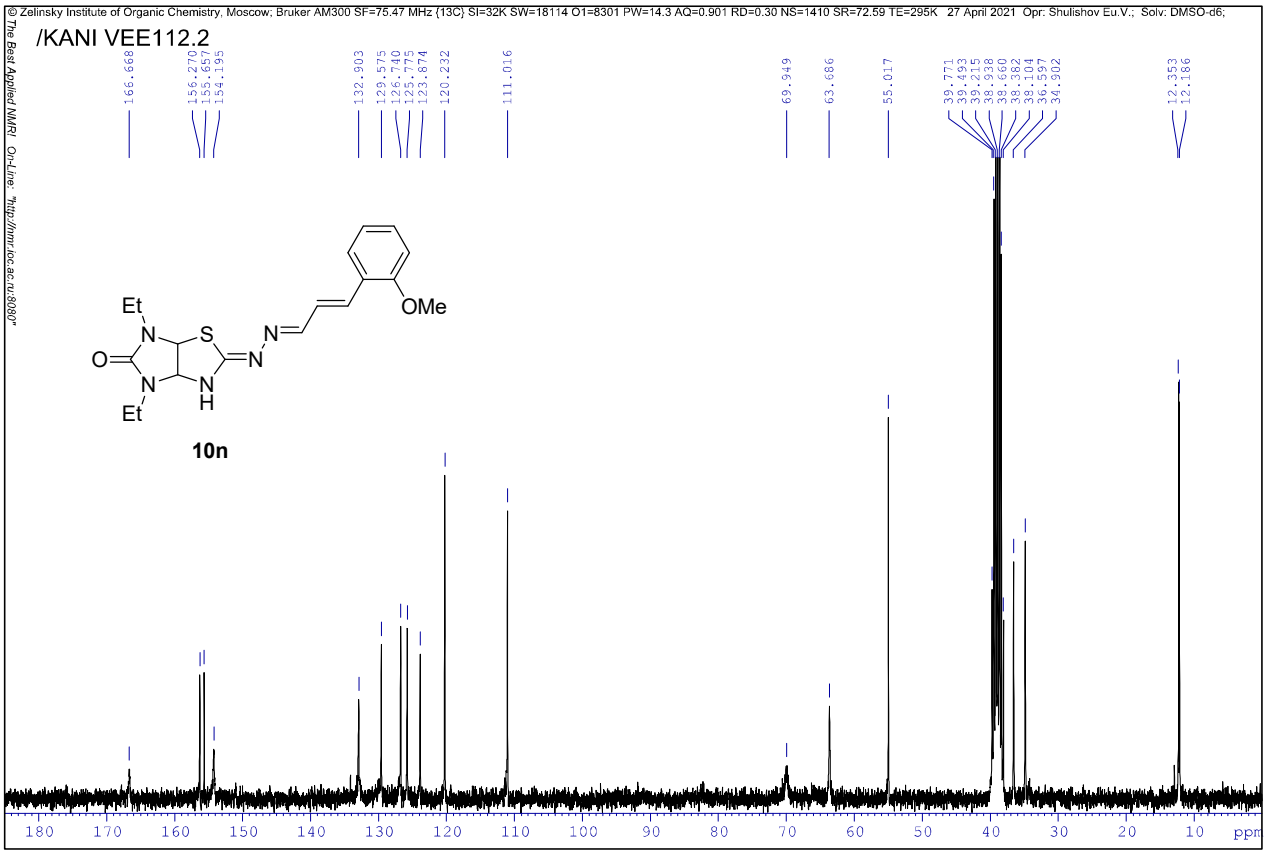


^{1}H NMR spectra of **10n** (in ppm and in Hz)

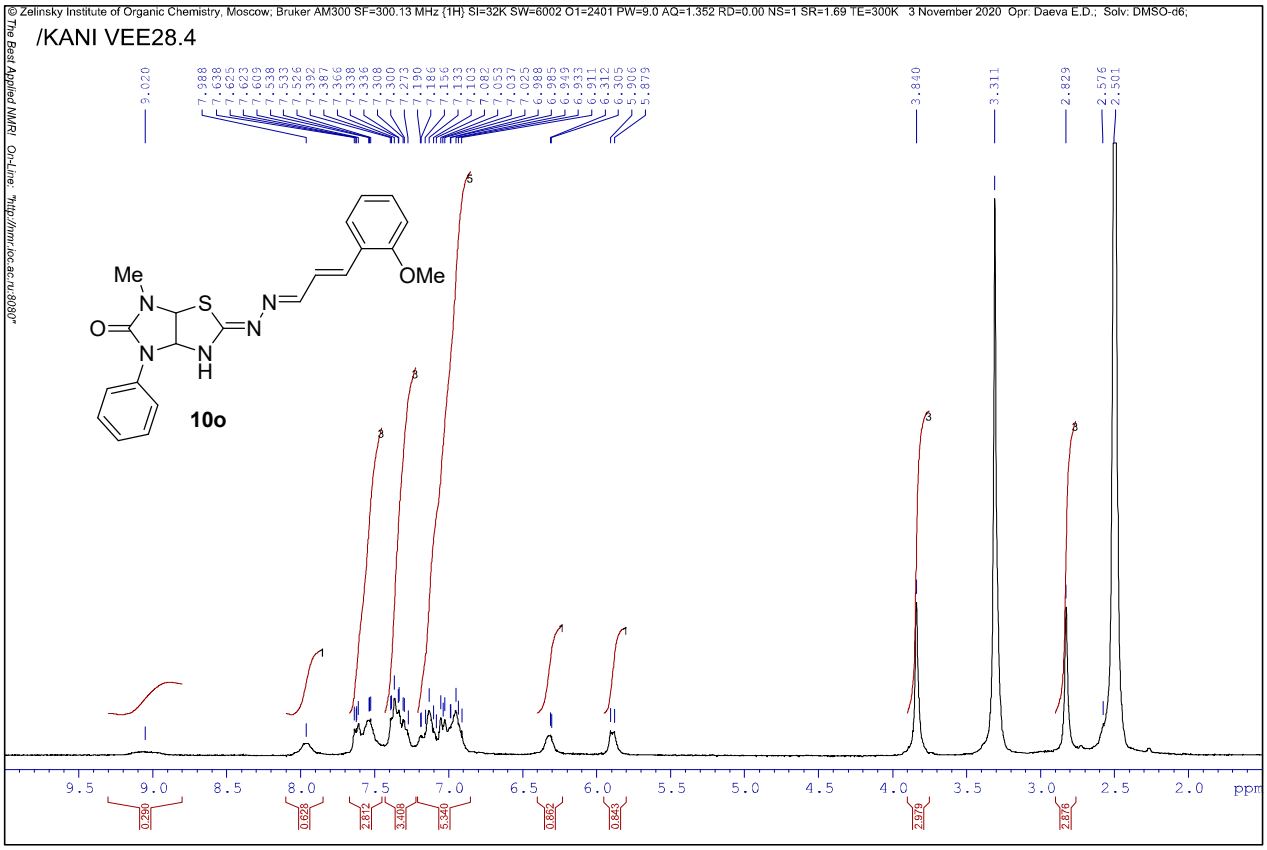




^{13}C NMR spectrum of **10n**



^{1}H NMR spectrum of **10o**



^{13}C NMR spectrum of **10o**