Electronic supplementary information

Catalytic [4+1]-annulation of thioamides with carbenoid precursors

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General information

All chemicals were obtained from commercial sources and were used without further purification. Dry solvents were obtained according to the literature protocols and stored over molecular sieves. Analytical thin-layer chromatography was performed on aluminum foil plates coated with 0.2 mm silica gel. Column chromatography was performed using 60–120 mesh silica gel. Melting points were determined on a melting point apparatus Stuart SMP10 and are uncorrected. Enantioselectivity was determined on an Azura P6.1L Knauer HPLC using a Chiralpak AD column (250 × 4.6 mm, 5 μm) (Daicel, Japan). The elution rate for the Chiralpak AD column was 1 mL min–1. Detection was carried out on a wavelength of 220 (230) nm (Diode Array Detector).. Optical rotation was measured using a PerkinElmer polarimeter 343 plus. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer equipped with a ZnSe ATR accessory. All NMR spectra were recorded at 400 MHz, 600 MHz (^{1}H NMR) and 100 MHz, 150 MHz (^{13}C NMR) in $CDCl_3$, DMSO-d_6, CD_3CN-d_3. The chemical shifts are given in parts per million (ppm) relative to the resonance of the solvents [^{1}H: δ ($CHCl_3$) = 7.26, ^{13}C: δ ($CDCl_3$) = 77.16 ppm; ^{1}H: δ (DMSO-d_6) = 2.50, ^{13}C: δ (DMSO-d_6) = 39.52 ppm; ^{1}H: δ (CD_3CN-d_3) = 1.94, ^{13}C: δ (CD_3CN-d_3) = 1.32, 118.26 ppm]. Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), and m (multiplet). Coupling constants are reported as *J* value in Hertz (Hz). The minor isomer (*Z*/*E*-isomerism) signal is highlighted with an asterisk (*). High-resolution mass spectra (HRMS) were recorded using an ultra-high-resolution quadrupole time-of-flight mass spectrometer with an electrospray ionization probe installed coupled with an Agilent 1260 HPLC system. The XRD analysis was carried out using equipment of the Center for Joint Use “Spectroscopy and Analysis of Organic Compounds” at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch). The experiments were accomplished on the automated X-ray diffractometer «Xcalibur 3» with CCD detector on standard procedure (MoKα-irradiation, graphite monochromator, ω-scans with 1o step at T= 295(2) K). Empirical absorption correction was applied. The solution and refinement of the structures were accomplished with using Olex program package.[1] The structures were solved by method of the intrinsic phases in ShelXT program and refined by ShelXL by full-matrix least-squared method for non-hydrogen atoms.[2] The H-atoms at were placed in the calculated positions and were refined in isotropic approximation. The XRD data were deposited in the Cambridge Structural Database with numbers CCDC 2288489–2288498. This data can be requested free of charge via www.ccdc.cam.ac.uk.

Preparation of starting reagents

3-Morpholino-3-thioxopropanenitrile (**S1a**),[3] 3-(piperidin-1-yl)-3-thioxopropanenitrile (**S1b**),[4] 3-(pyrrolidin-1-yl)-3-thioxopropanenitrile (**S1c**),[4] 3-(azepan-1-yl)-3-thioxopropanenitrile (**S1d**),[5] 2-cyano-*N*-(*p*-tolyl)ethanethioamide (**S1e**),[6] 4-morpholino-4-thioxobutan-2-one[7] (**S1f**), methyl 3-morpholino-3-thioxopropanoate[8] (**S1g**), 3-((4-chlorophenyl)amino)-2-(pyrrolidine-1-carbonothioyl)acrylonitrile[9] (**1t**), 2-morpholino-*N*-phenyl-2-thioxoacetohydrazonoyl cyanide[10] (**1u**), 3-(dimethylamino)-2-(pyrrolidine-1-carbonothioyl)acrylonitrile[9] (**1v**), 1-sulfonyl-1,2,3-triazoles **2a-c**,[11] **2d**,[12] **2e-f**,[13] diazo compounds **2h-o**,[14] **2q**,[15] **2r**,[16] **2t**,[17] **2v**,[18] 4,7-dibromoisobenzofuran-1,3-dione[19] (**S3**) were synthesized according to literature procedures. 3-Morpholino-3-thioxopropanethioamide[20] (**1e**), 4-cyclopropyl-1-tosyl-1*H*-1,2,3-triazole[21] (**2g**), *N*-(4-chlorophenyl)-*N*'-tosylformimidamide[22] (**3ta**) were synthesized according to modified literature procedures. 3-Diazo-7-methylindolin-2-one (**2p**) was purchased from commercial source and characterized. Copper, ruthenium, silver, palladium catalysts, $Rh_2(OAc)_4$, $Rh_2(Oct)_4$, $Rh_2(esp)_2$, Rh_2(*S*-PTAD)$_4$, Rh_2(*S*-DOSP)$_4$ were purchased from commercial sources. $Rh_2(Piv)_4$ was synthesized according to literature procedure.[23] Other chiral rhodium catalysts, Rh_2(*S*-PTTL)$_4$,[24] Rh_2(*S*-PTV)$_4$,[24] Rh_2(*S*-NTTL)$_4$,[25] were synthesized according to literature protocols. Heteroaromatic thioamides **T1-2**,[26] **T3**[14] were synthesized according to literature procedures.

Starting compounds were used in the research

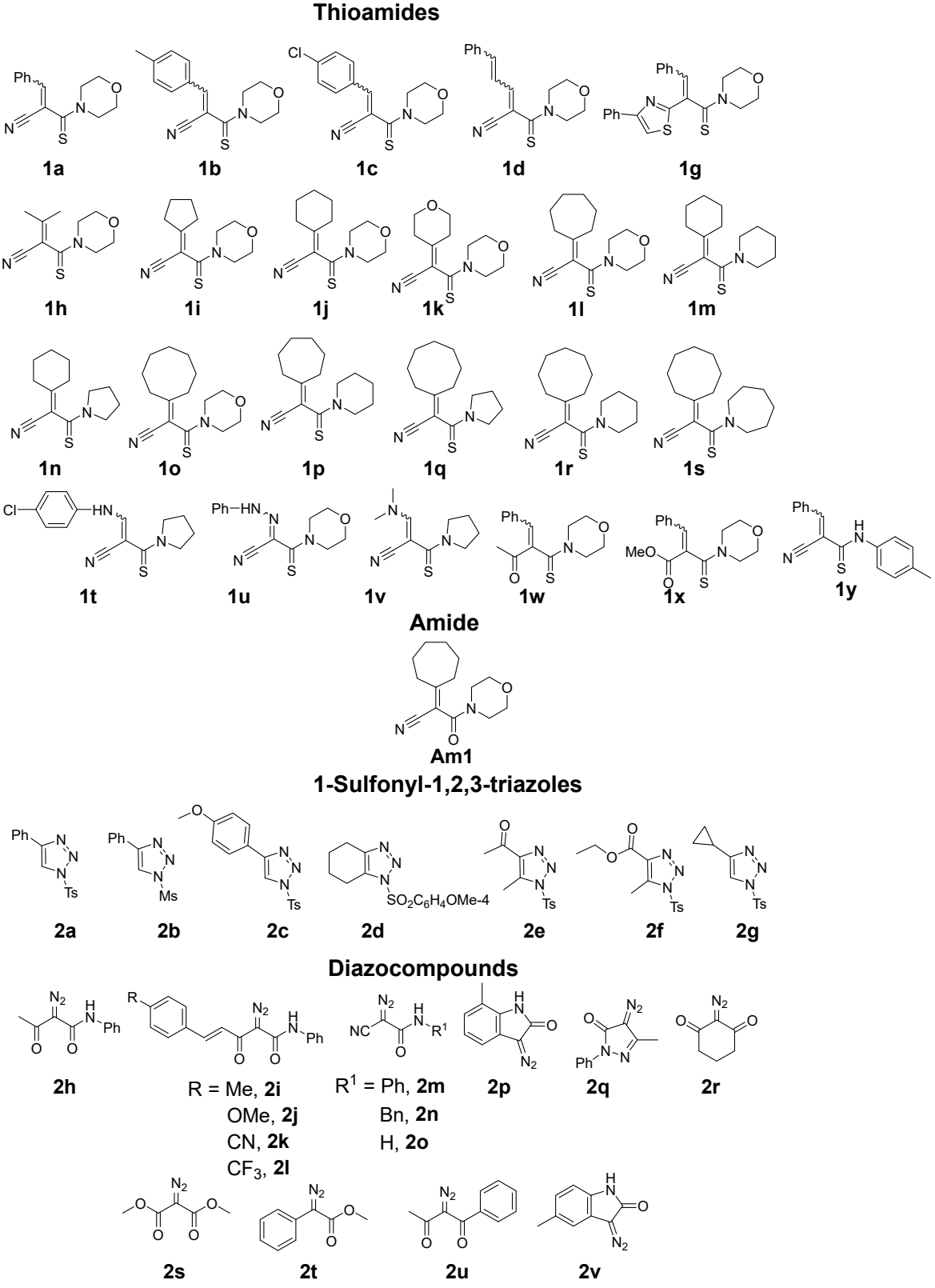


Figure S1. Starting compounds were used in the research

Chiral rhodium(II) catalysts were used in the research

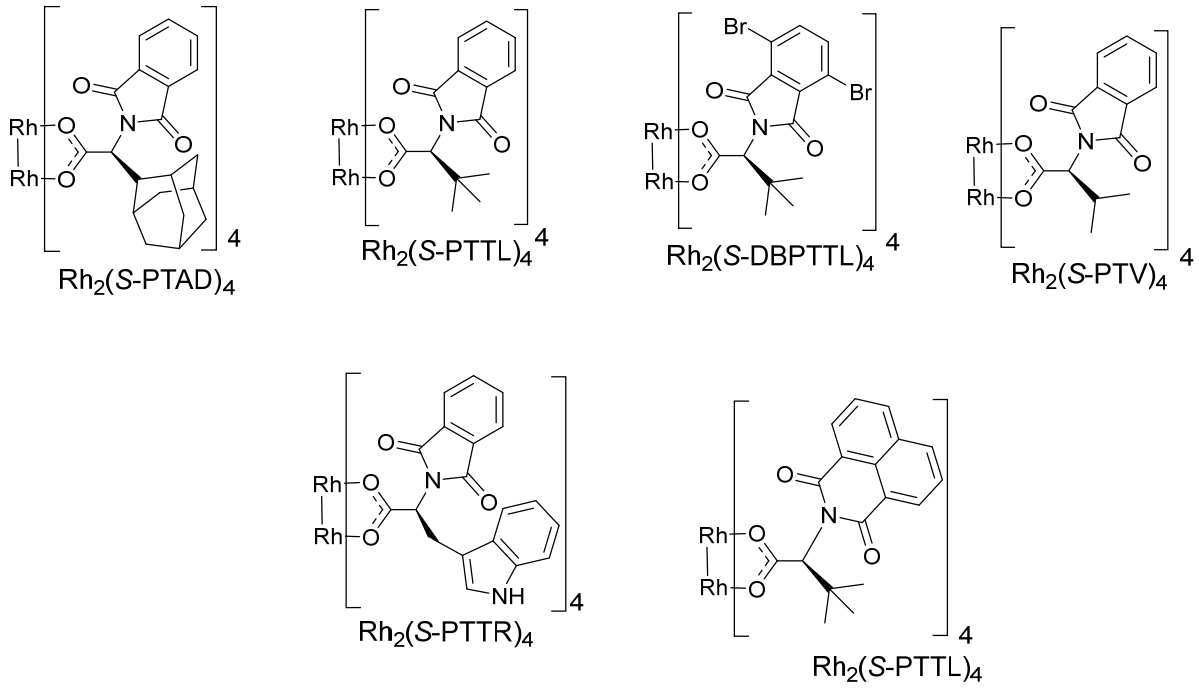
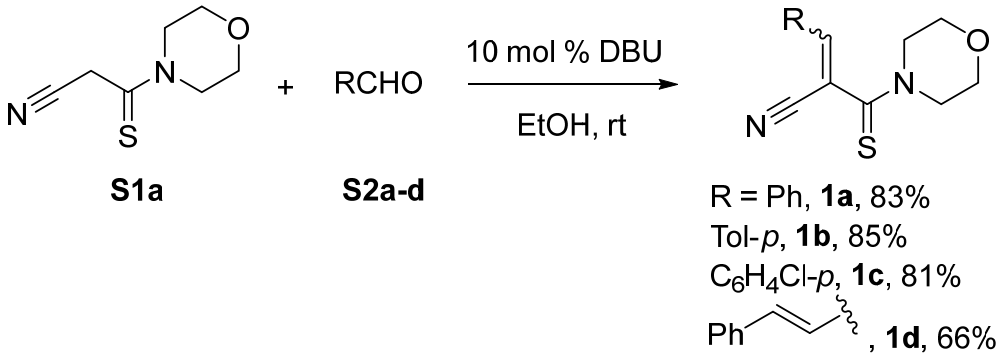


Figure S2. Chiral catalysts were used in the research

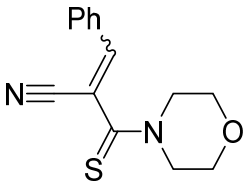
Synthesis of thioamides 1a-p

General procedure for the synthesis of thioamides 1a-d



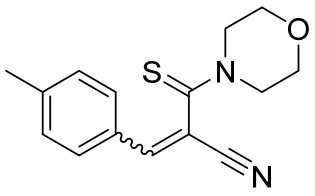
A mixture of 3-morpholino-3-thioxopropanenitrile (**S1a**) (1.0 equiv), appropriate aldehyde **S2a-d** (1.3–1.4 equiv) and DBU (0.1 equiv) in ethanol (2–5 mL) was stirred for 10–18 h at room temperature. The formed precipitate was filtered off and washed with cold ethanol and diethyl ether for **1a-b** or with cold ethanol with subsequent centrifugation with hexane for **1d**. The product **1c** after filtration was washed with ethanol and diethyl ether, the precipitate was dissolved in boiling methanol and filtered off. The mother liquor was evaporated under reduced pressure.

2-(Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**)



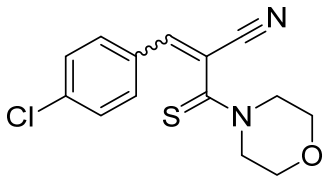
Compound **1a** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (1000 mg, 1.0 equiv, 5.87 mmol), benzaldehyde **S2a** (872 mg, 8.22 mmol, 1.4 equiv), DBU (89 mg, 0.1 equiv, 0.59 mmol), and ethanol (5 mL), reaction time is 15 h. Product **1a** was isolated as a yellow powder (1255 mg, 83%), mp 118–120 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.89 – 7.87 (m, 2H), 7.55 – 7.52 (m, 4H), 4.23 (br. s, 2H), 3.96 (br. s, 2H), 3.78 (br. s, 2H), 3.70 (br. s, 2H). ^{13}C{1H} NMR (150 MHz, DMSO-d_6): δ 189.2, 144.7, 132.3, 131.6, 129.3, 129.1, 116.2, 110.8, 65.9, 65.5, 52.7, 49.6. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{14}H_{14}N_2OSNa^+$ 281.0719; found 281.0719.

(*Z*/*E*)-2-(Morpholine-4-carbonothioyl)-3-(*p*-tolyl)acrylonitrile (**1b**)



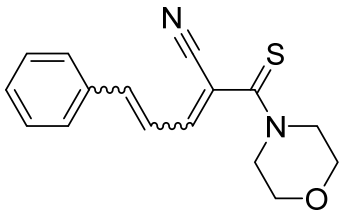
Compound **1b** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (600 mg, 1.0 equiv, 3.52 mmol), 4-methylbenzaldehyde (**S2b**) (593 mg, 4.93 mmol, 1.4 equiv), DBU (54 mg, 0.1 equiv, 0.35 mmol), and ethanol (5 mL), reaction time is 18 h. Product **1b** was isolated as a bright-yellow powder (815 mg, 85%), mp 160–162 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.42 (s, 1H), 7.39 (d, J = 4.2 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.28 – 4.16 (m, 2H), 3.80 – 3.72 (m, 2H), 3.68 – 3.62 (m, 1H), 3.52 – 3.47 (m, 2H), 3.08 – 3.02 (m, 1H), 2.34 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 189.6*, 187.5, 144.9, 142.0*, 141.4, 140.9, 129.7, 129.7, 129.5*, 129.4*, 117.4, 116.3*, 110.5, 109.7*, 65.8*, 65.5*, 65.2, 64.9, 52.7*, 51.4, 49.6*, 48.3, 21.1*, 21.1. HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{15}H_{16}N_2OSNa^+$ 295.0876; found 295.0876.

(*Z*/*E*)-3-(4-Chlorophenyl)-2-(morpholine-4-carbonothioyl)acrylonitrile (1c)



Compound **1c** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (1000 mg, 1.0 equiv, 5.87 mmol), 4-chlorobenzaldehyde (**S2c**) (1073 mg, 7.64 mmol, 1.3 equiv), DBU (89 mg, 0.1 equiv, 0.59 mmol), and ethanol (5 mL), reaction time is 14 h. Product **1c** was isolated as a yellow powder (1390 mg, 81%), mp 194–196 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.58 – 7.50 (m, 4H), 7.45 (s, 1H), 4.26 – 4.16 (m, 2H), 3.81 – 3.65 (m, 3H), 3.54 – 3.49 (m, 2H), 3.08 – 3.04 (m, 1H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 188.9*, 186.8, 143.2, 139.6, 136.1*, 135.7, 131.3, 131.3, 131.2*, 131.0*, 129.3, 129.2*, 117.0, 115.9*, 112.0, 111.3*, 65.3, 64.9, 51.5, 48.3. HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{14}H_{13}ClN_2OSNa^+$ 315.0329; found 315.0327.

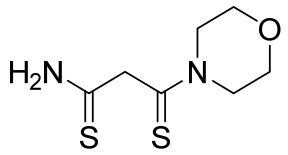
(*Z*/*E*)-2-(Morpholine-4-carbonothioyl)-5-phenylpenta-2,4-dienenitrile (1d)



Compound **1d** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (200 mg, 1.0 equiv, 1.17 mmol), 3-phenylacrylaldehyde (**S2d**) (217 mg, 1.64 mmol, 1.4 equiv), DBU (18 mg, 0.1 equiv, 0.12 mmol), and ethanol (2 mL), reaction time is 10 h. Product **1d** was isolated as a yellow powder (220 mg, 66%), mp 139–141 °C. ^{1}H

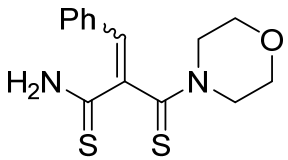
NMR (400 MHz, DMSO-d_6): δ 7.65 (d, J = 7.6 Hz, 2H), 7.47 – 7.34 (m, 5H), 7.15 – 7.09 (m, 1H), 4.32* and 4.20 (both br. s, 2H), 3.91 and 3.81* (both br. s, 2H), 3.73 and 3.64 – 3.61* (br. s and m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 188.9, 186.5*, 146.3, 144.9, 143.7*, 142.1*, 135.1, 135.0*, 130.2, 130.1*, 129.1, 129.0*, 128.0*, 127.9, 123.2, 121.9*, 117.4*, 115.26, 111.9, 110.8*, 66.0, 65.8*, 65.7*, 65.6, 52.8*, 52.0, 49.7*, 48.6. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{16}H_{17}N_2OS^+$ 285.1056; found 285.1056.

3-Morpholino-3-thioxopropanethioamide (1e)



Sodium (40 mg, 0.1 equiv, 1.76 mmol) was dissolved in dry ethanol (35 mL), and the solution was cooled to 0 °C. Then the solution was saturated with hydrogen sulfide obtained from sodium sulfide nonahydrate (50 g) and phosphoric acid (15 mL). The hydrogen sulfide-saturated solution was transferred to an autoclave containing 3-morpholino-3-thioxopropanenitrile (**S1a**) (3000 mg, 1.0 equiv, 17.62 mmol) and stirred at 70 °C for 5 h. The formed suspension was cooled to room temperature and kept in the fridge for 1 h. Filtration of the precipitate and washing with ethanol afforded **1e** in 83% (3000 mg) yield as a colorless powder, mp 167–170 °C (lit.[20] 143–150 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.59 (s, 1H, NH), 9.18 (s, 1H, NH), 4.20 – 4.17 (m, 4H), 3.84 (br. s, 2H), 3.72 – 3.66 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 200.0, 194.3, 65.9, 65.5, 56.7, 51.2, 49.7.

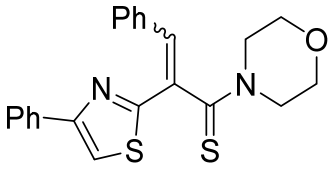
(*Z*/*E*)-2-(Morpholine-4-carbonothioyl)-3-phenylprop-2-enethioamide (1f)



3-Morpholino-3-thioxopropanethioamide (**1e**) (680 mg, 1.0 equiv, 3.33 mmol), benzaldehyde (**S2a**) (494 mg, 1.4 equiv, 4.66 mmol) and DIPEA (43 mg, 0.1 equiv, 0.33 mmol) were dissolved in *n*-butanol (4 mL), and the solution was stirred at 100 °C for 13.5 h. The solvent was evaporated, and the residue was purified by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 25:25) afforded **1f** (33%, 321 mg) as pale-yellow powder, mp 118–120 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.79 (s, 1H, NH), 9.42 (s, 1H, NH), 7.54 (d, J = 7.2 Hz, 2H), 7.43 – 7.35 (m, 3H), 6.86 (s, 1H), 4.24 – 4.14 (m, 2H), 3.73 – 3.61 (m, 2H), 3.58 – 3.51 (m, 2H), 3.31 – 3.27 (m, 1H), 2.87 – 2.82 (m, 1H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 197.0, 196.9*, 193.6, 139.1, 139.1*,

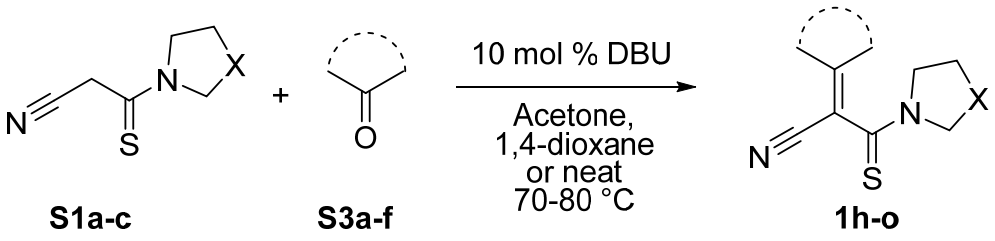
133.9, 129.4, 129.2, 128.8*, 128.7, 125.4, 65.0, 64.8, 51.5, 47.6. HRMS (ESI) m/z: $[M - H]^-$ calcd. for $C_{14}H_{15}N_2OS_2^-$ 291.0631; found 291.0628.

1-Morpholino-3-phenyl-2-(4-phenylthiazol-2-yl)prop-2-ene-1-thione (1g)

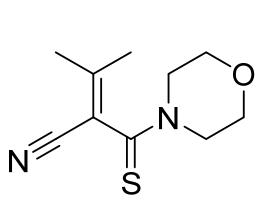


A mixture of 2-(morpholine-4-carbonothioyl)-3-phenylprop-2-enethioamide (**1f**) (100 mg, 1.0 equiv, 0.34 mmol) and freshly prepared 2-bromo-1-phenylethan-1-one (102 mg, 1.5 equiv, 0.51 mmol) in dry ethanol (2 mL) was stirred at room temperature for 3 h. The solvent was evaporated, and the residue was purified by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 40:10). The obtained precipitate was centrifugated with diethyl ether to afford **1g** (71 mg, 53%) as a pale-yellow powder, mp 167–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.94 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.3 Hz, 2H), 7.48 – 7.31 (m, 8H), 4.59 – 4.54 (m, 1H), 4.35 – 4.29 (m, 1H), 3.89 – 3.74 (m, 3H), 3.63 – 3.50 (m, 2H), 3.23 – 3.19 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 195.4, 165.6, 156.2, 134.4, 134.4, 134.0, 129.7, 129.2, 129.0, 128.9, 128.5, 126.9, 126.6, 113.9, 66.3, 66.1, 51.6, 48.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{21}N_2OS_2^+$ 393.1090; found 393.1095.

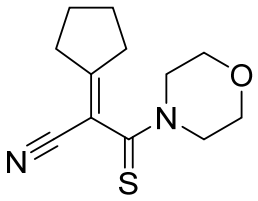
General procedure for the synthesis of thioamides 1h-s



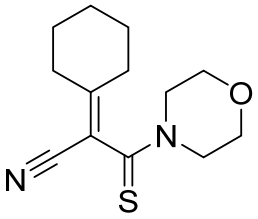
S1a-c **S3a-f** **1h-o**



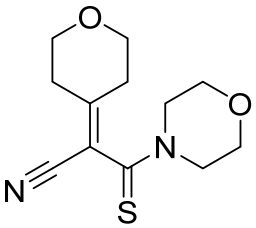
1h, 94%,
14 h, 80 °C



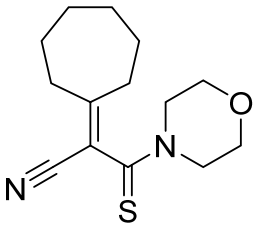
1i, 84%,
24 h, 70 °C



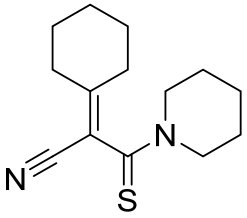
1j, 85%,
16 h, 80 °C



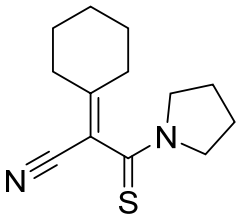
1k, 81%,
24 h, 80 °C



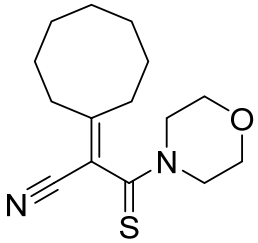
1l, 70%,
23 h, 80 °C



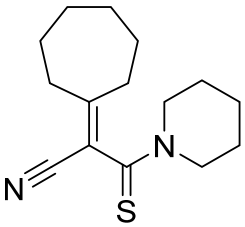
1m, 94%,
14 h, 80 °C



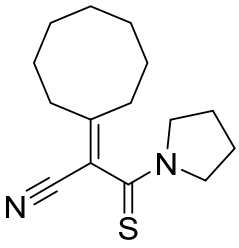
1n, 86%,
21 h, 80 °C



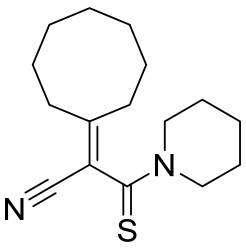
1o, 68%,
48 h, 80 °C



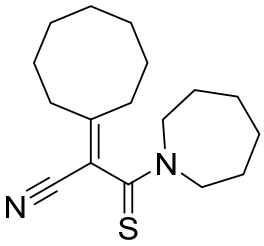
1p, 91%,
40 h, 80 °C



1q, 65%,
24 h, 85 °C



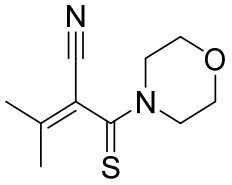
1r, 70%,
24 h, 85 °C



1s, 42%,
44 h, 85 °C

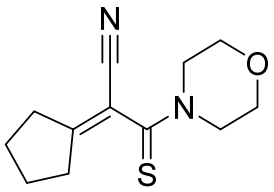
A mixture of 2-cyanothioacemamide **S1a-c** (1.0 equiv), appropriate ketone **S3a-g** (2.5–4.0 equiv) and DBU (0.1–1 equiv) in dry 1,4-dioxane (for **1k**) or in neat (for **1h**,**i**,**j**,**l-s**) was stirred for 14–48 h at 70–85 °C in an oven-dried 10 mL standard microwave vial. The vial was cooled to room temperature, then SiO_2 was added, and the solvent was evaporated under reduced pressure. The purification of the crude product by column chromatography on SiO_2 afforded the desired products **1h-s**.

3-Methyl-2-(morpholine-4-carbonothioyl)but-2-enenitrile (1h)



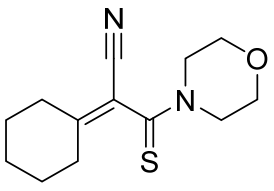
Compound **1h** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (500 mg, 1.0 equiv, 2.94 mmol), acetone **S3a** (2 mL), DBU (45 mg, 0.1 equiv, 0.29 mmol), 80 °C, reaction time is 14 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 40:10 to 20:30) afforded **1h** as a pale-yellow oil (94%, 580 mg). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 4.42 – 4.40 (m, 1H), 4.16 – 4.13 (m, 1H), 3.81 – 3.70 (m, 6H), 2.14 (s, 3H), 1.89 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 189.8, 154.7, 115.3, 111.7, 66.5, 66.2, 51.8, 48.8, 23.9, 21.4. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{10}H_{14}N_2OSNa^+$ 233.0719; found 233.0716.

2-Cyclopentylidene-3-morpholino-3-thioxopropanenitrile (1i)



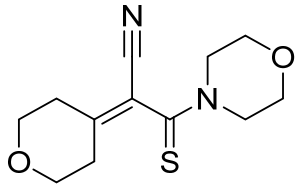
Compound **1i** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (400 mg, 1.0 equiv, 2.35 mmol), cyclopentanone (**S3b**) (791 mg, 4.0 equiv, 9.40 mmol), DBU (36 mg, 0.1 equiv, 0.24 mmol), 70 °C, reaction time is 24 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 50:0 to 30:20) afforded **1i** as a pale-yellow oil (84%, 465 mg) that crystallizes into powder when stored at room temperature, mp 109–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 4.26 (br. s, 2H), 3.82 – 3.74 (m, 6H), 2.69 (t, J = 6.0 Hz, 2H), 2.46 (br. s, 2H), 1.81 – 1.89 (m, 4H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 190.1, 169.2, 115.4, 107.5, 66.7, 66.4, 51.9, 49.0, 34.9, 33.1, 26.4, 25.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{12}H_{17}N_2OS^+$ 237.1056; found 237.1059.

2-Cyclohexylidene-3-morpholino-3-thioxopropanenitrile (1j)



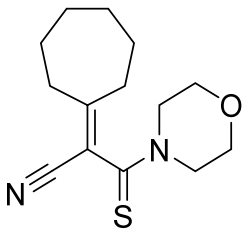
Compound **1j** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (1000 mg, 1.0 equiv, 5.87 mmol), cyclohexanone (**S3c**) (1730 mg, 3.0 equiv, 17.62 mmol), DBU (89 mg, 0.1 equiv, 0.59 mmol), 80 °C, reaction time is 16 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 50:0 to 25:25) afforded **1j** as a pale-yellow oil (85%, 1250 mg) that crystallizes into powder when stored at room temperature, mp 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 4.42 – 4.37 (m, 1H), 4.21 – 4.15 (m, 1H), 3.86 – 3.68 (m, 6H), 2.59 – 2.46 (m, 2H), 2.39 – 2.33 (m, 1H), 2.20 – 2.13 (m, 1H), 1.78 – 1.52 (m, 6H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 189.8, 161.4, 115.1, 108.3, 66.5, 66.3, 51.8, 48.9, 34.2, 31.7, 27.7, 27.1, 25.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{13}H_{19}N_2OS^+$ 251.1212; found 251.1214.

3-Morpholino-2-(tetrahydro-4*H*-pyran-4-ylidene)-3-thioxopropanenitrile (1k)



Compound **1k** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (300 mg, 1.0 equiv, 1.76 mmol), tetrahydro-4*H*-pyran-4-one (**S3d**) (529 mg, 3.0 equiv, 5.29 mmol), DBU (27 mg, 0.1 equiv, 0.18 mmol), 1,4-dioxane (1 mL), 80 °C, reaction time is 24 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 50:0 to 25:25) afforded **1k** as a colorless powder (81%, 360 mg), mp 191–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 4.45 – 4.41 (m, 1H), 4.17 – 4.12 (m, 1H), 3.87 – 3.72 (m, 10H), 2.73 – 2.57 (m, 3H), 2.34 – 2.29 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 188.6, 156.0, 114.6, 110.0, 68.1, 67.5, 66.5, 66.4, 52.0, 49.0, 34.5, 32.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{12}H_{17}N_2O_2S^+$ 253.1005; found 253.1005.

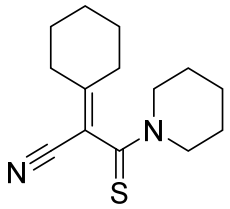
2-Cycloheptylidene-3-morpholino-3-thioxopropanenitrile (1l)



Compound **1l** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (300 mg, 1.0 equiv, 1.76 mmol), cycloheptanone (**S3e**) (593 mg, 3.0 equiv, 17.62 mmol), DBU (27 mg, 0.1 equiv, 0.18 mmol), 80 °C, reaction time is 23 h. The

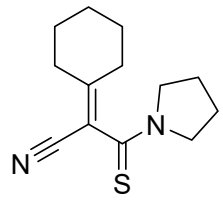
purification of the crude product by column chromatography (PE/EtOAc, gradient 50:0 to 35:15) afforded **1l** as a yellow oil (70%, 326 mg) that crystallizes into powder when stored at room temperature, mp 99–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 4.48 – 4.42 (m, 1H), 4.17 – 4.11 (m, 1H), 3.86 – 3.76 (m, 4H), 3.73 – 3.65 (m, 2H), 2.74 – 2.56 (m, 3H), 2.31 – 2.25 (m, 1H), 1.78 – 1.71 (m, 3H), 1.59 (br. s, 4H), 1.50 – 1.44 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 190.3, 164.0, 115.3, 110.9, 66.6, 66.4, 51.8, 48.8, 35.4, 33.1, 29.8, 29.0, 27.2, 25.9. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{14}H_{21}N_2OS^+$ 265.1369; found 265.1374.

2-Cyclohexylidene-3-(piperidin-1-yl)-3-thioxopropanenitrile (1m)



Compound **1m** was obtained according to the general procedure from 3-(piperidin-1-yl)-3-thioxopropanenitrile (**S1b**) (350 mg, 1.0 equiv, 2.08 mmol), cyclohexanone (**S3c**) (612 mg, 3.0 equiv, 6.24 mmol), DBU (32 mg, 0.1 equiv, 0.21 mmol), 80 °C, reaction time is 14 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 100:0 to 85:15) afforded **1m** as a pale-yellow powder (94%, 484 mg), mp 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 4.32 – 4.29 (m, 1H), 4.14 – 4.10 (m, 1H), 3.79 – 3.75 (m, 1H), 3.67 – 3.62 (m, 1H), 2.52 (br. s, 2H), 2.37 – 2.31 (m, 1H), 2.20 – 2.14 (m, 1H), 1.73 (br. s, 8H), 1.65 – 1.48 (m, 4H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 188.5, 160.0, 115.3, 108.9, 52.7, 50.0, 34.1, 31.7, 27.7, 27.1, 26.8, 25.6, 25.3, 24.0. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{14}H_{21}N_2S^+$ 249.1420; found 249.1422.

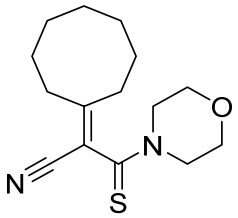
2-Cyclohexylidene-3-(pyrrolidin-1-yl)-3-thioxopropanenitrile (1n)



Compound **1n** was obtained according to the general procedure from 3-(pyrrolidin-1-yl)-3-thioxopropanenitrile (**S1c**) (400 mg, 1.0 equiv, 2.59 mmol), cyclohexanone (**S3c**) (764 mg, 3.0 equiv, 7.78 mmol), DBU (39 mg, 0.1 equiv, 0.26 mmol), 80 °C, reaction time is 21 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 100:0 to 80:20) afforded **1n** as a colorless powder (86%, 526 mg), mp 84–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*):

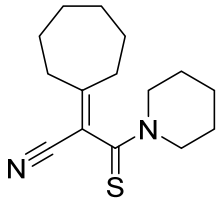
δ 3.82 – 3.52 (m, 4H), 2.52 (br. s, 2H), 2.31 (br. s, 2H), 2.06 (br. s, 2H), 1.73 – 1.61 (m, 6H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 186.7, 161.4, 115.1, 110.0, 53.0, 52.3, 34.2, 31.7, 27.8, 27.2, 26.3, 25.6, 24.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{13}H_{19}N_2S^+$ 235.1263; found 235.1265.

2-Cyclooctylidene-3-morpholino-3-thioxopropanenitrile (1o)



Compound **1o** was obtained according to the general procedure from 3-morpholino-3-thioxopropanenitrile (**S1a**) (360 mg, 1.0 equiv, 2.11 mmol), cyclooctanone (**S3f**) (801 mg, 3.0 equiv, 6.34 mmol), DBU (32 mg, 0.1 equiv, 0.21 mmol), 80 °C, reaction time is 48 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 100:0 to 70:30) afforded **1o** as a pale-yellow oil (68%, 401 mg) that crystallizes into powder when stored at room temperature, mp 117–119 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 4.45 – 4.40 (m, 1H), 4.20 – 4.14 (m, 1H), 3.84 – 3.75 (m, 4H), 3.72 – 3.63 (m, 2H), 2.69 – 2.63 (m, 1H), 2.50 – 2.42 (m, 2H), 2.25 – 2.19 (m, 1H), 1.93 – 1.84 (m, 2H), 1.80 – 1.76 (m, 2H), 1.66 – 1.60 (m, 1H), 1.56 – 1.43 (m, 5H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 190.4, 165.6, 115.4, 109.8, 66.6, 66.4, 51.7, 48.7, 33.2, 33.0, 29.2, 28.0, 25.6, 25.1, 23.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{15}H_{23}N_2OS^+$ 279.1525; found 279.1528.

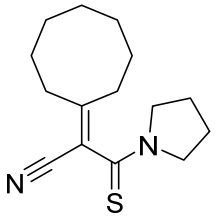
2-Cycloheptylidene-3-(piperidin-1-yl)-3-thioxopropanenitrile (1p)



Compound **1p** was obtained according to the general procedure from 3-(piperidin-1-yl)-3-thioxopropanenitrile (**S1b**) (300 mg, 1.0 equiv, 1.78 mmol), cycloheptanone (**S3e**) (600 mg, 3.0 equiv, 5.35 mmol), DBU (27 mg, 0.1 equiv, 0.18 mmol), 80 °C, reaction time is 40 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 100:0 to 70:30) afforded **1p** as a pale-yellow oil (91%, 468 mg) that crystallizes into powder when stored at room temperature, mp 87–88 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 4.42 – 4.36 (m, 1H), 4.05 – 3.99 (m, 1H), 3.82 – 3.76 (m, 1H), 3.63 – 3.57 (m, 1H), 2.70 – 2.53 (m, 3H), 2.31 – 2.24 (m, 1H), 1.78 –

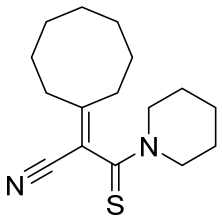
1.54 (m, 13H), 1.48 – 1.42 (m, 1H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 188.9, 162.5, 115.4, 111.5, 52.6, 49.9, 35.2, 32.9, 29.8, 29.0, 27.1, 26.8, 25.9, 25.3, 24.0. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{15}H_{23}N_2S^+$ 263.1576; found 263.1576.

2-Cyclooctylidene-3-(pyrrolidin-1-yl)-3-thioxopropanenitrile (1q)



Compound **1q** was obtained according to the general procedure from 3-(pyrrolidin-1-yl)-3-thioxopropanenitrile (**S1c**) (500 mg, 1.0 equiv, 3.24 mmol), cyclooctanone (**S3f**) (1023 mg, 2.5 equiv, 8.10 mmol), DBU (493 mg, 1 equiv, 3.24 mmol), 85 °C, reaction time is 24 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 50:0 to 42:8) afforded **1q** as a pale-yellow oil (65%, 558 mg) that crystallizes into powder when stored at room temperature, mp 81–83 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 3.86 – 3.83 (m, 2H), 3.62 (br s, 2H), 2.58 (br s, 2H), 2.40 (br s, 2H), 2.09 – 2.06 (m, 4H), 1.92 – 1.86 (m, 2H), 1.80 – 1.76 (m, 2H), 1.50 (br s, 6H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 187.2, 165.6, 115.3, 111.5, 52.8, 52.0, 33.2, 32.8, 28.9, 27.9, 26.3, 25.7, 25.2, 24.4, 23.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{15}H_{23}N_2S^+$ 263.1576; found 263.1575.

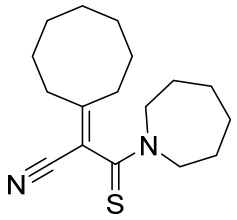
2-Cyclooctylidene-3-(piperidin-1-yl)-3-thioxopropanenitrile (1r)



Compound **1r** was obtained according to the general procedure from 3-(piperidin-1-yl)-3-thioxopropanenitrile (**S1b**) (500 mg, 1.0 equiv, 2.97 mmol), cyclooctanone (**S3f**) (1125 mg, 3.0 equiv, 8.91 mmol), DBU (821 mg, 1 equiv, 2.97 mmol), 85 °C, reaction time is 24 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 100:0 to 82:18) afforded **1r** as a pale-yellow oil (70%, 573 mg) that crystallizes into powder when stored at room temperature, mp 114–116 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 4.40 – 4.35 (m, 1H), 4.09 – 4.03 (m, 1H), 3.79 – 3.74 (m, 1H), 3.63 – 3.57 (m, 1H), 2.67 – 2.61 (m, 1H), 2.50 – 2.41 (m, 1H), 2.26 – 2.19 (m, 1H), 1.95 – 1.82 (m, 2H), 1.81 – 1.68 (m, 7H), 1.66 – 1.58 (m, 2H), 1.56 – 1.38 (m, 5H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 189.1, 164.0, 115.6, 110.5, 52.6, 49.9, 33.1, 32.9,

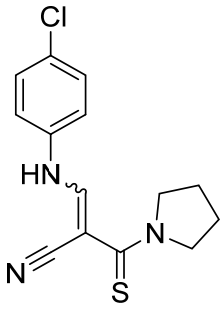
29.1, 28.0, 26.8, 25.6, 25.3, 25.1, 24.1, 23.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{16}H_{25}N_2S^+$ 277.1733; found 277.1733.

3-(Azepan-1-yl)-2-cyclooctylidene-3-thioxopropanenitrile (1s)



Compound **1s** was obtained according to the general procedure from 3-(azepan-1-yl)-3-thioxopropanenitrile (**S1d**) (500 mg, 1.0 equiv, 2.74 mmol), cyclooctanone (**S3f**) (1038 mg, 3.0 equiv, 8.23 mmol), DBU (417 mg, 1 equiv, 2.74 mmol), 85 °C, reaction time is 40 h. The purification of the crude product by column chromatography (PE/EtOAc, gradient 50:0 to 42:8) afforded **1s** as a pale-yellow oil (42%, 338 mg) that crystallizes into powder when stored at room temperature, mp 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 4.24 – 4.18 (m, 1H), 3.97 – 3.90 (m, 1H), 3.86 – 3.80 (m, 1H), 3.65 – 3.58 (m, 1H), 2.68 – 2.62 (m, 1H), 2.52 – 2.40 (m, 2H), 2.20 – 2.13 (m, 1H), 2.05 – 1.95 (m, 1H), 1.93 – 1.81 (m, 4H), 1.79 – 1.73 (m, 3H), 1.67 – 1.58 (m, 4H), 1.57 – 1.37 (m, 6H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 190.3, 163.8, 115.7, 110.9, 53.8, 52.8, 33.0, 32.9, 29.4, 28.7, 28.1, 27.8, 26.1, 25.5, 25.4, 25.1, 22.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{27}N_2S^+$ 291.1889; found 291.1887.

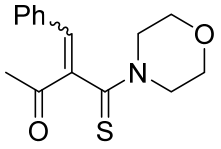
(*Z*/*E*)-3-((4-Chlorophenyl)amino)-2-(pyrrolidine-1-carbonothioyl)acrylonitrile (1t)



To a solution of 3-(dimethylamino)-2-(pyrrolidine-1-carbonothioyl)acrylonitrile (**S1d**) (261 mg, 1.0 equiv, 1.25 mmol), 4-chloroaniline (175 mg, 1.1 equiv, 1.375 mmol) in EtOH (5 mL) concentrated HCl (127 mg, 1.0 equiv, 1.25 mmol) was added and the mixture was stirred for 3 h at 60 °C. The suspension was cooled down to room temperature, filtered and washed with EtOH afforded **1p** as a yellow powder (65%, 238 mg), mp 159–161 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.52* and 10.46 (both d, J = 13.4* and 12.1 Hz, 1H), 8.52 and 7.95* (both d, J = 11.1 and 13.3* Hz, 1H), 7.42 – 7.34 (m, 4H), 3.81 – 3.72 (m, 4H), 1.96 (br. s, 4H). ^{13}C{1H} NMR (100 MHz,

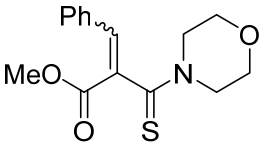
DMSO-d_6): δ 186.9, 183.8*, 152.2, 144.3*, 139.2, 138.6*, 129.4, 129.3*, 128.0, 127.4*, 119.2*, 119.1, 118.3*, 116.2, 86.9, 85.6*, 55.1, 53.4*, 53.3, 52.7*, 26.6, 26.0*, 24.0, 23.8*. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{14}H_{15}ClN_3S^+$ 292.0670; found 292.0672.

3-(Morpholine-4-carbonothioyl)-4-phenylbut-3-en-2-one (1w)



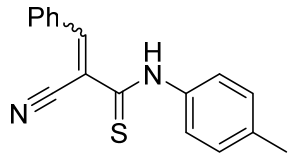
A mixture of 4-morpholino-4-thioxobutan-2-one (**S1f**) (374 mg, 1.0 equiv, 2.0 mmol), benzaldehyde **S2a** (261 mg, 1.25 equiv, 2.5 mmol), DBU (30 mg, 0.1 equiv, 0.20 mmol) and glacial acetic acid (12 mg, 0.1 equiv, 0.20 mmol) in toluene (3 mL) was stirred for 16 h at 80 °C. The solvent was evaporated under reduced pressure. Ethanol (3 mL) was added to a residue and the formed suspension was kept in the fridge for 1 h. The precipitate was filtered off and washed with cold ethanol afforded **1w** as a yellow powder (57%, 315 mg), mp 131–133 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.65 – 7.63 (m, 2H), 7.48 – 7.40 (m, 3H), 7.36 (s, 1H), 4.35 – 4.30 (m, 1H), 4.27 – 4.21 (m, 1H), 3.77 – 3.65 (m, 2H), 3.62 – 3.54 (m, 1H), 3.50 – 3.44 (m, 2H), 3.13 – 3.07 (m, 1H), 2.43 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 195.5, 194.3, 139.6, 133.8, 133.2, 130.2, 128.8, 65.5, 65.2, 51.1, 47.7, 26.6. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{15}H_{18}NO_2S^+$ 276.1053; found 276.1053.

Methyl 2-(morpholine-4-carbonothioyl)-3-phenylacrylate (1x)



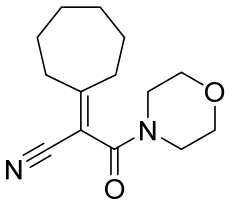
A mixture of methyl 3-morpholino-3-thioxopropanoate (**S1g**) (406 mg, 1.0 equiv, 2.0 mmol), benzaldehyde **S2a** (233 mg, 1.10 equiv, 2.2 mmol), DBU (30 mg, 0.1 equiv, 0.20 mmol) and glacial acetic acid (12 mg, 0.1 equiv, 0.20 mmol) in toluene (4 mL) was stirred for 16 h at 80 °C. The solvent was evaporated under reduced pressure. Ethanol (3 mL) was added to a residue and the formed suspension was kept in the fridge for 1 h. The precipitate was filtered off and washed with cold ethanol afforded **1x** as a yellow powder (71%, 412 mg), mp 138–139 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.62 – 7.60 (m, 2H), 7.47 – 7.43 (m, 3H), 7.35 (s, 1H), 4.30 – 4.27 (m, 2H), 3.77 (s, 3H), 3.73 – 3.63 (m, 3H), 3.58 – 3.47 (m, 2H), 3.20 – 3.14 (m, 1H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 192.4, 164.4, 134.3, 132.8, 131.0, 130.1, 128.8, 65.4, 65.1, 52.5, 51.3, 47.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{15}H_{18}NO_3S^+$ 292.1002; found 292.1001.

2-Cyano-3-phenyl-*N*-(*p*-tolyl)prop-2-enethioamide (1y)



A mixture of 2-cyano-*N*-(*p*-tolyl)ethanethioamide (**S1e**) (1000 mg, 1.0 equiv, 5.25 mmol), benzaldehyde **S2a** (781 mg, 1.4 equiv, 7.36 mmol) and DBU (80 mg, 0.1 equiv, 5.25 mmol) in ethanol (5 mL) was stirred for 15 h at room temperature. The formed suspension was kept in the fridge for 1 h. The precipitate was filtered off and washed with cold ethanol. The product was recrystallized from ethanol and filtered off. The mother liquor was evaporated under reduced pressure and the formed precipitate was filtered off and washed with cold ethanol afforded **1y** as a bright-red powder (27%, 400 mg), mp 131–132 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.02 (s, 1H), 8.02 (s, 1H), 8.00 – 7.97 (m, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.61 – 7.55 (m, 3H), 7.26 (d, J = 8.1 Hz, 2H), 2.33 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 188.4, 145.5, 136.6, 136.1, 132.1, 132.0, 130.0, 129.2, 129.1, 123.8, 116.5, 114.2, 20.7. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{15}N_2S^+$ 279.0950; found 279.0950.

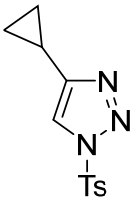
2-Cycloheptylidene-3-morpholino-3-oxopropanenitrile (Am-1)



A mixture of 3-morpholino-3-oxopropanenitrile (300 mg, 1.0 equiv, 1.94 mmol), cycloheptanone (**S3e**) (873 mg, 4.0 equiv, 7.78 mmol) and DBU (30 mg, 0.1 equiv, 0.19 mmol) was stirred for 24 h at 80 °C in an oven-dried 10 mL standard microwave vial. The vial was cooled to room temperature. The purification of the crude product by column chromatography on SiO_2 afforded **Am-1** as a white powder (75%, 364 mg), mp 60–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 3.70 – 3.65 (m, 3H), 3.51 – 3.49 (m, 1H), 2.71 – 2.68 (m, 1H), 2.50 – 2.47 (m, 1H), 1.76 – 1.65 (m, 2H), 1.60 – 1.53 (m, 2H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 171.1, 161.9, 115.2, 105.9, 66.8, 47.4, 42.5, 35.8, 33.7, 29.4, 29.1, 26.8, 26.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{14}H_{21}N_2O_2^+$ 249.1597; found 249.1599.

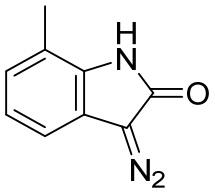
Synthesis of 1-Sulfonyl-1,2,3-Triazole 2g and Diazo Compounds 2p,s-v

4-Cyclopropyl-1-tosyl-1*H*-1,2,3-triazole (2g)



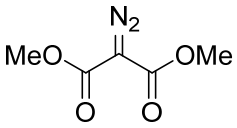
To a solution of ethynylcyclopropane (500 mg, 1.0 equiv, 7.56 mmol) and CuTC (144 mg, 0.1 equiv, 0.76 mmol) in toluene (17 mL) tosyl azide (1490 mg, 1.0 equiv, 7.56 mmol) in toluene (10 mL) was added dropwise at room temperature and the solution was stirred for 2 h. The solvent was evaporated, and the formed precipitate was triturated with the mixture of PE/DCM (8:1). Purification of the crude product by flash chromatography (PE/EtOAc, gradient 50:0 to 40:10) afforded **2g** (70%, 1390 mg) as a colorless powder, mp 105–106 °C (lit.[16] 105–106 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.96 (d, J = 8.3 Hz, 2H), 7.79 (s, 1H), 7.36 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H), 1.96 – 1.89 (m, 1H), 0.99 – 0.94 (m, 2H), 0.88 – 0.84 (m, 2H).

3-Diazo-7-methylindolin-2-one (2p)



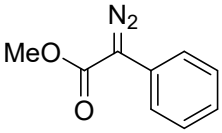
3-Diazo-7-methylindolin-2-one (**2p**) was purchased from a commercial source. Mp 178–176 °C (decomp.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.68 (br. s, 1H), 7.23 (d, J = 4.4 Hz, 1H), 6.92 (d, J = 4.4 Hz, 2H), 2.23 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 168.2, 131.2, 126.4, 121.3, 119.4, 116.7, 116.5, 60.2, 16.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_9H_8N_3O^+$ 174.0662; found 174.0661.

Dimethyl 2-diazomalonate (2s)



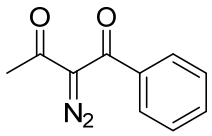
To a solution of dimethyl malonate (500 mg, 1.0 equiv, 3.78 mmol) and Et_3N (383 mg, 1.0 equiv, 3.78 mmol) in acetonitrile (10 mL) tosyl azide (830 mg, 1.1 equiv, 4.16 mmol) in acetonitrile (10 mL) was added dropwise at 0 °C and the solution was stirred for 16 h at room temperature. The solvent was evaporated, and the formed precipitate was triturated CCl_4 and filtered off. The mother liquor was evaporated under reduced pressure. The residue was dissolved in DCM and purified by flash chromatography (DCM/EtOAc, gradient 25:0 to 24:1) afforded **2s** (93%, 557 mg) as a pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$-d): δ 3.83 (s, 6H).

Methyl 2-diazo-2-phenylacetate (2t)



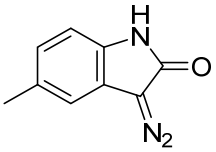
Red oil. ^{1}H NMR (400 MHz, $CDCl_3$-d): δ 7.48 (d, J = 8.3 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 3.87 (s, 3H).

2-Diazo-1-phenylbutane-1,3-dione (2u)



To a solution of 1-phenylbutane-1,3-dione (300 mg, 1.0 equiv, 1.85 mmol) and Et_3N (187 mg, 1.0 equiv, 1.85 mmol) in acetonitrile (4 mL) mesyl azide (246 mg, 1.1 equiv, 2.03 mmol) in acetonitrile (7 mL) was added dropwise at 0 °C and the solution was stirred for 16 h at room temperature. The solvent was evaporated, and the residue was dissolved in minimal volume of DCM and purified by flash chromatography (PE/EtOAc, gradient 9:1 to 4:1) afforded **2u** (80%, 280 mg) as a pale-yellow solid, mp 62–63 °C (lit.[27] 63.5–64.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.64 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 2.58 (s, 3H).

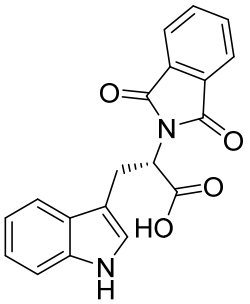
3-Diazo-5-methylindolin-2-one (2v)



Red powder, mp 178–180 °C (lit.[28] 184–185 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.53 (s, 1H), 7.21 (s, 1H), 6.90 (d, J = 7.9 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 2.27 (s, 3H).

Synthesis of catalysts Rh_2(*S*-DBPTTL)$_4$ and Rh_2(*S*-PTTR)$_4$

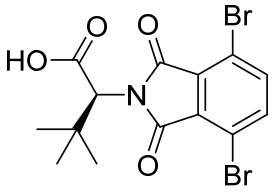
(*S*)-2-(1,3-Dioxoisoindolin-2-yl)-3-(1*H*-indol-3-yl)propanoic acid (L1)



A 50 mL round-bottom flask was charged with *L*-tryptophan (1000 mg, 4.9 mmol), phthalic anhydride (725 mg, 1.0 equiv, 4.9 mmol), triethylamine (50 mg, 0.1 equiv, 0.49 mmol), toluene (25 mL) and equipped with a Dean-Stark apparatus. The mixture was heated to reflux and stirred for 18 h. The solvent was evaporated and the crude product was purified by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 25:25) afforded after trituration in diethyl ether and *n*-hexane and filtration **L1** as a yellow powder (72%, 1182 mg), mp 172–174 °C (lit.[22] 170 °C), $[\alpha]_D^{20} = -184$ (C = 0.49, EtOH) (lit.[29] $[\alpha]_D^{20} = -212$ (C = 1, EtOH)) ^{1}H NMR (400

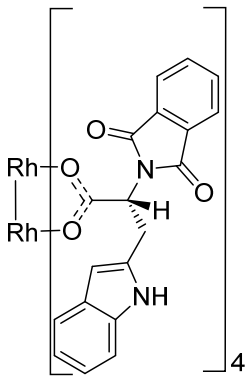
MHz, DMSO-d_6): δ 13.30 (s, 1H), 10.73 (s, 1H), 7.81 (s, 3H), 7.48 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.03 – 6.98 (m, 2H), 6.89 (t, J = 7.4 Hz, 1H), 5.14 – 5.10 (m, 1H), 3.62 – 3.54 (m, 2H).

(*S*)-2-(4,7-Dibromo-1,3-dioxoisoindolin-2-yl)-3,3-dimethylbutanoic acid (L2)



A 50 mL round-bottom flask was charged with *L-tert*-leucine (500 mg, 3.8 mmol), 4,7-dibromoisobenzofuran-1,3-dione (**S3**) (1170 mg, 1.0 equiv, 3.8 mmol), triethylamine (38 mg, 0.1 equiv, 0.38 mmol), dry toluene (15 mL) and equipped with a Dean-Stark apparatus. The mixture was heated to reflux and stirred for 15 h. The solvent was evaporated, and the crude product was purified by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 35:15) afforded after trituration in *n*-hexane and centrifugation **L2** as a colorless powder (80%, 1284 mg), mp 195–197 °C, $[\alpha]_D^{20} = +20{,}4$ (C = 1.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 10.67 (br. s, 1H), 8.10 (s, 2H), 4.69 (s, 1H), 1.16 (s, 9H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 173.6, 166.1, 131.9, 131.4, 128.9, 60.4, 35.9, 28.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{14}H_{14}Br_2NO_4^+$ 417.9285; found 417.9283.

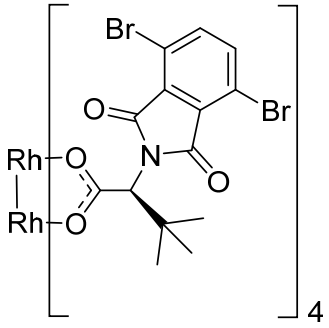
Rh_2(*S*-PTTR)$_4$



To a mixture of $Rh_2(OAc)_4$ (100 mg, 1.0 equiv, 0.23 mmol) and (*S*)-PTTR (454 mg, 6.0 equiv, 1.36 mmol) was added dry chlorobenzene (25 mL). The flask was adapted with a Soxhlet extractor containing a cartridge filled with a mixture of Na_2CO_3 and sand (1:1). The solution was heated to 150 °C for 24 h. The reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was dissolved in acetonitrile, concentrated under reduced pressure, then dissolved in ethyl acetate, the obtained solution was heated to reflux and filtered

off. The mother liquor was cooled down and washed with saturated solution of Na_2CO_3 (3 times) and with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The green residue was then dissolved in DCM and was purified by column chromatography on SiO_2 (DCM/EtOAc, gradient 30:0 to 25:5) to provide the title product as a green solid (256 mg, 73%), $[\alpha]_D^{20} = -5{,}1$ (C = 0.7, MeCN). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 10.74 (s, 4H, NH), 7.78 – 7.76 (m, 8H), 7.70 – 7.68 (m, 8H), 7.56 (d, *J* = 7.8 Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 4H), 7.07 (s, 4H), 7.01 (t, *J* = 7.5 Hz, 4H), 6.90 (t, *J* = 7.4 Hz, 4H), 5.21 (t, *J* = 7.9 Hz, 4H), 3.56 (d, *J* = 7.6 Hz, 8H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 188.5, 166.8, 136.0, 134.6, 130.9, 127.1, 123.4, 123.1, 120.9, 118.3, 118.0, 111.4, 109.7, 53.8, 24.7. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{76}H_{53}N_8O_{16}Rh_2^+$ 1539.1684; found 1539.1697.

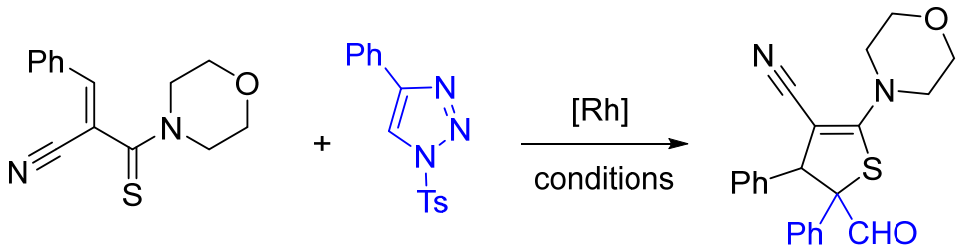
Rh$_2$(*S*-DBPTTL)$_4$



To a mixture of $Rh_2(OAc)_4$ (70 mg, 1.0 equiv, 0.16 mmol) and (*S*)-DBPTTL (398 mg, 6.0 equiv, 0.95 mmol) was added dry chlorobenzene (15 mL). The flask was adapted with a Soxhlet extractor containing a cartridge filled with a mixture of Na_2CO_3 and sand (1:1). The solution was heated to 150 °C for 24 h. The reaction mixture was cooled down and concentrated under reduced pressure. The residue was dissolved in DCM and washed with saturated solution of Na_2CO_3 (3 times) and with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The green residue was then dissolved in DCM and was purified by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 36:14) to provide the title product as a light green solid (281 mg, 95%), $[\alpha]_D^{20} = +55{,}3$ (C = 0.07, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.05 (br. s, 8H), 4.82 (s, 4H), 1.08 (s, 36H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 187.2, 166.1, 131.7, 131.5, 128.7, 62.0, 35.7, 28.0. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{56}H_{48}Br_8N_4O_{16}Rh_2Na^+$ 1892.4539; found 1892.4535.

Optimization study for the reaction of thioamide 1a with 1-sulfonyl-1,2,3-triazole 2a

Table S1. Optimization of the synthesis of dihydrothiophene **3aa**



1a **2a** **3aa**

Entry	Solvent (T, °C)	Catalyst (mol %)	Time, h	Equiv of 2a	Yield[a], %	dr[b]
1	$CHCl_3$ (80)	$Rh_2(Oct)_4$ (2.0)	13	1.1	52	83:17
2	$CHCl_3$ (80)	$Rh_2(OAc)_4$ (2.0)	13	1.1	35	75:25
3	$CHCl_3$ (80)	$Rh_2(esp)_2$ (2.0)	13	1.1	75	83:17
4	$CHCl_3$ (80)	$Rh_2(Piv)_4$ (2.0)	13	1.1	81	83:17
5	1,2-DCE (80)	$Rh_2(Piv)_4$ (2.0)	13	1.1	68	81:19
6	C_6H_6 (80)	$Rh_2(Piv)_4$ (2.0)	13	1.1	60	83:17
7	$CHCl_3$ (70)	$Rh_2(Piv)_4$ (2.0)	13	1.1	70	83:17
8	$CHCl_3$ (50)	$Rh_2(Piv)_4$ (2.0)	13	1.1	51	76:24
9	$CHCl_3$ (40)	$Rh_2(Piv)_4$ (2.0)	13	1.1	44	70:30
10	$CHCl_3$ (80)	Rh_2(*S*-PTAD)$_4$ (1.0)	13	1.1	NR	–
11	$CHCl_3$ (90)	Rh_2(*S*-PTAD)$_4$ (1.0)	13	1.1	NR	–
12	$CHCl_3$ (100)	Rh_2(*S*-PTAD)$_4$ (1.0)	13	1.1	NR	–
13	$CHCl_3$ (100)	Rh_2(*S*-DOSP)$_4$ (1.0)	13	1.1	NR	–
14	$CHCl_3$ (100)	Rh_2(*S*-PTTL)$_4$ (1.0)	13	1.1	NR	–
15	$CHCl_3$ (100)	Rh_2(*S*-NTTL)$_4$ (1.0)	13	1.1	NR	–

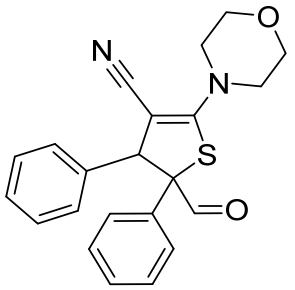
Conditions: thioamide **1a** (0.19 mmol), triazole **2a** (0.21 mmol, 1.1 equiv), solvent (1 mL).
[a]Isolated yields. [b](4*RS*,5*SR*:4*RS*,5*RS*). Determined by ^{1}H NMR analysis of the crude mixture.

Synthesis of dihydrothiophenes 3

General procedure for the synthesis of dihydrothiophenes 3

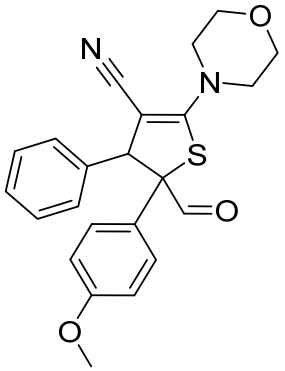
To an oven-dried 10 mL standard microwave vial, a mixture of rhodium (II) pivalate dimer (2.0 mol %), thioamide **1** (1.0 equiv), 1-sulfonyl-1,2,3-triazole **2** (1.1–1.5 equiv) and dry chloroform (1–1.5 mL) were added. The resulting solution was stirred for 9–17 h at 80 °C. Reaction solution was cooled down to room temperature and directly transferred on SiO_2 or neutral alumina (for **3da**) and purified.

(4*RS*,5*SR*)-5-Formyl-2-morpholino-4,5-diphenyl-4,5-dihydrothiophene-3-carbonitrile (3aa)



Compound **3aa** was obtained according to the general procedure from 2-(morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), 1-sulfonyl-1,2,3-triazole **2a** (64 mg, 1.1 equiv, 0.21 mmol), $Rh_2(Piv)_4$ (2.6 mg), chloroform (1 mL), 80 °C, reaction time is 13 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 35:15) afforded **3aa** as a colorless powder (81%, 59 mg), mp 213–214 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.43 (s, 1H), 7.21 – 7.18 (m, 3H), 7.13 – 7.02 (m, 7H), 4.88 (s, 1H), 3.73 – 3.71 (m, 4H), 3.65 – 3.61 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-*d*$_6$): δ 188.7, 159.2, 137.1, 130.1, 128.7, 128.6, 128.5, 128.1, 128.0, 127.3, 118.4, 75.2, 73.5, 65.5, 55.0, 50.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{21}N_2O_2S^+$ 377.1318; found 377.1320.

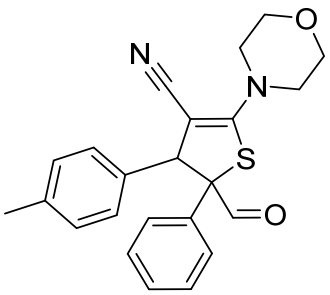
(4*RS*,5*SR*)-5-Formyl-5-(4-methoxyphenyl)-2-morpholino-4-phenyl-4,5-dihydrothiophene-3-carbonitrile (3ac)



Compound **3ac** was obtained according to the general procedure from 2-(morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), 1-sulfonyl-1,2,3-triazole **2c** (70 mg, 1.1 equiv, 0.21 mmol), $Rh_2(Piv)_4$ (2.6 mg), chloroform (1 mL), 80 °C, reaction time is 13 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 24:1) afforded **3ac** as a colorless gum. It was triturated with *n*-hexane and centrifugated afforded **3ac** as a colorless powder (85%, 53 mg), mp 174–179 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 9.35 (s, 1H), 7.10 – 7.06 (m, 3H), 7.01 – 6.99 (m, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 4.84 (s, 1H), 3.82 – 3.77 (m, 4H), 3.73 – 3.62 (m, 7H). ^{13}C{1H} NMR

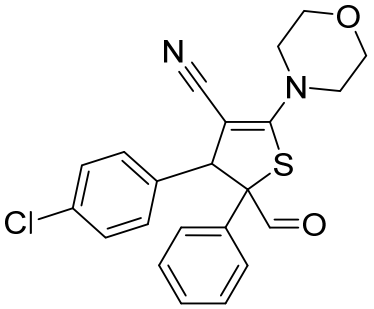
(100 MHz, $CDCl_3$-*d*): δ 188.1, 159.8, 159.3, 136.8, 129.5, 128.9, 128.2, 127.6, 121.6, 118.3, 114.2, 77.4, 73.9, 66.4, 55.9, 55.3, 50.9. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{23}N_2O_3S^+$ 407.1424; found 407.1425.

(4*RS*,5*SR*)-5-Formyl-2-morpholino-5-phenyl-4-(*p*-tolyl)-4,5-dihydrothiophene-3-carbonitrile (3ba)



Compound **3ba** was obtained according to the general procedure from 2-(morpholine-4-carbonothioyl)-3-(*p*-tolyl)acrylonitrile (**1b**) (40 mg, 1.0 equiv, 0.15 mmol), 1-sulfonyl-1,2,3-triazole **2a** (48 mg, 1.1 equiv, 0.16 mmol), $Rh_2(Piv)_4$ (2.0 mg), chloroform (1 mL), 70 °C, reaction is time 16 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 35:15) afforded **3ba** as a colorless powder (70%, 57 mg), mp 228–229 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.41 (s, 1H), 7.23 – 7.17 (m, 3H), 7.05 – 7.02 (m, 4H), 6.90 (d, *J* = 7.6 Hz, 2H), 4.85 (s, 1H), 3.71 (br. s, 4H), 3.66 – 3.61 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 188.8, 159.0, 136.3, 134.1, 130.2, 128.7, 128.6, 128.6, 128.5, 128.2, 118.4, 75.6, 73.5, 65.5, 54.6, 50.5, 20.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{23}N_2O_2S^+$ 391.1475; found 391.1473.

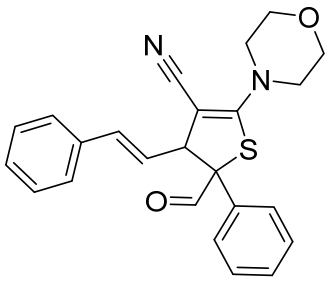
(4*RS*,5*SR*)-4-(4-Chlorophenyl)-5-formyl-2-morpholino-5-phenyl-4,5-dihydrothiophene-3-carbonitrile (3ca)



Compound **3ca** was obtained according to the general procedure from 3-(4-chlorophenyl)-2-(morpholine-4-carbonothioyl)acrylonitrile (**1c**) (50 mg, 1.0 equiv, 0.17 mmol), 1-sulfonyl-1,2,3-triazole **2a** (56 mg, 1.1 equiv, 0.19 mmol), $Rh_2(Piv)_4$ (2.3 mg), chloroform (1 mL), 80 °C, reaction time is 13 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc,

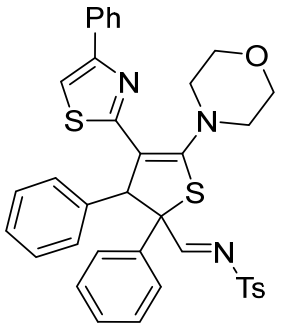
gradient 50:0 to 30:20) afforded **3ca** as a colorless powder (64%, 45 mg), mp 235–236 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.42 (s, 1H), 7.25 – 7.22 (m, 3H), 7.16 (br. s, 4H), 7.06 – 7.03 (m, 2H), 4.94 (s, 1H), 3.73 – 3.70 (m, 4H), 3.65 – 3.62 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 188.5, 159.3, 136.3, 131.9, 130.6, 130.0, 128.8, 128.7, 128.1, 127.9, 118.2, 74.7, 73.3, 65.5, 54.2, 50.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{20}ClN_2O_2S^+$ 411.0928; found 411.0929.

(*E*)-5-Formyl-2-morpholino-5-phenyl-4-styryl-4,5-dihydrothiophene-3-carbonitrile (3da)



Compound **3da** was obtained according to the general procedure from 2-(morpholine-4-carbonothioyl)-5-phenylpenta-2,4-dienenitrile (**1d**) (70 mg, 1.0 equiv, 0.25 mmol), 1-sulfonyl-1,2,3-triazole **2a** (81 mg, 1.1 equiv, 0.27 mmol), $Rh_2(Piv)_4$ (3.3 mg), chloroform (1.5 mL), 80 °C, reaction time is 13 h. The purification of the crude product by column chromatography on neutral Al_2O_3 (PE/EtOAc, gradient 50:0 to 35:15) with subsequent centrifugation with *n*-hexane afforded **3da** as a colorless powder (68%, 48 mg), mp 121–123 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.39 (s, 1H), 7.41 (t, J = 7.4 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.27 – 7.17 (m, 7H), 6.49 (d, J = 15.7 Hz, 1H), 5.86 (dd, J = 15.7, 9.1 Hz, 1H), 4.47 (d, J = 9.0 Hz, 1H), 3.70 – 3.68 (m, 4H), 3.60 – 3.59 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 189.6, 158.7, 136.2, 131.9, 130.5, 129.1, 128.8, 128.5, 128.4, 127.6, 126.2, 124.9, 118.4, 73.1, 72.5, 65.4, 53.2, 50.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{23}N_2O_2S^+$ 403.1475; found 403.1470.

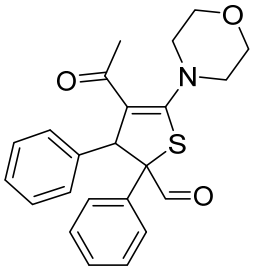
4-Methyl-*N*-((5-morpholino-2,3-diphenyl-4-(4-phenylthiazol-2-yl)-2,3-dihydrothiophen-2-yl)methylene)benzenesulfonamide (3ga)



Compound **3ga** was obtained according to the general procedure from 1-morpholino-3-phenyl-2-(4-phenylthiazol-2-yl)prop-2-ene-1-thione (**1g**) (44 mg, 1.0 equiv, 0.11 mmol), 1-sulfonyl-1,2,3-

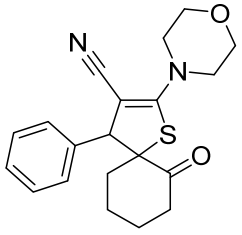
triazole **2a** (40 mg, 1.2 equiv, 0.13 mmol), $Rh_2(Piv)_4$ (1.6 mg), chloroform (1.0 mL), 80 °C, reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 40:10) with subsequent centrifugation with cold diethyl ether afforded **3ga** as a colorless powder (53%, 30 mg), mp 216–218 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.41 (s, 1H), 7.99 (s, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.9 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.33 – 7.19 (m, 8H), 7.12 (d, J = 6.7 Hz, 2H), 7.04 – 6.94 (m, 3H), 5.45 (s, 1H), 2.74 – 2.70 (m, 2H), 2.35 (s, 3H), 2.24 – 2.20 (m, 2H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 167.4, 158.5, 152.6, 149.0, 144.7, 136.4, 134.3, 134.1, 132.3, 129.9, 129.0, 128.7, 128.6, 128.4, 128.0, 127.9, 127.7, 127.3, 126.9, 126.8, 125.9, 114.2, 70.1, 65.7, 55.9, 51.4, 21.0. HRMS (ESI) m/z: [M + H]$^+$ calcd. for $C_{37}H_{34}N_3O_3S_3^+$ 664.1757; found 664.1768.

4-Acetyl-5-morpholino-2,3-diphenyl-2,3-dihydrothiophene-2-carbaldehyde (3wa)



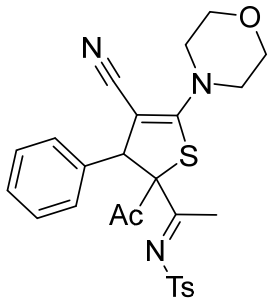
Compound **3wa** was obtained according to the general procedure from 3-(morpholine-4-carbonothioyl)-4-phenylbut-3-en-2-one (**1w**) (50 mg, 1.0 equiv, 0.18 mmol), 1-sulfonyl-1,2,3-triazole **2a** (65 mg, 1.2 equiv, 0.22 mmol), $Rh_2(Piv)_4$ (2.6 mg), chloroform (2.0 mL), 80 °C, reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 100:0 to 40:60) with subsequent flash chromatography on SiO_2 (DCM/EtOAc, gradient 50:0 to 25:25) afforded **3wa** as a pale-yellow gum (52%, 37 mg). ^{1}H NMR (400 MHz, $CDCl_3$-d): δ 9.42 (s, 1H), 7.14 – 7.10 (m, 3H), 7.06 - 6.97 (m, 7H), 5.10 (s, 1H), 3.96 – 3.90 (m, 2H), 3.85 – 3.79 (m, 2H), 3.70 – 3.65 (m, 2H), 3.45 – 3.40 (m, 2H), 2.06 (m, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-d): δ 189.1, 188.6, 162.4, 137.9, 130.4, 129.1, 128.7, 128.7, 128.3, 128.1, 127.2, 112.4, 73.9, 66.9, 57.0, 53.5, 30.4. HRMS (ESI) m/z: [M + H]$^+$ calcd. for $C_{23}H_{24}NO_3S^+$ 394.1471; found 394.1475.

(4*RS*,5*RS*)-2-Morpholino-6-oxo-4-phenyl-1-thiaspiro[4.5]dec-2-ene-3-carbonitrile (3ad)



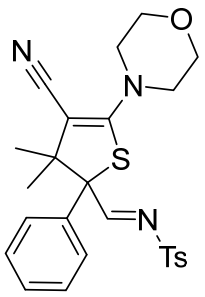
Compound **3ad** was obtained according to the general procedure from 2-(morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), 1-sulfonyl-1,2,3-triazole **2d** (79 mg, 1.4 equiv, 0.27 mmol), $Rh_2(Piv)_4$ (3.3 mg), chloroform (1.5 mL), 80 °C, reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 22.5:2.5) with subsequent flash chromatography on neutral Al_2O_3 (PE/EtOAc, gradient 100:0 to 85:15) afforded **3ad** as a colorless powder (69%, 48 mg), mp 164–166 °C. ^{1}H NMR (600 MHz, CD_3CN-*d*$_3$): δ 7.38 (t, J = 7.3 Hz, 2H), 7.34 – 7.31 (m, 3H), 4.70 (s, 1H), 3.69 (t, J = 4.9 Hz, 4H), 3.59 – 3.52 (m, 4H), 3.20 (td, J = 14.2, 6.3 Hz, 1H), 2.36 – 2.32 (m, 1H), 2.00 – 1.95 (m, 1H), 1.74 – 1.69 (m, 1H), 1.61 – 1.53 (m, 2H), 1.45 – 1.35 (m, 2H). ^{13}C{1H} NMR (150 MHz, CD_3CN-*d*$_3$): δ 205.5, 162.5, 138.6, 130.2, 129.5, 128.9, 119.8, 76.7, 67.8, 66.9, 56.8, 51.5, 37.7, 37.3, 27.2, 25.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{23}N_2O_2S^+$ 355.1475; found 355.1473.

(2*RS*,3*SR*)-(*E*)-*N*-(1-(2-Acetyl-4-cyano-5-morpholino-3-phenyl-2,3-dihydrothiophen-2-yl)ethylidene)-4-methylbenzenesulfonamide (3ae)



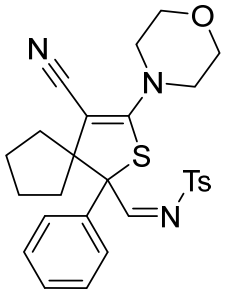
Compound **3ae** was obtained according to the general procedure from 2-(morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 1-sulfonyl-1,2,3-triazole **2e** (65 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (2.8 mg, 2 mol %), chloroform (1 mL), 80 °C, reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 80:20 to 50:50) afforded **3ae** as a pale-yellow gum. It was triturated with *n*-hexane until a powder was obtained and centrifugated with cold diethyl ether afforded **3ae** as a colorless powder (78%, 62 mg), mp 184–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.70 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.30 – 7.21 (m, 5H), 4.92 (s, 1H), 3.73 – 3.67 (m, 4H), 3.58 – 3.48 (m, 4H), 2.47 (s, 3H), 2.30 (s, 3H), 2.00 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 195.7, 180.4, 159.1, 144.6, 136.7, 136.7, 129.8, 129.1, 128.8, 128.5, 127.4, 118.0, 81.7, 66.2, 55.5, 50.6, 25.0, 21.9, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{28}N_3O_4S_2^+$ 510.1516; found 510.1520.

***N*-((4-Cyano-3,3-dimethyl-5-morpholino-2-phenyl-2,3-dihydrothiophen-2-yl)methylene)-4-methylbenzenesulfonamide (3ha)**



Compound **3ha** was obtained according to the general procedure from 3-methyl-2-(morpholine-4-carbonothioyl)but-2-enenitrile (**1h**) (40 mg, 1.0 equiv, 0.19 mmol), 1-sulfonyl-1,2,3-triazole **2a** (56 mg, 1.1 equiv, 0.21 mmol), $Rh_2(Piv)_4$ (2.3 mg), chloroform (1 mL), 80 °C, reaction time is 13 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 30:20) afforded **3ha** as a pale-yellow powder (68%, 63 mg), mp 173–175 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.65 (s, 1H), 7.81 (d, J = 8.1, 2H), 7.39 – 7.34 (m, 7H), 3.71 – 3.62 (m, 4H), 3.53 – 3.48 (m, 2H), 3.45 – 3.49 (m, 2H), 2.44 (s, 3H), 1.38 (s, 3H), 0.88 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 169.9, 157.8, 145.0, 135.0, 131.4, 130.0, 129.2, 128.9, 128.6, 128.1, 118.4, 82.2, 72.2, 66.2, 52.2, 50.8, 25.7, 21.8, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{28}N_3O_3S_2^+$ 482.1566; found 482.1569.

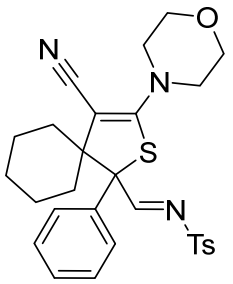
***N*-((4-Cyano-3-morpholino-1-phenyl-2-thiaspiro[4.4]non-3-en-1-yl)methylene)-4-methylbenzenesulfonamide (3ia)**



Compound **3ia** was obtained according to the general procedure from 2-cyclopentylidene-3-morpholino-3-thioxopropanenitrile (**1i**) (40 mg, 1.0 equiv, 0.17 mmol), 1-sulfonyl-1,2,3-triazole **2a** (56 mg, 1.1 equiv, 0.19 mmol), $Rh_2(Piv)_4$ (2.3 mg), chloroform (1 mL), 80 °C, reaction time is 10 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 24.5:0.5) afforded **3ia** as a pale-yellow powder (78%, 67 mg), mp 183–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.42 (s, 1H), 7.89 (d, J = 8.1 Hz, 2H), 7.38 – 7.37 (m, 7H), 3.59 – 3.49 (m, 4H), 3.39 – 3.34 (m, 2H), 3.25 – 3.20 (m, 2H), 2.57 – 2.50 (m, 1H), 2.45 (s, 3H), 1.80

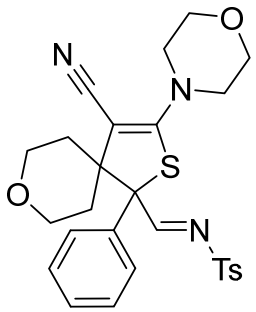
– 1.63 (m, 4H), 1.52 – 1.38 (m, 2H), 0.86 – 0.81 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 167.2, 157.0, 145.0, 135.3, 131.5, 130.0, 129.6, 129.1, 129.0, 128.2, 118.6, 85.4, 73.2, 66.2, 62.4, 50.8, 38.6, 31.7, 25.5, 23.9, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{27}H_{30}N_3O_3S_2^+$ 508.1723; found 508.1719.

***N*-((4-Cyano-3-morpholino-1-phenyl-2-thiaspiro[4.5]dec-3-en-1-yl)methylene)-4-methylbenzenesulfonamide (3ja)**



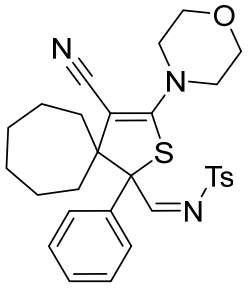
Compound **3ja** was obtained according to the general procedure from 2-cyclohexylidene-3-morpholino-3-thioxopropanenitrile (**1j**) (40 mg, 1.0 equiv, 0.16 mmol), 1-sulfonyl-1,2,3-triazole **2a** (53 mg, 1.1 equiv, 0.17 mmol), $Rh_2(Piv)_4$ (2.2 mg), chloroform (1 mL), 80 °C, reaction time is 12 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 24.5:0.5 to 24:1) afforded **3ja** as a yellow gum (81%, 67 mg), which solidified within 48 h when stored at room temperature, mp 187–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.57 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.42 – 7.35 (m, 7H), 3.68 – 3.63 (m, 2H), 3.61 – 3.56 (m, 2H), 3.54 – 3.48 (m, 2H), 3.33 – 3.28 (m, 2H), 2.53 – 2.45 (m, 4H), 2.24 – 2.12 (m, 1H), 2.01 (d, J = 12.5 Hz, 1H), 1.65 – 1.50 (m, 4H), 1.41 (td, J = 13.1, 4.7 Hz, 1H), 0.92 – 0.82 (m, 1H), 0.77 – 0.70 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 168.8, 161.1, 145.0, 135.0, 131.4, 130.0, 129.7, 129.4, 128.6, 128.2, 120.1, 80.9, 74.4, 66.4, 54.2, 51.1, 35.0, 28.8, 25.3, 22.2, 22.2, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{28}H_{32}N_3O_3S_2^+$ 522.1879; found 522.1874.

***N*-((4-Cyano-3-morpholino-1-phenyl-8-oxa-2-thiaspiro[4.5]dec-3-en-1-yl)methylene)-4-methylbenzenesulfonamide (3ka)**



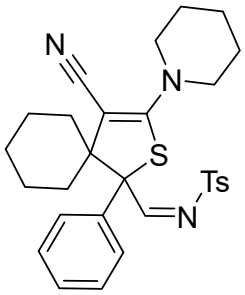
Compound **3ka** was obtained according to the general procedure from 3-morpholino-2-(tetrahydro-4*H*-pyran-4-ylidene)-3-thioxopropanenitrile (**1k**) (40 mg, 1.0 equiv, 0.16 mmol), 1-sulfonyl-1,2,3-triazole **2a** (52 mg, 1.1 equiv, 0.17 mmol), $Rh_2(Piv)_4$ (2.1 mg), chloroform (1 mL), 80 °C, reaction time is 9 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 30:20 to 15:35) afforded **3ka** as a pale-yellow powder (93%, 77 mg), mp 184–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.43 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.40 (m, 5H), 7.34 – 7.33 (m, 2H), 4.19 (t, *J* = 11.6, 1H), 3.80 (dd, *J* = 12.3, 5.6 Hz, 1H), 3.75 – 3.65 (m, 2H), 3.62 – 3.56 (m, 2H), 3.53 – 3.45 (m, 4H), 3.29 – 3.23 (m, 2H), 2.66 (d, *J* = 13.2, 1H), 2.48 (s, 3H), 1.86 – 1.73 (m, 2H), 1.36 – 1.29 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 166.3, 160.6, 145.1, 135.0, 130.6, 130.0, 129.9, 129.6, 129.1, 128.3, 119.7, 79.9, 74.4, 66.3, 64.2, 64.1, 51.2, 35.2, 29.8, 28.7, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{27}H_{30}N_3O_4S_2^+$ 524.1672; found 524.1669.

***N*-((4-Cyano-3-morpholino-1-phenyl-2-thiaspiro[4.6]undec-3-en-1-yl)methylene)-4-methylbenzenesulfonamide (3la)**



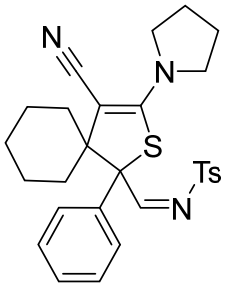
Compound **3la** was obtained according to the general procedure from 2-cycloheptylidene-3-morpholino-3-thioxopropanenitrile (**1l**) (40 mg, 1.0 equiv, 0.15 mmol), 1-sulfonyl-1,2,3-triazole **2a** (50 mg, 1.1 equiv, 0.17 mmol), $Rh_2(Piv)_4$ (2.0 mg), chloroform (1 mL), 80 °C, reaction time is 12 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 30:20) afforded **3la** as a pale-yellow powder (78%, 63 mg), mp 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.62 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.34 (m, 7H), 3.69 – 3.59 (m, 4H), 3.53 – 3.48 (m, 2H), 3.38 – 3.33 (m, 2H), 2.51 – 2.42 (m, 4H), 1.90 – 1.82 (m, 2H), 1.76 – 1.68 (m, 2H), 1.61 – 1.47 (m, 2H), 1.25 – 1.08 (m, 4H), 0.37 – 0.29 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.1, 159.0, 144.9, 135.0, 131.5, 130.0, 129.5, 129.4, 128.6, 128.2, 119.3, 84.1, 74.0, 66.4, 58.4, 50.9, 35.6, 34.1, 31.1, 30.9, 24.9, 22.9, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{29}H_{34}N_3O_3S_2^+$ 536.2036; found 536.2030.

***N*-((4-Cyano-1-phenyl-3-(piperidin-1-yl)-2-thiaspiro[4.5]dec-3-en-1-yl)methylene)-4-methylbenzenesulfonamide (3ma)**



Compound **3ma** was obtained according to the general procedure from 2-cyclohexylidene-3-(piperidin-1-yl)-3-thioxopropanenitrile (**1m**) (40 mg, 1.0 equiv, 0.16 mmol), 1-sulfonyl-1,2,3-triazole **2a** (53 mg, 1.1 equiv, 0.18 mmol), $Rh_2(Piv)_4$ (2.2 mg), chloroform (1 mL), 80 °C, reaction time is 12 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 35:15) with subsequent centrifugation with cold diethyl ether afforded **3ma** as a pale-yellow powder (65%, 55 mg), mp 174–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.58 (s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.35 – 7.34 (m, 7H), 3.51 – 3.46 (m, 2H), 3.36 – 3.31 (m, 2H), 2.44 (s, 3H), 2.23 – 2.13 (m, 1H), 1.95 (d, J = 13.2, 1H), 1.61 – 1.37 (m, 12H), 0.87 – 0.81 (m, 1H), 0.72 – 0.65 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 169.9, 161.2, 144.7, 135.0, 131.7, 129.9, 129.8, 129.1, 128.5, 128.2, 120.8, 77.8, 73.8, 54.1, 52.7, 35.2, 29.1, 26.1, 25.5, 24.2, 22.2, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{29}H_{34}N_3O_2S_2^+$ 520.2087; found 520.2085.

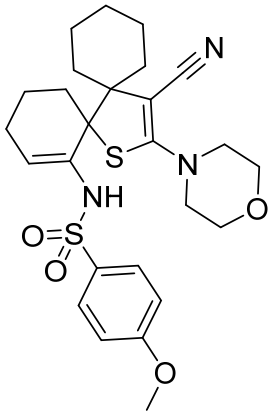
***N*-((4-Cyano-1-phenyl-3-(pyrrolidin-1-yl)-2-thiaspiro[4.5]dec-3-en-1-yl)methylene)-4-methylbenzenesulfonamide (3na)**



Compound **3na** was obtained according to the general procedure from 2-cyclohexylidene-3-(pyrrolidin-1-yl)-3-thioxopropanenitrile (**1n**) (40 mg, 1.0 equiv, 0.17 mmol), 1-sulfonyl-1,2,3-triazole **2a** (56 mg, 1.1 equiv, 0.19 mmol), $Rh_2(Piv)_4$ (2.3 mg), chloroform (1 mL), 80 °C, reaction time is 12 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 20:30) with subsequent centrifugation with cold diethyl ether afforded **3na** as a yellow powder (70%, 60 mg), mp 182–183 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.73 (s, 1H), 7.82 (d, J = 7.9 Hz, 2H), 7.37 – 7.32 (m, 7H), 3.54 – 3.47 (m, 4H), 2.43 (s, 3H), 2.27 – 2.15 (m, 2H),

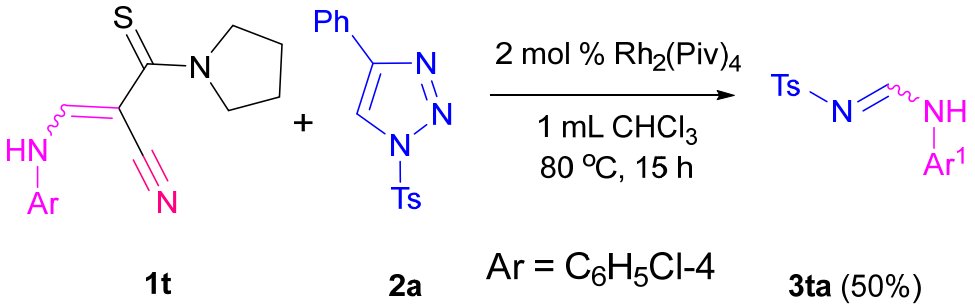
1.93 – 1.90 (m, 4H), 1.66 – 1.53 (m, 4H), 1.45 – 1.40 (m, 2H), 0.87 – 0.78 (m, 1H), 0.67 – 0.60 (m, 1H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 171.4, 157.7, 144.6, 135.2, 131.8, 129.9, 129.0, 128.3, 128.1, 121.9, 75.6, 74.4, 54.3, 51.9, 35.4, 29.8, 25.7, 25.5, 22.1, 22.0, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{28}H_{32}N_3O_2S_2^+$ 506.1930; found 506.1929.

_N_-(15-Cyano-14-morpholino-13-thiadispiro[5.0.57.36]pentadeca-8,14-dien-8-yl)-4-methoxybenzenesulfonamide (3jd)

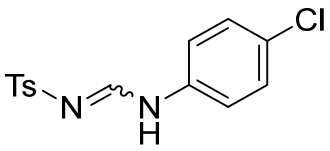


Compound **3jd** was obtained according to the general procedure from 2-cyclohexylidene-3-morpholino-3-thioxopropanenitrile (**1j**) **(**40 mg, 1.0 equiv, 0.16 mmol), 1-sulfonyl-1,2,3-triazole **2d** (56 mg, 1.2 equiv, 0.19 mmol), $Rh_2(Piv)_4$ (2.3 mg), chloroform (1 mL), 80 °C, reaction time is 17 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 24:1 to 23:2) with subsequent centrifugation with cold diethyl ether afforded **3jd** as a colorless powder (63%, 44 mg), mp 154–155 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.85 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 6.71 (s, 1H), 5.59 (dd, J = 5.8, 2.4 Hz, 1H), 3.89 (s, 3H), 3.81 – 3.71 (m, 5H), 3.63 – 3.58 (m, 2H), 2.30 – 2.19 (m, 1H), 2.15 – 2.07 (m, 2H), 2.03 – 1.45 (m, 11H), 1.36 – 1.26 (m, 2H), 1.18 – 1.06 (m, 1H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 167.5, 163.1, 135.2, 132.5, 129.6, 120.9, 115.1, 114.1, 76.9, 66.6, 64.7, 55.8, 54.0, 51.4, 34.4, 32.0, 29.3, 25.7, 24.5, 22.1, 22.1, 21.2. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{34}N_3O_4S_2^+$ 516.1985; found 516.1994.

The reaction of 3-amino-2-cyanothioacrylamide 1t with 1-sulfonyl-1,2,3-triazole 2a afforded *N*-sulfonylamidine 3ta

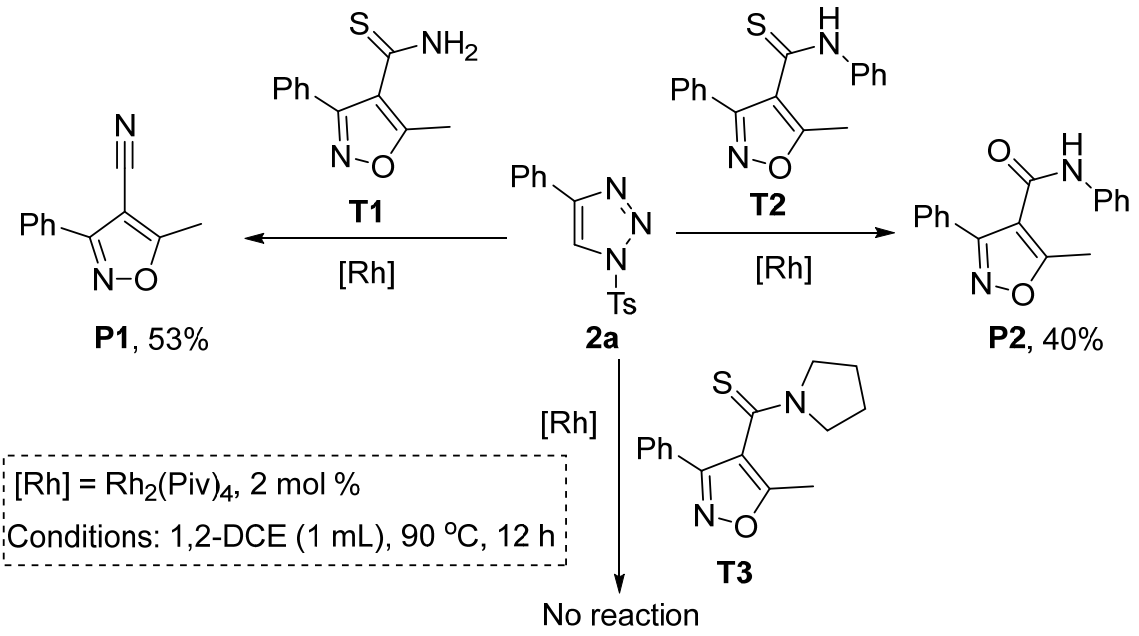


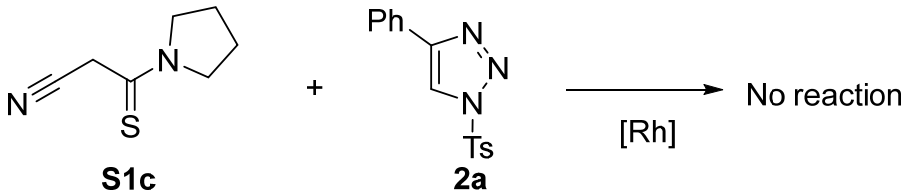
***(Z/E)-N*-(4-Chlorophenyl)-*N*'-tosylformimidamide (3ta)**



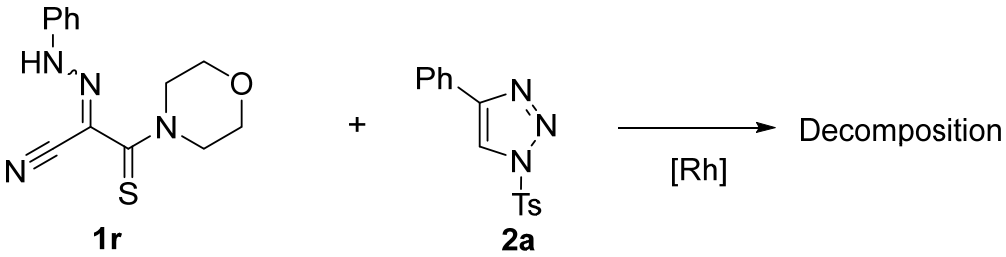
Compound **3ta** was obtained according to the general procedure from 3-((4-chlorophenyl)amino)-2-(pyrrolidine-1-carbonothioyl)acrylonitrile (**1t**) (40 mg, 1.0 equiv, 0.14 mmol), 1-sulfonyl-1,2,3-triazole **2a** (57 mg, 1.4 equiv, 0.19 mmol), $Rh_2(Piv)_4$ (2.3 mg), chloroform (1 mL), 80 °C, reaction time is 15 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 30:20) with subsequent centrifugation with cold diethyl ether and then with EtOAc afforded **3ta** as a pale-red powder (50%, 21 mg). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 11.29* and 10.87 (both d, J^* = 12.3 Hz, J = 5.3 Hz, 1H), 8.74* and 8.28 (both d, J^* = 12.0 Hz, J = 5.0 Hz, 1H), 7.76 – 7.66 (m, 3H), 7.46 – 7.42 (m, 2H), 7.38 – 7.32 (m, 3H), 2.36 (s, 3H).

The failure of experiments for the synthesis of dihydrothiophenes

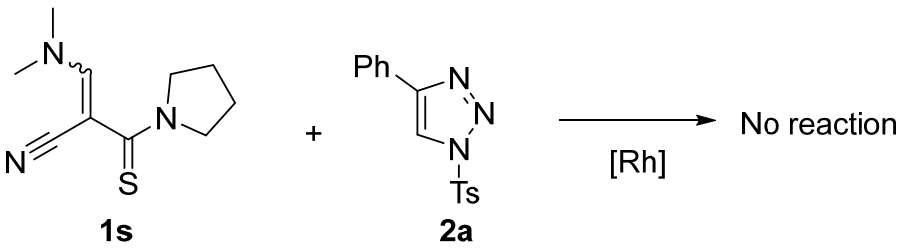




[Rh] = $Rh_2(Piv)_4$, 2 mol %
Conditions: 1,2-DCE (1 mL), 100 °C, 24 h



[Rh] = $Rh_2(Piv)_4$, 2 mol %
Conditions: 1,2-DCE (1 mL), 80 °C, 24 h



[Rh] = $Rh_2(Piv)_4$, 2 mol %
Conditions: 1,2-DCE (1 mL), 100 °C, 24 h

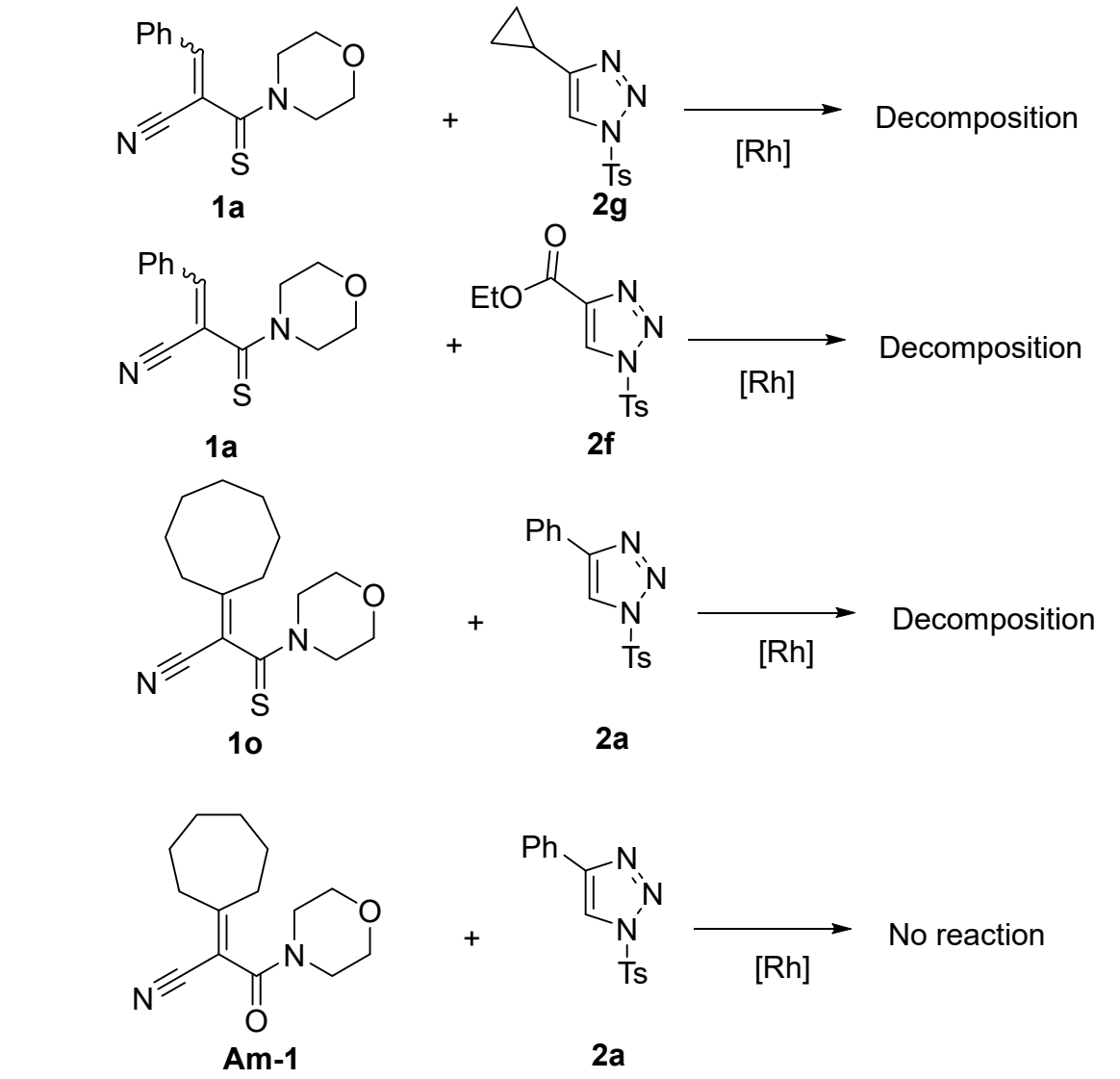
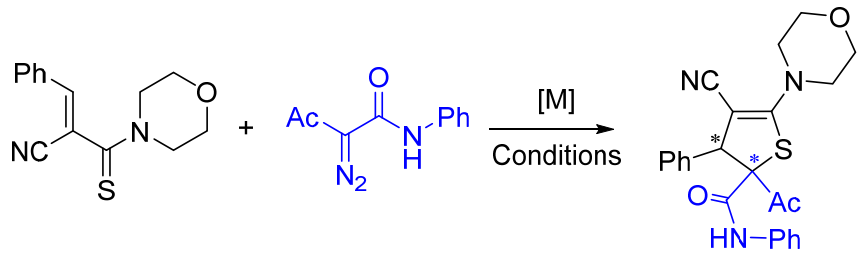


Figure S3. The failure of experiments for the synthesis of dihydrothiophenes

Optimization study for the reaction of thioamide 1a with diazo compound 2h

Table S2. Optimization of the synthesis of dihydrothiophenes **4ah**/**4′ah**



1a **2h** (2RS,3SR)-**4ah** and (2RS,3RS)-**4'ah**

Entry	Solvent (T, ˚C)	Catalyst (mol %)	Time, h	Equiv of 2h	Yield[a] 4ah/4′ah, %	dr[b]
1	$CHCl_3$ (rt)	$Rh_2(Piv)_4$ (2.0)	24	1.1	51/34	56:44
2	$CHCl_3$ (rt)	$Rh_2(esp)_2$ (0.5)	24	1.1	46/28	56:44
3	$CHCl_3$ (rt)	$Rh_2(OAc)_4$ (0.5) or $Rh_2(Oct)_4$ (0.5)	24	1.1	NR	–
4	$CHCl_3$ (75)	$Rh_2(OAc)_4$ (0.5)	3.5	1.1	52/34	51:49
5	$CHCl_3$ (75)	$Rh_2(Oct)_4$ (0.5)	3.5	1.1	57/28	54:46
6	$CHCl_3$ (rt)	$Rh_2(Piv)_4$ (0.5)	2	1.1	45/24	54:46
7	$CHCl_3$ (rt)	$Rh_2(Piv)_4$ (0.5)	24	1.1	49/33	56:44
8	$CHCl_3$ (rt)	$Rh_2(Piv)_4$ (0.5)	19	2.0	55/40	55:45
9	MeCN (rt)	$Rh_2(Piv)_4$ (0.5)	19	2.0	Trace	–
10	MeCN (75)	$Rh_2(Piv)_4$ (0.5)	3.5	2.0	48/22	53:47
11	C_6H_6 (rt)	$Rh_2(Piv)_4$ (0.5)	19	2.0	61/36	57:43
12	CCl_4 (rt)	$Rh_2(Piv)_4$ (0.5)	19	2.0	55/35	50:50
13	1,2-DCE (100)	$[CuOTf]_2{\cdot}C_6H_6$ (10.0)	24	2.0	24/52	28:72
14	1,2-DCE (100)	$[Cu(MeCN)_4]CF_3SO_3$ (10.0)	24	2.0	32/65	33:67
15	1,2-DCE (90)	$[Cu(MeCN)_4]CF_3SO_3$ (10.0)	24	2.0	31/57	29:71
16	1,2-DCE (100)	$[Cu(MeCN)_4]PF_6$ (10.0)	24	2.0	19/49	32:68
17	1,2-DCE (100)	AgOTf (10.0)	24	2.0	20/34	33:67
18	1,2-DCE (100)	$[Ru(p\text{-cymene})Cl_2]_2$ (5.0)	24	2.0	18/47	31:69
19	1,2-DCE (100)	$RuCl(PPh_3)_3Cp$	24	2.0	24/56	27:73
20	*n*-Hexane (rt)	$Rh_2(Piv)_4$ (0.5)	24	2.0	NR	–
21	1,4-Dioxane (rt)	$Rh_2(Piv)_4$ (0.5)	24	2.0	NR	–
22	$CHCl_3$ (rt)	$Pd_2(OAc)_4$ (2.0)	24	1.1	NR	–
23	$CHCl_3$ (75)	$Pd_2(OAc)_4$ (2.0)	3.5	1.1	NR	–

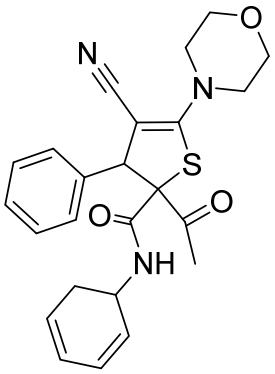
Conditions: thioamide **1a** (0.15 mmol), diazo compound **2h** (0.17 mmol, 1.1 equiv or 0.31 mmol, 2.0 equiv), solvent (1.5 mL). [a]Isolated yields. [b](2*RS*,3*SR*:2*RS*,3*RS*). Determined by ^{1}H NMR analysis of the crude mixture.

General procedure for the synthesis of dihydrothiophenes 4a,i-l and 4′a,i-l

Method A. A 10 mL standard microwave vial was charge with $Rh_2(Piv)_4$ (0.5–1.0 mol %), 2-(morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (1.0 equiv) and dry benzene (0.5 mL). A solution of diazo compounds **2h-o** (1.1–2.0 equiv) in dry benzene (0.5–3 mL) was added slowly to the vial at room temperature. The reaction solution was stirred for 19–27 h at room temperature, and then the solution was concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel.

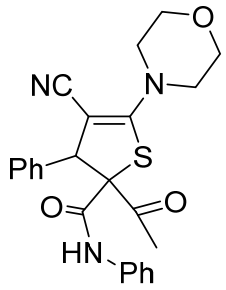
Method B. A 10 mL standard microwave vial was charge with $[Cu(MeCN)_4]CF_3SO_3$ (10 mol %), (morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (1.0 equiv), diazo compounds **2h-l** (1.2–2.0 equiv) and dry 1,2-DCE (1.0–1.5 mL). The reaction solution was stirred for 24 h at 70–100 °C, and then the solution was concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel.

(2*RS*,3*SR*)-2-Acetyl-4-cyano-*N*-(cyclohexa-2,4-dien-1-yl)-5-morpholino-3-phenyl-2,3-dihydrothiophene-2-carboxamide (4ah)



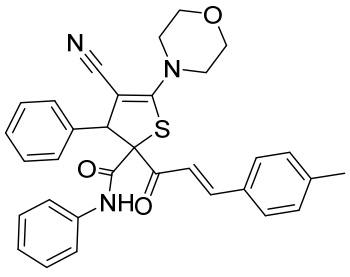
Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (63 mg, 2.0 equiv, 0.31 mmol), $Rh_2(Piv)_4$ (0.9 mg, 0.5 mol %), benzene (1 mL), reaction time is 19 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 21:4) afforded **4ah** as a colorless powder (61%, 41 mg), mp 105–106 °C. **Method B. 1a** (50 mg, 1.0 equiv, 0.19 mmol), **2h** (78 mg, 2.0 equiv, 0.39 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (14 mg), 1,2-DCE (1 mL), 100 °C, reaction time is 24 h. The product **4ah** was isolated as a colorless powder (32%, 27 mg), mp 105–106 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.13 (s, 1H), 7.64 (d, J = 7.8 Hz, 2H), 7.41 – 7.44 (m, 7H), 7.13 (t, J = 7.4 Hz, 1H), 5.33 (s, 1H), 3.71 – 3.68 (m, 4H), 3.59 – 3.56 (m, 4H), 1.78 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 199.0, 166.1, 161.4, 138.5, 136.5, 129.0, 128.7, 128.7, 128.4, 124.3, 120.4, 118.5, 78.2, 72.7, 65.5, 56.4, 50.2, 27.7. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{24}H_{25}N_3O_3SNa^+$ 456.1351; found 456.1352.

(2*RS*,3*RS*)-2-Acetyl-4-cyano-*N*-(cyclohexa-2,4-dien-1-yl)-5-morpholino-3-phenyl-2,3-dihydrothiophene-2-carboxamide (4′ah)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (63 mg, 2.0 equiv, 0.31 mmol), $Rh_2(Piv)_4$ (0.9 mg, 0.5 mol %), benzene (1 mL), reaction time is 19 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 21:4) afforded **4′ah** as an amorphous solid (36%, 25 mg). **Method B. 1a** (50 mg, 1.0 equiv, 0.19 mmol), **2h** (78 mg, 2.0 equiv, 0.39 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (14 mg), 1,2-DCE (1 mL), 100 °C, reaction time is 24 h. The product **4′ah** was isolated as an amorphous solid (65%, 55 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.82 (s, 1H), 7.50 (d, J = 7.3 Hz, 2H), 7.26 (t, J = 7.4 Hz, 2H), 7.22 – 7.18 (m, 3H), 7.12 – 7.09 (m, 2H), 7.03 (t, J = 7.3 Hz, 1H), 4.94 (s, 1H), 3.69 – 3.67 (m, 4H), 3.56 – 3.53 (m, 4H), 2.39 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 195.4, 162.3, 159.9, 137.5, 137.2, 128.5, 128.4, 128.2, 127.9, 124.7, 121.2, 118.5, 78.6, 74.8, 65.5, 53.4, 50.3, 24.3. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{24}H_{23}N_3O_3SNa^+$ 456.1352; found 456.1356.

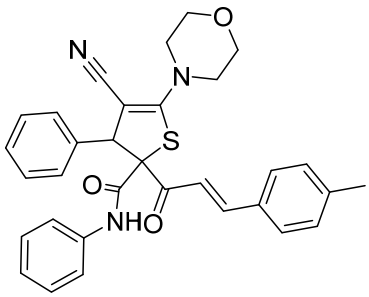
(*2RS*,*3SR*)-4-Cyano-5-morpholino-*N*,3-diphenyl-2-((*E*)-3-(*p*-tolyl)acryloyl)-2,3-dihydrothiophene-2-carboxamide (4ai)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-diazo-3-oxo-*N*-phenyl-5-(*p*-tolyl)pent-4-enamide (**2i**) (71 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (1.4 mg, 1 mol %), benzene (3 mL), reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 24.5:0.5) afforded **4ai** as a pale-yellow powder (54%, 45 mg), mp 204–206 °C. **Method B. 1a** (50 mg, 1.0 equiv,

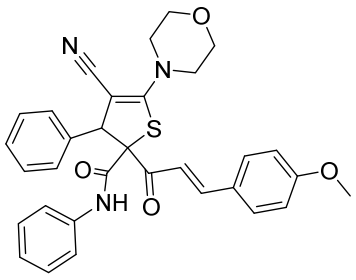
0.19 mmol), **2i** (89 mg, 1.5 equiv, 0.29 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (14.5 mg), 1,2-DCE (1.5 mL), 90 °C, reaction time is 24 h. The product **4ai** was isolated as a pale-yellow powder (27%, 28 mg), mp 204–206 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.13 (s, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.45 (br. s, 4H), 7.32 (t, J = 7.3 Hz, 2H), 7.24 – 7.07 (m, 7H), 6.84 (d, J = 15.8 Hz, 1H), 5.45 (s, 1H), 3.71 (br. s, 4H), 3.61 (br. s, 4H), 2.31 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 188.9, 166.3, 161.5, 143.1, 141.3, 138.6, 136.8, 131.0, 129.6, 129.0, 128.8, 128.7, 128.2 (2C), 124.2, 120.3, 120.1, 118.6, 78.2, 73.4, 65.5, 56.2, 50.3, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{30}N_3O_3S^+$ 536.2002; found 536.2001.

(2*RS*,3*RS*)-4-Cyano-5-morpholino-*N*,3-diphenyl-2-((*E*)-3-(*p*-tolyl)acryloyl)-2,3-dihydrothiophene-2-carboxamide (4′ai)



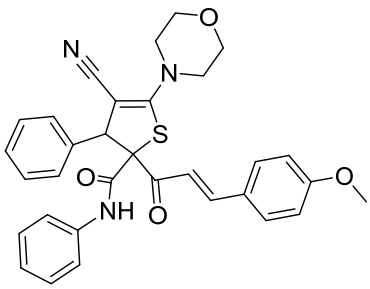
Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-diazo-3-oxo-*N*-phenyl-5-(*p*-tolyl)pent-4-enamide (**2i**) (71 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (1.4 mg, 1 mol %), benzene (3 mL), reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 24.5:0.5) afforded **4′ai** as a bright-yellow powder (30%, 25 mg), mp 217–219 °C. **Method B. 1a** (50 mg, 1.0 equiv, 0.19 mmol), **2i** (89 mg, 1.5 equiv, 0.29 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (14.5 mg), 1,2-DCE (1.5 mL), 90 °C, reaction time is 24 h. The product **4′ai** was isolated as a bright-yellow powder (49%, 51 mg), mp 217–219 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.90 (s, 1H), 7.86 (d, J = 15.6 Hz, 1H), 7.61 – 7.55 (m, 4H), 7.30 – 7.11 (m, 9H), 7.02 – 6.98 (m, 2H), 5.14 (s, 1H), 3.70 – 3.61 (m, 4H), 3.58 – 3.48 (m, 4H), 2.32 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 185.9, 162.3, 159.8, 144.8, 141.4, 137.4, 137.3, 131.0, 129.7, 128.7, 128.7, 128.4, 128.2, 127.9, 124.6, 121.1, 119.4, 118.6, 78.0, 75.2, 65.5, 53.3, 50.2, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{30}N_3O_3S^+$ 536.2002; found 536.1997.

(2*RS*,3*SR*)-4-Cyano-2-((*E*)-3-(4-methoxyphenyl)acryloyl)-5-morpholino-*N*,3-diphenyl-2,3-dihydrothiophene-2-carboxamide (4aj)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-diazo-5-(4-methoxyphenyl)-3-oxo-*N*-phenylpent-4-enamide (**2j**) (75 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (0.7 mg, 0.5 mol %), benzene (3 mL), reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 50:0 to 49:1) afforded **4aj** as a yellow amorphous solid (59%, 50 mg) that crystallizes into powder when stored at 40 °C for 12 h, mp 214–216 °C. **Method B. 1a** (50 mg, 1.0 equiv, 0.19 mmol), **2j** (93 mg, 1.5 equiv, 0.29 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (10.7 mg), 1,2-DCE (1.5 mL), 90 °C, reaction time is 24 h. The product **4aj** was isolated as a yellow amorphous solid (36%, 39 mg) that crystallizes into powder when stored at 40 °C for 12 h, mp 214–216 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 10.14 (s, 1H), 7.65 (d, J = 7.9 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.9 Hz, 2H), 7.24 – 7.13 (m, 4H), 7.09 (t, J = 7.4 Hz, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 15.6 Hz, 1H), 5.46 (s, 1H), 3.79 (s, 3H), 3.71 – 3.68 (m, 4H), 3.61 – 3.59 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-*d*$_6$): δ 188.6, 166.4, 161.7, 161.5, 143.2, 138.6, 136.9, 130.7, 129.0, 128.6, 128.2, 128.1, 126.3, 124.2, 120.4, 118.6, 118.6, 114.5, 78.5, 73.6, 65.5, 56.2, 55.4, 50.3. HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{32}H_{29}N_3O_4SNa^+$ 574.1771; found 574.1771.

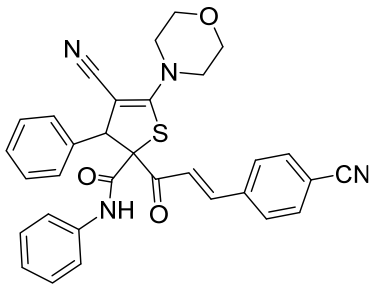
(2*RS*,3*RS*)-4-Cyano-2-((*E*)-3-(4-methoxyphenyl)acryloyl)-5-morpholino-*N*,3-diphenyl-2,3-dihydrothiophene-2-carboxamide (4′aj)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-diazo-5-(4-methoxyphenyl)-3-oxo-*N*-phenylpent-4-enamide (**2j**) (75 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (0.7 mg, 0.5 mol %), benzene (3 mL), reaction time is 24 h. The purification of

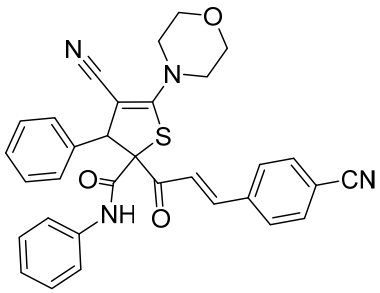
the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 50:0 to 46:4) afforded **4′aj** as a yellow powder (32%, 27 mg), mp 222–223 °C. **Method B. 1a** (50 mg, 1.0 equiv, 0.19 mmol), **2j** (93 mg, 1.5 equiv, 0.29 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (10.7 mg), 1,2-DCE (1.5 mL), 90 °C, reaction time is 24 h. The product **4′aj** was isolated as a yellow powder (56%, 60 mg), mp 222–223 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.90 (s, 1H), 7.85 (d, J = 15.5 Hz, 1H), 7.67 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 7.3 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.23 – 7.12 (m, 5H), 7.02 – 6.97 (m, 3H), 6.91 (d, J = 15.5 Hz, 1H), 5.14 (s, 1H), 3.79 (s, 3H), 3.69 – 3.64 (m, 4H), 3.58 – 3.49 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 186.0, 186.0*, 162.5, 162.4*, 161.7, 159.9, 144.6, 137.5, 137.3, 137.2*, 130.7, 128.7, 128.4, 128.2, 127.9, 126.4, 124.6, 121.1, 121.0*, 118.6, 117.8, 114.6, 78.0, 75.2, 65.5, 55.4, 53.3, 50.2. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{30}N_3O_4S^+$ 552.1951; found 552.1949.

(2*RS*,3*SR*)-4-Cyano-2-((*E*)-3-(4-cyanophenyl)acryloyl)-5-morpholino-*N*,3-diphenyl-2,3-dihydrothiophene-2-carboxamide (4ak)



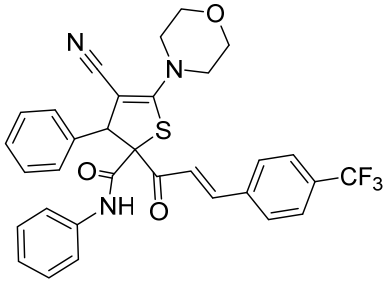
Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 5-(4-cyanophenyl)-2-diazo-3-oxo-*N*-phenylpent-4-enamide (**2k**) (73 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (1.4 mg, 1.0 mol %), benzene (3 mL), reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **4ak** as a yellow powder (59%, 50 mg), mp 166–168 °C. **Method B. 1a** (50 mg, 1.0 equiv, 0.19 mmol), **2k** (92 mg, 1.5 equiv, 0.29 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (10.9 mg), 1,2-DCE (1.5 mL), 90 °C, reaction time is 24 h. The product **4ak** was isolated as a yellow powder (21%, 20 mg), mp 166–168 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.16 (s, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.9 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.15 – 7.03 (m, 3H), 5.50 (s, 1H), 3.74 – 3.70 (m, 4H), 3.65 – 3.58 (m, 4H). ^{13}C{1H} NMR (150 MHz, DMSO-d_6): δ 189.4, 166.0, 161.5, 140.6, 138.6, 138.2, 136.6, 132.8, 129.3, 129.1, 128.7, 128.3 (2C), 124.2, 124.0, 120.3, 118.6, 118.5, 112.7, 77.6, 73.3, 65.5, 56.2, 50.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{27}N_4O_3S^+$ 547.1798; found 547.1789.

(2*RS*,3*RS*)-4-Cyano-2-((*E*)-3-(4-cyanophenyl)acryloyl)-5-morpholino-*N*,3-diphenyl-2,3-dihydrothiophene-2-carboxamide (4′ak)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 5-(4-cyanophenyl)-2-diazo-3-oxo-*N*-phenylpent-4-enamide (**2k**) (73 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (1.4 mg, 1.0 mol %), benzene (3 mL), reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **4′ak** as a yellow powder (28%, 24 mg), mp 242–244 °C. **Method B. 1a** (50 mg, 1.0 equiv, 0.19 mmol), **2k** (92 mg, 1.5 equiv, 0.29 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (10.9 mg), 1,2-DCE (1.5 mL), 90 °C, reaction time is 24 h. The product **4′ak** was isolated as a yellow powder (57%, 60 mg), mp 242–244 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.91 (s, 1H), 7.96 – 7.92 (m, 3H), 7.87 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 7.3 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.24 – 7.10 (m, 6H), 7.01 (t, J = 7.2 Hz, 1H), 5.14 (s, 1H), 3.69 – 3.65 (m, 4H), 3.59 – 3.49 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 185.5, 162.0, 159.7, 142.6, 138.2, 137.2, 137.1, 132.9, 129.3, 128.7, 128.4, 128.3, 128.0, 124.7, 123.9, 121.3, 118.5, 112.7, 77.7, 75.0, 65.5, 53.4, 50.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{27}N_4O_3S^+$ 547.1798; found 547.1792.

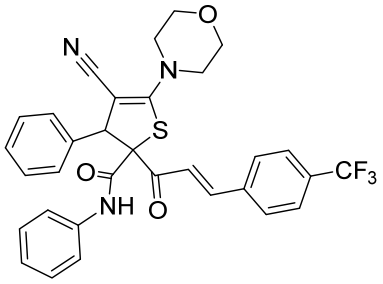
(2*RS*,3*SR*)-4-Cyano-5-morpholino-*N*,3-diphenyl-2-((*E*)-3-(4-(trifluoromethyl)phenyl)acryloyl)-2,3-dihydrothiophene-2-carboxamide (4al)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-diazo-3-oxo-*N*-phenyl-5-(4-(trifluoromethyl)phenyl)pent-4-enamide (**2l**) (83 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (1.4 mg, 1.0 mol %), benzene (3 mL), reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM) afforded **4al** as a yellow amorphous solid (59%, 54 mg), that crystallizes into powder when treated with cold diethyl

ether, mp 209–210 °C. **Method B**. **1a** (40 mg, 1.0 equiv, 0.15 mmol), **2l** (83 mg, 1.5 equiv, 0.23 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (8.7 mg), 1,2-DCE (1.5 mL), 90 °C, reaction time is 24 h. The product **4al** was isolated as a yellow amorphous solid (30%, 26 mg), that crystallizes into powder when treated with cold diethyl ether, mp 209–210 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.17 (s, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.16 – 7.02 (m, 3H), 5.50 (s, 1H), 3.73 – 3.71 (m, 4H), 3.66 – 3.62 (m, 4H). ^{19}F{1H} NMR (376 MHz, DMSO-d_6): δ -61.38. ^{13}C{1H} NMR (150 MHz, DMSO-d_6): δ 189.3, 166.1, 161.5, 140.9, 138.6, 137.7, 136.7, 130.4 (q, J = 31.9 Hz), 129.3, 129.1, 128.7, 128.4, 126.6, 125.8 (q, J = 3.1 Hz), 123.6 (q, J = 272 Hz), 121.2, 120.3, 118.6, 77.7, 73.3, 65.5, 56.3, 50.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{27}F_3N_3O_3S^+$ 590.1719; found 590.1709.

(2*RS*,3*RS*)-4-Cyano-5-morpholino-*N*,3-diphenyl-2-((*E*)-3-(4-(trifluoromethyl)phenyl)acryloyl)-2,3-dihydrothiophene-2-carboxamide (4′al)



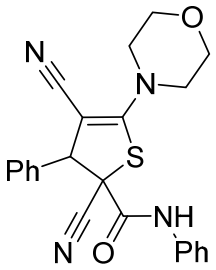
Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-diazo-3-oxo-*N*-phenyl-5-(4-(trifluoromethyl)phenyl)pent-4-enamide (**2l**) (83 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (1.4 mg, 1.0 mol %), benzene (3 mL), reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM) afforded **4′al** as a yellow amorphous solid (25%, 23 mg), that crystallizes into powder when treated with cold diethyl ether, mp 218–220 °C. **Method B**. **1a** (40 mg, 1.0 equiv, 0.15 mmol), **2l** (83 mg, 1.5 equiv, 0.23 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (8.7 mg), 1,2-DCE (1.5 mL), 90 °C, reaction time is 24 h. The product **4′al** was isolated as a yellow amorphous solid (60%, 51 mg), that crystallizes into powder when treated with cold diethyl ether, mp 218–220 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.93 (s, 1H), 7.98 – 7.94 (m, 3H), 7.77 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 7.3 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.24 – 7.10 (m, 6H), 7.01 (t, J = 7.2 Hz, 1H), 5.14 (s, 1H), 3.68 – 3.65 (m, 4H), 3.59 – 3.49 (m, 4H). ^{19}F{1H} NMR (376 MHz, DMSO-d_6): δ -61.37. ^{13}C{1H} NMR (150 MHz, DMSO-d_6): δ 185.6, 162.0, 159.7, 142.8, 137.7, 137.2, 137.1, 130.43 (q, J = 31.9 Hz), 129.4, 128.7, 128.4, 128.3, 128.0, 125.9 (q, J = 4.0 Hz), 124.7, 123.9 (q, J = 272.3 Hz), 123.2, 121.3, 118.5, 77.8, 75.1, 65.5, 53.4, 50.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{27}F_3N_3O_3S^+$ 590.1719; found 590.1713.

General procedure for the synthesis of dihydrothiophenes 4a,m-o and 4′a,m-o

Method A. A 10 mL standard microwave vial was charge with $Rh_2(Piv)_4$ (0.5 mol %), (morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (1.0 equiv) and dry chloroform (0.5 mL). A solution of diazo compounds **2m,n** (1.1 equiv) in dry chloroform (0.5 mL) was added slowly to the vial at 0 °C. The order of mixing the reagents for diazo compounds **2o** (1.6 equiv) was reversed. The reaction solution was stirred for 1 h at room temperature, and then the solution was directly subjected to SiO_2.

Method B. A 10 mL standard microwave vial was charge with $[Cu(MeCN)_4]CF_3SO_3$ (10 mol %), (morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (1.0 equiv), 2-cyano-2-diazo-*N*-phenylacetamide (**2m**) (1.2 equiv) and dry chloroform (1 mL). The reaction solution was stirred for 24 h at 70 °C, and then the solution was directly subjected to SiO_2 afforded **4f**.

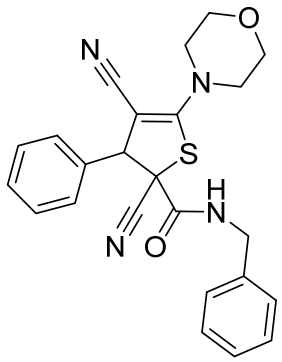
(2*RS*,3*RS*)-2,4-Dicyano-5-morpholino-*N*,3-diphenyl-2,3-dihydrothiophene-2-carboxamide (4am)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (40 mg, 1.0 equiv, 0.15 mmol), 2-cyano-2-diazo-*N*-phenylacetamide (**2m**) (35 mg, 1.1 equiv, 0.18 mmol), $Rh_2(Piv)_4$ (0.5 mg, 0.5 mol %), chloroform (1 mL), reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 0:50 to 30:20) afforded **4am** as a yellow amorphous solid, that crystallizes into colorless powder when treated with cold diethyl ether (56%, 36 mg, dr 93:7), mp 181–183 °C. **Method B**. **1a** (40 mg, 1.0 equiv, 0.15 mmol), **2m** (35 mg, 1.2 equiv, 0.23 mmol), $[Cu(MeCN)_4]CF_3SO_3$ (7.1 mg). The product **4am** was isolated as a yellow amorphous solid, that crystallizes into colorless powder when treated with cold diethyl ether (51%, 33 mg), mp 218–220 °C. Diastereomer **4′am** was isolated in a trace amount. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.76 (NH, s, 1H), 10.70 (NH, s, 1H, *minor isomer*), 7.64 (d, J = 7.7 Hz, 2H), 7.45 – 7.37 (m, 7H), 7.30 – 7.24 (m, *x*H, *minor isomer*), 7.18 (t, J = 7.2 Hz, 1H), 5.35 (s, 1H), 5.06 (s, 1H, *minor isomer*), 3.73 – 3.70 (m, 4H), 3.64 – 3.61 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 160.9, 160.8 (*minor isomer*), 160.5, 137.7, 137.6 (*minor isomer*), 135.2, 129.1, 128.9, 128.8 (*minor isomer*), 128.7, 128.4 (*minor isomer*), 125.1 (*minor isomer*), 125.0, 120.8, 120.6 (*minor*

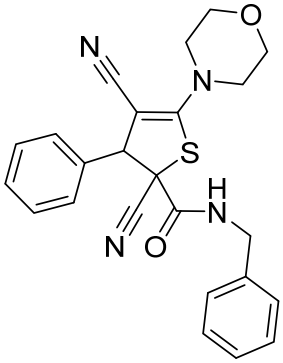
isomer), 118.0, 115.7, 70.4, 65.5, 58.0, 57.1, 50.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{21}N_4O_2S^+$ 417.1380; found 417.1384.

(2*RS*,3*RS*)-2,4-Dicyano-5-morpholino-*N*-phenethyl-3-phenyl-2,3-dihydrothiophene-2-carboxamide (4an)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (43 mg, 1.1 equiv, 0.21 mmol), $Rh_2(Piv)_4$ (0.65 mg, 0.5 mol %), chloroform (1 mL), reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 0:50 to 30:20) afforded **4an** as a colorless solid (44%, 37 mg, dr 96:4), mp 216–217 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.42 (t, J = 5.3 Hz, 2H, *minor isomer*), 9.31 (t, J = 5.5 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.30 (m, 3H), 7.28 – 7.23 (m, 3H), 6.94 – 6.92 (m, 2H), 5.16 (s, 1H, *minor isomer*), 4.86 (s, 1H), 4.10 (dd, J = 15.0, 5.9 Hz, 1H), 3.99 (dd, J = 15.1, 5.4 Hz, 1H), 3.73 – 3.71 (m, 4H), 3.67 – 3.64 (m, 4H). ^{13}C{1H} NMR (150 MHz, DMSO-d_6): δ 161.0, 159.6, 137.3, 134.6, 128.9, 128.6, 128.5, 128.3, 127.3, 127.1, 119.9, 118.2, 71.0, 65.5, 62.1, 57.8, 50.5, 43.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{23}N_4O_2S^+$ 431.1536; found 431.1537.

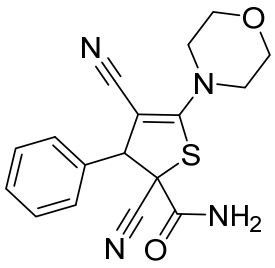
(2*RS*,3*SR*)-2,4-Dicyano-5-morpholino-*N*-phenethyl-3-phenyl-2,3-dihydrothiophene-2-carboxamide (4′an)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (43 mg, 1.1 equiv, 0.21 mmol), $Rh_2(Piv)_4$ (0.65 mg, 0.5 mol %), chloroform (1 mL), reaction time is 1 h. The purification of the crude product by

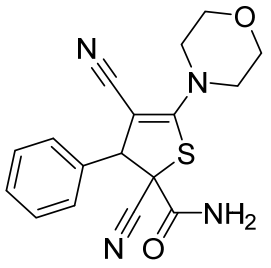
column chromatography on SiO_2 (PE/EtOAc, gradient 0:50 to 30:20) afforded **4′an** that crystallizes into colorless powder when treated with cold diethyl ether (44%, 37 mg, dr 96:4), mp 138–140 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.43 (t, J = 5.8 Hz, 2H), 9.31 (t, J = 5.3 Hz, 2H, *minor isomer*), 7.44 – 7.40 (m, 3H), 7.37 – 7.34 (m, 4H), 7.30 – 7.26 (m, 3H), 5.17 (s, 1H), 4.86 (s, 1H, *minor isomer*), 4.39 (d, J = 5.8 Hz, 2H), 3.71 – 3.69 (m, 4H), 3.63 – 3.61 (m, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 162.4, 160.5, 138.2, 135.0, 129.0, 129.0, 128.6, 128.4, 127.2, 127.1, 118.0, 115.9, 70.1, 65.5, 58.4, 56.8, 50.5, 43.7. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{23}N_4O_2S^+$ 431.1536; found 431.1533.

(2*RS*,3*RS*)-2,4-Dicyano-5-morpholino-3-phenyl-2,3-dihydrothiophene-2-carboxamide (4ao)



Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), 2-cyano-2-diazoacetamide (**2o**) (34 mg, 1.6 equiv, 0.31 mmol), $Rh_2(Piv)_4$ (0.94 mg, 0.5 mol %), chloroform (1 mL), reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 20:30 to 10:40) afforded **4ao** as a colorless solid (56%, 37 mg, single isomer), mp 208–209 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.25 (s, 1H, NH_2), 7.91 (s, 1H, NH_2), 7.48 – 7.46 (m, 2H), 7.38 – 7.34 (m, 3H), 4.81 (s, 1H), 3.73 – 3.71 (m, 4H), 3.66 – 3.65 (m, 4H). ^{13}C{1H} NMR (150 MHz, DMSO-d_6): δ 161.3, 161.0, 134.7, 128.9, 128.8, 128.4, 120.0, 118.2, 70.9, 65.5, 62.7, 57.7, 50.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{17}N_4O_2S^+$ 341.1067; found 341.1064.

(2*RS*,3*SR*)-2,4-Dicyano-5-morpholino-3-phenyl-2,3-dihydrothiophene-2-carboxamide (4′ao)



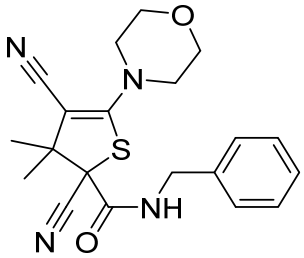
Method A. (Morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), 2-cyano-2-diazoacetamide (**2o**) (34 mg, 1.6 equiv, 0.31 mmol), $Rh_2(Piv)_4$ (0.94 mg, 0.5 mol %), chloroform (1 mL), reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 20:30 to 10:40) afforded **4′ao** as a yellow

amorphous solid (39%, 26 mg, single isomer). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.32 (s, 1H, NH_2), 8.19 (s, 1H, NH_2), 7.45 – 7.39 (m, 5H), 5.14 (s, 1H), 3.71 – 3.70 (m, 4H), 3.62 – 3.61 (m, 4H). ^{13}C{1H} NMR (150 MHz, DMSO-d_6): δ 164.0, 160.6, 135.3, 129.0, 128.9, 128.6, 118.1, 116.0, 70.0, 65.5, 58.2, 50.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{17}N_4O_2S^+$ 341.1067; found 341.1072.

General procedure for the synthesis of dihydrothiophenes 5

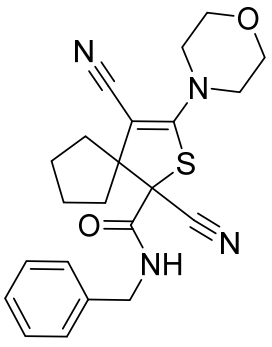
A 10 mL standard microwave vial was charge with $Rh_2(Piv)_4$ (0.5 mol %), thioamide **1** (1.0 equiv) and dry chloroform (0.5-1 mL). A solution of diazo compound **2n** (1.5 equiv), **2h** (1.5 equiv), **2p** (1.5–2.0 equiv), **2q** (1.5 equiv), **2s** (1.5 equiv) or **2t** (1.2 equiv) in dry chloroform (1-2 mL) was added slowly to the vial via syringe at room temperature. The reaction solution was stirred for 10 min–14 h at room temperature or at 40 °C (for **5kp**), 60 °C (for **5jq**) or 45 °C (for **5as**,**xs**), and then the solution was directly subjected to SiO_2 or neutral alumina (for **5at**).

***N*-Benzyl-2,4-dicyano-3,3-dimethyl-5-morpholino-2,3-dihydrothiophene-2-carboxamide (5hn)**



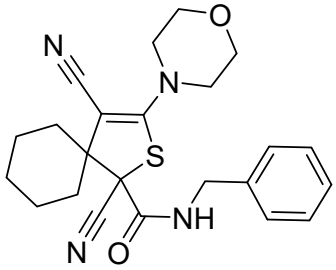
Product **5hn** was obtained according to the general procedure from 3-methyl-2-(morpholine-4-carbonothioyl)but-2-enenitrile (**1h**) (75 mg, 1.0 equiv, 0.36 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (107 mg, 1.5 equiv, 0.53 mmol), $Rh_2(Piv)_4$ (1.6 mg), chloroform (3.0 mL), reaction time is 13 min. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **5hn** as a yellow gum (98%, 134 mg). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.38 – 7.32 (m, 3H), 7.28 – 7.26 (m, 2H), 6.61 (t, J = 5.1 Hz, 1H), 4.55 – 4.42 (m, 2H), 3.74 – 3.72 (m, 4H), 3.58 – 3.56 (m, 4H), 1.63 (s, 3H), 1.25 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 160.7, 158.5, 136.5, 129.1, 128.4, 128.1, 117.6, 117.3, 79.2, 66.2, 63.4, 53.7, 50.9, 45.2, 25.0, 22.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{23}N_4O_2S^+$ 383.1536; found 383.1539.

***N*-Benzyl-1,4-dicyano-3-morpholino-2-thiaspiro[4.4]non-3-ene-1-carboxamide (5in)**



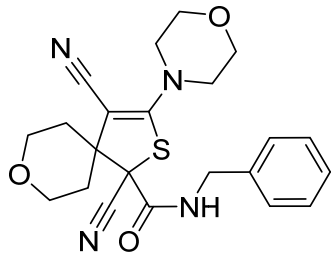
Product **5in** was obtained according to the general procedure from 2-cyclopentylidene-3-morpholino-3-thioxopropanenitrile (**1i**) (69 mg, 1.0 equiv, 0.29 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (88 mg, 1.5 equiv, 0.44 mmol), $Rh_2(Piv)_4$ (1.3 mg), chloroform (3.0 mL), reaction time is 15 min. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **5in** as a pale-yellow gum (83%, 99 mg), that crystallizes into powder when stored at 50 °C for 8 h, mp 143–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.38 – 7.27 (m, 5H), 6.66 (t, J = 5.8 Hz, 1H), 4.54 – 4.42 (m, 2H), 3.73 – 3.71 (m, 4H), 3.58 – 3.56 (m, 4H), 2.40 – 2.33 (m, 1H), 2.21 – 2.15 (m, 1H), 2.05 – 1.97 (m, 1H), 1.91 – 1.72 (m, 4H), 1.63 – 1.54 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 161.5, 159.3, 136.5, 129.1, 128.4, 128.1, 117.9, 117.3, 80.3, 66.3, 64.6, 62.1, 51.1, 45.1, 36.8, 35.7, 25.4, 24.9. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{25}N_4O_2S^+$ 409.1693; found 409.1695.

***N*-Benzyl-1,4-dicyano-3-morpholino-2-thiaspiro[4.5]dec-3-ene-1-carboxamide (5jn)**



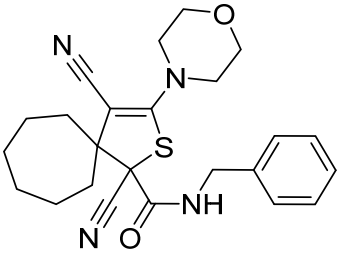
Product **5jn** was obtained according to the general procedure from 2-cyclohexylidene-3-morpholino-3-thioxopropanenitrile (**1j**) (68 mg, 1.0 equiv, 0.27 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (81 mg, 1.5 equiv, 0.40 mmol), $Rh_2(Piv)_4$ (1.2 mg), chloroform (3.0 mL), reaction time is 10 min. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 24:1) afforded **5jn** as a colorless powder (90%, 104 mg), mp 178–179 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.39 – 7.28 (m, 5H), 6.61 (t, J = 4.5 Hz, 1H), 4.55 (dd, J = 14.6, 5.8 Hz, 1H), 4.43 (dd, J = 14.5, 5.3 Hz, 1H), 3.74 – 3.72 (m, 4H), 3.64 – 3.54 (m, 4H), 2.28 (d, J = 11.1 Hz, 1H), 2.04 – 1.89 (m, 3H), 1.77 – 1.61 (m, 4H), 1.37 – 1.30 (m, 1H), 1.20 – 1.08 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 162.3, 161.0, 136.5, 129.1, 128.4, 128.1, 119.3, 117.1, 77.6, 66.4, 64.6, 56.0, 51.4, 45.2, 33.4, 32.7, 25.0, 22.3, 22.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{27}N_4O_2S^+$ 423.1849; found 423.1851.

***N*-Benzyl-1,4-dicyano-3-morpholino-8-oxa-2-thiaspiro[4.5]dec-3-ene-1-carboxamide (5kn)**



Product **5kn** was obtained according to the general procedure from 3-morpholino-2-(tetrahydro-4*H*-pyran-4-ylidene)-3-thioxopropanenitrile (**1k**) (50 mg, 1.0 equiv, 0.20 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (59 mg, 1.5 equiv, 0.30 mmol), $Rh_2(Piv)_4$ (0.9 mg), chloroform (3.0 mL), reaction time is 15 min. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 24:1 to 22.5:2.5) afforded **5kn** as a colorless solid (73%, 61 mg), mp 212–214 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.24 (t, J = 5.4 Hz, 1H), 7.35 – 7.24 (m, 5H), 4.35 (d, J = 5.6 Hz, 1H), 3.97 – 3.85 (m, 2H), 3.72 – 3.60 (m, 9H), 3.48 (t, J = 11.4 Hz, 1H), 2.31 – 2.23 (m, 1H), 1.93 (d, J = 13.7 Hz, 1H), 1.83 (d, J = 13.3 Hz, 1H), 1.51 – 1.44 (m, 1H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 163.0, 160.1, 138.1, 128.3, 127.4, 127.1, 119.4, 117.2, 73.2, 65.6, 64.7, 63.2, 63.2, 52.0, 51.0, 43.9, 32.6, 32.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{25}N_4O_3S^+$ 425.1642; found 425.1640.

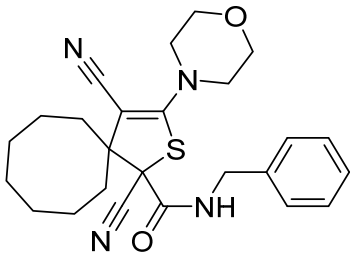
***N*-Benzyl-1,4-dicyano-3-morpholino-2-thiaspiro[4.6]undec-3-ene-1-carboxamide (5ln)**



Product **5ln** was obtained according to the general procedure from 2-cycloheptylidene-3-morpholino-3-thioxopropanenitrile (**1l**) (75 mg, 1.0 equiv, 0.28 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (85 mg, 1.5 equiv, 0.42 mmol), $Rh_2(Piv)_4$ (1.3 mg), chloroform (3.0 mL), reaction time is 10 min. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 24:1) afforded **5ln** as a pale-yellow gum (71%, 88 mg), that crystallizes into powder when stored at 50 °C for 8 h, mp 176–177 °C. ^{1}H NMR (400 MHz, $CDCl_3$-d): δ 7.39 – 7.29 (m, 5H), 6.69 (t, J = 4.9 Hz, 1H), 4.55 (dd, J = 14.5, 5.8 Hz, 1H), 4.39 (dd, J = 14.5, 5.0 Hz, 1H), 3.73 – 3.71 (m, 4H), 3.62 – 3.52 (m, 4H), 2.44 – 2.38 (m, 1H), 2.24 – 2.16 (m, 2H), 1.81 – 1.72 (m, 4H), 1.56 – 1.49 (m, 2H), 1.41 – 1.25 (m, 2H), 1.21 – 1.13 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-d): δ 160.7, 160.1, 136.3, 129.1, 128.4, 128.3, 118.5, 117.8, 80.9, 66.3,

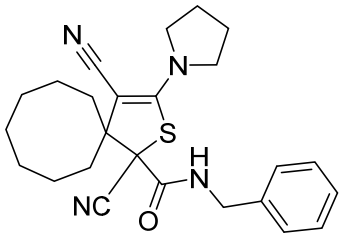
64.4, 60.1, 51.2, 45.4, 37.1, 33.4, 31.1, 30.9, 24.2, 23.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{29}N_4O_2S^+$ 437.2006; found 437.1999.

***N*-Benzyl-1,4-dicyano-3-morpholino-2-thiaspiro[4.7]dodec-3-ene-1-carboxamide (5on)**



Product **5on** was obtained according to the general procedure from 2-cyclooctylidene-3-morpholino-3-thioxopropanenitrile (**1o**) (50 mg, 1.0 equiv, 0.18 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (54 mg, 1.5 equiv, 0.27 mmol), $Rh_2(Piv)_4$ (0.8 mg), chloroform (3.0 mL), reaction time is 60 min. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 24:1 to 23:2) afforded **5on** as a pale-yellow gum (79%, 64 mg). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.38 – 7.29 (m, 5H), 6.63 (br. s, 1H, NH), 4.54 (dd, J = 14.3, 5.7 Hz, 1H), 4.42 (dd, J = 14.4, 5.0 Hz, 1H), 3.72 (br. s, 4H), 3.63 – 3.55 (m, 4H), 2.43 – 2.36 (m, 1H), 2.30 – 2.25 (m, 1H), 2.17 – 2.13 (m, 1H), 1.80 – 1.57 (m, 9H), 1.47 – 1.39 (m, 2H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): 162.0, 160.7, 136.5, 129.1, 128.4, 128.2, 118.7, 117.1, 78.7, 66.3, 60.3, 51.3, 45.2, 32.3, 29.6, 28.7, 28.1, 25.3, 23.0, 22.9. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{31}N_4O_2S^+$ 451.2162; found 451.2165.

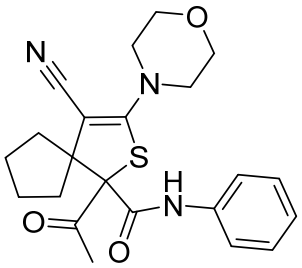
***N*-Benzyl-1,4-dicyano-3-(pyrrolidin-1-yl)-2-thiaspiro[4.7]dodec-3-ene-1-carboxamide (5qn)**



Product **5qn** was obtained according to the general procedure from 2-cyclooctylidene-3-(pyrrolidin-1-yl)-3-thioxopropanenitrile (**1q**) (40 mg, 1.0 equiv, 0.15 mmol), *N*-benzyl-2-cyano-2-diazoacetamide (**2n**) (46 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (0.7 mg), chloroform (3.0 mL), reaction time is 10 min. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 37.5:12.5) afforded **5qn** as a colorless solid (91%, 60 mg), mp 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.38 – 7.29 (m, 5H), 6.71 (t, J = 5.1 Hz, 1H), 4.54 (dd, J = 14.6, 5.9 Hz, 1H), 4.43 (dd, J = 14.6, 5.4 Hz, 1H), 3.62 (br. s, 4H), 2.44 – 2.38 (m, 1H), 2.29 – 2.23 (m, 1H), 2.16 – 2.10 (m, 1H), 1.96 – 1.94 (m, 4H), 1.78 – 1.73 (m, 2H), 1.68 – 1.56 (m, 7H),

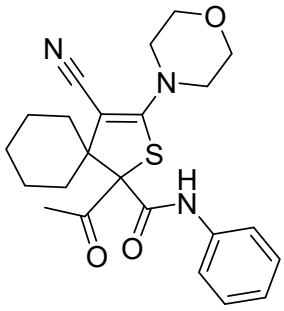
1.47 – 1.36 (m, 2H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): 162.4, 156.8, 136.7, 129.0, 128.2, 128.1, 120.2, 117.2, 73.6, 60.3, 52.0, 45.0, 32.7, 30.0, 28.7, 28.2, 25.7, 25.4, 23.1, 22.9. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{31}N_4OS^+$ 435.2213; found 435.2216.

1-Acetyl-4-cyano-3-morpholino-*N*-phenyl-2-thiaspiro[4.4]non-3-ene-1-carboxamide (5ih)



Product **5ih** was obtained according to the general procedure from 2-cyclopentylidene-3-morpholino-3-thioxopropanenitrile (**1i**) (155 mg, 1.0 equiv, 0.65 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (199 mg, 1.5 equiv, 0.98 mmol), $Rh_2(Piv)_4$ (3.0 mg), chloroform (3.5 mL), reaction time is 13 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.8:1.2) with subsequent centrifugation with *n*-hexane afforded **5ih** as a colorless powder (74%, 199 mg), mp 154–155 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 8.27 (s, 1H, NH), 7.50 (d, J = 8.1 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 6.9 Hz, 1H), 3.74 (br. s, 4H), 3.64 – 3.52 (m, 4H), 2.46 – 2.41 (m, 1H), 2.36 (s, 3H), 2.15 – 2.07 (m, 2H), 1.98 – 1.71 (m, 4H), 1.62 – 1.56 (m, 1H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): 197.1, 164.3, 158.5, 136.5, 129.4, 125.8, 120.6, 118.3, 84.0, 78.5, 66.39, 62.8, 51.0, 38.7, 34.1, 27.2, 25.3, 24.7. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{25}N_3O_3SNa^+$ 434.1509; found 434.1511.

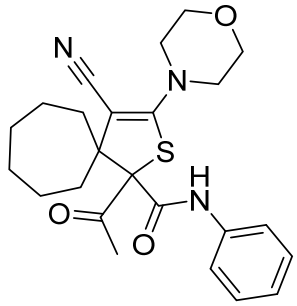
1-Acetyl-4-cyano-3-morpholino-*N*-phenyl-2-thiaspiro[4.5]dec-3-ene-1-carboxamide (5jh)



Product **5jh** was obtained according to the general procedure from 2-cyclohexylidene-3-morpholino-3-thioxopropanenitrile (**1j**) (128 mg, 1.0 equiv, 0.50 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (156 mg, 1.5 equiv, 0.77 mmol), $Rh_2(Piv)_4$ (2.3 mg), chloroform (3.5 mL), reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 25:25) afforded **5jh** as a colorless powder (82%, 178 mg), mp 198–

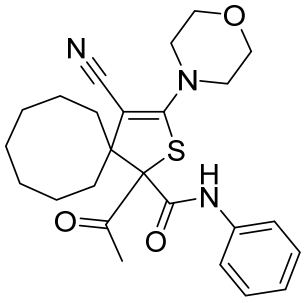
200 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.60 (s, 1H), 7.50 (d, J = 7.9 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 3.79 – 3.72 (m, 4H), 3.70 – 3.56 (m, 4H), 2.45 (s, 3H), 2.36 – 2.29 (m, 1H), 2.23 – 2.16 (m, 1H), 2.03 – 1.96 (m, 1H), 1.77 – 1.67 (m, 5H), 1.62 – 1.55 (m, 1H), 1.18 – 1.07 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 200.5, 163.6, 163.4, 136.8, 129.3, 125.5, 120.6, 119.9, 81.5, 79.3, 66.5, 55.4, 51.3, 34.4, 31.0, 29.6, 25.2, 22.6. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{28}N_3O_3S^+$ 426.1846; found 426.1840.

1-Acetyl-4-cyano-3-morpholino-*N*-phenyl-2-thiaspiro[4.6]undec-3-ene-1-carboxamide (5lh)



Product **5lh** was obtained according to the general procedure from 2-cycloheptylidene-3-morpholino-3-thioxopropanenitrile (**1l**) (80 mg, 1.0 equiv, 0.30 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (92 mg, 1.5 equiv, 0.45 mmol), $Rh_2(Piv)_4$ (1.4 mg), chloroform (2.0 mL), reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **5lh** as a colorless powder (92%, 123 mg), mp 174–175 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.51 (s, 1H, NH), 7.50 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 3.78 – 3.70 (m, 4H), 3.66 – 3.54 (m, 4H), 2.57 – 2.46 (m, 1H), 2.41 (s, 3H), 2.38 – 2.32 (m, 1H), 2.05 – 1.99 (m, 2H), 1.80 – 1.73 (m, 3H), 1.68 – 1.55 (m, 2H), 1.48 – 1.31 (m, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): 198.8, 164.2, 160.4, 136.8, 129.4, 125.6, 120.6, 119.1, 83.5, 80.9, 66.5, 58.9, 51.2, 35.8, 34.1, 30.8, 30.6, 28.5, 24.7, 24.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{29}N_3O_3SNa^+$ 462.1822; found 462.1823.

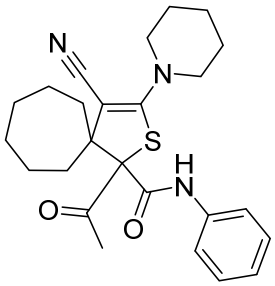
1-Acetyl-4-cyano-3-morpholino-*N*-phenyl-2-thiaspiro[4.7]dodec-3-ene-1-carboxamide (5oh)



Product **5oh** was obtained according to the general procedure from 2-cyclooctylidene-3-morpholino-3-thioxopropanenitrile (**1o**) (80 mg, 1.0 equiv, 0.29 mmol), 2-diazo-3-oxo-*N*-

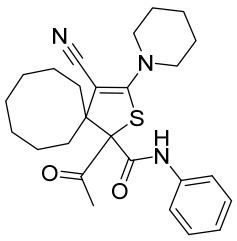
phenylbutanamide (**2h**) (87 mg, 1.5 equiv, 0.43 mmol), $Rh_2(Piv)_4$ (1.3 mg), chloroform (2.0 mL), reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **5oh** as a colorless powder (75%, 98 mg), mp 241–243 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.88 (s, 1H, NH), 7.51 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 3.79 – 3.58 (m, 8H), 2.51 (s, 3H), 2.31 – 2.10 (m, 3H), 1.99 – 1.92 (m, 1H), 1.73 – 1.40 (m, 10H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): 203.2, 163.4, 161.9, 136.9, 129.3, 125.4, 120.4, 119.4, 82.2, 81.0, 66.5, 59.9, 51.2, 31.6, 30.6, 30.2, 28.7, 28.2, 25.9, 23.2, 23.2. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{32}N_3O_3S^+$ 454.2159; found 454.2155.

1-Acetyl-4-cyano-N-phenyl-3-(piperidin-1-yl)-2-thiaspiro[4.6]undec-3-ene-1-carboxamide (5ph)



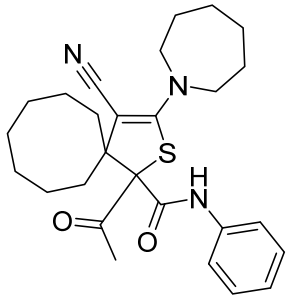
Product **5ph** was obtained according to the general procedure from 2-cycloheptylidene-3-(piperidin-1-yl)-3-thioxopropanenitrile (**1p**) (60 mg, 1.0 equiv, 0.23 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (70 mg, 1.5 equiv, 0.34 mmol), $Rh_2(Piv)_4$ (1.0 mg), chloroform (2.0 mL), reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 37.5:12.5) afforded **5ph** as a colorless powder (79%, 79 mg), mp 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.59 (s, 1H, NH), 7.52 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.9 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 3.65 – 3.60 (m, 4H), 2.50 – 2.32 (m, 5H), 2.12 – 1.96 (m, 2H), 1.82 – 1.59 (m, 11H), 1.53 – 1.45 (m, 2H), 1.39 – 1.32 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): 199.4, 164.8, 160.6, 136.8, 129.2, 125.3, 120.4, 119.8, 81.1, 80.4, 58.3, 52.6, 35.9, 34.1, 30.6, 30.2, 28.7, 26.1, 24.5, 24.3, 24.0. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{32}N_3O_2S^+$ 438.2201; found 438.2212.

1-Acetyl-4-cyano-*N*-phenyl-3-(piperidin-1-yl)-2-thiaspiro[4.7]dodec-3-ene-1-carboxamide (5rh)



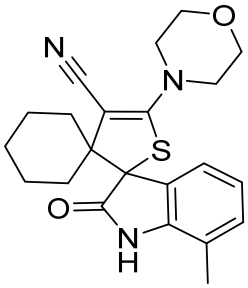
Product **5rh** was obtained according to the general procedure from 2-cyclooctylidene-3-(piperidin-1-yl)-3-thioxopropanenitrile (**1r**) (90 mg, 1.0 equiv, 0.32 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (99 mg, 1.5 equiv, 0.49 mmol), $Rh_2(Piv)_4$ (1.5 mg), chloroform (2.0 mL), reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 37.5:12.5) afforded **5rh** as a colorless powder (76%, 112 mg), mp 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.90 (s, 1H, NH), 7.51 (d, J = 7.7 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 3.66 – 3.58 (m, 4H), 2.51 (s, 3H), 2.35 – 2.08 (m, 3H), 1.99 – 1.93 (m, 1H), 1.77 – 1.68 (m, 10H), 1.60 – 1.39 (m, 6H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): *the product decomposes while recording a carbon spectrum*. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{34}N_3O_2S^+$ 452.2366; found 452.2369.

1-Acetyl-3-(azepan-1-yl)-4-cyano-*N*-phenyl-2-thiaspiro[4.7]dodec-3-ene-1-carboxamide (5sh)



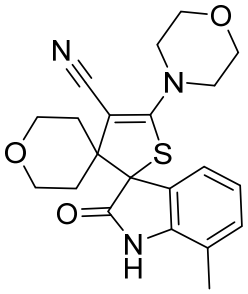
Product **5sh** was obtained according to the general procedure from 2-cyclooctylidene-3-(piperidin-1-yl)-3-thioxopropanenitrile (**1s**) (90 mg, 1.0 equiv, 0.31 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (94 mg, 1.5 equiv, 0.46 mmol), $Rh_2(Piv)_4$ (1.4 mg), chloroform (2.0 mL), reaction time is 14 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 37.5:12.5) afforded **5sh** as a colorless powder (83%, 119 mg), mp 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.93 (s, 1H, NH), 7.51 (d, J = 7.7 Hz, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 3.74 – 3.64 (m, 4H), 2.53 (s, 3H), 2.35 – 2.29 (m, 1H), 2.24 – 2.18 (m, 2H), 2.11 – 2.05 (m, 1H), 2.00 – 1.93 (m, 1H), 1.87 – 1.81 (m, 4H), 1.78 – 1.41 (m, 14H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): 203.8, 164.1, 161.0, 137.1, 129.3, 125.2, 120.7, 120.4, 83.0, 75.6, 59.6, 54.3, 31.8, 30.8, 30.7, 29.1, 28.9, 28.3, 26.9, 26.0, 23.4, 23.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{27}H_{36}N_3O_2S^+$ 466.2522; found 466.2524.

7''-Methyl-5'-morpholino-2''-oxodispiro[cyclohexane-1,3'-thiophene-2',3''-indoline]-4'-carbonitrile (5jp)



Product **5jp** was obtained according to the general procedure from 2-cyclohexylidene-3-morpholino-3-thioxopropanenitrile (**1j**) (40 mg, 1.0 equiv, 0.16 mmol), 3-diazo-7-methylindolin-2-one (**2p**) (41 mg, 1.5 equiv, 0.24 mmol), $Rh_2(Piv)_4$ (0.70 mg), chloroform (2.0 mL), reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 30:20 to 20:30) afforded **5jp** as a colorless powder (75%, 47 mg), mp 222–223 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 9.62 (s, 1H), 7.26 (d, J = 7.3 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 3.78 – 3.58 (m, 7H), 2.32 (s, 3H), 2.25 (d, J = 9.9 Hz, 1H), 2.14 – 2.00 (m, 2H), 1.70 – 1.61 (m, 4H), 1.51 (d, J = 14.1 Hz, 1H), 1.31 – 1.23 (m, 1H), 1.07 – 0.97 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 178.0, 165.6, 140.2, 131.4, 124.7, 124.3, 122.4, 121.0, 120.1, 78.1, 66.7, 66.5, 55.2, 51.4, 34.0, 30.5, 25.3, 22.3, 22.3, 16.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{26}N_3O_2S^+$ 396.1740; found 396.1740.

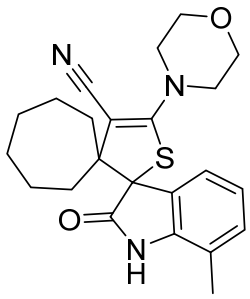
7-Methyl-5'-morpholino-2-oxo-2'',3'',5'',6''-tetrahydrodispiro[indoline-3,2'-thiophene-3',4''-pyran]-4'-carbonitrile (5kp)



Product **5kp** was obtained according to the general procedure from 3-morpholino-2-(tetrahydro-4*H*-pyran-4-ylidene)-3-thioxopropanenitrile (**1k**) (41 mg, 1.0 equiv, 0.15 mmol), 3-diazo-7-methylindolin-2-one (**2p**) (39 mg, 1.5 equiv, 0.24 mmol), $Rh_2(Piv)_4$ (0.70 mg), chloroform (2.0 mL), 40 °C, reaction time is 30 min. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 30:20 to 40:10) afforded **5kp** as a colorless powder (89%, 56 mg), mp 288–290 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.82 (s, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 3.87 (t, J = 11.1 Hz, 1H), 3.71 – 3.63

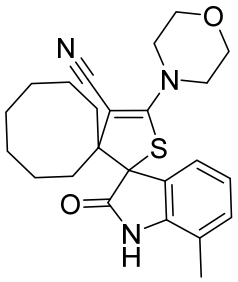
(m, 6H), 3.60 – 3.54 (m, 4H), 2.20 (s, 3H), 1.98 – 1.92 (m, 1H), 1.85 – 1.78 (m, 2H), 1.51 – 1.44 (m, 1H). $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6): δ 174.7, 165.3, 140.6, 131.2, 123.7, 123.7, 121.5, 120.2, 119.7, 74.7, 65.6, 63.1, 51.3, 50.8, 33.7, 30.6, 16.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{24}N_3O_3S^+$ 398.1533; found 398.1530.

7''-Methyl-5'-morpholino-2''-oxodispiro[cycloheptane-1,3'-thiophene-2',3''-indoline]-4'-carbonitrile (5lp)



Product **5lp** was obtained according to the general procedure from 2-cycloheptylidene-3-morpholino-3-thioxopropanenitrile (**1l**) (39 mg, 1.0 equiv, 0.15 mmol), 3-diazo-7-methylindolin-2-one (**2p)** (39 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (0.68 mg), chloroform (2.0 mL), reaction time is 20 min. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 30:20 to 25:25) afforded **5lp** as a colorless powder (79%, 49 mg), mp 209–211 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 9.34 (s, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 3.78 – 3.76 (m, 4H), 3.69 – 3.57 (m, 4H), 2.31 (s, 3H), 2.27 – 2.18 (m, 2H), 2.00 – 1.94 (m, 1H), 1.86 – 1.73 (m, 2H), 1.66 – 1.53 (m, 2H), 1.46 – 1.41 (m, 3H), 1.25 – 1.14 (m, 2H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 178.0, 163.1, 139.9, 131.4, 125.1, 124.2, 122.6, 120.0, 81.4, 66.6, 66.0, 59.6, 51.2, 35.0, 34.6, 31.0, 30.8, 24.4, 24.2, 16.6. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{28}N_3O_2S^+$ 410.1897; found 410.1897.

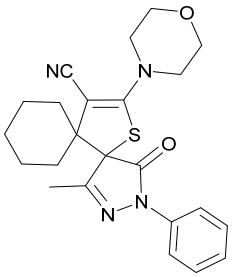
7''-Methyl-5'-morpholino-2''-oxodispiro[cyclooctane-1,3'-thiophene-2',3''-indoline]-4'-carbonitrile (5op)



A 10 mL standard microwave vial was charge with $Rh_2(Piv)_4$ (0.60 mg, 1.0 mol %), 2-cyclooctylidene-3-morpholino-3-thioxopropanenitrile (**1o**) (40 mg, 1.0 equiv, 0.14 mmol) and dry

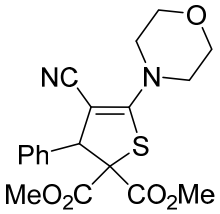
chloroform (1 mL). A solution of diazocompound **2p** (37 mg, 1.5 equiv, 0.21 mmol) in dry chloroform (1 mL) was added slowly to the vial at room temperature. The reaction solution was stirred for 20 min at room temperature, and then a portion of **2p** (25 mg, 1.0 equiv, 0.14 mmol) in 0.5 mL dry chloroform was added. The reaction solution was stirred for 40 min at room temperature, and then the solution was directly subjected to SiO_2. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 30:20 to 40:10) with subsequent centrifugation with cold diethyl ether afforded **5op** as a colorless powder (57%, 35 mg), mp 228–230 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 9.49 (s, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 3.77 – 3.75 (m, 4H), 3.70 – 3.58 (m, 4H), 2.45 – 2.37 (m, 1H), 2.29 (s, 3H), 2.24 – 2.21 (m, 2H), 2.06 – 2.00 (m, 1H), 1.66 (br. s, 1H), 1.55 (br. s, 4H), 1.47 – 1.42 (m, 1H), 1.32 (br. s, 3H), 0.91 (br. s, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 178.3, 163.4, 139.6, 131.3, 124.0, 122.5, 120.1, 120.0, 79.7, 66.6, 66.2, 58.8, 51.3, 30.1, 29.7, 29.3, 28.0, 25.4, 22.9, 22.1, 16.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{30}N_3O_2S^+$ 424.2053; found 424.2055.

1-Methyl-13-morpholino-4-oxo-3-phenyl-14-thia-2,3-diazadispiro[4.0.5^6.3^5]tetradeca-1,12-diene-12-carbonitrile (5jq)



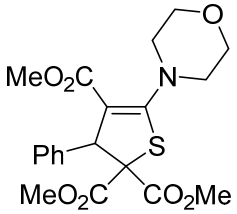
Product **5jq** was obtained according to the general procedure from 2-cyclohexylidene-3-morpholino-3-thioxopropanenitrile (**1j**) (40 mg, 1.0 equiv, 0.16 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2q**) (48 mg, 1.5 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (0.70 mg), chloroform (2.0 mL), 60 °C, reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 20:5) afforded **5jq** as a pale-yellow oil (79%, 53 mg). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.88 (d, J = 7.8 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 3.82 – 3.67 (m, 6H), 3.62 – 3.57 (m, 2H), 2.30 (s, 3H), 2.19 – 2.15 (m, 1H), 2.10 – 2.02 (m, 2H), 1.95 – 1.91 (m, 1H), 1.73 – 1.68 (m, 1H), 1.65 – 1.59 (m, 2H), 1.51 – 1.47 (m, 1H), 1.39 – 1.32 (m, 1H), 1.21 – 1.15 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 167.6, 163.9, 159.6, 137.6, 129.0, 125.7, 119.8, 119.0, 78.2, 68.5, 66.6, 55.6, 51.5, 32.6, 31.1, 25.1, 22.4, 22.4, 16.3. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{27}N_4O_2S^+$ 423.1849; found 423.1853.

Dimethyl 4-cyano-5-morpholino-3-phenylthiophene-2,2(3*H*)-dicarboxylate (5as)



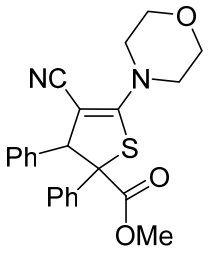
Product **5as** was obtained according to the general procedure from 2-(morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), dimethyl 2-diazomalonate (**2s**) (46 mg, 1.5 equiv, 0.29 mmol), $Rh_2(Piv)_4$ (0.90 mg), chloroform (2.0 mL), 45 °C, reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 20:30) afforded **5as** as a colorless powder (95%, 71 mg), mp 153–154 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.35 (br. s, 5H), 4.89 (s, 1H), 3.81 (s, 6H), 3.69 (br. s, 4H), 3.57 (br. s, 4H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 168.1, 165.0, 160.6, 136.2, 128.6, 128.5, 128.4, 118.3, 71.8, 68.9, 65.5, 56.7, 54.1, 53.2, 50.2. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{21}N_2O_5S^+$ 389.1165; found 389.1164.

Trimethyl 5-morpholino-3-phenylthiophene-2,2,4(3*H*)-tricarboxylate (5xs)



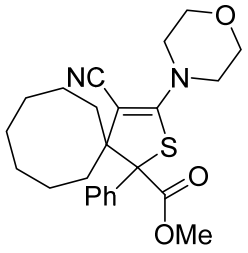
Product **5xs** was obtained according to the general procedure from methyl 2-(morpholine-4-carbonothioyl)-3-phenylacrylate (**1x**) (58 mg, 1.0 equiv, 0.20 mmol), dimethyl 2-diazomalonate (**2s**) (47 mg, 1.5 equiv, 0.30 mmol), $Rh_2(Piv)_4$ (0.90 mg), chloroform (2.0 mL), 45 °C, reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 25:25) with subsequent centrifugation with cold diethyl ether afforded **5xs** as a colorless powder (69%, 58 mg), mp 173–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.37 (d, J = 7.0 Hz, 2H), 7.29 – 7.24 (m, 3H), 5.25 (s, 1H), 3.87 – 3.75 (m, 7H), 3.67 – 3.59 (m, 2H), 3.55 (s, 3H), 3.40 – 3.35 (m, 2H), 3.29 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 169.1, 166.1, 164.1, 162.9, 138.3, 128.7, 128.2, 127.9, 99.5, 69.2, 66.9, 57.1, 53.9, 53.1, 53.0, 51.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{24}NO_7S^+$ 422.1268; found 422.1271.

Methyl 4-cyano-5-morpholino-2,3-diphenyl-2,3-dihydrothiophene-2-carboxylate (5at)



Product **5at** was obtained according to the general procedure from 2-(morpholine-4-carbonothioyl)-3-phenylacrylonitrile (**1a**) (50 mg, 1.0 equiv, 0.19 mmol), methyl 2-diazo-2-phenylacetate (**2t**) (41 mg, 1.2 equiv, 0.23 mmol), $Rh_2(Piv)_4$ (0.70 mg), chloroform (2.0 mL), rt, reaction time is 15 min. The purification of the crude product by column chromatography on neutral alumina (PE/EtOAc, gradient 25:0 to 35:15) afforded **5at** as a colorless powder (76%, 60 mg), mp 68–70 °C, *a mixture of diastereomers* (dr 65:35). ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.59 (d, J = 7.3 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.45 – 7.30 (m, 7H), 7.12 – 6.93 (m, 6H), 5.24 (s, 0.56H), 4.75 (s, 1H), 3.83 – 3.81 (m, 4H), 3.74 – 3.70 (m, 6H), 3.62 – 3.55 (m, 4H), 3.26 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 172.5, 169.5, 162.5, 161.8, 141.8, 137.6, 136.3, 134.5, 129.3, 129.0, 128.6, 128.5, 128.4, 128.4, 128.0, 128.0, 127.8, 127.5, 127.2, 125.6, 119.1, 118.8, 75.2, 74.1, 73.1, 69.9, 66.4, 66.3, 60.0, 59.6, 53.7, 52.8, 50.8, 50.7. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{23}N_2O_3S^+$ 407.1424; found 407.1423.

Methyl 4-cyano-3-morpholino-1-phenyl-2-thiaspiro[4.7]dodec-3-ene-1-carboxylate (5ot)



Method A. Product **5ot** was obtained according to the general procedure from 2-cyclooctylidene-3-morpholino-3-thioxopropanenitrile (**1o**) (50 mg, 1.0 equiv, 0.14 mmol), methyl 2-diazo-2-phenylacetate (**2t**) (30 mg, 1.2 equiv, 0.17 mmol), $Rh_2(Piv)_4$ (0.70 mg), chloroform (2.0 mL), rt, reaction time is 60 min. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 35:15) with subsequent centrifugation with a mixture of diethyl ether:hexane (0.4 mL : 1 mL) afforded **5ot** as a colorless powder (85%, 52 mg), mp 179–181 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.41 – 7.38 (m, 2H), 7.36 – 7.32 (m, 3H), 3.83 – 3.71 (m, 9H), 3.66 – 3.61 (m, 2H), 2.48 – 2.41 (m, 1H), 2.24 – 2.19 (m, 1H), 2.01 – 1.93 (m, 1H), 1.81 – 1.61 (m, 7H), 1.47 – 1.25 (m, 4H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 169.8, 163.6, 137.1, 128.5,

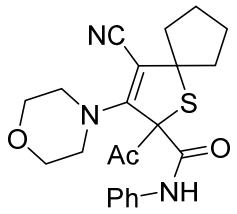
128.5, 127.4, 120.3, 80.7, 76.2, 66.7, 60.1, 53.2, 51.1, 30.7, 30.2, 29.7, 28.1, 25.8, 24.3, 22.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{31}N_2O_3S^+$ 427.2050; found 427.2051.

Method B. To an oven-dried 50 mL standard screw glass vial (50 mL) $[Cu(MeCN)_4]CF_3SO_3$ (19 mg, 10 mol %), thioamide (**1o**) (70 mg, 1.0 equiv, 0.25 mmol), methyl 2-diazo-2-phenylacetate (**2t**) (88 mg, 2.0 equiv, 0.50 mmol) and dry chloroform (3.5 mL) were added. Then, the reaction mixture was allowed to stir at 90 °C for 24 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 35:15) with subsequent centrifugation with a mixture diethyl ether:hexane (0.4 mL:1.0 mL) afforded **5ot** as a colorless powder (70%, 77 mg), mp 179–181 °C.

General procedure for the synthesis of dihydrothiophenes 6

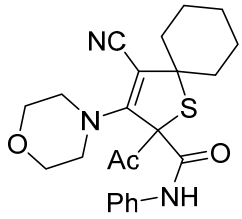
To an oven-dried 50 mL standard screw glass vial (50 mL) $[Cu(MeCN)_4]CF_3SO_3$ (10 mol %), thioamides (**1i,j,l,o**) (1.0 equiv), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (2.0 equiv) and dry chloroform were added. Then, the reaction mixture was allowed to stir at 90 °C for 24 h. Upon completion, the solution was directly subjected to SiO_2 afforded **6**.

2-Acetyl-4-cyano-3-morpholino-*N*-phenyl-1-thiaspiro[4.4]non-3-ene-2-carboxamide (6ih)



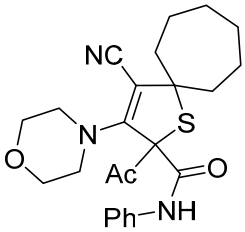
Product **6ih** was obtained according to the general procedure from 2-cyclopentylidene-3-morpholino-3-thioxopropanenitrile (**1i**) (203 mg, 1.0 equiv, 0.86 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (349 mg, 2.0 equiv, 1.72 mmol), $[Cu(MeCN)_4]OTf$ (65 mg), chloroform (6.0 mL), 90 °C, reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **6ih** as a yellow oily mass (116 mg). The latter was triturated with hexane:diethyl ether (1:1) and the formed precipitate was centrifugated afforded **6ih** as a colorless powder (23%, 80 mg), mp 164–166 °C. The second regioisomer was isolated by column chromatography on SiO_2 (DCM/EtOAc, gradient up to 23:2) as a brown oily mass (144 mg). The trituration with hexane:diethyl ether (1:1) and centrifugation of the formed precipitate afforded **5ih** as a colorless powder (31%, 109 mg), mp 154–155 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 9.29 (s, 1H), 7.54 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 3.71 – 3.62 (m, 4H), 3.58 – 3.52 (m, 2H), 3.38 – 3.33 (m, 2H), 2.49 (s, 3H), 2.35 – 2.20 (m, 2H), 2.16 – 2.11 (m, 1H), 2.02 – 1.97 (m, 1H), 1.87 – 1.80 (m, 2H), 1.76 – 1.68. $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$): δ 201.5, 165.7, 156.2, 137.2, 129.3, 125.3, 120.2, 117.4, 91.5, 71.8, 67.5, 66.5, 50.3, 42.4, 41.1, 26.6, 24.3, 24.0. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{26}N_3O_3S^+$ 412.1689; found 412.1687.

2-Acetyl-4-cyano-3-morpholino-*N*-phenyl-1-thiaspiro[4.5]dec-3-ene-2-carboxamide (6jh)



Product **6jh** was obtained according to the general procedure from 2-cyclohexylidene-3-morpholino-3-thioxopropanenitrile (**1j**) (192 mg, 1.0 equiv, 0.77 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (312 mg, 2.0 equiv, 1.53 mmol), $[Cu(MeCN)_4]OTf$ (58 mg), chloroform (6.0 mL), 90 °C, reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **6jh** as a yellow oily mass (253 mg). The latter was triturated with hexane:diethyl ether (1:1) and the formed precipitate was centrifugated afforded **6jh** as a colorless powder (57%, 185 mg), mp 195–196 °C. The second regioisomer was isolated by column chromatography on SiO_2 (DCM/EtOAc, gradient up to 23:2) as a brown gum (30 mg). The trituration with hexane:diethyl ether (1:1) and centrifugation of the formed precipitate afforded **6jh** as a colorless powder (5%, 16 mg), mp 198–200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (s, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 6.4 Hz, 1H), 3.67 – 3.62 (m, 4H), 3.57 – 3.51 (m, 2H), 3.37 – 3.32 (m, 2H), 2.49 (s, 3H), 2.04 – 1.96 (m, 3H), 1.88 – 1.79 (m, 3H), 1.67 (d, J = 13.4 Hz, 1H), 1.47 – 1.30 (m, 2H), 1.26 – 1.14 (m, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 201.7, 165.9, 155.8, 137.2, 129.3, 125.3, 120.2, 117.6, 93.9, 71.0, 66.5, 63.8, 50.3, 40.1, 39.0, 26.6, 24.5, 24.4, 23.9. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{28}N_3O_3S^+$ 426.1846; found 426.1846.

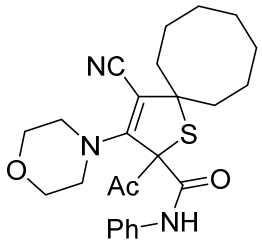
2-Acetyl-4-cyano-3-morpholino-*N*-phenyl-1-thiaspiro[4.6]undec-3-ene-2-carboxamide (6lh)



Product **6lh** was obtained according to the general procedure from 2-cycloheptylidene-3-morpholino-3-thioxopropanenitrile (**1l**) (200 mg, 1.0 equiv, 0.76 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (307 mg, 2.0 equiv, 1.51 mmol), $[Cu(MeCN)_4]OTf$ (57 mg), chloroform (6.0 mL), 90 °C, reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23:2) afforded **6lh** as a yellow oily mass (281 mg). The latter was triturated with hexane:diethyl ether (1:1) and the formed precipitate was

centrifugated afforded **6lh** as a colorless powder (56%, 187 mg), mp 168–170 °C. The second regioisomer was formed in a trace amount. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (s, 1H, NH), 7.53 (d, J = 8.6 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 3.69 – 3.60 (m, 4H), 3.56 – 3.50 (m, 2H), 3.35 – 3.29 (m, 2H), 2.48 (s, 3H), 2.26 – 2.18 (m, 3H), 2.05 – 2.00 (m, 1H), 1.83 – 1.77 (m, 2H), 1.61 – 1.48 (m, 6H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$): 201.6, 165.8, 155.4, 137.2, 129.3, 125.3, 120.2, 117.9, 95.3, 71.5, 66.5, 66.0, 50.4, 44.3, 42.6, 27.7, 27.7, 26.6, 24.5, 24.0. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{29}N_3O_3S^+$ 440.2002; found 440.1999.

2-Acetyl-4-cyano-3-morpholino-*N*-phenyl-1-thiaspiro[4.7]dodec-3-ene-2-carboxamide (6oh)

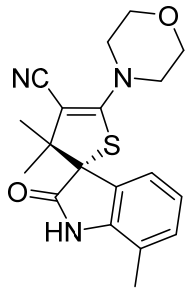


Product **6oh** was obtained according to the general procedure from 2-cyclooctylidene-3-morpholino-3-thioxopropanenitrile (**1o**) (200 mg, 1.0 equiv, 0.72 mmol), 2-diazo-3-oxo-*N*-phenylbutanamide (**2h**) (292 mg, 2.0 equiv, 1.44 mmol), $[Cu(MeCN)_4]OTf$ (54 mg), chloroform (6.0 mL), 90 °C, reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 23.5:1.5) afforded **6oh** as a yellow oily mass (276 mg). The latter was triturated with hexane:diethyl ether (1:1) and the formed precipitate was centrifugated afforded **6oh** as a colorless powder (67%, 218 mg), mp 241–243 °C. The second regioisomer was formed in a trace amount. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (s, 1H, NH), 7.53 (d, J = 7.9 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 3.70 – 3.60 (m, 4H), 3.56 – 3.52 (m, 2H), 3.36 – 3.30 (m, 2H), 2.43 (s, 3H), 2.41 – 2.31 (m, 2H), 2.26 – 2.20 (m, 1H), 2.08 – 2.02 (m, 1H), 1.90 – 1.85 (m, 2H), 1.65 – 1.51 (m, 9H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$): 201.5, 165.9, 156.0, 137.2, 129.3, 125.3, 120.2, 118.2, 94.6, 71.4, 66.6, 65.8, 50.5, 40.8, 38.8, 27.9, 27.8, 26.6, 24.5, 24.1, 24.0. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{32}N_3O_3S^+$ 454.2159; found 454.2159.

Asymmetric Synthesis of Dihydrithiophenes 5

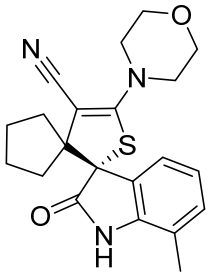
A 20 mL Schlenk tube was charge with Rh_2(*S*-NTTL)$_4$ (0.5 mol %), thioamide **1** (1.0 equiv) and dry chloroform (1 mL). A solution of diazo compound **2p** or **2v** (1.5 equiv) in dry chloroform (1 mL) was added slowly to the tube via syringe at 0 °C. Then the reaction solution was allowed to warm to room temperature and stirred for 40 min (for **5hp**) or stirred 30 min at 0 °C and 20 min at room temperature (for **5ip**, **jp′**, **lp′**, **op′**,**ov**), and then the solution was directly subjected to SiO_2.

(*S*)-3',3',7-Trimethyl-5'-morpholino-2-oxo-3'*H*-spiro[indoline-3,2'-thiophene]-4'-carbonitrile (5hp)



Product **5hp** was obtained according to the general procedure from thioamide **1h** (30 mg, 1.0 equiv, 0.14 mmol), diazo compound **2p** (37 mg, 1.5 equiv, 0.21 mmol), Rh_2(*S*-NTTL)$_4$ (1.3 mg), chloroform (2 mL). The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 20:5) afforded **5hp** as a colorless powder (96%, 49 mg, 1.4:98.6 e.r.), mp 131–133 °C, $[\alpha]_D^{20} = +59$ (C = 0.89, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on a Chiralpak AD column: 5:1 *n*-hexane/*i*-PrOH, flow rate 1 mL/min, λ = 220, 230 nm: TR Minor = 8.28 min, TR Major = 9.67 min. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.73 (s, 1H, NH), 7.27 (d, J = 7.0 Hz, 1H), 7.11 (d, J = 7.0 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 3.67 (br. s, 4H), 3.53 (br. s, 4H), 2.20 (s, 3H), 1.26 (s, 3H), 1.08 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 175.9, 161.4, 140.9, 131.3, 123.8, 123.5, 121.7, 119.6, 118.7, 78.2, 65.6, 63.6, 51.6, 50.4, 25.1, 22.1, 16.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{22}N_3O_2S^+$ 356.1427; found 356.1433.

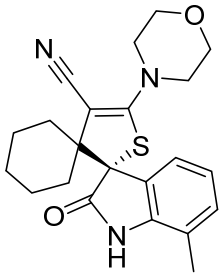
(*S*)-7''-Methyl-5'-morpholino-2''-oxodispiro[cyclopentane-1,3'-thiophene-2',3''-indoline]-4'-carbonitrile (5ip)



Product **5ip** was obtained according to the general procedure from thioamide **1i** (30 mg, 1.0 equiv, 0.13 mmol), diazo compound **2p** (33 mg, 1.5 equiv, 0.19 mmol), Rh_2(*S*-NTTL)$_4$ (1.4 mg), chloroform (2 mL). The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 20:5 to 20:20) afforded **5ip** as a colorless powder (83%, 40 mg, 3.9:96.1 e.r.), mp 102–104 °C, $[\alpha]_D^{20} = -7.7$ (C = 0.77, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on a Chiralpak AD column: 5:1 *n*-hexane/*i*-PrOH, flow rate 1 mL/min, λ = 220, 230 nm: TR Minor = 11.98 min, TR Major = 12.70 min. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 9.51 (s, 1H, NH), 7.33 (d, J = 7.5 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 3.78 – 3.76

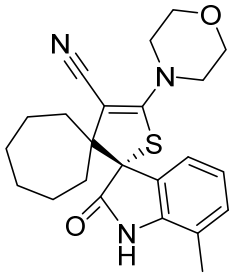
(m, 4H), 3.69 – 3.59 (m, 4H), 2.31 (s, 3H), 2.09 – 1.84 (m, 4H), 1.79 – 1.70 (m, 2H), 1.45 – 1.32 (m, 2H). $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6): δ 177.6, 162.3, 139.8, 131.5, 125.7, 123.6, 122.9, 120.1, 119.3, 80.8, 66.5, 64.2, 63.9, 51.2, 36.4, 33.6, 24.8, 24.7, 16.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{24}N_3O_2S^+$ 382.1584; found 382.1580.

(*S*)-7''-Methyl-5'-morpholino-2''-oxodispiro[cyclohexane-1,3'-thiophene-2',3''-indoline]-4'-carbonitrile (5jp′)



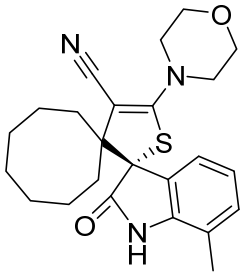
Product **5jp′** was obtained according to the general procedure from thioamide **1i** (30 mg, 1.0 equiv, 0.12 mmol), diazo compound **2p** (31 mg, 1.5 equiv, 0.18 mmol), Rh_2(*S*-NTTL)$_4$ (1.3 mg), chloroform (2 mL). The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 20:5 to 20:20) afforded **5jp′** as a colorless powder (72%, 34 mg, 4.1:95.9 e.r.), mp 218–219 °C, $[\alpha]_D^{20} = +12.0$ (C = 1.07, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on a Chiralpak AD column: 5:1 *n*-hexane/*i*-PrOH, flow rate 1 mL/min, λ = 220, 230 nm: TR Minor = 12.33 min, TR Major = 15.82 min. The spectral data are consistent with those reported previously for the racemate **5jp**.

(*S*)-7''-methyl-5'-morpholino-2''-oxodispiro[cycloheptane-1,3'-thiophene-2',3''-indoline]-4'-carbonitrile (5lp′)



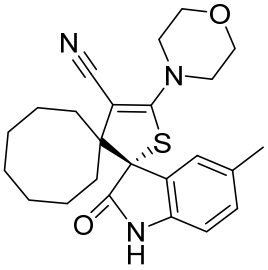
Product **5lp′** was obtained according to the general procedure from thioamide **1l** (30 mg, 1.0 equiv, 0.11 mmol), diazo compound **2p** (29 mg, 1.5 equiv, 0.17 mmol), Rh_2(*S*-NTTL)$_4$ (1.2 mg), chloroform (2 mL). The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 20:5 to 20:20) afforded **5lp′** as a colorless powder (83%, 38 mg, 4.3:95.7 e.r.), mp 213–215 °C, $[\alpha]_D^{20} = +23.0$ (C = 1.27, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on a Chiralpak AD column: 5:1 *n*-hexane/*i*-PrOH, flow rate 1 mL/min, λ = 220, 230 nm: TR Minor = 12.87 min, TR Major = 13.70 min. The spectral data are consistent with those reported previously for the racemate **5lp**.

(*S*)-7''-Methyl-5'-morpholino-2''-oxodispiro[cyclooctane-1,3'-thiophene-2',3''-indoline]-4'-carbonitrile (5op′)



Product **5op′** was obtained according to the general procedure from thioamide **1o** (30 mg, 1.0 equiv, 0.11 mmol), diazo compound **2p** (28 mg, 1.5 equiv, 0.16 mmol), Rh_2(*S*-NTTL)$_4$ (1.1 mg), chloroform (2 mL). The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 20:5 to 20:20) afforded **5op′** as a colorless powder (91%, 42 mg, 7.0:93.0 e.r.), mp 245–247 °C, $[\alpha]_D^{20} = +10.3$ (C = 1.17, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on a Chiralpak AD column: 5:1 *n*-hexane/*i*-PrOH, flow rate 1 mL/min, λ = 220, 230 nm: TR Minor = 28.18 min, TR Major = 12.95 min. The spectral data are consistent with those reported previously for the racemate **5op**.

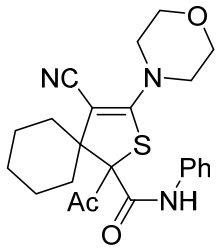
(S)-5''-Methyl-5'-morpholino-2''-oxodispiro[cyclooctane-1,3'-thiophene-2',3''-indoline]-4'-carbonitrile (5ov)



Product **5ov** was obtained according to the general procedure from thioamide **1o** (30 mg, 1.0 equiv, 0.11 mmol), diazo compound **2v** (28 mg, 1.5 equiv, 0.16 mmol), Rh_2(*S*-NTTL)$_4$ (1.1 mg), chloroform (2 mL). The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 20:5 to 20:20) afforded **5ov** as a pale-red powder (87%, 40 mg, 19:81 e.r.), mp 144–146 °C, $[\alpha]_D^{20} = -3.43$ (C = 0.67, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on a Chiralpak AD column: 5:1 *n*-hexane/*i*-PrOH, flow rate 1 mL/min, λ = 220, 230 nm: TR Minor = 23.70 min, TR Major = 11.45 min. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.62 (s, 1H, NH), 7.30 (s, 1H), 7.09 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 3.68 – 3.65 (m, 4H), 3.60 – 3.49 (m, 4H), 2.35 – 2.28 (m, 4H), 2.14 – 1.93 (m, 3H), 1.5 (br. s, 5H), 1.35 – 1.27 (m, 4H), 0.85 (br. s, 1H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 175.6, 162.9, 139.3, 130.5, 130.3, 119.8, 109.8, 77.8, 65.7, 64.6, 57.3, 50.7, 29.5, 29.4, 28.9, 27.5, 24.8, 22.2, 21.4, 20.8. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{30}N_3O_2S^+$ 424.2053; found 424.2057.

Grame-scale synthesis of dihydrithiophenes 5jh

1-Acetyl-4-cyano-3-morpholino-*N*-phenyl-2-thiaspiro[4.5]dec-3-ene-1-carboxamide (5jh)



To an oven-dried double neck round bottom flask (100 mL), rhodium (II) pivalate dimer (0.5 mol %, 24.4 mg), thioamide **1j** (1000 mg, 1.0 equiv, 3.99 mmol) and dry chloroform (10 mL) were added under an argon atmosphere. After stirring for 15 min at room temperature, a solution of diazoacetamide **2h** (811.5 mg, 1.0 equiv, 3.99 mmol) in dry chloroform (20 mL) was added via syringe to the flask. Then, the reaction mixture was allowed to stir at room temperature for 2 h. Two hours later a new portion of a solution of diazoacetamide **2h** (811.5 mg, 1.0 equiv, 3.99 mmol) in dry chloroform (20 mL) was added via syringe to the flask. Upon completion (14 h), chloroform was removed under reduced pressure and the product was isolated using column chromatography on SiO_2 (Eluent mixture PE/EtOAc, gradient 25:0 to 25:25) afforded **5jh** as a colorless powder (74%, 1258 mg), mp 198–200 °C and **6jh** as a colorless powder (3%, 51 mg), mp 195–196 °C.

X-Ray crystallographic data

A single crystal of **3aa** was obtained by crystallization via evaporation at room temperature from its ethyl acetate solution. The deposition number for **3aa** at the Cambridge Crystallographic Data Centre is CCDC 2288490.

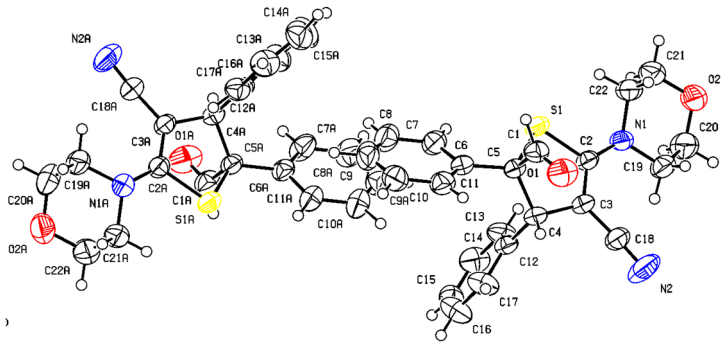


Figure S4. X-Ray crystallographic data of **3aa**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 3aa. $C_{22}H_{20}N_2O_2S$ (M =376.46 g/mol): triclinic, space group P-1 (no. 2), a = 11.9036(6) Å, b = 12.3656(5) Å, c = 13.5444(6) Å, α = 82.460(4)°, β = 80.987(4)°, γ = 79.478(4)°, V = 1925.11(16) Å3, Z = 4, T = 295(2) K, μ(Mo Kα) = 0.187 mm^{-1}, D_{calc} = 1.299 g/cm^3, 21912 reflections measured (7.214° ≤ 2Θ ≤ 60.952°), 10398 unique (R_{int} = 0.0410, R_{sigma} = 0.0692) which were used in all calculations. The final R_1 was 0.0606 (I > 2σ(I)) and wR_2 was 0.1979. GooF 1.007. Largest diff. peak/hole 0.36/-0.40.

A single crystal of **3ad** was obtained by crystallization via evaporation at room temperature from its ethyl acetate solution. The deposition number for **3ad** at the Cambridge Crystallographic Data Centre is CCDC 2288496.

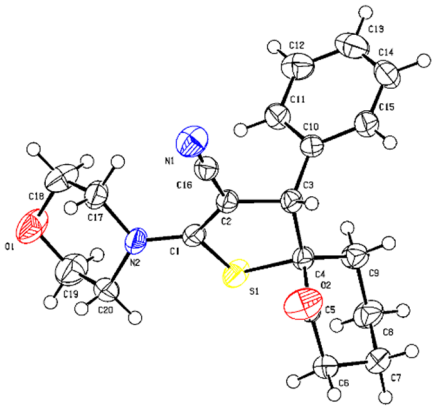


Figure S5. X-Ray crystallographic data of **3ad**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 3ad. $C_{20}H_{22}N_2O_2S$ (M =354.45 g/mol): orthorhombic, space group Pbca (no. 61), a = 9.1006(15) Å, b = 15.187(3) Å, c = 25.844(6) Å, V = 3572.0(12) Å3, Z = 8, T = 295.15 K, μ(Mo Kα) = 0.197 mm^{-1}, D_{calc} = 1.318 g/cm^3, 11055 reflections measured (5.364° ≤ 2Θ ≤ 58.934°), 4247 unique (R_{int} = 0.0351, R_{sigma} = 0.0456) which were used in all calculations. The final R_1 was 0.0485 (I > 2σ(I)) and wR_2 was 0.1245. GooF 1.038. Largest diff. peak/hol 0.30/-0.29.

A single crystal of **3ae** was obtained by crystallization via evaporation at room temperature from its ethyl acetate solution. The deposition number for **3ae** at the Cambridge Crystallographic Data Centre is CCDC 2288498.

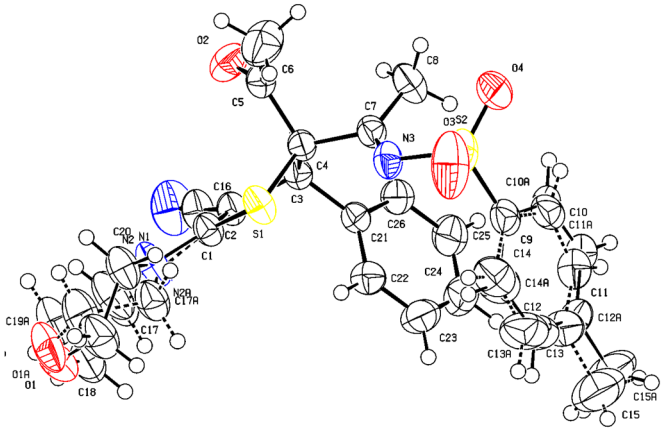


Figure S6. X-Ray crystallographic data of **3ae**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 3ae. $C_{26}H_{27}N_3O_4S_2$ (M =509.62 g/mol): orthorhombic, space group Pbca (no. 61), a = 18.539(3) Å, b = 11.4393(16) Å, c = 24.448(4) Å, V = 5184.6(14) Å3, Z = 8, T = 295.15 K, μ(Mo Kα) = 0.242 mm^{-1}, D_{calc} = 1.306 g/cm^3, 18665 reflections measured (4.504° ≤ 2Θ ≤ 58.838°), 6274 unique (R_{int} = 0.0344, R_{sigma} = 0.0433) which were used in all calculations. The final R_1 was 0.0579 (I > 2σ(I)) and wR_2 was 0.1450. GooF 1.034. Largest diff. peak/hole 0.28/-0.51.

A single crystal of **3ta** was obtained by crystallization via evaporation at room temperature from its ethyl acetate solution. The deposition number for **3ta** at the Cambridge Crystallographic Data Centre is CCDC 2288497.

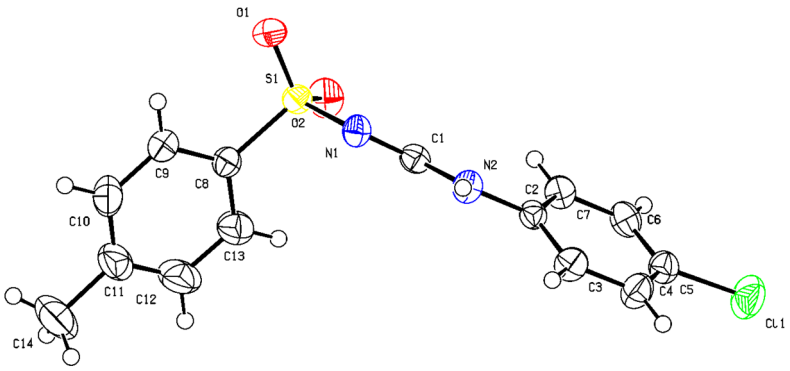


Figure S7. X-Ray crystallographic data of **3ta**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 3ta. $C_{14}H_{13}ClN_2O_2S$ (M =308.77 g/mol): monoclinic, space group P21/c (no. 14), a = 13.453(3) Å, b = 9.8748(18) Å, c = 11.570(3) Å, β = 107.97(3)°, V = 1462.0(6) Å3, Z = 4, T = 295(2) K, μ(Mo Kα) = 0.406 mm^{-1}, D_{calc} = 1.403 g/cm^3, 7161 reflections measured (5.21° ≤ 2Θ ≤ 58.988°), 3480 unique (R_{int} = 0.0368, R_{sigma} = 0.0491) which were used in all calculations. The final R_1 was 0.0508 (I > 2σ(I)) and wR_2 was 0.1446. GooF 1.052. Largest diff. peak/hole 0.46/-0.49.

A single crystal of **4ah** was obtained by crystallization via evaporation at room temperature from its mixture of methanol and acetonitrile solution. The deposition number for **4ah** at the Cambridge Crystallographic Data Centre is CCDC 2288491.

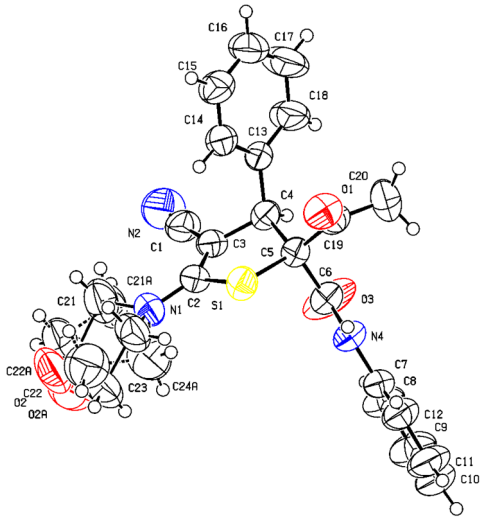


Figure S8. X-Ray crystallographic data of **4ah**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 4ah. $C_{24}H_{23}N_3O_3S$ (M =433.51 g/mol): orthorhombic, space group Pbca (no. 61), a = 13.4556(12) Å, b = 16.0823(15) Å, c = 21.045(2) Å, V = 4554.0(8) Å3, Z = 8, T = 295(2) K, μ(MoKα) = 0.172 mm^{-1}, D_{calc} = 1.265 g/cm^3, 14386 reflections measured (7.624° ≤ 2Θ ≤ 52.744°), 4622 unique (R_{int} = 0.0648, R_{sigma} = 0.0885) which were used in all calculations. The

final R_1 was 0.0672 ($I > 2\sigma(I)$) and wR_2 was 0.2266. GooF 1.015. Largest diff. peak/hole 0.21/-0.24.

A single crystal of **4ai** was obtained by crystallization via evaporation at room temperature from its mixture of methanol, ethyl acetate and acetonitrile solution. The deposition number for **4ai** at the Cambridge Crystallographic Data Centre is CCDC 2288493.

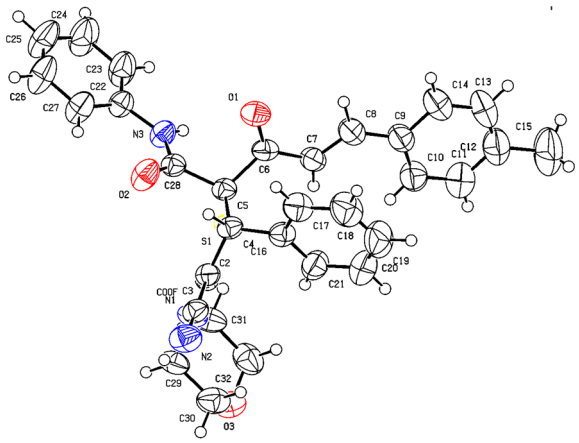


Figure S9. X-Ray crystallographic data of **4ai**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 4ai. $C_{32}H_{29}N_3O_3S$ (M =535.64 g/mol): monoclinic, space group P21/n (no. 14), a = 13.1630(12) Å, b = 11.7627(8) Å, c = 18.6294(17) Å, β = 99.090(8)°, V = 2848.2(4) Å3, Z = 4, T = 295(2) K, μ(MoKα) = 0.151 mm^{-1}, D_{calc} = 1.249 g/cm^3, 22624 reflections measured (7.082° ≤ 2Θ ≤ 60.996°), 7713 unique (R_{int} = 0.0677, R_{sigma} = 0.0971) which were used in all calculations. The final R_1 was 0.0670 ($I > 2\sigma(I)$) and wR_2 was 0.2342. GooF 1.012. Largest diff. peak/hole 0.28/-0.42.

A single crystal of **4ao** was obtained by crystallization via evaporation at room temperature from its methanol solution. The deposition number for **4ao** at the Cambridge Crystallographic Data Centre is CCDC 2288492.

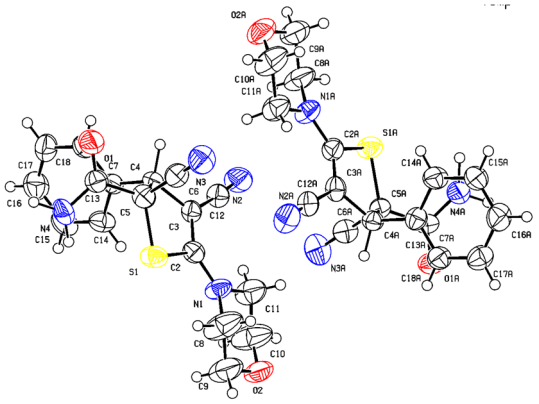


Figure S10. X-Ray crystallographic data of **4ao**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 4ao. $C_{17}H_{16}N_4O_2S$ (M =340.40 g/mol): orthorhombic, space group Pna21 (no. 33), a = 20.677(2) Å, b = 10.7808(7) Å, c = 15.1131(17) Å, V = 3369.0(6) Å3, Z = 8, T = 295(2) K, μ(MoKα) = 0.209 mm^{-1}, D_{calc} = 1.342 g/cm^3, 11968 reflections measured (7.518° ≤ 2Θ ≤ 60.962°), 6726 unique (R_{int} = 0.0686, R_{sigma} = 0.1152) which were used in all calculations. The final R_1 was 0.0660 (I > 2σ(I)) and wR_2 was 0.1816. GooF 1.002. Largest diff. peak/hole 0.29/-0.34.

A single crystal of **5in** was obtained by crystallization via evaporation at room temperature from its ethyl acetate solution. The deposition number for **5in** at the Cambridge Crystallographic Data Centre is CCDC 2288495.

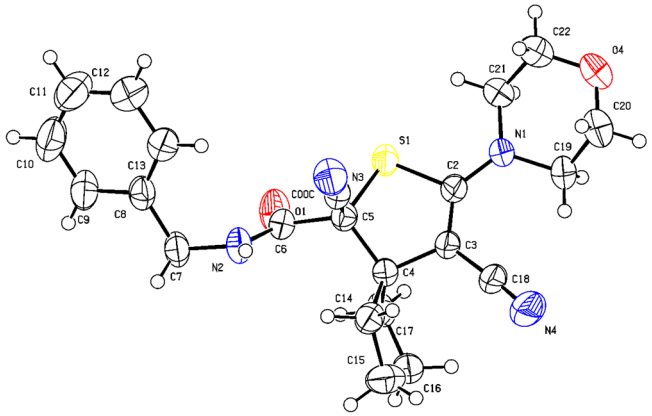


Figure S11. X-Ray crystallographic data of **5in**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 5in. $C_{22}H_{24}N_4O_2S$ (M =408.51 g/mol): monoclinic, space group C2/c (no. 15), a = 19.8227(18) Å, b = 8.1430(7) Å, c = 26.372(3) Å, β = 102.977(10)°, V = 4148.2(7) Å3, Z = 8, T = 295(2) K, μ(MoKα) = 0.182 mm^{-1}, Dcalc = 1.308 g/cm^3, 11495 reflections measured (7.526° ≤ 2Θ ≤ 56.564°), 4953 unique (R_{int} = 0.0634, R_{sigma} = 0.0960) which were used in all calculations. The final R_1 was 0.0648 (I > 2σ(I)) and wR_2 was 0.1999. GooF 1.016. Largest diff. peak/hole 0.30/-0.30.

A single crystal of **5hp** was obtained by crystallization via evaporation at room temperature from its mixture of ethyl acetate and dichloromethane solution. The deposition number for **5hp** at the Cambridge Crystallographic Data Centre is CCDC 2288489.

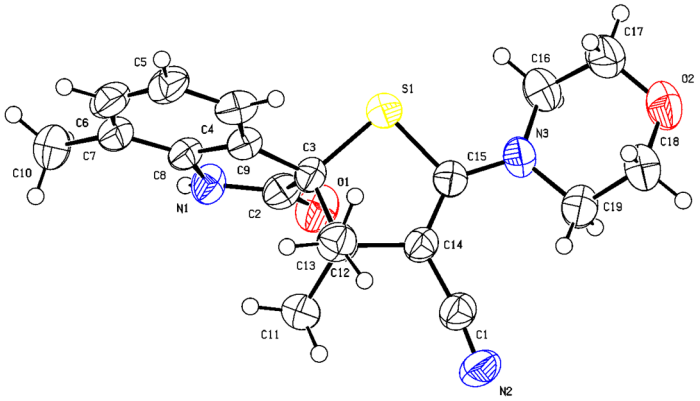


Figure S12. X-Ray crystallographic data of **5hp**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 5hp. $C_{19}H_{21}N_3O_2S$ (M =355.45 g/mol): monoclinic, space group P21/n (no. 14), a = 14.247(3) Å, b = 9.0994(10) Å, c = 15.279(4) Å, β = 117.13(3)°, V = 1762.8(8) Å3, Z = 4, T = 295(2) K, μ(MoKα) = 0.201 mm^{-1}, D_{calc} = 1.339 g/cm^3, 10192 reflections measured (4.700° ≤ 2Θ ≤ 62.280°), 5831 unique (R_{int} = 0.0271, R_{sigma} = 0.0497) which were used in all calculations. The final R_1 was 0.0770 (I > 2σ(I)) and wR_2 was 0.2509. GooF 1.055. Largest diff. peak/hole 0.22/-0.25.

A single crystal of **6jh** was obtained by crystallization via evaporation at room temperature from its ethyl acetate solution. The deposition number for **6jh** at the Cambridge Crystallographic Data Centre is CCDC 2306789.

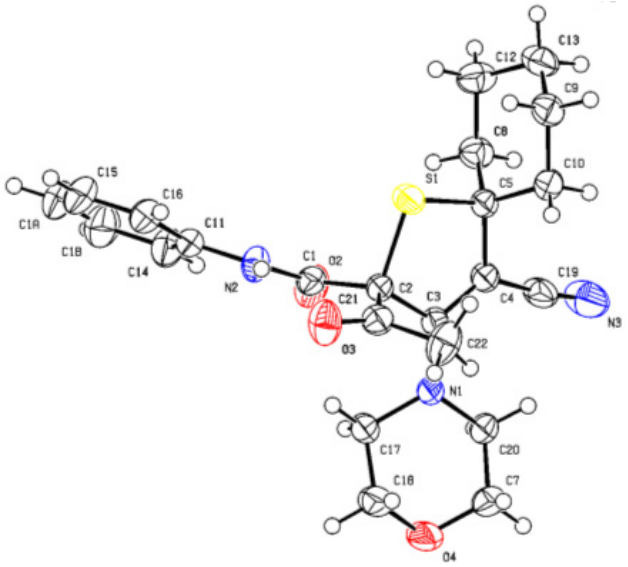


Figure S13. X-Ray crystallographic data of **6jh**. Thermal ellipsoids are shown at the 50% level.

Crystal Data for 6jh. $C_{23}H_{27}N_3O_3S$ (M =425.54 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 18.9394(6) Å, b = 9.8877(3) Å, c = 11.9483(3) Å, α = 90°, β = 107.354(3)°, γ = 90°, V = 2135.67(11) Å3, Z = 4, T = 295(2) K, μ(MoKα) = 0.182 mm^{-1}, D_{calc} = 1.324 g/cm^3, 9437 reflections

measured ($7.378^{\circ} \leq 2\Theta \leq 62^{\circ}$), 4252 unique ($R_{int}$ = 0.0407, R_{sigma} = 0.0545) which were used in all calculations. The final R_1 was 0.0510 ($I > 2\sigma(I)$) and wR_2 was 0.1397. GooF 1.011. Largest diff. peak/hole 0.29/-0.55.

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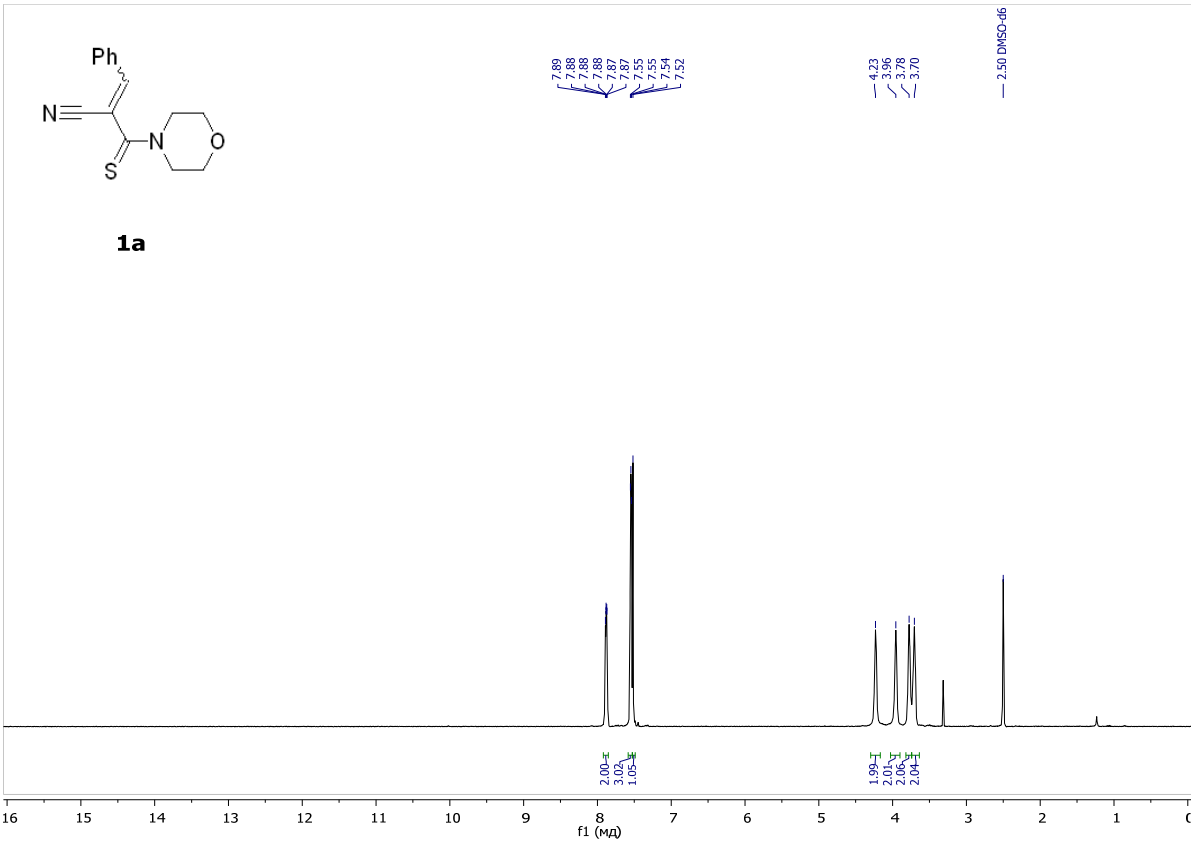
NMR ^{1}H, ^{13}C and ^{19}F Spectra



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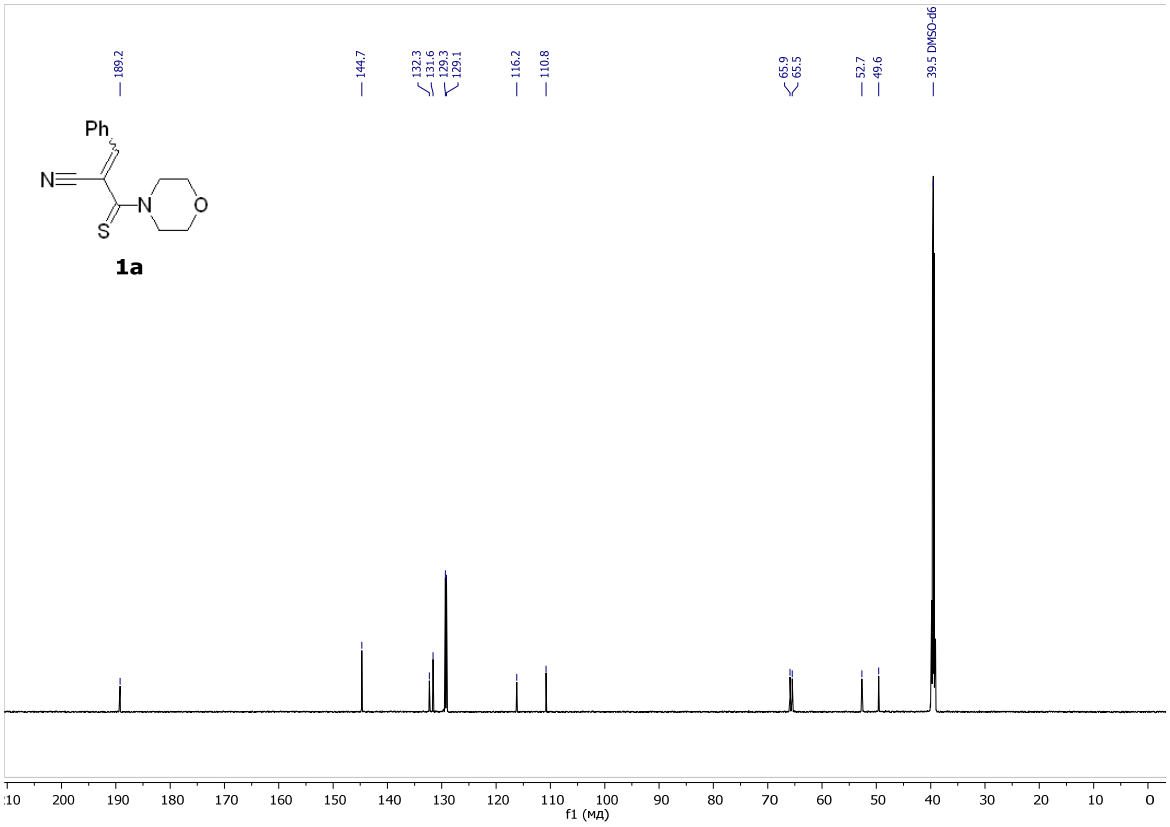

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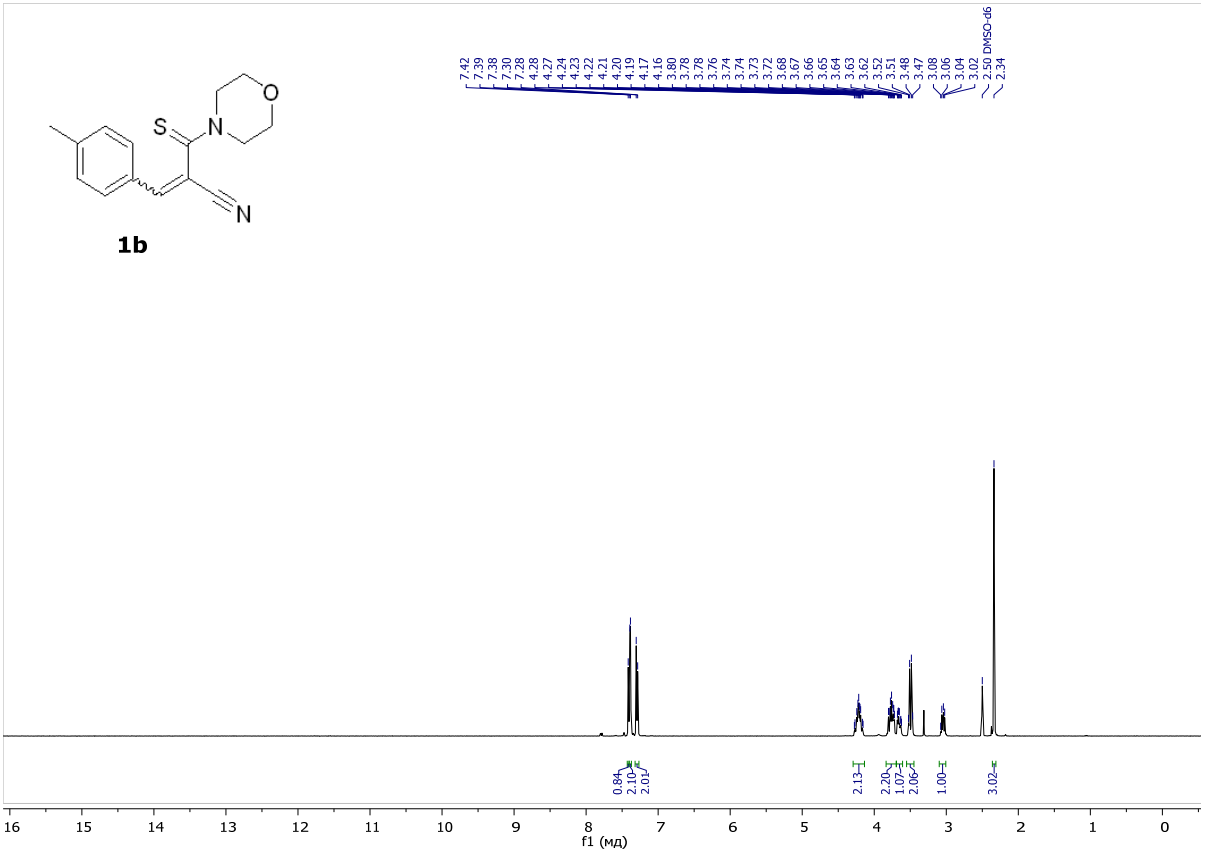

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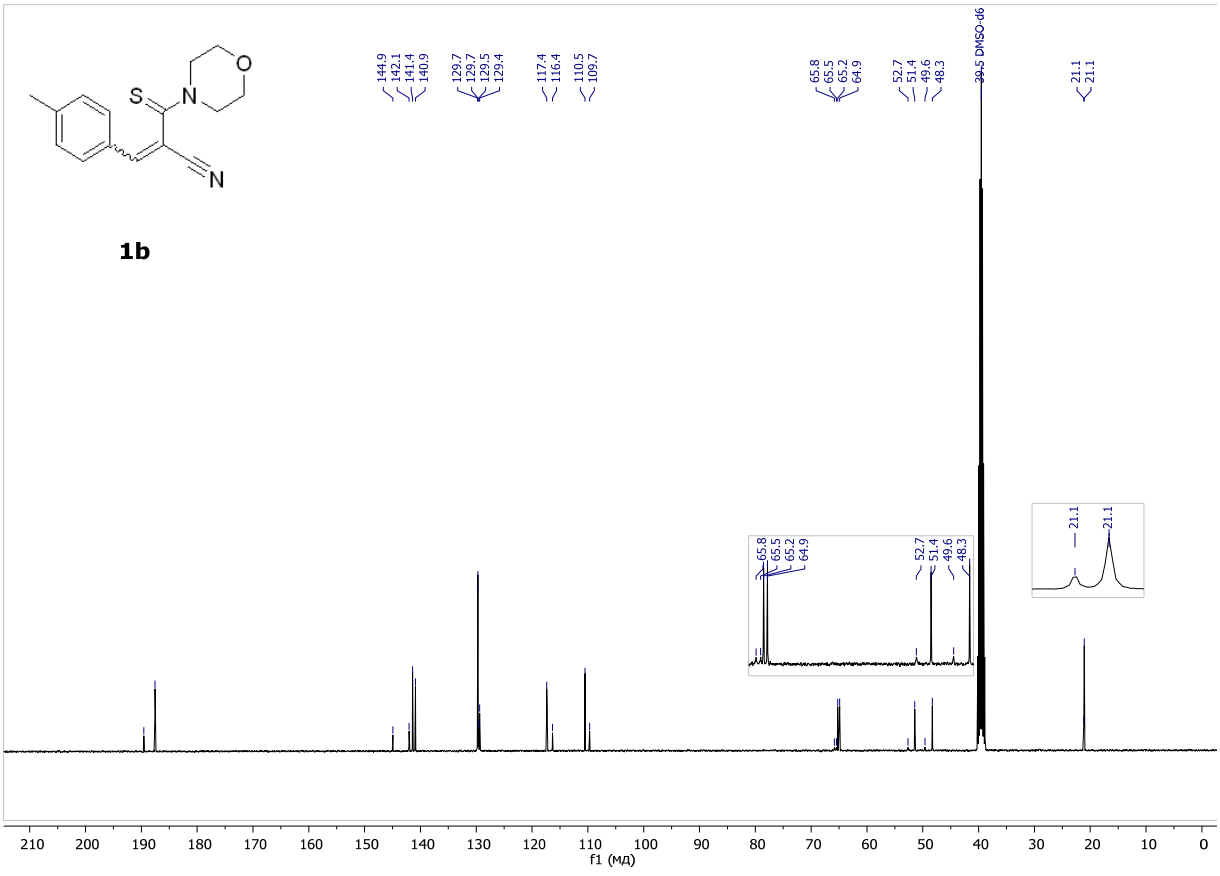

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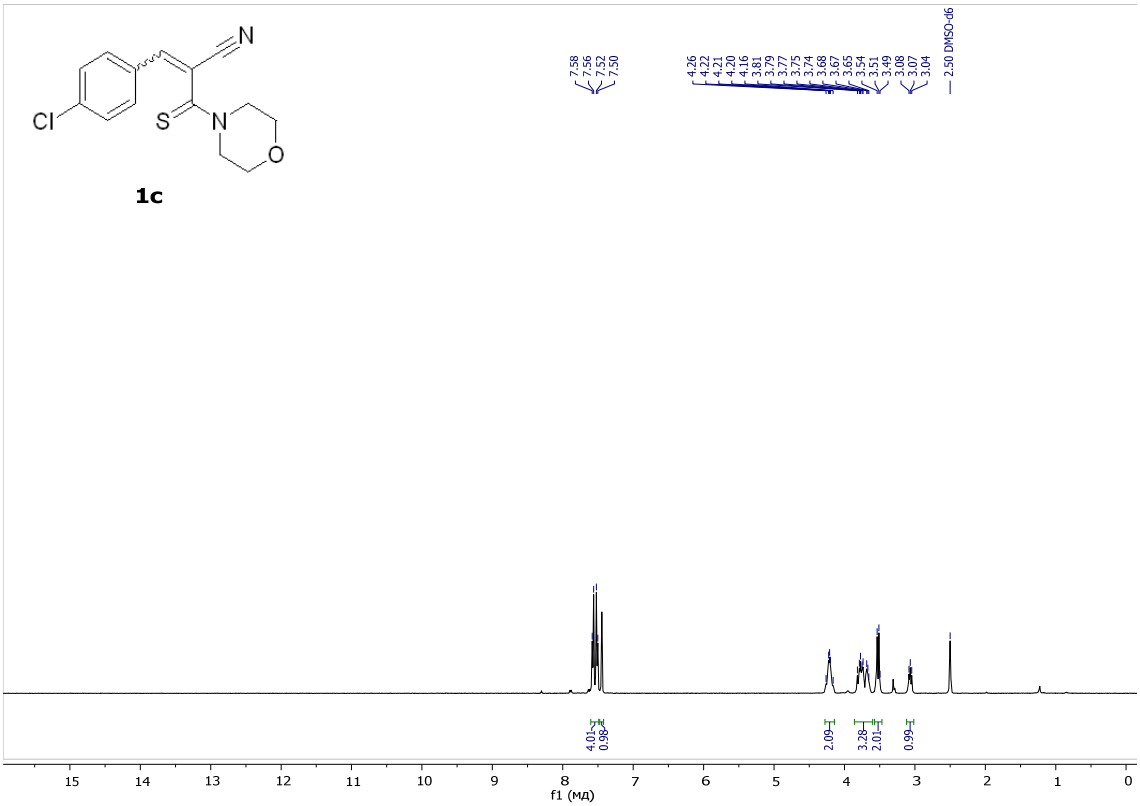

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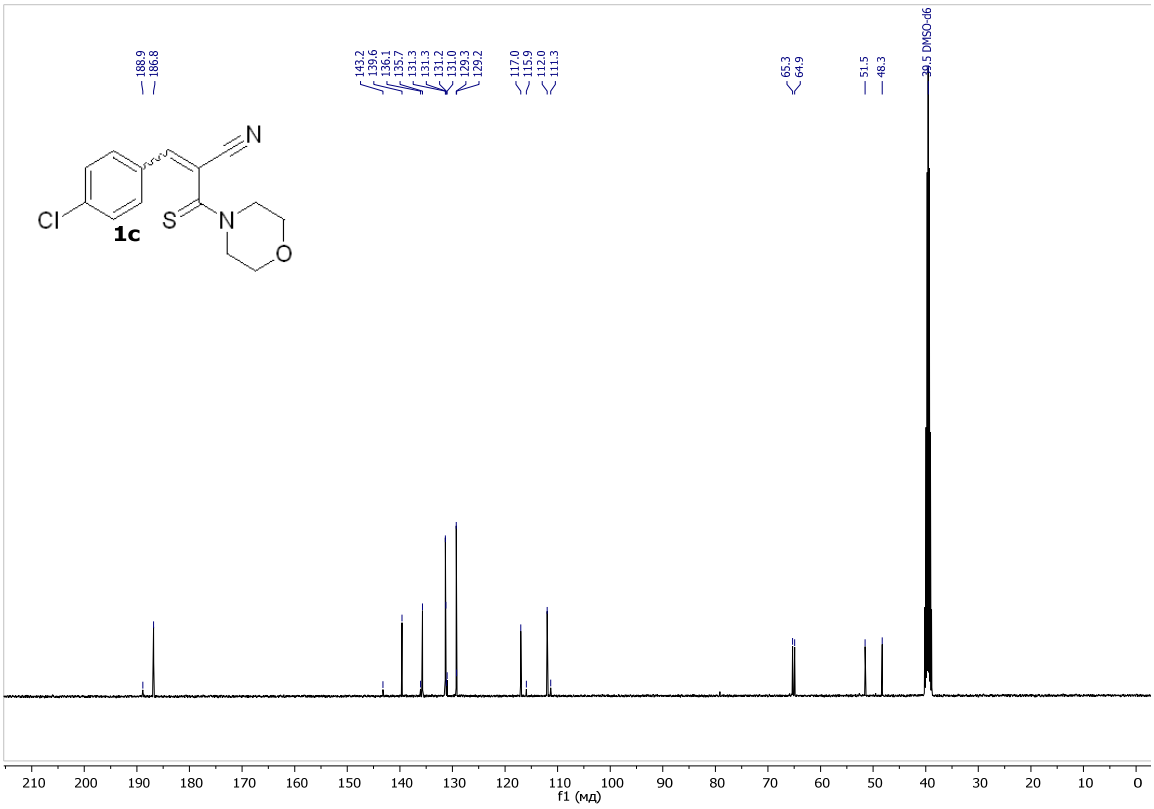

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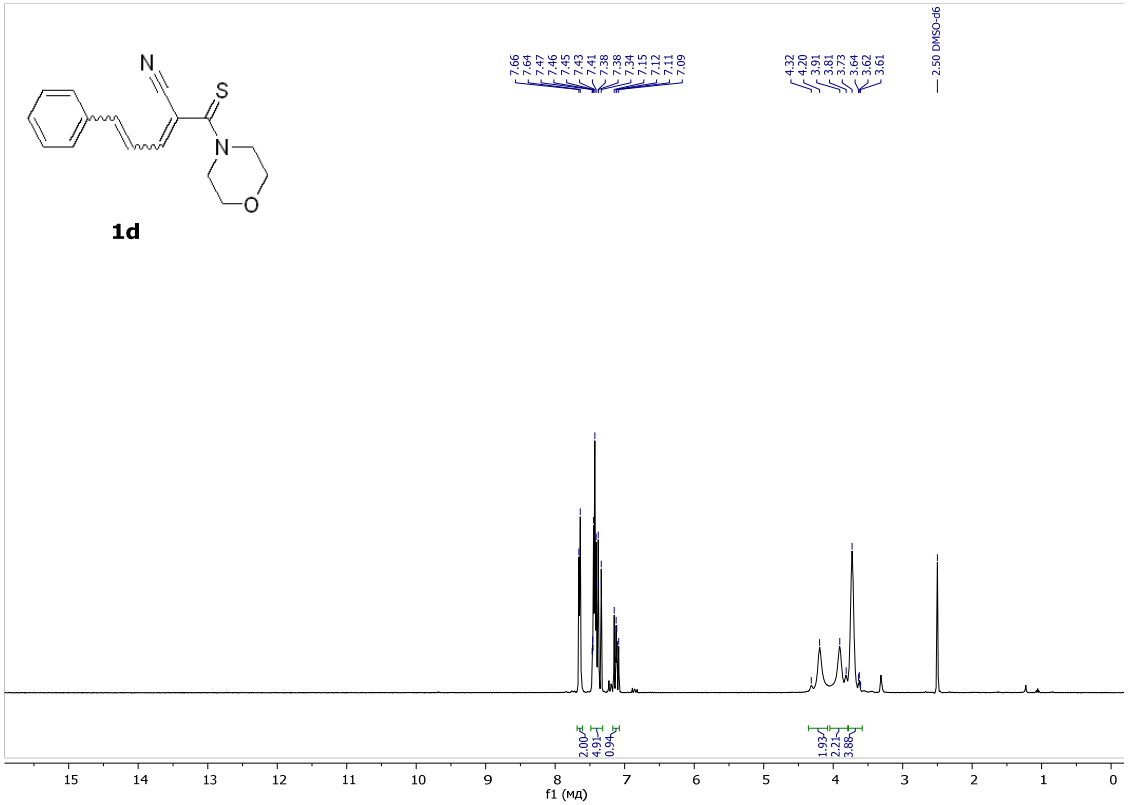

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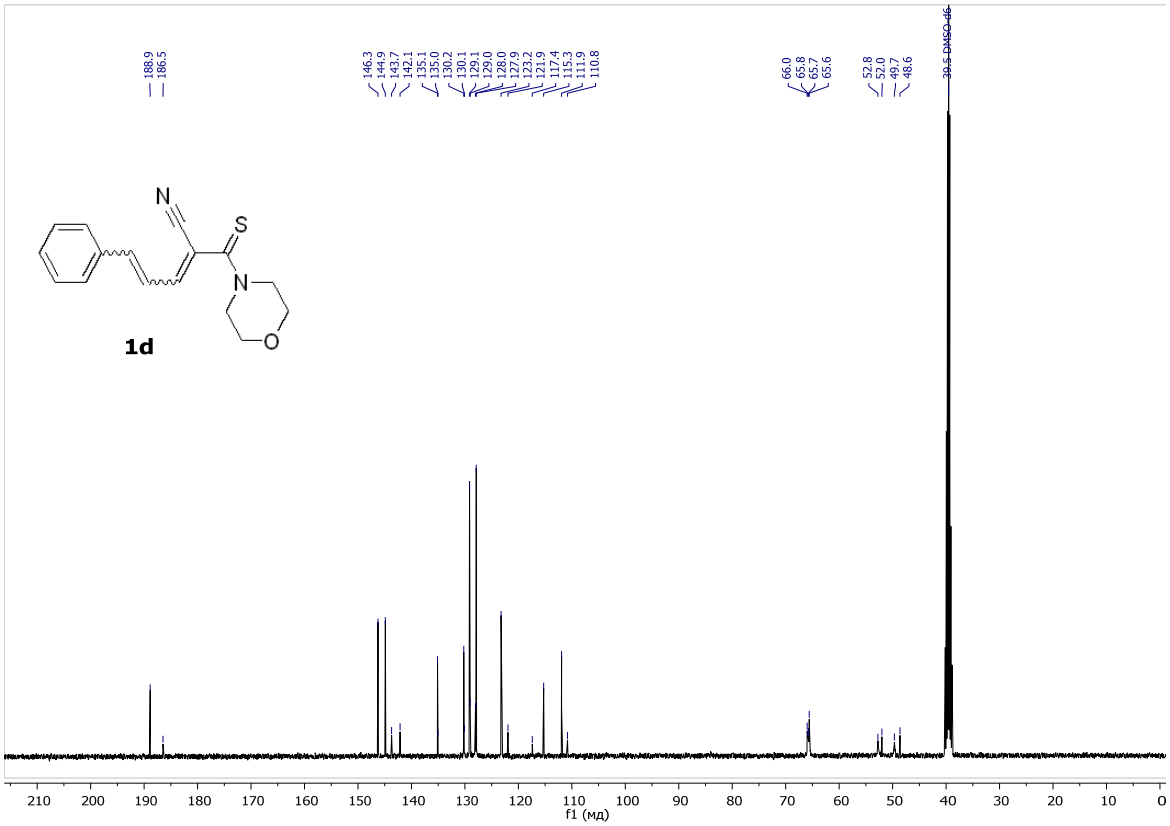

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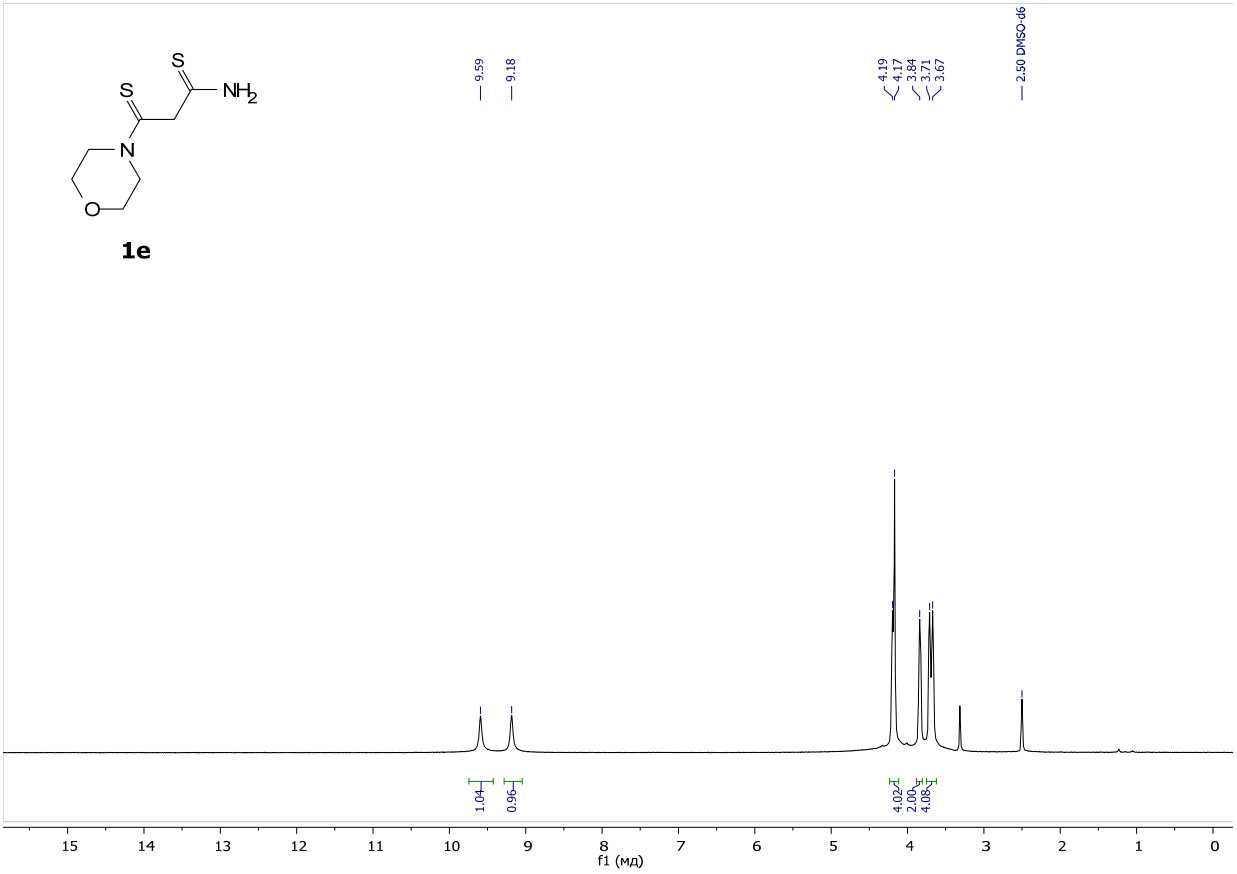

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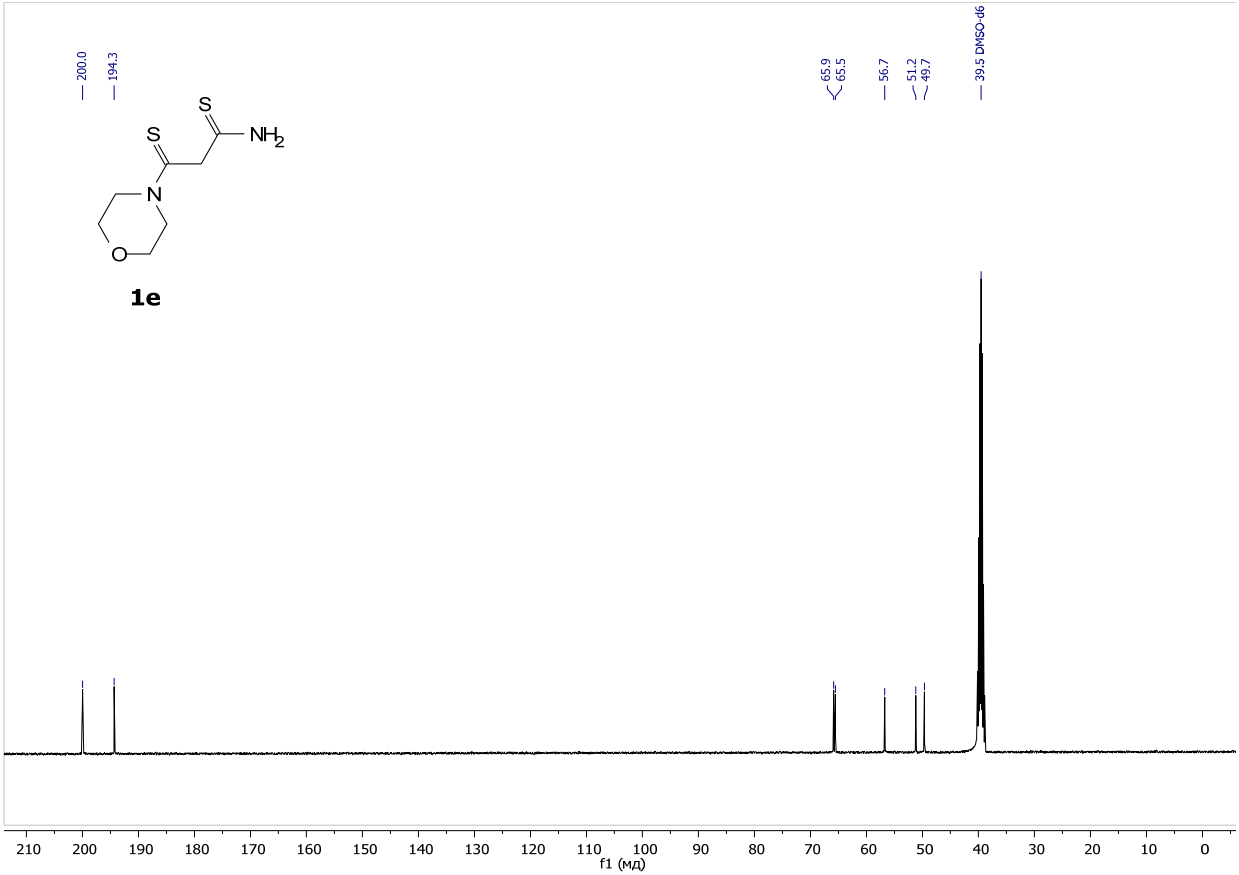

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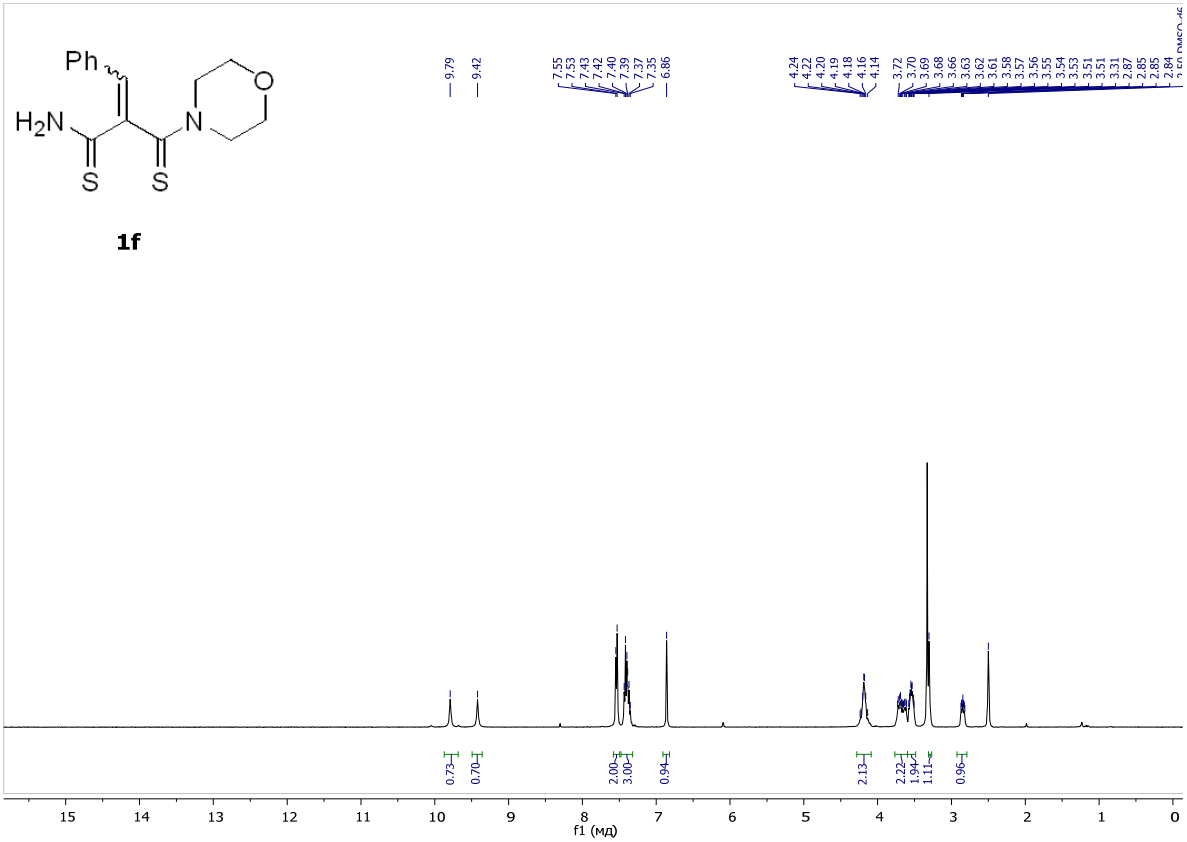

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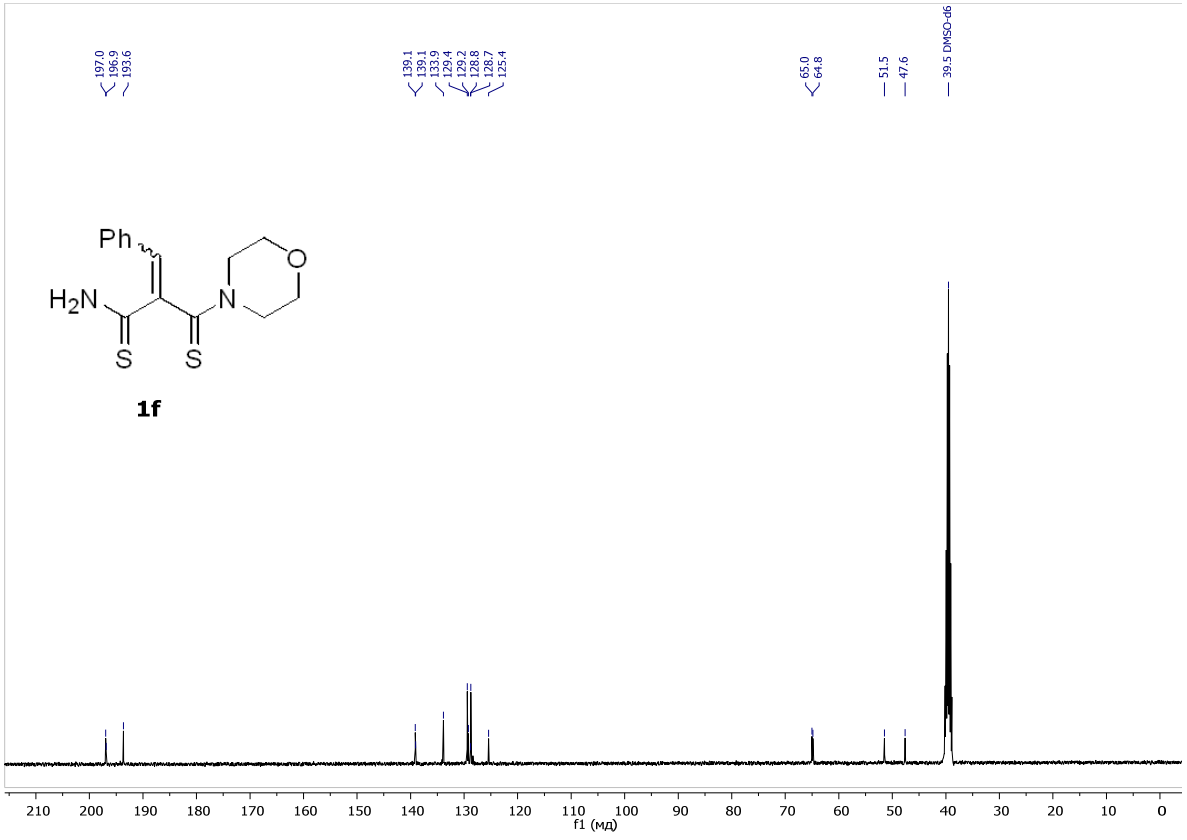

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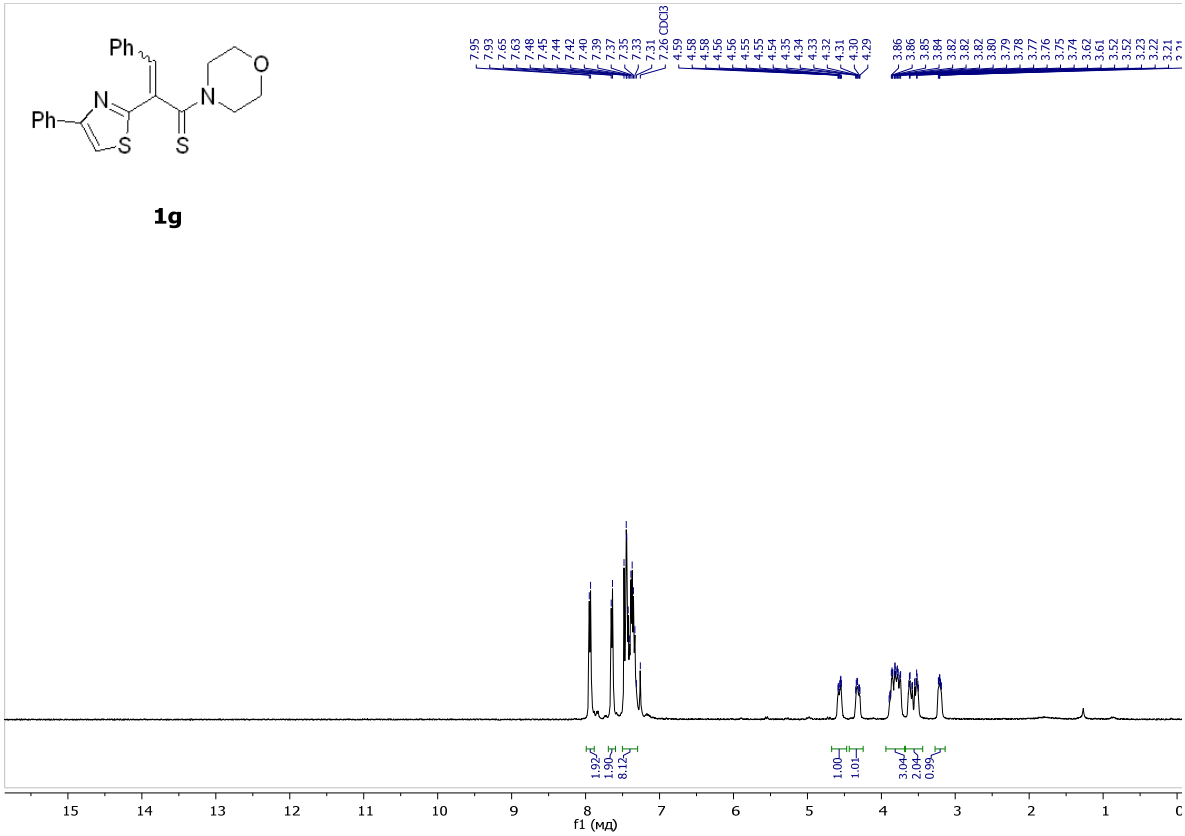

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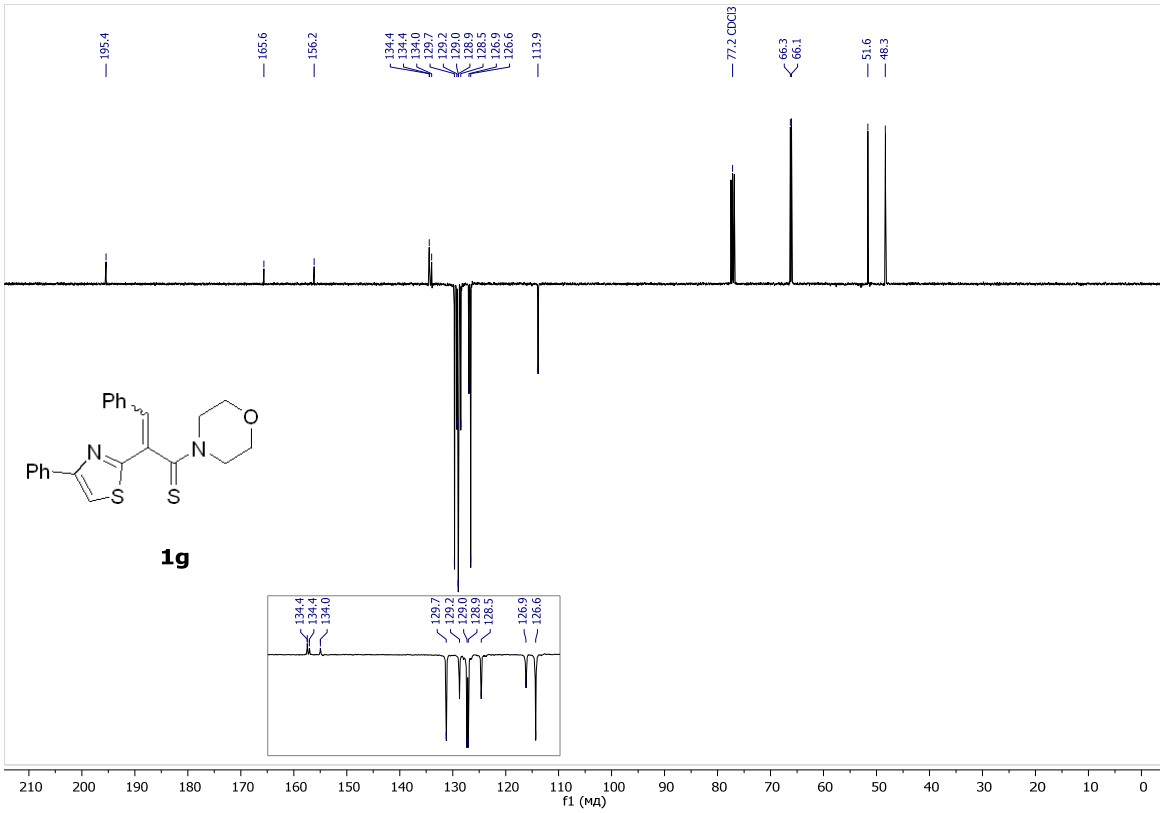

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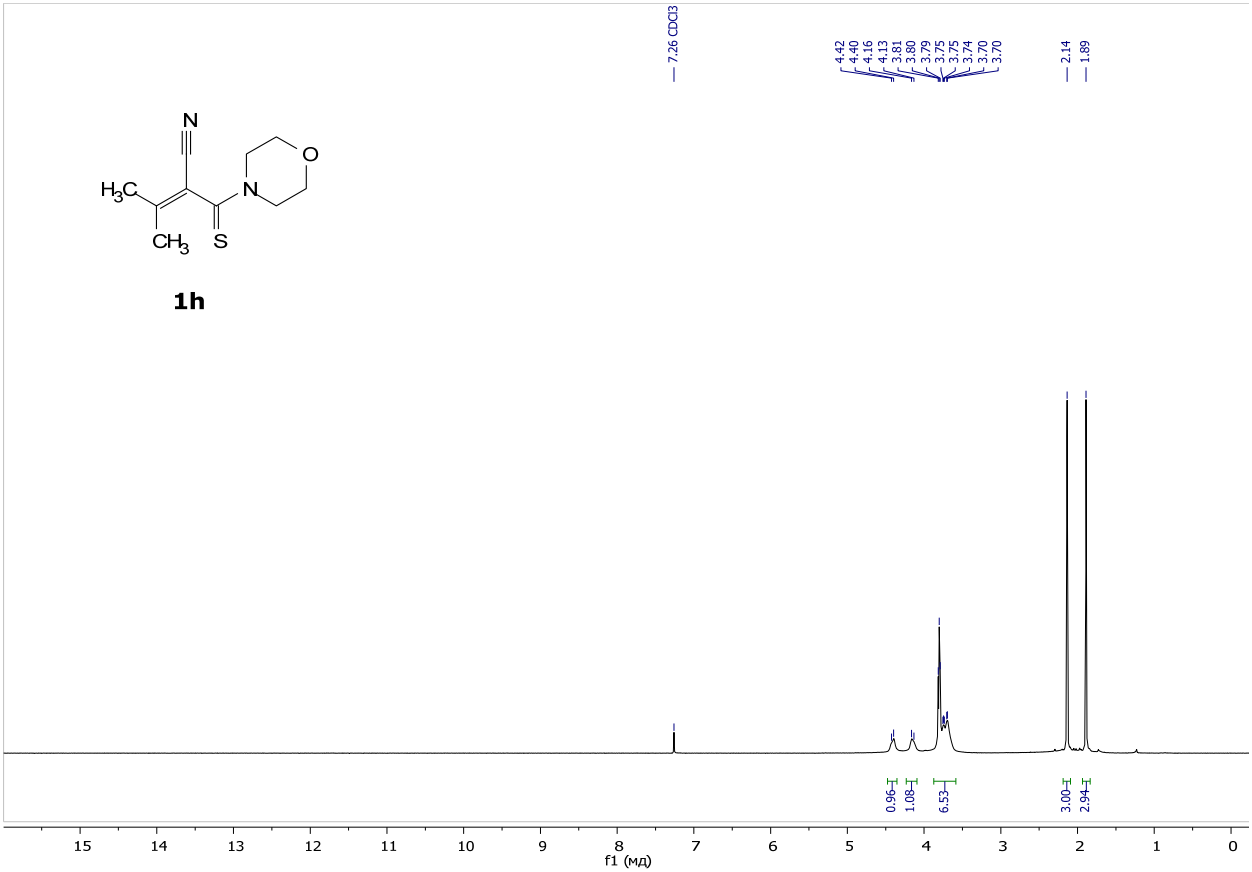

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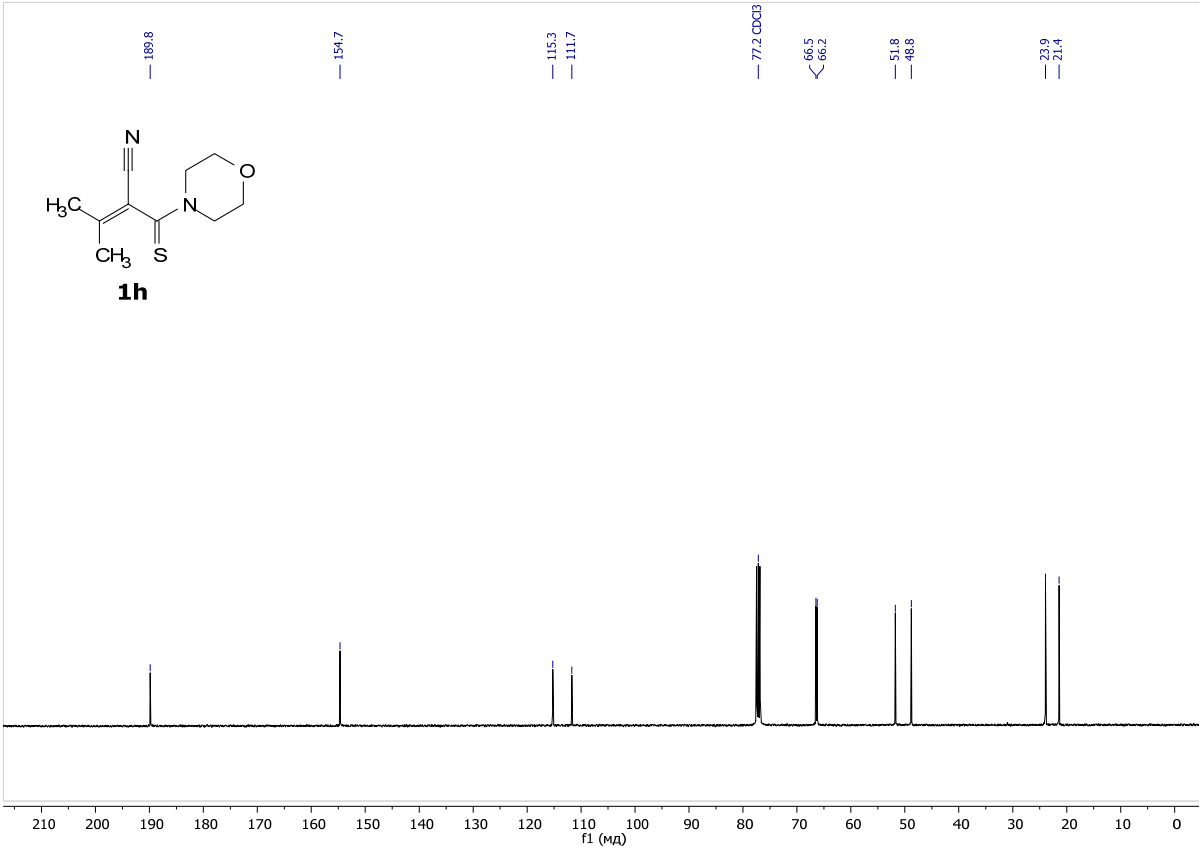

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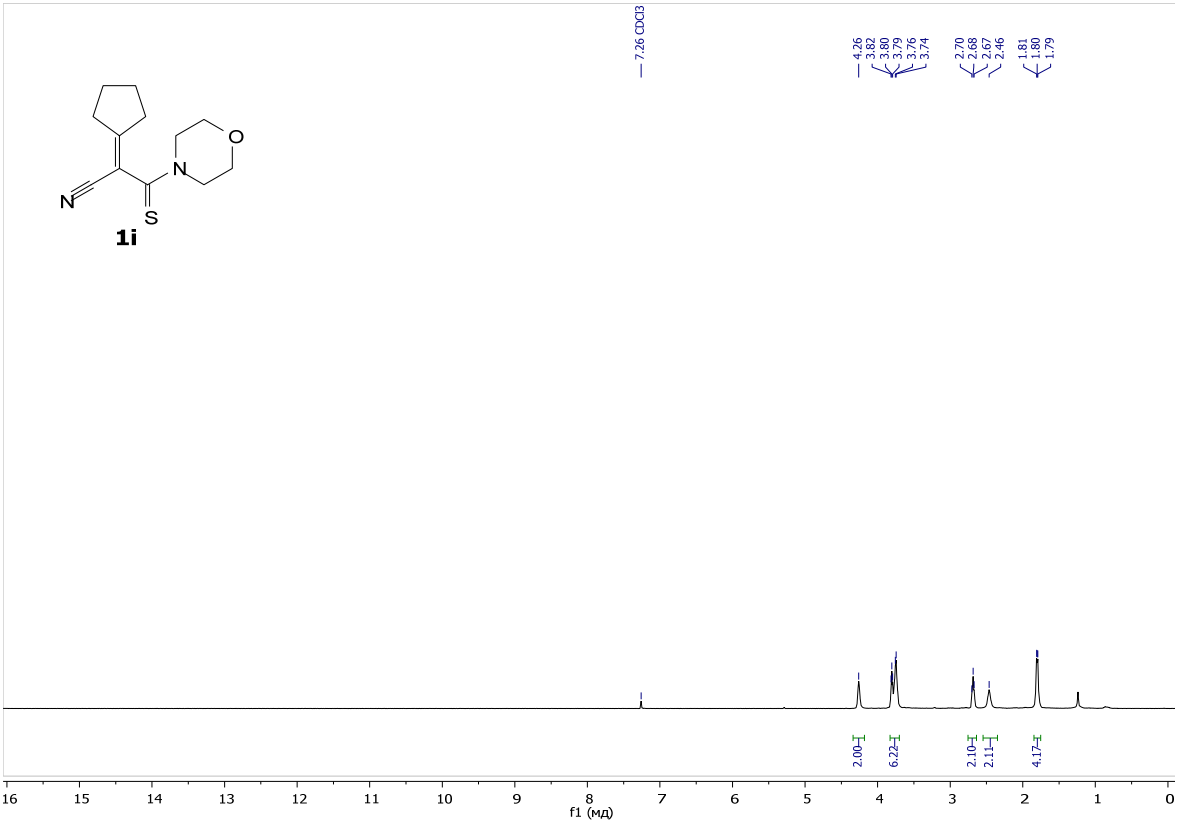

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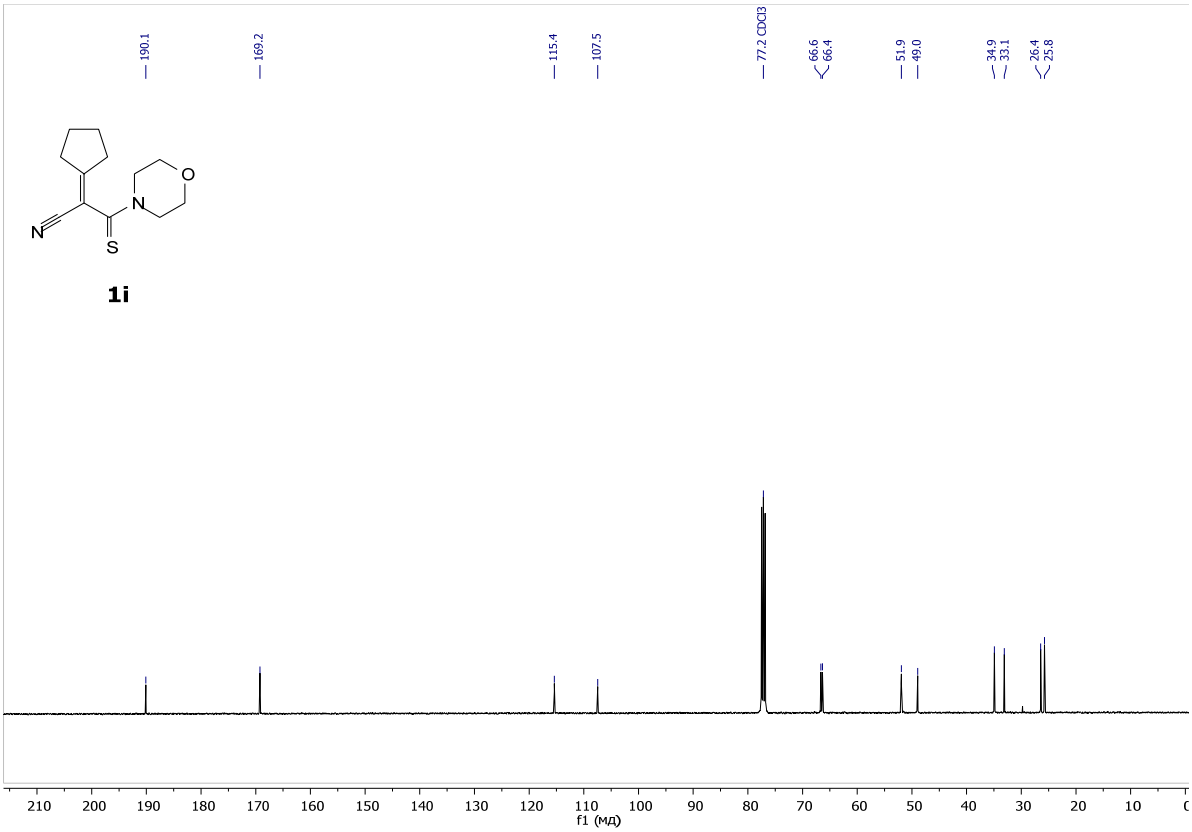

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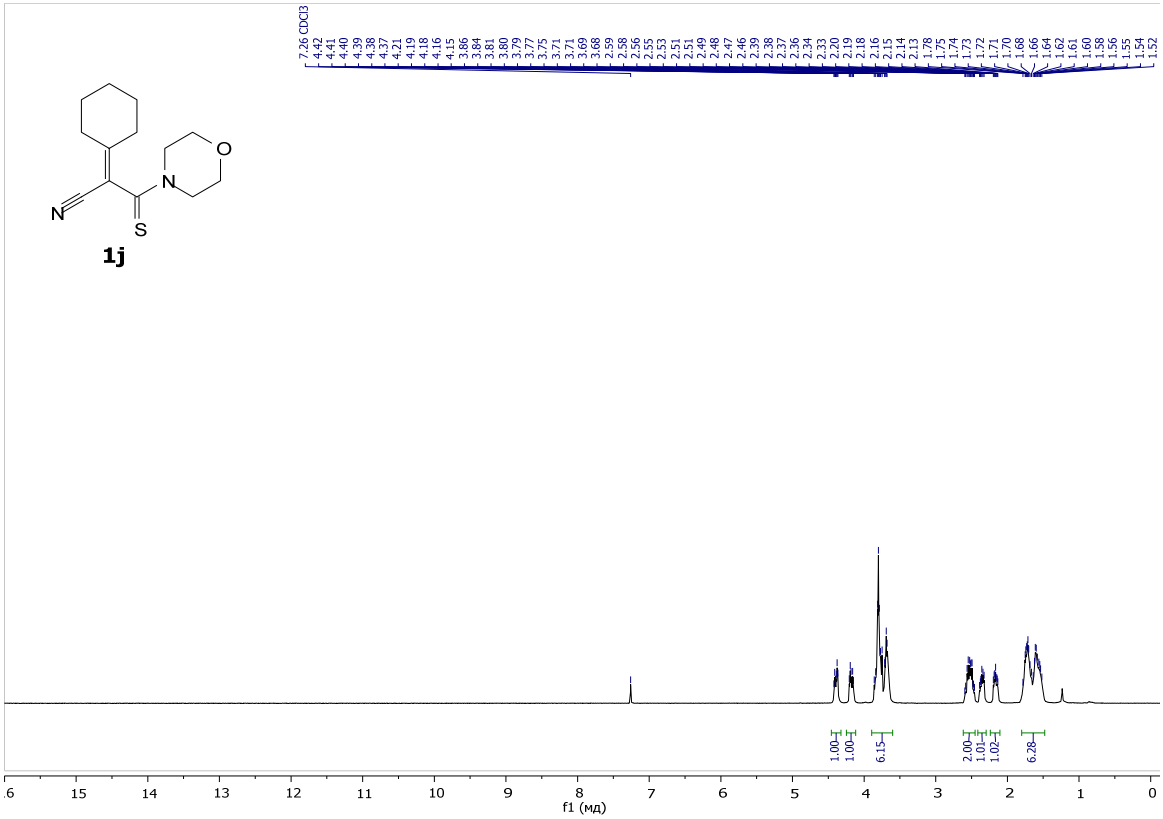

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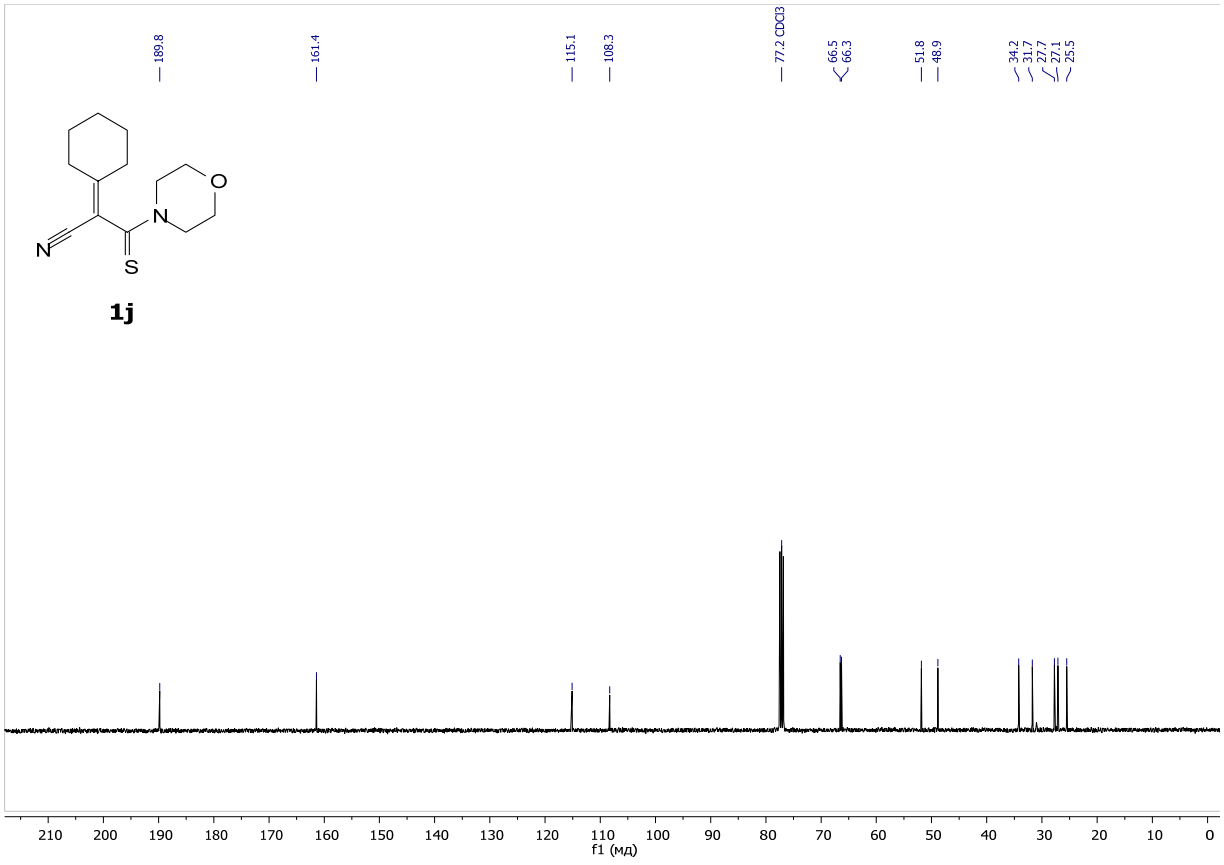

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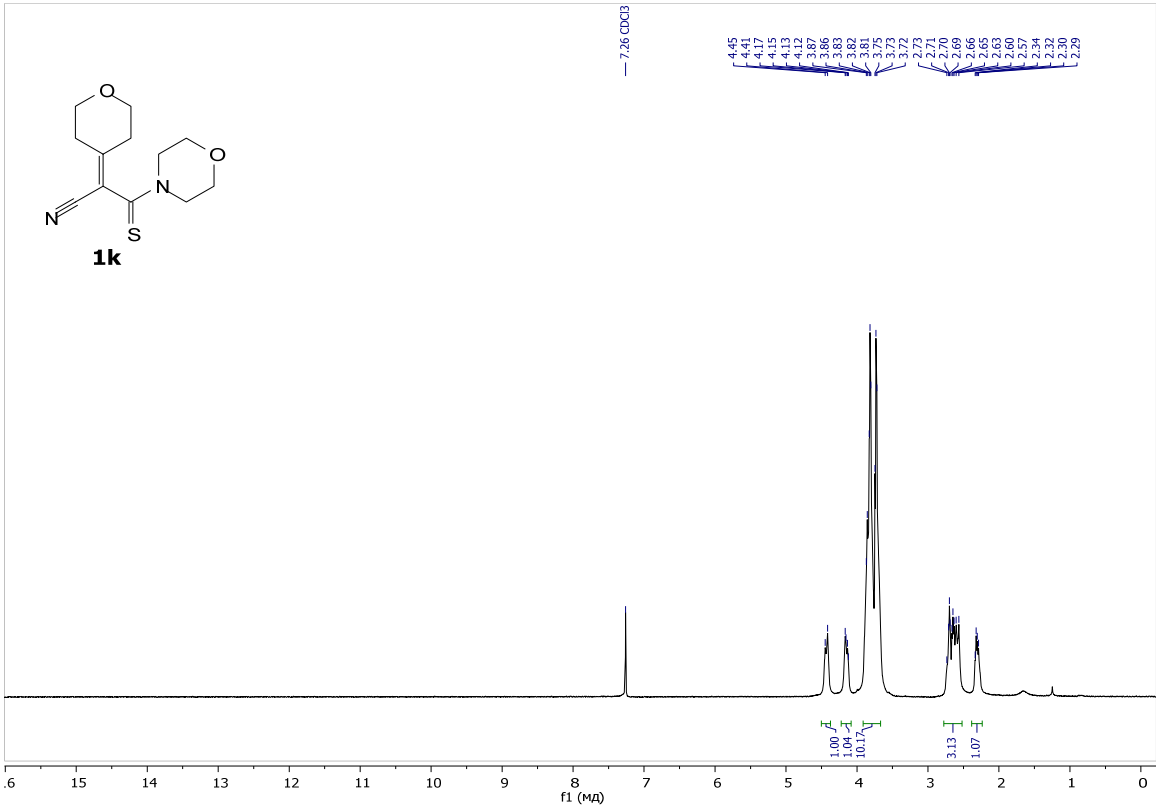

1k

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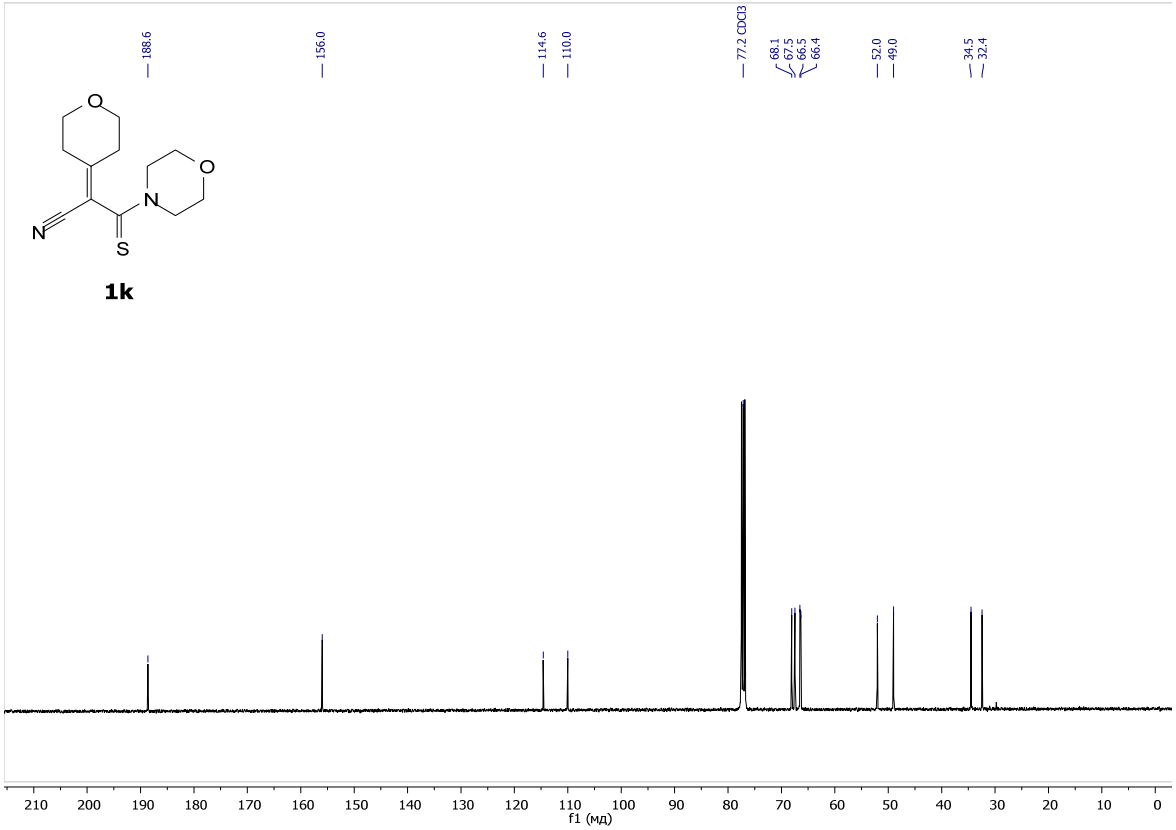

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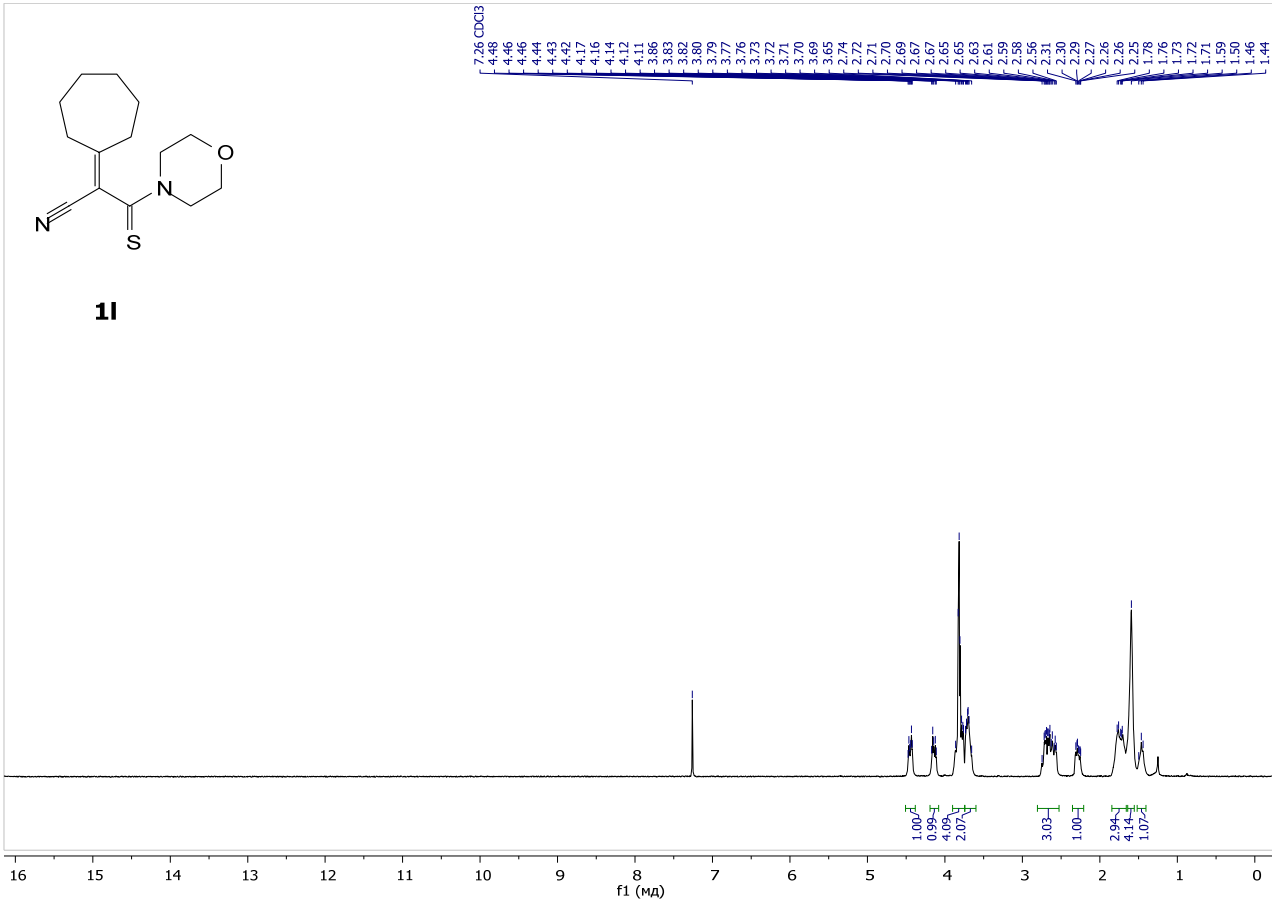

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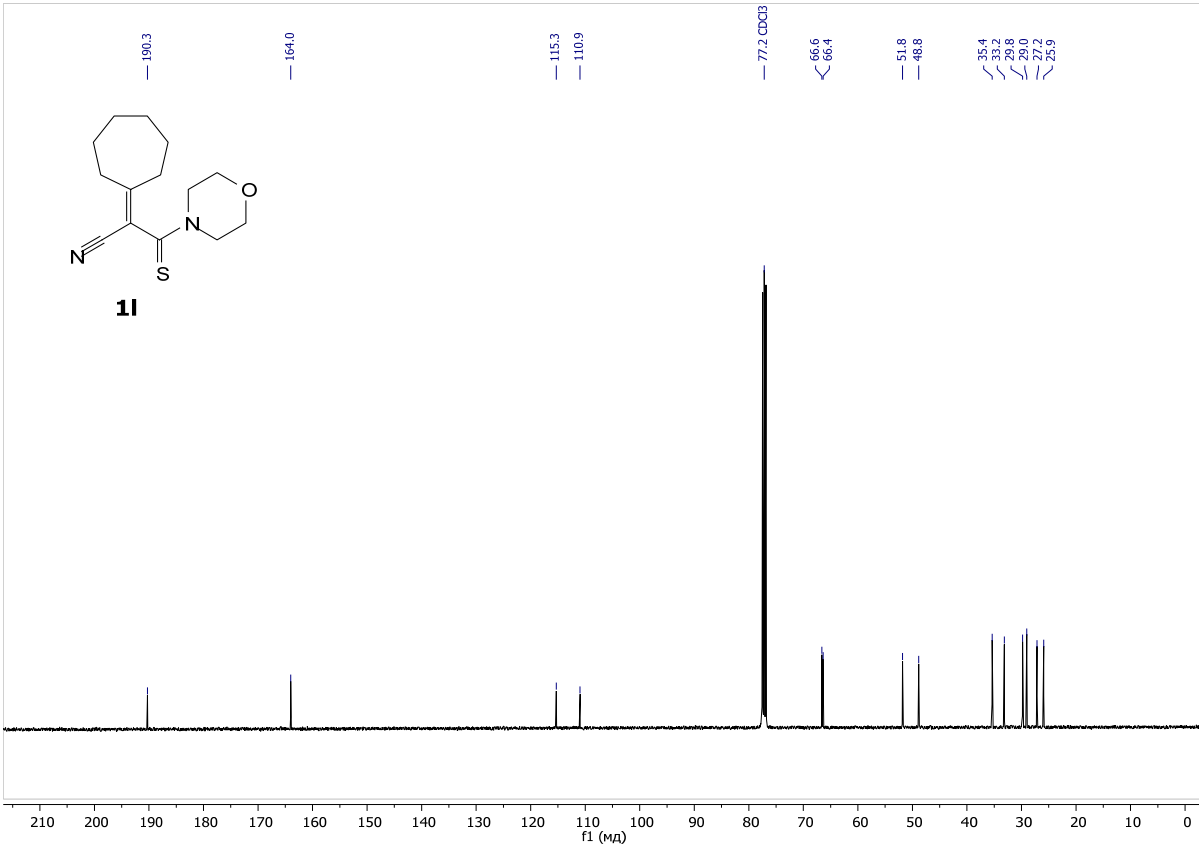

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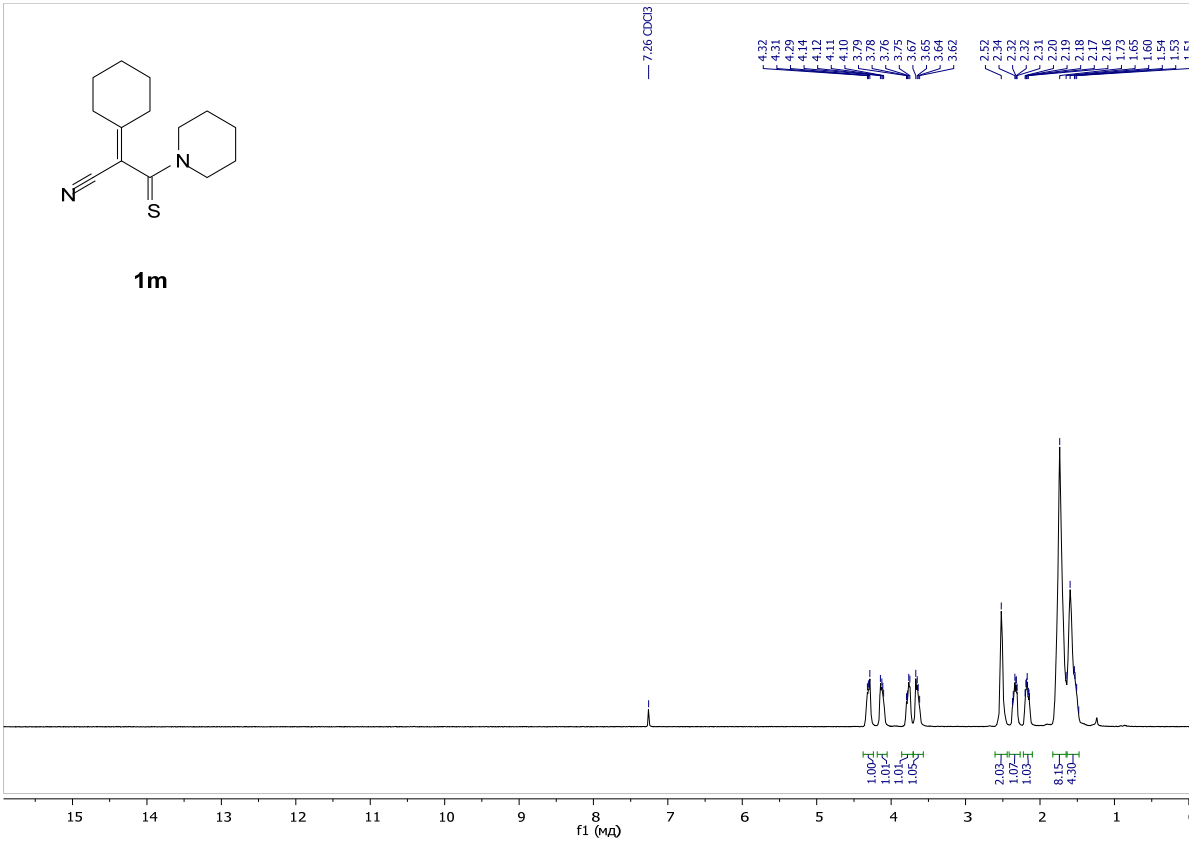

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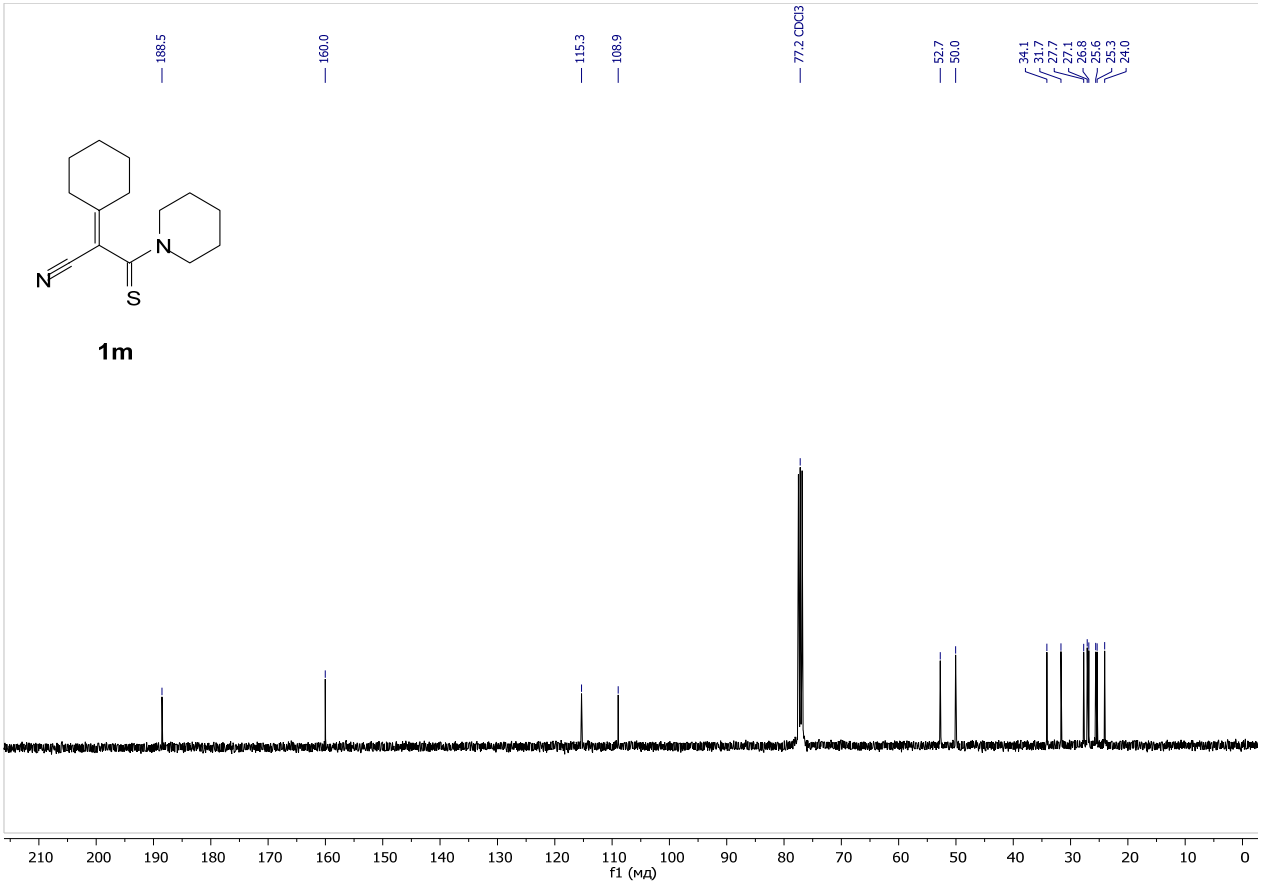

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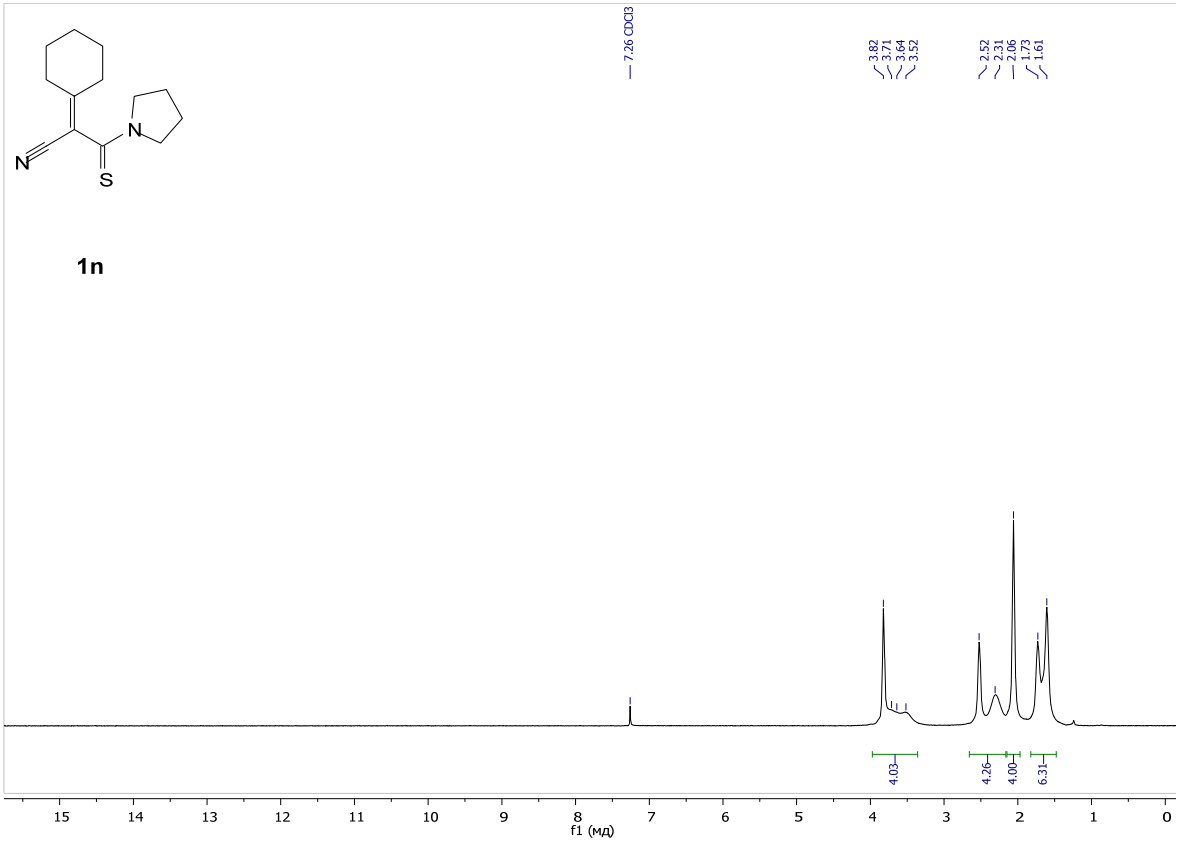

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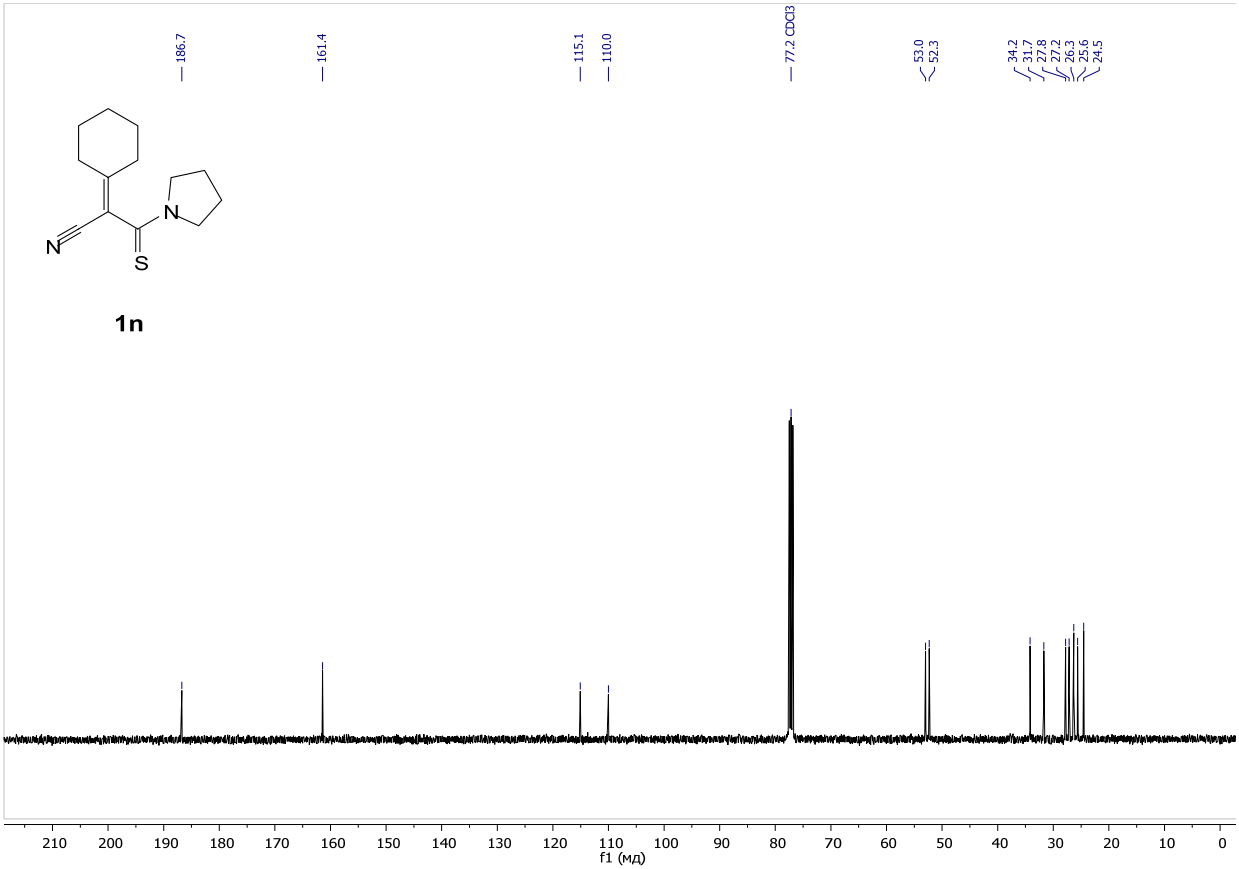

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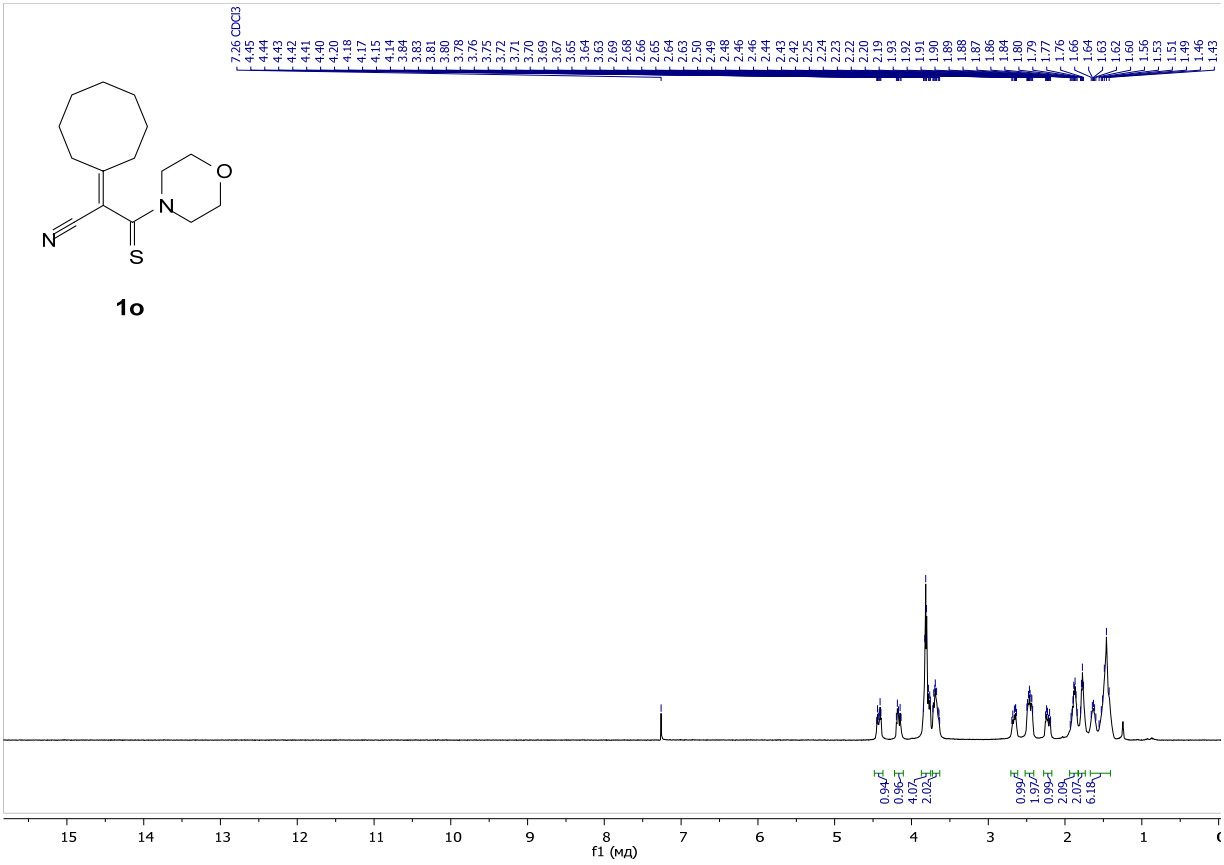

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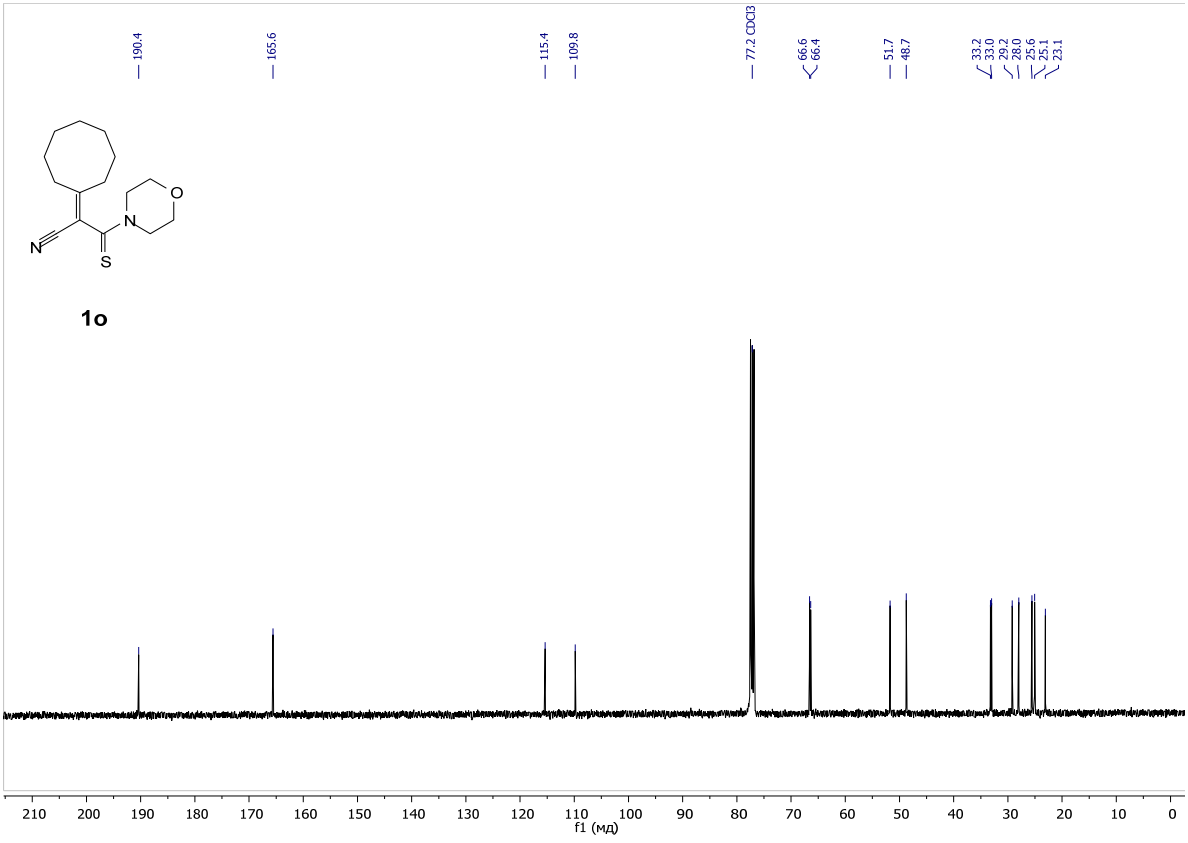

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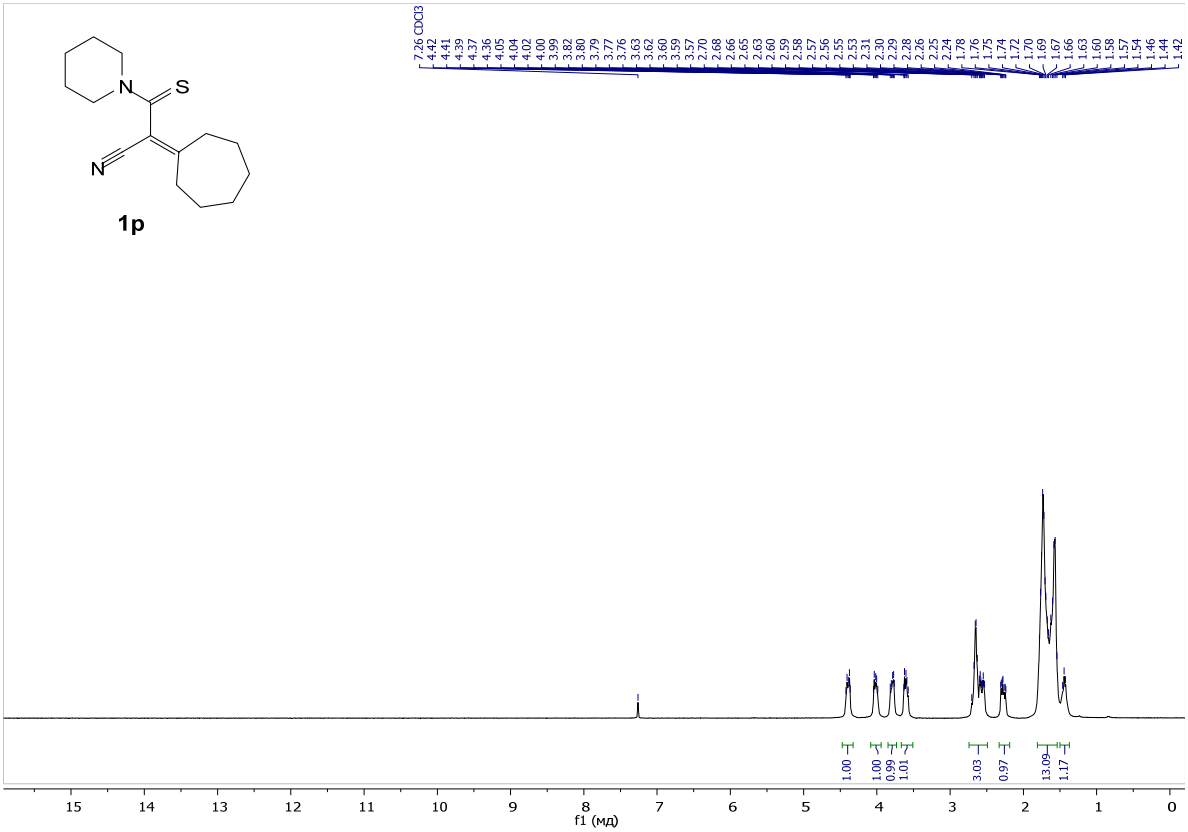
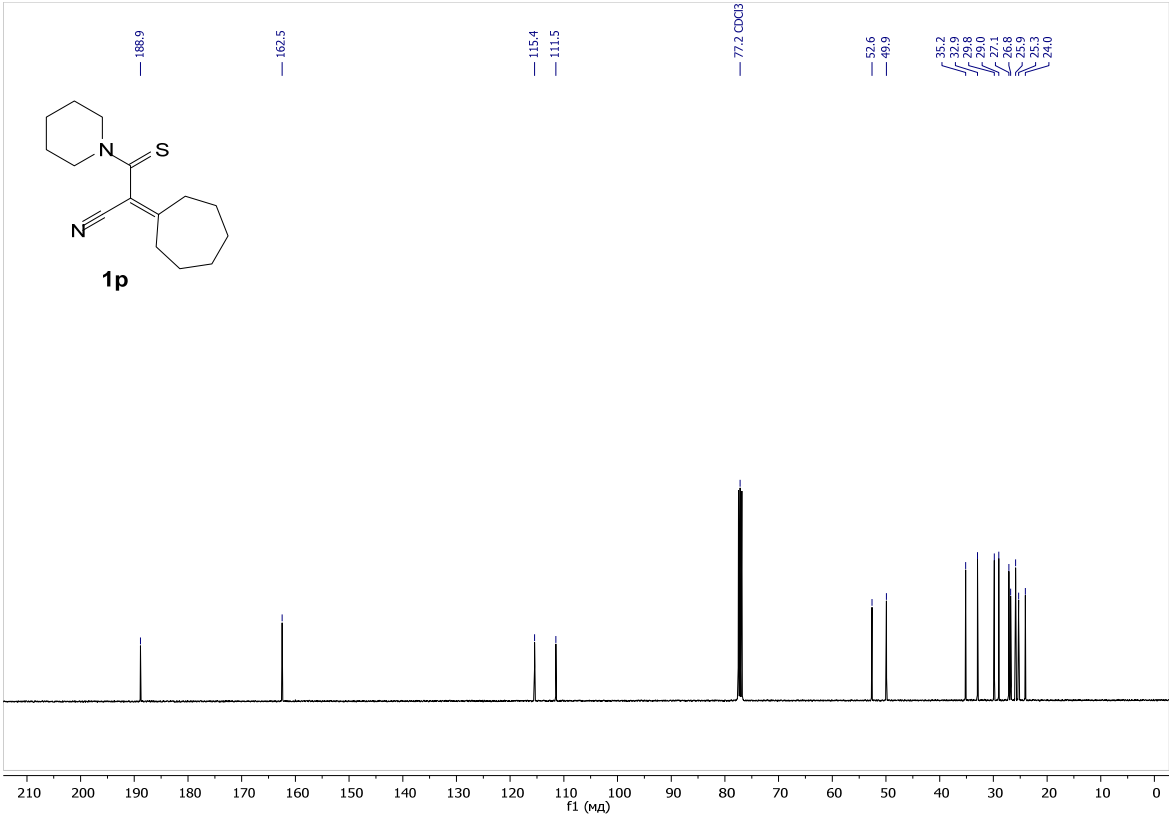
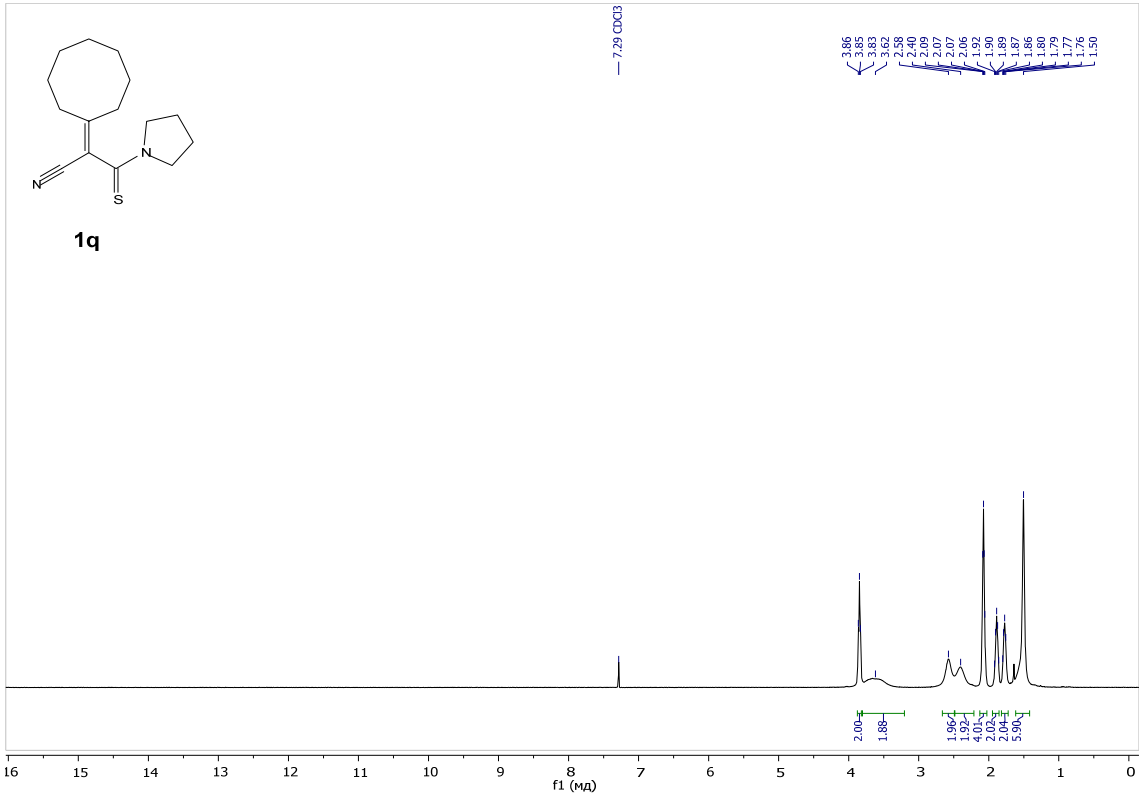


^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **1p**

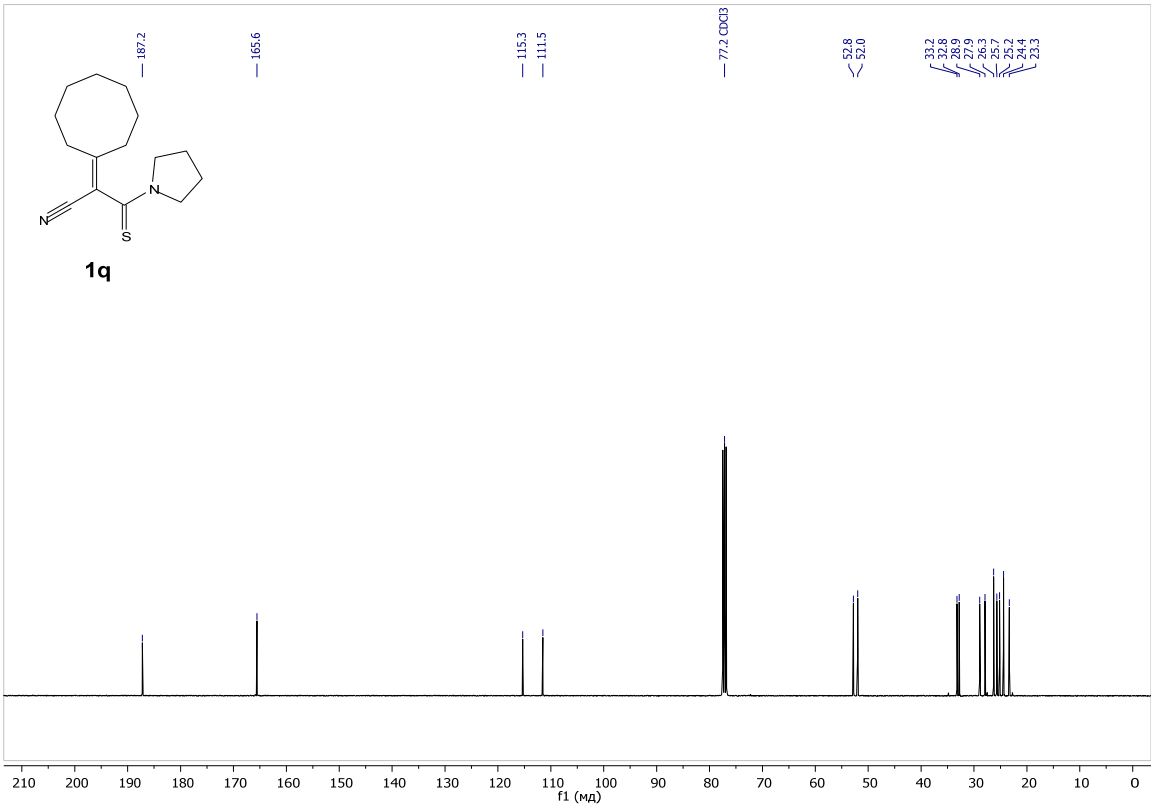


^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **1p**



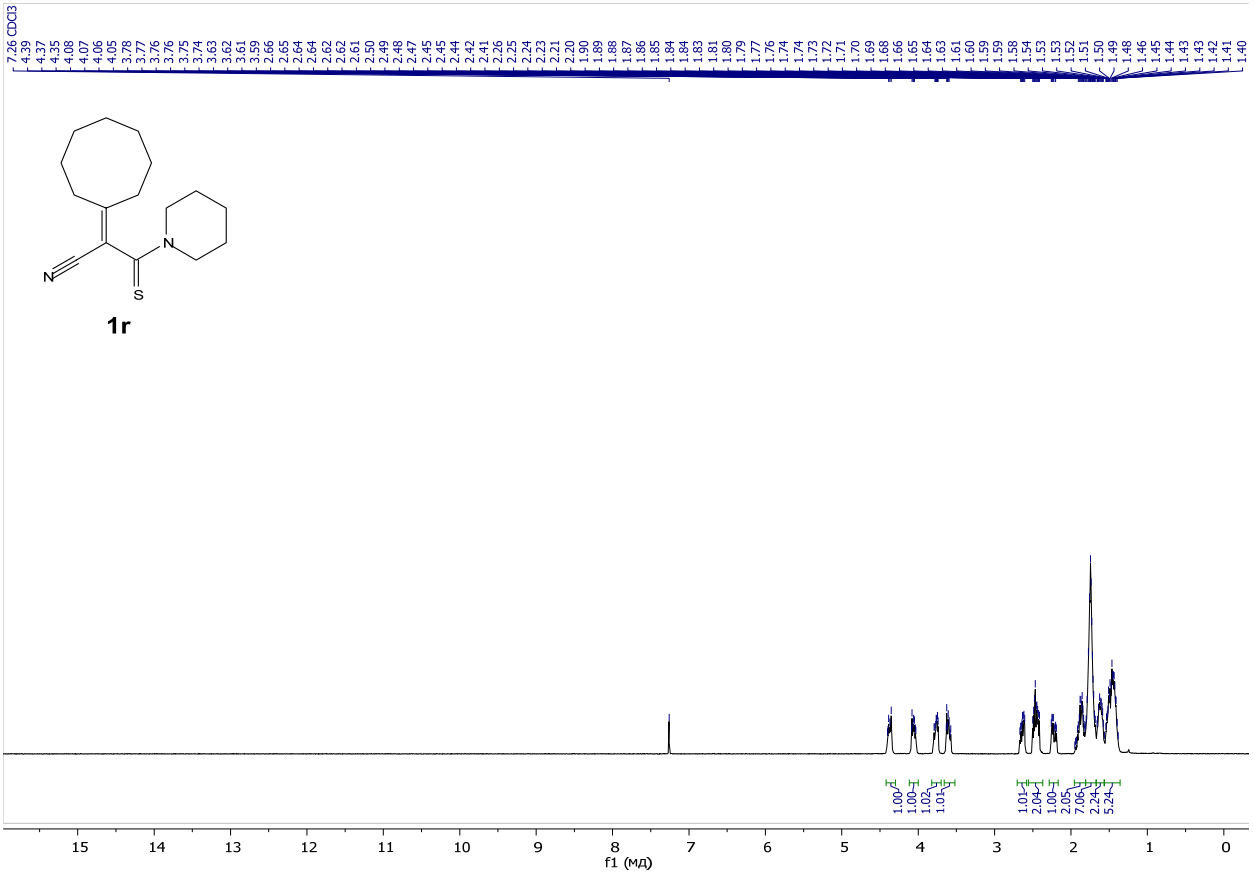
1q

^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **1q**

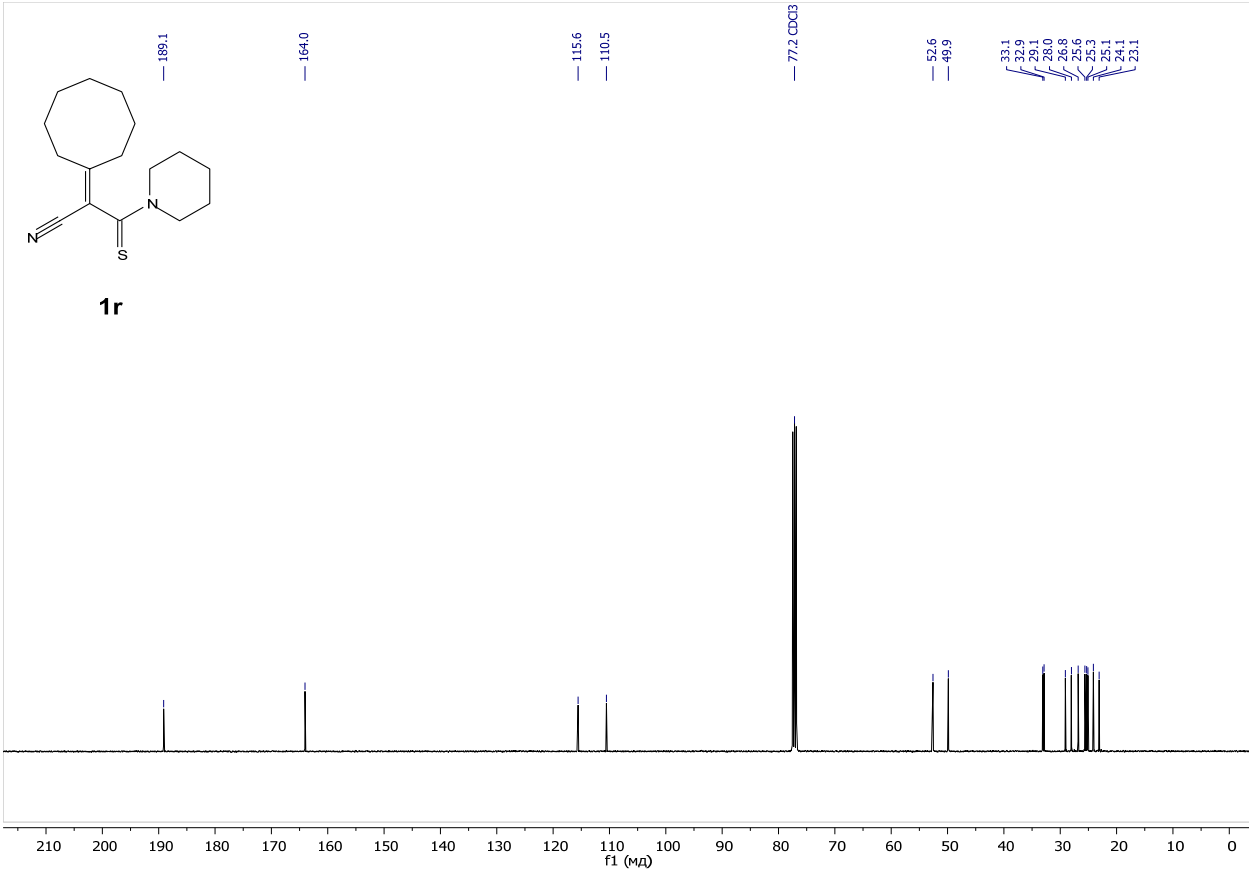


1q

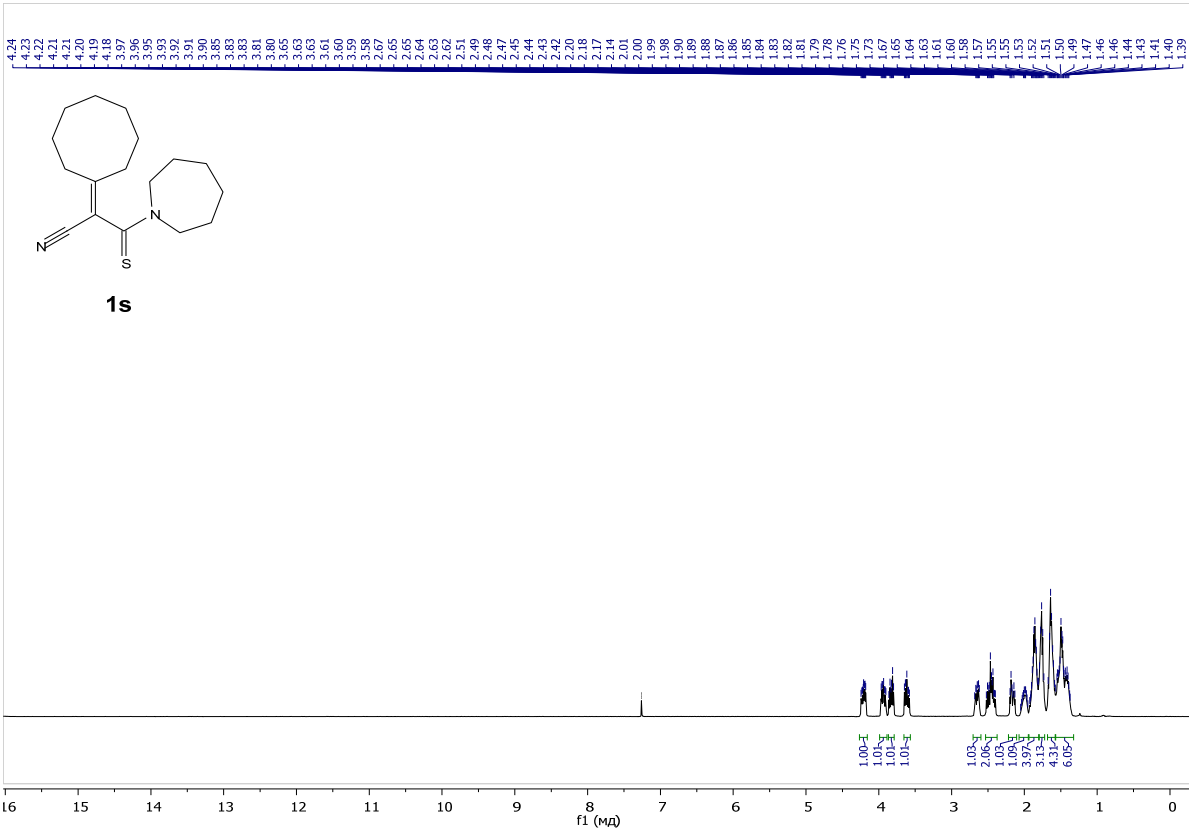
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **1q**



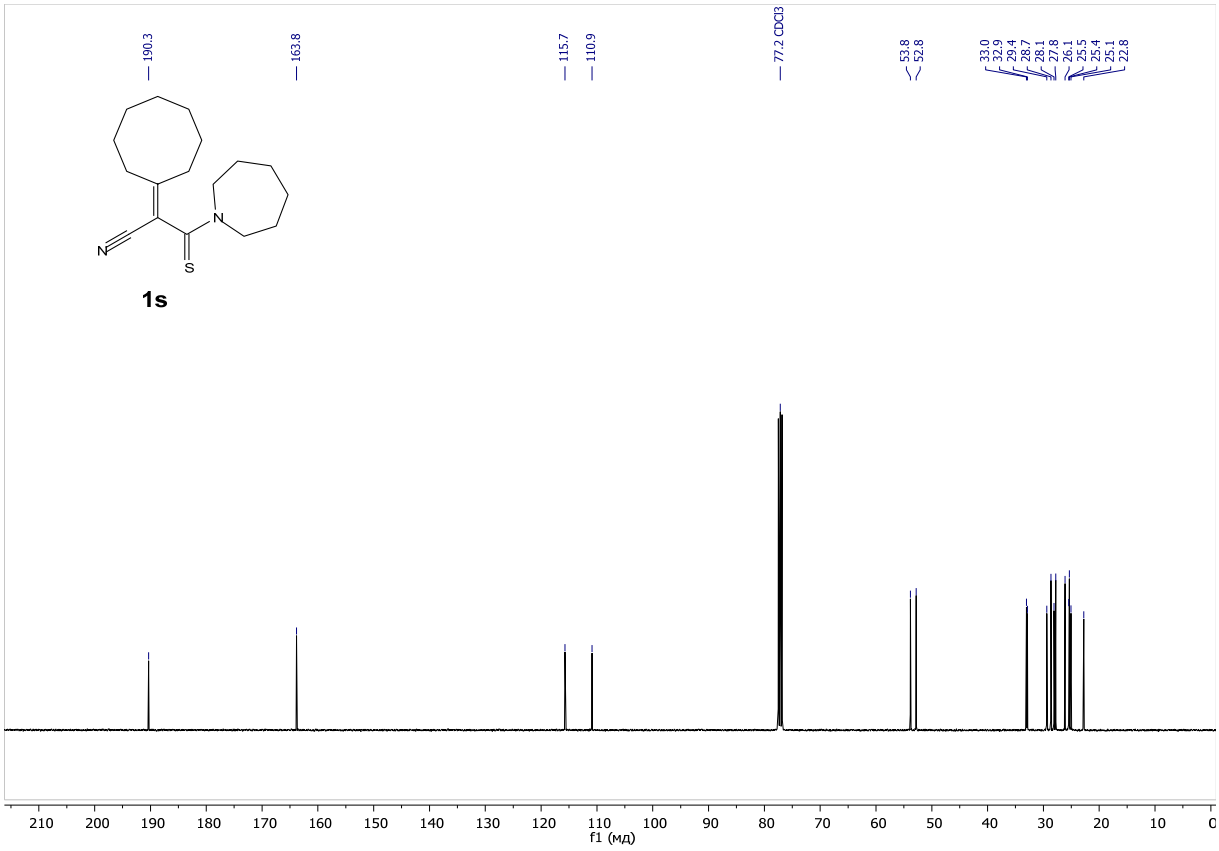
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **1r**



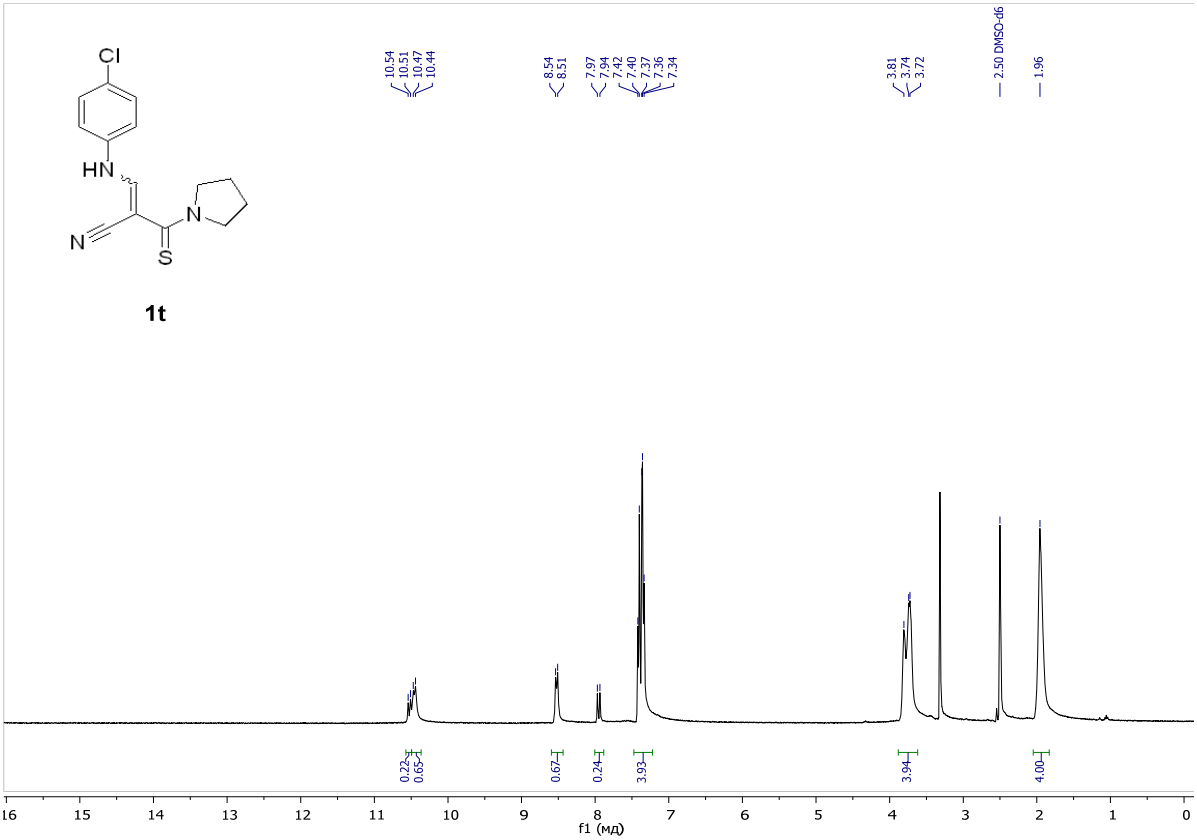
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **1r**



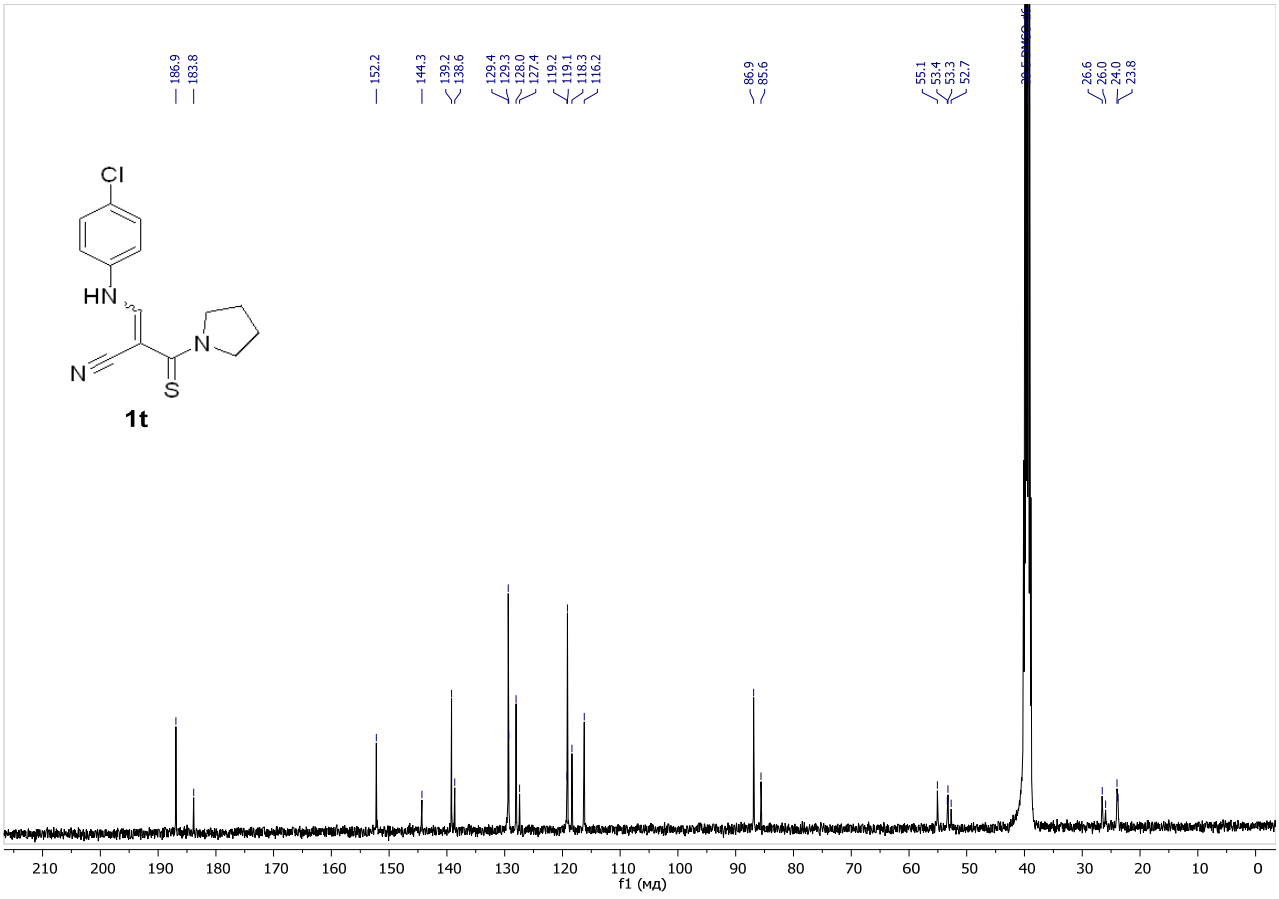
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **1s**



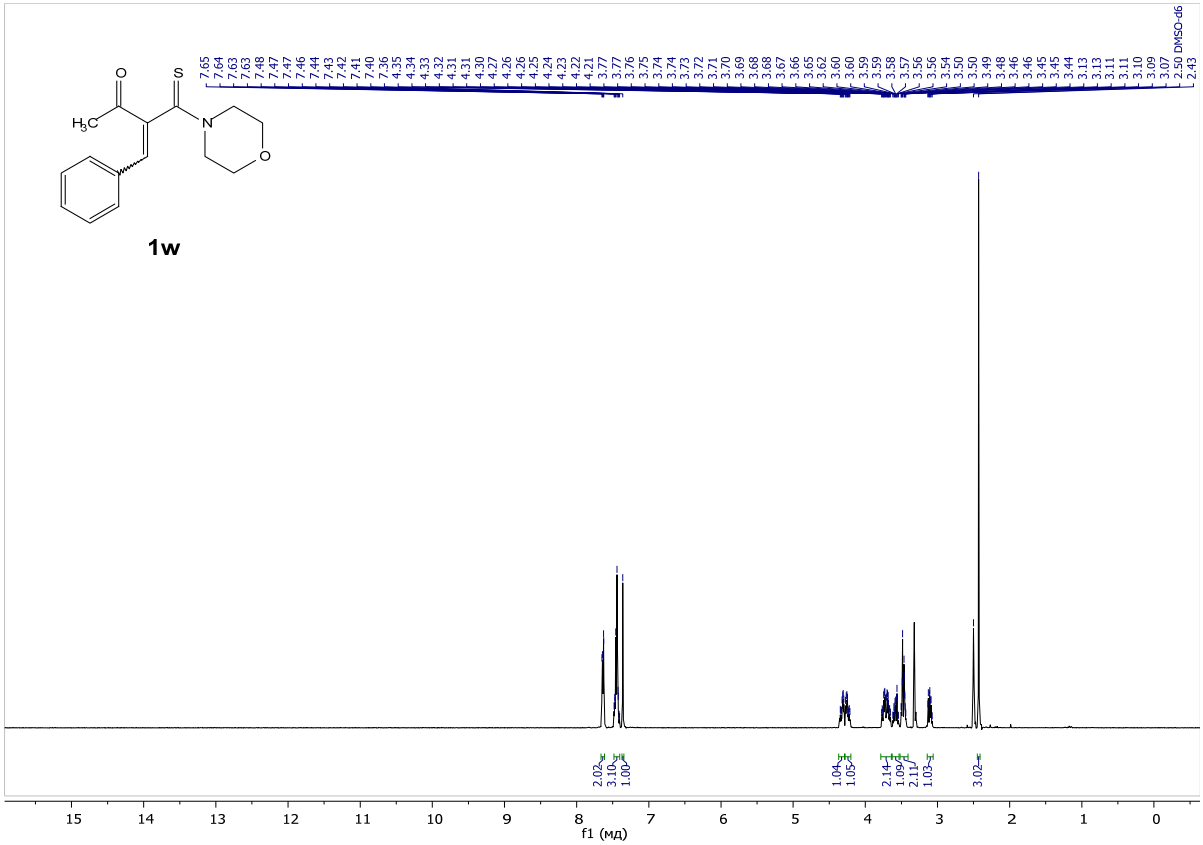
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **1s**



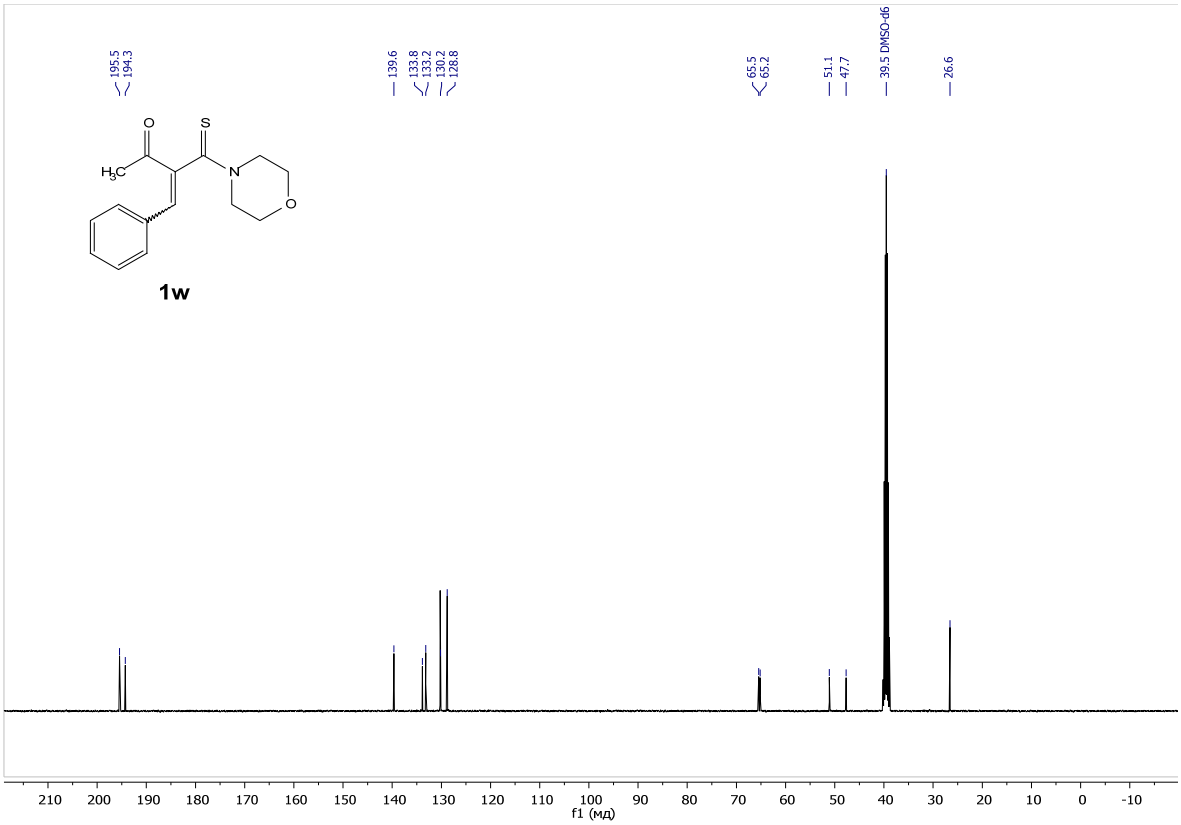
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **1t**



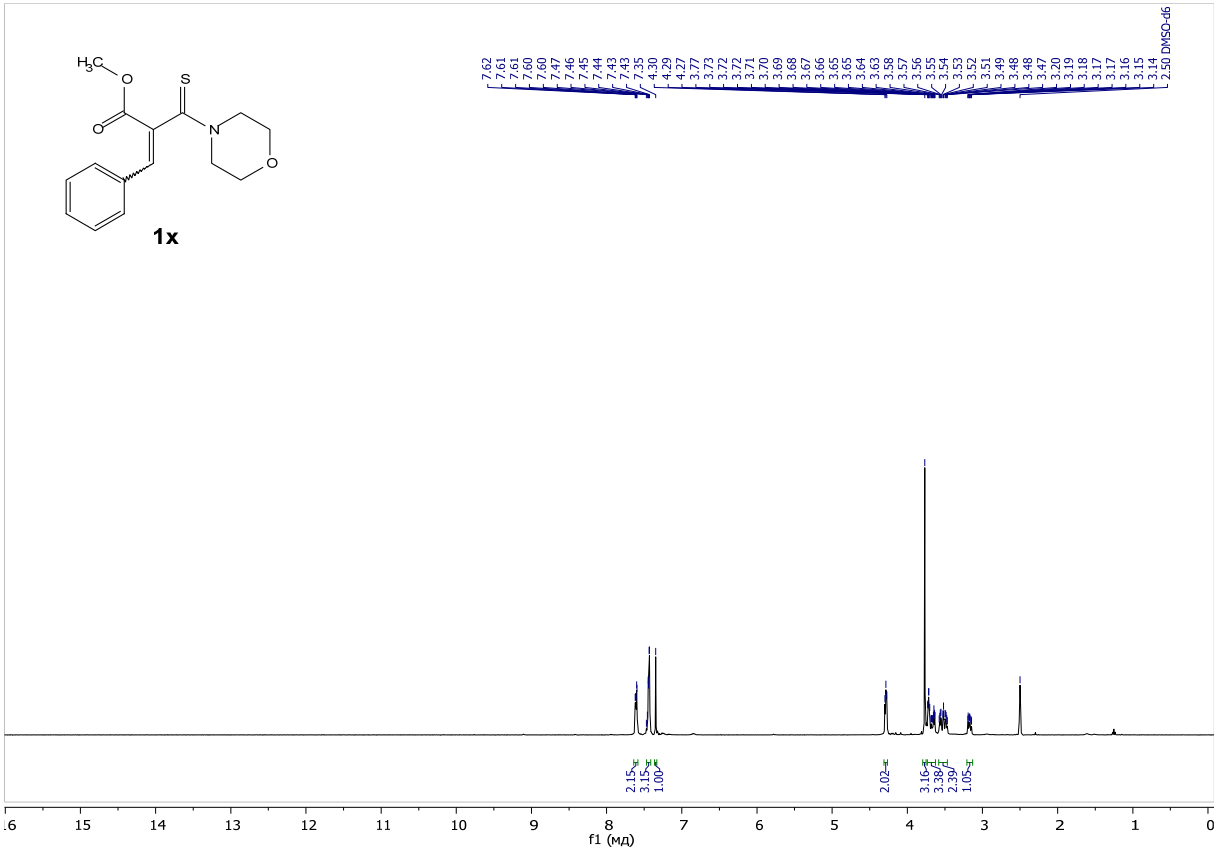
^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **1t**



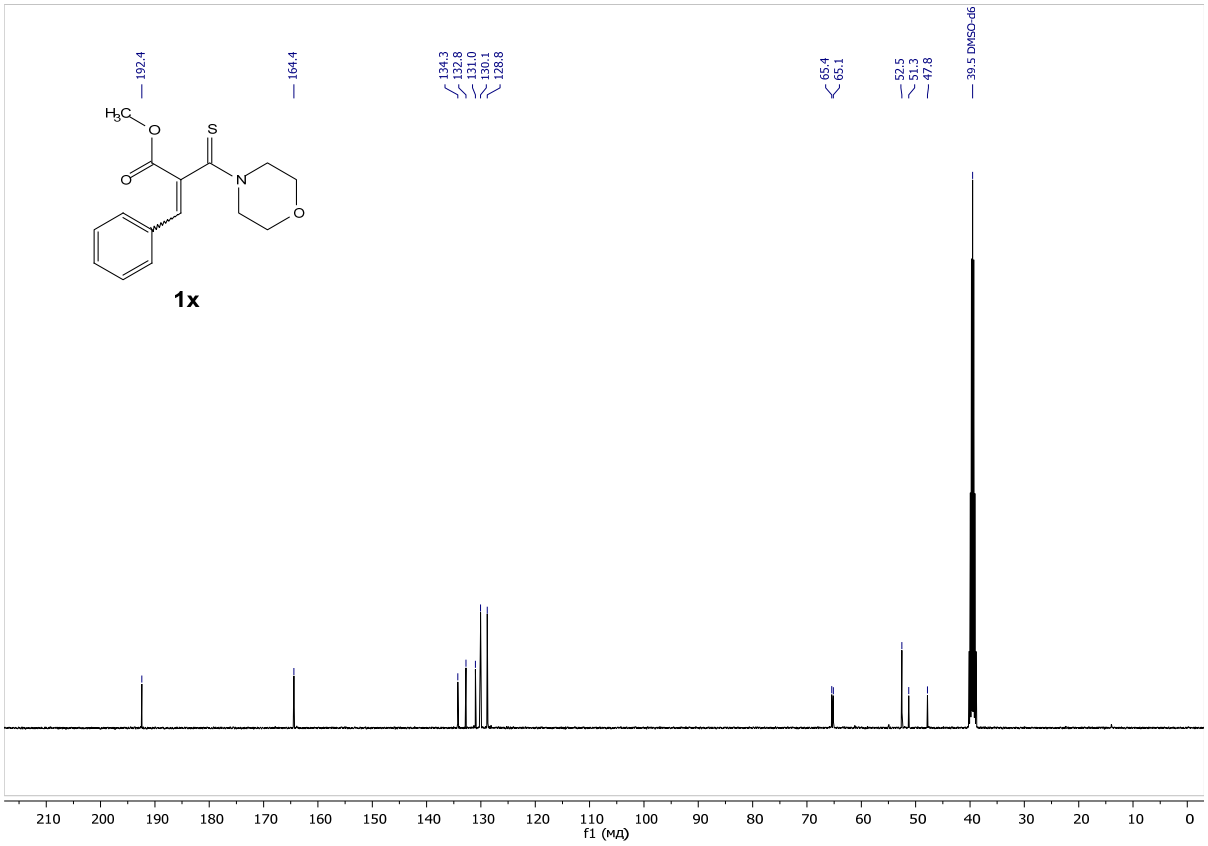
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **1w**



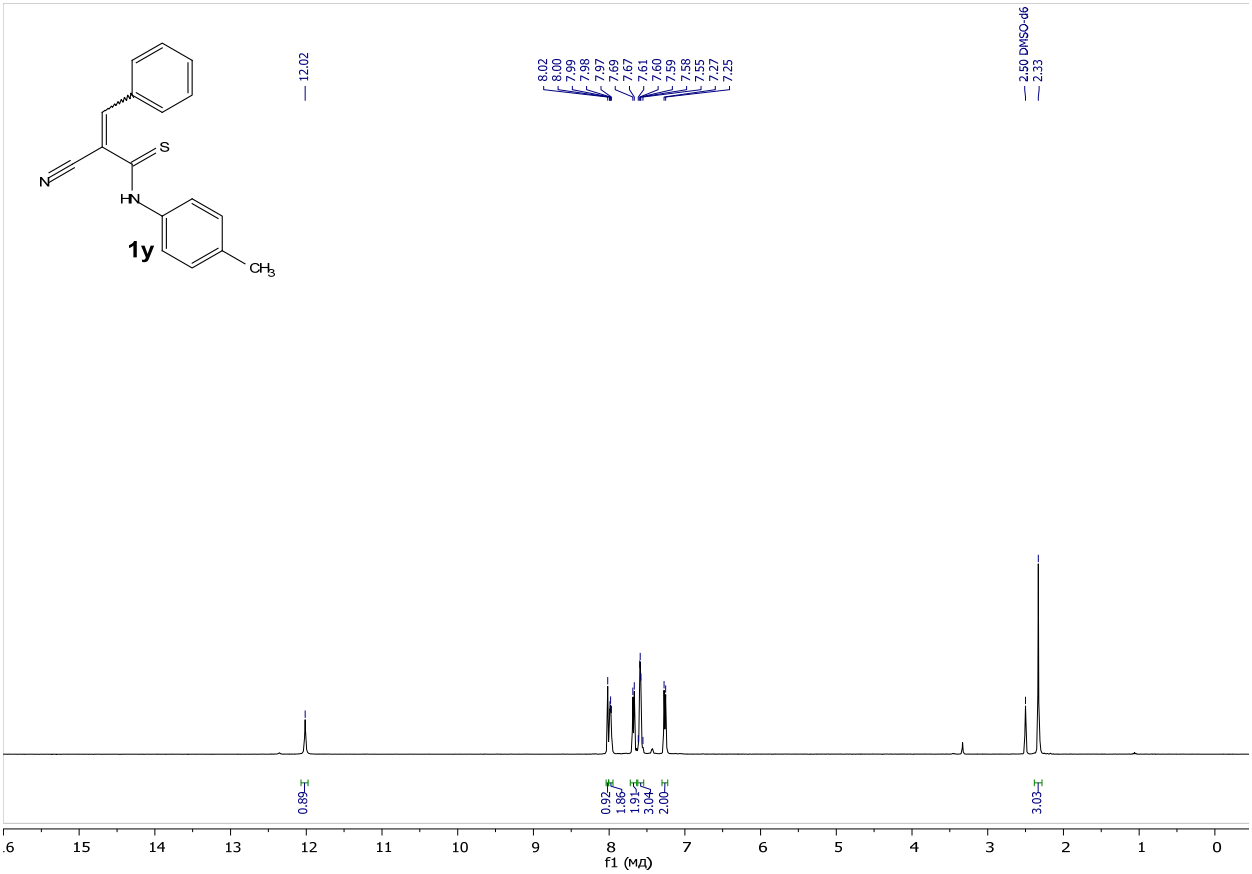
^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **1t**



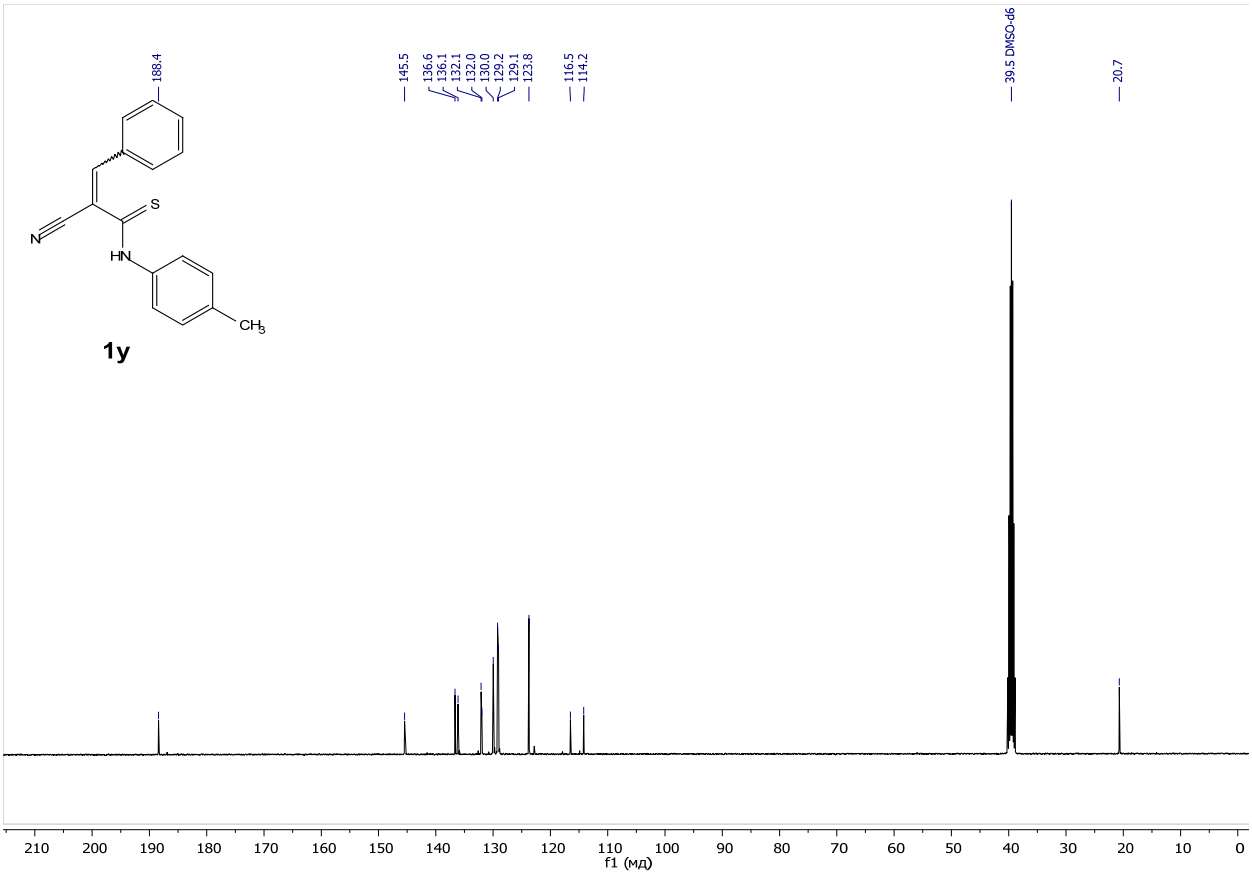
^{1}H NMR (400 MHz, DMSO–d_6) of **1x**



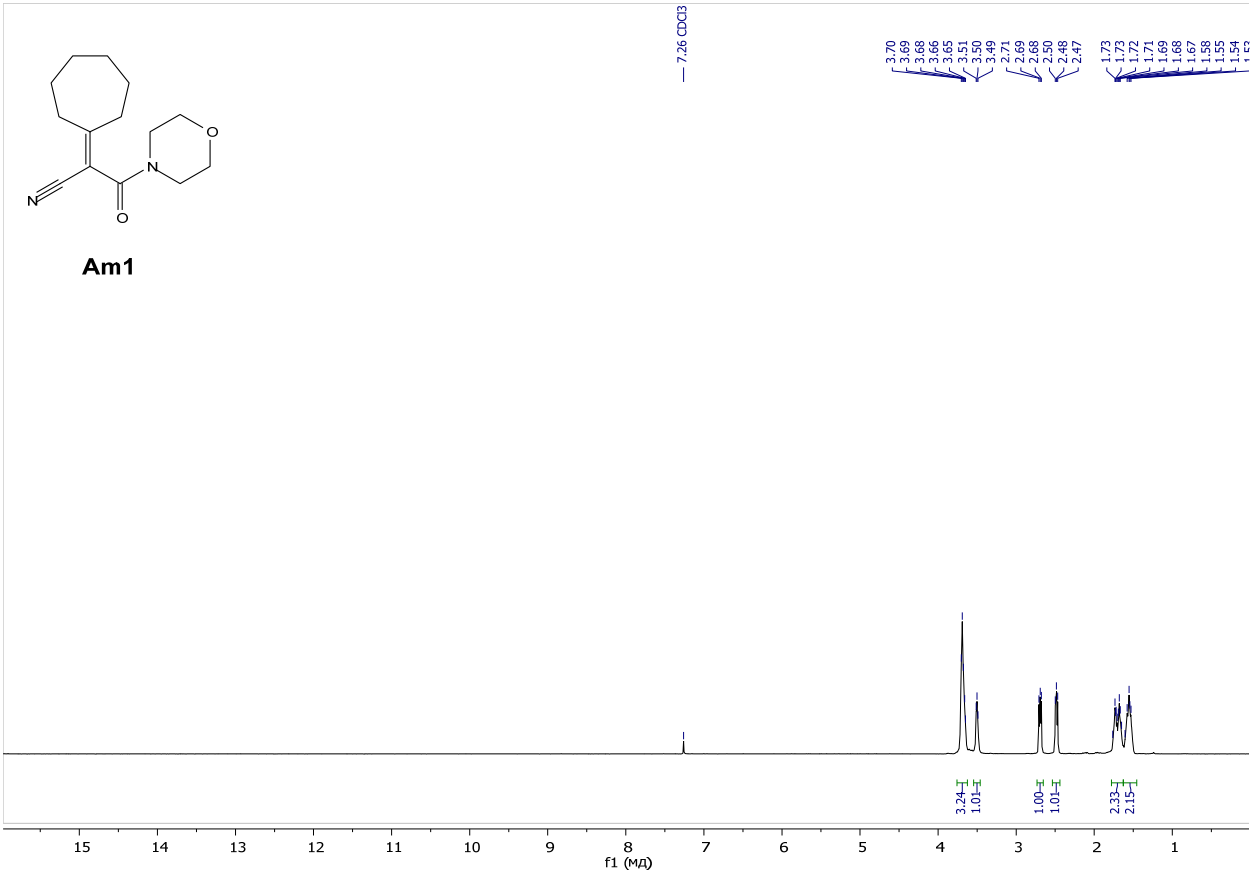
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **1x**



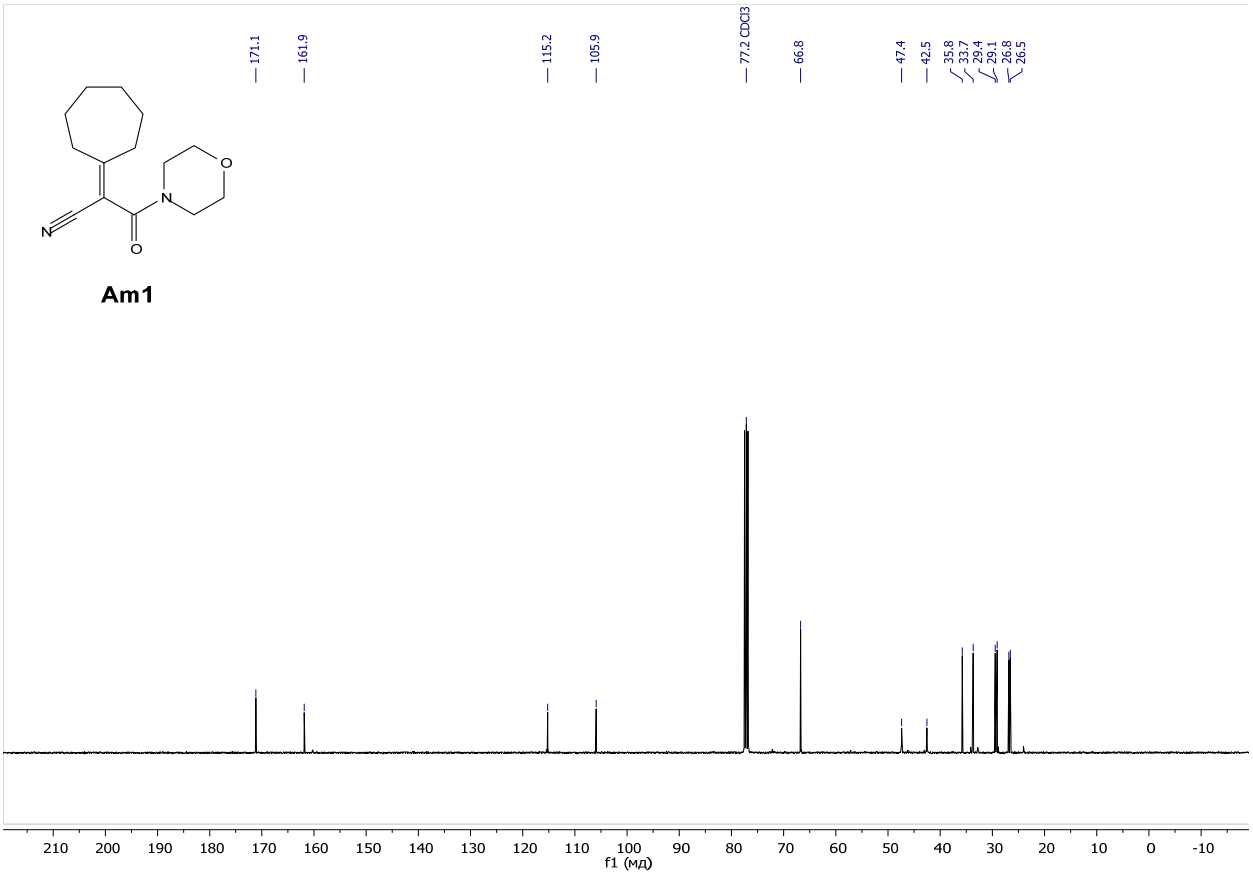
^{1}H NMR (400 MHz, DMSO–d_6) of **1y**



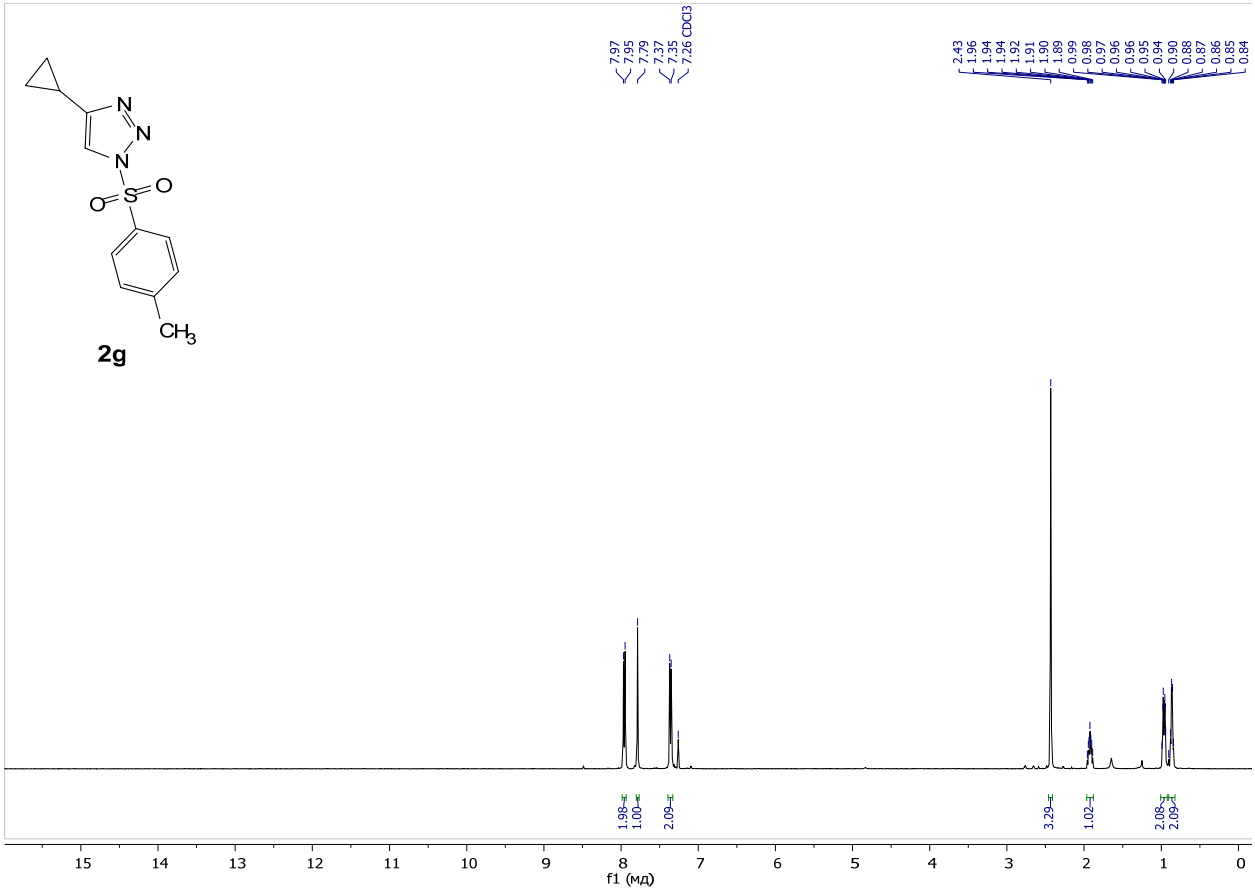
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **1y**



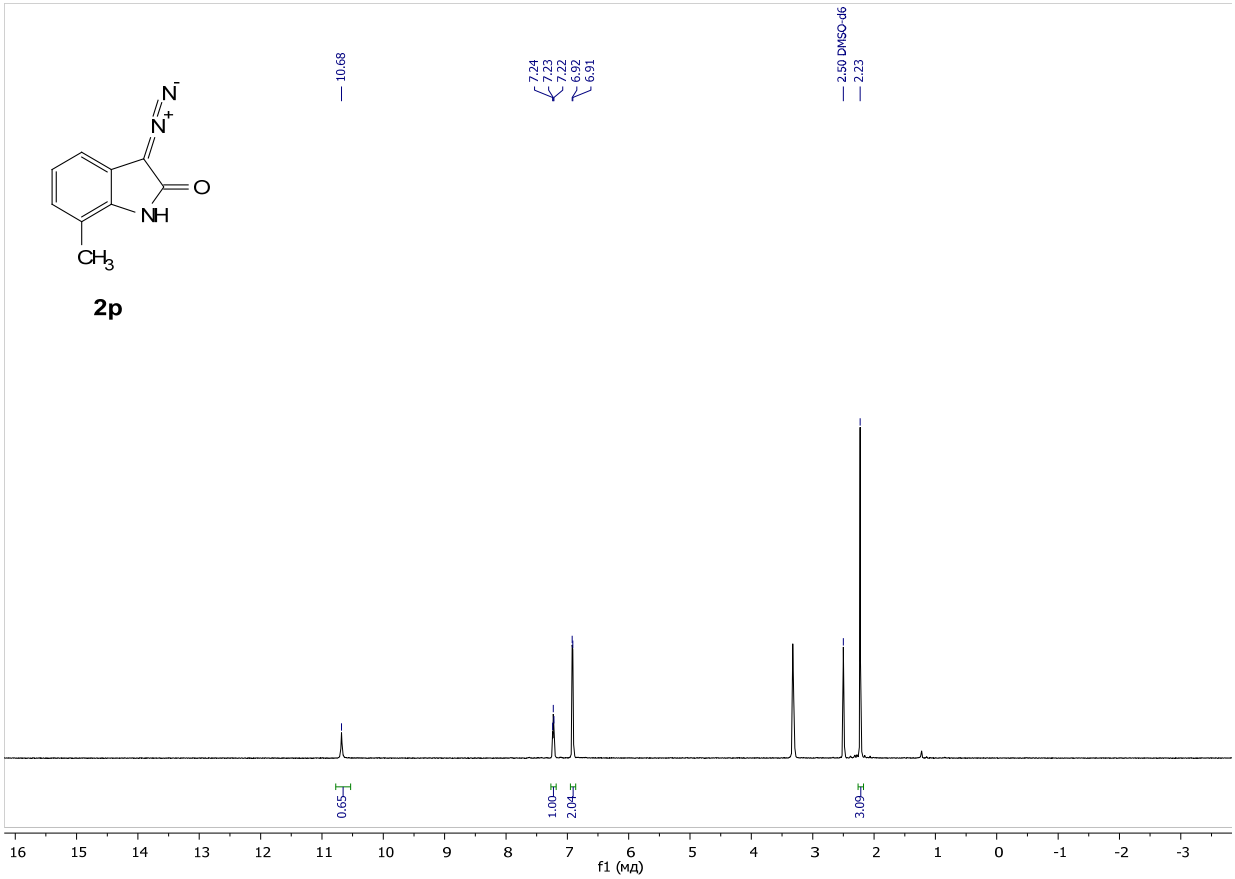
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **Am1**



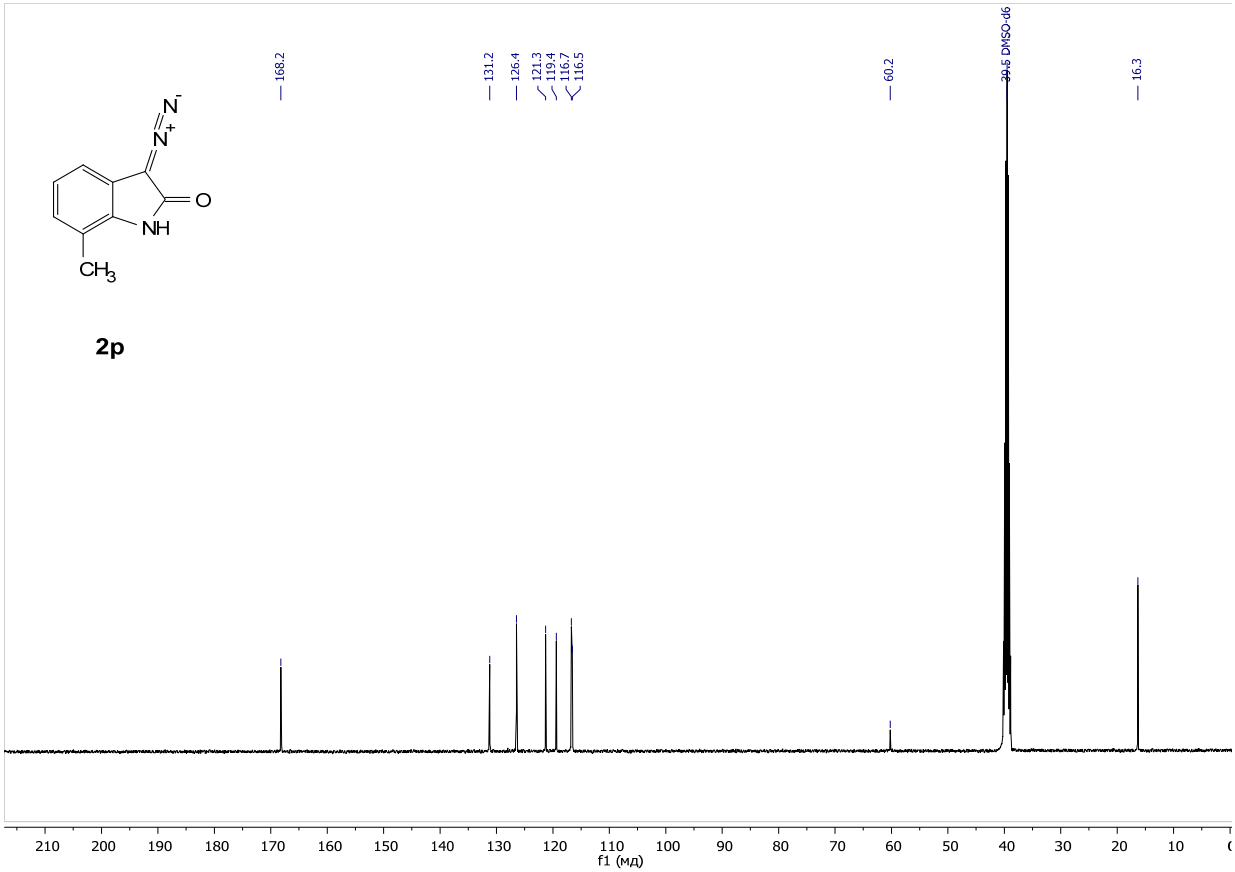
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **Am1**



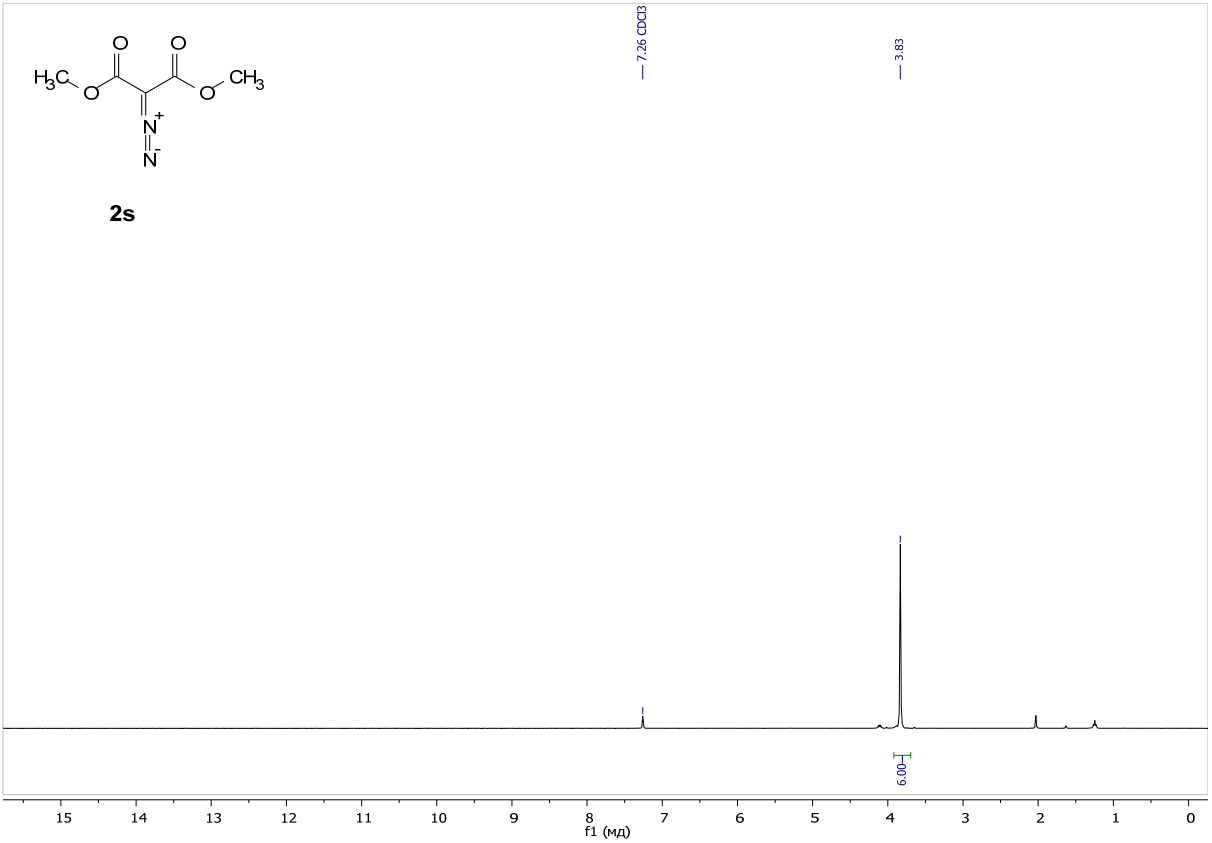
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **2g**



^{1}H NMR (400 MHz, DMSO–d_6) of **2p**

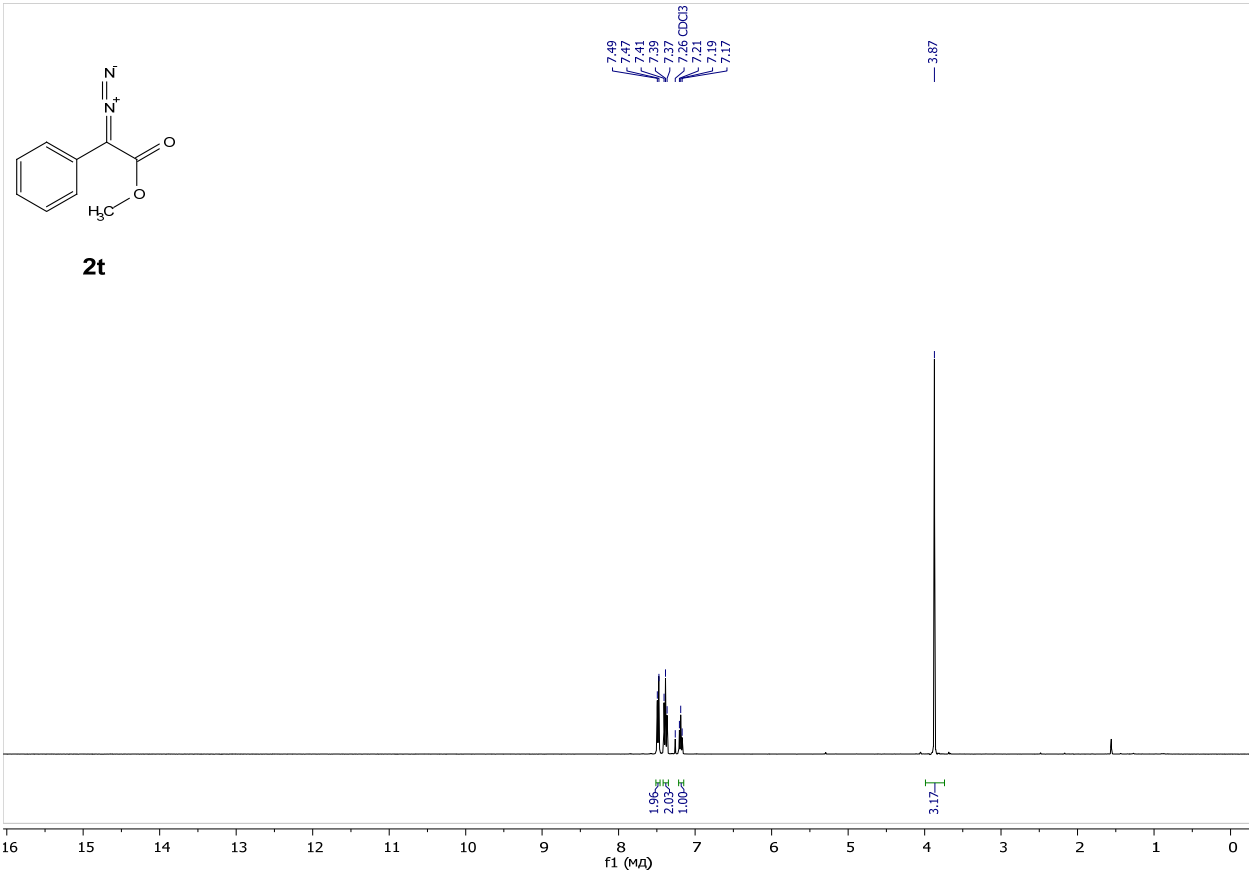


^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **2p**

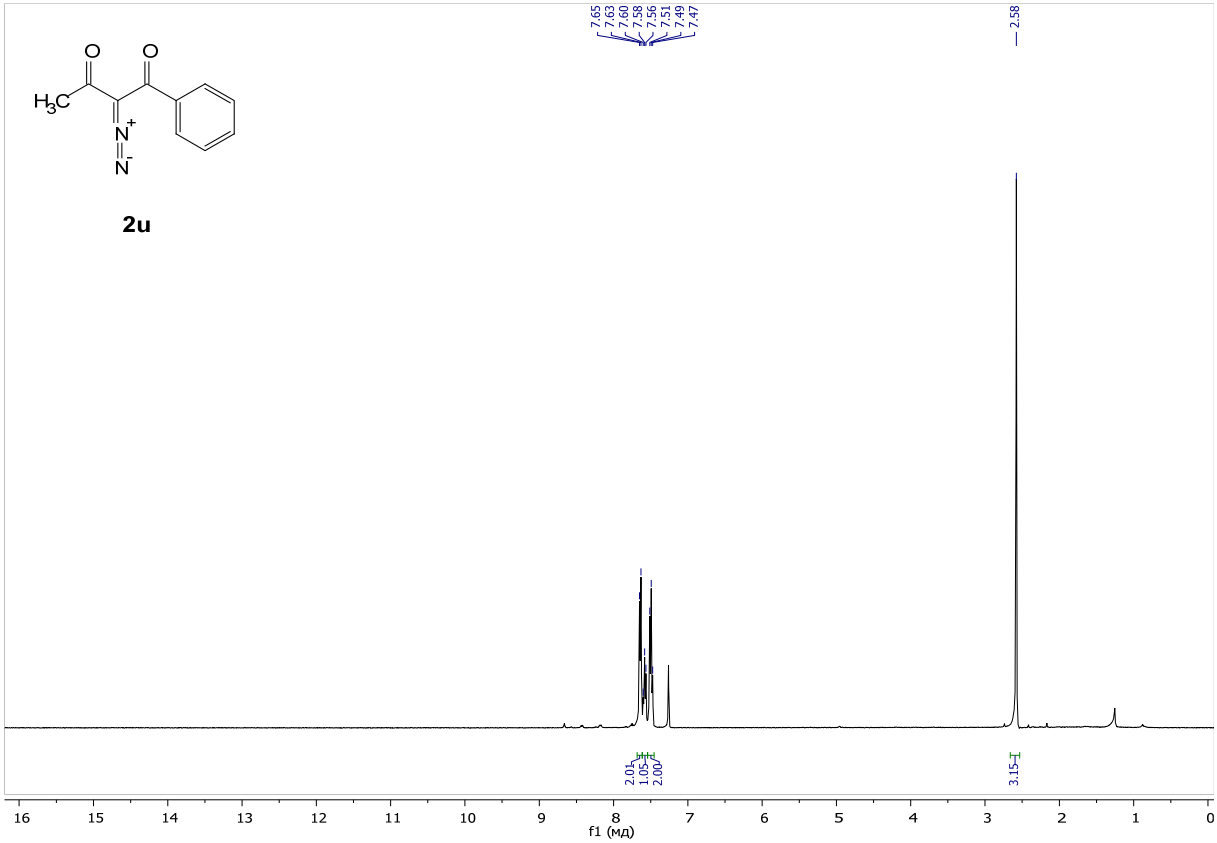


2s

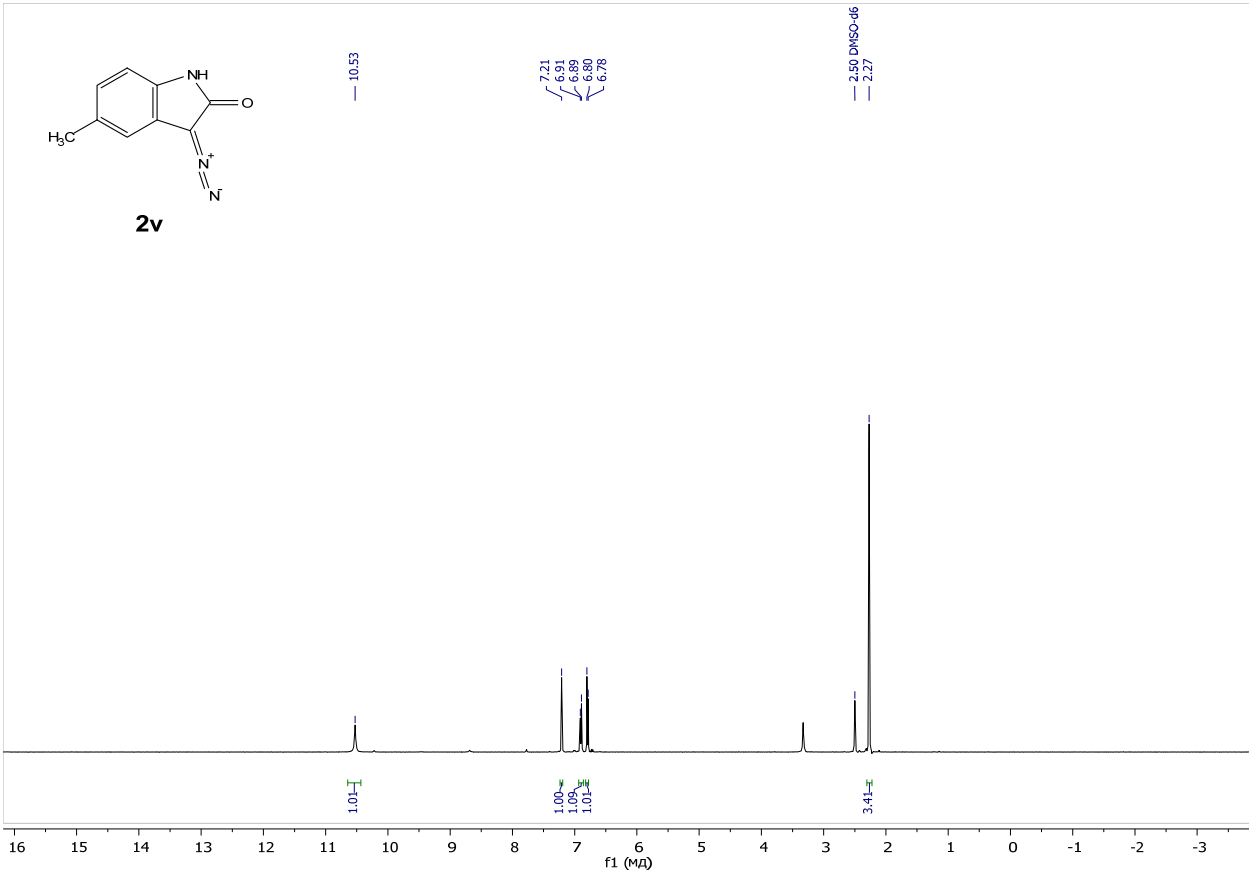
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **2s**



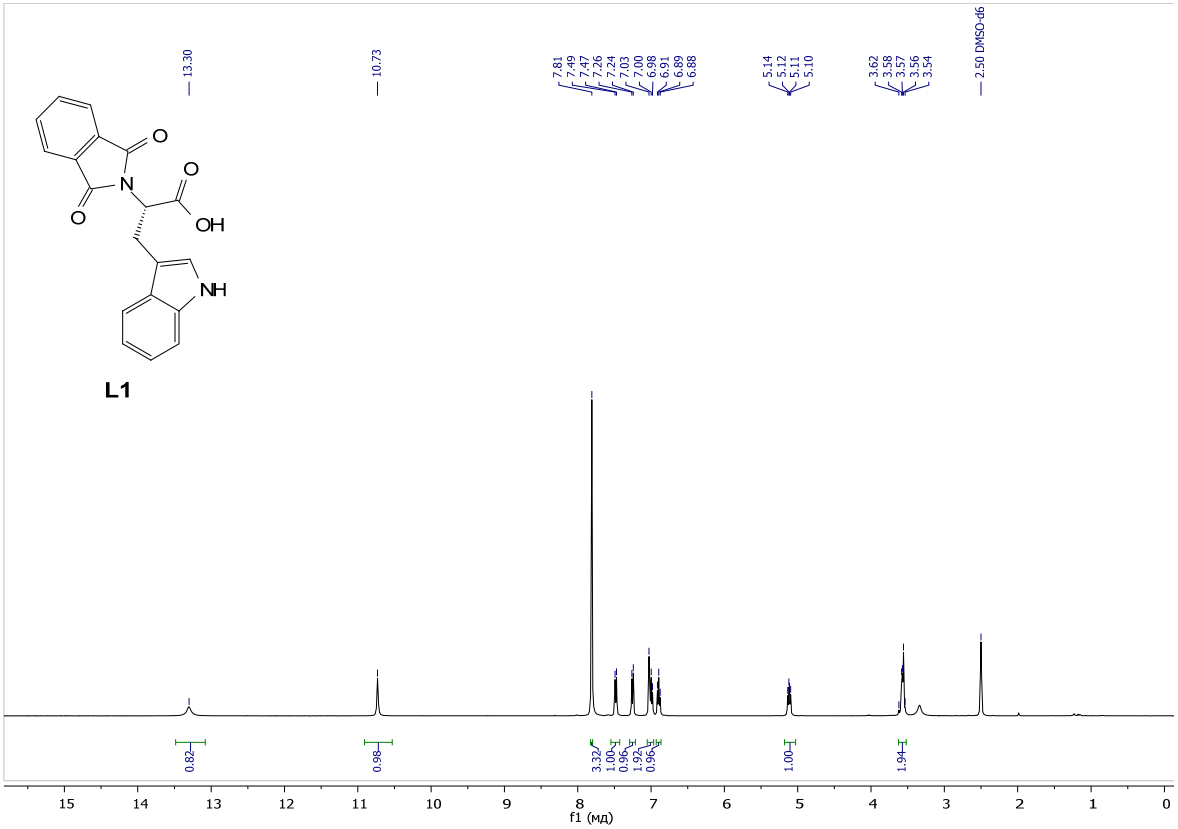
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **2t**



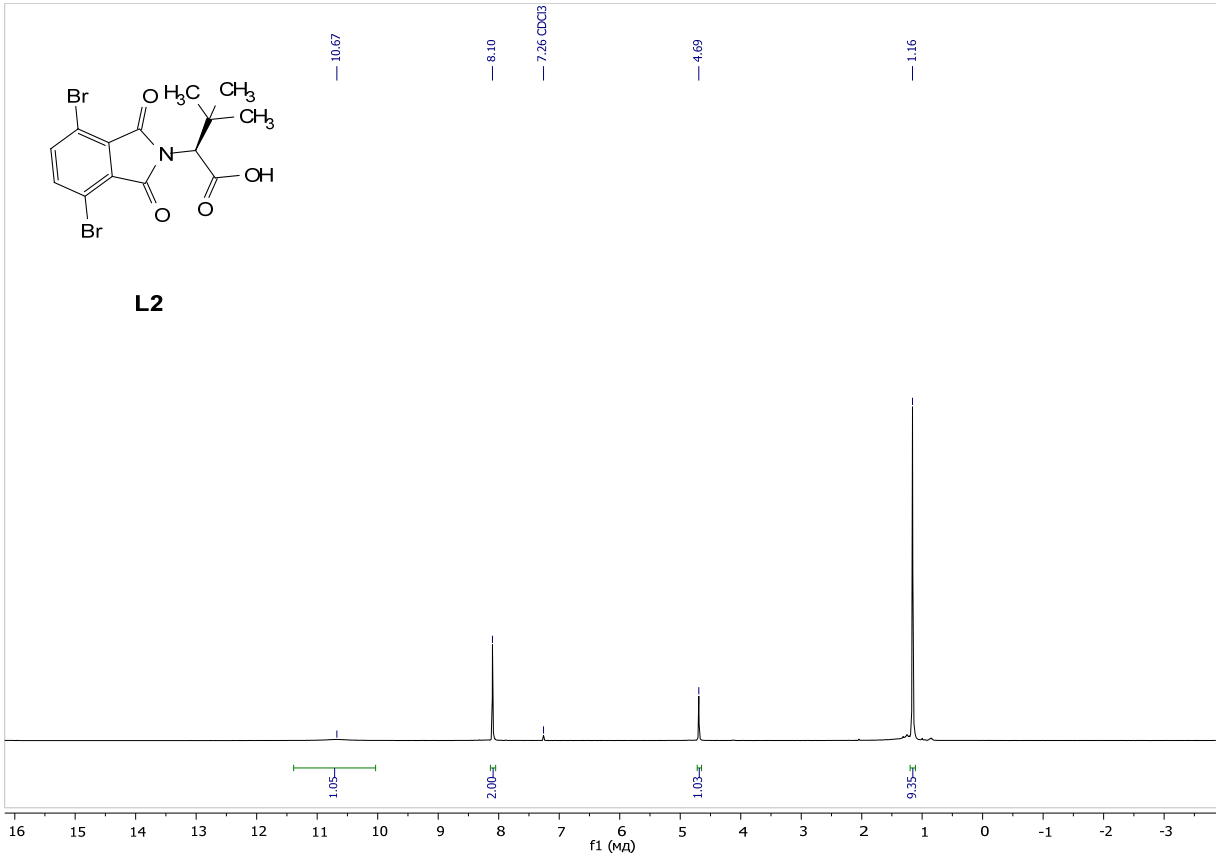
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **2u**



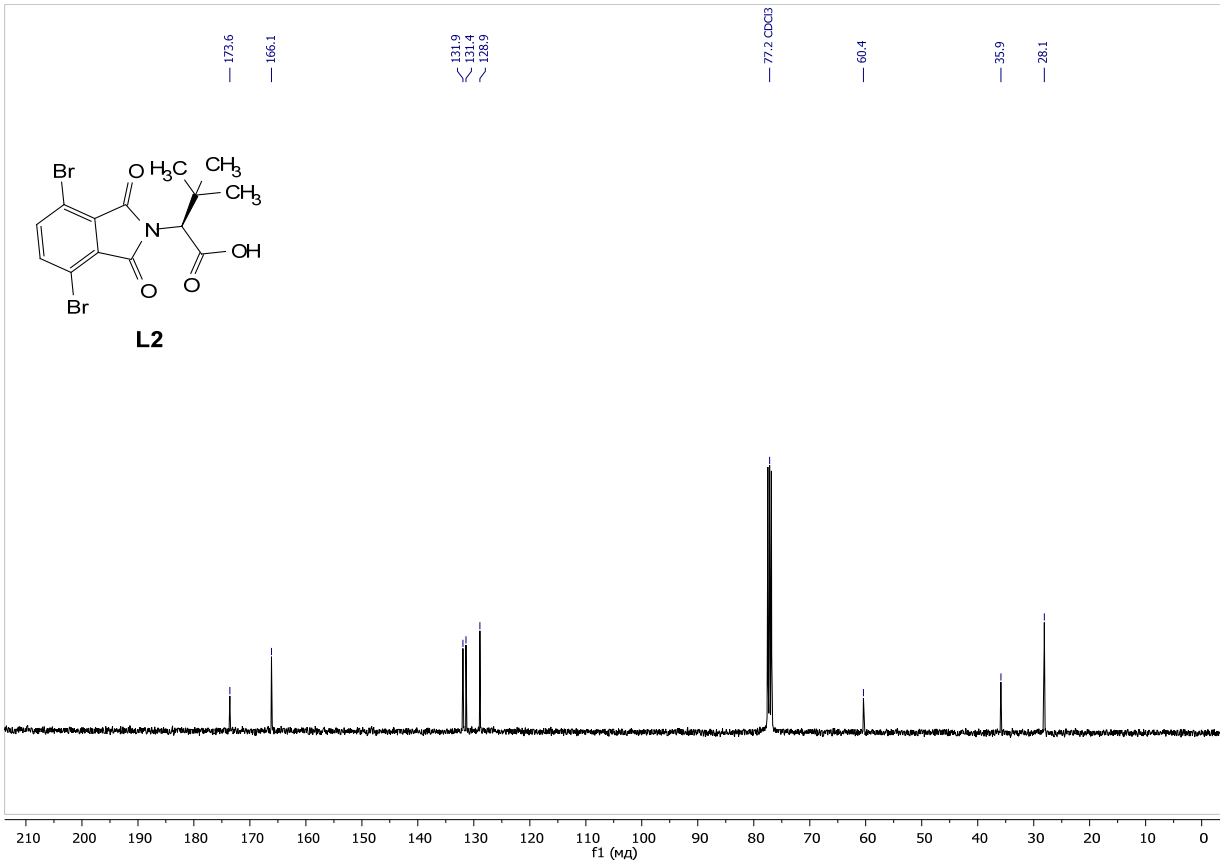
^{1}H NMR (400 MHz, DMSO–d_6) of **2v**



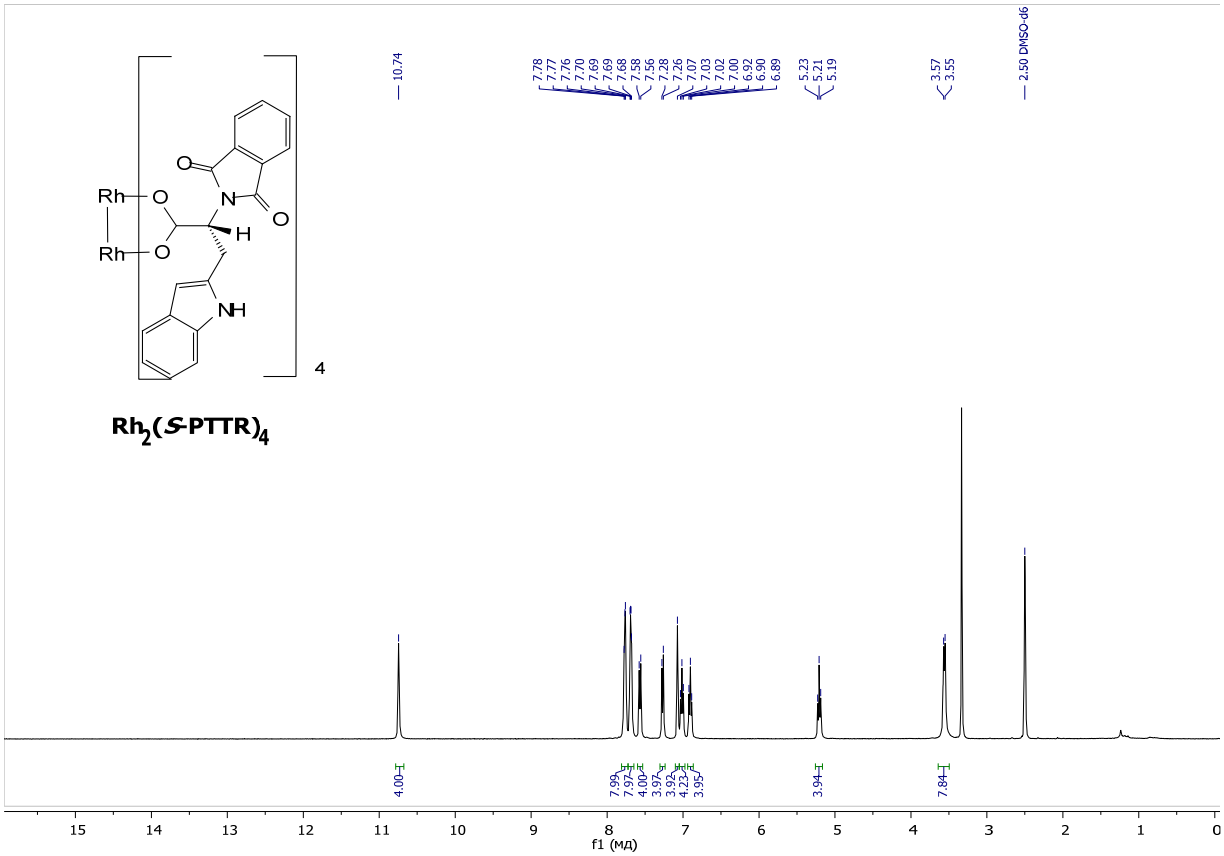
^{1}H NMR (400 MHz, DMSO–d_6) of **L1**



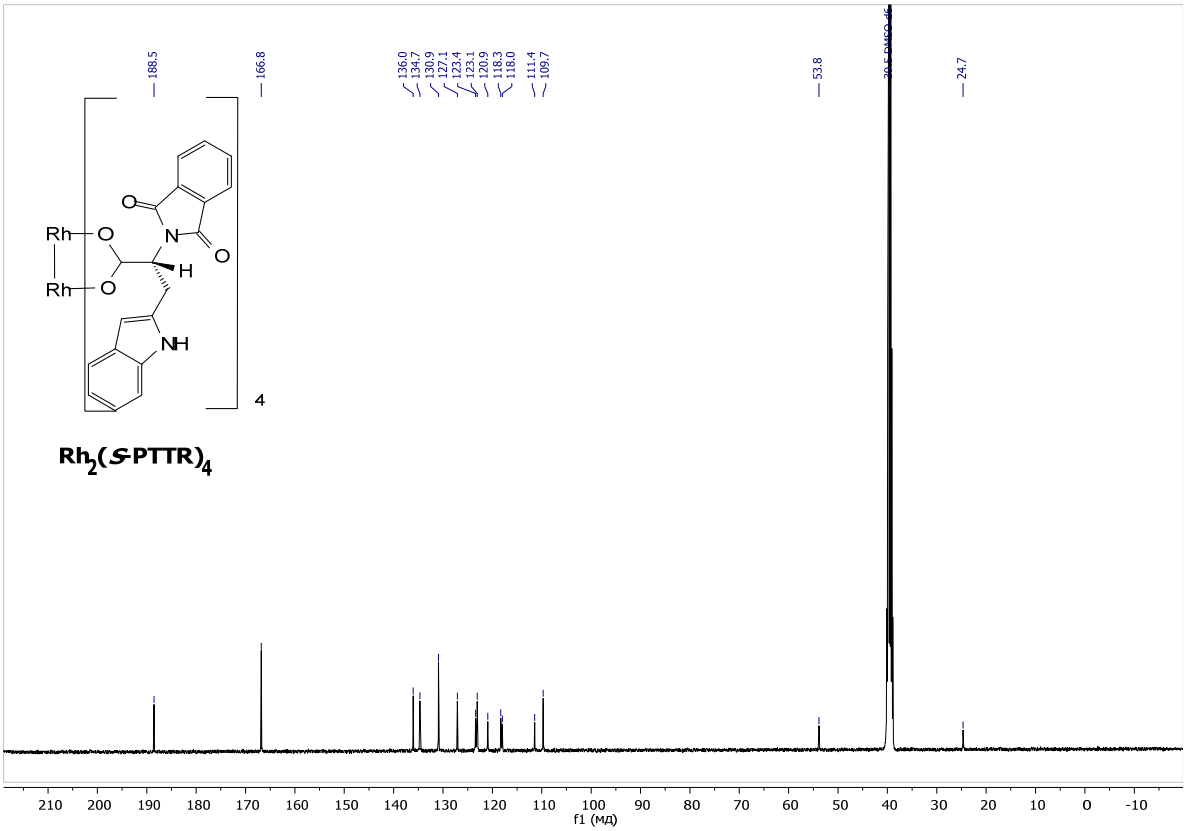
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **L2**



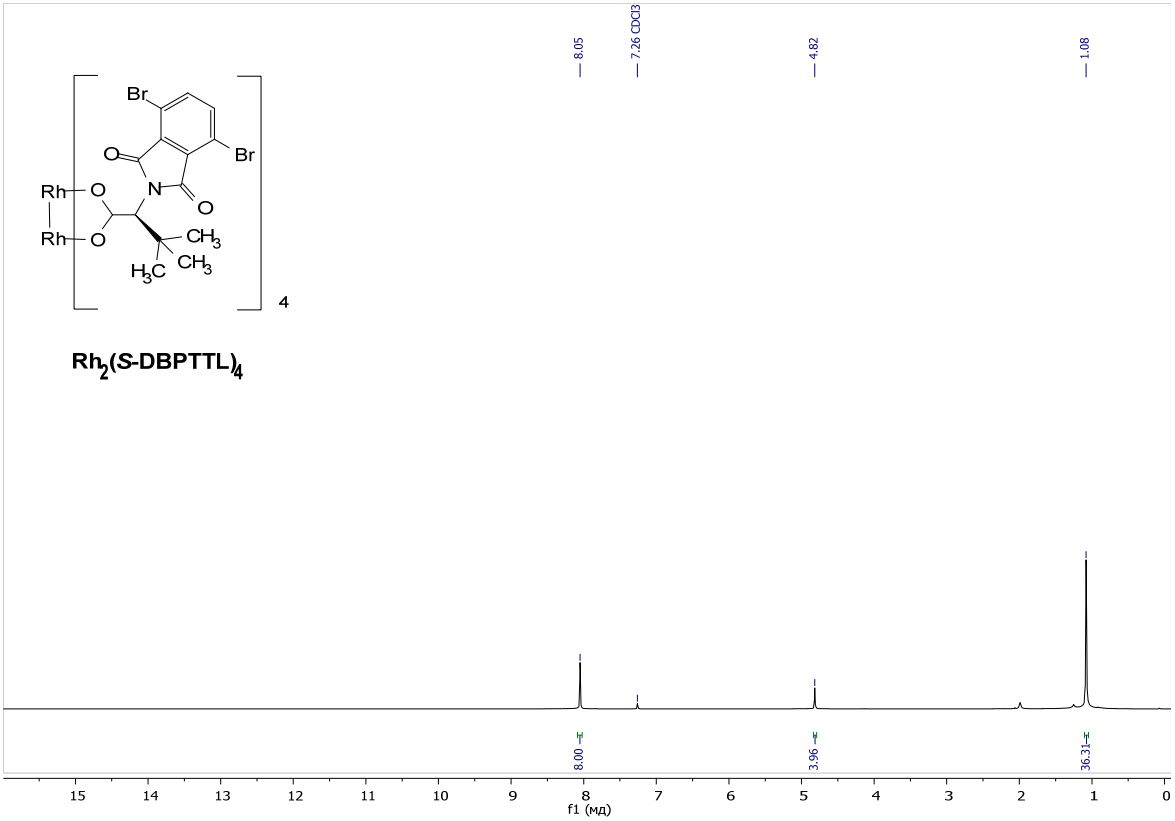
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **L2**



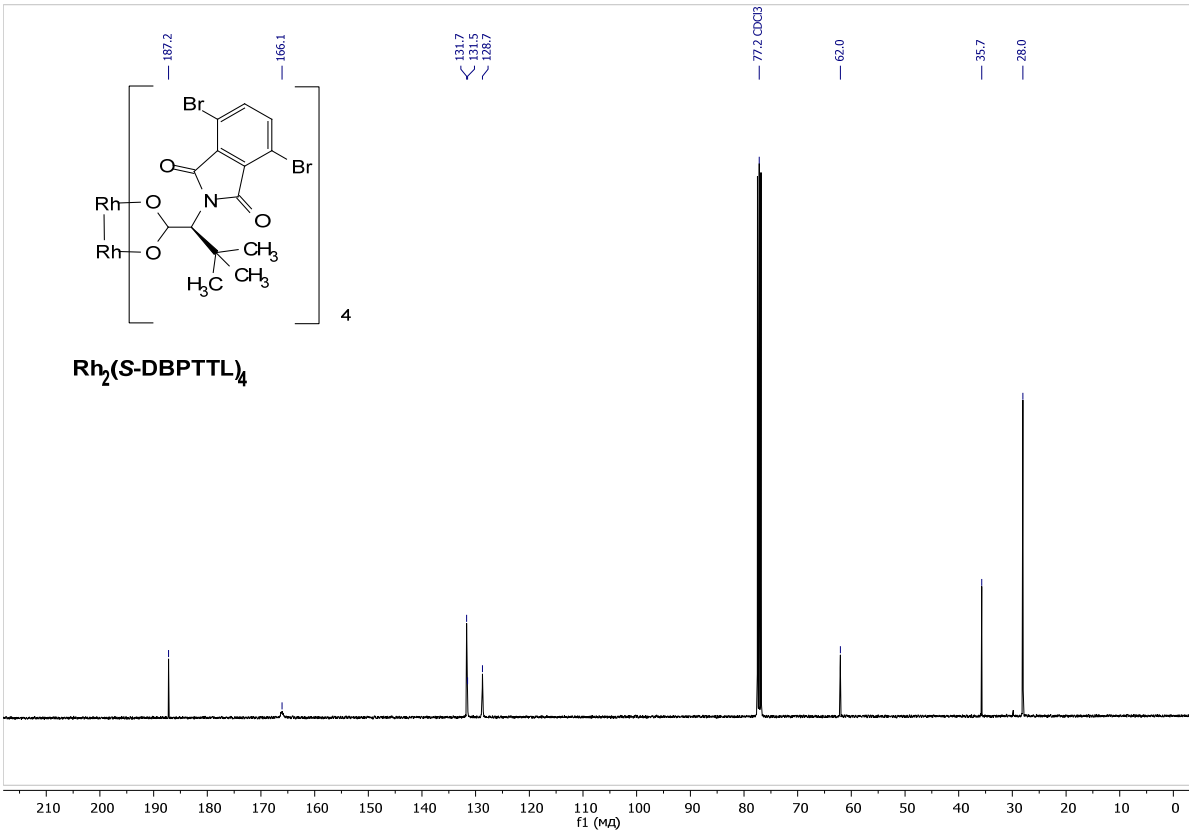
^{1}H NMR (400 MHz, DMSO–d_6) of **Rh$_2$(*S*-PTTR)$_4$**



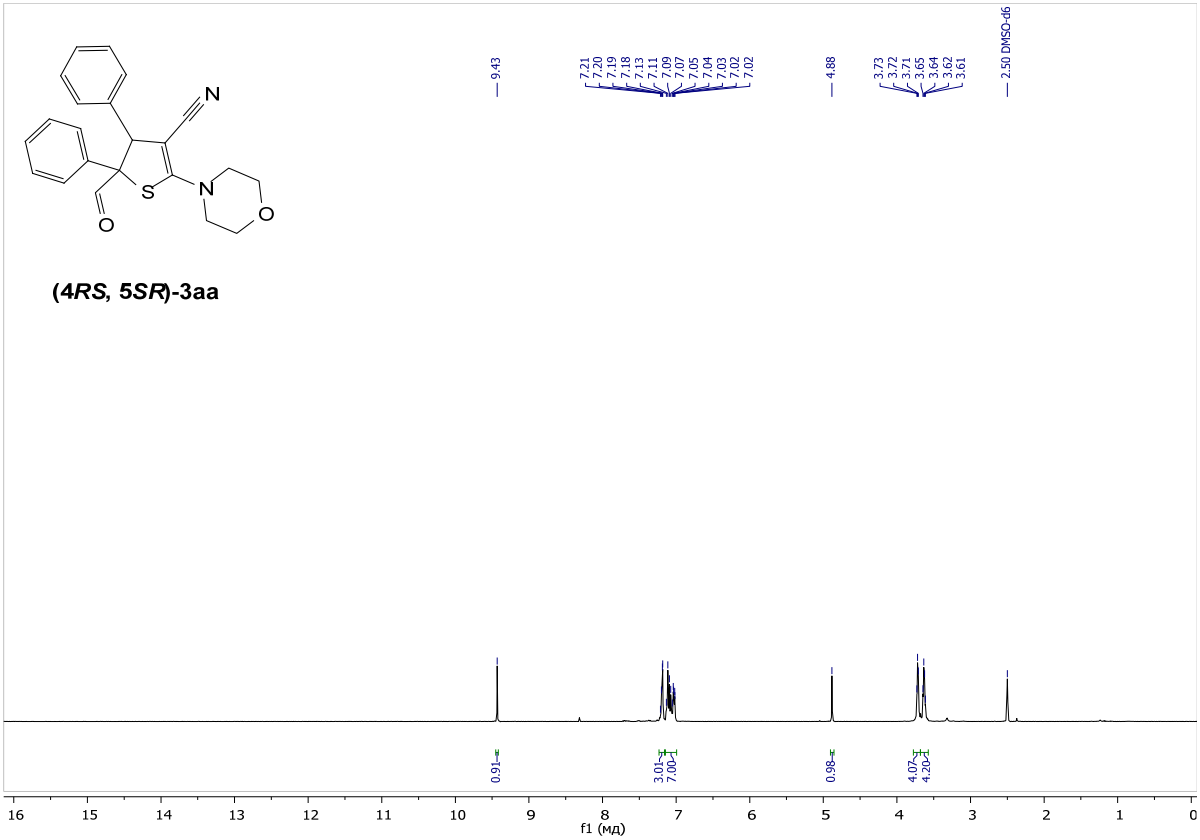
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **Rh$_2$(*S*-PTTR)$_4$**



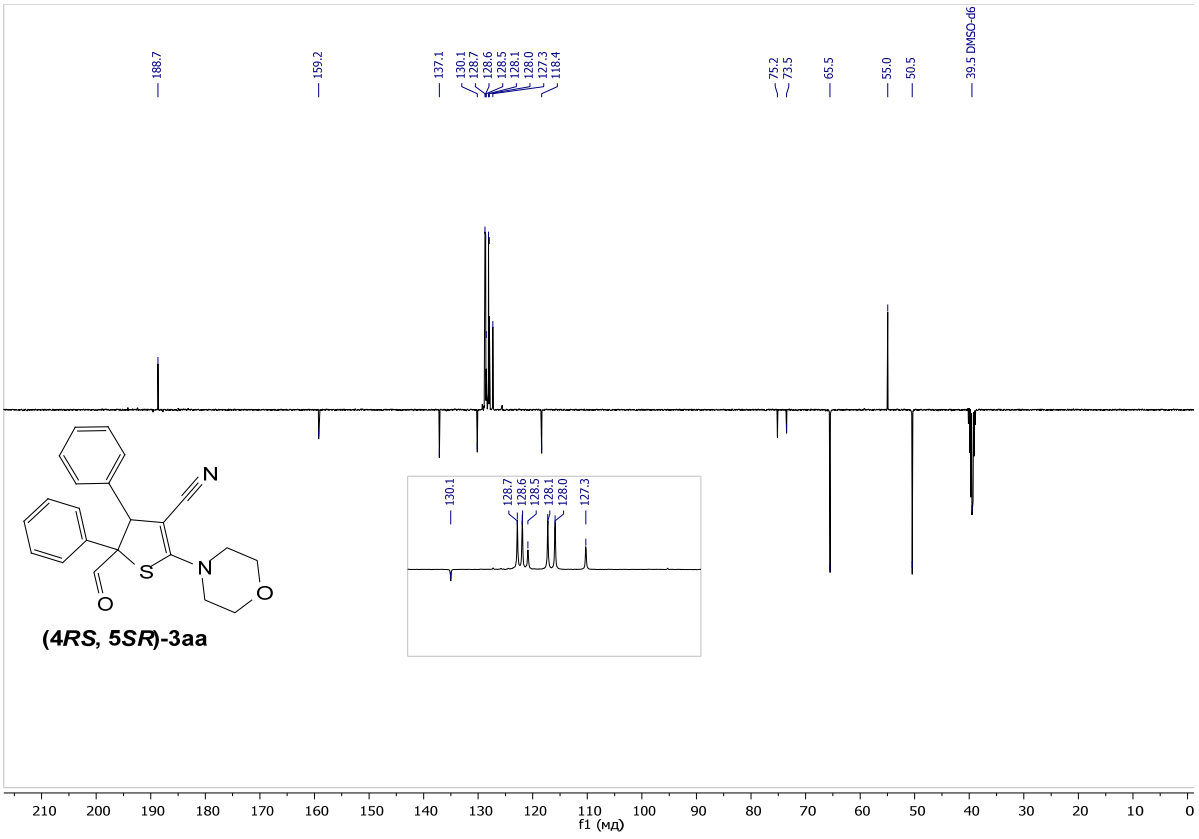
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **Rh_2(*S*-DBPTTL)$_4$**



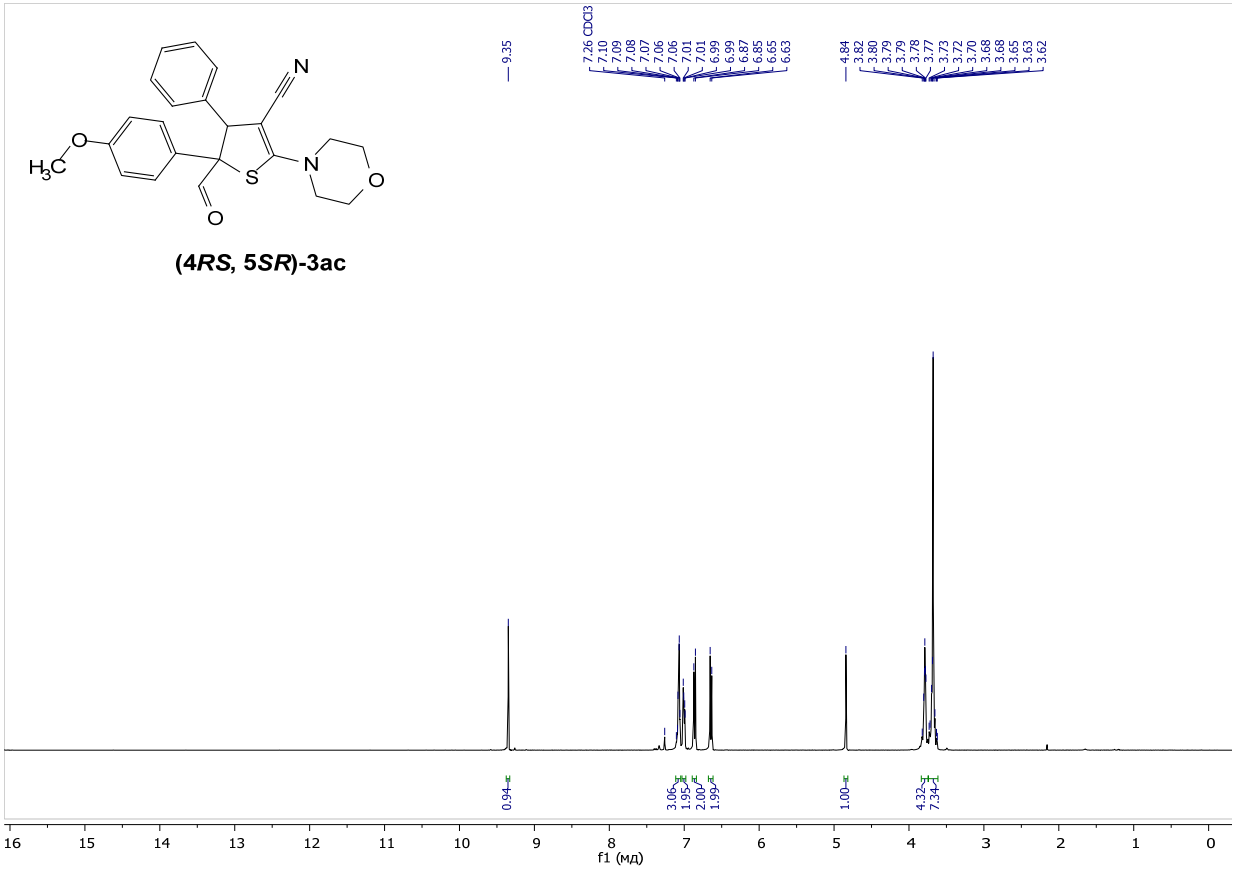
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **Rh_2(*S*-DBPTTL)$_4$**



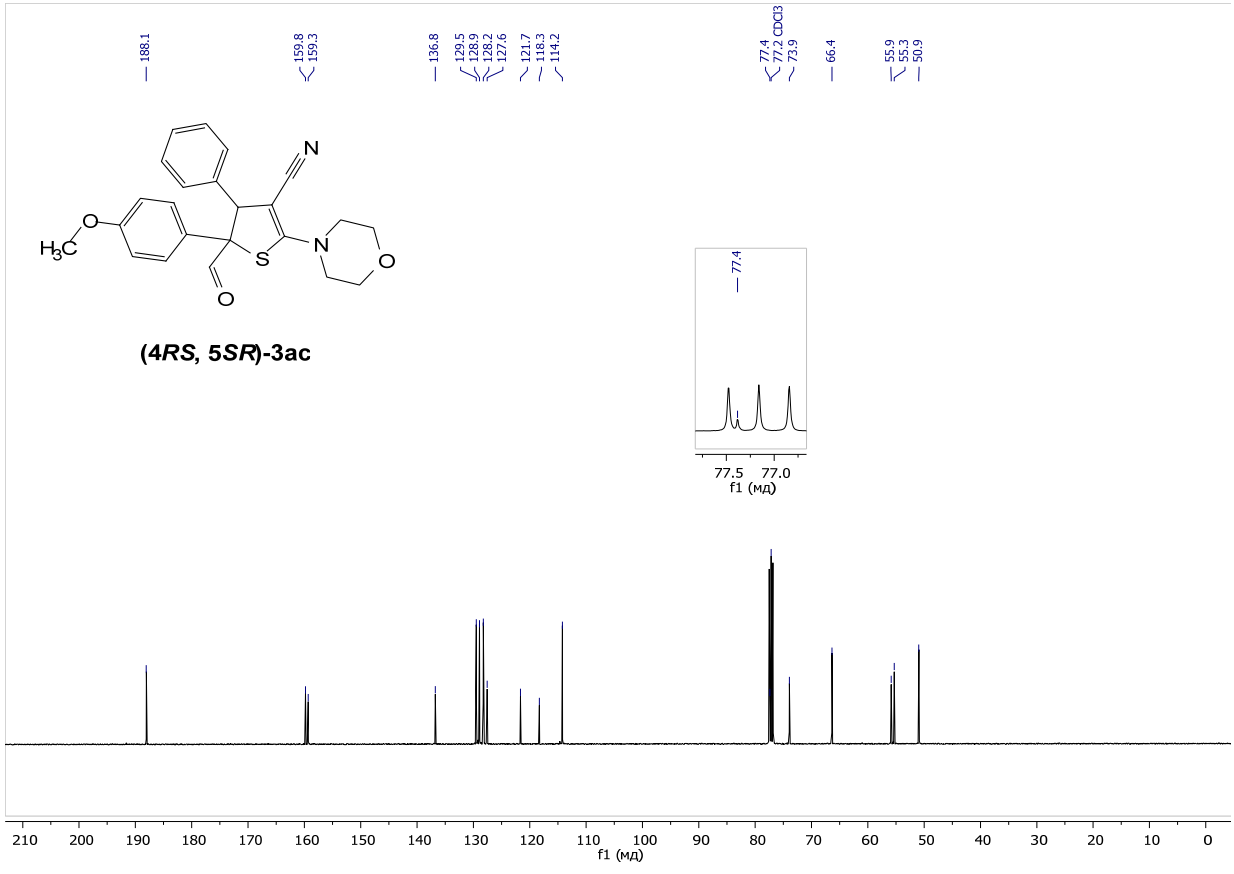
^{1}H NMR (400 MHz, DMSO–d_6) of **(4*RS*,5*SR*)-3aa**



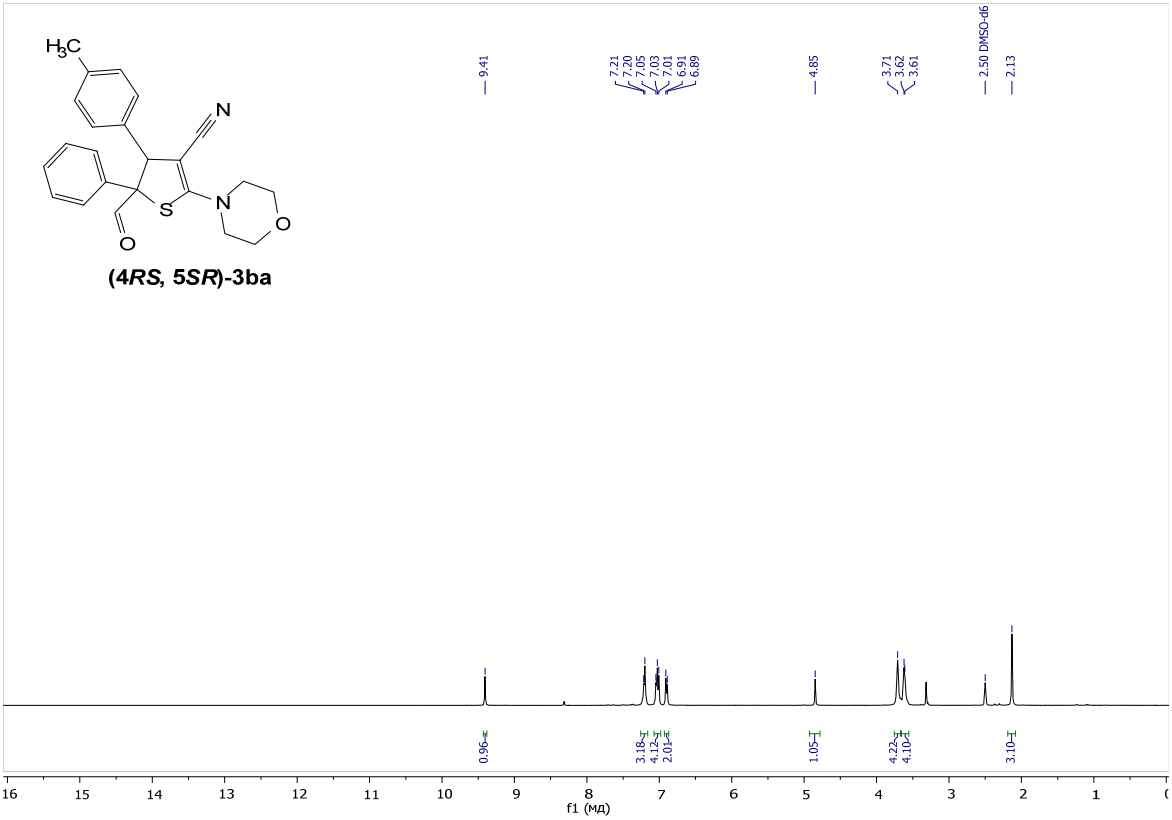
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(4*RS*,5*SR*)-3aa**



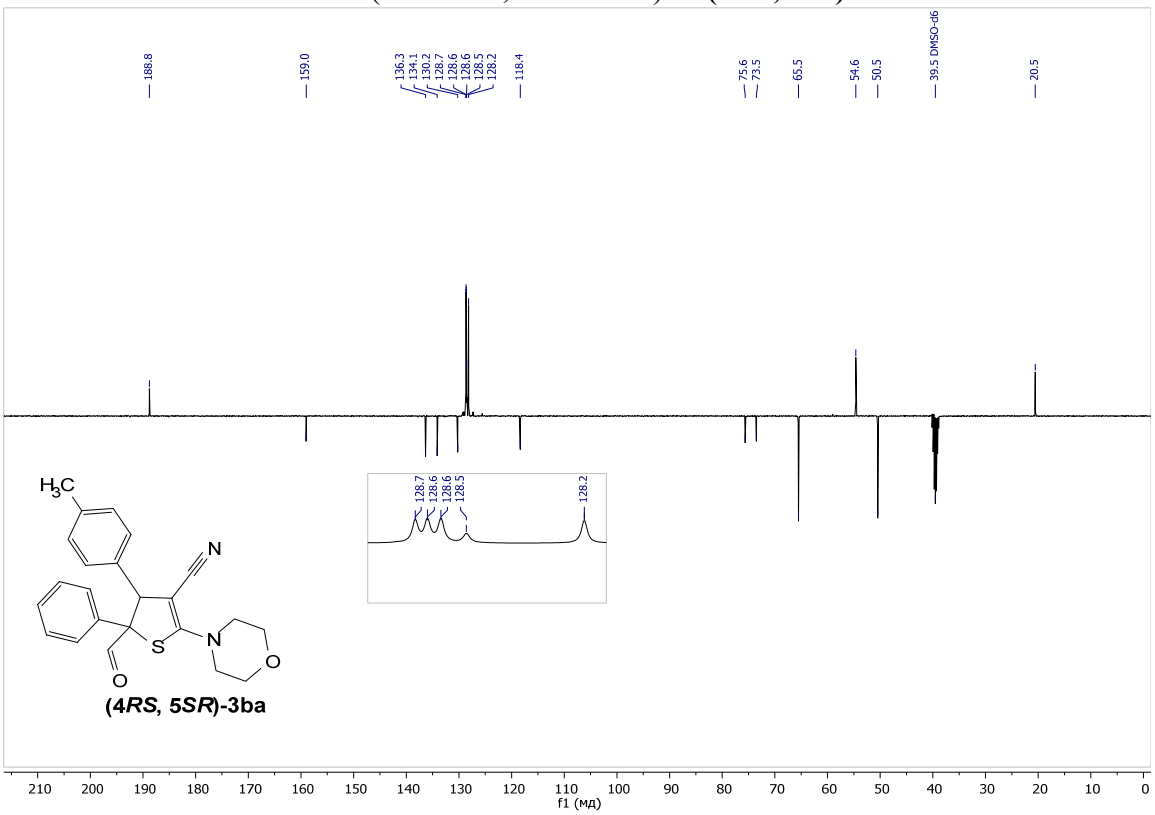
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **(4*RS*,5*SR*)-3ac**



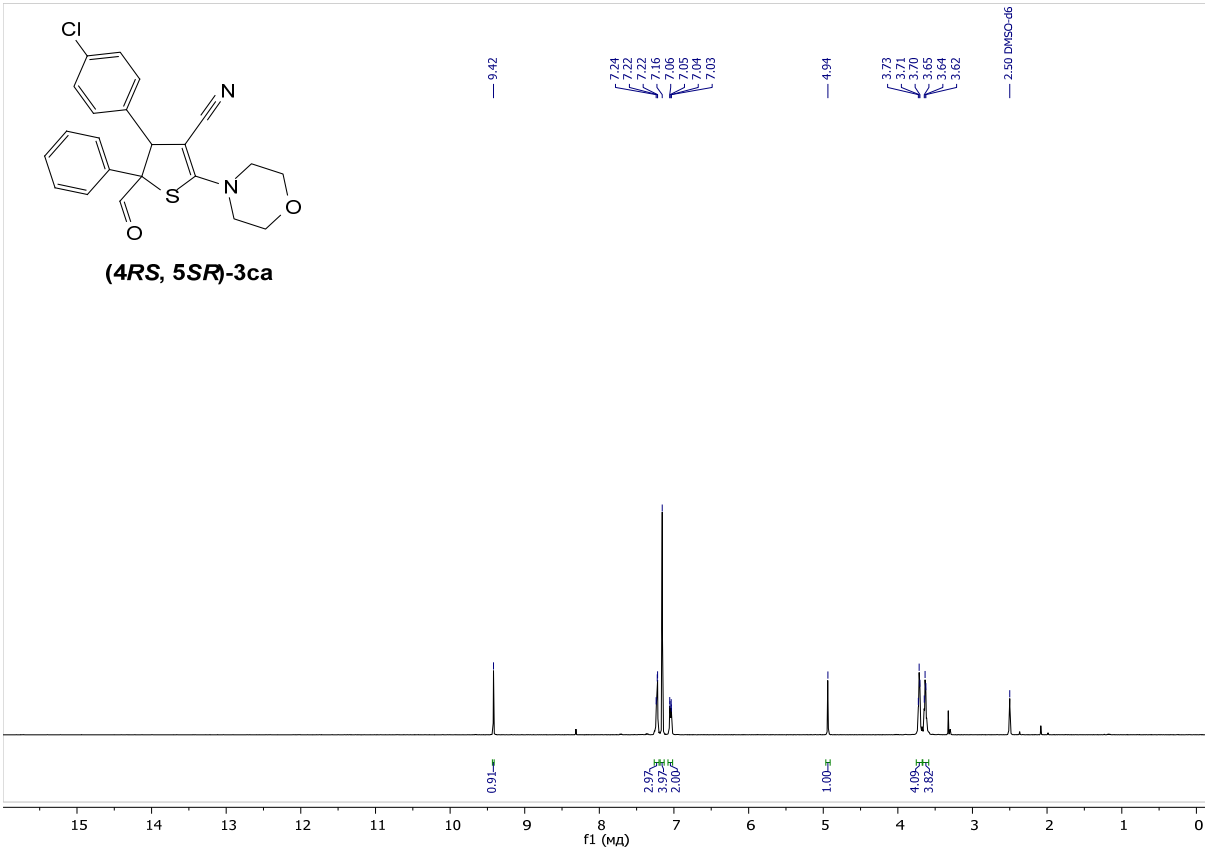
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **(4*RS*,5*SR*)-3ac**



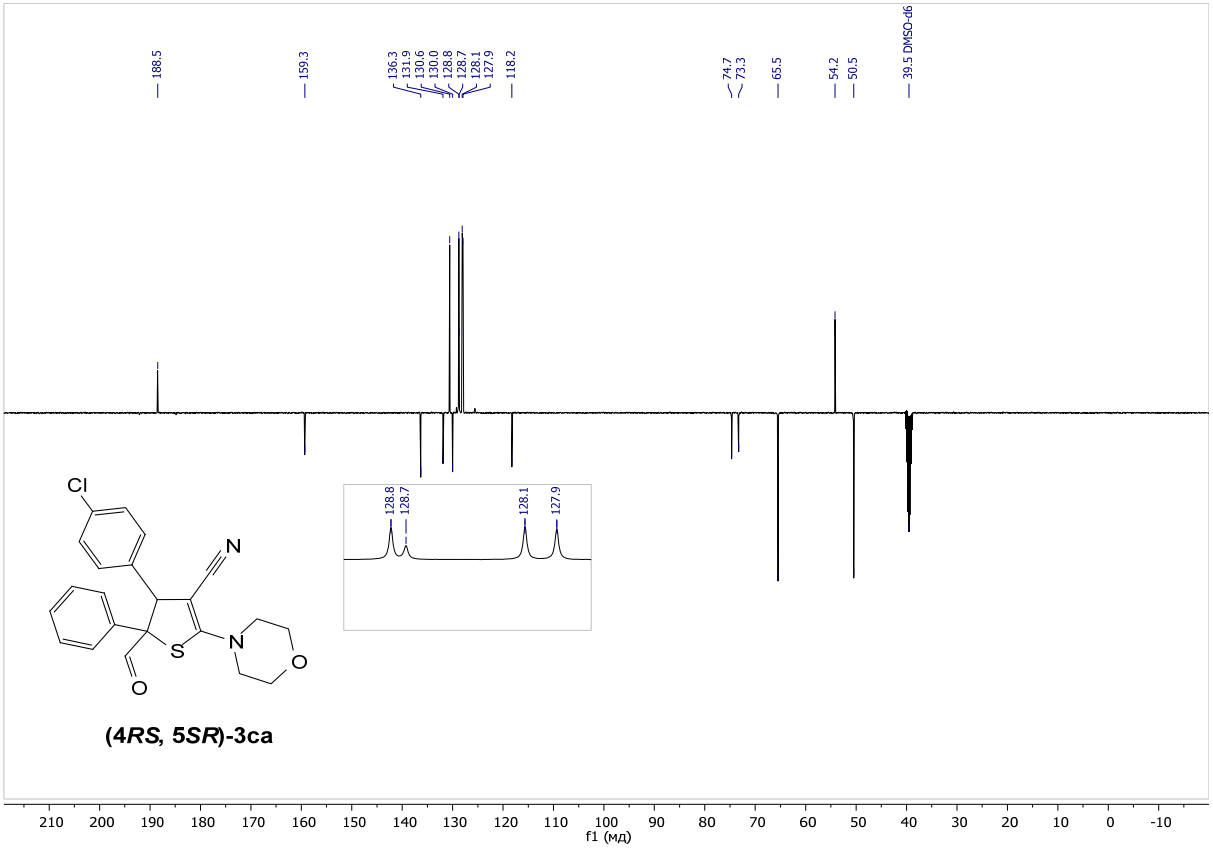
^{1}H NMR (400 MHz, DMSO–d_6) of **(4*RS*,5*SR*)-3ba**



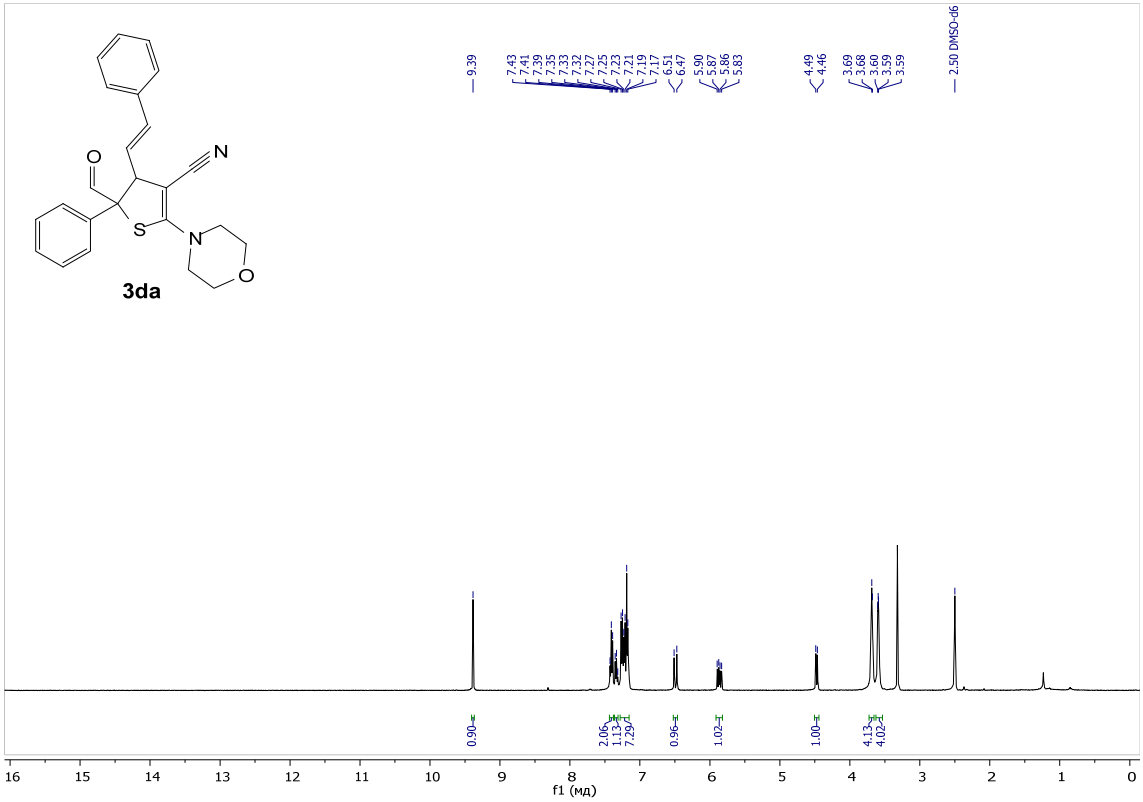
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(4*RS*,5*SR*)-3ba**



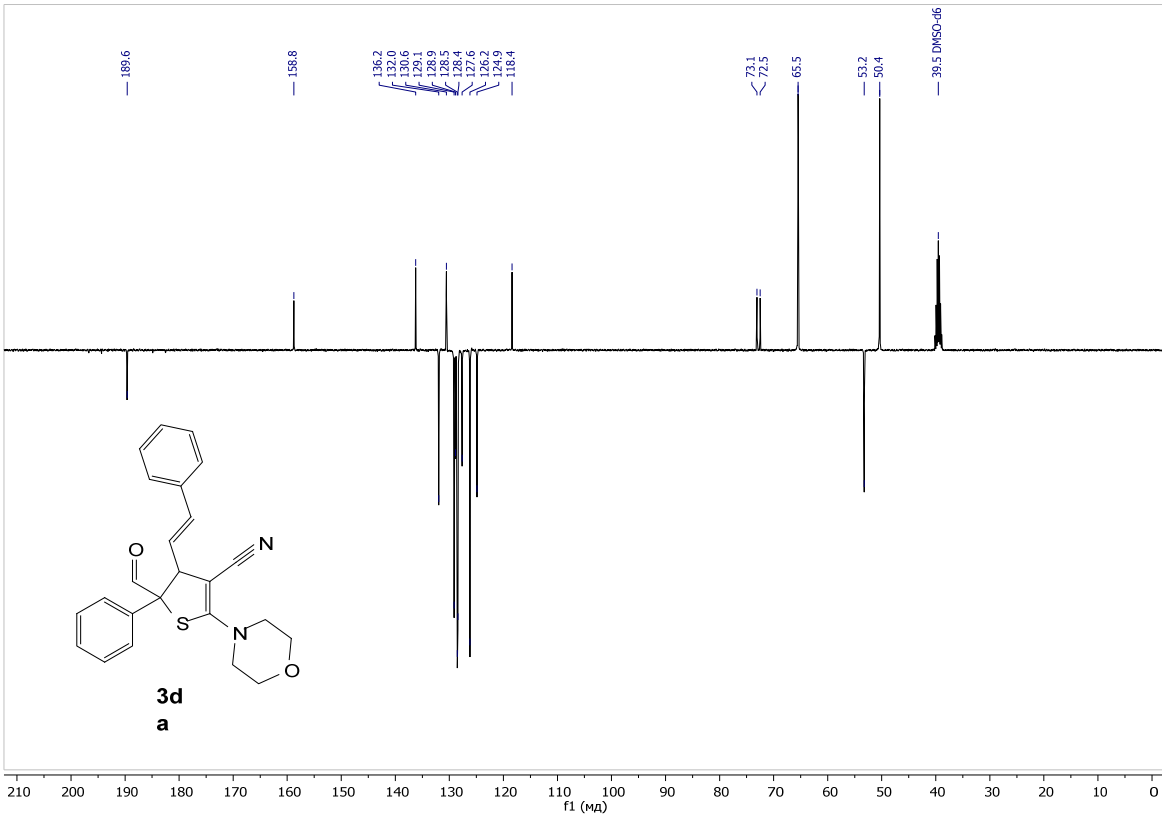
^{1}H NMR (400 MHz, DMSO–d_6) of **(4*RS*,5*SR*)-3ca**



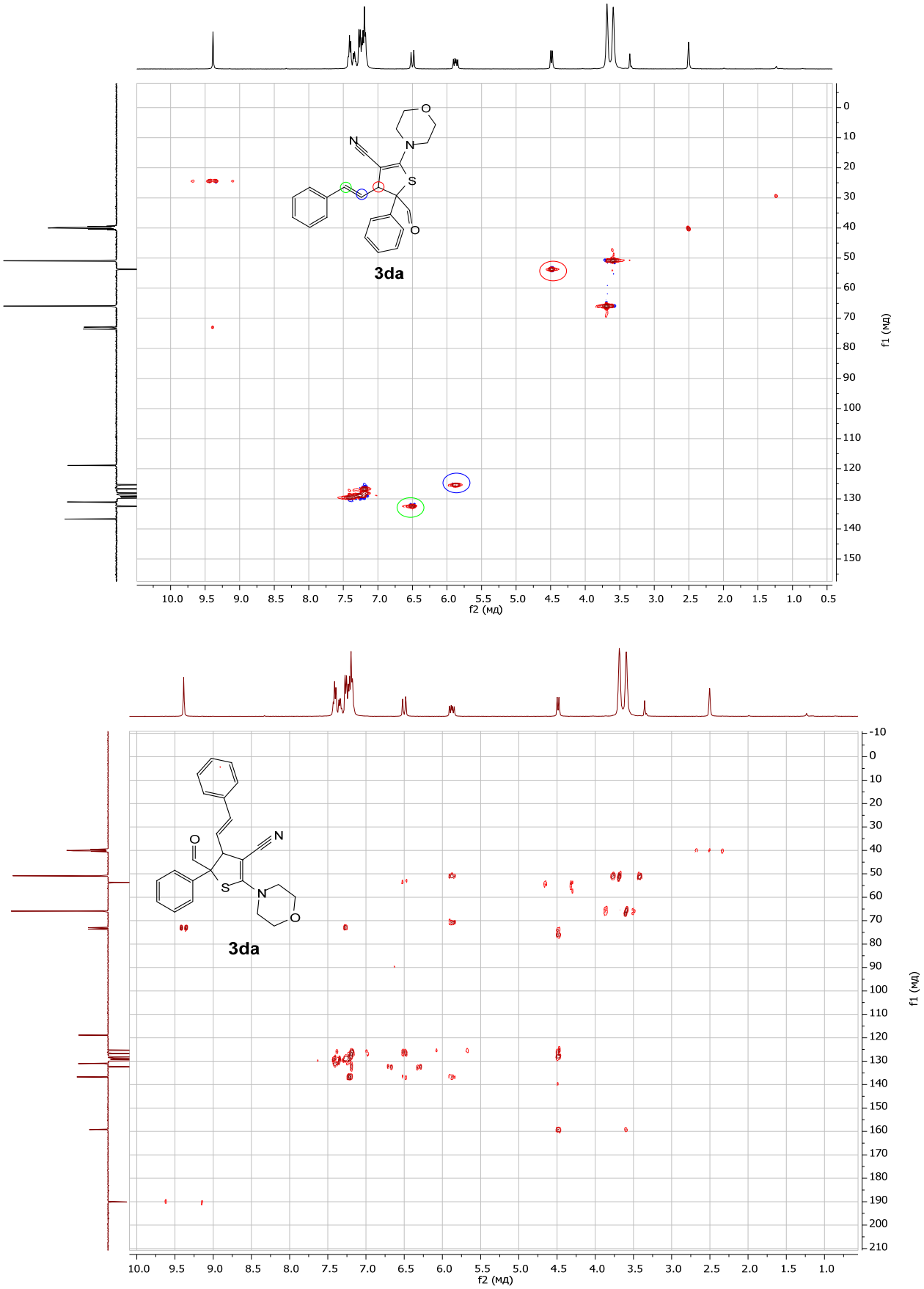
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(4*RS*,5*SR*)-3ca**



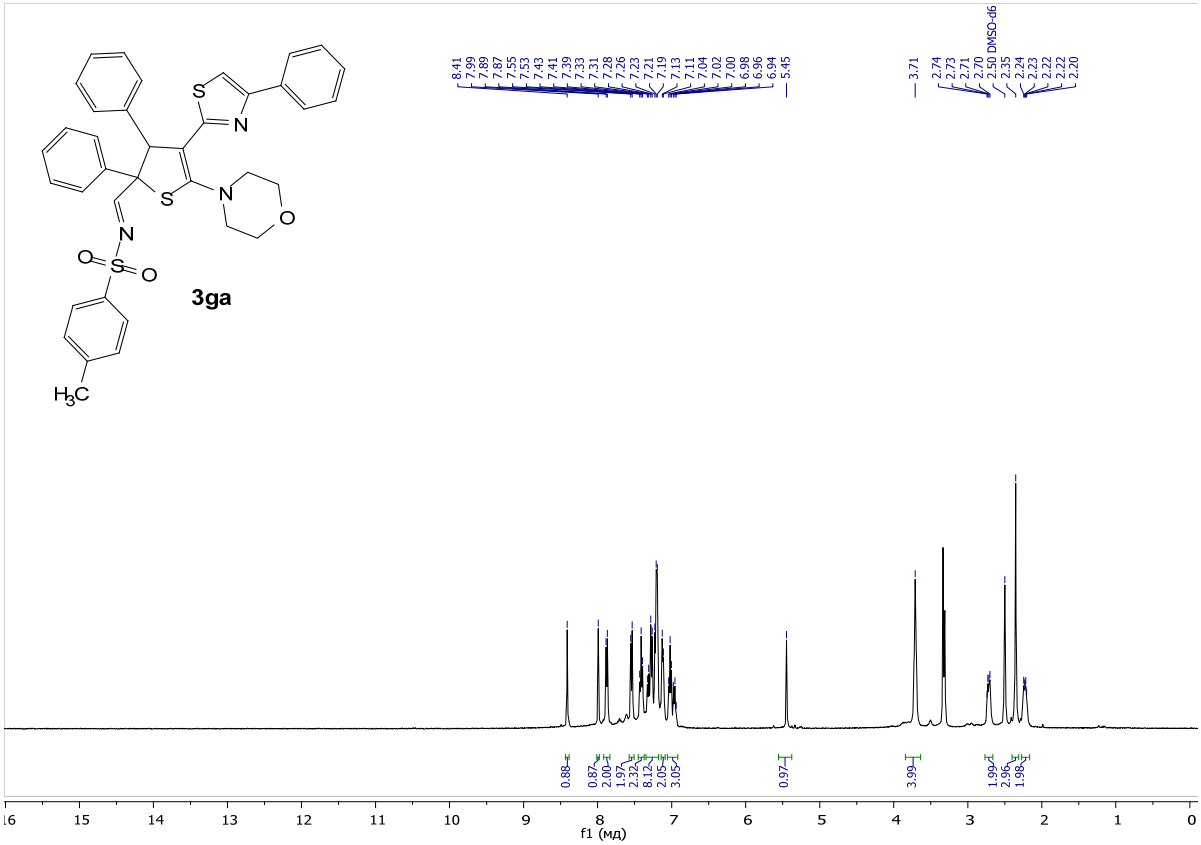
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **3da**



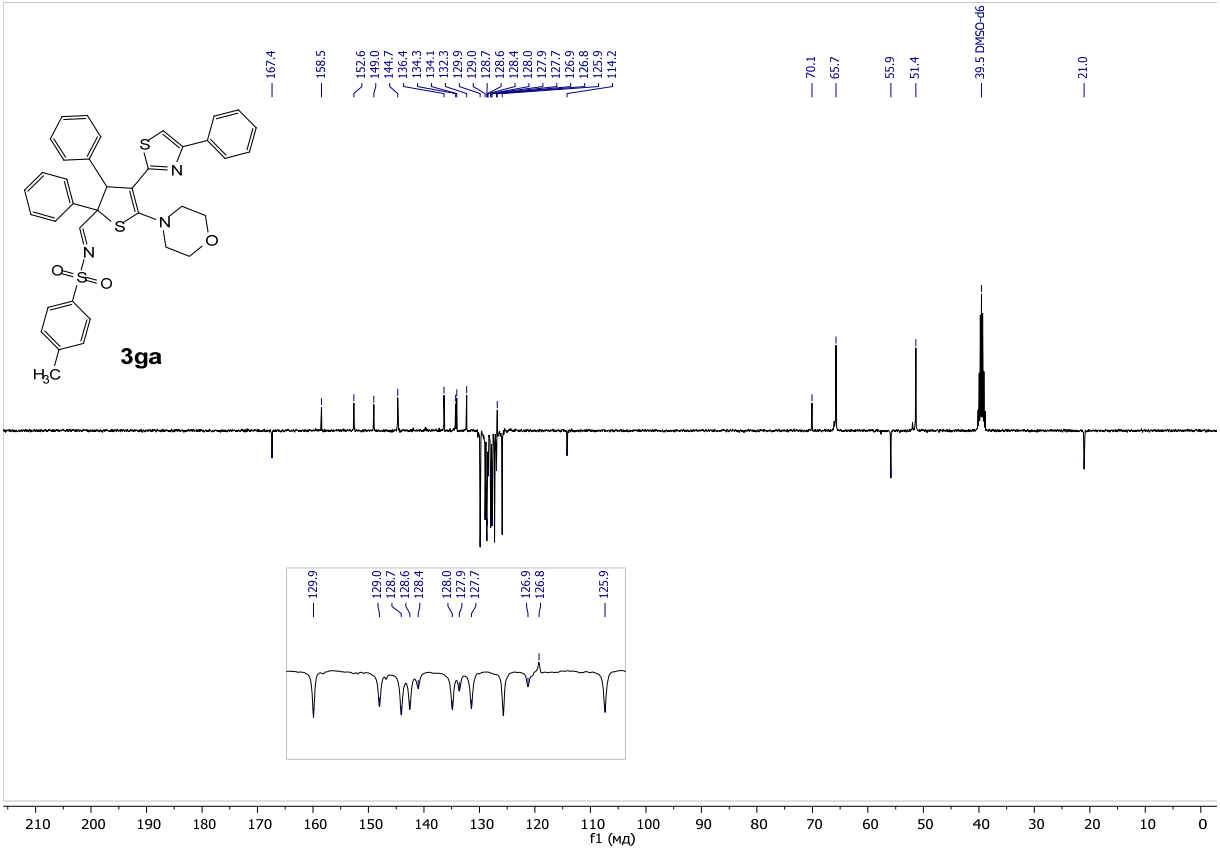
^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **3da**



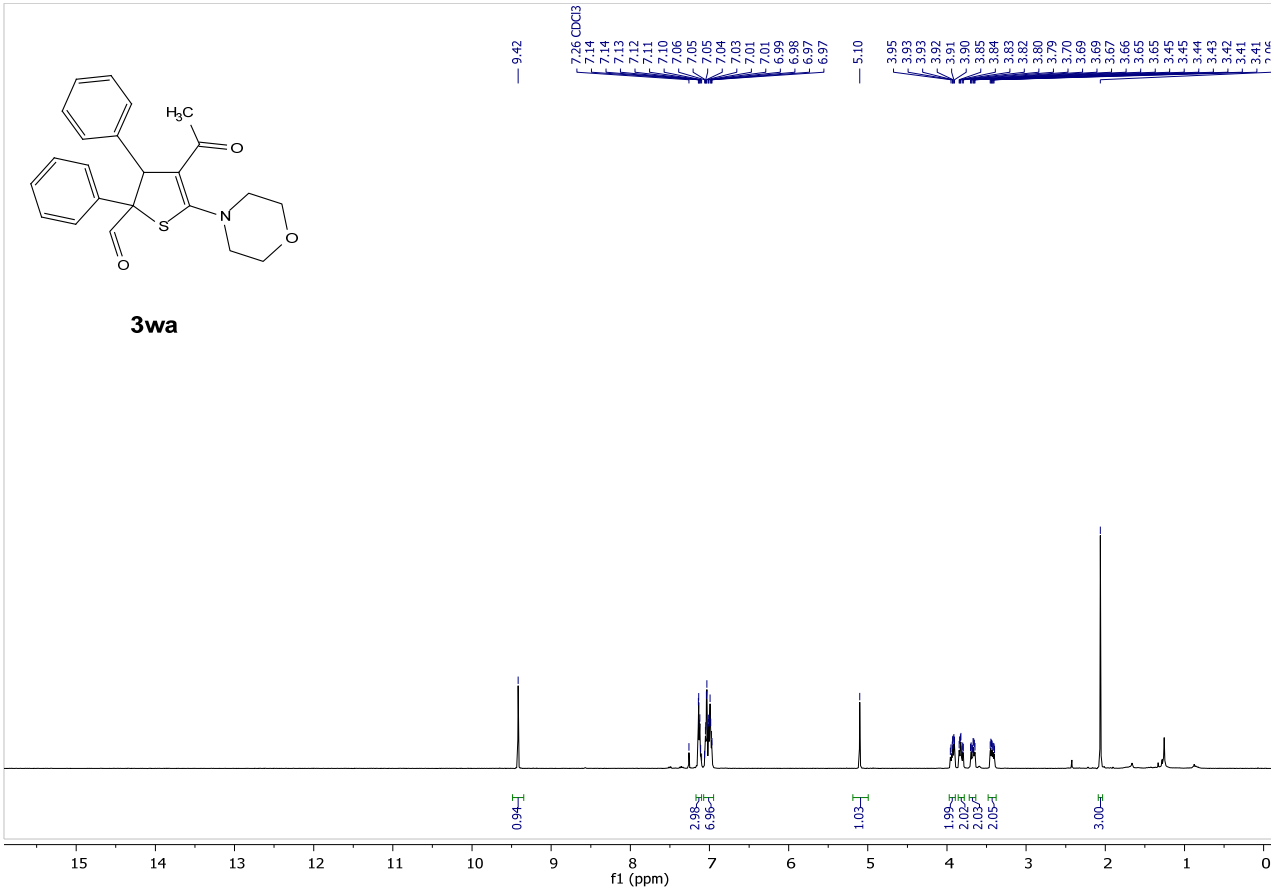
HSQC and HMBC spectra of **3da**



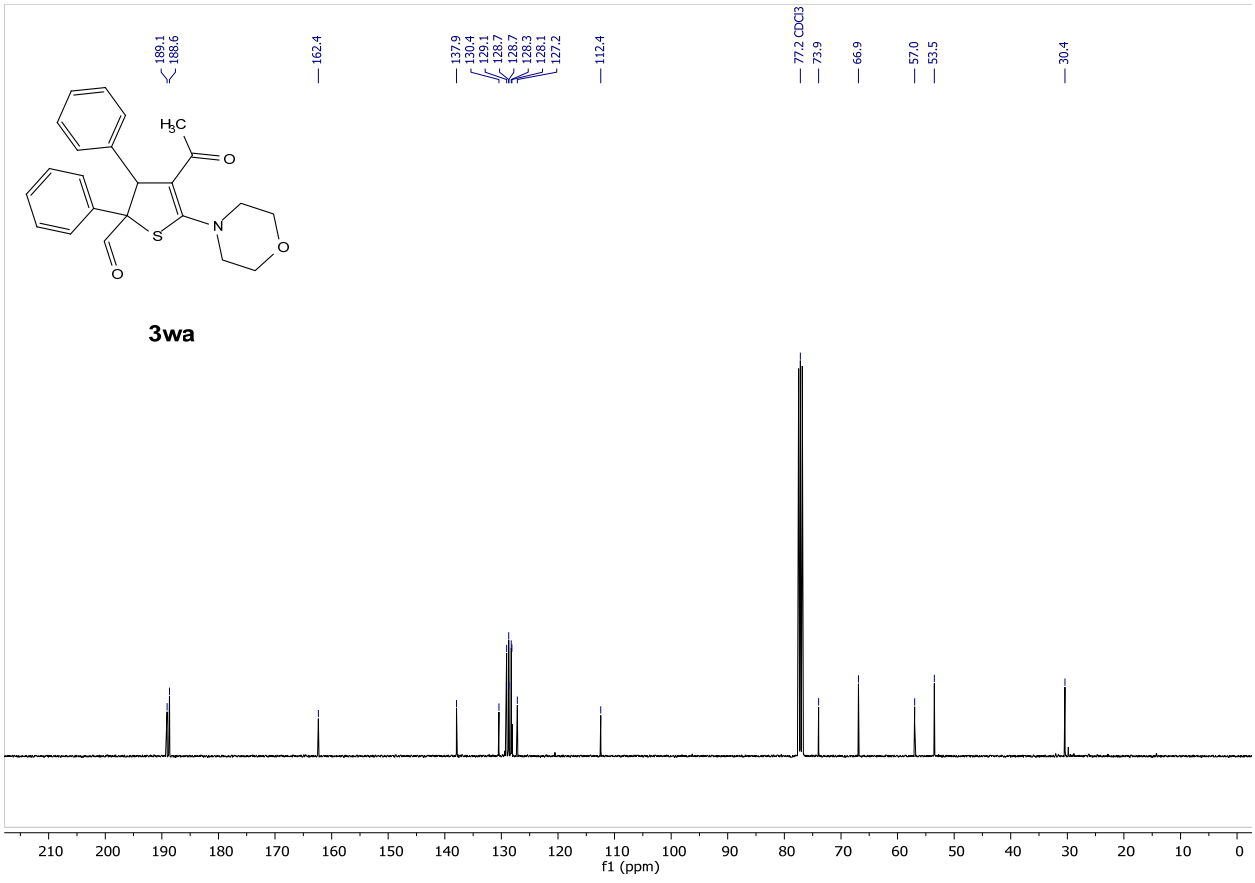
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **3ga**



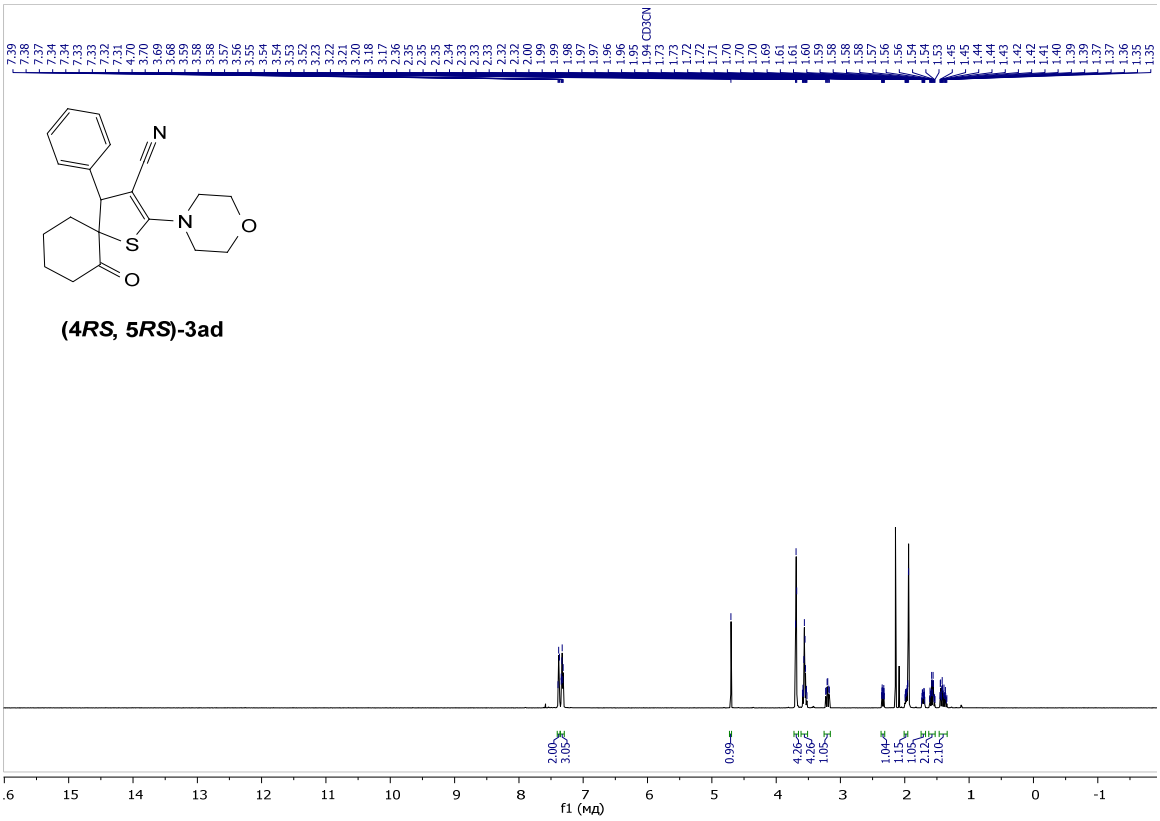
^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **3ga**



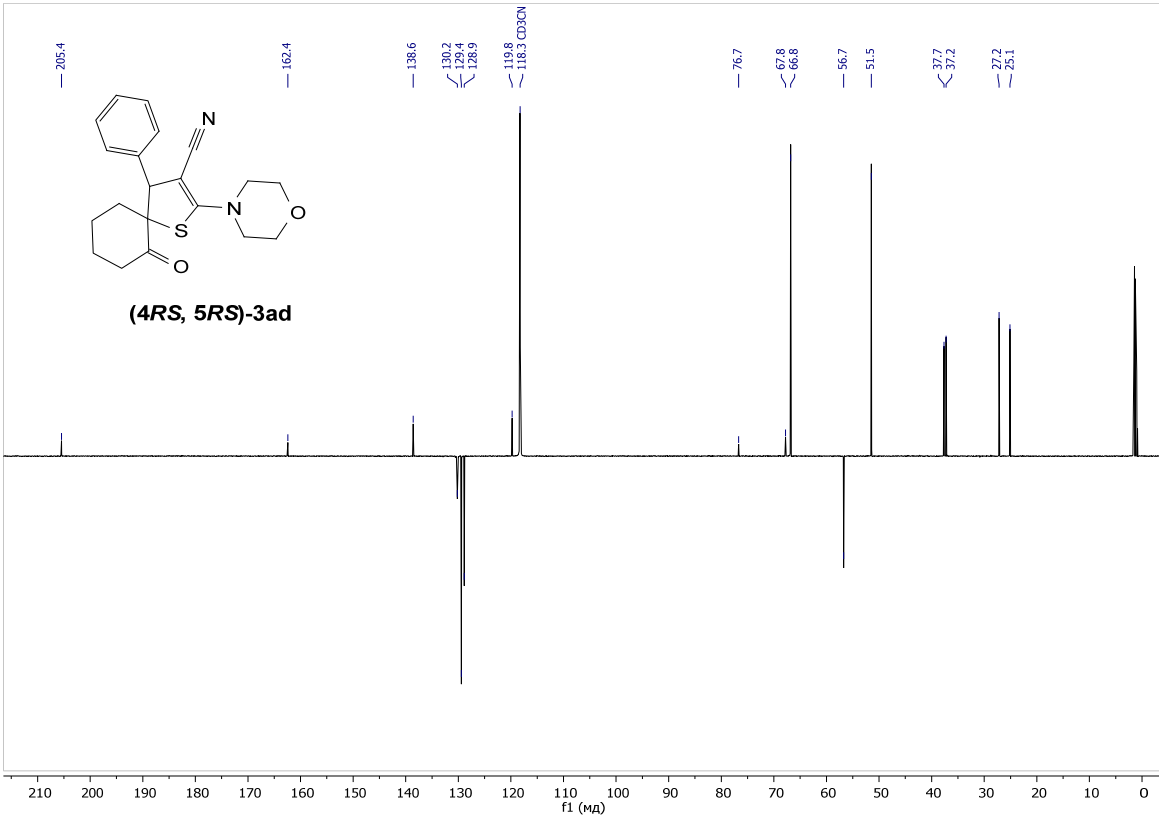
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3wa**



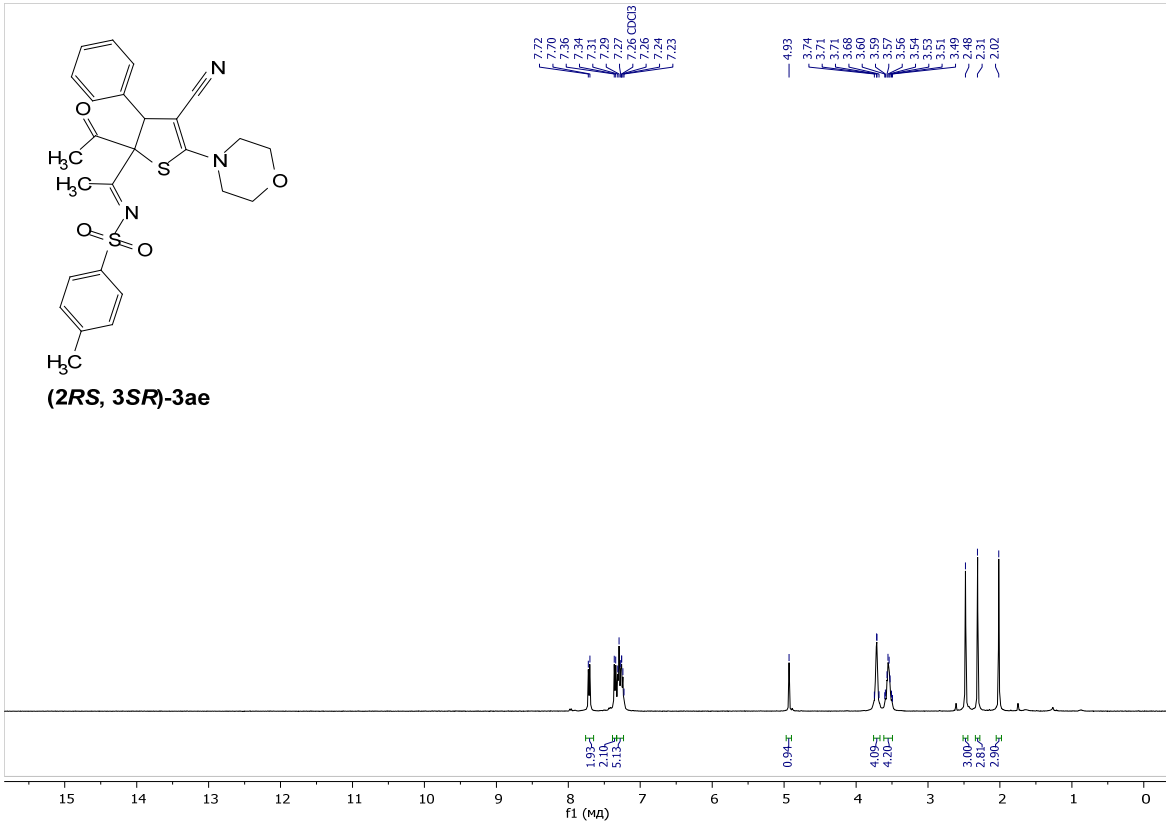
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3wa**



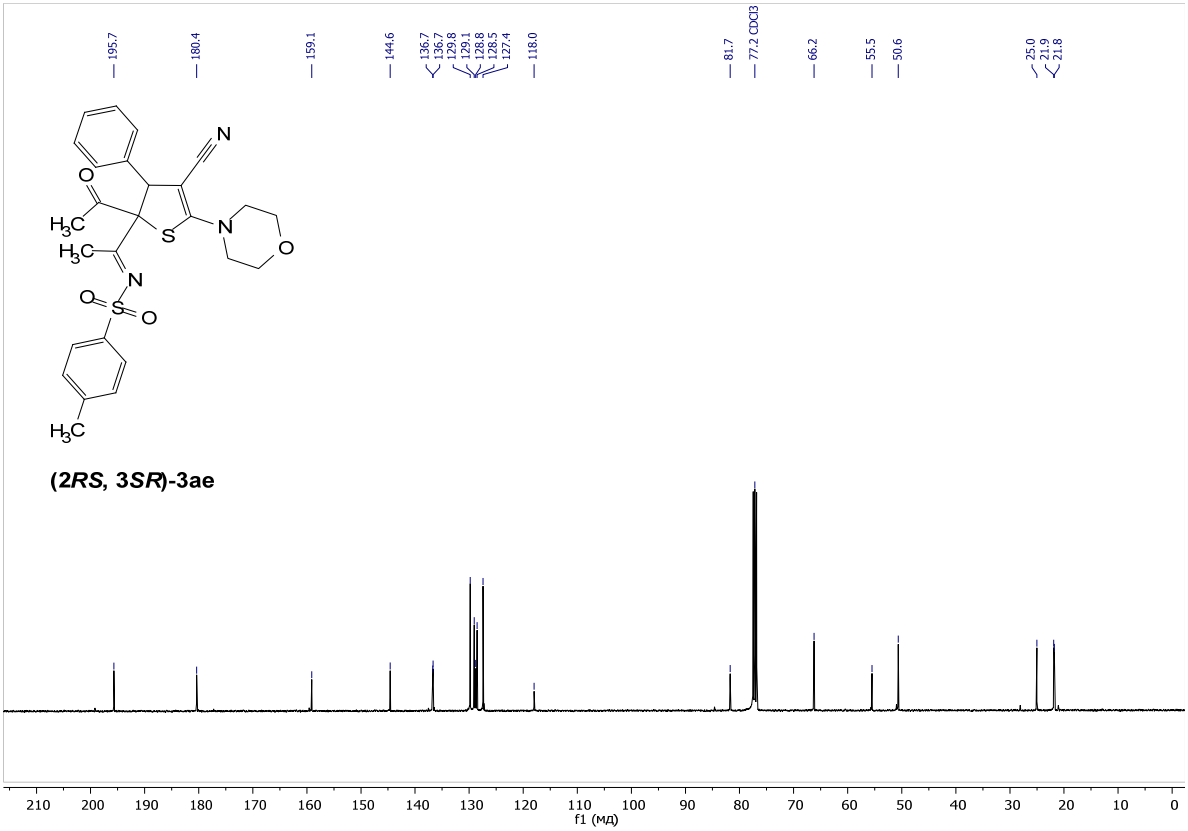
^{1}H NMR (600 MHz, CD_3CN–d_3) of **(4*RS*,5*RS*)-3ad**



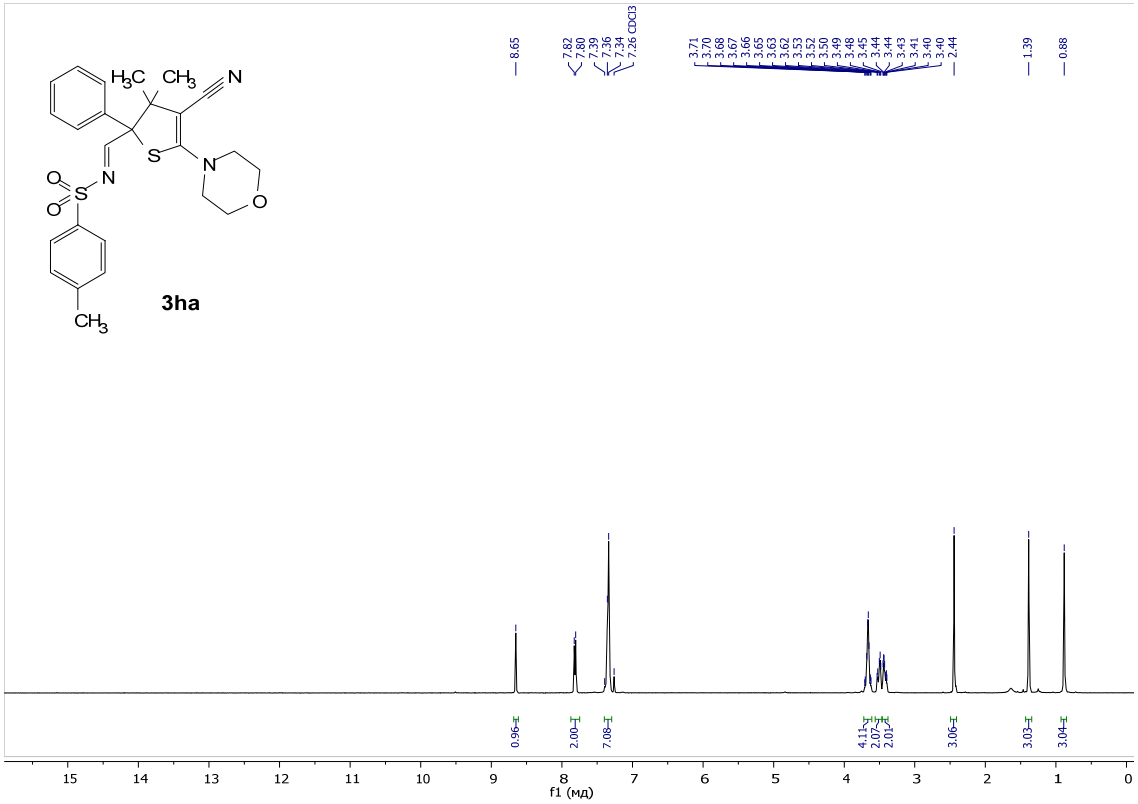
^{13}C{1H} NMR (150 MHz, CD_3CN–d_3) of **(4*RS*,5*RS*)-3ad**



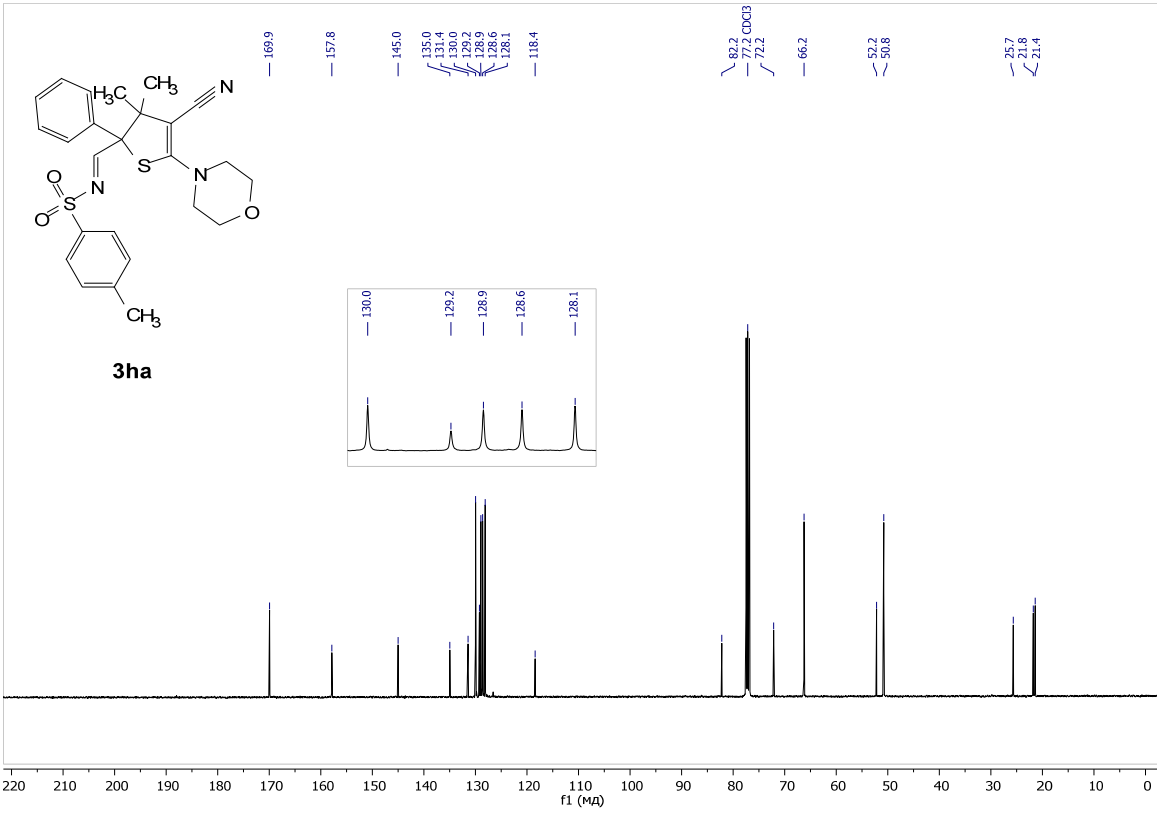
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **(2*RS*,3*SR*)-3ae**



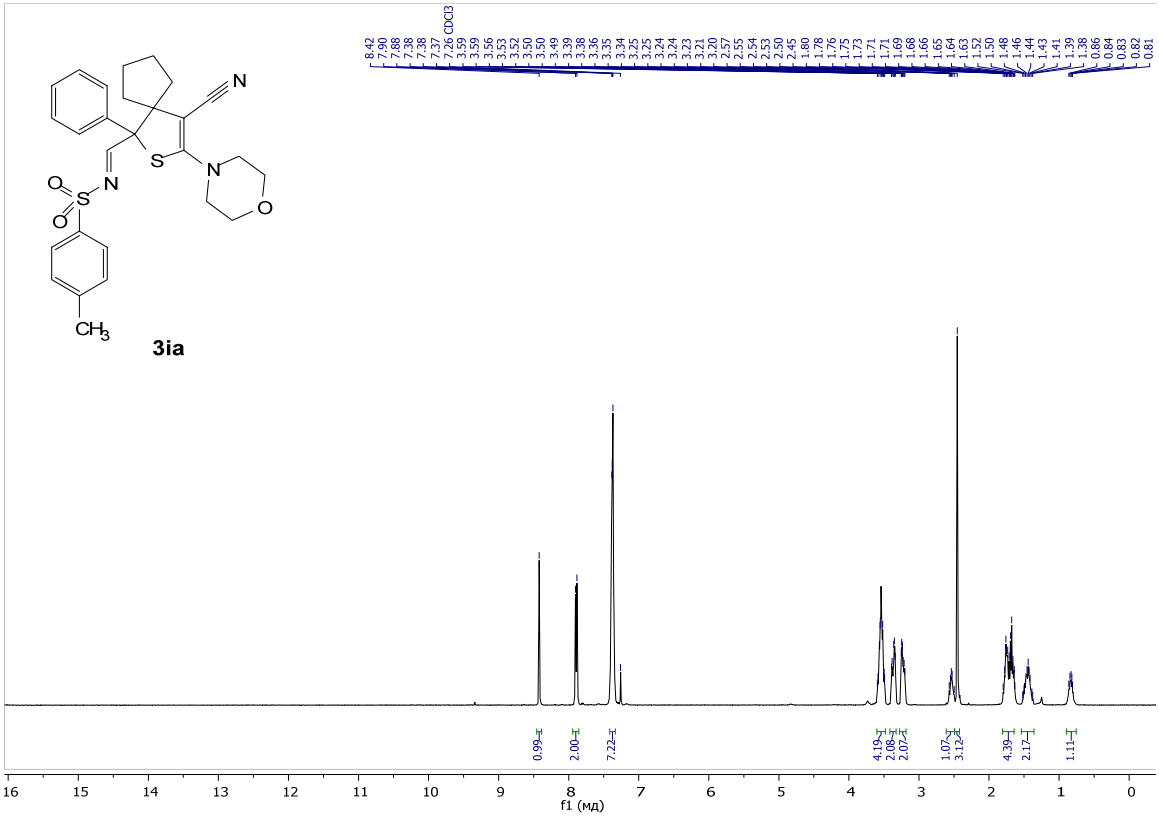
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **(2*RS*,3*SR*)-3ae**



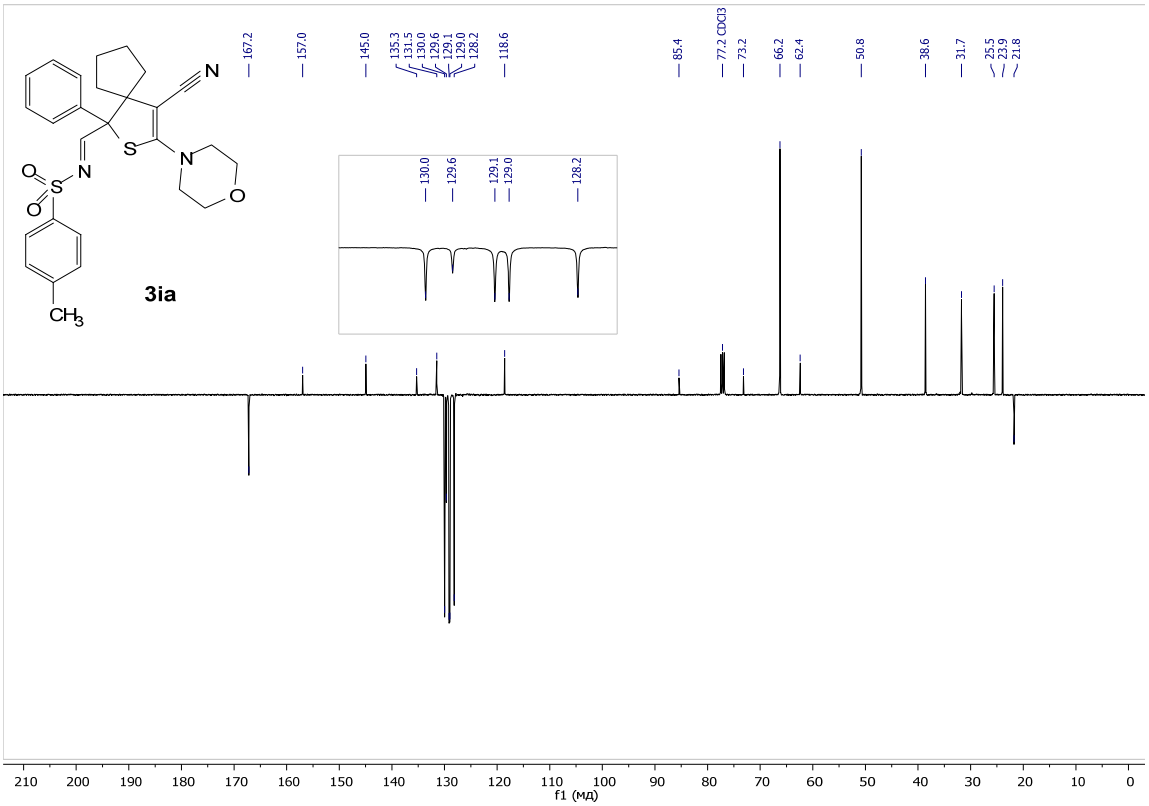
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ha**



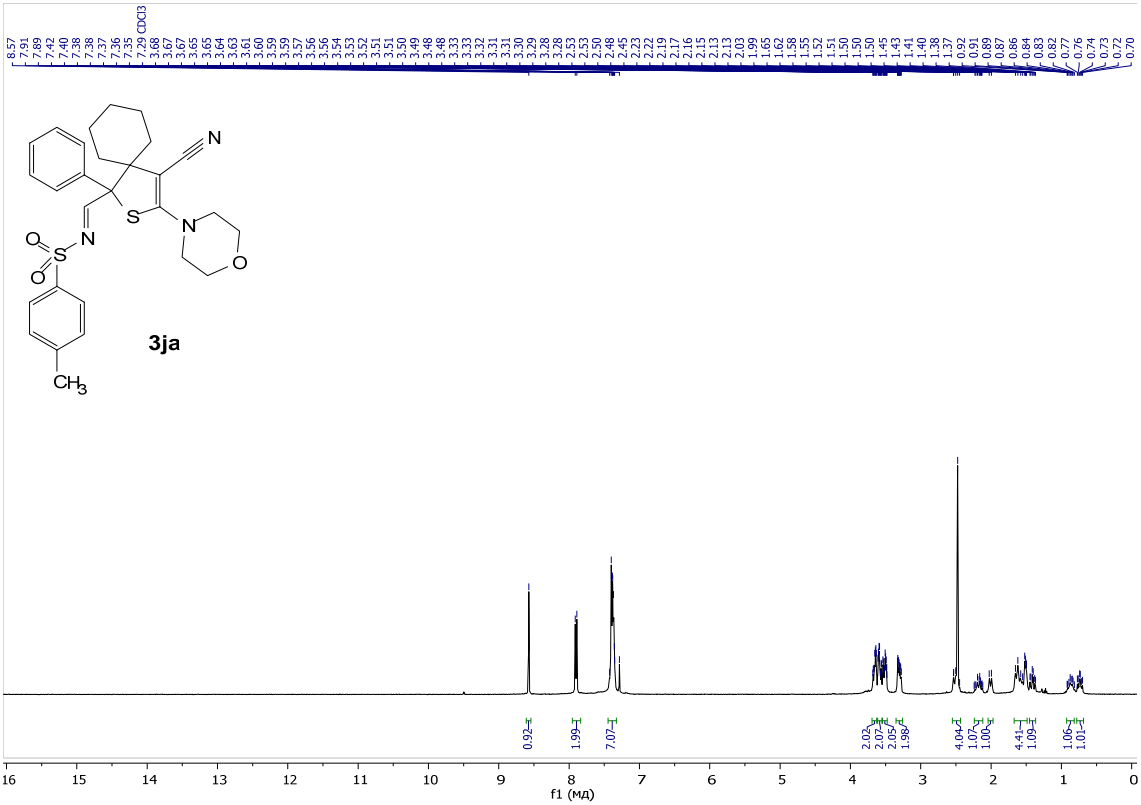
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3ha**



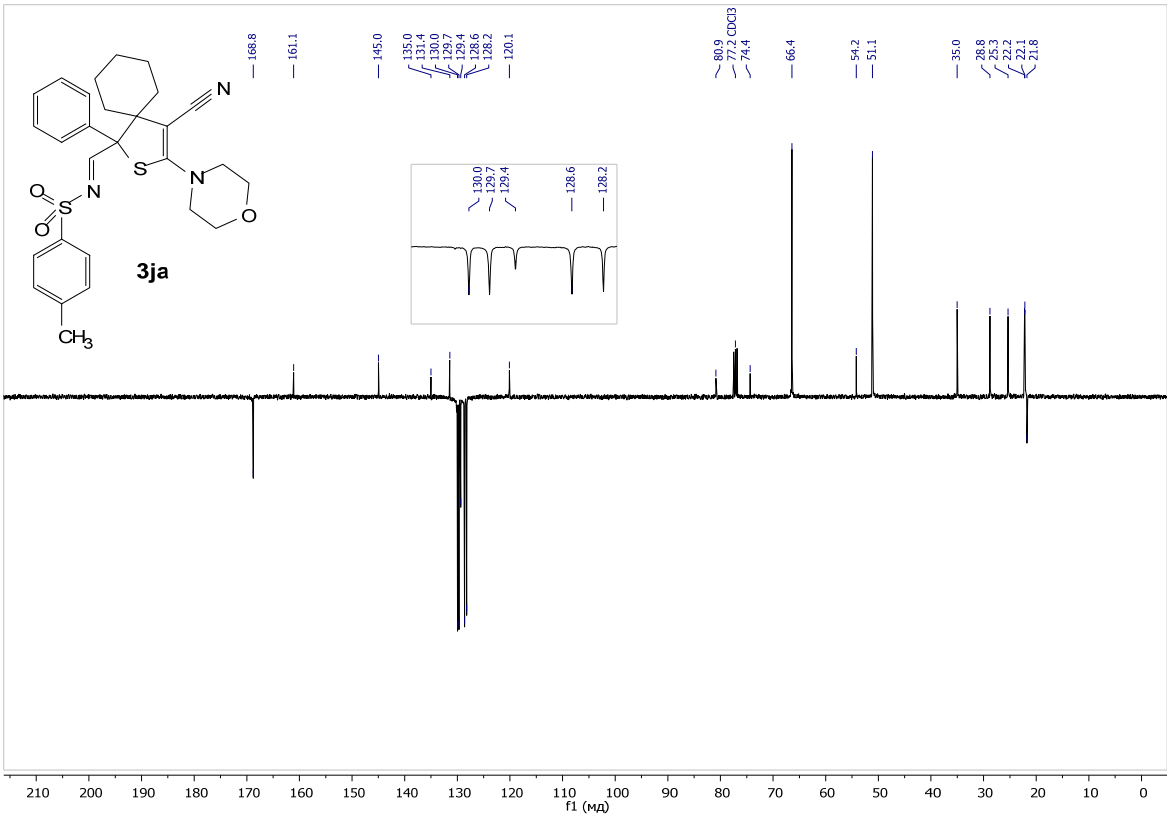
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ia**



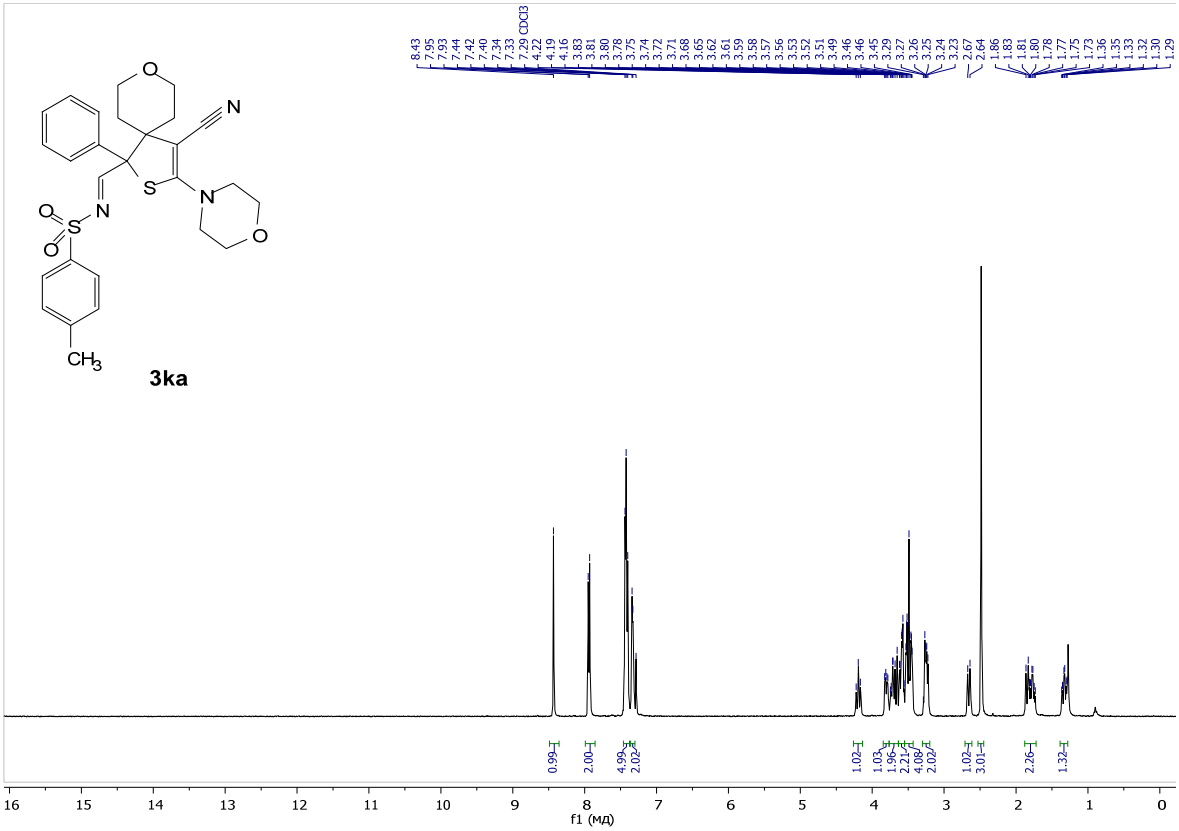
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3ia**



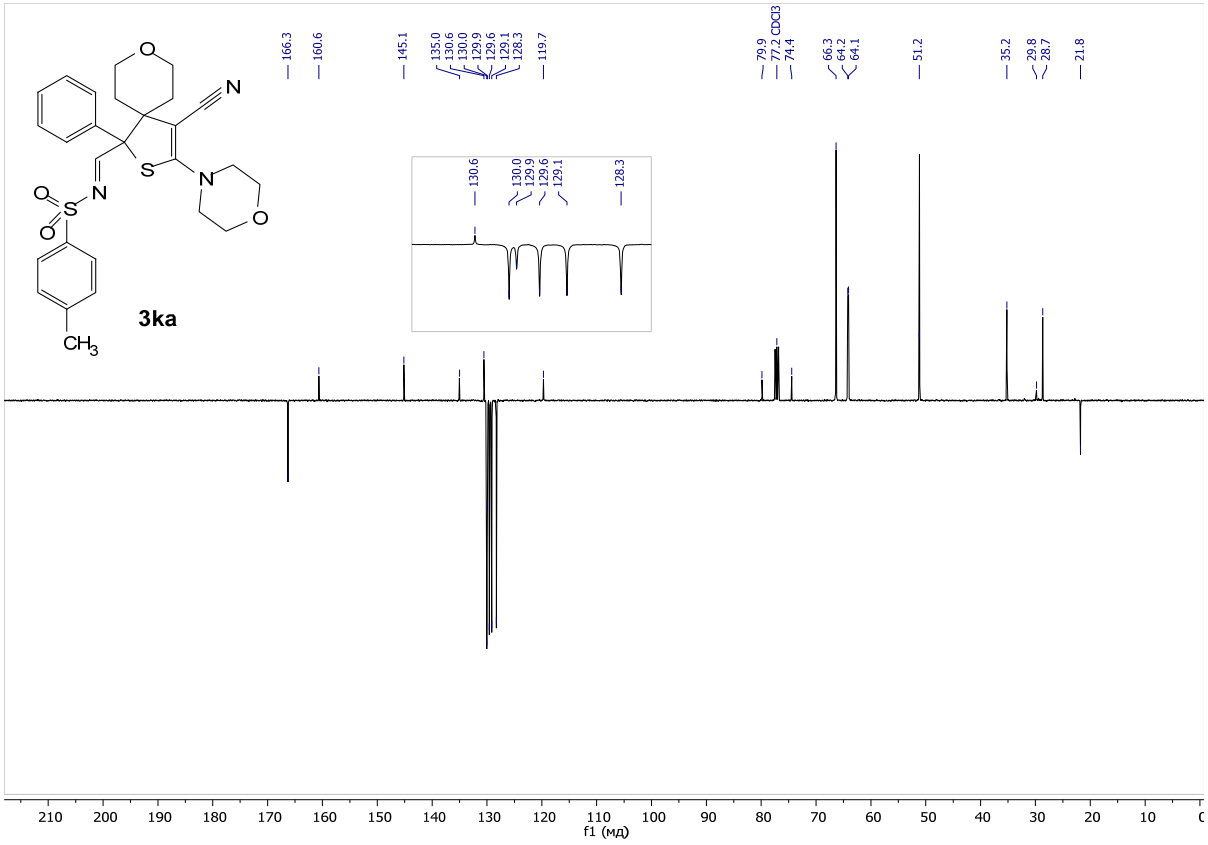
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ja**



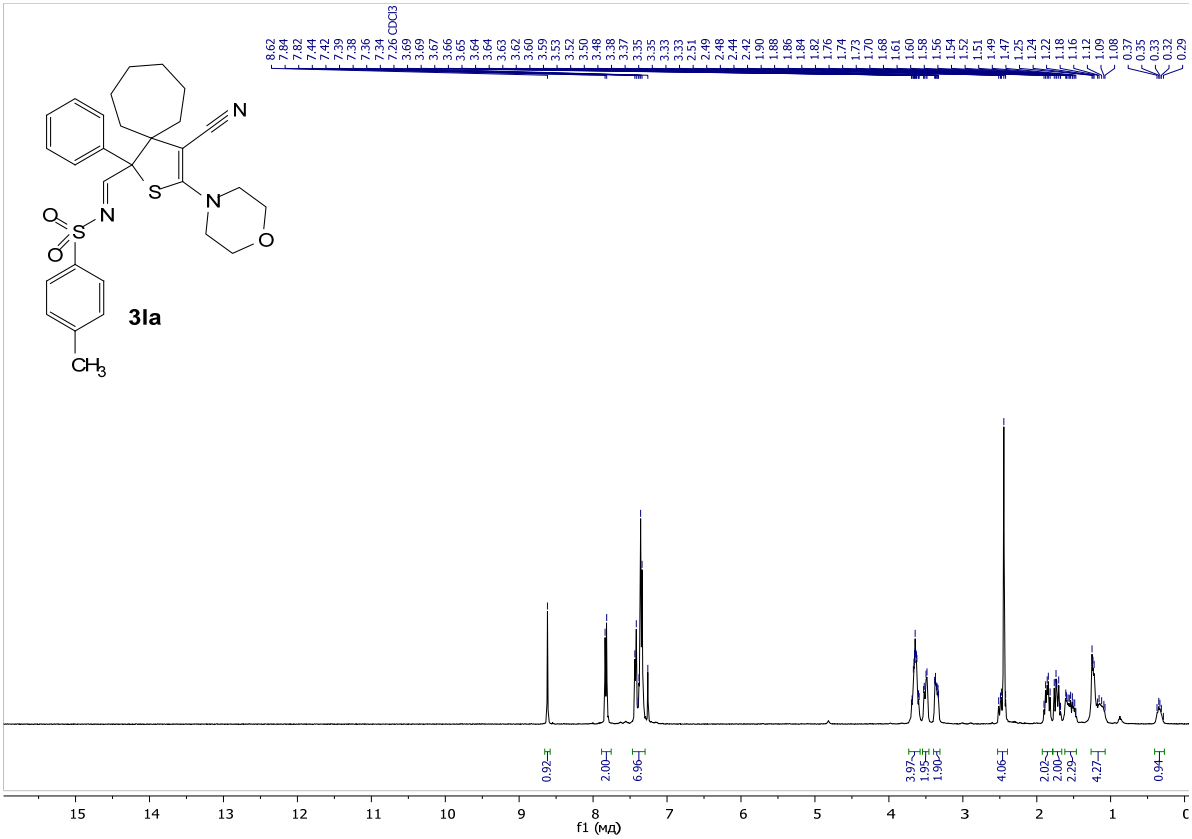
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3ja**



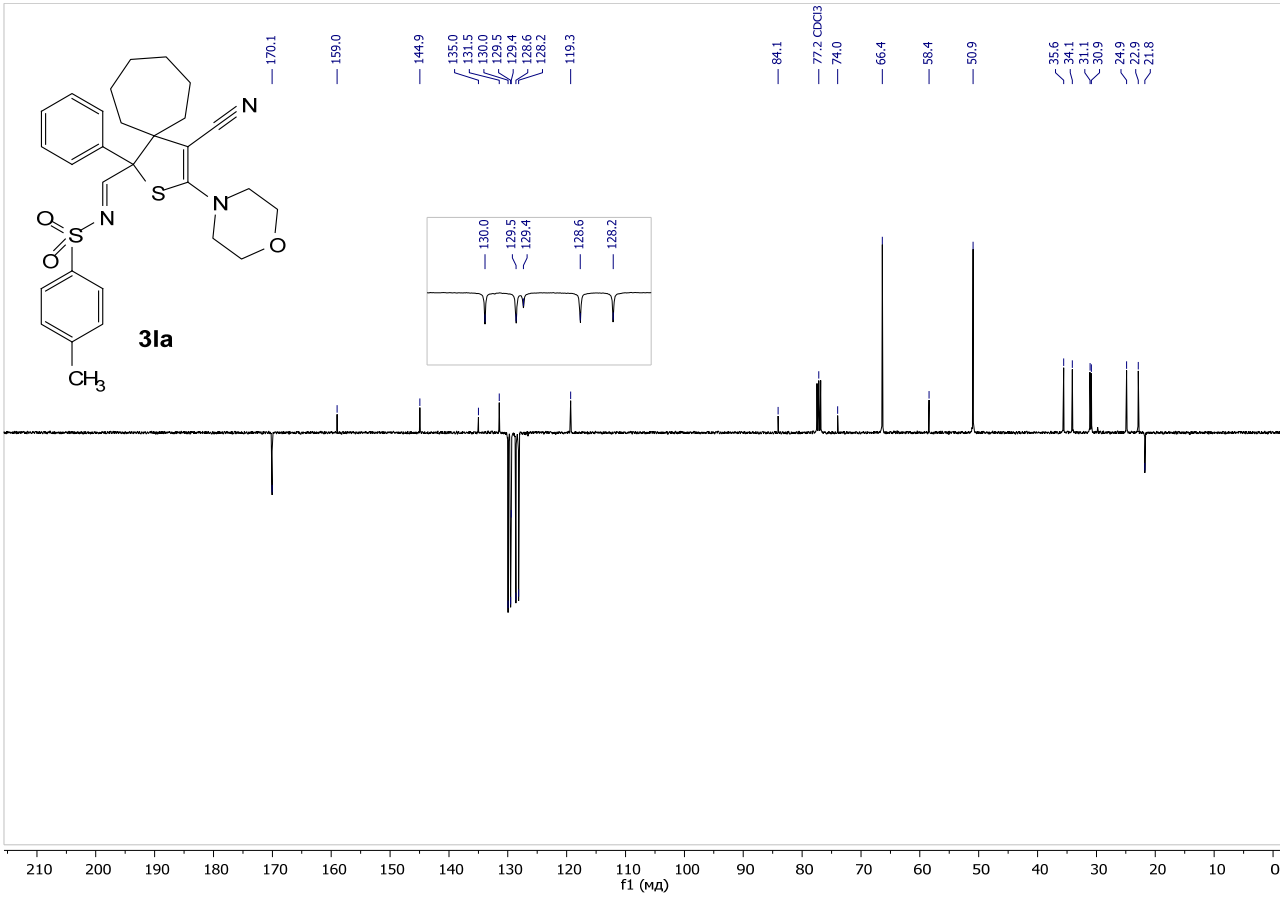
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ka**



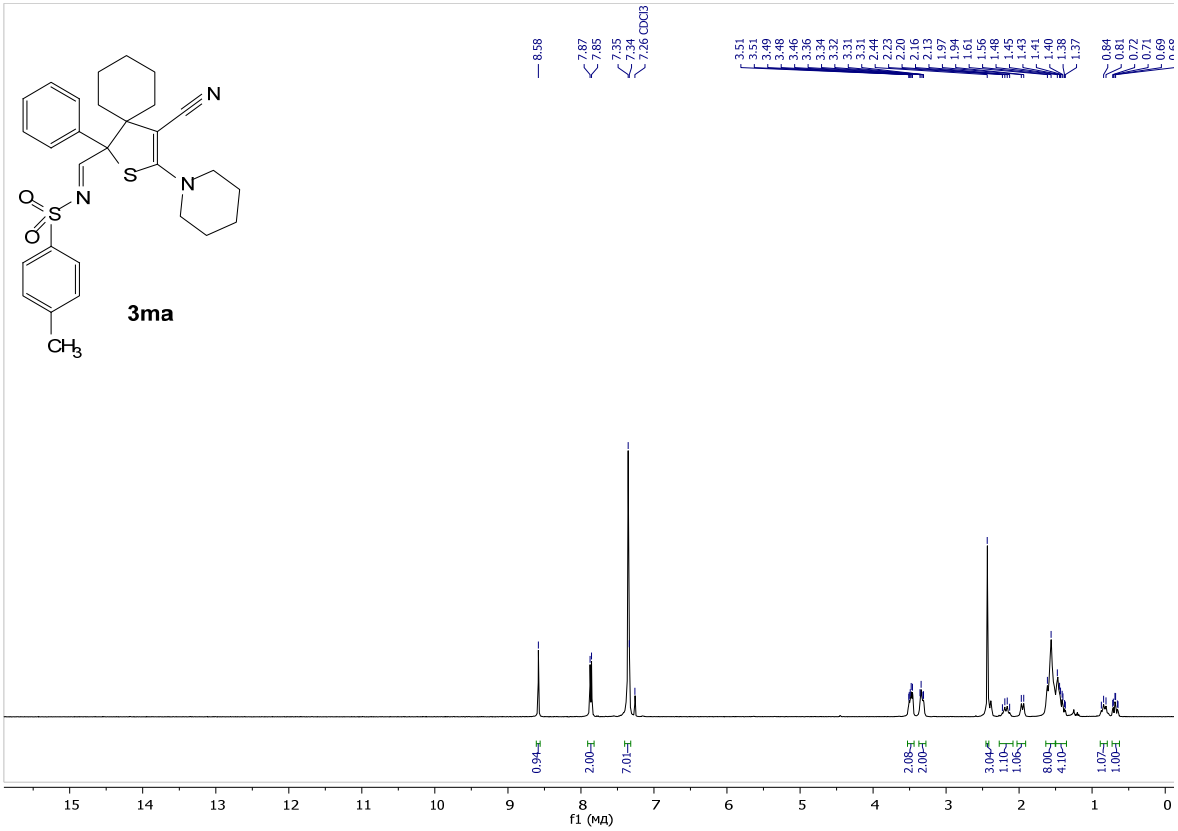
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3ka**



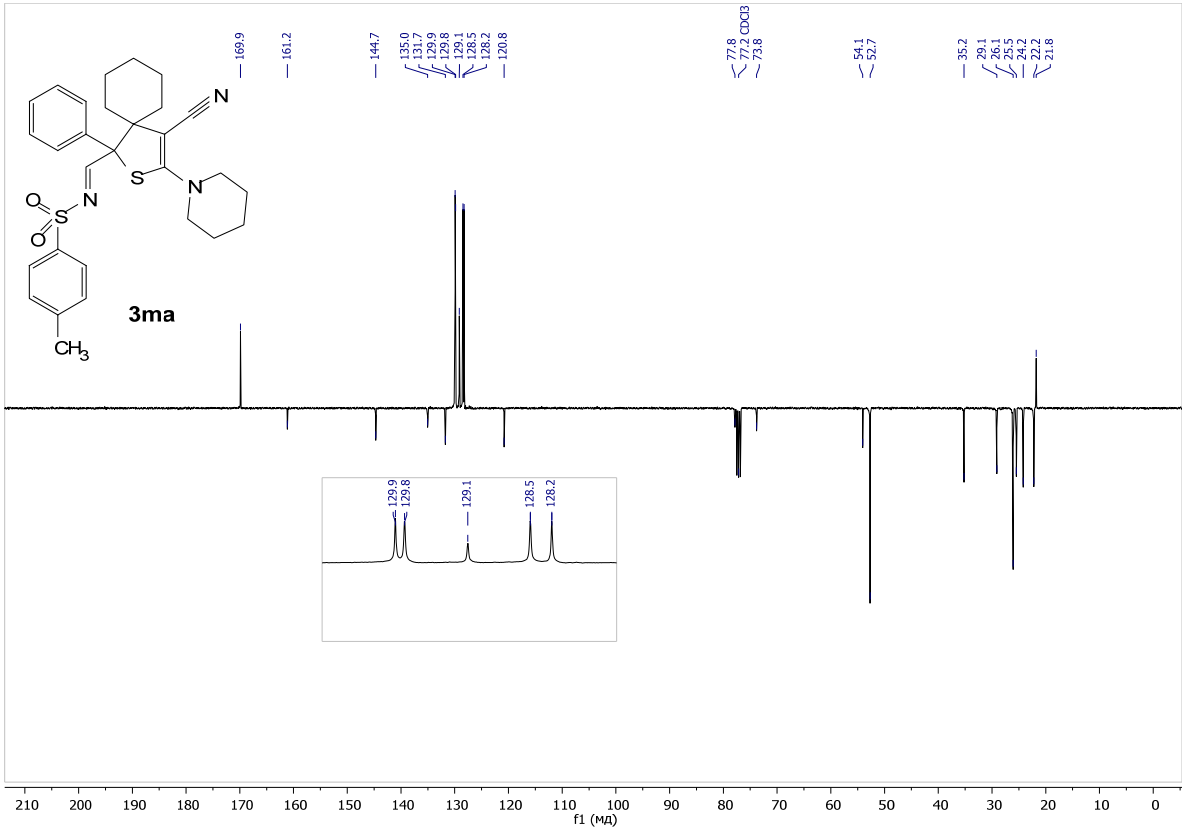
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3la**



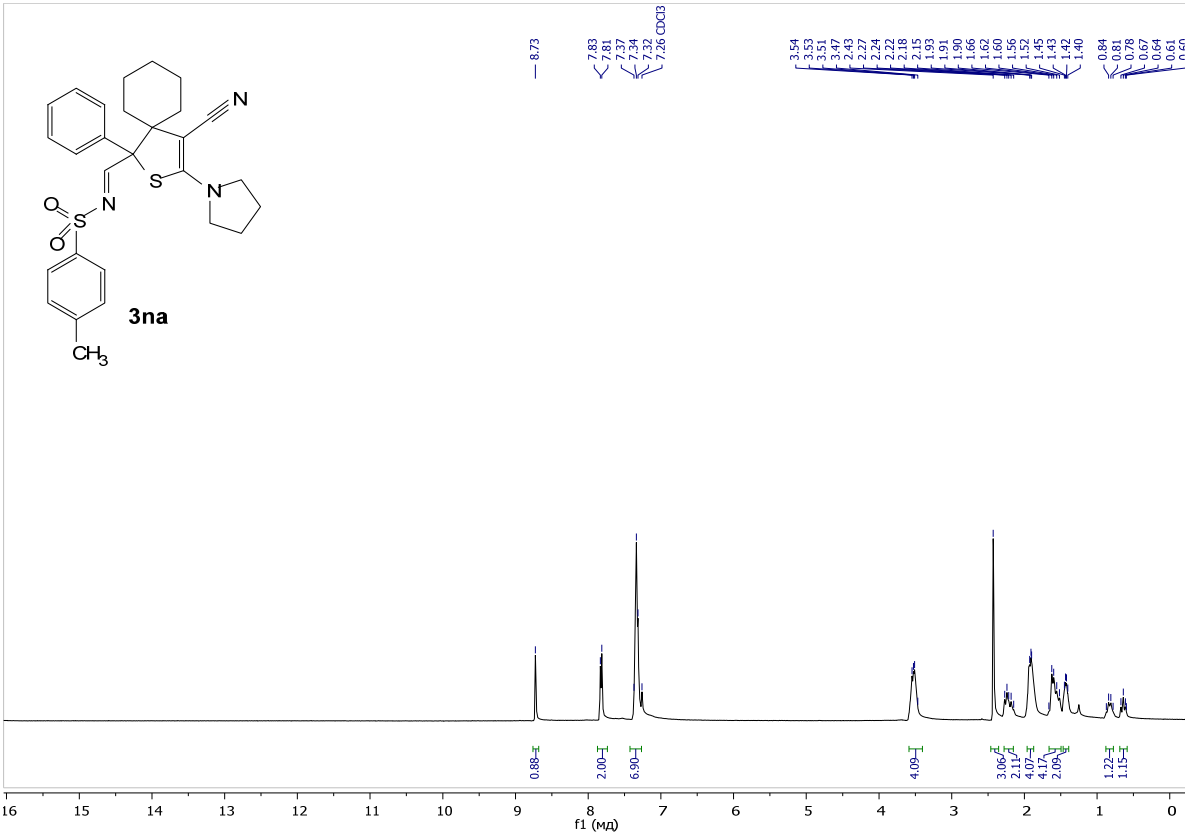
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3la**



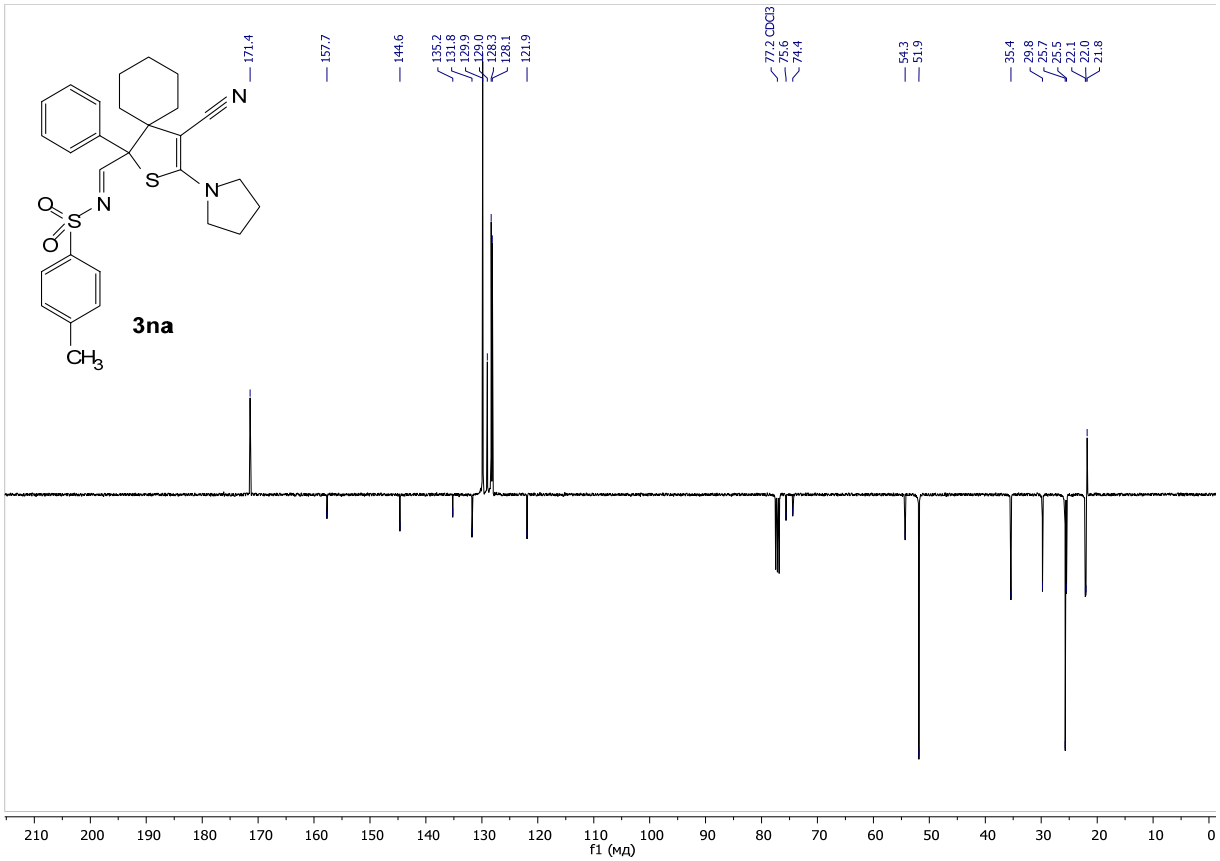
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ma**



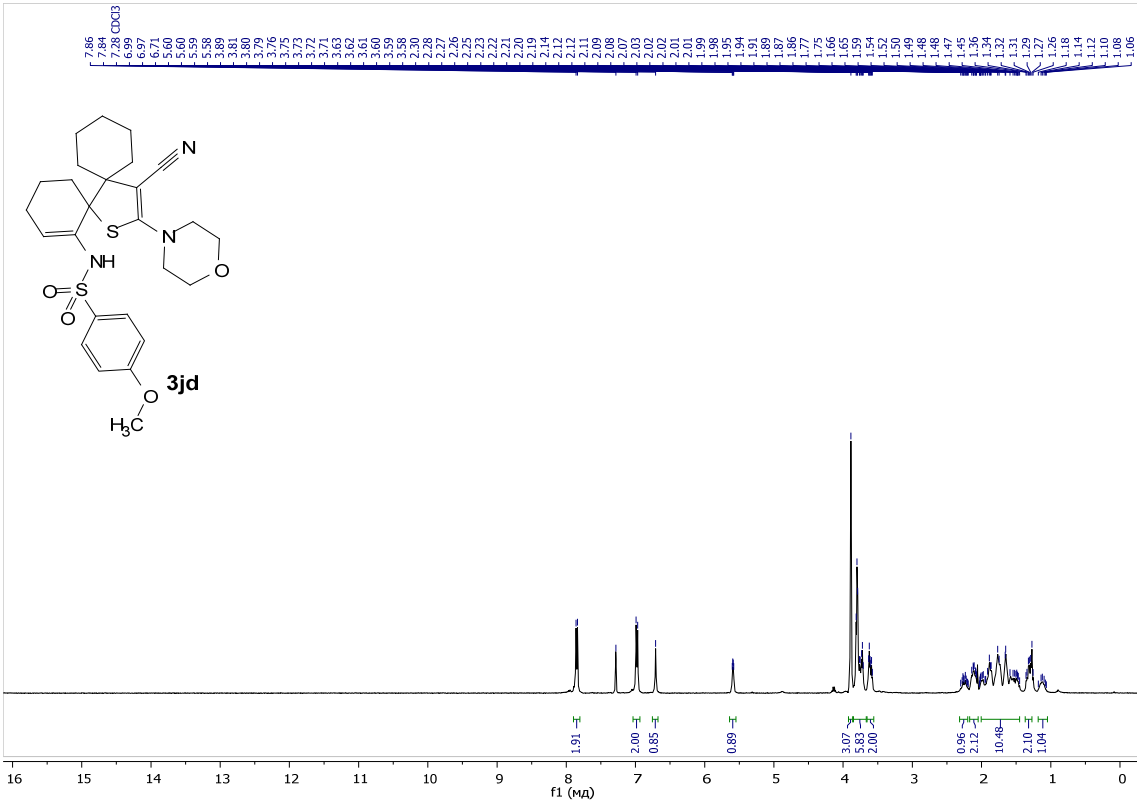
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3ma**



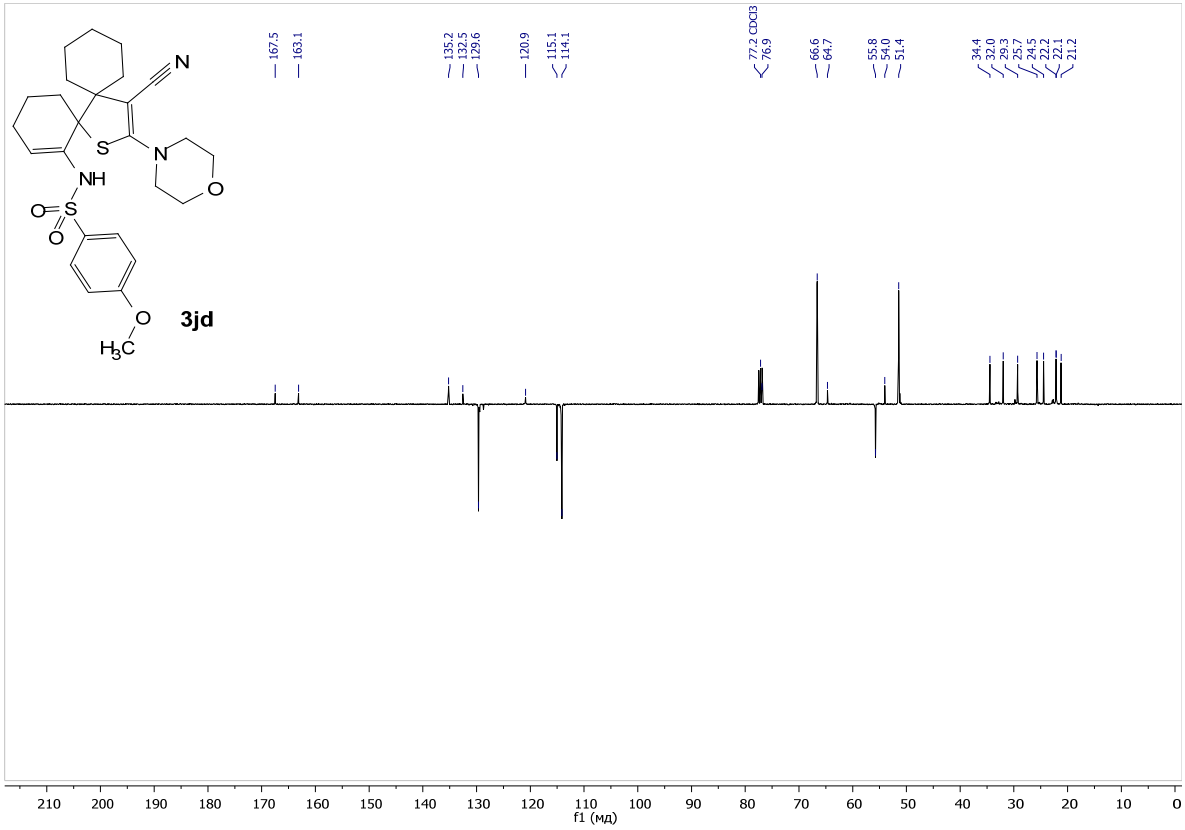
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3na**



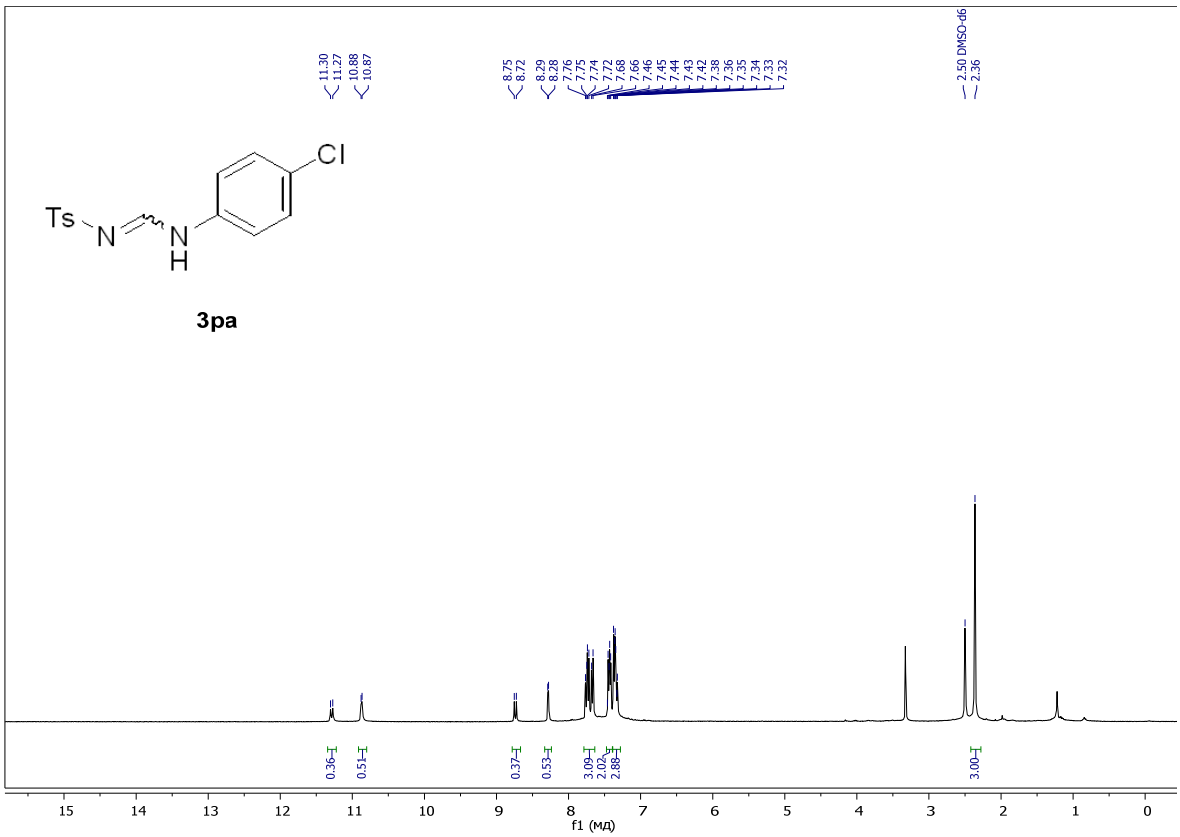
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3na**



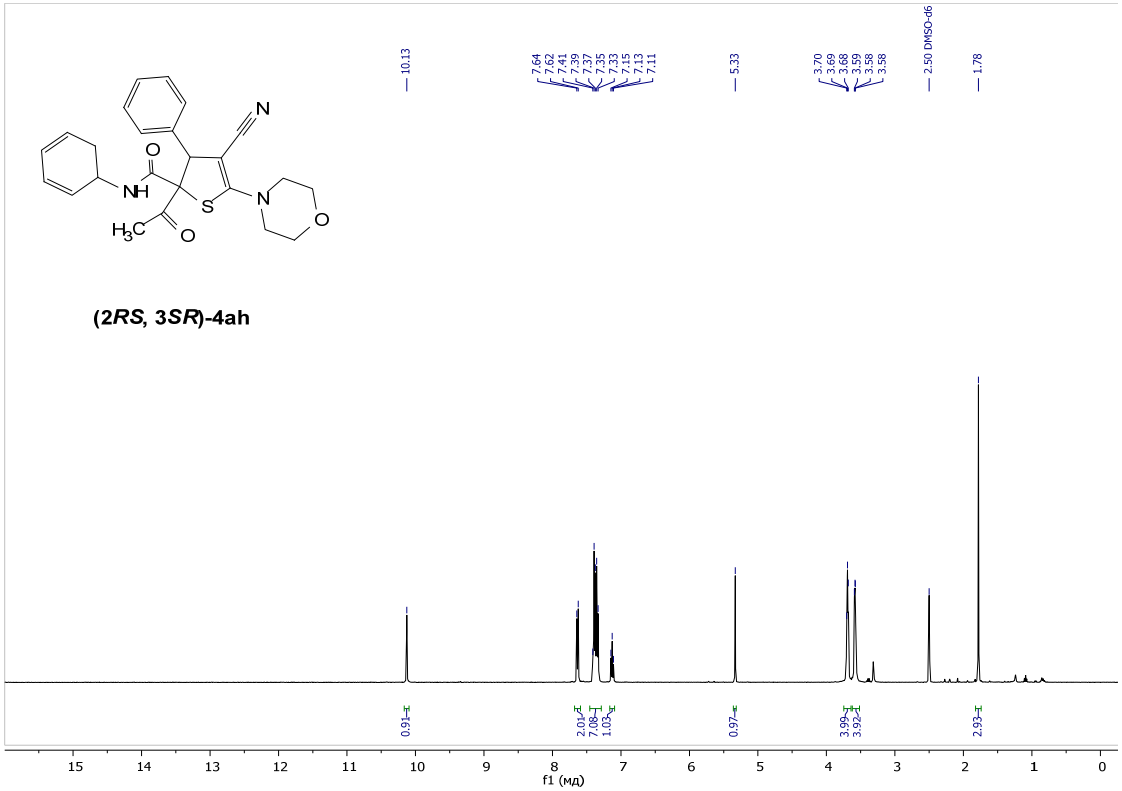
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3jd**



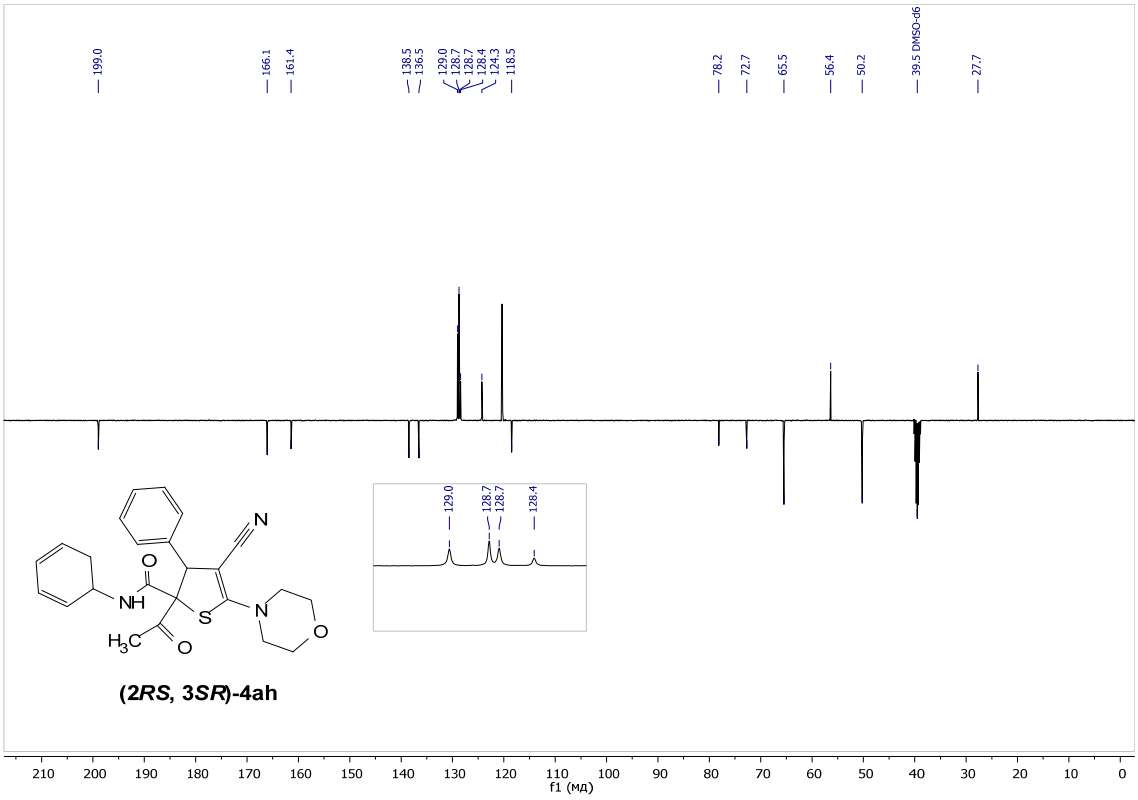
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **3jd**



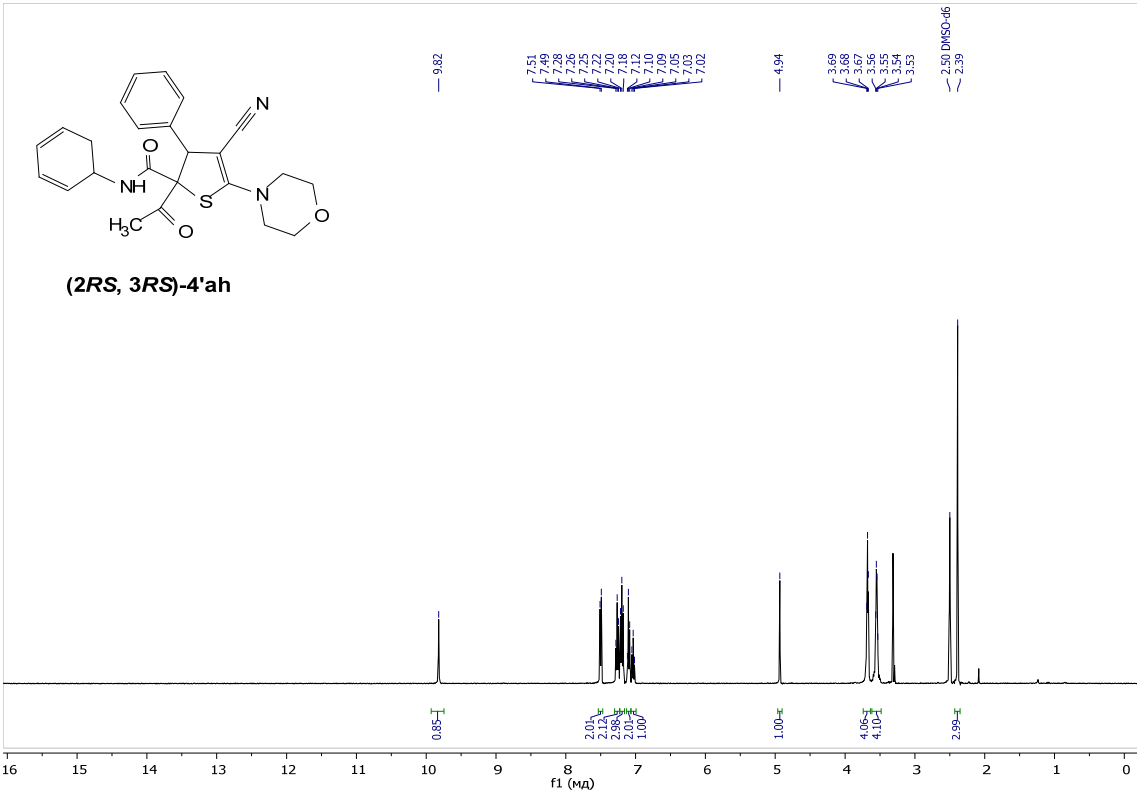
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **3ta**



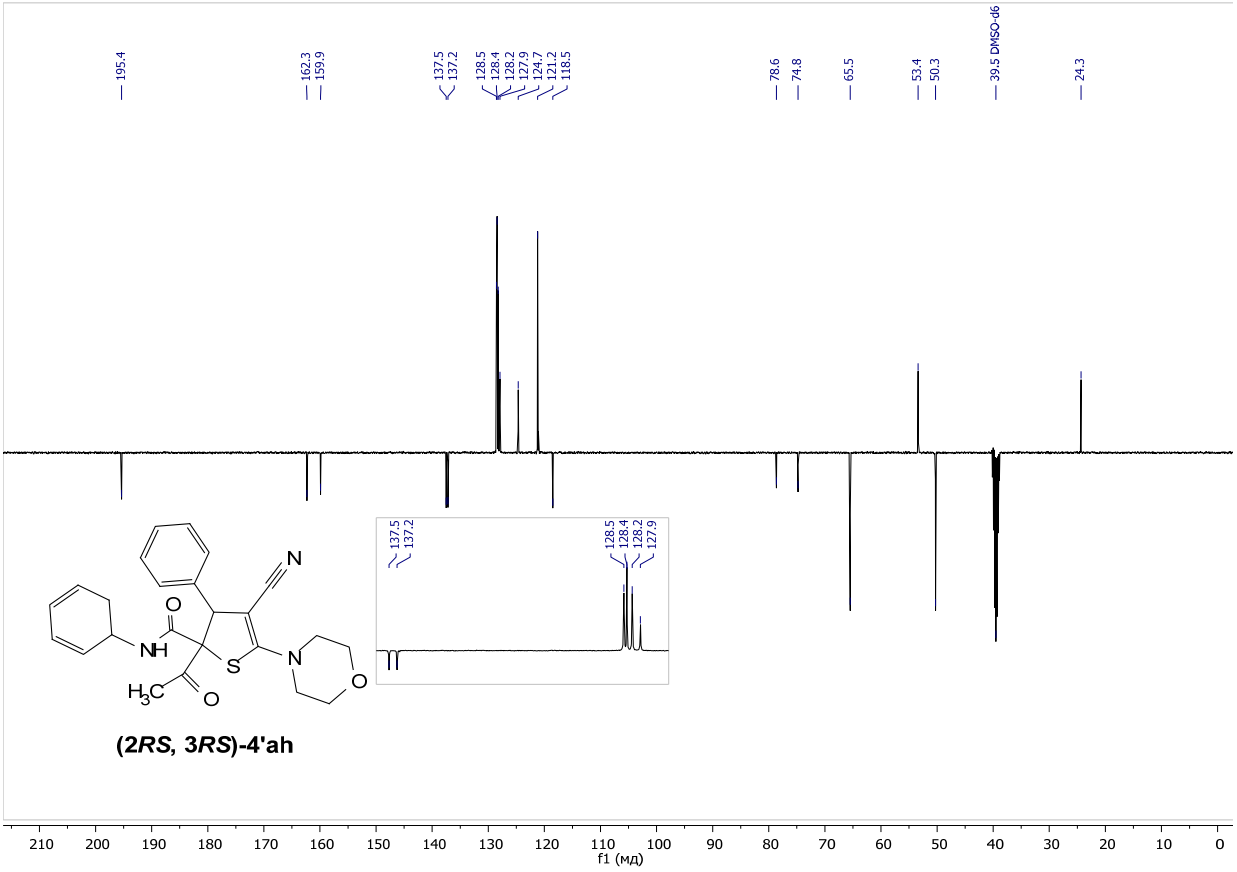
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4ah**



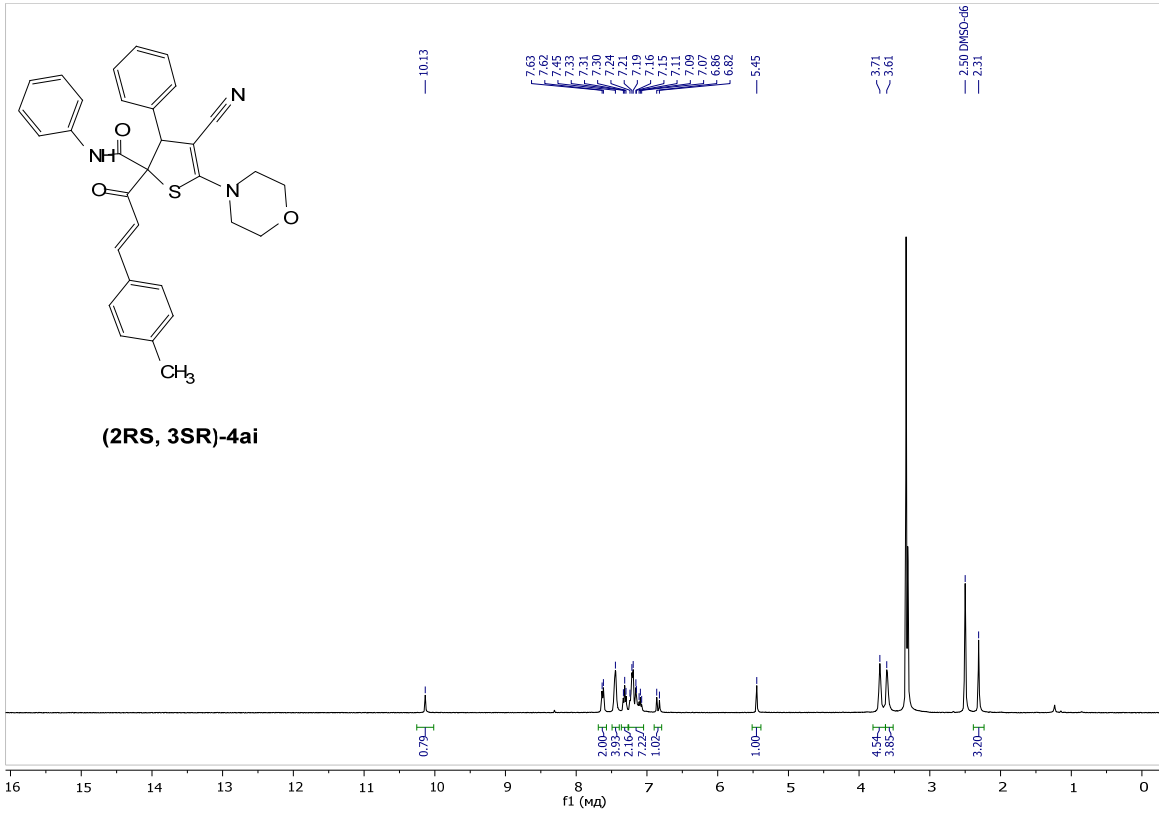
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4ah**



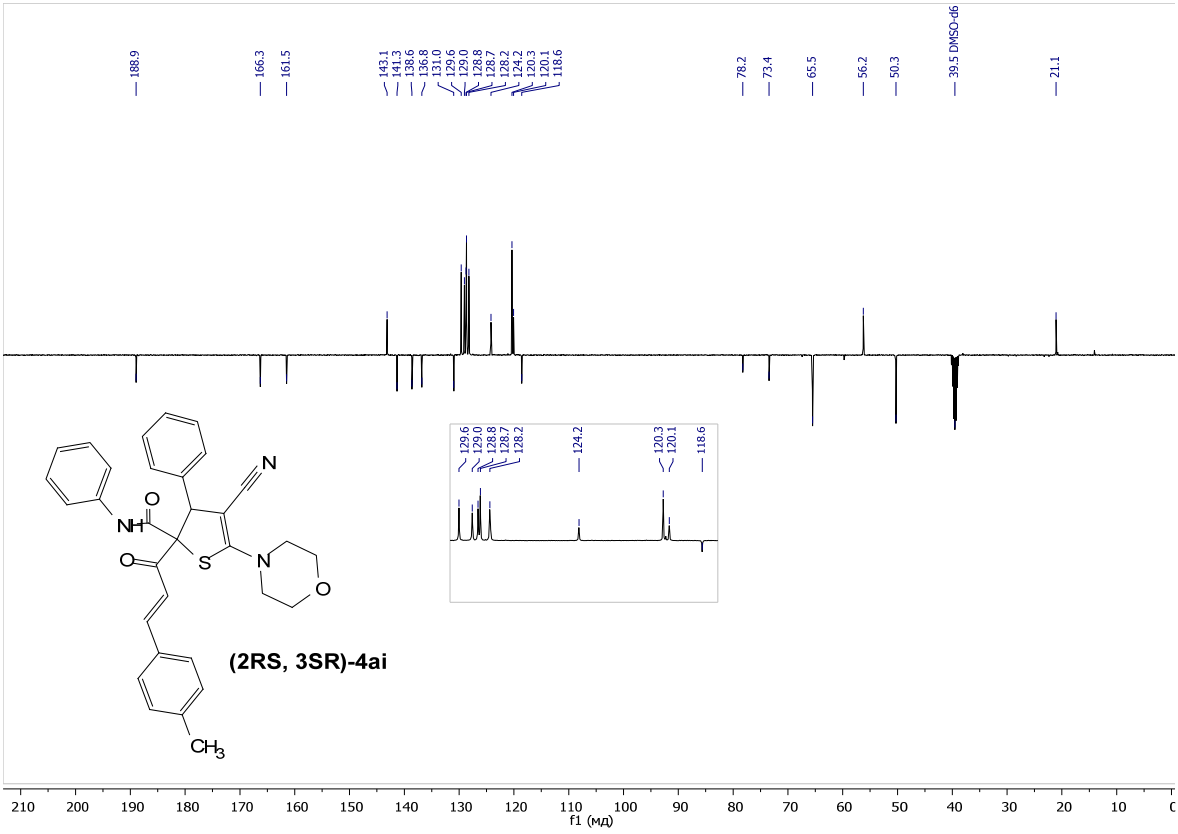
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′ah**



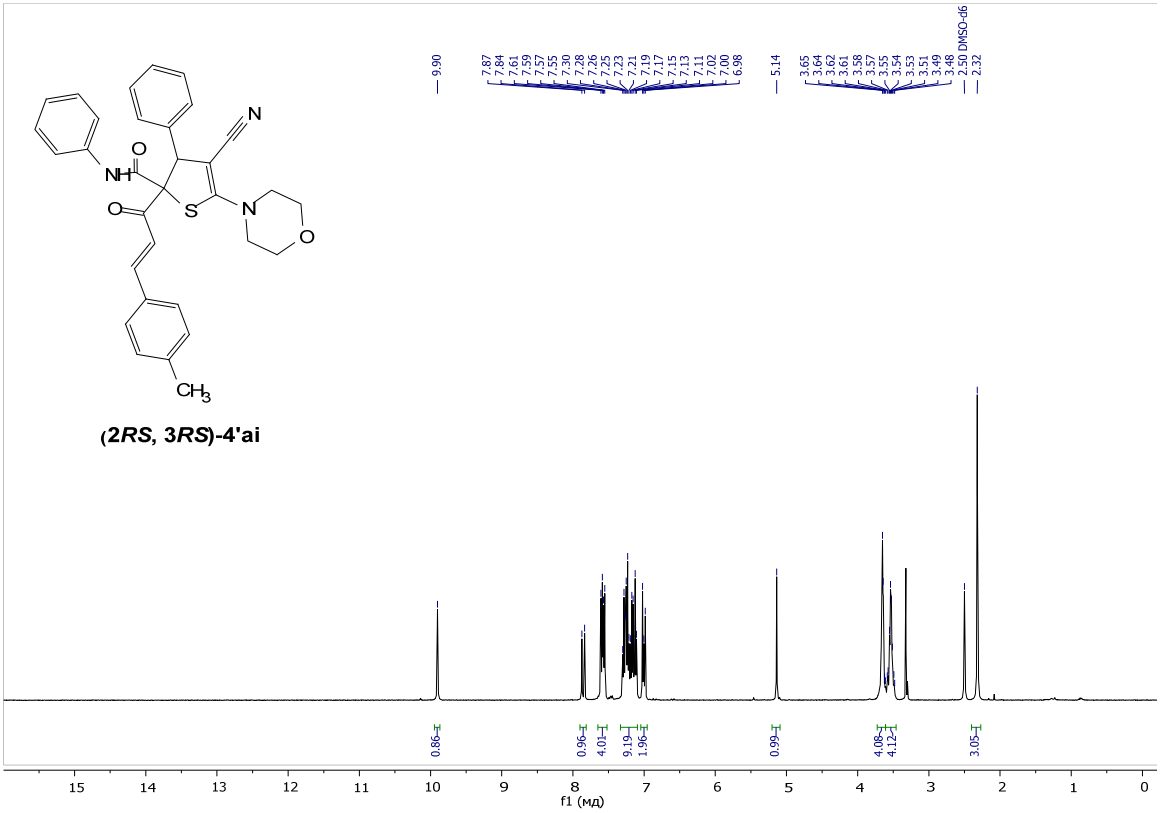
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′ah**



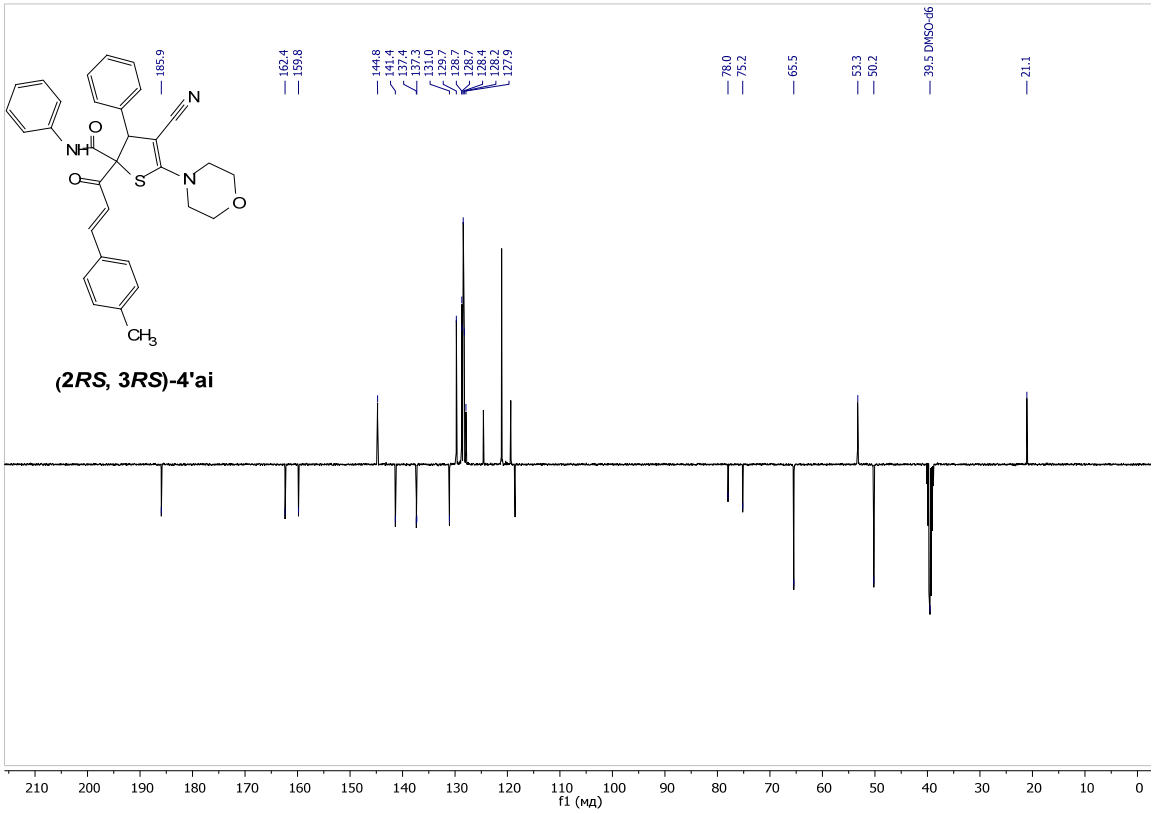
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4ai**



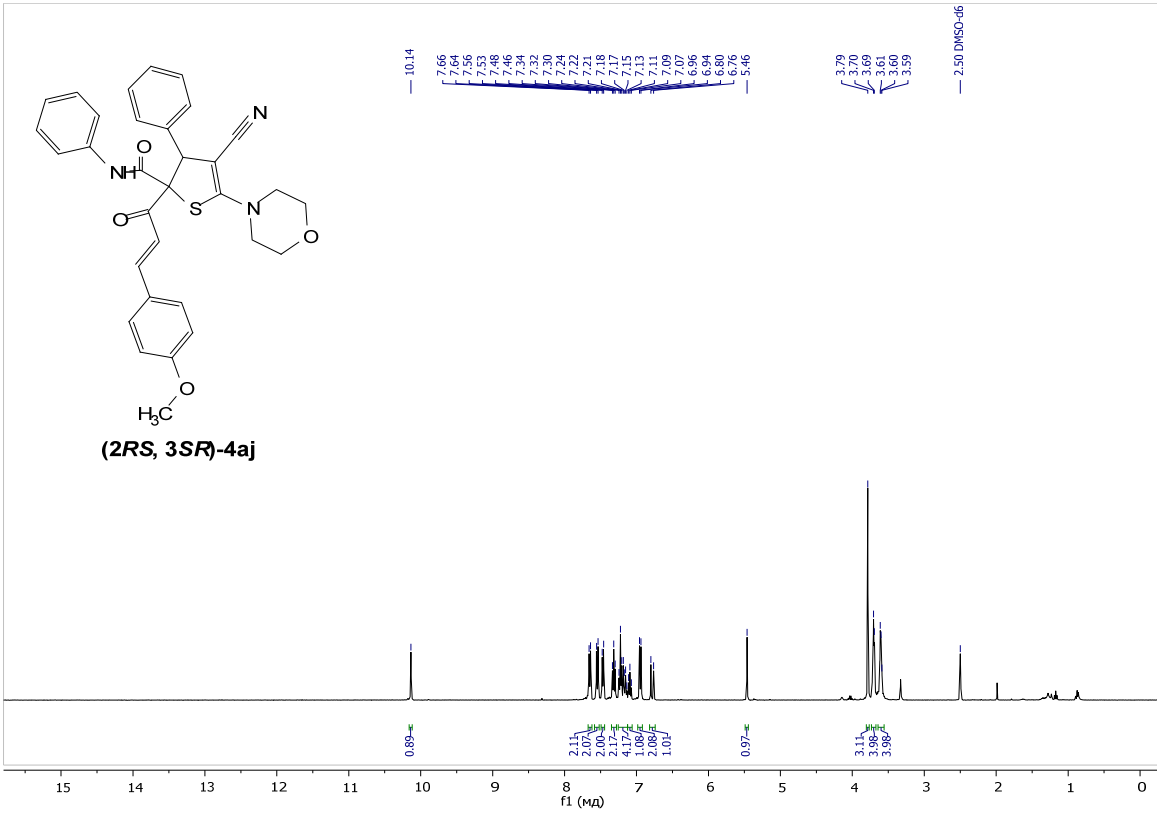
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4ai**



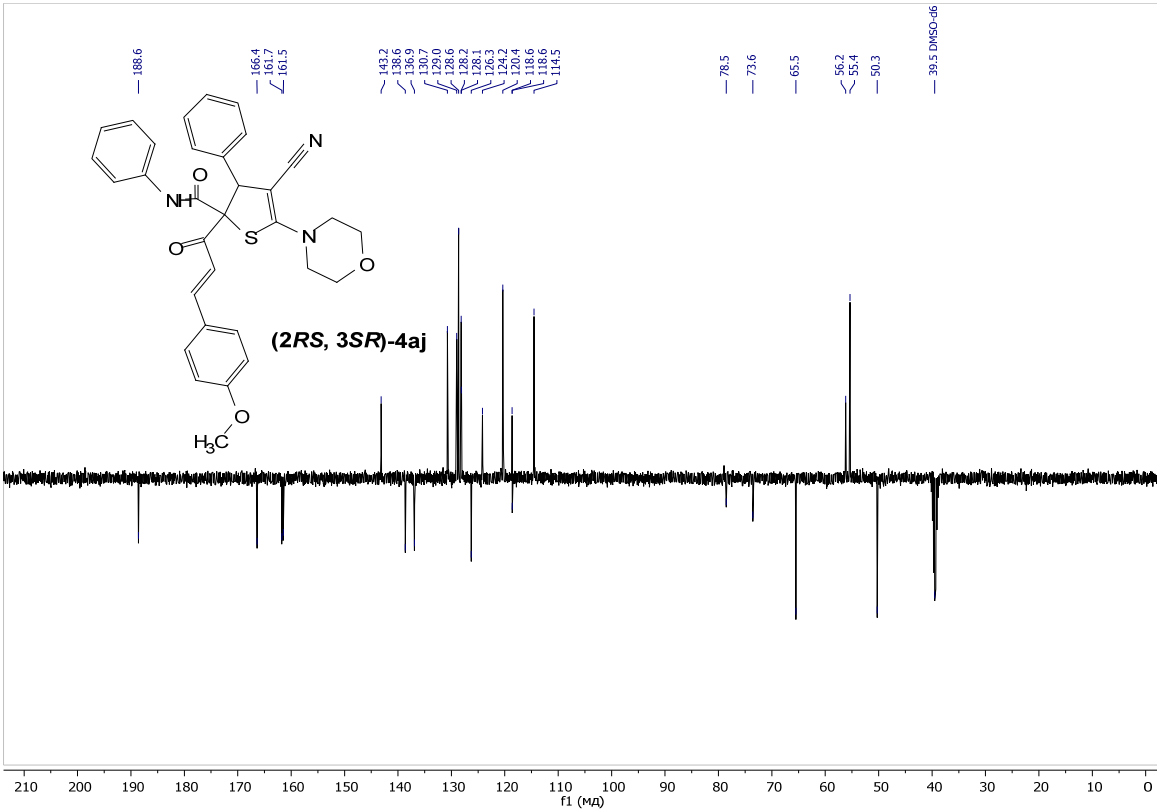
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′ai**



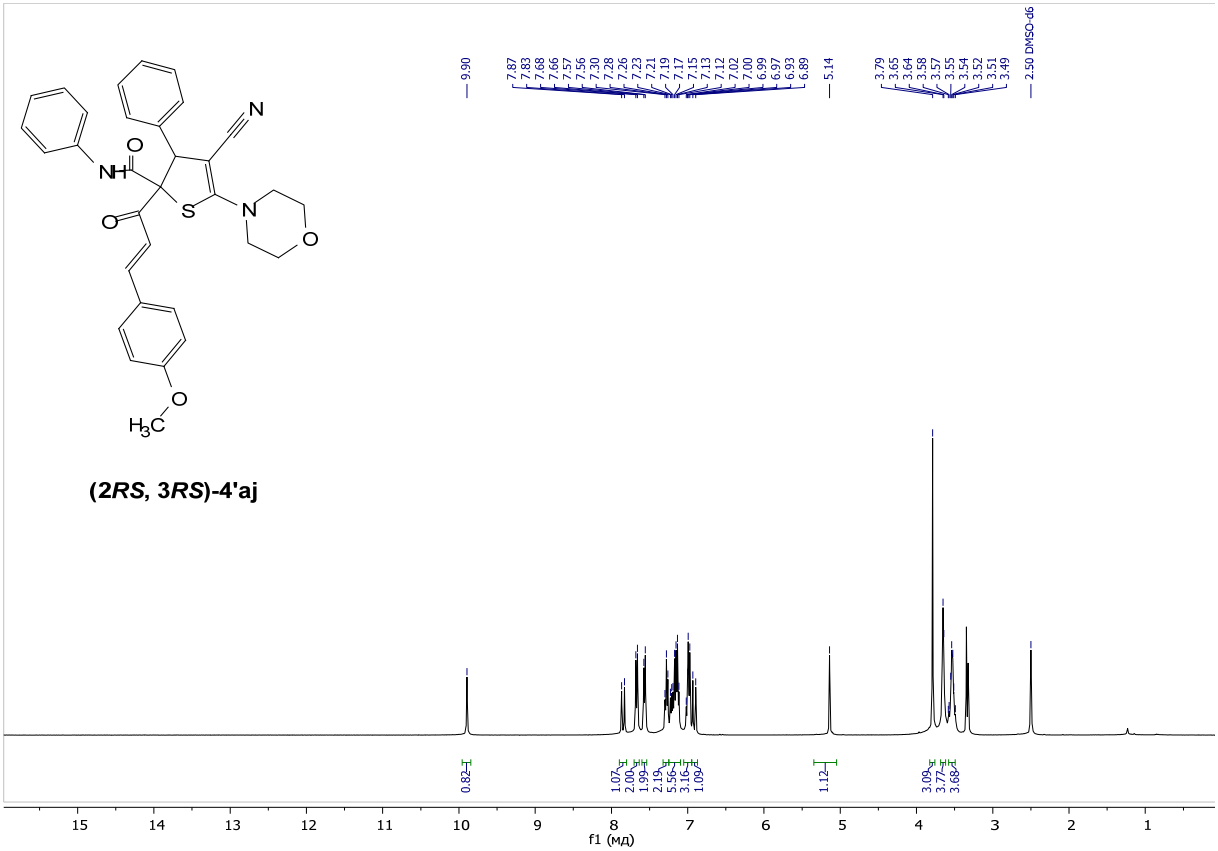
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′ai**



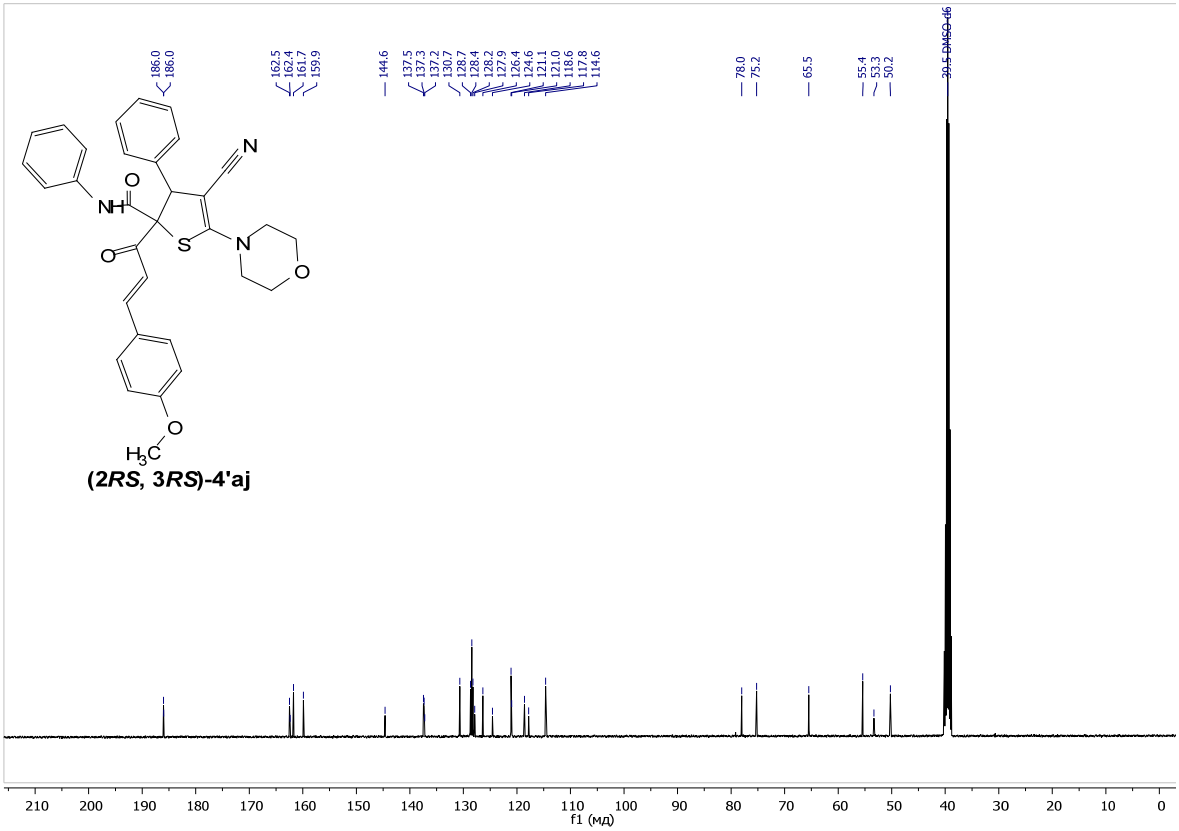
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **(2*RS*,3*SR*)-4aj**



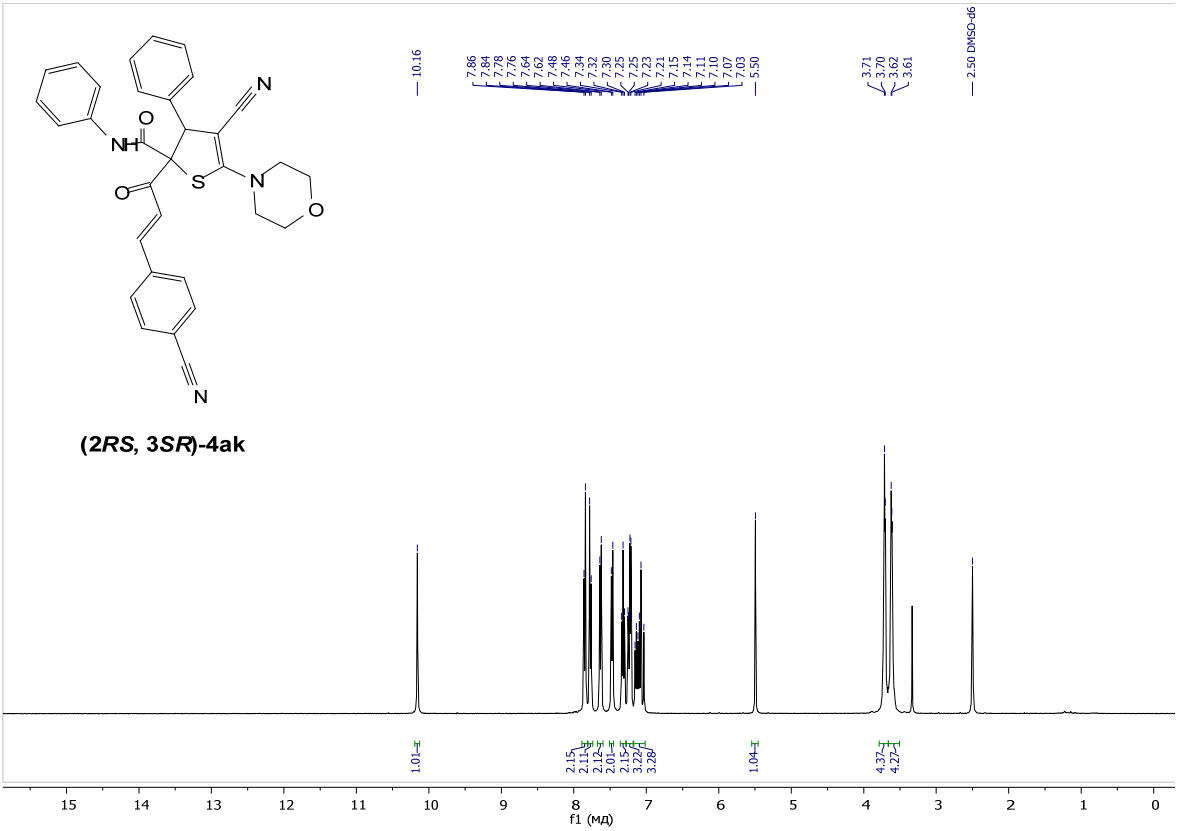
^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **(2*RS*,3*SR*)-4aj**



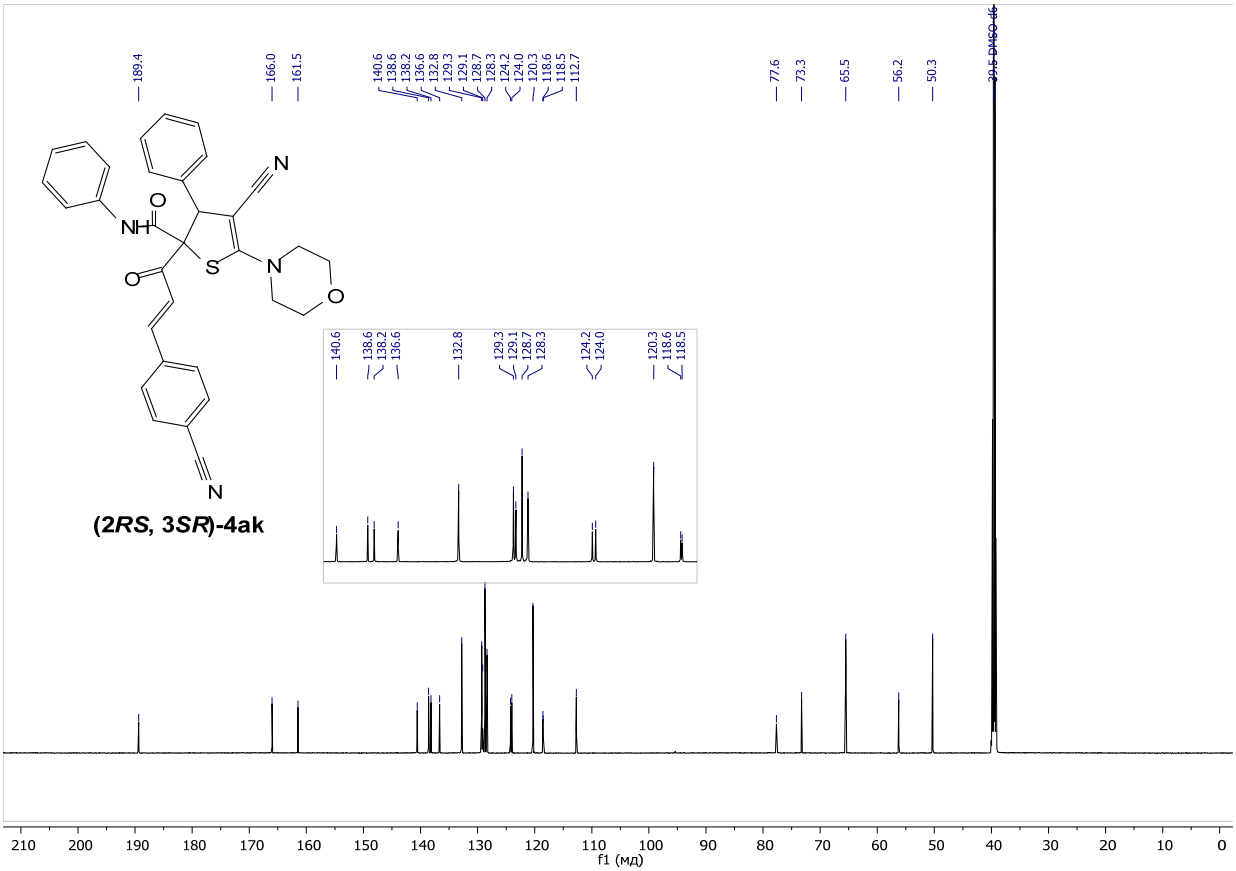
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′aj**



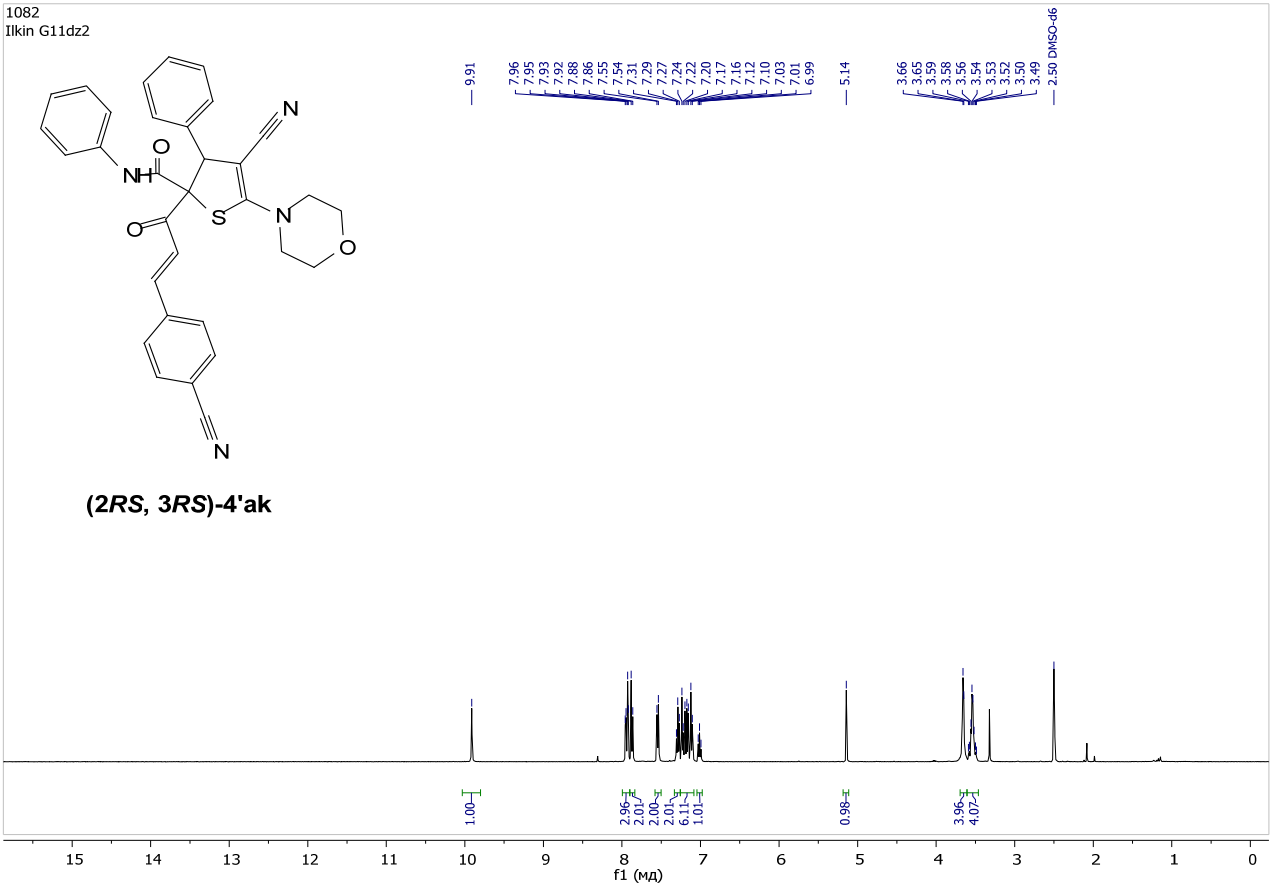
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(2*RS*,3*RS*)4′aj**



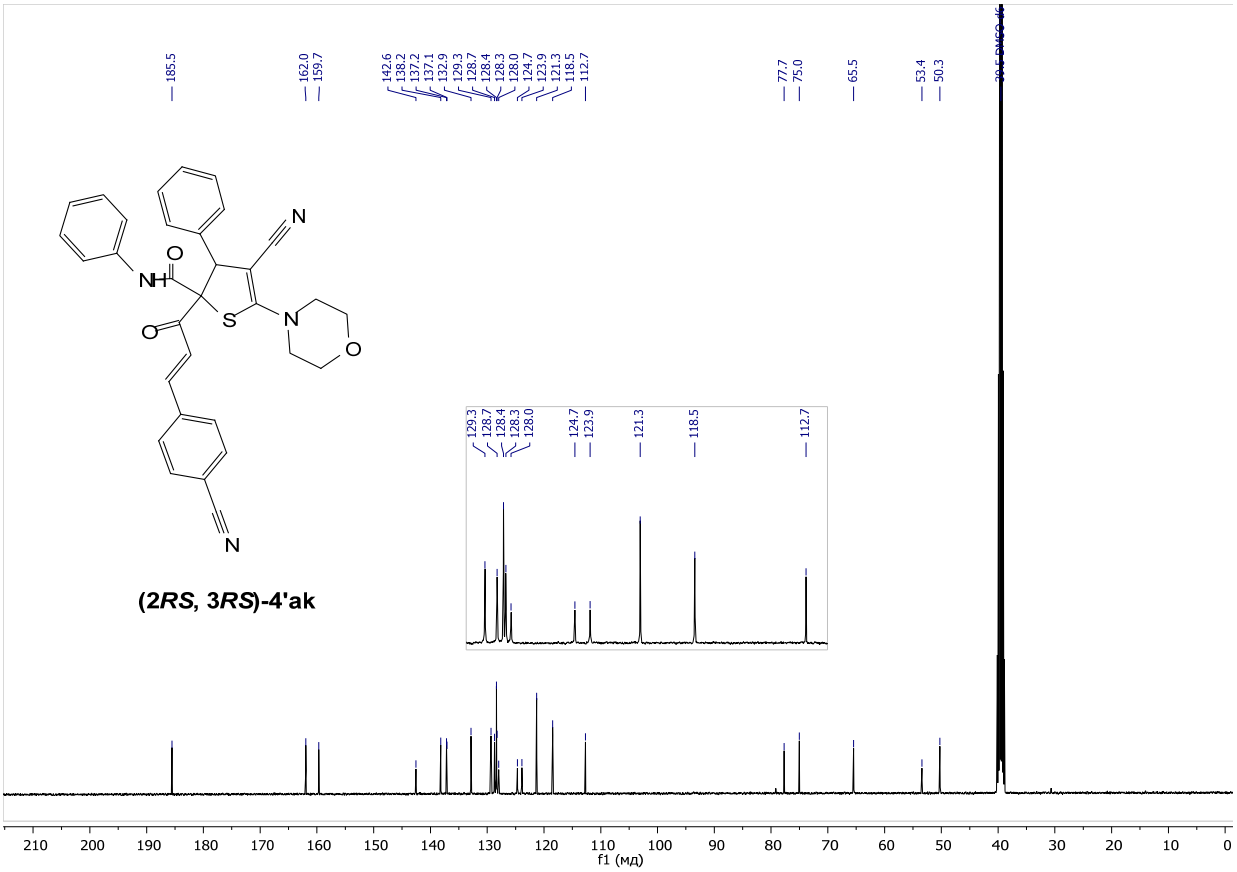
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4ak**



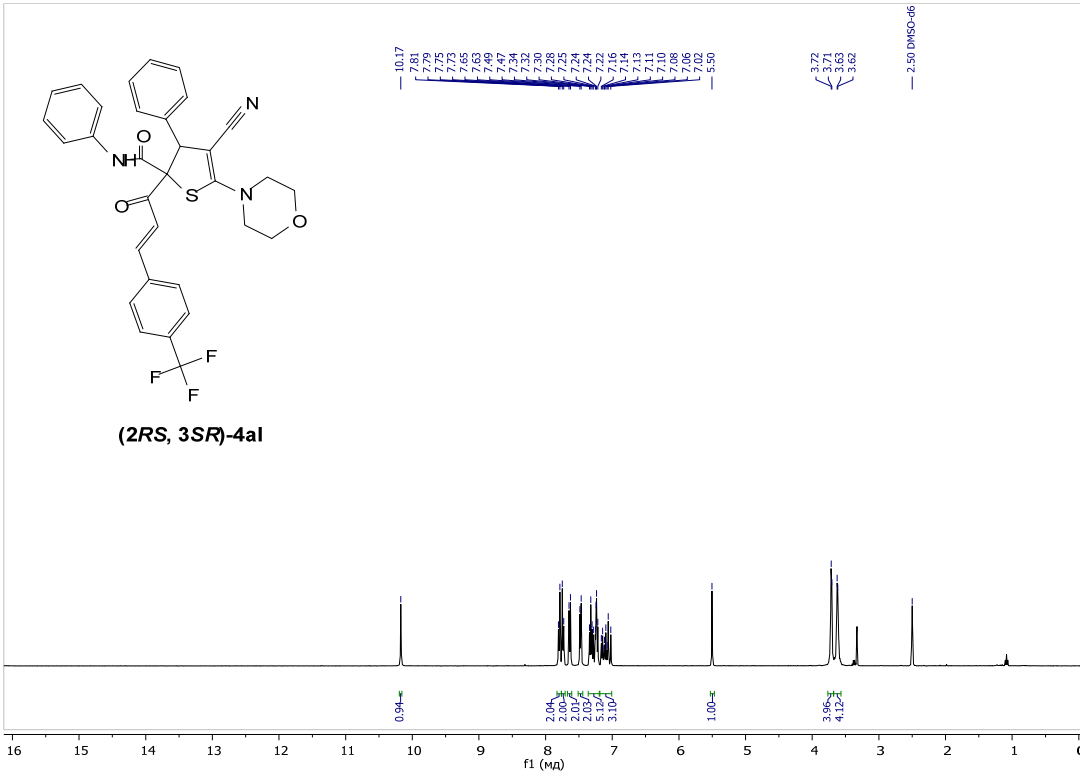
^{13}C{1H} NMR (150 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4ak**



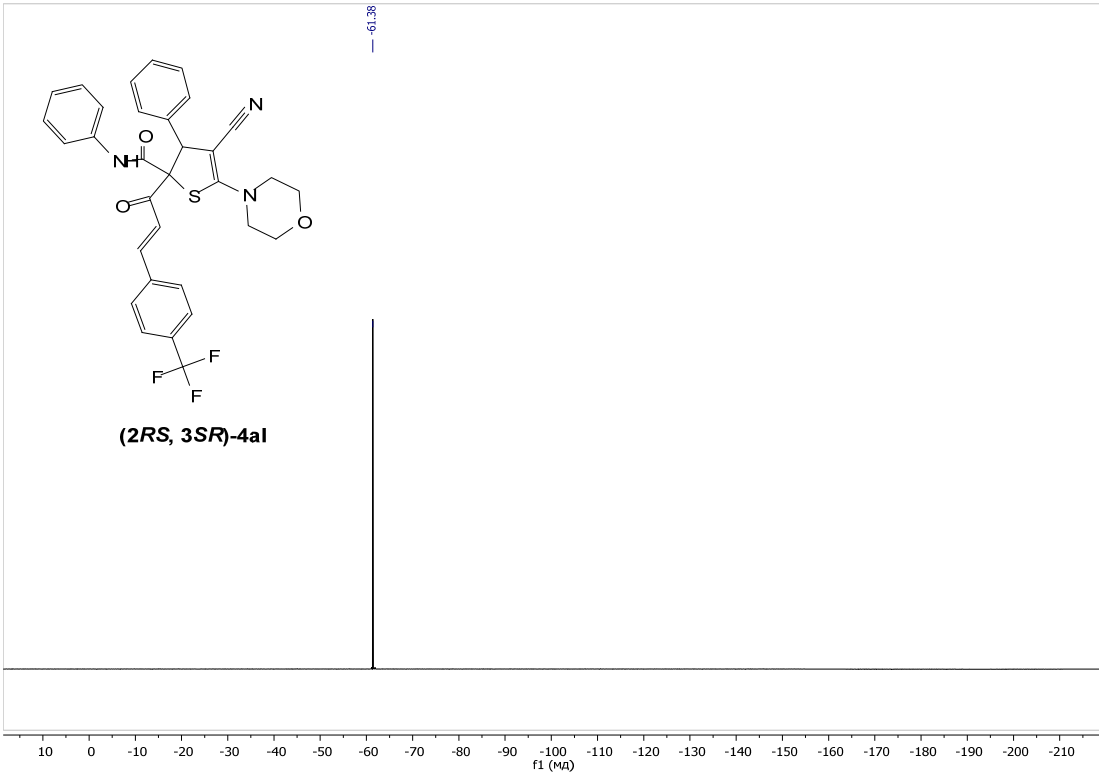
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′ak**



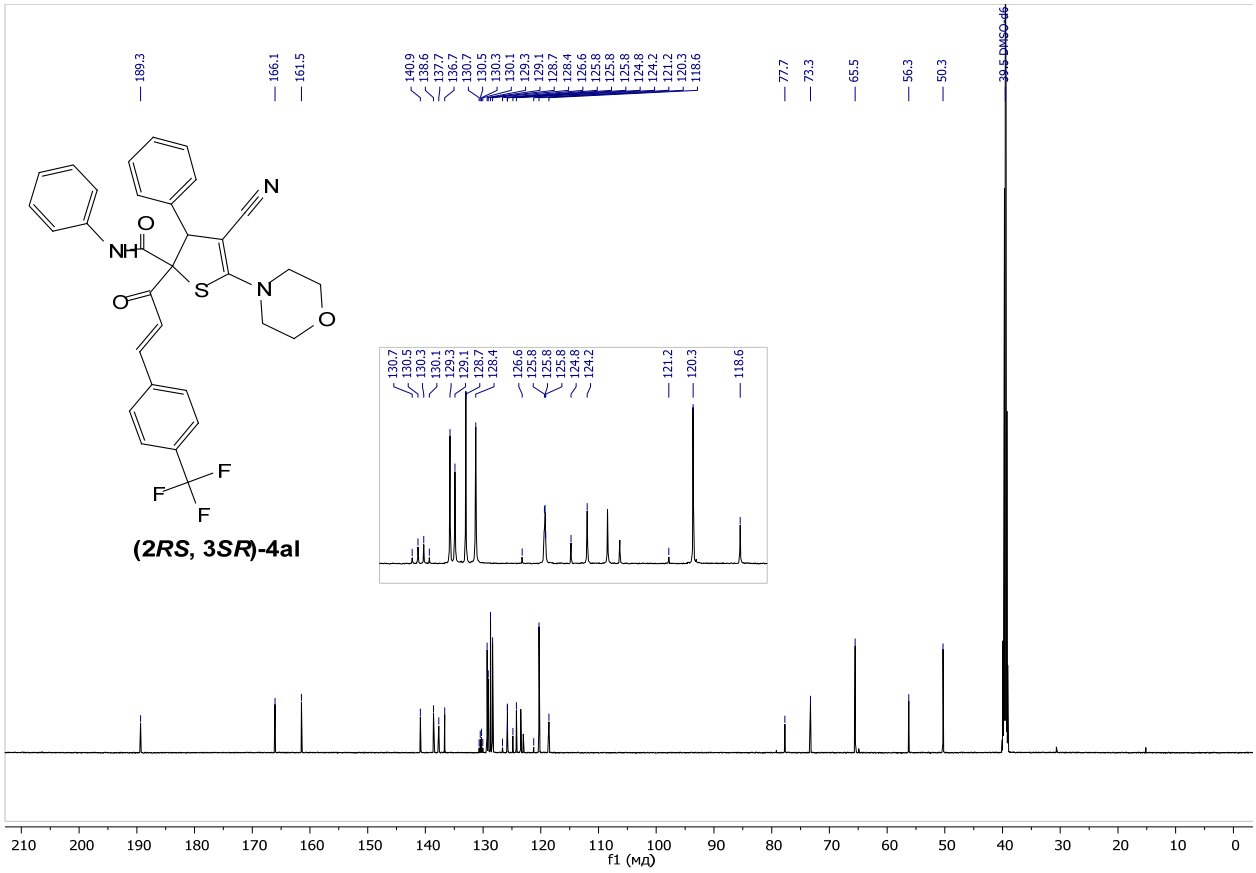
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′ak**



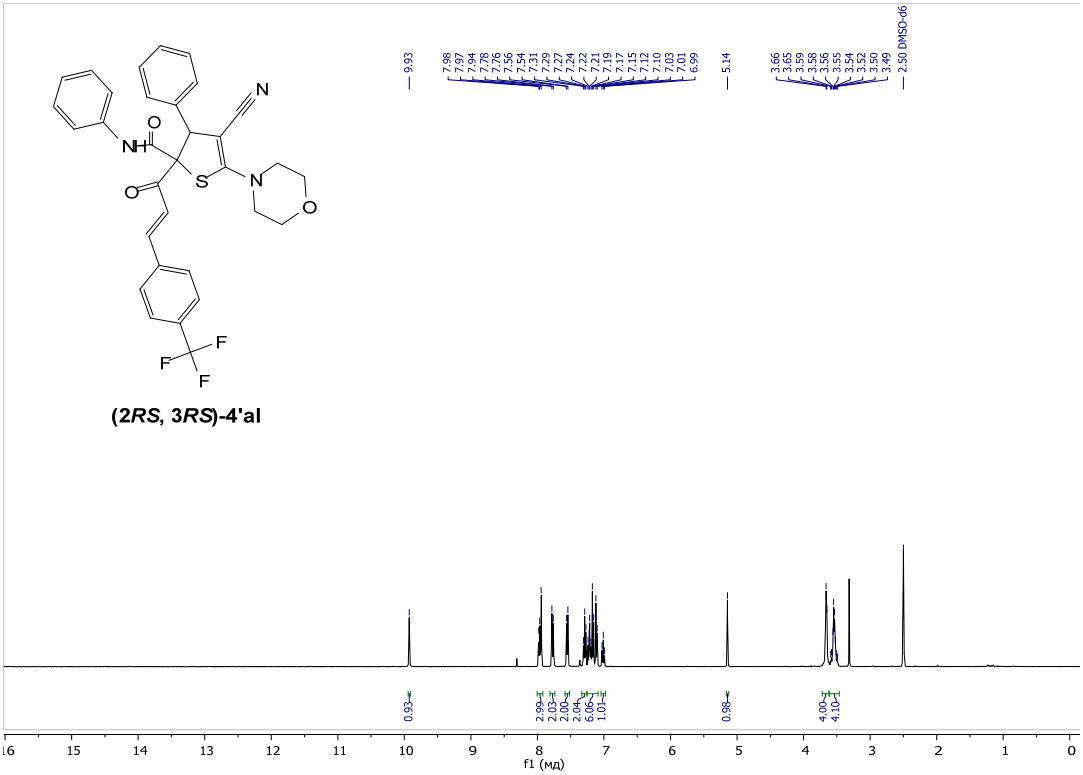
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4al**



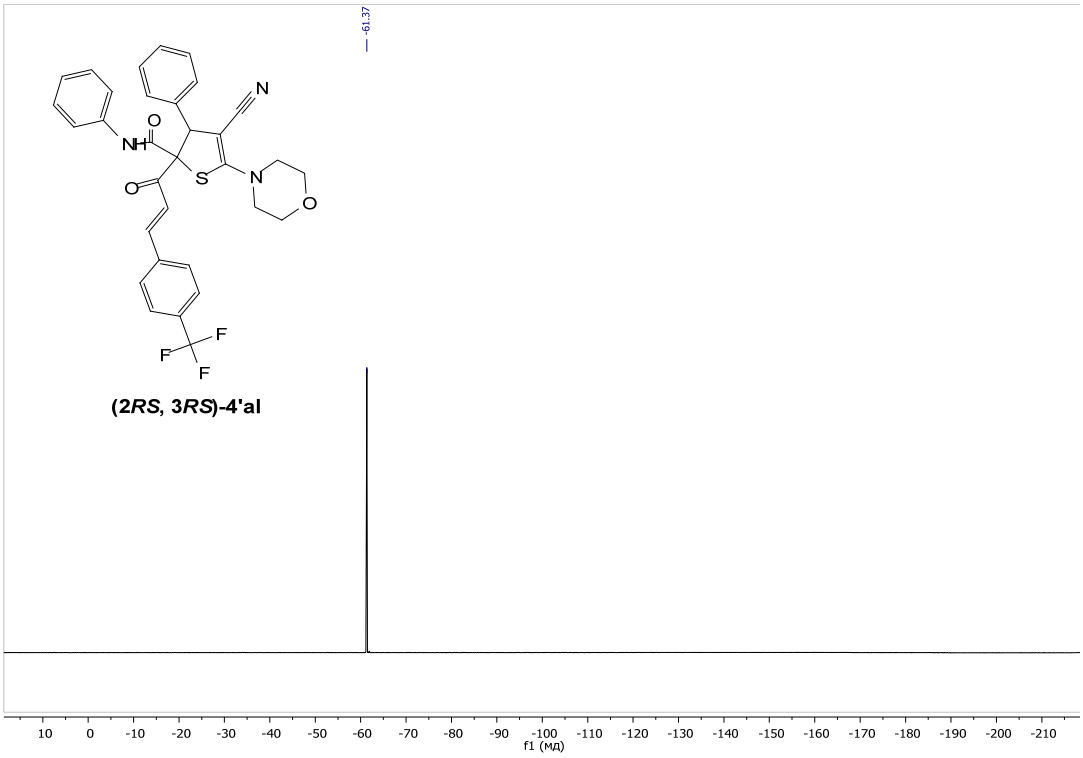
^{19}F NMR (376 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4al**



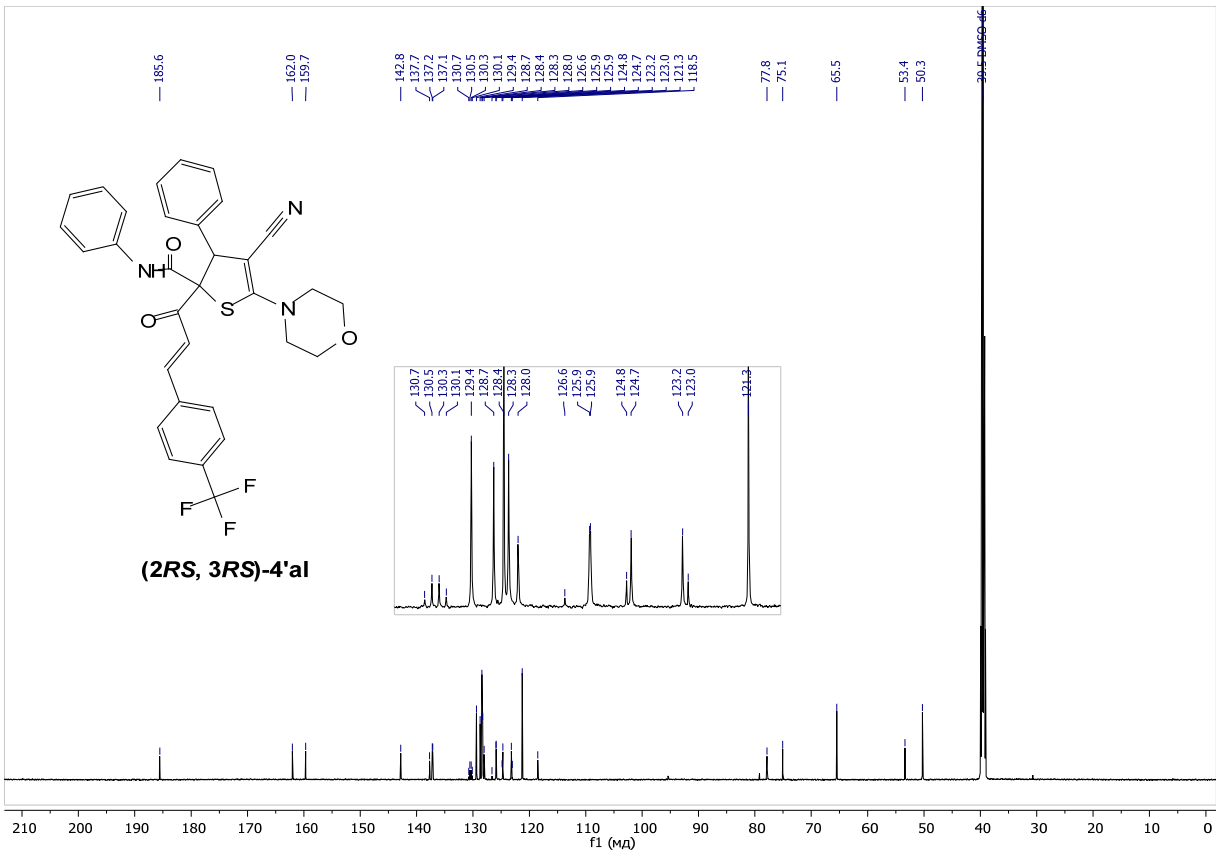
$^{13}C\{1H\}$ NMR (150 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4al**



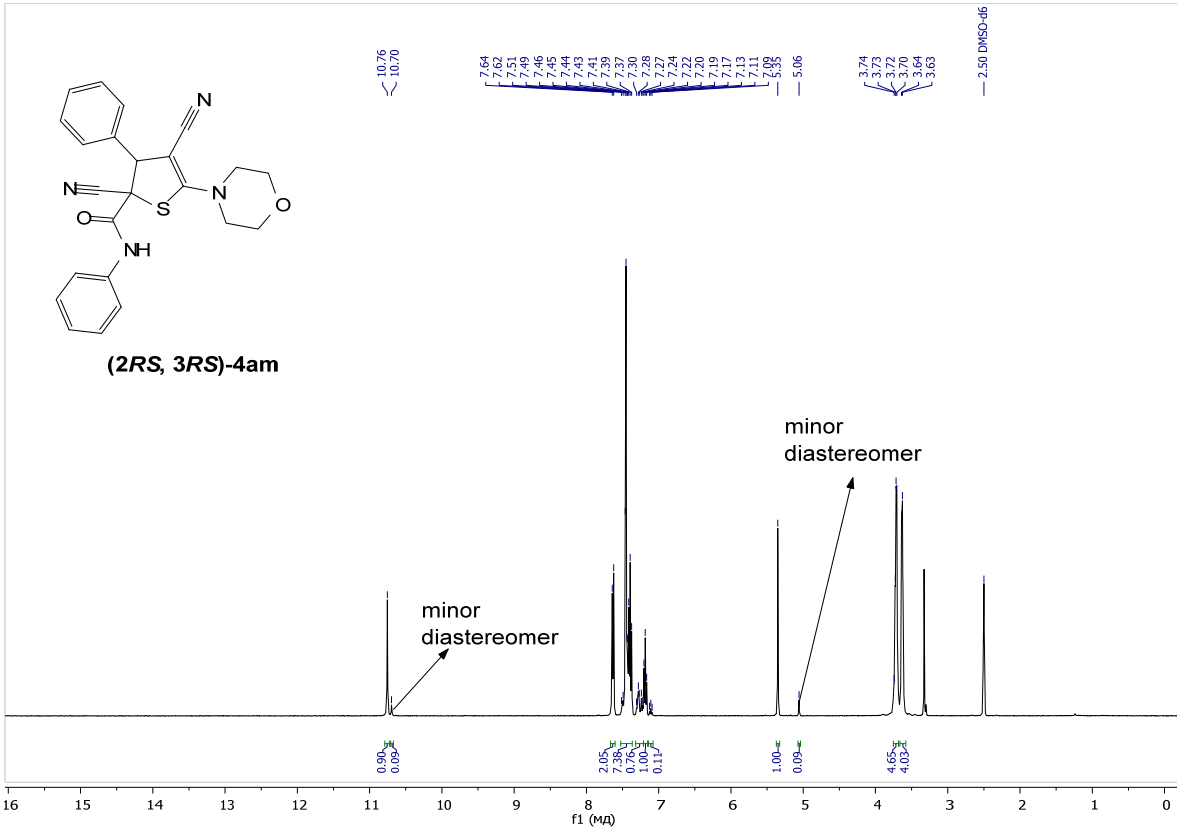
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′al**



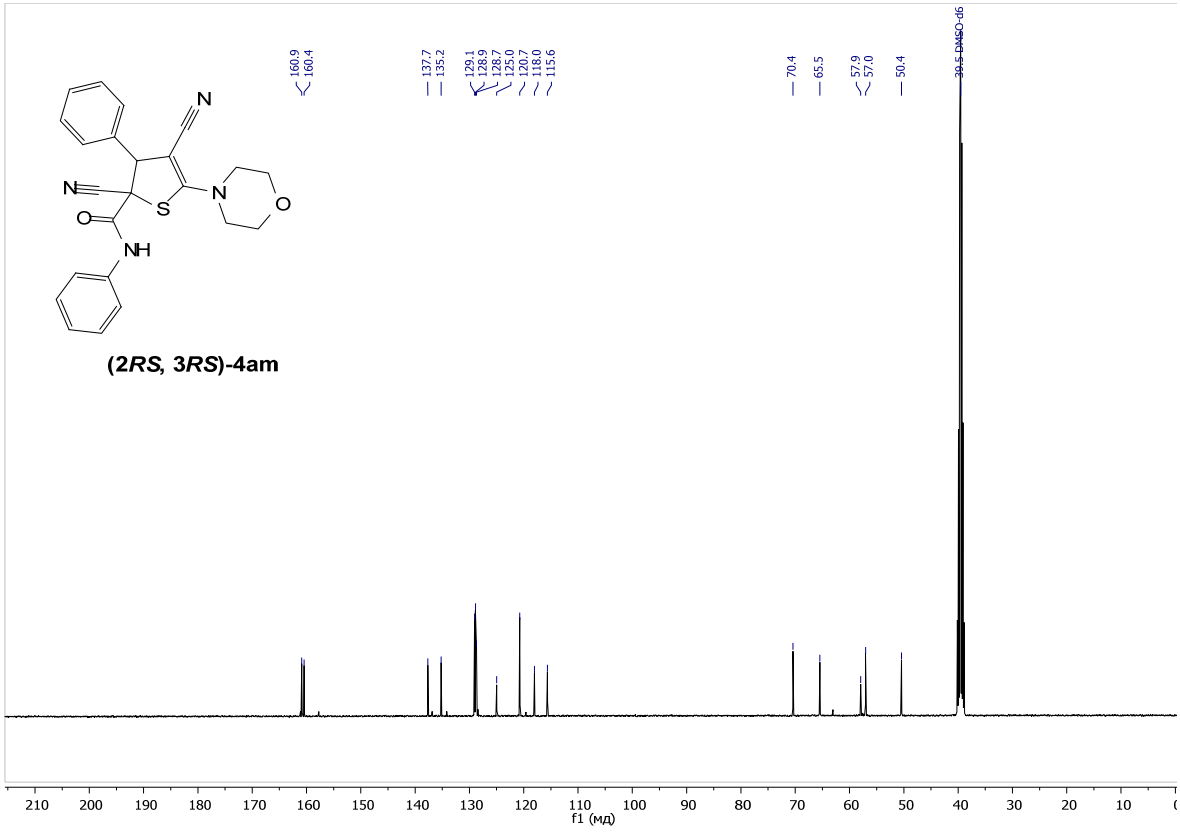
^{19}F NMR (376 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′al**



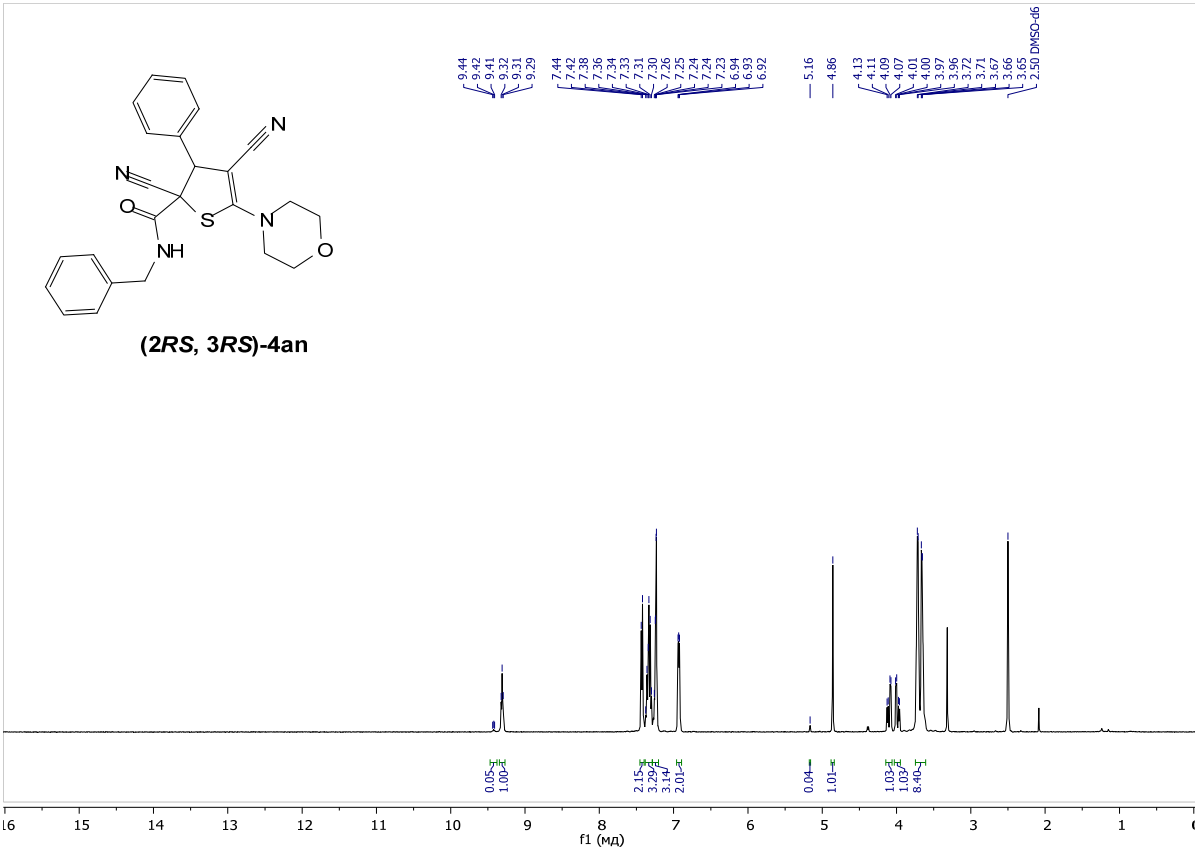
^{13}C{1H} NMR (150 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4′al**



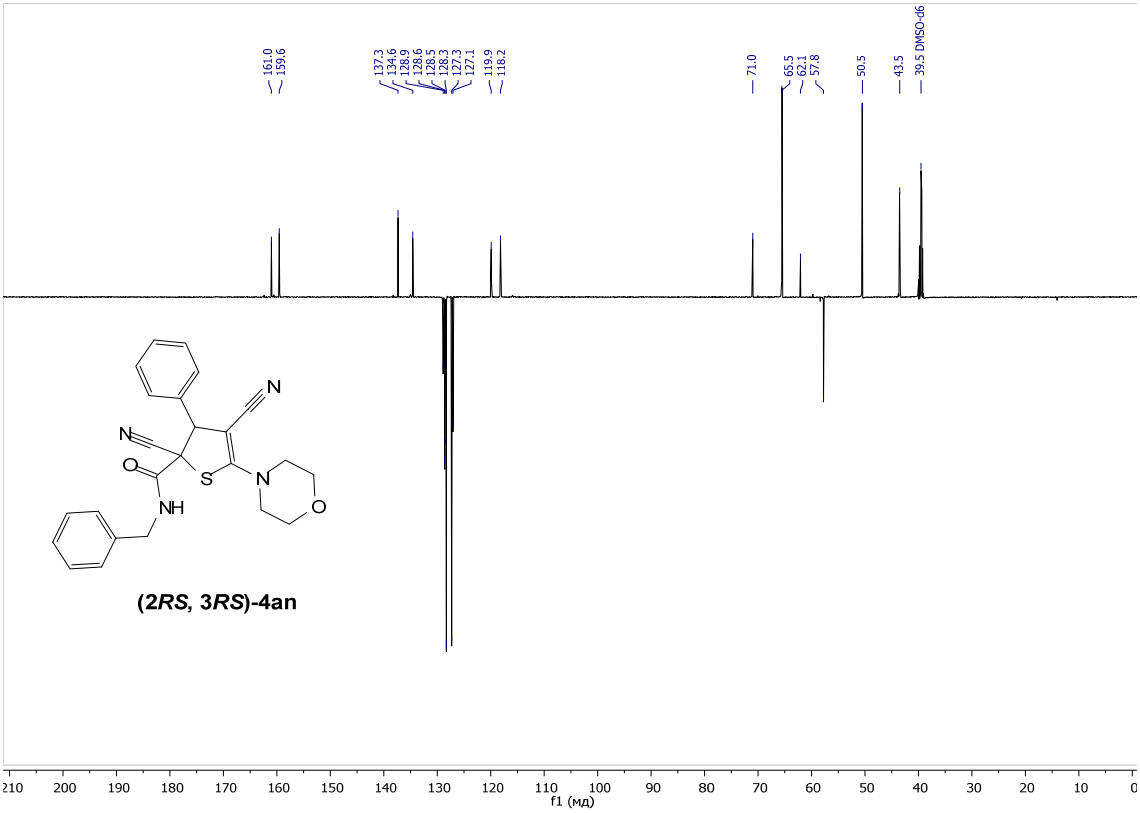
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **(2*RS*,3*RS*)-4am**



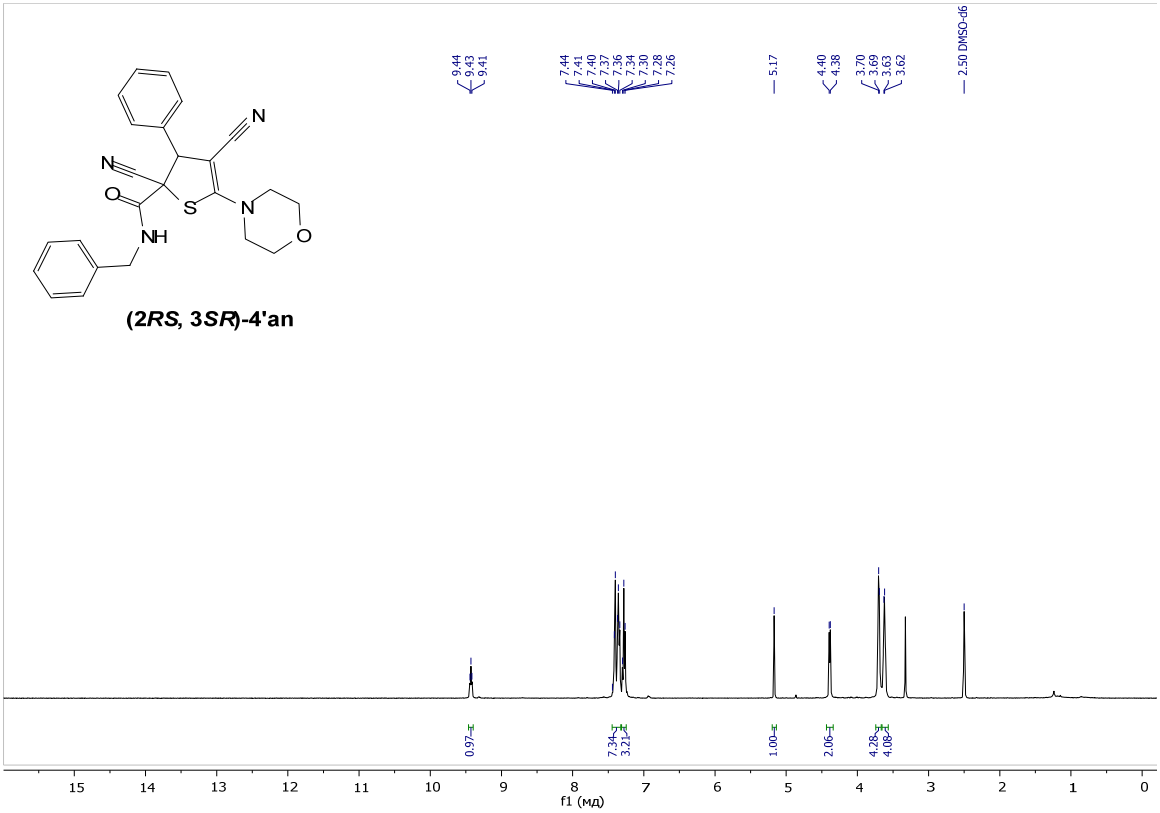
^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **(2*RS*,3*RS*)-4am**



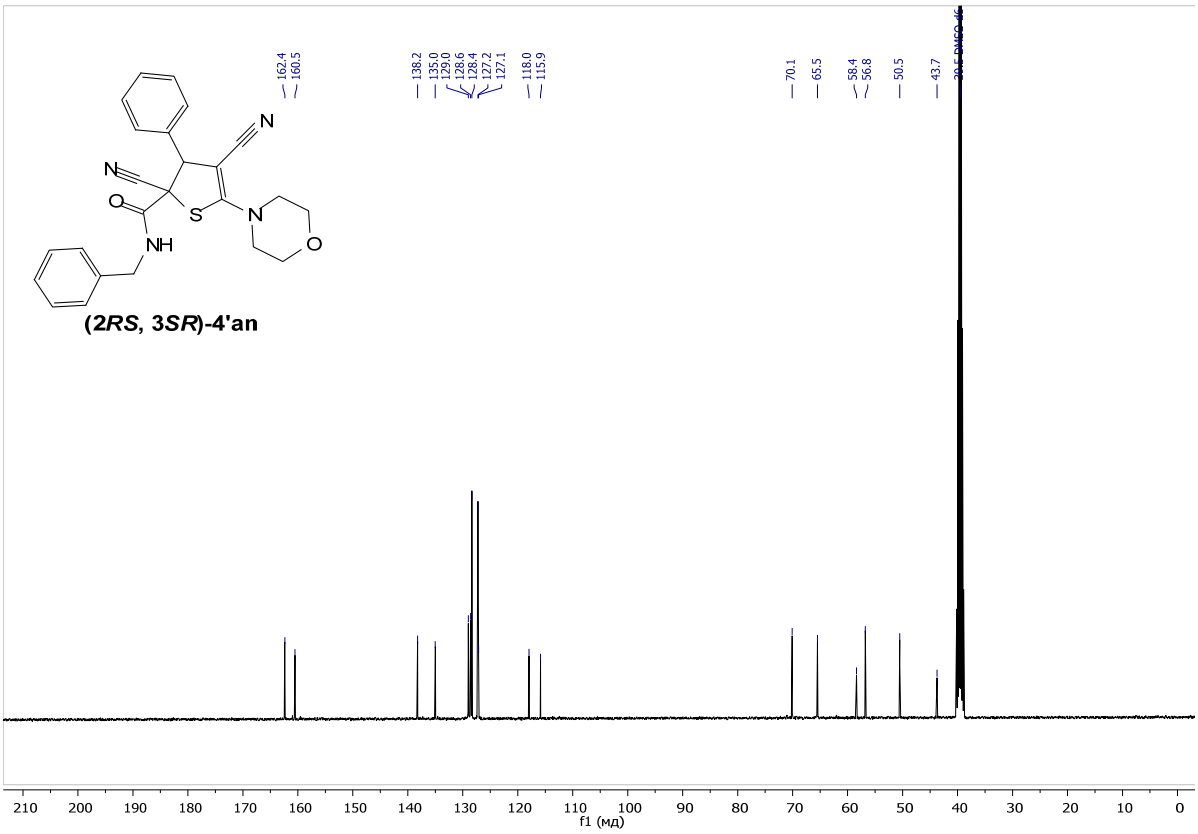
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4an**



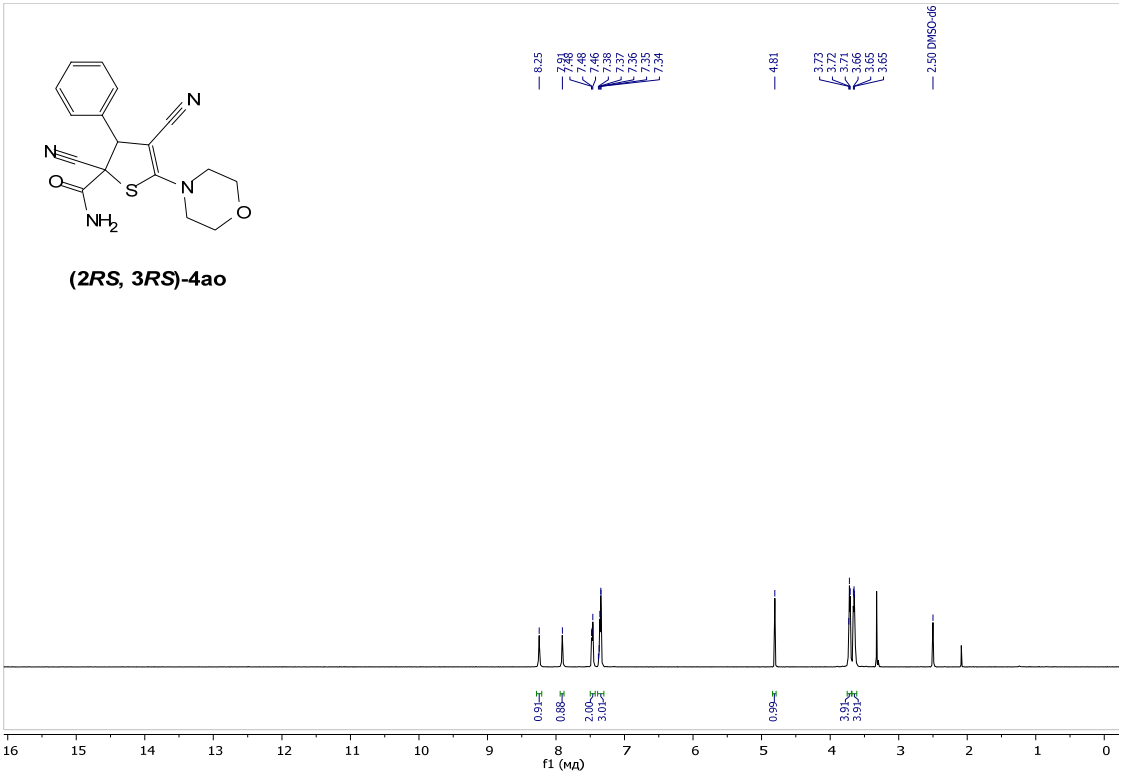
^{13}C{1H} NMR (150 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4an**



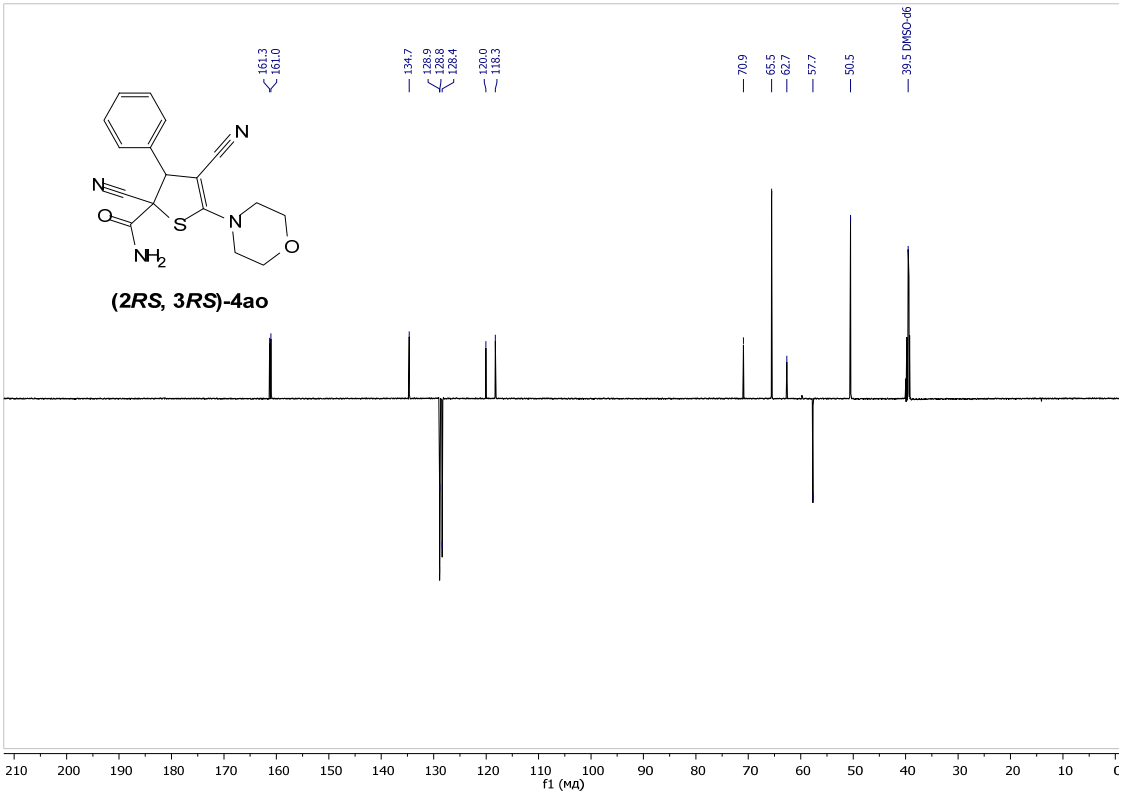
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4′an**



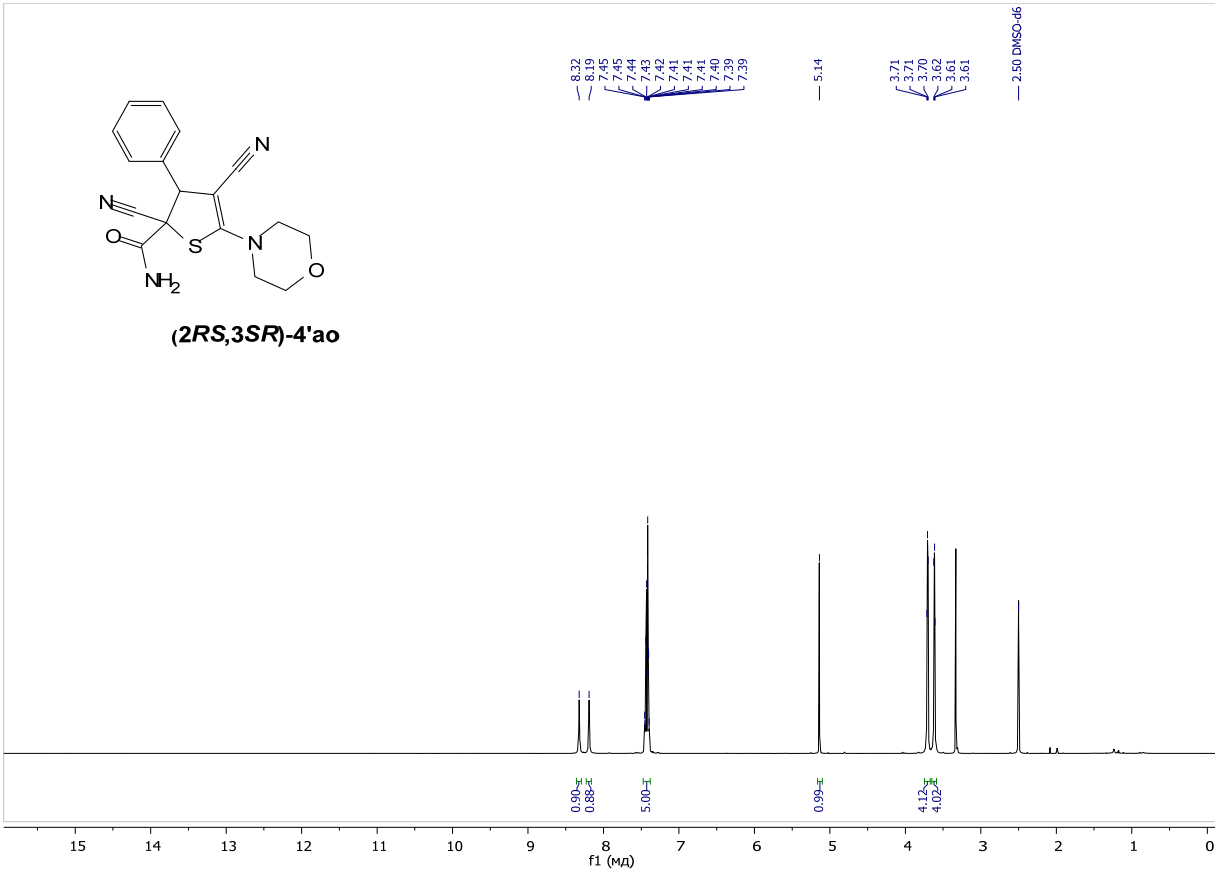
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4′an**



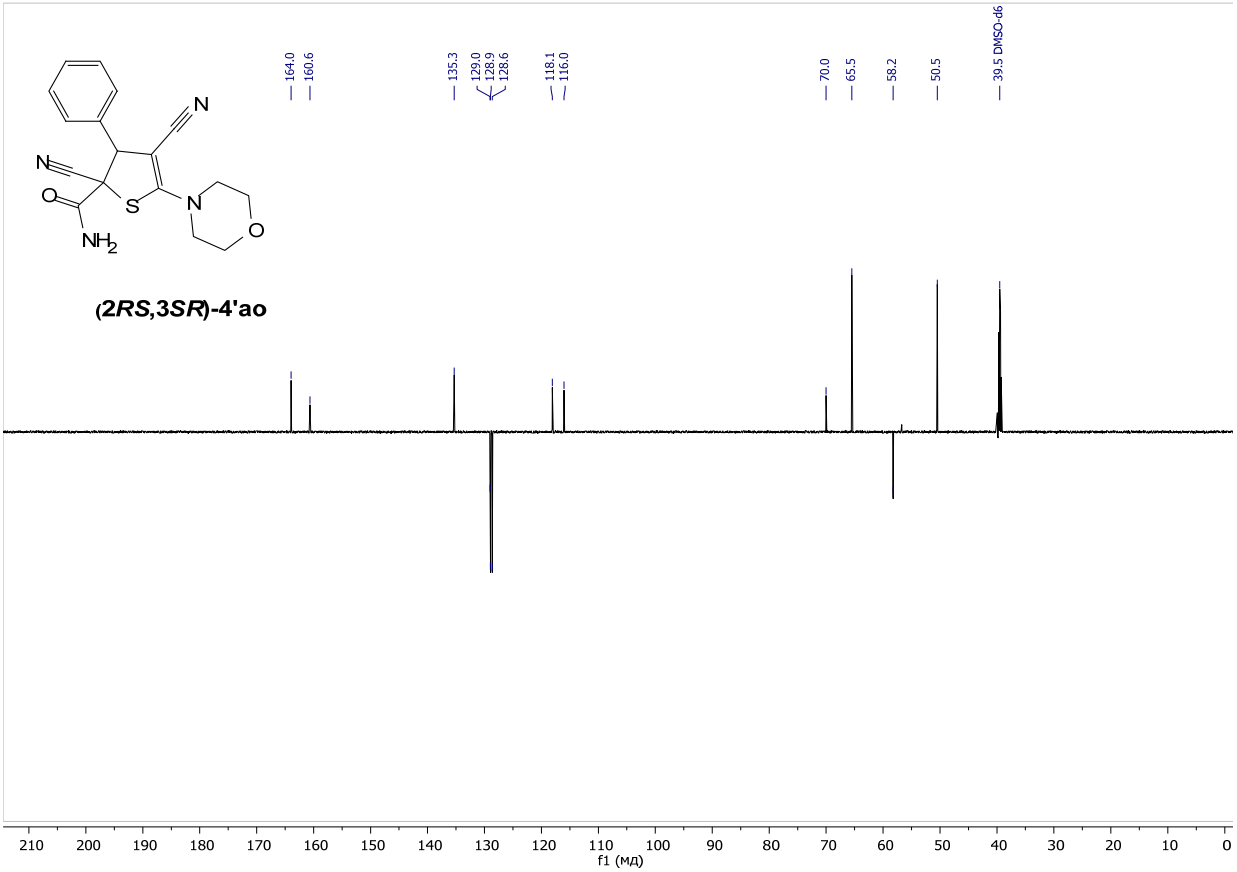
^{1}H NMR (400 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4ao**



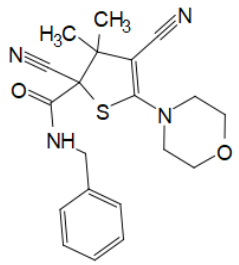
^{13}C{1H} NMR (150 MHz, DMSO–d_6) of **(2*RS*,3*RS*)-4ao**



^{1}H NMR (600 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4′ao**

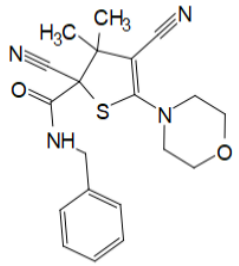


^{13}C{1H} NMR (150 MHz, DMSO–d_6) of **(2*RS*,3*SR*)-4′ao**



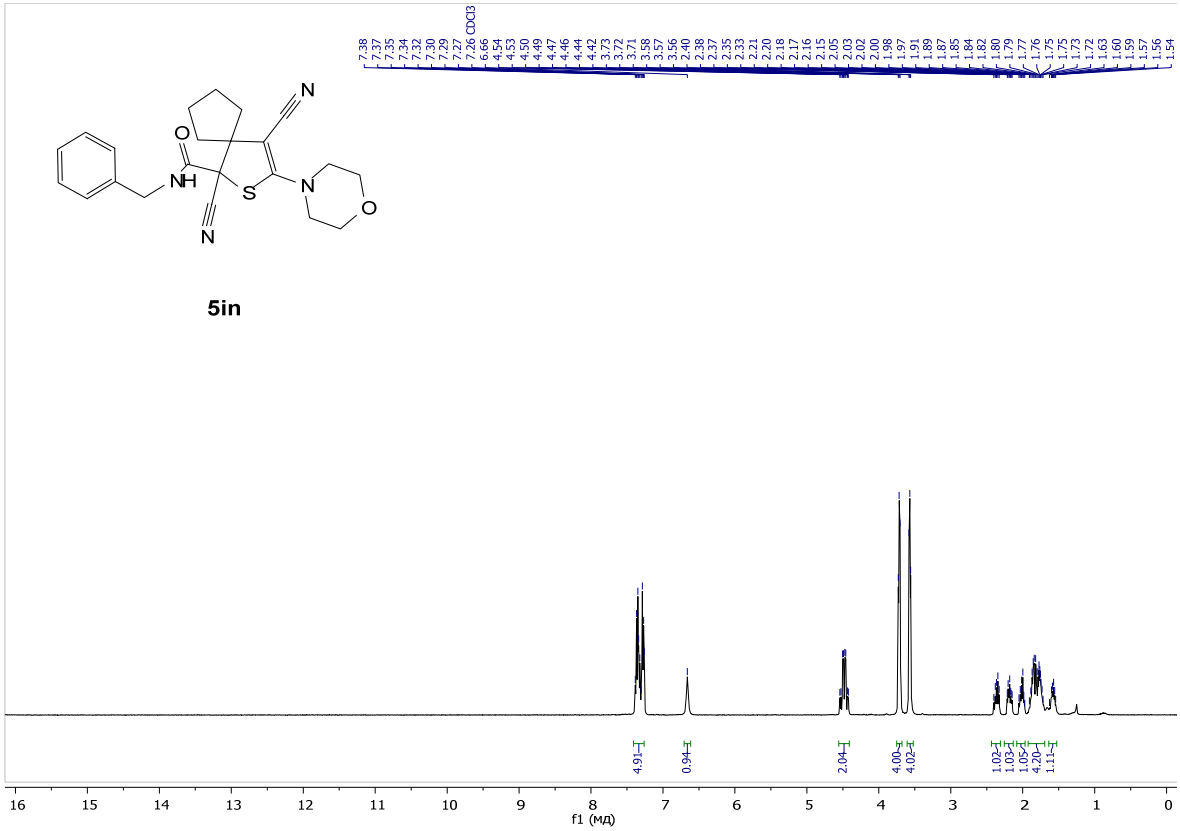
5hn

^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **5hn**

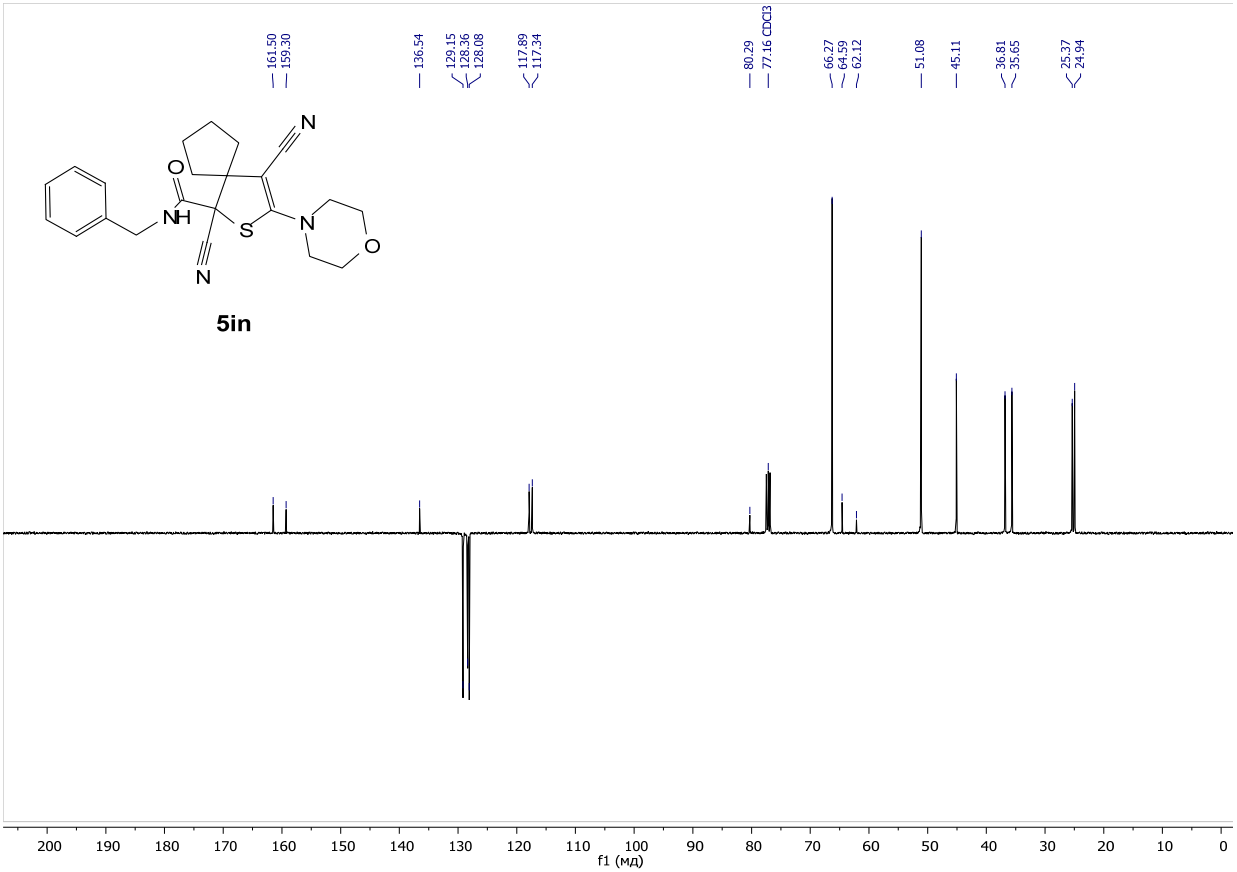


5hn

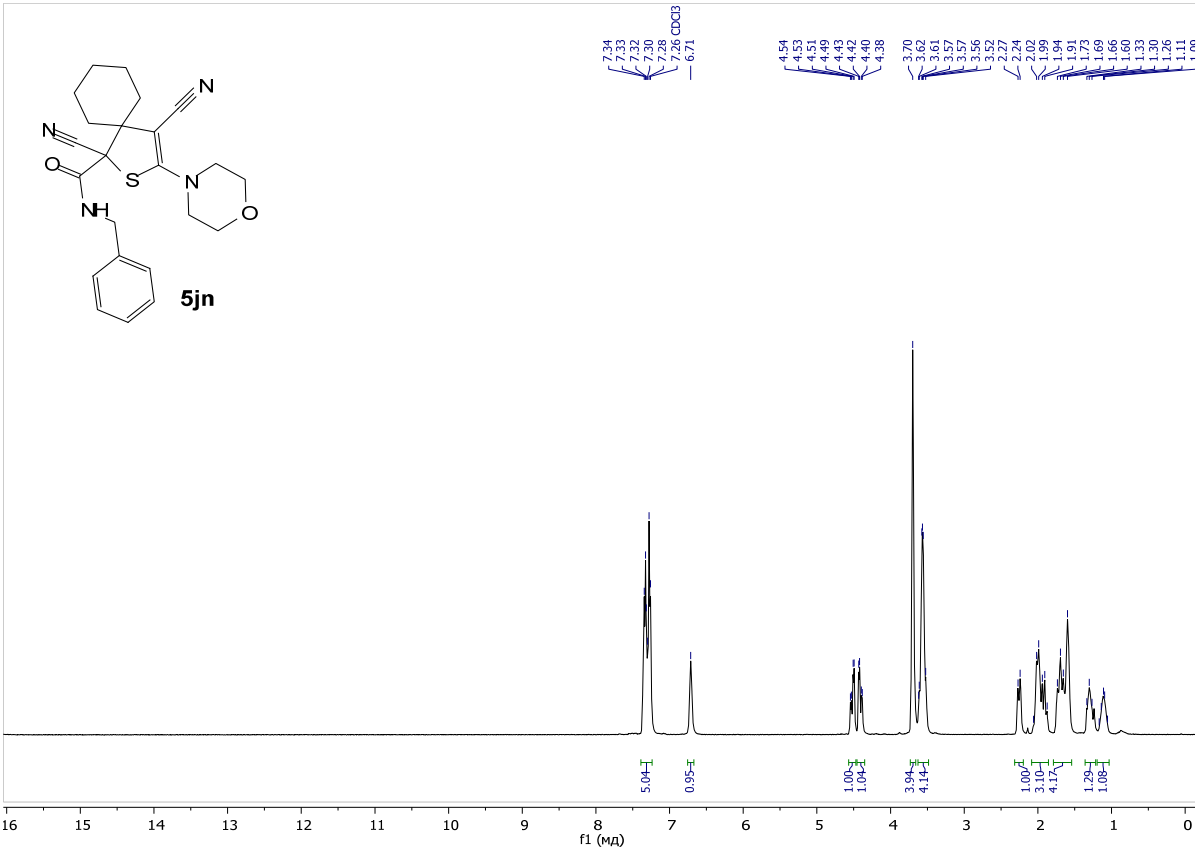
^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **5hn**



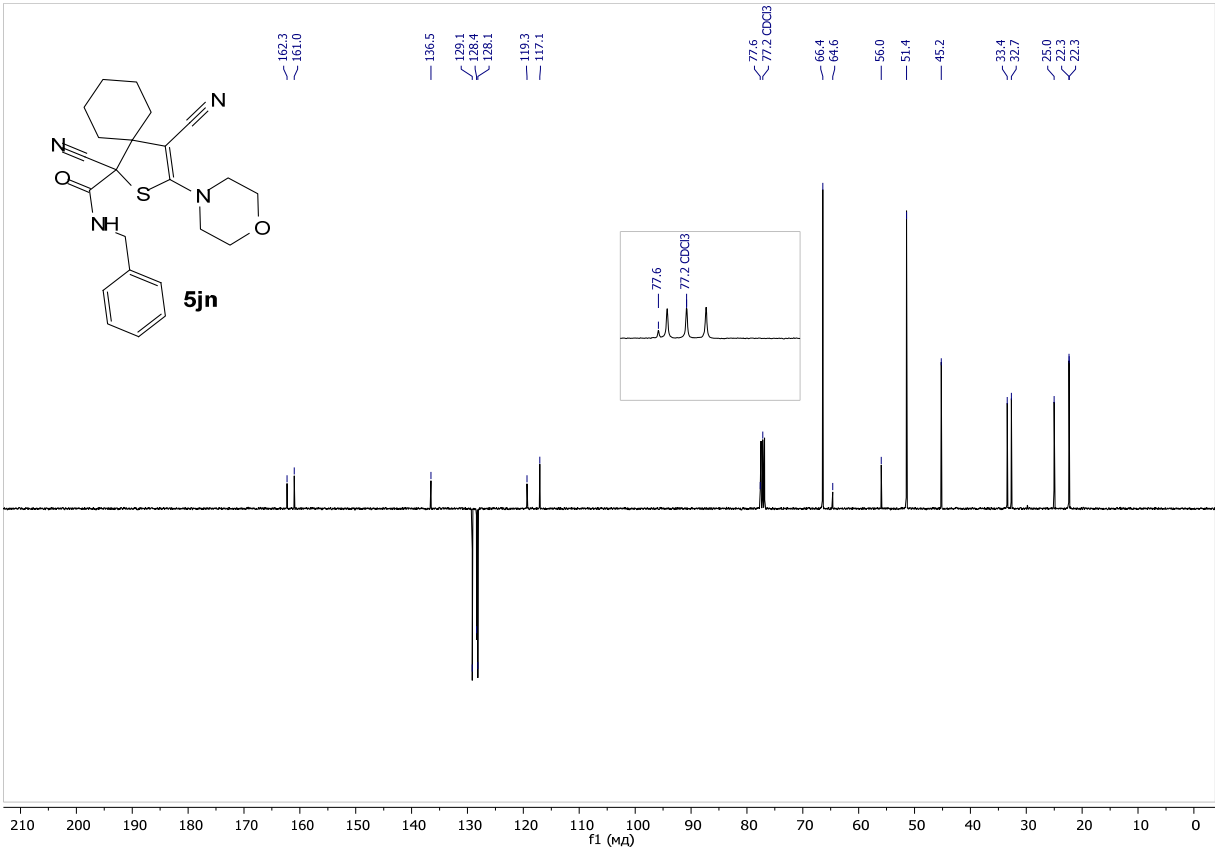
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5in**



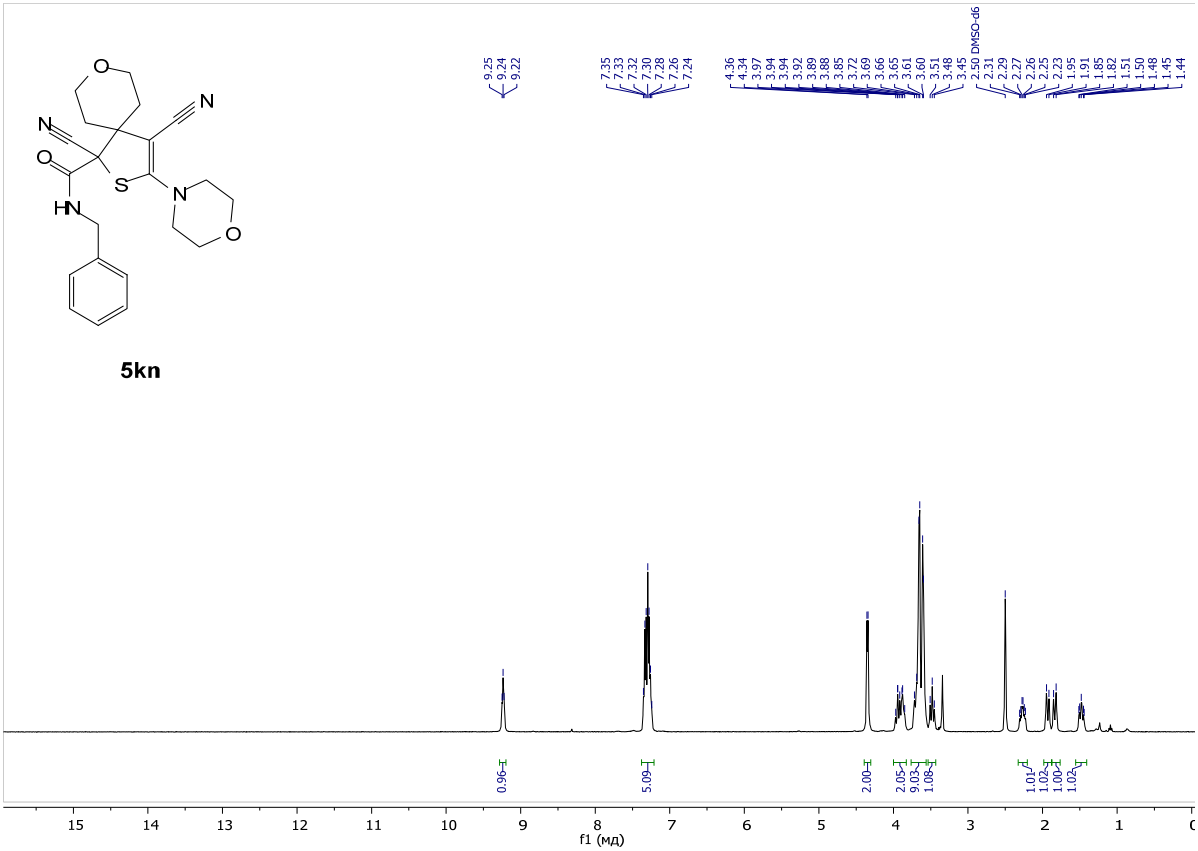
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5in**



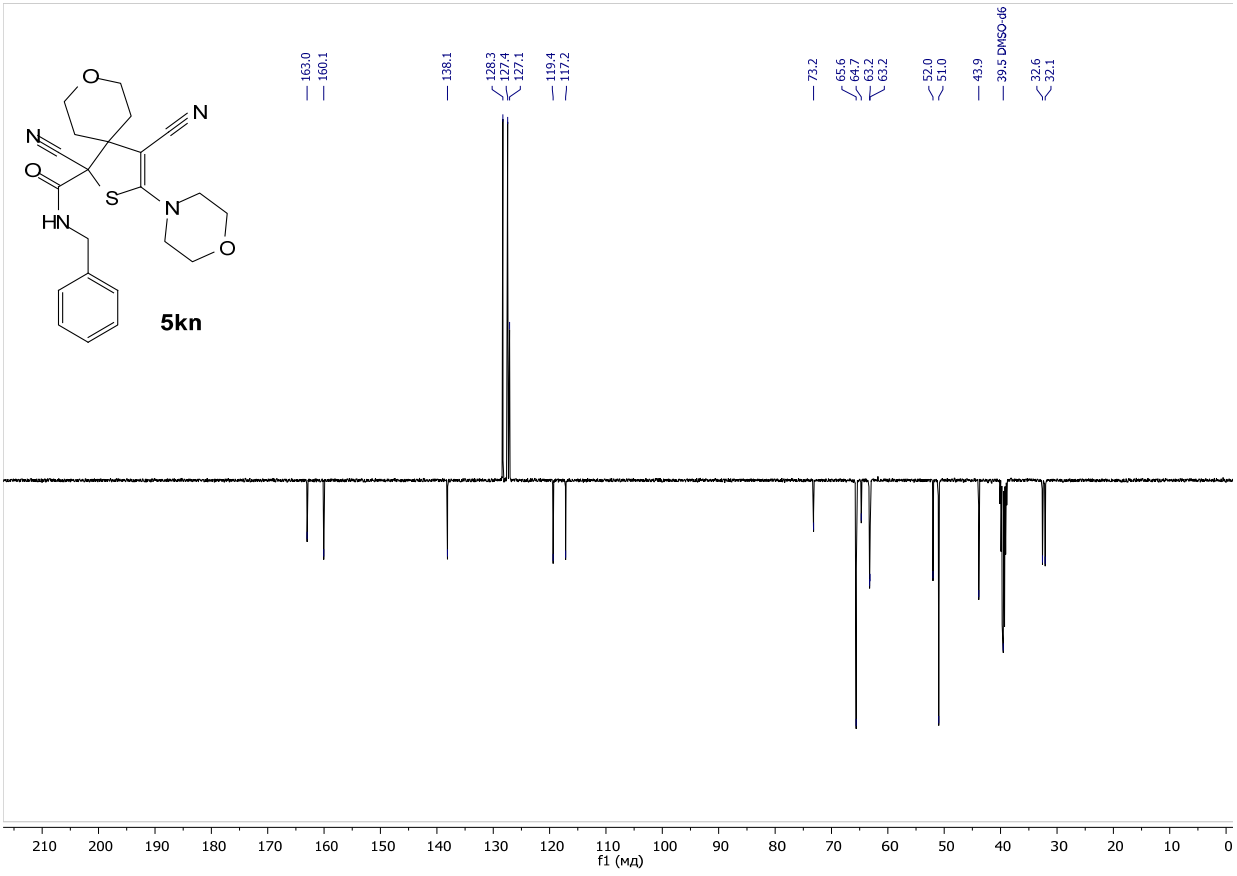
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5jn**



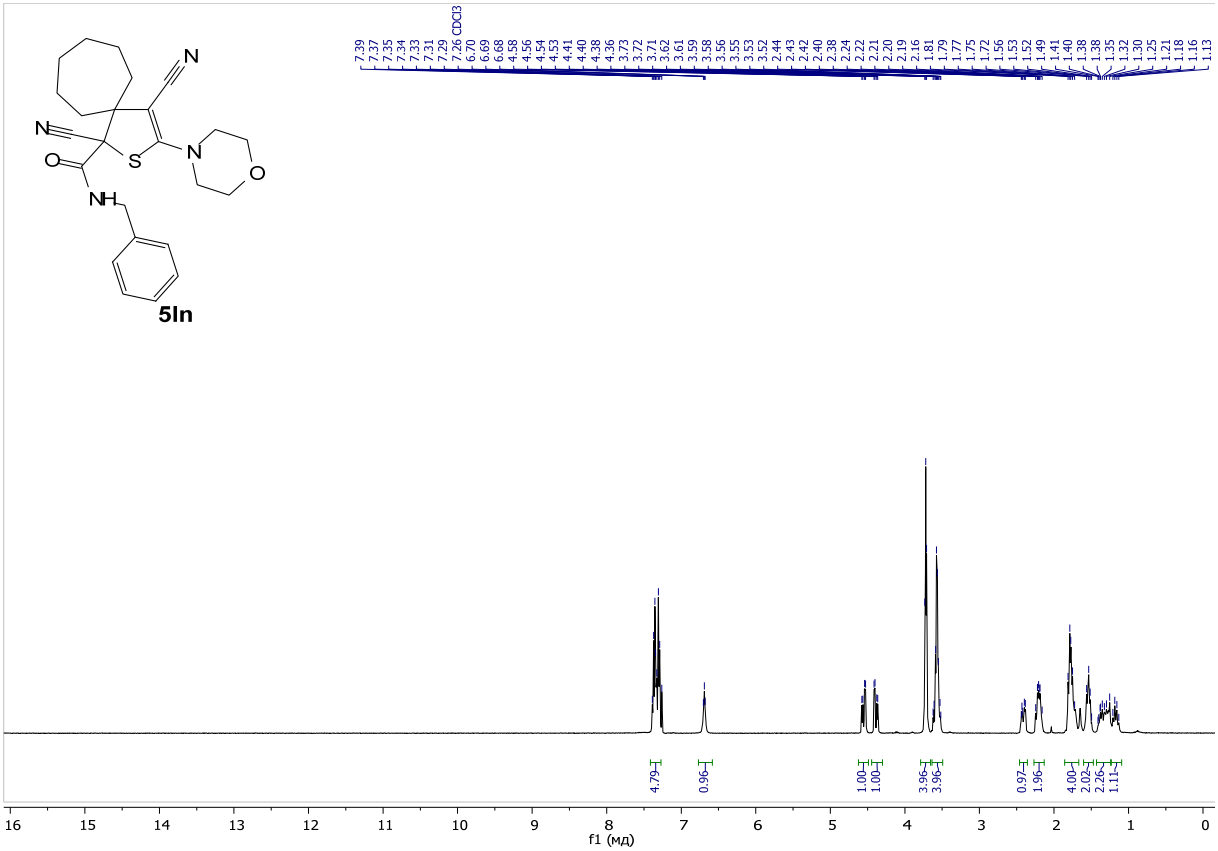
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5jn**



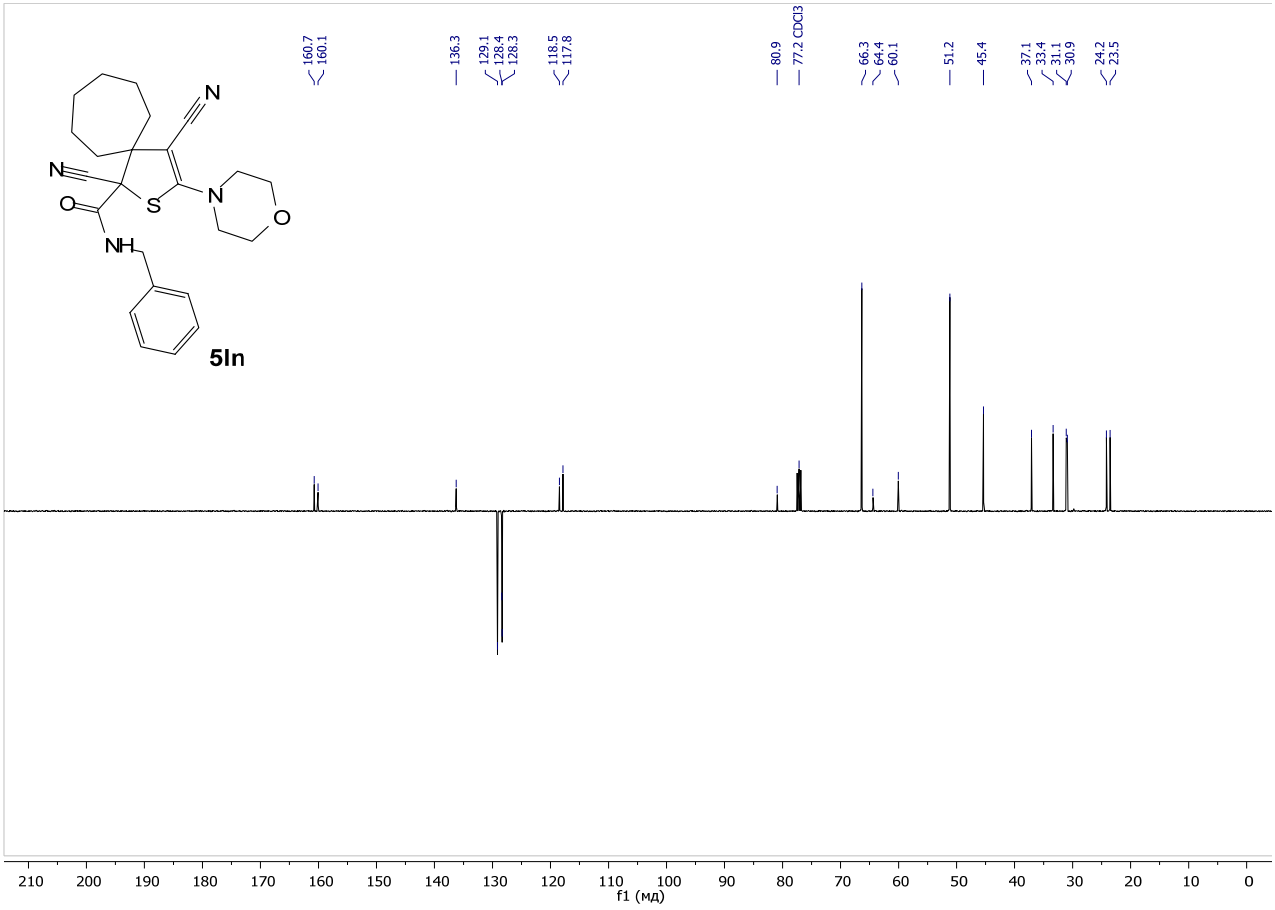
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **5kn**



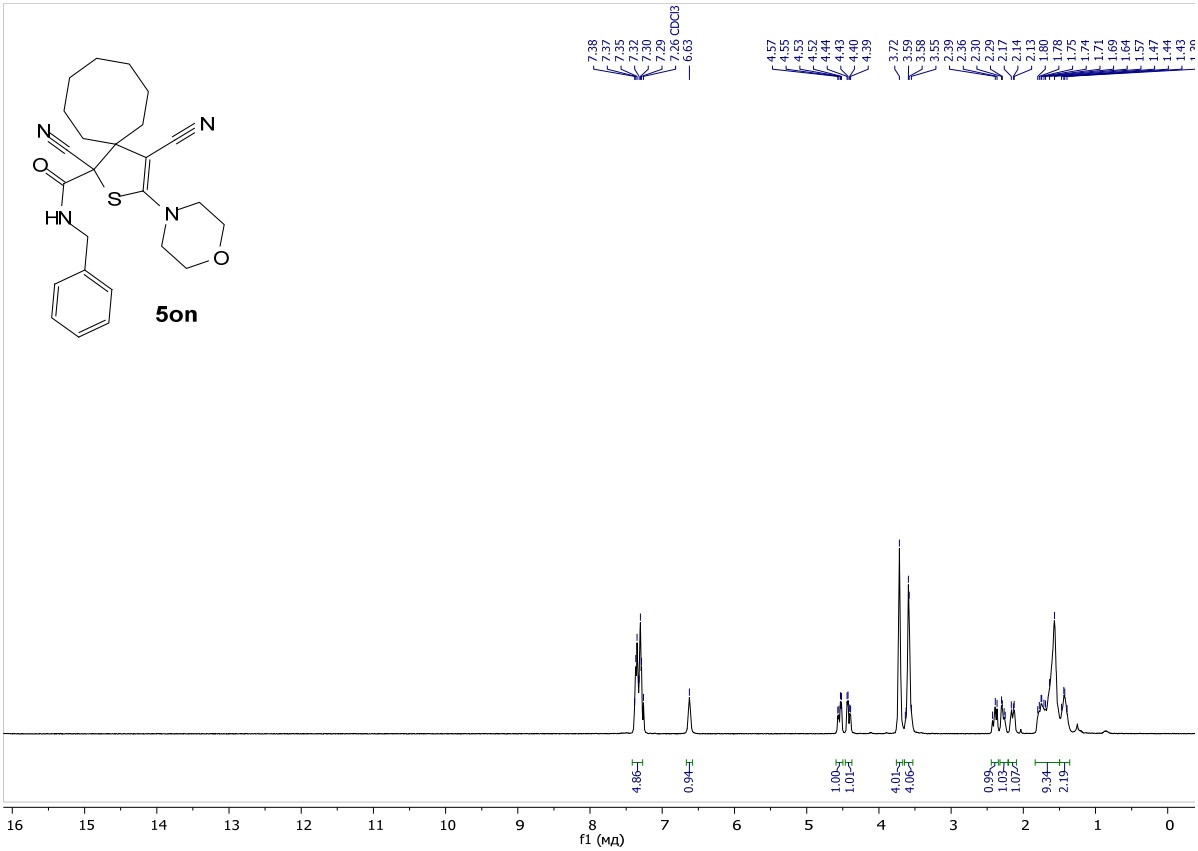
^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **5kn**



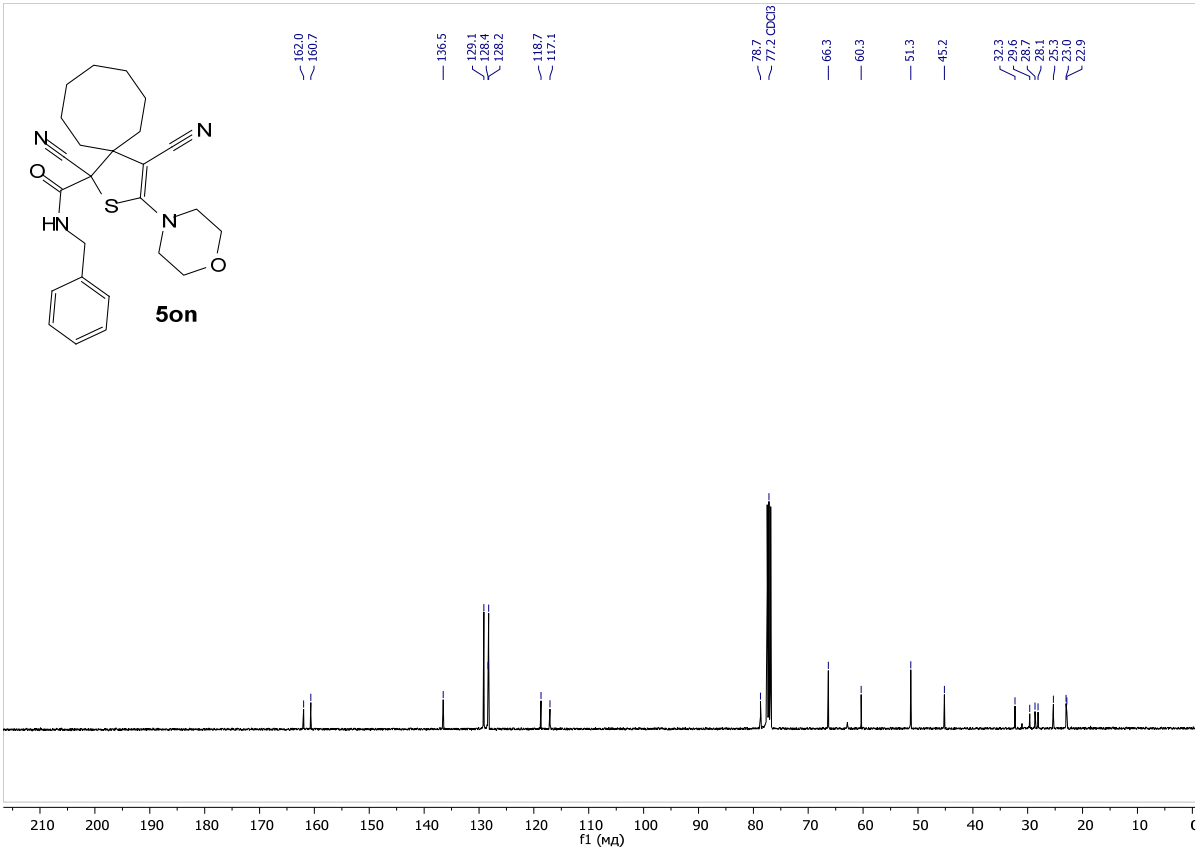
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ln**



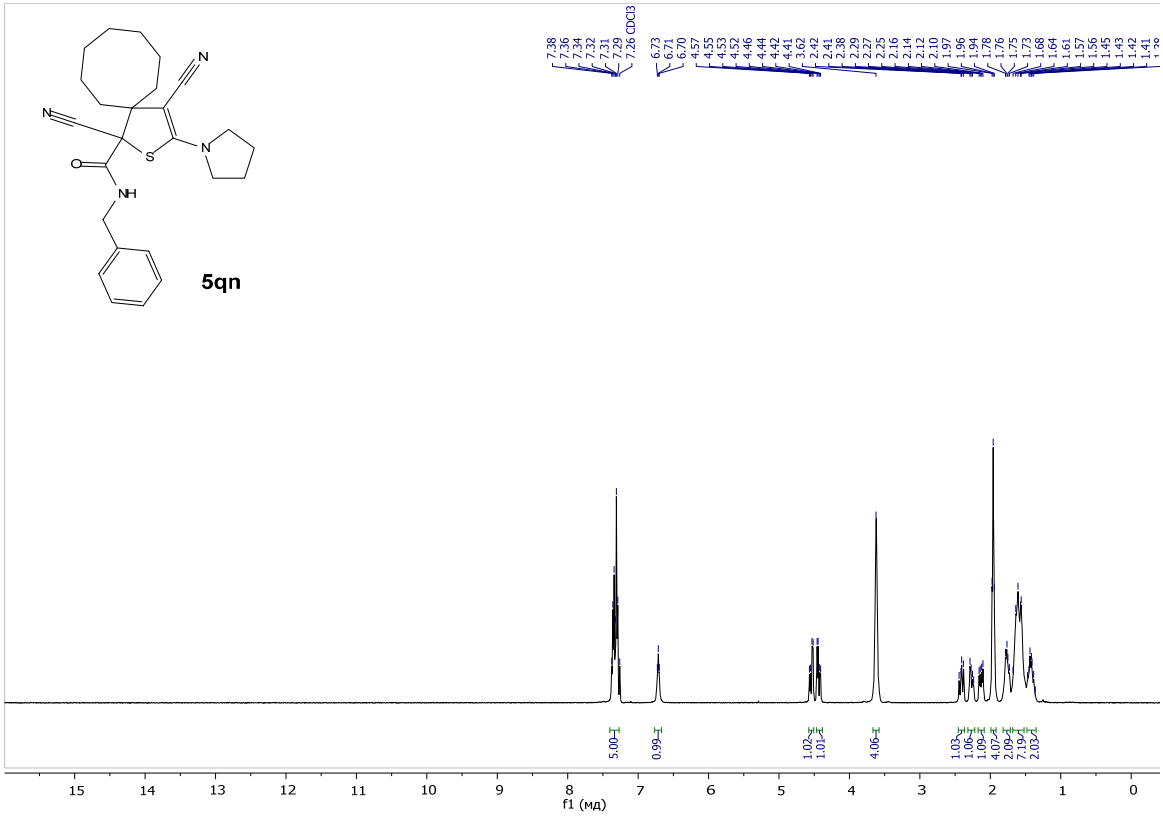
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5ln**



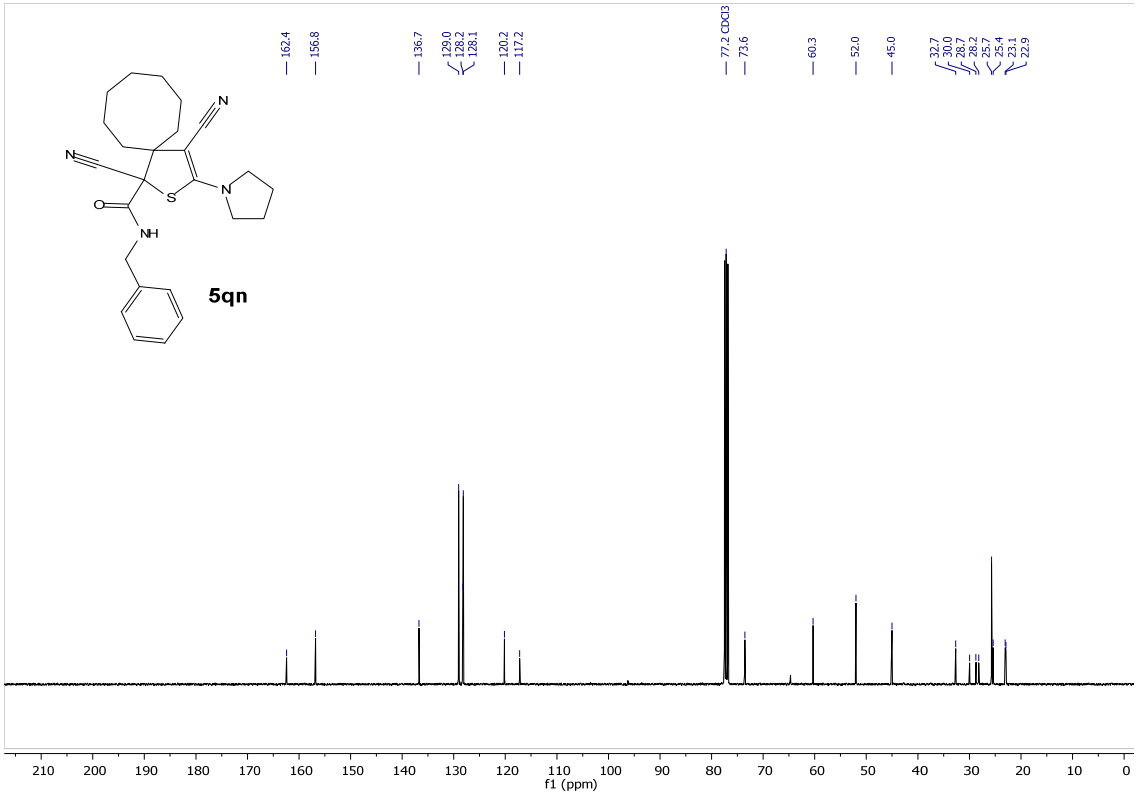
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5on**



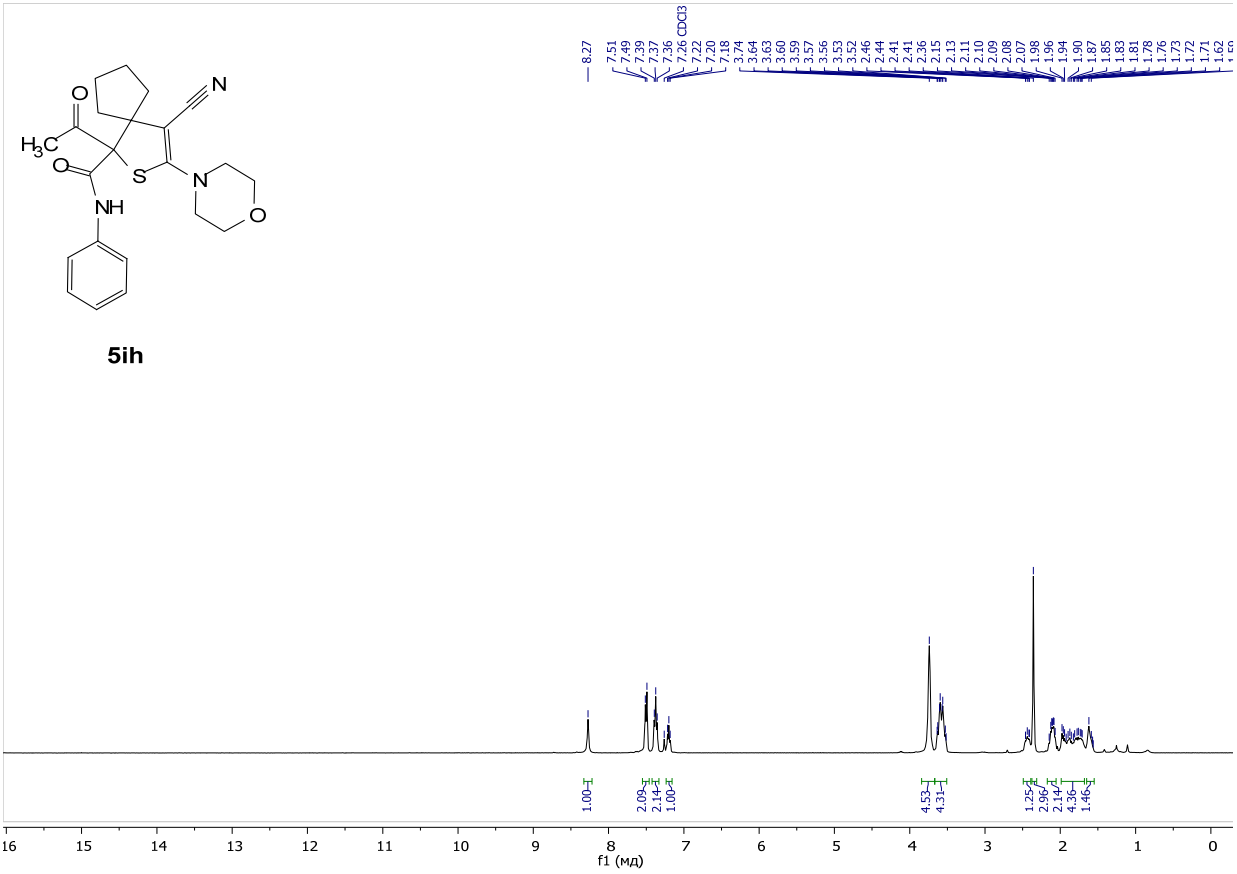
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5on**



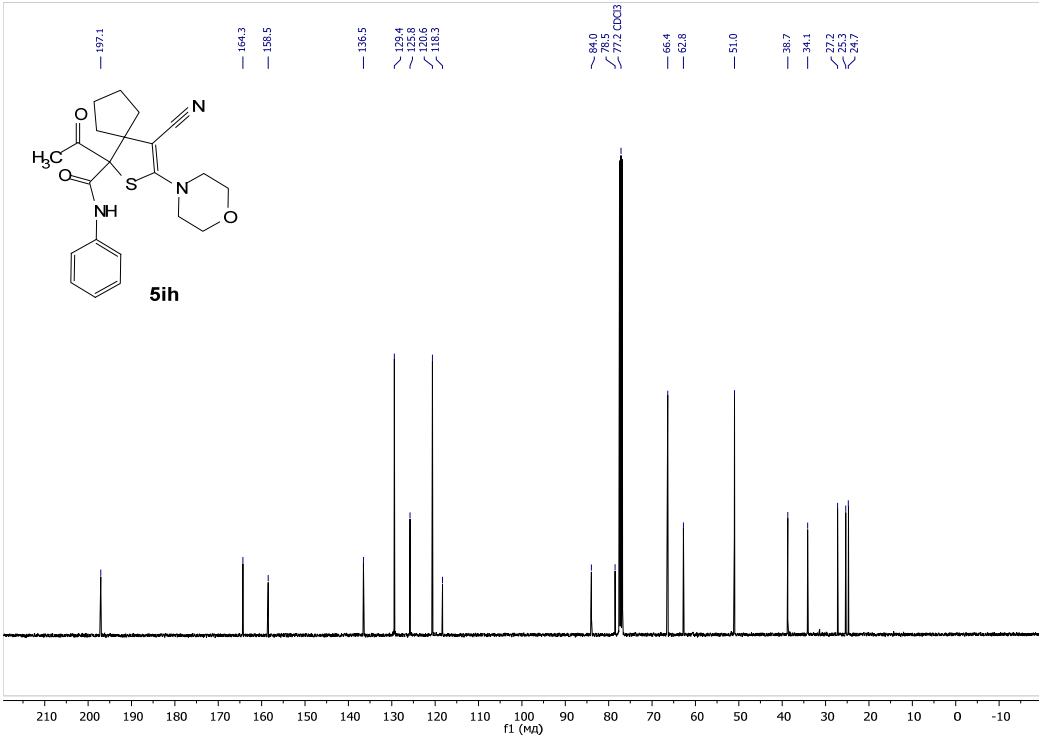
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5qn**



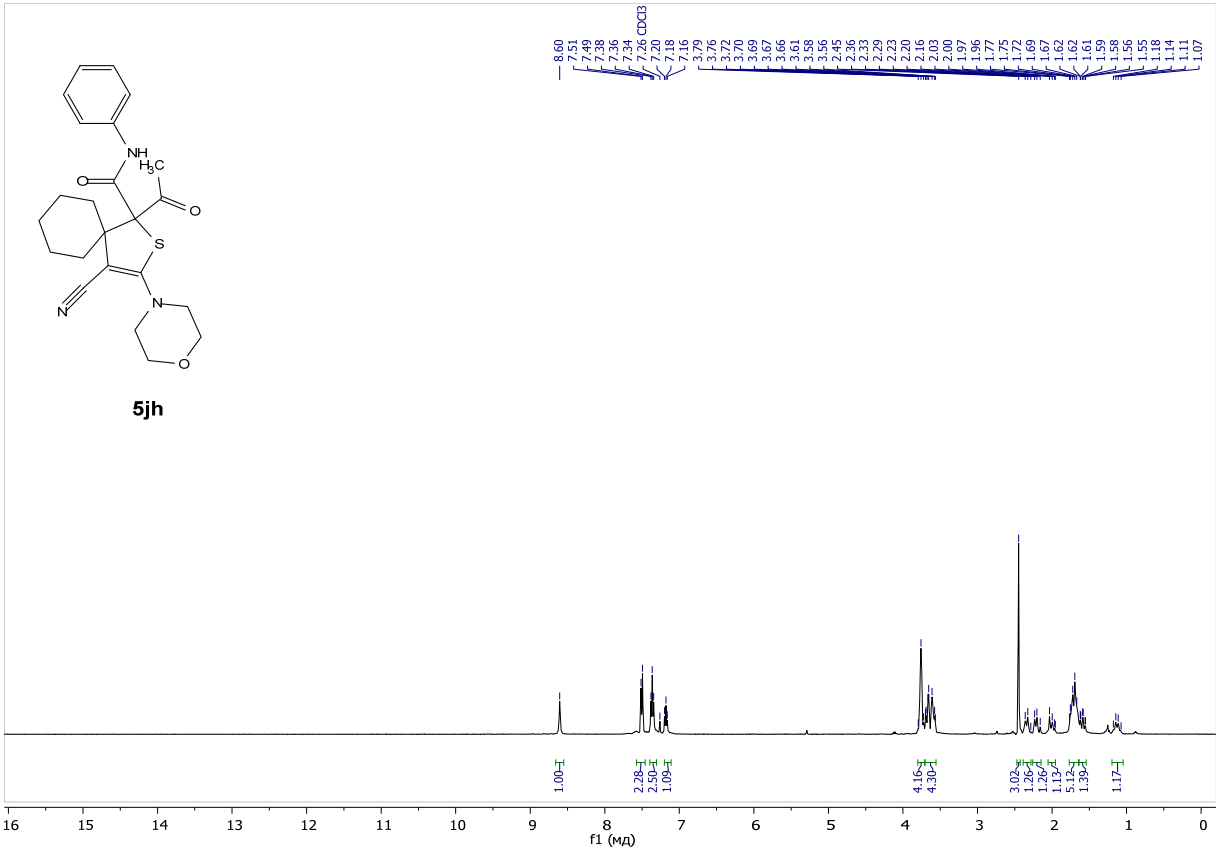
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5qn**



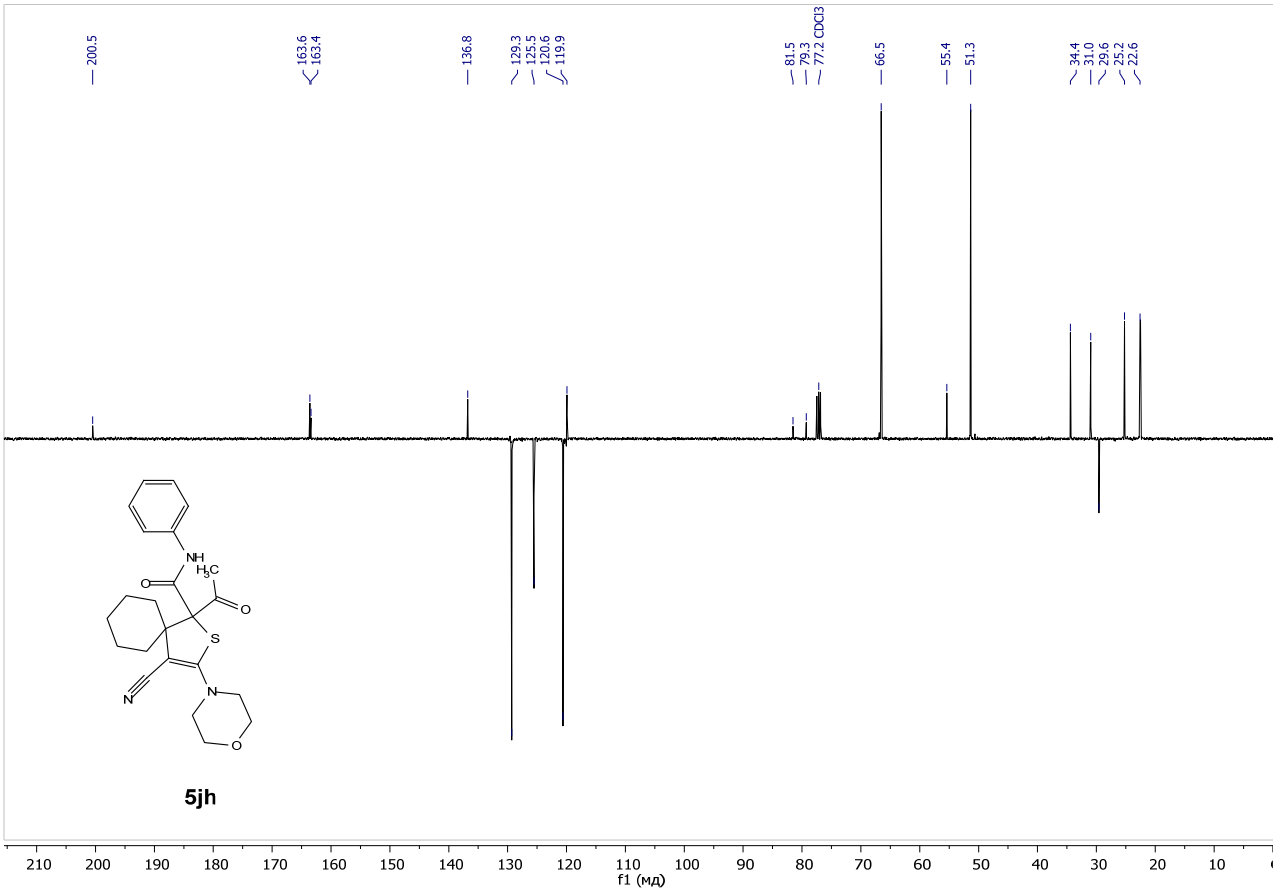
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ih**



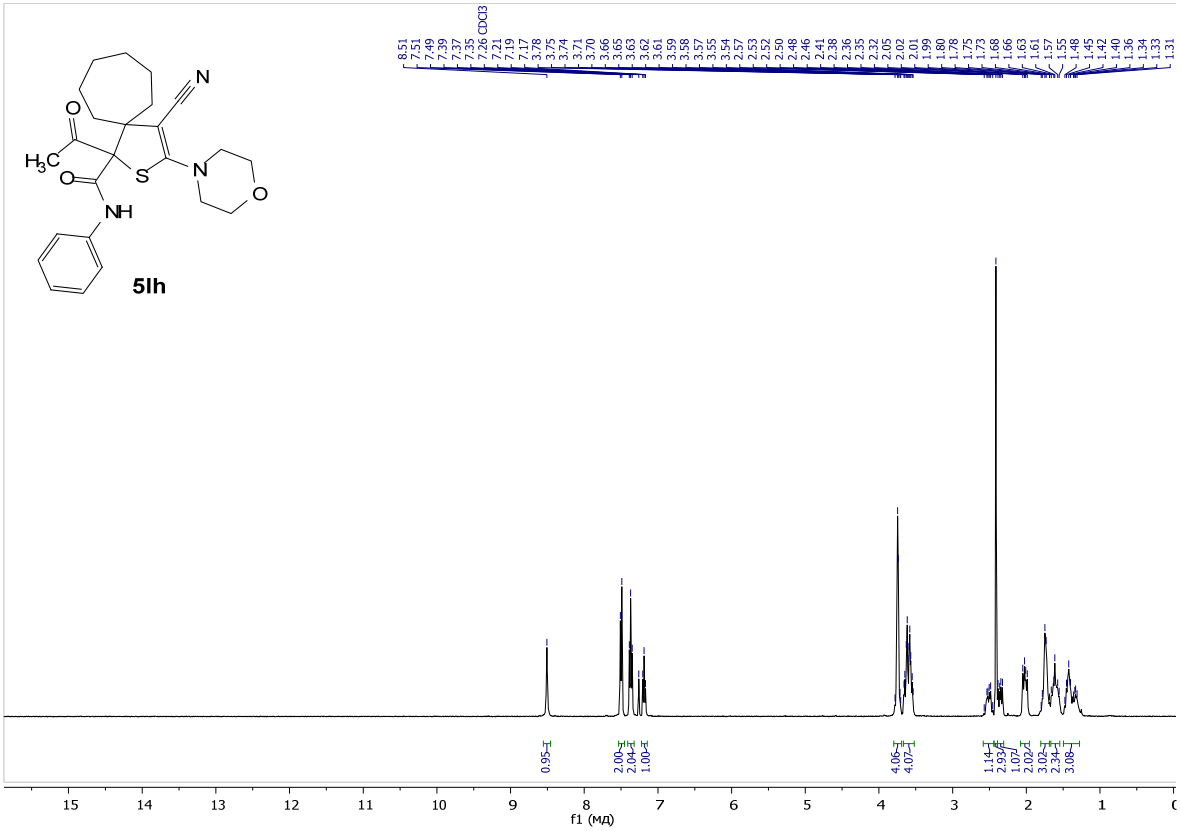
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5ih**



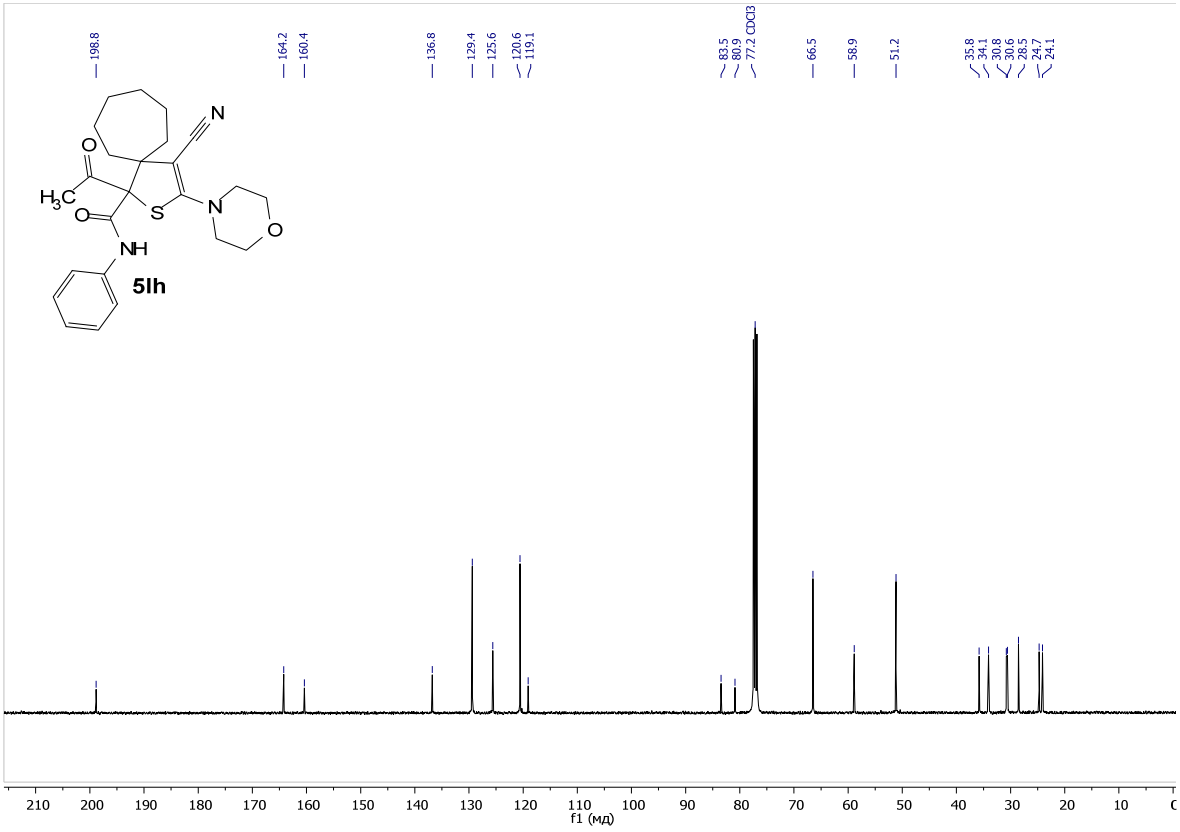
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5jh**



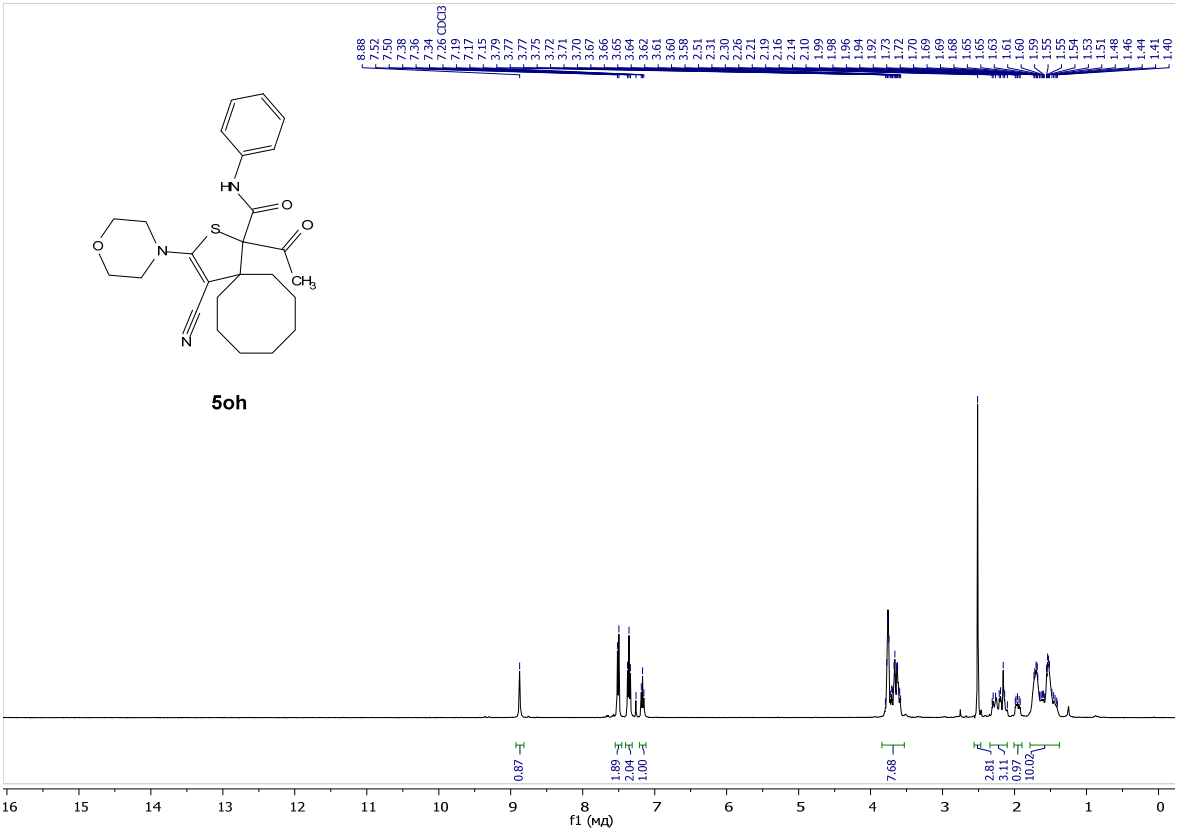
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5jh**



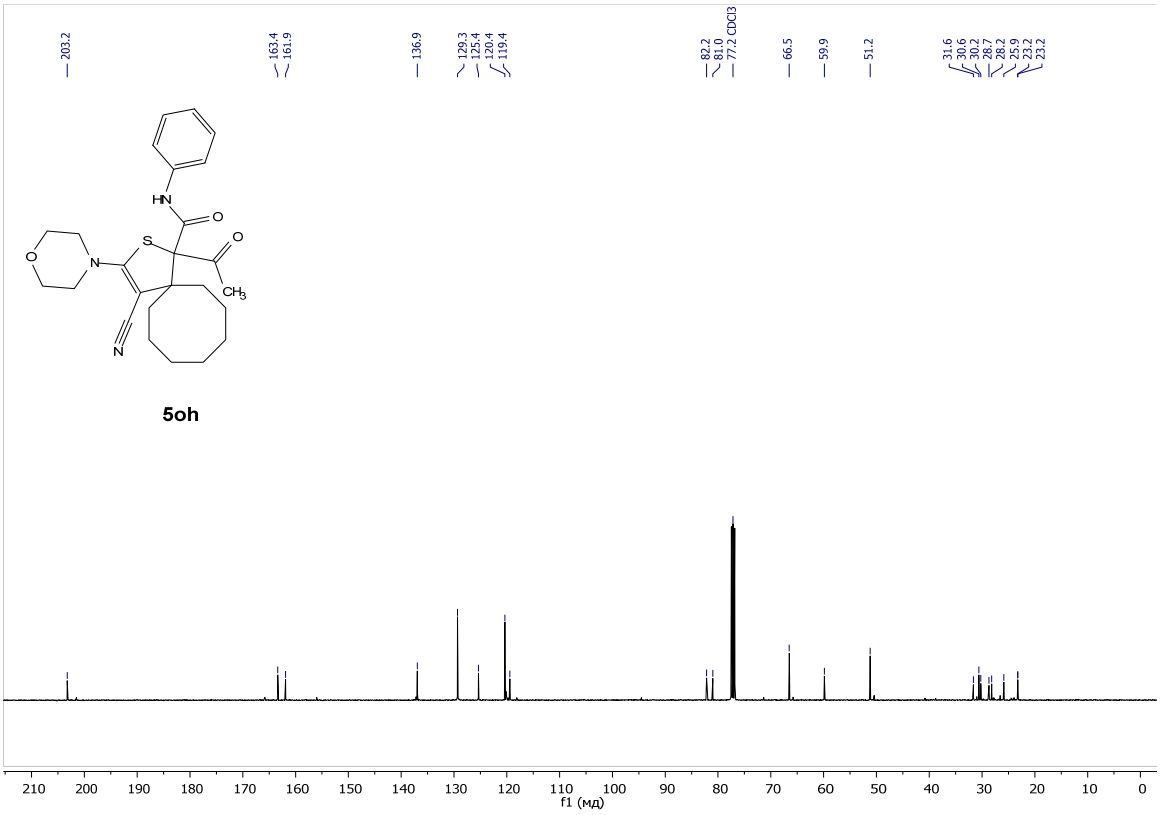
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5lh**



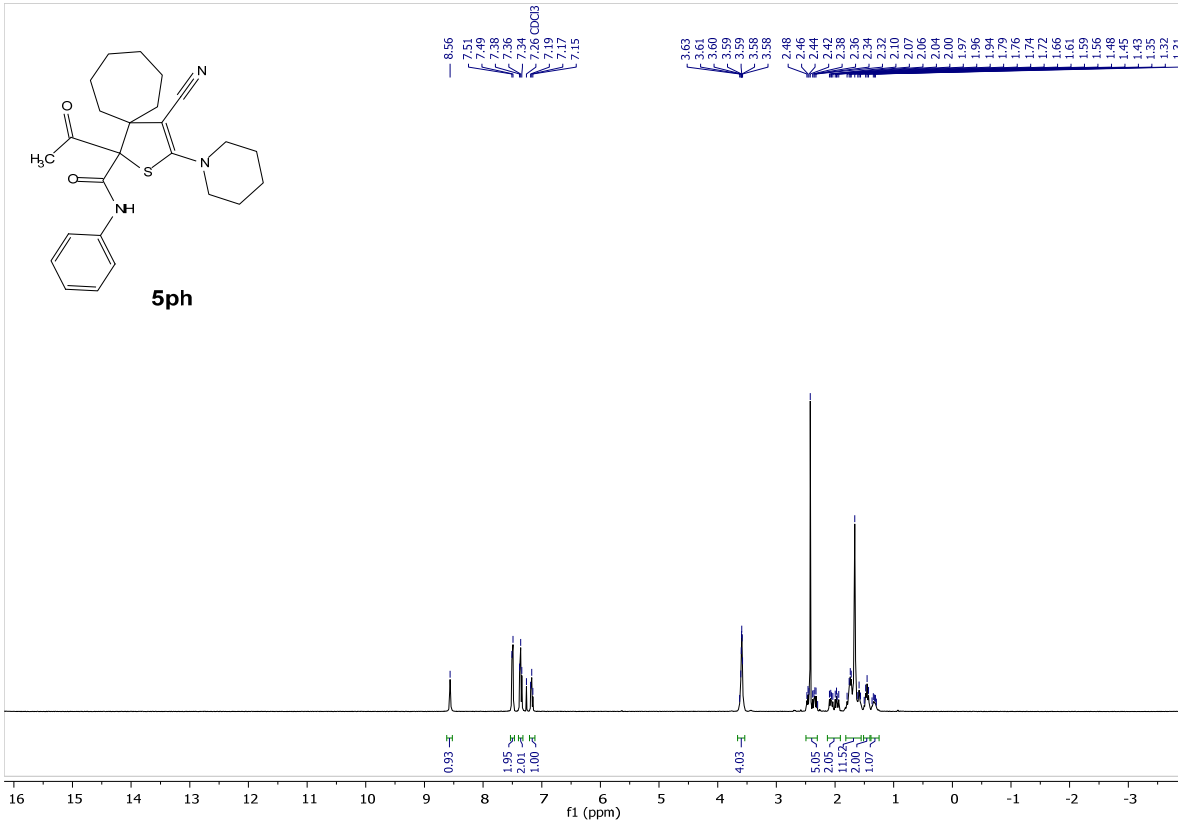
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5lh**



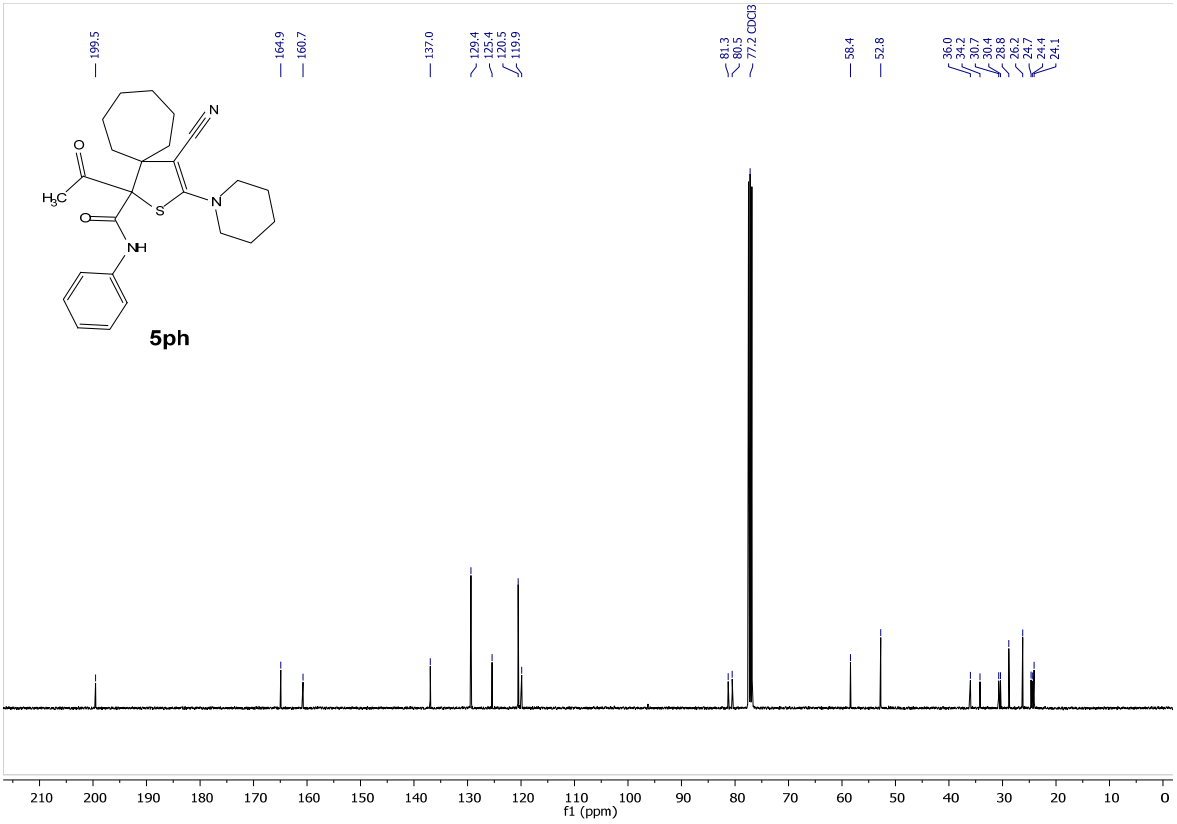
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5oh**



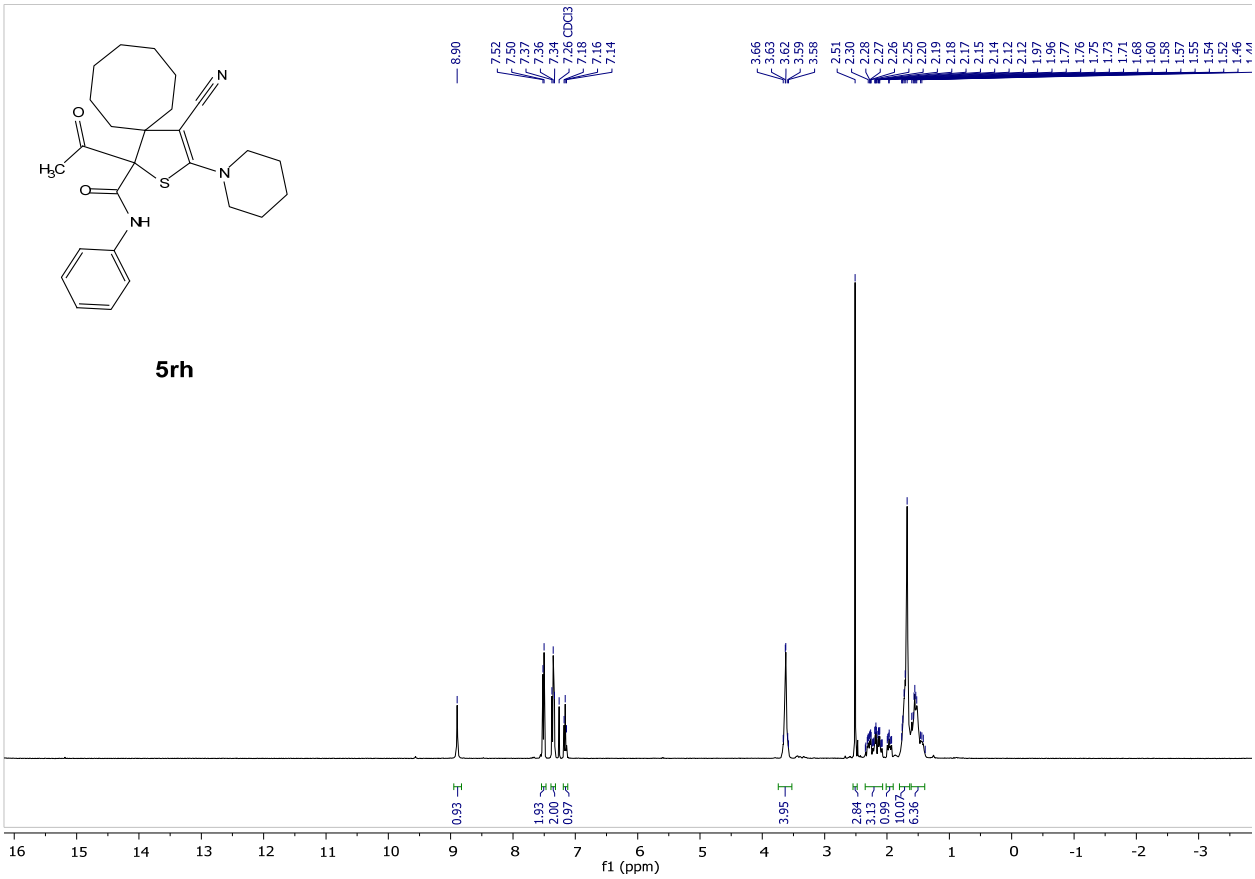
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5oh**



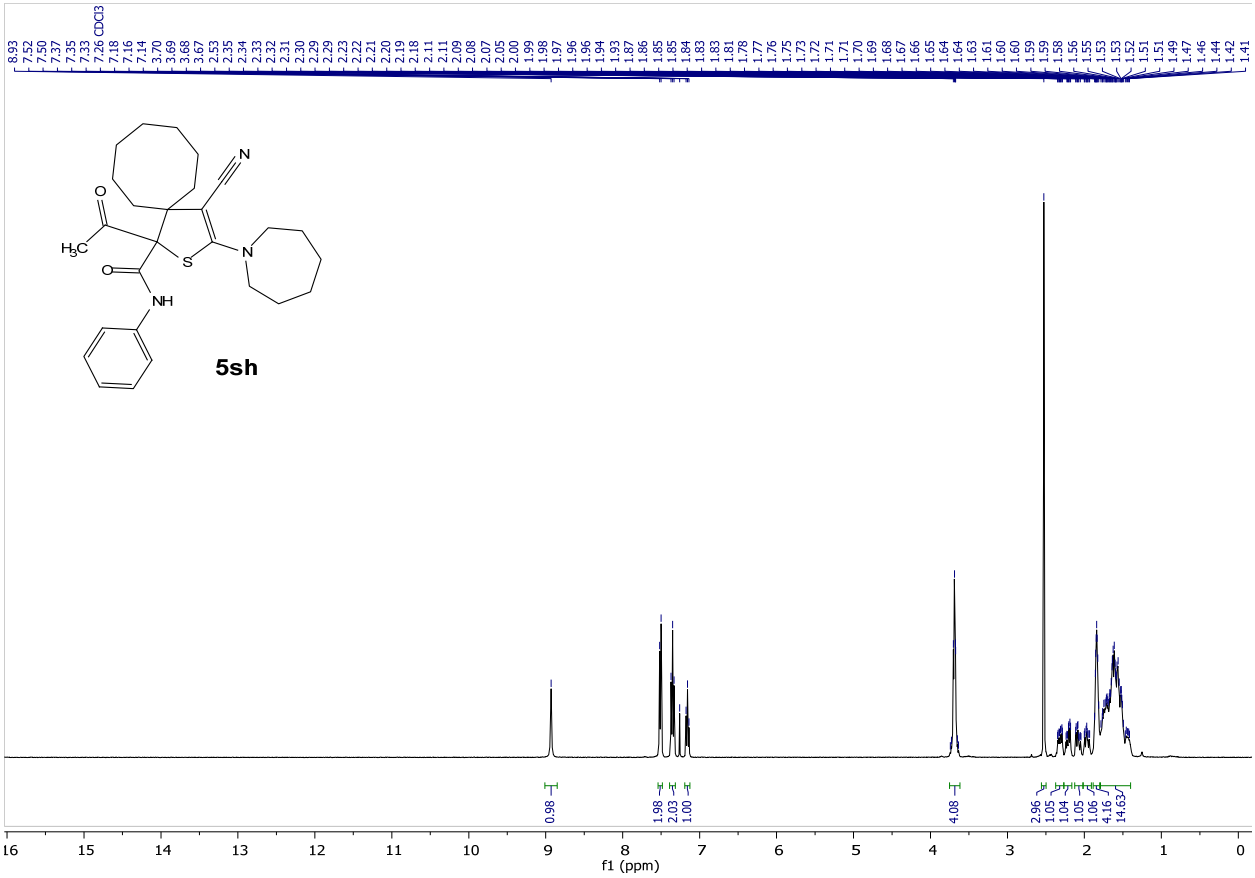
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ph**



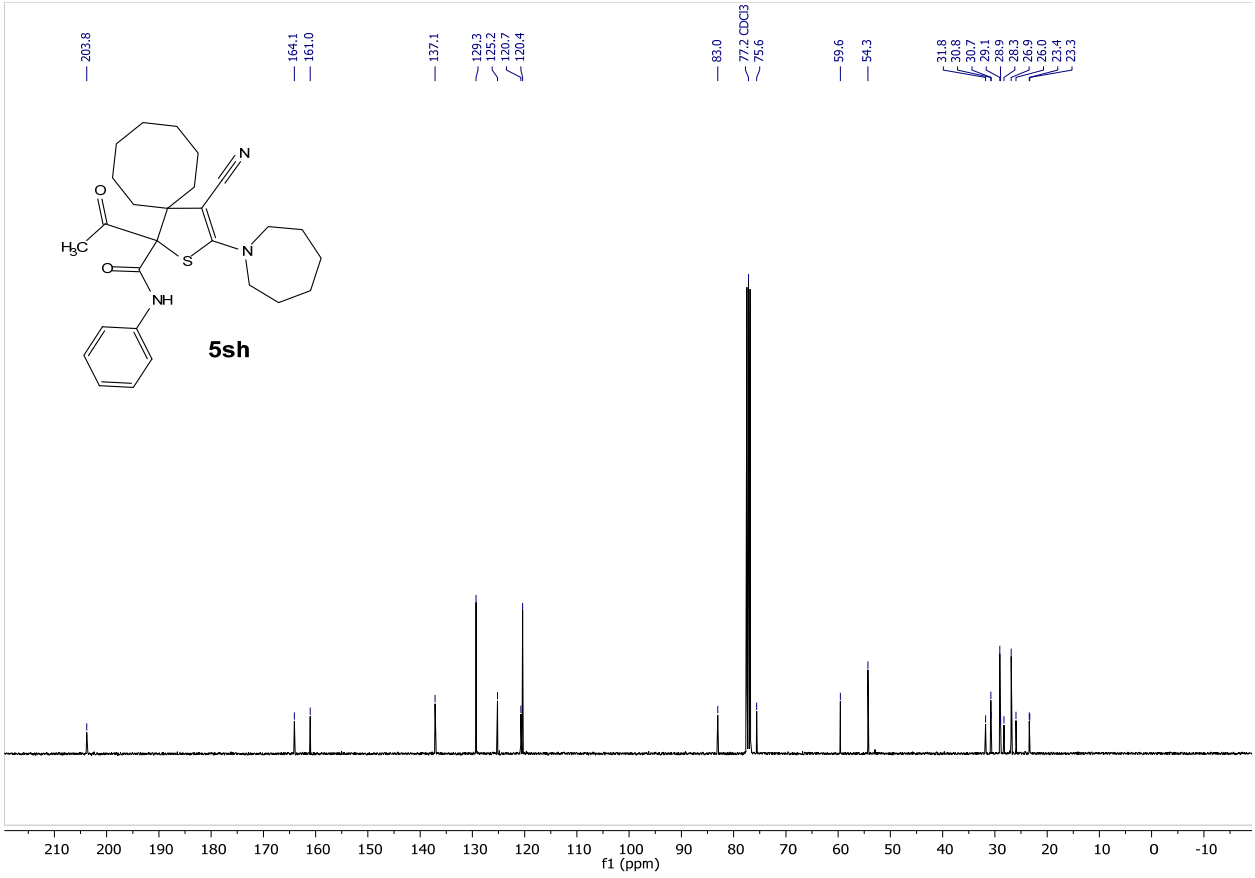
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5ph**



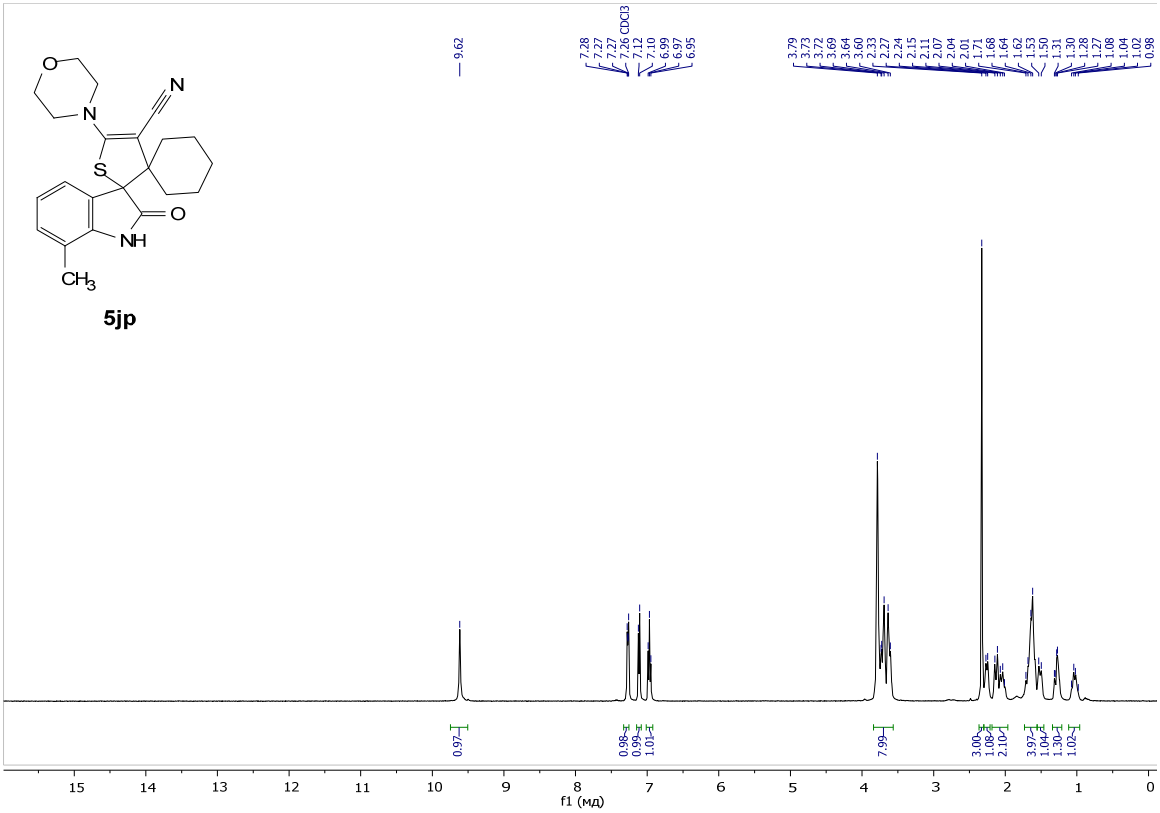
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5rh**



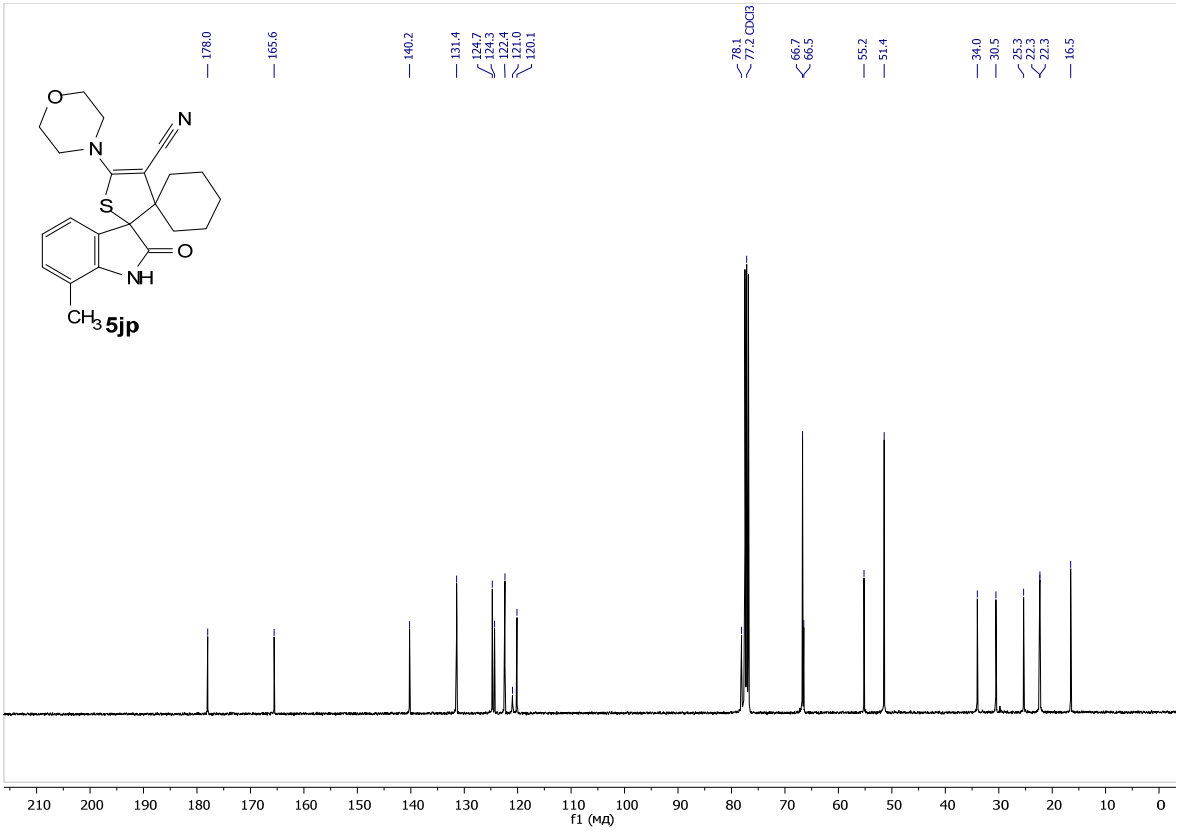
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5sh**



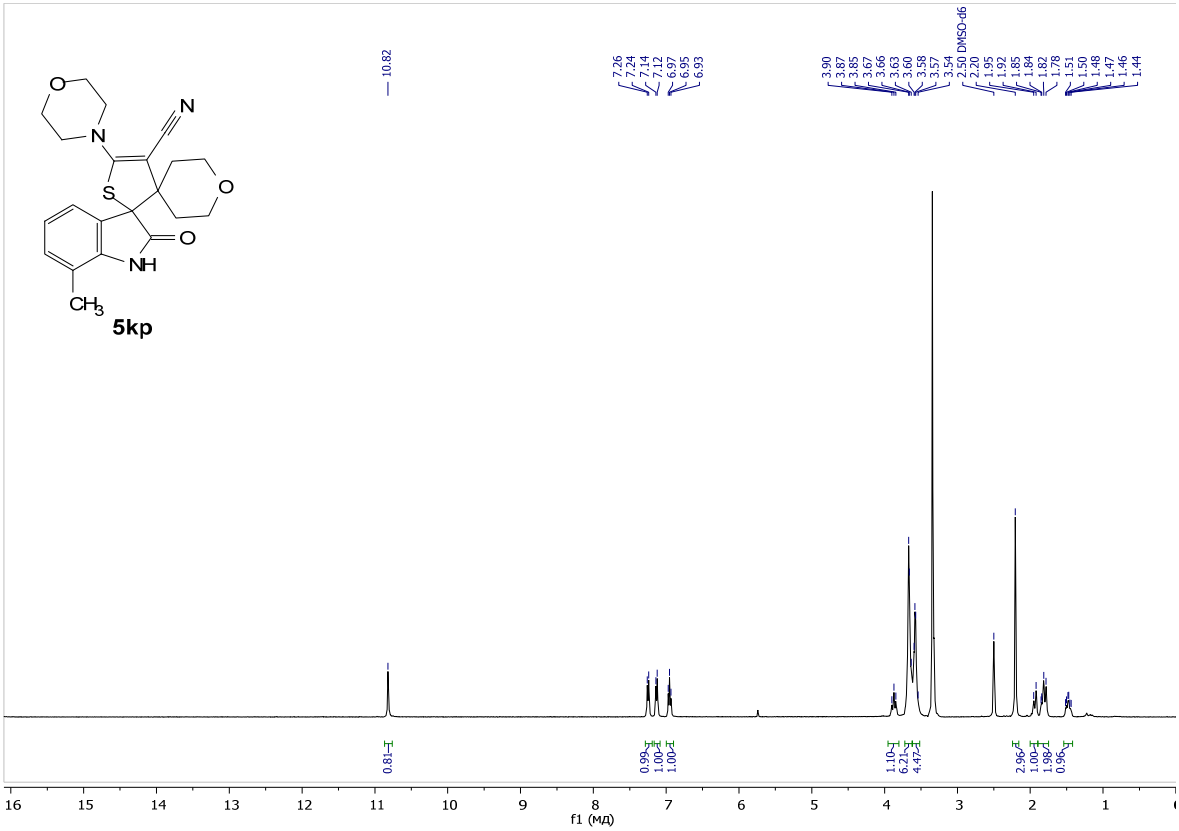
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5sh**



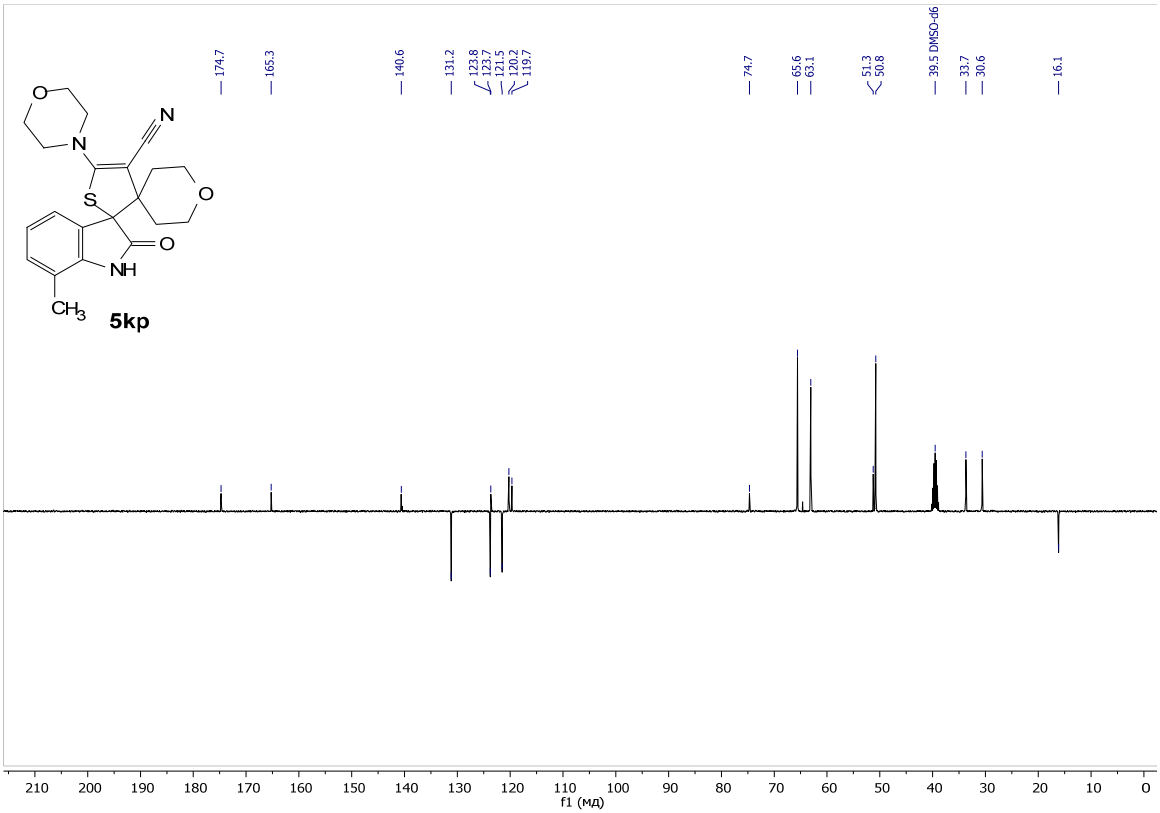
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5jp**



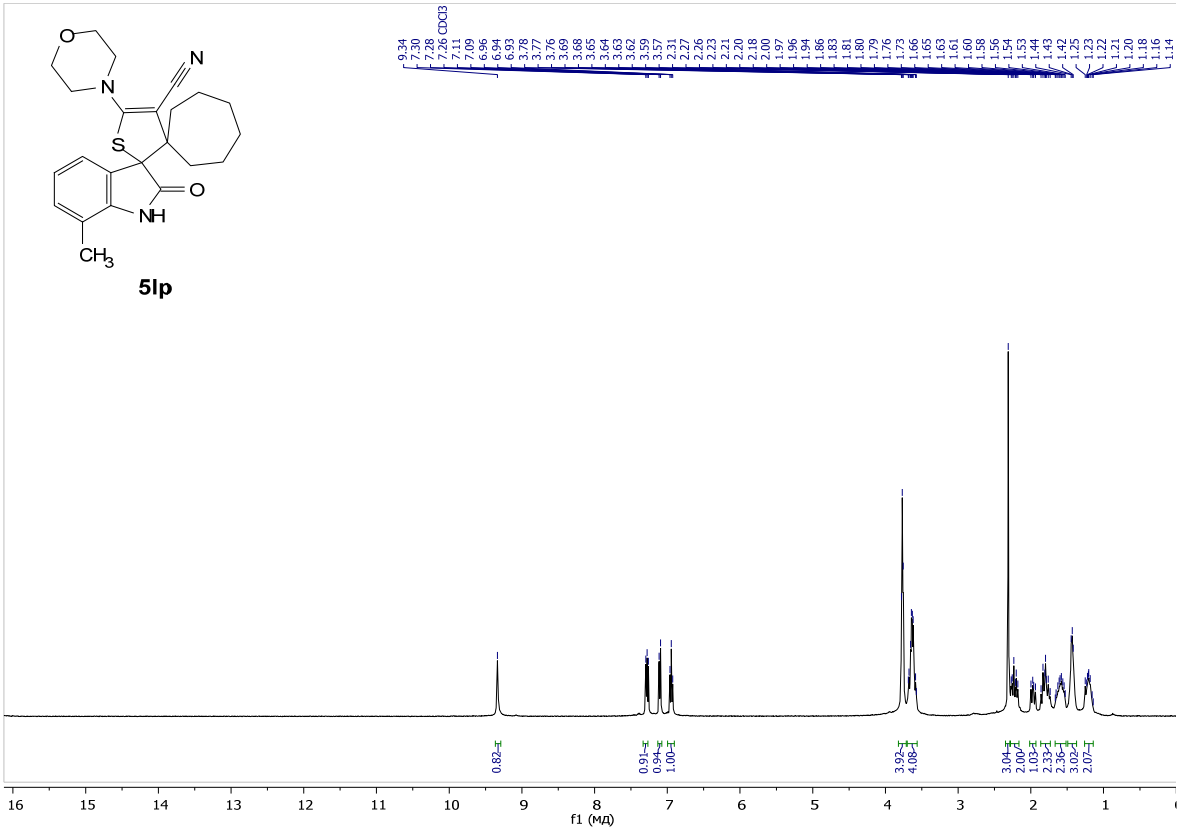
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5jp**



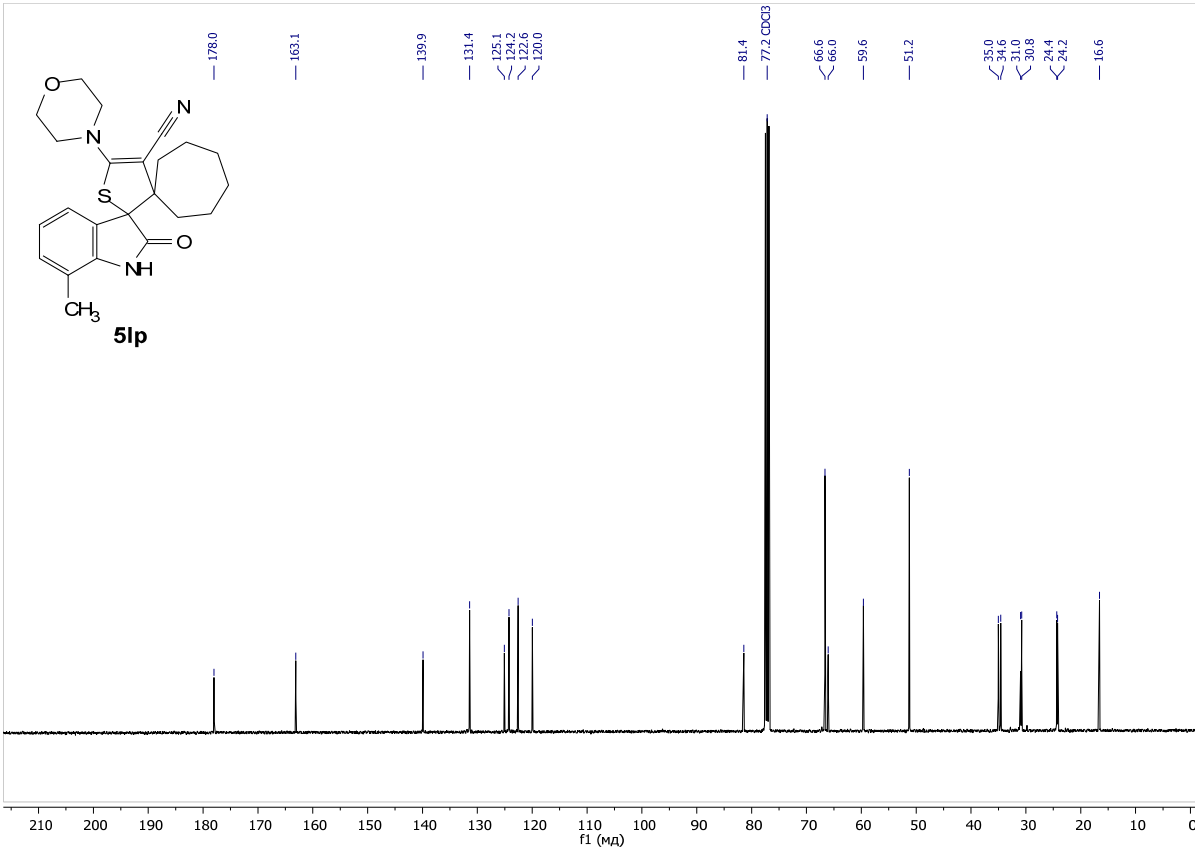
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **5kp**



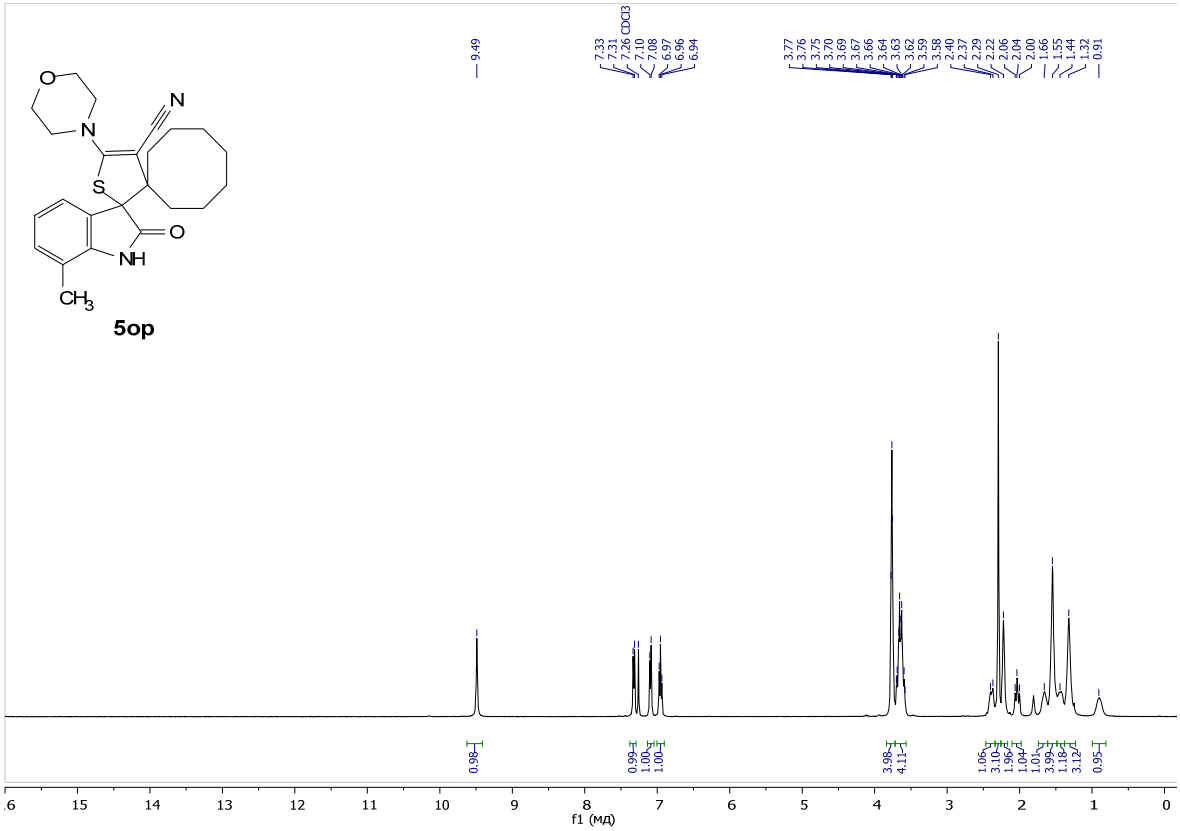
^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **5kp**



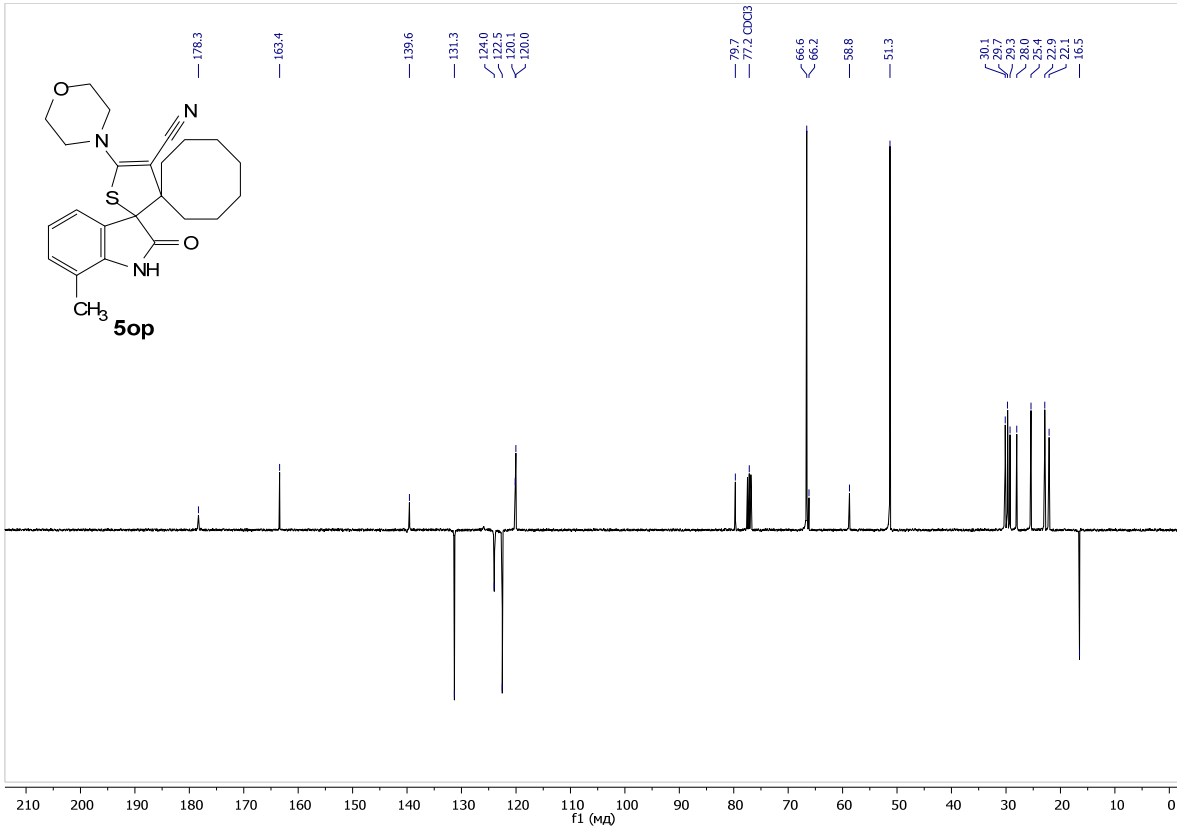
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5lp**



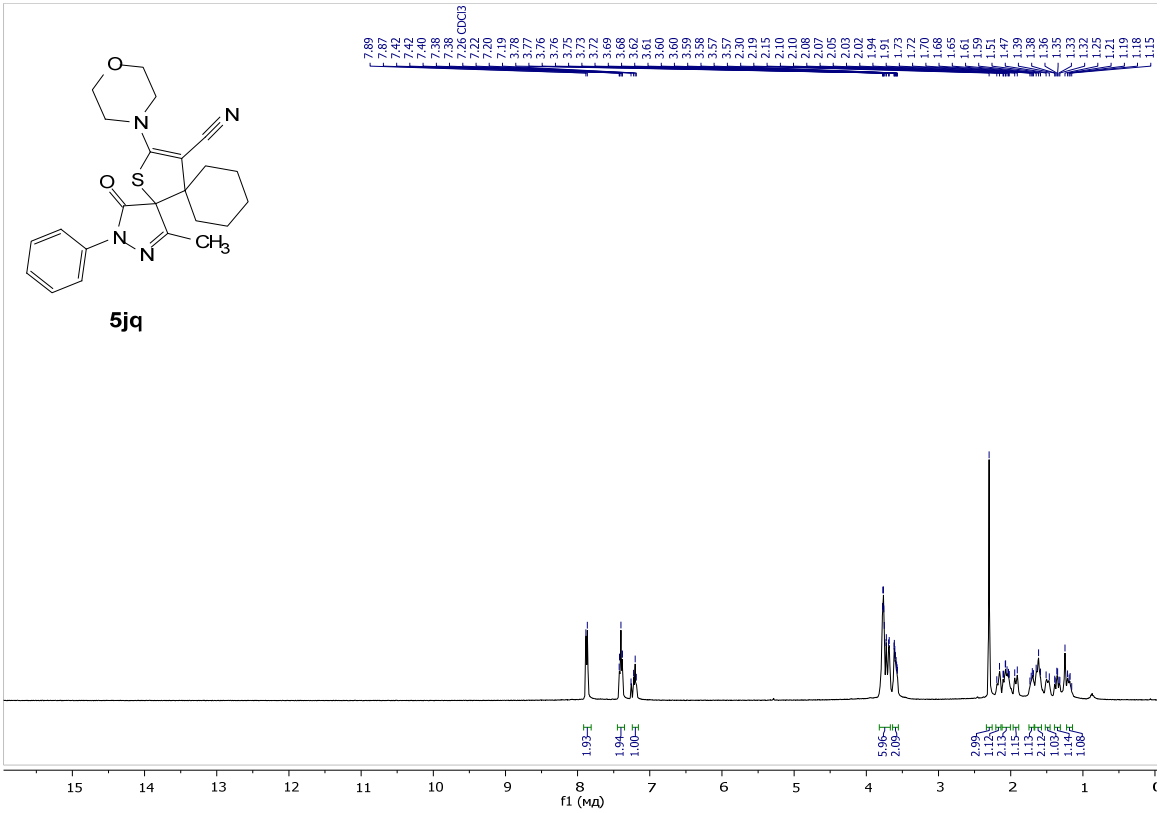
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5lp**



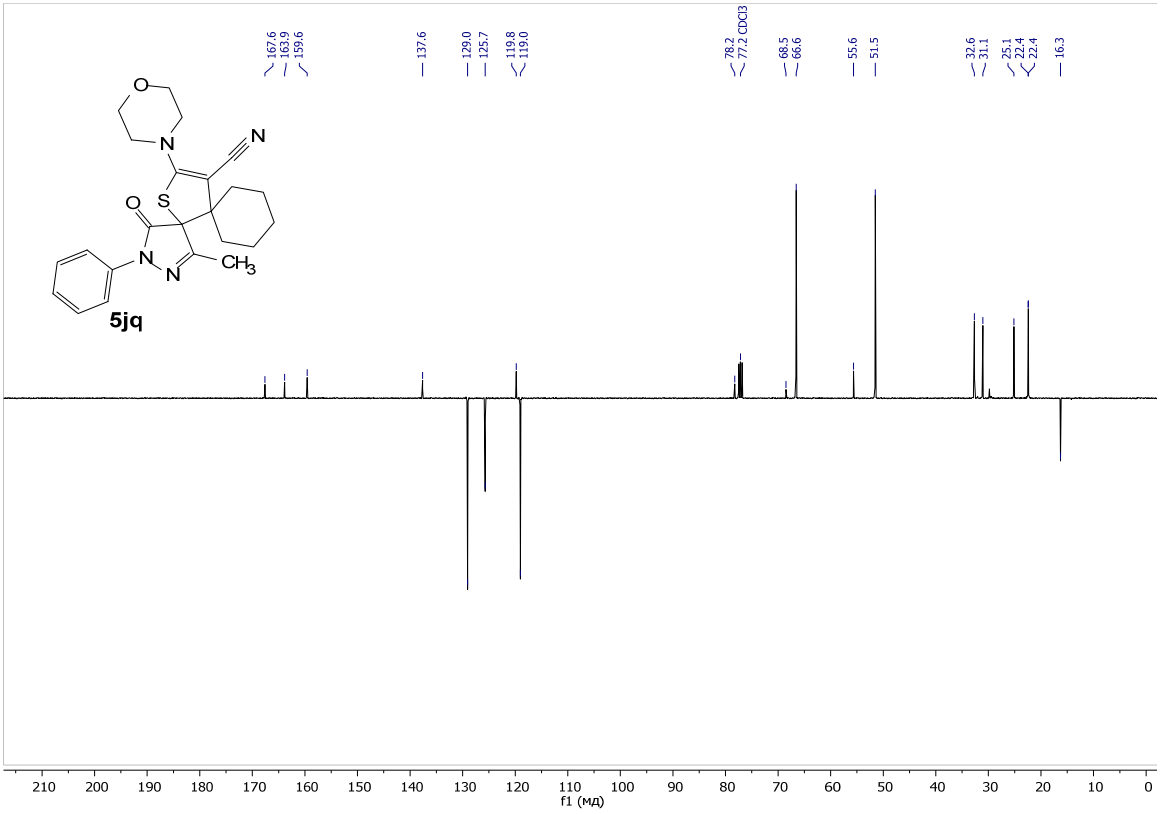
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5op**



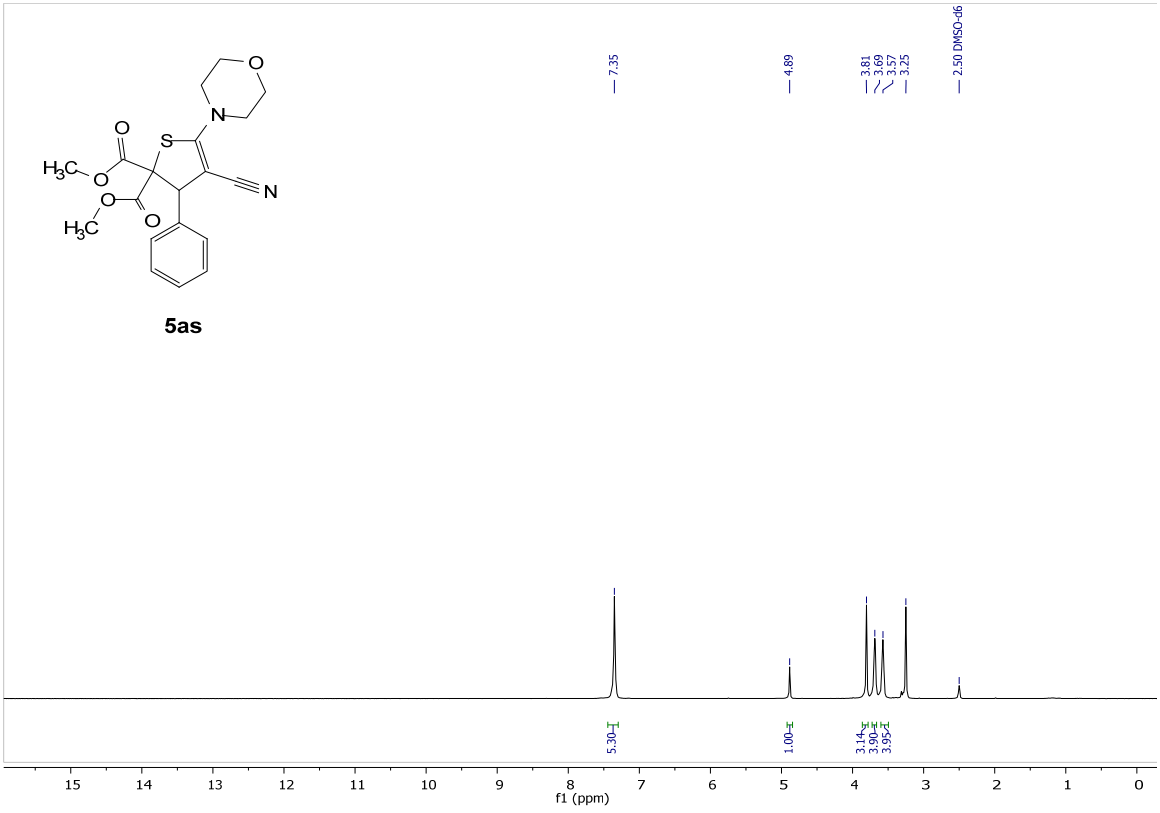
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5op**



^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5jq**

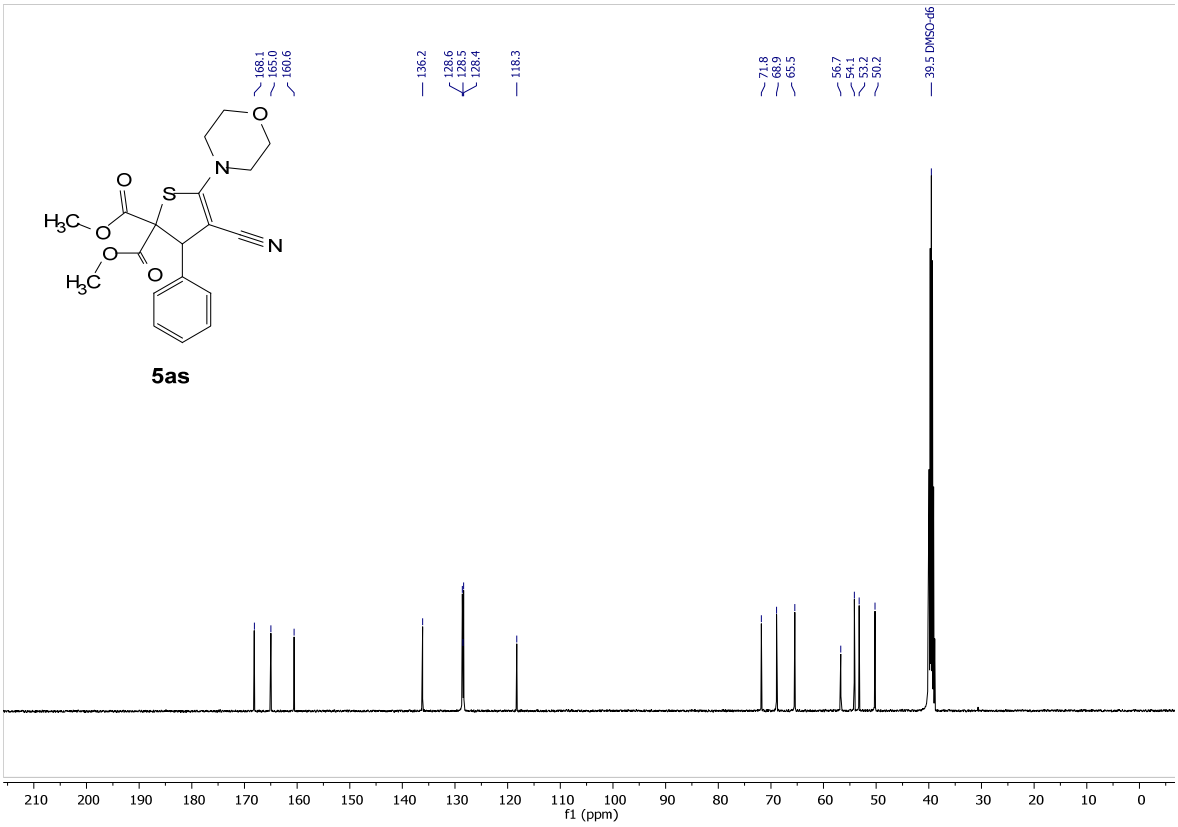


^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5jq**



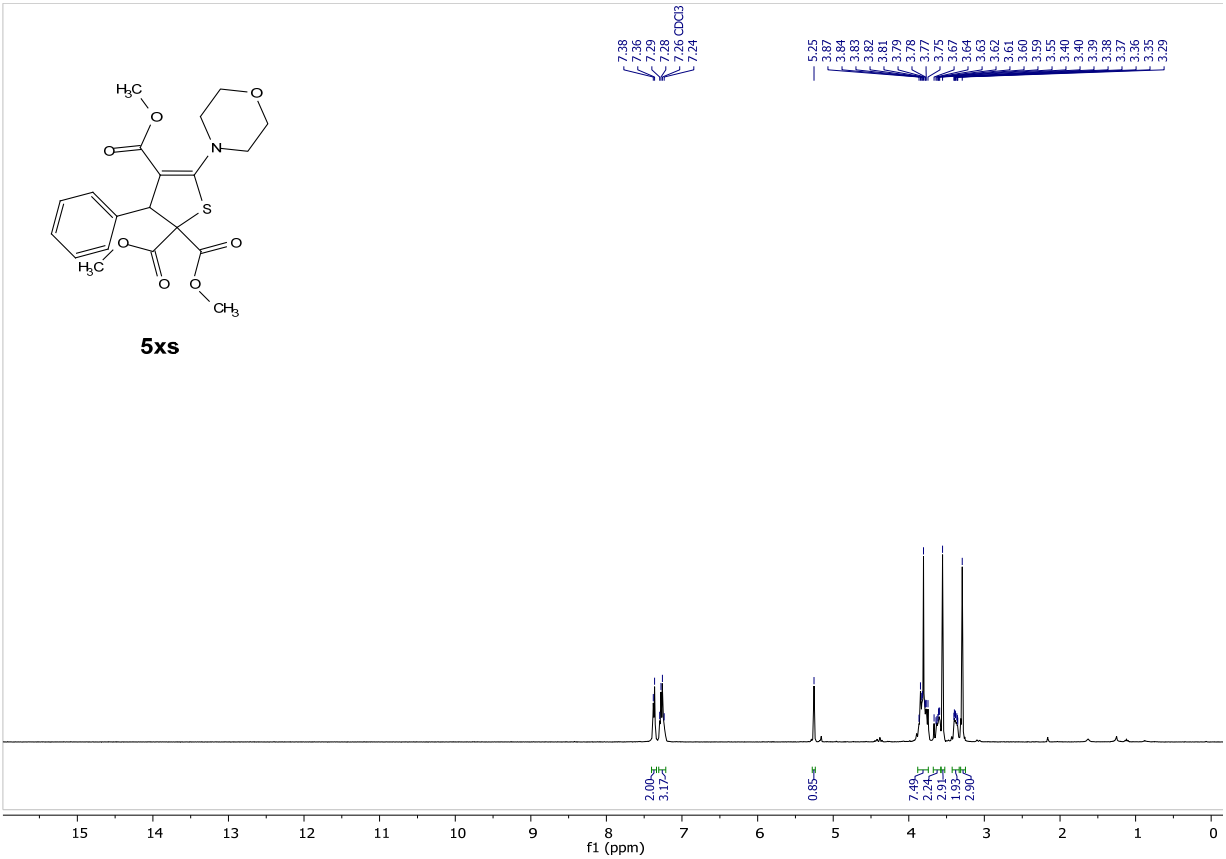
5as

^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **5as**



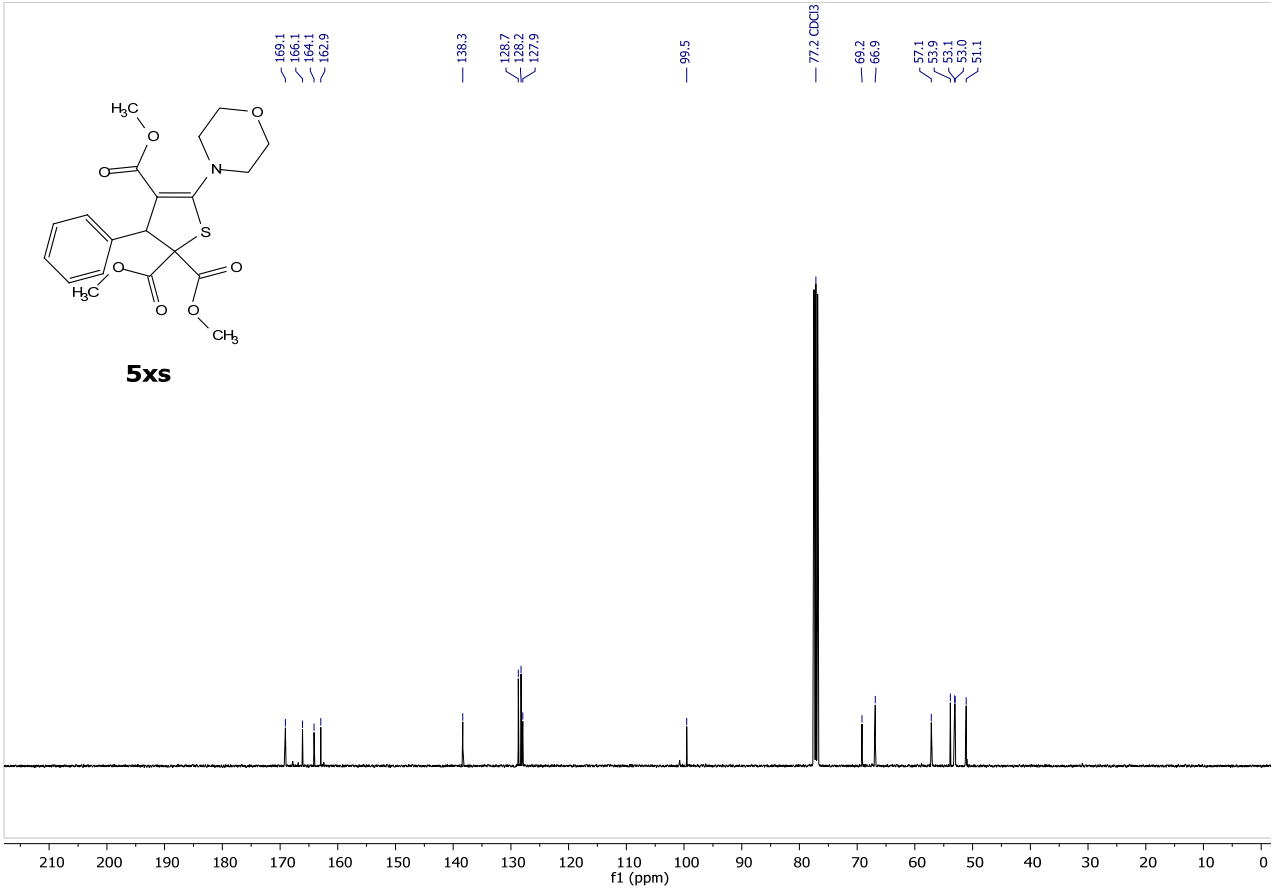
5as

^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **5as**



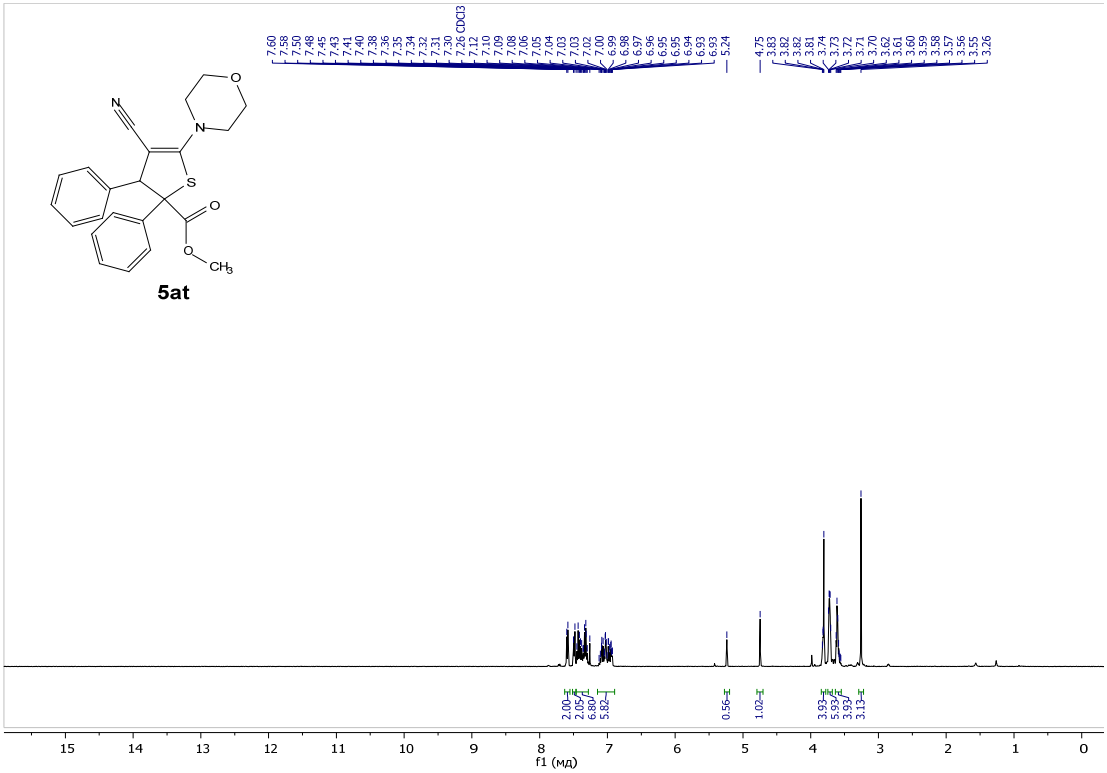
5xs

^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5xs**

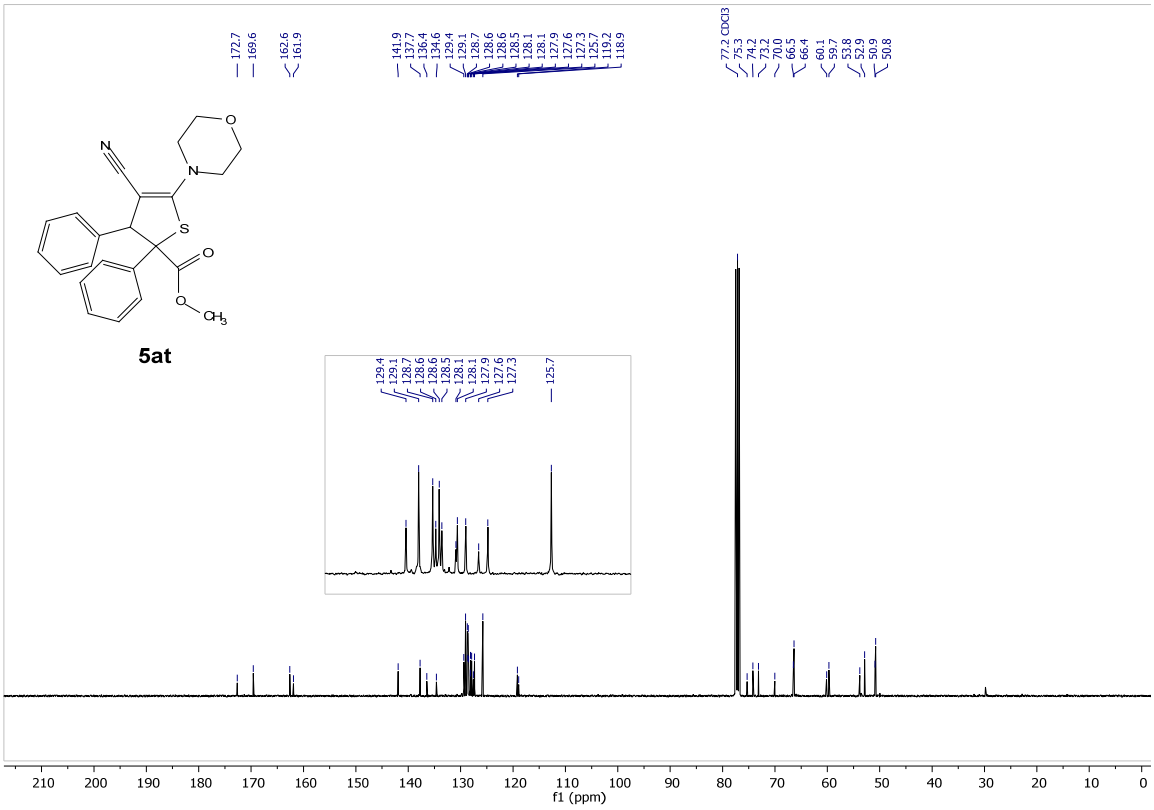


5xs

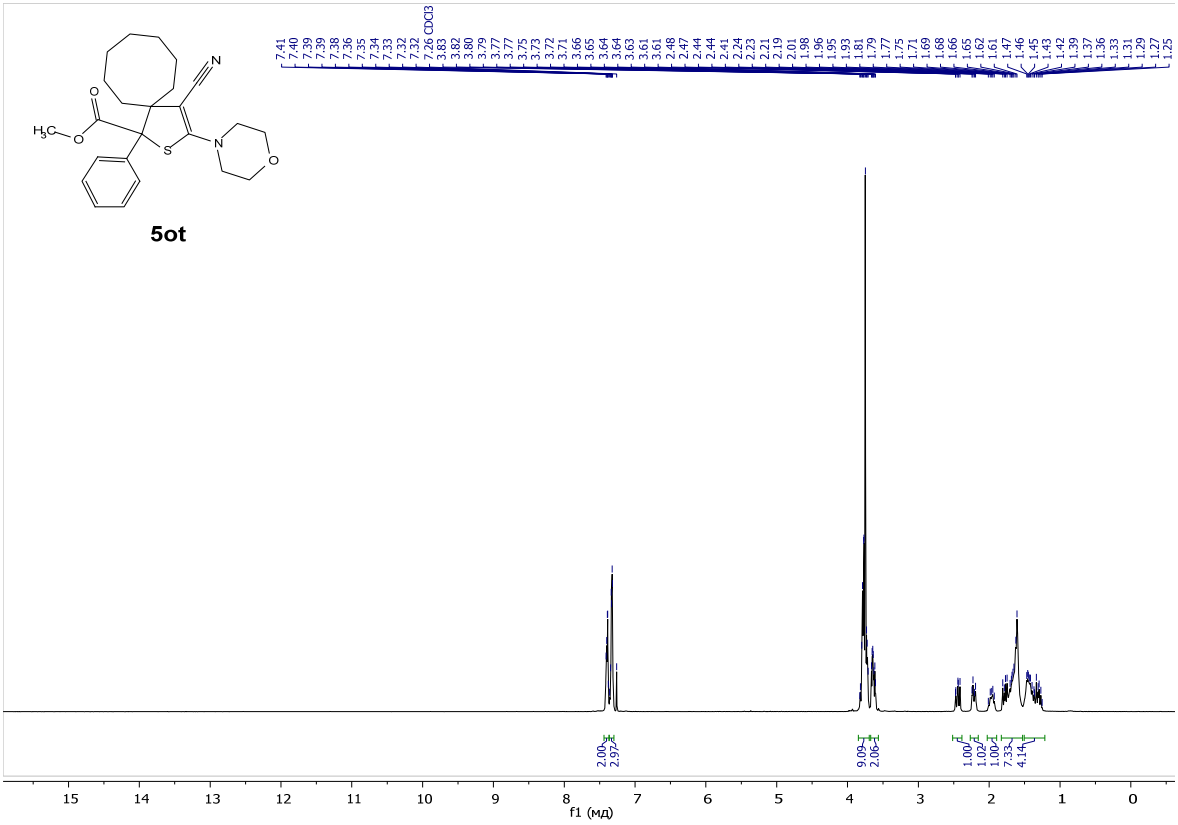
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5xs**



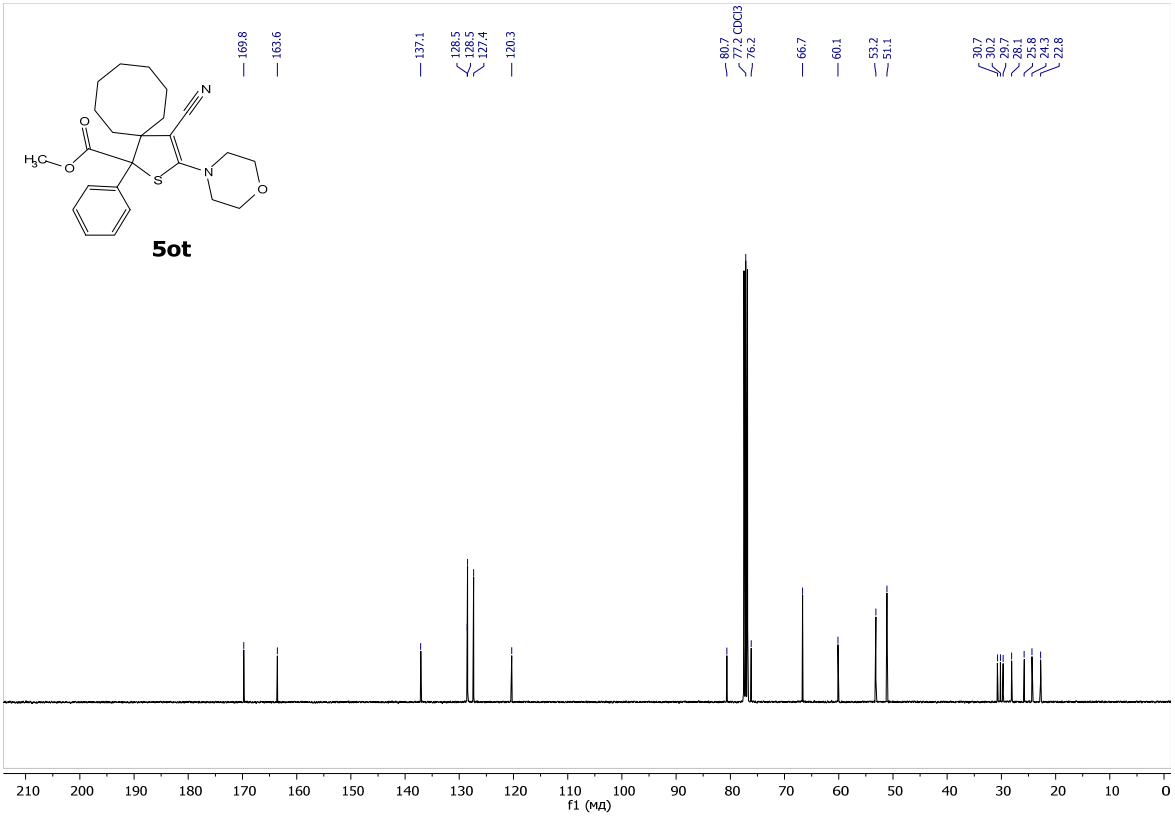
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5at**



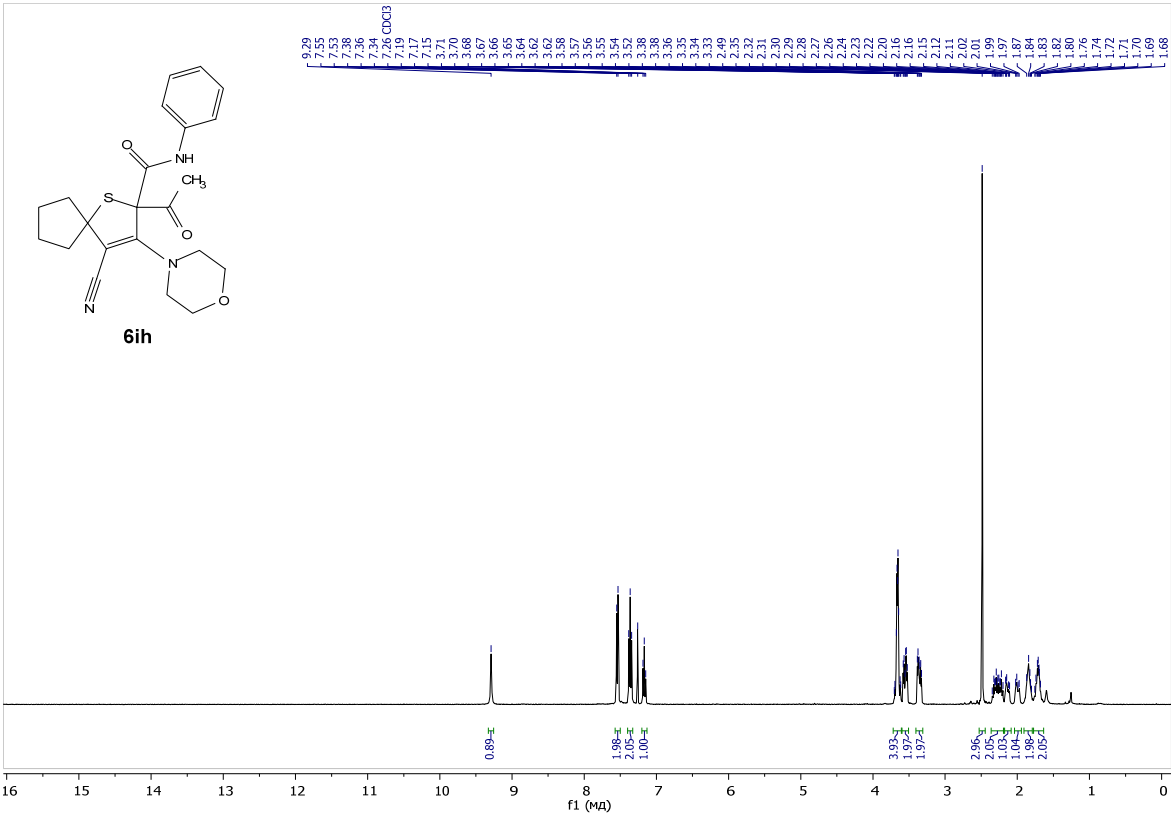
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5at**



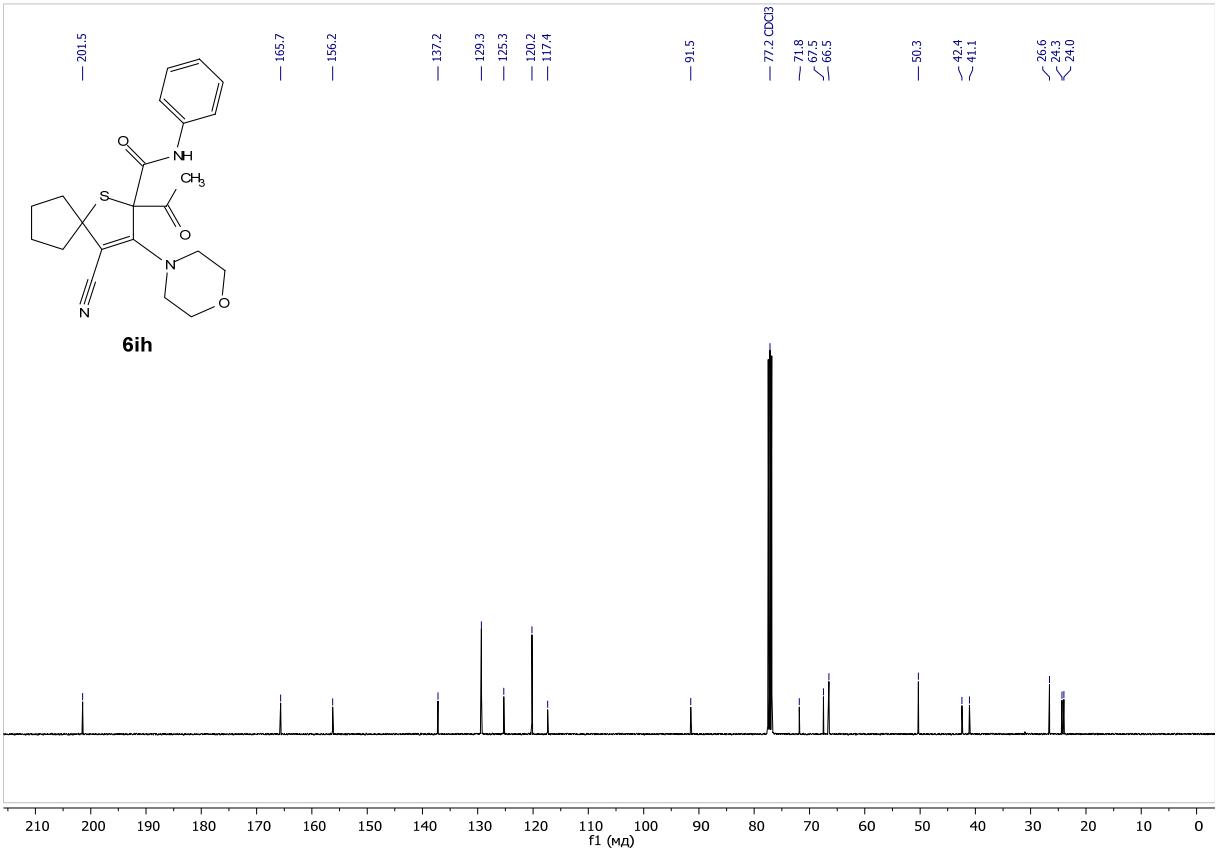
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ot**



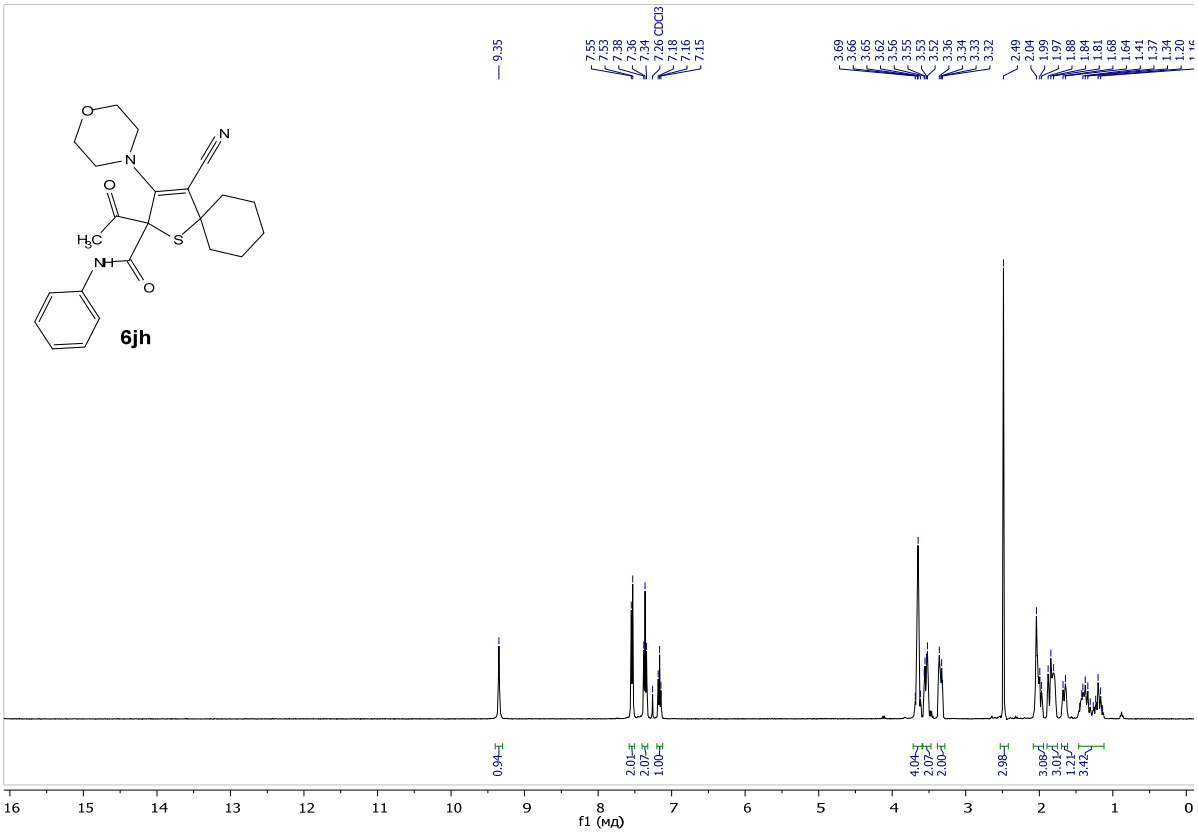
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **5ot**



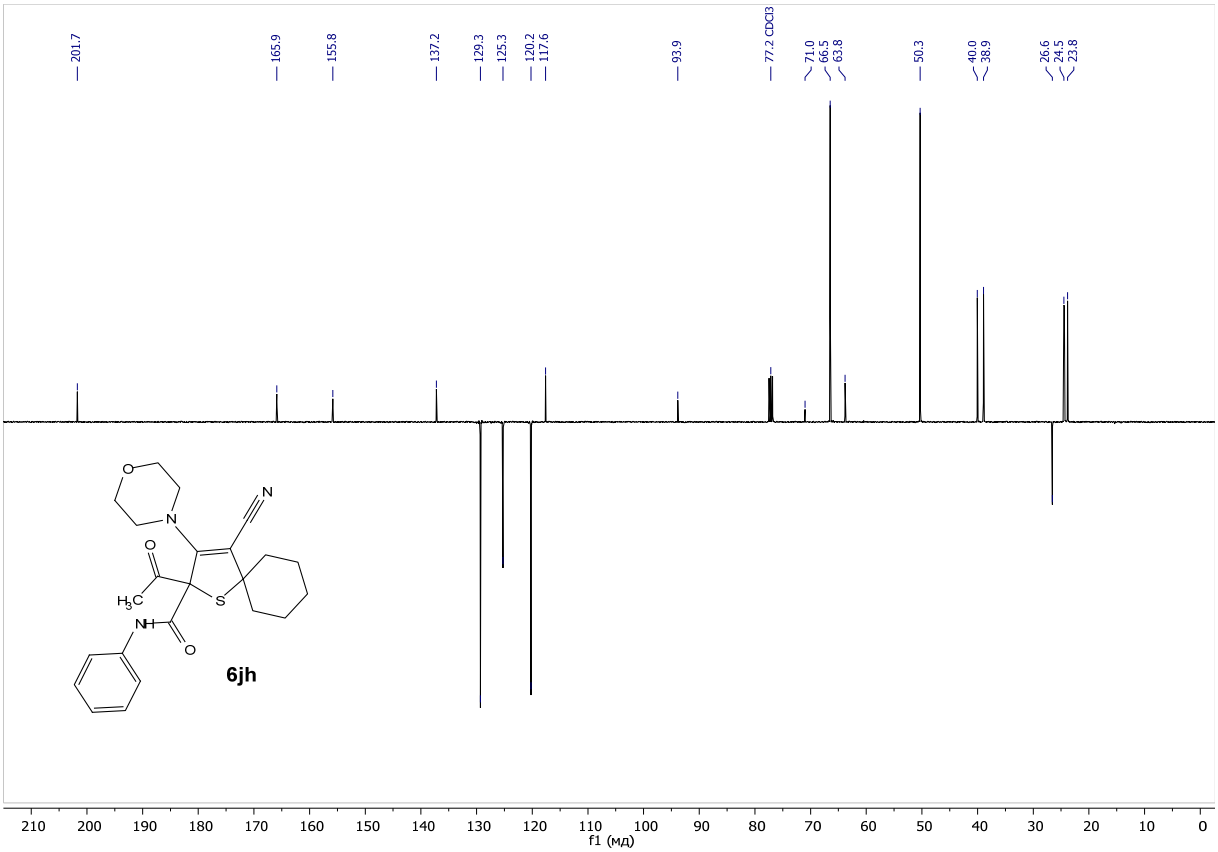
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **6ih**



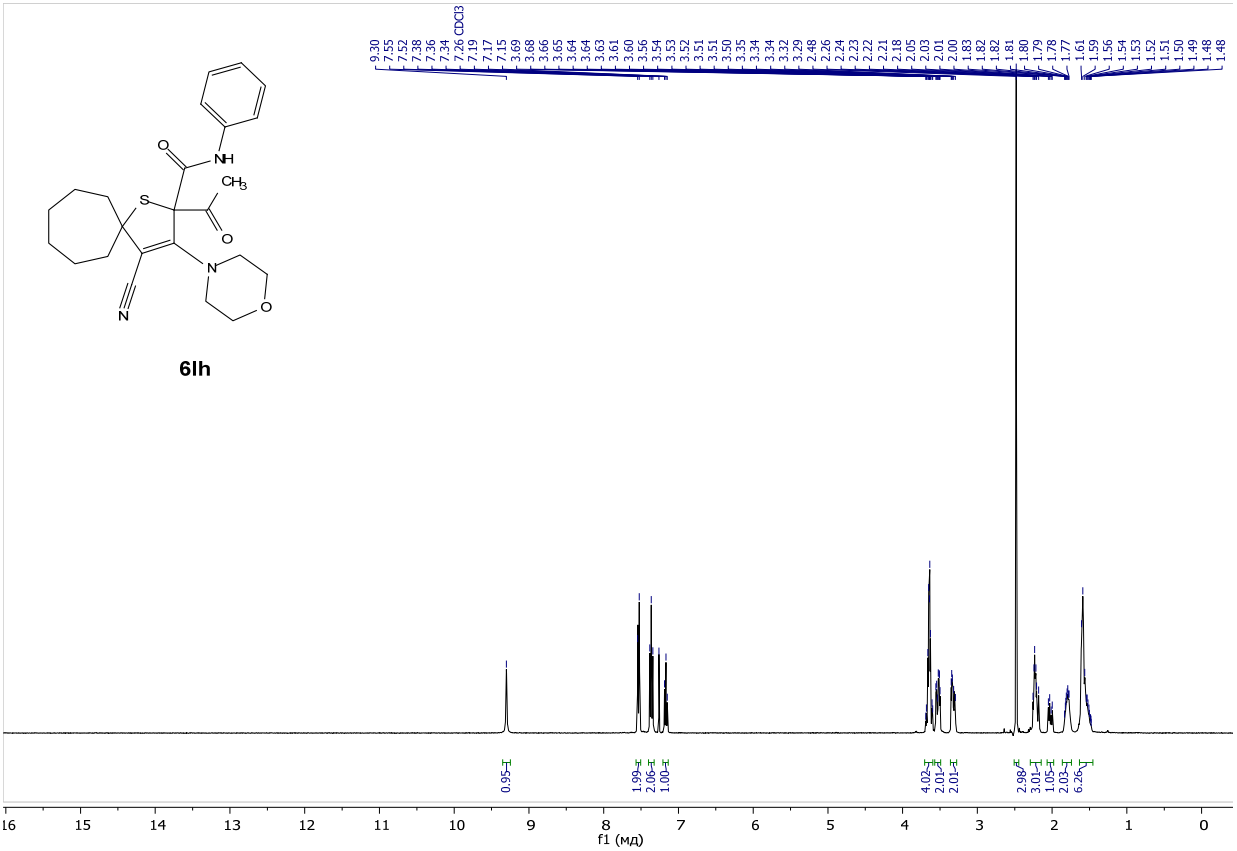
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **6ih**



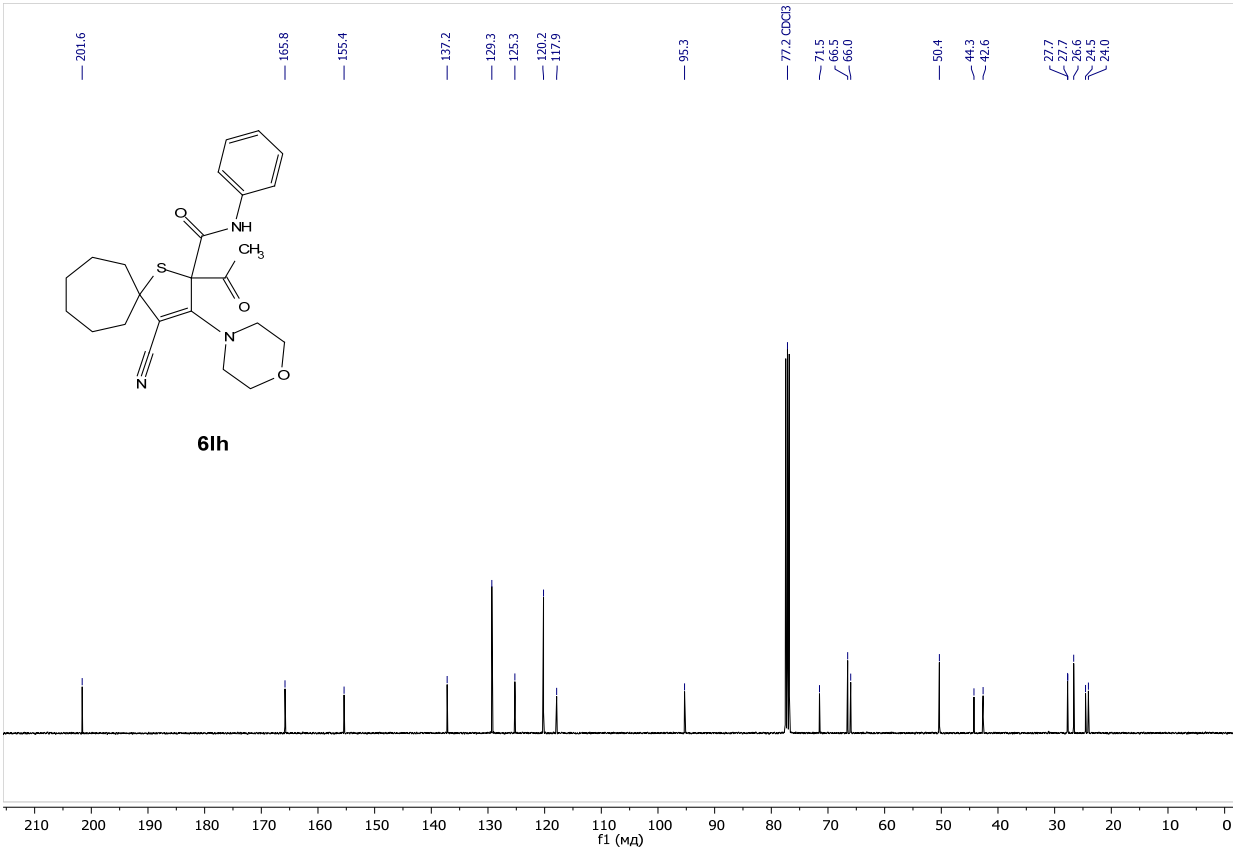
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **6jh**



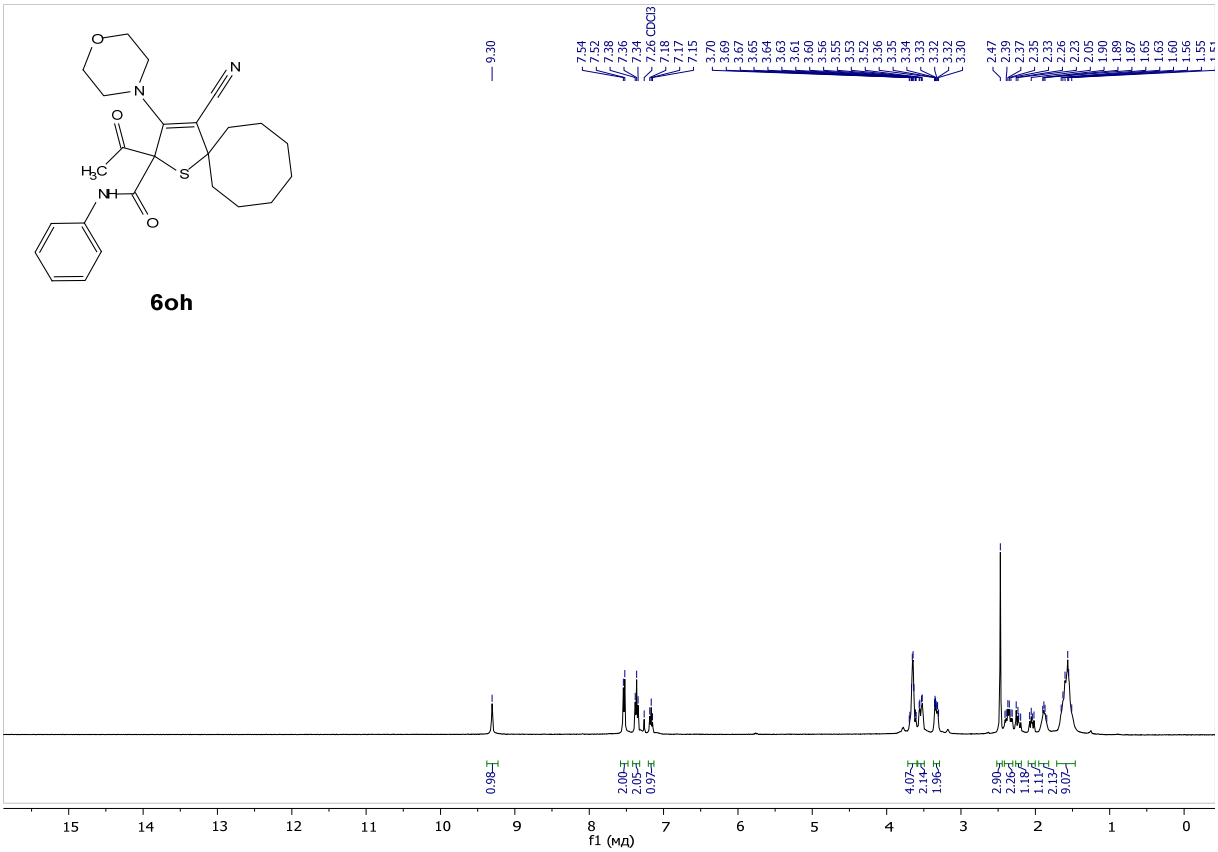
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **6jh**



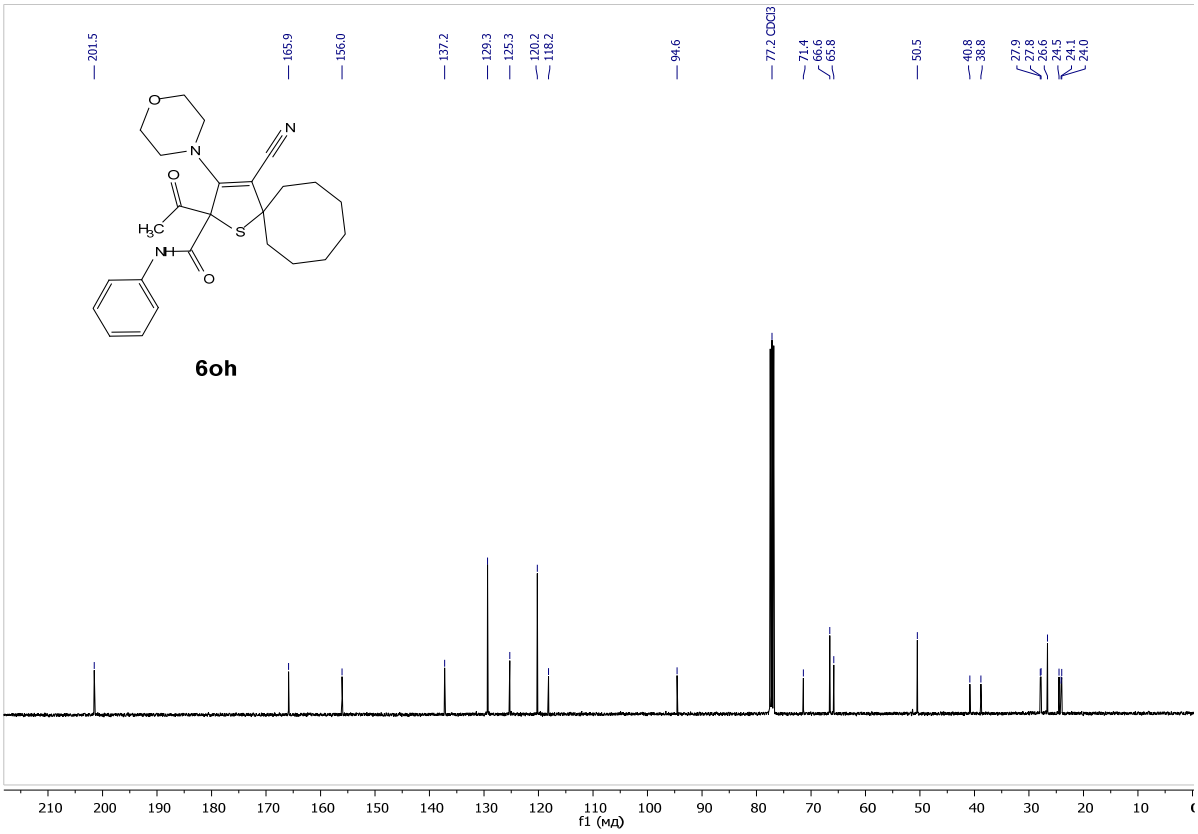
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **6lh**



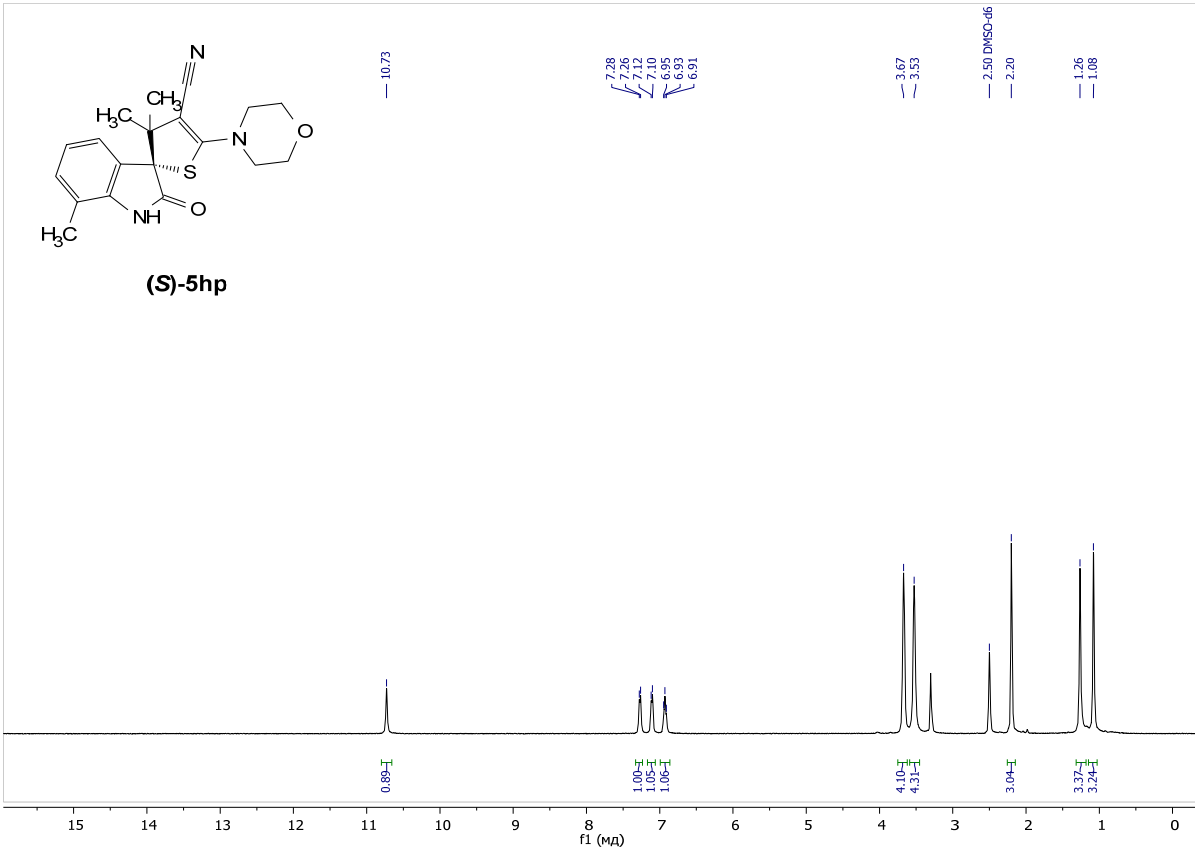
^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **6lh**



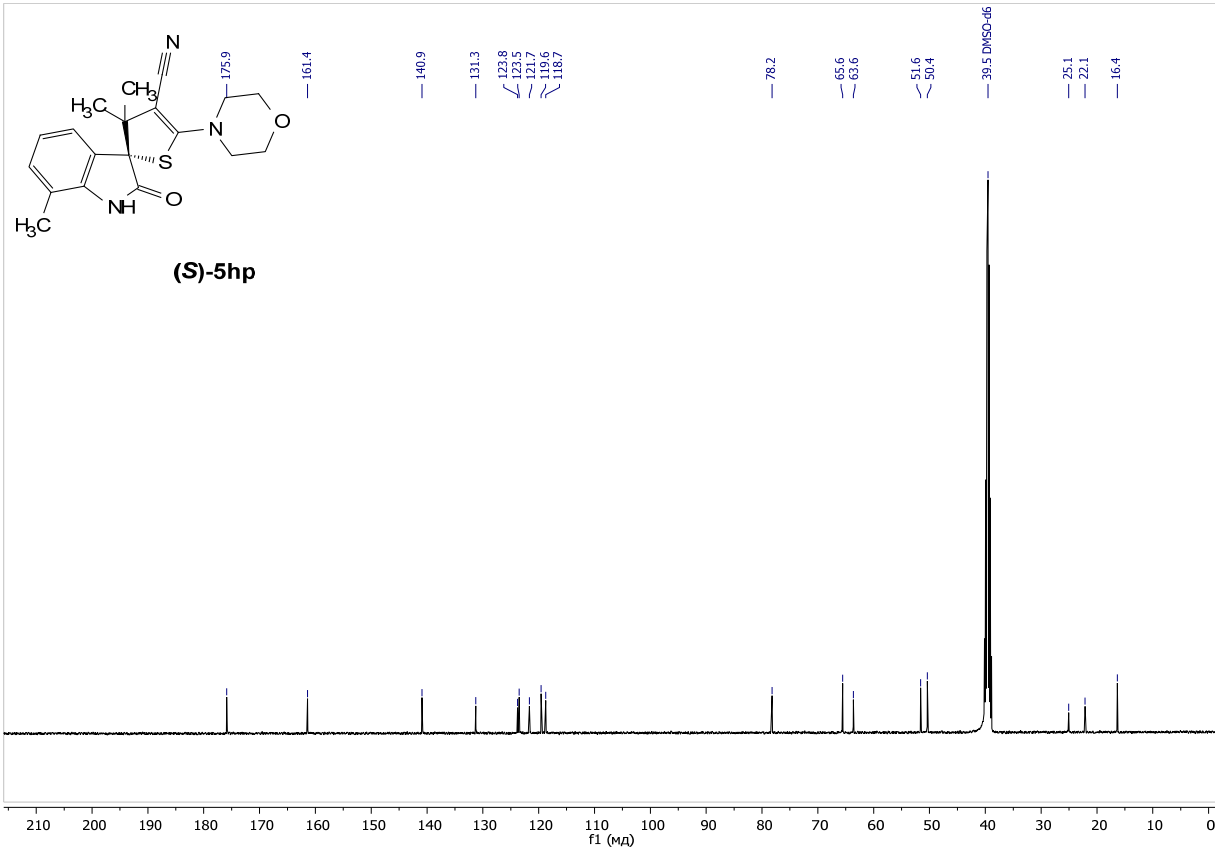
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **6oh**



^{13}C{1H} NMR (100 MHz, $CDCl_3$–*d*) of **6oh**



^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **(*S*)-5hp**



^{13}C{1H} NMR (100 MHz, DMSO–*d*$_6$) of **(*S*)-5hp**

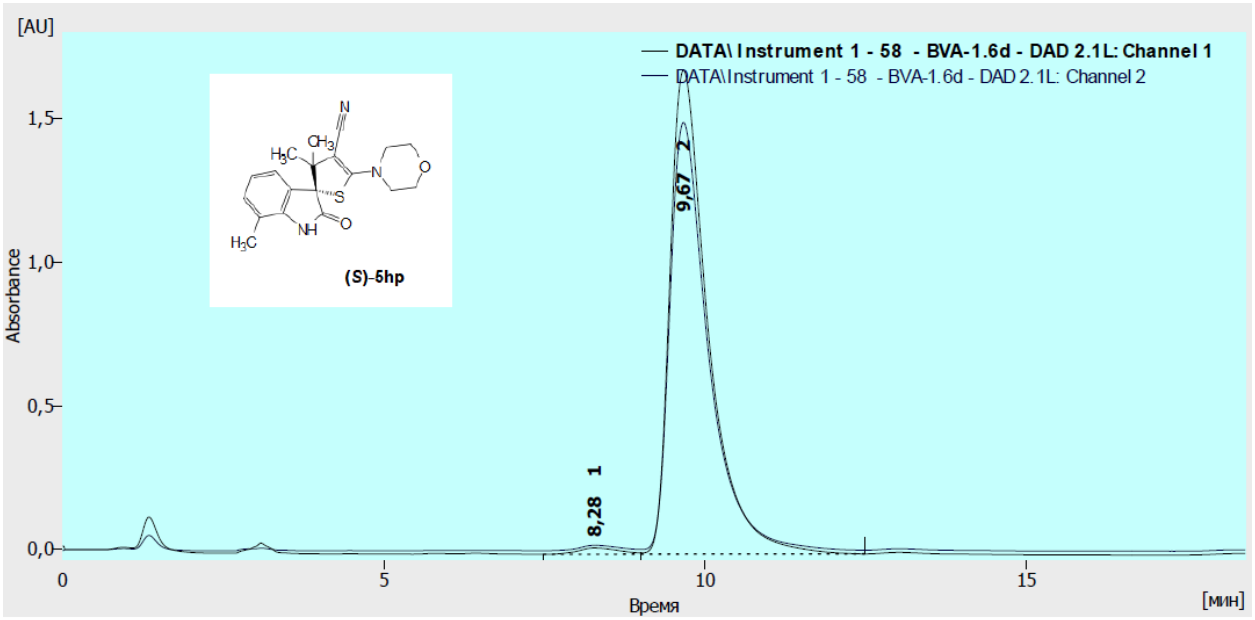
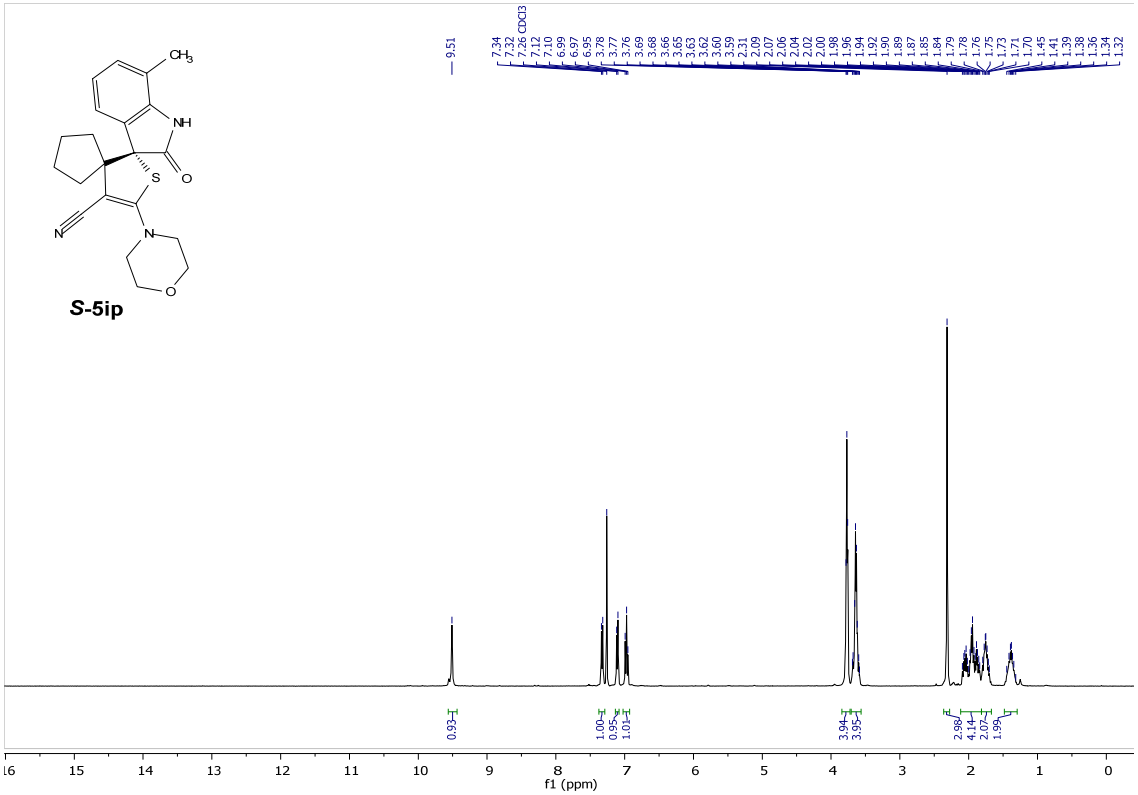
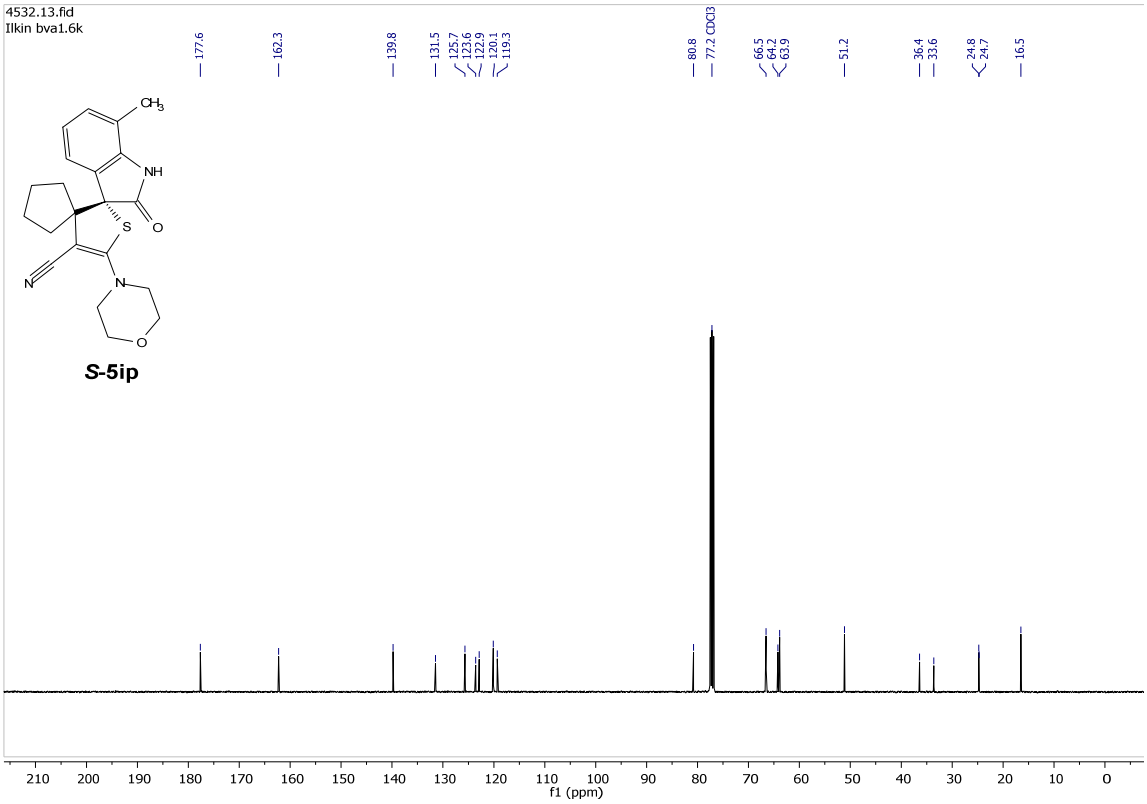


Таблица результатов (Без калибровки - DATA\Instrument 1 - 58 - BVA-1.6d - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	W05 [мин]	Название вещества
1	8,283	959,138	21,900	1,4	0,72	
2	9,667	69699,615	1686,517	98,6	0,62	
	Суммарное значение	70658,753	1708,417	100,0		



^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **(*S*)-5ip**



^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **(*S*)-5ip**

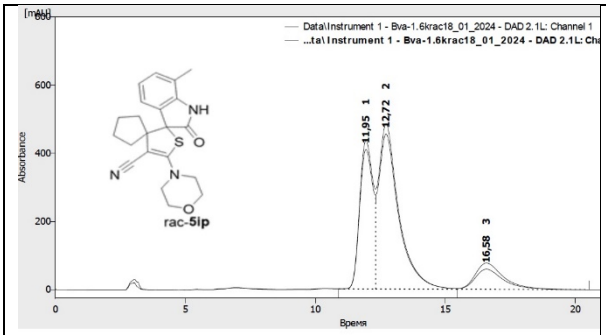


Таблица результатов (Без калибровки - Data\Instrument 1 - Bva-1.6krac18_01_2024 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	11,950	15298,130	415,623	32,0	43,7	0,65	
2	12,717	26573,977	484,562	55,5	48,6	0,87	
3	16,583	5968,077	77,203	12,5	7,7	1,12	
	Суммарное значение	47840,184	997,388	100,0	100,0		

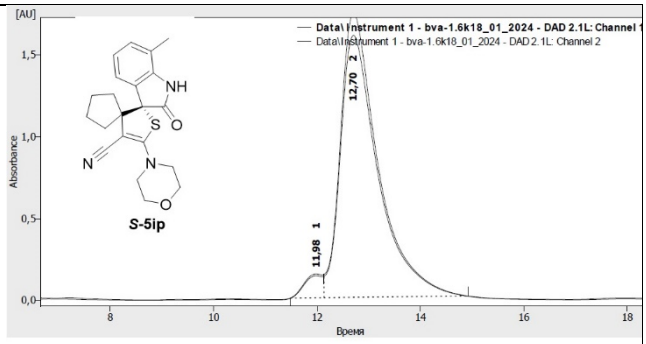
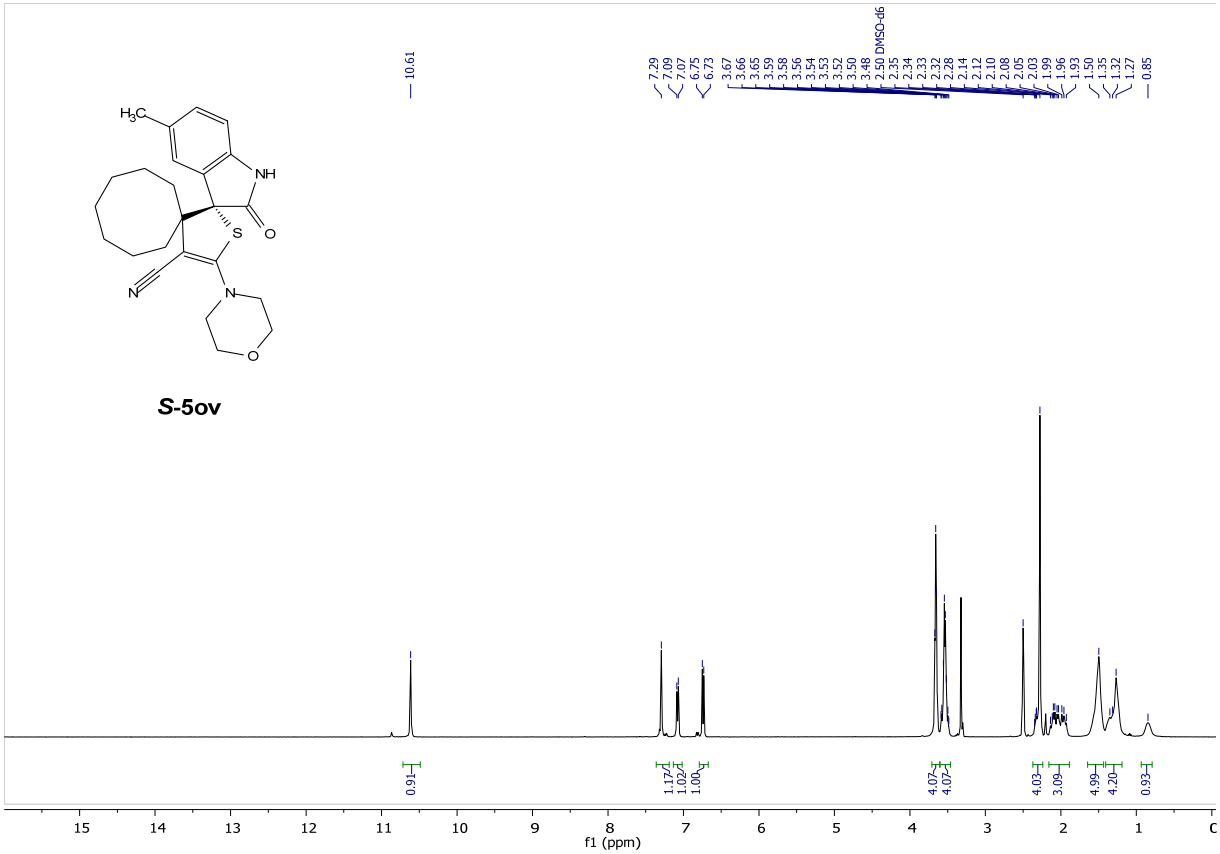
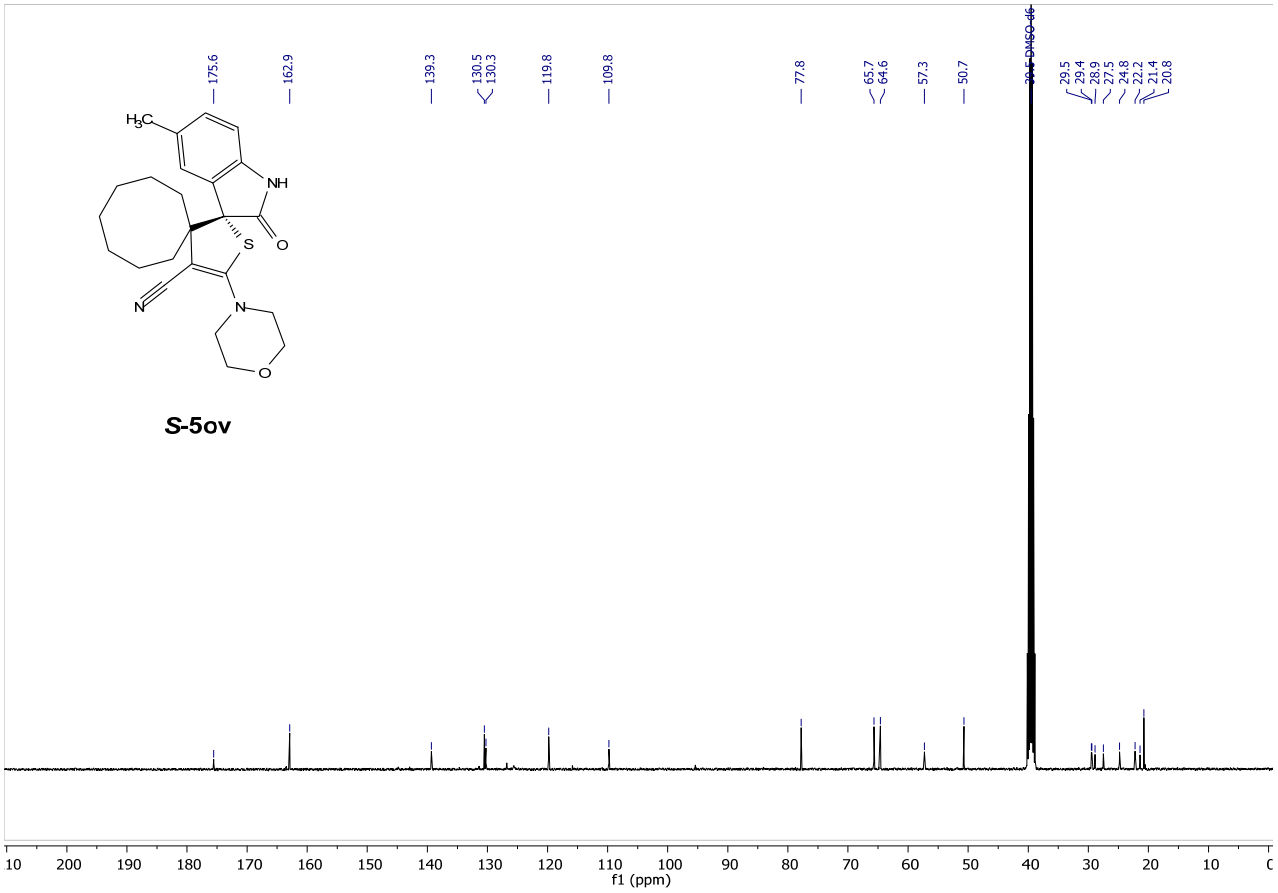


Таблица результатов (Без калибровки - Data\Instrument 1 - bva-1.6k18_01_2024 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	11,983	3565,098	145,403	3,9	7,7	0,43	
2	12,700	87846,016	1736,389	96,1	92,3	0,73	
	Суммарное значение	91411,114	1881,792	100,0	100,0		



^{1}H NMR (400 MHz, DMSO–d_6) of **(*S*)-5ov**



^{13}C{1H} NMR (100 MHz, DMSO–d_6) of **(*S*)- 5ov**

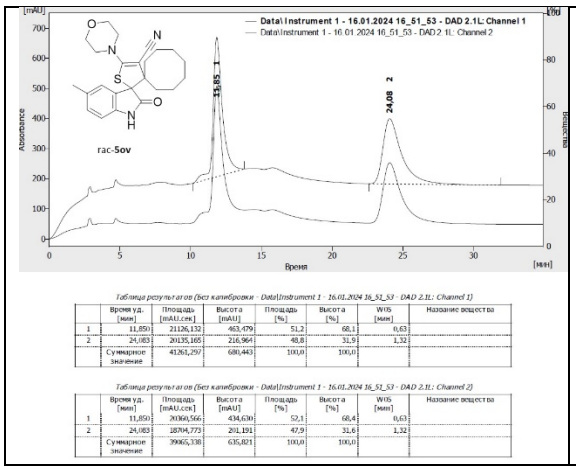


Таблица результатов (Без калибровки - Data\Instrument 1 - 16.01.2024 16_51_53 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	11,850	21126,132	463,479	51,2	68,1	0,63	
2	24,083	20135,165	216,964	48,8	31,9	1,32	
	Суммарное значение	41261,297	680,443	100,0	100,0		

Таблица результатов (Без калибровки - Data\Instrument 1 - 16.01.2024 16_51_53 - DAD 2.1L: Channel 2)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	11,850	20369,566	434,630	52,1	68,4	0,63	
2	24,083	18704,773	201,191	47,9	31,6	1,32	
	Суммарное значение	39065,338	635,821	100,0	100,0		

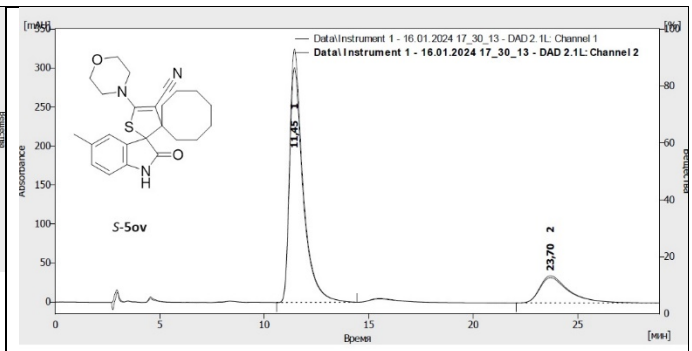


Таблица результатов (Без калибровки - Data\Instrument 1 - 16.01.2024 17_30_13 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	11,450	14585,295	325,009	81,0	90,3	0,65	
2	23,700	3424,014	35,015	19,0	9,7	1,40	
	Суммарное значение	18009,309	360,024	100,0	100,0		

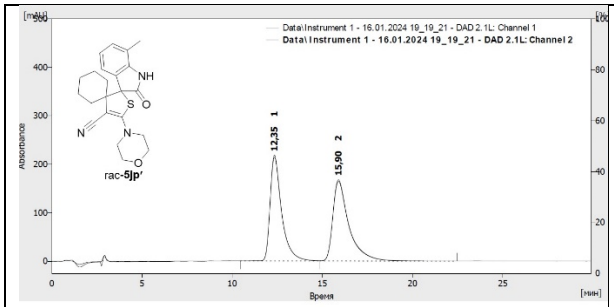


Таблица результатов (Без калибровки - Data\Instrument 1 - 16.01.2024 19_19_21 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	12,350	9660,081	217,892	48,3	56,6	0,65	
2	15,900	10335,646	167,338	51,7	43,4	0,87	
	Суммарное значение	19995,726	385,230	100,0	100,0		

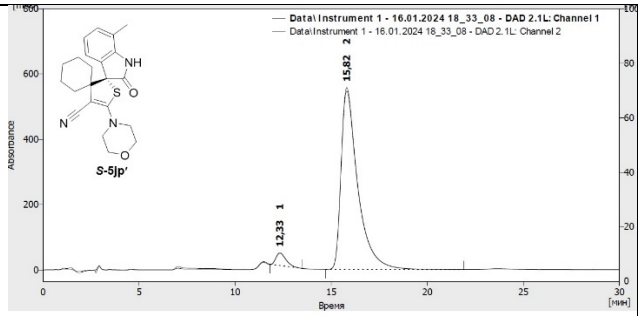


Таблица результатов (Без калибровки - Data\Instrument 1 - 16.01.2024 18_33_08 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	12,333	1445,871	39,394	4,1	6,6	0,57	
2	15,817	33697,178	556,958	95,9	93,4	0,87	
	Суммарное значение	35143,049	596,352	100,0	100,0		

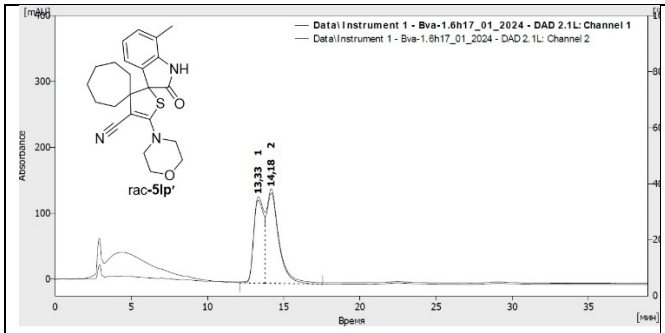


Таблица результатов (Без калибровки - Data\Instrument 1 - Bva-1.6h17_01_2024 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	13,333	5575,412	125,660	42,1	47,8	0,78	
2	14,183	7673,699	137,180	57,9	52,2	0,88	
	Суммарное значение	13249,111	262,840	100,0	100,0		

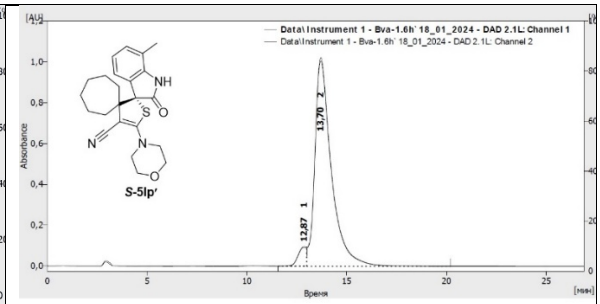


Таблица результатов (Без калибровки - Data\Instrument 1 - Bva-1.6h`18_01_2024 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	12,867	2566,746	92,460	4,3	8,4	0,47	
2	13,700	57573,963	1004,928	95,7	91,6	0,82	
	Суммарное значение	60140,709	1097,388	100,0	100,0		

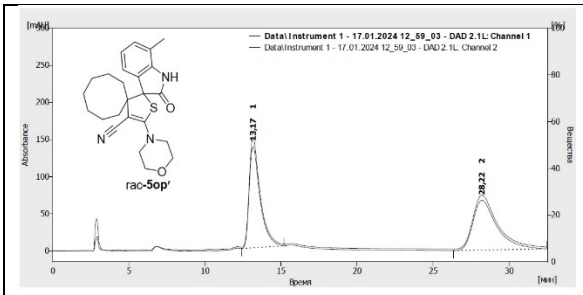


Таблица результатов (без калибровки - Data\Instrument 1 - 17.01.2024 12_59_03 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	13,167	6815,734	137,137	48,1	67,1	0,75	
2	28,217	7361,863	67,143	51,9	32,9	1,66	
	Суммарное значение	14177,597	204,280	100,0	100,0		

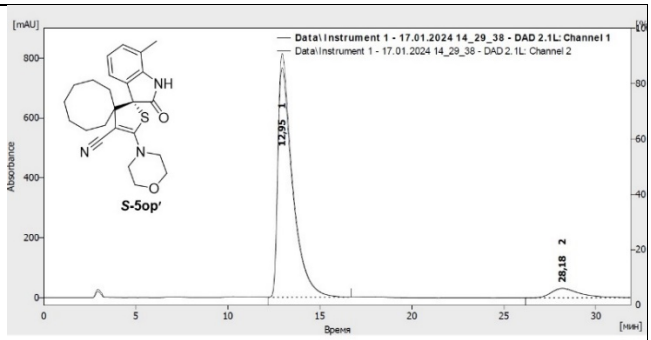


Таблица результатов (без калибровки - Data\Instrument 1 - 17.01.2024 14_29_38 - DAD 2.1L: Channel 1)

	Время уд. [мин]	Площадь [mAU.сек]	Высота [mAU]	Площадь [%]	Высота [%]	W05 [мин]	Название вещества
1	12,950	42499,829	766,442	93,0	96,2	0,80	
2	28,183	3210,571	29,885	7,0	3,8	1,60	
	Суммарное значение	45710,400	796,328	100,0	100,0		