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# Electrooxidative thiocyanation and halogenation of azopyrazoles

**Anastasia S. Kudinova, Vera L. Sigacheva, Boris V. Lyalin, Alla G. Tum, Natalia V. Gorpinchenko, Vladimir A. Kokorekin and Mikhail P. Egorov**

## Experimental

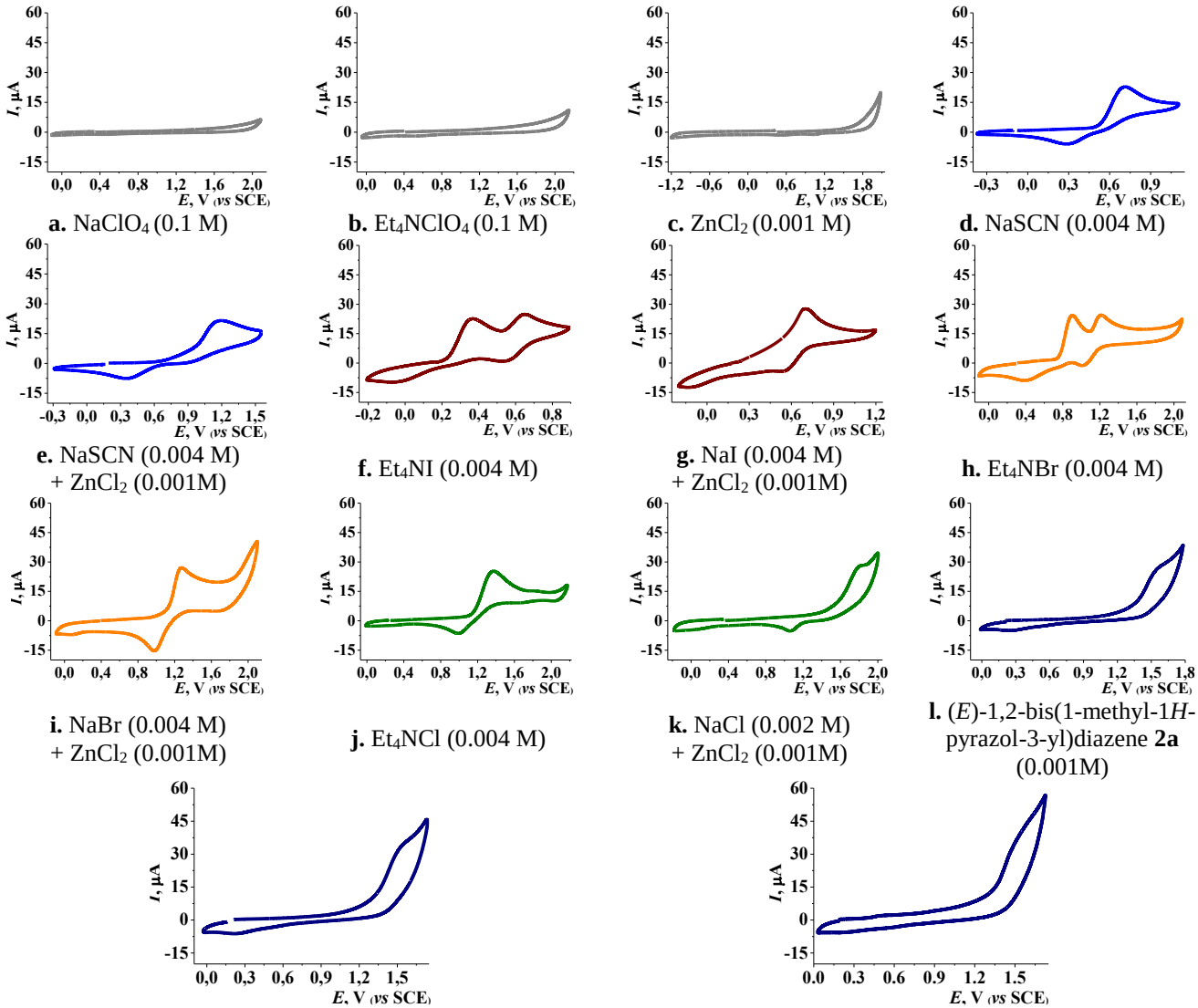
The $^{1}H$ and $^{13}C$ and spectra were recorded in $CDCl_3$ and DMSO-$d_6$ on Bruker Avance 300 (300 MHz for $^{1}H$ and 75 MHz for $^{13}C$) or Bruker DRX500 (126 MHz for $^{13}C$) instruments. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak as an internal reference: $^{1}H$ ($CDCl_3$ $\delta$: 7.26 ppm; DMSO-$d_6$ $\delta$ = 2.50 ppm), $^{13}C$ ($CDCl_3$ $\delta$ = 77.2 ppm; DMSO-$d_6$ $\delta$ = 39.5 ppm).[S1] Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet. High-resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II instrument using electrospray ionization (ESI) in positive ion mode (interface capillary voltage: 4500 V), with a mass range of m/z 50 – 3000.

Column chromatography was carried out using silica gel (particle size 0.040 - 0.063 mm, pore size 60 Å).

Azopyrazoles **2a-c** and thiocyanated pyrazole **$C_5H_6N_4S$** were prepared according to the described procedures.[S2,S3] Pyrazole **$C_4H_7N_3$**, acetonitrile (MeCN), acetone, sodium perchlorate ($NaClO_4$), tetraethylammonium perchlorate ($Et_4NClO_4$), sodium thiocyanate (NaSCN), zinc chloride ($ZnCl_2$), tetraethylammonium iodide ($Et_4NI$), sodium iodide (NaI), tetraethylammonium bromide ($Et_4NBr$), sodium bromide (NaBr), tetraethylammonium chloride ($Et_4NCl$), sodium chloride (NaCl), and anhydrous sodium sulfate ($Na_2SO_4$) were purchased from commercial suppliers and used as received. Light petroleum ether (PE), ethyl acetate (EtOAc), dichloromethane ($CH_2Cl_2$) and toluene were purified by distillation before use.

Electrochemical experiments (cyclic voltammetry and electrolysis) were performed using a computer-controlled potentiostat P-30JM (Elins, Russia).

Cyclic voltammetry (CV) experiments (see Scheme 1, Figure S1 and Table S1) were conducted under a nitrogen atmosphere at a scan rate of 0.10 V $s^{-1}$ in a temperature-controlled (20 °C) glass cell (10 ml) equipped with three electrodes (a Pt disk working electrode, $d$ = 2 mm; a Pt plate counter electrode, $S$ = 3 $cm^2$; saturated calomel reference electrode, SCE). Prior to each measurement, the working electrode was carefully polished and rinsed with acetone. The concentrations of the studied compounds ranged from 0.001 to 0.004 M in a 0.1 M solution of $NaClO_4$ ($Et_4NClO_4$) in MeCN as a supporting electrolyte.




**a.** $NaClO_4$ (0.1 M) **b.** $Et_4NClO_4$ (0.1 M) **c.** $ZnCl_2$ (0.001 M) **d.** NaSCN (0.004 M)

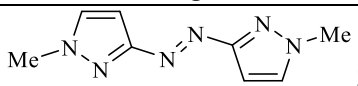
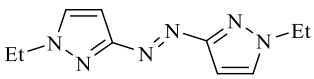
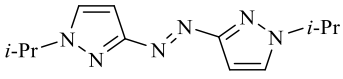
**e.** NaSCN (0.004 M) + $ZnCl_2$ (0.001M) **f.** $Et_4NI$ (0.004 M) **g.** NaI (0.004 M) + $ZnCl_2$ (0.001M) **h.** $Et_4NBr$ (0.004 M)

**i.** NaBr (0.004 M) + $ZnCl_2$ (0.001M) **j.** $Et_4NCl$ (0.004 M) **k.** NaCl (0.002 M) + $ZnCl_2$ (0.001M) **l.** (*E*)-1,2-bis(1-methyl-1*H*-pyrazol-3-yl)diazene **2a** (0.001M)

**m.** (*E*)-1,2-bis(1-ethyl-1*H*-pyrazol-3-yl)diazene **2b** (0.001M) **h.** (*E*)-1,2-bis(1-isopropyl-1*H*-pyrazol-3-yl)diazene **2c** (0.001M)

**Figure S1** CV curves of the reagents or their mixtures. Pt disk (working electrode), SCE (reference electrode), 0.1M solution of $NaClO_4$ ($Et_4NClO_4$) in MeCN (supporting electrolyte), scan rate 0.1 V $s^{-1}$

**Table S1** Reagents and oxidation potentials, $E_p^{ox}$, V [a]

| Reagent | $E_p^{ox}$, V | Reagent | $E_p^{ox}$, V |
|---|---|---|---|
| $ZnCl_2$ | >1.8 |  **2a** | ~1.5 (1.5[S4]) |
| $SCN^-$ | 0.7 (0.7 [S4,S5]) | | |
| $[Zn(SCN)_4]^{2-}$ [b] | 1.2 (1.1 – 1.2[S4-S6]) | | |
| $I^-$ | 0.4 (0.4 – 0.5[S7]) |  **2b** | ~1.5 |
| $[ZnI_4]^{2-}$ [b] | 0.7 | | |
| $Br^-$ | 0.9 (1.1[S7,S8]) | | |
| $[ZnBr_4]^{2-}$ [b] | 1.3 |  **2c** | ~1.5 |
| $Cl^-$ | 1.4 (1.4[S9]) | | |
| $[ZnCl_4]^{2-}$ [b] | 1.8 | | |

[a] Pt disk (working electrode), SCE (reference electrode), 0.1M solution of $NaClO_4$ в MeCN (supporting electrolyte), scan rate 0.1 V·$s^{-1}$, concentrations of compounds are 0.001 – 0.004 M

[b] This work only suggests the *in situ* formation of zinc (II) complex ions by mixing the corresponding reagents, while structurally related complexes have been described in detail in the literature[S10-S12]

Electrolyses (see Table 1) were performed in a temperature-controlled (20 °C) divided glass cell (70 ml) equipped with a three-layer tracing-paper diaphragm, Pt plate electrodes ($S_{anode}$ = 16.5 $cm^2$, $S_{cathode}$ = 3.5 $cm^2$) and SCE. The anolyte consisted a 0.1 M solution of $NaClO_4$ (or $Et_4NClO_4$) in MeCN (60 ml) containing the thiocyanating of halogenating reagent: NaSCN (0.5 – 4 mmol, 0.041 – 0.649 g, entries 1 – 5), $Et_4NI$ (0.5 mmol, 0.129 g, entry 6), NaI (4 mmol, 0.60 g, entry 7), $Et_4NBr$ (0.5 – 1 mmol, 0.105 – 0.211 g, entries 8 – 10), NaBr (1 mmol, 0.103 g, entry 11), $Et_4NCl$ (1 mmol, 0.166 g, entry 12), or NaCl (0.5 mmol, 0.029 g, entry 13); $ZnCl_2$ (0.25 – 1 mmol, 0.034 – 0.136 g, entries 2 – 5, 7, 11, 13); and azopyrazole **1a-c** (0.25 mmol, 0.048 – 0.062 g). In entries 2 – 5, 7, 11, the addition of $ZnCl_2$ resulted in the formation of a white precipitate (identified previously as NaCl[S5]) was observed which partially or completely dissolved during electrolysis. The catholyte was a 0.5 M solution of $NaClO_4$ (or $Et_4NClO_4$) in MeCN (10 ml). Electrolyses were conducted at anode potentials ($E_{anode}$) 0.4 – 1.8 V with vigorous magnetic stirring. The amounts of passed electricity ($Q$) were 48.25 – 386 C. The theoretical amount of passed electricity ($Q_t$) was calculated based on Faraday's law as 48.25 C for mono-functionalization (entries 1 – 7), corresponding to the generation of thiocyanogen or halogen from 0.5 mmol of the corresponding ion; or 96.5 C for bis-functionalization (entries 8 – 13). After electrolysis, the reaction mixture was concentrated *in vacuo*, dissolved in water (15 ml) and extracted with organic solvent (4 × 25 ml, $CH_2Cl_2$ in entries 1 – 5, 7, 11, 13; toluene in entries 6, 8 – 10, 12). The combined organic extracts were dried with $Na_2SO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel using PE / EtOAc (from 10 / 1 to 1 / 1 v/v) as eluent, affording the pure target products **3-5a-c** (0.028 – 0.213 mmol, 0.007 – 0.086 g, entries 2 – 5, 8 – 12). The products were characterized by $^1H$ and $^{13}C$ NMR spectroscopy and HRMS. In some cases, unreacted azopyrazoles **2a-c** were recovered (entries 1 – 4, 6 – 9), or a complex mixture of taring products was formed (entry 13).

**(*E*)-1-Methyl-3-((1-methyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole** (**3a**).[S4] Yellow powder, mp 95-97 °C (90 – 94 °C[S3]). $^1H$ NMR (300 MHz, DMSO-$d_6$) $\delta$: 3.97 (s, 3H, Me), 4.00 (s, 3H, Me), 6.55 (d, $^3J_{H,H}$ 2.6 Hz, 1H, CH), 7.84 (d, $^3J_{H,H}$ 2.6 Hz, 1H, CH), 8.11 (s, 1H, CH). $^{13}C$ NMR (126 MHz, DMSO-$d_6$) $\delta$: 39.5 (merge with DMSO), 40.2 (merge with DMSO), 93.1, 94.9, 111.5, 132.4, 133.6, 157.7, 162.0. HRMS (ESI), *m/z*: 270.0533 (calc. for $C_9H_9N_7SNa$, *m/z*: 270.0532 $[M + Na]^+$).

**(*E*)-1-Ethyl-3-((1-ethyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole** (**3b**). Yellow powder, mp 200-202 °C. $^1H$ NMR (300 MHz, DMSO-$d_6$) $\delta$: 1.40 – 1.50 (m, 6H, $C\underline{H_3}CH_2$), 4.21 – 4.36 (m, 4H, $CH_3C\underline{H_2}$), 6.56 (d, $^3J_{H,H}$ 2.6 Hz, 1H, CH), 7.90 (d, $^3J_{H,H}$ 2.6 Hz, 1H, CH), 8.16 (s, 1H, CH). $^{13}C$

NMR (75 MHz, DMSO-$d_6$) $\delta$: 15.0, 15.3, 47.3, 48.0, 92.8, 94.7, 111.4, 131.2, 132.2, 157.7, 162.0. HRMS (ESI), *m/z*: 298.0844 (calc. for $C_{11}H_{13}N_7SNa$, *m/z*: 298.0845 $[M + Na]^+$).

**(*E*)-1-Isopropyl-3-((1-isopropyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole** (**3c**). Yellow powder, mp 96-98 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 1.47 – 1.53 (m, 12H, CH(C$\underline{H_3}$)$_2$), 4.49 – 4.87 (m, 2H, C$\underline{H}$(CH$_3$)$_2$), 6.56 (d, $^3J_{H,H}$ 2.6 Hz, 1H, CH), 7.94 (d, $^3J_{H,H}$ 2.6 Hz, 1H, CH), 8.17 (s, 1H, CH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$: 22.2 (2C), 22.5 (2C), 54.2, 55.0, 92.5, 94.5, 111.4, 129.9, 130.5, 157.4, 161.8. HRMS (ESI), *m/z*: 326.1159 (calc. for $C_{13}H_{17}N_7SNa$, *m/z*: 326.1158 $[M + Na]^+$).

**(*E*)-1,2-Bis(4-bromo-1-methyl-1*H*-pyrazol-3-yl)diazene** (**4a**).[S3,S8] Yellow powder, mp 215-217 °C (211-213 °C[S8]). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 3.97 (s, 6H, Me), 8.13 (s, 2H, CH). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$: 40.1 (2C, merge with DMSO), 88.2 (2C), 134.2 (2C), 156.4 (2C). HRMS (ESI), *m/z*: 372.9033 (calc. for $C_8H_8{}^{81}Br_2N_6Na$, *m/z*: 372.9029 $[M + Na]^+$).

**(*E*)-1,2-Bis(4-bromo-1-ethyl-1*H*-pyrazol-3-yl)diazene** (**4b**).[S8] Yellow powder, mp 155-157 °C (154-156 °C[S8]). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 1.45 (t, $^3J_{H,H}$ 7.3 Hz, 6H, C$\underline{H_3}$CH$_2$), 4.22 (q, $^3J_{H,H}$ 7.3 Hz, 4H, CH$_3$C$\underline{H_2}$), 8.20 (s, 2H, CH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$: 15.0 (2C), 48.0 (2C), 87.5 (2C), 132.9 (2C), 156.3 (2C). HRMS (ESI), *m/z*: 376.9547 (calc. for $C_{10}H_{13}{}^{79}Br\,{}^{81}BrN_6$, *m/z*: 376.9543 $[M + H]^+$).

**(*E*)-1,2-Bis(4-bromo-1-isopropyl-1*H*-pyrazol-3-yl)diazene** (**4c**). Yellow powder, mp 175-177 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 1.46 (d, $^3J_{H,H}$ 6.6 Hz, 12H, CH(C$\underline{H_3}$)$_2$), 4.59 (sept, $^3J_{H,H}$ 6.6 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 8.24 (s, 2H, CH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$: 22.2 (4C), 55.0 (2C), 87.0 (2C), 131.4 (2C), 156.0 (2C). HRMS (ESI), *m/z*: 404.9854 (calc. for $C_{12}H_{17}{}^{79}Br{}^{81}BrN_6$, *m/z*: 404.9856 $[M + H]^+$).

**(*E*)-1,2-Bis(4-chloro-1-methyl-1*H*-pyrazol-3-yl)diazene** (**5a**).[S2,S8] Yellow powder, mp 213-215 °C (214–216 °C[S2]). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 3.98 (s, 6H, Me), 7.45 (s, 2H, CH). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$: 40.5 (2C), 106.6 (2C), 130.6 (2C), 156.5 (2C). HRMS (ESI), *m/z*: 259.0255 (calc. for $C_8H_9{}^{35}Cl_2N_6$, *m/z*: 259.0260 $[M + H]^+$).

**(*E*)-1,2-Bis(4-chloro-1-ethyl-1*H*-pyrazol-3-yl)diazene** (**5b**). Yellow powder, mp 155-157 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 1.43 (t, $^3J_{H,H}$ 7.3 Hz, 6H, C$\underline{H_3}$CH$_2$), 4.21 (q, $^3J_{H,H}$ 7.3 Hz, 4H,

$CH_3C\underline{H_2}$), 8.20 (s, 2H, CH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$: 14.9 (2C), 48.0 (2C), 103.0 (2C), 130.7 (2C), 155.2 (2C). HRMS (ESI), *m/z*: 287.0574 (calc. for $C_{10}H_{13}{}^{35}Cl_2N_6$, *m/z*: 287.0573 $[M + H]^+$).

**(*E*)-1,2-Bis(4-chloro-1-isopropyl-1*H*-pyrazol-3-yl)diazene** (**5c**). Yellow powder, mp 165-167 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 1.46 (d, $^3J_{H,H}$ 6.6 Hz, 12H, $CH(C\underline{H_3})_2$), 4.58 (sept, $^3J_{H,H}$ 6.6 Hz, 2H, $C\underline{H}(CH_3)_2$), 8.25 (s, 2H, CH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$: 22.2 (4C), 55.1 (2C), 102.6 (2C), 129.4 (2C), 155.0 (2C). HRMS (ESI), *m/z*: 317.0863 (calc. for $C_{12}H_{17}{}^{35}Cl^{37}ClN_6$, *m/z*: 317.0857 $[M + H]^+$).

Microbiological studies of compounds 1-methyl-1*H*-pyrazol-3-amine (**$C_4H_7N_3$**), 1-methyl-4-thiocyanato-1*H*-pyrazol-3-amine (**$C_5H_6N_4S$**), (*E*)-1,2-bis(4-bromo-1-methyl-1*H*-pyrazol-3-yl)diazene (**4a**) and (*E*)-1,2-bis(4-chloro-1-methyl-1*H*-pyrazol-3-yl)diazene (**5a**) (Table 2) were conducted using the double serial microdilution method in accordance with MUK 4.2.1890-0416,[S13] EUCAST,[S14,S15] and CLSI guidelines.[S16] *Candida albicans* ATCC 24433 and *Aspergillus niger* GNCA 37a were used as test cultures.

For testing, each sample (2 mg) was dissolved in 0.2 ml of DMSO to prepare a stock solution with a concentration of 10000 μg ml$^{-1}$. Serial dilutions were then prepared in RPMI 1640 medium supplemented with 2% glucose, covering a concentration range of 0.0015 – 500 μg ml$^{-1}$. To assess activity, 100 μl of each sample solution was added to wells (the inoculum titer was $2.5 \cdot 10^3$ CFU ml$^{-1}$). The plates were incubated for 48 – 72 h at 35 ± 2 °C.

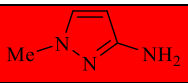
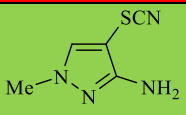
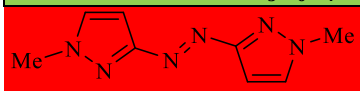
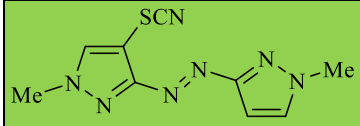
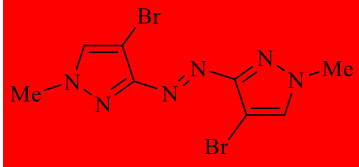
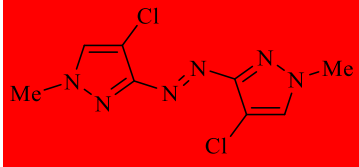
The minimum inhibitory concentration (MIC) was determined as the lowest concentration of the compound at which no visible growth of the test cultures was observed. Antifungal activity was evaluated by comparing the MIC values of the samples with that of the standard antifungal drug fluconazole.

Simultaneously, microbiological purity of the samples (*via* examination of sample solutions without inoculum), the activity of DMSO (via examination of inoculum solutions without samples), and growth controls (inoculum solutions without DMSO or samples) were monitored.

An additional comparative analysis to elucidate the proposed mechanism of antifungal activity (Table S2) was performed by integrating our experimental results with literature data[S4] on the test compounds and related SCN-containing pyrazole-type compounds,[S17] standard antifungal agents,[S18-S24] and predictive insights of the PASS online program.[S25] The table demonstrates that both the experimental and predicted activity profiles of the thiocyanate compounds **$C_5H_6N_4S$** and **3a** closely align with those of fluconazole and voriconazole. This alignment suggests that the antifungal

mechanism of the synthesized compounds may be similar to that of these drugs, likely involving inhibition of ergosterol biosynthesis through targeting the enzyme lanosterol 14α-demethylase.

**Table S2** Experimental data and calculations on probable activity (Pa-Pi) obtained using the PASS online program

| Compound | Bioassay data MIC / μg ml$^{-1}$ | | PASS online data[S25] | | | | |
|---|---|---|---|---|---|---|---|
| | *C. albicans* | *A. niger* | Lanosterol 14 alpha demethylase inhibitor | Steroid synthesis inhibitor | Membrane integrity antagonist | Membrane permeability enhancer | Squalene epoxidase inhibitor |
|  **$C_4H_7N_3$** | >500 | >500 | 0,1 | 0,2 | 0,2 | 0,3 | - |
|  **$C_5H_6N_4S$** | 32 | 125 | 0,1 | 0,1 | - | - | - |
|  **2a** | >500[S4] | >500[S4] | 0,1 | - | 0,1 | 0,3 | - |
|  **3a** | 32[S4] | 8[S4] | 0,1 | 0,1 | - | - | - |
|  **4a** | >500 | >500 | 0,1 | 0,2 | 0,1 | - | - |
|  **5a** | >500 | >500 | 0,1 | 0,1 | 0,4 | 0,1 | - |
| fluconazole[S18] | 8 | 125 | 0,8 | 0,7 | - | - | - |
| voriconazole[S18] | 0.06 – 8[S19] | 2 – 4[S19] | 0,7 | 0,5 | - | - | - |
| amphotericin B[S20] | 2 – 4[S19] | 4 – 8[S19] | - | - | 1,0 | 0,9 | - |
| caspofungin[S21] | 0.15 – 1[S19] | 0.25 – 1[S19] | - | - | - | - | - |
| terbinafine[S22] | 4[S23] | 0.02 – 2.5[S24] | - | 0,6 | 0,1 | 0,1 | 0,4 |

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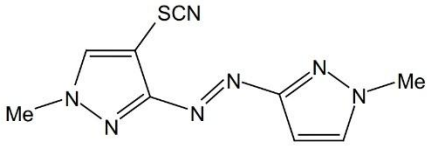
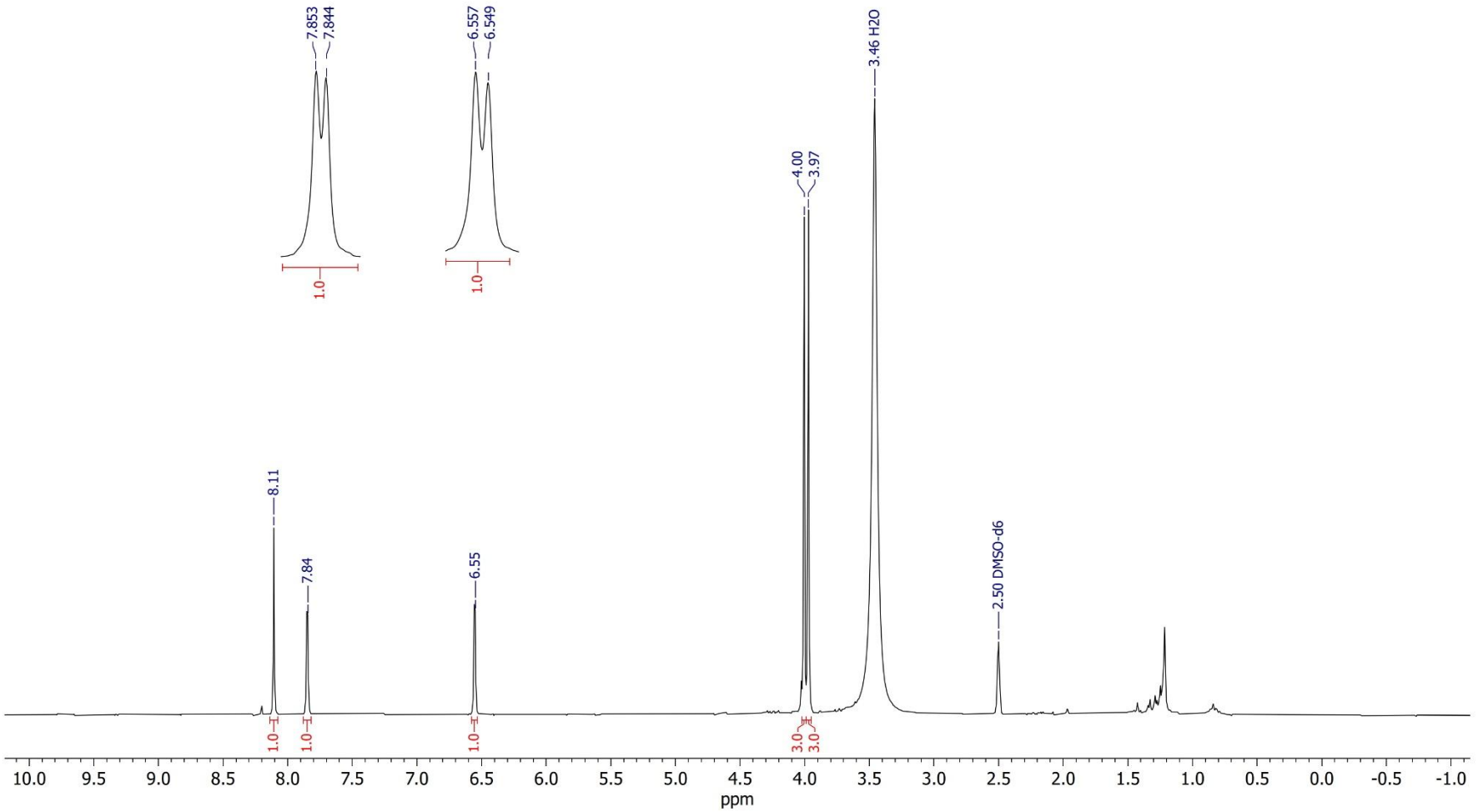
1H NMR (300.13 MHz, DMSO-d6)

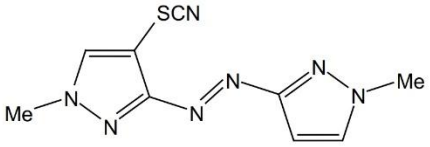
(*E*)-1-methyl-3-((1-methyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole (**3a**)

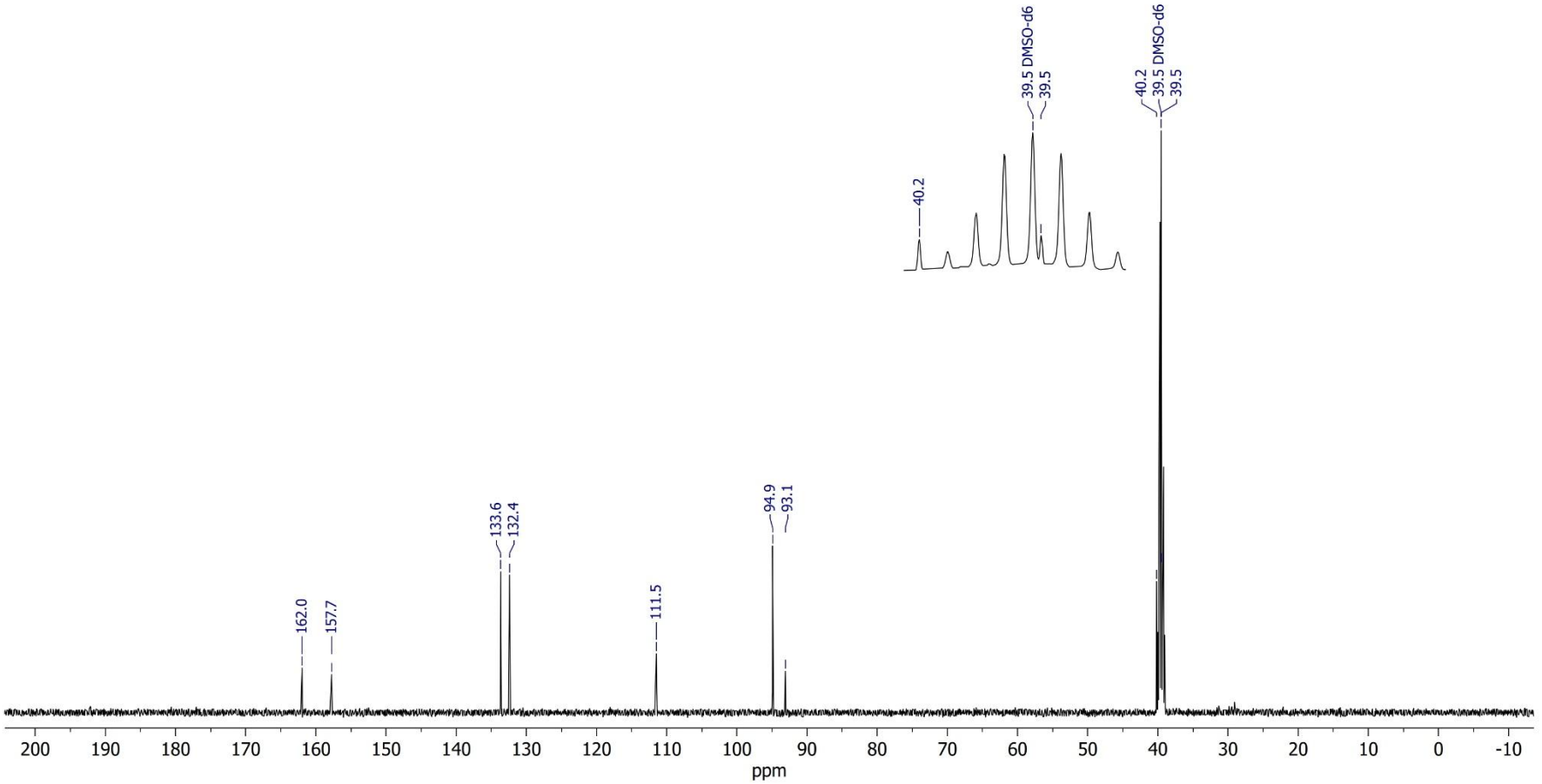


13C NMR (125.77 MHz, DMSO-d6)

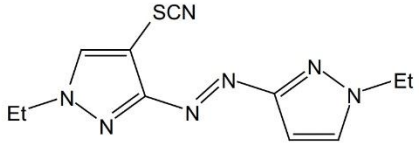
(*E*)-1-methyl-3-((1-methyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole (**3a**)

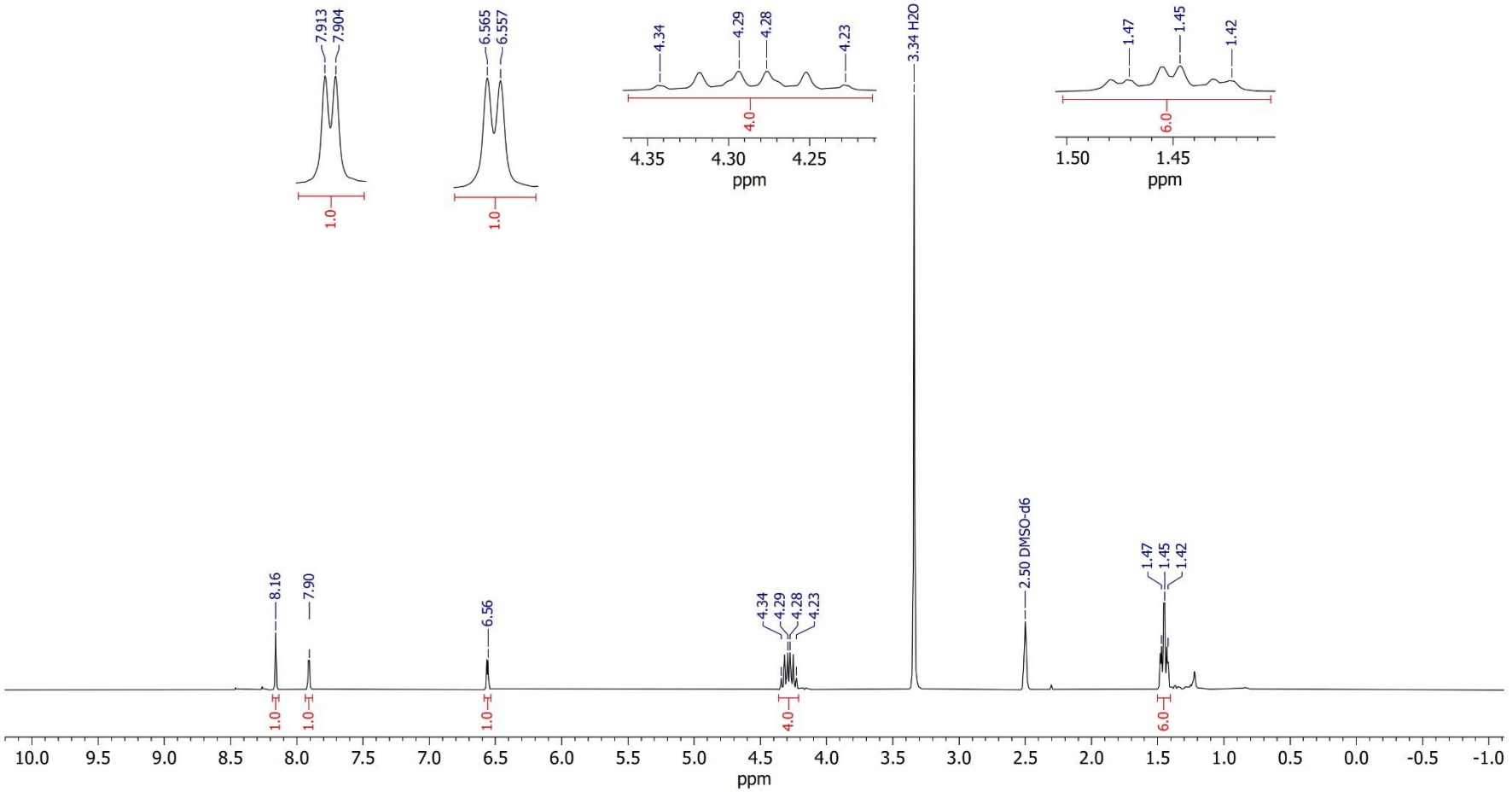


1H NMR (300.13 MHz, DMSO-d6)

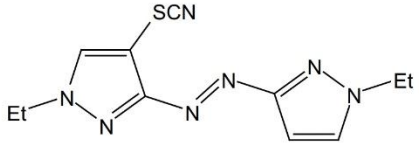
(*E*)-1-ethyl-3-((1-methyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole (**3b**)

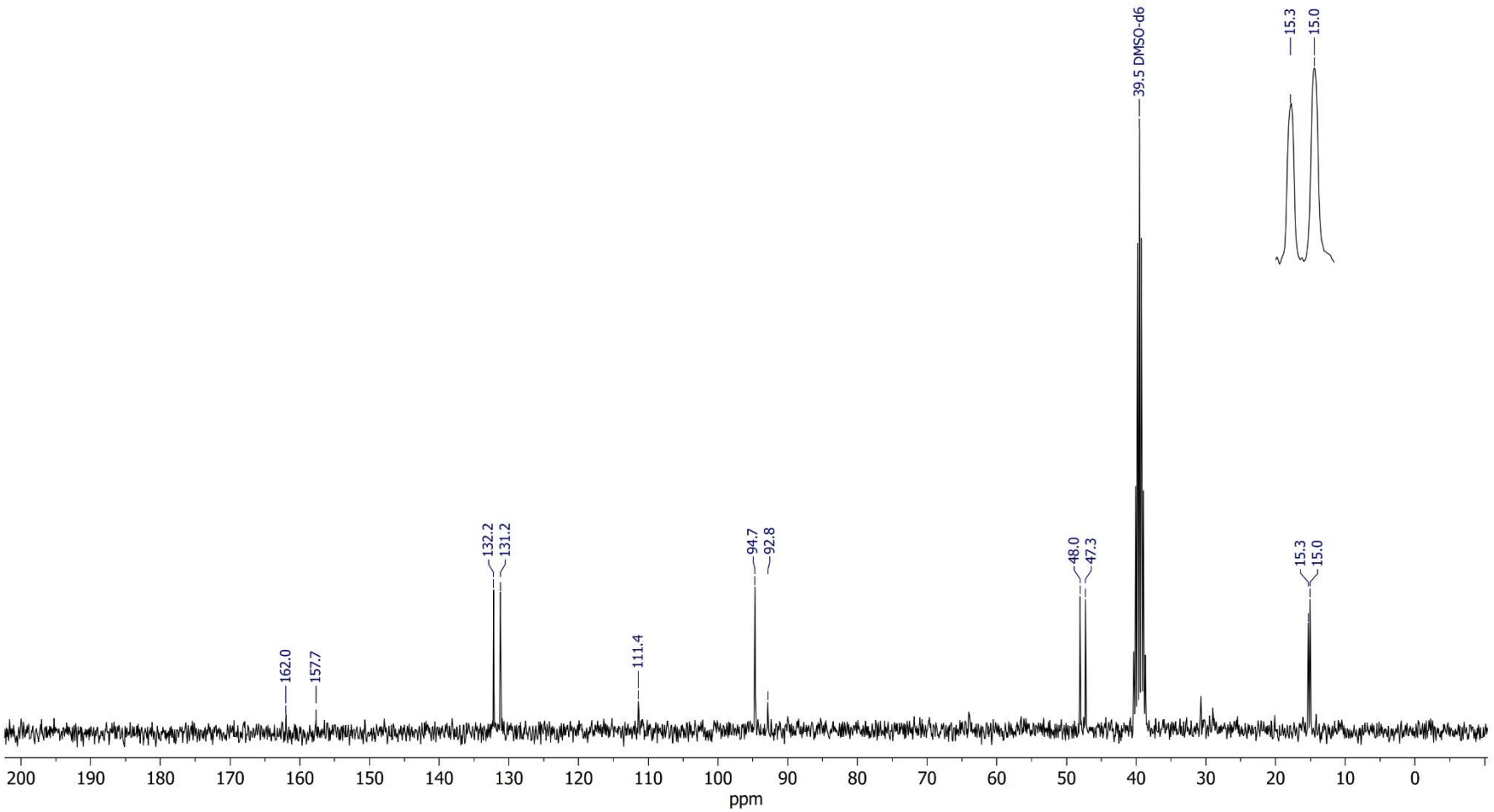


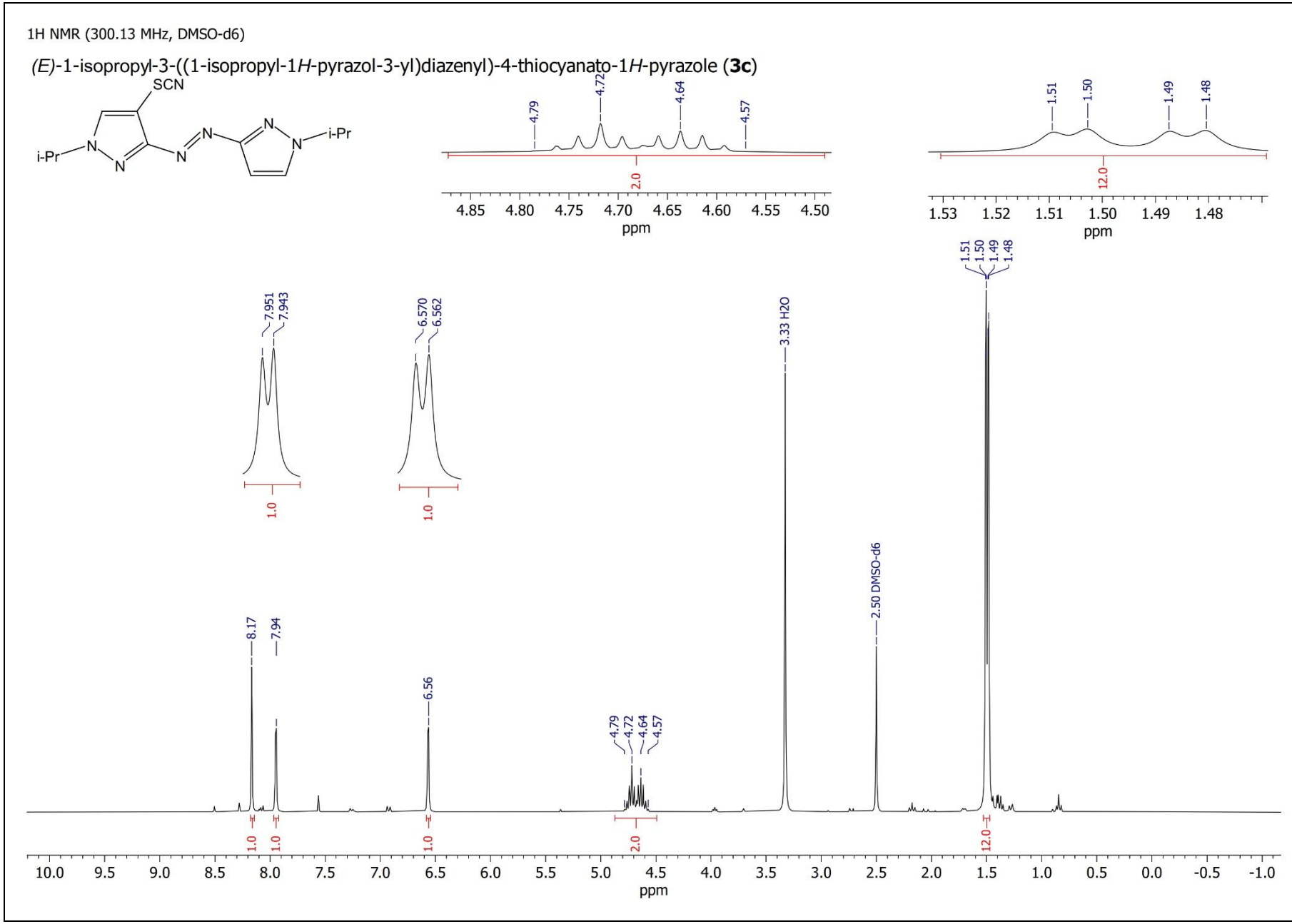



13C NMR (75.48 MHz, DMSO-d6)

(*E*)-1-ethyl-3-((1-methyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole (**3b**)

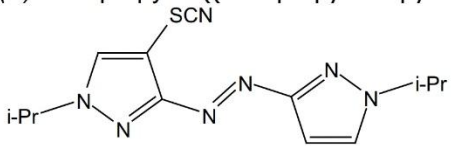


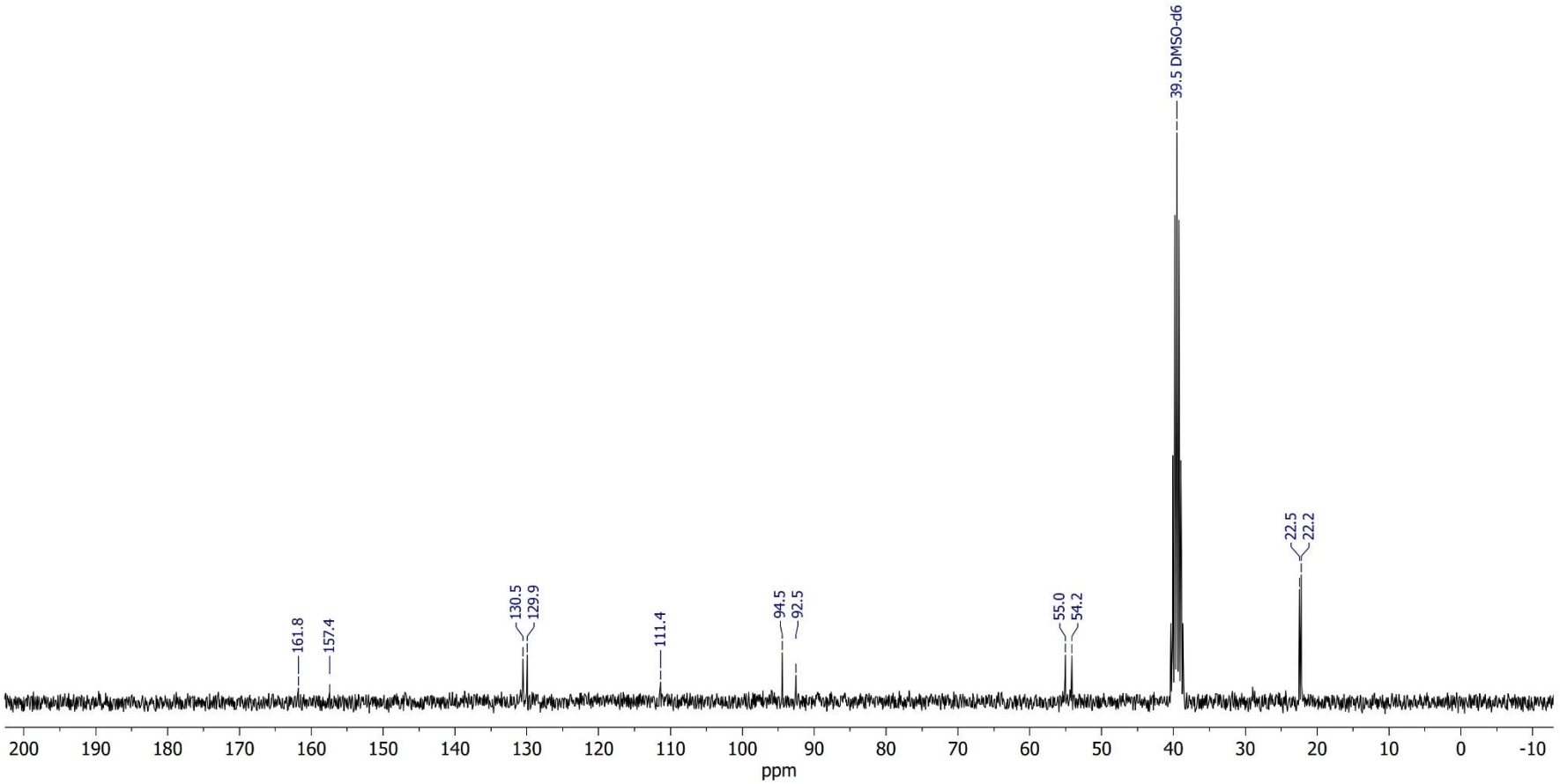




1H NMR (300.13 MHz, DMSO-d6)
(E)-1-isopropyl-3-((1-isopropyl-1H-pyrazol-3-yl)diazenyl)-4-thiocyanato-1H-pyrazole (3c)
SCN
i-Pr
i-Pr
4.79
4.72
4.64
4.57
2.0
1.51
1.50
1.49
1.48
12.0
ppm
7.951
7.943
6.570
6.562
3.33 H2O
2.50 DMSO-d6
8.17
7.94
6.56
1.0
2.0
12.0
ppm

13C NMR (75.48 MHz, DMSO-d6)

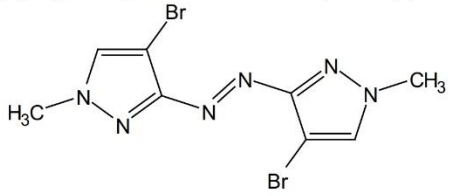
*(E)*-1-isopropyl-3-((1-isopropyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole (**3c**)

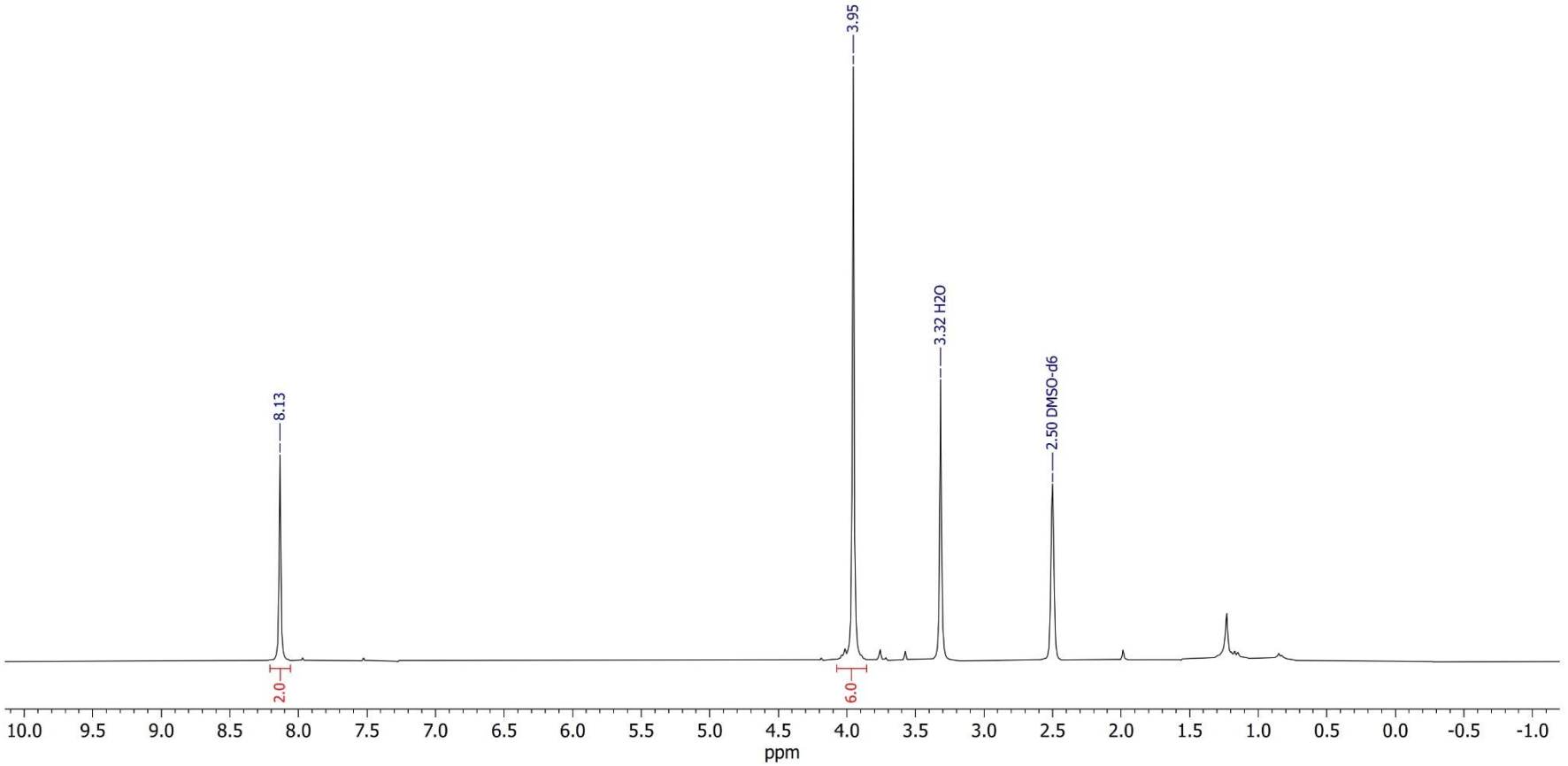


1H NMR (300.13 MHz, DMSO-d6)

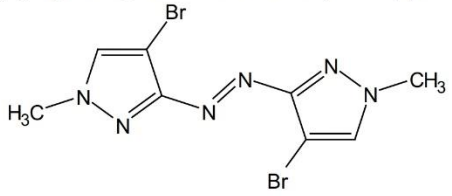
*(E)*-1,2-bis(4-bromo-1-methyl-1*H*-pyrazol-3-yl)diazene (**4a**)

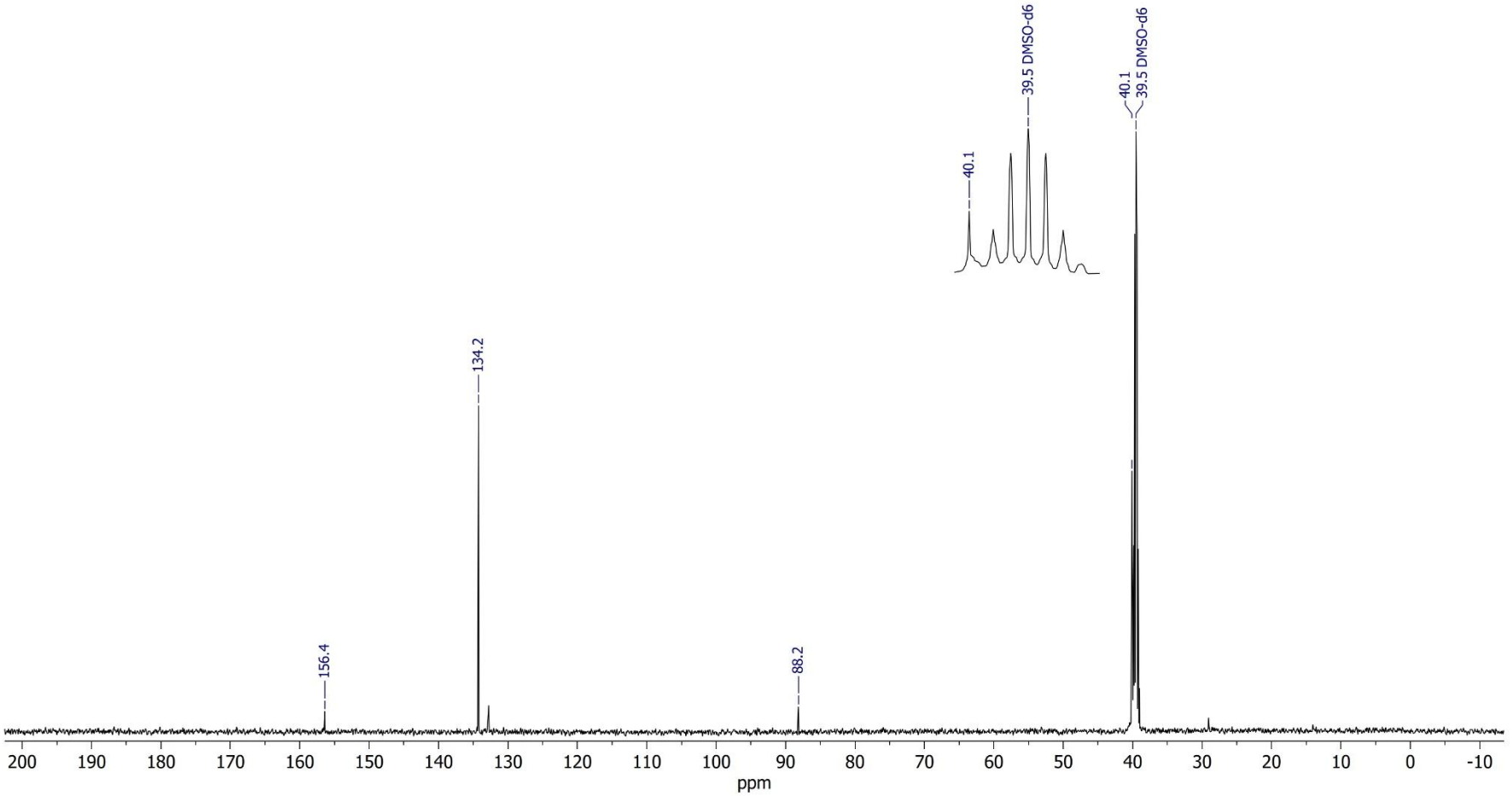


13C NMR (125.77 MHz, DMSO-d6)

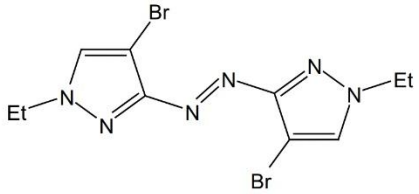
*(E)*-1,2-bis(4-bromo-1-methyl-1*H*-pyrazol-3-yl)diazene (**4a**)

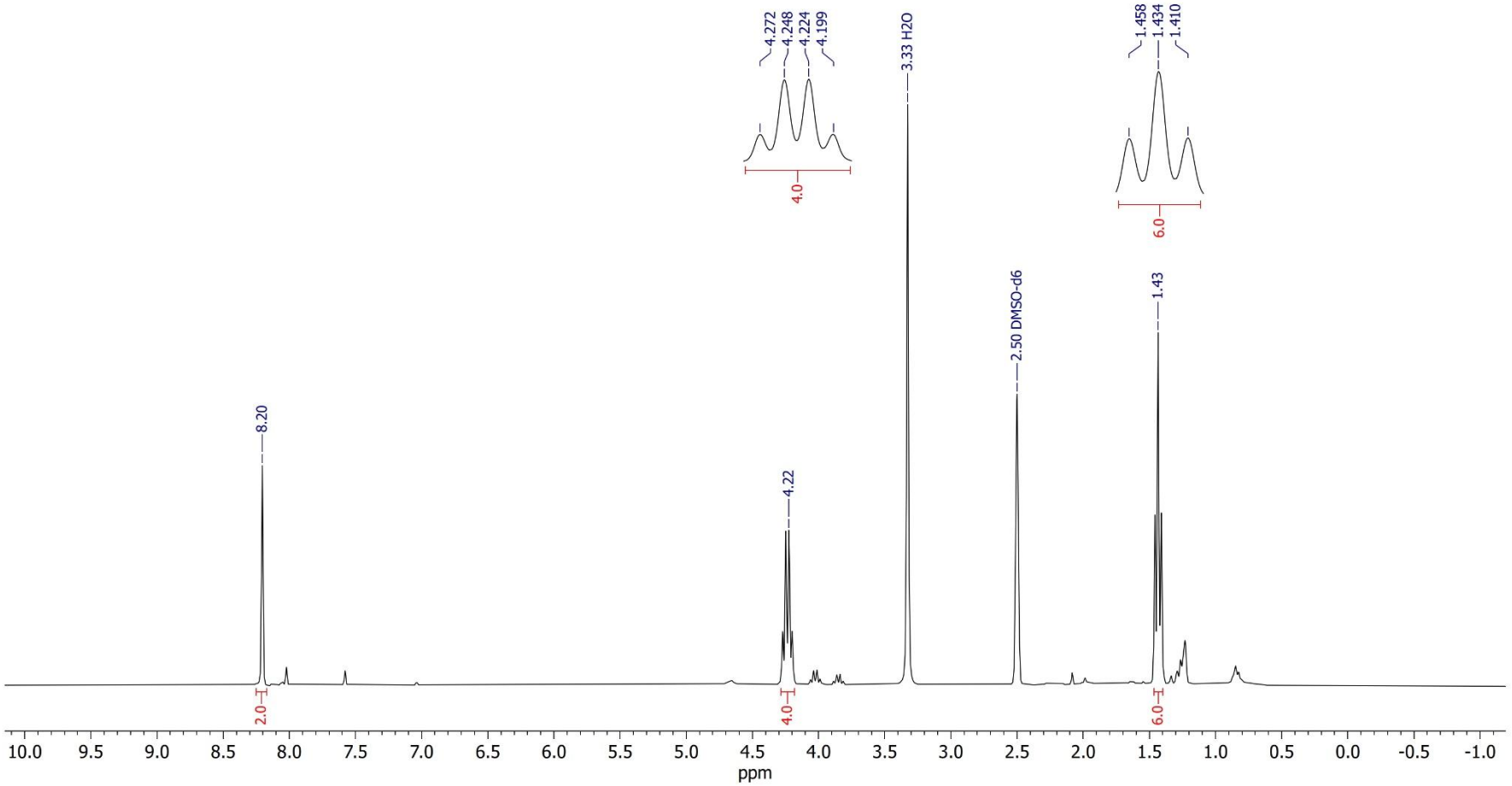


1H NMR (300.13 MHz, DMSO-d6)

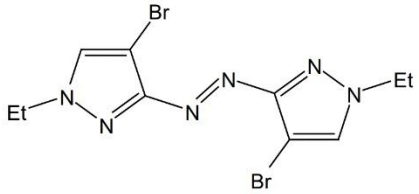
*(E)*-1,2-bis(4-bromo-1-ethyl-1*H*-pyrazol-3-yl)diazene (**4b**)

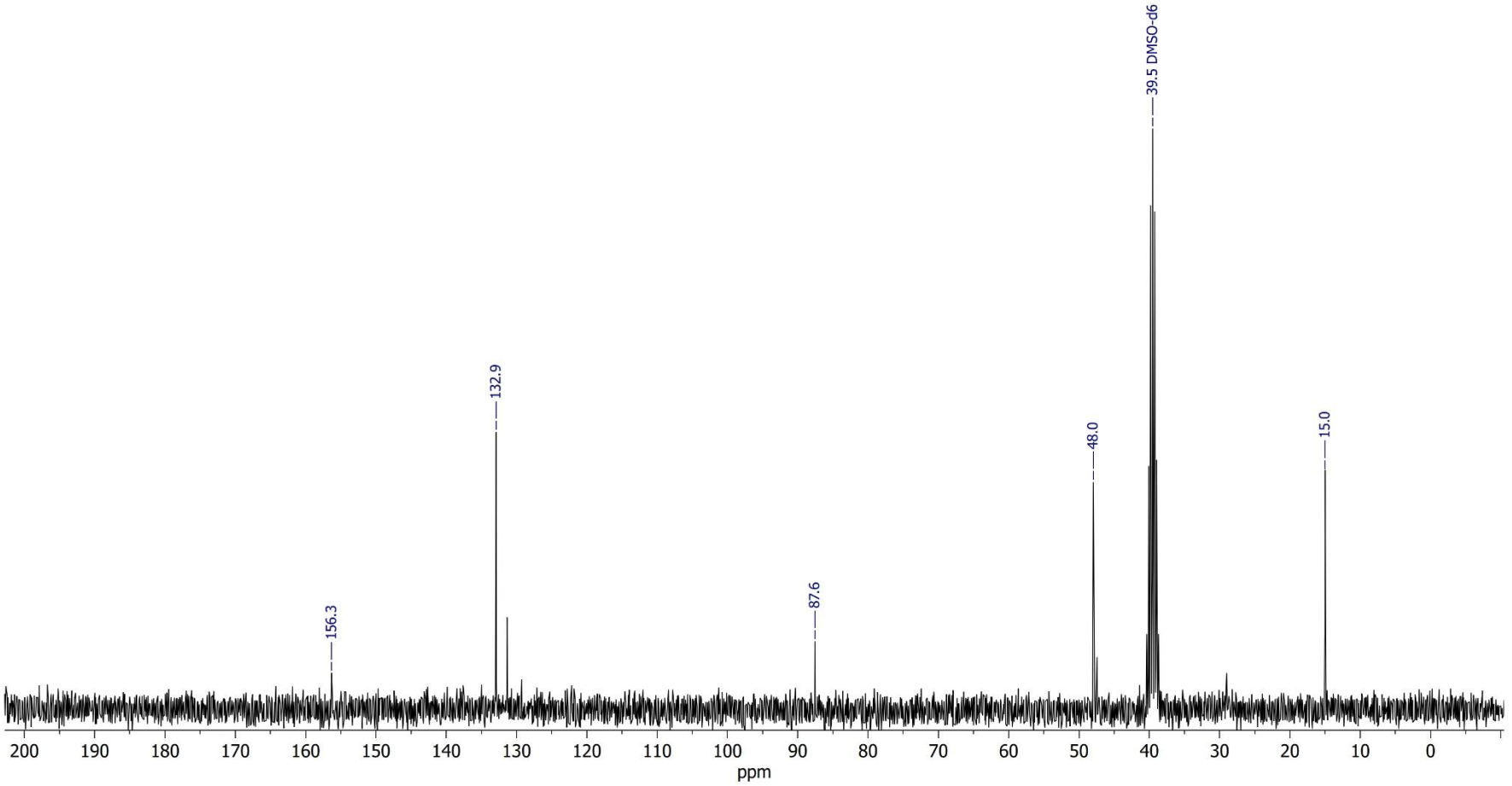


13C NMR (75.48 MHz, DMSO-d6)

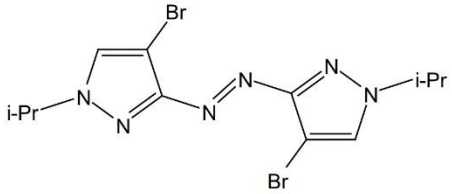
*(E)*-1,2-bis(4-bromo-1-ethyl-1*H*-pyrazol-3-yl)diazene (**4b**)

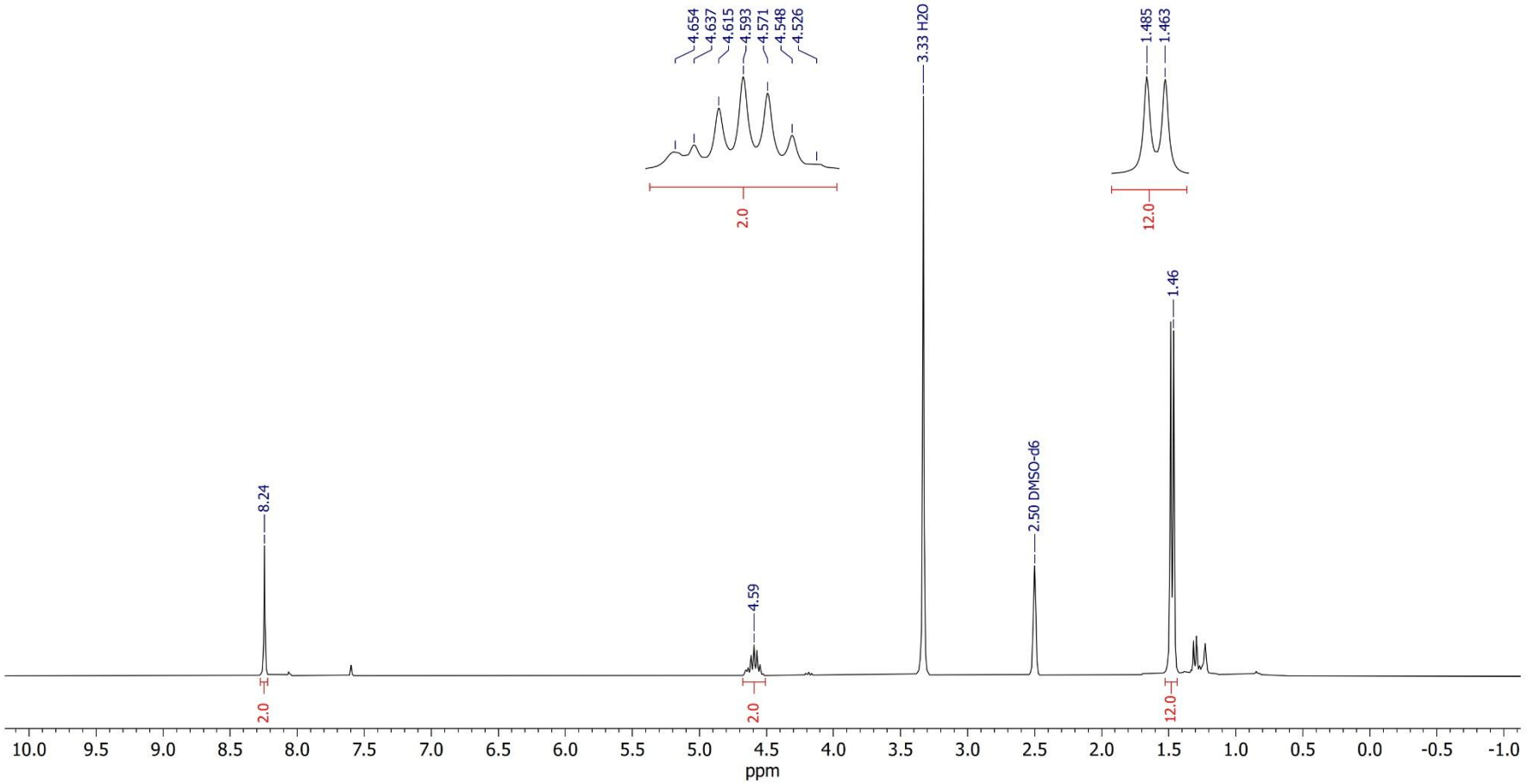


1H NMR (300.13 MHz, DMSO-d6)

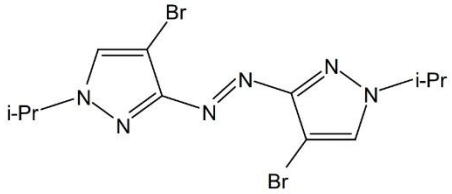
*(E)*-1,2-bis(4-bromo-1-isopropyl-1*H*-pyrazol-3-yl)diazene (**4c**)

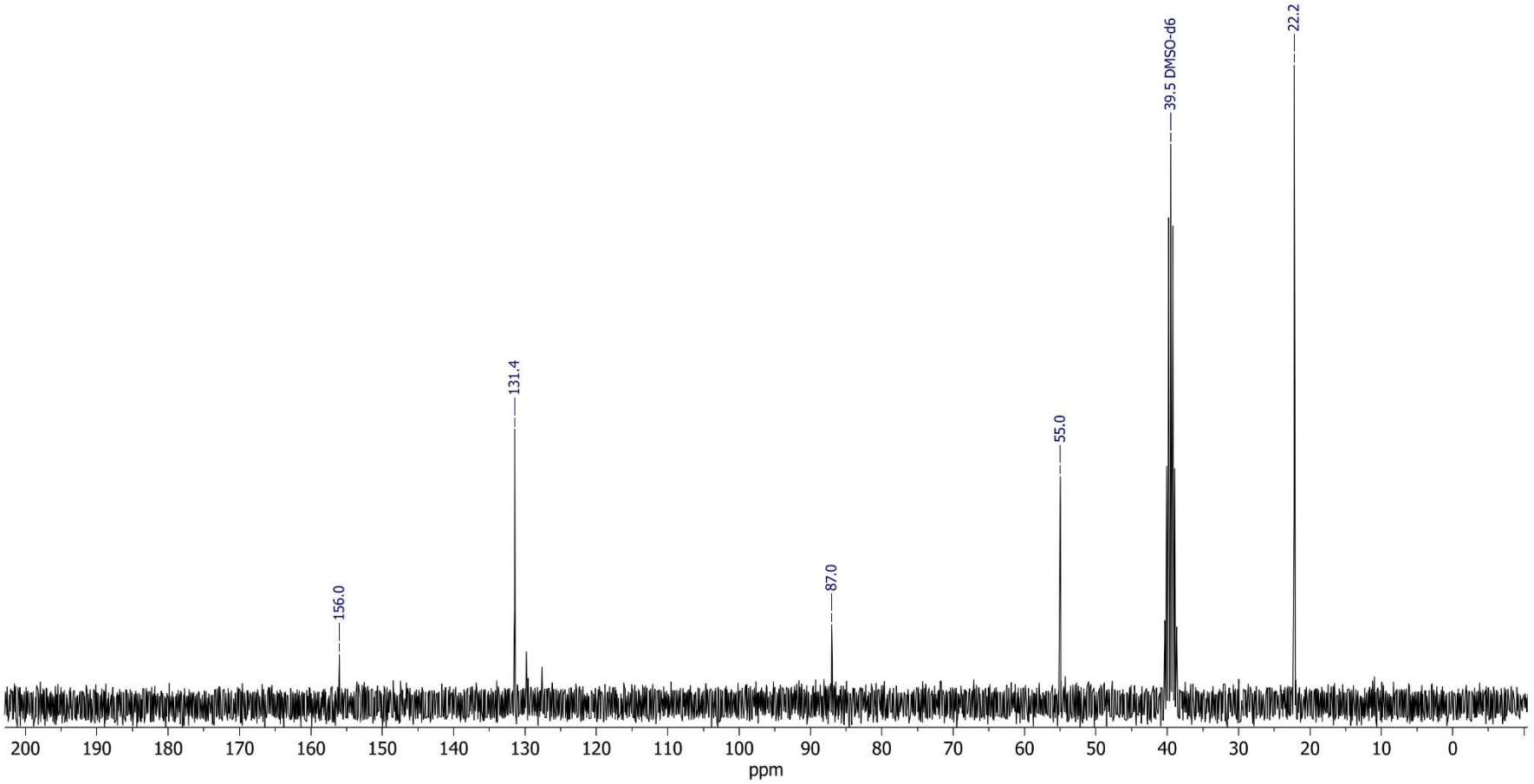


13C NMR (75.48 MHz, DMSO-d6)

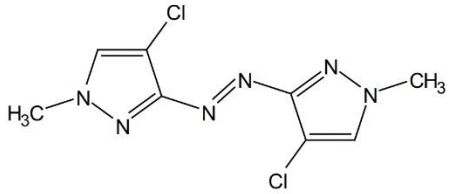
*(E)*-1,2-bis(4-bromo-1-isopropyl-1*H*-pyrazol-3-yl)diazene (**4c**)

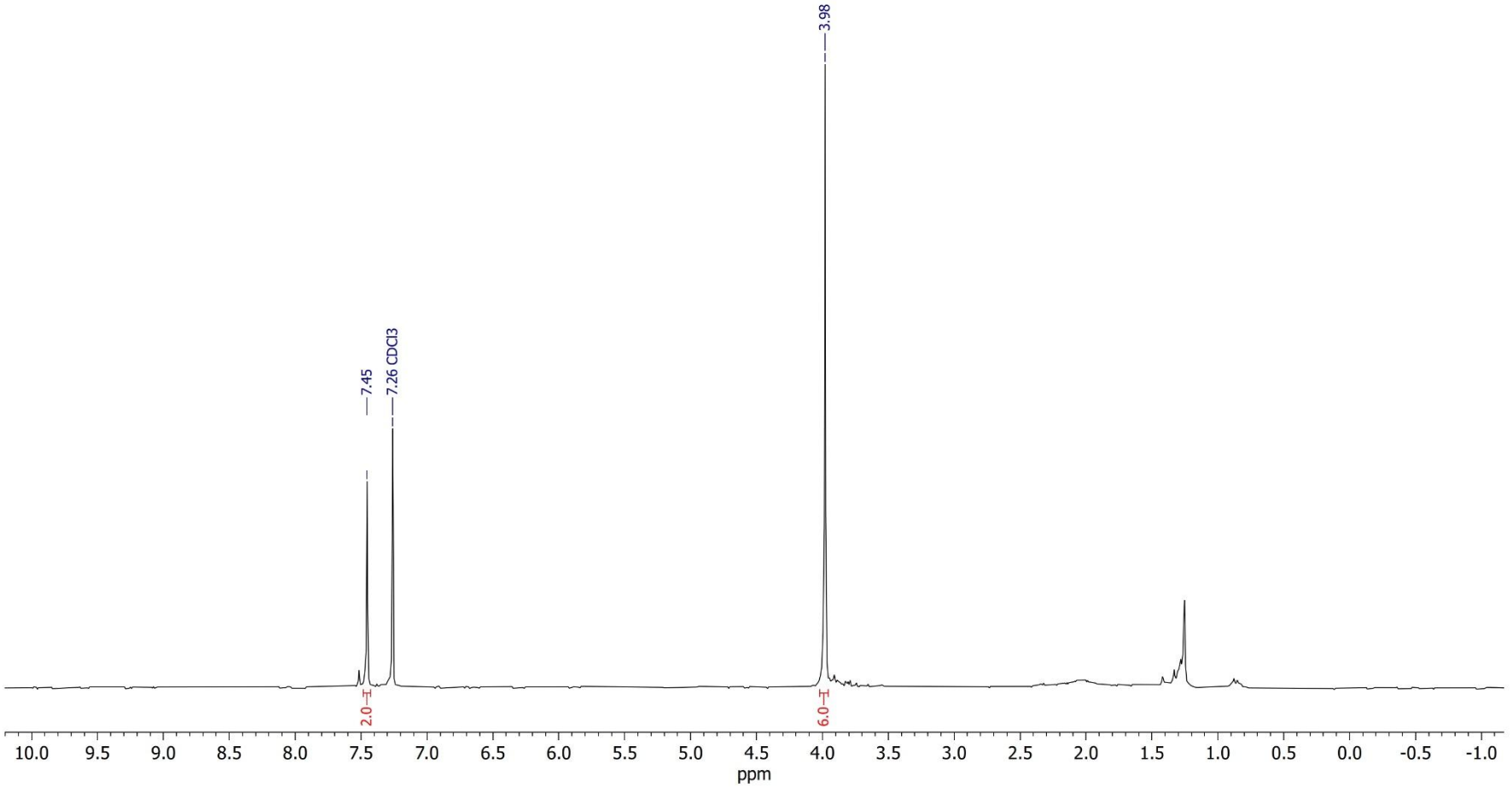


1H NMR (300.13 MHz, CDCl3)

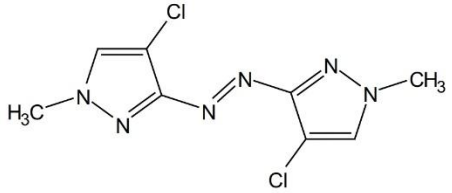
*(E)*-1,2-bis(4-chloro-1-methyl-1*H*-pyrazol-3-yl)diazene (**5a**)

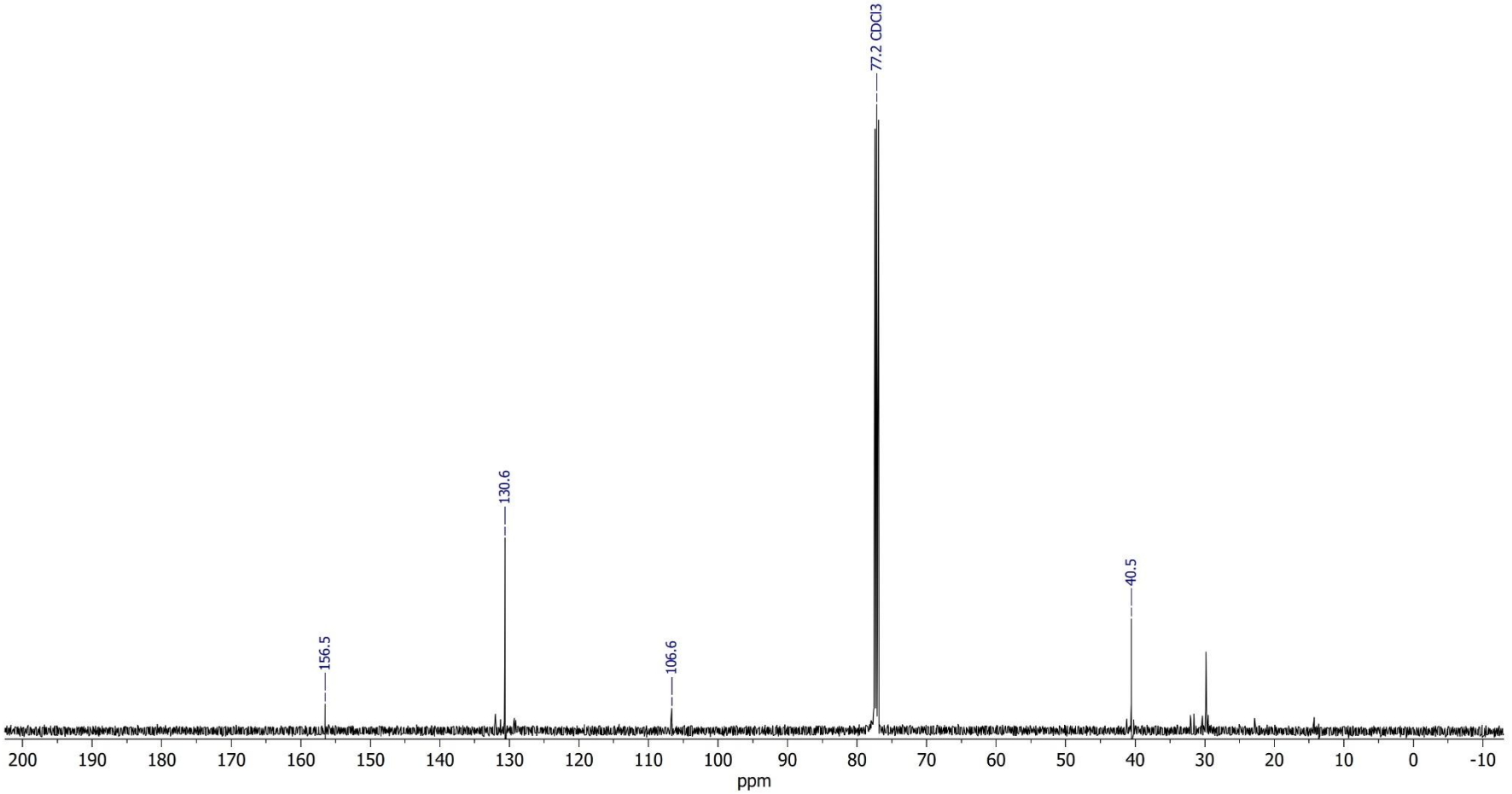


13C NMR (125.77 MHz, CDCl3)

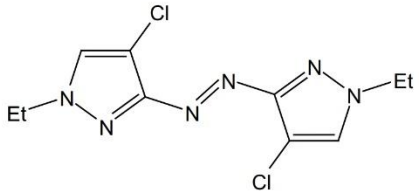
*(E)*-1,2-bis(4-chloro-1-methyl-1*H*-pyrazol-3-yl)diazene (**5a**)

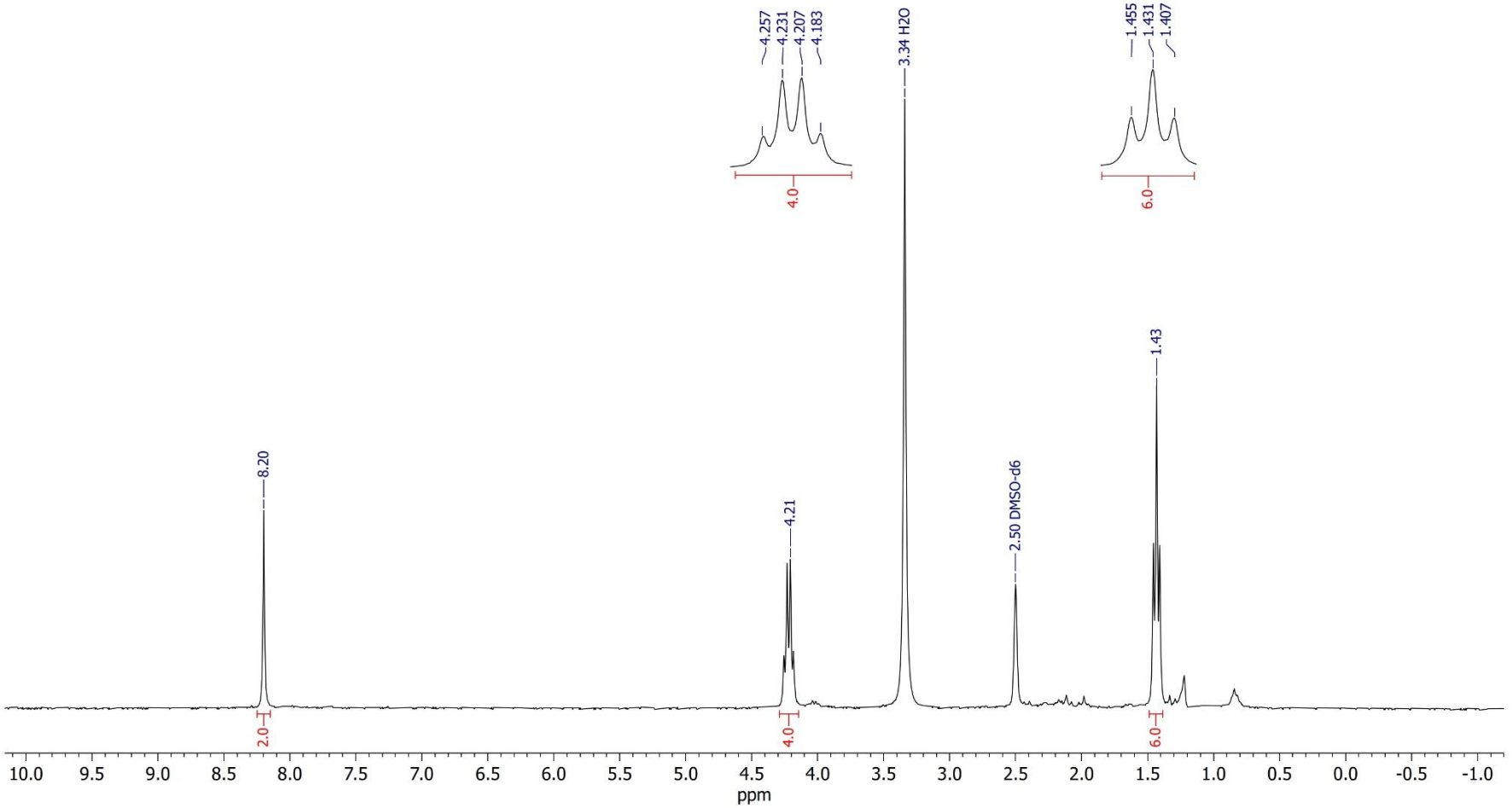


1H NMR (300.13 MHz, DMSO-d6)

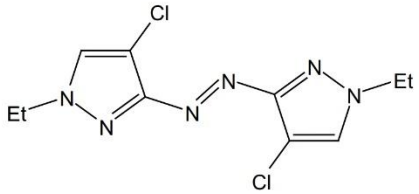
*(E)*-1,2-bis(4-chloro-1-ethyl-1*H*-pyrazol-3-yl)diazene (**5b**)

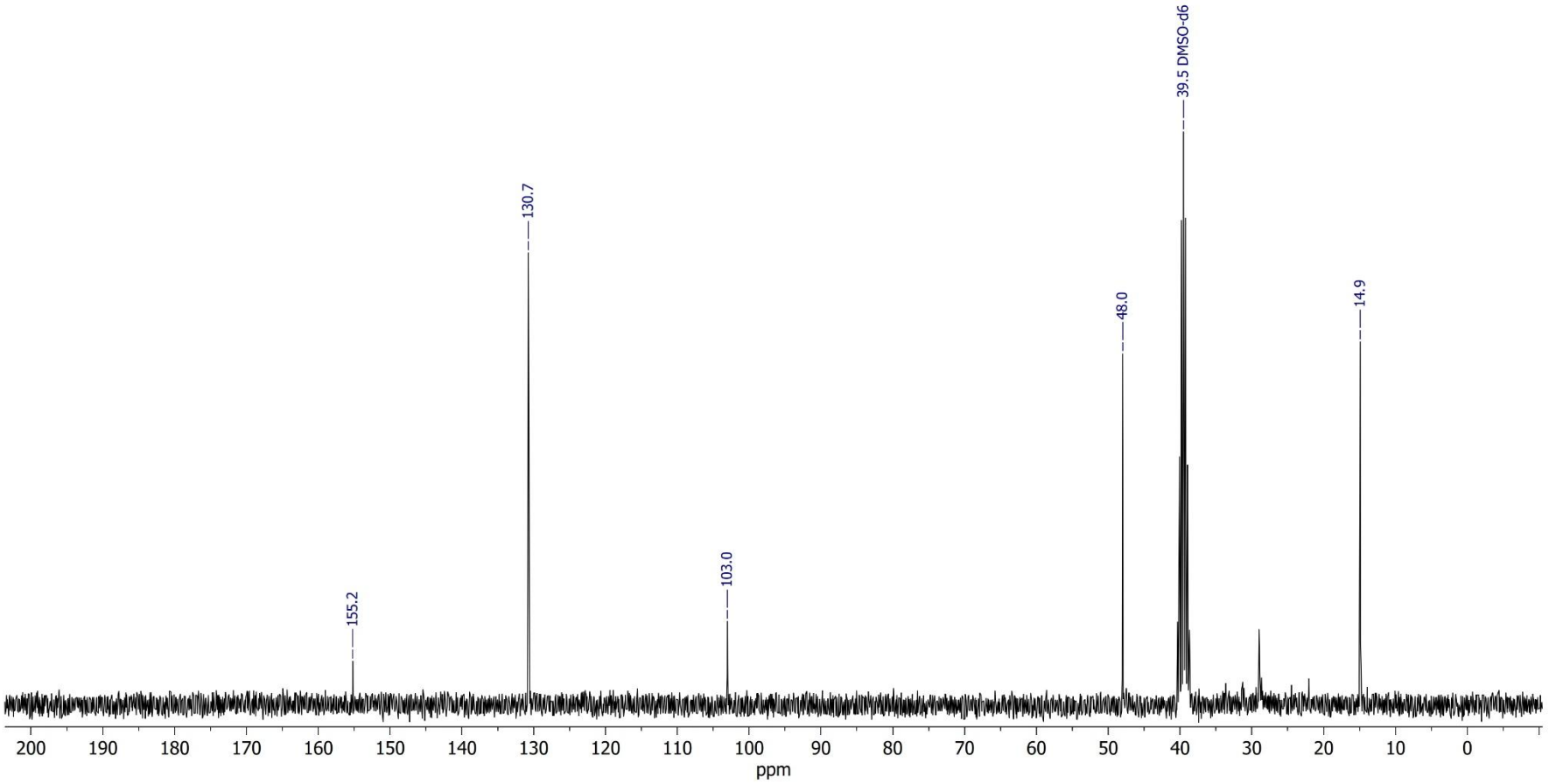


13C NMR (75.48 MHz, DMSO-d6)

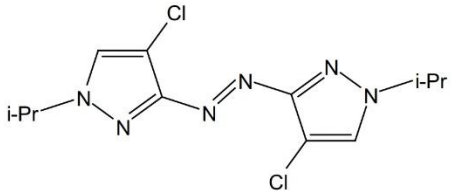
*(E)*-1,2-bis(4-chloro-1-ethyl-1*H*-pyrazol-3-yl)diazene (**5b**)

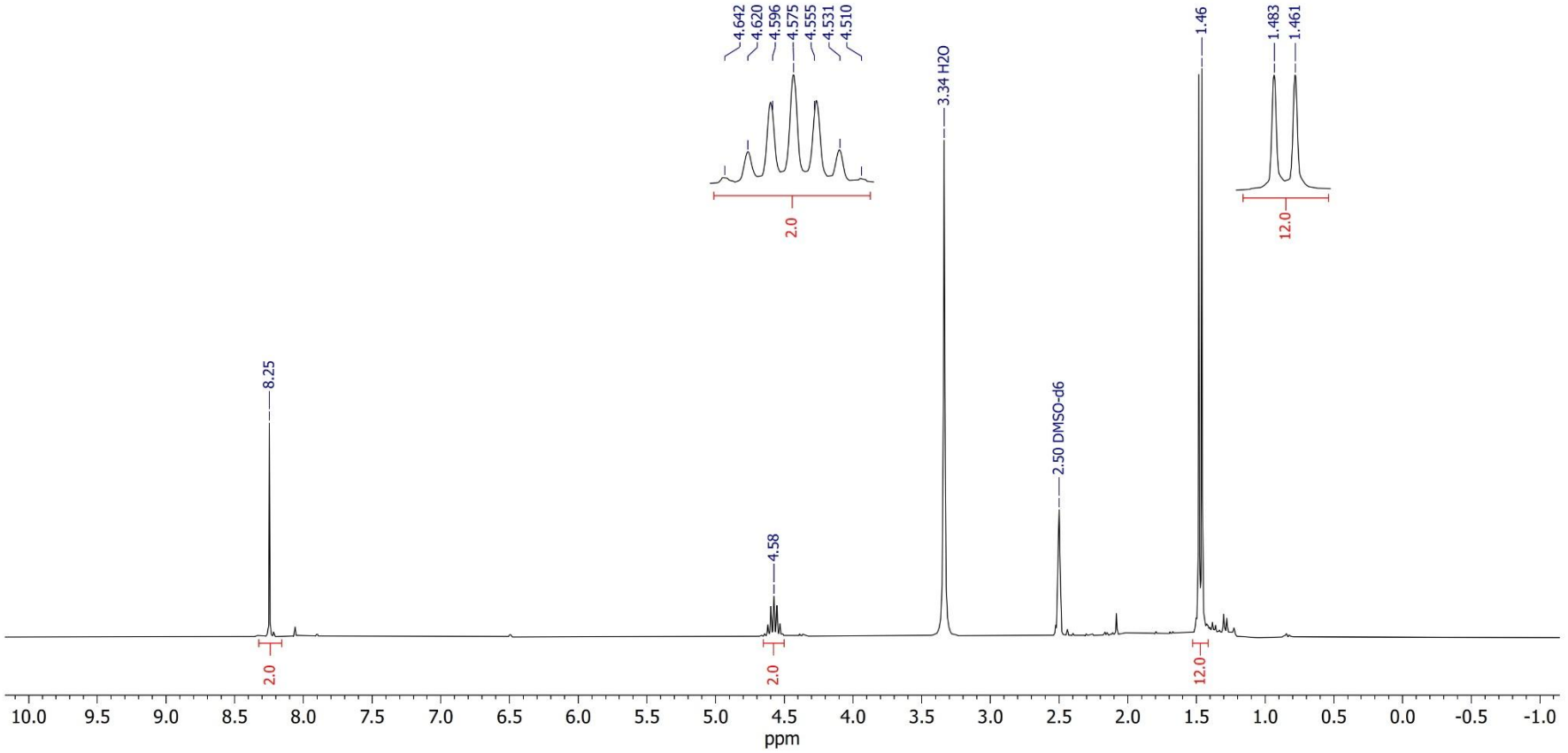


1H NMR (300.13 MHz, DMSO-d6)

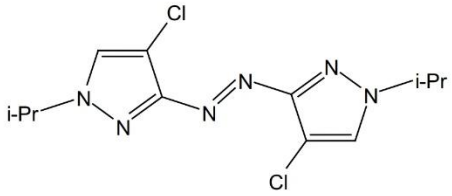
*(E)*-1,2-bis(4-chloro-1-isopropyl-1*H*-pyrazol-3-yl)diazene (**5c**)

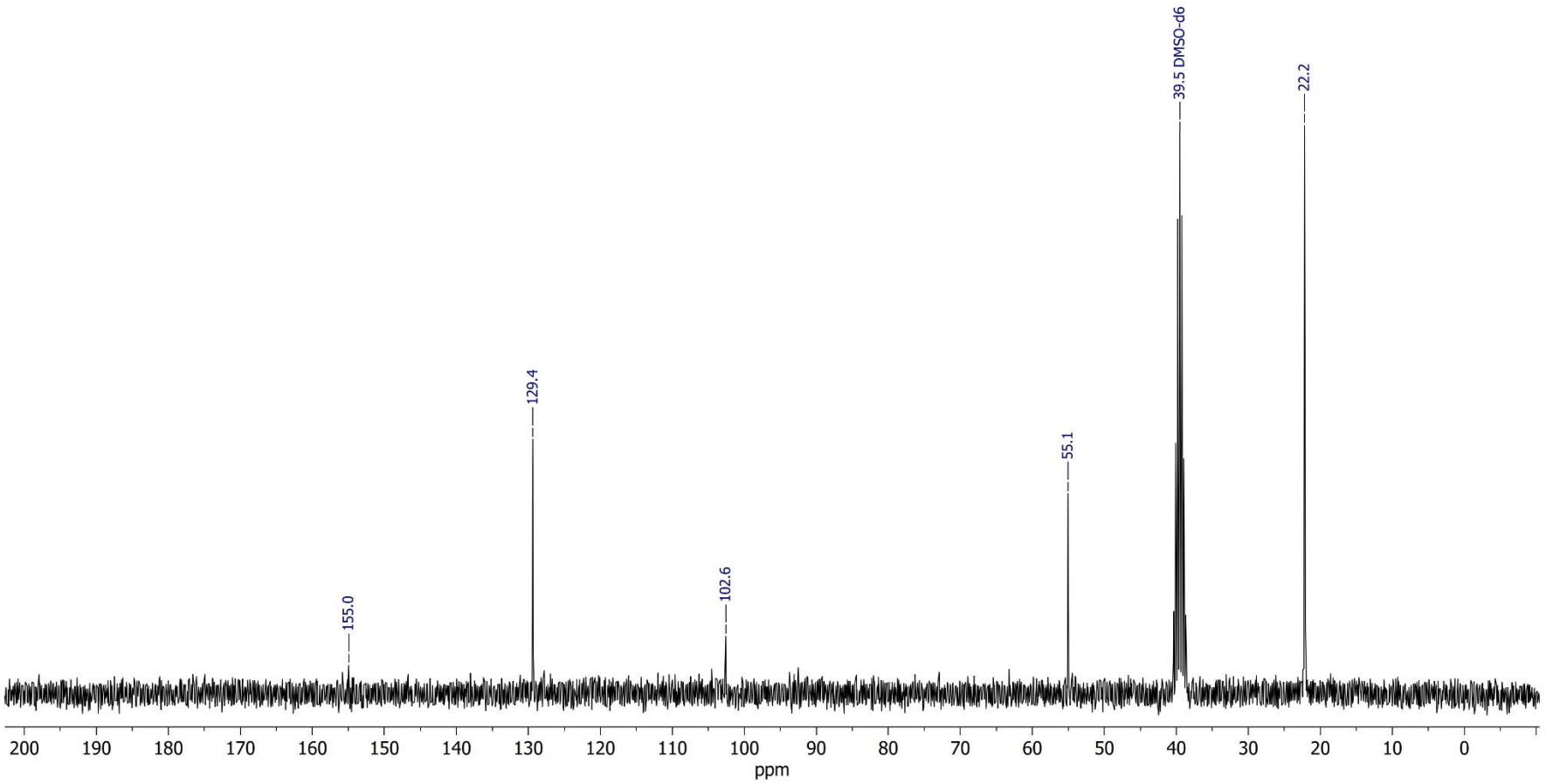


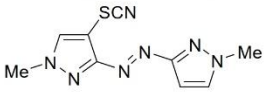
13C NMR (75.48 MHz, DMSO-d6)

*(E)*-1,2-bis(4-chloro-1-isopropyl-1*H*-pyrazol-3-yl)diazene (**5c**)



(*E*)-1-methyl-3-((1-methyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole (**3a**)




Chemical Formula: $C_9H_9N_7S$
Exact Mass: 247,06

**Analysis Info**

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| Analysis Name | D:\Data\Kolotyrkina\2025\Kudinova\0718025.d | Acquisition Date | 18.07.2025 17:11:52 |
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| Sample Name | /VAPP KAS320 | Instrument / Ser# | micrOTOF 10248 |
| Comment | C9H9N7S mH248.0712 calibrant added CH3CN | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
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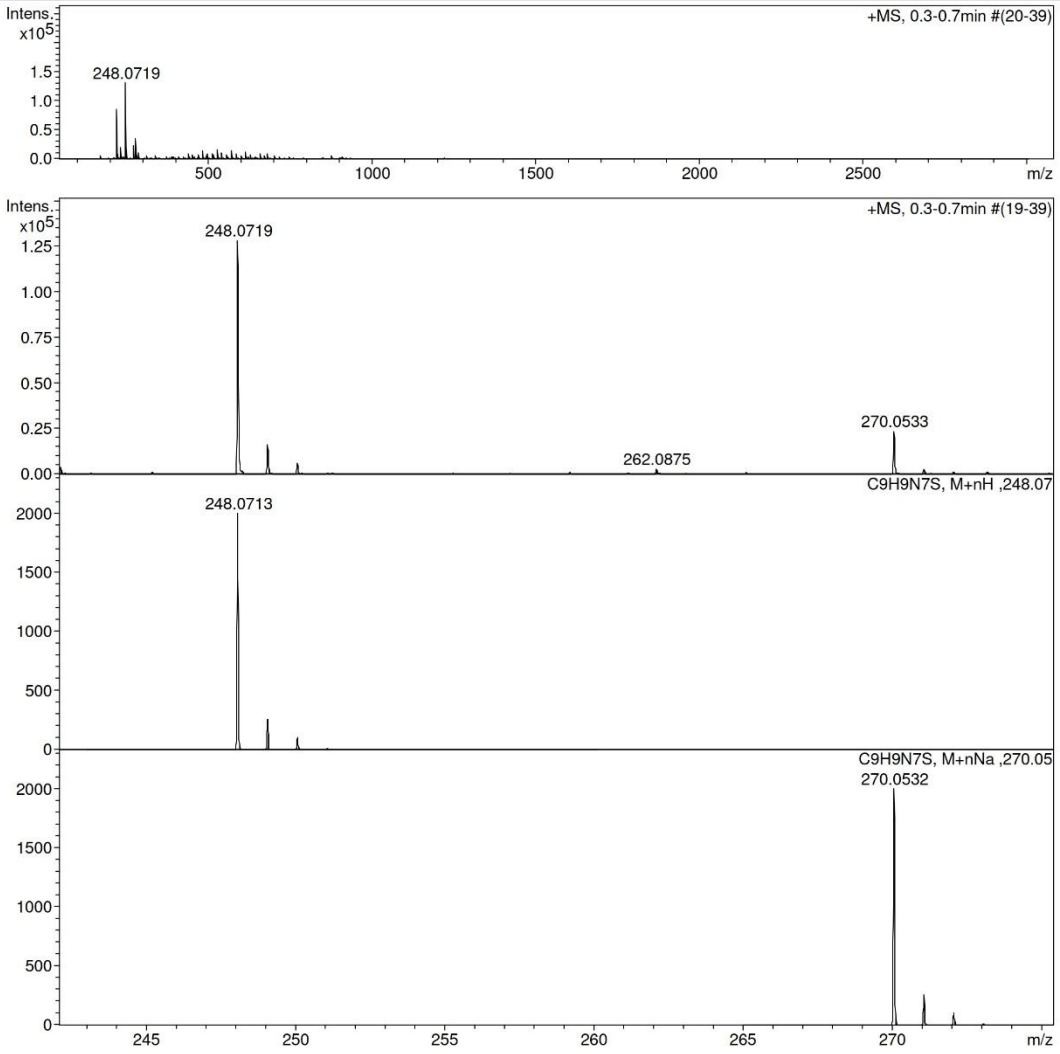
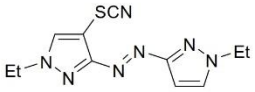


(*E*)-1-ethyl-3-((1-ethyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole (**3b**)




Chemical Formula: $C_{11}H_{13}N_7S$
Exact Mass: 275,10

**Analysis Info**

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| Comment | C11H13N7S clb added CH3CN | | |

**Acquisition Parameter**

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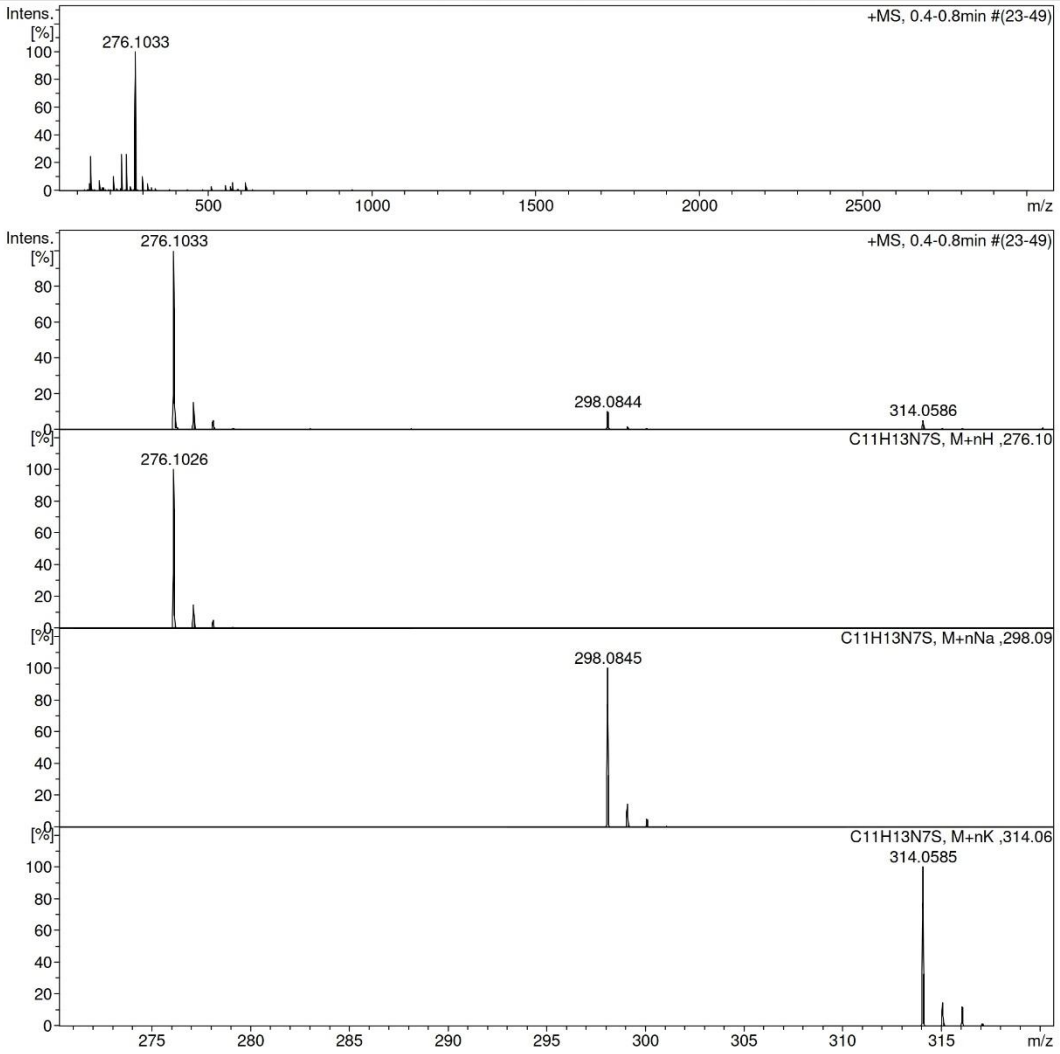
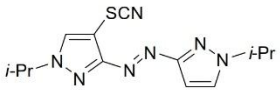
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



(*E*)-1-isopropyl-3-((1-isopropyl-1*H*-pyrazol-3-yl)diazenyl)-4-thiocyanato-1*H*-pyrazole (**3c**)



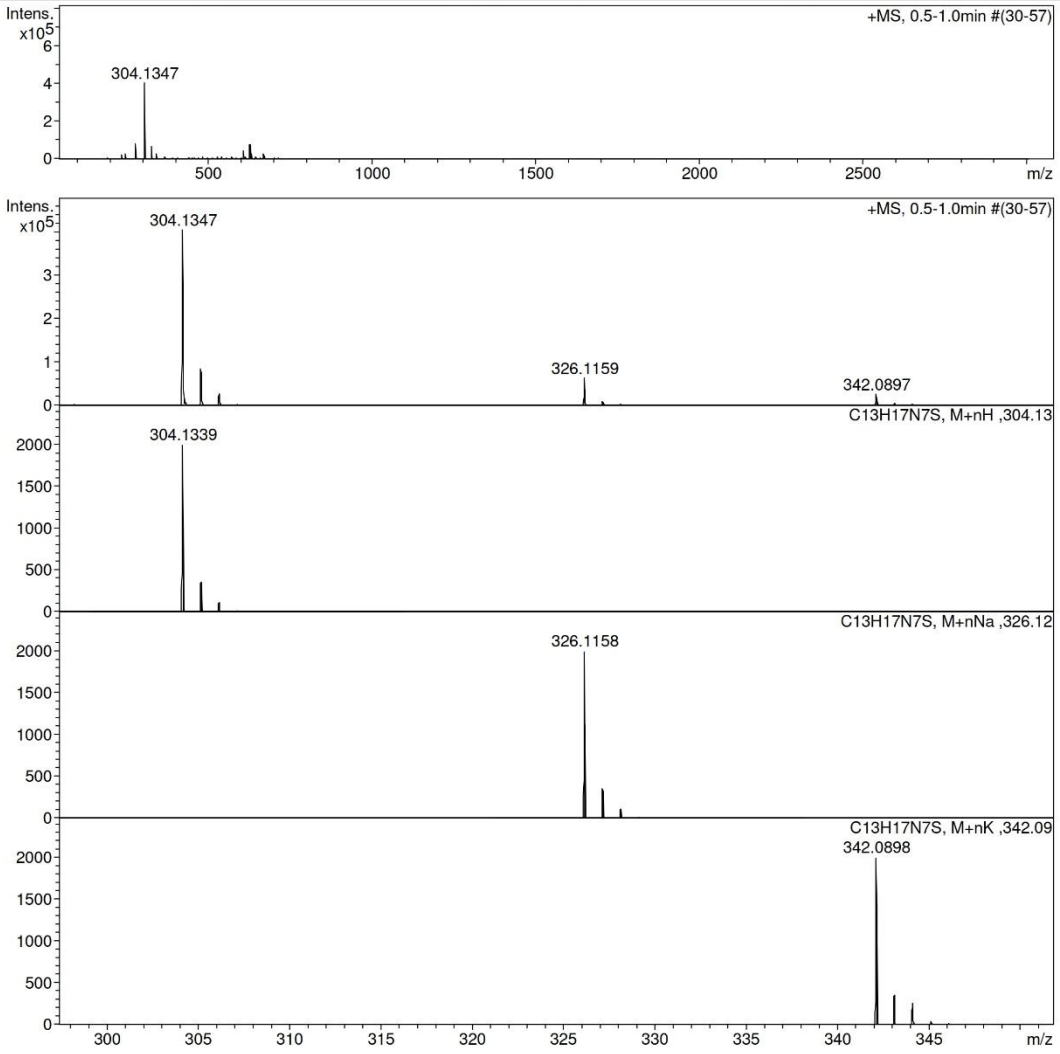

Chemical Formula: $C_{13}H_{17}N_7S$
Exact Mass: 303,13

**Analysis Info**

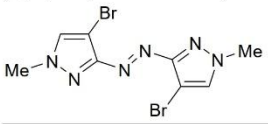
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Kolotyrkina\2025\Kudinova\0718025.d | Acquisition Date | 18.07.2025 17:23:12 |
| Method | tune_low.m | Operator | BDAL@DE |
| Sample Name | /VAPP KAS347 | Instrument / Ser# | micrOTOF 10248 |
| Comment | C13H17N7S mH304.1338 calibrant added CH3CN | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



(*E*)-1,2-bis(4-bromo-1-methyl-1*H*-pyrazol-3-yl)diazene (**4a**)



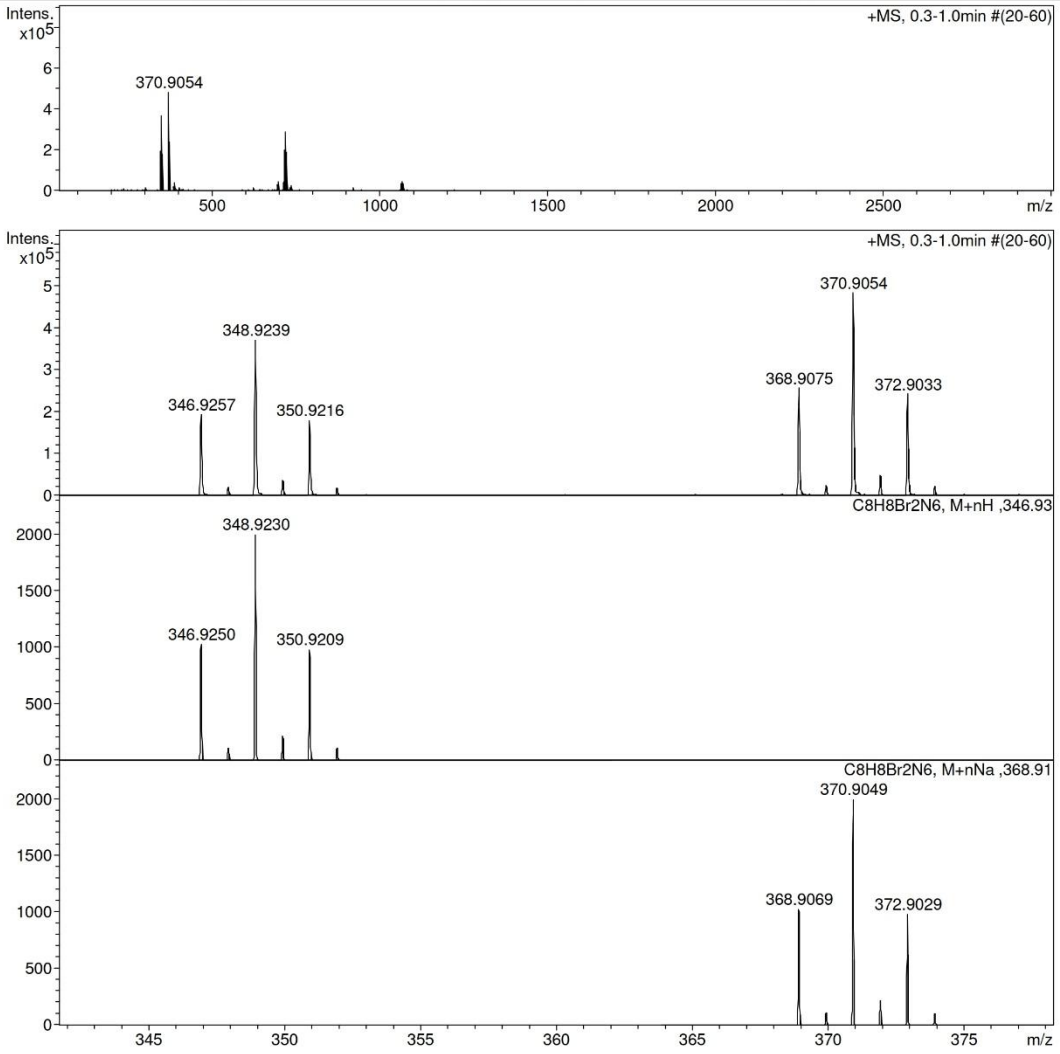
Chemical Formula: $C_8H_8Br_2N_6$
Exact Mass: 345,92

**Analysis Info**

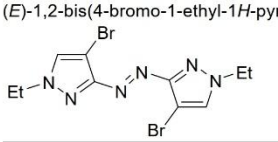
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Kolotyrkina\2025\Kudinova\0711025.d | Acquisition Date | 11.07.2025 17:08:36 |
| Method | tune_low.m | Operator | BDAL@DE |
| Sample Name | /VAPP KAS289 | Instrument / Ser# | micrOTOF 10248 |
| Comment | C8H8Br2N6 mH346.9249calibrant added CH3OH | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



(*E*)-1,2-bis(4-bromo-1-ethyl-1*H*-pyrazol-3-yl)diazene (**4b**)



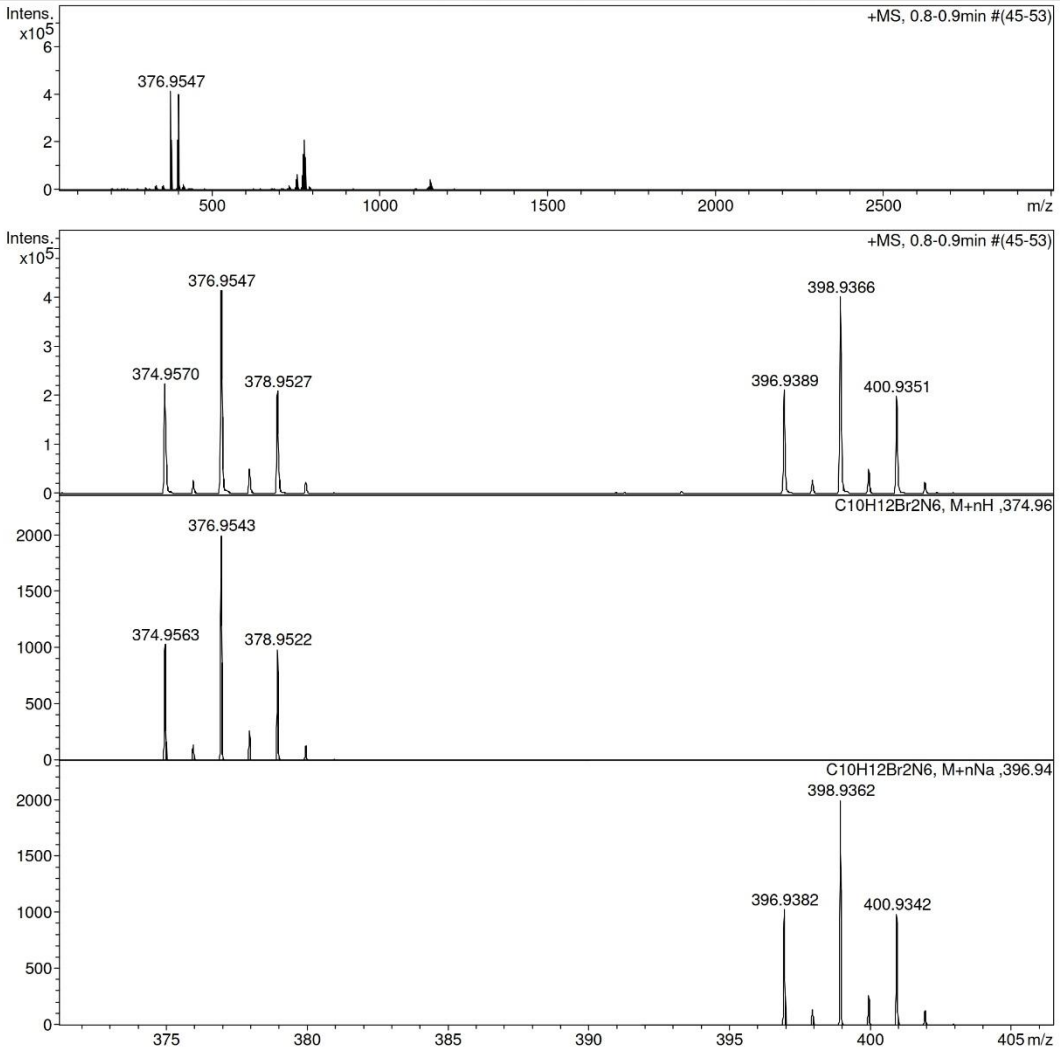
Chemical Formula: $C_{10}H_{12}Br_2N_6$
Exact Mass: 373,95

**Analysis Info**

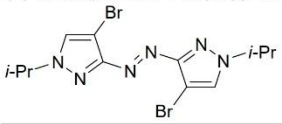
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Kolotyrkina\2025\Kudinova\0711025.d | Acquisition Date | 11.07.2025 17:14:17 |
| Method | tune_low.m | Operator | BDAL@DE |
| Sample Name | /VAPP KAS385 | Instrument / Ser# | micrOTOF 10248 |
| Comment | C10H12Br2N6 mH374.9562 calibrant added CH3OH | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



(*E*)-1,2-bis(4-bromo-1-isopropyl-1*H*-pyrazol-3-yl)diazene (**4c**)



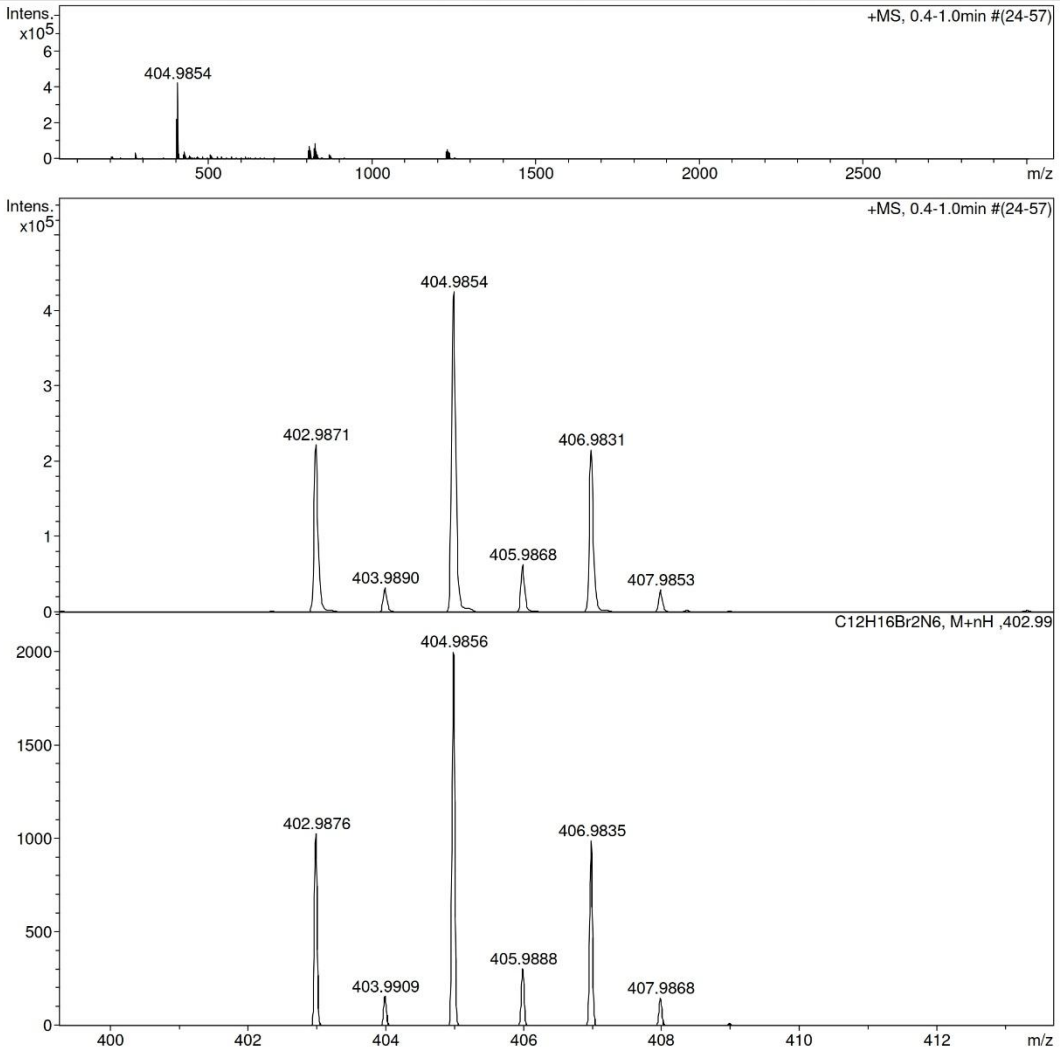
Chemical Formula: $C_{12}H_{16}Br_2N_6$
Exact Mass: 401,98

**Analysis Info**

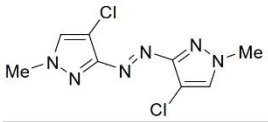
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Kolotyrkina\2024\Kudinova\0718025.d | Acquisition Date | 18.07.2025 17:18:43 |
| Method | tune_low.m | Operator | BDAL@DE |
| Sample Name | /VAPP KAS375 | Instrument / Ser# | micrOTOF 10248 |
| Comment | C12H16Br2N6 mH402.9875 calibrant added CH3CN | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



(*E*)-1,2-bis(4-chloro-1-methyl-1*H*-pyrazol-3-yl)diazene (**5a**)



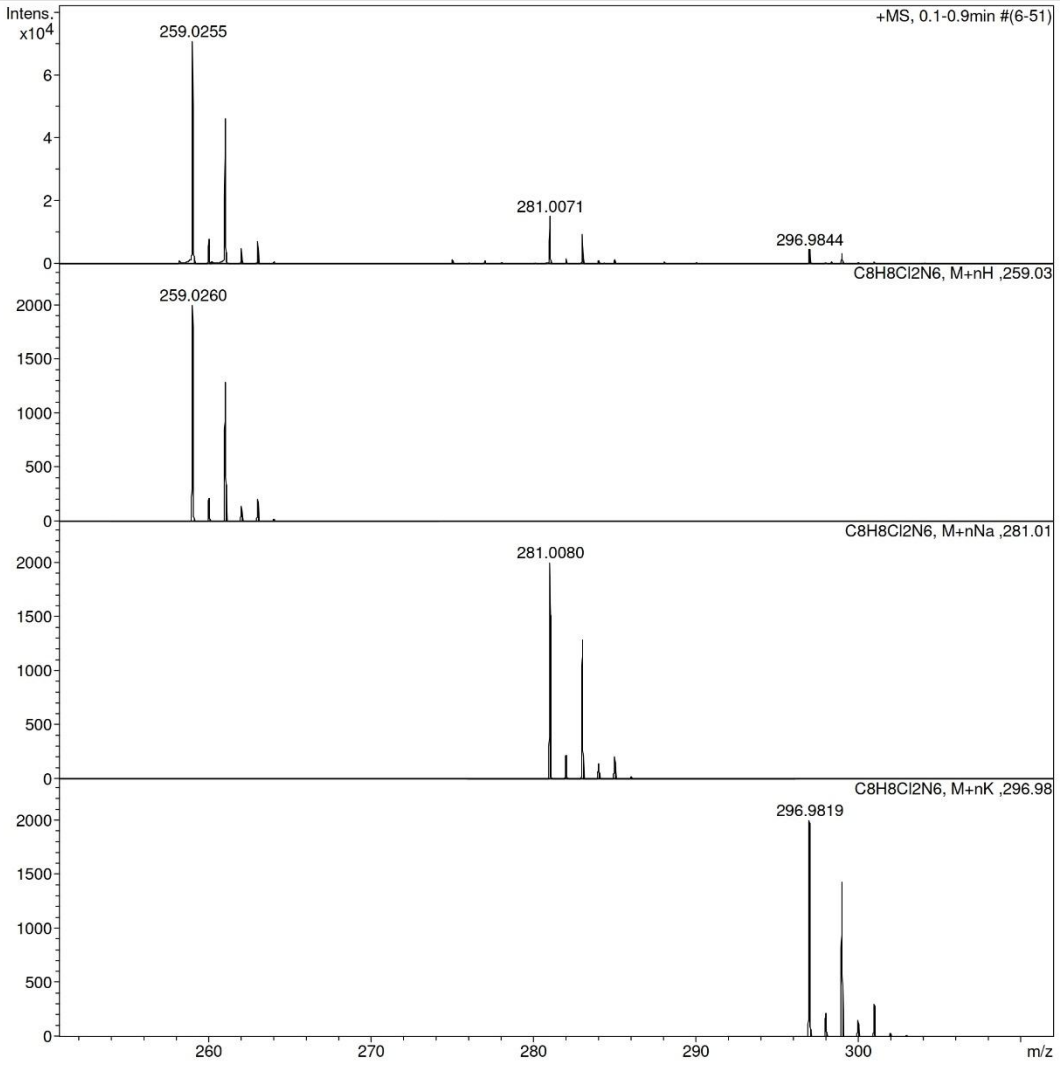
Chemical Formula: $C_8H_8Cl_2N_6$
Exact Mass: 258,02

**Analysis Info**

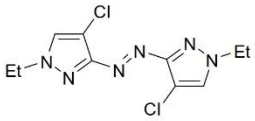
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Kolotyrkina\2025\Kudinova\0615025.d | Acquisition Date | 15.06.2025 16:33:26 |
| Method | tune_low.m | Operator | BDAL@DE |
| Sample Name | /VAPP KAS432 | Instrument / Ser# | micrOTOF 10248 |
| Comment | C8H8Cl2N6 mwH 259.026 clb added | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



(*E*)-1,2-bis(4-chloro-1-ethyl-1*H*-pyrazol-3-yl)diazene (**5b**)



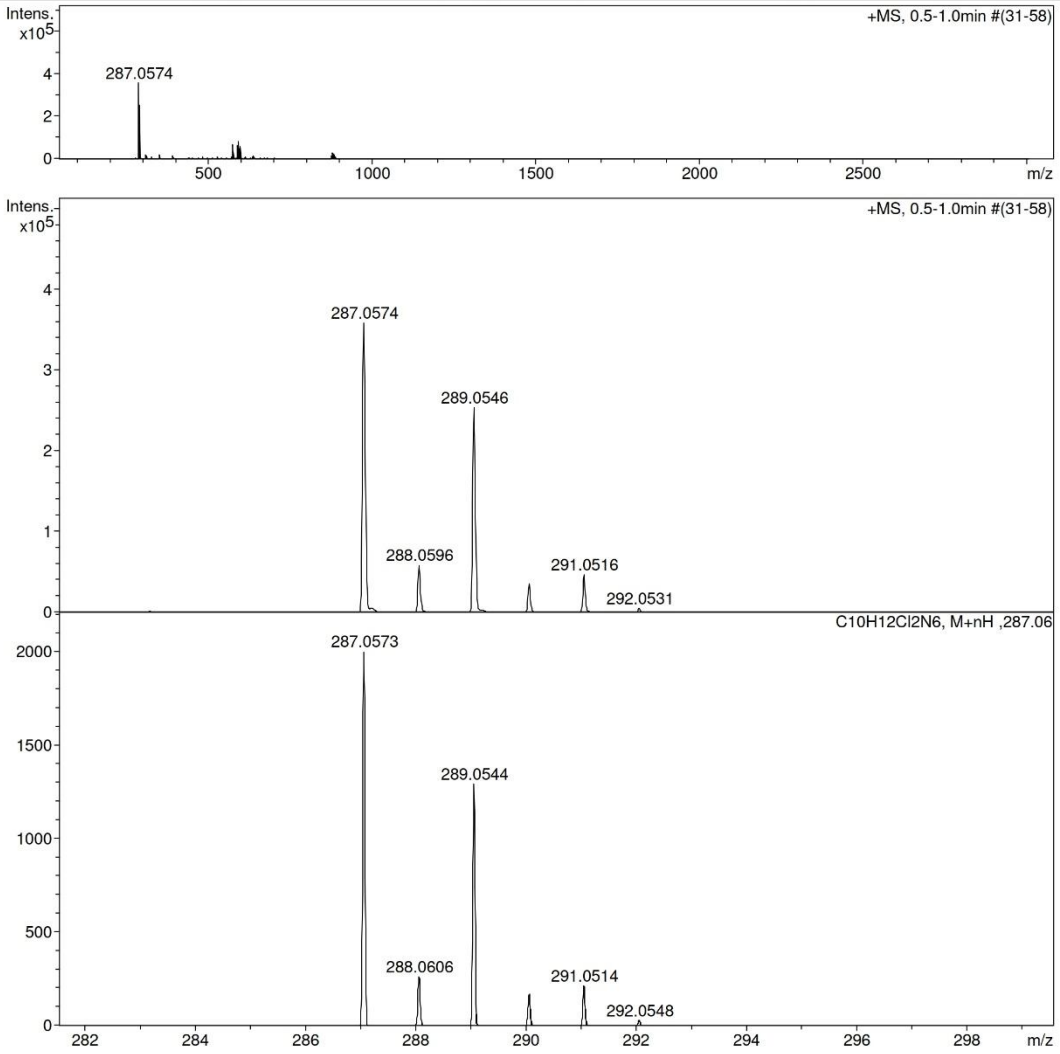
Chemical Formula: $C_{10}H_{12}Cl_2N_6$
Exact Mass: 286,05

**Analysis Info**

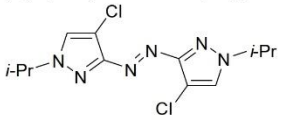
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Kolotyrkina\2025\Kudinova\0718025.d | Acquisition Date | 18.07.2025 17:28:22 |
| Method | tune_low.m | Operator | BDAL@DE |
| Sample Name | /VAPP KAS413 | Instrument / Ser# | micrOTOF 10248 |
| Comment | C10H12Cl2N6 mH287.0573 calibrant added CH3CN | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



(*E*)-1,2-bis(4-chloro-1-isopropyl-1*H*-pyrazol-3-yl)diazene (**5c**)



Chemical Formula: $C_{12}H_{16}Cl_2N_6$
Exact Mass: 314,08

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\Kolotyrkina\2024\Kudinova\0911038.d | Acquisition Date | 11.12.2024 17:01:39 |
| Method | tune_low.m | Operator | BDAL@DE |
| Sample Name | /VAPP KAS403 | Instrument / Ser# | micrOTOF 10248 |
| Comment | C12H16Cl2N6 mH315.0886 clb added CH3CN | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |