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Reactions of *N*-(2,2-Dichloro-1-cyanoethenyl)-*N*'-methyl(phenyl)ureas with Aliphatic Amines

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Abstract—Novel derivatives of 3,3-dichloroprop-2-enenitrile containing methylurea or phenylurea fragments have been synthesized. The obtained *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methyl(phenyl)ureas undergo intramolecular cyclization in the presence of triethylamine to form 4-(dichloromethylidene)-5-imino-1-methyl (phenyl)imidazolidin-2-ones. Reactions of *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methylurea with aliphatic amines have afforded 4-(alkylamino)-4-(dichloromethyl)-5-imino-1-methylimidazolidin-2-ones.

Keywords: cyclization, *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methyl(phenyl)urea, 4-(alkylamino)-4-(dichloromethyl)-5-imino-1-methylimidazolidin-2-one, 4-(dichloromethylidene)-5-imino-1-phenylimidazolidin-2-one

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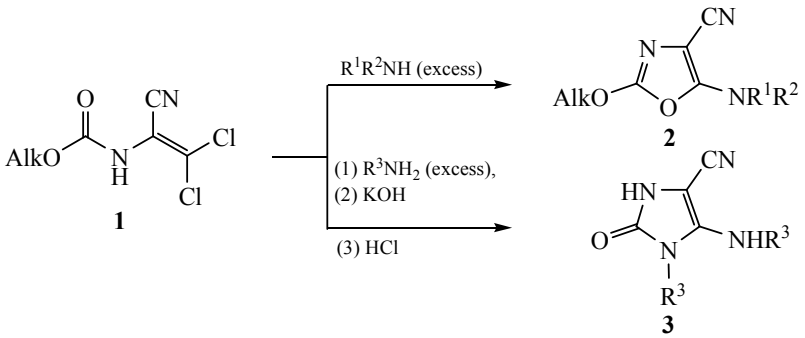
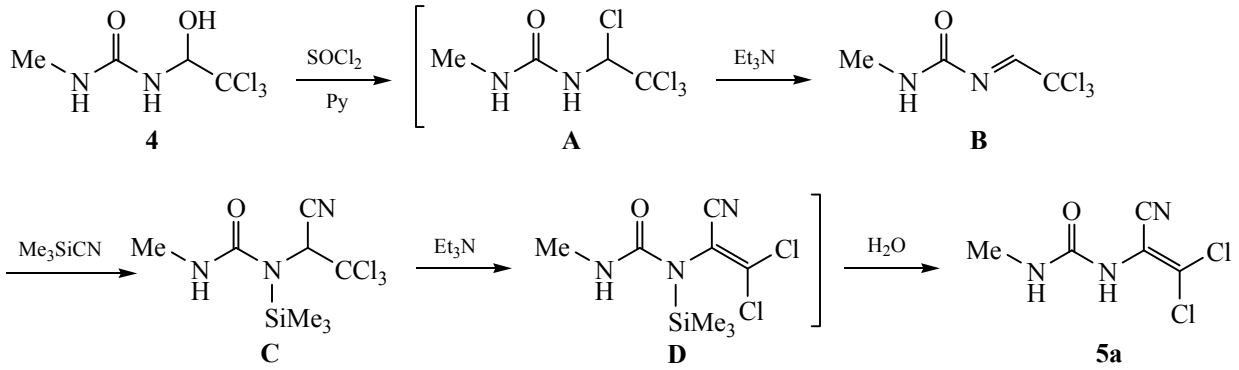
It has been previously shown that alkyl (2,2-dichloro-1-cyanoethenyl)carbamates **1** react with primary and secondary aliphatic amines to give 5-amino-2-alkoxy-1,3-oxazole-4-carbonitrile **2** [1] or 5-amino-2-oxo-2,3-dihydro-1*H*-imidazole-4-carbonitrile **3** derivatives [2], depending on the reaction conditions (Scheme 1).

Similar products could be expected when in the reaction of *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methyl(phenyl)ureas **5a** and **5b**, the analogs of compound **1**, with aliphatic amines. Compound **5b** has been described [3], however we failed to reproduce the procedure of its preparation. Therefore, we proposed other ways to synthesize compounds **5a** and **5b**. In detail, *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methylurea **5a** was obtained starting from *N*-methyl-*N*'-(2,2,2-trichloro-1-hydroxyethyl)urea **4** [4] via converting to tetrachloride **A**, which was treated successively with triethylamine, Me_3SiCN, and again with triethylamine

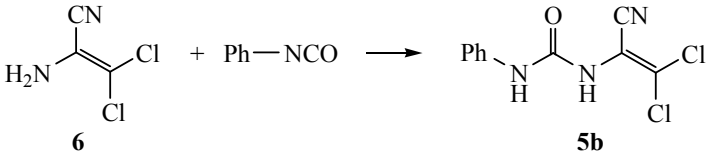
Scheme 1.



Scheme 2.



Scheme 3.



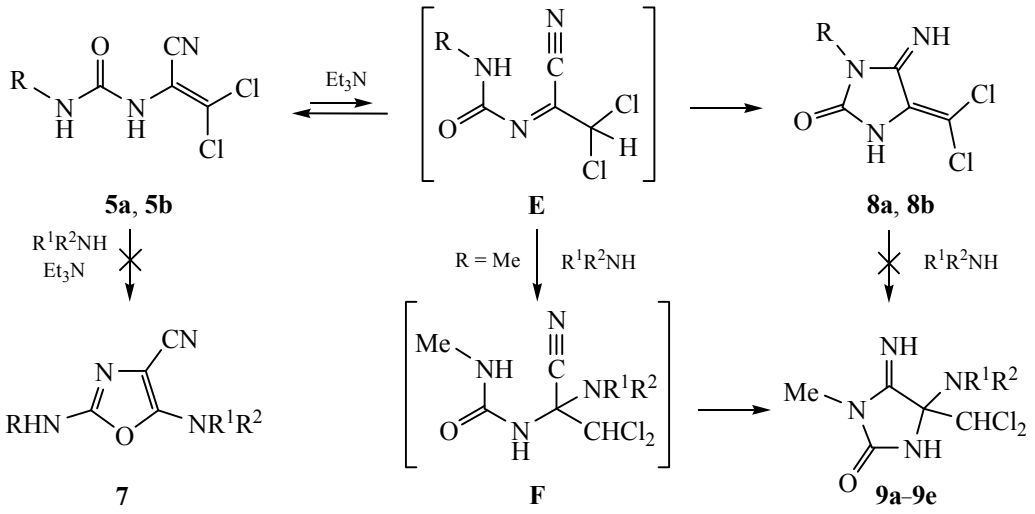
without isolation, to give intermediates **B**, **C**, and **D**. Hydrolysis of the latter gave *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methylurea **5a** in 52% yield (Scheme 2).

N-(2,2-Dichloro-1-cyanoethenyl)-*N*'-phenylurea **5b** was prepared via the reaction of 2-amino-3,3-dichloroprop-2-enenitrile **6** [5] with phenyl isocyanate in a DMF solution (Scheme 3). It should be noted that the melting points of compounds **5b** obtained by us and in [3] were significantly different.

To prepare 2,5-diamino-1,3-oxazole derivatives, we utilized the earlier developed [6] procedure for the synthesis of 2-alkyl(aryl)-5-amino-1,3-oxazole-4-carbonitrile, involving the treatment of compounds **5a** and **5b** with 2 eq. of Et_3N and 1 eq. of an aliphatic amine in methanol at 20–25°C. However, the expected oxazoles **7** were not formed under those conditions. The reactions of *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methylurea **5a** afforded 4-(alkylamino)-4-(dichloromethyl)-5-imino-1-methylimidazolidin-2-ones **9a**–**9d** in high yields (Scheme 4). Their formation could be represented in terms of a series of intermediate stages **5a**→**E**→**F**→**9a**–**9e**. In the case of *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-phenylurea **5b**, 4-(dichloromethylidene)-5-imino-1-phenylimidazolidin-2-one **8b** was obtained instead of the compounds **9**. It should be noted that conversion **5b**→**8b** proceeded also in the absence of an aliphatic amine, but only in the presence of triethylamine. A similar transformation of compound **5a** in the presence of triethylamine resulted in the formation of imidazole derivative in 76% yield. The suggested reaction mechanism **5a**→**E**→**F**→**9** was also confirmed by the fact that compounds **8a** and **8b** did not react with aliphatic amines and the transformation **8**→**9** did not occur. The indicated direction of the reaction of *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methylurea **5a** and *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-phenylurea **5b** with aliphatic amines in the presence of triethylamine was probably due to the different rates of cyclization of intermediate **E** into compounds **8a** and **8b**. In the case of R = Me, the intermediate **E** quickly added the aliphatic amine to the acylimine fragment, causing the **E**→**8a** transformation. Further intramolecular cyclization of the intermediate **F** afforded imidazolidines **9a**–**9e** (Scheme 4).

Structure and composition of the obtained compounds were reliably confirmed by the spectral methods and elemental analysis data. In the IR spectra of compounds **5a** and **5b**, there was the signal of the CN group (2230, 2233 cm^{-1}), disappearing as a result of the transformations **5**→**8** and **5**→**9**. In the ^{13}C NMR spectra of acrylonitriles **5a** and **5b**, the signals of carbonyl (154.1, 150.6 ppm) and nitrile groups were found (for the compound **5a**, it was identified at 123.9 ppm). In the case of compounds **8a**, **9a**–**9e**, the ^{13}C NMR spectra contained the signals of carbonyl and imino groups at 153.4–162.9 ppm. It was not possible to record the high-resolution ^{13}C NMR spectrum for compound **8b**.

Scheme 4.



R = Me (**a**), Ph (**b**); R^1R^2NH = $MeNH_2$ (**a**), $PhCH_2NH_2$ (**b**), $(Me)_2NH$ (**c**), 4-Boc-$N(CH_2)_4$ (**d**), $O(CH_2)_4NH$ (**e**).

Crystal structure of compounds **9** was confirmed by X-ray diffraction using imidazolidin-2-one **9b** as the example. The general view of the molecule and its basic geometry parameters are shown in Fig. 1.

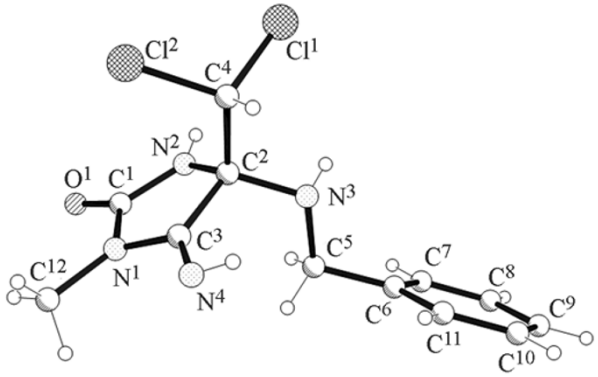
Similarly to the earlier studied 5-imino-1,4,4-triphenylimidazolidin-2-one [7], the imidazolidine ring in the molecule of compound **9b** was planar, the deviation of the atoms from the plane was 0.0197 Å. Most of the intracyclic bonds in the imidazolidine ring (except for C^2–C^3 and C^2–N^2 bonds, which had the usual values for single C–C and C–N bonds) exhibited the parameters characteristic of conjugate systems, being in the intermediate range of values for single and double bonds (Fig. 1). The atoms N^2 and N^3 had planar-trigonal environment: the sum of the bond angles for those atoms was close to 360° because of the effective coupling of their lone electron pairs with the neighboring π-systems of the double bonds C=O and C=N, while the sum of the bond angles for the pyramidal nitrogen atom N^3 isolated from such interactions was 326(2)°.

In a crystal, the molecules formed a branched 2D system of hydrogen bonds in which the layers of the molecules combined via hydrogen bonds were in a plane perpendicular to the axis *ac*. Parameters of the hydrogen bonds are summarized in Table 1.

In summary, the derivatives which are of interest as potential biologically active compounds [8, 9] were obtained starting from *N*-(2,2-dichloro-1-cyanoethenyl)-*N*'-methyl(phenyl)urea novel (5-imino)imidazolidin-2-one.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded using a Varian Mercury instrument (400 and 100 MHz) in DMSO-d_6 relative to internal TMS. IR spectra were registered with a Vertex-70 spectrometer (KBr pellets). Chromato–mass spectra were recorded using an Agilent 1100 Series liquid chromatography–mass spectrometry system equipped with a diode array and an Agilent LC\MSD SL mass-selective detector. Parameters of chromatography–mass spectral analysis: column Zorbax SB-C18, 1.8 μm, 4.6 × 15 mm; solvents: A, MeCN–H_2O, 95 : 5, 0.1% CF_3COOH; B,



General view of the molecule of compound **9b** in the crystal. Some geometric parameters are as follows: N^1–C^1 1.384(3), N^1–C^3 1.376(3), C^2–C^3 1.525(4), N^2–C^2 1.451(3), N^2–C^1 1.350(3), O^1–C^1 1.221(3), N^4–C^3 1.259(3), N^3–C^2 1.441(3), N^3–C^5 1.464(4), Cl^1–C^4 1.757(3), Cl^2–C^4 1.768(3) Å; $N^2C^1N^1$ 107.7(2)°, $C^3N^1C^1$ 111.5(2)°, $N^1C^3C^2$ 106.8(2)°, $N^2C^2C^3$ 101.2(2)°, $C^1N^2C^2$ 112.6(2)°, $C^2N^3C^5$ 113.7(2)°.

Hydrogen bonding parameters in the crystal of **9b**

D–H···A	D–H, Å	H···A, Å	∠D–H···A, deg	Symmetry operation
N^2–H(N^2)···O^1	0.83(3)	2.906(3)	166(3)	$1 - x, 1 - y, 1 - z$
N^3–H(N^3)···N^4	0.79(3)	3.109(3)	159(3)	$x + 0.5, 0.5 - y, z + 0.5$
N^4–H(N^4)···O^1	0.75(3)	3.110(3)	155(3)	$0.5 - x, y - 0.5, 0.5 - z$

0.1% aqueous CF_3COOH; flow of eluent 3 mL/min, injected volume 1 μL; UV detectors 215, 254, 285 nm; chemical ionization at atmospheric pressure. Elemental analysis was performed at the Analytical Chemistry Laboratory, Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine. The carbon and hydrogen content were determined via the Pregl method; the nitrogen and chlorine contents were determined via the Dumas micromethod and Schöniger titration method, respectively [10]. Melting points were measured with a Fisher–Johns apparatus.

Commercially available reagents and solvents were used. *N*-Methyl-*N*'-(2,2,2-trichloro-1-hydroxyethyl)urea **4** was synthesized as described elsewhere [4].

***N*-(2,2-Dichloro-1-cyanoethenyl)-*N*'-methylurea (5a).** Pyridine (4.36 mL, 0.054 mol) and $SOCl_2$ (3.4 mL, 0.047 mol) were subsequently added to a suspension of compound **4** (10.0 g, 0.045 mol) in dichloromethane (100 mL) with stirring at 20–25°C. While stirring the reaction mixture for 30–40 min, a clear solution was formed. Triethylamine (13.1 mL, 0.095 mol) and then $(CH_3)_3SiCN$ (6.2 mL, 0.05 mol) were added to that solution. The reaction mixture was stirred at 20–25°C for 30 min, then triethylamine (13.1 mL, 0.095 mol) was added. After stirring for 12 h, water (40–50 mL) was added, and the organic layer was separated. The extract was washed with water (4 × 5 mL), dried over Na_2SO_4, evaporated, and purified by recrystallization. Yield 52%, mp 166–168°C (benzene–hexane, 10 : 1). IR spectrum, ν, cm^{-1}: 1424, 1506, 1572, 1603, 1601, 1655, 2230 (CN), 3047–3362 (NH). ^{1}H NMR spectrum, δ, ppm: 2.61 d (3H, CH_3, $^3J_{HH}$ = 4.4 Hz), 6.51 br.s (1H, NH), 8.57 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.8 (CH_3), 112.8, 113.1, 123.9 (CN), 154.1 (C=O). Mass spectrum, *m*/*z*: 194 $[M + H]^+$. Found, %: C 30.80; H 2.79; Cl 36.67; N 21.62. $C_5H_5Cl_2N_3O$. Calculated, %: C 30.95; H 2.60; Cl 36.55; N 21.66.

***N*-(2,2-Dichloro-1-cyanoethenyl)-*N*'-phenylurea (5b).** PhNCO (8.7 g, 0.073 mol) was added to a solution of compound **6** (10.0 g, 0.073 mol) [5] in dimethylformamide (10 mL) with stirring at 20–25°C. The mixture was kept for 4 days, then the precipitate was filtered off and purified by recrystallization. Yield 45%, mp 215–217°C (propan-2-ol) (mp 184–186°C [3]). IR spectrum, ν, cm^{-1}: 1441, 1497, 1554, 1603, 1693, 2233 (CN), 3080–3354 (NH). ^{1}H NMR spectrum, δ, ppm: 7.00 t (1H, C_6H_5, $^3J_{HH}$ = 7.2 Hz), 7.30 t (2H, C_6H_5, $^3J_{HH}$ = 8.0 Hz), 7.42 t (2H, C_6H_5, $^3J_{HH}$ = 8.0 Hz), 8.66 s (1H, NH), 9.13 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 111.6, 112.4, 118.5, 122.8, 125.3, 128.9, 138.5, 150.6 (C=O). Mass spectrum, *m*/*z*: 256 $[M + H]^+$. Found, %: C 46.83; H 2.84; Cl 27.61; N 16.60. $C_{10}H_7Cl_2N_3O$. Calculated, %: C 46.90; H 2.76; Cl 27.69; N 16.41.

4-(Dichloromethylidene)-5-imino-1-methyl(phenyl)-imidazolidin-2-ones (8a, 8b). Triethylamine (2.11 mL, 0.015 mol) was added to a suspension of compound **5** (1.0 g, 0.005 mol) in methanol (10 mL) at 20–25°C with stirring. After 6 h, a clear solution was formed. The solvent was removed under reduced pressure, and the residue was treated with 10 mL of water. The precipitate was filtered off and recrystallized from propan-2-ol.

4-(Dichloromethylidene)-5-imino-1-methylimidazolidin-2-one (8a). Yield 76%, mp 177–179°C. IR spectrum, ν, cm^{-1}: 1404, 1466, 1626, 1673, 1792 (C=O), 3029–3363 (NH). ^{1}H NMR spectrum, δ, ppm: 2.93 s (3H, CH_3), 8.56 s (0.8H, NH), 8.73 s (0.2H, NH), 10.65 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.5 (CH_3), 102.7, 127.2, 153.4, 154.1. Mass spectrum, *m*/*z*: 194 $[M + H]^+$. Found, %: C 30.80; H 2.79; Cl 36.67; N 21.62. $C_5H_5Cl_2N_3O$. Calculated, %: C 30.95; H 2.60; Cl 36.55; N 21.66.

4-(Dichloromethylidene)-5-imino-1-phenylimidazolidin-2-one (8b). Yield 84%, mp 214–216°C. IR spectrum, ν, cm^{-1}: 1415, 1454, 1496, 1626, 1671, 1738 (C=O), 3092–3344 (NH). ^{1}H NMR spectrum, δ, ppm: 7.35–7.59 m (5H, C_6H_5), 8.58 br.s (1H, NH), 10.85 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 103.0,

128.6, 129.5, 132.2, 153.0 (C=O) (all the signals are broadened). Mass spectrum, *m*/*z*: 256 $[M + H]^+$. Found, %: C 46.83; H 2.84; Cl 27.61; N 16.60. $C_{10}H_7Cl_2N_3O$. Calculated, %: C 46.90; H 2.76; Cl 27.69; N 16.41.

4-(Dichloromethyl)-5-imino-1-methyl-4-(methylamino)imidazolidin-2-one (9a). 20% solution (5 mL) of methylamine in methanol was added with stirring at 20–25°C to a suspension of compound **5** (1.0 g, 0.005 mol) in methanol (5 mL). The mixture was stirred for 12 h, and a clear solution was formed. The solvent was removed under reduced pressure, and the residue was treated with 10 mL of water. The precipitate was filtered off and recrystallized from propan-2-ol. Yield 62%, mp 146–148°C. IR spectrum, ν, cm^{-1}: 1461, 1662, 1737 (C=O), 3000–3321 (NH). ^1H NMR spec-trum, δ, ppm: 2.05 s (3H, CH_3), 2.80 br.s (1H, NH), 2.85 s (3H, CH_3), 6.13 s (0.15H, CH), 6.38 s (0.85H, CH), 8.10 s (1H, NH), 8.29 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.1 (CH_3), 29.1 (CH_3), 75.8, 80.8, 157.6, 162.5. Mass spectrum, *m*/*z*: 225 $[M + H]^+$. Found, %: C 31.84; H 4.27; Cl 31.47; N 24.93. $C_6H_{10}Cl_2N_4O$. Calculated, %: C 32.02; H 4.48; Cl 31.50; N 24.89.

4-(Alkylamino)-4-(dichloromethyl)-5-imino-1-methylimidazolidin-2-ones 9b–9e. Triethylamine (2.11 mL, 0.015 mol) and the appropriate amine (0.005 mol) were added in sequence at 20–25°C to a stirred suspension of compound **5a** (1.0 g, 0.005 mol) in methanol (10 mL). The mixture was stirred for 12 h, and a clear solution was formed. The solvent was removed under reduced pressure, and the residue was treated with 10 mL of water. The precipitate was filtered off and recrystallized from propan-2-ol.

4-(Benzylamino)-4-(dichloromethyl)-5-imino-1-methylimidazolidin-2-one (9b). Yield 57%, mp 178–180°C. IR spectrum, ν, cm^{-1}: 1400, 1475, 1669, 1741 (C=O), 3030–3274 (NH). ^1H NMR spectrum, δ, ppm: 2.87 s (3H, CH_3), 3.12 br. t (1H, NH, $^3J_{HH}$ = 7.2 Hz), 3.53 d. d (1H, CH_2, $^3J_{HH}$ = 7.2, $^2J_{HH}$ = 12.8 Hz), 3.60 d. d (1H, CH_2, $^3J_{HH}$ = 7.2, $^2J_{HH}$ = 12.8 Hz), 6.25 s (0.15H, CH), 6.40 s (0.85H, CH), 7.24–7.33 m (5H, C_6H_5), 8.25 br.s (1H, NH), 8.47 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.3 (CH_3), 46.9 (CH_2), 75.9, 80.3, 127.6, 128.7, 128.9, 139.8, 157.6, 162.9. Mass spectrum, *m*/*z*: 301 $[M + H]^+$. Found, %: C 47.94; H 4.47; Cl 23.45; N 18.53. $C_{12}H_{14}Cl_2N_4O$. Calculated, %: C 47.86; H 4.69; Cl 23.54; N 18.60.

4-(Dimethylamino)-4-(dichloromethyl)-5-imino-1-methylimidazolidin-2-one (9c). Yield 43%, mp 147–149°C. IR spectrum, ν, cm^{-1}: 1476, 1674, 1752 (C=O), 2994–3297 (NH). ^1H NMR spectrum, δ, ppm: 2.15 s (0.8×6H, CH_3), 2.30 s (0.2×6H, CH_3), 2.82 s (0.2×3H, CH_3), 2.87 s (0.80×3H, CH_3), 6.62 s (0.8H, CH), 6.66 s (0.2H, CH), 7.86 s (0.8H, NH), 8.09 s (0.2H, NH), 8.39 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.0 (CH_3), 38.8 (CH_3), 74.0, 82.3, 157.7, 161.4. Mass spectrum, *m*/*z*: 239 $[M + H]^+$. Found, %: C 35.27; H 5.19; Cl 29.54; N 23.63. $C_7H_{12}Cl_2N_4O$. Calculated, %: C 35.16; H 5.06; Cl 29.65; N 23.43.

***tert*-Butyl-4-[4-(dichloromethyl)-5-imino-1-methyl-2-oxoimidazolidin-4-yl]piperazine-1-carboxylate (9d).** Yield 51%, mp 154–156°C. IR spectrum, ν, cm^{-1}: 1402, 1431, 1453, 1479, 1670, 1745 (C=O), 3087–3307 (NH). ^1H NMR spectrum, δ, ppm: 1.37 s (9H, CH_3), 2.23–2.51 m (2H, CH_2), 2.81 s (0.3×3H, CH_3), 2.86 s (0.7×3H, CH_3), 3.31 m (6H, CH_2), 6.70 s (1H, CH), 7.90 s (0.7H, NH), 8.14 s (0.3H, NH), 8.45 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.0 (CH_3), 28.5 (CH_3), 43.6, 46.3, 73.5, 79.5, 81.9, 154.0, 157.4, 160.8. Mass spectrum, *m*/*z*: 380 $[M + H]^+$. Found, %: C 44.28; H 5.99; Cl 18.82; N 18.50. $C_{14}H_{23}Cl_2N_5O_3$. Calculated, %: C 44.22; H 6.10; Cl 18.65; N 18.42.

4-(Dichloromethyl)-5-imino-1-methyl-4-(morpholin-4-yl)imidazolidin-2-one (9e). Yield 58%, mp 115–117°C. IR spectrum, ν, cm^{-1}: 1451, 1481, 1675, 1758 (C=O), 3077–3326 (NH). ^1H NMR spectrum, δ, ppm: 2.27–2.45 m (2H, CH_2), 2.82 s (0.3×3H, CH_3), 2.86 s (0.7×3H, CH_3), 3.30–3.40 m (2H, CH_2), 3.48–3.62 m (4H, CH_2), 6.70 s (1H, CH), 7.91 s (0.7H, NH), 8.18 s (0.3H, NH), 8.48 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.0 (CH_3), 46.7, 66.5, 73.4, 81.9, 157.5, 160.7. Mass spectrum, *m*/*z*: 281 $[M + H]^+$. Found, %: C 38.28; H 5.16; Cl 25.08; N 19.99. $C_9H_{14}Cl_2N_4O_2$. Calculated, %: C 38.45; H 5.02; Cl 25.22; N 19.93.

X-Ray diffraction study of a crystal of **9b** (0.15 × 0.18 × 0.28 mm) was carried out at room temperature with a Bruker Smart Apex II diffractometer (MoK_α-radiation, graphite monochromator, θ_{max} 26.42°, $-12 \le h \le 11$, $-17 \le k \le 15$, $-13 \le l \le 13$). In total, 15213 reflections were collected, of which 2908 were independent (*R*-factor 0.0737). Absorption was corrected for in SADABS software by the multiscanning method (T_{min}/T_{max} = 0.8365/0.9349). Crystals of compound **9b** were monoclinic, the unit cell parameters: space group $P2_1/n$, *a* 9.8504(18), *b* 13.725(3), *c* 11.139(3) Å, β 109.691(4)°, *V* 1417.9(5) $Å^3$, *Z* 4, d_{calc} 1.411, μ 0.455 mm^{-1}, *F*(000) 624. The structure was solved via the direct method and refined by the least squares method in the full-matrix anisotropic approximation

using the SHELXTL software [11]. Positions of the hydrogen CH atoms were geometrically calculated and refined via a *rider* model. Positions of the hydrogen NH atoms participating in the formation of hydrogen bonds were detected from the differential Fourier synthesis and refined isotropically. In the refinement, 2908 independent reflections were used, including 1669 reflections with $I > 2\sigma(I)$, (184 refined parameters, the number of reflections per parameter 15.8, weight $\omega = 1/[\sigma^2(Fo^2) + (0.0606P)^2 + 0.2293P]$, where $P = (Fo^2 + 2Fc^2)/3$, the ratio of the maximum (mean) shift to the error in the last cycle is 0.001 (0.000). Final divergence factors: $R_1(F)$ 0.0485, $wR_2(F^2)$ 0.1143 over the reflections with $I>2\sigma(I)$, $R_1(F)$ 0.1019, $wR_2(F^2)$ 0.1417, GOF 1.071 over all independent reflections. The residual electron density from the difference Fourier series after the last refinement cycle was 0.36 and –0.32 $e/Å^3$. Crystallographic data for compound **9b** were deposited at the Cambridge Structural Database (CCDC 1529645).

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