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SYNTHESIS AND PROPERTIES OF TRIETHYLAMMONIUM 4-ARYL(HETARYL)-3,5-DICYANO-6-OXO-1,4,5,6-TETRAHYDRO-PYRIDINE-2-SELENOLATES

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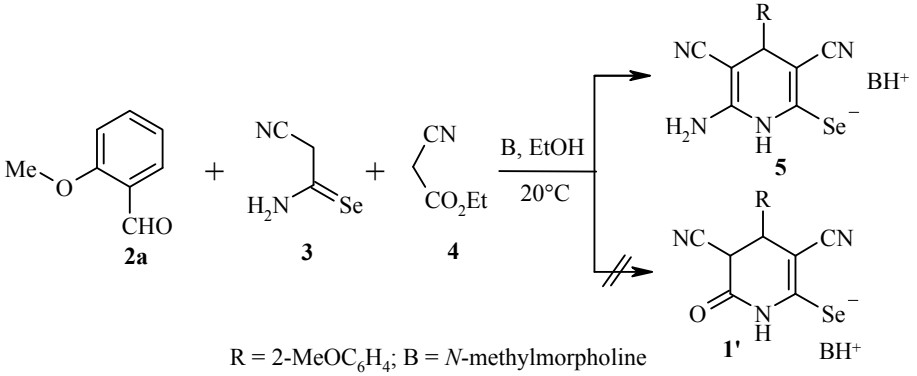
The reaction of (hetero)aromatic aldehydes, cyanoselenoacetamide, and 1-(cyanoacetyl)-3,5-dimethylpyrazole in the presence of triethylamine gives a mixture of the cis and trans diastereomers of triethylammonium 4-aryl(hetaryl)-3,5-dicyano-6-oxo-1,4,5,6-tetrahydropyridine-2-selenolates. The selenolates obtained react with alkyl halides to form the corresponding selenides.

Keywords: 1-cyanoacetyl-3,5-dimethylpyrazole, cyanoselenoacetamide, (hetero)aromatic aldehydes, tetrahydropyridine-2-selenolates, heterocyclization.

Despite the high toxicity of many selenium compounds, a series of effective medications, superconducting materials, and dyes have been prepared on the basis of selenium-containing heterocycles [1, 2]. Due to the limited range of methods of preparing selenium-containing pyridines, they remain to this time a poorly studied group of organic compounds [3, 4], and there are only single examples in the literature of the synthesis of their tetrahydropyridine analogs [5].



We have previously developed convenient methods for preparing polyfunctional reagents, namely, *N*-methylmorpholinium 4-aryl-3,5-dicyano-6-oxo-1,4,5,6-tetrahydropyridine-2-thiolates based on the reaction of

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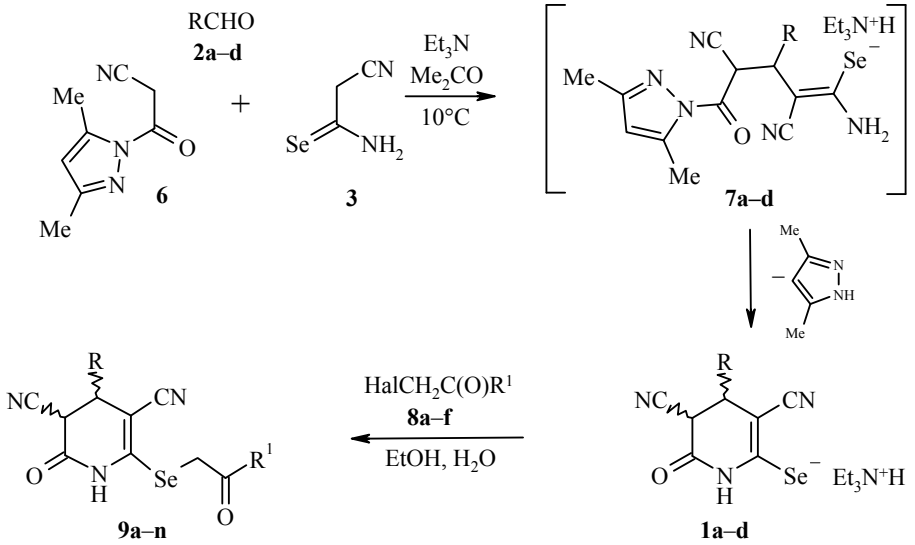
aromatic aldehydes with cyanothioacetamide and cyanoacetate ester or 2-(cyanoacetyl)-3,5-dimethylpyrazole [6-8]. In this work, we have studied the potential use of the indicated routes in preparing the triethylammonium 4-aryl(hetaryl)-3,5-dicyano-6-oxo-1,4,5,6-tetrahydropyridine-2-selenolates **1a-d**.

It was found that reaction of 2-methoxybenzaldehyde (**2a**) with cyanoselenoacetamide (**3**) and cyanoacetate (**4**) in the presence of *N*-methylmorpholine gave the known 6-amino-3,5-dicyano-4-(2-methoxyphenyl)-1,4-dihydropyridine-2-selenolate (**5**) [9] in 39% yield (as a result of a concurrent process of condensation of 2 equivalents of the selenoamide **3** with the aldehyde **2a**) instead of the expected selenolate **1'**.

The synthesis of selenolates **1a-d** was successfully achieved by exchanging the cyanoacetate **4** for the more active cyanoacetylating agent 1-(cyanoacetyl)-3,5-dimethylpyrazole (**6**). Hence, the aldehydes **2a-d**, cyanoselenoacetamide (**3**), and compound **6** in the presence of excess triethylamine in acetone take part in a multicomponent cascade heterocyclization to give the triethylammonium tetrahydropyridine-2-selenolates **1a-d** in 26-53% yield.



1a, 2a, 9a R = 2-$MeOC_6H_4$; **1b**, **2b**, **9b–f** R = 2-furyl; **1c**, **2c**, **9g,h** R = 2-thienyl; **1d, 2d**, **9i–n** R = Ph;
8a, **9b**,**i** R^1 = OMe; **8b**, **9j** R^1 = OEt; **8c**, **9a**,**c**,**g**,**k** R^1 = Ph; **8d**, **9d**,**h**,**l** R^1 = 4-MeC_6H_4;
8e, 9e,**m** R^1 = PhNH; **8f**, **9f**,**n** R^1 = 4-MeC_6H_4NH; **8a**,**b**,**e**,**f** Hal = Cl; **8c,d** Hal = Br;

Probably the intermediates in this reaction are the Michael adducts **7a-d**. Short heating of compounds **1a-d** with an equimolar amount of the alkyl halides **8a-f** gives the corresponding selenides **9a-n** in 24-96% yield. It was found that the selenolates **1a-d** and their derivatives **9a-n** exist as a mixture of diastereomers with different ratios of the mutually *cis*- and *trans*-orientated (het)aryl substituent at C-4 and the cyano group at C-5 in the pyridine ring.

The ^{1}H NMR spectra of compounds **1a-d** and **9a-n** show the H-4 and H-5 protons of the *cis* diastereomers as two doublets with spin-spin coupling of 6.1-8.2 Hz or as a broadened singlet whereas the corresponding protons of the *trans* diastereomers show a coupling of 11.5-13.0 Hz.

The IR spectra of the selenolates **1a-d** show the presence of a weak absorption band for the non-conjugated 5-CN group at 2260-2265 cm^{-1} and a strong band for the conjugated 3-CN group at 2175-2215 cm^{-1}. The spectroscopic data for compounds **1a-d** is in a good agreement with that for the corresponding sulfur analogs reported in the studies [8, 10]. It should be noted that the method developed by us remains the only method for the preparation of 4-aryl(hetaryl)-3,5-dicyano-6-oxo-1,4,5,6-tetrahydropyridine-2-selenolates since earlier attempts [11] led only to the formation of their dehydrogenation products - 4-aryl(hetaryl)-3,5-dicyano-6-oxo-1,6-dihydropyridine-2-selenolates.

EXPERIMENTAL

IR spectra were recorded on an IKS-29 spectrophotometer using vaseline oil. ^{1}H NMR spectra were recorded on a Bruker Avance II 400 instrument (400 MHz) using DMSO-d_6 with TMS as internal standard. The elemental analysis for compound **5** was performed on a Carlo-Erba 1106 elemental analyzer and the remaining compounds on a Perkin-Elmer CHN analyzer. Monitoring of the purity of the compounds prepared was carried out by TLC using Silufol UV-254 plates with acetone–hexane (1:1) as eluent and visualized using iodine vapor and a UV detector. Melting points were determined on a Koffler block and are not corrected. All of the syntheses were carried out in an argon atmosphere.

Triethylammonium 4-Aryl(hetaryl)-3,5-dicyano-6-oxo-1,4,5,6-tetrahydropyridine-2-selenolates (1a-d) (General Method). A mixture of the corresponding aldehyde **2a-d** (1.0 mmol), freshly prepared cyanoselenoacetamide (**3**) (1.47 g, 1.0 mmol), acetone (2 ml), and triethylamine (1 drop) was stirred at 10ºC for 10 min. 1-(Cyanoacetyl)-3,5-dimethylpyrazole (**6**) (1.67 g, 1.0 mmol) was added followed by dropwise addition of triethylamine (2 ml, 1.5 mmol). The mixture obtained was stirred for 30 min with cooling on an ice bath and then left for 12 h in a fridge (3-4ºC). The precipitate formed was filtered off and washed with acetone and hexane.

Triethylammonium 3,5-Dicyano-4-(2-methoxyphenyl)-6-oxo-1,4,5,6-tetrahydropyridine-2-selenolate (1a). Yield 2.34 g (53%). Yellow, finely crystalline substance, mp 146-148ºC. IR spectrum, ν, cm^{-1}: 1700 (C=O), 2190 and 2260 (2C≡N), 3180 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): (ratio of *cis* and *trans* isomers ~ 1:2): 1.22 (9H, t, ^3J = 7.1, N(CH$_2$C<u>H</u>$_3$)$_3$); 3.00 (6H, q, ^3J = 7.1, N(C<u>H</u>$_2$CH$_3$)$_3$); 3.78-3.86 (3H, m, OCH$_3$); 4.28 (0.33H, br. s, *cis*-4-CH); 4.43 (0.67H, d, ^3J = 12.2, *trans*-4-CH); 4.65 (0.67H, d, ^3J = 12.2, *trans*-5-CH); 4.77 (0.33H, br. s, *cis*-5-CH); 6.92-7.37 (4H, m, H Ar); 10.63 (1H, br. s, NH). Found, %: C 54.96; H 6.11; N 12.76. $C_{14}H_{10}N_3O_2Se\cdot C_6H_{16}N$. Calculated, %: C 55.42; H 6.05; N 12.93.

Triethylammonium 3,5-Dicyano-4-(2-furyl)-6-oxo-1,4,5,6-tetrahydropyridine-2-selenolate (1b). Yield 1.53 g (41%). Light-yellow, finely crystalline substance, mp 149-151ºC. IR spectrum, ν, cm^{-1}: 1695 (C=O), 2175 and 2265 (2C≡N), 3150 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 1:3): 1.07 (9H, t, ^3J = 6.9, N(CH$_2$C<u>H</u>$_3$)$_3$); 2.67 (6H, q, ^3J = 6.9, N(C<u>H</u>$_2$CH$_3$)$_3$); 4.28 (0.25H, br. s, *cis*-4-CH); 4.43 (0.75H, br. s, *trans*-4-H); 4.66 (0.75H, br. s, *trans*-5-CH); 4.75 (0.25H, br. s, *cis*-5-CH); 6.37-6.51 (2H, m, *cis*- and *trans*-3,4-CH furyl); 7.52 (0.75H, br. s, *trans*-5-CH furyl); 7.58 (0.25H, br. d, ^3J = 6.3, *cis*-5-CH furyl); 10.77 (1H, br. s, NH). Found, %: C 51.39; H 5.67; N 14.16. $C_{11}H_6N_3O_2Se\cdot C_6H_{16}N$. Calculated, %: C 51.91; H 5.64; N 14.24.

Triethylammonium 3,5-Dicyano-6-oxo-4-(2-thienyl)-1,4,5,6-tetrahydropyridine-2-selenolate (1c). Yield 1.75 g (43%). Light-yellow, finely crystalline substance, mp 153-155ºC. IR spectrum, ν, cm^{-1}: 1695 (C=O), 2190 and 2263 (2C≡N), 3148 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 3:2): 1.15 (9H, t, ^3J = 7.1, N(CH$_2$C<u>H</u>$_3$)$_3$); 2.89 (6H, q, ^3J = 7.1, N(C<u>H</u>$_2$CH$_3$)$_3$); 4.29 (0.4H, d, ^3J = 11.1, *trans*-4-CH); 4.37 (0.6H, br. s, *cis*-4-CH); 4.48 (0.4H, d, ^3J = 11.1, *trans*-5-CH); 4.73 (0.6H, br. s, *cis*-5-CH); 6.97-7.38 (3H, m, H thienyl); 10.33 (1H, br. s, NH). Found, %: C 49.61; H 5.45; N 13.51. $C_{11}H_6N_3OSSe\cdot C_6H_{16}N$. Calculated, %: C 49.87; H 5.42; N 13.68.

Triethylammonium 3,5-Dicyano-6-oxo-4-phenyl-1,4,5,6-tetrahydropyridine-2-selenolate (1d). Yield 1.05 g (26%). Yellow, finely crystalline substance, mp 155-157ºC. IR spectrum, ν, cm^{-1}: 1705 (C=O), 2200 and 2215 (sh), 2260 (2C≡N), 3140 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 1:1: 1.15 (9H, t, ^3J = 7.1, N(CH$_2$C<u>H</u>$_3$)$_3$); 2.95 (6H, q, ^3J = 6.9, N(C<u>H</u>$_2$CH$_3$)$_3$); 3.91 (0.5H, br. s, *cis*-4-CH); 4.02 (0.5H, d, ^3J = 10.5, *trans*-4-CH); 4.29 (0.5H, d, ^3J = 10.5, *trans*-5-CH); 4.69 (0.5H, br. s, *cis*-5-CH); 7.21-7.46 (5H, m, H Ph); 9.65 (1H, br. s, NH). Found, %: C 56.13; H 6.08; N 13.70. $C_{13}H_8N_3OSe\cdot C_6H_{16}N$. Calculated, %: C 56.57; H 6.00; N 13.89.

***N*-Methylmorpholinium 6-Amino-3,5-dicyano-4-(2-methoxyphenyl)-1,4-dihydropyridine-2-selenolate (5)**. A mixture of 2-methoxybenzaldehyde (**2a**) (1.63 ml, 1.36 mmol), cyanoselenoacetamide (**3**) (2.0 g, 1.36 mmol), and *N*-methylmorpholine (1-2 drops) was stirred in ethanol (20 ml) for 10 min at 20ºC. The

cyanoacetate **4** (1.45 ml, 1.36 mmol) and *N*-methylmorpholine (1.9 ml, 2 mmol) were added dropwise. The mixture obtained was stirred for 30 min and left for 12 h at 20ºC. The precipitate formed was filtered off and washed with acetone and hexane. Yield 2.27 g (39%). Bordeaux colored, finely crystalline substance, mp 170-172ºC. IR spectrum, ν, cm^{-1}: 2180, 2190 (2C≡N), 3255, 3315, 3420 (NH, NH_2). ^{1}H NMR spectrum, δ, ppm: 2.40 (3H, s, NMe); 2.64 (4H, m, $O(CH_2)_2$); 3.70 (4H, m, $N(CH_2)_2$); 3.86 (3H, s, OMe); 4.85 (1H, s, 4-CH); 5.74 (2H, s, NH_2); 6.85-7.27 (4H, m, H Ar); 9.27 (1H, s, NH). Found, %: C 52.84; H 5.39; N 16.04. $C_{15}H_{11}N_4OSe \cdot C_4H_{12}NO$. Calculated, %: C 52.78; H 5.36; N 16.20.

4-Aryl-2-oxo-6-[(2-oxo-2-phenylethyl)seleno]-1,2,3,4-tetrahydropyridine-3,5-dicarbonitriles 9a-n (General Method). A mixture of the corresponding selenolate **1a-d** (1 mmol) and the corresponding alkyl halide **8a-f** (1 mmol) in 70% aqueous ethanol (30 ml) was refluxed for 1-2 min and rapidly filtered through a plaited filter paper. The reaction mixture was allowed to stand for 24 h at 20ºC. The precipitate formed was filtered off and washed with ethanol and hexane to give the corresponding selenide **9** in an analytically pure state. If needed, the sample is crystallized from a suitable solvent.

4-(2-Methoxyphenyl)-2-oxo-6-[(2-oxo-2-phenylethyl)seleno]-1,2,3,4-tetrahydropyridine-3,5-dicarbonitrile (9a). Yield 0.2 g (48%). Yellow-green, finely crystalline substance, mp 61-63ºC (AcOH). IR spectrum, ν, cm^{-1}: 1710 (C=O), 2220, 2270 (2C≡N), 3135 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 4:3): 3.80 (0.57H, s, *cis*-OMe); 3.88 (0.43H, s, *trans*-OMe); 4.42 (0.57H, d, ^3J = 8.2, *cis*-4-CH); 4.42 (0.43H, d, ^3J = 13.0, *trans*-4-CH); 4.56 (0.43H, d, ^3J = 13.0, *trans*-3-CH); 4.67-4.81 (2.57H, m, *cis*-3-CH, $SeCH_2$); 6.95-8.03 (9H, m, H Ar); 10.90 (0.57H, s, *cis*-NH); 11.04 (0.43H, s, *trans*-NH). Found, %: C 58.25; H 3.84; N 9.27. $C_{22}H_{17}N_3O_3Se$. Calculated, %: C 58.67; H 3.80; N 9.33.

Methyl {[3,5-Dicyano-4-(2-furyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl]seleno}acetate (9b). Yield 0.16 g (47%). Light-brown crystalline substance, mp 150-152ºC. IR spectrum, ν, cm^{-1}: 1710 (C=O), 2210, 2270 (2C≡N), 3150 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 2:5): 3.67 (0.71H, s, *trans*-OMe); 3.72 (0.29H, s, *cis*-OMe); 3.80-3.90 (2H, m, $SeCH_2$); 4.42 (0.29H, m, *cis*-4-CH); 4.55 (0.71H, m, *trans*-4-CH); 4.64 (0.71H, m, *trans*-5-CH); 4.81 (0.29H, m, *cis*-5-CH); 6.39-6.48 (2H, m, H-3,4 furyl); 7.55 (0.71H, br. d, ^3J = 5.9, *trans*-H-5 furyl); 7.60 (0.29H, br. d, ^3J = 5.9, *cis*-H-5 furyl); 11.12 (0.71H, s, *trans*-NH); 11.14 (0.29H, s, *cis*-NH). Found, %: C 45.91; H 3.07; N 11.43. $C_{14}H_{11}N_3O_4Se$. Calculated, %: C 46.17; H 3.04; N 11.54.

4-(2-Furyl)-2-oxo-6-[(2-oxo-2-phenylethyl)seleno]-1,2,3,4-tetrahydropyridine-3,5-dicarbonitrile (9c). Yield 0.18 g (45%). White, finely crystalline substance, mp 197-199ºC (AcOH). IR spectrum, ν, cm^{-1}: 1725 (C=O), 2205, 2260 (2C≡N), 3135 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 2:1): 4.38 (0.67H, d, ^3J = 6.6, *cis*-4-CH); 4.53 (0.33H, d, ^3J = 12.2, *trans*-4-CH); 4.61 (0.33H, d, ^3J = 12.2, *trans*-3-CH); 4.79 (0.67H, d, ^3J = 6.6, *cis*-3-H); 4.70-4.83 (2H, m, $SeCH_2$); 6.38-7.64 (6H, m, H-3,4,5 Ph and H-3,4,5 furyl); 7.99 (2H, br. d, ^3J = 7.8, H-2,6 Ph); 11.04 (1H, br. s, NH). Found, %: C 55.31; H 3.22; N 10.17. $C_{19}H_{13}N_3O_3Se$. Calculated, %: C 55.62; H 3.19; N 10.24.

4-(2-Furyl)-6-{[2-(methylphenyl)-2-oxoethyl]seleno}-2-oxo-1,2,3,4-tetrahydropyridine-3,5-dicarbonitrile (9d). Yield 0.24 g (59%). White, finely crystalline substance, mp 193-195ºC (AcOH). IR spectrum, ν, cm^{-1}: 1712 (C=O), 2205, 2260 (2C≡N), 3120 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~2:1): 2.44 (3H, br. s, 4-CH_3); 4.37 (0.67H, d, ^3J = 6.6, *cis*-4-CH); 4.52 (0.33H, d, ^3J = 12.1, *trans*-4-CH); 4.59 (0.33H, d, ^3J = 12.1, *trans*-3-CH); 4.67-4.80 (2.67H, m, $SeCH_2$, *cis*-3-CH); 6.39-6.48 (2H, m, H-3,4 furyl); 7.29 (2H, m, H-3,5 Ar); 7.53 (0.67H, m, *cis*-H-5 furyl); 7.58 (0.33H, m, *trans*-H-5 furyl); 7.90 (2H, m, H-2,6 Ar); 11.02 (1H, br. s, NH). Found, %: C 56.26; H 3.59; N 9.86. $C_{20}H_{15}N_3O_3Se$. Calculated, %: C 56.61; H 3.56; N 9.90.

2-{[3,5-Dicyano-4-(2-furyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl]seleno}-*N*-phenylacetamide (9e). Yield 0.28 g (68%). Light-brown crystalline substance, mp 188-190ºC (AcOH). IR spectrum, ν, cm^{-1}: 1725 (C=O), 2200, 2265 (2C≡N), 3135, 3400 (2NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 5:2): 3.85-4.01 (2H, m, $SeCH_2$); 4.42 (0.71H, d, ^3J = 6.7, *cis*-4-CH); 4.63 (0.29H, d, ^3J = 12.5, *trans*-4-CH); 4.67 (0.29H, d, ^3J = 12.5, *trans*-5-CH); 4.87 (0.71H, d, ^3J = 6.7, *cis*-5-CH); 6.39 (1.42H, br. s, *cis*-H-3,4 furyl); 6.43 (0.29H, m) and 6.49 (0.29H, m, *trans*-H-3,4 furyl); 7.04-7.59 (6H, m, H-5 furyl, H Ph); 10.33

(0.71H, s, *cis*-NHPh); 10.36 (0.29H, s, *trans*-NHPh); 11.38 (0.71H, s, *cis*-NH); 11.42 (0.29H, s, *trans*-NH). Found, %: C 53.12; H 3.35; N 13.06. $C_{19}H_{14}N_4O_3Se$. Calculated, %: C 53.66; H 3.32; N 13.17.

2-{[3,5-Dicyano-4-(2-furyl)-6-oxo-1,4,5,6-tetrahydropyridin-2-yl]seleno}-*N*-(4-methylphenyl)acetamide (9f). Yield 0.25 g, (60%). Light-brown crystalline substance, mp 199-201ºC. IR spectrum, ν, cm^{-1}: 1720 (C=O), 2205, 2260 (2C≡N), 3165, 3375 (2NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 2:1): 2.31 (3H, br. s, 4-CH_3); 3.81-3.98 (2H, m, $SeCH_2$); 4.39 (0.67H, d, ^3J = 6.6, *cis*-4-CH); 4.60 (0.66H, br. s, *trans*-4-CH, *trans*-5-CH); 4.84 (0.67H, d, ^3J = 6.6, *cis*-5-CH); 6.38 (1.34H, br. s, *cis*-H-3,4 furyl); 6.42 (0.33H, m) and 6.46 (0.33H, m, *trans*-H-3,4 furyl); 7.06-7.46 (4H, m, H Ar); 7.52 (0.67H, br. s, *cis*-H-5 furyl); 7.56 (0.33H, br. s, *trans*-H-5 furyl); 10.22 (0.67H, s, *cis*-NH Ar); 10.25 (0.33H, s, *trans*-NH Ar); 11.43 (0.67H, s, *cis*-NH); 11.50 (0.33H, s, *trans*-NH). Found, %: C 53.92; H 3.71; N 12.61. $C_{20}H_{16}N_4O_3Se$. Calculated, %: C 54.68; H 3.67; N 12.75.

2-Oxo-6-[(2-oxo-2-phenylethyl)seleno]-4-(2-thienyl)-1,2,3,4-tetrahydropyridine-3,5-dicarbonitrile (9g). Yield 0.40 g (96%). White crystalline substance, mp 195-197ºC (AcOH). IR spectrum, ν, cm^{-1}: 1718 (C=O), 2200, 2260 (2C≡N), 3140 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 3:1): 4.54 (0.25H, d, ^3J = 11.7, *trans*-4-CH); 4.62 (0.75H, d, ^3J = 6.6, *cis*-4-CH); 4.75 (0.25H, d, ^3J = 11.7, *trans*-3-CH); 4.72-4.92 (2H, m, $SeCH_2$); 4.87 (0.75H, d, ^3J = 6.6, *cis*-3-CH); 7.02-7.17 (2H, m, H-3,4 thienyl); 7.42 (0.75H, m, *cis*-CH-5 thienyl); 7.46 (0.25H, m, *trans*-CH thienyl); 7.51-8.03 (5H, m, H Ph); 11.15 (0.25H, s, *trans*-NH); 11.20 (0.75H, s, *cis*-NH). Found, %: C 53.17; H 3.11; N 9.79. $C_{19}H_{13}N_3O_2SSe$. Calculated, %: C 53.52; H 3.07; N 9.86.

6-{[2-(4-Methylphenyl)-2-oxoethyl]seleno}-2-oxo-4-(2-thienyl)-1,2,3,4-tetrahydropyridine-3,5-dicarbonitrile (9h). Yield 0.33 g (76%). White crystalline substance, mp 200-202ºC (AcOH). IR spectrum, ν, cm^{-1}: 1715 (C=O), 2204, 2265 (2C≡N), 3180 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 5:2): 2.43 (3H, m, CH_3); 4.48 (0.29H, d, ^3J = 11.7, *trans*-4-CH); 4.57 (0.71H, d, ^3J = 6.1, *cis*-4-CH); 4.69-4.83 (2.29H, m, *trans*-3-CH, $SeCH_2$); 4.85 (0.71H, d, ^3J = 6.1, *cis*-4-CH); 7.01-7.15 (2H, m, H-3,4 thienyl); 7.29 (2H, br. d, ^3J = 8.3, H-3,5 Ar); 7.37-7.43 (1H, m, H-5 thienyl); 7.89 (1.42H, d, ^3J = 8.3, *cis*-H-2,6 Ar); 7.90 (0.58H, d, ^3J = 8.3, *trans*-H-2,6 Ar); 11.10 (0.29H, s, *trans*-NH); 11.14 (0.71H, s, *cis*-NH). Found, %: C 54.16; H 3.47; N 9.46. $C_{20}H_{15}N_3O_2SSe$. Calculated, %: C 54.55; H 3.43; N 9.54.

Methyl [(3,5-Dicyano-6-oxo-4-phenyl-1,4,5,6-tetrahydropyridin-2-yl)seleno]acetate (9i). Yield 0.2 g (54%). White crystalline substance, mp 178-180ºC. IR spectrum, ν, cm^{-1}: 1720 (C=O), 2205, 2270 (2C≡N), 3150 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 1:1): 3.67 (1.5H, s, *cis*-OCH_3); 3.73 (1.5H, s, *trans*-OCH_3); 3.83-3.90 (2H, m, $SeCH_2$); 4.24 (0.5H, d, ^3J = 6.9, *cis*-4-CH); 4.35 (0.5H, d, ^3J = 11.5, *trans*-4-CH); 4.55 (0.5H, d, ^3J = 11.5, *trans*-5-CH); 4.86 (0.5H, d, ^3J = 6.9, *cis*-5-CH); 7.23-7.44 (5H, m, H Ph); 11.11 (0.5H, s, *cis*-NH); 11.14 (0.5H, s, *trans*-NH). Found, %: C 50.64; H 3.54; N 11.13. $C_{16}H_{13}N_3O_3Se$. Calculated, %: C 51.35; H 3.50; N 11.23.

Ethyl [(3,5-Dicyano-6-oxo-4-phenyl-1,4,5,6-tetrahydropyridin-2-yl)seleno]acetate (9j). Yield 0.09 g (24%). White, finely crystalline substance, mp 154-156ºC. IR spectrum, ν, cm^{-1}: 1725 (C=O), 2200, 2265 (2C≡N), 3180 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 5:4): 1.25 (1.65H, t, ^3J = 7.1, *cis*-$OCH_2C\underline{H}_3$); 1.30 (1.35H, t, ^3J = 7.1, *trans*-$OCH_2C\underline{H}_3$); 3.82-3.90 (2H, m, $SeCH_2$); 4.12 (1.1H, q, ^3J = 7.1, *cis*-$OC\underline{H}_2CH_3$); 4.22 (0.9H, q, ^3J = 7.1, *trans*-$OC\underline{H}_2CH_3$); 4.25 (0.55H, d, ^3J = 6.9, *cis*-4-CH); 4.35 (0.45H, d, ^3J = 12.5, *trans*-4-CH); 4.56 (0.45H, d, ^3J = 12.5, *trans*-5-CH); 4.85 (0.55H, d, ^3J = 6.9, *cis*-5-CH); 7.23-7.45 (5H, m, H Ph); 11.12 (0.45H, s, *trans*-NH); 11.14 (0.55H, s, *cis*-NH). Found, %: C 52.11; H 3.93; N 10.78. $C_{17}H_{15}N_3O_3Se$. Calculated, %: C 52.59; H 3.89; N 10.82.

2-Oxo-6-[(2-oxo-2-phenylethyl)seleno]-4-phenyl-1,2,3,4-tetrahydropyridine-3,5-dicarbonitrile (9k). Yield 0.24 g (58%). White, finely crystalline substance, mp 195-197ºC. IR spectrum, ν, cm^{-1}: 1715 (C=O), 2207, 2265 (2C≡N), 3148 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 6:5): 4.23 (0.55H, d, ^3J = 7.1, *cis*-4-CH); 4.33 (0.45H, d, ^3J = 13.0, *trans*-4-CH); 4.55 (0.45H, d, ^3J = 13.0, *trans*-3-CH); 4.72-4.88 (2.55H, m, *cis*-3-CH, $SeCH_2$); 7.24-8.04 (10H, m, H Ph); 11.11 (1H, br. s, NH). Found, %: C 59.63; H 3.63; N 9.89. $C_{21}H_{15}N_3O_2Se$. Calculated, %: C 60.01; H 3.60; N 10.00.

6-{[2-(4-Methylphenyl)-2-oxoethyl]seleno}-2-oxo-4-phenyl-1,2,3,4-tetrahydropyridine-3,5-dicarbonitrile (9l). Yield 0.32 g (74%). White, finely crystalline substance, mp 205-207ºC. IR spectrum, ν, cm^{-1}: 1717 (C=O), 2202, 2265 (2C≡N), 3150 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 6:5): 2.44 (3H, br. s, CH_3); 4.23 (0.55H, d, ^3J = 7.1, *cis*-4-CH); 4.32 (0.45H, d, ^3J = 13.0, *trans*-4-CH); 4.54 (0.45H, d, ^3J = 13.0, *trans*-3-CH); 4.68-4.84 (2H, m, $SeCH_2$); 4.86 (0.55H, d, ^3J = 7.1, *cis*-3-CH); 7.24-7.93 (9H, m, H Ar); 11.07 (1H, br. s, NH). Found, %: C 60.41; H 3.98; N 9.57. $C_{22}H_{17}N_3O_2Se$. Calculated, %: C 60.83; H 3.94; N 9.67.

2-[(3,5-Dicyano-6-oxo-4-phenyl-1,4,5,6-tetrahydropyridin-2-yl)seleno]-*N*-phenylacetamide (9m). Yield 0.31 g (74%). White crystalline substance, mp 207-209ºC (AcOH). IR spectrum, ν, cm^{-1}: 1745 (C=O), 2202, 2260 (2C≡N), 3150, 3430 (2NH) ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 7:6): 3.88-4.06 (2H, m, $SeCH_2$); 4.26 (0.54H, d, ^3J = 7.0, *cis*-4-CH); 4.38 (0.46H, d, ^3J = 13.0, *trans*-4-CH); 4.64 (0.46H, d, ^3J = 13.0, *trans*-5-CH); 4.95 (0.54H, d, ^3J = 7.0, *cis*-5-CH); 7.04-7.62 (10H, m, H Ph); 10.35 (0.54H, s, *cis*-N<u>H</u>Ph); 10.37 (0.46H, s, *trans*-N<u>H</u>Ph); 11.42 (0.46H, s, *trans*-NH); 11.44 (0.54H, s, *cis*-NH). Found, %: C 57.36; H 3.74; N 12.79. $C_{21}H_{16}N_4O_2Se$. Calculated, %: C 57.94; H 3.70; N 12.87.

***N*-(4-Methylphenyl)-2-[(3,5-dicyano-6-oxo-4-phenyl-1,4,5,6-tetrahydropyridin-2-yl)seleno]acetamide (9n)**. Yield 0.31 g (70%). Light-yellow crystalline substance, mp 206-208ºC. IR spectrum, ν, cm^{-1}: 1725 (C=O), 2205, 2260 (2C≡N), 3148, 3400 (2NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (ratio of *cis* and *trans* isomers ~ 10:9): 2.32 (1.59H, s, *cis*-CH_3); 2.33 (1.41H, s, *trans*-CH_3); 3.85-4.02 (2H, m, $SeCH_2$); 4.21 (0.53H, d, ^3J = 6.9, *cis*-4-CH); 4.32 (0.47H, d, ^3J = 12.7, *trans*-4-CH); 4.56 (0.47H, d, ^3J = 12.7, *trans*-5-CH); 4.89 (0.53H, d, ^3J = 6.9, *cis*-5-CH); 7.07-7.50 (9H, m, H Ar); 10.24 (0.53H, s, *cis*-N<u>H</u>Ph); 10.26 (0.47H, s, *trans*-N<u>H</u>Ph); 11.48 (1H, br. s, NH). Found, %: C 58.47; H 4.08; N 12.32. $C_{22}H_{18}N_4O_2Se$. Calculated, %: C 58.80; H 4.04; N 12.47.

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