

4-Alkyl-6-amino-4- N^3, N^5 -diaryl-2-thioxo-1,2,3,4-tetrahydropyridine-3,5-dicarboxamides: I. Tandem Synthesis and Alkylation. Molecular and Crystal Structure of 6-Allylsulfanyl-2-amino-4-isobutyl- N^3, N^5 -di-*m*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide

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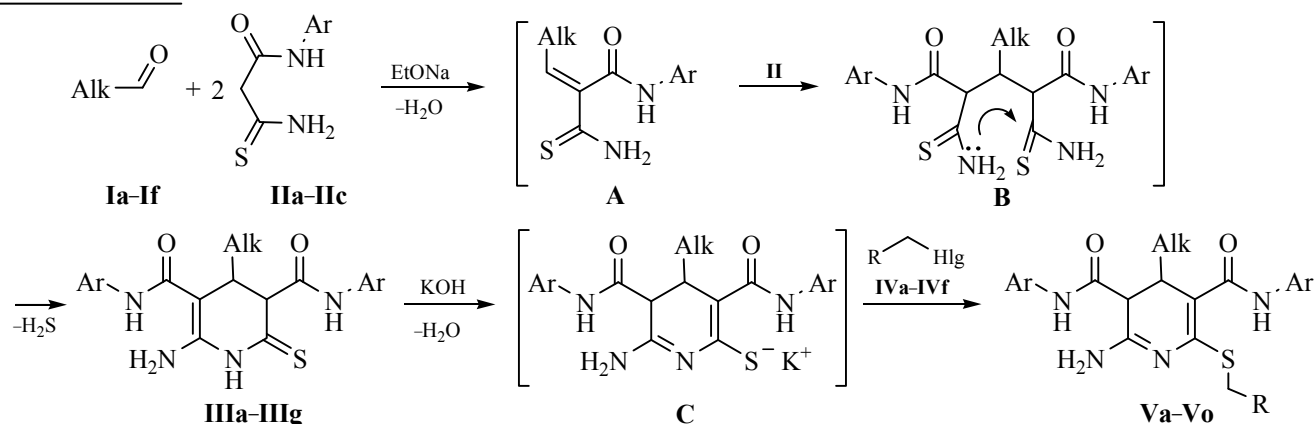
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Abstract—4-Alkyl-6-amino-4- N^3, N^5 -diaryl-2-thioxo-1,2,3,4-tetrahydropyridine-3,5-dicarboxamides were obtained via tandem synthesis involving the Knoevenagel reaction, Michael reaction and intramolecular condensation. Alkylation of the obtained dicarboxamides proceeds regioselectively at the S atom to form the corresponding thioethers. Structure of 6-allylsulfanyl-2-amino-4-isobutyl- N^3, N^5 -di-*m*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide was uniquely determined by XRD analysis.

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Currently tandem reactions are widely used in organic synthesis [1–3]. This approach to construct complex structures from simple molecules has been previously used by us to obtain the nitrogen-containing heterocyclic compounds: pyrrolines [4], pyridines [5], dihydropyridines [6], and fused pyrimidines [7].

In the present work we examined a condensation of aliphatic aldehydes **Ia–If** with a double excess of 3-amino-3-thioxopropane anilides **IIa–IIc** in anhydrous ethanol at 20°C in the presence of sodium ethoxide. This condensation consists in a tandem of several reactions and results in new 4-alkyl-6-amino- N^3, N^5 -



I, Alk = *i*-Bu (**a**), Et (**b**), *i*-Pr (**c**), Me (**d**), *n*-C₆H₁₃ (**e**), CH(Ph)CH₃ (**f**); **II**, Ar = Ph (**a**), 2-MeC₆H₄ (**b**), 3-MeC₆H₄ (**c**); **III**, Alk = *i*-Bu, Ar = 2-MeC₆H₄ (**a**); *i*-Bu, 3-MeC₆H₄ (**b**); *i*-Pr, 2-MeC₆H₄ (**c**); Et, 2-MeC₆H₄ (**d**); *n*-C₆H₁₃, 2-MeC₆H₄ (**e**); CH(Ph)CH₃, Ph (**f**); Me, Ph (**g**); **IV**, R = COOEt (**a**), Ph (**b**), 4-BrC₆H₄NHC(O) (**c**), 4-MeOC₆H₄NHC(O) (**d**), CH=CH₂ (**e**), *n*-C₈H₁₇ (**f**); **V**, Alk = *i*-Bu, Ar = 2-MeC₆H₄, R = CH=CH₂ (**a**); *i*-Bu, 2-MeC₆H₄, COOEt (**b**); *i*-Bu, 2-MeC₆H₄, 4-MeOC₆H₄NHC(O) (**c**); *i*-Bu, 3-MeC₆H₄, CH=CH₂ (**d**); *i*-Bu, 3-MeC₆H₄, Ph (**e**); *i*-Pr, 2-MeC₆H₄, CH=CH₂ (**f**); Et, 2-MeC₆H₄, CH=CH₂ (**g**); Et, 2-MeC₆H₄, COOEt (**h**); *n*-C₆H₁₃, 2-MeC₆H₄, CH=CH₂ (**i**); *n*-C₆H₁₃, 2-MeC₆H₄, Ph (**j**); CH(Ph)CH₃, Ph, CH=CH₂ (**k**); CH(Ph)CH₃, Ph, 4-BrC₆H₄NHC(O) (**l**); Me, Ph, 4-MeOC₆H₄NHC(O) (**m**); Me, Ph, CH=CH₂ (**n**); Me, Ph, *n*-C₈H₁₇ (**o**).

diaryl-2-thioxo-1,2,3,4-tetrahydropyridine-3,5-dicarboxamides **IIIa–IIIg**. Apparently, alkene **A** was initially formed as a result of the Knoevenagel reaction. Then the Michael reaction occurs to form the corresponding adduct **B**. The latter was chemoselectively transformed into the final product **III** via an intramolecular cyclocondensation.

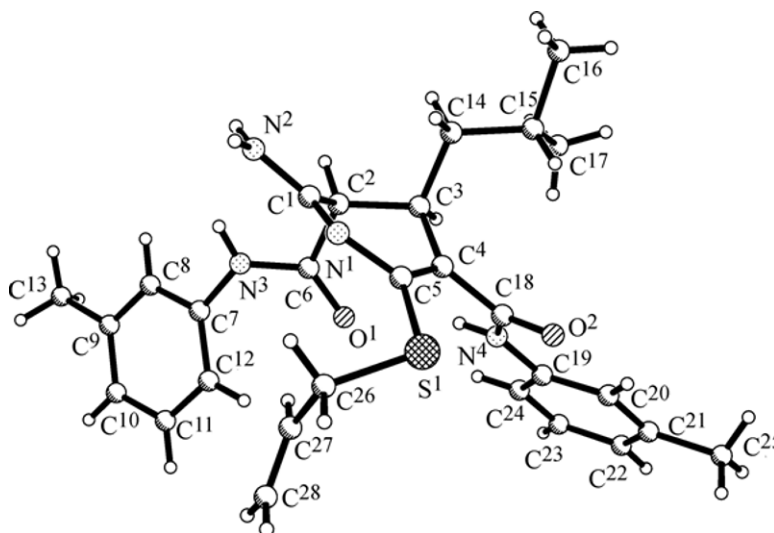
The structures of compounds **IIIa–IIIg** were confirmed by the spectral methods and also by chemical transformations. Thus, their alkylation with alkyl halides **IVa–IVf** results in the corresponding thioethers **Va–Vo**. This reaction proceeds smoothly in ethanol at 20°C in the presence of an equimolar amount of an aqueous KOH solution and apparently includes the formation of an intermediate salt **C**.

The ^1H NMR spectra of compounds **IIIa–IIIg** contain characteristic proton signals of the substituents of tetrahydropyridine ring in the respective areas and the signals of N^1H , C^3H and C^4H proton in the range of 12.45–13.25, 3.74–4.10 and 3.69–3.98 ppm, respectively. In the ^1H NMR spectra of compounds **Va–Vo** there are characteristic proton signals of C^3H and C^4H groups at δ 3.43–4.34 ppm, and the signals of amino group and a SCH_2 fragment. It should be noted that the nature of the proton signals of the last groups indicates the absence of free rotation. Thus, the signal of amino group is split in two broadened singlets instead of the expected one broad singlet, which may indicate the formation of a hydrogen bond confirmed by X-ray diffraction analysis for compound **Vd**. The absence of free rotation of alkylsulfanyl groups and non-equivalence of the SCH_2 -protons is also confirmed by

the presence of two doublet signals with the coupling constants 2J of 12–16 Hz characteristic of this type of compounds [8, 9]. The doubling with equal intensity of the signals from C^3H , C^4H , and CHMe protons in the ^1H NMR spectrum of compound **IIIg** indicates the presence of a chiral center in a phenylethyl moiety.

The structure of 6-allylsulfanyl-2-amino-4-isobutyl- N^3,N^5 -di-*m*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide **Vd** was studied by XRD in order to establish unambiguously the chemoselectivity of cyclization of the Michael adduct **B** and the regioselectivity of alkylation of compounds **IIIa–IIIg** and also to determine the position of double bonds in the dihydropyridine ring (commonly 2,5 location in the fully substituted 2-alkylsulfanyldihydropyridines [10–12]).

The molecule of compound **Vd** contains two chiral centers, the C^2 and C^3 atoms, with the same absolute configuration. The dihydropyridine ring has an intermediate conformation between a *semi-chair* and *twist-boat* (see figure). The fragment $\text{C}^1\text{N}^1\text{C}^5\text{C}^4$ is nonplanar [torsion angle $20.6(5)^\circ$], the C^2 and C^3 atoms are out of the median plane of this fragment by 0.404(7) and $-0.343(7)$ Å, respectively. The substituents at the C^2 and C^3 atoms have axial orientation [$\angle\text{C}^1\text{C}^2\text{C}^3\text{C}^{14} -70.3(4)^\circ$, $\angle\text{N}^2\text{C}^1\text{C}^2\text{C}^6 -99.5(4)^\circ$]. The carbonyl group of the $\text{O}^1\text{C}^6\text{N}^3$ amide fragment has *sc*-orientation with respect to the bond C^2-C^3 [$\angle\text{C}^3\text{C}^2\text{C}^6\text{O}^1 7.1(5)^\circ$], which is probably due to formation of an intramolecular hydrogen bond $\text{N}^4-\text{H}^4\cdots\text{O}^1$ ($\text{H}\cdots\text{O}$ 2.24°, $\text{N}-\text{H}\cdots\text{O}$ 147°). Tolylyl substituent at the N^3 atom is slightly turned with respect to the plane of the amide group [torsion angle is $\text{C}^6\text{N}^3\text{C}^7\text{C}^{12} 35.2(6)^\circ$]. Due to steric



General view of the molecule of **Vd** according to XRD data.

Table 1. The bond lengths (Å) in the structure of **Vd**

Bond		<i>d</i>	Bond		<i>d</i>
S ¹	C ⁵	1.775(3)	C ⁷	C ¹²	1.383(5)
S ¹	C ²⁶	1.822(5)	C ⁸	C ⁹	1.371(5)
O ¹	C ⁶	1.223(4)	C ⁹	C ¹⁰	1.379(5)
O ²	C ¹⁸	1.241(4)	C ⁹	C ¹³	1.503(5)
N ¹	C ¹	1.298(4)	C ¹⁰	C ¹¹	1.385(5)
N ¹	C ⁵	1.401(4)	C ¹¹	C ¹²	1.379(5)
N ²	C ¹	1.332(4)	C ¹⁴	C ¹⁵	1.519(5)
N ³	C ⁶	1.351(4)	C ¹⁵	C ¹⁶	1.535(6)
N ³	C ⁷	1.418(4)	C ¹⁵	C ¹⁷	1.520(7)
N ⁴	C ¹⁸	1.347(4)	C ¹⁹	C ²⁰	1.374(4)
N ⁴	C ¹⁹	1.418(4)	C ¹⁹	C ²⁴	1.377(4)
C ¹	C ²	1.508(5)	C ²⁰	C ²¹	1.392(4)
C ²	C ³	1.524(4)	C ²¹	C ²²	1.377(5)
C ²	C ⁶	1.527(5)	C ²¹	C ²⁵	1.505(5)
C ³	C ⁴	1.529(4)	C ²²	C ²³	1.371(5)
C ³	C ¹⁴	1.543(5)	C ²³	C ²⁴	1.371(5)
C ⁴	C ⁵	1.334(4)	C ²⁶	C ²⁷	1.487(6)
C ⁴	C ¹⁸	1.482(4)	C ²⁷	C ²⁸	1.279(7)
C ⁷	C ⁸	1.377(5)			

hindrances (a short intramolecular contact H^{3a}...H⁴ 2.07 Å against the sum of the van der Waals radii of 2.32 Å [13]) and also due to the intramolecular hydrogen bond N⁴–H⁴...O¹ there is a rotation of the amide group O²–C¹⁸–N⁴ relative to the plane of the double bond C⁴=C⁵ [$\angle$ C⁵C⁴C¹⁸O² –49.7(5)°]. Tolylyl substituent at the N⁴ atom is in the plane of the amide group [$\angle$ C¹⁸N⁴C¹⁹C²⁰ –6.9(6)°]. This orientation is additionally stabilized by the formation of an intramolecular hydrogen bond C²⁰–H²⁰...O² (H...O 2.35 Å, C–H...O 122°). The bond S¹–C²⁶ is non-co-planar with the heterocycle plane [$\angle$ C²⁶S¹C⁵N¹ 39.8(3)°], which should lead to some disruption of conjugation between the lone electron pairs of the sulfur atom and the π -system of the heterocycle. Probably, this is compensated by the formation of the shortened intramolecular contacts N¹...H^{26b} 2.48 Å (sum of the van der Waals radii 2.66 Å [13]). In the crystal, the molecules form dimers by hydrogen bonds

N²–H^{2a}...N¹ⁱ [*i*: 1/2 – *x*, 1/2 – *y*, *z*] (H...N 2.31 Å, N–H...N 146°). These dimers form the chains along the axis *a* due to the weak hydrogen bonding N³–H³...O²ⁱⁱ [*ii*: 1 + *x*, *y*, *z*] (H...O 2.47 Å, N–H...O 128°) and N²–H^{2b}...S¹ⁱⁱ (H...S 2.97 Å, N–H...S 132°).

EXPERIMENTAL

Crystals of compound **Vd** are rhombic, C₂₈H₃₄N₄O₂S; at 298 K: *a* 8.1384(5), *b* 36.179(3), *c* 18.5955(16) Å; *V* 5475.3(7) Å³, *M* 490.65, *Z* 8, space group *Pccn*, *d*_{calc} 1.19 g cm^{–3}, μ (MoK α) 0.149 mm^{–1}, *F*(000) 2096. The unit cell parameters and intensities of 40295 reflections (4857 independent, *R*_{int} 0.125) were measured on a Xcalibur 3 four-circle automatic diffractometer (MoK α , graphite monochromator, CCD-detector, ω -scanning, 2 θ _{max} 50.0°). The structure was solved by the direct method using SHELX-97 program [14]. Positions of the hydrogen atoms were calculated geometrically and refined in a *rider* model with *U*_{iso} = *nU*_{eq} of the carrier atom (*n* = 1.5 for methyl groups, *n* = 1.2 for the other hydrogen atoms). The structure was refined with respect to *F*² using a full-matrix anisotropic approximation for nonhydrogen atoms to *wR*₂ 0.173 for 4857 reflections [*R*₁ 0.067 for 2443 reflections with *F* > 4 σ (*F*), *S* 0.99]. In the crystal a disordered solvent molecule, apparently ethanol, is present whose contribution to the electron density was removed from *F*_o² at the final refining step by means of SQUEEZE procedure in PLATON program [15]. The bond lengths and bond angles are listed in Tables 1 and 2, respectively.

The ¹H NMR spectra were recorded on a Bruker AVANCE DRX-500 (500 MHz) (**Vd**, **Vh**, **VI**) and Bruker AVANCE II-400 (400 MHz) spectrometers (**IIIa–IIIg**, **Va–Vc**, **Ve–Vg**, **Vi–Vk**, **Vm–Vo**) in a DMSO-*d*₆ solution, internal reference TMS). The ¹³C NMR spectrum of compound **Vd** was taken on a Bruker AVANCE DRX-500 spectrometer (125.75 MHz). Mass spectra were registered on a Chrommas GC/MS-Hewlett-Packard 5890/5972 instrument (column HP-5MS, chemical ionization, 70 eV) in CH₂Cl₂ solutions. The IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR instrument from KBr pellets. Melting points were measured on a Koeffler heating block. The reaction progress and purity of the compounds obtained were monitored by TLC (Silufol UV-254 plates) eluting with an acetone–hexane mixture (3:5) and detecting with iodine vapors.

Synthesis of 4-alkyl-6-amino-*N*³,*N*⁵-diaryl-2-thioxo-1,2,3,4-tetrahydropyridine-3,5-dicarboxamides (IIIa–****

Table 2. Bond angles (deg) in the structure of **Vd**

Angle			deg	Angle			deg
C ⁵	S ¹	C ²⁶	100.78(19)	C ⁸	C ⁹	C ¹⁰	118.5(4)
C ¹	N ¹	C ⁵	117.1(3)	C ⁸	C ⁹	C ¹³	121.2(4)
C ⁶	N ³	C ⁷	128.5(3)	C ¹⁰	C ⁹	C ¹³	120.3(4)
C ¹⁸	N ⁴	C ¹⁹	130.9(3)	C ⁹	C ¹⁰	C ¹¹	119.6(4)
N ¹	C ¹	N ²	119.2(3)	C ¹²	C ¹¹	C ¹⁰	121.7(4)
N ¹	C ¹	C ²	122.6(3)	C ¹¹	C ¹²	C ⁷	118.3(4)
N ²	C ¹	C ²	118.1(3)	C ¹⁵	C ¹⁴	C ³	114.8(3)
C ¹	C ²	C ³	107.3(3)	C ¹⁴	C ¹⁵	C ¹⁶	109.0(4)
C ¹	C ²	C ⁶	111.7(3)	C ¹⁴	C ¹⁵	C ¹⁷	112.2(4)
C ³	C ²	C ⁶	112.0(3)	C ¹⁷	C ¹⁵	C ¹⁶	108.0(5)
C ²	C ³	C ⁴	108.0(3)	O ²	C ¹⁸	N ⁴	123.8(3)
C ²	C ³	C ¹⁴	111.0(3)	O ²	C ¹⁸	C ⁴	122.5(3)
C ⁴	C ³	C ¹⁴	111.8(3)	N ⁴	C ¹⁸	C ⁴	113.7(3)
C ⁵	C ⁴	C ³	117.5(3)	C ²⁰	C ¹⁹	N ⁴	123.4(3)
C ⁵	C ⁴	C ¹⁸	122.3(3)	C ²⁰	C ¹⁹	C ²⁴	119.2(3)
C ¹⁸	C ⁴	C ³	120.0(3)	C ²⁴	C ¹⁹	N ⁴	117.3(3)
N ¹	C ⁵	S ¹	114.2(3)	C ¹⁹	C ²⁰	C ²¹	120.9(3)
C ⁴	C ⁵	S ¹	122.2(2)	C ²⁰	C ²¹	C ²⁵	120.9(3)
C ⁴	C ⁵	N ¹	123.5(3)	C ²²	C ²¹	C ²⁰	119.0(3)
O ¹	C ⁶	N ³	122.6(3)	C ²²	C ²¹	C ²⁵	120.2(3)
O ¹	C ⁶	C ²	123.2(3)	C ²³	C ²²	C ²¹	119.8(3)
N ³	C ⁶	C ²	114.1(3)	C ²²	C ²³	C ²⁴	121.0(4)
C ⁸	C ⁷	N ³	118.0(3)	C ²³	C ²⁴	C ¹⁹	120.0(4)
C ⁸	C ⁷	C ¹²	119.5(3)	C ²⁷	C ²⁶	S ¹	112.7(3)
C ¹²	C ⁷	N ³	122.4(3)	C ²⁸	C ²⁷	C ²⁶	126.3(6)
C ⁹	C ⁸	C ⁷	122.3(4)				

IIIg) (general procedure). To a solution of 5 mmol (0.115 g) of metallic sodium in 20 ml of anhydrous ethanol was added under stirring 5 mmol of appropriate 3-amino-*N*-aryl-3-thioxopropanamide **IIa–IIc** and 5 mmol of aldehyde **Ia–If**. After 10 min to the mixture was added another 5 mmol of appropriate 3-amino-*N*-aryl-3-thioxopropanamide **IIa–Iic**. The mixture was kept for 48 h at room temperature. The formed precipitate was filtered off, washed with water, cold ethanol, and hexane.

6-Amino-4-isobutyl-2-thioxo- N^3,N^5 -di-*o*-tolyl-1,2,3,4-tetrahydropyridine-3,5-dicarboxamide (IIIa). Yield 1.18 g (52%), yellow powder, mp 162–164°C (EtOH). IR spectrum, ν , cm⁻¹: 3235–3412 (NH, NH₂),

1672 (CONH), 1646 [δ (NH₂)], 1211 (C=S). ¹H NMR spectrum, δ , ppm: 0.93 d (3H, CH₃, *J* 6.2 Hz), 0.97 d (3H, CH₃, *J* 6.2 Hz), 1.11–1.32 m (2H, CH₂), 1.51–1.77 m (1H, CHMe₂), 2.12 s (3H, CH₃), 2.34 s (3H, CH₃), 3.83 s (1H, C³H), 3.97 t (1H, C⁴H, *J* 7.0 Hz), 6.87 t (1H, H_{arom}, *J* 7.3 Hz), 6.96–7.28 m (8H, 6H_{arom}, NH₂), 8.20 d (1H, H_{arom}, *J* 7.9 Hz), 9.72 br.s (1H, NHCO), 10.18 br.s (1H, NHCO), 12.45 br.s (1H, N¹H). Mass spectrum, *m/z* (*I*_{rel}, %): 451.2 (100) [*M* + 1]⁺. Found, %: C 66.52; H 6.65; N 12.29. C₂₅H₃₀N₄O₂S. Calculated, %: C 66.64; H 6.71; N 12.43. *M* 450.608.

6-Amino-4-isobutyl-2-thioxo- N^3,N^5 -di-*m*-tolyl-1,2,3,4-tetrahydropyridine-3,5-dicarboxamide (IIIb). Yield 1.23 g (55%), yellow powder, mp 180–182°C

(EtOH). IR spectrum, ν , cm^{-1} : 3228–3411 (NH, NH_2), 1670 (CONH), 1640 [$\delta(\text{NH}_2)$], 1191 (C=S). ^1H NMR spectrum, δ , ppm: 0.88 d (3H, CH_3 , J 5.6 Hz), 0.96 d (3H, CH_3 , J 5.6 Hz), 1.08–1.29 m (2H, CH_2), 1.56–1.72 m (1H, CHMe_2), 2.26 s (6H, 2CH_3), 3.71–3.81 m (1H, C^4H), 3.84 s (1H, C^3H), 6.73 d (1H, H_{arom} , J 6.9 Hz), 6.87 d (1H, H_{arom} , J 7.0 Hz), 7.10 t (1H, H_{arom} , J 7.2 Hz), 7.17 t (1H, H_{arom} , J 7.2 Hz), 7.25–7.36 m (2H, H_{arom}), 7.36–7.48 m (2H, H_{arom}), 8.56 br.s (1H, NH_2), 9.48 br.s (1H, NH_2), 10.27 br.s (2H, 2NHCO), 13.18 br.s (1H, N^1H). Mass spectrum, m/z (I_{rel} , %): 451.2 (82) [$M + 1$] $^+$. Found, %: C 66.50; H 6.64; N 12.37. $\text{C}_{25}\text{H}_{30}\text{N}_4\text{O}_2\text{S}$. Calculated, %: C 66.64; H 6.71; N 12.43. M 450.608.

6-Amino-4-isopropyl-2-thioxo- N^3, N^5 -di-*o*-tolyl-1,2,3,4-tetrahydropyridine-3,5-dicarboxamide (IIIc). Yield 0.46 g (21%), white powder, mp 188–190°C (EtOH). IR spectrum, ν , cm^{-1} : 3195–3340 (NH, NH_2), 1681 (CONH), 1653 [$\delta(\text{NH}_2)$], 1200 (C=S). ^1H NMR spectrum, δ , ppm: 0.94 d (6H, 2CH_3 , J 6.3 Hz), 1.55–1.62 m (1H, CHMe_2), 2.10 s (3H, CH_3), 2.34 s (3H, CH_3), 3.70 d (1H, C^4H , J 7.4 Hz), 4.03 s (1H, C^3H), 6.88 t (1H, H_{arom} , J 7.2 Hz), 6.95–7.31 m (6H, H_{arom}), 8.19 d (1H, H_{arom} , J 8.0 Hz), 8.51 br.s (H, NH_2), 9.36 br.s (H, NH_2), 9.81 br.s (1H, NHCO), 10.25 br.s (1H, NHCO), 12.55 br.s (1H, N^1H). Mass spectrum, m/z (I_{rel} , %): 437.2 (100) [$M + 1$] $^+$. Found, %: C 66.18; H 6.35; N 12.74. $\text{C}_{24}\text{H}_{28}\text{N}_4\text{O}_2\text{S}$. Calculated, %: C 66.03; H 6.47; N 12.83. M 436.581.

6-Amino-2-thioxo- N^3, N^5 -di-*o*-tolyl-4-ethyl-1,2,3,4-tetrahydropyridine-3,5-dicarboxamide (IIIId). Yield 0.50 g (47%), white powder, mp 178–180°C (EtOH). IR spectrum, ν , cm^{-1} : 3314–3158 (NH, NH_2), 1668 (CONH), 1638 [$\delta(\text{NH}_2)$], 1195 (C=S). ^1H NMR spectrum, δ , ppm: 0.92 t (3H, CH_3 , J 6.9 Hz), 1.23–1.38 m (1H, CH_2), 1.40–1.51 m (1H, CH_2), 2.12 s (3H, CH_3), 2.34 s (3H, CH_3), 3.84 s (1H, C^3H), 3.86–3.91 m (1H, C^4H), 6.88 t (1H, H_{arom} , J 7.3 Hz), 7.00–7.25 m (6H, H_{arom}), 8.19 s (1H, H_{arom}), 8.21 br.s (1H, NH_2), 9.50 br.s (1H, NH_2), 9.73 br.s (1H, NHCO), 10.29 br.s (1H, NHCO), 12.45 br.s (1H, N^1H). Mass spectrum, m/z (I_{rel} , %): 423.2 (100) [$M + 1$] $^+$. Found, %: C 65.49; H 6.07; N 13.10. $\text{C}_{23}\text{H}_{26}\text{N}_4\text{O}_2\text{S}$. Calculated, %: C 65.38; H 6.20; N 13.26. M 422.53.

6-Amino-4-*n*-hexyl- N^3, N^5 -di-*o*-tolyl-2-thioxo-1,2,3,4-tetrahydropyridine-3,5-dicarboxamide (IIIe). Yield 1.27 g (53%), yellow powder, mp 188–190°C (EtOH). IR spectrum, ν , cm^{-1} : 3188–3415 (NH, NH_2), 1670 (CONH), 1635 [$\delta(\text{NH}_2)$], 1198 (C=S). ^1H NMR spectrum, δ , ppm: 0.82 t (3H, CH_3 , J 6.4 Hz), 1.10–

1.48 m (10H, 5CH_2), 2.11 s (3H, CH_3), 2.33 s (3H, CH_3), 3.81–3.94 br.s (2H, C^3H and C^4H), 6.84–6.91 m (1H, H_{arom}), 7.00–7.25 m (8H, 6H_{arom} , NH_2), 8.19 d (1H, H_{arom} , J 8.0 Hz), 9.75 br.s (1H, NHCO), 10.30 br.s (1H, NHCO), 12.46 br.s (1H, N^1H). Mass spectrum, m/z (I_{rel} , %): 479.2 (100) [$M + 1$] $^+$. Found, %: C 67.69; H 7.22; N 11.58. $\text{C}_{27}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$. Calculated, %: C 67.75; H 7.16; N 11.71. M 478.663.

6-Amino-2-thioxo- N^3, N^5 -diphenyl-4-(1-phenylethyl)-1,2,3,4-tetrahydropyridine-3,5-dicarboxamide (IIIff). Yield 0.65 g (28%), yellow powder, mp 188–190°C (EtOH). IR spectrum, ν , cm^{-1} : 2930–3444 (NH, NH_2), 1683 (CONH), 1601 [$\delta(\text{NH}_2)$], 1167 (C=S). ^1H NMR spectrum, δ , ppm: 1.08 d (3H, CH_3 , J 6.5 Hz), 2.83 br.s and 2.97 br.s (1H, CHMe), 3.98 br.s and 4.10 br.s (1H, C^3H), 4.27 br.s and 4.36 br.s (1H, C^4H), 6.70–7.65 m (17H, 15H_{arom} , NH_2), 9.68 br.s (1H, NHCO), 10.41 br.s (1H, NHCO), 13.24 br.s (1H, N^1H). Mass spectrum, m/z (I_{rel} , %): 471.2 (100) [$M + 1$] $^+$. Found, %: C 68.86; H 5.42; N 11.84. $\text{C}_{27}\text{H}_{26}\text{N}_4\text{O}_2\text{S}$. Calculated, %: C 68.91; H 5.57; N 11.91. M 470.598.

6-Amino-4-methyl-2-thioxo- N^3, N^5 -diphenyl-1,2,3,4-tetrahydropyridine-3,5-dicarboxamide (IIIg). Yield 0.65 g (34%), yellow powder, mp 211–213°C (EtOH). IR spectrum, ν , cm^{-1} : 3188–3398 (NH, NH_2), 1674 (CONH), 1615 [$\delta(\text{NH}_2)$], 1173 (C=S). ^1H NMR spectrum, δ , ppm: 1.02 d (3H, CH_3 , J 6.4 Hz), 3.75 d (1H, C^4H , J 6.4 Hz), 3.80 s (1H, C^3H), 6.92 t (1H, H_{arom} , J 7.2 Hz), 7.05 t (1H, H_{arom} , J 6.8 Hz), 7.22 t (2H, H_{arom} , J 7.2 Hz), 7.30 t (2H, H_{arom} , J 7.2 Hz), 7.45–7.72 m (4H, H_{arom}), 9.20 br.s (2H, NH_2), 10.44 br.s (2H, 2NHCO), 13.25 br.s (1H, N^1H). Mass spectrum, m/z (I_{rel} , %): 381.1 (100) [$M + 1$] $^+$. Found, %: C 63.22; H 5.37; N 14.84. $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$. Calculated, %: C 63.14; H 5.30; N 14.73. M 380.463.

Synthesis of compounds (Va–Vo) (general procedure). To a suspension of 0.5 mmol of compound **IIIa–IIIg** in 15 ml of ethanol under stirring was added 0.26 ml (0.5 mmol) of 10% aqueous KOH solution. After 10 min to the reaction mixture was added 0.5 mmol of appropriate alkyl halide **IVa–IVf**. The mixture was kept for 24 h. The formed precipitate was filtered off, washed with water, cold methanol and ethanol, then dried in a vacuum.

6-Allylsulfanyl-2-amino-4-isobutyl- N^3, N^5 -di-*o*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide (Va). Yield 0.12 g (50%), white powder, mp 224–226°C (EtOH). IR spectrum, ν , cm^{-1} : 3211–3412 (NH, NH_2), 1666 (CONH), 1641 [$\delta(\text{NH}_2)$]. ^1H NMR spectrum, δ ,

ppm: 0.93 d (6H, 2CH₃, *J* 5.3 Hz), 1.06–1.20 m (1H, CH₂), 1.28–1.40 m (1H, CH₂), 1.66–1.81 m (1H, CHMe₂), 2.16 s (3H, CH₃), 2.23 s (3H, CH₃), 3.39 br.s (2H, C³H and C⁴H), 3.47 d.d (1H, SCH₂, ²*J* 13.2, ³*J* 6.3 Hz), 3.74 d.d (1H, SCH₂, ²*J* 13.3, ³*J* 6.4 Hz), 4.87 d (1H, =CH₂, *J*_{cis} 9.4 Hz), 5.11 d (1H, =CH₂, *J*_{trans} 16.6 Hz), 5.76–5.90 m (1H, CH=), 7.02 t (1H, H_{arom}, *J* 8.0 Hz), 7.15–7.24 m (5H, H_{arom}), 7.34 d (1H, H_{arom}, *J* 7.6 Hz), 7.47 br.s (2H, NH₂), 7.65 d (1H, H_{arom}, *J* 7.7 Hz), 8.74 br.s (1H, NHCO), 8.88 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 491.2 (100) [*M* + 1]⁺. Found, %: C 68.37; H 6.84; N 11.37. C₂₈H₃₄N₄O₂S. Calculated, %: C 68.54; H 6.98; N 11.42. *M* 490.674.

Ethyl-2-[6-amino-4-isobutyl-3,5-di(*o*-tolylcarbamoyl)-4,5-dihydropyridine-2-ylsulfanyl]acetate (Vb). Yield 0.086 g (32%), white powder, mp 161–163°C (EtOH). IR spectrum, *v*, cm⁻¹: 3214–3433 (NH, NH₂), 1712 (C=O), 1666 (CONH), 1635 [δ(NH₂)]. ¹H NMR spectrum, δ, ppm: 0.80–1.05 m (6H, 2CH₃), 1.11 t (3H, CH₃, *J* 7.0, Hz), 1.20–1.37 m (2H, CH₂), 1.66–1.77 m (1H, CHMe₂), 2.15 s (3H, CH₃), 2.22 s (3H, CH₃), 3.35 br.s (2H, C³H and C⁴H), 3.68 d (1H, SCH₂, ²*J* 15.9 Hz), 3.85 d (1H, SCH₂, ²*J* 15.9 Hz), 3.97 m (2H, OCH₂), 7.00–7.35 m (7H, H_{arom}), 7.51 d (1H, H_{arom}, *J* 8.0 Hz), 7.54 br.s (1H, NH₂), 7.61 br.s (1H, NH₂), 8.64 br.s (1H, NHCO), 8.72 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 537.4 (100) [*M* + 1]⁺. Found, %: C 64.73; H 6.64; N 10.38. C₂₉H₃₆N₄O₄S. Calculated, %: C 64.90; H 6.76; N 10.44. *M* 536.70.

2-Amino-4-isobutyl-6-[2-(4-methoxyphenylamino)-2-oxoethylsulfanyl]-*N*³,*N*⁵-di-*o*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide (Vc). Yield 0.163 g (53%), yellowish green powder, mp 198–200°C (EtOH). IR spectrum, *v*, cm⁻¹: 3212–3415 (NH, NH₂), 1682 (CONH), 1633 [δ(NH₂)]. ¹H NMR spectrum, δ, ppm: 0.93 d (6H, 2CH₃, *J* 5.8 Hz), 1.09–1.22 m (1H, CH₂), 1.26–1.40 m (1H, CH₂), 1.68–1.82 m (1H, CHMe₂), 2.14 s (3H, CH₃), 2.20 s (3H, CH₃), 3.42 t (1H, C⁴H, *J* 7.6 Hz), 3.48 s (1H, C³H), 3.64 d (1H, SCH₂, ²*J* 14.2 Hz), 3.69 s (3H, OCH₃), 3.89 d (1H, SCH₂, ²*J* 14.2 Hz), 6.73 d (2H, H_{arom}, *J* 8.5 Hz), 6.98–7.27 m (7H, H_{arom}), 7.32 d (2H, H_{arom}, *J* 8.5 Hz), 7.46 d (1H, H_{arom}, *J* 7.6 Hz), 7.77 br.s (2H, NH₂), 8.86 br.s (1H, NHCO), 9.11 br.s (1H, NHCO), 9.95 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 614.4 (100) [*M* + 1]⁺. Found, %: C 66.63; H 6.32; N 11.47. C₃₄H₃₉N₅O₄S. Calculated, %: C 66.53; H 6.41; N 11.41. *M* 613.782.

6-Allylsulfanyl-2-amino-4-isobutyl-*N*³,*N*⁵-di-*o*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide (Vd).

Yield 0.19 g (79%) of yellow crystals, mp 158–160°C (EtOH). IR spectrum, *v*, cm⁻¹: 3154, 3304, 3429 (NH, NH₂), 1675 (CONH), 1627 [δ(NH₂)]. ¹H NMR spectrum, δ, ppm: 0.88 d (6H, 2CH₃, *J* 5.7 Hz), 1.03–1.11 m (1H, CH₂), 1.26–1.36 m (1H, CH₂), 1.63–1.73 m (1H, CHMe₂), 2.27 s (3H, CH₃), 2.28 s (3H, CH₃), 3.24 s (1H, C³H), 3.28–3.45 m (2H, C⁴H, SCH₂), 3.73 d.d (1H, SCH, ²*J* 13.5, ³*J* 6.3 Hz), 4.86 d (1H, =CH₂, *J*_{cis} 9.8 Hz), 5.07 d (1H, =CH₂, *J*_{trans} 16.7 Hz), 5.77–5.87 m (1H, CH=), 6.83 d (1H, H_{arom}, *J* 7.1 Hz), 6.89 d (1H, H_{arom}, *J* 7.2 Hz), 7.15 t (1H, H_{arom}, *J* 7.7 Hz), 7.20 t (1H, H_{arom}, *J* 7.8 Hz), 7.29–7.51 m (6H, 4H_{arom}, NH₂), 9.21 br.s (1H, NHCO), 9.60 br.s (1H, NHCO). ¹³C NMR spectrum, δ_C, ppm: 21.62, 21.67, 22.92, 23.94, 25.03, 33.17, 34.62, 42.91, 48.76, 111.45, 116.48, 117.10, 117.29, 120.39, 120.63, 123.91, 124.63, 128.81, 129.00, 136.47, 138.08, 138.30, 139.31, 139.90, 149.26, 159.04, 167.03, 167.08. Mass spectrum, *m/z* (*I*_{rel}, %): 491.2 (100) [*M* + 1]⁺. Found, %: C 68.38; H 6.87; N 11.30. C₂₈H₃₄N₄O₂S. Calculated, %: C 68.54; H 6.99; N 11.42. *M* 490.674.

2-Amino-6-benzylsulfanyl-4-isobutyl-*N*³,*N*⁵-di-*m*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide (Ve). Yield 0.16 g (58%), white powder, mp 192–194°C (EtOH). IR spectrum, *v*, cm⁻¹: 3198–3413 (NH, NH₂), 1677 (CONH), 1640 [δ(NH₂)]. ¹H NMR spectrum, δ, ppm: 0.89 d (6H, 2CH₃, *J* 4.3 Hz), 1.05–1.19 m (1H, CH₂), 1.23–1.37 m (1H, CH₂), 1.60–1.76 m (1H, CHMe₂), 2.25 s (3H, CH₃), 2.29 s (3H, CH₃), 3.36 t (1H, C⁴H, *J* 6.4 Hz), 3.43 s (1H, C³H), 4.07 d (1H, SCH₂, ²*J* 13.2 Hz), 4.33 d (1H, SCH₂, ²*J* 13.3 Hz), 6.80 d (1H, H_{arom}, *J* 7.3 Hz), 6.89 d (1H, H_{arom}, *J* 7.3 Hz), 7.01–7.65 m (13H, 11H_{arom}, NH₂), 8.96 br.s (1H, NHCO), 9.86 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 541.2 (100) [*M* + 1]⁺. Found, %: C 71.12; H 6.67; N 10.40. C₃₂H₃₆N₄O₂S. Calculated, %: C 71.08; H 6.71; N 10.36. *M* 540.73.

6-Allylsulfanyl-2-amino-4-isopropyl-*N*³,*N*⁵-di-*o*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide (Vf). Yield 0.09 g (37%), yellowish green powder, mp 192–194°C (EtOH). IR spectrum, *v*, cm⁻¹: 3208–3444 (NH, NH₂), 1666 (CONH), 1634 [δ(NH₂)]. ¹H NMR spectrum, δ, ppm: 0.93 d (3H, CH₃, *J* 6.3 Hz), 0.97 d (3H, CH₃, *J* 6.3 Hz), 1.56–1.74 m (1H, CHMe₂), 2.16 s (3H, CH₃), 2.22 s (3H, CH₃), 3.09 d (1H, C⁴H, *J* 7.2 Hz), 3.45 d.d (1H, SCH₂, ²*J* 13.4, ³*J* 6.6 Hz), 3.55 s (1H, C³H), 3.73 d.d (1H, CH₂, ²*J* 13.4, ³*J* 6.6 Hz), 4.85 d (1H, =CH₂, *J*_{cis} 9.4 Hz), 5.10 d (1H, =CH₂, *J*_{trans} 17.3 Hz), 5.73–5.90 m (1H, CH=), 7.02 t (1H, H_{arom}, *J* 7.2 Hz), 7.05–7.27 m (5H, H_{arom}), 7.34 d (1H, H_{arom},

J 7.6 Hz), 7.49 br.s (2H, NH₂), 7.57 d (1H, H_{arom}, *J* 7.6 Hz), 8.72 br.s (1H, NHCO), 8.86 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 477.2 (100) [*M* + 1]⁺. Found, %: C 68.11; H 6.82; N 11.59. C₂₇H₃₂N₄O₂S. Calculated, %: C 68.04; H 6.77; N 11.76. *M* 476.636.

6-Allylsulfanyl-2-amino-4-ethyl-*N*³,*N*⁵-di-*o*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide (VI). Yield 0.17 g (73%), white powder, mp 151–153°C (EtOH). IR spectrum, *v*, cm⁻¹: 3295–3416 (NH, NH₂), 1665 (CONH), 1639 [δ(NH₂)]. ¹H NMR spectrum, *δ*, ppm: 0.97 t (3H, CH₃, *J* 6.4 Hz), 1.25–1.40 m (1H, CH₂), 1.44–1.58 m (1H, CH₂), 2.15 s (3H, CH₃), 2.22 s (3H, CH₃), 3.39–3.54 m (3H, C³H, C⁴H and SCH₂), 3.75 d.d (1H, SCH₂, ²*J* 13.2, ³*J* 6.3 Hz), 4.89 d (1H, =CH₂, *J*_{cis} 9.9 Hz), 5.12 d (1H, =CH₂, *J*_{trans} 17.0 Hz), 5.78–5.93 m (1H, CH=), 7.02 t (1H, H_{arom}, *J* 7.1 Hz), 7.06–7.25 m (5H, H_{arom}), 7.31 d (1H, H_{arom}, *J* 7.6 Hz), 7.50 d (2H, NH₂, *J* 19.6 Hz), 7.58 d (1H, H_{arom}, *J* 7.9 Hz), 8.70 br.s (1H, NHCO), 8.95 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 463.2 (100) [*M* + 1]⁺. Found, %: C 67.42; H 6.37; N 12.09. C₂₆H₃₀N₄O₂S. Calculated, %: C 67.51; H 6.54; N 12.11. *M* 462.619.

Ethyl-2-[6-amino-3,5-di(*o*-tolylcarbonyl)-4-ethyl-4,5-dihydropyridine-2-ylsulfanyl]acetate (Vh). Yield 0.09 g (36%), white powder, mp 158–160°C (EtOH). IR spectrum, *v*, cm⁻¹: 3211–3408 (NH, NH₂), 1715 (C=O), 1661 (CONH), 1632 [δ(NH₂)]. ¹H NMR spectrum, *δ*, ppm: 0.96 t (3H, CH₃, *J* 7.1 Hz), 1.13 t (3H, CH₃, *J* 7.1 Hz), 1.23–1.35 m (1H, CH₂), 1.46–1.57 m (1H, CH₂), 2.16 s (3H, CH₃), 2.20 s (3H, CH₃), 3.31 t (1H, C⁴H, *J* 6.5 Hz), 3.49 s (1H, C³H), 3.66 d (1H, SCH₂, ²*J* 15.8 Hz), 3.84 d (1H, SCH₂, ²*J* 15.8 Hz), 3.91–4.04 m (2H, OCH₂), 6.99–7.24 m (6H, H_{arom}), 7.28 d (1H, H_{arom}, *J* 7.9 Hz), 7.41 d (1H, H_{arom}, *J* 7.9 Hz), 7.50 br.s (1H, NH₂), 7.66 br.s (1H, NH₂), 8.66 br.s (1H, NHCO), 8.69 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 509.1 (100) [*M* + 1]⁺. Found, %: C 63.60; H 6.27; N 11.18. C₂₇H₃₂N₄O₄S. Calculated, %: C 63.76; H 6.34; N 11.02. *M* 508.646.

6-Allylsulfanyl-2-amino-4-*n*-hexyl-*N*³,*N*⁵-di-*o*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide (Vi). Yield 0.07g (27%), yellowish green powder, mp 147–149°C (EtOH). IR spectrum, *v*, cm⁻¹: 3225–3407 (NH, NH₂), 1669 (CONH), 1641 [δ(NH₂)]. ¹H NMR spectrum, *δ*, ppm: 0.86 t (3H, CH₃, *J* 6.6 Hz), 1.05–1.60 m (10H, 5CH₂), 2.15 s (3H, CH₃), 2.22 s (3H, CH₃), 3.26–3.55 m (3H, C³H, C⁴H and SCH₂), 3.75 d.d (1H, SCH₂, ²*J* 13.2, ³*J* 6.5 Hz), 4.88 d (1H, =CH₂, *J*_{cis} 9.5 Hz), 5.11 d (1H, =CH₂, *J*_{trans} 16.9 Hz), 5.74–5.90 m

(1H, CH=), 6.90–7.65 m (10H, 8H_{arom}, NH₂), 8.71 br.s (1H, NHCO), 8.98 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 519.3 (100) [*M* + 1]⁺. Found, %: C 69.52; H 7.25; N 10.71. C₃₀H₃₈N₄O₂S. Calculated, %: C 69.46; H 7.38; N 10.80. *M* 518.729.

2-Amino-6-benzylsulfanyl-4-*n*-hexyl-*N*³,*N*⁵-di-*o*-tolyl-3,4-dihydropyridine-3,5-dicarboxamide (Vj). Yield 0.16g (58%), yellowish green crystals, mp 173–175°C (EtOH). IR spectrum, *v*, cm⁻¹: 3198–3446 (NH, NH₂), 1672 (CONH), 1630 [δ(NH₂)]. ¹H NMR spectrum, *δ*, ppm: 0.86 t (3H, CH₃, *J* 6.8 Hz), 1.10–1.55 m (10H, 5CH₂), 2.11 s (6H, 2CH₃), 3.45 m (1H, C⁴H), 3.50 s (1H, C³H), 4.12 d (1H, SCH₂, ²*J* 13.2 Hz), 4.32 d (1H, SCH₂, ²*J* 13.2 Hz), 7.00 t (1H, H_{arom}, *J* 7.2 Hz), 7.02–7.38 m (11H, H_{arom}), 7.53 d (1H, H_{arom}, *J* 7.6 Hz), 7.67 br.s (2H, NH₂), 8.63 br.s (1H, NHCO), 8.94 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 569.2 (100) [*M* + 1]⁺. Found, %: C 71.64; H 7.13; N 9.68. C₃₄H₄₀N₄O₂S. Calculated, %: C 71.80; H 7.09; N 9.85. *M* 568.784.

2-Allylsulfanyl-6-amino-*N*³,*N*⁵-diphenyl-4-(1-phenylethyl)-3,4-dihydropyridine-3,5-dicarboxamide (Vk). Yield 0.10 g (39%), white powder, mp 215–217°C (EtOH). IR spectrum, *v*, cm⁻¹: 3169–3403 (NH, NH₂), 1670 (CONH), 1631 [δ(NH₂)]. ¹H NMR spectrum, *δ*, ppm: 1.27 d (3H, CH₃, *J* 6.8 Hz), 2.64–2.77 m (1H, CHMe), 3.38–3.44 m (1H, SCH₂), 3.50 d (1H, C⁴H), 3.57 s (1H, C³H), 3.71 d.d (1H, SCH₂, ²*J* 13.4, ³*J* 6.5 Hz), 4.86 d (1H, =CH₂, *J*_{cis} 9.9 Hz), 5.07 d (1H, =CH₂, *J*_{trans} 17.0 Hz), 5.72–5.86 m (1H, CH=), 6.95 t (1H, H_{arom}, *J* 7.2 Hz), 7.05 t (2H, H_{arom}, *J* 7.2 Hz), 7.09–7.74 m (14H, 12H_{arom}, NH₂), 8.48 br.s (1H, NHCO), 9.52 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 511.2 (100) [*M* + 1]⁺. Found, %: C 70.42; H 5.80; N 10.84. C₃₀H₃₀N₄O₂S. Calculated, %: C 70.56; H 5.92; N 10.97. *M* 510.664.

2-Amino-6-[2-(4-bromophenylamino)-2-oxoethylsulfanyl]-*N*³,*N*⁵-diphenyl-4-(1-phenylethyl)-3,4-dihydropyridine-3,5-dicarboxamide (VI). Yield 0.17 g (51%), yellowish green powder, mp 216–218°C (EtOH). IR spectrum, *v*, cm⁻¹: 3176–3447 (NH, NH₂), 1666 (CONH), 1633 [δ(NH₂)]. ¹H NMR spectrum, *δ*, ppm: 1.27 d (3H, CH₃, *J* 6.9 Hz), 2.73–2.81 m (1H, CHMe), 3.55–3.65 m (2H, C³H and C⁴H), 3.80 d (1H, SCH₂, ²*J* 15.0 Hz), 3.90 d (1H, SCH₂, ²*J* 15.0 Hz), 6.91–7.61 m (21H, 19H_{arom}, NH₂), 9.14 br.s (1H, NHCO), 9.50 br.s (1H, NHCO), 10.29 br.s (1H, NHCO). Mass spectrum, *m/z* (*I*_{rel}, %): 684.2 (100) [*M* + 2]⁺. Found, %: C 61.63; H 4.67; N 10.18.

$C_{35}H_{32}BrN_5O_3S$. Calculated, %: C 61.58; H 4.73; N 10.26. M 682.64.

2-Amino-4-methyl-6-[2-(4-methoxyphenylamino)-2-oxoethylsulfanyl]- N^3, N^5 -diphenyl-3,4-dihydropyridine-3,5-dicarboxamide (Vm). Yield 0.15 g (54%), yellowish green powder, mp 194–196°C (EtOH). IR spectrum, ν , cm^{-1} : 3198–3456 (NH, NH_2), 1668 (CONH), 1632 [$\delta(NH_2)$]. 1H NMR spectrum, δ , ppm: 1.03 d (3H, CH_3 , J 6.6 Hz), 3.43 s (1H, C^3H), 3.45–3.49 m (1H, C^4H), 3.71 s (3H, OCH_3), 3.77 d (1H, SCH_2 , 2J 14.6 Hz), 3.86 d (1H, SCH_2 , 2J 14.6 Hz), 6.84 d (2H, H_{arom} , J 8.7 Hz), 6.99 t (1H, H_{arom} , J 7.1 Hz), 7.04 t (1H, H_{arom} , J 7.1 Hz), 7.15–7.33 m (4H, H_{arom}), 7.47 d (2H, H_{arom} , J 8.7 Hz), 7.58 d (2H, H_{arom} , J 8.0 Hz), 7.65 d (2H, H_{arom} , J 8.4 Hz), 7.79 br.s (2H, NH_2), 9.45 br.s (1H, $NHCO$), 9.93 br.s (1H, $NHCO$), 10.06 br.s (1H, $NHCO$). Mass spectrum, m/z (I_{rel} , %): 544.2 (100) [$M + 1$] $^+$. Found, %: C 64.01; H 5.22; N 12.97. $C_{29}H_{29}N_5O_4S$. Calculated, %: C 64.07; H 5.38; N 12.88. M 543.65.

6-Allylsulfanyl-2-amino-4-methyl- N^3, N^5 -diphenyl-3,4-dihydropyridine-3,5-dicarboxamide (Vp). Yield 0.09 g (44%), yellowish green powder, mp 155–157°C (EtOH). IR spectrum, ν , cm^{-1} : 3202–3415 (NH, NH_2), 1672 (CONH), 1638 [$\delta(NH_2)$]. 1H NMR spectrum, δ , ppm: 1.02 d (3H, CH_3 , J 6.5 Hz), 3.25–3.34 m (2H, C^3H and C^4H), 3.52 d.d (1H, SCH_2 , 2J 13.0, 3J 7.7 Hz), 3.75 d.d (1H, SCH_2 , 2J 13.0, 3J 7.7 Hz), 4.96 d (1H, $=CH_2$, J_{cis} 9.8 Hz), 5.15 d (1H, $=CH_2$, J_{trans} 17.0 Hz), 5.82–6.02 m (1H, $CH=$), 6.99 t (1H, H_{arom} , J 7.0 Hz), 7.03 t (1H, H_{arom} , J 7.0 Hz), 7.26 t (2H, H_{arom} , J 7.7 Hz), 7.31 t (2H, H_{arom} , J 7.7 Hz), 7.40 br.s (1H, NH_2), 7.48 br.s (1H, NH_2), 7.52–7.68 m (4H, H_{arom}), 9.10 br.s (1H, $NHCO$), 9.83 br.s (1H, $NHCO$). Mass spectrum, m/z (I_{rel} , %): 421.2 (100) [$M + 1$] $^+$. Found, %: C 65.74; H 5.52; N 13.28. $C_{23}H_{24}N_4O_2S$. Calculated, %: C 65.69; H 5.75; N 13.32. M 420.537.

2-Amino-4-methyl-6- n -nonylsulfanyl- N^3, N^5 -diphenyl-3,4-dihydropyridine-3,5-dicarboxamide (Vo).

Yield 0.05 g (20%), yellowish green powder, mp 156–158°C (EtOH). IR spectrum, ν , cm^{-1} : 3199–3418 (NH, NH_2), 1664 (CONH), 1641 [$\delta(NH_2)$]. 1H NMR spectrum, δ , ppm: 0.85 d (3H, CH_3 , J 6.4 Hz), 1.03 t (3H, CH_3 , J 6.8 Hz), 1.15–1.71 m (14H, $7CH_2$), 2.71–2.84 m (2H, SCH_2), 3.00–3.15 m (2H, C^3H and C^4H), 6.90–7.11 m (2H, H_{arom}), 7.18–7.44 m (4H, H_{arom}), 7.48–7.69 m (4H, H_{arom}), 8.40 br.s (1H, NH_2), 9.32 br.s (1H, NH_2), 9.85 br.s (1H, $NHCO$), 10.02 br.s (1H, $NHCO$). Mass spectrum, m/z (I_{rel} , %): 507.4 (100) [$M + 1$] $^+$. Found, %: C 68.61; H 7.62; N 11.11. $C_{29}H_{38}N_4O_2S$. Calculated, %: C 68.74; H 7.56; N 11.06. M 506.70.

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