The Mannich reaction in the synthesis of N,S-containing heterocycles
12.* First example of aminomethylation involving 2-thioxonicotinamide derivative: synthesis of 3,5,7,11-tetraazatricyclo[7.3.1.$0^{2,7}$]tridec-2-ene-9-carboxamides

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Piperidinium 6-amino-5-cyano-3-*N*-(4-methylphenyl)carbamoyl-4-phenyl-1,4-dihydropyridine-2-thiolate upon the action of primary amines and excess formaldehyde undergoes aminomethylation to form 3,5,7,11-tetraazatricyclo[7.3.1.$0^{2,7}$]tridec-2-ene-9-carboxamides in 36—52% yields.

Key words: the Mannich reaction, pyridine-2-thiolates, aminomethylation, 3,5,7,11-tetraazatricyclo[7.3.1.$0^{2,7}$]tridec-2-enes.

2-Thioxo(mercapto)-3-cyanopyridines and related δ-thiolactams are of significant practical interest due to a synthetic potential and a wide range of biological activity of their derivatives.[1] They can behave as C-, N-, or S-nucleophiles toward electrophilic agents depending on both the nature of a substrate and the structure of an electrophile. In this connection, aminomethylation reaction frequently leading to unpredictable results is of special interest. Thus, 2-mercaptopyridines or their 2-thioxo tautomers give in the Mannich reaction 2-(dialkylaminomethylthio)pyridines,[2] *N*-(dialkylaminomethyl)pyridine-2(1*H*)-thiones,[3] pyrido[2,1-*b*][1,3,5]thiadiazines,[4] bis-(pyrido[2,1-*b*][1,3,5]thiadiazin-7-yl)methanes,[5] 6-thioxopyrido[1,2-*a*][1,3,5]triazines,[6] 3,7-diazabicyclo[3.3.1]-nonanes (DABCN, bispydines),[7] and tricyclic structures, *viz.*, 3,5,7,11-tetraazatricyclo[7.3.1.$0^{2,7}$]tridec-2-enes[8] (Scheme 1).

In the present work, we made an attempt to study an aminomethylation reaction of piperidinium 6-amino-5-cyano-3-*N*-(4-methylphenyl)carbamoyl-4-phenyl-1,4-dihydropyridine-2-thiolate (**1**). Generally, despite availability of 2-mercaptopyridine-3-carboxamides,[9—13] their properties are studied poorly. Some known examples[10,12,13] indicate that reactions of 2-mercapto(thioxo)pyridine-3-carboxamides can essentially differ from those for the much more in detail studied 3-cyano-substituted analogs.[1] Since thiolate **1** has at least six nucleophilic centers (C(3), C(5), NH, NH_2, CONHAr, S^-) which can undergo aminomethylation, its behavior under the Mannich reaction conditions is hardly predictable. The only close example found by us in the literature is a reaction involving 2-thioxonicotinamide with formaldehyde,[9] leading to a mixture of pyrido[3,2-*e*][1,3]thiazines (Scheme 2).

Thiolate **1** was synthesized by a multi-component condensation of benzaldehyde, malononitrile, 3-amino-*N*-(4-methylphenyl)-3-thioxopropanamide (**2**), and piperidine. We found that compound **1** upon treatment with an excess of 37% aqueous formaldehyde and primary amines in the absence of a catalyst undergo the aminomethylation reaction at the centers C(3), C(5), NH, and NH_2 to form the DABCN-like structures, *viz.*, 3,5,7,11-tetraazatricyclo-[7.3.1.$0^{2,7}$]tridec-2-ene-9-carboxamide derivatives **3a—c**, in 36—52% yields instead of the expected, by analogy with the literature data,[9] aminomethylation products at the sulfur atom and the C(O)NHAr fragments, *i.e.*, thiazines **4** (Scheme 3). It should be noted that such a reaction has not been described in the series of 2-thioxonicotinamide derivatives.

After filtration, the mother liquor did not yield additional amount of the product: the residue after evaporation of the solvent is a yellow resin of a complex composition presumably containing products of competitive aminomethylation involving piperidine. Similarly, treatment

* For Part 11, see V. V. Dotsenko, S. G. Krivokolysko, V. P. Litvinov, *Izv. Akad. Nauk, Ser. Khim.*, 2012, 129 [*Russ. Chem. Bull., Int. Ed.*, 2012, **61**, 131].
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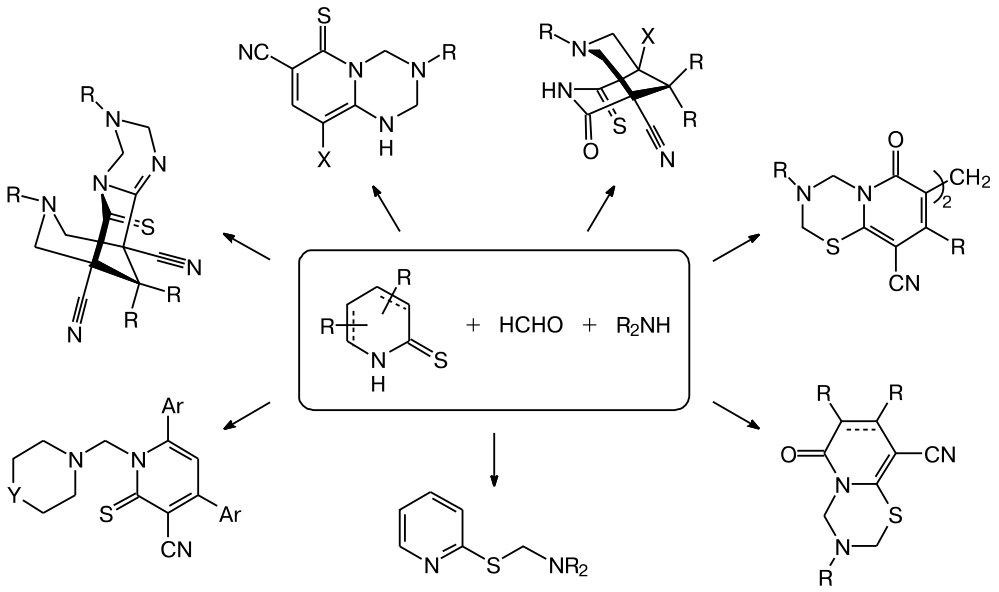
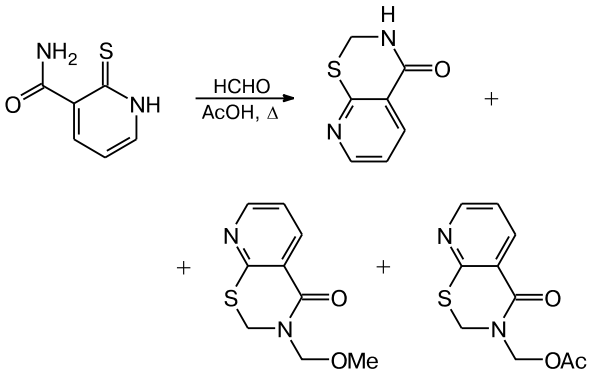
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 134—138, January, 2012.
1066-5285/12/6101-136

Scheme 1



X = CN, CO_2Alk; Y = O, CH_2; R = H, Alk, Ar

Scheme 2



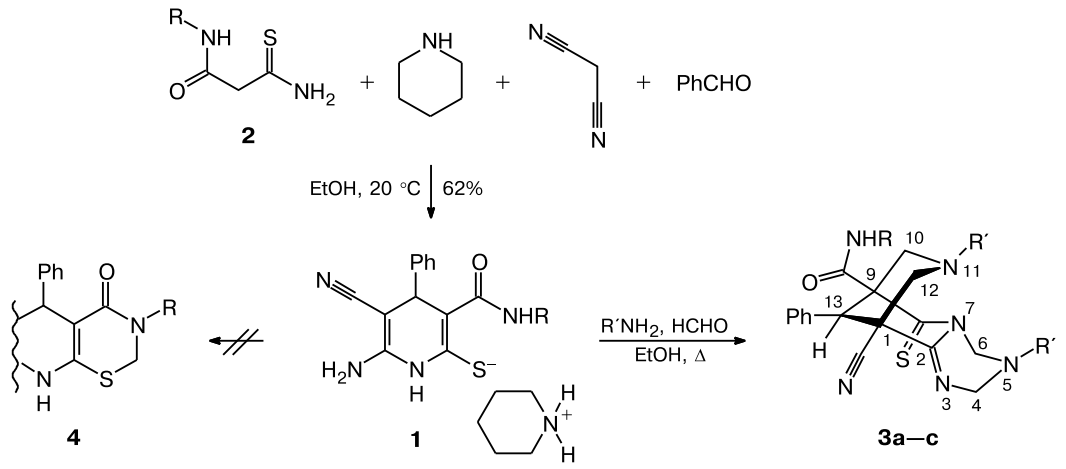
of thiolate **1** with formaldehyde in the absence of a primary amine in EtOH or AcOH leads to the resinification of the reaction mixture and formation of a complex mixture of products of unknown structure (TLC, LC/MS).

Compounds **3** are pale yellow finely crystalline powders, readily soluble in DMSO and DMF, moderately soluble in hot acetone, and insoluble in EtOH. The structure of compounds **3a—c** was confirmed by the spectral data. Thus, two pairs of doublets at δ 3.07—4.26 (^2J = = 10.30—11.75 Hz) corresponding to the methylene protons C(12)H_2 and C(10)H_2 are found in the ^{1}H NMR spectra. Two pairs of doublets with very pronounced "roof effect" (AB system) in the low field (δ 4.34—5.31, ^2J = 16.6—17.1 Hz; δ 5.23—5.99, ^2J = 12.5—13.7 Hz) should be attributed to the signals for the protons of the C(4)H_2 and C(6)H_2 groups; the signals for the C(13)H protons are found as a sharp singlet at δ 3.96—4.15. These data are in good agreement with the chemical shifts for the related DABCN-like structures.[8]

The structure of compound **3b** was confirmed by a combination of 2D NMR experiments with the ^{1}H—^{13}C HSQC and ^{1}H—^{13}C HMBC heteronuclear correlations (Fig. 1, 2). In the HMBC spectrum, the presence of the cross-peaks between the C=S group peak (δ 200.50) and the dd at δ 5.77 from the one hand and the doublet at δ 3.70 from the other hand enables an unambiguous assignment of the latter to the signals for the protons of the C(6)H_2 and C(10)H_2 groups, respectively. A HSQC method makes it possible to unambiguously assign the signals for the ^{13}C and ^{1}H nuclei of the C(4)H_2, C(12)H_2, and C(13)H fragments. The presence of correlations between the signal at δ 50.63 (C(13)) and the pair of dd C(10)H_2 and C(12)H_2, as well as between the singlet for the proton C(13)H (δ 3.97) and the peaks at δ 58.644 (C(12)), 62.887 (C(10)), 116.238 (C≡N), and 200.50 (C=S) in the ^{1}H—^{13}C HMBC spectrum excludes alternative interpretations and confirms the 3,5,7,11-tetraazatricyclo[7.3.1.0^{2,7}]tridec-2-ene structure suggested for compound **3b**.

The IR spectra of compounds **3a—c** do not contain absorption bands of the conjugated cyano groups at ν = 2200±30 cm^{-1}, exhibiting weak absorption bands at ν = 2250 cm^{-1} instead, which correspond to the stretching vibrations of the unconjugated C≡N group. Absorption bands in the region ν = 3425—3430 cm^{-1} and strong bands at ν = 1645—1650 and 1675—1690 cm^{-1} should be attri-

Scheme 3



R = 4-MeC_6H_4 (**1**–**3**)
3: R′ = Ph (**a**), 4-MeC_6H_4 (**b**), CH_2Ph (**c**)

buted to the stretching vibrations of the NHR, C=N, and C=O groups, respectively.

In conclusion, piperidinium 6-amino-5-cyano-3-*N*-(4-methylphenyl)carbamoyl-4-phenyl-1,4-dihydropyridine-2-thiolate under the Mannich reaction conditions undergo aminomethylation at C(3), C(5), NH, and NH_2 to form the earlier unknown compounds, 3,5,7,11-tetraazatricyclo[7.3.1.$0^{2,7}$]tridec-2-ene-9-carboxamide derivatives, promising polydentate ligands and new objects for bioscreening. Contrary to our expectations, no products of aminomethylation at the sulfur atom and C(O)NHAr were found. The new reaction is characterized by preparative simplicity, gives acceptable yields of the target products, and can serve as a convenient protocol for the preparation of combinatorial libraries.

It should be noted that the 3-carbonitrile analogs of compound **1** behave similarly under conditions of aminomethylation reaction. It can be suggested that formation of 3,5,7,11-tetraazatricyclo[7.3.1.$0^{2,7}$]tridec-2-enes upon treatment of 3,5-disubstituted 6-amino-1,4-dihydropyridine-2-thiolates with the primary amine—HCHO system is of fairly general character, with the amino group at

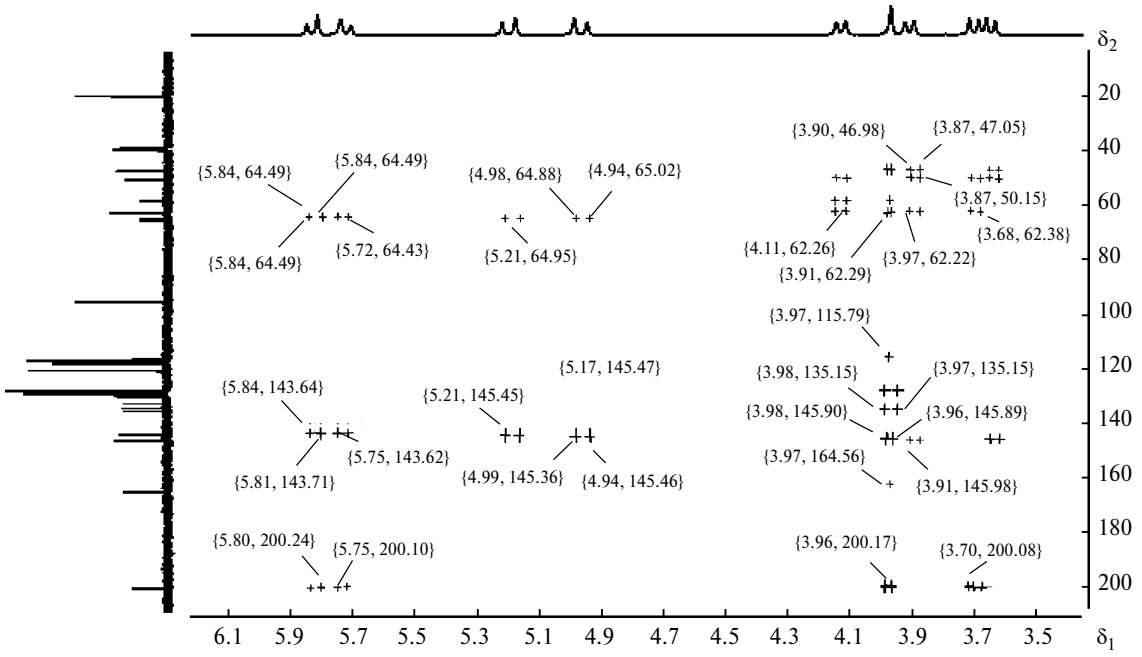


Fig. 1. The fragment of the HMBC spectrum of compound **3b**.

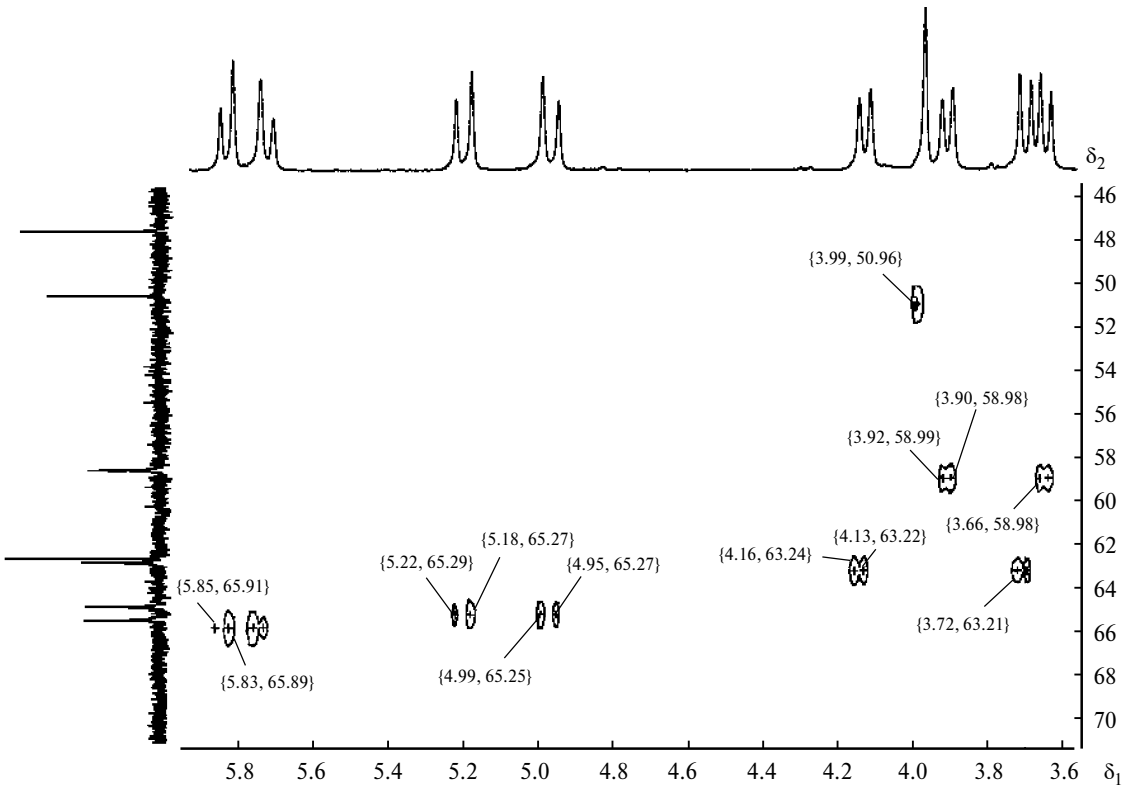


Fig. 2. The fragment of the HSQC spectrum of compound **3b**.

position 6 of dihydropyridine substrate playing a key role in the formation of a tricyclic system.

Experimental

^{1}H NMR spectra were recorded on a Bruker DRX-500 (500.13 MHz), Me_4Si internal standard. Heteronuclear ^{1}H—^{13}C HSQC and HMBC correlation experiments were performed on a Bruker Avance II 400 spectrometer (400.13 (^{1}H) and 100.62 MHz (^{13}C)) in CCl_4—DMSO-d_6, Me_4Si internal standard. IR spectra were recorded on an IKS-29 spectrophotometer in Nujol. Elemental analysis was performed on a Perkin—Elmer C,H,N-Analyzer apparatus. Purity of individual compounds was monitored by TLC on Silufol UV-254 plates, using the acetone—hexane (1 : 1) system as an eluent and visualization in iodine vapors or under UV light. Melting points were measured on a Kofler heating stage and were not corrected. 3-Amino-*N*-(4-methylphenyl)-3-thioxopropanamide (**2**) was obtained by the reaction of *N*-(4-methylphenyl)cyanoacetamide with H_2S in the pyridine—Et_3N mixture according to the known procedure.[10,12]

Piperidinium 6-aminol-5-cyano-3-*N*-(4-methylphenyl)carbamoyl-4-pheny-1,4-dihydropyridine-2-thiolate (1) was synthesized similarly to the known procedures[11b,11d,13b] as follows: a mixture of freshly distilled benzaldehyde (0.5 mL, 4.8 mmol), malononitrile (0.32 g, 4.8 mmol), and piperidine (1 drop) in EtOH (3 mL) was stirred for 0.5 h, followed by addition of 3-amino-*N*-(4-methylphenyl)-3-thioxopropanamide (**2**) (1.0 g, 4.8 mmol) and piperidine (0.8 mL, 8.1 mmol). The reaction mixture was stirred for 3 h at ~20 °C and kept for 24 h in refrigerator at 0...—4 °C. A precipitate that formed was filtered off and washed several times with acetone. The yield was 1.33 g (62%), yellow finely crystalline powder, m.p. 175—180 °C (decomp.). Found (%): C, 67.16; H, 6.56; N, 15.63. $C_{25}H_{29}N_5OS$ (M = 447.61). Calculated (%): C, 67.09; H, 6.53; N, 15.65. ^{1}H NMR (DMSO-d_6), δ: 1.54—1.62 (m, 6 H, $(CH_2)_3$); 2.21 (s, 3 H, $ArC\underline{H}_3$); 2.98 (m, 4 H, $^+NH_2(C\underline{H}_2)_2$); 4.66 (s, 1 H, C(4)H); 5.53 (br.s, 2 H, $C(6)NH_2$); 6.99, 7.43 (both d, 2 H each, $H_3CC_6\underline{H}_4$, ^3J = 8.0 Hz); 7.04—7.20 (m, 5 H, Ph); 7.72 (s, 1 H, C(O)NH); 13.42 (s, 1 H, NH_{Py}). No signal for the $^+NH_2$ protons was found because deuterium exchange with DMSO-d_6.

Synthesis of 3,5,7,11-tetraazatricyclo[7.3.1.0^{2,7}]tridec-2-ene-9-carboxamides 3a—c (general procedure). Thiolate **1** (0.3 g, 0.67 mmol) was suspended in EtOH (7—8 mL), followed by addition of excess of 37% aqueous formaldehyde (1.0 mL, 13.3 mmol, free of paraformaldehyde impurities), and the corresponding primary amine (2.5 equiv., 1.7 mmol). The mixture was refluxed for 2—3 min with vigorous stirring and then stirred for 3—4 h at ~20 °C. After 48 h, a precipitate that formed was filtered off and washed with EtOH. For purification, compounds **3** were suspended in the EtOH—acetone (1 : 2) mixtures, refluxed for 5 min and cooled. A pale yellow precipitate was filtered off, washed with EtOH—acetone and dried at 60 °C to obtain analytically pure samples of compounds **3a—c**.

1-Cyano-*N*-(4-methylphenyl)-5,11,13-triphenyl-8-thioxo-3,5,7,11-tetraazatricyclo[7.3.1.0^{2,7}]tridec-2-ene-9-carboxamide (3a). The yield was 38%, m.p. 238—240 °C (EtOH—acetone), R_f = 0.80 (acetone—hexane (1 : 1)). Found (%): C, 72.20; H, 5.43; N, 14.04. $C_{36}H_{32}N_6OS$ (M = 596.76). Calculated (%): C, 72.46; H, 5.41; N, 14.08. IR, ν/cm^{-1}: 3430 (NH), 2250 (C≡N),

1675 (C=O), 1650 (C=N). ^{1}H NMR (DMSO-d_6), δ: 2.21 (s, 3 H, ArC$\underline{H}_3$); 3.79 (m, 2 H, C(10)H and C(12)H, the overlap of two d); 3.99 (d, 1 H, C(12)H, ^2J = 11.25 Hz, a part of the AB system); 4.15 (s, 1 H, C(13)H); 4.26 (d, 1 H, C(10)H, ^2J = 11.75 Hz, a part of the AB system); 5.05, 5.31 (both d, 1 H each, C(4)H_2, ^2J = 17.1 Hz, AB system); 5.63, 5.99 (both d, 1 H each, C(6)H_2, ^2J = 13.7 Hz, AB system); 6.86—7.29 (m, 19 H, 4 Ar); 8.11 (s, 1 H, NH).

1-Cyano-*N*,5,11-tri(4-methylphenyl)-13-phenyl-8-thioxo-3,5,7,11-tetraazatricyclo[7.3.1.0^{2,7}]tridec-2-ene-9-carboxamide (3b). The yield was 52%, m.p. 208—210 °C (EtOH—acetone), R_f = 0.81 (acetone—hexane (1 : 1)). Found (%): C, 72.86; H, 5.83; N, 13.39. $C_{38}H_{36}N_6OS$ (M = 624.81). Calculated (%): C, 73.05; H, 5.81; N, 13.45. IR, ν/cm^{-1}: 3425 (NH), 2250 (C≡N), 1685 (C=O), 1650 (C=N). ^{1}H NMR (CCl_4—DMSO-d_6, 400 MHz), δ: 2.21, 2.24, 2.28 (three s, 3 H each, 3 ArC$\underline{H}_3$); 3.64, 3.91 (both d, 1 H each, C(12)H_2), ^2J = 11.2 Hz, AB system); 3.70, 4.13 (both d, 1 H each, C(10)H_2, ^2J = 11.8 Hz, AB system); 3.98 (s, 1 H, C(13)H); 4.97, 5.20 (both d, 1 H each, C(4)H_2, ^2J = 16.9 Hz, AB system); 5.77 (dd, 2 H, C(6)H_2, ^2J = 13.6 Hz, AB system); 6.69—7.01 (m, the overlap of six d, 12 H, 3 $C_6\underline{H}_4CH_3$); 7.09—7.16 (m, 4 H, Ph); 7.26 (m, 1 H, Ph); 7.75 (br.s, 1 H, NH). ^{13}C NMR (CCl_4—DMSO-d_6, 100 MHz), δ: 20.083 (2 Ar$\underline{C}H_3$); 20.389 (C(O)NH$C_6H_4\underline{C}H_3$); 47.628 (C(1)); 50.631 (C(13)); 58.644 (C(12)); 62.705 (C(9)); 62.887 (C(10)); 64.921 (C(4)); 65.548 (C(6)); 116.238 (C≡N); 117.247 (C_{Ar}); 118.180 (C_{Ar}); 120.696 (C_{Ar}); 127.928 (C_{Ar}); 128.256 (C_{Ar}); 128.664 (C_{Ar}); 128.781 (C_{Ar}); 129.153 (C_{Ar}); 129.401 (C_{Ar}); 129.612 (C_{Ar}); 130.341 (C_{Ar});132.798 (C_{Ar}); 134.446 (C(2)); 135.569 (C_{Ar}); 165.155 (C(O)NH); 200.500 (C=S).

5,11-Dibenzyl-1-cyano-*N*-(4-methylphenyl)-13-phenyl-8-thioxo-3,5,7,11-tetraazatricyclo[7.3.1.0^{2,7}]tridec-2-ene-9-carboxamide (3c). The yield was 36%, m.p. 197—199 °C (EtOH—acetone), R_f = 0.80 (acetone—hexane (1 : 1)). Found (%): C, 73.29; H, 5.80; N, 13.55. $C_{38}H_{36}N_6OS$ (M = 624.81). Calculated (%): C, 73.05; H, 5.81; N, 13.45. IR, ν/cm^{-1}: 3430 (NH), 2250 (C≡N), 1690 (C=O), 1645 (C=N). ^{1}H NMR (DMSO-d_6), δ: 2.18 (s, 3 H, ArC$\underline{H}_3$); 3.07, 3.38 (both d, 1 H each, C(12)H_2, ^2J = 11.0 Hz, AX system); 3.12, 3.49 (both d, 1 H each, C(10)H_2, ^2J = 10.3 Hz, AX system); 3.69, 3.82 (both d, 1 H each, NC$\underline{H}_2$Ph, ^2J = 13.70 Hz, AB system); 3.94 (m, 2 H, NC$\underline{H}_2$Ph); 3.96 (s, 1 H, C(13)H); 4.39, 4.57 (both d, 1 H each, C(4)H_2, ^2J = 16.6 Hz, AB system); 5.23, 5.56 (both d, 1 H each, C(6)H_2, ^2J = 12.5 Hz, AX system); 6.89 (dd, 4 H, $C_6\underline{H}_4CH_3$, ^3J = 8.05 Hz); 7.27—7.42 (m, 15 H, 3 Ph); 7.98 (s, 1 H, NH).

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Received November 12, 2010;
in revised form October 5, 2011