Synthesis of 2,2′-(1,4-Phenylene)bis-3,4-dihydro-2H-1,3-thiazin-4-ones and their Facile Recyclization to 2,2′-(1,4-Phenylene)bis(pyrimidin-4-one) and/or 2,2′-(1,4-Phenylene)-bis-(thieno[2,3-d]pyrimidin-4(1H)-one) Derivatives

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An efficient and direct procedure for the synthesis of 2,2′-(1,4-phenylene)bis-3,4-dihydro-2H-1,3-thiazin-4-one derivatives is described. Oxidation of the latter and their base-catalyzed recyclization has been studied. The products were characterized by elemental analyses, and IR, 1H NMR, and 13C NMR spectra.

Key words: Terephthalaldehyde, Cyanoacetamide, Phenyl (Phenethyl) Isothiocyanate, Bis-1,3-thiazin-4-one, Bis-pyrimidin-4-one, Bis-thieno[2,3-d]pyrimidin-4-one

Introduction

1,3-Thiazines are an important type of heterocycles showing a wide variety of pharmacological properties. Thus, 1,3-thiazine derivatives have recently been reported as cholecystokinin antagonists [1], antmycobacterial agents [2], cannabinoid receptor agonists [3], and inhibitors of NO synthase (NOS) [4], as antibacterial [5], antipyretic [6], anti-inflammatory [6, 7], analgesic [7], antitumor [8], and antioxidant [9] agents, and as calcium channel modulators [10]. Furthermore, the antibiotic activity of cephalosporin is due to the presence of the 1,3-thiazine moiety [11]. A few methods have been reported in the literature for the preparation of 1,3-thiazines [12 – 21], but to the best of our knowledge, there are no reports in the literature for the formation of 2,2′-(1,4-phenylene)bis(3,4-dihydro-2H-1,3-thiazin-4-one). Considering the above reports in conjunction with our recent work on the synthesis of bis- [22 – 26] and polyheterocyclic systems [27 – 35], we wish to describe herein an efficient and direct procedure for the synthesis of 2,2′-(1,4-phenylene)bis(3,4-dihydro-2H-1,3-thiazin-4-one) derivatives and their base-catalyzed recyclization to bis-pyrimidin-4-one and bis-thieno[2,3-d]pyrimidin-4-one derivatives.

Results and Discussion

The bis-1,3-thiazines 3a, b have been synthesized by the cyclocondensation of terephthalaldehyde (1) with 2 equivalents of 2a, b in the presence of catalytic amounts of p-toluenesulfonic acid (p-TSA) in boiling ethanol. High yields of the products 3 also resulted when the reaction was performed in boiling glacial acetic acid (Scheme 1). Compound 2a was readily prepared by treatment of cyanoacetamide with phenyl isothiocyanate according to a literature procedure [36].

Scheme 1. Synthesis of bis-1,3-thiazines 3.

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The proposed molecular structures of the bis-1,3-thiazines 3a, b are supported by elemental and spectral analyses. For example, compound 3a exhibits an IR spectrum with strong absorption bands at 3181 (NH), 2206 (CN), and 1645 cm⁻¹ (CO). Its 1H NMR spectrum shows a characteristic singlet at δ = 10.18 ppm for the two exocyclic NH protons, a doublet at 8.52 ppm for the two endocyclic NH protons (J = 3 Hz), and a multiplet at 7.22 – 7.48 ppm due to the phenyl protons and a multiplet at 6.13 ppm for the two thiazine protons (2H, J = 3 Hz). Moreover, the 13C NMR spectrum of 3a shows signals at δ = 57 (2 × C-2),
Considering the facile oxidation in the presence of nitrobenzene [37], 3a was converted into 4 in good yield (Scheme 2). The structure 4 was confirmed by elemental analysis and spectral data. The disappearance of 2-H and 3-NH in the 1H NMR spectrum indicated that only these protons were removed from 3a.

We also studied the alkylation of 3a, b with dimethyl sulfate and/or ethyl iodide under basic conditions. Unexpectedly, the reactions proved to involve the sulfur atom thus affording the S-alkylated-bis(pyrimidin-4-one) derivatives 5a, b and/or 6a, b, respectively, in high yields (Scheme 3). The structural assignments of compounds 5 and 6 were confirmed by their spectroscopic data. A distinction between the thiazine and pyrimidine structural types is clearly manifested in the 1H and 13C NMR spectra. For example, the 1H NMR spectrum of 77.51 (2 × C-5), 116.18 (CN), 162.07 (2 × C=O), and 164.93 (2 × C-6), in addition to those of the phenyl carbons at δ = 125.48 – 137.79.

Scheme 2. Oxidation of 3a.

Scheme 3. Alkylation of 3.

Scheme 4.

Scheme 5. Synthesis of bis-pyrimidines 5a and 6a.

5a showed the absence of exocyclic NH protons, and in its 13C NMR spectrum the resonances of the aminal carbon atoms in compounds 5a (δ = 73.71) are shifted downfield from those of the thioaminal carbon atoms in compound 3a.

The transformations shown in Scheme 3 can be accounted for by the following mechanism: A base causes proton abstraction from the nitrogen atom in position 3 and the thiazine ring opening [17]. Then the
resulting intermediate A cyclizes to the stable thiolate B, and alkylation of the latter in situ yields products 5 and 6, respectively (Scheme 4).

Compounds 5 and 6 were prepared independently from 2-cyano-3-(alkylthio)-3-(phenylamino)acrylamide 7a, b obtained from the reaction of cyanoacetamide with phenyl isothiocyanate in DMF and in the presence of potassium hydroxide, followed by treatment with dimethyl sulfate and/or ethyl iodide. Subsequent reaction of 7a, b with terephthalaldehyde (1) in boiling ethanol and in the presence of catalytic amounts of p-toluenesulfonic acid (p-TSA) afforded 5a and/or 6a in excellent yields (Scheme 5). The identity of the products prepared in Scheme 5 with those obtained previously in Scheme 3 was confirmed by comparison of their IR and 1H NMR spectra.

Next, we moved on to develop a facile and convenient route to polyfunctionally substituted thienopyrimidine derivatives using the 1,3-thiazines 3a, b as starting materials. Thus, benzyl chloride, ethyl bromoacetate and bromoacetonitrile were used as alkylating agents for further heterocyclization (Schemes 6–8). Benzylation of compounds 3a, b with benzyl chloride in ethanol in the presence of potassium hydroxide gave the S-benzylated bis-pyrimidines 8a, b in high yields (Scheme 6). Upon treatment of compound 8a with sodium ethoxide in ethanol, it underwent intramolecular Thorpe-Ziegler cyclization [38] and partial oxidation to furnish the thienopyrimidine 9 (Scheme 6). Compounds 8a, b and 9 gave satisfactory analytical and spectroscopic data. The IR and 1H NMR spectra of 9 revealed the absence of bands of CN and NH groups and signals attributable to the methylene, methene and NH protons of 8a, respectively.

Treatment of 3a with ethyl bromoacetate, in ethanol in the presence of potassium hydroxide, furnished the bis-{thieno[2,3-d]pyrimidin-4(1H)-one} 10 (Scheme 7).
The elemental analysis and the spectral data are in good agreement with the proposed structures. The IR and \(^1\)H NMR spectra of 10 revealed the absence of a band of a CN group and of signals attributable to the two exocyclic NH protons of 3a, respectively.

On the other hand, the condensation of 3b with ethyl bromoacetate under the previous conditions gave the bis S-substituted thiopyrimidine 11. The cyclization and partial oxidation of 11 to the bis-thienopyrimidine 12 proceeds upon treatment with sodium ethoxide in ethanol (Scheme 7). The structures of 11 and 12 were established on the basis of their correct elemental analyses as well as compatible spectral data. The IR and \(^1\)H NMR spectra of 12 revealed the absence of a CN and NH groups and of signals attributable to the SCH\(_2\), CH and NH protons of 11, respectively.

Finally, as described in Scheme 8, the thienopyrimidine derivatives 13a and 13b were prepared in aq. KOH by cycloalkylation of 3a, b with bromoacetoni- trile. Based on the spectroscopic data, the structure of compound 13 is undoubtedly confirmed.

Experimental Section

General procedures

Melting points were measured with a Gallenkamp apparatus and are uncorrected. The reactions and purity were monitored by thin layer chromatography (TLC) on aluminum plates coated with silica gel with fluorescence indicator (Merck, 60 F\(_{254}\)) using CHCl\(_3\)/CH\(_3\)OH (10:1) as eluent. The infrared spectra were recorded on a Jasco FT/IR-450 Plus infrared spectrophotometer. The NMR spectra were obtained on a JHA-LAA 400 WB-FT spectrometer (300 MHz for \(^1\)H NMR, 75 MHz for \(^13\)C NMR) with deuterated chloroform (CDCl\(_3\)) or dimethylsulfoxide ([D\(_6\)]DMSO) as solvent. Chemical shifts are quoted in \(\delta\) and are referenced to the solvent signal. Elemental analyses were measured with a Vario EL III CHNOS Elemental Analyzer, Germany, in the Microanalytical Center of Cairo University.

Compounds 2a [36] and 7a [39] were synthesized using the published procedures.

2-Cyano-3-mercapto-3-phenethylamino-acrylamide (2b)

This compound was prepared in 88% isolated yield by treatment of cyanoacetamide with phenyl isothiocyanate using the procedure described for the synthesis of 2a [36]: pale-yellow crystals, m. p. 148–150°C. – IR (film): \(\nu = 3423, 3340, 1653, 1527\) cm\(^{-1}\). – \(^1\)H NMR (300 MHz, [D\(_6\)]DMSO): \(\delta = 2.85\) (t, 2H, CH\(_2\), \(J = 7.5\) Hz), 3.72 (t, 2H, CH\(_2\), \(J = 7.5\) Hz), 6.97 (s, 2H, NH\(_2\)), 7.21 – 7.36 (m, 5H, ArH), 8.78 (s, 1H, SH), 10.45 (brs, 1H, NH).

2,2′-(1,4-Phenylen)-bis(5-cyano-6-arylamino-3,4-dihydro-2H-1,3-thiazin-4-ones) 3a, b

Method A: A mixture of terephthalaldehyde (1) (1.34 g, 0.01 mol), 2a, b (0.02 mol), and p-toluenesulfonic acid (0.076 g, 0.01 mol) in ethanol (20 mL) was refluxed, a pale-yellow precipitate was formed after 30 min, and stirring was continued for 2 h. The precipitate was filtered off, washed with ethanol, dried, and recrystallized from DMF/EtOH.

Method B: A mixture of terephthalaldehyde (1) (1.34 g, 0.01 mol) and 2a, b (0.02 mol), in glacial acetic acid (20 mL) was boiled, and a pale-yellow precipitate was formed after 30 min. Stirring was continued for 2 h, the precipitate was filtered off, washed with ethanol, dried, and recrystallized from DMF/EtOH.

2,2′-(1,4-Phenylen)-bis(5-cyano-6-phenylamino-3,4-dihydro-2H-1,3-thiazin-4-one) 3a [36]

Yellow powder, yield: method A: 84%; method B: 81%. m. p. 286 – 288°C. – IR (film): \(\nu = 3181, 3064, 1645, 1548\) cm\(^{-1}\). – \(^1\)H NMR (300 MHz, [D\(_6\)]DMSO): \(\delta = 6.13\) (d, 2H, 2CH, \(J = 3\) Hz), 7.22 – 7.48 (m, 14H, ArH), 8.52 (d, 2H, 2NH, \(J = 3\) Hz), 10.18 (s, 2H, 2NH). \(\delta = 13\)C NMR (75 MHz, [D\(_6\)]DMSO): \(\delta = 57.49\) (C-2, C-2′), 77.51 (C-5, C-5′), 116.18 (2CN), 125.48, 126.82, 127.46, 127.71, 128.91, 129.63, 137.49, 137.51, 137.79 (C-Ar), 162.07 (C-6, C-6′). – Anal. for C\(_{28}\)H\(_{20}\)N\(_6\)O\(_2\)S\(_2\): calcd. C 62.67, H 3.76, N 15.66, S 11.95; found C 62.59, H 3.87, N 15.76, S 11.84.

2,2′-(1,4-Phenylen)-bis(5-cyano-6-phenylamino-3,4-dihydro-2H-1,3-thiazin-4-one) 3b [39]

Pale-yellow powder, yield: method A: 82%; method B: 79%. m. p. 224 – 244°C. – IR (film): \(\nu = 3227, 3150, 3020, 2203, 1638, 1565\) cm\(^{-1}\). – \(^1\)H NMR (300 MHz, [D\(_6\)]DMSO): \(\delta = 2.78 – 2.87\) (t, 4H, 2CH\(_2\)N, \(J = 6\) Hz), 3.41 – 3.51 (t, 4H, 2CH\(_2\)Ph, \(J = 6\) Hz), 6.07 (d, 2H, 2CH, \(J = 2.4\) Hz), 7.14 – 7.30 (m, 14H, ArH), 7.49 (d, 2H, 2NH, \(J = 2.4\) Hz), 8.33 (t, 2H, 2 NH, \(J = 6\) Hz). – \(\delta = 13\)C NMR (75 MHz, [D\(_6\)]DMSO): 35.59 (2CH\(_2\)Ph), 46.59 (2CH\(_2\)N), 57.38 (C-2, C-2′), 73.72 (C-5, C-5′), 116.94 (CN), 126.37, 127.37, 127.68, 128.21, 128.36, 128.56, 128.70, 129.56, 136.27, 137.71, 137.80, 137.91.
A solution of compound 3a (2 mmol) was refluxed in DMF/PhNO₂ (1:5) for 2 h, and the solvent was evaporated under vacuum. The product 4 was crystallized by using chloroform/petroleum ether. Pale-grey powder, yield: 73%, m.p. 210 – 212 °C. – IR (film): ν = 3175, 3070, 2202, 1650 cm⁻¹. – 1H NMR (300 MHz, D₆DMSO): δ = 7.27 – 7.69 (m, 14H, ArH), 8.94 (s, 2H, ArH), 8.64 (d, 2H, 2NH), 7.23 – 7.35 (m, 14H, ArH), 8.60 (d, 2H, 2NH), 115.72 (2CN), 125.40, 125.44, 126.41, 126.69, 126.84, 127.46, 127.59, 129.70, 129.81, 139.33, 142.93 (C-5′, Ar), 160.40 (2CO), 165.02 (C-6′, C-6′). – Anal. for C₂₉H₂₆N₆O₂S₂: calcd. C 63.14, H 3.03, N 15.78, S 12.04; found C 63.04, H 3.16, N 15.69, S 11.96.

Synthesis of 5a, b

To a stirred 0.75 N aqueous KOH solution (20 mL), compound 3a b (10 mmol) and dimethyl sulfate (40 mmol) were added successively. The resulting precipitate was filtered off, washed with water, dried and recrystallized from DMF/EtOH.

2,2′-(1,4-Phenylene)bis(5-cyano-6-phenylamino-4H-1,3-thiazin-4-one) (4a)

Yellow crystals, yield: 80%, m.p. 296 – 298 °C. – IR (film): ν = 3175, 3060, 2206, 1650, 1545 cm⁻¹. – 1H NMR (300 MHz, D₆DMSO): δ = 2.12 (s, 6H 2CH₃), 6.14 (d, 2H, 2CH, J = 2.4 Hz), 7.39 – 7.60 (m, 14H, ArH), 8.94 (d, 2H, 2NH, D₂O-exchangeable, J = 2.4 Hz). – 13CN M R (75MHz, D₆DMSO): δ = 15.29 (2SCH₂), 73.71 (C-2, C-2′), 90.0 (C-5, C-5′), 115.72 (2CN), 125.40, 125.44, 126.41, 126.69, 126.84, 127.46, 127.59, 129.70, 129.81, 139.33, 142.93 (C-5′, Ar), 160.40 (2CO), 165.02 (C-6′, C-6′). – Anal. for C₃₀H₂₈N₂O₂S₂: calcd. C 63.81, H 4.28, N 14.88, S 11.36; found C 63.72, H 4.37, N 14.75, S 11.24.

2,2′-(1,4-Phenylene)bis(5-cyano-6-methylthio-4H-1,3-thiazin-4-one) (5a)

Pale-yellow crystals, yield: 67%, m.p. 278 – 279 °C. – IR (film): ν = 3163, 3045, 2203, 1665, 1515 cm⁻¹. – 1H NMR (300 MHz, D₆DMSO): δ = 1.01 (t, 6H, 2CH₃, J = 7.2 Hz), 2.80 (t, 4H, 2CH₂N, J = 7.2 Hz), 2.93 (t, 4H, 2CH₂Ph, J = 7.2 Hz), 4.41 (q, 4H, 2CH₂J, J = 7.2 Hz), 6.13 (d, 2H, 2CH, J = 1.5 Hz), 7.38 – 7.35 (m, 14H, ArH), 8.60 (d, 2H, 2NH, J = 1.5 Hz). – 13CN M R (75 MHz, D₆DMSO): δ = 14.55 (2SCH₂), 28.47 (2CH₂), 35.44 (2CH₂Ph), 53.79 (2CH₂N), 68.30 (C-2, C-2′), 86.31 (C-5, C-5′), 120.60 (CN), 125.69, 126.51, 128.31, 128.93, 137.57, 139.43 (C-5′, Ar), 161.60 (2CO), 162.89 (C-6′, C-6′). – Anal. for C₂₉H₂₆N₂O₂S₂: calcd. C 66.64, H 5.59, N 12.95, S 9.88; found C 66.52, H 5.48, N 12.86, S 9.77.

2-Cyano-3-ethylthio-3-phenylamino-acrylamide (7b)

This compound was prepared in 90% isolated yield by treatment of cyanoacetamide with phenyl isothiocyanate and ethyl iodide using the procedure described for the synthesis of 7a [39]; pale-yellow crystals, m.p. 128 – 130 °C. – IR (film): ν = 3383, 3201, 2195, 1652, 1555 cm⁻¹. – 1H NMR (300 MHz, D₆DMSO): δ = 1.20 (t, 3H, CH₃, J = 7.5 Hz), 2.63 (q, 2H, CH₂, J = 7.5 Hz), 7.25 – 7.42 (m, 7H, ArH + NH₂), 12.44 (s, 1H, NH).

Alternative synthesis of 5a and 6a

A mixture of terephthalaldehyde (I) (1.34 g, 0.01 mol), 7a b (0.02 mol), and p-toluenesulfonic acid (0.076 g, 0.01 mol) in ethanol (20 mL) was refluxed. A yellow precipitate was formed after 30 min, and stirring was continued for 2 h. The precipitate was filtered off, washed with ethanol, dried, and recrystallized from the appropriate solvents.
2H, 2NH, \( \nu = 3284, 2979, 2210, 1671, 1535 \text{ cm}^{-1} \). - 1H NMR (300 MHz, [D₆]DMSO): \( \delta = 3.91 \) (d, 2H, CH₂H, \( J = 13 \text{ Hz} \)), 6.09 (d, 2H, CH₂, \( J = 6.6 \text{ Hz} \)). - Anal. for C₄₂H₃₂N₆O₂S₂: calcd. C 70.37, H 4.50, N 11.72, S 8.95; found C 70.24, H 4.41, N 11.65, S 8.88.

2H, 2NH, \( \nu = 3745, 3352, 3028, 2921, 1637, 1591 \text{ cm}^{-1} \). - 1H NMR (300 MHz, [D₆]DMSO): \( \delta = 1.23 \) (t, 6H, 2CH₃), \( J = 6.3 \text{ Hz} \), 6.15 (d, 2H, 2CH₂, \( J = 6 \text{ Hz} \)). - Anal. for C₄₀H₄₀N₆O₆S₂: calcd. H 5.27, N 10.99, S 8.38; found C 62.70, H 5.35, N 10.91, S 8.29.

2H, 2NH, \( \nu = 3426, 3325, 3200, 2921, 1637, 1591 \text{ cm}^{-1} \). - 1H NMR (300 MHz, [D₆]DMSO): \( \delta = 1.23 \) (t, 6H, 2CH₃), \( J = 6.3 \text{ Hz} \), 6.15 (d, 2H, 2CH₂, \( J = 6 \text{ Hz} \)). - Anal. for C₄₀H₄₀N₆O₆S₂: calcd. H 5.27, N 10.99, S 8.38; found C 62.70, H 5.35, N 10.91, S 8.29.

Synthesis of 8a, b

To a stirred 75 N aqueous KOH solution (20 mL), 3a, b (10 mmol) and benzyl chloride (40 mmol) were added successively. The resulting precipitate was filtered off, washed with water, dried, and recrystallized from ethanol.

2H, 2NH, \( \nu = 3284, 2979, 2210, 1671, 1535 \text{ cm}^{-1} \). - 1H NMR (300 MHz, [D₆]DMSO): \( \delta = 2.87 \) (t, 4H, 2CH₂, \( J = 6 \text{ Hz} \)), 6.35 (t, 4H, 2CH₂, \( J = 6 \text{ Hz} \)). - Anal. for C₄₀H₄₀N₆O₆S₂: calcd. C 62.81, H 5.27, N 10.99, S 8.38; found C 62.70, H 5.35, N 10.91, S 8.29.

 synthesis of compound 11 (0.764 g, 1 mmol) with sodium ethoxide (0.046 g Na/15 mL ethanol) was heated under reflux for 2 h, and then allowed to cool. The solid product was collected by filtration and washed with water. Brown powder, yield: 74 %, m. p. 240 – 242 °C. - IR (film): \( \nu = 3286, 3060, 2210, 1727, 1670, 1535 \text{ cm}^{-1} \). - 1H NMR (300 MHz, [D₆]DMSO): \( \delta = 1.08 \) (t, 6H, 2CH₃, \( J = 4.8 \text{ Hz} \)), 2.99 (t, 4H, 2CH₂Ph, \( J = 6.3 \text{ Hz} \)), 3.82 (t, 4H, 2CH₂N, \( J = 6.3 \text{ Hz} \)), 3.98 (s, 4H, 2CH₂S), 4.28 (q, 4H, 2CH₂O, \( J = 6.6 \text{ Hz} \)), 6.15 (d, 2H, 2CH, \( J = 6 \text{ Hz} \)), 7.28 – 7.33 (m, 14H, ArH), 8.72 (d, 2H, 2NH, \( J = 6 \text{ Hz} \)). - Anal. for C₄₀H₄₀N₆O₆S₂: calcd. H 5.27, N 10.99, S 8.38; found C 62.70, H 5.35, N 10.91, S 8.29.

2H, 2NH, \( \nu = 3745, 3532, 3028, 2921, 1637, 1591 \text{ cm}^{-1} \). - 1H NMR (300 MHz, [D₆]DMSO): \( \delta = 1.23 \) (t, 6H, 2CH₃, \( J = 6 \text{ Hz} \)), 2.92 (t, 4H, 2CH₂Ph, \( J = 6 \text{ Hz} \)), 3.82 (t, 4H, 2CH₂N, \( J = 6 \text{ Hz} \)), 6.15 (d, 4H, 2CH₂O, \( J = 6.6 \text{ Hz} \)), 6.96 (s, 4H, 2NH), 7.27 – 7.51 (m, 24H, ArH). - Anal. for C₄₀H₄₀N₆O₆S₂: calcd. C 6314, H 4.77, N 11.05, S 8.43; found C 6305, H 4.77, N 11.05, S 8.33.

Synthesis of compounds 10 and 11

To a stirred 0.75 N aqueous KOH solution (20 mL), 3a b (10 mmol) and bromoacetonitrile (40 mmol) were added successively. The resulting precipitate was filtered off, washed with water, dried, and recrystallized from ethanol.

2H, 2NH, \( \nu = 3284, 3060, 2210, 1727, 1670, 1535 \text{ cm}^{-1} \). - 1H NMR (300 MHz, [D₆]DMSO): \( \delta = 1.23 \) (t, 6H, 2CH₃, \( J = 6 \text{ Hz} \)), 2.92 (t, 4H, 2CH₂Ph, \( J = 6 \text{ Hz} \)), 3.82 (t, 4H, 2CH₂N, \( J = 6 \text{ Hz} \)), 6.15 (d, 4H, 2CH₂O, \( J = 6.6 \text{ Hz} \)), 6.96 (s, 4H, 2NH), 7.27 – 7.51 (m, 24H, ArH). - Anal. for C₄₀H₄₀N₆O₆S₂: calcd. C 6314, H 4.77, N 11.05, S 8.43; found C 6305, H 4.77, N 11.05, S 8.33.
1659 cm$^{-1}$. – 1H NMR (300 MHz, [D$_6$]DMSO): $\delta = 6.29$
(d, 2H, 2CH, $J = 4.8$ Hz), 6.77 (s, 4H, N$_2$H$_2$), 7.24 – 7.41
(m, 14H, ArH), 8.55 (d, 2H, 2NH, $J = 4.8$ Hz). – 13C NMR
(75 MHz, [D$_6$]DMSO): $\delta = 73.77$ (C-2, C-2'), 101.28 (C-6, C-6'), 115.74 (2CN), 124.19, 126.89, 127.36, 129.70, 139.35
(C-Ar), 141.35 (C-5a, C-5a'), 155.18 (C-4a, C-4a'), 159.74
(SCN), 160.76 (2C=O). – Anal. for C$_{36}$H$_{30}$N$_8$O$_2$S$_2$: calcd.
C 64.38, H 4.62, N 16.59, S 9.48; found C 64.46, H 4.51, N 16.70, S 9.56;
for C$_{36}$H$_{30}$N$_8$O$_2$S$_2$: calcd. C 64.46, H 4.51, N 16.70, S 9.56;
found C 64.46, H 4.51, N 16.70, S 9.56.

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