Ring Transformation of 6-Acyl-1,1-dioxo-1,2-thiazines with Nitrogen Nucleophiles to Substituted Pyridinium-3-sulfonamidates

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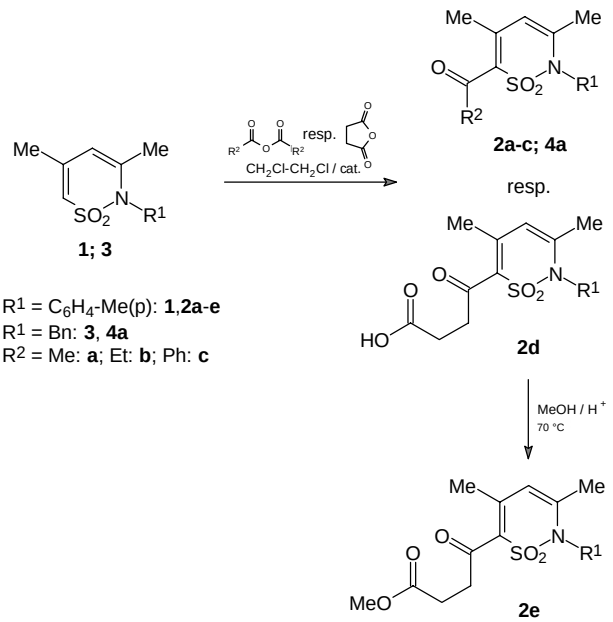
Abstract. 6-Acyl(benzoyl)-1,1-dioxo-1,2-thiazines **2** were synthesized by Friedel-Crafts acylation of the 3,5-dimethyl-1,1-dioxo-1,2-thiazines **1** and **3** using carboxylic anhydrides. The ketones **2** and **4** were transformed to substituted pyridinium-3-sulfonamidates **5**–**7** and **9** with nitrogen nucleophiles like alkylamines and hydrazine. A pyrido-pyridazinum-sulfonamidate **8** was formed from **2e** with hydrazinium hydroxide. The 6-benzoyl-1,1-dioxo-1,2-thiazine **2c** does not show the described ring transformation. The results demonstrate scope and limitations of the ring transformation reaction of 1,1-dioxo-1,2-thiazine-6-carbonyl compounds.

Ring transformations are valuable methods achieving structural modifications of heterocyclic compounds [1–7]. For instance, due to the masked 1,5-dicarbonyl structure 1,1-dioxo-1,2-thiazine-6-carbaldehydes are transformed into zwitterionic pyridinium-3-sulfonamidates with nitrogen nucleophiles [8, 9]. Correspondingly, pyrazoles [10] and pyrimidines [11] were obtained from 1,1-dioxo-1,2-thiazine-4-carbaldehydes as masked 1,3-dicarbonyl compounds.

In order to study limitations of the ring transformation of 1,1-dioxo-1,2-thiazine derivatives with masked 1,5-dicarbonyl structure, ketones should be examined despite their lower carbonyl activity in comparison with the corresponding carbaldehydes. 6-Acyl-1,1-dioxo-1,2-thiazines have not yet been described in the literature. It seemed to be possible to acylate the 3,5-dimethyl-1,1-dioxo-2-*p*-tolyl-1,2-thiazine **1** and the benzyl derivative **3**, because these compounds are easily substituted in 4- and 6-position by electrophiles. For instance, formylation with the very reactive reagent (dichloromethyl)methyl ether (DCME)/$TiCl_4$ afforded a 1:1 mixture of 1,2-thiazine-4- and -6-carbaldehydes [10], while the less reactive Vilsmeier-Haack reagent gave only the 6-carbaldehyde regiospecifically [12]. The *N*-benzyl compound **3** reacted with DCME/$TiCl_4$ to give mainly the 4-carbaldehyde.

Attempted Friedel-Crafts acylations with acid chlorides (acetyl chloride, propionyl chloride, pivaloyl chloride, benzoyl chloride, oxalyl dichloride) and a Lewis acid ($TiCl_4$, $SnCl_4$) as catalyst were moderately successful only in the case of acetyl chloride. Acetylation occured exclusively in 6-position of the thiazine ring. However, the products were contaminated with starting material, separation of which turned out to be difficult. Therefore, this acylation procedure was not further pursued, despite the positional selectivity of the reaction.

The positionally selective acylation of compound **1** succeeded in acceptable yields by use of carboxylic anhydrides (Scheme 1). While aliphatic carboxylic anhydrides reacted already at room temperature in the presence of $SnCl_4$ to furnish ketones **2a**,**b**, with benzoic and succinic anhydride higher reaction temperature and the more reactive $AlCl_3$ were needed for the preparation of ketones **2c**,**d**. Esterification of acid **2d** with MeOH afforded ketone **2e**.



Scheme 1

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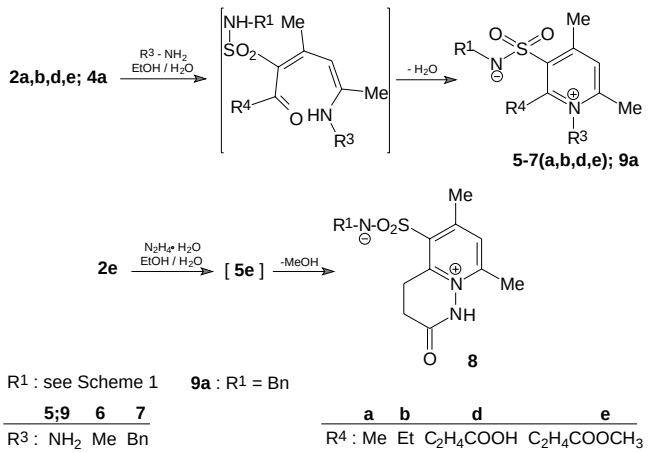
Similarly to 1,1-dioxo-1,2-thiazine-6-carbaldehydes [8, 9] 6-acyl-1,1-dioxo-1,2-thiazines **2a**,**b**,**d**,**e** and **4a** react with nitrogen nucleophiles to form the zwitterionic pyridinium-3-sulfonamidates **5**–**7** and **9**. As nitrogen nucleophiles methylamine, benzylamine and hydrazine were used. Obviously, the activating effect of the alkylketo group in 6-position of the 1,1-dioxo-1,2-thiazines **2**, **4** is strong enough to enable opening of the 1,1-dioxo-1,2-thiazine ring by amines in position 3. This reaction can be considered as a 1,5-Michael addition of the nitrogen base at the $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl compounds **2** and **3**, resp., followed by opening of the 1,2-thiazine ring. Subsequent ring closure results in formation of the pyridine derivatives **5**–**7** and **9** (see also [10]).



Scheme 2

In the case of **2e** the ring transformation to the 1-amino-pyridinium-3-sulfonamidate **5e** afforded the bicyclus **8** by ring closure between the ester group and the 1-amino function.

In contrast to the 6-acyl-1,1-dioxo-1,2-thiazines the corresponding benzoyl derivative **2c** did not react with nitrogen nucleophiles. The starting compound was recovered even at a higher reaction temperature (80 °C). The reason for this diminished reactivity could be the mesomeric interaction between the phenyl group and the carbonyl group, which reduces its electrophilic activity. This means that for the described ring transformation to occur a fine tuning of activation of the 1,1-dioxo-1,2-thiazine ring by substituents is required.

All new compounds were characterized by NMR spectroscopy. The obtained data confirm the proposed structures (see Experimental).

Like other pyridine derivatives [13–16], the new pyridinium-3-sulfonamidates are of interest as potential biological active compounds and for further chemical transformations.

Experimental

NMR spectra were measured using a Varian Gemini 300 spectrometer (^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz). IR spectra were recorded on a Philips PU 9624 FTIR spectrometer as KBr pellets. Microanalyses were performed on a Lenco CHNS-932 analyzer. Satisfactory microanalyses were obtained for all new substances (C, H, N, S, O ± 0.5%). Thin-layer chromatography was made on silica-gel aluminum sheets using cyclohexan/ethyl acetate (1:1) as solvent system. The 3,5-dimethyl-2-(4-methylphenyl)-1,1-dioxo-1,2-thiazine (**1**) and the 2-benzyl-3,5-dimethyl-1,1-dioxo-1,2-thiazine (**3**) were synthesized as described in the literature [17] and [10].

6-Acyl-3,5-dimethyl-2-(4-methylphenyl)-1,1-dioxo-1,2-thiazines (2a,b) (General Procedure)

A solution of the 1,2-thiazine **1** (200 mg, 0.8 mmol), $SnCl_4$ (0.47 ml, 0.4 mmol) and the acid anhydride (2.0 mmol) in 1,2-dichloroethane (20 ml) was stirred at room temperature for 24 h. The reaction mixture was hydrolyzed by adding chopped ice (45 cm^3) and stirred for 30 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 8 ml).

6-Acetyl-3,5-dimethyl-2-(4-methylphenyl)-1,1-dioxo-1,2-thiazine (**2a**) (by using acetic anhydride)

The combined organic layers were dried ($MgSO_4$) and the solvent removed *in vacuo*. The product **2a** was obtained by crystallization of the viscose residue from cyclohexane. Yield 150 mg (64%); *m.p.* = 90–92 °C (cyclohexane). – ^{1}H NMR (DMSO-d_6): δ/ppm = 1.90 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.36 (s, 3H, Ar–CH_3), 2.42 (s, 3H, $COCH_3$), 6.02 (s, 1H, C4-H), 7.23 (d, 2H, *J* = 7.2, Ar-H), 7.32 (d, 2H, *J* = 7.7, Ar-H).

3,5-Dimethyl-2-(4-methylphenyl)-1,1-dioxo-6-propionyl-1,2-thiazine (**2b**) (in a mixture with **1**) (by using propionic anhydride)

The combined organic layers were neutralized by shaking with sodium bicarbonate solution, separated from the aqueous layer and dried ($MgSO_4$). After evaporating the solvent a hardly separable viscose residue was obtained which is composed of the product **2b** (79%) and **1** (21%), as determined by ^{1}H NMR spectroscopic analysis. This mixture could be successfully used for further conversions. Yield **2b** 180 mg (73%). – ^{1}H NMR (DMSO-d_6): δ/ppm = 1.00 (t, 3H, *J* = 7.2, CH_3), 1.89 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.36 (s, 3H, Ar–CH_3), 2.78 (q, 2H, *J* = 7.3, CH_2), 6.01 (s, 1H, C4-H), 7.22 (d, 2H, *J* = 8.2, Ar-H), 7.32 (d, 2H, *J* = 8.0, Ar-H).

6-Benzoyl-3,5-dimethyl-2-(4-methylphenyl)-1,1-dioxo-1,2-thiazine (**2c**)

Benzoic anhydride (545 mg, 2.41 mmol), $AlCl_3$ (1043 mg, 7.82 mmol) and **1** (500 mg, 2.01 mmol) were added to 1,2-dichloroethane (40 ml), and the mixture was heated under reflux for 35 h. After cooling chopped ice (50 cm^3) and conc. HCl (3 ml) were added to the mixture and stirred as long as the organic layer became clear. After separation of the organic layer the aqueous phase was extracted with CH_2Cl_2 (4×6 ml). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. To separate the product **2c**

the remaining residue was recrystallized from MeOH. Yield 274 mg (39%); *m.p.* = 192–193 °C (MeOH). – ^{1}H NMR (DMSO-d_6): δ/ppm = 1.93 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.35 (s, 3H, Ar–CH_3), 6.07 (s, 1H, C4-H), 7.26 (d, 2H, *J* = 8.0, Ar-H), 7.31 (d, 2H, *J* = 8.1, Ar-H), 7.55 (m, 2H, Ar-H), 7.69 (t, 1H, *J* = 7.1, Ar-H), 7.83 (d, 2H, *J* = 7.7, Ar-H). – ^{13}C NMR (DMSO-d_6): δ/ppm = 20.9, 21.0, 21.3 (CH_3), 108.8, 123.2, 123.2, 129.3, 129.4, 129.5, 130.3, 131.4, 134.3, 137.7, 139.8, 147.4, 188.2 (CO). – IR (KBr): ν/cm^{-1} = 1664 (C=O).

Hydroxycarbonylethyl[3,5-dimethyl-2-(4-methylphenyl)-1,1-dioxo-1,2-thiazin-6-yl] ketone (**2d**)

Succinic anhydride (48 mg, 0.48 mmol), $AlCl_3$ (209 mg, 1.57 mmol) and **1** (100 mg, 0.40 mmol) were added to 1,2-dichloroethane (10 ml), and the mixture was heated under reflux for 96 h. By adding chopped ice (30 cm^3) the reaction mixture was hydrolyzed, and the formed precipitate dissolved with a small amount of conc. HCl. After separation of the organic layer, the aqueous phase was extracted with CH_2Cl_2 (4×3 ml). The combined organic layers were dried ($MgSO_4$). After evaporating the solvent *in vacuo* the obtained residue was dissolved in $CHCl_3$ (15 ml), and the product **2d** extracted by shaking with aqueous sodium bicarbonate solution (0.275 M). To precipitate **2d** the combined bicarbonate extracts were gradually acidified with HCl (2N). The product **2d** was separated by suction, washed with water and dried. Yield 36 mg (26%); *m.p.* = 193–195 °C. – ^{1}H NMR (DMSO-d_6): δ/ppm = 1.92 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.38 (s, 3H, Ar–CH_3), 2.51 (t, 2H, *J* = 6.4, CH_2), 3.00 (t, 2H, *J* = 6.4, CH_2), 6.05 (s, 1H, C4-H), 7.24 (d, 2H, *J* = 8.1, Ar-H), 7.34 (d, 2H, *J* = 8.1, Ar-H). – IR (KBr): ν/cm^{-1} = 1664 (C=O), 1709 (COOH).

Methoxycarbonylethyl[3,5-dimethyl-2-(4-methylphenyl)-1,1-dioxo-1,2-thiazin-6-yl] ketone (**2e**)

2d (30 mg, 0.086 mmol) was suspended in MeOH (2 ml), and a few droplets of conc. H_2SO_4 were added (pH = 2). After heating under reflux for 3h and cooling at room temperature ice water (10 cm^3) was added to the reaction mixture. The product **2e** precipitated as a white solid, which was separated by suction, washed with water and dried. Yield 28 mg (90%); *m.p.* = 135–136 °C. – ^{1}H NMR (DMSO-d_6): δ/ppm = 1.91 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.36 (s, 3H, Ar–CH_3), 2.57 (t, 2H, *J* = 6.4, CH_2), 3.04 (t, 2H, *J* = 6.4, CH_2), 3.56 (s, 3H, OCH_3), 6.04 (s, 1H, C4-H), 7.23 (d, 2H, *J* = 8.1, Ar-H), 7.33 (d, 2H, *J* = 8.0, Ar-H). – IR (KBr): ν/cm^{-1} = 1666 (C=O), 1739 ($COOCH_3$).

6-Acetyl-2-benzyl-3,5-dimethyl-1,1-dioxo-1,2-thiazine (**4a**) (in mixture with **3**)

The 1,2-thiazine **3** (500 mg, 2 mmol), $TiCl_4$ (0.65 ml, 6 mmol) and acetyl chloride (0.28 ml, 4 mmol) were added to 1,2-dichloroethane (10 ml) at 0 °C. After stirring for 90 min at this temperature stirring was continued for 3 h at room temperature. The reaction mixture was hydrolyzed by adding chopped ice (25 cm^3). The organic phase was separated, and polar impurities were removed by adding silica gel (about 100 mg). After filtration the solution was evaporated *in vacuo*. The remained viscose residue started to crystallize after 1 d. The ^{1}H NMR spectroscopic analysis showed that a mixture of two compounds was obtained composed of the product **4a** (30%) and **3** (70%). This mixture could be successfully used for the ring transformation with nitrogen nucleophiles. Yield **4a** 176 mg (30%). – ^{1}H NMR (DMSO-d_6): δ/ppm = 2.16 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.48 (s, 3H, $COCH_3$), 5.14 (s, 2H, CH_2), 5.96 (s, 1H, C4-H), 7.2–7.4 (m, 5H, Ar-H).

Pyridinium-3-sulfonamidates (5, 6, 7) (General Procedure)

The ketone **2** (0.17 mmol) and the corresponding amine were added to EtOH (7 ml)/H_2O (0.25 ml) and stirred as long as the ketone could not be longer detected by TLC (about 5–10 h). Then the solution was evaporated *in vacuo*, the obtained residue washed with little Et_2O, dried and dissolved in $CHCl_3$ (3 ml). In the case of **6** the product has to be leached from the residue. The products **5**, **6** and **7** were precipitated by gradually adding Et_2O to the $CHCl_3$ solution at 0 °C. After separation of **5**, **6** and **7** by suction the products were washed with Et_2O and dried. For the data of the products see Table 1.

1-Aminopyridinium-3-(N-4-methylphenyl)sulfonamidates (**5,b,d**)

by using hydrazinium hydroxide (17 µl, 0.34 mmol).

1-Methylpyridinium-3-(N-4-methylphenyl)sulfonamidates (**6a,b,d,e**)

by using methylamine hydrochloride (18 mg, 0.26 mmol) and Na_2CO_3 (26 mg, 0.26 mmol) dissolved in H_2O (6 ml).

1-Benzylpyridinium-3-(N-4-methylphenyl)sulfonamidates (**7a,b,d,e**)

by using benzylamine (37 µl, 0.34 mmol).

1H,2H-3,4-Dihydro-6,8-dimethyl-2-oxo-pyrido[1,2-b]pyridazinium-5-(N-4-methylphenyl)sulfonamidate (**8**)

The ketone **2e** (30 mg, 0.08 mmol) and hydrazinium hydroxide (30 µl, 0.61 mmol) were added to EtOH (5 ml)/H_2O (0.2 ml) and stirred as long as **2e** was not longer detected by TLC. After removing the solvent *in vacuo*, the remaining residue was washed with Et_2O (6 ml), dried and dissolved in $CHCl_3$ (1 ml). To precipitate the product **8** Et_2O was gradually added at 0 °C. **8** was separated by suction, washed with Et_2O and dried. Yield 28 mg (98%); *m.p.* = 125–140 °C (dec.). – ^{1}H NMR (DMSO-d_6): δ/ppm = 2.01 (t, 2H, *J* = 7.0, CH_2), 2.14 (s, 3H, Ar–CH_3), 2.46 (s, 3H, C4–CH_3), 2.54 (s, 3H, C2–CH_3), 3.55 (t, 2H, *J* = 7.0, CH_2), 6.78 (d, 2H, *J* = 7.0, Ar-H), 6.93 (d, 2H, *J* = 6.7, Ar-H), 7.53 (s, 1H, C3-H). – ^{13}C NMR (DMSO-d_6): δ/ppm = 20.5, 20.7, 22.5, 24.6, 25.2, 122.6, 128.8, 129.7, 132.5, 136.6, 137.6, 144.6, 147.7, 148.3, 173.6 (C=O). – IR (KBr): ν/cm^{-1} = 1616 (C=O).

1-Amino-2,4,6-trimethylpyridinium-3-(N-benzyl)sulfonamidate (**9a**)

The ketone **4a** (45 mg, 0.17 mmol) as mixture with **3** and hydrazinium hydroxide (8 µl, 0.18 mmol) were added to EtOH (7 ml)/H_2O (0.2 ml). The solution was stirred as long as **4a** was not longer detected by TLC. For reprocessing the white fine-crystalline precipitate **3** was removed by filtration, and the obtained solution evaporated under vacuum. The remaining solid residue was washed with Et_2O (5 ml). After drying the solid was dissolved in $CHCl_3$ (1 ml). The product **9** was precipitated by gradually adding Et_2O at 0 °C. After filtration

Table 1 Yields, melting points and spectroscopic data of the *N*-substituted pyridinium-3-(*N*-4-methylphenyl)sulfonamidates **5–7**

Prod.	Yield (%)	*m.p.* (°C)	^{1}H NMR (DMSO-d_6/TMS) δ (ppm), *J* (Hz)
5a	73	207–209	2.08 (s, 3H, Ar–CH_3), 2.62 (s, 3H, Py–CH_3), 2.71 (s, 3H, Py–CH_3), 3.12 (s, 3H, Py–CH_3), 6.58 (d, 2H, *J* = 7.8, Ar-H), 6.74 (d, 2H, *J* = 7.9, Ar-H), 6.90 (s, 2H, NH_2), 7.64 (s, 1H, C3-H)
5b	60	208–210	1.18 (t, 3H, *J* = 6.9, CH_3), 2.07 (s, 3H, Ar–CH_3), 2.65 (s, 3H, C4–CH_3), 2.77 (s, 3H, C2–CH_3), 3.79 (q, 2H, *J* = 7.0, CH_2), 6.58 (d, 2H, *J* = 7.7, Ar-H), 6.74 (d, 2H, *J* = 7.9, Ar-H), 6.84 (s, 2H, NH_2), 7.67 (s, 1H, C3-H)
5d	80	137–140	2.08 (s, 3H, Ar–CH_3), 2.49 (t, 2H, *J* = 6.5, CH_2), 2.64 (s, 3H, C4–CH_3), 2.73 (s, 3H, C2–CH_3), 3.90 (t, 2H, *J* = 6.3, CH_2), 6.58 (d, 2H, *J* = 7.7, Ar-H), 6.76 (d, 2H, *J* = 8.0, Ar-H), 7.67 (s, 1H, C3-H)
6a	85	196–198	2.23 (s, 3H, Ar–CH_3), 2.58 (s, 3H, Py–CH_3), 2.76 (s, 3H, Py–CH_3), 3.06 (s, 3H, Py–CH_3), 4.04 (s, 3H, N1–CH_3), 6.99 (d, 2H, *J* = 7.9, Ar-H), 7.11 (d, 2H, *J* = 8.0, Ar-H), 7.94 (s, 1H, C3-H)
6b	50	184–187	1.20 (t, 3H, *J* = 7.2, CH_3), 2.09 (s, 3H, Ar-CH_3), 2.66 (s, 3H, C4–CH_3), 2.79 (s, 3H, C2–CH_3), 3.77 (b, 2H, CH_2), 4.02 (s, 3H, N1–CH_3), 6.60 (d, 2H, *J* = 8.1, Ar-H), 6.75 (d, 2H, *J* = 8.0, Ar-H), 7.70 (s, 1H, C3-H)
6d	48	175–180 dec.	2.07 (s, 3H, Ar–CH_3), 2.27 (t, 2H, *J* = 6.2, CH_2), 2.62 (s, 3H, C4–CH_3), 2.75 (s, 3H, C2–CH_3), 3.52 (b, 2H, CH_2), 4.04 (s, 3H, N1–CH_3), 6.59 (d, 2H, *J* = 8.1, Ar-H), 6.73 (d, 2H, *J* = 8.2, Ar-H), 7.64 (s, 1H, C3-H)
6e	77	111–113	2.20 (s, 3H, Ar-H), 2.54 (s, 3H, CH_3), 2.60 (b, 2H, CH_2), 2.73 (s, 3H, CH_3), 3.57 (b, 2H, CH_2), 3.61 (s, 3H, CH_3), 4.04 (s, 3H, N1–CH_3), 6.92 (d, 2H, *J* = 7.9, Ar-H), 7.08 (d, 2H, *J* = 7.9, Ar-H), 7.98 (s, 1H, C3-H)
7a	80	98–100	2.11 (s, 3H, Ar–CH_3), 2.60 (s, 3H, Py–CH_3), 2.82 (s, 3H, Py–CH_3), 3.05 (s, 3H, Py–CH_3), 5.83 (s, 2H, N1–CH_2), 6.55 (d, 2H, *J* = 8.0, Ar-H), 6.76 (d, 2H, *J* = 7.9, Ar-H), 6.83 (m, 2H, Ar-H), 7.35 (m, 3H, Ar-H), 7.81 (s, 1H, C3-H)
7b	65	105–107	1.20 (t, 3H, *J* = 7.2, CH_3), 2.13 (s, 3H, Ar–CH_3), 2.55 (s, 3H, C4–CH_3), 2.87 (s, 3H, C2–CH_3), 3.66 (b, 2H, CH_2), 5.80 (s, 2H, N1–CH_2), 6.60 (d, 1H, *J* = 8.2, Ar-H), 6.77 (m, 1H, Ar-H), 6.81 (d, 1H, *J* = 8.1, Ar-H), 7.35 (m, 2H, Ar-H), 7.84 (s, 1H, C3-H)
7d	20	125–135 dec.	2.11 (s, 3H, Ar–CH_3), 2.50 (t, 2H, *J* = 6.8, CH_2), 2.54 (s, 3H, C4–CH_3), 2.83 (s, 3H, C2–CH_3), 2.96 (t, 2H, *J* = 6.9, CH_2), 5.81 (s, 2H, N1–CH_2), 6.57 (d, 2H, *J* = 8.1, Ar-H), 6.77 (m, 4H, Ar-H), 7.34 (m, 3H, Ar-H), 7.81 (s, 1H, C3-H)
7e	85	121–123	2.12 (s, 3H, Ar–CH_3), 2.56 (s, 3H, C4–CH_3), 2.70 (t, 2H, *J* = 5.2, CH_2), 2.84 (s, 3H, C2–CH_3), 3.33 (b, 2H, CH_2), 3.59 (s, 3H, OCH_3), 5.78 (s, 2H, N1–CH_2), 6.54 (d, 2H, *J* = 7.7, Ar-H), 6.78 (m, 3H, Ar-H), 7.36 (b, 4H, Ar-H), 7.85 (s, 1H, C3-H)

under suction **9** was washed with Et_2O and dried. Yield 17 mg (35%); *m.p.* = 119–123 °C (dec.). – ^{1}H NMR (DMSO-d_6): δ/ppm = 2.50 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 4.03 (s, 2H, CH_2), 7.15 (m, 5H, Ar-H), 7.32 (b, 1.5H, NH_2), 7.66 (s, 1H, C3-H). – IR (KBr): ν/cm^{-1} = 1088, 1126, 1159, 1338.

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