Synthesis of Novel Functionalized Derivatives of 5-Nitro-3,4-dihydropyrimidin-2(1*H*)-one by the Cyclocondensation of 1-Chlorobenzyl Isocyanates with *N*,*S*- and *N*,*N*-Nitroketeneacetals

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Abstract: The cyclocondensation of 1-chlorobenzyl isocyanates with *S*,*N*- and *N*,*N*-nitroketeneacetals has been employed to synthesize hitherto-unknown 6-methylthio-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones, 8-nitro-2,3,6,7-tetrahydroimidazo[1,2-c]pyrimidin-5(1*H*)-ones and 9-nitro-1,2,3,4,7,8-hexahydro-6*H*-pyrimido[1,6-a]pyrimidin-6(1*H*)-ones. Substitution of the methylthio group in 6-methylthio-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones provided 6-amino-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones, which exist in tautomeric equilibrium with 4-imino-5-nitro-3,4,5,6-tetrahydropyrimidin-2(1*H*)-ones. The compounds obtained, if boiled in dioxane in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), eliminate the nitro groups to give substituted 4-imino-3,4-dihydropyrimidin-2(1*H*)-ones.

Key words: heterocyclization, tautomerism, 1-chlorobenzyl isocyanates, *S*,*N*- and *N*,*N*-nitroketeneacetals, 3,4-dihydropyrimidones

The chemistry of 3,4-dihydropyrimidine (DHPM) derivatives, heterocyclic systems of the general formula **1** (Figure 1), has been under vigorous development over the past two decades.[1] Compounds of this class are remarkable for their diverse biological activity and the scaffold represented by structure **1** is hence of paramount importance in medicinal and combinatorial chemistry.[2] The DHPM nucleus is also contained in a number of biologically significant natural products as, for instance, in batzelladine alkaloids and saxitoxin.[3]

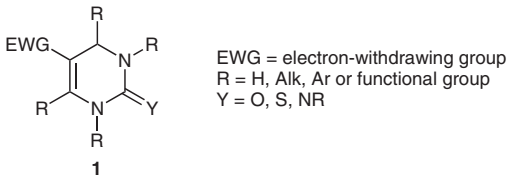

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Figure 1

Classical synthetic access to DHPMs **1** is based on the Biginelli reaction,[4] which has recently been notably developed through the use of new, efficient Lewis acid catalysts and by applying microwave exposure as well as solid-phase and fluorine-phase strategies.[5] Modified approaches to DHPM synthesis, for example those proposed by Atwald and Shutalev,[6] have also been reported. The condensed DHPM nucleus of the alkaloids batzelladines B and D was constructed using the condensation between acetoacetic ester and a complex derivative of *N*-α-hydroxyalkyl urea;[7] in a more recent example, vinyl carbodiimides were cycloadded to chiral cyclic imines.[8] To obtain partially hydrogenated derivatives of pyrrolo[1,2-c]pyrimidine, constituting the heterocyclic system of saxitoxin, Kishi suggested the condensation of 2-carbethoxymethylidenepyrrolidine with isocyanic acid and acetaldehyde.[9]

In contrast to the developments summarized above, the existing literature offers only scant evidence of 6-alkoxy-, 6-alkylthio-, and 6-amino-substituted DHPMs. Their condensed analogues, partially hydrogenated oxazolo(thiazolo)pyrimidines, result from the cycloaddition of alkenyloxazolines(thiazolines) to aryl and arylsulfonyl isocyanates.[10] The first representatives of 6-amino-3,4-dihydropyrimidin-2(1*H*)-ones were synthesized principally following the Biginelli reaction, with the difference being that malonodinitrile or cyanoacetic acid was used instead of acetoacetic ester.[11] It is only very recently that the derivatives of 6-ethoxy- and 6-thiocarbamido-3,4-dihydropyrimidin-2(1*H*)-one have been obtained.[12]

Our previous studies on the reaction of 1-chloroalkyl isocyanates with C,N-, C,O- and C,S binucleophilic reagents, led us to a new strategy of constructing functionalized 3,4-dihydropyrimidones **2**. This approach was based on the [3+3] cyclocondensation of bielectrophilic 1-chloroalkyl isocyanates **3**,[13] containing the synthon $[–C=N–C=O]^{2+}$, and binucleophilic, deactivated enamines **4**, representing the synthon $[–C=C–N–]^{2–}$ (see Scheme 1).

In this way, starting from 1-chlorobenzyl isocyanates and ethyl β-aminocrotonates or β-aminoenones, a number of hitherto-unknown 1-aryl-substituted 3,4-dihydropyrimidones and 2,3-dihydropyrimido[6,1-c][1,4]benzothiazin-1(1*H*)-ones have been obtained.[14] Further research along these lines was aimed at the synthesis of new dihydropyrimidine derivatives containing functional groups of various electronic nature at positions 5 and 6. It appeared, therefore, expedient to run cyclocondensations of this kind with another class of deactivated enamines, *S*,*N*-nitroketeneacetals **5**. Such compounds were chosen because

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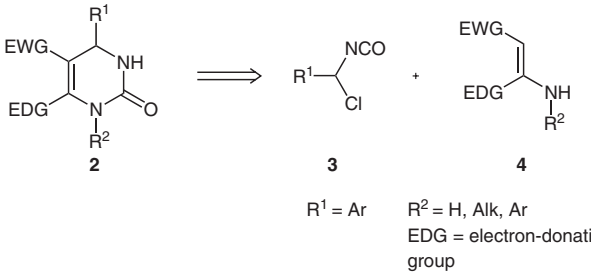
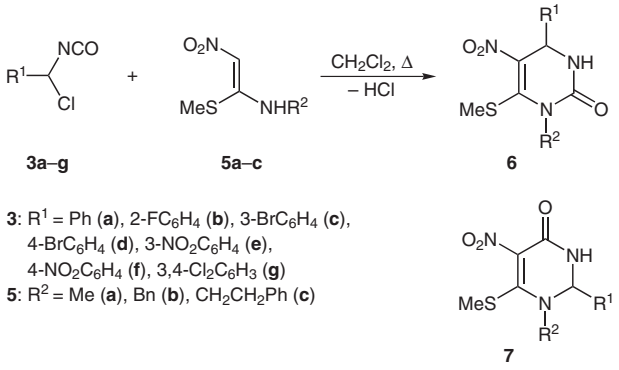


Scheme 1 Retrosynthetic route to functionalized 3,4-dihydropyrimidin-2(1*H*)-ones **2**

they are easily accessible and constitute highly reactive 1,3-C,N-binucleophiles.[15] Previously reported cyclizations of compounds **5** with such bielectrophiles as glyoxal, ethyl glyoxylate, oxalyl chloride and chlorothioformyl chloride, furnished pyrrole and thiazole derivatives.[16] The systematic research on the reactions of these highly versatile enamines with propargyl bromide,[17] 3-bromopropionyl chloride[18] and itaconic anhydride[19] enabled Junjappa and co-workers to develop synthetic routes to functionalized pyrroles and γ-lactones.

We have found that heating 1-chlorobenzyl isocyanate (**3a**) and *N*-methylnitroketeneacetal (**5a**) in methylene chloride for four hours, provided 1-methyl-6-methylthio-5-nitro-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (**6a**) in 36% yield. Conducting the reaction in the presence of triethylamine (Et_3N) or *N*,*N*-diisopropylethylamine (DIPEA), used as hydrogen chloride acceptors, resulted in a reduced yield of compound **6a**.



Scheme 2

To obtain compounds **6** with various substituents R^1 and R^2, we started from *N*-alkylnitroketeneacetals **5a**–**c** and 1-chlorobenzyl isocyanates **3a**–**g** (see Scheme 2 and Table 1). It can be seen that the yields of pyrimidones **6** increased up to 79% when acceptor substituents are present on the aromatic ring of the starting isocyanates **3**. With N-aryl-substituted *S*,*N*-nitroketeneacetals, a mixture of unidentifiable products was formed. The isomeric compound **7** was not detected in the reaction mixture.

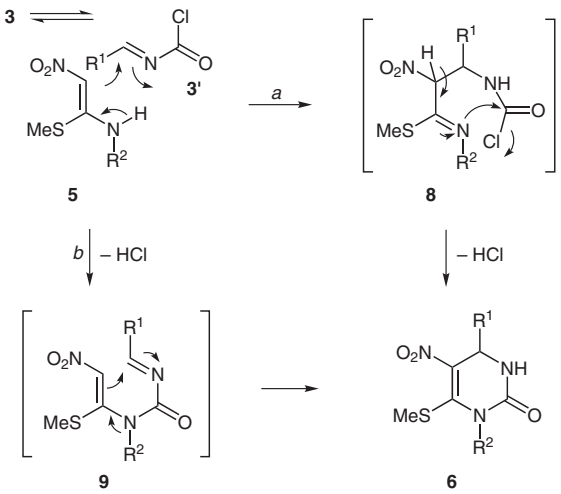
Since compounds **3** exist as equilibrium mixtures of the isocyanate and *N*-chloroformylimine tautomeric forms,[20] each having two electrophilic centers, there are several

Table 1 1-Alkyl-4-aryl-6-methylthio-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones **6**

6	R^1	R^2	Yield (%)[a]
a	Ph	Me	36
b	2-FC_6H_4	Me	62
c	3-BrC_6H_4	Me	60
d	3-$NO_2C_6H_4$	Me	79
e	4-BrC_6H_4	Me	55
f	4-$NO_2C_6H_4$	Me	77
g	3,4-$Cl_2C_6H_3$	Me	73
h	3-BrC_6H_4	Bn	56
i	3,4-$Cl_2C_6H_3$	CH_2CH_2Ph	44

[a] Pure, isolated yield.

possibilities for the initial step of the reaction between **3** and **5** (see Scheme 3). The reaction is most likely to start with the Mannich addition of the nucleophilic β-carbon atom in the enamine moiety of *S*,*N*-nitroketeneacetal **5** to the activated C=N double bond of the *N*-chloroformylimine form **3′** of 1-chlorobenzyl isocyanate **3** (path *a*). It is highly probable that the formation of new C–C and N–H bonds in this step proceeds by the diazaene mechanism,[21] as in the Michael addition and, as a result, intermediate **8** forms which rapidly cyclizes to the product **6**. An alternative reaction mechanism, discussed in our previous work,[14a] is assumed to proceed in two stages, namely isocyanatoalkylation of enamine **5** with the isocyanate form of compound **3**, followed by the intramolecular carbamoylation of the alkylamino group. However, the nature of the amino group in reagents **5** was found to affect the course of the reaction and, hence, one cannot rule out the possibility that the carbamoylation of the amino group is just the initial reaction step, which leads to intermedi-



Scheme 3

ates **9** and subsequently to the pyrimidine ring closure (path *b*).

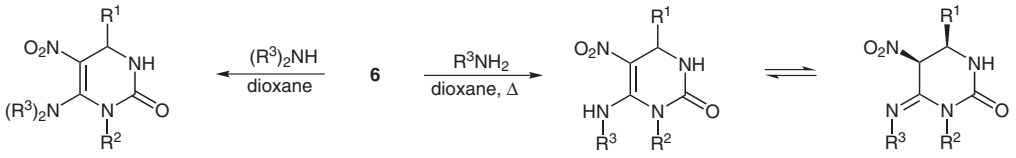
Though 5-nitro derivatives of classical DHPMs have so far been rather poorly studied, they are known to be efficient calcium channel modulators, antihypertensive agents and calcitonin mimetics.[22] It should be noted that compounds **6** constitute the first representatives of 3,4-dihydropyrimidin-2(1*H*)-ones containing the 6-methylthio group, which imparts pronounced nucleofugic properties to nucleophilic substitution reactions. It was found that compounds **6** readily reacted with aliphatic primary and secondary amines as well as ammonia, at room temperature in dioxane, so that the amino group replaced the methylthio group, affording 6-dialkylaminodihydropyrimidones **10a** and **10b** as well as 6-amino- and 6-alkylaminodihydropyrimidones **11d**,**f**,**i**,**k**,**l**,**p** in high yields (Table 2, entries 5, 9, 12, 14, 15 and 19).

Aromatic amines enter into this reaction only on boiling in dioxane to give 6-arylaminodihydropyrimidones in 51–91% yields (Table 2, entries 4–6, 8, 10, 11, 13, 16–18 and 20). For instance, aniline, *p*-toluidine and *p*-anisidine react on boiling for four hours, whereas less basic 4-chloroaniline requires boiling for 16 hours and 4-cyanoaniline is actually inert under such conditions.

To synthesize the condensed analogues of 6-amino-3,4-dihydropyrimidones, we started from cyclic *N*,*N*-nitroketeneacetals **12a** and **12b**.

Compounds **12** reacted with isocyanates **3** at room temperature, in methylene chloride, in the presence of a weakly nucleophilic organic base (DIPEA), to furnish the

Table 2 Synthesis of 1-Alkyl-6-amino-4-aryl-5-nitro-3,4-dihydropyrimidin-2-ones **10** and **11**

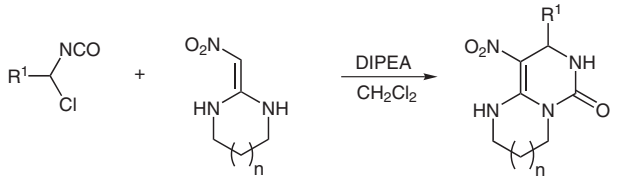


Entry	Compd	R^1	R^2	R^3	Ratio **11′**:**11″**, DMSO-d_6 ($CDCl_3$)	Yield (%)[a]
1	**10a**	Ph	Me	$(R^3)_2N$ = 1-pyrrolidinyl	–	55
2	**10b**	4-BrC_6H_4	Me	$(R^3)_2N$ = 4-morpholinyl	–	51
4	**11a**	Ph	Me	Ph	0:100 (0:100)	87
5	**11b**	Ph	Me	4-ClC_6H_4	0:100 (0:100)	82
6	**11c**	Ph	Me	4-$MeOC_6H_4$	16:84 (13:87)	90
7	**11d**	2-FC_6H_4	Me	H	100:0	64
8	**11e**	3-BrC_6H_4	Me	Ph	15:85 (13:82)	78
9	**11f**	3-BrC_6H_4	Bn	Bn	45:55 (80:20)	57
10	**11g**	3-BrC_6H_4	Bn	Ph	0:100 (0:100)	45
11	**11h**	4-BrC_6H_4	Me	4-$MeOC_6H_4$	31:69 (28:72)	85
12	**11i**	3-$NO_2C_6H_4$	Me	Bn	83:17 (100:0)	61
13	**11j**	3-$NO_2C_6H_4$	Me	4-$MeOC_6H_4$	54:46	91
14	**11k**	3-$NO_2C_6H_4$	Me	Me	98:2 (100:0)	58
15	**11l**	4-$NO_2C_6H_4$	Me	H	100:0	67
16	**11m**	4-$NO_2C_6H_4$	Me	Ph	24:76	87
17	**11n**	4-$NO_2C_6H_4$	Me	4-ClC_6H_4	11:89	75
18	**11o**	4-$NO_2C_6H_4$	Me	4-$MeOC_6H_4$	32:68	90
19	**11p**	3,4-$Cl_2C_6H_3$	Me	Bn	91:9 (100:0)	54
20	**11q**	3,4-$Cl_2C_6H_3$	Me	4-MeC_6H_4	27:73	83

[a] Pure, isolated yield.

derivatives of 8-nitro-2,3,6,7-tetrahydroimidazo[1,2-c]pyrimidin-5(1*H*)-one **13a** and **13d** and 9-nitro-1,2,3,4,7,8-hexahydro-6*H*-pyrimido[1,6-a]pyrimidin-6(1*H*)-one **13b** and **13c** in high yields (see Table 3). Starting from *N*,*N*′-dibenzylnitroketeneacetal (**12c**) and the corresponding isocyanate **3c**, compound **11f** was also thus-obtained in 43% yield.

Table 3 Synthesis of 8-Nitro-2,3,6,7-tetrahydroimidazo[1,2-c]pyrimidin-5(1H)-ones **13a** and **13d**, and 9-Nitro-1,2,3,4,7,8-hexahydro-6*H*-pyrimido[1,6-a]pyrimidin-6(1*H*)-ones **13b** and **13c**



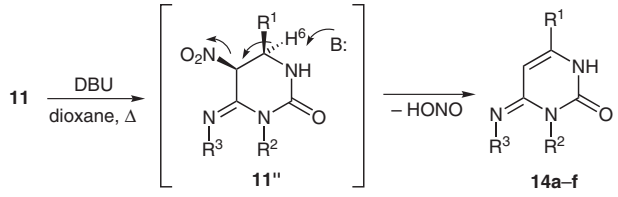
3a–g **12a,b** **13a–d**

Compd **13**	R^1; n	Yield (%)[a]
a	Ph; 0	70
b	3-$NO_2C_6H_4$; 1	85
c	4-$NO_2C_6H_4$; 1	83
d	3,4-$Cl_2C_6H_3$; 0	74

[a] Pure, isolated yield.

On heating a dioxane solution of 4-aryl-6-monoalkyl(aryl)amino-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones **11**, in the presence of catalytic amounts of a strong organic base (DBU), the nitro group is eliminated and the derivatives of 6-aryl-4-monoalkyl(aryl)imino-3,4-dihydropyrimidin-2(1*H*)-ones **14a–f** result in high yields (see Table 4).

Table 4 Synthesis of 3-Alkyl-6-aryl-4-alkyl(aryl)imino-3,4-dihydropyrimidin-2(1*H*)-ones **14**



Compd **14**	R^1	R^2	R^3	Yield (%)[a]
a	Ph	Me	Ph	84
b	3-BrC_6H_4	Bn	Ph	70
c	3-$NO_2C_6H_4$	Me	4-$MeOC_6H_4$	88
d	4-$NO_2C_6H_4$	Me	4-$MeOC_6H_4$	85
e	3,4-$Cl_2C_6H_3$	Me	Bn	65
f	3,4-$Cl_2C_6H_3$	Me	4-MeC_6H_4	90

[a] Pure, isolated yield.

An analogous process, in which a nitro group functions as a leaving group, has previously been observed for aliphatic nitro compounds[23] as well as in the Barton–Zard pyrrole synthesis.[24] Presumably, nitro group elimination proceeds through 1,2-*anti* elimination of nitrous acid from the amidine tautomeric form **11″**, as this process is much facilitated by the location of the proton H^6 and the nitro group in the stable *anti*-periplanar conformation. It is then evident that the elimination of this kind should be impossible for compounds **10**, which is indeed the case. Released nitrous acid rapidly decomposes and therefore a catalytic amount of DBU is needed for the reaction to go to completion. It has been ascertained that the basicity of the amine involved is of significance, since the conversion described above does not occur in the presence of triethylamine. 4-Iminopyrimidin-2-ones **14** thus synthesized represent hitherto-unknown cytosine derivatives.[25]

All solvents were purified and dried by standard methods. ^{1}H NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ on a Varian Mercury spectrometer (400 MHz) using TMS as internal standard. ^{13}C NMR spectra were recorded in DMSO-d_6 on a Varian Mercury spectrometer (125 MHz, TMS internal standard). APCI MS data were obtained on an Agilent 1100\DAD\MSD VL G1965a.

2-Methylamino-2-methylthionitroethene (**5a**) is commercially available and was used as received. 1-Chloroalkyl isocyanates **3a–g**,[14,26] 2-benzylamino-2-methylthionitroethene (**5b**),[27] 2-phenethylamino-2-methylthionitroethene (**5c**),[28] 2,2-dibenzylaminonitroethene (**12c**),[29] 2-(nitromethylen)imidazolidine (**12a**)[30] and 2-(nitromethylen)hexahydropyrimidine (**12b**)[31] were prepared according to literature procedures.

1-Alkyl-4-aryl-6-methylthio-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones 6; General Procedure

To a stirred solution of *S*,*N*-nitroketeneacetal (**5a–c**; 0.01 mol) in CH_2Cl_2 (30 mL) at r.t., a solution of the corresponding 1-chlorobenzyl isocyanate (**3a–g**; 0.01 mol) in CH_2Cl_2 (20 mL) was added. The reaction mixture was heated for 4 h then the solvent was evaporated in vacuo and the residue was crystallized from EtOH.

1-Alkyl-6-amino-4-aryl-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones 10 and 11; General Procedure

To a solution of dihydropyrimidone (**6a–h**; 0.01 mol) in anhyd dioxane (30 mL), the corresponding amine was added. The reaction mixture was stirred at r.t. for 24 h (in the case of aliphatic amines and ammonia) or heated for 6 h (in the case of *p*-chloraniline, 16 h). The solvent was evaporated in vacuo and the residue was crystallized from EtOH.

4-(3-Bromophenyl)-1,6-dibenzyl-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones (11f), 8-Nitro-2,3,6,7-tetrahydroimidazo[1,2-c]pyrimidin-5(1*H*)-ones (13a,d) and 9-Nitro-1,2,3,4,7,8-hexahydro-6*H*-pyrimido[1,6-a]pyrimidin-6-ones (13b,c); General Procedure

To a stirred solution of *N*,*N*-nitroketeneacetal (**12a–c**; 0.01 mol) and DIPEA (0.01 mol) in CH_2Cl_2 (30 mL) at r.t., a solution of the corresponding 1-chlorobenzyl isocyanate (**3a**,**e–g**; 0.01 mol) in CH_2Cl_2 (20 mL) was added. The reaction mixture was stirred for 12 h at r.t. and the precipitate formed was filtered, washed with H_2O (10 × 3 mL) and crystallized from EtOH.

3-Alkyl-6-aryl-4-benzyl(aryl)imino-3,4-dihydropyrimidin-2(1*H*)-ones (14a–f); General Procedure

To a solution of the corresponding 6-aminodihydropyrimidone (0.01 mol) in anhyd dioxane (30 mL), DBU (0.3 g, 0.002 mol) was added. The reaction mixture was heated for 6 h then the solvent was evaporated in vacuo and the residue was crystallized from EtOH.

Structure Assignments and Analytical Data

The structure of synthesized 3,4-dihydropyrimidones **6a–i** was confirmed by ^{1}H and ^{13}C NMR spectroscopic as well as APCI MS data. In DMSO-d_6, characteristic ^{1}H resonance doublets were observed at 5.6–5.8 and 8.5–8.9 ppm, arising from the CH and NH protons, respectively, with spin-spin coupling constants (SSCC) of 3.0–4.8 Hz. The ^{13}C resonance peaks for the carbon atom C-4 were exhibited at 52–53 ppm, unequivocally pointing to the 3,4-dihydropyrimidone structure and ruling out formation of regioisomeric 2,3-dihydropyrimidone **7**.[32]

The structure of the obtained 6-amino-substituted 5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones **10** and **11** was supported by ^{1}H and ^{13}C NMR spectroscopy as well as by APCI MS spectrometry. The ^{1}H NMR spectra of compounds **10** in DMSO-d_6 displayed doublets at 5.6–5.7 and 8.7–8.8 ppm, originating from the CH and NH protons, respectively, with SSCC of 3–4 Hz. 6-Aminopyrimidones **11d** and **11l** gave signals, arising from the NH_2 group, that appeared as two broadened singlets at 8.7–8.8 and 10.1–10.2 ppm as a result of the intramolecular hydrogen bond formation; 6-monoalkylaminopyrimidones **11f**,**i**,**k**,**p** were characterized by the broad signals from the exocyclic NH protons at 10.1–10.6 ppm. The ^{1}H NMR spectra of these compounds, when measured in DMSO-d_6, were indicative of another tautomeric form, 4-imino-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (**11″**), in addition to the main form **11′**, with the content ratio **11′** to **11″** of 45:55, 83:17, 98:2, and 91:9 for **11f**,**i**,**k** and **p**, respectively. In a $CDCl_3$ solution, the ^{1}H NMR spectra showed no evidence of the **11″** form or, in the case of **11f**, suggests its lowered content (see Table 2). The tautomerism between forms **11′** and **11″** can be regarded as a particular case of the keteneaminal–amidine tautomerism observed previously for some acyclic compounds.[33] Unlike 6-alkylaminopyrimidones, for which the keteneaminal form predominates, their 6-arylamino counterparts tend to exist in the amidine form (see Table 2), and it becomes the only possible form, both in DMSO-d_6 and $CDCl_3$ solutions, for compounds **11a**,**b**,**g**, suggesting that they should be considered as 4-imino-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one derivatives. The ^{1}H NMR signals from the protons H-5 and H-6 normally appear as slightly split multiplets. The resonance of the proton H-5 is exhibited as a doublet at 5.8–5.9 ppm with a very small SSCC of 2.0–2.5 Hz. The multiplet at 5.5–5.6 arises from the proton H-6 and its spin coupling with the NH proton is characterized by the SSCC of 4.4–4.5 Hz. The ^{13}C NMR spectrum displays signals arising from the carbon atoms H-6 and H-5 at 52–53 and 78–79 ppm, respectively.

The established relationships between the nature of the substituents and the tautomeric equilibrium position are consistent with the electronic and steric structure of compounds **11**. A strong electron-donor amino or alkylamino group at position 6 of 3,4-dihydropyrimidones, stabilizes form **11′** due to its efficient conjugation with the nitro group at position 5 through the double bond of the keteneaminal moiety. With an acceptor aryl substituent in the 6-arylamino group, the conjugation of the aromatic ring with the endocyclic nitrogen atom, through the imino group of the amidine moiety, becomes energetically preferable so that form **11″** tends to prevail and its content rises with increasing acceptor character of the aryl residue (Table 2, entries 4–6 and 16–18). It is notable that the equilibrium position is also highly dependent on the nature of the 4-aryl substituent, since the stronger its acceptor properties, the more stabilized is the keteneaminal form **11′** (entries 6, 11, 13 and 18). A more bulky benzyl substituent at position 1 causes the equilibrium to shift towards amidine form **11″** (*cf* entries 8 and 10). A distinctive feature of the tautomerism found for aminopyrimidones **11** is that the equilibrium between the tautomeric forms is established rather slowly. This is evidenced by the APCI MS spectra of compounds **11**, which exhibits two peaks on the chromatogram with much the same intensity ratio as the content ratio of the tautomeric forms derived from the ^{1}H NMR spectra in DMSO-d_6. Moreover, the mass spectra show two molecular ion peaks, with the values [M – 1] and [M + 1], corresponding to the deprotonated keteneaminal form **11′** (containing an acidic NH proton) and the protonated amidine form **11″** (containing a basic imino group), respectively. Two spots were also observed on the thin-layer chromatogram, however, attempts at separating these tautomers by preparatory TLC provided samples with varying ratios of the tautomeric forms.

Though structure **11″** permits the existence of the *cis* and *trans* isomers, only the isomer with the *cis* configuration of the protons H-5 and H-6 was observed in solution; it is evidently most thermodynamically stable due to the dynamic *cis–trans* equilibrium that is likely to involve the intermediate keteneaminal form **11′**. Structural determination of these compounds was performed by ^{1}H NMR spectroscopy with the difference NOE experiments in a DMSO-d_6 solution using compound **11b** as an example.

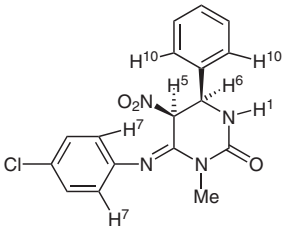


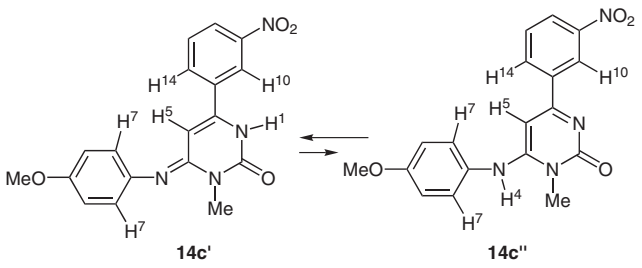
Figure 2 Structure of compound **11b**

The SSCC for the protons H-5 and H-6 was found to be 2.45 Hz. On irradiation of H-5, an NOE enhancement was detected for the proton H-6 and *ortho* protons H-10 and H-7 in the aryl rings, whereas irradiation of H-6 revealed a coupling with H-5 and also with H-10 and H-1 (see Figure 2). These observations suggest that the protons H-5 and H-6 reside on the same side of the pyrimidine ring[34] and the imino group has the *E*-configuration. The *cis* configuration is probably characteristic of all the other derivatives of structure **11″**.

The ^{1}H NMR spectra of condensed pyrimidines **13** in DMSO-d_6 showed characteristic doublets of the CH and NH protons at 5.4–5.6 and 9.4–11.1 ppm, respectively, with SSCC of 3–4 Hz. The ^{13}H NMR signal of the C-4 carbon atom was found at 52–53 ppm, as in the case of compounds **10** and **11** (in the ketenaminal form).

The structure of compounds **14** was determined using APCI MS spectrometry as well as ^{1}H and ^{13}C NMR spectroscopy. The molecular ion peaks in the APCI spectra were found at [M + 1]. The ^{1}H NMR spectra displayed singlets arising from the protons H-5 and H-1 at 5.6–6.2 and 10.8–11.0 ppm, respectively. The methylene group of the benzyl residue in compound **14e** was not spin-coupled to the NH proton and generated a singlet at 4.6 ppm, thus corroborating the structure of 6-aryl-4-benzyliminopyrimidin-2-one. The ^{13}C NMR signal of C-5 was observed at 90–92 ppm.

The structure of compound **14c** was thoroughly studied by ^{1}H NMR spectroscopy and difference NOE experiments in a $CDCl_3$, since the prevailing tautomeric form of pyrimidines **14a–d**,**f** which may be either 4-arylimino-3,4-dihydropyrimidin-2(1*H*)-one (**14c′**) or 6-arylaminopyrimidin-2(1*H*)-one (**14c″**) could not be unequivocally determined (Scheme 4).



Scheme 4 Structure of compound **14c**

Irradiation at the H-1 proton frequency give rise to an NOE enhancement of the signals arising from the *ortho* protons (H-10 and H-14) of the 6-aryl ring. The H-5 proton was spin-coupled to both the H-10 and H-14 protons and to the *ortho* protons (H-7) of the *p*-anisyl residue, but not to the H-1 proton. An NOE enhancement of the H-1 signal was also absent from the spectra recorded after irradiation of the H-7 protons. Taken together, this evidence suggests that only one tautomeric form, **14c′**, exists in a solution, since otherwise the NOE would manifest itself in a way that might be expected for structure **14c″**, i.e. an enhancement of the signal from the H-4 protons on irradiation at H-5, but not for H-10 and H-14 on irradiation of H-4.

Table 5 Analytical Data for Compounds **6**, **10**, **11**, **13** and **14**[a]

Compd	Mp (°C)[b]	^{1}H NMR, DMSO-d_6 (δ ppm)	^{13}C NMR, DMSO-d_6 (δ ppm)	MS (APCI), *m*/*z*
6a	178–180	2.47 (s, 3 H), 3.29 (s, 3 H), 5.69 (d, *J* = Hz, 1 H), 7.21 (d, *J* = 7.0 Hz, 2 H), 7.30 (t, *J* = 7.0 Hz, 1 H), 7.36 (t, *J* = 7.0 Hz, 2 H), 8.71 (d, *J* = Hz, 1 H)	18.20, 34.97, 52.99, 125.75, 128.20, 128.97, 140.64, 151.89, 155.46	280 [M + 1]
6b	144–146	2.48 (s, 3 H), 3.36 (s, 3 H), 5.85 (d, *J* = 3.9 Hz, 1 H), 7.10–7.42 (m, 4 H), 8.58 (d, *J* = 3.9 Hz, 1 H)	18.10, 35.02, 49.28, 115.82, 124.77, 127.23, 128.72, 130.41, 151.46, 155.08, 158.85, 160.82	299 [M + 1]
6c	195–197	2.48 (s, 3 H), 3.29 (s, 3 H), 5.71 (d, *J* = 4.0 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.41 (s, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 8.71 (d, *J* = 4.0 Hz, 1 H)	18.28, 34.85, 52.48, 122.02, 124.64, 127.97, 128.87, 131.08, 131.25, 143.27, 151.57, 156.14	360 [M + 1]
6d	165–167	2.48 (s, 3 H), 3.29 (s, 3 H), 5.87 (d, *J* = 3.6 Hz, 1 H), 7.67 (m, 2 H), 8.08 (s, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 8.17 (m, 1 H), 8.90 (d, *J* = 3.6 Hz, 1 H)	18.31, 34.70, 52.32, 120.74, 123.10, 127.23, 130.69, 132.28, 142.76, 147.99, 151.40, 156.82	325 [M + 1]
6e	200–202	2.48 (s, 3 H), 3.30 (s, 3 H), 5.68 (d, *J* = 4.5 Hz, 1 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 8.74 (d, *J* = 4.5 Hz, 1 H)	18.74, 35.28, 52.99, 121.83, 128.54, 132.34, 140.54, 152.15, 155.67, 156.32	360 [M + 1]
6f	181–183	2.49 (s, 3 H), 3.29 (s, 3 H), 5.85 (d, *J* = 4.0 Hz, 1 H), 7.52 (d, *J* = 8.5 Hz, 2 H), 8.23 (d, *J* = 8.5 Hz, 2 H), 8.91 (d, *J* = 4.0 Hz, 1 H)	18.35, 34.78, 52.53, 124.18, 127.27, 134.00, 147.28, 147.77, 151.46, 156.90	325 [M + 1]
6g	145–147	2.48 (s, 3 H), 3.28 (s, 3 H), 5.73 (d, *J* = 4.2 Hz, 1 H), 7.19 (dd, J^1 = 8.5 Hz, J^2 = 2 Hz, 1 H), 7.47 (d, *J* = 2 Hz, 1 H), 7.62 (d, *J* = 8.5 Hz, 1 H), 8.77 (d, *J* = 4.2 Hz, 1 H)	18.34, 34.75, 52.11, 126.02, 127.42, 128.17, 130.87, 131.21, 131.44, 141.65, 151.40, 156.49	350 [M + 1]
6h	131–133	2.48 (s, 3 H), 5.03 (d, *J* = 15.6 Hz, 1 H), 5.18 (d, *J* = 15.6 Hz, 1 H), 5.70 (d, *J* = 4.8 Hz, 1 H), 7.03–7.50 (m, 9 H), 8.89 (d, *J* = 4.8 Hz, 1 H)	19.03, 49.42, 52.79, 122.44, 125.20, 127.54, 127.85, 128.90, 129.24, 131.52, 137.66, 143.81, 151.56, 155.28	435 [M + 1]
6i	152–154	2.49 (s, 3 H), 2.74 (m, 2 H), 4.05 (m, 1 H), 4.20 (m, 1 H), 5.68 (d, *J* = 4.8 Hz, 1 H), 7.05–7.29 (m, 6 H), 7.43 (s, 1 H), 7.54 (d, *J* = 8.4 Hz, 1 H), 8.90 (d, *J* = 4.8 Hz, 1 H)	18.43, 35.08, 46.71, 51.75, 125.78, 126.31, 127.70, 127.93, 128.24, 128.38, 130.68, 131.04, 131.33, 137.61, 141.56, 150.62, 154.79	440 [M + 1]
10a	194–196	1.89 (m, 2 H), 2.06 (m, 2 H), 2.96 (s, 3 H), 3.09 (m, 2 H), 3.69 (m, 1 H), 5.71 (d, *J* = 3.0 Hz, 1 H), 7.21–7.35 (m, 5 H), 8.74 (d, *J* = 3.0 Hz, 1 H)	24.89, 34.80, 50.72, 51.85, 112.50, 125.13, 127.40, 128.62, 141.76, 152.65, 154.07	302 [M + 1]
10b	231–233	3.21 (m, 2 H), 3.36 (m, 2 H), 3.68 (m, 2 H), 3.78 (m, 2 H), 5.58 (d, *J* = 4.2 Hz, 1 H), 7.19 (d, *J* = 7.5 Hz, 2 H), 7.50 (d, *J* = 7.5 Hz, 2 H), 8.83 (d, *J* = 4.2 Hz, 1 H)	34.57, 50.29, 51.62, 65.85, 113.44, 121.16, 127.96, 132.07, 141.70, 154.19, 155.47	399 [M + 1]
11a	155–157	3.17 (s, 3 H), 5.26 (m, 1 H), 5.59 (s, 1 H), 6.10 (d, *J* = 7.2 Hz, 2 H), 7.02 (t, *J* = 7.2 Hz, 1 H), 7.15–7.42 (m, 7 H), 8.47 (d, *J* = 4.0 Hz, 1 H)	28.93, 52.60, 78.64, 119.53, 123.73, 125.78, 128.56, 129.00, 129.08, 135.99, 144.65, 146.84, 152.20	325 [M + 1]

Table 5 Analytical Data for Compounds **6**, **10**, **11**, **13** and **14**[a] (continued)

Compd	Mp (°C)[b]	^{1}H NMR, DMSO-d_6 (δ ppm)	^{13}C NMR, DMSO-d_6 (δ ppm)	MS (APCI), *m*/*z*
11b	196–198	3.19 (s, 3 H), 5.27 (m, 1 H), 5.72 (d, *J* = 2.45 Hz, 1 H), 6.09 (d, *J* = 8.4 Hz, 2 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 6.6 Hz, 2 H), 7.41 (m, 3 H), 8.51 (d, *J* = 4.5 Hz, 1 H)	28.97, 52.44, 78.69, 121.36, 125.64, 127.93, 118.55, 128.96, 128.99, 135.78, 145.29, 145.75, 152.03	360 [M + 1]
11c	164–166	2.72 (s, 0.57 H), 3.19 (s, 3 H), 3.72 (s, 3 H), 3.80 (s, 0.57 H), 5.28 (m, 1 H), 5.66 (s, 1 H), 5.75 (d, *J* = 4.0 Hz, 0.19 H), 6.09 (d, *J* = 8.4 Hz, 2 H), 6.76 (d, *J* = 8.4 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 0.38 H), 7.18 (d, *J* = 8.8 Hz, 0.38 H), 7.20–7.44 (m, 5.95 H), 8.44 (s, 1 H), 8.72 (d, *J* = 4.0 Hz, 0.19 H), 11.42 (s, 0.19 H) [2.77 (s, 0.45 H), 3.37 (s, 3 H), 3.71 (s, 3 H), 3.79 (s, 0.45 H), 5.32 (m, 2 H), 6.00 (d, *J* = 4.4 Hz, 0.15 H), 6.11 (d, *J* = 8.8 Hz, 2 H), 6.68 (m, 3.15 H), 6.90 (d, *J* = 8.4 Hz, 0.30 H), 7.03 (d, *J* = 8.4 Hz, 0.30 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.27–7.40 (m, 3.75 H), 11.73 (s, 0.15 H)][c]	–	355 [M + 1] 353 [M – 1]
11d	252–254	3.22 (s, 3 H), 5.64 (d, *J* = 3.0 Hz, 1 H), 7.06–7.14 (m, 2 H), 7.23–7.32 (m, 2 H), 8.48 (d, *J* = 3.0 Hz, 1 H), 8.73 (br s, 1 H), 10.28 (br s, 1 H)	29.09, 47.88, 115.43, 124.29, 128.79, 129.36, 129.60, 149.79, 153.48, 159.08, 161.03	265 [M – 1]
11e	167–169	2.73 (s, 0.51 H), 3.20 (s, 3 H), 5.28 (m, 1 H), 5.71–5.74 (m, 1.17 H), 6.18 (d, *J* = 7.2 Hz, 2 H), 7.06 (t, *J* = 7.4 Hz, 1 H), 7.19–7.53 (m, 7.53 H), 8.54 (d, *J* = 3.6 Hz, 1 H), 8.81 (d, *J* = 4.0 Hz, 0.17 H), 11.12 (s, 0.17 H)	–	405 [M + 1] 403 [M – 1]
11f	180–182	4.52–4.60 (m, 3.5 H), 5.09–5.14 (m, 1.5 H), 5.32 (m, 0.25 H), 5.64 (s, 0.25 H), 5.90 (d, *J* = 3.0 Hz, 1 H), 6.72–7.31 (m, 17.75 H), 10.42 (br s, 1 H)[c]	–	495 [M + 1] 493 [M – 1]
11g	186–188	5.03 (m, 2 H), 5.31 (m, 1 H), 5.78 (d, *J* = 2.4 Hz, 1 H), 6.14 (d, *J* = 7.5 Hz, 2 H), 7.04 (t, *J* = 6.6 Hz, 1 H), 7.21–7.38 (m, 9 H), 7.47 (s, 1 H), 7.55 (d, *J* = 8.1 Hz, 1 H), 8.63 (d, *J* = 4.0 Hz, 1 H)	45.17, 52.26, 78.75, 120.06, 122.79, 124.50, 125.53, 127.35, 127.91, 128.57, 129.49, 129.71, 131.60, 132.07, 137.90, 139.06, 144.46, 147.08, 152.41	481 [M + 1]
11h	171–173	2.80 (s, 1.14 H), 3.40 (s, 3 H), 3.76 (s, 3 H), 3.82 (1.14 H), 5.34 (m, 2 H), 5.99 (d, *J* = 0.38 H)[c]	–	435 [M + 1] 433 [M – 1]
11i	176–178	3.16 (s, 0.6 H), 3.22 (s, 3 H), 4.52 (d, *J* = 15.2 Hz, 0.2 H), 4.60 (d, *J* = 15.2 Hz, 0.2 H), 4.67 (d, *J* = 13.6 Hz, 0.2 H), 4.81 (d, *J* = 13.6 Hz, 0.2 H), 5.57 (s, 0.2 H), 5.76 (d, *J* = 4.4 Hz, 1 H), 6.93 (m, 0.2 H), 7.11 (m, 0.4 H), 7.30–7.68 (m, 8.4 H), 8.03–8.19 (m, 2.4 H), 8.47 (s, 0.2 H), 8.82 (d, *J* = 4.4 Hz, 1 H), 10.33 (br s, 1 H)	–	384 [M + 1] 382 [M – 1]
11j	236–238	2.74 (s, 3 H), 3.24 (s, 2.43 H), 3.73 (s, 2.43 H), 3.81 (s, 3 H), 5.43–5.46 (m, 1 H), 5.90–5.93 (m, 1.81 H), 6.18 (d, *J* = 8.1 Hz, 1.62 H), 6.76 (d, *J* = 8.1 Hz, 1.62 H), 7.00 (d, *J* = 7.8 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 1.62 H), 7.42–7.53 (m, 3.62 H), 8.15–8.27 (m, 3.62 H), 8.54 (d, *J* = 2.7 Hz, 0.81 H), 8.79 (d, *J* = 2.4 Hz, 1 H), 11.38 (s, 0.81 H)	–	400 [M + 1] 398 [M – 1]
11k	221–223	3.20 (s, 3 H), 3.23 (s, 3 H), 5.77 (d, *J* = 4.0 Hz, 1 H), 7.63 (m, 2 H), 8.08 (s, 1 H), 8.12 (s, 1 H), 8.77 (d, *J* = 4.0 Hz, 1 H), 10.13 (br s, 1 H)	33.49, 34.46, 51.49, 109.21, 121.10, 123.16, 130.89, 132.77, 144.48, 148.45, 153.15, 156.10	306 [M – 1]
11l	263–265	3.21 (s, 3 H), 5.62 (d, *J* = 2.7 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 8.15 (d, *J* = 8.1 Hz, 2 H), 8.67 (d, *J* = 2.7 Hz, 1 H), 8.79 (br s, 1 H), 10.19 (br s, 1 H)	29.42, 51.65, 105.33, 123.78, 127.85, 146.96, 149.45, 150.07, 153.51	292 [M – 1]

Table 5 Analytical Data for Compounds **6**, **10**, **11**, **13** and **14**[a] (continued)

Compd	Mp (°C)[b]	^{1}H NMR, DMSO-d_6 (δ ppm)	^{13}C NMR, DMSO-d_6 (δ ppm)	MS (APCI), *m*/*z*
11m	207–209	2.76 (s, 0.96 H), 3.22 (s, 3 H), 5.44 (m, 1 H), 5.82 (d, *J* = 4.4 Hz, 1 H), 5.88 (d, *J* = 4.8 Hz, 0.32 H), 6.23 (d, *J* = 7.6 Hz, 2 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 7.15–7.30 (m, 3.28 H), 7.42 (t, *J* = 8.0 Hz, 0.32 H), 7.55–7.62 (m, 2.64 H), 8.25 (d, *J* = 8.0 Hz, 0.32 H), 8.31 (d, *J* = 8.8 Hz, 2 H), 8.64 (d, *J* = 4.4 Hz, 1 H), 8.92 (d, *J* = 4.8 Hz, 0.32 H), 11.12 (s, 0.32 H)	–	370 [M + 1] 368 [M – 1]
11n	218–220	2.8 (s, 0.36 H), 3.20 (s, 3 H), 5.43 (m, 1 H), 5.86 (d, *J* = 2.0 Hz, 0.12 H), 5.93 (s, 1 H), 6.22 (d, *J* = 8.0 Hz, 2 H), 7.25 (m, 2.48 H), 7.40 (d, *J* = 8.4 Hz, 0.12 H), 8.26 (m, 2.24 H), 8.67 (d. *J* = 4.0 Hz, 1 H), 8.90 (d, *J* = 2.0 Hz, 0.12 H), 10.88 (s, 0.12 H)	–	405 [M + 1] 403 [M – 1]
11o	203–205	2.72 (s, 1.38 H), 3.20 (s, 3 H), 3.72 (3 H), 3.80 (s, 1.38 H), 5.43 (m, 1 H), 5.87 (m, 1.46 H), 6.17 (d, *J* = 8.1 Hz, 2 H), 6.78 (d, J = 8.1 Hz, 2 H), 6.99 (d, *J* = 8.1 Hz, 0.92 H), 7.18 (d, *J* = 8.1 Hz, 0.92 H), 7.54–7.60 (m, 2.92 H), 8.22 (d, *J* = 7.8 Hz, 0.92 H), 8.28 (d, *J* = 7.8 Hz, 2 H), 8.59 (d, *J* = 2.5 Hz, 1 H), 8.85 (d, *J* = 3.3 Hz, 0.46 H), 11.38 (s, 0.46 H)	–	400 [M + 1] 398 [M – 1]
11p	180–182	3.33 (s, 3 H), 4.64 (dd, J^1 = 5.2 Hz, J^2 = 12.8 Hz, 2 H), 5.89 (d, *J* = 4.0 Hz, 1 H), 6.42 (d, *J* = 4.0 Hz, 1 H), 7.05 (d, *J* = 8.4 Hz, 1 H), 7.15–7.39 (m, 7 H), 10.63 (br s, 1 H)[c]	–	409 [M + 1] 407 [M – 1]
11q	199–201	2.27 (s, 3 H), 2.33 (s, 1.11 H), 2.70 (s, 1.11 H), 3.20 (s, 3 H), 5.26 (m, 1 H), 5.74 (d, *J* = 3.3 Hz, 0.37 H), 5.79 (s, 1 H), 6.12 (d, *J* = 8.1 Hz, 2 H), 7.05 (d, *J* = 8.1 Hz, 2 H), 7.10–7.26 (m, 2.85 H), 7.47–7.65 (m, 2.74 H), 8.56 (d, *J* = 3.9 Hz, 1 H), 8.81 (d, *J* = 3.3 Hz, 0.37 H), 11.23 (s, 0.37 H)	–	409 [M + 1] 407 [M – 1]
13a	243–245	3.75–3.93 (m, 4 H), 5.43 (d, *J* = 3.0 Hz, 1 H), 7.27–7.30 (m, 5 H), 8.29 (d, *J* = 3.0 Hz, 1 H), 9.42 (br s, 1 H)	42.89, 43.35, 53.49, 103.53, 126.43, 127.56, 128.34, 142.55, 149.98, 151.81	261 [M + 1]
13b	239–241	2.01 (m, 2 H), 3.48–3.81 (m, 4 H), 5.62 (d, *J* = 3.3 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.69 (d, *J* = 7.5 Hz, 1 H), 8.10–8.14 (m, 2 H), 8.64 (d, *J* = 3.3 Hz, 1 H), 11.06 (br s, 1 H)	18.96, 38.78, 39.17, 51.58, 104.41, 121.36, 122.58, 130.15, 132.92, 144.40, 147.67, 149.56, 150.52	320 [M + 1]
13c	233–235	1.91 (m, 2 H), 3.45–3.83 (m, 4 H), 5.61 (d, *J* = 2.4 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 8.15 (d, *J* = 8.0 Hz, 2 H), 8.63 (d, *J* = 2.4 Hz, 1 H), 11.04 (s, 1 H)	19.45, 39.32, 40.36, 52.20, 104.90, 124.19, 128.40, 147.38, 150.00, 150.11, 150.97	320 [M + 1]
13d	258–260	3.78–3.96 (m, 4 H), 5.48 (d, *J* = 2.7 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 1 H), 7.49 (s, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 8.32 (d, *J* = 2.7 Hz, 1 H), 9.49 (br s, 1 H)	42.89, 43.40, 52.82, 102.63, 126.88, 128.74, 130.13, 130.59, 130.86, 143.53, 149.52, 151.66	331 [M + 1]
14a	216–218	5.57 (s, 1 H), 6.83 (d, *J* = 7.2 Hz, 2 H), 7.00 (t, *J* = 7.2 Hz, 1 H), 7.30–7.48 (m, 7 H), 10.95 (s, 1 H)	28.00, 90.92, 121.60, 122.25, 126.41, 128.81, 129.14, 130.58, 132.04, 146.46, 149.85, 150.84, 151.45	278 [M + 1]
14b	252–254	5.23 (s, 2 H), 5.60 (s, 1 H), 6.71 (d, *J* = 7.5 Hz, 2 H), 6.97 (t, *J* = 7.2 Hz, 1 H), 7.25–7.60 (m, 9 H), 7.59 (d, *J* = 7.2 Hz, 1 H), 7.70 (s, 1 H), 10.99 (s, 1 H)	43.30, 91.74, 121.34, 121.79, 122.30, 125.59, 126.68, 127.54, 128.00, 129.02, 129.13, 130.74, 133.16, 134.24, 137.52, 145.30, 149.23, 149.82, 151.11	434 [M + 1]
14c	238–240	3.47 (s, 3 H), 3.81 (s, 3 H), 5.99 (s, 1 H), 6.79 (d, *J* = 8.7 Hz, 2 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 7.63 (t, *J* = 8.1 Hz, 1 H), 7.86 (d, *J* = 7.5 Hz, 1 H), 8.31 (d, *J* = 7.5 Hz, 1 H), 8.59 (s, 1 H), 11.02 (s, 1 H)[c]	28.19, 55.06, 92.11, 114.44, 121.36, 122.72, 124.83, 130.29, 132.91, 147.77, 151.79, 155.15 (other signals absent)	353 [M + 1]

Table 5 Analytical Data for Compounds **6**, **10**, **11**, **13** and **14**[a] (continued)

Compd	Mp (°C)[b]	^{1}H NMR, DMSO-d_6 (δ ppm)	^{13}C NMR, DMSO-d_6 (δ ppm)	MS (APCI), *m/z*
14d	270–272	3.30 (s, 3 H), 3.74 (s, 3 H), 5.78 (s, 1 H), 6.84 (d, *J* = 8.1 Hz, 2 H), 6.90 (d, *J* = 8.1 Hz, 2 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 8.23 (d, *J* = 8.4 Hz, 2 H), 10.85 (br s, 1 H)	28.22, 55.07, 114.45, 122.82, 123.72, 128.00, 148.28, 151.66, 155.24 (other signals absent)	353 [M + 1]
14e	217–219	3.42 (s, 3 H), 4.60 (s, 2 H), 6.21 (s, 1 H), 7.23–7.41 (m, 5 H), 7.59 (d, *J* = 8.7 Hz, 1 H), 7.87 (d, *J* = 8.7 Hz, 1 H), 8.10 (s, 1 H), 8.13 (s, 1 H)	29.31, 45.21, 82.54, 126.87, 126.93, 127.06, 128.36, 128.60, 130.49, 131.29, 132.90, 137.87, 138.14, 155.66, 157.49, 162.28	362 [M + 1]
14f	263–265	2.28 (s, 3 H), 3.32 (s, 3 H), 5.62 (s, 1 H), 6.66 (d, *J* = 7.2 Hz, 2 H), 7.06 (d, *J* = 7.2 Hz, 2 H), 7.39 (d, *J* = 7.8 Hz, 1 H), 7.59 (d, *J* = 7.8 Hz, 1 H), 7.74 (s, 1 H), 10.94 (s, 1 H)	20.27, 27.99, 91.23, 121.52, 126.62, 128.36, 129.49, 130.73, 131.20, 131.43, 132.87, 132.97, 143.62, 146.04, 150.75, 151.43	362 [M + 1]

[a] Satisfactory microanalysis obtained: C ±0.30, H ±0.08, N ±0.16.
[b] Melting points are uncorrected.
[c] Recorded in $CDCl_3$.

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