Diaminomethylidene derivatives of β-oxo sulfones as potential reagents in heterocyclic synthesis and chelating ligands

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Active methylene β-oxo sulfones add to the C≡N bond of benzoylcyanamide in the presence of catalytic amounts of $Ni(acac)_2$. Debenzoylation of the reaction products under the action of MeONa in MeOH gives *N*,*N*´-unsubstituted diaminomethylidene derivatives of β-oxo sulfones (acyl(R-sulfonyl)ketene aminals), which can be used as reagents for heterocyclic synthesis and as chelating ligands. The syntheses of 2-amino-3-arylsulfonylpyridin-4(1*H*)-ones and 5-sulfonylcytosine derivatives are presented as examples.

Key words: β-oxo sulfones, benzoylcyanamide, nickel acetylacetonate, catalysis, diaminomethylidene derivatives of β-oxo sulfones, 5-sulfonylcytosines, diphenylboron chelates, 2-amino-3-arylsulfonylpyridin-4(1*H*)-ones, intramolecular cyclization.

We found two decades ago that active methylene β-diketones and β-oxo esters add to the C≡N bond of cyanamides in the presence of catalytic or stoichiometric amounts of $Ni(acac)_2$ or $Ni(OAc)_2$ to give α,α-dioxo ketene aminals,[1—5] which were used in various schemes of designing nitrogen-containing heterocyclic systems and in the synthesis of B and Ni chelate complexes.[6—11]

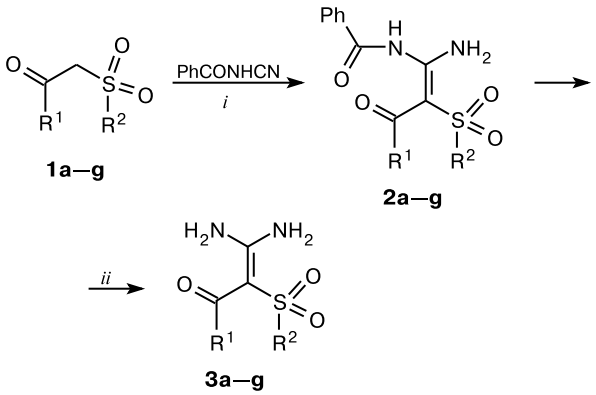
As reported in our latest communications,[12,13] ketene aminals with two unsubstituted NH_2 groups are most efficient in heterocyclization reactions, probably because of both electronic and steric effects. Such reagents can conveniently be prepared by debenzoylation of adducts of appropriate β-dicarbonyl compounds (including barbituric acid[14]) and benzoylcyanamide.

To obtain new diaminomethylidene reagents combining acyl and sulfonyl functions, we studied reactions of β-oxo sulfones **1a**—**g** with benzoylcyanamide. It turned out that these reactions in boiling dioxane in the presence of $Ni(acac)_2$ give *N*-benzoyl ketene aminals **2a**—**g** in moderate yields, which are easily converted into *N*,*N*´-unsubstituted diaminomethylidene derivatives of oxo sulfones **3a**—**g** upon treatment with MeONa in MeOH (Scheme 1).

It has been proved that the catalytic cycle in addition reactions of cyanamides with acyclic β-diketones and β-oxo esters involves the formation of nickel chelates with β-dicarbonyl compounds;[7] however, we detected no chelate intermediates in reaction mixtures of oxo sulfones and benzoylcyanamide.

Nevertheless, cyclic β-diketones, which cannot act as chelating ligands, have been found[2,14] to efficiently add to the C≡N bond of cyanamides in the presence of equimolar amounts of $Ni(OAc)_2$ (apparently, the reaction involves nickel derivatives of the enolized diketone). One could assume that oxo sulfones would behave alike. However, our attempts to promote the reactions of compounds **1a**—**g** with benzoylcyanamide using $Ni(OAc)_2$ failed. That is why the catalytic effect of $Ni(acac)_2$ in the synthesis of aminals **2** is rather difficult to explain. One can only assume that compounds **1** can produce enol intermediates that add to

Scheme 1



	R^1	R^2		R^1	R^2
a	Ph	Ph	**e**	Me	Ph
b	Ph	4-MeC_6H_4	**f**	Me	4-MeC_6H_4
c	Ph	4-$MeOC_6H_4$	**g**	Me	4-$MeOC_6H_4$
d	Ph	Me			

Reagents and conditions: *i.* 10 mol.% $Ni(acac)_2$, dioxane, Δ; *ii.* MeONa, MeOH, 20 °C.

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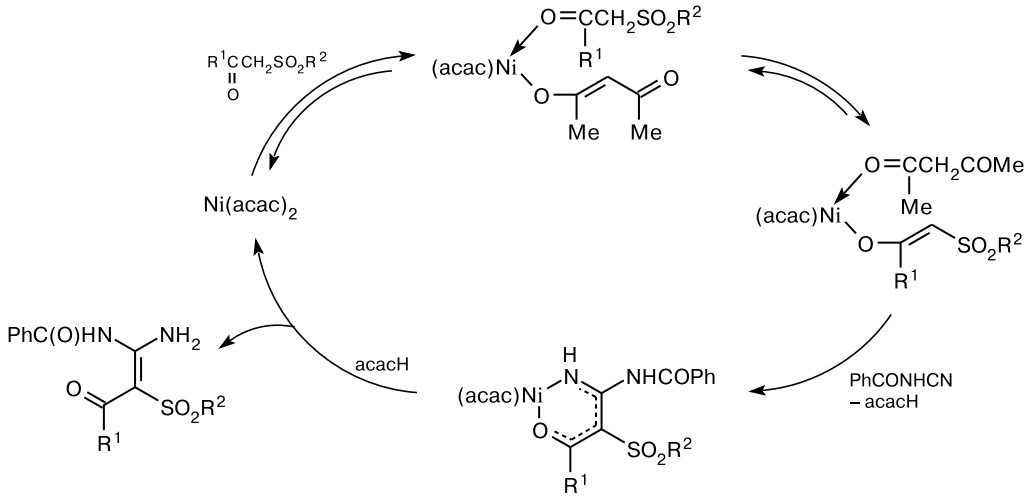
Scheme 2



benzoylcyanamide as illustrated in Scheme 2. Such metal enolates are believed to form, *e.g.*, in the alcoholysis of metal β-diketonates.[15]

Apparently, the formation of Ni enolates from $Ni(OAc)_2$ is prevented by the liberation of AcOH.

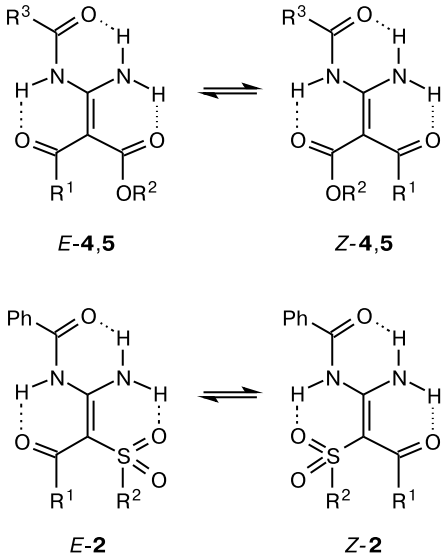
Ketene aminals **2** and **3** are colorless crystalline solids that are well soluble in acetone, DMSO, and DMF but are insoluble in hexane. Compounds **2** are well soluble in chloroform and moderately soluble in alcohols, while aminals **3** are poorly soluble in chloroform and well soluble in alcohols. Their mass spectra (EI) contain very weak molecular ion peaks and the intense peaks $[M - SO_2]^+$. The IR (KBr) and ^1H NMR spectra ($CDCl_3$, DMSO-d_6) fully agree with structures **2** and **3**.

Like previously described *N*-benzoyl and *N*-arylureido derivatives of acyl(alkoxycarbonyl)ketene aminals **4** and **5**, compounds **2** relate to push-pull systems with very low barriers to rotation about the C=C bond (see the reviews[16,17]). Their ^1H NMR spectra in DMSO-d_6 show one set of signals. In neutral solvents, however, the rotation is hindered by intramolecular hydrogen bonding (N—H···O bonds) and the spectra of compounds **4** and **5** in $CDCl_3$ indicate the presence of the *E*- and *Z*-isomers in dynamic equilibrium[13] (Scheme 3).

A similar pattern is observed in the spectra of sulfonyl ketene aminals (the ratio of the isomers is ~3.5 : 1). As with compounds **4** and **5** (for our arguments, see Ref. 13), the lowest-field signal for the NH proton at δ ~15.3—15.7 should be assigned to the dominant *E*-isomer (for the minor *Z*-isomer, the lowest-field signal for the NH proton appears at δ 12.4—12.7).

Compounds **2a**—**g** and **3a**—**g** are stable in air and remain unchanged when stored. Despite the low yields of *N*-benzoylaminals **2** (Table 1), their straightforward synthesis and smooth debenzoylation leading to *N*-unsubstituted ketene aminals **3** make compounds of the types **2** and **3** sufficiently promising reagents for heterocyclic synthesis and sulfonyl-containing chelating ligands.

Scheme 3



E-**4**,**5** *Z*-**4**,**5**

E-**2** *Z*-**2**

R^1 = Alk, Ar; R^2 = Alk; R^3 = Ph (**4**), ArNH (**5**)

This can be illustrated with the synthesis of 5-sulfonylcytosines from ketene aminals **3**. Like 2-(diaminomethylidene)-3-oxoalkanoic acid esters,[13] β-oxo sulfones **3e,f** react with phenyl isocyanate to give the corresponding ureas **6a,b**, which undergo cyclization in the presence of sodium methoxide into 4-amino-5-arylsulfonyl-6-methyl-1-phenylpyrimidin-2(1*H*)-ones **7a,b** (Scheme 4).

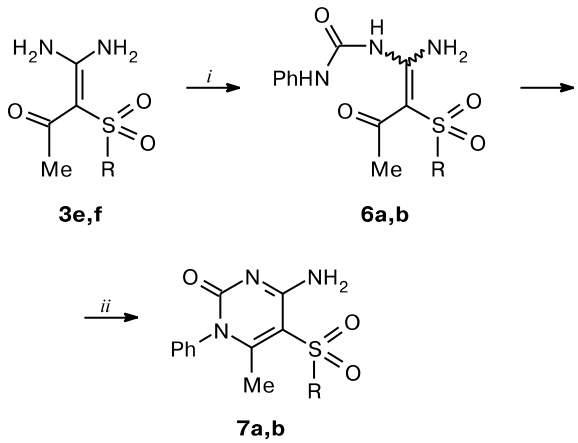
When slightly heated, crystalline ureas **6a,b** are soluble in DMSO and DMF but remain insoluble in chloroform.

Table 1. Yields, melting points, elemental analysis data, and IR spectra of compounds **2a**—**g** and **3a**—**g**

Compound	Yield (%)	M.p./°C	Found / Calculated (%)				Molecular formula	IR (KBr),[a] ν/cm^{-1}
			C	H	N	S		
2a[b]	36	187—188	64.59	4.53	6.94	7.82	$C_{22}H_{18}N_2O_4S$	3352, 3236, 1676, 1632, 1600, 1580,
			65.01	4.46	6.89	7.89		1556, 1328, 1284, 1136
2b[c]	42	240—241	65.73	4.77	6.52	7.60	$C_{23}H_{20}N_2O_4S$	3368, 3248, 1680, 1620, 1600, 1580,
			65.70	4.79	6.66	7.63		1552, 1320, 1284, 1132
2c[c]	39	212—213	62.99	4.64	6.63	7.34	$C_{23}H_{20}N_2O_5S$	3368, 3252, 1676, 1624, 1600, 1576,
			63.29	4.62	6.42	7.35		1552, 1496, 1332, 1284, 1136
2d[c]	38	232—233	59.02	4.71	8.30	9.25	$C_{17}H_{16}N_2O_4S$	3384, 3264, 1680, 1624, 1600, 1580,
			59.29	4.68	8.13	9.31		1544, 1348, 1280, 1128
2e[b]	20	147—148	59.54	4.69	8.13	9.34	$C_{17}H_{16}N_2O_4S$	3408, 3284, 1676, 1612, 1600, 1576,
			59.29	4.68	8.13	9.31		1556, 1364, 1300, 1128
2f[b]	20	134—135	60.31	5.00	7.71	9.00	$C_{18}H_{18}N_2O_4S$	3384, 3260, 1676, 1616, 1600, 1580,
			60.32	5.06	7.82	8.95		1560, 1496, 1364, 1300, 1132
2g[b]	24	153—154	57.75	4.93	7.51	8.82	$C_{18}H_{18}N_2O_5S$	3384, 3260, 1668, 1628, 1596, 1580,
			57.74	4.85	7.48	8.56		1556, 1500, 1364, 1300, 1128
3a[d]	84	127—128	59.23	4.74	8.96	10.72	$C_{15}H_{14}N_2O_3S$	3392, 3312, 3232, 1692, 1572,
			59.59	4.67	9.27	10.60		1536, 1504, 1312, 1148
3b	72	208—209	60.40	5.11	8.77	10.09	$C_{16}H_{16}N_2O_3S$	3424, 3332, 3252, 1636, 1572,
			60.74	5.10	8.85	10.13		1520, 1452, 1320, 1260, 1132
3c	77	217—218	57.65	4.72	8.50	9.49	$C_{16}H_{16}N_2O_4S$	3436, 3336, 3232, 1652, 1596,
			57.82	4.85	8.43	9.65		1556, 1496, 1312, 1260, 1132
3d[d]	91	183—184	50.20	4.96	11.80	12.98	$C_{10}H_{12}N_2O_3S$	3388, 3312, 3224, 1656, 1576,
			49.99	5.03	11.66	13.34		1520, 1412, 1304, 1256, 1120
3e[d]	77	155—156	50.22	4.96	11.85	12.94	$C_{10}H_{12}N_2O_3S$	3404, 3340, 3064, 1628, 1596,
			49.99	5.03	11.66	13.34		1520, 1492, 1360, 1248, 1124
3f[d]	96	163—164	52.34	5.42	11.20	12.45	$C_{11}H_{14}N_2O_3S$	3416, 3312, 3192, 1640, 1592,
			51.95	5.55	11.02	12.61		1520, 1496, 1320, 1272, 1144
3g[d]	44	157—158	49.03	5.13	10.40	11.73	$C_{11}H_{14}N_2O_4S$	3408, 3312, 3200, 1640, 1592,
			48.88	5.22	10.36	11.86		1556, 1496,1320, 1260, 1140

[a] The IR spectra of compounds **2a**—**g** and **3a**—**g** in the ranges 3450—3000 and 1700—1100 cm^{-1}.
[b] The melting points of the samples recrystallized from Pr^{i}OH—benzene.
[c] The melting points of the samples recrystallized from dioxane.
[d] The melting points of the samples recrystallized from benzene—methanol.

Scheme 4



R = Ph (**a**), 4-MeC$_6$H$_4$ (**b**)

Reagents and conditions: *i.* PhNCO, PhH, Δ; *ii.* MeONa, MeOH, 20 °C.

Their structures were confirmed by mass spectrometry. In their ^{1}H NMR spectra (DMSO-d$_6$), as in the spectra of similar push-pull compounds **5**, each of the four NH protons appears as a broadened singlet (δ ~9.5, 9.8, 10.4, and 13.2). The *E*- and *Z*-isomers keep indistinguishable because compounds **6a,b** are insoluble in $CDCl_3$.

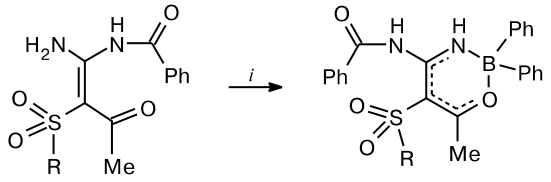
Cytosines **7a,b** are white crystalline solids that are well soluble in DMF and DMSO and moderately soluble in chloroform. In their mass spectra (EI), the peaks $[M - SO_2 - H]^+$ have a maximum intensity. The ^{1}H NMR spectra in DMSO-d$_6$ show, apart from signals for the protons of two aryl groups and a signal at δ ~2.15 (Me), two broadened singlets for the NH protons at ~7.60 and ~8.00. In the 2D spectrum (^{1}H/^{15}N HMBC NMR, DMSO-d$_6$), the signals for two NH protons at δ 7.58 and 8.02 correspond to the same chemical shift of the signal for the N atom (δ −278). Therefore, cytosine **7a** contains the NH_2 group, existing in the form of an amino rather than imino tautomer.

Current interest in 5-substituted cytosine derivatives is worth noting (see Ref. 13 and references cited therein). An earlier[18] proposed route to 4-amino-5-sulfonylcytosines, which are structural analogs of compounds **7a,b**, starts from (phenylsulfonyl)acetonitrile and *N*-cyano imidates. However, this approach seems to be unsuitable for the synthesis of 1-substituted cytosines.

Compounds **2** and **3** are functionalized aminovinyl ketones, so they could be expected to form chelate complexes with boron (see, *e.g.*, Refs 6, 10, and 11 about boron chelates with mono- and diacylketene aminals).

Indeed, borylation of aminals **2e,f** with methoxy(diphenyl)borane gave crystalline diphenylboron chelates **8a,b** (Scheme 5).

Scheme 5



R = Ph (**a**), 4-MeC_6H_4 (**b**)

Reagents and conditions: *i.* Ph_2BOMe, *o*-xylene, Δ.

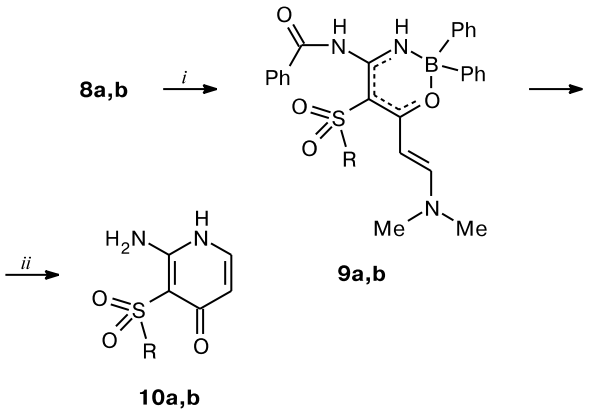
Diphenylboron chelates **8a,b** are air-stable white solids that are well soluble in most organic solvents, except for hexane. The ^{11}B NMR spectrum of chelate **8a** in *o*-xylene shows a signal characteristic of tetracoordinated boron (δ 2.0). The ^1H NMR spectra in $CDCl_3$ exhibit two broadened singlets for the NH protons and a downfield shift (δ 2.49) of the singlet for the methyl protons compared to the starting ketene aminals (δ 2.20), which suggests the coordination of the acetyl group of compounds **2e**,**f** to the B atom. The mass spectra of chelates **8a**,**b** contain characteristic intense peaks of the ions $[M - Ph]^+$.

Using our strategy developed earlier,[6] we obtained sulfonylpyridones (Scheme 6). Condensation of diphenylboron chelates **8a**,**b** with dimethylformamide dimethyl acetal (DMF DMA) in boiling THF yielded chelate complexes **9a**,**b** with an enamine fragment in the side chain.

Compounds **9a,b** are yellow crystalline solids that are insoluble only in hexane. Their mass spectra also contain intense peaks of the ions $[M - Ph]^+$. The ^1H NMR spectra in $CDCl_3$ show two singlets for the NMe_2 protons (δ 2.86 and 3.16) and two doublets for the protons at the double bond of the dimethylaminovinyl substituent (δ ~6.0 and ~7.9). The coupling constant (~12 Hz) suggests the *E*-configuration of the enamine fragment.

In boiling butanol, chelates **9a,b** decompose and the free ligands undergo cyclization into 2-amino-3-arylsulfonylpyridin-4(1*H*)-ones **10a,b**. It is interesting that the

Scheme 6



R = Ph (**a**), 4-MeC_6H_4 (**b**)

Reagents and conditions: *i.* DMF DMA, THF, Δ; *ii.* BuOH, Δ.

heterocyclization is accompanied by debenzoylation in the presence of a liberated base (dimethylamine), while in similar syntheses of pyridone derivatives from boron chelates prepared from diacetylketene aminals, the benzoyl group is retained.[6]

Pyridones **10a,b** are white crystalline solids well soluble in DMSO and DMF. Their mass spectra contain intense molecular ion peaks. The ^1H NMR spectra in DMSO-d_6 show, apart from signals for the aromatic protons (H(5), H(6) of pyridine, and RSO_2), two broadened singlets for the NH and NH_2 protons (δ ~10.50 and ~7.20, respectively). In the ^{13}C NMR spectrum (DMSO-d_6), the signals for the C(4), C(5), and C(6) atoms of the pyridine ring are strongly broadened, thus suggesting the dynamic equilibrium pyridone—hydroxypyridine. However, this equilibrium is appreciably shifted toward pyridone, which is evident from the chemical shifts of the signals for the C(4), C(5), and C(6) atoms (δ 173.77, 112.14, and 135.58, respectively; *cf.* data for 3-acetyl-2-amino-4-pyridone[19]).

The presented examples of the synthesis of pyridines and pyrimidines from ketene aminals **2** and **3** undoubtedly demonstrate that these reagents can be employed more widely for the design of sulfonyl-containing heterocyclic systems.

Experimental

^1H NMR spectra were recorded on a Bruker AM-300 instrument (300 MHz). ^{13}C NMR and 2D spectra ($^1H/^{13}C$ and $^1H/^{15}N$ HMBC) were recorded on a Bruker Avance 600 instrument (600 (^1H), 150 (^{13}C), and 60.8 MHz (^{15}N)) with residual signals of the nondeuterated solvent as the internal standards: δ 7.27 for $CDCl_3$ and δ 2.50 for DMSO-d_6 (^1H) and δ 39.50 for DMSO-d_6 (^{13}C). The ^{15}N chemical shifts are referenced to $MeNO_2$ as the external standard (high-field signals are cited with a minus sign). IR spectra were recorded on a Specord-M82 instrument; mass spectra were measured on a Kratos MS-30 instrument (EI, 70 eV,

ion source temperature 250 °C, direct inlet probe). High-resolution mass spectra were recorded on a Bruker micrOTOF II instrument (ESI,[20] positive ions (capillary voltage 4500 V), scan range m/z 50—3000 D, external calibration). Samples were syringed as solutions in acetonitrile, flow rate 3 mL min^{-1}, nitrogen as a spraying gas (4 L min^{-1}), interface temperature 180 °C. Phenyl isocyanate, dimethylformamide dimethyl acetal (Lancaster), and dry dioxane were used. Benzene and THF were dehydrated by distillation over Na; methanol and butanol were distilled before use. The starting β-oxo sulfones[21] and methyl diphenylboronate[22] were prepared according to known procedures.

Acyl(R-sulfonyl)ketene *N*-benzoylaminals 2a—g (general procedure). Nickel acetylacetonate (10 mol.%) was added to a solution of an appropriate oxo sulfone **1a—g** (1.9 mmol) and benzoylcyanamide (1.9 mmol) in dioxane (5 mL). The reaction mixture was refluxed for 10 h. Workup was carried out in two ways (methods A and B).

Method A. The solvent was evaporated *in vacuo* to dryness. The residue was diluted with Pr^iOH and heated. The undissolved precipitate was filtered off and washed with hot Pr^iOH. The filtrate was concentrated and the residue was recrystallized from Pr^iOH—benzene. This procedure was used to obtain 3-amino-3-benzoylamino-1-phenyl-2-phenylsulfonylprop-2-en-1-one (**2a**), 4-amino-4-benzoylamino-3-phenylsulfonylbut-3-en-2-one (**2e**), 4-amino-4-benzoylamino-3-(4-tolylsulfonyl)-but-3-en-2-one (**2f**), and 4-amino-4-benzoylamino-3-(4-methoxyphenylsulfonyl)but-3-en-2-one (**2g**).

Method B. The precipitate produced by the reaction was filtered off and washed with dioxane. The solvent was evaporated *in vacuo* to dryness and the residue was recrystallized from dioxane. This procedure was used to obtain 3-amino-3-benzoylamino-1-phenyl-2-(4-tolylsulfonyl)prop-2-en-1-one (**2b**), 3-amino-3-benzoylamino-2-(4-methoxyphenylsulfonyl)-1-phenylprop-2-en-1-one (**2c**), and 3-amino-3-benzoylamino-2-methylsulfonyl-1-phenylprop-2-en-1-one (**2d**). The yields, melting points, elemental analysis data, and IR spectra of the compounds obtained are given in Table 1; their ^{1}H NMR and mass spectra are presented in Table 2.

Acyl(R-sulfonyl)ketene aminals 3a—g (general procedure). Sodium methoxide (0.55 mmol) in MeOH (1 mL) was added to an appropriate ketene aminal **2a—g** (0.55 mmol) in MeOH (5 mL). The reaction mixture was stirred for 1 h and acidified with acetic acid. Workup was carried out in two ways (methods A and B).

Method A. The solvent was evaporated *in vacuo* to dryness and chloroform was added. The undissolved sodium acetate was filtered off, the filtrate was concentrated, and the residue was diluted with light petroleum. The resulting precipitate was filtered off and, if required, recrystallized from benzene—methanol. This procedure was used to obtain 3,3-diamino-1-phenyl-2-phenylsulfonylprop-2-en-1-one (**3a**), 3,3-diamino-2-methylsulfonyl-1-phenylprop-2-en-1-one (**3d**), 4,4-diamino-3-phenylsulfonylbut-3-en-2-one (**3e**), 4,4-diamino-3-(4-tolylsulfonyl)-but-3-en-2-one (**3f**), and 4,4-diamino-3-(4-methoxyphenylsulfonyl)but-3-en-2-one (**3g**).

Method B. The precipitate was filtered off and washed with diethyl ether. This procedure was used to obtain 3,3-diamino-1-phenyl-2-(4-tolylsulfonyl)prop-2-en-1-one (**3b**) and 3,3-diamino-2-(4-methoxyphenylsulfonyl)-1-phenylprop-2-en-1-one (**3c**). The yields, melting points, elemental analysis data, and IR spectra of the compounds obtained are given in Table 1; their ^{1}H NMR ($CDCl_3$ and DMSO-d_6) and mass spectra are presented in Table 2.

4-Amino-3-phenylsulfonyl-4-(*N*′-phenylureido)but-3-en-2-one (6a). Phenyl isocyanate (0.09 mL, 0.83 mmol) was added to ketene aminal **3e** (0.2 g, 0.83 mmol) in dry benzene (3 mL). The reaction mixture was refluxed for 16 h. The precipitate that formed was filtered off and washed with benzene. The resulting white crystalline solid is soluble only in DMF and DMSO on slight heating. Yield 0.25 g (84%), m.p. 164—165 °C. Found (%): C, 56.92; H, 4.76; N, 11.74; S, 8.61. $C_{17}H_{17}N_3O_4S$. Calculated (%): C, 56.81; H, 4.77; N, 11.69; S, 8.92. MS, m/z (I_{rel} (%)): 359 $[M]^+$ (3), 294 $[M - SO_2 - H]^+$ (29), 176 $[M - PhNCO - SO_2]^+$ (79), 175 $[M - PhNCO - SO_2 - H]^+$ (87), 161 $[M - PhNCO - SO_2 - Me]^+$ (42), 141 $[PhSO_2]^+$ (45), 119 $[PhNCO]^+$ (88), 101 (95), 93 $[PhNH_2]^+$ (100). IR (KBr, 3400—2900, 1710—1500 cm^{-1}), ν/cm^{-1}: 3364 (NH), 3260—2950 (NH, CH), 1708 (CO), 1640, 1532. ^{1}H NMR (DMSO-d_6), δ: 2.17 (s, 3 H, Me); 7.09 (t, 1 H, *p*-PhNH, J = 7.8 Hz); 7.33 (t, 2 H, *m*-PhNH, J = 7.8 Hz); 7.50 (d, 2 H, *o*-PhNH, J = 7.8 Hz); 7.64 (m, 3 H, *m*-$PhSO_2$, *p*-$PhSO_2$); 7.91 (d, 2 H, *o*-PhSO_2, J = 7.8 Hz); 9.50 (br.s, 1 H, NH); 9.84 (br.s, 1 H, NH); 10.43 (br.s, 1 H, NH); 13.20 (br.s, 1 H, NH).

4-Amino-4-(*N*′-phenylureido)-3-(4-tolylsulfonyl)but-3-en-2-one (6b) was obtained as described for urea **6a** from ketene aminal **3f** and PhNCO. Yield 79%, m.p. 174—175 °C. Found (%): C, 58.01; H, 5.08; N, 11.32; S, 8.45. $C_{18}H_{19}N_3O_4S$. Calculated (%): C, 57.90; H, 5.13; N, 11.25; S, 8.59. MS, m/z (I_{rel} (%)): 373 $[M]^+$ (1), 291 $[M - SO_2 - H_2O]^+$ (24), 290 $[M - SO_2 - H_2O - H]^+$ (74), 221 $[M - SO_2 - CO - NH_2CN - H_2O]^+$ (27), 189 (44), 155 $[SO_2C_6H_4Me]^+$ (45), 119 $[PhNCO]^+$ (100). IR (KBr, 3400—2900, 1710—1500 cm^{-1}), ν/cm^{-1}: 3368 (NH), 3280—3000 (NH, CH), 1708 (CO), 1640, 1532. ^{1}H NMR (DMSO-d_6), δ: 2.18 (s, 3 H, COMe); 2.39 (s, 3 H, Me); 7.08 (t, 1 H, *p*-Ph, J = 7.8 Hz); 7.33 (t, 2 H, *m*-Ph, J = 7.8 Hz); 7.42 (d, 2 H, *m*-C_6H_4Me, J = 7.8 Hz); 7.50 (d, 2 H, *o*-Ph, J = 7.8 Hz); 7.78 (d, 2 H, *o*-C_6H_4Me, J = 7.8 Hz); 9.51 (br.s, 1 H, NH); 9.79 (br.s, 1 H, NH); 10.36 (br.s, 1 H, NH); 13.17 (br.s, 1 H, NH).

4-Amino-6-methyl-1-phenyl-5-phenylsulfonylpyrimidin-2(1*H*)-one (7a). Sodium methoxide (0.7 mmol) in MeOH (1 mL) was added to urea **6a** (0.25 g, 0.7 mmol) in MeOH (5 mL). The reaction mixture was stirred for 1 h. The precipitate that formed was filtered off, washed with methanol, and dried. The resulting white crystalline solid is well soluble in DMF and moderately soluble in chloroform. Yield 0.18 g (75%), m.p. 293—294 °C. Found (%): C, 59.66; H, 4.48; N, 12.23; S, 8.93. $C_{17}H_{15}N_3O_3S$. Calculated (%): C, 59.81; H, 4.43; N, 12.31; S, 9.39. MS, m/z (I_{rel} (%)): 341 $[M]^+$ (11), 276 $[M - SO_2 - H]^+$ (100), 83 (25). High-resolution MS: found: m/z 342.0922 $[M + H]^+$. $C_{17}H_{15}N_3O_3S$. Calculated: $[M + H]^+$ = 342.0907. IR (KBr), ν/cm^{-1}: 3428 (NH), 3360—2920 (NH, CH), 1648, 1564, 1484, 1452, 1376, 1300, 1280, 1152, 1080, 1044, 784, 720, 704, 688, 628. ^{1}H NMR ($CDCl_3$), δ: 2.21 (s, 3 H, Me); 6.43 (br.s, 1 H, NH); 7.11 (d, 2 H, *o*-PhN, J = 7.8 Hz); 7.49 (m, 3 H, *m*-PhN, *p*-PhN); 7.58 (t, 2 H, *m*-$PhSO_2$, J = 7.8 Hz); 7.67 (t, 1 H, *p*-$PhSO_2$, J = 7.8 Hz); 7.93 (d, 2 H, *o*-$PhSO_2$, J = 7.8 Hz); 8.15 (br.s, 1 H, NH). ^{1}H NMR (DMSO-d_6), δ: 2.16 (s, 3 H, Me); 7.30 (d, 2 H, *o*-PhN, J = 7.8 Hz); 7.43 (t, 1 H, *p*-PhN, J = 7.8 Hz); 7.48 (t, 2 H, *m*-PhN, J = 7.8 Hz); 7.58 (br.s, 1 H, NH); 7.67 (t, 2 H, *m*-$PhSO_2$, J = 7.8 Hz); 7.75 (t, 1 H, *p*-$PhSO_2$, J = 7.8 Hz); 7.99 (d, 2 H, *o*-$PhSO_2$, J = 7.8 Hz); 8.02 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 19.97 (Me); 103.62 (C(5)); 125.95 (*o*-PhS); 128.22 (*o*-PhN); 128.60 (*p*-PhN);

Table 2. ^{1}H NMR ($CDCl_3$ and DMSO-d_6) and mass spectra of compounds **2a**—**g** and **3a**—**g**

Compound	^{1}H NMR (δ, *J*/Hz)		MS, *m/z* (I_{rel} (%))
	$CDCl_3$	DMSO-d_6	
2a[a]	*E*-isomer: 7.00—7.69 (m, 13 H, 3 Ph); 8.11 (d, 2 H, Ph, *J* = 7.8); 9.35, 10.38 (both br.s, 2 H, NH_2); 15.35 (br.s, 1 H, NH) *Z*-isomer (22%): 8.05 (d, 2 H, Ph, *J* = 7.8); 10.30, 11.84 (both br.s, 2 H, NH_2); 12.66 (br.s, 1 H, NH)	7.23—7.37 (m, 5 H, 2 Ph); 7.48—7.54 (m, 4 H, 2 Ph); 7.57—7.65 (m, 2 H, 2 Ph); 7.70 (d, 4 H, 2 Ph, *J* = 7.8); 9.18, 9.54 (both br.s, 2 H, NH_2); 12.93 (br.s, 1 H, NH)	342 $[M - SO_2]^+$ (17), 341 $[M - SO_2 - H]^+$ (29), 265 $[M - PhSO_2]^+$ (10), 105 $[COPh]^+$ (100)
2b[a]	*E*-isomer: 2.39 (s, 3 H, Me); 7.01—7.37 (m, 9 H, 2 Ph, C_6H_4); 7.50—7.66 (m, 3 H, 2 Ph); 8.11 (d, 2 H, Ph, *J* = 7.8); 9.33 и 10.35 (both br.s, 2 H, NH_2); 15.35 (br.s, 1 H, NH) *Z*-isomer (21%): 8.05 (d, 2 H, Ph, *J* = 7.8); 10.25, 11.80 (both br.s, 2 H, NH_2); 12.67 (br.s, 1 H, NH)	2.36 (s, 3 H, Me); 7.22—7.34 (m, 7 H, 2 Ph, C_6H_4); 7.51—7.56 (m, 4 H, Ph, C_6H_4); 7.66 (t, 1 H, Ph, *J* = 7.8); 7.74 (d, 2 H, Ph, *J* = 7.8); 9.36 (br.s, 2 H, NH_2); 13.10 (br.s, 1 H, NH)	420 $[M]^+$ (1), 355 $[M - SO_2 - H]^+$ (35), 265 $[M - MeC_6H_4SO_2]^+$ (12), 161 $[M - MeC_6H_4SO_2 - COPh + H]^+$ (22), 122 $[PhCONH_2 + H]^+$ (35), 105 $[COPh]^+$ (71), 91 $[C_6H_4Me]^+$ (84), 77 $[Ph]^+$ (100)
2c[a]	*E*-isomer: 3.83 (s, 3 H, OMe); 6.76 (d, 2 H, C_6H_4, *J* = 7.8); 7.03—7.34 (m, 7 H, 2 Ph, C_6H_4); 7.50—7.65 (m, 3 H, 2 Ph); 8.10 (d, 2 H, Ph, *J* = 7.8); 9.35, 10.34 (both br.s, 2 H, NH_2); 15.35 (br.s, 1 H, NH) *Z*-isomer (22%): 3.71 (s, 3 H, OMe); 8.05 (d, 2 H, Ph, *J* = 7.8); 10.24 и 11.79 (both br.s, 2 H, NH_2); 12.70 (br.s, 1 H, NH)	3.82 (s, 3 H, OMe); 7.00 (d, 2 H, C_6H_4, *J* = 7.8); 7.24—7.74 (m, 12 H, 2 Ph, C_6H_4); 9.24, 9.54 (both br.s, 2 H, NH_2); 13.10 (br.s, 1 H, NH)	254 $[M - COPh - Ph]^+$ (85), 206 $[M - COPh - Ph - SO]^+$ (34), 175 $[M - COPh - Ph - SO - OMe]^+$ (100), 147 $[M - COPh - Ph - SO - OMe - CO]^+$ (42), 120 $[PhCONH_2 - H]^+$ (70), 105 $[COPh]^+$ (96)
2d[a]	*E*-isomer: 2.93 (s, 3 H, Me); 7.37—7.68 (m, 8 H, 2 Ph); 8.11 (d, 2 H, Ph, *J* = 7.8); 8.98, 10.30 (both br.s, 2 H, NH_2); 15.26 (br.s, 1 H, NH) *Z*-isomer (20%): 8.00 (d, 2 H, Ph, *J* = 7.8); 10.25, 11.50 (both br.s, 2 H, NH_2); 12.37 (br.s, 1 H, NH)	3.16 (s, 3 H, Me); 7.37 (m, 3 H, Ph); 7.46 (m, 2 H, Ph); 7.54 (t, 2 H, Ph, *J* = 7.8); 7.67 (t, 1 H, Ph, *J* = 7.8); 7.74 (d, 2 H, Ph, *J* = 7.8); 9.10, 9.50 (both br.s, 2 H, NH_2); 12.96 (br.s, 1 H, NH)	344 $[M]^+$ (13), 265 $[M - SO_2Me]^+$ (38), 105 $[COPh]^+$ (92), 77 $[Ph]^+$ (100)
2e[a,b]	*E*-isomer: 2.34 (s, 3 H, Me); 7.50—7.67 (m, 6 H, 2 Ph); 7.91 (t, 2 H, Ph, *J* = 7.8); 8.07 (d, 2 H, Ph, *J* = 7.8); 9.36, 10.25 (both br.s, 2 H, NH_2); 15.73 (br.s, 1 H, NH) *Z*-isomer (25%): 2.25 (s, 3 H, Me); 8.00 (d, 2 H, Ph, *J* = 7.8); 12.21 (br.s, 1 H, NH); 12.65 (br.s, 1 H, NH)	2.20 (s, 3 H, Me); 7.61—7.75 (m, 6 H, 2 Ph); 7.95 (d, 4 H, 2 Ph, *J* = 7.8); 9.64, 14.82 (both br.s, 2 H, NH_2); 10.00 (br.s, 1 H, NH)	344 $[M]^+$ (7), 280 $[M - SO_2]^+$ (67), 279 $[M - SO_2 - H]^+$ (100), 265 $[M - SO_2 - Me]^+$ (26), 203 $[M - SO_2 - Ph]^+$ (36), 105 $[COPh]^+$ (92)
2f[a,b]	*E*-isomer: 2.34 (s, 3 H, MeCO); 2.44 (s, 3 H, Me); 7.33 (d, 2 H, C_6H_4, *J* = 7.8); 7.55 (t, 2 H, Ph, *J* = 7.8); 7.64 (t, 1 H, Ph, *J* = 7.8); 7.80 (d, 2 H, C_6H_4, *J* = 7.8); 8.06 (d, 2 H, Ph, *J* = 7.8); 9.37, 10.22 (both br.s, 2 H, NH_2); 15.73 (br.s, 1 H, NH) *Z*-isomer (24%): 2.26 (s, 3 H, MeCO); 7.99 (d, 2 H, Ph, *J* = 7.8); 12.18 (br.s, 1 H, NH); 12.68 (br.s, 1 H, NH)	2.20 (s, 3 H, MeCO); 2.40 (s, 3 H, Me); 7.43 (d, 2 H, C_6H_4, *J* = 7.8); 7.63 (t, 2 H, Ph, *J* = 7.8); 7.73 (t, 1 H, Ph, *J* = 7.8); 7.83 (d, 2 H, C_6H_4, *J* = 7.8); 7.95 (d, 2 H, Ph, *J* = 7.8); 9.63, 14.84 (both br.s, 2 H, NH_2); 9.98 (br.s, 1H, NH)	358 $[M]^+$ (15), 295 $[M - SO_2 + H]^+$ (100), 294 $[M - SO_2]^+$ (66), 280 $[M - Me - SO_2 + H]^+$ (33), 203 $[M - Ph - Me - SO_2 + H]^+$ (56), 187 $[M - Ph - 2\,Me - SO_2]^+$ (50), 105 $[COPh]^+$ (66)
2g[a,b]	*E*-isomer: 2.35 (s, 3 H, MeCO); 3.38 (s, 3 H, OMe); 7.00 (d, 2 H, C_6H_4, *J* = 7.8); 7.55 (t, 2 H, Ph, *J* = 7.8); 7.64 (t, 1 H, Ph, *J* = 7.8); 7.85 (d, 2 H, C_6H_4, *J* = 7.8); 8.06 (d, 2 H, Ph, *J* = 7.8); 9.38, 10.21 (both br.s, 2 H, NH_2); 15.74 (br.s, 1 H, NH) *Z*-isomer (25%): 2.27 (s, 3 H, MeCO); 8.00 (d, 2 H, Ph, *J* = 7.8); 12.17 (br.s, 1 H, NH); 12.70 (br.s, 1 H, NH)	2.21 (s, 3 H, MeCO); 3.85 (s, 3 H, OMe); 7.14 (d, 2 H, C_6H_4, *J* = 7.8); 7.63 (t, 2 H, Ph, *J* = 7.8); 7.73 (t, 1 H, Ph, *J* = 7.8); 7.87 (d, 2 H, C_6H_4, *J* = 7.8); 7.95 (d, 2 H, Ph, *J* = 7.8); 9.65, 14.86 (both br.s, 2 H, NH_2); 9.96 (br.s, 1 H, NH)	374 $[M]^+$ (5), 310 $[M - SO_2]^+$ (19), 309 $[M - SO_2 - H]^+$ (26), 235 $[M - SOC_6H_4 - Me]^+$ (25), 155 $[SOC_6H_4OMe]^+$ (91), 127 $[SOC_6H_4OMe - CO]^+$ (99), 105 $[COPh]^+$ (72), 77 $[Ph]^+$ (100)

(*to be continued*)

Table 2 (*continued*)

Compound	^{1}H NMR (δ, *J*/Hz)		MS, *m/z* (I_{rel} (%))
	$CDCl_3$	DMSO-d_6	
3a[c]	—	6.83—7.89 (m, 10 H, 2 Ph); 8.95 (br.s, 2 H, NH_2); 9.34 (br.s, 2 H, NH_2)	238 $[M - SO_2]^+$ (24), 133 $[M - SO_2 - COPh]^+$ (75), 77 $[Ph]^+$ (100)
3b[c]	—	2.37 (s, 3 H, Me); 6.80—8.01 (m, 9 H, Ph, C_6H_4); 8.89 (br.s, 2 H, NH_2); 9.29 (br.s, 2H, NH_2)	251 $[M - SO_2 - H]^+$ (42), 145 $[M - SO_2 - COPh - 2H]^+$ (17), 106 $[COPh + H]^+$ (56), 91 $[C_6H_4Me]^+$ (99); 77 $[Ph]^+$ (100)
3c[c]	—	3.82 (s, 3 H, OMe); 6.82—7.87 (m, 9 H, Ph, C_6H_4); 8.93 (br.s, 2 H, NH_2); 9.48 (br.s, 2 H, NH_2)	332 $[M]^+$ (1), 267 $[M - SO_2 - H]^+$ (15), 171 $[MeOC_6H_4SO_2]^+$ (17), 145 (38), 105 $[COPh]^+$ (66), 76 $[C_6H_4]^+$ (100)
3d[c]	—	2.92 (s, 3 H, Me); 7.27—7.36 (m, 5 H, Ph); 9.18 (br.s, 2 H, NH_2); 9.28 (br.s, 2 H, NH_2)	240 $[M]^+$ (24), 238 $[M - 2H]^+$ (69), 177 $[M - SO_2 + H]^+$ (24), 121 $[M - Me - COPh + H]^+$ (30), 105 $[COPh]^+$ (100)
3e	—	2.10 (s, 3 H, Me); 7.11 (br.s, 2 H, NH_2); 7.60 (m, 3 H, Ph); 7.80 (d, 2 H, Ph, *J* = 7.8); 9.06 (br.s, 2 H, NH_2)	240 $[M]^+$ (2), 225 $[M - Me]^+$ (13), 176 $[M - SO_2]^+$ (21), 175 $[M - SO_2 - H]^+$ (100), 141 $[PhSO_2]^+$ (25), 101 (34)
3f	—	2.09 (s, 3 H, MeCO); 2.37 (s, 3 H, Me); 7.37 (d, 2 H, C_6H_4, *J* = 7.8); 7.57 (br.s, 2 H, NH_2); 7.68 (d, 2 H, C_6H_4, *J* = 7.8); 9.00 (br.s, 2 H, NH_2)	254 $[M]^+$ (9), 239 $[M - Me]^+$ (5), 190 $[M - SO_2]^+$ (31), 189 $[M - SO_2 - H]^+$ (100), 91 $[C_6H_4Me]^+$ (56), 83 (96)
3g	—	2.09 (s, 3 H, MeCO); 3.82 (s, 3 H, OMe); 7.05 (br.s, 2 H, NH_2); 7.10 (d, 2 H, C_6H_4, *J* = 7.8); 7.72 (d, 2 H, C_6H_4, *J* = 7.8); 9.10 (br.s, 2H, NH_2)	270 $[M]^+$ (4), 206 $[M - SO_2]^+$ (19), 205 $[M - SO_2 - H]^+$ (44), 191 $[M - SO_2 - Me]^+$ (17), 189 $[M - SO_2 - Me - 2H]^+$ (33), 171 $[SO_2C_6H_4OMe]^+$ (25), 107 $[C_6H_4OMe]^+$ (32), 92 $[C_6H_4O]^+$ (71), 83 (100)

[a] In the ^{1}H NMR spectra in $CDCl_3$, the other signals of the minor isomer overlap the signals of the major isomer.
[b] In the ^{1}H NMR spectra in $CDCl_3$, one signal for the NH proton of the primary amino group in the minor isomer overlaps the signal of the major isomer at δ 10.20—10.25.
[c] To identify the NH_2 protons, the ^{1}H NMR spectra in DMSO-d_6 were recorded in the presence of CF_3COOH.

129.30 (*m*-PhN); 129.62 (*m*-PhS); 133.72 (*p*-PhS); 138.07 (*ipso*-PhN); 142.12 (*ipso*-PhS); 152.91 (C(2)); 160.73 (C(4)); 162.61 (C(6)). The signals in the ^{1}H and ^{13}C NMR spectra were assigned from the 2D experiment (^{1}H/^{13}C HMBC). 2D ^{1}H/^{15}N HMBC (DMSO-d_6), δ_H/δ_N: 7.58/−278 (N<u>H</u>/<u>N</u>H_2); 8.02/−278 (N<u>H</u>/<u>N</u>H_2) (correlation peaks of the protons and the N atoms across one bond); 7.30/−200 (*o*-N<u>Ph</u>/N(1)); 2.16/−200 (Me/N(1)); 7.58/−172 (N<u>H</u>/N(3)) (correlation peaks of the protons and the N atoms across three bonds).

4-Amino-6-methyl-1-phenyl-5-(4-tolylsulfonyl)pyrimidin-2(1*H*)-one (7b) was obtained as described for pyrimidine **7a** from urea **6b**. Yield 59%, m.p. 285—286 °C. Found (%): C, 60.95; H, 4.95; N, 11.88; S, 8.80. $C_{18}H_{17}N_3O_3S$. Calculated (%): C, 60.83; H, 4.82; N, 11.82; S, 9.02. MS, *m/z* (I_{rel} (%)): 355 $[M]^+$ (2), 291 $[M - SO_2]^+$ (63), 290 $[M - SO_2 - H]^+$ (100), 276 $[M - SO_2 - Me]^+$ (33), 263 $[M - SO_2 - CO]^+$ (26), 221 $[M - SO_2 - CO - NH_2CN]^+$ (58). High-resolution MS: found: *m/z* 356.1079 $[M + H]^+$. $C_{18}H_{17}N_3O_3S$. Calculated: $[M + H]^+$ = = 356.1063. IR (KBr), ν/cm^{-1}: 3420 (NH), 3380—2920 (NH, CH), 1652, 1560, 1480, 1452, 1372, 1300, 1276, 1152, 1080, 1048, 812, 784, 772, 700, 684, 668, 624. ^{1}H NMR ($CDCl_3$), δ: 2.20 (s, 3 H, Me); 2.47 (s, 3 H, <u>Me</u>C_6H_4); 6.40 (br.s, 1 H, NH); 7.11 (d, 2 H, *o*-PhN, *J* = 7.8 Hz); 7.37 (d, 2 H, *m*-C_6<u>H</u>$_4$Me, *J* = 7.8 Hz); 7.46 (m, 3 H, *m*-PhN, *p*-PhN); 7.80 (d, 2 H, *o*-C_6<u>H</u>$_4$Me, *J* = 7.8 Hz); 8.17 (br.s, 1 H, NH). ^{1}H NMR (DMSO-d_6), δ: 2.15 (s, 3 H, Me); 2.42 (s, 3 H, <u>Me</u>C_6H_4); 7.29 (d, 2 H, *m*-C_6<u>H</u>$_4$Me, *J* = 7.8 Hz); 7.44 (m, 5 H, *o*-PhN, *m*-PhN, *p*-PhN); 7.60 (br.s, 1 H, NH); 7.87 (d, 2 H, *o*-C_6<u>H</u>$_4$Me, *J* = 7.8 Hz); 8.00 (br.s, 1 H, NH).

Diphenylboron chelate of compound 2e (8a). Methyl diphenylboronate (0.2 mL, 1 mmol) was added to a solution of ketene aminal **2e** (0.14 g, 0.41 mmol) in *o*-xylene (3 mL). The reaction

mixture was refluxed for 3 h and concentrated. The residue was triturated with light petroleum to produce a crystalline precipitate, which was filtered off and washed with light petroleum. The resulting white crystalline solid is well soluble in benzene, chloroform, and acetone. Yield 0.16 g (78%), m.p. 118—119 °C. Found (%): C, 68.32; H, 4.90; N, 5.67; S, 6.41. $C_{29}H_{25}BN_2O_4S$. Calculated (%): C, 68.51; H, 4.96; N, 5.51; S, 6.31. MS, *m/z* (I_{rel} (%)): 508 $[M]^+$ (1), 431 $[M - Ph]^+$ (74), 105 $[PhCO]^+$ (100). High-resolution MS: found: *m/z* 531.1509 $[M + Na]^+$. $C_{29}H_{25}BN_2O_4S$. Calculated: $[M + Na]^+ = 531.1525$. IR ($CHCl_3$, 3400—2900, 1700—1500 cm^{-1}), ν/cm^{-1}: 3260 (NH), 3160—3000 (NH, CH), 1692 (CO), 1632, 1544. ^1H NMR ($CDCl_3$), δ: 2.49 (s, 3 H, COMe); 7.26—7.40 (m, 12 H, 3 Ph); 7.47 (m, 5 H, 2 Ph); 7.68 (t, 1 H, Ph, *J* = 7.5 Hz); 8.00 (d, 2 H, Ph, *J* = 7.5 Hz); 10.96 (br.s, 1 H, NH); 12.01 (br.s, 1 H, NH). ^{11}B NMR (*o*-xylene), δ: 2.0.

Diphenylboron chelate of compound 2f (8b) was obtained as described for compound **8a** from ketene aminal **2f** and methyl diphenylboronate. Yield 90%, m.p. 199—200 °C. Found (%): C, 68.78; H, 5.17; N, 5.43; S, 6.25. $C_{30}H_{27}BN_2O_4S$. Calculated (%): C, 68.97; H, 5.21; N, 5.36; S, 6.14. MS, *m/z* (I_{rel} (%)): 445 $[M - Ph]^+$ (4), 312 $[M - Ph - PhCO - CO]^+$ (53), 311 $[M - Ph - PhCO - CO - H]^+$ (71), 105 $[PhCO]^+$ (100). IR ($CHCl_3$, 3400—2900, 1700—1500 cm^{-1}), ν/cm^{-1}: 3260 (NH), 3170—2980 (NH, CH), 1692 (CO), 1632, 1540. ^1H NMR ($CDCl_3$), δ: 2.40 (s, 3 H, Me); 2.49 (s, 3 H, COMe); 7.12 (d, 2 H, Ph, *J* = 7.5 Hz); 7.26 (m, 6 H, 2 Ph); 7.38 (m, 6 H, 2 Ph); 7.56 (t, 2 H, Ph, *J* = 7.5 Hz); 7.68 (t, 1 H, Ph, *J* = 7.5 Hz); 8.00 (d, 2 H, Ph, *J* = 7.5 Hz); 10.93 (br.s, 1 H, NH); 12.04 (br.s, 1 H, NH).

Diphenylboron chelate of 1-amino-1-benzoylamino-5-dimethylamino-2-phenylsulfonylpenta-1,4-dien-3-one (9a). Dimethylformamide dimethyl acetal (0.03 mL, 0.24 mmol) was added to a solution of compound **8a** (0.12 g, 0.24 mmol) in THF (4 mL). The reaction mixture was refluxed for 5 h and concentrated. The residue was diluted with light petroleum and the precipitate that formed was filtered off. The resulting yellow crystalline solid is well soluble in chloroform and acetonitrile. Yield 0.12 g (93%), m.p. 248—249 °C. Found (%): C, 67.93; H, 5.35; N, 7.52; S, 5.76. $C_{32}H_{30}BN_3O_4S$. Calculated (%): C, 68.21; H, 5.37; N, 7.46; S, 5.69. MS, *m/z* (I_{rel} (%)): 563 $[M]^+$ (2), 486 $[M - Ph]^+$ (55), 56(100). High-resolution MS: found: *m/z* 564.2152 $[M + H]^+$. $C_{32}H_{30}BN_3O_4S$. Calculated: $[M + H]^+ = 564.2128$. IR ($CHCl_3$, 3400—2800, 1700—1500 cm^{-1}), ν/cm^{-1}: 3280 (NH), 3160—2850 (NH, CH), 1684 (CO), 1632, 1596, 1532. ^1H NMR ($CDCl_3$), δ: 2.86 (s, 3 H, NMe); 3.16 (s, 3 H, NMe); 5.99 (d, 1 H, CH, *J* = 12.0 Hz); 7.17—7.27 (m, 8 H, 2 Ph); 7.38 (m, 7 H, 2 Ph); 7.52 (t, 2 H, Ph, *J* = 7.5 Hz); 7.62 (t, 1 H, Ph, *J* = 7.5 Hz); 7.89 (d, 1 H, CH, *J* = 12.0 Hz); 8.00 (d, 2 H, Ph, *J* = 7.5 Hz); 10.52 (br.s, 1 H, NH); 11.94 (br.s, 1 H, NH).

Diphenylboron chelate of 1-amino-1-benzoylamino-5-dimethylamino-2-(4-tolylsulfonyl)penta-1,4-dien-3-one (9b) was obtained as described for compound **9a** from chelate **8b** and dimethylformamide dimethyl acetal. Yield 95%, m.p. 176—177 °C. Found (%): C, 68.35; H, 5.51; N, 7.38; S, 5.67. $C_{33}H_{32}BN_3O_4S$. Calculated (%): C, 68.63; H, 5.59; N, 7.28; S, 5.55. MS, *m/z* (I_{rel} (%)): 577 $[M]^+$ (1), 500 $[M - Ph]^+$ (100). High-resolution MS: found: *m/z* 578.2273 $[M + H]^+$. $C_{33}H_{32}BN_3O_4S$. Calculated: $[M + H]^+ = 578.2285$. IR ($CHCl_3$, 3400—2800, 1700—1500 cm^{-1}), ν/cm^{-1}: 3284 (NH), 3160—2860 (NH, CH), 1684 (CO), 1632, 1596, 1532. ^1H NMR ($CDCl_3$), δ: 2.34 (s, 3 H, Me); 2.86 (s, 3 H, NMe); 3.16 (s, 3 H, NMe); 6.01 (d, 1 H, CH, *J* = 12.0 Hz); 6.99 (d, 2 H, Ph, *J* = 7.5 Hz); 7.22—7.27 (m, 8 H, 2 Ph); 7.39 (m, 4 H, Ph); 7.52 (t, 2 H, Ph, *J* = 7.5 Hz); 7.62 (t, 1 H, Ph, *J* = 7.5 Hz); 7.89 (d, 1 H, CH, *J* = 12.0 Hz); 8.00 (d, 2 H, Ph, *J* = 7.5 Hz); 10.50 (br.s, 1 H, NH); 11.98 (br.s, 1 H, NH).

2-Amino-3-phenylsulfonylpyridin-4(1*H*)-one (10a). Compound **9a** (0.1 g, 0.18 mmol) was refluxed in butanol (5 mL) for 12 h. On cooling, the precipitate that formed was filtered off and washed with light petroleum. The resulting white crystalline solid is well soluble in DMF and DMSO. Yield 0.03 g (61%), m.p. 289—290 °C. Found (%): C, 52.53; H, 4.12; N, 11.48; S, 12.73. $C_{11}H_{10}N_2O_3S$. Calculated (%): C, 52.79; H, 4.03; N, 11.19; S, 12.81. MS, *m/z* (I_{rel} (%)): 250 $[M]^+$ (63), 184 $[M - SO_2 - 2H]^+$ (100). IR (KBr), ν/cm^{-1}: 3448 (NH), 3330—2900 (NH, CH), 1624, 1508, 1480, 1380, 1280, 1232, 1136, 1080, 820, 720, 680. ^1H NMR (DMSO-d_6), δ: 5.55 (m, 1 H, CH); 7.23 (m, 3 H, CH, NH_2); 7.52 (m, 3 H, Ph); 7.89 (m, 2 H, Ph); 10.54 (br.s, 1 H, NH).

2-Amino-3-(4-tolylsulfonyl)pyridin-4(1*H*)-one (10b) was obtained as described for compound **10a** from chelate **9b**. Yield 59%, m.p. 295—296 °C. Found (%): C, 54.05; H, 4.52; N, 10.67; S, 12.25. $C_{12}H_{12}N_2O_3S$. Calculated (%): C, 54.53; H, 4.58; N, 10.60; S, 12.13. MS, *m/z* (I_{rel} (%)): 264 $[M]^+$ (47), 199 $[M - SO_2 - H]^+$ (100); 185 $[M - SO_2 - Me]^+$ (35). IR (KBr), ν/cm^{-1}: 3440 (NH), 3330—2850 (NH, CH), 1636, 1520, 1480, 1380, 1280, 1232, 1140, 1080, 824, 704, 676. ^1H NMR (DMSO-d_6), δ: 2.35 (s, 3 H, Me); 5.53 (d, 1 H, CH, *J* = 7.5 Hz); 7.20 (br.s, 2 H, NH_2); 7.25 (d, 1 H, CH, *J* = 7.5 Hz); 7.30 (d, 2 H, C_6H_4, *J* = 7.5 Hz); 7.77 (d, 2 H, C_6H_4, *J* = 7.5 Hz); 10.50 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 20.92 (Me); 103.62 (C(3)); 112.14 (C(5)); 127.08 (*o*-C_6H_4); 128.58 (*m*-C_6H_4); 135.58 (C(6)); 140.52 (*ipso*-C_6H_4); 142.58 (*p*-C_6H_4); 153.15 (C(2)); 173.77 (C(4)).

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