Chemistry of Stable Iminopropadienones, RN=C=C=C=O

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Received November 5, 2001

The synthesis, spectroscopic properties, and chemical reactions of the stable (neopentylimino)-, (mesitylimino)-, and (*o-tert*-butylphenylimino)propadienones (**6**) are reported. Nucleophilic addition of amines affords the malonic amidoamidines **7** and **8**. 3,5-Dimethylpyrazole reacts analogously to form **9b**. Addition of 1,2-dimethylhydrazine produces pyrazolinones **10**−**12**. Addition of *N*,*N*′-dimethyldiaminoethane, -propane, and -butane gives diazepine, diazocine, and diazonine derivatives **13**−**15**, respectively (X-ray structures of **13c**, **14a**, and **15a** are available). The mesoionic pyridopyrimidinium olates **18** are obtained by addition of 2-(methylamino)pyridine (X-ray structure of **18b** available). Primary 2-aminopyridines afford the pyridopyrimidininones **20**−**29** and **31** (X-ray structure of **21a** available), and 2-aminopyrimidines and 2-aminopyrazine afford pyrimidopyrimidinones and pyrazinopyrimidinones **33**−**35**. Pyrimidoisoquinolinone **36** results from 1-aminoisoquinoline and pyridoquinolinone **40** from 8-aminoquinoline. 2-Aminothiazoline and 2-aminothiazole afford thiazolopyrimidinone derivatives **41**−**43** (X-ray structure of **43a** available).

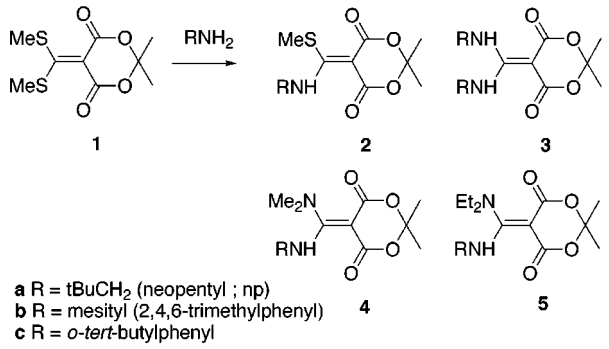
Introduction

The iminopropadienones, RN=C=C=C=O, constitute a recently discovered class of compounds.[1] While the simple alkyl derivatives (methyl,[1] isopropyl,[2] and *tert*-butyl[2]) are notoriously unstable compounds which can, however, be isolated and characterized in low-temperature matrixes, the aryl derivatives are more stable and undergo chemical reactions, often in good preparative yields, under controlled conditions at temperatures around −100 to −50 °C.[3−7]

We have now succeeded in preparing several iminopropadienones that are stable at room temperature, namely the neopentyl, mesityl,[8] and *o-tert*-butylphenyl derivatives. This has allowed a more thorough investigation of the preparative potential of these compounds. The results are reported herein.

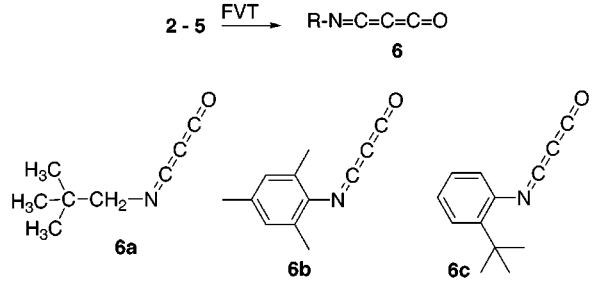
Results and Discussion

The 5-bis(methylthio)methylene derivative of Meldrum's acid, **1**, undergoes nucleophilic displacement of SMe groups on reaction with amines.[2−5,9] Thus, compounds **2a** and **3a** are obtained on reaction with 1 and 2 equiv of neopentylamine, respectively. The reaction of



compounds **2** with dimethyl- and diethylamine affords **4** and **5**, respectively. Compounds of type **2**−**5** can all be used to generate iminopropadienones **6** by flash vacuum thermolysis (FVT), but **4** is the best overall precursor, and therefore, most experiments were performed with these types of compounds (**4a**−**c**).

FVT of **4a** at 700 °C afforded CO_2, acetone, and (neopentylimino)propadienone (**6a**). Collection of the



products in a cold trap at −50 °C allowed the subsequent distillation of **6a** as a yellow oil, which is stable at room temperature. The IR spectrum of **6a** is dominated by a very intense and complex band centered around 2250 cm^{-1}, as is typical of iminopropadienones (see the Supporting Information).[1−6]

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(7) For a review of the chemistry of carbon suboxide, C_3O_2, see: Kappe, T.; Ziegler, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 491.
(8) Moloney, D. W. J. Ph.D. Thesis, The University of Queensland, Brisbane, Australia, 1997.
(9) Ben Cheikh, A.; Chuche, J.; Manisse, N.; Pommelet, J. C.; Netsch, K.-P.; Lorencak, P.; Wentrup, C. *J. Org. Chem.* **1991**, *56*, 970.

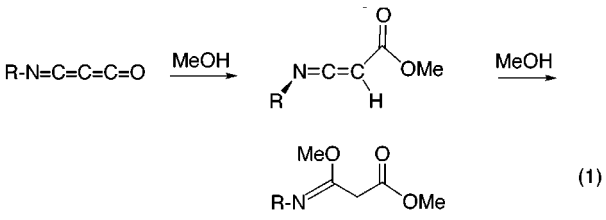
10.1021/jo0110552 CCC: $22.00
Published on Web 03/19/2002

(Mesitylimino)propadienone **6b** was similarly obtained by FVT of **4b** at 700 °C. Between 400 and 800 °C this was the only cumulene observed by IR spectroscopy (2234/2243/2248 (vs) cm^{-1}; 2149 (w) cm^{-1} (Ar matrix)). In CCl_4 solution at room temperature, it features an intense peak centered at 2214 cm^{-1}. The far-IR spectrum in polyethylene shows very low-frequency bands at 73 and 89 cm^{-1}, which, by analogy with C_3O_2,[10] may be due to the bending of the cumulene chain at the central carbon atom. However, due to the structural complexity of **6b**, further far-IR studies of simpler compounds would be required for a rigorous assignment of the vibrational modes. The Raman spectrum shows a relatively weak cumulenic band at 2217−2171 cm^{-1}. The spectra are available in the Supporting Information.

((*o*-*tert*-Butylphenyl)imino)propadienone (**6c**) was obtained by FVT of either **2c** or **4c** at 700 °C and purified by bulb-to-bulb distillation. The IR spectrum shows the characteristic bands at 2237 (vs) and 2139 (w) cm^{-1} (Ar matrix; see the Supporting Information).

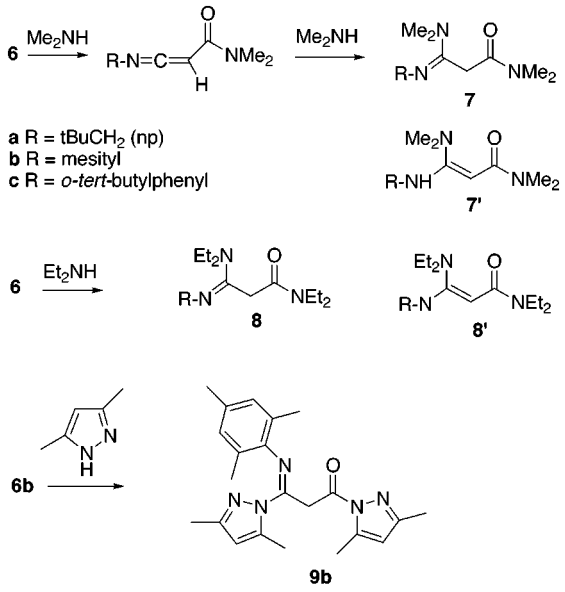
The ^{13}C NMR spectrum of **6a** shows highly characteristic carbon resonances at −11 (central cumulenic carbon, C2), 108.5 (C═N), and 130 ppm (C═O). **6b** has the corresponding signals at −7, 112, and 133 ppm, and **6c** at −3.8, 108, and 130 ppm (the ^1H and ^{13}C NMR spectra of **6a**−**c** are reproduced in the Supporting Information). Carbon suboxide, O═C═C═C═O, features analogous ^{13}C NMR resonances at −14.6 and 129.7 ppm.[11] Calculations at the MP2/6-31G*//HF/6-31G* level reproduce the ^{13}C NMR shifts of C_3O_2 and the iminopropadienones very accurately.[8,12] The imine carbon signal at 108−112 ppm in the iminopropadienones is very broad and weak at room temperature due to the adjacent nitrogen quadrupole moment (see e.g. Figure S2). The signal intensity improves by recording the spectrum at −30 °C.

Compounds **6** are quite long-lived at room temperature, even in the presence of mild nucleophiles such as alcohols and water. Compound **6a** has a half-life of almost 7 h in the presence of a 2-fold excess of methanol.[13] We have investigated this type of reaction for other iminopropadienones and found that ketenimines are formed first, followed by addition of a second molecule of methanol to afford malonic ester imides (eq 1).[5] Compounds **6** react



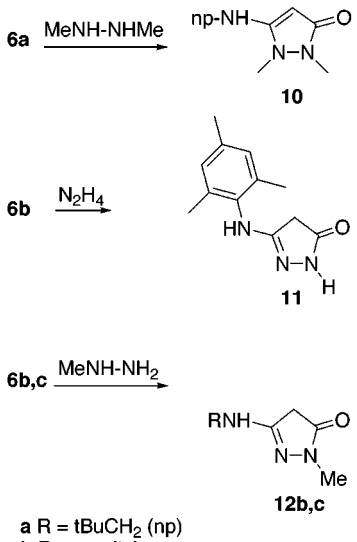
(1)

much faster with amines than with alcohols.[13] They react virtually spontaneously with dimethyl- and diethylamine to afford amidoamidines **7** and **8**, respectively. We have demonstrated that the initial reaction involves formation of an amidoketenimine by addition of dimethylamine to the C═O group in **6b**. This reaction takes place at −40 °C in CD_2Cl_2 solution, and the ketenimine was fully characterized by ^1H NMR and IR spectroscopy.[5] Subsequent slow addition of a second molecule of amine gives amidoamidines **7** and **8**. Such compounds are usually



obtained as the unconjugated tautomers (**7**); however, workup by Kugelrohr distillation caused incomplete tautomerization of **7a** and **8a** to **7a′**/**8a′**. 3,5-Dimethylpyrazole reacts with **6** like an amine, forming **9b** with (mesitylimino)propadienone.

The reaction of **6** with hydrazines and bis(amines) affords cyclic compounds. Thus, the pyrazolinone **10** is



obtained from **6a** and 1,2-dimethylhydrazine at room temperature. Pyrazolinone **11** is obtained from **6b** with hydrazine, and pyrazolinones **12b**,**c** are obtained with methylhydrazine, respectively. *N*,*N*′-Dimethyl-1,2-diaminoethane, -1,3-diaminopropane, and -1,4-diaminobutane afford the perhydrodiazepine, -diazocine, and -diazonine derivatives **13a**−**c**, **14**, and **15**, respectively. Compound **13a** undergoes partial tautomerization to the conjugated

(10) Millar, F. A.; Lemon, D. H.; Witkowski, R. E. *Spectrochim. Acta* **1965**, *21*, 1709. Smith, W. H.; Leroy, G. E. *J. Chem. Phys.* **1966**, *45*, 1767.

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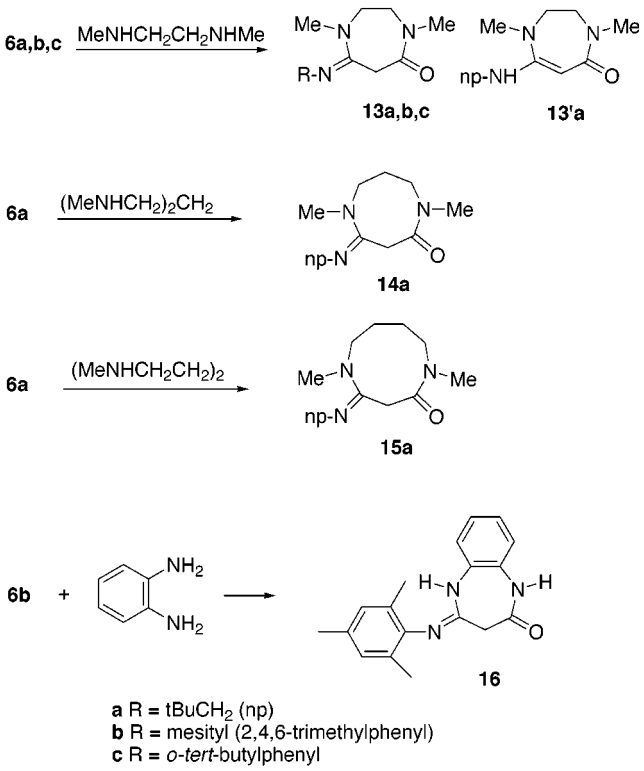
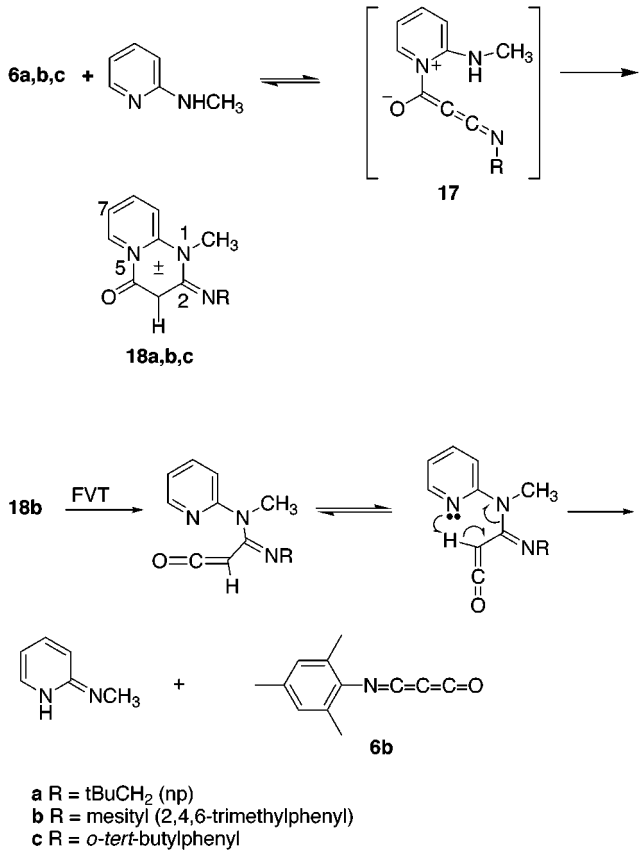
(13) More detailed kinetics of the reactions with alcohols and amines are under investigation. It is known that ketenes react faster with amines than with alcohols, and a nucleophilicity series has been published: De Lucas, N. C.; Netto-Ferreira, J.-C.; Andraos, J.; Scaiano, J. C. *J. Org. Chem.* **2001**, *66*, 5016. Acetylketene reacts with propanol and propanamine to give a product ratio of 1:2.3: Birney, D. M.; Xu, X.; Ham, S.; Huang, X. *J. Org. Chem.* **1997**, *62*, 7114.



13a′ on workup involving Kugelrohr distillation. *o*-Phenylenediamine reacted similarly with **6b** to afford the benzodiazepine derivative **16**. The structures of compounds **13c**, **14a**, and **15a** were confirmed by X-ray crystallography (see the Supporting Information). Compounds **6b**,**c** also reacted with *N*,*N*′-dimethyl-1,3-diaminopropane to afford diazocine derivatives (**14b**,**c**), but these have so far only been obtained as oils that were difficult to purify. No cyclic amidoamidines of structures related to **13**−**15** are known in the literature.

The reactions of iminopropadienones with N-heterocyclic amines is particularly interesting, because of the possibility of forming mesoionic (zwitterionic) compounds.[6b,14] Compounds **6** react with 2-(methylamino)-pyridine to afford pyridopyrimidinium olates **18** as red-orange solids (Scheme 1). The atom connectivity in **18a** was established by 2D ^{13}C NMR experiments (HMBC and HSQC) and by X-ray crystallography for **18b** (data in the Supporting Information). The structures of many mesoionic compounds show distortions toward ketene valence isomers, with long N−CO bonds and acute OCN angles.[14] Compound **18b** features a characteristically long N−CO bond (1.49 Å) and tilting of the C=O group toward the ring junction at N5a (∠O4−C4−N5 = 116°). A mechanism for the formation of **18** is given in Scheme 1. It is known that ketenes react with pyridine, even at very low temperatures (e.g. 40 K), to produce ketene−pyridine zwitterions.[15] Furthermore, carbon suboxide, O=C=C=C=O, reacts with pyridine and other amine nucleophiles in low-temperature matrixes to give, first, observable van

Scheme 1



der Waals complexes,[16] which can be transformed into covalent zwitterions of the type O=C=C=C(O$^-$)Nu$^+$.[17] It is postulated that the corresponding zwitterion **17** can form by interaction of 2-(methylamino)pyridine with **6**. Addition of the exocyclic amino group to the imine carbon atom in **17** affords the mesoionic heterocycle **18**. It would be possible to bypass **17** by postulating that the exocyclic amino group reacts with the less electrophilic C=N carbon of the cumulene **6**, but this goes against all our knowledge of the initial stages of these and similar reactions.[5,16,17] This reaction is reversible: FVT of **18b** at 350 °C regenerates 2-(methylamino)pyridine and **6b**, as proved by the IR spectrum of the products in Ar matrix at 10 K. However, the mechanisms of the synthesis and fragmentation of **18c** are likely to involve different intermediates. A rational mechanism for the FVT reaction is given in Scheme 1, and this is based on a previous investigation of ring opening and fragmentation in six-membered mesoionic compounds.[18] The 1,2-dihydro-2-(methylimino)pyridine initially formed in this mechanism undergoes rapid tautomerization to the observed 2-(methylamino)pyridine.[18]

The corresponding reactions of **6** with primary 2-aminopyridines would proceed via the analogous zwitterions **17′** to the mesoions **19**, followed by tautomerization to the pyridopyrimidinones **20**−**24** as final products (Scheme 2). These are indeed the major or exclusive products when the reactions are performed in methylene chloride solu-

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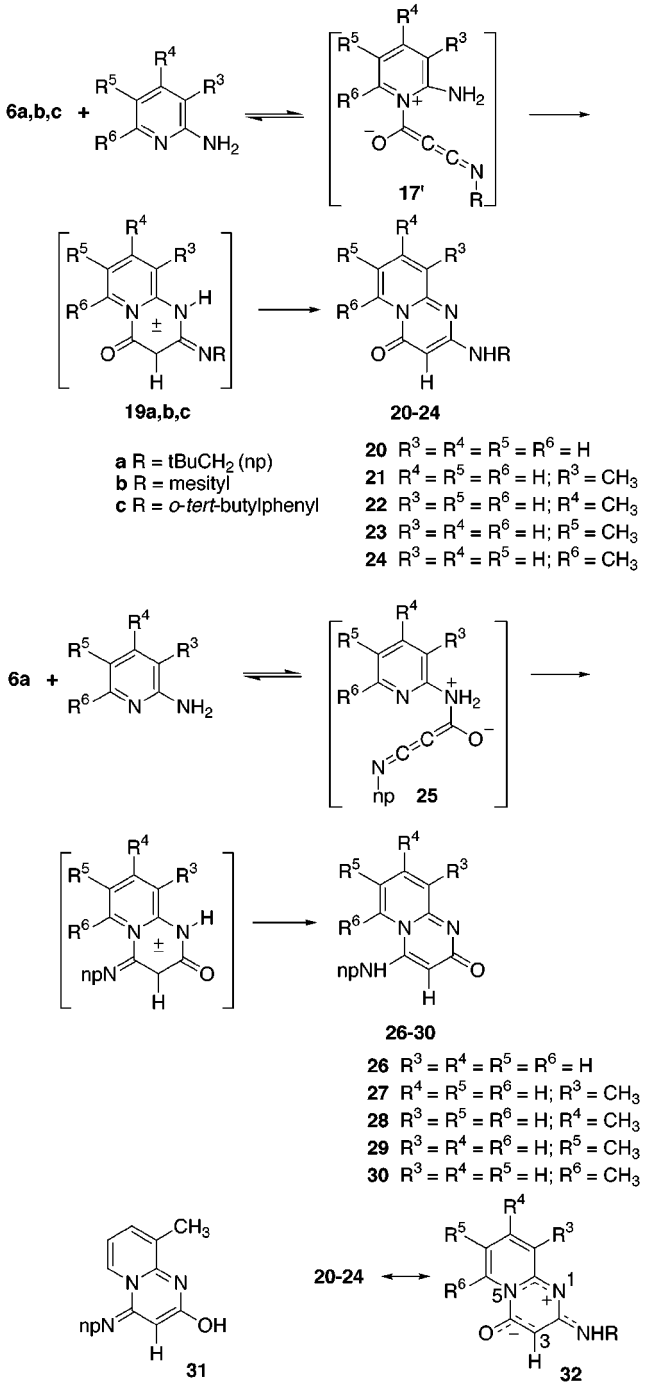
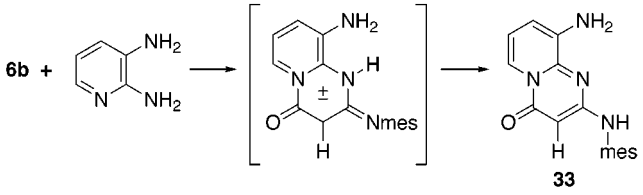
Scheme 2



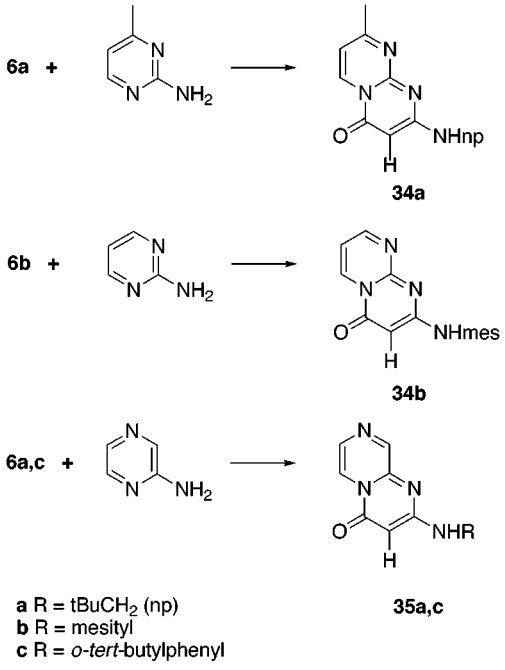
tion at room temperature, but small amounts of the alternate addition products **26**−**29** were also obtained from (neopentylimino)propadienone **6a**. 2-Amino-6-methylpyridine gave only **24**; compound **30** was not formed. Usually, the pyridine nitrogen atom is the most nucleophilic center in 2-aminopyridines, and the C=O group is more electrophilic than the C=N group in iminopropadienones, but the formation of both types of addition products, corresponding to the two alternate modes of nucleophile/electrophile interaction, has been described in a previous case.[6b] Moreover, the orientation of addition can be modulated by electronic substituent effects in the aromatic ring in (phenylimino)propadienones.[19] The proportions of the "abnormal" isomers **26**−**29** were found to increase when the reactions were performed in refluxing toluene, but **20a**−**23a** always remained the major isomer. Control experiments excluded the possibility of a rearrangement of **22a** to **28**. The formation of **26**−**29** is postulated to result from initial attack of the exocyclic amino group of the pyridine on the carbonyl group of **6**, leading to the zwitterions **25**. Subsequent attack of the pyridine nitrogen lone pair on the imine carbon in **25** gives **26**−**29**. In most cases, other possible tautomers of **20**−**30** are not observed, but in the case of 2-amino-3-methylpyridine, a small amount of the hydroxy tautomer **31a** was formed as well.

Compounds of type **20**−**24** are structurally interesting because, even though they are not mesoionic, they exist in a highly zwitterionic form, as expressed by resonance structure **32**.[14] The X-ray structure analysis of **21a** confirmed that this is the case, with short C10−N1 and N1−C2 bonds, long C2−C3 and C3−C4 bonds, an unusually long C4−N5 bond, and the C=O group at C4 tilted toward the ring junction at N5 (C10−N1 = 1.322 Å, N1−C2 = 1.353 Å, C2−C3 = 1.383 Å, C3−C4 = 1.380 Å, C4−N5 = 1.446 Å, N5−C10 = 1.376 Å; ∠C10−N1−C2 = 117.3°, N1−C2−N2 = 115.9°, N1−C2−C3 = 123.0°, C2−C3−C4 = 121.5°, C3−C4−N5 = 114.1°, O4−C4−N5 = 116.8°). Full data are reported in the Supporting Information.

2,3-Diaminopyridines react just like 2-aminopyridine, by using the pyridine ring nitrogen and the amino group in the 2-position, thus affording **33** with **6b**.



2-Aminopyrimidines and 2-aminopyrazine react in a similar manner with **6** to give pyrimido- and pyrazinopyrimidinones **34** and **35**. These rings are less nucleophilic



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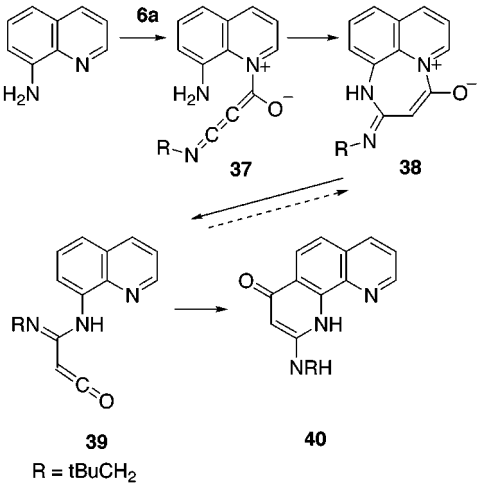
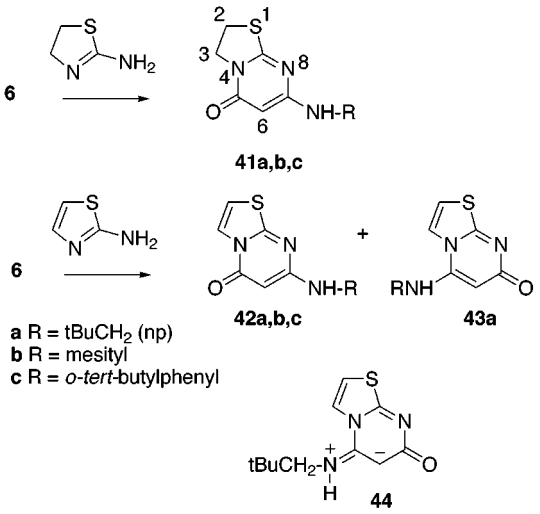
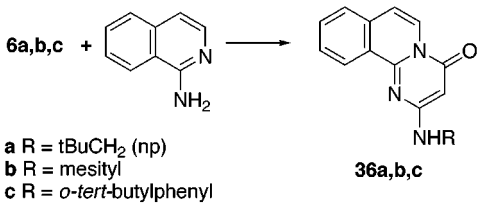
Scheme 3





than pyridine and react much more slowly. 1-Aminoisoquinoline reacts at room temperature to afford the cyclization products **36a**,**b**.



The reaction with 8-aminoquinoline in refluxing THF affords compound **40a**, the formation of which is rationalized in Scheme 3. Initial addition to **6a** by using the pyridine type lone pair leads to zwitterion **37**. Cyclization affords the new zwitterion **38**, which can be regarded as an intramolecular ketene−pyridine zwitterion.[6b,15] Such zwitterions can be in equilibrium with the ketene valence isomer **39**. The cyclization of **39** onto the C7 of the quinoline system can be described as an electrophilic aromatic substitution by a ketene. Another cyclization reaction analogous to **39** → **40** has been reported recently.[18] Again, it would be possible to bypass **37** and **38** by postulating direct formation of **39**. However, this would involve the initial attack of an amino group on the less electrophilic and more hindered C=N carbon in **6a** and go against our current knowledge of the reactivity of iminopropadienones.

Thiazole forms a van der Waals complex with C_3O_2 in the same manner as pyridine,[16,17] involving an interaction between the nitrogen lone pair and the cumulene system.[20] Therefore, it may be expected that thiazoles and thiazolines react with ketenes in much the same manner as pyridines and that reaction with **6** will proceed analogously to Schemes 1 and 2. 2-Aminothiazoline afforded the expected addition products **41a**−**c** in methylene chloride solution at room temperature. Similarly, 2-aminothiazole yielded compounds **42a**−**c** under the same reaction conditions, but in refluxing toluene a small amount of the "abnormal" tautomer **43a** was formed as well. The mechanism for its formation is expected to be analogous to the formation of **26**−**30** in Scheme 2. The structure of **43a** was confirmed by X-ray crystallography (see the Supporting Information). As mentioned above, the "normal" pyridopyrimidinones of types **20**−**24** are highly zwitterionic, as expressed in the canonical structure **32**. The bond lengths in **43a** suggest a different kind of zwitterionic contribution involving the exocyclic amino group, as expressed in canonical structure **44** (bond lengths (Å): C2−C3 = 1.320, C8a−N8 = 1.296, N8−C7 = 1.398, C7−C6 = 1.416, C6−C5 = 1.372, C5−N4 = 1.400, N4−C8a = 1.374; exocyclic NH−C5 = 1.330, exocyclic NH−CH_2 = 1.457).

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Conclusion

Whereas simple alkyliminopropadienones are highly unstable and have the character of reactive intermediates, the neopentyl, mesityl, and *o*-*tert*-butylphenyl derivatives **6** are sufficiently stable to permit isolation at room temperature. This may appear somewhat surprising, since the steric hindrance exerted by these substituents, especially to attack on the cumulenic carbonyl groups, would seem to be very modest. Cumulenes **6** undergo a multitude of nucleophilic addition reactions, usually initiated by attack of amines on the cumulenic carbonyl group, to generate zwitterion intermediates. Subsequent ring closure reactions lead to a multitude of heterocyclic compounds containing five-, six-, seven-, eight-, and nine-membered rings, including pyrazolinones, pyridopyrimidinones and mesoionic pyridopyrimidinium olates, pyrimidopyrimidinones, pyrazinopyrimidinones, and perhydrodiazepinone, -diazocinone, and -diazoninone derivatives.

Experimental Section

General Considerations. NMR spectra were recorded at 200 MHz for ^{1}H and 50.3 MHz for ^{13}C unless otherwise indicated. 2D ^{1}H−^{13}C COSY spectra were recorded using the HMBC or HSQC sequences. Mass spectra were obtained at 70 eV electron ionization. GC-MS employed a BP-4 capillary column (30 m × 0.25 mm; He carrier gas at 20 psi head pressure; injector 200 °C; detector 280 °C; column temperature 100−270 °C, programmed at 16 °C/min). Flash, column, and thin-layer chromatography were performed on silica gel. IR spectra were recorded on FT-IR spectrometers, usually at 0.5−1 cm^{-1} resolution. Melting points are uncorrected. The

apparatus used for flash vacuum thermolysis and matrix isolation has been described.[21]

5-[((2,2-Dimethylpropyl)amino)(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (2a). 2,2-Dimethylpropylamine (6.53 g, 75 mmol) and 5-(bis(methylthio)methylene-1,3-dioxane-4,6-dione (1;[4] 18.6 g, 75 mmol) were dissolved in 130 mL of THF and stirred for 2 days at room temperature. The solvent was reduced to half its volume under vacuum, and diethyl ether (100 mL) was added. A yellow precipitate formed immediately. The solution was decanted and the residue recrystallized from THF/diethyl ether to yield 18.3 g (85%) of 2a. Use of CH_3CN or EtOH as solvent gave yields of 71 and 75%, respectively. The compound was sublimed at 100 °C/10^{-7} mbar prior to use in FVT experiments: mp 130 °C; ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 1.73 (s, 6 H), 2.58 (s, 3 H), 3.11 (d, 2 H, ^3J = 5.62 Hz); ^{13}C NMR ($CDCl_3$) δ 18.2, 26.0, 27.2, 31.9, 57.6, 82.9, 102.5. 163.8, 178.7. Anal. Calcd for $C_{13}H_{21}NO_4S$: C, 54.33; H, 7.37; N, 4.87. Found: C, 54.45; H, 7.59; N, 4.81.

5-[(Bis((2,2-dimethylpropyl)amino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (3a). A mixture of 2,2-dimethylpropylamine (1.31 g, 15 mmol) and **1** (1.21 g, 5 mmol) in 30 mL of ethanol was refluxed for 5 h. The solvent was reduced to half its volume under vacuum, and diethyl ether (20 mL) was added. After the mixture was cooled to 0 °C in a refrigerator for 2 days, yellow crystals formed. The solution was decanted and the residue recrystallized from THF/diethyl ether to yield 0.78 g (2.4 mmol, 48%) of **3a** as a colorless powder. Compound **3a** can also be purified by chromatography on silica gel/diethyl ether (R_f = 0.68): mp 148 °C; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 18 H), 1.61 (s, 6 H), 3.10 (d, 2 H, ^3J = 4.88 Hz), 9.83 (s, br, 2H); ^{13}C NMR ($CDCl_3$) δ 25.7, 26.7, 32.2, 58.1, 73.7, 101.6, 165.2, 166.3. Anal. Calcd for $C_{17}H_{30}N_2O_4$: C, 62.55; H, 9.26; N, 8.58. Found: C, 62.59; H, 9.57; N, 8.22.

5-[(Dimethylamino)(2,2-(dimethylpropyl)amino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4a). Compound 2a (10 g, 35 mmol) was dissolved in 40 mL of dry THF. A stream of gaseous dimethylamine was bubbled via a pipet through the stirred solution at such a rate that the gas was just absorbed. After approximately 20 min, a colorless precipitate had formed. The addition of $HNMe_2$ was stopped, and the reaction mixture was stirred for another 1h. The precipitate was filtered, and the yellow solution was collected and treated with $HNMe_2$ as described above for another 20 min. After the mixture was stirred for a further 2 h, the pale yellow precipitate was filtered, and the combined solid fractions were recrystallized from hot THF to afford 7.56 g (26.6 mmol, 76%) of 4a: mp 202 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9 H), 1.66 (s, 6 H), 2.87 (d, 2 H, ^3J = 6.11 Hz), 3.15 (s, 6 H), 7.45 (s, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.4, 27.1, 31.8, 40.6, 57.6, 70.6, 102.5, 163.4, 164.6. Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.14; H, 8.51; N, 9.85. Found: C, 58.89; H, 8.73; N, 9.61.

5-[(Diethylamino)(2,2-(dimethylpropyl)amino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (5a). Compound **2a** (0.28 g, 1 mmol) and diethylamine (0.4 g, 5.5 mmol) were dissolved in 10 mL of freshly distilled dry THF, and the mixture was heated under reflux. Further diethylamine (0.5 g) was added after 3 h and again after 10 h. After 17 h the reaction was completed, and the solvent was evaporated under vacuum. The oily yellow residue was dissolved in methylene chloride (5 mL). Petroleum ether was added to precipitate 0.24 g (0.77 mmol, 77%) of **5a** as a pale yellow powder. To obtain analytical purity the crude product was sublimed at 120 °C/10^{-2} mbar to yield 0.22 g (0.71 mmol, 71%) of **5a** as a colorless compound: mp 172 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9 H), 1.32 (t, 6 H), 1.71 (s, 6 H), 2.03 (s, br, 1 H), 3.08 (d, 2 H, ^3J = 5.86 Hz), 3.53 (q, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.2 (br), 26.5, 27.1, 31.9, 43.8−46.8 (br), 57.2, 70.5−70.7, 102.3, 163.5, 164.6. The broad signals are ascribed to hindered rotation (CH_3 group at δ 13.2) or the presence of the nitrogen quadrupole moment (NCH_2 signal at δ 43.8−46.8). Anal. Calcd for $C_{16}H_{28}N_2O_4$: C, 61.51; H, 9.03; N, 8.97. Found: C, 61.49; H, 9.30; N, 8.78.

(21) Kuhn, A.; Plüg, C.; Wentrup, C. *J. Am. Chem. Soc.* **2000**, *122*, 1945. Wentrup, C.; Blanch, R.; Briehl, H.; Gross, G. *J. Am. Chem. Soc.* **1988**, *110*, 1874.

(Neopentylimino)propadienone (6a). This compound was prepared by preparative FVT as follows. In the course of ca. 1 h compound **4**a (100 mg, 0.35 mmol) was sublimed at 150−180 °C/10^{-4} mbar through an unpacked 300 × 20 mm (i.d.) horizontal quartz tube heated to 700 °C in a tube furnace (heating zone 250 mm). The iminopropadienone was collected in a U-tube cooled to −50 °C with dry ice/acetone and connected via an uncooled cold finger to a vacuum line equipped with an oil diffusion pump. After completion of the thermolysis, the dry ice/acetone bath was removed, and the U-tube was warmed to room temperature. The pump was isolated, and the cold finger was cooled to 77 K with liq. N_2. As soon as the U-tube containing the iminopropadienone was heated with a heat gun to a maximum of 150 °C, a yellow oil distilled and deposited on the cold finger as a pale yellow layer. The system pressure was equalized with N_2, the cold finger was warmed to room temperature, and the iminopropadienone was collected in a receiving NMR tube by rinsing the cold finger with a suitable solvent: ^{1}H NMR (CD_3OD) δ 1.00 (s, 9 H, *t*-Bu), 3.38 (s, 2 H, NCH_2); ^{13}C NMR (CD_3OD) δ −11.0, 27.1, 33.9, 57.5, 108.5, 130.0 (see the Supporting Information for the spectra); MS *m*/*z* 137.0843, calcd for $C_8H_{11}NO$ 137.0841.

Matrix Isolation of (Neopentylimino)propadienone (6a). In the course of 5 min, Meldrum's acid derivative **3a** was sublimed at 80 °C/4 × 10^{-6} mbar under an argon stream, pyrolyzed at 700 °C, and deposited on a CsI window in the cryostat at 7 K: IR (Ar matrix, 7 K) 2975 (m), 2313 (m), 2250 (vs), 2216 (s) cm^{-1}.

Kinetics of Reaction of 6a with Methanol. (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **3a** (100 mg, 0.3 mmol) and isolated in a dry ice/acetone cold trap was warmed to 0 °C, and 1 mL of CD_2Cl_2 was injected through a septum onto the cold finger to rinse **6a** into an NMR tube cooled in liquid N_2. A solution of 0.03 mL (0.74 mmol) of methanol in 1 mL of CD_2Cl_2 was added, and the tube was placed in the NMR spectrometer. The reaction was monitored during a period of 832 min (ca. 2 half-lives) in intervals of 6 min by integration of the *N*-methylene protons. By plotting −ln [np-NCCCO] versus time, a straight line was obtained, indicating a first-order reaction kinetics with respect to the decreasing concentration of **6a**. Regression analysis yielded −ln [npNCCCO] = 0.0017t + 0.0509, R^2 = 0.9905, rate constant $k_1 = 2.83 \times 10^{-5}$ s^{-1}, and $t_{1/2}$ = 408 min.

1,3-Bis(dimethylamino)-3-((2,2-dimethylpropyl)imino-)propan-1-one (7a) and 1,3-Bis(dimethylamino)-3-((2,2-dimethylpropyl)amino)propen-1-one (7′a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (300 mg, 1.1 mmol) was isolated on a cold finger as above, and 10 mL of a 1 N solution of dimethylamine in THF was injected through a septum onto the cold thermolysate. The red-brown reaction mixture was warmed to room temperature. After evaporation of the solvent, a ^{1}H NMR spectrum of the crude oil indicated an almost pure sample of **7a**/**7′a** in a 1:0.4 ratio. Kugelrohr distillation at 135 °C/10^{-4} mbar yielded **7a**/**7′a** in a 0.7:1 ratio as a yellow oil. Yield: 145 mg (0.64 mmol, 61%). **7a**: ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 2.83 (s, 2 H), 2.94 (s, br), 2.97 (s, br), 3.05 (s, br), 3.53 (s, br, 2 H). **7′a**: ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9 H), 2.67 (s, 6 H), 2.81 (d, 2 H), 2.92 (s, 6 H), 4.09 (s, 1 H), 8.99 (t, br, 1 H). **7a**/**7′a**: ^{13}C NMR ($CDCl_3$) δ 27.4, 27.7, 32.2, 32.5, 32.4, 33.6, 36.4, 37.3, 38.6, 40.4, 56.9, 60.9, 69.4, 154.9, 166.9, 168.1, 171.3. Anal. Calcd for $C_{12}H_{25}N_3O$: C, 63.40; H, 11.08; N, 18.48. Found: C, 63.11; H, 11.37; N, 18.60.

1,3-Bis(diethylamino)-3-((2,2-dimethylpropyl)imino)-propan-1-one (8a) and 1,3-Bis(diethylamino)-3-((2,2-dimethylpropyl)amino)propen-1-one (8′a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (300 mg, 1.1 mmol) was isolated on a cold finger as above, 10 mL of a 1 N solution of diethylamine in THF was injected, and the red-brown reaction mixture was warmed to room temperature. The solvent was evaporated, and the crude oil was distilled at 150−155 °C/10^{-4} mbar to yield **8a** and **8′a** in a 1:0.83 ratio as a yellow oil. Yield: 203 mg (0.72 mmol, 65%). **8**: ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9 H), 2.81 (s, 2 H), 3.35 (s, 2 H). **8′**: ^{1}H NMR ($CDCl_3$) δ 0.9 (s, 9 H), 2.80 (d, 2 H), 2.99 (q, 4 H),

4.18 (s, 1 H). ^{1}H NMR signals common to **8a** and **8′a**: δ 1.00−1.21 (m, 24 H, CH_3), 3.23−3.35 (m, 12 H NCH_2), 8.98 (t, br, 1 H). **8**, **8′**: ^{13}C NMR ($CDCl_3$) δ 11.9, 12.1, 13.4, 14.0, 14.2, 27.4, 27.8, 32.0, 32.0, 32.5, 40.4, 40.9, 42.3, 56.5, 60.9, 72.4, 150.5, 153.9 166.3, 169.9.

1,2-Dimethyl-5-((2,2-dimethylpropyl)amino)pyrazolin-3-one (10a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (100 mg, 0.36 mmol) was isolated on a cold finger as above and dissolved in 10 mL of dry CH_2Cl_2. A solution of 1,2-dimethylhydrazine in 10 mL of dry THF, previously prepared from 1,2-dimethylhydrazine dihydrochloride (40 mg, 0.3 mmol) and dry triethylamine (100 mg, 1 mmol), was added. The reaction mixture was stirred for 3 h at room temperature and was then concentrated to dryness. The brown residue was chromatographed (silica gel, CH_2Cl_2/MeOH = 100:15, R_f = 0.75) to afford 26 mg (37%) of **10a** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.90 (9 H), 2.80 (s, 2 H), 2.98 (s, 3 H), 3.01 (s, 3 H), 4.45 (s, 1 H), 4.80 (t, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.2, 31.3, 32.3, 36.7, 56.2, 75.5, 164.4, 172.0.

1,4-Dimethyl-7-((2,2-dimethylpropyl)imino)perhydro-[1,4]diazepin-5-one (13a) and 1,4-Dimethyl-7-((2,2-dimethylpropyl)amino)-1,2,3,4-tetrahydro-5*H*-1,4-diazepin-5-one (13′a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (300 mg, 1.1 mmol) was isolated in a cold trap and dissolved in 25 mL of dry CH_2Cl_2, and a solution of *N*,*N*′-dimethylethylenediamine (90 mg, 1 mmol) in dry diethyl ether (20 mL) was added via a dropping funnel within 1 h. The reaction mixture was stirred for another 6 h at room temperature and was then concentrated to dryness. The brown oily residue was distilled in a Kugelrohr apparatus at 150−160 °C/10^{-5} mbar to afford 141 mg (0.63 mmol, 57%) of **13a** and **13′a** in the ratio 1:0.13 as a colorless solid. For further purification **13a**/**13′a** was dissolved in 10 mL of diethyl ether and precipitated by addition of a few drops of hexane: mp 90−91 °C; GC retention time 9.6 min. **13**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83 (s, 9 H, *t*-Bu), 2.84 (s, 3 H, NMe), 2.88 (s, 3 H, NMe), 2.94 (s, 2 H, CH_2), 3.37−3.40 (m, 2 H, NCH_2), 3.46−3.49 (m, 2 H, NCH_2), 3.54 (s, 2 H, 6-H); ^{13}C NMR ($CDCl_3$, 100.62 MHz) δ 27.5 (C*Me*$_3$), 32.5 (*C*Me$_3$), 35.4 (NMe), 36.0 (C-6), 36.7 (NMe), 49.8 (NMe), 50.1 (NCH_2), 61.4 (NCH_2), 153.1 (C-5), 166.6 (C-7). **13′**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (s, 9 H, *t*-Bu), 2.75 (s, 2 H, NCH_2), 2.84 (s, 3 H, NMe), 2.92 (s, 3 H, NMe),), 3.33 (s, br, 4 H, 2x NCH_2), 4.3 (s, 1 H, 6-H_{olefin}); ^{13}C NMR ($CDCl_3$, 100.62 MHz) δ 27.4 (C*Me*$_3$), 31.6 (*C*Me$_3$), 36.7 (NMe), 38.6 (NMe), 52.9 (NCH_2), 55.7 (NCH_2), 78.1 (C-6) 156.9 (C-7), 168.5 (C-5) ppm. The ^{13}C NMR assignments are supported by an HSQC spectrum. **13**, **13′**: IR (KBr) 1651 (s), 1636 (vs), 1622 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{23}N_3O$: C, 63.96; H, 10.29; N, 18.65. Found: C, 63.83; H, 10.56 N, 18.80.

1,5-Dimethyl-4-((2,2-dimethylpropyl)imino)perhydro-[1,5]diazocin-2-one (14a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (300 mg, 1.1 mmol) was isolated in a cold trap as above and dissolved in 50 mL of dry CH_2Cl_2, and a solution of *N*,*N*′-dimethylpropylenediamine (36 mg, 0.35 mmol) in dry diethyl ether (40 mL) was added via an automatic syringe pump (flow rate 2.5 mL/h) within 16 h. The reaction mixture was stirred for another 5 h at room temperature and was then concentrated to dryness. A 10 mL portion of methanol was added, and the solution was filtered through cotton wool. After evaporation of the solvent under vacuum, the brown oil was subjected to a bulb to bulb distillation at 170−200 °C/10^{-5} mbar to afford a yellow oil. A subsequent Kugelrohr distillation at 160 °C/7 × 10^{-6} mbar gave **14a** as a colorless solid. Recrystallization in the cold from diethyl ether/hexane yielded 23 mg (0.08 mmol, 24%) of **14a**: mp 89−90 °C; GC retention time 10.1 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (s, 9 H, *t*-Bu), 1.75 (quin, 2 H, 3-H), 2.83 (s, 3 H, NMe), 2.95 (s, 3 H, NMe), 3.00 (s, 2 H, NCH_2), 3.3−3.4 (m_c, 4 H, 2x NCH_2), 3.52 (s, 2 H, 3-H) ppm; ^{13}C NMR ($CDCl_3$, 100.62 MHz) δ 27.1 (C-7) 27.8 (C*Me*$_3$), 32.7 (*C*Me$_3$), 34.5 (C-3), 36.2 (NMe), 36.4 (NMe), 47.3 (NCH_2), 47.2 (NCH_2), 62.0 (NCH_2), 155.5 (C-4), 169.1 (C-2) ppm (the ^{13}C NMR assignments are supported by an HSQC spectrum); MS *m*/*z* 257.2093 ($M^+ + H_2O$), calcd for $C_8H_{12}NO_2$ 257.2096. Anal. Calcd for $C_{13}H_{25}N_3O$: C, 65.23; H, 10.53; N, 17.56. Found: C, 65.53; H, 10.94; N, 17.47. For the X-ray structure, see the Supporting Information.

1,5-Dimethyl-4-((2,2-dimethylpropyl)imino)perhydro-[1,5]diazonin-2-one (15a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (300 mg, 1.1 mmol) was isolated in a cold trap as above and dissolved in 50 mL of dry CH_2Cl_2, and a solution of *N*,*N*′-dimethylbutylenediamine (41 mg, 0.35 mmol), dissolved in 40 mL of dry diethyl ether, was added via an automatic syringe pump over the course of 16 h. The reaction mixture was stirred for another 5 h at room temperature and was then concentrated to dryness. A 10 mL portion of methanol was added, and the solution was filtered through cotton wool. After evaporation of the solvent under vacuum, the brown oil was subjected to bulb to bulb distillation at 170−200 °C/10^{-5} mbar to afford a yellow oil. Subsequently, a very slow Kugelrohr distillation at 80−100 °C/7 × 10^{-6} mbar gave **15a** as a colorless semisolid compound: yield 20 mg (0.08 mmol, 23%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.94 (s, 9 H), 1.63−1.65 (m, 2 H), 1.69−1.73 (m, 2 H), 2.89 (s, 3 H), 2.14 (s, 3 H), 3.43 (s, 2 H), 3.58 (t, 2 H), 3.66 (t, 2 H), 3.8 (s, 2 H, 3-H); ^{13}C NMR ($CDCl_3$, 100.62 MHz) δ 24.2, 24.8, 27.7, 31.0, 38.3, 32.7, 34.2, 47.1, 48.7, 60.2, 156.2, 167.4. Anal. Calcd for $C_{14}H_{27}N_3O$: C, 65.23; H, 10.53; N, 17.56. Found: C, 66.15; H, 10.86 N, 16.03. For the X-ray structure, see the Supporting Information.

1-Methyl-2-((2,2-dimethylpropyl)imino)-1,2-dihydropyrido[1,2-*a*]pyrimidin-5-ium-4-olate (18a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (300 mg, 1.1 mmol) was isolated in a cold trap as above, and a solution of 2-(methylamino)pyridine (119 mg; 1.1 mmol) in 15 mL of dry CH_2Cl_2 was added. The red-brown solution was transferred to a round-bottom flask, heated for 15 min under reflux, and stirred at room temperature overnight. The solvent was evaporated, and the brown residue was flash-chromatographed using diethyl ether/methanol (100:10) as the mobile phase to remove unreacted starting material and impurities. **18a** was obtained as a red solid in 32% yield (86 mg, 0.35 mmol) by washing the column with a diethyl ether/methanol (100:70) mixture: mp 155−160 dec; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9 H, *t*-Bu), 2.74 (s, 2 H, NCH_2), 3.68 (s, 3 H, NMe), 5.02 (s, 1 H, 3-H), 7.02 (dt, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 7-H), 7.19 (d, 1 H, 9-H), 7.89 (dt, ^3J = 6.8 Hz, ^4J = 1.7 Hz, 1 H, 8-H), 9.17 (dd, ^3J = 6.8 Hz, ^4J = 1.5 Hz, 1 H, 6-H) ppm; ^{1}H NMR (CD_3CN, DMSO, 400.13 MHz) δ 0.88 (s, 9 H, *t*-Bu), 3.13 (d, 3J = 6.5 Hz, 2 H, NCH_2), 3.75 (s, 3 H, NMe), 5.81 (s, 1 H, 3-H), 7.65 (t, 7-H), 7.99 (t, br, 1 H, NH), 8.11 (d, 1 H, 9-H), 8.45 (dt, ^3J = 7.0 Hz, ^4J = 1.7 Hz, 1 H, 8-H), 9.17 (dd, ^3J = 6.8 Hz, ^4J = 1.2 Hz, 1 H, 6-H); ^{13}C NMR ($CDCl_3$, 50.32 MHz) δ 27.9 (C*Me*$_3$), 30.3 (NMe), 32.3 (*C*Me$_3$), 60.2 (NCH_2), 75.0 (C-3), 112.1 (C-9), 113.1 (C-7), 132.0 (C-6), 142.3 (C-8), 148.4 (C-9a), 149.9 (C-2), 151.2 (C-4); ^{13}C NMR (CD_3CN, DMSO, 100.6 MHz) 27.3 (C*Me*$_3$), 33.6 (NMe), 35.7 (*C*Me$_3$), 52.8 (NCH_2), 78.2 (C-3), 116.6 (C-9), 118.8 (C-7), 130.9 (C-6), 145.5 (C-8), 147.5 (C-9a), 153.3 (C-2), 154.8 (C-4) ppm (the ^{13}C NMR assignments are supported by HMBS and HSQC spectra); IR (KBr) 2959 (s), 2871 (sh), 1638 (vs, br), 1546 (s), 1478 (s), 1397 (s), 1369 (m), 1253 (m), 1207 (m), 1094 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.45; H, 7.90; N, 16.84.

2-((2,2-Dimethylpropyl)amino)pyrido[1,2-*a*]pyrimidin-4-one (20a) and 4-((2,2-Dimethylpropyl)amino)pyrido-[1,2-*a*]pyrimidin-2-one (26). Method A. (Neopentylimino)-propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (200 mg, 0.6 mmol) was isolated in a cold trap as above and dissolved in 50 mL of dry CH_2Cl_2. This solution was treated with a solution of 2-aminopyridine (56 mg, 0.6 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature overnight. The solvent was evaporated under vacuum, and the oily residue was chromatographed (MeOH/diethyl ether 2.5:100, R_f = 0.44) to afford 99 mg (0.43 mmol, 73%) of **20a** as a pale brown solid.

Method B. Iminopropadienone **6a** similarly obtained from Meldrum's acid derivative **4a** was treated with a solution of 2-aminopyridine (56 mg, 0.6 mmol) in 15 mL of toluene, and

the reaction mixture was refluxed in a preheated oil bath for 30 min. The solution was concentrated under vacuum to half volume, and diethyl ether was added until the solution became cloudy. The suspension was cooled to 0 °C for several hours, and the precipitate was collected by centrifugation, washed with diethyl ether, and dried under vacuum to afford 21 mg (15%) of **26** as yellow crystals (TLC with diethyl ether/MeOH 1:1; $R_f = 0.2$).

The supernatant was purified in the same way as described above for **20a** to yield 73 mg (0.32 mmol, 53%) of **20a**.

26: mp 216−218 °C dec; ^{1}H NMR ($CDCl_3$/MeOH) δ 0.86 (s, 9 H), 3.01 (s, 2 H), 5.65 (s, 1 H), 6.83 (t, $^3J = 7.2$ Hz, 1 H), 7.14 (d, $^3J = 9.2$ Hz, 2 H 9-H), 7.45 (t, $^3J = 7.4$, 1 H), 8.22 (d, $^3J = 7.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 27.1, 32.4, 54.4, 88.9, 113.7, 124.3, 126.1, 135.9, 150.3, 150.8, 170.3. **20a**: mp 123 °C; ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 0.96 (s, 9 H), 3.02 (s, br, 2 H), 4.97 (s, br, 1 H), 5.44 (s, 1 H), 6.81 (dt, 1 H), 7.18 (d, $^3J = 8.8$ Hz, 1 H), 7.53 (dt, 1 H), 8.82 (d, $^3J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$, 50.32 MHz) δ 27.3, 32.1, 53.5, 79.6, 112.2, 123.6, 127.7, 136.5, 151.0, 158.4, 162.0. Anal. Calcd for $C_{13}H_{17}N_3O$: C, 67.51; H, 7.41; N, 18.18. Found: C, 67.33; H, 7.66; N, 18.08.

2-((2,2-Dimethylpropyl)amino)-9-methylpyrido[1,2-*a*]-pyrimidin-4-one (21a), 4-((2,2-Dimethylpropyl)amino)-9-methylpyrido[1,2-*a*]pyrimidin-2-one (27), and 4-((2,2-Dimethylpropyl)amino)-9-methylpyrido[1,2-*a*]pyrimidin-2-ol (31). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (200 mg, 0.6 mmol) was isolated in a cold trap as above and treated with a solution of 2-amino-3-methylpyridine (65 mg, 0.6 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 90 min, and the solvent was evaporated under vacuum. A ^{1}H NMR of the crude product showed a mixture of **27** and **21a** in a 0.3:1 ratio. The oily residue was dissolved in 10 mL of THF, and a few drops of diethyl ether and hexane were added until the solution became milky. The suspension was stirred for 2 h, and the precipitate was collected by centrifugation, washed with diethyl ether, and dried under vacuum to afford **27**, which was then recrystallized from CH_2Cl_2/diethyl ether to yield 25 mg (17%) as a white powder. The supernatant was cooled to 0 °C overnight in a refrigerator, and the cloudy precipitate was isolated by centrifugation, washed with diethyl ether, and dried under vacuum to give **31** (5 mg, 0.02 mmol, 3%) as a red-brown solid. The supernatant was evaporated to dryness and purified by sublimation (105 °C/10^{-4} mbar) to give 45 mg (31%) of **21a** as a yellow powder. **27**: mp 220−228 °C dec; ^{1}H NMR δ 0.99 (s, 9 H), 2.28 (s, 3 H), 3.05 (s, 2 H), 5.75 (s, 1 H), 6.64 (t, $^3J = 6.24$ Hz, 1 H), 6.79 (s, br, 1 H), 7.25 (d, 1 H), 8.50 (d, $^3J = 7.04$ Hz); ^{13}C NMR (CD_3CN, $CDCl_3$, 100.62 MHz) δ 18.4, 27.2, 32.3, 54.4, 88.5, 112.9, 124.6, 133.2, 133.8, 150.3, 150.6, 169.5. **31**: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 0.99 (s, 9 H), 2.41 (s, 3 H), 3.15 (s, 2 H), 6.18 (s, 1 H), 6.96 (t, $^3J = 7.1$ Hz, 1 H), 7.48 (d, $^3J = 6.9$, 1 H), 7.77 (s, br, 1 H), 8.95 (d, $^3J = 7.1$ Hz, 1 H). **21a**: mp 183−184 °C; GC/MS 12.97 min; ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 0.97 (s, 9 H), 2.41 (s, 3 H), 3.08 (d, 2 H), 4.96 (t, br, 1 H), 5.45 (s, 1 H), 6.74 (t, $^3J = 6.8$ Hz, 1 H), 7.41 (s, 1 H), 8.77 (d, $^3J = 6.6$ Hz); ^{13}C NMR ($CDCl_3$) δ 18.0, 27.7, 32.3, 53.2, 80.2, 111.6, 125.6, 132.0, 135.0, 150.6, 159.0, 161.5. Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.34; H, 8.08; N, 16.95. For the X-ray structure of **21a** see the Supporting Information.

2-((2,2-Dimethylpropyl)amino)-8-methylpyrido[1,2-*a*]-pyrimidin-4-one (22a) and 4-((2,2-Dimethylpropyl)amino)-8-methylpyrido[1,2-*a*]pyrimidin-2-one (28). Method A. (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (100 mg, 0.3 mmol) was isolated in a cold trap as above and treated with a solution of 2-amino-4-methylpyridine (32 mg, 0.3 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 5 h. The solvent was evaporated under vacuum, and the oily residue was chromatographed (MeOH:diethyl ether 5:100) to afford 45 mg (61%) of **22a** as a pale brown solid.

Method B. (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (200 mg, 0.6 mmol) was isolated in a cold trap as above and treated with a solution of 2-amino-3-methylpyridine (65 mg, 0.6 mmol) in 15 mL of toluene. The reaction mixture was refluxed in a preheated oil bath for 30 min. The solution was concentrated under vacuum to half-volume, and diethyl ether was added until the solution became cloudy. The suspension was cooled to 0 °C for several hours, and the precipitate was collected by centrifugation, washed with diethyl ether, and dried under vacuum to afford 39 mg (0.16 mmol, 27%) of **28** as yellow crystals. The supernatant was purified as described above to yield 50 mg (0.2 mmol, 34%) of **22a**.

28: mp 238−239 °C; ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 1.01 (s, 9 H), 2.29 (s, 3 H), 2.99 (d, $^3J = 3.9$ Hz, 2 H), 5.70 (s, br, 1 H), 5.70 (s, 1 H), 6.60 (dd, $^3J = 7.3$ Hz, $^4J = 1.7$ Hz), 6.94 (s, 1 H), 8.2 (d, $^3J = 7.6$ Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.1, 27.7, 32.5, 54.8, 90.2, 115.4, 122.8, 125.9, 146.7, 149.9, 151.1, 170.6.

22a: mp 179−181 °C; ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 0.92 (s, 9 H), 2.23 (s, 3 H), 2.98 (s, br, 2 H), 4.95 (s, br, 1 H), 5.35 (s, 1 H), 6.63 (dd, $^3J = 7.4$ Hz, $^4J = 1.7$ Hz), 6.95 (s, 1 H), 8.71 (d, $^3J = 7.1$ Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.3, 27.3, 32.1, 53.5, 79.5, 115.0, 121.5, 127.0, 148.8, 150.9, 158.3, 162.0.

Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.31; H, 8.01, N, 16.83.

2-((2,2-Dimethylpropyl)amino)-7-methylpyrido[1,2-*a*]-pyrimidin-4-one (23a) and 4-((2,2-Dimethylpropyl)amino)-7-methylpyrido[1,2-*a*]pyrimidin-2-one (29). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (500 mg, 1.5 mmol) was isolated in a cold trap as above and treated with a solution of 2-amino-5-methylpyridine (162 mg, 15 mmol) in 20 mL of dry THF. The reaction mixture was refluxed for 6 h in a preheated oil bath. After the solvent had been evaporated, a ^{1}H NMR spectrum of the crude material was taken, indicating a mixture of **29** and **23a** in a 1:0.17 ratio. Attempts to precipitate **23a** from the crude mixture (in THF) with diethyl ether failed. The crude product was chromatographed (diethyl ether/methanol 100:5, $R_f = 0.5$) to yield 249 mg (1.0 mmol, 68%) of **29** as a pale orange solid, while **23a** failed to elute. **23a**: ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9 H, *t*-Bu), 2.20 (s, 3 H, Me), 3.16 (d, 2 H, NCH_2), 5.76 (s, 1 H, 3-H), 6.9512 (d, $^3J = 9.05$ Hz, 9-H), 7.28 (dd, $^4J = 2.44$ Hz, $^3J = 8.79$ Hz,8-H), 8.55 (s, 6-H). **29**: mp 138−140 °C; GC/MS 13.5 min; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9 H, *t*-Bu), 2.26 (s, 3 H, Me), 2.99 (d, 2 H, NCH_2), 5.10 (tr, br, 1 H, NH), 5.42 (s, 1 H, 3-H), 7.12 (d, $^3J = 9.03$ Hz, 9-H), 7.40 (dd, $^4J = 4.18$ Hz, $^3J = 9.03$ Hz, 8-H), 8.65 (s, 6-H). ^{13}C NMR ($CDCl_3$) δ 17.9 (Me), 27.3 (CMe_3), 32.1 (CMe_3), 53.4 (NCH_2), 80.0 (C-3), 122.3 (C-7), 122.7 (C-9), 125.2 (C-6), 139.7 (C-7), 149.6 (C-9a), 158.1 (C-2), 161.4 (C-4) ppm (the assignments are supported by a HMBC spectrum). Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.36; H, 8.05; N, 17.09.

2-((2,2-Dimethylpropyl)amino)-6-methylpyrido[1,2-*a*]-pyrimidin-4-one (24a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (100 mg, 0.3 mmol) was isolated in a cold trap as above and treated with a solution of 2-amino-6-methylpyridine (32 mg, 0.3 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature, and the course of the reaction was monitored by GC/MS. After 5 days the solvent was evaporated under vacuum and the oily residue was chromatographed on (diethyl ether/MeOH 100:5, $R_f = 0.41$) to afford 21 mg (0.08 mmol, 28%) of **24a** as a pale brown solid: mp 156−158 °C; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9 H), 2.96 (d, 2 H), 2,97 (s, 3 H), 5.03 (t, br, 1 H), 5.27 (s, 1 H), 6.43 (d, $^3J = 6.8$ Hz), 7.03 (d, $^3J = 8.81$ H), 7.29 (dd, $^3J = 6.8$ Hz, $^3J = 8.8$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.8, 27.3, 32.1, 53.5, 81.2, 116.3, 122.0, 136.2, 144.7, 153.0, 160.1, 162.3. Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.69; H, 8.17; N, 17.11.

2-((2,2-Dimethylpropyl)amino)-8-methylpyrimido[1,2-*a*]pyrimidin-4-one (34a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (100 mg, 0.3 mmol) was isolated in a cold trap as above and treated with a solution of 2-amino-4-methylpyrimidine (33 mg, 0.3 mmol) in 15 mL of dry THF. The reaction mixture was refluxed for 30 min. The solvent was evaporated, and the brown residue was flash chromatographed using a diethyl ether/methanol mixture (100:15, $R_f = 0.58$) as the mobile phase. The crude product

was recrystallized from THF to give 36 mg (42%): mp 242 °C; GC retention time 14.2 min; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9 H), 2.59 (s, 3 H), 2.98−3.04 (s, br, 2 H), 5.23 (s, br, 1 H), 5.36 (s, 1 H), 6.74 (d, ^3J = 7.1 Hz), 8.96 (d, ^3J = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.5, 27.3, 32.1, 53.6, 78.7, 110.1, 135.8, 158.0, 163.5, 173.3.

2-((2,2-Dimethylpropyl)amino)pyrazino[1,2-*a*]pyrimidin-4-one (35a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (200 mg, 0.6 mmol) was isolated in a cold trap as above and treated with a solution of 2-aminopyrazine (70 mg, 0.7 mmol) in 15 mL of dry THF. The reaction mixture was heated under reflux for 4 h. The solvent was evaporated, and the brown residue was flash-chromatographed using a diethyl ether/methanol mixture (100:15, R_f = 0.42) as the mobile phase. The crude product was recrystallized from THF to give 61 mg (37%) as a beige powder: mp 166 °C, GC retention time 12.3 min; ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 0.98 (s, 9 H), 3.06 (d, 2 H), 5.12 (s, br, 1 H), 5.54 (s, 1 H), 7.87 (d, ^3J = 4.7 Hz), 8.51 (d, ^3J = 4.7 Hz, 1 H), 8.69 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ27.3, 32.2, 53.5, 82.7, 117.6, 129.2, 144.4, 151.0, 156.9, 162.3.

4-((2,2-Dimethylpropyl)amino)pyrimido[2,1-*a*]isoquinolin-4-one (36a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (100 mg, 0.3 mmol) was isolated in a cold trap as above, treated with a solution of 1-aminoisoquinoline (51 mg, 0.32 mmol) in 10 mL of dry CH_2Cl_2, and stirred at room temperature for 16 h. The solvent was evaporated, and the brown oil was chromatographed (diethyl ether/methanol 100:7, R_f =0.68) to afford **36**, which was recrystallized from boiling THF to give 28 mg (0.1 mmol, 31%): mp 170 °C; GC retention time 17.2 min; ^{1}H NMR (CD_3OD, 400.13 MHz) δ 1.00 (s, 9 H), 3.06−3.1 (d, br, 2 H), 5.16 (tr, 1 H), 5.50 (s, 1 H), 6.99d, ^3J = 7.92 Hz), 7.57 (dt, 1 H), 7.59 (d, 1 H), 7.67 (dt, 1 H), 8.63 (d, ^3J = 7.62 Hz), 8.81 (d, 1 H); ^{13}C NMR ($CDCl_3$, 100.62 MHz) δ 27.4, 32.3, 53.4, 80.8, 112.0, 122.1, 126.0, 126.3, 126.9, 127.9, 132.2, 134.2, 149.6, 159.5, 161.5. Anal. Calcd for $C_{17}H_{19}N_3O$: C, 72.56; H, 6.81; N, 14.94. Found: C, 71.93; H, 6.73 N, 13.61.

1,4-Dihydro-2-[(2,2-dimethylpropyl)amino][1,10]-phenanthrolin-4-one (40). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (300 mg, 1.1 mmol) was isolated in a cold trap as above and treated with a solution of of 8-aminoquinoline (144 mg, 1 mmol) in 10 mL of THF. The brown reaction mixture was heated under reflux for 6 h (no reaction took place in CH_2Cl_2 at room temperature). After evaporation of the solvent **40** was chromatographed using a diethyl ether/methanol gradient (0% to 10% methanol, R_f = 0.52 using 10% methanol in diethyl ether) and recrystallized from THF to give 78 mg (28%) of a colorless solid: mp 288−312 °C dec; ^{1}H NMR (CD_3OD, 500 MHz) δ 1.06 (s, 9 H, *t*-Bu), 3.06 (s, 2 H, NCH_2), 5.82 (s, 1 H, 3-H), 7.61 (dd, 8-H), 8.9 (d, ^3J = 3.3 Hz, 9-H); ^{13}C NMR (CD_3OD, 125.7 MHz) δ 27.2 (CMe_3), 32.9 (CMe_3), 54.8 (NCH_2), 91.3 (C-3), 121.1 (C-4a), 121.9 (C-6), 123.1 (C-5), 124.6 (C-8), 130.5 (C-6a), 136.9 (C-10b), 137.4 (C-7), 139.2 (C-10a), 150.4 (C-9), 155.7 (C-2), 178.4 (C-4) (HMBC and HSQC spectra supported the assignments). Anal. Calcd for $C_{17}H_{19}N_3O$: C, 72.56; H, 6.81; N, 14.94. Found: C, 71.80; H, 6.97; N, 14.19.

7-((2,2-Dimethylpropyl)amino)-2,3-dihydro[1,3]thiazolo-[3,2-*a*]pyrimidin-5-one (41a). (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (200 mg, 0.6 mmol) was isolated in a cold trap as above and treated with a solution of 2-aminothiazole (62 mg, 0.6 mmol) in 10 mL of CH_2Cl_2. The yellow solution was stirred for 15 min at room temperature. The solvent was partly evaporated under vacuum, and diethyl ether was added to precipitate a brown solid. The solvent was decanted, and the residue was dissolved in a few drops of CH_2Cl_2. After a few drops of diethyl ether were slowly added, the solution turned into a milky suspension. After the mixture was cooled at 0 °C for 2 days, pale brown crystals formed. Yield: 90 mg (62%). For further purification **41a** was chromatographed using diethyl ether/methanol (100:10) as the mobile phase (R_f = 0.78): mp 112−114 °C; GC retention time 13.7 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (s, 9 H), 2.85 (d, ^3J = 6.1 Hz, 2 H), 3.36 (t, 2 H), 4.34 (t, 2 H), 4.98 (t, br, 1 H), 4.98 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100.62 MHz) δ 26.4, 27.3, 32.0, 48.3, 53.8, 79.9, 162.2, 163.0, 164.0.

Table 1

reagent	4-/2-pyrimidinone ratio: CH_2Cl_2, room temp, 5 h	4-/2-pyrimidinone ratio: toluene, reflux, 30 min
2-aminopyridine	1/0.3[a] **20a**/**26**	1/0.6[a] **20a**/**26**
2-amino-4-methylpyridine	1/0.25[b] **22a**/**28**	1/0.72[b] **22a**/**28**
2-aminothiazole	1/0[a] **42a**/**43a**	1/0.5[a] **42a**/**43a**

[a] By integration of *tert*-butyl signals. [b] By integration of pyridylmethyl signals.

7-((2,2-Dimethylpropyl)amino)[1,3]thiazolo[3,2-*a*]pyrimidin-5-one (42a) and 5-((2,2-Dimethylpropyl)amino)-[1,3]thiazolo[3,2-*a*]pyrimidin-7-one (43a). Method A. (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (200 mg, 0.6 mmol) was isolated in a cold trap as above and treated with a solution of 2-aminothiazole (61 mg, 0.6 mmol) in 10 mL of THF. The reaction mixture was refluxed for 1 h. The solvent was evaporated under vacuum, and the oily residue was chromatographed (MeOH/diethyl ether = 10:100) to afford 65 mg of **42a** (46%) as a pale brown solid.

Method B. (Neopentylimino)propadienone (**6a**) obtained from Meldrum's acid derivative **4a** (200 mg, 0.6 mmol) was isolated in a cold trap as above, treated with a solution of 2-aminothiazole (61 mg, 0.6 mmol) in 15 mL of toluene, and refluxed for 30 min. The solution was concentrated under vacuum to half-volume, and diethyl ether was added until the solution turned cloudy. After the mixture was cooled for 48 h at 0 °C, the precipitate was collected by centrifugation, washed with diethyl ether, and dried under vacuum. Recrystallization from ethanol afforded 19 mg (13%, 0.08 mmol) of **43a** as yellow crystals. The supernatant was purified as described above to yield 41 mg (35%) of **42a**.

42a: mp 82 °C; GC retention time 12.6 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.94 (s, 9 H), 2.97 (d, ^3J = 5.3 Hz, 2 H), 4.89 (t, br, 1 H), 5.2 (s, 1 H), 6.64 (d, ^3J = 4.7 Hz), 7.78 (d, ^3J = 4.7 Hz); ^{13}C NMR ($CDCl_3$, 100.62 MHz) δ 27.3, 32.1, 53.7, 78.9, 107.1, 122.2, 159.1, 162.4, 162.9. Anal. Calcd for $C_{11}H_{15}N_3OS$: C, 55.67; H, 6.37; N, 17.17 Found: C, 55.58; H, 6.47; N, 17.72.

43a: mp 276 °C dec; ^{1}H NMR (DMSO-d_6, 333 K) δ 0.96 (s, 9 H), 2.99 (d, ^3J = 4.9 Hz, 2 H), 5.31 (s, 1 H), 6.8 (s, br, 1 H), 7.26 (d, ^3J = 5.12 Hz), 8.12 (d, ^3J = 5.12 Hz); ^{13}C NMR (CD_3CN, DMSO-d_6) δ 27.0, 32.5, 53.0, 82.4, 108.4, 120.9, 149.6, 162.8, 168.0. Anal. Calcd for $C_{11}H_{15}N_3OS$: C, 55.67; H, 6.37; N, 17.71. Found: C, 55.37; H, 6.40 N, 17.42. For the X-ray structure, see the Supporting Information.

Temperature Effect on Isomer Ratio in Reactions of 6a with 2-Aminopyridines and 2-Aminothiazole. For each of the following experiments, iminopropadienone **6a** obtained from Meldrum's acid derivative **3a** (50 mg, 0.15 mmol) was isolated at −78 °C and subsequently treated with 2-aminopyridine (0.28 mmol, 28 mg), 2-amino-4-methylpyridine (0.28 mmol, 32 mg), or 2-aminothiazole (0.28 mmol, 30 mg), dissolved in either methylene chloride or toluene (the use of nitrobenzene at reflux caused mainly decomposition). The reaction mixture was stirred at room temperature for 5 h when methylene dichloride was used as solvent and for 30 min under reflux in toluene. The solvents were evaporated under vacuum, and the samples were analyzed by ^{1}H NMR spectroscopy to give the results shown in Table 1.

Attempted Isomerization of 2-((2,2-Dimethylpropyl)-amino)-8-methylpyrido[1,2-*a*]pyrimidin-4-one (22a) into 4-((2,2-Dimethylpropyl)amino)-8-methylpyrido[1,2-*a*]pyrimidin-2-one (28). 2-((2,2-Dimethylpropyl)amino)-8-methylpyrido[1,2-*a*]pyrimidin-4-one (**22a**) (10 mg) was dissolved in 1 mL of toluene-d_8 and placed in a NMR tube. The NMR tube was sealed and placed in the 200 MHz spectrometer. The probe was heated to 95 °C, and ^{1}H NMR spectra were recorded over a period of 12 h in intervals of 1 h. No change in the NMR patterns occurred, and the solution was therefore heated in

an oil bath at 140 °C for another 12 h. The ^{1}H NMR remained unchanged. Consequently, no equilibrium between **22a** and **28** was achieved under these conditions.

Standard Procedure for Synthesis and Chemistry of (Mesitylimino)propadienone (6b). 5-[(Dimethylamino)-(mesitylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**4b**;[22] 100 mg, 0.3 mmol) was subjected to FVT at 700 °C/ 1.5×10^{-5} mbar over the course of 4 h, collecting the product in an ice-cooled U-tube. Upon completion of the thermolysis, the apparatus was flushed with N_2, and an excess or 1 equiv of trapping agent in dilute solution (4 mL of dry CCl_4 or CH_2Cl_2) was injected through a septum onto the cold thermolysate. After the mixture stood for a further 30 min in the ice bath, the U-tube was warmed to room temperature, and the solvent was removed by rotary evaporation.

(Mesitylimino)propadienone (6b). After thermolysis of **4b** as above, 4 mL of CCl_4 was injected to give **6b** in 72−80% yield as a white solid (color changed rapidly to brown): mp 12 °C dec. Spectroscopy was performed immediately: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 2.29 (s, 6H), 6.74 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −6.8, 18.6, 21.1, 111.6, 126.2, 128.8, 132.5, 135.0, 137.3; IR (CCl_4) 2983, 2921, 2857, 2214, 2181, 1615, 1474, 1379, 1264, 1204, 855 cm^{-1}; IR (Ar, 14 K) 2248, 2243, 2234, 2149, 1583, 1483, 1440, 1145, 1032 cm^{-1}; far-IR (LLD polyethylene) 73, 90 cm^{-1}; Raman (CCl_4) 2925, 2217, 2204, 2180, 2171, 1610, 1475, 1309, 1207, 1151, 577 cm^{-1} (see the Supporting Information for IR, Raman, and NMR spectra); MS *m*/*z* 308 (M^+, 2), 292 (2), 247 (6), 213 (5), 173 (3), 141 (53), 135 (100), 120 (98), 112 (69), 85 (96), 70 (15), 56 (15), 42 (39); HRMS *m*/*z* calcd for $C_{12}H_{11}NO$ 185.0841, found 185.0480.

***N*,*N*-Diethyl 3-(Diethylamino)-3-(mesitylimino)propanamide (8b).** Diethylamine in dichlorormethane was added to **6b**. The resulting yellow solution was filtered through a pipet containing cotton wool, and the solvent was evaporated to give 39 mg of **8b** as a yellow oil. According to the ^{1}H and ^{13}C NMR spectra, the product was >98% pure: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.72 (t, 3 H, J = 7.2 Hz), 1.00 (t, 3 H, J = 7.1 Hz), 1.20 (t, 6 H, J = 7.0), 1.96 (s, 6 H), 2.16 (s, 3 H), 2.69 (q, 2 H, J = 7.2 Hz), 3.06 (s, 2 H), 3.20 (q, 2 H, J = 7.1 Hz), 3.46 (q, 4 H, J = 7.0 Hz), 6.72 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 152.5, 146.5, 130.4, 129.1, 128.4, 42.2, 42.0, 40.7, 31.9, 20.6, 18.4, 13.7, 13.6, 12.8. Anal. Calcd for $C_{20}H_{33}N_3O$: C, 72.42; H, 10.03; N, 12.68. Found: C, 72.47; H, 10.04; N, 12.60.

1,3-Bis(3,5-dimethylpyrazolyl)-3-(mesitylimino)propan-1-one (9b). 3,5-Dimethylpyrazole in dichloromethane was added to **6b**, and the solution was evaporated. NMR data showed the formation of only **9b** (>95% purity according to NMR). Dilution (1 equiv of trapping agent in 80 mL of dichloromethane) gave the same results: ^{1}H NMR ($CDCl_3$) δ 6.78 (s, 2 H), 5.86 (s, 1 H), 5.82 (s, 1 H), 4.34 (s, 2 H), 2.61 (s, 3 H), 2.34 (s, 3 H), 2.16 (s, 3 H), 2.11 (s, 3 H), 2.04 (s, 6 H), 2.01 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.2, 151.9, 151.8, 149.2, 143.9, 143.3, 142.6, 132.4, 128.7, 126.8, 111.0, 109.9, 37.3, 20.6, 18.3, 15.6, 14.2, 13.7, 13.6. HRMS *m*/*z* calcd for $C_{22}H_{27}N_5O$ 377.2210, found 377.2211.

3-(Mesitylamino)pyrazolin-5-one (11). Addition of an excess of anhydrous hydrazine in dichloromethane to **6b** resulted in the formation of an insoluble white solid. Filtration and washing with dichloromethane and acetone gave 35 mg of **11** as a white solid (yield 72%): mp 268−270 °C; ^{1}H NMR (DMSO-d_6) δ 9.92 (s, 1 H), 7.80 (s, 1 H), 6.83 (s, 2 H), 3.27 (s, 2 H), 2.19 (s, 3 H), 2.12 (s, 6 H); ^{13}C NMR (DMSO-d_6) δ 171.5, 154.6, 135.0, 134.7, 134.0, 128.4, 36.0, 20.5, 18.1. Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.38; H, 6.96; N, 19.35. Found: C, 66.11; H, 6.91; N, 19.19.

1-Methyl-3-(mesitylamino)pyrazolin-5-one (12b). Addition of an excess of anhydrous methylhydrazine in dichloromethane to **6b** resulted in the formation of a yellow solution. Evaporation of the solvent gave a brownish solid which was purified by recrystallization (THF/pentane) or by sublimation to give **12b** as a pale brown solid (yield 70%): mp 138−140 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.91 (s, 1 H), 5.90 (s, 1 H), 3.16 (s, 2 H), 3.15 (s, 3 H), 2.27 (s, 3 H), 2.23 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 168.1, 154.7, 137.2, 135.5, 132.4, 129.3, 36.7, 31.1, 20.9, 18.2. Anal. Calcd for $C_{13}H_{17}N_3O$: C, 67.49; H, 7.41; N, 18.18. Found C, 67.20; H, 7.46; N, 18.16.

1,4-Dimethyl-7-(mesitylimino)perhydro[1,4]diazepin-5-one (13b). Iminopropadienone **6b** obtained from **4b** (332 mg, 1.0 mmol) was treated with a solution of 97.0 mg (1.1 mmol) of *N*,*N*′-dimethylethylenediamine in 30 mL of diethyl ether, which was added dropwise to the stirred solution over a period of 6 h. The resulting mixture was stirred for 3 days. The solvent was evaporated, and the crude product was purified by flash chromatography (5% MeOH/ether) to give 150 mg (yield 55%) as a yellow oil which was difficult to purify to analytical accuracy: ^{1}H NMR (400 MHz, $CDCl_3$) δ1.91 (s, 6 H), 2.92 (s, NMe, 3 H), 3.14 (s, 3 H, NMe), 3.28 (s, 2 H), 3.49−3.51 (m, 2H), 3.63−3.66 (m, 2H), 6.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 20.7, 35.6, 37.4, 37.5, 50.0, 50.1, 128.5, 129.3, 134.6, 143.8, 153.1, 165.6.

4-(Mesitylimino)-2,3,4,5-tetrahydrobenzo[*b*][1,4]-diazepin-2-one (16). Iminopropadienone **6b** obtained from **4b** (332 mg, 1.0 mmol) was treated with 119.0 mg (1.1 mmol) of 1,2-phenylenediamine in 15 mL of dry THF, and the resulting mixture was stirred for 3 h. The solvent was evaporated, and the crude product was sublimed to remove excess 1,2-phenylenediamine and then purified by flash chromatography (5% MeOH/ether), sublimed, and washed with ethyl acetate to give 160 mg (yield 55%) as white crystals: mp 238−239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (s, 6 H), 2.30 (s, 3 H,), 3.20 (s, 2 H), 6.95 (s, 2 H), 7.19 (dd, ^3J = 7.6 Hz,^4J = 1.0 Hz, 1 H), 7.26−7.36 (m, 2 H), 7.54 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1 H), 8.58 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 21.0, 34.9, 122.7, 124.3, 126.8, 127.2, 128.4, 128.7, 129.2, 129.8, 135.7, 139.9, 160.9, 163.1. Anal. Calcd for $C_{18}H_{19}N_3O$: C, 73.69; H, 6.53; N, 14.32. Found: C, 73.84; H, 6.64; N, 14.05.

1-Methyl-2-(mesitylamino)pyrido[1,2-*a*]pyrimidin-5-ium-4-olate (18b). 2-(Methylamino)pyridine in dichloromethane was added to **6b** to give, after evaporation of the solvent and recrystallization of the crude product with methanol, 50 mg of **18b** as an orange solid (yield 79%): mp 237−240 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.00 (apparent d, 1H), 8.22 (appt t, 1 H), 7.71 (appt d, 1 H), 7.33 (appt t, 1 H), 6.80 (s, 2 H), 4.08 (s, 1 H), 3.80 (s, 3 H), 2.19 (s, 3 H), 1.94 (s, 6 H); ^{13}C NMR (DMSO-d_6) δ 150.7 (C-4), 149.0 (C-9a or C-2), 148.2 (C-2 or C-9a), 145.0 (C−N), 143.6 (C-8), 130.7 (C-6), 129.6 (C−CH_3), 128.4 (2x CH), 128.1 (2 × C−CH_3), 114.9 (C-7), 114.1 (C-9), 73.6 (C-3), 30.7 (CH_3−N), 20.4 (CH_3), 17.7 (2 × CH_3) (the NMR assignments are supported by HSQC and HMBC spectra); IR (KBr) 1710, 1638, 1616, 1603, 1561, 1415 1385 cm^{-1}; IR (Ar, 14 K) 1738, 1636, 1624, 1609, 1590, 1568, 1533, 1485, 1468, 1443, 1434, 1412, 1383, 1366, 1351, 1323, 1306, 1265, 1229, 1201, 1176, 1168, 1155, 1139, 1051, 1035, 1007, 930, 853, 778, 767, 742, 663, 552, 469 cm^{-1} (for medium effects on the IR spectra of mesoionic compounds, see ref 12). Anal. Calcd for $C_{18}H_{19}N_3O$: C, 73.68; H, 6.53; N, 14.33. Found: C, 73.86; H, 6.54; N, 14.27. For the X-ray structure, see the Supporting Information.

Flash Vacuum Thermolysis of 18b: Formation of 6b and 2-(Methylamino)pyridine. FVT of **18b** was carried out with deposition of the thermolysate in an Ar matrix at ca. 10 K. At 350 °C, only starting material was isolated (deposition for 10 min using 70 mbar of Ar; vacuum 5×10^{-5} mbar). At 450 °C, **18b** decomposed to give **6b** with the characteristic bands at 2248, 2243, and 2235 cm^{-1} and 2-(methylamino)-pyridine, which was identified by comparison with the IR spectrum of an authentic sample.

2-(Mesitylamino)pyrido[1,2-*a*]pyrimidin-4-one (20b). 2-Aminopyridine in dichloromethane was added to **6b**, and the solvent was evaporated to give a brownish solid. The starting material was removed by sublimation, and the crude product was washed with cold ether to give 40 mg of **20b** as a pale yellow solid (yield 66%): mp 240−242 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.89 (broad d, 1H, J = 7.0 Hz), 7.59 (ddd, 1H, J = 9.0, 7.0, 1.7 Hz), 7.23 (broad d, 1H, J = 9.0 Hz), 6.95 (s, 2H),

(22) Bernhardt, P. V.; Koch, R.; Moloney, D. W. J.; Shtaiwi, M.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 2*, in press.

6.88 (td, 1H, J = 7.0, 1.3 Hz), 6.52 (s, 1H, NH), 5.06 (s, 1H), 2.31 (s, 3H), 2.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 158.5, 151.4, 137.6, 136.7, 136.6, 131.7, 129.3, 127.8, 123.7, 112.5, 80.5, 20.9, 18.0; IR (KBr) 3230, 1661, 1642, 1568, 1544 cm^{-1}. Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.08; H, 6.14; N, 15.05. Found C, 72.68; H, 6.17; N, 14.93.

9-Amino-2-(mesitylamino)pyrido[1,2-*a*]pyrimidin-4-one (33). 2,3-Diaminopyridine in dichloromethane was added to 6b. Evaporation of the solvent and purification of the crude product by chromatography through a short column, with ethyl acetate as eluent, gave 40 mg of 33 as a pale brown solid (yield 63%): mp 230−232 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (dd, 1H, J = 7.0 Hz, 1.4 Hz), 6.94 (s, 2H), 6.79 (dd, 1H, J = 7.0, 1.4 Hz), 6.73 (t, 1H, J = 7.0 Hz), 6.12 (s, 1H, NH), 5.04 (s, 1H), 4.77 (s, 2H, NH_2), 2.30 (s, 3H), 2.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9 (C-4), 159.2 (C-9a or C-2), 144.0 (C-2 or C-9a), 138.6 (C-9), 137.4 (C−N), 136.6 (2 × *C*−CH_3), 131.8 (*C*−CH_3), 129.3 (2 × CH), 116.6 (C-6), 112.9 (C-8), 112.1 (C-7), 80.7 (C-3), 20.9 (CH_3), 18.1 (2 × CH_3) (the NMR assignments are supported by a HSQC spectrum); HRMS *m*/*z* calcd for $C_{17}H_{18}N_4O$ 294.1481, found 294.1478.

2-(Mesitylamino)pyrimido[1,2-*a*]pyrimidin-4-one (34b). 2-Aminopyrimidine in dichloromethane was added to **6b** to give, after evaporation of the solvent and purification of the crude product by chromatography ($CHCl_3$/MeOH 40:1), 45 mg of **34b** as a pale brown solid (yield 74%): mp 193−195 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.11 (dd, 1H, J = 6.8, 1.8 Hz), 8.82 (dd, 1H, J = 3.9, 1.8 Hz), 6.91 (s, 2H), 6.89 (dd, J = 6.8, 3.9 Hz), 6.87 (s, 1H), 4.97 (s, 1 H), 2.26 (s, 3 H), 2.17 (s, 6 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 162.7, 162.6, 158.1, 152.1, 137.9, 137.0, 136.4, 131.2, 129.4, 109.3, 80.0, 20.9, 18.0; IR (KBr) 3285, 3229, 1674, 1558, 1484, 1413, 1285, 804, 784 cm^{-1}; HRMS *m*/*z* calcd for $C_{16}H_{16}N_4O$ 280.1319. found 280.1321.

2-(Mesitylamino)isoquinolino[1,2-*a*]pyrimidin-4-one (36b). 1-Aminoisoquinoline in dichloromethane was added to **6b** to give, after evaporation of the solvent and purification by chromatography ($CHCl_3$), 60 mg of **36b** as a cream-colored solid (yield 84%): mp 288−290 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.91 (br d, 1 H), 8.67 (d, 1H, J = 7.6 Hz), 7.74 (ddd, J = 8.0, 7.0, 1.3 Hz, 1 H), 7.67−7.60 (m, 2 H), 7.05 (d, 1 H, J = 7.6 Hz), 6.94 (s, 2 H), 6.28 (s, 1 H), 5.09 (s, 1 H), 2.30 (s, 3 H), 2.22 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 159.7, 150.2, 137.6, 136.5, 134.4, 132.5, 131.7, 129.3, 128.0, 127.1, 126.4, 126.0, 122.2, 112.3, 81.5, 21.0, 18.1; HRMS *m*/*z* calcd for $C_{21}H_{19}N_3O$ 329.1410, found 329.1421.

2,3-Dihydro-7-(mesitylamino)[1,3]thiazolo[3,2-*a*]pyrimidin-5-one (41b). 2-Aminothiazoline in dichloromethane was added to **6b** to give, after evaporation of the solvent and chromatography ($CHCl_3$), 50 mg of **41b** as a cream-colored solid (yield 74%): mp 114−120 °C; ^{1}H NMR ($CDCl_3$) δ 6.89 (s, 2 H), 6.10 (s, 1 H), 4.59 (s, 1 H), 4.37 (t, 2 H, J = 7.6 Hz), 3.40 (t, 2 H, J = 7.6 Hz), 2.26 (s, 3 H), 2.15 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 164.7, 162.2, 162.1, 137.6, 136.2, 131.5, 129.2, 81.0, 48.3, 26.5, 20.9, 18.0. Anal. Calcd for $C_{15}H_{17}N_3OS$: C, 62.69; H, 5.97; N, 14.63. Found: C, 62.72; H, 6.16; N, 14.09.

7-(Mesitylamino)[1,3]thiazolo[3,2-*a*]pyrimidin-5-one (42b). 2-Aminothiazole in dichloromethane was added to **6b** to give, after evaporation of the solvent and chromatography ($CHCl_3$), 45 mg of **42b** as a cream-colored solid (yield 74%): mp 198−202 °C; ^{1}H NMR ($CDCl_3$) δ 7.81 (d, 1 H, J = 4.9 Hz), 6.91 (s, 2 H), 6.69 (d, 1 H, J = 4.9 Hz), 6.35 (s, 1 H), 4.80 (s, 1 H), 2.27 (s, 3 H), 2.17 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.2, 161.4, 159.1, 137.7, 136.4, 131.5, 129.3, 122.2, 107.6, 79.5, 20.9, 18.0. Anal. Calcd for $C_{15}H_{15}N_3OS$: C, 63.14; H, 5.30; N, 14.74. Found: C, 63.24; H, 5.44; N, 14.58.

5-[(2-*tert*-Butylanilino)(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (2c). A solution consisting of 10 g (40 mmol) of **1** and 7.5 g (50 mmol) in 50 mL of dry acetonitrile was refluxed for 30 h. The resulting solution was concentrated under reduced pressure, and 5 mL of *n*-hexane was added to precipitate white crystals, which were collected by filtration and recrystallized from hot THF to give 9.1 g (65%) as colorless crystals: mp 148−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9 H, *t*-Bu), 1.78 (s, 6 H, CMe_2), 2.32 (s, 3 H, SCH_3), 7.18 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H), 7.22−7.26 (m, 1H), 7.33 (td, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1H), 7.50 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz), 12.8 (s, br, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 26.1, 30.3, 34.9, 85.2, 102.7, 126.7, 127.5, 128.9, 129.2, 135.2, 144.8, 163.8, 178.3. Anal. Calcd for $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63; N, 4.01. Found: C, 61.62; H, 6.64; N, 4.04.

5-[(2-*tert*-Butylanilino)(dimethylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4c). Compound **2c** (12.2 g, 35 mmol) was dissolved in 50 mL of dry THF. A stream of gaseous dimethylamine was bubbled via a pipet through the stirred solution at such a rate that the gas just absorbed, and the solution was then heated at 50 °C for 24 h in a closed flask. The resulting solution was concentrated, causing precipitation of white crystals, which were collected by filtration and recrystallized from THF to give 9.1 g (75%) of colorless crystals: mp 117−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 9 H), 1.74 (s, 6 H), 2.79 (s, 6 H), 6.88 (dd, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 1 H), 7.14−7.22 (m, 2 H), 7.44 (dd, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 1 H) 10.2 (s, br, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2 (CH_3), 30.3 (CH_3 in *t*Bu), 35.1 (*C* in *t*Bu), 41.7 (NCH_3), 76.5 (*C*(CO)), 102.0 (C(O)), 124.3 (aryl-C3), 126.4 (aryl-C5), 126.9 (aryl-C4), 127.7 (aryl-C6), 137.1 (aryl-C2), 142.5 (aryl-C1), 162.8 (C(N)N), 164.7 (CO) (the assignments are supported by HSQC and HMBC spectra). Anal. Calcd for $C_{19}H_{26}N_2O_4$: C, 65.88; H, 7.56; N, 8.09. Found: C, 65.70; H, 7.50; N, 8.01.

5-[(2-*tert*-Butylanilino)(diethylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (5c). A solution consisting of 10 g (35 mmol) of **2c** and 10 mL (97 mmol) of diethylamine in 50 mL of dry acetonitrile was refluxed for 40 h. Concentration of the resulting solution caused precipitation of white crystals, which were filtered and recrystallized from THF to give 10.5 g (80%) of colorless crystals: mp 198−199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, ^3J = 7.2 Hz, 6 H), 1.40 (s, 9 H), 1.70 (s, 6 H), 3.17−3.18 (m, 4 H), 7.08−7.10 (m, 1 H), 7.15−7.18 (m, 2 H), 7.44−7.46 (m, 1 H), 10.1 (s, br, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 26.3, 35.1, 44.2, 76.4, 102.0, 124.1, 126.5, 126.8, 127.8, 137.5, 142.4, 163.1, 164.8. Anal. Calcd for $C_{20}H_{30}N_2O_4$: C, 61.87; H, 6.63; N, 4.01. Found: C, 61.77; H, 6.60; N, 3.98.

((2-*tert*-Butylphenyl)imino)propadienone (6c). This compound was prepared by preparative FVT as follows: 100 mg (0.29 mmol) of **4c** was sublimed at 150−180 °C/10^{-4} mbar and thermolyzed at 700 °C; the iminopropadienone **6c** was collected on a cold finger cooled to −30 °C using acetone/liquid nitrogen solution; this cold finger was connected via an uncooled cold finger to the oil diffusion vacuum pump. Upon completion of the thermolysis, the pump was closed, and the first cold finger was warmed to 20 °C for 30 min and then heated with a heat gun to distill **6c** to the second cold finger, which was cooled to 77 K in liquid nitrogen. This cold finger was now warmed to room temperature while the pressure was equalized with N_2, and iminopropadienone **6c** was rinsed into a receiving NMR tube with $CDCl_3$. The compound was stable for ca. 2 h at room temperature: IR ($CHCl_3$) 2794 m, 2219 s, 2189 s, 1603 m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9 H), 7.07−7.09 (m, 1 H), 7.11−7.15 (m, 2 H), 7.32−7.34 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.81, 29.7, 35.0, 107.6, 126.8, 127.2, 127.5, 128.6, 130.4, 132.6, 144.9 (see Supporting Information for NMR and matrix IR spectra).

Matrix Isolation of ((2-*tert*-Butylphenyl)imino)propadienone (6c). Compound **4c** (10 mg, 0.03 mmol) was sublimed at 50 °C through the FVT tube at 700 °C with Ar matrix isolation of the product on a BaF_2 disk at 7 K over the course of 15 min: IR (Ar, 7K) 2790 w, 2237 vs, 2138 w, 1624 m, 1354 w, 663 m cm^{-1}, Other IR peaks: acetone 1769 w, 1722 m, 1362 m, 1217 m, 1092 m cm^{-1}; dimethylamine 2975 w, 2832 w, 1486 w, 1148 w, 1021 w cm^{-1}; carbon dioxide 2346, 2340 cm^{-1}.

***N*,*N*-Diethyl 3-(Diethylamino)-3-((2-*tert*-butylphenyl)imino)propanamide (8c).** Iminopropadienone **6c** obtained from Meldrum's acid derivative **5c** (374 mg, 1.0 mmol) as above was treated with 0.21 mL (2.0 mmol) of diethylamine in 15 mL of dry CH_2Cl_2, and the resulting mixture was stirred for 12 h. The crude product was purified by flash chromatography (3% MeOH in ether) to yield 200 mg (58%) of a white solid: mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.819 (t, ^3J = 7.2 Hz, 3 H), 1.09 (t, ^3J = 6.9 Hz, 3 H), 1.20 (t, ^3J = 7.2 Hz, 6 H),

1.32 (s, 9 H), 2.90 (q, ^3J = 7.2 Hz, 2 H), 3.13 (s, 2 H), 3.31 (q, ^3J = 6.6 Hz, 2 H), 3.44 (q, ^3J = 6.5 Hz, 4 H), 6.57 (dd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H), 6.82 (td, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1 H), 6.96 (td, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H), 7.23 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 13.6, 13.9, 29.6, 33.9, 35.1, 40.6, 41.6, 42.2, 121.3, 123.4, 125.7, 126.4, 140.7, 150.4, 151.2, 167.1. Anal. Calcd for $C_{21}H_{35}N_3O$: C, 73.00; H, 10.21; N, 12.16. Found: C, 72.91; H, 10.47; N, 11.86.

3-((2-*tert*-Butylphenyl)imino)-1-methylpyrazolin-5-one (12c). To iminopropadienone **6c**, obtained from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol), was added a solution of 50.7 mg (1.1 mmol) of methylhydrazine in 30 mL of THF dropwise over a period of 3 h, and the resulting mixture was stirred for 2 days. The solvent was evaporated, and the crude product was purified by flash chromatography (5% MeOH/ether) to yield 135 mg (55%) of a pale yellow solid: mp 160−161 °C; ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 9 H), 3.21 (s, 3 H), 3.30 (s, 2 H), 6.29 (s, br, 1 H), 7.10−7.26 (m, 2 H), 7.38−7.43 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.6, 31.1, 34.7, 37.4, 125.8, 126.4, 127.0, 127.1, 136.9, 142.8, 153.8, 167.8.

1-Methyl-2-((2-*tert*-butylphenyl)imino)-1,2-dihydropyrido[1,2-*a*]pyrimidin-1-ium-4-olate (18c). Iminopropadienone **6c** obtained from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) as above was treated with 119 mg (1.1 mmol) of 2-(methylamino)pyridine in 15 mL of dry CH_2Cl_2. The resulting mixture was stirred for 24 h. The solvent was evaporated and the crude product purified by flash chromatography (50% MeOH/ether) to yield 200 mg (65%) of an orange solid: mp 198−199 °C; IR (KBr): 1716, 1694, 1636, 1615, 1560, 1473, 1458, 1417, 1355, 1301, 1265, 1050, 771, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 9 H, *t*-Bu), 4.97 (s, 1H, CH), 6.70 (td, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1H), 6.91 (td, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 1H), 7.06−7.12 (m, 1H), 7.30−7.34 (m, 1H), 7.97 (td, ^3J = 7.9 Hz, ^4J = 2.0 Hz, 1H), 9.25 (dd, ^3J = 6.5 Hz, ^4J = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3 (CMe_3), 35.2 (CMe_3), 67.1 (CH), 112.3, 113.9, 122.1, 122.6, 126.5, 126.8, 132.4, 141.6, 142.5, 148.5, 148.6, 149.3, 151.6 (CO). The assignments are supported by a HSQC spectrum. Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67. Found: C, 73.97; H, 7.09; N, 13.54.

2-((2-*tert*-Butylphenyl)imino)pyrido[1,2-*a*]pyrimidin-4-one (20c). Iminopropadienone **6c** obtained from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) was isolated on a cold finger at −30 °C. Subsequently, 103.5 mg (1.1 mmol) of 2-aminopyridine in 15 mL of dry CH_2Cl_2 was added to the iminopropadienone, and the resulting mixture was stirred for 16 h. The solvent was evaporated, and the crude product was sublimed to remove excess 2-aminopyridine and then purified by flash chromatography (5% MeOH/ether) to yield 195 mg (66%) as a pale yellow solid: mp 190−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 9 H, *t*-Bu), 5.38 (s, 1H, CH), 6.47 (s, br, 1 H, NH), 6.87 (td, ^3J = 7.0 Hz, ^4J = 1.4 Hz, 1H), 7.22−7.29 (m, 4H), 7.45−7.47 (m, 1H), 7.57 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H), 8.88 (dd, ^3J = 7.0 Hz, ^4J = 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7 (CMe_3), 35.1 (CMe_3), 81.92 (CH), 112.7, 123.9, 127.3, 127.4, 127.5, 127.9, 130.1, 136.0, 136.7, 146.7, 151.4, 158.5 (CO), 161.5 (the assignments are supported by HSQC and HMBC spectra). Anal. Calcd for $C_{18}H_{19}N_3O$: C, 73.69; H, 6.53; N, 14.32. Found: C, 73.42; H, 6.62; N, 14.25.

1,4-Dimethyl-7-((2-*tert*-butylphenyl)imino)perhydro-[1,4]diazepin-5-one (13c). Iminopropadienone **6c** obtained from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) was treated with 97.0 mg (1.1 mmol) of *N*,*N*′-dimethylethylenediamine in 30 mL of diethyl ether, which was added dropwise to the stirred solution over a period of 6 h. The resulting mixture was stirred at room temperature for 3 days. The solvent was evaporated, and the crude product was purified by flash chromatography (5% MeOH/ether), sublimed, and then washed with ether to yield 170 mg (59%) of white crystals: mp 126−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9 H), 2.96 (s, 3 H), 3.14 (s, 3 H), 3.47 (s, 2 H), 3.51 (t, ^3J = 5.3 Hz, 2 H), 3.69 (t, ^3J = 5.3 Hz, 2 H), 6.37 (dd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H), 6.91 (td, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1 H), 7.09 (td, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H), 7.26 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 35.1, 35.7, 36.9, 37.9, 49.5, 50.6, 122.4, 123.4, 126.0, 126.5, 141.1, 148.2, 151.2, 166.1. Anal. Calcd for $C_{17}H_{25}N_3O$: C, 71.04; H, 8.77; N, 14.62. Found: C, 70.94; H, 8.94; N, 13.79. For the X-ray structure, see the Supporting Information.

8-Methyl-2-((2-*tert*-butylphenyl)imino)pyrido[1,2-*a*]pyrimidin-4-one (22c). Iminopropadienone **6c** obtained from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) was treated with 119.0 mg (1.1 mmol) of 2-amino-4-picoline in 15 mL of dry THF, and the resulting mixture was stirred for 12 h. The solvent was evaporated, and the crude product was sublimed to remove excess 2-amino-4-picoline. Flash chromatography (5% MeOH/ether) yielded 200 mg (65%) as a pale yellow solid: mp 229−230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9 H), 2.32 (s, 3 H) 5.30 (s, 1 H), 6.95 (s, br, 1 H), 6.73 (d, ^3J = 7.0 Hz, 1 H), 7.23−7.29 (m, 4 H), 7.45−7.48 (m, 1 H), 8.77 (d, ^3J = 7.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.35, 30.7, 35.1, 81.0, 115.7, 121.4, 127.2, 127.3, 127.4, 127.6, 130.2, 136.0, 147.0, 149.5, 150.8, 158.1, 161.1. Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67. Found: C, 74.49; H, 6.99; N, 13.71.

7-Methyl-2-((2-*tert*-butylphenyl)imino)pyrido[1,2-*a*]pyrimidin-4-one (23c). Iminopropadienone **6c** obtained from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) was treated with 119.0 mg (1.1 mmol) of 2-amino-5-picoline in 15 mL of dry THF, and the resulting mixture was stirred for 12 h. The solvent was evaporated, and the crude product was sublimed to remove excess 2-amino-5-picoline. Flash chromatography (5% MeOH/ether) yielded 210 mg (68%) as a pale yellow solid: mp 200−201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 2.40 (s, 3 H) 5.30 (s, 1 H), 6.27 (s, br, 1 H), 7.19−7.29 (m, 3 H), 7.49−7.52 (m, 2 H), 7.69 (d, ^3J = 8.0 Hz, 1 H), 8.78 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 30.6, 35.1, 81.9, 122.7, 122.9, 125.2, 127.3, 127.4, 127.5, 130.4, 136.1, 147.1, 149.9, 158.2, 161.3. Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67. Found: C, 74.22; H, 7.00; N, 13.61.

2-((2-*tert*-Butylphenyl)imino)pyrazino[1,2-*a*]pyrimidin-4-one (35c). Iminopropadienone **6c** from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) was treated with 104.6 mg (1.1 mmol) of aminopyrazine in 15 mL of dry THF, and the resulting mixture was stirred at room temperature for 24 h. The solvent was evaporated, and the crude product was sublimed to remove excess aminopyrazine and then purified by flash chromatography (5% MeOH/ether) to yield 80 mg (27%) of a pale yellow solid: mp 156−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9 H), 5.50 (s, 1 H), 6.78 (s, br, 1 H), 7.24−7.31 (m, 3 H), 7.49−7.51 (m, 1 H), 7.94 (d, ^3J = 4.7 Hz, 1 H), 8.56 (dd, ^3J = 4.7 Hz, ^5J = 1.2 Hz, 1 H), 8.77 (d, ^5J = 1.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6, 35.0, 84.4, 117.5, 127.4, 127.5, 127.8, 129.5, 129.7, 135.2, 144.5, 146.7, 151.0, 156.9, 161.6.

2-((2-*tert*-Butylphenyl)imino)isoquinolino[1,2-*a*]pyrimidin-4-one (36c). Iminopropadienone **6c** from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) was treated with 158.6 mg (1.1 mmol) of 1-aminoisoquinoline in 15 mL of dry THF, and the resulting mixture was stirred at room temperature for 12 h. The crude product precipitated upon partial evaporation of the solvent, and it was recrystallized from THF/hexane to yield 275 mg (80%) of a white solid: mp 260−261 °C; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 9 H), 5.49 (s, 1 H), 6.60 (s, br, 1 H), 7.08 (d, ^3J = 7.6 Hz, 1 H), 7.23−7.36 (m, 3 H), 7.44−7.51 (m, 1 H), 7.60−7.80 (m, 3 H), 8.68 (d, ^3J = 7.6 Hz), 8.92 (br d, 1 H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 30.6, 35.0, 82.7, 112.4, 122.2, 125.9, 126.4, 127.0, 127.2, 127.28, 127.31, 128.0, 129.9, 132.5, 134.3, 136.1, 146.4, 150.1, 159.6, 160.7. Anal. Calcd for $C_{18}H_{19}N_3O$: C, 76.94; H, 6.16; N, 12.24. Found: C, 76.41; H, 6.16; N, 11.97.

2-((2-*tert*-Butylphenyl)imino)-2,3-dihydro[1,3]thiazolo-[3,2-*a*]pyrimidin-4-one (41c). Iminopropadienone **6c** obtained from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) as above was treated with 112.4 mg (1.1 mmol) of 2-aminothiazoline in 15 mL of dry THF, and the resulting mixture was stirred for 10 h. The solvent was evaporated, and the crude product was sublimed to remove excess trapping agent. Flash chromatography (5% MeOH/ether) yielded 211 mg (70%) of a pale yellow solid: mp 220−221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 9 H), 3.44 (t, 2 H, ^3J = 7.3), 4.40 (t, 2 H, ^3J = 7.3),

5.01 (s, 1 H), 6.48 (s, br, 1 H), 7.16−7.23 (m, 3 H), 7.40−7.44 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 30.6, 35.0, 48.4, 82.3, 127.2, 127.3, 127.5, 135.7, 146.6, 161.9, 162.0, 164.7. Anal. Calcd for $C_{16}H_{19}N_3OS$: C, 63.76; H, 6.35; N, 13.94. Found: C, 63.47; H, 6.47; N, 13.85.

2-((2-*tert*-Butylphenyl)imino)[1,3]thiazolo[3,2-*a*]pyrimidine-5-one (42c). Iminopropadienone **6c** obtained from Meldrum's acid derivative **4c** (346 mg, 1.0 mmol) was treated with 110.2 mg (1.1 mmol) of 2-aminothiazole in 15 mL of dry THF, and the resulting mixture was stirred for 10 h. The solvent was evaporated, and the crude product was sublimed to remove excess trapping agent. Flash chromatography (5% MeOH/ether) yielded 210 mg (70%) of a pale yellow solid: mp 229−330 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9 H, *t*-Bu), 5.16 (s, 1H, CH), 6.59 (s, br, 1 H, NH), 6.73 (d, 1H, ^3J = 5.0), 7.23−7.24 (m, 3H), 7.43−7.47 (m, 1H), 7.82 (d, 1H, ^3J = 5.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ M 30.6 (C*Me*$_3$), 35.0 (*C*Me$_3$), 80.8 (CH), 107.9, 122.2, 127.3, 127.4, 127.6, 130.0, 135.8, 146.7, 159.0, 161.6, 163.0 (CO). The assignments are supported by HSQC and HMBC spectra. Anal. Calcd for $C_{16}H_{17}N_3OS$: C, 64.19; H, 5.72; N, 14.04. Found: C, 64.06; H, 5.73; N, 13.91.

Acknowledgment. This work was supported by the Australian Research Council.

Supporting Information Available: Figures and tables giving vibrational spectra of **6a**−**c**, ^{1}H and ^{13}C NMR spectra of **6a**−**c**, **8a**, **8′a**, **9b**, **10a**, **12c**, **13b**,**c**, **14a**, **15a**, **17b**, **21a**, **22a**, **23a**, **24a**, **26a**, **33b**, **34a**, **34b**, **35a**,**c**, **36b**, **41a**, and **43a**, and X-ray structure data for **13c**, **14a**, **15a**, **18b**, **21a**, and **43a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0110552