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# *N*-Acyl- and *N*-Sulfonylformamidines from Cyanamides and Carbodiimides by Hydroalumination and Subsequent Treatment with Electrophiles

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Hydroalumination of cyanamides **1** with di(isobutyl)aluminium hydride affords intermediate compounds **3**, which have dimeric structures in the solid state with four-membered $Al_2N_2$ heterocycles and exocyclic N=C double bonds. The reactions of **3** with acyl chlorides yield *N*′,*N*′-disubstituted *N*-acylformamidines **5**, whereas reaction with sulfonyl chlorides give the corresponding *N*-sulfonylformamidines **7**. In contrast, carbodiimides **8** react with dialkylaluminium hydrides $R_2AlH$ (R = *t*Bu, *i*Bu) to give compounds **9** in which one C=N bond of the carbodiimide is reduced to form an amidinate ligand and a second molecule of the hydride is coordinated through an Al–N and an Al–H–Al bond. Treatment of **9** with acyl chlorides yields *N*,*N*′-disubstituted *N*-acylformamidines **10**, whereas reaction with sulfonyl chlorides gives the corresponding *N*-sulfonylformamidines **11**.

## Introduction

The Pauling electronegativities, as revised by Allred and Rochow, of aluminium and carbon or nitrogen differ by 1.03 and 1.60 units, respectively, thus indicating a substantial ionic character of the respective bonds.[1] Consequently, aluminium–carbon and aluminium–nitrogen compounds exhibit a pronounced nucleophilic character at carbon or nitrogen. Furthermore, considering the high Lewis acidity of aluminium, which may significantly influence reactivity and stereoselectivity, its compounds seem to offer valuable synthetic advantages. Interestingly, these two valuable and cooperative properties have not yet been fully explored in organic synthesis. Many intermediate aluminium compounds are simply hydrolyzed, introducing a proton as electrophile, e.g., in the hydrolytic workup of hydroalumination products in reductions with di(isobutyl)aluminium hydride (DIBAL-H). But hydroalumination is a facile procedure that can be used to generate organoaluminium derivatives from unsaturated organic substrates such as alkynes, to a lesser extent alkenes, and nitrogen-containing double and triple bonds.[2] To the best of our knowledge, only dimethylcyanamide has previously been used in a hydroalumination reaction, but the product has not been applied in synthesis.[3] Hydroalumination reactions of carbodiimides seem to be unknown. In this report we describe the hydroalumination reactions of cyanamides and carbodiimides followed by treatment with acylating or sulfonylating agents to synthesise *N*′,*N*′-disubstituted *N*-acyl-[4] and *N*-sulfonylformamidines[5] and the respective *N*,*N*′-disubstituted *N*′-acyl[6] and *N*′-sulfonyl[7] derivatives. These classes of compounds have found considerable use in the synthesis of organic heterocycles and in pharmacological studies.[8] *N*-Acylamidines are widely applicable as ligands for metal complexation.[9]

*N*-Substituted formamidines, e.g., acyl formamidines and sulfonyl formamidines, are usually synthesised by the reaction of amides with *N*,*N*-dimethylformamide diethyl acetal.[10] Due to the high importance of such compounds, new procedures for the synthesis were developed recently. Li et al. obtained *N*-sulfonyl formamidines unexpectedly from tertiary amines and sulfonyl azide in the presence of diethyl azodicarboxylate (DEAD) as dehydrogenation reagent.[11] Wang et al. reported a similar $FeCl_3$-mediated pathway to *N*-sulfonyl formamidines starting from triethylamine and sulfonyl azide.[12]

There is considerable interest in the synthesis and properties of unsaturated nitrogen-containing compounds, in particular of *N*-substituted formamidines starting from cyanamides and carbodiimides. In a first step we reduced the cyanamides and carbodiimides with DIBAL-H to yield the corresponding aluminium formamidinates. These intermediates show high reactivity towards electrophiles such as carboxylic and sulfonic acid chlorides.

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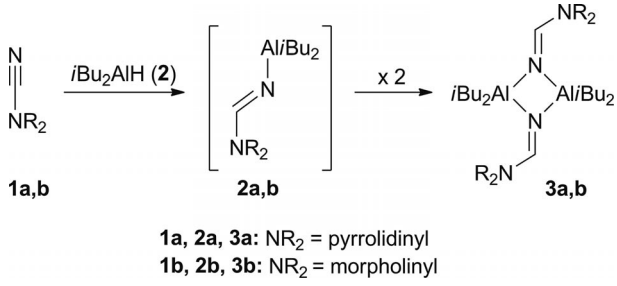
## Results and Discussion

### Cyanamides

In a first step, cyanamides **1** were treated in anhydrous toluene with DIBAL-H to obtain the corresponding dimeric aluminium formamidinates **3a** and **3b** by reduction of the C≡N triple bonds (Scheme 1). Both aluminium compounds were fully characterised, including by X-ray crystallography (Figure 1). They have centrosymmetric dimeric formula units in the solid state, with four-membered $Al_2N_2$ heterocycles and the former nitrile nitrogen atoms in the bridging positions. The amino groups are in *anti* positions. These results are in accordance with reports of Zakharkin and Khorlina,[13] Wade et al.,[14] Haley et al.[15] and Uhl et al.[16] on the hydroalumination of simple nitriles. The Al–N distances range from 1.909(1) to 1.926(1) Å, which is intermediate between typical covalent (ca. 1.8 Å) and dative Al–N bonds (ca. 2.0 Å).[17] The transannular Al–Al separations are 2.836 (av.) and 2.827 (av.) Å for **3a** and **3b**, respectively. The exocyclic C=N bond lengths are close to standard values [1.281(2) to 1.288(2) Å]. No Al–O interaction was observed in compound **3b**, in spite of the well-known oxophilicity of aluminium.[18]




Scheme 1. Hydroalumination of cyanamides **1a** and **1b**.

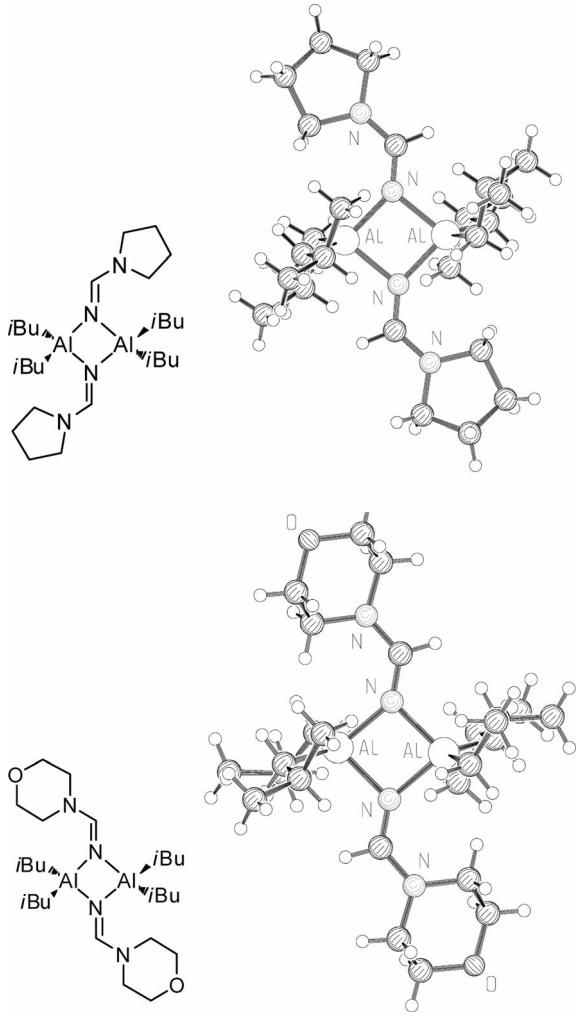


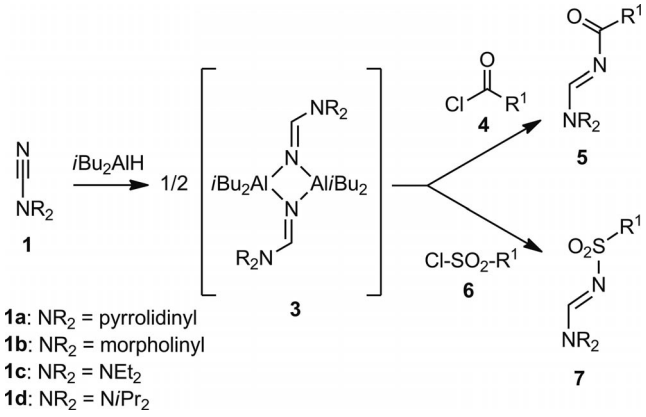
Figure 1. Molecular structures of **3a** (top) and **3b** (bottom) in the solid state.

The dimerisation of the coordinatively unsaturated monomers **2a** and **2b** to form the observed dimeric structures **3a** and **3b** is highly exothermic, as gas-phase quantum chemical calculations indicate. The geometries of the monomer **2b** and the dimer **3b** were completely optimised at the DFT-level B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p).[19] Relative energies were also obtained from SCS-MP2-single point calculations[20] and by correcting the DFT-energies using the D3-method,[21] which takes dispersion energy into account. The dimerisation energy for **2b** was calculated to be –45.8 kcal/mol at the DFT-level [SCS-MP2-level: –71.2 kcal/mol; D3-B3LYP/6-311+G(d,p): –68.0 kcal/mol] (all include zero point energy).

For synthetic application, it was not necessary to isolate the intermediate aluminium compounds **3**. The reaction of symmetrically disubstituted cyanamides **1** with DIBAL-H in anhydrous toluene and subsequent quenching with various carboxylic acid chlorides **4** yielded N-acyl-*N*′,*N*′-disubstituted formamidines **5**. Treatment with sulfonic acid chlorides **6** generated the related *N*-sulfonyl formamidines **7** (Scheme 2 and Table 1). In all cases, no hydrolytic workup was necessary. The crude reaction mixture was directly subjected to column chromatography over silica gel, enabling transformation into the ultimately isolated, aluminium-free products, probably by hydrolysis on the wet, polar silica gel. After optimisation of the reaction conditions it was found that the best cyanamide/DIBAL-H/electrophile ratio of reagents was 1:1:1.2, which led to moderate to good isolated yields. Toluene proved to be the best solvent. Aromatic acid chlorides gave better yields because the reaction products were easier to separate from the aluminium side products. Cyclic or acyclic cyanamides behaved similarly in these reactions.

Compounds **5c** and **5f** were characterised by single-crystal X-ray diffraction analysis (Figure 2). Both structures show *E*-configuration of the C=N bond and a sickle-type arrangement of the almost planar central O=C–N=C(H)–$N(R_2)$ chain with dihedral angles for the O=C–N=C unit of 17.4(2)° (**5c**) vs. 11.8(2)° (**5f**) and –168.2(2)° (**5c**) vs. –171.0(1)° (**5f**) for the C–N=C–N unit. The bond lengths along the O=C–N=CH–N chain are 1.224(2), 1.365(2), 1.299(2) and 1.313(2) Å for **5c**, and 1.233(2), 1.373(2),




Scheme 2. Synthesis of *N*-acyl- **5** and *N*-sulfonylformamidines **7** from cyanamides **1**.

Table 1. Substitution patterns and isolated yields of compounds **5a–j**, **7a** and **7b**.

| Product | $NR_2$ | $R^1$ | Yield [%] |
|---|---|---|---|
| **5a** | $NEt_2$ | Ph | 76 |
| **5b** | $NEt_2$ | 4-Me-$C_6H_4$ | 86 |
| **5c** | N*i*$Pr_2$ | Ph | 81 |
| **5d** | N*i*$Pr_2$ | 4-Me-$C_6H_4$ | 87 |
| **5e** | N*i*$Pr_2$ | *t*Bu | 30 |
| **5f** | pyrrolidinyl | Ph | 60 |
| **5g** | pyrrolidinyl | 4-Me-$C_6H_4$ | 81 |
| **5h** | pyrrolidinyl | *t*Bu | 30 |
| **5i** | morpholinyl | Ph | 70 |
| **5j** | morpholinyl | 4-Me-$C_6H_4$ | 68 |
| **7a** | N*i*$Pr_2$ | Ph | 81 |
| **7b** | N*i*$Pr_2$ | 4-Me-$C_6H_4$ | 64 |

1.317(2) and 1.311(2) Å for **5f**, indicating the dominating resonance interaction along the conjugated hetero system.[9j,9l]

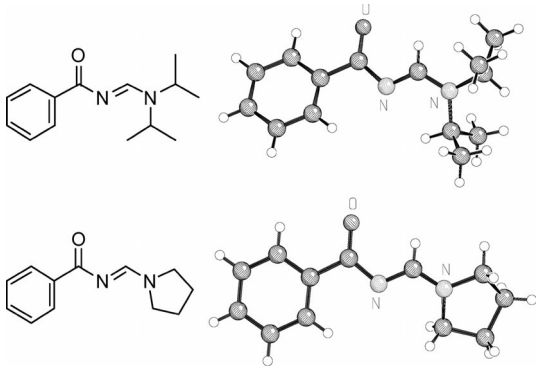


Figure 2. Molecular structures of compounds **5c** (top) and **5f** (bottom) in the solid state.

The molecular structure of **7b** (Figure 3) is also characterised by an almost planar O–S–N=C–N chain [torsion angles 8.1(2)°, –179.4(2)°] with an *E*-configuration across the C=N bond. The lengths of the S–O bonds are 1.422(1) and 1.437(1) Å, the S–N distance is 1.610(2) Å. Both N–C bonds of the amidine (N–C–N) subunit have the same length [1.307(2) Å], again indicating the importance of electron delocalisation in this part of the molecule.

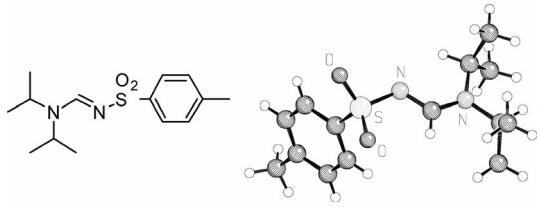


Figure 3. Molecular structures of compound **7b** in the solid state.

## Reaction Mechanism

To investigate the mechanism of the acylation of monomer **2** and dimer **3** in more detail, gas-phase quantum chemical calculations were performed. The geometries of the relevant species **A**–**H** were completely optimised at the DFT-Level B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p). Relative energies were also obtained from SCS-MP2-single point calculations[20] and by correcting the DFT-energies using the D3-method,[21] which considers dispersion energy. The following relative energies contain zero point corrections.

At first, calculations were performed to investigate the reaction of acetyl chloride with the monomeric product (such as **2**) resulting from the hydroalumination of the model compound *N*,*N*-dimethylcyanamide with di(*tert*-butyl)aluminium hydride (Figure 4). The hydroaluminated species forms a van der Waals complex **A** ($E_{rel}$ = 0.0 kcal/mol) with acetyl chloride. Starting from this complex, two different reaction pathways were investigated. One leads to a four-membered transition state **B**, in which the chlorine atom interacts with the aluminium atom and the carbonyl carbon atom approaches the iminic nitrogen atom [$E_{rel}$ = –1.6 (DFT), –1.6 (SCS-MP2), –1.7 (D3) kcal/mol with respect to van der Waals complex **A**]. The relevant atomic distances being C–Cl 2.167 Å; C–N 2.670 Å, N–Al 1.955 Å; Al–Cl 2.625 Å. The second pathway involves an approach of the carbonyl oxygen atom towards the aluminium centre, forming an intermediate complex **C** with an O–Al–distance of 2.075 Å [$E_{rel}$ = –6.1 (DFT), –6.1 (SCS-MP2), and –5.3 (D3) kcal/mol]. The next reaction step leads from **C** to a four-membered transition state **D** [$E_{rel}$ = 1.1 (DFT), 1.0 (SCS-MP2), –1.3 (D3) kcal/mol], which is characterised by a relative long carbon–nitrogen distance of 2.309 Å and a significant coordinative oxygen–aluminium interaction (1.996 Å). From both transition states **B** and **D**, in very exothermic steps, the final product **E** {–38.4 [DFT, –47.5 (SCS-MP2), –43.4 (D3) kcal/mol]} with the new carbon–nitrogen bond is formed, whereas the chlorine atom is bound to aluminium with bond lengths of Al–Cl: 2.197 Å, C–N: 1.438 Å; N–Al: 2.089 Å. In summary, both reaction pathways involve cyclic four-membered transition states. The geometrical and energetic parameters of the transition states strongly underline the cooperative character of this

bond-forming step, indicated by substantial Al–O or Al–Cl interactions in the first part of the mutual approach of both reaction partners.

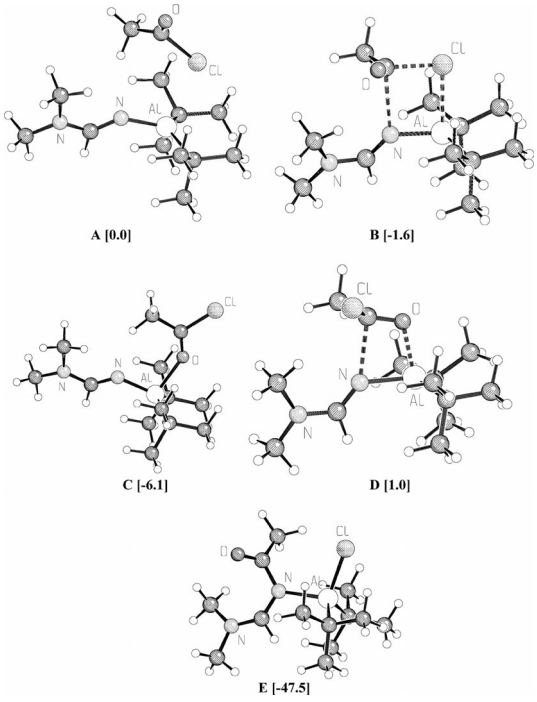



Figure 4. Van der Waals complex **A**, transition **B**, complex **C**, transition state **D** and final product **E** [kcal/mol; SCS-MP2/B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) + zero point correction].

Secondly, the acylation of dimer **3b** was also studied computationally (Figure 5). With regard to the huge dimerisation energy of **2**, we assume that this pathway gives a more realistic view of the reactions studied experimentally compared with the monomer reaction described above. Once more a weakly bound van der Waals complex **F** was identified ($E_{rel}$ = 0.0 kcal/mol). The approach of the carbonyl carbon atom of acetyl chloride to the respective nitrogen atom leads to a well-defined energy-rich transition state **G** [C–N: 1.970 Å; 44.7 (DFT), 36.5 (SCS-MP2), 31.1 (D3) kcal/mol with respect to **F**]. Because both aluminium atoms are already four-coordinate, no interaction of chloride to one of the two aluminium atoms can take place (Al–Cl: 3.295 Å). This transition state leads to the intermediate addition product **H**, resulting from bond formation between nitrogen and carbon; it is characterised by an Al–N–Al chain originating from the former A-N–Al–N four-membered ring. One of the two four-coordinate Al atoms carries the acylated amidine, the other has the chloride ion bound. This intermediate product **H** is lower in energy compared with the van der Waals complex **F** {–2.7 [DFT, –12.2 (SCS-MP2), –12.0 kcal/mol]}. We assume that this intermediate is then subject to a second acylation, leading finally by dissociation to two products of type **E** (see above) in a very exothermic reaction {–26.4 [DFT, –27.4 (SCS-MP2), –28.4 (D3) kcal/mol]}. Here again, the transition state and the products benefit from the cooperative properties of Al and N, respectively.

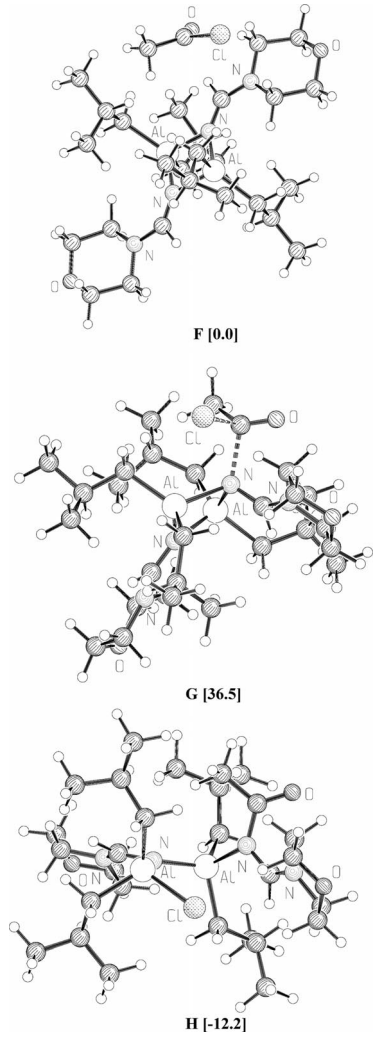
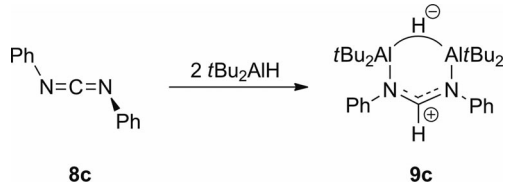



Figure 5. Van der Waals complex **F**, transition state **G**, and intermediate acylation product **H** [kcal/mol; SCS-MP2/B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) + zero point correction].

## Reactions with Carbodiimides

Similarly to the hydroalumination of cyanamides **1**, we investigated the reduction of carbodiimides **8** by dialkylaluminium hydrides. Reaction of *N*,*N*′-diphenylcarbodiimide (**8c**) with di(*tert*-butyl)aluminium hydride in a molar ration of 1:1 afforded only small quantities of the hydroalumination product **9c**. However, with a 1:2 ratio the yield was enhanced to 35%. Further compounds of unknown constitution were formed as by-products (Scheme 3).




Scheme 3. Hydroalumination of carboddimide **8c**.

The structure of **9c** may be described by single hydroalumination of **8c**, followed by the formation of an adduct with a second equivalent of the aluminium reagent forming the six-membered heterocycle of **9c** with a hydride bridge between both aluminium atoms.[22] Compound **9c** was fully characterised by NMR spectroscopic analysis and shows resonances of phenyl and *tert*-butyl groups in a molar intensity ratio of 1:2. The signal for the bridging hydride ion is observed at $\delta$ = 3.32 ppm, which is typical of aluminium hydrides. The CH group between the nitrogen atoms gave resonances at $\delta$ = 168.9 ppm ($^{13}$C NMR) and 7.43 ppm ($^{1}$H NMR). Boese et al. obtained the corresponding boron compounds by hydroboration of carbodiimides.[23]

Single crystals of **9c** were obtained from a solution in *n*-hexane at 2 °C. The compound crystallised in the centrosymmetric space group $P\bar{1}$ with two independent molecules per asymmetric unit (Figure 6 and the Supporting Information). The six-membered $Al_2N_2CH$ rings in the molecular centres adopt a twist form in the solid state. The dihedral angles for the endocyclic groups Al–N–C–N vary between 18.8(3) and 23.7(3)°, those for the C–N–Al–H moieties between 34.3 and 36.0°, and those for Al–H–Al–N groups between 8.9 and 16.5°. The C–N bonds in the six-membered ring exhibit lengths of 1.318(3) (C1–N1) to 1.329(3) Å (C1–N2), which is characteristic of delocalised N–C–N π-systems as in amidines. The Al–N distances [1.951(2) to 1.956(2) Å] as well as the Al–H distances [1.70(2) to 1.72(2) Å] reflect the symmetrical structure of the molecules with two almost identical molecular halves. The sum of the angles at the nitrogen atoms is always close to 360° [358.8 (N4) to 359.6° (N3)] and verifies the almost ideal planar coordination sphere with the π-conjugation across the bonds of the N3–C1–N15 group.

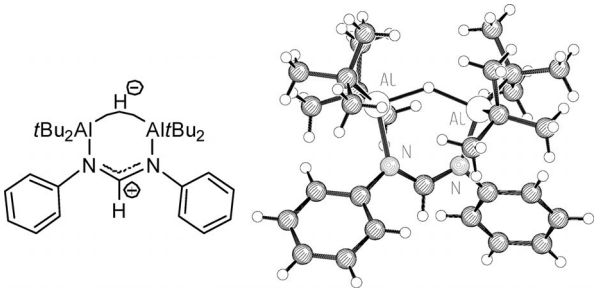
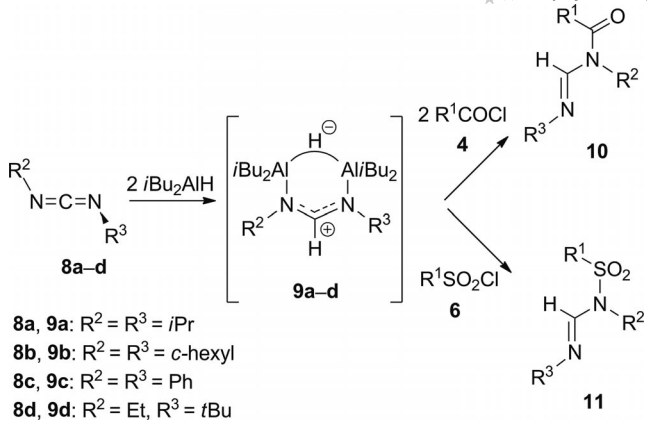



Figure 6. Molecular structure of **9c** in the solid state.

As in the case of hydroaluminated cyanamides **3**, the reaction of the aluminium intermediates **9** with organic electrophiles did not require their isolation. Thus, carbodiimides **8** were first treated with DIBAL-H and then quenched with acid chlorides to give access to *N*-acyl-*N*,*N*′-disubstituted formamidines **10**, whereas the reactions with sulfonic acid chlorides **6** yielded the related N-sulfonyl formamidines **11** (Scheme 4, Table 2). In accordance with the molecular structure of **9**, optimum yields were obtained by using two equivalents of DIBAL-H and 2.4 equivalents of the respective electrophile.




Scheme 4. Formation of *N*,*N*′-disubstituted *N*-acyl- **10** and *N*-sulfonylformamidines **11** from carbodiimides **8** via intermediate hydroalumination products **9**.

Table 2. Substitution patterns and isolated yields of compounds **10a**–**f** and **11a**–**c**.

| Product | $R^1$ | $R^2$ | $R^3$ | Yield [%] |
|---|---|---|---|---|
| **10a** | Ph | *i*Pr | *i*Pr | 75 |
| **10b** | 4-Me-$C_6H_4$ | *i*Pr | *i*Pr | 44 |
| **10c** | Ph | cyclohexyl | cyclohexyl | 98 |
| **10d** | Ph | Ph | Ph | 62 |
| **10e** | 4-Me-$C_6H_4$ | Et | *t*Bu | 50 |
| **10f** | *t*Bu | Et | *t*Bu | 15 |
| **11a** | 4-Me-$C_6H_4$ | *i*Pr | *i*Pr | 72 |
| **11b** | 4-Me-$C_6H_4$ | cyclohexyl | cyclohexyl | 73 |
| **11c** | 4-Me-$C_6H_4$ | Et | *t*Bu | 47 |

By employing an unsymmetrical carbodiimide, *N*-ethyl-*N*′-*tert*-butylcarbodiimide (**8d**), in this reaction sequence, the best yield of the products **10e**, **10f** and **11c** was 50%. Upon reaction with acid or sulfonyl chlorides we could isolate in each case only one of the two possible isomers (Table 2). Their constitutions were established by NMR spectroscopic analysis, EI mass spectrometry and, in the case of **11c**, by X-ray diffraction.

The *N*-acylated compounds **10c** and **10d** were characterised by X-ray crystal structure determination. They differ in the orientation of the central O=C–N–C(H)=N chain, possibly due to the differing substituents (cyclohexyl vs. phenyl) or because of packing effects (Figure 7). Compound **10c** shows a sickle-type structure [166.8(2)°, –162.0(2)°], whereas **10d** shows a W-type configuration [–0.1(2)°, –168.0(1)°]. In comparison to the electronically delocalised *N*′,*N*′-disubstituted *N*-acyl- and *N*-sulfonylformamidines **5** and **7**, the molecules **10c** and **10d** have isolated, relatively long C–N single bonds [**10c**: 1.401(2) Å, **10d**: 1.381(2) Å] and short C=N double bonds [**10c** and **10d**: 1.256(2) Å]. These differing structural properties underline nicely the electronic influence of a two-coordinate amidine nitrogen atom bound to the C=O or $SO_2$ group, respectively, as found in **5c**, **5f** and **7b** on the one hand (*N*-acylimine-type), compared with a three-coordinate central amidine nitrogen atom as found in **10c** and **10d** (amide-type) on the other hand.

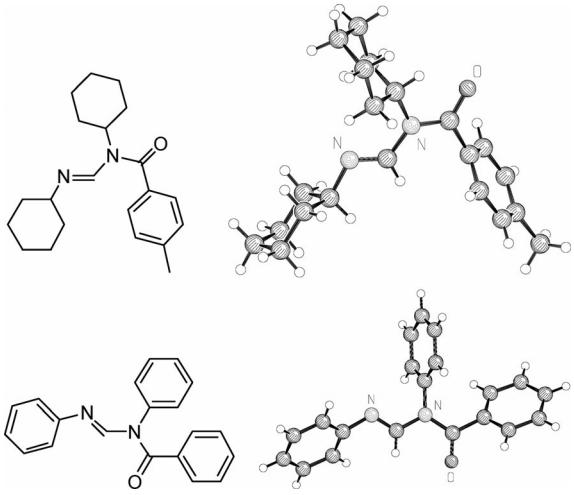


Figure 7. Molecular structures of **10c** and **10d** in the solid state.

The X-ray structures of **11b** and **11c** show – in spite of their different substitution pattern – similarities, with respect to both dihedral angles and bond lengths of the central $SO_2$–NR–CH=NR subunit (Figure 8). The group O–S–N–C–N of **11b** is characterised by dihedral angles of –145.4(2) and 179.6(2)°, and that of **11c** of 151.1(3) and 172.5(3)°, highlighting the relatively flat W-type configuration. As in compounds **10c** and **10d**, the C–N bond lengths differ significantly [C–N: 1.399(3) Å in **11b**, 1.405(5) Å in **11c**; C=N: 1.258(3) Å in **11b** and 1.257(5) Å in **11c**] indicating again the completely different electronic structure compared with the *N*′,*N*′-disubstituted *N*-sulfonylformamidines **7**.

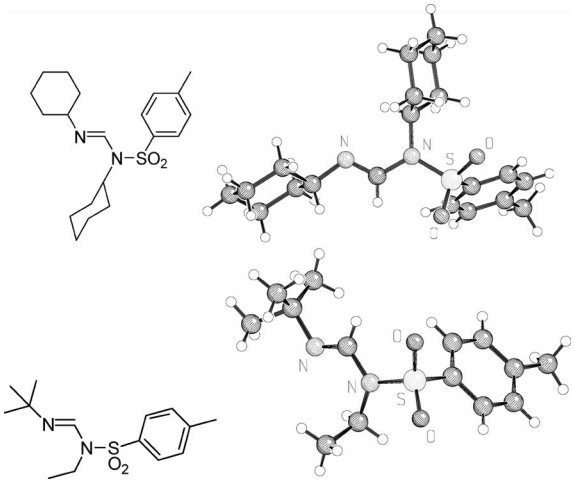


Figure 8. Molecular structures of **11b** (above) and **11c** (below) in the solid state.

## Conclusions

We have demonstrated the enormous synthetic potential of hydroalumination reactions of unsaturated nitrogen compounds such as cyanamides **1** and carbodiimides **8**. In a simple one-pot procedure the commercially available starting materials were first transformed into reactive aluminium compounds **3** and **9**, which were then treated with electrophiles such as acid or sulfonyl chlorides to yield, after work up on silica gel, a range of substituted *N*-acyl- and *N*-sulfonylformamidines **5**, **7**, **10** or **11** in satisfactory yield. The optimised reaction conditions do not involve a special hydrolytic workup step, and direct chromatographic separation was found to be superior for the isolation of the final products. The structures of several products in the solid state could be elucidated by X-ray crystallography, including the quite reactive hydroalumination intermediates **3** and **9**. This work should encourage organic chemists to use such aluminium compounds systematically as reactive intermediates for ambitious organic syntheses in place of the better known lithium or magnesium compounds.

## Experimental Section

**General:** Melting points are uncorrected. $^1$H, $^{13}$C, GCOSY, GHSQC and GHMBC spectroscopy used TMS ($^1$H) ($\delta$ = 0.00 ppm), $CD_2Cl_2$ ($^1$H: 5.32 ppm, $^{13}$C: 54.00 ppm), $CDCl_3$ ($^{13}$C: 77.16 ppm) or $C_6D_6$ ($^1$H: 7.16 ppm, $^{13}$C: 128.06 ppm) as internal references. When necessary, the experiments were carried out with complete exclusion of moisture. Compound **8c** was prepared according to the literature.[24]

**[*i*Bu$_2$Al-N=CH-NC$_4$H$_8$]$_2$ (3a):** 1-Cyanopyrrolidine (**1a**; 192 mg, 2.0 mmol) was dissolved in toluene (20 mL; dried with Na/benzophenone) and treated with DIBAL-H (**2**; 0.36 mL, 2.0 mmol) at room temperature under argon. After stirring for 2 h, the solution was concentrated and cooled to 4 °C to yield colourless crystals of **3a**. Yield 386 mg (0.81 mmol, 81%), m.p. 122 °C (argon, closed capillary). $^1$H NMR ($C_6D_6$, 400 MHz): $\delta$ = 0.47 (d, $^3J_{H,H}$ = 6.7 Hz, 8 H, AlC$H_2$CHMe$_2$), 1.09 and 1.27 (each br, 4 H, NCH$_2$C$H_2$), 1.32 (d, $^3J_{H,H}$ = 6.4 Hz, 24 H, AlCH$_2$CH*Me*$_2$), 2.25 (m, 4 H, AlCH$_2$C*H*Me$_2$), 2.66 (very br., 4 H, NC$H_2$), 3.46 (br., 4 H, NC$H_2$), 7.66 (s, 2 H, *H*C=N) ppm. $^{13}$C{$^1$H} NMR ($C_6D_6$, 100 MHz): $\delta$ = 24.6 (NCH$_2$*C*H$_2$), 26.5 (Al*C*H$_2$CHMe$_2$), 27.2 (AlCH$_2$C*H*Me$_2$), 29.1 (AlCH$_2$CH*Me*$_2$), 44.7 and 48.5 (N*C*H$_2$), 154.4 (*C*=N) ppm. IR (paraffin, CsI plates): $\tilde{\nu}$ = 1991 (m), 1956 (w), 1842 (m, br), 1694 (sh), 1639 (sh), 1611 (sh), 1578 [vs. $\nu$(C=N)], 1460 [vs. (paraffin)], 1402 [m $\delta$(CH$_3$)], 1375 [s (paraffin)], 1356 (sh), 1335 (m), 1310 (m), 1246 (m), 1223 [s $\delta$(CH$_3$)], 1167 (s), 1113 (m), 1059 (s), 1031 (m), 1009 (s), 970 (m), 945 (s), 930 (m), 914 (m), 872 (s), 814 (vs), 747 [s $\nu$(CC), $\nu$(CN)], 727 [s (paraffin)], 671 (m), 656 (sh), 627 (w), 602 (w), 588 (w), 542 (m), 494 (w), 457 [s $\delta$(CC), $\nu$(AlC), $\nu$(AlN)] cm$^{-1}$. MS (EI, 20 eV, 100 °C): *m*/*z* (%) = 475 (1) [M(dimer)$^+$ – H], 419 (100) [M$^+$ – CH$_2$CHMe$_2$], 363 (65) [M$^+$ – CH$_2$CHMe$_2$ – butene], 307 (44) [M$^+$ – CH$_2$CHMe$_2$ – 2butene].

**X-ray Crystal Structure Analysis of 3a:**[25] $C_{26}H_{54}Al_2N_4$; $M$ = 476.69; colourless crystal; 0.24 × 0.11 × 0.10 mm; $a$ = 10.5376(2), $b$ = 11.6532(2), $c$ = 13.3681(2) Å, $\alpha$ = 78.701(1)°, $\beta$ = 72.876(1)°, $\gamma$ = 79.582(1)°; $V$ = 1525.04(5) Å$^3$; $\rho_{calc}$ = 1.038 g cm$^{-3}$; $\mu$ = 0.984 mm$^{-1}$; empirical absorption correction (0.798 ≤ T ≤ 0.908); $Z$ = 2; triclinic; space group $P\bar{1}$ (No. 2); $\lambda$ = 1.54178 Å; $T$ = 153(2) K; $\omega$ and $\phi$ scans, 8720 reflections collected (±$h$, ±$k$, ±$l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 4861 independent ($R_{int}$ = 0.0197) and 4180 observed reflections [$I > 2\sigma(I)$], 297 refined parameters, $R$ = 0.0428, $wR^2$ = 0.1238, max. (min.) residual electron density 0.499 (–0.235) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**[*i*Bu$_2$Al-N=CH-NC$_4$H$_8$O]$_2$ (3b):** A solution of 4-morpholinecarbonitrile (**3b**; 224 mg, 2 mmol) in toluene (20 mL; dried with Na/

benzophenone) was treated with a solution of DIBAL-H (**2**; 2 mmol, 1.0 M in toluene, 2 mL) at room temperature under argon. The mixture was stirred for 16 h and concentrated. Cooling of the solution to –30 °C yielded colourless crystals of **3b**. Yield 260 mg (0.51 mmol, 51%), m.p. 169 °C (argon, closed capillary). $^1$H NMR ($C_6D_6$, 400 MHz): $\delta$ = 0.34 (d, $^3J_{H,H}$ = 6.4 Hz, 8 H, AlC$H_2$CHMe$_2$), 1.23 (d, $^3J_{H,H}$ = 6.7 Hz, 24 H, AlCH$_2$CH$Me_2$), 2.10 (m, 4 H, AlCH$_2$C$H$Me$_2$), 2.90 (br., 8 H, NC$H_2$), 3.18 (s, 4 H, OC$H_2$), 7.22 (s, 2 H, $H$C=N) ppm. $^{13}$C{$^1$H} NMR ($C_6D_6$, 100 MHz): $\delta$ = 25.2 (Al$C$H$_2$CHMe$_2$), 27.0 (AlCH$_2$C$H$Me$_2$), 28.9 (AlCH$_2$CH$Me_2$), 46.1 (br., N$C$H$_2$), 66.5 (O$C$H$_2$), 155.4 ($C$=N) ppm. IR (paraffin, CsI plates): $\tilde{\nu}$ = 1969 (m), 1934 (w), 1915 (w), 1883 (vw), 1838 (w), 1794 (w), 1603 (s, br), 1585 (s), 1575 [s $\nu$(C=N)], 1543 (m), 1466 (m), 1371 [m (paraffin)], 1312 (w), 1263 (w), 1231 [m $\delta$(CH$_3$)], 1169 (m), 1109 (m), 1067 (m), 1003 (w), 978 (w), 941 (m), 862 (s), 818 [s $\nu$(CC), $\nu$(CN)], 729 [s (paraffin)], 538 (w), 440 [m $\delta$(CC), $\nu$(AlC), $\nu$(AlN)] cm$^{-1}$. MS (EI, 20 eV, 50 °C): *m*/*z* (%) = 507 (0.2) [M$^+$], 451 (100) [M$^+$ – CH$_2$CMe$_3$], 395 (85) [M$^+$ – CH$_2$CHMe$_2$ – butene], 339 (48) [M$^+$ – CH$_2$CHMe$_2$ – 2 butene].

**X-ray Crystal Structure Analysis of 3b:**[25] $C_{26}H_{54}Al_2N_4O_2$; $M$ = 508.69; colourless crystals; 0.73 × 0.30 × 0.24 mm; $a$ = 15.6654(3), $b$ = 18.6875(4), $c$ = 17.6834(4) Å, $\beta$ = 112.727(1)°; $V$ = 4774.8(2) Å$^3$; $\rho_{calc}$ = 1.061 g cm$^{-3}$; $\mu$ = 1.019 mm$^{-1}$; empirical absorption correction (0.523 ≤ T ≤ 0.792); $Z$ = 6; monoclinic; space group $P2_1/c$ (No. 14); $\lambda$ = 1.54178 Å; $T$ = 153(2) K; $\omega$ and $\phi$ scans, 27654 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 8824 independent ($R_{int}$ = 0.030) and 7388 observed reflections [$I > 2\sigma(I)$], 550 refined parameters, $R$ = 0.0478, $wR^2$ = 0.1432, max. (min.) residual electron density 0.432 (–0.311) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**General Procedure for the Formation of *N*′,*N*′-Disubstituted *N*-Acylformamidines 5 and *N*-Sulfonylformamidines 7:** Cyanamide **1** (1 equiv.) was dissolved in toluene (5 mL per mmol) and DIBAL-H (1 M in toluene, 1 equiv.) was added. After stirring the reaction mixture for 30 min, the electrophile (1.2 equiv.) was added under ice-cooling and stirring was continued for at least 2 h. The solvent was removed under reduced pressure, then the crude product was purified by column chromatography and – if necessary – by HPLC and/or recrystallisation from the eluent.

***N*-[(Diethylamino)methylene]benzamide (5a):** Obtained from *N*,*N*-diethylcyanamide (**1c**; 0.196 g, 2 mmol) and benzoyl chloride (0.337 g, 2.4 mmol), according to the general procedure. Subsequent column chromatography (diethyl ether/*n*-pentane, 3:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 1:2) gave the pure product (0.310 g, 1.52 mmol, 76%) as a colourless solid (m.p. 48 °C). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 1.27 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, C$H_3$), 1.29 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, C$H_3$), 3.44 (q, $^3J_{H,H}$ = 7.2 Hz, NC$H_2$), 3.68 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, NC$H_2$), 7.22–7.70 (m, 3 H, C$H_{Ar}$), 8.11–8.45 (m, 2 H, C$H_{Ar}$), 8.64 (s, 1 H, C$H$) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = = 12.7, 15.0 (C$H_3$), 41.4, 47.5 (N$CH_2$), 128.4 (*p*-CH$_{Ar}$), 130.1 (*o*-CH$_{Ar}$), 132.1 (*m*-CH$_{Ar}$), 137.8 ($C_q$), 160.0 (N$C$N), 177.8 ($C$O) ppm. IR (neat): $\tilde{\nu}$ = 3080 (vw), 3061 (vw), 2980 (w), 2970 (m), 2936 (w), 2872 (vw), 1634 (vs), 1584 (s), 1568 (s), 1487 (w), 1450 (s), 1439 (s), 1354 (s), 1337 (vs), 1310 (s), 1252 (s), 1207 (s), 1173 (m), 1136 (s), 1105 (s), 1092 (s), 1063 (s), 1024 (m), 1015 (m), 1001 (m), 939 (m), 883 (w), 808 (w), 789 (w), 714 (vs), 691 (m). 667 (s) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{17}N_2O^+$ 205.1335; found 205.1339. $C_{12}H_{16}N_2O$ (204.27): calcd. C 70.56, H 7.90, N 13.71; found C 70.44, H 7.91, N 13.58.

***N*-[(Diethylamino)methylene]-4-methylbenzamide (5b):** Obtained from *N*,*N*-diethylcyanamide (**1c**; 0.196 g, 2 mmol) and 4-methylbenzoyl chloride (0.371 g, 2.4 mmol) according to the general procedure. Subsequent column chromatography (diethyl ether/*n*-pentane, 2:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 1:2) gave the pure product (0.376 g, 1.70 mmol, 86%) as a colourless solid (m.p. 46–47 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.27 (t, $^3J$ = 7.2 Hz, 3 H, C$H_3$), 1.27 (t, $^3J$ = 7.2 Hz, 3 H, C$H_3$), 2.40 (s, 3 H, Ar-C$H$), 3.44 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, C$H_2$), 3.67 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, C$H_2$), 7.23 (d, $J$ = 7.9 Hz, 2 H, *m*-C$H_{Ar}$), 8.14 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, *o*-C$H_{Ar}$), 8.63 (s, 1 H, NC$H$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 12.7, 15.0 (NCH$_2$C$H_3$), 21.8, 41.3 (N$CH_2$), 47.5 (*p*-C$CH_3$), 129.1, 130.2 (C$H_{Ar}$), 135.1 ($C_q$), 142.7 (*p*-$C$CH$_3$), 160.0 (N$C$N), 177.7 ($C$O) ppm. IR (neat): $\tilde{\nu}$ = 3026 (vw), 2976 (w), 2936 (w), 2874 (w), 1638 (s), 1609 (m), 1580 (vs), 1564 (vs), 1506 (w), 1449 (s), 1381 (m), 1337 (vs), 1306 (s), 1250 (vs), 1206 (m), 1169 (m), 1134 (m), 1078 (s), 1069 (s), 999 (m), 941 (w), 885 (w), 845 (w), 812 (w), 789 (w), 760 (s), 692 (w), 648 (m), 606 (s), 530 (w) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{18}N_2O^+$ 219.1492; found 219.1498. $C_{13}H_{18}N_2O$ (218.30): calcd. C 71.53, H 8.31, N 12.83; found C 71.83, H 8.27, N 12.66.

***N*-[(Diisopropylamino)methylene]benzamide(5c):**[26] Obtained from *N*,*N*-diisopropylcyanamide (**1d**; 0.252 g, 2 mmol) and benzoyl chloride (0.337 g, 0.24 mmol) according to the general procedure. Pure product **5c** (0.376 g, 1.62 mmol, 77%) was obtained by column chromatography (diethyl ether/*n*-pentane, 1:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 1:1) as a colourless solid (m.p. 104 °C). $^1$H NMR (600 MHz, $CD_2Cl_2$): $\delta$ = 1.37 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, NCH(C$H_3$)$_2$], 1.38 [d, $^3J_{H,H}$ = 7.1 Hz, 6 H, NCH(C$H_3$)$_2$], 3.76 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, NC$H$(CH$_3$)$_2$], 4.77 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, NC$H$(CH$_3$)$_2$], 7.40–7.43 (m, 2 H, *m*-C$H_{Ar}$), 7.47–7.51 (m, 1 H, *p*-C$H_{Ar}$), 8.23–8.25 (m, 2 H, *o*-C$H_{Ar}$), 8.79 (s, 1 H, NC$H$N) ppm. $^{13}$C NMR (150 MHz, $CD_2Cl_2$): $\delta$ = 20.2, 23.8 [NC$H$(CH$_3$)$_2$], 48.3 [N$C$H(CH$_3$)$_2$], 49.8 [br., N$C$H(CH$_3$)$_2$], 128.4 (*m*-C$H_{Ar}$), 130.1 (*o*-C$H_{Ar}$), 132.0 (*p*-C$H_{Ar}$), 138.0 (*i*-C$_{Ar}$), 158.7 (N$C$N), 177.6 ($C$O) ppm. IR (neat): $\tilde{\nu}$ = 3065 (s), 3028 (s), 2974 (s), 2930 (s), 2874 (s, CH$_3$), 2361 (s), 2336 (s), 1626 (s), 1582 (s), 1555 (s), 1452 (s), 1385 (s), 1342 (s), 1319 (s), 1304 (s), 1246 (s), 1198 (s), 1155 (s), 1111 (s), 1065 (s), 1026 (s), 1003 (s), 935 (s), 918 (s), 881 (s), 851 (s), 810 (s), 712 (s), 689 (s), 664 (s), 561 (s) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{21}N_2O^+$ 233.1647; found 233.1648. $C_{14}H_{20}N_2O$ (232.32): calcd. C 72.38, H 8.68, N 12.06; found C 72.14, H 8.55, N 11.95.

**X-ray Crystal Structure Analysis of 5c:**[25] $C_{14}H_{20}N_2O$; $M$ = 232.32; colourless crystal; 0.35 × 0.20 × 0.10 mm; $a$ = 11.6872(1), $b$ = 9.9337(1), $c$ = 12.0573(1) Å, $\beta$ = 110.842(1)°; $V$ = 1308.22(2) Å$^3$; $\rho_{calc}$ = 1.180 g cm$^{-3}$; $\mu$ = 0.588 mm$^{-1}$; empirical absorption correction (0.820 ≤ T ≤ 0.943); $Z$ = 4; monoclinic; space group $P2_1/c$ (No. 14); $\lambda$ = 1.54178 Å; $T$ = 223(2) K; $\omega$ and $\phi$ scans, 8653 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 2354 independent ($R_{int}$ = 0.043) and 2104 observed reflections [$I > 2\sigma(I)$], 159 refined parameters, $R$ = 0.041, $wR^2$ = 0.106, max. (min.) residual electron density 0.13 (–0.11) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

***N*-[(Diisopropylamino)methylene]-4-methylbenzamide (5d):** Obtained from *N*,*N*-diisopropylcyanamide (**1d**; 0.252 g, 2 mmol) and 4-methylbenzoyl chloride (0.371 g, 0.24 mmol) according to the general procedure. Pure product **5d** (0.430 g, 1.75 mmol, 87%) was obtained by column chromatography (diethyl ether/*n*-pentane, 1:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 2:1) as a colourless solid (m.p. 74 °C). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 1.35 (d, $^3J_{H,H}$ = 6.8 Hz, 5 H), 1.37 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, NCH(C$H_3$)$_2$], 2.40 (s, 3 H, Aryl-CH$_3$), 3.75 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, NC$H$(CH$_3$)$_2$], 4.76 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, NC$H$(CH$_3$)$_2$],

7.22 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, *m*-C*H*$_{Ar}$), 8.12 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, *o*-C*H*$_{Ar}$), 8.77 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 20.2, 23.9 [NCH(CH$_3$)$_2$], 48.3 f, 49.7 [NCH(*C*H$_3$)$_2$], 129.1 (*m*-*C*H$_{Ar}$), 130.2 (*o*-*C*H$_{Ar}$), 135.4 (*i*-*C*H$_{Ar}$), 142.6 (*p*-C$_{Ar}$), 158.6 (N*C*N), 177.6 (*C*O) ppm. IR (neat): $\tilde{\nu}$ = 3055 (vw), 3026 (w), 3003 (w), 2968 (m), 2928 (w), 2862 (w), 1682 (m), 1634 (vs), 1612 (s), 1510 (w), 1452 (w), 1414 (w), 1379 (m), 1366 (m), 1335 (vs), 1260 (vs), 1215 (w), 1186 (w), 1159 (w), 1128 (m), 1084 (vs), 1022 (w), 959 (m), 949 (w), 920 (w), 880 (w), 860 (w), 831 (s), 775 (s), 760 (m), 615 (s) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{23}N_2O^+$ 247.1805; found 247.1811. $C_{15}H_{22}N_2O$ (246.35): calcd. C 73.13, H 9.00, N 11.37; found C 73.15, H 8.09, N 11.19.

***N*-[(Diisopropylamino)methylene]pivalamide (5e):** Obtained from *N*,*N*-diisopropylcyanamide (**1d**; 0.252 g, 2 mmol) and pivaloyl chloride (0.289 g, 0.24 mmol) according to the general procedure. Pure product **5e** (0.430 g, 1.75 mmol, 87%) was obtained after column chromatography (diethyl ether/*n*-pentane, 1:5 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 1:5) as a colourless solid (m.p. 72 °C). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 1.15 [s, 9 H, C(O)C(C*H*$_3$)$_3$], 1.28 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, C*H*$_3$), 1.31 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, C*H*$_3$), 3.67 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, NC*H*(CH$_3$)$_2$], 4.38 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, NC*H*(CH$_3$)$_2$], 8.46 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 23.9, 20.2 [NCH(*C*H$_3$)$_2$], 28.0 [C(O)C(*C*H$_3$)$_3$], 48.3, 49.7, [N*C*H(CH$_3$)$_2$], 157.7 (N*C*N), 192.3 (*C*O) ppm. IR (neat): $\tilde{\nu}$ = 2994 (m), 2968 (s), 2955 (m), 2930 (w), 2901 (w), 2870 (w), 2361 (w), 2344 (w), 1636 (s), 1568 (vs), 1549 (s), 1477 (s), 1450 (m), 1387 (vs), 1371 (vs), 1356 (s), 1331 (m), 1283 (m), 1217 (w), 1207 (m), 1180 (m), 1165 (m), 1125 (s), 1109 (vs), 1030 (m), 1016 (s), 937 (w), 924 (m), 899 (w), 883 (w), 862 (w), 820 (w), 777 (w), 741 (w), 667 (w), 604 (m), 590 (w), 559 (m) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{25}N_2O^+$ 213.1961; found 213.1960. $C_{12}H_{24}N_2O$ (212.33): calcd. C 67.88, H 11.39, N 13.19; found C 67.65, H 11.07, N 13.16.

***N*-(Pyrrolidin-1-ylmethylene)benzamide (5f):** Obtained from pyrrolidine-1-carbonitrile (**1a**; 0.192 g, 2 mmol) and benzoyl chloride (0.337 g, 0.24 mmol) according to the general procedure. Pure product **5f** (0.241 g, 1.19 mmol, 60%) was obtained by column chromatography (diethyl ether/*n*-pentane, 3:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 1:2) as a colourless solid (m.p. 69–70 °C). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 1.95–2.01 (m, 4 H, NCH$_2$C*H*$_2$), 3.63–3.67 (m, 4 H, NC*H*$_2$), 7.38–7.41 (m, 2 H, *m*-C*H*$_{Ar}$), 7.46–7.49 (m, 1 H, *p*-C*H*$_{Ar}$), 8.15–8.31 (m, 2 H, *o*-CH$_{Ar}$), 8.78 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 24.9, 25.5 (NCH$_2$CH$_2$), 46.9, 50.3 (N*C*H$_2$), 128.4 (*m*-*C*H$_{Ar}$), 130.1 (*o*-*C*H$_{Ar}$), 132.1 (*p*-*C*H$_{Ar}$), 137.7 (*i*-*C*$_{Ar}$), 157.7 (N*C*N), 177.5 (*C*O) ppm. IR (neat): $\tilde{\nu}$ = 3080 (w), 3055 (w), 2963 (w), 2953 (w), 2878 (m), 1632 (s), 1580 (s), 1558 (vs), 1487 (m), 1477 (m), 1464 (m), 1450 (s), 1441 (s), 1344 (s), 1327 (s), 1310 (vs), 1290 (m), 1254 (s), 1244 (s), 1229 (s), 1186 (m), 1153 (s), 1117 (m), 1084 (s), 1063 (s), 1034 (s), 1018 (s), 974 (w), 961 (w), 930 (w), 918 (w), 903 (w), 874 (w), 853 (w), 816 (w), 808 (w), 787 (w), 714 (vs), 687 (s), 646 (m), 617 (w), 581 (w), 563 (w), 542 (w), 530 (w), 521 (w), 505 (w), 498 (w), 486 (m), 474 (s), 463 (s), 451 (vs), 424 (vs) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{15}N_2O^+$ 203.1179; found 203.1173. $C_{12}H_{14}N_2O$ (202.26): calcd. C 71.26, H 6.98, N 13.85; found C 71.17, H 7.08, N 13.55.

**X-ray Crystal Structure Analysis of 5f:**[25] $C_{12}H_{14}N_2O$; *M* = 202.25; colourless crystal; 0.40 × 0.20 × 0.15 mm; *a* = 9.6827(4), *b* = 10.7414(6), *c* = 11.2930(8) Å, $\beta$ = 114.543(3)°; *V* = 1068.42(11) Å$^3$; $\rho_{calc}$ = 1.257 g cm$^{-3}$; $\mu$ = 0.651 mm$^{-1}$; empirical absorption correction (0.780 ≤ T ≤ 0.908); *Z* = 4; monoclinic; space group $P2_1/n$ (No. 14); $\lambda$ = 1.54178 Å; *T* = 223(2) K; $\omega$ and $\phi$ scans, 6233 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 1852 independent ($R_{int}$ = 0.034) and 1668 observed reflections [$I > 2\sigma(I)$], 136 refined parameters, *R* = 0.038, $wR^2$ = 0.101, max. (min.) residual electron density 0.12 (–0.13) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**4-Methyl-*N*-(pyrrolidin-1-ylmethylene)benzamide (5g):** Obtained from pyrrolidine-1-carbonitrile (**1a**; 0.192 g, 2 mmol) and 4-methylbenzoyl chloride (0.371 g, 0.24 mmol) according to the general procedure. Pure product **5g** (0.352 g, 1.63 mmol, 81%) was obtained by column chromatography (diethyl ether/*n*-pentane, 3:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 1:1) as a colourless solid (m.p. 110 °C). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 1.99 (m, 4 H, NCH$_2$C*H*$_2$), 2.39 (s, 3 H, Aryl-C*H*$_3$), 3.64 (m, 4 H, NC*H*$_2$), 7.22 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, *m*-C*H*$_{Ar}$), 8.13 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, *o*-C*H*$_{Ar}$), 8.77 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 21.8 (Aryl-*C*H$_3$), 25.5, 24.9 (NCH$_2$*C*H$_2$), 50.3, 46.8 (N*C*H$_2$), 129.1 (*m*-CH$_{Ar}$), 130.2 (*o*-*C*H$_{Ar}$), 135.0 (*i*-C$_{Ar}$), 142.7 (*p*-*C*$_{Ar}$CH$_3$), 157.6 (N*C*HN), 177.6 (*C*O) ppm. IR (neat): $\tilde{\nu}$ = 3075 (vw), 3021 (w), 2970 (m), 2922 (w), 2876 (w), 2361 (vw), 2340 (vw), 1726 (vw), 1636 (s), 1591 (vs), 1562 (vs), 1504 (m), 1472 (m), 1441 (s), 1348 (s), 1333 (s), 1304 (s), 1294 (s), 1252 (s), 1190 (s), 1173 (s), 1161 (s), 1113 (m), 1082 (s), 1040 (s), 1016 (s), 993 (s), 970 (s), 932 (s), 916 (s), 901 (s), 856 (s), 841 (s), 806 (s), 777 (s), 760 (vs), 692 (s), 664 (m), 637 (s), 602 (m), 581 (m), 563 (m), 538 (m), 528 (m), 513 (m), 500 (s), 488 (vs) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{17}N_2O^+$ 217.1335; found 217.1339. $C_{13}H_{16}N_2O$ (216.28): calcd. C 72.19, H 7.46, N 12.95; found C 71.68, H 7.40, N 12.70.

***N*-(Pyrrolidin-1-ylmethylene)pivalamide (5h):** Obtained from pyrrolidine-1-carbonitrile (**1a**; 0.192 g, 2 mmol) and pivaloyl chloride (0.289 g, 0.24 mmol) according to the general procedure. Pure product **5h** (0.109 g, 0.60 mmol, 30%) was obtained by column chromatography (diethyl ether/*n*-pentane, 2:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 8:1) as a colourless solid (m.p. 61 °C). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 0.94–1.11 (m, 4 H, NCH$_2$C*H*$_2$), 1.54 [s, 9 H, C(CH$_3$)$_3$], 2.49 (t, $^3J_{H,H}$ = 6.7 Hz, 2 H, NC*H*$_2$), 3.08 (t, $^3J_{H,H}$ = 9.3 Hz, 2 H, NC*H*$_2$), 8.54 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 24.9, 25.5 (NCH$_2$*C*H$_2$), 28.3 [NC(*C*H$_3$)$_3$], 41.2 [N*C*(CH$_3$)$_3$], 45.6, 48.5 (N*C*H$_2$), 156.9 (N*C*HN), 191.3 (*C*O) ppm. IR (neat): $\tilde{\nu}$ = 2972 (m), 2961 (s), 2926 (m), 2864 (m), 2361 (m), 2344 (m), 1643 (vs), 1576 (vs), 1553 (s), 1477 (s), 1443 (s), 1410 (s), 1385 (m), 1346 (s), 1331 (s), 1310 (vs), 1292 (s), 1223 (m), 1177 (s), 1123 (vs), 1111 (vs), 1020 (m), 970 (w), 935 (m), 914 (m), 866 (m), 818 (m), 779 (m), 737 (m), 640 (m), 617 (m), 586 (s), 517 (w), 494 (vs) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{10}H_{19}N_2O^+$ 183.1492; found 183.1503.

***N*-(Morpholinomethylene)benzamide (5i):** Obtained from pyrrolidine-1-carbonitrile (**1a**; 0.192 g, 2 mmol) and benzoyl chloride (0.337 g, 0.24 mmol) according to the general procedure. Pure product **5i** (0.311 g, 1.39 mmol, 70%) was obtained by column chromatography (diethyl ether/*n*-pentane, 3:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 8:1) as a colourless solid (m.p. 100–102 °C). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 3.54 (t, $^3J_{H,H}$ = 5 Hz, 2 H, NC*H*$_2$), 3.73–3.77 [m, 4 H, O(C*H*$_2$)$_2$], 3.92 (t, $^3J_{H,H}$ = 5 Hz, 2 H, NC*H*$_2$), 7.37–7.45 (m, 2 H, *m*-C*H*$_{Ar}$), 7.47–7.53 (m, 1 H, *p*-C*H*$_{Ar}$), 8.24 (m, 2 H, *o*-C*H*$_{Ar}$), 8.66 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 44.8, 51.0 (NCH$_2$), 66.7, 67.6 (OCH$_2$), 128.5 (*m*-CH$_{Ar}$), 130.2 (*o*-*C*H$_{Ar}$), 132.4 (*p*-*C*H$_{Ar}$), 137.4 (*i*-C$_{Ar}$), 159.9 (N*C*HN), 177.9 (*C*O) ppm. IR (neat): $\tilde{\nu}$ = 3082 (vw), 3063 (vw), 2988 (vw), 2968 (m), 2932 (w), 2876 (w), 2361 (w), 2330 (vw), 1632 (m), 1582 (s), 1570 (s), 1555 (vs), 1485 (w), 1464 (m), 1441 (m), 1431 (m), 1339 (vs), 1325 (vs), 1310 (s), 1279 (m), 1269

(s), 1234 (vs), 1219 (m), 1182 (m), 1161 (m), 1123 (s), 1109 (m), 1092 (s), 1067 (s), 1020 (s), 999 (m), 926 (s), 893 (s), 849 (m), 789 (w), 725 (m), 712 (vs), 671 (s), 635 (m), 617 (m), 596 (m) $cm^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{15}N_2O_2^+$ 219.1128; found 219.1122. $C_{12}H_{14}N_2O_2$ (218.25): calcd. C 66.04, H 6.47, N 12.84; found C 65.95, H 6.59, N 12.47.

**4-Methyl-*N*-(morpholinomethylene)benzamide (5j):** Obtained from pyrrolidine-1-carbonitrile (**1a**; 0.192 g, 2 mmol) and 4-methylbenzoyl chloride (0.371 g, 0.24 mmol) according to the general procedure. Pure product **5j** (0.313 g, 1.35 mmol, 68%) was obtained by column chromatography (diethyl ether/*n*-pentane, 2:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 2:1) as a colourless solid (m.p. 112 °C). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 1.27 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, $NCH_2$), 2.40 (s, 3 H, Aryl-C$H_3$), 3.43 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, O$CH_2$), 3.67 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, O$CH_2$), 7.23 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, *m*-C$H_{Ar}$), 8.14 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, *o*-C$H_{Ar}$), 8.63 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 15.0, 12.7 ($NCH_2$), 21.8 (Aryl-C$H_3$), 41.2, 47.5 (O$CH_2$), 129.1 (*m*-$CH_{Ar}$), 130.2 (*o*-C$H_{Ar}$), 132.4 (*p*-$C_{Ar}$), 142.6 (*i*-$C_{Ar}$), 159.9 (N*C*HN), 177.7 (*C*O) ppm. IR (neat): $\tilde{\nu}$ = 3032 (w), 2995 (w), 2957 (w), 2930 (w), 2913 (w), 2870 (w), 2864 (w), 2361 (vw), 2326 (vw), 1630 (vs), 1603 (s), 1578 (vs), 1557 (vs), 1504 (m), 1468 (m), 1441 (s), 1362 (s), 1344 (vs), 1327 (vs), 1300 (s), 1269 (s), 1234 (s), 1219 (m), 1184 (w), 1157 (s), 1111 (vs), 1088 (s), 1070 (s), 1030 (m), 1015 (m), 988 (vs), 930 (s), 891 (m), 851 (m), 839 (m), 804 (w), 760 (vs), 691 (m), 644 (w), 638 (m), 606 (s), 594 (w), 507 (w) $cm^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{17}N_2O_2^+$ 233.1285; found 233.1278. $C_{13}H_{16}N_2O_2$ (232.28): calcd. C 67.22, H 6.97, N 12.06; found C 66.78, H 7.10, N 11.71.

***N*,*N*-Diisopropyl-*N*′-(phenylsulfonyl)formimidamide (7a):** Obtained from *N*,*N*-diisopropylcyanamide (**1d**; 0.252 g, 2 mmol) and benzenesulfonyl chloride (0.424 g, 0.24 mmol) according to the general procedure. Pure product **7a** (0.398 g, 1.48 mmol, 74%) was obtained by column chromatography (diethyl ether/*n*-pentane, 2:1 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 2:1) as a colourless solid (m.p. 112 °C; 114.5–115 °C[27]). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 1.22 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $NCH(CH_3)_2$], 1.30 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $NCH(CH_3)_2$], 3.71 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, $NCH(CH_3)_2$], 4.44 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, $NCH(CH_3)_2$], 7.44–7.52 (m, 3 H, C$H_{Ar}$), 7.80–7.83 (m, 2 H, *o*-$CH_{Ar}$), 8.22 (s, 1 H, NC*H*S) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 19.8, 23.7 [N*C*H$(CH_3)_2$], 48.6, 49.7 [N*C*H$(CH_3)_2$], 126.6 (*o*-$CH_{Ar}$), 129.2 (*m*-$CH_{Ar}$), 132.0 (*p*-$C_{Ar}$), 143.7 (S$C_{ipso}$), 157.2 (N*C*HS) ppm. IR (neat): $\tilde{\nu}$ = 3080 (vw), 2994 (w), 2976 (w), 2959 (w), 2878 (w), 1597 (vs), 1452 (s), 1375 (m), 1335 (s), 1319 (m), 1294 (m), 1279 (vs), 1194 (m), 1180 (m), 1138 (vs), 1103 (m), 1084 (s), 1001 (m), 916 (m), 889 (s), 837 (s), 770 (m), 748 (vs), 718 (m), 696 (m), 606 (vs), 586 (vs), 559 (vs), 546 (vs), 525 (vs), 513 (vs) $cm^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{20}N_2O_2SNa^+$ 291.1138; found 291.1128. $C_{13}H_{20}N_2O_2S$ (268.37): calcd. C 58.18, H 7.51, N 10.44; found C 58.40, H 7.73, N 10.41.

***N*,*N*-Diisopropyl-*N*′-tosylformimidamide (7b):**[28] Obtained from *N*,*N*-diisopropylcyanamide (**1d**; 0.252 g, 2 mmol) and 4-toluenesulfonyl chloride (0.458 g, 0.24 mmol) according to the general procedure. Pure product **7b** (0.458 g, 1.62 mmol, 81%) was obtained by column chromatography (diethyl ether/*n*-pentane, 1:4 + 10% triethylamine) and HPLC (ethyl acetate/cyclohexane, 2:1) as a colourless solid (m.p. 98–100 °C). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 0.63 [d, $^3J_{H,H}$ = 6.8 Hz, 1 H, $NCH(CH_3)_2$], 0.81 [d, $^3J_{H,H}$ = 6.9 Hz, 1 H, $NCH(CH_3)_2$], 1.89 (s, 3 H, Aryl-C$H_3$), 2.83 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, $NCH(CH_3)_2$], 4.03 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, $NCH(CH_3)_2$], 6.84 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, *m*-C$H_{Ar}$), 8.07 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, *o*-C$H_{Ar}$), 8.14 (s, 1 H, NC*H*S) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 19.8 [N*C*H$(CH_3)_2$], 21.1 (Aryl-$CH_3$), 22.6 [N*C*H$(CH_3)_2$], 47.6, 49.4 [N*C*H$(CH_3)_2$], 126.9 (*o*-$C_{Ar}$), 129.5 (*m*-$C_{Ar}$), 141.7 ($C_{q,Ar}$), 141.9 ($C_{q,Ar}$), 156.7 (N*C*HS) ppm. IR (neat): $\tilde{\nu}$ = 3069 (vw), 3048 (vw), 2986 (w), 2972 (w), 2959 (w), 2930 (w), 2878 (vw), 2359 (vw), 1595 (vs), 1495 (w), 1456 (m), 1387 (w), 1371 (w), 1329 (s), 1304 (s), 1294 (vs), 1283 (vs), 1196 (s), 1148 (vs), 1136 (s), 1086 (vs), 1042 (w), 1032 (w), 1018 (w), 916 (m), 887 (vs), 839 (vs), 818 (vs), 741 (s), 708 (vs), 669 (vs), 592 (vs), 569 (m), 538 (vs) $cm^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{23}N_2O_2S^+$ 283.1475; found 283.1472. $C_{14}H_{22}N_2O_2S$ (282.40): calcd. C 59.54, H 7.85, N 9.92; found C 59.65, H 7.93, N 9.98.

**X-ray Crystal Structure Analysis of 7b:**[25] $C_{14}H_{22}N_2O_2S$; *M* = 282.40; colourless crystal; 0.20 × 0.10 × 0.05 mm; *a* = 8.1168(1), *b* = 8.9201(1), *c* = 10.9206(1) Å, *α* = 97.435(1), *β* = 105.273(1), *γ* = 94.890(1)°; *V* = 750.43(1) Å$^3$; $\rho_{calc}$ = 1.250 g cm$^{-3}$; $\mu$ = 1.918 mm$^{-1}$; empirical absorption correction (0.700 ≤ T ≤ 0.910); *Z* = 2; triclinic; space group $P\bar{1}$ (No. 2); $\lambda$ = 1.54178 Å; *T* = 223(2) K; $\omega$ and $\phi$ scans, 8592 reflections collected (±*h*, ±*k*, ±*l*), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 2644 independent ($R_{int}$ = 0.042) and 2400 observed reflections [$I > 2\sigma(I)$], 177 refined parameters, *R* = 0.042, $wR^2$ = 0.110, max. (min.) residual electron density 0.20 (–0.37) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**Synthesis of 9c:** *N*,*N*′-Diphenylcarbodiimide (**8c**; 0.23 mL, 242 mg, 1.25 mmol) was added at room temperature to a solution of di(*tert*-butyl)aluminium hydride (354 mg, 2.49 mmol) in toluene (10 mL). The mixture was stirred for 14 h then the solvent was removed in vacuo and the residue was dissolved in *n*-hexane (8 mL); colourless crystals were formed at 2 °C. Yield 208 mg (0.44 mmol, 35%); m.p. 169 °C. $^1$H NMR (400 MHz, $C_6D_6$, 300 K): $\delta$ = 1.25 (s, 36 H, C$Me_3$), 3.32 (br. s, 1 H, Al*H*Al), 6.92 (m, 6 H, *p*-C*H* and *o*-C*H*), 7.00 (m, 4 H, *m*-C*H*); 7.43 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (100 MHz, $C_6D_6$, 300 K): $\delta$ = 16.4 (*C*$Me_3$), 31.5 (C*Me*$_3$), 123.9 (*o*-*C*), 126.5 (*p*-*C*), 129.8 (*m*-*C*), 145.9 (*ipso*-*C*), 168.9 (N*C*N) ppm. IR (paraffin, CsI plates): $\tilde{\nu}$ = 1663 [m $\nu$(AlH)], 1591 (vw), 1545 [s $\nu$(C=N), phenyl], 1462 (vs), 1377 [vs. (paraffin)], 1306 (w), 1236 [w $\delta$(CH$_3$)], 1211 (w), 1155 (w), 1078 (vw), 1001 (w), 972 (w), 918 (w), 810 (m), 772 (m), 758 [m $\nu$(CC), $\nu$(CN)], 723 [s (paraffin)], 571 (m), 527 (w), 432 [vw $\delta$(CC), $\nu$(AlC), $\nu$(AlN)] $cm^{-1}$. MS (EI, 20 eV, 80 °C): *m*/*z* (%) = 421 (47) [M$^+$ – $CMe_3$], 365 (5) [M$^+$ – $CMe_3$ – butene], 279 (27) [M$^+$ – Al*t*Bu$_2$ – butane], 196 (84) [M$^+$ – 2Al*t*Bu$_2$], 93 (100) [$PhNH_2$]. $C_{29}H_{48}Al_2N_2$ (478.65): calcd. C, 72.77; H, 10.11; N, 5.85; found C, 72.22, H, 9.95, N, 5.63.

**X-ray Crystal Structure Analysis of 9c:**[20] $C_{29}H_{48}Al_2N_2$; *M* = 478.65; colourless crystals; 0.35 × 0.22 × 0.09 mm; *a* = 11.3727(2), *b* = 16.6859(4), *c* = 16.7326(3) Å, *α* = 78.902(1), *β* = 73.841(1), *γ* = 89.181(1)°; *V* = 2990.16(10) Å$^3$; $\rho_{calc}$ = 1.063 g cm$^{-3}$; $\mu$ = 0.993 mm$^{-1}$; empirical absorption correction (0.772 ≤ T ≤ 0.915); *Z* = 4; triclinic; space group $P\bar{1}$ (No. 2); $\lambda$ = 1.54178 Å; *T* = 153(2) K; $\omega$ and $\phi$ scans, 17105 reflections collected (±*h*, ±*k*, ±*l*), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 9460 independent ($R_{int}$ = 0.0255), 7810 observed reflections [$I > 2\sigma(I)$], 627 refined parameters, *R* = 0.0469, $wR^2$ = 0.1345, max. (min.) residual electron density 0.477 (–0.241) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**General Procedure for the Preparation of *N*,*N*′-Disubstituted *N*-Acylformamidines 10 and *N*-Sulfonylformamidines 11:** The respective carbodiimide **8** (1 equiv.) was dissolved in toluene (5 mL per mmol) and DIBAL-H (1 M in toluene, 2 equiv.) was slowly added. After stirring the reaction mixture for 30 min, the electrophile (2.2 equiv.) was added and stirring was continued for at least 2 h. The solvent was removed under reduced pressure, then the

crude product was purified by column chromatography and – if necessary – by HPLC and/or recrystallisation.

***N*-Isopropyl-*N*′-[(isopropylimino)methyl]benzamide (10a):** Obtained from *N*,*N*-diisopropylcarbodiimide (**8a**; 0.252 g, 2 mmol) and benzoyl chloride (0.618 g, 0.44 mmol) according to the general procedure. Pure product **10a** (0.342 g, 1.50 mmol, 75%) was obtained by column chromatography (cyclohexane/ethyl acetate, 2:1 + 10% triethylamine) as a colourless oil. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 1.02 [d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH(C$H_3$)$_2$], 1.56 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C$H_3$)$_2$], 2.85 [hept, $^3J_{H,H}$ = 6.2 Hz, 1 H, C$H$(CH$_3$)$_2$], 5.18 [hept, $^3J_{H,H}$ = 6.9 Hz, 1 H, C$H$(CH$_3$)$_2$], 7.02 (m, 3 H, *o*- und *p*-C$H_{Ar}$), 7.36 (m, 2 H, *m*-C$H_{Ar}$), 7.95 (s, 1 H, NC$H$N) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 19.5 {N[CH(C$H_3$)$_2$]$_2$}, 25.0 {N[CH(C$H_3$)$_2$]$_2$}, 47.3 {N[C$H$(CH$_3$)$_2$]$_2$}, 57.4 {N[C$H$(CH$_3$)$_2$]$_2$}, 128.6 (*m*-C$H_{Ar}$), 128.7 (*o*-C$H_{Ar}$), 130.7 (*p*-C$H_{Ar}$), 136.9 (*i*-C$_{Ar}$), 147.8 (N$C$N), 171.6 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3305 (vw), 3062 (vw, CH$_{Ar}$), 2967 (m, CH$_{aliph.}$), 2934 (w, CH$_{aliph.}$), 2870 (w, CH$_{aliph.}$), 2608 (vw), 2359 (vw), 1705 (vw), 1602 (w, C=C), 1684 (w, C=C), 1670 (w, C=C), 1634 (vs, C=N), 1603 (w), 1582 (w), 1491 (vw), 1449 (w), 1412 (w), 1381 (mw), 1364 (w), 1327 (s, C-C), 1246 (s, C-C), 1204 (w), 1184 (w), 1159 (m), 1136 (w), 1088 (m), 1028 (w), 1001 (v), 961 (w), 930 (vw), 883 (w), 831 (vw), 818 (vw), 797 (w), 723 (m), 700 (m), 673 (m), 664 (m), 633 (s). HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{21}N_2O^+$ 233.1648; found 233.1644. $C_{14}H_{20}N_2O$ (232.32): calcd. C 72.38, H 8.68, N 12.06; found C 72.26, H 8.46, N 12.05.

***N*-Isopropyl-*N*-[(isopropylimino)methyl]-4-methylbenzamide (10b):** Obtained from *N*,*N*-diisopropylcarbodiimide (**8a**; 0.252 g, 2 mmol) and 4-methylbenzoyl chloride (0.763 g, 4.4 mmol) according to the general procedure. Pure product **10b** (0.216 g, 0.88 mmol, 44%) was obtained by column chromatography (*n*-pentane/diethyl ether, 2:1 + 10% triethylamine) and subsequent HPLC (cyclohexane/ethyl acetate, 1:3) as a colourless oil. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 1.06 [d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH(C$H_3$)$_2$], 1.60 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C$H_3$)$_2$], 1.98 (s, 3 H, C$H_3$), 2.90 [hept, $^3J_{H,H}$ = 6.3 Hz, 1 H, C$H$(CH$_3$)$_2$], 5.24 [hept, $^3J_{H,H}$ = 6.9 Hz, 1 H, C$H$(CH$_3$)$_2$], 6.83 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, *m*-C$H_{Ar}$), 7.35 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, *o*-C$H_{Ar}$), 8.02 (s, 1 H, NC$H$) ppm. $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 19.5, 25.0 [CH(C$H_3$)$_2$], 21.2 (C$H_3$), 47.3, 57.4 [C$H$(CH$_3$)$_2$], 128.0 (*o*-C$H_{Ar}$), 129.3 (*m*-C$H_{Ar}$), 134.1 (*i*-C$_{Ar}$), 141.0 (*p*-C$_{Ar}$), 148.1 (N$C$N), 164.83 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3063 (w, CH$_{Ar}$), 3032 (w, CH$_{Ar}$), 2967 (w, CH$_{aliph.}$), 2934 (w, CH$_{aliph.}$), 2870 (w, CH$_{aliph.}$), 2361 (vw), 2342 (vw), 1705 (w, C=C), 1684 (w, C=C), 1670 (m, C=N), 1634 (vs, C=O), 1603 (w), 1582 (w), 1491 (vw), 1449 (w), 1412 (w), 1381 (m), 1364 (w), 1327 (s), 1246 (s), 1204 (w), 1184 (w), 1159 (m), 1136 (w), 1088 (m), 1028 (w), 1001 (vw), 961 (w), 930 (vw), 883 (w), 831 (vw), 797 (w), 723 (m), 700 (m), 673 (m), 664 (m), 633 (s). HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{23}N_2O^+$ 247.1805; found 247.1800. $C_{15}H_{22}N_2O$ (246.17): calcd. C, 73.13; H, 9.00; N, 11.37; found C, 73.25; H, 9.01; N, 11.25.

***N*-Cyclohexyl-*N*′-[(cyclohexylimino)methyl]-4-methylbenzamide (10c):** Obtained from *N*,*N*-dicyclohexylcarbodiimide (**8b**; 0.412 g, 2 mmol) and 4-methylbenzoyl chloride (0.680 g, 4.4 mmol) according to the general procedure. Crude product **10c** (0.641 g, 1.96 mmol, 98%) was purified on two chromatographic columns (*n*-pentane/diethyl ether, 2:1 + 10% triethylamine, then cyclohexane/ethyl acetate, 5:1 + 10% triethylamine) and subsequent HPLC (cyclohexane/ethyl acetate, 5:1) to give a colourless solid (m.p. 106 °C). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 0.74–1.88 (m, 20 H, C$H_2$), 2.00 (m, 3 H, C$H_3$), 2.79 [m, 1 H, C$H$(CH$_2$)$_2$], 4.89 [m, 1 H, C$H$(CH$_2$)$_2$], 6.86 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *m*-C$H_{Ar}$), 7.40 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *o*-C$H_{Ar}$), 8.08 (m, 1 H, NC$H$) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 20.2 (C$H_3$), 24.8, 26.0, 26.1, 26.9, 29.4, 35.5 (C$H_2$), 55.7, 65.2 [C$H$(CH$_2$)$_2$],129.1, 129.3 (C$H_{Ar}$), 134.3 (*i*-C$_{Ar}$), 141.1 (*p*-C$_{Ar}$), 148.6 (N$C$N), 172.0 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3337 (w), 3154 (s, CH$_{Ar}$), 3059 (w, CH$_{Ar}$), 2918 (w, CH$_{aliph.}$), 2787 (w), 1665 (s, C=O), 1612 (s, C=N), 1568 (s, C=C), 1520 (m, C=C), 1439 (m, C=C), 1410 (s), 1396 (s), 1304 (w), 1287 (w), 1215 (w), 1188 (m), 1144 (w), 1123 (m), 1113 (w), 1040 (w), 1020 (w), 976 (w), 968 (w), 953 (w), 839 (m), 816 (w), 795 (w), 727 (w), 692 (w), 656 (w), 621 (w). HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{31}N_2O^+$ 327.2431; found 327.2439. $C_{21}H_{30}N_2O$ (326.24): calcd. C, 77.26; H, 9.26; N, 8.58; found C, 77.01; H, 9.20; N, 8.45.

**X-ray Crystal Structure Analysis of 10c:**[25] $C_{21}H_{30}N_2O$; $M$ = 326.47; colourless crystal; 0.35 × 0.20 × 0.20 mm; $a$ = 6.4959(3), $b$ = 14.2569(6), $c$ = 20.0837(9) Å; $V$ = 1859.98(14) Å$^3$; $\rho_{calc}$ = 1.166 g cm$^{-3}$; $\mu$ = 0.550 mm$^{-1}$; empirical absorption correction (0.830 ≤ T ≤ 0.898); $Z$ = 4; orthorhombic; space group $P2_12_12_1$ (No. 19); $\lambda$ = 1.54178 Å; $T$ = 223(2) K; $\omega$ and $\phi$ scans, 14210 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 3267 independent ($R_{int}$ = 0.045) and 3086 observed reflections [$I > 2\sigma(I)$], 218 refined parameters, $R$ = 0.037, $wR^2$ = 0.096, max. (min.) residual electron density 0.12 (–0.13) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms. Flack parameter was refined to 0.2(4).

***N*-Phenyl-*N*′-[(phenylimino)methyl]benzamide (10d):** Obtained from *N*,*N*-diphenylcarbodiimide (**8c**; 0.388 g, 2 mmol) and benzoyl chloride (0.763 g, 4.4 mmol) according to the general procedure. Pure product **10d** (0.185 g, 0.62 mmol, 31%) was obtained by column chromatography (*n*-pentane/diethyl ether, 2:1 + 10% triethylamine) and subsequent recrystallisation from the eluent as a colourless solid (m.p. 130–132 °C). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 6.75–7.15 (m, 13 H, C$H_{Ar}$), 7.35–7.40 (m, 2 H, C$H_{Ar}$), 9.25 (m, 1 H, NC$H$) ppm. $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 121.7, 125.3, 129.0, 129.4, 129.5, 129.6, 130.9 (C$H_{Ar}$), 137.1, 136.2 (*i*-C$_{Ar}$), 149.4 (N$C$N), 150.3 (*i*-C$_{Ar}$), 170.6 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3064 (m, CH$_{Ar}$), 3055 (m, CH$_{Ar}$), 3035 (m, CH$_{Ar}$), 2362 (m), 2341 (m), 1656 (s, C=O), 1627 (s, C=N), 1589 (s), 1577 (s), 1487 (s), 1444 (m), 1363 (s), 1315 (m), 1294 (m), 1217 (s), 1097 (m), 1026 (s), 983 (m), 912 (m), 844 (s), 754 (s), 715 (s), 688 (s), 661 (s). 651 (m) cm$^{-1}$. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{17}N_2O^+$ 301.1335; found 301.1334. $C_{20}H_{16}N_2O$ (300.36): calcd. C 79.98, H 5.37, N 9.33; found C 79.64, H 5.73, N 9.29.

**X-ray Crystal Structure Analysis of 10d:**[25] $C_{20}H_{16}N_2O_2$; $M$ = 300.35; colourless crystal; 0.40 × 0.15 × 0.10 mm; $a$ = 5.7474(1), $b$ = 10.9703(2), $c$ = 13.2155(3) Å, $\alpha$ = 112.298(1), $\beta$ = 93.933(1), $\gamma$ = 100.708(1)°; $V$ = 748.60(3) Å$^3$; $\rho_{calc}$ = 1.332 g cm$^{-3}$; $\mu$ = 0.657 mm$^{-1}$; empirical absorption correction (0.779 ≤ T ≤ 0.937); $Z$ = 2; triclinic; space group $P\bar{1}$ (No. 2); $\lambda$ = 1.54178 Å; $T$ = 223(2) K; $\omega$ and $\phi$ scans, 7914 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 2636 independent ($R_{int}$ = 0.039) and 2434 observed reflections [$I > 2\sigma(I)$], 209 refined parameters, $R$ = 0.036, $wR^2$ = 0.096, max. (min.) residual electron density 0.17 (–0.19) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**General Procedure for the Preparation of Unsymmetrical *N*,*N*′-Disubstituted Formamidines from *N*-*tert*-Butyl-*N*-ethylcarbodiimide (8d):** Carbodiimide **8d** (1 equiv.) was dissolved in toluene (5 mL per mmol) and DIBAL-H (1 M in toluene, 1 equiv.) was slowly added. After stirring the reaction mixture for 30 min, electrophile (1.1 equiv.) was added and stirring was continued for at least 2 h. The solvent was removed under reduced pressure, then the crude product was purified by column chromatography and – if necessary – by HPLC and/or recrystallisation.

***N*-[(*tert*-Butylimino)methyl]-*N*′-ethyl-4-methylbenzamide (10e):** Obtained from *N*-(*tert*-butyl)-*N*′-ethylcarbodiimide (**8d**; 0.252 g,

2 mmol) and 4-methylbenzoyl chloride (0.340 g, 2.2 mmol) according to the general procedure. Pure product **10e** (0.246 g, 1.0 mmol, 50%) was obtained by column chromatography (*n*-pentane/diethyl ether, 8:1 + 10% triethylamine) and subsequent HPLC (cyclohexane/ethyl acetate, 5:1) as a colourless oil. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 1.06 [s, 9 H, C(C$H_3$)$_3$], 1.28 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H, NCH$_2$C$H_3$), 1.98 (s, 3 H, Aryl-C$H_3$), 4.15 (q, $^3J_{H,H}$ = 6.9 Hz, 1 H, NC$H_2$CH$_3$), 6.84 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *m*-CH$_{Ar}$), 7.28 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, *o*-CH$_{Ar}$), 8.18 (s, 1 H, NC*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 13.3 (NCH$_2$*C*H$_3$), 21.2 (Aryl-CH$_3$), 30.3 [C(*C*H$_3$)$_3$], 37.6 (N*C*H$_2$CH$_3$), 54.9 [N*C*(CH$_3$)$_3$], 128.7 (*i*-C$_{Ar}$), 129.2 (*o*-C*H*$_{Ar}$), 133.5 (*m*-C*H*$_{Ar}$), 140.8 (Aryl-*C*H$_3$), 145.5 (N*C*HN), 171.3 (N*C*O) ppm. IR (neat): $\tilde{\nu}$ = 2968 (m), 2934 (w), 2874 (vw), 1668 (w), 1630 (vs), 1612 (s), 1510 (w), 1450 (w), 1433 (w), 1404 (m), 1366 (s), 1333 (s), 1258 (m), 1206 (m), 1177 (w), 1085 (s), 1022 (w), 937 (w), 874 (w), 754 (m), 631 (m), 606 (m), 550 (m), 540 (m), 515 (m), 494 (s), 459 (s), 447 (s), 420 (s). HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{23}N_2O^+$ 247.1805; found 247.1792. $C_{15}H_{22}N_2O$ (246.17): calcd. C, 73.13; H, 9.00; N, 11.37; found C, 72.90; H, 8.84; N, 11.45.

***N*-[(*tert*-Butylimino)methyl]-*N*-ethylpivalamide (10f):** Obtained from *N*-(*tert*-butyl)-*N*′-ethylcarbodiimide (**8d**; 0.252 g, 2 mmol) and pivaloyl chloride (0.265 g, 2.2 mmol) according to the general procedure. Pure **10f** (0.065 g, 0.31 mmol, 15%) was obtained by column chromatography (*n*-pentane/diethyl ether, 10:1 + 10% triethylamine) and subsequent HPLC (cyclohexane/ethyl acetate, 5:1) as a colourless oil. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 1.15 [s, 9 H, C(O)C(C$H_3$)$_3$], 1.16 [s, 9 H, NC(C$H_3$)$_3$], 1.19 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, NCH$_2$C$H_3$), 4.06 (q, $^3J_{H,H}$ = 6.9 Hz, 2 H, NC$H_2$CH$_3$), 8.45 (s, 1 H, NC*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 13.3 (NCH$_2$*C*H$_3$), 28.6 [C(O)C(*C*H$_3$)$_3$], 30.6 {NC(*C*H$_3$)$_3$, 37.7 [N*C*(CH$_3$)$_3$]}, 39.9 (N*C*H$_2$CH$_3$), 55.0 [C(O)*C*(CH$_3$)$_3$], 145.1 (N*C*HN), 177.0 (N*C*O) ppm. IR (neat): $\tilde{\nu}$ = 2970 (m), 2934 (w), 2911 (vw), 2876 (vw), 2361 (vw), 1670 (m), 1630 (vs), 1508 (vw), 1476 (m), 1433 (vw), 1408 (w), 1362 (m), 1344 (w), 1314 (m), 1261 (m), 1198 (s), 1107 (s), 1026 (vw), 947 (w), 885 (vw), 824 (w), 662 (w), 631 (s), 596 (w), 550 (s), 542 (s), 530 (s), 505 (vs), 491 (vs), 484 (vs), 474 (vs), 463 (vs), 432 (vs), 426 (vs), 417 (vs), 407 (vs). HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{25}N_2O^+$ 213.1961; found 213.1980. $C_{12}H_{24}N_2O$ (212.19): calcd. C, 67.88; H, 11.39; N, 13.19; found C, 67.51; H, 11.22; N, 13.18.

***N*,*N*′-Diisopropyl-*N*-tosylformimidamide (11a):** Obtained from *N*,*N*-diisopropylcarbodiimide (**8a**; 0.252 g, 2 mmol) and 4-toluenesulfonyl chloride (0.835 g, 4.4 mmol) according to the general procedure. Pure **11a** (0.407 g, 1.44 mmol, 72%) was obtained by column chromatography (*n*-pentane/diethyl ether, 2:1 + 10% triethylamine) and subsequent HPLC (cyclohexane/ethyl acetate, 2:1) as a colourless solid (m.p. 61 °C). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 1.06 [d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH(C$H_3$)$_2$], 1.33 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C$H_3$)$_2$], 1.83 (s, 3 H, C$H_3$), 3.13 [sept, $^3J_{H,H}$ = 6.3 Hz, 1 H, *H*(CH$_3$)$_2$], 4.44 [sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 6.70 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, *m*-C*H*$_{Ar}$), 7.64 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, *o*-C*H*$_{Ar}$), 8.49 (s, 1 H, NC*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 19.5, 25.1 [CH(*C*H$_3$)$_2$], 21.1 (*C*H$_3$), 50.5, 58.1 [*C*H(CH$_3$)$_2$], 127.3, 129.9 (*C*H$_{Ar}$), 138.5 (*i*-*C*$_{Ar}$), 143.6 (*p*-*C*$_{Ar}$), 144.8 (N*C*N) ppm. IR (neat): $\tilde{\nu}$ = 3001 (w, CH$_{Ar}$), 2986 (s, CH$_{aliph.}$), 2931 (s, CH$_{aliph.}$), 2872 (s, CH$_{aliph.}$), 2360 (w), 2341 (w), 1681 (w), 1651 (vs, C=N), 1598 (m), 1465 (m), 1454 (m), 1384 (s, SO2), 1348 (s), 1307 (w), 1236 (m), 1192 (s), 1168 (s), 1151 (m), 1085 (s), 1010 (s), 931 (s), 893 (w), 840 (m), 813 (w), 667 (s), 632 (s). HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{23}N_2O_2S^+$ 283.1475; found 283.1468. $C_{14}H_{22}N_2O_2S$ (282.23): C, 59.54; H, 7.85; N, 9.92; found C, 59.32; H, 7.94; N, 9.69.

***N*,*N*′-Dicyclohexyl-*N*-tosylformimidamide (11b):** Obtained from *N*,*N*-dicyclohexylcarbodiimide (**8c**; 0.412 g, 2 mmol) and 4-toluenesulfonyl chloride (0.763 g, 4.4 mmol) according to the general procedure. Pure **11b** (0.529 g, 1.46 mmol, 73%) was obtained by column chromatography (*n*-pentane/diethyl ether, 2:1 + 10% triethylamine), a second column chromatographic purification (cyclohexane/ethyl acetate, 5:1 + 10% triethylamine) and subsequent HPLC (cyclohexane/ethyl acetate, 5:1) as a colourless solid (m.p. 81–83 °C). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 0.90–1.78 (m, 20 H, C$H_2$), 1.86 (s, 3 H, C$H_3$), 2.90 [m, 1 H, C*H*(CH$_2$)$_2$], 4.22 [m, 1 H, C*H*(CH$_2$)$_2$], 6.76 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *m*-C*H*$_{Ar}$), 7.71 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *o*-C*H*$_{Ar}$), 8.55 (s, 1 H, NC*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 21.2 (*C*H$_3$), 24.8, 25.7, 26.2, 26.8, 29.6, 35.2 (*C*H$_2$), 58.7, 65.5, 127.2, 123.0 (*C*H$_{Ar}$), 139.0 (*i*-*C*$_{Ar}$), 143.6 (*p*-*C*$_{Ar}$), 145.3 (N*C*N) ppm. IR (neat): $\tilde{\nu}$ = 2929 (s, CH$_{aliph.}$), 2922 (s, CH$_{aliph.}$), 2827 (w, CH$_{aliph.}$), 2358 (m), 2343 (m), 2331 (m), 1645 (s, C=N), 1597 (m), 1494 (m), 1454 (s), 1361 (s), 1332 (s), 1219 (s), 1161 (s), 1153 (s), 1161 (s), 1153 (s), 1024 (s), 989 (s), 958 (s), 893 (m), 813 (s), 756 (s), 669 (s), 664 (m), 615 (m). HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{31}N_2O_2S^+$ 363.2101; found 363.2107. $C_{20}H_{30}N_2O_2S$ (362.53): calcd. C 66.26, H 8.34, N 7.73; found C 65.94, H 8.45, N 7.73.

**X-ray Crystal Structure Analysis of 11b:**[25] $C_{20}H_{30}N_2O_2S$; *M* = 362.52; colourless crystal; 0.50 × 0.12 × 0.05 mm; *a* = 5.6170(1), *b* = 19.7269(4), *c* = 17.5765(4) Å, $\beta$ = 90.706(1)°; *V* = 1947.43(7) Å$^3$; $\rho_{calc}$ = 1.236 g cm$^{-3}$; $\mu$ = 0.182 mm$^{-1}$; empirical absorption correction (0.914 ≤ T ≤ 0.991); *Z* = 4; monoclinic; space group $P2_1/c$ (No. 14); $\lambda$ = 0.71073 Å; *T* = 223(2) K; $\omega$ and $\phi$ scans, 14930 reflections collected (±*h*, ±*k*, ±*l*), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 3357 independent ($R_{int}$ = 0.056) and 2901 observed reflections [$I > 2\sigma(I)$], 227 refined parameters, *R* = 0.048, $wR^2$ = 0.128, max. (min.) residual electron density 0.22 (–0.39) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

***N*′-*tert*-Butyl-*N*-ethyl-*N*-tosylformimidamide (11c):** Obtained from *N*-(*tert*-butyl)-*N*′-ethylcarbodiimide (**8d**; 0.252 g, 2 mmol) and 4-toluenesulfonyl chloride (0.419 g, 2.2 mmol) according to the general procedure. Pure **11c** (0.065 g, 0.31 mmol, 15%) was obtained by column chromatography (*n*-pentane/diethyl ether, 4:1 + 10% triethylamine) and subsequent HPLC (cyclohexane/ethyl acetate, 5:1) as a colourless solid (m.p. 82–84 °C). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 1.11 [s, 9 H, NC(C$H_3$)$_3$], 1.16 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H, NCH$_2$C$H_3$), 1.84 (s, 3 H, Aryl-C$H_3$), 3.64 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, NC$H_2$CH$_3$), 6.71 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, *m*-C*H*$_{Ar}$), 7.62 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, *o*-C*H*$_{Ar}$), 8.44 (s, 1 H, NC*H*N) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ = 21.1 (Aryl-CH$_3$), 13.2 (NCH$_2$*C*H$_3$), 30.3 [NC(*C*H$_3$)$_3$], 39.2 (N*C*H$_2$CH$_3$), 55.1 [N*C*(CH$_3$)$_3$], 128.6 (*o*-*C*H$_{Ar}$), 130.0 (*m*-*C*H$_{Ar}$), 138.6 (*i*-*C*$_{Ar}$), 142.8 (*p*-*C*$_{Ar}$), 143.6 (N*C*HN) ppm. IR (neat): $\tilde{\nu}$ = 3053 (w), 2968 (m), 2934 (w), 2874 (w), 1649 (vs), 1599 (w), 1497 (w), 1452 (w), 1379 (w), 1362 (m), 1344 (m), 1331 (m), 1308 (m), 1250 (m), 1204 (m), 1177 (s), 1155 (s), 1123 (w), 1090 (m), 1032 (w), 1020 (m), 1009 (s), 978 (m), 961 (w), 893 (s), 816 (m), 800 (w), 772 (vw), 731 (s), 658 (s), 583 (s), 554 (s), 542 (s), 490 (s). HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{22}N_2O_2S^+$ 283.1475; found 283.1472. $C_{14}H_{21}N_2O_2S$ (281.39): calcd. C 59.54, H 7.85, N 9.92; found C 59.21, H 7.95, N 9.81.

**X-ray Crystal Structure Analysis of 11c:**[25] $C_{14}H_{22}N_2O_2S$; *M* = 282.40; colourless crystal; 0.20 × 0.13 × 0.02 mm; *a* = 18.1418(9), *b* = 7.3029(4), *c* = 12.9482(7) Å, $\beta$ = 104.649(2)°; *V* = 1659.71(15) Å$^3$; $\rho_{calc}$ = 1.130 g cm$^{-3}$; $\mu$ = 1.735 mm$^{-1}$; empirical absorption correction (0.723 ≤ T ≤ 0.966); *Z* = 4; monoclinic; space group $P2_1/c$ (No. 14); $\lambda$ = 1.54178 Å; *T* = 223(2) K; $\omega$ and $\phi$ scans, 13199 reflections collected (±*h*, ±*k*, ±*l*), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 2762 indepen-

dent ($R_{int}$ = 0.084) and 1900 observed reflections [$I > 2\sigma(I)$], 208 refined parameters, $R$ = 0.062, $wR^2$ = 0.179, max. (min.) residual electron density 0.23 (–0.30) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**Supporting Information** (see footnote on the first page of this article): $^1$H and $^{13}$C NMR spectra and results of quantum chemical calculations including optimised Cartesian coordinates [B3LYP/6-311+G(d,p) and SCS-MP2-single point energies as well as D3-corrected DFT energies including zero point correction].

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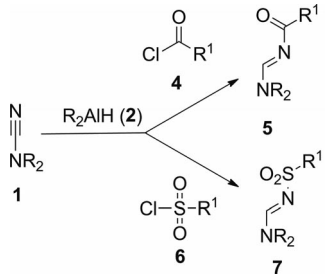
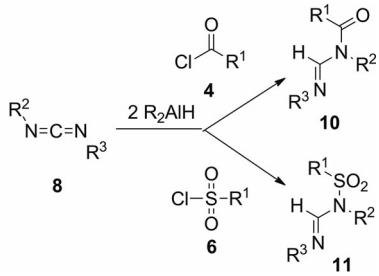
**Hydroalumination**




In a simple one-pot procedure cyanamides are converted into *N*′,*N*′-disubstituted *N*-acyl- or *N*-sulfonylformamidines by hydroalumination and subsequent treatment with acyl- or sulfonyl chlorides. Carbodiimides react similarly, forming *N*,*N*′-disubstituted *N*-acyl- and *N*-sulfonylformamidines. The intermediate aluminium compounds and several products were characterised, including by X-ray crystallography.

**J. Hellmann, I. Rhotert, H. Westenberg, R. Fröhlich, B. Wibbeling, W. Uhl, E.-U. Würthwein*** ..... **1–14**

*N*-Acyl- and *N*-Sulfonylformamidines from Cyanamides and Carbodiimides by Hydroalumination and Subsequent Treatment with Electrophiles

**Keywords:** Acylation / Aluminium / Synthetic methods / Hydrides / Density functional calculations