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Hydroalumination of Ketenimines and Subsequent Reactions with Heterocumulenes: Synthesis of Unsaturated Amide Derivatives and 1,3-Diimines

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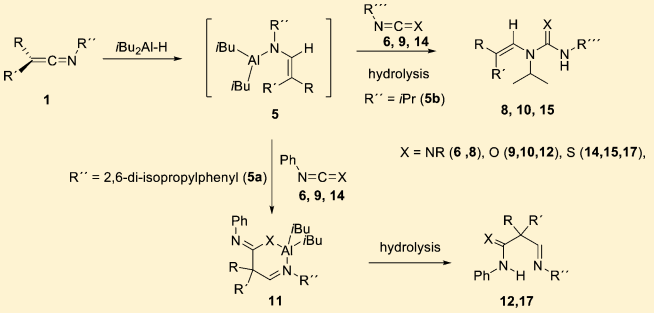
Supporting Information

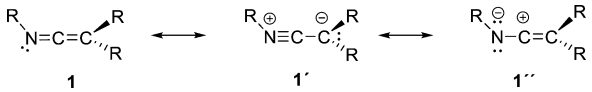
ABSTRACT: The series of differently substituted ketenimines **1** was hydroluminated using di-*iso*-butyl aluminum hydride. For the sterically congested ketenimine **1a**, preferred hydroalumination of the C═N-bond was proven by X-ray crystallography (compound **5a**). In situ treatment of the hydroaluminated ketenimines **5** with various heterocumulenes like carbodiimides, isocycanates, isothiocyanates and ketenimines as electrophiles and subsequent hydrolytic workup resulted in novel enamine derived amide species in case of *N*-attack (sterically less hindered ketenimines) under formation of a new C−N-bond or in 1,3-diimines by C−C-bond-formation in case of bulky substituents at the ketenimine-nitrogen atom. Furthermore, domino reactions with more than 1 equiv of the electrophile or by subsequent addition of two different electrophiles are possible and lead to polyfunctional amide derivatives of the biuret type which are otherwise not easily accessible.



INTRODUCTION

Ketenimines **1** belong to the class of heterocumulenes and might be described as imine analogues of ketenes.[1] Due to their high reactivity they are frequently used as starting materials for the synthesis of open-chain and heterocyclic compounds[2,3] and also of peptides (Scheme 1).[4]

Scheme 1



In heterocyclic chemistry ketenimines are not only used as nucleophiles,[5] but also for the addition of free radicals.[6] They are further employed for [2 + 2]-cycloaddition reactions[7] or for the synthesis of five- and six-membered ring systems.[8] Dijkstra and Backer reported on Lewis-acid-catalyzed electrophilic substitution reactions of arenes using ketenimines to obtain aromatic imine derivatives.[9] Ketenimines may be transformed into metal organic species by deprotonation. Schöllkopf et al.[10] reported the use of potassium-*t*-butoxide as base for the preparation of metalated ketenimines and Würthwein et al. observed the formation of 2-azabutadienes from ketenimines by deprotonation and subsequent reprotonation reaction.[11]

In 1919 Staudinger and Meyer[12] published the first synthesis of ketenimines using the nitrogen analogue of the later discovered Wittig-olefination by reacting isocyanates with triphenylphosphorylides. Staudinger et al. also succeeded in a related synthesis starting from ketenes and triphenyliminophosphoranes.[13] Later, Wadsworth et al. reported on a similar synthesis using dialkylphosphoramidates instead of triphenyliminophosphoranes.[14] The synthesis of *N*-silylketenimines by Watt[15] and our group[16] was achieved by treatment of acetonitrile derivatives with lithium diisopropylamid (LDA) and followed by *N*-silylation. In 1964 Stevens et al. published a versatile synthesis of ketenimines by dehydation of amides by phosphorus pentoxide in pyridine[2,17] A synthesis under milder conditions was described by Jochims et al. They used imidoyl chlorides, which were prepared from secondary amides, and subjected them to HCl-elimination reactions using various bases (see Scheme 1).[18]

In this article, we report on the first hydroalumination reactions of ketenimines. We were interested in the regio- and chemoselectivity of such reactions and in the structural properties of the metalated compounds of the aluminum enamide type. Due to their nucleophilic character, the organoaluminum intermediates should be applicable in

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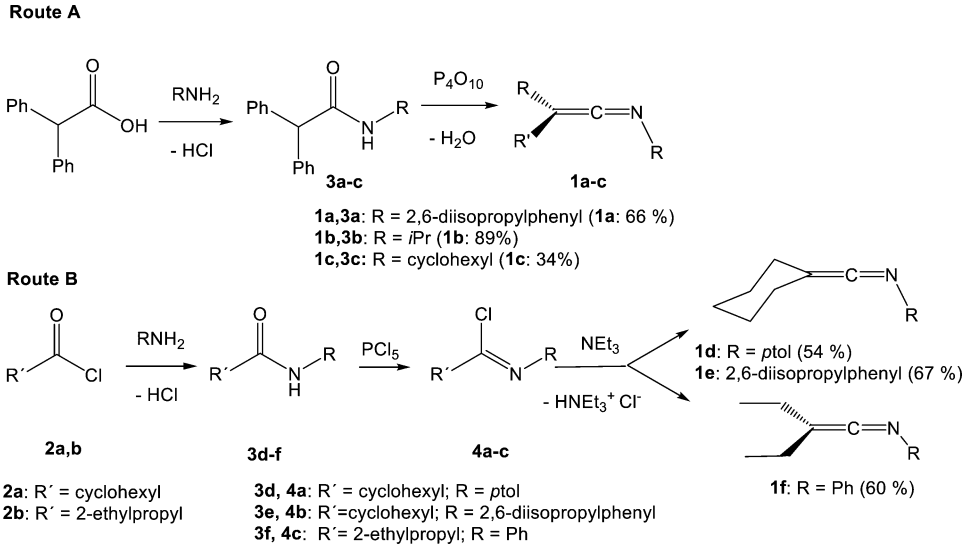
Scheme 2. Synthesis of Ketenimines 1 from Amides 3 or Imidoyl Chlorides 4



organic synthesis by treatment with functional electrophiles. We treated them with carbodiimides, isocyanates, isothiocyanates and a second equivalent of ketenimines. Even domino reactions involving the successive use of two different electrophiles are possible. After final aqueous workup, a great variety of interesting and novel functionalized organic molecules of the amide and 1,3-diimine type were isolated and fully characterized. With this study, we continue our investigations into the use of hydroalumination reactions of CN-multiple bonds in organic synthesis on cyanamides[19] and hydrazones.[20]

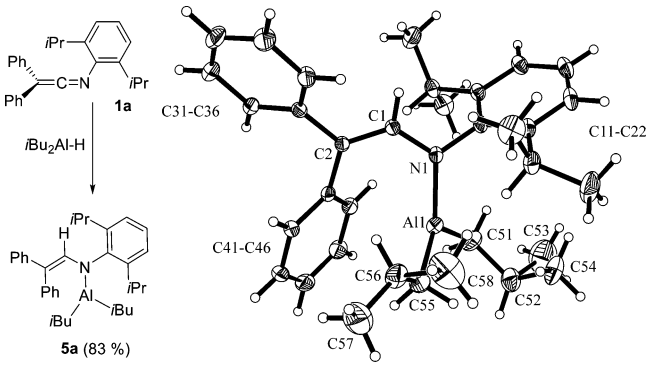
RESULTS AND DISCUSSION

Synthesis of Ketenimines. To investigate ketenimines with aromatic as well as aliphatic substitution patterns, two different synthetic pathways were used for their preparation. Thus, the *C*-diaromatic ketenimine derivates **1a−c** were generated following a literature procedure[17] by elimination of water from the corresponding secondary amides **3** using P_4O_{10} in excess of anhydrous pyridine or triethylamine (Scheme 2, Route A). The *C*-dialiphatic ketenimines **1d−f** were readily obtained by chlorination of the corresponding secondary amides **3** with phosphoryl chloride via established procedures to give imidoyl chlorides **4**, followed by their dehydrochlorination using an excess of triethylamine[18,21] (Scheme 2, Route B). These ketenimines reveal relatively low thermal stability and must be stored under argon at low temperatures (−20 °C).

Synthesis of the Monomeric Aluminum Enamide 5a by Hydroalumination of Ketenimine 1a. Ketenimine **1a** (*N*-(diphenylvinylidene)-2,6-diisopropylaniline) was treated with diisobutylaluminum hydride (DIBAL-H) in anhydrous *n*-hexane to obtain the monomeric aluminum enamide **5a** by selective hydroalumination in 83% yield (Scheme 3).

The crystal structure determination (Scheme 3) of **5a** shows that the aluminum atom is bonded to the nitrogen atom of the ketenimine moiety, which is also attached to the 2,6-diisopropylphenyl group, in spite of the steric shielding exerted by this bulky N-substituent. Thus, hydroalumination of the C═N-bond of **1** seems to be highly preferred over reduction of the C═C-bond, even in sterically unfavorable

Scheme 3. Hydroalumination of Ketenimine 1a Giving the Aluminum Compound 5a (Left), ORTEP Diagram of 5a with Ellipsoids Shown at the 30% Probability Level (Right)



cases. The negative partial charge of the aluminum bound hydrogen atom of DIBAL-H causes its addition to the central carbon atom of the ketenimine. As the respective nitrogen atom of ketenimine **1a** bears a relatively high negative partial charge (NBO-charges:[22] N −0.458, ═C= 0.506, ═C −0.285 at M062x/6-311+G(d,p)+gd3[23−25]), the attack of the electrophilic aluminum atom to give **5a** is electrostatically favored. The resulting Al−N distance (1.859(2) Å) in **5a** is in the upper range usually observed for Al−N compounds,[26] reflecting a relatively strong Al−N interaction between the tricoordinated Al and N atoms. The C═C bond length (1.352(3) Å) is close to standard values.[27] The NBO charges (N −1.007, Al 2.010, *β*-C −0.196) indicate the strong increase of nucleophilicity at the nitrogen atom upon hydroalumination, which is well in line with Gutmann's charge-density variation rules.[28] The presence of two adjacent Lewis-acidic and -basic atoms in a single molecule is an excellent prerequisite for their application in activation processes.

For comparison, the NBO-charges for the corresponding on nitrogen sterically less crowded *N*-propyl-substituted ketenimine **1b** and its hydroalumination product **5b** were also calculated. For **1b**, the NBO-charge at the nitrogen atom (−0.451) is quite similar compared to the one of **1a**; the *β*-carbon atom (−0.256), bears a slightly less negative charge

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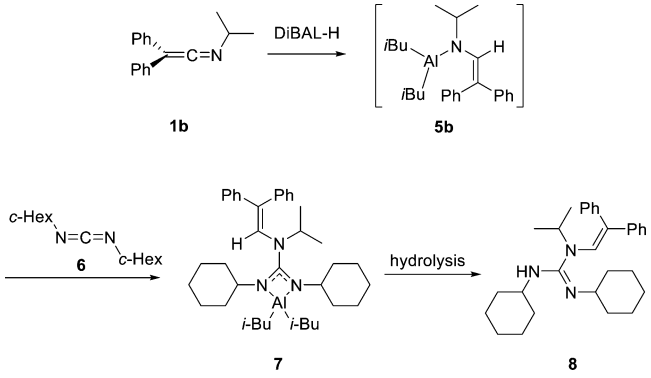
compared to **1a**. The corresponding aluminum compound **5b** shows a smaller negative charge on nitrogen (−0.976) and a less positive charge on aluminum (1.979) in comparison to **5a**. According to the calculations, in **5b**, the β-carbon atom (−0.226) is significantly more nucleophilic compared to one in **5a**.

Reactions of the Active Al/N Compounds with Heterocumulenes. *(a). Reaction of Ketenimine **1b** with DIBAL-H and Di(cyclohexyl)-carbodiimide **6**.* In a first reaction, we treated the ketenimine **1b** with DIBAL-H in anhydrous toluene at −78 °C and observed a complete consumption of the starting materials after stirring at room temperature for 2 h. The intermediate aluminum compound **5b** was neither isolated nor characterized, but was directly treated with di(cyclohexyl)-carbodiimide **6** at room temperature (12 h). Compound **7** was formed quantitatively and isolated in 42% yield after crystallization from the concentrated reaction mixture. Quenching of **7** with aqueous solution of NaOH (2 M) gave the unsaturated guanidine **8** in 55% yield (Scheme 4).

Scheme 4. Reaction of Ketenimine 1b with DIBAL-H and Di(cyclohexyl)-carbodiimide 6



The structure of aluminum compound **7** was elucidated by X-ray crystallography (Figure 1). It results from the hydroalumination of ketenimine **1b** at the C═N double bond giving **5b** and from the following insertion of the carbodiimide **6** into the Al−N bond. Both nitrogen atoms of the resulting guanidinate coordinate to the aluminum atom forming a four-membered AlN_2C heterocycle with a delocalized π-electronic system across the N−C−N group (C−N 1.333 Å; Al−N 1.936 Å (average)). Thus, the formation of the new C−N single bond (1.403(1) Å) between the former *N*-Al-enamine and the carbodiimide gives rise to a unique unsaturated aluminum guanidinate complex $(R_2Al)(RN)_2C-N(R)-C(H)=CR_2$. Insertion reactions of carbodiimides into Al−N bonds of simple AlR_2-(NR'_2) compounds to yield guanidinato complexes of aluminum have been reported previously.[29]

Single crystals of **8** (Figure 1) were obtained by crystallization from DMSO at room temperature and were characterized by X-ray crystallography. They show an almost planar $R_2N-C(NH)=N-C$ chain (torsion angles −6.7(9)° and 174.5(4)°). The length of the C4═N6 bond is 1.292(3) Å, the C4−N5(H) distance amounts to 1.355(3) Å. The newly formed C4−N3 single bond (1.412(1) Å) is only slightly longer compared to the corresponding C2−N4 bond (1.403(1) Å) of the corresponding aluminum guanidinato complex **7**.

*(b). Reaction of Ketenimines **1** with DIBAL-H and Isocyanates **9**.* In accordance with the synthesis of compound **8**, we treated the ketenimines **1a,b** with DIBAL-H in anhydrous *n*-hexane at −78 °C. The hydroalumination products **5a,b** were not isolated, but treated directly with 1 equiv of isocyanates **9a,b** at −78 °C. After a stirring step at room temperature, the urea derivates **10a,b**, derived from **1a**, were isolated in moderate to excellent yields after hydrolytic workup.

In case of compound **1b**, after addition of **9a** the aluminum compound **11** was formed almost quantitatively and was isolated in 85% yield after crystallization from the concentrated reaction mixture. It gave the amide **12** in 88% yield after quenching with aqueous NaOH-solution (2 M). Single crystals of **12** for X-ray structure analysis (see Supporting Information, Figure S39) were obtained from a 1:1 mixture of *n*-pentane and ethyl acetate (1:1) at room

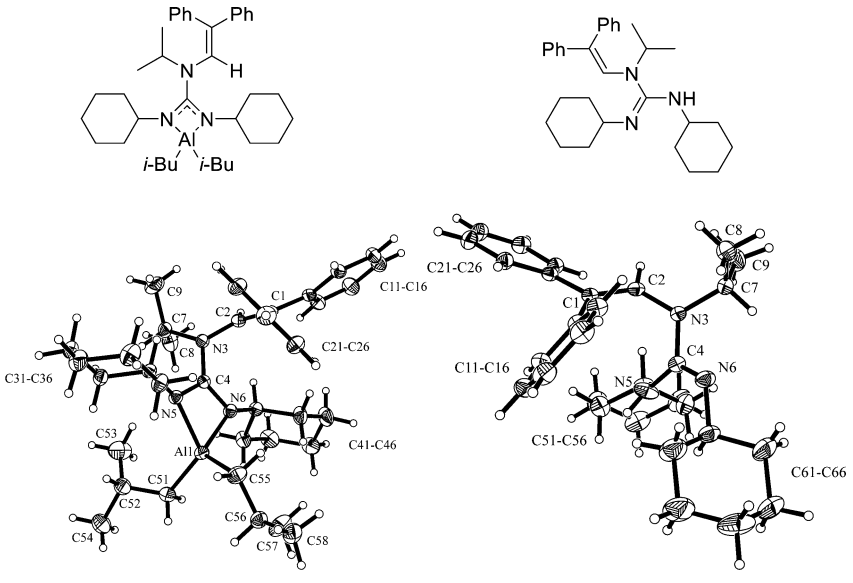


Figure 1. ORTEP diagram of **7** (left) and **8** (right) with ellipsoids shown at the 30% probability level.

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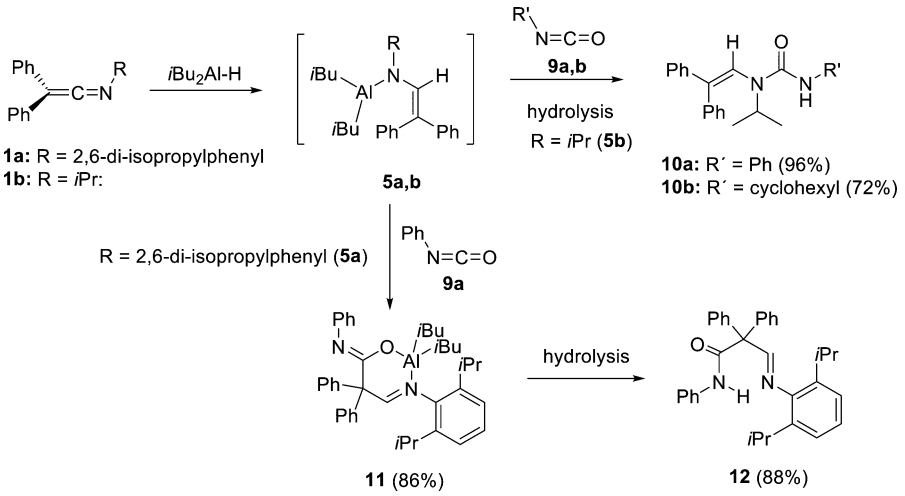
Scheme 5. Reactions of Ketenimine 1a,b with DIBAL-H and Isocyanates 9



temperature. In all cases, the crude products **10a,b** and **12** were purified by column chromatography over silica gel (Scheme 5).

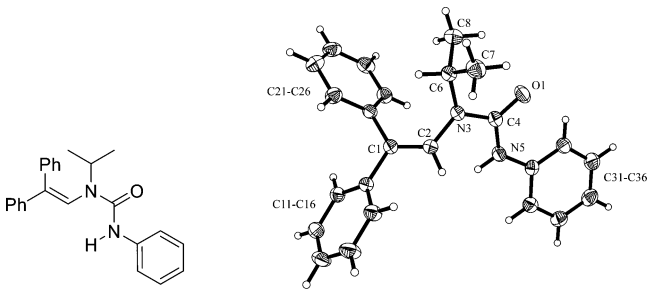


Figure 2. ORTEP diagram of **10a** with ellipsoids shown at the 30% probability level.

It is quite evident that the outcome of these reactions highly depends on the steric bulk of the N-substituent of the ketenimine **1**. Small substituents like the *i*Pr-group allow the attack of the isocyanate **9** at the more nucleophilic nitrogen atom to give the *n*-acylated enamines **10a,b**. The very bulky N-substituent in **1b**, however, directs the isocyanate to the *β*-carbon atom of the ketenimine subunit. Consequently, in the reaction course the aluminum compound **11** was formed, leading after hydrolysis to the imino amide **12**.

The X-ray structures of **10a** and **10b** indicate the formation of C−N single bonds between the nitrogen atom of the former ketenimine and the central carbon atom of the former isocyanate **9** (**10a**, Figure 2; **10b**, Supporting Information Figure S37).

Aluminum compound **11** was also characterized by single-crystal X-ray diffraction analysis (Figure 3, left). The six-membered $AlNC_3O$ heterocycle in **11** represents the stable intermediate formed by hydroalumination of ketenimine **1a** and subsequent addition of phenyl isocyanate **9a**. The formation of the C−C single bond is observed between the active *β*-carbon atom of the former ketenimine **1a** and the central carbon atom of the former isocyanate **9a**. The aluminum atom is bonded to the oxygen atom (Al−O

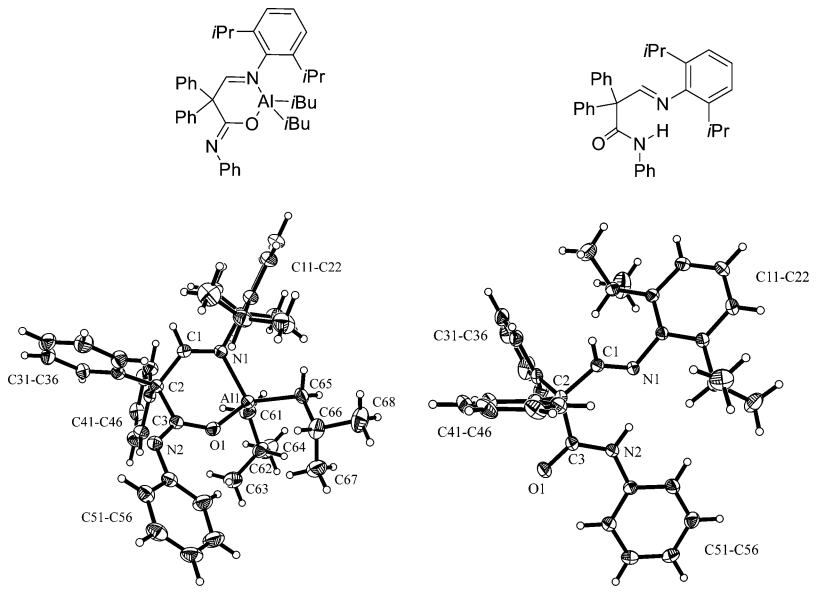


Figure 3. ORTEP diagram of **11** (left) and **12** (right) with ellipsoids shown at the 30% probability level.

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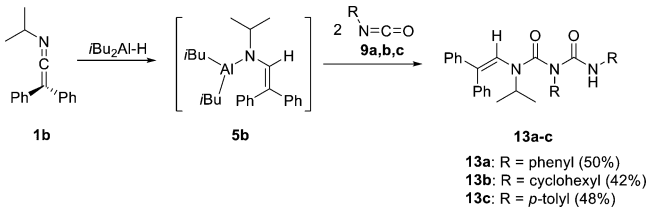
1.771 (6) Å) and further coordinated by the nitrogen atom via a dative Al−N bond with the expectedly long Al−N1 distance of 2.012 (0) Å.

In the X-ray structure of the hydrolysis product **12**, the intramolecular hydrogen bridge is the most interesting feature with an N1−N5-distance of 2.729 Å, which is significantly shorter than the sum of the nitrogen van der Waals radii (2.92 Å,[30]) (Figure 3, right).

Similarly to the synthesis of compounds **10a,b**, we treated the aluminum intermediate **5b** directly with 2 equiv of the isocyanates **9** at −78 °C. After optimization of the reaction conditions, the products of a domino-like reaction by subsequent addition of 2 equiv of isocyanates **9** were formed, leading in moderate isolated yields to the enamine-derived biuret-type compounds **13a−c** (Scheme 6).

Scheme 6. Reaction of Ketenimine 1b with DIBAL-H and 2 equiv of the Isocyanates 9



Single-crystal X-ray diffraction analyses confirm the constitution of compounds **13a** and **13b** (Figure 4).

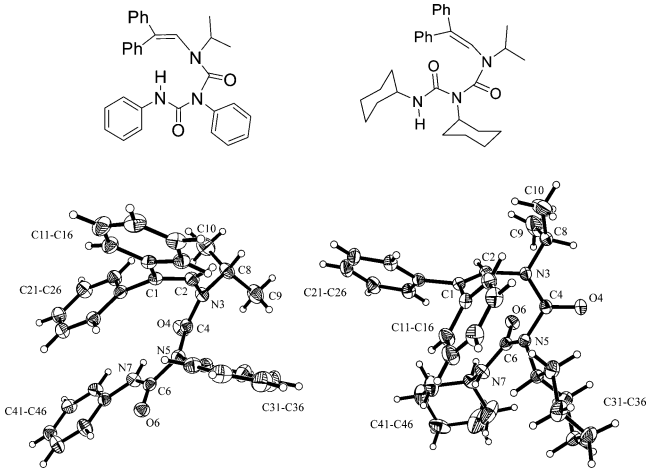


Figure 4. ORTEP diagram of **13a** (left) and **13b** (right) with ellipsoids shown at the 30% probability level.

Particularly noteworthy are the quite flexible biuret-substructures in the solid state (dihedral angles along the biuret-subunit: **13a**, N1−C6−N7−C8, 4.84°; C6−N7−C8−N9, 153.65°; **13b**, N1−C6−N7−C8, 61.19°; C6−N7−C8−N9, −170.61°). Thus, both compounds show significantly different conformations of the backbone.

*(c). Reaction of Ketenimine **1b** with DIBAL-H and Phenyl Isothiocyanate **14**.* Similarly to the synthesis of the aluminum compound **11**, the sterically less bulky ketenimine **1b** gave the vinyl thiourea derivative **15** as result of an electrophilic attack of the phenyl isocyanate **14** at the nitrogen atom of the former ketenimine after hydrolytic workup without isolating the hydroalumination intermediate **5b** (Scheme 7). No

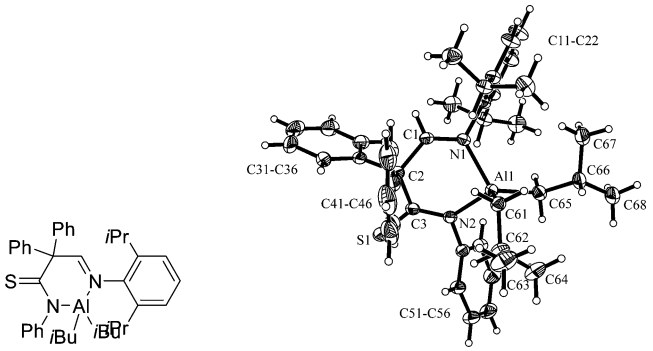


Figure 5. ORTEP diagram of **16** with ellipsoids shown at the 30% probability level.

domino-like reactions were observed when 2 equiv of phenyl isothiocyanate **14** were used.

In contrast, treatment of the bulky ketenimine **1a** with DIBAL-H and subsequent addition of 1 equiv of phenyl isothiocyanate **14** gave the aluminum compound **16** after stirring at −78 °C (2 h) and room temperature (1 h) in 53% yield. Hydrolysis and column chromatography over silica gel gave a few single crystals of the imino thioamide **17**, which could be characterized by X-ray crystallography (see Supporting Information Figure S43). However, preparative purification by column chromatography or recrystallization failed. Here also a C−C bond between the former ketenimine and the isothiocyanate was formed.

Single crystals of aluminum compound **16** were obtained by recrystallization from an anhydrous *n*-hexane/toluene = 2:1-mixture at −20 °C. The six-membered AlN_2C_3 ring in the molecular center shows the activation of C═N double bond of the phenyl isothiocyanate **14** in a similar mode as observed for **11** forming a coordination sphere of two nitrogen atoms at aluminum (Al−N: 1.924, 1.995 Å) (Figure 5).

*(d). Reaction of Ketenimines **1** with DIBAL-H and a Second Equivalent of Another Ketenimine **1**.* The compounds obtained by hydroalumination of ketenimines **1** should be able to react with a second equivalent of a ketenimine as an electrophile to form highly interesting oligomeric species. Therefore, we treated the ketenimine **1c** with DIBAL-H in anhydrous *n*-hexane at −78 °C. After stirring for 1 h (−78 °C), ketenimine **1d** was added directly at the same temperature. Compound **18** was formed almost quantitatively and isolated in 37% yield after crystallization from the concentrated reaction mixture (Scheme 8). Attempts to isolate the corresponding hydrolysis product by column chromatography over silica gel or alumina B failed.

The structure of aluminum compound **18** was elucidated by X-ray crystallography (Figure 6). In correspondence to the structure of compound **16**, the formation of a C−C single bond indicates that the *β*-carbon atom of ketenimine **1c** is activated by hydroalumination and reacts with the C═N double bond of the second ketenimine **1d** to form a chelating *N,N*-ligand. It is interesting to note that the cyclohexyl substituent at the nitrogen atom of **1c** leads to preferred C−C-bond formation, while the *N*-isopropyl substituent as in **1b** always gave C−N-bonding (see above).

In a similar way, the diimines **19a** and **19b** were obtained by treating the ketenimine **1e** or **1b** with DIBAL-H and afterward with a second equivalent of the ketenimine **1b** or **1e**. The crude products were subjected to column

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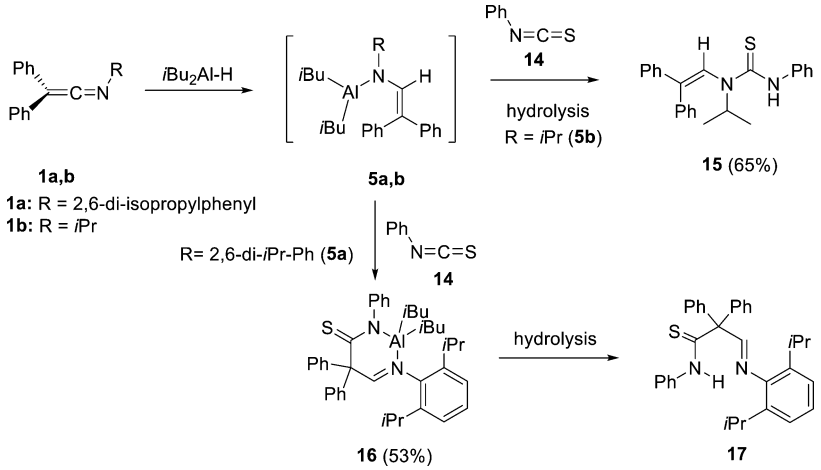
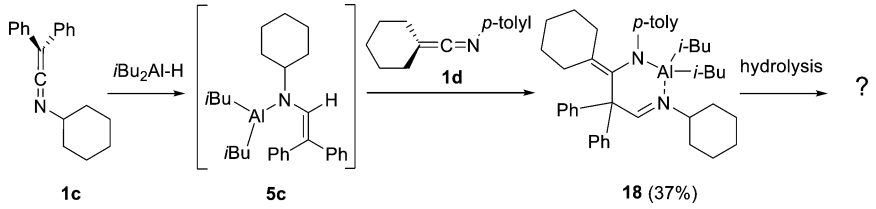
Scheme 7. Reaction of Ketenimine 1a,b with DIBAL-H and Phenyl Isothiocyanate 14



Scheme 8. Reaction of Ketenimine 1c with DIBAL-H and Subsequent Treatment with Ketenimine 1d



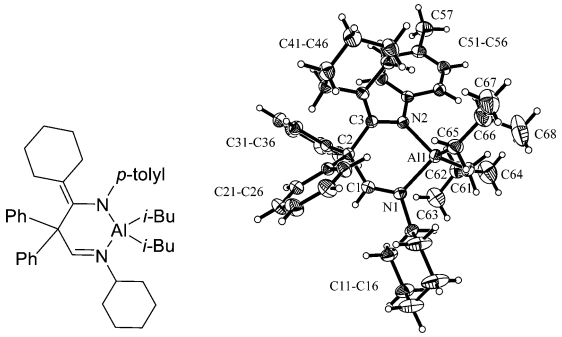


Figure 6. ORTEP diagram of **18** with ellipsoids shown at the 30% probability level.

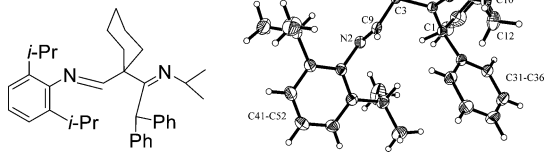


Figure 7. ORTEP diagram of **19a** with ellipsoids shown at the 30% probability level.

chromatography over Al_2O_3 (B) after hydrolytic workup (Scheme 9).

Single crystals of both compounds **19a** and **19b** were obtained by recrystallization from a solvent mixture (*n*-pentane/diethyl ether = 1:1) at room temperature (for **19a**, Figure 7; for **19b**, see Supporting Information Figure S46). Both structures indicate similar reactions as observed for the synthesis of **18**. Thus, a C−C single bond was formed

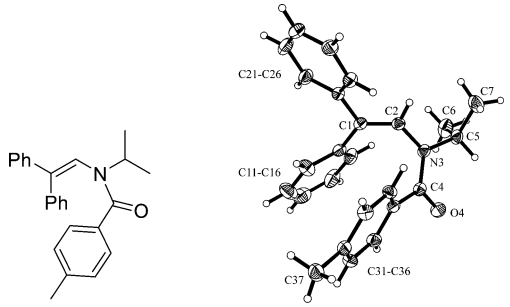


Figure 8. ORTEP diagram of **20a** with ellipsoids shown at the 30% probability level.

between the *β*-carbon atom of the first ketenimine and the *α*-carbon atom of the second ketenimine. In case of **19b**, the C−C-bond formation starting from the N-*i*-Pr compound **1b** is surprising and presents an exception among the reactions of this compound (see above). Possibly, the steric bulk of the reagent **1e** causes this different chemoselectivity. After hydrolytic workup, compounds **19a** and **19b** were isolated as multiply substituted diimines.

(e). Reactions of Ketenimines 1 with Carboxylic Chloride 2c. The aluminum intermediates **5b** or **5f** as nonisolated intermediates from the hydroalumination of ketenimine **1b** or **1f** reacted also with 2 equiv of carboxylic chloride **2c** in a one-pot reaction. The reactions mixtures were quenched with an aqueous solution of NaOH to yield the *N*-acyl enamides **20a** and **20b**. The crude products were subjected to column chromatography over silica gel and isolated in 22% and 61% yield (Scheme 10).

Single crystals of **20a** were obtained from toluene at room temperature (Figure 8). The structure shows the formation of a C−N single bond between the nitrogen atom originally

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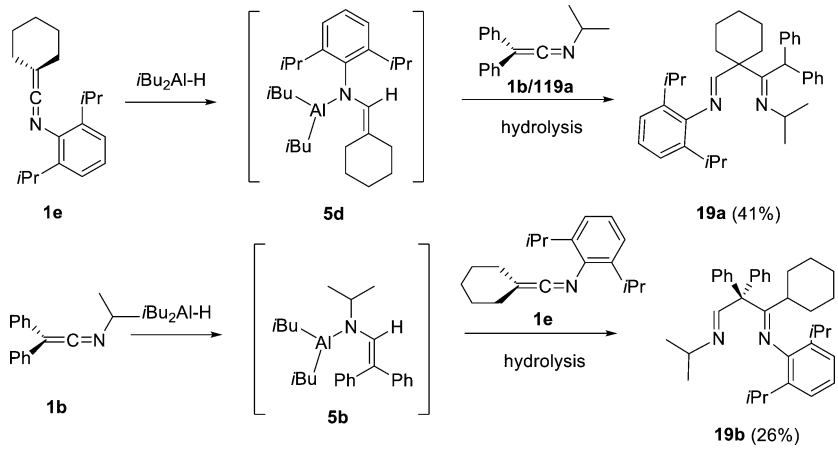
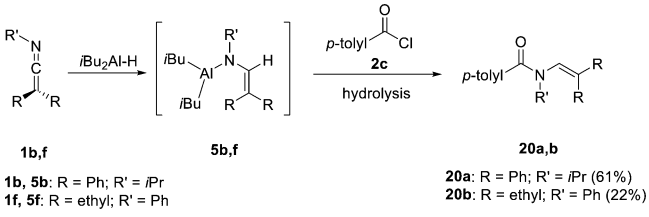
Scheme 9. Synthesis of Diimines 19a and 19b



Scheme 10. Synthesis of the *N*-Acyl Enamides 20a and 20b



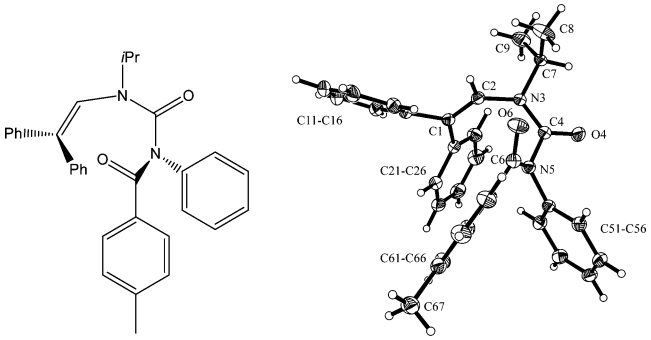


Figure 9. ORTEP diagram of **21a** with ellipsoids shown at the 30% probability level.

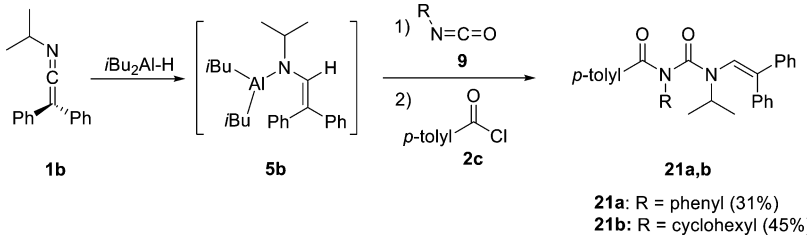
bonded to aluminum in the intermediate **5b** and the carbonyl carbon atom of the carboxylic acid.

*(f). One-Pot Reactions of Ketenimines **1** with Isocyanates **9** and Acid Chloride **2c**.* Finally, as a further example of a domino reaction involving successively two different electrophiles, the ketenimine **1b** was first treated with DIBAL-H. The addition of 1 equiv of isocyanate in a second step and finally of 2 equiv of acid chloride **2c** in a third step gave the *N*-imido-substituted enamides **21a,b** in a one-pot reaction 31% and 45% yield. The constitutions of **21a**, **b** were confirmed by X-ray diffraction of single crystals, which were obtained from a solution in DMSO at room temperature (for **21a**, Figure 9; for **21b**, see Supporting Information Figure S49). Two new C−N single bonds were formed, the first one between the nitrogen atom of the reduced ketenimine unit and the central carbon atom of the isocyanate and the second one after addition of acid chloride in the domino reaction (Scheme 11). The chains of **21a** and **21b** show helical conformations. These results underline the wide synthetic utility of hydroaluminated ketenimines for a multistep synthetic approach to multiply functionalized nitrogen compounds, which otherwise are not easily accessible.

■ CONCLUSIONS

In this study, we have investigated the hydroalumination of ketenimines and their unique reactivity toward various heterocumulenic electrophiles. In one case (**5a**), we determined the structure of the initial hydroalumination product in the solid state by X-ray crystallography, indicating that the hydroalumination of the C═N-bond is preferred over the reduction of the C═C-bond, even in those cases, in which the N-substituent is very bulky. These reactive intermediates with coordinatively unsaturated aluminum and nitrogen atoms showed an impressive reactivity in secondary reactions with an activation of heterocumulenic electrophiles such as carbodiimides, isocyanates, isothiocyanates and ketenimines. In general, the regioselectivity of these secondary reactions may be explained by the steric bulk of the N-substituent of the ketenimines. Thus, both types of reactions with electrophiles were found: Small N-substituents allow insertion reactions into the aluminum−nitrogen bond leading to various functionalized enamine and enamide derivatives,

Scheme 11. One-Pot Synthesis of the *N*-Imido-enamides 21a,b



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while bulky N-substituents lead to C−C-bond formation giving products of the 1,3-diimine type. In several cases, the constitution of the aluminum compounds before hydrolytic workup could be determined by X-ray structure analysis, showing coordination compounds with chelating *N,N*- or *N,O*-ligands. Hydrolytic workup gave the corresponding functionalized compounds in moderate to high yields. Even the successive addition of two electrophiles of the same or of different type was applied successfully and led to novel urea derivatives including such of the biuret type. These results verify convincingly the exceptional applicability of easily available aluminum based nucleophiles for C−C and C−N bond formation reactions and as efficient building blocks for the generation of new functionalized unsaturated organic nitrogen compounds. These reactions will clearly find wider application in preparative chemistry and will stimulate further experiments. Investigations into the synthesis of related or even more complicated compounds are presently in progress.

EXPERIMENTAL SECTION

General. All air and/or moisture sensitive experiments were performed under purified argon using standard Schlenk techniques. *n*-Hexane and toluene were dried over sodium/benzophenone. A solution of DIBAL-H in-*n*-hexane was applied as purchased. NMR spectra were recorded at 298 K (^{1}H, 300.13 MHz; ^{13}C, 75.48 MHz), (^{1}H, 400.03; ^{13}C, 100.59 MHz), (^{1}H, 499.85 MHz; ^{13}C, 125.67 MHz), (^{1}H, 599.79 MHz; ^{13}C, 150.83 MHz). Assignments of the resonances were supported by 2D experiments and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C NMR spectra were all proton decoupled. IR spectra were recorded as Nujol mull between CsI plates or with an ATR sampling system. Electron impact (EI) mass and electron spray ionization (ESI) spectra were recorded. Elemental analyses were determined by the microanalytic laboratory in our institute.

Precursors. *Synthesis of Amides.* **General Procedure A for 3a−c**: Thionyl chloride (2 equiv) was mixed with diphenylacetic acid (1 equiv) and refluxed until HCl gas evolution was no longer observed. Then, excess thionyl chloride was removed using a water jet pump. The resulting diphenylacetyl chloride **2a** was added without isolation to a solution of the corresponding acetamide (1 equiv) in sodium hydroxide solution (1 M, 500−600 mL) under ice-cooling and then stirred for 2 h at room temperature. The suspended solids were collected and treated with dichloromethane. Then, the solution was dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by crystallization from ethanol. **General Procedure B for 3d−f**: Carboxylic acid chloride (1 equiv) was added to a solution of the corresponding alkylamine or allylamine (1 equiv) in pyridine (150 mL) under ice-cooling, and then, the mixture stirred for 12 h at room temperature. Pyridine was then evaporated in vacuo. The collected reaction mixture was suspended in dichloromethane and washed with water three times. Drying over sodium sulfate and evaporation of the solvent gave the crude product, which was further purified by crystallization from ethanol.

*N-(2,6-Diisopropylphenyl)-2,2-diphenylacetamide (**3a**).* From diphenylacetic acid and 2,6-diisobutylaniline according to general procedure A. Yield: 29.3 g (79%), colorless solid. Mp 232 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.50−7.27 (m, 11H, C*H* of phenyl), 7.20 (d, J_{HH} = 6.9 Hz, 2H, C*H* of phenyl), 6.95 (br. s, 1H, N*H*), 5.17 (s, 1H, C*H*Ph$_2$), 2.97 (hept, J_{HH} = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.12 (d, J_{HH} = 6.9 Hz, 12H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 171.8 (*C*=O), 146.8 (*ipso*-*C*−CH(CH$_3$)$_2$), 139.9 (*ipso*-*C*-CHPh$_2$), 132.0 (*ipso*-*C*-NH), 129.5, 129.3, 128.9, 127.9, and 123.9 (CH, phenyl), 59.9 (*C*HPh$_2$), 29.3 (*C*H(CH$_3$)$_2$), 23.8 (*C*H$_3$). IR (ATR, cm^{-1}) = 3230 vw, ν (NH), 3030 w, 2968 m, 2924 w, 2868 w, 1647 s, ν(C=O), 1558 w, 1539 w, 1522 s, 1493 m, 1466 m, 1456 m, 1383 w, 1362 m, 1337 w, 1256 w, 1217 m, 1173 m, 1107 w, 1076 w, 1059 w, 1030 m, 988 w, 937 w, 880 m, 795 m, 737 s, 716 m, 696 s. HRMS (ESI$^+$): calcd for $C_{26}H_{29}NO$ + Na$^+$, 394.2141; found, 394.2140.

*N-Isopropyl-2,2-diphenylacetamide (**3b**).* From diphenylacetic acid and *i*-propylamine according to general procedure A. Yield: 20.0 g (79%, Lit. 70%[31]), colorless solid. Mp 159 °C (Lit.: 158−159 °C[31]). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50−7.27 (m, 10H, C*H*, phenyl), 5.62 (d, J_{HH} = 7.8 Hz, 1H, N*H*), 4.89 (s, 1H, C*H*Ph$_2$), 4.14 (dq, J_{HH} = 7.9, 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 1.11 (d, J_{HH} = 6.6 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 170.9 (*C*=O), 139.7 (*ipso*-*C*), 128.8, 128.6, and 127.2 (*C*H, phenyl.), 59.1 (*C*HPh$_2$), 41.7 (*C*H(CH$_3$)$_2$), 22.6 (*C*H$_3$).

*N-Cyclohexyl-2,2-diphenylacetamide (**3c**).* From diphenylacetic acid and cyclohexaneamine according to general procedure A. Yield: 22.1 g (75%, Lit. 50%[32]), colorless solid. Mp 150 °C (Lit.: 151−152 °C[32]). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.43−7.19 (m, 10H, C*H*, phenyl), 5.77 (d, J_{HH} = 6.9 Hz, 1H, N*H*), 4.85 (s, 1H, C*H*Ph$_2$), 3.87−3.70 (m, 1H, C*H*(CH$_2$)$_5$), 1.90−1.84 (m, 2H, C*H*$_2$), 1.69−1.56 (m, 3H, C*H*$_2$), 1.25 (m, 2H, C*H*$_2$), 1.25−1.01 (m, 3H, C*H*$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 170.8 (*C*=O), 140.4 (*ipso*-*C*), 129.3, 128.9, and 127.4 (*C*H, phenyl), 59.3 (*C*HPh$_2$), 48.8 (*C*H, cyclohexyl), 33.2, 25.9, and 25.2 (CH$_2$ of cyclohexyl).

*N-(p-Tolyl)cyclohexanecarboxamide (**3d**).* From *p*-toluidine (16.1 g, 150 mmol) and cyclohexanecarboxylic acid chloride **2a** (20.4 mL, 150 mmol) according to general procedure B. Yield: 30.5 g (106 mmol, 94%, Lit. 96%[33]), colorless solid. Mp 154 °C (Lit.: 154−156 °C[33]). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.10−1.39 (m, 3H, C*H*$_2$), 1.42−2.00 (m, 7H, C*H*$_2$), 2.14−2.41 (m, 4H, C*H* and C*H*$_3$), 7.08 (d, J_{HH} = 8.3 Hz, 2H, C*H*$_{arom.}$), 7.42 (d, J_{HH} = 8.4 Hz, 2H, C*H*$_{arom.}$), 7.67 (br s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 20.8 (CH$_3$), 25.7 (3C, CH$_2$), 29.6 (2C, CH$_2$), 46.4 (CH), 120.1, 129.4 (4C, CH$_{arom.}$), 133.6, 135.7 (2C, *i*-C$_{arom.}$), 174.7 (C=O).

*N-(2,6-Diisopropylphenyl)-cyclohexanecarboxamide (**3e**).* From cyclohexanecarboxylic acid chloride **2a** and 2,6-di-*i*-propylaniline according to general procedure B. Yield: 33.9 g (118 mmol, 95%), colorless solid. Mp 315 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.31−7.01 (m, 3H, C*H*, phenyl.), 6.60 (br. s, 1H, N*H*), 2.97 (hept, J_{HH} = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.29 (tt, J_{HH} = 18.3, 3.5 Hz, 1H, C*H*(CH$_2$)$_5$), 2.06−1.87 (m, 2H, C*H*$_2$), 1.86−1.40 (m, 6H, C*H*$_2$ of cyclohexyl), 1.40−0.78 (m, 14H, C*H*$_2$, cyclohexyl, and C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 175.2 (C=O), 146.2 (2C, *ipso*-C−CH(CH$_3$)$_2$), 131.1 (*ipso*-C-NH), 123.3 and 128.2 (CH, phenyl), 45.9 (CHC=O), 29.9 (CH(CH$_3$)$_2$), 28.7, 25.8, and 25.7 (CH$_2$, cyclohexyl), 23.6 (CH(CH$_3$)$_2$). IR (ATR, cm^{-1}) = 3213 w, ν(NH), 2963 m, 2924 s, 2855 m, 1645 s, ν(C=O), 1558 m, 1539 s, 1522 s, 1472 s, 1447 s, 1381 m, 1362 w, 1339 m, 1258 m, 1217 s, 1180 w, 1136 w, 1101 w, 1061 m, 1045 m, 962 m, 937 (w), 897 w, 797 m, 766 m, 727 s. HRMS (ESI$^+$): calcd for $C_{19}H_{29}NO$ + H$^+$, 288.2327; found, 288.2322.

*2-Ethyl-N-phenylbutanamide (**3f**).* From 2-ethyl-butanoyl chloride **2b** (57.0 g, 424 mmol) and aniline (38.8 mL, 425 mmol) according to general procedure B. Yield: 53.3 g (279 mmol, 56%, Lit 40%[34]), white solid.

*Synthesis of Imidoyl Chlorides **4**.* **General Procedure C**: 1.0 equiv of phosphorus pentachloride was added to a solution of the corresponding amide **3** (1 equiv) in dry chloroform (120−180 mL) under ice-cooling. The reaction mixture was vigorously stirred and heated to reflux for 2 h. Then, chloroform and phosphoryl chloride were evaporated in vacuo. The raw product was purified by fractional vacuum distillation. The products were air and moisture sensitive and had to be stored under argon at −20 °C.

*N-(p-Tolyl)cyclohexanecarbimidoyl Chloride (**4a**).* From **3d** and phosphorus pentachloride according to the general procedure C. Yield: 27.4 g (83%), yellow liquid. Bp 125 °C (1.4×10^{-2} mbar). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20−7.12 (m, 2H, C*H*, phenyl), 6.85−6.77 (m, 2H, C*H*, phenyl), 2.69 (tt, J_{HH} = 11.3, 3.4 Hz, 1H, C*H*, cyclohexyl), 2.35(s, 3H, C*H*$_3$), 2.20−2.09 (m, 2H, C*H*$_2$, cyclohexyl), 1.92−1.81 (m, 2H, C*H*$_2$, cyclohexyl), 1.77−1.50 (m, 3H, C*H*$_2$, cyclohexyl), 1.46−1.20 (m, 3H, C*H*$_2$, cyclohexyl). ^{13}C{^{1}H}

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NMR (75 MHz, $CDCl_3$): δ = 151.85 (*C*=N), 144.3 and 134.7 (*ipso*-C, phenyl), 129.5, 120.4 (4C, *C*H, phenyl), 50.8 (*C*H, cyclohexyl), 30.7 (CH_2, cyclohexyl), 25.9 (CH_2,cyclohexyl), 25.7 (CH_2, cyclohexyl), 21.1 (CH_3). IR (ATR, cm^{-1}) = 3040 w, 2934 s, 2857 s, 1690 s, ν (C=N), 1659 s, 1599 m, 1535 w, 1504 s, 1450 m, 1348 w, 1250 w, 1215 w, 1140 w, 1105 s, 1018 w, 966 s, 899 m, 841 s, 818 s, 764 m, 743 m, 714 m, 685 w, 646 m, 583 s. Elemental analysis Calcd (%) for $C_{14}H_{18}NCl$ (235.1): C, 71.32; H, 7.70; N, 5.94. Found: C, 71.22; H, 7.87; N 5.93.

*N-(2,6-Diisopropylphenyl)cyclohexanecarbimidoyl Chloride (**4b**).* From **3e** and phosphorus pentachloride according to the general procedure C. Yield: 27.0 g (76%), colorless liquid. Bp 185 °C (4×10^{-3} mbar). ^1H NMR (400 MHz, C_6D_6): δ = 7.36−7.12 (m, 3H, C*H*, phenyl). 3.23−2.97 (m, 2H, C*H*(CH_3)$_2$), 2.63 (tt, *J* = 11.1, 3.5 Hz, 1H, C*H*, cyclohexyl), 2.21 (*pseudo*d, 2H, CH_2, cyclohexyl), 1.82−1.51 (m, 5H, partially covered, CH_2, cyclohexyl), 1.48−1.09 (m, 15H, partially covered, CH_2, cyclohexyl and CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 150.6 (*C*=N). 143.7 and 136.7 (*ipso*-C, phenyl), 125.1 (*C*H, phenyl), 123.4 (*C*H, phenyl), 51.0 (CH, cyclohexyl), 31.1 (CH_2, cyclohexyl), 28.9 (*C*H(CH_3)$_2$), 26.0 and 25.8, (CH_2, cyclohexyl), 23.4 and 23.1 (4C, CH(CH_3)$_2$). IR (ATR, cm^{-1}) = 3040 w, 2963 w, 2934 s, 2859 s, 1738 br. s, ν (C=N), 1726 s) 1715 s, 1553 w, 1468 m, 1450 m, 1366 s, 1229 w, 1217 s, 1211 s, 968 m, 826 w, 791 w, 756 w, 723 w, 596 w, 581 s. Elemental analysis Calc (%) for $C_{19}H_{28}NCl$ (305.2): C, 74.60; H, 9.23; N, 4.58. Found: C, 74.27; H, 9.44; N, 4.52.

*2-Ethyl-N-phenylbutanimidoyl Chloride (**4c**).* From **3e** and phosphorus pentachloride according to the general procedure C. Yield: 49.5 g (85%, Lit 93%[34]), colorless liquid. Bp 66−68 °C (0.4 mbar, Lit: 60 °C, 0.3 mbar[34]). ^1H NMR (300 MHz, C_6D_6): δ = 7.41−7.37 (m, 2H, C*H* of phenyl), 7.24−7.08 (m, 3H, C*H* of phenyl), 2.81−2.70 (m, 1H, C*H*), 1.99−1.87 (m, 2H, CH_2), 1.70−1.58 (m, 2H, CH_2), 1.15 (t, $^3J_{HH}$ = 7.4 Hz, 6H, CH_3).

Synthesis of Ketenimines. **General Procedure D for 1a−c**: 5.4 equiv of phosphorus pentoxide with sea sand (75 g) were added to a solution of the corresponding carboxylic amide **VV** (1 equiv) in dry triethylamine or pyridine and were diluted with 200 mL of dry triethylamine or pyridine. The reaction mixture was vigorously stirred and heated to reflux for 7 h. Then, the suspended solids were filtered off and freed from the solvent in vacuo. This raw product was purified by crystallization from *n*-heptane. **General Procedure E for 1d−f:** Dry triethylamine (8.4 equiv) was added to a solution of the corresponding imidoyl chloride **V** (1 equiv) in dry toluene. Then, the mixture was heated to reflux for 20 h. The suspended solids were filtered off. Evaporation of the solvent gave the raw product, which was purified by fractional vacuum distillation. The products were air and moisture sensitive and had to be stored under argon at −20 °C.

*N-(2,2-Diphenylvinylidene)-2,6-diisopropylaniline (**1a**).* From **3a** and phosphorus pentoxide according to the general procedure D. Yield: 11.6 g (66%, lit. 82%[35]), yellow solid. Mp 92 °C. ^1H NMR (600 MHz, C_6D_6): δ = 7.34 (dd, J_{HH} = 8.4, 1.1 Hz, 4H, C*H*, phenyl). 7.12−7.08 (m, 4H, C*H*, phenyl), 7.04−7.02 (m, 3H, C*H*, phenyl), 6.97 (*pseudo*-s, 2H, C*H*, phenyl), 3.39 (hept, J_{HH} = 6.9 Hz, 2H, C*H*(CH_3)$_2$), 1.07 (d, J_{HH} = 6.9 Hz, 12H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ = 184.3 (C=*C*=N); 141.3 (*ipso*-*C*(*i*-Pr.)), 136.9 (*ipso*-*C*-N), 135.5 (*ipso*-*C*−N-C=C, phenyl), 129.2, 128.4, 127.0, and 126.3 (*C*H, phenyl), 124.0 (*C*H−C(*i*-Pr)), 72.7 (C=C=N), 29.0 (2C, CH(CH_3)$_2$), 23.7 (4C, CH(CH_3)$_2$). IR (ATR, cm^{-1}) = 3028 w, 2963 m, 2928 w, 2862 w, 2010 s, ν (C=C=N), 1593 m, 1493 m, 1456 m, 1433 m, 1383 w, 1360 w, 1325 w, 1256 w, 1167 m, 1121 w, 1107 w, 1063 w, 1030 w, 934 m, 926 m, 797 m, 754 s, 692 w, 662 w, 644 w. Elemental analysis Calcd (%) for $C_{26}H_{27}N$ (353.2): C, 88.34; H, 7.70; N, 3.96. Found: C, 88.08; H, 7.54; N, 3.94.

*N-(2,2-Diphenylvinylidene)propan-2-amine (**1b**).* From **3b** and phosphorus pentoxide according to the general procedure D. Yield: 10.5 g (89%, Lit. 54%[36]), yellow solid. Mp 45 °C (Lit.: 45−46 °C[36]). ^1H NMR (300 MHz, C_6D_6): δ = 7.58−7.43 (m, 4H, C*H*, phenyl), 7.29−7.20 (m, 4H, C*H*, phenyl), 7.17−7.06 (m, 2H, C*H*, phenyl), 3.36 (dt, J_{HH} = 12.9, 6.5 Hz, 1H, C*H*), 1.16 (d, J_{HH} = 6.5 Hz, 6H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 183.7 (C=C=N), 136.0 (*ipso*-C, phenyl), 129.1, 127.9, and 126.1 (*C*H, phenyl), 76.2 (C=C=N), 55.0 (CH), 23.6 (2C, CH_3). HRMS (ESI^+): calcd for $C_{17}H_{17}N$ +Na^+, 258.1253; found:, 258.1248.

*N-(2,2-Diphenylvinylidene)cyclohexanamine (**1c**).* From **3c** and phosphorus pentoxide according to the general procedure D. Yield: 4.80 g (34%, Lit. 50%[32]), yellow solid. Mp 58 °C). ^1H NMR (300 MHz, C_6D_6): δ = 7.54−7.36 (m, 4H, C*H*, phenyl), 7.25−7.12 (m, 4H, C*H*, phenyl), 7.09−6.98 (m, 2H, C*H*, phenyl), 3.30 (tt, J_{HH} = 10.1, 3.9 Hz, 1H, C*H*, cyclohexyl), 1.93−1.78 (m, 2H, CH_2, cyclohexyl), 1.64−1.21 (m, 5H, CH_2, cyclohexyl), 1.10−0.84 (m, 3H, CH_2, cyclohexyl). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 183.6 (C=*C*=N), 136.1 (*ipso*-C, phenyl), 127.9, 129.4, and 126.1 (CH, phenyl), 75.6 (C=C=N), 61.8 (CH, cyclohexyl), 34.3(CH_2, cyclohexyl), 25.4 and 24.8 (CH_2, cyclohexyl).

*N-(Cyclohexylidenemethylene)-4-methylaniline (**1d**).* From **4a** according to the general procedure E. Yield: 9.50 g (54%), yellow liquid. Bp 100 °C, 6.0×10^{-3} mbar. ^1H NMR (300 MHz, C_6D_6): δ = 7.40−7.27 (m, 2H, C*H*, phenyl), 7.01−6.96 (m, 2H, C*H*, phenyl), 2.12−1.96 (m, 7H, CH_3 and CH_2), 1.47−1.35 (m, 4H, CH_2, cyclohexyl), 1.31−1.23 (m, 4H, CH_2, cyclohexyl). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 192.4 (C=*C*=N), 142.3 (*ipso*-*C*-CH_3), 136.4 (*ipso*-*C*-N), 130.2 and 123.5 (CH, phenyl), 65.8 (*C*=C=N), 27.5, 27.1, and 26.3 (CH_2), 21.0 (CH_3). IR (ATR, cm^{-1}) = 3048 w, 2976 m, 2928 w, 2920 w, 2880 w, 2012 s, ν (C=C=N), 1738 s, br. (C=C), 1504 w, 1443 w, 1366 s, 1356 s, 1319 w, 1229 s, 1217 s, 1206 s, 1092 w, 895 w, 820 w.

*N-(Cyclohexylidenemethylene)-2,6-diisopropylaniline (**1e**).* From **4b** according to the general procedure E. Yield: 9.00 g (67%), colorless liquid. Bp 111 °C, 4.0×10^{-3} mbar. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.26−7.04 (m, 3H, C*H*, phenyl), 2.89−2.69 (m, 3H, C*H*(CH_3)$_2$), 2.42−2.16 (m, 2H, CH_2, cyclohexyl), 1.96−1.59 (m, 5H, partially covered, CH_2, cyclohexyl), 1.51−1.03 (m, 15H, partially covered, CH_2, cyclohexyl and CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 176.3 (C=*C*=N), 143.6 (*ipso*-*C*-N), 137.3 (2C, *ipso*-*C*(*i*-Pr)$_2$), 125.2 and 123.6 (CH, phenyl), 75.6 (C=C=N), 31.4 (CH_2, cyclohexyl), 28.9 (*C*H(CH_3)$_2$), 26.5 and 26.3 (CH_2, cyclohexyl), 23.4 (CH_3). IR (ATR, cm^{-1}) = 3010 w, 2959 m, 2930 w, 2859 w, 2033 s, ν(C=C=N), 1738 s. br, ν(C=N), 1728 s, 1462 w, 1441 w, 1371 m, 1229 m, 1223 m, 1211 m, 972 w, 895 w, 758 w, 652 w.

*N-(2-Ethylbut-1-en-1-ylidene)aniline (**1f**).* From **4c** according to the general procedure E. Yield: 9.50 g (54.8 mmol, 60%, Lit 55%[34]), colorless liquid. Bp 64 °C, 8.0×10^{-3} mbar (lit.: 60−64 °C, 0.04 mbar[34]). ^1H NMR (300 MHz, C_6D_6): δ = 7.43−7.34 (m, 3H, C*H*, phenyl), 7.15−7.05 (m, 2H, C*H*, phenyl), 7.02−6.92 (m, 1H, C*H*, phenyl), 1.86 (q, $^3J_{HH}$ = 7.4 Hz, 4H, CH_2), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 195.0 (C=*C*=N), 144.9 (*ipso*-*C*), 129.6, 126.8, and 123.4 (*C*H, phenyl), 72.8 (*C*=C=N), 22.6 (CH_2), 12.9 (CH_3).

*(2,6-Diisopropylphenyl)(2,2-diphenylvinyl)amino)di(iso-butyl)-aluminum **5a**.* Ketenimine **1a** (410 mg, 1.16 mmol, 1.0 equiv) was dissolved in 20 mL of *n*-hexane and treated with DIBAL-H (1.16 mL, 1 M in *n*-hexane, 1.16 mmol, 1.0 equiv) at −78 °C with stirring. Stirring was continued for 2 h at −78 °C; then, the mixture was slowly warmed to room temperature over 2 h. Red crystals (360 mg, 726 mmol, 63%, moisture sensitive) were obtained upon concentration of the reaction mixture at −20 °C. Mp 151 °C. ^1H NMR (400 MHz, C_6D_6): δ = 7.32−7.06 (m, 11H, C*H*, phenyl), 7.04−6.78 (m, 2H, C*H*, phenyl), 6.75 (s, 1H, C*H*=C), 3.69 (hept, J_{HH} = 6.8 Hz, 2H, C*H*Me_2), 1.69 (dp, J_{HH} = 13.4, 6.8 Hz, 2H, Al-CH_2C*H*), 1.39 (d, J_{HH} = 6.9 Hz, 6H, CHMe_2), 1.26 (d, J_{HH} = 6.7 Hz, 6H, CHMe_2), 0.92 (d, J_{HH} = 6.5 Hz, 12H, Al-CH_2−CHMe_2), 0.10 (d, J_{HH}= 7.1 Hz, 4H, Al−CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 146.6 (CH=N), 146.5 and 144.7 (*ipso*-*C*(*i*-Pr), 144.2 (*ipso*-*C*-N), 130.9, 129.6, 129.0, 128.7, 124.9, and 126.3 (CH, phenyl), 110.8 (CPh_2), 29.5 (*C*HMe_2), 28.2 (Al-CH_2−CHMe_2), 25.8 (Al-CH_2−CH), 25.7 (CHMe_2), 23.6 (Al-CH_2), 23.5 (CHMe_2). IR (CsI-plates, nujol, cm^{-1}): 3418 w, 3167 w, 3146 w, 3061 s, 3055 s, 2953−2851 vs, (nujol), 2679 s, 2641 m, 2606 m, 2548 w, 2498 w, 2336 w,

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2313 w, 1958 w, 1937 m, 1877 w, 1811 w, 1587 s, 1557 s, ν(C═C), 1454−1435 vs, (nujol), 1362 s, 1304 w, 1254 m, 1231 w, 1177 w, 1157 m, 1126 w, 1111 w, 1072 m, 1057 w, 1032 w, 1015 w, 972 w, 953 w, 918 w, 887 m, 802 s, 779 m, 754 s, 721 s, 698 m, 638 w, 592 w, 556 w, 505 m, 436 s, 401 s, ν(AlC), ν(AlN). MS (EI, 20 eV, 25 °C): *m/z* (%) = 495 (32) $[M]^+$, 438 (34) $[M - i\text{-Bu}]^+$, 382 (16) $[M - (i\text{-Bu})_2 + H]^+$, 355 (80) $[M - Al(i\text{-Bu})_2 + H]^+$, 188 (100) $[M - Al(i\text{-Bu})_2 - CPh_2]^+$, 146 (76), 130 (8), 128 (2), 77 (2), 56 (3), 43 (5).

Reactions of Active Al/N Compounds with heterocumulenes. *Reactions with Carbodiimides* ***6****. N,N′-Dicyclohexyl-3-(2,2-diphenylvinyl)-3-isopropylguanidino-di(iso-butyl)-aluminum* ***7****.* Ketenimine **1b** (454 mg, 1.93 mmol) was dissolved in 20 mL of dry toluene and treated with DIBAL-H (1.93 mL, 1.16 mmol, 1 M in *n*-hexane, 1.0 equiv) at −78 °C with stirring. Stirring was continued for 2 h at −78 °C. Then, the reaction mixture was slowly warmed to room temperature over 2 h, and dicyclohexylcarbodiimide **6** (398 mg, 1.93 mmol) in 20 mL of toluene was added followed by stirring overnight. Colorless crystals **7** (475 mg, 0.84 mmol, 42%) were obtained upon concentration of the reaction mixture at −20 °C. Mp 162 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.49−7.09 (m, 10H, C*H*, phenyl), 6.67 (s, 1H, C*H*═C), 3.73 (hept, J_{HH} = 6.6 Hz, 1H, NC*H*$(CH_3)_2$), 2.96−3.21 (m, 2H, N−C*H*, cyclohexyl), 2.25 (dp, J_{HH} = 13.3, 6.7 Hz, 2H, Al-CH_2C*H*), 1.57−1.89 (m, 10H, N−CH−CH_2), N−CH-CH_2−CH_2), 1.38 (d, J_{HH} = 6.5 Hz, 12H, Al-CH_2−CHMe_2), 1.22−1.52 (m, 8H, N−CH-CH_2−CH_2 and N−CH-CH_2−CH_2−CH_2), 1.04−1.20 (m, 2H, N−CH-CH_2−CH_2−CH_2), 1.15 (d, J_{HH} = 6.7 Hz, 6H, NCH(CH_3)$_2$), 0.10−0.53 (m, 4H, Al−CH_2). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 164.8 (N-*C*-N), 142.3 (C═CH), 139.5 and 133.2 (*ipso-C*), 130.5, 129.1, 128.6, 127.4, and 127.3 (*C*H of phenyl), 124.1 (C═*C*H), 54.4 (N-*C*H, cyclohexyl), 52.1 (NC*H*$(CH_3)_2$), 36.5 (N−CH-CH_2), 29.1 (Al-CH_2−CHMe_2), 27.2 (Al-CH_2−CH), 26.5 (N−CH-CH_2−CH_2), 26.1 (N−CH-CH_2−CH_2−CH_2), 23.9 (Al-CH_2), 20.6 (NCHMe_2). IR (CsI-plates, nujol, cm-^{1}): 3076 w, 3048 w, 3019 w, 2922 vs, 2853 vs, (nujol), 2668 w, 2594 w, 1622 s, ν(C═N), 1612 m, 1595 s, 1456 vs, (nujol), 1375 s (nujol), 1362s, 1344 w, 1312 s, 1260 s, 1248 s, 1209 s, 1173 m, 1146 m, 1125 m, 1084 s, 1072 s, 1053 s, 1028 m, 995 m, 935 w, 881 m, 866 m, 843 m, 791 m, 773 m, 760 s, 721 w, 696 s, 687 s, 664 m, 635 m, 606 w, 575 w, 505 m, 478 w, 442 w, 401 s, ν(AlC), ν(AlN). MS (EI, 20 eV, 25 °C): *m/z* (%) = 528 (6), 527 (37), 526 (100) $[M - i\text{-Bu}]^+$, 471 (3) $[M - i\text{-Bu} - \text{Buten}]^+$, 470 (9), 427, 346 (4), 290 (11), 237 (32), 222 (6), 125 (1). Elemental analysis Calcd (%) for $C_{38}H_{58}AlN_3$ (583.8): C, 78.17; H, 10.01; N, 7.20. Found: C, 78.08; H, 9.91; N, 7.32.

2,3-Dicyclohexyl-1-(2,2-diphenylvinyl)-1-(iso-propyl)guanidine ***8****.* Ketenimine **1b** (560 mg, 2.38 mmol, 1 equiv) was dissolved in 20 mL of dry *n*-hexane and treated with DIBAL-H (2.40 mL, 2.40 mmol, 1 M in *n*-hexane, 1 equiv) at −78 °C with stirring. Stirring was continued for 4 h at −78 °C. Then, the reaction mixture was slowly warmed to room temperature over 4 h. Dicyclohexylcarbodiimide **3** (491 mg, 2.38 mmol, 1 equiv) was added at room temperature and stirring was continued for at least 12 h. The reaction was quenched with NaOH-solution (2 M), and the organic layer was washed twice with alkaline solution and brine and dried over magnesium sulfate. The solvent was removed under reduced pressure; then the crude product was purified by recrystallization from DMSO (573 mg, 1.29 mmol, 55%) as colorless crystals (mp 154 °C). ^{1}H NMR (600 MHz, d_8-toluene,): δ = 7.35−7.00 (m, 10H, C*H*, phenyl), 6.97 (s, 1H, N*H*), 6.42 (s, 0.4H, C*H*═C), 6.37 (s, 0.6H, C*H*═C), 4.24 (hept, J_{HH} = 6.9 Hz, 0.6H, NC*H*$(CH_3)_2$), 3.41 (dp, J_{HH} = 13.7, 6.8 Hz, 0.4H, NC*H*$(CH_3)_2$), 3.32−3.09 (m, 2H, partially covered, N−CH−CH_2 and N−C*H*, cyclohexyl), 2.86−2.74 (m, 1H, N−C*H*, cyclohexyl), 1.87−1.26 (m, partially covered, 12H, N−CH-CH_2−CH_2 and N−CH−CH_2), 1.34−0.62 (m, 13H, partially covered, N−CH-CH_2−CH_2−CH_2 and N−CH-CH_2−CH_2, NCH-(CH_3)$_2$).* ^{13}C{^{1}H} NMR (160 MHz, d_8-toluene): δ = 149.6 (N-*C*═N), 146.9 (*C*═CH), 144.5 (*ipso-C*-C═CH(0.4C)), 143.4 (*ipso-C*-C═CH), 140.7 and 141.0 (*ipso-C*-C═CH(0.6C)), 129.6 (0.4C, C═*C*H), 130.5 and 131.3 (*C*H, phenyl), 128.5, 128.4, 128.3, and 128.2 (*C*H, phenyl), 127.2 (0.6C, C═*C*H), 126.6, 126.5, 126.2, and 125.9 (*C*H, phenyl), 55.9 (N-*C*H, cyclohexyl), 53.0 (0.4C, NC*H*$(CH_3)_2$), 52.7 (NH-*C*H, cyclohexyl), 51.7 (0.6C, NC*H*$(CH_3)_2$), 58.1 and 50.1 (partially covered, N−CH−CH_2), 35.0 (N−CH-CH_2), 34.9, 32.9, 26.7, and 25.9 (N−CH-CH_2−CH_2), 25.7 and 25.2, (N−CH-CH_2−CH_2−CH_2), 21.7 (NCHMe_2), 21.3 (NCHMe_2), *(Resonances of the main isomer are assigned (ration 6:4)). IR (ATR, cm^{-1}) = 3412 w, ν(NH), 3128 w, 3012 w, 2922 s, 2845 m, 1626 s, ν(C═N), 1587 m, 1570 w, 1493 w, 1462 w, 1443 m, 1400 m, 1364 m, 1327 w, 1308 m, 1238 s, 1180 m, 1150 m, 1128 m, 1117 w, 1067 m, 1028 w, 880 s, 866 s, 845 w, 758 s, 694 s, 640 w, 606 w. HRMS (ESI$^+$): calcd for $C_{30}H_{41}N_3 + H^+$, 444.3373; found, 444.3375. Elemental analysis Calcd (%) for $C_{30}H_{41}N_3$ (443.6): C, 81.21; H, 9.31; N, 9.47. Found: C, 80.84; H, 9.41; N, 9.34.

Reactions of Active Al/N Compounds 5 with Isocyanates 9 and Isothiocyanates 14. *General Procedure F for the Synthesis of* ***10a−d****.* A solution of DIBAL-H (1 M in *n*-hexane, 1 equiv) was added to a cooled (−78 °C) solution of the ketenimine **1** (1 equiv) in dry *n*-hexane (20 mL). After 2 h stirring at −78 °C, the solution was allowed to warm to room temperature and stirred for 2 h. The dry isocyanate **9** (1 or 2 equiv) or isothiocyanate **14** was added at −78 °C and stirring was continued for 2 h. The solution was warmed to room temperature and quenched with NaOH-solution (2 M). The organic layer was washed twice with NaOH-solution (2 M) and brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography and/or recrystallization for X-ray analysis.

1-(2,2-Diphenylvinyl)-1-isopropyl-3-phenylurea ***10a****.* From ketenimine **1b** (591 mg, 2.52 mmol) and phenyl isocyanate **9a** (605 mg, 5.08 mmol, 2.0 equiv) according to the general procedure F. The reaction mixture was quenched with NaOH-solution (2 M). Subsequent column chromatography (TBME/cyclohexane, 1:1) gave the pure product (873 mg, 2.45 mmol, 96%) as colorless solid (mp 139 °C). Colorless crystals were obtained by recrystallization from toluene. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 7.41−7.22 (m, 10H, C*H*, phenyl), 7.21−7.06 (m, 4H, C*H*, phenyl), 6.98−6.92 (m, 1H, C*H*, phenyl), 6.84 (br s, 1H, N*H*), 6.51 (s, 1H, C═C*H*), 4.61 (hept, J_{HH} = 6.9 Hz, 1H, NC*H*$(CH_3)_2$), 1.24 (d, J_{HH} = 6.9 Hz, 6H, NCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ =153.0 (*C*═O), 141.4 (*C*═CH), 141.3, 139.4 and 138.5(*ipso-C*), 129.9, 129.1, 129.0, 128.8, 128.8, 128.7, and 128.6 (*C*H, phenyl), 123.6 (C═*C*H), 123.2 and 120.0 (*C*H, phenyl), 48.7 (NCH$(CH_3)_2$), 20.8 (2C, NCH$(CH_3)_2$). IR (ATR, cm^{-1}) = 3420 s, ν(NH), 3057 w, 3030 w, 2968 w, 2934 w, 1682 s, ν(C═O), 1614 m, 1593 m, 1520 s, ν(C═C), 1497 m, 1439 s, 1396 w, 1312 s, 1231 s, 1179 w, 1155 w, 1126 m, 1076 w, 1036 w, 1001 w, 903 s, 868 w, 858 w, 773 s, 750 s, 718 s, 700 s, 692 s, 644 w, 629 w, 611 m. HRMS (ESI$^+$): calcd for $C_{24}H_{24}N_2O + H^+$, 357.1961; found, 357.1965. Elemental analysis Calcd (%) for $C_{24}H_{24}N_2O$ (356.4): C, 80.87; H, 6.79; N, 7.86. Found: C, 80.74; H, 6.91; N, 7.91.

3-Cyclohexyl-1-(2,2-diphenylvinyl)-1-isopropylurea ***10b****.* From ketenimine **1b** (373 mg, 1.59 mmol) and cyclohexyl isocyanate **9b** (198 mg, 1.59 mmol, 1 equiv) according to the general procedure F. The crude reaction mixture was quenched with NaOH-solution (2 M). Subsequent column chromatography on Al_2O_3 (B, (V)) (cyclohexane/ethyl acetate, 12:1) gave the pure product (415 mg, 1.14 mmol, 72%) as colorless solid. Mp 99 °C. Colorless crystals were obtained by recrystallization from DMSO. ^{1}H NMR (600 MHz, CD_2Cl_2): δ (ppm) = 7.24−7.38 (m, 10H, C*H*, phenyl), 6.33 (s, 1H, C═C*H*), 4.75 (d, J_{HH} = 7.8 Hz, 1H, N*H*), 4.55 (hept, J_{HH} = 6.9 Hz, 1H, NC*H*$(CH_3)_2$), 3.31−3.39 (m, 1H, NC*H*$(CH_2)_5$), 1.55−1.49 (m, 5H, CH_2, cyclohexyl), 1.29−1.18 (m, 2H, CH_2, cyclohexyl), 1.14 (d, J_{HH} = 6.9 Hz, 6H, NCH(CH_3)$_2$), 1.09−0.98 (m, 1H, CH_2 of cyclohexyl), 0.80−0.71 (m, 2H, CH_2, cyclohexyl). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2): δ = 154.7 (NH-*C*═O), 141.9 (*C*═CH), 140.5, 139.1(*ipso-C*), 130.1, 129.0, 128.9, 128.7, 128.5, and 128.3 (*C*H, phenyl), 124.6 (C═*C*H), 49.7 (NCH$(CH_2)_5$), 48.2 (NCH-$(CH_3)_2$), 33.9, 26.2, and 25.6 (CH_2, cyclohexyl), 20.7 (CH$(CH_3)_2$). IR (ATR, cm^{-1}) = 3248 w, ν(NH), 3024 w, 2976 w, 2936 w, 2918 w, 2853 w, 1651 m, 1628 s, ν(C═O), 1528 s, ν(C═C), 1495 m,

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1445 m, 1398 m, 1315 m, 1277 s, 1256 s, 1233 s, 1184 m, 1144 w, 1132 w, 1125 w, 1074 m, 868 m, 764 m, 696 s, 637 m. HRMS (ESI^+): calcd for $C_{24}H_{30}N_2O + Na^+$, 385.2250; found:, 385.2250. Elemental analysis Calcd (%) for $C_{24}H_{30}N_2O$ (362.5): C, 79.52; H, 8.34; N, 7.73. Found: C, 79.14; H, 8.22; N, 7.76.

(3-((2,6-Diisopropylphenyl)imino)-2,2-diphenyl-1-(phenylimino)-propoxy)-di(iso-butyl)aluminum ***11***. Ketenimine **1a** (537 mg, 1.52 mmol) was treated dropwise with di(*iso*-butylaluminum hydride (1.52 mL, 1.52 mmol, 1 M in *n*-hexane, 1.0 equiv) in 20 mL of dry *n*-hexane at −78 °C with stirring. After 2 h stirring at −78 °C, the mixture was slowly warmed to room temperature and stirred for additional 2 h. Then, the reaction mixture was cooled to −78 °C, and phenyl isocyanate **9a** (198 mg, 1.67 mmol, 1.1 equiv) was added. Stirring was continued for 1 h and then at room temperature for 2 h. Colorless crystals (810 mg, 1.32 mmol, 87%) were obtained upon concentration of the reaction mixture at −20 °C. Mp 144 °C. ^1H NMR (400 MHz, C_6D_6): δ = 8.21 (s, 1H, C*H*=N), 7.47−7.38 (m, 5H, C*H*, phenyl), 7.26−7.19 (m, 2H, C*H*, phenyl), 7.18−6.99 (m, 8H, C*H*, phenyl), 6.96−6.88 (m, 3H, C*H*, phenyl), 2.84 (dh, J_{HH} = 13.3, 6.6 Hz, 2H, C*H*(CH_3)$_2$), 1.92 (dp, J_{HH} = 13.4, 6.7 Hz, 2H, Al-CH_2−C*H*), 1.28−1.16 (m, 6H, CH(C*H*$_3$)$_2$), 1.05 (d, J_{HH} = 6.5 Hz, 6H, Al-CH_2−CH−C*H*$_3$), 0.98 (d, J_{HH} = 6.5 Hz, 6H, Al-CH_2−CH−C*H*$_3$), 0.90−0.76 (m, 6H, CH(C*H*$_3$)$_2$), −0.01 (qd, J_{HH} = 14.0, 7.3 Hz, 4H, Al−C*H*$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 185.6 (*ipso*-C-N=*C*H), 159.6 (*ipso*-*C*-N=C-O), 149.2 (*ipso*-C-N=*C*−O), 142.0 (*ipso*-*C*), 141.8 (*ipso*-*C*(*i*-Pr.)$_2$), 141.6 (*ipso*-*C*-N=CH), 130.3, 129.0, 128.8, 128.4, 128.2, 124.9, 123.8, and 123.1 (*C*H, phenyl), 66.5 (*C*Ph$_2$), 28.5 (CH(*C*H$_3$)$_2$), 28.4 (Al-CH_2−*C*H*Me*$_2$), 26.5 (CH(*C*H$_3$)$_2$), 26.4 (Al-CH_2−*C*H), 23.6 (CH(*C*H$_3$)$_2$), 21.6 (Al-CH_2). IR (CsI-plates, nujol, cm^{-1}): 3993 m, 3850 m, 3645 w, 2953−2849 vs, (nujol), 2720 m, 2704 m, 2666 w, 2644 m, 2602 m, 1948 m, 1892 m, 1867 m, 1800 m, 1645 m, ν(C=N), 1611 m, 1516 s, 1447 s, 1435 s, 1354 s, 1339 w, 1304 w, 1292 w, 1273 w, 1153 m, 1057 w, 1003 w, 968 m, 926 m, 907 m, 837 m, 806 m, 772−723 s, (nujol), 694 s, 679 m, 652 w, 637 w, 608 w, 559 m, 542 w, 517 m, 451 w, 428 w, 401 w, ν(AlC), ν(AlN). MS (EI, 20 eV, 25 °C): *m*/*z* (%) = 557 (12) [M − *i*-Bu]$^+$, 439 (15), 438 (47), 356 (22), 355 (80) [M − *i*-Bu_2Al − PhCNO + H]$^+$, 271 (8), 269 (12) [PhCN-Ph_2]$^+$, 189 (15) [M − *i*-Bu_2Al − PhCNO-Ph_2 + H]$^+$, 188 (100) [M − *i*-Bu_2Al − PhCNO-Ph_2]$^+$, 172 (10), 168 (11), 167 (12), 165 (15), 146 (71), 131 (9), 130 (15), 119 (35) [PhNCO]$^+$, 91 (9), 43 (22), 42 (10). Elemental analysis Calcd (%) for $C_{41}H_{51}AlN_2O$ (614.8): C, 80.09; H, 8.36; N, 4.56. Found: C, 79.66; H, 8.39; N, 4.46.

3-((2,6-Diisopropylphenyl)imino)-N,2,2-triphenylpropanamide ***12***. From ketenimine **1a** (382 mg, 1.08 mmol) and phenyl isocyanate **9a** (143 mg, 1.2 mmol) according to the general procedure F. The crude reaction mixture was quenched with NaOH-solution (2 M). Subsequent column chromatography (*n*-pentane/ethyl acetate, 100:1) gave the pure product (451 mg, 0.95 mmol, 88%), as colorless solid (mp 168 °C). Colorless crystals were obtained by recrystallization from a mixture of solvents (*n*-pentane/ethyl acetate, 1:1). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 11.87 (s, 1H, N*H*), 8.11 (s, 1H, C*H*=N), 7.66 (dd, J_{HH} = 8.6, 1.1 Hz, 2H, C*H*, phenyl.), 7.48−7.37 (m, 10H, C*H*, phenyl.), 7.37−7.32 (m, 2H, C*H*, phenyl.), 7.18−7.08 (m, 4H, C*H*, phenyl), 2.75 (hept, J_{HH} = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 1.08 (d, J_{HH} = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ =169.4 (*C*=O), 169.1 (CH=*N*), 146.5 (*ipso*-*C*-N=CH), 140.8 (*ipso*-*C*-NH), 139.0 (*ipso*-*C*), 138.9 (*ipso*-*C*−CH(CH_3)$_2$, 130.1, 129.2, 128.5, 125.9, 124.8, 123.8, and 120.6 (*C*H, phenyl), 66.3 (*C*-C=O), 28.4 (*C*H(CH_3)$_2$), 23.9 (CH(*C*H$_3$)$_2$). IR (ATR, cm^{-1}) = 3309 w, ν(NH), 3069 w, 3030 w, 2965 m, 2926 w, 2868 w, 1684 s, ν(C=O), 1647 m, ν(C=N), 1599 m, 1558 s, 1543 w, 1489 s, 1443 s, 1312 s, 1260 s, 1217 w, 1177 w, 1121 w, 1103 m, 1043 w, 1032 w, 1005 w, 962 w, 912 m, 885 m, 835 w, 806 s, 777 m, 752 s, 692 s, 673 w, 660 w. HRMS (ESI^+): calcd for $C_{33}H_{34}N_2O + H^+$, 475.2744,; found, 475.2732. Elemental analysis Calcd (%) for $C_{33}H_{34}N_2O$ (474.6): C, 83.51; H, 7.22; N, 5.90. Found: C, 83.12; H, 7.26; N, 5.78.

1-(2,2-Diphenylvinyl)-1-isopropyl-3-phenyl-3-(phenylcarbamoyl)-urea ***13a***. From ketenimine **1b** (272 mg, 1.07 mmol) and phenyl isocyanate **9a** (256 mg, 2.15 mmol, 2.0 equiv) according to the general procedure F. The crude reaction mixture was quenched with NaOH-solution (2 M). Subsequent column chromatography (*n*-pentane/ethyl acetate, 10:1) gave the pure product (261 mg, 0.55 mmol, 50%) as colorless solid. Mp 158 °C. Colorless crystals were obtained by recrystallization from ethyl acetate. ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.39 (s, 1H, N*H*), 7.49−6.99 (m, 18H, C*H*, phenyl), 6.78−6.71 (m, 2H, C*H*, phenyl), 5.50 (s, 1H, C=C*H*), 4.50 (sept, J_{HH} = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 1.34 (d, J_{HH} = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 158.6 (N-*C*=O), 152.0 (NH-*C*=O), 141.0 (*C*=CH), 139.6 138.9, 138.8, and 138.2 (*ipso*-*C*), 129.9, 129.8, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 128.3, 127.5, and 123.6 (*C*H, phenyl), 122.0 (C=*C*H), 120.3 (*C*H, phenyl), 51.4 (*C*H(CH_3)$_2$), 20.5 (2C, CH(*C*H$_3$)$_2$). IR (ATR, cm^{-1}) = 3269 w, 3239 w, ν(NH), 3061 w, 3034 w, 2991 w, 2968 w, 1702 s, ν(C=O), 1651 m, 1590 s, ν(C=O), 1549 s, ν(C=C), 1490 m, 1436 m, 1300 m, 1271 m, 1229 s, 1178 m, 1118 w, 1089 m, 1028 w, 895 m, 757 s, 723 m, 693 s, 658 w, 626 w, 584 m. HRMS (ESI^+): calcd for $C_{31}H_{29}N_3O_2 + Na^+$, 498.2152; found, 498.2157. Elemental analysis Calcd (%) for $C_{31}H_{29}N_3O_2$ (475.5): C, 78.29; H, 6.15; N, 8.84. Found: C, 78.09; H, 6.25; N, 8.78.

1-Cyclohexyl-1-(cyclohexylcarbamoyl)-3-(2,2-diphenylvinyl)-3-isopropylurea ***13b***. From ketenimine **1b** (508 mg, 2.01 mmol) and cyclohexyl isocyanate **9b** (502 mg, 4.01 mmol, 2.0 equiv) according to the general procedure F. The crude reaction mixture was quenched with NaOH-solution (2 M). Subsequent column chromatography (*n*-pentane/ethyl acetate, 5:1) gave the pure product (412 mg, 0.84 mmol, 42%), as colorless solid. Mp 136 °C. Colorless crystals were obtained by recrystallization from ethyl acetate. ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 7.38−7.18 (m, 10H, C*H*, phenyl), 6.29 (s, 1H, C=C*H*), 5.05 (d, J_{HH} = 7.7 Hz, 1H, N*H*), 4.29 (sept, J_{HH} = 6.9 Hz, 1 H, NC*H*(CH_3)$_2$), 3.54−3.34 (m, 2H, NC*H*(CH_2)$_5$), 1.84−1.54 (m, 10H, C*H*$_2$, cyclohexyl), 1.37−0.87 (m, 16H, CH(C*H*$_3$)$_2$, C*H*$_2$, cyclohexyl). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 158.5 (N(*i*-Pr)*C*=O), 155.3 (NH-*C*=O), 142.2 (*C*=CH), 139.2 and 137.3 (*ipso*-*C*), 130.2, 129.0, 128.7, 128.6, 128.5, 128.3 and 128.1(*C*H, phenyl), 124.2 (C=*C*H), 60.2 (NC*H*(CH_2)$_5$), 51.3 (NCH(*C*H$_3$)$_2$), 50.0 (NC*H*(CH_2)$_5$), 33.6, 31.3, 27.3, 26.2, 26.1, and 25.5 (*C*H$_2$, cyclohexyl), 20.7 (2C, CH(*C*H$_3$)$_2$). IR (ATR, cm^{-1}) = 3315 m, ν(NH), 3061 w, 3034 w, 2974 w, 2935 m, 2851 m, 1628 s, ν(C=O), 1528 s, ν(C=C), 1496 m, 1444 m, 1398 m, 1315 m, 1250 m, 1235 m, 1186 m, 1074 m, 869 m, 765 m, 752 m, 696 s, 639 w, 607 m. HRMS (ESI^+): calcd for $C_{31}H_{41}N_3O_2 + Na^+$, 510.3091; found, 510.3097. Elemental analysis Calcd (%) for $C_{31}H_{41}N_3O_2$ (487.7): C, 76.35; H, 8.47; N, 8.62. Found: C, 76.23; H, 8.47; N, 8.63.

1-(2,2-Diphenylvinyl)-1-isopropyl-3-(p-tolyl)-3-(p-tolylcarbamoyl)urea ***13c***. From ketenimine **1b** (295 mg, 1.17 mmol) and *p*-tolyl isocyanate **9c** (310 mg, 2.33 mmol, 2.0 equiv) according to general procedure F. The crude reaction mixture was quenched with NaOH-solution (2 M). Subsequent column chromatography (*n*-pentane/ethyl acetate, 15:1) gave the pure product (282 mg, 0.56 mmol, 48%) as colorless solid. Mp 170 °C. Colorless crystals were obtained by recrystallization from ethyl acetate. ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.25 (s, 1H, N*H*), 7.32−7.19 (m, 10H, C*H*, phenyl), 7.11−7.04 (m, 4H, C*H*, phenyl), 7.02−6.97 (m, 2H, C*H*, phenyl), 6.77−6.74 (m, 2H, C*H*, phenyl), 5.51 (s, 1H, C=C*H*), 4.48 (sept., J_{HH} = 6.9 Hz, 1H, C*H*(CH_3)$_2$), 2.44 (s, 3H, *ipso*-C(*C*H$_3$)), 2.30 (s, 3H, *ipso*-C(*C*H$_3$)), 1.31 (d, J_{HH} = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 158.6 (N(*i*-Pr.)*C*=O), 152.2 (NH-*C*=O), 141.0 (*C*=CH), 138.6, 138.2, 137.4, 137.0, 136.2, and 133.2 (*ipso*-*C*), 129.8, 129.5, 129.4, 129.0, 128.7, 128.6, 128.5, 128.3, and 128.2 (*C*H, phenyl), 122.3 (C=*C*H), 120.3 (*C*H, phenyl), 51.3 (*C*H(CH_3)$_2$), 21.4 (*ipso*-CMe), 21.0 (*ipso*-C(*C*H$_3$), 20.5 (CH(*C*H$_3$)$_2$). IR (ATR, cm^{-1}) = 3293 s br, ν(NH), 3059 w, 3030 w, 2967 w, 2942 w, 1707 s, ν(C=O), 1644 m, ν(C=O), 1590 s, 1540 s, ν(C=C), 1510 s, 1434 m, 1407 m, 1311 m, 1299 m, 1273 m, 1231 m, 1180 m, 1170 m, 1116 m, 1082 m, 1027 w, 889 m, 821 m, 771 m, 762 s, 740 m, 697 s, 666 m, 598 w. HRMS (ESI^+): calcd. for $C_{33}H_{33}N_3O_2 + H^+$,

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504.2646; found, 504.2640. Elemental analysis Calcd (%) for $C_{33}H_{33}N_3O_2$(503.6): C, 78.70; H, 6.60; N, 8.34. Found: C, 78.42; H, 6.78; N, 8.08.

1-(2,2-Diphenylvinyl)-1-isopropyl-3-phenylthiourea ***15***. From ketenimine **1b** (275 mg, 1.09 mmol) and phenyl isothiocyanate **14** (294 mg, 2.18 mmol, 2.0 equiv) according to general procedure F. The crude reaction mixture was quenched with NaOH-solution (2 M). Subsequent column chromatography (*n*-pentane/ethyl acetate, 15:1) gave the pure product (264 mg, 0.71 mmol, 65%) as yellow solid. Mp 109 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.61 (s, 1H, N*H*), 7.44−7.06 (m, 13H, C*H*, phenyl), 6.91−6.81 (m, 2H, C*H*, phenyl), 6.41 (s, 1 H, C=C*H*), 5.70 (hept, J_{HH} = 6.8 Hz, 1H, NC*H*$(CH_3)_2$), 1.29 (d, J_{HH} = 6.8 Hz, 6H, CH$(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 180.6 (C=S). 143.0(C=CH), 140.7, 139.7 and 137.9, (*ipso*-C), 129.5, 129.0, 128.9, 128.8, 128.7, 128.6, 126.2, and 126.1 (CH, phenyl), 122.1 (C=CH), 53.4 (NCH-$(CH_3)_2$), 20.3 (CH$(CH_3)_2$). IR (ATR, cm^{-1}) = 3193 w, ν(NH), 3176 w, ν(NH), 3106 w, 3055 w, 3023 w, 2969 w, 1591 m, 1528 m, ν(C=C), 1496 m, 1449 m, 1418 s, 1357 m, 1317 m, 1253 s, δ(C=S), 1179 m, 1157 m, 1119 m, 1079 w, 1044 m, 1026 m, 854 m, 759 s, 733 m, 690 s, 642 m, 616 w, 582 m. HRMS (ESI$^+$): calcd. for $C_{24}H_{24}N_2S$ + H^+, 373.1733; found, 373.1732. Elemental analysis Calcd (%) for $C_{24}H_{24}N_2S$ (372.53): C, 77.38; H, 6.49; N, 7.52. Found: C, 77.24; H, 6.59; N, 7.47.

(3-((2,6-Diisopropylphenyl)imino)-N,2,2-triphenylpropanethioamido)-di(iso-butyl)aluminum ***16***. From ketenimine **1a** (1.06 g, 2.99 mmol) and phenyl isothiocyanate **14** (441 mg, 3.26 mmol, 1.1 equiv) in 25 mL of *n*-hexane at −78 °C with stirring for 2 h and then at room temperature for 2 h according to the general procedure F. Red crystals (648 mg, 1.59 mmol, 53%) were obtained upon concentration of the reaction mixture and by recrystallization from *n*-hexane and toluene at −20 °C. Mp 170 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.99 (s, 1H, C*H*=N), 7.67−7.62 (m, 4H, C*H*, phenyl), 7.61−7.51 (m, 4H, C*H*, phenyl), 7.44−7.22 (m, 9H, C*H*, phenyl), 7.14 (*pseudo*s, 1H, C*H*, phenyl), 3.14 (hept, J_{HH} = 6.6 Hz, 2H, C*H*Me_2), 1.85−1.69 (m, 2H, Al-CH_2C*H*), 1.49 (d, J_{HH} = 6.7 Hz, 6H,CH(Me)$_2$), 1.20 (d, J_{HH} = 6.8 Hz, 6H, CHMe_2), 1.06 (d, J_{HH} = 6.4 Hz, 6H, Al-CH_2−CHMe_2), 0.96 (d, J_{HH} = 6.6 Hz, 6H, Al-CH_2−CHMe_2), 0.02 (dd, J_{HH} = 14.1, 8.5 Hz, 2H, Al−CH_2), −0.30 (dd, J_{HH} = 14.1, 5.7 Hz, 2H, Al−CH_2). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 206.4 (S=*C*), 190.7 (CH=N), 148.8 (*ipso*-*C*-N(S=C)), 145.2 (*ipso*-*C*.), 142.2 (*ipso*-*C*-N=CH), 141.7 (*ipso*-*C*-CHMe_2), 130.6, 129.4, 129.0, 128.6, 128.1, 128.0, 126.3, and 125.0 (CH, phenyl), 72.7 (Ph_2C), 29.0 (Al-CH_2−CHMe_2), 28.5 (C*H*Me_2), 27.7 (Al-CH_2−CHMe_2), 26.6 (CHMe_2), 26.0 (Al-CH_2−CH), 23.4 (CHMe_2), 22.2 (Al-CH_2). IR (CsI-plates, nujol, cm^{-1}): 3630 m, 3616 m, 2951−2852 vs, (nujol), 2723 s, 2669 m, 2603 m, 2341 m, 1951 w, 1888 w, 1805 w, 1616 m, ν(C=N), 1595 m, 1462 s, (nujol), 1377 s, 1344 m, 1307 w, 1155 w, 1041 s, δ(C=S), 1026 s, 931 w, 912 w, 858 m, 804 w, 779 m, 748 m, 723 s, (nujol), 623 w, 551 m,528 m, 505 w, 453 s, 447 s, 422 w, 401s, ν(AlC), ν(AlN). MS (EI, 20 eV, 150 °C): m/z (%) = 573 (13) [M − *i*-Bu]$^+$, 495 (22), 382 (17), 355 (99) [M − *i*-Bu_2Al − PhCNS + H]$^+$, 269 (4), 188 (100) [M − *i*-Bu_2Al − PhCNS − CPh_2]$^+$, 167 (13) [Ph_2C]$^+$, 146 (65), 135 (63) [PhCNS]$^+$, 91 (3), 77 (9), 56 (5). Elemental analysis Calcd (%) for $C_{41}H_{51}AlN_2S$ (630.90): C, 78.05; H, 8.15; N, 4.44. Found: C, 77.99; H, 8.15; N, 4.38.

3-((2,6-Diisopropylphenyl)imino)-N,2,2-triphenylthiopropanamide ***17***. From ketenimine **1a** (580 mg, 1.64 mmol) and phenyl thioisocyanate **14** (330 mg, 2.43 mmol) according to the general procedure F. The crude reaction mixture was quenched with NaOH-solution (2 M). Subsequent column chromatography (*n*-pentane/ethyl acetate, 100:1) did not lead to pure product, but inseparable mixtures of compounds were obtained. A few single crystals suitable for X-ray were obtained by recrystallization from a mixture of solvents (*n*-pentane/ethyl acetate, 1:1).

Reactions of Active Al/N Compounds 5 with Ketenimines 1. *General Procedure G for the Synthesis of Diimines* ***19***. A solution of DIBAL-H (1 M in *n*-hexane, 1 equiv) was added to a cooled (−78 °C) solution of the ketenimine **1b** or **1e** (1 equiv) in dry *n*-hexane (20 mL). After 2 h stirring at −78 °C, the solution was allowed to warm to room temperature and was stirred for 12 h. The second ketenimine **1e** or **1b** (1 equiv) was added at −78 °C and stirring was continued for 2 h. The solution was warmed to room temperature and quenched with saturated Na_2CO_3-solution. The organic layer was washed twice with saturated Na_2CO_3-solution and brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. Then, the crude product was purified by column chromatography and/or recrystallization for X-ray analysis.

((1-Cyclohexylidene-3-(cyclohexylimino)-2,2-diphenylpropyl)(p-tolyl)amino)-di(iso-butyl)aluminum ***18***. From ketenimine **1c** (270 mg, 0.98 mmol) and *N*-(cyclohexylidenemethylene)-4-methylaniline **1d** (195 mg, 0.98 mmol) in 20 mL of *n*-hexane at −78 °C after stirring for 2 h and then at room temperature for 12 h according to the general procedure G, but without aqueous workup. Yellow solid (225 mg, 0.36 mmol, 37%) was obtained upon concentration of the reaction mixture. Mp 157 °C. Yellow sensitive crystals were obtained by recrystallization from cyclopentane at −20 °C. ^{1}H NMR (500 MHz, C_6D_6, 343 K): δ = 7.59−7.50 (m, 5H, partially covered, C*H*, phenyl and C*H*=N), 7.23−7.18 (m, 4H, C*H*, phenyl), 7.13−7.08 (m, 2H, C*H*, phenyl), 6.81−6.77 (m, 2H, C*H*, phenyl), 6.28−6.24 (m, 2H, C*H*, phenyl), 3.66−3.73 (m, 1H, N−C*H*, cyclohexyl), 2.33−2.18 (m, 4H, partially covered, Al-CH_2−C*H*Me_2 and CH_2, cyclohexyl), 1.89−1.80 (m, 4H, CH_2, cyclohexyl), 2.10 (s, 3H, *ipso*-C−CH_3), 1.46−1.19 (m, 21H, partially covered, Al-CH_2−CHMe_2 and CH_2, cyclohexyl), 0.77−0.65 (m, 2H, CH_2, cyclohexyl), 1.06−0.99 (m, 2H, CH_2, cyclohexyl), 0.62−0.49 (m, 5H, partially covered, Al−CH_2 and CH_2,cyclohexyl). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 343 K): δ = 175.2 (CH=N), 153.4 (*ipso*-*C*−N-Al), 140.7 (Al−N-*C*=$C_{c\text{-hex}}$), 140.1 (*ipso*-*C*), 130.0 (*ipso*-*C*-CH_3), 129.8, 129.4, 128.3 (CH, phenyl), 125.3 (Al−N−C=*C*$_{c\text{-hex}}$), 119.3 (CH, phenyl), 67.2 (*spiro*-*C*), 62.1 (Al−N-CH, cyclohexyl), 34.1, 33.2, and 32.0 (CH_2, cyclohexyl), 29.2 (Al-CH_2−CHMe_2), 28.8 (CH_2, cyclohexyl), 27.1 (2C, Al-CH_2−CH), 26.8, 26.6, 25.9, 25.5, 25.2 (CH_2, cyclohexyl), 20.5 (*ipso*-C-CH_3). IR (CsI-plates, nujol, cm^{-1}): 3451 w, 2949−2848 vs, (nujol), 2754 w, 2719 w, 2657 w, 2609 w, 2333 w, 1651 s, ν(C=N), 1577 s, ν(C=C), 1454 s, (nujol), 1446 s, 1373 s, 1276 w, 1157 w, 1087 w, 1033 s, 1026 s, 891 w, 813 w, 719 s, 516 s, 460 s, 401 s, ν(AlC), ν(AlN). MS (EI, 30 eV, 25 °C): m/z (%) = 477 (20), 476 (54) [M − (*i*-Bu)$_2$Al + H]$^+$, 400 (7), 399 (23), 393 (14), 367 (18), 365 (24), 338 (6), 309 (8), 283 (35), 277 (59) [Ph_2C + C=NC_6H_{12} + H]$^+$, 260 (33), 234 (21), 217 (53), 216 (100) [(Me)PhN + C=NC_6H_{12} + H]$^+$, 200 (48), 193 (40), 167 (25), 165 (15), 110 (18), 107 (62), 91 (15), 83 (7).

*2,6-Diisopropyl-N-((1-((E)-1-(isopropylimino)-2,2-diphenylethyl)-cyclohexyl)-methylene)aniline (****19a****)*. From ketenimine **1e** (1.48 g, 5.52 mmol) and ketenimine **1b** (1.30 g, 5.52 mmol), according to the general procedure G. Subsequent column chromatography on alumina B. act. I (cyclohexane/TBME, 200:1) gave the pure product (1.14 g, 2.25 mmol, 41%) as colorless solid. Colorless crystals were obtained by recrystallization from *n*-pentane/diethyl ether (1:1). Mp 149 °C. ^{1}H NMR (400 MHz, C_6D_6): δ (ppm) = 7.71 (s, 1H, C*H*=N), 7.36−7.27 (m, 3H, C*H*, phenyl), 7.27−7.21 (m, 3H, C*H*, phenyl), 7.19−7.08 (m, 6H, C*H*, phenyl), 7.04 (dd, 1H, J_{HH} = 8.5, 6.7 Hz, C*H*, phenyl), 3.74 (hept, 1H, J_{HH} = 5.9 Hz, NC*H*$(CH_3)_2$), 5.64 (s, 1H, C*H*Ph_2), 3.20 (hept, 2H, J_{HH} = 5.9 Hz, C*H*$(CH_3)_2$), 2.10−1.93 (m, 4H, C$(CH_2)_2(CH_2)_2CH_2$), 1.73−1.51 (m, 5H, partially covered, C$(CH_2)_4$CH*H* and C$(CH_2)_2(CH_2)_2CH_2$), 1.36−1.24 (m, 1H, partially covered, C$(CH_2)_4$C*H*H), 1.15 (d, J_{HH} = 6, 9 Hz, 12H, CH$(CH_3)_2$), 0.69 (d, J_{HH} = 5.9 Hz, 6H, NCH$(CH_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 171.7 (CH=N), 168.8 (C=NCH$(CH_3)_2$), 149.9 (*ipso*-*C*-N), 141.6 (*ipso*-*C*-CH.), 138.2 (*ipso*-*C*−CH$(CH_3)_2$), 129.9, 128.9, 127.0, 124.1, and 123.2 (CH, phenyl), 55.8 (C$(CH_2)_5$), 53.8 ($CHPh_2$), 52.2 (NCH$(CH_3)_2$), 32.4 (partially covered, C$(CH_2)_2(CH_2)_2CH_2$ and C$(CH_2)_2(CH_2)_2CH_2$), 27.9 (CH-$(CH_3)_2$), 26.2 (partially covered, C$(CH_2)_4CH_2$ and C-$(CH_2)_2(CH_2)_2CH_2$), 23.7 (CH$(CH_3)_2$), 23.1 (NCH$(CH_3)_2$), 23.0 (C$(CH_2)_2$). IR (ATR, cm^{-1}) = 3089 w, 3040 w, 2967 s, 2936 s, 2864 m, 2860 m, 1636 s, ν(C=N), 1601 m, 1539 w, 1495 m, 1452 s, 1439 s, 1379 m, 1362 m, 1339 m, 1321 m, 1256 w, 1179 m, 1150 m,

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1117 m, 1096 w, 1042 m, 991 m, 968 m, 935 m, 932 m, 880 m, 849 s, 843 s, 729 m, 698 s. HRMS (ESI$^+$): calcd for $C_{36}H_{46}N_2$ + H^+, 507.3734; found, 507.3725. Elemental analysis Calcd (%) for $C_{36}H_{46}N_2$ (506.76): C, 85.32; H, 9.15; N, 5.53. Found: C, 85.26; H, 9.14; N, 5.39.

*N-(1-Cyclohexyl-3-(isopropylimino)-2,2-diphenylpropylidene)-2,6-diisopropyl-aniline (**19b**).* From ketenimine **1b** (972 mg, 4.13 mmol) and ketenimine **1e** (1.11 g, 5.52 mmol) according to the general procedure G. Subsequent column chromatography on alumina B. act. I (cyclohexane/TBME, 10:1) gave the pure product (550 mg, 1.08 mmol, 26%) as colorless solid. Mp 166 °C. Colorless crystals were obtained by recrystallization from *n*-pentane/diethyl ether (1:1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.17 (s, 1H, C*H*=N), 7.52−7.46 (m, 4H, C*H* of phenyl), 7.42−7.25 (m, 6H, C*H*, phenyl), 7.11−6.98 (m, 2H, C*H*, phenyl), 6.93 (dd, J_{HH} = 8.3, 6.8 Hz, 1H, C*H*, phenyl), 3.25 (m, 1H, NC*H*$(CH_3)_2$), 2.90 (hept, J_{HH} = 6.7 Hz, 2H, C*H*$(CH_3)_2$), 2.34 (tt, J_{HH} = 11.7, 2.3 Hz, 1H, C*H*$(CH_2)_5$), 1.37−0.98 (m, 23H, NCH$(CH_3)_2$, CH$(CH_3)_2$, partially covered, CH$(CH_2)_2$(CH*H*)$_2$CH$_2$ and CH$(CH_2)_2CH_2$), 0.97−0.53 (m, 5H, partially covered, CH$(CH_2)_4CH_2$, CH$(CH_2)_2$(CH*H*)$_2$CH$_2$) and CH$(CH_2)_2$(C*H*H)$_2$CH$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 173.6 (*C*=N), 163.7 (*C*H=N), 146.5 (*ipso*-*C*-N), 140.5 (*ipso*-*C*), 134.9 (*ipso*-*C*−CH$(CH_3)_2$), 131.6, 128.2, 127.5, 122.8, and 122.3 (*C*H, phenyl), 71.0 (*C*Ph$_2$), 61.9 (NCH$(CH_3)_2$), 48.9 (*C*H$(CH_2)_5$), 30.9 (CH$(CH_2CH_2)_2CH_2$), 29.0 (CH$(CH_3)_2$), 27.2 (CH-$(CH_2CH_2)_2CH_2$), 26.4 (CH$(CH_2CH_2)_2CH_2$), 24.2 (CH$(CH_3)_2$), 23.9 (NCH$(CH_3)_2$), 20.4 (CH$(CH_3)_2$). IR (ATR, cm^{-1}) = 3059 w, 2962 s, 2929 s, 2864 m, 2852 m, 1670 s, ν(C=N), 1653 s, ν(C=N), 1591 w, 1491 m, 1448 s, 1431 s, 1379 m, 1361 m, 1323 m, 1257 w, 1242 w, 1188 w, 1143 m, 1112 w, 1080 w, 1033 m, 974 m, 895 m, 840 w, 813 m, 756 s, 740 s, 704 vs. HRMS (ESI$^+$): calcd for $C_{36}H_{46}N_2$ + H^+, 507.3734; found, 507.3734. Elemental analysis Calcd (%) for $C_{36}H_{46}N_2$ (506.76): C, 85.32; H, 9.15; N, 5.53. Found: C, 85.18; H, 9.30; N, 5.43.

Reactions of Active Al/N Compounds with Acid Chlorides. *General Procedure H for the Synthesis of Enamides (N-Alkenylamines) **20a** and **20b**.* A solution of DIBAL-H (1 M in *n*-hexane, 1 equiv) was added to a cooled (−78 °C) solution of the ketenimine **1** (1 equiv) in dry *n*-hexane (5 mL per mmol). After 2 h stirring at −78 °C, the reaction mixture was slowly warmed to room temperature and then stirred for 2 h at room temperature. The electrophiles (2.0 equiv) were added under ice-cooling or −78 °C and stirring was continued for 4 h. The reaction was then quenched with alkaline solution (NaOH). The organic layer was washed twice with alkaline solution and brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and then the crude product was purified by column chromatography and/or recrystallization for X-ray analysis.

*N-(2,2-Diphenylvinyl)-N-isopropyl-4-methylbenzamide (**20a**).* From ketenimine **1b** (1.44 g, 6.11 mmol) and 4-methylbenzoyl chloride **2c** (1.89 g, 12.2 mmol) after quenching with NaOH-solution (2 M) according to the general procedure H. Subsequent column chromatography (*n*-pentane/DCM, 8:2) gave the pure product (1.33 g, 3.76 mmol, 61%) as yellow solid. Mp 163 °C. Yellow crystals were obtained by recrystallization from toluene. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.36−7.06 (m, 8H, C*H*, phenyl), 6.94 (*pseudos*, 4H, C*H*, phenyl), 6.68 (d, J_{HH} = 6.4 Hz, 2H, C*H*, phenyl), 6.49 (s, 1H, C=C*H*), 4.77 (dq, J_{HH} = 27.2, 13.4, 7.0 Hz, 1H, NC*H*$(CH_3)_2$), 2.27 (s, 3H, C*H*$_3$), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 6H, NCH$(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 170.3 (*C*=O), 142.2 (*C*=CH), 140.3 (*ipso*-*C*-CH$_3$), 138.7 (*ipso*-*C*), 134.4 (*ipso*-*C*-C=O), 130.1, 128.7, 128.6, 128.5, 128.3, 128.1, and 127.6 (*C*H, phenyl), 124.4 (C=*C*H), 48.7 (NCH$(CH_3)_2$), 21.6 (*C*H$_3$), 20.9 (NCH$(CH_3)_2$). IR (ATR, cm^{-1}) = 3049 w, 3018 w, 2984 w, 2968 w, 2916 w, 1614 s ν(C=O), 1574 w, 1495 m, 1443 m, 1414 s, 1337 s, 1310 s, 1277 m, 1240 s, 1182 s, 1128 m, 1123 m, 1078 m, 1032 w, 1020 w, 964 w, 878 s, 827 m, 775 s, 745 s, 696 s, 640 s, 600 m, 581 m. HRMS (ESI$^+$): calcd for $C_{25}H_{25}NO$ + Na^+, 378.1828; found, 378.1834. Elemental analysis Calcd (%) for $C_{25}H_{25}NO$ (355.47): C, 84.47; H, 7.09; N, 3.94. Found: C, 84.21; H, 7.09; N, 4.04.

*N-(2-Ethylbut-1-en-1-yl)-4-methyl-N-phenylbenzamide (**20b**).* From ketenimine **1f** (1.22 g, 7.05 mmol) and 4-methylbenzoyl chloride **2c** (2.20 g, 15.2 mmol) after quenching with NaOH-solution (2 M) according to the general procedure H. Subsequent column chromatography (*n*-pentane/ethyl acetate, 100:1) gave the pure product (460 mg, 1.57 mmol, 22%) as colorless liquid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.49−7.39 (m, 2H, C*H*, phenyl). 7.38−7.09 (m, 7H, C*H*, phenyl), 6.09 (s, 1H, C*H*=C), 2.37 (s, 3H, C*H*$_3$), 2.01 (dqd, J_{HH} = 39.3, 7.6, 1.2 Hz, 4H, C*H*$_2$CH$_3$), 0.95 (t, J_{HH} = 7.5 Hz, 3H, CH$_2$C*H*$_3$), 0.76 (t, J_{HH} = 7.6 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 170.9 (C=O), 143.7 (*ipso*-*C*-CH$_3$), 142.9 (*ipso*-*C*), 141.1 (*ipso*-*C*-C=O), 134.3 (C=CH), 129.4, 129.1, 128.8, 126.5, and 126.1 (CH, phenyl), 124.5 (C=CH), 26.4 (CH$_2$CH$_3$), 22.5 (CH$_2$CH$_3$), 21.7 (CH$_3$), 12.6 (CH$_2$CH$_3$), 11.3 (CH$_2$CH$_3$), IR (ATR, cm^{-1}) = 3012 w, 2967 w, 2945 w, 2878 w, 1649 s ν(C=O), 1611 w, 1595 w, 1493 m, 1474 w, 1339 s, 1302 s, 1182 m, 1069 w, 876 w, 831 w, 633 s, 600 s. HRMS (ESI$^+$): calcd for $C_{20}H_{23}NO$ + H^+, 294.1852; found, 294.1848.

*One-Pot Reactions of Hydroaluminated Ketenimines **1** with Isocyanates **9** and Acid Chloride **2c**. N-((2,2-Diphenylvinyl)-(isopropyl)carbamoyl)-4-methyl-N-phenylbenzamide (**21a**).* In analogy to general procedure F, ketenimine **1b** (514 mg, 2.18 mmol) was reacted with di(*iso*-butyl) aluminum hydride (2.18 mL, 2.18 mmol, 1 M in *n*-hexane, 1.0 equiv) in 20 mL of *n*-hexane at −78 °C. Phenyl isocyanate **9a** (258 mg, 2.18 mmol, 1 equiv) was added at −78 °C and the mixture was stirred at this temperature for 1 h and then at room temperature for 24 h. Then, 4-methylbenzoyl chloride **2c** (0.77 g, 4.36 mmol) was added at room temperature. The reaction mixture was quenched with saturated Na_2CO_3-solution. Subsequent column chromatography (*n*-pentane/ethyl acetate, 20:1) gave the pure product (464 mg, 0.98 mmol, 45%) as colorless solid. Mp 150 °C. Colorless crystals were obtained by recrystallization from DMSO. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.61−7.24 (m, 12H, C*H*, phenyl), 7.20−7.00 (m, 5H, C*H*, phenyl), 6.45−6.35 (m, 2H, C*H*, phenyl), 6.34 (s, 1 H, C*H*=C), 4.66 (hept, J_{HH} = 6.6 Hz, 1H, NC*H*$(CH_3)_2$), 2.40 (s, 3H, C*H*$_3$), 1.48 (d, J_{HH} = 6.6 Hz, 6H, NCH$(CH_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 171.2 (*p*-tolyl-*C*=O), 156.3 (N$_2$C=O), 142.3 (*ipso*-*C*-CH$_3$), 141.2 (CH=*C*), 140.6, 138.0, and 131.6 (*ipso*-*C*), 130.3, 129.8, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 127.7, 127.4, and 126.6 (*C*H, phenyl), 124.5 (*C*H=C), 51.7 (*C*H$(CH_3)_2$), 21.6 (*C*H$_3$), 19.9 (*C*H$_3$). IR (ATR, cm^{-1}) = 3024 w, 2984 w, 2874 w, 1668 s, ν(C=O), 1626 m, 1605 m, 1574 w, 1549 w, 1495 m, 1445 m, 1408 m, 1319 m, 1265 s, 1207 s, 1180 s, 1150 m, 1125 w, 1074 w, 1034 w. HRMS (ESI$^+$): calcd for $C_{32}H_{30}N_2O_2$ + Na^+, 497.2199; found, 497.2194. Elemental analysis Calcd (%) for $C_{32}H_{30}N_2O_2$ (474.59): C, 80.98; H, 6.37; N, 5.90. Found: C, 80.79; H, 6.35; N, 5.97.

*N-Cyclohexyl-N-((2,2-diphenylvinyl)(isopropyl)carbamoyl)-4-methylbenzamide (**21b**).* In analogy to general procedure F, ketenimine **1b** (502 mg, 2.13 mmol) was treated with di(*iso*-butyl) aluminum hydride (2.13 mL, 2.13 mmol, 1 M in *n*-hexane, 1.0 equiv) in 25 mL of *n*-hexane at −78 °C. Cyclohexyl isocyanate **9b** (265 mg, 2.13 mmol, 1 equiv) was added with stirring at −78 °C for 1 h and then at room temperature for 24 h. Then, 4-methylbenzoyl chloride **2c** (329 mg, 2.13 mmol, 1 equiv) was added at room temperature. The reaction mixture was quenched with saturated Na_2CO_3-solution. Subsequent column chromatography (*n*-pentane/ethyl acetate, 50:1) gave the pure product (318 mg, 0.66 mmol, 31%) as colorless solid. Mp 148 °C. Colorless crystals were obtained by recrystallization from DMSO. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm): = 7.57 (d, J_{HH} = 8.1 Hz, 2H C*H*, phenyl), 7.31−7.15 (m, 8H, C*H*, phenyl), 7.09 (m, 2H, C*H*, phenyl), 6.48 (d, J_{HH} = 6.7 Hz, 2H, C*H*, phenyl), 6.15 (s, 1H, C=C*H*), 4.13 (dt, J_{HH} = 3.3, 11.8 Hz, 1H, NC*H*$(CH_2)_5$), 3.57 (sept, J_{HH} = 6.8, 13.2 Hz, 1H, NC*H*$(CH_3)_2$), 2.46 (s, 3H, *p*-tolyl−C*H*$_3$), 1.12−1.80 (m, 10H, C*H*$_2$ of cyclohexyl), 1.02 (d, J_{HH} = 6.8 Hz, 6H, CH$(CH_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.1 (*p*-tolyl-C=O), 156.6 (N$_2$C=O), 142.8 (*ipso*-*C*-CH$_3$), 142.5 (C=CH), 138.4 and 135.0 (*ipso*-*C*), 130.2, 129.6,

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129.0, 128.7, 128.5, 128.3, and 128.1 (CH, phenyl), 125.8 (C═CH), 58.1 ($NCH(CH_2)_5$), 53.5 ($NCH(CH_3)_2$), 31.0, 26.8, and 26.1 (CH_2, cyclohexyl), 21.8 (*p*-tolyl-CH_3), 19.4 ($CH(CH_3)_2$). IR (ATR, cm^{-1}) = 3063 w, 3036 w, 3008 w, 2932 w, 2849 w, 1689 m, ν(C═O), 1638 s, ν(C═O), 1611 m, 1498 w, 1444 m, 1410 m, 1334 m, 1275 m, 1234 s, 1184 w, 1128 w, 1092 w, 1005 w, 881 m, 867 m, 834 m, 740 s, 723 m, 696 m, 646 w, 610 m. HRMS (ESI^+): calcd for $C_{32}H_{36}N_2O_2$ + H^+, 481.2850; found, 481.2852. Elemental analysis Calcd (%) for $C_{32}H_{36}N_2O_2$ (480.64): C, 79.96; H, 7.55; N, 5.83. Found: C, 79.79; H, 7.58; N, 5.71.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details (NMR-spectra and detailed X-ray data) and quantum chemical DFT results. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00466.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Dr. Christian Reichardt at the occasion of his 80th birthday.

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