Amino-*Claisen* Rearrangements[1]) and *Diels-Alder* Reactions of Ketene N,O-Acetals: Reactivity Studies. On the Way to a Novel Tandem Process?

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We report the synthesis of *N*-benzyl-*N*-[(*E*)-buta-1,3-dienyl]propanamide (**6**) and its corresponding *O*-silyl-substituted ketene N,O-acetal **7** and their *Diels-Alder* reaction. Propanamide **6** reacted smoothly, whereas the yield obtained from **7** was low, probably due to polymerization of the dienophile induced by electron transfer. The ketene N,O-acetals **27a**–**g** were synthesized starting from the corresponding benzamides **25a**–**e** (*Scheme 9*). The ketene N,O-acetals **27a**–**g** showed increased stabilities and underwent amino-*Claisen* rearrangements under thermal conditions. Using catalysts, interesting side reactions leading either to the annulated systems *rac*-**35**–**37** or to a β-lactam *rac*-**34** were observed.

1. Introduction. – Despite the power of modern synthesis, Nature's pathways are still impressive due to their high selectivity and their great efficiency [2a]. One of Nature's strategies attractive for synthetic chemists combines two or several transformations in one reaction step [2b]. The length of a synthesis is determined by the average complexity increase per operation. An important strategy to shorten a total synthesis is, therefore, the search for synthetic steps which increase the gain of complexity. To obtain shorter syntheses, chemists search for reactions that can be combined in one synthetic operation [3], often copying the lessons from Nature. Such processes involving two or more consecutive reactions are called tandem [2b][4], domino [2a][5], or cascade reactions [6]. In the last years, many natural-product syntheses involving tandem reactions have been published [7]. Pericyclic reactions such as *Diels-Alder* reactions and [3,3]-sigmatropic rearrangements are extremely useful transformations [5a]. Combining two or more pericyclic reactions, a transformation with considerably enhanced synthetic potential should be obtainable. For several years, the research efforts of our group are focused on the development of tandem reactions involving the sequence *Diels-Alder* cycloaddition/[3,3]-sigmatropic rearrangement [8]. For the first tandem reaction in this sequence, a moderately active thiocyanatobuta-1,3-diene **1** was used (*Scheme 1*) [8a,e]. After the initial *Diels-Alder* cycloaddition, the

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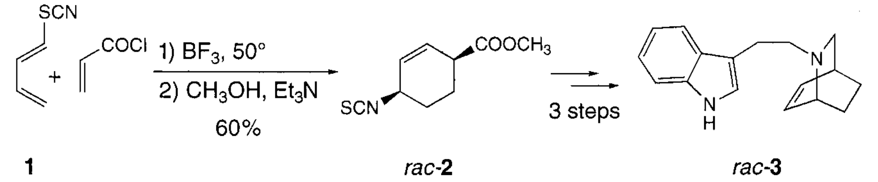
[1]) For the [3,3]-sigmatropic rearrangements where N–C bonds are broken, a systematic naming has been proposed [1a], based on *Cope* rearrangement and *IUPAC* replacement nomenclature. Following this proposal, the reaction studied would be a 3-aza-*Cope* rearrangement [1b–d]. However, for the [3,3]-sigmatropic rearrangements where the enol part of the starting material is in the oxidation state of an ester group, the following trivial names have been used by most authors in the field: The variants of the *Ireland-Claisen* rearrangement, in which one of the O-atoms is replaced by an N-atom, are called *Eschenmoser* rearrangement [1e] if the *exocyclic* O-atom is replaced, or aza-*Claisen* rearrangement [1f–h] if the *endocyclic* O-atom is replaced.

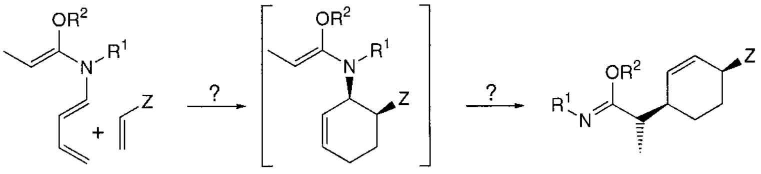
[3,3]-sigmatropic shift was successfully accomplished, leading directly to a 1,4-disubstituted cyclohexene-ring system *rac*-**2**.

Scheme 1. Diels-Alder *Cycloaddition/[3,3]-Sigmatropic Shift Tandem Reaction Applied to the Synthesis of the Precursor* rac-**3** *of the Ibogain Skeleton*



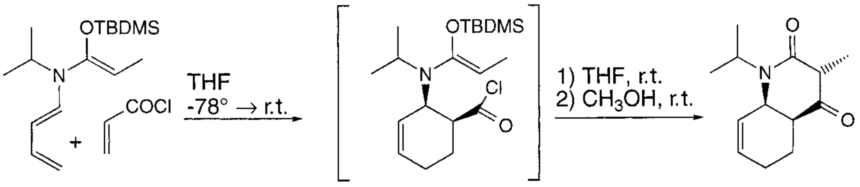
The relative configurations at C(1) and C(4) of the cyclohexene ring in *rac*-**2** are a consequence of the selectivities of the two individual reactions. This tandem product was successfully used for the synthesis of a precursor *rac*-**3** of the ibogain skeleton [8c]. To increase the synthetic utility of this tandem sequence, we tried to combine the *Diels-Alder* cycloaddition with an amino-*Claisen* rearrangement (*Scheme 2*).

Scheme 2. *Planned* Diels-Alder *Cycloaddition/Amino*-Claisen *Rearrangement Tandem Reaction*



This process would create a total of three C–C bonds allowing to control the relative configuration of the two chiral centers in the ring as well as the relative configuration of the exocyclic chiral C-atom. In contrast to the deactivated diene **1**, the N-substituted dienes should be electron-rich and thereby more reactive in the *Diels-Alder* reaction. To test this idea, a series of differently *N*-butadienyl-*N*-alkyl-*O*-silyl-substituted ketene N,O-acetals **4** have been prepared [8d][9] (*Scheme 3*). Instead of the expected tandem reaction, an unexpected *Diels-Alder* cycloaddition/acylation process was detected which led to the bicyclic product *rac*-**5** (*Scheme 3*). As the amino-*Claisen* rearrangements require reaction temperatures of 135–150° [10], the intramolecular acylation reaction is preferred. The bicyclic skeleton *rac*-**5** formed was

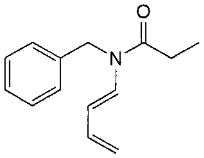
Scheme 3. Diels-Alder *Cycloaddition/Acylation Tandem Reaction Leading to the Bicyclic Skeleton* rac-**5**. TBDMS = ^{t}BuMe$_2$Si.



4 *rac*-**5** (56%)

sufficiently interesting to suggest the investigation of the scope and limitations of its formation [8d][9].

The synthetic potential of the initially planned tandem process (*Scheme 2*) motivated us to study the individual steps of the tandem reaction with the hope to combine them into one tandem reaction at a later stage. For this purpose, we prepared model compounds for the starting materials and the intermediates of the planned tandem reaction which should allow us to evaluate the scope and limitations of the *Diels-Alder* cycloaddition and the amino-*Claisen* rearrangement separately. We also hoped to increase our understanding of some earlier preliminary results. The *N*-benzyl-*N*-butadienylpropanamide **6**, the precursor of the ketene acetal **7**, reacted with methyl acrylate [11] (experiment not shown), but the ketene acetal **7** underwent almost no cycloaddition (see also *Scheme 8*). On reaction of the strong dienophile *N*-phenylmaleimide with a *N*-benzyl-*N*-butadienyl-substituted ketene N,O-acetal, only small amounts of the *Diels-Alder* adduct could be isolated, and only traces of the tandem product were obtained. Assuming that the ketene acetal **7** is a more electron-rich diene, we expected a higher reactivity in the *Diels-Alder* reaction for **7** compared to **6**. Based on these results, we planned to introduce a benzoyl substituent at the N-atom of the ketene N,O-acetal. The stability of such a ketene acetal should be enhanced due to resonance stabilization. We hoped that this protecting group would activate the amino-*Claisen* rearrangement as well, due to the higher polarization of the C–N bond, which will be broken.



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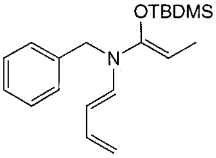
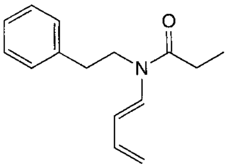


7 TBDMS = ^{t}BuMe$_2$Si



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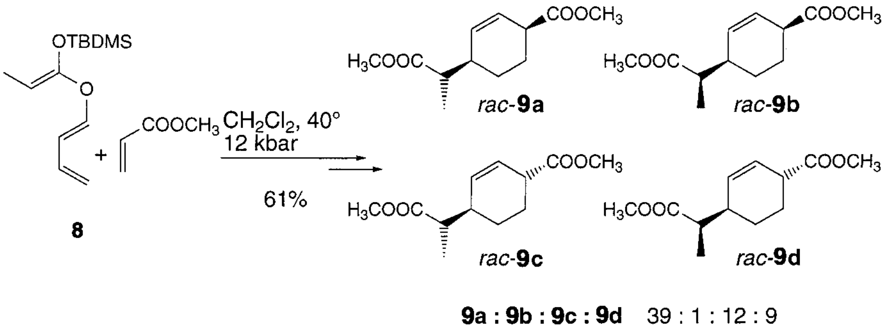
In our group, we developed a synthesis for *O*-butadienyl-*O*-(trialkylsilyl)-substituted ketene O,O-acetals like **8** and tested their potential for the tandem reaction *Diels-Alder* cycloaddition/*Ireland-Claisen* rearrangement in the presence of cyclic and acyclic dienophiles (*Scheme 4*). The temperatures needed for the rearrangement of *O*-allyl-*O*-(trialkylsilyl)-substituted ketene O,O-acetals are much lower than the temper-

Scheme 4. Diels-Alder *Cycloaddition/Amino-*Claisen *Rearrangement Tandem Reaction under High-Pressure Conditions Starting from* O-*(Trialkylsilyl)-Substituted Ketene O,O-Acetal* **8**. TBDMS = ^{t}BuMe$_2$Si.

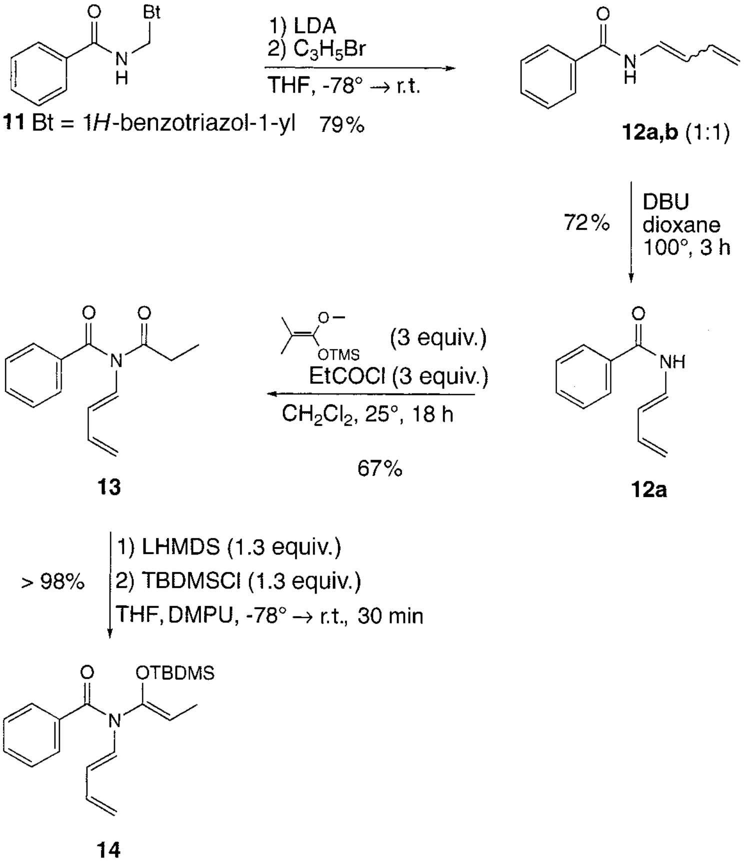


atures needed for amino-*Claisen* rearrangements [12], which is an advantage of this former process. The major difficulty of this approach to the tandem process *Diels-Alder* reaction/[3,3]-sigmatropic rearrangement is the extremely low temperature needed for the synthesis of the *O*-(trialkylsilyl)-substituted ketene O,O-acetals **8** [13].

2. Results and Discussion. – 2.1. Diels-Alder *Reactions.* 2.1.1. *Starting Materials.* The dienes used for the *Diels-Alder* studies were prepared as follows: *N*-Benzyl-*N*-[(*E*)-buta-1,3-dienyl]propanamide (**6**), its *O*-silyl-substituted ketene N,O-acetal **7**, and *N*-[(*E*)-buta-1,3-dienyl]-*N*-phenethylpropanamide (**10**) were synthesized as previously described [9].

For the preparation of *N*-[(*E*)-buta-1,3-dienyl]-*N*-propanoylbenzamide (**13**) (*Scheme 5*), we modified the procedure published by *Katritzky* and co-workers [14]. The reported method led to a mixture **12a**/**12b** of the (*E*)- and (*Z*)-isomers, which was separated by crystallization. At best, 34% of the (*E*)-isomer **12a** could be isolated. Allylation of *N*-(1*H*-benzotriazol-1-ylmethyl)benzamide (**11**) in the presence of lithium diisopropylamide (LDA) as base and heating to room temperature yielded

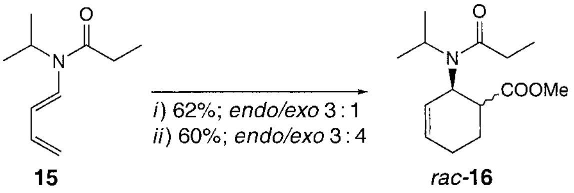
Scheme 5. *Synthesis of Diene* **14** *by a Modified Procedure First Reported by* Katritzky *and Co-workers* [14]. TBDMS = ^{t}BuMe$_2$Si.



12a/12b in a reproducible manner and allowed the elimination of 1*H*-benzotriazole in one step, without the use of NaH as reported, thus shortening the initial procedure. The 1:1 mixture **12a/12b** obtained after flash chromatography was then refluxed in dioxane in the presence of DBU [15]. This induced an isomerization to the favored (*E*)-isomer **12a**, which was isolated in 72% yield after 3 h. Subsequent acylation by 1-methoxy-2-methyl-1-[(trimethylsilyl)oxy]prop-1-ene [16] as neutral base gave imide **13** (67%). The latter was then converted in 98% yield to its ketene acetal **14** by a known procedure [9] which we modified by using lithium hexamethyldisilazanide (LHMDS) instead of LDA and by substituting the toxic hexamethylphosphoric triamide (HMPA) with the nontoxic *N,N'*-dimethylpropyleneurea (DMPU) [17]. With **14**, a *N*-butadienyl-substituted ketene N,O-acetal could be purified for the first time by flash chromatography. Indeed, as expected, **14** showed considerably enhanced stability towards hydrolysis.

2.1.2. Diels-Alder *Cycloadditions.* For our investigations on the *Diels-Alder* reaction, we used methyl acrylate as dienophile, although its reactivity is much lower than that of acryloyl chloride (*Scheme 6*). *N*-[(*E*)-Butadienyl]-*N*-isopropylpropanamide (**15**) reacted already at 0° with acryloyl chloride, and after methanolysis, we isolated 62% of the *Diels-Alder* product *rac*-**16** as a 3:1 *endo*/*exo* mixture [11]. With the methyl ester instead, the reaction temperature had to be increased to 85°. At this temperature, we observed the opposite selectivity, favoring now slightly the *exo*-product, which is probably the thermodynamically more stable compound.

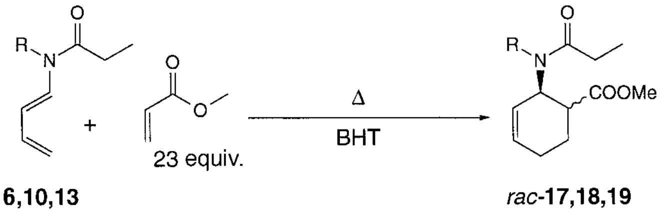
Scheme 6. *Comparision of the* Diels-Alder *Reaction of* **15** *with Acryloyl Chloride and Methyl Acrylate*



i) 1. Acryloyl chloride (2 equiv.), CH_2Cl_2, 0°, 18 h; 2. MeOH, r.t. *ii*) Methyl acrylate, toluene, 85°, 36 h.

We then varied the conditions of the *Diels-Alder* reaction involving methyl acrylate. The reaction was run without solvent using an excess of methyl acrylate (23 equiv.), with the aim to lower the reaction temperature, which could result in better *endo*/*exo* selectivities and yields, and traces of 2,6-di(*tert*-butyl)-*p*-cresol (BHT) were added as a radical trap to suppress polymerization. First we investigated the *N*-butadienylamides **6** and **10** and the *N*-butadienylimide **13** (*Scheme 7, Table 1*). All three butadienyl derivatives reacted smoothly in a *Diels-Alder* reaction. Due to the high concentration of the dienophile, cycloaddition occurred already at 60°. With **6**, the reaction led, after 67 h, to 95% of *rac*-**17**, with a slight *endo*-selectivity of 2:1. After 117 h reaction time, **10** gave *rac*-**18** in 71% yield with a 2.7:1 *endo*/*exo* selectivity, and **13** produced after 149 h 78% of *rac*-**19** as a 1:1 mixture of diastereoisomers. Thus, the substitution pattern at the N-atom seems to have no major influence on the reactivity of the butadienyl derivatives. The *Diels-Alder* reactions showed a slight *endo* selectivity. Probably, the long reaction time is responsible for the poor selectivity, due to epimerization at the

*Scheme 7*a)



a) For R, see *Table 1*.

Table 1. Diels-Alder *Cycloadditions of* **6**, **10**, *and* **13** (see *Scheme 7*)

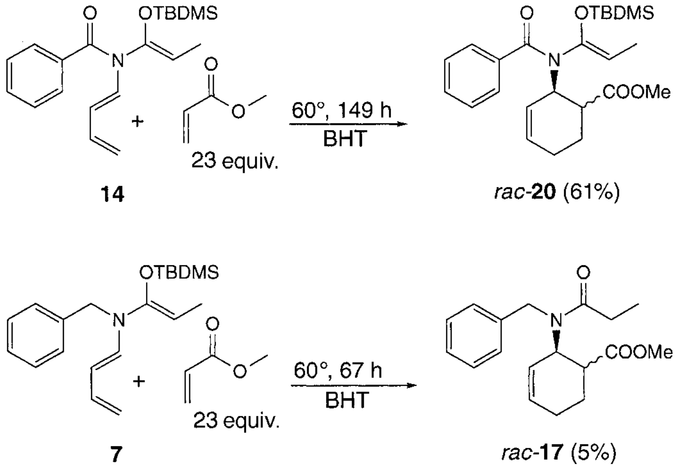
Starting material	R	*T*/°	*t*/h	Product	Yield [%]	*endo*/*exo* (*cis*/*trans*)
6	$PhCH_2$	60	67	*rac*-**17**	95	2 : 1
10	$Ph_2CH_2CH_2$	60	117	*rac*-**18**	71a)	2.7 : 1
13	PhCO	60	149	*rac*-**19**	78	1 : 1

a) Total yield; the *cis*/*trans* diastereoisomers were separated.

C-atom in α-position to the ester function. However, if this epimerization occurs after the cycloaddition, it would have no influence on our planned tandem reaction. Indeed, under tandem conditions, the *Diels-Alder* product would immediately undergo a [3,3]-sigmatropic rearrangement, prior to epimerization.

Applying the *Diels-Alder* conditions elaborated above to the ketene acetal **14** led to 61% of the silylated product *rac*-**20**, indicating the high stability of the *N*-benzoyl-substituted N,O-acetal moiety against hydrolysis (*Scheme 8*). However, ketene acetal **7** gave only 5% of the cycloaddition product *rac*-**17**. Despite the presence of the radical trap, most of the organic material was lost due to polymerization. As a consequence, the

Scheme 8. *Comparison of the* Diels-Alder *Reactivity of the Dienes* **7** *and* **14**. TBDMS = ^{t}BuMe$_2$Si.



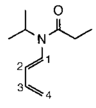
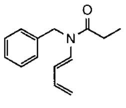
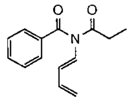
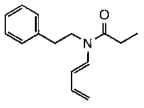
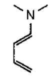
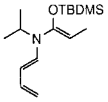
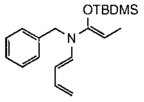
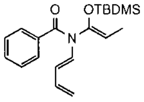
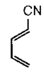
N-benzoyl-substituted N,O-acetal **14** should be preferred to the *N*-benzyl-substituted compound **7** as starting material for the planned tandem reaction.

It is known that substituents at C(1) of a butadiene have a strong influence on the energy levels of the FMO and, therefore, on the reaction rate in *Diels-Alder* reactions [18]. The total electron density at a C-atom can be linearly correlated with the ^{13}C-NMR chemical shifts [19]. It should, therefore, be possible to predict the reactivities of the dienes by comparing their ^{13}C-NMR data. If the electron lone pair at the N-atom is more available to activate the dienyl system by conjugation, positions C(2) and C(4) should become more electron-rich. In the ^{13}C-NMR spectra, high-field shifts of the corresponding C-atoms should be observed, the position C(1) should be slightly less electron-rich, resulting in a small down-field shift of δ(C(1)), and position C(3) should stay unchanged. In *Table 2*, the ^{13}C-NMR data of our dienes **4**, **6**, **7**, **10**, and **13**–**15** are compared to some representative known dienes, *i.e.* **21**–**24**. Thus, the 1-substituted dienes **21** and **22** show clearly the effect of electron-releasing substituents, when compared to buta-1,3-diene (**24**), and **23** demonstrates the influence of an electron-attracting substituent like the CN group. All amides **15**, **6**, and **10** and the imide **13** show roughly the same δ for C(1) which is downfield shifted by *ca.* 12–15 ppm with respect to the C(1) signal of **24**. The C(2) signals of **6** and **10** are upfield-shifted by *ca.* 24 ppm, a value almost twice as high as the shift difference obtained for **15** and **13** ($\Delta\delta \approx -13$ ppm). The δ(C(2)) of benzoyl-substituted imide **13** is very similar to that of the isopropyl-substituted amide **15**. At first, these observations are not in accordance with the electronic-effect analysis of the substituents. One would expect that the amides **15**, **6**, and **10** show similar δ(C(2)) values, whereas the C(2) signal of imide **13** with a reduced delocalization of the N-lone pair into the butadiene system should appear at lower field compared to **15**, **6**, and **10**. According to this argument, the δ(C(2)) value of the isopropyl-substituted amide **15** is unusual. A probable rationale for this behavior is a slight twist of the planar amide moiety of **15** out of the plane of the butadiene system due to the steric interaction of the bulky ^{i}Pr substituent with the diene, thus reducing the overlap between the N-lone pair and the butadiene. In summary, the ^{13}C-NMR chemical shifts of the amides **15**, **6**, and **10** and the imide **13** predict an activation of their diene moiety. The ketene acetals **4**, **7**, and **14** should even be more activated than their synthetic precursors **15**, **6**, and **13** (see *Table 2*).

The amides **15**, **6**, and **10** and the imide **13** underwent *Diels-Alder* addition with similar rates and yielded comparable amounts of cycloadducts, and also the ketene acetals **14** and **4** showed a good *Diels-Alder* reactivity. However, the benzyl-substituted ketene acetal **7** yielded only 5% of product (see also above). The only reasonable explanation for this result is to invoke a stability difference of the starting material and/or the product. It seems that **7** or its *Diels-Alder* product *rac*-**17** are less stable than **4** and **14**. Experimentally, besides the small quantities of *Diels-Alder* product, large amounts of polymerized material were obtained from **7**. The use of BHT should reduce radical polymerization. At the moment, we can only guess the mechanism responsible for this enhanced propensity for polymerization in the case of **7**.

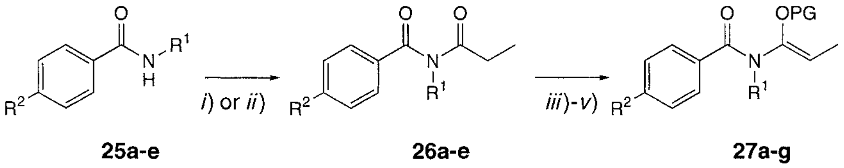
2.2. *Amino-*Claisen *Rearrangements.* 2.2.1. *Starting Materials.* The starting materials for the amino-*Claisen* rearrangement, the ketene N,O-acetals **27a**–**g**, were synthesized in two steps from the corresponding benzamides **25a**–**e** (*Scheme 9*, *Table 3*), which were obtained in turn by reported methods [22].

Table 2. *^{13}C-NMR Chemical Shifts* [ppm] *of 1-Substituted Dienes.* TBDMS = ^{t}BuMe$_2$Si

	 **15**	 **6**	 **13**	 **10**	 **21** [20]	
C(1)	128.8	130.0	128.1	130.2	143.4	
C(2)	123.0	112.5	123.6	111.5	99.9	
C(3)	134.4	135.4	133.7	135.4	136.6	
C(4)	115.8	113.2	117.4	113.0	104.7	
	 **4**	 **7**	 **14**	 **22** [21]	 **23** [19]	 **24** [19]
C(1)	138.1	137.3	139.0	152.9	98.9	116.0
C(2)	104.1	104.3	115.9	113.1	149.7	136.9
C(3)	138.0	137.1	134.6	135.9	133.1	136.9
C(4)	106.6	108.6	115.0	109.1	127.3	116.0

The allyl- and but-2-enyl-substituted benzamides **25a** and **25b** gave the corresponding imides **26a** and **26b** in 88 and 93% yield, respectively, *via* the imidoyl chlorides which were acylated under phase-transfer conditions [23]. This method failed in the case of the cyclohex-2-enyl-substituted benzamide **25c**. Thus, the latter was transformed under mild and neutral conditions by the elegant method developed by *Weinstock* and co-workers [24] who used the ethyl silylcarbamate **28** (see *Scheme 9*) as

Scheme 9



	R^1	R^2	PG
a	CH$_2$=CHCH$_2$	H	^{t}BuMe$_2$Si
b	(*E*)-MeCH=CHCH$_2$	H	^{t}BuMe$_2$Si
c	cyclohex-2-enyl	H	^{t}BuMe$_2$Si
d	CH$_2$=CHCH$_2$	Me	^{t}BuMe$_2$Si
e	CH$_2$=CHCH$_2$	MeO	^{t}BuMe$_2$Si
f	CH$_2$=CHCH$_2$	H	P(O)(OEt)$_2$
g	CH$_2$=CHCH$_2$	H	Et$_3$Si

i) 1. SOCl$_2$ (9 equiv.), 90°, 3 h; 2. NaOH, Bu$_4$NBr, EtCOOH, H$_2$O/CH$_2$Cl$_2$, r.t. 3 h. *ii*) Me$_3$SiNHCOOEt (**28**; 3 equiv.), EtCOCl (3 equiv.), CH$_2$Cl$_2$, 40°, 14 h. *iii*) 1. LHMDS (2 equiv.); 2. ^{t}BuMe$_2$SiCl (2 equiv.), THF/HMPA (10 vol-%), $-78° \rightarrow$ r.t., 1 h. *iv*) 1. LHMDS (1.5 equiv.); 2. Et$_3$SiCl (1.5 equiv.), THF/DMPU (10 vol-%), $-78° \rightarrow$ r.t., 1 h. *v*) 1. LHMDS (1.2 equiv.); 2. P(O)(OEt)$_2$Cl (1.5 equiv.), THF/DMPU (10 vol-%), $-78° \rightarrow$ r.t., 1 h.

Table 3. *Synthesis of the Ketene N,O-Acetals* **27a**–**g** (see *Scheme 9*)

Amide	Imide			Ketene acetal		
		Method	Yield[a])/%		Method	Yield[a])/%
25a	**26a**	*i*)	88	**27a**	*iii*)	85
25b	**26b**	*i*)	93	**27b**	*iii*)	93
25c	**26c**	*ii*)	97	**27c**	*iii*)	90
25d	**26d**	*ii*)	90	**27d**	*iii*)	93
25e	**26e**	*ii*)	96	**27e**	*iii*)	86
	26a			**27f**	*iv*)	71
	26a			**27g**	*v*)	64

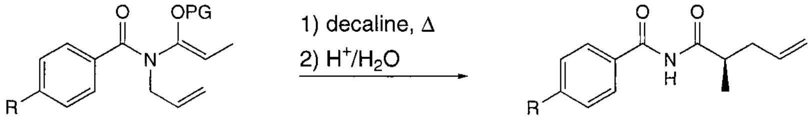
[a]) Isolated yields.

a HCl-sponge to push the equilibrium to the product side. Under these conditions, the imides **26c**–**e** were prepared in excellent yields (90–97%).

The corresponding *N*-alkenyl-*N*-benzoyl-*O*-silyl-substituted ketene N,O-acetals **27a**–**e**,**g** were prepared in good to excellent yields (64–93%) according to a previously published method [9] (*Scheme 9*, *Table 3*) which was modified. Thus, the imides **26a**–**e** were treated at −78° in THF with the milder base LHMDS [25] (instead of LDA) in the presence of a co-solvent (HMPA or DMPU) and quenched with ^{t}BuMe$_2$SiCl or Et$_3$SiCl. The phosphate-protected ketene acetal **27f** was prepared in the same way from **26a** using diethyl phosphorochloridate [26]. The stabilities of the benzoyl-substituted ketene acetals were much higher than the stabilities of the known *N*-benzyl-*N*-butadienyl- or *N*-isopropyl-*N*-butadienyl-substituted ketene acetals [9], allowing their purification by FC. Only the (*Z*)-enolates were formed, due to the allylic strain in the ground state [27].

2.2.2. *Thermal Amino*-Claisen *Rearrangements.* It is known that neutral [3,3]-sigmatropic rearrangements of ketene N,O-acetals require high reaction temperatures ranging from 135–190° [1f–h][10][25b][28]. Using the enolate derived from *N*-acyl-vinylaziridin lowered the rearrangement temperature to room temperature due to the release of the ring strain [29]. The best results with acyclic ketene acetals were achieved when the enolates were prepared *in situ* [10b]. However, due to the planned application of the amino-*Claisen* rearrangement in the tandem reaction, we were interested to study the protected ketene acetals only. Thus, the allyl-substituted ketene acetal **27a** rearranged to **29a** at 135° as expected, but unfortunately not very efficiently (yield *ca.* 36%) (*Scheme 10*, *Table 4*). Reproducibly, 9% of the hydrolysis product *N*-allylbenzamide (**25a**) were formed, maybe by a thermal sigmatropic rearrangement process [30] followed by hydrolysis during workup, along with other by-products that were not isolated. Different hydrolysis and workup conditions did not increase the yield of **29a**. The change of the protecting groups did not improve the yields either. Thus, the more stable phosphate-protected **27f**, which required a higher rearrangement temperature (153°), gave only 7% of the rearranged product **29f**, and the (triethylsilyl)-protected **27a** rearranged to 40% (*Table 4*). Interestingly, a *p*-substituent at the benzoyl group of the ketene N,O-acetals has a stabilizing effect, the *p*-Me-substituted **27d** yielding up to 49% of *rac*-**29d** and the *p*-MeO-substituted **27e** yielding 41% of *rac*-**29e**.

Scheme 10



27a,d-g *rac*-**29a,d-g**

	R	PG
a	H	$^{t}BuMe_2Si$
d	Me	$^{t}BuMe_2Si$
e	MeO	$^{t}BuMe_2Si$
f	H	$P(O)(OEt)_2$
g	H	Et_3Si

Table 4. *Amino-*Claisen *Rearrangements of Ketene Acetals* **27a,d–g** *with Different Protecting Groups*

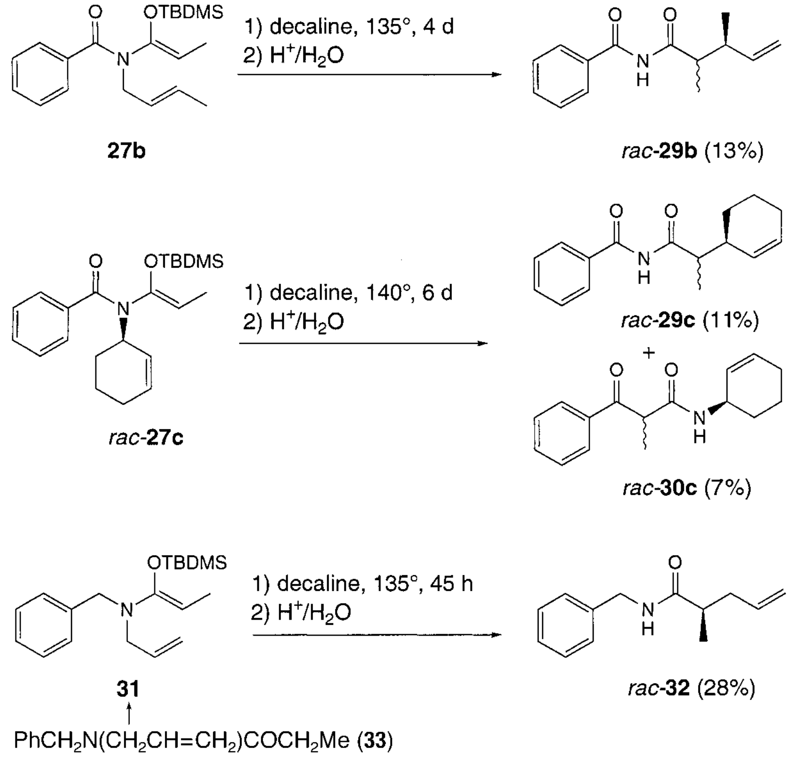
Starting material	*T*/°	*t*/h	Yield/%	Product
27a	135	18	36	**29a**
27d	135	40	49	**29d**
27e	135	30	41	**29e**
27f	153	18	7	**29f**
27g	135	21	40	**29g**

The rearrangement of compounds **27b** and **27c**, structurally closer to the intermediate of the planned tandem reaction, was significantly less efficient (*Scheme 11*). The but-2-enyl-substituted ketene acetal **27b** led, after 4 days, to only 13% of the diastereoisomer mixture *rac*-**29b**, the epimerization at C(α) being caused by the high reaction temperature and long reaction time. This problem has already been reported by *Kurth et al.* [10c]. In the case of the cyclohexenyl-substituted ketene acetal **27c**, the reaction time was even longer (6 days), and only 11% of *rac*-**29c** were isolated, along with 7% of the by-product *rac*-**30c**. The formation of *rac*-**30c** is due to an intramolecular acylation process (see discussion in *Sect. 2.2.3*).

For comparison, the benzyl-protected ketene acetal **31**, prepared from *N*-allyl-*N*-benzylpropanamide (**33**) [31] according to [9b], was also submitted to the amino-*Claisen* rearrangement (*Scheme 11*). However, the reduced stability of **31** had also a negative effect on the rearrangement, only 28% of the rearranged product *rac*-**32** could be isolated.

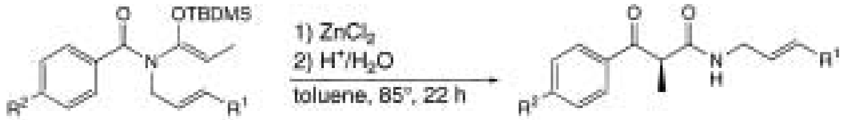
2.2.3. *Catalyzed Amino-*Claisen *Rearrangements.* [3,3]-Sigmatropic rearrangements can be catalyzed by different methods [32], *Lewis* acids having been successfully applied [1b][33]. It is assumed that the *Lewis* acid interacts with the N-lone pair, facilitating the bond breaking between the C-atom of the olefin-containing part of the molecule and the N-atom. Only amino-*Cope* rearrangements catalyzed by *Lewis* acids are known. No catalyst has been reported for the [3,3]-sigmatropic rearrangement of ketene N,O-acetals. We now tested $ZnCl_2$ as catalyst in the rearrangement of the *O*-silyl-substituted ketene N,O-acetals **27a,b,d**, assuming that complexation of $ZnCl_2$ to the carbonyl O-atom should facilitate the bond-breaking process. Applying the described conditions, *i.e.* 0.7 equiv. of catalyst in toluene [34], at 85° to **27a**, complete

Scheme 11. *Amino*-Claisen *Rearrangements under Thermal Conditions.* TBDMS = ^{t}BuMe$_2$Si.



transformation was indicated by TLC, but on FC, the product decomposed completely. However, normal workup was possible after addition of an excess of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and removal of the solid [Zn(TMEDA)] complex. After hydrolysis, 85% of *rac*-**30a** were isolated (*Scheme 12*). We rationalize the product formation by assuming that the *Lewis* acid activates the carbonyl group and facilitates the intramolecular attack of the ketene acetal.

Scheme 12. *ZnCl$_2$-Catalyzed Intramolecular Acylation.* TBDMS = ^{t}BuMe$_2$Si.

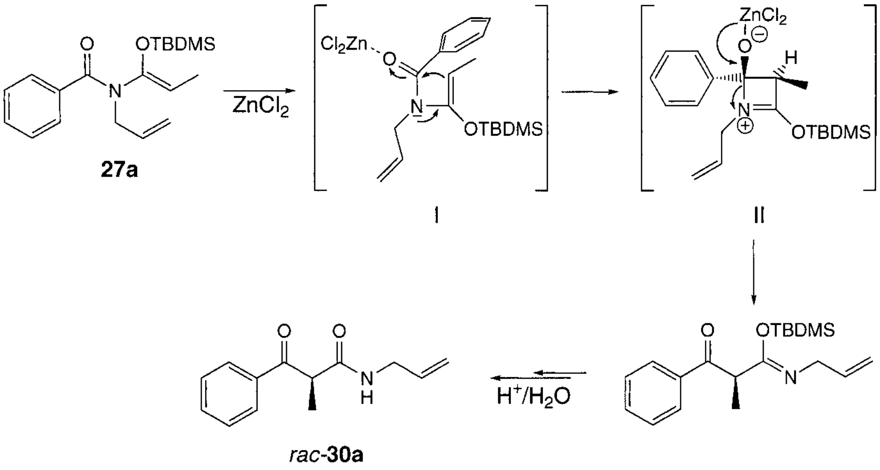


27a	R^1 = R^2 = H	85%	*rac*-**30a**	R^1 = R^2 = H
b	R^1 = Me, R^2 = H	84%	*rac*-**30b**	R^1 = Me, R^2 = H
d	R^1 = H, R^2 = Me	61%	*rac*-**30d**	R^1 = H, R^2 = Me

To determine whether the mechanism of the reaction **27a** → **30a** is inter- or intramolecular, we made a cross-over experiment. Submitting the isomeric acetals **27b** and **27d** separately to the catalyzed rearrangement, the acylation occurred with 84 (*rac*-**30b**) and 61% yield (*rac*-**30d**), respectively (*Scheme 12*). Submitting the 1:1 mixture

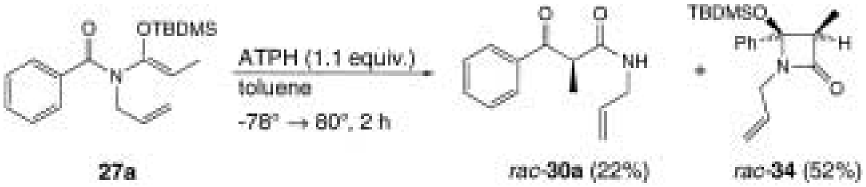
27b/**27d** allowed us to distinguish between the inter- and the intramolecular mechanism: MS and NMR analysis of the reaction mixture showed only two compounds, no cross-over products were observed. The acylation follows, therefore, an intramolecular pathway (*Scheme 13*).

Scheme 13. *Proposed Mechanism for the Intramolecular Acylation.* TBDMS = ^{t}BuMe$_2$Si.



Other *Lewis* acids showed either no activity as catalysts or induced intramolecular acylation as observed with $ZnCl_2 \cdot Sc(OTf)_3$, $[Zr(Cp)_2Cl_2]$, $AlCl_3$, and $BF_3 \cdot OEt_2$ were inactive. $TiCl_4$ catalyzed the intramolecular acylation like $ZnCl_2$. A very interesting reaction was observed with a catalyst developed by *Yamamoto* and co-workers [35], *i.e.* aluminium tris(2,6-diphenylphenoxide) (ATPH), which possesses sterically highly demanding ligands and allows to block efficiently the carbonyl groups. We hoped to activate the N-atom *via* the carbonyl O-atom and to block at the same time sterically the C-atom of the carbonyl group. However, no amino-*Claisen* rearrangement of ketene acetal **27a** was observed in the presence of ATPH, only the acylation product *rac*-**30a** and a diastereoisomerically pure product *rac*-**34** were isolated (*Scheme 14*). Compound *rac*-**34** is the silylated equivalent of the postulated intermediate **II** of the intramolecular acylation process (*Scheme 13*), suggesting a competition between hydrolysis of **II** to form *rac*-**30a** and trans-silylation to form *rac*-**34**.

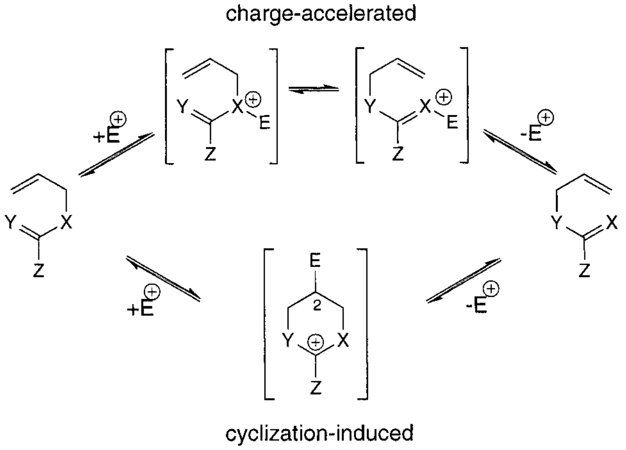
Scheme 14. *Reaction Catalyzed by the Sterically Highly Demanding* Lewis *Acid ATPH* [35]. TBDMS = ^{t}BuMe$_2$Si.



The structure of *rac*-**34** was deduced as follows: the IR spectra show the C=O absorption at 1764 cm^{-1}. This value is relatively high for amides and is compatible with the β-lactam structure. The ^{13}C-NMR chemical shift of the silyloxy-substituted C(4) is *ca.* 90 ppm. Ketene N,O-acetals would show a value of *ca.* 140 ppm. The $CH_2{=}CHCH_2$ protons are diastereotopic; therefore, the molecule must have at least one asymmetric center. In the ^{1}H,^{1}H-NOESY plot, the ^{t}BuMe$_2$Si protons show a cross-peak with the Ph protons indicating their neighborhood. The relative *cis* configuration at the two chiral centers is indicated by a ^{1}H,^{1}H-NOESY cross-peak H–C(3)/Ph.

Another possibility to catalyze *Claisen* rearrangements is the use of 'weak' electrophiles like Pd^{II} in the form of [Pd(PhCN)$_2$Cl$_2$] [32][36]. In contrast to a 'charge-accelerated' mechanism using *Lewis* acids, this catalysis proceeds *via* a 'cyclization-induced' pathway [37] (*Scheme 15*). *Overman et al.* suggest that in the 'cyclization-induced' mechanism, the Pd^{II} forms first a complex with the less substituted double bond. Cyclization to the cationic intermediate which can be stabilized by a electron-donating group Z and fragmentation yield the rearranged product. Pd^{II} belongs to the catalyst group of type 1 [38], forming the same rearrangement products as the thermal reaction since the 'cyclization-induced' pathway resembles the thermal, concerted mechanism. Chiral Pd^{II}-catalysts have also been used successfully for asymmetric rearrangements of allyl imidates [33c][39].

Scheme 15. *Postulated Mechanisms for the Catalysis of [3,3]-Sigmatropic Rearrangements According to* Overman [36]



The allyl-substituted ketene acetal **27a** was rearranged under standard conditions [36] with 50 mol-% of [Pd(PhCN)$_2$Cl$_2$] (1 h at 0°) to 48% of *rac*-**29a** (*Scheme 16*, *Table 5*). We were unable to improve this yield by varying the catalyst amount or by changing the workup.

The reaction of the cyclohexenyl-substituted ketene acetal **27c** in the presence of [Pd(PhCN)$_2$Cl$_2$] gave 37% of *rac*-**35**, 8% of *rac*-**36**, and 12% of *rac*-**37** (*Scheme 16*). Astonishingly, no rearrangement occurred. Isomerization product *rac*-**35** is probably formed *via* complexation of Pd^{II} with the ketene-acetal C=C bond. The Pd^{II} complex can now rotate around the formal single bond to give, after elimination, the thermodynamically more stable (*E*)-diastereoisomer *rac*-**35**. The cyclization products

Scheme 16. *Pd-Catalyzed Reaction of* **27a** *and of* rac-**27c**

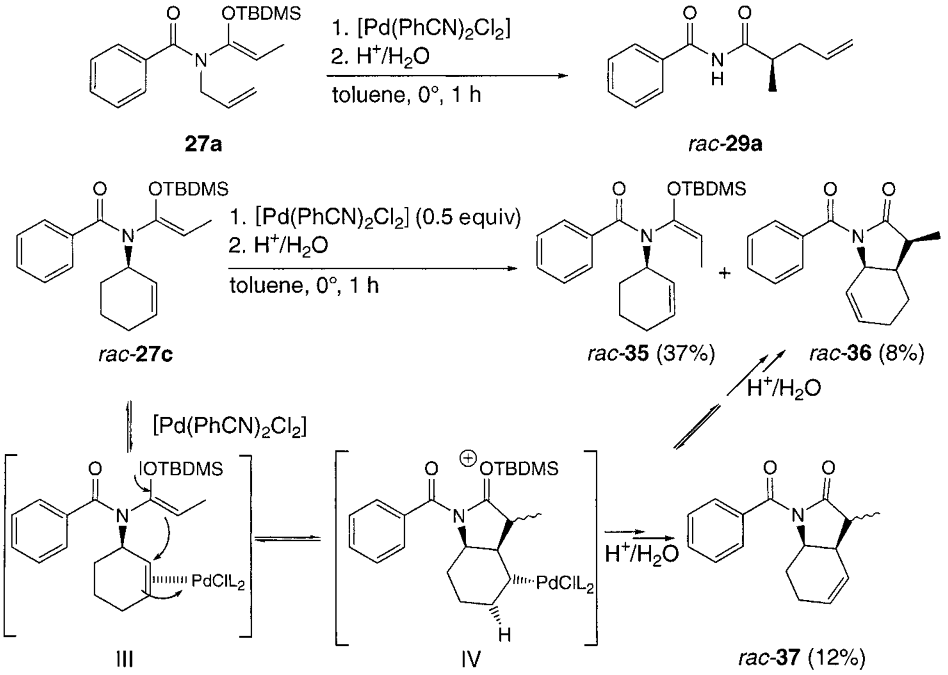


Table 5. *Yields of* rac-**27a** *Depending on the Amount of Catalyst Used*

mol-% of [Pd(PhCN)$_2$Cl$_2$]	Yield/%		
	rac-**29a**	**27a** (isolated)	recovered organic material
10	21	70	91
30	28	–	–
40	43	10	53
50	48	0	48
100	0	0	0

rac-**36** and *rac*-**37** can arise *via* a π-complex **III**, which is in equilibrium with a σ-complex **IV** by nucleophilic addition of the ketene-acetal moiety to the palladium-olefin complex. Subsequent hydride elimination from the β-position and hydrolysis lead to *rac*-**37**. A second addition of the palladium hydride at the regenerated double bond followed by elimination yield the regioisomeric olefin *rac*-**36**. The relative configuration of the Me substituent at the five-membered ring of *rac*-**37** could not be determined. But if the proposed pathway to the two cyclization products is correct, it should be the same for both *rac*-**36** and *rac*-**37**, assuming that no epimerization occurs after cyclization.

Other weak electrophiles like Hg(OCOCF$_3$)$_2$ as well as other Pd-catalysts like Pd(OAc)$_2$, [Pd(allyl)$_2$Cl$_3$], PdCl$_2$, Li$_2$PdCl$_2$, or [Pd(PPh$_3$)$_4$] showed no effect on our rearrangement [32][40]. Also Ni^0 prepared *in situ* was not catalyzing our rearrangement [32][41].

3. Conclusions. – The goal of our study has been to analyze the two parts of our planned tandem reaction separately. We studied the *Diels-Alder* reactivity first and developed a synthesis for *N*-butadienyl-substituted imides. The known synthesis for *N*-butadienylamides was shortened, and the process was optimized to yield the (*E*)-diastereoisomer preferentially. The *Diels-Alder* reactions of the newly synthesized *N*-butadienyl-substituted imides were tested. The benzoyl-substituted ketene acetal **14** showed the desired stability towards hydrolysis as well as sufficient reactivity in the *Diels-Alder* reaction. The benzyl-substituted ketene acetal **7** polymerized under our reaction conditions, due to a mechanism not known at the moment. The ketene acetals substituted by an electron-attracting substituent showed enhanced stability and reduced propensity for polymerization.

To evaluate the second part of the planned tandem reaction *Diels-Alder* cycloaddition/amino-*Claisen* rearrangement, we tested the reactivity of differently substituted ketene N,O-acetals under thermal conditions to undergo an amino-*Claisen* rearrangement. In this context, we developed a synthesis under mild and neutral conditions for differently *N*-substituted imides, using the silylcarbamate **28** as neutral base. These imides were then transformed by LHMDS into their corresponding ketene N,O-acetals in excellent yields. The ketene N,O-acetals substituted by benzoyl groups are more stable towards hydrolysis than the ketene N,O-acetals substituted by a benzyl group. The ketene acetals **27a – g** underwent the rearrangement under thermal conditions; however, the yields obtained were low, due to the high reaction temperatures needed, and the stereoselectivity was lost due to epimerization after the rearrangement. No catalytic system allowing lower temperatures could be found. *Lewis*-acid catalysis promoted an interesting intramolecular acylation process, producing the diastereoisomerically pure β-lactam *rac*-**34** instead. Catalysis by a Pd^{II} complex gave the desired rearranged product, but only from the allyl-substituted ketene acetal **27a**. In the case of the cyclohexenyl-substituted ketene acetal **27c**, the two interesting cyclization products *rac*-**36** and *rac*-**37** were formed. Other catalysts were ineffective.

The conditions found for the individual steps of our planned tandem reaction are, at the moment, incompatible with each other. However, the reactivity studies clearly indicate that the highly electron-rich ketene-acetal moiety is responsible for most of the problems observed. It will, therefore, be necessary to reduce the electron density in this part of the molecule to successfully combine them in our tandem reaction.

The NMR spectra (400 MHz) were measured by *Heinz Bursian* and Dr. *Saturnin Claude*, the MS by Dr. *Guy-Marie Dubin*, *Armelle Michel*, and *Christine Poliart*, and the HR-MS by *Fredy Nydegger* at the University of Fribourg.

We gratefully acknowledge the University of Neuchâtel and the *Swiss National Science Foundation* for support of this work.

Experimental Part

General. All moisture-sensitive reactions were carried out under Ar or N_2 using oven-dried glassware. All reagents were of commercial quality if not otherwise mentioned. Solvents were freshly distilled prior to use from the following drying agents: THF (K), toluene (K), CH_2Cl_2 (CaH_2), Et_2O ($LiAlH_4$). Flash chromatography: *Merck* silica gel *60*, 230 – 400 mesh, under positive pressure, 0.5 – 0.9 bar. TLC: precoated silica gel *60* F_{254} thin-layer sheets from *Merck*, detection by UV or/and basic $KMnO_4$. M.p.: *Gallenkamp MFB-595*; uncorrected.

Refraction index (n_D): *Carl Zeiss*. UV/VIS Spectra: *Perkin-Elmer-320* spectrophotometer; λ_{max} (ε) in nm. IR Spectra: *Perkin Elmer FT-IR 1720 X*; in cm^{-1}. NMR Spectra: *Bruker AMX-400* (400 and 100 MHz) or *Varian Gemini XL-2000* (200 and 50 MHz); at r.t., if not specified, chemical shifts in ppm rel. to $SiMe_4$ (=0 ppm) as internal reference; internal standard for ^{31}P-NMR, $(PhO)_3PO$ (= −18 ppm); coupling constants *J* in Hz. MS: *Nermag RC 30-10*; EI, 70 eV; DCl, NH_4^+. ESI-MS: *Finnigan LCQ*. HR-MS: *Bruker FTMS 4.7T BioAPEX II*.

Starting Materials. They were prepared according to literature procedures. *N*-Benzyl-*N*-[(*E*)-buta-1,3-dienyl] propanamide (**6**) [9], *N*-[(*E*)-buta-1,3-dienyl]-*N*-((*Z*)-1-([(*tert*-butyl)dimethylsilyl]oxy}prop-1-enyl)-benzenemethanamine (**7**) [9], *N*-(1*H*-benzotriazol-1-ylmethyl)benzamide (**11**) [14], (2*E*)-*N*-(2-phenylethyl)-but-2-en-1-imine **38** [42], *N*-prop-2-enylbenzamide (**25a**) [22a,b], *N*-[(*E*)-but-2-enyl]benzamide (**25b**) [22b][43], *N*-cyclohex-2-enylbenzamide (**25c**) [22b,d], 4-methyl-*N*-prop-2-enylbenzamide (**25d**) [22c,e], 4-methoxy-*N*-prop-2-enylbenzamide (**25e**) [22a,f], ethyl (trimethylsilyl)carbamate (**28**) [17], *N*-benzyl-*N*-prop-2-enylpropanamide (**33**) [31].

N-*[(*E*)-Buta-1,3-dienyl]-*N-*(2-phenylethyl)propanamide* (**10**). From (2*E*)-*N*-(2-phenylethyl)but-2-en-1-imine (**38**) according to [9]: **10** (26.6 g, 72%). Slightly yellow and very viscous oil. n_D^{20} = 1.5708. R_f (hexane/AcOEt 4:1 +1% MeOH) 0.63. IR (film): 3086*w*, 3063*w*, 3028*w*, 2980*m*, 2940*m*, 2877*w*, 1677*s*, 1636v*s*, 1604*m*, 1498*m*, 1456*m*, 1427*s*, 1387*s*, 1346*m*, 1308*m*, 1265*m*, 1239*m*, 1165*s*, 1074*m*, 1033*m*, 1000*m*, 886*m*, 748*m*, 701*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO, 353 K): 7.32–7.10 (*m*, 5 arom. H, CH=C*H*N); 6.40 (*dtd*, ^3J = 16.9, 10.2, 10.2, ^4J = 0.6, CH_2=C*H*); 5.85 (*dd*, ^3J = 14.0, 10.3, C*H*=CHN); 5.14 (*dd*, ^3J = 16.9, ^2J = 1.9, 1 H, CH_2=CH (*cis*)); 4.94 (*dd*, ^3J = 10.2, ^2J = 1.9, 1 H, CH_2=CH(*trans*)); 3.81 (*t*, ^3J = 7.7, CH_2CH_2N); 2.81 (*t*, ^3J = 7.7, C$H_2$$CH_2$N); 2.42 (*q*, ^3J = 7.2, MeCH_2); 1.01 (*t*, ^3J = 7.3, *Me*CH_2). ^{13}C-NMR (100 MHz, (D_6)DMSO 353 K): 171.6 (C=O); 138.4 (arom. C); 135.4 (*C*H=CH_2); 130.2 (CH=*C*HN); 128.3, 128.0, 125.9 (arom. C); 113.0 (*C*H_2=CH); 111.5 (*C*H=CHN); 44.0 (CH_2*C*H_2N); 32.6 (*C*$H_2$$CH_2$N); 25.9 (Me*C*$H_2$); 8.6 (*Me*$CH_2$). EI-MS: 230 (13, M^+), 175 (11), 122 (50), 105 (87), 96 (33), 79 (12), 77 (100), 69 (21), 68 (39), 67 (29), 58 (25), 53 (11), 51 (26). HR-ESI-MS: 230.1541 ([M+H]$^+$, $C_{15}H_{20}NO^+$; calc. 230.1539).

N-*[(*E*/*Z*)-Buta-1,3-dienyl]benzamide* (**12a/b**). To a freshly prepared LDA soln. (16.5 ml (117 mmol) of ^{i}Pr$_2$NH, 74 ml (118 mmol) of 1.6M BuLi in 80 ml of THF) kept at −78°, a soln. of **11** (13.9 g; 55.1 mmol) in THF (300 ml) was added in 30 min. After the first drop, the soln. became dark-violet. After 2 h stirring at −78°, allyl bromide (4.70 ml; 672 mg, 55.5 mmol) was quickly added. After 10 min, the mixture was allowed to warm to r.t. and stirred overnight. The orange mixture was then diluted with AcOEt and washed with sat. NaCl soln. (3 ×). The combined org. phases were dried (Na_2SO_4). FC (SiO_2, hexane/AcOEt 12:1 → 7:1): **12a/b** (7.58 g, 79%), mixture of isomers.

(*E*)-Isomer **12a**: M.p. 122.1°. R_f (hexane/CH_2Cl_2 4:1 +1% MeOH) 0.13. IR (KBr): 3294*s*, 3088*w*, 3062*w*, 3049*w*, 3032*w*, 3000*w*, 2923*w*, 2851*w*, 2385*w*, 1963*w*, 1904*w*, 1782*w*, 1645v*s*, 1605*s*, 1581*m*, 1516*s*, 1490*m*, 1447*m*, 1407*m*, 1317*s*, 1246*w*, 1200*m*, 1157*w*, 1097*w*, 1075*w*, 1028*w*, 694*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.06 (br. *d*, ^3J = 9.8, NH); 7.82–7.80 (*m*, 2 arom. H); 7.55–7.50 (*m*, 1 arom. H); 7.46–7.42 (*m*, 2 arom. H); 7.21 (*dd*, ^3J = 14.1, 10.9, CH=C*H*N); 6.35 (*ddd*, ^3J = 16.9, 10.4, 10.4, C*H*=CH_2); 5.99 (*dd*, ^3J = 14.1, 10.7, C*H*=CHN); 5.11 (*ddd*, ^3J = 16.9, $^2J \approx {}^4J$ = 0.7, 1 H, CH_2=CH (*cis*)); 5.00 (*dt*, ^3J = 10.6, $^2J \approx {}^4J$ = 0.7, 1 H, CH_2=CH(*trans*)). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.5 (C=O); 134.5 (*C*H=CH_2); 133.3, 132.1, 128.7, 127.1 (arom. C); 126.1 (CH=*C*HN); 114.8 (*C*H=CHN, *C*H_2=CH). EI-MS: 173 (27, M^+), 106 (9), 105 (100), 77 (50).

(*Z*)-Isomer **12b**: M.p. 93.5°. R_f (hexane/CH_2Cl_2 4:1 +1% MeOH) 0.08. IR (KBr): 3271*m*, 3162*w*, 3068*w*, 3016*w*, 2982*w*, 2926*w*, 2789*w*, 2642*w*, 2555*w*, 2323*w*, 1965*w*, 1922*w*, 1819*w*, 1734*w*, 1655*s*, 1638v*s*, 1601*s*, 1578*m*, 1510*s*, 1485*s*, 1425*m*, 1364*m*, 1307*m*, 1279v*s*, 1187*m*, 1160*w*, 1132*m*, 1104*w*, 1077*m*, 1045*m*, 1028*w*, 1001*m*, 704*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.02 (br. *d*, ^3J = 9.1, NH); 7.82–7.80 (*m*, 2 arom. H); 7.57–7.48 (*m*, 1 arom. H); 7.47–7.45 (*m*, 2 arom. H); 6.94 (br. *dd*, $^3J \approx$ 10.0, 10.0, CH=C*H*N); 6.54 (*dddd*, ^3J = 16.6, 11.3, 10.3, ^4J = 1.0, C*H*=CH_2); 5.54 (*dd*, ^3J = 10.9, 9.5, C*H*=CHN); 5.29 (*ddd*, ^3J = 16.6, ^2J = 1.6, ^4J = 0.8, 1 H, CH_2=CH(*cis*)); 5.15 (*ddd*, ^3J = 10.3, ^2J = 2.5, ^5J = 1.5, 1 H, CH_2=CH(*trans*)). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.2 (C=O); 133.5, 132.2 (arom. C); 128.8 (arom. C, *C*H=CH_2); 127.1 (arom. C); 121.8 (CH=*C*HN); 117.2 (*C*H_2=CH); 111.4 (*C*H=CHN). EI-MS: 173 (24, M^+), 105 (100), 86 (14), 84 (22), 77 (57), 51 (20), 49 (18).

N-*[(*E*)-Buta-1,3-dienyl]benzamide* (**12a**). To a soln. of **12a/b** (336 mg, 1.94 mmol) in degassed dioxane (15 ml), DBU (0.90 ml, 917 mg, 6.02 mmol) was added. The soln. was stirred under reflux for 4 h, then diluted with AcOEt, and washed with H_2O. The combined org. phase was dried (Na_2SO_4). FC (SiO_2, hexane/AcOEt 12:1): **12a** (242 mg, 72%). Slightly yellow solid.

N-*[(*E*)-Buta-1,3-dienyl]-*N-*propanoylbenzamide* (**13**). At r.t., 1-methoxy-2-methyl-1-[(trimethylsilyl)oxy]-propene (13.6 ml, 67.1 mmol) and propanoyl chloride (6 ml, 68.7 mmol) were added to a soln. of **12a** (3.91 g, 22.6 mmol) in CH_2Cl_2 (50 ml). After 18 h stirring at r.t., the mixture was diluted with CH_2Cl_2 and washed with sat. $NaHCO_3$ soln. (2 ×) and sat. NaCl soln. The combined org. phase was dried ($MgSO_4$). FC (SiO_2, hexane/

AcOEt 10:1): **13** (3.46 g, 67%). Yellow oil. R_f (hexane/AcOEt 4:1 +1% MeOH) 0.40. IR (KBr): 3064*m*, 2983*s*, 2943*m*, 2882*m*, 2450*w*, 1975*w*, 1696v*s*, 1644*s*, 1600*s*, 1452*s*, 1421*s*, 1360*s*, 1329*s*, 1291*s*, 1253*s*, 1226*s*, 1179*s*, 1148*s*, 1077*s*, 1042*m*, 1001*s*, 937*s*, 888*s*, 809*s*, 724*s*, 693*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.80–7.77 (*m*, 2 arom. H); 7.59–7.55 (*m*, 1 arom. H); 7.48–7.43 (*m*, 2 arom. H); 6.97 (*dm*, $^3J = 14.1$, CH=C*H*N); 6.24 (*dt*, $^3J = 17.1$, 10.2, 10.2, C*H*=CH_2); 5.59 (*dddd*, $^3J = 14.4$, 10.6, $^4J = 0.8$, 0.8, C*H*=CHN); 5.00–4.95 (*m*, CH_2=CH); 2.55 (*q*, $^3J = 7.4$, MeCH_2); 1.16 (*t*, $^3J = 7.4$, *Me*CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): 174.0 (Ph*C*O); 172.4 (MeCH_2*C*O); 133.7 (*C*H=CH_2, arom. C); 133.2, 130.1, 128.9 (arom. C); 128.1 (CH=*C*HN); 123.7 (*C*H=CHN); 117.4 (*C*H_2=CH); 29.7 (Me*C*H_2); 9.2 (*Me*CH_2). EI-MS: 230 (9, $[M+1]^+$), 229 (11, M^+), 174 (9), 173 (31), 105 (100), 86 (12), 84 (19), 77 (54), 57 (14), 51 (11). HR-ESI-MS: 230.1200 ($[M+H]^+$, $C_{14}H_{16}NO_2^+$; calc. 230.1176).

N-*[(*E*)-Buta-1,3-dienyl]*-N-*((*Z*)-1-{[(*tert-*butyl)dimethylsilyl]oxy}prop-1-enyl)benzamide* (**14**). Under N_2, a mixture of THF (2.2 ml) 1M LHMDS (2.2 ml, 2.2 mmol), and DMPU (1.0 ml, 8 vol.-%) was cooled to −85°. A soln. of **13** (0.38 g, 1.66 mmol) in THF (4.4 ml) was added in 15 min, and the mixture was stirred for 30 min. The temp. was lowered to −90°, and a soln. of ^{t}BuMe$_2$SiCl (0.33 g, 2.20 mmol) in THF (2.2 ml) was quickly added. After 1 h stirring at −78°, the mixture was allowed to warm to r.t., diluted with pentane, and washed successively with sat. NH_4Cl and sat. NaCl soln. The combined org. phase was dried (Na_2SO_4) and evaporated: **14** (0.56 g, 99%). Yellow oil. R_f (hexane/AcOEt 4:1 +1% MeOH) 0.56. IR (KBr): 3317*w*, 3061*m*, 3038*w*, 2957*s*, 2931*s*, 2887*m*, 2859*s*, 2712*w*, 1737*m*, 1667v*s*, 1581*m*, 1493*w*, 1473*s*, 1464*m*, 1447*m*, 1420*m*, 1385*m*, 1333v*s*, 1255v*s*, 1154v*s*, 1127*s*, 1083*s*, 1031*m*, 1006*s*, 956*m*, 939*m*, 905*m*, 889*m*, 840v*s*, 784*s*, 708*s*, 698*s*, 682*m*, 672*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63 (*dd*, $^3J = 7.0$, $^4J = 1.5$, 2 arom. H); 7.42 (*tt*, $^3J = 7.3$, $^4J = 1.7$, 1 arom. H); 7.36 (*td*, $^3J = 6.6$, 6.6, $^4J = 1.5$, 2 arom. H); 7.20–7.10 (br. CH=C*H*N); 6.36 (*dt*, $^3J = 16.9$, 10.3, 10.3, C*H*=CH_2); 5.96 (*dd*, $^3J = 14.1$, 10.8, C*H*=CHN); 5.13 (*ddt*, $^3J = 16.9$, $^2J = 1.6$, $^4J \approx {}^5J = 0.8$, 1 H, CH_2=CH(*cis*)); 5.00 (*ddt*, $^3J = 10.2$, $^2J = 1.5$, $^4J \approx {}^5J = 0.7$, 1 H, CH_2=CH(*trans*)); 4.67 (*q*, $^3J = 6.5$, MeC*H*=C); 1.57 (*d*, $^3J = 6.8$, *Me*CH=C); 0.87 (*s*, ^{t}BuSi); 0.13 (*s*, Me$_2$Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 168.6 (C=O); 140.0 (*C*OSi); 135.2 (arom. C); 134.6 (*C*H=CH_2); 130.6 (arom. C); 130.0 (CH=*C*HN); 128.0, 127.8 (arom. C); 115.9 (*C*H=CHN); 115.0 (*C*H_2=CH); 105.9 (Me*C*H=C); 25.5 (*Me*$_3$CSi); 18.1 (Me$_3$*C*Si); 10.7 (*Me*CH=C); −4.2 (Me$_2$Si). EI-MS: 344 (2, $[M+1]^+$), 286 (4), 238 (4), 212 (2), 156 (14), 106 (15), 105 (100), 77 (29), 75 (13), 73 (36). HR-ESI-MS: 344.2041 ($[M+H]^+$, $C_{20}H_{30}NO_2Si^+$; calc. 344.2040).

2-[Benzyl(propanoyl)amino]cyclohex-3-ene-1-carboxylic Acid Methyl Ester (*rac*-**17**). Typical procedure: A mixture of **6** (1.24 g, 5.76 mmol), methyl acrylate (12.0 ml, 133 mmol), and BHT (50 mg, 0.23 mmol) was heated under protection from light at 60° during 67 h. The excess methyl acrylate was evaporated: *rac*-**17** (1.65 g, 95%), *cis*/*trans* ratio 2:1. Colorless oil. R_f (hexane/AcOEt 4:1 +1% MeOH) 0.16. IR (film): 3087*w*, 3063*w*, 3029*w*, 2977*m*, 2947*m*, 2882*m*, 2840*w*, 1955*w*, 1734*s*, 1651*s*, 1606*w*, 1496*m*, 1453*m*, 1435*s*, 1412*s*, 1365*m*, 1314*m*, 1269*m*, 1232*s*, 1199*m*, 1175*s*, 1076*w*, 1041*m*, 1029*m*, 967*m*, 754*m*, 734*m*, 669*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO, 373 K; *trans-rac*-**17**): 7.31–7.15 (*m*, 5 arom. H)^2); 5.86–5.82 (*m*, H−C(4)); 5.41 (*dq*, $^3J = 10.1$, $J = 2.2$, H−C(3)); 5.02 (br., H−C(2)); 4.64–4.25 (*m*, PhCH_2)^2); 3.53, 3.52 (*s*, MeO (rotamers)); 2.72–2.66 (*m*, H−C(1)); 2.35–2.18 (*m*, MeCH_2))^2); 2.12–1.96 (*m*, CH_2(5))^2); 1.92–1.67 (*m*, CH_2(6))^2); 1.03 (*t*, $^3J = 7.2$, *Me*CH_2). ^{13}C-NMR (100 MHz, (D_6)DMSO, 373 K; *trans-rac*-**17**): 174.1, 174.0 (COO, MeCH_2*C*O); 139.5 (arom. C); 130.5 (C(4)); 128.3 (arom. C); 127.7 (C(3)); 126.8, 126.7 (arom. C); 51.4 (MeO); 50.4 (C(2)); 48.4 (Ph*C*H_2); 43.8 (C(1)); 26.4 (Me*C*H_2); 25.4, 23.7 (C(6), C(5)); 9.5 (*Me*CH_2). ^{1}H-NMR (400 MHz, (D_6)DMSO, 373 K; *cis-rac*-**17**): 7.31–7.15 (*m*, 5 arom. H)^2); 5.89 (*m*, H−C(4)); 5.54 (*ddt*, $^3J = 10.1$, $J = 4.2$, 2.1, H−C(3)); 5.25 (br., H−C(2)); 4.64–4.25 (*m*, PhCH_2)^2); 3.57, 3.56 (*s*, MeO (rotamers)); 2.97 (*ddd*, $J = 10.4$, 6.1, 4.2, H−C(1)); 2.35–2.18 (*m*, MeCH_2)^2); 2.12–1.96 (*m*, CH_2(5))^2); 1.92–1.67 (*m*, CH_2(6))^2); 0.96 (*t*, $^3J = 7.2$, *Me*CH_2).^{13}C-NMR (100 MHz, (D_6)DMSO, 373 K; *cis-rac*-**17**): 174.1, 174.0 (COO, MeCH_2*C*O); 139.5 (arom. C); 130.5 (C(4)); 128.3 (arom. C); 127.7 (C(3)); 126.8, 126.7 (arom. C); 51.4 (MeO); 50.4 (C(2)); 48.4 (Ph*C*H_2); 43.8 (C(1)); 26.4 (Me*C*H_2); 25.4, 23.7 (C(6), C(5)); 9.5 (*Me*CH_2). EI-MS: 302 (1, $[M+1]^+$), 301 (1, M^+), 244 (14), 162 (13), 154 (47), 106 (38), 91 (100), 79 (27), 77 (14), 65 (14), 57 (19). HR-ESI-MS: 302.1755 ($[M+H]^+$, $C_{18}H_{24}NO^+$; calc. 302.1751). Anal. calc. for $C_{18}H_{23}NO$ (301.17): C 71.73, H 7.69, N 4.65; found: C 71.76, H 7.90, N 4.53.

2-[(2-Phenylethyl)propanoylamino)cyclohex-3-ene-1-carboxylic Acid Methyl Ester (*rac*-**18**). From **10**, according to *rac*-**17** (117 h): *rac*-**18**. (1.29 g, 71%), ratio *cis*/*trans* 2.7:1 (*trans-rac*-**18**; 13%; *cis-rac*-**18**, 36%; *cis*/*trans-rac*-**18** (7:3), 22%). Colorless oil.

trans-rac-**18**: R_f (hexane/AcOEt 4:1 +1% MeOH) 0.14. IR (film): 3456*w*, 3278*w*, 3086*w*, 3062*m*, 3027*s*, 2975*s*, 2939*s*, 2878*m*, 2841*m*, 2666v*w*, 2361v*w*, 2063v*w*, 1950v*w*, 1875v*w*, 1734v*s*, 1652v*s*, 1604*m*, 1497*m*, 1455v*s*, 1436v*s*, 1418v*s*, 1373*s*, 1314*m*, 1236*s*, 1217*s*, 1192*s*, 1171v*s*, 1073*m*, 1041*s*, 1000*m*, 918*m*. ^{1}H-NMR (400 MHz,

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^{2}) The *cis*- and *trans*-isomers cannot be distinguished.

(D_6)DMSO, 373 K): 7.14 – 7.04 (*m*, 5 arom. H); 5.69 (br., H–C(4)); 5.24 (*d*, $^3J = 9.9$, H–C(3)); 4.68 (br., H–C(2)); 3.45 (*s*, MeO); 3.24 – 3.12 (2*m*, PhCH$_2$CH_2); 2.75 – 2.63 (*m*, PhCH_2CH$_2$, H–C(1)); 2.20 (*q*, $^3J = 7.2$, MeCH_2); 1.96 – 1.87 (*m*, CH$_2$(5)); 1.83 – 1.80 (*m*, H–C(6)); 1.67 – 1.57 (*m*, H–C(6)); 0.88 (*t*, $^3J = 7.3$, Me). ^{13}C-NMR (100 MHz, (D_6)DMSO, 373 K): 173.4, 172.7 (COO, MeCH$_2$CO); 138.9 (arom. C); 129.3 (br. C(4)); 127.9, 127.8 (arom. C); 127.4 (C(3)); 125.6 (arom. C), 54.5 (br., C(2)); 50.8 (br., MeO); 45.1 (br., PhCH$_2$$CH_2$); 43.3 (br., C(1)); 35.2 (br., PhCH$_2$CH$_2$); 25.4 (MeCH$_2$); 24.7 (C(6)); 23.1 (C(5)); 8.9 (*Me*CH$_2$). EI-MS: 317 (23, $[M+2]^+$), 316 (86, $[M+1]^+$), 315 (14, M^+), 259 (12), 258 (65), 224 (56), 178 (51), 169 (17), 168 (95), 154 (17), 140 (11), 139 (100), 108 (11), 107 (31), 105 (36), 104 (14), 103 (11), 91 (51), 86 (14), 82 (18), 81 (17), 80 (27), 79 (99), 78 (12), 77 (36), 65 (19), 59 (15), 57 (60), 55 (18). HR-ESI-MS: 316.1908 ($[M+\mathrm{H}]^+$, $C_{19}H_{26}NO_3^+$; calc. 316.1907).

cis-rac-**18**: R_f (hexane/AcOEt 4 : 1 + 1% MeOH) 0.11. IR (film): 3475*w*, 3278*w*, 3085*w*, 3062*w*, 3026*m*, 2948*s*, 2880*m*, 2840*m*, 2669*w*, 1951*w*, 1874*w*, 1734*vs*, 1646*vs*, 1604*m*, 1497*m*, 1455*s*, 1436*s*, 1413*s*, 1370*s*, 1342*m*, 1304*s*, 1265*s*, 1232*s*, 1215*s*, 1199*s*, 1162*s*, 1088*m*, 1071*m*, 1044*s*, 1032*s*, 999*m*, 981*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO, 373 K): 7.00 – 6.86 (*m*, 5 arom. H); 5.74 – 5.71 (*m*, H–C(4)); 5.28 (*dm*, $^3J = 7.9$, H–C(3)); 4.74 (br., H–C(2)); 3.252, 3.247 (2*s*, MeO (rotamers)); 3.21 – 3.05 (*m*, PhCH$_2$CH_2); 2.62 (br., H–C(1)); 2.51 – 2.47 (*m*, PhCH_2CH$_2$); 2.11 – 2.08 (*m*, MeCH_2); 1.98 – 1.93 (*m*, H–C(5)); 1.77 – 1.67 (*m*, H–C(5)); 1.57 – 1.53 (*m*, CH$_2$(6)); 0.79 – 0.74 (*m*, *Me*CH$_2$). ^{13}C-NMR (100 MHz, (D_6)DMSO, 373 K): 173.2, 172.5 (COO, MeCH$_2$$C$O); 139.1 (br., arom. C); 130.8 (C(4)); 128.0, 125.7 (arom. C); 125.1 (C(3)); 50.6 (MeO); 49.4 (br., C(2)); 46.0 (br., PhCH$_2$$CH_2$); 43.3 (br., C(1)); 35.4 (br., PhCH$_2$CH$_2$); 25.6 (MeCH$_2$); 22.7 (C(5)); 20.6 (C(6)); 9.1 (*Me*CH$_2$). EI-MS: 317 (10, $[M+2]^+$), 316 (57, $[M+1]^+$), 315 (9, M^+), 284 (11), 259 (16), 258 (79), 224 (53), 178 (41), 173 (10), 169 (27), 168 (100), 154 (17), 140 (11), 139 (93), 108 (11), 107 (29), 106 (10), 105 (45), 104 (19), 103 (12), 91 (54), 86 (17), 82 (43), 81 (24), 80 (43), 79 (99), 78 (15), 77 (48), 67 (14), 65 (25), 61 (16), 59 (23), 57 (77), 55 (29), 53 (14), 51 (11). HR-ESI-MS: 316.1906 ($[M+\mathrm{H}]^+$, $C_{19}H_{26}NO_3^+$; calc. 316.1907).

2-[Benzoyl(propanoyl)amino]cyclohex-3-ene-1-carboxylic Acid Methyl Ester (*rac*-**19**). From **13**, according to *rac*-**17** (in a sealed tube for 149 h): *rac*-**19** (0.14 g, 78%), *cis-trans* 1 : 1. Colorless oil. R_f (hexane/AcOEt 4 : 1 + 1% MeOH) 0.24. IR (film): 3362*w*, 3028*m*, 2943*s*, 2840*m*, 1734*vs*, 1665*vs*, 1599*m*, 1582*m*, 1450*s*, 1436*s*, 1369*s*, 1279*vs*, 1197*vs*, 1073*m*, 1045*s*, 924*m*, 797*m*, 755*s*, 700*s*, 669*m*. ^{1}H-NMR (400 MHz, CDCl$_3$; *trans-rac*-**19**): 7.71 – 7.41 (*m*, 5 arom. H)[2]); 5.83 – 5.79 (*m*, H–C(4)); 5.57 – 5.54 (*m*, H–C(3)); 5.03 (*ddd*, *J* = 10.2, 4.1, 2.2, H–C(2)); 3.58 or 3.55 (*s*, MeO)[2]) 3.50 (*ddd*, *J* = 13.1, 10.1, 3.0, H–C(1)); 2.42 – 1.69 (*m*, CH$_2$(5), CH$_2$(6))[2]); 2.32 (*q*, $^3J =$ 7.5, 1 H, MeCH_2); 2.22 (*q*, $^3J = 7.3$, 1 H, MeCH_2); 0.98 (*t*, $^3J = 7.4$, *Me*CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$; *trans-rac*-**19**; assignments from a *cis*/*trans* 1 : 2 mixture): 177.3, 177.0, 174.7, 174.5, 173.5, 173.4 (COO, MeCH$_2$$CO, PhC$O)[2]); 136.0, 132.6 (arom. C); 129.0, 128.9, 128.7, 128.7, 128.6 (arom. C, C(4))[2]); 126.9 (C(3)); 56.8 (C(2)); 51.7, 51.5 (MeO)[2]), 43.2 (C(1)); 32.3 (MeCH$_2$); 26.2 (C(5)); 24.2 (C(6)); 9.5 (*Me*CH$_2$). ^{1}H-NMR (400 MHz, CDCl$_3$; *cis-rac*-**19**): 7.71 – 7.41 (*m*, 5 arom. H)[2]); 5.96 – 5.92 (*m*, H–C(4)); 5.49 – 5.44 (*m*, H–C(2), H–C(3)); 3.58 or 3.55 (*s*, MeO)[2]); 2.90 (*ddd*, *J* = 10.3, 6.5, 3.9, H–C(1)); 2.42 – 1.69 (*m*, CH$_2$(5), CH$_2$(6))[2]); 2.02 (*q*, $^3J =$ 7.3, MeCH_2); 0.90 (*t*, $^3J = 7.3$, *Me*CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$; *cis-rac*-**19**; assignments from a *cis*/*trans* 1 : 2 mixture): 177.3, 177.0, 174.7, 174.5, 173.5, 173.4 (COO, MeCH$_2$$CO, PhC$O)[2]); 136.6, 132.9 (arom. C); 131.7 (C(4)); 129.0, 128.9, 128.7, 128.7, 128.6 (arom. C, C(4))[2]); 123.0 (C(3)); 51.7, 51.5 (MeO)[2]); 51.2 (C(2)); 42.9 (C(1)); 33.4 (MeCH$_2$); 23.4 (C(6)); 20.4 (C(5)); 9.6 (*Me*CH$_2$). EI-MS: 316 (14, $[M+1]^+$), 260 (27), 259 (12), 226 (29), 210 (44), 178 (27), 154 (66), 139 (18), 122 (15), 106 (11), 105 (100), 79 (24), 77 (68). HR-ESI-MS: 316.1540 ($[M+\mathrm{H}]^+$, $C_{18}H_{22}NO_4^+$; calc. 316.1443). Anal. calc. for $C_{18}H_{21}NO_4$ (315.15): C 68.55, H 6.71, N 4.44; found: C 68.14, H 6.78, N 4.18.

*2-[Benzoyl((*Z*)-1-{[(*tert*-butyl)dimethylsilyl]oxy}prop-1-enyl)amino]cyclohex-3-ene-1-carboxylic Acid Methyl Ester* (*rac*-**20**). From **14**, according to *rac*-**19**: *rac*-**20** (0.16 g, 61%). Colorless oil. R_f (hexane/AcOEt 4 : 1 + 1% MeOH) 0.30. ESI-MS: 430.1 ($[M+\mathrm{H}]^+$, $C_{24}H_{36}NO_4Si^+$). HR-ESI-MS: 430.2405 ($[M+\mathrm{H}]^+$, $C_{24}H_{36}NO_4Si^+$; calc. 430.2408).

N-*Propanoyl*-N-*prop-2-enylbenzamide* (**26a**). A mixture of **25a** (7.03 g, 43.6 mmol) and thionyl chloride (31.6 ml, 51.9 mmol) was heated to reflux (90°) for 3 h. The excess thionyl chloride was evaporated, and the residue and 260 ml of CH$_2$Cl$_2$ were transferred to a mixture of propanoic acid (4.70 ml, 4.20 g, 56.7 mmol), NaOH (2.26 g, 56.7 mmol), Bu$_4$NBr (457 mg, 1.41 mmol), and H$_2$O (260 ml). The mixture was shaken vigorously for 3 h at r.t. The aq. phase was extracted with AcOEt (2 × 100 ml) and the combined org. phase dried (Na$_2$SO$_4$). FC (SiO$_2$, hexane/AcOEt 6 : 1): **26a** (8.35 g, 88%). Colorless oil. B.p. 160°/4 · 10^{-2} mbar. $n_D^{20} = 1.5351$. R_f (hexane/AcOEt 5 : 1) 0.23. IR (CHCl$_3$): 3084*w*, 2982*w*, 2941*w*, 2882*w*, 1689*vs*, 1663*s*, 1449*m*, 1428*m*, 1346*s*, 1284*m*, 1249*m*, 1206*s*, 1177*m*, 1071*m*, 1027*m*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.62 – 7.59 (*m*, 2 arom. H); 7.56 – 7.52 (*m*, 1 arom. H); 7.47 – 7.42 (*m*, 2 arom. H); 5.86 (*ddt*, $^3J = 17.2, 10.4, 5.6$, CH$_2$=CHCH$_2$); 5.15 (*ddt*, $^3J = 10.4$, $^2J \approx {}^4J = 1.3$, CH_2=CHCH$_2$(*trans*)); 5.10 (*dtd*, $^3J = 17.2$, $^4J = 1.5$, $^2J = 1.3$, CH_2=CHCH$_2$(*cis*)); 4.35 (*ddd*, $^3J = 5.6$,

$^4J = 1.5$, 1.5, CH$_2$=CHC*H*$_2$); 2.52 (*q*, $^3J = 7.4$, MeC*H*$_2$); 1.11 (*t*, $^3J = 7.4$, *Me*CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$): 177.3 (MeCH$_2$*C*O); 174.2 (Ph*C*O); 135.8 (arom. C); 133.0 (CH$_2$=*C*HCH$_2$); 132.2, 128.7, 128.2 (arom. C); 117.4 (*C*H$_2$=CHCH$_2$); 48.5 (CH$_2$=CH*C*H$_2$); 31.6 (Me*C*H$_2$); 9.4 (*Me*CH$_2$). EI-MS: 217 (5, M^+), 216 (10), 161 (11), 112 (11), 106 (10), 105 (100), 77 (50), 57 (16), 51 (16). Anal. calc. for $\mathrm{C_{13}H_{15}NO_2}$ (217.27): C 71.87, H 6.96, N 6.45; found: C 71.80, C 7.21, N 6.36.

N-*[(*E*)-But-2-enyl]*-N-*propanoylbenzamide* (**26b**). From **25b**, according to **26a**: **26b** (8.6 g, 93%), (*E*)/(*Z*) 5.3 : 1. Colorless oil. B.p. 138° ($6 \cdot 10^{-2}$ mbar). $n_D^{20} = 1.5327$. R_f (hexane/AcOEt 5 : 1) 0.30. IR (KBr): 3029*w*, 2979*m*, 2941*m*, 1449*s*, 1351*s*, 1289*s*, 1242*m*, 1201*s*, 1177*m*, 1158*m*, 1075*m*, 961*s*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.62 – 7.58 (*m*, 2 arom. H); 7.56 – 7.51 (*m*, 1 arom. H); 7.46 – 7.42 (*m*, 2 arom. H); 5.53 – 5.50 (*m*, CH=CH); 4.31 – 4.27 (*m*, CH$_2$N); 2.48 (*q*, $^3J = 7.4$, MeC*H*$_2$); 1.65 (*dm*, $^3J = 4.7$, *Me*CH=CH); 1.10 (*t*, $^3J = 7.4$, *Me*CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$): 177.3 (MeCH$_2$C*O*); 174.2 (Ph*C*O); 135.9, 132.1 (arom. C); 129.3 (Me*C*H=CH); 128.6, 128.2 (arom. C); 125.7 (MeCH=*C*H); 47.9 (CH$_2$N); 31.5 (Me*C*H$_2$); 17.6 (*Me*CH$_2$); 9.5 (*Me*CH=CH). EI-MS: 232 (47, $[M + \mathrm{H}]^+$), 231 (13, M^+), 176 (15), 175 (17), 174 (27), 126 (47), 105 (100), 77 (41), 70 (44). Anal. calc. for $\mathrm{C_{14}H_{17}NO_2}$ (231.29): C 72.70, H 7.41, N 6.06; found: C 72.54, H 7.56, N 6.09.

N-*Cyclohex-2-enyl*-N-*propanoylbenzamide* (*rac*-**26c**). A mixture of *rac*-**25c** (8.39 g, 41.7 mmol), **28** (19.4 g, 120 mmol), propanoyl chloride (10.5 ml, 125 mmol) and $\mathrm{CH_2Cl_2}$ (150 ml) was heated during 14 h to 40°. The mixture was extracted with sat. $\mathrm{NH_4Cl}$ soln. (2 ×) and $\mathrm{H_2O}$ (2 ×). The combined org. phases were dried ($\mathrm{Na_2SO_4}$) and evaporated. FC ($\mathrm{SiO_2}$, hexane/AcOEt 6 : 1) and bulb-to-bulb distillation (175°/$6 \cdot 10^{-2}$ mbar) gave *rac*-**26c** (9.7 g, 97%). Viscous colorless oil. B.p. 175°/$6 \cdot 10^{-2}$ mbar. $n_D^{20} = 1.5461$. R_f (hexane/AcOEt 5 : 1) 0.23. IR (KBr): 3027*m*, 2939*m*, 1704*s*, 1664v*s*, 1450*m*, 1372*m*, 1333*m*, 1285*s*, 1212*s*, 1176*m*, 700*m*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.72 – 7.69 (*m*, 2 arom. H); 7.58 – 7.54 (*m*, 1 arom. H); 7.48 – 7.43 (*m*, 2 arom. H); 5.82 – 5.77 (*dm*, $^3J = 10.2$, H–C(2)); 5.55 (*d*, $^3J = 10.2$, H–C(3)); 5.07 – 5.00 (*m*, H–C(1)); 2.19 (*q*, $^3J = 7.5$, 1 H, MeC*H*$_2$); 2.18 (*q*, $^3J = 7.3$, 1 H, MeC*H*$_2$); 2.16 – 2.05, 2.00 – 1.87 (2*m*, CH$_2$(6), CH$_2$(4)); 1.90 – 1.84, 1.68 – 1.56 (2*m*, CH$_2$(5)); 1.00 (*t*, $^3J = 7.4$, 1.5 H, *Me*CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$): 176.8 (MeCH$_2$*C*O); 174.6 (Ph*C*O); 136.6, 132.9 (arom. C); 129.3 (C(3)); 128.9, 128.8 (arom. C); 127.8 (C(2)); 54.9 (C(1)); 32.5 (Me*C*H$_2$); 27.6 (C(6)); 24.3 (C(4)); 22.0 (C(5)); 9.7 (*Me*CH$_2$). EI-MS: 257 (2, M^+), 200 (41), 177 (10), 152 (58), 106 (12), 105 (100), 96 (48), 81 (16), 80 (11), 79 (22), 77 (75), 57 (43), 51 (14). Anal. calc. for $\mathrm{C_{16}H_{19}NO_2}$ (257.33): C 74.68, H 7.44, N 5.44; found: C 74.68, H 7.52, N 5.39.

4-Methyl-N-*propanoyl*-N-*prop-2-enylbenzamide* (**26d**). From **25d**, according to **26c**: **26d** (5.9 g, 90%). Colorless oil. B.p. 127°/$7 \cdot 10^{-2}$ mbar. $n_D^{20} = 1.5365$. R_f (hexane/AcOEt 5 : 1) 0.30. IR (KBr): 2982*m*, 2941*m*, 1689v*s*, 1664*s*, 1610m, 1428*m*, 1343*s*, 1289*m*, 1251*m*, 1207*s*, 1181*s*, 1109*m*, 1074*m*, 1021*m*, 962*m*, 835*m*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.52 (*d*, $^3J = 8.1$, 2 arom. H); 7.24 (*dd*, $^3J = 8.5$, $^4J = 0.7$, 2 arom. H); 5.86 (*ddt*, $^3J = 17.1$, 10.4, 5.6, CH$_2$=C*H*CH$_2$); 5.14 (*ddt*, $^3J = 10.4$, $^2J \approx {}^4J = 1.3$, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 5.11 (*dtd*, $^3J = 17.1$, $^4J = 1.6$, $^2J = 1.3$, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 4.35 (*ddd*, $^3J = 5.6$, $^4J = 1.5$, 1.5, CH$_2$=CHC*H*$_2$); 2.48 (*q*, $^3J = 7.4$, MeC*H*$_2$); 2.41 (*s*, *Me*C$_6$H$_2$); 1.10 (*t*, $^3J = 7.4$, *Me*CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$): 177.1 (MeCH$_2$*C*O); 174.0 (Ac*C*O); 143.0 (arom. C); 133.0 (CH$_2$=*C*HCH$_2$); 132.7, 129.2, 128.4 (arom. C); 117.1 (*C*H$_2$=CHCH$_2$); 48.3 (CH$_2$=CH*C*H$_2$); 31.3 (Me*C*H$_2$); 21.4 (*Me*–C$_6$H$_4$); 9.5 (*Me*CH$_2$). EI-MS: 231 (18, M^+), 230 (15), 215 (20), 175 (11), 120 (21), 91 (79), 89 (18), 65 (33). Anal. calc. for $\mathrm{C_{14}H_{15}NO_2}$ (231.29): C 72.70, H 7.41, N 6.06; found: C 72.60, H 7.52, N 6.04.

4-Methoxy-N-*propanoyl*-N-*prop-2-enylbenzamide* (**26e**). From **25e** according to **26c**: **26e** (21.9 g, 96%). Colorless oil. B.p. 108°/$6 \cdot 10^{-2}$ mbar. $n_D^{20} = 1.5495$. R_f (hexane/AcOEt 5 : 1) 0.20. IR (KBr): 2982*w*, 2979*m*, 2940*m*, 2880*m*, 1660*s*, 1605*s*, 1578*m*, 1511*s*, 1462*m*, 1442*m*, 1421*m*, 1341*s*, 1313*s*, 1256v*s*, 1211*s*, 1170*s*, 1112*m*, 1072*m*, 1027*s*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.62 (*dm*, $^3J = 9.8$, 2 arom. H); 6.93 (*dm*, $^3J = 8.9$, 2 arom. H); 5.86 (*ddt*, $^3J = 17.1$, 10.4, 5.6, CH$_2$=C*H*CH$_2$); 5.15 – 5.11 (*m*, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 5.10 (*ddt*, $^3J = 10.7$, $^2J = 1.4$, 1.4, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 3.86 (*s*, MeO); 4.35 (*ddd*, $^3J = 5.6$, $^4J = 1.5$, 1.5, CH$_2$=CHC*H*$_2$); 2.43 (*q*, $^3J = 7.4$, MeC*H*$_2$); 1.09 (*t*, $^3J = 7.4$, *Me*CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$): 177.1 (MeCH$_2$*C*O); 173.7 (Ar*C*O); 163.2 (arom. C); 133.1 (CH$_2$=*C*HCH$_2$); 130.9, 127.6 (arom. C); 117.4 (*C*H$_2$=CHCH$_2$); 114.0 (arom. C); 55.5 (MeO); 48.6 (CH$_2$=CH*C*H$_2$); 31.2 (Me*C*H$_2$); 9.7 (*Me*CH$_2$). EI-MS: 247 (10, M^+); 136 (14), 135 (100), 107 (11), 92 (22), 77 (33), 64 (10), 57 (11). Anal. calc. for $\mathrm{C_{14}H_{17}NO_3}$ (247.29): C 68.00, H 6.93, N 5.66; found: C 67.77, H 7.13, N 5.56.

N-*((*Z*)-1-{[(*tert-*Butyl)dimethylsilyl]oxy}prop-1-enyl)*-N-*prop-2-enylbenzamide* (**27a**). A mixture of THF (15 ml), 1M LHMDS in THF (12.7 ml, 12.7 mmol), and HMPA[3] (4 ml) was cooled to – 78° under N$_2$, and a soln. of **26a** (1.38 g, 6.36 mmol) in THF (6 ml) was added slowly during 30 min. After 1 h, the mixture was cooled to – 85°, and 1M ^{t}BuMe$_2$SiCl in THF (12.7 ml, 12.7 mmol) was added quickly. After 45 min, the mixture was warmed to r.t. and stirred for 1 h. The mixture was diluted with pentane (50 ml) and extracted with sat.

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[3] DMPU can also be used. In this case, the yields are *ca.* 5 – 10% lower.

NH_4Cl soln. (2 × 50 ml) and half-sat. NaCl soln. (2 × 50 ml). The combined org. phase was dried (Na_2SO_4). FC (SiO_2, hexane/AcOEt 10:1): **27a** (1.79 g, 85%). Pale-yellow oil. B.p. 160°/4 · 10^{-2} mbar (slight dec.) n_D^{20} = 1.5078. R_f (hexane/AcOEt 5:1) 0.40. IR (CH_2Cl_2): 3059*vw*, 2958*m*, 2932*m*, 2860*m*, 1681*m*, 1640v*s*, 1391*m*, 1326*m*, 1299*m*, 1211*m*, 1133*m*, 1076*m*, 841*m*, 832*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO, 353 K): 7.60–7.47 (*m*, 2 arom. H); 7.40–7.35 (*m*, 3 arom. H); 5.91 (*ddt*, ^3J = 17.2, 10.3, 5.9, CH_2=C*H*CH_2); 5.22 (*ddt*, ^3J = 17.2, $^2J \approx {}^4J$ = 1.6, 1 H, C*H*$_2$=$CHCH_2$(*cis*)); 5.18 (*ddt*, ^3J = 10.2, $^2J \approx {}^4J$ = 1.5, 1 H, C*H*$_2$=$CHCH_2$(*trans*)); 4.58 (*q*, ^3J = 6.8, MeC*H*); 4.14 (*d*, ^3J = 5.8, CH_2=CHC*H*$_2$); 1.41 (*d*, ^3J = 6.8, *Me*CH); 0.84 (*s*, ^{t}Bu); 0.13 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.7 (Ph*C*O); 144.5 (C–O–Si); 136.2 (arom. C); 133.2 (CH_2=*C*HCH_2); 129.9, 127.7, 127.6 (arom. C); 117.4 (*C*H$_2$=$CHCH_2$); 102.1 (Me*C*H); 50.9 (CH_2=CH*C*H$_2$); 25.4 (*Me*$_3$CSi); 18.1 (Me_3*C*Si); 10.8 (*Me*CH); –4.1 (Me_2Si). EI-MS: 332 (50, $[M+1]^+$), 331 (55, M^+), 330 (36), 316 (16), 304 (14), 276 (18), 275 (56), 274 (100), 234 (13), 233 (22), 232 (12), 144 (23), 105 (93), 77 (16), 73 (11). Anal. calc. for $C_{19}H_{29}NO_2Si$ (331.53): C 68.84, H 8.82, N 4.22; found: C 68.52, H 8.94, N 4.06.

N-*[(*E*)-But-2-enyl]*-N-*((*Z*)-1-{[(*tert-*butyl)dimethylsilyl]oxy}prop-1-enyl)benzamide* (**27b**). From **26b**, according to **27a**: **27b** (2.79 g, 93%), (*E*)/(*Z*) 4.7:1 (butenyl). Pale-yellow oil. n_D^{20} = 1.5109. R_f (hexane/AcOEt 5:1) 0.42. IR (KBr): 3029*w*, 2957*s*, 2931*s*, 2886*m*, 2859*s*, 1679*s*, 1651v*s*, 1473*m*, 1448*m*, 1429*m*, 1391*s*, 1371*s*, 1317*s*, 1257*s*, 1203*s*, 1128*m*, 1075*s*, 835*s*, 783*s*. ^{1}H-NMR (400 MHz, (D_6)DMSO, 353 K): 7.55–7.51 (*m*, 2 arom. H); 7.44–7.34 (*m*, 3 arom. H); 5.66–5.61 (*dqm*, ^3J = 15.4, 6.0, MeC*H*=CH); 5.55 (*dtq*, ^3J = 15.4, 5.8, ^4J = 1.3, CH=C*H*CH_2); 4.56 (*q*, ^3J = 6.8, MeC*H*); 4.07 (*d*, ^3J = 5.7, CH_2=CHC*H*$_2$); 1.68 (*dd*, ^3J = 6.0, ^4J = 1.1, *Me*CH=CH); 1.42 (*d*, ^4J = 6.8, *Me*CH); 0.84 (*s*, ^{t}BuSi); 0.12 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.5 (Ph*C*O); 144.5 (C–O–Si); 136.4, 129.8 (arom. C); 128.8 (Me*C*H=CH); 127.7, 127.5 (arom. C); 126.0 (CH=*C*HCH_2); 101.8 (Me*C*H); 50.2 (CH=CH*C*H$_2$); 25.3 (*Me*$_3$CSi); 18.0 (Me_3*C*Si), 17.6 (*Me*CH); 10.7 (*Me*CH=CH); –4.3 (Me_2Si). EI-MS: 347 (26), 346 (38, $[M+H]^+$), 345 (46, M^+), 290 (13), 289 (20), 288 (62), 264 (10), 240 (30), 234 (42), 233 (27), 232 (26), 179 (14), 178 (21), 105 (100), 77 (55), 75 (22), 73 (46). HR-ESI-MS: 368.2010 ($[M+Na]^+$, $C_{20}H_{31}NNaO_2Si$; calc. 368.2016.

N-*{(*Z*)-1-{[(*tert-*Butyl)dimethylsilyl]oxy}prop-1-enyl}*-N-*cyclohex-2-enylbenzamide* (*rac*-**27c**). From *rac*-**26c**, according to **27a**: *rac*-**27c** (5.19 g, 90%). Pale-yellow oil. n_D^{20} = 1.5233. R_f (hexane/AcOEt 5:1) 0.36. IR (KBr): 3059*w*, 3028*w*, 2931*s*, 2859*s*, 1678*m*, 1646v*s*, 1473*m*, 1463*m*, 1447*m*, 1384*s*, 1349*s*, 1337*s*, 1304*s*, 1255*s*, 1232*m*, 1212*m*, 1195*m*, 1136*m*, 1078*s*, 1017*m*, 895*m*, 840*s*, 783*s*. ^{1}H-NMR (400 MHz, (D_6)DMSO, 353 K): 7.49 (*dd*, ^3J = 7.7, ^4J = 1.8, 2 arom. H); 7.41–7.38 (*m*, 3 arom. H); 5.79–5.75 (*m*, H–C(3)); 5.64 (*dd*, ^3J = 10.2, 2.2, H–C(2)); 4.66 (*m*, H–C(1)); 4.63 (*q*, ^3J = 6.9, MeC*H*); 2.00–1.86 (*m*, CH_2(6), CH_2(4)); 1.84–1.79, 1.58–1.53 (2*m*, CH_2(5)); 1.45 (*d*, ^3J = 6.9, *Me*CH); 0.86 (*s*, ^{t}BuSi); 0.10/0.09 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, (D_6)DMSO, 353 K): 175.7 (Ph*C*O); 141.6 (C–O–Si); 136.8, 129.1, 128.4 (arom. C); 128.3 (C(3)); 127.8 (C(2)); 127.4 (arom. C); 103.7 (Me*C*H); 53.5 (C(1)); 26.7 (C(6)); 25.1 (*Me*$_3$CSi); 23.7 (C(4)); 20.9 (C(5)); 17.6 (Me_3*C*Si); 10.3 (*Me*CH); –4.2 (Me_2Si). EI-MS: 371 (0.1, M^+), 314 (5), 266 (8), 234 (25), 178 (25), 135 (12), 106 (11), 105 (100), 81 (45), 79 (35), 77 (57), 75 (40), 73 (50). HR-ESI-MS: 394.2175 ($[M+Na]^+$, $C_{22}H_{33}NNaO_2Si$; calc. 394.2173.

N-*((*Z*)-1-{[(*tert-*Butyl)dimethylsilyl]oxy}prop-1-enyl)-4-methyl*-N-*prop-2-enylbenzamide* (**27d**). From **26d**, according to **27a**: **27d** (3.96 g, 93%). Pale-yellow oil. n_D^{20} = 1.5102. R_f (hexane/AcOEt 5:1) 0.36. IR (KBr): 3081*w*, 2957*s*, 2930*s*, 2887*m*, 2860*s*, 1680*s*, 1651v*s*, 1613*m*, 1573*w*, 1473*m*, 1463*m*, 1407*m*, 1389*s*, 1364*s*, 1327*s*, 1297*s*, 1257*s*, 1213*s*, 1184*m*, 1132*m*, 1076*s*, 838*s*. ^{1}H-NMR (400 MHz, (D_6)DMSO, 353 K): 7.46 (*d*, ^3J = 8.1, 2 arom. H); 7.18 (*d*, ^3J = 7.8, 2 arom. H); 5.90 (*ddt*, ^3J = 17.2, 10.3, 5.9, CH_2=C*H*CH_2); 5.20 (*ddt*, ^3J = 17.0, $^2J = {}^4J$ = 1.5, 1 H, C*H*$_2$=$CHCH_2$(*cis*)); 5.17 (*ddt*, ^3J = 10.1, $^2J = {}^4J$ = 1.4, 1 H, C*H*$_2$=$CHCH_2$(*trans*)); 4.54 (*q*, ^3J = 6.8, MeC*H*); 4.12 (*dm*, ^3J = 5.8, CH_2=CHC*H*$_2$); 2.33 (*s*, *Me*–C_6H_4); 1.43 (*d*, ^3J = 6.8, *Me*CH); 0.85 (*s*, ^{t}BuSi); 0.13 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.7 (Ar*C*O); 144.6 (C–O–Si); 140.1 (arom. C); 133.4 (*C*H=CH_2); 128.3 (2 arom. C); 127.9 (arom. C); 117.3 (*C*H$_2$=$CHCH_2$); 101.9 (Me*C*H); 50.9 (CH_2=CH*C*H$_2$); 25.4 (*Me*$_3$CSi); 21.3 (*Me*–C_6H_4); 18.1 (Me_3*C*Si); 10.8 (*Me*CH); –4.1 (Me_2Si). EI-MS: 346 (38, $[M+H]^+$), 345 (11, M^+), 288 (15), 247 (16), 119 (100), 91 (41), 86 (22), 84 (36), 75 (10), 73 (38), 65 (11). HR-ESI-MS: 368.2000 ($[M+Na]^+$, $C_{20}H_{31}NNaO_2Si$; calc. 368.2016).

N-*((*Z*)-1-{[(*tert-*Butyl)dimethylsilyl]oxy}prop-1-enyl)-4-methoxy*-N-*prop-2-enylbenzamide* (**27e**). From **26e**, according to **27a**: **27e** (4.47 g, 86%). Pale-yellow oil. n_D^{20} = 1.5995. R_f (hexane/AcOEt 5:1) 0.26. IR (KBr): 3080*w*, 2957*m*, 2930*s*, 2859*m*, 1679*m*, 1644v*s*, 1608*s*, 1513*s*, 1473*m*, 1463*m*, 1419*m*, 1389*s*, 1364*s*, 1327*s*, 1303*s*, 1255v*s*, 1212*m*, 1176*s*, 1131*m*, 1109*m*, 1075*s*, 1034*m*, 840*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.69–7.62 (*m*, 2 arom. H); 6.84–6.80 (*m*, 2 arom. H); 5.93 (*ddt*, ^3J = 17.2, 10.3, 6.0, CH_2=C*H*CH_2); 5.22 (*ddt*, ^3J = 17.2, $^2J \approx {}^4J$ = 1.4, 1 H, C*H*$_2$=$CHCH_2$(*cis*)); 5.17 (*ddt*, ^3J = 10.2, $^2J \approx {}^4J$ = 1.4, 1 H, C*H*$_2$=$CHCH_2$(*trans*)); 4.52 (*q*, ^3J = 6.8, MeC*H*); 4.18 (br. CH_2=CHC*H*$_2$); 3.81 (*s*, MeO); 1.46 (*d*, ^3J = 6.8, *Me*CH); 0.84 (*s*, ^{t}BuSi); 0.13 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.1 (Ar*C*O); 161.1 (MeO–*C*); 145.0 (C–O–Si); 133.5 (CH_2=*C*HCH_2); 130.0, 128.4 (arom. C); 117.2 (*C*H$_2$=CHCH$_2$); 112.9 (arom. C); 101.5 (Me*C*H); 55.3 (MeO); 51.3 (CH$_2$=CH*C*H$_2$); 25.4 (*Me*$_3$CSi); 18.1 (Me$_3$*C*Si); 10.8 (*Me*CH); –4.1 (Me$_2$Si). EI-MS: 361 (8, M^+), 360 (10), 305 (11), 304 (24), 263 (19), 136 (11), 135 (100), 107 (18), 92 (11), 77 (27), 73 (27). HR-ESI-MS: 384.1956 ($[M+\mathrm{Na}]^+$, $C_{22}H_{31}NNaO_3Si$; calc. 384.1965).

*Phosphoric Acid (*Z*)-1-[Benzoyl(prop-2-enyl)amino]prop-1-enyl Diethyl Ester* (**27f**). From **26a**, with LHMDS (1.2 equiv.) and diethyl phosphorochloridate (1.5 equiv.): **27f** (646 mg, 64%). Pale-yellow oil. n_D^{20} = 1.5068. R_f (hexane/AcOEt 1:1) 0.24. IR (KBr): 3062*w*, 2985*m*, 1693*m*, 1661*s*, 1447*m*, 1370*s*, 1306*s*, 1281*s*, 1216*m*, 1030v*s*, 963*s*. ^{1}H-NMR (CDCl$_3$, 400 MHz): 7.61–7.58 (*m*, 2 arom. H); 7.37–7.28 (*m*, 3 arom. H); 5.89 (*ddt*, ^3J = 17.0, 10.4, 6.1, CH$_2$=C*H*CH$_2$); 5.25–5.21 (*m*, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 5.17 (*dd*, ^3J = 10.2, ^2J = 1.2, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 4.79 (*q*, ^3J = 6.6, MeC*H*); 4.30 (br., CH$_2$=CHC*H*$_2$); 4.18–4.06 (*m*, 2 MeC*H*$_2$O); 1.49 (*dd*, ^3J = 6.9, ^5J(Me,^{31}P) = 2.3, *Me*CH); 1.31 (*ttd*, ^3J = 7.1, ^4J(Me,^{31}P) = 1.0, 2 *Me*CH$_2$O). ^{13}C-NMR (CDCl$_3$, 100 MHz): 170.3 (Ph*C*O); 141.0 (C–O–P); 135.5 (arom. C); 132.6 (CH$_2$=*C*HCH$_2$); 130.1, 127.8, 127.6 (arom. C); 117.9 (*C*H$_2$=CHCH$_2$); 111.7 (Me*C*H); 64.4 (*d*, ^2J(C,P) = 6.1, Me*C*H$_2$O); 50.0 (CH$_2$=CH*C*H$_2$); 15.9 (*d*, ^3J(C,P) = 7.0, *Me*CH$_2$O); 10.9 (*Me*CH). DCI-MS: 355 (16, $[M+2]^+$), 354 (76, $[M+1]^+$), 353 (2, M^+), 200 (49), 105 (44), 96 (24), 95 (100), 94 (11), 77 (12), 58 (14). Anal. calc. for $C_{17}H_{24}NO_5P$ (353.35): C 57.79, H 6.85, N 3.96, P 8.77; found: C 57.56, H 6.77, N 4.09, P 9.33. HR-CI-MS (isobutane): 354.1464 ($[M+\mathrm{H}]^+$, $C_{17}H_{25}NO_5P$; calc. 354.1465).

N-*Prop-2-enyl-*N-*{(*Z*)-1-[(triethylsilyl)oxy]prop-1-enyl}benzamide* (**27g**). From **26a**, according to **27a**, with triethylchlorosilane (1.5 equiv.), LHMDS (1.5 equiv.), and DMPU instead of HMPA: **27g** (423 mg, 71%). Pale-yellow oil. n_D^{20} = 1.5013. R_f (hexane/AcOEt 5:1) 0.34. IR (KBr): 3082*w*, 3063*w*, 3028*w*, 2958*s*, 2938*m*, 2915*m*, 2877*m*, 1679*s*, 1653v*s*, 1458*m*, 1448*m*, 1417*m*, 1368*s*, 1344*m*, 1323*s*, 1297*m*, 1241*m*, 1212*s*, 1135*m*, 1078*s*, 1003*m*, 746*s*, 729*s*. ^{1}H-NMR (CDCl$_3$, 400 MHz): 7.62 (*d*, ^3J = 6.9, 2 arom. H); 7.38–7.28 (*m*, 3 arom. H); 5.92 (*ddt*, ^3J = 17.2, 10.3, 5.9, CH$_2$=C*H*CH$_2$); 5.24–5.16 (*m*, C*H*$_2$=CHCH$_2$); 4.43 (*q*, ^3J = 6.5, MeC*H*); 4.18 (br., CH$_2$=CHC*H*$_2$); 1.37 (*d*, ^3J = 6.8, *Me*CH); 0.94 (*t*, ^3J = 7.9, 3 *Me*CH$_2$Si); 0.67 (*q*, ^3J = 7.9, 3 MeC*H*$_2$Si). ^{13}C-NMR (CDCl$_3$, 100 MHz): 169.9 (Ph*C*O); 144.3 (C–O–Si); 136.3 (arom. C); 133.2 (CH$_2$=*C*HCH$_2$); 129.9, 127.7, 127.6 (arom. C); 117.2 (*C*H$_2$=CHCH$_2$); 102.4 (Me*C*H); 50.3 (CH$_2$=CH*C*H$_2$); 10.9 (*Me*CH); 6.6 (*Me*CH$_2$Si); 5.4 (Me*C*H$_2$Si). DCI-MS: 331 (<1, M^+), 302 (11), 115 (17), 105 (100), 95 (10), 87 (35), 77 (93), 75 (11), 59 (22). HR-CI-MS (isobutane): 332.2040 ($[M+\mathrm{H}]^+$, $C_{19}H_{30}NO_2Si$; calc. 2332.2040).

N-*((*Z*)-1-{[(*tert*-Butyl)dimethylsilyl]oxy}prop-1-enyl)-*N*-prop-2-enylbenzenemethanamine* (**31**). To a freshly prepared LDA soln. (from 12.5 ml (20.0 mmol) of 1.6M BuLi and 3.1 ml (21 mmol) of ^{i}Pr$_2$NH in 50 ml of THF) at –78°, a soln. of *N*-benzyl-*N*-prop-2-enylpropanamide (**33**; 2.91 g, 14.3 mmol) in THF (10 ml) was added dropwise and stirred for 30 min. Then ^{t}BuMe$_2$SiCl (2.52 g, 16.7 mmol) in THF (10 ml) was added quickly. After addition, the mixture was allowed to warm slowly to r.t. and stirred for 2 h. The mixture was diluted with pentane and washed with H$_2$O and half-sat. NaCl soln. The combined org. phase was dried (MgSO$_4$) and evaporated: **31** (4.43 g). The crude product was used directly for ^{1}H-NMR. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.36–7.16 (*m*, 5 arom. H); 5.79 (*ddt*, ^3J = 17.2, 10.3, 6.5, CH$_2$=C*H*CH$_2$); 5.12 (*dm*, ^3J = 9.6, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 5.02 (*dm*, ^3J = 17.2, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 3.93 (*d*, ^2J = 3.5, 1 H, PhC*H*$_2$); 3.92 (*d*, ^2J = 3.1, 1 H, PhC*H*$_2$); 3.69 (*q*, ^3J = 6.5, MeC*H*); 3.32 (*dm*, ^3J = 6.5, CH$_2$=CHC*H*$_2$); 1.54 (*d*, ^3J = 6.5, *Me*CH); 1.00 (*s*, ^{t}BuSi); 0.18 (*s*, Me$_2$Si).

N-*(2-Methylpent-4-enoyl)benzamide* (*rac*-**29a**) [44]. In a dried *Schlenk* tube, degassed and filled with Ar, **27a** (237 mg, 715 mmol) and decaline (2.3 ml) were heated to 135° for 20 h. The mixture was then cooled, diluted with Et$_2$O (20 ml), and extracted with sat. NH$_4$Cl soln. (2 × 20 ml) and H$_2$O. The org. phase was dried (Na$_2$SO$_4$) and evaporated. FC (SiO$_2$, hexane/AcOEt 6:1): *rac*-**29a** (56 mg, 36%). Colorless crystals. M.p. 93.4°. R_f (hexane/AcOEt 5:1) 0.20. IR (KBr): 3269*s*, 3160*s*, 3078*m*, 2973*s*, 2931*s*, 2874*m*, 1731v*s*, 1682v*s*, 1644*s*, 1603*s*, 1582*m*, 1489v*s*, 1379*m*, 1302*m*, 1274*s*, 1229*s*, 1168*s*, 1080*m*, 1026*m*, 993*m*, 909*s*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO): 10.90 (*s*, NH); 7.88–7.85 (*m*, 2 arom. H); 7.64–7.60 (*m*, 1 arom. H); 7.58–7.49 (*m*, 2 arom. H); 5.78 (*ddt*, ^3J = 17.1, 10.2, 6.9, CH$_2$=C*H*CH$_2$); 5.09–5.05 (*dm*, ^3J = 17.4, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 5.04–5.01 (*dm*, ^3J = 10.2, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 3.11 (*qt*, ^3J = 6.9, 6.9, MeC*H*); 2.41 (*ddddd*, ^2J = 14.0, ^3J = 6.9, 6.9, ^4J = 1.3, 1.3, 1 H, CH$_2$=CHC*H*$_2$); 2.11 (*ddd*, ^2J = 14.0, ^3J = 7.0, 7.0, 1 H, CH$_2$=CHC*H*$_2$); 1.09 (*d*, ^3J = 6.9, *Me*CH). ^{13}C-NMR (100 MHz, (D$_6$)DMSO): 176.7 (CH*C*O); 166.5 (Ph*C*O); 136.0 (CH$_2$=*C*HCH$_2$); 133.7, 132.6, 128.5, 128.4 (arom. C); 116.8 (*C*H$_2$=CHCH$_2$); 39.6 (Me*C*H); 37.2 (CH$_2$=CH*C*H$_2$); 16.6 (*Me*CH). EI-MS: 217 (13, M^+), 175 (11), 122 (50), 105 (87), 96 (33), 79 (12), 77 (100), 69 (21), 68 (39), 67 (29), 58 (25), 53 (11), 51 (26). Anal. calc. for $C_{13}H_{15}NO_2$ (217.27): C 71.87, H 6.96, N 6.45; found: C 71.81, H 7.03, N 6.51.

N-*(2-Methylpent-4-enoyl)-4-methylbenzamide* (*rac*-**29d**). From **27d**, according to *rac*-**29a**: *rac*-**29d** (633 mg, 49%). Colorless crystals. M.p. 90.3–91.6°. R_f (hexane/AcOEt 5:1) 0.18. IR (KBr): 3287*s*, 3156*m*, 3112v*s*, 3074*m*, 2971*m*, 2932*m*, 1747*s*, 1723v*s*, 1679*s*, 1652*m*, 1644*m*, 1612*s*, 1575*m*, 1557*m*, 1521*s*, 1490v*s*, 1456*s*, 1436*m*, 1415*m*, 1379*m*, 1322*m*, 1269*s*, 1228*m*, 1191*s*, 1163*s*, 1142*s*, 1119*s*, 1021*m*, 992*m*, 911*m*, 838*m*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO): 10.81 (*m*, NH); 7.80–7.78 (*m*, 2 arom. H); 7.31 (*d*, $^3J = 7.9$, 2 arom. H); 5.77 (*ddt*, $^3J = 17.0$, 10.1, 7.0, CH$_2$=C*H*CH$_2$); 5.06 (*ddt*, $^3J = 17.2$, $^2J = 2.1$, $^4J = 1.5$, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 5.02 (*ddm*, $^3J = 10.3$, $^2J = 1.0$, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 3.13 (*qt*, $^3J = 6.8$, 6.8, MeC*H*); 2.44–2.38 (*m*, 1 H, CH$_2$=CHC*H*$_2$); 2.14–2.07 (*m*, 1 H, CH$_2$=CHC*H*$_2$); 1.09 (*d*, $^3J = 6.7$, *Me*CH); 2.37 (*s*, *Me*–C$_6$H$_4$). ^{13}C-NMR (100 MHz, (D$_6$)DMSO): 176.8 (CH*C*O); 166.3 (Ar*C*O); 143.0 (arom. C); 136.1 (CH$_2$=*C*HCH$_2$); 130.8, 129.0, 128.5 (arom. C); 116.8 (*C*H$_2$=CHCH$_2$); 39.6 (Me*C*H); 37.3 (CH$_2$=CH*C*H$_2$); 21.2 (*Me*–C$_6$H$_4$); 16.7 (*Me*CH). EI-MS: 231 (7, M^+), 136 (20), 119 (94), 96 (13), 91 (36), 65 (14), 58 (28), 43 (100), 41 (21), 39 (12). Anal. calc. for C$_{14}$H$_{17}$NO$_2$ (231.29): C 72.70, H 7.41, N 6.06; found: C 72.47, H 7.61, N 6.02.

*4-Methoxy-*N*-(2-methylpent-4-enoyl)benzamide* (*rac*-**29e**). From **27e**, according to *rac*-**29a**: *rac*-**29e** (619 mg, 41%). Colorless crystals. M.p. 122.2°. R_f (hexane/AcOEt 5 :1) 0.08. IR (KBr): 3279*s*, 3154*m*, 3006*m*, 2978*m*, 2933*m*, 2908*m*, 2844*m*, 1720v*s*, 1677*s*, 1643*m*, 1605v*s*, 1495v*s*, 1441*s*, 1379*m*, 1311*s*, 1259v*s*, 1233*s*, 1181*s*, 1158*s*, 1117*s*, 1071*m*, 1025*s*, 994*m*, 963*m*, 923*m*, 845*s*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO): 10.75 (*s*, NH); 7.89 (*dm*, $^3J = 9.0$, 2 arom. H); 7.03 (*dm*, $^3J = 9.0$, 2 arom. H); 5.77 (*ddt*, $^3J = 16.9$, 10.0, 6.9, CH$_2$=C*H*CH$_2$); 5.06 (*ddm*, $^3J = 17.1$, $^2J = 1.6$, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 5.04–5.00 (*m*, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 3.83 (*s*, MeO); 3.15 (*qt*, $^3J = {}^3J = 6.9$, MeC*H*); 2.40 (*ddddd*, $^2J = 13.7$, $^3J = 6.9$, 6.9, $^4J = 1.3$, 1.3, 1 H, CH$_2$=CHC*H*$_2$); 2.10 (*ddddd*, $^2J =$ 14.1, $^3J = 7.1$, 7.1, $^4J = 1.1$, 1.1, 1 H, CH$_2$=CHC*H*$_2$); 1.09 (*d*, $^3J = 6.9$, *Me*CH). ^{13}C-NMR (100 MHz, (D$_6$)DMSO): 176.9 (CH*C*O); 165.7 (Ar*C*O); 162.9 (arom. C); 136.1 (CH$_2$=*C*HCH$_2$); 130.7, 125.6 (arom. C); 116.8 (*C*H$_2$=CHCH$_2$); 113.8 (arom. C); 55.6 (MeO); 39.5 (Me*C*H); 37.3 (CH$_2$=CH*C*H$_2$); 16.7 (*Me*CH). EI-MS: 247 (9, M^+), 152 (7), 136 (9), 135 (100), 107 (9), 107 (9), 96 (5), 92 (12), 77 (19), 69 (6), 64 (5). Anal. calc. for C$_{14}$H$_{17}$NO$_3$ (247.29): C 68.00, H 6.93, N 5.66; found: C 68.00, H 6.81, N 5.68.

N*-(2,3-Dimethylpent-4-enoyl)benzamide* (*rac*-**29b**). From **27b**, according to *rac*-**29a** (4 d): *rac*-**29b** (445 mg, 13%), diastereoisomer ratio 1:1.5. Colorless crystals. M.p. 114.2°. R_f (hexane/AcOEt 5 :1) 0.18. IR (KBr): 3278*s*, 3158*m*, 3064*m*, 2970*s*, 2932*m*, 2877*m*, 1724v*s*, 1677*s*, 1642*m*, 1602*m*, 1583*m*, 1507*s*, 1488v*s*, 1420*m*, 1377*m*, 1306*m*, 1271*s*, 1182*s*, 1142*s*, 1100*m*, 1075*m*, 1027*m*, 1001*m*, 705*s*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO; major isomer): 10.87 (*s*, NH); 7.88–7.83 (*m*, 2 arom. H); 7.64–7.59 (*m*, 1 arom. H); 7.54–7.49 (*m*, 2 arom. H); 5.70 (*ddd*, $^3J = 17.2$, 10.3, 8.2, CH$_2$=C*H*); 5.08–4.97 (*m*, C*H*$_2$=CH); 2.95–2.88 (*m*, COC*H*(Me)CH(Me)); 2.51–2.38 (*m*, COCH(Me)C*H*(Me)); 1.03 (*m*, $^3J = 6.9$, COCH(Me)CH(*Me*)); 1.01 (*d*, $^3J = 7.8$, COCH(*Me*)-CH(Me)). ^{1}H-NMR (400 MHz, (D$_6$)DMSO; minor isomer): 10.92 (*s*, NH); 7.88–7.83 (*m*, 2 arom. H); 7.65–7.60 (*m*, 1 arom. H); 7.54–7.49 (*m*, 2 arom. H); 5.83 (*ddd*, $^3J = 17.4$, 10.4, 7.1, CH$_2$=C*H*); 5.08–4.97 (*m*, C*H*$_2$=CH); 3.01 (*qd*, $^3J \approx {}^3J = 6.8$, COC*H*(Me)CH(Me); 2.51–2.38 (*m*, COCH(Me)C*H*(Me)); 1.03 (*d*, $^3J = 6.9$, COCH(Me)CH(*Me*)); 0.97 (*d*, $^3J = 6.9$, COCH(*Me*)CH(Me)). ^{13}C-NMR (100 MHz, (D$_6$)DMSO; 2 isomers): 176.5, 176.2 (CH*C*O); 166.5 (Ph*C*O); 142.0, 141.1 (CH$_2$=*C*H); 133.8, 133.7, 132.7, 128.5, 128.4 (arom. C); 115.2, 114.2 (*C*H$_2$=CH); 44.9, 44.5 (CO*C*H(Me)CH(Me)); 40.5, 39.5 (COCH(Me)*C*H(Me)); 18.3, 15.5 (COCH(*Me*)CH(Me)); 14.7, 13.2 (COCH(Me)CH(*Me*)). EI-MS: 232 (29, $[M+\mathrm{H}]^+$), 231 (7, M^+), 122 (32), 110 (33), 105 (91), 104 (11), 95 (21), 83 (15), 82 (25), 79 (10), 77 (100), 67 (35), 55 (35), 53 (10), 51 (21), 41 (12). Anal. calc. for C$_{14}$H$_{17}$NO$_2$ (231.29): C 72.70, H 7.41, N 6.06; found: C 72.44, H 7.68, N 6.02.

N*-[2-(Cyclohex-2-enyl)-1-oxopropyl]benzamide* (*rac*-**29c**). From **27c**, similarly to *rac*-**29a**. The mixture was stirred for 6 d at 140°, diluted with Et$_2$O (50 ml) and extracted with 5M H$_2$SO$_4$, sat. NaHCO$_3$ soln., and H$_2$O (20 ml each). The combined org. phase was dried (Na$_2$SO$_4$) and evaporated. FC (SiO$_2$, hexane/AcOEt 10 :1 → 1:1): *rac*-**29c** (145 mg, 10%), diastereoisomer ratio 55 :45. Colorless crystals. M.p. 112.9–113.5°. R_f (hexane/AcOEt 5 :1) 0.16. IR (KBr): 3298*s*, 3158*m*, 3067*m*, 3026*m*, 2979*m*, 2932*s*, 2878*m*, 2860*m*, 1724v*s*, 1682*s*, 1650*m*, 1602*m*, 1584*m*, 1506*s*, 1486*s*, 1368*m*, 1265*s*, 1249*s*, 1190*m*, 1154*s*, 1074*m*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO, 2 isomers): 10.89, 10.87 (2*s*, NH); 7.87–7.82 (*m*, 2 arom. H); 7.64–7.60 (*m*, 1 arom. H); 7.53–7.49 (*m*, 2 arom. H); 5.78–5.72 (*m*, H–C(3)(chx)); 5.66 (*dd*, $^3J = 10.3$, 2.2, 0.5 H, H–C(2)(chx)); 5.48 (*dd*, $^3J = 10.2$, 1.8, 0.5 H, H–C(2)(chx)); 2.99–2.91 (*m*, CHCO); 2.51–2.38, 1.94–1.93, 1.72–1.66, 1.51–1.42, 1.39–1.24 (5*m*, 3 CH$_2$(chx)); 1.08 (*d*, $^3J = 6.8$, 1.5 H, Me); 1.05 (*d*, $^3J = 6.9$, 1.5 H, Me). ^{13}C-NMR (100 MHz, (D$_6$)DMSO; 2 isomers): 176.52, 176.46 (CH*C*O); 166.52, 166.43 (Ph*C*O); 133.72, 133.69, 132.65 (arom. C); 129.87, 128.66, 128.16 (*C*H=*C*H); 128.49, 128.40 (arom. C); 44.57, 44.15 (*C*HCO); 37.66, 37.48, 26.80, 24.74, 24.69, 21.18, 21.16 (CH$_2$(chx)); 13.71, 13.48 (Me). EI-MS: 257 (14, M^+), 177 (15), 145 (13), 136 (15), 122 (78), 109 (14), 108 (87), 105 (93), 93 (31), 91 (12), 85 (51), 83 (63), 81 (29), 80 (19), 79 (84), 78 (19), 77 (100), 67 (29), 65 (12), 55 (16), 53 (15), 51 (19). Anal. calc. for C$_{16}$H$_{19}$NO$_2$ (257.33): C 74.68, H 7.44, N 5.44; found: C 74.34, H 7.64, N 5.17.

N*-(Cyclohex-2-enyl)-2-methyl-3-oxo-3-phenylpropanamide* (*rac*-**30c**). From *rac*-**27c**, exactly according to *rac*-**29a**: *rac*-**30c** (162 mg, 11%), diastereoisomer ratio 53 :47. Colorless crystals. M.p. 144.9°. R_f (hexane/AcOEt 2 :1) 0.34; IR (KBr): 3284*s*, 3063*m*, 3026*m*, 2990*m*, 2982*m*, 2932*s*, 2862*m*, 2839*m*, 1688v*s*, 1633v*s*, 1597*s*, 1583*m*, 1547*s*, 1492*m*, 1449*s*, 1389*m*, 1374*m*, 1338*s*, 1313*m*, 1240*s*, 1207*s*, 1182*m*, 1101*m*, 1076*m*, 1029*m*. ^{1}H-NMR

(400 MHz, (D$_6$)DMSO; 2 isomers): 8.49, 8.34 (2*s*, $^3J = 8.0$, NH); 7.96 – 7.94 (*m*, 2 arom. H); 7.64 – 7.59 (*m*, 1 arom. H); 7.53 – 7.48 (*m*, 2 arom. H); 5.85 – 5.76 (*m*, H–C(3)(chx)); 5.55 – 5-51, 5.40 – 5.36 (2*dm*, $^3J = 10.1$, H–C(2)(chx)); 4.38, 4.37 (2*q*, $^3J = 6.8$, MeC*H*); 4.15 – 4.13 (*m*, H–C(1)(chx)); 2.02 – 2.90, 1.73 – 1.29 (2*m*, 3 CH$_2$(chx)); 1.26 (*d*, $^3J = 6.8$, Me). ^{13}C-NMR (100 MHz, (D$_6$)DMSO; 2 isomers): 196.40, 196.35 (Ph*C*O); 169.68, 169.61 (CON); 136.27, 136.23, 133.16, 133.12 (arom. C); 130.09, 129.62 (C(3)(chx)); 128.66, 128.58, 128.07 (arom. C); 128.12, 127.90 (C(2)(chx)); 48.82, 48.69 (Me*C*H); 44.09, 43.88 (C(1)(chx)); 28.81, 28.59 (C(6)(chx)); 24.46, 24.40 (C(4)(chx)); 19.69, 19.24 (C(5)(chx)); 14.09, 13.91 (Me). EI-MS: 257 (1, M^+), 145 (12), 133 (10), 105 (43), 97 (13), 96 (100), 85 (58), 83 (75), 81 (17), 79 (20), 77 (51), 69 (21), 55 (13). Anal. calc. for $C_{16}H_{19}NO_2$ (257.33): C 74.68, H 7.44, N 5.44; found: C 74.65, H 7.40, N 5.30.

N-*Benzyl-2-methylpent-4-enamide* (*rac*-**32**) [45]. From **31**, according to *rac*-**29a** (sealed tube; stirring at 135° for 45 h): *rac*-**32** (61 mg, 28%). R_f (hexane/AcOEt 5 : 1) 0.08. IR (KBr): 3289*s*, 3077*m*, 3031*m*, 2972*s*, 2932*m*, 2876*m*, 1646v*s*, 1548v*s*, 1497*s*, 1455*s*, 1437*m*, 1359*m*, 1300*m*, 1285*m*, 1250*s*, 1221*m*, 1080*m*, 1029*m*, 699*s*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO): 8.33 (*dd*, $^3J = 5.6, 5.6$, NH); 7.33 – 7.21 (*m*, 5 arom. H); 5.73 (*ddt*, $^3J = 17.1, 10.3, 6.8$, CH$_2$=C*H*CH$_2$); 5.03 (*ddt*, $^3J = 17.2$, $^2J = 2.2$, $^4J = 1.5$, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 4.98 (*ddt*, $^3J = 10.2$, $^2J = 2.2$, $^4J = 1.1$, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 4.30 (*dd*, $^2J = 15.2$, $^3J = 6.1$, 1 H, PhC*H*$_2$); 4.24 (*dd*, $^2J = 15.2$, $^3J = 5.9$, 1 H, PhC*H*$_2$); 2.40 (*qt*, $^3J = 6.9, 6.9$, MeC*H*); 2.30 (*ddddd*, $^2J = 13.9$, $^3J = 7.0, 7.0$, $^4J = 1.3, 1.3$, 1 H, CH$_2$=CHC*H*$_2$); 2.05 (*ddddd*, $^2J = 13.8$, $^3J = 7.0, 7.0$, $^4J = 1.1, 1.1$, 1 H, CH$_2$=CHC*H*$_2$); 1.03 (*d*, $^3J = 6.8$, Me). ^{13}C-NMR (100 MHz, (D$_6$)DMSO): 175.2 (CON); 139.9 (arom. C); 136.7 (CH$_2$=*C*HCH$_2$); 128.4, 127.3, 126.9 (arom. C); 116.4 (*C*H$_2$=CHCH$_2$); 42.1 (CH$_2$N); 39.6 (Me*C*H); 38.1 (CH$_2$=CH*C*H$_2$); 17.7 (Me). EI-MS: 204 (11, $[M + H]^+$), 203 (23, M^+), 188 (11), 162 (17), 160 (11), 106 (14), 91 (100), 69 (15), 65 (14). Anal. calc. for $C_{13}H_{17}NO$ (203.28): C 76.81, H 8.43, N 6.89; found: C 76.53, H 8.32, N 6.99.

N-*[(*E*)-But-2-enyl]-2-methyl-3-oxo-3-phenylpropanamide* (*rac*-**30b**). Anh. ZnCl$_2$ (170 mg, 24 mmol) **27b** (677 mg, 1.96 mmol), and toluene (7 ml) were stirred in a dried *Schlenk* tube under Ar at 85° during 20 h. The mixture was cooled to r.t., and an excess of TMEDA was added, forming a white precipitate, which was filtered off. The filtrate was diluted with Et$_2$O (75 ml) and extracted with 5M H$_2$SO$_4$, sat. NaHCO$_3$ soln., and half-sat. NaCl soln. (2 × 75 ml each). The combined org. layer was dried (MgSO$_4$). FC (SiO$_2$, hexane/AcOEt 2 : 1): *rac*-**30b** (308 mg, 84%), (*E*)/(*Z*) 5.4 : 1. Colorless crystals. M.p. 107.5°. R_f (hexane/AcOEt 5 : 1) 0.16. IR (KBr): 3286*s*, 3075*m*, 2991*m*, 2964*m*, 2939*m*, 2874*m*, 1691v*s*, 1632v*s*, 1599*m*, 1584*m*, 1555*s*, 1449*s*, 1435*m*, 1372*m*, 1361*m*, 1313*m*, 1242*s*, 1207*s*, 1185*m*, 965*s*, 953*m*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO): 8.36 (*t*, $^3J = 4.8$, NH); 7.95 (*dd*, $^3J = 8.4, 1.2$, 2 arom. H); 7.64 – 7.60 (*m*, 1 arom. H); 7.53 – 7.49 (*m*, 2 arom. H); 5.50 (*dqm*, $^3J = 15.3, 6.4$, MeC*H*=CHCH$_2$); 5.31 (*dqm*, $^3J = 15.3$, $^4J = 1.5$, MeCH=C*H*CH$_2$); 4.40 (*q*, $^3J = 6.9$, MeC*H*); 3.60 – 3.57 (*m*, MeCH=CHC*H*$_2$); 1.59 (*ddt*, $^3J = 6.4$, $^4J = 1.5$, $^5J = 1.3$, *Me*CH=CHCH$_2$); 1.27 (*d*, $^3J = 6.9$, *Me*CH). ^{13}C-NMR (100 MHz, (D$_6$)DMSO): 196.5 (Ph*C*O); 169.9 (CON); 136.2, 133.2, 128.7 (arom. C); 128.2 (Me*C*H=CHCH$_2$); 127.7 (arom. C); 126.2 (MeCH=*C*HCH$_2$); 48.7 (Me*C*H); 40.4 (MeCH=CH*C*H$_2$); 17.5 (*Me*CH=CHCH$_2$); 14.2 (*Me*CH). EI-MS: 231 (8, M^+), 133 (18), 105 (97), 77 (60), 70 (100), 55 (9). Anal. calc. for $C_{14}H_{17}NO_2$ (231.29): C 72.70, H 7.41, N 6.06; found: C 72.63, H 7.36, N 6.15.

*2-Methyl-3-oxo-3-phenyl-*N*-prop-2-enylpropanamide* (*rac*-**30a**). From **27a**, according to *rac*-**30b**: *rac*-**30a** (80 mg, 85%). Colorless crystals. M.p. 108.5°. R_f (hexane/AcOEt 5 : 1) 0.16. IR (KBr): 3293*s*, 3064*m*, 2986*m*, 2936*m*, 2874*m*, 1692v*s*, 1632v*s*, 1582*m*, 1548*s*, 1447*s*, 1421*m*, 1372*m*, 1348*s*, 1315*m*, 1243*s*, 1205*s*, 1179*m*, 1093*m*, 998*s*, 956*s*, 946*s*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO): 8.04 – 8.01 (*m*, 2 arom. H); 7.62 – 7.58 (*m*, 1 arom. H); 7.51 – 7.46 (*m*, 2 arom. H); 6.59 (br. NH); 5.78 (*ddt*, $^3J = 17.2, 10.3, 5.3$, CH$_2$=C*H*CH$_2$); 5.11 (*ddt*, $^3J = 17.2$, $^2J \approx {}^4J = 1.5$, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 5.09 (*ddt*, $^3J = 10.3$, $^2J \approx {}^3J = 1.5$, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 4.42 (*q*, $^3J = 7.2$, MeC*H*); 3.89 (*ddddd*, $^2J = 15.9$, $^3J = 5.6, 5.6$, $^4J = 1.6, 1.6$, 1 H, CH$_2$=CHC*H*$_2$); 3.83 (*ddddd*, $^2J = 15.9$, $^3J = 5.7, 5.7$, $^4J = 1.6, 1.6$, 1 H, CH$_2$=CHC*H*$_2$); 1.54 (*d*, $^3J = 7.2$, *Me*CH). ^{13}C-NMR (100 MHz, CDCl$_3$): 199.9 (Ph*C*O); 169.8 (CON); 135.8 (arom. C); 133.9, 133.7 (CH$_2$=*C*HCH$_2$, arom. C); 128.9, 128.7 (arom. C); 116.2 (*C*H$_2$=CHCH$_2$); 49.6 (Me*C*H); 41.9 (CH$_2$=CH*C*H$_2$); 17.1 (*Me*CH). EI-MS: 217 (4, M^+), 133 (10), 105 (100), 77 (61), 58 (10), 57 (12), 56 (27), 51 (18). Anal. calc. for $C_{13}H_{15}NO_2$ (217.27): C 71.87, H 6.96, N 6.45; found: C 71.73, H 6.98, N 6.31.

*2-Methyl-3-(4-methylphenyl)-3-oxo-*N*-prop-2-enylpropanamide* (*rac*-**30d**). From **27d**, according to *rac*-**30b**: *rac*-**30d** (285 mg, 61%). Colorless crystals. M.p. 123.4°. R_f (hexane/AcOEt 5 : 1) 0.16. IR (KBr): 3283*s*, 3068*m*, 2980*m*, 2936*m*, 2873*m*, 1685*s*, 1636v*s*, 1610*s*, 1547*s*, 1454*m*, 1424*m*, 1373*m*, 1353*m*, 1336*m*, 1318*m*, 1246*m*, 1208*m*, 1185*m*, 996*m*, 953*m*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO): 8.41 (*t*, $^3J = 5.5$, NH); 7.87 (*d*, $^3J = 8.2$, 2 arom. H); 7.31 (*d*, $^3J = 8.1$, 2 arom. H); 5.74 (*ddt*, $^3J = 17.2, 10.3, 5.1$, CH$_2$=C*H*CH$_2$); 5.08 (*ddt*, $^3J = 17.2$, $^2J = {}^4J = 1.8$, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 5.02 (*ddt*, $^3J = 10.3$, $^2J = 1.9$, $^4J = 1.6$, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 4.40 (*q*, $^3J = 6.9$, MeC*H*); 3.68 (*ddddd*, $^2J = 16.6$, $^3J = 5.4, 5.4$, $^4J = 1.8, 1.8$, 1 H, CH$_2$=CHC*H*$_2$); 3.63 (*ddddd*, $^2J = 16.4$, $^3J = 5.4, 5.4$, $^4J = 1.8, 1.8$, 1 H, CH$_2$=CHC*H*$_2$); 2.37 (*s*, *Me*–C$_6$H$_4$); 1.27 (*d*, $^3J = 6.9$, *Me*CH). ^{13}C-NMR (100 MHz, (D$_6$)DMSO): 195.9 (Ar*C*O); 170.1 (CON); 143.6 (arom. C); 135.1 (CH$_2$=*C*HCH$_2$); 133.7, 129.3, 128.3 (arom. C); 115.1

(CH$_2$=CHCH$_2$); 48.5 (MeCH); 40.9 (CH$_2$=CHCH$_2$); 21.2 (*Me*−C$_6$H$_4$); 14.3 (*Me*CH). EI-MS: 231 (1, M^+), 148 (4), 133 (6), 120 (10), 119 (100), 91 (27), 65 (7). Anal. calc. for $C_{14}H_{17}NO_2$ (231.29): C 72.70, H 7.41, N 6.06; found: C 72.51, H 7.52, N 6.02.

*4-{[(*tert*-Butyl)dimethylsilyl]oxy}-3-methyl-4-phenyl-1-(prop-2-enyl)azetidin-2-one* (*rac*-**34**). To a mixture of 2,6-diphenylphenol (1.63 g, 6.62 mmol) and toluene (16 ml) under Ar, 2M AlMe$_3$ in hexane (1.1 ml) was added slowly. After 30 min, the mixture was cooled to −78°. A soln. of **27a** (661 mg, 1.99 mmol) in toluene (6 ml) was added at −78°. After 10 min, the mixture was heated to 80° during 2.5 h, then cooled, diluted with AcOEt, and extracted with half-sat. NaCl soln. (2 ×). The combined org. phase was dried (Na$_2$SO$_4$). FC (SiO$_2$, hexane/AcOEt 13:1 → 6:1): *rac*-**30a** (95 mg, 22%; colorless crystals) and *rac*-**34** (340 mg, 52%). *rac*-**34**: Colorless oil. n_D^{20} = 1.5895. R_f(hexane/AcOEt 5:1) 0.38. IR (KBr): 3062*w*, 3031*w*, 2958*m*, 2931*m*, 2895*m*, 2858*m*, 1764v*s*, 1762v*s*, 1473*m*, 1463*m*, 1449*m*, 1382*m*, 1361*m*, 1316*s*, 1287*m*, 1254*s*, 1191*m*, 1143*s*, 1078*m*, 1041*s*, 1028*m*, 872*s*, 837*s*, 778*s*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.44–7.30 (*m*, 5 arom. H); 6.02 (*dddd*, ^3J = 17.0, 10.3, 6.2, 6.2, CH$_2$=C*H*CH$_2$); 5.22 (*ddt*, ^3J = 17.0, $^2J \approx {}^4J$ = 1.4, 1 H, C*H*$_2$=CHCH$_2$(*cis*)); 5.19 (*ddt*, ^3J = 10.2, $^2J \approx {}^4J$ = 1.4, 1 H, C*H*$_2$=CHCH$_2$(*trans*)); 3.88 (*dddd*, ^2J = 15.7, ^3J = 5.9, ^4J = 1.4, 1.4, 1 H, CH$_2$=CHC*H*$_2$); 3.73 (*dddd*, ^2J = 15.7, ^3J = 6.4, ^4J = 1.2, 1.2, 1 H, CH$_2$=CHC*H*$_2$); 3.32 (*q*, ^3J = 7.4, H−C(3)); 1.30 (*d*, ^3J = 7.4, Me−C(3)); 0.97 (*s*, ^{t}BuSi); 0.02 (*s*, 1 MeSi); 0.003 (*s*, 1 MeSi). ^{13}C-NMR (100 MHz, CDCl$_3$): 171.9 (CON); 141.3 (arom. C); 132.5 (CH$_2$=CHCH$_2$); 128.39, 128.37, 126.0 (arom. C); 118.0 (CH$_2$=CHCH$_2$); 90.0 (C(4)); 59.4 (C(3)); 44.5 (CH$_2$=CHCH$_2$); 26.0 (*Me*$_3$CSi); 18.8 (Me$_3$$C$Si); 9.8 (Me−C(3)); −2.75, −2.79 (Me$_2$Si). EI-MS 330 (3, $[M-1]^+$), 274 (11), 200 (10), 117 (10), 105 (13), 75 (22), 73 (15), 43 (31), 41 (100). HR-ESI-MS: 332.2042 ($[M+H]^+$, $C_{19}H_{30}NO_2Si$; calc. 332.2040).

N-*((*E*)-1-{[(*tert*-Butyl)dimethylsilyl]oxy}prop-1-enyl)-*N*-cyclohex-2-enylbenzamide* (*rac*-**35**). To *rac*-**27c** (1.99 g, 5.36 mmol) and toluene (20 ml) in a dried *Schlenk* tube under Ar at 0°, bis(benzonitrile)palladium(II) chloride (411 mg, 1.07 mmol) was added. More Pd^{II} complex (411 mg) was added after 20 min and after another 20 min (205 mg). After 30 min, the mixture was diluted with AcOEt (50 ml) and extracted with H$_2$O and half-sat. NaCl soln. (2 × 30 ml each). The combined org. phase was dried (Na$_2$SO$_4$). FC (SiO$_2$, hexane/AcOEt 15:1 → 5:1): *rac*-**35** (739 mg, 37%), rotamer ratio 1.4:1.0 (^{1}H-NMR). Pale yellow solid. M.p. 53.0–54.9°. R_f (hexane/AcOEt 5:1) 0.20. IR (KBr): 3062*w*, 3029*w*, 2931*s*, 2859*s*, 2711*w*, 1959*w*, 1899*w*, 1813*w*, 1670*s*, 1648v*s*, 1602*w*, 1581*w*, 1492*m*, 1472*m*, 1463*m*, 1448*s*, 1397*m*, 1372*s*, 1355*s*, 1296v*s*, 1255*s*, 1215*s*, 1142*s*, 1131*s*, 1111*m*, 1073*w*, 1056*w*, 1028*w*, 1006*w*, 840v*s*, 759*s*, 701*s*, 689*s*. ^{1}H-NMR (400 MHz, CDCl$_3$, major rotamer): 7.61–7.59 (*m*, 2 arom. H); 7.38–7.34 (*m*, 1 arom. H); 7.31–7.27 (*m*, 2 arom. H); 5.85–5.70 (*m*, H−C(2)(chx)); 5.57–5.54 (*m*, H−C(3)(chx)); 5.04 (br., H−C(1)(chx)); 4.21 (*q*, ^3J = 6.5, MeC*H*=C); 2.14–1.65 (*m*, 3 CH$_2$(chx)); 1.26 (*d*, ^3J = 6.9, *Me*CH=C); 0.961 (*s*, ^{t}BuSi); 0.07 (*s*, Me$_2$Si). ^{1}H-NMR (400 MHz, CDCl$_3$; minor rotamer): 7.61–7.59 (*m*, 2 arom. H); 7.38–7.34 (*m*, 1 arom. H); 7.31–7.27 (*m*, 2 arom. H); 5.85–5.70 (*m*, CH=CH(chx)); 5.20 (br., H−C(1)(chx)); 4.20 (*q*, ^3J = 6.5, MeC*H*=C); 2.14–1.65 (*m*, 3 CH$_2$(chx)); 1.24 (*d*, ^3J = 7.9, *Me*CH=C); 0.957 (*s*, ^{t}BuSi); 0.15 (*s*, 1 MeSi); 0.14 (*s*, 1 MeSi). ^{13}C-NMR (100 MHz, CDCl$_3$; both rotamers): 170.9, 170.7 (PhCO); 144.8, 144.4 (C−O−Si); 137.4, 137.3 (arom. C); 130.3 (C(2)(chx)); 129.8 (arom. C); 127.6, 126.6 (C(3)(chx)); 127.3 (arom. C); 127.0 (arom. C); 100.2, 100.0 (MeCH=C); 51.9, 51.8 (C(1)(chx)); 28.1, 26.0 (C(6)(chx)); 25.7, 25.6 (*Me*$_3$CSi); 24.8, 24.5 (C(4)(chx)); 21.7, 21.4 (C(5)(chx)); 18.1, 18.0 (Me$_3$$C$Si); 12.4, 12.2 (*Me*CH=C); −4.95, −4.97, −5.0, −5.1 (Me$_2$Si). EI-MS: 371 (1, M^+), 235 (12), 234 (52), 233 (21), 183 (30), 179 (12), 178 (59), 135 (11), 105 (100), 81 (26), 79 (25), 77 (47), 75 (40), 73 (46). Anal. calc. for $C_{22}H_{33}NO_2Si$ (371.59): C 71.11, H 8.59, N 3.77; found: C 70.76, H 9.01, N 3.96. HR-ESI-MS: 394.2174 ($[M+Na]^+$, $C_{22}H_{33}NNaO_2Si$; calc. 394.2173).

*1-Benzoyl-1,3,3a,4,5,7a-hexahydro-3-methyl-2*H*-indol-2-one* (*rac*-**36**). From *rac*-**27c**, according to *rac*-**35**, but not in the same batch: *rac*-**36** (248 mg, 8%). Colorless crystals. M.p. 147.4°. R_f (hexane/AcOEt 5:1) 0.16. IR (KBr): 3059*w*, 3044*w*, 2979*w*, 2943*m*, 2916*m*, 2892*m*, 2863*w*, 2851*m*, 2840*w*, 1968*w*, 1923*w*, 1903*w*, 1737v*s*, 1674v*s*, 1599*m*, 1582*m*, 1488*w*, 1461*w*, 1447*s*, 1429*m*, 1392*m*, 1376*m*, 1349*m*, 1331*s*, 1313*s*, 1291v*s*, 1280v*s*, 1233*s*, 1210*s*, 1196*s*, 1173*s*, 1159*m*, 1143*s*, 1110*m*, 1076*m*, 1065*m*, 1053*m*, 1044*m*, 1028*m*, 1020*m*, 1002*m*. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.66–7.63 (*m*, 2 arom. H); 7.54–7.50 (*m*, 1 arom. H); 7.45–7.38 (*m*, 2 arom. H); 6.26 (*dddd*, ^2J = 10.0, ^3J = 4.2, ^4J = 2.8, 1.4, H−C(7)); 6.07 (*ddm*, ^2J = 10.0, ^3J = 4.9, H−C(6)); 4.52 (*ddm*, $^3J \approx$ 4.3, 4.3, H−C(7a)); 2.78 (*qd*, $^3J = {}^2J$ = 7.3, H−C(3)); 2.42 (*dddd*, ^3J = 13.4, 7.6, 5.7, 4.1, H−C(3a)); 2.23 (*dtm*, ^2J = 18.3, ^3J = 5.3, 5.3, 1 H−C(5)); 2.09 (*ddddd*, ^2J = 18.2, ^3J = 11.8, 4.9, 4.9, ^4J = 2.1, 1 H−C(5)); 1.83–1.80 (*dm*, ^2J = 13.1, 1 H−C(4)); 1.32 (*ddd*, $^2J \approx {}^3J$ = 13.3, ^3J = 11.8, 5.1, 1 H−C(4)); 1.19 (*d*, ^3J = 6.9, Me−C(3)). ^{13}C-NMR (100 MHz, CDCl$_3$): 176.6 (C(2)); 171.5 (PhCO); 134.9 (arom. C); 133.2 (C(5)); 132.3 (arom. C); 129.6 (arom. C); 127.8 (arom. C); 122.9 (C(4)); 53.5 (C(7a)); 42.2 (C(3)); 34.6 (C(3a)); 24.3 (C(6)); 20.0 (C(7)); 9.2 (*Me*−C(3)). EI-MS: 256 (16, $[M+H]^+$), 255 (23, M^+), 150 (73), 107 (10), 105 (100), 79 (10), 77 (65). Anal. calc. for $C_{16}H_{17}NO_2$ (255.31): C 75.27, H 6.71, N 5.49; found: C 75.22, H 6.71, N 5.49.

*1-Benzoyl-1,3,3a,6,7,7a-hexahydro-3-methyl-2*H*-indol-2-one* (*rac*-**37**). From *rac*-**27c**, according to *rac*-**35**: *rac*-**37** (147 mg, 12%). Colorless crystals. M.p. 84.5°. R_f (hexane/AcOEt 5:1) 0.22. IR (KBr): 3092*w*, 3061*w*, 3026*m*, 2967*m*, 2947*m*, 2935*m*, 2917*m*, 2889*m*, 2859*m*, 2832*w*, 1960*w*, 1896*w*, 1741v*s*, 1667v*s*, 1603*m*, 1583*w*, 1527*w*, 1492*w*, 1447*m*, 1425*m*, 1392*m*, 1376*m*, 1333v*s*, 1306v*s*, 1225*m*, 1209*s*, 1195*s*, 1155*s*, 1104*m*, 1090, 1081*m*, 1067*m*, 1029*m*, 1012*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.69 – 7.47 (*m*, 3 arom. H); 7.44 – 7.37 (*m*, 2 arom. H); 5.91 (*dddd*, $^3J = 10.0$, 3.4, 3.4, $^4J = 0.9$, H–C(5)); 5.77 (*ddddd*, $^3J \approx {}^4J \approx {}^4J \approx {}^5J = 1.9$, H–C(4)); 4.54 (*ddd*, $^3J = 11.1$, 7.0, 4.3, H–C(7a)); 2.54 – 2.44 (*m*, H–C(3), H–C(3a)); 2.33 (*dddd*, $^2J = 12.5$, $^3J = 4.2$, 4.2, 4.2, 1 H–C(7)); 2.15 – 2.00 (*m*, CH_2(6)); 1.64 (*dddd*, $^2J = 11.2$, 8.9, 7.0, 1 H–C(7)); 1.24 (*d*, $^3J = 6.6$, Me–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): 176.3 (C(2)); 170.3 (Ph*C*O); 135.1 (arom. C); 131.5 (arom. C); 128.6 (C(3a)); 128.3 (arom. C); 127.7 (arom. C); 125.6 (C(4)); 54.3 (C(7a)); 44.2 (C(3)); 39.8 (C(3a)); 24.2 (C(7)); 23.1 (C(6)); 13.6 (Me–C(3)). EI-MS: 255 (31, M^+), 106 (12), 105 (100), 85 (23), 83 (32), 79 (11), 77 (55). Anal. calc. for $C_{16}H_{17}NO_2$ (255.31): C 75.27, H 6.71, N 5.49; found: C 75.06, H 6.78, N 5.15.

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