N,N-Bis(trimethylsilyl)ynamines: Cycloaddition Reactions with Dimethyl Acetylenedicarboxylate and Ketenes

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N,N-Bis(trimethylsilyl)ynamines **1** react with dimethyl acetylenedicarboxylate (**2**) in a molar ratio of 1:2 to afford 3-cyclopropenylfurans **3**. Configuration and conformation of **3a** are confirmed by X-ray crystallography. Addition of a further mol of **1** furnishes the fumarates **4**. With ketenes **5** (**5c**, **d** are prepared in situ) a competition between the formation of cyclic butenone derivatives **6** and allenic imidates **7** is observed, depending on the substitution pattern of **1**. After hydrolytic workup, the corresponding amides **10** or the vinylogous amides **9** are obtained in good yield. These experiments indicate that the silylated ynamines **1** show a completely different, more selective reactivity towards dimethyl acetylenedicarboxylate compared to *N,N*-dialkyl-substituted ynamines, yielding furan derivatives instead of anilines. Towards ketenes, however, a similar cycloaddition reactivity as for *N,N*-dialkylynamines is observed.

Ynamines are very useful building blocks in organic synthesis[1]. However, until recently their use was limited with respect to the substitution pattern at the nitrogen atom, since only tertiary ynamines are accessible[2]. The synthesis of *N,N*-bis(trimethylsilyl)ynamines **1** as synthetic equivalents of primary ynamines was reported recently by our laboratory[3]. In the course of subsequent work concerning the nucleophilic reactivity of the bissilylated nitrogen atom it became evident, that the ynamines **1** show only very limited reactivity at nitrogen. In all cases studied, conjugate addition to the triple bond by electrophiles was observed[3,4].

In this paper, we report on our results of addition reactions of dimethyl acetylenedicarboxylate (**2**) and ketenes **5** to the triple bonds of **1**. We use the relatively easily accessible *n*-butyl- and phenyl-substituted compounds **1a,b** as examples for other aliphatically and aromatically substituted derivatives of **1**. We are particularly interested in the chemical reactivity of the *N,N*-bissilylated ynamines **1** in comparison with those of known *N,N*-dialkyl derivatives. Furthermore, these experiments are aimed at the synthesis of cycloadducts of ynamines possessing primary amine functionalities after hydrolytic cleavage of the N–Si bonds.

Reactions of the Ynamines 1 with Dimethyl Acetylenedicarboxylate (2)

Reports on reactions of ynamines with electron-poor alkynes are rare[5–8]. Ficini and Barbara describe the cycloaddition of one mol equivalent of ynamine to two equivalents of dimethyl acetylenedicarboxylate (**2**) forming a persubstituted aniline derivative[8].

The reaction of the *N,N*-bis(trimethylsilyl)ynamines **1** with two mol equivalents of **2** takes a completely different course. After mixing of ethereal solutions of the starting materials at −78°C, slow warming up to room temperature and stirring for 16 h the bicyclic compounds **3** are obtained in 79 and 67% yield, respectively. The synthesis of **3b** is accompanied by the formation of small amounts (approx. 3%) of a 2:4 adduct of **1b** and **2**. However, we have not yet been able to assign a satisfactory structure to this material; indications for aniline-type structures (compare ref.[8]) were not obtained.

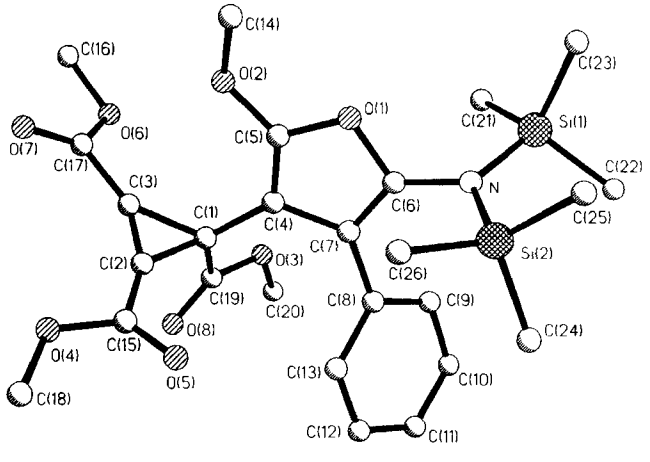

Figure 1. XS plot of the molecular structure of **3a**; crystallographic numbering and thermal ellipsoids (SHELXTL-PLUS[18])

The constitution and configuration of **3a** are determined by *X-ray crystallography*[9]. Compound **3a** crystallizes with 0.3 mol of cyclohexane (from the recrystallization) per for-

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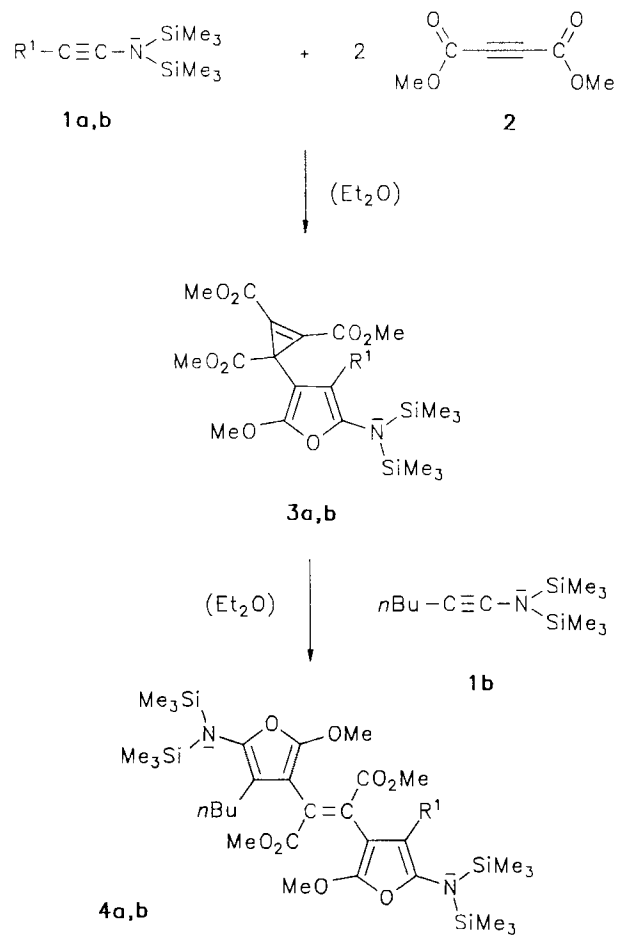


	1a, 3a, 4b	1b, 3b, 4a
R^1	Ph	Bu

mula unit (Figure 1). Because of steric and electronic reasons the furan ring system in **3a** is highly unsymmetric with O(1)–C(6) and O(1)–C(5) bonds of 1.414(8) and 1.344(7) Å, respectively. Both C=C bonds are similar in length [C(6)–C(7) 1.333(8), C(4)–C(5) 1.330(9), resp.]. The phenyl ring is twisted by 53° with respect to the plane of the furan ring, indicating reduced conjugative interaction due to steric interferences. The methoxy group and the bissilylamino function are similarly bent out of the plane of the furan ring. The C(2)=C(3) bond of the cyclopropene ring is comparably short [1.284(8) Å], due to the adjacent carboxylate groups.

The spectroscopic data of **3a** and **3b** are well explained from the results of the X-ray study. The *IR spectrum* is dominated by a strong absorption at 1855–1860 cm^{-1} due to the C=C valence stretching vibration in the three-membered ring; the ester C=O absorptions are found at 1720 cm^{-1}.

The ^{13}C-NMR spectra of **3a,b** are characterized by the cyclopropene signals (approx. δ = 32.5 for the sp^3 atom and 116–117 for the C=C carbon atoms). The signals for the furan carbon atoms reflect the strong polarization of the C=C bonds with chemical shifts of δ ≈ 142 and 171 for the hetero-substituted carbon atoms and δ ≈ 97 and 114 for the carbon atoms in β positions of the enamine and enol ether subunits.

The unexpected formation of a mixed furan/cyclopropene-type molecule **3** has prompted us to investigate the addition of a further mol equivalent of **1b** to **3a** and **3b**. In analogy to the studies of Ege and Gilbert[10] as well as Eicher and Pfister[11] we have expected the formation of a bisfuran system from such reactions. Indeed, as anticipated, a symmetrical bisfuryl-substituted dimethyl fumarate **4a** is obtained in 60% yield after addition of **1b** to **3b** at room temperature. Similarly, a mixed product **4b** is formed in 33% yield from **1b** and **3a**. The synthesis of a symmetrical biphenyl system from **1a** and **3a** fails because of the diminished reactivity of **3a** and uncontrollable polymerizations at higher temperatures. Compound **4a** is also obtained directly from equimolar amounts of **1b** and **2** after mixing of the starting materials at −78°C and stirring at room temperature for 2 days. In analogy to a proposal of Ege and Gilbert[10] the mechanism is best explained by a nucleophilic attack of the β atom of the ynamine **1** at the cyclopropene double bond forming a zwitterionic intermediate which collapses to the second furan ring in a 1,5 electrocyclization.

The constitution and configuration of the products **4** are mainly determined by *^{13}C-NMR spectral analysis*. The symmetry of **4a** is clearly seen at room temperature, but at low temperature (213 K) a complicated dynamic behavior is observed, probably due to freezing of rotations of the furan rings in the neighborhood of the ester functions of the fumarate systems. Otherwise, the chemical shifts of the furan systems of the compounds **4** are similar to those of **3** with the central C=C bond giving rise to signals at δ = 127–131.

The formation of mixed furan-cyclopropene-type molecules has been discussed in connection with the mechanism of the tetramerization of dimethyl acetylenedicarboxylate[12].

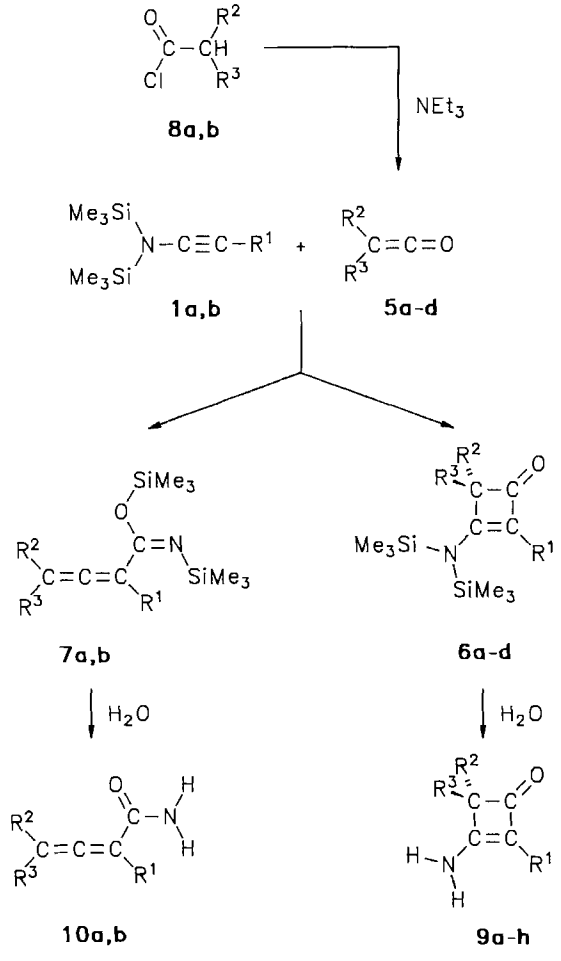
These experiments indicate that the protected primary ynamines **1** react differently from other tertiary ynamines[1,8]; they are obviously less reactive and more selective because of the reduced polarity of the C≡C triple bond as a consequence of the diminished nucleophilic character of the bissilylamino moiety.

Reactions of the Ynamines 1 with the Ketenes 5

Reactions of ynamines with ketenes mainly occur by [2+2] cycloadditions, depending on the substitution patterns of both starting materials[1]. Cycloaddition of the C=C bonds of the ketenes leads to 3-aminocyclobutenones, whereas involvement of the C=O bond of the ketenes yields allenic carboxamides by an intermediate formation of 2-methyleneoxetes[13–17].

Regarding the reactivity towards ketenes, *N,N*-bissilylated ynamines **1** behave similar to other known *N*-trisubstituted ynamines. Thus, mixing of the ynamines **1** with the stable ketenes **5a,b** at −78°C in diethyl ether and warming up to room temperature within 8 h yields the cyclic (**6**) and allenic products **7** in good yield (Table 1) after evaporation of the

solvent. Reactions of the unstable ketenes **5c,d** are performed by in situ generation of the ketenes by adding the corresponding acyl chloride **8** to a mixture of one aliquot of ynamine **1** and a threefold excess of triethylamine. In these cases, aqueous workup leads exclusively to the cyclic primary vinylogous amides **9e–h**; indications for the formation of allenic products under these reaction conditions have not been found. As Table 1 indicates, the regiochemistry of the cycloaddition with regard to the ketenes is governed by the substitution pattern of the ynamine **1**. The reaction of the phenyl derivative **1a** gives exclusively the cyclobutenone system **6** or **9**, whereas the reaction of the butyl derivative **1b** leads to mixtures of cyclic and allenic products. The allenic bissilylated imidates **7a,b** are very sensitive to moisture and can only be detected by spectroscopic methods, but are not isolated. The cyclic products **6**, however, are all isolated in pure form.



	5a	5b	5c, 8a	5d, 8b
R^2	Ph	Et	Ph	H
R^3	Ph	Ph	H	H

Both types of products **6** and **7** can be easily hydrolyzed in satd. aqueous sodium hydrogencarbonate solution, supporting the idea of using the *N,N*-bissilylated ynamines as synthetic equivalents of the inaccessible primary ynamines. Hence, the primary vinylogous amides **9** and the primary amides **10** are obtained in good yield. In cases where mixtures of products are obtained, separation of the components is easily achieved by flash chromatography on silica gel.

Table 1. Yields and substitution pattern for **6**, **9**, and **10**

	R^1	R^2	R^3	Yield (%)	From
6a	Ph	Ph	Ph	64	**1a**, **5a**
6b	Ph	Et	Ph	86	**1a**, **5b**
6c	Bu	Ph	Ph	21	**1b**, **5a**
6d	Bu	Et	Ph	24	**1b**, **5b**
9a	Ph	Ph	Ph	91	**6a**
9b	Ph	Et	Ph	83	**6b**
9c	Bu	Ph	Ph	85	**6c**
9d	Bu	Et	Ph	79	**6d**
9e	Ph	Ph	H	71	**1a**, **8a**
9f[a]	Ph	Bu	H	32	**1b**, **8a**
9g	Ph	H	H	65	**1a**, **8b**
9h	Bu	H	H	38	**1b**, **8b**
10a	Bu	Ph	Ph	45	**1b**, **5a**
10b	Bu	Et	Ph	35	**1b**, **5b**

[a] After 1,3-H shift.

Interestingly, in the formation of the cyclic vinylogous amide **9f** from ynamine **1b** and phenylketene, a 1,3-H shift has to be assumed, yielding the better conjugated system with the phenyl group in a sp^2 position instead of its expected isomer with the *n*-butyl group in this position.

The cyclobutenones **6** and **9** are best characterized by *^{13}C-NMR* data: The signals for the carbonyl carbon atoms are found at $\delta = 181-197$ and those for the sp^3 carbon atoms C-4 at 46–77. As anticipated, the strong push-pull olefinic character of the double bond is reflected in the chemical shifts of C-2 (112–144) and C-3 (164–184).

The allenic compounds **7** and **10** are easily identified by a weak antisymmetric cumulene stretching absorption at 1920–1940 cm^{-1}. Furthermore, characteristic shifts are found in the ^{13}C-NMR spectra: the central cumulenic carbon atom gives rise to a signal at $\delta = 206-208$; the other cumulenic carbon atoms show up between $\delta = 105$ and 115.

In conclusion, the results presented here indicate, that the *N,N*-bissilylated ynamines **1** show similar reactivity in cycloadditions towards ketenes compared to the much better known dialkyl-substituted ynamines; therefore, these compounds **1** may be regarded as synthetic equivalents of the preparatively inaccessible primary ynamines as far as products from cycloaddition reactions are concerned.

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Experimental

IR: Perkin-Elmer PE 298. – ^{1}H NMR: Bruker WM 300 (300 MHz) and AM 360 (360 MHz), internal reference tetramethylsilane. – ^{13}C NMR: Bruker WM 300 (75.47 MHz) and AM 360 (90.56 MHz), internal reference tetramethylsilane. – MS: Finnigan MAT C 312. – Flash chromatography: Silica gel 60 (Merck),

0.040–0.063 mm. – CHN: Perkin Elmer CHN Analysator 240. – Melting points are not corrected. – All solvents are purified by distillation. – Absolute diethyl ether is dried by distillation from sodium, THF by distillation from sodium/potassium alloy. Dimethyl acetylenedicarboxylate (**2**) (Janssen, 98%) was used without further purification. – All experiments are carried out with the exclusion of moisture (Ar).

(Phenylethynyl)bis(trimethylsilyl)amine (**1a**): See ref.[3].

1-Hexynylbis(trimethylsilyl)amine (**1b**) is prepared in analogy to **1a**[3] from 10.00 g (27 mmol) of *O*-(2,4,6-trimethylphenylsulfonyl)-*N*,*N*-bis(trimethylsilyl)hydroxylamine, 2.16 g (27 mmol) of 1-hexyne and 17.90 ml (27 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane) by using THF as solvent. Colorless oil, yield 4.15 g (64%), b.p. 57°C/0.1 Torr. – IR (neat): $\tilde{\nu}$ = 2940 cm^{-1}, 2920, 2860 (s, C–H aliph.), 2215 (s, C≡C), 1440 (w, br.), 1390 (vw), 1245 (s), 1220 (s). – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.20 [s, 18H, $Si(CH_3)_3$], 0.89 (t, ^3J = 7.1 Hz, 3H, CH_3), 1.39–1.43 (m, 4H, CH_2CH_2), 2.15 (t, ^3J = 6.8 Hz, 2H, ≡CCH_2). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 0.67 [$Si(CH_3)_3$], 13.63 (CH_3), 18.31 (≡C–CH_2), 21.98 ($CH_2CH_2CH_3$), 32.40 (CH_2CH_3), 53.57 (C≡C–N), 82.30 (C≡C–N). – MS (70 eV), *m/z* (%): 241 (8) [M^+], 226 (18) [M^+ – CH_3], 97 (34), 84 (38), 75 (84), 73 (100) [$Si(CH_3)_3^+$], 57 (80) [$C_4H_9^+$]. – $C_{12}H_{27}NSi_2$ (241.5): calcd. C 59.68, H 11.27, N 5.80; found C 59.18, H 11.49, N 6.13.

Reactions of the Ynamines **1a**, **b** *with Dimethyl Acetylenedicarboxylate* (**2**). – *General Procedure for the Synthesis of* **3a**, **b**: To a solution of the corresponding ynamine **1** in THF (30 ml) two equivalents of **2** are slowly added at −78°C. During warming to room temp. the reaction mixture turns red. After stirring for 2 d, the solvent is removed in vacuo. The crude product is purified by recrystallization.

Trimethyl 3-{5-[Bis(trimethylsilyl)amino]-2-methoxy-4-phenyl-3-furyl}-1-cyclopropene-1,2,3-tricarboxylate (**3a**): From 1.31 g (5.02 mmol) of **1a** and 1.42 g (10.0 mmol) of **2** triester **3a** is obtained as an orange solid after recrystallization from cyclohexane/petroleum ether (5:1); yield 2.16 g (79%), m.p. 89°C (orange crystals). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3040 (w, C–H arom.), 2960, 2940, 2890 (m, C–H aliph.), 1855 (m, C=C cyclopropene), 1720 (s, C=O), 1635 (m, C=C furan), 1610 (m, C=C), 1590 (sh, m, C=C arom.), 1430 (m), 1320 (m), 1240 (vs, br), 1100 (m), 1060 (m), 1015 (m). – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.02 [s, 18H, $Si(CH_3)_3$], 3.28 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.86 (s, 6H, OCH_3), 7.17–7.20 (m, 1H, *p*-H), 7.26–7.32 (m, 2H, *m*-H), 7.53–7.46 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 0.54 [$Si(CH_3)_3$], 32.52 (C), 51.62 (OCH_3), 52.54 (2× OCH_3), 58.59 (OCH_3), 97.08 (C-3), 114.1 (C-4), 116.0 (2× =*C*–C=O), 125.8 (*p*-C), 127.5, 128.4 (*o*-/*m*-C), 133.7 (*i*-C), 142.2 (C-5), 151.3 (C–*C*=O), 157.2 (2× =C–*C*=O), 170.3 (C-2). – MS (70 eV), *m/z* (%): 545 (10) [M^+], 530 (11) [M^+ – CH_3], 486 (8) [M^+ – CO_2CH_3], 278 (20), 77 (14) [$C_6H_5^+$], 73 (100) [$Si(CH_3)_3^+$], 59 (38) [$CO_2CH_3^+$]. – UV (diethyl ether): λ_{max} (lg ε) = 220 nm (4.125), 260 (3.804). – $C_{26}H_{35}NO_8Si_2$ (545.7): calcd. C 57.23, H 6.46, N 2.57; found C 57.48, H 6.52, N 2.65.

X-Ray Diffraction Analysis of **3a**[9]: A red, prismatic crystal, $C_{26}H_{35}NO_8Si_2 \cdot 0.3\ C_6H_{12}$ (from cyclohexane/petroleum ether, 5:1), crystal size 0.7 × 0.3 × 0.3 mm^3, is measured at room temp. by using an automatic CAD4 Turbo diffractometer (Enraf-Nonius) with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. 11600 reflexions are collected in the 2-Θ range 4.0 ≤ 2Θ ≤ 50.0° (scan speed variable; 1.50 to 3.30°/min). Crystal system: Triclinic, space group $P\bar{1}$, Z = 2, a = 8.331(5), b = 11.868(4), c = 16.830(6) Å, α = 93.27(3), β = 95.28(3), γ = 92.20(3)°; V = 1652.7(3) $Å^3$; D_x = 1.099 g · cm^{-1}. After absorption correction the structure is solved by direct methods (SHELXTL-PLUS program[18]) by using 3032 observed reflexions [$F_o > 4.0\sigma(F)$] for the non-hydrogen atoms. With the addition of the hydrogen atoms (coupled in position and temperature parameters to the corresponding carbon atoms) the anisotropic refinement leads to agreement factors R = 0.0863 and R_w = 0.1339 [weighting with $w^{-1} = \sigma^2(F) + 0.0766 \cdot F^2$] [3032 reflections with $I_0 > 4.0\sigma(I_0)$, 346 variable parameters, program SHELXTL-PLUS]. In this final refinement an isotropic extinction coefficient χ of 0.0001(6) is obtained. The molecular shape is presented in Figure 1.

Trimethyl 3-{5-[Bis(trimethylsilyl)amino]-4-butyl-2-methoxy-3-furyl}-1-cyclopropene-1,2,3-tricarboxylate (**3b**): From 1.21 g (5.02 mmol) of **1b** and 1.42 g (10.0 mmol) of **2** triester **3b** is obtained as red solid after recrystallization from cyclohexane/petroleum ether (5:1); yield 1.76 g (67%) (red crystals); m.p. 41°C. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2890 (m, C–H aliph.), 2850 (w), 1860 (w, C=C cyclopropene), 1720 (vs, C=O), 1640 (m, C=C furan), 1605 (s), 1430 (s), 1260 (vs), 1160 (m), 1060 (m), 1040 (m). – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.08 [s, 18H, $Si(CH_3)_3$], 0.91 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.29–1.48 (m, 4H, CH_2CH_2), 2.18 (t, ^3J = 7.8 Hz, 2H, CH_2), 3.69 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.90 (s, 6H, OCH_3). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 1.19 [$Si(CH_3)_3$], 13.73 (CH_3), 23.25, 24.43 (CH_2CH_2), 31.27 (=C–CH_2), 32.44 (C), 52.46 (OCH_3), 52.85 (2× OCH_3), 59.06 (OCH_3), 97.25 (C-3), 113.4 (C-4), 116.9 (2× =*C*–C=O), 141.5 (C-5), 151.6 (C–*C*=O), 157.6 (2× =C–*C*=O), 171.1 (C-2). – MS (70 eV), *m/z* (%): 525 (20) [M^+], 510 (22) [M^+ – CH_3], 468 (18) [M^+ – C_4H_9], 172 (46), 89 (62), 73 (100) [$Si(CH_3)_3^+$], 59 (71) [$CO_2CH_3^+$], 57 (32) [$C_4H_9^+$]. – UV (diethyl ether): λ_{max} (lg ε) = 221 nm (4.060). – $C_{24}H_{39}NO_8Si_2$ (525.7): calcd. C 54.83, H 7.48, N 2.66; found C 54.61, H 7.53, N 2.66.

Reaction of **1b** *with One Equivalent of Dimethyl Acetylenedicarboxylate* (**2**)

Dimethyl 2,3-Bis{5-[bis(trimethylsilyl)amino]-4-butyl-2-methoxy-3-furyl}fumarate (**4a**): To a solution of 1.21 g (5.02 mmol) of **1b** in diethyl ether (30 ml) 0.71 g (5.00 mmol) of **2** is added at −78°C. After warming to room temp. the orange-red reaction mixture is stirred for 2 d. The solvent is removed and the red oil filtered through silica gel 60. After removal of the solvent at reduced pressure, the crude product is purified by recrystallization from cyclohexane/petroleum ether (10:1). Yield 1.15 g (60%); m.p. 75°C (yellow solid). – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2900, 2850 (m, C–H aliph.), 1720 (s, C=O), 1605 (s), 1450 (m), 1430 (m), 1245 (s), 1220 (s), 1200 (m, sh), 1160 (m), 1070 (m), 1100 (w). – ^1H NMR (360 MHz, $CDCl_3$): δ = 0.08 [s, 36H, $Si(CH_3)_3$], 0.88 (t, ^3J = 7.2 Hz, 6H, CH_3), 1.23–1.43 (m, 8H, CH_2CH_2), 1.95 (s, br, 4H, CH_2), 3.68 (s, 6H, OCH_3), 3.75 (s, 6H, OCH_3). – ^{13}C NMR (90.56 MHz, $CDCl_3$): δ = 1.37 [$Si(CH_3)_3$], 13.91 (CH_3), 23.24, 24.50 (CH_2CH_2), 31.49 (br, CH_2), 52.25 (OCH_3), 57.92 (br, OCH_3), 96.04 (C-3, C-3'-Furyl), 113.1 (C-5, C-5'-Furyl), 129.2 (C=C), 141.7 (C-4, C-4'-Furyl), 151.6 (2 C=O), 169.1 (C-2, C-2'-Furyl). – MS (70 eV), *m/z* (%): 767 (19) [M^+ + H], 766 (14) [M^+], 751 (16) [M^+ – CH_3], 646 (18), 227 (20), 84 (38), 73 (100) [$Si(CH_3)_3^+$], 57 (40) [$C_4H_9^+$]. – UV (diethyl ether): λ_{max} (lg ε) = 215 nm (4.374), 221 (4.383), 331 (3.871). – $C_{36}H_{66}N_2O_8Si_4$ (766.2): calcd. C 56.43, H 8.68, N 3.65; found C 56.29, H 8.82, N 3.64.

Reaction of **3a** *with* **1b**

Dimethyl 2-{5-[Bis(trimethylsilyl)amino]-4-butyl-2-methoxy-3-furyl}-3-{5-[bis(trimethylsilyl)amino]-2-methoxy-4-phenyl-3-furyl}-fumarate (**4b**): To a solution of 1.00 g (1.83 mmol) of **3a** in diethyl ether (30 ml) 0.44 g (1.83 mmol) of **1b** is added at −78°C. After warming to room temp., the orange-red reaction mixture is stirred for 1 d. The solvent is removed in vacuo and the red oil purified

by flash chromatography [diethyl ether/petroleum ether, 1:10; R_f (DC) = 0.84]. Yield 0.47 g (33%), red resinous substance (purity 92%). – IR (neat): $\tilde{\nu}$ = 3040 cm^{-1}, 3020 (vw, sh, C–H arom.), 2960, 2900, 2850 (m, C–H aliph.), 1720 (s, C=O), 1600 (s), 1490 (w), 1450 (m), 1430 (m), 1400 (w), 1370 (w), 1340 (m), 1250 (s), 1220 (s), 1200 (m), 1160 (m), 1130 (m), 1070 (m), 1050 (w), 1015 (m). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.09 [s, 36 H, $Si(CH_3)_3$], 0.89 (t, ^3J = 7.0 Hz, 3H, CH_3), 1.15–2.3 (m, 6H, $CH_2CH_2CH_2$), 3.06 (s, br, 3H, OCH_3), 3.67 (s, 6H, OCH_3), 3.71 (s, 3H, OCH_3), 7.10–7.15 (m, 1H, *p*-H), 7.22–7.28 (m, 2H, *m*-H), 7.34 (s, br, 2H, *o*-H). – ^{13}C NMR (90.56 MHz, $CDCl_3$): δ = 1.30, 1.41 [$Si(CH_3)_3$], 13.81 (CH_3), 23.24 (CH_2), 24.56 (CH_2), 31.27 (=C–CH_2), 51.52 (OCH_3), 52.17 (OCH_3), 57.36 (OCH_3), 95.30, 96.23 [C-3 (furan)], 113.4, 113.9 [C-5 (furan)], 125.7 (*p*-C), 127.1 (=*C*–C=O), 127.7, 128.1 (*o*-, *m*-C), 130.7 (=*C*–C=O), 133.7 (*i*-C), 141.2, 141.8 [C-4 (furan)], 149.6 (C=O), 150.1 (C=O), 168.3, 169.6 [C-2 (furan)]. – MS (70 eV), *m/z* (%): 786 (18) [M^+], 770 (12) [M^+ – CH_4], 667 (12), 73 (100) [$Si(CH_3)_3^+$], 57 (66) [$C_4H_9^+$]. – $C_{38}H_{62}N_2O_8Si_4$: calcd. 786.3583, found 786.3598 (MS).

Reactions of the Ynamines **1a, b** *with Ketene* **5**

General Procedure for the Synthesis of **6a–d** *and* **10a–b**: A solution of the ynamine **1** in 30 ml of diethyl ether is cooled to –78°C and slowly treated with an equimolar solution of the ketene **5** in 10 ml of diethyl ether. Then, the solution is allowed to warm up to room temp. and stirred for 8 h. After removal of the solvent, the residue is purified by recrystallization or flash chromatography.

3-[Bis(trimethylsilyl)amino]-2,4,4-triphenyl-2-cyclobuten-1-one (**6a**): From 1.31 g (5.00 mmol) of **1a** and 0.97 g (5.00 mmol) of diphenylketene (**5a**)[19] **6a** is obtained as a colorless solid after recrystallization (petroleum ether/diethyl ether, 9:1). Yield 1.46 g (64%), m.p. 191°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3020 (m, C–H arom.), 1745 (vs, C=O), 1610 (m, C=C), 1590 (m, C=C arom.), 1490 (m), 1445 (m), 1305 (m), 1250 (s), 1175 (s), 1015 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.01 [s, 18H, $Si(CH_3)_3$], 7.21–7.33 (m, 9H, arom. H), 7.43–7.47 (m, 4H, *o*-H), 7.70–7.73 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 2.81 [$Si(CH_3)_3$], 78.28 (C), 126.9, 127.2, 127.9, 128.1, 128.3, 128.5 (arom. CH), 129.6 (*i*-C), 139.2 (*i*-C), 139.6 (*C*=C–N), 179.6 (=C–N), 191.0 (C=O). – MS (70 eV), *m/z* (%): 455 (12) [M^+], 440 (15) [M^+ – CH_3], 352 (14), 261 (12) [$C_{14}H_{23}NSi_2^+$], 189 (22), 188 (31) [261 – $Si(CH_3)_3$], 73 (100) [$Si(CH_3)_3^+$]. – $C_{28}H_{33}NOSi_2$ (455.7): calcd. C 73.79, H 7.36, N 3.07; found C 73.74, H 7.50, N 3.09.

3-[Bis(trimethylsilyl)amino]-4-ethyl-2,4-diphenyl-2-cyclobuten-1-one (**6b**): From 1.31 g (5.00 mmol) of **1a** and 0.73 g (5.00 mmol) of ethylphenylketene (**5b**)[19] **6b** is obtained as a colorless solid after recrystallization (petroleum ether/diethyl ether, 9:1). Yield 1.75 g (86%), m.p. 98°C. – IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1}, 3020 (m, C–H arom.), 2960, 2940, 2890 (s, C–H aliph.), 1735 (vs, C=O), 1615 (s, C=C), 1590 (s, C=C arom.), 1490 (m), 1445 (m), 1330 (s), 1300 (s), 1250 (s), 1180 (m), 1140 (m), 1070 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.12 [s, 18H, $Si(CH_3)_3$], 1.00 (t, ^3J = 7.2 Hz, 3H, CH_3), 2.15–2.24 (m, 2H, CH_2), 7.22–7.26 (m, 2H, *p*-H), 7.29–7.36 (m, 4H, *m*-H), 7.46–7.49 (m, 2H, *o*-H), 7.76–7.79 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 2.66 [$Si(CH_3)_3$], 10.41 (CH_3), 29.40 (CH_2), 74.88 (C), 126.7, 126.9, 127.0, 127.8, 128.0, 128.1 (arom. CH), 129.8 (*i*-C), 136.2 (*C*=C–N), 138.6 (*i*-C), 182.0 (=C–N), 194.1 (C=O). – MS (70 eV), *m/z* (%): 407 (9) [M^+], 392 (3) [M^+ – CH_3], 261 (26) [$C_{14}H_{23}NSi_2^+$], 246 (26) [261 – CH_3], 188 (42) [261 – $Si(CH_3)_3$], 73 (100) [$Si(CH_3)_3^+$]. – $C_{24}H_{33}NOSi_2$ (407.7): calcd. C 70.70, H 8.16, N 3.43; found C 70.69, H 8.13, N 3.41.

3-[Bis(trimethylsilyl)amino]-2-butyl-4,4-diphenyl-2-cyclobuten-1-one (**6c**) *and 2-Butyl-4,4-diphenyl-2,3-butadienamide* (**10a**): From 1.21 g (5.02 mmol) of **1b** and 0.97 g (5.00 mmol) of diphenylketene (**5a**)[19] a crude light yellow mixture of the products **6c** and **10a** is obtained which is separated by flash chromatography. The first fraction (eluent: petroleum ether/diethyl ether, 20:1) consists of **6c**. Colorless crystals (from cyclohexane/petroleum ether, 10:1), R_f (DC) = 0.46 (petroleum ether/diethyl ether, 20:1), yield 0.46 mg (21%), m.p. 83°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020 (w, C–H arom.), 2960, 2920, 2860 (m, C–H aliph.), 1745 (s, C=O), 1610 (s, C=C), 1595 (s, C=C), 1490 (m), 1460 (w), 1440 (m), 1330 (m), 1305 (m), 1275 (m), 1250 (s), 1210 (m), 1160 (m), 1090 (w), 1030 (w), 945 (w), 910 (m), 895 (s), 850 (vs), 830 (s, sh), 755 (m), 730 (m), 700 (s), 655 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 [s, 18H, $Si(CH_3)_3$], 0.97 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.45 (sext, ^3J = 7.3 Hz, 2H, CH_2CH_3), 1.69 (quint, ^3J = 7.3 Hz, 2H, $CH_2CH_2CH_2$), 2.12 (t, ^3J = 7.3 Hz, 2H, =C–CH_2), 7.21–7.32 (m, 6H, arom. H), 7.38–7.41 (m, 4H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 2.53 [$Si(CH_3)_3$], 13.80 (CH_3), 22.96 (CH_2CH_3), 23.65 ($CH_2CH_2CH_2$), 29.47 (=C–CH_2), 76.82 (C), 127.0 (*p*-C), 128.1, 128.3 (arom. CH), 139.6 (*i*-C), 143.4 (*C*=C–N), 181.4 (C=*C*–N), 193.2 (C=O). – MS (70 eV), *m/z* (%): 436 (8) [M^+ + H], 435 (18) [M^+], 420 (20) [M^+ – CH_3], 363 (8), 226 (12), 188 (26) [$C_6H_5C_2NSi(CH_3)_3^+$], 73 (100) [$Si(CH_3)_3^+$]. – $C_{26}H_{37}NOSi_2$ (436.3): calcd. C 71.67, H 8.56, N 3.21; found C 72.04, H 8.59, N 3.14.

The second fraction (eluent: petroleum ether/diethyl ether, 2:1) consists of **10a**. Colorless crystals, R_f (DC) = 0.28 (petroleum ether/diethyl ether, 2:1), yield 0.63 g (45%), m.p. 118°C. – IR (KBr): $\tilde{\nu}$ = 3440, 3260, 3190, 3140 (m, N–H), 3040 (w, sh, C–H arom.), 2950, 2920 (m, C–H aliph.), 1925 (w, C=C=C), 1675 (s, N–C=O), 1590 (m, C=C arom.), 1490 (m), 1350 (m), 765 (m), 690 (s). – ^{1}H NMR (300 MHz, [D_6]acetone): δ = 0.84 (t, ^3J = 7.2 Hz, 3H, CH_3), 1.32 (sext, ^3J = 7.2 Hz, 2H, CH_2CH_3), 1.52 (quint, ^3J = 7.2 Hz, 2H, $CH_2CH_2CH_2$), 2.42 (t, ^3J = 7.2 Hz, 2H, =C–CH_2), 6.48 (s, 1H, NH), 6.78 (s, 1H, NH), 7.32–7.43 (m, 10H, arom. H). – ^{13}C NMR (75.47 MHz, [D_6]acetone): δ = 13.61 (CH_3), 22.41 (CH_2CH_3), 27.97 ($CH_2CH_2CH_3$), 30.27 (=C–CH_2), 105.6, 114.7 (*C*=C=*C*), 128.1 (*p*-C), 128.3, 128.7 (arom. CH), 168.1 (O=C–N), 207.8 (C=*C*=C). – MS (70 eV), *m/z* (%): 291 (46) [M^+], 290 (64) [M^+ – H], 248 (52) [M^+ – HNCO], 230 (72), 111 (90), 91 (98), 77 (62) [$C_6H_5^+$], 57 (100) [$C_4H_9^+$]. – $C_{20}H_{21}NO$ (291.4): calcd. C 82.44, H 7.26, N 4.80; found C 82.42, H 7.44, N 4.84.

3-[Bis(trimethylsilyl)amino]-2-butyl-4-ethyl-4-phenyl-2-cyclobuten-1-one · 0.8 $CHCl_3$ (**6d**) *and 2-Butyl-4-phenyl-2,3-hexadienamide* (**10b**): From 1.21 g (5.02 mmol) of **1b** and 0.73 g (5.00 mmol) of ethylphenylketene (**5b**)[19] a light yellow mixture of the products **6d** and **10b** is obtained, which is separated by flash chromatography. The first fraction (eluent: petroleum ether/diethyl ether, 20:1) consists of **6d**. Colorless crystals after recrystallization from $CHCl_3$, R_f (DC) = 0.48 (petroleum ether/diethyl ether, 20:1), yield 0.58 g (24%), m.p. 57°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020 (w, C–H arom.), 2950, 2920, 2860 (s, C–H aliph.), 1745 (s, C=O), 1610 (m, C=C–N), 1590 (s, C=C arom.), 1490 (m), 1420 (m), 1250 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10 [s, 18H, $Si(CH_3)_3$], 0.91 (t, ^3J = 7.0 Hz, 3H, CH_3), 0.92 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.36 (sext, ^3J = 7.0 Hz, 2H, CH_2CH_3), 1.51 (quint, 2H, CH_2), 1.98 (m, 2H, CH_2CH_3), 2.02 (t, ^3J = 7.2 Hz, 2H, =C–CH_2), 7.19–7.24 (m, 1H, *p*-H), 7.27–7.32 (m, 2H, *m*-H), 7.37–7.40 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 2.51 [$Si(CH_3)_3$], 10.40 (CH_3), 13.65 (CH_3), 22.75, 22.81 (CH_2CH_2), 28.96, 29.99 (CH_2, CH_2), 73.41 (C), 126.5 (*p*-C), 126.7 (*m*-C), 128.0 (*o*-C), 139.5 (*i*-C),

140.3 (*C*=C−N), 183.7 (C=*C*−N), 196.4 (C=O). − MS (70 eV), *m/z* (%): 387 (40) [M^+], 372 (42) [$M^+ - CH_3$], 314 (40) [$M^+ - Si(CH_3)_3$], 227 (22) [$M^+ - N(Si(CH_3)_3)_2$], 226 (42), 188 (58), 75 (56), 73 (100) [$Si(CH_3)_3^+$]. − $C_{22}H_{37}NOSi_2 \cdot 0.8\ CHCl_3$ (387.2 · 0.8 $CHCl_3$): calcd. C 56.67, H 7.85, N 2.89; found C 56.38, H 7.82, N 2.80.

The second fraction (eluent: petroleum ether/diethyl ether, 2:1) consists of **10b**, colorless oil, R_f (DC) = 0.29 (petroleum ether/diethyl ether, 2:1), yield 0.43 g (35%). − IR (film): $\tilde{\nu}$ = 3460 cm^{-1}, 3300, 3180 (m, N−H), 3020 (w, sh, C−H arom.), 2940, 2920, 2850 (m, C−H aliph.), 1925 (w, C=C=C), 1660 (s, O=C−N), 1590 (m, C=C arom.), 1490 (m), 1440 (m), 1360 (m), 750 (m), 690 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 7.2 Hz, 3H, CH_3), 1.21 (t, ^3J = 7.2 Hz, 3H, =C−CH_2CH_3), 1.39−1.51 (m, 4H, $CH_2CH_2CH_3$), 2.40 (t, ^3J = 7.2 Hz, 2H, =C−CH_2), 2.59 (q, ^3J = 7.2 Hz, 2H, CH_2CH_3), 5.68 (s, broad, 1H, NH), 5.88 (s, broad, 1H, NH), 7.26−7.42 (m, 5H, arom. H). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.43 (CH_3), 13.83 (CH_3), 22.47, 23.13, 27.69, 30.41 ($CH_2CH_2CH_2$, =C−CH_2), 106.7, 113.6 (*C*=C=*C*), 125.9, 127.6, 128.6 (arom. CH), 134.7 (*i*-C), 168.8 (O=C−N), 206.3 (C=*C*=C). − MS (70 eV), *m/z* (%): 243 (8) [M^+], 228 (18) [$M^+ - CH_3$], 200 (24) [M^+ − HNCO], 169 (30), 149 (31), 77 (30) [$C_6H_5^+$], 69 (80), 57 (100) [$C_4H_9^+$]. − $C_{16}H_{21}NO$ (243.4): calcd. C 78.96, H 8.70, N 5.75; found C 78.80, H 8.92, N 5.74.

Synthese of the 3-Aminocyclobutenones **9a**−**d**: A solution of the corresponding cyclobutenone **6** in 20 ml of diethyl ether is treated with an excess of a saturated $NaHCO_3$ solution and is then stirred for 7 d at room temp. The colorless crystals are removed by filtration and washed with water and cold diethyl ether.

3-Amino-2,4,4-triphenyl-2-cyclobuten-1-one (**9a**): From 1.00 g (2.20 mmol) of **6a**. Colorless crystals, yield 0.62 g (91%), m.p. 192°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1}, 3260, 3160 (m, N−H), 3040, 3020 (w, C−H arom.), 1720 (s, C=O), 1620 (vs, C=C−N), 1590 (m, C=C arom.), 1560 (vs, N−H), 1485 (m), 1420 (m), 1300 (m), 1245 (m), 1130 (m), 1070 (m), 1010 (m). − ^{1}H NMR (300 MHz, [D_6]acetone): δ = 7.11−7.16 (m, 1H, *p*-H), 7.26−7.36 (m, 8H, arom. H), 7.43−7.46 (m, 4H, *o*-H), 7.73−7.76 (m, 2H, *o*-H), 7.77−7.90 (s, broad, 2H, NH_2). − ^{13}C NMR (75.47 MHz, [D_6]acetone): δ = 76.58 (C), 114.6 (*C*=C−N), 126.4 (*p*-CH), 126.7 (*p*-CH), 128.1, 129.0, 129.4, 129.6 (arom. CH), 133.1 (*i*-C), 141.7 (*i*-C), 168.8 (C=*C*−N), 184.3 (C=O). − MS (70 eV), *m/z* (%): 311 (40) [M^+], 310 (32) [M^+ − H], 265 (24), 126 (20), 69 (33), 58 (100), 57 (96). − $C_{22}H_{17}NO$ (311.4): calcd. C 84.86, H 5.50, N 4.50; found C 84.80, H 5.48, N 4.55.

3-Amino-4-ethyl-2,4-diphenyl-2-cyclobuten-1-one (**9b**): From 1.00 g (2.45 mmol) of **6b**. Colorless crystals, yield 0.54 g (83%), m.p. 152°C. − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1}, 3320, 3200 (m, N−H), 3040 (m, C−H arom.), 2980, 2920, 2880 (m, C−H aliph.), 1725 (m, C=O), 1630 (m, C=C−N), 1600 (m, C=C arom.), 1570 (s, N−H), 1480 (m), 1405 (m), 1250 (m), 690 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.5 Hz, 3H, CH_3), 2.04−2.31 (m, 2H, CH_2), 5.66 (s, 2H, NH_2), 7.16−7.21 (m, 1H, *p*-H), 7.26−7.38 (m, 5H, arom. H), 7.44−7.47 (m, 2H, *o*-H), 7.53−7.56 (m, 2H, *o*-H). − ^{13}C NMR (75.47 MHz, [D_6]acetone/$CDCl_3$, 1:1): δ = 8.85 (CH_3), 24.17 (CH_2), 70.34 (C), 112.7 (*C*=C−N), 124.4, 124.5, 125.5, 125.8, 127.4, 127.5 (arom. CH), 130.9 (*i*-C), 139.8 (*i*-C), 167.7 (C=*C*−N), 185.5 (C=O). − MS (70 eV), *m/z* (%): 263 (44) [M^+], 248 (100) [$M^+ - CH_3$], 202 (42), 115 (58), 77 (42) [$C_6H_5^+$]. − $C_{18}H_{17}NO$ (263.3): calcd. C 82.10, H 6.51, N 5.31; found C 81.97, H 6.56, N 5.11.

3-Amino-2-butyl-4,4-diphenyl-2-cyclobuten-1-one (**9c**): From 0.30 g (0.69 mmol) of **6c**. Colorless crystals, yield 0.17 g (85%), m.p. 115°C. − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1}, 3270, 3160 (m, N−H), 3040 (w, C−H arom.), 2940, 2920 (m, C−H aliph.), 1720 (m, C=O), 1620 (s, C=C−N), 1590 (m, C=C arom.), 1560 (s), 1490 (m), 1425 (m), 1150 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, ^3J = 7.2 Hz, 3H, CH_3), 1.34 (sext, ^3J = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 1.51 (quint, ^3J = 7.2 Hz, 2H, $CH_2CH_2CH_2$), 2.06 (t, ^3J = 7.2 Hz, 2H, =C−CH_2), 5.33 (s, br., 2H, NH_2), 7.20−7.32 (m, 6H, arom. H), 7.36−7.40 (m, 4H, *o*-H). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.09 (CH_3), 22.15, 23.19 (CH_2CH_2), 30.71 (=C−CH_2), 74.86 (C), 116.1 (*C*=C−N), 127.3 (*p*-CH), 128.5, 128.8 (arom. CH), 142.1 (*i*-C), 170.5 (C=*C*−N), 185.2 (C=O). − MS (70 eV), *m/z* (%): 291 (38) [M^+], 248 (76) [$M^+ - C_3H_7$], 205 (72), 115 (50), 91 (100) [$C_7H_7^+$], 77 (40) [$C_6H_5^+$]. − $C_{20}H_{21}NO$ (291.4): calcd. C 82.44, H 7.26, N 4.80; found C 82.04, H 7.49, N 4.80.

3-Amino-2-butyl-4-ethyl-4-phenyl-2-cyclobuten-1-one (**9d**): From 0.30 g (0.62 mmol) of **6d**. Colorless crystals, yield 0.12 g (79%), m.p. 110°C. − IR (KBr): $\tilde{\nu}$ = 3400, 3300, 3150 (m, N−H), 3020 (w, sh, C−H arom.), 2960, 2920, 2860 (m, C−H aliph.), 1730 (m, C=O), 1630 (s, C=C−N), 1590 (m, C=C arom.), 1550 (vs), 1490 (m), 1440 (m), 1050 (w), 690 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85−0.94 (m, 6H, CH_3), 1.29 (sext, ^3J = 7.3 Hz, 2H, CH_2CH_3), 1.41 (quint, ^3J = 7.3 Hz, 2H, $CH_2CH_2CH_2$), 1.85−2.04 (m, 4H, CH_2), 5.82 (s, br., 2H, NH_2), 7.16−7.28 (m, 3H, arom. H), 7.32−7.35 (m, 2H, *o*-H). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 9.44 (CH_3), 13.47 (CH_3), 21.03, 22.29, 23.95 (CH_2CH_2, CH_2CH_3), 29.37 (=C−CH_2), 69.24 (C), 115.8 (*C*=C−N), 126.2 (*p*-CH), 125.8, 127.9 (arom. CH), 140.4 (*i*-C), 170.3 (=C−N), 188.2 (C=O). − MS (70 eV), *m/z* (%): 243 (41) [M^+], 228 (100) [M^+ − CH_3], 200 (42), 174 (5), 156 (58), 143 (62), 129 (62), 115 (82), 91 (79), 77 (52) [$C_6H_5^+$], 55 (59). − $C_{16}H_{21}NO$ (243.3): calcd. C 78.94, H 8.70, N 5.75; found C 79.05, H 9.07, N 5.79.

Reactions of the Ynamines **1a**, **b** *with in situ Prepared Ketenes* **5c**, **d**: A solution of 5.02 mmol of the corresponding ynamine **1** in diethyl ether (50 ml) is cooled to −78°C and dropwise treated with a solution of 5.00 mmol of acyl chloride **8** in diethyl ether. Then 0.50 g (5.00 mmol) of triethylamine is added slowly. The solution is allowed to warm up to room temp. (4 h) and is then treated with a satd. aqueous $NaHCO_3$ solution (30 ml). After stirring for 3 d, the aqeous layer is extracted twice with diethyl ether (30 ml). The combined organic layers are dried with Na_2SO_4, and the solvent is removed in vacuo. The colorless residue is washed with water (50 ml) and cold diethyl ether (5 ml).

3-Amino-2,4-diphenyl-2-cyclobuten-1-one (**9e**): From 1.31 g (5.02 mmol) of **1a**, 0.77 g (5.00 mmol) of phenylacetyl chloride (**8a**) and 0.50 g (5.00 mmol) of triethylamine. Colorless crystals, yield 0.83 g (71%), m.p. 165°C (ref.[20] 170−172°C). − IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1}, 3320, 3120 (m, N−H), 3060 (w, sh C−H arom.), 2940 (vw, C−H aliph.), 1720 (m, C=O), 1635 (s, C=C−N), 1590 (m, C=C arom.), 1555 (vs), 1490 (m), 1435 (m), 1150 (w), 765 (w), 690 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.61 (s, 1H, CH), 5.61 (s, br., 2H, NH_2), 7.27−7.33 (m, 8H, arom. H), 7.70−7.74 (m, 2H, *o*-H). − ^{13}C NMR (75.47 MHz, [D_6]acetone): δ = 66.51 (CH), 114.9 (*C*=C−N), 125.7 (arom. CH), 126.1 (*p*-CH), 127.7 (*p*-CH), 128.2, 129.1, 129.2 (arom. CH), 132.8 (*i*-C), 135.5 (*i*-C), 165.8 (=C−N), 182.5 (C=O). − MS (70 eV), *m/z* (%): 235 (88) [M^+], 206 (38), 101 (36), 59 (58), 58 (100). − $C_{16}H_{13}NO$ (235.3): calcd. C 81.68, H 5.57, N 5.95; found C 81.69, H 5.59, N 5.98.

3-Amino-4-butyl-2-phenyl-2-cyclobuten-1-one (**9f**): From 1.21 g (5.02 mmol) of **1b**, 0.77 g (5.00 mmol) of phenylacetyl chloride (**8a**), and 0.50 g (5.02 mmol) of triethylamine. Colorless crystals, yield 0.34 g (32%), m.p. 132°C. − IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1}, 3300 (w, N−H), 3240 (m, N−H), 2960 (m), 2920 (m), 2860 (m, C−H

aliph.), 1720 (s, C=O), 1640 (s, C=C−N), 1600 (w, C=C ar.), 1570 (vs, N−H), 1490 (m), 1430 (m), 1225 (m), 1165 (m). − ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 0.87 (t, ^3J = 7.2 Hz, 3H, CH$_3$), 1.29−1.74 (m, 6H, CH$_2$CH$_2$CH$_2$), 3.88 (t, ^3J = 4.8 Hz, 1H, CH), 7.03−7.09 (m, 1H, *p*-H), 7.24−7.29 (m, 2H, *m*-H), 7.52 (s, br., 2H, NH$_2$), 7.62−7.65 (m, 2H, *o*-H). − ^{13}C NMR (75.47 MHz, [D$_6$]acetone): δ = 14.19 (CH$_3$), 23.51 (*C*H$_2$CH$_3$), 28.56, 29.54 (CH$_2$CH$_2$), 60.40 (CH), 112.7 (*C*=C−N), 125.5 (*p*-CH), 125.4 (*m*-CH), 128.9 (*o*-CH), 133.2 (*i*-C), 168.5 (=C−N), 186.3 (C=O). − MS (70 eV), *m/z* (%): 215 (36) [M$^+$], 172 (100) [M$^+$ − C$_3$H$_7$], 144 (72), 127 (48), 96 (46), 77 (30) [C$_6$H$_5^+$]. − C$_{14}$H$_{17}$NO (215.3): calcd. C 78.10, H 7.96, N 6.50; found C 77.85, H 8.13, N 6.58.

3-Amino-2-phenyl-2-cyclobuten-1-one (**9g**): From 1.31 g (5.00 mmol) of **1a**, 0.39 g (5.00 mmol) of acetyl chloride (**8b**), and 0.50 g (5.00 mmol) of triethylamine **9g** is obtained as a green crude product. After flash chromatography [R_f (DC): 0.22, petroleum ether/diethyl ether, 3:1; the crude product is dissolved in little acetone before applying it to the column] colorless crystals are isolated. Yield 0.51 g (65%), m.p. 166°C. − IR (KBr): ṽ = 3300 (m, N−H), 3180 (s, N−H), 2900 (w, sh, C−H aliph.), 1710 (s, C=O), 1645 (s, C=C−N), 1595 (C=C ar.), 1550 (vs, N−H), 1490 (m), 1430 (m), 1255 (m), 1150 (m), 1000 (w), 990 (w), 755 (m), 690 (s), 640 (m). − ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 3.16 (s, 2H, CH$_2$), 7.04−7.09 (m, 1H, *p*-H), 7.24−7.29 (m, 2H, *m*-H), 7.61−7.74 (m, br., 4H, *o*-H, NH$_2$). − ^{13}C NMR (75.47 MHz, [D$_6$]acetone): δ = 48.92 (CH$_2$), 113.8 (*C*=C−N), 125.2 (*m*-CH), 125.6 (*p*-CH), 129.0 (*o*-CH), 133.2 (*i*-C), 164.1 (=C−N), 181.6 (C=O). − MS (70 eV), *m/z* (%): 159 (80) [M$^+$], 131 (82) [M$^+$ − CO], 130 (100) [M$^+$ − HCO], 103 (60) [PhCN$^+$], 89 (44), 77 (52) [C$_6$H$_5^+$]. − C$_{10}$H$_9$NO (159.2): calcd. C 75.45, H 5.69, N 8.79; found C 75.43, H 5.61, N 8.95.

3-Amino-2-butyl-2-cyclobuten-1-one (**9h**): From 1.21 g (5.02 mmol) of **1b**, 0.39 g (5.00 mmol) of acetyl chloride (**8b**), and 0.50 g (5.00 mmol) of triethylamine **9h** is obtained as a colorless solid after flash chromatography [R_f (DC) = 0.19, petroleum ether/diethyl ether, 3:1]. Colorless crystals, yield 0.26 g (38%), m.p. 102°C. − IR (Film): ṽ = 3300 cm^{-1}, 3160 (m, N−H), 2960, 2920, 2860 (s, C−H aliph.), 1730 (C=O), 1630 (s, C=C−N), 1555 (vs, N−H), 1440 (m), 1380 (m), 1250 (m), 1220 (m), 1150 (m), 1000 (vw), 930 (vw), 840 (w). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.86 (t, ^3J = 7.2 Hz, 3H, CH$_3$), 1.27−1.42 (m, 4H, CH$_2$CH$_2$), 1.88 (tt, ^5J = 1.6, ^3J = 7.3 Hz, 2H, =C−CH$_2$), 2.91 (t, ^5J = 1.6 Hz, 2H, CH$_2$), 6.85 (s, 2H, NH$_2$). − ^{13}C NMR (75.47 MHz, [D$_6$]acetone): δ = 13.79 (CH$_3$), 22.03, 22.77 (CH$_2$CH$_2$), 30.26 (=C−*C*H$_2$), 46.94 (CH$_2$), 115.0 (*C*=C−N), 166.0 (=C−N), 182.8 (C=O). − MS (70 eV), *m/z* (%): 139 (28) [M$^+$], 111 (37) [M$^+$ − CO], 96 (71) [M$^+$ − C$_3$H$_7$], 83 (76), 69 (100), 57 (50), 55 (98). − C$_8$H$_{13}$NO (139.2): calcd. C 69.03, H 9.40, N 10.06; found C 68.72, H 9.52, N 10.02.

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[20/94]