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Efficient Tandem Synthesis of 3-Alkylaminoprop-2-enamides from 3-Trimethylsilylprop-2-ynamides

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Abstract—A tandem synthetic approach to previously unknown 3-aminoprop-2-enamides has been developed. It is based on Si–C_{sp} desilylation of 3-trimethylsilylprop-2-ynamides and subsequent addition of an amine to the triple bond of intermediate terminal propynamides. The effects of the reaction conditions and amine nature on the efficiency of the process have been studied.

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α,β-Unsaturated enamide moiety constitutes the key structural fragment of natural antibiotics exhibiting a broad spectrum of antimicrobial [1] and antitumor activity [2] and 2′,3′-dideoxy-2′,3′-didehydro nucleosides of the uracil series, which are efficient against human immunodeficiency (HIV-1) and hepatitis B viruses [3]. α,β-Unsaturated enamides can be used as intermediate products in the synthesis of natural products, e.g., doubly unsaturated amides [4], biologically important polycyclic alkaloids containing a 2-oxopiperidine ring [5], pharmacologically valuable β-amino amides [6], and isoxazolidines [7]; they are also promising as ligands [8] and monomers. β-Amino enamides may be regarded as poorly explored compounds. There are very limited published data on the synthesis and application of β-amino enamides. Efficient procedures for the synthesis of 2-alkylidene-1,3-dicarbonyl compounds [9], 1,2,3-triazolecarboxamides [10], and β-amino acid derivatives [11] have been developed on the basis of "push–pull" amino enamides; they can also be used as bidentate ligands [9].

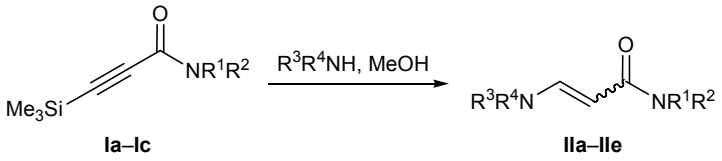
The synthesis of β-amino enamides via aminolysis of β-keto esters [12] and subsequent reaction of β-keto amides with amines [9] is known. However, this procedure involves some difficulties. Amination of β-keto esters requires fairly severe conditions (elevated temperature, sometimes above 200°C), base catalyst [13], and the absence of a solvent [14]. In addition, only tertiary keto amides can be obtained in this way, and the reaction is accompanied by formation of β-enamino esters as by-products, especially under acidic conditions [15].

An alternative method for the synthesis of β-aminoacrylamides is based on the addition of amines to terminal propynamides. Secondary amines readily add to propynamides in acetonitrile to give the corresponding amino enamides in high yield [16]. However, preparation of the initial terminal propynamides requires the use of inflammable propiolic acid or its highly toxic derivatives [17]. We recently developed an efficient one-step procedure for the synthesis of trimethylsilylpropynamides from accessible and safe trimethylsilylpropynoic acid [18]. The presence of trimethylsilyl group in silicon-containing acetylene derivatives stabilizes the triple bond and increases the solubility in organic solvents [19].

The present study was aimed at developing a general procedure for the synthesis of β-amino enamides containing primary, secondary, or tertiary amide group from accessible trimethylsilylpropynamides via tandem desilylation–amination reaction and elucidating the effects of the reactant nature and reaction conditions on the efficiency of the process.

We previously reported on highly efficient Si–C_{sp}-desilylation of 3-trimethylsilylprop-2-ynamides, which ensured preparation of terminal acetylenic amides in high yield under mild conditions (in methanol) [20]. Our attempt to synthesize the corresponding β-amino enamide by reaction of 1-(morpholin-4-yl)-3-tri-

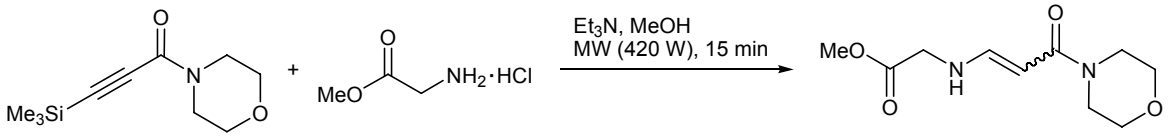
Scheme 1.



Ia–Ic **IIa–IIe**

Ia, **IIa**, $R^1 = R^2 = H$; **Ib**, **IIb**, $R^1 = H$, $R^2 = Ph$; **Ic**, **IIc**–**IIe**, R^1R^2N = morpholin-4-yl; **IIa**–**IIc**, $R^3 = H$, $R^4 = Me$; **IId**, $R^3 = H$, $R^4 = PhCH_2$; **IIe**, R^3R^4N = morpholin-4-yl.

Scheme 2.



Ic **III**

methylsilylprop-2-yn-1-one (**Ic**) with morpholine in anhydrous acetonitrile at room temperature was unsuccessful, and only the initial amide was isolated. Presumably, unlike terminal analog [16], weak polarization of the triple bond due to oppositely directed and comparable in strength electron-withdrawing effects of the trimethylsilyl and amide groups and steric effect of the trimethylsilyl group strongly reduce the reactivity of propynamide **Ic.**

Tandem transformation of trimethylsilylpropynamides **Ia**–**Ic** into previously unknown "push–pull" (*Z,E)*-3-aminoprop-2-enamides **IIa**–**IIc** smoothly occurred in methanol at room temperature by the action of primary and secondary amines (yield 60–76%; Scheme 1; Table 1, run nos. 1–5). (*Z,E*)-3-(Benzylamino)-1-(morpholin-4-yl)prop-2-en-1-one (**IId**) was obtained at 65°C.

Amino acid derivatives can also be subjected to tandem Si–C_{sp}-desilylation–amination. By reaction of 1-(morpholin-4-yl)-3-trimethylsilylprop-2-yn-1-one (**Ic**) with glycine methyl ester hydrochloride in the presence of triethylamine under microwave irradiation we synthesized previously unknown methyl (*Z,E*)-(morpholin-4-yl-3-oxoprop-1-en-1-ylamino)acetate (**III**) in 44% yield (isomer ratio 0.64:0.36; Scheme 2).

Amide **Ic** was also converted in one-pot reaction into polyfunctional diamide **V** containing both double and triple bonds. Tandem desilylation–addition and subsequent acylation of the amino nitrogen atom gave methyl [(*E*)-3-(morpholin-4-yl)-3-oxoprop-1-en-1-yl]-3-(trimethylsilyl)prop-2-ynamide (**V**) in an overall yield of 37% (after column chromatography; intermediate **IIc** was not isolated; Scheme 3).

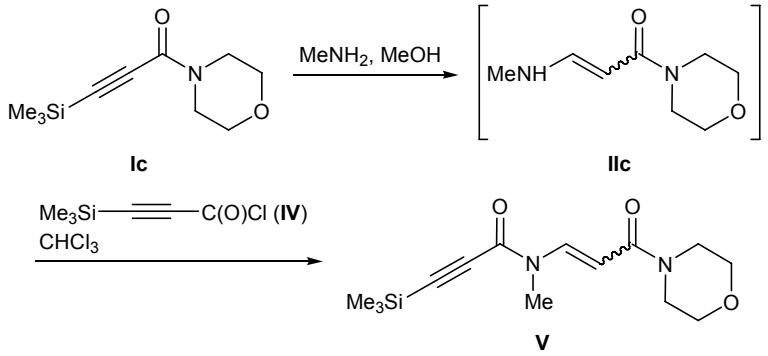
Using 1-(morpholin-4-yl)-3-trimethylsilylprop-2-yn-1-one (**Ic**) as model substrate we examined how the reactant nature and reaction conditions affect the efficiency of the formation of enamides **IIc**–**IIe**. The reactivity of amines toward amide **Ic** in methanol (25°C, 1 h) depended on the pK_a value of amines and changed in the following series: methylamine (pK_a 10.66) > benzylamine (pK_a 9.34) > morpholine (pK_a 8.70) > ammonia (pK_a 9.25) ≈ pyridin-2-amine (pK_a 6.86) (Table 2). On the whole, this series is consistent with the pK_a values [21], except for

Table 1. Synthesis of β-amino enamides $R^3R^4NCH{=}CHCONR^1R^2$ (**IIa**–**IIe**, **III**) in MeOH

Run no.	Compound no.	Reaction conditions	Yield,[a] %	*Z*/*E* Isomer ratio (^{1}H NMR)
1	**IIa**	25°C, 1 h	69	0.16:0.84
2	**IIb**	25°C, 1 h	72	0.75:0.25
3	**IIc**	25°C, 1 h	76	0.79:0.21
4	**IId**	65°C, 1 h	60	0.97:0.03
5	**IIe**	25°C, 7 h	75	0.00:1.00
6	**III**	MW, 15 min	44	0.64:0.36

[a] Yield of purified product.

Scheme 3.



ammonia. The reaction of the latter with amide **Ic** resulted in protodesilylation of amide (**Ic**) (Table 2, run no. 6). Increase of the reaction time from 1 to 7 h and elevated temperature (65°C) favored quantitative formation of aminopropenamides **IId** and **IIe** (Table 2, run nos. 2–5).

Being a weak base, pyridin-2-amine in methanol induced only protodesilylation of substrate **Ic** (1 h, reflux) with formation of propynamide **VI** (Scheme 4; Table 2, run no. 7). When the reaction was carried out under microwave irradiation (420 W, 15 min), β-methoxypropenamide **VII** was formed in quantitative yield as a result of addition of methanol to the triple bond (Table 2, run no. 8). Obviously, the addition was preceded by desilylation of initial amide **Ic**, as followed from the data of IR (2100 cm^{-1}, C≡C) and ^{1}H NMR spectroscopy (δ 2.9–3.12 ppm, HC≡) [20].

The structure of 3-aminoprop-2-enamides **IIa**–**IId** and **III** was confirmed by elemental analyses and IR and ^{1}H and ^{13}C NMR spectra. The addition of amines to trimethylsilylpropynamide **Ic** was stereoselective only in the reaction with morpholine, which afforded (*E*)-1,3-bis(morpholin-4-yl)prop-2-en-1-one (**IIe**). This is consistent with published data on the addition of secondary amines to terminal tertiary propynamides [16]. Predominant formation of the *E* isomer was also observed in the reaction of primary amide **Ia** with methylamine (*Z*/*E* ratio 0.16:0.84). The reactions of amides **Ic** and **Ib** with primary amines gave the corresponding *Z* isomers as major products (Table 1); their formation is likely to be favored by intramolecular hydrogen bond NH···O=C–N.

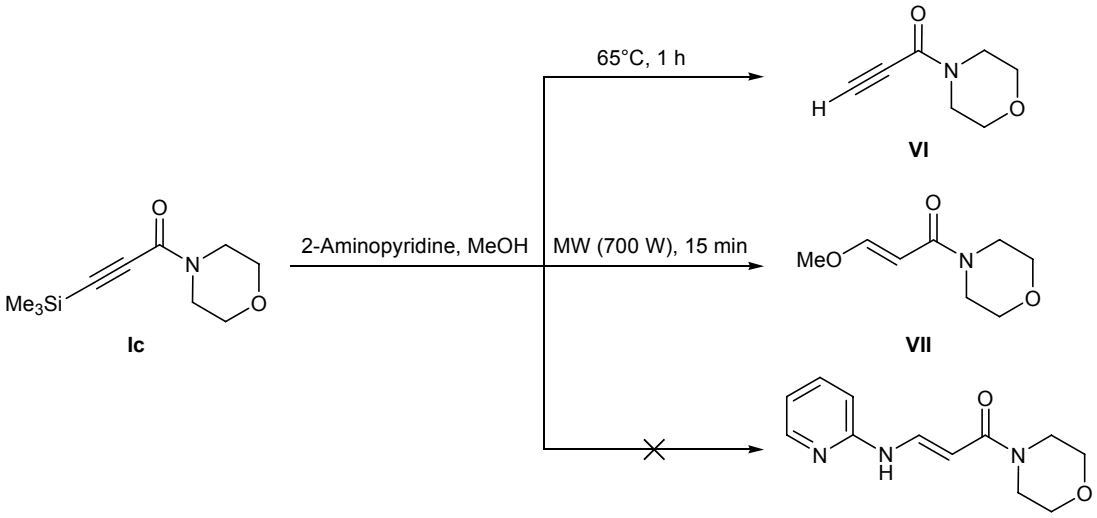
To conclude, we have developed a highly efficient procedure for the synthesis of 3-aminoprop-2-enamides via tandem desilylation–amination of accessible trimethylsilylpropynamides. The procedure is advantageous due to its experimental simplicity, mild conditions (room temperature), the possibility of using various initial amides and amines, including amino acid esters, and high yields of the target products. We

Table 2. Reaction of 1-(morpholin-4-yl)-3-trimethylsilylprop-2-yn-1-one (**Ic**) with amines R^3R^4NH

Run no.	Amine		Reaction conditions	Product (yield,[a] %)
	R^3	R^4		
1[b]	$(CH_2)_2O(CH_2)_2$		25°C, MeCN, 1 h	–
2	$(CH_2)_2O(CH_2)_2$		25°C, MeOH, 1 h	**IIe** (50), **VI** (50)
3	$(CH_2)_2O(CH_2)_2$		25°C, MeOH, 7 h	**IIe** (100)
4	H	$PhCH_2$	25°C, MeOH, 1 h	**IId** (66), **VI** (34)
5	H	$PhCH_2$	65°C, MeOH, 1 h	**IId** (100)
6	H	H	25°C, MeOH, 1 h	**IIc** (14), **VI** (86)
7	H	Pyridin-2-yl	65°C, MeOH, 1 h	**VI** (100)
8	H	Pyridin-2-yl	MW, MeOH, 15 min	**VII** (100)
9	H	Me	25°C, MeOH, 1 h	**IIc** (100)

[a] According to the ^{1}H NMR data.
[b] Initial amide **Ic** was recovered.

Scheme 4.



also have demonstrated the possibility for one-pot transformation of initial propynamide into polyfunctional diamides containing both double and triple bonds. Polyfunctionalized aminopropenamides can be used as building blocks in fine organic synthesis, biologically active substances, and multidentate ligands for metal-complex catalysis.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS-25 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument from solutions in $CDCl_3$ using hexamethyldisiloxane as internal reference. Microwave-assisted reactions were carried out in an unmodified LG MS-1904H microwave furnace (700 W); the reaction mixture was placed into a 25-ml Teflon high-pressure reactor. Initial 3-trimethylsilylprop-2-ynamides were synthesized according to the procedure described in [18].

3-(Methylamino)prop-2-enamides IIa–IIc (*general procedure*). Gaseous methylamine was passed over a period of 1 h at room temperature through a solution of 0.47 mmol of 3-trimethylsilylprop-2-ynamide **Ia**–**Ic** in 10 ml of methanol. The solvent was removed under reduced pressure, and the residue was recrystallized from 1,4-dioxane.

(*Z*,*E*)-3-(Methylamino)prop-2-enamide (IIa). Yield 33 mg (69%), mp 89–91°C. IR spectrum (KBr), ν, cm^{-1}: 1650 (C=O), 1550 (C–N, δNH, C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.56 d (3H, CH_3N, J = 4.88 Hz, *E*), 2.81 d (3H, CH_3N, J = 4.88 Hz, *Z*), 4.29 d (1H, =CHCO, J = 8.04 Hz, *Z*), 4.53 d (1H, =CHCO, J = 12.56 Hz, *E*), 6.36 m (1H, NCH=, J = 8.36 Hz, *Z*), 7.17 m (1H, NCH=, J = 12.96 Hz, *E*), 6.27 br.s (3H, NH, NH_2, *E*), 6.53 br.s (2H, NH_2, *Z*), 7.97 br.s (1H, NH, *Z*); *Z*/*E* ratio 0.16:0.84. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 30.64 (CH_3N, *E*), 35.13 (CH_3N, *Z*), 85.7 (=**C**HCO, *Z*), 88.10 (=**C**HCO, *E*), 147.96 (NCH=, *E*), 151.53 (NCH=, *Z*), 171.04 (C=O, *E*), 173.50 (C=O, *Z*). Found, %: C 47.84; H 8.02; N 28.30. $C_4H_8N_2O$. Calculated, %: C 47.99; H 8.05; N 27.98.

(*Z*,*E*)-3-(Methylamino)-*N*-phenylprop-2-enamide (IIb). Yield 60 mg (72%), mp 123–125°C. IR spectrum (KBr), ν, cm^{-1}: 1660 (C=O), 1590, 1580, 1560 (C=C, C=C_{arom}), 1530 (C–N, δNH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.76 d (3H, CH_3N, J = 4.92 Hz, *E*), 2.95 d (3H, CH_3N, J = 4.59 Hz, *Z*), 4.43 d (1H, =CHCO, J = 7.68 Hz, *Z*), 4.76 d (1H, =CHCO, J = 12.56 Hz, *E*), 6.49 m (1H, NCH=, J = 7.92 Hz, *Z*), 7.58 m (1H, NCH=, J = 12.72 Hz, *E*), 6.73 br.s (1H, N**H**Ph, *Z*), 6.87 br.s (1H, N**H**Ph, *E*), 6.99 t (1H, *p*-H, J = 7.08 Hz), 7.24 t (2H, *m*-H, J = 7.12 Hz), 7.42 d (2H, *o*-H, J = 8.08 Hz, *Z*), 7.48 d (2H, *o*-H, J = 8.04 Hz, *E*), 7.76 br.s (1H, N**H**Me, *E*), 8.23 br.s (1H, N**H**Me, *Z*); *Z*/*E* ratio 0.75:0.25. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.71 and 35.10 (CH_3N), 84.72 (=**C**HSO, *E*), 88.45 (=**C**HCO, *Z*); 119.98, 123.25, 129.05, 139.27, 139.50 (C_{arom}); 148.77 (NCH=, *E*), 152.34 (NCH=, *Z*), 169.65 (C=O, *E*), 167.50 (C=O, *Z*). Found, %: C 67.75; H 6.89; N 15.93. $C_{10}H_{12}N_2O$. Calculated, %: C 68.16; H 6.86; N 15.90.

(*Z*,*E*)-3-(Methylamino)-1-(morpholin-4-yl)prop-2-en-1-one (IIc). Yield 61 mg (76%), mp 135–136°C. IR spectrum (KBr), ν, cm^{-1}: 1650 (C=O), 1580 (C=C),

1530 (C–N, δNH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.74 d (3H, CH_3N, J = 5.04, *E*), 2.90 d (3H, CH_3N, J = 4.92 Hz, *Z*), 3.46 m (4H, NCH_2, *Z*), 3.54 m (4H, NCH_2, *E*), 3.62 m (4H, OCH_2, *Z*, *E*), 4.56 d (1H, =CHCO, J = 8.08 Hz, *Z*), 4.92 d (1H, =CHCO, J = 12.52 Hz, *E*), 6.50 m (1H, NCH=, J = 8.20 Hz, *Z*), 7.60 m (1H, NCH=, J = 12.52 Hz, *E*), 8.41 br.s (1H, NH); *Z*/*E* ratio 0.79:0.21. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.82 (CH_3N), 42.34 and 43.98 (NCH_2), 66.91 and 66.98 (OCH_2), 80.18 (=**C**HCO, *E*), 83.61 (=**C**HCO, *Z*), 149.86 (NCH=, *Z*), 152.32 (NCH=, *E*), 168.62 (C=O, *Z*), 170.48 (C=O, *E*). Found, %: C 56.60; H 8.64; N 16.70. $C_8H_{14}N_2O_2$. Calculated, %: C 56.45; H 8.29; N 16.46.

(*Z*,*E*)-3-(Benzylamino)-1-(morpholin-4-yl)prop-2-en-1-one (IId). A mixture of 0.5 g (2.4 mmol) of 4-(3-trimethylsilyl-1-oxoprop-2-yn-1-yl)morpholine (**Ic**) and 0.25 g (2.4 mmol) of benzylamine in methanol was heated for 1 h at 65°C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using methanol–chloroform (1:40) as eluent. Yield 0.35 g (60%), oily substance. IR spectrum (film), ν, cm^{-1}: 1630 (C=O), 1570 (C=C, C–N, δNH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.49 m (4H, NCH_2), 3.65 m (4H, OCH_2), 4.21 d (2H, C**H**$_2$Ph, J = 5.04 Hz, *E*), 4.30 d (2H, C**H**$_2$Ph, J = 6.08 Hz, *Z*), 4.65 d (1H, =CHCO, J = 8.16 Hz, *Z*), 5.04 d (1H, =CHCO, J = 12.72 Hz, *E*), 6.63 m (1H, NCH=, J = 8.32 Hz, *Z*), 7.67 m (1H, NCH=, J = 12.60 Hz, *E*), 7.24–7.31 m (5H, Ph), 8.94 br.s (1H, NH); *Z*/*E* ratio 0.97:0.03. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 43.00–46.50 (NCH_3), 48.88 (**C**H$_2$Ph, *Z*), 52.11 (**C**H$_2$Ph, *E*), 66.88 (OCH_2), 81.18 (=**C**HCO, *E*), 85.35 (=**C**HCO, *Z*); 127.15, 127.42, 128.36, 128.69, 139.02 (C_{arom}, *E*, *Z*), 148.61 (NCH=, *Z*), 150.94 (NCH=, *E*), 170.22 (C=O, *E*). Found, %: C 67.81; H 7.33; N 10.86. $C_{14}H_{18}N_2O_2$. Calculated, %: C 68.27; H 7.37; N 11.37.

(2*E*)-1,3-Bis(morpholin-4-yl)prop-2-en-1-one (IIe). A mixture of 100 mg (0.47 mmol) of compound **Ic** and 41 mg (0.47 mmol) of morpholine in methanol was stirred for 7 h at 25°C. The solvent was removed under reduced pressure, and the crystalline residue was washed with diethyl ether. Yield 80 mg (75%), mp 131–132°C (no melting point was given in [16]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.18 m (4H, 3-NCH_2, J = 4.64 Hz); 3.53 m, 3.64 m, and 3.70 m (12H, OCH_2, NCH_2, J = 4.76 Hz); 4.93 (1H, =CHCO, J = 12.60 Hz), 7.38 d (1H, NCH=, J = 12.60 Hz). Found, %: C 58.65; H 8.13; N 12.31. $C_{11}H_{18}N_2O_3$. Calculated, %: C 58.39; H 8.02; N 12.38.

Methyl 2-[(*Z*,*E*)-3-(morpholin-4-yl)-3-oxoprop-1-en-1-ylamino]acetate (III). A mixture of 70 mg (0.33 mmol) of amide **Ic**, 42 mg (0.33 mmol) of methyl 2-aminoacetate hydrochloride, and 33 mg (0.33 mmol) of triethylamine in 5 ml of methanol was placed into a Teflon reactor and was subjected to microwave irradiation (420 W) over a period of 15 min. The mixture was then treated with 5 ml of water and extracted with diethyl ether, and the extract was dried over $MgSO_4$ and evaporated to isolate 36 mg (44%) of **III** with mp 131–132°C. IR spectrum (film), ν, cm^{-1}: 1720 (C=O, ester), 1620 (C=O, amide), 1570 (C=C), 1530 (C–N, δNH), 1510, 1090 (C–O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.53 m (4H, NCH_2), 3.67 m (4H, OCH_2), 3.76 s (3H, CH_3O, *Z*), 3.81 s (3H, CH_3O, *E*), 3.90 d (2H, CH_2CO, J = 6.36 Hz), 4.78 d (1H, =CHCO, J = 8.56 Hz, *Z*), 5.02 d (1H, =CHCO, J = 12.72 Hz, *E*), 6.53 m (1H, NCH=, J = 8.56 Hz, *Z*), 7.64 m (1H, NCH=, J = 12.48 Hz, *E*), 8.82 br.s (NH); *Z*/*E* ratio 0.64:0.36. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 45.40 (NCH_2), 49.27 (CH_2CO), 52.27 (OCH_3), 66.82 and 66.98 (OCH_2), 82.87 (=**C**HCO), 150.35 (NCH=), 169.74 and 170.60 (C=O). Found, %: C 48.28; H 7.07; N 10.98. $C_{10}H_{16}N_2O_4 \cdot H_2O$. Calculated, %: C 48.77; H 7.37; N 11.38.

***N*-Methyl-*N*-[(*E*)-3-(morpholin-4-yl)-3-oxoprop-1-en-1-yl]-3-trimethylsilylprop-2-ynamide (V).** Gaseous methylamine was passed over a period of 1 h at room temperature through a solution of 0.97 g (4.6 mmol) of compound **Ic** in 10 ml of methanol. The solvent was removed under reduced pressure, the residue was dissolved in 20 ml of chloroform, a solution of 0.74 g (4.6 mmol) of 3-trimethylsilylprop-2-ynoyl chloride (**IV**) in 10 ml of chloroform was added dropwise, and the mixture was stirred for 1 h. The mixture was then treated with a 5% solution of sodium hydrogen carbonate and extracted with diethyl ether, the extract was dried over $MgSO_4$ and evaporated under reduced pressure, and the residue, 1.13 g (84%), was purified by column chromatography using ethyl acetate–methanol (100:1) as eluent. Yield 0.5 g (37%), mp 83–84°C. IR spectrum (KBr), ν, cm^{-1}: 1630 (C=O), 1580 (C=C), 1250, 830 (Si–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.13 s (3H, CH_3N), 3.61 m (4H, NCH_2), 3.68 m (4H, OCH_2), 5.66 d and 5.74 d* (1H, =CHCO, J = 13.08 Hz, *E*), 8.60 d (1H, NCH=, J = 13.08 Hz, *E*). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm 29.40 (CH_3N), 41.94–47.15 (NCH_2), 66.92 (OCH_2), 98.98 (=**C**HCO); 94.02, 100.81, 102.66 [C≡C,

* Rotamer concentration 15%.

=**C**HCO (rotamer)]; 143.27 (NCH=), 153.52 (≡C–**C**=O), 163.12 (=C–**C**=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –14.78 ppm. Found, %: C 57.63; H 7.82; N 9.65; Si 9.19. $C_{14}H_{22}N_2O_3Si$. Calculated, %: C 57.11; H 7.53; N 9.51; Si 9.54.

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