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Synthesis of 3-Chloro-3-(trimethylsilyl)prop-2-enoic Acid Amides and Hydrazides from 3-(Trimethylsilyl)propynoic Acid

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Abstract—A number of previously unknown and difficultly accessible polyfunctional β-chloro-β-(trimethylsilyl)prop-2-enoic acid amides and hydrazides have been synthesized by amination of 3-chloro-3-(trimethylsilyl)prop-2-enoyl chloride with the corresponding amines, amino alcohols, 2-amino-4-methylpentanoic acid, and hydrazines. Initial 3-chloro-3-(trimethylsilyl)prop-2-enoyl chloride has been prepared by hydrohalogenation of 3-trimethylsilylpropynoic acid with thionyl chloride in DMF, followed by treatment with oxalyl chloride.

Keywords: amides, hydrazides, acylation, chlorination, 3-(trimethylsilyl)propynoic acid, amines, amino alcohols, leucine, vinyl chlorides

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INTRODUCTION

An enamide fragment is present in molecules of many biologically active natural products [1]. These include fungal and cytotoxic antibiotics crocacins [2], macrocyclic lactones salicylihalamides A and B [3], apicularen A [4], cruentaren [5], zampanolides [6], and lactam macrolides such as cryptophycin [7], apratoxin A [8], poecillastrins [9, 10], and herbimycin A [11]. Pepper alkaloids containing an enamide fragment showed high anticancer, gastroprotective, and anxiolytic activities [12–14]. Synthetic cinnamic acid amides exhibited high fungicidal and insecticidal effects [15], and their *N*-aryl-substituted analogs efficiently acted as antibiotics against staphylococci and tuberculosis bacteria [16]. Acrylamides were used to create a number of known antitumor drugs such as afatinib, canertinib, panobinostat, ibrutinib, anthramycin, and belinostat, antitubercular drug rifampicin, and anticonvulsant medication entacapone [17].

α,β-Unsaturated amides can be involved in Michael reaction with aromatic amines to protect the amino group and obtain benzothiazepine and benzodiazepine lactames [18], Morita–Baylis–Hillman reactions with the formation of both linear olefinic alcohols [19] and cyclic ones (intramolecular cyclization products) [20], arylation with aryl iodides at the β-position of the double bond in the presence of $Pd(OAc)_2$ or AgOAc [21], trifluoromethylation using Umemoto's reagent [22], C^2-alkylation of benzimidazoles in the presence of a rhodium(I) complexes [23], annulation of alkynoates leading to biologically important 6-oxo-1,6-dihydropyridine-3-carboxylic acid esters [24], aerobic rhodium(III)-catalyzed oxidative cross-coupling with alkenes to produce dienamides [25], and reaction with 2-thiocyanato-2,3-dihydro-1*H*-benzimidazole accompanied by cyclization of the amide fragment to 1,2-thiazole derivative [26]. (*Z*)-3-Azidoprop-2-enamides generated in situ from 3-(trimethylsilyl)propynamides and ammonium azide underwent cyclization to 5-amino-1,2-oxazoles on heating under solvent-free conditions [27]. Acrylamides are widely used in the synthesis of polymers [28] and copolymers [29], including those widely used in petroleum industry to increase oil recovery [30, 31], and for the preparation of functional polyacrylamide nanoparticles as potential vehicles for targeted drug delivery to macrophages [32].

α,β-Unsaturated amides can be synthesized by acylation of amines with acryloyl chlorides [15, 16], as well as by multicomponent Ugi reaction of isocyanide, amine, aldehyde, and substituted cinnamic or benzoic acid, which produced α-(acylamino)acrylamides [33].

[†] Deceased.

β-Functionalized prop-2-enamides were synthesized by nucleophilic addition of amines [34], sodium selenide [35], or benzeneselenolate [36] to terminal prop-2-ynamides generated in situ from 3-(trimethylsilyl)prop-2-ynamides. Base-catalyzed hydration of 3-(trimethylsilyl)prop-2-ynamides in the presence of DABCO (10 mol %) afforded symmetrical (*E*,*E*)-β,β′-oxybisacrylamides in good yields [37, 38].

Herein we describe a new synthetic approach to previously unknown difficultly accessible polyfunctional 3-chloro-3-(trimethylsilyl)prop-2-enoic acid amides and hydrazides starting from 3-(trimethylsilyl)propynoic acid.

RESULTS AND DISCUSSION

Examples of geminally substituted (Si, Cl) alkenes containing an electron-withdrawing group are 2-chloro-2-(trialkylsilyl)vinyl ketones [39] and 3-chloro-3-(trimethylsilyl)prop-2-enal [40] which were synthesized by reaction of the corresponding trimethylsilyl-substituted acetylenic carbonyl compounds with gaseous hydrogen chloride. We have found that, unlike 3-(trimethylsilyl)prop-2-ynal and structurally related ketones, 3-(trimethylsilyl)prop-2-ynamides **1a** and **1b** failed to react with gaseous HCl under similar conditions ($CHCl_3$, 25°C, 6 h). On the other hand, terminal propynamides **2a** and **2b** were thus converted to (*E*,*Z*)-3-chloroprop-2-enamides **4a** and **4b** in 3 h and were isolated in 63–90% yield (Scheme 1).

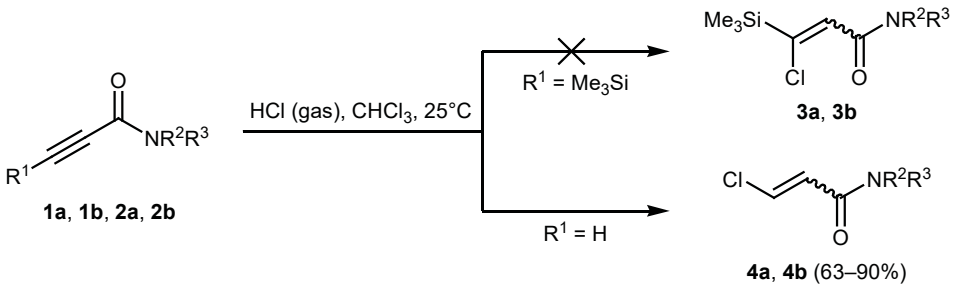
A probable reason for the inertness of the triple bond of 3-(trimethylsilyl)prop-2-ynamides with respect to electrophiles is its low polarizability in comparison to trimethylsilylpropynal and ketones, which can be rationalized by comparability of the electron-withdrawing effects of the trimethylsilyl and amide groups.

We previously showed that 3-chloro-3-(trimethylsilyl)prop-2-enoyl chloride can be obtained in 20% yield [in a mixture with 3-(trimethylsilyl)prop-2-ynoyl chloride] by the solvent-free reaction of 3-(trimethylsilyl)prop-2-ynoic acid with thionyl chloride [41]. (*E*,*Z*)-3-Chloroalk-2-enoic acids were previously synthesized in good yields by reaction of propynoic acid and alkyl(phenyl)propynoic acids with thionyl chloride in DMF at room temperature [42].

We isolated 3-chloroacrylates instead of aryl propynoates while attempting to perform esterification of propynoic acids using thionyl chloride as chlorinating and dehydrating agent, followed by treatment with ethanol in the presence of 4-(dimethylamino)pyridine [43]. Urdaneta et al. [44] synthesized (*E*,*Z*)-3-chloroprop-2-enamides in 70–82% yield by reacting 3-phenylpropynoic and but-2-ynoic acids with oxalyl chloride in DMF at 0°C and subsequent amination in methylene chloride at –50°C. However, we failed to obtain 3-chloro-*N*-phenyl-3-(trimethylsilyl)prop-2-enamide (**3a**) from trimethylsilylpropynoic acid **5** in the system oxalyl chloride–DMF according to the procedure described in [44] at –25 or 0°C. The C≡C triple bond of **5** turned out to be inert toward addition of HCl, and the only product was *N*-phenyl-3-(trimethylsilyl)-prop-2-ynamide (**1a**) which was isolated in 86 and 81% yield, respectively (Table 1; entry nos. 1, 2). When oxalyl chloride was added to acid **5** at a higher temperature, 10 or 25°C, the reaction was accompanied by appreciable decomposition (the mixture turned dark brown). Presumably, the reaction involved oligomerization and heterolytic dissociation of the Si–C_{sp^2} bond in 3-chloro-3-(trimethylsilyl)prop-2-enoyl chloride (**7**). According to the ^{1}H NMR data, the yield of target amide **3a** at 10°C was very low (5%), whereas the major product was compound **1a** (52%); at 25°C, the yield of **3a** increased to 25%, and 13% of 3-chloroprop-2-enamide (**4a**) was also formed (Table 1; run nos. 3, 4; the yields were based on the initial acid **5**).

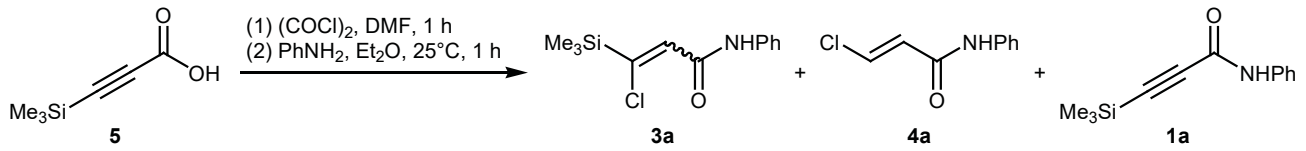
We previously showed that silicon-containing propynamide **1a** can be obtained with a high yield from acid **5** by a one-pot procedure including chlorination of

Scheme 1.



1, R^1 = Me_3Si; **2**, R^1 = H; NR^2R^3 = NHPh (**a**); morpholin-4-yl (**b**).

Table 1. Synthesis of 3-chloro-3-(trimethylsilyl)prop-2-enamide (**3a**) from 3-(trimethylsilyl)prop-2-ynoic acid (**5**) using the system oxalyl chloride–DMF



5 **3a** **4a** **1a**

Entry no.	Temperature,[a] °C	Yield, %		
		3a	**4a**	**1a**
1	–25	0	0	86[b]
2	0	0	0	81[b]
3	10	5[c] (*E*/*Z* = ~2:1)	0	52[c]
4	25	25[d] (*E*/*Z* = ~3:1)	13[d] (*E*)	0
5	25[e]	0	0	84[b]

[a] Temperature of the reaction mixture at the stage of addition of oxalyl chloride to acid **5**.
[b] Isolated yield.
[c] A mixture of **3a** and **1a** was isolated; the yield (based on acid **5**) was determined from the ^{1}H NMR data. The reaction was accompanied by formation of tars.
[d] A mixture of **3a** and **4a** was isolated; the yield (based on acid **5**) was determined from the ^{1}H NMR data. The reaction was accompanied by strong formation of tars.
[e] A catalytic amount of DMF (4 mol %) was used [45].

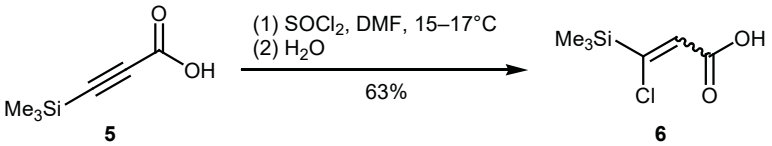
5 with oxalyl chloride in the presence of a catalytic amount of DMF and subsequent amination [45] (Table 1, entry no. 5).

Our failure to obtain 3-chloro-3-(trimethylsilyl)-prop-2-enamide (**3a**) under the above conditions prompted us to examine the possibility of synthesizing target compounds from 3-(trimethylsilyl)propynoic acid in several preparative steps. We synthesized 3-chloro-3-(trimethylsilyl)prop-2-enoic acid (**6**) in 63% yield according to the procedure described in [42] by hydrochlorination of acid **5** with thionyl chloride in DMF (Scheme 2). 3-Chloro-3-(trimethylsilyl)prop-2-enoyl chloride **7** was obtained by treatment of acid **6** with oxalyl chloride in the presence of DMF (4 mol %) without a solvent (Scheme 3). The yield of **7** was 40% based on the initial acid **5**.

Previously unknown (*Z*/*E*)-3-chloro-3-(trimethylsilyl)prop-2-enamides **3a**–**3e** were synthesized in 63–78% yield by adding acid chloride **7** to a solution of 2 equiv of amine **8a**–**8d** in diethyl ether at room temperature (Table 2, entry nos. 1–5). The reaction was chemoselective. For example, no substitution of chlorine at the double bond was observed even when compound **7** was treated with 4 equiv of morpholine (**8b**). Presumably, the reactivity of the β-chlorine atom toward nucleophilic substitution is reduced due to steric effect of the neighboring trimethylsilyl group.

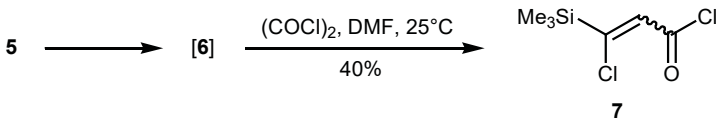
The reaction of **7** with an equimolar amount of *N*,*O*-bis-trimethylsilyl leucine derivative **8f** in diethyl ether at 25°C, followed by hydrolysis, gave 2-[(*E*,*Z*)-3-chloro-3-(trimethylsilyl)prop-2-enoylamino]-4-methylpentanoic acid (**3f**) in 91% yield (Table. 2, entry no. 6).

Scheme 2.



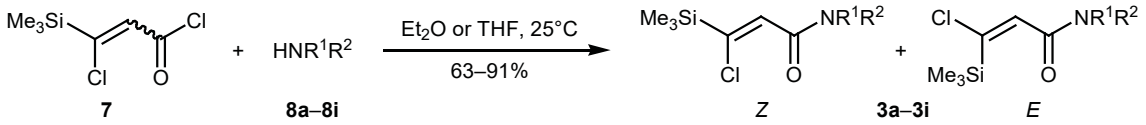
5 **6**

Scheme 3.

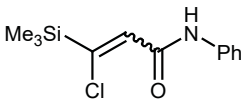
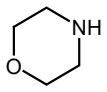
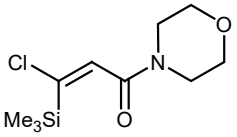
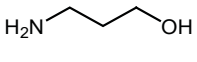
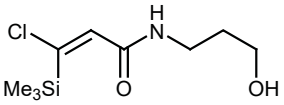
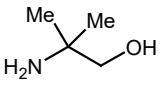
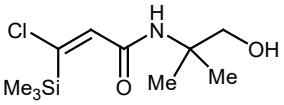
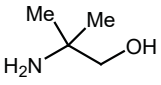
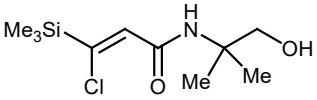
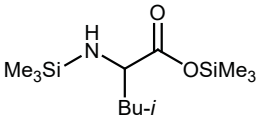
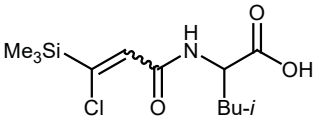
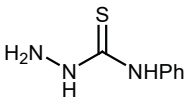
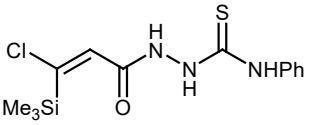
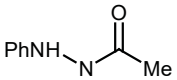
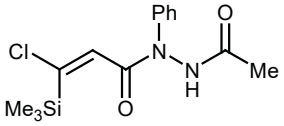
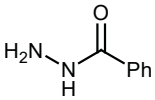
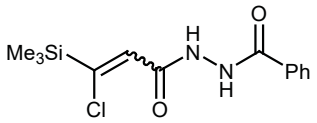


7

Table 2. Synthesis of 3-chloro-3-(trimethylsilyl)prop-2-enamides **3a**–**3f** and hydrazides **3g**–**3i**

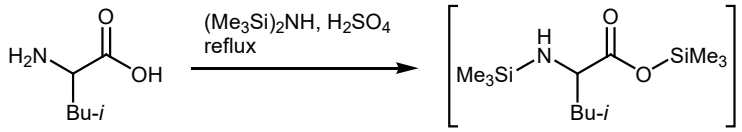


7 **8a–8i** *Z* **3a–3i** *E*

Entry no.	Initial amine (hydrazine)	Product	δ(=CH), ppm (*E*, *Z*)	$^3J_{SiH}$, Hz (*E*, *Z*)	Yield,[a] %
1	**8a**	 **3a** (*E*/*Z* = ~ 5:1)[a]	6.83, 6.48	7.7, 4.6	78
2	 **8b**	 **3b** (*E*)[a]	6.89	8.2	70
3	 **8c**	 **3c** (*E*)[a]	6.66	8.1	76
4	 **8d**	 **3d** (*E*)[a]	6.70	7.8	63
5	 **8d**	 **3e** (*Z*)[a]	6.34	–	2
6	 **8f**	 **3f** (*E*/*Z* = ~ 5:1)[a]	6.89, 6.54	7.9, 4.2	91
7	 **8g**	 **3g** (*E*)[a]	6.64	6.6	73
8	 **8h**	 **3h** (*E*)[a]	6.65	–	33
9	 **8i**	 **3i** (*E*/*Z* = ~ 20:1)[a]	6.64, 6.44	6.6, –	76

[a] Isolated yield.

Scheme 4.



8e **8f**

Bis-silyl derivative **8f** was prepared by treatment of leucine (**8e**) with hexamethyldisilazane in the presence of a catalytic amount of sulfuric acid on heating under reflux (Scheme 4).

We previously demonstrated the efficiency of using silylated amino acids and amino alcohols generated in in situ in the synthesis of *N*-[3-(trimethylsilyl)prop-2-ynoyl] amino acids [46] and *N*-(hydroxyalkyl) 3-(trimethylsilyl)prop-2-ynamides [47]. Acid chloride **7** reacted with *N*-phenylhydrazinecarbothioamide (**8g**), *N*′-phenylacetohydrazide (**8h**), and benzohydrazide (**8i**) in THF in the presence of pyridine at room temperature to afford 33–76% of the corresponding (*E*)-3-chloro-3-(trimethylsilyl)prop-2-enehydrazides **3g**–**3i** (Table 2, entry nos. 7–9).

The structure of compounds **3a**–**3i** was proved by IR and ^{1}H, ^{13}C, and ^{29}Si NMR spectra. Their configuration was determined on the basis of the vicinal ^{1}H–^{29}Si spin–spin coupling constant ($^{3}J_{SiH}$). It is known that the *trans* coupling constant is higher than *cis* coupling constant [48]. The $^{3}J_{SiH}$ values for the *E* (*trans*) isomers ranged from 6 to 8 Hz against 3–5 Hz for the *Z* (*cis*) isomers. It should also be noted that the olefinic proton of the *E* isomers resonated at a lower field (δ 6.64–6.89 ppm) than that of the *Z* isomer (δ 6.34–6.54 ppm, Table 2).

As follows from the data in Table 2, compounds **3b**, **3c**, **3g**, and **3h** were isolated as *E* isomers (entry nos. 2, 3, 7, 8). Compounds **3a**, **3f**, and **3i** were mixtures of the *Z* and *E* isomers, the latter prevailing (entry nos. 1, 6, 9). Pure (*E*)- and (*Z*)-3-chloro-*N*-(3-hydroxy-2-methylpropan-2-yl)-3-(trimethylsilyl)prop-2-enamides **3d** and **3e** were isolated by column chromatography (entry nos. 4, 5).

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13, 101.62, and 79.49 MHz, respectively. The ^{1}H and ^{13}C chemical shifts were measured relative to the residual proton and carbon signals of the deuterated solvents ($CHCl_3$, δ 7.27 ppm; $CDCl_3$, δ_C 77.1 ppm; DMSO-d_5, δ 2.50 ppm; DMSO-d_6, δ_C 39.6 ppm); the ^{29}Si chemical shifts were measured relative to hexamethyldisiloxane as internal standard (δ_{Si} 7.5 ppm). The IR spectra were recorded on a Bruker Vertex-70 spectrometer. The melting points were measured with a PolyTherm A micro hot stage. Silica gel (0.060–0.2 mm, 70–230 mesh; Alfa Aesar) was used for column chromatography. Elemental analyses were obtained using a Flash EA 1112 CHNS-O analyzer.

3-(Trimethylsilyl)prop-2-ynoic acid (**5**) [49] and 3-(trimethylsilyl)prop-2-ynamides **1a** and **1b** [45] were synthesized according to reported procedures. (*E*)-3-Chloroacrylamides **4a** and **4b** were described previously [50, 51], and only their ^{1}H NMR spectra were recorded.

3-Chloro-3-(trimethylsilyl)prop-2-enamides 3a–3e (*general procedure*). A solution of 3 mmol of 3-chloro-3-(trimethylsilyl)prop-2-enoyl chloride (**7**) in 5 mL of diethyl ether was added dropwise with stirring at room temperature to a solution of 6 mmol of amine **8a**–**8d** in 20 mL of diethyl ether. The mixture was stirred for 1 h, washed with 5 mL of 5% aqueous HCl, and extracted with diethyl ether, the organic phase was dried over $MgSO_4$ and evaporated under reduced pressure, and the product was isolated by recrystallization or column chromatography.

(*E*,*Z*)-3-Chloro-*N*-phenyl-3-(trimethylsilyl)prop-2-enamide (3a) was synthesized from 0.60 g (5.0 mmol) of **7**. Yield 0.60 g (78%), white crystalline solid, mp 66–67°C (from hexane). IR spectrum (KBr), ν, cm^{-1}: 3237 br (NH), 1664 m (C=O), 1643 s (C=O), 1596 s (C=C_{arom}), 1583 m (C=C_{arom}), 1542 s (δNH), 1252 s (Si–C), 847 s (Si–C), 757 s (Si–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.31 s (9H, CH_3Si, *Z*), 0.34 s (9H, CH_3Si, *E*), 6.48 s (1H, =CH, $^{3}J_{SiH}$ = 4.6 Hz, *Z*), 6.83 s (1H, =CH, $^{3}J_{SiH}$ = 7.7 Hz, *E*), 7.06 t (1H, *p*-H, *J* = 7.6 Hz, *Z*), 7.12 t (1H, *p*-H, *J* = 7.8 Hz, *E*), 7.26 t (2H, *m*-H, *J* = 7.6 Hz, *Z*), 7.31 t (2H, *m*-H, *J* = 7.8 Hz, *E*), 7.51 d (2H, *o*-H, *J* = 7.6 Hz, *Z*), 7.56 d (2H, *o*-H, *J* = 7.8 Hz, *E*), 8.06 br.s (1H, NH, *E*), 8.46 br.s (1H, NH, *Z*); *E*/*Z* = ~5:1. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –2.4 (CH_3Si, *Z*), –0.2 (CH_3Si, *E*), 120.2 (C^{o}, *E*), 120.6 (C^{o}, *Z*), 124.5 (C^{p}, *E*), 125.1 (C^{p}, *Z*), 129.0 (C^{m}, *E*), 129.2 (C^{m}, *Z*), 131.8 (=CH, *Z*), 136.1 (=CH, *E*), 137.3 (C^{i}, *Z*), 138.0 (C^{i}, *E*), 146.6 (SiC=, *Z*), 157.4

(SiC=, *E*), 161.9 (C=O, *Z*), 162.4 (C=O, *E*). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: 1.9 (*E*), 3.1 (*Z*). Found, %: C 56.61; H 6.55; Cl 13.71; N 5.83; Si 11.20. $C_{12}H_{16}ClNOSi$. Calculated, %: C 56.79; H 6.35; Cl 13.97; N 5.52; Si 11.07.

(*E*)-3-Chloro-1-(morpholin-4-yl)-3-(trimethylsilyl)prop-2-en-1-one (3b) was synthesized from 0.60 g (3.0 mmol) of **7**. Yield 0.52 g (70%), yellow oil which crystallized after storage for a month, mp 30–32°C. IR spectrum (KBr), ν, cm^{-1}: 1630 s (C=O), 1570 m (C=C), 1240 s (Si–C), 840 s (Si–C), 760 s (Si–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.20 s (9H, CH_3Si), 3.45 t and 3.56 t (4H, NCH_2, $^3J_{HH}$ = 4.9 Hz), 3.52–3.65 m (4H, OCH_2), 6.89 s (1H, =CH, $^3J_{SiH}$ = 8.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –1.2 (CH_3Si), 41.7, 46.6 (CH_2N), 66.5 (CH_2O), 134.3 (=CH), 151.2 (SiC=), 164.4 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 1.0 ppm. Found, %: C 48.61; H 7.51; Cl 14.49; N 5.94; Si 11.53. $C_{10}H_{18}ClNO_2Si$. Calculated, %: C 48.47; H 7.32; Cl 14.31; N 5.65; Si 11.33.

(*E*)-3-Chloro-*N*-(3-hydroxypropyl)-3-(trimethylsilyl)prop-2-enamide (3c) was synthesized from 1.00 g (5.1 mmol) of **7**. Yield 0.90 g (76%), white crystalline solid, mp 104–105°C (from hexane). IR spectrum (KBr), ν, cm^{-1}: 3275 br (NH, OH), 1630 s (C=O), 1575 s (C=C), 1540 m (δNH), 1235 s (Si–C), 865 s (Si–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.31 s (9H, CH_3Si), 1.66–1.75 m (2H, C**H**$_2$CH$_2$O), 3.02 br.s (1H, OH), 3.42–3.51 m (2H, CH_2N), 3.64 t (2H, CH_2O, *J* = 5.5 Hz), 5.89 br.s (1H, NH), 6.66 s (1H, =CH, $^3J_{SiH}$ = 8.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –0.1 (CH_3Si), 32.4 (**C**CH_2N), 36.7 (CH_2N), 59.4 (CH_2O), 134.7 (=CH), 157.7 (SiC=), 165.3 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 1.9 ppm. Found, %: C 46.09; H 7.89; Cl 14.96; N 5.89; Si 11.67. $C_9H_{18}ClNO_2Si$. Calculated, %: C 45.85; H 7.69; Cl 15.04; N 5.94; Si 11.91.

(*E*)-3-Chloro-*N*-(3-hydroxy-2-methylpropan-2-yl)-3-(trimethylsilyl)prop-2-enamide (3d) was synthesized from 1.17 g (5.9 mmol) of **7**; the product was isolated by silica gel column chromatography using diethyl ether as eluent. Yield 0.95 g (63%), white crystalline solid, mp 89–90°C. IR spectrum (KBr), ν, cm^{-1}: 3270 br (NH, OH), 1639 s (C=O), 1585 s (C=C), 1549 s (δNH), 1242 s, 846 s (Si–C), 750 m (Si–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.30 s (9H, CH_3Si), 1.31 s (6H, CH_3C), 3.60 s (2H, CH_2), 4.75 br.s (1H, OH), 5.64 br.s (1H, NH), 6.70 s (1H, =CH, $^3J_{SiH}$ = 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –0.4 (CH_3Si), 24.8 (CH_3C), 56.6 (CH_3S), 70.7 (CH_2), 135.6 (=CH), 156.8 (SiC=), 165.3 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 1.6 ppm. Found, %: C 48.26; H 8.06; Cl 13.91; N 5.89; Si 11.36. $C_{10}H_{20}ClNO_2Si$. Calculated, %: C 48.08; H 8.07; Cl 14.19; N 5.61; Si 11.24.

(*Z*)-3-Chloro-*N*-(3-hydroxy-2-methylpropan-2-yl)-3-(trimethylsilyl)prop-2-enamide (3e) was synthesized from 1.17 g (5.9 mmol) of **7**; the product was isolated by silica gel column chromatography using diethyl ether as eluent. Yield 22 mg (2%), white crystalline solid, mp 98–99°C. IR spectrum (KBr), ν, cm^{-1}: 3270 br (NH, OH), 1630 s (C=O), 1590 s (C=C), 1530 m (δNH), 1230 s (Si–C), 830 s (Si–C), 750 m (Si–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.24 s (9H, CH_3Si), 1.37 s (6H, CH_3C), 3.65 s (2H, CH_2), 4.46 br.s (1H, OH), 6.34 s (1H, =CH), 6.54 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –2.8 (CH_3Si), 25.0 (**C**H_3C), 57.2 (CH_3**C**), 70.7 (CH_2), 132.2 (=CH), 145.7 (SiC=), 164.7 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 2.7 ppm. Found, %: C 47.92; H 8.06; Cl 14.40; N 5.79; Si 11.36. $C_{10}H_{20}ClNO_2Si$. Calculated, %: C 48.08; H 8.07; Cl 14.19; N 5.61; Si 11.24.

2-{[(*E*,*Z*)-3-Chloro-3-(trimethylsilyl)prop-2-enoyl]amino}-4-methylpentanoic acid (3f). A mixture of 0.73 g (5.6 mmol) of *dl*-leucine **8e**, 2.30 g (14.0 mmol) of hexamethyldisilazane, and a catalytic amount of concentrated sulfuric acid was refluxed for 30 min. Excess hexamethyldisilazane was removed under reduced pressure, the residue was dissolved in 30 mL of anhydrous diethyl ether, and a solution of 1.10 g (5.6 mmol) of acid chloride **7** in 10 mL of diethyl ether was added dropwise with stirring. The mixture was stirred at room temperature for 1 h, washed with 10 mL of 5% aqueous HCl, and extracted with diethyl ether, the organic phase was dried over $MgSO_4$, the solvent was removed, and the residue was purified by recrystallization. Yield 1.47 g (91%), white crystalline solid, mp 113–114°C (from heptane). IR spectrum (KBr), ν, cm^{-1}: 3400–2500 br (NH, OH), 1720 s (C=O, acid), 1640 s (C=O, amide), 1580 s (C=C), 1530 (δNH), 1260 s (Si–C), 850 s (Si–C), 760 m (Si–C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.23 s (9H, CH_3Si), 0.89–0.94 m (6H, CH_3), 1.52–1.55 m (2H, CH_2), 1.60–1.74 m [1H, C**H**$(CH_3)_2$], 4.25–4.31 m (1H, CHCO), 6.54 s (1H, =CH, $^3J_{SiH}$ = 4.2 Hz, *Z*), 6.89 s (1H, =CH, $^3J_{SiH}$ = 7.9 Hz, *E*), 8.10 d (1H, NH, *J* = 7.9 Hz, *Z*), 8.28 d (1H, NH, *J* = 8.2 Hz, *E*), 12.38 br.s (1H, COOH), *E*/*Z* = ~5:1. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: –2.3 (CH_3Si, *Z*), 0.0 (CH_3Si, *E*), 21.57 (**C**H_3C, *E*), 21.61 (**C**H_3C, *Z*), 23.2 (CH_3**C**), 24.7 (CH**C**H_2, *Z*), 24.8 (CH**C**H_2, *E*), 50.5 (**C**HCO, *Z*), 50.6 (**C**HCO, *E*), 131.1 (=CH, *Z*), 136.9 (=CH, *E*) 146.0 (SiC=, *Z*), 153.7, (SiC=, *E*), 163.0

(NC=O, *Z*), 163.9 (NC=O, *E*), 174.1 (OC=O, *E*), 174.3 (OC=O, *Z*). ^{29}Si NMR spectrum (DMSO-d_6), δ_{Si}, ppm: 1.3 (*Z*), 2.3 (*E*). Found, %: C 49.63; H 7.89; Cl 12.35; N 4.99; Si 9.47. $C_{12}H_{22}ClNO_3Si$. Calculated, %: C 49.39; H 7.60; Cl 12.15; N 4.80; Si 9.62.

3-Chloro-3-(trimethylsilyl)prop-2-enehydrazides 3g–3i (*general procedure*). A solution of 3.0 mmol of **7** in anhydrous diethyl ether (20 mL) was added dropwise with stirring at room temperature to a mixture of 3.0 mmol of hydrazine **8g**–**8i** and 3.0 mmol of pyridine in 15 mL of THF. The mixture was stirred for 8 h, washed with 10 mL of water, and extracted with diethyl ether (**3g**, **3h**) or chloroform (**3i**). The extract was dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was subjected to further purification.

2-[(*E*)-3-Chloro-3-(trimethylsilyl)prop-2-enoyl]-*N*-phenylhydrazine-1-carbothioamide (3g) was synthesized from 0.60 g (3.0 mmol) of **7**; the product was isolated by silica gel column chromatography using chloroform–diethyl ether (1:1) as eluent. Yield 0.73 g (73%), white crystalline solid, mp 134–135°C. IR spectrum (KBr), ν, cm^{-1}: 3450 br (NH), 1660 s (C=O), 1590 s (C=C), 1525 m (δNH), 1240 s (Si–C), 835 s (Si–C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.24 s (9H, CH_3Si), 6.64 s (1H, =CH, $^3J_{SiH}$ = 6.6 Hz), 7.16 t (1H, *p*-H, *J* = 7.2 Hz), 7.33 t (2H, *m*-H, *J* = 7.2 Hz), 7.45 d (2H, *o*-H, *J* = 7.2 Hz), 9.67 br.s and 9.70 br.s (2H, NH–NH), 10.16 br.s (1H, N**H**Ph). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: –2.7 ($SiMe_3$), 125.0 (C^p), 125.2–126.2 (C^o), 128.0 (C^m), 129.3 (C^i), 139.1 (=CH), 147.4 (SiC=), 162.0 (C=O), 180.8 (C=S). ^{29}Si NMR spectrum (DMSO-d_6): δ_{Si} 1.3 ppm. Found, %: C 47.90; H 5.69; Cl 11.10; N 13.14; S 10.04; Si 8.28. $C_{13}H_{18}ClN_3OSSi$. Calculated, %: C 47.62; H 5.53; Cl 10.81; N 12.81; S 9.78; Si 8.57.

(*E*)-*N*′-Acetyl-3-chloro-*N*-phenyl-3-(trimethylsylyl)prop-2-enehydrazide (3h) was synthesized from 50 mg (0.25 mmol) of **7**; the product was isolated by silica gel column chromatography using chloroform–diethyl ether (1:1) as eluent. Yield 21 mg (33%), white crystalline solid, mp 101–102°C. IR spectrum (KBr), ν, cm^{-1}: 3430 br (NH), 1660 br (C=O), 1590 s (C=C), 1525 m (δNH), 1240 m (Si–C), 840 s (Si–C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.24 s (9H, CH_3Si), 1.95 s (3H, CH_3), 6.65 s (1H, =CH), 7.41 br.m (5H, Ph), 10.86 br.s (1H, NH). Found, %: C 54.30; H 6.43; Cl 11.25; N 9.19; Si 8.79. $C_{14}H_{19}ClN_2O_2Si$. Calculated, %: C 54.09; H 6.16; Cl 11.41; N 9.01; Si 9.04.

(*E*,*Z*)-*N*′-Benzoyl-3-chloro-3-(trimethylsilyl)-prop-2-enehydrazide (3i) was synthesized from 0.46 g (2.34 mmol) of **7**. Yield 0.52 g (76%), white crystalline solid, mp 211–212°C (from Et_2O). IR spectrum (KBr), ν, cm^{-1}: 3225 (NH), 1678 m (PhC=O), 1637 s (NC=O), 1604 w (C=C), 1528 m (δNH), 1252 m (Si–C), 843 s (Si–C), 710 m (Si–C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.11 s (9H, CH_3Si, *Z*), 0.27 s (9H, CH_3Si, *E*), 6.44 s (1H, =CH, *Z*), 6.64 s (1H, =CH, $^3J_{SiH}$ = 6.6 Hz, *E*), 7.46 t (2H, *m*-H, *J* = 7.3 Hz, *E*), 7.54 t (1H, *p*-H, *J* = 7.3 Hz, *E*), 7.82 d (2H, *o*-H, *J* = 8.5 Hz, *Z*), 7.92 d (2H, *o*-H, *J* = 7.3 Hz, *E*), 10.06 d (1H, **H**NCOPh, *J* = 1.9 Hz), 10.41 d (1H, HNCOC=, *J* = 1.9 Hz). *E*/*Z* = ~20:1. ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: –2.7 (CH_3Si), 127.5, 128.0 (C^o, C^m), 128.7 (C^p), 131.3 (=CH), 132.4 (C^i), 147.5 (SiC=), 161.2 (PhC=O), 164.9 (NC=O). ^{29}Si NMR spectrum (DMSO-d_6), δ, ppm: 1.5. Found, %: C 52.87; H 5.51; Cl 12.03; N 9.43; Si 9.38. $C_{13}H_{17}ClN_2O_2Si$. Calculated, %: C 52.60; H 5.77; Cl 11.94; N 9.44; Si 9.46.

General procedure for hydrochlorination of prop-2-ynamides. Gaseous hydrogen chloride was passed through a solution of 1 mmol of prop-2-ynamide **2a** or **2b** in 15 mL of chloroform at room temperature over a period of 3 h. The solvent was removed, and the residue was purified by recrystallization from benzene (**4a**) or column chromatography on silica gel (**4b**; $CHCl_3$–MeOH, 10:1).

(*Z*,*E*)-3-Chloro-*N*-phenylprop-2-enamide (4a) was synthesized from 0.15 g (1 mmol) of *N*-phenylprop-2-ynamide (**2a**). Yield 0.17 g (90%), yellowish powder, mp 120–121°C (from benzene); published data [42]: mp 152–153°C, *E* isomer. IR spectrum (KBr), ν, cm^{-1}: 3298 br (NH), 1657 s (C=O), 1597 m (C=C$_{arom}$), 1546 m (δNH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.32 d (1H, =CHCO, *J* = 8.4 Hz, *Z*), 6.34 d (1H, =CHCO, *J* = 12.9 Hz, *E*), 6.61 d (1H, ClCH=, *J* = 8.4 Hz, *Z*), 7.06–7.18 m (1H, *p*-H), 7.24–7.36 m (2H, *m*-H), 7.39 d (1H, ClCH=, *J* = 12.9 Hz, *E*), 7.42 br.s (1H, NH, *E*), 7.53 d (2H, *o*-H, *J* = 6.0 Hz, *E*), 7.57 d (2H, *o*-H, *J* = 8.0 Hz, *Z*), 8.00 br.s (1H, NH, *Z*), *E*/*Z* = ~1:1; published data [50]: ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.45 d (1H, =CHSO, *J* = 14 Hz, *E*), 7.52 d (1H, ClCH=, *J* = 14.0 Hz, *E*), 7.52 m (5H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 120.4 (C^o), 124.9 (C^p, *Z*), 125.1 (C^p, *E*), 125.9, 126.2 (=**C**CO), 127.4 (ClC=, *Z*), 129.1 (C^m, *E*), 129.2 (C^m, *Z*), 135.2 (ClC=, *E*), 137.2, 137.5 (C^i, *E*), 161.4 (C=O). Found, %: C 59.81; H 4.42, Cl 19.29; N 7.60. C_9H_8ClNO. Calculated, %: C 59.52; H 4.44; Cl 19.52; N 7.71.

(*Z*,*E*)-3-Chloro-1-(morpholin-4-yl)prop-2-en-1-one (4b) was synthesized from 0.30 g (1.4 mmol) of 1-(morpholin-4-yl)prop-2-yn-1-one (**2b**). Yield 0.24 g (63%), orange oil. IR spectrum (film), ν, cm^{-1}: 1630 s (C=O), 1580 m (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.37–3.50 m (2H, NCH_2), 3.51–3.78 m (6H, NCH_2, OCH_2), 6.22 d (1H, =CHCO, *J* = 8.1 Hz, *Z*), 6.33 d (1H, ClCH=, *J* = 8.1 Hz, *Z*), 6.59 d (1H, =CHCO, *J* = 12.8 Hz, *E*), 7.19 d (1H, ClCH=, *J* = 12.8 Hz, *E*); *E*/*Z* = ~1:1; published data [51]: ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.66 br.s (8H, NCH_2CH_2O), 6.65 d (1H, =CHCO, *J* = 12.9 Hz, *E*), 7.31 d (1H, ClCH=, *J* = 12.9 Hz, *E*). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 42.4, 42.9, 46.8, 47.3 (CH_2N), 67.3, 67.6 (CH_2O), 123.9, 124.5, 125.3 (=**C**CO, ClC=), 136.2 (ClC=, *E*), 163.4, 164.2 (C=O). Found, %: C 47.71; H 5.99; Cl 20.42; N 8.19. $C_7H_{10}ClNO_2$. Calculated, %: C 47.88; H 5.74; Cl 20.19; N 7.98.

Reaction of 3-(trimethylsilyl)prop-2-ynoic acid (5) with oxalyl chloride in DMF, followed by amination. Oxalyl chloride, 0.28 g (2.20 mmol), was added dropwise with stirring over a period of 1 h at room temperature to a solution of 0.15 g (1.05 mmol) of acid **5** in anhydrous DMF (1.0 mL). The mixture turned dark brown due to strong tarring, excess oxalyl chloride was removed under reduced pressure, and the black viscous residue was extracted with diethyl ether (4×5.0 mL). The combined extracts were added dropwise to a solution of 0.20 g (2.10 mmol) of aniline (**8a**) in 10 mL of diethyl ether. The mixture was stirred for 1 h and washed with 10 mL of 5% aqueous HCl, the aqueous phase was extracted with diethyl ether, the extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure to obtain 0.78 g of a mixture containing compounds **3a** and **4a**. The ^1H NMR spectrum of the reaction mixture showed two singlets at δ 6.48 ($^3J_{SiH}$ = 4.6 Hz) and 6.84 ppm ($^3J_{SiH}$ = 7.7 Hz) due to vinylic protons of the *Z* and *E* isomers of **3a** and two doublets at δ 6.35 (*J* = 12.9 Hz) and 7.39 ppm (*J* = 12.9 Hz) due to vinylic protons of *E*-**4a**. According to the ^1H NMR data, the ratio **3a**:**4a** is 67:33, which corresponds to 25 and 13% yields of **3a** and **4a**, respectively, based on the initial acid **5**.

(*E*,*Z*)-3-Chloro-3-(trimethylsilyl)prop-2-enoyl chloride (7). Thionyl chloride, 1.35 g (11.39 mmol), was added dropwise with stirring at 15–17°C over a period of 2 h to a solution of 1.34 g (9.42 mmol) of acid **5** in anhydrous DMF (8.5 mL). Excess thionyl chloride was removed under reduced pressure, and the residue was poured onto ice. The aqueous phase was separated and extracted with diethyl ether, the extract was dried over Na_2SO_4, and the solvent was removed under reduced pressure to obtain 3-chloro-3-(trimethylsilyl)prop-2-enoic acid (**6**) as an amorphous substance. Yield 1.06 g (63%). IR spectrum (KBr), ν, cm^{-1}: 2500–3400 br (OH), 1670 s (C=O), 1600 s (C=O), 1220 m (Si–C), 840 s (Si–C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.28 s (9H, CH_3Si, *Z*), 0.32 s (9H, CH_3Si, *E*), 6.39 s (1H, =CH, *Z*), 6.75 s (1H, =CH, *E*), 10.76 br.s (1H, COOH); *E*/*Z* = ~1.5:1. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –2.3 (CH_3Si), 126.3 (=CH), 157.5 (SiC=), 168.4 (C=O). A mixture of 1.06 g (5.9 mmol) of acid **6**, 0.86 g (6.8 mmol) of oxalyl chloride, and a catalytic amount of DMF (4 mol %) was stirred for 1 h. Compound **7** was isolated by fractional distillation. Yield 0.74 g (40%, based on **5**), bp 84–85°C (17 mm Hg). IR spectrum (film), ν, cm^{-1}: 1778 s (C=O), 1744 m (C=O), 1660 m (C=C), 1640 s (C=C), 1253 s (Si–C), 845 s (Si–C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.29 s (9H, CH_3Si, *Z*), 0.31 s (9H, CH_3Si, *E*), 6.65 s (1H, =CH, *Z*), 7.00 s (1H, =CH, *E*), *E*/*Z* = ~4:1. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –2.6, –1.4 (CH_3Si), 131.1, 138.0 (=CH), 159.3, 160.0 (SiC=), 163.8, 168.0 (C=O). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: 4.6, 3.4. Found, %: C 36.40; H 5.23; Cl 35.70; Si 14.03. $C_6H_{10}Cl_2OSi$. Calculated, %: C 36.56; H 5.11; Cl 35.97; Si 14.25.

CONCLUSIONS

Previously unknown difficultly accessible polyfunctional β-chloro-β-(trimethylsilyl)propenoic acid amides and hydrazides were synthesized from 3-(trimethylsilyl)propynoic acid using available reagents, mainly at room temperature, without purification of intermediate 3-chloro-3-(trimethylsilyl)prop-2-enoic acid. The obtained amides and hydrazides attract interest as polyfunctional reagents containing four interrelated reaction centers, ligands, potential biologically active compounds, and substrates for the design of new bioactive molecules.

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CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

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