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A New Family of Vinyl Selenocyanates with the Amide Function Based on the Reaction of Potassium Selenocyanate with 3-Trimethylsilyl-2-Propynamides

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Abstract: An efficient approach to a novel family of (Z)-3-amino-3-oxo-1-propenyl selenocyanates was developed based on the reaction of KSeCN with 3-trimethylsilyl-2-propynamides in the presence of ammonium chloride in methanol. The reaction was accompanied by a desilylation process. The products were not formed under the same reaction conditions in the absence of ammonium chloride, which was used for the first time in the reactions of selenocyanates with acetylenes. The use of this new methodology allowed the reaction to carry out in a regio- and stereoselective fashion as anti-addition affording vinyl selenocyanates with a (Z)-configuration in high yields.

Keywords: potassium selenocyanate; 3-trimethylsilyl-2-propynamides; ammonium chloride; methanol; vinyl selenocyanates; acetylenes

1. Introduction

Selenium is recognized as a vital trace element. The selenium atom is included in the active center of enzymes of the body's antioxidant defense system [1–3]. Organoselenium compounds exhibit a variety of biological activities [3–19] including antitumor [8–11], antiviral [13,14], antibacterial [11,12], and glutathione peroxidase-like properties [15–17].

The intensively studied selenium drug ebselen has a number of valuable biological properties such as anti-inflammatory, neuroprotective and glutathione peroxidase-like activities [20–22]. Ebselen is being clinically evaluated as a therapeutic agent in several other areas, including the treatment of COVID-19, hearing loss, and bipolar disorder [20–22]. Ebselen and a number of organoselenium compounds with biological activity contain the amide group [20–22]. The presence of the amide function can be considered favorable for the manifestation of possible biological activity.

A very convenient and promising approach to the introduction of the selenium atom is based on alkali metal selenocyanates [23–26]. This approach to organoselenium compounds has been widely developed due to the ease of the reaction of metallic selenium with alkali metal cyanides and the high synthetic potential of organic selenocyanates [23–26].

Treatment of organic selenocyanates with bases and reducing agents such as LiEt$_3$BH, DIBAL [27], NaBH$_4$ [28,29], KOH, K$_3$PO$_4$ [30,31], and K$_2$CO$_3$ [32] leads to the formation of dialkyl(diaryl)diselenides, which are in turn very important reagents for organoselenium chemistry [33]. The reduction of organic selenocyanates to selenolates with sodium borohydride followed by the reaction of the generated selenolates with vinyl halides [31] or with terminal acetylenes in the presence of t-BuOK [34] makes it possible to obtain a wide range of functionalized organyl vinyl selenides. Disubstituted selenides with different substituents at selenium were also obtained from arylselenocyanates by the direct substitution of the cyano group for a hydrocarbon fragment in the reaction with alcohols in the presence of tributylphosphine [35,36], as well as by the reaction of benzylselenocyanates with lithium

acetylenides [37]. Aryl selenocyanates, upon boiling in water in the presence of monovalent copper iodide and 1,2-cyclohexyldiamine, yield symmetric diaryl selenides [38].

Organic selenocyanates react with alkali metal nitrites to form Se-linked triazoles or tetrazoles [39–42]. Styryl selenocyanates undergo intramolecular cyclization to benzoselenophenes in high yield by a transition-metal-free reaction under the action of a catalytic amount of iodine [43]. The hydrochloride derivatives of 2-aminoethylselenocyanates are cyclized to 2-imino-1,3-selenazolidines [44–46]. The cyclization of the intermediate selenocyanate derivative of 1,2-anhydroglucopyranose to cis-1,2-fused 1,3-oxaselenolan-2-imine carbohydrate derivatives proceeds in a similar fashion [47].

Examples of selenocyanates with interesting biological properties are present in the literature and shown in Figure 1. Selenocyanates exhibit high anticancer [48–52], antimicrobial [53,54], antioxidant [55], and fungicidal [54,55] activity. The selenocyanate group has been shown to be an important pharmacophore that often enhances anticancer activity [48]. The SeCN-containing derivative of the drug vorinostat (**A**, Figure 1) demonstrates high cytotoxicity against the WM115 melanoma cell line [49,50].
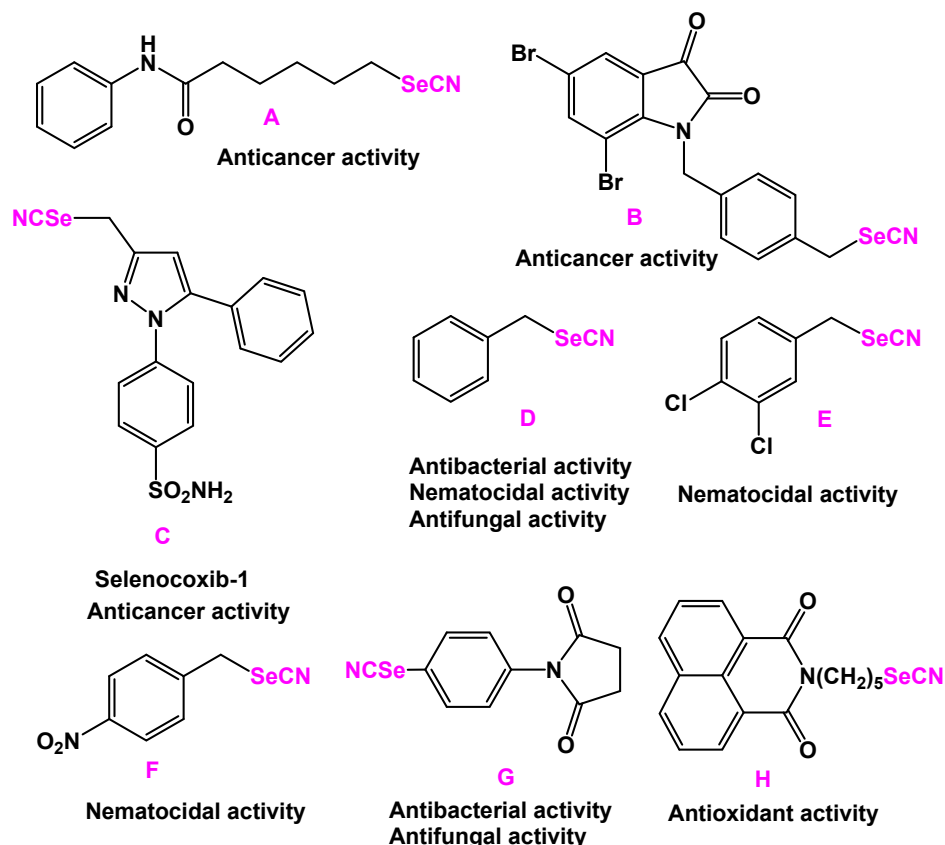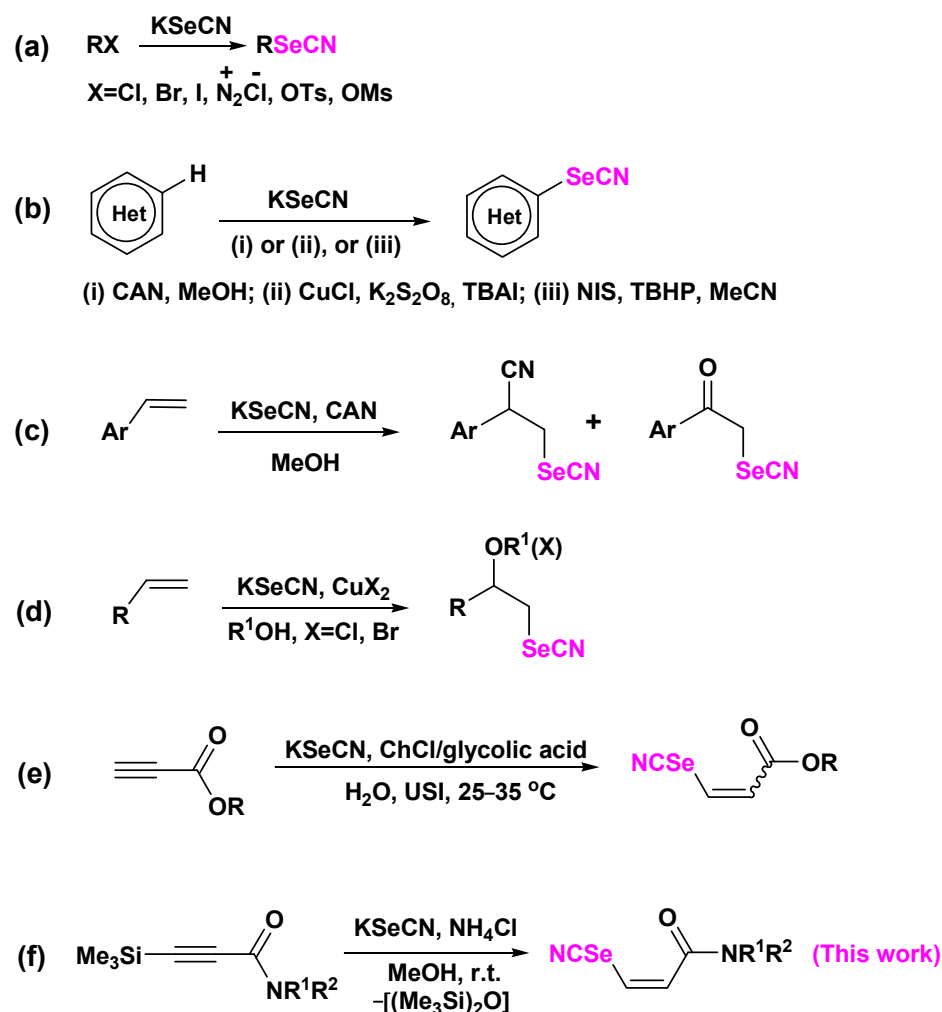

Figure 1. Examples of organic selenocyanates with biological activity.

5,7-Dibromo-N-(4′-selenocyanatobutyl)isatin (**B**, Figure 1) exhibits in vitro cytotoxicity against breast cancer cells and is superior in activity to its thiocyanate analogue [51]. Selenocoxib-1 (**C**, Figure 1) inhibits the development prostate cancer cells [52]. Benzyl selenocyanate (**D**, Figure 1) shows antimicrobial and nematocidal activities almost one-hundred times higher than that of the reference drug oxacillin; its analogs **E** and **F** (Figure 1) exhibit high nematicidal activity [53]. Compound **G** (Figure 1) shows high antimicrobial and antifungal activities [54].

The preparation of organyl selenocyanates is most often carried out by the reaction of potassium selenocyanate with organyl halides [28–32,39,42–44,46,50–56], diazonium salt [40,41], O-methanesulfonates [45], toluenesulfonates (or tosylate) [57,58] (Scheme 1a).

(a)　RX $\xrightarrow{\text{KSeCN}}$ R**SeCN**

　　X=Cl, Br, I, N₂⁺Cl⁻, OTs, OMs

(b)　
KSeCN, (i) or (ii), or (iii)

(i) CAN, MeOH; (ii) CuCl, K₂S₂O₈, TBAI; (iii) NIS, TBHP, MeCN

(c)　Ar $\xrightarrow[\text{MeOH}]{\text{KSeCN, CAN}}$

(d)　R $\xrightarrow[\text{R}^1\text{OH, X=Cl, Br}]{\text{KSeCN, CuX}_2}$

(e)　$\xrightarrow[\text{H}_2\text{O, USI, 25–35 °C}]{\text{KSeCN, ChCl/glycolic acid}}$

(f)　Me₃Si $\xrightarrow[\substack{\text{MeOH, r.t.} \\ -[(Me_3Si)_2O]}]{\text{KSeCN, NH}_4\text{Cl}}$ **(This work)**

Scheme 1. The known syntheses of organic selenocyanates [28–32,39,42–44,46,50–64] compared to the synthetic method of this work.

Direct selenocyanation into the aromatic ring of arenes and heteroarenes is known to be initiated by CAN (cerium (IV) ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$) [59], CuCl–$K_2S_2O_8$–TBAI [60], tert-butyl hydroperoxide (TBHP)–NIS [61], affording the corresponding aromatic and heteroaromatic selenocyanates (Scheme 1a) [26]. However, methods for the preparation of organylselenocyanates based on the addition of inorganic selenocyanates to multiple bonds of olefins and acetylenes can rarely be found in the literature. The development of such a direction would expand the synthetic potential of the selenocyanate reagents and open up new ways to obtain novel organoselenium compounds, including poorly studied vinyl selenocyanates [43,62–65].

One of the few known examples is the addition of potassium selenocyanate at the double bond of substituted styrenes (Scheme 1c) initiated by transition metal salts (CAN or $CuCl_2$, $CuBr_2$) giving saturated bis(selenocyanates) or oxo selenocyanates in the presence of oxygen [59], as well as the addition of selenocyanate to olefins (Scheme 1d) to obtain saturated alkoxy selenocyanates in alcohols or halogen selenocyanates in acetonitrile [63].

The method of the catalytic addition of potassium selenocyanate to organyl propiolates giving the mixture of corresponding (Z)- and (E)-vinyl selenocyanates was recently developed (Scheme 1e) [64]. The reaction was catalyzed by a deep eutectic solvent (DES) choline chloride/glycolic acid under the action of ultrasound at 25–35 °C. (Scheme 1d).

We developed an efficient approach to a novel family of (Z)-3-amino-3-oxo-1-propenyl selenocyanates based on the reaction of potassium selenocyanate with 3-trimethylsilyl-2-propynamides in the presence of ammonium chloride in methanol (Scheme 1f). This

approach is superior to the known methods regarding efficiency and selectivity, high yields, mild reaction conditions (room temperature), the use of cheap and available reagent such as ammonium chloride, and green solvent such as methanol.

An alternative approach is to use terminal propynamides; however, as terminal propynamides are known to be difficult to obtain, methods for their preparation are limited. 3-Trimethylsilylpropynamides can be easily obtained from 3-trimethylsilylpropiolic acid by the methods developed in this institute [66].

2. Results and Discussion

The aim of our research is to develop an efficient and selective approach to novel vinyl selenocyanates, containing the amide function at the double bond, based on 3-trimethylsilyl-2-propynamides and potassium selenocyanate. It should be emphasized that to date, not a single representative of 3-amino-3-oxo-1-propenylselenocyanates has been described in the literature.

The reaction of N-phenyl-3-trimethylsilyl-2-propynamide **1a** with potassium selenocyanate was studied in order to find favorable conditions for the synthesis of vinyl selenocyanates.

The reaction of propynamide **1a** with excess potassium selenocyanate (3.5 eq) at room temperature in methanol for 23 h was accompanied by gumming. The isolated mixture contained the product **3** (87 mol%) of the methanol addition to the triple bond of propynamide [67] and diadduct **4** (13 mol%) [68], resulted from the addition of methanol to the double bond of the product **3** (Table 1, entry 1). The expected selenocyanate **2a** was not detected (^{1}H-NMR data). Refluxing propynamide **1a** with 1.0 equivalent of potassium selenocyanate in methanol for 3 h also resulted in strong gumming and only methanol addition with the formation of a mixture of mono-adduct **3** (35 mol%) and diadduct **4** (65 mol%) was observed (Table 1, entry 2).

Table 1. The use of NH$_4$Cl in the reaction of 3-trimethylsilyl-2-propynamide **1a** with KSeCN.
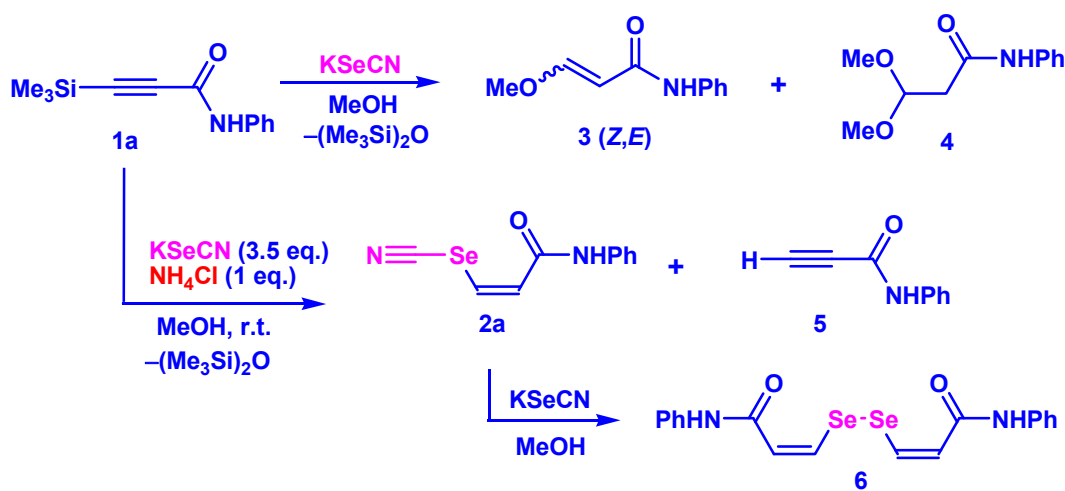
| Entry | KSeCN [a] (Equiv) | MeOH (mL) | Conditions [b] | NH$_4$Cl (Equiv) | Time (h) | Content (mol %) | | | | | Yield, 2a (%) |
						2a	3	4	5	6	
1	3.5	0.6	r.t. [b]	–	23	–	87	13	–	–	–
2	1.0	3.0	reflux [b]	–	3	–	35	65	–	–	–
3	3.5	0.6	r.t. [b]	1.0	23	63	–	–	31	6	65
4	3.5	0.6	r.t. [b]	1.0	68	38	–	–	–	62	36

[a] Potassium selenocyanate was prepared from elemental selenium and potassium cyanide in methanol at room temperature. [b] The reaction was accompanied by the formation of tars.

We found that the reaction of propynamide with potassium selenocyanate proceeded efficiently in the presence of ammonium chloride. Thus, the reaction of propynamide **1a** with excess potassium selenocyanate (3.5 eq) in the presence of ammonium chloride (1 eq) at room temperature for 23 h gave Z-3-anilino-3-oxo-1-propenyl selenocyanate **2a** in 65% yield. Along with selenocyanate **2a** and unreacted terminal amide **5** (31 mol%), the mixture contained diselenide **6** (6 mol%, Table 1, entry 3). Under these conditions, the reaction was completed for 68 h, giving the target product **2a** in 36% yield along with diselenide **6** (62 mol%) (Table 1, entry 4).

Previously, we obtained amide-containing divinyl diselenide **6** and their analogues by the reaction of N-substituted 3-trimethylsilyl-2-propynamides with sodium diselenide in aqueous THF [69]. In this case, the formation of diselenide **6** in the reaction mixture is obviously due to the cleavage of the Se–CN bond of organyl selenocyanate **2a** under the action of an excess potassium selenocyanate. It should be emphasized that the addition of methanol to the triple bond in the presence of ammonium chloride was not observed.

When amide **1a** was refluxed with potassium selenocyanate (1:1) and ammonium chloride in methanol for 5 h, the precipitation of elemental selenium was observed and the yield of organyl selenocyanate **2a** was only 51% (Table 2, entry 1). With a 1.5-fold excess of potassium selenocyanate in the presence of ammonium chloride, selenocyanate **2a** in 60% yield was formed in 5 h along with propynamide **5** (23 mol%) and diselenide **6** (10 mol%) (Table 2, entry 2). With an increase in the heating duration to 10 h, the content of selenocyanate **2a** increased from 67% (5 h) to only 72% (10 h) and the yield of compound **2a** increased to 62% (Table 2, entries 2,3). Only an increase in the content of potassium selenocyanate to 4.5 equivalents made it possible to complete the reaction for 3 h and to obtain selenocyanate **2a** in 73% yields (Table 2, entry 4).

Table 2. Influence of the KSeCN content on the product yield in presence of NH_4Cl at reflux.

Entry	KSeCN [a] (eq)	Time (h) [b]	Content (mol %)			Yield of 2a [c] (%)
			2a	5	6	
1	1.0	5	60	36	4	51
2	1.5	5	67	23	10	60
3	1.5	10	72	18	10	62
4	4.5	3	86	–	14	73

[a] Potassium selenocyanate was prepared by stirring elemental selenium with potassium cyanide in methanol at room temperature. [b] 3-(Trimethylsilyl)-2-propynamide (0.47 mmol) and NH_4Cl (126 mg, 2.35 equiv.) were added to methanol solution (3.0 mL) of potassium selenocyanate (0.47–2.12 mmol). The mixture was refluxed with stirring. [c] The yield was determined based on the ^1H NMR data.

At room temperature, in the presence of excess ammonium chloride, the reaction of *N*-phenyl-3-trimethylsilyl-2-propynamide **1a** with selenocyanate proceeded more slowly (19–29 h) (Table 3) compared to heating (3–5 h) (Table 2). However, when multiple excesses of ammonium chloride were used without heating, side diselenide **6** was not formed (^1H-NMR) and resinification of the reaction mixture and precipitation of selenium were not observed. According to ^1H-NMR and elemental analysis, the resulting target organylselenocyanate **2a** was of high purity and did not require additional purification (Table 3).

Table 3. Optimization of the conditions of the reaction of 3-trimethylsilyl-2-propynamide **1a** with KSeCN [a] in presence of NH$_4$Cl at room temperature: [b].

| Entry	Time (h)	NH$_4$Cl (Equiv)	MeOH (mL)	Conc. 1a (mmol/L)	Conversion 2a (%)	Yield 2a (%)
1	23	5	0.6	0.78	77	69 [c]
2	23	10	0.6	0.78	83	78 [c]
3	23	20	0.6	0.78	90	82 [c]
4	23	30	0.6	0.78	92	82 [c]
5	29	20	0.6	0.78	100	90 [d]
6	**19**	**5**	**0.4**	**1.18**	**100**	**91 [d]**
7	19	10	0.4	1.18	100	90 [d]
8	19	3	0.4	1.18	89	–

[a] Potassium selenocyanate was prepared by stirring elemental selenium (130 mg, 1.65 mmol) with potassium cyanide (115 mg, 1.77 mmol) in 0.4 mL of methanol at room temperature for 1.5 h. [b] NH$_4$Cl (126–756 mg, 2.35–14.10 mmol) and 3-(trimethylsilyl)-2-propynamide **1a** (102 mg, 0.47 mmol) were added to a methanol solution of potassium selenocyanate (1.65 mmol) and the reaction mixture was stirred at room temperature. [c] The yield was determined from the ^{1}H NMR data. [d] Isolated yield.

In search of the optimal conditions of the method, we studied the effect of the amount of ammonium chloride taken into the reaction, as well as the volume of the solvent, on the efficiency of the reaction. With an increase in the amount of ammonium chloride in the series, 5, 10, and 20 equivalents in a solvent volume of 0.6 mL, which corresponds to an initial amide concentration of 0.78 mmol/L for 23 h, the conversion of the target product **2a** increases in the sequence 77, 83, 90%, respectively, and the yield of **2a** by ^{1}H NMR also increases by 69, 78, 82% (Table 3, entries 1,2,3)

Further increase in the amount of NH$_4$Cl up to 30 equiv leads to a slight increase in the conversion of selenocyanate **1a** from 90% (at 20 equiv.) to 92% (30 equiv.), while the NMR yield of **2a** did not change—having a value of 82% (Table 3, entries 3,4). The increase in the duration of the process up to 29 h at a concentration of the original **1a** 0.78 mol/L in the presence of NH$_4$Cl (20 equiv) resulted in complete conversion and high isolated yield (90%) of organyl selenocyanate **2a** (Table 3, entry 5).

A decrease in the volume of the solvent also leads to an increase in the efficiency of the reaction. The best result was achieved using 0.4 mL of methanol (amide concentration 1.18 mmol/L); the reaction was completed within 19 h in the presence of 5–10 equivalents of ammonium chloride-affording Z-3-anilino-2-oxo-1-propenyl selenocyanate **2a** in 90% yield (Table 3, example 6,7). When the amount of ammonium chloride was reduced to 3 equivalents, the conversion dropped to 89% at a 19 h reaction time (Table 3, entry 8). Thus, the optimal reaction conditions found include the following: 3-trimethylsilyl-2-propynamide **1a** (0.47 mmol), selenocyanate (3.5 equiv), ammonium chloride (5 equiv), methanol (0.4 mL), and stirring for 19 h at room temperature. The use of 0.4 mL of methanol (Table 3, entry 6,7) instead of 0.6 mL (Table 3, entry 1–5) decreases the reaction time and reduces the required amount of ammonium chloride to 5 equiv.

Using these optimal conditions for the preparation of **2a**, we synthesized a number of novel N-substituted (Z)-3-amino-3-oxo-1-propenyl selenocyanates **2b–l** in 64–95% yields based on 3-trimethylsilyl-2-propynamides **1a–l** including primary amide **1b**, aromatic secondary amides **1c–m**, and tertiary amides **1n,l** (Scheme 2).
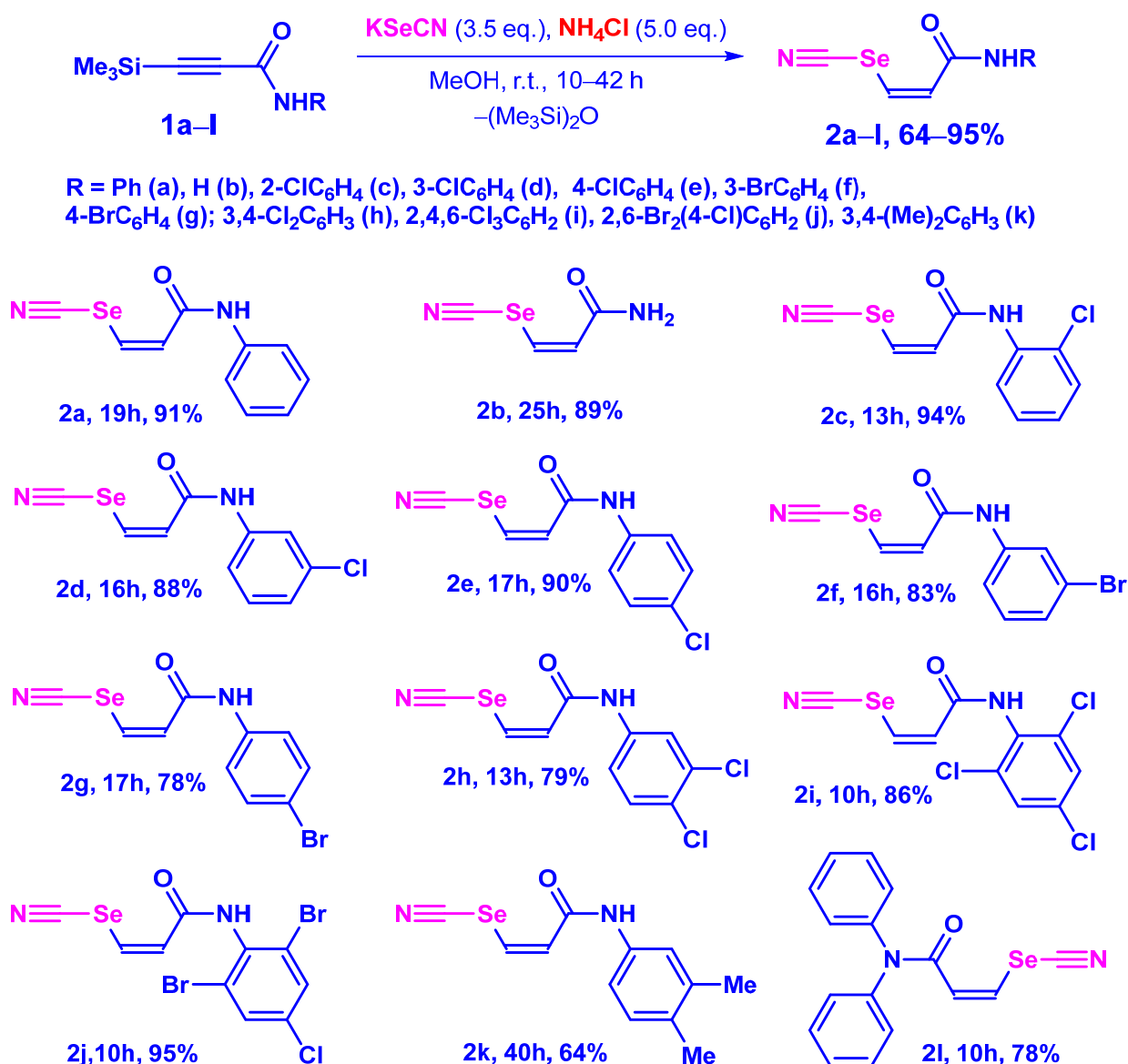
Scheme 2. Synthesis of selenocyanates **2a–l** by the reaction of 3-trimethylsilyl-2-propynamide **1a–l** with KSeCN in the presence of NH$_4$Cl.

In the course of the study, the influence of the nature of the *N*-substituent of the amide group of the starting acetylenic amides **1a–l** on their reactivity in the nucleophilic addition of selenocyanate at the triple bond was found. Obviously, the different reactivity in the series of acetylenic amides **1a–l** depends on the magnitude of the electron-withdrawing effect of the amide group, which polarizes the triple bond to a different degree, depending on the donor–acceptor properties of the *N*-substituent [70].

Thus, if the addition of selenocyanate to *N*-phenylacetylenic amide **1a** took 19 h, then in the case of amides with more electron-withdrawing amide groups 3- and 4-mono-halophenylamides **1d–g**, the reaction was completed in 16–17 h, and 2-chloroanilide **1c** and 3,4-dichlorophenylamide **1h** reacted for 13 h. The addition of selenocyanate to propy-namides containing strongly electron-withdrawing *N*-substituents 2,4,6-trihalophenylamides **1i,j** and diphenylamide **1l** was completed in 10 h. Electron-donating substituents (two methyl groups) in the benzene ring of the amide **1k** decrease the reactivity of the triple bond.

Thus, the reactivity of the starting propynamides **1a–l** with substituents NR$_1$R$_2$ increases approximately in the following order: 3,4-(Me)$_2$C$_6$H$_3$NH (**1k**) < NH$_2$ (**1b**) < PhNH (**1a**) < 4-ClC$_6$H$_4$NH (**1e**)~4-BrC$_6$H$_4$NH (**1g**) < 3-ClC$_6$H$_4$NH (**1d**)~3-BrC$_6$H$_4$NH (**1f**)

< 2-ClC$_6$H$_4$NH (**1c**)~3,4-Cl$_2$C$_6$H$_3$NH (**1h**) < 2,4,6-Cl$_3$C$_6$H$_2$NH (**1i**)~2,6-Br$_2$(4-Cl)C$_6$H$_2$NH (**1j**)~NPh$_2$ (**1l**).

The method of the catalytic addition of KSeCN to the triple bond of activated terminal acetylenes, propiolates, propynthioates, methylpropynones, and 1-(ethynylsulfonyl)-4-methylbenzene proceeding with the formation of the mixture of corresponding Z- and E-vinyl selenocyanates was reported [64]. The reaction was catalyzed by a deep eutectic solvent: choline chloride/glycolic acid under the action of ultrasound. The supposed mechanism includes the activation of the triple bond by intermolecular H-bonding of the carbonyl group [64]. Taking into account that ammonium chloride can be the source of protons, a similar mechanism of activation of the triple bond by the bonding of the carbonyl group can be assumed in this case (Scheme 3).
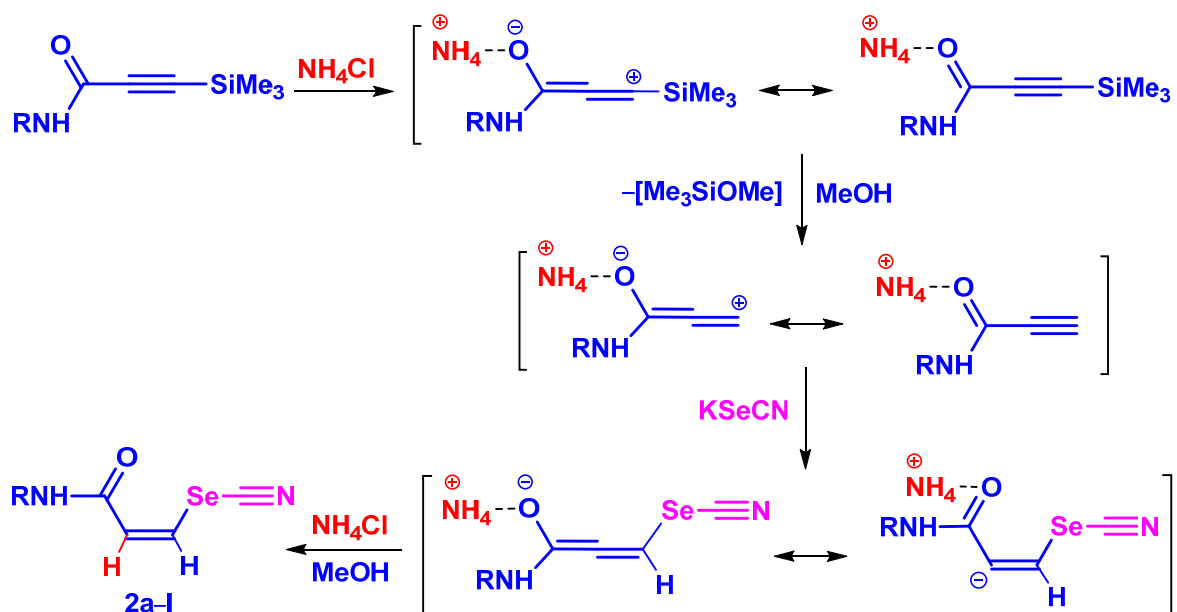
**Scheme 3.** A plausible mechanism of the formation of the products **2a–l**.

Besides the activation of the triple bond, ammonium chloride played a role of a proton donor to intermediate carbanion. Certain weak acidity of the reaction media is very important, which should be suitable for the addition of selenocyanate anion to the triple bond as well as for the protonation of intermediate carbanion, stabilized by the carbonyl group (Scheme 3).

It is worth noting that the reaction proceeded in a regio- and stereoselective fashion as anti-addition-affording vinyl selenocyanates only with a (Z)-configuration in high yields.

Most of the obtained compounds do not contain impurities of by-products (elemental analysis and NMR data) and do not require additional purification after removing the solvent.

Starting 3-trimethylsilyl-2-propynamides **1a—l** were prepared from 3-trimethylsilyl-propiolic acid and amines by the methods which were previously developed in this institute [66,70]. Trimethylsilyl-2-propynamides **1c** and **1i—k** are new compounds and were prepared for the first time (Scheme 4).

The structural assignment of the obtained compounds was carried out based on the multinuclear NMR investigations and confirmed by FTIR data and elemental analysis.
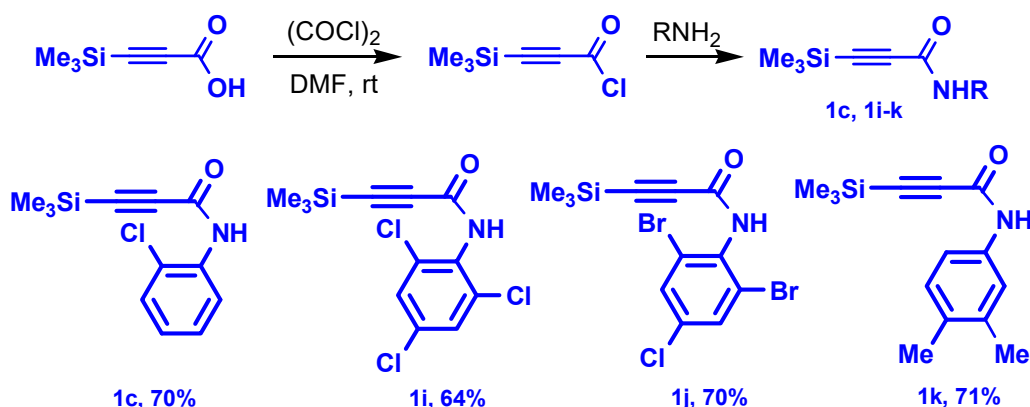
Scheme 4. Synthesis of trimethylsilyl-2-propynamides **1c** and **1i**−**k**.

3. Materials and Methods

3.1. General Information

The ^{1}H (400.1 MHz), ^{13}C (100.6 MHz), ^{77}Se (76.3 MHz), ^{29}Si (79.5 MHz) and ^{15}N (40.6 MHz) NMR spectra (the spectra can be found in Supplementary Materials) were recorded on a Bruker DPX-400 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) in CDCl$_3$ or DMSO-d_6 solutions and referred to the residual solvent peaks (CDCl$_3$, δ = 7.27 and 77.1 ppm; DMSO-d_6, δ = 2.50 and 39.6 ppm for ^{1}H- and ^{13}C-NMR, respectively), tetramethylsilane (^{29}Si), nitromethane (^{15}N) and dimethyl selenide (^{77}Se).

FTIR spectra were taken on an Bruker Vertex-70 spectrometer. Elemental analysis was performed on a Thermo Scientific Flash 2000 Elemental Analyzer (Thermo Fisher Scientific Inc., Milan, Italy). Melting points were determined on a Kofler Hot-Stage Microscope PolyTherm A apparatus (Wagner & Munz GmbH, München, Germany). The distilled organic solvents and degassed water were used in syntheses.

Compounds **1i** and **1j** contain two amide rotamers [71] (the signals of the minor rotamer are given with an asterisk).

3.2. Synthesis of New 3-Trimethylsilyl-2-Propynamides

N-(2-Chlorophenyl)-3-(trimethylsilyl)prop-2-ynamide (**1c**). Compound **1c** was prepared by the method in [66]. Yield: 70%; white powder; mp 81–82 °C (hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.29 (s, 9H, Me$_3$Si), 7.08 (dd, ^3J = 8.3, 7.8 Hz, 1H, H^4), 7.28 (dd, ^3J = 8.3, 7.9 Hz, 1H, H^5), 7.39 (d, ^3J = 7.8 Hz, 1H, H^2), 7.90 (br.s, 1H, NH), 8.33 (d, ^3J = 7.9 Hz, 1H, H^6). ^{13}C NMR (100 MHz, CDCl$_3$): δ −0.9 (Si−C), 93.2 (SiC≡), 97.4 (≡CCO), 122.0 (C^6), 122.5 (C^2), 125.2 (C^4), 127.5 (C^5), 128.9 (C^3), 133.8 (C^1), 149.9 (C=O). ^{15}N NMR (40 MHz, CDCl$_3$): δ −249.5 ($^1J_{\text{N−H}}$ = 92.3 Hz). ^{29}Si NMR (79 MHz, CDCl$_3$): δ −14.7. IR (KBr): 3251, 3219, 3162, 3108, 3033, 2962, 2899, 2169 (C≡C), 1643 (C=O), 1588, 1527, 1472, 1441, 1297, 1248, 1218, 1132, 1035, 976, 870, 846, 756, 739, 704, 682, 628, 610, 506 cm^{-1}. C$_{12}$H$_{14}$ClNOSi (251.78): calcd. C 57.24, H 5.60, Cl 14.08, N 5.56, Si 11.15; found: C 57.16, H 5.72, Cl 14.03, N 5.29, Si 10.98.

N-(2,4,6-Trichlorophenyl)-3-(trimethylsilyl)prop-2-ynamide (**1i**). Compound **1i** was prepared by the method in [70]. Yield: 64%; grey powder; mp 146–148 °C (hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.07*, 0.29 (s, 9H, Me$_3$Si), 6.96*, 7.19 (br.s, 1H, NH), 7.41, 7.43* (s, 2H, =CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ −1.2*, −0.8 (Si−C), 94.1, 94.6* (SiC≡), 96.6, 98.9 (≡CCO), 128.2, 128.5* (C^{3,5}), 129.6, 131.0* (C^4), 133.7 (C^1), 134.2, 136.2* (C^{2,6}), 150.5, 155.0* (C=O). ^{15}N NMR (40 MHz, CDCl$_3$): δ −255.7 ($^1J_{\text{N−H}}$ = 93.5 Hz). ^{29}Si NMR (79 MHz, CDCl$_3$): δ −14.7. IR (KBr): 3189, 3154, 3056, 2984, 2964, 2900, 2166 (C≡C), 1670 (C=O), 1653 (C=O), 1573, 1563, 1512, 1448, 1384, 1370, 1280, 1247, 1224, 1190, 1143, 1078, 981, 885, 851, 821, 762, 719, 704, 677, 549 cm^{-1}. C$_{12}$H$_{12}$Cl$_3$NOSi (320.67): calcd. C 44.95, H 3.77, Cl 33.17, N 4.37, Si 8.76; found: C 45.00, H 3.68, Cl 33.09, N 4.50, Si 8.74.

N-(2,6-Dibromo-4-chlorophenyl)-3-(trimethylsilyl)prop-2-ynamide (**1j**). Compound **1j** was prepared by the method in [70]. Yield: 70%; grey powder; mp 156–158 °C (hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.06*, 0.29 (s, 9H, Me$_3$Si), 7.08*, 7.22 (br.s, 1H, NH), 7.61, 7.67* (s,

2H, =CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ –1.3, –0.7 (Si–C), 93.9, 94.8* (SiC≡), 96.7, 98.9* (≡$\underline{C}$CO), 123.8, 125.9* (C^{2,6}), 131.0*, 131.7 (C^{3,5}), 132.4, 133.7* (C^4), 134.2, 135.0* (C^1), 150.3, 154.9* (C=O). ^{15}N NMR (40 MHz, CDCl$_3$): δ –247.9 ($^1J_{\text{N–H}}$ = 95.1 Hz). ^{29}Si NMR (79 MHz, CDCl$_3$): δ –14.8. IR (KBr): 3186, 3140, 3053, 2957, 2927, 2902, 2831, 2784, 2167 (C≡C), 1642 (C=O), 1571, 1571, 1551, 1510, 1444, 1373, 1359, 1280, 1251, 1228, 1134, 1114, 1068, 975, 882, 848, 786, 761, 744, 701, 679, 623 cm^{-1}. C$_{12}$H$_{12}$Br$_2$ClNOSi (409.58): calcd. C 35.19, H 2.95, Br 39.02, Cl 8.66, N 3.42, Si 6.86; found: C 35.25, H 2.93, Br 39.16, Cl 8.87, N 3.25, Si 6.57.

(Z)-N-(3,4-Dimethylphenyl)-3-(trimethylsilyl)prop-2-ynamide (**1k**). Compound **1k** was prepared by the method in [66]. Yield: 71%; beige powder; mp 136–137 °C (hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.20 (s, 9H, Me$_3$Si), 2.17 (s, 3H, Me^4), 2.19 (s, 3H, Me^3), 7.01 (d, ^3J = 7.8 Hz, 1H, H^5), 7.26 (d, ^3J = 7.8 Hz, 1H, H^6), 7.29 (s, 1H, H^2), 8.11 (br.s, 1H, NH). ^{13}C NMR (100 MHz, CDCl$_3$): δ –0.8 (Si–C), 19.1 (Me^4), 19.7 (Me^3), 92.1 (SiC≡), 98.1 (≡$\underline{C}$CO), 117.7 (C^6), 121.4 (C^2), 129.9 (C^5), 133.1 (C^4), 135.0 (C^3), 137.1 (C^1), 150 (C=O). IR (KBr): 3271, 3185, 3060, 3022, 2960, 2921, 2901, 2860, 2168 (C≡C), 1641 (C=O), 1616, 1598, 1537, 1503, 1448, 1400, 1312, 1253, 1239, 1162, 1119, 1019, 980, 927, 847, 819, 762, 716, 626, 570 cm^{-1}. C$_{14}$H$_{19}$NOSi (245.39): calcd. C 68.52, H 7.80, N 5.71, Si 11.45; found: C 68.63, H 7.76, N 5.93, Si 11.28.

3.3. Synthesis of (Z)-3-Amino-3-Oxo-1-Propenyl Selenocyanates 2a–l

General Procedure. A mixture of metallic selenium (130 mg, 1.65 mmol) and KCN (115 mg, 1.77 mmol) in MeOH (0.4 mL) was stirred for 1.5 h at room temperature. NH$_4$Cl (126 mg, 2.35 mmol) and 3-(trimethylsilyl)-2-propynamide **1a–l** (0.47 mmol) were added to the prepared methanol solution of potassium selenocyanate (1.65 mmol). The reaction mixture was stirred for 10–42 h at room temperature and target selenocyanates (**2a–l**) were isolated according to the procedures described below.

(Z)-3-Anilino-3-oxo-1-propenyl selenocyanate (**2a**). Reaction mixture was stirred for 19 h at room temperature and was treated with water (8.0 mL) and CH$_2$Cl$_2$ (5.0 mL). The aqueous layer was extracted (3 × 5 mL) with CH$_2$Cl$_2$ and the extract was dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure. After removal of the solvent, the product did not require further purification. Yield: 107 mg (91%); beige powder; mp 164–166 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.95 (d, ^3J = 7.9 Hz, 1H, =CHCO), 7.13 (t, ^3J = 7.8 Hz, 1H, H^4), 7.36 (dd, ^3J = 7.8 Hz, 2H, H^{3,5}), 7.60 (d, ^3J = 7.8 Hz, 2H, H^{2,6}), 8.07 (d, ^3J = 7.9 Hz, 1H, SeCH=), 10.77 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 108.2 (C≡N, $^1J_{\text{Se–C}}$ = 227.4 Hz), 119.6 (C^{2,6}), 122.2 (=$\underline{C}$CO), 124.5 (C^4), 129.1 (C^{3,5}), 137.5 (SeC=, $^1J_{\text{Se–C}}$ = 109.3 Hz, $^1J_{\text{C–H}}$ = 190.0 Hz), 137.9 (C^1), 166.2 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 408.5. ^{15}N NMR (40 MHz, DMSO-d_6): δ –243.8 (NH, $^1J_{\text{N–H}}$ = 91.0 Hz). IR (KBr): 3305, 3249, 3204, 3145, 3062, 2161 (C≡N), 1645 (C=O), 1596, 1565, 1554, 1499, 1443, 1359, 1304, 1254, 1304, 1254, 1206, 1136, 1029, 976, 898, 806, 796, 754, 734, 687, 630, 508, 451 cm^{-1}. C$_{10}$H$_8$N$_2$OSe (251.14): calcd. C 47.82, H 3.21, N 11.15, Se 31.44; found: C 47.68, H 3.00, N 11.21, Se 31.27.

(Z)-3-Amino-3-oxo-1-propenyl selenocyanate (**2b**). The reaction mixture was stirred for 25 h at room temperature and the solvent was removed. Hot THF (3.0 mL) was added to the residue and the solution was filtered. Then, CH$_2$Cl$_2$ (5.0 mL) and degassed water (5.0 mL) were added. The aqueous layer was extracted (2 × 4 mL) with CH$_2$Cl$_2$ and the extract was dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure. After the removal of the solvent, the product did not require further purification. Yield: 75 mg (89%); yellow powder; mp 146–148 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.73 (d, ^3J = 7.8 Hz, 1H, =CHCO), 7.83 (br s, 1H, NH), 7.88 (d, ^3J = 7.8 Hz, 1H, SeCH=), 8.11 (br s, 1H, NH). ^{13}C NMR (100 MHz, d_6-DMSO): δ 109.1 (C≡N, $^1J_{\text{Se–C}}$ = 226.3 Hz), 121.7 (=$\underline{C}$CO), 136.9 (SeC=, $^1J_{\text{Se–C}}$ = 106.5 Hz), 169.8 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 405.0. ^{15}N NMR (40 MHz, DMSO-d_6): δ –148.6 (C≡N), –268.6 (NH$_2$, $^1J_{\text{N–H}}$ = 88.5, 89.5 Hz). IR (KBr): 3388, 3341, 3282, 3184, 3081, 2156 (C≡N), 1672 (C=O), 1679 (C=O), 1568 (C=C), 1417, 1285, 1163, 918, 797, 743, 645, 591, 545, 479 cm^{-1}. C$_4$H$_4$N$_2$OSe (175.05): calcd. C 27.45, H 2.30, N 16.00, Se 45.11; found: C 27.59, H 2.48, N 15.89, Se 45.03.

(Z)-3-(2-Chlorophenyl)amino]-3-oxo-1-propenyl selenocyanate (**2c**). The reaction mixture was stirred for 13 h at room temperature and was treated with water (8.0 mL) and CH_2Cl_2 (5.0 mL). The aqueous layer was extracted (3 × 5 mL) with CH_2Cl_2 and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure. After the removal of the solvent, the product did not require further purification. Yield: 126 mg (94%); beige powder; mp 130–132 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.18 (d, ^3J = 8.0 Hz, 1H, =CHCO), 7.25 (dd, ^3J = 8.8, 7.9 Hz, 1H, H^5), 7.35 (dd, ^3J = 8.8, 7.8 Hz, 1H, H^4), 7.52 (d, ^3J = 7.8 Hz, 1H, H^3), 7.75 (d, ^3J = 7.9 Hz, 1H, H^6), 8.11 (d, ^3J = 8.0 Hz, 1H, SeCH=), 10.38 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 108.0 (C≡N, $^1J_{Se-C}$ = 227.2 Hz), 121.8 (=$\underline{C}$CO), 126.2 (C^6), 126.6 (C^2), 127.3 (C^5), 127.6 (C^4), 129.7 (C^3), 133.7 (C^1), 138.5 (SeC=, $^1J_{Se-C}$ = 110.0 Hz), 166.8 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 409.4. ^{15}N NMR (40 MHz, DMSO-d_6): −249.8 (NH, $^1J_{N-H}$ = 92.9 Hz). IR (KBr): 3332, 3073, 2921, 2852, 2155 (C≡N), 1642 (C=O), 1595, 1566, 1534, 1465, 1443, 1354, 1297, 1238, 1205, 1157, 1131, 1055, 1038, 984, 810, 792, 754, 745, 708, 698, 684, 626, 605, 492, 466, 439 cm^{-1}. $C_{10}H_7ClN_2OSe$ (285.59): calcd. C 42.06, H 2.47, Cl 12.41, N 9.81, Se 27.65; found: C 41.98, H 2.32, Cl 12.59, N 9.74, Se 27.63.

(Z)-3-(3-Chlorophenyl)amino]-3-oxo-1-propenyl selenocyanate (**2d**). The reaction mixture was stirred for 16 h at room temperature and H_2O (8 mL) was added. Precipitate was filtered off, washed with water and was dried. The product did not require further purification. Yield: 118 mg (88%); yellow powder; mp 124–126 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.92 (d, ^3J = 8.2 Hz, 1H, =CHCO), 7.18 (d, ^3J = 8.0 Hz, 1H, H^4), 7.36, 7.38 (dd, ^3J = 8.2 Hz, 8.0 Hz, 1H, H^5), 7.45 (d, ^3J = 8.2 Hz, 1H, H^6), 7.78 (s, 1H, H^2), 8.10 (d, ^3J = 8.2 Hz, 1H, SeC=), 10.94 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 108.1 (N≡C, $^1J_{Se-C}$ = 227.0 Hz), 118.1 (C^6), 119.1 (C^2), 122.0 (=$\underline{C}$CO), 124.3 (C^4), 130.9 (C^5), 133.5 (C^3), 138.6 (SeC=, $^1J_{Se-C}$ = 110.1 Hz), 139.4 (C^1), 166.5 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 411.1. ^{15}N NMR (40 MHz, DMSO-d_6): δ −244.0 (NH, $^1J_{N-H}$ = 90.5 Hz). IR (KBr): 3302, 3247, 3199, 3130, 3115, 3077, 2160 (C≡N), 1647 (C=O), 1612, 1594, 1546, 1478, 1427, 1352, 1302, 1271, 1256, 1203, 1144, 1078, 996, 979, 907, 864, 809, 775, 724, 694, 673, 605, 485, 452 cm^{-1}. $C_{10}H_7ClN_2OSe$ (285.59): calcd. C 42.06, H 2.47, Cl 12.41, N 9.81, Se 27.65; found: C 42.30, H 2.44, Cl 12.14, N 9.92, Se 27.59.

(Z)-3-[(4-Chlorophenyl)amino]-3-oxo-1-propenyl selenocyanate (**2e**). The reaction mixture was stirred for 17 h at room temperature and H_2O (8 mL) was added. Precipitate was filtered off, washed with water and was dried. The product did not require further purification. Yield: 120 mg (90%); light brown powder; mp 194–196 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.92 (d, ^3J = 7.9 Hz, 1H, =CHCO), 7.38 (d, ^3J = 8.8 Hz, 2H, H^{3,5}), 7.62 (d, ^3J = 8.8 Hz, 2H, H^{2,6}), 8.07 (d, ^3J = 7.9 Hz, 1H, SeCH=), 10.86 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 108.0 (N≡C, $^1J_{Se-C}$ = 225.6 Hz), 121.1 (C^{2,6}), 122.0 (=$\underline{C}$CO), 128.1 (C^4), 128.9 (C^{3,5}), 136.8 (C^1), 138.0 (SeC=, $^1J_{Se-C}$ = 110.6 Hz), 166.2 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 409.8. ^{15}N NMR (40 MHz, DMSO-d_6): δ −243.1 (NH, $^1J_{N-H}$ = 90.1 Hz). IR (KBr): 3314, 3248, 3205, 3134, 3083, 2153 (C≡N), 1649 (C=O), 1610, 1596, 1548, 1490, 1404, 1358, 1304, 1289, 1249, 1206, 1151, 1088, 1011, 981, 825, 809, 782, 707, 614, 504, 472, 416 cm^{-1}. $C_{10}H_7ClN_2OSe$ (285.59): calcd. C 42.06, H 2.47, Cl 12.41, N 9.81, Se 27.65; found: C 41.91, H 2.25, Cl 12.62, N 9.83, Se 27.87.

(Z)-3-[(3-Bromophenyl)amino]-3-oxo-1-propenyl selenocyanate (**2f**). The reaction mixture was stirred for 16 h at room temperature and H_2O (8 mL) and CH_2Cl_2 (5.0 mL) were added. The aqueous layer was extracted (3 × 5 mL) with CH_2Cl_2 and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure. After the removal of the solvent, the residue was dissolved in CH_2Cl_2 and precipitated by cold hexane. Yield: 129 mg (83%); beige powder; mp 150–152 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.92 (d, ^3J = 8.1 Hz, 1H, =CHCO), 7.33 (d, ^3J = 5.2 Hz, 2H, H^{4,6}), 7.45–7.61 (m, 1H, H^5), 7.94 (s, 1H, H^2), 8.12 (d, ^3J = 8.1 Hz, 1H, SeCH=), 10.91 (br s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 108.0 (N≡C, $^1J_{Se-C}$ = 227.2 Hz), 118.4 (C^5), 121.8 (C^3), 121.9 (C^2), 122.0 (=$\underline{C}$CO), 127.1 (C^6), 131.0 (C^4), 138.4 (SeC=, $^1J_{Se-C}$ = 110.3 Hz), 139.5 (C^1), 166.4 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 411.2. ^{15}N NMR (40 MHz, DMSO-d_6): δ −244.8 (NH, $^1J_{N-H}$ = 90.0 Hz). IR (KBr): 3304, 3242, 3193, 3123, 3067, 2160 (C≡N), 1647 (C=O), 1606, 1591, 1536, 1474, 1423,

1351, 1300, 1272, 1249, 1207, 1143, 1070, 994, 981, 879, 807, 785, 772, 721, 672, 630, 607, 454 cm^{-1}. $C_{10}H_7BrN_2OSe$ (330.04): calcd. C 36.39, H 2.14, Br 24.21, N 8.49, Se 23.92; found: C 36.54, H 2.30, Br 23.97, N 8.52, Se 23.72.

(Z)-3-[(4-Bromophenyl)amino]-3-oxo-1-propenyl selenocyanate (**2g**). The reaction mixture was stirred for 17 h at room temperature and H_2O (8 mL) and CH_2Cl_2 (5.0 mL) were added. The aqueous layer was extracted (3 × 4 mL) with CH_2Cl_2 and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure. The product did not require further purification. Yield: 121 mg (78%); beige powder; mp 153–155 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.93 (d, ^3J = 8.0 Hz, 1H, =CHCO), 7.53 (d, ^3J = 9.0 Hz, 2H, H^{3,5}), 7.57 (d, ^3J = 9.0 Hz, 2H, H^{2,6}), 8.10 (d, ^3J = 8.0 Hz, 1H, SeCH=), 10.87 (br s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 108.0 (N≡C, $^1J_{Se–C}$ = 226.0 Hz), 116.2 (C^4), 121.5 (C^{2,6}), 122.0 (=$\underline{C}$CO), 131.9 (C^{3,5}), 137.2 (C^1), 138.1 (SeC=, $^1J_{Se–C}$ = 109.9 Hz) 166.2 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 410.1. ^{15}N NMR (40 MHz, DMSO-d_6): δ –242.8 (NH, $^1J_{N–H}$ = 90.4 Hz). IR (KBr): 3309, 3246, 3204, 3130, 3073, 2154 (C≡N), 1649 (C=O), 1610, 1589, 1548, 1487, 1397, 1356, 1302, 1288, 1247, 1205, 1146, 1071, 1006, 981, 823, 807, 783, 719, 613, 501, 464 cm^{-1}. $C_{10}H_7BrN_2OSe$ (330.04): calcd. C 36.39, H 2.14, Br 24.21, N 8.49, Se 23.92; found: C 36.50, H 2.21, Br 24.17, N 8.60, Se 23.76.

(Z)-3-[(3,4-Dichlorophenyl)amino]-3-oxo-1-propenyl selenocyanate (**2h**). The reaction mixture was stirred for 13 h at room temperature and H_2O (8 mL) was added. Precipitate was filtered off, washed with water and was dried. The product did not require further purification. Yield: 118 mg (79%); beige powder; mp 145–147 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 6.91 (d, ^3J = 8.0 Hz, 1H, =CHCO), 7.50 (dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, 1H, H^6), 7.61 (d, ^3J = 8.8 Hz, H^5), 7.95 (d, ^4J = 2.4 Hz, 1H, H^2), 8.14 (d, ^3J = 8.0 Hz, 1H, SeCH=), 11.02 (s, 1H, NH). ^{13}C NMR (100 MHz, d_6-DMSO) δ 107.8 (N≡C, $^1J_{Se–C}$ = 224.7 Hz), 119.6 (C^6), 120.8 (C^2), 121.8 (=$\underline{C}$CO), 126.1 (C^3), 130.9 (C^5), 131.4 (C^4), 138.0 (C^1), 138.7 (SeC=, $^1J_{Se–C}$ = 111.2 Hz, $^1J_{C–C}$ = 92.7 Hz), 166.4 (C=O). ^{77}Se NMR (76 MHz, d_6-DMSO): δ 412.3. ^{15}N NMR (40 MHz, d_6-DMSO): δ –245.5. IR (KBr): 3296, 3243, 3187, 3109, 3072, 2157 (C≡N), 1647 (C=O), 1607, 1590, 1535, 1473, 1449, 1395, 1348, 1293, 1237, 1206, 1143, 1130, 1026, 983, 866, 810, 784, 706, 675, 675, 617, 576, 527, 480, 435, 403 cm^{-1}. $C_{10}H_6Cl_2N_2OSe$ (320.03): calcd. C 37.53, H 1.89, Cl 22.16, N 8.75, Se 24.67; found: C 37.30, H 1.91, Cl 22.17, N 8.57, Se 24.70.

(Z)-3-[(2,4,6-Trichlorophenyl)amino]-3-oxo-1-propenyl selenocyanate (**2i**). The reaction mixture was stirred for 10 h at room temperature and H_2O (8 mL) was added. Precipitate was filtered off, washed with water and was dried. The product did not require further purification. Yield: 143 mg 86%; beige powder; mp 193–195 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.03 (d, ^3J = 8.3 Hz, 1H, =CHCO), 7.78 (s, 2H, H^{3,5}), 8.14 (d, ^3J = 8.3 Hz, 1H, SeCH=), 10.77 (br s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 107.6 (N≡C, $^1J_{Se–C}$ = 227.2 Hz), 120.6 (=CHCO), 128.5 (C^{3,5}), 131.0 (C^4), 133.1 (C^1), 134.0 (C^{2,6}), 139.4 (SeC=, $^1J_{Se–C}$ = 110.6 Hz), 166.6 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 410.8. ^{15}N NMR (40 MHz, DMSO-d_6): δ –255.3 (NH, $^1J_{N–H}$ = 92.9 Hz). IR (KBr): 3223, 3202, 3158, 3126, 3066, 3011, 2165 (C≡N), 1643 (C=O), 1569, 1519, 1446, 1379, 1348, 1266, 1246, 1216, 1187, 1139, 1075, 990, 876, 853, 825, 792, 682, 641, 616, 570, 553, 522, 478, 411 cm^{-1}. $C_{10}H_5Cl_3N_2OSe$ (354.48): calcd. C 33.88, H 1.42, Cl 30.00, N 7.90, Se 22.28; found: C 34.01, H 1.56, Cl 29.85, N 7.98, Se 22.42.

(Z)-3-[(2,6-Dibromo-4-chlorophenyl)amino]-3-oxo-1-propenyl selenocyanate (**2j**). The reaction mixture was stirred for 10 h at room temperature and H_2O (8 mL) was added. Precipitate was filtered off, washed with water and dried in vacuum. The product did not require further purification. Yield: 199 mg (95%); beige powder; mp 185–187 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.03 (d, ^3J = 7.9 Hz, 1H, =CHCO), 7.91 (s, 2H, H^{3,5}), 8.12 (d, ^3J = 7.9 Hz, 1H, SeCH=), 10.75 (br s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 107.8 (N≡C, $^1J_{Se–C}$ = 228.7 Hz), 120.7 (=CHCO), 124.2 (C^{2,6}), 131.8 (C^{3,5}), 133.7 (C^1, $^3J_{H–C}$ = 4.8 Hz) 133.9 (C^4, $^2J_{H–C}$ = 8.0 Hz), 139.3 (SeC=, $^1J_{Se–C}$ = 111.4 Hz), 166.5 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 410.7. ^{15}N NMR (40 MHz, DMSO-d_6): δ –248.1. IR (KBr): 3082, 2152 (C≡N), 1628 (C=O), 1591, 1552 (C=C), 1493, 1450, 1381, 1279, 1142, 1073, 1035, 1004, 997, 909, 839, 782, 764, 756, 698, 633, 623, 537, 520, 457 cm^{-1}. $C_{10}H_5Br_2ClN_2OSe$ (443.38): calcd.

C 27.09, H 1.14, Br 36.04, Cl 8.00, N 6.32, Se 17.81; found: C 27.17, H 1.23, Br 35.89, Cl 8.07, N 6.11, Se 18.06.

(Z)-3-[(3,4-Dimethylphenyl)amino]-3-oxo-1-propenyl selenocyanate (**2k**). The reaction mixture was stirred for 40 h at room temperature and H_2O (8 mL) and CH_2Cl_2 (5.0 mL) were added. The aqueous layer was extracted (2 × 4 mL) with CH_2Cl_2 and the extract was dried over Na_2SO_4. After the removal of the solvent, the residue was dissolved in $CHCl_3$ and precipitated by cold hexane. Yield: 84 mg (64%); beige powder; mp 154–155 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.16 (s, 3H, Me[4]), 2.19 (s, 3H, Me[3]), 6.92 (d, [3]J = 8.0 Hz, 1H, =CHCO), 7.08 (d, [3]J = 8.4 Hz, 1H, H[5]), 7.32 (d, [3]J = 8.4 Hz, 1H, H[6]), 7.39 (s, 1H, H[2]), 8.01 (d, [3]J = 8.0 Hz, 1H, SeCH=), 10.60 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 18.9 (Me[4]), 19.6 (Me[3]), 108.3 (N≡C, [1]J_{Se-C} = 227.0 Hz), 117.0 (C[6]), 120.2 (C[2]), 122.2 (=$\underline{C}$CO, [2]J_{Se-C} = 62.1 Hz), 129.9 (C[5]), 132.4 (C[4]), 135.6 (C[3]), 136.8 (C[1]), 137.0 (SeC=, [1]J_{Se-C} = 109.1 Hz), 165.9 (C=O). ^{77}Se NMR (76 MHz, DMSO-d_6): δ 407.2. ^{15}N NMR (40 MHz, DMSO-d_6): δ −244.0. (NH, [1]J_{N-H} = 90.0 Hz). IR (KBr): 3338, 3142, 3062, 2943, 2917, 2854, 2155 (C≡N), 1643 (C=O), 1603, 1547 (C=C), 1504 (C=C), 1451, 1413, 1348, 1306, 1258, 1227, 1147, 1020, 1000, 977, 878, 807, 788, 701, 686, 615, 590, 568, 478, 440 cm^{-1}. $C_{12}H_{12}N_2OSe$ (279.20): calcd. C 51.62, H 4.33, N 10.03, Se 28.28; found: C 51.78, H 4.19, N 10.02, Se 28.46.

(Z)-3-(Diphenylamino)-3-oxo-1-propenyl selenocyanate (**2l**). The reaction mixture was stirred for 10 h at room temperature and H_2O (8 mL) was added. Precipitate was filtered off, washed with water and was dried. The product did not require further purification. Yield: 120 mg (78%); beige powder; mp 153–155 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.63 (d, [3]J = 8.2 Hz, 1H, =CHCO), 7.18–7.33 (m, 4H, C[2,6]), 7.33–7.54 (m, 6H, C[3,4,5]), 7.75 (d, [3]J = 8.2 Hz, 1H, SeCH=). ^{13}C NMR (100 MHz, CDCl$_3$): δ 108.1 (N≡C, [1]J_{Se-C} = 225.9 Hz), 119.5 (=$\underline{C}$CO), 126.0 (C[2,6]), 127.0 (C[4]), 128.2 (C[2',6']), 128.6 (C[4']), 129.2 (C[3,5]), 130.1 (C[3',5']), 140.7 (SeC=, [1]J_{Se-C} = 111.6 Hz), 141.1 (C[1]), 141.2 (C[1']), 167.7 (C=O). ^{77}Se NMR (76 MHz, CDCl$_3$): δ 420.2. ^{15}N NMR (40 MHz, CDCl$_3$): δ −231.0 (NPh). IR (KBr): 3082, 2152 (C≡N), 1628 (C=O), 1591, 1552, 1493, 1450, 1381, 1279, 1142, 1073, 1035, 997, 839, 782, 764, 756, 698, 660, 633, 623, 537, 520, 457 cm^{-1}. $C_{16}H_{12}N_2OSe$ (327.24): calcd. C 58.72, H 3.70, N 8.56, Se 24.13; found: C 58.77, H 3.63, N 8.34, Se 24.36.

4. Conclusions

We have developed an efficient approach to novel N-substituted (Z)-3-amino-3-oxo-1-propenyl selenocyanates based on the reaction of 3-trimethylsilyl-2-propynamides with the potassium selenocyanate catalyzed by ammonium chloride in methanol. The reaction did not realize under the same conditions in the absence of ammonium chloride, which was used for the first time in the reactions of selenocyanates with acetylenes. The reaction proceeded in a regio- and stereoselective fashion as anti-addition-affording vinyl selenocyanates with a (Z)-configuration in high yields.

The known methods for the preparation of vinyl selenocyanates are technically difficult and expensive. Some reactions were carried out under the action of ultrasound in a deep eutectic solvent (DES) containing glycolic acid as one of the components [64] or in lactic acid [65] and gave a mixture of (Z)- and (E)-isomers. In our case, mild reaction conditions (room temperature), cheap and available reagent such as ammonium chloride, and green solvent such as methanol were used. We developed a stereoselective method (unlike the known methods), which gives vinyl selenocyanates with only (Z)-configuration.

It should be emphasized that, to date, not a single representative of 3-amino-3-oxo-1-propenylselenocyanates has been described in the literature. It is worth noting that the amide function is usually favorable for the manifestation of biological activity.

The products obtained are a new family of vinyl selenocyanates, which can be used as intermediates for organic synthesis and compounds with possible biological activity.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/catal13091257/s1: ^{1}H and ^{13}C NMR spectra of the obtained compounds.

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