Studies on the reactivity of *N*-(3-thienyl)carbamates

Delphine Brugier, Francis Outurquin and Claude Paulmier *

Laboratoire de Synthèse Thio- et Séléno-organique, IRCOF-UFR Sciences, Université de Rouen, F-76821 Mont Saint Aignan Cedex, France

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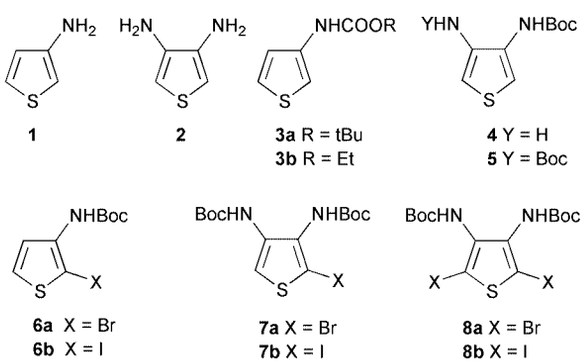
tert-Butyl 2-allyl- and *N*-allyl-3-thienylcarbamates were used as substrates for the preparation of thieno-[3,2-*b*]pyrroles **9** and 5,6-dihydrothieno[3,2-*b*]pyrroles **10**. Pd-catalyzed cyclization of *N*-allyl-(2-bromo-3-thienyl)carbamates **12** has allowed access to thienopyrroles **9**. The radical route has led to the formation of a dihydrothienopyrrole **10** or a tetrahydrothienopyridine **19** according to the β-substitution of the allyl substituent. The nucleophilic participation of the *tert*-butoxycarbonyl group occurred during the selenium or iodine-induced cyclization of *tert*-butyl 2-allyl- or N-allyl-3-thienylcarbamates. The formation of the thienooxazepinone **25** and *N*-(3-thienyl)oxazolidinones **28** and **29** was observed.

Indole derivatives display a wide range of biological activity.[1] For comparison, the study of thiophene isosteres is of great interest. The synthesis of thieno[3,2-*b*]pyrroles has been described but low yields were observed.[2–4] The multistep methods used involve cyclization of 3-aminothiophene derivatives according to Reissert, Bischler or Fischer modified procedures. More recently, Gronowitz *et al.* have prepared thieno[3,2-*b*]pyrroles using Pd-catalyzed coupling reactions.[5] Few works are devoted to 5,6-dihydrothieno[3,2-*b*]pyrroles[5] and, in particular, to their preparation.[6]

We are interested in the reactivity of 3-aminothiophene **1**, 3,4-diaminothiophene **2** and their carbamates: alkyl (3-thienyl)-carbamates **3**, *tert*-butyl (4-amino-3-thienyl)carbamate **4** and di-*tert*-butyl (thiophene-3,4-diyl)dicarbamate **5**[7] (Scheme 1).

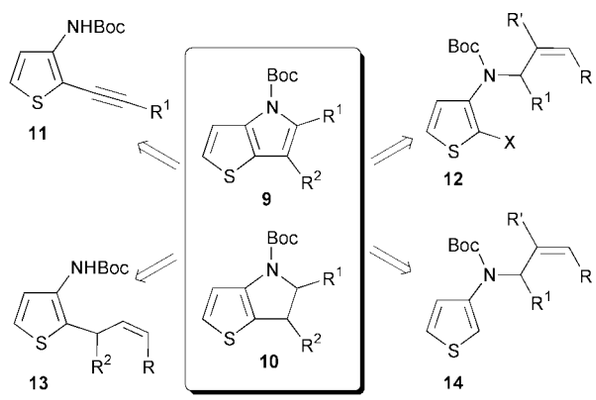


Scheme 1

Halogenation of these compounds was recently studied and carbamates **6**–**8** are now readily available.[8]

We now report our results concerning the access to 4-*tert*-butoxycarbonylthieno[3,2-*b*]pyrroles **9** and 4-*tert*-butoxy-carbonyl 5,6-dihydrothieno[3,2-*b*]pyrroles **10** from 3-amino-thiophene derivatives. Four routes were tested (Scheme 2). The cyclization of alkyl (2-alkynyl-3-thienyl)carbamates **11** was studied first. Methods involving Pd-catalyzed coupling reactions, radical and anionic cyclizations were then investigated. *tert*-Butyl *N*-allyl(2-bromo-3-thienyl)carbamates **12**, *tert*-butyl (2-allyl-3-thienyl)carbamates **13** and *tert*-butyl *N*-allyl(3-thienyl)carbamates **14** were considered as potential precursors.

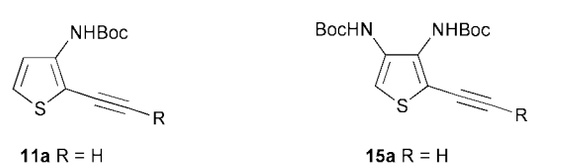
We have recently described the synthesis of alkyl (2-ethynyl-3-thienyl)carbamates **11** by Pd-catalyzed coupling reaction between acetylene compounds and the bromo carbamate **6a**.[8]



Scheme 2

According to recent preparations of indoles and azaindoles, we have tried to achieve the cyclization of compounds **11** in the presence of palladium(II) salts[9] or copper(I) iodide,[10] but the reactions were unsuccessful. Gronowitz *et al.* reported a two step procedure with both Pd-catalyzed carbon–carbon bond formation and cyclization.[5a] Our result seems to demonstrate that carbamates **11** and **15b** (R = $SiMe_3$) were not intermediates in this reaction.

The carbamate **11b** (R = $SiMe_3$) was treated with sodium ethoxide in ethanol.[11] The formation of thienopyrrole was not



observed and only the 2-ethynylthiophenes **11a** and **15a** were respectively obtained. This result shows that this method, efficient for the synthesis of indoles, cannot be transposed to the thiophene isosteres.

We then prepared several *N*-allylated [2-halo or 2-phenylselanyl-3-thienyl]carbamates **12** with the goal to test the palladium-catalyzed, radical and ionic routes. Compounds **12** were easily obtained by *N*-allylation of (2-halo or 2-phenylselanyl-3-thienyl)carbamates **6** (Scheme 3, Table 1). The same reaction was carried out on halo dicarbamates **7b**, **8a** and **8b** providing the bis(*N*-allylcarbamates) **16** and **17** in good yields

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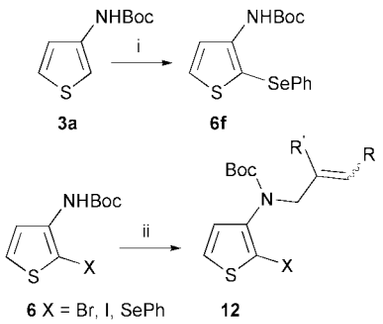
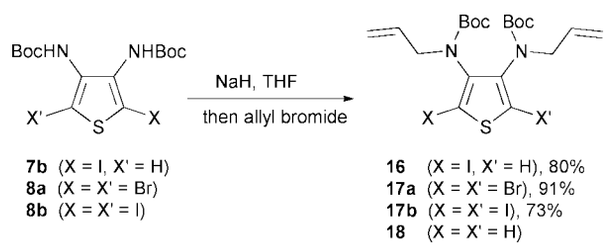
Table 1 *N*-Allyl 2-substituted 3-thienylcarbamates **12**

No.	X	R	R′	*E*:*Z*	Yield (%)
12a	Br	H	H	—	72
12b	Br	H	Me	—	87
12c	Br	Me	H	90:10	51
12d	Br	Ph	H	100:0	50
12e	I	H	H	—	94
12f	SePh	H	H	—	68



Scheme 3 *Reagents and conditions*: (i) nBuLi (2.5 eq.), THF, −78 °C then PhSeSePh, −20 °C; (ii) NaH, THF then allylic halide, 20 °C.

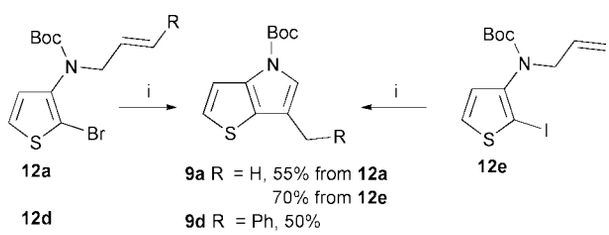


Scheme 4

(Scheme 4). Compounds **16** and **17** have given very complex ^{1}H and ^{13}C NMR spectra, which indicate stabilized conformers resulting from an important steric hindrance.

tert-Butyllithium treatment of *N*,*N*-diallylated 2-haloanilines, in a polar solvent or in the presence of a chelating agent, allows cyclization at room temperature.[12] The mechanism involves the successive formation of two carbanionic species. In our hand, the lithium–bromine exchange occurred but no cyclization took place. We have observed the quantitative formation of the debrominated compounds **14a** from **12a** (R = R′ = R^1 = H, X = Br) and **18** from **17a**.

The palladium-catalyzed cyclization of a *tert*-butyl *N*-allylated (2-iodo-3-thienyl)carbamate, leading to a thieno[3,2-*b*]pyrrole derivative, has been described[5c] but the reaction was not extensively studied. We have applied this procedure to the synthesis of the 6-methyl and 6-benzylthieno[3,2-*b*]pyrrole derivatives **9a** (R = H) and **9d** (R = Ph). The iodothiophene **12e** was a better substrate than the bromo analog **12a** for access to **9a** (Scheme 5).

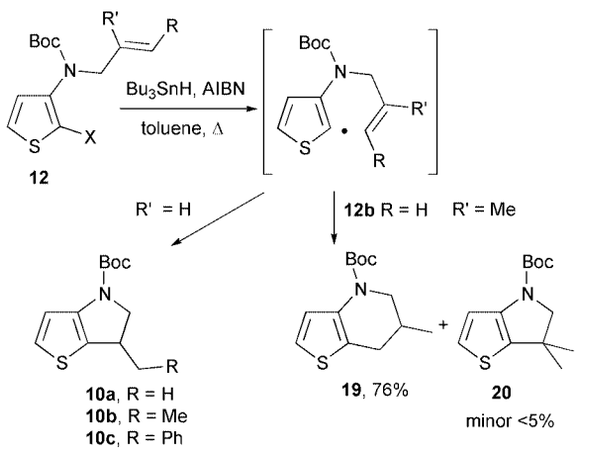


Scheme 5 *Reagents and conditions*: (i) $Pd(PPh_3)_4$, K_2CO_3, DMF, 60 °C.

The radical cyclization[13] of carbamates **12** (X = Br, I, SePh) was also achieved (Scheme 6, Table 2). When R′ = H, the initial thienyl radical underwent exclusively 5-*exo* trigonal cyclization

Table 2 Thieno[3,2-*b*]pyrrole and thieno[3,2-*b*]pyridine derivatives **10** and **19**

Entry	X	R	R′	Product	Yield (%)
1	Br	H	H	**10a**	68
2	I	H	H	**10a**	73
3	SePh	H	H	**10a**	69
4	Br	H	Me	**19**	76
5	Br	Me	H	**10b**	67
6	Br	Ph	H	**10c**	85

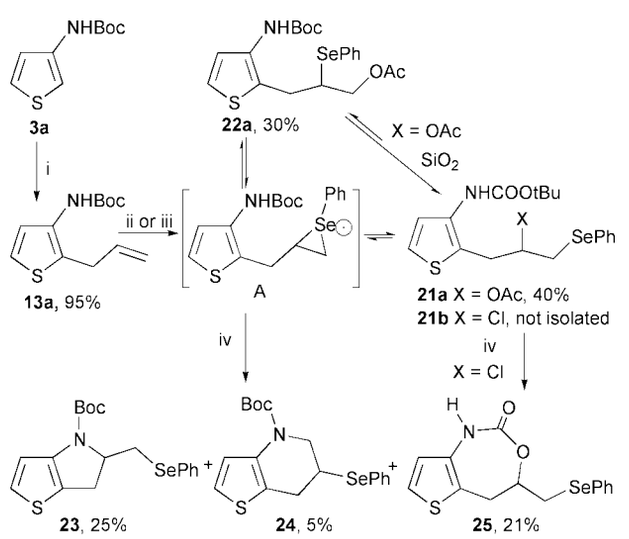


Scheme 6

providing the dihydrothienopyrrole **10** with a good yield. Comparable results were observed for X = Br, I and SePh (compare entries 1, 2 and 3). According to a 6-*endo* process, the tetrahydrothienopyridine **19** was the major product formed from **12b** (76% yield). The corresponding dihydrothienopyrrole **20** was also present as a minor product (**19**–**20**, 95:5).

Palladium-catalyzed and radical cyclizations were unsuccessful in the case of dicarbamates **16** and **17**. The cleavage of the C–X bond was never observed. Steric hindrance probably prevents palladium insertion or radical formation.

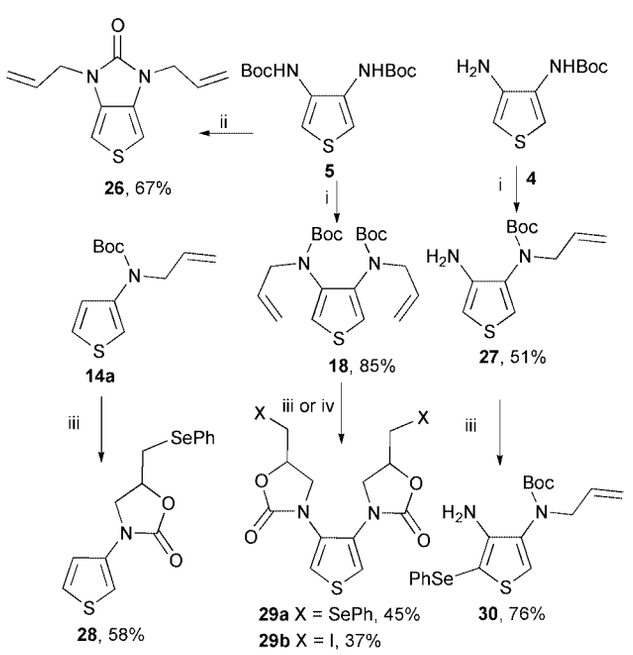
The electrophilic selenium-induced cyclization method[14] was then considered. *tert*-Butyl (2-allyl-3-thienyl)carbamate **13a**, prepared in a quantitative yield by metallation–allylation of **3a**, was treated with an electrophilic selenium reagent (Scheme 7). Using PhSeBr or *N*-(phenylselanyl)phthalimide (NPSP), no reaction was observed even after several days. Phenylselanyl



Scheme 7 *Reagents and conditions*: (i) *n*-BuLi (2.5 eq.), THF, −78 °C then allylbromide, −10 °C; (ii) PhSeCl (1.5 eq.), CH_2Cl_2, Na_2CO_3 (1eq.); (iii) PhSeSePh (0.6 eq.), $PhI(OAc)_2$ (excess), CH_3CN; (iv) SiO_2, CH_2Cl_2.

triflate† led to a complex and untractable mixture with consumption of the substrate. The generation of $PhSe^+$ from diphenyl diselenide and $PhI(OAc)_2$[15] has led to the formation of the regioisomeric addition products **21a** and **22a** (thermodynamic and kinetic adducts, respectively). A slow and partial isomerisation **22a** ⟶ **21a** occurred during the chromatographic separation. This reaction could be considered as a formal addition of "PhSeOAc" (Scheme 7). With PhSeCl, only the thermodynamic adduct **21b** was formed, but was not isolated in a pure form. The cyclization occurred during silica gel chromatography. Three heterocyclic products were formed and isolated: the expected dihydrothienopyrrole **23**, the tetrahydrothienopyridine **24** and the thienooxazepine **25** (ratio: **23**–**24**–**25**, 50 : 15 : 35). The formation of **23** and **24** was the result of 5- and 7-*exo* cyclization processes involving the thermodynamic addition product **21b** or the seleniranium ion **A** with respective attacks of the nitrogen and oxygen atoms of the carbamate functional group (Scheme 7).

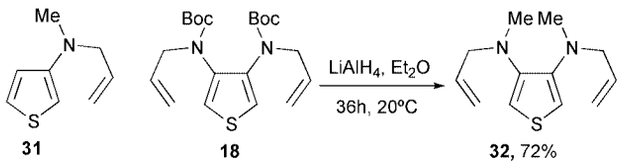
We have previously studied the strong enamine character of β-aminothiophenes **1** and **2**.[7] Under acid catalysis, α-alkylation of the nucleus was efficiently achieved using an aldehyde and PhSeH as reducing agent. We were interested in evaluating the nucleophilicity of the α-carbon towards that of a seleniranium ion. We have therefore prepared the *N*-allylated compounds **14a**, **18** (already obtained by debromination of **12a** and **17a**), and **27** (Scheme 8). The synthesis of the *tert*-butyl *N*-allyl-3-thienylcarbamate **14a** has been previously described.[16] NaH treatment of the dicarbamate **5**, followed by addition of allyl bromide, afforded the dicarbamate **18** or the thienoimidazolone **26** depending on the reaction time. The monoallyl diamine derivative **27** was prepared, in good yield, from the aminocarbamate **4**. In the reaction of PhSeCl with the *N*-allylated thienylcarbamates **14a** and **18**, the *O*-nucleophilicity of the carbamate group was also efficient and the oxazolidinones **28** and **29a** were formed respectively. An analogous reactivity was observed in the reaction of *N*-iodosuccinimide with the dicarbamate **18**. The bis(oxazolidinone) **29b** was obtained albeit in a poor yield (37%).



Scheme 8 *Reagents and conditions*: (i) NaH, THF, allyl bromide, 5 h; (ii) NaH, THF, allyl bromide, 20 h; (iii) PhSeCl, CH_2Cl_2, 20 °C, 12 h; (iv) *N*-iodosuccinimide, CCl_4, Δ, 12 h.

PhSeCl treatment of the *N*-allylated thiophenediamine derivative **27** has led to an electrophilic aromatic substitution providing the 2-phenylselanylthiophene derivative **30** isolated in a good yield (Scheme 8).

To prevent the participation of the functional group, we have applied the reaction to tertiary *N*-allyl amines. *N*-Allyl-3-(methylamino)thiophene **31**[16] and *N*,*N*′-diallyl-3,4-bis(methylamino)thiophene **32** were prepared by $LiAlH_4$ reduction of the *N*-allylated carbamates **14a** and **18**, respectively (Scheme 9).



Scheme 9

In each case, the reaction with PhSeCl (1.5 eq.) has not allowed the cyclization. Complex and untractable mixtures of products were formed. The reaction was not investigated further.

This work has shown that the synthesis of thieno[3,2-*b*]pyrroles from 3-aminothiophene derivatives cannot be achieved by the methods which are efficient for the preparation of indoles from 2-allyl or *N*-allylanilines. We succeeded, however, in the synthesis of *tert*-butyl 6-alkylthieno[3,2-*b*]pyrrole-4-carboxylates **9** by Pd-catalyzed cyclization of *tert*-butyl *N*-allyl(2-halo-3-thienyl)carbamates **12**. The radical cyclization of the same substrates **12** (X = Br, I, SePh) has given an access to the 5,6-dihydrothieno[3,2-*b*]pyrroles **10** and 4,5,6,7-tetrahydrothieno[3,2-*b*]pyridine **19** according to the nature of the allyl substituent. The PhSe-induced cyclization of *tert*-butyl 2-allyl-3-thienylcarbamate **13a** has shown competitive participation of the functional group with formation of the thienooxazepinone **25**. A comparable *O*-nucleophilic attack by the Boc group was observed with the formation of the the oxazolidinones **28** and **29** during selenium- or iodine-induced cyclization of the *N*-allylated thienylcarbamates **14a** and **18**, respectively.

Experimental

Di-*tert*-butyl (thiophene-3,4-diyl)dicarbamate **5**,[17] *tert*-butyl (4-amino-3-thienyl)carbamate **4**,[7e] *tert*-butyl (2-bromo-3-thienyl)carbamate **6a**,[18] the halothiophene derivatives **6**–**8**[8] and acetylene compounds **11b** and **15b**[8] were prepared as described elsewhere. All solvents were distilled before use and light petroleum refers to the fraction with bp 40–60 °C. THF was distilled over sodium–benzophenone and triethylamine was dried over sodium hydride. The chromatographic separations were achieved on silica gel (0.060–0.200 nm, pore diameter *ca.* 4 nm) available from ACROS. ^1H and ^{13}C NMR spectrum were recorded on Brucker AC 200 and DPX 300 instruments.

Attempted cyclization of 2-(trimethylsilylethynyl)thiophenes 11b and 15b

The carbamate **11b** (0.295 g, 1 mmol) was added to a freshly prepared solution of NaOEt (5 mmol) in ethanol (10 ml). The mixture was heated on reflux for 9 h under argon. The solvent was eliminated and the residue was treated with water and extracted with CH_2Cl_2. The organic layer was concentrated and silica gel chromatography (eluent: AcOEt) afforded the thienylacetylene **11a**. With the same treatment, **15b** has led to **15a**.

***tert*-Butyl (2-ethynyl-3-thienyl)carbamate 11a.** Oil. Yield = 62%. ^1H NMR ($CDCl_3$), δ: 7.61 (d, 1H, H^5, J = 5.5 Hz), 7.14 (d, 1H, H^4, J = 5.5 Hz), 6.91 (br s, 1H, NH), 3.63 (s, 1H, CH), 1.50 (s, 9H, CH_3). Anal. calc. for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27; found: C, 58.67; H, 6.02; N, 5.94%.

Di-*tert*-butyl (2-ethynylthiophene-3,4-diyl)dicarbamate 15a. Oil. Yield = 68%. ^1H NMR ($CDCl_3$), δ: 8.00 (br s, 1H, NH),

† The IUPAC name for triflic acid is trifluoromethanesulfonic acid.

7.37 (s, 1H, H^5), 6.54 (br s, 1H, NH), 3.58 (s, 1H, CH), 1.51 (s, 9H), 1.48 (s, 9H,). ^{13}C NMR ($CDCl_3$), δ: 153.8, 152.9 (CO), 132.3, 130.5 (C^3, C^4), 110.9 (C^5, CH), 88.2 (C), 81.9, 80.2 ($C(CH_3)_3$), 28.1, 27.9 (CH_3). Anal. calc. for $C_{16}H_{22}N_2O_4S$: C, 56.79; H, 6.55; N, 8.28; found: C, 56.55; H, 6.08; N, 8.18%.

N-Allylation of halocarbamates 6

A solution of bromocarbamate **6a** (0.278 g, 1 mmol) and sodium hydride (0.120 g, 5 mmol) in THF (50 ml) was stirred for 30 min at room temperature. Allyl bromide (0.605 g, 5 mmol) was then added and the mixture was stirred for 5 h. After cooling to 0 °C, the reaction was treated with a sat. aq. NaCl solution (10 ml). The organic layer was dried and the solvent was eliminated. The oily residue was chromatographed (eluent: CH_2Cl_2–light petroleum, 1:1) affording *N*-allyl(2-bromo-3-thienyl)carbamate **12a**. The other compounds **12** were obtained in a similar way from the corresponding carbamates **6** and the appropriate allylic bromide. The *N*-allylated halodicarbamates **16**, **17a** and **17b** were prepared from dicarbamates **7b**, **8a** and **8b** respectively, using double the amount of NaH and allyl bromide.

***tert*-Butyl *N*-allyl(2-bromo-3-thienyl)carbamate 12a.** Mp = 38 °C, yield = 72%. ^{1}H NMR ($CDCl_3$), δ: 7.17 (d, 1H, H^4, J = 5.8 Hz), 6.75 (br s, 1H, H^5), 5.92–5.77 (m, 1H, H_β), 5.14–5.05 (m, 2H, H_γ), 4.10 (d, 2H, H_α, J = 5.6 Hz), 1.37 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.0 (CO), 139.0 (C^3), 132.9 (C^β), 126.2 (C^5), 124.0 (C^4), 116.9 (C_γ), 108.7 (C^2), 79.7 ($C(CH_3)_3$), 50.9 (C_α), 27.6 (CH_3). Anal. calc. for $C_{12}H_{16}BrNO_2S$: C, 45.29; H, 5.07; N, 4.40; S, 10.07; found: C, 45.25; H, 4.97; N, 4.60; S, 10.21%.

***tert*-Butyl *N*-(2-methylprop-2-enyl)(2-bromo-3-thienyl)carbamate 12b.** Mp = 64 °C, yield = 87%. ^{1}H NMR ($CDCl_3$), δ: 7.14 (d, 1H, H^4, J = 5.8 Hz), 6.76 (br s, 1H, H^5), 4.77 (s, 2H, H_γ), 4.06 (s, 2H, H_α), 1.73 (s, 3H, CH_3), 1.37 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.3 (CO), 140.4 (C_β), 139.2 (C^3), 126.0 (C^5), 123.9 (C^4), 112.3 (C_γ), 108.4 (C_2), 79.7 ($C(CH_3)_3$), 54.0 (C_α), 27.6 ($C(CH_3)_3$),19.6 (CH_3). Anal. calc. for $C_{13}H_{18}BrNO_2S$: C, 46.99; H, 5.46; N, 4.22; found: C, 46.98; H, 5.69; N, 4.07%.

***tert*-Butyl *N*-but-2-enyl(2-bromo-3-thienyl)carbamate 12c.** Oil. yield = 51%, (90:10 *E*:*Z* mixture). *E* Isomer: ^{1}H NMR ($CDCl_3$), δ: 7.12 (d, 1H, H^4, J = 5.8 Hz), 6.67 (br s, 1H, H^5), 5.55–5.37 (m, 2H, H_β, H_γ), 3.98 (m, 2H, H_α), 1.54 (d, 3H, H_δ, J = 7.4 Hz), 1.32 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.5 (CO), 139.4 (C^3), 128.6 (C_β), 126.6 (C_γ), 125.9 (C^5), 124.0 (C^4), 109.1 (C^2), 79.9 ($C(CH_3)_3$), 50.5 (C_α), 27.9 (CH_3),17.4 (C_δ). Anal. calc. for $C_{13}H_{18}BrNO_2S$: C, 46.99; H, 5.46; N, 4.22; found: C, 47.31; H, 5.72; N, 4.58%. *Z* isomer not isolated: ^{1}H NMR ($CDCl_3$), δ: 7.12 (d, 1H, H^4, J = 5.8 Hz), 6.67 (br s, 1H, H^5), 5.55–5.37 (m, 2H, H_β, H_γ), 4.12 (m, 2H, H_α), 1.45 (d, 3H, H_δ, J = 7.1 Hz), 1.32 (s, 9H, CH_3).

***tert*-Butyl *N*-(3-phenylprop-2-enyl)(2-bromo-3-thienyl)carbamate 12d.** Oil. Yield = 50%. *E* Isomer: ^{1}H NMR ($CDCl_3$), δ: 7.30–7.10 (m, 6H, Ph, H^4), 6.70 (br s, 1H, H^5), 6.35 (d, 1H, H_γ, J = 16 Hz), 6.16 (dt, 1H, H_β, J = 16, 6.5 Hz), 4.14 (d, 2H, H_α, J = 6.5 Hz), 1.34 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.4 (CO), 136.2 (C_β), 132.3, 129.0, 127.1, 126.3, 126.2, 125.9 (C_{Ph}, C_γ, C^5), 124.0 (C^4), 109.2 (C^2), 80.0 ($C(CH_3)_3$), 50.5 (C_α), 27.7 (CH_3). Anal. calc. for $C_{18}H_{20}BrNO_2S$: C, 54.83; H, 5.11; N, 3.55; S, 8.13; found: C, 55.02; H, 5.02; N, 3.88; S, 8.56%.

***tert*-Butyl *N*-allyl(2-iodo-3-thienyl)carbamate 12e.** Oil. Yield = 94%. ^{1}H NMR ($CDCl_3$), δ: 7.17 (d, 1H, H^4, J = 5.8 Hz), 6.75 (br s, 1H, H^5), 5.92–5.77 (m, 1H, H_β), 5.14–5.05 (m, 2H, H_γ), 4.10 (d, 2H, H_α, J = 5.6 Hz), 1.37 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.6 (CO), 133.5 (C_β), 129.6 (C^5), 123.5 (C^4), 117.5 (C_γ), 116.0 (C^2), 80.3 ($C(CH_3)_3$), 51.6 (C_α), 28.1 (CH_3). Anal. calc. for $C_{12}H_{16}INO_2S$: C, 39.46; H, 4.42; N, 3.84; found: C, 40.00; H, 4.52; N, 4.10%.

***tert*-Butyl *N*-allyl(2-phenylselanyl-3-thienyl)carbamate 12f.** Oil. Yield = 68%. ^{1}H NMR ($CDCl_3$), δ: 7.32–7.28 (m, 6H, Ph, H^4), 6.81 (br s, 1H, H^5), 5.82–5.71 (m, 1H, H_β), 5.11–4.96 (m, 2H, H_γ), 4.07 (m, 2H, H_α), 1.35 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 154.1 (CO), 144.6 (C^3), 133.7 (C_β), 130.4 (C^5), 132.5, 129.0, 127.4 (Ph), 126.7 (C^4), 117.1 (C_γ), 80.9 ($C(CH_3)_3$), 52.2 (C_α), 28.0 (CH_3). Anal. calc. for $C_{18}H_{21}NO_2SSe$: C, 54.82; H, 5.37; N, 3.55; S, 8.13; found: C, 54.86; H, 6.05; N, 2.96; S, 8.52%.

Di-*tert*-butyl *N*,*N*′-diallyl(2-iodothiophene-3,4-diyl)dicarbamate 16. Oil. Yield = 80%. ^{1}H NMR ($CDCl_3$), δ: 7.17 (s, 1H, H^5), 6.05–5.65 (m, 2H, H_β), 5.13–5.02 (m, 4H, H_γ), 4.35–3.85 (m, 4H, H_α), 1.40 (s, 9H, CH_3), 1.38 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.8, 152.9 (CO), 133.3 (C_β), 125.9 (C^5), 117.6, 116.5 (C_γ), 80.3, 80.1 ($C(CH_3)_3$), 51.9, 50.9 (C_α), 27.8 (CH_3). Anal. calc. for $C_{20}H_{29}IN_2O_4S$: C, 46.16; H, 5.62; N, 5.38; S, 6.16; found: C, 46.35; H, 5.98; N, 5.66; S, 6.02%.

Di-*tert*-butyl *N*,*N*′-diallyl(2,5-dibromothiophene-3,4-diyl)dicarbamate 17a. Oil. Yield = 91%. ^{1}H NMR ($CDCl_3$), δ: 5.97–5.75 (m, 2H, H_β), 5.14–5.02 (m, 4H, H_γ), 4.45–3.50 (m, 4H, H_α), 1.46 (s, 9H, CH_3), 1.37 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 152.9 (CO), 133.5, 133.0 (C_β), 118.6, 118.0, 117.4 (C_γ), 80.9 ($C(CH_3)_3$), 50.8 (C_α), 28.0 (CH_3). Anal. calc. for $C_{20}H_{28}Br_2N_2O_4S$: C, 43.49; H, 5.11; N, 5.07; S, 5.80; found: C, 43.56; H, 5.16; N, 5.02; S, 5.64%.

Di-*tert*-butyl *N*,*N*′-diallyl(2,5-diiodothiophene-3,4–diyl)dicarbamate 17b. Mp = 105–120 °C, yield = 73%. ^{1}H NMR ($CDCl_3$), δ: 6.03–5.80 (m, 2H, H_β), 5.15–5.02 (m, 4H, H_γ), 4.45–3.50 (m, 4H, H_α), 1.50 (s, 9H, CH_3), 1.39 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 152.7 (CO), 133.8, 133.2, 132.8 (C_β), 118.6, 117.9, 117.4 (C_γ), 81.0, 80.9, 79.9 ($C(CH_3)_3$), 52.3, 50.9 (C_α), 28.1 (CH_3). Anal. calc. for $C_{20}H_{28}I_2N_2O_4S$: C, 37.17; H, 4.37; N, 4.33; S, 4.96; found: C, 37.27; H, 4.64; N, 4.11; S, 4.95%.

Preparation of thienopyrroles 9a and 9d

Potassium carbonate (0.512 g, 4 mmol) and $Pd(PPh_3)_4$ (0.057 g, 0.05 mmol) were successively added to a degassed solution of *N*-allyl(2-halo-2-thienyl)carbamate **12a** (**12d** or **12e**) (1 mmol) in DMF (3 ml). The reaction mixture was stirred for 30 min at room temperature and 5 h at 60 °C and then diluted with ether (25 ml) and water (10 ml) and filtered through a Celite pad. The organic layer was dried and evaporated. The thienopyrrole **9a** (or **9d**) was isolated after silica gel chromatography of the oily residue (eluent: light petroleum–CH_2Cl_2, 75:25).

***tert*-Butyl 6-methyl-4*H*-thieno[3,2-*b*]pyrrole-4-carboxylate 9a.** Oil. Yield = 55% from **12a** and 70% from **12e**. ^{1}H NMR ($CDCl_3$), δ: 7.30 (br s, 1H, H^2), 7.13 (m, 2H, H^3, H^5), 2.20 (s, 3H, CH_3), 1.63 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 148.3 (CO), 137.4 (C^{3a}), 128.2 (C^{6a}), 124.2 (C^2), 120.8 (C^5), 115.7 (C^6), 114.9 (C^3), 82.8 ($C(CH_3)_3$), 27.7 (CH_3), 10.8 (CH_3). Anal. calc. for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90; S, 13.51; found: C, 60.13; H, 6.02; N, 5.23; S, 13.54%.

***tert*-Butyl 6-benzyl-4*H*-thieno[3,2-*b*]pyrrole-4-carboxylate 9d.** Oil. Yield = 50%. ^{1}H NMR ($CDCl_3$), δ: 7.40–7.20 (m, 7H, Ph, H^2, H^5), 7.11 (d, 1H, H^3, J = 5.5 Hz), 4.90 (s, 2H, CH_2), 1.63 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 148.6 (CO), 140.3, 128.3, 127.3, 125.2 (C_{Ph}), 138.4 (C^{3a}), 128.2 (C^{6a}), 124.9 (C^2), 120.8 (C^5), 114.8 (C_6), 111.1 (C^3), 83.3 ($C(CH_3)_3$), 32.6 (CH_2), 27.7 (CH_3). Anal. calc. for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47; S, 10.23; found: C, 69.05; H, 6.35; N, 4.63; S, 10.22%.

Radical cyclization of *N*-allyl(2-halo-3-thienyl)carbamates 12

A degassed solution of carbamate **12** (1 mmol) in toluene (10 ml) containing AIBN (0.01 g) and tributyltin hydride (0.437 g, 1.5 mmol) was stirred under reflux for 8 h. The solvent was evaporated and silica gel chromatography (eluent: light petroleum–CH_2Cl_2, 80:20, then CH_2Cl_2) afforded the dihydrothienopyrrole **10** (or the tetrahydrothienopyridine **19** for **12b**).

***tert*-Butyl 5,6-dihydro-6-methyl-4*H*-thieno[3,2-*b*]pyrrole-4-carboxylate 10a.** Oil. Yield = 68%. ^{1}H NMR ($CDCl_3$), δ: 7.16, 6.87 (2br s, 1H, H^2), 7.06 (d, 1H, H^3, J = 5.1 Hz), 4.47–4.37 (m, 1H, H^5), 3.85–3.76 (m, 1H, H^5), 3.59–3.48 (m, 1H, H_6), 1.53 (s, 9H, CH_3), 1.29 (d, 3H, CH_3, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 151.2, 150.9 (CO), 144.5, 143.7 (C^{3a}), 128.9, 128.4 (C^{6a}), 126.7 (C^2), 116.0, 115.6 (C^3), 80.2, 79.6 ($C(CH_3)_3$), 60.3, 59.8 (C^5), 33.7, 33.0 (C^6), 28.0, 27.7 (CH_3), 21.3 (CH_3). Anal. calc. for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85; found: C, 59.84; H, 7.02; N, 5.86%. MS (EI, 70 eV): 239 ($M^{+\bullet}$, 15), 183 (90), 168 (87), 124 (81), 57 (100), 41 (69).

***tert*-Butyl 6-ethyl-5,6-dihydro-4*H*-thieno[3,2-*b*]pyrrole-4-carboxylate 10b.** Oil. Yield = 67%. ^{1}H NMR ($CDCl_3$), δ: 7.16, 6.86 (2br s, 1H, H^2), 7.02 (d, 1H, H^3, J = 4.8 Hz), 4.37–4.30 (m, 1H, H^5), 3.88–3.82 (m, 1H, H^6), 3.35–3.23 (m, 1H, H^5), 1.57 (m, 2H, CH_2), 1.49 (s, 9H, CH_3), 0.94 (t, 3H, CH_3, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 151.2 (CO), 145.0, 144.5 (C^{3a}), 127.4 (C^{6a}), 126.8 (C^2), 116.1, 115.7 (C^3), 80.5, 79.9 ($C(CH_3)_3$), 58.6, 58.1 (C^5), 41.0, 40.2 (C^6), 28.9 (CH_2), 28.2 (CH_3), 11.4 (CH_3). Anal. calc. for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53; found: C, 62.09; H, 7.08; N, 5.74%.

***tert*-Butyl 6-benzyl-5,6-dihydro-4*H*-thieno[3,2-*b*]pyrrole-4-carboxylate 10c.** Oil. Yield = 85%. ^{1}H NMR ($CDCl_3$), δ: 7.24–6.82 (m, 7H, Ph, H^3, H^2), 4.34–4.10 (m, 1H, H^5), 3.95–3.76 (m, 1H, H^5), 3.72–3.55 (m, 1H, H^6), 2.85–2.60 (m, 2H, CH_2), 1.53 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 151.1 (CO), 144.4 (C^{3a}), 138.5, 128.8, 128.3, 127.2, 126.4 (C_{Ph}, C^2, C^{6a}), 115.8 (C^3), 80.2 ($C(CH_3)_3$), 57.8 (C^5), 41.8(CH_2), 40.2 (C_6), 28.2 (CH_3). Anal. calc. for $C_{18}H_{21}NO_2S$: C, 68.54; H, 6.71; N, 4.44; found: C, 68.18; H, 6.44; N, 4.37%.

***tert*-Butyl 4,5,6,7-tetrahydro-6-methylthieno[3,2-*b*]pyridine-4-carboxylate 19.** Oil. Yield = 76%. ^{1}H NMR ($CDCl_3$), δ: 7.42 (br s, 1H, H^2), 6.98 (d, 1H, H^3, J = 5.5 Hz), 4.00 (m, 1H, H^5), 3.06 (dd, 1H, H^5, J = 9.7, 12.6 Hz), 2.86 (dd, 1H, H^7, J = 5.6, 16.2 Hz), 2.37 (dd, 1H, H^7, J = 9.0, 16.2 Hz), 2.22–2.02 (m, 1H, H^6), 1.52 (s, 9H, CH_3), 0.88 (d, 3H, CH_3, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 152.6 (CO), 135.0 (C^{3a}), 123.0 (C^2), 121.0 (C^{6a}), 120.3 (C^3), 80.4 ($C(CH_3)_3$), 49.8 (C^5), 31.2 (C^7), 28.2 (CH_3), 28.1 (C^6), 18.1 (CH_3). Anal. calc. for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53; S, 12.65; found: C, 61.47; H, 7.55; N, 5.48; S, 12.65%.

***tert*-Butyl 5,6-dihydro-6,6-dimethyl-4*H*-thieno[3,2-*b*]pyrrole-4-carboxylate 20.** Not isolated in a pure form. ^{1}H NMR ($CDCl_3$), δ: 7.04 (d, 1H, H^2, J = 5.1 Hz), 6.85 (d, 1H, H^3, J = 5.1 Hz), 3.97 (m, 2H, H^5), 1.51 (s, 9H, CH_3), 1.36 (s, 6H, CH_3).

Preparation of *tert*-butyl 2-allyl-3-thienylcarbamate 13a[16]

The carbamate **3a** (0.398 g, 2 mmol) in THF (20 ml) was treated with *n*-BuLi (2.5 M solution in hexane, 2 ml) at −78 °C. Allyl bromide (0.423 g, 3 mmol) was added at −10 °C. The mixture was stirred for 2 h at this temperature and quenched with sat. aq. NaCl solution. The organic layer was evaporated and the product **13a** was purified by silica gel chromatography (eluent: light petroleum–CH_2Cl_2, 50:50). Mp = 70 °C, yield = 95%. ^{1}H NMR ($CDCl_3$), δ: 7.30 (br s, 2H, H^5), 7.02 (d, 1H, H^4, J = 5.4 Hz), 6.50 (br s, 1H, NH), 5.80 (m, 1H, H_β), 5.07 (m, 2H, H_γ), 3.40 (d, 2H, H_α, J = 6.5 Hz).

Formal "PhSeOAc" addition to the 2-allylthiophene 13a

Diphenyl diselenide (0.375 g, 1.2 mmol) and (diacetoxy-λ^3-iodanyl)benzene (0.754 g, 2.6 mmol) were added to a solution of **13a** (0.478 g, 2 mmol) in CH_3CN (6 ml). The mixture was stirred overnight and treated with sat. aq. NaCl solution. The organic layer was dried and evaporated. The addition products **21a** and **22a** were separated by silica gel chromatography (eluent: light petroleum–CH_2Cl_2, 1:1). A partial isomerization of **22a** into **21a** was observed during the purification.

***tert*-Butyl {2-[2-acetoxy-3-(phenylselanyl)propyl]-3-thienyl}-carbamate 21a.** Oil. Yield = 40%. ^{1}H NMR ($CDCl_3$), δ: 7.48–7.44 (m, 2H, Ph), 7.24–7.19 (m, 4H, Ph, H^5), 7.02 (d, 1H, H^4, J = 5.5 Hz), 6.90 (br s, 1H, NH), 4.99 (m, 1H, CHOAc), 3.12–2.93 (m, 4H, CH_2, CH_2), 1.92 (s, 3H, CH_3), 1.44 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 170.2 (CO), 152.9 (CO), 134.2, 132.6, 129.1, 128.1 (Ph), 122.4 (C^5), 80.3 ($C(CH_3)_3$), 74.0 (CHOAc), 31.5 (CH_2), 30.3 (CH_2), 28.2 (CH_3), 20.9 (CH_3). IR (KBr): 3344, 3058, 2978, 2931, 1731, 1582, 1368 cm^{-1}. Anal. calc. for $C_{20}H_{25}NO_4SSe$: C, 52.86; H, 5.54; N, 3.08; S, 7.05; found: C, 52.88; H, 5.65; N, 3.18; S, 6.98%.

***tert*-Butyl {2-[3-acetoxy-2-(phenylselanyl)propyl]-3-thienyl}-carbamate 22a.** Oil. Yield = 30%. ^{1}H NMR ($CDCl_3$), δ: 7.50–7.48 (m, 2H, Ph), 7.25–7.19 (m, 4H, Ph, H^5), 7.05 (d, 1H, H^4, J = 5.5 Hz), 6.60 (br s, 1H, NH), 4.25 (dd, 1H, CH_2OAc, J = 4.7, 11.6 Hz), 4.11 (dd, 1H, CH_2OAc, J = 7.7, 11.6 Hz), 3.46–3.40 (m, 1H, CHSePh), 3.17–3.02 (m, 2H, CH_2), 2.04 (s, 3H, CH_3), 1.43 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 170.2 (CO), 152.9 (CO), 134.7, 133.5, 129.2, 128.1 (Ph), 122.4 (C^5), 80.0 ($C(CH_3)_3$), 65.5 (CH_2OAc), 43.9 (CHSePh), 29.2 (CH_2), 28.2 (CH_3), 20.8 (CH_3). Anal. calc. for $C_{20}H_{25}NO_4SSe$: C, 52.86; H, 5.54; N, 3.08; S, 7.05; found: C, 52.78; H, 5.73; N, 3.22; S, 6.97%.

PhSeCl addition to the 2-allylthiophene 13a

The carbamate **13a** (0.717 g, 3 mmol) in CH_2Cl_2 was treated with PhSeCl (0.862 g, 4.5 mmol) in the same solvent (50 ml). The mixture was stirred overnight and sat. aq. NaCl solution was added. The organic layer was dried and evaporated. The chloroselenide **21b** was obtained as a mixture with the substrate **13a** (**21b**–**13a**, 85:15). The chromatographic separation was unsuccessful.

***tert*-Butyl {2-[2-chloro-3-(phenylselanyl)propyl]-3-thienyl}-carbamate 21b.** ^{1}H NMR ($CDCl_3$), δ: 7.52–7.47 (m, 2H, Ph), 7.24–7.17 (m, 4H, Ph, H^5), 7.06 (d, 1H, H^4, J = 5.4 Hz), 6.60 (br s, 1H, NH), 4.15–4.05 (m, 1H, CHCl), 3.37 (dd, 1H, J = 3.9 H, 15.7 Hz), 3.28 (dd, 1H, J = 4.7, 12.8 Hz), 3.14 (dd, 1H, J = 7.3, 15.7 Hz), 3.11 (dd, 1H, J = 9.3, 12.8 Hz), 1.43 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.1 (CO), 134.0, 133.2, 129.3, 127.7 (Ph), 122.6 (C^5), 117.0 (C^4), 80.3 ($C(CH_3)_3$), 61.8 (CHCl), 34.3 (CH_2), 33.7 (CH_2), 28.2 (CH_3).

Cyclization of the β-chloro phenylselenide 21b

A solution of the crude addition product **21b** (0.862 g, 2 mmol) in CH_2Cl_2 was stirred overnight in the presence of silica gel (1 g). After filtration and concentration, the solid was recrystallized. The oxazepine **25** was isolated as white crystals. The solution resulting from the recrystallization was evaporated and chromatographed (eluent: CH_2Cl_2–light petroleum, 50:50). The dihydrothienopyrrole **23**, tetrahydrothienopyridine **24** and thienooxazepine **25** were successively isolated in 25, 5 and 21% yields respectively.

***tert*-Butyl 5,6-dihydro-5-(phenylselanylmethyl)-4*H*-thieno-[3,2-*b*]pyrrole-4-carboxylate 23.** Oil. Yield = 25%. ^{1}H NMR ($CDCl_3$), δ: 7.46–7.44 (m, 2H, Ph), 7.30 (br s, 1H, H^2), 7.21–7.19

(m, 3H, Ph), 6.97 (d, 1H, H^3, J = 5.4 Hz), 3.73–3.83 (m, 1H, H^5), 3.05–2.73 (m, 4H, H^6, CH_2), 1.42 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.4 (CO), 134.5, 133.3, 129.2, 127.5 (Ph), 121.5 (C^2), 110.3 (C^3), 71.0 (C^5), 35.5 (CH_2), 32.9 (CH_2), 28.3 (CH_3). Anal. calc. for $C_{18}H_{21}NO_2SSe$: C, 54.82; H, 5.37; N, 3.55; S, 8.13; found: C, 54.51; H, 5.56; N, 3.79; S, 7.97%.

***tert*-Butyl 4,5,6,7-tetrahydro-6-(phenylselanyl)thieno[3,2-*b*]pyridine-4-carboxylate 24.** Oil. Yield = 5%. ^{1}H NMR ($CDCl_3$), δ: 7.50–7.48 (m, 2H, Ph), 7.31 (br s, 1H, H^2), 7.21–7.19 (m, 3H, Ph), 7.03 (d, 1H, H^3, J = 5.2 Hz), 3.52 (m, 2H, H^5), 3.41–3.37 (m, 1H, H^6), 3.11–3.08 (m, 2H, H_7), 1.42 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 154.0 (CO), 134.8, 129.2, 128.1 (Ph), 62.0 (C^5), 48.8 (C^6), 28.3 (C^7), 28.2 (CH_3). Anal. calc. for $C_{18}H_{21}NO_2SSe$: C, 54.82; H, 5.37; N, 3.55; S, 8.13; found: C, 54.86; H, 5.71; N, 3.19; S, 7.92%.

4,5,7,8-Tetrahydro-5-oxo-7-(phenylselanylmethyl)thieno[3,2-*d*][1,3]oxazepine 25. Mp = 151 °C, yield = 21%. ^{1}H NMR ($CDCl_3$), δ: 8.67 (br s, 1H, NH), 7.49–7.46 (m, 2H, Ph), 7.23–7.19 (m, 3H, Ph), 6.98 (d, 1H, H^2, J = 5.3 Hz), 6.57 (d, 1H, H^3, J = 5.3 Hz), 4.66–4.63 (m, 1H), 3.35–3.25 (m, 2H, CH_2), 3.12–3.03 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 156.2 (CO), 133.4, 131.6, 129.3, 127.6 (Ph), 121.4 (C^2), 117.0 (C^3), 78.4 (C^7), 33.0 (CH_2), 31.4 (CH_2). Anal. calc. for $C_{14}H_{13}NO_2SSe$: C, 49.71; H, 3.87; N, 4.14; S, 9.48; found: C, 49.40; H, 4.16; N, 3.69; S, 9.18%. MS (EI, 70 eV): 339 ($M^{+\bullet}$, 18), 314 (58), 182 (50), 157 (81), 136 (100), 124 (82), 77 (82).

N-Allylation of the amino carbamate 4 and dicarbamate 5

A mixture of amino carbamate **4** (0.214 g, 1 mmol) and NaH (0.24 g, 10 mmol) in THF (20 ml) was stirred for 30 min. Allyl bromide (1.21 g, 10 mmol) was added and the stirring continued for 5 h. The mixture was quenched at 0 °C with sat. aq. NaCl solution. The organic layer was evaporated and silica gel chromatography provided the monoallylated product **27** (eluent: light petroleum–CH_2Cl_2, 50 : 50). The diallylated dicarbamate **18** was prepared from dicarbamate **5** using double amounts of NaH and allyl bromide, after 5 h of stirring at room temperature. The diallyl thienoimidazolone **26** was obtained after 20 h of reaction. All compounds were purified by silica gel chromatography (eluent: light petroleum–CH_2Cl_2, 50 : 50).

***tert*-Butyl *N*-allyl-3-thienylcarbamate 14a.**[16] Oil. Yield = 51%. ^{1}H NMR ($CDCl_3$), δ: 7.13 (m, 1H, H^5), 7.07 (m, 1H, H^4), 6.97 (m, 1H, H^2), 6.00–5.80 (m, 1H, H_β), 5.27–5.11 (m, 2H, H_γ), 4.09 (d, 2H, H_α, J = 5.7 Hz), 1.44 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 154.0 (CO), 127.5, 126.5, 124.6, 123.5, 113.1 (C_γ), 51.4 (C_α), 28.2.

Di-*tert*-Butyl *N*,*N*′-diallylthiophene-3,4-diyldicarbamate 18. Oil. Yield = 85%. ^{1}H NMR ($CDCl_3$), δ: 7.00 (br s, 2H, H^2, H^6), 5.98–5.84 (m, 2H, H_β), 5.17–5.09 (m, 4H, H_γ), 3.98 (d, 4H, H_α, J = 5.7 Hz), 1.41 (s, 18H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 154.1 (CO), 134.0 (C_β), 131.7 (C^3, C^4), 118.0 (C^2, C^5), 116.4 (C_γ), 80.1 ($C(CH_3)_3$), 44.7 (C_α), 28.1 (CH_3). MS (EI, 70 eV): 294 ($M^{+\bullet}$, 2), 238 (6), 194 (4), 165 (63), 57 (100), 41 (60).

***N*,*N*′-Diallyl-2-oxo-2,3-dihydro-1*H*-thieno[3,4-*d*]imidazole 26.** Oil. Yield = 67%. ^{1}H NMR ($CDCl_3$), δ: 6.24 (s, 2H, H^4, H^6), 5.97–5.77 (m, 2H, H_β), 5.32–5.20 (m, 4H, H_γ), 4.36 (m, 4H, H_α). ^{13}C NMR ($CDCl_3$), δ: 217.8 (CO), 131.7 (C_β), 131.6 (C^{2a}, C^{2b}), 116.0 (C_γ), 93.8 (C^{3a}, C^{6a}), 44.7 (C_α). Anal. calc. for $C_{11}H_{12}N_2OS$: C, 59.98; H, 5.49; N, 12.72; found: C, 60.14; H, 5.98; N, 12.98%. IR (KBr): 3102, 2980, 2916, 1713, 1645, 1552 cm^{-1}. MS (EI, 70 eV): 220 ($M^{+\bullet}$, 100), 187 (26), 179 (25), 151 (63), 136 (22), 123 (30), 80 (39), 41 (80), 39 (78).

***tert*-Butyl *N*-allyl(4-amino-3-thienyl)carbamate 27.** Oil. Yield = 51%. ^{1}H NMR ($CDCl_3$), δ: 6.90 (d, 1H, H^2, J = 3.4 Hz), 6.14 (d, 1H, H^5, J = 3.4 Hz), 6.00–5.80 (m, 1H, H_β), 5.27–5.11 (m, 2H, H_γ), 4.09 (d, 2H, H_α, J = 5.7 Hz), 3.57 (br s, 2H, NH^2), 1.44 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 154.0 (CO), 141.2 (C^3), 133.7 (C^4), 133.2 (C_β), 117.8 (C^2), 116.6 (C_γ), 99.8 (C^5), 80.5 ($C(CH_3)_3$), 52.9 (C_α), 27.9 (CH_3). Anal. calc. for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.01; found: C, 56.77; H, 7.02; N, 10.53%.

Reaction of *N*-allyl compounds 14a, 18 and 27 with PhSeCl

N-Allylthienylcarbamate **14a** (0.478 g, 2 mmol) in CH_2Cl_2 (30 ml) was treated with PhSeCl (0.575 g, 3 mmol) dissolved in the same solvent (30 ml) containing sodium carbonate (0.848 g, 8 mmol). The reaction mixture was stirred overnight and sat. aq. NaCl solution was added. The organic layer was dried and evaporated. Silica gel chromatography afforded the oxazolidinone **28** (eluent: CH_2Cl_2). The same procedure gave the bis(oxazolidinone) **29a** from dicarbamate **18** and the 2-(phenylselanyl)thiophene derivative **30** from the monoallyl diamine derivative **27**. The chromatographic purification was achieved on silica gel (eluent: light petroleum–CH_2Cl_2, 50 : 50).

5-(Phenylselanylmethyl)-3-(3-thienyl)-1,3-oxazolidin-2-one 28. Oil. Yield = 58%. ^{1}H NMR ($CDCl_3$), δ: 7.51–7.50 (m, 2H, Ph), 7.32–7.29 (m, 5H, Ph, $H^{4'}$, $H^{5'}$), 6.87 (s, 1H, $H^{2'}$), 4.71–4.64 (m, 1H, H^5), 4.00 (t, 1H, H^4, J = 8.8 Hz), 3.66 (dd, 1H, H^4, J = 8.8, 6.3 Hz), 3.27 (dd, 1H, CH_2Se, J = 4.3, 12.9 Hz), 2.97 (dd, 1H, CH_2Se, J = 9.2, 12.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 153.8 (C^2), 136.4 ($C^{3'}$), 133.4, 129.3, 127.9 (Ph), 125.4 ($C^{4'}$), 119.4 ($C^{5'}$), 107.2 ($C^{2'}$) 72.1 (C^5), 51.5 (C^4), 30.9 (CH_2Se). Anal. calc. for $C_{14}H_{13}NO_2SSe$: C, 49.71; H, 3.87; N, 4.14; S, 9.48; found: C, 49.98; H, 3.87; N, 4.52; S, 9.58%.

3,4-Bis[2-oxo-5-(phenylselanylmethyl)-1,3-oxazolidin-3-yl]-thiophene 29a. Yield = 45%. ^{1}H NMR ($CDCl_3$), δ: 7.48–7.46 (m, 4H, Ph), 7.22–7.19 (m, 6H, Ph), 7.03 (s, 2H, $H^{2,}$ H^5), 4.66–4.61 (m, 2H, $H^{5'}$), 4.02 (t, 2H, $H^{4'}$, J = 8.6 Hz), 3.75–3.67 (m, 2H, $H^{4'}$), 3.27 (dd, 2H, CH_2Se, J = 3.4, 12.8 Hz), 3.08–3.00 (m, 2H, CH_2Se). ^{13}C NMR ($CDCl_3$), δ: 155.2 ($C^{2'}$), 133.3, 132.0, 129.3, 127.8 (Ph), 128.0 (C^4), 119.2 (C^5), 73.1 ($C^{5'}$), 52.5 ($C^{4'}$), 30.7 (CH_2Se). Anal. calc. for $C_{24}H_{22}N_2O_4SSe_2$: C, 48.66; H, 3.74; N, 4.73; S, 5.41; found: C, 48.98; H, 3.72; N, 4.97; S, 5.02%.

***tert*-Butyl *N*-allyl[5-(phenylselanyl)-4-amino-3-thienyl]carbamate 30.** Oil. Yield = 76%. ^{1}H NMR ($CDCl_3$), δ: 7.59–7.55 (m, 2H, Ph), 7.23–7.19 (m, 3H, Ph), 7.12 (s, 1H, H^2), 5.96–5.78 (m, 1H, H_β), 5.19–5.08 (m, 2H, H_γ), 3.91–4.11 (m, 4H, H_α, NH^2), 1.43 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 153.9 (CO), 147.1 (C^4), 133.7 (C^3), 133.4, 129.0, 127.8, 125.9 (Ph), 132.9 (H_β), 117.3 (H_γ), 53.6 (H_α), 80.8 ($C(CH_3)_3$), 28.1 (CH_3). Anal. calc. for $C_{18}H_{22}N_2O_2SSe$: C, 52.81; H, 5.42; N, 6.84; found: C, 53.00; H, 5.64; N, 6.42%.

N-Iodosuccinimide-induced cyclization of di-*tert*-butyl *N*,*N*′-diallyl(thiophene-3,4-diyl)dicarbamate 18

NIS (0.9 g, 4 mmol) was added to *N*,*N*′-diallyldicarbamate **18** (0.394 g, 1 mmol) in CCl_4 (20 ml). The mixture was stirred overnight at room temperature. The oxazolidinone **29b** was isolated and purified as described for **29a**.

3,4-Bis(5-iodomethyl-2-oxo-1,3-oxazolidin-3-yl)thiophene 29b. Yield = 37%. ^{1}H NMR ($CDCl_3$), δ: 7.19 (s, 1H, H^2), 7.18 (s, 1H, H^5), 4.80–4.61 (m, 2H, $H^{5'}$), 4.16 (t, 2H, $H^{4'}$, J = 8.7 Hz), 3.83–3.74 (m, 2H, $H^{4'}$), 3.42 (d, 4H, CH_2I, J = 6.4 Hz). Anal. calc. for $C_{12}H_{12}I_2N_2O_4S$: C, 26.99; H, 2.26; N, 5.24; found: C, 27.42; H, 2.35; N, 5.63%. MS (EI, 70 eV): 534 ($M^{+\bullet}$, 17), 406 (30), 363 (100), 254 (75), 235 (27), 144 (50), 127 (53). MS (desorption chemical ionisation, DCI, pos., isobutane): 585 ($(MH + C_4H_9)^+$, 100), 365 (45), 100 (43).

Preparation of *N*,*N*′-diallyl-3,4-bis(methylamino)thiophene 32

Dicarbamate **18** (0.394 g, 1 mmol) in dry ether (30 ml) was added to a suspension of $LiAlH_4$ (0.8 g, 20 mmol) in the same solvent (20 ml). The mixture was stirred overnight, cooled to 0 °C and treated with sat. aq. NaCl. The aqueous solution was extracted twice with ether and the combined organic layers were dried and evaporated. Silica gel chromatography (eluent: light petroleum–CH_2Cl_2, 80 : 20) afforded the diamine **32**. Yield: 72%. ^{1}H NMR ($CDCl_3$), δ: 6.31 (s, 2H, H^2, H^5), 5.92–5.75 (m, 2H, H_β), 5.25–5.12 (m, 4H, H_γ), 3.75 (d, 4H, H_α, J = 6.3 Hz), 2.68 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 145.2 (C^3, C^4), 135.3 (C_β), 116.9 (C_γ), 104.7 (C^2, C^5), 56.1 (C_α), 39.0 (CH_3). Anal. calc. for $C_{12}H_{18}N_2S$: C, 64.82; H, 8.16; N, 12.60; found: C, 64.97; H, 8.22; N, 12.77%.

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