

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

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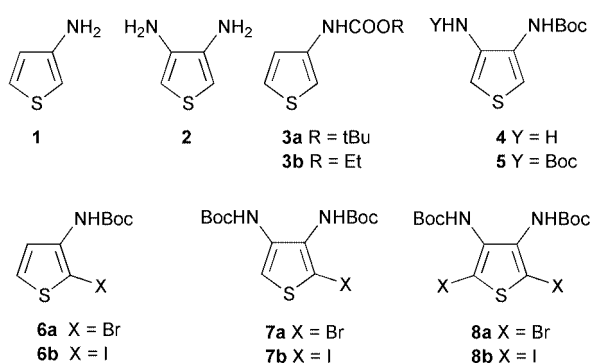
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tert-Butyl 2-allyl- and *N*-allyl-3-thienylcarbamates were used as substrates for the preparation of thieno[3,2-*b*]pyrroles **9** and 5,6-dihydrothieno[3,2-*b*]pyrroles **10**. Pd-catalyzed cyclization of *N*-allyl-(2-bromo-3-thienyl)carbamates **12** 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*]pyrroles⁵ 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).

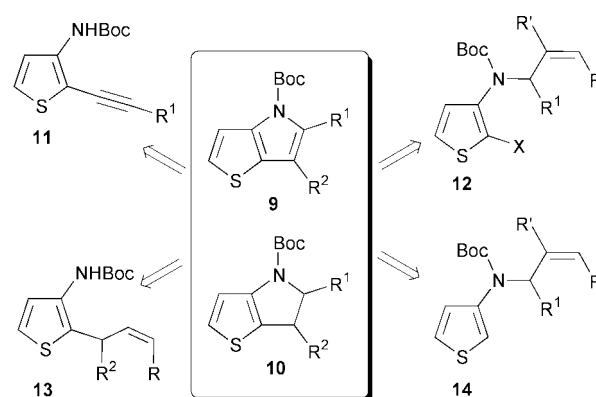


Scheme 1

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*-butoxycarbonyl 5,6-dihydrothieno[3,2-*b*]pyrroles **10** from 3-aminothiophene 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.

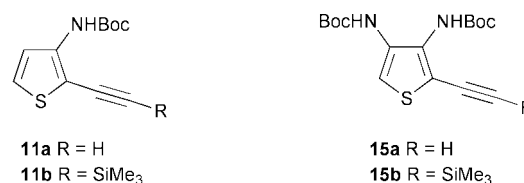
We have recently described the synthesis of alkyl (2-ethynyl-3-thienyl)carbamates **11** by Pd-catalyzed coupling reaction between acetylene compounds and the bromo carbamate **6a**.⁸



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) salts⁹ 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** ($R = \text{SiMe}_3$) were not intermediates in this reaction.

The carbamate **11b** ($R = \text{SiMe}_3$) was treated with sodium ethoxide in ethanol.¹¹ The formation of thienopyrrole was not

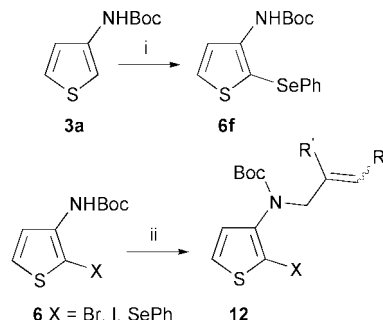
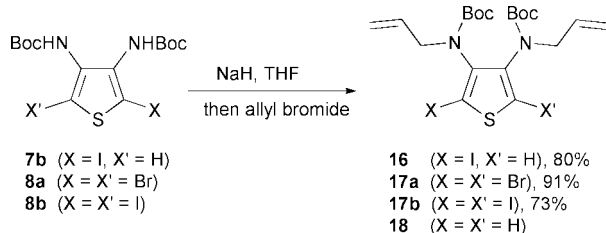


observed and only the 2-ethynylthiophenes **11a** and **15a** were respectively obtained. This result shows that this method, efficient for the synthesis of indoles, cannot be transposed to the thiophene isosteres.

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

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

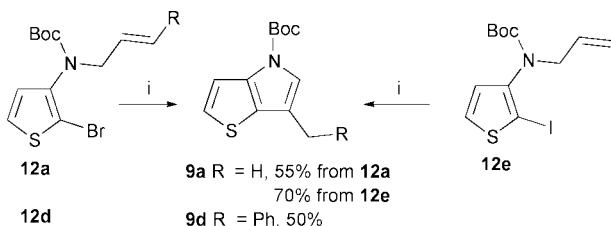
No.	X	R	R'	<i>E</i> : <i>Z</i>	Yield (%)
12a	Br	H	H	—	72
12b	Br	H	Me	—	87
12c	Br	Me	H	90:10	51
12d	Br	Ph	H	100:0	50
12e	I	H	H	—	94
12f	SePh	H	H	—	68

**Scheme 3** Reagents and conditions: (i) *n*BuLi (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 ^1H 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** ($\text{R} = \text{R}' = \text{R}'' = \text{H}$, $\text{X} = \text{Br}$) and **18** from **17a**.

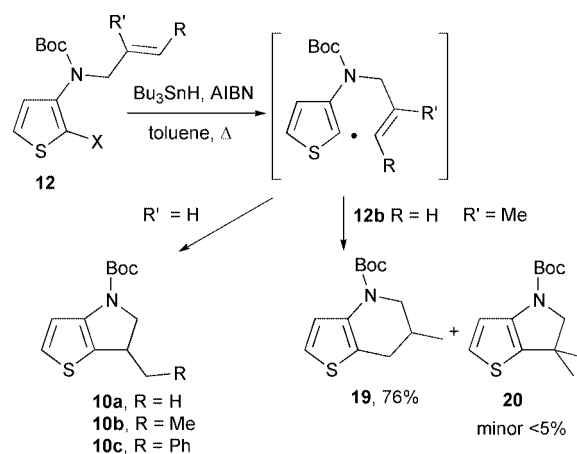
The palladium-catalyzed cyclization of a *tert*-butyl *N*-allylated (2-iodo-3-thienyl)carbamate, leading to a thieno[3,2-*b*]pyrrole derivative, has been described^{5c} but the reaction was not extensively studied. We have applied this procedure to the synthesis of the 6-methyl and 6-benzylthieno[3,2-*b*]pyrrole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

**Scheme 5** Reagents and conditions: (i) $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , DMF, 60°C .

The radical cyclization¹³ of carbamates **12** ($\text{X} = \text{Br}$, I , SePh) was also achieved (Scheme 6, Table 2). When $\text{R}' = \text{H}$, 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**

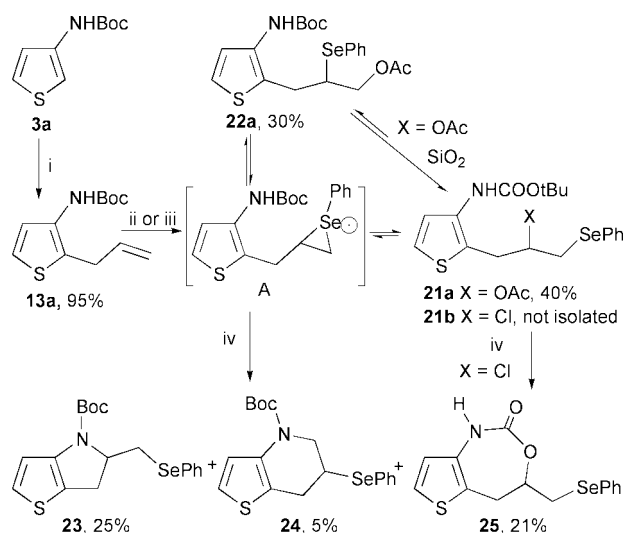
Entry	X	R	R'	Product	Yield (%)
1	Br	H	H	10a	68
2	I	H	H	10a	73
3	SePh	H	H	10a	69
4	Br	H	Me	19	76
5	Br	Me	H	10b	67
6	Br	Ph	H	10c	85

**Scheme 6**

providing the dihydrothienopyrrole **10** with a good yield. Comparable results were observed for $\text{X} = \text{Br}$, 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).

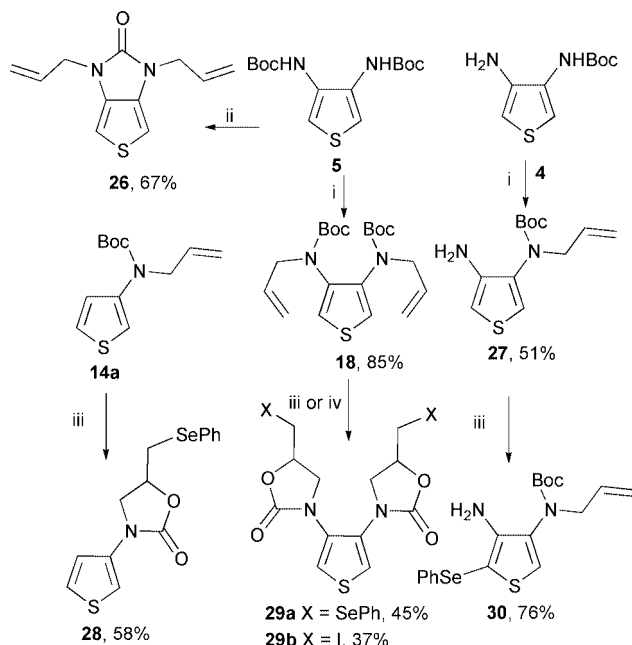
Palladium-catalyzed and radical cyclizations were unsuccessful in the case of dicarbamates **16** and **17**. The cleavage of the C–X bond was never observed. Steric hindrance probably prevents palladium insertion or radical formation.

The electrophilic selenium-induced cyclization method¹⁴ 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*-(phenylselenanyl)phthalimide (NPSP), no reaction was observed even after several days. Phenylselenanyl

**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 (1 eq.); (iii) PhSeSePh (0.6 eq.), $\text{PhI}(\text{OAc})_2$ (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)₂¹⁵ 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-



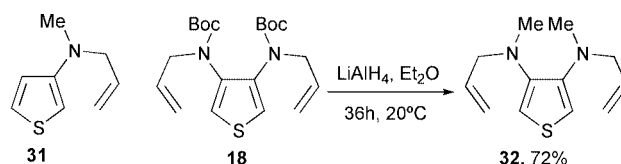
Scheme 8 Reagents and conditions: (i) NaH, THF, allyl bromide, 5 h; (ii) NaH, THF, allyl bromide, 20 h; (iii) PhSeCl, CH₂Cl₂, 20 °C, 12 h; (iv) *N*-iodosuccinimide, CCl₄, Δ, 12 h.

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 amino-carbamate **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%).

PhSeCl treatment of the *N*-allylated thiophenediamine derivative **27** has led to an electrophilic aromatic substitution

providing the 2-phenylselenanylthiophene 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 LiAlH₄ 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 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**,^{7c} *tert*-butyl (2-bromo-3-thienyl)carbamate **6a**,¹⁸ the halothiophene derivatives **6–8** 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 mm, pore diameter *ca.* 4 nm) available from ACROS. ¹H and ¹³C NMR spectrum were recorded on Bruker 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 CH₂Cl₂. 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 (CDCl₃), δ: 7.61 (d, 1H, H⁵, *J* = 5.5 Hz), 7.14 (d, 1H, H⁴, *J* = 5.5 Hz), 6.91 (br s, 1H, NH), 3.63 (s, 1H, CH), 1.50 (s, 9H, CH₃). Anal. calc. for C₁₁H₁₃NO₂S: 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 (CDCl₃), δ: 8.00 (br s, 1H, NH),

[†] The IUPAC name for triflic acid is trifluoromethanesulfonic acid.

7.37 (s, 1H, H⁵), 6.54 (br s, 1H, NH), 3.58 (s, 1H, CH), 1.51 (s, 9H), 1.48 (s, 9H). ¹³C NMR (CDCl₃), δ: 153.8, 152.9 (CO), 132.3, 130.5 (C³, C⁴), 110.9 (C⁵, CH), 88.2 (C), 81.9, 80.2 (C(CH₃)₃), 28.1, 27.9 (CH₃). Anal. calc. for C₁₆H₂₂N₂O₄S: 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: CH₂Cl₂–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%. ¹H NMR (CDCl₃), δ: 7.17 (d, 1H, H⁴, *J* = 5.8 Hz), 6.75 (br s, 1H, H⁵), 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, CH₃). ¹³C NMR (CDCl₃), δ: 153.0 (CO), 139.0 (C³), 132.9 (C⁶), 126.2 (C⁵), 124.0 (C⁴), 116.9 (C_γ), 108.7 (C²), 79.7 (C(CH₃)₃), 50.9 (C_α), 27.6 (CH₃). Anal. calc. for C₁₂H₁₆BrNO₂S: 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%. ¹H NMR (CDCl₃), δ: 7.14 (d, 1H, H⁴, *J* = 5.8 Hz), 6.76 (br s, 1H, H⁵), 4.77 (s, 2H, H_γ), 4.06 (s, 2H, H_α), 1.73 (s, 3H, CH₃), 1.37 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 153.3 (CO), 140.4 (C_β), 139.2 (C³), 126.0 (C⁵), 123.9 (C⁴), 112.3 (C_γ), 108.4 (C₂), 79.7 (C(CH₃)₃), 54.0 (C_α), 27.6 (C(CH₃)₃), 19.6 (CH₃). Anal. calc. for C₁₃H₁₈BrNO₂S: 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: ¹H NMR (CDCl₃), δ: 7.12 (d, 1H, H⁴, *J* = 5.8 Hz), 6.67 (br s, 1H, H⁵), 5.55–5.37 (m, 2H, H_β, H_γ), 3.98 (m, 2H, H_α), 1.54 (d, 3H, H_β, *J* = 7.4 Hz), 1.32 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 153.5 (CO), 139.4 (C³), 128.6 (C_β), 126.6 (C_γ), 125.9 (C⁵), 124.0 (C⁴), 109.1 (C²), 79.9 (C(CH₃)₃), 50.5 (C_α), 27.9 (CH₃), 17.4 (C_β). Anal. calc. for C₁₃H₁₈BrNO₂S: C, 46.99; H, 5.46; N, 4.22; found: C, 47.31; H, 5.72; N, 4.58%. *Z* isomer not isolated: ¹H NMR (CDCl₃), δ: 7.12 (d, 1H, H⁴, *J* = 5.8 Hz), 6.67 (br s, 1H, H⁵), 5.55–5.37 (m, 2H, H_β, H_γ), 4.12 (m, 2H, H_α), 1.45 (d, 3H, H_β, *J* = 7.1 Hz), 1.32 (s, 9H, CH₃).

tert-Butyl *N*-(3-phenylprop-2-enyl)(2-bromo-3-thienyl)carbamate 12d. Oil. Yield = 50%. *E* Isomer: ¹H NMR (CDCl₃), δ: 7.30–7.10 (m, 6H, Ph, H⁴), 6.70 (br s, 1H, H⁵), 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, CH₃). ¹³C NMR (CDCl₃), δ: 153.4 (CO), 136.2 (C_β), 132.3, 129.0, 127.1, 126.3, 126.2, 125.9 (C_{ph}, C_γ, C⁵), 124.0 (C⁴), 109.2 (C²), 80.0 (C(CH₃)₃), 50.5 (C_α), 27.7 (CH₃). Anal. calc. for C₁₈H₂₀BrNO₂S: 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%. ¹H NMR (CDCl₃), δ: 7.17 (d, 1H, H⁴, *J* = 5.8 Hz), 6.75 (br s, 1H, H⁵), 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, CH₃). ¹³C NMR (CDCl₃), δ: 153.6 (CO), 133.5 (C_β), 129.6 (C⁵), 123.5 (C⁴), 117.5 (C_γ), 116.0 (C²), 80.3 (C(CH₃)₃), 51.6 (C_α), 28.1 (CH₃). Anal. calc. for

C₁₂H₁₆INO₂S: 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%. ¹H NMR (CDCl₃), δ: 7.32–7.28 (m, 6H, Ph, H⁴), 6.81 (br s, 1H, H⁵), 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, CH₃). ¹³C NMR (CDCl₃), δ: 154.1 (CO), 144.6 (C³), 133.7 (C_β), 130.4 (C⁵), 132.5, 129.0, 127.4 (Ph), 126.7 (C⁴), 117.1 (C_γ), 80.9 (C(CH₃)₃), 52.2 (C_α), 28.0 (CH₃). Anal. calc. for C₁₈H₂₁NO₂SSe: 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%. ¹H NMR (CDCl₃), δ: 7.17 (s, 1H, H⁵), 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, CH₃), 1.38 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 153.8, 152.9 (CO), 133.3 (C_β), 125.9 (C⁵), 117.6, 116.5 (C_γ), 80.3, 80.1 (C(CH₃)₃), 51.9, 50.9 (C_α), 27.8 (CH₃). Anal. calc. for C₂₀H₂₉IN₂O₄S: 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%. ¹H NMR (CDCl₃), 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, CH₃), 1.37 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 152.9 (CO), 133.5, 133.0 (C_β), 118.6, 118.0, 117.4 (C_γ), 80.9 (C(CH₃)₃), 50.8 (C_α), 28.0 (CH₃). Anal. calc. for C₂₀H₂₈Br₂N₂O₄S: 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%. ¹H NMR (CDCl₃), 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, CH₃), 1.39 (s, 9H, CH₃). ¹³C NMR (CDCl₃), 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(CH₃)₃), 52.3, 50.9 (C_α), 28.1 (CH₃). Anal. calc. for C₂₀H₂₈I₂N₂O₄S: 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(PPh₃)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–CH₂Cl₂, 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**. ¹H NMR (CDCl₃), δ: 7.30 (br s, 1H, H²), 7.13 (m, 2H, H³, H⁵), 2.20 (s, 3H, CH₃), 1.63 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 148.3 (CO), 137.4 (C^{3a}), 128.2 (C^{6a}), 124.2 (C²), 120.8 (C⁵), 115.7 (C⁶), 114.9 (C³), 82.8 (C(CH₃)₃), 27.7 (CH₃), 10.8 (CH₃). Anal. calc. for C₁₂H₁₅NO₂S: 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%. ¹H NMR (CDCl₃), δ: 7.40–7.20 (m, 7H, Ph, H², H⁵), 7.11 (d, 1H, H³, *J* = 5.5 Hz), 4.90 (s, 2H, CH₂), 1.63 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 148.6 (CO), 140.3, 128.3, 127.3, 125.2 (C_{ph}), 138.4 (C^{3a}), 128.2 (C^{6a}), 124.9 (C²), 120.8 (C⁵), 114.8 (C₆), 111.1 (C³), 83.3 (C(CH₃)₃), 32.6 (CH₂), 27.7 (CH₃). Anal. calc. for C₁₈H₁₉NO₂S: 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–CH₂Cl₂, 80:20, then CH₂Cl₂) 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%. ¹H NMR (CDCl₃), δ: 7.16, 6.87 (2br s, 1H, H²), 7.06 (d, 1H, H³, *J* = 5.1 Hz), 4.47–4.37 (m, 1H, H⁵), 3.85–3.76 (m, 1H, H⁵), 3.59–3.48 (m, 1H, H₆), 1.53 (s, 9H, CH₃), 1.29 (d, 3H, CH₃, *J* = 6.7 Hz). ¹³C NMR (CDCl₃), δ: 151.2, 150.9 (CO), 144.5, 143.7 (C^{3a}), 128.9, 128.4 (C^{6a}), 126.7 (C²), 116.0, 115.6 (C³), 80.2, 79.6 (C(CH₃)₃), 60.3, 59.8 (C⁵), 33.7, 33.0 (C⁶), 28.0, 27.7 (CH₃), 21.3 (CH₃). Anal. calc. for C₁₂H₁₇NO₂S: 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⁺, 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%. ¹H NMR (CDCl₃), δ: 7.16, 6.86 (2br s, 1H, H²), 7.02 (d, 1H, H³, *J* = 4.8 Hz), 4.37–4.30 (m, 1H, H⁵), 3.88–3.82 (m, 1H, H⁶), 3.35–3.23 (m, 1H, H⁵), 1.57 (m, 2H, CH₂), 1.49 (s, 9H, CH₃), 0.94 (t, 3H, CH₃, *J* = 7.4 Hz). ¹³C NMR (CDCl₃), δ: 151.2 (CO), 145.0, 144.5 (C^{3a}), 127.4 (C^{6a}), 126.8 (C²), 116.1, 115.7 (C³), 80.5, 79.9 (C(CH₃)₃), 58.6, 58.1 (C⁵), 41.0, 40.2 (C⁶), 28.9 (CH₂), 28.2 (CH₃), 11.4 (CH₃). Anal. calc. for C₁₃H₁₉NO₂S: 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%. ¹H NMR (CDCl₃), δ: 7.24–6.82 (m, 7H, Ph, H², H³), 4.34–4.10 (m, 1H, H⁵), 3.95–3.76 (m, 1H, H⁵), 3.72–3.55 (m, 1H, H⁶), 2.85–2.60 (m, 2H, CH₂), 1.53 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 151.1 (CO), 144.4 (C^{3a}), 138.5, 128.8, 128.3, 127.2, 126.4 (C_{Ph}, C², C^{6a}), 115.8 (C³), 80.2 (C(CH₃)₃), 57.8 (C⁵), 41.8 (CH₂), 40.2 (C⁶), 28.2 (CH₃). Anal. calc. for C₁₈H₂₁NO₂S: 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%. ¹H NMR (CDCl₃), δ: 7.42 (br s, 1H, H²), 6.98 (d, 1H, H³, *J* = 5.5 Hz), 4.00 (m, 1H, H⁵), 3.06 (dd, 1H, H⁵, *J* = 9.7, 12.6 Hz), 2.86 (dd, 1H, H⁷, *J* = 5.6, 16.2 Hz), 2.37 (dd, 1H, H⁷, *J* = 9.0, 16.2 Hz), 2.22–2.02 (m, 1H, H⁶), 1.52 (s, 9H, CH₃), 0.88 (d, 3H, CH₃, *J* = 7.7 Hz). ¹³C NMR (CDCl₃), δ: 152.6 (CO), 135.0 (C^{3a}), 123.0 (C²), 121.0 (C^{6a}), 120.3 (C⁵), 80.4 (C(CH₃)₃), 49.8 (C⁵), 31.2 (C⁷), 28.2 (CH₃), 28.1 (C⁶), 18.1 (CH₃). Anal. calc. for C₁₃H₁₉NO₂S: 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. ¹H NMR (CDCl₃), δ: 7.04 (d, 1H, H², *J* = 5.1 Hz), 6.85 (d, 1H, H³, *J* = 5.1 Hz), 3.97 (m, 2H, H⁵), 1.51 (s, 9H, CH₃), 1.36 (s, 6H, CH₃).

Preparation of *tert*-butyl 2-allyl-3-thienylcarbamate 13a¹⁶

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–CH₂Cl₂, 50:50). Mp = 70 °C, yield = 95%. ¹H NMR (CDCl₃), δ: 7.30 (br s, 2H, H⁵), 7.02 (d, 1H, H⁴, *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-λ³-iodanyl)benzene (0.754 g, 2.6 mmol) were added to a solution of **13a** (0.478 g, 2 mmol) in CH₃CN (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–CH₂Cl₂, 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%. ¹H NMR (CDCl₃), δ: 7.48–7.44 (m, 2H, Ph), 7.24–7.19 (m, 4H, Ph, H⁵), 7.02 (d, 1H, H⁴, *J* = 5.5 Hz), 6.90 (br s, 1H, NH), 4.99 (m, 1H, CHOAc), 3.12–2.93 (m, 4H, CH₂, CH₂), 1.92 (s, 3H, CH₃), 1.44 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 170.2 (CO), 152.9 (CO), 134.2, 132.6, 129.1, 128.1 (Ph), 122.4 (C⁵), 80.3 (C(CH₃)₃), 74.0 (CHOAc), 31.5 (CH₂), 30.3 (CH₂), 28.2 (CH₃), 20.9 (CH₃). IR (KBr): 3344, 3058, 2978, 2931, 1731, 1582, 1368 cm^{–1}. Anal. calc. for C₂₀H₂₅NO₄Se: 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%. ¹H NMR (CDCl₃), δ: 7.50–7.48 (m, 2H, Ph), 7.25–7.19 (m, 4H, Ph, H⁵), 7.05 (d, 1H, H⁴, *J* = 5.5 Hz), 6.60 (br s, 1H, NH), 4.25 (dd, 1H, CH₂OAc, *J* = 4.7, 11.6 Hz), 4.11 (dd, 1H, CH₂OAc, *J* = 7.7, 11.6 Hz), 3.46–3.40 (m, 1H, CHSePh), 3.17–3.02 (m, 2H, CH₂), 2.04 (s, 3H, CH₃), 1.43 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ: 170.2 (CO), 152.9 (CO), 134.7, 133.5, 129.2, 128.1 (Ph), 122.4 (C⁵), 80.0 (C(CH₃)₃), 65.5 (CH₂OAc), 43.9 (CHSePh), 29.2 (CH₂), 28.2 (CH₃), 20.8 (CH₃). Anal. calc. for C₂₀H₂₅NO₄Se: 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 CH₂Cl₂ 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. ¹H NMR (CDCl₃), δ: 7.52–7.47 (m, 2H, Ph), 7.24–7.17 (m, 4H, Ph, H⁵), 7.06 (d, 1H, H⁴, *J* = 5.4 Hz), 6.60 (br s, 1H, NH), 4.15–4.05 (m, 1H, CHCl), 3.37 (dd, 1H, *J* = 3.9 Hz, 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, CH₃). ¹³C NMR (CDCl₃), δ: 153.1 (CO), 134.0, 133.2, 129.3, 127.7 (Ph), 122.6 (C⁵), 117.0 (C⁴), 80.3 (C(CH₃)₃), 61.8 (CHCl), 34.3 (CH₂), 33.7 (CH₂), 28.2 (CH₃).

Cyclization of the β-chloro phenylselenide 21b

A solution of the crude addition product **21b** (0.862 g, 2 mmol) in CH₂Cl₂ 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: CH₂Cl₂–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%. ¹H NMR (CDCl₃), δ: 7.46–7.44 (m, 2H, Ph), 7.30 (br s, 1H, H²), 7.21–7.19

(m, 3H, Ph), 6.97 (d, 1H, H³, $J = 5.4$ Hz), 3.73–3.83 (m, 1H, H⁵), 3.05–2.73 (m, 4H, H⁶, CH₂), 1.42 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ : 153.4 (CO), 134.5, 133.3, 129.2, 127.5 (Ph), 121.5 (C²), 110.3 (C³), 71.0 (C⁵), 35.5 (CH₂), 32.9 (CH₂), 28.3 (CH₃). Anal. calc. for C₁₈H₂₁NO₂SSe: 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%. ¹H NMR (CDCl₃), δ : 7.50–7.48 (m, 2H, Ph), 7.31 (br s, 1H, H²), 7.21–7.19 (m, 3H, Ph), 7.03 (d, 1H, H³, $J = 5.2$ Hz), 3.52 (m, 2H, H⁵), 3.41–3.37 (m, 1H, H⁶), 3.11–3.08 (m, 2H, H₇), 1.42 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ : 154.0 (CO), 134.8, 129.2, 128.1 (Ph), 62.0 (C⁵), 48.8 (C⁶), 28.3 (C⁷), 28.2 (CH₃). Anal. calc. for C₁₈H₂₁NO₂SSe: 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%. ¹H NMR (CDCl₃), 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, H², $J = 5.3$ Hz), 6.57 (d, 1H, H³, $J = 5.3$ Hz), 4.66–4.63 (m, 1H), 3.35–3.25 (m, 2H, CH₂), 3.12–3.03 (m, 2H, CH₂). ¹³C NMR (CDCl₃), δ : 156.2 (CO), 133.4, 131.6, 129.3, 127.6 (Ph), 121.4 (C²), 117.0 (C³), 78.4 (C⁷), 33.0 (CH₂), 31.4 (CH₂). Anal. calc. for C₁₄H₁₃NO₂SSe: 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⁺, 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–CH₂Cl₂, 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–CH₂Cl₂, 50 : 50).

tert-Butyl *N*-allyl-3-thienylcarbamate 14a.¹⁶ Oil. Yield = 51%. ¹H NMR (CDCl₃), δ : 7.13 (m, 1H, H⁵), 7.07 (m, 1H, H⁴), 6.97 (m, 1H, H²), 6.00–5.80 (m, 1H, H_β), 5.27–5.11 (m, 2H, H_α), 4.09 (d, 2H, H_α, $J = 5.7$ Hz), 1.44 (s, 9H, CH₃). ¹³C NMR (CDCl₃), 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-diyl dicarbamate 18. Oil. Yield = 85%. ¹H NMR (CDCl₃), δ : 7.00 (br s, 2H, H², H⁶), 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, CH₃). ¹³C NMR (CDCl₃), δ : 154.1 (CO), 134.0 (C_β), 131.7 (C³, C⁴), 118.0 (C², C⁵), 116.4 (C_γ), 80.1 (C(CH₃)₃), 44.7 (C_α), 28.1 (CH₃). MS (EI, 70 eV): 294 (M⁺, 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%. ¹H NMR (CDCl₃), δ : 6.24 (s, 2H, H⁴, H⁶), 5.97–5.77 (m, 2H, H_β), 5.32–5.20 (m, 4H, H_γ), 4.36 (m, 4H, H_α). ¹³C NMR (CDCl₃), 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 C₁₁H₁₂N₂O₂S: 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⁺, 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%. ¹H NMR (CDCl₃), δ : 6.90 (d, 1H, H², $J = 3.4$ Hz),

6.14 (d, 1H, H⁵, $J = 3.4$ Hz), 6.00–5.80 (m, 1H, H_β), 5.27–5.11 (m, 2H, H_α), 4.09 (d, 2H, H_α, $J = 5.7$ Hz), 3.57 (br s, 2H, NH²), 1.44 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ : 154.0 (CO), 141.2 (C³), 133.7 (C⁴), 133.2 (C_β), 117.8 (C²), 116.6 (C_γ), 99.8 (C⁵), 80.5 (C(CH₃)₃), 52.9 (C_α), 27.9 (CH₃). Anal. calc. for C₁₂H₁₈N₂O₂S: 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 CH₂Cl₂ (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: CH₂Cl₂). 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–CH₂Cl₂, 50 : 50).

5-(Phenylselanylmethyl)-3-(3-thienyl)-1,3-oxazolidin-2-one

28. Oil. Yield = 58%. ¹H NMR (CDCl₃), δ : 7.51–7.50 (m, 2H, Ph), 7.32–7.29 (m, 5H, Ph, H⁴, H⁵), 6.87 (s, 1H, H²), 4.71–4.64 (m, 1H, H⁵), 4.00 (t, 1H, H⁴, $J = 8.8$ Hz), 3.66 (dd, 1H, H⁴, $J = 8.8$, 6.3 Hz), 3.27 (dd, 1H, CH₂Se, $J = 4.3$, 12.9 Hz), 2.97 (dd, 1H, CH₂Se, $J = 9.2$, 12.9 Hz). ¹³C NMR (CDCl₃), δ : 153.8 (C²), 136.4 (C³), 133.4, 129.3, 127.9 (Ph), 125.4 (C⁴), 119.4 (C⁵), 107.2 (C²), 72.1 (C⁵), 51.5 (C⁴), 30.9 (CH₂Se). Anal. calc. for C₁₄H₁₃NO₂SSe: 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

29a. Yield = 45%. ¹H NMR (CDCl₃), δ : 7.48–7.46 (m, 4H, Ph), 7.22–7.19 (m, 6H, Ph), 7.03 (s, 2H, H², H⁵), 4.66–4.61 (m, 2H, H⁵), 4.02 (t, 2H, H⁴, $J = 8.6$ Hz), 3.75–3.67 (m, 2H, H⁴), 3.27 (dd, 2H, CH₂Se, $J = 3.4$, 12.8 Hz), 3.08–3.00 (m, 2H, CH₂Se). ¹³C NMR (CDCl₃), δ : 155.2 (C²), 133.3, 132.0, 129.3, 127.8 (Ph), 128.0 (C⁴), 119.2 (C⁵), 73.1 (C⁵), 52.5 (C⁴), 30.7 (CH₂Se). Anal. calc. for C₂₄H₂₂N₂O₄SSe₂: 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

30. Oil. Yield = 76%. ¹H NMR (CDCl₃), δ : 7.59–7.55 (m, 2H, Ph), 7.23–7.19 (m, 3H, Ph), 7.12 (s, 1H, H²), 5.96–5.78 (m, 1H, H_β), 5.19–5.08 (m, 2H, H_γ), 3.91–4.11 (m, 4H, H_α, NH²), 1.43 (s, 9H, CH₃). ¹³C NMR (CDCl₃), δ : 153.9 (CO), 147.1 (C⁴), 133.7 (C³), 133.4, 129.0, 127.8, 125.9 (Ph), 132.9 (H_β), 117.3 (H_γ), 53.6 (H_α), 80.8 (C(CH₃)₃), 28.1 (CH₃). Anal. calc. for C₁₈H₂₂N₂O₂SSe: 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 CCl₄ (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%. ¹H NMR (CDCl₃), δ : 7.19 (s, 1H, H²), 7.18 (s, 1H, H⁵), 4.80–4.61 (m, 2H, H⁵), 4.16 (t, 2H, H⁴, $J = 8.7$ Hz), 3.83–3.74 (m, 2H, H⁴), 3.42 (d, 4H, CH₂I, $J = 6.4$ Hz). Anal. calc. for C₁₂H₁₂I₂N₂O₄S: 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⁺, 17), 406 (30), 363 (100), 254 (75), 235 (27), 144 (50), 127 (53). MS (desorption chemical ionisation, DCI, pos., isobutane): 585 ((MH + C₄H₉)⁺, 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%. ^1H 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 $\text{C}_{12}\text{H}_{18}\text{N}_2\text{S}$: C, 64.82; H, 8.16; N, 12.60; found: C, 64.97; H, 8.22; N, 12.77%.

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