



α -Vinylolation of β -Aminothiophene Derivatives. Synthesis of 6-Functionalized Thieno[3,2-b]pyridines

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Abstract : The acid-catalyzed reductive α -alkylation of β -aminothiophenes was applied to the N-(thien-3-yl)acetamide and alkyl N-(thien-3-yl)carbamates. Without reduction, β -amino α -vinylthiophenes were obtained when α -branched aldehydes were used. β -(3-Aminothiien-2-yl) α,β -unsaturated ketones, esters and nitriles were also prepared from the corresponding α -functionalized acetals. These amines are intermediates in the formation of thieno[3,2-b]pyridines bearing a functional group at the β -position of the pyridine ring. © 1998 Elsevier Science Ltd. All rights reserved.

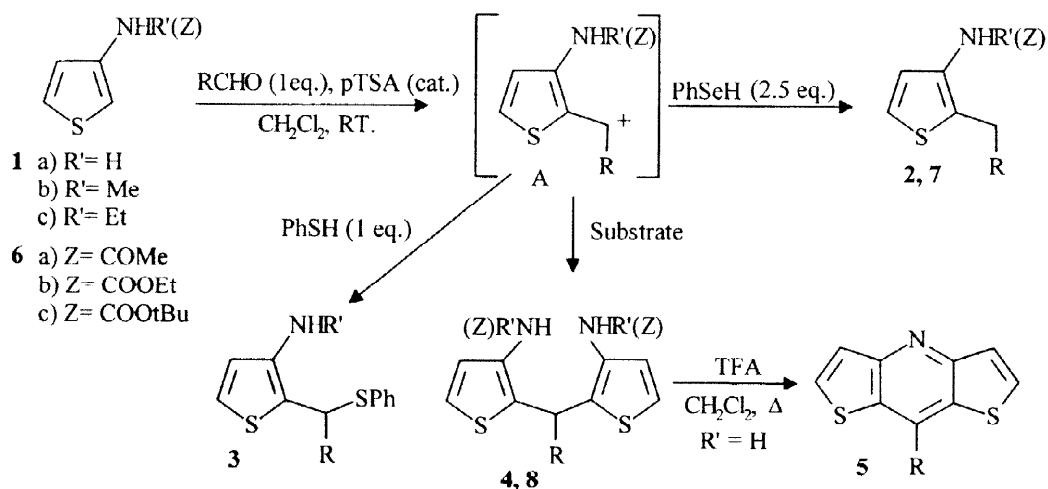
The strong enamino character of β -aminothiophenes and β,β' -diaminothiophenes allows reactions with various electrophilic reagents¹. We have prepared 2-alkyl 3-thiophenamines **2** in good yields, by treatment of amine **1**, at room temperature, with an aldehyde and an excess of selenophenol in dichloromethane under acid catalysis. Without PhSeH, one-half equivalent of aldehyde led to 2,2'-alkylidenebis(3-thiophenamines) **4**^{2,3}. As shown in Scheme 1, the intermediate carbonium ion A is reduced by selenophenol leading to compound **2** but which can be trapped by thiophenol giving the thioether **3**. For the formation of **4**, the intermediate A is a good electrophile for a second molecule of substrate. A loss of hydrogen followed by an acid-catalyzed "transamination" were proposed to explain the cyclization of the free amines **4** (R' = H) into dithienopyridines **5**. In continuation of this work, we have found that the same reactions can be carried out on acetamide **6a** and alkyl thien-3-ylcarbamates **6b** and **6c**. 2-Alkyl 3-thiophenamine derivatives **7** and (alkylidene-2,3-thienylene) bisacetamides and biscarbamates **8** were prepared in good yields. Compounds **8** were obtained with one-half equivalent of aldehyde under pTSA catalysis but also in the presence of a conc. HCl solution (Scheme 1, Table 1).

We observed, as for amines **1**, that the reaction failed with ketones and that α -methylation of the thiophene ring of carbamate **6c** can be achieved, in a clean reaction, with an aqueous solution of formaldehyde (Table 1, entry 5), although 3-thiophenamines **1** have led to complex mixtures^{2,3}.

We have previously noted lower yields of alkylated thiophenes **2** when amines **1** were treated with α -branched aldehydes^{2,3} and that bis(aminothiienyl)methane derivatives **4** were obtained when one-half equivalent of the same aldehyde was added in the presence of a conc. HCl solution at room temperature. We

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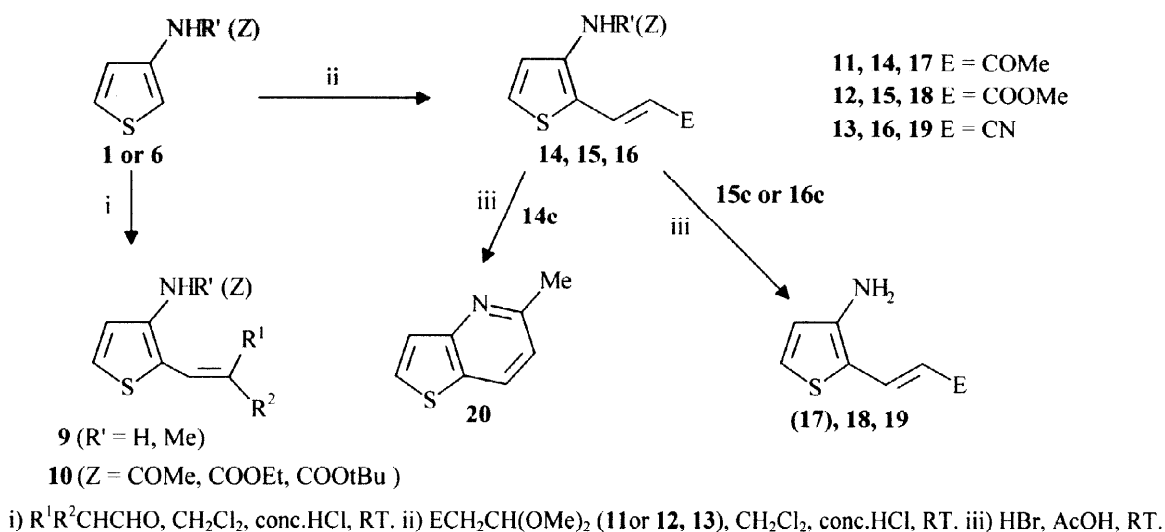
were however surprised to isolate 2-(alk-1-enyl) 3-aminothiophenes **9** when one equivalent of α -branched aldehyde was used. Comparable results were obtained with acetamide **6a**, carbamates **6b** and **6c**. The corresponding acetamides and carbamates **10** were prepared in good yields (Scheme 2, Table 2). A cis/trans isomer mixture was isolated for $R^1, R^2 \neq H$. Noe experiments have shown that the E isomer is the major product.



Scheme 1

Table 1 : (2-Alkyl 3-thienyl) acetamides and carbamates **7**, bisacetamides and biscarbamates **8**.

Entry	N°	Z	R	Yield (%)
1	7a	COMe	Et	50
2	7b	COMe	Ph	68
3	7c	COOEt	Et	75
4	7d	COOEt	Ph	66
5	7e	COOtBu	H	70
6	7g	COOtBu	Ph	65
7	8a	COMe	Et	85
8	8b	COMe	Ph	90
9	8c	COOEt	Et	87
10	8d	COOEt	Ph	80
11	8e	COOtBu	Ph	63



Scheme 2

Table 2 : Preparation of 2-(alk-1-enyl) 3-aminothiophenes **9**, acetamides and carbamates **10**.

Entry	N°	R' or Z	R ¹	R ²	Yield %
1	9a	H	Me	Me	70
2	9b	H	Me	Et	60
3	9c	H	Me	iPr	58
4	9d	H	Me	Ph	57
5	9e	H	-(CH ₂) ₅ -		60
6	9f	Me	Me	Me	75
7	10a	COMe	Me	Me	80
8	10b	COMe	Me	Et	75
9	10c	COOEt	Me	Me	82
10	10d	COOEt	Me	Et	80
11	10e	COOEt	Me	nPr	77
12	10f	COOEt	Et	Et	65
13	10g	COOEt	-(CH ₂) ₅ -		75
14	10h	COOEt	H	Ph	66
15	10i	COOtBu	H	Ph	87

From these results, we can conclude that whatever the nature of the aliphatic aldehyde, the reduction of the carbonium ion A, with PhSeH, occurs faster than its capture by a second molecule of substrate. The elimination reaction, leading to the α -vinyl substituent, is only efficient when two alkyl groups are present on the vicinal carbon atom of the carbonium ion. With linear aldehydes, no olefinic compounds were isolated and the dithienylmethane derivatives **4** were only formed. The small difference of stability of the carbonium ions

A controls the second reaction. The elimination is favoured when an R¹ (or R²) is an aryl substituent (Table 2, entries 14 and 15).

This result has led us to study the reaction with α -functionalized aldehydes. Considering their instability, we used the acetals **11** (E = COMe), **12** (E = COOMe) and **13** (E = CN) which were opposed to the acetamide **6a**, carbamates **6b**, **6c** in the presence of a conc. HCl aqueous solution. As expected, the corresponding α,β -unsaturated ketones **14**, esters **15** and nitriles **16** were obtained in good yields (Scheme 2, Table 3).

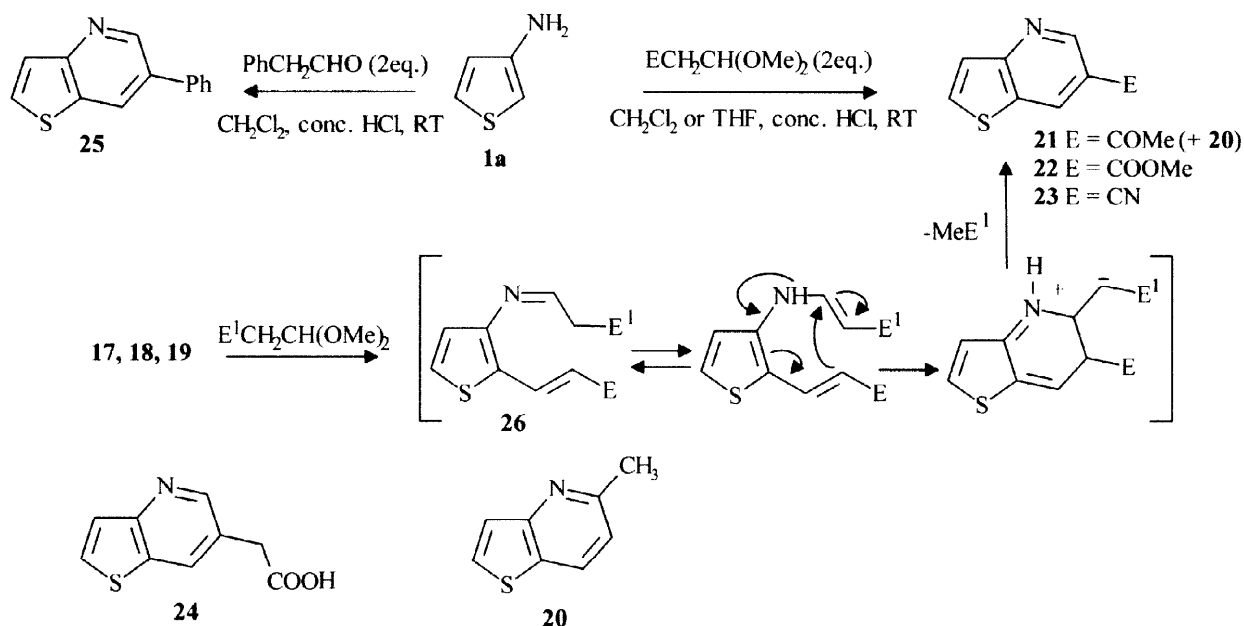
Table 3 : β -(3-Amino 2-thienyl) α,β -unsaturated ketone, ester and nitrile derivatives **14**, **15** and **16**.

Entry	N°	Z	E	Yield (%)
1	14a	COMe	COMe	70
2	14b	COOEt	COMe	67
3	14c	COOtBu	COMe	80
4	15a	COMe	COOMe	88
5	15b	COOEt	COOMe	85
6	15c	COOtBu	COOMe	75
7	16a	COMe	CN	63
8	16b	COOEt	CN	70
9	16c	COOtBu	CN	83

The ¹H NMR spectra showed, in each case, the formation of the E isomer except for the nitrile **16b** (E/Z = 55/45). In the next step, we were able to isolate the amino-ester **18** and the amino-nitrile **19** through the acidic cleavage of the corresponding t-butyl carbamates **15c** and **16c**. The hydrolysis of the keto-carbamate **14c** has caused the fast cyclization into 5-methylthieno[3,2-b]pyridine **20** without isolation of the amino-ketone **17** (Scheme 2). The thienopyridine **20** was previously obtained from one equivalent of the diethylacetal analogous to **11**, and the bis(3-thienylammonium) hexachlorostannate, in the presence of ZnCl₂ in ethanol at reflux⁴. Later, Klemm and coll.⁵ have observed the formation of 5-acetylthieno[3,2-b]pyridine **21** when a conc. HCl aqueous solution was used instead of ZnCl₂. The methylthienopyridine **20** was not formed when the reaction was carried out in n-butanol⁶. In these works, however, five equivalents of ketoacetal were added. Formation of acetone was observed during the formation of acetylthienopyridine **21**⁵.

In our hands, the reaction of amine **1a** with acetal **11** (2 eq.) in CH₂Cl₂ at room temperature under acidic conditions, has led to a 35/65 mixture of methylthienopyridine **20** and acetylthienopyridine **21**. The methyl ester **22** and the nitrile **23** were prepared using to the same procedure with acetals **12** and **13**, respectively. Another compound, not isolated in a pure form, probably the 5-(thieno[3,2-b]pyridyl) acetic acid **24** was obtained besides the nitrile **23** (**23/24** : 70/30). The formation of **24** was not explained but can be avoided when the reaction was achieved in THF. To complete our study, we have verified that amine **1a** and phenylethanal led to the 6-phenylthienopyridine **25**.

Our results agree with the mechanism shown in Scheme 3 excluding the precedent proposition⁵. α -Vinyl β -aminothiophenes **17–19** are intermediates in the reaction giving the thienopyridines **21–23**. They react with a second molecule of functionalized aldehyde leading to imines **26** whose enaminic forms cyclise by formation of a bond between the β -carbon of the vinyl group and the iminic carbon. The aromatization of the structure is provided by the loss of acetone (for **21**), methyl acetate (for **22**) and acetonitrile (for **23**).



Scheme 3

To confirm the proposed mechanism, we have verified that the reaction of amino-ester **18** with the acetal **11** gave also the ester **22** and that amino-nitrile **19** treated with acetal **12** led to nitrile **23**. The functional group E present at the 5-position of the thienopyridine ring is introduced during the α -vinylation of the thiophene nucleus. The study concerning the reactivity of amines **1** and derivatives **6** is now directed to the synthesis of α -allyl β -aminothiophenes.

EXPERIMENTAL SECTION

Amine **1a** was prepared by the method described by Reinecke and Coll.⁷, stored in the refrigerator, in ethereal solution and distilled under reduced pressure just before use. N-Methylamine (**1b**) was obtained by N-methylation of **1a**⁸ and the acetamide **6a** by acylation of the same amine⁹. The carbamates **6b** (Z= COOEt)⁷ and **6c** (Z= COOtBu)¹⁰ were synthesized according to conventional procedures: **6b** (M.p. 71°C, Yield: 80%), **6c** (M.p. 137°C, Yield: 86%). ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker AC 200 spectrometer. Elemental analysis were performed on a Carlo Erba CHNS-01106 automatic analyzer. The

chromatographic purifications were carried out on silica gel (0.060-0.200mm pore diameter ca. 4nm)(Acros) or on basic activated aluminium oxide (Brockman I, standard grade)(Aldrich).

Synthesis of the (2-alkylthien-3-yl)acetamides and carbamates 7 : A cold solution of aldehyde (1.1mmol) in dichloromethane (10ml) containing selenophenol (392mg ; 2.5mmol) was quickly added under stirring to the amide **6a** (carbamates **6b** or **6c**) (1mmol) in dichloromethane (20ml) at 0°C. A solution of p-toluenesulfonic acid (20mg) in the same solvent (dissolved on heating) was then added dropwise. The mixture was stirred for 3 h at r.t. and treated with a 4N NaOH solution (10ml). The organic layer was separated, washed with water, dried and evaporated. The residue was purified by chromatography on silica gel (elution: hexane/ CH₂Cl₂ 50/50). An aqueous solution of formaldehyde (37%) was used for the preparation of **7f**.

N-(2-Propylthien-3-yl)acetamide 7a. Yield : 50%. M.p. 50°C ; ¹H NMR (CDCl₃), δ: 7.17(d, 1H, H₅, J= 5.4Hz), 6.99(d, 1H, H₄, J= 5.4Hz), 2.61(t, 2H), 1.82(m, 2H), 1.03(t, 3H), 2.16(s, 3H). Anal. Calc.for C₉H₁₃NOS (183.268) : C, 58.97 ; H, 7.15 ; N, 7.64. Found : C, 59.18; H, 7.23; N, 7.72.

N-(2-Benzylthien-3-yl)acetamide 7b. Yield : 68%. M.p. 70°C ; ¹H NMR (CDCl₃), δ: 7.19(d, 1H, H₅, J= 5.4Hz) ; 7.01(d, 1H, H₄, J= 5.4Hz) ; 3.39(s, 2H) ; 7.23(brs, 5H) ; 2.17(s, 3H). Anal. Calc.for C₁₃H₁₃NOS (231.308) : C, 67.52 ; H, 5.66 ; N, 6.06. Found : C, 67.13; H, 5.47; N, 5.82.

Ethyl (2-propylthien-3-yl)carbamate 7c. Yield : 75%. oil ; ¹H NMR (CDCl₃), δ: 7.17(d, 1H, H₅, J= 5.4Hz), 7.01(d, 1H, H₄, J= 5.4Hz), 2.61(t, 2H), 1.79(m, 2H), 0.97(t, 3H), 1.29(t, 3H) ; 4.14(q, 2H). Not obtained in a pure form.

Ethyl (2-benzylthien-3-yl)carbamate 7d. Yield : 66%. M.p. 85°C ; ¹H NMR (CDCl₃), δ: 7.22(d, 1H, H₅, J= 5.4Hz) ; 7.07(d, 1H, H₄, J= 5.4Hz) ; 4.01(s, 2H) ; 7.24(brs, 5H) ; 1.26(t, 3H).4.17(q, 2H). Anal. Calc.for C₁₄H₁₅NO₂S (261.334) : C, 64.34 ; H, 5.78 ; N, 5.36. Found : C, 64.57; H, 5.53; N, 5.47.

t-Butyl (2-methylthien-3-yl)carbamate 7e. Yield : 70%. M.p. 102°C ; ¹H NMR (CDCl₃), δ: 7.22(d, 1H, H₅, J= 5.4Hz) ; 6.98(d, 1H, H₄, J= 5.4Hz) ; 2.27(s, 3H) ; 1.48(s, 9H). Anal. Calc.for C₁₀H₁₅NO₂S (213.294) : C, 56.31 ; H, 7.09 ; N, 6.57. Found : C, 56.23; H, 7.32; N, 6.72.

t-Butyl (2-benzylthien-3-yl)carbamate 7f. Yield : 65%. M.p. 87°C ; ¹H NMR (CDCl₃), δ: 7.21(d, 1H, H₅, J= 5.4Hz) ; 7.03(d, 1H, H₄, J= 5.4Hz) ; 4.03(s, 2H) ; 7.27(brs, 5H) ; 1.47(s, 9H). Anal. Calc.for C₁₆H₁₉NO₂S (289.38) : C, 66.40 ; H, 6.61 ; N, 4.84. Found : C, 66.35; H, 6.28; N, 4.82.

Synthesis of the bisacetamides and biscarbamates 8 : The aldehyde (1.1mmol) was added to a solution of the amide **6a** (carbamate **6b** or **6c**) (2mmol) in CH₂Cl₂ (20ml). A conc. HCl solution (0.5ml) was introduced dropwise. A precipitate appeared after 2 min. The mixture was stirred for 40 min. at r.t. and the solid was isolated and washed with CH₂Cl₂ (30ml). After treatment with a 1N NaOH solution (10ml), the organic layer was separated and the aqueous solution extracted with the same solvent(25ml). The organic fractions were dried and evaporated under reduced pressure and the solid residue was crystallized in hexane.

N,N'-[2,2'-Propylidenebis(thien-3-yl)]bisacetamide 8a. Yield : 85%. M.p. 150°C ; ¹H NMR (CDCl₃), δ: 7.12(d, 2H, H₅, J= 5.4Hz), 7.06(d, 2H, H₄, J= 5.4Hz), 4.27(t, 1H), 2.12(m, 2H), 1.02(t, 3H), 2.19(s, 6H). ¹³C NMR (CDCl₃), δ: 122.4(C₄) ; 123.9(C₅) ; 41.15(C₆) ; 28.4(CH₂) ; 13.5(CH₃). Anal. Calc.for C₁₅H₁₈N₂O₂S₂ (332.442) : C, 55.87 ; H, 5.63 ; N, 8.69. Found : C, 56.09; H, 5.72; N, 8.53.

N,N'-[2,2'-Benzylidenebis(thien-3-yl)]bisacetamide 8b. Yield : 90%. M.p. 200°C ; ¹H NMR (CDCl₃), δ: 7.21(d, 2H, H₅, J= 5.4Hz), 7.07(d, 2H, H₄, J= 5.4Hz), 5.78(s, 1H), 7.33(brs, 5H), 2.17(s, 6H). ¹³C NMR

(CDCl₃), δ : 122.5(C₄); 124.1(C₅); 41.2(C₆); 127.8–128.9(C_{Ph}); 13.5(CH₃). Anal. Calc. for C₁₉H₁₈N₂O₂S₂ (370.482): C, 61.59; H, 4.90; N, 7.56. Found: C, 61.06; H, 4.96; N, 8.04.

Diethyl [2,2'-propylidenebis(thien-3-yl)]biscarbamate 8c. Yield: 87%. M.p. 105°C; ¹H NMR (CDCl₃), δ : 7.20(d, 2H, H₅, J = 5.4Hz), 7.08(d, 2H, H₄, J = 5.4Hz), 4.35(t, 1H); 2.18(m, 2H); 1.1(t, 3H), 4.16(q, 2H), 1.26(t, 3H). ¹³C NMR (CDCl₃), δ : 122.7(C₄); 124.2(C₅); 41.4(C₆); 27.7(CH₂); 14(CH₃). Anal. Calc. for C₁₇H₂₂N₂O₄S₂ (382.494): C, 53.38; H, 5.79; N, 7.32. Found: C, 53.61; H, 5.93; N, 7.47.

Diethyl [2,2'-benzylidenebis(thien-3-yl)]biscarbamate 8d. Yield: 80%. M.p. 154°C; ¹H NMR (CDCl₃), δ : 7.23(d, 2H, H₅, J = 5.4Hz), 7.11(d, 2H, H₄, J = 5.4Hz), 5.80(s, 1H); 7.26(m, 5H); 4.18(q, 2H); 1.29(t, 3H). ¹³C NMR (CDCl₃), δ : 123 (C₄); 124.7(C₅); 41.4(C₆); 127.5–128.6(C_{Ph}). Anal. Calc. for C₂₁H₂₂N₂O₄S₂ (430.534): C, 58.59; H, 5.15; N, 6.50. Found: C, 58.96; H, 5.30; N, 6.15.

Di-*t*-Butyl [2,2'-benzylidenebis(thien-3-yl)]biscarbamate 8e. Yield: 63%. M.p. 205°C; ¹H NMR (CDCl₃), δ : 7.22(d, 2H, H₅, J = 5.4Hz), 7.10(d, 2H, H₄, J = 5.4Hz), 5.79(s, 1H); 7.3(m, 5H); 1.49(s, 9H). ¹³C NMR (CDCl₃), δ : 122.8(C₄); 124.3(C₅); 41.4(C₆); 127.3–128.5(C_{Ph}). Anal. Calc. for C₂₅H₃₀N₂O₄S₂ (486.638): C, 61.69; H, 6.21; N, 5.76. Found: C, 61.46; H, 5.91; N, 5.28.

Synthesis of the 2-(alk-1-enyl)3-aminothiophenes 9, acetamides and carbamates 10: The α -branched aldehyde (1,1mmol) was quickly added to a solution of the amine **1** (acetamide **6a**, carbamate **6b** or **6c**) (1mmol) in CH₂Cl₂ (30ml). A 12N HCl solution (0.5ml) was then introduced dropwise. The mixture was stirred for 2 h. at r.t. and treated with a 4N NaOH solution (10ml). The organic phase was separated and the aqueous solution extracted two times with CH₂Cl₂ (2x20ml). The organic layers were washed with water, dried and evaporated under vacuum. The residual oil was purified by chromatography on silica gel (elution: hexane/CH₂Cl₂ 60/40).

3-Amino 2-(2-methylprop-1-enyl)thiophene 9a. Yield: 70%. ¹H NMR (CDCl₃), δ : 7.05(d, 1H, H₅, J = 5.4Hz), 6.56(d, 1H, H₄, J = 5.4Hz), 6.05(m, 1H); 1.88(d, 6H, 2xCH₃); 3.52(brs, 2H, NH₂). ¹³C NMR (CDCl₃), δ : 26.5(Me), 114.9(C_{1'}), 120.7(C₄), 122.6(C₅). Anal. Calc. for C₈H₁₁NS (153.24): C, 62.70; H, 7.23; N, 9.14. Found: C, 62.45; H, 7.35; N, 9.31.

3-Amino 2-(2-methylbut-1-enyl)thiophene 9b. Yield: 60%. ¹H NMR (CDCl₃), E isomer (70%): δ : 7.01 (d, 1H, H₅, J = 5.4Hz), 6.56(d, 1H, H₄, J = 5.4Hz), 6.06(m, 1H); 3.41(brs, 2H, NH₂); 2.18(q, 2H, CH₂); 1.87(brs, 3H, CH₃), 1.02(t, 3H, CH₃). Z isomer (30%): δ : 7.01(d, 1H, H₅, J = 5.4Hz), 6.56(d, 1H, H₄, J = 5.4Hz), 6.01(m, 1H); 2.24(q, 2H, CH₂); 1.87(brs, 3H, CH₃), 1.06(t, 3H, CH₃). ¹³C NMR (CDCl₃), δ : 12.9(CH₃), 33.3(CH₂), 26.7(Me), 113.4(C_{1'}), 120.6(C₄), 122.6(C₅). Not isolated in a pure form.

3-Amino 2-(2-methylpent-1-enyl)thiophene 9c Yield: 58%. ¹H NMR (CDCl₃), E isomer (75%): δ : 7.00(d, 1H, H₅, J = 5.4Hz), 6.56(d, 1H, H₄, J = 5.4Hz), 6.06(m, 1H); 3.42(brs, 2H, NH₂); 0.89(t, 3H, CH₃); 1.46(3, 2H, CH₂); 1.82(s, 3H, CH₃), 2.13(m, 2H, CH₂), Z isomer (25%): δ : 7.00(d, 1H, H₅, J = 5.4Hz), 6.56(d, 1H, H₄, J = 5.4Hz), 6.00(m, 1H). ¹³C NMR (CDCl₃), δ : 13.2(CH₃), 19.8(CH₂), 36.7(CH₂), 26.7(Me), 113.8(C_{1'}), 120.6(C₄), 122.6(C₅). Not isolated in a pure form.

3-Amino 2-(2-phenylprop-1-enyl)thiophene 9d. Yield: 57%. ¹H NMR (CDCl₃), E isomer (92%): δ : 7.14(d, 1H, H₅, J = 5.4Hz), 6.60(d, 1H, H₄, J = 5.4Hz), 6.67(m, 1H); 2.12(s, 3H, CH₃); 7.21–7.33(m, 5H, Ph), 3.53(brs, 2H, NH₂). Z isomer (8%): δ : 7.14(d, 1H, H₅, J = 5.4Hz), 6.60(d, 1H, H₄, J = 5.4Hz), 6.60(m, 1H).

2.10(s, 3H, CH₃) ; 7.21-7.33(m, 5H, Ph), 3.53(brs, 2H, NH₂). Anal. Calc. for C₁₃H₁₃NS (215.308) : C, 72.51 ; H, 6.09 ; N, 6.51. Found : C, 72.39; H, 5.95; N, 6.82.

3-Amino 2-(Cyclohexylidenemethyl)thiophene 9e. Yield : 60%. ¹H NMR (CDCl₃). δ: 6.99(d, 1H, H₅, J= 5.4Hz), 6.55(d, 1H, H₄, J= 5.4Hz), 5.95(m, 1H) ; 1.53(m, 6H), 2.22(m, 4H) ; 3.43(brs, 2H, NH₂). ¹³C NMR (CDCl₃), δ: 114.2(C₁'), 120.7(C₄), 122.6(C₅), 22.1, 23.5, 24.3, 29.6, 34.2. Not isolated in a pure form.

3-Methylamino 2-(methylprop-1-enyl)thiophene 9f. Yield : 75%. ¹H NMR (CDCl₃). δ: 7.07(d, 1H, H₅, J= 5.4Hz), 6.68(d, 1H, H₄, J= 5.4Hz), 6.02(m, 1H) ; 2.76(s, 3H, CH₃) ; 1.86(brs, 6H, 2xCH₃) ; 3.45(brs, 1H, NH). Anal. Calc. for C₉H₁₃NS (167.268) : C, 64.62 ; H, 7.83 ; N, 8.37. Found : C, 64.33 ; H, 7.61 ; N, 8.24.

N-[2-(2-Methylprop-1-enyl)thien-3-yl]acetamide 10a. Yield : 80%. ¹H NMR (CDCl₃). δ: 7.41(d, 1H, H₅, J= 5.4Hz), 7.05(d, 1H, H₄, J= 5.4Hz), 6.08(m, 1H) ; 2.02(s, 3H, CH₃) ; 1.82(brs, 6H, 2xCH₃), 7.95(brs, 1H, NH). ¹³C NMR (CDCl₃), δ: 114.7(C₁'), 121.1(C₄), 123.7(C₅), 166.5(CO), 19.9(CH₃), 26.8(CH₃), 23.4(CH₃). Anal. Calc. for C₁₀H₁₃NOS(195.278) : C, 61.50 ; H, 6.71 ; N, 7.17. Found : C, 61.73 ; H, 6.25 ; N, 7.09.

N-[2-(2-Methylbut-1-enyl)thien-3-yl]acetamide 10b. Yield : 75%. ¹H NMR (CDCl₃), E isomer (74%). δ: 7.51(d, 1H, H₅, J= 5.4Hz), 7.11(d, 1H, H₄, J= 5.4Hz), 6.08(m, 1H) ; 1.07(t, 3H, CH₃), 1.88(s, 3H, CH₃) ; 2.18(q, 2H, CH₂) ; 7.10(brs, 1H, NH) Z isomer(26%) : δ: 7.51(d, 1H, H₅, J= 5.4Hz), 7.11(d, 1H, H₄, J= 5.4Hz), 6.02(m, 1H) ; 1.05(t, 3H, CH₃), 1.87(s, 3H, CH₃) ; 2.18(q, 2H, CH₂) ; 7.10(brs, 1H, NH). Anal. Calc. for C₁₁H₁₅NOS (209.304) : C, 63.12 ; H, 7.22 ; N, 6.69. Found : C, 63.27; H, 7.51; N, 6.87.

Ethyl [2-(2-methylprop-1-enyl)thien-3-yl]carbamate 10c. Yield : 82%. ¹H NMR (CDCl₃). δ: 7.43 (d, 1H, H₅, J= 5.4Hz), 7.11(d, 1H, H₄, J= 5.4Hz), 6.05(m, 1H) ; 1.28(t, 3H, CH₃) ; 6.40(brs, 1H, NH) ; 4.18(q, 2H, CH₂) ; 1.89(d, 3H, CH₃, J= 1.6Hz) ; 1.82(d, 3H, CH₃, J= 0.7Hz) ¹³C NMR (CDCl₃), δ: 114.7(C₁'), 120.7(C₄), 122.6(C₅), 61.3(CH₂), 14.5(CH₃), 26.5(CH₃). Anal. Calc. for C₁₁H₁₅NO₂S (225.304) : C, 58.64 ; H, 6.71 ; N, 6.22. Found : C, 58.52 ; H, 6.83 ; N, 6.41.

Ethyl [2-(2-methylbut-1-enyl)thien-3-yl]carbamate 10d. Yield : 75%. ¹H NMR (CDCl₃), E isomer(58%). δ: 7.43(d, 1H, H₅, J= 5.4Hz), 7.11(d, 1H, H₄, J= 5.4Hz), 6.08(m, 1H) ; 6.50(brs, 1H, NH) ; 4.19(q, 2H, CH₂) ; 1.85(q, 2H, CH₂) ; 1.87(d, 3H, CH₃, J= 1.4Hz) ; 1.26(t, 3H, CH₃) ; 1.07(t, 3H, CH₃). Z isomer(42%) : δ: 7.43(d, 1H, H₅, J= 5.4Hz), 7.11(d, 1H, H₄, J= 5.4Hz), 6.01(m, 1H) ; 6.50(brs, 1H, NH) ; 4.19(q, 2H, CH₂) ; 1.87(q, 2H, CH₂) ; 1.84(d, 3H, CH₃, J= 0.8Hz) . ¹³C NMR (CDCl₃), δ: 113.6(C₁'), 120.2(C₄), 122.4(C₅), 61.3(CH₂), 14.5(CH₃), 26.3(CH₃), 33.2(CH₃), 12.7(CH₂). Anal. Calc. for C₁₂H₁₇NO₂S (239.33) : C, 60.22 ; H, 7.16 ; N, 5.85. Found : C, 60.17; H, 7.43; N, 5.73.

Ethyl [2-(2-methylpent-1-enyl)thien-3-yl]carbamate 10e. Yield : 77%. ¹H NMR (CDCl₃) : E isomer (64%). δ: 7.40(d, 1H, H₅, J= 5.4Hz), 7.08(d, 1H, H₄, J= 5.4Hz), 6.09(m, 1H) ; 6.62(brs, 1H, NH) ; 4.17(q, 2H, CH₂) ; 2.12(m, 2H, CH₂) ; 1.83(s, 3H, CH₃) ; 1.46(m, 2H, CH₂) ; 1.25(t, 3H, CH₃) ; 0.89(t, 3H, CH₃). Z isomer(36%) : δ: 7.40(d, 1H, H₅, J= 5.4Hz), 7.08(d, 1H, H₄, J= 5.4Hz), 6.03(m, 1H) ; 6.62(brs, 1H, NH) ; 4.17(q, 2H, CH₂) ; 2.12(m, 2H, CH₂) ; 1.83(s, 3H, CH₃) ; 1.46(m, 2H, CH₂) ; 1.25(t, 3H, CH₃) ; 0.89(t, 3H, CH₃). ¹³C NMR (CDCl₃), δ: 114.1(C₁'), 120.3(C₄), 122.4(C₅), 61.4(CH₂), 14.4(CH₃), 26.3(CH₃), 40.6(CH₂), 20.4(CH₂), 13.6(CH₃). Anal. Calc. for C₁₃H₁₉NO₂S (253.356) : C, 61.62 ; H, 7.56 ; N, 5.53. Found : C, 61.45; H, 7.39; N, 5.27.

Ethyl [2-(2-methylbut-1-enyl)thien-3-yl]carbamate 10f. Yield : 65%. ¹H NMR (CDCl₃). δ: 7.45(d, 1H, H₅, J= 5.4Hz), 7.08(d, 1H, H₄, J= 5.4Hz), 5.99(m, 1H) ; 6.45(brs, 1H, NH) ; 4.18(q, 2H, CH₂) ; 2.21(m, 4H, 2xCH₂) ; 1.26(t, 3H, CH₃) ; 1.04(t, 6H, 2xCH₃). ¹³C NMR (CDCl₃), δ: 111.7(C₁'), 120.1(C₄), 122.3(C₅),

61.3(CH₂), 14.5(CH₃), 29.6(CH₂), 24.6(CH₂), 12.6(CH₃). Anal. Calc. for C₁₃H₁₉NO₂S (253.356) : C, 61.62 ; H, 7.56 ; N, 5.53. Found : C, 61.83; H, 7.72; N, 5.68.

Ethyl [2-(cyclohexyldenemethyl)thien-3-yl]carbamate 10g. Yield : 75%. ¹H NMR (CDCl₃) δ: 7.44(d, 1H, H₅, J= 5.4Hz), 7.07(d, 1H, H₄, J= 5.4Hz), 5.95(m, 1H) ; 6.50(brs, 1H, NH) ; 4.18(q, 2H, CH₂) ; 2.26(m, 4H); 1.56(m, 6H); 1.25(t, 3H, CH₃). ¹³C NMR (CDCl₃), δ: 110.7(C₁), 120.2(C₄), 122.4(C₅), 61.2(CH₂), 14.5(CH₃), 37.2, 30.2, 27.6, 26.5, 26.3. Anal. Calc. for C₁₄H₁₉NO₂S(265.366) : C, 63.36 ; H, 7.22 ; N, 5.28. Found : C, 63.25; H, 7.47; N, 5.36.

Ethyl [2-(2-phenylprop-1-enyl)thien-3-yl]carbamate 10h. Yield : 66%. ¹H NMR (CDCl₃). δ: 7.08(d, 1H, H₄, J= 5.4Hz), 6.77(d, 1H, H_α, J_{αβ}= 15.9Hz), 7.05(d, 1H, H_β, J_{αβ}= 15.9Hz), 4.16(q, CH₂), 1.29(t, CH₃) ; 7.22-7.40(m, 6H, H₅+Ph). ¹³C NMR (CDCl₃), δ: 115.8(C₇), 118.35(C₈) ; 127.4(C₄), 128.55(C₅), 61.3(CH₂), 14.5(CH₃). Anal. Calc. for C₁₅H₁₅NO₂S (273.34) : C, 65.91 ; H, 5.53 ; N, 5.12. Found : C, 65.83; H, 5.46; N, 5.08.

t-Butyl [2-(2-phenylprop-1-enyl)thien-3-yl]carbamate 10i. Yield : 87%. M.p. 129°C ¹H NMR (CDCl₃). δ: 7.07(d, 1H, H₄, J= 5.4Hz), 6.81(d, 1H, H_α, J_{αβ}= 15.9Hz), 7.07(d, 1H, H_β, J_{αβ}= 15.9Hz), 1.46(s, 9H), 7.22-7.46(6H, Ph+ H₅). ¹³C NMR (CDCl₃), δ: 117.9(C₇), 122.65(C₈)127.6(C₄), 128.1(C₅) 28.3(CH₃), 80.93(C(CH₃)₃), 133.49(C₂), 136.9(C₃). Anal. Calc. for C₁₇H₁₉NO₂S (301.396) : C, 67.74 ; H, 6.35 ; N, 4.65. Found : C, 67.59; H, 6.27; N, 4.43.

Preparation of the functional thiophene derivatives 14, 15, 16 : The acetal [ECH₂CH(OMe)₂ ; (11 : E = COCH₃, or 12 : E = CO₂CH₃, or 13 : E = CN] (1,1mmol) was quickly added to a solution of acetamide **6a** (or carbamate **6b** or **6c**) (1mmol) in CH₂Cl₂ (30ml). A 12N HCl solution (0.5ml) was then introduced dropwise. The mixture was stirred vigorously for 2 h. at r.t. After treatment with a 4N NaOH solution (10ml), the organic phase was separated and the aqueous solution extracted two times with CH₂Cl₂(2x20ml). The combined organic layers were washed with water, dried and evaporated under vacuum. The solid residue was crystallized in hexane.

4-(3-Acylaminothien-2-yl)butenone 14a. Yield : 70%. M.p.163°C. ¹H NMR (CDCl₃). δ: 7.50(d, 1H, H₅, J= 5.4Hz), 7.27(d, 1H, H₄, J= 5.4Hz), 7.70(d, 1H, H_α, J_{αβ}= 15.3Hz), 6.42(d, 1H, H_β, J_{αβ}= 15.3Hz) ; 2.30(s, 3H, CH₃) ; 2.17(s, 3H, CH₃). Anal. Calc. for C₁₀H₁₁NO₂S (209.262) : C, 57.39 ; H, 5.29 ; N, 6.73. Found : C, 57.09; H, 5.38; N, 6.27.

4-(3-Ethoxycarbonylaminothien-2-yl)butenone 14b. Yield : 67%. M.p.105°C. ¹H NMR (CDCl₃). δ: 7.51(d, 1H, H₅, J= 5.4Hz), 7.28(d, 1H, H₄, J= 5.4Hz), 7.70(d, 1H, H_α, J_{αβ}= 15.3Hz), 6.45(d, 1H, H_β, J_{αβ}= 15.3Hz) ; 4.20(q, 2H, CH₂) ; 2.29(s, 3H, CH₃) ; 1.27(t, 3H, CH₃). Not isolated in pure form.

4-(3-tert-Butoxycarbonylaminothien-2-yl)butenone 14c. Yield : 80%. M.p.128°C. ¹H NMR (CDCl₃). δ: 7.51(d, 1H, H₅, J= 5.4Hz), 7.27(d, 1H, H₄, J= 5.4Hz), 7.66(d, 1H, H_α, J_{αβ}= 15.2Hz), 6.43(d, 1H, H_β, J_{αβ}= 15.2Hz) ; 6.96(brs, 1H, NH) ; 2.3(s, 3H, CH₃) ; 1.49(s, 9H). Anal. Calc. for C₁₃H₁₇NO₃S (267.340) : C, 58.40 ; H, 6.41 ; N, 5.24. Found : C, 58.89; H, 6.67; N, 4.98.

Methyl 3-(3-acylaminothien-2-yl)propenoate 15a. Yield : 88%. M.p.127°C. ¹H NMR (CDCl₃). δ: 7.47(d, 1H, H₅, J= 5.4Hz), 7.16(d, 1H, H₄, J= 5.4Hz), 7.78(d, 1H, H_α, J_{αβ}= 15.4Hz), 5.98(d, 1H, H_β, J_{αβ}= 15.4Hz) ; 3.65(s, 3H, CH₃) ; 2.10(s, 3H, CH₃). Anal. Calc. for C₁₀H₁₁NO₃S (225.262) : C, 53.33 ; H, 4.92 ; N, 6.22. Found : C, 52.96; H, 5.09; N, 6.14.

Methyl 3-(3-Ethoxycarbonylaminothien-2-yl)propenoate 15b. Yield : 85%. M.p.118-120°C. ^1H NMR (CDCl_3). δ : 7.47(d, 1H, H_5 , $J = 5.4\text{Hz}$), 7.26(d, 1H, H_4 , $J = 5.4\text{Hz}$), 7.81(d, 1H, H_α , $J_{\alpha\beta} = 15.4\text{Hz}$), 6.10(d, 1H, H_β , $J_{\alpha\beta} = 15.4\text{Hz}$) ; 7.28(brs, 1H, NH) ; 4.21(q, 2H, CH_2) ; 3.75(s, 3H, CH_3) ; 1.28(t, 3H, CH_3). Anal. Calc.for $\text{C}_{11}\text{H}_{13}\text{NO}_4\text{S}$ (255.288) : C, 51.075 ; H, 5.13 ; N, 5.49. Found : C, 51.65; H, 4.92; N, 5.37.

Methyl 3-(3-tert-butoxycarbonylaminothien-2-yl)propenoate 15c. Yield : 75%. M.p. 124°C. ^1H NMR (CDCl_3). δ : 7.50(d, 1H, H_5 , $J = 5.4\text{Hz}$), 7.24(d, 1H, H_4 , $J = 5.4\text{Hz}$), 7.76(d, 1H, H_α , $J_{\alpha\beta} = 15.3\text{Hz}$), 6.07(d, 1H, H_β , $J_{\alpha\beta} = 15.3\text{Hz}$) ; 3.72(s, 3H, CH_3) ; 1.46(s, 9H). Not isolated in a pure form.

3-(3-Acylaminothien-2-yl)propenenitrile 16a. Yield : 63%. M.p.150°C. ^1H NMR (CDCl_3). δ : 7.65(d, 1H, H_5 , $J = 5.4\text{Hz}$), 7.32(d, 1H, H_4 , $J = 5.4\text{Hz}$), 7.77(d, 1H, H_α , $J_{\alpha\beta} = 15.9\text{Hz}$), 5.48(d, 1H, H_β , $J_{\alpha\beta} = 15.9\text{Hz}$), 8.4(brs, 1H, NH) ; 2.17(s, 3H, CH_3).

3-(3-Ethoxycarbonylaminothien-2-yl)propenenitrile 16b. Yield : 70%. M.p.82°C. ^1H NMR (CDCl_3). E. isomer (55%), δ : 7.40(d, 1H, H_5 , $J = 5.4\text{Hz}$), 7.25(d, 1H, H_4 , $J = 5.4\text{Hz}$), 7.65(d, 1H, H_α , $J_{\alpha\beta} = 16\text{Hz}$), 5.45(d, 1H, H_β , $J_{\alpha\beta} = 16\text{Hz}$) ; 4.20(q, 2H, CH_2) ; 1.28(t, 3H, CH_3). Z. isomer (45%), δ : 7.40(d, 1H, H_5 , $J = 5.4\text{Hz}$), 7.25(d, 1H, H_4 , $J = 5.4\text{Hz}$), 7.20(d, 1H, H_α , $J_{\alpha\beta} = 11.75\text{Hz}$), 5.14(d, 1H, H_β , $J_{\alpha\beta} = 11.75\text{Hz}$) ; 4.20(q, 2H, CH_2) ; 1.28(t, 3H, CH_3). Anal. Calc.for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ (222.262) : C, 54.04 ; H, 4.54 ; N, 12.60. Found : C, 54.17 ; H, 4.73 ; N, 12.81.

3-(3-tert-Butoxycarbonylaminothien-2-yl)propenenitrile 16c. Yield : 83%. M.p.130°C. ^1H NMR (CDCl_3). δ : 7.62(d, 1H, H_5 , $J = 5.4\text{Hz}$), 7.25(d, 1H, H_4 , $J = 5.4\text{Hz}$), 7.60(d, 1H, H_α , $J_{\alpha\beta} = 15.9\text{Hz}$), 5.43(d, 1H, H_β , $J_{\alpha\beta} = 15.9\text{Hz}$) ; 1.46(s, 9H). Anal. Calc.for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ (250.314) : C, 57.56 ; H, 5.64 ; N, 11.19. Found : C, 57.67 ; H, 5.94 ; N, 11.37.

Synthesis of the amino-ester 18 and the amino-nitrile 19 : The carbamate **15c** (or **16c**) (1 mmol), in a 20% HBr solution of in acetic acid (0,450 g, 1 mmol) for 0.3 h. at r.t. Anhydrous ether (20 ml) was then added. The reaction was stirred for another 15 min. The thienylammonium salt was separated, washed with ether and dissolved in water (20ml). After neutralisation with a 1N NaOH solution, the residue was extracted with ether (3x20ml).The ester **18** (or nitrile **19**) was obtained in a pure form after elimination of the solvent. The amino-nitrile **19** was isolated as a Z/E isomer mixture (33/67).

Methyl 3-(3-aminothien-2-yl)propenoate 18. Brown oil. Yield : 55 %. ^1H NMR (CDCl_3). δ : 3.68 (s, 3H, CH_3), 4.16(brs, 2H, NH_2) ; 5.85 (d, 1H, H_β , $J_{\alpha\beta} = 15.4\text{ Hz}$), 6.46 (d, 1H, H_4 , $J_{45} = 5.4\text{ Hz}$), 7.10 (d, 1H, H_5 , $J_{45} = 5.4\text{ Hz}$), 7.71 (d, 1H, H_α , $J_{\alpha\beta} = 15.4\text{ Hz}$). Anal. Calc.for $\text{C}_8\text{H}_9\text{NO}_2\text{S}$ (183.22) : C, 52.44, H, 4.94, N, 7.64. Found : C, 52.21, H, 4.81, N, 7.27.

3-(3-aminothien-2-yl)propenenitrile 19. Yellow oil. Yield : 65 %.E.isomer (67%). ^1H NMR (CDCl_3). δ : 4.35(brs, 2H, NH_2) ; 5.22 (d, 1H, H_β , $J_{\alpha\beta} = 16.6\text{ Hz}$), 6.51 (d, 1H, H_4 , $J_{45} = 5.5\text{ Hz}$), 7.18 (d, 1H, H_5 , $J_{45} = 5.5\text{ Hz}$), 7.37 (d, 1H, H_α , $J_{\alpha\beta} = 16.6\text{ Hz}$). Z. isomer (33%). ^1H NMR (CDCl_3). δ : 4.93 (d, 1H, H_β , $J_{\alpha\beta} = 11.62\text{ Hz}$), 6.62 (d, 1H, H_4 , $J_{45} = 5.4\text{ Hz}$), 7.21 (d, 1H, H_5 , $J_{45} = 5.4\text{ Hz}$), 7.05 (d, 1H, H_α , $J_{\alpha\beta} = 11.6\text{ Hz}$). Anal. Calc.for $\text{C}_7\text{H}_6\text{N}_2\text{S}$ (150.20). Calc: C: 55.98, H: 3.99, N: 18.65. Found : C, 55.63, H, 3.98, N, 18.53.

Synthesis of the 5-methylthieno[3,2-b]pyridine 20⁵: The carbamate **14c** (267mg, 1mmol) was treated as for **15c** (or **16c**). After neutralisation with a 1N NaOH solution, the thienopyridine **20** was extracted with ether (3x20ml). The work-up of the organic phases has led to a crude product purified by chromatography on silica gel (elution CH_2Cl_2 /light petroleum: 40/60) . The thienopyridine **20** were isolated as a yellow oil.. Yield :

40%. ^1H NMR (CDCl_3). δ : 2.67 (s, 3H, CH_3), 7.12 (d, 1H, H_6 , $J_{67} = 8.32$ Hz), 7.46 (d, 1H, H_3 , $J_{23} = 5.52$ Hz), 7.68 (d, 1H, H_2 , $J_{23} = 5.52$ Hz), 8.03 (d, 1H, H_7 , $J_{67} = 8.32$ Hz).

Synthesis of the functionalized thieno[3,2-b]pyridines 21–24 :

1. Direct synthesis : To a solution of amine **1a** (198mg, 2 mmol) in CH_2Cl_2 (20 ml), the acetal $[\text{ECH}_2\text{CH}(\text{OMe})_2]$; (**11** : $\text{E} = \text{COCH}_3$ or **12** : $\text{E} = \text{CO}_2\text{CH}_3$ or **13** : $\text{E} = \text{CN}$) (4,5 mmol) and a solution of 12N hydrochloric acid (0,5 ml) were successively added at r.t.. The mixture was stirred for 2 h. and neutralized with a 4N NaOH solution. The organic phase was separated and the aqueous solution extracted with the same solvent. The combined organic fractions were washed with water, dried and evaporated. With the acetal **11**, a mixture of **21**⁵ and methylthienopyridine **20**⁵ (65/35) was obtained. These compounds were separated by chromatography on silica gel (elution : light petroleum/ CH_2Cl_2 : 40 / 60). In the case of the acetal **13**, ^1H RMN and mass spectra have shown the formation of the (thieno[3,2-b]pyridin-6-yl)acetic acid **24** besides the thienopyridine **23** (**23/24** : 70/30). When the reaction was achieved in THF instead of CH_2Cl_2 , and the mixture stirred for 12 h. at r.t., the thienopyridine **23** was obtained without formation of the acid **24**.

Methyl thieno[3,2-b]pyridine-6-carboxylate 22. Yield : 66%. M.p. 98°C . ^1H NMR (CDCl_3). δ : 3.93 (s, 3H, CH_3), 7.60 (d, 1H, H_3 , $J_{23} = 5.56$ Hz), 7.93 (s, 1H, H_2 , $J_{23} = 5.56$ Hz), 8.81 (d, 1H, H_7 , $J_{57} = 1.86$ Hz), 9.26 (d, 1H, H_5 , $J_{57} = 1.86$ Hz). Anal. Calc. for $\text{C}_9\text{H}_7\text{NO}_2\text{S}$ (193.23): C, 55.95 ; H, 3.65 ; N, 7.25 . Found : C, 60.02 ; H, 3.78 ; N, 7.43.

Thieno[3,2-b]pyridine-6-carbonitrile 23¹¹. Yield : 57%. M.p. 143°C (litt. : 142°C). ^1H NMR (CDCl_3). δ : 7.63 (d, 1H, H_3 , $J_{23} = 5.54$ Hz), 7.95 (d, 1H, H_2 , $J_{23} = 5.4$ Hz), 8.48 (d, 1H, H_7 , $J_{57} = 1.86$ Hz), 8.89 (d, 1H, H_5 , $J_{57} = 1.86$ Hz). Anal. Calc. for $\text{C}_8\text{H}_4\text{N}_2\text{S}$ (160.198): C, 59.98 ; H, 2.52 ; N, 17.49. Found : C, 60.25 ; H, 2.62 ; N, 17.73.

2. Synthesis of 22 and 23 from amino-ester 18 and amino-nitrile 19 respectively : To a solution of ester **18** (183mg, 1mmol) in CH_2Cl_2 (30 ml), the acetal **12** ($\text{E} = \text{CO}_2\text{Me}$) or **13** ($\text{E} = \text{CN}$) (1,1 mmol) and a 12N HCl solution (0,5ml) were successively added. The mixture was stirred for 2 h. at r.t. and neutralized with 4N NaOH solution. After separation, the aqueous phase was extracted with the same solvent and the combined organic layers washed with water, dried and evaporated. The thienopyridine **22** was crystallized in hexane. The thienopyridine **23** was obtained, according to the same protocol from the nitrile **19**. The 6-acetylthieno[3,2-b]pyridine **21** was formed after hydrolysis of the carbamate **14c**, in the presence of acetal **11**.

Synthesis of 6-phenylthieno[3,2-b]pyridine 25

Phenylethanal (300mg, 2.5mmol) and a 12N HCl solution (0.5ml) were successively added, under stirring, to a solution of the amine **1a** (198mg, 2mmol) in CH_2Cl_2 . The mixture was stirred for 2 h. at r.t. and then neutralized with a 4N NaOH solution. The aqueous phase was separated and extracted with CH_2Cl_2 (2x20ml). The combined organic fractions were dried and concentrated . The residue was crystallized in light petroleum. Yield : 70%. M.p. $107\text{--}109^\circ\text{C}$. ^1H NMR (CDCl_3). δ : 7.72 (d, 1H, H_2 , $J_{23} = 5.45$ Hz), 8.30 (d, 1H, H_7 , $J_{57} = 1.86$ Hz), 8.81 (d, 1H, H_5 , $J_{57} = 1.86$ Hz), 7.41–7.63 (m, 6H). Anal. Calc. For : $\text{C}_{13}\text{H}_9\text{NS}$ (211.28) Calc: C: 73.90, H: 4.29, N: 6.63; Tr: C: 74.06, H: 4.41, N: 6.57.

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