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α-Vinylation 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-Aminothien-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.

The strong enaminic character of β-aminothiophenes and β,β'-diaminothiophenes allows reactions with various electrophilic reagents[1]. We have prepared 2-alkyl 3-thiophenamines **2** in good yields, by treatement 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 traped 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(aminothienyl)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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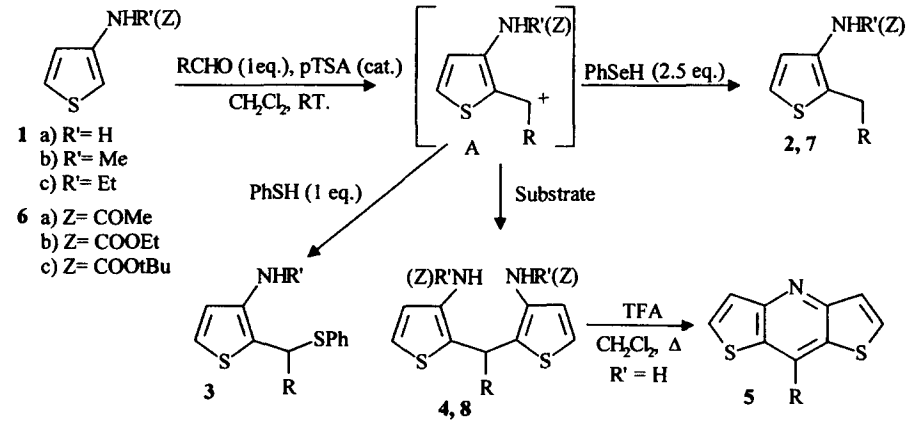
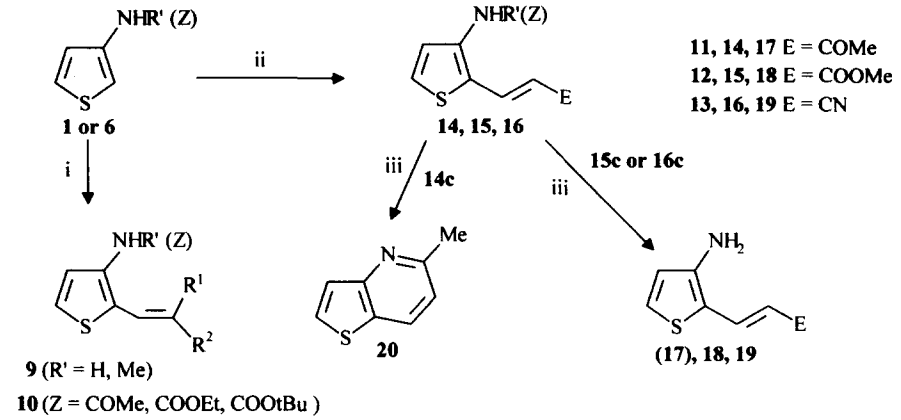
were however surprised to isolate 2-(alk-1-enyl) 3-aminothiophenes **9** when one equivalent of α-branched aldehyde was used. Comparable results were obtained with acetamide **6a**, carbamates **6b** and **6c**. The corresponding acetamides and carbamates **10** were prepared in good yields (Scheme 2, 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



i) R^1R^2CHCHO, CH_2Cl_2, conc.HCl, RT. ii) $ECH_2CH(OMe)_2$ (11or 12, 13), CH_2Cl_2, conc.HCl, RT. iii) HBr, AcOH, RT.

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 R^1 (or R^2) 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).

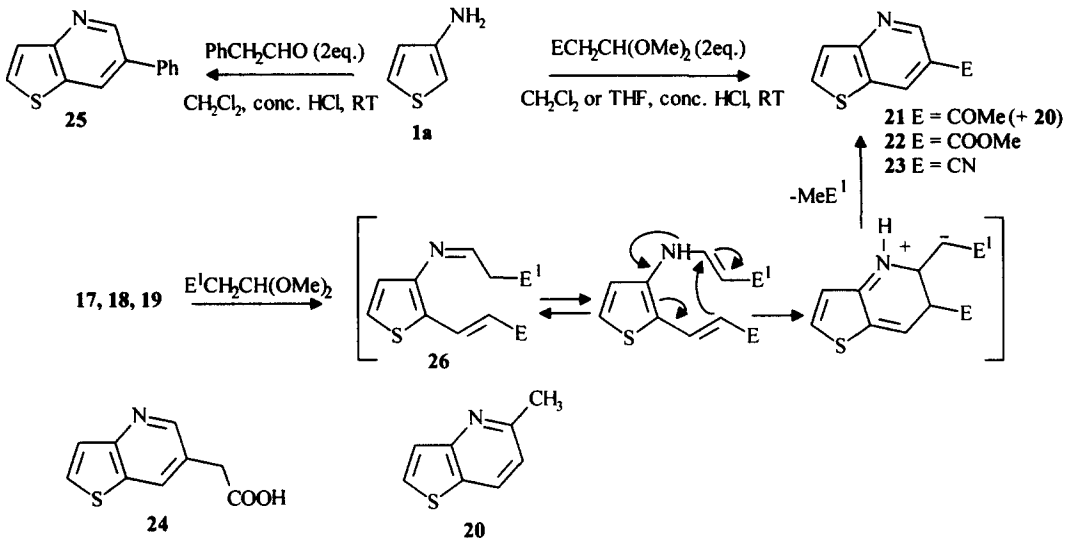
Table 3 : β-(3-Amino 2-thienyl) α,β-unsaturated ketone, ester and nitrile derivatives **14**, **15** and **16**.

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 ^{1}H 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 $ZnCl_2$ in ethanol at reflux[4]. 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 $ZnCl_2$. The methylthienopyridine **20** was not formed when the reaction was carried out in n-butanol[6]. 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 CH_2Cl_2 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 proposition[5]. 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 etheral solution and distillated 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 amine[9]. The carbamates **6b** (Z= COOEt) [7] and **6c** (Z= COOtBu)[10] were synthetized according to conventional procedures : **6b**(M.p. 71°C, Yield: 80%), **6c**(M.p. 137°C. Yield: 86%). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker 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/ CH_2Cl_2 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 ; ^{1}H NMR ($CDCl_3$), δ: 7.17(d, 1H, H_5, J= 5.4Hz), 6.99(d, 1H, H_4, J= 5.4Hz), 2.61(t, 2H), 1.82(m, 2H), 1.03(t, 3H), 2.16(s, 3H). Anal. Calc.for $C_9H_{13}NOS$ (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 ; ^{1}H NMR ($CDCl_3$), δ: 7.19(d, 1H, H_5, J= 5.4Hz) ; 7.01(d, 1H, H_4, J= 5.4Hz) ; 3.39(s, 2H) ; 7.23(brs, 5H) ; 2.17(s, 3H). Anal. Calc.for $C_{13}H_{13}NOS$ (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 ; ^{1}H NMR ($CDCl_3$), δ: 7.17(d, 1H, H_5, J= 5.4Hz), 7.01(d, 1H, H_4, 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 ; ^{1}H NMR ($CDCl_3$), δ: 7.22(d, 1H, H_5, J= 5.4Hz) ; 7.07(d, 1H, H_4, J= 5.4Hz) ; 4.01(s, 2H) ; 7.24(brs, 5H) ; 1.26(t, 3H).4.17(q, 2H). Anal. Calc.for $C_{14}H_{15}NO_2S$ (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 ; ^{1}H NMR ($CDCl_3$), δ: 7.22(d, 1H, H_5, J= 5.4Hz) ; 6.98(d, 1H, H_4, J= 5.4Hz) ; 2.27(s, 3H) ; 1.48(s, 9H). Anal. Calc.for $C_{10}H_{15}NO_2S$ (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 ; ^{1}H NMR ($CDCl_3$), δ: 7.21(d, 1H, H_5, J= 5.4Hz) ; 7.03(d, 1H, H_4, J= 5.4Hz) ; 4.03(s, 2H) ; 7.27(brs, 5H) ; 1.47(s, 9H). Anal. Calc.for $C_{16}H_{19}NO_2S$ (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 CH_2Cl_2 (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 CH_2Cl_2 (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 ; ^{1}H NMR ($CDCl_3$), δ: 7.12(d, 2H, H_5, J= 5.4Hz), 7.06(d, 2H, H_4, J= 5.4Hz), 4.27(t, 1H), 2.12(m, 2H), 1.02(t, 3H), 2.19(s, 6H). ^{13}C NMR ($CDCl_3$), δ: 122.4(C_4) ; 123.9(C_5) ; 41.15(C_6) ; 28.4(CH_2) ; 13.5(CH_3). Anal. Calc.for $C_{15}H_{18}N_2O_2S_2$ (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 ; ^{1}H NMR ($CDCl_3$), δ: 7.21(d, 2H, H_5, J= 5.4Hz), 7.07(d, 2H, H_4, J= 5.4Hz), 5.78(s, 1H), 7.33(brs, 5H), 2.17(s, 6H). ^{13}C NMR

($CDCl_3$), δ: 122.5(C_4) ; 124.1(C_5) ; 41.2(C_6) ; 127.8-128.9(C_{Ph}) ; 13.5(CH_3). Anal. Calc.for $C_{19}H_{18}N_2O_2S_2$ (370.482) : C, 61.59 ; H, 4.90 ; N, 7.56. Found : C, 61.06 ; H, 4.96 ; N, 8.0.4.

Diethyl [2,2'-propylidenebis(thien-3-yl)]biscarbamate 8c. Yield : 87%. M.p. 105°C ; ^1H NMR ($CDCl_3$), δ: 7.20(d, 2H, H_5, J= 5.4Hz) , 7.08(d, 2H, H_4, J= 5.4Hz) , 4.35(t, 1H) ; 2.18(m, 2H) ; 1.1(t, 3H), 4.16(q, 2H), 1.26(t, 3H). ^{13}C NMR ($CDCl_3$), δ: 122.7(C_4) ; 124.2(C_5) ; 41.4(C_6) ; 27.7(CH_2) ; 14(CH_3). Anal. Calc.for $C_{17}H_{22}N_2O_4S_2$ (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 ($CDCl_3$), δ: 7.23(d, 2H, H_5, J= 5.4Hz), 7.11(d, 2H, H_4, J= 5.4Hz), 5.80(s, 1H) ; 7.26(m, 5H) ; 4.18(q, 2H) ; 1.29(t, 3H). ^{13}C NMR ($CDCl_3$), δ: 123 (C_4) ; 124.7(C_5) ; 41.4(C_6) ; 127.5-128.6(C_{Ph}) . Anal. Calc.for $C_{21}H_{22}N_2O_4S_2$ (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 ($CDCl_3$), δ: 7.22(d, 2H, H_5, J= 5.4Hz), 7.10(d, 2H, H_4, J= 5.4Hz), 5.79(s, 1H) ; 7.3(m, 5H) ; 1.49(s, 9H). ^{13}C NMR ($CDCl_3$), δ: 122.8(C_4) ; 124.3(C_5) ; 41.4(C_6) ; 127.3-128.5(C_{Ph}) . Anal. Calc.for $C_{25}H_{30}N_2O_4S_2$ (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 CH_2Cl_2 (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 CH_2Cl_2(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/ CH_2Cl_2 60/40).

3-Amino 2-(2-methylprop-1-enyl)thiophene 9a. Yield : 70%. ^1H NMR ($CDCl_3$), δ: 7.05(d, 1H, H_5, J= 5.4Hz), 6.56(d, 1H, H_4, J= 5.4Hz), 6.05(m, 1H); 1.88(d, 6H, 2xCH_3) ; 3.52(brs, 2H, NH_2). ^{13}C NMR ($CDCl_3$), δ: 26.5(Me), 114.9($C_{1'}$), 120.7(C_4), 122.6(C_5). Anal. Calc.for $C_8H_{11}NS$ (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 ($CDCl_3$), E isomer (70%). δ: 7.01 (d, 1H, H_5, J= 5.4Hz), 6.56(d, 1H, H_4, J= 5.4Hz), 6.06(m, 1H) ; 3.41(brs, 2H, NH_2) ; 2.18(q, 2H, CH_2) ; 1.87(brs, 3H, CH_3), 1.02(t, 3H, CH_3). Z isomer(30%) : δ: 7.01(d, 1H, H_5, J= 5.4Hz), 6.56(d, 1H, H_4, J= 5.4Hz), 6.01(m, 1H) ; 2.24(q, 2H, CH_2) ; 1.87(brs, 3H, CH_3), 1.06(t, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 12.9(CH_3), 33.3(CH_2), 26.7(Me), 113.4($C_{1'}$), 120.6(C_4), 122.6(C_5). Not isolated in a pure form.

3-Amino 2-(2-methylpent-1-enyl)thiophene 9c Yield : 58%. ^1H NMR ($CDCl_3$), E isomer (75%). δ: 7.00(d, 1H, H_5, J= 5.4Hz), 6.56(d, 1H, H_4, J= 5.4Hz), 6.06(m, 1H) ; 3.42(brs, 2H, NH_2) ; 0.89(t, 3H, CH_3) ; 1.46(3, 2H, CH_2) ; 1.82(s, 3H, CH_3), 2.13(m, 2H, CH_2) , Z isomer(25%) : δ: 7.00(d, 1H, H_5, J= 5.4Hz), 6.56(d, 1H, H_4, J= 5.4Hz), 6.00(m, 1H). ^{13}C NMR ($CDCl_3$), δ: 13.2(CH_3), 19.8(CH_2), 36.7(CH_2) 26.7(Me), 113.8($C_{1'}$), 120.6(C_4), 122.6(C_5). Not isolated in a pure form.

3-Amino 2-(2-phenylprop-1-enyl]thiophene 9d. Yield : 57%. ^1H NMR ($CDCl_3$), E isomer (92%). δ: 7.14(d, 1H, H_5, J= 5.4Hz), 6.60(d, 1H, H_4, J= 5.4Hz), 6.67(m, 1H) ; 2.12(s, 3H, CH_3) ; 7.21-7.33(m, 5H, Ph), 3.53(brs, 2H, NH_2). Z isomer(8%) : δ: 7.14(d, 1H, H_5, J= 5.4Hz), 6.60(d, 1H, H_4, J= 5.4Hz), 6.60(m, 1H).

2.10(s, 3H, CH_3) ; 7.21-7.33(m, 5H, Ph), 3.53(brs, 2H, NH_2). Anal. Calc.for $C_{13}H_{13}NS$ (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 ($CDCl_3$). δ: 6.99(d, 1H, H_5, J= 5.4Hz), 6.55(d, 1H, H_4, J= 5.4Hz), 5.95(m, 1H) ; 1.53(m, 6H), 2.22(m, 4H) ; 3.43(brs, 2H, NH_2). ^{13}C NMR ($CDCl_3$), δ: 114.2($C_{1'}$), 120.7(C_4), 122.6(C_5), 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 ($CDCl_3$). δ: 7.07(d, 1H, H_5, J= 5.4Hz), 6.68(d, 1H, H_4, J= 5.4Hz), 6.02(m, 1H) ; 2.76(s, 3H, CH_3) ; 1.86(brs, 6H, 2xCH_3) ; 3.45(brs, 1H, NH). Anal. Calc.for $C_9H_{13}NS$ (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 ($CDCl_3$), δ: 7.41(d, 1H, H_5, J= 5.4Hz), 7.05(d, 1H, H_4, J= 5.4Hz), 6.08(m, 1H) ; 2.02(s, 3H, CH_3) ; 1.82(brs, 6H, 2xCH_3), 7.95(brs, 1H, NH). ^{13}C NMR ($CDCl_3$), δ: 114.7($C_{1'}$), 121.1(C_4), 123.7(C_5), 166.5(CO), 19.9(CH_3), 26.8(CH_3), 23.4(CH_3). Anal. Calc. for $C_{10}H_{13}NOS$(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 ($CDCl_3$), E isomer (74%). δ: 7.51(d, 1H, H_5, J= 5.4Hz), 7.11(d, 1H, H_4, J= 5.4Hz), 6.08(m, 1H) ; 1.07(t, 3H, CH_3), 1.88(s, 3H, CH_3) ; 2.18(q, 2H, CH_2) ; 7.10(brs, 1H, NH) Z isomer(26%) : δ: 7.51(d, 1H, H_5, J= 5.4Hz), 7.11(d, 1H, H_4, J= 5.4Hz), 6.02(m, 1H) ; 1.05(t, 3H, CH_3), 1.87(s, 3H, CH_3) ; 2.18(q, 2H, CH_2) ; 7.10(brs, 1H, NH). Anal. Calc.for $C_{11}H_{15}NOS$ (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 ($CDCl_3$). δ: 7.43 (d, 1H, H_5, J= 5.4Hz), 7.11(d, 1H, H_4, J= 5.4Hz), 6.05(m, 1H) ; 1.28(t, 3H, CH_3) ; 6.40(brs, 1H, NH) ; 4.18(q, 2H, CH_2) ; 1.89(d, 3H, CH_3, J= 1.6Hz) ; 1.82(d, 3H, CH_3, J= 0.7Hz) ^{13}C NMR ($CDCl_3$), δ: 114.7($C_{1'}$), 120.7(C_4), 122.6(C_5), 61.3(CH_2), 14.5(CH_3), 26.5(CH_3). Anal. Calc.for $C_{11}H_{15}NO_2S$ (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 ($CDCl_3$), E isomer(58%). δ: 7.43(d, 1H, H_5, J= 5.4Hz), 7.11(d, 1H, H_4, J= 5.4Hz), 6.08(m, 1H) ; 6.50(brs, 1H, NH) ; 4.19(q, 2H, CH_2) ; 1.85(q, 2H, CH_2) ; 1.87(d, 3H, CH_3, J= 1.4Hz) ; 1.26(t, 3H, CH_3) ; 1.07(t, 3H, CH_3). Z isomer(42%) : δ: 7.43(d, 1H, H_5, J= 5.4Hz), 7.11(d, 1H, H_4, J= 5.4Hz), 6.01(m, 1H) ; 6.50(brs, 1H, NH) ; 4.19(q, 2H, CH_2) ; 1.87(q, 2H, CH_2) ; 1.84(d, 3H, CH_3, J= 0.8Hz) . ^{13}C NMR ($CDCl_3$), δ: 113.6($C_{1'}$), 120.2(C_4), 122.4(C_5), 61.3(CH_2), 14.5(CH_3), 26.3(CH_3), 33.2(CH_3), 12.7(CH_2). Anal. Calc.for $C_{12}H_{17}NO_2S$ (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 ($CDCl_3$) : E isomer (64%). δ: 7.40(d, 1H, H_5, J= 5.4Hz), 7.08(d, 1H, H_4, J= 5.4Hz), 6.09(m, 1H) ; 6.62(brs, 1H, NH) ; 4.17(q, 2H, CH_2) ; 2.12(m, 2H, CH_2) ; 1.83(s, 3H, CH_3) ; 1.46(m, 2H, CH_2); 1.25(t, 3H, CH_3) ; 0.89(t, 3H, CH_3). Z isomer(36%) : δ: 7.40(d, 1H, H_5, J= 5.4Hz), 7.08(d, 1H, H_4, J= 5.4Hz), 6.03(m, 1H) ; 6.62(brs, 1H, NH) ; 4.17(q, 2H, CH_2) ; 2.12(m, 2H, CH2) ; 1.83(s, 3H, CH_3) ; 1.46(m, 2H, CH_2); 1.25(t, 3H, CH_3) ; 0.89(t, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 114.1($C_{1'}$), 120.3(C_4), 122.4(C_5), 61.4(CH_2), 14.4(CH_3), 26.3(CH_3), 40.6(CH_2), 20.4(CH_2), 13.6(CH_3),. Anal. Calc.for $C_{13}H_{19}NO_2S$ (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 ($CDCl_3$). δ: 7.45(d, 1H, H_5, J= 5.4Hz), 7.08(d, 1H, H_4, J= 5.4Hz), 5.99(m, 1H) ; 6.45(brs, 1H, NH) ; 4.18(q, 2H, CH_2) ; 2.21(m, 4H, 2xCH_2) ; 1.26(t, 3H, CH_3) ; 1.04(t, 6H, 2xCH_3). ^{13}C NMR ($CDCl_3$), δ: 111.7($C_{1'}$), 120.1(C_4), 122.3(C_5),

61.3(CH_2), 14.5(CH_3), 29.6(CH_2), 24.6(CH_2), 12.6(CH_3). Anal. Calc.for $C_{13}H_{19}NO_2S$ (253.356) : C, 61.62 ; H, 7.56 ; N, 5.53. Found : C, 61.83; H, 7.72; N, 5.68.

Ethyl [2-(cyclohexylidenemethyl)thien-3-yl]carbamate 10g. Yield : 75%. ^1H NMR ($CDCl_3$) δ: 7.44(d, 1H, H_5, J= 5.4Hz), 7.07(d, 1H, H_4, J= 5.4Hz), 5.95(m, 1H) ; 6.50(brs, 1H, NH) ; 4.18(q, 2H, CH_2) ; 2.26(m, 4H); 1.56(m, 6H); 1.25(t, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 110.7($C_{1'}$), 120.2(C_4), 122.4(C_5), 61.2(CH_2), 14.5(CH_3), 37.2, 30.2, 27.6, 26.5, 26.3. Anal. Calc.for $C_{14}H_{19}NO_2S$(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 ($CDCl_3$). δ: 7.08(d, 1H, H_4, J= 5.4Hz), 6.77(d, 1H, H_α, $J_{\alpha\beta}$= 15.9Hz), 705(d, 1H, H_β, $J_{\alpha\beta}$= 15.9Hz), 4.16(q, CH_2), 1.29(t, CH_3) ; 7.22-7.40(m, 6H, H_5+Ph). ^{13}C NMR ($CDCl_3$), δ: 115.8(C_7), 118.35(C_8) ; 127.4(C_4), 128.55(C_5), 61.3(CH_2), 14.5(CH_3). Anal. Calc.for $C_{15}H_{15}NO_2S$ (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 ($CDCl_3$). δ: 7.07(d, 1H, H_4, J= 5.4Hz), 6.81(d, 1H, H_α, $J_{\alpha\beta}$= 15.9Hz), 7.07(d, 1H, H_β, $J_{\alpha\beta}$= 15.9Hz), 1.46(s, 9H), 7.22-7.46(6H, Ph+ H_5). ^{13}C NMR ($CDCl_3$), δ: 117.9(C_7), 122.65(C_8)127.6(C_4), 128.1(C_5) 28.3(CH_3), 80.93($\underline{C}(CH_3)_3$), 133.49(C_2), 136.9(C_3). Anal. Calc.for $C_{17}H_{19}NO_2S$ (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 [$ECH_2CH(OMe)_2$; (**11** : E = $COCH_3$, or **12** : E = CO_2CH_3, or **13** : E = CN] (1,1mmol) was quickly added to a solution of acetamide **6a** (or carbamate **6b** or **6c**) (1mmol) in CH_2Cl_2 (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 CH_2Cl_2(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 ($CDCl_3$). δ: 7.50(d, 1H, H_5, J= 5.4Hz), 7.27(d, 1H, H_4, J= 5.4Hz), 7.70(d, 1H, H_α, $J_{\alpha\beta}$= 15.3Hz), 6.42(d, 1H, H_β, $J_{\alpha\beta}$= 15.3Hz) ; 2.30(s, 3H, CH_3) ; 2.17(s, 3H, CH_3). Anal. Calc.for $C_{10}H_{11}NO_2S$ (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 ($CDCl_3$). δ: 7.51(d, 1H, H_5, J= 5.4Hz), 7.28(d, 1H, H_4, J= 5.4Hz), 7.70(d, 1H, Hα, $J_{\alpha\beta}$= 15.3Hz), 6.45(d, 1H, Hβ, $J_{\alpha\beta}$= 15.3Hz) ; 4.20(q, 2H, CH_2) ; 2.29(s, 3H, CH_3) ; 1.27(t, 3H, CH_3). Not isolated in pure form.

4-(3-tert-Butoxycarbonylaminothien-2-yl)butenone 14c. Yield : 80%. M.p.128°C. ^1H NMR ($CDCl_3$). δ: 7.51(d, 1H, H_5, J= 5.4Hz), 7.27(d, 1H, H_4, J= 5.4Hz), 7.66(d, 1H, H_α, $J_{\alpha\beta}$= 15.2Hz), 6.43(d, 1H, H_β, $J_{\alpha\beta}$= 15.2Hz) ; 6.96(brs, 1H, NH) ; 2.3(s, 3H, CH_3) ; 1.49(s, 9H). Anal. Calc.for $C_{13}H_{17}NO_3S$ (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 ($CDCl_3$). δ: 7.47(d, 1H, H_5, J= 5.4Hz), 7.16(d, 1H, H_4, J= 5.4Hz), 7.78(d, 1H, H_α, $J_{\alpha\beta}$= 15.4Hz), 5.98(d, 1H, H_β, $J_{\alpha\beta}$= 15.4Hz) ; 3.65(s, 3H, CH_3) ; 2.10(s, 3H, CH_3). Anal. Calc.for $C_{10}H_{11}NO_3S$ (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. ^{1}H NMR ($CDCl_3$). δ: 7.47(d, 1H, H_5, J= 5.4Hz), 7.26(d, 1H, H_4, J= 5.4Hz), 7.81(d, 1H, H_α, $J_{\alpha\beta}$= 15.4Hz), 6.10(d, 1H, H_β, $J_{\alpha\beta}$= 15.4Hz) ; 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 $C_{11}H_{13}NO_4S$(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. ^{1}H NMR ($CDCl_3$). δ: 7.50(d, 1H, H_5, J= 5.4Hz), 7.24(d, 1H, H_4, J= 5.4Hz), 7.76(d, 1H, H_α, $J_{\alpha\beta}$= 15.3Hz), 6.07(d, 1H, H_β, $J_{\alpha\beta}$= 15.3Hz) ; 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. ^{1}H NMR ($CDCl_3$). δ: 7.65(d, 1H, H_5, J= 5.4Hz), 7.32(d, 1H, H_4, J= 5.4Hz), 7.77(d, 1H, H_α, $J_{\alpha\,\beta}$= 15.9Hz), 5.48(d, 1H, H_β, $J_{\alpha\,\beta}$= 15.9Hz), 8.4(brs, 1H, NH) ; 2.17(s, 3H, CH_3).

3-(3-Ethoxycarbonylaminothien-2-yl)propenenitrile 16b. Yield : 70%. M.p.82°C. ^{1}H NMR ($CDCl_3$). E. isomer (55%), δ: 7.40(d, 1H, H_5, J= 5.4Hz), 7.25(d, 1H, H_4, J= 5.4Hz), 7.65(d, 1H, H_α, $J_{\alpha\beta}$= 16Hz), 5.45(d, 1H, H_β, $J_{\alpha\beta}$= 16Hz) ; 4.20(q, 2H, CH_2) ; 1.28(t, 3H, CH_3). Z. isomer (45%), δ: 7.40(d, 1H, H_5, J= 5.4Hz), 7.25(d, 1H, H_4, J= 5.4Hz), 7.20(d, 1H, H_α, $J_{\alpha\beta}$= 11.75Hz), 5.14(d, 1H, H_β, $J_{\alpha\beta}$= 11.75Hz); 4.20(q, 2H, CH_2) ; 1.28(t, 3H, CH_3). Anal. Calc.for $C_{10}H_{10}N_2O_2S$ (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. ^{1}H NMR ($CDCl_3$). δ: 7.62(d, 1H, H_5, J= 5.4Hz), 7.25(d, 1H, H_4, J= 5.4Hz), 7.60(d, 1H, H_α, $J_{\alpha\beta}$= 15.9Hz), 5.43(d, 1H, H_β, $J_{\alpha\beta}$= 15.9Hz) ; 1.46(s, 9H). Anal. Calc.for $C_{12}H_{14}N_2O_2S$ (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 %. ^{1}H 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 Hz), 6.46 (d, 1H, H_4, J_{45} = 5.4 Hz), 7.10 (d, 1H, H_5, J_{45} = 5.4 Hz), 7.71 (d, 1H, H_α, $J_{\alpha\beta}$ = 15.4 Hz). Anal. Calc.for $C_8H_9NO_2S$ (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%). ^{1}H NMR ($CDCl_3$). δ: 4.35(brs, 2H, NH_2) ; 5.22 (d, 1H, H_β, $J_{\alpha\beta}$= 16.6 Hz), 6.51 (d, 1H, H_4, J_{45} = 5.5 Hz), 7.18 (d, 1H, H_5, J_{45} = 5.5 Hz), 7.37 (d, 1H, H_α, $J_{\alpha\beta}$ = 16.6 Hz). Z. isomer (33%). ^{1}H NMR ($CDCl_3$). δ: 4.93 (d, 1H, H_β, $J_{\alpha\beta}$ = 11.62 Hz), 6.62 (d, 1H, H_4, J_{45} = 5.4 Hz), 7.21 (d, 1H, H_5, J_{45} = 5.4 Hz), 7.05 (d, 1H, H_α, $J_{\alpha\beta}$ = 11.6 Hz). Anal. Calc.for $C_7H_6N_2S$(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 20[5]: 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%. ^{1}H 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 fonctionalized 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 [$ECH_2CH(OMe)_2$; (**11** : E = $COCH_3$ or **12** : E = CO_2CH_3 or **13** : E = 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**, ^{1}H 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. ^{1}H 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 $C_9H_7NO_2S$ (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 23[11]**.** Yield : 57%. M.p. 143°C (litt. : 142°C). ^{1}H 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. $C_8H_4N_2S$ (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**(E = CO_2Me) or **13**(E = 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. 107-109°C. ^{1}H 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 : $C_{13}H_9NS$ (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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