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α-Substitution of β-Thienylcarbamates: Alkylation, Vinylation and Pd-Catalyzed Coupling Reactions

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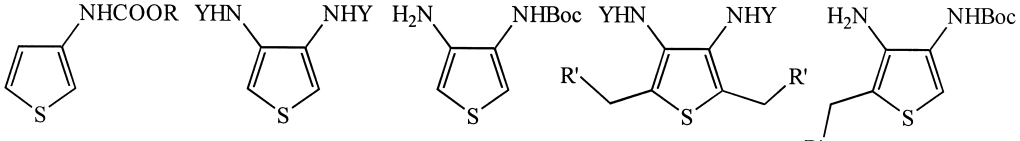
Abstract—Reaction of the trilithio derivative of di-*t*-butyl thiophene-3,4-diyldicarbamate **4** with alkyl halides has led to 2-alkylthiophenedicarbamates **9** and **11** and 4-alkylthieno[3,4−d]imidazolones **12**. Acid catalyzed α-alkylation of **4**, using α-branched or functionalized aldehydes, has allowed the synthesis of divinylthiophenes **13** and thieno[3,2−b]pyridines **14**–**16**, respectively. Pd-catalyzed coupling reactions involving halo- or dihalothienylcarbamates **10**, **17**, **18** were studied. One or two alkenyl, alkynyl, aryl groups were introduced on the thiophene nucleus.

We have recently described an efficient method for the α-alkylation of the thiophene nucleus of 3-thienylcarbamates **1**, **2**,[1–3] 3,4-diaminothiophene **3** and dicarbamate derivative **4**.[4] The enaminic character of **3** and **4** has allowed the preparation of 2,5-dialkyl-3,4-diaminothiophenes **6** and their corresponding dicarbamates **7** using an aldehyde and selenophenol as reducing agents. Monoalkylation of the nucleus was achieved on the aminocarbamate **5**.[4] The products **8** were attractive intermediates for the synthesis of biotin analogs.



1 R = *t*-Bu
2 R = Et

3 Y = H
4 Y = Boc

5

6 Y = H
7 Y = Boc

8

This method, using simple and mild experimental conditions, was very efficient. The preparation of the aminocarbamate **5** was, however, a limiting step and could not be achieved on a multigram scale with a yield not exceeding 60%. Furthermore, linear alkyl substituents are only introduced on the thiophene nucleus. This drawback led us to investigate other methods allowing the introduction of various substituents. In this paper, we describe our results concerning the alkylation of **4** after metalation or coupling reactions applied to α-halothiophenic compounds derived from **1** and **4**.

Lithiation of thien-3-ylcarbamate **1** was described[5,6] and needs two equivalents of *n*-butyllithium. The formed dianion was trapped by various electrophilic species, such as dimethyl sulfate, trimethyltin chloride or 2-chlorocyclohexanone affording *t*-butyl (2-substituted thien-3-yl)carbamates in modest yields. The dipivalamide derived from **3** has led to the corresponding mono or dicarboxylic acids depending on the experimental conditions.[7]

Treatment of dicarbamate **4** with *n*-BuLi (3.5 equiv.) and an excess of methyl iodide has provided the trimethylated compound **9** in 92% yield (Scheme 1). This result demonstrates the efficiency of the deprotonation and the intermediate formation of the trianion A. Reaction of A with various electrophilic reagents (1.2 equiv.) has led to the corresponding 2-substituted thiophenes **10a**, **11a** and **11b**, which were, however, isolated in poor to modest yields (Scheme 1; Table 1). The yield dramatically depends on the nature of the electrophilic reagent. With ethyl 5-bromovalerate, 25% of the subtrate was consumed after one hour. The α-proton acidity of the ester was probably responsible for the protonation of the trianion A. HMPA or LiCl addition, which must prevent acid–base reaction between the substrate and the electrophilic reagent, has no substantial effect on the yield.

During this study, we have observed the formation of a

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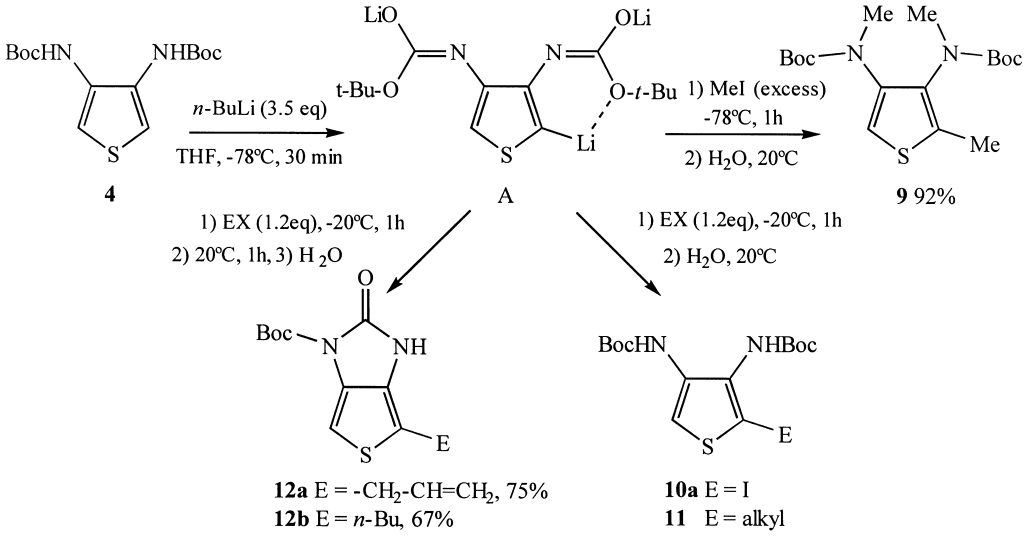


Scheme 1.

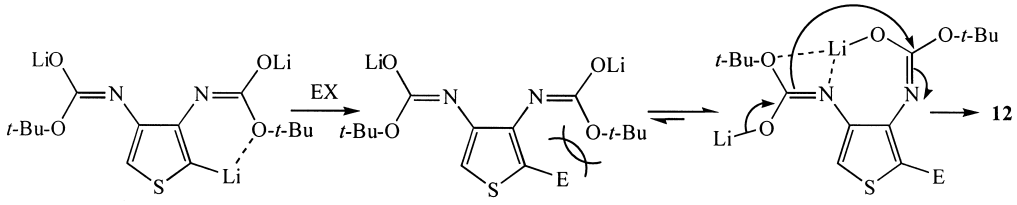
Table 1.

Number	Electrophile	Conversion (%)	Yield (%)
10a	I_2	100	60
11a	CH_2=CH–CH_2Br	90	56
11b	nBuBr	75	27
11c	EtOOC–$(CH_2)_4$Br	25	0

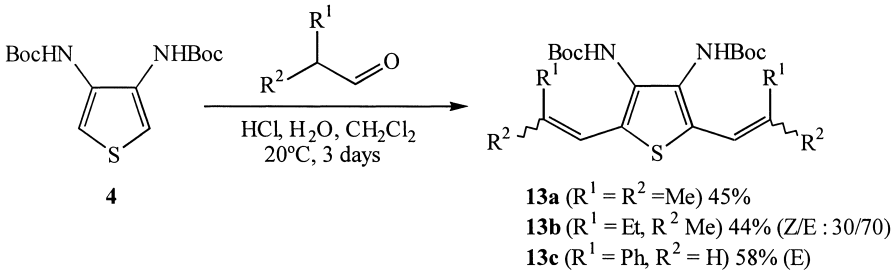
thienoimidazolone **12** when the reaction mixture was allowed to stand for one hour at room temperature before hydrolysis. The position of the remaining Boc group was assigned according to the ^{13}C NMR spectra. This cyclization probably results from a new chelation between the two functional groups. The regioselectivity was the consequence of the steric hindrance generated by the α-substituent (Scheme 2). No cyclization occurred after addition of 3.5 molar equivalents of *n*-BuLi. The formation of the thienoimidazolone **12** (R=H)[8] was partially observed with two equivalents of *n*-BuLi but the cyclization took place about 10 times slower than for the access to **12a** or **12b**. These two results pointed out the importance of both chelation and steric hindrance for the success of the thienoimidazolone formation. The efficiency of this reaction was similar to that observed for the preparation of dicarbamates **11**, but the difficulties encountered during the purification have led to lower yields.

In a previous work,[3] we described the introduction of vinyl substituents on carbamates **1** and **2** using α-branched or α-functionalized aldehydes under acidic conditions. In an analogous manner, dicarbamate **4** gave the 2,5-divinyl thiophenes **13** in moderate yields (Scheme 3). The stereochemistry of **13b** and **13c** was assigned by comparing their NMR spectra with those of similar products of the 3-aminothiophene series.[3]

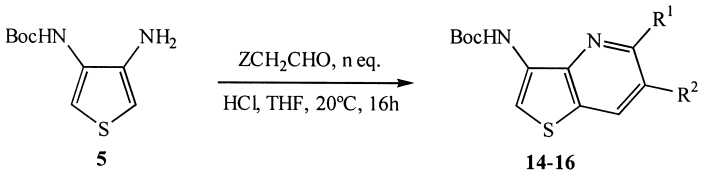
With the goal to introduce one vinyl group on the thiophene



Scheme 2.



Scheme 3.



Scheme 4.

Table 2.

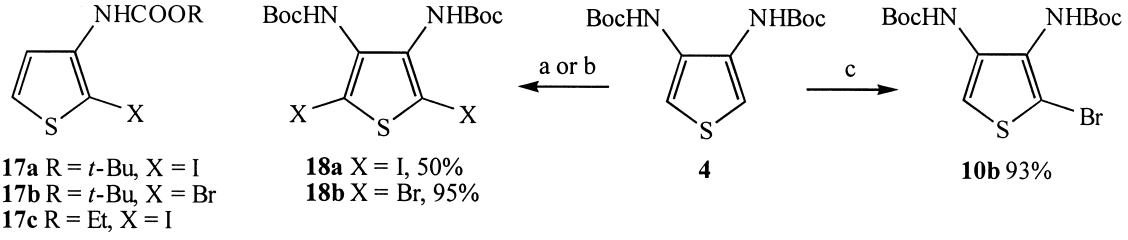
Number	Z	*n* equiv.	R^1	R^2	Yield (%)
14	COMe	1	Me	H	45
15	COMe	2	H	COMe	55
16	Ph	2	CH_2Ph	Ph	70

ring, the same reaction was carried out on the aminocarbamate **5**. Complex mixtures were obtained with α-branched aldehydes. This result points out the absence of regioselectivity in this case. The thienopyridines **14**–**16** were isolated when α-functionalized aldehydes were used (Scheme 4, Table 2).

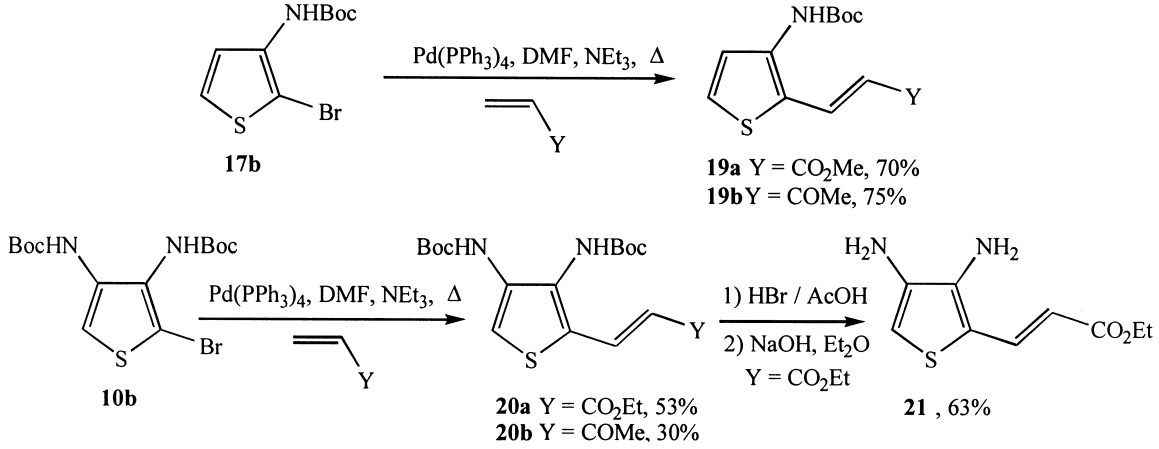
The thienopyridine **14** was isolated with 1 equiv. of 3-oxobutanal. Using an excess of aldehyde, the formed 2-vinyl-3-aminothiophene gave an imine by reaction with a second molecule of aldehyde. The cyclization occurred with the loss of acetone or hydrogen, affording the thienopyridine **15** or **16** according to the mechanism proposed in the case of the 3-aminothiophene.[3] We observe, however, that an oxidation giving **16** has occurred instead of the loss of toluene.[3]

The introduction of vinyl, alkynyl and aryl substituents was successfully achieved by coupling reactions. Gronowitz et al.[6,9] have carried out such reactions on *t*-butyl thien-3-ylcarbamate derivatives affording azaheterocycles. In the 3,4-diaminothiophene series, a double coupling process between di-*t*-butyl [2,5-bis(tributylstannyl)thiophene-3,4-diyl]dicarbamate and deactivated dihaloarenes was achieved for the synthesis of polymers.[10]

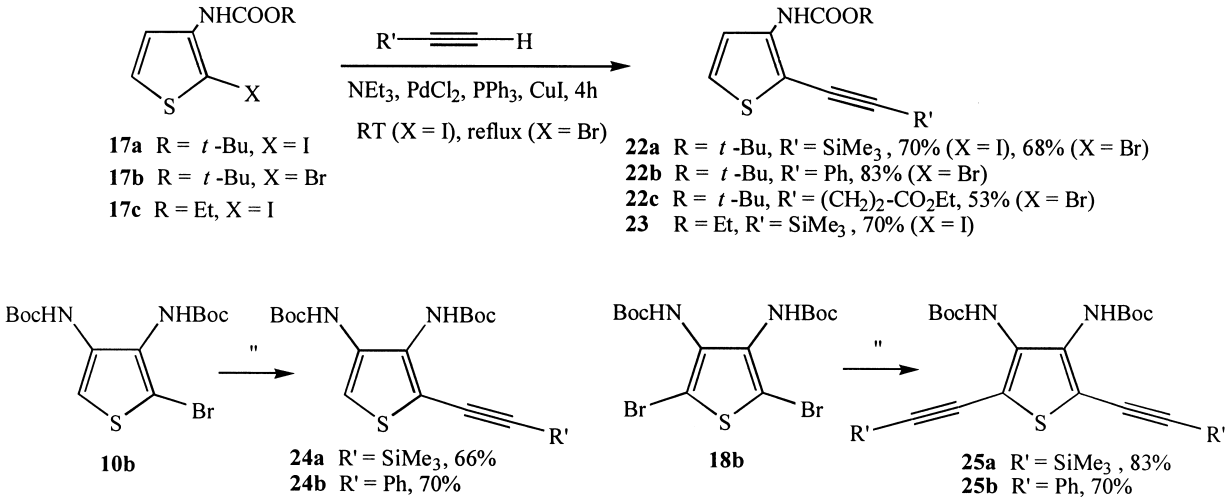
t-Butyl 2-bromothien-3-ylcarbamate **17b** was prepared as described.[11] 2-Iodothien-3-ylcarbamates **17a** and **17c** were synthesized by iodine treatment of the dilithio derivative of carbamate **1** and **2** in a more efficient way than that proposed.[9] Halo derivatives **10** and **18** were prepared by electrophilic substitution (Scheme 5), except **10a** previously described (Scheme 1). These mono and dihalothiophenes were then subjected to coupling reactions with acetylenic, olefinic compounds or with boronic acids. Heck coupling reaction[12] has allowed the access to monovinylated thienylcarbamates **19** and monovinylated dicarbamates **20** (Scheme 6). The unsaturated ester and ketone **19** are known compounds.[3] The products of double coupling reaction were not formed from dibromothiophene **18b**. The dicarbamate **20a**, an interesting synthon for the



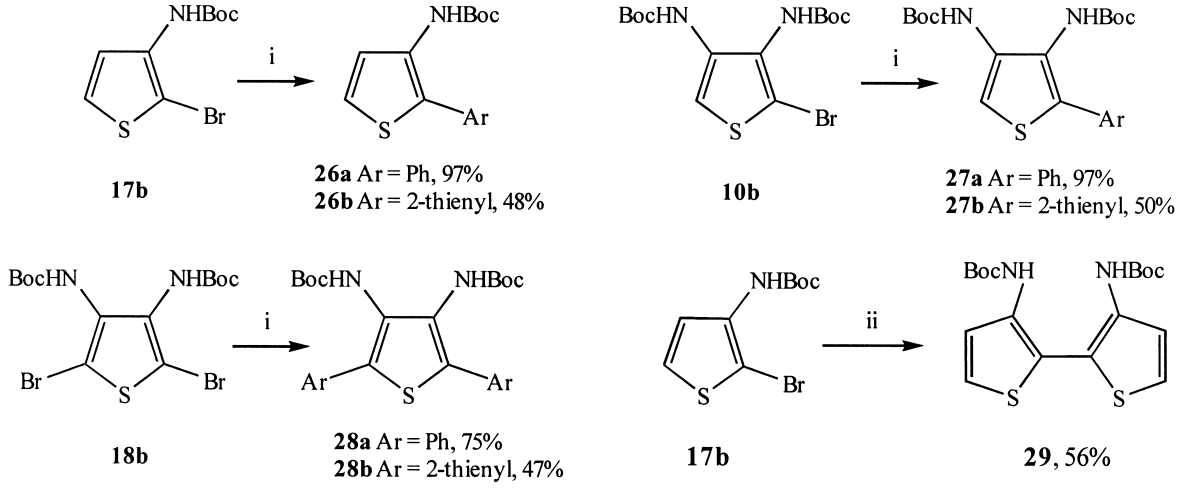
Scheme 5. (a) NIS (5 equiv.), CCl_4, Δ, 10 h; (b) Br_2 (2 equiv.), MeOH, 20 min; (c) NBS (1 equiv.), CCl_4, 15 h.



Scheme 6.



Scheme 7.



Scheme 8. (i) $ArB(OH)_2$, $Pd(PPh_3)_4$, DME, Na_2CO_3, H_2O, reflux; (ii) K_2CO_3, $(n\text{-}Bu)_4NBr$, $Pd(OAc)_2$, DMF, EtOH, H_2O, Δ.

synthesis of a biotin analog, afforded the diamine **21** by acidic treatment[13] without formation of the corresponding thienopyridinone.

We then studied the introduction of an alkynyl group. A preliminary study was carried out on the 2-halothien-3-ylcarbamates **17**. Sonogashira type reaction,[14a] already achieved in the thiophene series,[14b] proceeded smoothly with iodo derivatives as shown in Scheme 7. With the bromo derivative **17b**, the reaction succeeded only on heating. No steric effect was observed when a *t*-butyl carbamate was used (**22a** and **23**: 70% yield). Halo dicarbamates **10** and **18** were also subjected to this coupling reaction. Surprisingly, with iodo derivatives **10a** and **18a** no reaction occurred, even on heating. The bromo compounds **10b** and **18b** have led to the coupling products **24** and **25**, respectively, with correct yields.

The Suzuki coupling reaction[15] has allowed the introduction of aryl substituents using the bromothiophenes **10b**, **17b** and **18b** (Scheme 8). In all cases, the reagent was totally consumed. The modest yield observed with 2-thiopheneboronic acid resulted from difficulties encountered during the purification. In this reaction, the iodo derivatives were also unreactive. The dithienylbiscarbamate **29** was prepared from the bromocarbamate **17b** by homocoupling reaction[16] carried out for the first time in the thiophene series (Scheme 8). When applied to dicarbamate **10b**, no homocoupling product was formed.

Different methods were applied for the introduction of alkyl, aryl, alkenyl and alkynyl substituents on the α-position of β-aminothiophenes. Reaction of electrophilic species with the trianion derived from dicarbamate **4** has led to 2-substituted dicarbamates **11** or thienoimidazolones **12**. The efficient preparation of monobromo and dibromothiophene derivatives **10b**, **17b** and **18b** has allowed Pd-catalyzed coupling reactions leading to the 2-alkenyl, 2-alkynyl or 2-aryl thienylcarbamates and dicarbamates **19**–**29**.

Experimental

Di-*t*-butyl (thiophene-3,4-diyl)dicarbamate **4**,[8] *t*-butyl (4-aminothien-3-yl)carbamate **5**[4] and *t*-butyl (2-bromothien-3-yl)carbamate **17b**[11] were prepared according to known

procedures. All solvents were distilled before use and light petroleum refers to the fraction with bp 40–60°C. The chromatographic separations were achieved on silica gel (0.060–0.200 nm pore diameter ca. 4 nm) available from ACROS. ^{1}H and ^{13}C NMR spectrum were recorded in $CDCl_3$ on a Bruker AC 200 or DPX 300.

Preparation of dicarbamates 9, 10a and 11. *n*-BuLi in hexane (1.4 ml, 2.5N) was added to a stirred solution of dicarbamate **4** (0.314 g, 1 mmol) in THF (40 ml) cooled at −78°C under argon. The mixture was stirred for 30 min at −78°C and methyl iodide (1.42 g, 10 mmol) was added at −10°C. For the preparation of **10a** and **11**, the appropriate electrophilic reagent (I_2 or RBr, 1.5 mmol) was added in place of methyl iodide. The mixture was stirred for 1 h at this temperature and treated with a saturated NaCl solution (2 ml). The organic layer was dried and evaporated. The residue was chromatographed on silica gel (eluent CH_2Cl_2/light petroleum: 30/70).

Di-*t*-butyl *N*,*N*′-dimethyl (2-methylthiophene-3,4-diyl)-dicarbamate 9. Yield: 92%. ^{1}H NMR, δ: 6.73 (bs, 1H, H_5), 3.04, 3.00, 2.99, 2.95 (4s, 6H, N-CH_3), 2.21, 2.19, 2.15, 2.12 (4s, 3H, CH_3), 1.43, 1.36, 1.30 (3s, 18H, CH_3). ^{13}C NMR, δ: 155.0 (CO), 132.0 (C_3), 115.3 (C_5), 79.9 (C), 35.4 (N-CH_3), 28.0 (CH_3), 12.7 (CH_3). Anal. Calcd for $C_{17}H_{28}N_2O_4S$: C, 57.28; H, 7.92; N, 7.86; found: C, 57.32; H, 7.85; N, 7.52. MS (E.I., 70 eV): 356 ($M^{+\cdot}$,3), 256 (8), 156 (71), 57 (100).

Di-*t*-butyl (2-iodothiophene-3,4-diyl)dicarbamate 10a. Yield: 60%.^{1}H NMR, δ: 7.53 (bs, NH), 7.33 (bs, 1H, H_5), 6.06 (bs, NH), 1.47, 1.50 (2s, 18H, CH_3). ^{13}C NMR, δ: 153.8 (CO), 131.6, 131.2 (C_3, C_4), 114.8 (C_2), 108.2 (C_5), 81.7 (C), 28.0 (CH_3). Anal. Calcd for $C_{14}H_{21}N_2IO_4S$: C, 38.19; H, 4.81; N, 6.36; found: C, 37.96; H, 4.69; N, 5.98.

Di-*t*-butyl (2-allylthiophene-3,4-diyl)dicarbamate 11a. Mp=96°C, Yield: 56%. ^{1}H NMR, δ: 7.03 (bs, 1H, H_5), 6.79 (bs, NH), 5.77 (m, 2H, NH, C*H*=CH_2), 5.06–4.94 (m, 2H, CH=C*H*$_2$), 3.28 (d, 2H, CH_2, J=6.2 Hz), 1.38 (s, 18H, CH_3). ^{13}C NMR, δ: 153.8, 152.7 (CO), 134.7 (*C*H=CH_2), 131.5 (C_3), 127.0 (C_4), 123.5 (C_2), 116.2 (CH=*C*H$_2$), 105.9 (C_5), 80.7, 79.9 (C), 31.6 (CH_2), 27.8, 27.6 (CH_3). Anal. Calcd for $C_{17}H_{26}N_2O_4S$: C, 57.60; H, 7.39; N, 7.90; S, 9.05; found: C, 57.47; H, 7.12; N, 7.83; S, 8.82.

Di-*t*-butyl (2-butylthiophene-3,4-diyl)dicarbamate 11b. Yield: 27%. ^{1}H NMR, δ: 7.06 (bs, 1H, H_5), 6.90 (bs, NH), 5.97 (bs, 1H,NH), 2.63 (t, 2H, CH_2, J=7.6 Hz), 1.76–1.38 (m, 20H, CH_2, CH_3), 1.22 (m, 2H, CH_2), 0.88 (t, 3H, CH_3, J=7.4 Hz). ^{13}C NMR, δ: 153.6, 152.9 (CO), 131.4 (C_3), 129.0 (C_4), 123.0 (C_2), 106.3 (C_5), 80.9, 80.2 (C), 38.8 (CH_2), 28.0, 27.9 (CH_3), 25.5 (CH_2), 23.2 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{18}H_{30}N_2O_4S$: C, 58.35; H, 8.16; N, 7.56; S, 8.65; found: C, 58.19; H, 7.72; N, 7.35; S, 8.52.

Thienoimidazolones 12. The procedure described for the preparation of compounds **11** was used but the reaction mixture was allowed to stand for 1 h at room temperature before hydrolysis. Thienoimidazolones **12** were obtained after chromatographic purification (eluent: ether).

***t*-Butyl (1-allyl-5,6-dihydro-5-oxothieno[3,4−d]imidazol-4-yl)carboxylate 12a.** Mp=143°C, Yield: 75%. ^{1}H NMR, δ: 9.62 (bs, NH), 6.63 (s, 1H, H_3), 5.90 (m, 1H, CH=), 5.22–5.09 (m, 2H, =CH_2), 3.44 (d, 2H, CH_2, J=6.6 Hz), 1.60 (s, 9H, CH_3). ^{13}C NMR, δ: 155.9 (C_5), 147.9 (CO), 134.6 (*C*H=CH_2), 127.6 (C_{3a}), 124.8 (C_{6a}), 117.1 (CH=*C*H$_2$), 112.0 (C_1), 100.3 (C_3), 84.4 (C), 30.9 (CH_2), 28.0 (CH_3). Anal. Calcd for $C_{13}H_{16}N_2O_3S$: C, 55.70; H, 5.75; N, 9.99; found: C, 55.43; H, 5.66; N, 9.96.

***t*-Butyl (1-butyl-5,6-hydro-5-oxothieno[3,4−d]imidazol-4-yl)carboxylate 12b.** Yield: 67%. ^{1}H NMR, δ: 8.98 (bs, NH), 6.58 (s, 1H, H_3), 2.66 (t, 2H, CH_2, J=7.5 Hz), 1.57 (m, 11H, CH_2, CH_3), 1.32 (m, 2H, CH_2), 0.86 (t, 3H,CH_3, J=7.3 Hz). ^{13}C NMR, δ: 156.1 (C_5), 147.8 (CO), 128.7 (C_{3a}), 127.4 (C_{6a}), 115.1 (C_1), 99.4 (C_3), 83.9 (C), 32.5 (CH_2), 27.8 (CH_3), 26.1 (CH_2), 21.8 (CH_2), 13.6 (CH_2). Anal. Calcd for $C_{14}H_{20}N_2O_3S$: C, 56.74; H, 6.80; N, 9.45; found: C, 56.26; H, 6.67; N, 9.28.

Double vinylation of dicarbamate 4. The aldehyde (6 mmol) and conc. aq. HCl (0.5 ml) were added to dicarbamate **4** (0.314 g, 1 mmol) in CH_2Cl_2 (30 ml). After stirring for 4 days at room temperature and further addition of aldehyde (2 mmol) each day, the mixture was treated with NaOH aq. solution. The organic phase was dried and evaporated. The oily residue was chromatographed (eluent: ethyl acetate/light petroleum: 20/80) to give the dicarbamate **13**.

Di-*t*-butyl [2,5-di(2-methylpropen-1-yl)thiophene-3,4-diyl]-dicarbamate 13a. Mp=153°C, Yield=45%. ^{1}H NMR, δ: 6.27 (bs, 2H, NH), 6.17 (s, 2H, CH=C), 1.91 (s, 6H, CH_3), 1.89 (s, 6H, CH_3), 1.46 (s, 18H, CH_3). ^{13}C NMR, δ: 153.9 (CO), 135.5 (C_3, C_4), 129.2 (*C*=CH), 127.3 (C_2, C_5), 115.5 (*C*H=C), 80.1 (C), 28.0 (CH_3), 27.1 (CH_3), 20.1 (CH_3). Anal. Calcd for $C_{22}H_{34}N_2O_4S$: C, 62.53; H, 8.11; N, 6.63; S, 7.59; found: C, 62.08; H, 7.76; N, 6.02; S, 6.99.

Di-*t*-butyl [2,5-di(2-methylbuten-1-yl)thiophene-3,4-diyl]-dicarbamate 13b. Yield=44%. Z/E mixture: 30/70. ^{1}H NMR, δ: 6.35 (bs, 2H, NH), 6.17 and 6.11 (2s, 2H, CH=C), 2.33 and 2.16 (2q, 4H, CH_2, J=7.4 Hz), 1.91 and 1.85 (2s, 6H, CH_3), 1.45 (s, 18H, CH_3), 1.05 (t, 6H, CH_3, J=7.4 Hz). ^{13}C NMR, δ: 153.8 (CO), 140.3 (C_3, C_4), 129.5 and 128.1 (*C*=CH), 127.5 (C_2, C_5), 115.0 and 114.1 (*C*H=C), 79.8 (C), 33.5 and 26.5 (CH_2), 27.9 (CH_3), 23.8 and 18.4 (CH_3), 12.4 and 11.9 (CH_3). Anal. Calcd for $C_{24}H_{38}N_2O_4S$: C, 63.97; H, 8.50; N, 6.22; found: C, 64.13; H, 8.12; N, 6.01.

Di-*t*-butyl [2,5-di(2-phenylethen-1-yl)thiophene-3,4-diyl]-dicarbamate 13c. Mp=223°C, Yield=58%. ^{1}H NMR, δ: 7.23–7.46 (m, 10H, Ph), 7.12 (d, 2H, Ph-C*H*=CH, J=16.1 Hz), 6.84 (d, 2H, PhCH=C*H*, J=16.1 Hz), 6.50 (bs, 2H, NH), 1.50 (s, 18H, CH_3). ^{13}C NMR, δ: 154.0 (CO), 136.8 (C_3, C_4), 129.2, 129.0, 128.6, 128.1, 127.7, 127.7, 118.8 (Ph, C_2, C_5, Ph*C*H=CH, PhCH=*C*H), 80.1 (C), 28.1(CH_3). Anal. Calcd for $C_{30}H_{34}N_2O_4S$: C, 69.47; H, 6.61; N, 5.40; S, 6.18; found: C, 69.31; H, 6.44; N, 5.37; S, 6.06.

Thienopyridines 14–16. A solution of aminocarbamate **5**

(0.214 g, 1 mmol) in THF (10 ml) containing conc. aq. HCl (0.5 ml), was quickly added to 3-oxobutanal (0.086 g, 1 mmol) in the same solvent (10 ml). The mixture was stirred for 16 h and washed with 4N aqueous NaOH (10 ml). The organic layer was dried and concentrated. The thienopyridine **14** was purified by chromatography on silica gel (eluent: CH_2Cl_2/light petroleum: 1/1) and recrystallization (light petroleum). For the preparation of **15** and **16**, 2 equiv. of 3-oxobutanal (0.172 g, 2 mmol) and 2-phenylacetaldehyde (0.236 g, 2 mmol) were used respectively.

***t*-Butyl (5-methylthieno[3,2-b]pyridin-3-yl)carbamate 14.** Mp=57°C, Yield=45%. ^{1}H NMR, δ: 7.97 (d, 1H, H_6, J=8.2 Hz), 7.83 (bs, 1H, H_2), 7.75 (bs, NH), 7.13 (d, 1H, H_7, J=8.2 Hz), 2.64 (s, 3H, CH_3), 1.54 (s, 9H, CH_3). ^{13}C NMR, δ: 155.2 (C_5), 152.9 (CO), 146.6 (C_{3a}), 130.7 (C_7), 130.0 (C_3), 129.4 (C_{7a}), 119.9 (C_6), 109.2 (C_2), 80.2 (C), 28.2 (CH_3), 24.1 (CH_3). Anal. Calcd for $C_{13}H_{16}N_2O_2S$: C, 56.11; H, 7.65; N, 8.18; found: C, 56.03; H, 7.65; N, 8.13.

***t*-Butyl (6-acetylthieno[3,2-b]pyridin-3-yl)carbamate 15.** Mp=135°C, Yield=55%. ^{1}H NMR, δ: 9.11 (d, 1H, H_5, J=1.8 Hz), 8.66 (d, 1H, H_7, J=1.8 Hz), 8.02 (bs, NH), 7.86 (bs, 1H, H_2), 2.68 (s, 3H, CH_3), 1.53 (s, 9H, CH_3). ^{13}C NMR, δ: 195.9 (CO), 152.5 (CO), 149.3 (C_{3a}), 146.1 (C_5), 130.0 (C_6), 129.9 (C_7), 129.9 (C_3), 128.1 (C_{7a}), 113.9 (C_2), 80.8 (C), 28.0 (CH_3), 26.7 (CH_3). Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 57.51; H, 5.52; N, 9.58; found: C, 57.53; H, 5.51; N, 9.20.

***t*-Butyl (6-benzyl-5-phenylthieno[3,2−b]pyridin-3-yl)carbamate 16.** Mp=123°C, Yield=70%. ^{1}H NMR, δ: 7.93 (s, 1H, H_7), 7.84 (bs, 1H, H_2), 7.39–7.36 (m, 3H, Ph), 7.20–7.13 (m, 6H, Ph, NH), 6.98–6.94 (m, 2H, Ph), 4.25 (s, 2H, CH_2), 1.59 (s, 9H, CH_3). ^{13}C NMR, δ: 154.7 (C_5), 152.7 (CO), 147.8 (C_{3a}), 131.9 (C_7), 129.4 (C_3), 129.4 (C_{7a}), 139.4, 139.3, 134.2, 129.2, 128.6, 128.1, 127.8, 127.6, 125.7 (C_{Ph}, C_6), 109.3 (C_2), 80.5 (C), 41.4 (CH_2), 28.1 (CH_3). Anal. Calcd for $C_{25}H_{24}N_2O_2S$: C, 72.09; H, 5.81; N, 6.73; found: C, 72.28; H, 5.59; N, 6.56. M/S (I.E., 70eV): 416 ($M^{+\cdot}$, 18), 341 (17), 316 (100), 237 (8); (C.I., isobutane): 473 ($(M+C_4H_9)^+$, 10), 417 (MH^+, 100).

Monoiodo thiophenes 17a and 17c. Alkyl (2-iodothien-3-yl)carbamates **17a** and **17c** were prepared by addition of *n*-BuLi (2.5N solution in hexane, 1 ml) to a stirred solution of *t*-butyl or (ethyl) thien-3-ylcarbamate **1** (or **2**) (1 mmol) in THF (40 ml) cooled at −78°C under argon. After 30 min at this temperature, the mixture was warmed up to −10°C and iodine (0.305 g, 1.2 mmol) was added. The solution was allowed to stand 1 h at this temperature and a saturated NaCl solution was added. The iodo compound **17b** (or **17c**) was obtained after silica gel chromatography (eluent: AcOEt/light petroleum: 5/95).

***t*-Butyl (2-iodothien-3-yl)carbamate 17a.**[5] Mp=71°C, Yield: 82%. ^{1}H NMR, δ: 7.45 (m, 2H, H_4, H_5), 6.60 (bs, NH), 1.31 (t, 3H, CH_3).

Ethyl (2-iodothien-3-yl)carbamate 17c. Mp=88°C, Yield: 84%. ^{1}H NMR, δ: 7.45 (m, 2H, H_4, H_5), 6.60 (bs, NH), 4.22 (q, 2H, CH_2, J=7.1 Hz), 1.31 (t, 3H, CH_3).

***t*-Butyl (2,5-diiodothiophene-3,4-diyl)dicarbamate 18a.** *N*-Iodosuccinimide (1.35 g, 6 mmol) was added to a solution of dicarbamate **4** (0.314 g, 1 mmol) in CCl_4 (50 ml). The mixture was heated under reflux for 10 h, filtered, washed with water and the solvent was evaporated. The di-*t*-butyl (2,5-diiodo thiophene-3,4-diyl)dicarbamate **18a** was used without further purification. *F* dec.=151°C, Yield: 50%. ^{1}H NMR, δ: 6.49 (bs, 2H, NH), 1.46 (s, 18H, CH_3). ^{13}C NMR, δ:153.1 (CO), 135.8 (C_3,C_4), 81.2 (C), 28.1 (CH_3).

Di-*t*-butyl (2-bromothiophene-3,4-diyl)dicarbamate 10b. *N*-Bromosuccinimide (0.178 g, 1 mmol) was added to a solution of dicarbamate **4** (0.314 g, 1 mmol) in CCl_4 (20 ml). The mixture was stirred overnight, filtered and washed with water. The organic layer was dried and evaporated under reduced pressure. The bromothienylcarbamate **10b** was purified by chromatography (eluent: CH_2Cl_2). Yield: 93%. ^{1}H NMR, δ: 7.48 (bs, NH), 7.34 (bs, 1H, H_5), 6.15 (bs, NH), 1.49, 1.47 (2s, 18H, CH_3). ^{13}C NMR, δ: 153.7, 152.5 (CO), 131.1 (C_4), 127.0 (C_3), 108.5 (C_5), 81.2, 80.2 (C), 27.9, 27.7 (CH_3). Anal. Calcd for $C_{14}H_{21}N_2BrO_4S$: C, 42.75; H, 5.38; N, 7.12; S, 8.15; found: C, 42.73; H, 5.21; N, 7.18; S, 7.96.

Di-*t*-butyl (2,5-dibromothiophene-3,4-diyl)dicarbamate 18b. Bromine (0.32 g, 2 mmol) dissolved in MeOH (10 ml) was added dropwise to a solution of dicarbamate **4** (0.314 g, 1 mmol) in MeOH (12 ml). The mixture was stirred for 20 min at 20°C and poured in water (25 ml). The dibromothiophene **18b** was isolated after rapid filtration and recrystallization ($CHCl_3$/heptane: 1/1). Mp >230°C, Yield: 95%. ^{1}H NMR, δ: 6.47 (bs, 2H, NH), 1.47 (s, 18H, CH_3). ^{13}C NMR, δ: 152.9 (CO), 131.1 (C_3, C_4), 81.1 (C), 27.9 (CH_3). Anal. Calcd for $C_{14}H_{20}N_2Br_2O_4S$: C, 35.61; H, 4.27; N, 5.93; found: C, 35.65; H, 4.27; N, 5.93.

Heck type coupling reaction. $Pd(PPh_3)_4$ (0.116 g, 0.1 mmol), NEt_3 (0.808 g, 8 mmol) and methyl acrylate (6 mmol) were added to a degased solution of bromocarbamate **17b** (or **10b**) (1 mmol) in DMF (1 ml). The mixture was heated at 150°C for 10 h, diluted with water (10 ml) and extracted with ether (3×10 ml). The dried organic solution was concentrated and the product **19a** (or **20a**) was purified by silica gel chromatography (eluent: CH_2Cl_2). Enones **19b** and **20b** were prepared by the same procedure, using vinyl methyl ketone in place of methyl acrylate.

Methyl 3-(3-*t*-butoxycarbonylaminothien-2-yl)propenoate 19a.[3] Mp=124°C, Yield: 70%. ^{1}H NMR, δ: 7.74 (d, 1H, C*H*=CH, J=15.3 Hz), 7.50 (dl, 1H, H_5, J=5.4 Hz), 7.25 (d, 1H, H_4, J=5.4 Hz), 6.91 (bs, NH), 6.10 (d, 1H, CH=C*H*, J=15.3 Hz), 3.68 (s, 3H, CH_3), 1.49 (s, 9H, CH_3).

4-[3-(*t*-Butoxycarbonylamino)thien-2-yl]butenone 19b.[3] Mp=128°C, Yield: 75%. ^{1}H NMR, δ: 7.70 (d, 1H, C*H*=CH, J=15.3 Hz), 7.51 (m, 2H, NH, H_5), 7.27 (d, 1H, H_4, J=5.7 Hz), 6.42 (d, 1H, CH=C*H*, J=15.3 Hz), 2.29 (s, 3H, CH_3), 1.49 (s, 9H, CH_3).

Ethyl 3-[3,4-bis(*t*-butoxycarbonylamino)thien-2-yl]propenoate 20a. Mp=123°C, Yield: 53%. ^{1}H NMR, δ: 7.69

(d, 1H, C*H*═CH, *J*=15.6 Hz), 7.38 (bs, 1H, H_5), 7.22 (bs, NH), 6.70 (bs, NH), 6.14 (d, 1H, CH═C*H*, *J*=15.6 Hz), 4.20 (q, 2H, CH_2, *J*=7.1 Hz), 1.48, 1.47 (2s, 18H, CH_3),1.28 (t, 3H, CH_3, *J*=7.1 Hz). ^{13}C NMR, δ: 166.7 (CO), 153.9, 152.9 (CO), 133.8 (*C*H═CH), 132.6 (C_3), 128.7 (C_4), 116.3 (CH═*C*H), 81.8, 80.6 (C), 60.4 (CH_2), 28.1, 27.9 (CH_3), 14.1 (CH_3). Anal. Calcd for $C_{19}H_{28}N_2O_6S$: C, 55.32; H, 6.84; N, 6.79; S, 7.77; found: C, 55.41; H, 6.86; N, 6.81; S, 7.33.

4-[3,4-Bis(*t*-butoxycarbonylamino)thien-2-yl]butenone 20b. Yield: 30%. ^{1}H NMR, δ: 7.55 (d, 1H, C*H*═CH, *J*=15.7 Hz), 7.41 (bs, 1H, H_5), 7.20 (bs, NH), 6.75 (bs, NH), 6.45 (d, 1H, CH═C*H*, *J*=15.7 Hz), 2.28 (s, 3H, CH_3), 1.49, 1.47 (2s, 18H, CH_3). ^{13}C NMR, δ: 154.6, 153.1 (CO), 132.6 (*C*H═CH), 134.1 (C_3), 124.6 (CH═*C*H), 107.2 (C_2), 81.6, 80.7 (C), 29.7 (CH_3), 28.0, 27.9 (CH_3). Anal. Calcd for $C_{18}H_{26}N_2O_5S$: C, 56.53; H, 6.85; N, 7.32; S, 8.38; found: C, 56.68; H, 7.14; N, 7.42; S, 7.55.

Ethyl 3-(3,4-diaminothien-2-yl)propenoate 21. Dicarbamate **20a** (0.412 g, 1 mmol) in a 20% solution of hydrobromic acid in acetic acid (0.450 g, 1 mmol) was stirred for 20 min at room temperature and anhydrous ether (20 ml) was added. The reaction was stirred for another 15 min. The filtered salt was washed with ether and dissolved in water (20 ml). After neutralization with diluted NaOH aq. solution, the diamine **21** was extracted with ether (3×10 ml) and obtained in a pure form after concentration. Yield=63%. ^{1}H NMR, δ: 7.70 (d, 1H, C*H*═CH, *J*= 15.3 Hz), 6.25 (s, 1H, H_5), 5.91 (d, 1H, CH═C*H*, *J*=15.3 Hz), 4.19 (q, 2H, CH_2, *J*=7.1 Hz), 4.00 (bs, 4H, NH_2), 1.28 (t, 3H, CH_3, *J*=7.1 Hz). ^{13}C NMR, δ: 166.2 (CO), 140.6 (C4), 136.0 (C3), 134.6 (*C*H═CH), 111.2 (CH═*C*H), 105.5 (C5), 60.1 (CH_2), 14.2 (CH_3). Anal. Calcd for $C_9H_{12}N_2O_2S$: C, 50.93; H, 5.70; N, 13.20; S, 15.10; found: C, 51.45; H, 6.02; N, 12.98; S, 14.98.

Sonogashira type coupling reaction. To a degased solution of bromocarbamate **17b** (0.695 g, 2.5 mmol) in triethylamine (5 ml) was added, successively, the acetylenic reagent (3.75 mmol), $PdCl_2$ (0.022 g, 0.125 mmol), PPh_3 (0.066 g, 0.25 mmol.), and CuI (0.024 g, 0.125 mmol). The mixture was stirred on heating for 4 h under argon and then diluted with ether (50 ml) and water (10 ml). After filtration, the organic layer was dried and evaporated. The product was purified by silica gel chromatography (eluent CH_2Cl_2/light petroleum: 1/1). Using the same experimental procedure, iodocarbamates **17a** and **17c** have led at room temperature to the carbamates **22** and **23**, respectively. Dicarbamates **24** were obtained by the same way from **10b**. Dicarbamates **25** were prepared using double amounts of the acetylenic reagent, $PdCl_2$, PPh_3 and CuI. Compounds **24** and **25** were purified by silica gel chromatography (eluent: CH_2Cl_2).

***t*-Butyl (2-trimethylsilylethynylthien-3-yl)carbamate 22a.** Yield: 70%. ^{1}H NMR, δ: 7.57 (bs, 1H, H_5), 7.10 (d, 1H, H_4, *J*=5.4 Hz), 6.87 (bs, NH), 1.50 (s, 9H, CH_3), 0.24 (s, 9H, SiC*H*$_3$). ^{13}C NMR, δ: 151.4 (CO), 141.6 (C_3), 125.9 (C_5), 120.0 (C_4), 104.0 (C), 102.8 (C_2), 94.9 (C), 80.6 (C), 27.9 (CH_3), −0.3 ($SiCH_3$). Anal. Calcd for $C_{14}H_{21}NO_2SSi$: C, 56.91; H, 7.16; N, 4.74; found: C, 56.95; H, 6.84; N, 5.27.

Ethyl (2-trimethylsilylethynylthien-3-yl)carbamate 23. Yield: 70%. ^{1}H NMR, δ: 7.58 (bs, 1H, H_5), 7.12 (d, 1H, H_4, *J*=5.5 Hz), 6.99 (bs, NH), 4.22 (q, 2H, CH_2, *J*=7.1 Hz), 1.31 (t, 3H, CH_3, *J*=7.1 Hz), 0.24 (s, 9H, SiC*H*$_3$). ^{13}C NMR, δ: 152.7 (CO), 141.2 (C_3), 126.3 (C_5), 120.3 (C_4), 104.4 (C), 94.8 (C), 61.5 (CH_2), 14.4 (CH_3), 0.1 ($SiCH_3$). Anal. Calcd for $C_{12}H_{17}NO_2SSi$: C, 53.89; H, 6.41; N, 5.24; S, 11.99; found: C, 53.06; H, 6.21; N, 5.82; S, 11.72.

***t*-Butyl (2-phenylethynylthien-3-yl)carbamate 22b.** Mp= 83°C, Yield: 83%. ^{1}H NMR, δ: 7.65 (bs, 1H, H_5), 7.53–7.47 (m, 2H, Ph), 7.35–7.33 (m, 3H, Ph), 7.17 (d, 1H, H_4, *J*=5.5 Hz), 6.96 (bs, NH), 1.53 (s, 9H, CH_3). ^{13}C NMR, δ: 151.5 (CO), 140.5 (C_3), 131.0, 128.1, 128.0, 122.3 (Ph) 125.9 (C_5), 120.5 (C_4), 103.0 (C_2), 97.8 (C), 80.6 (C), 79.5 (C), 27.9 (CH_3). Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68; found: C, 68.49; H, 5.91; N, 4.64.

Ethyl 5-(3-*t*-butoxycarbonylaminothien-2-yl)pent-4-ynoate 22c. Yield: 53%. ^{1}H NMR, δ: 7.55 (bs, 1H, H_5), 7.01 (d, 1H, H_4, *J*=5.5 Hz), 6.91 (bs, NH), 4.13 (q, 2H, CH_2, *J*=7.1 Hz), 2.74 (t, 2H, CH_2, *J*=7.2 Hz), 2.56 (t, 2H, CH_2, *J*=7.2 Hz), 1.46 (s, 9H, CH_3), 1.21 (t, 3H, CH_3, *J*=7.1 Hz). ^{13}C NMR, δ: 171.3 (C_{10}), 150.6 (CO), 140.4 (C_3), 124.5 (C_5), 119.9 (C_4), 102.9 (C_2), 96.8 (C_6), 80.3 (C), 71.4 (C_7), 60.2 (CH_2), 33.0 (C_9), 27.7 (CH_3), 15.5 (C_8), 13.7 (CH_3). Anal. Calcd for $C_{16}H_{21}NO_4S$: C, 58.23; H, 6.19; N, 4.53; S, 10.36; found: C, 58.30; H, 6.58; N, 4.08; S, 9.99.

Di-*t*-butyl (2-trimethylsilylethynylthiophen-3,4-diyl)dicarbamate 24a. Mp=135°C, Yield: 66%. ^{1}H NMR, δ: 8.50 (bs, NH), 7.35 (s, 1H, H_5), 6.47 (bs, NH), 1.48 (s, 18H, CH_3), 0.23 (s, 9H, $SiCH_3$). ^{13}C NMR, δ: 153.7, 152.8 (CO), 131.8, 130.3 (C_3, C_4), 110.2 (C_5), 104.1 (C), 95.0 (C), 81.6, 80.1 (C), 28.1, 27.9 (CH_3), −0.3 (SiC*H*$_3$). Anal. Calcd for $C_{19}H_{30}N_2O_4SSi$: C, 55.58; H, 7.36; N, 6.82; S, 7.81; found: C, 55.44; H, 7.25; N, 6.92; S, 7.37.

Di-*t*-butyl (2-phenylethynylthiophen-3,4-diyl)dicarbamate 24b. Mp=178°C, Yield: 70%. ^{1}H NMR, δ: 8.71 (bs, NH), 7.51–7.32 (m, 6H, Ph, H_5), 6.58 (bs, NH), 1.50 (s, 18H, CH_3). ^{13}C NMR, δ: 153.9, 153.0 (CO), 130.7 (C_3, C_4), 131.2, 128.6, 128.3, 122.3 (Ph), 110.6 (C_5), 97.8 (C), 81.9, 80.3 (C), 80.0 (C), 28.1, 28.0 (CH_3). Anal. Calcd for $C_{22}H_{26}N_2O_4S$: C, 63.75; H, 6.32; N, 6.76; S, 7.73; found: C, 63.62; H, 5.98; N, 6.92; S, 7.64.

Ethyl 5-[3,4-bis(*t*-butoxycarbonylamino)thien-2-yl]pent-4-ynoate 24c. Yield: 46%. ^{1}H NMR, δ: 8.00 (bs, NH), 7.08 (s, 1H, H_5), 6.48 (bs, NH), 4.11 (q, 2H, CH_2, *J*=7.2 Hz), 2.72 (t, 2H, CH_2, *J*=7.1 Hz), 2.54 (t, 2H, CH_2, *J*=7.1 Hz), 1.46,1.42 (s, 18H, CH_3), 1.18 (t, 3H, CH_3, *J*=7.2 Hz). ^{13}C NMR, δ: 171.5 (C_{10}), 153.9, 153.0 (CO), 130.8, 129.3 (C_3, C_4), 109.5 (C_5), 97.2 (C_6), 81.7 (C_7), 80.7, 80.1 (C), 60.6 (CH_2), 33.2 (C_9), 28.1, 28.0 (CH_3), 15.7 (C_8), 14.0 (CH_3). Anal. Calcd for $C_{21}H_{30}N_2O_6S$: C, 56.59; H, 6.65; N, 6.60; S, 7.55; found: C, 56.68; H, 7.14; N, 6.42; S, 7.92.

Di-*t*-butyl [2,5-bis(trimethylsilylethynyl)thiophen-3,4-diyl]-dicarbamate 25a Mp=145°C, Yield: 83%. ^{1}H NMR, δ: 6.75 (bs, 2H, NH), 1.46 (s, 18H, CH_3), 0.20 (s, 18H, $SiCH_3$). ^{13}C NMR, δ: 152.6 (CO), 133.9 (C_3, C_4), 104.2 (C), 94.9 (C), 80.6 (C), 27.8 (CH_3), −0.5 ($SiCH_3$). Anal.

Calcd for $C_{24}H_{38}N_2O_4SSi_2$: C, 56.88; H, 7.56; N, 5.53; S, 6.33; found: C, 56.68; H, 7.82; N, 5.82; S, 6.83.

Di-*t*-butyl (2,5-diphenylethynylthiophen-3,4-diyl)dicarbamate 25b. Mp=155°C, Yield: 70%. ^{1}H NMR, δ: 7.52–7.30 (m, 10H, Ph), 6.95 (bs, 2H, NH), 1.50 (s, 18H, CH_3). ^{13}C NMR, δ: 152.9 (CO), 133.4 (C_3, C_4), 131.3, 128.6, 128.2, 122.4 (Ph), 98.3 (C), 81.0 (C), 80.4 (C), 28.0 (CH_3). Anal. Calcd for $C_{30}H_{30}N_2O_4S$: C, 70.02; H, 5.88; N, 5.44; found: C, 69.32; H, 6.34; N, 5.13.

Suzuki type coupling reaction. $Pd(PPh_3)_4$ (0.060 g, 0.05 equiv.) was added to a degased solution of bromocarbamate **17b** (0.278 g, 1 mmol) in dimethoxyethane (5 ml). After stirring for 10 min, the boronic acid (1.5 equiv.), water (2.5 ml) and sodium carbonate (0.318 g, 3 equiv.) were added. The reaction mixture was heated on reflux for 4 h, cooled and poured in ether (50 ml) and water (10 ml). The usual work-up has led to **26a** with benzeneboronic acid and **26b** with 2-thiopheneboronic acid. The same experimental procedure gave the monoaryl dicarbamates **27** from **10b** and the diaryl derivatives **28** from **18b** using double amount of reagents.

***t*-Butyl (2-phenylthien-3-yl)carbamate 26a.** Mp=56°C, Yield: 97%. ^{1}H NMR, δ: 7.65 (bs, 1H, H_5), 7.45–7.39 (m, 5H, Ph), 7.22 (d, 1H, H_4,J=5.5 Hz), 6.62 (bs, NH), 1.48 (s, 9H, CH_3). ^{13}C NMR, δ: 152.7 (CO), 132.7 (C_3), 131.7, 130.7, 129.0, 128.5 (Ph), 127.5 (C_5), 123.2 (C_4), 80.4 (C), 28.1 (CH_3). Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.42; H, 6.22; N, 5.09; S, 11.65; found: C, 65.58; H, 6.56; N, 4.66; S, 11.23.

***t*-Butyl [2-(thien-2-yl)thien-3-yl]carbamate 26b.** Mp=57°C, Yield: 48%. ^{1}H NMR, δ: 7.55 (bs, 1H, H_5), 7.34–7.31 (dd, 1H, $H_{5'}$, J_1=1.5 Hz, J_2=4.9 Hz), 7.17 (d, 1H, H_4, J=5.5 Hz), 7.13–7.06 (m, 2H, $H_{4'}$, $H_{3'}$), 6.69 (bs, NH), 1.48 (s, 9H, CH_3). ^{13}C NMR, δ: 152.6 (CO), 133.8 (C_6), 132.5 (C_3), 127.7 (C_5, C_8), 125.7 (C_9, C_{10}), 123.4 (C_4), 80.5 (C), 28.1 (CH_3). Anal. Calcd for $C_{13}H_{15}NO_2S_2$: C, 55.49; H, 5.37; N, 4.98; S, 22.79; found: C, 55.27; H, 5.21; N, 5.10; S, 22.19.

***t*-Butyl (2-phenylthiophene-3,4-diyl)dicarbamate 27a.** Mp=50°C, Yield: 97%. ^{1}H NMR, δ: 7.41–7.27 (m, 6H, Ph, H_5), 7.20 (bs, NH), 6.00 (bs, NH), 1.50, 1.43 (2s, 18H, CH_3). ^{13}C NMR, δ: 154.5, 152.8 (CO), 132.7 (C_3), 132.4, 128.6, 127.8, 127.7 (Ph), 122.6 (C_2), 115.0 (C_5), 81.1, 80.2 (C), 28.0, 27.8 (CH_3). Anal. Calcd for $C_{20}H_{26}N_2O_4S$: C, 61.52; H, 6.71; N, 7.17; found: C, 61.44; H, 6.80; N, 6.70.

***t*-Butyl [2-(thien-2-yl)thiophene-3,4-diyl]dicarbamate 27b.** Mp=119°C, Yield: 50%. ^{1}H NMR, δ: 7.28–7.24 (m, 2H, H_5, $H_{5'}$), 7.15 (m, 1H, $H_{3'}$), 7.04–6.99 (dd, 1H, $H_{4'}$, J_1=3.8 Hz, J_2=4.9 Hz) 6.20 (bs, NH), 1.49, 1.45 (2s, 18H, CH_3). ^{13}C NMR, δ: 154.4, 152.7 (CO), 134.0 (C_6), 132.6 (C_3), 127.1 (C_8), 125.4, 125.0 (C_9, C_{10}), 122.4 (C_2), 81.7, 80.4 (C), 28.0, 27.9 (CH_3). Anal. Calcd for $C_{18}H_{24}N_2O_4S_2$: C, 54.52; H, 6.10; N, 7.07; S, 16.17; found: C, 54.35; H, 6.46; N, 7.12; S, 15.77.

***t*-Butyl (2,5-diphenylthiophene-3,4-diyl)dicarbamate 28a.** Mp=198°C, Yield: 75%. ^{1}H NMR, δ: 7.56–7.23 (m, 10H, Ph), 6.53 (bs, 2H, NH), 1.45 (s, 18H, CH_3). ^{13}C NMR, δ: 154.0 (CO), 132.1, 128.6, 127.7, 127.6 (Ph), 80.4 (C), 28.0 (CH_3). Anal. Calcd for $C_{26}H_{30}N_2O_4S$: C, 66.93; H, 6.48; N, 6.00; S, 6.87; found: C, 66.57; H, 6.38; N, 5.90; S, 6.65.

***t*-Butyl [2-(thien-2-yl)thiophene-3,4-diyl]dicarbamate 28b.** Mp=166°C, Yield: 47%. ^{1}H NMR, δ: 7.28–7.24 (m, 2H, $H_{5'}$), 7.20–7.15 (m, 2H, $H_{3'}$), 7.04–6.99 (m, 2H, $H_{4'}$) 6.45 (bs, 2H, NH), 1.51 (s, 18H, CH_3). ^{13}C NMR, δ: 153.9 (CO), 133.9 (C_6), 126.7 (C_8), 125.5, 124.7 (C_9, C_{10}), 80.4 (C), 28.1 (CH_3). Anal. Calcd for $C_{22}H_{26}N_2O_4S_3$: C, 55.21; H, 5.47; N, 5.85; found: C, 55.65; H, 5.78; N, 5.88.

Di-*t*-butyl 2,2′-bis(thien-3-ylcarbamate) 29. Potassium carbonate (0.276 g, 2 mmol), tetrabutylammonium bromide (0.322 g, 1 mmol) and palladium acetate (0.024 g, 0.1 mmol) were added to the bromothienyl carbamate **17b** (0.556 g, 2 mmol) in DMF (1.5 ml), ethanol (1 ml) and water (1 ml). The reaction was heated on reflux for 8 h then diluted with ether (30 ml) and water (10 ml). A usual work-up has allowed the isolation of dicarbamate **29**. Mp=175°C, Yield: 56%. ^{1}H NMR, δ: 7.69 (d, 2H, H_5, $H_{5'}$, J=5.7 Hz), 7.32 (d, 2H, H_4, $H_{4'}$, J=5.7 Hz), 6.48 (bs, 2H, NH), 1.45 (s, 18H, CH_3). ^{13}C NMR, δ: 152.3 (CO), 135.4 (C_3), 126.3 (C_5), 122.2 (C_4), 80.8 (C), 28.1 (CH_3). Anal. Calcd for $C_{18}H_{24}N_2O_4S_2$: C, 54.52; H, 6.10; N, 7.06; S, 16.17; found: C, 54.22; H, 6.02; N, 6.83; S, 15.88.

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