Pergamon

Tetrahedron Vol. 51, No. 7, pp. 2129-2136, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01086-2

Stannylcupration of γ-Heterosubstituted Acetylenic Esters: a New Route to 4-Stannylated Five Membered N- and O- Heterocycles.

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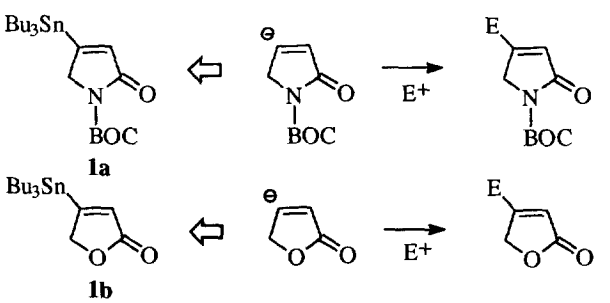
Abstract: *4-Tributylstannyl,2-(5H)-furanone and pyrrolone have been prepared in good yields by addition of mixed stannylcuprate reagent on γ-amino and γ-hydroxy acetylenic esters. The use of these compounds as useful intermediates for the selective functionalization of these heterocyclic rings is discussed.*

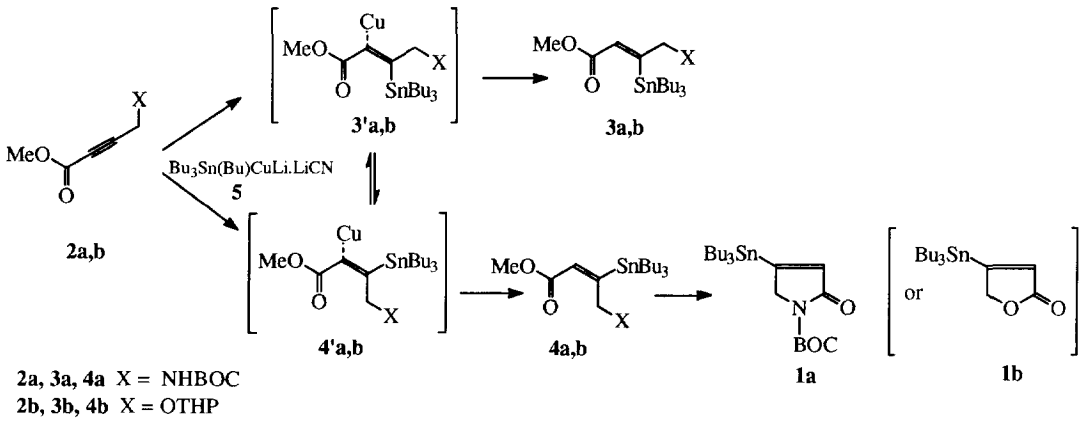
INTRODUCTION

It is known[1] that the presence of a vinyltin mojety in a molecular structure allows further structural transformations which can be performed via a cross-coupling reaction in the presence of Pd(II) as catalyst or *via* transmetallation to a vinyllithium species and subsequent interception with electrophiles: this reactions sequence affords a good methodology to transfer a large number of electrophiles on the vinyl unit[2]. On these premises we thought that compounds like the 4-stannylated α,β-usaturated-γ-lactam **1a** and γ-lacton **1b** could be regarded as very good intermediates for achieving 4-substituted furanones and pyrrolones, which are very interesting targets in organic synthesis[3] (scheme1).This hypothesis has been recently confirmed in the case of **1b**[3].



Scheme 1

The hydrostannation of alkynes provides a simple general route to alkenylstannanes, but lacks quite often in stereo and regioselectivity[4]; on the other hand the addition of trialkylstannylcopper and cuprate reagents to α,β-acetylenic esters has been widely explored in recent years[5]: these considerations, coupled with our interest[6] in exploiting the synthetic potentialities of metallometalation of alkynes bearing heteroatoms on the lateral chain, prompted us to investigate the addition of tin-copper reagents on suitably protected γ-amino (**2a**) and γ-hydroxy (**2b**) α,β-acetylenic esters: stereospecific *cis* addition on the triple bond, in fact, could afford the γ-stannylated *E* allylic aminoester **4a** and hydroxyester **4b**, which upon cyclization reaction could lead to the desired five membered heterocyclic systems (scheme 2).

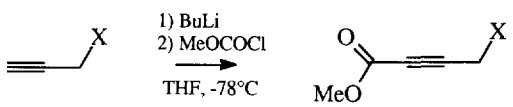


Scheme 2

We wish to report here our studies on stannylcupration of compounds **2a** and **2b** showing how the stereo selectivity of the reaction can be driven to afford, in effect, an easy route to **1b** or to the previously unreported **1a**. As a further step some examples of selective functionalization of position 4, through the palladium catalyzed coupling of the vinyltin moiety with electrophiles, are discussed.

RESULTS AND DISCUSSION

Compounds **2a**,**2b** have been prepared following the procedure described by Corriu[7]. Propargylamine and propargyl alcohol have been suitably protected, then treated with BuLi at low temperature and subsequently reacted with methylchloroformate to give, after purification, the desired products in good yields (scheme 3).



2a X = NHBOC (63%)
2b X = OTHP (68%)

Scheme 3

It has been shown[6b] that the high order mixed cuprate $Bu_3Sn(Bu)CuLi{\cdot}LiCN$[8] **5** adds very rapidly to the triple bond of BOC protected propargylamine affording quantitatively the corresponding stannylated E-allylic amines in a very good regioisomeric ratio, therefore **5** has been the reagent of choice for a preliminary text of reactivity of our substrates.

Addition of **5** to compound **2a** occurs very rapidly at -78 °C; upon quenching the reaction mixture with NH_4OH/NH_4Cl buffer at the same temperature after 5 minutes, a roughly 1:1 mixture of the desired cyclic compound **1a** and of the open chain stannylated allylic amino ester **3a** (derived from the *trans* addition of the cuprate), is detected in the crude after ^1H NMR spectroscopic analysis, the starting material being completely consumed. The observed ratio seems not to be affected by increasing the reaction time or quenching the reaction mixture at higher temperature. It is known[5] that when a mixed Gilman stannylcuprate adds to an acetylenic ester a careful control of the reaction conditions can lead to excellent *E* or *Z* stereoselectivities. In particular when the addition is conducted in THF at low temperature and in the presence of methanol only the product of *cis* addition can be obtained. We decided to check if this behaviour could be observed even by using reagent **5** and therefore we carried out the reaction by adding the substrate at -78°C together with methanol and then hydrolizing with NH_4Cl/NH_4OH buffer at the same temperature after 10 minutes. ^1H NMR spectroscopic analysis of the crude mixture showed, indeed, that only compound **4a** was present. Treatment of **4a** with BuLi at -78°C afforded cyclization to **1a** in good yield. A very similar behaviour has been observed in the stannylcupration of compound **2b**. Addition of cuprate **5** is *trans* stereospecific affording **3b** as the only product, in good agreement with what reported by Piers and Tillyer[9] on the addition of stannylcuprate reagents on compound related to **1b**. On the other hand, once again, the reaction can be easily driven toward the formation of the desired **4b** simply by adding a mixture of **2b** and methanol to the solution of the cuprate **5** at -78°C. Treating the crude mixture with trace of *p*-toluen-sulfonic acid in methanol at room temperature, afforded the cyclized product **1b** in 68% overall yield after purification.

Structures of compound **3a, 3b** and **4a, 4b** have been unequivocally established looking at difference in coupling constants between the vinylic proton and the ^{117}Sn and ^{119}Sn isotopes: typically[5],[10] they show to be higher in compound **3a** ($J_{Sn\text{-}H}$ = 96 Hz) or **3b** ($J_{Sn\text{-}H}$ = 102 Hz) where there is a *trans* relationship between H and Sn across the double bond, than in compound **4a** ($J_{Sn\text{-}H}$ = 60 Hz) or **4b** ($J_{Sn\text{-}H}$ = 60 Hz) where the relationship is *cis*. Moreover by irradiation of the allylic protons (δ = 4.07 and δ = 4.41) a positive Overhauser enhancement is measured on the vinyl proton of **3a** and **3b** respectively and is not observed carrying out the same experiment on **4a** and **4b.**

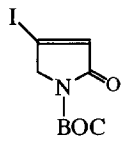
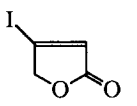
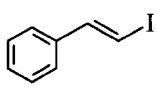
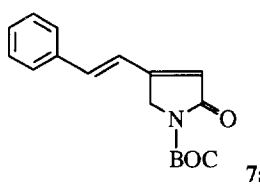
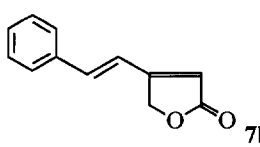
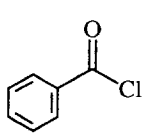
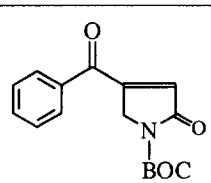
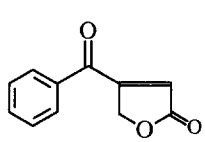
In order to evaluate their synthetic potentialities, compounds **1a** and **1b** have been reacted with three different class of electrophiles: in particular we checked the reactivity toward vinyl and acyl halogenide in the well known coupling reactions catalysed by Pd(II) complexes [11].

The obtained results are reported in Table 1 and show how both of our substrates can bee regarded, indeed, as useful intermediates for obtaining 4-substituted lactams and lactons derivatives.

Treatment with iodine at room temperature afforded the corresponding 4-iodo derivatives (**6a**, **6b**) in good yields; reactions with *trans*,β-iodostyrene[12] or with benzoylchloride in the presence of the appropriate Pd(II) catalyst allowed an easy route for the synthesis of polyunsaturated derivatives.

All the obtained compounds were precedently unreported.

Table 1 - Reactivity of compounds **1a** and **1b** with electrophiles.

Substrate	Electrophile (rection conditions)	Obtained compound	Yield (%) (isolated)
1a	I_2 $CHCl_3$, RT, overnight	 **6a**	78%
1b		 **6b**	66%
1a	 $PdCl_2(CH_3CN)_2$, DMF overnight	 **7a**	57%
1b		 **7b**	72%
1a	 $PdCl(Bz)(PPh_3)_2$, $CHCl_3$, reflux, overnight	 **8a**	54%
1b		 **8b**	87%

In conclusion the stannylcupration of γ–amino- and γ–hydroxy- acetylenic esters **2a** and **2b** shows how this reaction can be used in the synthesis of 4-stannylated furanone and pyrrolinone. Compounds **1a** and **1b** have been obtained in good yield and fully characterized and their use as intermediates for the synthesis of functionalized five membered unsaturated lactams and lactones has been shown. Further synthetic potentialities of this metallated heterocyclic systems are still under investigation.

EXPERIMENTAL SECTION

1. General remarks

Starting materials are commercially available unless otherwise stated. Commercial reagents were used without further purification. All the experiments were carried out under an atmosphere of 99.99% pure nitrogen. *BuLi* was used as 1.6 M hexane solution. *Tetrahydrofuran* was obtained anhydrous by distillation from sodium wire and by two subsequent distillations on $LiAlH_4$. *Chloroform* has been washed with water, dried on $CaCl_2$ and stored on molecular sieves. *DMF* has been distilled over CaH_2. *Ethereal extracts were dried* with sodium sulfate.

The temperature of dry ice/ethanol baths is consistently indicated as -78°C and that of ice baths as 0°C. Purifications by *flash column chromatography* were performed using glass columns (10-50 mm wide); silica gel 230-400 mesh was chosen as stationary phase (15 cm high), with an elution rate of 5 cm/ min [13], the boiling range of petroleum ether was 40-70°C.

Nuclear magnetic resonance spectra of hydrogen nuclei were recorded at 200 MHz or 300 MHz. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$: 7.26 ppm). Coupling constants (*J*) are measured in Hz. Coupling patterns are described by abbreviations: s (singlet), d (doublet), t (triplet), dd (doublet of a doublet), m (multiplet), bs (broad singlet). Nuclear magnetic resonance spectra of carbon-13 nuclei were recorded at 50 MHz or 75 M. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$: 77.0 ppm). *Mass spectra* were obtained at a 70 eV ionization potential by direct introduction. When tin is present the fragmentation is referred to ^{120}Sn isotope. *IR spectra* have been recorded in solution using 0.1 mm KBr cells.

*2. Preparation of methyl-4,N(tert-butoxycarbonyl)amino,but-2-ynoate (**2a**).*

To a solution of 3,N(*tert*-butoxycarbonyl)amino-prop-1-yne (1.48 gr, 10 mmol) in THF (20 ml) at 0°C, 16 ml (25 mmol) of BuLi are added and let to react at this temperature for 30 min. The reaction mixture is cooled at -78°C and methylchloroformiate (0.700 ml, 11 mmol) is added and let to react at this temperature for 2 hours. After quenching with a 0.1 M NaOH acqueous solution, extraction with ether and drying, the solvent is evaporated and the crude purified by flash-chromatography (eluent: petroleum ether/ethyl acetate = 2/1) affording 1.34 gr (63%) of (**2a**) as a low melting solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.82 (1H, bs, N-H); 4.06 (2H, m, CH_2); 3.76 (3H, s, CH_3); 1.43 (9H, s, $C(CH_3)_3$) - ^{13}C-NMR (75 MHz, $CDCl_3$): 155.49; 154.10; 84.68; 80.96; 75.03; 53.26; 30.81; 28.74 - MS: 198 (11%; M-15$^+$); 158 (47%); 157 (37%); 140 (49%); 127 (35%); 57 (100%)

*3. Preparation of methyl-4,O(tetrahydropyranyl)oxy-but-2-ynoate (**2b**).*

To a solution of 3,O(tetrahydropyranyl)oxy-prop-1-yne (1.43 gr, 10 mmol) in THF (20 ml) cooled at -45°C, 8 ml (12 mmol) of BuLi are added and let to react at this temperature for 1 hour. The reaction mixture is cooled at -78°C and methylchloroformate (0.700 ml, 11 mmol) is added and let to react for 1 hour. After quenching with NaCl saturated solution, extraction with ether and drying, the solvent is evaporated and the crude purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 10/1) affording 1.36 gr of **2b** (68%) as a pale yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): 4.81 (1H, t, J = 2.5 Hz, OCHO); 4.38 (2H, m,≡CCH_2O); 3.83 (1H, m, CHO); 3.78 (3H, s, OCH_3); 3.54 (1H, m, CHO); 1.49-1.38 (6H, m, 3xCH_2) - ^{13}C-NMR (50 MHz, $CDCl_3$): 153.59; 97.08; 83.93; 77.21; 61.92; 53.55; 52.76; 29.99; 25.19; 18.72 - MS: 197 (10%; M-1$^+$); 111 (73%); 98 (72%); 85 (100%); 66 (63%); 41 (80%).

4. General procedure of stannylcupration.

Tributyltincuprate (**5**) is prepared according to the general route outlined by Lipshutz[8]: CuCN (88 mg, 1 mmol) is suspended in THF (3 ml), cooled at -78°C and then treated with BuLi (1.400 ml, 2.2 mmol). The mixture is allowed to react for 15 min and then Bu_3SnH (0.600 ml, 2.2 mmol) is added dropwise. After stirring for 15 minutes the substrate is added and after quenching with NH_4Cl/NH_4OH buffer solution at -78°C, drying and evaporation of the solvent, the crude has been analyzed and purified as described below.

*(Z)-Methyl,3-tributylstannyl,4-N(ter-butoxycarbonyl)ammino,but-2-enoate (**3a**).* 210 mg (1 mmol) of (**2a**) are dissolved in 1 ml of THF, added dropwise and let to react at -78°C for 10 min. After workup the analysis of the crude shows the presence of compound (**3a**) and of the cyclized compound (**1a**) in a roughly 1/1 ratio. After flash chromatography (eluent: petroleum ether/ethyl acetate = 10/1) 178 mg (36%) of compound (**3a**) are obtained as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): 6.48 (1H, t, J = 1.9 Hz, $^3J_{Sn\text{-}H\ trans}$ = 96 Hz, =CH); 4.66 (1H, bt, J = 5.7 Hz, NH); 4.06 (2H, bm, NCH_2); 3.72 (3H, s, OCH_3); 1.56-1.20 (12H, m, 3xCH_2CH_2); 1.44 (9H, s, $C(CH_3)_3$); 1.02-0.81 (15H, m, 3x$SnCH_2CH_2CH_2CH_3$) - ^{13}C-NMR (50 MHz, $CDCl_3$): 170.66; 168.06; 155.47; 125.77; 79.55; 51.58; 48.23; 29.10; 28.34; 27.38; 13.67; 10.89 - MS: 448 (8%; M-57$^+$); 392 (100%); 346 (10%); 276 (12%); 202 (10%); 177 (16%); 149 (22%); 57 (25%).

*(E)-Methyl,3-tributylstannyl,4-N(tert-butoxycarbonyl)ammino-but-2-enoate (**4a**).* 212 mg (1 mmol) of (**2a**) are dissolved in 1 ml of THF together with 0.200 ml of MeOH, added dropwise and let to react at -78°C for 10 min. After workup the mixture is purified by chromatography (Florisil (10 cm), eluent: petroleum ether/ethyl acetate, gradient) affording 397 mg (79%) of (**4a**).

^{1}H NMR (200 MHz, $CDCl_3$): 6.01 (1H, t , J = 2.0 Hz $^3J_{Sn\text{-}H\ cis}$ = 60 Hz, =C<u>H</u>); 4.96 (1H, bs, N<u>H</u>); 4.41 (2H, m, NC<u>H</u>$_2$); 3.71 (3H, s, OC<u>H</u>$_3$); 1.57-1.21 (12H, m, 3xC<u>H</u>$_2$C<u>H</u>$_2$); 1.45 (9H, s, C(C<u>H</u>$_3$)$_3$) 1.03-0.84 (15H, m, 3xSnC<u>H</u>$_2$CH$_2$CH$_2$C<u>H</u>$_3$) - ^{13}C-NMR (50 MHz, $CDCl_3$): 172.26; 164.64; 155.60; 128.23; 79.80; 51.19; 42.10; 29.00; 28.42; 27.31; 13.69; 10.15 - MS: 448 (5%; M-57$^+$); 392 (100%); 202 (25%); 177 (34%); 121 (22%); 57 (97%) - IR (CCl_4): 1708 cm^{-1} (ν C=O). Calc. for $C_{22}H_{43}NO_4Sn$ (504.27) C 52.40, H 8.59, N 2.78; found C 52.56, H 8.63, N 2.77.

*(Z)-Methy,3-tributylstannyl,4-(tetrahydropyranyl)oxy,but-2-enoate (**3b**).* 199 mg (1 mmol) of (**2b**) are dissolved in 1 ml of THF, added to the solution of stannylcuprate and let to react at -78°C for 10 min. After workup and flash chromatography (eluent : petroleum ether/ ethyl acetate = 10/1) 326 mg (66%) of (**3b**) are obtained as a colorless oil.^{1}H NMR (200 MHz, $CDCl_3$): 6.72 (1H, t, J = 2.2 Hz $^3J_{Sn\text{-}H\ trans}$ = 102 Hz, =C<u>H</u>); 4.65 (1H, bt, J = 3.3 Hz, OC<u>H</u>O); 4.53 (1H, dd B part of an AB system J = 17.2 Hz, J = 2.3 Hz, =CC<u>H</u>$_2$O); 4.25 (1H, dd A part of an AB system J = 17.2 Hz, J = 2.2 Hz, =CC<u>H</u>$_2$O); 3.92-3.79 (1H, m, C<u>H</u>$_2$O); 3.73 (3H, s, OC<u>H</u>$_3$); 3.58-3.48 (1H, m, C<u>H</u>$_2$O); 1.78-1.19 (18H, m, 3xC<u>H</u>$_2$C<u>H</u>$_2$ + C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$); 1.02-0.75 (15H, m, 3xSnC<u>H</u>$_2$CH$_2$CH$_2$C<u>H</u>$_3$) - ^{13}C-NMR (50 MHz, $CDCl_3$): 169.92; 168.39; 125.24; 97.95; 72.02; 62.02; 51.52; 29.27; 29.14; 27.36; 25.44; 19.27; 13.72; 10.84 - MS: 433 (100%; M-57$^+$); 251 (42%); 179 (37%); 177 (48%); 85 (39%); 41 (93%).

*(E)-Methy,3-tributylstannyl,4-(tetrahydropyranyl)oxy,but-2-enoate (**4b**).* 202 mg (1 mmol) of (**2b**) are dissolved in THF (2 ml) together with 0.200 ml of MeOH, added dropwise and let to react at -78°C for 10 min. After workup and purification by flash chromatography (eluent: petroleum ether/ ethyl acetate = 10/1) 368 mg (75%) of (**4b**) are obtained as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): 5.93 (1H, t, J = 2.3 Hz $^3J_{Sn\text{-}H\ cis}$ = 60 Hz, =C<u>H</u>); 5.06 (1H, dd B part of an AB system J = 17.5 Hz, J = 2.8 Hz, =CC<u>H</u>$_2$O); 4.69 (1H, bt, J = 3.3 Hz, OC<u>H</u>O); 4.56 (1H, dd A part of an AB system J = 17.5 Hz, J = 2.8 Hz, =CC<u>H</u>$_2$O); 3.89-3.76 (1H, m, C<u>H</u>$_2$O); 3.70 (3H, s, OC<u>H</u>$_3$); 3.59-3.47 (1H, m, C<u>H</u>$_2$O); 1.86-1.21 (18H, m, 3xC<u>H</u>$_2$C<u>H</u>$_2$ + C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$); 1.02-0.82 (15H, m, 3xSnC<u>H</u>$_2$CH$_2$CH$_2$C<u>H</u>$_3$) - ^{13}C-NMR (50 MHz, $CDCl_3$): 175.21; 164.76; 123.92; 98.70; 72.20; 61.90; 51.07; 30.51; 29.06; 27.34; 25.39; 19.44; 13.69; 10.91 - MS: 433 (5%; M-57$^+$); 335 (75%); 177 (39%); 85 (56%); 57 (100%); 41 (85%) - IR (CCl_4): 1706 cm^{-1} (ν C=O). Calc. for $C_{22}H_{42}O_4Sn$ (489.26) C 54.01, H 8.65; found C 53.85, H 8.59.

5. *Preparation of N-(tert-butoxycarbonyl),4-tributilstannyl, 2(5H)-pirrolone (**1a**).*

397 mg (0.6 mmol) of (**4a**) are dissolved in THF (4ml) and cooled to -78°C. 0.500 ml of BuLi are then added and let to this temperature for 4 hours. After workup and purification by column chromatography (Florisil (10 cm), eluent: petroleum ether/ethyl acetate = 5/1), 242 mg (85%) of (**1a**) are obtained. ^{1}H NMR (300 MHz, $CDCl_3$): 6.23 (1H, t, J = 1.8 Hz $^3J_{Sn\text{-}H\ cis}$ = 27 Hz, =C<u>H</u>); 4.41 (2H, m, =CC<u>H</u>$_2$N); 1.58-1.45 (6H, m, 3xSnCH$_2$C<u>H</u>$_2$C<u>H</u>$_2$CH$_3$); 1.56 (9H, s, C(C<u>H</u>$_3$)$_3$); 1.37-1.22 (6H, m, 3xSnCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$); 1.09-1.02 (6H, m, 3xSnC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$); 0.9 (9H, t, J = 7.8Hz, 3xSnCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$) - ^{13}C-NMR (75 MHz, $CDCl_3$): 168.85; 165.69; 149.87; 136.62; 82.65; 57.94; 28.94; 28.14; 27.22; 13.61; 9.80 - MS: 416 (64% M-57$^+$); 316 (100%); 260 (65%); 202 (72%); 177 (62%); 57 (88%) - IR (CCl_4): 1775, 1745 cm^{-1} (ν C=O). Calc. for $C_{21}H_{39}NO_3Sn$ (472.24) C 53.41, H 8.32, N 2.97; found C 53.58, H 8.23, N 2.92.

6. *Preparation of 4-tributylstannyl-2(5H)-furanone (**1b**).*

320 mg (0.65 mmol of (**4b**) are dissolved in MeOH (4ml), a small amount of PTSA is added and the mixture is refluxed for 3 hours. After workup and purification by chromatography (Florisil (10 cm), eluent: petroleum ether/ethyl acetate = 5/1) 203 mg (83%) of (**1b**) are obtained. ^{1}H NMR (300 MHz, $CDCl_3$): 6.18 (1H, t, J = 2.2 Hz $^3J_{Sn\text{-}H\ cis}$ = 23 Hz, =C<u>H</u>); 4.96 (2H, m, =CC<u>H</u>$_2$N); 1.68-1.44 (6H, m, 3xSnCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$); 1.41-1.22 (6H, m, 3xSnCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$); 1.12-1.06 (6H, m, 3xSnC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$); 0.9 (9H, t, J = 8.0 Hz, 3xSnCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$) - ^{13}C-NMR (75 MHz, $CDCl_3$): 174.17; 129.36; 78.61; 34.13; 28.94; 27.20; 13.60; 9.96 - MS: 317 (82% M-57$^+$); 261 (100%); 205 (81%); 177 (34%); 121 (33%); 41 (86%) - IR (CCl_4): 1739 cm^{-1} (ν C=O). Calc. for $C_{16}H_{30}O_2Sn$ (373.10) C 51.51, H 8.10; found C 51.36, H 8.02.

7. *Preparation of N-(tert-butoxycarbonyl),4iodo,2(5H)-pirrolone(**6a**).*

100 mg (0.21 mmol) of (**1a**) are dissolved in chloroform (1ml), 55 mg (0.22 mmol) of I_2 are then added and let to react at room temperature overnight. After this time the solvent is evaporated and the crude is chromatographated (SiO_2 (5cm) eluent: petroleum ether/ethyl acetate = 3/1) affording 51 mg of (**6a**) (78%) as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): 6.56 (1H, t, J = 1.2 Hz, =C<u>H</u>); 4.41 (2H, d, J = 1.2 Hz, =CC<u>H</u>$_2$N), 1.55 (9H, s, C(C<u>H</u>$_3$)$_3$) - ^{13}C-NMR (50 MHz, $CDCl_3$): 167.40; 148.87; 136.82; 111.43; 84.02; 60.88; 31.41 - MS: 252 (7% M-57$^+$); 236 (46%), 209 (38%); 127 (10%); 57 (100%); 41 (62%).

8. *Preparation of 4-iodo,2(5H)-furanone(**6b**).*

97 mg (0.26 mmol) of (**1b**) are dissolved in chloroform (1ml), 70 mg (0.28 mmol) of I_2 are then added and let to react at room temperature overnight. After evaporation of the solvent and chromatography (SiO_2 (5cm) eluent: petroleum ether/ethyl acetate = 3/1) 36 mg of (**6b**) (66%) are obtained as a pale yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): 6.58 (1H, t, J = 2.0 Hz, =C<u>H</u>); 4.86

(2H, d, J = 2.0 Hz, =CC$\underline{H}_2$O) - ^{13}C-NMR (50 MHz, $CDCl_3$): 171.15; 129.44; 118.14; 78.80 - MS: 210 (100% M-57$^+$);209 (22%); 152 (22%); 127 (55%); 83 (64%) - IR (CCl_4): 1785 cm^{-1} (ν C=O).

9. Coupling with trans, β-iodo-styrene.

0.25 mmol of **(1a,1b)** are dissolved in DMF (1 ml) added with a small amount of $PdCl_2(CH_3CN)_2$ and with 65 mg (0.28 mmol) of trans,β-iodo styrene[12]. The reaction is let overnight then DMF is evaporated under high vacuum, the residue filtered over a 2 cm silica gel column, eluted with ether and purified by TLC.

N-(tert-butoxycarbonyl),4,(E-2-phenylethenyl),2(5H)pirrolone (7a). (Eluent: petroleum ether/ethyl acetate = 3/1) 41 mg (57%) of (**7a**) are obtained. ^{1}H NMR (200 MHz, $CDCl_3$): 7.41-7.31 (4H, m, arom.); 7.28-7.22 (1H, m, arom.); 7.03 (1H, d, J = 18.9 Hz, =C$\underline{H}$Ph); 6.91 (1H, dd, J = 18.9 Hz J = 1.1 Hz, =C$\underline{H}$-CH=); 6.06 (1H, bs, =C$\underline{H}$-C=O); 4.57 (2H, m, C$\underline{H}_2$N); 1.58 (9H, s, C(C$\underline{H}_3$)$_3$) - ^{13}C-NMR (50 MHz, $CDCl_3$): 169.60; 154.39; 149.71; 138.54; 136.54; 129.00; 128.63; 127.93; 124.68; 122.44; 82.57; 52.51; 28.16 - MS: 228 (23% M-57$^+$); 185 (44%); 184 (100%); 156 (59%); 128 (58%); 57 (94%)

4,(E-2-phenylethenyl),2(5H)furanone (7b). (Eluent petroleum ether/ ethyl acetate = 4/1, two runs) 33 mg (72%) of (**7a**) are obtained. ^{1}H NMR (200 MHz, $CDCl_3$): 7.52-7.45 (2H, m, arom.); 7.43-7.36 (3H, m, arom.); 7.07 (1H, d, J = 16.1 Hz, =C$\underline{H}$Ph); 6.86 (1H, d, J = 16.1 Hz, =C$\underline{H}$-CH=); 6.04 (1H,t, J = 1Hz, =C$\underline{H}$-C=O); 5.11 (2H, m, C$\underline{H}_2$O); - ^{13}C-NMR (50 MHz, $CDCl_3$): 161.84; 137.20; 135.51; 134.84; 130.02; 129.08; 127.49; 118.68; 115.65; 70.48 - MS: 186 (6% M$^+$); 142 (45%); 141 (100%);128 (59%); 77 (23%); 51 (46%).

10. Coupling with benzoylchloride.

0.25 mmol of **1a,b** are dissolved in $CHCl_3$ (2ml), added with a small amount of $Pd(PPh_3)_2ClBz$ and with 40 mg (0.28 mmol) of benzoylchlorode. The reaction mixture is let to reflux for 18 hours, then the solvent is evaporated and the residue purified by TLC.

N-(tert-butoxycarbonyl),4,(benzoyl),2(5H)pirrolone (8a). (eluent: petroleum ether/ethyl acetate = 3/1, 3 runs). 39 mg (54%) of (**8a**) are obtained. ^{1}H NMR (300 MHz, $CDCl_3$): 7.87-7.83 (1H, m, arom.); 7.72-7.64 (2H, m, arom.); 7.57-7.46 (2H, m, arom.); 6.51 (1H, t, J = 1.3 Hz, =C$\underline{H}$); 4.67 (2H, d, J = 1.3 Hz, C$\underline{H}_2$N); 1.58 (9H, s, C(C$\underline{H}_3$)$_3$) - ^{13}C-NMR (75 MHz, $CDCl_3$): 189.55; 167.89; 152.08; 149.06; 135.90; 132.17; 128.68; 128.41; 126.20; 83.70; 51.07; 28.07 - MS: 230 (15% M-57$^+$); 186 (94%); 158 (45%); 130 (38%); 128 (46%); 77 (16%); 57 (100%).

4,(benzoyl),2(5H)furanone (8b) (eluent: petroleum ether/ethyl acetate = 3/1,). 41 mg (87%) of (**8b**) are obtained. ^{1}H NMR (200 MHz, $CDCl_3$): 7.93-7.88 (2H, m, arom.); 7.75-7.51 (3H, m, arom.); 6.50 (1H, t J = 2.2 Hz, =C$\underline{H}$); 5.20 (2H, d,, J = 2.2 Hz, C$\underline{H}_2$O);- ^{13}C-NMR (75 MHz, $CDCl_3$): 189.10; 172.20; 159.55; 135.68; 134.48; 129.13; 126.43; 125.12; 71.62 - MS: 188 (50% M$^+$); 106 (58%); 105 (74%); 77 (100%); 51 (58%); 43 (51%).

Acknowledgement. We wish to thank Professor Alfredo Ricci (University of Bologna) for helpful discussions.

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(*Received in UK* 12 *October* 1994; *revised* 5 *December* 1994; *accepted* 9 *December* 1994)