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ORGANOTIN HOMOENOLATE EQUIVALENTS - ACCESS TO β-ACYL- AND β-ARYL-PROPIONALDEHYDES THROUGH HETEROSUBSTITUTED ALLYLTINS AND VINYLTINS

Jean-Baptiste VERLHAC* and Michel PEREYRE

Laboratoire de Chimie Organique et Organométallique, URA 35 CNRS, Université Bordeaux I, 351, cours de la Libération, 33405 - Talence Cedex, France

Jean-Paul QUINTARD

Laboratoire de Synthèse Organique Sélective et Matériaux, URA 475 CNRS, Université de Nantes, 2, rue de la Houssinière, 44072 - Nantes Cedex, France.

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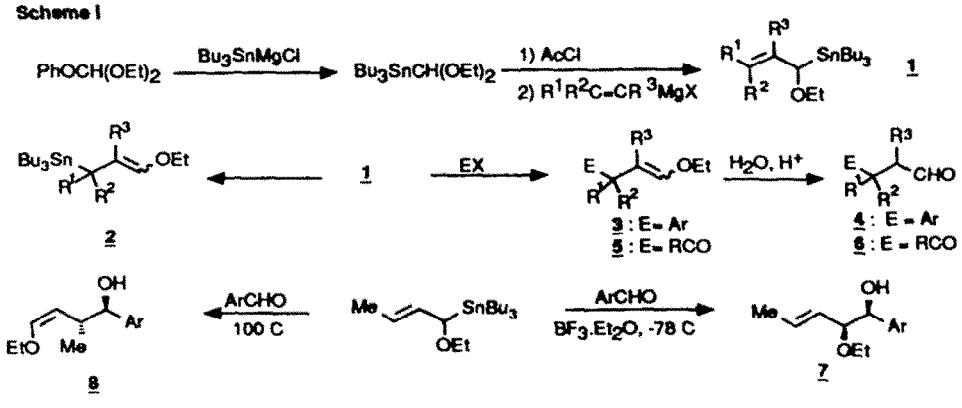
ABSTRACT.Although, α-ethoxycrotyltributyltin can be used as an equivalent of the homoenolate anion $CH_3^-CHCH_2CHO$ in reactions with acyl chlorides, the non-substituted α-ethoxyallyltributyltin could not be employed in this way. γ-Methoxyvinyltins, easily prepared by hydrostannation of propargylic ethers, are successfully employed as synthetic equivalents of the homoenolate anions $^-CH_2CH_2CHO$ and $^-CH_2CH_2COCH_3$ in reactions with acyl chlorides. A silylated γ-methoxyvinyltin, which is both a vinyltin and an allylsilane, reacts with acyl chlorides and aryl bromides as a promising equivalent of the homoenolate anion $^-CH_2CH_2CHO$ and tolerates a wide range of other reactive functional groups.

INTRODUCTION

There are numerous methods available for the homologation by a three-carbon reagent[1,2] but the introduction of a terminal reactive group is not always an easy task. This is the case for aldehyde groups which require protecting groups such as acetals, enol ethers or vinyl halides. Although several lithiated species have been proposed as homoenolate equivalents (d^3 propionaldehyde synthons[3]) such highly nucleophilic species do not tolerate various functional groups.

Organotin reagents, usually less reactive, more selective and easier to prepare, store and handle, have been used for three-carbon homologations[4]. Thus α-ethoxyallyltins **1** can be considered as homoenolate equivalents in reactions involving allylic rearrangement if no isomerization to the thermodynamically more stable γ-ethoxyallyltins **2** occurs (Scheme I).

Scheme I



We have reported a general method for the preparation of differently substituted α-ethoxyallyltributyltins (Scheme I) and shown that the palladium catalyzed cross-coupling with aryl bromides is indeed an efficient route to β-arylpropionaldehydes **4** [5-8] even in the case of the more unstable reagent **1** (R^1=R^2=R^3=H) which rearranges completely to **2** on standing alone, on heating or on attempted liquid chromatography. The regio- and stereo-chemistry of condensations of **1** with aldehydes depends on the conditions employed (Scheme I)[5-16].

We report here the utilization of α-ethoxyallyltins **1** in coupling reactions with acyl chlorides in order to gain access to β-acylpropionaldehydes. Our results, although positive, clearly show the limitations of the method. In addition a detailed study of the utilization of substituted vinyltins for the synthesis of β-aryl- and β-acyl- propionaldehydes is presented. A part of these data has already been briefly reported in a preliminary paper[17].

RESULTS AND DISCUSSION

α-Ethoxyallyltins as homoenolate equivalents for access to β-acylpropionaldehydes

It has been shown that the transition metal catalyzed cross-coupling of organotins with acyl chlorides leads to ketones[18-19]. The application of this reaction to α-ethoxyallyltins could thus possibly open a route to 1,4-ketoaldehydes **6** (Scheme I).

The catalyst used was benzylchlorobis(triphenylphosphine)palladium, $BnClPd(PPh_3)_2$, usually the best catalyst for the cross-coupling of organotins with acyl chlorides[20,21]. After a first encouraging result[6,7] using benzene as solvent, which was difficult to reproduce in reasonable yields, we found that α-ethoxycrotyltributyltin **1** ((R^1=Me;R^2=R^3=H)(E)-isomer in majority) reacted well with acyl chlorides in THF to give enol ethers **5**. Subsequently the hydrolytic cleavage of **5** was performed and yielded 1,4-ketoaldehydes **6**. These results are presented in Table I.

Table I. α-Ethoxycrotyltributyltin (1 ; R^1=Me ; R^2=R^3=H (E) in majority) in the synthesis of 1,4-ketoaldehydes 6

Entry	Acyl chloride	Enol ether yields %[a]	1,4-ketoaldehyde yields%[a]
1	C_6H_5COCl	**5a** 72 (E/Z=75/25)	**6a** 81
2	3-$MeOC_6H_4COCl$	**5b** 67 (E/Z=55/45)	**6b** 85
3	2-MeC_6H_4COCl	**5c** 52 (E/Z=75/25)	c
4	4-BrC_6H_4COCl	**5d** 69 (E/Z=75/25)	c
5	n-$C_6H_{13}COCl$	**5e** 51[b] (E/Z=80/20)	**6e** 82

[a]Isolated yields

[b]Reaction performed in HMPA instead of THF - [c]Hydrolysis not performed

It should be noted that no coupling at the aromatic site was observed with 4-bromobenzoyl chloride (entry 4) : the reaction is fully chemoselective when a competition between an aryl bromide and an acyl halide is involved.

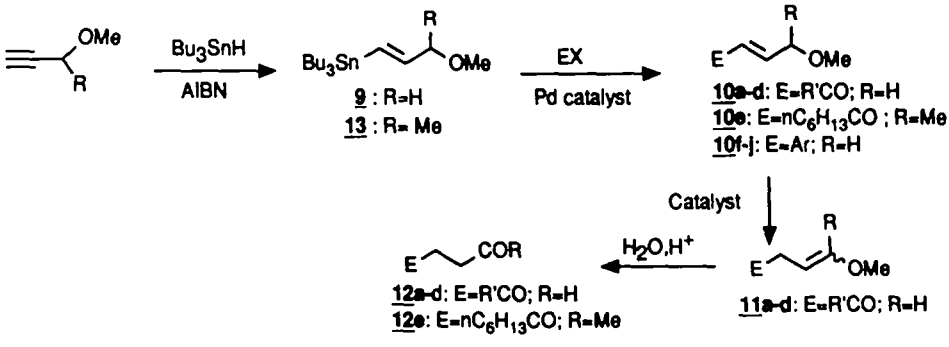
The next step was to try experiments with unsubstituted **1**, which is the more easily isomerized reagent in the series. All attempts to perform the expected coupling with benzoyl chloride failed, the organotin reagent being partly isomerized into **2**, unreactive in our experimental conditions. This result contrasts sharply with the already reported successful coupling of **1** (R^1=R^2=R^3=H) with aryl bromides[5-8]. The difference is probably due to the higher Lewis acidity of the catalyst, $BnClPd(PPh_3)_2$ compared to $(Ph_3P)_4Pd$, or of acyl chlorides compared to aryl bromides. Electrophiles, as well as nucleophiles, are known to catalyze the metallotropic rearrangement of allyltins[22].

In summary although unsubstituted α-ethoxyallyltributyltin could not be used with acyl chlorides as an equivalent of the simplest homoenolate anion $^-CH_2CH_2CHO$, coupling can be conveniently performed with a reagent substituted at the terminal carbon atom, and thus less readily isomerized, such as α-ethoxycrotyltributyltin, an equivalent of the homoenolate anion $CH_3{}^-CHCH_2CHO$. An alternative might be the use of α-siloxyallylsilanes[23] , which react with acyl halides in the presence of $TiCl_4$, but this approach does not tolerate various functional groups on the substrate. Instead we decided to explore the ability of the easily accessible γ-heterosubstituted vinyltins to react as homoenolate equivalents.

γ-Methoxyvinyltins as homoenolate equivalents for access to β-acylpropionaldehydes

Scheme II outlines the approach. γ-Methoxyvinyltins **9** and **13** can be easily prepared by free radical hydrostannation of methyl propargyl ethers which can be directed to give in majority the (E) isomer[4]. The vinyl group linked to tin can be stereospecifically transfered, either through transmetallation with butyllithium or more directly by Pd-catalyzed coupling to various electrophiles[4], yielding the allyl ethers **10**. Since it is in principle possible to isomerize allyl ethers into enol ethers **11**, for instance with Wilkinson's catalyst[24], a final hydrolytic work-up would lead to aldehyde **12** (starting from **9**) corresponding to the transfer of "CH_2CH_2CHO" to the substrate. The hydrostannation step was performed in good yield giving a majority of (E)-isomer. Upon Pd-catalyzed coupling with acyl halides we were gratified to observe that in some circumstances the isomerization step can be omitted since the coupling gave **11** directly. The results are collected in Table II.

Scheme II



It can be seen that in benzene an increase of reaction time and temperature leads to **11** (entries 1 and 2). There are experimental conditions where aromatic benzoyl chlorides exclusively yield enol ethers **11** (entries 2 and 4) which means that the Pd catalyst not only allows the coupling but also isomerizes the primarily formed allyl ether **10**. In this case reagent **9** is a direct equivalent of the simplest homoenolate $^-CH_2CH_2CHO$ since a hydrolytic work-up would lead to aldehydes **12** a-c in a one-pot process. On the other hand the use of methylene chloride instead of benzene as solvent only gives the allyl ethers **10** (entries 3,5 and 6). Surprisingly an aliphatic acyl chloride such as heptanoyl chloride gives only the allyl ether even in conditions in which aromatic acyl chlorides lead to enol ethers (entry 7).

Table II. Cross-coupling of 9 with acyl chlorides and aryl bromides (EX), in the presence of $BnClPd(PPh_3)_2$

Entry	EX	Experimental conditions solvent,temperature,time	Overall yield %[a]	Allyl ether[b]	Enol ether[b,c]
1	C_6H_5COCl	C_6H_6;90°C;16h	69	**10a** 25	**11a** 75
2	C_6H_5COCl	C_6H_6;100°C;48h	85	**10a** 0	**11a** 100
3	C_6H_5COCl	CH_2Cl_2;65°C;4h	71	**10a** 100	**11a** 0
4	$4\text{-}MeOC_6H_4COCl$	C_6H_6;100°C;36h	78	**10b** 0	**11b** 100
5	$4\text{-}MeOC_6H_4COCl$	CH_2Cl_2;70°C;4h	76	**10b** 100	**11b** 0
6	$4\text{-}ClC_6H_4COCl$	CH_2Cl_2;70°C;8h	71	**10c** 100	**11c** 0
7	$nC_6H_{13}COCl$	C_6H_6;100°C;24h	82	**10d** 100	**11d** 0
8	C_6H_5Br	C_6H_6;100°C;20h	81	**10f** 100	**11f** 0
9	$4\text{-}MeOC_6H_4Br$	C_6H_6;100°C;20h	82	**10g** 100	**11g** 0
10	$4\text{-}ClC_6H_4Br$	C_6H_6;100°C;20h	79	**10h** 100	**11h** 0
11	$4\text{-}CNC_6H_4Br$	C_6H_6;100°C;20h	73	**10i** 100	**11i** 0
12	$4\text{-}NO_2C_6H_4Br$	C_6H_6;100°C;20h	75	**10j** 100	**11j** 0

[a]Isolated yields - [b]Compositions - [c](Z):(E) mixtures

The reason why the isomerization **10** ⟶ **11** occurs in C_6H_6 and not in CH_2Cl_2 is not yet clear ; it is possible that at the stage of the intermediate Π-allylpalladium complex CH_2Cl_2 reacts with the Pd-H bond, thus preventing the isomerization process[25].

The isomerization can however be carried out using $RhCl(PPh_3)_3$ in ethanol: for instance, the allyl ether obtained from entry 3 (**10a**) was transformed into the corresponding enol ether **11a** in 81% yield in pure absolute ethanol. If the reaction is performed in 95% ethanol the process leads mainly to the diethyl acetal which can be subsequently hydrolyzed to the aldehyde. A similar behavior was found in the case of the allyl ether **10b** obtained in entry 5. The rhodium-catalyzed isomerization is especially important in the case of heptanoyl chloride, since no direct transformation to the enol ether occurred even in benzene. In this case the complete process including an intramolecular aldol condensation of the 1,4-ketoaldehyde **12d** led to the expected alkyl-substituted cyclopentenone[26].

We have extended this work by preparing an organotin equivalent for the homoenolate $^-CH_2CH_2COCH_3$ by hydrostannation of 3-methoxy-1-butyne. This reagent, **13**,mainly in the (E)-configuration, works nicely as exemplified by the synthesis of a 1,4-diketone (**12e**) which is a precursor for dihydrojasmone. It should be noted that the isomerization step, performed in 95% ethanol, led directly to the diketone.

γ-Methoxyvinyltins as homoenolate equivalents for access to β-arylpropionaldehydes

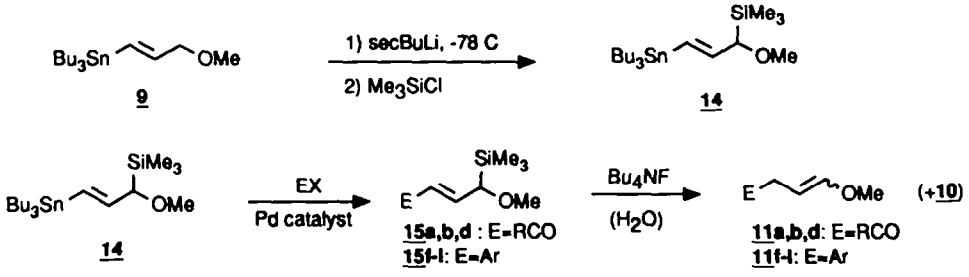
Scheme II summarizes the approach in which aryl bromides (E=Ar) are coupled with reagent **9**. Although the cross-coupling occurs nicely in benzene with $BnClPd(PPh_3)_2$ as shown in Table II, with various other functional groups being preserved, we did not succeed in obtaining enol ethers **11** either directly or through isomerization of allyl ethers **10** with Wilkinson's catalyst or other catalysts such as Pd/C, $PdCl_2$ or $Pd(OAc)_2$.

In summary γ-methoxyvinyltins, which are efficient for the synthesis of β-acylpropionaldehydes, cannot be used as homoenolate equivalents for the access to β-arylpropionaldehydes because of the failure of the catalytic isomerization step. The search for a general route must by-pass the transition metal-catalyzed isomerization or improve it. We have done the first by using a silicon-containing γ-methoxyvinyltin.

Silyl-substituted γ-methoxyvinyltins as homoenolate equivalents for access to β-acyl and β-aryl-propionaldehydes

Allylsilanes usually react with allylic rearrangement[27]. Introduction of a trimethylsilyl group at the allylic position of reagent **9** and subsequent cleavage after the cross-coupling step would solve the isomerization problem. Allylic deprotonation by sec-BuLi, a relatively hindered base, avoid competing transmetallation. On trapping with trimethylchlorosilane the silylated γ-methoxyvinyltin **14** was obtained in a non-optimized 60% isolated yield (Scheme III).

Scheme III



The subsequent steps, cross-coupling and desilylation, are presented in Scheme III and occurred as expected : the allylsilane moiety does not interfere with the cross-coupling of the vinyl-tin bond.

Cross-coupling was performed in the presence of $BnClPd(PPh_3)_2$ and desilylation, run with commercial tetrabutylammonium fluoride (containing water), led to the protodesilylated products[28].

In the cross-coupling of **14** with acyl chlorides, the silylated enones **15** (E=RCO), which are not very stable, were not isolated. The reaction mixtures were treated directly with Bu_4NF (two equivalents, the second exchanging with tributyltin chloride to give insoluble tributyltin fluoride) giving the expected enol ethers **11**. A few examples are shown in Table III.

For cross-coupling of **14** with aryl bromides, the silylated intermediates **15** were isolated, purified and subsequently desilylated. The desilylation yielded the expected enol ethers **11**, contaminated in some cases with small amounts of allyl ethers **10**.

Table III. Cross-coupling of 14 with acyl chlorides and aryl bromides, in the presence of a palladium catalyst and subsequent desilylation of the intermediates 15

Entry	EX	15 (yield %[a])	Enol ether 11 (yield %)	Allyl ether 10 (yield %)
1	C_6H_5COCl	b	**11a**(56)	-
2	4-$MeOC_6H_4COCl$	b	**11b**(53)	-
3	$nC_6H_{13}COCl$	b	**11d**(51)	-
4	C_6H_5Br	**15f** (76)	**11f** (64)	**10f** (8)
5	4-$MeOC_6H_4Br$	**15g** (75)	**11g** (56)	**10g** (11)
6	4-ClC_6H_4Br	**15h** (72)	**11h** (60)	**10h** (11)
7	4-CNC_6H_4Br	**15i** (65)	**11i** (77)	**10i** (0)
8	4-$NO_2C_6H_4Br$	**15j** (58)	c	
9	4-AcC_6H_4Br	**15k** (73)	**11k** (87)	**10k** (0)
10	4-$MeOCOC_6H_4Br$	**15l** (71)	**11l** (82)	**10l** (0)

[a]Isolated yield - [b]Not isolated - [c]Desilylation not performed

It can be noted that the desilylation step does not produce allyl ethers **10** when strongly electron-withdrawing substituents are present on the aromatic ring. This is probably due to the stabilization of a negative charge at the benzylic carbon atom, since the fluoride ion generates an allylic anion from the allylsilane. The anion is rapidly protonated *in situ* since commercial Bu_4NF always contains water.

CONCLUSIONS

α-Ethoxyallyltins **1** can act as d^3 propionaldehyde synthons in the transformation of acyl chlorides into β-acylpropionaldehydes. α-Ethoxycrotyltributyltin has been successfully employed as an equivalent of the homoenolate anion $CH_3^-CHCH_2CHO$. However the simplest non-substituted reagent α-ethoxyallyltributyltin cannot be employed as an equivalent of $^-CH_2CH_2CHO$. This failure in combination with the rather long access to the organotin reagents (scheme I), constitutes a limitation to the use of α-ethoxyallyltributyltins in organic synthesis.

On the other hand, γ-methoxyvinyltin **9**, conveniently prepared by hydrostannation of a propargylic ether was found to couple easily with acyl chlorides. Isomerization of initially formed allyl ethers **10**, either in situ or subsequently, generated vinyl ethers **11**, precursors of 1,4-ketoaldehydes. Reagent **9**, thus, constitutes a direct equivalent of the homoenolate anion $^{-}CH_2CH_2CHO$. The hydrostannation of a substituted propargylic ether provided an organotin reagent **13** equivalent of the homoenolate anion $^{-}CH_2CH_2COCH_3$ in the synthesis of 1,4-diketones. However, γ-methoxyvinyltins also show a limitation in their use for the preparation of β-arylpropionaldehydes. Cross-coupling of reagent **9** with aryl bromides was successfully performed, however neither spontaneous nor rhodium-catalyzed isomerization of the allyl ethers into enol ethers occurred in our hands.

Finally, an efficient method of performing the double bond shift to the desired enol ethers was developed using the silylated reagent **14**, which is both a vinyltin and an allylsilane. In Pd catalyzed cross-coupling with acyl chlorides and aryl halides **14** reacted as a vinyltin, generating allylsilanes **15**. Desilylation, using fluoride anion in wet medium, occured exclusively or mainly with the usual allylic rearrangement and moved the double bond in the correct position. Reagent **14**, easily obtained, tolerates a wide range of reactive functional groups, and can be considered as a promising equivalent of the homoenolate anion $^{-}CH_2CH_2CHO$. It is also a versatile polyfunctional reagent with a number of potential applications.

EXPERIMENTAL SECTION

Unless otherwise specified Proton Magnetic Resonance (^1H NMR) was recorded at 60 MHz on Perkin-Elmer R 12 and R 24B instruments in carbon tetrachloride with tetramethylsilane as internal standard. Other spectra were recorded at 200 MHz on a Bruker AC 200 instrument in the specified solvent. Carbon Magnetic Resonance (^{13}C NMR) spectra were recorded on a Bruker WH 90 instrument at 22.63 Mz and Tin Magnetic Resonance spectra (^{119}Sn NMR) on Bruker WH 90 (33.54 MHz) or AC 200 (74.63 MHz) instruments in the specified solvents (concentrations around 30-40 %) with tetramethyltin as internal standard. Mass spectra (MS) were recorded at 70 eV on VG Micromass (16F or 7070F) spectrometers and infrared spectra on a Perkin-Elmer 683 spectrophotometer. Gaz liquid chromatography analyses have been performed on a Intersmat IGC 120 FL apparatus.

Organotin starting materials

Tributyltin hydride was obtained from polymethylhydrosiloxane and tributyltin oxide[29] in 85% yield.

Tributylstannylmagnesium chloride was prepared by reacting isopropylmagnesium chloride with Bu_3SnH[30]. To freshly distilled Bu_3SnH (16g, 55 mmol) was added dropwise iPrMgCl (55 mmol in c.a. 1N ether solution) within 30 minutes. At the end of the addition, the reaction mixture was heated with a sun lamp until the end of the gas emission. The reagent $Bu_3SnMgCl$ (45 mmol, 82%) contains hexabutylditin and traces of tetrabutyltin which do not interfere with further reactions.

Diethoxymethyltributyltin was obtained from diethylphenyl orthoformate and $Bu_3SnMgCl$[31] according to a previously described procedure.

α-Ethoxyallyltins (**1**) were obtained, according to already published procedures[8], by reaction of the required vinyl Grignard reagent with α-chloro α-ethoxymethyltributyltin initially prepared from diethoxymethyltributyltin and acetyl chloride[31-32].

Palladium catalysts. Tetrakis(triphenylphosphine)palladium[33], $Pd(PPh_3)_4$, and benzylchlorobis-(triphenylphosphine)palladium[34], $BnClPd(PPh_3)_2$ were prepared according to litterature.

Pd-catalyzed coupling of α-ethoxycrotyltributyltin with benzoyl chlorides

In a typical experiment, benzoyl chloride (0.7g, 5 mmol), α-ethoxycrotyltributyltin (2.5g, 6.4 mmol) and $BnClPd(PPh_3)_2$ (30 mg, 0.04 mmol) in dry THF (5 ml) were heated in a sealed tube at 100°C over a period of 16 hours. After hexane-acetonitrile partition and concentration of the acetonitrile phase, the crude enol ether **5a** was purified by liquid chromatography on florisil (eluent : 15% ether in petroleum ether). Similar experimental conditions were used for the other benzoyl chlorides (excepted for the preparation of **5e** where HMPA was used instead of THF).

5a : ^1H NMR (C_6D_6, 200 MHz) : (E)-isomer, δ, 0.95 (t, J=6.7Hz, 3H), 1.29 (d, J=6.7Hz, 3H), 3.28 (m, J=6.7Hz, 2H), 3.80 (double q, J=6.7 and 9 Hz, 1H), 4.86 (double d, J=9 and 14 Hz, 1H), 6.36 (d, J=14Hz, 1H), 7.17 (m, 3H), 7.97 (m,2H). (Z)-isomer, δ, 0.98 (t, J=6.7 Hz, 3H), 1.34 (d, J=6.7Hz, 3H), 3.42 (m, J=6.7Hz, 2H), 4.42 (double d, J=6 and 9.8Hz, 1H), 4.61 (double q, J=6.7 and 9.8 Hz, 1H), 5.67 (d, J=6Hz, 1H), 7.17 (m, 3H), 8.17 (m, 2H) ;
MS:M/Z, 204 (6.7), 158 (7), 129 (5), 105 (21.3), 90 (100), 77 (20), 71 (84).

5b : ^1H NMR ($CDCl_3$, 200 MHz) : (E)-isomer, δ, 1.22 (t, J=6.7Hz, 3H), 1.30 (d, J=6.6Hz, 3H), 3.68 (q, J=6.7Hz, 2H), 3.82 (s, 3H), 4.0 (double q, J=6.6 and 8.9Hz, 1H), 4.89 (double d, J=8.9 and 12.9Hz, 1H), 6.39 (d, J=12.9, 1H), 7.0-7.36 (m, 4H). (Z)-isomer, δ, 1.27 (t, J=6.7Hz, 3H), 1.31 (d, J=6.5Hz, 3H), 3.82 (s, 3H), 3.92 (q, J=6.7Hz, 2H), 4.37 (double d, J=9.8 and 5.9Hz, 1H), 4.54 (double q, J=6.5 and 9.8Hz, 1H), 5.97 (d, J=5.9Hz, 1H), 7.1-7.7 (m,4H).

5c : ^1H NMR (C_6D_6, 200MHz) : (E)-isomer, δ, 0.94 (t, J=6.7Hz, 3H), 1.26 (d, J=6.8Hz, 3H), 2.41 (s, 3H), 3.27 (q, J=6.7Hz, 2H), 3.57 (double q, J=6.8 and 9Hz, 1H), 4.77 (double d, J=9 and 12.6Hz, 1H), 6.17 (d, J=12.6Hz, 1H), 6.9-7.4 (m, 4H). (Z)-isomer, δ, 0.87 (t, J=6.7Hz, 3H), 1.32 (d, J=6.8Hz, 3H), 2.49 (s, 3H), 3.25 (q, J=6.7Hz, 2H), 4.44 (m, 2H), 5.51 (d, J=6Hz, 1H), 6.9-7.9 (m, 4H) ;
MS:M/Z, 218 (6.9), 119 (78.3), 99 (100), 91 (28), 71 (67.7).

5d : ^1H NMR (C_6D_6, 200MHz) : (E)-isomer, d, 0.93 (t, J=7Hz, 3H), 1.24 (d, J=6.6Hz, 3H), 3.24 (m, J=7Hz, 2H), 3.54 (double q, J=6.6 and 9Hz, 1H), 4.76 (double d, J=9 and 12.6Hz, 1H), 6.27 (d, J=12.6Hz, 1H), 7.20-7.56 (AB q, J=8.3Hz, 4H). (Z)-isomer, d, 0.89 (t, J=7Hz, 3H), 1.31 (d, J=6.6Hz, 3H), 3.29 (m, J=7Hz, 2H), 4.34 (m, 2H), 5.56 (d, J=5.5Hz, 1H), 7.25-7.83 (AB system, J=8.3Hz, 4H).

5e : ^1H NMR : δ, 0.7-1.5 (m, 11H), 1.10 (d, J=6.7Hz, 3H) 1.21 (t, J=6.7 Hz, 3H), 2.33 (m, 2H), 3.27 (m, 1H), 3.65 (q, J=6.7 Hz, 2H), 4.11 (m, 1H, (Z)-isomer), 4.53 (double d, J=8.7 and 13.3Hz, 1H, (E)-isomer), 5.99 (d, J=6Hz, 1H, (Z)-isomer), 6.48 (d, J=13.3Hz, 1H, (E)-isomer).

Hydrolysis of enol ethers 5 ; obtention of 1,4-ketoaldehydes 6

The enol ether (1g) was added to a 30% H_2SO_4 solution (10 ml) and the heterogeneous mixture was stirred at 50°C during 1 hour. The organic phase was extracted with ether, washed with a potassium hydrogenocarbonate solution and dried over magnesium sulfate. Subsequent elimination of the solvent afforded the 1,4-ketoaldehydes.

6a : ^1H NMR : δ, 1.12 (d, J=7Hz, 3H), 2.42 (double d, J=6.1 and 17.9Hz, 1H), 3.04 (double d, J=7.9 and 17.9Hz, 1H), 3.79 (m, J=7.0, 6;1 and 7.9Hz, 1H), 7.2-8 (m, 5H), 9.73 (broad s, 1H) ;
IR cm^{-1} : 1720, 1675. The spectroscopic data of **6a** agree with those of the litterature [35]

6b : ^1H NMR (C_6D_6, 200MHz) : δ, 0.89 (d, J=7.9Hz, 3H), 1.89 (double d, J=5.1 and 18.5Hz, 1H), 2.72 (double d, J=8.2 and 18.5Hz, 1H), 3.25 (s, 3H), 3.61 (m, J=7.9, 5.1 and 8.2Hz, 1H), 6.86 (m, 1H), 7.03 (m, 1H), 7.41 (m, 1H), 7.63 (m, 1H), 9.27 (broad s, 1H). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.47; H, 7.01.

6c : ^1H NMR : δ, 1.10 (d, J=7Hz, 3H), 0.8-1.5 (m, 11H), 2.31 (m, 4H), 2.65 (m, 1H), 9.78 (broad s, 1H). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.54; H, 11.00. Found: C, 71.13; H, 10.79

Attempted cross-coupling of α-ethoxyallyltributyltin with benzoyl chloride

In the experimental conditions already described for α-ethoxycrotyltributyltin, after 5 hours, different compounds were obtained from which γ-ethoxyallyltributyltin was observed in poor yield.
^{1}H NMR : d, 0.5-1.8 (m, 27H), 1.20 and 1.23 (t, J=6.7Hz, 3H), 1.56 and 1.63 (d, J=8.4Hz, 2H), 3.67 (q,J=6.7Hz, 2H), 4.43 (m, J=5.7 and 8.4Hz, 1H) (Z-isomer), 4.78 (m, J=8.4 and 12.5Hz, 1H) (E-isomer), 5.67 (d, J=5.7Hz, 1H) (Z-isomer), 6.10 (d, J=12.5Hz, 1H) (E-isomer)

^{119}Sn NMR : δ, -16,4 (Z-isomer), -19.6 (E-isomer)

Hydrostannation of methyl propargyl ether.: Synthesis of 9

A mixture of Bu_3SnH (18g, 62 mmol), methyl propargyl ether (4.2g, 60 mmol) and AIBN (100mg) was slowly heated and maintained at 100°C during 1 hour in toluene (100ml). After evaporation of the solvent, the distillation gave **9** (17.9g, 83%), bp 120-123°C (0.05 mmHg)[21]. ^{1}H NMR : δ, 0.7-1.6 (m, 27H), 3.27 (s, 3H), 3.89 (m, 2H), 6.13 (m, 2H). The hydrostannation yielded a 70:30 mixture of (E):(Z) isomers (analysis by g.l.c on a FFAP column). The mixture was enriched to a 98:2 (E)(Z) mixture by column chromatography on silica gel (eluent : 3% ethyl acetate in petroleum ether).

Cross-coupling of γ-methoxyvinyltin 9 with acyl chlorides

In a typical experiment a mixture of vinyltin **9** (2.2g, 6 mmol), benzoyl chloride (0.7g, 5 mmol), $BnClPd(PPh_3)_2$ (30mg) was heated at 90°C for 16 hours in benzene (5ml) in a sealed tube. After liquid chromatography on silica gel (eluent 7.5% ether in petroleum ether) the enol ether **11a** (Z+E mixture) (460mg) and the allyl ether **10a** (150mg) were isolated. In another experiment, performed at 100°C for 48 hours, only enol ethers **11a** were obtained.

When performed in CH_2Cl_2 (4 hours at 65°C) the reaction gave only the allyl ether **10a** in 71% yield. In all cases, the cross-coupling occurred with clean retention of configuration the ratio **10a**(E)/**10a**(Z) being the same as the ratio **9**(E)/**9**(Z). Two experiments were made from **9**(E)/**9**(Z) = 98/2 and 70/30 and the reaction mixtures were analyzed by g.l.c on a FFAP column. Similar experimental conditions were used for the other acyl chlorides.

10a : ^{1}H NMR : δ, 3.49 (s, 3H), 4.12 (d, J=3.5Hz, 2H), 7.10 (m, 2H), 7.51 (m, 3H), 7.99 (m, 2H).
IR cm^{-1} : 1680, 1630, 1450.

11a : ^{1}H NMR : (Z)-isomer, δ, 3.59 (s, 3H), 3.71 (double d, J=1 and 6.7Hz, 2H), 4.67 (double t, J=6.7 and 6.5Hz, 1H), 5.97 (double t, J=1 and 6.5Hz, 1H), 7.52 (m, 3H), 7.97 (m, 2H). (E)-isomer, δ, 3.51 (s, 3H), 3.62 (m, 2H), 4.99 (double t, J=6.7 and 13Hz, 1H), 6.48 (d, J=13Hz, 1H), 7.43 (m, 3H), 7.94 (m, 2H).

10b : ^{1}H NMR : δ, 3.33 (s, 3H), 3.76 (s, 3H), 4.04 (d, J=3Hz, 2H), 6.91 (m, 2H), 6.82-7.83 (AB system, J=8.7Hz, 4H).
IR cm^{-1} : 1670, 1630, 1600, 1420.

11b : ^{1}H NMR : (Z)-isomer, δ, 3.61 (s, 3H), 3.63 (double d, J=1 and 6.5Hz, 2H), 3.81 (s, 3H), 4.68 (apparent q, J=6.5Hz, 1H), 5.98 (double t, J=1 and 6.5Hz, 1H), 6.86-7.92 (AB system, J= 8.7Hz, 4H). (E)-isomer, δ, 3.52 (s, 3H), 3.55 (m, 2H), 3.81 (s, 3H), 4.93 (double t, J=6.5 and 12.5Hz, 1H), 6.43 (d, J=12.5Hz, 1H), 6.86-7.90 (AB system, J=8.7Hz, 4H).

10c : ^{1}H NMR : δ, 3.41 (s, 3H), 4.16 (d, J=3Hz, 2H), 7.09 (m, 2H), 7.45-7.94 (AB system, J=8Hz, 4H).

10d : [Obtained after Kugelrohr distillation, bp 80°C (0.05 mmHg)].
^{1}H NMR : (E)-isomer (major), δ, 0.8-1.5 (m, 11H), 2.47 (t, J=6.5Hz, 2H), 3.35 (s, 3H), 4.05 (double d, J=3.9 and 1.2Hz, 2H), 6.21 double t, J=16.7 and 1.2Hz, 1H), 6.73 (double t, J=3.9 and 16.7Hz, 1H).
IR cm^{-1} : 1710, 1640, 1470.
MS: M/Z, 184 (2.3), 139 (38.5), 114 (22), 113 (11.3), 99 (100), 71 (50.5).

Isomerization of allyl ether 10a into enol ether 11a

The isomerizations were run in sealed tubes with either 95% ethanol or absolute ethanol as solvent, in the presence of $RhCl(PPh_3)_3$ (1-2% molar) at 110°C during 20 hours. At the end of the heating, insoluble clear yellow crystals were present. After elimination of solvent the crude residue was chromatographied on Florisil (eluent : 10% ether in petroleum ether). Enol ether **11a** ((E)-isomer) was obtained in 81% yield for the reaction in absolute ethanol while in 95% ethanol the ketoaldehyde diethylacetal was obtained in 75% yield.

Hydrolysis of enol ether 11a

11a (1g) was heated for 1 hour at 50°C in HCl 3N or 30% H_2SO_4 (10 ml), under nitrogen. After extraction with ether, washing with 5% $NaHCO_3$ and drying over $MgSO_4$,. β-benzoylpropionaldehyde was obtained in 92% yield.

12a : ^1H NMR : δ, 2.72-3.18 (m, 4H), 7.42 (m, 3H), 7.92 (m, 2H), 9.78 (apparent s, 1H). Litt.[36]

Isomerization of allyl ether 10b into diethylacetal and subsequent hydrolysis

The reaction was performed in 95% ethanol and gave the diethylacetal corresponding to the ketoaldehyde in 73% yield.

^1H NMR : δ, 1.16 (t, J=7Hz, 6H), 1.94 (double t, J=7.3 and 5.3Hz, 2H), 2.89 (t, J=7.3Hz, 2H), 3.46 (m, 4H), 3.82 (s, 3H), 4.48 (t, J=5.3Hz, 1H), 6.85-7.88 (AB system, J=8.7Hz, 4H).

The hydrolysis in HCl 3N gave the corresponding 1,4-ketoaldehyde **12b** in 93% yield.

12b : ^1H NMR : δ, 2.69-3.13 (m, 4H), 3.73 (s, 3H), 6.78-7.80 (AB system, J=8.7Hz, 4H), 9.73 (apparent s, 1H). Litt.[36]

Isomerization of allyl ether 10d into enol ether 11d and subsequent hydrolysis

An isomeric mixture (Z/E=70/30) of enol ethers **11d** was obtained in 84% yield in absolute ethanol.

11d : ^1H NMR : (Z)-isomer, δ, 0.8-1.5 (m, 11H), 2.34 (m, 2H), 3.02 (d, J=7Hz, 2H), 3.61 (s, 3H), 4.45 (m, J=7 and 6Hz, 1H), 5.93 (d, J=6Hz, 1H) ; (E)-isomer, δ, 0.8-1.5 (m, 11H), 2.34 (m, 2H), 2.88 (d, J=7Hz, 2H), 3.52 (s, 3H), 4.72 (double t, J=7 and 12,5Hz, 1H), 6.27 (d, J=12.5Hz, 1H).

IR cm^{-1} (Z + E mixture) : 1720, 1610, 1410.

A sample of the isomeric mixture (1g) was added to 30% H_2SO_4 (10 ml) and treated as above. β-heptanoylpropionaldehyde **12d** (0.84g, 91%) was obtained.

12d : ^1H NMR : δ, 0.8-1.5 (m, 11H), 2.38 (m, 2H), 2.61 (apparent s, 4H), 9.72 (apparent s, 1H).

IR cm^{-1} : 1720, 1410, 1380. Litt.[37]

Intramolecular aldol condensation of β-heptanoylpropionaldehyde

To a mixture of water (40 ml), dioxane (40 ml) and 10% NaOH solution (10 ml) at reflux, was added dropwise, over 1.5 hour, a solution of β-heptanoylpropionaldehyde (0.85g, 5 mml)(**12d**) in dioxane (10 ml). The reflux was maintained 10 minutes and the mixture was neutralized with 1N HCl. After extraction with ether, drying and evaporation of the solvent, the product was distilled (Kugelrohr) to give 2-pentyl-cyclopent-2-ene-1-one (0.53g). bp 89-91°C (0.1 mmHg).

^1H NMR : δ, : 0.8-1.5 (m, 9H) ; 2.00-2.70 (m, 6H) ; 7.21 (m, 1H).

^{13}C NMR ($CDCl_3$, 22,6 MHz) : ring carbons 210.2 ; 157.5 ; 146.7 ; 34.6 ; 31.6 ; chain carbons : 27.4 ; 26.5 ; 24.7 ; 22.5 ; 14.0.

IR cm^{-1} : 1710, 1635, 1450. Litt.[37]

Hydrostannation of 3-methoxy-1-butyne. Synthesis of γ-methoxyvinyltin 13

A solution of Bu_3SnH (6.2g, 21 mmol), 3-methoxy-1-butyne (1.8g, 21 mmol), prepared by methylation of 1-butyne-3-ol, and AIBN (50 mg) in toluene (20ml) was slowly heated and maintained at 100°C during 1 hour. Distillation of the reaction mixture gave the γ-methoxyvinyltin **13** (E/Z=80/20) (5.25g, 67%). bp 111-113°C (0.1 mmHg).

^1H NMR ((E)-isomer) : δ, 0.7-1.6 (m, 30H), 3.19 (s, 3H), 3.62 (double q, J = 4.8 and 6 Hz, 1H), 5.72 (double d, J = 4.8 and 18.7 Hz, 1H), 6.13 (d, J = 18.7 Hz, 1H).

Cross-coupling of γ-methoxyvinyltin 13 with heptanoyl chloride

The cross-coupling was performed in benzene as already described for **9** and the product **10e** was isolated by liquid chromatography on silica gel (eluent : 10% ether in petroleum ether) in 79% yield.

10e : ^{1}H NMR : δ, 0.8-1.5 (m, 14H), 2.51 (m, 2H), 3.29 (s, 3H), 3.84 (m, 1H), 6.09 (d, J = 16.7 Hz, 1H), 6.62 (double d, J = 16.7 and 5 Hz), 1H).

Isomerization of 2-methoxy-3-undecene-5-one

The allyl ether (1g, 5 mmol) was heated at 100°C during 24 hours, in a sealed tube, in the presence of Wilkinson's catalyst (90 mg) in 95% ethanol (15 ml). After chromatography on silica, 2,5-undecanedione (650 mg, 71%) (**12e**) was isolated.

12e : ^{1}H NMR : δ, 0.8-1.5 (m, 11H), 2.10 (s, 3H), 2.38 (t, J = 6 Hz), 2.56 (apparent s, 4H). Litt.[37]

Cross-coupling of γ-methoxyvinyltin 9 with aryl bromides

In a typical experiment a mixture of bromobenzene (0.95g, 6 mmol), reagent **9** (2.16g, 6 mmol) and $BnClPd(PPh_3)_2$ (30 mg) was dissolved in benzene and heated at 100°C (sealed tube) over a period of 14-20 hours, until the apparition of a black precipitate. The reaction mixture was then chromatographied on silica gel (eluent : 7.5% ether in petroleum ether) to give the alkyl ether **10f** (81%) mainly as the (E)-isomer. Similar experimental conditions were used for the other aryl bromides.

10f : ^{1}H NMR : δ, 3.30 (s, 3H), 4.01 (d, J = 5 Hz, 2H), 6.19 (double t, J = 5 and 16 Hz, 1H), 6.64 (d, J = 16 Hz, 1H), 7.32 (apparent s, 5H).

10g : ^{1}H NMR : δ, 3.29 (s, 3H),3.73 (s, 3H), 3.99 (d, J = 5.3 Hz, 2H), 6.02 (double t, J = 5.3 and 16 Hz, 1H), 6.52 (d, J = 16 Hz, 1H), 6.8-7.29 (AB system, J = 8.7 Hz, 4H).

10h : ^{1}H NMR : δ, 3.30 (s, 3H), 3.99 (d, J = 5 Hz, 2H), 6.09 (double t, J = 5 and 16 Hz, 1H), 6.53 (d, J = 16 Hz, 1H), 7.25 (apparent s, 4H).

10i : (elution with CH_2Cl_2)
^{1}H NMR ($CDCl_3$) : δ, 3.34 (s, 3H), 4.05 (d, J = 4 Hz, 2H), 6.28 (m, J = 4 and 16 Hz, 1H), 6.60 (d, J = 16 Hz, 1H), 7.52 (AB system, J = 8.9 Hz, 4H).

10j : (elution with CH_2Cl_2)
^{1}H NMR ($CDCl_3$) : δ, 3.39 (s, 3H), 4.20 (d,J = 4 Hz, 2H), 6.39 (m, J = 4 and 16.5 Hz, 1H), 6.77 (d, J = 16.5 Hz, 1H), 7.53-8.22 (AB system, J = 8.7 Hz, 4H).

Synthesis of the silylated γ-methoxyvinyltin 14

To a solution of γ-methoxyvinyltin **9** (21.7g, 60 mmol) in THF (150 ml), 43.5 ml of sec-BuLi (1.4M in cyclohexane) were added at -78°C under nitrogen. The mixture turned yellow-brown and was quenched with freshly distilled Me_3SiCl (6.5g, 60 mmol) at -78°C and kept under stirring for 1 hour. The temperature was slowly rised to -10°C and the mixture hydrolyzed with a saturated solution of ammonium chloride in water. The organic phase was dried over $MgSO_4$ and **14** was obtained in 60% yield (14.5g) (Kugelrohr distillation).

14 : ^{1}H NMR : δ, 0.12 (s, 9H), 0.7-1.6 (m, 27H), 3.25 (s, 3H), 3.44 (m, 1H), 5.89 (m, 2H).
^{119}Sn NMR (C_6D_6) : δ, -45.52. Anal. Calcd for $C_{19}H_{42}OSiSn$: C, 52.66; H, 9.77. Found: C, 52.79; H, 9.87.

Cross-coupling of 14 with acyl chlorides, followed by desilylation

In a typical procedure reagent **14** (2.5g, 5.8 mmol), the acyl chloride (5 mmol) and $BnClPd(PPh_3)_2$ (20 mg) were heated at 80°C, under nitrogen, in THF (10 ml) until a black precipitate appeared. The mixtures were cooled to 0°C and a solution of Bu_4NF (Aldrich) in THF (1M, 10 ml) was added. After hydrolysis and extraction of the organic phase, the enol ethers **11** were isolated by liquid chromatography on Florisil (eluent : 10% ether + 90% petroleum ether).The already described enol ethers **11a, 11b, and 11d,** were obtained mainly as (Z)-isomers.

Cross-coupling of 14 with aryl bromides and subsequent desilylation.

In a typical procedure a mixture of bromobenzene (1.57g, 10 mmol), reagent **14** (5.2g, 13 mmol) and $Pd(PPh_3)_4$ (50mg) in benzene (10 ml) was heated under nitrogen at 110°C during 20 hours in a sealed tube. The reaction mixture was treated with a 30% KF solution in water in order to precipitate tributyltin fluoride. The silylated ether **15f** was isolated by liquid chromatography on silica gel (eluent : 5% ether in petroleum ether).

15f : ^{1}H NMR : δ, 0.10 (s, 9H), 3.38 (s, 3H), 3.56 (d, J = 6 Hz, 1H), 6.19 (double d, J = 6 Hz and 16 Hz, 1 H), 6.54 (d, J = 16Hz, 1H), 7.34 (apparent s, 5H).
IR cm^{-1} : 1500, 1450, 1250, 1080. Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.84; H,9.15. Found: C, 70.05; H, 9.14.

The desilylation of **15f** was performed by adding 10 ml of a Bu_4NF solution (1M in THF) to **15f** (1.92g, 10 mmoles in 20 ml THF) at 0°C. After stirring for 5 minutes the reaction mixture was hydrolyzed and the organic phase extracted with pentane. After concentration and liquid chromatography on silica gel (eluent : 5% ether in petroleum ether) the enol ether **11f** was isolated as a (Z):(E) mixture in addition to a small amount of the already described **10f**. Similar experimental conditions were used for the other aryl bromides.

11f : ^{1}H NMR: (E)-isomer (25%), δ, 3.21 (d, J = 7.2 Hz, 2H), 3.41 (s, 3H), 4.78 (double t, J = 7.2 and 13 Hz, 1H), 6.45 (d, J = 13 Hz, 1H), 7.19 (m, 5H) ; (Z)-isomer (75%), δ, 3.35 (d, J = 7 Hz, 2H), 3.56 (s, 3H), 4.48 (double t, J = 7 and 6 Hz, 1H), 5.90 (d, J = 6 Hz, 1H), 7.19 (m, 5H). Litt.[38].

15g : (eluent : 2% ethyl acetate in petroleum ether).

^{1}H NMR : δ, 0.11 (s, 9H), 3.39 (s, 3H), 3.55 (d, J = 6 Hz, 1H), 3.81 (s, 3H), 6.09 (double d, J = 6 and 16 Hz, 1H), 6.57 (d, J = 16 Hz, 1H), 6.9-7.39 (AB system, J = 8.7 Hz, 4H). Anal. Calcd for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86. Found: C, 66.96; H, 8.76.

11g : (mainly (Z) isomer)
^{1}H NMR : δ, 3.30 (d, J = 7.3 Hz, 2H), 3.59 (s, 3H), 3.78 (s, 3H), 4.48 (double t, J = 7.3 and 6 Hz, 1H), 5.95 (d, J = 6 Hz, 1H), 6.74-7.11 (AB system, J = 8.7 Hz, 4H).

15h : (eluent : 2% ethyl acetate in petroleum ether). mp 70-71°C ;
^{1}H NMR : δ, 0.12 (s, 9H), 3.37 (s, 3H), 3.57 (d, J = 5.3 Hz, 1H), 6.11 (m, J = 5.3 Hz and 16 Hz, 1H), 6.50 (d, J = 16H,1H), 7.33 (apparent s, 4H). Anal. Calcd for $C_{13}H_{19}ClOSi$: C, 61.27; H, 7.51. Found: C, 61.12; H, 7.43.

11h (Z/E = 60/40)
^{1}H NMR : (E)-isomer, δ, 3.15 (d, J = 7.2 Hz, 2H), 3.43 (s, 3H), 4.68 (double t, J = 7.2 and 13 Hz, 1H), 6.31 (d, J = 13 Hz, 1H), 7.14 (apparent s, 4H) ; (Z)-isomer, δ, 3.30 (d, J = 7.3 Hz, 2H), 3.55 (s,3H), 4.41 (double t, J = 7.3 and 6 Hz, 1H), 5.91 (d, J = 6 Hz, 1H), 7.14 (apparent s, 4H).

15i : (eluent : 3% ethyl acetate in pretroleum ether).
^{1}H NMR : δ, 0.12 (s, 9H), 3.40 (s,3H), 3.64 (m, 1H), 6.43 (m, 2H), 7.55 (AB system, J = 8 Hz, 4H). Anal. Calcd for $C_{14}H_{19}NOSi$: C, 68.52; H, 7.80. Found: C, 68.13; H, 7.67.

11i : mainly (Z)-isomer (eluent : 10% ether in petroleum ether)
^{1}H NMR : δ, 3.30 (d, J = 7.3 Hz, 2H), 3.52 (s, 3H), 4.45 (apparent q, J = 7.3 and 6 Hz, 1H), 5.90 (d, J = 6 Hz, 1H), 7.16-7.43 (AB system, J = 6 Hz, 4H).

15j : (eluent : 4% ethyl acetate in petroleum ether). mp 106-107°C.
^{1}H NMR : δ, 0.10 (s, 9H), 3.39 (s, 3H), 3.65 (m, 1H), 6.48 (m, 2H), 7.48-8.18 (AB system, J = 8.7 Hz, 4 H). Anal. Calcd for $C_{13}H_{19}NO_3Si$: C, 58.83; H, 7.22. Found: C, 58.45; H, 7.10.

15k : (eluent : 10% ether in petroleum ether). mp 57-58°C.
^{1}H NMR : δ, 0.11 (s, 9H), 2.52 (s, 3H), 3.39 (s, 3H), 3.54 (d, J = 3.8 Hz, 1H), 6.32 (m, J = 3.8 and 15 Hz, 1H), 6.56 (d, J = 15 Hz, 1H), 7.44-7.83 (AB system, J = 8 Hz, 4H). Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.43; H, 8.53.

11k : mainly (Z)-isomer (eluent : 7% ether in petroleum ether)
^{1}H NMR : δ, 2.35 (s, 3H), 3.30 (d, J = 7 Hz, 2H), 3.52 (s, 3H), 4.39 (apparent q, J = 7 and 6 Hz, 1H), 5.89 (d, J = 6 Hz, 1H), 7.15-7.71 (AB system, J = 8 Hz, 4H).

^{1}H NMR : δ, 0.12 (s, 9H), 3.38 (s, 3H), 3.59 (d, J = 4 Hz, 1H), 3.90 (s, 3H), 6.43 (m, 2H), 7.43-8.02 (AB system, J = 8 Hz, 4H). Anal. Calcd for $C_{15}H_{22}O_3Si$: C, 64.70; H, 7.96. Found: C, 64.25; H, 7.74.

11l, mainly (Z)-isomer (eluent : 10% ether in petroleum ether)
^{1}H NMR : δ, 3.38 (d, J = 7 Hz, 2H), 3.49 (s, 3H), 3.81 (s, 3H), 4.45 (apparent q, J = 7 and 6 Hz, 1H), 5.93 (d, J = 6 Hz, 1H), 7.21-7.88 (AB system, J = 8 Hz, 4H).

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