Tetrahedron Vol 45, No 14, pp 4627 to 4636, 1989
Printed in Great Britain

0040-4020/89 $3.00+.00
Maxwell Pergamon Macmillan plc

SYNTHESIS OF γ,δ-UNSATURATED α-AMINO ACIDS FROM ALLYLSILANES AND GLYCIDYL CATION EQUIVALENTS

Hendrik H. Mooiweer, Henk Hiemstra*, and W. Nico Speckamp*

Laboratory of Organic Chemistry, University of Amsterdam

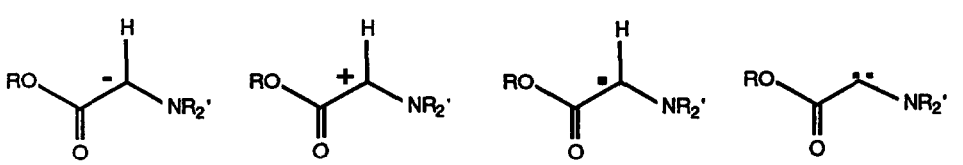
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands.

(*Received in UK 2 May* 1989)

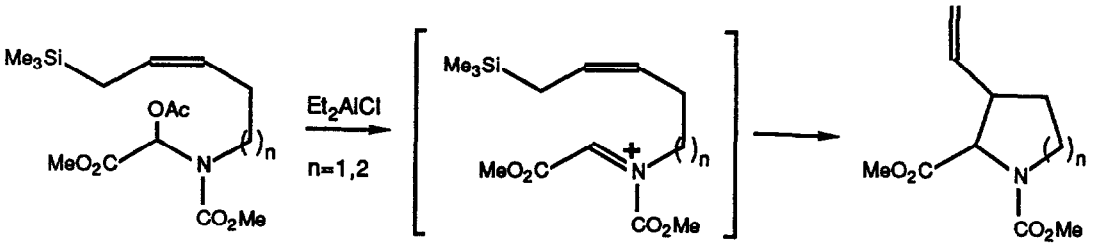
Summary: The synthesis of a series of γ,δ-unsaturated *N*-protected α-amino acid methyl esters from the coupling of different allylsilanes and glycidyl cation equivalents **6** and **7** is described. Reactions with methoxyglycine derivative **6** are induced with $BF_3{\cdot}OEt_2$; in the case of chloroglycine derivative **7** $SnCl_4$ is used as Lewis acid. Reactions are fully regioselective, but show low stereoselectivity. The conversion of the reaction products into unprotected α-amino acids is described for two cases.

INTRODUCTION

The synthesis of natural and unnatural α-amino acids continues to attract considerable attention.[1] A conceptually appealing approach, which enjoys frequent use, is the alkylation of reactive glycidyl equivalents.[1] By far, most attention has been devoted to the anionic type (1), of which still novel applications are being reported, especially in the field of asymmetric synthesis.[2] The cationic glycidyl equivalent (2), pioneered by Ben-Ishai and co-workers,[3,4] has received less attention, but in recent years asymmetric modifications are rapidly gaining interest.[5] The glycidyl radical (3)[6] and glycidyl carbene (4)[7] have become a subject of investigation only very recently.



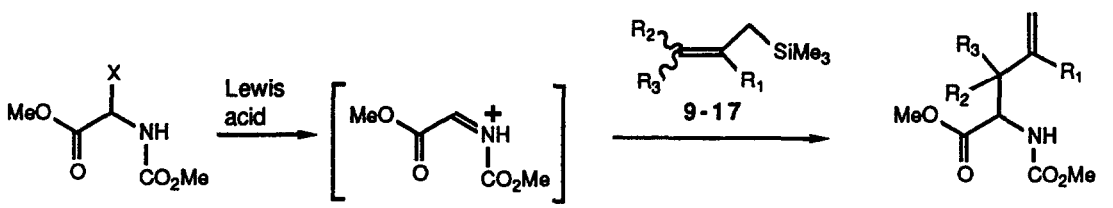
Extending our research on silicon-assisted *N*-acyliminium ion cyclizations,[8] we recently reported the synthesis of cyclic α-amino acid derivatives through use of *C,N*-bis(alkoxycarbonyl)iminium ions **5**,[9] which are in fact reactive cationic glycidyl equivalents of type **2** (Scheme 1; n=1,2). We then became aware of a lack of information in the literature on the corresponding intermolecular reaction with allylsilanes (Scheme 2). This is remarkable, because the methoxy- and chloroglycine derivatives **6** and **7**, suitable precursors towards **8**, are readily accessible in high yield from inexpensive starting materials.[10] Furthermore, γ,δ-unsaturated α-amino acid derivatives (**18-26**) are expected to be formed highly regioselectively with respect to the position of the double bond due to the β-effect of silicon.[11]



Scheme 1

5

Simple olefins instead of allylsilanes have been shown to lead to mixtures of double bond isomers in many cases.[3b] It was recently reported that β,γ-unsaturated α-amino acids can be prepared with high selectivity by using vinylsilanes as π-nucleophiles in reactions with 8.[12] Reactions with allylsilanes have been published for a cyclic, chiral analogue of intermediate 8.[5d] A very recent article [13] describing a simple allylsilane reaction, prompted us to report our work in this area, the details of which are described herein.



6 X=OMe
7 X=Cl

8

18-26

Scheme 2

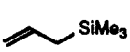
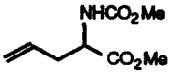
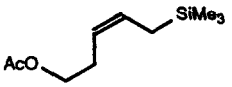
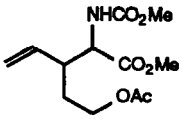
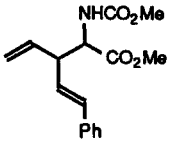
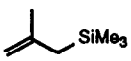
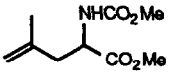
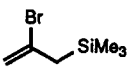
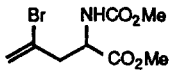
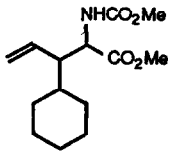
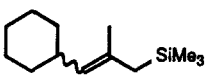
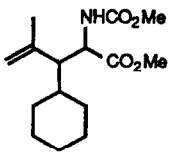
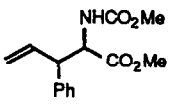
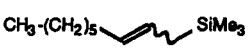
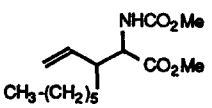
RESULTS AND DISCUSSION

The results are collected in Table 1. The allylsilanes 11, 14-17 were prepared by using the Wittig methodology, developed by Seyferth et al,[14] and refined by Fleming et al.[15] The yields were around 70% after vacuum distillation, and the products obtained as E/Z mixtures were employed as such in the coupling reactions with 6 and 7.

Generation of the intermediate 8 from methoxy precursor 6 was effected with 4 equiv of boron trifluoride etherate. Tin tetrachloride (2 equiv) was preferred as Lewis acid if chloroglycine derivative 7 was used as starting material. The results show that the chloro precursor 7 gave somewhat better yields than the methoxy compound 6 (cf entries 1 and 4; 2 and 9). Yields starting from chloro precursor 7 varied from moderate for the bromine containing allylsilane 13 (entry 6) to excellent for allylsilane 14 (entry 7).

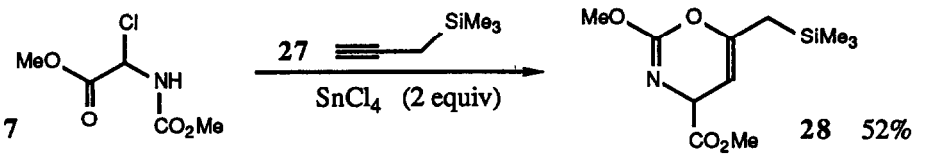
The products in Table 1 were obtained as single regioisomers, emphasizing the value of silicon as a regiochemical control element. This is particularly remarkable for silane 11 (entry 3) which solely reacted at the γ-position relative to silicon [16], although the yield of 20 was rather poor. In those cases where stereoisomers were formed little

Table 1

entry	glycidyl cation precursor	Lewis acid (equiv)	allylsilane (equiv, Z/E ratio)	product (yield, isomer ratio)
1	**6**	$BF_3.OEt_2$ (4)	 **9** (1.8)	 **18** (54%)
2	**6**	$BF_3.OEt_2$ (4)	 **10** (1.1)	 **19** (66%, 37:63)
3	**6**	$BF_3.OEt_2$ (4)	 **11** (1.2, 40:60)	 **20** (34%, 38:62)
4	**7**	$SnCl_4$ (2)	**9** (1.0)	**18** (75%)
5	**7**	$SnCl_4$ (2)	 **12** (1.1)	 **21** (58%)
6	**7**	$SnCl_4$ (2)	 **13** (1.1)	 **22** (51%)
7	**7**	$SnCl_4$ (2)	 **14** (1.0, 14:86)	 **23** (99%, 41:59)
8	**7**	$SnCl_4$ (2)	 **15** (1.0, 33:67)	 **24** (68%, 50:50)
9	**7**	$SnCl_4$ (2)	**10** (1.1)	**19** (74% , 40 : 60)
10	**7**	$SnCl_4$ (2)	 **16** (1.1, 19:81)	 **25** (73%, 44:56)
11	**7**	$SnCl_4$ (2)	 **17** (1.1, 18:82)	 **26** (84%, 45:55)

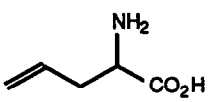
stereoselectivity was observed, and the product isomers could not be separated. The stereoisomer ratio's were determined from the ^{1}H NMR spectra by integration of the hydrogens located α or β to nitrogen. The formation of stereoisomer mixtures is not due to the use of E/Z mixtures of allylsilanes, since the reaction with pure Z-allylsilane **10** (entry 2) also led to a stereoisomer mixture of **19**. When this reaction was performed with the chloroglycine precursor **7** bearing a benzyloxycarbonyl instead of a methoxycarbonyl group at nitrogen, an isomer ratio of 42 : 58 was obtained. Thus, the nature of the substituent at nitrogen does not have a great influence on the stereoselectivity of the coupling reaction.

In analogy with earlier results,[9,17] we also attempted to use 2-propynyltrimethylsilane (**27**) as π-nucleophile in reaction with the glycidyl cation equivalent **8**, aiming at the preparation of protected allenylglycine.[18] However, reaction of **7** with 3 equiv of silane **27** in the presence of tin tetrachloride (2 equiv) led to cyclization product **28** in 52% yield. Thus, whereas **8** reacts in an S_E2' fashion with allylsilanes, **8** gives a (formal) Diels Alder reaction with 2-propynyltrimethylsilane (**27**).[19]

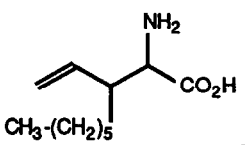


Scheme 3

In conclusion, reactions of chloroglycine derivative **7** with various allylsilanes in the presence of tin tetrachloride constitute a facile synthesis of γ,δ-unsaturated α-amino acid derivatives. The products can be easily converted into the unprotected amino acids by successive treatment with trimethylsilyl iodide in CCl_4 [20] and dilute aqueous hydrochloric acid, as is described for the synthesis of allylglycine (**29**) and the more complex amino acid **30**. γ,δ-Unsaturated α-amino acids may be interesting compounds in their own right.[1,5d] In addition, the double bond can be a suitable handle for further synthetic manipulations.



29



30

EXPERIMENTAL

General information. All reactions were carried out in an inert atmosphere of dry nitrogen, unless otherwise described. Standard syringe techniques were applied for transfer of Lewis acids and dry solvents. Infrared spectra (IR) were obtained from $CHCl_3$ solutions, or liquid capilary (liq. cap.) using NaCl platelets, using a Perkin-Elmer 298 or Perkin-Elmer 1310 spectrophotometer and are reported in cm^{-1}. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were determined in $CDCl_3$ as solvent using a Varian XL-100 (100 MHz), a Bruker AC 200 (200 MHz) or a

Bruker WM 250 (250 MHz) spectrometer. ^{13}C-NMR spectra were recorded on a Bruker AC 200 or Bruker WM 250 instrument. Chemical shifts are given in ppm downfield from tetramethylsilane. Mass spectra were recorded on a Varian MAT 711 or a VG Micromass ZAB-2HF instrument. R_f values were obtained by using thin layer chromatography (TLC) on silica-gel-coated plastic sheets (Merck silica gel 60 F_{254}) with the indicated solvent (mixture). Chromatographic purification refers to flash chromatography with Merck silica gel 60 (230-400 mesh). Melting and boiling points are uncorrected. CH_2Cl_2 was distilled from P_2O_5 and kept under an atmosphere of dry nitrogen. $BF_3{\cdot}OEt_2$ and $SnCl_4$ were distilled and stored under an atmosphere of dry nitrogen, $SnCl_4$ as a 1.2 M solution in CH_2Cl_2. Dry THF and Et_2O were distilled under an atmosphere of dry nitrogen from sodium benzophenone ketyl prior to use. 2-Bromo-3-trimethylsilane (13), and 2-propynyltrimethylsilane (27) were purchased from Fluka.

1-Acetoxy-5-trimethylsilyl-3-pentene (10). To a solution of 9.24 g (58.4 mmol) of 5-trimethylsilyl-3-penten-1-ol [21] in 91.0 ml of pyridine was added at room temperature 6.61 mL (7.15 g, 70.1 mmol) of acetic anhydride and 713.5 mg (5.84 mmol) of 4-dimethylaminopyridine. After stirring for 20 h, the reaction mixture was worked up by pouring it into water (~100 ml). The water layer was extracted with CH_2Cl_2 (3x40 mL). After drying over $MgSO_4$ the organic fractions were concentrated *in vacuo*. The temperature should be kept below 30 °C (15 mm Hg), because of product volatility. Toluene was added to the residue (~50 ml), and the solvent evaporation was repeated for the azeotropic removal of pyridine. This procedure was repeated twice with toluene and then with CH_2Cl_2 in order to remove toluene. The product was purified by flash chromatography (EtOAc : hexane = 1:7), to yield 11.11 g (55.5 mmol, 95%) of 10 as a colourless oil. R_f 0.40 (EtOAc : hexane = 1:7). IR ($CHCl_3$): 3005, 2990-2850, 1730, 1245, 850. ^{1}H-NMR (100 MHz): 5.72-5.08 (m, 2 H, -C<u>H</u>=C<u>H</u>-), 4.03 (t, 2 H, *J* 6 Hz, -C<u>H</u>$_2$-OAc), 2.32 (q, 2 H, *J* 6Hz, -C<u>H</u>$_2$-C<u>H</u>$_2$-OAc), 2.04 (s, 3 H, C<u>H</u>$_3$), 1.48 (d, 2 H, *J* 8 Hz, -C<u>H</u>$_2$-Si(CH$_3$)$_3$), 0.00 (s, 9 H, Si(C<u>H</u>$_3$)$_3$).

1-Phenyl-5-trimethylsilyl-1,3-pentadiene (11). To a suspension of 4.88 g (13.66 mmol) of methyltriphenylphosphonium bromide in 30 mL of dry THF was added at 0° C, under a dry nitrogen atmosphere, 9.48 mL (15.16 mmol, 1.6 M solution in hexane) of n-butyllithium. The mixture was allowed to warm up to room temperature, stirred for 1 h at this temperature and recooled to 0 °C. Iodomethyltrimethylsilane (2.92 g; 13.66 mmol) was added over 10 min. The mixture was again allowed to warm up to room temperature to precipitate the phosphonium salt. After stirring for 1 h at room temperature, the reaction mixture was again treated with 9.48 mL (15.16 mmol, 1.6 M solution in hexane) of n-butyllithium at -78 °C. The mixture was allowed to warm up to room temperature and was stirred for a further 1.5 h to give a dark red solution of the ylid. *trans*- Cinnamaldehyde (1.59 g, 12.02 mmol) in 7 mL of dry THF was then added dropwise over 15 min to the ylid solution at -78 °C. After stirring for 30 min at -78 °C, the mixture was allowed to warm up to room temperature and stirred for a further 16 h. The reaction mixture was then poured out into saturated aq ammonium chloride (~60 mL) and extracted with ether (3x100 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated *in vacuo*. Purification by flash chromatography (hexane) yielded 2.06 g (9.54 mmol, 80%) of 11 as a colourless oil, as a mixture of isomers (E : Z = 60 : 40). R_f 0.38 (hexane). IR (liq.cap.): 3080, 3030, 2990-2850, 1650, 1590, 1495, 1245, 840. ^{1}H-NMR (250 MHz): 7.46-7.17 (m, 5 H, Ph), 7.06 (dd, 1 H, *J* 11, 15.5 Hz, Ph-CH=C<u>H</u>-, cis isomer), 6.80 (dd, 1 H, *J* 10.2, 15.6 Hz, Ph-CH=C<u>H</u>-, trans isomer), 6.52 (d, 1 H, *J* 15.5 Hz, Ph-C<u>H</u>=, cis isomer), 6.40 (d, 1 H, *J* 15.6 Hz, Ph-C<u>H</u>=, trans isomer), 6.14 (t, 1 H, *J* 7.5 Hz, Ph-CH=CH-C<u>H</u>=, cis isomer), 6.13 (dd, 1 H, *J* 11, 15.8 Hz, Ph-CH=CH-C<u>H</u>=, trans isomer), 5.88 (dt, 1 H, *J* 8.3, 15 Hz, =C<u>H</u>-CH$_2$-, trans isomer), 5.64 (q, 1 H, *J* 9 Hz, =C<u>H</u>-CH$_2$-, cis isomer), 1.81 (d, 2 H, *J* 9 Hz, -C<u>H</u>$_2$-Si(CH$_3$)$_3$, cis isomer), 1.65 (d, 2 H, *J* 8.3 Hz, -C<u>H</u>$_2$-Si(CH$_3$)$_3$, trans isomer), 0.10 (s, 9 H, Si(C<u>H</u>$_3$)$_3$, cis isomer), 0.08 (s, 9 H, Si(C<u>H</u>$_3$)$_3$, trans isomer). ^{13}C-NMR (50 MHz): 137.9 (cis isomer) and 137.8 (trans isomer), 132.7, 130.5, 129.8, 129.7, 129.3, 128.5, 128.4, 128.0, 126.9, 126.6, 126.5, 126.1, 125.8, 124.6, 24.0 (trans isomer) and 20.0 (cis isomer,-<u>C</u>H$_2$-Si(CH$_3$)$_3$)), -1.8 (cis isomer) and -2.0 (trans isomer, Si(CH$_3$)$_3$). Exact mass 216.1343 (calcd. for $C_{14}H_{20}Si$ 216.1334).

1-Cyclohexyl-2-methyl-3-trimethylsilyl-1-propene (15). Synthesis according to the procedure for 11 with 5.57 g (15.00 mmol) of ethyltriphenylphosphonium bromide, 30 mL dry THF, 10.31 mL (16.50 mmol, 1.6 M solution in hexane) of n-butyllithium and, 3.21 g (15.00 mmol) of iodomethyltrimethylsilane. After stirring for 1.75 h (in one case 4.5 h, because of long precipitation time) at room temperature, 10.31 mL (16.50 mmol, 1.6 M solution in hexane) of n-butyllithium was added. After stirring for 2.25 h at room temperature 1.50 g (13.32 mmol)

of cyclohexane carboxaldehyde in 7 mL dry THF was added. For work up see procedure for **11** ; eluent: hexane. The allylsilane was further purified by distillation (bp 140-142 °C / 17 mmHg) to yield 2.05 g (9.74 mmol, 73%) of **13** as a colourless oil, as a mixture of isomers (E : Z = 66 : 34). R_f 0.65 (hexane). IR (liq. cap.): 3010, 3000-2800, 1245, 840. ^{1}H-NMR (250 MHz): 4.82 (d, 1 H, *J* 10.0 Hz , -C<u>H</u>=, major isomer), 4.77 (d, 1 H, *J* 12.0 Hz, -C<u>H</u>= , minor isomer), 2.22-2.05 (m, 1 H, C<u>H</u>-CH= , minor isomer), 2.05-1.85 (m, 1 H, C<u>H</u>-CH=, major isomer), 1.70-1.54 (m, 7 H, CH_3-, =CH-CH-(CH_2-)$_2$), 1.49 (s, 2 H, $(CH_3)_3$Si-C<u>H</u>$_2$-, major isomer), 1.42 (s, 2 H, $(CH_3)_3$Si-C<u>H</u>$_2$-, minor isomer), 1.37-0.84 (m, 6 H, -CH_2-C<u>H</u>$_2$-CH_2-C<u>H</u>$_2$-CH_2-), 0.02 (s, 9 H, $(CH_3)_3$Si, major isomer), -0.02 (s, 9 H, $(CH_3)_3$Si, minor isomer). ^{13}C-NMR (50 MHz): 130.7 and 130.6 (-CH=<u>C</u>), 129.4 (minor) and 128.9 (major, -<u>C</u>H=C), 37.3 (<u>C</u>H-CH=C), 33.7 and 33.5 (-<u>C</u>H$_2$-CH-<u>C</u>H$_2$-), 29.7 (-<u>C</u>H$_2$-Si$(CH_3)_3$), 26.3 (major) and 18.7 (minor, <u>C</u>H$_3$-CH=CH-), 26.2 (-<u>C</u>H$_2$-CH_2-<u>C</u>H$_2$-), 23.1 (-CH_2-<u>C</u>H$_2$-CH_2-), -0.7 (major) and -1.3 (minor, $(CH_3)_3$Si). Exact mass 210.1812 (Calcd. for $C_{13}H_{26}Si$ 210.1804).

General procedure for the coupling of 6 with allyltrimethylsilanes using BF_3·OEt_2. (Procedure A). An excess of the allyltrimethylsilane (1.1-1.8 equiv) was added at room temperature to a 0.5 M solution of methoxylactam **6** [10] in dry CH_2Cl_2. The reaction mixture was cooled to 0 °C. An excess of boron trifluoride etherate (4 equiv) was added slowly to the reaction mixture. After stirring for 15 min at 0 °C, the reaction mixture was allowed to warm up to room temperature. The reaction mixture was worked up after stirring for 3 h at room temperature, by pouring it into brine and extraction with $CHCl_3$ (3x). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed, to give colourless oils in all cases.

General procedure for the coupling of 7 with allyltrimethylsilanes using $SnCl_4$. (Procedure B). The allyltrimethylsilane (1.0-1.1 equiv) was added at room temperature to a 0.3 M solution of moisture sensitive chloride **7** [10] in dry CH_2Cl_2 (**7** was weighed under nitrogen). The reaction mixture was cooled to -78 °C. Tin tetrachloride (2 equiv) was added slowly to the reaction mixture. After a further 15 min at -78 °C, the reaction mixture was allowed to warm up to room temperature and was stirred for a further 3 h. The reaction mixture was then carefully poured out into ice-cold saturated aq $NaHCO_3$. Tin salts were removed by filtration through a sintered glass funnel with the aid of Celite. The filter was rinsed with $CHCl_3$. The organic filtrate was washed with aq $NaHCO_3$ (2x), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed, to give colourless oils in all cases.

Carbamate 18. According to procedure A, starting from 143.2 mg (1.254 mmol) of allyltrimethylsilane (**9**), 124.6 mg (0.703 mmol) of **6**, 2.0 mL CH_2Cl_2, and 474.4 mg (3.343 mmol; 411 µL) of BF_3·OEt_2, there was obtained 71.0 mg (0.379 mmol, 54%) of **18** after flash chromatography. R_f 0.40 (EtOAc : hexane = 53:47).
According to procedure B, starting from 737.9 mg (6.458 mmol) of allyltrimethylsilane (**9**), 1173.0 mg (6.458 mmol) of **7**, 20 mL CH_2Cl_2, and 10.76 mL (12.916 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 904.6 mg (4.831 mmol, 75%) of **18** after flash chromatography. IR (liq.cap.): 3500-3200, 3080, 2995-2850, 1790-1650, 995, 940. ^{1}H-NMR (250 MHz) : 5.72-5.55 (m, 1 H, H_2C=C<u>H</u>-), 5.29 (d, 1 H, *J* 6.5 Hz, N<u>H</u>), 5.11-5.04 (m, 2 H, <u>H</u>$_2$C=CH-), 4.38 (q, 1 H, *J* 6.5 Hz, C<u>H</u>-N), 3.69 (s, 3 H, C<u>H</u>$_3$OC(O)-C), 3.62 (s, 3 H, C<u>H</u>$_3$OC(O)-N), 2.47 (dt, 2H, *J* 6.8, 7.2 Hz, =CH-C<u>H</u>$_2$-). ^{13}C-NMR (50 MHz) : 172.2 (NH-<u>C</u>(O)-O), 156.3 (<u>C</u>(O)-O), 132.0 (H_2C=<u>C</u>H-), 119.1 (H_2<u>C</u>=CH-), 53.2 (<u>C</u>H-N), 52.2 (<u>C</u>H$_3$O, <u>C</u>H$_3$O), 36.6 (=CH-<u>C</u>H$_2$-). Mass spectrum : $M^{+\cdot}$ = 187.

Carbamate 19. According to procedure A, starting from 186.9 mg (0.933 mmol) of **10**, 150.3 mg (0.848 mmol) of **6**, 2 ml CH_2Cl_2, and 481.4 mg (3.392 mmol; 417.2 µl) of BF_3·OEt_2, there was obtained 153.0 mg (0.560 mmol, 66%) of **19** after flash chromatography, as a mixture of isomers (63 : 37). R_f 0.35 (EtOAc : hexane = 53:47).
According to procedure B, starting from 14.38 g (71.773 mmol) of **10**, 11.86 g (65.267 mmol) of **7**, 200 ml CH_2Cl_2, and 108.78 ml (130.534 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 13.11 g (47.961 mmol, 74%) of **19**, after flash chromatography, as a mixture of isomers (63 : 37). IR (liq. cap.): 3500-3200, 3080, 3000-2840, 1790-1650, 1230, 995, 950. ^{1}H-NMR (250 MHz): 5.57-5.40 (m, 1 H, H_2C=C<u>H</u>-), 5.32-5.24 (m, 1 H, NH), 5.13-5.00 (m, 2 H, <u>H</u>$_2$C=CH-), 4.42 (dd, 1 H, *J* 4.0, 9.0 Hz, C<u>H</u>-N, minor isomer), 4.31 (dd, 1 H, *J* 5.7, 8.5 Hz, C<u>H</u>-N, major isomer), 4.13-4.00 (m, 1 H, O-C<u>H</u>$_2$-CH_2-), 3.99-3.86 (m, 1 H, O-C<u>H</u>$_2$-CH_2-), 3.66 (s, 3 H, C<u>H</u>$_3$O-C(O)-C), 3.62 (s, 3 H, C<u>H</u>$_3$O-C(O)-N), 2.71-2.65 (m, 1 H, =CH-C<u>H</u>, minor isomer), 2.55-2.44 (m, 1 H, =C<u>H</u>-C<u>H</u>, major isomer), 1.97 (s, 3 H, C<u>H</u>$_3$-C(O)), 1.93-1.82 (m, 1 H, O-CH_2-C<u>H</u>$_2$-), 1.80-1.51 (m, 1 H,

O-CH_2-CH_2-). ^{13}C-NMR (50 MHz): 171.6 and 171.4 (CH_3O-C(O)-C), 170.8 (CH_3-C(O)-O), 156.8 and 156.3 (CH_3O-C(O)-N), 135.6 (major) and 135.0 (minor, H_2C=CH-), 119.1 (H_2C=CH-), 61.9 (O-CH_2-), 57.1 (minor) and 57.0 (major, CH-N), 52.2 and 52.0 (CH_3O, CH_3O), 44.2 (major) and 43.1 (minor, =CH-CH), 29.4 (O-CH_2-CH_2-), 20.7 (CH_3-C(O)-O). Exact mass 273.1216 (calcd. for $C_{12}H_{19}NO_6$ 273.1212).

Carbamate 20. According to procedure A, starting from 255.3 mg (1.191 mmol) of **11**, 175.8 mg (0.992 mmol) of **6**, 4 mL CH_2Cl_2, and 563.2 mg (3.968 mmol; 488.0 µL) of BF_3·OEt_2, there was obtained 97.7 mg (0.338 mmol, 34%) of **20**, after flash chromatography, as a mixture of isomers (62 : 38). R_f 0.42 (EtOAc : hexane = 42:58). IR (liq. cap.): 3500-3400, 3100-3000, 2955, 2850-2810, 1800-1650, 1600, 1500, 1000, 905. ^{1}H-NMR (200 MHz): 7.35-7.16 (m, 5 H, Ph), 6.50-6.07 (m, 2 H, Ph-CH=CH-), 5.99-5.93 (m, 1 H, H_2C=CH-, major isomer), 5.89-5.85 (m, 1 H, H_2C=CH-, minor isomer), 5.38-5.03 (m, 3 H, H_2C=CH-, NH), 4.72-4.66 (m, 1 H, CH-N), 3.83-3.52 (m, 7 H, CH_3O-C(O)-C, CH_3O-C(O)-N, =CH-CH-). ^{13}C-NMR (62 MHz): 171.6 (CH_3O-C(O)-C), 156.3 (CH_3O-C(O)-N), 138.9 (major) and 138.6 (minor, Ph), 136.2 (H_2C=CH-), 135.4-126.0 (Ph-CH=CH-), 117.9 (minor) and 117.3 (major, H_2C=CH-), 58.5 (minor) and 58.0 (major, CH-N), 52.5-51.0 (CH_3O, CH_3O, =CH-CH-CH=). Exact mass 289.1315 (Calcd. for $C_{16}H_{19}NO_4$ 289.1314).

Carbamate 21. According to procedure B, starting from 337.2 mg (2.628 mmol) of 2-methyl-3-trimethylsilylpropene (**12**) [22], 434.0 mg (2.389 mmol) of **7**, 5 mL CH_2Cl_2, and 3.98 mL (4.778 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 281.3 mg (1.398 mmol, 58%) of **21**, after flash chromatography. R_f 0.40 (EtOAc : hexane = 47:53). IR ($CHCl_3$): 3500-3200, 3080-3000, 2995-2840, 1790-1660. ^{1}H-NMR (200 MHz): 5.19 (d, 1 H, *J* 6.3 Hz, NH), 4.83 (s, 2 H, H_2C=), 4.43 (q, 1 H, *J* 6.6 Hz, CH-N), 3.71 (s, 3 H, CH_3OC(O)-C), 3.65 (s, 3 H, CH_3OC(O)-N), 2.43 (ddd, 2 H, *J* 5.5, 8.4, 13.9 Hz, =CH-CH_2-), 1.71 (s, 3 H, CH_3-C=). ^{13}C-NMR (50 MHz) : 172.8 (NH-C(O)-O), 156.4 (C(O)-O), 140.3 (H_2C=C), 114.5 (H_2C=CH-), 52.3 (CH-N), 52.1 (CH_3O, CH_3O), 40.6 (=C-CH_2-), 21.7 (CH_3-C=). Mass spectrum : $M^{+\cdot}$-CH_3-O-C(O) = 142.

Carbamate 22. According to procedure B, starting from 567.3 mg (2.937 mmol) of 2-bromo-3-trimethylsilylpropene (**13**), 485.0 mg (2.670 mmol) of **7**, 7 mL CH_2Cl_2, and 4.45 mL (5.340 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 360.0 mg (1.353 mmol, 51%) of **22**, after flash chromatography. R_f 0.40 (EtOAc : hexane = 55:45). IR ($CHCl_3$): 3500-3200, 3080-3005, 2900-2840, 1790-1660, 1075-1030. ^{1}H-NMR (250 MHz): 5.61 (d, 1 H, *J* 0.6 Hz, NH), 5.48 (s, 1 H, H_2C=), 5.47 (s, 1 H, H_2C=), 4.53 (q, 1 H, *J* 7.6 Hz, CH-N), 3.70 (s, 3 H, CH_3OC(O)-C), 3.62 (s, 3 H, CH_3OC(O)-N), 2.87 (ddd, 2 H, *J* 5.1, 7.4, 14.7 Hz, =CH-CH_2-). ^{13}C-NMR (62 MHz) : 171.4 (NH-C(O)-O), 156.2 (C(O)-O), 127.5 (H_2C=C), 120.6 (H_2C=CH-), 52.4 (CH-N), 52.3 (CH_3O, CH_3O), 43.4 (=C-CH_2-). Mass spectrum : $M^{+\cdot}$-CH_3-O-C(O) = 206, 208.

Carbamate 23. According to procedure B, starting from 570.9 mg (2.922 mmol) of **14**, [14,15] 530.7 mg (2.922 mmol) of **7**, 10 mL CH_2Cl_2, and 4.87 mL (5.844 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 780.9 mg (2.897 mmol, 99%) of **23**, after flash chromatography, as a mixture of isomers (59 : 41). R_f 0.38 (EtOAc : hexane = 1 : 2). IR (liq. cap.): 3500-3200, 3080, 3020, 3000-2850, 1790-1650, 1235, 995, 920. ^{1}H-NMR (250 MHz): 5.56-5.38 (m, 1 H, H_2C=CH-), 5.23-4.92 (m, 3 H, H_2C=CH-, NH), 4.57 (dd, 1 H, *J* 4.4, 9.4 Hz, CH-N, minor isomer), 4.49 (dd, 1 H, *J* 6.6, 8.8 Hz, CH-N, major isomer), 3.66 (s, 3 H, CH_3O-C(O)-C), 3.63 (s, 3 H, CH_3O-C(O)-N), 2.30-2.21 (m, 1 H, =CH-CH, minor isomer), 2.07-1.98 (m, 1 H, =CH-CH, major isomer), 1.83-1.52 (m, 5 H, -CH_2-CH-CH_2-), 1.45-0.92 (m, 6H, -CH_2-CH_2-CH_2-). ^{13}C-NMR (62 MHz): 171.9 (CH_3O-C(O)-C), 156.5 (CH_3O-C(O)-N), 135.5 (major) and 135.4 (minor, H_2C=CH-), 118.9 (H_2C=CH-), 54.2 (minor) and 54.1 (major, CH-N), 52.3, 52.0, 51.7 (CH_3O, CH_3O, =CH-CH-), 37.4 and 37.3 (-CH_2-CH-CH_2-), 31.3, 30.8, 30.6, and 30.0 (-CH_2-CH-CH_2-), 26.4, 26.3, 26.2 and 26.1 (-CH_2-CH_2-CH_2-). Exact mass 269.1627 (Calcd. for $C_{14}H_{23}NO_4$ 269.1627).

Carbamate 24. According to procedure B, starting from 170.1 mg (0.812 mmol) of **15**, 134.0 mg (0.738 mmol) of **7**, 4 mL CH_2Cl_2, and 1.23 mL (1.475 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 142.0 mg (0.501 mmol, 68%) of **24**, after flash chromatography, as a mixture of isomers (50 : 50). R_f 0.38 (EtOAc : hexane = 1: 2). IR (liq. cap.): 3500-3380, 3080, 3030, 3005, 2980-2820, 1780-1680, 1230, 790. ^{1}H-NMR (200 MHz): 5.27 (d, 1 H, *J* 8.1 Hz, NH, single isomer), 5.09 (d, 1 H, *J* 9.4 Hz, NH, single isomer),

4.87 (s, 2 H, H_2C=, single isomer), 4.68 (s, 2 H, H_2C=, single isomer), 4.64-4.51 (m, 1 H, C*H*-N), 3.65 (s, 3 H, CH_3O-C(O)-C), 3.63 (s, 3 H, CH_3O-C(O)-N), 2.29 (dd, 1 H, *J* 4.7, 10.1 Hz, =C-C*H*-, single isomer), 2.17 (dd, 1 H, *J* 5.5, 9.7 Hz, =C-C*H*-, single isomer), 2.01-1.85 (m, 1 H, -CH_2-C*H*-CH_2-), 1.75-0.75 (m, 10 H, cyclohexane, =C-CH_3). ^{13}C-NMR (50 MHz): 173.0 and 172.2 (CH_3O-C(O)-C), 156.2 (CH_3O-C(O)-N), 143.0 and 142.9 (H_2C=C), 115.9 and 114.7 (H_2C=C), 56.4 (CH-N), 53.8 (=C-CH), 51.8 (CH_3O-C(O)-N, CH_3O-C(O)-N), 36.6 and 36.2 (-CH_2-CH-CH_2-), 31.2, 31.0, 30.9 and 30.6 (-CH_2-CH-CH_2-), 26.3-25.8 (-CH_2-CH_2-CH_2-), 22.5 and 20.0 (=C-CH_3). Exact mass 283.1772 (Calcd. for $C_{15}H_{25}NO_4$ 283.1784).

Carbamate 25. According to procedure B, starting from 278.9 mg (1.465 mmol) of **16**, [14] 241.9 mg (1.332 mmol) of **7**, 3 mL CH_2Cl_2, and 2.22 mL (2.663 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 257.5 mg (0.978 mmol, 73%) of **25**, after flash chromatography, as a mixture of isomers (56 : 44). R_f 0.40 (EtOAc : hexane = 40:60). IR($CHCl_3$): 3500-3380, 3080, 3060-3000, 2980-2930, 2850, 1800-1650, 1600, 1510, 990, 925. ^{1}H-NMR (250 MHz): 7.34-7.14 (m, 5 H, Ph), 6.13-5.99 (m, 1 H, H_2C=CH-), 5.28-4.82 (m, 3 H, H_2C=CH-, NH), 4.72 (t, 1 H, *J* 8.8 Hz, CH-N, major isomer), 4.63 (t, 1 H, *J* 8.0 Hz, CH-N, minor isomer) , 3.83-3.53 (m, 7 H, CH_3O-C(O)-C, CH_3O-C(O)-N, =CH-CH). ^{13}C-NMR (50 MHz): 171.7 (CH_3O-C(O)-C), 156.4 (CH_3O-C(O)-N), 138.9 and 138.5 (Ph), 136.2 and 136.0 (H_2C=CH-), 128.7-126.7 (Ph), 117.6 (H_2C=CH-), 58.2 and 57.7 (CH-N), 52.7, 52.6, 52.3, 52.0, 51.9 (CH_3O, CH_3O, =CH-CH). Exact mass 263.1171 (Calcd. for $C_{14}H_{17}NO_4$ 263.1158).

Carbamate 26. According to procedure B, starting from 337.8 mg (1.702 mmol) of **17**, [14,15] 281.0 mg (1.548 mmol) of **7**, 6.0 mL CH_2Cl_2, and 2.83 mL (3.404 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 353.7 mg (1.303 mmol, 84 %) of **26**, after flash chromatography, as a mixture of isomers (55 : 45). R_f 0.42 (EtOAc : hexane = 45:55). IR ($CHCl_3$): 3600-3300, 3070, 3020, 3005, 2980-2820, 1780-1670, 1230. ^{1}H-NMR (200 MHz): 5.60-5.38 (m, 1 H, H_2C=CH-), 5.30-4.99 (m, 3 H, H_2C=CH-, NH), 4.42-4.26 (m, 1 H, CH-N), 3.68 (s, 3 H, CH_3O-C(O)-C), 3.64 (s, 3 H, CH_3O-C(O)-N), 2.62-2.44 (m, 1 H, =CH-CH, minor isomer), 2.41-2.23 (m, 1 H, =CH-CH, major isomer), 1.50-1.07 (m, 10 H, -$(CH_2)_5$-), 0.83 (t, 3 H, *J* 6 Hz, CH_3-CH_2-). ^{13}C-NMR (50 MHz): 172.1 and 171.8 (CH_3O-C(O)-C), 156.8 and 156.3 (CH_3O-C(O)-N), 137.1 and 136.6 (H_2C=CH-), 118.0 (H_2C=CH-), 57.2 (CH-N), 52.2, 52.0 and 51.8 (CH_3O), 47.4 and 46.1 (=CH-CH-), 31.6, 30.4, 29.0, 26.9, 22.5 (-$(CH_2)_5$-), 13.9 (CH_3-CH_2-). Exact mass 271.1768 (Calcd. for $C_{14}H_{25}NO_4$ 271.1784).

2-Methoxy-4-methoxycarbonyl-6-trimethylsilylmethyl-4*H*-1,3-oxazine (28). According to procedure B, starting from 148.3 mg (1.321 mmol) of 2-propynyltrimethylsilane (**27**), 160.0 mg (0.881 mmol) of **7**, 3 mL CH_2Cl_2, and 1.47 mL (1.762 mmol; 1.2 M solution in CH_2Cl_2) of $SnCl_4$, there was obtained 117.0 mg (0.455 mmol, 52%) of **28**, after flash chromatography. R_f 0.38 (EtOAc : hexane = 37:63). IR ($CHCl_3$): 3010, 2995-2850, 1730, 1660, 1245, 850. ^{1}H-NMR (200 MHz): 4.65-4.58 (m, 2 H, =CH-, N-CH), 3.74 (s, 3 H, CH_3O), 3.67 (s, 3 H, CH_3O), 1.51 (s, 2 H, -CH_2-Si$(CH_3)_3$), 0.00 (s, 9 H, Si$(CH_3)_3$). ^{13}C-NMR (50 MHz): 172.1 (CH_3O-C(O)-C), 152.3 (N=C), 151.2 (-CH=C(H)(O)(CH_2-Si$(CH_3)_3$), 92.6 (-CH=C(H)(O)(CH_2-Si$(CH_3)_3$), 56.3, 54.8, 52.1 (CH_3O, CH_3O, N-C), 22.6 (-CH_2-Si$(CH_3)_3$), -1.8 (Si$(CH_3)_3$). Mass spectrum : $M^{+\cdot}$ = 257.

Allylglycine (29). To a solution of 4.062 g (21.70 mmol) of **18** in 50.0 mL of CCl_4, was added at room temperature under an atmosphere of dry nitrogen, 8.684 g (43.40 mmol, 6.18 mL) of iodotrimethylsilane. After being stirred for 2 h at 50-55 °C, the reaction mixture was poured out into 5% aq $NaHSO_4$ and washed with CH_2Cl_2 (3x30 mL). The water layer was made basic with K_2CO_3 and extracted with CH_2Cl_2 (4x50 mL). The combined organic fractions containing the free amine were dried (K_2CO_3) and concentrated *in vacuo*, to yield 1.820 g (14.091 mmol, 65%) of allylglycine methyl ester as a colourless oil. IR ($CHCl_3$): 3600-3200, 3080, 3020, 3000-2840, 1730. ^{1}H-NMR (60 MHz): 6.1-5.4 (m, 1 H, H_2C=CH-), 5.2-4.9 (m, 2 H, H_2C=CH-), 3.6 (s, 3 H, CH_3O-), 3.4 (d, 1 H, *J* 7 Hz, CH-N), 2.3 (t, 2 H, *J* 7 Hz, =CH-CH_2-), 1.6 (s, 2 H, NH_2).

A solution of 515.0 mg (3.988 mmol) of allylglycine methyl ester in 10.0 mL 6N HCl (aq) was stirred at 30-40 °C for 18 h. The mixture was evaporated *in vacuo*, dissolved in distilled water (5.0 mL) and applied to a 1 cm x 20 cm Amberlite CG-120 (H^+) ion exchange column. The column was eluted with distilled water until the eluent tested negative for chloride ion using 5% ethanolic $AgNO_3$. The column was then eluted with a 5% ammonium hydroxide solution in distilled water, until the eluent tested negative with ninhydrin. The fractions showing a positive test with ninhydrin were degassed and freeze-dried to give 376.8 mg (3.273 mmol, 82%) of allylglycine as a white solid; mp

243-245 °C dec (lit : 243-244 °C [23] : 245-250 °C [24]). IR (KBr): 3500-3000, 2500, 2100, 1650, 1580, 1525, 1410. ^{1}H-NMR (200 MHz, D_2O): 5.90-5.69 (m, 1 H, H_2C=C<u>H</u>-), 5.34-5.25 (m, 2 H, <u>H_2</u>C=CH-), 3.82 (dd, 1 H, *J* 5.2, 6.8 Hz, C<u>H</u>-N), 2.74-2.53 (m, 2 H, =CH-<u>CH_2</u>-).

2-Amino-3-vinylnonanoic acid (30). According to the procedure for allylglycine (**29**), starting from 233.2 mg (0.859 mmol) of **26**, 4.0 mL of CCl_4, and 367.9 mg (1.719 mmol, 255 µl) of iodotrimethylsilane, there was obtained 132.5 mg (0.583 mmol, 68%) of the methyl ester of **30** as a colourless oil, as a mixture of isomers (46 : 54). IR ($CHCl_3$): 3500-3200, 3080, 3020 , 3000-2800, 1730. ^{1}H-NMR (200 MHz): 5.67-5.48 (m, 1 H, H_2C=C<u>H</u>-), 5.14-4.98 (m, 2 H, <u>H_2</u>C=CH-), 3.70 and 3.68 (s, 3 H, <u>CH_3</u>O-, both isomers), 3.42 (d, 1 H, *J* 4.9 Hz, C<u>H</u>-N), 2.45-2.20 (m, 1 H, =CH-<u>CH_2</u>-), 1.50-1.20 (m, 12 H, -(<u>CH_2</u>)$_5$-, <u>NH_2</u>), 0.85 (t, 3 H, *J* 5.7 Hz, <u>CH_3</u>-CH_2-). ^{13}C-NMR (50 MHz): 175.3 (CH_3O-<u>C</u>(O)-C), 138.2 and 137.7 (H_2C=<u>C</u>H-), 117.5 and 117.1 (H_2<u>C</u>=CH-), 58.2 and 57.9 (<u>C</u>H-N), 51.6 and 51.4 (<u>CH_3</u>O-C(O)-O), 48.6 and 47.8 (=CH-<u>C</u>H), 31.6, 31.5, 30.9, 29.9, 29.0, 27.0, 22.4 (-(<u>CH_2</u>)$_5$-), 13.8 (<u>CH_3</u>-CH_2-).

A solution of 125.9 mg (0.554 mmol) of the methyl ester of **30** in 5.0 mL 6N HCl (aq) was refluxed for 18 h. The reaction mixture was evaporated *in vacuo*, dissolved in distilled water (2.0 mL) and applied to a 1 cm x 20 cm Amberlite CG-120 (H^+) ion exchange column. Following the same isolation procedure as for allylglycine (**29**), there was obtained 88.4 mg (0.414 mmol, 75%) of **30** as a white solid; mp 154-158 °C, as a mixture of isomers (49 : 51). IR (KBr): 3300-3000 , 2950, 2930, 2850, 2490, 1590, 1515, 1405. ^{1}H-NMR (200 MHz, D_2O-NaOD): 5.65-5.44 (m, 1 H, H_2C=C<u>H</u>-), 5.08-4.79 (m, 4 H, <u>H_2</u>C=CH-, <u>NH_2</u>), 3.08 (d, 1 H, *J* 5.5 Hz, C<u>H</u>-N), 2.30-2.06 (m, 1 H, =CH-C<u>H</u>-), 1.45-1.07 (m, 10 H, -(<u>CH_2</u>)$_5$-), 0.78 (t, 3 H, *J* 6.2 Hz, <u>CH_3</u>-CH_2-). ^{13}C-NMR (50 MHz, D_2O-NaOD): 183.4 and 183.1 (HO-<u>C</u>(O)-C), 141.4 and 140.3 (H_2C=<u>C</u>H-), 119.3 and 118.4 (H_2<u>C</u>=CH-), 62.5 and 62.0 (<u>C</u>H-N), 51.2 and 50.4 (=CH-<u>C</u>H), 33.6, 33.5, 32.9, 31.7, 30.9, 29.1, 24.3 (-(<u>CH_2</u>)$_5$-), 15.6 (<u>CH_3</u>-CH_2-).

ACKNOWLEDGEMENTS

We thank Mr. C. Kruk and his staff for their help in obtaining en interpreting the NMR spectra.

REFERENCES AND NOTES

1. (a) Barrett, G.C., Ed.; *Chemistry and Biochemistry of the Amino Acids* ; Chapman and Hall: London, 1985. (b) O'Donnell, M.J., Ed.; *α-Amino Acid Synthesis; Tetrahedron Symposia-in-Print number 33* ; Pergamon: Oxford, 1988, p. 5253.
2. See e.g. (a) Schöllkopf, U. *Tetrahedron* **1983**, *39*, 2085. (b) Evans, D.A.; Weber, A.E. *J.Am.Chem.Soc.* **1986**, *108*, 6757. (c) Schmidt, U.; Siegel, W. *Tetrahedron Lett.* **1987**, *28*, 2849. (d) Duhamel, P.; Eddine, J.J.; Valnot, J.-Y. *Tetrahedron Lett.* **1987**, *28*, 3801. (e) Williams, R.M.; Im, M.-N. *Tetrahedron Lett.* **1988**, *29*, 6075. (f) Dellaria, Jr.,J.F.; Santarsiero, B.D. *Tetrahedron Lett.* **1988**, *29*, 6079.
3. (a) Ben-Ishai, D.; Sataty, I.; Bernstein, Z. *Tetrahedron* **1976**, *32*, 1571. (b) Ben-Ishai, D.; Moshenberg, R.; Altman, J. *Tetrahedron* **1977**, *33*, 1533. (c) Ben-Ishai D.; Altman J.; Peled, N. *Tetrahedron*, **1977**, *33*, 2715. (d) Ben-Ishai, D.; Altman, J.; Bernstein, Z.; Peled, N. *Tetrahedron* **1978**, *34*, 467.
4. Reviews : (a) Zaugg, H.E. *Synthesis* **1985**, 85. (b) Zaugg, H.E. *Synthesis* **1985**, 181.
5. (a) Harding, K.E.; Davis, C.S. *Tetrahedron Lett.* **1988**, *29*, 1891. (b) Kober, R.; Papadopoulos, K.; Miltz, W.; Enders, D.; Steglich, W.; Reuter, H.; Puff, H. *Tetrahedron* **1985**, *41*, 1693. (c) Allmendinger, T.; Rihs, G.; Wetter, H. *Helv.Chim.Acta* **1988**, *71*, 395. (d) Williams, R.M.; Sinclair, P.J.; Zhai, D.; Chen, D. *J.Am.Chem.Soc.* **1988**, *110*, 1547. (e) Ermert, P.; Meyer, I.; Stucki, C.; Schneebeli, J.; Obrecht, J.P.

Tetrahedron Lett. **1988**, *29*, 1265. (f) Yamamoto, Y.; Nishii, S.; Maruyama, K.; Komatsu, T.; Ito, W. *J.Am.Chem.Soc.* **1986**, *108*, 7778.

6. (a) Easton, C.J.; Scharfbillig, I.M.; Tan, E.W. *Tetrahedron Lett.* **1988**, *29*, 1565. (b) Baldwin, J.E.; Adlington, R.M.; Lowe, C.; O'Neil, I.A.; Sanders, G.L.; Schofield, C.J.; Sweeney, J.B. *J.Chem.Soc.,Chem. Commun.* **1988**, 1030.
7. (a) Schöllkopf, U.; Hauptreif, M.; Dippel, J.; Nieger, M.; Egert, E. *Angew.Chem.,Int.Ed. Engl.* **1986**, *25*, 192. (b) Schöllkopf, U.; Hupfeld, B.; Küper, S.; Egert, E.; Dysbusch, M. *Angew.Chem.,Int.Ed.Engl.* **1988**, *27*, 432.
8. Hiemstra, H.; Fortgens H.P.; Speckamp, W.N. *Tetrahedron Lett.* **1985**, *26*, 3155.
9. Mooiweer, H.H.; Hiemstra, H.; Fortgens, H.P.; Speckamp, W.N. *Tetrahedron Lett.* **1987**, *28*, 3285.
10. (a) Zoller, U.; Ben-Ishai, D. *Tetrahedron* **1975**, *31*, 863. (b) Bernstein, Z.; Ben-Ishai, D. *Tetrahedron* **1977**, *33*, 881.
11. (a) Colvin, E.W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W.P. *Silicon Reagents for Organic Synthesis*, Springer-Verlag: Berlin, 1983.
12. Angst, C. *Pure.Appl.Chem.* **1987**, *59*, 373.
13. Castelhano, A.L.; Horne, S.; Taylor, G.J.; Billedeau, R.; Krantz, A. *Tetrahedron* **1988**, *44*, 5451.
14. Seyferth, D.; Wursthorn, K.R.; Lim, T.F.O.; Sepelak, D.J. *J.Organomet.Chem.* **1979**, *181*, 293.
15. Fleming, I.; Paterson, I. *Synthesis* **1979**, 446.
16. For related reactions of dienylmethylsilanes see: (a) Seyferth, D.; Pornet, J.; Wernstein, R.M. *Organometallics* **1982**, *1*, 1651. (b) Jones, M.; Kitching, W. *Austr. J. Chem.* **1984**, *37*, 1863. (c) Fleming, I.; Kindon, N.D.; Sarkar, A.K. *Tetrahedron Lett.* **1987**, *28*, 5921.
17. Hiemstra, H.; Fortgens, H.P.; Speckamp, W.N. *Tetrahedron Lett.* **1984**, *25*, 3115.
18. Castelhano, A.L.; Pliura, D.H.; Taylor, G.J.; Hsieh, K.C.; Krantz, A. *J.Am.Chem.Soc.* **1984**, *106*, 2734.
19. For analogy see: Esch, P.M.; Hiemstra, H.; Speckamp, W.N. *Tetrahedron Lett.* **1988**, *29*, 367.
20. Jung, M.E.; Lyster, M.A. *J.Chem.Soc.,Chem.Commun.* **1978**, 315.
21. Hiemstra, H.; Sno, M.A.H.M.; Vijn, R.J.; Speckamp, W.N. *J. Org. Chem.* **1985**, *50*, 4014.
22. Carr, S.A.; Weber, W.P. *J. Org. Chem.* **1985**, *50*, 2782.
23. O'Donnell, M.J.; Bennett, W.D. *Tetrahedron* **1988**, *44*, 5389.
24. Drinkwater, D.J.; Smith, P.W.G. *J.Chem.Soc. (C)* **1971**, 1305.