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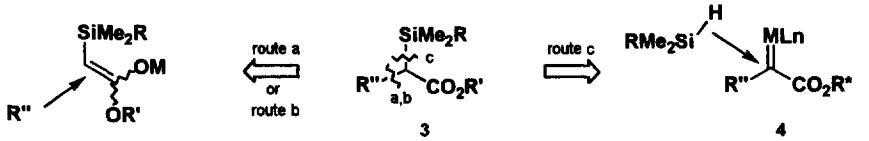
Preparation of Optically Active α-Silylcarbonyl Compounds using Asymmetric Alkylation of α-Silylacetic Esters and Asymmetric Metal-Carbene Insertion into the Si-H Bond.

Yannick Landais,* Denis Planchenault

Institut de Chimie Organique, Université de Lausanne
Collège Propédeutique, 1015 Lausanne-Dorigny, Switzerland
Fax: (41) 021 692 40 05. Email : ylandais@ulys.unil.ch

Abstract : Substituted α-silylacetic esters have been prepared in good yields and with reasonable diastereoselectivities by three different routes. The first two involved alkylation of the parent α-silylacetic ester enolates, with the chiral auxiliaries being present either on silicon or on the ester function. The third route involving asymmetric insertion of metal-carbenoids into the Si-H bond was found to afford better diastereoselectivities, using pantolactone as chiral auxiliary. © 1997 Elsevier Science Ltd. All rights reserved.

We recently reported on the preparation of α-silylacetic esters such as **3** and their subsequent transformations into 1,2-diols and polysubstituted tetrahydrofurans.[1] Further extension of this work logically implicated the development of a stereoselective access to these substrates.[2] Three different routes were envisioned as illustrated in Scheme 1. The first two methods involve diastereoselective alkylations of prochiral α-silylacetic esters **1** and **2** and the third implicates a diastereoselective insertion of metal-carbenoid **4** into the Si-H bond. In the first approach (*route a*), the R" substituent is introduced through an asymmetric alkylation with the chiral auxiliary supported by the silicon centre (R). In *route b*, the R" group is introduced similarly but control of the stereoselectivity is ensured by a chiral auxiliary attached to the ester function (R'). Finally, in *route c*, the C-Si bond is formed in the last stage of the sequence through an asymmetric insertion of a metal-carbenoid species into the Si-H bond with the chiral vector attached to the ester function.[1e] The metal-carbenoid intermediate is itself generated from the corresponding α-diazoester. We report here a full account of our results in this area and demonstrate that *route c* generally leads to higher diastereoselectivities than the corresponding alkylations.



Route a **: R chiral auxiliary, 1**
Route b **: R' chiral auxiliary, 2**

Scheme 1

In *route a*, we reasoned that a chiral auxiliary attached to the silicon centre would control efficiently the diastereofacial selectivity through a chelation of the metal (Li^+, Na^+,...) by its co-ordinating moiety. The preformed tightly bound metal-complex would then hinder one face of the π-system ensuring a selective attack of the alkylating agent from the opposite face (Fig.-1). Different chiral amino-ethers likely to co-ordinate the lithium enolate were thus attached to the silicon centre, using our two steps-one pot procedure[1b,c] starting from ethyl diazoacetate (EDA) and HMe_2SiCl (Scheme 2). Rhodium-carbenoid insertion into the Si-H bond of HMe_2SiCl followed by nucleophilic displacement of chloride with suitable amino-alcohols thus afforded **5a-c** in

good yield. Alkylation of the enolate of **5a** with MeI gave the expected α-silylpropionic ester **6a** in 80% yield but with no diastereoselectivity at all !. Similarly, the alkylation of **5b-c** gave the desired product in good yield but with 0% d.e. The exact reasons for these failures are not obvious to us but we assume that the co-ordination illustrated in Fig.-1 requires an enolate of Z-configuration, and the conditions we employed presumably would not lead to such enolate geometry.[3] Our attempts to determine the geometry of the enolate through its silyl ketene acetal unfortunately failed. The addition of HMPA to change the geometry of the enolate also failed leading to extensive decomposition of **5a**.

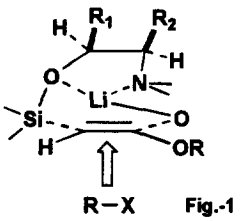
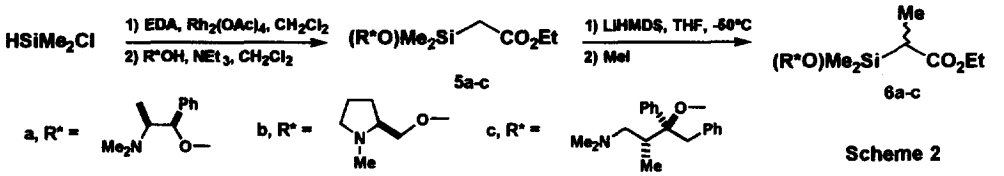
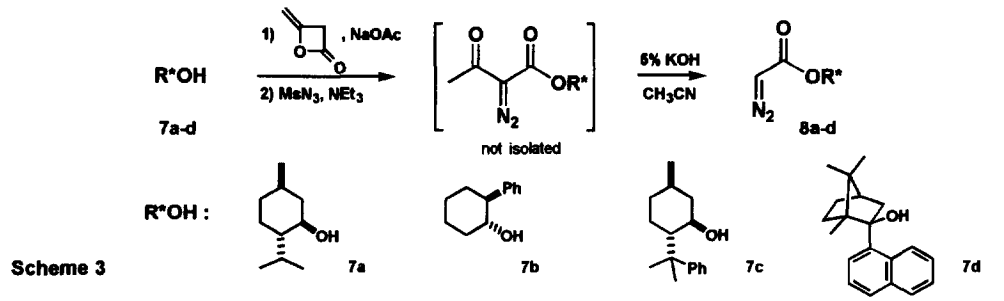


Fig.-1



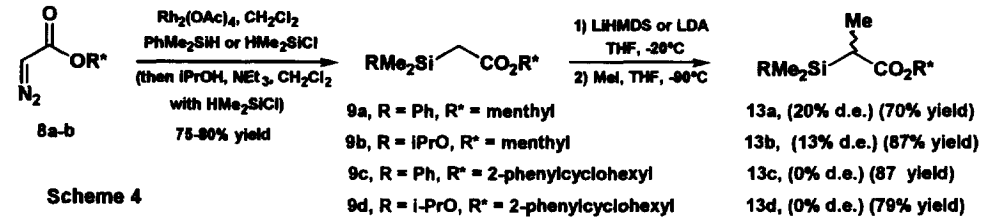
Scheme 2

These disappointing results led us to turn our attention to the alternative diastereoselective *route b*. The α-silylester precursors were prepared from compounds **8a-d** synthesized using a 3-step protocol as depicted in scheme 3.[1e,4] Reaction of diketene with chiral alcohols **7a-d**[5] afforded the acetoacetate which was then submitted to diazo-transfer conditions[4,6] (MsN_3, base) producing an α-aceto-α-diazoester intermediate which was directly deacetylated with KOH, affording **8a-d**[4] as stable oils in 40-70% overall yield.



Scheme 3

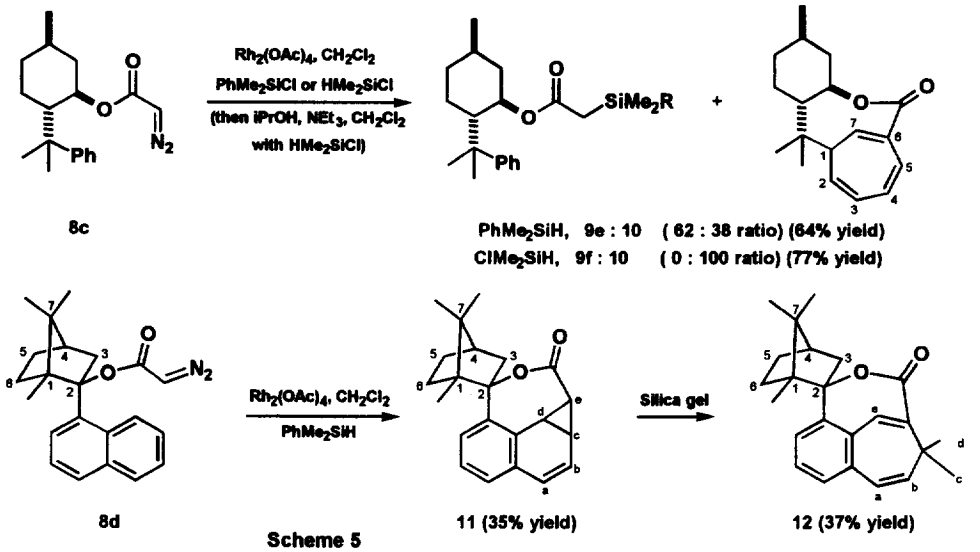
The insertion was then carried out by slowly adding the solution of α-diazoesters in CH_2Cl_2 to a suspension of $Rh_2(OAc)_4$ and silane in CH_2Cl_2. With HMe_2SiCl, the chlorine was then displaced by isopropanol in the presence of NEt_3.[1b,c] The insertion of rhodium-carbenoids generated from **8a** and **8b** gave, as expected, the corresponding esters **9a-d** in good yields (Scheme 4).



Scheme 4

However, with the analogues **8c-d**, cyclopropanation of the chiral auxiliary's aromatic ring was found to compete to a large extent giving after ring rearrangement, the corresponding 7-membered ring (Scheme 5).[7] α-Diazoester **8c** gave, in the presence of $PhMe_2SiH$, the α-silylester **9e** along with the cycloheptatriene **10**. In

contrast with **8c**, diazoester **8d** afforded only the cyclopropanation product **11** which could be isolated before its rearrangement into **12** during flash chromatography through silica gel.

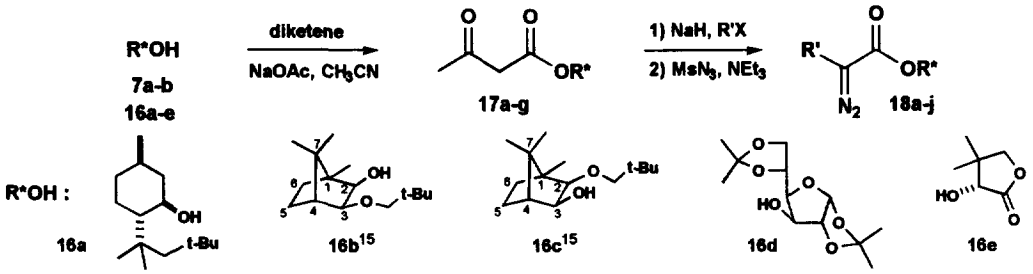


Scheme 5

The difference in reactivity between **8c-d** and their analogue **8b** may be attributed to the proximity of the phenyl ring to the metallo-carbenoid species during the process. Alignment of both reactive moieties in **8c** and **8d** is likely to be at the origin of the competitive cyclopropanation of the aromatic ring. On the other hand, in **8b**, the phenyl ring is relatively far away from the carbenoid centre, and hence the intermolecular insertion process is favoured. Interestingly, replacement of the phenyl ring in **8c** with an isobutyl substituent eventually allowed us to perform the Si-H insertion reaction in reasonable yield (*vide supra*).

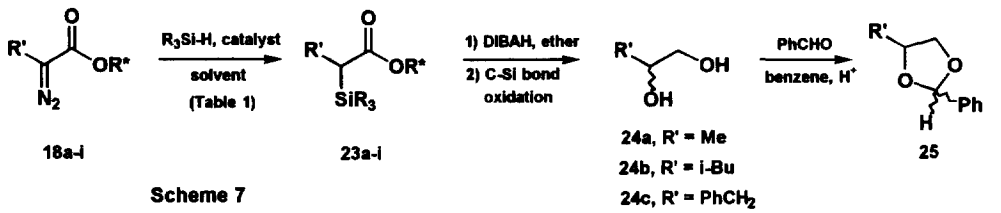
Alkylation of **9a-d** in the same conditions as the above (Scheme 4) led to the expected products **13a-d** in good yields but again with disappointing diastereoselectivities (10-20% d.e.). In all cases, the major ester possessed the S configuration (for the determination of absolute configuration, see below). Similar results have been described in the past by Paquette et al.[2h] on similar menthyl substrates. More surprising were the diastereoselectivities attained with Whitesell's chiral auxiliary (*i.e.* **7b**) if one makes a comparison with the high level of selectivity generally reported in the literature.[8] Similarly, ester **9d** afforded no diastereoselectivity at all.[9]

The disappointing results described previously prompted us to employ the alternative *route c* which involves the formation of the carbon-silicon bond in a latter stage of the sequence. This approach was initiated in the early 70's by Kagan *et al.*[12] as an efficient route for the preparation of amino acids through insertion of a copper-carbenoid into the N-H bond of an amine. More recently, we and others have extended this process to the insertion into Si-H and O-H bonds.[1,13] This strategy relies on the assumption that the approach of a sterically hindered silicon group should experience larger steric interactions with the chiral auxiliaries than the alkyl group in the diastereoselective alkylation described previously, which could lead to increased diastereofacial selectivity. The diazo precursors were prepared as above with the R' group introduced through alkylation of the α-acetoacetates **17a-g** prior to the diazo-transfer process.[4,6,14] Deacetylation occurs during the diazo-transfer leading to the α-diazoesters **18a-j** in 50-70% overall yield. As outlined in scheme 6, various types of chiral auxiliaries are easily introduced using this methodology.[15] As the 8-phenylmenthyl derivative (*i.e.* **8c**) underwent predominantly cyclopropanation of its phenyl ring, we devised an analogue having a t-BuCH_2 group instead of the phenyl ring. **16a** was thus prepared in two steps from pulegone **19** following Corey's protocol (see experimental part).[16] Independently, the α-diazobenzylester of pantolactone (*i.e.* R' = Ph, **22**) was directly prepared from the corresponding ester **21** (itself prepared through condensation of phenylacetic acid and **16e**) through the diazo-transfer process (see experimental part).[13a,17]



Scheme 6

With α-diazoesters **18a-i** in hand, we then investigated the asymmetric insertion on varying parameters such as the nature of the silane, the catalyst and the solvent (Scheme 7, Table 1). The diastereoselectivities are generally modest but are in any case far superior to those observed during the alkylation following *route b*. Best results were obtained using $Rh_2(OAc)_4$ as catalyst (compare entry 1-4). $Cu(acac)_2$ was found to be less efficient both in terms of yield and diastereoselectivity.[1a,e] Increasing the reactivity of the catalyst using instead $Cu(OTf)_2$ proved unsuccessful. However, the association of $Cu(OTf)_2$ with sparteine as a ligand led to yields approaching those obtained with $Rh_2(OAc)_4$.[1c] The low selectivity observed in this case was attributed to mismatching of the two chiral auxiliaries (sparteine and menthol). As sparteine occurs naturally as only one enantiomer, we decided to repeat the reaction using (+)-menthyl **18a** and clearly observed an improvement of the stereoselectivity along with the expected reversal of the diastereoselectivity (32:68, 62% yield). The nature of the silane was next investigated (entry 5-7) and was found to have little effect on the diastereoselectivity. Surprisingly, the sterically hindered Ph_3Si group led to little or no selectivity. Similarly, changing the polarity of the solvent little affected the diastereoselectivity, with benzene giving lower yields (entry 8-9). This is in good agreement with a more or less concerted mechanism with little charge development in the transition state.[18] The small difference in diastereoselectivity observed on changing the substitution at the silicon centre might be connected with the occurence of an early transition state in which both reactants are far away from each other, the steric interactions hence being relatively weak.[19] This is further corroborated by the similar diastereoselectivities obtained by changing the size of the R' group on α-diazoesters (entry 10-12). Similarly, changing the nature of the chiral auxiliary had no effect on the diastereoselectivity with the best results being obtained using menthol (entry 13-18). This is also in good agreement with what is suggested above. It is noteworthy that the lower yield obtained with precursor **18c** is due to a competitive β-hydride elimination leading to the undesired menthyl cinnamate.[1e,20] Intriguing observations have been made with camphor auxiliaries **18g** and **18h**. In contrast with the observations of Oppolzer[15] made during Diels-Alder reactions using these chiral auxiliaries, **18g** and **18h** reacted with the same topicity (entry 16-17). A better diastereoselectivity is however obtained with **18g**, indicating, as proposed by Oppolzer, that the angular methyl group in C-1 (Scheme 6) prevents any rotation of the diazoester moiety thus leading to an amplification of the diastereofacial selectivity.



Scheme 7

The absolute configurations of the newly created chiral centres in **13a-b** and **23a-i** were determined through the following two-step sequence : reduction of the ester function and recovery of the chiral auxiliary then oxidation of the C-Si bond with retention of configuration[21] to produce the desired diols **24a-c** in good overall yield (40-60%, 2 steps)(Scheme 7). The value and the sign of the optical rotation of the diols were compared with those described in the literature.[22] It must be emphasized that the reduction of the ester function takes place with no

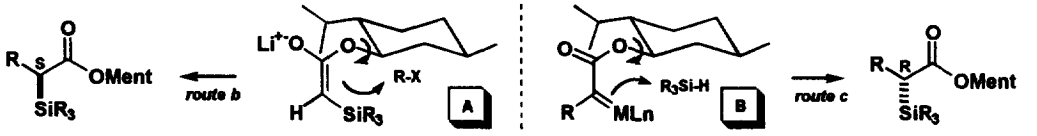
epimerization since the enantiomeric excesses of the diols, measured from ^1H NMR and $Eu(hfc)_3$ of the corresponding acetals **25**,[23] were identical with the diastereoisomeric excesses summarized in Table 1.

Table 1. Metal-catalyzed decomposition of chiral α-diazoesters **18a-i** in the presence of silanes (Scheme 7).

Entry	α-diazoester	Silane[a]	Catalyst[b]	Solvent	α-Silylester	Yield (%)[c]	Ratio[d]	config[e] diol
1	**18a**	$PhMe_2SiH$	$Rh_2(OAc)_4$	CH_2Cl_2	**13a**	70	72 :28	R
2	**18a**	"	$Cu(acac)_2$	"	**13a**	50	66 : 34	R
3	**18a**	"	$Cu(OTf)_2$	"	**13a**	33	56 : 44	R
4	**18a**	"	$Cu(OTf)_2$-sparteine	"	**13a**	68	55 : 45	R
5	**18a**	$ClMe_2SiH$	$Rh_2(OAc)_4$	"	**13b**	74	67 : 33	R
6	**18a**	Et_3SiH	"		**23a**	72	72 : 28	-
7	**18a**	Ph_3SiH	"	"	**23b**	66	53 : 47	-
8	**18a**	$PhMe_2SiH$	$Rh_2(OAc)_4$	benzene	**13a**	48	67 : 33	R
9	**18a**	"	"	pentane	**13a**	66	65 : 35	R
10	**18b**	$PhMe_2SiH$	$Rh_2(OAc)_4$	CH_2Cl_2	**23c**	75	70 : 30	R
11	**18c**	"	"	"	**23d**	52	61 : 39	R
12	**18d**	"	"	"	**23e**	70	66 : 34	-
13	**18e**	$PhMe_2SiH$	$Rh_2(OAc)_4$	CH_2Cl_2	**13c**	56	42 : 58	S
14	**18e**	$ClMe_2SiH$	"	"	**13d**	70	42 : 58	S
15	**18f**	$PhMe_2SiH$	$Rh_2(OAc)_4$	"	**23f**	32	68 : 32	-
16	**18g**	"	"	"	**23g**	73	69 : 31	-
17	**18h**	"	"	"	**23h**	74	59 : 41	-
18	**18i**	"	"	"	**23i**	66	50 : 50	-

[a] 2 equivalents. [b] Anhydrous $Rh_2(OAc)_4$ (0.5 mol%); $Cu(acac)_2$ (10 mol%); $Cu(OTf)_2$ (10 mol%); sparteine (10 mol%). [c] Isolated yield. [d] Estimated from the ^1H NMR of the crude reaction mixture. [e] Obtained by comparison with literature data. [22]

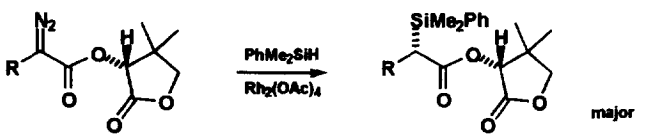
We observed that the configuration of α-silylesters **13a-b** obtained from alkylation of **9a-b** (Scheme 4) and the configuration of the same esters obtained through asymmetric insertion into the Si-H bond were opposite. This indicates that similar factors govern the stereocontrol in alkylation and asymmetric insertion since the order of introduction of the substituents at the newly created chiral centre is opposite in the two processes. Steric effects are likely to be involved in these reactions with the isopropyl substituent of the menthol shielding one face of the enolate (alkylation) or one face of the metal-carbenoid species (insertion). As depicted in Scheme 8, we assumed, although it has not been proved, that an enolate of *E*-configuration[3] (**A**) and a metal-carbenoid in a *s-trans* conformation[24] (**B**) were involved in these processes. It is clear from the conformations **A** and **B** that a rotation around the C-O bond would leave the opposite face free for the approach of the alkylating agent or the silane, leading to the opposite diastereoisomer. Such a rotation is likely to be relatively easy, explaining the modest stereoselectivities obtained with all these chiral auxiliaries.[1d,2h]



Scheme 8

Considering what is suggested above, it appears that any method which would prevent the rotation of the C-O bond might allow for a higher level of diastereocontrol. The carbon centre of the metallo-carbene possesses electrophilic character and therefore may co-ordinate with electron-rich groups such as carbonyl functions. Recently, Davies and co-workers[25] showed that the carbonyl group of amides and lactones effectively interacts with the carbenoid centre presumably forming a cyclic complex. These authors used this attractive feature of metal-carbenoids as an efficient way to control the diastereoselectivity during cyclopropanations. Readily available pantolactone was used for this purpose. It was shown that the carbonyl group of this chiral auxiliary could interact with the electrophilic carbenoid centre leading to a rigid and stabilized transition state where one face of the metal-carbenoid species was masked. While the efficiency of the methodology was firmly established for asymmetric cyclopropanations, such an approach has never been used in insertion reactions.

Using the same conditions as before, we were pleased to find that the $Rh_2(OAc)_4$-catalyzed reaction of α-diazoesters **18j** and **22** with $PhMe_2SiH$ led to the desired α-silylesters in good yields with much higher diastereoselectivities than those observed with menthyl esters (up to 80% d.e. !), thus supporting Davies' hypothesis[25] (Scheme 9, Fig.-2). The absolute configurations of the α-silylesters were determined using the same route as before (reduction and oxidation of the C-Si bond). However, and in contrast with the other chiral auxiliaries, partial epimerization was observed during the reduction of pantolactone, leading to diols of lower e.e.[26] Nevertheless, we proved that high levels of diastereocontrol can be achieved during insertion into Si-H bonds using chiral auxiliaries capable of co-ordinating the reactive carbenoid centre. Further studies are now under way to find a suitable chiral auxiliary possessing the required features and which can be recovered without epimerization at the chiral centre.



18j, R = Me
22, R = Ph

27a, R = Me (67% d.e.)
27b, R = Ph (80% d.e.)

Scheme 9

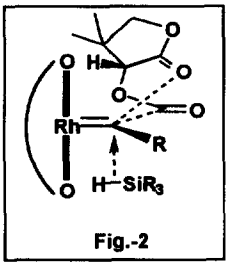


Fig.-2

In summary, we have described here an asymmetric route to substituted α-silylacetic esters starting either from the corresponding α-silylacetic esters or from the α-diazoester. In both cases, the chiral auxiliary is attached to the ester function. We observed that better diastereoselectivities are generally obtained with asymmetric metal-carbene insertion. Menthol and related chiral auxiliaries induce the chirality mainly through steric interactions which are not sufficient to efficiently prevent attack on both faces of the π-system. On the contrary, we found that pantolactone leads to higher selectivities. In this case, co-ordination between the chiral auxiliary and the reacting centre probably introduces a stabilization and a rigidification of the transition state. Such a feature is clearly absent with chiral auxiliaries **7a-b** and **16a-d**. The preliminary results obtained with pantolactone are encouraging and indicate the direction which might be followed in order to get higher diastereoselectivities. Work along these lines is now in progress in our laboratory.

EXPERIMENTAL SECTION

^1H NMR spectra were recorded on a BRUKER 250FT (250 MHz) and BRUKER WH-360FT (360 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. IR spectra were recorded on a Perkin-Elmer 1710 spectrophotometer. All commercial products were used without further purification.

CH_2Cl_2, hexamethyldisilazane and triethylamine were distilled from CaH_2. THF and ether were distilled from sodium and benzophenone. Toluene was distilled from sodium. HMe_2SiCl was distilled from magnesium before use. (+) and (-)-Menthol, (+)-camphor, (+)-camphorquinone, **7b**, **7c**, **16d**, **16e**, pulegone **19** are commercially available (Fluka) and were

used without further purifications. ABSA (Acetylbenzenesulfonyl azide) was prepared according to Davies procedure.[6,27] Methanesulfonyl azide was prepared following Taber's procedure.[6,28]
Elemental analyses were performed by the I. Beetz laboratory, W-8640 Kronach (Germany). Mass spectra were recorded on a Nermag R10-10C (Chemical ionization mode, NH_3).
The numbering of the protons in the ^1H NMR spectra of substrates **8d**, **10**, **11** and **12** have been made according to the numbering outlined in Scheme 5. The numbering of the protons in the ^1H NMR spectra of substrates **17d-e**, **18g-h** and **23g-h** have been made according to the numbering outlined in Scheme 6.

General procedure for the preparation of α-silylacetic esters 5a-c. A solution of ethyl diazoacetate (0.9 ml, 8.7 mmol) in dry CH_2Cl_2 (2 ml) was added slowly at room temperature, using a syringe pump (2 mmol/h), to a solution of dimethylchlorosilane (1 ml, 9.2 mmol) and $Rh_2(OAc)_4$ (12 mg, 0.025 mmol) in dry CH_2Cl_2 (3 ml). The mixture was cooled to 0°C and a solution of triethylamine (1.55 ml, 11 mmol) in dry CH_2Cl_2 (1 ml) was added, followed by N-methylephedrine (1.25 g, 7 mmol) in dry CH_2Cl_2 (7 ml). The suspension was stirred at room temperature for 2h then treated with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were washed with brine then dried over $MgSO_4$. The solvents were then evaporated *in vacuo* to give a brown oil which was purified by Kugelrohr distillation (130°C, 0.02 mbar) to afford the ester **5a** as a colourless oil (1.78 g, 79%). $[\alpha]_D^{25}$ = +36.2 (C 1.25, $CHCl_3$). ^1H **NMR** (δ ppm) : 7.34-7.19 (5H, m, Aromatic H), 4.86 (1H, d, J 4.5, ArC<u>H</u>), 4.06 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.69-2.64 (1H, m, $C\underline{H}CH_3$), 2.28 (6H, s, $N(CH_3)_2$), 1.96 (1H, d, J 12.0, $SiC\underline{H}_aCH_b$), 1.90 (1H, d, J 12.0, $SiCH_aC\underline{H}_b$), 1.22 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.98 (3H, d, J 6.6, $C\underline{H}_3CH$), 0.14 (3H, s, $SiCH_3$), 0.10 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2)(υ_{max}) : 1710 (C=O), 1600 (C=C), 1090, 1070 (Si-O), 1025 cm^{-1}. **MS** (CI, NH_3): 324 (M^++1, 2), 236 (M^+-$CH_2CO_2C_2H_5$, 2), 91 ($C_7H_7^+$, 3), 77 ($C_6H_5^+$, 4), 75 ($C_6H_3^+$, 4), 73 ($CO_2C_2H_5^+$, 8), 72 ($^+CH_3CHN(CH_3)_2$, 100). **Anal.** Calcd for $C_{17}H_{29}O_3SiN$: C, 63.12; H, 9.04; Si, 8.68; N, 4.33. Found : C, 63.02; H, 9.10; Si, 8.65; N, 4.36.
5b. (73%) $[\alpha]_D^{25}$ = -50.4 (C 0.23, $CHCl_3$). ^1H **NMR** (δ ppm) : 4.10 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 3.68 (1H, dd, J 5.1, 10.1, $NCHC\underline{H}_aH_bO$), 3.52 (1H, dd, J 6.1, 10.1, $NCHCH_a\underline{H}_bO$), 3.08-3.01 (1H, m, $NC\underline{H}CH_aH_bO$), 2.40 (3H, s, NCH_3), 2.38-2.16 (2H, m, NCH_2), 2.04 (1H, d, J 8.3, $SiC\underline{H}_aCH_b$), 2.01 (1H, d, J 8.3, $SiCH_aC\underline{H}_b$), 1.90-1.56 (4H, m, 2 x CH_2), 1.25 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.24 (6H, s, $Si(CH_3)_2$). **IR** (CH_2Cl_2)(υ_{max}) : 2790, 1710 (C=O), 1540, 1100 (Si-O), 910 cm^{-1}. **MS** (CI, NH_3) : 260 (M^+ +1, 5), 173 (M^+-$CHCO_2C_2H_5$, 3), 149 (2), 87 ($CH_2CO_2C_2H_5^+$, 9), 85 ($C_4H_5O_2^+$, 53), 83 ($C_4H_3O_2^+$, 100), 84 ($C_4H_4O_2^+$, 52). **Anal.** Calcd for $C_{12}H_{25}O_3SiN$: C, 55.56; H, 9.71; Si, 10.83; N, 5.40. Found : C, 55.43; H, 9.65; Si, 10.97; N, 5.56.
5c. (75%) $[\alpha]_D^{25}$ = -20.1 (C 1.3, $CHCl_3$). ^1H **NMR** (δ ppm) : 7.28-7.08 (8H, m, Aromatic H), 6.86-6.82 (2H, m, Aromatic H), 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 3.57 (1H, d, J 14.3, $ArC\underline{H}_aH_b$), 3.12 (1H, d, J 14.3, $ArCH_a\underline{H}_b$), 2.28 (6H, s, $N(CH_3)_2$), 2.27-2.04 (3H, m, Aliphatic H), 1.98 (2H, s, $SiCH_2$), 1.23 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.84 (3H, d, J 6.4, $C\underline{H}_3CH$), 0.27 (3H, s, $SiCH_3$), 0.19 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2)(υ_{max}) : 1710 (C=O), 1600 (C=C), 1100, 1070 (Si-O) cm^{-1}. **MS** (CI, NH_3) : 428 (M^++1, 32), 382 (M^+-C_2H_5, 8), 370 (M^+-C_4H_9, 7), 341 (14), 340 (M^+-$CH_2CO_2C_2H_5$, 17), 105 (26), 103 (44), 91 ($C_7H_7^+$, 67), 77 ($C_6H_5^+$, 39), 75 ($Si(CH_3)_2OH^+$, 100). **Anal.** Calcd for $C_{25}H_{37}O_3SiN$: C, 70.21; H, 8.72; Si, 6.57; N, 3.28. Found : C, 70.08; H, 8.78; Si, 6.69; N, 3.36.
General procedure for the alkylation of α-silylacetic esters 5a-c. To a solution of hexamethyldisilazane (0.14 ml, 0.64 mmol) in dry THF (3 ml) was added at -20°C a 1.6<u>M</u> solution of n-BuLi in hexane (0.35 ml, 0.55 mmol). The solution was stirred at -5°C for 15 minutes then cooled to -60°C and a solution of the ester **5a** (0.15 g, 0.46 mmol) in dry THF (1 ml) was added dropwise. The mixture was stirred at -50°C for 2h then a solution of MeI (0.15 ml, 2.3 mmol) in dry THF (1 ml) was added dropwise at -80°C. The mixture was stirred at -80°C for 2h then treated with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine then dried over $MgSO_4$. The solvents were then evaporated *in vacuo* to give a yellow oil which was purified by Kugelrohr distillation (130°C, 0.02 mbar) to afford the ester **6a** as a colourless oil (0.125 g, 80%). ^1H **NMR** (δ ppm) (2 diastereoisomers) : 7.34-7.20 (10H, m, Aromatic H), 4.83 (1H, d, J 4.5, ArC<u>H</u>), 4.79 (1H, d, J 5.0, ArC<u>H</u>), 4.08 (4H, q, J 7.1, 2 x $CO_2C\underline{H}_2CH_3$), 2.70-2.62 (2H, m, 2 x $C\underline{H}CH_3$), 2.27 (6H, s, $N(CH_3)_2$), 2.26 (6H, s, $N(CH_3)_2$), 2.15 (1H, q, J 7.1, $SiC\underline{H}CH_3$), 2.07 (1H, q, J 7.1, $SiC\underline{H}CH_3$), 1.22 (6H, t, J 7.1, 2 x $CO_2CH_2C\underline{H}_3$), 1.20 (3H, d, J 7.1, $SiCHC\underline{H}_3$), 1.18 (3H, d, J 7.1, $SiCHC\underline{H}_3$), 1.0 (3H, d, J 6.7, $C\underline{H}_3CH$), 0.98 (3H, d, J 6.7, $C\underline{H}_3CH$), 0.14 (3H, s, $SiCH_3$), 0.13 (3H, s, $SiCH_3$), -0.03 (3H, s, $SiCH_3$), -0.05 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}) : 2960, 2940 (C-H), 2870, 2810, 2780, 1705 (C=O), 1450, 1375, 1365, 1315, 1255 (Si-C), 1180, 1065 (Si-O), 970, 865 cm^{-1}. **MS** (CI, NH_3) : 354 (M^++NH_3, 10), 353 (15), 351 (11), 338 (M^++1, 1), 247 (1), 94 (1), 79 (3), 77 ($C_6H_5^+$, 5), 75 ($C_6H_3^+$, 97), 74 ($HCO_2C_2H_5^+$, 100), 73 ($CO_2C_2H_5^+$, 15), 72 (78). **Anal.** Calcd for $C_{18}H_{31}O_3SiN$: C, 64.05; H, 9.26. Found : C, 63.93; H, 9.01.
General procedure for the preparation of α-diazoesters 8c-d. To a solution of 1,7,7-trimethyl-2-naphtylbicyclo[2.2.1]heptan-2-ol[5] (3 g, 10.7 mmol), sodium acetate (0.4 g, 4.3 mmol) and methanesulfonyl azide (1.7 g,

13.9 mmol) in dry acetonitrile (10 ml) was added dropwise a solution of diketene (1.65 ml, 21.4 mmol) in dry acetonitrile (3 ml). The mixture was stirred at room temperature overnight, then an additional amount of methanesulfonyl azide (0.64 g, 5.3 mmol) and triethylamine (0.74 ml, 5.3 mmol) were added at 0°C. The mixture was stirred at 0°C for 2h then treated with water. The solution was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and the solvents were evaporated *in vacuo*. The residue was dissolved in acetonitrile (60 ml) and a 5% solution of KOH (60 ml) was slowly added. The mixture was stirred at room temperature for 5h then extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and the solvents were evaporated *in vacuo*. Flash chromatography (Petroleum ether/triethylamine 99.5:0.5) and crystallization in cold pentane afforded **8d** as pale yellow crystals (1.33 g, 40%). mp 133-136°C (pentane). $[\alpha]_D^{25}$ = -274.4 (C 0.94, $CHCl_3$). **^{1}H NMR** (δ ppm) : 8.56-8.52 (1H, m, Aromatic H), 7.85-7.71 (3H, m, Aromatic H), 7.48-7.38 (3H, m, Aromatic H), 4.69 (1H, broad s, CHN_2), 2.96 (1H, d, J 15.5, H-3 *endo*), 2.62 (1H, dt, J 3.6, 15.5, H-3 *exo*), 1.99 (1H, t, J 4.2, H-5 *exo*), 1.83-1.72 (1H, m, H-4), 1.50-1.39 (1H, m, H-5 *endo*), 1.28 (3H, s, CH_3), 1.24-1.01 (2H, m, H-6 *exo*, H-6 *endo*), 1.14 (3H, s, CH_3), 0.98 (3H, s, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2940 (C-H), 2110 (C=N=N), 1690 (C=O), 1370 cm^{-1}. **MS** (CI, NH_3) : 321 (3), 263 ($M^{+\cdot}$-OCOCHN$_2$, 100), 262 (14), 219 (5), 210 (11), 170 (12), 168 (14). **Anal.** Calcd for $C_{22}H_{24}O_2N_2$: C, 75.83; H, 6.94; N, 8.04. Found : C, 75.65; H, 7.18; N, 8.08.

8c. As above, **8c** was obtained after chromatography as a yellow oil (42%). $[\alpha]_D^{25}$ = +1.95 (C 1.23, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.29-7.27 (4H, m, Aromatic H), 7.18-7.13 (1H, m, Aromatic H), 4.89 (1H, dt, J 4.2, 10.7, C<u>H</u>OCO), 4.23 (1H, broad s, CHN_2), 2.05-1.89 (2H, m, Aliphatic H), 1.74-1.60 (2H, m, Aliphatic H), 1.32 (3H, s, CH_3), 1.23 (3H, s, CH_3), 1.58-0.80 (4H, m, Aliphatic H), 0.88 (3H, d, J 6.5, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2860, 2110 (CHN_2), 1675 (C=O), 1385, 1250, 1190, 1010 cm^{-1}. **MS** (CI, NH_3) : 272 ($M^{+\cdot}$-N_2, 20), 215 ($M^{+\cdot}$-OCOCHN$_2$, 51), 135 (6), 120 (11), 119 ((CH$_3$)$_2$CPh$^{+\cdot}$, 100), 118 (23), 105 (24), 91 ($C_7H_7^{+\cdot}$, 71), 81 (18), 77 ($C_6H_5^{+\cdot}$, 12). **Anal.** Calcd for $C_{18}H_{24}O_2N_2$: C, 71.97; H, 8.05; N, 9.33. Found : C, 71.84; H, 8.15; N, 9.23.

General procedure for the preparation of α-(phenyldimethylsilyl)acetic esters 9a,c,e. A solution of menthyl diazoacetate[4] (0.5 g, 2.22 mmol) in dry CH_2Cl_2 (2 ml) was added slowly at room temperature, using a syringe pump (1.5 mmol/h), to a solution of dimethylphenylsilane (0.38 ml, 2.45 mmol) and $Rh_2(OAc)_4$ (8 mg, 0.017 mmol) in dry CH_2Cl_2 (3 ml). The solvent was then evaporated *in vacuo* and the residue purified by flash chromatography (Petroleum ether/EtOAc/NEt_3 98.5/1/0.5) to give **9a** as a colourless oil (0.59 g, 80%). $[\alpha]_D^{25}$ = -37.4 (C 1.28, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.57-7.52 (2H, m, Aromatic H), 7.40-7.35 (3H, m, Aromatic H), 4.61 (1H, dt, J 4.4, 10.8, CHOCO), 2.15 (1H, d, J 12.0, SiC<u>H$_a$</u>H$_b$), 2.09 (1H, d, J 12.0, SiCH$_a$<u>H$_b$</u>), 1.89-0.80 (9H, m, Aliphatic H), 0.87 (3H, d, J 6.6, CH_3), 0.84 (3H, d, J 7.0, CH_3), 0.71 (3H, d, J 6.9, CH_3), 0.41 (6H, s, Si(CH$_3$)$_2$). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2860, 1700 (C=O), 1255, 1115, 1095, 990, 835 cm^{-1}. **MS** (CI, NH_3) : 317 ($M^{+\cdot}$-CH_3, 8), 275 (7), 255 ($M^{+\cdot}$-Ph, 29), 179 (65), 154 (8), 138 ($C_{10}H_{18}^{+\cdot}$, 21), 137 ($C_{10}H_{17}^{+\cdot}$, 51), 135 (PhSi(CH$_3$)$_2^{+\cdot}$, 61), 117 (100), 95 (21), 83 (36). **Anal.** Calcd for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.70; Si, 8.45. Found : C, 72.26; H, 9.79; Si, 8.41.

9c. (70%). $[\alpha]_D^{25}$ = -32.6 (C 1.11, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.44-7.15 (10H, m, Aromatic H), 5.0 (1H, dt, J 4.5, 10.5, ArC<u>H</u>), 2.64 (1H, dt, J 4.0, 11.4, CHOCO), 2.15-2.02 (1H, m, Aliphatic H), 1.96-1.29 (7H, m, Aliphatic H), 1.92 (1H, d, J 11.9, SiC<u>H$_a$</u>H$_b$), 1.86 (1H, d, J 11.9, SiCH$_a$<u>H$_b$</u>), 0.15 (3H, s, $SiCH_3$), 0.08 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}) : 2920 (C-H), 2880, 1700 (C=O), 1600 (C=C), 1250, 1095, 1020 (Si-O), 840 cm^{-1}. **MS** (CI, NH_3): 295 (15), 275 ($M^{+\cdot}$-Ph, 11), 233 (6), 177 (42), 158 ($C_{12}H_{14}^{+\cdot}$, 100), 135 (PhSi(CH$_3$)$_2^{+\cdot}$, 66), 117 (12), 91 ($C_7H_7^{+\cdot}$, 54). **Anal.** Calcd for $C_{22}H_{28}O_2Si$: C, 74.95; H, 8.01; Si, 7.97. Found : C, 75.28; H, 8.05; Si, 7.45.

9e. (49%). $[\alpha]_D^{25}$ = +19.2 (C 1.4, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.46-7.28 (9H, m, Aromatic H), 7.15-7.10 (1H, m, Aromatic H), 4.70 (1H, dt, J 4.2, 10.7, CHOCO), 1.94 (1H, dt, J 3.6, 10.7, C<u>H</u>CHOCO), 1.72-0.63 (7H, m, Aliphatic H), 1.69 (1H, d, J 12.0, SiC<u>H$_a$</u>H$_b$), 1.42 (1H, d, J 12.0, SiCH$_a$<u>H$_b$</u>), 1.28 (3H, s, CH_3), 1.19 (3H, s, CH_3), 0.82 (3H, d, J 6.5, CH_3), 0.29 (3H, s, $SiCH_3$), 0.28 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}) : 2950, 2920 (C-H), 2870, 1690 (C=O), 1440, 1250 (Si-C), 1140, 1110, 1000, 910, 840 cm^{-1}. **MS** (CI, NH_3) : 331 ($M^{+\cdot}$-Ph, 4), 289 ($M^{+\cdot}$-PhSiCH$_2$, 11), 215 (8), 214 (16), 137 (9), 136 (11), 135 (PhSi(CH$_3$)$_2^{+\cdot}$, 34), 120 (PhSi(CH$_3$)$^{+\cdot}$, 12), 119 (PhSiCH$_2^{+\cdot}$, 100), 118 (PhSiCH$^{+\cdot}$, 70), 117 (24), 105 (PhSi$^{+\cdot}$, 15), 91 ($C_7H_7^{+\cdot}$, 29), 75 (10). **Anal.** Calcd for $C_{26}H_{36}O_2Si$: C, 76.42; H, 8.88; Si, 6.87. Found : C, 76.38; H, 8.77; Si, 6.80.

General procedure for the preparation of α-(phenyldimethylsilyl)acetic esters 9b,d. A solution of menthyl diazoacetate[4] (1.6 g, 7.2 mmol) in dry CH_2Cl_2 (6 ml) was added slowly at room temperature, using a syringe pump (1.5 mmol/h), to a solution of dimethylchlorosilane (0.82 ml, 7.5 mmol) and $Rh_2(OAc)_4$ (8 mg, 0.017 mmol) in dry CH_2Cl_2 (3 ml). The mixture was then cooled to 0°C and a solution of triethylamine (1.26 ml, 9 mmol) in dry CH_2Cl_2 (1 ml) was added, followed by a solution of isopropanol (0.69 ml, 9 mmol) in dry CH_2Cl_2 (1 ml). The suspension was stirred at room temperature for 2h then treated with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were washed with brine, dried ($MgSO_4$) and the solvents were evaporated *in vacuo* to give a brown oil which was purified by Kugelrohr distillation (130°C, 0.04 mbar) to afford the ester **9b** as a colourless oil (1.72 g, 76%). $[\alpha]_D^{25}$ = -44.3 (C 1.06, $CHCl_3$). **^{1}H NMR** (δ ppm) : 4.65 (1H, dt, J 4.4, 10.9,

CHOCO), 4.06 (1H, sept, J 6.0, OC<u>H</u>$(CH_3)_2$), 2.02 (1H, d, J 12.0, SiC<u>H</u>$_a$H$_b$), 1.99 (1H, d, J 12.0, SiCH$_a$<u>H</u>$_b$), 2.01-1.87 (1H, m, Aliphatic H), 1.69-0.83 (8H, m, Aliphatic H), 1.17 (6H, d, J 6.0, OCH(C<u>H</u>$_3)_2$), 0.90 (3H, d, J 6.2, CH_3), 0.89 (3H, d, J 7.1, CH_3), 0.76 (3H, d, J 6.9, CH_3), 0.23 (6H, s, Si$(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 2960, 2920 (C-H), 2870, 1700 (C=O), 1450 ($SiCH_3$), 1370, 1260, 1095, 1015 (Si-O), 885, 835 cm^{-1}. **MS** (CI, NH_3) : 295 (7), 282 ($M^{+\cdot}$-CH_3OH, 10), 281 (20), 265 (15), 251 (20), 221 (10), 207 (19), 191 (42), 177 (10), 138 (18), 95 (39), 85 (45), 83 (100), 81 (43). **Anal.** Calcd for $C_{17}H_{34}O_3Si$: C, 64.92; H, 10.90; Si, 8.93. Found : C, 64.71; H, 10.72; Si, 9.06.

9d. (80%). $[\alpha]_D^{25}$ = -35.9 (C 1.16, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.29-7.14 (5H, m, Aromatic H), 5.0 (1H, dt, J 4.3, 10.4, ArC<u>H</u>), 3.89 (1H, sept, J 6.1, OC<u>H</u>$(CH_3)_2$), 2.66 (1H, dt, J 3.5, 11.5, CHOCO), 2.17-2.14 (1H, m, Aliphatic H), 1.94-1.29 (7H, m, Aliphatic H), 1.81 (1H, d, J 11.6, SiC<u>H</u>$_a$H$_b$), 1.75 (1H, d, J 11.6, SiCH$_a$<u>H</u>$_b$), 1.09 (6H, d, J 6.0, OCH(C<u>H</u>$_3)_2$), -0.04 (3H, s, $SiCH_3$), -0.08 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2920 (C-H), 2860, 1700 (C=O), 1600 (C=C), 1450, 1250, 1100, 1020 (Si-O), 890, 835 cm^{-1}. **MS** (CI, NH_3) : 336 ($M^{+\cdot}$+2, 32), 335 ($M^{+\cdot}$+1, 41), 292 ($M^{+\cdot}$-C_3H_6, 7), 275 (19), 207 (9), 158 ($C_{12}H_{14}^{+\cdot}$, 52), 159 (17), 134 (17), 117 (39), 91 ($C_7H_7^+$, 100), 83 (99), 75 ($Si(CH_3)_2OH^+$, 91). **Anal.** Calcd for $C_{19}H_{30}O_3Si$: C, 68.22; H, 9.04; Si, 8.40. Found : C, 68.32; H, 9.00; Si, 8.43.

10. Same procedure than that described for **9a**. $[\alpha]_D^{25}$ = -37.1 (C 1.12, $CHCl_3$). **^{1}H NMR** (δ ppm) : 6.70 (1H, d, J 5.2, H-5), 6.22-6.14 (2H, m, H-3, H-4), 5.82-5.67 (2H, m, H-2, H-7), 3.79 (1H, dt, J 4.0, 10.7, CHOCO), 3.56 (1H, dd, J 7.7, 7.7, H-1), 2.18-0.80 (8H, m, Aliphatic H), 1.31 (3H, s, CH_3), 1.18 (3H, s, CH_3), 0.88 (3H, d, J 6.5, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 1715 (C=O), 1465, 1295, 1255, 1185, 1000 cm^{-1}. **MS** (CI, NH_3) : 273 ($M^{+\cdot}$+1, 22), 272 ($M^{+\cdot}$, 46), 257 ($M^{+\cdot}$-CH_3, 20), 214 (14), 185 (34), 145 (45), 137 ($C_{10}H_{17}^{+\cdot}$, 35), 135 (40), 132 (67), 119 (45), 117 (99), 115 (21), 105 (19), 95 (45), 91 ($C_7H_7^{+\cdot}$, 100), 81 (51). **Anal.** Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found : C, 76.74; H, 8.78.

11. Same procedure than that described for **9a**, except that the crude product was crystallized from pentane. mp 161-164°C (pentane). $[\alpha]_D^{25}$ = -45.3 (C 1.0, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.49-7.29 (3H, m, Aromatic H), 7.12 (1H, d, J 11.6, H-a), 6.55 (1H, dd, J 5.5, 11.6, H-b), 6.28 (1H, ddd, J 1.8, 5.5, 9.6, H-c), 5.79 (1H, dd, J 5.1, 9.6, H-d), 3.77 (1H, dd, J 1.8, 5.1, H-e), 2.70 (1H, dt, J 3.8, 14.8, H-3 *exo*), 2.27 (1H, d, J 14.8, H-3 *endo*), 2.03 (1H, t, J 4.3, H-5 *exo*), 1.95-1.82 (1H, m, H-4), 1.49-1.18 (3H, m, H-5 *endo*, H-6 *exo*, H-6 *endo*), 1.38 (3H, s, CH_3), 0.97 (3H, s, CH_3), 0.89 (3H, s, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 1710 (C=O), 1455, 1320, 1255, 1000 cm^{-1}. **MS** (CI, NH_3) : 338 ($M^{+\cdot}$+NH_4, 9), 321 ($M^{+\cdot}$+1, 39), 320 ($M^{+\cdot}$, 7), 263 (5), 211 (30), 210 (100), 182 (9), 139 (6), 109 (5), 95 (22). **Anal.** Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found : C, 82.35; H, 7.66.

12. Obtained after flash chromatography of **11** (37%). mp > 190°C (pentane). $[\alpha]_D^{25}$ = +11.4 (C 1.12, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.42-7.34 (3H, m, Aromatic H), 7.01 (1H, dd, J 6.0, 8.5, H-e), 6.71 (1H, ddd, J 1.0, 2.3, 10.0, H-a), 5.91 (1H, ddd, J 4.6, 8.2, 10.0, H-b), 3.01 (1H, dddd, J 1.0, 8.4, 8.4, 13.5, H-c), 2.65 (1H, ddd, J 3.1, 4.3, 14.8, H-3 *exo*), 2.35 (1H, d, J 14.8, H-3 *endo*), 2.14-2.04 (1H, m, H-d), 2.01 (1H, t, J 4.3, H-5 *exo*), 1.95-1.79 (1H, m, H-4), 1.45-1.18 (3H, m, H-5 *endo*, H-6 *exo*, H-6 *endo*), 1.36 (3H, s, CH_3), 0.93 (3H, s, CH_3), 0.80 (3H, s, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 1700 (C=O), 1630 (C=C), 1455, 1310, 1295, 1060, 980, 910 cm^{-1}. **MS** (CI, NH_3) : 321 ($M^{+\cdot}$+1, 9), 273 (30), 251 (5), 222 (10), 212 (16), 211 (73), 210 (100), 181 (22), 169 (28), 153 (27), 109 (36), 98 (17), 95 (35), 85 (38), 83 (52), 81 (21), 78 (33), 75 (51), 71 (35). **Anal.** Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.55; H, 7.52.

General procedure for the alkylation of α-silylacetic esters 9a-d. Following the procedure described for the synthesis of **5a-c**, **13a** was obtained from **9a** as a colourless oil (0.146 g, 70%). **^{1}H NMR** (δ ppm)(2 diastereoisomers) : 7.55-7.51 (4H, m, Aromatic H), 7.40-7.34 (6H, m, Aromatic H), 4.62 (2H, dt, J 4.4, 10.8, 2 CHOCO), 2.26 (1H, q, J 7.2, SiC<u>H</u>CH_3), 2.25 (1H, q, J 7.2, SiC<u>H</u>CH_3), 1.96-0.80 (18H, m, Aliphatic H), 1.17 (3H, d, J 7.2, SiCHC<u>H</u>$_3$), 1.15 (3H, d, J 7.2, SiCHC<u>H</u>$_3$), 0.89 (3H, d, J 6.5, CH_3CHC<u>H</u>$_3$), 0.87 (6H, d, J 6.8, CH(C<u>H</u>$_3)_2$), 0.82 (3H, d, J 7.0, C<u>H</u>$_3$CHC<u>H</u>$_3$), 0.73 (3H, d, J 6.9, CH_3), 0.68 (3H, d, J 6.9, CH_3), 0.39 (3H, s, $SiCH_3$), 0.38 (9H, s, 3 $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960, 2920 (C-H), 2870, 1695 (C=O), 1450, 1425, 1370, 1310, 1250 (Si-C), 1190, 1145, 1110, 1080, 1035, 980, 960, 835, 820 cm^{-1}. **MS** (CI, NH_3) : 269 ($M^{+\cdot}$-Ph, 3), 193 (7), 138 ($C_{10}H_{18}^{+\cdot}$, 11), 135 ($PhSi(CH_3)_2^+$, 27), 131 (24), 130 (100), 95 (6), 83 (21). **Anal.** Calcd for $C_{21}H_{34}O_2Si$: C, 72.78; H, 9.89; Si, 8.10. Found : C, 72.92; H, 9.78; Si, 8.14.

13b. Same procedure as described above except that hexamethyldisilazane (2.2 eq.) was used instead of diisopropylamine (87%). **^{1}H NMR** (δ ppm)(2 diastereoisomers) : 4.67 (2H, dt, J 4.4, 10.8, 2 CHOCO), 4.04 (2H, sept, J 6.0, 2 OC<u>H</u>$(CH_3)_2$), 2.10 (1H, q, J 7.1, SiC<u>H</u>CH_3), 2.0-0.81 (19H, m, Aliphatic H), 1.22 (3H, d, J 7.2, SiCHC<u>H</u>$_3$), 1.16 (6H, d, J 6.0, OCH(C<u>H</u>$_3)_2$), 1.15 (3H, d, J 6.0, CH_3CHC<u>H</u>$_3$), 1.14 (3H, d, J 6.0, C<u>H</u>$_3$CHC<u>H</u>$_3$), 0.89 (6H, d, J 7.0, CH(C<u>H</u>$_3)_2$), 0.88 (6H, d, J 7.1, CH(C<u>H</u>$_3)_2$), 0.75 (3H, d, J 7.0, CH_3), 0.74 (3H, d, J 6.9, CH_3), 0.19 (6H, s, $Si(CH_3)_2$), 0.19 (3H, s, $SiCH_3$), 0.18 (6H, s, $Si(CH_3)_2$), 0.17 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 2860, 1695 (C=O), 1450, 1365, 1250, 1115, 1100, 1030 (Si-O), 880 cm^{-1}. **MS** (CI, NH_3) : 329 ($M^{+\cdot}$+1, 24), 315 (6), 190 (40), 173 (19), 130 (100), 117 (18), 92 (38), 83 (58), 75 ($Si(CH_3)_2OH^+$, 94). **Anal.** Calcd for $C_{18}H_{36}O_3Si$: C, 65.80; H, 11.04; Si, 8.55. Found : C, 65.14; H, 10.91; Si, 8.84.

13c. (87%). ^{1}H **NMR** (δ ppm) (2 diastereoisomers) : 7.45-7.08 (20H, m, Aromatic H), 5.05 (1H, dt, J 4.2, 10.5, PhC<u>H</u>), 4.96 (1H, dt, J 4.5, 10.6, PhC<u>H</u>), 2.72-2.54 (2H, m, 2 C<u>H</u>OCO), 2.18-1.18 (18H, m, Aliphatic H), 0.89 (3H, d, J 7.1, SiCHC<u>H</u>$_3$), 0.85 (3H, d, J 7.2, SiCHC<u>H</u>$_3$), 0.22 (3H, s, SiC<u>H</u>$_3$), 0.18 (3H, s, SiC<u>H</u>$_3$), 0.08 (3H, s, SiC<u>H</u>$_3$), 0.03 (3H, s, SiC<u>H</u>$_3$). **IR** ($CHCl_3$)(υ_{max}) : 2940 (C-H), 2860, 1700 (C=O), 1600 (C=C), 1450, 1250, 1180, 1110, 820 cm^{-1}. **MS** (CI, NH_3) : 351 ($M^{+\cdot}$-CH_3, 2), 295 (6), 289 ($M^{+\cdot}$-Ph, 8), 233 (5), 191 ($COCH(Me)Si(CH_3)_2Ph^{+\cdot}$ or $PhC_6H_{10}O^{+\cdot}$, 16), 159 (18), 158 (19), 135 ($PhSi(CH_3)_2^{+\cdot}$, 27), 130 (33), 91 ($C_7H_7^{+\cdot}$, 100). **Anal.** Calcd for $C_{23}H_{30}O_2Si$: C, 75.36; H, 8.25; Si, 7.66. Found : C, 75.42; H, 8.34; Si, 7.24.

13d. (79%). ^{1}**H NMR** (δ ppm)(2 diastereoisomers) : 7.29-7.13 (10H, m, Aromatic H), 5.04 (1H, dt, J 4.3, 10.4, PhC<u>H</u>), 5.0 (1H, dt, J 4.4, 10.3, PhC<u>H</u>), 3.92 (1H, sept, J 6.0, OC<u>H</u>$(CH_3)_2$), 3.87 (1H, sept, J 6.0, OC<u>H</u>$(CH_3)_2$), 2.72-2.60 (2H, m, 2 x CHOCO), 2.18-1.30 (18H, m, Aliphatic H), 1.13-1.06 (12H, m, 2 x OCH(C<u>H</u>$_3)_2$), 0.97 (6H, d, J 7.1, 2 x C<u>H</u>$_3$), 0.02 (3H, s, SiC<u>H</u>$_3$), -0.01 (3H, s, SiC<u>H</u>$_3$), -0.14 (6H, s, Si$(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 2980, 2965 (C-H), 2860, 1700 (C=O), 1600 (C=C), 1450, 1320, 1250, 1120, 1030 (Si-O), 880, 830 cm^{-1}. **MS** (CI, NH_3) : 349 ($M^{+\cdot}$+1, 17), 289 (31), 251 (5), 190 (12), 173 (15), 159 (37), 158 (33), 130 (35), 91 ($C_7H_7^{+\cdot}$, 100), 75 ($Si(CH_3)_2OH^{+\cdot}$, 56). **Anal.** Calcd for $C_{20}H_{32}O_3Si$: C, 68.92; H, 9.25; Si, 8.06. Found : C, 69.00; H, 9.26; Si, 8.22.

(4*S*)-N-(chloroacetyl)-4-isopropyloxazolidone 15. Same procedure than that described for the preparation of **9b-d**. (90% yield). mp 58-60°C (Ether/pentane). $[\alpha]_D^{25}$ = +5.0 (C 1.33, $CHCl_3$). ^{1}**H NMR** (δ ppm) : 4.73 (2H, s, CH_2Cl), 4.16 (1H, dd, J 11.1, 11.1, OC<u>H$_a$H$_b$</u>CH), 3.92 (1H, ddd, J 3.8, 9.7, 11.1, OCH$_a$H$_b$C<u>H</u>), 3.82 (1H, dd, J 3.8, 11.1, OCH$_a$<u>H$_b$</u>CH), 2.40-2.28 (1H, m, C<u>H</u>$(CH_3)_2$), 1.05 (3H, d, J 6.7, CH_3), 0.94 (3H, d, J 6.7, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 1820, 1810, 1740 (C=O), 1440, 1410, 1380, 1260, 1160, 1120, 1060, 910 cm^{-1}. **MS** (CI, NH_3) : 225 (24), 223 ($M^{+\cdot}$+NH_3, 100), 189 (11), 156 (21), 127 (19), 102 (38), 83 (33), 72 (62). **Anal.** Calcd for $C_8H_{12}O_3NCl$: C, 46.73; H, 5.88; Cl, 17.24. Found : C, 46.86; H, 5.77; Cl, 17.19.

(1*R*, 2*S*, 5*R*)-5-Methyl-2-[(1,1,3,3-tetramethyl)butyl]cyclohexanol 16a. To a suspension of sodium (0.24 g, 10.4 mmol) in dry refluxing toluene (5 ml) was added dropwise a solution of ketones **20** (0.8 g, 3.56 mmol) in isopropanol (0.8 ml). The reaction mixture was then refluxed for an additionnal 20h and cooled to 0°C. The mixture was diluted with ether (20 ml) and carefully poured into ice-water. The organic layer was decanted and the aqueous layer was saturated with sodium chloride and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and the solvents were evaporated *in vacuo*. Flash chromatography (Petroleum ether/EtOAc 98:2) afforded recovered starting material (0.23 g) and the alcohol **16a** (0.3 g, corrected yield: 52%) as a colourless oil. $[\alpha]_D^{25}$ = -24.2 (C 1.0, $CHCl_3$). ^{1}**H NMR** (δ ppm) : 3.62-3.52 (1H, m, CHOCO), 2.05-0.74 (8H, m, Aliphatic H), 1.46 (1H, d, J 14.4, C<u>H$_a$H$_b$</u>t-Bu), 1.38 (1H, d, J 14.4, CH$_a$<u>H$_b$</u>t-Bu), 1.13 (3H, s, CH_3), 1.09 (3H, s, CH_3), 1.0 (9H, s, t-Bu), 0.90 (3H, d, J 6.5, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 3600 (O-H), 2950, 2920 (C-H), 1450, 1360, 1090, 1015, 1000, 910 cm^{-1}. **MS** (CI, NH_3) : 244 ($M^{+\cdot}$+NH_4, 14), 226 ($M^{+\cdot}$, 2), 137 (8), 113 (18), 112 (51), 97 (54), 96 (28), 95 (35), 83 (23), 81 (100), 71 (t-Bu$CH_2^{+\cdot}$, 10). **Anal.** Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36. Found : C, 79.69; H, 13.27.

General procedure for the preparation of acetoacetate 17a-g.[4] To a solution of (-)-menthol (15 g, 96 mmol) and sodium acetate (0.5 g, 6.1 mmol) in acetonitrile (80 ml) was added dropwise at room temperature a solution of diketene (14.8 ml, 192 mmol) in acetonitrile (20 ml). The mixture was refluxed for 2h then treated at 0°C with water (20 ml) and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and the solvents were evaporated *in vacuo*. Flash chromatography (Petroleum ether/EtOAc 95:5) gave **17a** as a colourless oil (22.1 g, 96%). ^{1}**H NMR** (δ ppm) : 4.74 (1H, dt, J 4.4, 10.8, CHOCO), 3.44 (2H, s, $COCH_2CO$), 2.27 (3H, s, $COCH_3$), 2.10-2.0 (1H, m, Aliphatic H), 1.87 (1H, dsept, J 2.7, 7.0, CH_3CHCH_3), 1.72-1.30 (4H, m, Aliphatic H), 1.12-0.80 (3H, m, Aliphatic H), 0.91 (3H, d, J 6.5, C<u>H</u>$_3$CHC<u>H</u>$_3$), 0.89 (3H, d, J 7.0, CH_3CHC<u>H</u>$_3$), 0.77 (3H, d, J 7.0, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 1730 (C=O), 1710 (C=O), 1640, 1450, 1410, 1360, 1310, 1240, 1095, 1080, 1025, 1010, 980, 960, 910 cm^{-1}.

17c (86%). $[\alpha]_D^{25}$ = -35.0 (C 1.13, $CHCl_3$). ^{1}**H NMR** (δ ppm) : 4.87 (1H, dt, J 4.3, 10.7, CHOCO), 3.41 (2H, s, $COCH_2CO$), 2.28 (3H, s, $COCH_3$), 2.05-1.85 (3H, m, Aliphatic H), 1.70-0-80 (4H, m, Aliphatic H), 1.39 (1H, d, J 14.5, C<u>H$_a$H$_b$</u>t-Bu), 1.21 (1H, d, J 14.5, CH$_a$<u>H$_b$</u>t-Bu), 0.98 (15H, s, 5 x CH_3), 0.89 (3H, d, J 6.6, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 1725 (C=O), 1710 (C=O), 1640, 1450, 1360, 1315, 1240, 1150, 910 cm^{-1}. **MS** (CI, NH_3) : 239 ($M^{+\cdot}$-CH_2t-Bu, 14), 209 ($M^{+\cdot}$-$OCOCH_2COCH_3$, 7), 208 (10), 199 (10), 137 (12), 112 (21), 103 (73), 97 (36), 95 (34), 85 (46), 81 (100), 71 (t-Bu$CH_2^{+\cdot}$, 12). **Anal.** Calcd for $C_{19}H_{34}O_3$: C, 73.50; H, 11.04. Found : C, 73.58; H, 10.96.

17d (88%). $[\alpha]_D^{25}$ = +88.9 (C 1.73, $CHCl_3$). ^{1}**H NMR** (δ ppm) : 4.62 (1H, d, J 7.0, H-2), 3.49 (1H, d, J 15.2, $COCH_aH_bCO$), 3.48 (1H, d, J 6.7, H-3), 3.40 (1H, d, J 15.2, $COCH_aH_bCO$), 3.13 (1H, d, J 8.2, OC<u>H$_a$H$_b$</u>t-Bu), 2.95 (1H, d, J 8.2, OCH$_a$<u>H$_b$</u>t-Bu), 2.30 (3H, s, $COCH_3$), 1.85 (1H, d, J 4.7, Aliphatic H), 1.75-1.47 (2H, m, Aliphatic H), 1.08 (3H, s, CH_3), 1.06-0.90 (2H, m, Aliphatic H), 0.88 (3H, s, CH_3), 0.85 (9H, s, t-Bu), 0.81 (3H, s, CH_3). **IR** ($CHCl_3$) (υ_{max}) : 2950 (C-H), 2870, 1730 (C=O), 1710 (C=O), 1645, 1360, 1320, 1240, 1140 cm^{-1}. **MS** (CI, NH_3) : 325 ($M^{+\cdot}$+1, 26), 237 ($M^{+\cdot}$-OCH_2t-Bu, 6), 223 (68), 222 (100), 194 (28), 153 (18), 152 (21), 135 (29), 123 (24), 109 (64), 95 (52), 85 ($COCH_2COCH_3^{+\cdot}$, 58). **Anal.** Calcd for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94. Found : C, 70.24; H, 10.00.

17e (92%). $[\alpha]_D^{25}$ = -25.7 (C 1.23, $CHCl_3$). **^{1}H NMR** (δ ppm) : 4.74 (1H, d, J 6.8, H-3), 3.48 (1H, d, J 15.5, $COCH_aH_bCO$), 3.38 (1H, d, J 15.5, $COCH_aH_bCO$), 3.28 (1H, d, J 6.8, H-2), 3.10 (1H, d, J 7.9, OCH_aH_bt-Bu), 3.03 (1H, d, J 7.9, OCH_aH_bt-Bu), 2.28 (3H, s, $COCH_3$), 1.78 (1H, d, J 4.8, Aliphatic H), 1.75-1.42 (2H, m, Aliphatic H), 1.12-0.95 (2H, m, Aliphatic H), 1.07 (3H, s, CH_3), 0.91 (3H, s, CH_3), 0.87 (9H, s, t-Bu), 0.79 (3H, s, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 2870, 1730 (C=O), 1710 (C=O), 1645, 1470, 1410, 1150, 1110 cm^{-1}. **MS** (CI, NH_3) : 325 ($M^{+\cdot}$+1, 4), 237 ($M^{+\cdot}$-OCH_2t-Bu, 14), 222 (77), 207 (12), 194 (20), 153 (28), 121 (46), 109 (49), 108 (53), 95 (70), 85 ($COCH_2COCH_3^+$, 91), 81 (41), 71 (CH_2t-Bu^+, 100). **Anal.** Calcd for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94. Found : C, 70.31; H, 9.92.

17f (98%). $[\alpha]_D^{25}$ = -19.8 (C 1.0, $CHCl_3$). **^{1}H NMR** (δ ppm) : 5.88 (1H, d, J 3.7, Aliphatic H), 5.31 (1H, broad s, Aliphatic H), 4.58 (1H, d, J 3.7, Aliphatic H), 4.24-3.98 (4H, m, Aliphatic H), 3.55 (1H, d, J 15.8, $COCH_aH_bCO$), 3.48 (1H, d, J 15.8, $COCH_aH_bCO$), 2.28 (3H, s, $COCH_3$), 1.52 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.32 (6H, s, 2 x CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2990, 2940 (C-H), 2900, 1750 (C=O), 1720 (C=O), 1625, 1450, 1405, 1365, 1255, 1150, 1075, 1020, 945, 885, 840 cm^{-1}. **MS** (CI, NH_3) : 362 ($M^{+\cdot}$+NH_4, 42), 346 ($M^{+\cdot}$+2, 27), 345 ($M^{+\cdot}$+1, 100), 329 ($M^{+\cdot}$-CH_3, 47), 287 ($M^{+\cdot}$-CH_2COCH_3, 32), 271 (3), 229 (4), 185 (5), 127 (7), 113 (17), 101 (58), 85 (20), 81 (9), 72 (8). **Anal.** Calcd for $C_{16}H_{24}O_8$: C, 55.81; H, 7.02. Found : C, 55.79; H, 6.93.

17g (96%). mp 52-54°C (Ether/petroleum ether). $[\alpha]_D^{25}$ = -6.9 (C 2.5, $CHCl_3$). **^{1}H NMR** (δ ppm) : 5.42 (1H, s, COCHOCO), 4.06 (1H, d, J 9.1, CH_aH_bO), 4.02 (1H, d, J 9.1, CH_aH_bO), 3.67 (1H, d, J 16.0, $COCH_aH_bCO$), 3.58 (1H, d, J 16.0, $COCH_aH_bCO$), 2.30 (3H, s, $COCH_3$), 1.24 (3H, s, CH_3), 1.11 (3H, s, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 3020, 2970 (C-H), 2930, 2900, 1800 (C=O), 1750 (C=O), 1720 (C=O), 1660, 1630, 1465, 1400, 1310, 1150, 1085, 1030, 1000 cm^{-1}. **MS** (CI, NH_3) : 232 ($M^{+\cdot}$+NH_4, 100), 215 ($M^{+\cdot}$+1, 18), 172 ($M^{+\cdot}$-$COCH_2$, 5), 86 (9), 85 (22). **Anal.** Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found : C, 56.09; H, 6.54.

General procedure for the preparation of α-diazoesters 18a-j. To a suspension of NaH (60% dispersion in oil), previously washed with anhydrous hexane (0.25 g, 10.5 mmol) in dry THF (40 ml) was added dropwise at 0°C, a solution of **17a** (2.78 g, 11.6 mmol) in dry THF (10 ml). The mixture was stirred at 0°C for 30 minutes then a solution of MeI (0.65 ml, 10.5 mmol) in dry THF (3 ml) was added dropwise. The solution was stirred at room temperature for 12h then treated at 0°C with a saturated solution of $NaHCO_3$ and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo* to afford the crude acetoacetate as an oil which was dissolved in a mixture of acetonitrile (15 ml) and triethylamine (2.3 ml, 16.6 mmol). Methanesulfonyl azide (2 g, 16.6 mmol) was then slowly added at room temperature and the mixture was stirred at room temperature for 4 days. The mixture was treated with water (10 ml) and extracted with ether. The combined extracts were washed with a 5% solution of KOH in water (3 x 20 ml), brine, dried ($MgSO_4$) and the solvent were evaporated *in vacuo*. Flash chromatography (Petroleum ether/EtOAc 99:1) gave **18a** as a yellow oil (1.28 g, 64 %). $[\alpha]_D^{25}$ = -88.1 (C 1.93, $CHCl_3$). **^{1}H NMR** (δ ppm) : 4.73 (1H, dt, J 4.4, 10.8, CHOCO), 2.06-0.83 (10H, m, Aliphatic H), 1.95 (3H, s, N_2CCH_3), 0.89 (3H, d, J 6.5, CH_3CHCH_3), 0.88 (3H, d, J 6.9, CH_3CHCH_3), 0.77 (3H, d, J 6.9, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2960, 2930 (C-H), 2870, 2080 (C=N=N), 1675 (C=O), 1455, 1350, 1305, 1155, 1140, 990, 950 cm^{-1}. **MS** (CI, NH_3) : 238 ($M^{+\cdot}$, 12), 169 (4), 139 (9), 138 (11), 95 (26), 83 ($COC(N_2)CH_3^+$, 100), 81 (37), 77 (12), 71 (12). **Anal.** Calcd for $C_{13}H_{22}O_2N_2$: C, 65.52; H, 9.30; N, 11.75. Found : C, 65.49; H, 9.28; N, 11.86.

18b (62%). $[\alpha]_D^{25}$ = -49.9 (C 1.35, $CHCl_3$). **^{1}H NMR** (δ ppm) : 4.74 (1H, dt, J 4.4, 10.9, CHOCO), 2.16 (2H, d, J 6.9, N_2CCH_2), 2.07-0.80 (10H, m, Aliphatic H), 0.96 (6H, d, J 6.6, CH_3CHCH_3), 0.91 (3H, d, J 6.6, CH_3CHCH_3), 0.89 (3H, d, J 7.0, CH_3CHCH_3), 0.78 (3H, d, J 7.0, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 2080 (C=N=N), 1675 (C=O), 1455, 1370, 1270, 1140, 980, 960 cm^{-1}. **MS** (CI, NH_3) : 297 ($M^{+\cdot}$+NH_3, 7), 280 ($M^{+\cdot}$, 3), 272 (15), 255 (16), 253 (12), 170 (18), 169 (21), 155 (9), 139 (27), 138 (60), 132 (31), 115 (16), 112 (16), 97 (42), 84 (14), 83 (100), 81 (62). **Anal.** Calcd for $C_{16}H_{28}O_2N_2$: C, 68.53; H, 10.06; N, 9.99. Found : C, 68.40; H, 10.02; N, 10.08.

18c (56%). $[\alpha]_D^{25}$ = -64.8 (C 1.73, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.37-7.22 (5H, m, Aromatic H), 4.78 (1H, dt, J 4.4, 10.8, CHOCO), 3.64 (2H, s, CH_2Ph), 2.09-2.01 (1H, m, Aliphatic H), 1.90-1.31 (6H, m, Aliphatic H), 1.14-0.94 (2H, m, Aliphatic H), 0.91 (3H, d, J 6.6, CH_3CHCH_3), 0.88 (3H, d, J 7.0, CH_3CHCH_3), 0.78 (3H, d, J 6.9, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2080 (C=N=N), 1675 (C=O), 1450, 1355, 1295, 1170, 1110, 980, 960 cm^{-1}. **MS** (CI, NH_3) : 332 ($M^{+\cdot}$+NH_4, 2), 306 (43), 182 (6), 171 (14), 170 (100), 169 (28), 124 (8), 95 (6), 91 ($C_7H_7^+$, 7), 77 ($C_6H_5^+$, 5). **Anal.** Calcd for $C_{19}H_{26}O_2N_2$: C, 72.58; H, 8.33; N, 8.91. Found : C, 72.52; H, 8.25; N, 8.98.

18d (76%). $[\alpha]_D^{25}$ = -58.7 (C 1.44, $CHCl_3$). **^{1}H NMR** (δ ppm) : 4.75 (1H, dt, J 4.4, 10.9, CHOCO), 3.22 (2H, s, CH_2CO_2t-Bu), 2.05-0.80 (9H, m, Aliphatic H), 1.47 (9H, s, t-Bu), 0.91 (3H, d, J 6.6, CH_3CHCH_3), 0.89 (3H, d, J 7.0, CH_3CHCH_3), 0.78 (3H, d, J 6.9, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 2090 (C=N=N), 1725 (C=O), 1675 (C=O), 1450, 1370, 1150, 1110 cm^{-1}. **MS** (CI, NH_3) : 237 ($M^{+\cdot}$-CO_2t-Bu, 2), 209 (6), 169 (8), 155 (5), 139 (28), 138 (46), 137 (13), 123 (26), 96 (19), 95 (62), 83 (55), 81 (100), 79 (26), 74 (47), 71 (26). **Anal.** Calcd for $C_{18}H_{30}O_4N_2$: C, 63.88; H, 8.93; N, 8.28. Found : C, 63.97; H, 8.78; N, 8.19.

18e (60%). $[\alpha]_D^{25}$ = -125.7 (C 1.4, $CHCl_3$). ^{1}H NMR (δ ppm) : 7.32-7.25 (2H, m, Aromatic H), 7.22-7.16 (3H, m, Aromatic H), 4.96 (1H, dt, J 4.4, 10.6, CHOCO), 2.66 (1H, dt, J 3.6, 10.9, CHPh), 2.23-2.19 (1H, m, Aliphatic H), 1.76 (3H, s, CH_3CN_2), 1.97-1.18 (7H, m, Aliphatic H). IR ($CHCl_3$)(υ_{max}) : 2930 (C-H), 2850, 2080 (C=N=N), 1660 (C=O), 1450, 1330, 1300, 1245, 1220, 1010 cm^{-1}. MS (EI) : 158 (24), 129 (9), 117 (10), 115 (10), 91 ($C_7H_7^+$, 100), 81 (14), 67 (10), 55 (17). Anal. Calcd for $C_{15}H_{18}O_2N_2$: C, 69.74; H, 7.02; N, 10.84. Found : C, 69.89; H, 7.07; N, 10.74.

18f (52%). $[\alpha]_D^{25}$ = -33.0 (C 0.8, $CHCl_3$). ^{1}H NMR (δ ppm) : 4.90 (1H, dt, J 4.4, 10.6, CHOCO), 1.97 (3H, s, CH_3CN_2), 2.01-0.80 (8H, m, Aliphatic H), 1.43 (1H, d, J 14.6, CH_aH_bt-Bu), 1.20 (1H, d, J 14.6, CH_aH_bt-Bu), 1.0 (3H, s, CH_3), 0.98 (12H, s, 4 x CH_3), 0.87 (3H, d, J 6.5, CH_3). IR ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 2080 (C=N=N), 1675 (C=O), 1455, 1410, 1360, 1140 cm^{-1}. MS (CI, NH_3) : 301 (14), 300 (37), 298 (15), 226 (26), 225 (4), 209 (29), 170 (19), 137 (27), 112 (27), 97 (32), 90 (100), 83 (23), 81 (32). Anal. Calcd for $C_{18}H_{32}O_2N_2$: C, 70.09; H, 10.46; N, 9.08. Found : C, 70.18; H, 10.54; N, 8.95.

18g (57%). $[\alpha]_D^{25}$ = +43.0 (C 1.32, $CHCl_3$). ^{1}H NMR (δ ppm) : 4.70 (1H, d, J 6.8, H-2), 3.45 (1H, d, J 6.8, H-3), 3.12 (1H, d, J 8.1, CH_aH_bt-Bu), 2.94 (1H, d, J 8.1, CH_aH_bt-Bu), 1.94 (3H, s, CH_3CN_2), 1.83 (1H, d, J 4.7, Aliphatic H), 1.75-1.45 (2H, m, Aliphatic H), 1.08 (3H, s, CH_3), 1.16-0.87 (2H, m, Aliphatic H), 0.86 (3H, s, CH_3), 0.85 (9H, s, t-Bu), 0.81 (3H, s, CH_3). IR ($CHCl_3$)(υ_{max}) : 2950 (C-H), 2870, 2080 (C=N=N), 1675 (C=O), 1475, 1460, 1380, 1305, 1145, 1100, 1075, 905 cm^{-1}. MS (EI) : 222 (10), 135 (11), 124 (9), 108 (14), 100 (4), 94 (17), 84 (26), 72 (CH_3t-Bu$^+$, 100), 56 (44). Anal. Calcd for $C_{18}H_{30}O_3N_2$: C, 67.05; H, 9.38; N, 8.69. Found : C, 67.15; H, 9.33; N, 8.71.

18h (58%). $[\alpha]_D^{25}$ = +19.8 (C 0.9, $CHCl_3$). ^{1}H NMR (δ ppm) : 4.83 (1H, d, J 6.7, H-3), 3.27 (1H, d, J 6.7, H-2), 3.11 (1H, d, J 7.9, CH_aH_bt-Bu), 3.02 (1H, d, J 7.9, CH_aH_bt-Bu), 1.93 (3H, s, CH_3CN_2), 1.74-1.42 (3H, m, Aliphatic H), 1.07 (3H, s, CH_3), 1.05-0.92 (2H, m, Aliphatic H), 0.91 (3H, s, CH_3), 0.87 (9H, s, t-Bu), 0.79 (3H, s, CH_3). IR ($CHCl_3$)(υ_{max}) : 2950 (C-H), 2870, 2080 (C=N=N), 1675 (C=O), 1475, 1385, 1330, 1305, 1150, 1100, 910 cm^{-1}. MS (EI) : 322 ($M^{+\cdot}$, 2), 222 (11), 194 (8), 153 (13), 135 (19), 109 (17), 96 (28), 93 (24), 84 (51), 82 (25), 72 (CH_3t-Bu$^+$, 100), 56 (86). Anal. Calcd for $C_{18}H_{30}O_3N_2$: C, 67.05; H, 9.38; N, 8.69. Found : C, 65.96; H, 9.18; N, 8.54.

18i (72%). $[\alpha]_D^{25}$ = -53.2 (C 1.0, $CHCl_3$). ^{1}H NMR (δ ppm) : 5.88 (1H, d, J 3.7, Aliphatic H), 5.28 (1H, d, J 3.8, Aliphatic H), 4.58 (1H, d, J 3.7, Aliphatic H), 4.27-3.98 (4H, m, Aliphatic H), 1.98 (3H, s, CH_3CN_2), 1.53 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.33 (3H, s, CH_3), 1.31 (3H, s, CH_3). IR ($CHCl_3$)(υ_{max}) : 2990, 2930 (C-H), 2090 (C=N=N), 1690 (C=O), 1450, 1370, 1290, 1250, 1130, 1075, 1020 cm^{-1}. MS (CI, NH_3) : 343 ($M^{+\cdot}$+1, 36), 327 ($M^{+\cdot}$-CH_3, 22), 315 (36), 299 (26), 285 (48), 257 (33), 185 (6), 174 (5), 155 (5), 138 (6), 113 (17), 109 (18), 101 (100), 95 (15), 85 (16), 83 (20), 81 (36), 72 (16). Anal. Calcd for $C_{15}H_{22}O_7N_2$: C, 52.63; H, 6.48; N, 8.18. Found : C, 52.60; H, 6.55; N, 8.10.

18j (64%). $[\alpha]_D^{25}$ = +12.9 (C 1.0, $CHCl_3$). ^{1}H NMR (δ ppm) : 5.43 (1H, s, COCHOCO), 4.07 (1H, d, J 9.1, CH_aH_bO), 4.03 (1H, d, J 9.1, CH_aH_bO), 2.02 (3H, s, CH_3CN_2), 1.23 (3H, s, CH_3), 1.11 (3H, s, CH_3). IR ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2900, 2100 (C=N=N), 1790 (C=O), 1690 (C=O), 1465, 1370, 1365, 1130, 1010 cm^{-1}. MS (CI, NH_3) : 230 ($M^{+\cdot}$+NH_4, 46), 213 ($M^{+\cdot}$+1, 17), 204 (27), 185 (35), 184 ($M^{+\cdot}$-N_2, 13), 170 (27), 132 (22), 99 (9), 86 (13), 83 (15), 74 (12). Anal. Calcd for $C_9H_{12}O_4N_2$: C, 50.94; H, 5.70; N, 13.20. Found : C, 50.80; H, 5.72; N, 13.04.

(2*R, 5*R**)-5-Methyl-2-[(1,1,3,3-tetramethyl)butyl]cyclohexanone 20**. To a suspension of magnesium (0.9 g, 36.8 mmol) in dry ether (10 ml) under nitrogen was added a small portion of a solution of t-BuCH_2Br (4.7 ml, 36.8 mmol) in dry ether (15 ml). The reaction mixture was then heated under reflux and the remaining of the solution of t-BuCH_2Br was added at such a rate to maintain a gentle reflux. After the addition was complete, the reaction mixture was refluxed for 1h. The solution was cooled down to room temperature and slowly added to a suspension of copper iodide (0.7 g, 3.7 mmol) in dry ether (20 ml) at -30°C. The reaction mixture was then stirred at -20°C for 30 minutes and a solution of R-(+)-pulegone **19** (5 ml, 30.7 mmol) in dry ether (10 ml) was slowly added at -30°C over a period of 10 minutes. The resulting mixture was stirred at -20°C for 6h then allowed to warm to room temperature overnight and finally refluxed for 4h. The solution was cooled down to room temperature and was poured into a cooled 1M solution of HCl. The organic layer was decanted, then filtered. The aqueous layer was saturated with ammonium chloride and extracted with ether. The combined extracts were washed with a saturated solution of $NaHCO_3$, dried ($MgSO_4$) and the solvents evaporated *in vacuo*. Flash chromatography (CH_2Cl_2/MeOH 99.5:0.5) afforded pulegone (3.5 g) and a 1/1 mixture (^{1}H NMR) of diastereoisomers **20** (1.12 g, corrected yield: 57%). A mixture of the preceding ketones **20** (1.12 g, 5 mmol) in ethanol (11 ml), water (1.5 ml) and KOH (1 g, 23 mmol) was then refluxed for 4h. The solution was concentrated *in vacuo*, saturated with sodium chloride and extracted with ether. The combined extracts were dried ($MgSO_4$) and the solvents evaporated *in vacuo*. Flash chromatography of the residue (CH_2Cl_2/MeOH 99:1) afforded a 78:22 mixture of diastereoisomers **20** (0.84 g, 75%) as a colourless oil. ^{1}H NMR (δ ppm)(2 diastereoisomers) : 2.33-0.90 (32H, m, Aliphatic H), 1.07 (3H, s, CH_3), 1.06 (3H, s, CH_3), 0.98 (9H, s, t-Bu), 0.97 (9H, s, t-Bu). IR ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 1700 (C=O), 1450, 1260, 1120, 1000 cm^{-1}. MS (CI, NH_3) : 231 (41), 230 (100), 224 ($M^{+\cdot}$, 1), 216 (11), 215 (85), 186 (5), 170 (5), 112 (15), 94 (21), 91 (9), 78 (22), 71 (t-Bu$CH_2^{+\cdot}$, 6). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found : C, 81.28; H, 11.37.

Pantolactone phenylacetic ester 21. To a solution of phenylacetic acid (3.45 g, 25.3 mmol) in dry CH_2Cl_2 (30 ml) was added dropwise freshly distilled $SOCl_2$ (5.5 ml, 75.9 mmol). The solution was refluxed for 20h then concentrated under vacuum. The residue was dissolved in dry CH_2Cl_2 (20 ml) then a solution of D-pantolactone (3 g, 25.3 mmol), pyridine (2.05 ml, 27.8 mmol) and dimethylaminopyridine (0.14 g, 1.26 mmol) in dry CH_2Cl_2 (10 ml) was added slowly at 0°C. The mixture was stirred at room temperature for 15h then washed successively with a 1M solution of HCl, a saturated solution of $NaHCO_3$, brine, dried ($MgSO_4$) and the solvents were evaporated *in vacuo*. Flash chromatography of the residue (CH_2Cl_2/MeOH 99.5:0.5) gave **21** as a colourless oil (3.77 g, 66%). $[\alpha]_D^{25}$ = +11.9 (C 1.0, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.41-7.25 (5H, m, Aromatic H), 5.37 (1H, s, COCHOCO), 4.06 (1H, d, J 19.2, C$\underline{H_a}H_b$O), 3.97 (1H, d, J 19.2, CH$_a\underline{H_b}$O), 3.79 (2H, s, CH_2Ph), 1.12 (3H, s, CH_3), 0.99 (3H, s, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 3020, 2960 (C-H), 2900, 1790 (C=O), 1740 (C=O), 1600 (C=C), 1495, 1460, 1400, 1370, 1295, 1240, 1140, 1085, 1030, 1000 cm^{-1}. **MS** (CI, NH_3) : 249 ($M^{+\cdot}$+1, 2), 119 ($PhCH_2CO^+$, 9), 118 ($PhCHCO^{+\cdot}$, 78), 91 ($C_7H_7^+$, 100), 89 (5). **Anal.** Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found : C, 67.57; H, 6.38.

Pantolactone α-diazophenylacetic ester 22. To a solution of **21** (0.78 g, 3.14 mmol) and ABSA (0.98 g, 4.08 mmol) in acetonitrile (30 ml), DBU (0.47 ml, 3.14 mmol) was added dropwise at 0°C. The solution was stirred at room temperature for 15h then treated with a saturated solution of NH_4Cl. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and the solvents evaporated *in vacuo*. Flash chromatography of the residue (Petroleum ether/EtOAc 6:4) gave **22** as a brown oil (0.53 g, 62%). $[\alpha]_D^{25}$ = +7.0; $[\alpha]_{546}^{25}$ = +13.9 (C 0.95, $CHCl_3$). **^{1}H NMR** (δ ppm) : 7.51-7.19 (5H, m, Aromatic H), 5.55 (1H, s, COCHOCO), 4.09 (2H, s, CH_2O), 1.28 (3H, s, CH_3), 1.15 (3H, s, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2910, 2100 (C=N=N), 1790 (C=O), 1745, 1705 (C=O), 1600 (C=C), 1495, 1460, 1370, 1360, 1240, 1210, 1140, 1010 cm^{-1}. **MS** (CI, NH_3) : 274 ($M^{+\cdot}$, 2), 247 (11), 118 ($PhCHCO^{+\cdot}$, 45), 114 (27), 106 (12), 105 (100), 99 (42), 91 ($C_7H_7^{+\cdot}$, 48), 89 (25), 77 ($C_6H_5^{+\cdot}$, 35). **Anal.** Calcd for $C_{14}H_{14}O_4N_2$: C, 61.31; H, 5.14; N, 10.21. Found : C, 61.42; H, 5,18; N, 10.03.

General procedure for asymmetric insertion of chiral rhodium-carbenoid into $PhMe_2SiH$ (and Et_3SiH, Ph_3SiH). Following the procedure described above for the synthesis of **9a**, compound **13a** was obtained from **18a** as a colourless oil (208 mg, 70%)(see table 1). This material was identical (IR, ^{1}H NMR) with the one prepared by alkylation.

General procedure for asymmetric insertion of chiral rhodium-carbenoid into $ClSiMe_2H$. Following the procedure described above for the synthesis of **9b**, compound **13b** was obtained from **18a** as a colourless oil (0.52 g, 74%)(see table 1). This material was identical (IR, ^{1}H NMR) with the one prepared by alkylation.

23a. **^{1}H NMR** (δ ppm) (2 diastereoisomers) : 4.66 (2H, dt, J 4.3, 10.8, 2 x CHOCO), 2.14 (2H, q, J 7.1, 2 x SiC$\underline{H}$CH$_3$), 2.07-1.81 (4H, m, Aliphatic H), 1.71-1.61 (4H, m, Aliphatic H), 1.56-0.79 (10H, m, Aliphatic H), 1.21 (3H, d, J 7.1, SiCHC$\underline{H_3}$), 1.19 (3H, d, J 7.1, SiCHC$\underline{H_3}$), 0.98 (18H, t, J 7.9, 2 x Si($CH_2C\underline{H_3}$)$_3$), 0.92-0.84 (12H, m, 2 x C$\underline{H_3}$CHC$\underline{H_3}$), 0.76 (3H, d, J 6.9, CH_3), 0.75 (3H, d, J 7.0, CH_3), 0.63 (12H, q, J 7.7, 2 x Si($C\underline{H_2}CH_3$)$_3$). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 2870, 1690 (C=O), 1450, 1370, 1310, 1180, 1140, 1005, 905 cm^{-1}. **MS** (EI) : 297 ($M^{+\cdot}$-C_2H_5, 5), 241 (8), 159 (90), 131 (13), 115 ($Si(C_2H_5)_3^{+\cdot}$, 18), 103 (100), 84 (43), 76 (44), 60 (43), 58 ($C_2H_5SiH^{+\cdot}$, 34), 56 (63). **Anal.** Calcd for $C_{19}H_{38}O_2Si$: C, 69.88; H, 11.73; Si, 8.60. Found : C, 69.95; H, 11.62; Si, 8.51.

23b. **^{1}H NMR** (δ ppm)(2 diastereoisomers) : 7.68-7.57 (6H, m, Aromatic H), 7.49-7.33 (9H, m, Aromatic H), 4.54 (1H, dt, J 4.1, 10.8, CHOCO), 4.48 (1H, dt, J 4.1, 10.8, CHOCO), 2.96 (2H, q, J 7.3, 2 x SiC$\underline{H}$CH$_3$), 1.75-0.80 (18H, m, Aliphatic H), 1.38 (3H, d, J 7.3, SiCHC$\underline{H_3}$), 1.36 (3H, d, J 7.3, SiCHC$\underline{H_3}$), 0.83 (3H, d, J 7.0, CH_3), 0.80 (3H, d, J 6.6, CH_3), 0.69 (3H, d, J 6.3, CH_3), 0.67 (3H, d, J 7.0, CH_3), 0.62 (3H, d, J 7.0, CH_3), 0.50 (3H, d, J 7.0, CH_3). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 1700 (C=O), 1450, 1425, 1370, 1305, 1250, 905 cm^{-1}. **MS** (EI) : 393 ($M^{+\cdot}$-Ph, 6), 259 ($Si(Ph)_3^{+\cdot}$, 67), 254 (82), 199 (42), 181 (36), 138 (17), 105 ($PhSi^{+\cdot}$, 27), 95 (31), 84 (67), 82 (42), 70 (50), 58 (32), 56 (100). **Anal.** Calcd for $C_{31}H_{38}O_2Si$: C, 79.10; H, 8.14; Si, 5.97. Found : C, 79.01; H, 8.22; Si, 6.00.

23c. **^{1}H NMR** (δ ppm) (2 diastereoisomers) : 7.57-7.53 (4H, m, Aromatic H), 7.40-7.33 (6H, m, Aromatic H), 4.68 (2H, dt, J 4.4, 10.9, 2 x CHOCO), 2.30 (2H, m, 2 x SiCH), 1.71-0.88 (24H, m, Aliphatic H), 0.92-0.89 (24H, m, 4 x C$\underline{H_3}$CHC$\underline{H_3}$), 0.78 (3H, d, J 7.0, CH_3), 0.76 (3H, d, J 7.0, CH_3), 0.34 (12H, s, 2 x Si$(CH_3)_2$). This sensitive product was used in the next step without further purification.

23d. **^{1}H NMR** (δ ppm) (2 diastereoisomers) : 7.61-7.57 (4H, m, Aromatic H), 7.42-7.37 (6H, m, Aromatic H), 7.23-7.08 (10H, m, Aromatic H), 4.60-4.45 (2H, m, 2 CHOCO), 3.10-2.95 (2H, m, C$\underline{H_2}$Ph), 2.80-2.60 (2H, m, C$\underline{H_2}$Ph), 2.56 (2H, dd, J 2.6, 12.4, SiC$\underline{H}$CH$_2$), 1.80-0.70 (18H, m, Aliphatic H), 0.82 (12H, d, J 6.5, 2 x C$\underline{H_3}$CHC$\underline{H_3}$), 0.70 (3H, d, J 7.0, CH_3), 0.66 (3H, d, J 7.0, CH_3), 0.53-0.48 (12H, m, 2 x Si$(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 1690 (C=O), 1635, 1600 (C=C), 1490, 1450, 1370, 1310, 1250 (Si-C), 1160, 1150, 1115, 1010, 980, 910, 850, 815 cm^{-1}. **MS** (CI, NH_3) : 207 (43), 206 (100), 205 (35), 138 (12), 135 ($PhSi(CH_3)_2^{+\cdot}$, 26), 131 (4), 95 (9), 91 ($C_7H_7^{+\cdot}$, 14), 83 (26), 77 ($C_6H_5^{+\cdot}$, 7). **Anal.** Calcd for $C_{27}H_{38}O_2Si$: C, 76.72; H, 9.06; Si, 6.64. Found : C, 76.81; H, 9.11; Si, 6.67.

23e. **^{1}H NMR** (δ ppm)(2 diastereoisomers) : 7.53-7.49 (4H, m, Aromatic H), 7.39-7.34 (6H, m, Aromatic H), 4.67 (2H, dt, J 4.3, 10.8, 2 CHOCO), 2.76-2.64 (4H, m, 2 x SiCHC$\underline{H_2}$), 2.12 (2H, dd, J 4.8, 9.1, 2 x SiC$\underline{H}$CH$_2$), 2.0-0.80 (18H, m,

Aliphatic H), 1.39 (18H, s, 2 x t-Bu), 0.88 (6H, d, J 6.5, $C\underline{H}_3CHC\underline{H}_3$), 0.86 (6H, d, J 6.6, $C\underline{H}_3CHC\underline{H}_3$), 0.72 (6H, d, J 6.9, 2 x CH_3), 0.41 (6H, s, $Si(CH_3)_2$), 0.38 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}) : 2950, 2920 (C-H), 2870, 1720 (C=O), 1700 (C=O), 1450, 1365, 1310, 1250 (Si-C), 1210, 1145, 1110, 910 cm^{-1}. **MS** (CI, NH_3) : 447 (M^++1, 2), 375 (9), 314 (8), 313 (23), 237 (67), 176 (15), 175 (100), 174 (62), 138 (19), 137 (41), 135 ($PhSi(CH_3)_2^+$, 64), 129 (32), 83 (74), 81 (40), 75 (49). **Anal.** Calcd for $C_{26}H_{42}O_4Si$: C, 69.91; H, 9.48; Si, 6.29. Found : C, 69.85; H, 9.54; Si, 6.15.

23f. ^{1}**H NMR** (δ ppm)(2 diastereoisomers) : 7.57-7.51 (4H, m, Aromatic H), 7.40-7.31 (6H, m, Aromatic H), 4.81 (1H, dt, J 4.2, 10.7, CHOCO), 4.75 (1H, dt, J 4.2, 10.7, CHOCO), 2.22 (1H, q, J 7.3, $SiC\underline{H}CH_3$), 2.21 (1H, q, J 7.1, $SiC\underline{H}CH_3$), 1.88-0.80 (20H, m, Aliphatic H), 1.20 (3H, d, J 7.3, $SiCHC\underline{H}_3$), 1.15 (3H, d, J 7.1, $SiCHC\underline{H}_3$), 0.98 (12H, s, 4 x CH_3), 0.97 (12H, s, 4 x CH_3), 0.96 (6H, s, 2 x CH_3), 0.84 (3H, d, J 6.5, CH_3), 0.83 (3H, d, J 6.4, CH_3), 0.42 (3H, s, $SiCH_3$), 0.41 (3H, s, $SiCH_3$), 0.40 (3H, s, $SiCH_3$), 0.38 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2950, 2920 (C-H), 2870, 1695 (C=O), 1600 (C=C), 1455, 1365, 1310, 1250 (Si-C), 1185, 1110, 910, 835, 815 cm^{-1}. **MS** (CI, NH_3): 434 ($M+NH_4^+$, 41), 417 (M^++1, 14), 345 (M^+-CH_2t-Bu, 7), 304 (16), 300 (39), 226 (42), 209 (20), 193 (17), 152 (36), 135 ($PhSi(CH_3)_2^+$, 40), 131 (68), 130 (84), 110 (18), 105 ($PhSi^+$, 10), 95 (15), 92 (100), 91 ($C_7H_7^+$, 13), 81 (23).

23g. ^{1}**H NMR** (δ ppm) (2 diastereoisomers) : 7.57-7.51 (4H, m, Aromatic H), 7.39-7.31 (6H, m, Aromatic H), 4.54 (1H, d, J 6.9, H-2), 4.47 (1H, d, J 6.9, H-2), 3.43 (1H, d, J 6.9, H-3), 3.42 (1H, d, J 6.9, H-3), 3.10 (1H, d, J 8.3, $OC\underline{H}_aH_b$t-Bu), 3.08 (1H, d, J 8.3, $OC\underline{H}_aH_b$t-Bu), 2.96 (2H, d, J 8.1, 2 x $OCH_a\underline{H}_b$t-Bu), 2.32 (1H, q, J 7.2, $SiC\underline{H}CH_3$), 2.25 (1H, q, J 7.2, $SiC\underline{H}CH_3$), 1.82 (2H, d, J 4.7, Aliphatic H), 1.73-1.40 (4H, m, Aliphatic H), 1.18 (3H, d, J 7.2, $SiCHC\underline{H}_3$), 1.13 (3H, d, J 7.2, $SiCHC\underline{H}_3$), 1.08 (6H, s, 2 x CH_3), 1.04-0.87 (4H, m, Aliphatic H), 0.85 (9H, s, t-Bu), 0.84 (9H, s, t-Bu), 0.79 (3H, s, CH_3), 0.78 (3H, s, CH_3), 0.75 (3H, s, CH_3), 0.73 (3H, s, CH_3), 0.40 (3H, s, $SiCH_3$), 0.39 (3H, s, $SiCH_3$), 0.37 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 2870, 1700 (C=O), 1475, 1460, 1360, 1250 (Si-C), 1180, 1140, 1100, 1050, 910, 835, 820 cm^{-1}. **MS** (EI) : 222 (19), 191 (31), 169 (7), 152 (8), 135 (Ph $Si(CH_3)_2^+$, 100), 109 (14), 94 (11), 72 (81), 58 (22), 56 (26). **Anal.** Calcd for $C_{26}H_{42}O_3Si$: C, 72.51; H, 9.83; Si, 6.52. Found : C, 72.39; H, 9.94; Si, 6.62.

23h. ^{1}**H NMR** (δ ppm)(2 diastereoisomers) : 7.54-7.49 (4H, m, Aromatic H), 7.39-7.32 (6H, m, Aromatic H), 4.65 (1H, d, J 6.8, H-3), 4.56 (1H, d, J 6.8, H-3), 3.24 (1H, d, J 6.0, H-2), 3.19 (1H, d, J 5.7, H-2), 3.09 (2H, d, J 8.3, 2 x $C\underline{H}_aH_b$t-Bu), 2.98 (2H, d, J 8.1, 2 x $CH_a\underline{H}_b$t-Bu), 2.29 (1H, q, J 7.2, $SiC\underline{H}CH_3$), 2.21 (1H, q, J 7.2, $SiC\underline{H}CH_3$), 1.74-1.39 (6H, m, Aliphatic H), 1.18 (3H, d, J 7.2, $SiCHC\underline{H}_3$), 1.13 (3H, d, J 7.2, $SiCHC\underline{H}_3$), 1.05 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.02-0.92 (4H, m, Aliphatic H), 0.90 (3H, s, CH_3), 0.89 (3H, s, CH_3), 0.87 (18H, s, 2 x t-Bu), 0.76 (3H, s, CH_3), 0.75 (3H, s, CH_3), 0.41 (3H, s, $SiCH_3$), 0.40 (3H, s, $SiCH_3$), 0.39 (3H, s, $SiCH_3$), 0.38 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 2870, 1695 (C=O), 1470, 1455, 1310, 1250 (Si-C), 1180, 1140, 905 cm^{-1}. **MS** (EI) : 430 (M^+,3), 222 (19), 191 (30), 153 (11), 135 ($PhSi(CH_3)_2^+$, 100), 121 (17), 109 (21), 95 (12), 82 (16), 72 (66), 56 (46). **Anal.** Calcd for $C_{26}H_{42}O_3Si$: C, 72.51; H, 9.83; Si, 6.52. Found : C, 72.47; H, 9.86; Si, 6.34.

23i. ^{1}**H NMR** (δ ppm)(2 diastereoisomers) : 7.55-7.50 (4H, m, Aromatic H), 7.42-7.35 (6H, m, Aromatic H), 5.64 (1H, d, J 3.7, Aliphatic H), 5.43 (1H, d, J 3.7, Aliphatic H), 5.11 (1H, d, J 2.7, Aliphatic H), 5.09 (1H, d, J 2.9, Aliphatic H), 4.14-3.93 (9H, m, Aliphatic H), 3.75 (1H, d, J 3.7, Aliphatic H), 2.33 (1H, q, J 7.0, $SiC\underline{H}CH_3$), 2.31 (1H, q, J 7.1, $SiC\underline{H}CH_3$), 1.49 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.40 (6H, s, 2 x CH_3), 1.31 (3H, s, CH_3), 1.30 (3H, s, CH_3), 1.27 (6H, s, 2 x CH_3), 1.23 (3H, d, J 7.1, $SiCHC\underline{H}_3$), 1.21 (3H, d, J 7.1, $SiCHC\underline{H}_3$), 0.42 (3H, s, $SiCH_3$), 0.41 (3H, s, $SiCH_3$), 0.40 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3000, 2950 (C-H), 1720 (C=O), 1460, 1380, 1320, 1250 (Si-C), 1165, 1080, 1020, 820 cm^{-1}. **MS** (CI, NH_3) : 435 (M^+-CH_3, 67), 393 (16), 349 (3), 219 (6), 191 (21), 156 (9), 135 ($PhSi(CH_3)_2^+$, 77), 101 (100), 91 ($C_7H_7^+$, 6), 75 (20). **Anal.** Calcd for $C_{23}H_{34}O_7Si$: C, 61.31; H, 7.61; Si, 6.23. Found : C, 60.61; H, 7.54; Si, 6.13.

Propane-1,2-diol 24a.[22] To a solution of **13b** (0.32 g, 0.97 mmol) in dry ether (12 ml) was added dropwise at -65°C a 1M solution of DIBAH in toluene (1.94 ml, 1.94 mmol). The mixture was stirred at -65°C for 30 minutes, then treated with a 1M solution of HCl at room temperature for 30 minutes and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo*. To a solution of the resulting silane in a 1:1 mixture of MeOH-THF (6 ml) was added at room temperature, $KHCO_3$ (0.29 g, 2.91 mmol), KF (0.17 g, 2.91 mmol) then a 30% solution of H_2O_2 (1.94 ml, 19.4 mmol). The mixture was stirred for 15h then treated cautiously at 0°C with $Na_2S_2O_3$ (1.8 g). The mixture was stirred at room temperature for 30 minutes, then diluted with ether, dried ($MgSO_4$) and the solvents were evaporated *in vacuo* to give a yellow oil which was purified by chromatography on silica gel (CH_2Cl_2/MeOH 99:1) to afford (-)-menthol (128 mg, 85%) and **24a** (46 mg, 62%).

Similarly, to a solution of **13a** (0.24 g, 0.69 mmol) in dry ether (8 ml) was added dropwise at -65°C a 1M solution of DIBAH in toluene (1.38 ml, 1.38 mmol). The mixture was stirred at -65°C for 30 minutes, then treated with a 1M solution of HCl at room temperature for 30 minutes and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and the solvents were evaporated *in vacuo*. To the resulting oil in solution in peracetic acid (32% in acetic acid) (3.6 ml) and acetic anhydride (0.5 ml) was added $Hg(OAc)_2$

(0.33 g; 1.03 mmol). The mixture was stirred at room temperature for 2h and evaporated *in vacuo*. Ether was then added to the residue and the mixture was filtered and the solvent evaporated *in vacuo*. Flash chromatography on silica gel (CH_2Cl_2/MeOH 99:1) gave (-)-menthol (87 mg, 80%) and **24a** (25 mg, 48%). **^{1}H NMR** (δ ppm) : 3.92 (1H, ddq, J 2.9, 6.4, 7.8, $CH_3C\underline{H}OH$), 3.64 (1H, dd, J 2.9, 11.0, $C\underline{H}_a\underline{H}_bOH$), 3.40 (1H, dd, J 7.8, 11.0, $CH_a\underline{H}_bOH$), 2.51 (2H, broad s, 2 x OH), 1.17 (3H, d, J 6.4, $CHC\underline{H}_3$). **IR** ($CHCl_3$) (υ_{max}) : 3400 (O-H), 2970, 2920 (C-H), 2880, 1450, 1375, 1130, 1035, 990, 920, 835 cm^{-1}.

4-Methylpentane-1,2-diol 24b.[22] (45%, 2 steps). **^{1}H NMR** (δ ppm) : 3.86-3.78 (1H, m, $CH_2C\underline{H}OH$), 3.67 (1H, dd, J 3.0, 11.1, $C\underline{H}_a\underline{H}_bOH$), 3.43 (1H, dd, J 7.8, 11.1, $CH_a\underline{H}_bOH$), 2.09 (2H, broad s, 2 x OH), 1.84-1.73 (1H, m, $CH_3C\underline{H}CH_3$), 1.47-1.33 (1H, m, $C\underline{H}_c\underline{H}_dCHOH$), 1.25-1.14 (1H, m, $CH_c\underline{H}_dCHOH$), 0.95 (3H, d, J 6.6, $CH_3CHC\underline{H}_3$), 0.93 (3H, d, J 6.6, $C\underline{H}_3CHCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3580, 3400 (O-H), 2950, 2920 (C-H), 2870, 1465, 1365, 1260, 1070, 910 cm^{-1}.

3-Phenylpropane-1,2-diol 24c.[22] (50%, 2 steps). **^{1}H NMR** (δ ppm) : 7.37-7.22 (5H, m, Aromatic H), 3.97 (1H, dddd, J 3.2, 5.7, 7.0, 7.7, $CH_2C\underline{H}OH$), 3.71 (1H, dd, J 3.2, 11.1, $C\underline{H}_a\underline{H}_bOH$), 3.53 (1H, dd, J 7.0, 11.1, $CH_a\underline{H}_bOH$), 2.80 (1H, dd, J 5.7, 13.6, $PhC\underline{H}_c\underline{H}_d$), 2.78 (1H, dd, J 7.7, 13.6, $PhCH_c\underline{H}_d$), 2.18 (2H, broad s, 2 x OH). **IR** ($CHCl_3$) (υ_{max}) : 3400 (O-H), 2970, 2920 (C-H), 2880, 1450, 1375, 1130, 1035, 990, 920, 835 cm^{-1}.

General procedure for the conversion of diols 24 into the corresponding acetals 25. A solution of propane- 1,2-diol **24a** (3 mg, 0.04 mmol), benzaldehyde (0.005 ml, 0.048 mmol) and *p*-toluenesulfonic acid (5 mg, 0.026 mmol) in dry benzene (5 ml) was refluxed for 20 minutes. The mixture was then cooled down to room temperature and washed successively with a 2% solution of Na_2CO_3, water, a 35% solution of $NaHSO_3$, water, dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. The mixture was analyzed without further purification using ^{1}H NMR (360 MHz) and $Eu(hfc)_3$.

27a. **27a** was prepared according to the general asymmetric insertion protocol described for **13a**. (62%). **^{1}H NMR** (δ ppm)(2 diastereoisomers) : 7.58-7.52 (4H, m, Aromatic H), 7.40-7.34 (6H, m, Aromatic H), 5.34 (2H, s, 2 x COCHOCO), 4.0 (2H, s, CH_2O), 3.97 (2H, s, CH_2O), 2.46 (1H, q, J 7.1, $SiC\underline{H}CH_3$), 2.40 (1H, q, J 7.1, $SiC\underline{H}CH_3$), 1.26 (3H, d, J 7.1, $SiCHC\underline{H}_3$), 1.18 (3H, d, J 7.1, $SiCHC\underline{H}_3$), 1.15 (3H, s, CH_3), 1.06 (3H, s, CH_3), 1.01 (3H, s, CH_3), 0.93 (3H, s, CH_3), 0.47 (3H, s, $SiCH_3$), 0.46 (3H, s, $SiCH_3$), 0.44 (3H, s, $SiCH_3$), 0.43 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2900, 2880, 1790 (C=O), 1720 (C=O), 1460, 1400, 1380, 1370, 1310, 1260 ($Si(CH_3)$), 1160, 1130, 1110, 1100, 1010, 1000, 840, 820 cm^{-1}. **MS** (CI, NH_3) : 320 ($M^{+\cdot}$, 9), 305 ($M^{+\cdot}$-CH_3, 3), 264 (10), 249 (8), 207 (26), 191 (20), 187 (19), 186 (18), 171 (18), 137 (21), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 107 (11), 105 ($PhSi^{+\cdot}$, 20), 91 ($C_7H_7^{+\cdot}$, 13), 83 (13), 75 (24). **Anal.** Calcd for $C_{17}H_{24}O_4Si$: C, 63.72; H, 7.55; Si, 8.76. Found : C, 63.71; H, 7.52; Si, 8.78. This product was converted into diol **24a** according to the general procedure.

27b. **27b** was prepared as above (67%). **^{1}H NMR** (δ ppm)(2 diastereoisomers) : 7.62-7.16 (10H, m, Aromatic H), 5.36 (1H, s, COCHOCO), 5.34 (1H, s, COCHOCO), 4.00 (2H, s, CH_2O), 3.96 (2H, s, CH_2O), 3.79 (1H, s, SiCH), 3.74 (1H, s, SiCH), 1.14 (3H, s, CH_3), 1.12 (3H, s, CH_3), 1.00 (3H, s, CH_3), 0.99 (3H, s, CH_3), 0.47 (3H, s, $SiCH_3$), 0.42 (3H, s, $SiCH_3$), 0.35 (6H, s, 2 x $SiCH_3$). This sensitive product was converted into 1-phenylethane-1,2-diol following the general procedure described for **24a**.

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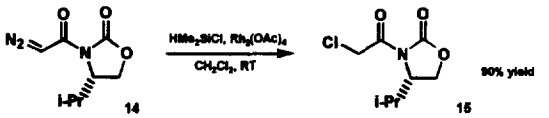

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