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Mukaiyama Aldol and Michael Reactions Catalyzed by Lanthanide Iodides

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Abstract : Samarium diiodide is an efficient catalyst precursor which allows the formation of condensation products between various carbonyl compounds and ketene silyl acetals or enoxysilanes. With α,β-unsaturated carbonyl compounds, 1,2- or 1,4-additions are observed according to the structure of the substrate. α,β-Unsaturated ketones yield to enoxysilanes by selective Michael additions. Aldol poducts are isolated as silyl ethers. The mechanisms of the reactions are discussed.

Keywords : Aldol reactions; Michael additions; samarium diiodide; lanthanides.

INTRODUCTION

Mukaiyama aldol and Michael reactions are important tools for carbon-carbon bond forming reactions[1] and have been widely developed since the initial report on the $TiCl_4$ mediated reaction between ketene silyl acetals and carbonyl compounds[2].

A great variety of Lewis acids have been described as promoters or catalysts for these reactions. After the first generation of Lewis acids, titanium tetrachloride, tin tetrachloride or boron trifluoride etherate[3] which where used in stoichiometric amounts, different types of catalysts have been reported such as tin (II) chloride[4], trityl or silver perchlorates[5] or transition metal complexes[6]. The introduction of electronegative ligands such as triflates or pentafluorophenyl ligands enhance the catalytic activity by increasing the Lewis acidity of the compounds[7, 8] . The activity of the catalysts can also be exalted by the presence of an activating agent such as metallic iodides for the reactions induced by $BiCl_3$[9]. Promoted or catalyzed aldol reactions have also been reported, using titanium silicate molecular sieves, sulfated zirconia, neutral alumina[10] or fluoride derivatives[11].

Recently the Lewis acid properties of lanthanides compounds have found numerous applications in catalysis. The first example of Mukaiyama aldol reactions catalyzed by lanthanides was described by Kagan and Vougioukas and involved addition of ketene trimethylsilyl acetal of methyl isobutyrate on aldehdes using lanthanide trichlorides as catalysts[12]. A similar reactivity was observed with a bis disubstituted-cyclopentadienyl ytterbium chloride[13]. $Eu(dppm)_3$ catalyzes aldol reactions with various aldehydes and diastereoselective additions were obtained when a chelating group is present in α-position of the carbonyl

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compounds[14]. Other europium derivatives such as $EuCl_3$ or $Eu(tfc)_3$ catalyze Michael additions of α,β-unsaturated ketones with 1,3-dicarbonyl compounds[15]. Divalent and trivalent samarium alkoxides promote the reaction of ketene silyl acetals with aldehydes and the samarium bis-menthoxide gives modest enantioselectivities[16]. The condensation of α-chloroketones on aldehydes is catalyzed by lanthanide tert-butoxides or more efficiently by $Sm(HMDS)_3$[17]. Since the first report of Kobayashi in 1991 on the activity of ytterbium triflate for the catalysis of the reaction of formaldehyde with silyl enol ethers[18], lanthanide and scandium triflates have been largely developed for aldol and Michael reactions[19] as well as for various Lewis acid-induced reactions [20]. The great interest of lanthanide and scandium triflates lies in their stability in the presence of water and also the possibility to reuse the catalyst. Recently Shibasaki *et al.* described several asymmetric lanthanide catalysts for aldol and Michael reactions. Catalysts prepared from lanthanum isopropoxide, either alkali metal free La-BINOL, or La-Na-BINOL (LSB), give high enantioselectivities for Michael and nitroaldol reactions[21]. Moderate enantiomeric excesses were obtained in Mukaiyama aldol reactions with catalysts prepared from lanthanide triflates and a chiral sulfonamide ligand[22].

Samarium diiodide, for most applications, is employed for its reductive character as a stoichiometric reagent or in excess[23]. Recently however, samarium diiodide has been used in catalytic amounts for coupling reactions through *in situ* regeneration of the divalent samarium by magnesium or zinc amalgam[24]. In an other hand reactions such as MPVO[25] Tischenko[26] or rearrangement of epoxides[27], using samarium diiodide as precatalysts have been reported. Moreover we have previously disclosed that samarium diiodide is also interesting owing to its Lewis acid properties for the catalysis of aldolization, Diels-Alder reactions and ring opening of epoxides[28]. The catalytic activity of samarium diiodide for ene-like cyclization in similar conditions was recently described[29]. We now report on the activity of samarium diiodide as a precatalyst for Mukaiyama aldol or Michael reactions, but also on the activities of other lanthanide iodides for these reactions with a discussion of reaction mechanisms.

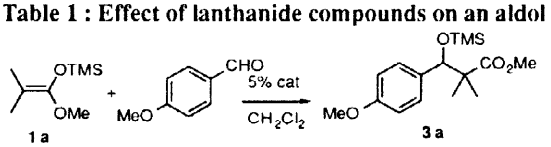
RESULTS

We found that samarium diiodide can be used in methylene chloride and catalyzes some aldol reactions involving the trimethylsilyl ketene acetal of methyl isobutyrate with aldehydes or acetophenone. The catalyst was easily prepared by the following procedure : the solvent of the 0.1 M solution of diiodosamarium in tetrahydrofuran[30] was evaporated, leaving a blue powder of $SmI_2(THF)_2$[31,32]. The bis tetrahydrofuran samarium diiodide is insoluble in methylene chloride and the suspension is sufficiently stable to be stored under argon without oxidation. After standing 24h, the methylene chloride is evaporated, THF is added, and the reductive power of the solution of samarium diiodide is restored, indicating that $SmI_2(THF)_2$ does not react with methylene chloride. In a typical experiment, at room temperature, to the blue suspension of $SmI_2(THF)_2$ in methylene chloride were added successively the silyl derivative (ketene silyl acetal or enoxysilane) and the carbonyl compound. The aldol product was formed as its silyl ether. The color of the reaction mixture turned rapidly yellow and this color was maintained until the end of the reaction. This observation suggests that samarium diiodide is only a precursor of the catalyst and that the active species is trivalent. With the aim at studying the importance of the divalent state for the formation of the actual catalytic species, we have compared the activity of various divalent and trivalent lanthanides derivatives in the reaction of *p*-anisaldehyde with trimethylsilyl ketene acetal of methyl isobutyrate **1a** (Table 1). For all the investigated

iodides (entries 1-8) the reaction is very fast (100 % conversion after 5 min at -78 °C) irrespective of the divalent or trivalent state of the lanthanide derivatives and no difference in the reaction rates with the different metals could be detected. The use of samarium dibromide, samarium and ytterbium trichlorides and samarium triisopropoxide, gives lower rates of reaction than lanthanide iodides. These results allow to attribute the increased catalytic activity of samarium diiodide for the aldolisation reaction compared to that of lanthanides trichlorides[12], to the presence of iodide and not to the divalent state of the catalyst precursor.

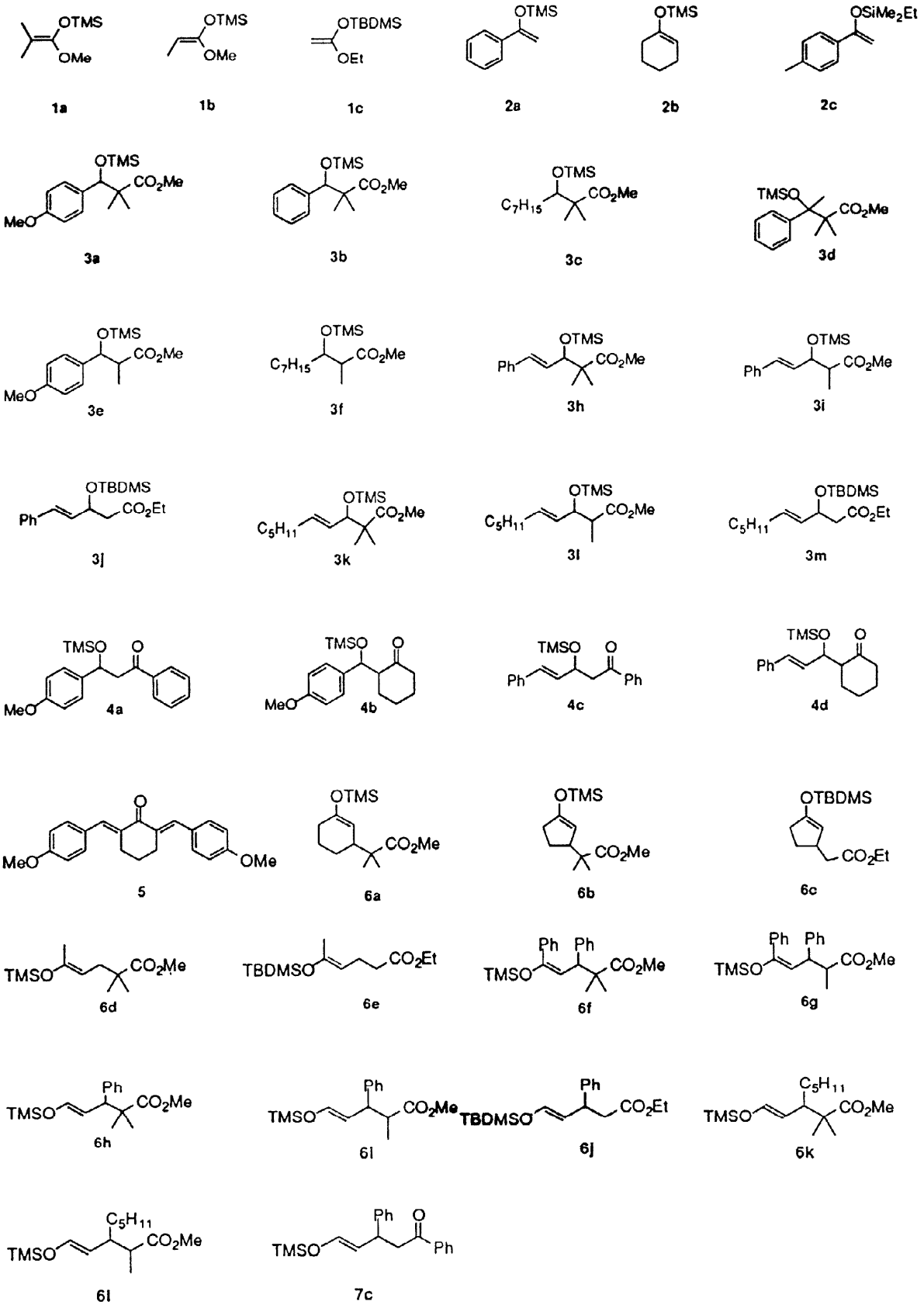
The solvent was found to have a dramatic influence on the reaction rate. For the addition of *p*-anisaldehyde on ketene silyl acetal **1a** the use of 5 % samarium diiodide in acetonitrile or in methylene chloride, led to comparable reaction rates (100 % conversion after 5 min at -78 °C). For total conversion in THF or toluene longer reaction times were needed, 4 h and 24 h at room temperature respectively. However the coordination of the samarium diiodide by at least two THF molecules is necessary to maintain the catalytic activity[31], perhaps because of the polymeric structure of samarium diiodide in the absence of a coordinating solvent. As it will be described below, the reactions involving ketene silyl acetals proceeded faster than those involving enoxysilanes. The former can be realized in a mixture of solvents, THF/CH_2Cl_2 which allows a very easy procedure for the preparation of the catalytic species : methylene chloride is added to the solution of samarium diiodide 0.1 M in tetrahydrofuran in a volume ratio 5:1 to 10:1. In this case the catalyst must be used immediately after mixing the solvents, due to the fast oxidation of samarium diiodide in diluted solutions.

Table 1 : Effect of lanthanide compounds on an aldol reaction



Entry	catalyst	temp.	time[a]
1	$SmI_2(THF)_2$	-78 °C	5 min
2	*t*-$BuOSmI_2(THF)_3$	-78 °C	5 min
3	$SmI_3(THF)_3$	-78 °C	5 min
4	$(ArCHOSmI_2)_2$	-78 °C	5 min
5	$EuI_2(THF)_2$	-78 °C	5 min
6	$YbI_2(THF)_2$	-78 °C	5 min
7	$LaI_3(DME)_2$	-78 °C	5 min
8	$YbI_3(DME)_2$	-78 °C	5 min
9	$SmBr_2(THF)_n$	25 °C	1.5 h
10	$SmCl_3(THF)_n$	25 °C	12 h
11	$YbCl_3(THF)_n$	25 °C	4 d
12	$Sm(OiPr)_3$	25 °C	14 d

[a]: Reaction time for 100 % conversion in the reaction of *p*-anisaldehyde (2 mmol) and **1a** (3 mmol) using 5 % catalyst (0.1 mmol).


OTMS
OMe
1a
OTMS
OMe
1b
OTBDMS
OEt
1c
OTMS
2a
OTMS
2b
OSiMe2Et
2c
OTMS
CO2Me
MeO
3a
OTMS
CO2Me
3b
OTMS
C7H15
CO2Me
3c
TMSO
CO2Me
3d
OTMS
CO2Me
MeO
3e
OTMS
C7H15
CO2Me
3f
OTMS
Ph
CO2Me
3h
OTMS
Ph
CO2Me
3i
OTBDMS
Ph
CO2Et
3j
OTMS
C5H11
CO2Me
3k
OTMS
C5H11
CO2Me
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TMSO
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MeO
4a
TMSO
O
MeO
4b
TMSO
O
Ph
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4c
TMSO
O
Ph
4d
O
MeO
OMe
5
OTMS
CO2Me
6a
OTMS
CO2Me
6b
OTBDMS
CO2Et
6c
TMSO
CO2Me
6d
TBDMSO
CO2Et
6e
Ph
Ph
TMSO
CO2Me
6f
Ph
Ph
TMSO
CO2Me
6g
Ph
TMSO
CO2Me
6h
Ph
TMSO
CO2Me
6i
Ph
TBDMSO
CO2Et
6j
C5H11
TMSO
CO2Me
6k
C5H11
TMSO
CO2Me
6l
Ph
O
TMSO
Ph
7c

Chart 1

Table 2 : Mukaiyama aldol reactions catalyzed by samarium iodides

entry	carbonyl compound	silylated derivative	catalyst[a]	temp.	time	product	yield[b] %
1			$SmI_2(THF)_2$		5 min		95
2	*p*-anisaldehyde	**1a**	$SmI_3(THF)_3$	-78 °C	5 min	**3a**	95
3			*t*-BuO$SmI_2(THF)_3$		5 min		95
4	benzaldehyde	**1a**	$SmI_2(THF)_2$	-78 °C	5 min	**3b**	95
5			$SmI_2(THF)_2$		4.5 h	**3c**	90
6	octanal	**1a**	$SmI_3(THF)_3$	-20 °C	4.5 h	**3c**	73
7			*t*-BuO$SmI_2(THF)_3$		5 h	**3c**	69
8	acetophenone	**1a**	$SmI_2(THF)_2$	-20 °C	2 h	**3d**	85
9			$SmI_3(THF)_3$		2 h	**3d**	76
10			$SmI_2(THF)_2$		72 h	**2b**	100[c]
11	cyclohexanone	**1a**	$SmI_3(THF)_3$	rt	10 min	**2b**	100[c]
12			*t*-BuO$SmI_2(THF)_3$		18 h	**2b**	100[c]
13			$SmI_2(THF)_2$		24 h	**4a**	89
14	*p*-anisaldehyde	**2a**	$SmI_3(THF)_3$	rt	24 h	**4a**	100[c]
15			*t*-BuO$SmI_2(THF)_3$		24 h	**4a**	80
16			$SmI_2(THF)_2$		48 h	**4b**[d]	57
17	*p*-anisaldehyde	**2b**	$SmI_3(THF)_3$	0 °C	48 h	**4b**[e]	62[g]
18			*t*-BuO$SmI_2(THF)_3$		48 h	**4b**[f]	66[g]
19	*p*-anisaldehyde	**1b**[h]	$SmI_2(THF)_2$	rt	1.5 h	**3e**[i]	75
20	octanal	**1b**[h]	$SmI_2(THF)_2$	-20°C	4.5 h	**3f**[j]	95

[a]: 5 % catalyst in 10 mL CH_2Cl_2 ; [b]: Isolated yield ;[c]: Yield in crude product ; [d]: *anti/syn* : 33/67; [e]: *anti/syn* : 46/54; [f] *anti/syn* : 50/50 ; [g] 15% of product **5** was obtained; [h]*E/Z* : 84/16; [i] *anti/syn* : 64/36; [j] *anti/syn* : 59/41

The catalytic ratio could be lowered down to 0.5 % $SmI_2(THF)_2$ in the case of the formation of **3a** in methylene chloride. However to investigate the scope of the reaction most of the studies were carried out in methylene chloride using 5% $SmI_2(THF)_2$ as a precatalyst, in order to insure good reproducibility and precision (lower catalytic ratios involve the manipulation of small quantities of samarium diiodide, at the scale of the experiments). The catalytic activities of samarium triiodide and samarium diiodotert-butoxide have been compared to that of samarium diiodide in several cases. The results of the reactions of condensation of ketene silyl acetals (KSA) **1** or silyl enol ethers **2** with various aldehydes and ketones are reported in Table 2. The reaction of trimethylsilyl ketene acetal of methyl isobutyrate **1a** with aromatic or aliphatic aldehydes and acetophenone gives the aldol products as their trimethylsilyl ethers with excellent yields using samarium diiodide, samarium triiodide or samarium diiodotert-butoxide as catalysts (entries 1-9). At room temperature, the reaction of cyclohexanone with **1a** in the presence of 5% samarium iodides affords the corresponding enoxysilane quantitatively whatever the catalyst is (entries 10-12). These results have been

extended to various cyclic and acyclic aliphatic ketones and to bulky aldehydes, allowing a rapid and easy method of preparation of enoxysilanes[33]. The reaction of the trimethylsilyl enol ether **2a** with *p*-anisaldehyde at room temperature yields to the trimethyl silyl ether **4a** in good yield when the catalyst is $SmI_2(THF)_2$, $SmI_3(THF)_3$ or *t*-BuO$SmI_2(THF)_3$ (entries 13-15). The addition reaction of *p*-anisaldehyde with the trimethylsilyl enol ether **2b** was performed at 0°C to avoid the formation of by-product **5** occuring from the condensation of two molecules of *p*-anisaldehyde on the cyclohexanone ring. No appreciable difference in the rate of the reactions catalyzed with the above three samarium iodides compounds could be detected but the diastereoselectivity of the reaction leading to compound **4b** depends on the catalyst. Samarium diiodide gives a higher *syn/anti* ratio than samarium triiodide or samarium diiodotertiobutylate.

The diastereoselectivity of the aldol reaction of trimethylsilyl ketene acetal of methyl propionate **1b** (*E/Z* : 84/16) using $SmI_2(THF)_2$ as a precatalyst has been examined. With *p*-anisaldehyde and octanal the addition products were isolated as the trimethylsilyl ethers **3e** and **3f**, with modest *anti* selectivity, respectively *anti/syn* : 64/36 (entry 19) and *anti/syn* : 59/41 (entry 20). These *anti/syn* ratios are similar or slightly higher than those reported for other catalysts such as zirconium triflate, Eu(dppm)$_3$ or HgI_2[5b, 6a, 14a, 34].

The reaction of α,β-unsaturated aldehydes and ketones with ketene silyl acetals **1** and enoxysilanes **2** in the presence of 5 % samarium diiodide has been examined and the results are collected in Table 3. α,β-Unsaturated ketones react with ketene silyl acetals by a selective Michael addition and the products are isolated as enoxysilanes **6** in all cases. The reactions with cyclic ketones give quantitatively the Michael adducts at low temperatures (entries 1-5) and only a very small excess of ketene silyl acetal is needed. With linear ketones only 1,4-addition reactions of the ketene silyl acetals are observed and the silyl enol ethers are isolated in good yields (entries 6-9). The reaction of cinnamaldehyde with various substrates has been studied and the regioselectivity depends on the nature of the silyl derivative. With KSA **1a** a 50/50 mixture of 1,2- and 1,4-addition (adducts **3h** and **6h**) was observed while the monosubstituted ketene silyl acetal **1b** gives higher ratio of 1,2-addition (**3i/6i** : 66/34) (entries 12 and 13). With an aliphatic α,β-unsaturated aldehyde selective 1,2-addition was observed with the unsubstituted ketene silyl acetal **1c** (entry 19) while the substituted ketene silyl acetals **1a** and **1b** lead to a small amount of 1,4 addition (entries 17, 18). The enoxysilanes are much less reactive than ketene silyl acetals and they do not react with chalcone at room temperature. With cinnamaldehyde the aldol silyl ether was the major product of the reaction with **2a** or the sole product with **2b** (entries 15 and 16). The difference of regioselectivity between α,β-unsaturated ketones and α,β-unsaturated aldehydes which give preferentially 1,4- or 1,2-additions respectively could be explained by steric effects. Similarly the comparison of the reactivity of the different silyl ketene acetals with each α,β-unsaturated aldehyde reveals that the ratio of Michael addition is increased with the bulkier KSA. The temperature does not influence the regioselectivity, as reaction of octen-2-al and **1c** both gives the aldol silyl ether as the sole product at -20°C or at room temperature (entries 19 and 20).

Table 3 : Reaction of α,β-unsaturated aldehydes and ketones with silyl derivatives : 1,2- versus 1,4- addition

entry	carbonyl compound	silyl derivative	temp.	time	ratio 1,2-/1,4-[b]	product	yield[c] (%)
1	cyclohexen-2-one	**1a**[a]	-20 °C	5 h	0/100	**6a**	65
2	cyclopenten-2-one	**1a**[a]	-20 °C	15 min	0/100	**6b**	95
3	cyclopenten-2-one	**1a**[a]	-78 °C	60 min	0/100	**6b**	95
4	cyclopenten-2-one	**1c**[a]	-20 °C	2 min	0/100	**6c**	95
5	cyclopenten-2-one	**1c**[a]	-78 °C	30 min	0/100	**6c**	95
6	buten-3-one	**1a**[a]	rt	12 h	0/100	**6d**[d]	86
7	buten-3-one	**1c**	rt	24 h	0/100	**6e**[e]	90
8	chalcone	**1a**	-20 °C	5 h	0/100	**6f**[f]	85
9	chalcone	**1b**	-20°C	4.5 h	0/100	**6g**[g]	95
10	chalcone	**2a**	rt	72 h			0
11	chalcone	**2b**	rt	72 h			0
12	cinnamaldehyde	**1a**	-20 °C	45 min	50/50	**3h+6h**[f]	90
13	cinnamaldehyde	**1b**	-20°C	45 min	66 /34	**3i**[h]**+6i**[i]	94
14	cinnamaldehyde	**1c**	- 20°C	45 min	90/10	**3j+6j**	83
15	cinnamaldehyde	**2a**	rt	4 h	85/15	**4c+7c**	68
16	cinnamaldehyde	**2b**	rt	6.5 h	100/0	**4d**[j]	52
17	octen-2-al	**1a**	- 20°C	4.5 h	80/20	**3k+6k**	95
18	octen-2-al	**1b**	- 20°C	4.5 h	87/13	**3l**[k]**+6l**[l]	95
19	octen-2-al	**1c**[a]	- 20°C	4.5 h	100/0	**3m**	80
20	octen-2-al	**1c**[a]	rt	30 min	100/0	**3m**	90

[a]: 1.1 eq. of silyl derivative; [b]: determined by ^{1}H NMR and/or GC; [c]: isolated yield ; [d]: *E/Z*, 55/45; [e]: *E/Z*, 80/20; [f] Only one isomer was detected, presumably *E* ; [g]: *anti/syn* 50/50 ; [h] *anti/syn* 54/46; [i] *anti/syn* 70/30; [j] *anti/syn* 50/50; [k] *anti/syn* 50/50; [l] *anti/syn* 55/45.

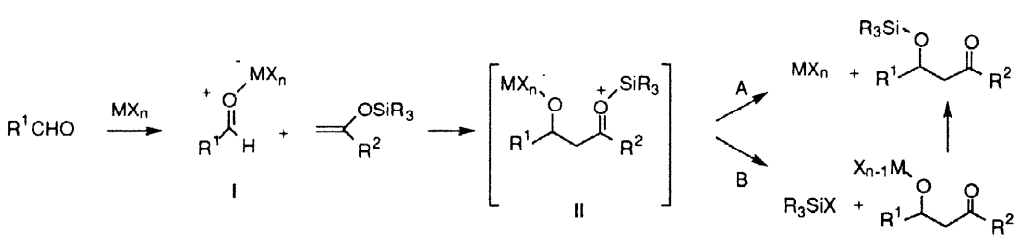
DISCUSSION

Samarium diiodide and other lanthanides derivatives compare well with other Lewis acids for catalytic activity and appear useful since they allow the steady isolation of silyl ethers as addition products[35]. Samarium diiodide used as a precatalyst for Michael reactions generates a species of high activity compared

to other reported catalysts[19b, 36], as milder conditions and a lower catalytic ratio are used. A selective 1,4-addition is usually observed for the reaction of KSA or enoxysilanes with α,β-unsaturated ketones catalyzed by Lewis acids, while for α,β-unsaturated aldehydes the regioselectivity varies with the catalyst. The reaction of KSA **1a** with cinnamaldehyde catalyzed by a zirconium triflate derivative[7] affords a 60/40 1,2- and 1,4-addition mixture while $(C_6F_5)_2SnBr_2$[8] in catalytic amount leads to the Michael addition as the major product. The preferred 1,2 selectivity displayed by samarium diiodide for reactions of KSA on α,β-unsaturated aldehydes has been also previously observed for other lanthanides derivatives such as bis disubstituted cyclopentadienyl ytterbium chloride[13] and Eu(dppm)$_3$ [14a]. In the latter case it was found, similarly to our observations, that the regioselectivity of the addition of ketene silyl acetals to α,β-unsaturated aldehydes is related to the bulkiness of the substrates. When one or two methyl substituents are present in β-position as in **1b** or **1a** a larger ratio of 1,4-addition is observed. Noteworthy is the selective formation of the aldol silyl ether from the reaction of **1c** with octen-2-al. As will be shown below, aldol reactions catalyzed by samarium diiodide are not reversible and the kinetic products are obtained.

Study of the mechanism of aldolisation and Michael reactions

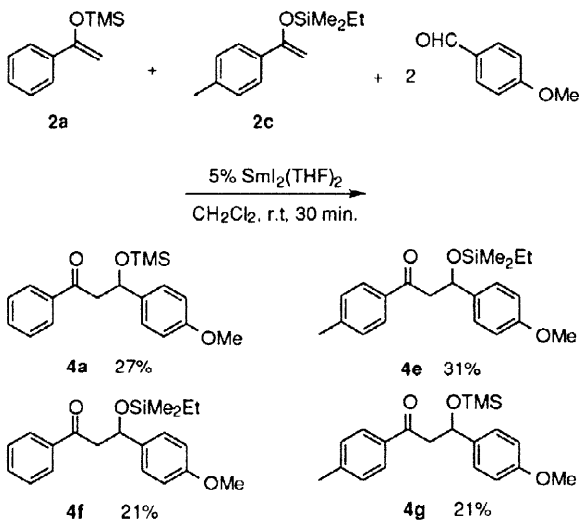
Several mechanisms have been proposed for Lewis acids catalyzed Mukaiyama aldol and Michael reactions, and the main different pathways proposed for the aldolisation reaction are depicted in Scheme 1 [37-39]. In a first step the Lewis acid coordinates the carbonyl compound to form an intermediate I which reacts with the silyl derivative to give the adduct II. The next step can be a concerted path A, or a non concerted process B. The concerted mechanism in path A involves an intramolecular transfer of the silyl group, while in the non concerted process B there is formation of an aldolate intermediate and intermolecular silylation in a second step. In the latter process the release of a silyl species R_3SiX allows a silicon-catalyzed competing process if the silylation of the aldolate is slow. A trichlorotitanium aldolate has been characterized in an aldol reaction between ketene silyl acetal and preformed $TiCl_4$ carbonyl adduct[40]. The Mukaiyama-Michael reactions catalyzed by Lewis acids, can be explained by the same reaction pathways as described above, or by the radical mechanism suggested by Otera, involving an electron transfer from KSA to the Lewis acid[41]. The mechanism varies depending on the structure of KSA (β-methyl substitution and bulkiness of substituents on silyl and alkoxy groups) as well as on the Lewis acid[42].



Scheme 1

During all the reactions involving $SmI_2(THF)_2$ as a precatalyst, the samarium species seems to be in the trivalent state and we tried to get informations on its possible structure. The change of color from blue to yellow after the introduction of the aldehyde or of the ketone leads to the hypothesis of their transformation in samarium pinacolates since this reaction is well known in THF[43]. We performed the pinacolisation of *p*-

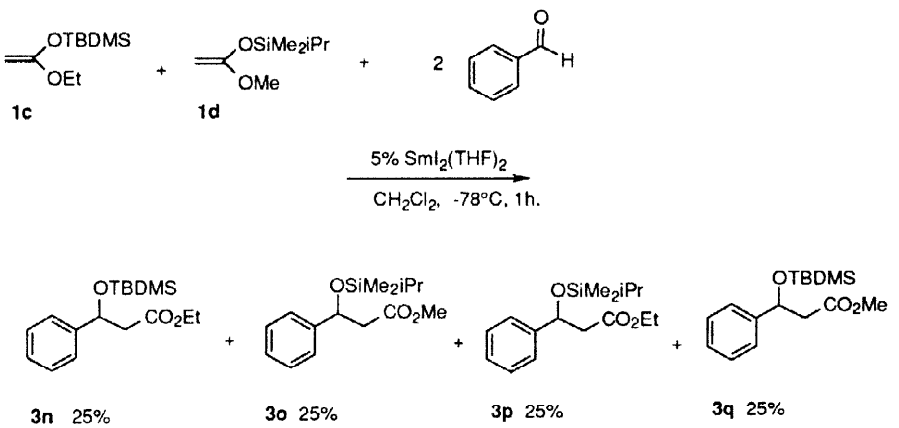
anisaldehyde by SmI_2 in THF and checked that after evaporation of the THF, the samarium pinacolate employed in catalytic amount (5%) in methylene chloride yields to the silyl ether **3a** quantitatively (Table 1, entry 4). However, no trace of pinacol could be detected in the aldol reactions involving *p*-anisaldehyde. Furthermore when *p*-anisaldehyde and **1a** are added to a stoichiometric amount of $SmI_2(THF)_2$ under the conditions of the formation of compound **3a** (-78°C, in CH_2Cl_2) the change of color of samarium diiodide is not observed and the reaction afforded no pinacol, but exclusively **3a**. This reveals that *the reducing properties of samarium diiodide decrease in a non coordinating solvent, while Lewis acidity is enhanced.* Therefore we did not confirm the *in situ* formation of a samarium pinacolate that could act as the active species. For the Michael additions on cyclopenten-2-one catalyzed by samarium diiodide the rate of the reaction is lower with the β-disubstituted KSA **1a** than with **1c**. This is not in agreement with a radical mechanism which requires the reduction of the Lewis acid by the ketene silyl acetal[42]. Moreover this radical process implying the reduction of samarium (II) or lanthanide (III) derivatives, seems an unfavourable path with lanthanide iodides as catalysts.



Equation 1

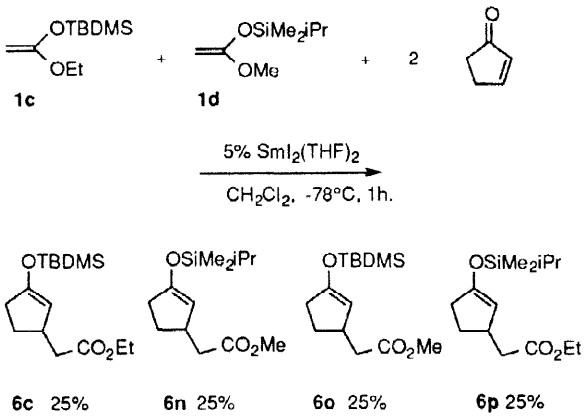
Crossover experiments are a useful tool to distinguish between the different mechanisms. Using doubly-labelled silyl ketene acetals or enoxysilanes, no scrambling should be obtained in the case of an intramolecular transfer of the silyl group. This was indeed found by Mikami for asymmetric reactions of ketene silyl acetals of thioesters with aldehydes catalyzed by (*R*)-BINOL-$TiCl_2$[44]. With most of the other catalysts such as triflates or perchlorates of various metals, scrambling was observed in reactions involving either ketene silyl acetals or enoxysilanes[37-38]. To determine whether the samarium diiodide induces a catalytic process with intramolecular silyl transfer or initiates the reaction and liberates another catalytic species such as TMSI, we carried out several crossover experiments using two doubly-labelled enoxysilanes **2a** and **2c** and two doubly-labelled ketene silyl acetals **1c** and **1d**. In both cases the pairs of substrates selected have similar bulkiness in order to minimize the difference of their reaction rates. The aldol reactions between *p*-anisaldehyde and enoxysilanes (eq 1) and between benzaldehyde and ketene silyl acetals (eq 2) using samarium diiodide as a precatalyst yield to scrambling (ratios of aldol products determined by GC/MS). We checked also that the silyl exchange is not occurring in the reaction mixture after the end of the reaction as

following. The silyl ethers **3n** and **3o** were independently prepared at -78°C and the two reaction mixtures were mixed at the same temperature. No scrambling was observed in these conditions, neither when the mixture of **3n** and **3o** was allowed to stand at room temperature. Then this mixture of **3n** and **3o** was added on fresh $SmI_2(THF)_2$, which did not permit to detect any trace of ethers **3p** and **3q**. Furthermore these two last experiments show unambiguously the non reversibility of the reactions at low temperature as well as at room temperature.



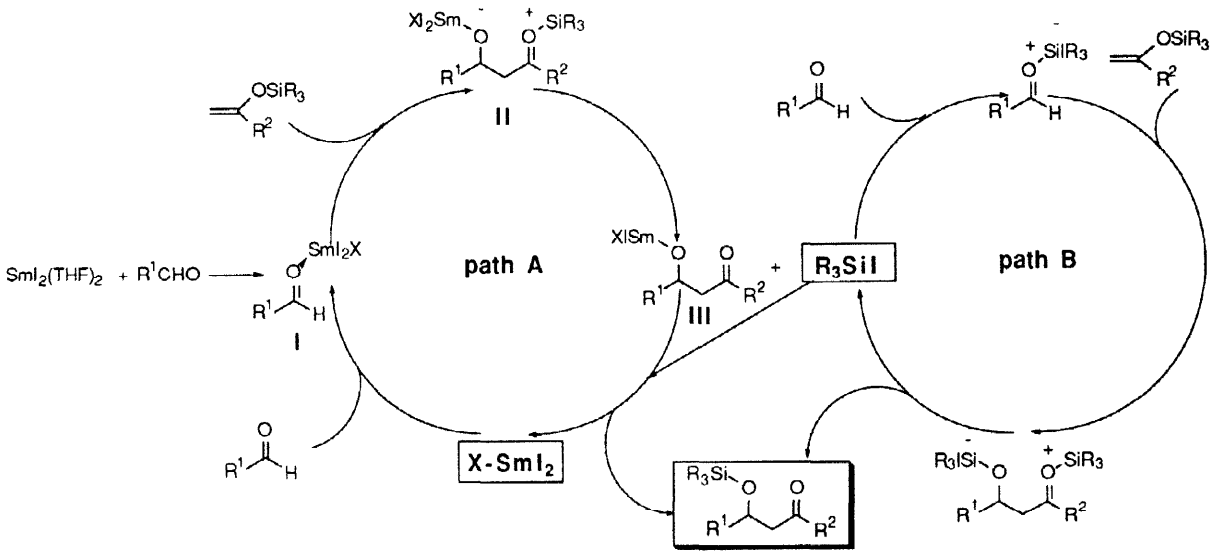
Equation 2

Similarly, the crossover Michael addition of cyclopenten-2-one to the mixture of silyl ketene acetals **1c** and **1d** (eq 3) furnishes the enoxysilanes with equimolar amounts of scrambling and non scrambling products. The observation of scrambling products allows to discard an intramolecular transfer of the silyl group when samarium diiodide is used as a precatalyst and may involve the liberation of silyl iodide in the reaction mixture. The observation of intramolecular transfer of the silyl group does not however necessarily rules out a catalysis by a metal species. This was well demonstrated by Evans who obtained excellent asymmetric induction in aldol reactions catalyzed by copper triflate, while this catalyst in crossover reactions with doubly-labelled silyl compounds provided scrambling[45]. In this case the catalysis by the silyl species is slow and does not compete with the catalysis with the copper compound. To get insight in the mechanism of the presently reported reactions we tried to detect silyl iodide and to determine the nature of the true catalyst, silicon or lanthanide species. Bosnich[39] found that for Mukaiyama aldol reactions catalyzed by $[Ti(Cp)_2(OTf)_2]$, Ph_3COTf, Ph_3CClO_4, in all cases the true catalyst is either Me_3SiOTf or Me_3SiClO_4. The titanium complex acts as an initiator which liberates the silicon species while for the reactions involving trityl salts, Me_3SiOTf or Me_3SiClO_4 are formed by trace amounts of water *in situ*. For reactions involving samarium diiodide as a precatalyst, we envisage preferentially that silyl iodide could be formed by a metal initiated process : the reaction of $SmI_2(THF)_2$ with traces of water should induce a change of the colour of the reaction mixture, which was not observed before the addition of the carbonyl compound. We found no evidence of the presence of trimethylsilyl iodide in the reaction mixture : the corresponding signal could not be detected by following with ^{29}Si NMR at -20°C the aldol reaction of *p*-anisaldehyde with enoxysilane **2a**. This result may indicate that the reaction involving trimethylsilyl iodide is a rapid step of the catalytic process.



Equation 3

Variations of the diastereomer ratios with various catalysts in aldolizations involving enoxysilane **2b** have been used to discuss the nature of the true catalytic species[19e, 38, 39]. For aldol reactions catalyzed by lanthanide iodides the diastereoselectivity depends both on the ligands and the metal. The kinetic control of these reactions has been checked by GC monitoring of the diastereoisomers ratio during the reaction : no variation could be detected, neither during the reaction nor after total conversion. In the reaction of *p*-anisaldehyde with enoxysilane **2b** the three samarium iodides lead to the condensation product **4b** with different *anti /syn* ratios (Table 2, entries 16, 18). $LaI_3(DME)_2$ and $YbI_3(DME)_2$ yield to **4b** with *anti /syn* ratios 33/67 and 70/30 repectively. These results allow us to propose that, at least for this reaction, the true catalyst may be a lanthanide species, and not TMSI which would provide the same diastereoselectivity in all experiments. Such an interpretation was suggested by Denmark when triaryl carbenium compounds were used as precatalysts[38] and by Kobayashi with aldolization involving lanthanide triflates[19c]. Nevertheless this cannot be considered as definitive evidence of catalysis by lanthanide species as Bosnich on the basis of NMR and kinetic experiments[39] claimed that when triaryl carbenium triflates are employed the variation of the diastereoselectivity is due to changes in the concentration of ions OTf^-.



Scheme 2

The proposed mechanism of the aldol reaction using samarium diiodide as a precatalyst is indicated on Scheme 2. In the first step the carbonyl compound is activated by the samarium iodide SmI_2X considered as a Lewis acid, and the second step is the reaction of the ketene silyl acetal or of the enoxysilane to form a samarium aldolate of type II. This samarium aldolate liberates silyl iodide in the reaction mixture and the samarium aldolate III. The reaction of III with silyl iodide produces the aldol as its silyl ether and regenerates the catalyst (cycle A). The same catalytic cycle can be realized with the silyl iodide as the catalyst (cycle B). The increase of activity of lanthanides iodides compared to lanthanides chlorides (similarly observed between $BiCl_3$ and BiI_3)[9] can be explained by the similar energies of dissociation Sm-I and Si-I[46]. According to the nature of the substrate and to the rate of silylation of the aldolate, process can be lanthanide-catalyzed (A, probably for reaction involving enoxysilane **2b**), or silicon-catalyzed (B), or both species are the actual catalysts[47].

CONCLUSION

Samarium diiodide and other lanthanide iodides are very efficient catalysts for Mukaiyama aldol and Michael reactions. Noteworthy Michael addition of KSA to α,β-unsaturated ketones affords selectively 1,4-addition products as enoxysilanes in mild conditions through an easy procedure. These catalysts exhibit high activity compared to other Lewis acids. The role of the lanthanide iodide, either to initiate the formation of silyl iodide acting as the catalyst, either to form a lanthanide species acting as the true catalyst, could not be elucidated. Nevertheless the variations of diastereoselectivity recorded through changing the nature of metal and ligands allow to envisage the preparation of enantioselective catalysts for aldol and Michael reactions based on lanthanide iodides, which we are currently investigating.

EXPERIMENTAL

All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. THF was distilled from sodium benzophenone ketyl, methylene dichloride from CaH_2 and solvents were degassed immediately prior to use.

Bruker AM 200 and AM 250 spectrometers, operating at 200 and 250 MHz for ^1H, 50.4 and 63 MHz for ^{13}C, 49.7 for ^{29}Si were used for the NMR spectra. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane for spectra in $CDCl_3$. Infrared spectra were recorded as Nujol mulls using KBr plates on a Perkin-Elmer 883 spectrometer and are reported in cm^{-1}. GC analyses were performed with a 25 m BP 1 capillary column connected with a computing integrator. Mass spectra (MS) (70 eV) data were determined on a Ribermag R-10 GC/MS and high resolution mass spectra on a Varian 3400 GC-LC/MS. Column chromatographies were realized on silica desactivated by Et_3N or on desactivated alumina, using hexane/ethyl acetate mixtures as eluents. $LnI_2(THF)_n$, (Ln = Sm, Yb, Eu), *t*-$BuOSmI_2(THF)_3$ and $SmBr_2(THF)_n$, were prepared according to published methods[48-50]. $SmI_3(THF)_3$ was obtained by reacting SmI_2 and I_2 in THF in the molar ratio 1/0.5 at room temperature. $LaI_3(DME)_2$ and $YbI_3(DME)_2$ were prepared from La or Yb powder and iodine[51]. Silyl ketene acetals were purchased from Aldrich or prepared according to Tamura's method[52]. Methyl 3-phenyl-2,2-dimethyl-3-trimethylsilyloxypropanoate **3b** has been previously

described[34]. Column chromatographies were realized on silica desactivated by Et_3N or on desactivated alumina, using hexane/ethyl acetate mixtures as eluents.

General procedures for aldol and Michael reactions

Procedure A : A solution of SmI_2 in THF (0.1 M, 1.0 mL, 0.1 mmol) was carefully evaporated *in vacuo* to give $SmI_2(THF)_2$ as a blue powder, (alternatively $SmI_2(THF)_2$ (0.055 g, 0.1 mmol) was weighted in a glove-box). This was suspended in CH_2Cl_2 (5 mL) and then the silyl ketene acetal or enoxysilane (2.2 to 3.0 mmol) was added, followed by the carbonyl compound (2.0 mmol). The resulting yellow solution was then stirred under argon. The reaction mixture was hydrolyzed with a solution of 0.1 M HCl (5 mL) and extracted with ether, washed with water and dried over $MgSO_4$. After evaporation of the solvent, the product was purified by column chromatography.

Procedure B : Same procedure as above. At the end of the reaction instead of hydrolysis the reaction was stopped by the addition of hexane (50 mL) which precipitates samarium salts. After filtration through celite the solvents were removed under reduced pressure to give the desired product.

Procedure C : To a blue solution of SmI_2 in THF (0.1 M, 1.0 mL, 0.1 mmol) was added, under argon, CH_2Cl_2 (5 mL) giving a pale blue solution. The silyl ketene acetal (2.2 to 3.0 mmol) was then introduced immediately, followed by the carbonyl compound (2.0 mmol). The resulting yellow solution was stirred under argon. The reaction was stopped by the addition of hexane (50 mL) which precipitates samarium salts. After filtration through celite the solvents were removed under reduced pressure to give the desired product.

The *procedures A* and *B* allow the preparation of all products described above, procedure B should be preferred when enoxysilanes are formed. *Procedure C* has been successfully employed for the preparation of compounds **3a, 3c, 6a, 6b, 3j+6j, 3k+6k**.

Crossover experiment 1: To a suspension of $SmI_2(THF)_2$ (0.055 g, 0.05 mmol) in CH_2Cl_2 (5mL) were successively added 1-phenyl-1-trimethylsiloxy ethene (0.192 g, 1.0 mmol), 1-(4-methylphenyl)-1-dimethylethylsilyloxy ethene (0.220g, 1 mmol) and *p*-anisaldehyde (0.243 mL, 2.0 mmol) at room temperature. The reaction mixture immediately turned yellow and was hydrolyzed after 30 mn. The crude product was analyzed by GC and GC/MS.

Crossover experiment 2: To a suspension of $SmI_2(THF)_2$ (0.055 g, 0.1 mmol) in CH_2Cl_2 (5mL) were successively added 1-dimethyl-*t*-butylsilyloxy-1-ethoxy ethene (0.202 g, 1 mmol), 1-dimethyl-*i*-propylsilyloxy-1-methoxy ethene (0.174 g, 1 mmol), and *p*-anisaldehyde (0.243 mL, 2.0 mmol) at -78°C. After 1h, 50 mL hexane were added, samarium salts were filtrated and after evaporation the crude product was analyzed by GC and GC/MS.

Crossover experiment 3: To a suspension of $SmI_2(THF)_2$ (0.055 g, 0.1 mmol) in CH_2Cl_2 (5mL) were successively added 1-dimethyl-*t*-butylsilyloxy-1-ethoxy ethene (0.202 g, 1 mmol), 1-dimethyl-*i*-propylsilyloxy-1-methoxy ethene (0.174 g, 1 mmol), and cyclopenten-2-one (0.164 g , 2.0 mmol) at -78°C. After 1h, 50 mL hexane were added, samarium salts were filtrated and after evaporation the crude product was analyzed by GC and GC/MS.

Methyl 3-(4-methoxyphenyl)-2,2-dimethyl-3-trimethylsilyloxypropanoate (3a) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.15 [d, ^3J (H, H) = 8.7 Hz, 2H; Ar], 6.80 [d, ^3J (H, H) = 8.7Hz, 2H; Ar] 4.90 (s, 1H; CH), 3.80 (s, 3H; OCH_3), 3.65 (s, 3H; CO_2CH_3), 1.10 (s, 3H; CH_3), 0.95 (s, 3H; CH_3), 0.10 (s, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 178.00, 132.90, 128.80, 112.70, 78.40, 54.00, 51.00, 49.10, 22.00, 19.00, 1.00; GC/MS (EI) m/z (intensity): 310 (M^+, 0.05) ; IR (Nujol) : 1731, 1613 ; Anal. Calcd for $C_{16}H_{26}O_4Si$: C, 61.93; H, 8.39 ; Found : C, 62.12; H, 8.17 ; mp = 54-56°C.

Methyl 2,2-dimethyl-3-trimethylsilyloxydecanoate (3c) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 3.85 (m, 1H; CH), 3.60 (s, 3H; OCH_3), 1.30 (m, 12H, 6 CH_2), 1.10 (s, 3H, C-CH_3), 1.05 (s, 3H; C-CH_3), 0.85 [t, ^3J (H, H) =7 Hz, 3H; CH_3], 0.05 (s, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 177.76, 77.63, 51.57, 48.17, 29.62, 29.22, 26.98, 22.60, 21.57, 20.13, 14.06, 0.74; GC/MS (EI) m/z (intensity): 302 (M^+, 0.06) ; IR (Neat) : 1731 ; HRMS (EI) Calcd for $C_{16}H_{34}O_3Si$-CH_3 : 287.2042 ; Found : 287.2032.

Methyl 2,2-dimethyl-3-phenyl-3-trimethylsilyloxybutanoate (3d) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.25 (m, 5H; Ph), 3.60 (s, 3H; OCH_3), 1.80 (s, 3H, CH_3), 1.15 (s, 3H; C-CH_3), 1.05 (s, 3H; C-CH_3), 0.05 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 142.25, 126.96, 126.86, 126.65, 52.22, 51.34, 24.82, 21.65, 21.29, 2.13 ; GC/MS (EI) m/z (intensity): 279 (M-15, 2) ; IR (Neat) : 1724 ; Anal. Calcd for $C_{16}H_{26}O_3Si$: C 65.31, H 8.84 Found : C 65.54, H 8.97 .

Methyl 3-(4-methoxyphenyl)-2-methyl-3-trimethylsilyloxypropanoate (3e) : ^{1}H NMR ($CDCl_3$, 250 MHz) *Anti* δ: 7.66 (m, 2H; Ar), 7.28 (m, 2H; Ar), 5.08 [d, ^3J (H, H) = 7.2Hz, 1H; CH-OTMS], 4.23 (s, 3H; OCH_3), 4.15 (s, 3H; CO_2CH_3), 3.15 (m, 1H; CH), 1.28 [d, ^3J (H, H) = 7.2Hz, 3H; CH_3], 0.36 (s, 9H; $Si(CH_3)_3$) ; *Syn* δ: 7.66 (m, 2H; Ar), 7.28 (m, 2H; Ar), 5.35 [d, ^3J (H, H) = 6.6Hz, 1H; CH-OTMS], 4.22 (s, 3H; OCH_3), 3.98 (s, 3H; CO_2CH_3), 3.15 (m, 1H; CH), 1.57 [d, ^3J (H, H) = 6.6Hz, 3H; CH_3], 0.43 (s, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) *Anti* δ: 158.83, 134.87, 133.90, 127.79, 127.03, 113.20, 113.00, 77.00, 75.09, 54.86, 48.99, 13.55, -0.35; *Syn* δ: 175.65, 134.87, 133.90, 127.79, 127.03, 113.20, 113.00, 77.24, 76.73, 51.22, 48.68, 11.70, -0.82; GC/MS (EI) m/z (intensity): 296 (M^+, 0.35) ; IR (Neat) : 1741, 1613 ; Anal. Calcd for $C_{15}H_{24}O_4Si$: C, 60.78; H, 8.16 ; Found : C, 60.61; H, 8.27

Methyl 2-methyl-3-trimethylsilyloxydecanoate (3f) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 3.89 (m, 1H; CH-OTMS), 3.64 (s, 3H; CO_2CH_3), 2.50 (m, 1H; CH), 1.24 (m, 12H; 6 CH_2) , [*syn*, [(1.09 [d, ^3J (H, H) = 7.0Hz], *anti* , 1.05 [d, ^3J (H, H) = 7.2 Hz], 3H; *anti* + *syn*, C-CH_3], 0.85 [t, ^3J (H, H) = 6.6Hz, 3H; CH_3], 0.060 (s, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) *anti* + *syn* δ: 175.16, 175.2, 73.59, 73.08, 50.97, 50.93, 45.63, 44.70, 34.95, 32.99, 31.29, 31.28, 29.16, 29.09, 28.71, 25.04, 24.26, 22.12, 13.57, 12.06, 11.10, -0.12, -0.20; GC/MS (EI) m/z (intensity): 273 (M-CH_3, 23) ; IR (Neat) : 1742 ; HRMS (EI) Calcd for $C_{15}H_{32}O_3Si$: 288.2136 ; Found : 288.2103.

3-(4-methoxyphenyl)-1-phenyl-3-trimethylsilyloxypropan-1-one (4a) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.95 (d, ^3J (H, H) = 10Hz, 2H; Ar), 7.55-7.30 (m, 5H; Ph), 6.75 (d, ^3J (H, H) = 10Hz, 2H; Ar), 5.30 (m, 1H; CH), 3.80 (s, 3H; OCH_3 , 3.55-3.00 (m, 2H, CH_2), 0.05 (s, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 214.51, 132.90, 128.40, 128.34, 126.90, 113.60, 55.19, 49.65, 30.90, -0.11; GC/MS (EI) m/z (intensity): 328 (M^+, 3) ; IR (Neat) : 1687, 1612 ; Calcd for $C_{19}H_{24}O_3Si$: C, 69.47; H, 7.36 ; Found : C, 69.17; H, 7.31.

2-(1-(4-methoxyphenyl)-1-trimethylsilyloxymethyl)-cyclohexan-1-one (4b) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.19 (m, 2H; Ar), 6.81 (m, 2H; Ar), (5.19 [d, ^3J (H, H) = 4.8Hz, *anti*, 4.98 (d, ^3J (H, H) = 8.1Hz, *syn*, 1H, *anti* + *syn* ; CH-OTMS], [3.78 (s, *syn*), 3.77 (s, anti), 3H *anti* + *syn*; OCH_3], 2.70-2.55 (m, 1H; CH), 2.55-2.10 (m, 2H; CH_2-C=O), 2.0-1.4 (m, 6H; 3 CH_2), [-0.03 (s, *anti*), -0.05 (s, *syn*), 9H, *anti* + *syn* ; $Si(CH_3)_3$] ; ^{13}C

NMR ($CDCl_3$, 62.9 MHz) δ: 211.76, 211.37, 158.85, 158.44, 136.29, 134.80, 128.08, 127.40, 113.35, 113.21, 72.99, 71.45, 65.83, 59.39, 58.65, 42.36, 42.04, 30.33, 28.38, 27.17, 26.90, 24.35, 24.10, 0.99, 0.10; GC/MS (EI) m/z (intensity): (isomer Anti) : 306 (M^+, 0.93) ; IR (Neat) : 1715, 1612 ; HRMS (EI) Calcd for $C_{17}H_{26}O_3Si$: 306.1651 ; Found : 305.1687. Anal. Calcd for $C_{17}H_{26}O_3Si$: C, 66.62; H, 8.55 ; Found : C, 66.51; H, 8.72.

Methyl 2-(3-trimethylsilyloxycyclohex-2-enyl)-2-methyl-propanoate (6a) : ^1H NMR ($CDCl_3$, 200 MHz) δ: 4.65 [d, ^3J (H, H) = 1Hz, 1H; C=CH], 3.65 (s, 3H; CO_2CH_3), 2.55 (m, 1H; CH), 2.10-1.40 (m, 6H; 3 CH_2), 1.15 (s, 3H; CH_3), 1.05 (s, 3H; CH_3), 0.15 (s, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 152.00, 104.95, 65.8, 51.45, 45.35, 42.60, 29.65, 23.75, 22.30, 21.75, 21.45, 0.15. GC/MS (EI) m/z (intensity): 270 (M^+, 0.50) ; IR (Neat) : 1737; 1666 ; Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 62.22; H, 9.63 ; Found : C, 62.41; H, 9.85.

Methyl 2-(3-trimethylsilyloxycyclopent-2-enyl)-2-methyl-propanoate (6b) : ^1H NMR ($CDCl_3$, 200MHz) δ: 4.50 [d, ^3J (H, H) = 2Hz, 1H; C=CH], 3.60 (s, 3H; CO_2CH_3), 1.85 (m, 2H; CH_2-C=), 1.55 (m, 1H; CH), 1.15 (m, 2H, CH_2), 1.07 (s, 3H; CH_3), 1.04 (s, 3H; CH_3), 0.15 (s, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) : 178.36, 156.24, 102.97, 51.57, 50.10, 45.87, 33.40, 23.28, 22.69, 21.19, -0.015 ; IR (Neat) : 1734, 1646 ; HRMS (EI) Calcd for $C_{13}H_{24}O_3Si$-CH_3: 241.1254 ; Found : 241.1251.

Ethyl (3-tert-butydimethylsilyloxycyclopent-2-enyl)-ethanoate (6c) :
^1H NMR ($CDCl_3$, 250 MHz) δ: 4.55 [d, ^3J (H, H) = 2Hz, 1H; HC=], 4.10 [q, ^3J (H, H) = 7.2Hz, 2H; CO_2CH_2], 2.70-1.80 (m, 6H; 3 CH_2), 1.50 (m, 1H; CH) 1.25 [t, ^3J (H, H) = 7.2Hz, 3H, CH_3], 0.90 (s, 9H, $C(CH_3)_3$), 0.10 (s, 6H; $Si(CH_3)_3$);^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 171.79, 105.70, 101.81, 60.29, 39.55, 38.10, 33.33, 29.04, 25.50, 17.94, 15.07, -3.15 ; GC/MS (EI) m/z (intensity): 284 (M^+, 3.1) ; IR (Neat): 1737, 1646 ; HRMS (EI) Calcd for $C_{15}H_{28}SiO_3$: 284.1807; Found : 284.1812

Methyl 2,2-dimethyl-5-trimethylsilyloxyhex-4-enoate (6d) : ^1H NMR ($CDCl_3$, 200MHz) δ: *E* : 4.60 [t, ^3J (H, H) = 6Hz, 1H; C=CH], 3.65 (s, 3H; CO_2CH_3), 2.19 (m, 2H; CH_2) 1.72 (s, 3H; CH_3), 1.16 (s, 6H; $C(CH_3)_2$), 0.17 (s, 9H; $Si(CH_3)_3$); *Z* : 4.32 [t, ^3J (H, H) = 6Hz, 1H; C=CH], 3.65 (s, 3H; CO_2CH_3), 2.19 (m, 2H) CH_2), 1.77 (s, 3H; CH_3), 1.14 (s, 6H; $C(CH_3)_2$), 0.19 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: *E* +*Z* : 149.89, 148.25, 103.58, 51.53, 38.20, 35.97, 24.74, 24.62, 22.65, 17.14, 0.69, 0.18; GC/MS (EI) m/z (intensity): *E* 244 (M^+, 3), *Z* 244 (M^+, 2); IR (Neat) : 1738, 1672 ; HRMS (EI) Calcd for $C_{12}H_{24}O_3Si$: 244.1494; Found : 244.1484.

Ethyl 5-tert-butyldimethylsilyloxyhex-4-enoate (6e) : ^1H NMR ($CDCl_3$, 200 MHz) δ: 4.60 [t, ^3J (H, H) = 7.4 Hz], *E* , 4.38 [t, ^3J (H, H) = 6.7 Hz], *Z* , 1H, *E*+*Z*; C=CH, 4.05 [q, ^3J (H, H) = 7 Hz, 2H; CO_2CH_2] *E*+*Z*, 2.28 (m, 4H; 2 CH_2) *E*+*Z*, (1.72 (s) *Z*, 1.70 (s) *E*, 3H, *E*+*Z* ; C=CH_3), 1.23 [t, ^3J (H, H) = 7 Hz] *E*, 1.22 [t, ^3J (H, H) =7 Hz] *Z*, 3H, *E*+*Z*; CH_3), (0.88 (s), *Z*, 0.86 (s) *E*, 9H, *E*+*Z*; $C(CH_3)_3$), (0.09 (s) *E*, 0.08 (s) *E*+*Z* , 6H; $Si(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ *E*+*Z* : 173.25, 149.17, 147.50, 106.20, 106.07, 60.20, 35.12, 34.51, 31.55, 25.74, 25.63, 22.88, 22.65, 17.94, 17.63, 14.19, 14.14, -3.62, -4.57; GC/MS (EI) m/z (intensity): 258 (M^+,0.53) ; IR (Neat) : 1739, 1672 ; HRMS (EI) Calcd for $C_{14}H_{28}O_3Si$: 272.1808; Found : 272.1812.

Methyl 2,2-dimethyl-3,5-diphenyl-5-trimethylsilyloxypent-4-enoate (6f) : ^1H NMR ($CDCl_3$, 250 MHz) δ: 7.45 (m, 2H; Ph), 7.25 (m, 8H; Ph), 5.50 [d, ^3J (H, H) = 11Hz, 1H; C=CH], 4.15 [d, ^3J (H, H) = 11Hz, 1H; CH], 3.60 (s, 3H; CO_2CH_3), 1.20 (s, 3H; CH_3), 1.10 (s, 3H; CH_3), 0.05 (s, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 198.12, 177.52, 150.86, 141.22, 139.25, 129.22, 127.78, 127.73, 126.38, 125.99, 109.19, 51.45, 49.14, 47.20, 23.20, 22.18, 0.56; GC/MS (EI) m/z (intensity): 367 (M-15, 0.7) ; IR (Neat) : 1731, 1643, 1600 ; Anal. Calcd for $C_{23}H_{30}O_3Si$: C, 72.25; H, 7.85 ; Found : C, 72.41; H, 7.91.

Methyl 2-methyl-3,5-diphenyl-5-trimethylsilyloxypent-4-enoate (6g) : *Anti +syn* : 50/50 : ^{1}H NMR ($CDCl_3$, 200MHz) δ: 7.44 (m, 10H; Ph), (5.48 [d, ^3J (H, H) = 10Hz], 5.33 [d, ^3J (H, H) = 10Hz], *Anti +syn* , 1H; C=CH), (4.07 [t, ^3J (H, H) = 10Hz] 3.95 [t, ^3J (H, H) = 10Hz], *Anti +syn* , 1H; CH-Ph), (3.63 (s), 3.44 (s), *Anti +syn* , 3H; CO_2CH_3), 2.77 (m, *Anti +syn* , 1H; CH), 1.20 (m, *Anti +syn* , 3H; CH_3), 0.05 (s, *Anti +syn* , 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ *Anti +syn* : 175.86, 150.30, 143.16, 142.61, 139.15, 128.38, 128.29, 128.06, 128.01, 127.97, 127.88, 127.81, 126.39, 126.31, 126.00, 111.60, 110.94, 51.47, 51.31, 46.90, 46.26, 45.73, 45.36, 15.31, 15.25, 0.69, 0.63 ; GC/MS (EI) m/z (intensity): 368 (M^+, 0.9) ; IR (Neat) : 1738, 1646 ; HRMS (EI) Calcd for $C_{22}H_{28}O_3Si$: 368.1808; Found : 368.1773.

Methyl 2,2-dimethyl-5-phenyl-3-trimethylsilyloxypent-4-enoate (3h) + Methyl 2,2-dimethyl-3-phenyl-5-trimethylsilyloxypent-4-enoate (6h)

(6h) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.25 (m, 5H; Ph), 6.30 [d, ^3J (H, H) = 12.0Hz, 1H; CH-OTMS], 5.45 [dd, ^3J (H, H) = 12.0Hz, ^3J (H, H) = 10.8Hz, 1H; C=CH], 3.60 (s, 3H; CO_2CH_3), 3.45 [d, ^3J (H, H) = 10.8Hz, 1H; CH-Ph], 1.20 (s, 3H; CH_3), 1.10 (s, 3H; CH_3), 0.15 (s, 9H, $Si(CH_3)_3$) ; GC/MS (EI) m/z (intensity): 291 (M-15, 1).

(3h) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.25 (m, 5H; Ph), 6.50 [d, ^3J (H, H) = 15Hz, 1H; C=CH-Ph], 6.10 [dd, ^3J (H, H) = 15Hz, ^3J (H, H) = 7.2 Hz, 1H; C=CH], 4.50 [d, ^3J (H, H) = 7.2Hz, 1H; CH-OTMS], 3.65 (s, 3H; CO_2CH_3), 1.15 (s, 3H; CH_3), 1.00 (s, 3H; CH_3), 0.05 (s, 9H; $Si(CH_3)_3$) ; GC/MS (EI) m/z (intensity): 306 (M^+, 0.22).

(3h+ 6h) : ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ:177.50, 176.75, 136.80, 131.95, 129.42, 128.95, 128.80, 128.54, 127.84, 127.58, 126.45, 78.40, 51.64, 48.46, 47.34, 22.85, 22.33, 22.20, 21.26, 19.83, 0.30, -0.46; IR (Neat) : 1728, 1658 ; Anal. Calcd for $C_{17}H_{26}O_3Si$: C, 66.62; H, 8.55 ; Found : C, 66.76; H, 8.68.

Methyl 2-methyl-3-phenyl-5-trimethylsilyloxypent-4-enoate (6i) + Methyl 2-methyl-5-phenyl-3-trimethylsilyloxypent-4-enoate (3i) :

(6i) : ^{1}H NMR ($CDCl_3$, 250 MHz) (*Anti +syn*) δ: 7.4-7.10 (m, 5H; Ph), 6.30-6.01 (m, 1H; C=CH-OTMS), 5.24-5.09 (m, 1H; C=CH), 3.62 (s, 3 H; CO_2CH_3), 3.23 (m, 1 H; CH-Ph), 2.77-2.54 (m, 1H; CH), 0.15, 0.12 (*Z* + *E*) (2 s, 9H; $Si(CH_3)_3$); GC/MS (EI) m/z (intensity): 292 (M^+, 4).

(3i) : ^{1}H NMR ($CDCl_3$, 250 MHz) (*anti* + *syn*) δ: 7.4-7.10 (*anti* + *syn*) (m, 5H; Ph), 6.50 (*syn*) [dd, ^3J (H, H) = 4 Hz, ^3J (H, H) = 1Hz, 1H; C=CH], 6.46 (*anti*) [d, ^3J (H, H) = 4 Hz, ^3J (H, H) = 1Hz, 1H; C=CH], 6.30-6.01 (*anti* + *syn*) (m, 1H, C=CH-Ph), 4.50 (*syn*) [dd, ^3J (H, H) = 7 Hz, ^3J (H, H) =1Hz, 1H; CH-OTMS], 4.36 (*anti*) [dd, ^3J (H, H) = 7 Hz, ^3J (H, H) = 1 Hz, 1H; CH-OTMS], 3.68 (*anti*) (s, 3H; CO_2CH_3), 3.65 (*syn*) (s, 3H; CO_2CH_3), 2.77-2.54 (*anti* + *syn*) (m, 1H; CH), 1.17 (*syn*) [d, ^3J (H, H) = 7Hz, 3H; CH_3], 1.07 (*anti*) [d, ^3J (H, H) = 7Hz, 3H; CH_3], 0.07(*syn*) (s, 9H; $Si(CH_3)_3$), 0.09 (*anti*) (s, 9H; $Si(CH_3)_3$) ; GC/MS (EI) m/z (intensity) (*anti* + *syn*) : 292 (M^+, 0.6).

(3i)+ (6i) : ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 176.16, 175.37, 174.76, 143.36, 142.49, 141.29, 140.71, 136.71, 136.52, 131.89, 130.69, 130.53, 129.79, 128.78, 128.56, 128.51, 128.31, 128.00, 127.73, 127.68, 127.54, 127.35, 126.47, 126.44, 126.29, 113.12, 111.59, 76.11, 74.69, 51.51, 51.41, 51.30, 48.25, 47.59, 47.33, 46.89, 46.35, 45.82, 15.88, 14.92, 13.30, 12.14, 1.29, 0.15, -0.53. IR (Neat) : 1739, 1661, 1252 ; HRMS (EI) Calcd for $C_{16}H_{24}O_3Si$: 292.1494; Found : 292.1485.

Ethyl 5-phenyl-3-terbutyldimethylsilyloxypent-4-enoate (3j) + Ethyl 3-phenyl-5-terbutyldimethylsilyloxypent-4-enoate (6j) :

(3j) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.55-7.20 (m, 5H; Ph), 6.56 [d, ^3J (H, H) =16Hz, 1H; CH-Ph], 6.17 [dd, ^3J (H, H) = 16Hz, ^3J (H, H) = 6.6Hz, 1H; C=CH], 4.75 (m, 1H; CH-OTBDMS), 4.09 (m, 2H; CO_2CH_2), 2.55 (m, 2H; CH_2), 1.25 [t, ^3J (H, H) = 7.2Hz, 3H; CH_3], 0.88 (s, 9H; $C(CH_3)_3$), 0.05 (s, 6H; $Si(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 171.02, 136.65, 131.67, 129.89, 128.55, 127.60, 126.45, 70.72, 60.42, 44.02, 25.74, 18.08, 14.20, -4. 25, -5.06 ; GC/MS (EI) m/z (intensity) 319 (M-15, 0.5) ; HRMS (EI) Calcd for $C_{19}H_{20}O_3Si$-C_4H_9 : 277.1260; Found : 277.1241.

(6j) : ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.55-7.20 (m, 5H; Ph), 6.30 (m, 1H; C=CH-OTBDMS), 5.15 (m, 1H; C=CH), 4.09 (m, 2H; CO_2CH_2), 3.21 (m, 1H; CH-Ph), 2.55 (m, 2H; CH_2), 1.25 [t, ^3J (H, H) = 7.2Hz, 3H; CH_3]), 0.88 (s, 9H; $C(CH_3)_3$), 0.09 (s, 6H; $Si(CH_3)_2$) ; GC/MS (EI) m/z (intensity) 319 (M-15, 0.9) ; HRMS (EI) Calcd for $C_{19}H_{20}O_3Si$-C_4H_9 : 277.1260; Found : 277.1254.

(3j) + (6j) IR (neat) : 1737 ; Anal. Calcd for $C_{19}H_{20}O_3Si$-C_4H_9 : C, 68.22; H, 9.04 ; Found : C, 68.04; H, 9.21.

1,5-diphenyl-3-trimethylsilyloxy-4-penten-1-one (4c) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.90-7.20 (m, 10H; Ph), 6.60 [d, ^3J (H, H) = 15Hz, 1H; C=CH-Ph], 6.30 [dd, ^3J (H, H) = 15Hz, ^3J (H, H) = 7Hz, 1H; C=CH] 4.95 (m, 1H; CH-OTMS), 3.45-2.95 (m, 2H; CH_2), 0.05 (s, 9H; $Si(CH_3)_3$) ; GC/MS (EI) m/z (intensity): 324 (M^+, 6) ; Anal. Calcd for $C_{20}H_{24}O_2Si$: C, 74.07; H, 7.41 ; Found : C, 74.09; H, 7.26.

1,3-diphenyl-5-trimethylsilyloxy-4-penten-1-one (7c) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.90-7.10 (m, 10H; Ph), 6.30 (m, 1H; CH-OTMS), 5.32 (m, 1H; C=CH), 4.05 (m, 1H; CH-Ph), 3.50-3.00 (m, 2H; CH_2), 0.10 (s, 9H; $Si(CH_3)_3$) ; GC/MS (EI) m/z (intensity): 324 (M^+, 6).

2-(1-phenyl-3-trimethylsilyloxy-2-propenyl)-cyclohexanone (4d) (*Syn -Anti* : 50-50): ^{1}H NMR ($CDCl_3$, 250 MHz) δ: (*Syn+Anti*): 7.30 (m, 5H; Ph), 6.55 [d, ^3J (H, H) = 16Hz, 0.5H; C=CH-Ph], 6.50 [d, ^3J (H, H) = 16Hz, 0.5H; C=CH-Ph], 6.35 [dd, ^3J (H, H) = 16Hz, ^3J (H, H) = 5Hz, 0.5H; C=CH], 6.25 [dd, ^3J (H, H) = 16Hz, ^3J (H, H) = 6Hz, 0.5H; C=CH)], 4.75 (m, 1H; CH-OTMS), 2.55 (m, 1H; CH), 2.40-1.50 (m, 8H; $4CH_2$), 0.15 (m, 9H; $Si(CH_3)_3$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (*Syn +Anti*) : 211.37, 211.34, 136.97, 136.88, 131.85, 130.43, 130.26, 129.33, 128.46, 127.10, 126.34, 71.43, 70.60, 57.46, 57.02, 42.51, 42.13, 28.60, 28.43, 27.63, 27.45, 24.50, 24.32, 0.24, 0.22 ; GC/MS (EI) m/z (intensity): 302 (M^+, 1) ; HRMS (EI) Calcd for $C_{18}H_{26}O_2Si$: 302.1702 ; Found : 302.1693 ; Anal. Calcd for $C_{18}H_{26}O_2Si$: C, 71.50; H, 8.60 ; Found : C, 72.12; H, 8.68.

Methyl 2,2-dimethyl-3-trimethylsilyloxydec-4-enoate (3k) + Methyl 2,2-dimethyl-3-(2-trimethylsilyloxy-ethyliden)-octanoate (6k)

(3k) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 5.55 (m, 1H; C=CH), 5.31 (m, 1H; C=CH), 4.22 [d, ^3J (H, H) = 7.5Hz, 1H; CH-OTMS], 3.62 (s, 3H; CO_2CH_3), 1.98 (m, 2H; CH_2), 1.25 (m, 6H; 3 CH_2), 1.09 (s, 3H; C-CH_3), 1.00 (s, 3H; C-CH_3), 0.86 [t, ^3J (H, H) = 6.5Hz, 3H; CH_3], 0.02 (s, 9H; $SiCH_3)_3$). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 177.41, 133.83, 128.89, 78.55, 51.53, 32.22, 31.34, 28.88, 22.47, 21.16, 19.72, 14.07, 0.34; GC/MS (EI) m/z (intensity): 300 (M^+, 0,1) ; HRMS (EI) Calcd for $C_{16}H_{32}O_3Si$-CH_3 : 285.1885; Found : 285.1931.

(6k) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 6.12 [d, ^3J (H, H) = 11.8Hz, 1H; C=CH-OTMS], 4.67 [dd, ^3J (H, H) = 11.8Hz, ^3J (H, H) = 10.7Hz, 1H; C=CH], 3.65 (s, 3H; CO_2CH_3), 1.98 (m, 3H; CH + CH_2), 1.25 (m, 6H; 3 CH_2), 1.06 (s, 3H; C-CH_3), 1.04 (s, 3H; C-CH_3), 0.86 [t, ^3J (H, H) = 6.5, 3H; CH_3], 0.17 (s, 9H; $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 178.68, 141.50, 111.71, 48.05, 45.80, 31.46, 30.30, 27.51, 23.95, 22.60, 20.73, 14.04, -0.50; GC/MS (EI) m/z (intensity): 300 (M^+, 0.2) ; HRMS (EI) Calcd for $C_{16}H_{32}O_3Si$-CH_3 : 285.1885; Found : 285.1927.

(3k+6k) IR (neat) : 1741, 1653.

Methyl 2-methyl-3-trimethylsilyloxydec-4-enoate (3l) + Methyl 2-methyl-3-(2-trimethylsilyloxy-ethyliden)-octanoate (6l):

(3l) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: *syn* + *anti* 5.48 (m, 1H *syn* + *anti*; C=CH), 5.23 (m, 1H *syn* + *anti*; C=CH), 4.13 [t, ^3J (H, H) = 6Hz, 1H *syn*; CH-OTMS], 4.02 [t, ^3J (H, H) =6 Hz, 1H *anti*; CH-OTMS], 3.54, 3.51 (2s, 3H *syn* + *anti*; CO_2CH_3), 2.38 (m, 2H *syn* + *anti* =C-CH_2), 1.88 (m, 2H *syn* + *anti*; CH_2), 1.15 (m, 4H *syn* + *anti*; 2 CH_2), 1.02 [d, ^3J (H, H) = 8Hz], 0.91 [d, ^3J (H, H) = 8Hz], 3H *syn* + *anti*; CH_3)], 0.75 [t, ^3J (H, H) = 6Hz, 3H *syn* + *anti*; CH_3], -0.05, -0.04 (2s, 9H *syn* + *anti*; $Si(CH_3)_3$); GC/MS (EI) m/z (intensity) : 286 (M^+, 0.3) HRMS (EI) Calcd for $C_{15}H_{30}O_3Si$: 286.1956; Found : 286.1968.

(6l) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: *syn* + *anti* 6.20 [d, ^3J (H, H) = 10Hz, 1H; C=CH-OTMS], 4.75 (m, 1H; C=CH), 3.54 (s, 3H; CO_2CH_3), 2.38 (m, 3H ; CH + CH_2), 1.88 (m, 2H; CH_2), 1.15 (m, 4H; 2 CH_2), 1.09 [d, ^3J (H, H) = 8Hz, 3H; CH_3], 0.75 [t, ^3J (H, H) = 6Hz, 3H; CH_3], 0.06 (s, 9H; $Si(CH_3)_3$) ; GC/MS (EI) m/z (intensity): 286 (M^+, 5.8) ; HRMS (EI) Calc for $C_{15}H_{30}O_3Si$-CH_3 : 271.1721; Found : 271.1771.

(3l+6l) ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 176.01, 175.35, 175.32, 141.31, 141.03, 134.26, 132.74, 132.72, 131.32, 130.68, 128.61, 128.17, 125.90, 113.60, 113.16, 76.78, 75.29, 51.72, 51.70, 47.55, 47.42, 45.26, 44.95, 41.90, 41.72, 33.90, 33.77, 32.45, 32.39, 32.04, 31.94, 31.69, 31.66, 30.49, 30.45, 29.20, 29.15, 27.33, 27.21, 23.00, 22.96, 22.82, 22.81, 15.95, 14.89, 14.36, 13.71, 12.76, 12.75, 0.60, 0.58, -0.17, -0.21; IR (Neat) 1741.

Ethyl 3-terbutyldimethylsilyloxydec-4-enoate (3m) : ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 5.55 [dt, ^3J (H, H) = 19Hz, ^3J (H, H) = 11Hz, 1H; C=CH], 5.35 [dd, ^3J (H, H) = 8.5Hz, ^3J (H, H) = 19Hz, 1H; C=CH], 4.50 (m, 1H; CH-OTBDMS), 4.05 [q, ^3J (H, H) *J*= 7Hz, 2H; CO_2CH_2], 2.40 (m, 2H; =C-CH_2), 1.90 (m, 2H; CH_2), 1.25 (m, 8H; 4 CH_2), 0.85 (m, 15H; $C(CH_3)_3$) + 2 CH_3), 0.00 (s, 6H, $Si(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 171.40, 132.05, 131.55, 70.90, 60.20, 44.15, 31.95, 31.30, 28.75, 25.70, 22.45, 14.15, 14.13, -4.25 ; GC/MS (EI) m/z (intensity): 313 (M-15, 1) ; IR (Neat) : 1743 ; Anal. Calcd for $C_{18}H_{36}O_3Si$: C, 65.79; H, 11.04 ; Found : C, 65.81; H, 10.88.

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REFERENCES and NOTES

1. a) Mukaiyama, T. *Org. React.* **1982**, *28*, 203-331; b) Mukaiyama, T. *Challenges in Synthetic Organic Chemistry*; Oxford Science Publications, 1990; 177-213; c) Gennari C. 629-660; d) Colvin E. in *Silicon in Organic Synthesis*; Butterworths, **1981**; pp. 199-287.
2. a) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503-7509; b) Mukaiyama, T. *Angew. Chem. Int. Ed. Eng.* **1977**, *16*, 817-826.
3. a) Heathcock, C.H.; Norman, M.H.; Uehling, D.E. *J. Am. Chem. Soc.* **1985**, *107*, 2797-2799; b) Heathcock, C.H.; Davidsen, S.K.; Hug, K.T.; Flippin, L.A. *J. Org. Chem.* **1986**, *51*, 3027-3037; c) Heathcock, C.H.; Oare D.A. in *Topics in Stereochemistry* (Ed. Eliel, E.L.; Wilen, S.H.) Interscience Publication, **1991**,vol. 20, pp. 87-170.
4. a) Mukaiyama, T.; Kobayashi, S .; Tamura, M.; Sagawa, Y. *Chem. Lett.* **1987**, 491-494; b) Iwasawa, N. ; Mukaiyama, T. *Chem. Lett.* **1987**, 463-466.

5. a) Mukaiyama, T.; Kobayashi, S.; Murakami, M. *Chem. Lett.* **1985**, 447-450; b) Mukaiyama, T.; Saito, K.; Kitagawa, H.; Shimomura, N. *Chem. Lett.* **1994**, 789-792.
6. a) Hong, Y.; Norris, D. J.; Collins, S. *J. Org. Chem.* **1993**, *58*, 3591-3594; b) Faller, J.W.; Gundersen, L.L. *Tetrahedron Lett.* **1993**, *34*, 2275-2278; c) Hollis, T.K.; Odenkirk, W.; Robinson, N.P.; Whelan, J.; Bosnich, B. *Tetrahedron* **1993**, *49*, 5415-5430.
7. Cozzi, P.G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Synlett* **1994**, 857-858.
8. a) Ishihara, K.; Hananki, N.; Yamamoto, H. *Synlett* **1993**, 577-579; b) Chen, J.; Sakamoto, K.; Orita, A.; Otera J. ***Synlett*, 1996**, 877-879.
9. a) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J.; Jaud, J.; Vignaux, P. *J. Org. Chem.* **1993**, *58*, 1835-1839; b) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J. *Bull. Soc. Chim. Fr.* **1993**, *130*, 832-842.
10. a) Sasidharan, M.; Raju, S.V.N.; Srinivasan, K.N.; Paul, V.; Kumar, R. *J. C. S., Chem. Commun.* **1996**, 129-130; b) Raju, S.V.N.; Ponratham, S.; Rajan, C.R.; Srinivasan, K.V. *Synlett* **1996**, 239-240. c) Ranu, B.C.; Saha, M.; Bhar, .S;. *Tetrahedron Lett.* **1993**, *34*,1989-1990. d) Ranu, B.C.; Chakraborty, B.C. *Tetrahedron* **1993**, *49*, 5333-5338.
11. a) Noyori, R.; Yokoyama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1265-1267; b) Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokohama, K;. Noyori, R. *J. Org. Chem.* **1983**, *48*, 932-945; c) Csuk, R.; Schaade, M. *Tetrahedron Lett.* **1993**, *49*, 7907-7910; d) RajanBabu, T.V. *J. Org. Chem.* **1984**, *49*, 2083-2089.
12. Vougioukas, A.E ; Kagan, H.B. *Tetrahedron Lett.* **1987**, *28*, 5513-5516.
13. Gong, L.; Streitwieser, A. *J. Org. Chem.* **1990**, *55*, 6235-6236.
14. a) Mikami, K.; Terada, M.; Nakai, T. *J. Org. Chem.* **1991**, *56*, 5456-5459; b) Mikami, K.; Terada, M.; Nakai, T. *Tetrahedron: Asymm.* **1991**, *2*, 993-996; c) Terada., M ; Gu, J.-H.; Deka, D.C.; Mikami, K.; Nakai T. *Chem. Lett.* **1992**, 29-32; d) Gu, J.-H.; Terada, M.; Mikami, K.; Nakai, T. *Tetrahedron Lett.* **1992**, *33*, 1465-1468.
15. Bonadies, F.; Lattanzi, A.; Orelli, L.R.; Pesci, S ; Scettri, A. *Tetrahedron Lett.* **1993**, *34*, 7649-7650.
16. Makioka, Y.; Nakagawa, I.; Taniguchi, Y.; Takaki, K ; Fujiwara, Y. *J. Org. Chem.* **1993**, *58*, 4771-4774.
17. a) Sasai, H.; Suzuki, T.; Arai, S.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1992**, *115*, 4418-4420; b) Sasai, H.; Arai, S.; Shibasaki, M. *J. Org. Chem.* **1994**, *59*, 2661-2664.
18. Kobayashi, S. *Chem. Lett.* **1991**, 2087-2090.
19. a) Kobayashi, S.; Hachiya, I. *Tetrahedron Lett.* **1992**, *33*, 1625-1628; b) Kobayashi, S.; Hachiya, I.; Takahori, T.; Araki, M.; Ishitani, H. *Tetrahedron Lett.* **1992**, *33*, 6815-6818; c) Kobayashi, S.; Hachiya, I.; Araki, M. *Synlett* **1993**, 472-474; d) Kobayashi, S.; Hachiya, I.;Takahori, T. *Synthesis* **1993**, 371-373; e) Kobayashi, S.; Hachiya, I. *J. Org. Chem.* **1994**, *59*, 3590-3596; f) Keller, E.B.; Feringa, L. *Tetrahedron Lett.* **1996**, *37*, 1879-1882.
20. Kobayashi, S. *Synlett* **1994**, 689-701.
21. a) Sasai, H.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1994**, *116*, 1571-1572; b) Sasai, H.; Arai, T.; Satow, Y.; Houk, K.N.; Shibasaki, M. *J. Am. Chem. Soc.* **1995**, *117*, 6194-; d) Arai, T.; Yamada, M.A.;Yamamoto, N.; Sasai, H.; Shibasaki, M. *Chem. Eur.* **1996**, *2*, 1368-1372; e) Shibasaki, M. *Pure Appl. Chem.* **1996**, *68*, 523-530.
22. Uotsu, K.; Sasai, H.; Shibasaki, M. *Tetrahedron: Asymm* **1995**, *6*, 71-74.
23. a) Kagan, H.B.; Namy, J.L *Tetrahedron* **1986**, *42*, 6573-6614; b) Molander, G.A. *Chem. Rev.* **1992**, *92*, 29-68.
24. a) Nomura, R.; Matsuno, T. Endo T. *J. Am. Chem. Soc.*, **1996**, *118*, , 11666-11667; b) Corey, E.J.; Zheng, G. Z. *Tetrahedron Lett.* **1997**, *38*, 2045-2048.
25. Collin, J.; Namy, J.L.; Kagan, H.B. *New J. Chem.* **1986**, *10*, 229-232.
26. Evans, D.A.; Hoveyda, A.H. *J. Am. Chem. Soc.* **1990**, *112*, 6447-6449.

27. Prandi, J.; Namy, J.L.; Menoret, G.; Kagan, H.B. *J. Organometal. Chem.* **1985**, *285*, 449-460.
28. a) Van de Weghe, P.; Collin, J. *Tetrahedron Lett.* **1993**, *34*, 3881-3884; b) Van de Weghe, P.; Collin, J. *Tetrahedron Lett.* **1994**, *35*, 2545-2548; c) Van de Weghe, P.; Collin, J. *Tetrahedron Lett.* **1995**, *36*, 1649-1652.; Collin, J.; Giuseppone, N.; Van de Weghe, P. *Coord. Chem. Rev.* in press.
29. Sarkar, T.K.; Nandy, S.K. *Tetrahedron Lett.* **1996**, *37*, 5195-5198.
30. Namy, J.L.; Girard, P.; Kagan, H.B. *New. J. Chem.* **1977**, *1*, 5-7.
31. The composition of this powder was checked by elemental analysis. A sample of SmI_2 commercially available as a powder from Aldrich exhibits no catalytic activity for aldol reaction.
32. Watson, P.L.; Tulip, T.H.; Williams, I. *Organometallics* **1990**, *9*, 1999-2009.
33. Hydrio, J. Van de Weghe, P.; Collin, J. *Synthesis* **1997**, 68-72.
34. Dicker, I.B. *J. Org. Chem.* **1993**, *58*, 2324-2327.
35. We compared the activity of $Yb(OTf)_3$ and $Sc(OTf)_3$ in the aldolisation reaction leading to **1a** and in the Michael reactions giving **6b** and **3h+6h**. In all cases the rate of the reactions were similar using triflates and samarium diiodide or slightly higher with the latter. Yet with $Yb(OTf)_3$ and $Sc(OTf)_3$ the aldol reaction yields to the aldol instead of its silyl ether and the Michael reactions give a mixture of the enoxysilane and the corresponding ketone.
36. Otera, J.; Fujita, K.; Hirai, S.; Gu, J.; Nakai, T. *Tetrahedron Lett.* **1995**, *36*, 95-98.
37. Carreira, E.M.; Singer, R. *Tetrahedron Lett.* **1994**, *35*, 4323-4326.
38. Denmark, S.C.; Chen, C.T. *Tetrahedron Lett.* **1994**, *35*, 4327-4330.
39. Hollis, T. K.; Bosnich, B. *J. Am. Chem .Soc.* **1995**, *117*, 4570-4581.
40. Cozzi, P.G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 2131-2134.
41. a) Sato, T.; Wakahara,Y.;. Otera, J.; Nozaki,H.; Fukuzumi, S. *J. Am. Chem. Soc.* **1991**, *113*, 4028-4030; b) Fukuzumi, S.; Fujita, M.; Otera, J.; Fujita, Y. *J. Am. Chem .Soc.* **1992**, *114*, 10271-10278.
42. a) Otera, J.; Fujita, Y.; Sato, T.; Nozaki,H.; Fukuzumi, S.; Fujita, M. *J. Org. Chem.* **1992**, *57*, 5054-5055; b) Otera, J.; Fujita, Y.; Sakuta, N.; Fujita, M.; Fukuzumi, S. *J. Org. Chem.* **1996**, *61*, 2951-2962; c) Otera, J.; Fujita, Y.; Fukuzumi, S. *Tetrahedron*, **1996**, *52*, 9409-9418.
43. Namy, J.L.; Souppe, J.; Kagan, H.B. *Tetrahedron Lett.* **1983**, *24*, 765-766.
44. Mikami, K.; Matsukawa, S. *J. Am. Chem. Soc.* **1994**, *116*, 4077-4078.
45. Evans, D.A.; Murry, J.A.; Kozlowski, M.C. *J. Am. Chem. Soc.* **1996**, *118*, 5814-5815.
46. The difference between the energies of dissociation of Sm-X and Si-X bonds is quite smaller for X=I than for X= Br, Cl, O. *Handbook of Chemistry and Physics*, CRC Press Inc, Boca Raton Florida, 1984, F176-F181.
47. An example of asymmetric aldol reactions catalyzed by chiral triaryl carbenium ions has given modest enantioselectivities explained by the intervention of a silicon catalyzed process : Chen, C-T.; Chao, S-D.; Yen, K-C.; Chen, C-H.; Chou, I-C ; Hon, S-W. *J. Am. Chem. Soc.* **1997**, *119*, 11341-11342.
48. Girard, P. ; Namy, J.L.; Kagan, H.B. *J. Am. Chem. Soc.* **1980**, *102*, 2693-2698.
49. Namy, J.L.; Souppe, J.; Collin, J.; Kagan, H.B. *J. Org. Chem.* **1984**, *49*, 2045-2049.
50. Lebrun, A.; Rantze, E.; Namy, J.L.; Kagan, H.B. *New. J. Chem.* **1995**, *19*, 699-705.
51. Qian, C.; Zheng, P.; Wang, B. ; Deng, D.; Sun, J. *Organomet. Chem.* **1994**, *466*, 101-105.
52. Kita, Y.; Segewa, J.; Haruta, J.; Yasuda, H.; Tamura, Y. *J. Chem. Soc. Perkin Trans. 1*, **1982**, 1099-1104.