Tetrahedron 66 (2010) 265–273

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of functionalised β-lactones via silylcarbocyclisation/desilylation reactions of propargyl alcohols

Laura Antonella Aronica *, Caterina Mazzoni, Anna Maria Caporusso

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

ARTICLE INFO

Article history:
Received 29 July 2009
Received in revised form 9 October 2009
Accepted 29 October 2009
Available online 1 November 2009

Keywords:
Lactones
Silylformylation
Silylcarbocyclisation
Desilylation

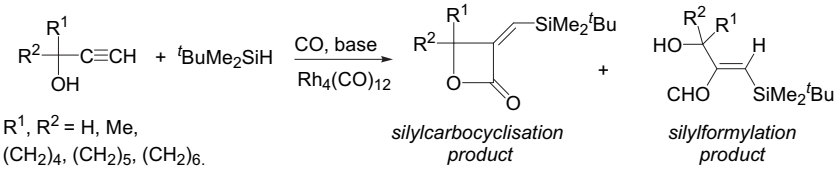
ABSTRACT

Functionalised β-lactones were prepared starting from propargyl alcohols by means of an efficient rhodium-catalysed silylcarbocyclisation reaction. This process took place in high yields and complete stereoselectivity using DBU as the base, a sterically hindered alcohol and/or hydrosilane. Otherwise, a silylformylation competitive reaction occurred affording 3-hydroxy-2-[(aryldimethylsilyl)methylene]alkanals with complete regioselectivity. Indeed, while α-(aryldimethylsilylmethylene)-β-lactones were generated exclusively starting from an alkynol characterised by two alkyl groups on the propargyl carbon atom, significant amounts of the aldehydes were observed for secondary alcohols. In these cases, the use of *ortho*-substituted arylsilanes improved the chemoselectivity towards the α-methylene-β-lactones. Such molecules were then successfully converted into α-methylaryl-β-lactones by a fluoride-induced rearrangement of the aryl group that migrates from silicon to carbon with retention of configuration.

1. Introduction

β-Lactones (2-oxetanones) have recently emerged as important synthetic targets due to their occurrence in a variety of natural compounds such as lipstatin, esterastin, valilactone, ebelactones, anisatin and lupeolactone,[1] which are efficient inhibitors of several enzymes.[2] Moreover, their utility as versatile organic intermediates is well recognized since they combine the structural features of a masked aldol product with the exceptional reactivity of a strained ring system that may be readily opened by nucleophiles, undergo enolate formation and reactions towards electrophiles. In addition they can be transformed into unsaturated products by decarboxylation, undergo Lewis acid-promoted rearrangements leading to ring expansion[3] and polymerised by various initiators and catalysts.[4]

Considering the significant synthetic value of β-lactones, it is not surprising that many synthetic methods have been developed to achieve selective and efficient syntheses. The fundamental approaches for the preparation of 2-oxetanones are based on the lactonization of β-hydroxyl acids via hydroxyl or carboxyl group activations, lactonization of β-halocarboxylic acids, tandem Mukayama aldol-lactonization and [2+2] cycloaddition of ketenes and carbonyl compounds.[5] Another attractive route to β-lactones is the ring-expansive carbonylation of epoxides, promoted by cobalt-based catalysts.[6] In 1990 Matsuda and co-workers[7] reported the first example of rhodium-catalysed silylcarbocyclisation of propargyl alcohols that generated α-(triorganosilyl)methylene-β-lactones in good yields, provided that a suitable base and a sterically hindered hydrosilane were used (Scheme 1). In fact, silylformylation by-products (i.e., β-silylalkenals), derived from the direct addition of CO and silane to the triple bond without cyclisation, were often observed.



Scheme 1.

The data described by Matsuda and further examples reported by the author in a Japanese patent published in 1991,[8] prompted us to take into account the silylcarbocyclisation of several acetylenic

* Corresponding author. Tel.: +39 0502219274; fax: +39 0502219260.
E-mail address: aronica@dcci.unipi.it (L.A. Aronica).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.10.112

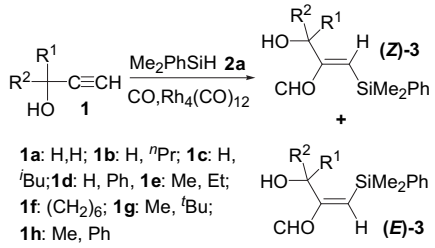
alcohols with aryldimethylsilanes. We were particularly intrigued by the possibility of applying the silylation-aryl migration protocol that we had already developed for the synthesis of linear aldehydes and heterocycles[9] to the preparation of functionalised β-lactones. Indeed, we have shown that an aryldimethylsilyl moiety present on a β-lactam or a β-silylalkenal could act as carrier of the aryl group from silicon to the adjacent carbon atom when tetrabutylammonium fluoride was added. The two-step sequence of silylcarbocyclisation–desilylation and aryl migration was applied to terminal acetylenes containing functional groups in the ω-position such as double and triple bonds, epoxide, esters, nitrile and hydroxyl. As far as propargyl derivatives, while propargyl amides have been recently[10] employed in the synthesis of 2-benzylalkenals and 3-methylaryl-β-lactams, in our opinion the reactivity of propargyl alcohols as not yet been investigated comprehensively.

In this paper, we describe a detailed study on the silylformylation of several propargyl alcohols characterized by different steric and electronic requirements. Subsequently, the silylcarbocyclisation process is considered and an analysis of the factors that can influence the chemoselectivity of such reaction is reported. Finally, the fluoride-induced aryl migration step will be extended to the derivatives obtained.

2. Results and discussion

2.1. Silylformylation of propargyl alcohols

The silylformylation reactions of propargyl alcohols were performed in a stainless steel autoclave charged with carbon monoxide and an equivalent amount of the alcohol and the silane, in the presence of 0.1% mmol of $Rh_4(CO)_{12}$. The results are summarised in Table 1 and indicate that the substrates **1a**–**h** (Scheme 2) selected reacted readily with complete chemo- and regioselectivity, affording the corresponding 3-hydroxy-2-[(dimethylphenylsilyl)methylene]alkanals **3** in good yields.



Scheme 2.

Table 1
Silylformylations of propargyl alcohols with Me_2PhSiH[a]

Entry	1	R^1	R^2	P_{CO} (atm)	t (h)	Conv[b]. (%)	3	Yield (%)[c]	
								(*Z*)-3	(*E*)-3
1	a	H	H	10	12	100	aa	83(71)	17(11)
2	b	H	^{n}Pr	10	24	99	ba	84(53)	16(10)
3	c	H	^{i}Bu	30	24	80	ca	96(60)	4
4	d	H	Ph	30	24	100	Da	79(66)	21(12)
5	e	Me	Et	20	24	86	ea	85(55)	15(8)
6	f			30	24	100	fa	97(90)	3
7	g	Me	^{t}Bu	30	96	51	ga	23(7)[d]	—
8	h	Me	Ph	30	24	85	ha	100(55)	—

[a] Reaction conditions: 3 mmol of Me_2PhSiH, 3 mmol of alcohol, $3\cdot10^{-3}$ mmol of $Rh_4(CO)_{12}$, 3 mL of CH_2Cl_2, room temperature.
[b] Calculated by GLC conversion of the hydrosilane.
[c] Determined by GLC and ^1H NMR spectroscopic analysis of the reaction mixture after work up. In parentheses the isolated yields of pure compounds are reported.
[d] Hydrosilylation by-products were detected by ^1H NMR spectroscopy.

The reaction time was highly affected by the steric hindrance of the alkyl and aromatic substituents on the propargyl carbon atom. Indeed, when the steric requirements of the R^2 group of the substrates were increased from a hydrogen atom to an isobutyl group, both the reaction time and the CO pressure had to be raised to gain a nearly complete conversion of the reagents (Table 1, entries 1–3). We determined that 30 atm of carbon monoxide and 24 h reaction time were required for almost all the alcohols. Only in the case of the most hindered 3,4,4-trimethyl-1-pentyn-3-ol **3g** (Table 1, entry 7), the conversion reached 50% after four days, and the formation of relevant amounts of hydrosilylation by-products was detected.

As described in Scheme 2, the silylformylation reaction proceeded with complete regioselectivity, i.e., the silicon moiety added to the terminal carbon atom while the aldehydic group was introduced into the internal position of the triple bond. The kinetically favoured (*Z*)-**3** isomers were principally formed together with small amounts (4–21%) of the corresponding (*E*)-**3** compounds. The configuration of the two stereoisomers was confirmed by means of NOESY experiments. For instance, in the cases of the carbonyl compounds (*Z*)-**3ea** and (*E*)-**3ea** generated starting from 3-methyl-1-pentyn-3-ol **1e**, relevant NOE effects between the aldehydic proton and the methyl groups bonded to the silicon atom were detected in the (*Z*)-product as shown in Figure 1a; on the other hand, the NOESY spectra confirmed the interaction between the CHO proton and the vinyl hydrogen in the *E*-isomer (Fig. 1b).

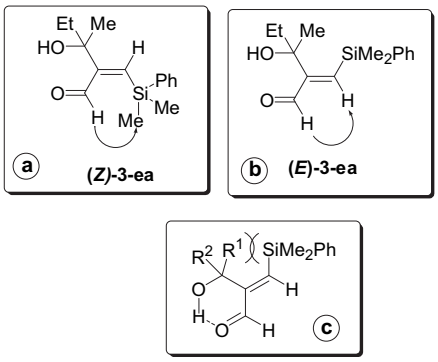


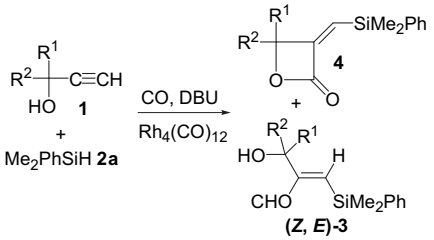
Figure 1.

It is well known that (*Z*)-silylalkenals can isomerise to the *E*-structure in the presence of protic acids and high temperatures[11], but they have seldom been observed under the typical experimental conditions of the silylformylation (10–30 atm CO, aprotic solvent, room temperature). The unexpected *E* isomers could be caused by the presence of the hydroxyl group that could favour an *s-trans* conformation stabilized by a hydrogen bond between the OH proton and the CO moiety (Fig. 1c). However, the increase of the steric requirements of the propargyl substituents R^1 and R^2 determined a reduction of stability of the *E*-geometry (Fig. 1c) and consequently an improvement of the selectivity towards the *Z* products as observed in entries 3 and 6–8 of Table 1.

2.2. Silylcarbocyclisation of propargyl alcohols

The silylcarbocyclisation reactions were initially performed under the experimental conditions (3 mmol silane, 3 mmol alcohol, 0.1 mol % $Rh_4(CO)_{12}$, 100 °C, 4 h, 10% DBU), previously optimised for the synthesis of β-lactams starting from propargyl tosyl amides.[10] Contrary to what was observed for the silylformylation reaction, the cyclisation process (Scheme 3) was favoured by a steric

environment around the propargyl carbon atom as shown in Table 2 (entries 3–5). In these examples the reactions were stereoselective yielding the (*Z*)-(dimethylphenylsilyl)methylene-β-lactones **4ea**–**ga** as almost sole products. An opposite behaviour was observed in the reaction of 2-propyn-1-ol **1a** giving exclusively the corresponding β-silylalkenals (*E*, *Z*)-**3aa** together with small amounts of unidentified by-products. When a secondary propargyl alcohol (**1b**) was tested, a slight improvement in the silylcarbocyclisation process was detected (Table 2, entry 2, 36% β-lactone), the major products still being aldehydes. Indeed, besides the β-silylalkenals (*Z*, *E*)-**3ba**, significant quantities (30%) of (*Z*)-2-[(dimethylphenylsilyl)methyl]-2-hexenal **5ba** (Fig. 2) were identified by means of ^{1}H NMR spectroscopic analysis.



Scheme 3.

Table 2
Silylcarbocyclisation of propargyl alcohols with Me_2PhSiH[a]

Entry	1	R^1	R^2	Conv.(%)[b]	3,4	Yield (%)[c]	
						4[d]	3 (*Z*/*E*)
1	a	H	H	100	aa	0	70(66/34)[e]
2	b	H	^{n}Pr	100	ba	36(24)	29(46/54)[f]
3	e	Me	Et	100	ea	93(76)	7(100/0)
4	f			100	fa	99(85)	1(100/0)
5	g	Me	^{t}Bu	99	ga	96(85)	4(100/0)
6	h	Me	Ph	85	ha	0	8(100/0)[g]

[a] Reaction conditions: 3 mmol of Me_2PhSiH, 3 mmol of alcohol, 0.3 mmol DBU, 3×10^{-3} mmol of $Rh_4(CO)_{12}$, 3 mL of CH_2Cl_2, 100 °C, 4 h, 30 atm CO.
[b] Calculated by GLC conversion of the hydrosilane.
[c] Determined by GLC and ^{1}H NMR spectroscopic analysis of the reaction mixture after work up.
[d] In parentheses the isolated yields of pure compounds are reported.
[e] Unidentified by-products were detected.
[f] (*Z*)-3-[(dimethylphenylsilyl)methyl]-2-hexenal (30%) was detected by ^{1}H NMR spectroscopic analysis.
[g] A complex mixture of several compounds was detected (Scheme 5).

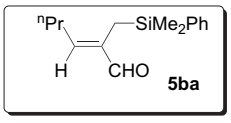
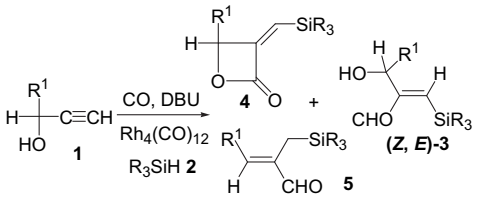


Figure 2.

Matsuda and co-workers[12] observed the formation of similar products when they ran the silylformylation reaction of propargyl amides with two equivalents of dimethylphenylsilane. The authors demonstrated that 2-[(dimethylphenylsilyl)methyl]-2-alkenals derived from the interaction of β-silylalkenals with an extra mole of silane. In the case of **1b,** the lack of bulkiness of the propargyl carbon probably reduces the rate of the silylcarbocyclisation reaction favouring the silylformylation process and the subsequent transformation of the resulting β-silylalkenals (*Z*, *E*)-**3ba** into **5ba**.

In order to minimize the formation of the aldehydic by-products, 1-hexyn-3-ol **1b** was reacted with several arylsilanes containing hindered substituents (Scheme 4, Table 3, **2a**–**g**). While **2a**–**c** and **2f** are commercially available, *o*-tolyldimethylsilane **2d**, *p*-phenylphenyldimethylsilane **2e**[13] and di-*t*-butylphenylsilane **2g** were easily prepared by reaction of the corresponding chlorosilane R_2ClSiH (R=Me, ^{t}Bu) with a suitable Grignard reagent (ArMgBr, Ar=*o*-tolyl, *p*-Ph-Ph, Ph). The data listed in Table 3 clearly indicate that the choice of the silane plays a crucial role in the silylcarbocyclisation process. In particular the substitution of Me_2PhSiH **2a** with $MePh_2SiH$ **2b** resulted in a significant increase of the lactone yield from 36 to 50% (Table 3, entries 1, 2). Unfortunately, more hindered phenylsilanes such as **2c** and **2g** were completely inactive (Table 3, entries 3, 8). When *p*-phenyl-phenyldimethylsilane **2e** was reacted with **1b** the complete consumption of the reagents was observed together with a low chemoselectivity (Table 3, entry 6). Much better results were obtained in the reactions with *o*-tolyldimethylsilane **2d**. Indeed, propargyl alcohols **1b** and **1c** were readily transformed into the corresponding β-lactones **4bd** and **4cd** (Table 3, entries 4, 5) highlighting the importance of an *ortho* substituent on the phenyl group bonded to the silicon atom.



Scheme 4.

Contrary to what was observed in the silylcarbocyclisation of alkyl propargyl alcohols (vide supra), the reaction of 2-phenyl-3-butyn-2-ol **1h** with Me_2PhSiH (Table 2, entry 6) did not afford any lactone derivative but a complex mixture of products as depicted in Scheme 5.

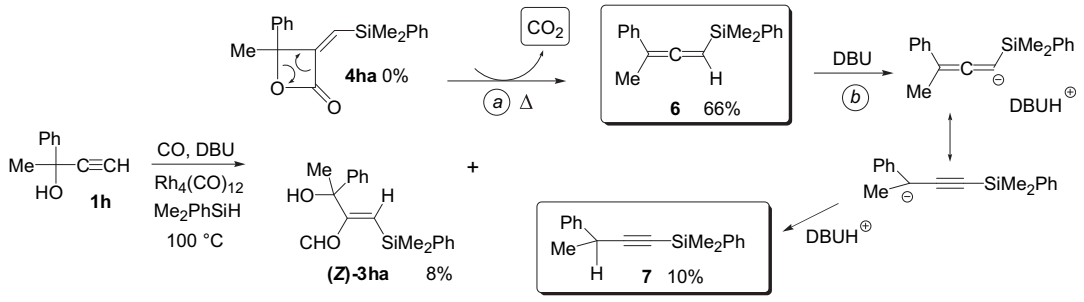
The formation of 1-(dimethylphenylsilyl)-3-phenyl-1,2-butadiene **6** can be ascribed to a thermal decarboxylation process of the corresponding β-lactone **4ha**. Indeed, it has already been demonstrated[14] that α-alkylidene-β-lactones can be converted into allenes via a [2+2] cycloreversion mechanism (Scheme 5, step a), which is favored by high temperature, polar solvents and electron donating groups such as phenyl and vinyl. The decarboxylation reaction generally takes place with complete retention of configuration of the β-lactone substituents and has been applied to the synthesis of polyfunctionalised allenes. After its formation, allene **6** may undergo a prototropic rearrangement[15], probably catalyzed by the base (DBU), thus generating dimethylphenylsilyl acetylene **7** (Scheme 5, step b). It is noteworthy that allenylsilanes are versatile substrates, which have been shown to react efficiently with several types of electrophiles.[16]

We tried to get the silylcarbocyclisation reaction of propargyl alcohol **1h** more chemoselective towards the corresponding β-lactone acting on the experimental condition. Considering that a polar solvent may favour the formation of the allene, a few reactions were performed using toluene instead of dichloromethane (Table 4). A significant improvement in the yield of the lactone ring was thus observed (Table 4, entry 2), although significant amounts of by-products were still present in the reaction mixture. Subsequently we investigated the influence of the temperature on the reaction progress. When the temperature was lowered from 100 °C to 70 °C, the allene by-product disappeared and the lactone resulted nearly the sole product, even if a longer reaction time was requested to achieve a high conversion of the reagents (Table 4, entry 5). The results show that the silylcarbocyclisation reactions

Table 3
Silylcarbocyclisation of secondary propargyl alcohols with different hydrosilanes[a]

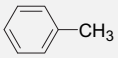
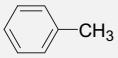
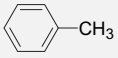
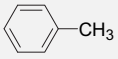
Entry	1	R^1	2	R_3SiH	Conv.(%)[b]	Yield (%)[c]			
						3–5	4[d]	3(*Z*/*E*)	5
1	**b**	^{n}Pr	**a**	Me_2PhSiH	100	**ba**	36(24)	29(46/54)	30[e]
2	**b**	^{n}Pr	**b**	$MePh_2SiH$	100	**bb**	50(32)	22(78/22)	28
3	**b**	^{n}Pr	**c**	Ph_3SiH	0	**bc**	—	—	—
4	**b**	^{n}Pr	**d**	*o*-$TolMe_2SiH$	100	**bd**	78(43)	22(100/0)	—
5	**c**	^{i}Bu	**d**	*o*-$TolMe_2SiH$	98	**cd**	81(53)	19(58/42)	—
6	**b**	^{n}Pr	**e**	*p*-Ph-$PhMe_2SiH$	100	**be**	22(12)	22(36/64)	37[e]
7	**b**	^{n}Pr	**f**	^{t}$BuMe_2SiH$	80	**bf**	66	6(100/0)	—[f]
8	**b**	^{n}Pr	**g**	^{t}Bu_2PhSiH	0	**bg**	—	—	—

[a] Reaction conditions: 3 mmol of Me_2PhSiH, 3 mmol of alcohol, $3\cdot10^{-3}$ mmol of $Rh_4(CO)_{12}$, 0.3 mmol DBU, 3 mL of CH_2Cl_2, 30 atm CO, 100 °C, 4 h.
[b] Calculated by GLC conversion of the hydrosilane.
[c] Determined by GLC and ^{1}H NMR spectroscopic analysis of the reaction mixture after work up.
[d] In parentheses the isolated yields of pure compounds are reported.
[e] Unidentified aldehydic by-products were detected.
[f] Several unidentified aldehydic by-products were detected by ^{1}H NMR spectroscopic analysis together with small amounts of (*E*)-2-[(terbutyldimethylsilyl)methylene]-2-hexanoic acid (9%).



Scheme 5.

Table 4
Silylcarbocyclisation of 2-phenyl-3-butyn-2-ol **1h** with Me_2PhSiH: temperature and solvent effects[a]

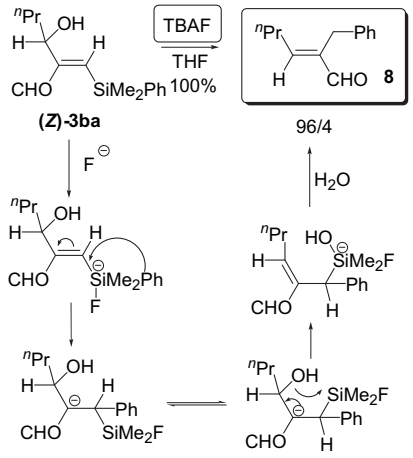
Entry	Solvent	*T* (°C)	*t* (h)	Conv. (%)[b]	Yield (%)[c]			
					4ha[d]	6[d]	7	(*Z*)-4ha
1	CH_2Cl_2	100	4	85	—	66(41)	10	8[e]
2		100	4	79	44	16	18	5[e]
3		80	4	80	66	12	11	10
4		70	4	42	87	—	—	13
5		70	6	70	99 (53)	—	—	1

[a] Reaction conditions: 3 mmol of Me_2PhSiH, 3 mmol of alcohol, 3×10^{-3} mmol of $Rh_4(CO)_{12}$, 0.3 mmol DBU, 30 atm CO, 3 mL of solvent.
[b] Calculated by GLC conversion of the hydrosilane.
[c] Determined by GLC and ^{1}H NMR spectroscopic analysis of the reaction mixture after work up.
[d] In parentheses the isolated yields of pure compounds are reported.
[e] Unidentified aldehydic by-products were detected.

represent a versatile and direct method for the synthesis of α-alkylidene-β-lactones, useful building blocks generally obtained by means of multi-steps sequences.[17]

2.3. Fluoride promoted aryl migration reactions

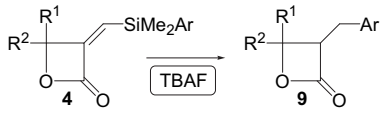
The reactivity of 3-hydroxy-2-[(dimethylphenylsilyl)methylene]alkanals (*Z*, *E*)-3 and (*Z*)-(aryldimethylsilyl)methylene-β-lactones **4** were evaluated in the fluoride-mediated aryl migration-desilylation process. The reactions were performed under very mild experimental conditions, i.e., excess tetrabutylammonium fluoride (2.5/1, TBAF) in THF, at room temperature.[10] Unfortunately, when (*Z*)-**3ba** was tested as model compound, 2-benzylhexanal **8** was recovered as sole identified product, after column chromatography on silica gel, in low yield (35%). Nevertheless, a complete conversion of the reagents was observed by gas-chromatography (Scheme 6) together with the formation of significant amounts of unidentified by-products. As already observed for carboxylic esters and tosyl amides derivatives[10], in this case the 1,2-anionotropic rearrangement is coupled with an elimination step, which generates double bonds with high



Scheme 6.

regioselectivity (96/4=*E*/*Z*). The formation of **8** may be explained considering the high affinity of silicon towards oxygen that can transform OH in a good leaving group as described by the mechanism hypothesised in Scheme 6.

At this point, we investigated the transformation of silyl lactones **4** into the corresponding α-methylaryl-β-lactones via the aryl migration process promoted by fluoride ions (Scheme 7). The reactions proceeded smoothly affording lactones **9** in good yields, as summarized in Table 5. Only in the case of compound **9ha** the purification process needs to be optimized (Table 5, entry 4), probably due to the ease of decomposition of the 3-benzyl-4-phenyl-4-methyl-oxetan-2-one as previously observed for its precursor **4ha** (see Scheme 5 and Table 4). The reaction conducted with **4cd** (Table 5, entry 5) showed that the desilylation process was also successful for the β-lactone derived from a secondary propargyl alcohol (**1c**), and that the aryl migration takes place with complete retention of the configuration of the aryl group (i.e., *o*-tolyl).



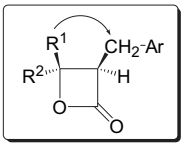
Scheme 7.

Table 5
Fluoride promoted synthesis of α-arylmethyl-β-lactones **9**[a]

Entry	4	R^1	R^2	Ar	Conv.(%)[b]	9	Yield (%)[c]	Diastereomeric ratio (*trans*/*cis*)[b]
1	**ea**	Me	Et	Ph	100	**ea**	66	70/30
2	**fa**			Ph	100	**fa**	68	—
3	**ga**	Me	^{t}Bu	Ph	93	**ga**	59	100
4	**ha**	Me	Ph	Ph	100	**ha**	30	100
5	**cd**	H	^{i}Bu	*o*-Tol	100	**cd**	60	89/11

[a] Reaction conditions: 2 mmol of lactones **4**, 4.5 mmol of TBAF (1 M in THF), 15 mL of THF.
[b] Calculated by GLC and ^{1}H NMR spectroscopic analyses.
[c] Isolated yields of the major isomer are reported.

The rearrangement process resulted highly diastereoselective affording mainly α-methylaryl-β-lactones **9** with the two bulky substituents *trans* to each other. The configuration of the diastereomers was evaluated by means of NOESY spectra (Fig. 3). For instance, in the case of 3-benzyl-4-ethyl-4-methyl-oxetan-2-one **9ea,** significant NOE contacts between the benzyl protons and the methyl group were observed.



R^1 = H, Me; **9 ea-cd**
R^2 = Et, ^{i}Bu, ^{t}Bu, Ph, *o*-Tol

Figure 3.

It is noteworthy that the diastereoselectivity of the rearrangement reaction depended on the steric requirements of the two groups R^1 and R^2 of the propargyl carbon. Indeed, while the reaction generated the main isomer in 70–90% yield for lactones **4ea** and **4cd** (Table 5, entries 1 and 5), the selectivity was complete in the cases of the more hindered substrates **4ga** and **4ha** (Table 5 entries 3, 4).

Finally, two homopropargylic alcohols, 5-hexyn-3-ol (**10a**) and 1-phenyl-3-butyn-1-ol (**10b**) were taken into account as model substrates to be tested in the silylcarbocyclisation-desilylation and aryl migration sequence (Scheme 8). As could be expected, both steps proceeded smoothly, affording the corresponding γ-lactones **11a**,**b** and **12a**,**b** in good yields (61–72%). Moreover, the TBAF-promoted phenyl anionotropic rearrangement took place with a good diastereoselectivity. NOESY experiments indicated the preferential formation of the isomer characterized by the benzyl moiety in the *cis* position respect to the R group. Preliminary results by molecular mechanics analysis revealed a higher stability (ca. 4 Kcal/mol) of the *cis* isomer respect to the corresponding *trans* isomer.

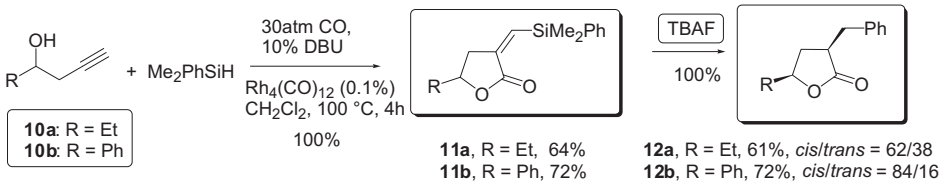
3. Conclusions

In conclusion, according to Matsuda's previous results, we have shown that functionalised β-lactones can be accessed by a silylcarbocyclisation of propargyl alcohols with arylsilanes, which is favoured by the presence of bulky substituents on both reagents. Indeed, alcohols with two alkyl groups on the propargyl carbon atom generated the corresponding (*Z*)-(dimethylphenylsilyl)-methylene β-lactones in high yields with complete stereoselectivity. The presence on the acetylenic carbinol of a phenyl instead of an alkyl group requested a simple optimisation process, i.e., the replacement of dichloromethane with toluene as solvent and the reduction of the temperature to 70 °C. Analogously, monoalkylated propargyl alcohols were smoothly converted into β-lactones when bulky aryldimethylsilanes were employed. On the contrary, 2-propynol afforded exclusively the corresponding aldehydic products, confirming the trend observed for the silylformylation process, which takes place easily if poorly hindered alcohols are used. The aryl migration step was then successfully applied to the (aryldimethylsilyl)methylene β-lactones. No ring opening was observed and the aryl group was transferred from silicon to the adjacent carbon atom with complete retention of configuration and with high stereoselectivity, thus affording α-methylaryl-β-lactones useful building blocks for organic synthesis[18] and potentially valuable as enzymes inhibitors.[19] Finally, the process of cyclisation-aryl migration was extended to the preparation of α-benzyl-γ-lactones, thus demonstrating the high versatility of the developed protocol.

4. Experimental section

4.1. General remarks

All solvents were reagent grade materials purified by standard methods. THF was distilled from sodium, CH_2Cl_2 from P_2O_5 and DBU from KOH immediately before use. All silanes **2** were distilled and stored under inert gas. Non-commercial silanes **2d**, **2e**[13] and **2g**



10a: R = Et
10b: R = Ph

11a, R = Et, 64%
11b, R = Ph, 72%

12a, R = Et, 61%, *cis*/*trans* = 62/38
12b, R = Ph, 72%, *cis*/*trans* = 84/16

Scheme 8.

were prepared from the corresponding Grignard reagents according to the method described by Hiyama and co-workers.[20] Propargyl alcohols **1a**–**h** were purchased from Sigma–Aldrich and distilled before use. TBAF solution (1 M in THF) was purchased from Fluka and used without purification. $Rh_4(CO)_{12}$ was prepared and purified as previously reported.[21] ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ solution with Me_4Si or $CHCl_3$ as internal standards; δ values are given in ppm and coupling constants (J) in Hertz. The *Z*/*E* and *cis*/*trans* configurations were determined by means of NOE experiments. Infrared absorption spectra were recorded as neat films. Mass spectra were obtained with a Varian Saturn connected to a Varian 3800 gas chromatograph. GLC analyses were performed with a Perkin Elmer Clarus 500 (30 m×0.52 mm, 5 μm) using He as the carrier gas and a flame ionization detector (FID). Column chromatography was performed on silica gel 60 (230–400 mesh). All products were identified and characterized by spectroscopic and analytical data.

4.2. General procedure for the silylformylation of propargyl alcohols with aryldimethylsilanes catalyzed by $Rh_4(CO)_{12}$

Catalytic runs were performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, freshly distilled CH_2Cl_2 (3 mL), previously degassed $ArMe_2SiH$ (3 mmol), the required propargyl alcohol (3 mmol), and 3×10^{-3} mmol of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex 'Schlenk' tube. This solution was introduced in the autoclave, previously placed under vacuum (0.1 mm Hg), by a steel syphon. The reactor was pressurized with carbon monoxide and the mixture was stirred at room temperature for the requested time. After removal of excess CO (fume hood), the reaction mixture was diluted with CH_2Cl_2, filtered on Celite and concentrated in vacuum. The reagents conversion and the products composition were determined by GLC and ^1H NMR. The purification of the crude oil by column chromatography on silica gel afforded the pure β-silylalkenals.

*4.2.1. (Z)-2-Hydroxymethyl-3-[(dimethylphenylsilyl)methylene]propanal (Z)-**3aa**.* The crude oil was purified by column chromatography on silica gel using hexane/AcOEt=90/10 as eluent (71% yield); ^1H NMR δ 0.52 (6H, s), 2.00 (1H, sb), 4.35 (2H, d, J=1.4 Hz), 7.17 (1H, t, J=1.4 Hz), 7.34–7.38 (3H, m), 7.49–7.53 (2H, m), 9.78 (1H, s); ^{13}C NMR δ −0.2, 64.7, 128.8, 130.2, 134.1, 137.8, 140.5, 144.8, 193.8; IR ν 3422, 3066, 2955, 2700, 1950, 1885, 1811, 1677, 1422, 1250. Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32; found: C, 65.45; H, 7.30.

*4.2.2. (E)-2-Hydroxymethyl-3-[(dimethylphenylsilyl)methylene]propanal (E)-**3aa**.* The crude oil was purified by column chromatography on silica gel using hexane/AcOEt=90/10 as eluent (11% yield); ^1H NMR δ 0.49 (6H, s), 2.40 (1H, sb), 4.38 (2H, d, J=1.8 Hz), 7.24 (1H, t, J=0.7 Hz), 7.34–7.38 (3H, m), 7.49–7.53 (2H, m), 9.74 (1H, s); IR ν 3422, 3066, 2955, 2700, 1950, 1885, 1811, 1677, 1422, 1250.

*4.2.3. (Z)-2-[(Dimethylphenylsilyl)methylene]-3-hydroxy-hexanal (Z)-**3ba**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=70/30 as eluent (53% yield); ^1H NMR δ 0.51 (6H, s), 0.91 (3H, t, J=7.1 Hz), 1.20–1.70 (4H, m), 2.40 (1H, sb), 4.50 (1H, m), 7.16 (1H, s), 7.30–7.45 (3H, m), 7.47–7.60 (2H, m), 9.77 (1H, s); ^{13}C NMR δ −0.3, 13.9, 18.9, 38.3, 71.2, 128.2, 129.6, 133.5, 137.5, 148.6, 158.0, 193.3; MS (EI) m/z (rel int.%): 247 (M^+-15, 15), 219 (13), 205 (24), 185(11), 141 (19), 135 (23), 129 (13), 105 (13), 91 (12), 75 (100), 43 (29); IR ν 3422, 3055, 2955, 2722, 1955, 1894, 1822, 1761, 1677, 1586, 1422, 1250. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45; found: C, 68.94; H, 8.37.

*4.2.4. (E)-2-[(Dimethylphenylsilyl)methylene]-3-hydroxy-hexanal (E)-**3ba**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=70/30 as eluent (10% yield); ^1H NMR δ 0.50 (3H, s), 0.53 (3H, s), 0.80 (3H, t, J=7.0 Hz), 1.00–1.70 (4H, m), 2.64–2.69 (1H, d, J=9.5 Hz), 4.30–4.40 (1H, m), 6.81 (1H, s), 7.36–7.40 (3H, m), 7.51–7.56 (2H, m), 9.42 (1H, d, J=1.8 Hz); ^{13}C NMR δ −1.7, −1.3, 13.7, 19.1, 38.7, 71.8, 128.1, 129.6, 133.6, 137.1, 152.8, 158.0, 196.6; MS (EI) m/z (rel int.%): 244 (M^+-18, 3); 169 (13); 155 (12); 141 (38); 135 (34); 129 (14); 113 (11); 105 (18); 93 (13); 91 (20); 77 (58); 75 (100); IR ν 3444, 3055, 2955, 2722, 1955, 1894, 1822, 1761, 1677, 1594, 1422, 1250.

*4.2.5. (Z)-2-[(Dimethylphenylsilyl)methylene]-3-hydroxy-5-methylhexanal (Z)-**3ca**.* The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (60% yield); ^1H NMR δ 0.54 (6H, s), 0.93–0.98 (6H, m), 1.35–1.55 (2H, m), 1.75–1.89 (1H, m), 2.41 (1H, sb), 7.19 (1H, s), 7.36–7.40 (3H, m), 7.52–7.55 (2H, m), 9.80 (1H, s); ^{13}C NMR δ −0.1, 21.9, 23.7, 25.1, 46.1, 70.2, 128.5, 129.9, 133.8, 137.7, 148.7, 158.6, 193.6; IR ν 3425, 3054, 2955, 1955, 1882, 1815, 1680, 1595, 1428, 1252. Anal. Calcd for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75; found: C, 69.58; H, 8.72.

*4.2.6. (Z)-2-[(Dimethylphenylsilyl)methylene]-3-hydroxy-3-phenylpropanal (Z)-**3da**.* The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (66% yield); ^1H NMR δ 0.71 (3H, s), 0.73 (3H, s), 2.78 (1H, sb), 5.79 (1H, s), 7.39–7.72 (11H, m), 9.94 (1H, s); ^{13}C NMR δ−0.4, 72.9, 126.6, 127.8, 128.2, 128.4, 129.6, 133.5, 137.3, 141.4, 148.8, 156.6, 192.7; MS (EI) m/z (rel int.%): 281 (M^+-15, 12), 217 (15), 203 (88), 165 (29), 135 (66), 115 (24), 103 (36), 75 (100); IR ν 3433, 3055, 2955, 2722, 1950, 1877, 1822, 1760, 1678, 1586, 1422, 1250. Anal. Calcd for $C_{18}H_{20}O_2Si$: C, 72.93; H, 6.80; found: C, 73.24; H, 6.71.

*4.2.7. (E)-2-[(Dimethylphenylsilyl)methylene]-3-hydroxy-3-phenylpropanal (E)-**3da**.* The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (12% yield); ^1H NMR δ 0.54 (3H, s), 0.55 (3H, s), 3.27 (1H, d, J=9 Hz), 5.55 (1H, d, J=9 Hz), 7.06 (1H, s), 7.22–7.65 (11H, m); 9.46 (1H, d, J=1 Hz); ^{13}C NMR δ −1.4, 73.0, 126.0, 127.4, 128.2, 128.3, 129.7, 133.8, 136.9, 141.4, 153.6, 156.0, 196.0; MS (EI) m/z (rel int.%): 281 (M^+-15, 2), 217 (45), 203 (17), 135 (49), 115 (28), 105 (28), 91 (19), 77 (48), 75 (100); IR ν 3444, 3066, 2944, 2722, 1950, 1877, 1822, 1760, 1683, 1600, 1422, 1250.

*4.2.8. (Z)-2-[(Dimethylphenylsilyl)-methylene]-3-hydroxy-3-methylpentanal (Z)-**3ea**.* The crude oil was purified by column chromatography on silica gel using hexane/AcOEt=80/20 as eluent (55% yield); ^1H NMR δ 0.51 (6H, s), 0.80 (3H, t, J=7.3 Hz), 1.38 (3H, s), 1.62–1.90 (2H, m), 3.19 (1H, s), 7.21 (1H, s), 7.32–7.37 (3H, m), 7.47–7.52 (2H, m), 9.79 (1H, s); ^{13}C NMR δ −0.3, 8.3, 26.6, 33.7, 75.5, 128.1, 129.4, 133.4, 137.6, 149.4, 159.6, 193.9; MS (EI) m/z (rel int.%): 247 (M^+-15, 32), 229 (100), 185 (25), 169 (39), 167 (47), 165 (50), 155 (51), 145 (45), 137 (46), 135 (88), 121 (21), 103 (41), 91(22), 75 (39); IR ν 3444, 3056, 2967, 2744, 1950, 1889, 1817, 1761, 1678, 1422, 1250. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45; found: C, 68.71; H, 8.38.

*4.2.9. (E)-2-[(Dimethylphenylsilyl)-methylene]-3-hydroxy-3-methylpentanal (E)-**3ea**.* The crude oil was purified by column chromatography on silica gel using hexane/AcOEt=80/20 as eluent (8% yield); ^1H NMR δ 0.51 (6H, s), 0.58 (3H, t, J=7.2 Hz), 1.29 (3H, s), 1.42 (1H, s), 1.46–2.03 (2H, m), 6.86 (1H, s), 7.32–7.37 (3H, m), 7.50–7.56 (2H, m), 9.51 (1H, s); ^{13}C NMR δ 0.0, 7.7, 27.7, 32.6, 75.5, 128.1, 128.9, 133.2, 140.4, 155.5, 162.3, 194.8; MS (EI) m/z (rel int.%): 247 (M^+-15, 32), 229 (100), 185 (25), 169 (39), 167 (47), 165 (50), 155 (51), 145 (45), 137 (46), 135 (88), 121 (21), 103 (41), 91 (22), 75 (39); IR ν 3456, 3056, 2956, 2722, 1955, 1895, 1823, 1684, 1422, 1250.

*4.2.10. (Z)-2-[(Dimethylphenylsilyl)-methylene]-2-(1-hydroxy-cyclohexyl)-propenal (Z)-**3fa**.* The crude oil was purified by column

chromatography on silica gel using CH_2Cl_2 as eluent (90% yield); ^{1}H NMR δ 0.49 (6H, s), 1.50–1.75 (10H, m), 2.87 (1H, s), 7.15 (1H, s), 7.39–7.51 (5H, m), 9.79 (1H, s); ^{13}C NMR δ −0.3, 21.5, 25.5, 36.1, 73.7, 128.2, 129.5, 133.5, 137.6, 147.9, 161.2, 194.8; MS (EI) *m*/*z* (rel int.%): 255 (M^+-33, 17), 193 (11), 167 (11), 145 (10), 135 (44), 119 (15), 105 (22), 91 (30), 75 (100), 61 (15); IR ν 3444, 3055, 2922, 2733, 1843, 1887, 1816, 1766, 1677, 1422, 1250. Anal. Calcd for $C_{17}H_{24}O_2Si$: C, 70.78; H, 8.39; found: C, 70.83; H, 8.41.

*4.2.11. (Z)-2-[(Dimethylphenylsilyl)-methylene]-3-hydroxy-3,4,4-trimethyl-pentanal (Z)-**3ga**.* The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (7% yield); ^{1}H NMR δ 0.51 (6H, s), 0.89 (9H, s), 1.38 (3H, H_c), 1.62 (1H, s), 7.02 (1H, s), 7.31–7.52 (5H, m), 9.75 (1H, s); MS (EI) *m*/*z* (rel int.%): 273 (M^+-15, 81), 231 (29), 211 (100), 195 (20), 145 (30), 135 (80), 105 (34); IR ν 3467, 3055, 2955, 2710, 1955, 1877, 1811, 1666, 1422, 1250. Anal. Calcd for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9.02; found: C, 69.90; H, 8.93.

*4.2.12. (Z)-2-[(Dimethyl-phenyl-silyl)-methylene]-3-hydroxy-3-phenyl-butanal (Z)-**3ha**.* The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (55% yield); ^{1}H NMR δ 0.56 (6H, s), 1.65 (3H, s), 4.06 (1H, sb), 7.24–7.72 (11H, m), 9.70 (1H, s); ^{13}C NMR δ −0.4, 29.1, 76.9, 124.6, 127.0, 128.2, 128.3, 129.7, 133.5, 137.3, 146.1, 148.8, 158.7, 194.4; MS (EI) *m*/*z* (rel int.%): 295 (M^+-15, 9), 217 (22), 199 (18), 165 (34), 141 (20), 103 (33), 91 (11), 75 (67), 135 (100); IR ν 3455, 3056, 2977, 2733, 1950, 1883, 1811, 1760, 1678, 1583, 1427, 1256. Anal. Calcd for $C_{19}H_{22}O_2Si$: C, 73.50; H, 7.14; found: C, 73.17, H, 7.22.

4.3. General procedure for the silylcarbocyclisation of propargyl alcohols with hydrosilanes catalyzed by $Rh_4(CO)_{12}$

Catalytic runs were performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, 3 mmol of alcohol, 3 mL of a freshly distilled solvent, 3 mmol of R_3SiH, 0.3 mmol of DBU and 3×10^{-3} mmol of $Rh_4(CO)_{12}$ were put, via syringe and under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, previously placed under vacuum (0.1 mmHg), by a steel syphon. The reactor was pressurised to 30 atm of CO and stirred at 100 °C for 4 h. The autoclave was then cooled to room temperature and the excess of CO was removed under fume hood. The reaction mixture was diluted with CH_2Cl_2, filtered on silica gel and concentrated under reduced pressure. The reagents conversion and the products composition were determined by GLC and ^{1}H NMR. The purification of the crude oil by column chromatography on silica gel afforded the pure β-lactones.

*4.3.1. (Z)-3-[(Dimethylphenylsilyl)-methylene]-4-propyl-oxetan-2-one (Z)-**4ba**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=90/10 as eluent (24% yield); ^{1}H NMR δ 0.59 (6H, s), 0.98 (3H, t, *J*=7.8 Hz), 1.42–1.59 (2H, m), 1.74–1.86 (2H, m), 4.84 (1H, t, *J*=6.6 Hz), 6.29 (1H, s), 7.34–7.42 (3H, m), 7.58–7.61 (2H, m); ^{13}C NMR δ −2.5, 13.7, 17.9, 35.2, 79.9, 127.9, 129.4, 133.6, 141.1, 135.4, 152.7, 163.8; MS (EI) *m*/*z* (rel int.%): 260 (M^+, 4); 245 (33); 217 (35); 149 (29); 145 (89); 135 (100); 105 (44); 75 (41); IR ν 3055, 2955, 1805, 1461, 1422, 1244, 1105. Anal. Calcd for $C_{15}H_{20}O_2Si$: C, 69.19; H, 7.74; found: C, 69.25; H, 7.69.

*4.3.2. (Z)-3-[(Dimethylphenylsilyl)-methylene]-4-ethyl-4-methyl-oxetan-2-one (Z)-**4ea**.* The crude oil was purified by column chromatography on silica gel using hexane/AcOEt=90/10 as eluent (76% yield); ^{1}H NMR δ 0.54 (6H, s), 0.95 (3H, t, *J*=7.3 Hz), 1.51 (3H, s), 1.75–1.90 (2H, m), 6.13 (1H, s), 7.23–7.52 (5H, m); ^{13}C NMR δ 7.8, 22.8, 30.9, 87.4, 127.9, 129.4, 133.4, 133.6, 137.0, 156.0, 163.8; MS (EI) *m*/*z* (rel int.%): 260 (M^+, 14), 245 (45), 231 (44), 183 (23), 169 (16), 145 (100), 135 (28), 123 (20), 105 (28), 75 (23); IR ν 3074, 2967, 1808, 1455, 1422, 1250, 1249, 1114. Anal. Calcd for $C_{15}H_{20}O_2Si$: C, 69.19; H, 7.74; found C, 69.37; H, 7.81.

*4.3.3. (Z)-3-[(Dimethylphenylsilyl)-methylene]-1-oxa-spiro[3.5]nonan-2-one (Z)-**4fa**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=70/30 as eluent (76% yield); ^{1}H NMR δ 0.54 (6H, s), 1.55–1.84 (10H, m), 6.22 (1H, s), 7.36–7.39 (3H, m), 7.55–7.59 (2H, m); ^{13}C NMR δ 22.6, 24.2, 34.3, 87.1, 128.0, 129.5, 133.6, 137.0, 132.9, 156.7, 164.1; MS (EI) *m*/*z* (rel int.%): 242 (M^+-44, 10), 277 (5), 145 (14), 136 (17), 135 (100), 107 (12), 105 (15); IR ν 3055, 2938, 1800, 1444, 1422, 1255, 1111. Anal. Calcd for $C_{17}H_{22}O_2Si$: C, 71.28; H, 7.74; found: C, 70.97; H, 7.65.

*4.3.4. (Z)-4-tert-Butyl-3-[(dimethyl-phenyl-silyl)-methylene]-4-methyl-oxetan-2-one (Z)-**4ga**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=70/30 as eluent (85% yield); ^{1}H NMR δ 0.55 (6H, s), 1.01 (9H, s), 1.53 (3H, s), 6.18 (1H, s), 7.35 (3H, m), 7.55 (2H, m); ^{13}C NMR δ 2.3,19.6, 25.0, 36.6, 91.6, 128.0, 129.5, 133.6, 133.8, 137.1, 155.8, 164.2; MS (EI) *m*/*z* (rel int.%): 273 (M^+-15, 81), 231 (29), 211 (100), 195 (20), 145 (30), 135 (80), 105 (34); IR ν 3066, 2967, 1806, 1450, 1428, 1250, 1111. Anal. Calcd for $C_{17}H_{24}O_2Si$: C, 70.78; H, 8.39; found C, 71.11, H, 8.47.

*4.3.5. (Z)-3-[(Methyldiphenylsilyl)-methylene]-4-propyl-oxetan-2-one (Z)-**4bb**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=70/30 as eluent (32% yield); ^{1}H NMR δ 0.59 (6H, s), 0.98 (3H, t, *J*=7.8 Hz), 1.42–1.59 (2H, m), 1.74–1.86 (2H, m), 4.84 (1H, t, *J*=6.6 Hz), 6.29 (1H, s), 7.34–7.42 (3H, m), 7.58–7.61 (2H, m); MS (EI) *m*/*z* (rel int.%): 322 (M^+, 10), 321 (27), 303 (39), 245 (24), 207 (54), 197 (100), 181(27), 145 (31), 137 (63), 129 (29), 105 (89), 77 (19), 53 (58). IR ν 3066, 2944, 1889, 1811, 1461, 1422, 1250, 1107. Anal. Calcd for $C_{20}H_{22}O_2Si$: C, 74.49; H, 6.88; found: C, 74.43; H, 6.90.

*4.3.6. (Z)-3-[(Dimethyl-o-tolyl-silyl)-methylene]-4-propyl-oxetan-2-one (Z)-**4bd**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=90/10 as eluent (43% yield); ^{1}H NMR δ 0.75 (3H, s), 0.74 (3H, s), 1.15 (3H, t, *J*=7.4 Hz), 1.28–1.54 (2H, m), 1.76–1.87 (2H, m), 2.57 (3H, s), 4.86 (1H, dt, *J*=7, 1 Hz), 6.33 (1H, d, *J*=1 Hz), 7.14–7.56 (4H, m); ^{13}C NMR δ 1.5, 13.7, 17.9, 23.0, 35.3, 79.8, 124.6, 125.1, 129.4, 129.7, 133.9, 134.6, 143.0, 152.3, 163.6; MS (EI) *m*/*z* (rel int.%): 259 (M^+-15, 21), 231 (64), 183 (85), 159 (69), 149 (90), 121 (51), 115 (46), 91 (100), 75 (78); IR ν 3044, 2944, 1811, 1460, 1283, 1250, 1127. Anal. Calcd for $C_{16}H_{22}O_2Si$: C, 70.03; H, 8.08; found: C, 70.19; H, 8.01.

*4.3.7. (Z)-3-[(Dimethyl-o-tolyl-silyl)-methylene]-4-isobutyl-oxetan-2-one (Z)-**4cd**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=80/20 as eluent (53% yield); ^{1}H NMR δ 0.62 (6H, s), 1.00 (6H, d, *J*=6.6 Hz), 1.61–1.74 (2H, m), 1.78–1.95 (1H, m), 2.44 (3H, s), 4.87–4.95 (1H, m), 6.32 (1H, d, *J*=1.6 Hz), 7.14–7.37 (2H, m), 7.49–7.56 (2H, m); ^{13}C NMR δ 22.3, 22.7, 23.0, 25.2, 42.4, 78.9, 125.1, 129.9, 134.0, 136.1, 134.6, 136.1, 143.4, 152.8, 163.9; MS (EI) *m*/*z* (rel int.%): 288 (M^+, 1), 273 (27), 231 (39), 197 (97), 159 (57), 149 (91), 121(76), 105 (36), 91 (85), 75 (100), 53 (59); IR ν 3044, 2944, 1811, 1461, 1283, 1255, 1111. Anal. Calcd for $C_{17}H_{24}O_2Si$: C, 70.78; H, 8.39; found: C, 70.61, H, 8.45.

*4.3.8. (Z)-3-[(Biphenyl-4-yl-dimethyl-silyl)-methylene]-4-propyl-oxetan-2-one (Z)-**4be**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=95/5 as eluent (12% yield); ^{1}H NMR δ 0.61 (6H, s), 0.98 (3H, t, *J*=7.2 Hz), 1.41–1.56 (2H, m), 1.75–1.86 (2H, m), 4.85 (1H, m), 6.29 (1H, s), 7.25–7.80 (9H, m); ^{13}C NMR δ 2.4, 13.8, 18.0, 35.3, 80.0, 126.7, 127.3, 127.1, 127.4, 135.3, 135.5, 137.3, 141.0, 141.2, 141.9, 142.3, 152.9, 165.6; MS (EI) *m*/*z* (rel int.%): 336 (M^+, 26), 293 (52), 221 (90), 211 (100), 195 (70), 181 (74), 165 (82), 152

(68), 105 (56), 75 (94); IR ν 3055, 2955, 1811, 1461, 1250, 1111. Anal. Calcd for $C_{21}H_{24}O_2Si$: C, 74.96; H, 7.19; found C, 75.91; H, 7.07.

*4.3.9. (Z)-3-[(tert-Butyldimethylsilyl)-methylene]-4-propyl-oxetan-2-one (Z)-**4bf**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=95/5 as eluent (30%); ^{1}H NMR δ 0.21 (3H, s), 0.22 (3H, s), 0.90 (9H, s), 0.96 (3H, t, J=7.4 Hz), 1.36–1.55 (2H, m), 1.70–1.82 (2H, m), 4.81 (1H, ddd, J=6.9, 5.4, 1.5 Hz), 6.13 (1H, d, J=1.5 Hz); ^{13}C NMR δ 5.6, 13.8, 16.9, 18.0, 26.2, 35.4, 79.9, 135.4, 153.0, 163.9; MS (EI) m/z (rel int.%): 225 (M^+-15, 1), 197 (3), 184 (30), 139 (12), 109 (12), 85 (9), 75 (100), 59 (15); IR ν 2951, 1812, 1682, 1253, 1280, 1113. Anal. Calcd for $C_{13}H_{24}O_2Si$: C, 64.95; H, 10.06; found: C, 65.25; H, 10.16.

*4.3.10. (Z)-4-Methyl-4-phenyl-3-[(dimethylphenyllsilyl)methylene]-oxetan-2-one (Z)-**4ha**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=70/30 as eluent (53%); ^{1}H NMR δ 0.47 (3H, s), 0.51 (3H, s), 1.83 (3H, s), 6.30 (1H, s), 7.27–7.36 (6H, m), 7.46–7.51 (4H, m); ^{13}C NMR δ −2.5, 25.7, 86.1, 124.6, 128.0, 128.2, 128.6, 129.5, 133.6, 136.7, 140.2, 134.8, 156.6, 163.8; MS (EI) m/z (rel int.%): 264 (M^+-44, 6), 205 (5), 135 (100), 128 (6), 119 (3), 105 (9), 51 (12); IR ν 3066, 2944, 1955, 1889, 1811, 1450, 1422, 1250, 1105. Anal. Calcd for $C_{19}H_{20}O_2Si$: C, 73.98; H, 6.54; found: C, 74.04; H, 6.61.

*4.3.11. 1-(Dimethylphenylsilyl)-3-phenyl-1,2-butadiene **6**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=70/30 as eluent (41%); ^{1}H NMR δ 0.33 (6H, s), 2.18 (3H, d, J=3.6 Hz), 5.45 (1H, q, J=3.6 Hz), 7.14–7.50 (10H, m); ^{13}C NMR δ 1.02, 24.6, 84.2, 94.2, 125.1, 125.8, 126.9, 127.7, 127.8, 128.3, 129.2, 133.0, 133.6, 133.6, 203.13; MS (EI) m/z (rel int.%): 264 (M^+, 23), 249 (36), 145 (48), 135 (100), 129 (26), 121 (86), 105 (39). Anal. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62; found: C, 81.68; H, 7.67.

*4.3.12. 1-(Dimethylphenylsilyl)-3-phenyl-1-butyne **7**.* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=70/30 as eluent (5%); ^{1}H NMR δ 0.42 (6H, s), 1.64 (3H, d, J=7 Hz), 3.86 (1H, q, J=7 Hz), 7.12–7.60 (10H, m); MS (EI) m/z (rel int.%): 264 (M^+, 10), 249 (1), 204 (2), 135 (100), 128 (4), 105 (12). Anal. Calcd for C18H20Si: C, 81.76; H, 7.62; found: C, 81.65; H, 7.55.

*4.3.13. (Z)-3-[(Dimethylphenylsilyl)methylene]-5-ethyl-2(3H)-dihydrofuran (Z)-**11a**.* The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (64%); ^{1}H NMR δ 0.51 (3H, s), 0.52 (3H, s), 0.98 (3H, t, J=7.3 Hz), 1.57–1.84 (2H, m), 2.61 (1H, ddd, J=17.3, 6.3, 2.7 Hz), 3.04 (1H, ddd, J=17.3, 7.5, 2.7 Hz), 4.44 (1H, m), 6.50 (1H, m), 7.35–7.38 (3H, m), 7.58–7.61 (2H, m), ^{13}C NMR δ −2.04, −2.07, 9.29, 29.42, 37.04, 78.81, 127.96, 129.13, 133.97, 139.51, 141.94, 142.53, 169.93; MS (EI) m/z (rel int.%): 245 (M+-15, 100), 183 (87), 169 (4), 135 (4), 105 (5), 77 (4), 75 (6); IR ν 3067, 2956, 1956, 1889, 1828, 1465, 1426, 1245, 1111. Anal. Calcd for $C_{15}H_{20}O_2Si$: C, 69.19; H, 7.74; found: C, 69.33, H, 7.78.

*4.3.14. (Z)-3-[(Dimethylphenylsilyl)methylene]-5-phenyl-2(3H)-dihydrofuran (Z)-**11b**.* The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (72%); ^{1}H NMR δ 0.58 (3H, s), 0.59 (3H, s), 2.95 (1H, ddd, J=17.1, 6.6, 2.4 Hz), 3.40 (1H, ddd, J=17.1, 7.8, 2.4 Hz), 5.52 (1H, dd, J=7.8, 6.6 Hz), 6.60 (1H, t, J=2.4 Hz), 7.30–7,79 (10H, m); ^{13}C NMR δ −2.33, 40.01, 77.96, 125.40, 127.75, 128.44, 128.76, 128.97, 133.74, 138.99, 139.98, 141.50, 142.61, 165.45. Anal. Calcd for $C_{19}H_{20}O_2Si$: C, 73.98; H, 6.54; found: C, 74.10; H, 6.57.

4.4. General procedures for the TBAF promoted rearrangements

To a solution of 2 mmol of β-silylalkenal or (*Z*)-(dimethylary lsilyl)methylene-β-lactone in 10 mL of THF, were added, at room temperature, 2 mL of TBAF (1 M in THF). The reaction mixture was immediately hydrolysed with water, extracted with Et_2O and the organic layers were dried over Na_2SO_4. After concentration under vacuum, the crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent, unless otherwise specified.

*4.4.1. (E)-2-Benzyl-hex-2-enal **8**[22].* The crude oil was purified by column chromatography on silica gel using hexane/Et_2O=80/20 as eluent (35%); ^{1}H NMR δ 1.04(3H, t J=7.4 Hz); 1.52–1.70 (2H, m); 2.44–2.55 (2H, m); 3.72 (2H, s); 6.70 (1H, t J=7.3 Hz); 7.21–7.39 (5H, m); 9.55 (1H, s); ^{13}C NMR δ 13.77, 21.69, 29.64, 31.21, 125.98, 128.27, 128.33, 139.18, 142.49, 156.02, 194.56; MS (EI) m/z (rel int.%) 188 (M^+, 37), 145 (100), 129 (33), 117 (45), 91 (94), 77 (20), 65 (20); IR ν 3022, 2955, 2333, 1938, 1883, 1805, 1693, 1638, 1455.

*4.4.2. 3-Benzyl-4-ethyl-4-methyl-oxetan-2-one **9ea**.* Major isomer: 66%, ^{1}H NMR δ 0.79 (3H, t, J=7.4 Hz), 1.46 (3H, s), 1.68–1.95 (2H, m), 2.83–2.95 (1H, m), 3.51–3.64 (1H, m), 3.10–3.15 (1H, m), 7.20–7.40 (5H, m); ^{13}C NMR δ 7.9, 19.1, 30.6, 33.4, 57.3, 82.9, 126.6, 128.2, 128.5, 137.5, 170.8; MS (EI) m/z (rel int.%): 203 (M^+-1, 2), 160 (26), 131 (100), 115(15), 104 (14), 91 (60); IR ν 2966, 1811, 1450. Minor isomer: ^{1}H NMR δ 1.0 (3H, t, J=7.4 Hz), 1.51 (3H, s), 1.80–2.00 (2H, m), 2.95–3.04 (2H, m), 3.55–3.68 (2H, m), 3.18–3.23 (1H, m), 7.20–7.40 (5H, m); ^{13}C NMR δ 7.6, 23.9, 29.8, 27.8, 59.1, 82.5, 126.5, 128.3, 128.5, 137.6, 170.8. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; found: C, 76.14; H, 7.98.

*4.4.3. 3-Benzyl-1-oxa-spiro[3.5]nonan-2-one **9fa**[23].* 68% Yield, ^{1}H NMR δ 1.36–2.11 (10H, m), 3.00–3.14 (2H, 2 dd, J=9.2, 6.9, 15.0 Hz), 3.54–3.62 (1H, dd, J=9.2, 6.9 Hz), 7.33–7.45 (5H, m); ^{13}C NMR δ 21.9, 22.6, 24.8, 29.7, 31.3, 37.2, 58.6, 82.5, 126.7, 128.2, 128.7, 137.9, 171.3; MS (EI) m/z (rel int.%) 186 (M^+-44, 26), 129 (13), 115 (10), 104 (100), 95 (10), 91 (27); IR ν 2922, 1800, 1444.

*4.4.4. -3-Benzyl-4-tert-butyl -4-methyl-oxetan-2-one **9ga**.* 59% Yield, ^{1}H NMR δ 0.88 (9H, s), 1.57 (3H, s), 2.78–3.25 (2H, 2 dd, J=8.6, 7.0, 14.7 Hz), 3.78 (1H, dd, J=8.6, 7.0 Hz), 7.26–7–38 (5H, m); ^{13}C NMR δ 16.8, 24.3, 31.3, 36.2, 53.9, 86.8, 126.7, 128.6, 128.7, 137.8, 171.1; MS (EI) m/z (rel int.%) 188 (M^+-44, 2), 132 (36), 131 (100), 91 (36), 84 (21), 69 (15), 57 (13); IR ν 2955, 1811, 1450. Anal. Calcd for C15H20O2: C, 77.55; H, 8.68; found: C, 77.36; H, 8.76.

*4.4.5. 3-Benzyl-4-phenyl-4-methyl-oxetan-2-one **9ha**.* 30% Yield, ^{1}H NMR δ 2.03 (3H, s), 2.48–2.89 (2H, 2 dd, J=7.8, 8.8, 15.0 Hz), 4.00 (1H, dd, J=7.8, 8.8 Hz), 7.29–7.47 (10H, m); ^{13}C NMR δ 27.46, 32.0, 61.3, 82.5, 125.5, 126.6, 128.3, 128.4, 128.5, 128.6, 137.0, 137.5, 170.3; IR ν 2955, 1816, 1444. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39; found: C, 81.20; H, 6.48.

*4.4.6. 4-Isobutyl-3-(2-methylbenzyl)-oxetan-2-one **9cd**.* Major isomer: 60%, ^{1}H NMR δ 0.85 (6H, 2 d, J=6.4, 7.0 Hz), 1.36–1.58 (2H, m), 1.64–1.75 (1H, m), 2.32 (3H, s), 2.93–3.24 (2H, 2 dd, J=6.3, 9.5, 14.7 Hz), 3.39–3.49 (1H, m), 4.31–4.39 (1H, m), 7.10–7.16 (4H, m); ^{13}C NMR δ 19.4, 22.5, 22.2, 25.1, 30.9, 43.4, 56.4, 76.6, 126.3, 127.1, 128.9, 130.6, 135.3, 135.8, 170.9; MS (EI) m/z (rel int.%) 188 (M^+-44, 35), 131 (49), 117 (44), 105 (46), 41 (100), 39 (79); IR ν 2955, 1816, 1461. Minor isomer: ^{1}H NMR δ 0.91–0.98 (6H, m), 1.62–1.75 (2H, m), 2.49 (3H, s), 2.93–3.24 (2H, m), 3.98–4.09 (1H, m), 4.71–4.81 (1H, m), 7.10–7.16 (4H, m). Anal. Calcd for C15H20O2: C, 77.55; H, 8.68; found: C, 77.75; H, 8.75.

*4.4.7. 3-Benzyl-5-ethyl-dihydro-furan-2-one **12a**[24].* 61% Yield of a diastereoisomeric mixture; major isomer (*Z*): ^{1}H NMR δ 0.94 (3H, t, J=7.5), 1.55 (1H, m), 1.46–1.78 (2H, m), 2.27 (1H, ddd, J=12.6, 8.4, 5.4 Hz), 2.70 (1H, dd, J=13.8, 9.6 Hz), 2.91 (1H, m), 3.28 (1H, dd, J=13.8, 4.2 Hz), 4.24 (1H, m), 7.24 (5H, m); ^{13}C NMR δ 9.20, 28.18,

34.09, 36.08, 42.73, 79.98, 126.76, 128.78, 128.91, 138.82, 178.21. Minor isomer (*E*) 0.93 (3H, t, *J*=7.5 Hz), 1.46–1.78 (2H, m), 1.92 (1H, ddd, *J*=13.2, 9.3, 5.1 Hz), 2.08 (1H, dt, *J*=13.2, 7.5 Hz), 2.76 (1H, dd, *J*=13.5, 9.6 Hz), 2.91 (1H, m), 3.18 (1H, dd, *J*=13.5, 4.2 Hz), 4.24 (1H, m), 7.24 (5H, m); ^{13}C NMR δ 9.36, 28.33, 31.97, 36.43, 40.96, 79.88, 126.86, 128.79, 129.02, 138.49, 178.77.

4.4.8. 3-Benzyl-5-phenyl-dihydro-furan-2-one ***12b***[24c,25]. 72% Yield of a diastereoisomeric mixture; major isomer (*Z*): ^{1}H NMR δ 1.84–1.99 (1H, m), 2.56–2.65 (1H, m), 2.78 (1H, dd, *J*=13.8, 9.6 Hz), 3.02–3.12 (1H, m), 3.35 (1H, dd, *J*=13.8, 4.2 Hz), 5.33 (1H, dd, *J*=10.8, 5.8 Hz), 7.16–7.40 (10H, m); ^{13}C NMR δ 36.07, 37.49, 43.30, 79.45, 124.85, 125.38, 126.68, 128.44, 128.67, 128.80, 138.41, 138.96, 177.65. Minor isomer (*E*): ^{1}H NMR δ 2.22–2.26 (1H, m), 2.41–2.51 (1H, m), 2.86 (1H, dd, *J*=13.2, 9.6 Hz), 2.93–3.20 (1H, m), 3.23 (1H, dd, *J*=13.2, 4.2 Hz), 5.33 (1H, dd, *J*=10.8, 5.8 Hz), 7.16–7.40 (10H, m).

References and notes

1. (a) Pommier, A.; Pons, J. M. *Synthesis* **1995**, 729; (b) Lower, C.; Vederas, J. C. *Org. Prep. Proced. Int.* **1995**, *27*, 305 and references therein.
2. (a) Borgstrom, B. *Biochim. Biophys. Acta* **1988**, *962*, 308; (b) Stalder, H.; Schneider, P. R.; Oesterhelt, G. *Helv. Chim. Acta* **1990**, *73*, 1022; (c) Zhi, J.; Melia, A. T.; Guerciolini, R.; Chung, J.; Kinberg, J.; Hauptman, J. B.; Patel, I. H. *Clin. Pharmacol. Ther.* **1994**, *56*, 82; (d) Majama, M.; Kuribayashi, Y.; Ikeda, Y.; Adachi, K.; Kato, H.; Katori, M.; Aoyagi, T. *Jpn. J. Pharmacol.* **1994**, *65*, 79; (e) Scaloni, A.; Jones, W. M.; Barra, D.; Pospischil, M.; Sassa, S.; Popowicz, A.; Manning, L. R.; Schneewind, O.; Manning, J. M. *J. Biol. Chem.* **1992**, *267*, 3811; (f) Koller, W.; Trail, F.; Parker, D. M. *J. Antibiot.* **1990**, *43*, 734; (g) Kondo, S.; Uotani, K.; M; Miyamoto, M.; Hazato, T.; Naganawa, H.; Aoyagi, T. *J. Antibiot.* **1978**, *31*, 797; (h) Umezawa, H.; Aoyagi, T.; Hazato, T.; Uotani, K.; Kojima, F.; Hamada, M.; Takeuchi, T. *J. Antibiot.* **1978**, *31*, 639; (i) Imanaka, T.; Moriyama, Y.; Ecsedi, G. G.; Aoyagi, T.; Amanuma-Muto, K.; Ohkuma, S.; Takano, T. *J. Biochem.* **1983**, *94*, 1017; (j) Kudo, Y.; Oka, J.-I.; Yamada, K. *Neurosci. Lett.* **1981**, *25*, 83.
3. Wang, Y.; Tennyson, R. L.; Romo, D. *Heterocycles* **2004**, *64*, 605 and references therein.
4. (a) Jedlinski, Z.; Kurcok, P. Kowalcuzuk, M.; Matuszowicz, A.; Dubois, P.; Jerome, R.; Kricheldorf, A.R. Macromolecules 28, 7276 (b) Jedlinski, Z. *J. Heterocycl. Chem.* **2001**, *38*, 1249; (c) Jaipuri, F. A.; Bower, B. D.; Pohl, N. L. *Tetrahedron: Asymmetry* **2003**, *14*, 3249.
5. (a) Pommier, A.; Pons, J. M. *Synthesis* **1993**, 441; (b) Yang, H. W.; Romo, D. *Tetrahedron* **1999**, *55*, 6403; (c) Collins, I. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1377; Tidwell, T. T. *Eur. J. Org. Chem.* **2006**, 563; Purohit, V. C.; Matla, A. S.; Romo, D. *Heterocycles* **2008**, *76*, 949 and references therein.
6. (a) Lee, J. T.; Thomas, P. J.; Alper, H. *J. Org. Chem.* **2001**, *66*, 5424; (b) Getzler, Y. D. Y. L.; Mahedevan, V.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1174; (c) Molnar, F.; Luinstra, G. A.; Allmendinger, M.; Rieger, B. *Chem.— Eur. J.* **2003**, *9*, 1273; (d) Schimdt, J. A. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 11426; (e) Nakano, K.; Nozaki, K. *Top. Organomet. Chem.* **2006**, *12*, 223; (f) Church, T. L.; Getzler, Y. D. Y. L.; Byrne, C. M.; Coates, G. W. *Chem. Commun.* **2007**, 657; (g) Kramer, J. W.; Coates, G. W. *Tetrahedron* **2008**, *64*, 6973.
7. Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120.
8. Matsuda, I.; JP Patent 3148271, 1995; Chem. Abstr. 1991, 232059.
9. Aronica, L. A.; Caporusso, A. M.; Salvadori, P. *Eur. J. Org. Chem.* **2008**, 3039 and references therein.
10. Aronica, L. A.; Valentini, G.; Caporusso, A. M.; Salvadori, P. *Tetrahedron* **2007**, *63*, 6843.
11. Aronica, L. A.; Morini, F.; Caporusso, A. M.; Salvadori, P. *Tetrahedron Lett.* **2002**, *43*, 5813.
12. Matsuda, I.; Niikawa, N.; Kuwabara, R.; Inoue, H.; Nagashima, H.; Itoh, K. *J. Organomet. Chem.* **1999**, *574*, 133.
13. Aronica, L. A.; Raffa, P.; Caporusso, A. M.; Salvadori, P. *J. Org. Chem.* **2003**, *68*, 9292.
14. (a) Adam, W.; Albert, R.; Hasemann, L.; Nava Salgado, V. O.; Nestker, B.; Peters, E.-M.; Peters, K.; Prechtl, F.; Georg Von Shenering, H. *J. Org. Chem.* **1991**, *56*, 5782; (b) Danheiser, R. L.; Choi, Y. M.; Meninchincheri, M.; Stoner, E. J. *J. Org. Chem.* **1993**, *58*, 322; (c) Morao, I.; Lecea, B.; Arrieta, A.; Cossio, F. P. *J. Am. Chem. Soc.* **1997**, *119*, 816.
15. (a) Jones, E. R. H.; Mansfield, G. H.; Whiting, M. C. *J. Chem. Soc.* **1954**, 3208; (b) Pourcelot, G.; Cadiot, P. *Tetrahedron* **1982**, *38*, 2123; (c) Banert, K. *Chem. Ber.* **1989**, *122*, 1963; (d) Leise, M.; Lang, H.; Imohof, W.; Zsolnai, L. *Chem. Ber.* **1993**, *126*, 1077; (e) Banert, Klaus. *Targets in Heterocyclic Systems*; Società Chimica Italiana: Roma, 1999; Vol. 3, 1; (f) Trofimov, B. A. *Curr. Org. Chem.* **2002**, *6*, 1121.
16. (a) Fleming, I.; Waterson, D. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1809; (b) Fleming, I.; Terrett, N. K. *J. Organomet. Chem.* **1984**, *264*, 99; (c) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293; (d) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063; (e) Marshall, J. A.; Adams, N. D. *J. Org. Chem.* **1997**, *62*, 8976; (f) Marshall, J. A.; Maxson, K. *J. Org. Chem.* **2000**, *65*, 630; (g) Guitchin, B. K.; Bienz, S. *Organometallics* **2004**, 4944.
17. (a) Adam, W.; Hasemann, L.; Prechtl, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1536; (b) Cheikh, A. B.; Pommelet, J.-C.; Chuche, J. *J. Chem. Soc., Chem. Commun.* **1990**, 615; (c) Campi, E. M.; Dyall, K.; Fallon, G.; Jackson, W. R.; Perlmutter, P.; Smallridge, A. J. *Synthesis* **1990**, 855; (d) Adam, W.; Rainer, A.; Dachs Grau, N.; Hasemann, L.; Nestler, B.; Peters, E.-M.; Peters, K.; Prechtl, F.; Georg Von Shenering, H. *J. Org. Chem.* **1991**, *56*, 5778; (e) Qing, F.-L.; Jiang, Z.-X. *J. Fluorine Chem.* **2002**, *114*, 177; (f) Martinez, I.; Andrews, A. E.; Emch, J. D.; Ndakala, A. J.; Wang, J.; Howell, A. R. *Org. Lett.* **2003**, *5*, 399.
18. (a) Mulzer, J.; Kerkmann, T. *J. Am. Chem. Soc.* **1980**, *102*, 3620; (b) Carriere, F.; Blottiau, R.; Sekiguchi, H. *Eur. Polym. J.* **1986**, *22*, 285; (c) Carriere, F.; Blottiau, R. *Bull. Soc. Chim. Fr.* **1991**, 717; (d) Scherowsky, G.; Sefkov, M. *Chimia* **1993**, *47*, 19.
19. (a) Kim, D. H.; Ryoo, J. J. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 1287; (b) Kim, D. H.; Park, J.; Chung, S. J.; Park, J. D.; Park, N.-K.; Han, J. H. *Bioorg. Med. Chem. Lett.* **2002**, *10*, 2553; (c) Purohit, V. C.; Richardson, R. D.; Smith, J. W.; Romo, D. *J. Org. Chem.* **2006**, *71*, 4549.
20. Fujita, M.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 5405.
21. Martinengo, S.; Giordano, G.; Chini, P. *Inorg. Synth.* **1990**, *28*, 242.
22. Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503.
23. Wedler, C.; Kleiner, K.; Kunath, A.; Schick, H. *Lieb. Ann.* **1996**, *6*, 881.
24. (a) Li, B.; Buzon, R. A.; Castaldi, M. J. *Org. Process Res. Dev.* **2001**, *5*, 609; (b) Oswald, M. F.; Parsons, A. F.; Yang, W.; Bowden, M. *Tetrahedron Lett.* **2005**, *46*, 8087; (c) Domingo, L. R.; Gil, S.; Parra, M.; Segura, J. *Molecules* **2008**, *13*, 1303.
25. (a) McWilliams, J. C.; Armstrong, J. D.; Zheng, N.; bhupathy, M.; Volante, R. P.; Reider, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 11970; (b) Ghosh, A. K.; Shurrush, K.; Kulkarni, S. *J. Org. Chem.* **2009**, *74*, 4508.