Pergamon

Tetrahedron 56 (2000) 2025–2036

TETRAHEDRON

The Phenylthiocyclopropylsilyl Group: a Useful Latent Hydroxy Group

Rémy Angelaud[a] and Yannick Landais[a,b,*]

[a]*University of Lausanne, Institute of Organic Chemistry, Collège Propédeutique, 1015 Lausanne-Dorigny, Switzerland*
[b]*Université Bordeaux-I, Laboratoire de Chimie Organique et Organométallique, 351 Cours de la Libération, 33405 Talence Cedex, France*

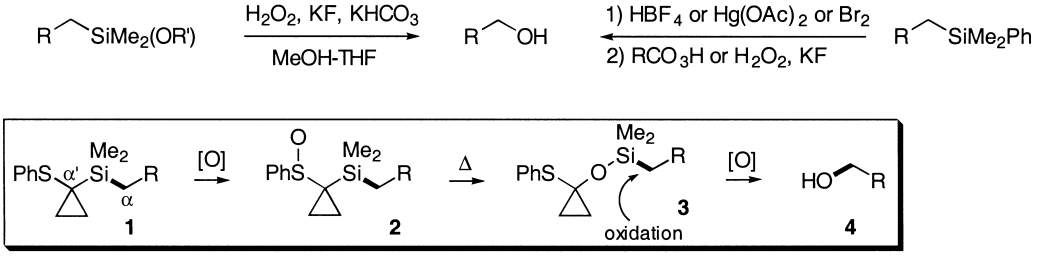
Received 15 December 1999; accepted 11 February 2000

Abstract—The α-dimethyl(1-phenylthio)cyclopropylsilyl group was used as a new masked hydroxy group. Three procedures have been devised to allow the oxidation of this silicon group in the presence of various functionalities. The desired alcohols are obtained in high yields with *retention of configuration* at the carbon centre.

The conversion of a silicon group into a hydroxy group, discovered independently by Kumada, Tamao and Fleming,[1] is a very useful process that has widened the scope of application of organosilicon compounds in organic synthesis.[2] Its application in the synthesis of complex natural products demonstrates that it can be used with confidence in the preparation of multifunctional substrates. Various silicon groups can be employed as latent hydroxy groups, but alkoxy- (i.e. *t*-BuO, *i*-PrO,…) and arylsilanes (i.e. $PhMe_2Si$, Ph_2MeSi,…) are the most frequently used since they are readily available. Amongst the masked hydroxy groups, $PhMe_2Si$ holds a special place since it is easy to introduce on a carbon framework through silylcupration, and its stability allows its use throughout long synthetic sequences (which is not the case for alkoxysilanes). Nonetheless, the oxidation of $PhMe_2Si$ requires that the phenyl substituent is removed through protodesilylation prior to the oxidation of the silicon group by a peroxide or a peracid.[1c,d] This preliminary electrophilic step has been shown to cause problems, which has prompted several laboratories to propose alternative routes through the design of new silicon groups.[2,3]

In this context, we recently proposed the utilisation of the stable phenylthiocyclopropylsilyl group **1** as a masked hydroxy group[4] (Scheme 1). Our approach relied upon the selective oxidation of the thioether group into the corresponding sulfoxide **2**, which would then undergo a sila-Pummerer rearrangement[5] to provide the alkoxysilane **3** required for the oxidation into the desired alcohol **4**. The thioether group is stable enough to be used in various reaction conditions and the alkoxysilane **3** is the real masked hydroxy group, which is revealed only in the last step of the sequence. We therefore have in hand a group which is as stable as $ArMe_2Si$ groups but can be oxidised in the same conditions as those of alkoxysilyl groups. We report here a full account of our studies on this masked hydroxy group and propose three oxidation procedures compatible with most useful organic functions.

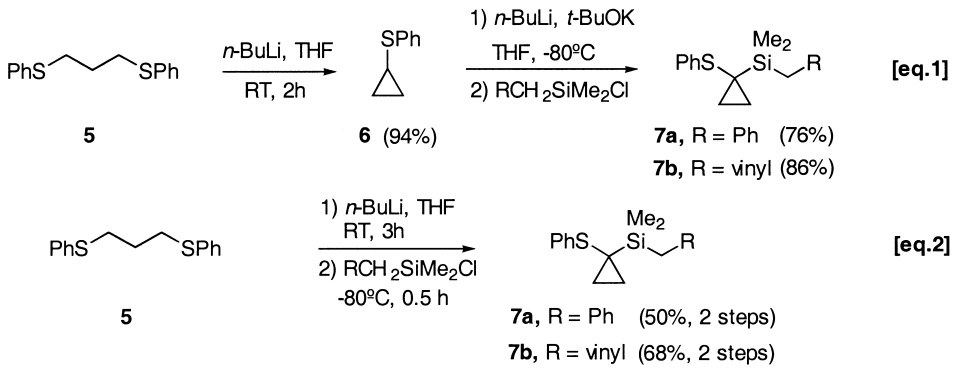
The dimethyl(1-phenylthiocyclopropyl)silyl group (DMPTCS) in **1** was selected since it is readily available and is known to be stable under various reaction conditions. The absence of acidic protons at C-α′ also allowed for a possible functionalisation of the α-position using basic conditions (vide



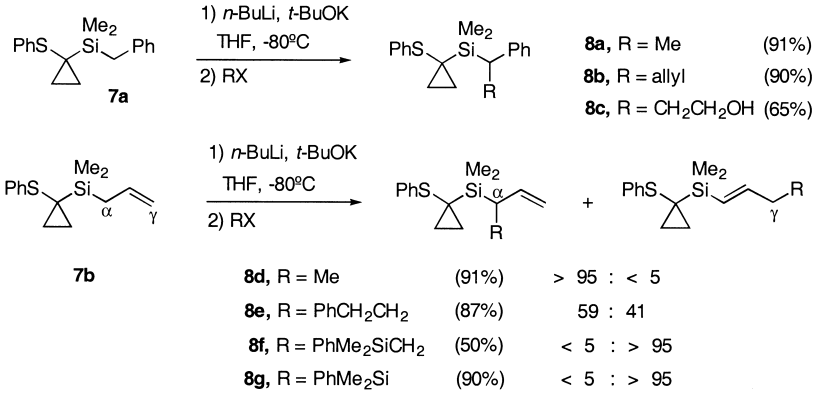
Scheme 1.

Keywords: silicon and compounds; Pummerer reactions; sulfoxides; oxidation.
* Corresponding author. Fax: +33-5-56-84-46-64; e-mail: y.landais@lcoo.u.-bordeaux.fr

0040–4020/00/$ - see front matter
PII: S0040-4020(00)00112-5



Scheme 2.



Scheme 3.

infra). A simpler analogue such as dimethyl(1-phenylthiomethyl)silyl would suffer from competitive deprotonation at C-α′. Moreover, it was envisioned that the cyclopropane ring strain would keep the silicon and the sulfoxide groups apart, slowing down the sila-Pummerer rearrangement. Each step of the sequence in Scheme 1 would then be controlled so that intermediates **2** and **3** could be isolated if necessary. Pioneering studies by Cohen[6] effectively showed that the dimethyl(1-phenylthiomethyl)silyl analogue led directly to the siloxane **3** at room temperature.

In order to validate our strategy, we first prepared simple precursors having a DMPTCS group. Benzyl- and allylsilanes **7a**–**b** were prepared using two alternative procedures starting from commercially available bisphenylthiopropane **5** (Scheme 2). The first method was a two-step sequence involving the formation of the cyclopropane **6** followed by its metallation using superbases[7] (*n*-BuLi/*t*-BuOK) and silylation of the resulting carbanion with the suitable chlorosilane (Eq. 1, Scheme 2). It was later found that these two steps could be realised in one-pot, but with somewhat lower yields (Eq. 2, Scheme 2).

Metallation of **7a**–**b** at the α position and alkylation afforded an easy access to substituted benzyl- and allylsilanes **8a**–**g**. Our preliminary attempts to deprotonate **7a**–**b** using *n*-BuLi, *s*-BuLi or *t*-BuLi, with or without additives (TMEDA) unfortunately failed, leading to recovered starting material. Fortunately, superbases (*n*-BuLi/*t*-BuOK) were found to be much more efficient leading after alkylation to **8a**–**g** in high yields (Scheme 3).

8c was prepared by alkylation with ethylene glycol sulfate[8] followed by catalytic acidic hydrolysis (H_2SO_4) of the sulfate group. It is noteworthy that alkylation of allylsilane **7b** with MeI proceeded with higher regioselectivity than that reported with the simpler allyltrimethylsilane.[9] This selectivity was attributed to the occurrence of a favourable 5-membered ring chelate resulting from the co-ordination of Li^+ (or K^+) by the sulfur atom (Fig. 1). However, the regioselectivity seems to be controlled mainly by the size of the electrophile, the γ-regioisomer being formed as the sole product with hindered electrophiles. It is also noteworthy that double bonds in **8e** (γ-isomer), **8f** and **8g** possess exclusively the *E*-configuration.

Precedent in the literature[10] finally prompted us to study an enantioselective version of these metallation–alkylations. We thus simply repeated the alkylation of benzylsilane **7a** in the presence of 1.5 equiv. of (−)-sparteine. **8a** was produced as before in good yield but with no enantioselectivity.

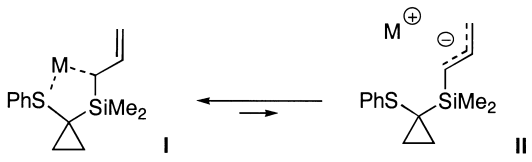
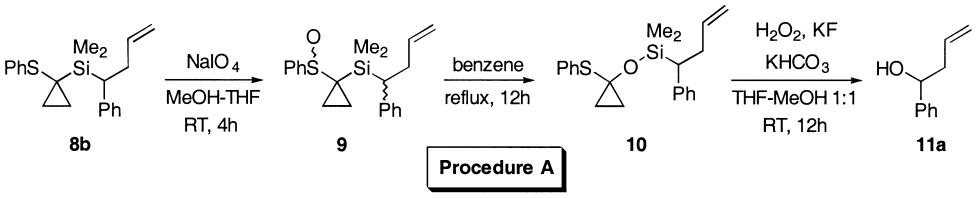


Figure 1.



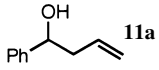
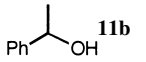
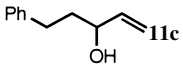
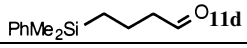
Scheme 4.

Transmetallation of the lithium–potassium carbanion with Cu(I)Cl was then carried out in order to generate an organometallic species such as **I** where the softer metal would be more tightly bound to sulfur. Unfortunately, under these conditions **8a** was again obtained as a racemic mixture. These few unsuccessful trials then led us to give up this route but further studies are now under way in our laboratories to devise an enantioselective version of our methodology.

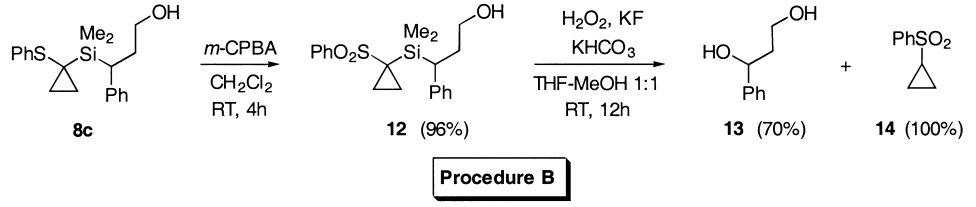
With our silanes in hand, we then investigated the oxidation of the DMPTCS group starting from benzylsilane **8b**. The thioether function in **8b** was thus oxidised using $NaIO_4$ in MeOH–H_2O to afford a 1:1 mixture of the diastereomeric sulfoxides **9**. These were isolated and heated under reflux in toluene to produce quantitatively the desired siloxane **10**. Tamao–Kumada oxidation of **10** eventually afforded the alcohol **11a** in 78% overall yield.[11] This sequence, which we refer to as procedure **A**, was then applied to analogues of **8b** without purification of the sulfoxide and siloxane intermediates (Scheme 4, Table 1).

Using the procedure **A**, benzyl- and allylsilanes **8a**–**b** and **8e** were readily converted into the desired alcohols **11a**–**c** (entries 1–3, Table 1) and the vinylsilane **8f** led in similar conditions to the aldehyde **11d** (entry 4, Table 1). However, this approach cannot be applied to substrates having a free hydroxy group. The presence of an OH function probably interferes with the sila-Pummerer rearrangement leading to unknown by-products. We therefore devised an alternative route which we called procedure **B**, based on the known nucleofugal ability of a sulfonyl substituent at silicon.[12] The oxidation of the sulfur group onto a sulfone, followed by the displacement of the cyclopropylsulfonyl group by a fluoride source, should afford a fluorosilyl intermediate which could be oxidised further into the desired alcohol. This was demonstrated starting from the silane **8c** which was converted into the sulfone **12** using *m*-CPBA (Scheme 5). The sulfone was then oxidised into the alcohol **13** under the standard Tamao–Kumada conditions. The cyclopropylsulfone **14** was recovered quantitatively after chromatography and could be reused for other transformations (vide infra).

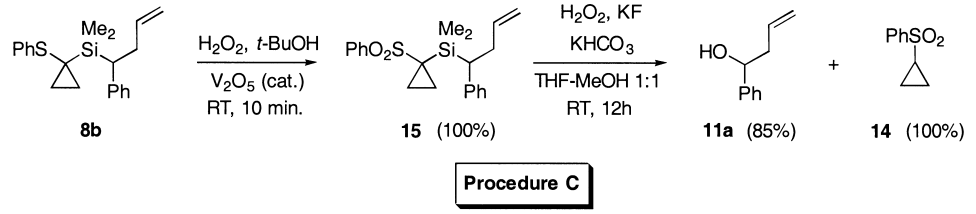
Table 1. Oxidation of silanes **8a**–**b** and **8e**–**f** according to Procedure **A** (Scheme 4)

Entry	Substrate	Product	Yield[a]
1	**8b**	 **11a**	78
2	**8a**	 **11b**	86
3	**8e**	 **11c**	77[b]
4	**8f**	 **11d**	50

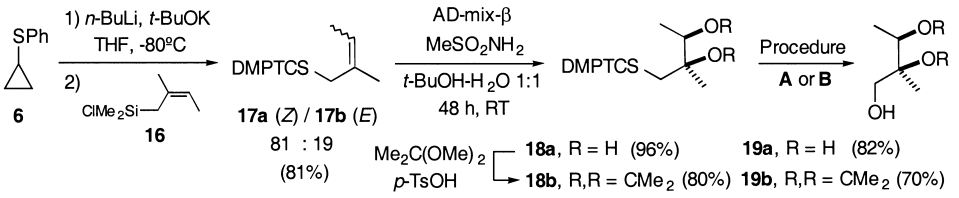
[a] Overall yield (3 steps without purification of the intermediates).
[b] Calculated from the amount of the α-regioisomer in **8e**.



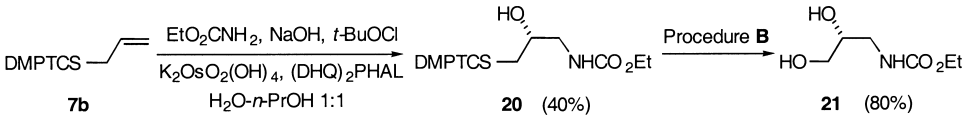
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

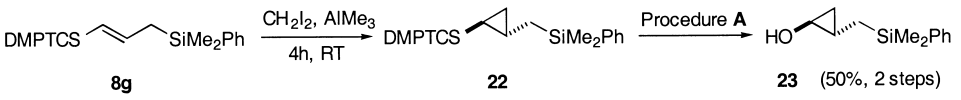
Although we have demonstrated that route **B** is very straightforward, we noticed that when applied to silanes such as **8b**, the double bond was partially epoxidised during the *m*-CPBA oxidation. This prompted us to develop a modification of route **B** called procedure **C** for the oxidation of silanes having double bonds. This was based on a report by Senning[13] who showed that ethylenic thioethers could be selectively oxidised into ethylenic sulfones using H_2O_2 in *t*-BuOH in the presence of a catalytic amount of V_2O_5. Using these conditions, **8b** was converted cleanly into the sulfone **15**, which was then oxidised into the alcohol **11a** in 85% overall yield (Scheme 6). As above, **14** was recovered quantitatively.

With these three complementary routes in hand we then studied the scope and limitation of our methodology using a range of silanes possessing group functionalities which were reported to interfere with the $PhMe_2Si$ group oxidation. This started with oxidation of β-hydroxysilanes which are prone to Peterson elimination and from time to time cause problems during the $PhMe_2Si$ group oxidation (particularly during the protodesilylation step).[2] The required β-hydroxysilanes were prepared starting from **6** using a two steps sequence (Scheme 7). Deprotonation of **6** using *n*-BuLi/*t*-BuOK and silylation of the carbanion with (*Z*)-chlorosilane **16**[14] provided a mixture of *Z*- and *E*-allylsilane **17**. The partial isomerisation of the double bond was attributed to the strongly basic medium and could not be avoided whatever the reaction conditions. **17** was submitted to the Sharpless asymmetric dihydroxylation (AD-mix-β®)[15] leading to the diol **18a** in 96% yield (calculated from **17a**) which was in turn protected as the acetonide **18b**. Oxidation of **18a** and **18b** following procedure **B** and **A**, respectively, finally led to the diol **19a**[16] and the acetonide **19b**[16] in 82 and 70% yield, with 25% e.e. [measured by ^1H NMR using $Eu(hfc)_3$]. It is worth noting that the DMPTCS group is compatible with the Sharpless dihydroxylation conditions (no sulfur oxidation) and that no trace of elimination product could be detected during the oxidation process.

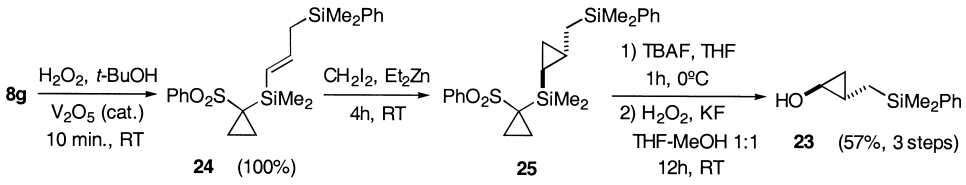
Similarly, allylsilane **7b** was submitted to the asymmetric Sharpless amino-hydroxylation[17] to afford the hydroxycarbamate **20** in 40% yield and 40% e.e. (Mosher's ester). This modest yield may be attributed to a reaction of excess $EtO_2CNClNa$ onto the thioether function.[18] Oxidation of this sensitive β-hydroxysilane using procedure **B** led to the diol **21** in 80% yield, again without Peterson elimination (Scheme 8).

Cyclopropanes constitute another challenging case since they are readily opened in acidic and electrophilic conditions. Therefore, not surprisingly, the oxidation of a $PhMe_2Si$ group was found to be incompatible with the presence of cyclopropanes.[19] We thus decided to extend our approach to this case using the cyclopropane **22** as a model. **22** was prepared from **8g** using the Yamamoto cyclopropanation method (Scheme 9).[20] Oxidation of the DMPTCS using procedure **A** finally afforded the desired alcohol **23** with *retention of configuration* at the carbon centre as reported previously by Tamao–Kumada and Fleming for other silicon groups.[1,2]

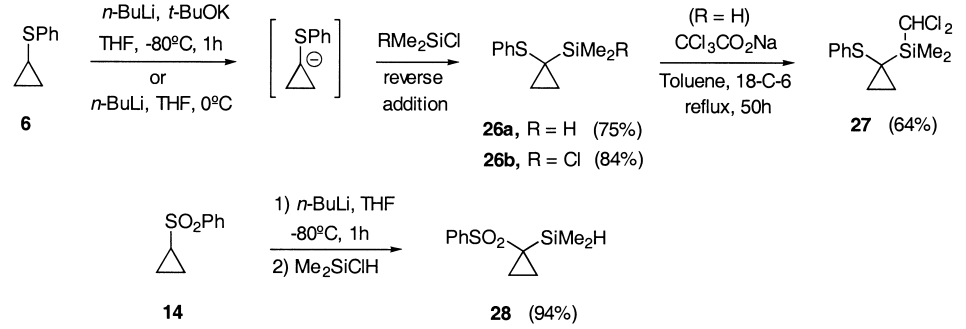
The modest yields observed in this two steps sequence prompted us to devise an alternative pathway. As the thioether group was likely to be at the origin of the low yield and poor reproducibility of the cyclopropanation process,[21] we converted quantitatively **8g** into its sulfone analogue **24**, which was then cyclopropanated using Furukawa conditions[22] to afford the crude cyclopropane **25** (Scheme 10). The attempt to directly oxidise **25** unfortunately failed, probably due to steric congestion around the silicon centre. Therefore, the sulfone moiety was first displaced using fluoride, producing a putative fluorosilane intermediate, which was oxidised according to the Tamao–Kumada conditions. **23** was thus obtained in 3 steps with a



Scheme 9.



Scheme 10.



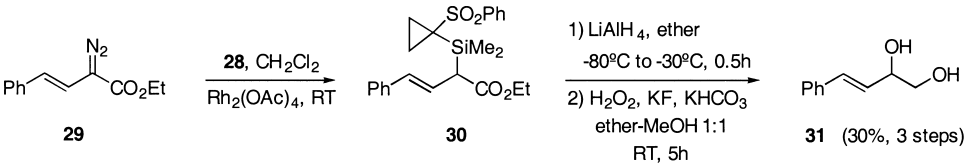
Scheme 11.

57% overall yield, again with complete *retention of configuration* at the carbon centre. It is noteworthy that the oxidation of the DMPTCS is not only compatible with the presence of a cyclopropane ring but also with that of a $PhMe_2Si$ group, which indicates that the selective sequential oxidation of different silicon groups should be possible.

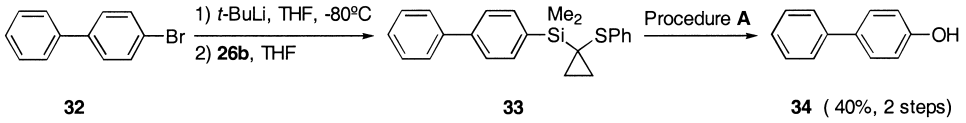
In the few examples above, the DMPTCS group was prepared through metallation of **6** followed by silylation using simple chlorosilanes. Functionalised chlorosilanes are not commercially available and their preparation may sometimes be quite tedious. Therefore, in order to extend the scope of application of the DMPTCS group, we developed an access to new organosilanes having a phenylthiocyclopropyl substituent. This was readily achieved through metallation of **6** followed by silylation with HMe_2SiCl or Me_2SiCl_2 (Scheme 11). Chlorosilane **26b** is thus obtained in excellent yield and may be introduced onto a carbon framework through simple silylation. Silanes **26a** and **28** were also prepared in high yields from the corresponding sulfide **6** and sulfone **14**, respectively, and should be useful for hydrosilylation and for carbene and carbenoid insertions. As an illustration, **26a** was converted into the dichloromethylsilane **27** through insertion of a dichlorocarbene species into the Si–H bond.[23] As recently demonstrated by Tamao, such synthons are useful diradical synthon equivalents.[24] It is worth noting that our efforts to convert **26a** and **26b** into the corresponding silyl-lithium, which would eventually give an access to silyl-cuprate reagents, have failed so far.

The reactivity of silanes **26a** and **28** towards carbenes and carbenoid species was then investigated.[25] We recently showed that $Rh_2(OAc)_4$-mediated decomposition of diazo-esters such as **29** in the presence of R_3SiH led to the corresponding allylsilanes with retention of the double bond configuration.[26] We thus studied the rhodium-catalysed decomposition of diazo-ester **29** in the presence of silane **26a** in order to get an allylsilane which could be oxidised further. Unfortunately, using $Rh_2(OAc)_4$ or Cu(I)OTf as catalysts, no insertion product could be detected, probably owing to the complexation of the metal to the sulfur centre. However, when the reaction was carried out with sulfone **28**, the unstable allylsilane **30** was formed and directly reduced into an alcohol and the silicon group was oxidised using the standard Tamao–Kumada conditions (Scheme 12). **31** was thus isolated in 30% overall yield in 3 steps, demonstrating the versatility of our silicon group.

A last example of the utility of the DMPTCS as a latent hydroxy group was finally provided by the oxidation of a C_{Ar}–Si bond. Such a transformation is not possible using a $PhMe_2Si$ group since in this case both aryl groups could react with the electrophile during the protodesilylation step.[27] The DMPTCS was easily introduced on a biaryl model through silylation of the bromide **32** with the chlorosilane **26b** (Scheme 13). This provided the organosilane **33** which was directly oxidized using procedure **A** into the phenol **34**, thus obtained pure in 40% overall yield.



Scheme 12.



32 33 34 (40%, 2 steps)

Scheme 13.

As a summary, we reported here on the development of a masked hydroxy group that can be an efficient surrogate to the widely used $PhMe_2Si$ and $(RO)Me_2Si$ groups. Its oxidation can be performed in the presence of cyclopropanes, allylic and non-allylic double bonds, hydroxy groups in β-position, all situations where the oxidation of the $PhMe_2Si$ group was reported to be troublesome. The DMPTCS is more stable than alkoxysilanes and can withstand strong bases, electrophiles, reducing agents and organometallic reagents. The real masked hydroxy group (i.e. **3**, Scheme 1) is revealed late in the oxidation sequence, which is particularly useful in the context of a multistep synthesis. Finally, its oxidation can be performed in the presence of other silicon groups which indicates that orthogonal unmasking of latent hydroxy groups should be possible.

Experimental

^1H NMR and ^{13}C NMR were recorded on a Bruker AC-250 FT (^1H: 250 MHz, ^{13}C: 62.9 MHz), Bruker WH-360 FT (^1H: 360 MHz, ^{13}C: 90.55 MHz), Bruker ARX-400 FT (^1H: 400 MHz, ^{13}C: 100.6 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin–Elmer 1710 spectrophotometer or on a Perkin–Elmer Paragon 500 FT-IR spectrophotometer. Mass spectra were recorded on a Finnigan 1020 and Nermag R10-10C, chemical ionisation (CI) with NH_3. Specific rotatory powers were recorded on a Perkin–Elmer 241 polarimeter. Elemental analyses were performed by the I. Beetz laboratory, W-8640 Kronach (Germany). Merck silica gel 60 (70–230 mesh) and (230–400 mesh ASTM) were used for flash chromatography. CH_2Cl_2 was distilled from CaH_2. THF was distilled from potassium. Benzene, toluene, ether and hexane were distilled from sodium. Chlorosilanes were distilled over magnesium.

Phenylthiocyclopropane (6). In a dry 500 mL three-necked flask equipped with a magnetic stirrer, an inlet for nitrogen, a thermometer and a septum was placed a solution of 1,3-diphenylthiopropane **5** (20 g, 77 mmol) in dry THF (200 mL). A 1.5 M solution of *n*-BuLi in hexane (62 mL, 92 mmol) was then added at −80°C. The mixture was stirred for 2 h at rt, then quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with Et_2O. The combined extracts were washed with a 10% solution of NaOH (3×), then with a saturated solution of NaCl, dried over $MgSO_4$ and the solvents were evaporated in vacuo. The residue was purified by distillation (72–74°C, 4 mbar) to give pure **6** (10.8 g, 94%). Spectroscopic data were identical with those described in the literature.[28]

General procedure for the synthesis of organosilylphenylthiocyclopropane 7

Two steps procedure from 5 (7b). In a dry 250 mL three-necked flask equipped with a magnetic stirrer, an inlet for nitrogen, a thermometer and a septum was placed a solution of phenylthiocyclopropane **6** (6 g, 40 mmol) in dry THF (100 mL) then *t*-BuOK (6.7 g, 60 mmol). A 1.5 M solution of *n*-BuLi in hexane (40 mL, 60 mmol) was then added at −80°C. The mixture was stirred for 0.75 h at −80°C, then allyldimethylchlorosilane (9 mL, 60 mmol) was added at −80 °C. The resulting mixture was stirred for 5 min at −80°C then quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with ether. The combined extracts were washed with a saturated solution of NaCl, and dried over $MgSO_4$ and the solvents were evaporated in vacuo. The residue was then purified by distillation (84°C, 0.4 mbar) to give pure **7b** (8.5 g, 86%). **7b** can also be purified using flash chromatography over silica gel (petroleum ether/NEt_3 99:1). ^1H NMR δ 7.4–7.1 (5H, m), 5.75 (1H, m), 4.85 (2H, m), 1.55 (2H, d, J=8.1 Hz), 0.98 (4H, m), −0.05 (6H, s). IR (KBr) ν 3080, 3000, 2900, 1615, 1590, 1480, 1440, 1250, 1030, 900, 840, 740, 700 cm^{-1}. MS m/z (%): 248 ($M^{+\cdot}$, 7), 224 (2), 207 (52), 191 (4), 167 (100), 151 (24), 117 (4), 91 (8). Anal. Calcd for $C_{14}H_{20}SSi$: C 67.71, H 8.12, S 12.89, Si 11.28. Found: C 67.80, H 8.09, S 12.83, Si 11.30.

General procedure for the synthesis of organosilylphenylthiocyclopropane

One-pot procedure from 5 (7b). In a dry 500 mL three-necked flask equipped with a magnetic stirrer, an inlet for nitrogen, a thermometer and a septum was placed a solution of 1,3-diphenylthiopropane **5** (20 g, 77 mmol) in dry THF (200 mL). A 1.5 M solution of *n*-BuLi in hexane (108 mL, 162 mmol) was then added at −80°C and the mixture was stirred for 3 h at rt. Allyldimethylchlorosilane (17.3 mL, 115.5 mmol) was then added at −80°C and the mixture was stirred for 30 min. at rt. The reaction mixture was then quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with ether. The combined extracts were washed with a 10% solution of NaOH (3×), then with a saturated solution of NaCl, and dried over $MgSO_4$, and the solvents were evaporated in vacuo. The residue was then purified by distillation to give pure **7b** (13 g, 68%). The purification by distillation is recommended in this procedure because the residual **6** is difficult to separate from the desired products using flash chromatography. Spectroscopic data of **7b** are identical with those obtained through the above procedure.

Benzyldimethyl(1-thiophenyl)cyclopropylsilane (7a). Following the two-step procedure described above, **7a** (9 g, 76%) was obtained after purification through

Kugelrohr distillation (145°C, 0.1 mbar). **7a** can also be purified using flash chromatography over silica gel (petroleum ether/NEt_3 99:1). Following the one-pot procedure described above, **7a** was obtained after purification through Kugelrohr distillation (11.5 g, 50%). ^{1}H NMR δ 7.40–7.00 (10H, m), 2.17 (2H, s), 1.00 (4H, m), −0.09 (6H, s). IR (KBr) ν 3060, 3000, 2900, 1620, 1470, 1440, 1250, 900, 840, 730 cm^{-1}. MS *m/z* (%): 298 ($M^{+\cdot}$, 13), 207 (58), 167 (100), 151 (17), 135 (3), 121 (13), 105 (4), 91 (29). Anal. Calcd for $C_{18}H_{22}SSi$: C 72.45, H 7.44, S 10.72, Si 9.38. Found: C 72.51, H 7.48, S 10.70, Si 9.34.

General procedure for the alkylation of allyl- and benzylsilanes 7a–b

(8a). In a dry 50 mL three-necked flask equipped with a magnetic stirrer, an inlet for nitrogen, a thermometer and a septum was placed a solution of benzylsilane **7a** (0.2 g, 0.67 mmol) in dry THF (20 mL); then *t*-BuOK (0.11 g, 1 mmol) was added. A 1.5 M solution of *n*-BuLi in hexane (0.7 mL, 1 mmol) was then added at −80°C. The mixture was stirred for 0.75 h at −80°C, then methyl iodide (0.6 g, 2.6 mmol) was added at −80°C. The resulting mixture was stirred for 5 min at −80°C, then quenched with a saturated solution of NH_4Cl, and the aqueous layer was extracted with Et_2O. The combined extracts were washed with a saturated solution of NaCl, dried over $MgSO_4$ and the solvents were evaporated in vacuo. The residue was then purified by flash chromatography over silica gel (petroleum ether/NEt_3 99:1) to give pure **8a** (0.19 g, 91%). ^{1}H NMR δ 7.45–7.00 (10H, m), 2.53 (1H, q, *J*=7.5 Hz), 1.42 (3H, d, *J*=7.5 Hz), 0.58 (4H, m), −0.1 (3H, s), −0.23 (3H, s). IR (KBr) ν 3100, 3050, 3000, 2900, 1600, 1590, 1460, 1240, 900, 820, 780, 720, 700 cm^{-1}. MS *m/z* (%): 312 ($M^{+\cdot}$, 13), 224 (4), 207 (99), 167 (100), 151 (36), 135 (17), 105 (21), 91 (15). Anal. Calcd for $C_{19}H_{24}SSi$: C 73.04, H 7.75, S 10.24, Si 8.96. Found: C 73.12, H 7.67, S 10.18, Si 9.03.

Allylsilane (8b). Following the general procedure described above, allylation of **7a** (1 g, 3.4 mmol) with allyl bromide (0.65 g, 5.4 mmol) gave after flash chromatography over silica gel (petroleum ether/NEt_3 99:1) the pure olefin **8b** (1.03 g, 90%). ^{1}H NMR δ 7.45–7.02 (10H, m), 5.64 (1H, m), 4.99–4.82 (2H, m), 2.65–2.45 (3H, m), 1.00–0.73 (4H, m), −0.06 (3H, s), −0.24 (3H, s). IR (KBr) ν 3050, 3000, 2990, 1680, 1600, 1500, 1450, 1260, 920, 850, 820, 780, 720 cm^{-1}. MS *m/z* (%): 339 ($M^{+\cdot}$+1, 100), 207 (65), 167 (33), 151 (6), 91 (7), 74 (16). Anal. Calcd for $C_{21}H_{26}SSi$: C 74.52, H 7.75, S 9.45, Si 8.27. Found: C 74.57, H 7.69, S 9.37, Si 8.23.

Alcohol (8c). Following the general procedure described above, **7a** (0.4 g, 1.3 mmol) was alkylated with ethylene glycol sulfate[8] (0.33 g, 2.7 mmol). The crude product was dissolved in Et_2O (20 mL) and a 20% aqueous solution of H_2SO_4 (20 mL) was added dropwise. After 1 h at rt, the organic layer was decanted and the aqueous layer extracted with Et_2O. The combined extracts were then washed with NaOH 10%. After drying and evaporation of the solvent in vacuo, the crude alcohol was purified by flash chromatography over silica gel (petroleum ether/EtOAc 8:2) to afford the pure alcohol **8c** (0.13 g, 65%). ^{1}H NMR δ 7.43–7.04 (10H, m), 3.60–3.35 (2H, m), 2.49 (1H, m), 2.13–2.05 (2H, m), 1.05–0.73 (4H, m), −0.06 (3H, s), −0.26 (3H, s). IR (KBr) ν 3350, 3090, 3000, 2960, 1600, 1580, 1470, 1245, 1020, 900, 840, 715, 700 cm^{-1}. MS *m/z* (%): 342 ($M^{+\cdot}$+1, 1), 207 (100), 167 (12), 135 (40), 74 (6). Anal. Calcd for $C_{20}H_{26}OSSi$: C 70.25, H 7.66, S 9.34. Found: C 70.19, H 7.77, S 9.27.

Allylsilane (8d). Following the general procedure described above, alkylation of **7b** (1 g, 4 mmol) with methyl iodide (0.5 mL, 6 mmol) gave after flash chromatography over silica gel (petroleum ether/NEt_3 99:1) the alkylated product **8d** (0.95 g, 91%) (α/γ ratio>95:5 measured from ^{1}H NMR of the crude alkylation mixture). ^{1}H NMR δ 7.40–7.09 (5H, m), 5.95 (1H, ddd, *J*=17.6, 10.5 and 7.2 Hz), 4.86 (2H, m), 1.91 (1H, tquint, *J*=7.2 and 1.4 Hz), 1.11 (3H, d, *J*=7.2 Hz), 1.05 (4H, m), −0.10 (3H, s), −0.11 (3H, s). IR (KBr) ν 3100, 3000, 2950, 1640, 1600, 1490, 1260, 910, 845, 770 cm^{-1}. MS *m/z* (%): 248 ($M^{+\cdot}$+1+NH_3, 4), 207 (37), 179 (3), 167 (100), 151 (13), 117 (7), 91 (11). Anal. Calcd for $C_{15}H_{22}SSi$: C 68.67, H 8.46, S 12.20, Si 10.67. Found: C 68.75, H 8.43, S 12.22, Si 10.59.

Allyl- and vinylsilane (8e). Following the general procedure described above, alkylation of **7b** (0.5 g, 2 mmol) with 2-bromoethylbenzene (0.5 mL, 3.7 mmol) gave **8e** (0.62 g, 87%) as a 59:41 mixture of the α/γ regioisomers (measured from ^{1}H NMR of the crude alkylation mixture), after flash chromatography over silica gel (petroleum ether/NEt_3 99:1). ^{1}H NMR δ 7.38–7.05 (20H, m), 6.06 (1H, dt, *J*=18.6 and 6.1 Hz), 5.72 (1H, ddd, *J*=17, 10.3 and 9.1 Hz), 5.50 (1H, dt, *J*=18.6 and 1.4 Hz), 4.94 (2H, m), 2.81–1.60 (11H, m), 1.05–0.93 (8H, m), 0.05 (6H, s, $Si(CH_3)_2$ γ), −0.11 (3H, s, $SiCH_3$ α), −0.13 (3H, s, $SiCH_3$ α). MS *m/z* (%): 353 ($M^{+\cdot}$+1, 43), 224 (7), 207 (100), 167 (29), 151 (4), 116 (3), 74 (11).

Vinylsilane (8f). Following the general procedure described above, alkylation of **7b** (0.8 g, 3.2 mmol) with bromomethyldimethylphenylsilane (1.18 g, 5.2 mmol) gave the pure olefin **8f** (0.64 g, 50%) after flash chromatography over silica gel (petroleum ether/NEt_3 99:1). ^{1}H NMR δ 7.52–7.06 (10H, m), 6.11 (1H, dt, *J*=18.5 and 5.7 Hz), 5.45 (1H, dt, *J*=18.5 and 1.4 Hz), 2.06 (2H, m), 0.97 (4H, m), 0.76 (2H, m), 0.28 (6H, s), 0.03 (6H, s). IR (KBr) ν 3100, 3000, 2950, 1620, 1600, 1400, 1260, 1120, 840, 750, 710 cm^{-1}. MS *m/z* (%): 248 ($M^{+\cdot}$+1, 100), 207 (84), 167 (26), 135 (44), 75 (8). Anal. Calcd for $C_{23}H_{32}SSi_2$: C 69.67, H 8.14, S 8.07, Si 14.12. Found: C 69.64, H 8.16, S 8.12, Si 14.03.

Vinylsilane (8g). Following the general procedure described above, silylation of **7b** (1 g, 4 mmol) with phenyldimethylchlorosilane (1.3 mL, 6.5 mmol) gave the pure olefin **8g** (1.5 g, 90%) after flash chromatography over silica gel (petroleum ether/NEt_3 99:1). ^{1}H NMR δ 7.53–7.10 (10H, m), 6.04 (1H, dt, *J*=18.5 and 7.8 Hz), 5.30 (1H, dt, *J*=18.5 and 1.1 Hz), 1.86 (2H, dd, *J*=8 and 1.1 Hz), 0.94 (4H, m), 0.29 (6H, s), 0.16 (6H, s). IR (KBr) ν 3090, 3000, 2950, 1600, 1480, 1440, 1260, 1140, 920, 850, 720 cm^{-1}. MS *m/z* (%): 399 ($M^{+\cdot}$+1+NH_3, 3), 343 (100), 233 (4), 193 (47), 167 (13), 150 (14), 117 (21), 91 (11), 74 (21). Anal. Calcd for $C_{22}H_{30}SSi_2$: C 69.08, H 7.91, S 8.37, Si 14.64. Found: C 69.14, H 8.02, S 8.37, Si 14.75.

General procedure for the oxidation of the C–Si bond

Procedure A. 1-Phenylbut-3-enol (11a). To a solution of **8b** (0.85 g, 2.5 mmol) in MeOH (50 mL) was added at 0°C, water (2 mL) and $NaIO_4$ (0.65 g, 3 mmol). The white slurry was stirred for 4 h at rt, then the solvent was evaporated under vacuum and Et_2O (20 mL) was added to the residue. The solution was dried over $MgSO_4$, filtered and the solvent was evaporated in vacuo to afford the crude sulfoxide **9** as a 1:1 mixture of two diastereomers (estimated from the ^1H NMR of the crude mixture) used in the next step without further purification: ^1H NMR δ (2 diastereomers): 7.75–7.49 (10H, m), 7.25–6.94 (10H, m), 5.69–5.50 (2H, m), 5.00–4.81 (4H, m), 2.57–2.48 (4H, m), 2.32 (2H, m), 1.48–1.34 (2H, m), 1.26 (1H, m), 1.15 (1H, m), 0.84 (2H, m), 0.65 (2H, m), −0.11 (3H, s), −0.23 (3H, s), −0.40 (3H, s), −0.52 (3H, s). IR (KBr) 3055, 3000, 2900, 1640, 1600, 1450, 1260, 1100, 1060 (S=O), 920, 880, 860, 820, 720 cm^{-1}. The crude sulfoxides **9** in benzene (10 mL) were then refluxed for 18 h to afford after evaporation of the solvent, the crude siloxane **10** used in the next step without further purification: ^1H NMR (C_6D_6) δ 7.58–6.91 (10H, m), 5.75–5.59 (1H, m), 4.96–4.81 (2H, m), 2.57–2.46 (2H, m), 2.20 (1H, dd, J=9.0 and 6.7 Hz), 0.94–0.92 (4H, m), 0.16 (3H, s), 0.15 (3H, s). IR (KBr) ν 3060, 3000, 2995, 1620, 1580, 1470, 1420, 1250, 1180, 1040, 880, 710 cm^{-1}.

General procedure for the Tamao–Kumada oxidation

To a solution of crude **10** in MeOH (20 mL) and THF (20 mL) was added at 0°C, KF (0.44 g, 7.5 mmol), $KHCO_3$ (0.75 g, 7.5 mmol) and a 35% solution of H_2O_2 in water (4.3 mL, 50 mmol). The reaction mixture was stirred overnight at rt then $Na_2S_2O_3$ was added and the solvents were evaporated under vacuum. Et_2O (50 mL) was added to the residue and the mixture was dried over $MgSO_4$, filtered and the solvent was evaporated in vacuo. The crude alcohol was purified by flash chromatography over silica gel (petroleum ether/EtOAc 8:2) to give pure **11a** (0.29 g, 78%, 3 steps). Spectroscopic data of **11a** were identical with those described in the literature.[29]

1-Phenylethanol (11b). Following the general procedure **A**, **8a** (0.17 g, 0.54 mmol) gave, after flash chromatography over silica gel (petroleum ether/EtOAc 7:3), the alcohol **11b** (0.06 g, 86%). Spectroscopic data of **11b** were identical with those of the commercially available material.

5-Phenylpenten-3-ol (11c). Following the general procedure **A**, **8e** (0.85 g, 2.5 mmol) gave, after flash chromatography over silica gel (petroleum ether/EtOAc 8:2), the alcohol **11c** (0.06 g, 77% from the α-regioisomer). Spectroscopic data of **11c** were identical with those described in the literature.[30]

4-phenyldimethylsilylbutanal (11d). Following the general procedure **A**, **8f** (0.45 g, 1.1 mmol) gave, after flash chromatography over silica gel (petroleum ether/EtOAc 9:1), the pure aldehyde **11d** (0.11 g, 50%). ^1H NMR δ 9.73 (1H, t, J=1.8 Hz), 7.53–7.36 (5H, m), 2.45 (2H, dt, J=7.2 and 1.8 Hz), 1.67 (2H, m), 0.78 (2H, m,), 0.29 (6H, s). IR (KBr) ν 3100, 3000, 2950, 1620, 1600, 1400, 1260, 1120, 840, 750, 710 cm^{-1}. MS m/z (%): 207 ($M^{+\cdot}$+1, 0.2), 191 (16), 178 (5), 163 (39), 135 (100), 104 (37), 91 (7). Anal. Calcd for $C_{12}H_{18}OSi$: C 69.86, H 8.80, Si 13.57. Found: C 69.88, H 8.76, Si 13.61.

General procedure for the oxidation of the C–Si bond

Procedure B. 1-Phenylpropan-1,3-diol (13). The alcohol **8c** (0.61 g, 1.8 mmol) was dissolved in CH_2Cl_2 (30 mL) and a solution of *m*-CPBA (70%, 1 g, 4 mmol) in CH_2Cl_2 (60 mL) was added dropwise at 0°C. The reaction mixture was stirred at rt for 2 h then a saturated solution of $NaHCO_3$ (150 mL) was added and the aqueous layer was extracted with EtOAc. The combined extracts were washed with brine, dried over $MgSO_4$ and the solvents were evaporated in vacuo to give the crude sulfone **12** (0.64 g, 96%) used in the next step without further purification: ^1H NMR δ 7.97–7.01 (10H, m), 3.58 (1H, m), 3.42 (1H, m), 2.74 (1H, dd, J=11.9 and 3.6 Hz), 2.10 (2H, m), 1.80 (1H, br s), 1.65–1.39 (2H, m), 1.04–0.67 (2H, m), −0.11 (3H, s), −0.52 (3H, s). IR (KBr) ν 3500, 3100, 3000, 2995, 2950, 1450, 1300, 1250, 1150, 910, 800, 600 cm^{-1}. Following the general Tamao–Kumada oxidation procedure, the preceding sulfone **12** (0.28 g, 0.75 mmol) gave, after flash chromatography over silica gel (CH_2Cl_2/Et_2O 3:2), the pure diol **13**[31] (0.08 g, 70%) and the sulfone **14**[32] (0.32 g, 100%) which spectroscopic data were identical with those described in the literature.

General procedure for the oxidation of the C–Si bond

Procedure C. (11a). A solution of V_2O_5 in *t*-BuOH was prepared as follows: a 35% solution of H_2O_2 in water (100 mL) was mixed with *t*-BuOH (400 mL) under vigorous stirring, then the organic layer was decanted and dried over Na_2SO_4 (3×), then over K_2SO_4. To the preceding solution (ca. 6% H_2O_2, 50 mL) was added V_2O_5 (50 mg, 0.27 mmol) and the resulting orange mixture was stirred for 1 h at rt. This freshly prepared mixture (ca. 20 mL) was then added dropwise to a solution of **8b** (0.5 g, 1.5 mmol) in *t*-BuOH (5 mL), until the complete disappearance of the starting material (monitored by TLC). The solvent was then evaporated to afford the crude sulfone **15** (0.55 g, 100%): ^1H NMR δ 7.97–7.54 (5H, m), 7.25–6.99 (5H, m), 5.62–5.51 (1H, m), 4.96–4.81 (2H, m), 2.60–2.41 (3H, m), 1.59–1.39 (2H, m), 0.95 (1H, m), 0.64 (1H, m), −0.08 (3H, s), −0.37 (3H, s). IR (KBr) ν 3062, 2973, 1638, 1599, 1492, 1447, 1299, 1254 (SO_2), 1172, 1137 (SO_2), 1082, 918, 805, 702, 691 cm^{-1}. The crude **15** was then submitted to the general Tamao–Kumada oxidation procedure to give, after flash chromatography over silica gel (petroleum ether/EtOAc 8:2), the sulfone **14**[32] (0.27 g, 100%) and the pure alcohol **11a**[29] (0.19 g, 85%) identical (^1H NMR, IR) with that prepared according to procedure **A**.

Allylsilanes (17a–b). Following the general procedure, silylation of **6** (1.2 g, 4.8 mmol) with *Z*-(2-methylbut-2-enyl)dimethylchlorosilane[14] (2 g, 7.2 mmol) gave, after flash chromatography over silica gel (petroleum ether/NEt_3 99:1), a 81:19 mixture of allylsilanes **17a/17b** respectively (1.8 g, 81%). *Major* **17a**: ^1H NMR δ 7.39–7.08 (5H, m), 5.07 (1H, q, J=6.7 Hz), 1.67–1.42 (8H, m), 1.05 (4H, m), −0.03 (6H, s). IR (KBr) ν 3050, 3000, 2990, 1600,

1490, 1450, 1260, 1040, 910, 850 cm^{-1}. MS *m/z* (%): 276 ($M^{+\cdot}$, 18), 224 (4), 207 (66), 167 (100), 151 (23), 117 (7), 91 (23), 74 (62). Anal. Calcd for $C_{16}H_{24}SSi$: C 69.50, H 8.75, S 11.59, Si 10.16. Found: C 69.45, H 8.70, S 11.46, Si 10.08.

Acetonide (18b). To a mixture of AD-mix-β® (0.7 g) and $MeSO_2NH_2$ (0.048 g, 0.5 mmol) in *t*-BuOH (3 mL) and H_2O (3 mL) at 0°C, was added the olefin **17a** (0.14 g, 0.5 mmol) and the resulting orange solution was stirred at rt for 48 h. A saturated solution of Na_2SO_3 was then added and the organic layer decanted. The aqueous layer was extracted with EtOAc and the combined extracts were washed with brine, dried over $MgSO_4$ and the solvent was evaporated in vacuo to afford the crude diol **18a** (0.15 g, 96%). **18a** was then dissolved in dimethoxypropane (10 mL) and *p*-TsOH (10 mg) was added. After 2 h at rt, a saturated solution of $NaHCO_3$ (20 mL) was added and the aqueous layer extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over $MgSO_4$ and the solvent was evaporated in vacuo. The crude product was purified by flash chromatography over silica gel (petroleum ether/EtOAc 95:5) to afford the pure acetonide **18b** (0.14 g, 80%). ^1H NMR δ 7.38–7.10 (5H, m), 3.78 (1H, q, J=6.3 Hz), 1.38 (3H, s), 1.31 (3H, s), 1.22 (3H, s), 1.04 (9H, m), 0.10 (3H, s), 0.05 (3H). IR (KBr) ν 3070, 3000, 2950, 1580, 1480, 1380, 1240, 1020, 910, 740, 700 cm^{-1}. MS *m/z* (%): 351 ($M^{+\cdot}$+1, 2), 335 (3), 293 (5), 225 (2), 201 (26), 167 (13), 143 (51), 109 (32), 75 (100). Anal. Calcd for $C_{19}H_{30}O_2SSi$: C 65.11, H 8.63, S 9.13, Si 7.99. Found: C 65.23, H 8.62, S 9.01, Si 8.06.

(2*S*,3*R*)-2-methylbutan-1,2,3-triol (19a). Following the general procedure **B**, the crude diol **18a** prepared through dihydroxylation of **17a** as above (0.32 g, 1 mmol) gave, after flash chromatography over silica gel (CH_2Cl_2/MeOH 9:1), the pure triol **19a** (0.1 g, 82%). Spectroscopic data were identical with those described in the literature.[16]

Alcohol (19b). Following the general procedure **A**, the thioether **18b** (0.28 g, 0.8 mmol) gave, after flash chromatography over silica gel (petroleum ether/EtOAc 7:3), pure **19b** (0.08 g, 70%) [25% ee measured from the ^1H NMR of **19b** in the presence of Eu(hfc)$_3$]. $[\alpha]_D^{25}=-7.9$ (*c* 1.1, $CHCl_3$). Spectroscopic data were identical with those described in the literature.[16]

Hydroxy-carbamate (20). In a 100 mL flask equipped with a magnetic stirrer, urethane (0.75 g, 8.5 mmol) was dissolved in *n*-propanol (11 mL). To this solution was added a freshly prepared solution of NaOH (0.34 g, 8.5 mmol) in water (21 mL), followed by *t*-BuOCl (1.3 mL, 11.3 mmol) and a solution of the ligand $(DHQ)_2PHAL$ (0.11 g, 0.14 mmol) in *n*-propanol (10 mL). The flask was then immersed in a water bath (15°C), and after stirring for a few minutes, $K_2OsO_2(OH)_4$ (42 mg, 0.11 mmol) was added, followed by the allylsilane **7b** (0.7 g, 2.8 mmol). The green reaction mixture was stirred for 1.5 h then quenched with sodium sulfite, followed by EtOAc (20 mL). After stirring for 15 min, the organic layer was decanted and the aqueous layer extracted with EtOAc (3×20 mL). The combined extracts were washed with water, brine and then dried over $MgSO_4$ and the solvents were evaporated in vacuo. The residue was purified by chromatography through silica gel (EtOAc/petroleum ether 1:1) to give **20** (0.4 g, 40%) (40% ee measured from the ^1H NMR of the Mosher ester of **20**). $[\alpha]_D^{25}=+2.8$ (*c* 1.3, $CHCl_3$). ^1H NMR δ 7.38–7.11 (5H, m), 5.11 (1H, br s), 4.12 (2H, q, J=7 Hz), 3.87 (1H, m), 3.28 (1H, m), 2.96 (1H, m), 2.47 (1H, br s), 1.25 (3H, t, J=7 Hz), 1.16–0.99 (4H, m), 0.84 (2H, m), 0.00 (6H, s). ^{13}C NMR δ 157 (s), 138.0 (s), 128.5–125.4 (3d), 69.0 (d, J=141 Hz), 60.9 (t, J=146 Hz), 49.6 (t, J=133 Hz), 21.4 (t, J=115 Hz), 14.6 (q, J=126 Hz), 13.6 (t, J=163 Hz), −3.1 (q, J=119 Hz), −3.3 (q, J=119 Hz). IR (KBr) ν 3442, 3074, 1698, 1529, 1479, 1440, 1252, 1090, 1026, 839, 739 cm^{-1}. MS *m/z* (%): 353 ($M^{+\cdot}$, 0.1), 336 (5), 251 (5), 204 (83), 158 (45), 135 (10), 121 (37), 75 (100). Anal. Calcd for $C_{17}H_{27}NO_3SSi$: C 57.77, H 7.71, N 3.97, S 9.05, Si 7.92. Found: C 57.65, H 7.74, N 3.94, S 9.01, Si 7.89.

3-*N*-Ethoxycarbonylpropan-1,2-diol (21).[33] **20** was submitted to the general oxidation procedure **B** described above to give, after flash chromatography through silica gel (petroleum ether/EtOAc 4:6), the pure diol **21** (0.15 g, 80%). ^1H NMR δ 5.70 (1H, br s), 4.21–4.04 (2H, m), 4.09 (2H, t, J=7.3 Hz), 3.64–3.54 (3H, m), 3.35–3.13 (2H, m), 1.22 (3H, t, J=7.4 Hz). ^{13}C NMR δ 158 (s), 71.2 (d), 63.8 (t), 61.2 (t), 43.2 (t), 14.5 (q). IR (KBr) ν 3335 (OH), 1698 (C=O), 1538, 1268, 1037 cm^{-1}. MS *m/z* (%): 164 ($M^{+\cdot}$, 3.5), 132 (55), 115 (8), 102 (93), 90 (9), 74 (43), 60 (45), 44 (28). HRMS. Calcd for $C_6H_{14}NO_4$: 164.0923. Found: 164.0926.

***trans*-2-(Dimethylphenylsilyl)methylcyclopropanol (23). (Procedure A).** To a solution of olefin **8g** (0.5 g, 1.3 mmol) in CH_2Cl_2 (10 mL) was added at 0°C a 1*M* solution of Me_3Al in hexane (6.5 mL, 6.5 mmol) and CH_2I_2 (0.53 mL, 6.5 mmol). The reaction mixture was stirred at rt for 4 h then quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$ and the solvents were evaporated in vacuo. The crude cyclopropane **22** was then submitted to the general procedure **A** to afford, after flash chromatography through silica gel (petroleum ether/EtOAc 8:2), the cyclopropanol **23** (0.13 g, 50%). ^1H NMR δ 7.57–7.52 (2H, m), 7.39–7.20 (3H, m), 3.07 (1H, dt, J=6.3 and 2.6 Hz), 1.85 (1H, br s), 0.90–0.69 (3H, m), 0.60 (1H, dd, J=14.7 and 7.5 Hz), 0.36 (3H, s), 0.34 (3H, s), 0.27 (1H, q, J=6 Hz). ^{13}C NMR δ 140 (s), 133.5, 128.9 and 127.7 (3d), 54.2 (d, J=183 Hz), 18.5 (t), 16.6 (t), 16.3 (d), −2.9 (q, J=119 Hz), −3.1 (q, J=119 Hz). IR (KBr) ν 3413, 3070, 2957, 1428, 1253, 1190, 1118, 1065, 981, 832, 795, 730, 700 cm^{-1}. MS *m/z* (%): 206 ($M^{+\cdot}$, 2), 178 (7), 143 (54), 102 (100), 86 (38). Anal. Calcd for $C_{12}H_{18}OSi$: C 69.86, H 8.80, Si 13.57. Found: C 69.79, H 8.81, Si 13.65.

Sulfone (24). Following the sulfide oxidation described in procedure **C**, the thioether **8g** (0.5 g, 1.3 mmol) gave, after flash chromatography over silica gel (petroleum ether/EtOAc/NEt_3 90:9:1), the sulfone **24** (0.53 g, 100%). ^1H NMR δ 7.85–7.32 (10H, m), 5.92 (1H, dt, J=18.4 and 7.8 Hz), 5.00 (1H, dt, J=18.5 and 1.2 Hz), 1.79 (2H, dd, J=7.8 and 1.2 Hz), 1.52 (2H, m), 0.86 (2H, m), 0.25 (6H, s), −0.06 (6H, s). IR (KBr) ν 3060, 3000, 2950, 1600, 1440, 1420, 1300, 1140, 920, 850, 740, 600 cm^{-1}. MS *m/z* (%):

432 ($M^{+\cdot}+1+NH_3$, 23), 375 (1), 297 (44), 139 (100), 209 (9), 135 (92), 83 (16). Anal. Calcd for $C_{22}H_{30}O_2SSi_2$: C 63.74, H 7.30, S 7.72, Si 13.51. Found: C 63.82, H 7.22, S 7.67, Si 13.62.

***trans*-2-(Dimethylphenylsilyl)methylcyclopropanol (23) from sulfone (24).** To a solution of **24** (0.53 g, 1.28 mmol) in CH_2Cl_2 (10 mL) was added CH_2I_2 (0.53 mL, 6.5 mmol) and a 1 M solution of Et_2Zn in hexane (6.5 mL, 6.5 mmol). The reaction mixture was stirred at rt for 4 h then quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$ and the solvents were evaporated in vacuo. The crude cyclopropane **25** was then diluted in THF (20 mL) and a 1 M solution of TBAF in THF (2 mL, 1.95 mmol) was added at 0°C. After stirring for 1 h at 0°C, the solvent was evaporated in vacuo and the residue was submitted to the general Tamao–Kumada oxidation procedure to afford, after flash chromatography through silica gel (petroleum ether/EtOAc 8:2) the cyclopropanol **23** (0.15 g, 57%, 3 steps) identical to that obtained above.

Dimethyl(1-phenylthio)cyclopropylsilane (26a). In a dry 500 mL three-necked flask equipped with a magnetic stirrer, an inlet for nitrogen, a thermometer and a septum was placed a solution of **6** (8 g, 53.3 mmol) in dry THF (150 mL) and *t*-BuOK (7.8 g, 69.3 mmol) was added. A 1.5 M solution of *n*-BuLi in hexane (46.2 mL, 69.29 mmol) was then added at −80°C. The orange mixture was stirred for 0.75 h at −80°C then slowly canulated onto a solution of dimethylchlorosilane (17.4 mL, 160 mmol) in dry THF (50 mL) at −80°C. The reaction mixture was stirred for 5 min. at −80°C then quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with Et_2O. The combined extracts were washed with a saturated solution of NaCl, dried over $MgSO_4$ and the solvents were evaporated in vacuo. The residue was then purified by distillation (62°C, 0.06 mbar) to give pure silane **26a** (8.3 g, 75%). ^{1}H NMR δ 7.40–7.10 (5H, m), 3.91 (1H, sept, J=3.6 Hz), 1.04 (4H, m), 0.09 (6H, d, J=3.6 Hz). IR (KBr) ν 3050, 3000, 2950, 2140 (Si-H), 1590, 1480, 1440, 1090, 1025, 880 (Si-C), 740 cm^{-1}. MS *m/z* (%): 208 ($M^{+\cdot}$, 23), 191 (5), 165 (9), 151 (31), 135 (39), 117 (100), 91 (51), 71 (32). Anal. Calcd for $C_{11}H_{16}SSi$: C 63.44, H 7.75, Si 13.45. Found: C 63.28, H 7.62, Si 13.53.

Dimethyl(1-phenylthio)cyclopropylchlorosilane (26b). In a dry 500 mL three-necked flask equipped with a magnetic stirrer, an inlet for nitrogen, a thermometer and a septum was placed a solution of **6** (7.5 g, 50 mmol) in dry THF (150 mL) and a 1.5 M solution of *n*-BuLi in hexane (40 mL, 60 mmol) was then added at 0°C. The yellow mixture was stirred for 4 h at 0°C, cooled to −80°C then slowly canulated onto a solution of dimethyldichlorosilane (10.3 mL, 85 mmol) in dry THF (50 mL) at −80°C. The resulting mixture was stirred for 5 min at −80°C then warmed to rt. The solvent was evaporated in vacuo and the residue was purified by distillation (80°C, 0.04 mbar) to afford pure chlorosilane **26b** (10.2 g, 84%). ^{1}H NMR δ 7.40–7.12 (5H, m), 1.32 (2H, m), 1.09 (2H, m), 0.40 (6H, s). IR (KBr) ν 3061, 3000, 2965, 1583, 1480, 1439, 1256, 1222, 1090, 1026, 908, 844, 819, 791, 737, 691, 673 cm^{-1}. MS *m/z* (%): 242 ($M^{+\cdot}$, 100), 225 (89), 207 (46), 168 (9), 149 (30), 134 (9), 117 (71), 91 (77).

Dichloromethylsilane (27). To a solution of silane **26a** (0.43 g, 2.06 mmol) in dry toluene (30 mL) was added sodium trichloroacetate (1.12 g, 6.18 mmol) and a catalytic amount of 18-crown-6. The mixture was refluxed for 50 h and the solvent evaporated in vacuo. The residue was purified by flash chromatography over silica gel (petroleum ether/NEt_3 99:1) to give the silane **27** (0.42 g, 64%). ^{1}H NMR δ 7.43–7.17 (5H, m), 5.28 (1H, s), 1.19 (4H, m), 0.18 (6H, s). IR (KBr) ν 3100, 3000, 2950, 1580, 1480, 1240, 900, 850, 700 cm^{-1}. MS *m/z* (%): 291 ($M^{+\cdot}$+1, 11), 167 (45), 149 (36), 134 (9), 117 (100), 91 (47), 77 (15). Anal. Calcd for $C_{12}H_{16}Cl_2SSi$: C 49.65, H 5.56, Cl 24.12, S 11.02, Si 9.65. Found: C 49.66, H 5.56, Cl 24.12, S 10.92, Si 9.76.

Dimethyl(1-phenylsufonyl)cyclopropylsilane (28). In a dry 250 mL three-necked flask equipped with a magnetic stirrer, an inlet for nitrogen, a thermometer and a septum was placed a solution of sulfone[32] **14** (2.1 g, 11.5 mmol) in dry THF (100 mL). A 1.5 M solution of *n*-BuLi in hexane (8.5 mL, 12.7 mmol) was then added at −80°C. The mixture was stirred for 45 min. at −40°C, then dimethylchlorosilane (0.61 mL, 12.7 mmol) was added at −80°C. The resulting mixture was stirred for 1 h at −80°C then quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with Et_2O. The combined extracts were washed with a saturated solution of NaCl, dried over $MgSO_4$ and the solvents were evaporated in vacuo. The residue was then purified by Kugelrohr distillation (140–150°C, 0.1 mbar) to give the silane **28** (2.6 g, 94%). ^{1}H NMR δ 7.91–7.50 (5H, m), 3.80 (1H, sept, J=3.7 Hz), 1.66 (2H, m), 0.98 (2H, m), 0.02 (6H, d, J=3.7 Hz). IR (KBr) ν 3100, 3000, 2950, 2150, 1440, 1300, 1120, 880, 560 cm^{-1}. MS *m/z* (%): 358 ($M^{+\cdot}+1+NH_3$, 72), 239 (100), 225 (7), 199 (3), 135 (10), 121 (4), 74 (4). Anal. Calcd for $C_{11}H_{16}O_2SSi$: C 54.99, H 6.72, S 13.32, Si 11.65. Found: C 54.93, H 6.66, S 13.31, Si 11.58.

4-Phenylbut-3-en-1,2-diol (31). To a solution of the diazoester **29**[26] (0.31 g, 1.43 mmol) and the silane **28** (0.34 g, 1.42 mmol) in dry CH_2Cl_2 (20 mL) was added $Rh_2(OAc)_4$ (2 mg) at rt. N_2 rapidly evolved and the resulting green solution was stirred for 0.5 h. The solvent was evaporated in vacuo to afford the crude α-silylester **30** (0.70 g) used in the next step without purification. **30** (0.48 g, 1.12 mmol) was then dissolved in ether (20 mL) and a 0.8 *M* solution of $LiAlH_4$ in ether (1.4 mL, 1.12 mmol) was added dropwise at −60°C. The reaction mixture was then allowed to warm slowly to −30°C and stirred at this temperature for 0.5 h then quenched with a 1 M solution of HCl. The organic layer was decanted and the aqueous layer extracted with ether (3×). The combined extracts were washed with brine, dried over $MgSO_4$ and ether was partially evaporated (*ca.* 15 mL remaining). To this solution was then added at 0°C, MeOH (15 mL) $KHCO_3$ (0.4 g, 4 mmol), KF (0.24 g, 4 mmol), then a 35% solution of H_2O_2 in water (2.6 mL, 30 mmol). The reaction mixture was stirred for 15 h at rt, then quenched following the general Tamao–Kumada procedure to afford, after flash chromatography over silica gel (CH_2Cl_2/MeOH 95:5), the

diol **31** (55 mg, 30%, 3 steps) whose spectroscopic data were identical with those described in the literature.[26]

4-Phenylphenol (34). In a dry 150 mL three-necked flask equipped with a magnetic stirrer, an inlet for nitrogen, a thermometer and a septum was placed a solution of 4-bromobiphenyl (0.5 g, 2.1 mmol) in dry THF (50 mL). A 1.5 M solution of *t*-BuLi in pentane (1.5 mL, 2.2 mmol) was then added at −80°C. The mixture was stirred for 30 min at −80°C, then chlorosilane **26b** (0.56 g, 2.3 mmol) was added at −80°C. The resulting mixture was stirred for 30 min at −80°C then quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with Et_2O. The combined extracts were washed with a saturated solution of NaCl, dried over $MgSO_4$ and the solvents were evaporated in vacuo to afford crude **33** as a pale yellow oil. **33** was then submitted to the general procedure **A** to afford, after flash chromatography over silica gel (petroleum ether/EtOAc 9:1), the biaryl **34** (0.14 g, 40%) whose spectroscopic data were identical with those of the commercially available compound.[34]

Acknowledgements

R. A and Y. L. gratefully acknowledge the Swiss National Science Foundation, the Office Fédéral de L'Education et de la Science (COST program) and the Fondation Agassiz for generous support. Special thanks goes to Prof. C. Maignan (University of Le Mans, France), Dr F. L. van Delft and Prof. J. H. van Boom (University of Leiden, The Netherlands) for helpful discussions.

References

1. (a) Tamao, K.; Ishida, N.; Tanaka, P.; Kumada, M. *Organometallics* **1983**, *2*, 1694–1696. (b) Tamao, K.; Ishida, N. *J. Organomet. Chem*. **1984**, *269*, C37–C39. (c) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29–31. (d) Fleming, I.; Henning, R.; Parker, D. C.; Plaut, H. E.; Sanderson, P. E. J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 317–337.

2. (a) Fleming, I. *Chemtracts: Org. Chem.* **1996**, 1–64. (b) Landais, Y.; Jones, G. *Tetrahedron* **1996**, *52*, 7599–7662. (c) Tamao, K. In *Advances in Silicon Chemistry*, Jai Press Inc., 1996; Vol. 3, pp 1–62.

3. For recent reports addressing this problem, see: (a) Itami, K.; Mitsudo, K.; Yoshida, J.-I. *Tetrahedron Lett.* **1999**, *40*, 5537–5540. (b) Groaning, M. D.; Brengel, G. P.; Meyers, A. I. *J. Org. Chem.* **1998**, *63*, 5517–5522. (c) Knölker, H. J.; Jones, P. G.; Wanzl, G. *Synlett*, **1998**, 613–616; (d) Shaw, J. T.; Woerpel, K. A. *Tetrahedron* **1997**, *53*, 16597–16606; (d) Fleming, I.; Winter, S. B. D. *Tetrahedron Lett.* **1995**, *36*, 1733–1734.

4. Angelaud, R.; Landais, Y.; Maignan, C. *Tetrahedron Lett.* **1995**, *36*, 3861–3864.

5. (a) Oae, S.; Numata, T. The Pummerer type of reactions. In *Isotopes in Organic Synthesis*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1980; Vol. 5, chap. 2. (b) Ager, D. J. *Tetrahedron Lett.* **1980**, *21*, 4759–4762.

6. (a) Bhupathy, M.; Cohen, T. *Tetrahedron Lett.* **1987**, *28*, 4793–4796. (b) Bhupathy, M.; Cohen, T. *Tetrahedron Lett.* **1987**, *28*, 4797–4800.

7. For a review on superbases, see: Schlosser, M. Organoalkali reagents. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: Chichester, 1994; pp 1–166.

8. Lohray, B. B. *Synthesis* **1992**, 1035–1052.

9. (a) Chan, T. H.; Labrecque, D. *Tetrahedron Lett.* **1992**, *33*, 7997–8000. (b) Li, L.-H.; Wang, D.; Chan, T. H. *Tetrahedron Lett.* **1991**, *32*, 2879–2882. (c) Tamao, K.; Nakajo, E.; Ito, Y. *Synth. Commun.* **1987**, *17*, 1637–1646. (d) Muchowski, J. M.; Naef, R.; Maddox, L. *Tetrahedron Lett.* **1985**, *26*, 5375–5378.

10. (a) Hoppe, D.; Hintze, H.; Tebben, P.; Paetow, M.; Ahrens, H.; Schwerdtfeger, J.; Sommerfeld, P.; Haller, J.; Guarnieri, W.; Kolczewski, S.; Hense, T.; Hoppe, I. *Pure Appl. Chem.* **1994**, *66*, 1479–1486. (b) Beak, P.; Du, H. *J. Am. Chem. Soc.* **1993**, *115*, 2516–2518. (c) Schlosser, M.; Limat, D. *J. Am. Chem. Soc*. **1995**, *117*, 12342–12343.

11. A report by van Boom et al. led to sensibly opposite conclusions. Their studies on the closely related dimethyl(phenylthio)-methylsilyl group indicate that its oxidation into the alcohol did not proceed through sila-Pummerer rearrangement but rather by direct displacement of the sulfoxide group by fluoride as demonstrated by the recovery of phenylmethylsulfoxide: (a) van Delft, F. L.; van der Marel, G. A.; van Boom, J. H. *Synlett* **1995**, 1069–1070. (b) van Delft, F. L. PhD Thesis, University of Leiden, 1996.

12. Magar, S. S.; Desai, R. C.; Fuchs, P. L. *J. Org. Chem.* **1992**, *57*, 5360–5369.

13. Miklos, P.; Senning, A. *Tetrahedron* **1987**, *43*, 249–254.

14. Ojima, I.; Kumagai, M. *J. Organomet. Chem.* **1978**, *157*, 359–372.

15. Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483–2547.

16. Fuganti, C.; Grasselli, P.; Servi, S.; Lazzarani, A.; Casati, P. *Tetrahedron* **1988**, *44*, 2575–2582.

17. For a review on Sharpless asymmetric amino-hydroxylation, see: O'Brien, P. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 326–329.

18. *N*-haloamides and carbamates have been used as electrophilic nitrogen sources in the preparation of sulfilimines, see: (a) Tomooka, C. S.; LeCloux, D. D.; Sasaki, H.; Carreira, E. M. *Org. Lett.* **1999**, *1*, 149–152. (b) Celentano, G.; Colonna, S.; Gaggero, N.; Richelmi, C. *J. Chem. Soc., Chem. Commun.* **1998**, 701–702. (c) Bach, T.; Körber, C. *Tetrahedron Lett.* **1998**, *39*, 5015–5016. (d) Genêt, J.-P.; Mallart, S.; Greck, C.; Piveteau, E. *Tetrahedron Lett.* **1991**, *32*, 2359–2362.

19. Abd. Rahman, N.; Fleming, I. *Synth. Commun.* **1993**, *23*, 1583–1594.

20. Maruoka, K.; Fukutani, Y.; Yamamoto, H. *J. Org. Chem.* **1985**, *50*, 4412–4414.

21. The irreproducibility of the cyclopropanation reaction was attributed to the presence of the thioether group known to generate sulfur ylides in the presence of carbenoid species, see: Kosarych, Z.; Cohen, T. *Tetrahedron Lett.* **1982**, *23*, 3019–3022.

22. Morikawa, T.; Sasaki, H.; Hanai, R.; Shibuya, A.; Taguchi, T. *J. Org. Chem.* **1994**, *59*, 97–103.

23. Larson, G. L.; Klesse, R.; Cartledge, F. K. *Organometallics* **1987**, *6*, 2250–2252.

24. Tamao, K.; Nagata, K.; Ito, Y.; Maeda, K.; Shiro, M. *Synlett* **1994**, 257–259.

25. Landais, Y. *Main Group Chemistry News* **1997**, *5*, 4–13.

26. Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.* **1997**, *62*, 1630–1641.

27. Eaborn, C.; Bott, R. W. In *Organometallic Compounds of the IV Elements*, MacDiarmid, A. G. Ed.; Marcel Dekker: New York, 1968; Vol. 1 (Part 1).

28. Tanaka, K.; Uneme, H.; Matsui, S. *Chem. Lett.* **1980**, 287–288.

29. Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2292–2299.
30. Julia, M.; Mansuy, D. *Bull. Soc. Chim. Fr.* **1972**, 2684–2689.
31. Medlik-Balan, A.; Klein, J. *Tetrahedron* **1980**, *36*, 299–304.
32. Truce, W. E.; Hollister, K. R.; Lindy, L. B.; Parr, J. E. *J. Org. Chem.* **1968**, *33*, 43–47.
33. Angelaud, R.; Landais, Y.; Schenk, K. *Tetrahedron Lett.* **1997**, *38*, 1407–1411.
34. Aldrich No. 42,462-5.