Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
Tetrahedron 61 (2005) 657–663

Evaluation of C-trialkylsilyl enol and thioenol ethers as intermediates in the synthesis of acylsilanes

Catherine Hammaecher, Imad Ouzzane, Charles Portella* and Jean-Philippe Bouillon*,†

UMR 6519 'Réactions Sélectives et Applications', CNRS-Université de Reims Champagne-Ardenne, B. P. 1039, 51687 REIMS Cedex 2, France

Received 23 August 2004; revised 27 October 2004; accepted 28 October 2004

Available online 18 November 2004

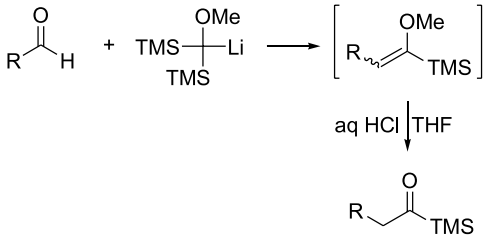
Abstract—C-silyl enol ethers or thioenol ethers have been prepared by a Peterson reaction, as intermediates for acylsilane synthesis. Bis(trialkylsilyl)(methoxy)- or -(methylsulfanyl)methanes bearing identical or different trialkylsilyl groups were used as starting materials in order to assess the selectivity of the Peterson elimination step. A good selectivity was observed only with ethers bearing the TMS and TBDMS groups. However, there is no practical interest to use such reagents owing to the difficulty to obtain them in correct yields. Bis(trimethylsilyl)(methylsulfanyl)methane proved to be a good reagent for the preparation of C-silyl thioenol ethers, which are hydrolyzed under classical acid conditions to give acylsilanes in fair overall yields. This convenient procedure was extended to the synthesis of bis(acylsilanes).

1. Introduction

Acylsilanes are interesting compounds exhibiting specific properties beside the usual ones of carbonyl derivatives.[1] The interest of their chemistry is strongly dependant on their more or less easy synthesis. Several strategies were reported, starting from compounds as various as aldehydes,[2,3] esters,[4] acyl chlorides,[5] alkyl halides or triflates,[6] epoxides,[7] diols,[8] and others. One of the more general methods, proposed simultaneously by Brook's and Corey's groups,[2] is based on the reversed polarity (umpolung) concept and uses dithioacetals as key intermediates. First developed essentially via the thioacetalization of aldehydes as starting materials, the methodology was further extended to the alternative approach using alkylation of 2-lithio-2-trimethylsilyldithiane as silylcarbonyl moiety equivalent.[6–8] These dithioacetal routes are very useful, and they were involved in the preparation of a wide range of acylsilanes, including functionalized acylsilanes and bis(acylsilanes).[6–8]

The dithioacetal methodology suffers some drawbacks inherent to the last step of carbonyl releasing, which needs oxidative hydrolytic conditions. Even if one can avoid the mercury salts initially proposed, the conditions are not trivial and not compatible with various functional groups. On the other hand, aldehydes are starting materials of choice, a lot of them being commercially available. Very few attention has been paid to other methods of preparation of acylsilanes from aldehydes. The one reported by Yoshida and co-workers[3] seems to have not been exploited much.[9] Based on a Peterson reaction, this method is interesting because the last step requires classical hydrolytic conditions (Scheme 1).

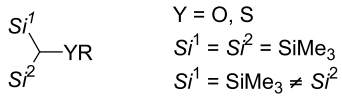
Being involved in some aspects of the chemistry of acylsilanes, especially functionalized ones, we were interested in a possible extension of this 'Peterson' approach. Our goals were to investigate the building blocks described in Scheme 2, as precursors of C-trialkylsilyl enol or thioenol ether type intermediates. Our interest for bis(acylsilanes) prompted us to also investigate a possible selectivity in the



Scheme 1.

Keywords: Organosilicon; Peterson olefination; Acylsilane; Enol ether; Thioenol ether.
* Corresponding authors. Tel.: +33 32 691 3234; fax: +33 32 691 3166 (C.P.); e-mail addresses: charles.portella@univ-reims.fr; jean-philippe.bouillon@univ-rouen.fr
† Present address: Sciences et Méthodes Séparatives-EA 3233, Université de Rouen. IRCOF. F-76821 Mont-Saint-Aignan Cedex, France.

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.10.082



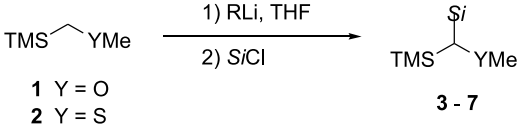
Scheme 2.

Peterson elimination step by differentiating the two trialkylsilyl groups.

2. Results and discussion

2.1. Synthesis of the bis(silylated) building blocks

The procedure and results are depicted in Scheme 3 and Table 1. The methoxy derivatives **3–5** have been prepared by applying to methoxymethyl(trimethyl)silane **1** the metallation–silylation sequence reported by Yoshida's group.[3] The reaction works well for bis(trimethylsilyl)-(methoxy)methane **3** as reported by Yoshida, but proved to be more difficult with (*tert*-butyl)dimethylsilyl (TBDMS) derivative **4**. Surprisingly, a better yield was obtained for the tris(isopropylsilyl) (TIPS) derivative **5**.



Scheme 3.

Table 1. Preparation of bis(silylated) building blocks **3–7**

Y	RLi	Si[a]	Product (%)
O	*s*-Bu	TMS	**3** (85)[3]
O	*s*-Bu	TBDMS	**4** (28)
O	*s*-Bu	TIPS	**5** (56)
S	*n*-Bu	TMS	**6** (65)[11]
S	*n*-Bu	TBDMS	**7** (62)

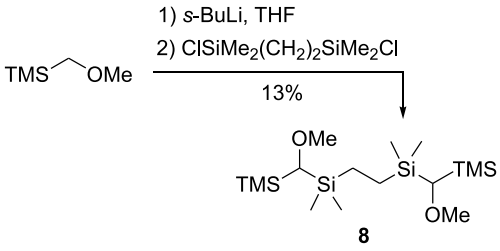
[a] TMS = trimethylsilyl, TBDMS = (*tert*-butyl)dimethylsilyl, TIPS = tris-(isopropylsilyl).

The bis(silylated) methylsulfanyl derivatives **6–7** were prepared from methylsulfanyl (trimethylsilyl)methane[10] according to a similar procedure, except that the presence of sulfur allows to use *n*-butyllithium (Scheme 3). As for oxygen series, only the bis(trimethylsilyl) derivative **6** had already been prepared, for different purposes.[11] In contrast to the oxygen analogue, the TBDMS derivative **7** has been obtained in fairly good yield (Table 1).

Just as variously substituted silyl groups are introduced to assess a possible selectivity in the Peterson reaction, the tetrasilyl reagent **8** has been synthesized, though in poor yield, in order to investigate a possible application in bis(acylsilane) synthesis (Scheme 4).

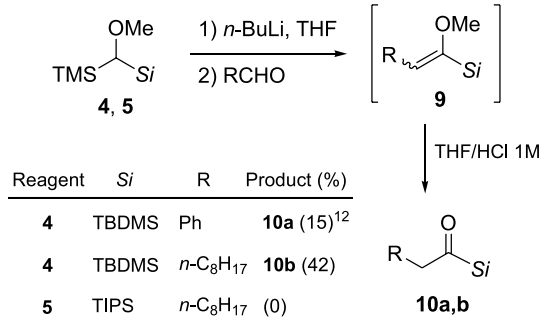
2.2. Peterson reaction using reagents 3–7

To the best of our knowledge, the chemoselectivity of the elimination step of the Peterson olefination process had never been investigated on bis(silylated) organometallic species. One could expect that the intramolecular formation



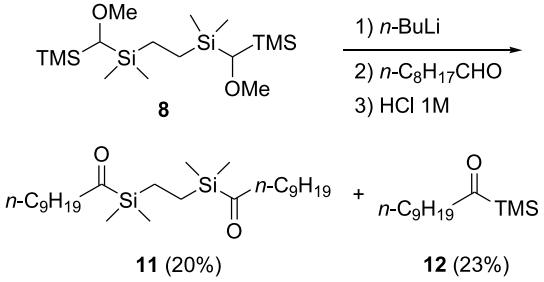
Scheme 4.

of the Si–O bond would be favoured with the less bulky TMS group. Indeed, when the reagent **4** is reacted with *n*-butyllithium and then with an aldehyde, a single acylsilane (**10a**[12] or **10b**) is isolated, albeit in low yield, after hydrolysis of the corresponding enol ether intermediate **9** (Scheme 5). No reaction was observed with the TIPS derivative **5** treated in the same conditions.



Scheme 5.

The steric hindrance around one silicon is a critical point since the reaction is no longer selective with the reagent **8**. In this case, the expected bis(acylsilane) **11** and decanoyltrimethylsilane **12**[13] are obtained in similar yields, owing to a too weak difference in the bulk around the silicon atoms (Scheme 6).



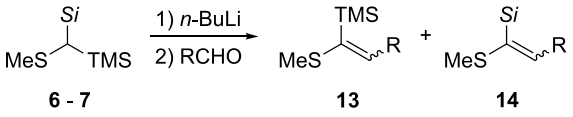
Scheme 6.

Except the bis(TMS) reagent **3**, which proved to be useful for acyl(trimethyl)silane synthesis,[3] the oxygenated reagents **4**, **5** and **8** are definitely not convenient owing to the low yields at the successive stages of the synthesis (Schemes 5 and 6). Hence we turned our attention to the methylsulfanyl analogues (Scheme 7, Table 2). Reagent **6**, which had never been considered in Peterson reaction, reacts effectively with benzaldehyde to give a high yield of the thioenol ether **13a**, as a 58/42 *E*/*Z* diastereomers mixture (NOE determination). The reaction was applied to a series

Table 2. Peterson reactions of reagents **6** and **7**

Si	R	Conversion (%)	Product (%)	**13/14**	Diast. ratio[a] (%)
TMS	Ph	100	**13a** (91)	—	58/42
TMS	Bn	64	**13b** (38)	—	67/33
TMS	$BnCH_2$	86	**13c** (52)	—	79/21
TMS	n-C_8H_{17}	100	**13d** (65)	—	52/48
TMS	Et_2CH	90	**13e** (67)	—	51/49
TMS	$EtCH{=}CH(CH_2)_4$	90	**13f** (68)	—	57/43
TBDMS	Ph	100	**13a**+**14g** (94)[b]	28/72[b]	[b]
TBDMS	n-C_8H_{17}	100	**13d**+**14h** (93)[b]	30/70[b]	[b]

[a] The nature of the diastereomers was determined only for **13a** (see text).
[b] Crude product; ratio **13/14** determined by ^1H NMR and GC; diaster. ratio undetermined.



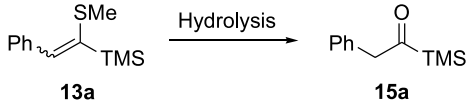
6 - 7 13 14

Scheme 7.

of aldehydes to give reasonable yields of the corresponding thioenol ethers **13b–13f**, sometimes accompanied by a minor amount of unreacted starting materials (Table 2). Owing to the loss of stereochemical information in the subsequent hydrolysis step, the nature of the stereomers was not further determined. In contrast to the methoxy derivative **4**, reaction in the same conditions of the *tert*-butyl substituted reagent **7** with aldehyde gives a mixture of the two thioenol ethers **13a**+**14g** or **13d**+**14h**. As expected, the major product results from elimination of the TMS group, but the selectivity is too weak to consider any application to bis(acylsilane) synthesis.

2.3. Conversion of thioenol ethers to acylsilanes

The starting purpose of this study was to find a route to acylsilane which does not need the strong oxidative conditions required for the removal of the dithioacetal functionality. We have thus studied the conditions of the final hydrolysis step. Hydrolysis of thioenol ether is not a trivial reaction, since either additives ($TiCl_4$, $CuSO_4$, HgO)[14] or very strong acids[15] are often necessary, even if some more classical conditions have been mentioned.[16] We have tried various conditions, among which only the one reported in Scheme 8 for **13a** as model compound gave satisfactory results. This C-silyl thioenol ether **13a** is cleanly but very slowly hydrolyzed using trifluoroacetic acid in a biphasic medium, or aqueous HCl in THF or acetone. Owing to the long reaction time, by-products resulting from cleavage of THF are formed and can make the purification process more complex. Hence refluxing aqueous HCl–acetone mixture was chosen as standard procedure and applied to compounds **13a–13f**, giving in fair yields the acylsilanes **15a–15f** (Table 3). It is noteworthy that these conditions are compatible with unsaturated compounds since **15f** is obtained in good yield, without isomerization.



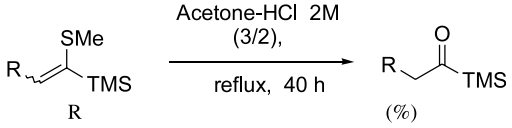
13a 15a

Conditions	% Yield
THF-HCl 3M (3/2), reflux, 40h	74[a]
Acetone-HCl 2M (3/2), reflux, 40h	75
Dichloroethane-H_2O (8/2) TFA (10 eq.), reflux, 40h	75

[a] By-product: $O[(CH_2)_4Cl)]_2$

Scheme 8.

Table 3. Hydrolysis of C-silyl thioenol ethers **13**



(%)

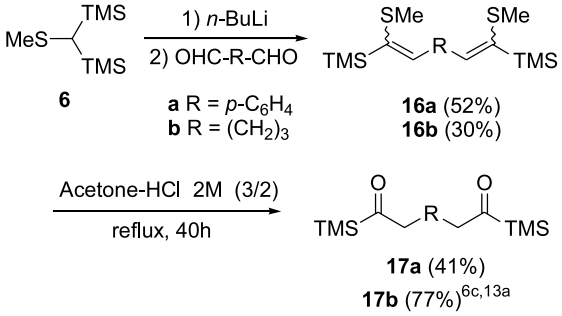
R	(%)
Ph	**15a** (75)[17]
Bn	**15b**[a] (74)[13c,17a]
$BnCH_2$	**15c** (60)[18]
n-C_8H_{17}	**15d** (54)[13]
Et_2CH	**15e** (67)
$EtCH{=}CH(CH_2)_4$	**15f** (76)

[a] Conv.=85% (total conv. for all other compounds).

The reaction sequence was finally applied to dialdehydes to prepare the bis(acylsilanes) **17** (Scheme 9). However, the overall transformation is less effective than previously reported synthesis.[6c]

3. Conclusion

A Peterson approach has been studied for the synthesis of acylsilanes via C-silyl enol–ether or thioenol ether. A good



6

a R = p-C_6H_4
b R = $(CH_2)_3$

16a (52%)
16b (30%)

17a (41%)
17b (77%)[6c,13a]

Scheme 9.

selectivity was observed with enol ethers bearing a TMS and a TBDMS group, which decreases significantly for less differentiated silyl groups, making this strategy unsuitable for the synthesis of bis(acylsilanes) with internal silicon. However, there is no practical interest to use such reagents owing to the difficulty to reach correct yields. In contrast, bis(trimethylsilyl)methylsulfanylmethane **6** proved to be a good reagent for the preparation of C-silyl thioenol ether **13**, which are converted to acylsilanes **15** by classical acid hydrolysis. The procedure is convenient, even if some yields should be optimized to make it more attractive.

4. Experimental

4.1. Materials and general methods

Melting points are uncorrected. FT-IR spectra were recorded on a MIDAC Corporation Spectrafile IR apparatus. ^{1}H, and ^{13}C spectra were recorded on a Bruker AC-250 or AC-500 spectrometer with $CDCl_3$ as the solvent. Tetramethylsilane ($\delta=0.00$ ppm) or $CHCl_3$ ($\delta=7.27$ ppm) were used as internal standards for ^{1}H, $CDCl_3$ ($\delta=77.23$ ppm) for ^{13}C NMR spectra. The abbreviations q and qu are used to design quartet and quintet, respectively, in the description of ^{1}H NMR spectra. GCMS spectra were obtained on Trace MS Thermoquest apparatus (70 eV) in electron impact mode. Elemental analyses were performed with a Perkin–Elmer CHN 2400 apparatus. High Resolution Mass Spectra (HRMS) were performed on Q-TOF Micromass in positive ESI mode (CV=30 V). Reactions were monitored by TLC (Merck F 254 silica gel). All anhydrous reactions were carried out under dry argon. THF was dried and distilled from sodium/benzophenone. Starting material **1**, **2** and aldehydes were distilled before use. TMSCl and TIPSCl were distilled on triphenylamine. Products were separated by chromatography on silica gel using a mixture of petroleum ether and ethyl acetate.

4.2. Preparation of compounds (4, 5 and 7) (Scheme 3, Table 1)

The methoxy derivatives **4** and **5** have been prepared by applying the metallation–silylation sequence[3] to methoxymethyl(trimethyl)silane **1**. The methylsulfanyl derivative **7** has been prepared according to the procedure reported by Seebach's group.[11]

4.2.1. Methoxy(*tert*-butyldimethylsilyl) trimethylsilyl methane (4). Yield: 28%; oil; ^{1}H NMR ($CDCl_3$, 250 MHz) δ −0.04 (s, 3H, Si*Me*$_2^t$Bu), 0.06 (s, 3H, Si*Me*$_2^t$Bu), 0.10 (s, 9H, $SiMe_3$), 0.94 (s, 9H, C(*CH*$_3$)$_3$), 2.75 (s, 1H, CH), 3.33 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ −6.6 (Si*Me*$_2^t$Bu), −4.9 (Si*Me*$_2^t$Bu), −0.7 ($SiMe_3$), 17.4 (*C*(CH$_3$)$_3$), 27.1 (C(*CH*$_3$)$_3$), 62.5 (OCH_3), 68.8 (CH); IR (film) 2955, 2929, 2857, 1471, 1249, 1087 cm^{-1}; GCMS (EI) *m/e* 232 (M^+), 73 (100).

4.2.2. Methoxy(triisopropylsilyl) trimethylsilyl methane (5). Yield: 56%; oil; ^{1}H NMR ($CDCl_3$, 250 MHz) d 0.15 (s, 9H, Si(CH$_3$)$_3$), 1.0–1.1 (m, 3H, 3×*CH*(CH$_3$)$_2$), 1.12 (d, $^{3}J=6.0$ Hz, 18H, 3×CH(*CH*$_3$)$_2$), 2.97 (s, 1H, CH), 3.34 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 62.9 MHz) d 0.0 (Si(CH$_3$)$_3$), 11.8 (*C*H(CH$_3$)$_2$), 19.2 (CH(*C*H$_3$)$_2$), 19.3 (CH(*C*H$_3$)$_2$), 62.9 (OCH_3), 68.3 (CH); IR (film) 2946, 2867, 2810, 1464, 1248, 1085, 845 cm^{-1}; GCMS (EI) *m/e* 274 (M^+), 115 (100).

4.2.3. Methylthio(*tert*-butyldimethylsilyl) trimethylsilyl methane (7). Yield: 62%; oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.04 (s, 3H, Si*Me*$_2^t$Bu), 0.07 (s, 3H, Si*Me*$_2$ ^{t}Bu), 0.14 (s, 9H, $SiMe_3$), 0.97 (s, 9H, C(CH$_3$)$_3$), 1.56 (s, 1H, CH), 2.12 (s, 3H, SCH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −5.2 (Si*Me*$_2^t$Bu), −2.8 (Si*Me*$_2^t$Bu), −0.1 ($SiMe_3$), 16.2 (CH or SCH_3), 18.2 (*C*(CH$_3$)$_3$), 21.0 (SCH_3 or CH), 27.4 (C(*CH*$_3$)$_3$); IR (film) 2955, 2928, 2856, 1470, 1250 cm^{-1}; GCMS (EI) *m/e* (%) 248 (M^+), 191 (100), 105, 75, 59.

4.3. Preparation of compound (8) (Scheme 4)

To a solution of (methoxymethyl)trimethylsilane **1** (1.37 g, 11.6 mmol) in dry THF (25 mL) cooled at −78 °C and under argon atmosphere, was added a 0.9 M ether solution of *s*-BuLi (13.5 mL, 12.2 mmol). The mixture was allowed to reach −25 °C then was stirred at this temperature for 40 min. After cooling at −78 °C, 1,2-bis(chlorodimethylsilyl)ethane (1.1 g, 5.3 mmol) was added. The cooling bath was removed and the resulting mixture was stirred for 2 h at room temperature. The crude was hydrolysed with brine (20 mL) then the aqueous phase was extracted with ether (3×25 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel using petroleum ether–EtOAc (98/2) to give the compound **8** (0.26 g, 13%).

4.3.1. Compound 8. Oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.03 (s, 6H, 2×SiCH$_3$), 0.05 (s, 6H, 2×SiCH$_3$), 0.07 (s, 18H, 2×SiMe$_3$), 0.51 (m, 4H, CH_2CH_2), 2.56 (s, 2H, 2×CH), 3.33 (s, 6H, 2×OCH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −4.0 (SiCH$_3$), −3.7 (SiCH$_3$), −1.3 ($SiMe_3$), 7.2 (CH_2), 63.1 (OCH_3), 70.3 (CH); IR (film) 2958, 2902, 1250, 1053, 839 cm^{-1}; GCMS (EI) *m/e* 379 (M^++1, 2), 73 (100).

4.4. Preparation of acylsilanes (10a,b) (Scheme 5)

The procedure described by J.-I. Yoshida and co-workers[3] was used to prepare acylsilanes **10a**,**b** starting from compounds **4** and **5**.

4.4.1. Decanoyl(*tert*-butyldimethyl)silane (10b). Yield: 42%; oil; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.18 (s, 6H, $SiMe_2$), 0.88 (t, $^{3}J=6.7$ Hz, 3H, CH_3), 0.93 (s, 9H, C(CH$_3$)$_3$), 1.2–1.5 (m, 12H, 6×CH_2), 1.50 (qu, $^{3}J=7.3$ Hz, 2H, *CH*$_2$CH$_2$CO), 2.59 (t, $^{3}J=7.3$ Hz, 2H, CH_2CO); Selected ^{13}C NMR data ($CDCl_3$, 62.9 MHz) δ −7.1 ($SiMe_2$), 14.0 (CH_3), 16.4 (*C*(CH$_3$)$_3$), 21.8 (CH_2), 22.6 (CH_2), 26.3 (C(*CH*$_3$)$_3$), 31.8 (CH_2), 50.2 (*C*H$_2$CO), 247.6 (CO); IR (film) 2930, 2860, 1630, 1460, 1250, 835 cm^{-1}; GCMS (EI) *m/e* 271 (M^++1, 1), 115 (100).

4.5. Preparation of bis(acylsilane) (11) (Scheme 6)

To a solution of compound **8** (0.19 g, 0.5 mmol) in THF (7 mL) was added *n*-butyllithium 2.5 M in hexane (0.4 mL, 1.0 mmol) at −78 °C. The mixture was warmed up to 0 °C and stirred at this temperature for 30 min. The solution was then recooled to −78 °C and nonylaldehyde (0.17 mL,

1.0 mmol) was added. The mixture was stirred at this temperature for 1 h and warmed up to room temperature for 2 h. Brine (10 mL) was added and the organic materials were extracted with ether (3×10 mL) and dried over $MgSO_4$. The solvents were removed under reduced pressure then the residue was dissolved in THF (7 mL). Hydrochloric acid (1 M, 1 mL) was added, and the mixture was stirred at room temperature overnight. The mixture was partitioned between saturated aqueous Na_2CO_3 and ether (10 mL). The organic layer was separated and the aqueous phase was extracted twice with ether (2×10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether–EtOAc (98/2)) to give the bis(acylsilane) **11** (45 mg, 20%) and the acylsilane **12**[13] (26 mg, 23%).

4.5.1. 1,2-Bis[2′-(decanoyldimethylsilyl)]ethane (11). Oil; ^{1}H NMR ($CDCl_3$, 250 MHz,) δ 0.19 (s, 12H, 2×$SiMe_2$), 0.58 (s, 4H, 2×$SiCH_2$), 0.88 (t, ^3J=6.5 Hz, 6H, 2×CH_3), 1.2–1.3 (m, 24H, 12×CH_2), 1.4–1.5 (m, 4H, 2×CH_2CH_2-CO), 2.57 (t, ^3J=7.1 Hz, 4H, 2×CH_2CO); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ −5.3 ($SiMe_2$), 5.6 ($SiCH_2$), 14.1 (CH_3), 22.0 (CH_2), 22.6 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 49.2 (CH_2CO), 248.2 (CO); IR (film) 2925, 1643, 1249, 837 cm^{-1}; GCMS (EI) *m/e* 454 (M^+), 387, 314, 189 (100).

4.6. General procedure for the Peterson olefination: preparation of compounds 13 and 14 (Scheme 7, Table 2)

To a solution of the (methylsulfanyl)bis(trialkylsilyl)-methane **6** or **7** (2.5 mmol) in 25 mL of THF was added *n*-butyllithium 2.5 M in hexane (1 mL, 2.5 mmol, 1.0 equiv) at −78 °C. The mixture was warmed up to 0 °C and stirred at this temperature for 1 h. The light yellow solution was cooled to −78 °C and the aldehyde (2.5 mmol, 1.0 equiv) was added. The mixture was stirred at this temperature for 1 h and warmed up to room temperature for 2 h. Brine (20 mL) was added and the organic materials were extracted with ether (3×10 mL) and dried over $MgSO_4$. The solvents were removed under reduced pressure, and the residue was purified by flash silica gel chromatography using petroleum ether (PE) to give the corresponding thioenol ether **13** and **14** (Scheme 7, Tables 2 and 4).

4.6.1. Selected data for compound 14g. First stereomer: ^{1}H NMR ($CDCl_3$) δ 0.340 (s, 3H, $SiMe^t_2Bu$), 0.344 (s, 3H, $SiMe^t_2Bu$), 1.10 (s, 9H, $SiMe^t_2Bu$), 2.13 (d, ^5J=0.8 Hz, 3H, SMe), 7.08 (br s, 1H, =CH), 7.3–7.7 (m, 5H, Ph); GCMS (EI) *m/e* (%) 264 (M^+), 207, 105 (100), 73. Second stereomer: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 6H, $SiMe^t_2Bu$), 1.05 (s, 9H, $SiMe^t_2Bu$), 2.47 (s, 3H, SMe), 7.03 (s, 1H, =CH), 7.2–7.8 (m, 5H, Ph); GCMS (EI) *m/e* (%) 264 (M^+), 207, 105 (100), 73.

4.6.2. Selected data for compound 14h. First stereomer: selected ^{1}H NMR ($CDCl_3$) δ 6.26 (t, ^3J=7.6 Hz, 1H, =CH); GCMS (EI) *m/e* (%) 300 (M^+), 243, 195, 105 (100), 73. Second stereomer: selected ^{1}H NMR ($CDCl_3$) δ 5.74 (t, ^3J=7.6 Hz, 1H, =CH); GCMS (EI) *m/e* (%) 300 (M^+), 243, 195, 105 (100), 73.

4.7. Preparation of acylsilanes 15

4.7.1. Hydrolysis with THF–hydrochloric acid 3 M (3/2) (Scheme 8). The compound **15a** was obtained in 74% yield using the same procedure described for the preparation of bis(acylsilane) **11** except that 3 M hydrochloric acid was employed.

4.7.2. Hydrolysis with dichloroethane–H_2O (8/2), trifluoroacetic acid (10 equiv) (Scheme 8). To a solution of thioenol ether **13a** (0.11 g, 0.5 mmol) in a mixture of 1,2-dichloroethane–H_2O (8/2) was added trifluoroacetic acid (0.39 mL, 5 mmol). The mixture was heated under reflux and the reaction was followed by TLC until the disappearance of the starting compound (40 h). Then the reaction mixture was neutralized using saturated aqueous solution of $NaHCO_3$ (3 mL). The organic materials were extracted with ethyl acetate (3×5 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash silica gel chromatography using PE–EtOAc (97/3) as eluent to give the acylsilane **15a** (72 mg, 75%).

4.7.3. Hydrolysis with acetone–hydrochloric acid 2 M 3:2 (Schemes 8 and 9, Table 3). To a solution of thioenol ether **13** (0.5 mmol, 1.0 equiv) in acetone (3 mL) was added a solution of 2 M hydrochloric acid (2 mL). The mixture was heated under reflux and the reaction was followed by TLC until the disappearance of the starting compound (40 h). Then the reaction mixture was neutralized using saturated aqueous solution of $NaHCO_3$ (3 mL). The organic materials were extracted with ethyl acetate (3×5 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash silica gel chromatography using a mixture of petroleum ether/EtOAc as eluent to give the acylsilanes **15** (Schemes 8 and 9, Table 3).

4.7.4. Compound 15e. Yield: 67%; oil; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H, $SiMe_3$), 0.82 (t, ^3J=7.3 Hz, 6H, 2×CH_3), 1.1–1.3 (m, 4H, 2×CH_2), 1.89 (m, 1H, CH), 2.51 (d, ^3J=6.6 Hz, 2H, CH_2CO); ^{13}C NMR ($CDCl_3$) δ −3.1 ($SiMe_3$), 11.0 (2×CH_3), 26.1 (2×CH_2), 34.9 (CH), 52.8 (CH_2CO), 249.3 (C=O); IR (film) 2962, 2930, 2876, 1642, 1250 cm^{-1}; GCMS (EI) *m/e* (%) 186 (M^+), 171, 101, 75, 73 (100). Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.25; H, 11.55.

4.7.5. Compound 15f. Yield: 76%; oil; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9H, $SiMe_3$), 0.93 (t, ^3J=7.5 Hz, 3H, CH_3CH_2), 1.2–1.4 (m, 4H, $CH_2CH_2CH_2CH$), 1.50 (tt, ^3J=^3J=7.3 Hz, 2H, CH_2CH_2CO), 1.9–2.0 (m, 4H, 2×CH_2CH=), 2.57 (t, ^3J=7.3 Hz, 2H, CH_2CO), 5.3–5.4 (m, 2H, 2×CH=); ^{13}C NMR ($CDCl_3$) δ −3.2 ($SiMe_3$), 14.3 (CH_3), 20.5 (CH_2CH=), 22.0 (CH_2CH_2CO), 26.9 (CH_2CH=), 28.9 ($CH_2CH_2CH_2$-CO), 29.5 (CH_2CH_2CH=), 48.4 (CH_2CO), 129.0 (CH=), 131.7 (CH=), 248.6 (C=O); IR (film) 2961, 2933, 1644, 1462, 1249 cm^{-1}; GCMS (EI) *m/e* (%) 226 (M^+), 197, 183, 101, 75, 73 (100); HRMS (ESI) calcd for $C_{13}H_{26}ONaSi$ *m/e*=249.1651; found 249.1650.

Table 4. Spectral data of compounds **13a–13f**

Compound	IR (cm^{-1})[a]	GC–MS[a] *m/z*	^1H NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ, *J* (Hz)
13a[b]	2955, 1601, 1489, 1248	222 (M^+), 207, 134, 105, 73 (100)	0.05 (s, 9H, $SiMe_3$), 2.35 (d, ^5J=0.6 Hz, 3H, SMe), 6.81 (br s, 1H, =CH), 7.2–7.6 (m, 5H, Ph)	0.1 ($SiMe_3$), 15.0 (SMe), 126.6 (CH), 127.8 (2×CH), 128.5 (2×CH), 132.1 (CH), 137.6 (C_q), 140.1 (C_q)
13a[c]			0.28 (s, 9H, $SiMe_3$), 2.19 (s, 3H, SMe), 6.93 (s, 1H, =CH), 7.2–7.6 (m, 5H, Ph)	−0.5 ($SiMe_3$), 17.8 (SMe), 127.2 (CH), 127.9 (2×CH), 129.3 (2×CH), 138.7 (CH), 139.7 (C_q), 140.4 (C_q)
13b[b]	2955, 1602, 1581, 1494, 1248	236 (M^+), 221, 115, 105, 73 (100)	0.30 (s, 9H, $SiMe_3$), 2.36 (s, 3H, SMe), 3.86 (d, ^3J=6.7 Hz, 2H, CH_2), 6.41 (t, ^3J=6.7 Hz, 1H, =CH), 7.3–7.5 (m, 5H, Ph)	−0.7 ($SiMe_3$), 18.0 (SMe), 36.7 (CH_2), 126.0 (CH), 128.46 (2×CH), 128.53 (2×CH), 138.0 (C_q), 140.3 (C_q), 144.6 (CH)
13b[c]			0.41 (s, 9H, $SiMe_3$), 2.29 (s, 3H, SMe), 3.70 (d, ^3J=7.6 Hz, 2H, CH_2), 5.83 (t, ^3J=7.6 Hz, 1H, =CH), 7.3–7.5 (m, 5H, Ph)	0.0 ($SiMe_3$), 14.6 (SMe), 38.2 (CH_2), 126.1 (CH), 128.3 (2×CH), 130.9 (CH), 135.7 (C_q), 140.8 (C_q)[d]
13c[b]	3027, 2955, 1587, 1496, 1453, 1248	250 (M^+), 159 (100), 111, 105, 73	0.16 (s, 9H, $SiMe_3$), 2.15 (s, 3H, SMe), 2.6–2.8 (m, 4H, 2×CH_2), 6.18 (t, ^3J=6.0 Hz, 1H, =CH), 7.2–7.3 (m, 5H, Ph)	−0.8 ($SiMe_3$), 17.9 (SMe), 32.2 (CH_2), 35.1 (CH_2), 125.76 (CH), 128.2 (2×CH), 128.4 (2×CH), 137.7 (C_q), 141.6 (C_q) 145.6 (CH)
13c[c]			0.22 (s, 9H, $SiMe_3$), 2.19 (d, ^5J=2.0 Hz, 3H, SMe), 2.6–2.8 (m, 4H, 2×CH_2), 5.66 (t, ^3J=7.3 Hz, 1H, =CH), 7.2–7.3 (m, 5H, Ph)	−0.2 ($SiMe_3$), 14.5 (SMe), 34.4 (CH_2), 36.6 (CH_2), 125.84 (CH), 128.3 (2×CH), 132.2 (CH), 134.4 (C_q), 141.5 (C_q)[d]
13d[b]	2924, 1587, 1465, 1248	258 (M^+), 243, 159, 105, 73 (100)	0.23 (s, 9H, $SiMe_3$), 0.89 (t, ^3J=6.6 Hz, 3H, =CH_3), 1.1–1.5 (m, 14H), 2.19 (s, 3H, SMe), 6.15 (t, ^3J=6.7 Hz, 1H, =CH)	−0.1 ($SiMe_3$), 14.1 (CH_3), 18.1 (CH_3), 22.7 (CH_2), 28.8–29.6 (4×CH_2), 30.5 (CH_2), 31.9 (CH_2), 136.6 (C_q), 147.3 (CH)
13d[c]			0.17 (s, 9H, $SiMe_3$), 0.89 (t, ^3J=6.2 Hz, 3H, CH_3), 1.1–1.5 (m, 14H), 2.20 (s, 3H, SMe), 5.64 (t, ^3J=7.4 Hz, 1H, =CH)	−0.8 ($SiMe_3$), 14.7 (CH_3), 20.3 (CH_3), 30.4 (CH_2), 32.5 (CH_2), 133.2 (C_q), 134.1 (CH)[d]
13e[b]	2960, 1548, 1460, 1248	216 (M^+), 187, 105, 73 (100)	0.19 (s, 9H, $SiMe_3$), 0.87 (t, ^3J=7.3 Hz, 6H, 2×CH_3), 1.1–1.3 (m, 4H, 2×CH_2), 2.21 (s, 3H, SMe), 2.7–2.9 (m, 1H), 5.88 (d, ^3J=9.3 Hz, 1H, =CH)	0.40 ($SiMe_3$), 11.8 (2×CH_3), 15.2 (SMe), 27.5 (2×CH_2), 44.6 (CH), 136.7 (C_q), 152.6 (CH)
13e[c]			0.25 (s, 9H, $SiMe_3$), 0.85 (t, ^3J=7.3 Hz, 6H, 2×CH_3), 1.4–1.6 (m, 4H, 2×CH_2), 2.19 (s, 3H, SMe), 2.7–2.9 (m, 1H); 5.43 (d, ^3J=10.6 Hz, 1H, =CH)	−0.44 ($SiMe_3$), 11.6 (2×CH_3), 18.4 (SMe), 28.1 (2×CH_2), 42.9 (CH), 140.3 (CH)[d]
13f[b]	2961, 1587, 1460, 1248	256 (M^+), 241, 105, 73 (100)	0.16 (s, 9H, $SiMe_3$), 0.95 (t, ^3J=7.5 Hz, 3H, CH_3), 1.4–1.6 (m, 4H, 2×CH_2), 2.0–2.1 (m, 4H, 2×CH_2), 2.22 (s, 3H, SMe), 2.37 (q, ^3J=6.9 Hz, 2H, CH_2), 5.3–5.4 (m, 2H, 2×=CH), 6.14 (t, ^3J=6.9 Hz, 1H, =CH)	−0.8 ($SiMe_3$), 14.4 (CH_3), 18.1 (CH_3), 20.5 (CH_2), 26.9 (CH_2), 28.6 (CH_2), 29.5 (CH_2), 30.3 (CH_2), 129.0 (CH), 131.72 (CH), 136.8 (C_q), 147.1 (CH)
13f[c]			0.23 (s, 9H, $SiMe_3$), 0.95 (t, ^3J=7.5 Hz, 3H, CH_3), 1.4–1.6 (m, 4H, 2×CH_2), 2.0–2.1 (m, 4H, 2×CH_2), 2.1–2.3 (m, 2H, CH_2), 2.22 (s, 3H, SMe), 5.3–5.4 (m, 2H, 2×=CH), 5.60 (t, ^3J=7.7 Hz, 1H, =CH)	−0.1 ($SiMe_3$), 14.7 (CH_3), 18.1 (CH_3), 20.5 (CH_2), 27.0 (CH_2), 29.4 (CH_2), 29.9 (CH_2), 32.4 (CH_2), 128.9 (CH), 131.75 (CH), 133.9 (CH), 143.1 (C_q)

[a] IR and GC–MS spectra on the mixture of stereomers.
[b] Major isomer.
[c] Minor isomer.
[d] Selected data.

4.8. Preparation of compounds (16a,b) and bis(acylsilanes) (17a,b) (Scheme 9)

The compounds **16a**,**b** were obtained in 52 and 30% yields respectively using the general procedure for the Peterson olefination (Scheme 7) except that 2 equiv of **6**, 2 equiv of *n*-BuLi and 1 equiv of bis(aldehyde) were used. The compounds **17a**,**b** were obtained in 41 and 77% yields respectively using the hydrolysis with acetone–hydrochloric acid 2 M (3:2) (Schemes 8 and 9).

4.8.1. Compound 16a. Yield: 52%; Mixture of 3 stereomers (54/21/25, determined by GC); oil; ^1H NMR ($CDCl_3$) δ 0.10 (s, $SiMe_3$), 0.29 (s, $SiMe_3$), 2.23 (s, SMe), 2.36 (s, SMe), 6.79 (s, =CH), 6.91 (s, =CH), 7.13 (s, Ar sym.), 7.19 (d, ^3J=8.0 Hz, Ar unsym.), 7.61 (d, ^3J=8.0 Hz, Ar unsym.), 7.66 (s, Ar sym.); ^{13}C NMR ($CDCl_3$) δ −0.52 ($SiMe_3$), −0.47 ($SiMe_3$), 0.28 ($SiMe_3$), 0.34 ($SiMe_3$), 15.2 (2× SMe), 17.8 (SMe), 17.9 (SMe), 128.1 (CH Ar), 128.2 (CH Ar), 129.0 (CH Ar), 129.1 (CH Ar), 131.97 (=CH), 132.04 (=CH), 136.0 (C_q), 136.5 (C_q), 138.3 (=CH), 138.4 (=CH), 139.0 (C_q), 139.5 (C_q), 140.3 (C_q), 140.8 (C_q); IR (film) 2953, 2908, 1553, 1494, 1247 cm^{-1}; GCMS (EI) *m/e* (%) 366 (M^+), 215, 207, 105, 73 (100).

4.8.2. Compound 16b. Yield: 30%; Mixture of 3 stereomers (49/20/31 determined by GC); oil; ^1H NMR ($CDCl_3$) δ 0.17 (s, $SiMe_3$), 0.23 (s, $SiMe_3$), 1.4–1.6 (m, $CH_2CH_2CH_2$), 2.19 (s, SMe), 2.24 (q, ^3J=7.4 Hz, =CHCH_2), 2.41 (q, ^3J=7.4 Hz, =CHCH_2), 5.61 (t, ^3J=7.2 Hz, =CH), 5.64 (t, ^3J=7.2 Hz, =CH), 6.14 (t, ^3J=6.4 Hz, =CH), 6.17 (t, ^3J=6.4 Hz, =CH); Selected ^{13}C NMR data ($CDCl_3$) δ −0.7 ($SiMe_3$), −0.0 ($SiMe_3$), 14.6 (SMe), 14.7 (SMe), 18.0 (SMe), 18.1 (SMe), 28.4 (CH_2), 29.6 (CH_2), 30.0 (CH_2), 30.2 (CH_2), 32.1 (CH_2), 32.2 (CH_2), 133.1 (=CH), 133.3 (=CH), 137.3 (C_q), 146.2 (=CH), 146.5 (=CH); IR (film) 2955, 1640, 1587, 1438, 1248 cm^{-1}; GCMS (EI) *m/e* (%) 332 (M^+), 317, 197, 181, 105, 73 (100).

4.8.3. Compound 17a. Yield: 41%; oil; ^1H NMR ($CDCl_3$) δ 0.10 (s, 18H, 2×$SiMe_3$), 3.82 (s, 4H, 2×CH_2), 7.07 (s, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ −2.8 ($SiMe_3$), 55.1 (CH_2),

130.1 (CH Ar), 131.6 (C_q Ar), 244.1 (C=O); IR (film) 3026, 2957, 1638, 1510, 1421, 1249 cm^{-1}, GCMS (EI) *m/e* (%) 306 (M^+), 278, 205, 175, 147, 75, 73 (100); HRMS (ESI) calcd for $C_{16}H_{26}NaO_2Si_2$ *m/e*=329.1369; found 329.1356.

Acknowledgements

The authors are grateful to the 'Région Champagne Ardenne' for a doctoral fellowship (CH). They thank Sylvie Lanthony, Henri Baillia and Dominique Harakat for their effective contribution in analytical work.

References and notes

1. (a) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647–660. (b) Bulman-Page, P. C.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147–195. (c) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proc.* **1992**, *24*, 555–582. (d) Patrocinio, A. F.; Moran, P. J. S. *J. Brazilian Chem. Soc.* **2001**, *12*, 7–31.
2. (a) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434–436. (b) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431–434.
3. Yoshida, J.; Matsunaga, S.; Ishichi, Y.; Isoe, S. *J. Org. Chem.* **1991**, *56*, 1307–1309.
4. Dunogues, J.; Ekonya, A.; Calas, R.; Picard, J. P.; Duffaut, N. *J. Organomet. Chem.* **1974**, *66*, C39–C42.
5. (a) Dunogues, J.; Bolourtchian, M.; Calas, R.; Duffaut, N.; Picard, J. P. *J. Organomet. Chem.* **1972**, *43*, 139–155. (b) Kang, J.; Lee, J. H.; Kim, K. S.; Jeong, J. U.; Pyun, C. *Tetrahedron Lett.* **1987**, *28*, 3261–3262. (c) Capperucci, A.; Degl'Innocenti, A.; Faggi, C.; Ricci, A. *J. Org. Chem.* **1988**, *53*, 3612–3614. (d) Bonini, B. F.; Comes-Franchini, M.; Mazzanti, G.; Passamonti, U.; Ricci, A.; Zani, P. *Synthesis* **1995**, 92–96. (e) Bonini, B. F.; Comes-Franchini, M.; Mazzanti, G.; Ricci, A.; Sala, M. *J. Org. Chem.* **1996**, *61*, 7242–7243. (f) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *Synlett* **1999**, 486–488. (g) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A.; Varchi, G. *Tetrahedron Lett.* **1999**, *40*, 6473–6476.
6. (a) Chuang, T.-H.; Fang, J.-M.; Jiaang, W.-T.; Tsai, Y.-M. *J. Org. Chem.* **1996**, *61*, 1794–1804. (b) Plantier-Royon, R.; Portella, C. *Tetrahedron Lett.* **1996**, *37*, 6113–6114. (c) Bouillon, J.-P.; Portella, C. *Eur. J. Org. Chem.* **1999**, 1571–1580. (d) Saleur, D.; Bouillon, J.-P.; Portella, C. *Tetrahedron Lett.* **2000**, *41*, 321–324.
7. (a) Plantier-Royon, R.; Portella, C. *Synlett* **1994**, 527–529. (b) Bouillon, J.-P.; Portella, C. *Tetrahedron Lett.* **1997**, *38*, 6595–6598.
8. Gérard, S.; Plantier-Royon, R.; Nuzillard, J.-M.; Portella, C. *Tetrahedron Lett.* **2000**, *41*, 9791–9795.
9. Chanteau, F.; Plantier-Royon, R.; Portella, C. *Synlett* **2004**, 512–516.
10. Peterson, D. J. *J. Org. Chem.* **1967**, *32*, 1717–1720.
11. Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852–866.
12. (a) Bartoli, G.; Bosco, M.; Dalpozzo, R.; Marcantoni, E. *Tetrahedron Lett.* **1999**, *31*, 6935–6936. (b) Murakami, M.; Amii, H.; Takizawa, N.; Ito, Y. *Organometallics* **1993**, *12*, 4223–4227.
13. (a) Mandai, T.; Yamaguchi, M.; Nakayama, Y.; Otera, J.; Kawada, M. *Tetrahedron Lett.* **1985**, *26*, 2675–2676. (b) Nakada, M.; Nakamura, S.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1991**, *32*, 4929–4932. (c) Suda, K.; Watanabe, J.; Takanami, T. *Tetrahedron Lett.* **1992**, *33*, 1355–1356.
14. (a) Mukaiyama, T.; Kamio, K.; Kobayashi, S.; Takei, H. *Bull. Chem. Soc. Jpn* **1972**, *45*, 3723–3729. (b) Ogura, K.; Iihama, T.; Kiuchi, S.; Kajiki, T.; Koshikawa, O.; Takahashi, K.; Iida, H. *J. Org. Chem.* **1986**, *51*, 700–705. (c) Dieter, R. K.; Fishpaugh, J. R. *J. Org. Chem.* **1988**, *53*, 2031–2046.
15. Satoh, T.; Taguchi, D.; Suzuki, C.; Fujisawa, S. *Tetrahedron* **2001**, *57*, 493–500.
16. Yamamoto, I.; Tanaka, S.; Fujimoto, T.; Ohta, K. *J. Org. Chem.* **1989**, *54*, 747–750.
17. (a) Aoyama, T.; Shioiri, T. *Tetrahedron Lett.* **1986**, *27*, 2005–2006. (b) Patrocinio, A. F.; Moran, P. J. S. *J. Organomet. Chem.* **2000**, *603*, 220–224.
18. (a) Yoshida, J.; Itoh, M.; Matsunaga, S.; Isoe, S. *J. Org. Chem.* **1992**, *57*, 4877–4882. (b) Bhat, N. G.; Tamm, A.; Gorena, A. *Synlett* **2004**, 297–298.