Tetrahedron 65 (2009) 5527–5534

Contents lists available at ScienceDirect

Tetrahedron

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

Towards bis(acylsilanes) and cyclic unsaturated acylsilanes via metathesis: an exploratory study

Catherine Hammaecher [a], Jean-Philippe Bouillon [b], Charles Portella [a,*]

[a] Université de Reims Champagne-Ardenne, Institut de Chimie Moléculaire de Reims, CNRS UMR 6229, UFR Sciences Exactes et Naturelles, BP 1039, 51687 Reims Cedex 2, France
[b] Université de Rouen, Laboratoire Sciences et Méthodes Séparatives, EA 3233, UFR Sciences et Techniques, IRCOF, F-76821 Mont-Saint-Aignan cedex, France

ARTICLE INFO

Article history:
Received 15 December 2008
Received in revised form 5 February 2009
Accepted 6 February 2009
Available online 14 April 2009

ABSTRACT

New acyl(allyl)- and acyl(vinyl)silanes have been synthesized in order to explore cross metathesis or ring-closing metathesis as a new way towards bis(acyl)silanes or unsaturated cyclic acylsilanes, respectively. Metathesis from acylsilanes did not work but their precursors, in particular in benzotriazol series, proved to be good candidates. Two new benzotriazolyl substituted silacyclic compounds (tetrahydrosiline and dihydrosilol) were thus prepared by RCM. Their conversion into the corresponding acylsilane failed. In contrast, the preparation of a bis(acylsilane) bearing the silicon atoms in internal position was achieved by a two-step sequence: cross metathesis of an allyl(dimethylsilyl) benzotriazolyl intermediate–hydrolysis.

1. Introduction

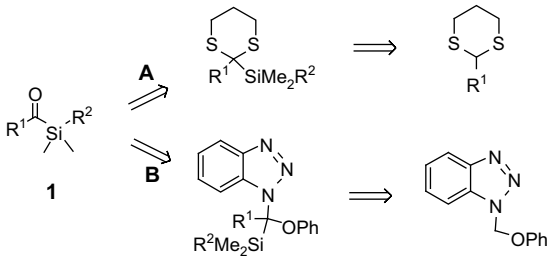
Acylsilanes are versatile intermediates in organic synthesis.[1] Bis(acylsilanes) (BAS) have been less investigated, in spite of interesting properties; they indeed can undergo domino processes combining nucleophilic addition and Brook rearrangement. Two kinds of bis(acylsilanes) have to be considered: compounds with external trialkylsilyl or triarylsilyl groups (Type 1 BAS, Fig. 1) and those having internal silicon and external acyl moieties (Type 2 BAS, Fig. 1). If several studies on synthesis and/or reactivity of Type 1 BAS were reported in the literature,[2] those related to type 2 BAS (internal silyl groups) are rare, probably because the proposed methodologies for their preparation are not effective or may not be generalized.[3] We hypothesize that type 2 BAS could be prepared via a cross metathesis reaction between acyl(vinyl)- or acyl(allyl)silanes, which led us to undertake the synthesis of a series of allyl- and vinylacylsilanes. During these synthesis compounds bearing a second unsaturation on the acyl moiety were also prepared in order to explore their ring-closing metathesis. The difficulties encountered in trying to engage these compounds in metathesis prompted us to consider also their precursors in such reactions. This paper discloses the results of this exploratory study.

Figure 1.

2. Results and discussion

2.1. Preparation of starting acylsilanes

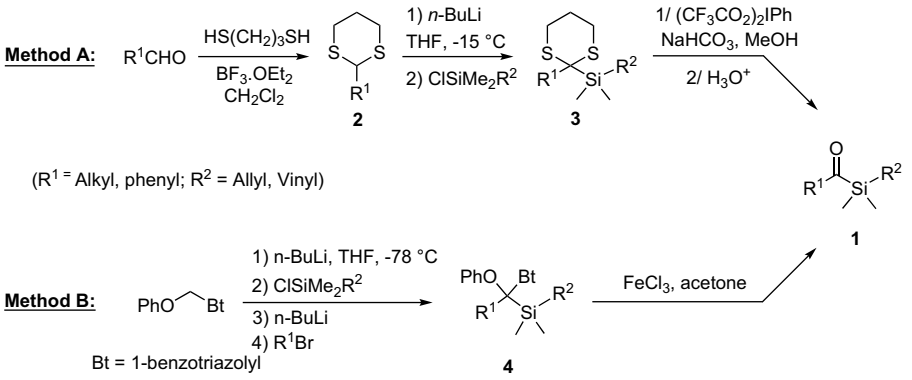
Surprisingly, before this study, acyl(allyl)silanes seemed to have been reported only by Tsai's group who studied intramolecular radical addition on the allyl unsaturation,[4] and by our group, which very recently reported their remarkable photochemical behaviour.[5] Similarly, only one paper was found mentioning an acyl(vinyl)silane obtained in very low yield.[6] We have prepared a series of acyl(allyl)- and acyl(vinyl)dimethylsilanes (Table 1) according to the retrosynthetic routes depicted in Scheme 1. A Brook–Corey type strategy (method A)[7] or a Katritzky type strategy (method B),[8] both modified in the last step, allowed us to obtain the desired



Scheme 1. Retrosynthesis of acyl(allyl)- and acyl(vinyl)silanes.

* Corresponding author. Tel.: +33326913234; fax: +33326913166.
E-mail address: charles.portella@univ-reims.fr (C. Portella).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.02.085



Scheme 2. Synthesis of acyl(allyl)- and acyl(vinyl)silanes **1a**–**1k**.

compounds. The reaction conditions and the results are depicted in Scheme 2 and Table 1.

Owing to the presence of the unsaturation, the conditions for releasing the carbonyl group in the last step are not trivial. In the dithiane series (Scheme 2: method A), after some unsuccessful attempts with reagents either ineffective or which gave complex mixtures, we have used bis(trifluoroacetoxy)iodobenzene. This reagent was shown to release aldehydes or ketones from their corresponding dithio(a)cetals including those bearing a double bond.[9] It was also reported to yield acyl(allyl)silanes from dithiane precursors.[4] When **3a** was treated under the reported conditions for direct obtention of the acylsilane, a low conversion and partial degradation of the product were observed. A previous conversion of the dithioketal moiety into a ketal function and aqueous acidic work-up allowed us to obtain the desired acylsilane in acceptable yield. These conditions were applied for all allyl- and vinyl-(acyl)silanes prepared through dithiane intermediates **3** (Table 1).

Similarly, after numerous attempts to hydrolyze the benzotriazole-substituted intermediates **4**, we decided to investigate ferric chloride (method B), a Lewis acid, which catalyzes effectively ketal hydrolysis.[10] The conversion of intermediates **4** into the corresponding acylsilanes **1** was eventually achieved using anhydrous ferric chloride in acetone (Table 1). The products were obtained in high yields except for but-3-enoyl derivatives **1g** and **1k**. The direct obtention of the final acylsilane via in situ hydrolysis by diluted hydrochloric acid according to Katritzky procedure[8] was achieved only for the allyl compound **1e** (67% overall yield).

2.2. Metathesis experiments

Having these acylsilanes in hand, we were interested to attempt self cross metathesis reaction (SCM) and, for compounds bearing a double bond on both acyl and silyl moieties, ring-closing metathesis (RCM). Metathesis reactions on such substrates are unprecedented, but are well documented for vinyl and allylsilanes. The later gave selectively a cross metathesis (CM)[11] or RCM[12] with olefinic double bonds. Metathesis of vinylsilanes was deeply studied and was shown to proceed via metallacarbene or transsilylation mechanisms depending on catalyst and silicon substituents.[13] The metathesis reactivity of vinylsilanes strongly depends on the substituents on silicon, and the selectivity CM versus SCM also depends on the alkene structure.[14] SCM giving bis(silyl)alkenes seems to occur effectively only with alkoxysubstituted vinylsilanes.[15]

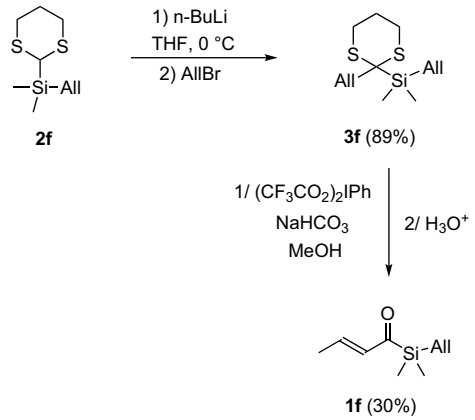
Grubbs second generation (Grubbs II) catalyst has been chosen to explore the RCM of bis(unsaturated) acylsilanes. The RCM of acylsilane **1g** was unsuccessful: the starting material was recovered whatever the reaction conditions (solvent, temperature), possibly because of the presence of acidic allylic hydrogens able to deactivate the catalyst. We reasoned that a cyclization on the intermediate **3f**, followed by hydrolytic removal of dithioketal could give the targeted acylsilane. Indeed, an analogous non-silylated 2-allyl-2-homoallyl-1,3-dithiane was reported to cyclize under Grubbs II catalysis.[16] Compound **3f** proved to react in the presence of Grubbs II catalyst (2×5%), but the reaction led to a compound, which exhibits spectral characteristics in agreement with the CM product **5** (Scheme 4). Unfortunately, the reaction was not reproducible and we were unable to have a correct elemental analysis of this product. Lowering the substrate concentration did not change the course of the reaction. These results may be due to some competitive oligomerization.

We then turn to the intermediates prepared following the benzotriazole route. The results of RCM of compounds **4** are summarized in Table 2. Good yields of tetrahydrosiline **6g** (from **4g**) and

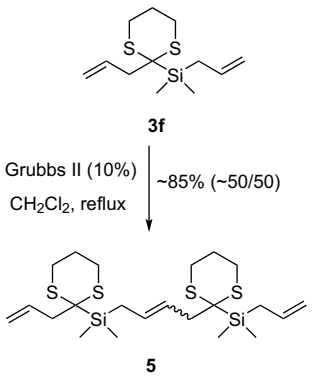
Table 1
Synthesis of acyl(allyl)- and acyl(vinyl)silanes **1a**–**1k**

R^1	R^2	Method	Intermediate **2** (%)	Intermediate **3** (%)	Intermediate **4** (%)	Acylsilane **1** (%)
Ph	All	**A**	**2a**[a]	**3a** (94)	—	**1a** (62)
c-C_6H_{11}	All	**A**	**2b** (80)	**3b** (72)	—	**1b** (88)
$PhCH_2CH_2$	All	**A**	**2c** (90)	**3c** (75)	—	**1c** (60)
$PhCH_2$	All	**A**	**2d** (93)	**3d** (70)	—	**1d** (75)
n-$C_{10}H_{21}$	All	**B**	—	—	**4e** (70)	**1e** (95)
All	All	**A**	**2f**[b]	**3f** (89)	—	**1f** (30)[c]
All	All	**B**	—	—	**4g** (75)	**1g** (25)
Pent-4-enyl	All	**B**	—	—	**4h** (58)	**1h** (80)
Ph	Vin	**A**	**2i**[a]	**3i** (89)	—	**1i** (60)
n-$C_{10}H_{21}$	Vin	**B**	—	—	**4j** (60)	**1j** (94)
All	Vin	**B**	—	—	**4k** (65)	**1k** (35)

[a] 2-Phenyl-1,3-dithiane is commercially available.
[b] From 2-[allyl(dimethyl)silyl]dithiane (yield: 78%).
[c] Isomerization to but-2-enoylsilane during hydrolysis (see Scheme 3).

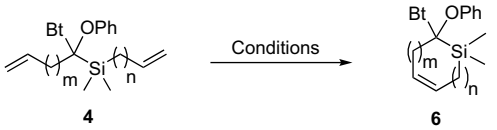


Scheme 3. Synthesis of but-2-enoyl(dimethyl)allylsilane **1f**.

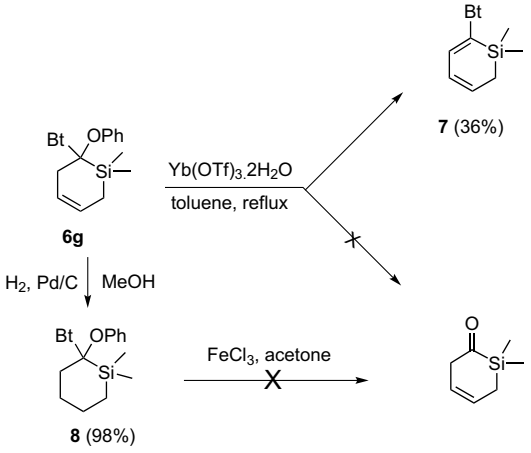


Scheme 4. CM of 2-allyl-2-allylsilyl-1,3-dithiane **3f**.

Table 2
RCM of benzotriazole derived intermediates **4**



Substrate	*m*	*n*	Conditions	Products (%)
4g	1	1	10% Grubbs II, CH_2Cl_2, reflux, 5 h	**6g** (82)
4h	3	1	15% Grubbs II, toluene, 80 °C, 24 or CH_2Cl_2, reflux, 5 h	—
4k	1	0	7×2% Grubbs II, toluene, 80 °C, 24 h	**6k** (80)



Scheme 5. Hydrolysis and hydrogenation of tetrahydrosiline **6g**.

dihydrosilol **6k** (from **4k**) were obtained using at least 10% of catalyst. The reaction failed for higher homologue **4h**. The geminal substitution by two sterically hindered and electro rich groups might account for the successful cyclization of intermediates **6** comparatively to the dithiane intermediate **3f**.

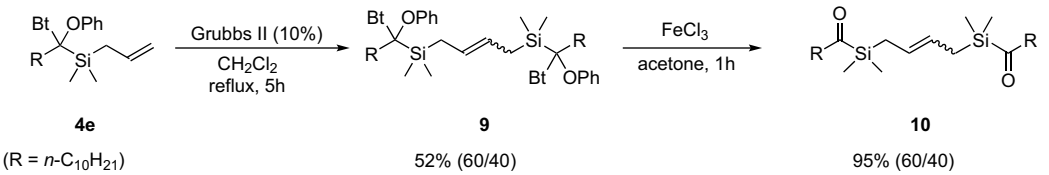
Compounds **6** were expected to be synthetic equivalents of the corresponding cyclic unsaturated acylsilanes so far unprecedented. Unfortunately, hydrolysis experiments either gave unexpected or degradation products. Various Bronsted or Lewis acid conditions were investigated. Using ytterbium triflate hydrate as Lewis acid, an elimination occurred leading to the benzotriazolyldihydrosiline **7** (36% yield) from a rather complex mixture (Scheme 5). In order to prevent a degradation possibly due to the presence of the double bond, hydrogenation of **6g** was carried out giving compound **8** in 98% yield. Treatment of **8** under the conditions optimized for the preparation of acylsilanes **1** from intermediates **4** (method B) seemed to convert cleanly **8** but we were unable to isolate any compound (Scheme 5).

After these somewhat disappointing results in RCM, we have explored the possibility to engage vinyl- and allyl(acyl)silanes **1** in SCM in order to have a new access to type 2 BAS. Grubbs first and second generation and Hoveyda–Grubbs catalysts were screened. No reaction was observed with Grubbs I and Hoveyda–Grubbs catalysts, whatever the vinylsilyl or allylsilyl nature of the substrate and the solvent/temperature conditions. In toluene at 80 °C a slow conversion of **1a** was observed but the bis(acylsilane) degrades as it is formed. CM reactions between allylsilyl and vinylsily**l** derivatives (**1a**+**1i** or **1e**+**1j**) were unsuccessful as well. As for RCM, we then attempted to perform the metathesis before the final hydrolysis. We did not observed any SCM or CM from each possible combination between dithiane intermediates **3a**–**3d** and/or **3i**. The experiments on benzotriazole derivatives were much more gratifying. The intermediate **4j** did not react under Grubbs II catalysis in dichloromethane, but in these conditions, the allyl analogue **4e** was totally converted within 5 h and the 1,6-disilahex-3-ene **9** was isolated in 52% yield as a (60:40) mixture of stereomers (Scheme 6). This result is interesting since homocoupling between allylsilanes, when observed, is a very minor reaction compared to cross coupling with various alkenes.[11] Finally, compound **9** was cleanly and quantitatively converted into the type 2 BAS **10** under treatment with Fe(III) chloride in acetone.

3. Conclusion

We have synthesized a variety of new acylsilanes **1** with an allyl or a vinyl group linked to silicon. The objective to prepare type 2 bis(acylsilanes) and unsaturated cyclic acylsilanes via cross metathesis or ring-closing metathesis proved to be difficult to achieve. Coupling from acyl(allyl)- or acyl(vinyl)silanes being difficult, we tried to overcome the problem by treatment of their precursors under metathesis conditions. Two new benzotriazole-substituted five and six membered silacyclic compounds **6** were thus prepared by RCM. They were submitted to hydrolytic treatment but the corresponding acylsilanes could not be obtained. In contrast, we achieved the preparation of a bis(acylsilane) of type 2, bearing the silicon atoms in internal position, by a two-step sequence: cross metathesis of an allyl(dimethylsilyl) benzotriazolyl intermediate–hydrolysis.

Owing to the exploratory character of this study, we have not insights on the scope and limitation of this route, which however seems to be valuable for acyclic compounds bearing a four carbon spacer between silicon atoms.



Scheme 6. Synthesis of bis(acylsilane) **10** via SCM of benzotriazole derivative **4e**.

4. Experimental

4.1. Materials and general methods

Melting points are uncorrected. FTIR 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 (δ=0.00 ppm) or $CHCl_3$ (δ=7.27 ppm) was used as internal standards for ^{1}H, $CDCl_3$ (δ=77.23 ppm) for ^{13}C NMR spectra. GC–MS spectra were obtained on Trace MS Thermoquest apparatus (70 eV) in electron impact mode (EI). High Resolution Mass Spectra (HRMS) were performed on Q-TOF Micromass in positive ESI mode (CV=30 V). Elemental analyses were performed with a Perkin–Elmer CHN 2400 apparatus. Reactions were monitored by TLC (Merck F_{254} silica gel). All anhydrous reactions were carried out under dry argon. THF and toluene were dried and distilled from sodium/benzophenone. Dichloromethane was dried and distilled over calcium hydride. All other commercially available starting materials were used without further purification. Products were usually separated by chromatography on silica gel using a mixture of petroleum ether (EP) and ethyl acetate.

2-Phenyl-1,3-dithiane **2a** is commercially available. The 2-alkyl-1,3-dithianes **2b–2d** used for the preparation of acylsilanes (method A) were prepared from the corresponding aldehydes and propane-1,3-dithiol in dichloromethane under $BF_3{\cdot}OEt_2$ catalysis. Their spectral data were consistent with those reported in literature: **2b** and **2c**,[17] **2d**.[18] 2-Allyl(dimethyl)silyl-1,3-dithiane[4] used in the preparation of **3f** and 1-phenoxymethylbenzotriazole[19] used in method B were prepared according to reported procedures.

4.2. General procedure for the preparation of 2-alkyl (or 2-phenyl)-2-allyldimethyl (or dimethylvinyl)silyl-1,3-dithianes 3 (Scheme 2: method A)

To a solution of 2-alkyl (or 2-phenyl)-1,3-dithianes **2a–2d** (4.95 mmol) in THF (50 mL), cooled at −15 °C, was added a solution of *n*-butyllithium (2.5 M in hexane, 1.98 mL, 1.0 equiv). The reaction mixture was stirred for 3 h and was allowed to reach room temperature then chloroallyldimethylsilane (or chlorovinyldimethylsilane) (4.95 mmol, 1.0 equiv) was added. The stirring was maintained (12–15 h) until the disappearance of the starting material (checked by TLC, eluent: EP/AcOEt 99:1). At the end of the reaction, aqueous saturated solution of $NaHCO_3$ (25 mL) was added and then the two phases were separated. The aqueous phase was extracted three times with ether (3×20 mL). The combined organic phases were dried over $MgSO_4$ and filtered off. After evaporation of solvent, the residue was purified by silica gel column chromatography (eluent: EP/AcOEt 99:1) affording the corresponding silyl-1,3-dithianes **3** (Table 1).

4.2.1. 2-(Allyldimethylsilyl)-2-phenyl-1,3-dithiane **3a**

Yield: 1.27 g (94%). Oil. TLC: R_f=0.34 (EP/AcOEt 99:1). IR (film): 2953, 2903, 1628, 1591, 1477, 1441, 1421, 1248 cm^{-1}. ^{1}H NMR: δ=−0.02 (s, 6H, $Si(CH_3)_2$), 1.56 (d, 2H, $SiCH_2$, J=7.8 Hz), 1.8–2.0 (m, 2H, $SCH_2CH_2CH_2S$), 2.35 (dt, 2H, SCH_2, J=14.2, 3.2 Hz), 2.76 (td, 2H, SCH_2, J=14.2, 2.4 Hz), 4.73 (dd, 2H, J_{trans}=13.9 Hz, J_{gem}=1.2 Hz), 5.5–5.8 (m, 1H), 7.21 (td, 1H$_{para}$, J=7.4, 1.2 Hz), 7.32 (dt, 2H$_{meta}$, J=7.4, 1.5 Hz), 7.84 (dd, 2H$_{ortho}$, J=7.4, 1.2 Hz). ^{13}C NMR: δ=−6.2 ($Si(CH_3)_2$), 20.1 ($SiCH_2$), 25.0 (3×CH_2, $SCH_2CH_2CH_2S$), 47.3 (C_q), 114.0 (CH_2=), 125.3 (CH Ph), 128.3 (2×CH Ph), 129.5 (2×CH Ph), 134.0 (CH=), 140.2 (C_q Ph). GC–MS: m/z (%) 294 (M^+), 253, 195, 163, 135, 121 (100), 99, 77. Anal. Calcd for $C_{15}H_{20}S_2Si$ (294.093): C 61.16, H 7.53; found C 61.04, H 7.84.

4.2.2. 2-(Allyldimethylsilyl)-2-cyclohexyl-1,3-dithiane **3b**

Yield: 0.76 g (72%). Oil. TLC: R_f=0.32 (EP/AcOEt 99:1). IR (film): 2926, 2851, 1628, 1449, 1246, 824 cm^{-1}. ^{1}H NMR: δ=0.22 (s, 6H, $Si(CH_3)_2$), 1.1–1.3 (m, 5H), 1.6–2.4 (m, 10H), 2.46 (dt, 2H, SCH_2, J=14.3, 3.6 Hz), 2.96 (dt, 2H, SCH_2, J=12.5, 3.0 Hz), 4.8–4.9 (m, 2H), 5.7–5.9 (m, 1H). ^{13}C NMR: δ=−3.0 ($Si(CH_3)_2$), 22.9 ($SiCH_2$), 23.8 (2×SCH_2), 24.4 ($SCH_2CH_2CH_2S$), 26.3 (CH_2), 27.4 (2×CH_2), 31.1 (2×CH_2), 43.8 (C_q), 45.6 (CH), 113.5 (CH_2=), 134.6 (CH=). GC–MS: m/z (%) 300 (M^+), 259, 217, 201 (100). Anal. Calcd for $C_{15}H_{28}S_2Si$ (300.590): C 59.93, H 9.39; found C 60.04, H 9.63.

4.2.3. 2-(Allyldimethylsilyl)-2-phenethyl-1,3-dithiane **3c**

Yield: 0.89 g (75%). Oil. TLC: R_f=0.33 (EP/AcOEt 99:1). IR (film): 3061, 2948, 1628, 1495, 1454, 1249, 699 cm^{-1}. ^{1}H NMR: δ=0.14 (s, 6H, $Si(CH_3)_2$), 1.74 (d, 2H, $SiCH_2$, J=8.1 Hz), 1.8–2.0 (m, 2H), 2.2–2.4 (m, 2H), 2.6–2.8 (m, 4H), 2.87 (t, 2H, J=12.8 Hz), 4.8–4.9 (m, 2H, CH_2=), 5.6–5.8 (m, 1H, CH=), 7.0–7.1 (m, 5H, Ph). ^{13}C NMR: δ=−4.9 ($Si(CH_3)_2$), 21.0 ($SiCH_2$), 23.0 (2×SCH_2), 24.7 ($SCH_2CH_2CH_2S$), 34.1 (CH_2), 38.3 (C_q), 39.5 (CH_2), 113.9 (CH_2=), 125.6 (CH Ph), 128.0 (2×CH Ph), 128.2 (2×CH Ph), 134.0 (CH=), 141.9 (C_q). GC–MS: m/z (%) 322 (M^+), 281, 223 (100), 191, 149, 115, 91. Anal. Calcd for $C_{17}H_{22}S_2Si$ (322.604): C 63.64, H 8.12, S 19.88; found C 63.29, H 8.10, S 20.22.

4.2.4. 2-(Allyldimethylsilyl)-2-benzyl-1,3-dithiane **3d**

Yield: 0.75 g (70%). Oil. TLC: R_f=0.31 (EP/AcOEt 99:1). IR (film): 3060, 2915, 1628, 1493, 1453, 1248 cm^{-1}. ^{1}H NMR: δ=0.10 (s, 6H, $Si(CH_3)_2$), 1.69 (d, 2H, $SiCH_2$, J=8.1 Hz), 1.8–2.0 (m, 2H, $SCH_2CH_2CH_2S$), 2.28 (dt, 2H, SCH_2, J=14.0, 3.8 Hz), 2.6–2.8 (m, 2H), 3.35 (s, 2H, CH_2Ph), 4.8–4.9 (m, 2H, CH_2=), 5.7–5.9 (m, 1H, CH=), 7.3–7.5 (m, 5H, Ph). ^{13}C NMR: δ=−5.6 ($Si(CH_3)_2$), 20.7 ($SiCH_2$), 24.0 ($SCH_2CH_2CH_2S$), 24.1 (2×SCH_2), 37.7 (C_q), 45.0 (CH_2), 113.8 (CH_2=), 126.7 (CH Ph), 127.8 (2×CH Ph), 131.0 (2×CH Ph), 134.5 (CH=), 138.6 (C_q). GC–MS: m/z (%) 308 (M^+), 267, 217 (100), 209, 134, 99, 91.

4.2.5. 2-(Allyldimethylsilyl)-2-(prop-2-enyl)-1,3-dithiane **3f**

The procedure was similar to the general one, but consisted in metallation (BuLi)-allylation (AllBr) of 2-allyl(dimethyl)silyl-1,3-dithiane **2f**.

Yield: 0.62 g (89%). Oil. TLC: R_f=0.25 (EP/AcOEt 99:1). IR (film): 3075, 2954, 1629, 1422, 1248, 1029, 915, 825 cm^{-1}. ^{1}H NMR: δ=0.16 (s, 6H, $Si(CH_3)_2$), 1.78 (d, 2H, $SiCH_2$, J=8.0 Hz), 1.7–2.2 (m, 2H, $SCH_2CH_2CH_2S$), 2.45 (dt, 2H, H_2C=CH–CH_2, J=10.2, 3.7 Hz), 3.0–3.2 (m, 4H, $SCH_2CH_2CH_2S$), 4.8–4.9 (m, 2H), 5.0–5.2 (m, 2H), 5.6–5.8 (m, 1H), 5.9–6.1 (m, 1H). ^{13}C NMR: δ=−5.1 ($Si(CH_3)_2$), 21.0 ($SiCH_2$), 23.2 (2×CH_2, $SCH_2CH_2CH_2S$), 24.9 ($SCH_2CH_2CH_2S$), 37.7 (C_q), 41.5 (CH_2), 113.8 ($SiCH_2CH$=CH_2), 116.6 (CH_2=), 134.3 ($SiCH_2CH$=CH_2), 136.4 (CH=). GC–MS: m/z (%) 258 (M^+), 217, 159 (100), 127, 121, 99, 59. Anal. Calcd for $C_{12}H_{22}S_2Si$ (258.518): C 55.75, H 8.58, S 24.81; found C 56.14, H 8.53, S 25.01.

4.2.6. 2-Dimethyl(vinyl)silyl-2-phenyl-1,3-dithiane **3i**

Yield: 1.10 g (89%). White solid. Mp 81 °C (recrystallized from EtOH). TLC: R_f=0.26 (EP/AcOEt 99:1). IR (film): 2945, 2897, 1590, 1477, 1417, 1244 cm^{-1}. ^{1}H NMR: δ=0.11 (s, 6H, $Si(CH_3)_2$), 1.9–2.2 (m, 2H, $SCH_2CH_2CH_2S$), 2.41 (dt, 2H, SCH_2, J=14.2, 3.4 Hz), 2.76 (td, 2H, SCH_2, J=14.2, 2.9 Hz), 5.66 (dd, 1H, J_{trans}=18.6 Hz, J_{gem}=5.3 Hz), 6.09 (dd, 1H, J_{cis}=14.7 Hz, J_{gem}=5.3 Hz), 6.13 (dd, 1H, J_{trans}=18.6 Hz, J_{cis}=5.3 Hz), 7.18 (tt, 1H$_{para}$, J=7.7, 1.2 Hz), 7.35 (td, 2H$_{meta}$, J=7.7, 1.2 Hz), 7.89 (dt, 2H$_{ortho}$, J=7.7, 1.2 Hz). ^{13}C NMR: δ=−5.9 ($Si(CH_3)_2$), 25.0 (3×CH_2, $SCH_2CH_2CH_2S$), 46.7 (C_q), 125.2 (CH Ph), 128.2 (2×CH Ph), 129.6 (2×CH Ph), 134.3 (CH_2=), 134.4 (CH=), 140.0 (C_q Ph). GC–MS: m/z (%) 280 (M^+), 195 (100), 163, 121, 85, 77. Anal. Calcd for $C_{14}H_{20}S_2Si$ (280.520): C 59.94, H 7.19; found C 59.61, H 7.39.

4.3. General procedure for the oxidative hydrolysis of 1,3-dithianyl derivatives 3 into allyl- (or vinyl-) (acyl)silanes 1 (Scheme 2: method A)

To a solution of 2-alkyl (or 2-phenyl)-1,3-dithianes **3** (0.67 mmol) in methanol (3 mL) were successively added $NaHCO_3$ (2.68 mmol,

4 equiv) and bis(trifluoroacetoxy)iodobenzene (1.34 mmol, 2 equiv). The mixture was stirred at room temperature until the disappearance of the starting material (45–75 min) then, it was poured into a mixture of 1 M hydrochloric acid (15 mL) and ether (15 mL). After the separation of the two phases, the aqueous layer was extracted three times with ether (3×5 mL). The combined organic phases were dried over $MgSO_4$, filtered off and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: EP/AcOEt 99:1) affording the corresponding acylsilanes **1** (Table 1).

4.3.1. Allyl(benzoyl)dimethylsilane ***1a***

Yield: 51 mg (62%). Yellow oil. TLC: R_f=0.60 (EP/AcOEt 99:1). IR (film): 2957, 2826, 1629, 1447, 1249 cm^{-1}. ^1H NMR: δ=0.18 (s, 6H, $Si(CH_3)_2$), 1.67 (d, 2H, $SiCH_2$, J=8.0 Hz), 4.6–4.8 (m, 2H, CH_2=), 5.5–5.6 (m, 1H, CH=), 7.1–7.9 (m, 5H, Ph). ^{13}C NMR: δ=−3.7 ($Si(CH_3)_2$), 22.1 ($SiCH_2$), 114.2 (CH_2=), 127.1 (2×CH Ph), 128.3 (2×CH Ph), 132.5 (CH Ph), 132.9 (CH=), 141.1 (C_q Ph), 234.0 (C=O). GC–MS: m/z (%) 204 (M^+), 203 (100), 189, 135, 130, 99, 77, 59. HRMS (ESI): calcd for $C_{12}H_{16}ONaSi$: m/z 227.0868, found: 227.0870.

4.3.2. Cyclohexyl(allyldimethylsilyl)ketone ***1b***

Yield: 111 mg (88%). Oil. R_f=0.18 (EP/AcOEt 99:1). IR (film): 2928, 1636, 1449, 1258, 822 cm^{-1}. ^1H NMR: δ=0.21 (s, 6H, $Si(CH_3)_2$), 1.1–1.3 (m, 6H), 1.6–1.8 (m, 6H), 2.68 (t, 1H, J=9.6 Hz), 4.8–4.9 (m, 2H, CH_2=), 5.6–5.8 (m, 1H, CH=). ^{13}C NMR: δ=−4.6 ($Si(CH_3)_2$), 21.6 ($SiCH_2$), 25.6 (2×CH_2), 26.0 (CH_2), 26.5 (2×CH_2), 55.7 (CH), 114.2 (CH_2=), 133.3 (CH=), 249.3 (C=O). GC–MS: m/z (%) 210 (M^+), 127, 99 (100), 83, 73.

4.3.3. Allyl(dimethyl)(3-phenylpropanoyl)silane ***1c***

Yield: 56 mg (60%). Oil. R_f=0.22 (EP/AcOEt 99:1). IR (film): 2955, 1643, 1497, 1250, 825, 698 cm^{-1}. ^1H NMR: δ=0.29 (s, 6H, $Si(CH_3)_2$), 1.78 (d, 2H, $SiCH_2$, J=8.0 Hz), 2.9–3.0 (m, 4H), 4.9–5.0 (m, 2H, CH_2=), 5.7–5.9 (m, 1H, CH=), 7.2–7.4 (m, 5H, Ph). ^{13}C NMR: δ=−5.3 ($Si(CH_3)_2$), 21.0 ($SiCH_2$), 28.0 (CH_2), 50.8 (CH_2), 114.4 (CH_2=), 125.9 (CH Ph), 128.3 (2×CH Ph), 128.5 (2×CH Ph), 133.0 (CH=), 141.5 (C_q), 245.7 (C=O). GC–MS: m/z (%) 232 (M^+), 141, 99, 91 (100), 75, 59. HRMS (ESI): calcd for $C_{14}H_{20}ONaSi$: m/z 255.1181, found: 255.1175.

4.3.4. Allyl(dimethyl)(2-phenylethanoyl)silane ***1d***

Yield: 82 mg (75%). Oil. R_f=0.18 (EP/AcOEt 99:1). IR (film): 2959, 1634, 1495, 1257, 838, 701 cm^{-1}. ^1H NMR: δ=0.12 (s, 6H, $Si(CH_3)_2$), 1.61 (dd, 2H, $SiCH_2$, J=8.0, 0.9 Hz), 3.85 (s, 2H, CH_2CO), 4.8–4.9 (m, 2H, CH_2=), 5.6–5.8 (m, 1H, CH=), 7.12 (d, 2H, 2×CH Ph, J=6.9 Hz), 7.2–7.3 (m, 3H Ph). ^{13}C NMR: δ=−4.7 ($Si(CH_3)_2$), 21.6 ($SiCH_2$), 56.2 (CH_2), 114.6 (CH_2=), 127.0 (CH Ph), 128.8 (2×CH Ph), 130.1 (2×CH Ph), 133.0 (C_q), 133.2 (CH=), 243.0 (C=O). GC–MS: m/z (%) 218 (M^+), 149, 121, 99 (100), 91, 59. HRMS (ESI): calcd for $C_{13}H_{18}ONaSi$: m/z 241.1025, found: 241.1023.

4.3.5. Allyl(but-2-enoyl)dimethylsilane ***1f***

Yield: 10 mg (30%). Yellow oil. R_f=0.20 (EP/AcOEt 98:2). IR (film): 2986, 1633, 1265, 738 cm^{-1}. ^1H NMR: δ=0.18 (s, 6H, $Si(CH_3)_2$), 1.67 (d, 2H, $SiCH_2$, J=8.0 Hz), 1.88 (dd, 3H, CH_3, J=6.8, 1.4 Hz), 4.7–4.9 (m, 2H), 5.5–5.8 (m, 1H), 6.07 (d, 1H, =CHCO, J_{trans}=15.9 Hz), 6.6–6.8 (m, 1H). ^{13}C NMR: δ=−3.7 ($Si(CH_3)_2$), 21.4 ($SiCH_2$), 21.5 (CH_3), 113.8 (CH_2=), 133.5 (CH=), 133.7 (CH=), 144.2 (CH=), 236.2 (C=O).

4.3.6. Benzoyl(dimethyl)vinylsilane ***1i***

Yield: 46 mg (60%). Yellow oil. R_f=0.20 (EP/AcOEt 99:1). IR (film): 3053, 2966, 1629, 1615, 1577, 1446, 1250 cm^{-1}. ^1H NMR: δ=0.44 (s, 6H, $Si(CH_3)_2$), 5.89 (dd, 1H,=C$H_a$$H_b$, J_{trans}=20.0 Hz, J_{gem}=3.5 Hz), 6.14 (dd, 1H, =$CH_a$$H_b$, J_{cis}=14.6 Hz, J_{gem}=3.5 Hz), 6.39 (dd, 1H, SiCH=, J_{trans}=20.0 Hz, J_{cis}=14.6 Hz), 7.4–8.1 (m, 5H Ph). ^{13}C NMR: δ=−3.8 ($Si(CH_3)_2$), 127.4 (2×CH Ph), 128.3 (2×CH Ph), 132.5 (CH Ph), 134.1 (CH_2=), 135.5 (CH=), 141.0 (C_q Ph), 233.2 (C=O). GC–MS: m/z (%) 190 (M^+), 189 (100), 175, 105, 85, 77, 59. HRMS (ESI): calcd for $C_{11}H_{14}ONaSi$: m/z 213.0712, found: 213.0716.

4.4. Preparation of allyl(1-benzotriazolyl-1-phenoxyalkyl)dimethylsilane and 1-benzo-triazolyl-1-phenoxyalkyl(dimethyl)vinylsilane: general procedure (Scheme 2: method B)

To a solution of 1-phenoxymethylbenzotriazole (5.0 mmol) in THF (70 mL), at −78 °C, was added a solution of *n*-butyllithium (2.5 M in hexane, 2.0 mL, 1 equiv) and then the reaction mixture was stirred for 2 min at the same temperature. Chloroallyldimethylsilane (or chlorovinyldimethylsilane) (5.0 mmol, 1 equiv.) was added and the resulting mixture was stirred for 5 min, at −78 °C. One more equivalent of *n*-butyllithium (2.5 M, 2.0 mL) was added and the resulting mixture was again stirred for 2 min at −78 °C. Finally, alkyl or allyl bromide (5.0 mmol, 1 equiv) was added. The reaction was stirred for 5 min at −78 °C then for 5 min at room temperature. Water (40 mL) was added to the resulting solution then the aqueous phase was extracted three times with ether (3×50 mL). The combined organic phases were dried over $MgSO_4$, filtered off and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: EP/AcOEt 97:3) affording the corresponding 1*H*-benzotriazoles **4** (Table 1).

4.4.1. Allyl(1-(benzotriazol-1-yl)-1-phenoxyundecyl)dimethylsilane ***4e***

Yield: 1.13 g (70%). Oil. R_f=0.28 (EP/AcOEt 97:3). IR (film): 2925, 2854, 1629, 1589, 1489, 1250 cm^{-1}. ^1H NMR: δ=0.21 (s, 3H, $SiCH_3$), 0.22 (s, 3H, $SiCH_3$), 0.87 (t, 3H, CH_3, J=6.7 Hz), 1.1–1.5 (m, 16H), 1.77 (d, 2H, $SiCH_2$, J=7.6 Hz), 2.4–2.7 (m, 2H), 4.8–4.9 (m, 2H), 5.6–5.8 (m, 1H), 6.46 (d, 2H, 2×CH Ph, J=7.9 Hz), 6.8–7.0 (m, 3H, 3×CH Ph), 7.2–7.3 (m, 2H, 2×CH Bt), 7.5–7.6 (m, 1H, CH Bt), 8.0–8.1 (m, 1H, CH Bt). ^{13}C NMR: δ=−3.1 ($Si(CH_3)_2$), 13.9 (CH_3), 22.4 (CH_2), 22.4 (CH_2), 23.5 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.6 (CH_2), 31.6 (CH_2), 37.2 (CH_2), 95.9 (C_q), 113.2 (CH Bt), 114.1 (CH_2=), 119.5 (CH Bt), 120.6 (2×CH Ph), 123.3 (CH Ph), 123.7 (CH Bt), 127.0 (CH Bt), 128.9 (2×CH Ph), 133.2 (C_q Bt), 133.6 (CH=), 146.0 (C_q Bt), 155.0 (C_q Ph). HRMS (ESI): calcd for $C_{28}H_{41}N_3ONaSi$: m/z 486.2917, found: 486.2926.

4.4.2. Allyl(1-(benzotriazol-1-yl)-1-phenoxybut-3-enyl)dimethylsilane ***4g***

Yield: 1.01 g (75%). Oil. TLC: R_f=0.36 (EP/AcOEt 96:4). IR (film): 3076, 2959, 1629, 1588, 1488, 1250 cm^{-1}. ^1H NMR: δ=0.21 (s, 6H, $Si(CH_3)_2$), 1.78 (d, 2H, $SiCH_2$, J=8.1 Hz), 3.34 (dd, 1H, CH_2=CH$CH_a$$CH_b$, J=15.3, 7.0 Hz), 3.51 (dd, 1H, CH_2=CH$CH_a$$CH_b$, J=15.3, 7.0 Hz), 4.7–5.1 (m, 4H), 5.5–5.8 (m, 2H), 6.3–6.5 (m, 2H, 2×CH Ph), 6.8–7.2 (m, 3H, 3×CH Ph), 7.2–7.3 (m, 2×CH Bt), 7.6–7.7 (m, 1H, CH Bt), 7.9–8.0 (m, 1H, 1CH Bt). ^{13}C NMR: δ=−3.2 ($Si(CH_3)_2$), 22.3 (CH_2), 41.5 (CH_2), 94.8 (C_q), 113.4 (CH Bt), 114.2 (CH_2=), 119.3 (CH_2=), 119.4 (CH Bt), 120.5 (2×CH Ph), 122.9 (CH Ph), 123.1 (CH Bt), 127.1 (CH Bt), 129.0 (2×CH Ph), 132.6 (CH=), 133.3 (C_q Bt), 133.5 (CH=), 146.0 (C_q Bt), 158.1 (C_q Ph). HRMS (ESI): calcd for $C_{21}H_{25}N_3ONaSi$: m/z 386.1665, found: 386.1674.

4.4.3. Allyl(1-(benzotriazol-1-yl)-1-phenoxyhex-5-enyl)dimethylsilane ***4h***

Yield: 0.66 g (58%). Oil. TLC: R_f=0.26 (EP/AcOEt 97:3). IR (film): 3075, 2957, 1629, 1595, 1250, 842, 694 cm^{-1}. ^1H NMR: δ=0.20 (s, 6H, $Si(CH_3)_2$), 1.1–1.6 (m, 2H), 1.81 (d, 2H, $SiCH_2$, J=8.1 Hz), 2.0–2.2 (m, 2H), 2.8–3.1 (m, 2H), 4.8–5.0 (m, 4H), 5.5–5.9 (m, 2H), 6.51 (d, 2H, 2×CH Ph, J=8.5 Hz), 6.9–7.1 (m, 3H, 3×CH Ph), 7.2–7.3 (m, 2×CH Bt), 7.6–7.7 (m, 1H, CH Bt), 8.0–8.2 (m, 1H, CH Bt). ^{13}C NMR: δ=−3.2 ($Si(CH_3)_2$), 22.3 (CH_2), 22.8 (CH_2), 33.5 (CH_2), 36.8 (CH_2), 95.9 (C_q),

113.3 (CH Bt), 114.3 (CH_2=), 115.2 (CH_2=), 119.6 (CH Bt), 120.5 (2×CH Ph), 123.4 (CH Ph), 123.9 (CH Bt), 127.1 (CH Bt), 129.0 (2×CH Ph), 133.2 (C_q Bt), 133.6 (CH=), 137.3 (CH=), 146.0 (C_q Bt), 155.1 (C_q Ph). HRMS (ESI): calcd for $C_{23}H_{29}N_3ONaSi$: *m*/*z* 414.1978, found: 414.1975.

4.4.4. *(1-(Benzotriazol-1-yl)-1-phenoxyundecyl)(dimethyl)-vinylsilane* ***4j***

Yield: 0.81 g (60%). Oil. TLC: R_f=0.39 (EP/AcOEt 97:3). IR (film): 2925, 2854, 1592, 1489, 1249, 926 cm^{-1}. ^1H NMR: δ=0.10 (s, 3H, $SiCH_3$), 0.19 (s, 3H, $SiCH_3$), 0.78 (t, 3H, CH_3, *J*=6.3 Hz), 0.9–1.5 (m, 16H), 2.42 (t, 1H, *J*=12.1 Hz), 2.59 (t, 1H, *J*=10.9 Hz), 5.5–5.7 (m, 1H), 5.8–5.9 (m, 1H), 6.1–6.3 (m, 1H), 6.36 (d, 2H, 2×CH Ph, *J*=8.1 Hz), 6.8–7.0 (m, 3H, 3×CH Ph), 7.1–7.3 (m, 2×CH Bt), 7.5–7.6 (m, 1H, CH Bt), 7.9–8.1 (m, 1H, CH Bt). ^{13}C NMR: δ=−2.8 ($SiCH_3$), −2.5 ($SiCH_3$), 14.1 (CH_3), 22.6 (CH_2), 23.6 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 37.8 (CH_2), 95.8 (C_q), 113.5 (CH Bt), 119.7 (CH Bt), 120.6 (2×CH Ph), 123.4 (CH Ph), 124.0 (CH Bt), 127.1 (CH Bt), 129.0 (2×CH Ph), 133.3 (C_q Bt), 133.5 (CH_2=), 136.7 (CH=), 146.2 (C_q Bt), 155.5 (C_q Ph). HRMS (ESI): calcd for $C_{27}H_{39}N_3ONaSi$: *m*/*z* 472.2760, found: 472.2756.

4.4.5. *(1-(Benzotriazol-1-yl)-1-phenoxybut-3-enyl)-(dimethyl)vinylsilane* ***4k***

Yield: 0.67 g (65%). White solid, mp 62–64 °C. TLC: R_f=0.33 (EP/AcOEt 97:3). IR (film): 3054, 2950, 1588, 1488, 1252 cm^{-1}. ^1H NMR: δ=0.26 (s, 3H, $SiCH_3$), 0.28 (s, 3H, $SiCH_3$), 3.28 (dd, 1H, CH_2=CH$CH_a$$CH_b$, *J*=15.2, 7.3 Hz), 3.43 (dd, 1H, CH_2=CH$CH_a$$CH_b$, *J*=15.2, 7.3 Hz), 4.9–5.0 (m, 2H), 5.6–5.8 (m, 2H), 5.9–6.3 (m, 2H), 6.45 (d, 2H, 2×CH Ph, *J*=8.3 Hz), 6.9–7.1 (m, 3H, 3×CH Ph), 7.3–7.4 (m, 2×CH Bt), 7.65–7.71 (m, 1H, CH Bt), 7.0–8.1 (m, 1H, CH Bt). ^{13}C NMR: δ=−2.8 ($SiCH_3$), −2.5 ($SiCH_3$), 42.1 (CH_2), 94.7 (C_q), 113.6 (CH Bt), 119.4 (CH_2=), 119.6 (CH Bt), 120.6 (2×CH Ph), 123.5 (CH Ph), 124.0 (CH Bt), 127.1 (CH Bt), 129.0 (2×CH Ph), 131.6 (CH=), 133.1 (C_q Bt), 133.8 (CH_2=), 136.4 (CH=), 146.0 (C_q Bt), 155.4 (C_q Ph). HRMS (ESI): calcd for $C_{20}H_{23}N_3ONaSi$: *m*/*z* 372.1508, found: 372.1512.

4.5. Hydrolysis of intermediates 4 into (acyl)(dimethyl)-allylsilanes or acyl(dimethyl)-vinylsilanes 1 (Scheme 2: method B)

To a solution of compound **4** (0.80 mmol) in acetone (2 mL) was added a solution of anhydrous $FeCl_3$ (0.48 mmol, 0.6 equiv) in acetone (2 mL). The reaction mixture was stirred (45–75 min) at room temperature until the disappearance of the starting material (checked by TLC, eluent: EP/AcOEt 96:4). At the end of the reaction, the resulting mixture was filtered on silica gel to remove $FeCl_3$. After evaporation of the solvent, the residue was purified by silica gel column chromatography (eluent: EP/CH_2Cl_2 85:15) affording the corresponding acylsilane **1** (Table 1).

4.5.1. *Allyl(dimethyl)undecanoylsilane* ***1e***

Yield: 190 mg (95%). Oil. TLC: R_f=0.28 (EP/AcOEt 98:2). IR (film): 2925, 2854, 1644, 1250 cm^{-1}. ^1H NMR: δ=0.21 (s, 6H, $Si(CH_3)_2$), 0.89 (t, 3H, CH_3, *J*=5.9 Hz), 1.1–1.4 (m, 14H), 1.50–1.61 (m, 2H), 1.71 (d, 2H, $SiCH_2$, *J*=8.1 Hz), 2.58 (t, 2H, CH_2CO, *J*=7.2 Hz), 4.9–5.0 (m, 2H), 5.6–5.8 (m, 1H). ^{13}C NMR: δ=−5.3 ($Si(CH_3)_2$), 14.0 (CH_3), 21.1 (CH_2), 21.9 (CH_2), 22.6 (CH_2), 22.9 (CH_2), 25.4 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 49.1 (CH_2CO), 114.1 (CH_2=), 133.9 (CH=), 246.6 (C=O). GC–MS: *m*/*z* (%) 155, 142, 127, 99 (100), 75, 59. HRMS (ESI): calcd for $C_{16}H_{32}ONaSi$: *m*/*z* 291.2120, found: 291.2112.

4.5.2. *Allyl(but-3-enoyl)dimethylsilane* ***1g***

Yield: 8 mg (25%). Oil. TLC: R_f=0.42 (EP/AcOEt 99:1). IR (film): 2919, 2855, 1643, 1251 cm^{-1}. ^1H NMR: δ=0.23 (s, 6H, $Si(CH_3)_2$), 1.72 (d, 2H, $SiCH_2$, *J*=8.9 Hz), 3.36 (dt, 2H, *J*=6.9, 1.3 Hz), 4.9–5.2 (m, 4H), 5.6–5.7 (m, 2H). ^{13}C NMR: δ=−5.0 ($Si(CH_3)_2$), 21.3 (CH_2Si), 53.8 (CH_2CO), 114.5 (CH_2=), 119.0 (CH_2=), 129.8 (CH=), 133.0 (CH=), 244.0 (C=O). GC–MS: *m*/*z* (%) 168 (M^+), 153, 99 (100), 71, 59.

4.5.3. *Allyl(dimethyl)hex-5-enoylsilane* ***1h***

Yield: 100 mg (80%). Oil. TLC: R_f=0.35 (EP/AcOEt 98:2). IR (film): 2927, 2855, 1641, 1261 cm^{-1}. ^1H NMR: δ=0.16 (s, 6H, $Si(CH_3)_2$), 1.45–1.60 (m, 2H, CH_2CH_2CO), 1.66 (d, 2H, $SiCH_2$, *J*=7.8 Hz), 1.94 (m, 2H, CH_2=CH–CH_2), 2.53 (t, 2H, CH_2CO, *J*=7.4 Hz), 4.8–5.0 (m, 4H), 5.5–5.7 (m, 2H). ^{13}C NMR: δ=−5.0 ($Si(CH_3)_2$), 21.1 (CH_2), 21.3 (CH_2), 33.3 (CH_2), 48.4 (CH_2), 114.4 (CH_2=), 115.2 (CH_2=), 133.3 (CH=), 138.4 (CH=), 247.1 (C=O). GC–MS: *m*/*z* (%) 196, 115, 99 (100), 97, 81.

4.5.4. *Dimethyl(vinyl)undecanoylsilane* ***1j***

Yield: 183 mg (94%). Oil. TLC: R_f=0.25 (EP/AcOEt 98:2). IR (film): 2927, 2855, 1639, 1252 cm^{-1}. ^1H NMR: δ=0.18 (s, 6H, $Si(CH_3)_2$), 0.88 (t, 3H, CH_3, *J*=6.3 Hz), 1.1–1.4 (m, 14H), 1.50–1.59 (m, 2H, CH_2CH_2CO), 2.59 (t, 2H, CH_2CO, *J*=7.3 Hz), 5.60–6.51 (m, 3H). ^{13}C NMR: δ=−5.1 ($Si(CH_3)_2$), 14.1 (CH_3), 22.1 (CH_2), 22.8 (CH_2), 23.6 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 30.9 (CH_2), 31.8 (CH_2), 49.0 (CH_2), 134.6 (CH_2=), 137.2 (CH=), 246.9 (C=O). GC–MS: *m*/*z* (%) 254 (M^+), 141, 113, 85 (100), 75, 59. HRMS (ESI): calcd for $C_{15}H_{30}ONaSi$: *m*/*z* 277.1964, found: 277.1958.

4.5.5. *But-3-enoyl(dimethyl)vinylsilane* ***1k***

Yield: 15 mg (35%). Oil. TLC: R_f=0.4 (EP/AcOEt 99:1). IR (film): 2925, 2854, 1638, 1249 cm^{-1}. ^1H NMR: δ=0.28 (s, 6H, $Si(CH_3)_2$), 3.36 (d, 2H, CH_2CO, *J*=7.0 Hz), 4.9–5.0 (m, 2H), 5.7–5.9 (m, 2H), 6.0–6.2 (m, 2H). ^{13}C NMR: δ=−5.0 ($Si(CH_3)_2$), 53.6 (CH_2), 115.6 (CH_2=), 119.2 (CH_2=), 134.5 (CH=), 137.3 (CH=), 245.2 (C=O).

4.6. Ring-closing metathesis experiments (Table 2)

4.6.1. *2-(Benzotriazol-1-yl)-1,1-dimethyl-2-phenoxy-1,2,3,6-tetrahydrosiline* ***6g***

To compound **4g** (200 mg, 0.55 mmol) was added 10% solution of Grubbs II catalyst (51 mg, 0.06 mmol) in CH_2Cl_2 (18 mL). The reaction mixture was refluxed for 5 h until the disappearance of the starting material (TLC, eluent: EP/AcOEt 96:4) and then it was filtered through silica gel. After evaporation of solvent, the residue was purified by silica gel column chromatography (eluent: EP/AcOEt 97:3) affording the compound **6g** (151 mg, yield: 82%).

White solid, mp 75–81 °C. TLC: R_f=0.21 (EP/AcOEt 97:3). IR (film): 3018, 2901, 1650, 1594, 1490, 1253 cm^{-1}. ^1H NMR: δ=0.02 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 1.51 (dd, 2H, $SiCH_2$, *J*=3.4, 1.5 Hz), 3.19 (dd, 2H, CH_2C(OPh)(Bt), *J*=2.6, 1.5 Hz), 5.3–5.5 (m, 1H, CH=), 5.7–5.9 (m, 1H, CH=), 6.35 (d, 2H, 2×CH Ph, *J*=8.6 Hz), 6.9–7.1 (m, 3H, 3×CH Ph), 7.2–7.4 (m, 2H, 2×CH Bt), 7.85 (d, 1H, CH Bt, *J*=8.5 Hz), 8.07 (d, 1H, CH Bt, *J*=8.1 Hz). ^{13}C NMR: δ=−2.7 ($SiCH_3$), −2.4 ($SiCH_3$), 15.1 ($SiCH_2$), 36.0 (CH_2), 92.1 (C_q), 113.0 (CH Bt), 120.0 (CH Bt), 120.8 (2×CH Ph), 123.5 (CH=), 123.8 (CH Ph), 124.2 (CH Bt), 127.2 (CH Bt), 127.5 (CH=), 129.1 (2×CH Ph), 132.3 (C_q Bt), 146.7 (C_q Bt), 155.6 (C_q Ph). HRMS (ESI): calcd for $C_{19}H_{22}N_3OSi$: *m*/*z* 336.1532, found: 336.1539.

4.6.2. *2-(Benzotriazol-1-yl)-1,1-dimethyl-2-phenoxy-2,3-dihydro-1H-silol* ***6k***

To compound **4k** (192.0 mg, 0.550 mmol) was added 2% solution of Grubbs II catalyst (9.3 mg, 0.011 mmol) in toluene (18 mL). The reaction mixture was heated at 80 °C. Grubbs II catalyst (9.3 mg, 0.011 mmol) was added after each 3 h (seven portions for ~24 h) until the disappearance of the starting material (TLC, eluent: EP/AcOEt 96:4). The resulting mixture was then filtered through silica gel. After evaporation of solvent, the residue was purified by silica gel column chromatography (eluent: EP/AcOEt 97:3) affording compound **6k** (141 mg, yield: 80%).

White solid, mp 77–80 °C. TLC: R_f=0.25 (EP/AcOEt 97:3). IR (film): 3019, 2962, 2400, 1591, 1490, 1261, 1216 cm^{-1}. ^1H NMR: δ=0.00 (s, 3H, $SiCH_3$), 0.62 (s, 3H, $SiCH_3$), 3.51 (ddd, 1H, CH_aCH_bCH=, J=18.3, 2.8, 1.9 Hz), 4.05 (dt, 1H, CH_aCH_bCH=, J=18.3, 2.8 Hz), 6.19 (dt, 1H, CH=, J=11.1, 1.9 Hz), 6.56 (d, 2H, 2×CH Ph, J=8.0 Hz), 6.83 (dt, 1H, CH=, J=11.1, 2.8 Hz), 6.97 (t, 1H, CH Ph, J=8.0 Hz), 7.13 (t, 2H, 2×CH Ph, J=8.0 Hz), 7.3–7.5 (m, 2H, 2×CH Bt), 7.80 (d, 1H, CH Bt, J=7.4 Hz), 8.12 (d, 1H, CH Bt, J=7.4 Hz). ^{13}C NMR: δ=1.0 ($Si(CH_3)_2$), 41.2 (CH_2), 94.8 (C_q), 112.1 (CH Bt), 119.7 (2×CH Ph), 120.8 (CH Bt), 123.0 (CH Ph), 124.1 (CH Bt), 127.3 (CH Bt), 128.6 (CH=), 129.6 (2×CH Ph), 133.2 (C_q Bt), 146.8 (CH=), 147.0 (C_q Bt), 155.0 (C_q Ph). HRMS (ESI): calcd for $C_{18}H_{19}N_3ONaSi$: m/z 344.1195, found: 344.1190.

4.7. Hydrolysis of benzotriazole 6g (Scheme 5)

To a solution of benzotriazole **6g** (60 mg, 0.18 mmol) in toluene (2 mL) was added ytterbium triflate dihydrate (217 mg, 0.36 mmol). The reaction mixture was refluxed for almost 4 h until the disappearance of the starting material (TLC, eluent: EP/AcOEt 97:3). After hydrolysis with saturated aqueous $NaHCO_3$ (5 mL), the aqueous phase was extracted with ether (3×5 mL). The combined organic phases were dried over $MgSO_4$, filtered off and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: EP/AcOEt 97:3) affording the dihydrosiline **7** (14 mg, yield: 36%).

4.7.1. 1(-Benzotriazol-1-yl)-(1,1-dimethyl)-1,6-dihydrosiline 7

Oil. TLC: R_f=0.35 (EP/AcOEt 97:3). IR (film): 2926, 1592, 1452, 1260, 1041, 757 cm^{-1}. ^1H NMR: δ=0.32 (s, 6H, $Si(CH_3)_2$), 1.70 (d, 2H, $SiCH_2$, J=4.6 Hz), 5.9–6.1 (m, 2H, 2×CH=), 6.95 (d, 1H, CH=, J=6.3 Hz), 7.2–7.5 (m, 2H, 2×CH Bt), 7.75 (d, 1H, CH Bt, J=8.4 Hz), 8.02 (d, 1H, CH Bt, J=8.3 Hz). ^{13}C NMR: δ=−1.7 ($Si(CH_3)_2$), 15.9 ($SiCH_2$), 111.9 (CH Bt), 120.3 (CH Bt), 123.5 (CH=), 124.2 (CH Bt), 127.4 (*CH*=CBt), 127.6 (CH Bt), 129.3 (CH=), 131.4 (C_q Bt), 138.9 (C_q), 146.4 (C_q Bt). GC–MS: m/z (%) 241 (M^+), 212 (100), 198, 119, 95.

4.8. Hydrogenation of compound 6g (Scheme 5)

A suspension of **6g** (100 mg, 0.29 mmol) and 10% Pd/C catalyst (10 mg) in methanol (6 mL) was hydrogenated under 1 atm of hydrogen. The reaction mixture was stirred for 12 h at room temperature, and then was filtered through Celite. Evaporation of the solvent under reduced pressure afforded the benzotriazole **8** as a pure compound (96 mg, yield: 98%).

4.8.1. 2-(Benzotriazol-1-yl)-1,1-dimethyl-2-phenoxysilinane 8

Oil. TLC: R_f=0.21 (EP/AcOEt 97:3). IR (film): 3072, 2930, 1594, 1489, 1250 cm^{-1}. ^1H NMR: δ=0.12 (s, 3H, $SiCH_3$), 0.20 (s, 3H, $SiCH_3$), 0.7–1.8 (br m, 6H), 2.62 (t, 1H, J=14.5 Hz), 2.81 (dd, 1H, J=21.8, 14.5 Hz), 6.39 (d, 2H, 2×CH Ph, J=8.0 Hz), 6.8–7.1 (m, 3H, 3×CH Ph), 7.2–7.4 (m, 2H, 2×CH Bt), 7.85 (d, 1H, CH Bt, J=5.8 Hz), 8.0–8.2 (m, 1H, CH Bt). ^{13}C NMR: δ=−3.6 ($SiCH_3$), −1.6 ($SiCH_3$), 13.8 (CH_2), 23.3 (CH_2), 24.2 (CH_2), 36.8 (CH_2), 94.2 (C_q), 113.4 (CH Bt), 115.7 (CH Bt), 119.6 (2×CH Ph), 123.2 (CH Ph), 124.5 (CH Bt), 127.3 (CH Bt), 129.5 (2×CH Ph), 132.3 (C_q Bt), 146.5 (C_q Bt), 155.9 (C_q Ph). HRMS (ESI): calcd for $C_{19}H_{23}N_3ONaSi$: m/z 360.1508, found: 360.1518.

4.9. Cross metathesis of compound 4e (Scheme 6)

The same procedure as for compound **4g** was applied affording compound **9** (261 mg, yield: 52%) as a mixture (60:40) of stereomers.

4.9.1. 1,4-Bis[(1-(benzotriazol-1-yl)-1-phenoxyundecyl)-dimethylsilyl]but-2-ene 9

Oil. IR (film): 2926, 2855, 1590, 1489, 1251, 1216 cm^{-1}. HRMS (ESI): calcd for $C_{54}H_{79}N_6O_2Si_2$: m/z 899.5803, found: 899.5817.

Major stereomer: TLC: R_f=0.27 (EP/AcOEt 96:4). ^1H NMR: δ=0.0 (s, 6H, $Si(CH_3)_2$), 0.8–0.9 (m, 3H, CH_3), 1.1–1.7 (m, 18H, 9×CH_2), 2.4–2.8 (m, 2H), 5.1–5.2 (m, 1H), 6.4–6.5 (m, 2H, 2×CH Ph), 6.8–7.1 (m, 3H, 3×CH Ph), 7.2–7.3 (m, 2H, 2×CH Bt), 7.5–7.6 (m, 1H, CH Bt), 8.0–8.1 (m, 1H, CH Bt). ^{13}C NMR: δ=−3.0 ($Si(CH_3)_2$), 14.1 (CH_3), 20.8 (CH_2), 22.6 (CH_2), 23.6 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 37.3 (CH_2), 96.2 (C_q), 113.4 (CH Bt), 119.6 (CH Bt), 120.6 (2×CH Ph), 123.4 (CH Ph), 123.9 (CH Bt), 124.7 (CH=), 127.1 (CH Bt), 129.1 (2×CH Ph), 133.4 (C_q Bt), 146.1 (C_q Bt), 155.2 (C_q Ph).

Minor stereomer (selected data): R_f=0.20 (EP/AcOEt 96:4). ^1H NMR: δ=5.3–5.4 (m, 1H). ^{13}C NMR: δ=−2.8 ($Si(CH_3)_2$), 123.4 (CH=).

4.10. Conversion of compound 9 into bis(acylsilane) 10

Treatment of compound **9** (151 mg, 0.17 mmol) by anhydrous $FeCl_3$ in acetone according to the procedure above described (4.5) gave bis(acyl)silane **10** (41 mg, 95%) as a mixture (60:40) of stereomers.

4.10.1. But-2-ene-1,4-diylbis[dimethyl(undecanoyl)silane] 10

Oil. TLC: R_f=0.25 (EP/AcOEt 98:2). IR (film): 2927, 2855, 1639, 1467, 1258, 1053 cm^{-1}. HRMS (ESI): calcd for $C_{30}H_{60}NaO_2Si_2$: m/z 277.1964, found: 277.1958.

Major stereomer: ^1H NMR: δ=0.18 (s, 6H, $Si(CH_3)_2$), 0.87 (t, 3H, CH_3, J=6.9 Hz), 1.1–1.7 (m, 18H, 9×CH_2), 2.5–2.7 (m, 2H), 5.2–5.3 (m, 1H). ^{13}C NMR: δ=−5.3 ($Si(CH_3)_2$), 14.1 (CH_3), 14.8 (CH_2), 19.5 (CH_2), 22.1 (CH_2), 22.7 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 31.0 (CH_2), 31.8 (CH_2), 49.2 (*CH*$_2$CO), 124.1 (CH=), 247.6 (C=O).

Minor stereomer (selected data): ^1H NMR: δ=5.3–5.4 (m, 2H). ^{13}C NMR: δ=−4.8 ($Si(CH_3)_2$), 122.1 (CH=).

4.11. Cross metathesis of the dithianyl derivative 3f (Scheme 4)

The same procedure as for compound **6g** (Table 2) was applied to compound **3f** (31 mg, 0.12 mmol, refluxing CH_2Cl_2, 5 h) affording the compound **5** (49 mg, 85%) as a mixture (~50:50) of stereomers non-separable over silica gel column chromatography (eluent: EP/AcOEt 99:1).

4.11.1. 1-[(2-Allyl-1,3-dithian-2-yl)(dimethyl)silyl]-4-[2-(allyldimethylsilyl)-1,3-dithian-2-yl]but-2-ene 5

Oil. TLC: R_f=0.35 (EP/AcOEt 99:1). IR (film): 3074, 2905, 1629, 1422, 1248, 1050, 839 cm^{-1}. ^1H NMR (mixture of stereomers): δ=0.19 (s, 6H, $Si(CH_3)_2$), 0.23 (s, 6H, $Si(CH_3)_2$), 1.80 (m, 4H, 2×$SiCH_2$), 1.9–2.2 (m, 4H), 2.4–2.6 (m, 4H), 3.0–3.2 (m, 8H), 4.8–5.0 (m, 2H), 5.1–5.3 (m, 2H), 5.5–5.6 (m, 1H), 5.7–5.9 (m, 2H), 5.9–6.1 (m, 1H). ^{13}C NMR (mixture of stereomers): δ=−5.5 ($SiCH_3$), −5.1 ($SiCH_3$), 12.2 ($SiCH_2$), 21.0 ($SiCH_2$), 23.1 (2×CH_2), 23.3 (2×CH_2), 25.0 (CH_2), 25.5 (CH_2), 37.1 (CH_2), 37.8 (2×C_q), 41.5 (CH_2), 113.9 (CH_2=), 116.8 (CH_2=), 126.0 (CH=), 126.5 (CH=), 134.4 (CH=), 136.5 (CH=).

Acknowledgements

We are grateful to CNRS and University of Reims for supporting this work and to Région Champagne-Ardenne for a Ph.D. grant (C.H.). The authors thank Dr. D. Harakat for HRMS analyses and they acknowledge a referee for relevant remarks regarding metathesis reactions.

References and notes

1. (a) Brook, A. G.; Mauris, R. J. *J. Am. Chem. Soc.* **1957**, *79*, 971–973; (b) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647–660; (c) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147–195; (d) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proced. Int.* **1992**, *24*, 555–582; (e) Najera, C.; Yus, M. *Org. Prep. Proced. Int.* **1995**, *27*, 385–456; (f) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *Gazz. Chim. Ital.* **1997**, *127*, 619–628; (g) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *J. Organomet. Chem.* **1998**, *567*, 181–189; (h) Page, P. C. B.; McKenzie, M. J.; Klair, S. S.; Rosenthal, S. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, UK, 1998; Vol. 2, Part 2, p 1599.
2. (a) Nocentini, T.; Bouillon, J.-P.; Capperucci, A.; Portella, C.; Degl'Innocenti, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2005**, *180*, 1303–1307; (b) Bouillon, J.-P.; Capperucci, A.; Portella, C.; Degl'Innocenti, A. *Tetrahedron Lett.* **2004**, *45*, 87–90; (c) Saleur, D.; Bouillon, J.-P.; Portella, C. *Tetrahedron Lett.* **2001**, *42*, 6535–6537; (d) Bouillon, J.-P.; Didier, B.; Dondy, B.; Pascale, D.; Plantier-Royon, R.; Portella, C. *Eur. J. Org. Chem.* **2001**, 187–192; (e) Saleur, D.; Bouillon, J.-P.; Portella, C. *J. Org. Chem.* **2001**, *66*, 4543–4548; (f) Bouillon, J.-P.; Portella, C.; Bouquant, J.; Humbel, S. *J. Org. Chem.* **2000**, *65*, 5823–5830; (g) Saleur, D.; Bouillon, J.-P.; Portella, C. *Tetrahedron Lett.* **2000**, *41*, 321–324; (h) Bouillon, J.-P.; Saleur, D.; Portella, C. *Synthesis* **2000**, 843–849; (i) Bouillon, J.-P.; Portella, C. *Eur. J. Org. Chem.* **1999**, 1571–1580; (j) Saleur, D.; Bouillon, J.-P.; Portella, C. *Tetrahedron Lett.* **1999**, *40*, 1885–1886; (k) Saleur, D.; Brigaud, T.; Bouillon, J.-P.; Portella, C. *Synlett* **1999**, 432–434; (l) Chuang, T.-H.; Fang, J.-M.; Jiaang, W.-T.; Tsai, Y.-M. *J. Org. Chem.* **1996**, *61*, 1794–1805; (m) Capperucci, A.; Degl'Innocenti, A.; Faggi, C.; Ricci, A. *J. Org. Chem.* **1988**, *53*, 3612–3614.
3. (a) Bouillon, J.-P.; Huguenot, F.; Portella, C. *Synthesis* **2002**, 552–556; (b) Hammaecher, C.; Ouzzane, I.; Portella, C.; Bouillon, J.-P. *Tetrahedron* **2005**, *61*, 657–663.
4. Tang, K.-H.; Liao, F.-Y.; Tsai, Y.-M. *Tetrahedron* **2005**, *61*, 2037–2045.
5. Hammaecher, C.; Portella, C. *Chem. Commun.* **2008**, 5833–5835.
6. Tongco, E. C.; Wang, Q.; Prakash, G. K. S. *Synth. Commun.* **1997**, *27*, 2117–2123.
7. Brook, G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431–434; Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434–436.
8. Katritzky, A. R.; Lang, H.; Wang, Z.; Lie, Z. *J. Org. Chem.* **1996**, *61*, 7551–7557.
9. Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 287–290.
10. Sen, S. E.; Roach, S. L.; Boggs, J. K.; Ewing, G. J.; Margrath, J. *J. Org. Chem.* **1997**, *62*, 6684–6686.
11. (a) Huber, J. D.; Perl, N. R.; Leighton, J. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 3037–3039; (b) Boldon, S.; Moore, J. E.; Gouverneur, V. *Chem. Commun.* **2008**, 3622–3624; (c) BouzBouz, S.; Boulard, L.; Cossy, J. *Org. Lett.* **2007**, *9*, 3765–3768; (d) BouzBouz, S.; De Lemos, E.; Boulard, L.; Cossy, J. *Adv. Synth. Catal.* **2002**, *344*, 627–630; (e) Crowe, W. E.; Goldberg, D. R.; Zhang, Z. J. *Tetrahedron Lett.* **1996**, *37*, 2117–2120; (f) Berglund, M.; Andersson, C.; Larsson, R. *J. Organomet. Chem.* **1986**, *314*, 61–73.
12. Adam, J.-M.; De Fays, L.; Laguerre, M.; Ghosez, L. *Tetrahedron* **2004**, *60*, 7325–7344.
13. (a) Marciniec, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003–2004 and references therein; (b) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *New J. Chem.* **2000**, *24*, 671–675.
14. Pietraszuk, C.; Fischer, H.; Rogalski, S.; Marciniec, B. *J. Organomet. Chem.* **2005**, *690*, 5912–5921.
15. Marciniec, B.; Maciejewski, H.; Gulinski, J.; Rzejak, L. *J. Organomet. Chem.* **1989**, *362*, 273–279.
16. Spagnol, G.; Heck, M.-P.; Nolan, S. P.; Mioskowski, C. *Org. Lett.* **2002**, *4*, 1767–1770.
17. Hon, Y.-S.; Lee, C.-F.; Chen, R.-J.; Huang, Y.-F. *Synth. Commun.* **2003**, *33*, 2829–2842.
18. Anderson, A. S.; Hwang, J.-T.; Greenberg, M. M. *J. Org. Chem.* **2000**, *65*, 4648–4654.
19. Katritzky, A. R.; Rachwal, S.; Rachwal, B. *J. Org. Chem.* **1989**, *54*, 6022–6029.