Tetrahedron 65 (2009) 5472–5483

Contents lists available at ScienceDirect

Tetrahedron

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

Silylated azolium salts and their applications in the synthesis of azolines and β-enaminoketones bearing allyl-, vinyl-, and acylsilane or α-silylketone units

Ana M. González-Nogal *, Mariola Calle

Departamento de Química Orgánica, Facultad de Ciencias and Centro de Innovación en Química y Materiales Avanzados (CINQUIMA), Universidad de Valladolid, Dr. Mergelina s/n, 47011Valladolid, Spain

ARTICLE INFO

Article history:
Received 12 January 2009
Received in revised form 23 January 2009
Accepted 24 January 2009
Available online 14 April 2009

Keywords:
Silicon heterocycles
Silylisoxazolines
Silylpyrazolines
β-Enaminoacylsilanes

ABSTRACT

Differently silylated 3- or 4-isoxazolines and 3-pyrazolines, bearing versatile vinyl- or allylsilane moieties in various positions of the heterocyclic system, have been synthesized starting from new silylazolium salts by reduction with metal complex hydrides or alkylation with organolithium reagents. On the other hand, the reductive ring-opening of silylated isoxazolium salts with lithium dimethylcuprate led to interesting β-enamino acylsilanes and α′-silylmethyl-β-enaminoketones. These polysynthetic equivalents are useful building blocks in organic synthesis.

1. Introduction

Following on with our current research in the synthesis of silylated azole derivatives, we were especially interested in the regioselective synthesis of azolines bearing silyl groups in different positions of the heterocyclic ring. Previously, we have reported[1] the synthesis of monometalated and dimetalated 1- and 2-pyrazolines by 1,3-dipolar cycloaddition of silicon and tin alkenes with *N*-phenylsydnone or trimethylsilyldiazomethane. Moreover, although pyrazolium salts are not reactive toward organolithium reagents, we prepared[2] 5-silyl-3-pyrazolines and 3-silylindazolines by silyl lithiation from pyrazolium and indazolium salts. These substrates were opened by lithium silylcuprate reagents[3] to give versatile *N*-silylated β-enaminoimines stabilized by coordination of the silyl group with both nitrogen atoms.

In this paper we describe the regioselective synthesis of new pyrazolines and isoxazolines bearing distinct silyl groups (trimethyl, dimethylphenyl, and *tert*-butyldiphenyl) by reaction of differently silylated isoxazolium and pyrazolium salts with metal complex hydrides and organolithium reagents. On the other hand, the reaction of isoxazolium salts with lithium dimethylcuprate led to silylated β-enaminoketones.

2. Results and discussion

2.1. Synthesis of silylated azolium salts

The starting silylazolium salts have not been previously described. We have prepared, for the first time, a variety of 4-, 5-silyl, 3-, 4-, and 5-silylmethyl isoxazolium and pyrazolium salts by quaternization of corresponding silylated isoxazoles (Scheme 1) and pyrazoles (Scheme 2) with tetraethyloxonio tetrafluoroborate and occasionally with methyl iodide (Scheme 3). The necessary silylated azoles have been synthesized by methodologies previously described by us[4–7] and others.[8]

2.1.1. *Synthesis of silyl isoxazolium tetrafluoroborates*

See Scheme 1.

2.1.2. *Synthesis of silyl pyrazolium tetrafluoroborates*

See Scheme 2.

2.1.3. *Synthesis of silylated pyrazolium iodides*

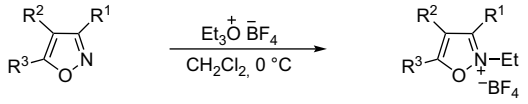
See Scheme 3.

2.2. Reactions of silylated azolium salts with metal complex hydrides

Isoxazolium and pyrazolium salts were reduced with sodium borohydride in methanol and/or lithium aluminum hydride in dry ether, giving the corresponding isoxazolines and pyrazolines.

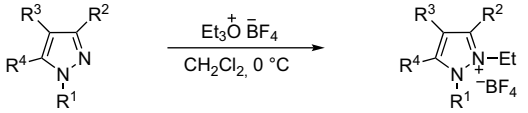
* Corresponding author. Tel.: +34 983423213; fax: +34 983423013.
E-mail address: agn@qo.uva.es (A.M. González-Nogal).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.01.114



1a; R^1= R^3= Me, R^2= $SiMe_3$	**2a** (94%)
1b; R^1= R^3= Me, R^2= $SiMe_2Ph$	**2b** (95%)
1c; R^1= R^3= Ph, R^2= $SiMe_2Ph$	**2c** (80%)
1d; R^1= Me,R^3= Ph, R^2= $SiMe_2Ph$	**2d** (90%)
1e; R^1= Ph, R^2= H, R^3= $SiPh_2Bu^t$	**2e** (95%)
1f; R^1= Me, R^2= H, R^3= $SiPh_2Bu^t$	**2f** (95%)
1g; R^1= Me, R^2= H, R^3= $SiMe_3$	**2g** (75%)
1h; R^1= Ph, R^2= H, R^3= $SiMe_2Ph$	**2h** (65%)
1i; R^1= $CH_2SiPh_2Bu^t$, R^2= H, R^3= Bu^t	**2i** (95%)
1j; R^1= $CH_2SiPh_2Bu^t$, R^2= H, R^3= Ph	**2j** (90%)
1k; R^1= $CH_2SiPh_2Bu^t$, R^2= H, R^3= Ph-OMe(p)	**2k** (50%)
1l; R^1= Me, R^2= CH_2SiMe_2Ph, R^3= Me	**2l** (95%)
1m; R^1= Me, R^2= H, R^3= $CH_2SiPh_2Bu^t$	**2m** (88%)
1n; R^1= Bu^t, R^2= H, R^3= $CH_2SiPh_2Bu^t$	**2n** (94%)
1o; R^1= Ph, R^2= H, R^3= $CH_2SiPh_2Bu^t$	**2o** (90%)
1p; R^1= Ph-Cl(p), R^2= H, R^3= $CH_2SiPh_2Bu^t$	**2p** (80%)

Scheme 1.



3a; R^1= Ph, R^2=R^4= Me, R^3=$SiMe_3$	**4a** (95%)
3b; R^1= Ph, R^2=R^4= Me, R^3=$SiMe_2Ph$	**4b** (96%)
3c; R^1= R^2=R^4= Ph, R^3=$SiMe_2Ph$	**4c** (90%)
3d; R^1= R^4= Me, R^2=$CH_2SiPh_2Bu^t$, R^3= H	**4d** (94%)
3e; R^1= R^2= Me, R^3= H, R^4=$CH_2SiPh_2Bu^t$	**4e** (92%)
3f; R^1= Ph,R^2= Me, R^3= H, R^4=$CH_2SiPh_2Bu^t$	**4f** (90%)

Scheme 2.

2.2.1. Reduction of isoxazolium salts with sodium borohydride or lithium aluminum hydride

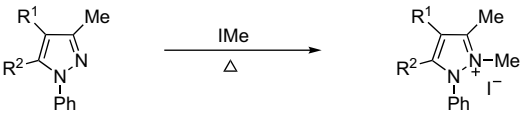
4-Silyl isoxazolium tetrafluoroborates **2a**–**d** reacted easily at rt with sodium borohydride in methanol or lithium aluminum hydride in dry ether to give 4-silylated 4-isoxazolines **5a**–**d** in the same yields with both hydrides (Scheme 4).

The same regiochemistry was observed in the reduction of 5-silyl isoxazolium salts with sodium borohydride or lithium aluminum hydride. Starting from 5-*tert*-butyldiphenylsilyl isoxazolium tetrafluoroborates **2e** and **2f**, 5-silyl-4-isoxazolines **5e** and **5f** were obtained with good yields. However, when the 5-trimethylsilylisoxazolium salt **2g** and 5-dimethylphenylsilylisoxazolium salt **2h** were treated with the same hydrides we could not isolate any reduction product. Although **2g** and **2h** were sufficiently stable to be isolated and recrystallized, in the reaction medium they were decomposed because, in both cases, an identifiable mixture was detected (Scheme 5).

Besides the synthetic utility of the vinylsilane unit,[9] the silyl group confers on these 4-isoxazolines a special reactivity. Thus, the MCPBA peracid oxidation of 5-silyl-4-isoxazolines afford α,β-unsaturated acylsilanes in excellent yields[10a] and the $[Co_2(CO)_8]$ promotes the rearrangement of 4- and 5-silyl-4-isoxazolines to silylated acylaziridines.[10b] Moreover, the silyl group is easily eliminated with concomitant cleavage of N–O bond by treatment with fluoride ion to provide β-lactam derivatives or α,β-unsaturated amides.[11]

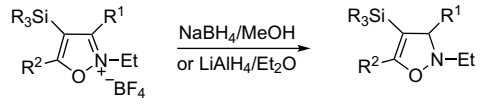
We have also prepared for the first time 2,3-dihydroisoxazoles **5i**–**k**, bearing the *tert*-butyldiphenylsilylmethyl group in C-3 from the corresponding isoxazolium tetrafluoroborates **2i**–**k** by reduction with sodium borohydride or lithium aluminum hydride (Scheme 6).

The 4-dimethylphenylsilylmethyl-4-isoxazoline **5l** was also synthesized from the 4-silylmethylisoxazolium tetrafluoroborate **2l** by the same procedure (Scheme 7).



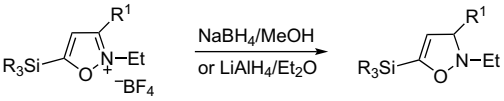
3g; R^1= $SiMe_2Ph$, R^2= Me	**4g** (45%)
3h; R^1= H, R^2= $SiMe_2Ph$	**4h** (90%)
3i; R^1= H, R^2= $SiPh_2Bu^t$	**4i** (95%)

Scheme 3.



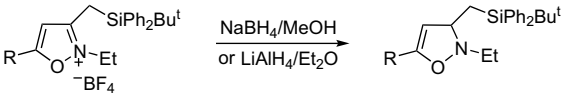
2a; R^1= R^2= Me, R_3= Me_3	**5a** (87%)
2b; R^1= R^2= Me, R_3= Me_2Ph	**5b** (90%)
2c; R^1= R^2= Ph, R_3= Me_2Ph	**5c** (72%)
2d; R^1= Me,R^2= Ph, R_3= Me_2Ph	**5d** (76%)

Scheme 4.



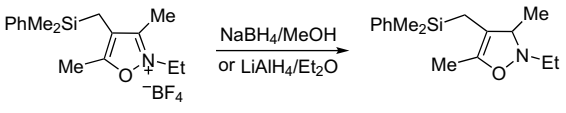
2e; R^1= Ph, R_3= Ph_2Bu^t	**5e** (95%)
2f; R^1= Me, R_3= Ph_2Bu^t	**5f** (92%)
2g; R^1= Me, R_3= Me_3	——
2h; R^1= Ph, R_3= Me_2Ph	——

Scheme 5.



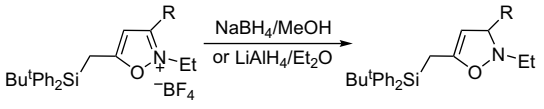
2i; R= Bu^t	**5i** (65%)
2j; R= Ph	**5j**(72%)
2k; R= Ph-OMe(p)	**5k**(50%)

Scheme 6.



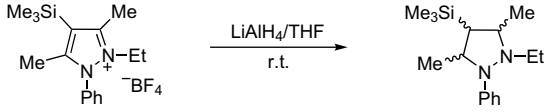
2l **5l** (63%)

Scheme 7.



2m; R= Me — **5m** (90%)
2n; R= Bu^t — **5n** (75%)
2o; R=Ph — **5o** (70%)
2p R=Ph-Cl(p) — **5p** (65%)

Scheme 8.



4a — *t,t*-**6a** (63%) + ***c,t*-6a** (14%) + ***t,c*-6a** (23%)

Scheme 9.

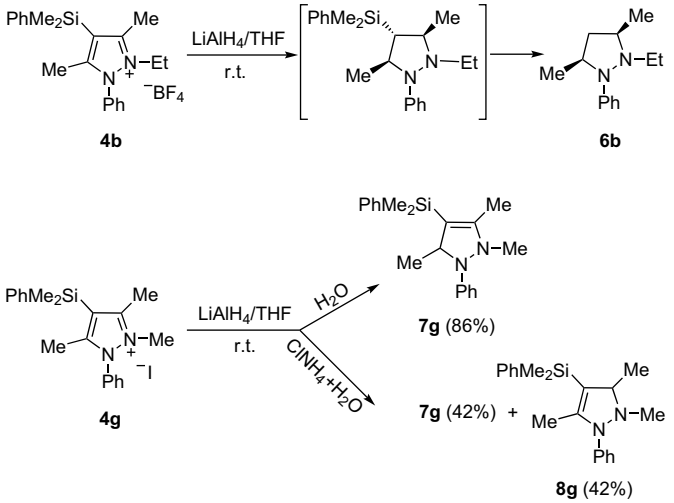
Finally, 5-*tert*-butyldiphenylsilylmethylisoxazolium salts **2m**–**p** were reduced to the corresponding 5-silylmethyl-4-isoxazolines **5m**–**p** by treatment with $NaBH_4$ or $LiAlH_4$ (Scheme 8).

It is noteworthy that 4-isoxazolines **5l**–**p** are versatile building blocks in the construction of more complex molecules. The presence in these isoxazolines of allylsilane moieties allows the transfer of the heterocyclic system to any electrophilic substrate.[12]

2.2.2. *Reduction of silylated pyrazolium salts with lithium aluminum hydride*

Although the pyrazolium ring can be reduced by complex metal hydrides ($NaBH_4$ and $LiAlH_4$), the presence of the silyl group decreases its reactivity, and the reduction with sodium borohydride did not take place. Nevertheless, its total or partial reduction was possible with lithium aluminum hydride in dry THF. Thus, the 3,5-dimethyl-2-ethyl-1-phenyl-4-trimethylsilylpyrazolium tetrafluoroborate **4a** by treatment with $LiAlH_4$ in THF at rt afforded a mixture of diastereomeric pyrazolidines resulting from the total ring-reduction in which the trans,trans-diastereoisomer **6a** was the main product (Scheme 9).

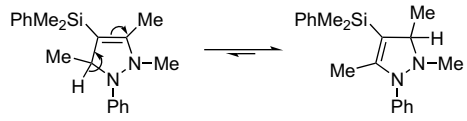
The reaction of the 4-dimethylphenylsilylpyrazolium tetrafluoroborate **4b** with lithium aluminum hydride in the same conditions led to a complex mixture in which the only product identified was the corresponding *trans*,*trans*-pyrazolidine that could not be isolated because it lost the silyl group in the purification process (flash chromatography on silica gel) giving the *cis*-2-ethyl-1-phenyl-3,5-dimethylpyrazolidine **6b** (Scheme 10). Surprisingly, the change of counter-ion in the pyrazolium salt exerted a pronounced effect on its behavior. Thus, the 4-dimethylphenylsilylpyrazolium iodide **4g** in the same conditions afforded the 4-silyl-3-pyrazolines resulting from the partial reduction of the ring. The regiochemistry observed (attack of hydride at C-3 or C-5) depends on the hydrolysis conditions. When the reaction mixture of **4g** with $LiAlH_4$ in THF at rt was hydrolyzed with water, only the 4-dimethylphenylsilyl-1-phenyl-2,3,5-trimethyl-3-pyrazoline **7g** was isolated. However, when the hydrolysis was carried out with a saturated aqueous solution of ammonium chloride, an equimolecular mixture of the two possible regioisomers 3-pyrazolines **7g** and **8g** resulting from attack of hydride at C-5 and C-3 were obtained, respectively (Scheme 10).



4b — **6b**

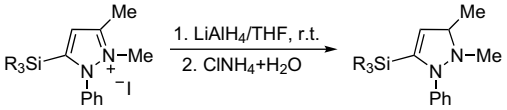
4g — **7g** (86%); **7g** (42%) + **8g** (42%)

Scheme 10.



7g — **8g**

Scheme 11.



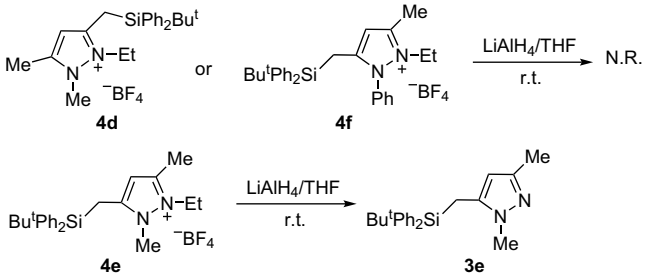
4h; R_3= Me_2Ph — **8h** (80%)
4i; R_3= Ph_2Bu^t — **8i** (85%)

Scheme 12.

Moreover, the 3-pyrazoline **7g** and the mixture of **7g** and **8g** were converted to the 3-pyrazoline **8g** after several days at rt. Therefore, we think that the 3-pyrazoline **7g** resulting from the nucleophilic attack at C-5 is the kinetic product, probably as a consequence of less steric hindrance in this position and the 3-pyrazoline **8g** formed by attack of hydride at C-3 is the thermodynamic product, because of its greater stability due to the conjugation of the double bond with the NPh group. This isomerization was favored by acid medium when the hydrolysis was carried out with an aqueous solution of ammonium chloride (Scheme 11).

On the other hand, the reduction of 5-silyl pyrazolium iodides **4h**,**i** with $LiAlH_4$ was shown to be regioselective, affording the 3-silyl-3-pyrazolines resulting from the attack of hydride at C-3, exclusively (Scheme 12).

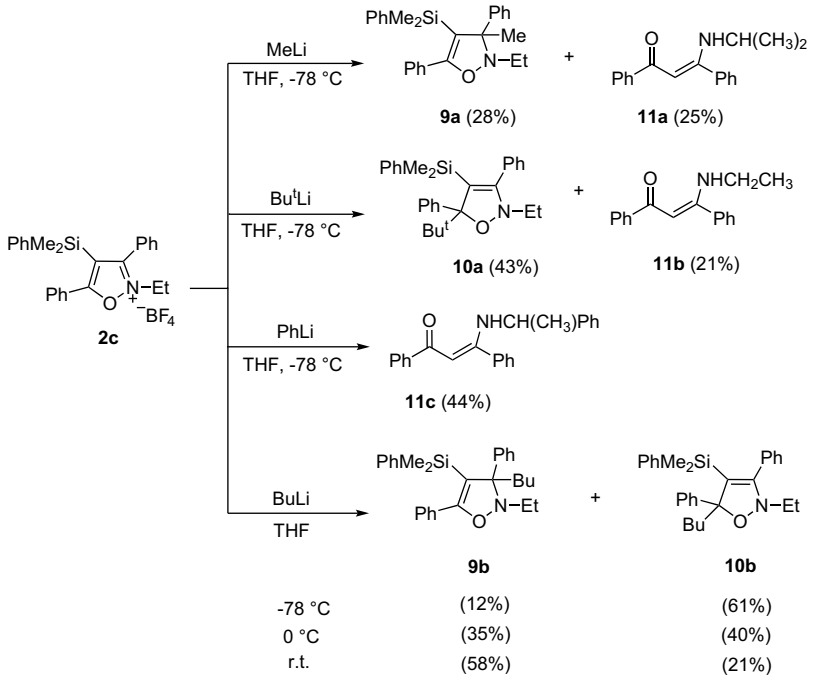
Conversely, 3- or 5-silylmethyl substituted pyrazolium salts did not undergo ring-reduction. The 3-(*tert*-butyldiphenylsilylmethyl)-1-methylpyrazolium salt **4d** was recovered. The same lack of reactivity was observed for the 5-(*tert*-butyldiphenylsilylmethyl)-1-phenylpyrazolium salt **4f**, while its analogous 1-methyl **4e** experienced dequaternization to give the corresponding silylated pyrazole **3e** (Scheme 13).



4d — **4f**

4e — **3e**

Scheme 13.



Scheme 14.

2.3. Reactions of silylated azolium salts with organometallic reagents

As described in Introduction, pyrazolium salts were shown to be unreactive toward organolithium and Grignard reagents[13] except when they bear a nitro group[14] at C-4. On the other hand, we have not found the behavior of these substrates toward lithium carbocuprates described but we have verified[3] their lack of reactivity. The 2,3,5-trimethyl-1-phenylpyrazolium iodide was recovered by treatment with lithium dimethylcuprate. Therefore, we have limited our research to the study of the reactivity of isoxazolium salts toward organometallic reagents.

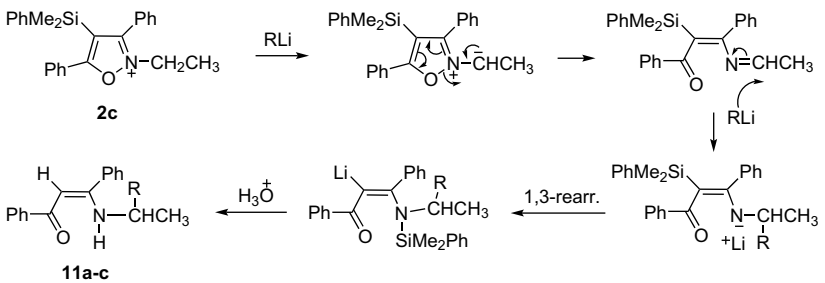
2.3.1. Reactions of silyl isoxazolium salts with organolithium reagents

We have studied the behavior of 4- and 5-silylated and 3-, 4-, and 5-silylmethyl isoxazolium salts toward the following organolithium reagents: MeLi, BuLi, ^{t}BuLi, and PhLi.

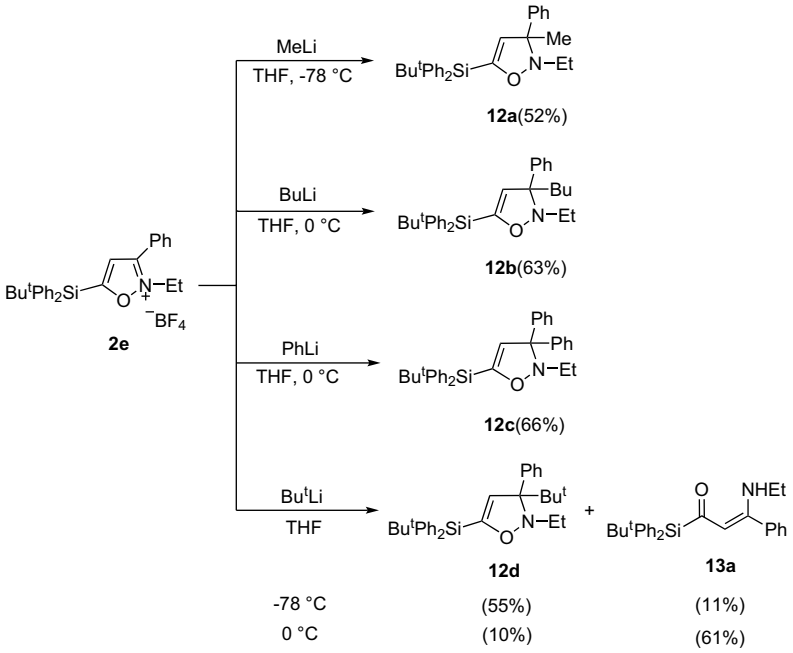
4-Silylated 3- and/or 5-methyl substituted isoxazolium salts **2a**,**b**,**d** did not react with the cited organolithium. A hydrogen–lithium exchange in the acidic methyl groups took place and the isoxazolium salts were regenerated in the final hydrolysis. Thus, we have used as a starting product the 3,5-diphenyl-4-silyl isoxazolium salt **2c** toward methyl-, butyl-, *tert*-butyl-, and phenyllithium.

The results obtained depend on the nature of the organolithium reagent. When MeLi was used the nucleophilic addition took place exclusively at C-3, giving the 4-isoxazoline **9a**, while the bulky ^{t}BuLi attacked the less hindered C-5 position affording the 3-isoxazoline **10a**. In both cases the β-enaminones **11a** and **11b** resulting from ring opening and loss of the silyl group were obtained. With BuLi, a mixture of both silylated isoxazolines **9b** and **10b** was isolated. Their relative ratio depends on the temperature. At −78 °C the majority product is the 3-isoxazoline **10b**, while at rt the principal product was the 4-isoxazoline **9b** and at 0 °C an equimolecular mixture was obtained. The addition of PhLi was not observed and only the β-enaminoketone **11c** was isolated (Scheme 14).

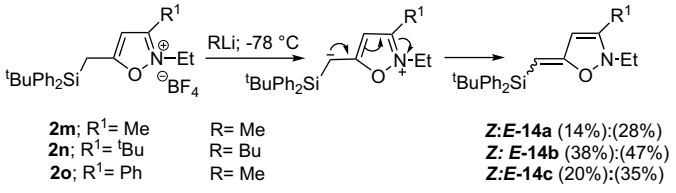
The formation of desilylated β-enaminones **11a**–**c** could be explained by the action of the organolithium as a base extracting a proton of the methylene attached to the quaternary nitrogen (CH_2N^+), followed by ring opening. The addition of organolithium at the imine group, less hindered than the carbonyl group, could afford a lithium amide, which undergoes a 1,3-rearrangement of silicon from carbon to nitrogen,[6] followed by the easy cleavage of the N–Si bond in the final hydrolysis (Scheme 15).



Scheme 15.



Scheme 16.



Scheme 17.

On the other hand, we have studied the behavior of 5-silylated 3-phenylisoxazolium salts **2e** and **2h** toward the cited organolithium reagents. The 5-dimethylphenylsilyl isoxazolium tetrafluoroborate **2h** is unstable in the reaction medium and we were not able to obtain any product of organometallic addition in its reaction with methyl-, butyl, *tert*-butyl-, and phenyllithium. Nevertheless, the 5-*tert*-butyldiphenylsilyl isoxazolium tetrafluoroborate **2e** reacted regioselectively with organolithium reagents, affording the 5-silyl-4-isoxazolines **12a–d** resulting from the nucleophilic attack at C-3. When ^{t}BuLi was used, a mixture of the 5-silyl-4-isoxazoline **12d** and the silylated β-enaminone **13a** resulting from ring opening was obtained. The product ratio depends on the temperature. At −78 °C the 5-silyl-4-isoxazoline **12d** was the majority product while at 0 °C the β-enaminone **13a**, bearing an acylsilane moiety, was the main product (Scheme 16).

These new silylated and highly substituted 3- and 4-isoxazolines are difficult to prepare by other methods.

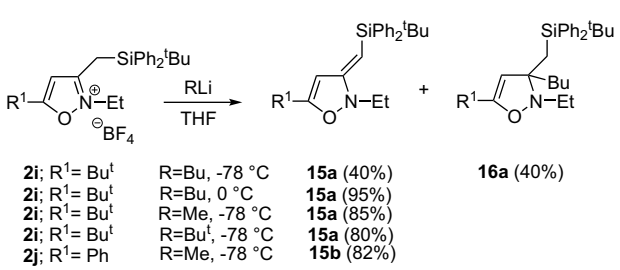
On the other hand, 5-silylmethyl isoxazolium salts **2m–o** did not undergo nucleophilic addition of the organolithium reagents. In all cases tested the organolithium behaves as a base, extracting a proton from the adjacent methylene to the silicon group. The resulting intermediate carbanion stabilized by the α-silyl group led to the corresponding silylated 5-methylen-3-isoxazolines **14a–c**, as a mixture of *Z*/*E* stereoisomers in which the *E*-isomer is the main product (Scheme 17).

3-Silylmethylisoxazolium salts **2i,j** showed the same behavior, affording *E*-3-silylmethylen-4-isoxazolines **15a**,**b**. The *E* geometry of **15a**,**b** was confirmed by NOE experiments.[15] When **2i** was treated with BuLi at −78 °C, an equimolecular mixture of the **15a** and the 3-butyl-4-isoxazoline **16a** resulting from nucleophilic addition was isolated. The PhLi was shown to be unreactive at −78 and 0 °C (Scheme 18).

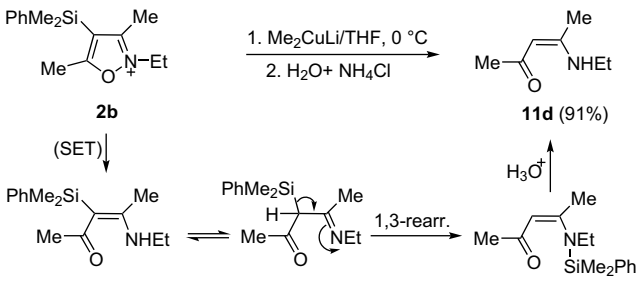
The silylated methylenisoxazolines **14a–c** or **15a**,**b** are especially interesting for their novelty and versatility due to the presence of an *exo* vinylsilane moiety conjugated with the heterocyclic double bond.

2.3.2. *Reactions of silyl isoxazolium salts with lithium dimethylcuprate*

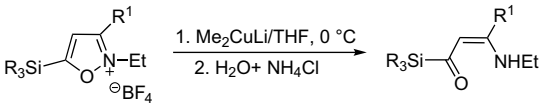
In general, when silyl isoxazolium salts reacted with the lithium dimethylcuprate they underwent reductive ring opening, possibly



Scheme 18.

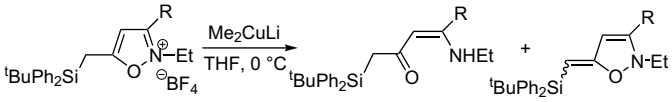


Scheme 19.



2e; R^1 = Ph, R_3 = Ph_2Bu^t **13a** (91%)
2f; R^1 = Me, R_3 = Ph_2Bu^t **13b** (52%)
2g; R^1 = Me, R_3 = Me_3 **13c** (75%)

Scheme 20.



2m; R= Me **17a** (73%) —
2n; R= ^{t}Bu — ***Z: E*-14b** (36%):(47%)
2o; R= Ph **17b** (79%) —

Scheme 21.

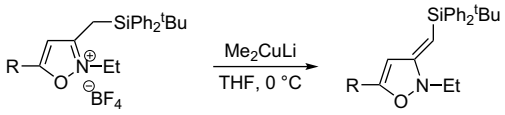
through a single-electron-transfer (SET) process, giving silylated β-enaminoketones. Nevertheless, the 4-dimethylphenylsilyl isoxazolium tetrafluoroborate **2b** reacted with the lithium dimethylcuprate in THF at 0 °C affording the desilylated β-enaminoketone **11d**. The loss of the silyl group occurs after the ring opening as we had observed in the opening of 4-silyl isoxazolium salts with catalytic hydrogenation[6] and it probably takes place by Brook 1,3-rearrangement of the silyl group from carbon to nitrogen. The labile N–Si bond is easily hydrolyzed in the final acidic workup (Scheme 19).

When the silyl group is attached at C-5, the ring underwent reductive opening, without the loss of the silyl group, affording the corresponding β-enamino acylsilanes **13a**–**c** (Scheme 20).

The behavior of this reagent toward isoxazolium salts bearing silylmethyl substituent in C-5 is analogous to that previously indicated. The 3-methyl- and 3-phenyl-5-silylmethyl derivatives **2m**,**o** reacted with lithium dimethylcuprate yielding the silylated β-enaminoketones **17a**,**b.** Meanwhile, the cuprate reagent behaves as a base toward the hindered 3-*tert*-butylisoxazolium **2n** leading to the 3-isoxazoline **14b** resulting from α-deprotonation to the silicon group (Scheme 21).

Finally, the higher acidity of the 3-silylmethyl group in the isoxazolium tetrafluoroborates **2i**,**j**, determined the exclusive behavior of the lithium dimethylcuprate as a basic reagent, giving the same 3-silylmethylen-4-isoxazolines **15a**,**b** previously obtained by reaction with organolithium reagents (Scheme 22).

The silylated β-enaminoketones **13a**–**c** and **17a**,**b** have proved to be interesting synthons in the creation of silyl penta- and hexaheterocycles.[6,7] Moreover, the well-known versatility of the β-enaminoketones[16] is increased by the presence of acylsilane[17] and α-silylketone[18] moieties.



2i; R= ^{t}Bu **15a** (90%)
2j; R= Ph **15b** (56%)

Scheme 22.

3. Conclusions

For the first time, we have synthesized 3- or 4-isoxazolines and 3-pyrazolines, bearing different silyl groups (trimethyl, dimethylphenyl, and *tert*-butyldiphenyl) in distinct positions of the heterocyclic ring, by reduction or alkylation of new silylated azolium salts. These results are interesting because isoxazolines and pyrazolines are frequently found in a diverse array of compounds, including biological active agents and intermediates in organic synthesis. In addition, the presence in these azolines of vinyl- or allylsilane moieties can be used for the transfer of heterocyclic frameworks to electrophilic substrates. Therefore, they are versatile building blocks in the construction of more complex molecules. On the other hand, the reductive ring-opening of silyl isoxazolium salts by reaction with lithium dimethylcuprate has allowed us to synthesize β-enaminoketones bearing versatile acylsilane or α-silylketone units.

4. Experimental

4.1. General

THF was distilled from sodium benzophenone ketyl in a recycling still. Dichloromethane was distilled from P_2O_5. All chromatographic and workup solvents were distilled prior to use. $LiAlH_4$, $NaBH_4$, MeLi, ^{n}BuLi, ^{t}BuLi, and PhLi were commercially available. Reactions involving $LiAlH_4$ and organometallic reagents were carried out under N_2. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ as an internal standard. Carbon multiplicities were assigned by DEPT experiments. Reactions were monitored by TLC on a precoated plate of silica gel 60 (nano-SIL-20, Macheray-Nagel). Flash chromatography was performed on silica gel 60 (230–240 mesh, M-N).

4.2. Preparation of silyl isoxazolium and pyrazolium salts

New 4-, 5-silyl, 3-, 4-, and 5-silylmethyl isoxazolium and pyrazolium tetrafluoroborates or iodides were prepared by quaternization of corresponding silylated isoxazoles and pyrazoles with tetraethyloxonio tetrafluoroborate in dry methylene chloride at rt for 24 h or by heating with methyl iodide in a pressure tube. The necessary silylated azoles were synthesized by methodologies previously described by us[4–7] and others.[8] Their spectroscopic data are given below.

*4.2.1. 2-Ethyl-3,5-dimethyl-4-(trimethylsilyl)isoxazolium tetrafluoroborate (**2a**)*

Yield 94%; white crystal, mp 51–52 °C (from acetone–ether); IR ($CHCl_3$) 1574, 1522, 1258, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9H), 1.57 (t, J=7.3 Hz, 3H), 2.56 (s, 3H), 2.60 (s, 3H), 4.53 (q, J=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −1.60, 12.04, 12.79, 46.37, 113.85, 162.01, 175.56.

*4.2.2. 2-Ethyl-3,5-dimethyl-4-(dimethylphenylsilyl)isoxazolium tetrafluoroborate (**2b**)*

Yield 95%; white crystal, mp 80–81 °C (from acetone–ether); IR ($CHCl_3$) 1575, 1522, 1250, 1100, 1059 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.67 (s, 6H), 1.59 (t, J=7.3 Hz, 3H), 2.31 (s, 3H), 2.44 (s, 3H), 4.55 (q, J=7.3 Hz, 2H), 7.44 (m, 3H), 7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −2.43, 12.63, 12.71, 13.26, 47.15, 113.34, 128.59, 130.54, 133.78, 133.99, 162.77, 176.72.

*4.2.3. 2-Ethyl-4-(dimethylphenylsilyl)-3,5-diphenylisoxazolium tetrafluoroborate (**2c**)*

Yield 80%; white crystal, mp 188–190 °C (from acetone–ether); IR ($CHCl_3$) 1605, 1547, 1448, 1256, 1110, 1058 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 6H), 1.54 (t, J=7.2 Hz, 3H), 4.54 (q, J=7.2 Hz, 2H), 7.27–7.66

(m, 15H); ^{13}C NMR ($CDCl_3$) δ −2.28, 13.03, 48.03, 114.70, 124.10, 124.69, 128.09, 128.61, 128.92, 129.38, 129.82, 130.02, 132.17, 132.56, 133.85, 134.43, 164.20, 177.50.

*4.2.4. 2-Ethyl-3-methyl-4-(dimethylphenylsilyl)-5-phenyl-isoxazolium tetrafluoroborate (**2d**)*

Yield 90%; white crystal, mp 84–85 °C (from acetone–ether); IR ($CHCl_3$) 1608, 1563, 1258, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.46 (s, 6H), 1.62 (t, J=7.3 Hz, 3H), 2.45 (s, 3H), 4.63 (q, J=7.3 Hz, 2H), 7.28–7.54 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −2.06, 12.31, 13.11, 47.41, 113.60, 124.63, 128.33, 128.56, 129.58, 130.12, 132.38, 133.91, 134.35, 163.35, 175.89.

*4.2.5. 5-(tert-Butyldiphenylsilyl)-2-ethyl-3-phenylisoxazolium tetrafluoroborate (**2e**)*

Yield 95%; white crystal, mp 102–103 °C (from acetone–ether); IR (KBr) 1601, 1566, 1470, 1110, 1051 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9H), 1.68 (t, J=7.1 Hz, 3H), 4.94 (q, J=7.1 Hz, 2H), 6.91 (s, 1H), 7.45–7.76 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 13.16, 18.80, 27.26, 49.67, 120.55, 121.85, 128.34, 128.65, 129.40, 129.95, 131.15, 133.46, 136.01, 157.61, 161.21.

*4.2.6. 5-(tert-Butyldiphenylsilyl)-2-ethyl-3-methylisoxazolium tetrafluoroborate (**2f**)*

Yield 95%; white crystal, mp 115–117 °C (from acetone–ether); IR (KBr) 1605, 1554, 1110, 1078 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 9H), 1.63 (t, J=7.3 Hz, 3H), 2.72 (s, 3H), 4.71 (q, J=7.3 Hz, 2H), 6.86 (s, 1H), 7.41–7.58 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.67, 12.68, 18.67, 27.20, 48.21, 121.62, 128.44, 128.56, 131.05, 135.90, 157.68, 179.29.

*4.2.7. 2-Ethyl-3-methyl-5-(trimethylsilyl)isoxazolium tetrafluoroborate (**2g**)*

Yield 75%; white crystal, mp 68–70 °C (from acetone–ether); IR (KBr) 1605, 1573, 1255, 1084 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 9H), 1.62 (t, J=7.3 Hz, 3H), 2.68 (s, 3H), 4.65 (q, J=7.3 Hz, 2H), 7.08 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −2.82, 11.14, 12.57, 47.55, 118.27, 157.35, 182.45.

*4.2.8. 2-Ethyl-5-(dimethylphenylsilyl)-3-phenylisoxazolium tetrafluoroborate (**2h**)*

Yield 65%; white crystal, mp 148–150 °C (from acetone–ether); IR (KBr) 1605, 1588, 125o, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 6H), 1.62 (t, J=7.3 Hz, 3H), 4.75 (q, J=7.3 Hz, 2H), 7.06 (s, 1H), 7.43–7.71 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −4.17, 13.18, 49.14, 117.99, 122.13, 127.95, 128.63, 129.14, 129.92, 131.50, 132.95 134.16, 157.70, 183.20.

*4.2.9. 5-tert-Butyl-3-(tert-butyldiphenylsilylmethyl)-2-ethyl-isoxazolium tetrafluoroborate (**2i**)*

Yield 95%; white crystal, mp 156–157 °C (from acetone–ether); IR ($CHCl_3$) 1590, 1566, 1464, 1110, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (t, J=7.2 Hz, 3H), 1.17 (s, 9H), 1.21 (s, 9H), 3.14 (s, 2H), 3.98 (q, J=7.2 Hz, 2H), 5.97 (s, 1H), 7.37–7.54 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.92, 13.20, 18.62, 27.22, 27.81, 33.39, 46.91, 104.68, 128.32, 130.45, 130.62, 135.80, 162.87, 181.52.

*4.2.10. 3-(tert-Butyldiphenylsilylmethyl)-2-ethyl-5-phenylisoxazolium tetrafluoroborate (**2j**)*

Yield 90%; white crystal, mp 174–175 °C (from acetone–ether); IR (KBr) 1606, 1573, 1462, 1104, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9H), 1.18 (t, J=7.2 Hz, 3H), 3.25 (s, 2H), 3.91 (q, J=7.2 Hz, 2H), 6.73 (s, 1H), 7.39–7.64 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 12.09, 13.57, 18.65, 27.25, 46.97, 104.31, 122.79, 127.02, 128.42, 129.56, 130.45, 130.66, 133.62, 135.90, 163.52, 169.22.

*4.2.11. 3-(tert-Butyldiphenylsilylmethyl)-2-ethyl-5-(p-methoxy-phenyl)isoxazolium tetrafluoroborate (**2k**)*

Yield 50%; white crystal, mp 188–190 °C (from acetone–ether); IR ($CHCl_3$) 1605, 1575, 1100, 1082 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9H), 1.54 (t, J=7.2 Hz, 3H), 2.66 (s, 2H), 3.87 (s, 3H), 4.64 (q, J=7.2 Hz, 2H), 7.20 (d, J=8.9 Hz, 2H), 7.34–7.41 (m, 6H), 7.61 (s, 1H), 7.67 (m, 4H), 7.97 (d, J=8.9 Hz, 2H).

*4.2.12. 2-Ethyl-3,5-dimethyl-4-(dimethylphenylsilylmethyl)-isoxazolium tetrafluoroborate (**2l**)*

Yield 95%; white crystal, mp 62–64 °C (from acetone–ether); IR ($CHCl_3$) 1618, 1540, 1480, 1255, 1072 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 6H), 1.47 (t, J=7.3 Hz, 3H), 2.06 (s, 3H), 2.11 (s, 3H), 2.13 (s, 2H), 4.44 (q, J=7.3 Hz, 2H), 7.30–7.40 (m, 5H), 7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.90, 10.11, 10.64, 11.341, 12.47, 47.33, 117.95, 128.16, 129.87, 133.50, 133.66, 157.68, 167.28.

*4.2.13. 5-(tert-Butyldiphenylsilylmethyl)-2-ethyl-3-methylisoxazolium tetrafluoroborate (**2m**)*

Yield 88%; white crystal, mp 86–88 °C (from acetone–ether); IR (KBr) 1592, 1523, 1468, 1109, 1083 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9H), 1.16 (t, J=7.2 Hz, 3H), 2.41 (s, 3H), 3.03 (s, 2H), 4.24 (q, J=7.2 Hz, 2H), 6.16 (s, 1H), 7.37–7.55 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.42, 12.46, 13.60, 18.59, 27.26, 46.93, 106.58, 128.19, 130.34, 130.71, 135.61, 159.06, 176.04.

*4.2.14. 3-(tert-Butyl-5-tert-butyldiphenylsilylmethyl)-2-ethylisoxazolium tetrafluoroborate (**2n**)*

Yield 94%; white crystal, mp 145–147 °C (from acetone–ether); IR ($CHCl_3$) 1576, 1479, 1104, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 9H), 1.22 (t, J=7.2 Hz, 3H), 1.26 (s, 9H), 3.12 (s, 2H), 4.39 (q, J=7.2 Hz, 2H), 5.97 (s, 1H), 7.36–7.56 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 13.14, 13.86, 18.67, 27.27, 28.19, 32.71, 49.74, 104.76, 128.12, 130.31, 130.89, 135.70, 168.70, 176.96.

*4.2.15. 5-(tert-Butyldiphenylsilylmethyl)-2-ethyl-3-phenylisoxazolium tetrafluoroborate (**2o**)*

Yield 90%; white crystal, mp 133–135 °C (from acetone); IR ($CHCl_3$) 1575, 1491, 1464, 1100, 1058 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 9H), 1.19 (t, J=7.2 Hz, 3H), 3.21 (s, 2H), 4.32 (q, J=7.2 Hz, 2H), 6.38 (s, 1H), 7.38–7.61 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 12.83, 13.96, 18.62, 27.21, 48.25, 105.87, 122.01, 128.13, 128.74, 129.84, 130.30, 130.70, 133.26, 135.64, 159.31, 177.62.

*4.2.16. 5-(tert-Butyldiphenylsilylmethyl)-3-(p-chlorophenyl)-2-ethylisoxazolium tetrafluoroborate (**2p**)*

Yield 80%; white crystal, mp 159–160 °C (from acetone–ether); IR (KBr) 1587, 1567, 1491, 1456, 1092, 1052, 830, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 9H), 1.20 (t, J=7.1 Hz, 3H), 3.22 (s, 2H), 4.32 (q, J=7.1 Hz, 2H), 6.21 (s, 1H), 7.38–7.61 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 12.82, 14.13, 18.73, 27.28, 48.32, 105.88, 120.61, 128.22, 130.26, 130.39, 130.78, 135.74, 139.95, 158.47, 177.96.

*4.2.17. 2-Ethyl-3,5-dimethyl-4-(trimethylsilyl)-1-phenylpyrazolium tetrafluoroborate (**4a**)*

Yield 95%; white crystal, mp 126–127 °C (from acetone–ether); IR ($CHCl_3$) 1593, 1500, 1470, 1256, 1061 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 9H), 1.13 (t, J=7.2 Hz, 3H), 2.13 (s, 3H), 2.51 (s, 3H), 4.10 (q, J=7.2 Hz, 2H), 7.52 (m, 2H), 7.64 (m, 3H); ^{13}C NMR ($CDCl_3$) δ −0.10, 12.54, 13.10, 14.03, 46.63, 114.11, 128.75, 130.70, 131.05, 132.45, 150.93, 151.01.

*4.2.18. 2-Ethyl-3,5-dimethyl-4-(dimethylphenylsilyl)-1-phenylpyrazolium tetrafluoroborate (**4b**)*

Yield 96%; white crystal, mp 96–97 °C (from acetone–ether); IR ($CHCl_3$) 1594, 1500, 1256, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.61 (s, 6H), 1.18 (t, J=7.3 Hz, 3H), 1.96 (s, 3H), 2.38 (s, 3H), 4.09 (q, J=7.3 Hz, 2H), 7.40–7.70 (m, 10H), 7.64 (m, 3H); ^{13}C NMR ($CDCl_3$) δ −1.34, 12.62, 13.15, 14.09, 42.82, 112.70, 128.36, 128.87, 129.92, 130.87, 131.16, 132.58, 133.92, 135.87, 151.61, 151.82.

*4.2.19. 2-Ethyl-4-(dimethylphenylsilyl)-1,3,5-triphenyl pyrazolium tetrafluoroborate (**4c**)*

Yield 90%; white crystal, mp 155–157 °C (from acetone–ether); IR (KBr) 1594, 1494, 1254, 1100, 1083, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.99 (t, J=7.2 Hz, 3H), 4.16 (q, J=7.2 Hz, 2H), 7.15–7.25 (m, 10H), 7.44–7.70 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −3.11, 19.43, 49.16, 119.52, 132.46, 132.95, 133.43, 134.24, 134.65, 134.75, 135.17, 135.59, 136.31, 136.71, 137.43, 138.75, 141.50, 158.35, 159.20.

*4.2.20. 3-(tert-Butyldiphenylsilylmethyl)-2-ethyl-1,5-dimethylpyrazolium tetrafluoroborate (**4d**)*

Yield 94%; white crystal, mp 149–150 °C (from acetone–ether); IR (KBr) 1563, 1460, 1110, 1059 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 9H), 1.13 (t, J=7.5 Hz, 3H), 2.25 (s, 3H), 2.70 (s, 2H), 3.75 (s, 3H), 3.83 (q, J=7.5 Hz, 2H), 5.80 (s, 1H), 7.35–7.57 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 10.35, 11.71, 13.61, 18.23, 27.29, 33.48, 41.36, 107.18, 128.07, 130.30, 131.11, 135.63, 146.01, 147.22.

*4.2.21. 5-(tert-Butyldiphenylsilylmethyl)-2-ethyl-1,3-dimethylpyrazolium tetrafluoroborate (**4e**)*

Yield 92%; white crystal, mp 181–182 °C (from acetone–ether); IR (KBr) 1561, 1470, 1110, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (t, J=7.2 Hz, 3H), 1.14 (s, 9H), 2.29 (s, 3H), 2.79 (s, 2H), 3.34 (s, 3H), 4.39 (q, J=7.2 Hz, 2H), 5.93 (s, 1H), 7.33–7.47 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.02, 11.41, 14.13, 18.25, 27.28, 32.73, 41.77, 106.86, 128.04, 130.19, 131.26, 135.63, 144.52, 148.31.

*4.2.22. 5-(tert-Butyldiphenylsilylmethyl)-2-ethyl-3-methyl-1-phenylpyrazolium tetrafluoroborate (**4f**)*

Yield 90%; white crystal, mp 165–166 °C (from acetone–ether); IR (KBr) 1552, 1495, 1471, 1110, 1054 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 9H), 0.95 (t, J=7.1 Hz, 3H), 2.42 (s, 3H), 2.51 (s, 2H), 3.96 (q, J=7.1 Hz, 2H), 6.07 (s, 1H), 6.63 (m, 2H), 7.40–7.60 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 11.07, 11.77, 14.43, 18.02, 27.05, 42.59, 107.25, 128.12, 128.98, 130.34, 130.42, 130.54, 131.59, 132.42, 135.97, 146.90, 149.97.

*4.2.23. 2,3,5-Trimethyl-4-(dimethylphenylsilyl)-1-phenylpyrazolium iodide (**4g**)*

Yield 45%; yellow crystal, mp 75–77 °C (from acetone–ether); IR ($CHCl_3$) 1592, 1499, 1256, 1116 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.62 (s, 6H), 1.96 (s, 3H), 2.41 (s, 3H), 3.77 (s, 3H), 7.29–7.73 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −1.26, 13.21, 13.83, 36.15, 111.52, 127.13, 127.74, 128.94, 130.13, 132.19, 133.62, 135.29, 138.72, 150.46, 151.66.

*4.2.24. 2,3-Dimethyl-5-(dimethylphenylsilyl)-1-phenylpyrazolium iodide (**4h**)*

Yield 90%; yellow crystal, mp 155–157 °C (from acetone–ether); IR ($CHCl_3$) 1602, 1495, 1256, 1113 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.36 (s, 6H), 2.64 (s, 3H), 3.82 (s, 3H), 6.62 (s, 1H), 7.20–7.63 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −3.53, 13.33, 36.41, 116.30, 128.09, 129.28, 129.92, 130.26, 132.36, 132.62, 133.66, 147.05, 150.96.

*4.2.25. 5-(tert-Butyldiphenylsilyl)-2,3-dimethyl-1-phenylpyrazolium iodide (**4i**)*

Yield 95%; yellow crystal, mp 205–207 °C (from acetone–ether); IR ($CHCl_3$) 1605, 1554, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (s, 9H), 2.80 (s, 3H), 3.79 (s, 3H), 6.95 (m, 4H), 7.09 (s, 1H), 7.18–7.40 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 13.93, 18.63, 27.27, 36.99, 117.79, 128.19, 129.32, 129.62, 130.15, 131.57, 132.36, 135.76, 147.27, 147.63.

4.3. Reduction of silylated azolium salts with metal complex hydrides. Typical procedure

To a stirred solution of the silylated isoxazolium or pyrazolium salt (0.5 mmol) in MeOH (6 mL) or THF (10 mL), $NaBH_4$ or $LiAlH_4$ (0.5 mmol) was added, respectively. The mixture was stirred at rt until TLC indicated complete reaction. The mixture was quenched with aqueous NH_4Cl, workup with Et_2O, and the ethereal layer was dried ($MgSO_4$). The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography to give the following products.

*4.3.1. 2-Ethyl-3,5-dimethyl-4-(trimethylsilyl)-4-isoxazoline (**5a**)*

Yield 87%; oil; R_f 0.42 (CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H), 1.11 (d, J=6.3 Hz, 3H), 1.12 (t, J=7.2 Hz, 3H), 1.82 (s, 3H), 2.57 (dq, J=12.1, 7.2 Hz, 1H), 2.85 (dq, J=12.1, 7.2 Hz, 1H), 3.69 (q, J=6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.28, 12.09, 12.37, 22.93, 52.60, 70.08, 102.19, 155.46. Anal. Calcd for $C_{10}H_{21}NOSi$: C, 60.24; H, 10.62; N, 7.03. Found: C, 60.37; H, 10.39; N, 6.86.

*4.3.2. 2-Ethyl-3,5-dimethyl-4-(dimethylphenylsilyl)-4-isoxazoline (**5b**)*

Yield 90%; oil; R_f 0.39 (CH_2Cl_2); IR ($CHCl_3$) 1640, 1255, 1111 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.42 (s, 3H), 0.43 (s, 3H), 1.14 (d, J=6.5 Hz, 3H), 1.19 (t, J=7.0 Hz, 3H), 1.73 (s, 3H), 2.65 (m, 1H), 2.95 (m, 1H), 3.76 (q, J=6.5 Hz, 1H), 7.38 (m, 3H), 7.56 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −1.37, −1.35, 12.34, 12.44, 23.08, 52.80, 70.17, 100.54, 127.82, 128.99, 133.74, 138.67, 157.29. Anal. Calcd for $C_{15}H_{23}NOSi$: C, 68.91; H, 8.87; N, 5.36. Found: C, 69.23; H, 9.01; N, 5.55.

*4.3.3. 2-Ethyl-4-(dimethylphenylsilyl)-3,5-diphenyl-4-isoxazoline (**5c**)*

Yield 72%; oil; R_f 0.22 (CH_2Cl_2); IR ($CHCl_3$) 1635, 1596, 1490, 1258, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 3H), 0.19 (s, 3H), 1.35 (t, J=7.2 Hz, 3H), 2.96 (dq, J=12.2, 7.2 Hz, 1H), 3.29 (dq, J=12.2, 7.2 Hz, 1H), 4.80 (s, 1H), 7.32 (m, 13H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −1.87, −1.54, 12.42, 53.70, 79.84, 102.96, 127.43, 127.56, 127.84, 128.49, 129.06, 129.48, 130.02, 133.71, 138.20, 142.45, 159.18. Anal. Calcd for $C_{25}H_{27}NOSi$: C, 77.88; H, 7.06; N, 3.63. Found: C, 77.65; H, 6.89; N, 3.91.

*4.3.4. 2-Ethyl-3-methyl-4-(dimethylphenylsilyl)-5-phenyl-4-isoxazoline (**5d**)*

Yield 76%; oil; R_f 0.44 (CH_2Cl_2); IR ($CHCl_3$) 1632, 1597, 1490, 1251, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 3H), 0.34 (s, 3H), 1.29 (d, J=6.4 Hz, 3H), 1.29 (t, J=7.0 Hz, 3H), 2.70 (dq, J=12.2, 7.0 Hz, 1H), 3.11 (dq, J=12.2, 7.0 Hz, 1H), 3.87 (q, J=6.4 Hz, 1H), 7.23–7.56 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −1.40, −1.28, 12.61, 22.77, 52.35, 71.21, 103.56, 127.80, 128.99, 129.30, 130.42, 133.81, 138.75, 158.58. Anal. Calcd for $C_{20}H_{25}NOSi$: C, 74.25; H, 7.79; N, 4.33. Found: C, 74.48; H, 7.92; N, 4.10.

*4.3.5. 5-(tert-Butyldiphenylsilyl)-2-ethyl-3-phenyl-4-isoxazoline (**5e**)*

Yield 95%; oil, R_f 0.55 (CH_2Cl_2); IR ($CHCl_3$) 1662, 1616, 1556, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9H), 1.35 (t, J=7.1 Hz, 3H), 3.00 (dq, J=12.0, 7.1 Hz, 1H), 3.32 (dq, J=12.0, 7.1 Hz, 1H), 4.81 (d, J=2.5 Hz, 1H), 5.10 (d, J=2.5 Hz, 1H), 7.35–7.78 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 12.82, 18.28, 27.68, 73.79, 116.25, 126.93, 127.69, 127.96, 128.54, 129.61, 132.86, 132.97, 136.09, 142.71, 153.35. Anal. Calcd for $C_{27}H_{31}NOSi$: C, 78.40; H, 7.55; N, 3.39. Found: C, 78.22; H, 7.33; N, 3.61.

*4.3.6. 5-(tert-Butyldiphenylsilyl)-2-ethyl-3-methyl-4-isoxazoline (**5f**)*

Yield 92%; oil, R_f 0.60 (CH_2Cl_2); IR ($CHCl_3$) 1645, 1601, 1471, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 9H), 1.20 (d, J=6.5 Hz, 3H), 1.28 (t, J=7.0 Hz, 3H), 2.72 (dq, J=12.2, 7.0 Hz, 1H), 3.11 (dq, J=12.2, 7.0 Hz, 1H), 3.77 (dq, J=2.4, 6.5 Hz, 1H), 4.96 (d, J=2.4 Hz, 1H), 7.35–7.46 (m, 6H), 7.68–7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.86, 18.17, 22.65, 27.61, 53.50, 65.22, 118.07, 127.65, 129.52, 133.03, 133.17, 136.04, 152.61. Anal. Calcd for $C_{22}H_{29}NOSi$: C, 75.16; H, 8.31; N, 3.98. Found: C, 75.32; H, 8.49; N, 4.15.

*4.3.7. 5-tert-Butyl-3-(tert-butyldiphenylsilylmethyl)-2-ethyl-4-isoxazoline (**5i**)*

Yield 65%; oil, R_f 0.47 (CH_2Cl_2); IR ($CHCl_3$) 1663, 1601, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (s, 9H), 1.01 (s, 9H), 1.10 (t, J=7.1 Hz, 3H), 1.51 (dd, J=10.3, 14.5 Hz, 1H), 1.67 (dd, J=10.3, 14.5 Hz, 1H), 2.36 (dq, J=12.3, 7.1 Hz, 1H), 2.77 (dq, J=12.3, 7.1 Hz, 1H), 3.59 (ddd, J=2.5, 4.2, 10.3 Hz, 1H), 3.84 (d, J=2.5 Hz, 1H), 7.33–7.45 (m, 6H), 7.64–7.75 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.60, 18.10, 19.94, 27.68, 27.96, 30.89, 52.68, 67.84, 94.95, 127.62, 127.86, 129.08, 134.15, 136.11, 136.36, 161.29. Anal. Calcd for $C_{26}H_{37}NOSi$: C, 76.60; H, 9.15; N, 3.44. Found: C, 76.41; H, 8.92; N, 3.66.

*4.3.8. 3-(tert-Butyldiphenylsilylmethyl)-2-ethyl-5-phenyl-4-isoxazoline (**5j**)*

Yield 72%; oil, R_f 0.53 (CH_2Cl_2); IR ($CHCl_3$) 1633, 1600, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 9H), 1.20 (t, J=7.1 Hz, 3H), 1.66 (dd, J=10.3, 14.6 Hz, 1H), 1.80 (dd, J=4.2, 14.6 Hz, 1H), 2.50 (dq, J=12.3, 7.1 Hz, 1H), 2.91 (dq, J=12.3, 7.1 Hz, 1H), 3.85 (ddd, J=2.8, 4.2, 10.3 Hz, 1H), 4.62 (d, J=2.8 Hz, 1H), 7.27–7.48 (m, 11H), 7.68–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.68, 18.12, 19.72, 27.66, 53.01, 68.57, 98.22, 125.49, 127.52, 127.72, 128.14, 129.22, 133.92, 134.69, 134.77, 136.13, 136.36, 150.94. Anal. Calcd for $C_{28}H_{33}NOSi$: C, 78.64; H, 7.78; N, 3.28. Found: C, 78.43; H, 7.59; N, 3.51.

*4.3.9. 3-(tert-Butyldiphenylsilylmethyl)-2-ethyl-5-(p-methoxyphenyl)-4-isoxazoline (**5k**)*

Yield 50%; oil, R_f 0.56 (CH_2Cl_2); IR ($CHCl_3$) 1655, 1608, 1510, 1464, 1253, 1106 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 9H), 1.19 (t, J=7.0 Hz, 3H), 1.65 (dd, J=10.1, 14.5 Hz, 1H), 1.78 (dd, J=4.3, 14.5 Hz, 1H), 2.50 (dq, J=12.2, 7.0 Hz, 1H), 2.91 (dq, J=12.2, 7.0 Hz, 1H), 3.81 (s, 3H), 3.81 (ddd, J=2.5, 4.3, 10.1 Hz, 1H), 4.50 (d, J=2.5 Hz, 1H), 6.82 (d, J=8.7 Hz, 2H), 7.25 (d, J=8.7 Hz, 2H), 7.36–7.48 (m, 6H), 7.68–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.70, 18.11, 19.78, 27.68, 52.96, 55.22, 68.57, 96.34, 113.55, 121.99, 126.94, 127.54, 127.69, 129.14, 129.18, 134.77, 136.13, 136.77, 150.74, 159.78. Anal. Calcd for $C_{29}H_{35}NO_2Si$: C, 76.10; H, 7.71; N, 3.06. Found: C, 75.84; H, 7.87; N, 3.33.

*4.3.10. 2-Ethyl-3,5-dimethyl-4-(dimethylphenylsilylmethyl)-4-isoxazoline (**5l**)*

Yield 63%; oil; R_f 0.46 (CH_2Cl_2); IR ($CHCl_3$) 1622, 1599, 1480, 1251, 1114 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (s, 6H), 1.07 (d, J=6.3 Hz, 3H), 1.09 (t, J=7.1 Hz, 3H), 1.60 (s, 3H), 1.98 (s, 2H), 2.50 (dq, J=12.2, 7.1 Hz, 1H), 2.84 (dq, J=12.2, 7.1 Hz, 1H), 3.33 (q, J=6.3 Hz, 1H), 7.31–7.59 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −3.29, −2.79, 9.95, 12.34, 12.46, 19.72, 53.17, 68.65, 104.71, 127.79, 129.13, 133.46, 138.69, 141.24. Anal. Calcd for $C_{24}H_{33}NOSi$: C, 75.93; H, 8.76; N, 3.69. Found: C, 76.18; H, 8.97; N, 3.42.

*4.3.11. 5-(tert-Butyldiphenylsilylmethyl)-2-ethyl-3-methyl-4-isoxazoline (**5m**)*

Yield 90%; oil, R_f 0.57 (CH_2Cl_2); IR ($CHCl_3$) 1667, 1591, 1447, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (d, J=6.0 Hz, 3H), 1.02 (t, J=7.2 Hz, 3H), 1.07 (s, 9H), 2.18 (d, J=15.2 Hz, 1H), 2.26 (d, J=15.2 Hz, 1H), 2.45 (dq, J=12.1, 7.2 Hz, 1H), 2.64 (dq, J=12.1, 7.2 Hz, 1H), 3.54 (dq, J=2.0, 6.0 Hz, 1H), 4.08 (d, J=2.0 Hz, 1H), 7.32–7.46 (m, 6H), 7.66–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 9.35, 12.41, 18.28, 22.36, 27.55, 53.36, 66.51, 96.55, 127.30, 129.06, 133.62, 135.92, 150.83. Anal. Calcd for $C_{23}H_{31}NOSi$: C, 75.56; H, 8.55; N, 3.83. Found: C, 75.36; H, 8.73; N, 4.06.

*4.3.12. 3-tert-Butyl-5-(tert-butyldiphenylsilylmethyl)-2-ethyl-4-isoxazoline (**5n**)*

Yield 75%; oil, R_f 0.66 (CH_2Cl_2); IR ($CHCl_3$) 1670, 1625, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.65 (s, 9H), 0.97 (t, J=7.1 Hz, 3H), 1.05 (s, 9H), 2.18 (d, J=15.6 Hz, 1H), 2.29 (d, J=15.6 Hz, 1H), 2.38 (dq, J=12.3, 7.1 Hz, 1H), 2.59 (dq, J=12.3, 7.1 Hz, 1H), 3.08 (d, J=1.1 Hz, 1H), 3.96 (d, J=1.1 Hz, 1H), 7.28–7.45 (m, 6H), 7.64–7.75 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 8.96, 12.37, 18.36, 25.41, 27.66, 34.78, 55.05, 80.75, 92.04, 127.44, 129.19, 133.63, 136.02, 136.16, 151.43. Anal. Calcd for $C_{26}H_{37}NOSi$: C, 76.60; H, 9.15; N, 3.44. Found: C, 76.45; H, 8.96; N, 3.69.

*4.3.13. 5-(tert-Butyldiphenylsilylmethyl)-2-ethyl-3-phenyl-4-isoxazoline (**5o**)*

Yield 70%; oil, R_f 0.48 (CH_2Cl_2); IR ($CHCl_3$) 1666, 1602, 1491, 1107 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, J=7.0 Hz, 3H), 1.09 (s, 9H), 2.28 (d, J=15.2 Hz, 1H), 2.37 (d, J=15.2 Hz, 1H), 2.65 (dq, J=12.2, 7.0 Hz, 1H), 2.79 (dq, J=12.2, 7.0 Hz, 1H), 4.23 (d, J=2.2 Hz, 1H), 4.54 (d, J=2.2 Hz, 1H), 7.10–7.74 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 9.51, 12.60, 18.44, 27.70, 54.34, 76.65, 95.48, 127.11, 127.52, 128.32, 129.29, 133.59, 136.09, 143.09, 151.98. Anal. Calcd for $C_{28}H_{33}NOSi$: C, 78.64; H, 7.78; N, 3.28. Found: C, 78.43; H, 7.57; N, 3.57.

*4.3.14. 5-(tert-Butyldiphenylsilylmethyl)-3-(p-chlorophenyl)-2-ethyl-4-isoxazoline (**5p**)*

Yield 65%; oil, R_f 0.47 (CH_2Cl_2); IR ($CHCl_3$) 1605, 1503, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (t, J=7.1 Hz, 3H), 1.07 (s, 9H), 2.26 (d, J=15.1 Hz, 1H), 2.33 (d, J=15.1 Hz, 1H), 2.60 (dq, J=12.2, 7.1 Hz, 1H), 2.78 (dq, J=12.2, 7.1 Hz, 1H), 4.17 (d, J=2.2 Hz, 1H), 4.49 (d, J=2.2 Hz, 1H), 6.98 (d, J=8.2 Hz, 2H), 7.16 (d, J=8.2 Hz, 2H), 7.30–7.45 (m, 6H), 7.65–7.74 (m, 4H). Anal. Calcd for $C_{28}H_{32}ClNOSi$: C, 72.78; H, 6.98; N, 3.03. Found: C, 73.01; H, 7.23; N, 2.80.

*4.3.15. trans,trans-2-Ethyl-3,5-dimethyl-4-(trimethylsilyl)-1-phenylpyrazolidine (t,t-**6a**)*

Yield 63%; oil, R_f 0.48 (hexane–CH_2Cl_2, 1:1); IR ($CHCl_3$) 1493, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 9H), 1.22 (t, J=7.1 Hz, 3H), 1.24 (d, J=6.7 Hz, 3H), 1.38 (dd, J=9.5, 12.1 Hz, 1H), 1.46 (d, J=6.3 Hz, 3H), 2.62 (dq, J=11.2, 7.1 Hz, 1H), 2.85 (dq, J=11.2, 7.1 Hz, 1H), 2.97 (dq, J=11.2, 7.1 Hz, 1H), 3.47 (dq, J=9.5, 6.3 Hz, 1H), 6.71 (tt, J=1.2, 7.2 Hz, 1H), 7.02 (dd, J=1.2, 8.8 Hz, 2H), 7.19 (dd, J=7.2, 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −2.02, 12.02, 16.18, 25.41, 41.29, 44.01, 60.87, 64.62, 112.61, 117.26, 128.50, 152.35. Anal. Calcd for $C_{16}H_{28}N_2Si$: C, 69.50; H, 10.21; N, 10.13. Found: C, 69.36; H, 10.43; N, 9.85.

*4.3.16. cis,trans-2-Ethyl-3,5-dimethyl-4-(trimethylsilyl)-1-phenylpyrazolidine (c,t-**6a**)*

Yield 14%; oil, R_f 0.57 (hexane–CH_2Cl_2, 1:1); IR ($CHCl_3$) 1595, 1492, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H), 0.80 (d, J=6.8 Hz, 3H), 1.12 (t, J=7.1 Hz, 3H), 1.48 (d, J=5.9 Hz, 3H), 1.80 (dd, J=6.0, 10.6 Hz, 1H), 2.76 (m, 2H), 1.46 (d, J=6.3 Hz, 3H), 3.29 (dq, J=6.0, 6.8 Hz, 1H), 3.57 (dq, J=10.6, 5.9 Hz, 1H), 6.70 (t, J=7.5 Hz, 1H), 7.02 (d, J=7.5 Hz, 2H), 7.18 (t, J=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −0.97, 13.55, 19.30, 25.03, 39.08, 52.48, 60.84, 62.45, 112.08, 116.61, 128.39, 152.95. Anal. Calcd for $C_{16}H_{28}N_2Si$: C, 69.50; H, 10.21; N, 10.13. Found: C, 69.73; H, 10.39; N, 10.36.

*4.3.17. trans,cis-2-Ethyl-3,5-dimethyl-4-(trimethylsilyl)-1-phenylpyrazolidine (t,c-**6a**)*

Yield 26%; oil, R_f 0.55 (hexane–CH_2Cl_2, 1:1); IR ($CHCl_3$) 1595, 1492, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H), 1.04 (t, J=7.2 Hz, 3H), 1.22 (dd, J=6.4, 11.6 Hz, 1H), 1.29 (d, J=6.0 Hz, 3H), 1.34 (d, J=7.0 Hz, 3H), 2.82 (dq, J=11.6, 7.2 Hz, 1H), 2.91 (dq, J=11.6, 7.2 Hz, 1H), 3.08 (dq, J=11.6, 6.0 Hz, 1H), 3.80 (dq, J=6.4, 7.0 Hz, 1H), 6.80 (m, 1H), 7.20 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −1.19, 14.36, 21.35, 21.54, 39.71, 53.42, 62.38, 67.23, 116.91, 119.29, 128.10, 155.17. Anal. Calcd for $C_{16}H_{28}N_2Si$: C, 69.50; H, 10.21; N, 10.13. Found: C, 69.79; H, 9.99; N, 10.41.

*4.3.18. cis-2-Ethyl-3,5-dimethyl-1-phenylpyrazolidine (**6b**)*

Yield 45%; oil, R_f 0.25 (hexane–CH_2Cl_2, 2:1); ^1H NMR ($CDCl_3$) δ 1.13 (t, J=7.0 Hz, 3H), 1.29 (d, J=6.8 Hz, 3H), 1.50 (d, J=6.4 Hz, 3H),

1.82 (dt, J=8.5, 11.9 Hz, 1H), 2.36 (ddd, J=11.9, 7.8, 5.7 Hz, 1H), 2.62 (dq, J=11.3, 7.0 Hz, 1H), 2.90 (dq, J=11.3, 7.0 Hz, 1H), 3.13 (ddq, J=11.9, 7.8, 6.8 Hz, 1H), 3.69 (ddq, J=5.7, 8.5, 6.4 Hz, 1H), 6.75 (t, J=7.4 Hz, 1H), 7.07 (d, J=8.8 Hz, 2H), 7.21 (dd, J=8.8, 7.4 Hz, 2H). Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.22; H, 10.02; N, 13.54.

4.3.19. 2,3,5-Trimethyl-4-(dimethylphenylsilyl)-1-phenyl-3-pyrazoline (**7g**)

Yield 86% (when the reaction mixture was hydrolyzed with water) and 42% (hydrolyzed with aqueous NH_4Cl); oil, R_f 0.62 (CH_2Cl_2); IR ($CHCl_3$) 1600, 1490, 1250, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.49 (s, 3H), 0.51 (s, 3H), 1.20 (d, J=6.4 Hz, 3H), 1.80 (s, 3H), 2.63 (s, 3H), 3.53 (q, J=6.4 Hz, 1H), 7.10 (t, J=7.8 Hz, 1H), 7.23 (d, J=8.1 Hz, 2H), 7.32 (dd, J=7.8, 8.1 Hz, 2H), 7.40–7.70 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.15, 0.24, 14.36, 31.13, 43.22, 56.40, 112.63, 120.31, 125.31, 127.36, 128.66, 129.62, 133.42, 138.65, 139.86, 151.36. Anal. Calcd for $C_{20}H_{26}N_2Si$: C, 74.48; H, 8.13; N, 8.69. Found: C, 74.30; H, 7.96; N, 8.92.

4.3.20. 1,3,5-Trimethyl-4-(dimethylphenylsilyl)-2-phenyl-3-pyrazoline (**8g**)

Yield 42%; oil, R_f 0.61 (CH_2Cl_2); IR ($CHCl_3$) 1601, 1494, 1255, 1119 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.43 (s, 3H), 1.12 (d, J=6.4 Hz, 3H), 2.09 (s, 3H), 2.51 (s, 3H), 3.37 (q, J=6.4 Hz, 1H), 6.79 (t, J=7.8 Hz, 1H), 6.87 (d, J=7.8 Hz, 2H), 7.22 (t, J=7.8 Hz, 2H), 7.31–7.75 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −0.01, 15.19, 30.81, 42.01, 57.60, 113.30, 119.29, 124.58, 127.65, 129.08, 129.20, 132.94, 139.24, 139.75, 148.40. Anal. Calcd for $C_{20}H_{26}N_2Si$: C, 74.48; H, 8.13; N, 8.69. Found: C, 74.66; H, 8.28; N, 8.43.

4.3.21. 1,5-Dimethyl-3-(dimethylphenylsilyl)-2-phenyl-3-pyrazoline (**8h**)

Yield 80%; oil, R_f 0.46 (CH_2Cl_2); IR ($CHCl_3$) 1591, 1489, 1255, 1118 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 3H), 0.25 (s, 3H), 1.12 (d, J=6.4 Hz, 3H), 2.65 (s, 3H), 3.49 (dq, J=2.5, 6.4 Hz, 1H), 5.30 (d, J=2.5 Hz, 1H), 6.77 (t, J=7.2 Hz, 1H), 6.90 (d, J=7.7 Hz, 2H), 7.01 (t, J=7.0 Hz, 2H), 7.09–7.68 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −2.40, −2.19, 22.73, 45.31, 68.06, 114.23, 119.27, 123.10, 123.92, 127.63, 128.48, 133.90, 137.64, 145.12, 149.79. Anal. Calcd for $C_{19}H_{24}N_2Si$: C, 73.97; H, 7.84; N, 9.08. Found: C, 74.21; H, 8.01; N, 8.86.

4.3.22. 3-(tert-Butyldiphenylsilyl)-1,5-dimethyl-2-phenyl-3-pyrazoline (**8i**)

Yield 85%; oil, R_f 0.38 (CH_2Cl_2); IR ($CHCl_3$) 1600, 1500, 1108 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 9H), 1.06 (d, J=6.5 Hz, 3H), 2.79 (s, 3H), 3.52 (dq, J=2.6, 6.5 Hz, 1H), 5.85 (d, J=2.6 Hz, 1H), 6.75 (m, 1H), 6.82 (m, 2H), 7.23–7.39 (m, 6H), 7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.04, 22.64, 28.05, 47.08, 68.19, 122.35, 122.88, 127.33, 127.50, 127.87, 129.10, 133.72, 136.05, 139.69, 150.41. Anal. Calcd for $C_{27}H_{32}N_2Si$: C, 78.59; H, 7.82; N, 6.79. Found: C, 78.84; H, 7.66; N, 7.05.

4.4. Reactions of silylated isoxazolium salts with organolithium reagents. General procedure

To a stirred solution of the isoxazolium salt (1 mmol) in dry THF (10 mL) at −78, 0 °C or rt, under N_2, was added the organolithium (1 mmol). The reaction mixture was stirred at this temperature until TLC indicated complete reaction. When the reaction was carried out at 0 °C or rt, the mixture was quenched with aqueous NH_4Cl, and with methanol in the reactions at −78 °C and workup with Et_2O. The ethereal layer was dried ($MgSO_4$) and the solvents removed. The residue was purified by flash chromatography to give the following products.

4.4.1. 2-Ethyl-3-methyl-4-(dimethylphenylsilyl)-3,5-diphenyl-4-isoxazoline (**9a**)

Yield 28%; oil, R_f 0.58 (CH_2Cl_2); IR ($CHCl_3$) 1632, 1597, 1490, 1250, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0. 08 (s, 3H), −0.03 (s, 3H), 1.15 (t, J=7.0 Hz, 3H), 1.77 (s, 3H), 2.54 (m, 2H), 7.18–7.54(m, 15H); ^{13}C NMR ($CDCl_3$) δ −1.00, 13.94, 23.38, 46.45, 77.59, 110.44, 127.32, 127.58, 127.73, 127.83, 128.04, 128.51, 129.01, 130.96, 133.88, 139.19, 142.29, 160.78. Anal. Calcd for $C_{26}H_{29}NOSi$: C, 78.15; H, 7.31; N, 3.51. Found: C, 77.93; H, 7.48; N, 3.76.

4.4.2. 3-Butyl-2-ethyl-4-(dimethylphenylsilyl)-3,5-diphenyl-4-isoxazoline (**9b**)

Yield 12% (at −78 °C), 35% (at 0 °C), and 58% (at rt); oil, R_f 0.42 (hexane–CH_2Cl_2, 1:2); IR ($CHCl_3$) 1636, 1593, 1490, 1257, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 3H), 0.02 (s, 3H), 0.93 (t, J=7.2 Hz, 3H), 1.11 (t, J=7.0 Hz, 3H), 1.31 (m, 4H), 1.80 (m, 1H), 2.03 (m, 1H), 2.33 (dq, J=13.0, 7.0 Hz, 1H), 2.53 (dq, J=13.0, 7.0 Hz, 1H), 7.14–7.57 (m, 15H); ^{13}C NMR ($CDCl_3$) δ −0.99, −0.76, 14.09, 14.27, 23.26, 27.55, 36.50, 47.76, 81.20, 108.19, 127.15, 127.24, 127.67, 127.78, 128.30, 128.45, 129.02, 129.20, 131.17, 132.94, 133.96, 138.61, 141.84, 160.55. Anal. Calcd for $C_{29}H_{35}NOSi$: C, 78.86; H, 7.99; N, 3.17. Found: C, 79.08; H, 8.22; N, 2.89.

4.4.3. 5-tert-Butyl-2-ethyl-4-(dimethylphenylsilyl)-3,5-diphenyl-3-isoxazoline (**10a**)

Yield 43%; oil, R_f 0.44 (hexane–AcOEt, 10:1); IR ($CHCl_3$) 1630, 1600, 1490, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 3H), 0.33 (s, 3H), 0.98 (s, 9H), 1.13 (t, J=7.0 Hz, 3H), 2.81 (dq, J=13.5, 7.0 Hz, 1H), 3.00 (dq, J=13.5, 7.0 Hz, 1H), 7.28–7.47 (m, 15H). Anal. Calcd for $C_{29}H_{35}NOSi$: C, 78.86; H, 7.99; N, 3.17. Found: C, 78.61; H, 8.19; N, 3.42.

4.4.4. 5-Butyl-2-ethyl-4-(dimethylphenylsilyl)-3,5-diphenyl-3-isoxazoline (**10b**)

Yield 61% (at −78 °C), 40% (at 0 °C), and 21% (at rt); oil, R_f 0.21 (hexane–CH_2Cl_2, 1:2); IR ($CHCl_3$) 1625, 1593, 1490, 1255, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.38 (s, 3H), 0.47 (s, 3H), 0.86 (t, J=7.0 Hz, 3H), 1.19 (t, J=7.0 Hz, 3H), 1.31 (m, 4H), 1.98 (m, 2H), 2.95 (dq, J=13.6, 7.1 Hz, 1H), 3.09 (dq, J=13.6, 7.1 Hz, 1H), 7.24–7.50 (m, 15H). Anal. Calcd for $C_{29}H_{35}NOSi$: C, 78.86; H, 7.99; N, 3.17. Found: C, 78.53; H, 7.84; N, 3.36.

4.4.5. Z-3-(Isopropylamino)-1,3-diphenylprop-2-en-1-one (**11a**)

Yield 25%; oil, R_f 0.34 (CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.22 (d, J=6.4 Hz, 6H), 3.65 (d, sep, J=7.2, 6.4 Hz, 1H), 5.70 (s, 1H), 7.31–7.54 (m, 8H), 7.90 (m, 2H), 11.33 (br d, J=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.65, 51.32, 103.77, 120.96, 122.06, 123.89, 127.43, 128.47, 129.26, 133.46, 135.47, 159.62, 196.43. Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.23; H, 6.99; N, 5.44.

4.4.6. Z-3-(Ethylamino)-1,3-diphenylprop-2-en-1-one (**11b**)

Yield 21%; oil, R_f 0.46 (CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.23 (t, J=7.2 Hz, 3H), 3.27 (q, J=7.2 Hz, 2H), 5.77 (s, 1H), 7.35–7.98 (m, 10H), 11.37 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.82, 40.12, 104.31, 126.65, 127.15, 127.62, 128.72, 130.07, 131.08, 133.21, 138.75, 172.35, 192.04. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 80.96; H, 7.08; N, 5.77.

4.4.7. Z-1,3-Diphenyl-3-(1-phenylethylamino)prop-2-en-1-one (**11c**)

Yield 44%; oil, R_f 0.44 (CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.55 (d, J=6.3 Hz, 3H), 4.60 (dq, J=7.1, 6.3 Hz, 1H), 5.70 (s, 1H), 6.80–8.10 (m, 15H), 11.85 (br d, J=7.1 Hz, 1H). Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.63; H, 6.59; N, 4.47.

*4.4.8. 5-(tert-Butyldiphenylsilyl)-2-ethyl-3-methyl-3-phenyl-4-isoxazoline (**12a**)*

Yield 52%; oil, R_f 0.50 (hexane–CH_2Cl_2, 1:10); ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9H), 1.23 (t, J=7.0 Hz, 3H), 1.64 (s, 3H), 2.51–2.69 (m, 2H), 5.24 (s, 1H), 7.25–7.73 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 13.72, 18.28, 27.62, 47.78, 72.90, 123.05, 127.14, 127.66, 128.10, 129.54, 133.08, 136.07, 153.75. Anal. Calcd for $C_{28}H_{33}NOSi$: C, 78.64; H, 7.78; N, 3.28. Found: C, 78.86; H, 7.61; N, 2.97.

*4.4.9. 3-Butyl-5-(tert-butyldiphenylsilyl)-2-ethyl-3-phenyl-4-isoxazoline (**12b**)*

Yield 63%; oil, R_f 0.33 (hexane–CH_2Cl_2, 1:1); IR ($CHCl_3$) 1625, 1500, 1107 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J=7.0 Hz, 3H), 0.88–1.30 (m, 9H), 1.20 (s, 9H), 1.25 (t, J=7.3 Hz, 3H), 2.07 (dt, J=14.5, 7.0 Hz, 1H), 2.19 (m, 2H), 2.52 (dq, J=12.8, 7.3 Hz, 1H), 5.40 (s, 1H), 7.28–7.45 (m, 11H), 7.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.57, 13.81, 18.27, 23.07, 26.64, 27.56, 40.61, 48.03, 120.59, 127.34, 127.64, 128.04, 128.13, 129.52, 133.15, 136.04, 139.70, 154.56. Anal. Calcd for $C_{31}H_{39}NOSi$: C, 79.26; H, 8.37; N, 2.98. Found: C, 78.93; H, 8.52; N, 3.28.

*4.4.10. 5-(tert-Butyldiphenylsilyl)-2-ethyl-3,3-diphenyl-4-isoxazoline (**12c**)*

Yield 66%; oil, R_f 0.68 (hexane–CH_2Cl_2, 1:10); IR ($CHCl_3$) 1593, 1471, 1109 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 9H), 1.27 (t, J=7.0 Hz, 3H), 2.31 (q, J=7.0 Hz, 2H), 5.58 (s, 1H), 7.26–7.74 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 13.77, 18.31, 26.74, 49.12, 79.90, 121.26, 126.89, 127.12, 127.21, 127.65, 127.99, 128.21, 129.03, 129.50, 133.02, 133.40, 135.48, 135.96, 141.19, 143.90, 154.20. Anal. Calcd for $C_{33}H_{35}NOSi$: C, 80.93; H, 7.20; N, 2.86. Found: C, 81.26; H, 7.35; N, 3.11.

*4.4.11. 3-tert-Butyl-5-(tert-butyldiphenylsilyl)-2-ethyl-3-phenyl-4-isoxazoline (**12d**)*

Yield 63% (at −75 °C), 10% (at 0 °C); oil, R_f 0.75 (hexane–CH_2Cl_2, 1:10); IR ($CHCl_3$) 1596, 1500, 1108 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.20 (t, J=7.2 Hz, 3H), 1.20 (s, 9H), 2.30 (dq, J=13.0, 7.2 Hz, 1H), 2.71 (dq, J=13.0, 7.2 Hz, 1H), 5.26 (s, 1H), 7.21–7.48 (m, 10H), 7.74 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.95, 18.28, 27.28, 27.63, 39.37, 51.11, 83.42, 118.04, 126.91, 127.63, 129.50, 130.56, 133.36, 135.46, 136.21, 138.78, 152.85. Anal. Calcd for $C_{31}H_{39}NOSi$: C, 79.26; H, 8.37; N, 2.98. Found: C, 79.49; H, 8.18; N, 2.73.

*4.4.12. Z-1-(tert-Butyldiphenylsilyl)-3-(ethylamino)-3-phenylprop-2-en-1-one (**13a**)*

Yield 11% (at −75 °C), 61% (at 0 °C); oil, R_f 0.43 (hexane–CH_2Cl_2, 1:10); IR ($CHCl_3$) 3155, 1610, 1589, 1564, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J=7.3 Hz, 3H), 1.21 (s, 9H), 3.20 (q, J=7.3 Hz, 2H), 5.39 (s, 1H), 7.31–7.45 (m, 11H), 7.72 (m, 4H), 12.23 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.00, 18.48, 28.04, 39.38, 106.79, 127.47, 127.58, 128.29, 129.06, 129.24, 133.98, 134.62, 136.38, 162.75, 217.95. Anal. Calcd for $C_{27}H_{31}NOSi$: C, 78.40; H, 7.55; N, 3.39. Found: C, 78.65; H, 7.71; N, 3.63.

*4.4.13. Z-5-(tert-Butyldiphenylsilylmethylen)-2-ethyl-3-methyl-3-isoxazoline (Z-**14a**)*

Yield 14%; oil, R_f 0.68 (CH_2Cl_2); IR ($CHCl_3$) 1610, 1105, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.74 (t, J=7.0 Hz, 3H), 1.05 (s, 9H), 1.87 (s, 3H), 3.01 (q, J=7.0 Hz, 2H), 3.97 (s, 1H), 5.38 (s, 1H), 7.30–7.75 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.03, 18.56, 27.76, 28.47, 51.63, 69.36, 104.12, 127.31, 128.32, 135.45, 136.81, 163.25, 171.22. Anal. Calcd for $C_{23}H_{29}NOSi$: C, 75.98; H, 8.04; N, 3.85. Found: C, 76.20; H, 7.88; N, 4.11.

*4.4.14. E-5-(tert-Butyldiphenylsilylmethylen)-2-ethyl-3-methyl-3-isoxazoline (E-**14a**)*

Yield 28%; oil, R_f 0.68 (CH_2Cl_2); IR ($CHCl_3$) 1610, 1105, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 9H), 1.20 (t, J=7.0 Hz, 3H), 1.70 (s, 3H), 3.25 (q, J=7.0 Hz, 2H), 4.32 (s, 1H), 4.53 (s, 1H), 7.30–7.75 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.57, 17.64, 27.31, 28.83, 50.43, 68.41, 103.61, 127.68, 128.91, 134.31, 137.71, 162.43, 170.12. Anal. Calcd for $C_{23}H_{29}NOSi$: C, 75.98; H, 8.04; N, 3.85. Found: C, 75.73; H, 8.23; N, 3.59.

*4.4.15. Z-3-tert-Butyl-5-(tert-butyldiphenylsilylmethylen)-2-ethyl-3-isoxazoline (Z-**14b**)*

Yield 38%; oil, R_f 0.66 (CH_2Cl_2); IR ($CHCl_3$) 1609, 1106, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75 (t, J=6.9 Hz, 3H), 1.05 (s, 9H), 1.22 (s, 9H), 3.12 (q, J=6.9 Hz, 2H), 3.99 (s, 1H), 5.42 (s, 1H), 7.35 (m, 6H), 7.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 10.84, 18.23, 27.83, 29.49, 31.62, 50.48, 68.73, 103.59, 127.06, 128.28, 136.05, 136.75, 164.45, 170.46. Anal. Calcd for $C_{26}H_{35}NOSi$: C, 76.98; H, 8.70; N, 3.45. Found: C, 77.25; H, 8.83; N, 3.22.

*4.4.16. E-3-tert-Butyl-5-(tert-butyldiphenylsilylmethylen)-2-ethyl-3-isoxazoline (E-**14b**)*

Yield 47%; oil, R_f 0.66 (CH_2Cl_2); IR ($CHCl_3$) 1609, 1106, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 9H), 1.07 (s, 9H), 1.23 (t, J=6.9 Hz, 3H), 3.37 (q, J=6.9 Hz, 2H), 4.32 (s, 1H), 4.43 (s, 1H), 7.35 (m, 6H), 7.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 11.39, 18.44, 27.60, 29.23, 31.54, 50.37, 67.22, 101.62, 127.34, 128.64, 136.35, 136.75, 165.21, 169.61. Anal. Calcd for $C_{26}H_{35}NOSi$: C, 76.98; H, 8.70; N, 3.45. Found: C, 76.74; H, 8.55; N, 3.71.

*4.4.17. Z-5-(tert-Butyldiphenylsilylmethylen)-2-ethyl-3-phenyl-3-isoxazoline (Z-**14c**)*

Yield 20%; oil, R_f 0.62 (CH_2Cl_2); IR ($CHCl_3$) 1613, 1102, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.72 (t, J=7.0 Hz, 3H), 1.06 (s, 9H), 3.02 (q, J=7.0 Hz, 2H), 4.24 (s, 1H), 5.84 (s, 1H), 7.14–7.75 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 10.31, 18.29, 27.83, 50.46, 72.36, 105.07, 126.93, 127.17, 128.45, 128.71, 129.14, 134.80, 136.04, 156.55, 170.54. Anal. Calcd for $C_{28}H_{31}NOSi$: C, 79.01; H, 7.34; N, 3.29. Found: C, 78.84; H, 7.49; N, 3.56.

*4.4.18. E-5-(tert-Butyldiphenylsilylmethylen)-2-ethyl-3-phenyl-3-isoxazoline (E-**14c**)*

Yield 35%; oil, R_f 0.62 (CH_2Cl_2); IR ($CHCl_3$) 1613, 1102, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9H), 1.19 (t, J=7.0 Hz, 3H), 3.30 (q, J=7.0 Hz, 2H), 4.56 (s, 1H), 4.92 (s, 1H), 7.14–7.79 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 10.88, 18.43, 27.53, 50.39, 70.43, 102.95, 127.05, 127.50, 128.71, 128.81, 129.14, 134.80, 136.29, 157.43, 169.88. Anal. Calcd for $C_{28}H_{31}NOSi$: C, 79.01; H, 7.34; N, 3.29. Found: C, 78.91; H, 7.18; N, 2.96.

*4.4.19. E-5-tert-Butyl-3-(tert-butyldiphenylsilylmethylen)-2-ethyl-4-isoxazoline (**15a**)*

Yield 40 and 95% (with BuLi at −78 and 0 °C, respectively), 85% (with MeLi at −78 °C), 80% (with ^{t}BuLi at −78 °C); oil, R_f 0.67 (CH_2Cl_2); IR ($CHCl_3$) 1624, 1578, 1104, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9H), 1.05 (s, 9H), 1.22 (t, J=7.0 Hz, 3H), 3.57 (q, J=7.0 Hz, 2H), 3.98 (s, 1H), 4.43 (s, 1H), 7.28–7.45 (m, 6H), 7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 9.53, 18.51, 27.68, 27.78, 31.90, 50.55, 71.06, 96.67, 127.35, 128.61, 135.32, 136.28, 164.70, 172.49. Anal. Calcd for $C_{26}H_{35}NOSi$: C, 76.98; H, 8.70; N, 3.45. Found: C, 77.29; H, 8.88; N, 3.69.

*4.4.20. E-3-(tert-Butyldiphenylsilylmethylen)-2-ethyl-5-phenyl-4-isoxazoline (**15b**)*

Yield 40 and 95% (with BuLi at −78 and 0 °C, respectively), 82%; oil, R_f 0.60 (CH_2Cl_2); IR ($CHCl_3$) 1625, 1599, 1579, 1450, 1104, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9H), 1.36 (t, J=7.0 Hz, 3H), 3.69 (q, J=7.0 Hz, 2H), 4.20 (s, 1H), 5.19 (s, 1H), 7.31–7.43 (m, 10H), 7.80 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.15, 18.44, 27.60, 51.05, 73.83, 98.67, 125.42, 127.52, 127.61, 128.37, 128.78, 136.02, 136.24, 160.50, 164.27.

Anal. Calcd for $C_{28}H_{31}NOSi$: C, 79.01; H, 7.34; N, 3.29. Found: C, 79.23; H, 7.48; N, 3.51.

*4.4.21. 3-Butyl-5-tert-butyl-3-(tert-butyldiphenylsilylmethyl)-2-ethyl-4-isoxazoline (**16a**)*

Yield 40; oil, R_f 0.45 (hexane–CH_2Cl_2, 1:2); ^{1}H NMR ($CDCl_3$) δ 0.68 (t, J=7.1 Hz, 3H), 0.84–1.15 (m, 6H), 0.98 (s, 9H), 1.02 (s, 9H), 1.19 (t, J=6.9 Hz, 3H), 1.56 (d, J=14.4 Hz, 1H), 1.79 (d, J=14.4 Hz, 1H), 2.73 (q, J=6.9 Hz, 2H), 3.94 (s, 1H), 7.32–7.42 (m, 6H), 7.68 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.61, 13.90, 18.45, 22.91, 26.82, 27.89, 28.02, 29.69, 31.06, 37.40, 45.22, 72.81, 99.85, 127.17, 127.35, 128.95, 129.01, 135.16, 135.38, 136.55, 160.93. Anal. Calcd for $C_{30}H_{45}NOSi$: C, 77.69; H, 9.78; N, 3.02. Found: C, 77.92; H, 9.95; N, 2.80.

4.5. Reactions of silyl isoxazolium salts with lithium dimethylcuprate. General procedure

To a stirred solution of the isoxazolium salt (1 mmol) under N_2, in dry THF (3 mL) at 0 °C, was added a THF solution of the lithium dimethylcuprate reagent [prepared from Me Li and cuprous iodide] (1 mmol). The reaction mixture was stirred at this temperature until TLC indicated that the reaction was complete. The mixture was quenched with aqueous NH_4Cl. The organic layer was extracted with Et_2O, dried with $MgSO_4$, and the solvents removed under reduced pressure. The residue was purified by flash chromatography to give the following products.

*4.5.1. Z-4-(Ethylamino)pent-3-en-2-one (**11d**)*

Yield: 91%; oil, R_f 0.57 (CH_2Cl_2); IR ($CHCl_3$) 3240, 1620, 1595, 1501, 752, 680 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, J=7.1 Hz, 3H), 1.92 (s, 3H), 2.00 (s, 3H), 3.24 (dq, J=5.9, 7.1 Hz, 2H), 4.95 (s, 1H), 10.80 (br s, 1H). Anal. Calcd for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 65.97; H, 10.11; N, 10.79.

*4.5.2. Z-1-(tert-Butyldiphenylsilyl)-3-(ethylamino)-3-phenylprop-2-en-1-one (**13a**)*

Yield 91%.

*4.5.3. Z-1-(tert-Butyldiphenylsilyl)-3-(ethylamino)but-2-en-1-one (**13b**)*

Yield 52%; oil, R_f 0.42 (CH_2Cl_2); IR ($CHCl_3$) 3150, 1592, 1517, 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 9H), 1.27 (t, J=7.1 Hz, 3H), 1.83 (s, 3H), 3.28 (dq, J=6.2, 7.1 Hz, 2H), 5.27 (s, 1H), 7.33–7.46 (m, 6H), 7.68–7.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 15.14, 18.24, 18.44, 28.08, 37.78, 106.35, 127.49, 129.01, 134.25, 136.39, 161.53, 215.63. Anal. Calcd for $C_{22}H_{29}NOSi$: C, 75.16; H, 8.31; N, 3.98. Found: C, 74.93; H, 8.45; N, 4.27.

*4.5.4. Z-3-(Ethylamino)-1-(trimethylsilyl)but-2-en-1-one (**13c**)*

Yield 75%; oil, R_f 0.10 (CH_2Cl_2); IR ($CHCl_3$) 3150, 1592, 1517, 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.26 (t, J=7.1 Hz, 3H), 1.95 (s, 3H), 3.29 (dq, J=7.3, 7.1 Hz, 2H), 5.42 (s, 1H), 12.20 (br s, 1H). Anal. Calcd for $C_9H_{19}NOSi$: C, 58.32; H, 10.33; N, 7.56. Found: C, 58.55; H, 10.47; N, 7.31.

*4.5.5. Z-3-tert-Butyl-5-(tert-butyldiphenylsilylmethylen)-2-ethyl-3-isoxazoline (Z-**14b**)*

Yield 36%.

*4.5.6. E-3-tert-Butyl-5-(tert-butyldiphenylsilylmethylen)-2-ethyl-3-isoxazoline (E-**14b**)*

Yield 47%.

*4.5.7. E-5-tert-Butyl-3-(tert-butyldiphenylsilylmethylen)-2-ethyl-4-isoxazoline (**15a**)*

Yield 90%.

*4.5.8. E-3-(tert-Butyldiphenylsilylmethylen)-2-ethyl-5-phenyl-4-isoxazoline (**15b**)*

Yield 56%.

*4.5.9. Z-1-(tert-Butyldiphenylsilyl)-4-(ethylamino)pent-3-en-2-one (**17a**)*

Yield 72%; oil, R_f 0.16 (CH_2Cl_2); IR ($CHCl_3$) 3155, 1605, 1561, 1104 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9H), 1.14 (t, J=7.1 Hz, 3H), 1.63 (s, 3H), 2.51 (s, 2H), 3.15 (q, J=7.1 Hz, 2H), 4.46 (s, 1H), 7.31–7.43 (m, 6H), 7.61–7.74 (m, 4H), 10.36 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 15.56, 18.47, 18.68, 27.72, 30.39, 37.43, 96.54, 127.32, 128.99, 134.70, 136.21, 161.01, 195.25. Anal. Calcd for $C_{23}H_{31}NOSi$: C, 75.56; H, 8.55; N, 3.83. Found: C, 75.78; H, 8.41; N, 4.06.

*4.5.10. Z-1-(tert-Butyldiphenylsilyl)-4-(ethylamino)-4-phenylbut-3-en-2-one (**17b**)*

Yield 79%; oil, R_f 0.30 (CH_2Cl_2); IR ($CHCl_3$) 3155, 1610, 1599, 1107 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (t, J=7.1 Hz, 3H), 1.12 (s, 9H), 2.62 (s, 2H), 3.02 (q, J=7.1 Hz, 2H), 4.58 (s, 1H), 6.94 (m, 2H), 7.24–7.43 (m, 9H), 7.74 (m, 4H), 10.29 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.31, 18.70, 27.67, 30.95, 39.00, 98.44, 127.40, 127.58, 128.02, 128.86, 129.03, 134.48, 135.63, 136.23, 163.26, 196.20. Anal. Calcd for $C_{28}H_{33}NOSi$: C, 78.64; H, 7.78; N, 3.28. Found: C, 78.38; H, 7.91; N, 2.93.

Acknowledgements

We thank the Ministerio de Ciencia y Tecnología of Spain for supporting this work.

References and notes

1. González-Nogal, A. M.; Calle, M.; Cuadrado, P.; Valero, R. *Tetrahedron* **2007**, *63*, 224–231.
2. (a) Cuadrado, P.; González-Nogal, A. M. *Tetrahedron Lett.* **1998**, *39*, 1449–1452; (b) González-Nogal, A. M.; Calle, M.; Calvo, L. A.; Cuadrado, P.; González-Ortega, A. *Eur. J. Org. Chem.* **2005**, 4663–4669.
3. González-Nogal, A. M.; Calle, M.; Cuadrado, P. *Eur. J. Org. Chem.* **2007**, 6089–6096.
4. Calle, M.; Cuadrado, P.; González-Nogal, A. M.; Valero, R. *Synthesis* **2001**, 1949–1958.
5. Cuadrado, P.; González-Nogal, A. M.; Valero, R. *Tetrahedron* **2002**, *58*, 4975–4980.
6. Calvo, L. A.; González-Nogal, A. M.; González-Ortega, A.; Sañudo, M. C. *Tetrahedron Lett.* **2001**, *42*, 8981–8984.
7. Calle, M.; Calvo, L. A.; González-Ortega, A.; González-Nogal, A. M. *Tetrahedron* **2006**, *62*, 611–618.
8. Nesi, R.; Ricci, A.; Taddei, M.; Tedeschi, P.; Seconi, G. *J. Organomet. Chem.* **1980**, *195*, 275–283.
9. Oshima, K. In *Science of Synthesis. Houben-Weyl Methods of Molecular Transformations*; Fleming, I., Ed.; Thieme: Stuttgart, 2001; Vol. 4, pp 743–754.
10. (a) Padwa, A.; Kline, D. N.; Perumattan, J. *Tetrahedron Lett.* **1987**, *28*, 913–916; (b) Ishikawa, T.; Kudoh, T.; Yoshida, J.; Yasuhara, A.; Manabe, S.; Saito, S. *Org. Lett.* **2002**, *4*, 1907–1910.
11. Ahn, C.; Kennington, J. W.; DeShong, P. *J. Org. Chem.* **1994**, *59*, 6282–6286.
12. (a) Fleming, I. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, pp 563–593; (b) Sarkar, T. K. In *Science of Synthesis. Houben-Weyl Methods of Molecular Transformations*; Fleming, I., Ed.; Thieme: Stuttgart, 2001; Vol. 4, pp 837–838 901–919.
13. Elguero, J.; Jacquier, R.; Tizané, D. *Bull. Soc. Chim. Fr.* **1970**, 1121–1129.
14. Cuadrado, P.; González-Nogal, A. M.; Martínez, S. *Tetrahedron* **1997**, *53*, 8585–8598.
15. Irradiation of the exocyclic olefinic proton showed enhancement of the CH_2N group.
16. (a) Kuckländer, U. Enaminones as Synthones. In *The Chemistry of Functional Groups*; Rappoport, Z., Ed.; Wiley-Interscience: New York, NY, 1994; Part 1, Chapter 10; (b) Lue, P.; Greenhill, J. V. *Adv. Heterocycl. Chem.* **1997**, *67*, 207–215.
17. (a) Page, P. C. B.; Mc Kenzie, M. J. In *Science of Synthesis. Houben-Weyl Methods of Molecular Transformations*; Fleming, I., Ed.; Thieme: Stuttgart, 2001; Vol. 4, pp 513–514, 543–561; (b) Linghu, X.; Potnick, J. R.; Johonson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 3070–3071; (c) Nahm, M. R.; Linghu, X.; Potnick, J. R.; Yates, C. M.; White, P. S.; Johnson, J. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2377–2379; (d) Mattson, A. E.; Bharadwa, A. R.; Zuhl, A. M.; Scheidt, K. A. *J. Org. Chem.* **2006**, *71*, 5715–5724.
18. Landais, Y. In *Science of Synthesis. Houben-Weyl Methods of Molecular Transformations*; Fleming, I., Ed.; Thieme: Stuttgart, 2001; Vol. 4, pp 757–760.