Tetrahedron

1,3-Dipolar cycloadditions of silicon and tin alkynes and alkenes. Regiospecific synthesis of silyl and stannylpyrazoles and pyrazolines

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Abstract—Silicon and tin 3-, 3,5-, and 3,4,5-metalated pyrazoles have been synthesized by 1,3-dipolar cycloadditions of silyl-, disilyl-, and silylstannylacetylenes with *N*-phenylsydnone or trimethylsilyldiazomethane. On the other hand, 1- and 2-pyrazolines monometalated and dimetalated in different positions of the heterocycle have been prepared by reaction of vinylsilanes and vinylstannanes with the same 1,3-dipolar reagents. Other interesting products resulting from homologation were obtained by cycloaddition of trimethylsilyldiazomethane with β-silyl enones and esters. Moreover, for the first time a 3-silylpyrazole has been converted into a 3-cyanopyrazole.
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1. Introduction

1,3-Dipolar cycloadditions of silicon or tin metalated alkynes[1–3] and alkenes[4–9] with nitrile oxides have been used largely to prepare metalated isoxazoles and isoxazolines. Nevertheless, the use of these substrates to synthesize silyl and stannylpyrazoles and pyrazolines have not been very explored. The synthesis of 4-silyl- and 3,4-disilylpyrazoles by cycloaddition of silyl and disilylacetylenes with diazomethane has been described.[10,11] Disubstituted diazomethanes afforded 4-silyl-3*H*-pyrazole derivatives.[12] One single reference has been reported with regard to the cycloaddition of tributylstannylacetylene[13] with diazomethane or ethyl diazoacetate and *N*-phenylsydnone, to give regioselectively the corresponding 3-tributylstannylpyrazole. On the other hand, the reaction of vinylsilanes[14] with diazomethane or monosubstituted diazomethanes led to unstable 4-silyl-1-pyrazolines, which are opened with rearrangement of the silyl group, affording acyclic products. Meanwhile, the 3-silyl-1-pyrazolines resulting from the cycloaddition of these substrates to disubstituted diazomethanes could be isolated at room temperature. Birkofer and Kühn[15] synthesized, for the first time, 3,4-bis-trimethylsilyl-1-pyrazolines by reaction of *trans*-1,2-bis-trimethylsilylethylenes with diazomethane.

Previously, we reported[16] the regioselective synthesis of 4- or 5-silylated and stannylated pyrazoles by silyl and stannylcuprations of 4-halopyrazoles or lithiation with LDA of 5-unsubstituted pyrazoles and the subsequent treatment with chlorosilanes or chlorostannanes. Furthermore, starting from 5-unsubstituted 4-halopyrazoles using both procedures, we were able to synthesize a variety of 4,5-dimetalated pyrazoles bearing different silyl and tin groups. Moreover, we synthesized 5-silylpyrazoles by heating β-silylalkynones with hydrazines or 4-functionalized 5-silylpyrazoles by cyclization of the resulting hydrazones in the presence of some electrophiles.[17] More recently, we have regioselectively synthesized 3- or 5-silylpyrazoles and 3-, 4-, or 5-silylmethylpyrazoles by reaction with hydrazines of β-enaminoenones substituted by different silyl groups in various positions of the enaminoketonic system.[18] We have also prepared for the first time, 5-silyl 3-pyrazolines and 3-silylindazolines by reaction of pyrazolium and indazolium salts with silyllithium reagents.[19] This is a reaction without counterpart in carbon chemistry due to the fact that the pyrazolium salts were shown to be unreactive toward organolithium reagents.

In this paper, we describe the results obtained in the regiospecific synthesis of silicon and tin 3-, 3,5-, or 3,4,5-metalated pyrazoles by 1,3-dipolar cycloadditions of silyl-, disilyl-, or silylstannylalkynes with *N*-phenylsydnone or trimethylsilyldiazomethane. Moreover, the regiospecific synthesis of 1- and 2-pyrazolines metalated in different positions of the heterocycle has been possible using vinylsilanes and vinylstannanes as substrates in the cycloaddition reactions with the cited 1,3-dipolar reagents.

2. Results and discussion

### 2.1. Silyl- and stannylacetylenes as dipolarophiles

2.1.1. Cycloadditions with trimethylsilyldiazomethane.
Although the presence of a silyl or tin group reduces the reactivity as dipolarophiles of alkynes, we have prepared 3,5-disilyl-, 3,4,5-trisilyl-, and 3,5-disilyl-4-stannylpyrazoles by reaction of silyl-, disilyl-, and silylstannylalkynes with trimethylsilyldiazomethane at reflux of THF (Scheme 1).
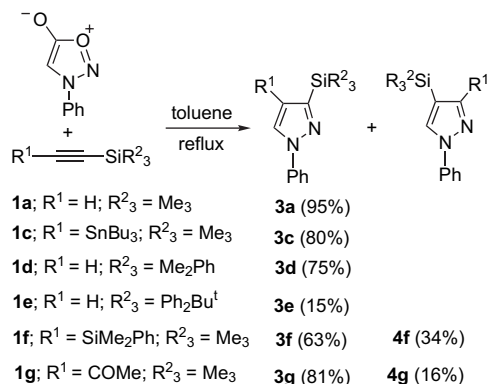

1a; R = H
1b; R = SiMe$_3$
1c; R = SnBu$_3$

2a; R = H
2b; R = SiMe$_3$
2c; R = SnBu$_3$
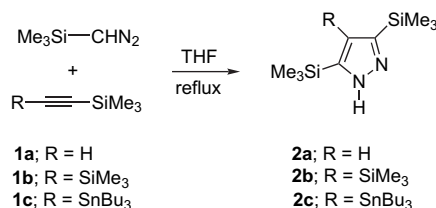
Scheme 1.

These results can be explained by considering the initial formation of the corresponding 3*H*-pyrazoles, which undergo a sigmatropic [1,3]-hydrogen shift leading to the thermodynamically more stable 1*H*-pyrazoles **2**. The regioselectivity observed suggests a steric control, keeping both silyl groups as far away as possible (Scheme 2).


R = H, SnBu$_3$
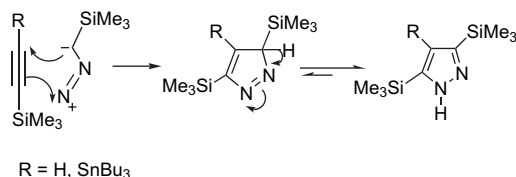
Scheme 2.

2.1.2. Cycloadditions with *N*-phenylsydnone.
The 1,3-dipolar cycloaddition of these substrates with *N*-phenylsydnone has permitted us to synthesize 1-phenyl-3-silylpyrazoles for the first time with good yields (Scheme 3).

1a; R^1 = H; R$^2_3$ = Me$_3$ **3a** (95%)
1c; R^1 = SnBu$_3$; R$^2_3$ = Me$_3$ **3c** (80%)
1d; R^1 = H; R$^2_3$ = Me$_2$Ph **3d** (75%)
1e; R^1 = H; R$^2_3$ = Ph$_2$Bu^t **3e** (15%)
1f; R^1 = SiMe$_2$Ph; R$^2_3$ = Me$_3$ **3f** (63%) **4f** (34%)
**1g**; R^1 = COMe; R$^2_3$ = Me$_3$ **3g** (81%) **4g** (16%)

Scheme 3.

The reaction is also regiospecific and takes place by the elimination of carbon dioxide from the initial adduct, formed via the orientation shown in Scheme 4. Only when the

β-substituent (R^1) is other silyl or acetyl group the inverse orientation was competitive.
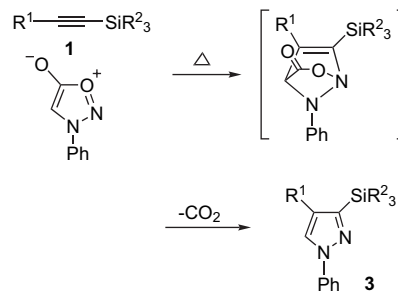
Scheme 4.

This result is very interesting because, as far as we know, the synthesis of *N*-phenyl-3-silylpyrazoles has not been previously described. Moreover, it is worth pointing out that, also for the first time, we have carried out the conversion of a 3-silylpyrazole into a 3-cyanopyrazole. This transformation is especially important because the cyanopyrazoles are compounds with great synthetic applications and difficult to prepare because a cyano group is impossible to introduce directly into the pyrazole nucleus. We have converted the 3-trimethylsilyl group of **3a** in a cyano group by acid hydrolysis of the intermediate resulting from the electrophilic *ipso*-substitution with chlorosulphonyl isocyanate (Scheme 5).


3a

1. ClSO$_2$N=C=O
2. HCl, 0.1 N

5a (86%)
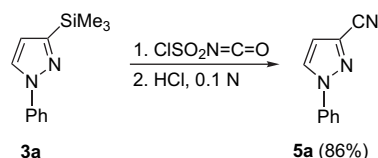
Scheme 5.

### 2.2. Silyl- and stannylalkenes as dipolarophiles

2.2.1. Cycloadditions with trimethylsilyldiazomethane.
We have also investigated the cycloaddition reaction of several vinylsilanes **6a**–**c** and the vinylstannane **6d** with trimethylsilyldiazomethane. We have proved that the silyl- and stannylalkenes are less reactive than the analogous alkynes toward this 1,3-dipole. Even at toluene reflux, only the trimethylsilylalkene **6a** was shown to be reactive toward the trimethylsilyldiazomethane, giving regiospecifically a 2.5:1 mixture of *trans*- and *cis*-3,5-bis-trimethylsilyl-1-pyrazoline **7a**, resulting from the approach shown in Scheme 6 (both silyl groups as far away as possible).

With the aim of increasing the reactivity of silylalkenes as dipolarophiles, we have used vinylsilanes β-substituted by withdrawing groups (acetyl or carbomethoxy). These substrates were shown to be more reactive toward the trimethylsilyldiazomethane, but the reaction was more complex. The cycloaddition of the methyl *E*-3-tert-butyldiphenylsilylpropenoate **6e** was not regioselective, affording a mixture of *trans*-1-*tert*-butyldiphenylsilyl-4-carbomethoxy-5-trimethylsilyl-2-pyrazoline **8a**, methyl *E*-4-*tert*-butyldiphenylsilyl-4-trimethylsilylcrotonate **9a**, and methyl *E*-2-*tert*-butyldiphenylsilyl-4-trimethylsilylbut-3-enoate **10a** (Scheme 7).
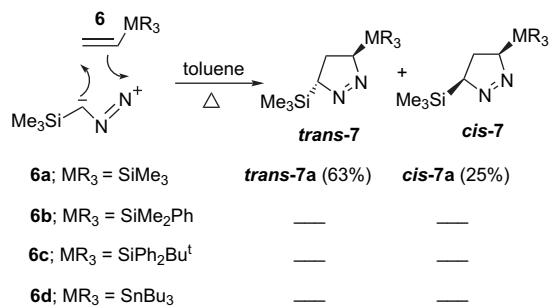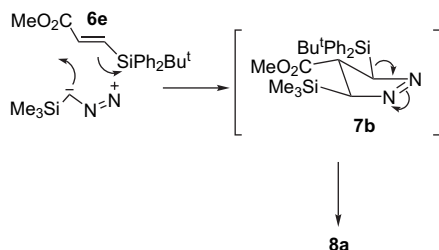
Scheme 6.
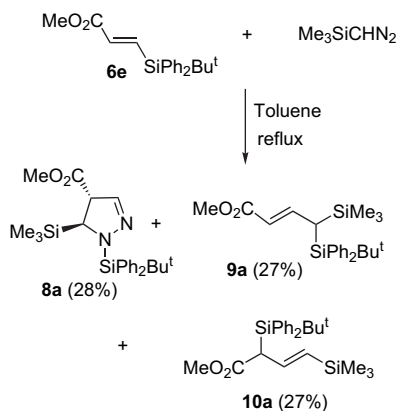
Scheme 7.

It can be postulated that the stereospecific formation of *trans*-2-pyrazoline **8a** arises by way of the cycloadduct **7b** resulting from the orientation in which there are the minimum steric interactions (trimethylsilyl and *tert*-butyldiphenylsilyl groups far away), followed by the 1,3-rearrangement of the *tert*-butyldiphenylsilyl group from carbon to nitrogen. The stereochemistry assigned to the intermediate 1-pyrazoline **7b** has been based on the well-established stereospecificity (retention of the dipolarophile configuration) of 1,3-dipolar cycloadditions and steric control (*anti* relationship between the carbomethoxy and trimethylsilyl groups), the three substituents assuming a pseudoequatorial position in a folded conformation (Scheme 8).
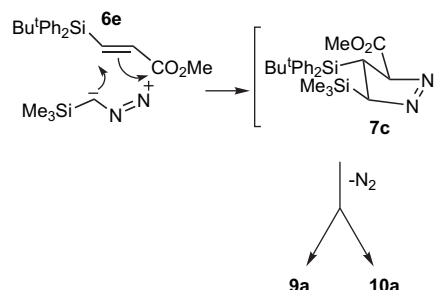

Scheme 8.

The trans geometry of 2-pyrazoline **8a** was confirmed by NOE experiments.[20]

On the other hand, the carbomethoxy group induced the inverse orientation, in which the carbon of the trimethylsilyl-diazomethane is bonded with the β-carbon of the α,

β-unsaturated ester. The initial 1-pyrazoline **7c** experiences nitrogen extrusion with concomitant *tert*-butyldiphenylsilyl migration from C-4 to C-3 and C-5, giving an almost equimolecular mixture of esters **9a** and **10a**. The pseudoequatorial position of the *tert*-butyldiphenylsilyl group at C-4 has an *anti* relationship with the breaking (3)C–N and (5)C–N bonds. This would explain the easily concerted 'backside' migration process and the stereospecific generation of disilylated *trans*-olefinic esters **9a** and **10a** (Scheme 9).
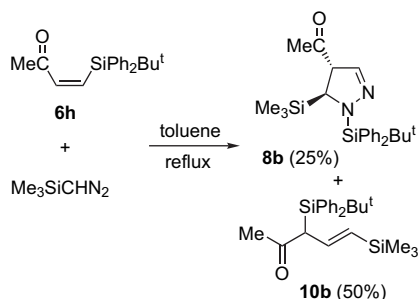

Scheme 9.

The chemical behavior of the trimethylsilyldiazomethane toward *E*-β-silylenones **6f** or **6g** was different to the previously indicated. In both cases, the cycloaddition was regioselective to give a mixture of disilylenones **9b** and **10b** or **9c** and **10c**, respectively (Scheme 10). The acetyl group, more activating[21] than the carbomethoxy group, determines a total preference by the addition of the dipole carbon to the more positive β-carbon of the α,β-unsaturated ketone. The resulting 1-pyrazolines **7d,e** lost nitrogen with concerted *tert*-butyldiphenylsilyl or dimethylphenylsilyl migration from C-4 to C-3 and C-5, to afford the homologation products **9b,c** and **10b,c** (Scheme 10).
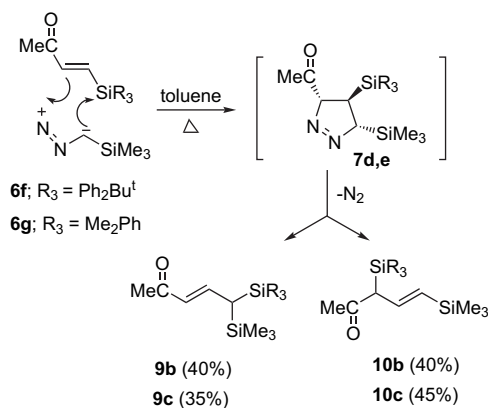
Scheme 10.

Surprisingly, the cycloaddition of this 1,3-dipolar reagent to the *Z*-4-*tert*-butyldiphenylsilyl-3-buten-2-one **6h** was not regioselective, yielding a mixture of *trans*-2-pyrazoline **8b** and the disilylketone **10b** (Scheme 11).

The addition of dipole carbon to α-position of β-silylenone led to the 4-acetyl-3-*tert*-butyldiphenylsilyl-5-trimethyl-silyl-1-pyrazoline **7f**, which was converted into the more
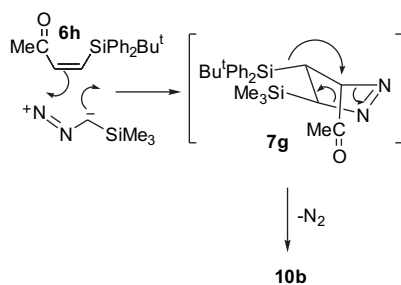
Scheme 11.

stable 4-acetyl-1-*tert*-butyldiphenylsilyl-5-trimethylsilyl-2-pyrazoline **8b** by 1,3-rearrangement of the *tert*-butyl-diphenylsilyl group from carbon to nitrogen. The reaction was stereoselective affording only the trans-isomer (Scheme 12).
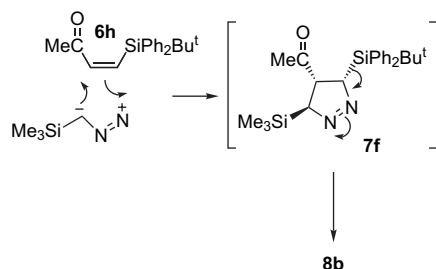
Scheme 12.

The 1-pyrazoline **7g** resulting from the reverse addition was opened with a nitrogen loss and simultaneous *tert*-butyldi-phenylsilyl-rearrangement from C-4 to C-3, exclusively (Scheme 13).
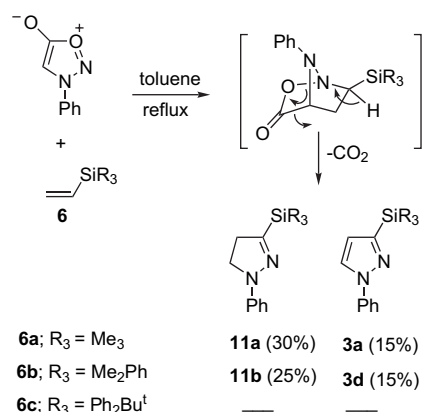

Scheme 13.

Probably, the lack of regioselectivity observed in the reaction with the *Z*-β-silylenone **6h** could be due to the hindered *tert*-butyldiphenylsilyl group, which prevents the co-planarity and conjugation of the acetyl group with the double bond and consequently decreases the activity of the β-position making both orientations competitive. This steric inhibition of the resonance is made clear when the spectroscopy data[22] of the *Z*-β-silylenone **6h** and of its *E*-isomer **6f** are compared.

2.2.2. Cycloadditions with *N*-phenylsydnone. The cycloaddition reactions of *N*-phenylsydnone with vinylsilanes and vinylstannanes proceeded with difficulty. Higher

temperatures and longer reaction times than in the cycloadditions with the silyl and stannylacetylenes were necessary, but the regiochemistry observed was the same. Heating *N*-phenylsydnone with trimethyl- and dimethylphenylsilyl-alkenes **6a** and **6b**, at reflux of toluene, 3-silylated 1-phenyl-2-pyrazolines **11a** and **11b** were obtained, together with the corresponding pyrazoles **3a** and **3d** resulting from their spontaneous aromatization in reaction conditions. These 2-pyrazolines could arise by loss of CO_2 in the adduct resulting from the orientation in which the carbon terminus of *N*-phenylsydnone is bonded to the unsubstituted carbon of the vinylsilane. The more hindered *tert*-butyldiphenylsilyl alkene **6c** was shown to be unreactive (Scheme 14).

Scheme 14.

The evolution of the initial adduct obtained in the cycloaddition of *N*-phenylsydnone with the vinylstannane **6d** was different. In this case, a 5-carbotributylstannoxy-2-pyrazoline **11c** was obtained by cleavage of the O–N bond with simultaneous tin-migration from carbon to oxygen (Scheme 15).
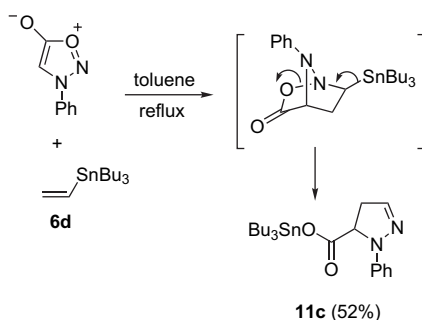
Scheme 15.

The 1,2-disilylalkene **6i** and the 1-phenylstannylalkene **6j** were recovered after prolonged heating (20 h) with this 1,3-dipolar reagent at reflux of toluene or decalin (Scheme 16).

Finally, when we used silylalkenes functionalized by withdrawing groups (β-silylated α,β-unsaturated esters or ketones) **6e–h** as dipolarophiles, only the *E*-β-dimethylphenylsilylenone **6g** experienced cycloaddition reaction. It was necessary to heat at reflux of decalin for the reaction to take place. In these conditions, the 4-dimethylphenylsilyl-
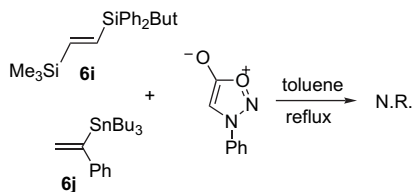
Scheme 16.

1-phenylpyrazole **12**, resulting from the concerted loss of CO_2 and acetaldehyde, was isolated (Scheme 17).
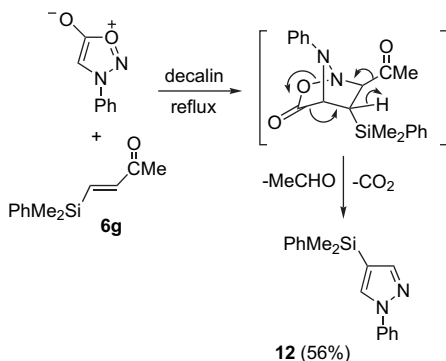
Scheme 17.

In conclusion, we have regioselectively synthesized 3,5-disilyl-, 3,4,5-trisilyl-, and 3,5-disilyl-4-stannylpyrazoles **2** by reaction of silyl-, disilyl-, and silylstannylalkynes with trimethylsilyldiazomethane. Moreover, the use of *N*-phenyl-sydnone as a 1,3-dipolar reagent has allowed us to prepare, for the first time, *N*-phenyl-3-silylpyrazoles **3**. In addition, the 3-silyl group could be converted into cyano, a group impossible to introduce directly into the pyrazole nucleus. On the other hand, we have synthesized interesting 1-pyrazolines **7** and 2-pyrazolines **8**, mono- and disilylated by different silyl groups through cycloaddition reactions of these 1,3-dipolar reagents with vinylsilanes. Finally, the unsaturated esters and ketones **9** and **10** bearing two silyl groups of very different electrofugacities (trimethyl and *tert*-butyl-diphenyl) in allylic and vinylic positions,[23] are versatile synthons in the selective substitution by a variety of carbon or heteroatomic electrophiles.

3. Experimental

3.1. General

THF was distilled from sodium benzophenone ketyl in a re-cycling still. All solvents were distilled prior to use. The ace-tylenes **1a**, **1b**, and **1g** were purchased from Aldrich. The remaining alkynes **1c**–**f** were obtained by reaction of the cor-responding lithium acetylide with chlorosilanes or chloro-stannanes according to the general procedure described by us[17] for the preparation of **1f**. The vinylsilane **6a** was bought (Aldrich). The vinylsilane **6b** was prepared by dimethylphe-nylsilylcupration[24] of acetylene and silylalkenes **6c** and **6e**–**i** as previously described.[25] The vinylstannanes **6d** and **6j** were obtained by stannylcupration[26] at −78 °C of acetylene and

phenylacetylene, respectively. The trimethylsilyldiazome-thane is commercial (Aldrich) and the *N*-phenylsydnone was synthesized starting from *N*-phenylglicine.[27] Reactions involving 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 chroma-tography was performed on silica gel 60 (230–240 mesh, M–N).

3.2. Cycloadditions with trimethylsilyldiazomethane: typical procedure

To a stirred solution of the trimethylsilyldiazomethane (2 mmol, 1 mL of a solution 1 M in hexane) under N_2, in dry THF (5 mL) or in toluene (5 mL) the alkenes **6a**–**h** (2 mmol) or the alkynes **1a**–**c** (2 mmol) were added, respec-tively. The mixture was refluxed until TLC indicated com-plete reaction. The solvent was evaporated under reduced pressure and the residue was chromatographed to give the following products:

3.2.1. 3,5-Bis(trimethylsilyl)pyrazole (2a). Yield 45%; oil, R_f=0.42 (CH_2Cl_2); IR (film) 3210, 1615, 1580, 1460, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 18H), 6.23 (s, 1H); MS (EI) *m/z* 212 (M$^+$, 20%), 211 (75), 139 (12), 125 (43), 98 (45), 73 (100). Anal. Calcd for $C_9H_{20}N_2Si_2$: C, 50.88; H, 9.49; N, 13.19. Found: C, 50.66; H, 9.83; N, 12.96.

3.2.2. 3,4,5-Tris(trimethylsilyl)pyrazole (2b). Yield 53%; oil, R_f=0.44 (CH_2Cl_2); IR (film) 3200, 1620, 1590, 1455, 1253 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 27H); ^{13}C NMR δ 2.05, 110.09, 129.42; MS (EI) *m/z* 284 (M$^+$, 18%), 283 (65), 212 (15), 197 (100), 73 (75). Anal. Calcd for $C_{12}H_{28}N_2Si_3$: C, 50.64; H, 9.92; N, 9.84. Found: C, 50.82; H, 10.07; N, 9.65.

3.2.3. 4-Tributylstannyl-3,5-bis(trimethylsilyl)pyrazole (2c). Yield 75%; oil, R_f=0.45 (CH_2Cl_2); IR (film) 3200, 1615, 1590, 1450, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 18H), 0.93 (t, *J*=7.2 Hz, 9H), 1.19 (t, *J*=7.2 Hz, 6H), 1.33 (m, 6H), 1.60 (m, 6H); ^{13}C NMR δ 3.11, 13.52, 15.82, 26.97, 27.76, 111.23, 129.01. Anal. Calcd for $C_{21}H_{46}N_2Si_2Sn$: C, 50.30; H, 9.25; N, 5.59. Found: C, 49.91; H, 9.38; N, 5.36.

3.2.4. *trans*-3,5-Bis-trimethylsilyl-1-pyrazoline (*trans*-**7a**). Yield 63%; oil, R_f=0.53 (CH_2Cl_2); IR (film) 1260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18H), 1.62 (t, *J*=9.2 Hz, 2H), 4.21 (t, *J*=9.2 Hz, 2H); ^{13}C NMR δ −3.45, 20.89, 82.82. Anal. Calcd for $C_9H_{22}N_2Si_2$: C, 50.41; H, 10.34; N, 13.06. Found: C, 50.76; H, 10.54; N, 12.89.

3.2.5. *cis*-3,5-Bis-trimethylsilyl-1-pyrazoline (*cis*-**7a**). Yield 25%; oil, R_f=0.51 (CH_2Cl_2); IR (film) 1260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 18H), 1.09 (q, *J*=11.5 Hz, 1H), 1.93 (q, *J*=11.5 Hz, 1H), 3.79 (t, *J*=11.5 Hz, 2H); ^{13}C NMR δ −2.93, 20.89, 81.49. Anal. Calcd for $C_9H_{22}N_2Si_2$: C, 50.41; H, 10.34; N, 13.06. Found: C, 50.28; H, 10.57; N, 13.33.

3.2.6. *trans*-1-*tert*-Butyldiphenylsilyl-4-carbomethoxy-5-trimethylsilyl-2-pyrazoline (8a).

Yield 28%; oil, R_f=0.26 (CH$_2$Cl$_2$–hexane, 1:1); IR (film) 1731, 1616, 1471, 1250, 1106 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.35 (s, 9H), 1.00 (s, 9H), 3.68 (dd, J=1.9, 5.0 Hz, 1H), 3.98 (d, J=5.0 Hz, 1H), 6.71 (d, J=1.9 Hz, 1H), 7.34–7.46 (m, 6H), 7.83 (m, 4H); ^{13}C NMR δ −3.84, 20.81, 27.78, 52.28, 53.05, 53.54, 127.32, 127.79, 129.55, 129.68, 134.00, 134.24, 135.63, 135.94, 136.20, 171.71. Anal. Calcd for C$_{24}$H$_{34}$N$_2$O$_2$Si$_2$: C, 65.71; H, 7.81; N, 6.39. Found: C, 65.34; H, 7.99; N, 6.58.

3.2.7. *trans*-4-Acetyl-1-*tert*-butyldiphenylsilyl-5-trimethylsilyl-2-pyrazoline (8b).

Yield 25%; oil, R_f=0.15 (hexane–AcOEt, 20:1); IR (film) 1712, 1600, 1491, 1250, 1109 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.37 (s, 9H), 0.96 (s, 9H), 2.26 (s, 3H), 3.67 (dd, J=2.1, 5.0 Hz, 1H), 4.06 (d, J=5.0 Hz, 1H), 6.75 (d, J=2.1 Hz, 1H), 7.38–7.45 (m, 6H), 7.73 (m, 2H), 7.82 (m, 2H); ^{13}C NMR δ −3.77, 20.79, 27.80, 28.01, 51.41, 62.41, 127.59, 129.29, 129.75, 133.51, 134.33, 134.76, 135.88, 136.46, 203.05. Anal. Calcd for C$_{24}$H$_{34}$N$_2$OSi$_2$: C, 68.19; H, 8.11; N, 6.63. Found: C, 67.96; H, 8.32; N, 6.85.

3.2.8. Methyl *E*-4-*tert*-butyldiphenylsilyl-4-trimethylsilylcrotonate (9a).

Yield 27%; oil, R_f=0.26 (CH$_2$Cl$_2$–hexane, 1:1); IR (film) 1731, 1616, 1471, 1250, 1106 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.33 (s, 9H), 0.96 (s, 9H), 2.37 (d, J=13.2 Hz, 1H), 3.76 (s, 3H), 5.80 (d, J=15.0 Hz, 1H), 7.40 (dd, J=13.2, 15.0 Hz, 1H), 7.34–7.46 (m, 6H), 7.64–7.72 (m, 4H); ^{13}C NMR δ −0.60, 20.31, 25.12, 27.86, 51.21, 118.13, 127.55, 129.27, 133.28, 136.45, 151.67, 167.06. Anal. Calcd for C$_{24}$H$_{34}$O$_2$Si$_2$: C, 70.19; H, 8.34. Found: C, 70.32; H, 8.18.

3.2.9. *E*-5-*tert*-Butyldiphenylsilyl-5-trimethylsilylpent-3-en-2-one (9b).

Yield 40%; oil, R_f=0.11 (CH$_2$Cl$_2$–hexane, 1:1); IR (film) 1693, 1606, 1491, 1255, 1105 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.32 (s, 9H), 0.97 (s, 9H), 2.26 (s, 3H), 2.37 (d, J=13.0 Hz, 1H), 6.10 (d, J=15.3 Hz, 1H), 7.40 (dd, J=13.0, 15.3 Hz, 1H), 7.37–7.47 (m, 6H), 7.65 (m, 2H), 7.82 (m, 2H); ^{13}C NMR δ −0.54, 20.35, 25.48, 26.95, 27.89, 127.37, 127.85, 129.34, 129.45, 129.63, 133.25, 133.82, 136.17, 136.37, 151.35, 197.26. Anal. Calcd for C$_{24}$H$_{34}$OSi$_2$: C, 73.03; H, 8.68. Found: C, 72.87; H, 8.41.

3.2.10. *E*-5-Dimethylphenylsilyl-5-trimethylsilylpent-3-en-2-one (9c).

Yield 35%; oil, R_f=0.23 (CH$_2$Cl$_2$–hexane, 1:1); IR (film) 1690, 1600, 1496, 1255, 1105 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.32 (s, 9H), 0.97 (s, 9H), 2.26 (s, 3H), 2.37 (d, J=13.0 Hz, 1H), 6.10 (d, J=15.3 Hz, 1H), 7.40 (dd, J=13.0, 15.3 Hz, 1H), 7.37–7.47 (m, 6H), 7.65 (m, 2H), 7.82 (m, 2H). Anal. Calcd for C$_{16}$H$_{26}$OSi$_2$: C, 66.14; H, 9.02. Found: C, 66.36; H, 8.89.

3.2.11. Methyl *E*-2-*tert*-butyldiphenylsilyl-4-trimethylsilylbut-3-enoate (10a).

Yield 27%; oil, R_f=0.50 (CH$_2$Cl$_2$–hexane, 1:1); IR (film) 1730, 1600, 1471, 1248, 1105 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.11 (s, 9H), 1.12 (s, 9H), 3.52 (s, 3H), 3.65 (d, J=9.7 Hz, 1H), 5.33 (d, J=18.6 Hz, 1H), 6.10 (dd, J=9.7, 18.6 Hz, 1H), 7.36 (m, 6H), 7.66 (m, 4H); ^{13}C NMR δ −0.23, 20.97, 29.33, 46.53, 52.56, 128.59, 130.65, 132.47, 133.70, 137.99, 141.71, 174.54.

Anal. Calcd for C$_{24}$H$_{34}$O$_2$Si$_2$: C, 70.19; H, 8.34. Found: C, 70.38; H, 8.52.

3.2.12. *E*-3-*tert*-Butyldiphenylsilyl-5-trimethylsilylpent-4-en-2-one (10b).

Yield 40%; oil, R_f=0.64 (CH$_2$Cl$_2$–hexane, 1:1); IR (film) 1713, 1605, 1496, 1250, 1105 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.01 (s, 9H), 1.04 (s, 9H), 1.91 (s, 3H), 5.30 (d, J=18.1 Hz, 1H), 5.39 (d, J=10.5 Hz, 1H), 6.46 (dd, J=10.6, 18.1 Hz, 1H), 7.36–7.44 (m, 6H), 7.71 (m, 4H); ^{13}C NMR δ −0.06, 19.67, 20.56, 27.79, 115.17, 128.56, 128.95, 131.05, 134.54, 136.63, 141.24, 204.00. Anal. Calcd for C$_{24}$H$_{34}$OSi$_2$: C, 73.03; H, 8.68. Found: C, 72.88; H, 8.93.

3.2.13. *E*-3-Dimethylphenylsilyl-5-trimethylsilylpent-4-en-2-one (10c).

Yield 45%; oil, R_f=0.69 (CH$_2$Cl$_2$–hexane, 1:1); IR (film) 1710, 1600, 1496, 1250, 1100 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.32 (s, 9H), 0.97 (s, 9H), 2.26 (s, 3H), 2.37 (d, J=13.0 Hz, 1H), 6.10 (d, J=15.3 Hz, 1H), 7.40 (dd, J=13.0, 15.3 Hz, 1H), 7.37–7.47 (m, 6H), 7.65 (m, 2H), 7.82 (m, 2H). Anal. Calcd for C$_{16}$H$_{26}$OSi$_2$: C, 66.14; H, 9.02. Found: C, 66.31; H, 8.87.

3.3. Cycloadditions with *N*-phenylsydnone: general procedure

A mixture of *N*-phenylsydnone (1.5 mmol) and the alkynes **1a**, **1c**–**g** or the alkenes **6a**–**d**, **6g**, **6i**,**j** (1.5 mmol) in toluene (5 mL) or decalin (5 mL) was stirred at reflux. At the end of the reaction (monitored by TLC) the solvent was evaporated under reduced pressure and the residue was extracted with ether and washed with water. The organic layer was dried (MgSO$_4$) and concentrated. The residue was purified by flash chromatography on silica gel using as eluent CH$_2$Cl$_2$–hexane (20:1–10:1) to give the following products:

3.3.1. 3-Trimethylsilyl-1-phenylpyrazole (3a).

Yield 95%; oil, R_f=0.27 (CH$_2$Cl$_2$); IR (film) 1600, 1510, 1445, 1250 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.35 (s, 9H), 6.57 (d, J=2.1 Hz, 1H), 7.49 (t, J=8.0 Hz, 1H), 7.62 (t, J=8.0 Hz, 2H), 7.74 (d, J=8.0 Hz, 2H), 7.93 (d, J=2.1 Hz, 1H); ^{13}C NMR δ −0.99, 113.61, 119.74, 126.38, 129.38, 131.01, 140.41, 155.09; MS (EI) *m/z* 216 (M$^+$, 8%), 215 (25), 200 (20), 143 (10), 77 (52), 73 (100). Anal. Calcd for C$_{12}$H$_{16}$N$_2$Si: C, 66.62; H, 7.45; N, 12.95. Found: C, 66.43; H, 7.59; N, 13.15.

3.3.2. 4-Tributylstannyl-3-trimethylsilyl-1-phenylpyrazole (3c).

Yield 80%; oil, R_f=0.21 (CH$_2$Cl$_2$); IR (film) 1640, 1590, 1490, 1240 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.07 (s, 9H), 0.92 (t, J=7.3 Hz, 9H), 1.43 (m, 12H), 1.68 (m, 6H), 7.33–7.56 (m, 5H), 8.22 (s, 1H); MS (EI) *m/z* 504 (M$^+$, 2%), 489 (15), 448 (10), 431 (15), 213 (22), 105 (13), 77 (28), 73 (30), 57 (100). Anal. Calcd for C$_{24}$H$_{42}$N$_2$SiSn: C, 57.04; H, 8.38; N, 5.54. Found: C, 56.84; H, 8.53; N, 5.27.

3.3.3. 3-Dimethylphenylsilyl-1-phenylpyrazole (3d).

Yield 75%; oil, R_f=0.26 (CH$_2$Cl$_2$); IR (film) 1600, 1500, 1460, 1250, 1100 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.65 (s, 6H), 6.58 (d, J=2.0 Hz, 1H), 7.30 (t, J=8.0 Hz, 1H), 7.32 (m, 3H), 7.47 (t, J=8.0 Hz, 2H), 7.69 (m, 2H), 7.77 (d, J=8.0 Hz, 2H), 7.96 (d, J=2.0 Hz, 1H); ^{13}C NMR δ −2.29, 114.43, 119.58, 126.33, 126.86, 127.76, 129.11,

129.31, 134.07, 138.02, 140.32, 153.01; MS (EI) *m/z* 278 (M⁺, 34%), 263 (20), 201 (8), 135 (88), 105 (39), 77 (100). Anal. Calcd for $C_{17}H_{18}N_2Si$: C, 73.33; H, 6.52; N, 10.06. Found: C, 73.58; H, 6.36; N, 9.89.

3.3.4. 3-*tert*-Butyldiphenylsilyl-1-phenylpyrazole (3e).
Yield 15%; oil, R_f=0.13 (CH_2Cl_2); IR (film) 1610, 1500, 1460, 1100 cm⁻¹; ¹H NMR (CDCl₃) δ 1.11 (s, 9H), 6.75 (d, *J*=1.8 Hz, 1H), 7.43–7.85 (m, 15H), 7.92 (d, *J*=1.8 Hz, 1H). Anal. Calcd for $C_{25}H_{26}N_2Si$: C, 78.49; H, 6.85; N, 7.32. Found: C, 78.26; H, 6.72; N, 7.48.

3.3.5. 4-Dimethylphenylsilyl-3-trimethylsilyl-1-phenyl-pyrazole (3f).
Yield 63%; oil, R_f=0.30 (CH_2Cl_2); IR (film) 1600, 1500, 1450, 1250, 1100 cm⁻¹; ¹H NMR (CDCl₃) δ 0.25 (s, 9H), 0.60 (s, 6H), 7.20–7.80 (m, 10H), 7.95 (s, 1H). Anal. Calcd for $C_{20}H_{26}N_2Si_2$: C, 68.51; H, 7.47; N, 7.99. Found: C, 68.76; H, 7.22; N, 8.11.

3.3.6. 3-Dimethylphenylsilyl-4-trimethylsilyl-1-phenyl-pyrazole (4f).
Yield 34%; oil, R_f=0.29 (CH_2Cl_2); IR (film) 1600, 1500, 1450, 1250, 1100 cm⁻¹; ¹H NMR (CDCl₃) δ 0.10 (s, 9H), 0.72 (s, 6H), 7.20–7.80 (m, 10H), 7.90 (s, 1H). Anal. Calcd for $C_{20}H_{26}N_2Si_2$: C, 68.51; H, 7.47; N, 7.99. Found: C, 68.36; H, 7.21; N, 7.73.

3.3.7. 4-Acetyl-3-trimethylsilyl-1-phenylpyrazole (3g).
Yield 81%; oil, R_f=0.17 (CH_2Cl_2); IR (film) 1685, 1600, 1510, 1450, 1250 cm⁻¹; ¹H NMR (CDCl₃) δ 0.45 (s, 9H), 2.51 (s, 3H), 7.28–7.56 (m, 5H), 8.41 (s, 1H); ¹³C NMR δ −1.52, 28.31, 119.45, 119.86, 127.66, 129.89, 131.55, 139.72, 157.01, 192.36. Anal. Calcd for $C_{14}H_{18}N_2OSi$: C, 65.08; H, 7.02; N, 10.84. Found: C, 65.29; H, 6.85; N, 11.03.

3.3.8. 3-Acetyl-4-trimethylsilyl-1-phenylpyrazole (4g).
Yield 16%; oil, R_f=0.18 (CH_2Cl_2); IR (film) 1695, 1600, 1500, 1460, 1250 cm⁻¹; ¹H NMR (CDCl₃) δ 0.22 (s, 9H), 2.67 (s, 3H), 7.28–7.56 (m, 5H), 7.73 (s, 1H); ¹³C NMR δ 1.25, 26.96, 103.43, 119.74, 127.32, 129.97, 134.75, 139.86, 156.14, 195.05. Anal. Calcd for $C_{14}H_{18}N_2OSi$: C, 65.08; H, 7.02; N, 10.84. Found: C, 64.81; H, 7.23; N, 10.69.

3.3.9. 3-Trimethylsilyl-1-phenyl-2-pyrazoline (11a).
Yield 30%; oil, R_f=0.70 (CH_2Cl_2–hexane, 2:1); IR (film) 1600, 1500, 1470, 1245 cm⁻¹; ¹H NMR (CDCl₃) δ 0.26 (s, 9H), 2.89 (t, *J*=10.4 Hz, 2H), 3.57 (t, *J*=10.4 Hz, 2H), 6.83 (t, *J*=7.3 Hz, 1H), 7.10 (d, *J*=8.5 Hz, 2H), 7.27 (dd, *J*=7.3, 8.5 Hz, 2H); ¹³C NMR δ −0.77, 38.18, 47.50, 114.36, 120.15, 130.28, 147.32, 157.49. Anal. Calcd for $C_{12}H_{18}N_2Si$: C, 66.00; H, 8.31; N, 12.83. Found: C, 66.21; H, 8.49; N, 12.66.

3.3.10. 3-Dimethylphenylsilyl-1-phenyl-2-pyrazoline (11b).
Yield 25%; oil, R_f=0.75 (CH_2Cl_2–hexane, 1:1); IR (film) 1600, 1500, 1475, 1250, 1105 cm⁻¹; ¹H NMR (CDCl₃) δ 0.54 (s, 6H), 2.84 (t, *J*=10.2 Hz, 2H), 3.56 (t, *J*=10.2 Hz, 2H), 6.84 (t, *J*=7.5 Hz, 1H), 7.10 (d, *J*=8.6 Hz, 2H), 7.28 (dd, *J*=7.5, 8.6 Hz, 2H), 7.39 (m, 3H), 7.59 (m, 2H); ¹³C NMR δ −3.48, 37.02, 46.23, 113.08, 118.96, 127.90, 128.98, 129.36, 133.87, 136.57, 145.80, 154.23. Anal. Calcd for $C_{17}H_{20}N_2Si$: C, 72.81; H, 7.19; N, 9.99. Found: C, 73.04; H, 7.28; N, 10.25.

3.3.11. 5-Tributylstannoxycarbonyl-2-pyrazoline (11c).
Yield 52%; oil, R_f=0.70 (CH_2Cl_2–hexane, 1:1); IR (film) 1652, 1599, 1500, 1464 cm⁻¹; ¹H NMR (CDCl₃) δ 0.89 (t, *J*=7.2 Hz, 9H), 1.20–1.35 (m, 12H), 1.51–1.61 (m, 6H), 3.09 (ddd, *J*=1.7, 7.0, 17.7 Hz, 1H), 3.30 (ddd, *J*=1.7, 12.4, 17.7 Hz, 1H), 4.58 (dd, *J*=7.0, 12.4 Hz, 1H), 6.75 (t, *J*=1.7 Hz, 1H), 6.82 (t, *J*=7.1 Hz, 1H), 7.05 (d, *J*=8.0 Hz, 2H), 7.23 (dd, *J*=7.1, 8.0 Hz, 2H); ¹³C NMR δ 13.58, 16.64, 26.91, 27.63, 39.87, 60.63, 113.02, 119.20, 128.84, 138.49, 145.32, 176.29; MS (EI) *m/z* 480 (M⁺, 3%), 423 (13), 291 (10), 145 (100), 119 (51), 77 (9). Anal. Calcd for $C_{22}H_{36}N_2O_2Sn$: C, 55.14; H, 7.57; N, 5.85. Found: C, 55.31; H, 7.74; N, 5.69.

3.3.12. 4-Dimethylphenylsilyl-1-phenylpyrazole (12).
Yield 56%; oil, R_f=0.30 (hexane–AcOEt, 10:1); IR (film) 1590, 1500, 1474, 1250, 1105 cm⁻¹; ¹H NMR (CDCl₃) δ 0.56 (s, 6H), 7.29 (t, *J*=7.7 Hz, 1H), 7.39 (m, 3H), 7.45 (dd, *J*=7.7, 8.1 Hz, 2H), 7.52–7.64 (m, 2H), 7.60 (d, *J*=8.1 Hz, 2H), 7.74 (s, 1H), 7.86 (s, 1H); ¹³C NMR δ −1.54, 114.88, 119.34, 126.46, 127.85, 129.20, 129.35, 132.12, 133.80, 138.27, 139.88, 146.10. Anal. Calcd for $C_{17}H_{18}N_2Si$: C, 73.33; H, 6.52; N, 10.06. Found: C, 73.18; H, 6.67; N, 9.91.

3.4. 3-Cyano-1-phenylpyrazole (5a)

To a stirred solution of **3a** (1 mmol) in CCl_4 (1 mL) at 0 °C was added dropwise chlorosulfonyl isocyanate (1 mmol) in CCl_4 (1 mL). The mixture was then stirred at room temperature until the starting material had disappeared (TLC). The solvent was removed and the residue was dissolved in acetone (3 mL) and hydrolyzed by refluxing with 0.1 N HCl (1 mL) for 5 min. The reaction mixture was extracted with ether, dried ($MgSO_4$), the solvent removed, and the residue chromatographed using CH_2Cl_2 as eluent to give 0.145 g (86%) of **5a**; R_f=0.27 (CH_2Cl_2); IR (film) 2230, 1600, 1500, 1450 cm⁻¹; ¹H NMR (CDCl₃) δ 6.80 (d, *J*=2.0 Hz, 1H), 7.29 (t, *J*=8.0 Hz, 1H), 7.48 (t, *J*=8.0 Hz, 2H), 7.71 (t, *J*=8.0 Hz, 2H), 8.09 (d, *J*=2.0 Hz, 1H); ¹³C NMR δ 112.57, 119.98, 120.32, 126.53, 128.32, 129.25, 132.43, 151.32; MS (EI) *m/z* 169 (M⁺, 100%), 143 (23), 105 (41), 77 (4), 64 (14). Anal. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.84. Found: C, 71.26; H, 4.28; N, 24.67.

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20. No NOE was observed between 4-H and 5-H.

21. It has been proved that a vinylsilane bearing the acetyl group is an order of magnitude more reactive than the vinylsilane bearing the carbomethoxy group toward 2-diazopropane (Ref. 5b).

22. Spectroscopy data for Z-β-silylenone **6h**: IR 1690 cm^{-1} (CO); ^{1}H NMR δ 7.22 (β-H to COMe); ^{13}C NMR δ 203.51 (CO). Spectroscopy data for the *E*-isomer **6f**: IR 1680 cm^{-1} (CO); ^{1}H NMR δ 7.51 (β-H to COMe); ^{13}C NMR δ 197.43 (CO).

23. In the course of our investigations concerning the behavior toward electrophiles of dimetalated alkenes bearing silicon groups in vinylic and allylic positions, we have substituted the allylic *tert*-butyldiphenylsilyl group in the presence of a vinylic better electrofugal group like dimethylphenylsilyl (unpublished results).

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