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Silylated β-enaminones as precursors in the regioselective synthesis of silyl pyrazoles

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Abstract—Silyl β-enaminones have been synthesized by reductive cleavage of 5-silyl, 3-, 4- and 5-silylmethylisoxazoles.These versatile synthons bearing different silyl groups in various positions of the enaminoketonic system are of great interest in the regioselective synthesis of 3- or 5-silylpyrazoles and 3-, 4- or 5-silylmethylpyrazoles, which can serve as building blocks in heterocyclic chemistry.

1. Introduction

In a preliminary communication[1] we described the synthesis of silylated β-enaminoketones by catalytic hydrogenation of 4- and 5-silylisoxazoles, as well as those resulting from the reductive cleavage of their 4- and 5-homologues. Moreover, we used these synthons as substrates in the synthesis of silylated pyrroles, pyrazoles, pyrimidines and pyridinones.

Following on with our current research in the synthesis and applications of silylated azoles, we were especially interested in the regioselective synthesis of azoles bearing silyl groups in different positions of the heterocyclic ring. Previously, we had reported[2] the synthesis of regioisomeric silicon and tin 4- or 5-metalated pyrazoles by silyl- or stannylcupration of 4-halopyrazoles or lithiation with LDA of 5-unsubstituted pyrazoles and the subsequent treatment with chlorosilanes or chlorostannanes, respectively. 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. This methodology could be applied to the preparation of 4-silyl- and 4-stannylisoxazoles, but not to the synthesis of 5-silyl- or 5-stannylisoxazoles, because the 5-lithio intermediate is opened by fission of N–O and C_3–C_4 bonds.[3] Fortunately, we synthesized 5-silylisoxazoles by reaction of β-silylalkynones with hydroxylamine.[4] The reaction of these substrates with hydrazines is more complex. The cyclization to the 5-silylpyrazole or the exclusive formation of the corresponding hydrazone depends on the nature of the hydrazine substituents (H, Me, Ph) and silyl group (Me_3, Me_2Ph, $tBuPh_2$). When hydrazine or methyl hydrazine were used the 4-trimethylsilyl- and 4-dimethylphenylsilyl-3-butyn-2-one gave the corresponding 5-silylpyrazoles. Nevertheless, heating of the hindered 4-*tert*-butyldiphenylsilyl-3-butyn-2-one with hydrazine or methyl hydrazine afforded the respective hydrazones. On the other hand, when phenylhydrazine was used as a 1,2-dinucleophile (free, in the form of hydrochloride or with acid catalysis) cyclization did not take place. The reaction with trimethyl-, dimethylphenyl- and *tert*-butyldiphenyl silyl alkynones led to the appropriate phenyl hydrazones. Interestingly, the trimethylsilyl- and dimethylphenylsilyl *N*-phenyl hydrazones, but not the *tert*-butyldiphenylsilyl derivative, could be cyclized to 4-functionalized 5-trimethylsilyl- and 5-dimethylphenylsilylpyrazoles by reaction with electrophiles.

In this paper, we describe the full results in the preparation of β-enaminones bearing different silyl groups in distinct positions of the enaminoketonic system[5] and their reaction with various hydrazines with the aim of knowing the scope of this methodology in the regioselective synthesis of a variety of new silylpyrazoles impossible or difficult to synthesize by other procedures.

2. Results and discussion

Differently silylated β-aminoenones have been synthesized by catalytic hydrogenation of 5-silyl-, 3-, 4-, and 5-silylmethylisoxazoles (Scheme 1).

Keywords: Silicon isoxazoles; Silicon β-enaminones; Silicon pyrazoles.
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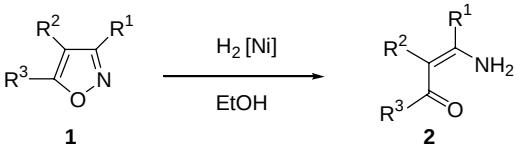


1 2

1a; R^1 = Me, R^2 = H, R^3 = $SiMe_3$ — **2a** (91%)

1b; R^1 = Me, R^2 = H, R^3 = $SiMe_2Ph$ — **2b** (95%)

1c; R^1 = Me, R^2 = H, R^3 = $SiPh_2Bu^t$ — **2c** (92%)

1d; R^1 = Me, R^2 = CH_2SiMe_3, R^3 = Me — **2d** (89%)

1e; R^1 = Me, R^2 = H, R^3 = CH_2SiMe_3 — **2e** (90%)

1f; R^1 = Me, R^2 = H, R^3 = $CH_2SiMePh_2$ — **2f** (90%)

1g; R^1 = Me, R^2 = H, R^3 = $CH_2SiPh_2Bu^t$ — **2g** (95%)

1h; R^1 = Pr^i, R^2 = H, R^3 = $CH_2SiPh_2Bu^t$ — **2h** (96%)

1i; R^1 = Ph, R^2 = H, R^3 = CH_2SiMe_3 — **2i** (91%)

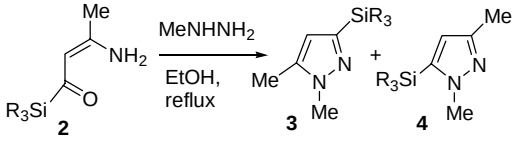
1j; R^1 = Ph, R^2 = H, R^3 = $CH_2SiPh_2Bu^t$ — **2j** (98%)

1k; R^1 = CH_2SiMe_3, R^2 = H, R^3 = Ph — **2k** (95%)

1l; R^1 = $CH_2SiPh_2Bu^t$, R^2 = H, R^3 = Ph — **2l** (96%)

Scheme 1.

The catalytic hydrogenation of 5-silylisoxazoles **1a–c** afforded stable acylsilane derivatives **2a–c**, which reacted regioselectively with hydrazines to give 3- or 5-silyl pyrazoles. The formation of the 3- or 5-regioisomer depends exclusively on the nature of the hydrazine. When methylhydrazine was used as a nucleophile, the trimethyl, dimethylphenyl and *tert*-butyldiphenylsilyl β-enaminones **2a–c** led to 3-silylpyrazoles **3a–c** with acceptable regioselectivity (Scheme 2).



2 3 4

2a; R_3 = Me_3 — **3a** (55%) + **4a** (18%)

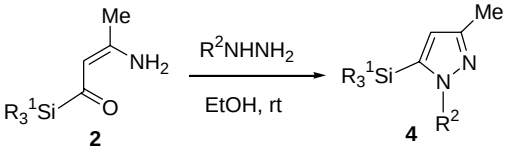
2b; R_3 = Me_2Ph — **3b** (50%) + **4b** (15%)

2c; R_3 = Ph_2Bu^t — **3c** (75%) + **4c** (16%)

Scheme 2.

This result is very interesting because, as far as we know, general procedures for synthesizing *N*-methyl-3-silyl pyrazoles have not been previously described.

However, the reaction of these substrates with other hydrazines (ethyl, *tert*-butyl or phenylhydrazine) afforded only the respective 5-silylpyrazoles **4d–k** (Scheme 3).



2 4

2a; $R^1{}_3$ = Me_3 — **4d** (91%); $R^1{}_3$ = Me_3, R^2 = Et

2a — **4e** (85%); $R^1{}_3$ = Me_3, R^2 = Ph

2a — **4f** (80%); $R^1{}_3$ = Me_3, R^2 = $CONH_2$

2b; $R^1{}_3$ = Me_2Ph — **4g** (<5%); $R^1{}_3$ = Me_2Ph, R^2 = Bu^t

2b — **4h** (69%); $R^1{}_3$ = Me_2Ph, R^2 = Ph

2c; $R^1{}_3$ = Ph_2Bu^t — **4i** (80%); $R^1{}_3$ = Ph_2Bu^t, R^2 = Bn

2c — **4j** (<5%); $R^1{}_3$ = Ph_2Bu^t, R^2 = Bu^t

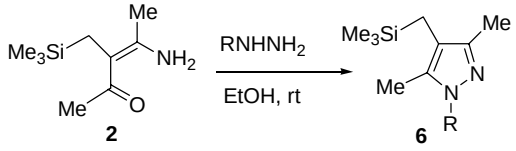
2c — **4k** (75%); $R^1{}_3$ = Ph_2Bu^t, R^2 = Ph

Scheme 3.

The low reactivity (<5%) of β-enaminoacylsilanes **2b** and **2c** with *tert*-butylhydrazine may be due to the steric hindrance between the bulky *tert*-butyl and silyl groups.

Although we had previously synthesized 5-silylpyrazoles by reaction of β-silylalkynones with hydrazines,[4] the cyclization of *N*-phenylhydrazones and all types of hydrazones bearing the bulky *tert*-butyldiphenylsilyl group had not taken place. Therefore, this is a complementary method for preparing, with acceptable yields, 5-silylated *N*-phenylpyrazoles **4e**, **4h** and *N*-alkyl- or *N*-phenyl 5-*tert*-butyldiphenylsilylpyrazoles **4i** or **4k**, respectively.

The silylated β-aminoenone **2d**, obtained by reductive cleavage of 4-trimethylsilylmethylisoxazole **1d**, is very stable despite containing an allylsilane moiety and it was shown to be reactive toward phenylhydrazine and semicarbazide giving 4-trimethylsilylmethylpyrazoles **6a** and **6b**, respectively (Scheme 4).



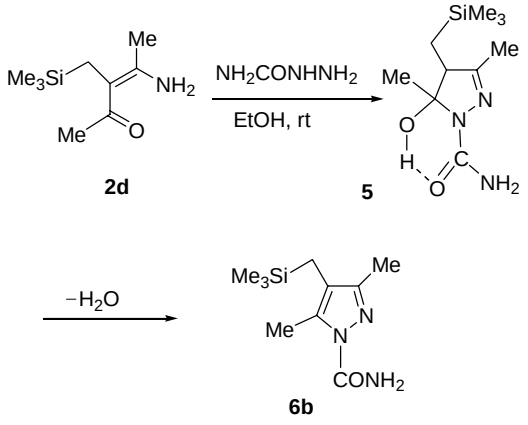
2 6

2d — **6a** (72%); R = Ph

2d — **6b** (78%); R = $CONH_2$

Scheme 4.

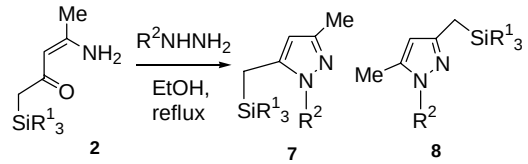
The formation of 4-trimethylsilylmethylpyrazoles **6a** and **6b** should take place through the respective 5-hydroxypyrazoline, because the stabilized intermediate **5** resulting from the reaction of **2d** with semicarbazide was identified by ^{1}H NMR spectroscopy from the reaction mixture (Scheme 5).



Scheme 5.

It is interesting to point out that this methodology has allowed us to prepare 4-silylmethylpyrazoles, for the first time, impossible to obtain by the procedure used to synthesize the analogous isoxazoles (starting from 4-chloromethylisoxazoles by treatment with chlorosilanes) because, in contrast to the isoxazole ring, which can be chloromethylated in the 4-position, the pyrazole nucleus does not undergo chloromethylation reaction.

Conversely, the stability of the silyl β-enaminones **2e–j** resulting from catalytic hydrogenolysis of 5-silylmethyl isoxazoles **1e–j**, depends on the nature of the silyl group (Schemes 6 and 7). When this is trimethylsilyl, the α′-silyl-β-enaminoketones **2e** and **2i** were unstable in the acidic reaction medium. In their treatment with hydrazine hydrochlorides or oxalates, desilylated pyrazoles were obtained. Nevertheless, β-aminoenones bearing silyl groups of minor nucleofugacity such as diphenylmethyl **2f** and *tert*-butyldiphenyl **2g**,**h** furnished, in general, the corresponding 5-silylmethylpyrazoles. The unstable α′-trimethylsilyl enaminone **2e** reacted only with free methylhydrazine but unfortunately the regioselectivity was lost and a mixture almost equimolecular of 3-trimethylsilylmethyl- **7a** and 5-trimethylsilylmethyl pyrazole **8a** was obtained. The same behavior was observed in the reaction of this hydrazine with the *tert*-butyldiphenylsilyl derivative **2g** and a mixture of the two possible regioisomers **7b** and **8b** was again isolated, in which the first was the majority product. On the other hand, when **2g** was treated with semicarbazide only the 5-silylmethylpyrazole **7c** was obtained which, left to stand at rt, was slowly transformed

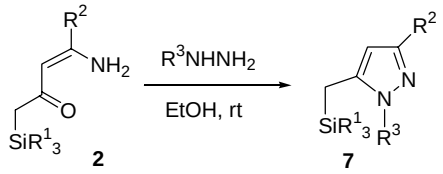


2e; $R^1_3 = Me_3$ — **7a** (40%) + **8a** (38%); R^2 = Me

2g; $R^1_3 = Ph_2Bu^t$ — **7b** (51%) + **8b** (28%); R^2 = Me

2g; $R^1_3 = Ph_2Bu^t$ — **7c** (75%); $R^2 = CONH_2$

Scheme 6.



2f; $R^1_3 = MePh_2$, R^2 = Me — **7d** (93%); R^3 = Et

2f — **7e**(79%); $R^3 = CONH_2$

2g; $R^1_3 = Ph_2Bu^t$, R^2 = Me — **7f** (85%); $R^3 = Bu^t$

2g — **7g** (91%); R^3 = Et

2g — **7h** (89%); R^3 = Ph

2h; $R^1_3 = Ph_2Bu^t$, $R^2 = Pr^i$ — **7i** (60%); R^3 = Ph

2i; $R^1_3 = Me_3$, R^2 = Ph — ———

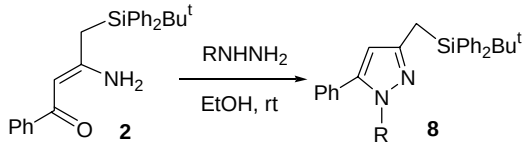
2j; $R^1_3 = Ph_2Bu^t$, R^2 = Ph — ———

Scheme 7.

into its 3-silylmethyl regioisomer **8c** ($R^1_3 = Ph_2Bu^t$, $R^2 = CONH_2$) (Scheme 6).

The reaction of β-enaminones **2f–h** with other hydrazines was regioselective leading to 5-silylmethylpyrazoles **7d–i** exclusively. The reactivity of β-aryl enaminones **2i**,**j** toward hydrazines at reflux from ethanol was low. Attempts to increase the yields by heating the reaction mixture at higher temperatures led to decomposition of the substrate (Scheme 7).

Finally, the presence of the phenyl group in the γ-silyl-β-enaminones **2k**,**l**, resulting from catalytic hydrogenation of 3-silylmethyl-5-phenylisoxazoles **1k**,**l**, decreases their reactivity toward hydrazines. Moreover, the trimethylsilyl derivative **2k** is not very stable, affording desilylated pyrazoles. Fortunately, the *tert*-butyldiphenylsilyl counterpart **2l** could be condensed with different hydrazines, yielding regioselectively the corresponding 3-*tert*-butyldiphenylsilylmethylpyrazoles **8d**,**e** (Scheme 8).



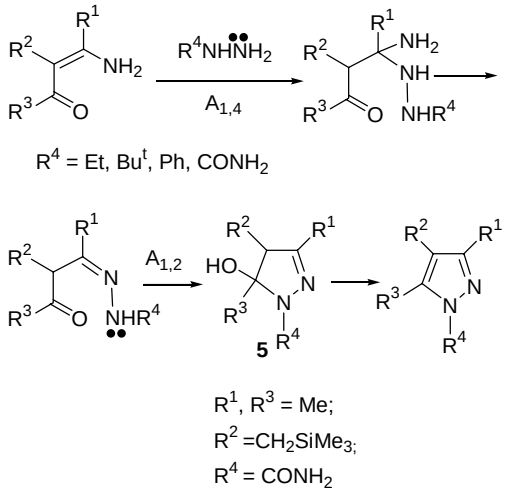
2l — **8d** (45%); R = Bu^t

2l — **8e** (34%); R = Ph

Scheme 8.

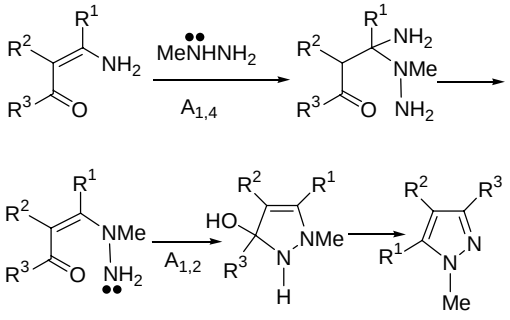
The regioselectivity observed when ethyl, *tert*-butyl and phenylhydrazine or semicarbazide were used, can be explained by initial 1,4-addition of the NH_2 group to

the enaminoketone, followed by 1,2-addition of the NH group to give a 5-hydroxy-2-pyrazoline intermediate **5** (R^1, R^3=Me; R^2=CH_2SiMe_3; R^4=$CONH_2$), which was identified by ^1H NMR in the reaction of the enaminone **2d** with semicarbazide (Scheme 9).



Scheme 9.

On the other hand, the loss of regioselectivity in the reactions with methylhydrazine could be due to the competitive 1,4-addition of the more nucleophilic NHMe group to the enaminone and subsequent 1,2-addition of the NH_2 group to afford the corresponding regioisomer (Scheme 10).



Scheme 10.

In conclusion, we have easily prepared β-enamino acylsilanes, α-silylmethyl-, α′-silyl- and γ-silyl-β-enaminones by reductive cleavage of 5-silyl-, 4-silylmethyl, 5-silylmethyl and 3-silylmethylisoxazoles, respectively. Moreover, we demonstrated[1] that they are interesting synthons in the creation of pyrroles, pyrazoles, pyrimidines and pyridinones bearing arylsilane, arylmethylsilane and α-silylketone moieties. In this paper, we have used these substrates for synthesizing regioselectively a variety of 3- or 5-silylpyrazoles, 3-silylmethyl-, 4-silylmethyl- and 5-silylmethylpyrazoles, of which no general method of synthesis is known. The easy electrophilic *ipso*-substitution in heteroarylsilanes[2,6] may permit the introduction, through the silyl group, of carbon or heteoatomic groups. Likewise, arylmethylsilanes[7] are synthetic equivalents of silicon-stabilized carbanions with wide synthetic possibilities.

3. Experimental

3.1. General

THF was distilled from sodium benzophenone ketyl in a recycling still and ethanol was dried by refluxing with Mg. All chromatographic and workup solvents were distilled prior to use. Reactions involving organometallic reagents were carried out under N_2. ^1H 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).

3.2. Preparation of silylisoxazoles

5-Silylisoxazoles **1a**, **1b** and **1c** have been prepared by a procedure described by us.[3] The 4-silylmethylisoxazole **1d** and 5-silylmethylisoxazole **1e** have also been previously described.[8] The remaining 5-silylmethyl- **1h–j** and 3-silylmethylisoxazoles **1k**,**l** were synthesized by the same procedure[8] starting from the corresponding 5-methyl- or 3-methylisoxazoles by hydrogen–lithium exchange and quenching with the suitable chlorosilane. The following products were obtained:

3.2.1. 3-Methyl-5-(methyldiphenylsilylmethyl)isoxazole (1f). Yield 83%; bp 132–134 °C/0.1 mmHg; IR (film) 1596, 1427, 1114, 818, 798, 731, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.65 (s, 3H), 2.20 (s, 3H), 2.74 (s, 2H), 5.49 (s, 1H), 7.39–7.55 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −4.42, 11.33, 15.44, 100.99, 127.93, 129.69, 134.36, 134.91, 159.79, 170.49. Anal. Calcd for $C_{18}H_{19}NOSi$: C, 73.68; H, 6.53; N, 4.77. Found: C, 73.91; H, 6.49; N, 4.91.

3.2.2. 5-(*tert*-Butyldiphenylsilylmethyl)-3-methylisoxazole (1g). Yield 75%; bp 164–167 °C/0.5 mmHg; IR (film) 1595, 14.27, 1108, 734, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (s, 9H), 2.08 (s, 3H), 2.82 (s, 2H), 5.21 (s, 1H), 7.35–7.63 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.30, 11.66, 18.38, 27.49, 101.40, 127.68, 129.52, 133.01, 135.79, 159.67, 170.50. Anal. Calcd for $C_{21}H_{25}NOSi$: C, 75.18; H, 7.51; N, 4.17. Found: C, 74.95; H, 7.62; N, 4.20.

3.2.3. 5-(*tert*-Butyldiphenylsilylmethyl)-3-isopropylisoxazole (1h). Yield 62%; mp 59–60 °C (from hexane); IR (KBr) 1588, 1467, 1100, 794, 731, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (s, 9H), 1.10 (d, J=7.11 Hz, 6H), 2.80 (s, 2H), 2.84 (m, J=7.11 Hz, 1H), 5.17 (s, 1H), 7.33–7.65 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.97, 18.36, 21.57, 26.27, 27.53, 98.81, 127.65, 129.49, 133.14, 135.88, 169.30, 170.27. Anal. Calcd for $C_{23}H_{29}NOSi$: C, 75.98; H, 8.04; N, 3.85. Found: C, 76.10; H, 7.99; N, 3.82.

3.2.4. 5-(Trimethylsilylmethyl)-3-phenylisoxazole (1i). Yield 95%; mp 51 °C (from hexane); IR (KBr) 1594, 1575, 1469, 1251, 846, 769, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H), 2.29 (s, 2H), 6.12 (s, 1H), 7.43–7.82 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −1.75, 17.90, 97.21, 126.62, 128.72, 129.52, 129.60, 162.36, 172.89. Anal. Calcd for

$C_{13}H_{17}NOSi$: C, 67.49; H, 7.41; N, 6.05. Found: C, 67.61; H, 7.35; N, 5.99.

3.2.5. 5-(*tert*-Butyldiphenylsilylmethyl)-3-phenylisoxazole (1j). Yield 82%; mp 103 °C (from hexane); IR (KBr) 1592, 1575, 1467, 1109, 767, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (s, 9H), 2.92 (s, 2H), 5.66 (s, 1H), 7.38–7.67 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 12.09, 18.41, 27.55, 98.71, 126.56, 127.76, 128.65, 129.42, 129.54, 129.63, 133.95, 135.87, 162.23, 171.47. Anal. Calcd for $C_{26}H_{27}NOSi$: C, 78.54; H, 6.84; N, 3.52. Found: C, 78.43; H, 6.82; N, 3.61.

3.2.6. 3-(Trimethylsilylmethyl)-5-phenylisoxazole (1k). Yield 61%; mp 59–60 °C (from hexane); IR (KBr) 1613, 1590, 1573, 1423, 1248, 1150, 819, 767, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 2.21 (s, 2H), 6.31 (s, 1H), 7.40–7.85 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −1.90, 15.91, 99.57, 125.39, 128.62, 128.77, 129.49, 162.22, 168.80. Anal. Calcd for $C_{13}H_{17}NOSi$: C, 67.49; H, 7.41; N, 6.05. Found: C, 67.38; H, 7.46; N, 6.12.

3.2.7. 3-(*tert*-Butyldiphenylsilylmethyl)-5-phenylisoxazole (1l). Yield 31%; mp 90–91 °C (from hexane); IR (KBr) 1686, 1574, 1425, 1415, 1111, 765, 740, 702, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 9H), 2.79 (s, 2H), 5.49 (s, 1H), 7.40–7.69 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 10.70, 18.52, 27.65, 100.00, 125.52, 127.61, 127.74, 128.71, 129.53, 129.65, 133.40, 136.07, 161.93, 168.62. Anal. Calcd for $C_{26}H_{27}NOSi$: C, 78.54; H, 6.84; N, 3.52. Found: C, 78.65; H, 6.75; N, 3.59.

3.3. Synthesis of silyl β-aminoenones. Typical procedure

A mixture of silylated isoxazole (20 mmol) and 1.0 g of Raney nickel in 10 mL of dry ethanol was stirred under 400 psi of hydrogen at rt for 24 h. Then, the catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The concentrate was chromatographed on silica gel using CH_2Cl_2–Et_2O (20/1) as eluent. The following silyl β-aminoenones were obtained:

3.3.1. 3-Amino-1-(trimethylsilyl)but-2-en-1-one (2a). Yield 91%; mp 84 °C (from hexane); IR (KBr) 3255, 3097, 1618, 1522, 1385, 1269, 1246, 867, 840, 752, 679 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9H), 1.90 (s, 3H), 5.46 (s, 1H), 5.62 (br, 1H), 10.76 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 2.95, 22.00, 102.19, 159.78, 225.08. Anal. Calcd for $C_7H_{15}NOSi$: C, 53.45; H, 9.61; N, 8.91. Found: C, 53.38; H, 9.73; N, 9.00.

3.3.2. 3-Amino-1-(dimethylphenylsilyl)but-2-en-1-one (2b). Yield 95%; mp 88–89 °C (from hexane); IR (KBr) 3213, 1590, 1427, 1253, 1118, 830, 797, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.48 (s, 6H), 1.89 (s, 3H), 5.17 (br, 1H), 5.49 (s, 1H), 7.27–7.61 (m, 5H), 10.85 (br, 1H). Anal. Calcd for $C_{12}H_{17}NOSi$: C, 65.71; H, 7.81; N, 6.39. Found: C, 65.50; H, 7.71; N, 6.48.

3.3.3. 3-Amino-1-(*tert*-butyldiphenylsilyl)but-2-en-1-one (2c). Yield 92%; mp 155–156 °C (from hexane); IR (KBr) 3310, 1624, 1507, 1383, 1288, 1102, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (s, 9H), 1.80 (s, 3H), 5.24 (br, 1H), 5.39 (s, 1H), 7.35–7.42 (m, 6H), 7.70–7.73 (m, 4H), 10.94 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 0.48, 22.16, 27.97, 105.77, 127.55, 129.15, 133.83, 136.33, 159.31, 220.75. Anal. Calcd for $C_{20}H_{25}NOSi$: C, 74.25; H, 7.79; N, 4.33. Found: C, 74.38; H, 7.60; N, 4.51.

3.3.4. 4-Amino-3-(trimethylsilylmethyl)pent-3-en-2-one (2d). Yield 89%; mp 58 °C (from hexane); IR (KBr) 3338, 2953, 1602, 1480, 1247, 851, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 9H), 1.63 (s, 2H), 1.90 (s, 3H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$) δ −0.67, 17.20, 22.24, 28.77, 101.80, 156.96, 197.13. Anal. Calcd for $C_9H_{19}NOSi$: C, 58.32; H, 10.33; N, 7.56. Found: C, 58.56; H, 10.31; N, 7.40.

3.3.5. 4-Amino-1-(trimethylsilyl)pent-3-en-2-one (2e). Yield 90%; mp 69 °C (from hexane); IR (KBr) 3300, 3138, 1605, 1530, 1249, 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 1.87 (s, 3H), 1.97 (s, 2H), 4.86 (s, 1H), 4.87 (br, 1H), 9.56 (br, 1H); ^{13}C NMR ($CDCl_3$) δ −1.20, 22.28, 37.08, 96.13, 159.15, 198.26. Anal. Calcd for $C_8H_{17}NOSi$: C, 56.09; H, 10.00; N, 8.18. Found: C, 55.91; H, 9.83; N, 8.30.

3.3.6. 4-Amino-1-(methyldiphenylsilyl)pent-3-en-2-one (2f). Yield 90%; mp 76 °C (from hexane); IR (KBr) 3303, 3134, 1606, 1530, 1288, 1126, 1062, 777, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69 (s, 3H), 1.75 (s, 3H), 2.54 (s, 2H), 4.76 (s, 1H), 4.93 (br, 1H), 7.26–7.61 (m, 10H), 9.56 (br, 1H); ^{13}C NMR ($CDCl_3$) δ −4.04, 22.05, 34.29, 96.65, 127.68, 129.25, 134.49, 136.28, 159.51, 196.72. Anal. Calcd for $C_{18}H_{21}NOSi$: C, 73.17; H, 7.16; N, 4.77. Found: C, 72.95; H, 7.22; N, 4.91.

3.3.7. 4-Amino-1-(*tert*-butyldiphenylsilyl)pent-3-en-2-one (2g). Yield 95%; mp 117 °C (from hexane); IR (KBr) 3310, 3073, 1613, 1471, 1205, 789, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (s, 9H), 1.6 (s, 3H), 2.6 (s, 2H), 4.5 (s, 1H), 4.65 (br, 1H), 7.35–7.50 (m, 6H), 7.55–7.7 (m, 4H), 9.40 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 18, 22, 27, 31, 97, 126, 129, 135, 137, 149, 197. Anal. Calcd for $C_{21}H_{27}NOSi$: C, 74.73; H, 8.06; N, 4.15. Found: C, 75.00; H, 7.92; N, 4.18.

3.3.8. 4-Amino-1-(*tert*-butyldiphenylsilyl)-5-methylhex-3-en-2-one (2h). Yield 96%; mp 63–64 °C (from hexane); IR (KBr) 3300, 3105, 1599, 1520, 1277, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (d, J=6.9 Hz, 6H), 1.09 (s, 9H), 1.97 (m, J=6.9 Hz, 1H), 2.60 (s, 2H), 4.54 (s, 1H), 4.71 (br, 1H), 7.27–7.41 (m, 6H), 7.66–7.69 (m, 4H), 9.30 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 18.59, 20.71, 27.55, 31.38, 34.41, 94.01, 127.32, 129.00, 134.35, 136.11, 168.37, 197.45. Anal. Calcd for $C_{23}H_{31}NOSi$: C, 75.56; H, 8.55; N, 3.83. Found: C, 75.63; H, 8.61; N, 3.81.

3.3.9. 4-Amino-1-(trimethylsilyl)4-phenylbut-3-en-2-one (2i). Yield 91%; mp 64 °C (from hexane); IR (KBr) 3324, 3153, 1609, 1534, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H), 2.13 (s, 2H), 5.11 (br, 1H), 5.30 (s, 1H), 7.42–7.55 (m, 5H), 9.83 (br, 1H); ^{13}C NMR ($CDCl_3$) δ −1.14, 37.89, 95.73, 126.18, 128.81, 130.23, 137.64, 159.42, 198.90. Anal. Calcd for $C_{13}H_{19}NOSi$: C, 66.90; H, 8.21; N, 6.00. Found: C, 67.10; H, 8.02; N, 6.20.

3.3.10. 4-Amino-1-(*tert*-butyldiphenylsilyl)-4-phenylbut-3-en-2-one (2j). Yield 98%; mp 88–89 °C (from hexane);

IR (KBr) 3456, 1602, 1571, 1520, 1484, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (s, 9H), 2.73 (s, 2H), 4.90 (br, 1H), 4.94 (s, 1H), 7.03–7.76 (m, 15H), 9.60 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 18.71, 27.63, 32.05, 96.89, 126.04, 127.54, 128.50, 129.14, 130.07, 134.29, 136.19, 137.19, 158.79, 197.81. Anal. Calcd for $C_{26}H_{29}NOSi$: C, 78.15; H, 7.31; N, 3.51. Found: C, 78.32; H, 7.02; N, 3.50.

3.3.11. 3-Amino-4-(trimethylsilyl)-1-phenyl-but-2-en-1-one (2k). Yield 95%; mp 89 °C (from hexane); IR (KBr) 3430, 1594, 1569, 1523, 852, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.79 (s, 2H), 5.17 (br, 1H), 5.57 (s, 1H), 7.40 (m, 3H), 7.87 (m, 2H), 10.43 (br, 1H); ^{13}C NMR ($CDCl_3$) δ −1.52, 29.42, 91.24, 126.95, 128.12, 130.47, 140.60, 167.17, 188.20. Anal. Calcd for $C_{13}H_{19}NOSi$: C, 66.90; H, 8.21; N, 6.00. Found: C, 66.75; H, 8.30; N, 5.91.

3.3.12. 3-Amino-4-(*tert*-butyldiphenylsilyl)-1-phenylbut-2-en-1-one (2l). Yield 96%; mp 138 °C; IR (KBr): 3270, 1593, 1521, 1324, 1107, 769, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 9H), 2.42 (s, 2H), 4.99 (br, 1H), 5.61 (s, 1H), 7.35–7.50 (m, 9H), 7.65–7.70 (m, 6H), 10.17 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 18.60, 22.75, 27.54, 93.01, 126.88, 127.87, 129.69, 130.34, 133.09, 135.89, 140.36, 165.98, 188.95. Anal. Calcd for $C_{26}H_{29}NOSi$: C, 78.15; H, 7.31; N, 3.51. Found: C, 78.43; H, 7.10; N, 3.60.

3.4. Synthesis of silylpyrazoles. General procedure

A mixture of silylated β-aminoenone (2 mmol) and free methylhydrazine, *tert*-butyl- and phenylhydrazine hydrochloride, ethylhydrazine oxalate or semicarbazide hydrochloride (3 mmol) in 8 mL of dry ethanol was stirred at rt or at reflux. At the end of the reaction (monitored by TLC) the solvent was evaporated under reduced pressure and the residue was extracted with CH_2Cl_2/H_2O. The organic layer was dried and concentrated. The residue was purified by flash chromatography on silica gel using as eluent CH_2Cl_2–Et_2O (20/1–10/1) to give the following products:

3.4.1. 1,5-Dimethyl-3-(trimethylsilyl)pyrazole (3a). Yield 60%; oil, bp 95–98 °C/0.5 mmHg; IR (film) 1247, 842, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9H), 2.25 (s, 3H), 3.80 (s, 3H), 6.13 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 1.13, 10.86, 35.90, 111.60, 138.16, 151.36. Anal. Calcd for $C_8H_{16}N_2Si$: C, 57.09; H, 9.58; N, 16.64. Found: C, 58.21; H, 9.60; N, 16.41.

3.4.2. 1,5-Dimethyl-3-(dimethylphenylsilyl)pyrazole (3b). Yield 50%; oil, R_f 0.38 (CH_2Cl_2/Et_2O, 20:1); IR (film) 1537, 1425, 1245, 1109, 831, 814, 776, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.66 (s, 6H), 2.30 (s, 3H), 3.86 (s, 3H), 6.21 (s, 1H), 7.42–7.71 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −2.37, 10.83, 35.93, 112.54, 127.57, 128.83, 133.84, 138.14, 138.21, 149.28. Anal. Calcd for $C_{13}H_{18}N_2Si$: C, 67.77; H, 7.88; N, 12.16. Found: C, 67.99; H, 7.78; N, 12.10.

3.4.3. 3-(*tert*-Butyldiphenylsilyl)-1,5-dimethylpyrazole (3c). Yield 68%; oil, R_f 0.55 (CH_2Cl_2); IR (film) 1540, 1427, 1107, 821, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (s, 9H), 2.27 (s, 3H), 3.89 (s, 3H), 6.04 (s, 1H), 7.35–7.38 (m, 6H), 7.71–7.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 11.02, 18.51, 27.83, 36.35, 115.15, 127.39, 128.93, 135.10, 136.42, 137.47, 146.23. Anal. Calcd for $C_{21}H_{26}N_2Si$: C, 75.40; H, 7.83; N, 8.37. Found: C, 75.21; H, 7.70; N, 8.51.

3.4.4. 1,3-Dimethyl-5-(trimethylsilyl)pyrazole (4a). Yield 18%; oil, R_f 0.27 (hexane/ethyl acetate, 10:1); IR (film) 1589, 1500, 1470, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.29 (s, 9H), 2.31 (s, 3H), 3.87 (s, 3H), 6.08 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −1.02, 12.80, 39.14, 114.07, 143.51, 147.63. Anal. Calcd for $C_8H_{16}N_2Si$: C, 57.09; H, 9.58; N, 16.64. Found: C, 57.40; H, 9.22; N, 16.28.

3.4.5. 1,3-Dimethyl-5-(dimethylphenylsilyl)pyrazole (4b). Yield 15%; oil, R_f 0.28 (hexane/ethyl acetate, 10:1); IR (film) 1580, 1500, 1470, 1270, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (s, 6H), 2.29 (s, 3H), 3.68 (s, 3H), 6.21, (s, 1H), 7.39–7.73 (m, 5H). Anal. Calcd for $C_{13}H_{18}N_2Si$: C, 67.77; H, 7.88; N, 12.16. Found: C, 67.43; H, 7.52; N, 12.49.

3.4.6. 5-(*tert*-Butyldiphenylsilyl)-1,3-dimethylpyrazole (4c). Yield 16%; oil, R_f 0.33 (hexane/ethyl acetate, 3:1); IR (film) 1516, 1471, 1106 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (s, 9H), 2.37 (s, 3H), 3.28 (s, 3H), 6.60 (s, 1H), 7.35–7.59 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 13.11, 18.43, 27.63, 40.03, 116.78, 127.94, 129.61, 133.01, 135.84, 137.50, 147.56. Anal. Calcd for $C_{21}H_{26}N_2Si$: C, 75.40; H, 7.83; N, 8.37. Found: C, 75.68; H, 7.72; N, 8.51.

3.4.7. 1-Ethyl-3-methyl-5-(trimethylsilyl)pyrazole (4d). Yield 91%; oil, bp 108–110 °C/1 mmHg; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9H), 1.44 (t, 3H, J=7.13 Hz), 2.28 (s, 3H), 4.13 (q, 2H, J=7.13 Hz), 6.09 (s, 1H). Anal. Calcd for $C_9H_{18}N_2Si$: C, 59.28; H, 9.95; N, 15.36. Found: C, 59.42; H, 10.01; N, 15.15.

3.4.8. 3-Methyl-1-phenyl-5-(trimethylsilyl)pyrazole (4e). Yield 85%; oil, bp 175–180 °C/1.5 mmHg; IR (film) 1600, 1501, 1252, 844, 762, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H), 2.34 (s, 3H), 6.33 (s, 1H), 7.33–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −0.62, 12.84, 115.65, 125.74, 127.83, 128.53, 142.28, 144.26, 148.74. Anal. Calcd for $C_{13}H_{18}N_2Si$: C, 67.77; H, 7.88; N, 12.16. Found: C, 67.45; H, 8.00; N, 12.21.

3.4.9. 3-Methyl-5-(trimethylsilyl)pyrazole-1-carboxamide (4f). Yield 80%; mp 78–80 °C (from hexane); IR (KBr) 3462, 3233, 1725, 1584, 1438, 1371, 947 cm^{-1}; H NMR ($CDCl_3$) δ 0.31 (s, 9H), 2.27 (s, 3H), 5.57 (br, 1H), 6.30 (s, 1H), 7.27 (br, 1H); ^{13}C NMR ($CDCl_3$) δ −0.90, 13.11, 118.99, 146.17, 151.43, 152.36. Anal. Calcd for $C_8H_{15}N_3OSi$: C, 48.70; H, 7.66; N, 21.30. Found: C, 48.82; H, 7.60; N, 21.52.

3.4.10. 3-Methyl-5-(dimethylphenylsilyl)-1-phenylpyrazole (4h). Yield 69%; oil, R_f 0.50 (CH_2Cl_2); IR (film) 1598, 1500, 1250, 1111, 779, 734, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.35 (s, 6H), 2.38 (s, 3H), 6.42 (s, 1H), 7.15–7.50 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −0.19, 13.31, 117.22, 125.46, 127.75, 127.90, 128.49, 129.15, 133.80, 137.10, 142.00, 142.50, 148.92. Anal. Calcd for $C_{18}H_{20}N_2Si$: C, 73.92; H, 6.89; N, 9.58. Found: C, 74.10; H, 6.81; N, 9.72.

3.4.11. 1-Benzyl-5-(*tert*-butyldiphenylsilyl)-3-methylpyrazole (4i). Yield 80%; oil, R_f 0.52 (CH_2Cl_2); IR (film) 1428, 1107, 820, 731, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (s, 9H), 2.44 (s, 3H), 4.84 (s, 2H), 6.71 (s, 1H), 6.98–7.60 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 13.37, 18.51, 27.78, 55.51, 116.88, 126.62, 126.77, 127.53, 127.77, 129.39, 132.70, 135.95, 137.23, 137.87, 148.40. Anal. Calcd for $C_{27}H_{30}N_2Si$: C, 78.97; H, 7.36; N, 6.82. Found: C, 79.10; H, 7.24; N, 6.75.

3.4.12. 5-(*tert*-Butyldiphenylsilyl)-3-methyl-1-phenylpyrazole (4k). Yield 75%; mp 145–146 °C (from hexane); IR (KBr) 1599, 1499, 1108, 817, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 9H), 2.46 (s, 3H), 6.87 (s, 1H), 6.88–7.49 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 13.21, 18.71, 28.08, 118.57, 126.34, 127.27, 127.52, 127.98, 129.18, 133.43, 135.89, 138.56, 141.86, 148.84. Anal. Calcd for $C_{26}H_{28}N_2Si$: C, 78.74; H, 7.12; N, 7.06. Found: C, 78.46; H, 7.02; N, 7.26.

3.4.13. 4,5-Dihydro-5-hydroxy-3,5-dimethyl-4-(trimethylsilylmethyl)pyrazole-1-carboxamide (5). ^1H NMR ($CDCl_3$) δ −0.20 (s, 9H), 0.85 (dd, 1H, J=8.3, 14.8 Hz), 1.11 (dd, 1H, J=6.6, 14.8 Hz), 1.77 (s, 3H), 2.14 (s, 3H), 3.43 (dd, 1H, J=6.6, 8.3 Hz), 5.62 (br, 1H), 7.05 (br, 1H).

3.4.14. 3,5-Dimethyl-4-(trimethylsilylmethyl)-1-phenylpyrazole (6a). Yield 72%; mp 190–191 °C (from hexane); IR (KBr) 1598, 1502, 1364, 1246, 857, 760, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.47 (s, 9H), 1.76 (s, 2H), 2.18 (s, 3H), 2.22 (s, 3H), 7.45–7.47 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −1.56, 11.31, 11.96, 12.48, 115.22, 124.01, 126.32, 128.51, 133.81, 139.90, 146.67. Anal. Calcd for $C_{15}H_{22}N_2Si$: C, 69.71; H, 8.58; N, 10.84. Found: C, 70.00; H, 8.41; N, 10.80.

3.4.15. 3,5-Dimethyl-4-(trimethylsilylmethyl)pyrazole-1-carboxamide 6b. Yield 78%; mp 103–104 °C (from hexane); IR (KBr) 3431, 3332, 1731, 1700, 1400, 863, 575 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9H), 1.69 (s, 2H), 2.12 (s, 3H), 2.42 (s, 3H), 5.33 (br, 1H), 7.07 (br, 1H); ^{13}C NMR ($CDCl_3$) δ −1.32, 12.30, 12.47, 12.86, 118.60, 137.38, 149.69, 152.65. Anal. Calcd for $C_{10}H_{19}N_3OSi$: C, 53.29; H, 8.50; N, 18.65. Found: C, 53.57; H, 8.49; N, 18.40.

3.4.16. 1,3-Dimethyl-5-(trimethylsilylmethyl)pyrazole 7a. Yield 40%; oil, bp 100–105 °C/0.2 mmHg; IR (film) 1542, 1249, 852 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9H), 1.93 (s, 2H), 2.16 (s, 3H), 3.61 (s, 3H), 5.61 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −1.74, 13.31, 15.55, 35.53, 103.10, 141.25, 146.91. Anal. Calcd for $C_9H_{18}N_2Si$: C, 59.28; H, 9.95; N, 15.36. Found: C, 59.42; H, 10.00; N, 15.22.

3.4.17. 5-(*tert*-Butyldiphenylsilylmethyl)-1,3-dimethylpyrazole (7b). Yield 51%; mp 70–71 °C; IR (KBr) 1543, 1426, 1106, 734, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (s, 9H), 2.07 (s, 3H), 2.56 (s, 2H), 3.23 (s, 3H), 5.47 (s, 1H), 7.31–7.52 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 9.25, 13.35, 18.24, 27.63, 35.18, 104.50, 127.60, 129.43, 133.28, 135.86, 139.62, 145.61. Anal. Calcd for $C_{22}H_{28}N_2Si$: C, 75.81; H, 8.10; N, 8.04. Found: C, 75.99; H, 8.00; N, 8.18.

3.4.18. 5-(*tert*-Butyldiphenylsilylmethyl)-3-methylpyrazole-1-carboxamide (7c). Yield 75%; mp 106–108 °C; IR (KBr) 3401, 3236, 1690, 1590, 1395, 1107, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (s, 9H), 2.04 (s, 3H), 3.37 (s, 2H), 5.21 (br, 1H), 5.50 (s, 1H), 6.81 (br, 1H), 7.30–7.55 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.07, 13.51, 18.43, 27.58, 109.03, 127.36, 129.13, 133.72, 136.04, 145.37, 150.09, 152.74. Anal. Calcd for $C_{22}H_{27}N_3OSi$: C, 69.99; H, 7.21; N, 11.13. Found: C, 70.20; H, 7.26; N, 10.99.

3.4.19. 1-Ethyl-3-methyl-5-(methyldiphenylsilylmethyl)pyrazole (7d). Yield 93%; bp 200–205 °C/1 mmHg; IR (film) 1540, 1427, 1113, 808, 733, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.62 (s, 3H), 1.22 (t, J=7.2 Hz, 3H), 2.20 (s, 3H), 2.52 (s, 2H), 3.71 (q, J=7.2 Hz, 2H), 5.56 (s, 1H), 7.36–7.52 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −4.48, 13.27, 13.50, 15.29, 42.90, 104.06, 127.92, 129.60, 134.39, 135.48, 138.71, 147.00. Anal. Calcd for $C_{20}H_{24}N_2Si$: C, 74.95; H, 7.55; N, 8.74. Found: C, 75.24; H, 7.50; N, 8.53.

3.4.20. 3-Methyl-5-(methyldiphenylsilylmethyl)pyrazole-1-carboxamide (7e). Yield 79%; mp 113–114 °C; IR (KBr) 3461, 3304, 3248, 1727, 1562, 1427, 1387, 1113, 732, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.54 (s, 3H), 2.15 (s, 3H), 3.23 (s, 2H), 5.24 (br, 1H), 5.62 (s, 1H), 6.98 (br, 1H), 7.33–7.65 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −4.62, 13.58, 15.86, 108.55, 127.75, 129.36, 134.57, 135.87, 145.38, 150.50, 152.61. Anal. Calcd for $C_{19}H_{21}N_3OSi$: C, 68.02; H, 6.31; N, 12.53. Found: C, 67.93; H, 6.40; N, 12.65.

3.4.21. 1-(*tert*-Butyl-5-(*tert*-butyldiphenylsilylmethyl))-3-methylpyrazole (7f). Yield 85%; oil, R_f 0.45 (CH_2Cl_2); IR (film) 1653, 1540, 1471, 1427, 1236, 1106, 1011, 820, 734, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (s, 9H), 1.61 (s, 9H), 2.01 (s, 3H), 2.85 (s, 2H), 5.46 (s, 1H), 7.35–7.80 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 10.73, 13.48, 18.35, 27.79, 30.61, 58.94, 108.11, 127.59, 129.29, 133.60, 135.91, 138.48, 144.47. Anal. Calcd for $C_{25}H_{34}N_2Si$: C, 76.87; H, 8.77; N, 7.17. Found: C, 76.99; H, 8.73; N, 7.22.

3.4.22. 5-(*tert*-Butyldiphenylsilylmethyl)-1-ethyl-3-methylpyrazole (7g). Yield 91%; mp 45–47 °C; IR (KBr) 1540, 1470, 1427, 1107, 732, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 9H), 1.21 (t, 3H, J=7.2 Hz), 2.09 (s, 3H), 2.59 (s, 2H), 3.64 (q, 2H, J=7.2 Hz), 5.44 (s, 1H), 7.31–7.55 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 8.70, 13.43, 15.15, 18.23, 27.63, 42.70, 104.69, 127.56, 129.36, 133.34, 135.82, 138.62, 146.65. Anal. Calcd for $C_{23}H_{30}N_2Si$: C, 76.19; H, 8.34; N, 7.73. Found: C, 76.23; H, 8.40; N, 7.68.

3.4.23. 5-(*tert*-Butyldiphenylsilylmethyl)-3-methyl-1-phenylpyrazole (7h). Yield 89%; oil, bp 250 °C/0.5 mmHg; IR (film) 1598, 1501, 1107, 732, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (s, 9H), 2.12 (s, 3H), 2.68 (s, 2H), 5.51 (s, 1H), 7.13–7.51 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 9.26, 13.48, 18.19, 27.50, 105.92, 126.04, 127.42, 127.59, 128.78, 129.37, 133.47, 135.94, 139.61, 140.36, 148.53. Anal. Calcd for $C_{27}H_{30}N_2Si$: C, 78.97; H, 7.36; N, 6.82. Found: C, 79.08; H, 7.29; N, 6.93.

3.4.24. 5-(*tert*-Butyldiphenylsilylmethyl)-3-isopropyl-1-phenylpyrazole (7i). Yield 60%; oil, R_f 0.45 (CH_2Cl_2); IR (film) 1598, 1501, 1380, 1106, 733, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (s, 9H), 1.13 (d, J=6.9 Hz, 6H), 2.72 (s, 2H), 2.87 (m, J=6.9 Hz, 1H), 5.51 (s, 1H), 7.12–7.46 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 9.51, 18.12, 22.76, 27.44,

27.65, 102.82, 126.09, 127.29, 127.46, 128.72, 129.26, 133.54, 135.94, 139.65, 139.97, 150.04. Anal. Calcd for $C_{29}H_{34}N_2Si$: C, 79.40; H, 7.81; N, 6.39. Found: C, 79.71; H, 7.75; N, 6.22.

3.4.25. 1,5-Dimethyl-3-(trimethylsilylmethyl)pyrazole (8a). Yield 38%; oil, bp 95–99 °C/0.1 mmHg; IR (film) 1550, 1453, 1247, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9H), 1.96 (s, 2H), 2.19 (s, 3H), 3.66 (s, 3H), 5.64 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −1.69, 11.09, 18.07, 35.46, 103.83, 138.61, 148.91. Anal. Calcd for $C_9H_{18}N_2Si$: C, 59.28; H, 9.95; N, 15.36. Found: C, 59.43; H, 10.01; N, 15.28.

3.4.26. 3-(*tert*-Butyldiphenylsilylmethyl)-1,5-dimethylpyrazole (8b). Yield 28%; oil, R_f 0.39 (CH_2Cl_2/Et_2O, 30:1); IR (film) 1619, 1549, 1427, 1107, 734, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (s, 9H), 2.00 (s, 3H), 2.72 (s, 2H), 3.62 (s, 3H), 5.15 (s, 1H), 7.35–7.71 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 10.91, 11.85, 18.34, 27.66, 35.28, 104.53, 127.30, 128.87, 134.56, 136.04, 138.31, 147.45. Anal. Calcd for $C_{22}H_{28}N_2Si$: C, 75.81; H, 8.10; N, 8.04. Found: C, 76.01; H, 7.95; N, 8.15.

3.4.27. 3-(*tert*-Butyldiphenylsilylmethyl)-5-methylpyrazole-1-carboxamide (8c). IR (film) 3430, 3330, 1720, 1690, 1100, 763, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 9H), 2.37 (s, 3H), 2.65 (s, 2H), 5.00 (br, 1H), 5.45 (s, 1H), 6.81 (br, 1H), 7.30–7.55 (m, 10H). Anal. Calcd for $C_{22}H_{27}N_3OSi$: C, 69.99; H, 7.21; N, 11.13. Found: C, 70.31; H, 7.55; N, 11.45.

3.4.28. 1-*tert*-Butyl-3-(*tert*-butyldiphenylsilylmethyl)-5-phenylpyrazole (8d). Yield 45%; oil, R_f 0.47 (CH_2Cl_2); IR (film) 1605, 1427, 1110, 821, 738, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (s, 9H), 1.45 (s, 9H), 2.31 (s, 2H), 5.95 (s, 1H), 7.26–7.76 (m, 15H). Anal. Calcd for $C_{30}H_{36}N_2Si$: C, 79.59; H, 8.02; N, 6.19. Found: C, 79.21; H, 7.90; N, 6.55.

3.4.29. 3-(*tert*-Butyldiphenylsilylmethyl)-1,5-diphenylpyrazole (8e). Yield 34%; oil, R_f 0.44 (CH_2Cl_2); IR (film) 1595, 1361, 1109, 970, 868 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (s, 9H), 2.41 (s, 2H), 6.34 (s, 1H), 7.22–7.74 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 13.51, 18.96, 26.51, 107.69, 125.10, 127.04, 127.59, 128.01, 128.34, 128.57, 128.78, 129.47, 130.67, 134.78, 135.36, 140.04, 143.64, 149.41. Anal. Calcd for $C_{32}H_{38}N_2Si$: C, 81.31; H, 6.82; N, 5.93. Found: C, 81.63; H, 6.97; N, 6.10.

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References and notes

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