Regioselective Synthesis of Silylated Pyrazolines and Indazolines by Reaction of Pyrazolium and Indazolium Salts with Silyllithium Reagents

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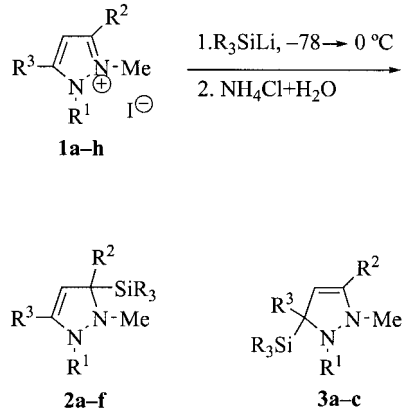
Pyrazolium salts react with dimethylphenylsilyl- and *tert*-butyldiphenylsilyllithium to give, in general, only one of the two possible 5-silyl-3-pyrazolines. On the other hand, indazolium and isoindazolium salts lead to 3-silylindazolines and occasionally to compounds resulting from the opening or expansion of the heterocyclic ring. All of these compounds are interesting synthons in organic chemistry.

Introduction

Pyrazolium salts are not reactive toward organometallic reagents[1] except when they bear a nitro group[2] at C-4. Nevertheless, in a preliminary communication[3] we reported the regioselective synthesis of 5-silylated 3-pyrazolines by reaction of 1,3,5-trisubstituted-2-methylpyrazolium iodides with dimethylphenylsilyl- and *tert*-butyldiphenylsilyllithium. We have extended this methodology to functionalized pyrazolium, indazolium and isoindazolium salts with the aim of knowing their scope and with the purpose of synthesising new silylated pyrazolines and indazolines. In this paper, we describe the full results obtained in the addition of silyllithium reagents to pyrazolium or benzopyrazolium salts with various substitution patterns.



Scheme 1.

Results and Discussion

1,3,5-Trisubstituted-2-methylpyrazolium iodides **1a**–**f** react easily with dimethylphenylsilyl- and *tert*-butyldiphenylsilyllithium leading to 5-silyl-3-pyrazolines **2a**–**f** or **3a**–**c** regioselectively, while 3- or 5-unsubstituted pyrazolium salts **1g** and **1h** were shown to be unreactive (Scheme 1). The results obtained are collected in Table 1.

When R^1 = Ph, the C-3 and C-5 positions of 2-methylpyrazolium salts are different and the attack of the silyl anion at C-3 or C-5 could lead to regioisomeric 5-silyl-3-pyrazolines. The reaction of the 2-methylpyrazolium iodide **1b** with dimethylphenylsilyllithium gave the 3-pyrazoline **2c** resulting from the attack of the silyl anion at the more electron-deficient C-3. However, the bulky *tert*-butyldiphenylsilyllithium attacked the less hindered C-5 to give the 3-pyrazoline **3a**.

Moreover, when the substituents at C-3 and C-5 are different, the selective formation of either of the 3-pyrazolines also depends on the nature of the 3- and 5-substituents. Thus, the reaction of pyrazolium iodides **1c** (R^2 = Me, R^3 = Ph) and **1d** (R^2 = Ph, R^3 = Me) with dimethylphenylsilyllithium afforded exclusively the 5-dimethylphenylsilyl-3-pyrazolines **2d** and **3b**, respectively, in which the double bond C=C is conjugated with the phenyl group. Although in a preliminary communication[3] we described that the reaction of **1c** with dimethylphenylsilyllithium between –78 and 0 °C led to a mixture of the two possible 5-silyl-3-pyrazolines, we have now verified that the product to which we had assigned the structure of the 3-pyrazoline regioisomer of **2d**, was a cleavage product whose ratio in the mixture increased with the reaction time at 0 °C. If the reaction is carried out at –78 °C, only the pyrazoline **2d** is isolated.

On the other hand, we have been unable to repeat the result described[3] in the reaction of **1c** with *tert*-butyldi-

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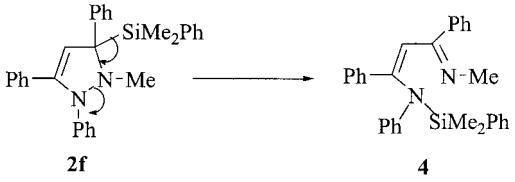
Table 1. Reactions of 2-methylpyrazolium iodides with silyllithium reagents.[a]

Substrate	R^1	R^2	R^3	R_3Si	Products and yields (%)
1a	Me	Me	Me	Me_2Ph	**2a** (5%)[b]
1a	Me	Me	Me	$tBuPh_2$	**2b** (25%)
1b	Ph	Me	Me	Me_2Ph	**2c** (82%)
1b	Ph	Me	Me	$tBuPh_2$	**3a** (57%)
1c	Ph	Me	Ph	Me_2Ph	**2d** (91%)[c]
1c	Ph	Me	Ph	$tBuPh_2$	–[d]
1d	Me	Ph	Me	Me_2Ph	**3b** (89%)
1d	Me	Ph	Me	$tBuPh_2$	**3c** (73%)
1e	Me	Ph	Ph	Me_2Ph	**2e** (84%)
1e	Me	Ph	Ph	$tBuPh_2$	–[d]
1f	Ph	Ph	Ph	Me_2Ph	**2f** (58%) + **4** (26%)[e]
1f	Ph	Ph	Ph	$tBuPh_2$	–[d]
1g	Ph	H	Me	Me_2Ph	–[d]
1g	Ph	H	Me	$tBuPh_2$	–[d]
1h	Ph	Me	H	Me_2Ph	–[d]
1h	Ph	Me	H	$tBuPh_2$	–[d]

[a] Reactions were carried out using a molar ratio of pyrazolium/R_3SiLi = 1:1 in THF as a solvent. [b] 5-Dimethylphenylsilyl-3-pyrazoline (**2a**) is very unstable and was only identified by ^1H NMR spectroscopy. [c] The reaction was carried out at –78 °C and hydrolysed with methanol at this temperature. [d] The starting product was recovered. [e] Even at –78 °C, **2f** is partially opened to **4**.

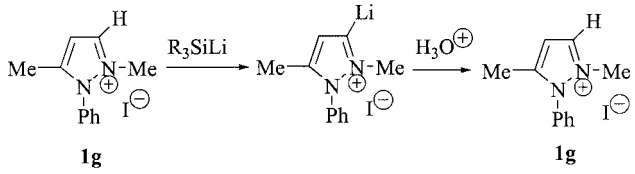
phenylsilyllithium. In all conditions (–78 to 0 °C, 0 °C, 0 °C to room temp.) we have recovered **1c**. The phenyl group attached to the less-hindered C-5 increases the steric hindrance and probably prevents the approach of the bulky *tert*-butyldiphenylsilyl group at C-3 and C-5. Furthermore, the 1,2-dimethylpyrazolium iodide **1d**, in which the C-3 and C-5 positions are interchangeable, afforded the 5-*tert*-butyldiphenylsilyl-3-pyrazoline (**3c**) in its reaction with *tert*-butyldiphenylsilyllithium.

The 3,5-diphenylpyrazolium iodides **1e** and **1f** reacted with dimethylphenylsilyllithium, but not with the bulkier *tert*-butyldiphenylsilyl reagent, affording the 5-silyl-3-pyrazolines **2e** and **2f**. In the latter case, we also obtained the *N*-silylated β-enamino imine **4**. This product was probably formed by the opening of the pyrazoline **2f** with the concomitant 1,3-rearrangement of the silyl group from carbon to nitrogen[4,5] (Scheme 2).



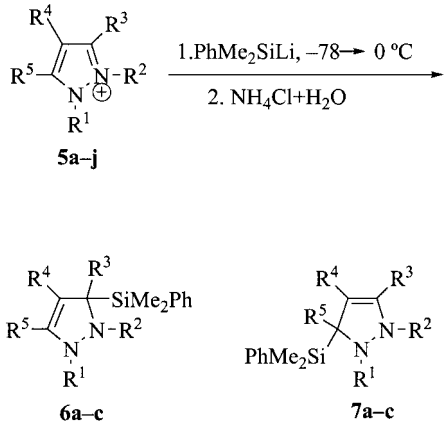
Scheme 2.

When C-3 or C-5 of the starting salts is unsubstituted, the reaction with neither silyllithium reagent took place. The pyrazolium iodides **1g** and **1h** were recovered even using an excess of silyllithium (2 equiv.) at room temperature for 24 h. Probably, the reagent behaves as a base, eliminating the acidic H-3 or H-5 proton[6] to give the corresponding lithium derivative which regenerates the starting product in the final hydrolysis (Scheme 3).



Scheme 3.

We have also studied the behaviour of functionalized pyrazolium salts toward these silyllithium reagents. Bulky *tert*-butyldiphenylsilyllithium was shown to be unreactive with all the pyrazolium salts tested (Scheme 4). The results with dimethylphenylsilyllithium are summarised in Table 2.



Scheme 4.

Although the electron-withdrawing groups increase the electron deficiency of the pyrazolium salts, and consequently their reactivity toward the nucleophilic silyllithium reagent, the 4-nitro and 4-bromo derivatives **5a** and **5b** were shown to be unreactive. Possibly, the large 4-nitro and 4-bromo groups prevent coplanarity and hinder the addition of the silyl group at C-3 or C-5. Meanwhile, the less bulky 4-ethoxycarbonyl group in the 1-methylpyrazolium salt **5d** increases the electronic deficiency of C-5 by conjugation and favours the formation of pyrazoline **7b** resulting from the addition of the silyl group at that position. The presence of the *N*-phenyl group in the pyrazolium salt **5c** increases the steric hindrance at C-5 and leads to a mixture of 3-pyrazolines **6a** and **7a** resulting from the addition of the silyl group at C-3 and at C-5, respectively.

On the other hand, a 3-ethoxycarbonyl group does not sufficiently activate C-3 or C-5. Despite the fact that this functional group enhances the electron deficiency of the 3-position by an inductive effect, it also increases its steric hindrance. The 3-(ethoxycarbonyl)pyrazolium salt **5f** was shown to be unreactive toward dimethylphenylsilyllithium.

Obviously, the presence at C-4 of an electron-donating silyl group decreases the reactivity of the pyrazolium salts **5g** and **5h** and increases the steric hindrance at C-3 and C-5, making the addition of the dimethylphenylsilyl anion more difficult. Nevertheless, the 3,5-dimethyl-4-(dimethylphenylsilyl)pyrazolium salt **5g** leads to an interesting 4,5-disilylated 3-pyrazoline **6b**, bearing an allyl- and a vinylsilane

Table 2. Reactions of 4- or 5-functionalized pyrazolium salts with dimethylphenylsilyllithium.[a]

Substrate	R^1	R^2	R^3	R^4	R^5	Products and yields (%)
5a	Ph	Et	Me	NO_2	Me	– [b]
5b	Ph	Et	Me	Br	Me	– [b]
5c	Ph	Et	Me	CO_2Et	Me	**6a** (33%) + **7a** (49%)
5d	Me	Et	Me	CO_2Et	Me	**7b** (67%)
5e	Ph	Et	Me	H	CO_2Et	**7c** (84%)[c]
5f	Ph	Et	CO_2Et	H	Me	– [b]
5g	Ph	Et	Me	Me_2PhSi	Me	**6b** (75%)
5h	Ph	Et	Ph	Me_2PhSi	Ph	–[b]
5i	Ph	Me	Me	H	Me_2PhSi	–[d]
5j	Ph	Me	Me	H	tBuPh$_2$Si	**6c** (68%)

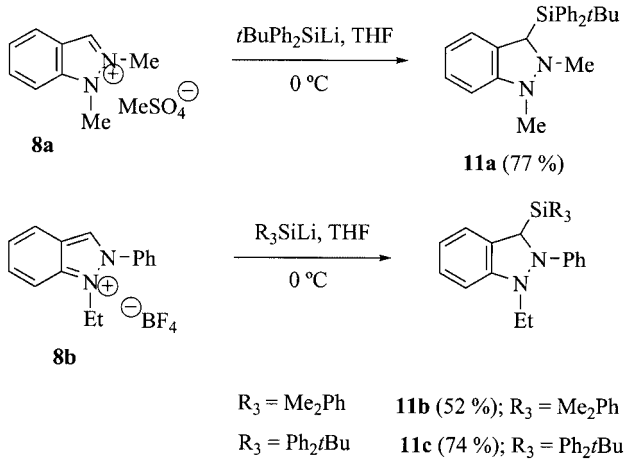
[a] Reactions were carried out using a molar ratio of pyrazolium/R_3SiLi = 1:1 in THF as a solvent. [b] The starting product was recovered. If the temperature or the time reaction was increased, the corresponding pyrazoles resulting from dequaternization were obtained. [c] The 5-silyl-3-pyrazoline **7c** lost the silyl group and was isolated as ethyl 2-ethyl-3-methyl-1-phenyl-3-pyrazoline-5-carboxylate (**7c**; $SiMe_2Ph$ = H). [d] Only unidentified decomposition products were detected.

moiety. The more hindered 3,5-diphenylpyrazolium salt **5h** was recovered from its treatment with the dimethylphenylsilyllithium reagent. Although the 5-silylpyrazolium salts **5i** and **5j** were shown to be reactive toward the dimethylphenylsilyllithium reagent, only 3-*tert*-butyldiphenylsilyl-5-dimethylphenylsilyl-3-pyrazoline (**6c**), resulting from the attack of the silyl anion at C-3 of the 5-(*tert*-butyldiphenylsilyl)pyrazolium salt **5j**, was sufficiently stable to be isolated.

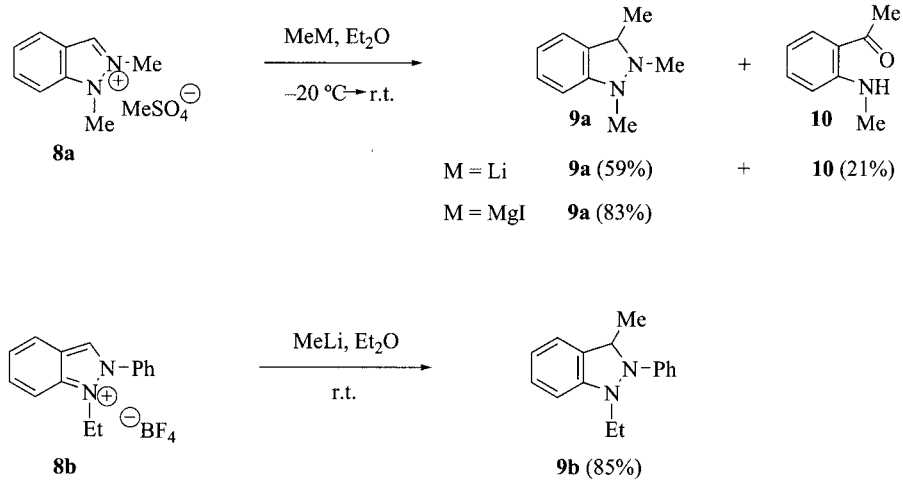
We were also interested to know the behaviour of benzopyrazolium salts toward silyllithium reagents. Since we did not find any references concerning the reactivity of these substrates with organometallic compounds, we initially studied the reaction of 1,2-dimethylindazolium methyl sulfate (**8a**) and 1-ethyl-2-phenylindazolium tetrafluoroborate (**8b**) with methyllithium and methylmagnesium iodide (Scheme 5).

The indazolium salt **8a** reacted easily with both organometallic reagents leading to 3-methylindazoline **9a**, resulting from the addition of the organometallic reagent at C-3. When methyllithium was used as a nucleophile, the amino ketone **10** formed by ring-cleavage, together with **9a**, were obtained. The isoindazolium salt **8b** was shown to be less reactive. It was necessary to carry out the reaction with methyllithium at room temperature in order to obtain the 3-methylindazoline **9b**.

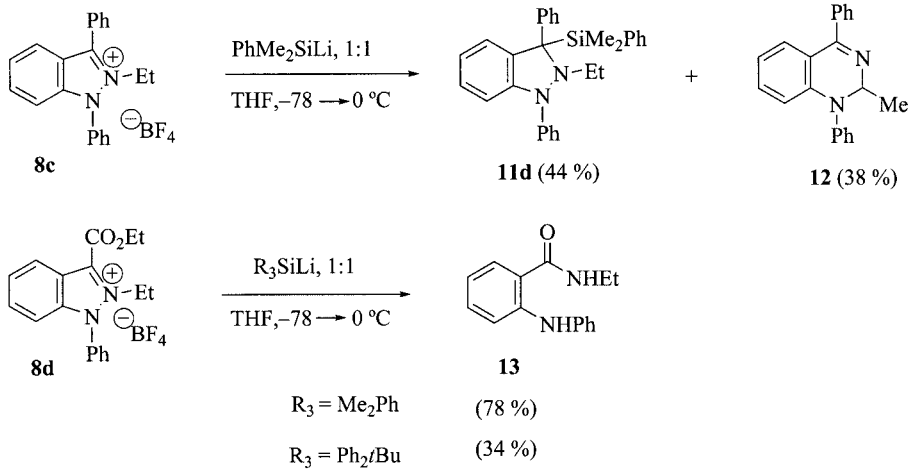
These 3-unsubstituted indazolium salts **8a** and **8b** were shown to be very reactive toward dimethylphenyl- and *tert*-butyldiphenylsilyllithium to give exclusively the corresponding 3-silylindazolines **11a**–**c** with good yields (Scheme 6).



Scheme 6.



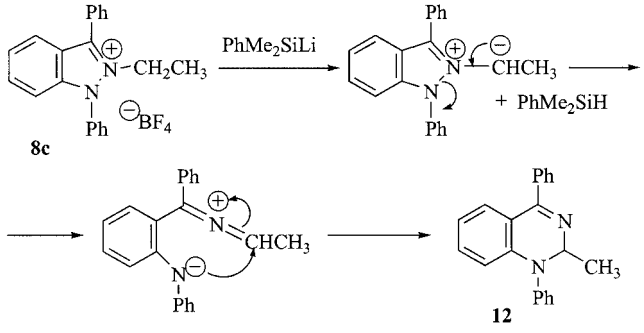
Scheme 5.



Scheme 7.

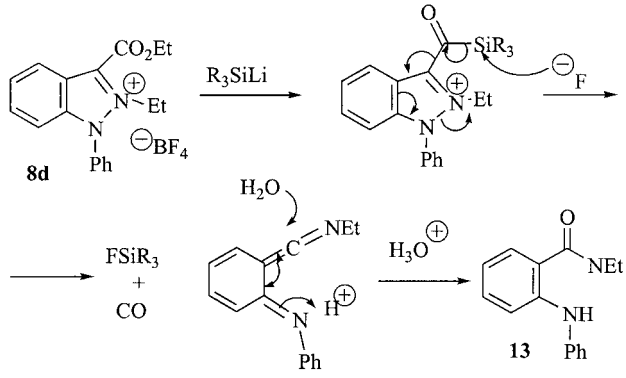
The indazolium salt **8a** also reacted with dimethylphenylsilyllithium but the 1,2-dimethyl-3-dimethylphenylsilylindazoline product turned out to be very unstable and could not be isolated.

The behaviour of the 3-substituted indazolium salts is different and depends on the nature of the substituent (Scheme 7). When 3-methylpyrazolium tetrafluoroborates were treated with dimethylphenyl- or *tert*-butyldiphenylsilyllithium at 0 °C for 8 h, the starting salt was recovered. The silyllithium probably extracted a proton from the acidic 3-methyl group,[7] and the resulting lithium derivative became the starting product in the final hydrolysis. On the other hand, the 3-phenylpyrazolium salt **8c** reacted with dimethylphenylsilyllithium to give a mixture of the corresponding 3-silylindazoline **11c** and 2-methyl-1,4-diphenyl-1,2-dihydroquinazoline (**12**). The latter, which is the major product if a salt/silyllithium ratio = 1:2 is used, might be formed by a heterocyclic opening/closing mechanism (Scheme 8).



Scheme 8.

Finally, the 3-(ethoxycarbonyl)indazolium tetrafluoroborate **8d** reacted with both silyllithium reagents, affording the β-enamino amide **13** exclusively (Scheme 7). This result could be explained by the initial reaction of the silyllithium with the ester group leading to an acylsilane, which is attacked by the fluoride ion with concomitant carbon monoxide elimination and ring opening to give a ketenimine intermediate, which yields **13** in the final hydrolysis (Scheme 9).



Scheme 9.

Conclusions

We have developed a simple and suitable method to regioselectively prepare 5-silylated 3-pyrazolines for the first time, and with wide substitution patterns. Moreover, we have studied the influence of the nature of the substituent on the reactivity and regioselectivity of the reaction. These 5-silyl-3-pyrazolines are interesting compounds in organic synthesis because their allylsilane moiety is easily substituted by electrophiles with double bond rearrangement to give new 5-substituted 3-pyrazolines. We were able[3] to prove the proto-, acetyl- and iododesilylation.

In addition, the application of this methodology to indazolium salts has allowed us to synthesise 3-silylindazolines and other interesting products obtained by the opening or expansion of the heterocyclic ring.

Experimental Section

General: THF was distilled from sodium benzophenone ketyl in a recycling still. All chromatographic and workup solvents were dis-

tilled prior to use. All reactions involving organometallic reagents were carried out under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ as an internal standard. Carbon multiplicities were assigned by DEPT experiments. Reactions were monitored by TLC on pre-coated plates of silica gel 60 (nano-SIL-20, Macherey–Nagel). Flash chromatography was performed on silica gel 60 (230–400 mesh, M–N). The 2-methylpyrazolium or indazolium iodides were prepared by heating of corresponding pyrazoles or indazoles with methyl iodide in a pressure tube, and 2-ethylpyrazolium tetrafluoroborates were prepared by treatment of the respective pyrazoles and indazoles with triethyloxonium fluoroborate in dry dichloromethane at room temperature for several hours (12–20 h). All pyrazolium and indazolium salts were recrystallized from acetone-ether.

We prepared new 4-silyl- and 5-silylpyrazolium salts **5g–j** by quaternization of the corresponding 4-silyl- and 5-silylpyrazoles.[8] Their spectroscopic data are given below.

2-Ethyl-3,5-dimethyl-4-dimethylphenylsilyl-1-phenylpyrazolium Tetrafluoroborate (5g): Yield 1.98 g (94%). M.p. 96–97 °C (recrystallised from MeCOMe/Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.61 (s, 6 H), 1.12 (t, J = 7.3 Hz, 3 H), 1.93 (s, 3 H), 2.32 (s, 3 H), 4.09 (q, J = 7.3 Hz, 2 H), 7.35–7.64 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.34, 12.62, 13.15, 14.09, 42.83, 112.70, 128.36, 128.87, 129.92, 130.81, 131.17, 132.59, 133.92, 135.87, 151.62, 151.83 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1593, 1499, 1256, 1100 cm^{-1}.

2-Ethyl-4-dimethylphenylsilyl-1,3,5-triphenylpyrazolium Tetrafluoroborate (5h): Yield 2.45 g (90%). M.p. 144.3–145.6 °C (recrystallised from MeCOMe/Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 6 H), 0.99 (t, J = 7.2 Hz, 3 H), 4.16 (q, J = 7.2 Hz, 2 H), 7.15–7.25 (m, 10 H), 7.44–7.70 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.11, 19.43, 49.16, 119.52, 132.46, 132.95, 133.43, 134.24, 135.17, 135.59, 136.31, 136.71, 137.43,138.75, 141.50, 158.35, 159.20 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1598, 1509, 1254, 1103 cm^{-1}.

2,3-Dimethyl-5-dimethylphenylsilyl-1-phenylpyrazolium Iodide (5i): Yield 1.97 g (91%). M.p. 155–157 °C (recrystallised from MeCOMe/Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.36 (s, 6 H), 2.64 (s, 3 H), 3.82 (s, 3 H), 6.62 (s, 1 H), 7.20–7.63 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.53, 13.33, 36.41, 116.30, 128.09, 129.28, 129.92, 130.26, 132.26, 132.36, 132.62, 133.66, 147.05, 150.95 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3019, 1495, 1458, 1256, 1113 cm^{-1}.

5-*tert*-Butyldiphenylsilyl-2,3-dimethyl-1-phenylpyrazolium Iodide (5j): Yield 2.50 g (93%). M.p. 205–207 °C (recrystallized from MeCOMe/Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 9 H), 2.80 (s, 3 H), 3.79 (s, 3 H), 6.91–6.98 (m, 4 H), 7.09 (s, 1 H), 7.18–7.40 (m, 11 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.93, 18.63, 27.77, 36.99, 117.79, 128.19, 129.32, 129.62, 130.15, 131.57, 132.36, 135.75, 147.27, 147.63 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3019, 1590, 1493, 1109 cm^{-1}.

General Procedure for the Reaction of Pyrazolium and Indazolium Salts with Silyllithium Reagents: To a stirred solution of pyrazolium or indazolium salt (2.0 mmol) in dry THF (20 mL) at –78 °C or 0 °C, under N_2, was added a THF solution of dimethylphenylsilyl[9] or *tert*-butyldiphenylsilyllithium[10] (2 mmol). The reaction mixture (when cooled to –78 °C) was slowly allowed to warm to 0 °C and was stirred at room temperature until TLC indicated that the reaction was complete. The mixture was quenched with aqueous NH_4Cl and extracted with Et_2O.The ethereal layer was dried with $MgSO_4$ and the solvent was removed. The residue was purified by flash chromatography (silica gel, hexanes/CH_2Cl_2 = 1:1) to give the following products:

1,2,3,5-Tetramethyl-5-dimethylphenylsilyl-3-pyrazoline (2a): Yield 26 mg (5%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.53 (s, 3 H), 0.54 (s, 3 H), 0.99 (s, 3 H), 2.01 (s, 3 H), 2.43 (s, 3 H), 2.80 (s, 3 H), 4.06 (s, 1 H), 7.36–7.74 (m, 5 H) ppm.

5-*tert*-Butyldiphenylsilyl-1,2,3,5-tetramethyl-3-pyrazoline (2b): Yield 182 mg (25%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (s, 3 H), 1.22 (s, 9 H), 1.97 (s, 3 H), 2.35 (s, 3 H), 2.78 (s, 3 H), 4.43 (s, 1 H), 7.46–7.78 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.96, 20.09, 27.47, 29.12, 31.82, 34.42, 51.08, 98.90, 127.50, 129.32, 133.71, 134.78, 147.06 ppm. IR (film): $\tilde{\nu}$ = 3020, 1598, 1509, 1100, 810 cm^{-1}. MS (EI, 70 eV): m/z (%) = 110 (M^+ – tBuPh$_2$SiMe, 100%), 95 (34), 82 (9). $C_{23}H_{32}N_2Si$ (364.23): calcd. C 75.77, H 8.85, N 7.68; found C 75.70, H 8.91, N 7.73.

1,3,5-Trimethyl-5-dimethylphenylsilyl-2-phenyl-3-pyrazoline (2c): Yield 528 mg (82%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.46 (s, 3 H), 0.48 (s, 3 H), 1.30 (s, 3 H), 1.70 (s, 3 H), 2.36 (s, 3 H), 4.70 (s, 1 H), 7.25–7.70 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.01, –4.82, 13.73, 17.59, 37.02, 59.74, 108.23, 126.14, 127.48, 128.67, 130.81, 132.97, 133.94, 137.33, 140.98, 146.76 ppm. IR (film): $\tilde{\nu}$ = 3020, 1608, 1504, 1250, 1110, 820 cm^{-1}. MS (EI, 70 eV): m/z (%) = 322 (M^+, 1%), 200 (16), 135 (30), 120 (20), 77 (100). $C_{20}H_{26}N_2Si$ (322.19): calcd. C 74.48, H 8.13, N 8.69; found C 74.57, H 8.03, N 8.59.

1,5-Dimethyl-5-dimethylphenylsilyl-2,3-diphenyl-3-pyrazoline (2d): Yield 699 mg (91%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.21 (s, 3 H), 0.24 (s, 3 H), 1.26 (s, 3 H), 2.67 (s, 3 H), 5.47 (s, 1 H), 6.76–7.60 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.79, –4.57, 18.07, 40.73, 62.56, 115.23, 117.21, 119.45, 126.15, 127.35, 127.49, 127.96, 128.20, 132.74, 134.17, 137.28, 139.47, 141.63, 147.98 ppm. IR (film): $\tilde{\nu}$ = 3020, 1608, 1504, 1250, 1120, 825 cm^{-1}. MS (EI, 70 eV): m/z (%) = 234 (M^+ – SiMe$_3$Ph, 100%), 218 (14), 77 (21). $C_{25}H_{28}N_2Si$ (384.20): calcd. C 78.07, H 7.34, N 7.28; found C 78.15, H 7.26, N 7.37.

1,2-Dimethyl-5-dimethylphenylsilyl-3,5-diphenyl-3-pyrazoline (2e): Yield 645 mg (84%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.44 (s, 3 H), 0.45 (s, 3 H), 2.43 (s, 3 H), 2.56 (s, 3 H), 5.55 (s, 1 H), 7.13–7.62 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –2.59, –2.15, 41.72, 43.16, 70.82, 107.86, 127.26, 127.63, 127.66, 128.26, 128.84, 129.00, 132.90, 133.02, 134.79, 137.91, 139.66, 141.63, 145.88, 150.03 ppm. IR (film): $\tilde{\nu}$ = 3020, 1608, 1504, 1250, 1100, 815 cm^{-1}. MS (EI, 70 eV): m/z (%) = 234 (M^+ – SiMe$_3$Ph, 100%), 188 (10), 77 (18). $C_{25}H_{28}N_2Si$ (384.20): calcd. C 78.07, H 7.34, N 7.28; found C 77.98, H 7.41, N 7.16.

1-Methyl-5-dimethylphenylsilyl-2,3,5-triphenyl-3-pyrazoline (2f): Yield 517 mg (58%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.38 (s, 3 H), 0.41 (s, 3 H), 2.78 (s, 3 H), 6.18 (s, 1 H), 6.96–7.69 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.82, 43.30, 72.64, 111.18, 117.65, 119.69, 124.28, 125,62, 126.88, 127.01, 127.98, 128.19, 128.61, 129.19, 132.92, 133.77, 136.82, 138.87, 139.52, 139,69, 143.06 ppm. IR (film): $\tilde{\nu}$ = 3020, 1600, 1504, 1250, 1100, 810 cm^{-1}. $C_{30}H_{30}N_2Si$ (446.22): calcd. C 80.67, H 6.77, N 6.27; found C 80.54, H 6.82, N 6.19.

5-*tert*-Butyldiphenylsilyl-2,3,5-trimethyl-1-phenyl-3-pyrazoline (3a): Yield 485 mg (57%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 9 H), 1.41 (s, 3 H), 2.26 (s, 3 H), 2.58 (s, 3 H), 3.90 (s, 1 H), 7.36–7.77 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.90, 26.47, 28.68, 28.87, 35.23, 51.43, 108.78, 124.26, 126.68, 127.29, 129.04, 130.57, 133.64, 135.45, 146.58, 148.39 ppm. IR (film): $\tilde{\nu}$ = 3020, 1600, 1500, 1100, 815 cm^{-1}. MS (EI, 70 eV): m/z (%) = 172 (M^+ – tBuPh$_2$SiMe, 100%), 157 (8), 95 (5), 77 (32). $C_{29}H_{34}N_2Si$ (426.25): calcd. C 78.82, H 8.03, N 6.57; found C 78.95, H 7.97, N 6.70.

1,2,5-Trimethyl-5-dimethylphenylsilyl-3-phenyl-3-pyrazoline (3b): Yield 573 mg (89%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.42 (s, 3

H), 0.44 (s, 3 H), 1.26 (s, 3 H), 2.44 (s, 3 H), 2.55 (s, 3 H), 4.92 (s, 1 H), 7.27–7.64 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.92, –3.96, 18.73, 38.06, 42.07, 61.96, 110.07, 126.61, 127.63, 128.14, 128.34, 133.73, 134.52, 137.40, 138.77, 149.07 ppm. IR (film): $\tilde{\nu}$ = 3040, 1605, 1500, 1250, 1110, 805 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 172 (M^+ – $SiMe_3Ph$, 100%), 157 (5), 77 (35), 56 (75). $C_{20}H_{26}N_2Si$ (322.19): calcd. C 74.48, H 8.13, N 8.69; found C 74.64, H 8.05, N 8.80.

5-*tert*-Butyldiphenylsilyl-1,2,5-trimethyl-3-phenyl-3-pyrazoline (3c): Yield 622 mg (73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (s, 9 H), 1.33 (s, 3 H), 1.99 (s, 3 H), 2.51 (s, 3 H), 5.25 (s, 1 H), 7.29–7.74 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.08, 18.84, 28.73, 35.75, 38.98, 57.11, 107.19, 127.50, 127.84, 128.88, 129.26, 129.82, 130.81, 136.14, 145.60, 147.85 ppm. IR (film): $\tilde{\nu}$ = 3020, 1600, 1500, 1090, 800 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 172 (M^+ – *t*$BuPh_2SiMe$, 100%), 157 (10), 130 (40), 95 (5), 77 (50). $C_{29}H_{34}N_2Si$ (426.25): calcd. C 78.82, H 8.03, N 6.57; found C 78.99, H 8.10, N 6.68.

3-Phenyl-3-[(dimethylphenylsilyl)phenylamino]-2-propen-1-phenylmethylimine (4): Yield 232 mg (26%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.33 (s, 6 H), 2.96 (s, 3 H), 5.03 (s, 1 H), 6.75 (dd, *J* = 1.2, 8.3 Hz, 2 H), 6.86 (tt, *J* = 1.2, 7.1 Hz, 1 H), 7.13 (dd, *J* = 7.2, 8.3 Hz, 2 H), 7.18–7.48 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.00, 32.12, 97.54, 118.83, 121.71, 122.57, 125,12, 125.68, 127.60, 127.90, 128.14, 128.32, 128.75, 129.16, 133.71, 136.76, 138.77, 139.47, 150.16, 161.88, 166.55 ppm. IR (film): $\tilde{\nu}$ = 3020, 1600, 1504, 1250, 1100, 800 cm^{-1}. $C_{30}H_{30}N_2Si$ (446.22): calcd. C 80.67, H 6.77, N 6.27; found C 80.82, H 6.84, N 6.14.

Ethyl 1-Ethyl-3,5-dimethyl-5-dimethylphenylsilyl-2-phenyl-3-pyrazoline-4-carboxylate (6a): Yield 269 mg (33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.35 (s, 3 H), 0.38 (s, 3 H), 0.73 (t, *J* = 7.1 Hz, 3 H), 1.18 (s, 3 H), 1.20 (t, *J* = 7.0 Hz, 3 H), 2.20 (s, 3 H), 2.66 (dq, *J* = 14.1, 7.1 Hz, 1 H), 2.78 (dq, *J* = 14.1, 7.1 Hz, 1 H), 3.99 (dq, *J* = 10.8, 7.0 Hz, 1 H), 4.19 (dq, *J* = 10.8, 7.0 Hz, 1 H), 7.06–7.65 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.40, –2.61, 11.99, 12.66, 14.21, 16.50, 42.33, 58.10, 61.37, 105.46, 118.32, 124.96, 127.45, 127.72, 128.98, 132.93, 139.91, 146.87, 153.85, 166.06 ppm. IR (film): $\tilde{\nu}$ = 1725, 1605, 1500, 1250, 1110, 820 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 408 (M^+, 1%), 335 (5), 273 (20), 244 (54), 215 (30), 199 (100), 135 (51), 77 (91). $C_{24}H_{32}N_2O_2Si$ (408.22): calcd. C 70.55, H 7.89, N 6.86; found C 70.69, H 7.80, N 6.98.

1-Ethyl-3,5-dimethyl-4,5-bis(dimethylphenylsilyl)-2-phenyl-3-pyrazoline (6b): Yield 705 mg (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 3 H), 0.13 (s, 3 H), 0.22 (s, 3 H), 0.33 (s, 3 H), 1.03 (t, *J* = 7,1 Hz, 3 H), 1.47 (s, 3 H), 1.96 (s, 3 H), 3.15 (dq, *J* = 7.1, 14.6 Hz, 1 H), 3.46 (dq, *J* = 7.1, 14.6 Hz, 1 H), 6.74 (t, *J* = 7.1 Hz, 1 H), 7.02 (d, *J* = 8.6 Hz, 2 H), 7.15 (dd, *J* = 7.1, 8.6 Hz, 2 H), 7.30–7.69 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.97, –3.92, –3.82, –2.52, 14.11, 14.74, 15.03, 48.45, 61.92, 110.03, 112.89, 122.17, 127.46, 128.30, 128.81, 131.18, 132.34, 133.40, 133.48, 139.35, 139.74, 141.23, 151.55 ppm. IR (film): $\tilde{\nu}$ = 1608, 1504, 1250, 1110 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 306 (M^+ – $SiMe_2EtPh$, 61%), 291 (26), 229 (10), 135 (40), 77 (100). $C_{29}H_{39}N_2Si_2$ (470.26): calcd. C 73.98, H 8.14, N 5.95; found C 74.12, H 8.22, N 6.13.

3-*tert*-Butyldiphenylsilyl-1,5-dimethyl-5-dimethylphenylsilyl-2-phenyl-3-pyrazoline (6c): Yield 742 mg (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.36 (s, 3 H), 0.38 (s, 3 H), 1.05 (s, 9 H), 1.29 (s, 3 H), 2.59 (s, 3 H), 5.75 (s, 1 H), 6.65–6.76 (m, 5 H), 7.30–7.82 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.14, –4.09, 19.07, 19.15, 28.31, 40.28, 63.08, 108.83, 120.93, 121.38, 127.31, 127.37, 127.63, 128.15, 128.96, 129.46, 132.98, 134.31, 134.38, 137.59, 137.99, 148.62 ppm. IR (film): $\tilde{\nu}$ = 1594, 1491, 1255, 1108 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 396 (M^+ – $SiMe_3Ph$, 23%), 339 (46), 262 (10), 239 (15), 135 (34), 77 (100). $C_{35}H_{42}N_2Si_2$ (546.29): calcd. C 76.87, H 7.74, N 5.12; found C 76.71, H 7.67, N 5.25.

Ethyl 2-Ethyl-3,5-dimethyl-5-dimethylphenylsilyl-1-phenyl-3-pyrazoline-4-carboxylate (7a): Yield 400 mg (49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.43 (s, 3 H), 0.48 (s, 3 H), 0.85 (t, *J* = 7.2 Hz, 3 H), 1.20 (t, *J* = 7.0 Hz, 3 H), 1.63 (s, 3 H), 2.22 (s, 3 H), 2.91 (m, 2 H), 4.00 (dq, *J* = 10.6, 7.0 Hz, 1 H), 4.14 (dq, *J* = 10.6, 7.0 Hz, 1 H), 7.06–7.65 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.35, –4.14, 12.12, 13.86, 14.04, 18.36, 44.05, 61.37, 65.02, 112.02, 115.44, 122.79, 126.96, 127.45, 128.48, 132.75, 137.59, 149.59, 157.01, 160.82 ppm. IR (film): $\tilde{\nu}$ = 1720, 1600, 1508, 1250, 1110, 825 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 408 (M^+, 1%), 273 (20), 244 (54), 215 (30), 199 (100), 135 (51), 105 (18), 77 (91). $C_{24}H_{32}N_2O_2Si$ (408.22): calcd. C 70.55, H 7.89, N 6.86; found C 70.76, H 7.96, N 6.74.

Ethyl 2-Ethyl-1,3,5-trimethyl-5-dimethylphenylsilyl-3-pyrazoline-4-carboxylate (7b): Yield 463 mg (67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.41 (s, 3 H), 0.43 (s, 3 H), 1.09 (t, *J* = 7.0 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.36 (s, 3 H), 2.10 (s, 3 H), 2.72 (s, 3 H), 2.95 (dq, *J* = 14.8, 7.0 Hz, 1 H), 3.15 (dq, *J* = 14.8, 7.0 Hz, 1 H), 4.06 (dq, *J* = 10.9, 7.2 Hz, 1 H), 4.18 (dq, *J* = 10.9, 7.2 Hz, 1 H), 7.30–7.60 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.35, –2.14, 11.45, 12.06, 14.12, 15.22, 42.36, 48.03, 58.67, 63.41, 104.53, 127.45, 132.75, 134.07, 139.59, 155.21, 160.37 ppm. IR (film): $\tilde{\nu}$ = 1720, 1600, 1500, 1250, 1110 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 346 (M^+, 1%), 331 (15), 273 (10), 211 (24), 182 (30), 137 (100), 135 (46). $C_{19}H_{30}N_2O_2Si$ (346.21): calcd. C 65.85, H 8.73, N 8.08; found C 65.97, H 8.80, N 7.92.

Ethyl 2-Ethyl-3-methyl-1-phenyl-3-pyrazoline-5-carboxylate (7c): Yield 437 mg (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.0 Hz, 3 H), 1.36 (t, *J* = 7.1 Hz, 3 H), 1.89 (s, 3 H), 3.16 (q, *J* = 7.0 Hz, 2 H), 4.31 (q, *J* = 7.1 Hz, 2 H), 4.74 (d, *J* = 2.4 Hz, 1 H), 4.84 (d, *J* = 2.4 Hz, 1 H), 6.97 (t, *J* = 7.4 Hz, 1 H), 7.10 (d, *J* = 7.9 Hz, 2 H), 7.28 (dd, *J* = 7.4, 7.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.08, 12.70, 14.28, 46.59, 61.15, 73.28, 98.88, 114.73, 120.33, 127.83, 145.14, 152.46, 172.22 ppm. IR (film): $\tilde{\nu}$ = 1735, 1600, 1508, 825 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 260 (M^+, 3%), 245 (42), 231 (4), 215 (30), 187 (51), 77 (100). $C_{15}H_{20}N_2O_2$ (260.15): calcd. C 69.20, H 7.74, N 10.76; found C 69.08, H 7.67, N 10.92.

3-*tert*-Butyldiphenylsilyl-1,2-dimethylindazoline (11a): Yield 594 mg (77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 9 H), 2.40 (s, 3 H), 2.56 (s, 3 H), 4.38 (s, 1 H), 6.38 (d, *J* = 7.9 Hz, 1 H), 6.57 (m, 2 H), 6.95 (m, 1 H), 7.19–7.60 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.22, 28.62, 41.30, 48.08, 62.21, 110.19, 120.16, 122.72, 126.71, 127.22, 127.27, 127.62, 129.11, 130.69, 132.75, 134.95, 136.75, 136.87, 150.24 ppm. IR (film): $\tilde{\nu}$ = 1598, 1490, 1106 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 329 (M^+ – Bu, 100%), 309 (15), 224 (22), 146 (31), 77 (40), 57 (53). $C_{25}H_{30}N_2Si$ (386.22): calcd. C 77.67, H 7.82, N 7.25; found C 77.83, H 7.90, N 7.41.

1-Ethyl-3-dimethylphenylsilyl-2-phenylindazoline (11b): Yield 372 mg (52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.45 (s, 3 H), 0.47 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 2.85 (dq, *J* = 14.2, 7.2 Hz, 1 H), 3.12 (dq, *J* = 14.2, 7.2 Hz, 1 H), 4.61 (s, 1 H), 6.74 (d, *J* = 7.5 Hz, 1 H), 6.86 (m, 2 H), 7.10–7.64 (m, 11 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.97, 14.22, 45.03, 53.27, 112.37, 112.75, 116.25, 120.98, 123.87, 127.65, 128.37, 129.21, 132.45, 132.94, 133.80, 139.74, 149.64, 155.25 ppm. IR (film): $\tilde{\nu}$ = 3015, 1590, 1486, 1250, 1100 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 343 (M^+ – Me, 16%), 281

(5), 223 (100), 194 (19), 135 (31), 77 (14). $C_{23}H_{26}N_2Si$ (358.19): calcd. C 77.05, H 7.31, N 7.81; found C 76.91, H 7.26, N 7.98.

3-*tert*-Butyldiphenylsilyl-1-ethyl-2-phenylindazoline (11c): Yield 684 mg (74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, J = 7.2 Hz, 3 H), 1.33 (s, 9 H), 2.25 (dq, J = 14.1, 7.2 Hz, 1 H), 2.51 (dq, J = 14.1, 7.2 Hz, 1 H), 5.28 (s, 1 H), 6.61 (m, 2 H), 6.94 (m, 2 H), 7.14–7.54 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.03, 19.01, 28.45, 50.93, 63.27, 111.95, 117.23, 121.02, 121.15, 122.22, 126.46, 127.17, 127.79, 128.69, 129.36, 132.45, 133.89, 134.77, 135.66, 137.01, 137.08, 150.02, 157.18 ppm. IR (film): $\tilde{\nu}$ = 3018, 1596, 1486, 1105 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 405 (M^+ – Bu, 100%), 300 (18), 222 (11), 105 (15), 77 (20), 57 (54). $C_{31}H_{34}N_2Si$ (462.25): calcd. C 80.47, H 7.41, N 6.05; found C 80.65, H 7.48, N 6.22.

2-Ethyl-3-dimethylphenylsilyl-1,3-diphenylindazoline (11d): Yield 382 mg (44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.45 (s, 3 H), 0.47 (s, 3 H), 1.11 (t, J = 7.1 Hz, 3 H), 2.82 (dq, J = 14.2, 7.1 Hz, 1 H), 3.02 (dq, J = 14.2, 7.1 Hz, 1 H), 6.90 (t, J = 7.5 Hz, 1 H), 7.05 (m, 3 H), 7.18 (dd, J = 7.6, 8.0 Hz, 1 H), 7.21–7.58 (m, 14 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.72, –4.05, 12.13, 52.19, 66.15, 112.05, 119.34, 121.60, 122.72, 124.11, 127.21, 127.45, 127.68, 127.90, 128.38, 128.90, 132.31, 132.75, 134.07, 139.59, 143.17, 145.38, 147.55 ppm. IR (film): $\tilde{\nu}$ = 3015, 1605, 1500, 1246, 1100 cm^{-1}. $C_{29}H_{30}N_2Si$ (434.22): calcd. C 80.14, H 6.96, N 6.45; found C 80.29, H 7.05, N 6.58.

2-Methyl-1,4-diphenyl-1,2-dihydroquinazoline (12): Yield 226 mg (38%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (d, J = 6.3 Hz, 3 H), 5.79 (q, J = 6.3 Hz, 1 H), 6.80 (t, J = 7.3 Hz, 1 H), 7.06 (d, J = 8.1 Hz, 2 H), 7.14 (dd, J = 7.3, 8.1 Hz, 2 H), 7.27–7.64 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.31, 71.91, 117.64, 118.77, 119.86, 122.65, 123.71, 128.08, 128.39, 128.58, 129.15, 129.35, 132.05, 138.02, 143.21, 144.70, 163.30 ppm. IR (film): $\tilde{\nu}$ = 3018, 1664, 1607, 1494, 762, 690 cm^{-1}. $C_{21}H_{18}N_2$ (298.15): calcd. C 84.53, H 6.08, N 9.39; found C 84.71, H 6.01, N 9.22.

***N*-Ethyl-2-(phenylamino)benzamide (13):** Yield: 374 mg (78%) from dimethylphenylsilyllithium and 163 mg (34%) from *tert*-butyldiphenylsilyllithium. M.p. 74–75 °C (recrystallised from cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.3 Hz, 3 H), 3.48 (dq, J = 5.4, 7.3 Hz, 2 H), 6.21 (s br, 1 H), 6.76 (t, J = 8.0 Hz, 1 H), 7.01 (dd, J = 7.1, 7.6 Hz, 1 H), 7.18–7.43 (m, 7 H), 9.32 (s. 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.77, 34.68, 115.40, 117.91, 118.69, 120.47, 122.20, 127.42, 129.21, 131.95, 141.54, 145.15, 169.44 ppm. IR (film): $\tilde{\nu}$ = 3300 br, 3015, 1630, 1590, 1500, 740, 690 cm^{-1}. $C_{15}H_{16}N_2O$ (240.13): calcd. C 74.97, H 6.71, N 11.66; found C 75.11, H 6.68, N 11.53.

Reaction of Indazolium Salts with Organometallic Reagents. Typical Procedure: To a stirred solution of indazolium salt **8a** or isoindazolium salt **8b** (1.5 mmol) in dry Et_2O (10 mL) at –20 °C or room temperature, under N_2, was added an ethereal solution of methylmagnesium iodide or methyllithium (1.5 mmol). The reaction mixture (when cooled to –20 °C) was slowly allowed to warm to room temperature and stirred at room temperature until TLC indicated that the reaction was complete. The mixture was quenched with aqueous NH_4Cl and extracted with Et_2O. The ethereal layer was dried with $MgSO_4$, the solvent was removed, and the residue was purified by chromatography on silica gel, with dichloromethane/hexanes (1:1) as eluent to give the following products:

1,2,3-Trimethylindazoline (9a): Yield 143 mg (59%) from methyllithium and 201 mg (83%) from methylmagnesium iodide; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (d, J = 7.0 Hz, 3 H), 2.47 (s, 3 H), 2.75 (s, 3 H), 3.72 (q, J = 7.0 Hz, 1 H), 6.35–7.14 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.05, 39.47, 43.40, 60.68, 111.24, 119.46, 121.70, 126.71, 128.32, 145.63 ppm. IR (film): $\tilde{\nu}$ = 1598, 1490, 720 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 162 (M^+, 1%), 146 (100), 103 (50), 91 (12), 77 (41). $C_{10}H_{14}N_2$ (162.12): calcd. C 74.03, H 8.70, N 17.27; found C 74.14, H 8.83, N 17.15.

1-Ethyl-3-methyl-2-phenylindazoline (9b): Yield 303 mg (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (t, J = 7.2 Hz, 3 H), 1.52 (d, J = 7.1 Hz, 3 H), 3.23 (q, J = 7.2 Hz, 2 H), 4.55 (q, J = 7.1 Hz, 1 H), 6.30–7.20 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.05, 19.13, 48.77, 57.03, 111.47, 112.69, 118.25, 119.06, 124.62, 127.32, 128.44, 129.87, 139.49, 143.12 ppm. IR (film): $\tilde{\nu}$ = 3015, 1600, 1493, 780, 752, 695 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 238 (M^+, 5%), 223 (21), 160 (100), 77 (54). $C_{16}H_{18}N_2$ (238.15): calcd. C 80.63, H 7.61, N 11.75; found C 80.74, H 7.73, N 11.91.

***o*-(Methylamino)acetophenone (10):** Yield 47 mg (21%). See ref.[11]

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