The effective preparation of secondary amines bearing a vinylsilane functionality via the reaction of primary amines with α-chlorine-substituted allylsilanes catalysed by CuCl

Makoto Kozuka and Michiharu Mitani*

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato 4-17-1, Nagano 380-8551, Japan

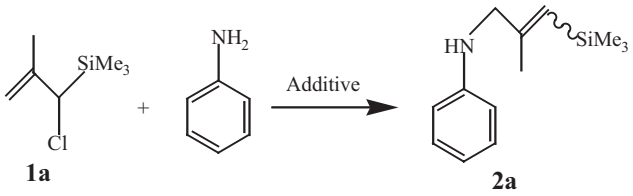
The reaction of α-chlorine-substituted allylsilanes with primary amines was promoted by CuCl to result in the selective formation of secondary amines bearing the vinylsilane functionality by a probable S_N2'-allylation keeping the silyl group intact.

Keywords: vinylsilane, allylsilane, copper catalyst, secondary amine

The preparation of secondary amines has commonly been accomplished by the reactions of primary amines with a range of electrophiles including alkyl halides. Alkylated secondary amines, however, tend to undergo further alkylation because of their enhanced nucleophilicity compared with that of the parent primary amines. Thus, primary amines usually incline to the formation of a complex mixture by multi-alkylation caused by reaction with electrophiles. Therefore, the selective formation of secondary amines has necessitated some manipulation in order to avoid multi-alkylation, such as the introduction of a protecting group on the nitrogen atom,[1] the use of primary amines in a large excess,[2] the effecting of reactions via π-allylpalladium complexes,[3] and employment of a method utilising the intermediary generation of a reactive amide anion species.[4]

We have recently reported that a CuCl catalyst promoted the formation of the three-component coupling products of primary amines with α-halogen-substituted allylsilanes and electrophiles such as electron-deficient olefins, alkyl halides, alkyl tosylates or epoxides.[5] In the present investigation, we have shown that the selective formation of secondary amines with an allyl group is readily brought about by the CuCl-catalysed reaction of primary amines with α-chlorine-substituted allylsilanes in the absence of another electrophile. A mixture of copper(II) perchlorate and copper metal has been reported to promote the reaction of allyl chlorides with amines to form allyl amines.[6] In this previous method, however, use of the copper promoter in an equivalent amount was necessary, and the concomitant formation of diallylated amines in large amounts occurred. Allylamines are an interesting class of compounds leading to useful synthetic intermediates[7] along with their physiological properties.[8] Furthermore, the carbon–carbon double bond of the allyl group in the obtained secondary amines is substituted with a silyl group to constitute a vinylsilane functionality. Vinylsilanes are building blocks that allow versatile transformations by reactions with a range of electrophiles,[9] *e.g.* acyl halides to form conjugated enones.

Initially, (1-chloro-2-methyl-2-propenyl)trimethylsilane **1a** was subjected to the reaction with aniline (3 equiv.) in a *t*-BuOH solution in the absence of a promoter as a control experiment. The result was a sluggish consumption of **1a** (700 min) and formation of the secondary amine **2a**, *i.e.*, *N*-(2-methyl-3-trimethylsilyl-2-propenyl)aniline in a low yield (12%) (Table 1, run 1). Thus, activation of **1a** by a Lewis acid seems to be requisite for the effective allylation of aniline with **1a**. However, common Lewis acids may not bring about activation of halides owing to the complex-formation with amines and, furthermore, halogen-containing ones such as



Scheme 1

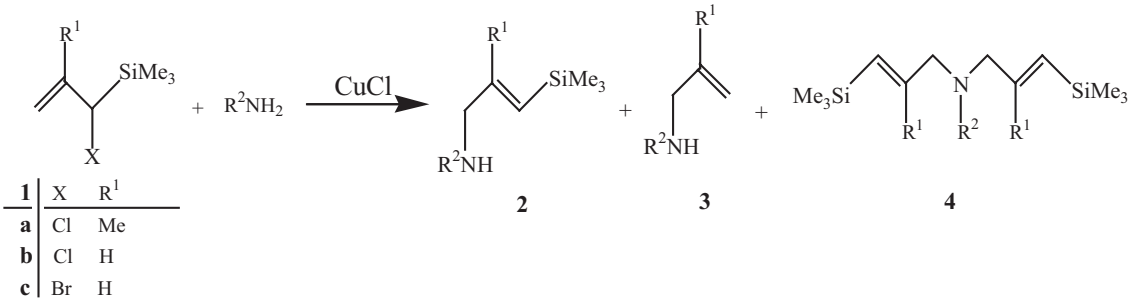
$TiCl_4$ are destroyed with protic compounds containing a N–H or O–H bond. Actually, the reaction of **1a** and aniline in the presence of $TiCl_4$ in a *t*-BuOH or CH_2Cl_2 solution resulted in no formation of **2a** along with recovery of **1a** (Table 1, runs 2 and 3, Scheme 1). The reaction in the presence of $B(OMe)_3$ also failed to give the enhanced formation of **2a** compared with the reaction without a promoter (Table 1, run 4). Next, copper(I) chloride was examined, resulting in the selective formation of **2a** (93%) along with accelerated consumption of **1a**. The catalytic activity of the copper(I) halide for the selective formation of **2a** proved to descend in the order chloride, bromide and iodide (Table 1, runs 5–7), and copper(II) chloride afforded a low yield of **2a** (Table 1, run 8). Furthermore, the reaction using a palladium catalyst, in which the formation of the allyl amine derivatives *via* a π-allyl complex might be expected,[3] was examined. The result after the reaction in 200 min was only recovery of **1a** or the production of **2a** in a trace amount (Table 1, runs 9–11). From the above-mentioned results, it seems certain that copper(I) halide, especially chloride, does not diminish the nucleophilicity of the amine by formation of a complex, but rather it enhances the susceptibility of the α-chlorine-substituted allylsilane to nucleophilic attack by the amine.

Table 1 Effect of metallic species on the reaction of **1a** and aniline[a]

Run No.	Additive	solvent	Time/min[b]	**2a**[c]Yield/%[d]
1	none	*t*-BuOH	700	12
2	$TiCl_4$	*t*-BuOH	100	0
3	$TiCl_4$	CH_2Cl_2	100	0
4	$B(OMe)_3$	*t*-BuOH	700	12
5	CuCl	*t*-BuOH	20	93(92)[e]
6	CuBr	*r*-BuOH	20	65
7	CuI	*t*-BuOH	20	20
8	$CuCl_2$	*t*-BuOH	20	25
9	$Pd(OAc)_2$[f]	DMF	200	7
10	$Pd(OAc)_2$[f]	*t*-BuOH	200	7
11	$Pd(OAc)_2$[f]	CH_3CN	200	0

[a]Reaction conditions; **1a** (1 mmol), aniline (3 mmol), additive (0.2 mmol), solvent (2.5 ml). [b]Time at which **1a** was consumed. [c]A 3/1 mixture of (*E*) and (*Z*) stereoisomers. [d]Determioned by GC analysis. [e]Determined by column chromatography isolation. [f]In the presence of PPh_3 as a ligand.

* Correspondent. E-mail: mitanim@shinshu-u.ac.jp



1	X	R^1
a	Cl	Me
b	Cl	H
c	Br	H

Scheme 2

We next investigated the effects of the molar ratio of aniline to **1a** on the formation of **2a**. While use of an equivalent amount gave only a moderate yield of **2a** (48%), use of aniline in two times excess brought about an almost quantitative yield of **2a** (92%).

The reactions of some α-halogen-substituted allylsilanes with a range of amines were performed under the best conditions examined above, *i.e.*, use of 2 equiv. of an amine and a CuCl catalyst (0.1 equiv.) in a *t*-BuOH solution. The results are collected in Table 2 (Scheme 2).

(1-Chloro-2-propenyl)trimethylsilane **1b** gave the corresponding secondary amine in an almost quantitative yield by the reaction with aniline in 20 min., similar to the case using **1a** (runs 1–2). The reactions of **1a** with aniline derivatives bearing alkyl substituents or the amines of aromatic systems other than benzene (*i.e.*, 2-naphthylamine and 2-aminofluorene) also gave the products of type **2** in excellent to good yields (runs 3–7). In the reaction of **1a** with aniline derivatives bearing an electron-withdrawing group (*i.e.*, nitro or cyano), however, a secondary amine **3** based on introduction of a 2-methylallyl group without a silyl group was selectively obtained (runs 8 and 9). The basicities of the aniline derivatives bearing these electron-withdrawing groups are low. Thus, hydrogen chloride generated by the reaction with **1a** is rather hard to trap with these amines and may promote desilylation of the product of type **2** to result in the formation of **3**. Also, in the reactions of **1a** with *o*-chloroaniline or *m*-anisidine, the products of type **3** were formed, although in low yields, along with the products of type **2**. Formation of **3** in these reactions probably results from the lower basicities of *o*-chloroaniline (pKa = 2.65) and *m*-anisidine (pKa = 4.23) compared with aniline (pKa = 4.63).[10] Next, alkyl amines instead of aromatic amines were subjected to the reaction with **1**. As a result, the reactions of **1a** with benzylamine, and **1b** with ethanolamine gave the products of type **2** in good yields, although formation of doubly alkylated tertiary amines **4** in trace amounts was observed (runs 12 and 13). Furthermore, the reaction of the α-bromine-substituted allylsilane **1c** with ethanolamine brought about diminution in the yield of the product of type **2** and increase of the product of type **4**, compared with the reaction of the α-chlorine analogue **1b** (runs 13 and 14). While **1c** disappeared after 3 hours in the reaction with ethanolamine in the absence of CuCl, **1b** was not consumed without CuCl in a reaction time of 3 hours (runs 16 and 17).

Finally, 2-methylallyl chloride was subjected to the CuCl-catalysed reaction with aniline in order to evaluate the effect of the silyl substituent. The result was promotion of multi-allylation compared with the reaction of **1a**, as revealed in Scheme 3.

The silyl group in **1** appears to allow avoidance of multi-alkylation and promote the selective formation of the secondary amine.

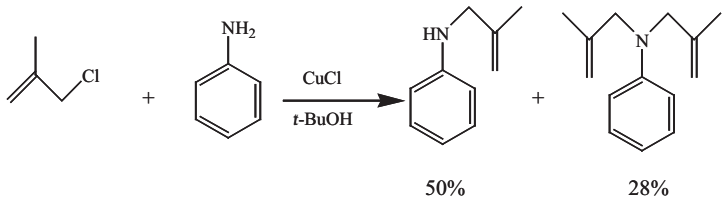
Experimental

^{1}H and ^{13}C NMR spectra were recorded on a JNM QX400 (400 and 100 MHz) spectrometer for solutions in $CDCl_3$ using TMS as internal standard (δ = 0). MS and HRMS were obtained using Shimadzu GCMS-QP5000 and Hitachi M-80B GC-MS instruments equipped with a 30 m DB-1 columun.

Table 2 Reaction of α-chlorine substituted allylsilanes with amines[a]

Run No.	1	R^2NH_2	Time/min[b]	Yield/%[c]		
				2	3	4
1	**a**	$PhNH_2$	20	**a**[d]	92	0	0
2	**b**	$PhNH_2$	20	**b**	90	0	0
3	**a**	4-$EtC_6H_4NH_2$	25	**c**[d]	90	0	0
4	**a**	2,4-$Me_2C_6H_3NH_2$	25	**d**[e]	95	0	0
5	**a**	2,4,6-$Me_3C_6H_2NH_2$	35	**e**[f]	90	0	0
6	**a**	2-naphthylamine*	45	**f**[d]	94	0	0
7[g]	**a**	2-aminofluorene	20	**g**[h]	90	0	0
8	**a**	4-$NO_2C_6H_4NH_2$	35	**h**	0	88	0
9[i]	**a**	4-$NCC_6H_4NH_2$	40	**i**	0	85	0
10[i]	**a**	2-$ClC_6H_4NH_2$	15	**j**[d]	62	31	0
11	**a**	3-$MeOC_6H_4NH_2$	25	**k**[j]	72	25	0
12	**a**	$PhCH_2NH_2$	40	**l**[f]	83	0	1.5
13	**b**	$HO(CH_2)_2NH_2$	60	**m**	88	0	1
14	**c**	$HO(CH_2)_2NH_2$	40	**m**	61	0	10
15[k]	**c**	$HO(CH_2)_2NH_2$	180	**m**	65	0	13
16[k]	**b**	$HO(CH_2)_2NH_2$	180[l]	**m**	0	0	0

[a]Reaction conditions; **1a** (1 mmol), amine (2 mmol), CuCl (0.1 mmol), *t*-BuOH (2.5 ml) under reflux. [b]Time at which **1** was consumed. [c]Determined by column chromatography isolation. [d]*E*/*Z* = 3/1. [e]*E*/*Z* = 2/1. [f]*E*/*Z* = 1/1. [g]Conditions; **1a** (1 mmol)/amine (2 mmol)/CuCl (0.1 mmol)/EtOH (12 ml). [h]*E*/*Z* = 5/1. [i]Conditions; **1a** (0.5 mmol)/amine (2 mmol)/CuCl (0.1 mmol)/EtOH (2.5 ml). [j]*E*/*Z* = 4/1. [k]Without CuCl. [l]**1b** was not consumed.



Scheme 3

CAUTION: The importation, manufacture and use of 2-naphthylamine for all purposes is prohibited in the UK due to its potent human carcinogenicity (COSHH Regulations).

An amine (2 mmol), **1** (1 mmol), CuCl (0.01 g, 0.1 mmol) and tert-BuOH (2.5 mmol) were added to a flask. The resulting solution was stirred under reflux. The reaction mixture was then poured into H_2O and extracted with Et_2O. After the solvent was mostly removed under reduced pressure, the residue was subjected to column chromatography using hexane/ethyl acetate (1 : 2) as an eluent.

(**2a**, *E* and *Z* mixture): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 1.74 and 1.82 (s, 3H, MeC=CSi), 3.57 and 3.66 (s, 2H, CH_2C=CSi), 4.78 (s, 1H, NH), 5.40 and 5.43 (s, 1H, C=CHSi), 6.52–7.10 (m, 5H, phenyl); ^{13}C NMR δ –0.3, 19.6, 25.2, 49.3, 53.1, 112.5, 117.9, 128.1, 128.7, 148.0, 152.3; MS (GC-EI) *m/z* (%) component A = 219 (M^+, 27), 204 (42), 178 (22), 146 (49), 106 (100), 73 (65, 59 (28): component B = 219 (M^+, 19), 204 (22), 178 (11), 146 (37), 106 (100), 73 (49), 59 (19); (Found: M^+ 219.1473. $C_{13}H_{21}NSi$ requires M, 219.1443).

(**2b**): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 3.68 (d, *J* = 4.8 Hz, 2H, CH_2CH=CSi), 3.90 (s, 1H, NH), 5.84 (d, *J* = 18.8 Hz, 1H, C=CHSi), 6.04 (dt, ^2J = 18.8 Hz, ^3J = 4.8 Hz, 1H, CH=CSi), 6.49–7.10 (m, 5H, phenyl); ^{13}C NMR δ –0.4, 48.5, 112.6, 117.0, 128.6, 130.6, 142.6, 144.9; MS (GC-EI) *m/z* (%) 205 (M^+, 30), 190 (28), 132 (100), 106 (81), 77 (46), 73 (68), 59 (46); (Found: M^+ 205.1283. $C_{12}H_{19}NSi$ requires M, 205.1285).

(**2c**, *E* and *Z* mixture): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 1.05 (t, *J* = 7.6 Hz, 3H, $\underline{CH_3}CH_2$), 1.68 and 1.77 (s, 3H, MeC=CSi), 2.40 (q, *J* = 7.6 Hz, $\underline{CH_2}CH_3$), 3.45 (s, 1H, NH), 3.49 and 3.59 (s, 2H, CH_2C=CSi), 5.34 and 5.40 (s, 1H, C=CHSi), 6.42 (d, *J* = 8.4 Hz, 2H, aromatic C(2)H), 6.87 (d, *J* = 8.4 Hz, 2H, aromatic C(3)H); ^{13}C NMR δ –0.3, 15.6, 19.3, 24.9, 27.5, 49.3, 53.2, 112.3, 127.5, 132.3, 145.7, 152.3; MS (GC-EI) *m/z* (%) component A = 247 (M^+, 38), 232 (56), 206 (35), 174 (35), 134 (1009, 83 (31), 73 (87), 59 (42): component B = 247 (M^+, 18), 232 (17), 206 (10), 174 (20), 134 (100), 83 (18), 73 (46), 59 (25); (Found: M^+ 247.1770. $C_{15}H_{25}NSi$ requires 247.1755).

(**2d**, *E* and *Z* mixture): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 1.70 and 1.79 (s, 3H, MeC=CSi), 1.95 (s, 3H, aromatic C(4)Me), 2.09 (s, 3H, aromaticC(2)Me), 3.25 (s, 1H, NH), 3.55 and 3.62 (s, 2H, CH_2C=CSi), 5.36 and 5.40 (s, 1H, C=CHSi), 6.40 (d, *J* = 8.4 Hz, 1H, aromatic C(2)H), 6.74 (s, 1H, aromatic C(3)H), 6.79 (d, *J* = 8.4 Hz, 1H, aromatic C(3)H); ^{13}C NMR δ –0.3, 17.1, 19.3, 20.0, 25.0, 49.3, 53.1, 109.4, 121.3, 125.5, 126.7, 130.2, 143.5, 152.4; MS (GC-EI) *m/z* (%) component A = 247 (M^+, 36), 232 (31), 206 (8), 190 (11), 174 (55), 134 (100), 73 (64), 59 (37): component B = 247 (M^+, 22), 232 (10), 206 (5), 190 (5), 174 (22), 134 (100), 73 (57), 59 (25); (Found: M^+ 247.1759. $C_{15}H_{25}NSi$ requires 247.1755).

(**2e**, *E* and *Z* mixture): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 1.75 and 1.77 (s, 3H, MeC=CSi), 2.11 (s, 3H, aromatic C(4)Me), 2.19 (s, 6H, aromatic C(2) and C(6)Me), 3.31 and 3.44 (s, 2H, CH_2C=CSi), 5.30 and 5.51 (s, 1H, C=CHSi), 6.70 (s, 2H, aromatic C(3) and C(5)H); ^{13}C NMR δ –0.4, 18.1, 18.4, 20.4, 25.4, 53.8, 57.9, 123.1, 127.7, 129.0, 130.7, 143.4, 152.3; MS (GC-EI) *m/z* (%) component A = 261 (M^+, 50), 246 (29), 188 (74), 148 (100), 134 (59), 91 (24), 73 (55), 59 (37): component B = 261 (M^+, 20), 246 (7), 188 (30), 105 (100), 134 (28), 91 (13), 73 (30), 59 (24); (Found: M^+ 261.1934. $C_{16}H_{27}NSi$ requires 261.1911).

(**2f**, *E* and *Z* mixture): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 1.70 and 1.81 (s, 3H, MeC=CSi), 3.61 and 3.71 (s, 2H, CH_2C=CSi), 4.30 (s, 1H, NH), 5.42 and 5.44 (s, 1H, C=CHSi), 6.45–7.61 (m, 7H, naphthyl); ^{13}C NMR δ –0.3, 19.7, 25.2, 49.2, 52.0, 104.0, 117.0, 119.2, 122.8, 124.1, 125.1, 126.0, 128.0, 128.1, 133.7, 142.8, 151.8; MS (GC-EI) *m/z* (%) component A = 269 (M^+, 67), 254 (42), 196 (62), 156 (46), 127 (25), 92 (40), 73 (100), 59 (49): component B = 269 (M^+, 40), 254 (21), 196 (48), 156 (65), 127 (33), 115 (26), 73 (100), 59 (52); (Found: M^+ 269.1578. $C_{17}H_{23}NSi$ requires 269.1597).

(**2g**, *E* and *Z* mixture): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 1.72 and 1.78 (s, 3H, MeC=CSi), 3.51 and 3.60 (s, 2H, CH_2C=CSi), 3.62 (s, 2H, fluoren CH_2), 3.87 (s, 1H, NH), 5.34 and 5.37 (s, 1H, C=CHSi), 6.43–7.44 (m, 7H, benzene ring); ^{13}C NMR δ –0.3, 20.1, 24.9, 36.5, 49.3, 49.7, 108.6, 111.4, 117.7, 119.9, 124.0, 125.9, 127.7, 131.3, 141.4, 141.6, 144.4, 147.3, 152.0; MS (GC-EI) *m/z* (%) component A = 307 (M^+, 94), 292 (59), 266 (51), 234 (33), 194 (64), 180 (36), 165 (47), 73 (100): component B = 307 (M^+, 74), 292 (25), 266 (18), 234 (25), 194 (100), 180 (29), 165 (37), 73 (51); (Found: M^+ 307.1785. $C_{20}H_{25}NSi$ requires 307.1755).

(**3h**): ^{1}H NMR δ 1.71 (s, 3H, MeC=C), 2.95 (s, 1H, NH), 3.71 (s, 2H, CH_2C=C), 4.86 (s, 2H, C=CH_2), 6.46 (d, *J* = 8.4 Hz, 2H, aromatic C(2) and C(6)H), 7.99 (d, *J* = 8.4 hz, aromatic C(3) and C(5)H); ^{13}C NMR δ 20.3, 49.2, 111.1, 111.6, 126.2, 137.6, 140.6, 153.0; MS (DI) *m/z* (%) 192 (M^+, 45), 177 (25), 151 (100), 130 (14), 105 (45), 76 (15), 55 (30); (Found: M^+ 192.0917. $C_{10}H_{12}N_2O_2$ requires 192.0898).

(**3i**): ^{1}H NMR δ 1.63 (s, 3H, MeC=C), 3.58 (s, 2H, CH_2C=C), 4.42 (s, 1H, NH), 4.78 (s, 2H, C=CH_2), 6.42 (d, *J* = 8.9 Hz, 2H, aromatic C(2) and C(6)H), 7.26 (d, *J* = 8.9 Hz, aromatic C(3) and C(5)H); ^{13}C NMR δ 20.1, 49.0, 109.5, 111.6, 122.3, 114.5, 133.7, 133.9, 141.3; MS (GS-EI) *m/z* (%) 172 (M^+, 62), 157 (71), 131 (100), 102 (19), 55 (23); (Found: M^+ 172.0971. $C_{11}H_{12}N_2$ requires 172.0999).

(**2j**, *E* and *Z* mixture): ^{1}H NMR δ 0.06 (s, 9H, $SiMe_3$), 1.68 and 1.79 (s, 3H, MeC=CSi), 3.59 and 3.67 (s, 2H, CH_2C=CSi), 4.23 (s, 1H, NH), 5.41 and 5.44 (s, 1H, C=CHSi), 6.46–7.13 (m, 4H, aromatic); ^{13}C NMR δ –0.86, 20.0, 24.9, 49.1, 52.4, 110.5, 111.0, 116.6, 118.4, 127.1, 128.4, 143.6, 151.3; MS (GC-EI) *m/z* (%) component A = 255 [$M(Cl^{37})^+$, 8], 253 [$M(Cl^{35})^+$, 21], 238 (46), 180 (44), 140 (53), 73 (100), 59 (38): component B = 255 [$M(Cl^{37})^+$, 10], 253 [$M(Cl^{35})^+$, 28], 238 (33), 180 (53), 140 (76), 73 (100), 59 (30); [Found: $M(Cl^{35})^+$ 253.1039. $C_{13}H_{20}NSiCl$ requires 253.1052].

(**2k**, *E* and *Z* mixture): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 1.68 and 1.77 (s, 3H, MeC=CSi), 3.51 (s, 1H, NH), 3.58 and 3.61 (s, 2H, CH_2C=CSi), 3.61 (s, 3H, OMe), 5.34 and 5.39 (s, 1H, C=CHSi), 6.04 (s, 1H, aromatic C(2)H), 6.09–6.95 (m, 3H, aromatic C(4), C(5) and C(6)H); ^{13}C NMR δ –1.0, 19.5, 24.9, 49.0, 52.9, 54.5, 98.2, 102.0, 105.4, 127.8, 129.3, 149.1, 152.0, 160.0; MS (GC-EI) *m/z* (%) component A = 249 (M^+, 40), 234 (50), 176 (68), 136 (100), 73 (85): component B = 249 (M^+, 30), 234 (25), 176 (42), 136 (100), 73 (48); (Found: M^+ 249.1559. $C_{14}H_{23}NOSi$ requires 249.1548).

(**2l**, *E* and *Z* mixture): ^{1}H NMR δ 0.07 (s, 9H, $SiMe_3$), 1.67 and 1.79 (s, 3H, MeC=CSi), 3.06 and 3.14 (s, 2H, CH_2C=CSi), 3.61 (s, 2H, $PhCH_2N$), 3.98 (s, 1H, NH), 5.25 and 5.32 (s, 1H, C=CHSi), 7.18 (s, 5H, phenyl); ^{13}C NMR δ –1.0, 19.9, 25.0, 53.0, 54.2, 58.2, 126.4, 127.3, 127.7, 128.0, 140.1, 153.2; MS (GC-EI) *m/z* (%) component A = 218 (6), 178 (10), 160 (14), 142 (35), 120 (24), 91 (100), 73 (68): component B = 218 (5), 178 (10), 160 (15), 142 (25), 120 (32), 91 (100), 73 (37); MS (GC-CI) *m/z* component A = 234 $(M + 1)^+$: component B = 234 $(M + 1)^+$; [Found: $(M - Me)^+$ 218.1369. $C_{13}H_{20}NSi$ requires 218.1364].

(**2m**): ^{1}H NMR δ 0.05 (s, 9H, $SiMe_3$), 2.61 (t, *J* = 5.6 Hz, 2H, N$\underline{CH_2}CH_2OH$), 2.80 (s, 2H, OH and NH), 3.08 (d, *J* = 4.8 Hz, 2H, N$\underline{CH_2}$CH=C), 3.53 (2H, *J* = 5.6 Hz, 2H, N$CH_2\underline{CH_2}$OH, 5.62 (d, *J* = 18.8 Hz, 1H, C=CHSi), 5.83 (dt, ^2J = 18.8 Hz, ^3J = 4.8 Hz, 1H, CH=CSi); ^{13}C NMR δ –1.0, 50.5, 54.2, 60.6, 123.1, 127.9; MS (GC-EI) *m/z* (%) 173 (M^+, 8), 158 (10), 142 (36), 128 (17), 73 (100), 59 (42); (Found: M^+ 173.3021. $C_8H_{19}NOSi$ requires 173.3042).

Received 14 June 2007; accepted 2 August 2007
Paper 07/4699 doi: 10.3184/030823407X237795

References

1(a) J. Jacobus, M. Raban and K. Mislow, *J. Org. Chem*., 1968, **33**, 1142; (b) P. Nussbaumer, K. Baumann, T. Dechat and M. Harasek, *Tetrahedron*, 1991, **47**, 4591; (c) M.B. Sassaman, *Tetrahedron*, 1996, **52**, 10835.
2 (a) J.H. Speer and A.J. Hill, *J. Org. Chem*., 1937, **2**, 139; (b) W.J. Hickinbottom, *J. Chem. Soc*., 1930, 992.

3 (a) S.-I. Murahashi, Y. Imada, Y. Taniguchi and Y. Kodera, *Terahedron Lett*., 1988, **29**, 2973; (b) S.-C. Yang and C.-W. Hung, *Synthesis*, 1999, 1747.
4 W. Ando and H. Tsumaki, *Chem. Lett*., 1981, 693.
5 M. Kozuka, A. Inoue, T. Tsuchida and M. Mitani, *Adv. Synth. Cat*., 2006, **348**, 953.
6 J.B. Baruah and A.G. Samuelson, Tetrahedron, 1991, **47**, 9449.
7 A. Stutz, *Angew. Chem., Int. Ed. Engl*., 1987, **26**, 320.
8 (a) Y. Genisson, M. Mehmandoust, C. Marazano and B.C. Das, *Heterocycles*, 1994, **39**, 811; (b) P. Jain, H.M. Garraffo, T.F. Spande, H.J.C. Yeh and J.W. Daly, *J. Nat. Prod*., 1995, **58**, 100.
9 (a) E.W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, 1988, p. 14; (b) I. Fleming, A. Barbero and D. Walter, *Chem. Rev*., 1997, **97**, 2063.
10 *CRC Handbook of Chemistry and Physics,* D.R. Lide (ed.), CRC Press, Boca Raton, 1993, pp.8-43.