

# One-Pot Synthesis of $\beta$ - and $\gamma$ -Aminofunctionalised Amines and Silanes via Hydroaminomethylation of Enamines and Vinylsilanes

Lars Bärffacker, Thorsten Rische, Peter Eilbracht\*

*Organische Chemie I (FB 3), Universität Dortmund, Otto-Hahn Str. 6, D-44221 Dortmund, Germany*

Received 24 February 1999; accepted 19 April 1999

## Abstract

Heterofunctionalised enamines and vinylsilanes under hydroformylation conditions in the presence of primary or secondary amines are converted to form diamines or aminosilanes in one step. This selective one-pot hydroaminomethylation procedure establishes an easy and convenient access to  $\beta$ - and  $\gamma$ -aminofunctionalised amines and silanes with potential biological activity. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* hydroaminomethylation, rhodium(I)-catalysis,  $\beta$ - and  $\gamma$ -aminofunctionalised amines, enamines, vinylsilanes

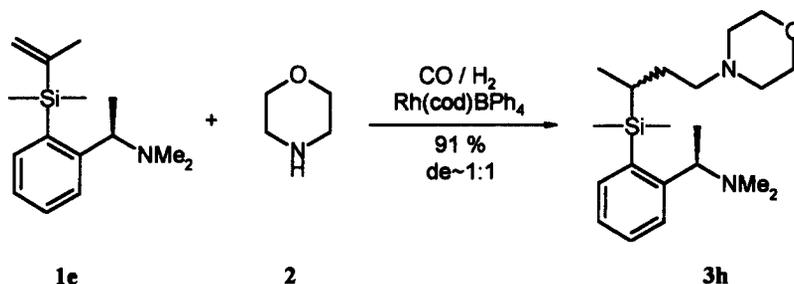
Due to their biological activity  $\beta$ - and  $\gamma$ -aminofunctionalised amines and silanes have attracted considerable interest. Thus 1,2-diamines and 1,3-diamines proved to be of analgesic [1], antipsychotic [2] and of antitumor activity [3]. Likewise  $\gamma$ -aminosilanes possess antimicrobial [4], antifungal [5] and antimuscarinic [6] properties. Numerous methodologies towards their synthesis have been developed usually starting from 1,2- or 1,3-difunctionalised precursors. Alternatively these compounds should be more easily accessible via a hydroformylation - reductive amination sequence starting from enamines or vinylsilanes. We recently reported that this overall hydroaminomethylation reaction as a one-pot version is a convenient and efficient method for selective preparation of secondary and tertiary amines [7]. Here we present use of this procedure by converting enamines and vinylsilanes under hydroformylation conditions in presence of a rhodium(I)-catalyst and primary or secondary amines into the corresponding  $\beta$ - and  $\gamma$ -aminofunctionalised amines and silanes, respectively.

Fax: (+49)(0)231-7555363; e-mail: eilbrach@citrin.chemie.uni-dortmund.de





The hydroaminomethylation of vinylsilane **1e** with morpholine leads to  $\gamma$ -aminosilane **3h** in high yield. However, no significant asymmetric induction at the new stereogenic centre was observed (scheme 3, table 1, entry 9). Obviously the methodology published by Breit [11] employing chiral phosphine ligands instead of amines is more effective in asymmetric hydroformylation.

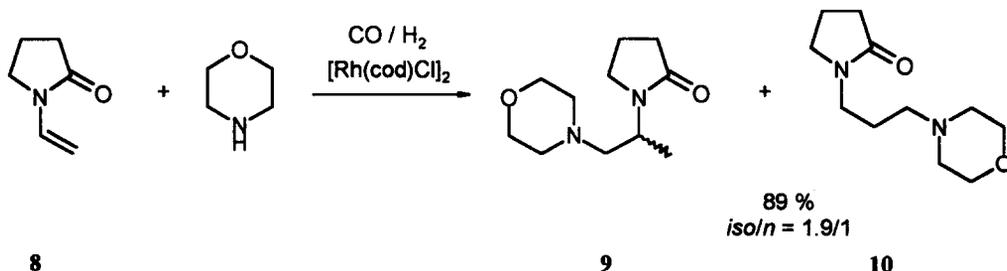


**Scheme 3.** Hydroaminomethylation of *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-(1-methylethenyl)-silyl]-phenyl-ethyl-amine

### Synthesis of $\beta,\gamma$ -diamines

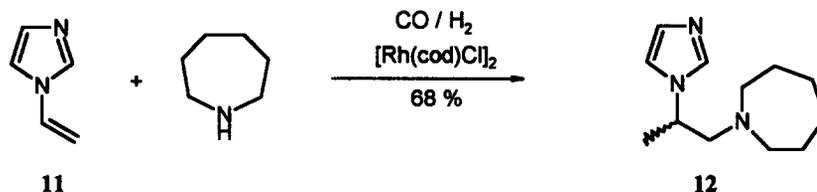
The synthesis of aldehydes starting from enamines via hydroformylation is well established in literature [12]. Similar to vinylsilanes **1** the combination of this hydroformylation with a subsequent reductive amination to a one-pot hydroaminomethylation procedure allows a direct synthesis of 1,2- and 1,3-diamines starting from enamines.

Under typical hydroaminomethylation conditions *N*-vinylpyrrolidinone (**8**) reacts with morpholine, carbon monoxide and hydrogen in presence of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  to form the 1,2- and 1,3-diamines **9**, **10** in good yield. In contrast to olefins possessing no donor-functionality like silanes **1** enamines are predominantly converted to the branched regioisomers (*iso/n*-ratio = 1.9/1). This may be due to a precoordinating effect of the nitrogen moiety influencing the formation of the acyl rhodium species [13].



**Scheme 4.** Hydroaminomethylation of *N*-vinylpyrrolidinone

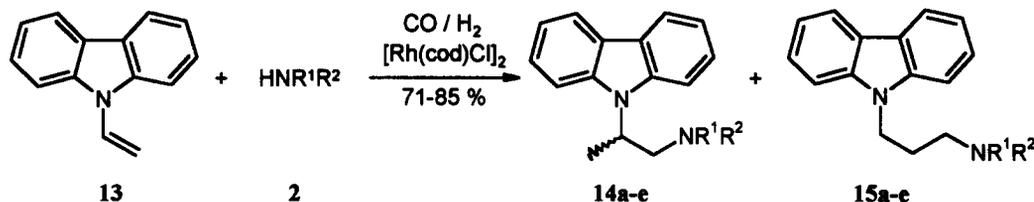
The aromatic *N*-vinylimidazole (11), however, under similar reaction conditions in presence of hexamethylenimine exclusively leads to corresponding 1,2- diamine 12 in 68 % yield.



Scheme 5. Hydroaminomethylation of *N*-vinylimidazole

A comparison with hydroaminomethylation of other aromatic systems such as styrenes suggests that electronical effects induce the high *iso*-regioselectivity [7a].

Similarly the conversion of aromatic *N*-vinylcarbazole (13) proceeds with various primary and secondary amines in good yields and selectivities (scheme 6, table 2). In analogy to the hydroaminomethylation of *N*-vinylimidazole (11) independent from the amine used the generation of the *iso*-product 14 is always preferred due to reasons given above.



Scheme 6. Hydroaminomethylation of *N*-vinylcarbazole

Table 2. Hydroaminomethylation of *N*-vinylcarbazole

entry	olefin	amine	product	<i>iso</i> -/ <i>n</i> - ratio	yield
1	13	morpholine	14a/15a	8/1	71
2	13	pyrrolidine	14b/15b	14/1	83
3	13	isopropylamine	14c/15c	10/1	85
4	13	<i>n</i> -butylamine	14d/15d	22/1	81
5	13	benzylamine	14e/15e	10/1	83

In conclusion we have shown that the rhodium(I)-catalysed one-pot hydroaminomethylation sequence is an efficient method to generate  $\beta$ - and  $\gamma$ -aminofunctionalised amines and silanes. All enamines and vinylsilanes are converted to give the corresponding secondary or tertiary amines in high yields. Further investigation towards an extension of the synthetic potential of this method are in progress.

## Experimental Section

All chemicals were purchased from commercial sources. The catalyst precursors  $[\text{Rh}(\text{cod})\text{Cl}]_2$  [14] and  $\text{Rh}(\text{cod})\text{BPh}_4$  [15] were prepared as described. Column chromatography was carried out on alumina N (act. I) from ICN Biomedicals, Eschwege, or with silica gel 60 from Merck, Darmstadt.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 300 or DRX 400 spectrometer using  $\text{CDCl}_3$  as the solvent and  $\text{CH}_2\text{Cl}_2$  or TMS as internal standards. IR spectra were performed on a Nicolet Impact 400 D, mass spectra on a Finnigan CA 5 and elementary analysis on a Leco, CHNS-932. Analytical gas chromatography was performed on a Fisons 8130 gas chromatograph with 30 m CP sil-5 capillaries. GC-MS spectra were obtained by using a comparable capillary and a Finnigan MAT 8320 (MS). Pressure reactions have been carried out in autoclaves (type A, 250 ml, PTFE-insert) from Berghof, Eningen, Germany. The vinyl silanes **1** are prepared according to typical Grignard procedures [16]. (*R*)-*N,N*-Dimethylphenylethylamine (**6**) was prepared as described by Ollis et al. [17].

### *General procedure for the preparation of $\beta$ -aminosilanes (3a-3g) and $\gamma$ -aminosilane (4a)*

A mixture of the vinylsilane, amine, Rh catalyst and dry toluene (in the case of **3a** and **4a** dioxane was employed as solvent) was placed in an autoclave. After flushing with argon the reactor was pressurized with hydrogen and carbon monoxide and heated to 120 °C for 20 h. Then the autoclave was allowed to cool to room temperature and the solvent was removed by rotary evaporation. The residue was dissolved in methyl *t*-butyl ether and filtered through neutral alumina. The isolation of the products was carried out via kugelrohr distillation or column chromatography.

### *Preparation of 4-(3-triethylsilyl-propyl)-morpholine (3a) and 4-(3-triethylsilyl-propionyl)-morpholine (4a) with $[\text{RhCl}(\text{cod})]_2$ as catalyst precursor in dioxane as solvent*

1.00 g (7.03 mmol) Triethylvinylsilane, 0.58 g (7.03 mmol) morpholine and 0.017 g (1 mol%)  $[\text{RhCl}(\text{cod})]_2$  in 10 ml dioxane are converted at 80 °C and a pressure of 100 bar ( $p(\text{CO}) / p(\text{H}_2) = 4$ ) for 20 h. The *n*-isomer **3a** and the amide **4a** were separated by column chromatography on alumina (petrol ether / MTBE = 2 / 1) yielding in 0.95 g (3.90 mmol, 56 %) 4-(3-triethylsilyl-propyl)-morpholine (**3a**) and 0.36 g (1.41 mmol, 20 %) 4-(3-triethylsilyl-propionyl)-morpholine (**4a**).

**Preparation of 4-(3-triethylsilyl-propyl)-morpholine (3a) with Rh(cod)BPh<sub>4</sub> as catalyst precursor in toluene as solvent**

0.50 g (3.51 mmol) Triethylvinylsilane, 0.37 g (4.21 mmol) morpholine and 0.019 g (1 mol-%) Rh(cod)BPh<sub>4</sub> are converted in 10 ml toluene at 120 °C and a pressure of 80 bar ( $p(\text{CO}) / p(\text{H}_2) = 1$ ) for 20 h. After removal of the catalyst by column filtration 0.73 g (3.01 mmol, 86 %) 4-[3-(triethylsilyl)-propyl]-morpholine (**3a**) were obtained.

**4-(3-Triethylsilyl-propyl)-morpholine (3a):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ [ppm] = 0.44 (2 H), 0.44 (q, 6 H, <sup>3</sup>J = 8.0 Hz), 0.86 (t, 9 H, <sup>3</sup>J = 8.0 Hz), 1.42 (m, 2 H), 2.21 (t, 2 H, <sup>3</sup>J = 7.7 Hz), 2.38 (m, 4 H), 3.66 (m, 4 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ [ppm] = 3.2 (CH<sub>2</sub>), 7.4 (CH<sub>3</sub>), 8.8 (CH<sub>2</sub>), 20.8 (CH<sub>2</sub>), 53.7 (CH<sub>2</sub>), 63.0 (CH<sub>2</sub>), 66.9 (CH<sub>2</sub>). IR (neat):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 2955 vs, 2761 s, 1456 s, 1233 s, 1120 vs, 1006 s, 753 s, 726 s. GC-MS (EI, 70 eV): m/z (%) = 243 (M<sup>+</sup>, 61), 214 (31), 115 (20), 100 (100), 87 (67), 59 (68).

**4-(3-Triethylsilyl-propionyl)-morpholine (4a):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ [ppm] = 0.50 (6 H, <sup>3</sup>J = 7.9 Hz), 0.80 (m, 2 H), 0.90 (t, 9 H, <sup>3</sup>J = 7.9 Hz), 2.23 (m, 2 H), 3.40 (m, 2 H), 3.56 (m, 2 H), 3.63 (m, 4 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ [ppm] = 2.8 (CH<sub>2</sub>), 6.7 (CH<sub>2</sub>), 7.3 (CH<sub>3</sub>), 27.5 (CH<sub>2</sub>), 41.9 (CH<sub>2</sub>), 44.9 (CH<sub>2</sub>), 66.6 (CH<sub>2</sub>), 66.9 (CH<sub>2</sub>), 173.2 (CH<sub>2</sub>). IR (neat):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 2955 s, 2010 s, 1652 s, 1233 s, 1117 s, 965 m, 734 s. GC-MS (EI, 70 eV): m/z (%) = 228 (M<sup>+</sup>-29, 100), 126 (20), 115 (26), 100 (61), 87 (67), 59 (71).

**Preparation of 4-[3-(methyl-diphenylsilyl)-propyl]-morpholine (3b)**

0.80 g (3.56 mmol) Methyl-diphenylvinylsilane, 0.35 g (4.02 mmol) morpholine and 0.019 g (1 mol-%) Rh(cod)BPh<sub>4</sub> are converted in 10 ml toluene at 120 °C and a pressure of 100 bar ( $p(\text{CO}) / p(\text{H}_2) = 1$ ) for 20 h. After removal of the catalyst by column filtration 1.29 g (3.41 mmol, 96 %) 4-[3-(methyl-diphenylsilyl)-propyl]-morpholine (**3b**) were obtained.

**4-[3-(Methyl-diphenylsilyl)-propyl]-morpholine (3b):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ [ppm] = 0.58 (s, 3H), 1.08 (m, 2H), 1.59 (m, 2H), 2.41-2.52 (6H), 3.70 (t\*, 4H, <sup>3</sup>J = 4.8 Hz), 7.30-7.70 (10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ [ppm] = -4.5 (CH<sub>3</sub>), 11.7 (CH<sub>2</sub>), 20.7 (CH<sub>2</sub>), 53.6 (CH<sub>2</sub>), 62.3 (CH<sub>2</sub>), 66.8 (CH<sub>2</sub>), 127.8 (CH), 129.1 (CH), 134.4 (CH), 137.0 (Cq). IR (neat):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 700 s, 790 s, 1116 s, 1258 s, 1412 s; GC-MS (EI, 70V): m/z (%) = 326 (M<sup>+</sup>, 5), 248 (13), 100 (100), 70 (11); Anal. Calcd. for C<sub>20</sub>H<sub>27</sub>NOSi: C: 73.8 %, H: 8.4 %, N: 4.3 %; found: C: 73.7 %, H: 8.1 %, N: 4.0 %.

**Preparation of 4-[3-(triphenylsilyl)-propyl]-morpholine (3c)**

1.00 g (3.49 mmol) Methyl-diphenylvinylsilane, 0.33 g (3.84 mmol) morpholine and 0.018 g (1 mol-%) Rh(cod)BPh<sub>4</sub> are converted in 10 ml toluene at 120 °C and a pressure of 100 bar ( $p(\text{CO}) / p(\text{H}_2) = 1$ ) for 20 h. After removal of the catalyst by column filtration 1.10 g (2.86 mmol, 82 %) 4-[3-(triphenylsilyl)-propyl]-morpholine (**3c**) were obtained.

**4-[3-(Triphenylsilyl)-propyl]-morpholine (3c):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ[ppm] = 1.40 (m, 2H), 1.68 (m, 2H), 2.32–2.42 (6H), 3.70 (t\*, 4H, <sup>3</sup>J = 4.6 Hz), 7.33–7.58 (15H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ[ppm] = 10.7 (CH<sub>2</sub>), 20.9 (CH<sub>2</sub>), 53.6 (CH<sub>2</sub>), 62.3 (CH<sub>2</sub>), 66.9 (CH<sub>2</sub>), 127.8 (CH), 129.4 (CH), 134.9 (Cq), 135.5 (CH); mp.: 120–121 °C; IR (neat):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 699 s, 713 s, 730 s, 1113 s, 1427 s; MS (EI, 70V): m/z (%) = 387 (M<sup>+</sup>-1, 22), 309 (67), 259 (74), 181 (63), 105 (51), 100 (100), 56 (70); Anal. calcd. for C<sub>25</sub>H<sub>29</sub>NOSi (MG: 387.59): C: 77.5 %, H: 7.5 %, N: 3.6 %; found: C: 77.0 %, H: 7.5 %, N: 3.6 %.

**Preparation of 4-[3-phenyl-3-(trimethylsilyl)-propyl]-morpholine (3d)**

0.30 g (1.70 mmol) α-Trimethylsilylstyrene, 0.16 g (1.87 mmol) morpholine and 0.005 g (1 mol-%) Rh(acac)(CO)<sub>2</sub> are converted in 5 ml toluene at 60 °C and a pressure of 100 bar ( $p(\text{CO}) / p(\text{H}_2) = 1$ ) for 24 h. After removal of the catalyst by column filtration (alumina, MTBE) 0.47 g (1.69 mmol, 98 %) 4-[3-phenyl-3-(trimethylsilyl)-propyl]-morpholine (**3d**) was obtained.

**4-[3-Phenyl-3-(trimethylsilyl)-propyl]-morpholine (3d):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ[ppm] = -0.03 (s, 9H), 1.91 - 2.08 (3H), 2.21 (m, 1H), 2.30 (m, 1H), 2.42 (m, 4H), 3.72 (t\*, 4H, <sup>3</sup>J = 4.8 Hz), 7.05 (m, 2H), 7.11 (m, 1H), 7.25 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ[ppm] = -3.1 (CH<sub>3</sub>), 26.1 (CH<sub>2</sub>), 34.7 (CH), 53.7 (CH<sub>2</sub>), 58.9 (CH<sub>2</sub>), 66.9 (CH<sub>2</sub>), 124.3 (CH), 127.4 (CH), 128.0 (CH), 143.1 (Cq); IR (neat):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 701 s, 837 s, 1119 s, 1248 s, 1450 s; GC-MS (EI, 70V): m/z (%) = 277 (M<sup>+</sup>, 6), 262 (8), 100 (100), 73 (9), 56 (6); Anal. calcd. for C<sub>16</sub>H<sub>27</sub>NOSi (MG: 277.48): C: 69.3 %, H: 9.8 %, N: 5.1 %; found: C: 69.2 %, H: 9.5 %, N: 5.2 %.

**Preparation of [3-(triethylsilyl)-propyl]-benzylic amine (3e)**

0.40 g (2.81 mmol) Triethylvinylsilane, 0.33 g (3.09 mmol) benzylic amine and 0.015 g (1 mol-%) Rh(cod)BPh<sub>4</sub> are converted in 5 ml toluene at 120 °C and a pressure of 100 bar ( $p(\text{CO}) / p(\text{H}_2) = 1$ ) for 20 h. After separation by column chromatography (silica gel, petrol ether:MTBE = 1:2) 0.47 g (1.80 mmol, 64 %) [3-(triethylsilyl)-propyl]-benzylic amine (**3e**) were obtained.

**[3-(Triethylsilyl)-propyl]-benzylamine (3e):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ [ppm] = 0.54 (m, 2H), 0.55 (q, 6H,  $^3J = 8.0$  Hz), 0.96 (t, 9H,  $^3J = 8.0$  Hz), 1.45 (sbr, 1H), 1.54 (m, 2H), 2.65 (t, 2H,  $^3J = 7.3$  Hz), 3.82 (s, 2H), 7.25–7.38 (5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ [ppm] = 3.2 ( $\text{CH}_2$ ), 7.4 ( $\text{CH}_3$ ), 8.7 ( $\text{CH}_2$ ), 24.3 ( $\text{CH}_2$ ), 53.1 ( $\text{CH}_2$ ), 54.0 ( $\text{CH}_2$ ), 126.8 (CH), 128.1 (CH), 128.3 (CH), 140.5 (Cq); IR (film, NaCl):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 730 s, 755 s, 1015 s, 1454 s. GC-MS (EI, 70V):  $m/z$  (%) = 264 ( $\text{M}^+$ , 26), 224 (14), 192 (6), 147 (29), 120 (91), 91 (100), 59 (9); Anal. Calcd. for  $\text{C}_{16}\text{H}_{29}\text{NSi}$  (MG: 263.50): C: 72.9 %, H: 11.1 %, N: 5.3 %; found: C: 73.0 %, H: 10.6 %, N: 5.6 %.

**Preparation of [3-(methyldiphenylsilyl)-propyl]-benzylamine (3f)**

0.50 g (3.49 mmol) Methyldiphenylvinylsilane, 0.24 g (2.23 mmol) benzylamine, 0.45 g (4.46 mmol) triethylamine and 0.018 g (1 mol-%)  $\text{Rh}(\text{cod})\text{BPh}_4$  are converted in 10 ml toluene at 90 °C and a pressure of 60 bar ( $p(\text{CO}) / p(\text{H}_2) = 1/2$ ) for 20 h. After separation by column chromatography (silica gel,  $\text{CHCl}_3$ :*i*-PrOH = 50:1) 0.35 g (1.03 mmol, 46 %) [3-(methyldiphenylsilyl)-propyl]-benzylamine (3f) were obtained.

**[3-(Methyldiphenylsilyl)-propyl]-benzylamine (3f):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ [ppm] = 0.58 (s, 3H), 1.12 (mc, 2H), 1.62 (m, 2H), 2.69 (t, 2H,  $^3J = 7.1$  Hz), 3.77 (s, 2H), 7.25–7.58 (15H), NH-proton was not detected;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ [ppm] = -4.5 ( $\text{CH}_3$ ), 11.7 ( $\text{CH}_2$ ), 24.3 ( $\text{CH}_2$ ), 52.6 ( $\text{CH}_2$ ), 53.7 ( $\text{CH}_2$ ), 126.8 (CH), 127.8 (CH), 128.1 (CH), 128.3 (CH), 129.1 (CH), 134.4 (CH), 137.0 (Cq), 140.4 (Cq); IR (neat):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 698 vs, 786 s, 1112 s, 1427 s, 2924 m, 3067 m, 3318 w; GC-MS (EI, 70V):  $m/z$  (%) = 346 ( $\text{M}^+$ , 21), 268 (25), 176 (14), 120 (61), 91 (100).

**Preparation of [3-(methyldiphenylsilyl)-propyl]-isopropylamine (3g)**

1.07 g (4.78 mmol) Methyldiphenylvinylsilane, 0.37 g (6.21 mmol) isopropylamine, 0.029 g (4 mol-%) 2,2'-bipyridyl and 0.012 g (1 mol-%)  $\text{Rh}(\text{acac})(\text{CO})_2$  are converted in 10 ml toluene at 100 °C and a pressure of 80 bar ( $p(\text{CO}) / p(\text{H}_2) = 1$ ) for 20 h. After separation by kugelrohr distillation 0.78 g (2.63 mmol, 55 %) [3-(methyldiphenylsilyl)-propyl]-isopropylamine (3g) was obtained.

**[3-(Methyldiphenylsilyl)-propyl]-isopropylamine (3g):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ [ppm] = 0.57 (s, 3H), 1.03 (d, 6H,  $^3J = 6.3$  Hz), 1.08 (m, 2H), 1.56 (m, 2H), 2.60 (t, 2H,  $^3J = 7.3$  Hz), 2.75 (sept, 1H,  $^3J = 6.3$  Hz), 7.32–7.40 (6H), 7.48–7.60 (4H), NH-proton was not detected;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ [ppm] = -4.5 ( $\text{CH}_3$ ), 11.9 ( $\text{CH}_2$ ), 23.0 ( $\text{CH}_3$ ), 24.7 ( $\text{CH}_2$ ), 48.6 (CH), 50.9 ( $\text{CH}_2$ ), 127.8 (CH), 129.1 (CH), 134.4 (CH), 137.1 (Cq); IR (neat):

$\tilde{\nu}$  [cm<sup>-1</sup>] = 699 vs, 1112 s, 1250 m, 1427 s, 2961 m; GC-MS (EI, 70V): m/z (%) = 298 (M<sup>+</sup>, 100), 220 (15), 204 (12), 176 (9), 72 (82), 59 (13); Anal. calcd. for C<sub>19</sub>H<sub>27</sub>NSi (MG: 297.51): C: 76.7 %, H: 9.2 %, N: 4.7 %; found: C: 76.4 %, H: 9.2 %, N: 4.7 %.

#### **Preparation of *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-methoxy-silyl]-phenylethylamine (7)**

According to a lithiation procedure published by Corriu et al. [10] 24.2 ml *n*-BuLi (1.24 M in hexane) was added dropwise to a solution of 4.6 g (*R*)-*N,N*-dimethyl-phenylethylamine in 30 ml abs. Et<sub>2</sub>O. After 72 h the solution was dropped to a solution of 3.61 g (30 mmol) dimethyl-dimethoxy-silane in 30 ml abs. Et<sub>2</sub>O. The reaction mixture is stirred for additional 2 days at ambient temperature and then the precipitate was filtered off and washed with pentane. The organic layers were combined and the solvent removed. After isolation by distillation 2.42 g (0.01 mol, 30 %; bp. 140 °C, 20 mbar) *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-methoxy-silyl]-phenylethyl-amine (7) was obtained. The spectroscopic datas are identical to those in the literature [10b].

#### **Preparation of *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-(1-methylethenyl)-silyl]-phenyl-ethyl-amine (1e)**

The isopropenyl magnesia bomide solution is generated starting from 0.49 g (0.020 mol) magnesia and 2.54 g (0.021 mol) 2-bromopropene in 20 ml abs. THF. After complete conversion of magnesia the a solution of 2.32 g (8.8 mmol) *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-methoxy-silyl]-phenylethylamine in 5 ml abs. THF was added dropwise. After stirring overnight the reaction mixture was hydrolysed with 10 ml of water. The water phase was extracted with ether (3x20 ml) and the combined organic layers were dried with MgSO<sub>4</sub>. After removal of the solvent the isolation of the vinyl silane was carried out by column chromatography (silica gel, petrol ether/MTBE = 1/1) to give 1.48 g (6.0 mmol, 67 %) *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-(1-methylethenyl)-silyl]-phenylethylamine (1e).

#### ***ortho*-(*R*)-*N,N*-Dimethyl-[(dimethyl)-(1-methylethenyl)-silyl]-phenylethylamine (1e):**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ[ppm] = 0.50 (s, 3H), 0.51 (s, 3H), 1.33 (d, 3H, <sup>3</sup>J = 6.3 Hz), 1.86 (t, 3H, <sup>4</sup>J = 1.5 Hz), 2.26 (s, 6H), 3.51 (q, 1H, <sup>3</sup>J = 6.3 Hz), 5.49 (mc, 1H), 5.76 (mc, 1H), 7.27 (dt, 1H, <sup>3</sup>J = 7.3 Hz, <sup>4</sup>J = 1.3 Hz), 7.43 (dt, 1H, <sup>3</sup>J = 7.3 Hz, <sup>4</sup>J = 1.3 Hz), 7.54 (dd, 1H, <sup>3</sup>J = 7.6 Hz, <sup>4</sup>J = 1.3 Hz), 7.66 (d, 1H, <sup>3</sup>J = 7.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ[ppm] = -1.3 (CH<sub>3</sub>), -1.2 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 43.8 (CH<sub>3</sub>), 64.8 (CH), 125.8 (CH), 126.1 (CH), 129.7 (CH), 135.1 (CH), 126.3 (CH<sub>2</sub>), 134.5 (Cq), 147.2 (Cq), 152.7 (Cq); IR (neat):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 761 s, 825 s, 833 s, 1080 s, 1256 s, 2972 s; GC-MS (EI, 70V): m/z (%) = 248 (M<sup>+</sup>+1, 21), 232 (13), 190 (49), 146 (12), 105 (10), 72 (100), 59 (39).

**Preparation of *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-(1-methyl-3-(morpholin-4-yl)-propyl)-silyl]-phenylethylamine (**3h**)**

0.40 g (1.52 mmol) *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-(1-methylethenyl)-silyl]-phenylethylamine (**1e**), 0.15 g (1.67 mmol) morpholine and 0.008 g (1 mol-%) Rh(cod)BPh<sub>4</sub> are converted in 5 ml toluene at 120 °C and a pressure of 100 bar ( $p(\text{CO}) / p(\text{H}_2) = 1$ ) for 44 h. After removal of the catalyst by kugelrohr distillation 0.48 g (1.38 mmol, 91 %) *ortho*-(*R*)-*N,N*-dimethyl-[(dimethyl)-(1-methyl-3-(morpholin-4-yl)-propyl)-silyl]-phenylethylamine (**3h**) were obtained as a 1:1-mixture of the epimers.

***ortho*-(*R*)-*N,N*-Dimethyl-[(dimethyl)-(1-methyl-3-(morpholin-4-yl)-propyl)-silyl]-phenylethylamine (**3h**) as 1:1-mixture of the epimers:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ [ppm] = 0.28 (s, 3H), 0.28 (s, 3H), 0.29 (s, 3H), 0.29 (s, 3H), 0.91 (2xd, 6H, <sup>3</sup>J = 7.0 Hz), 1.05 (m, 2H), 1.21 (m, 2H), 1.26 (2xd, 6H, <sup>3</sup>J = 3.5 Hz), 1.64 (m, 2H), 2.15 (m, 2H), 2.16 (s, 12 H), 2.33 (m, 8H), 2.42 (m, 2H), 3.34 (m, 2H), 3.67 (mc, 8H), 7.15 (dt, 2H, <sup>3</sup>J = 7.3 Hz, <sup>4</sup>J = 1.0 Hz), 7.32 (t, 2H, <sup>3</sup>J = 7.3 Hz), 7.39 (d, 2H, <sup>3</sup>J = 7.3 Hz), 7.56 (d, 2H, <sup>3</sup>J = 7.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ [ppm] = -2.8 (CH<sub>3</sub>), -2.8 (CH<sub>3</sub>), -2.7 (CH<sub>3</sub>), -2.7 (CH<sub>3</sub>), 14.2 (CH<sub>3</sub>), 14.3 (CH<sub>3</sub>), 17.7 (CH), 17.7 (CH), 23.1 (CH<sub>3</sub>), 23.2 (CH<sub>3</sub>), 28.4 (CH<sub>3</sub>), 28.4 (CH<sub>3</sub>), 44.1 (CH<sub>2</sub>), 44.1 (CH<sub>2</sub>), 53.8 (CH<sub>2</sub>), 58.5 (CH<sub>2</sub>), 58.6 (CH<sub>2</sub>), 65.3 (CH), 65.4 (CH), 66.9 (CH<sub>2</sub>), 125.9 (CH), 126.2 (CH), 129.6 (CH), 135.1 (CH), 135.1 (CH), 135.2 (Cq), 152.5 (Cq). <sup>29</sup>Si NMR (59.6 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 0.52; IR (neat):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 811 s, 827 s, 1119 s, 1258 s, 2954 s; GC-MS (EI, 70V):  $m/z$  (%) = 349 (M<sup>+</sup>, 36), 206 (61), 200 (31), 140 (25), 100 (100), 72 (53); Anal. Calcd. for C<sub>20</sub>H<sub>36</sub>N<sub>2</sub>OSi (MG: 348.60): C: 68.9 %, H: 10.4 %, N: 8.0 %; found: C: 68.9 %, H: 10.3 %, N: 8.2 %.

**General procedure for synthesis of 1,2- and 1,3-diamines**

A mixture of the olefin (4.8 mmol), the corresponding primary or secondary amine (4.8 mmol) and [Rh(cod)Cl]<sub>2</sub> (1 mol %) in 10 mL anhydrous dioxane was heated for 24 h at 110 °C in an autoclave under 90 bar carbon monoxide and 20 bar hydrogen ( $p_{\text{total}} = 110$  bar) pressure. The residue was dissolved in Et<sub>2</sub>O and filtered through neutral alumina. Product mixtures were separated by column chromatography on neutral alumina using a mixture of MTBE/PE as eluent or by kugelrohr distillation.

**1-(1-Methyl-2-morpholinoethyl)-2-pyrrolidinone (**9**) and 1-(3-morpholinopropyl)-2-pyrrolidinone (**10**) (iso/n-ratio = 1.9/1):** Obtained from *N*-vinylpyrrolidone (**8**) and morpholine as a colourless oil in 89 %.

**1-(1-Methyl-2-morpholinoethyl)-2-pyrrolidinone (9):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 0.86 (d,  $^3J = 6.9$  Hz, 3H,  $\text{CH}_3$ ), 2.12 (br s, 4H, 2 x  $\text{NCH}_2$ ), 2.30 (m, 6H, 2 x  $\text{NCH}_2$ ,  $\text{CH}_2$ ), 3.16 (m, 2H,  $\text{CH}_2$ ), 3.44 (br s, 4H, 2 x  $\text{OCH}_2$ ), 4.17 (m, 1H, CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 15.5 ( $\text{CH}_3$ ), 17.7 ( $\text{CH}_2$ ), 31.0 ( $\text{CH}_2$ ), 41.3 ( $\text{NCH}_2$ ), 42.4 ( $\text{NCH}$ ), 53.1 (2 x  $\text{NCH}_2$ ), 60.6 ( $\text{NCH}_2$ ), 66.6 (2 x  $\text{OCH}_2$ ), 174.2 (Cq, C=O). GC-MS (EI, 70 eV):  $m/z$  (%) = 213 ( $\text{M}^+ + 1$ , 24), 126 (15), 100 (100), 70 (16), 56 (10). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 2958 s, 2892 m, 2853 s, 2808 m, 1682 vs, 1459 s, 1426 s, 1286 s, 1272 s, 1258 m, 1117 vs.

**1-(3-Morpholinopropyl)-2-pyrrolidinone (10):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 1.77 (m, 2H,  $\text{CH}_2$ ), 2.11 (br s, 4H, 2 x  $\text{NCH}_2$ ), 2.17 (m, 6H, 2 x  $\text{NCH}_2$ ,  $\text{CH}_2$ ), 3.06 (m, 2H,  $\text{NCH}_2$ ), 3.39 (m, 2H,  $\text{NCH}_2$ ), 3.43 (br s, 4H, 2 x  $\text{OCH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 17.4 ( $\text{CH}_2$ ), 23.9 ( $\text{CH}_2$ ), 30.5 ( $\text{CH}_2$ ), 40.2 ( $\text{NCH}_2$ ), 46.7 ( $\text{NCH}_2$ ), 53.2 (2 x  $\text{NCH}_2$ ), 55.7 ( $\text{NCH}_2$ ), 66.4 (2 x  $\text{OCH}_2$ ), 174.3 (Cq, C=O). GC-MS (EI, 70 eV):  $m/z$  (%) = 213 ( $\text{M}^+ + 1$ , 100), 181 (9), 126 (47), 114 (6), 100 (76), 70 (15), 56 (6).

**1-[2-(1H-1-Imidazolyl)propyl]azepane (12):** Obtained from *N*-vinylimidazole (11) and hexamethylenimine as a yellow oil in 68 %.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  = 1.46 (d,  $^3J = 6.8$  Hz, 3 H,  $\text{CH}_3$ ), 1.53 (m, 8 H, 4 x  $\text{CH}_2$ ), 2.60 (m, 4 H, 2 x  $\text{NCH}_2$ ), 2.71 (d,  $^3J = 6.8$  Hz, 2 H,  $\text{NCH}_2$ ), 4.19 (q\*,  $J = 6.8$  Hz, 1 H,  $\text{NCH}$ ), 6.96 (d,  $J = 1.0$  Hz, 1 H,  $\text{N}=\text{CH}$ ), 7.03 (d,  $J = 0.8$  Hz, 1 H,  $\text{N}=\text{CH}$ ), 7.54 (s, 1 H,  $\text{N}=\text{CH}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  = 19.1 ( $\text{CH}_3$ ), 26.7 (2 x  $\text{CH}_2$ ), 28.3 (2 x  $\text{CH}_2$ ), 52.4 ( $\text{NCH}$ ), 55.5 (2 x  $\text{NCH}_2$ ), 64.4 ( $\text{NCH}_2$ ), 116.5 (CH), 128.5 (CH), 135.9 (CH). GC-MS (EI, 70 eV):  $m/z$  (%) = 208 ( $\text{M}^+ + 1$ , 4), 140 (15), 112 (100), 58 (75). IR (NaCl/film):  $\tilde{\nu}$  = 3105 w, 2925 vs, 2853 vs, 2820 s, 1495 s, 1453 s, 1373 m, 1359 m, 1226 s, 1079 s, 665  $\text{cm}^{-1}$  s.

**4-[2-(9H-9-Carbazolyl)propyl]morpholine (14a):** Obtained from *N*-vinylcarbazole (13) and morpholine as a colourless oil in 71 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 1.57 (d,  $^3J = 7.0$  Hz, 3H), 2.23 (m, 4H), 2.76 (dd,  $^2J = 13.0$  Hz,  $^3J = 6.5$  Hz, 1H), 2.92 (dd,  $^2J = 13.0$  Hz,  $^3J = 7.3$  Hz, 1H), 3.40 (t,  $^3J = 4.5$  Hz, 4H), 4.81 (sextet\*,  $J = 7.0$  Hz, 1H), 7.14 (m, 2H), 7.33 (m, 4H), 8.03 (d,  $J = 7.7$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 17.4 ( $\text{CH}_3$ ), 49.0 ( $\text{NCH}$ ), 53.6 (2 x  $\text{NCH}_2$ ), 61.7 ( $\text{NCH}_2$ ), 66.6 (2 x  $\text{OCH}_2$ ), 109.9 (2 x PhH), 118.5 (2 x PhH), 120.1 (2 x PhH), 123.1 (2 x Cq), 125.2 (2 x PhH), 139.6 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 294 ( $\text{M}^+$ , 8), 194 (9), 128 (7), 100 (100), 70 (8), 56 (7). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3059 w, 2961 m, 2935 m, 2891 m, 2854 m, 2811 m, 1595 m, 1483 s, 1454 vs, 1333 s, 1236 m, 1224 s, 1158 m, 1117 s, 1069 m, 1013 m, 751 s, 724 s.

**9-(1-Methyl-tetrahydro-1H-1-pyrrolylethyl)-9H-carbazole (14b):** Obtained from *N*-vinylcarbazole (13) and pyrrolidine as a yellow oil in 83 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 1.57 (br s, 4H), 1.62 (d,  $^3J = 7.0$  Hz, 3H), 2.37 (br s, 4H), 2.96 (dd,  $^2J = 12.3$  Hz,  $^3J = 6.8$  Hz, 1H), 3.14 (dd,  $^2J = 12.3$  Hz,  $^3J = 7.0$  Hz, 1H), 4.86 (sextet\*,  $J = 7.0$  Hz, 1H), 7.15 (t\*,  $J = 7.4$  Hz, 2H), 7.36 (t\*,  $J = 7.7$  Hz, 2H), 7.44 (d,  $^3J = 8.3$  Hz, 2H), 8.03 (d,  $^3J = 7.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 17.5 ( $\text{CH}_3$ ), 23.3 (2 x  $\text{CH}_2$ ), 50.8 (NCH), 54.1 (2 x NCH $_2$ ), 59.6 (NCH $_2$ ), 110.0 (2 x PhH), 118.4 (2 x PhH), 120.1 (2 x PhH), 123.1 (2 x Cq), 125.2 (2 x PhH), 139.4 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 279 ( $\text{M}^+ + 1$ , 16), 112 (7), 84 (100). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3060 w, 3023 w, 2969 m, 2934 m, 1596 m, 1483 s, 1454 s, 1334 m, 1237 m, 1224 m, 1158 m, 1123 m, 909 s, 749 s, 724 s.

***N*-[2-(9H-9-Carbazolyl)propyl]-*N*-isopropylamine (14c):** Obtained from *N*-vinylcarbazole (13) and isopropylamine as a colourless oil in 85 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 0.84 (d,  $^3J = 6.1$  Hz, 3H), 0.88 (d,  $^3J = 6.1$  Hz, 3H), 1.58 (d,  $^3J = 6.9$  Hz, 3H), 2.67 (sextet,  $J = 6.1$  Hz, 1H), 3.05 (dd,  $^2J = 12.2$  Hz,  $^3J = 5.1$  Hz, 1H), 3.40 (m, 1H), 4.66 (sextet,  $^3J = 6.9$  Hz, 1H), 7.19 (t,  $J = 7.3$  Hz, 2H), 7.38 (m, 2H), 7.48 (d,  $J = 8.3$  Hz, 2H), 8.05 (d,  $J = 7.6$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 17.0 ( $\text{CH}_3$ ), 22.66 ( $\text{CH}_3$ ), 22.72 ( $\text{CH}_3$ ), 48.2 (NCH), 50.5 (NCH $_2$ ), 51.3 (NCH), 110.0 (2 x PhH), 118.7 (2 x PhH), 120.2 (2 x PhH), 123.3 (2 x Cq), 125.4 (2 x PhH), 139.8 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 267 ( $\text{M}^+ + 1$ , 100), 250 (5), 195 (70), 167 (3), 100 (30), 72 (24), 56 (7). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3061 w, 3023 w, 2967 s, 2934 m, 1595 m, 1483 vs, 1453 s, 1380 m, 1333 s, 1237 m, 1223 s, 1157 m, 1124 m, 909 s, 750 vs, 724 vs. Anal. Calcd. for  $\text{C}_{18}\text{H}_{22}\text{N}_2$  (266.4): C, 81.2%; H, 8.3%; N, 10.5%; found C, 81.3%; H, 8.7%; N, 10.1%.

***N*-Butyl-*N*-[2-(9H-9-carbazolyl)propyl]amine (14d):** Obtained from *N*-vinylcarbazole (13) and *n*-butylamine in 81 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 0.73 (t,  $^3J = 7.1$  Hz, 3H), 1.08 (m, 2H), 1.17 (m, 2H), 1.57 (d,  $^3J = 6.9$  Hz, 3H), 2.38-2.52 (m, 2H), 2.98 (dd,  $^2J = 12.2$  Hz,  $^3J = 4.6$  Hz, 1H), 3.43 (m, 1H), 4.89 (m, 1H), 7.18 (d,  $J = 7.4$  Hz, 2H), 7.38 (m, 2H), 7.47 (d,  $J = 8.2$  Hz, 2H), 8.05 (d,  $J = 7.5$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$ [ppm] = 13.7 ( $\text{CH}_3$ ), 16.9 ( $\text{CH}_3$ ), 20.1 ( $\text{CH}_2$ ), 31.8 ( $\text{CH}_2$ ), 49.2 (NCH $_2$ ), 51.1 (NCH), 52.9 (NCH $_2$ ), 109.9 (2 x PhH), 118.7 (2 x PhH), 120.1 (2 x PhH), 123.2 (2 x Cq), 125.4 (2 x PhH), 139.5 (2 x NCq). GC-MS (EI, 70 eV):  $m/z$  (%) = 281 ( $\text{M}^+$ , 100), 195 (54), 114 (5). IR (NaCl/film):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3060 w, 2957 m, 2930 m, 1596 m, 1483 s, 1453 vs, 1333 s, 1225 m, 909 m, 750 vs, 724 vs. Anal. Calcd. for  $\text{C}_{19}\text{H}_{24}\text{N}_2$  (280.4): C, 81.4%; H, 8.6%; N, 10.0%; found C, 80.9%; H, 8.7%; N, 10.0%.

***N*-Benzyl-*N*-[2-(9*H*-9-carbazolyl)propyl]amine (14e):** Obtained from *N*-vinylcarbazole (13) and benzylamine as a colourless oil in 83 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C): δ[ppm] = 1.49 (d, <sup>3</sup>*J* = 7.0 Hz, 3H), 2.93 (m, 1H), 3.37 (m, 1H), 3.55 (s, 2H), 4.87 (m, 1H), 7.20 (m, 11H), 8.05 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C): δ[ppm] = 16.9 (CH<sub>3</sub>), 51.2 (NCH), 51.9 (NCH<sub>2</sub>Ph), 53.1 (NCH<sub>2</sub>), 110.0 (2 x PhH), 118.8 (2 x PhH), 120.2 (2 x PhH), 123.2 (2 x Cq), 125.4 (2 x PhH), 126.7 (PhH), 127.7 (2 x PhH), 128.1 (2 x PhH), 139.8 (Cq), 140.0 (2 x NCq). IR (NaCl/film):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3061 w, 3025 w, 2976 w, 2934 w, 1595 m, 1483 s, 1453 vs, 1333 s, 1237 m, 1225 m, 909 s, 750 vs, 725 vs.

**Acknowledgements:** Financial support of this work by the Fonds der Chemischen Industrie and the State of Nordrhein-Westfalen is gratefully acknowledged. We also thank the Degussa AG, Hanau for donation of chemicals.

## References

1. Rohet, F.; Rubat, C.; Coudert, P. *Chem Pharm. Bull* **1996**, *44*, 980.
2. Wise, L. D.; Pattison, I. C.; Butler, D. E. *J. Med. Chem.* **1985**, *28*, 1811.
3. Cherney R. J.; Swartz S. G.; Patten A.D.; Akamike E.; Sun J. H.; Kaltenbach R. F.; Seitz S. P.; Behrens C. H.; Getahun Z.; Trainor G. L.; Vavala M.; Kirshenbaum M. R.; Papp L. M.; Stafford M. P.; Czerniak P. M.; Diamond R. J.; McRipley R. J.; Page R. J.; Gross J. L. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 163.
4. Lukevits, E. Y.; Voronkov, M. G. *Dokl. Chem.* **1974**, *216*, 301.
5. Garandeau, J.-M.; Chollet, J. F.; Mignac, L. *Helv. Chim. Acta* **1997**, *80*, 706.
6. Steiling, L.; Tacke, R.; Wannagat, U. *Liebigs Ann. Chem.* **1979**, 1554.
7. a) Rische, T.; Eilbracht, P. *Synthesis* **1997**, 1331. b) Kranemann, C. L., Eilbracht, P. *Synthesis* **1998**, 71. c) Rische, T.; Kitsos-Rzychon, B.; Eilbracht, P. *Tetrahedron* **1998**, *54*, 2723. d) Bäracker, L.; Hollmann, C.; Eilbracht, P. *Tetrahedron* **1998**, *54*, 4493. e) Rische, T.; Eilbracht, P. *Tetrahedron* **1998**, *54*, 8441. f) Rische, T.; Bäracker, L.; Eilbracht, P. *Eur. J. Org. Chem.* accepted for publication. g) Rische, T.; Eilbracht, P. *Tetrahedron* **1999**, *55*, 1915.
8. a) Burkhard, C. A.; Hurd, D. T. *J. Org. Chem.* **1952**, *17*, 1107. b) Morozova, L. V.; Magomedov, G. K.-I.; Sheludyakov, V. D. *J. Gen. Chem. USSR* **1977**, *47*, 1395. c) Doyle, M. M.; Jackson, W. R.; Perlmutter, P. *Aust. J. Chem.* **1989**, *42*, 1907. d) Doyle, M. M.; Jackson, W. R.; Perlmutter, P. *Tetrahedron Lett.* **1989**, *30*, 233. e) Takeuchi, R.; Sato, N. *J. Organomet. Chem.* **1990**, *393*, 1. f) Crudden, C. M.; Alper, H. *J. Org. Chem.* **1994**, *59*, 3091.
9. Blegg, J.; Davis, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Perkin Trans I* **1987**, 1805.
10. a) Boyer, J.; Brelière, C.; Carré, F.; Corriu, R. J. P.; Kpton, A.; Poirier, M.; Royo, G.; Young, J. C. *J. Chem. Soc. Dalton Trans.* **1989**, 43. b) Corriu, R. J. P.; Kpton, A.; Poirier, M.; Royo, G.; de Saxcé, A.; Young, J. C. *J. Organomet. Chem.* **1990**, *395*, 1.
11. a) Breit, B. *Tetrahedron Lett.* **1998**, *39*, 5163. b) Breit, B. *Liebigs Ann./Recueil* **1997**, 1841.
12. a) Parrinello, G; Stille, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 7122. b) Settambolo, R.; Caiazzo, A.; Lazzaroni, R. *J. Organomet. Chem.* **1996**, *506*, 337.
13. Zhang, Z., Ojima, I. *J. Organomet. Chem.* **1993**, *454*, 281.
14. Giordano, G.; Crabtree, R. *Inorg. Synth.* **1979**, *19*, 218.
15. Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339.
16. Nagel, R.; Post, H. W.; *J. Org. Chem.* **1952**, *17*, 1379.
17. Ollis, W. D.; Rey, M.; Sutherland, I. O.; *J. Chem. Soc. Perkin Trans I* **1983**, 1009.