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One-Pot Synthesis of β- and γ-Aminofunctionalised Amines and Silanes via Hydroaminomethylation of Enamines and Vinylsilanes

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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 β- and γ-aminofunctionalised amines and silanes with potential biological activity.

Keywords: hydroaminomethylation, rhodium(I)-catalysis, β- and γ-aminofunctionalised amines, enamines, vinylsilanes

Due to their biological activity β- and γ-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 γ-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 β- and γ-aminofunctionalised amines and silanes, respectively.

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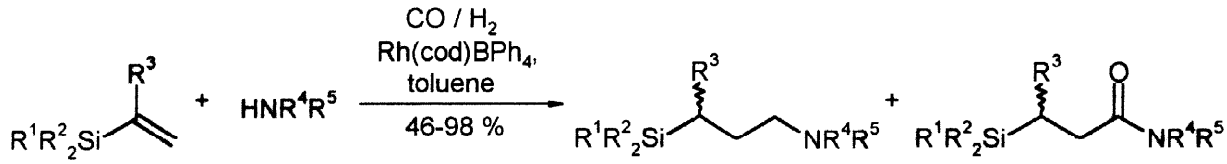
Synthesis of β,γ-aminofunctionalised silanes

Hydroformylation of vinylsilanes is well established for the preparation of the corresponding aldehydes [8]. The combination of hydroformylation and subsequent reductive amination as a one-pot hydroaminomethylation procedure leads directly to β,γ-aminofunctionalised silanes if starting from vinylsilanes. As listed in table 1 cyclic amines like morpholine react with triethylvinylsilane under hydroformylation conditions to form a 2.8/1-mixture of the linear alkylation product **3a** accompanied by small amounts of the hydrocarboxylation product **4a** (table 1, entry 1, scheme 1). The carbonylation is observed to occur in the β-position of the silyl moiety due to the steric hindrance of the silyl substituent.



1a-e **2** **3a-h** **4a**

Scheme 1. Hydroaminomethylation of vinylsilanes 1a-e with primary and secondary amines

Table 1. Hydroaminomethylation of vinylsilanes 1a-e

entry	silane (1)	R^1, R^2	R^3	amine (2)	product	yield 3 [%] / (3a /4a)
1[a)]	**a**	Et, Et	H	morpholine	**3a, 4a**	64 / (>2.8/1)
2	**a**	Et, Et	H	morpholine	**3a**	86
3	**b**	Me, Ph	H	morpholine	**3b**	96
4	**c**	Ph, Ph	H	morpholine	**3c**	82
5	**d**	Me, Me	Ph	morpholine	**3d**	98
6	**a**	Et, Et	H	benzylamine	**3e**	64
7[b,c)]	**b**	Me, Ph	H	benzylamine	**3f**	46
8[b,d)]	**b**	Me, Ph	H	isopropylamine	**3g**	55
9	**e**	[e)], Me	H	morpholine	**3h**	55

a) dioxane was used as solvent b) catalyst precursor: $Rh(acac)(CO)_2$; c) additive: 200 mol-% NEt_3; d) additive: 2 mol-% 2,2'-bipyridyl; e) *ortho-(R)-N,N*-dimethylaminoethyl-phenyl

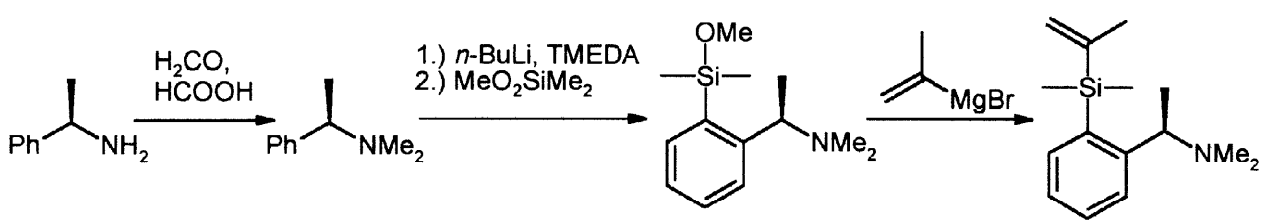
By replacing the solvent dioxane with toluene and the catalyst precursor $[Rh(cod)Cl]_2$ by $Rh(cod)BPh_4$ the product selectivity and yields are significantly increased and **3a** is isolated as

the sole product (table 1, entry 1 and 2). In order to suppress the formation of amides **4** the latter catalyst precursor was chosen for all further conversions. Methyl-diphenyl-vinylsilane and triphenyl-vinylsilane similarly react with morpholine leading to the corresponding tertiary amines in excellent yields (table 1, entry 3,4). 1-Phenyl-vinylsilanes and secondary amines afford the corresponding amines in almost quantitative yields (table 1, entry 5).

With primary amines like isopropyl- or benzylamine, however, the vinylsilane bond is cleaved leading to the generation of (diphenyl)-methylsilanol. This vinylsilane bond cleavage is depending on the substituents in the silyl moiety. If trialkyl substituents instead of aryl functionalities are introduced in the hydroaminomethylation sequence can be performed in medium yields without vinylsilane cleavage (table 1, entry 6).

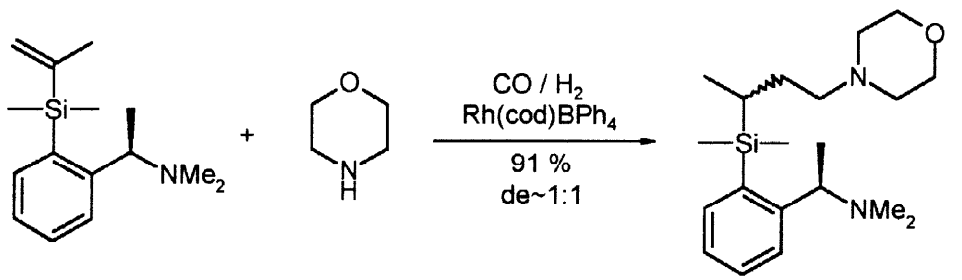
The Si-C bond cleavage observed can be interpreted as an acid or Lewis acid catalysed desilylation. If, however, triethylamine is added as a base even the conversion of methyl-diphenyl-vinylsilane and benzylamine proceeds towards the hydroaminomethylation product **3** in 46 % yield (table 1, entry 7). Likewise bidentate amine ligands like 2,2'-bipyridyl can effectively be used as a cocatalyst (table 1, entry 8). Here again the conversion of methyl-diphenylsilane with isopropylamine leads to the formation of the secondary amine in moderate yield.

The chiral vinylsilane **1e** was prepared in order to test a possible stereocontrol of hydroaminomethylation by a built-in chiral auxiliary. Starting from the commercially available *R*-(+)-phenylethylamine the N-alkylation was carried out employing the Leuckart-Wallach methodology [9]. *ortho*-Lithiation with *n*-butyllithium followed by addition of dimethoxy-dimethylsilane leads to arylsilane **7** [10]. A subsequent conversion with isopropenyl magnesia bromide gives vinylsilane **1e** (scheme 2).



Scheme 2. Preparation of ortho-R-N,N-dimethyl-[(dimethyl)-(1-methylethenyl)-silyl]-phenylethylamine

The hydroaminomethylation of vinylsilane **1e** with morpholine leads to γ-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.



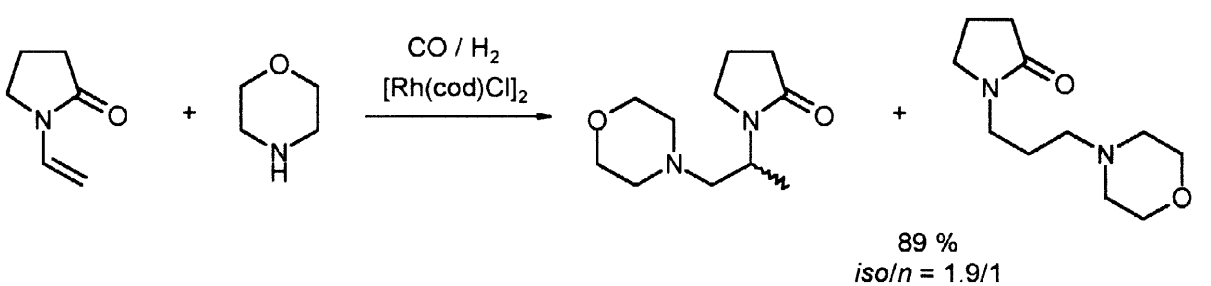
1e **2** **3h**

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

Synthesis of β,γ-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.

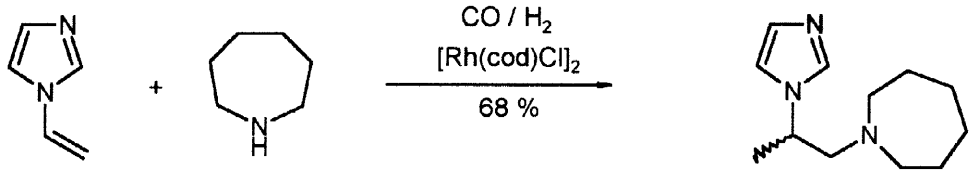
Under typical hydroaminomethylation conditions *N*-vinylpyrrolidinone **(8)** reacts with morpholine, carbon monoxide and hydrogen in presence of $[Rh(cod)Cl]_2$ to form the 1,2- and 1,3-diamines **9**, **10** in good yield. In contrast to olefins possessing no donor-functionality like silanes **1** 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].



8 **9** **10**

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.

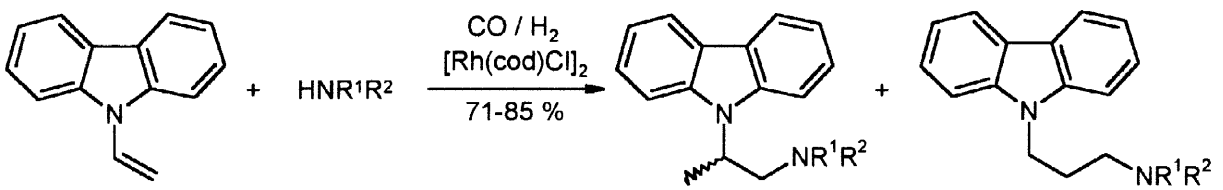


11 **12**

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.



13 **2** **14a-e** **15a-e**

Scheme 6. *Hydroaminomethylation of N-vinylcarbazole*

Table 2. *Hydroaminomethylation of N-vinylcarbazole*

entry	olefin	amine	product	*iso*-/*n*- 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**	*n*-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 β- and γ-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 $[Rh(cod)Cl]_2$ [14] and $Rh(cod)BPh_4$ [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. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 or DRX 400 spectrometer using $CDCl_3$ as the solvent and CH_2Cl_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*-Dimethyl-phenylethylamine **(6)** was prepared as described by Ollis et al. [17].

General procedure for the preparation of β-aminosilanes (3a-3g) and γ-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 $[RhCl(cod)]_2$ 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%) $[RhCl(cod)]_2$ in 10 ml dioxane are converted at 80 °C and a pressure of 100 bar ($p(CO) / p(H_2) = 4$) 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$_4$ 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$_4$ are converted in 10 ml toluene at 120 °C and a pressure of 80 bar (p(CO) / p (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)*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 0.44 (2 H), 0.44 (q, 6 H, ^3J= 8.0 Hz), 0.86 (t, 9 H, ^3J= 8.0 Hz), 1.42 (m, 2 H), 2.21 (t, 2 H, ^3J= 7.7 Hz), 2.38 (m, 4 H), 3.66 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm] = 3.2 (CH_2), 7.4 (CH_3), 8.8 (CH_2), 20.8 (CH_2), 53.7 (CH_2), 63.0 (CH_2), 66.9 (CH_2). IR (neat): $\tilde{\nu}$ [cm^{-1}] = 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^+, 61), 214 (31), 115 (20), 100 (100), 87 (67), 59 (68).

***4-(3-Triethylsilyl-propionyl)-morpholine (4a)*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 0.50 (6 H, ^3J= 7.9 Hz), 0.80 (m, 2 H), 0.90 (t, 9 H, ^3J= 7.9 Hz), 2.23 (m, 2 H), 3.40 (m, 2 H), 3.56 (m, 2 H), 3.63 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm] = 2.8 (CH_2), 6.7 (CH_2), 7.3 (CH_3), 27.5 (CH_2), 41.9 (CH_2), 44.9 (CH_2), 66.6 (CH_2), 66.9 (CH_2), 173.2 (CH_2). IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2955 s, 2010 s, 1652 s, 1233 s, 1117 s, 965 m, 734 s. GC-MS (EI, 70 eV): m/z (%) = 228 (M^+-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) Methyldiphenylvinylsilane, 0.35 g (4.02 mmol) morpholine and 0.019 g (1 mol-%) Rh(cod)BPh$_4$ are converted in 10 ml toluene at 120 °C and a pressure of 100 bar (p(CO) / p (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)*:** ^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 0.58 (s, 3H), 1.08 (m, 2H), 1.59 (m, 2H), 2.41-2.52 (6H), 3.70 (t*, 4H, ^3J= 4.8 Hz), 7.30-7.70 (10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ[ppm] = -4.5 (CH_3), 11.7 (CH_2), 20.7 (CH_2), 53.6 (CH_2), 62.3 (CH_2), 66.8 (CH_2), 127.8 (CH), 129.1 (CH), 134.4 (CH), 137.0 (Cq). IR (neat): $\tilde{\nu}$ [cm^{-1}] = 700 s, 790 s, 1116 s, 1258 s, 1412 s; GC-MS (EI, 70V): m/z (%) = 326 (M^+, 5), 248 (13), 100 (100), 70 (11); Anal. Calcd. for $C_{20}H_{27}NOSi$: 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) Methyldiphenylvinylsilane, 0.33 g (3.84 mmol) morpholine and 0.018 g (1 mol-%) $Rh(cod)BPh_4$ are converted in 10 ml toluene at 120 °C and a pressure of 100 bar (p(CO) / p (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): ^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 1.40 (m, 2H), 1.68 (m, 2H), 2.32-2.42 (6H), 3.70 (t*, 4H, ^3J= 4.6 Hz), 7.33-7.58 (15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ[ppm] = 10.7 (CH_2), 20.9 (CH_2), 53.6 (CH_2), 62.3 (CH_2), 66.9 (CH_2), 127.8 (CH), 129.4 (CH), 134.9 (Cq), 135.5 (CH); mp.: 120-121 °C; IR (neat): $\tilde{\nu}$ [cm^{-1}] = 699 s, 713 s, 730 s, 1113 s, 1427 s; MS (EI, 70V): m/z (%) = 387 (M^+-1, 22), 309 (67), 259 (74), 181 (63), 105 (51), 100 (100), 56 (70); Anal. calcd. for $C_{25}H_{29}NOSi$ (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-%) $Rh(acac)(CO)_2$ are converted in 5 ml toluene at 60 °C and a pressure of 100 bar (p(CO) / p (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): ^{1}H NMR (400 MHz, $CDCl_3$): 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, ^3J = 4.8 Hz), 7.05 (m, 2H), 7.11 (m, 1H), 7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ[ppm] = -3.1 (CH_3), 26.1 (CH_2), 34.7 (CH), 53.7 (CH_2), 58.9 (CH_2), 66.9 (CH_2), 124.3 (CH), 127.4 (CH), 128.0 (CH), 143.1 (Cq); IR (neat): $\tilde{\nu}$ [cm^{-1}] = 701 s, 837 s, 1119 s, 1248 s, 1450 s; GC-MS (EI, 70V): m/z (%) = 277 (M^+, 6), 262 (8), 100 (100), 73 (9), 56 (6); Anal. calcd. for $C_{16}H_{27}NOSi$ (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-%) $Rh(cod)BPh_4$ are converted in 5 ml toluene at 120 °C and a pressure of 100 bar (p(CO) / p (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]-benzylic amine (3e): ^{1}H NMR (400 MHz, $CDCl_3$): δ[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}C NMR (100 MHz, $CDCl_3$): δ[ppm] = 3.2 (CH_2), 7.4 (CH_3), 8.7 (CH_2), 24.3 (CH_2), 53.1(CH_2), 54.0 (CH_2), 126.8 (CH), 128.1 (CH), 128.3 (CH), 140.5 (Cq); IR (film, NaCl): $\tilde{\nu}$ [cm^{-1}] = 730 s, 755 s, 1015 s, 1454 s. GC-MS (EI, 70V): m/z (%) = 264 (M^+, 26), 224 (14), 192 (6), 147 (29), 120 (91), 91 (100), 59 (9); Anal. Calcd. for $C_{16}H_{29}NSi$ (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]-benzylic amine (3f)

0.50 g (3.49 mmol) Methyldiphenylvinylsilane, 0.24 g (2.23 mmol) benzylic amine, 0.45 g (4.46 mmol) triethylamine and 0.018 g (1 mol-%) Rh(cod)BPh_4 are converted in 10 ml toluene at 90 °C and a pressure of 60 bar (p(CO) / p (H_2) = 1/2) for 20 h. After separation by column chromatography (silica gel, $CHCl_3$:*i*-PrOH = 50:1) 0.35 g (1.03 mmol, 46 %) [3-(methyldiphenylsilyl)-propyl]-benzylic amine **(3f)** were obtained.

[3-(Methyldiphenylsilyl)-propyl]-benzylic amine (3f): ^{1}H NMR (400 MHz, $CDCl_3$): δ[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}C NMR (100 MHz, $CDCl_3$): δ[ppm] = -4.5 (CH_3), 11.7 (CH_2), 24.3 (CH_2), 52.6 (CH_2), 53.7 (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): $\tilde{\nu}$ [cm^{-1}] = 698 vs, 786 s, 1112 s, 1427 s, 2924 m, 3067 m, 3318 w; GC-MS (EI, 70V): m/z (%) = 346 (M^+, 21), 268 (25), 176 (14), 120 (61), 91 (100).

Preparation of [3-(methyldiphenylsilyl)-propyl]-isopropylic amine (3g)

1.07 g (4.78 mmol) Methyldiphenylvinylsilane, 0.37 g (6.21 mmol) isopropylic amine, 0.029 g (4 mol-%) 2,2'-bipyridyl and 0.012 g (1 mol-%) Rh(acac)$(CO)_2$ are converted in 10 ml toluene at 100 °C and a pressure of 80 bar (p(CO) / p (H_2) = 1) for 20 h. After separation by kugelrohr distillation 0.78 g (2.63 mmol, 55 %) [3-(methyldiphenylsilyl)-propyl]-isopropylic amine **(3f)** was obtained.

[3-(Methyldiphenylsilyl)-propyl]-isopropylic amine (3g): ^{1}H NMR (400 MHz, $CDCl_3$): δ[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}C NMR (100 MHz, $CDCl_3$): δ[ppm] = -4.5 (CH_3), 11.9 (CH_2), 23.0 (CH_3), 24.7 (CH_2), 48.6 (CH), 50.9 (CH_2), 127.8 (CH), 129.1 (CH), 134.4 (CH), 137.1 (Cq); IR (neat):

$\tilde{\nu}$ [cm^{-1}] = 699 vs, 1112 s, 1250 m, 1427 s, 2961 m; GC-MS (EI, 70V): m/z (%) = 298 (M^+, 100), 220 (15), 204 (12), 176 (9), 72 (82), 59 (13); Anal. calcd. for $C_{19}H_{27}NSi$ (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_2O. After 72 h the solution was dropped to a solution of 3.61 g (30 mmol) dimethyl-dimethoxy-silane in 30 ml abs. Et_2O. 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 $MgSO_4$. 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):

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 0.50 (s, 3H), 0.51 (s, 3H), 1.33 (d, 3H, ^3J = 6.3 Hz), 1.86 (t, 3H, ^4J = 1.5 Hz), 2.26 (s, 6H), 3.51 (q, 1H, ^3J = 6.3 Hz), 5.49 (mc, 1H), 5.76 (mc, 1H), 7.27 (dt, 1H, ^3J = 7.3 Hz, ^4J = 1.3 Hz), 7.43 (dt, 1H, ^3J = 7.3 Hz, ^4J = 1.3 Hz), 7.54 (dd, 1H, ^3J = 7.6 Hz, ^4J = 1.3 Hz), 7.66 (d, 1H, ^3J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ[ppm] = -1.3 (CH_3), -1.2 (CH_3), 22.4 (CH_3), 22.7 (CH_3), 43.8 (CH_3), 64.8 (CH), 125.8 (CH), 126.1 (CH), 129.7 (CH), 135.1 (CH), 126.3 (CH_2), 134.5 (Cq), 147.2 (Cq), 152.7 (Cq); IR (neat): $\tilde{\nu}$ [cm^{-1}] = 761 s, 825 s, 833 s, 1080 s, 1256 s, 2972 s; GC-MS (EI, 70V): m/z (%) = 248 (M^++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-%) $Rh(cod)BPh_4$ are converted in 5 ml toluene at 120 °C and a pressure of 100 bar ($p(CO) / p(H_2) = 1$) 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]-phenylethylamin **(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]-phenylethyl-amine (3h) as 1:1-mixture of the epimers: ^1H NMR (400 MHz, $CDCl_3$): δ[ppm] = 0.28 (s, 3H), 0.28 (s, 3H), 0.29 (s, 3H), 029 (s, 3H), 0.91 (2xd, 6H, ^3J = 7.0 Hz), 1.05 (m, 2H), 1.21 (m, 2H), 1.26 (2xd, 6H, ^3J = 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, ^3J = 7.3 Hz, ^4J = 1.0 Hz), 7.32 (t, 2H, ^3J = 7.3 Hz), 7.39 (d, 2H, ^3J = 7.3 Hz), 7.56 (d, 2H, ^3J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ[ppm] = -2.8 (CH_3), -2.8 (CH_3), -2.7 (CH_3), -2.7 (CH_3), 14.2 (CH_3), 14.3 (CH_3), 17.7 (CH), 17.7 (CH), 23.1 (CH_3), 23.2 (CH_3), 28.4 (CH_3), 28.4 (CH_3), 44.1 (CH_2), 44.1 (CH_2), 53.8 (CH_2), 58.5 (CH_2), 58.6 (CH_2), 65.3 (CH), 65.4 (CH), 66.9 (CH_2), 125.9 (CH), 126.2 (CH), 129.6 (CH), 135.1 (CH), 135.1 (CH), 135.2 (Cq), 152.5 (Cq). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ [ppm] = 0.52; IR (neat): $\tilde{\nu}$ [cm^{-1}] = 811 s, 827 s, 1119 s, 1258 s, 2954 s; GC-MS (EI, 70V): m/z (%) = 349 (M^+, 36), 206 (61), 200 (31), 140 (25), 100 (100), 72 (53); Anal. Calcd. for $C_{20}H_{36}N_2OSi$ (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 $[Rh(cod)Cl]_2$ (1 mol %) in 10 mL anhydous dioxane was heated for 24 h at 110 °C in an autoclave under 90 bar carbon monoxide and 20 bar hydrogen (p_{total} = 110 bar) pressure. The residue was dissolved in Et_2O 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*-vinypyrolidone **(8)** and morpholine as a colourless oil in 89 %.

1-(1-Methyl-2-morpholinoethyl)-2-pyrrolidinone (9): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ[ppm] = 0.86 (d, ^{3}J = 6.9 Hz, 3H, CH_3), 2.12 (br s, 4H, 2 x NCH_2), 2.30 (m, 6H, 2 x NCH_2, CH_2), 3.16 (m, 2H, CH_2), 3.44 (br s, 4H, 2 x OCH_2), 4.17 (m, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ[ppm] = 15.5 (CH_3), 17.7 (CH_2), 31.0 (CH_2), 41.3 (NCH_2), 42.4 (NCH), 53.1 (2 x NCH_2), 60.6 (NCH_2), 66.6 (2 x OCH_2), 174.2 (Cq, C=O). GC-MS (EI, 70 eV): m/z (%) = 213 (M^++1, 24), 126 (15), 100 (100), 70 (16), 56 (10). IR (NaCl/film): $\tilde{\nu}$ [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}H NMR (400 MHz, $CDCl_3$, 20 °C): δ[ppm] = 1.77 (m, 2H, CH_2), 2.11 (br s, 4H, 2 x NCH_2), 2.17 (m, 6H, 2 x NCH_2, CH_2), 3.06 (m, 2H, NCH_2), 3.39 (m, 2H, NCH_2), 3.43 (br s, 4H, 2 x OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ[ppm] = 17.4 (CH_2), 23.9 (CH_2), 30.5 (CH_2), 40.2 (NCH_2), 46.7 (NCH_2), 53.2 (2 x NCH_2), 55.7 (NCH_2), 66.4 (2 x OCH_2), 174.3 (Cq, C=O). GC-MS (EI, 70 eV): m/z (%) = 213 (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}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.46 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.53 (m, 8 H, 4 x CH_2), 2.60 (m, 4 H, 2 x NCH_2), 2.71 (d, ^3J = 6.8 Hz, 2 H, NCH_2), 4.19 (q*, J = 6.8 Hz, 1 H, NCH), 6.96 (d, J = 1.0 Hz, 1 H, N=CH), 7.03 (d, J = 0.8 Hz, 1 H, N=CH), 7.54 (s, 1 H, N=CH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 19.1 (CH_3), 26.7 (2 x CH_2), 28.3 (2 x CH_2), 52.4 (NCH), 55.5 (2 x NCH_2), 64.4 (NCH_2), 116.5 (CH), 128.5 (CH), 135.9 (CH). GC-MS (EI, 70 eV): m/z (%) = 208 (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 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}H NMR (400 MHz, $CDCl_3$, 20 °C): δ[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}C NMR (100 MHz, $CDCl_3$, 20 °C): δ[ppm] = 17.4 (CH_3), 49.0 (NCH), 53.6 (2 x NCH_2), 61.7 (NCH_2), 66.6 (2 x 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 (M^+, 8), 194 (9), 128 (7), 100 (100), 70 (8), 56 (7). IR (NaCl/film): $\tilde{\nu}$ [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}H NMR (400 MHz, $CDCl_3$, 20 °C): δ[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}C NMR (100 MHz, $CDCl_3$, 20 °C): δ[ppm] = 17.5 (CH_3), 23.3 (2 x 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 (M^++1, 16), 112 (7), 84 (100). IR (NaCl/film): $\tilde{\nu}$ [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}H NMR (400 MHz, $CDCl_3$, 20 °C): δ[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}C NMR (100 MHz, $CDCl_3$, 20 °C): δ[ppm] = 17.0 (CH_3), 22.66 (CH_3), 22.72 (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 (M^++1, 100), 250 (5), 195 (70), 167 (3), 100 (30), 72 (24), 56 (7). IR (NaCl/film): $\tilde{\nu}$ [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 $C_{18}H_{22}N_2$ (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}H NMR (400 MHz, $CDCl_3$, 20 °C): δ[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}C NMR (100 MHz, $CDCl_3$, 20 °C): δ[ppm] = 13.7 (CH_3), 16.9 (CH_3), 20.1 (CH_2), 31.8 (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 (M^+, 100), 195 (54), 114 (5). IR (NaCl/film): $\tilde{\nu}$ [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 $C_{19}H_{24}N_2$ (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-(9H-9-carbazolyl)propyl]amine (14e): Obtained from N-vinylcarbazole **(13)** and benzylamine as a colourless oil in 83 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ[ppm] = 1.49 (d, ^3J = 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). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ[ppm] = 16.9 (CH_3), 51.2 (NCH), 51.9 (NCH_2Ph), 53.1 (NCH_2), 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^{-1}] = 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.

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