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Selective One-Pot Synthesis of Symmetrically and Unsymmetrically Substituted Amines via Rhodium Catalysed Multiple Alkylations of Ammonia or Primary Amines under Hydroformylation Conditions

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Abstract: Symmetrically and unsymmetrically substituted secondary and tertiary amines are selectively prepared in high yields by a one-pot multiple alkylation procedure from ammonia or primary amines with styrenes and/or cyclic olefins, carbon monoxide and hydrogen in the presence of [Rh(cod)Cl]$_2$ as catalyst. Similarly unsymmetrically substituted tertiary amines are obtained under hydroformylation conditions from primary amines by a one-pot reductive bisalkylation procedure using preformed aldehydes or ketones in one step and the hydroformylation products in the second step of a combined amine condensation - reduction - hydroaminomethylation reaction sequence.
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The synthesis of secondary and tertiary amines with different substituents usually requires selective stepwise procedures.[1,2] Therefore one-pot methods with simultaneous introduction of two different alkyl substituents into an amine appears to be extremely difficult, if not impossible. We recently reported that [Rh(cod)Cl]$_2$ effectively catalyses carbonylative hydroaminomethylation of alkenes, which on the other hand is an efficient, and selective method to alkylate either primary to secondary amines or secondary to tertiary amines.[3,4] Now we present use of this method for a selective bisalkylation of ammonia or primary amines, the latter even with simultaneous introduction of two different alkyl substituents in an efficient one-pot procedure.

Synthesis of Symmetrically Substituted Secondary and Tertiary Amines

As earlier reported carbonylative reductive hydroaminomethylation of α-methylstyrene (**1**) with primary amines **2a-d** exclusively leads to secondary amines **3a-d** (Scheme 1).[3] No further alkylation of the amine product is observed under the reaction conditions if equivalent amounts of the amine and the alkene are used. On the other hand, however, secondary amines can also be alkylated to form tertiary amines with comparable rates and yields if using the same procedure and conditions. These results pose the question whether a one-pot double alkylation of primary amines to tertiary amines is possible, if more than one equivalent of the alkene is used. In addition, a mechanistic explanation must be found, why opposed to other alkylation methods, here a selective monoalkylation of primary to secondary amines is possible at all.
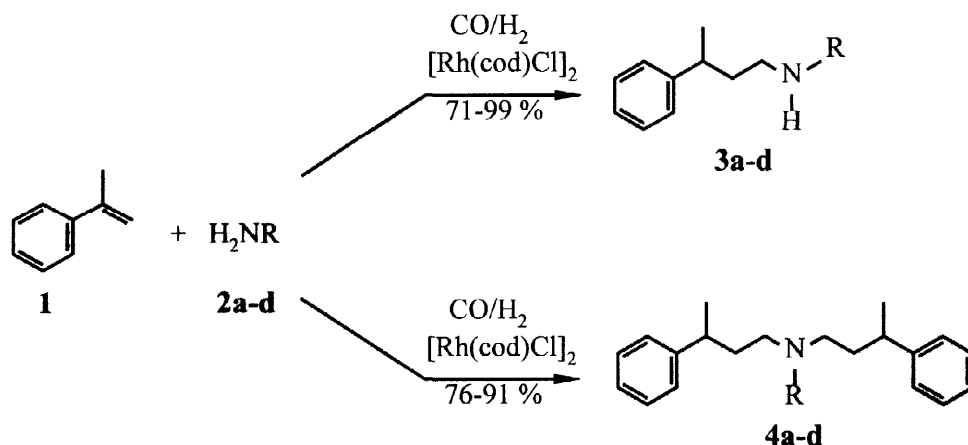
Scheme 1: Carbonylative mono- and bisalkyation of the primary amines 2a-d with
α-methylstyrene (1) and CO/H$_2$

As summarised in table 1 bisalkylation of primary amines 2a-d to tertiary amines 4a-d is achieved (see scheme 1) in good to excellent yields, if two equivalents of α-methylstyrene (1) are used. Several amines were tested, all without formation of by-products such as secondary amines 3, enamines or aldehydes.

Table 1. Bisalkylation of primary amines 2a-d with α-methylstyrene (1)

|	amine	product	yield (isolated) [%]
2a	n-butylamine	4a	76
2b	isopropylamine	4b	79
2c	benzylamine	4c	91
2d	aniline	4d	87

Using the same procedure bisalkylation of the primary amine 2c with two equivalents of styrene (5) proceeds much faster than that with α-methylstyrene and leads to the tertiary amine 7 in good yield (see scheme 2) with high iso-selectivity (iso,iso-/iso,n-/n,n-ratio = 2/1/0). This regioselectivity is in agreement with the hydroformylation and hydroaminomethylation of styrene (5) and is explained by electronic effects. [5-7]

As earlier reported, equivalent amounts of styrene (5) and benzylamine (2c) give the secondary amine 6 with high iso-selectivity as the main product in high yield without formation of detectable amounts of 7. This somewhat unexpected result may be due to the fact that primary amines add to aldehydes much faster than secondary amines. In addition, if hydroformylation, too, is a fast step, compared to the following reductive amination, all olefin, aldehyde and primary amine should be consumed before a significant concentration of the secondary amine is established.
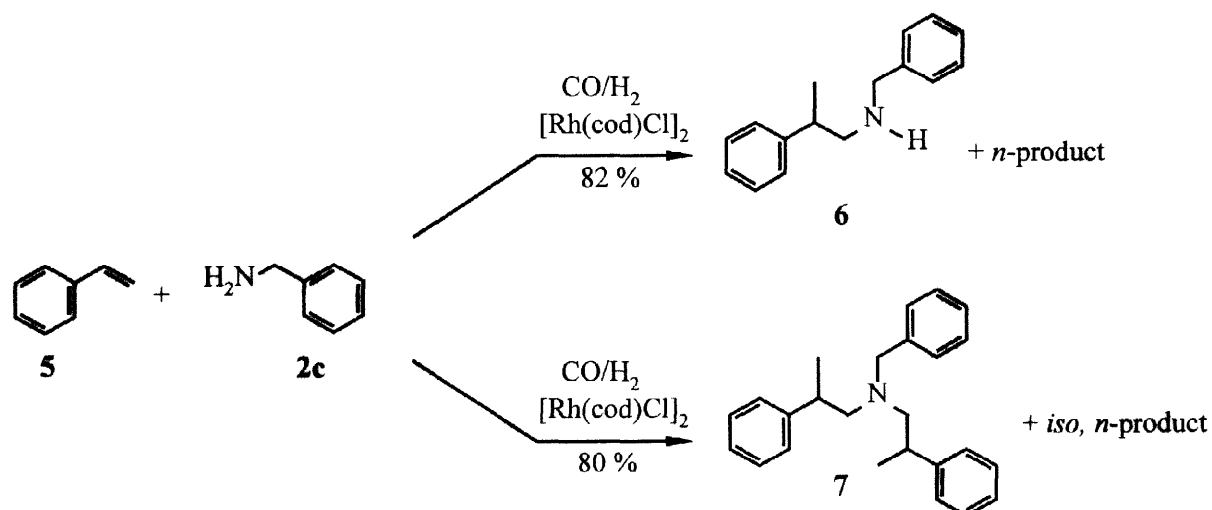
Scheme 2: Carbonylative mono- and bisalkylation of benzylamine (2c) with styrene (5)

In a control experiment conversion of α-methylstyrene (1) in presence of one equivalent of the primary amine 2b and one equivalent of the secondary amine 3b in 89 % yield predominantly leads to the secondary amine 3b. The tertiary amine 4b arising from 1 and 3b is only formed as a minor product with 2 % yield. In a further control experiment conversion of styrene (5) in presence of one equivalent of the primary amine 2b and one equivalent of the sterically hindered secondary amine 8 in 96 % yield exclusively leads to the secondary amine 9 (iso-hydroformylation) and the secondary amine 10 (n-hydroformylation) (iso-/n-ratio = 5/1) (Scheme 3). These experiments show that under the reaction conditions used the imines, arising from the hydroformylated α-methylstyrene (1) or styrene (5) and the primary amine 2b are formed preferentially compared to the enamines from the secondary amines. The secondary amines 3b and 8 therefore appear to be much less reactive towards the intermediate hydroformylation products compared to the primary amine 2b.
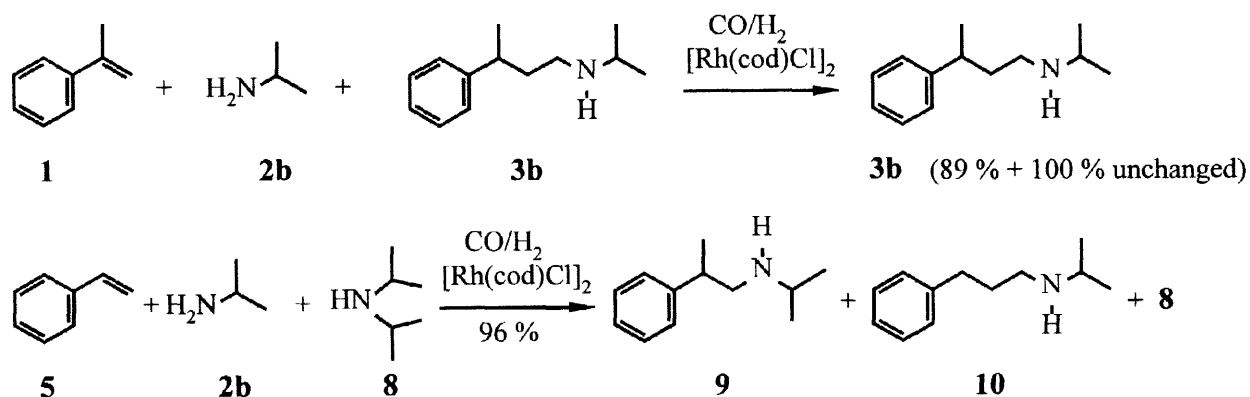

Scheme 3: Competitive carbonylative monoalkylation reaction of the primary amines 2b and the secondary amine 3b or 8

In a third control experiment competitive hydrogenation of enamine **11** and imine **13** is examined under typical hydroformylation conditions (Scheme 4/Diagram 1). Here nearly quantitative hydrogenation of enamine **11** is observed within 35 minutes, whereas for hydrogenation of imine **13** the fourfold reaction time is required.
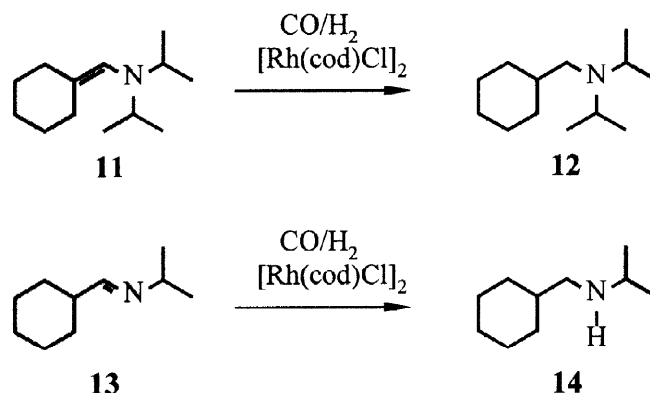
**Scheme 4:** Hydrogenation of enamine **11** and imine **13**
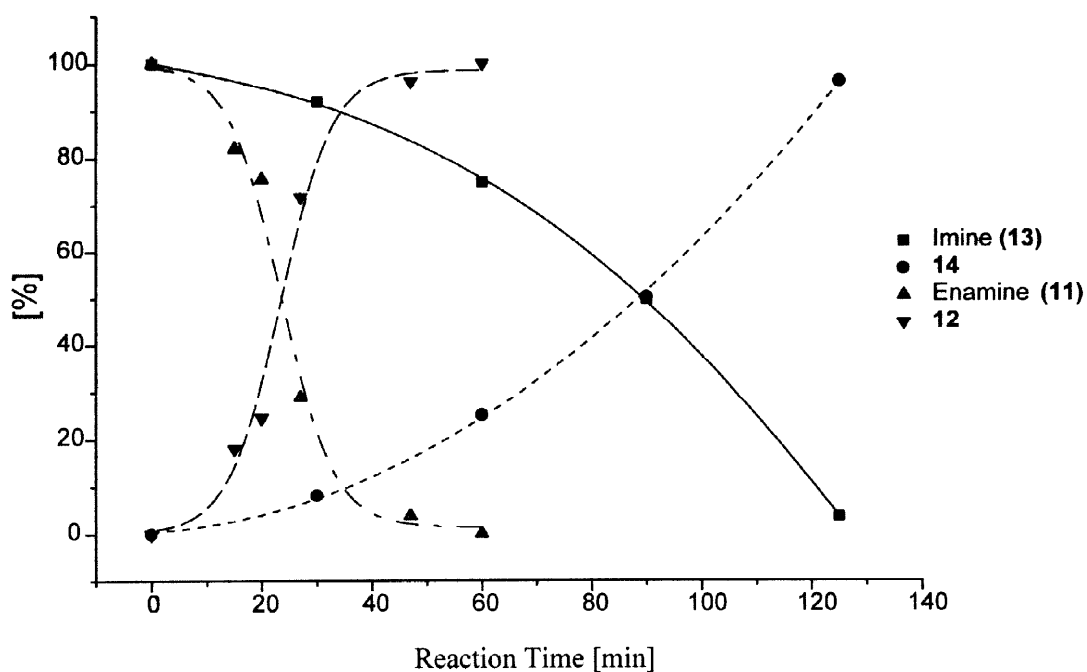
**Diagram 1.** Hydrogenation of enamine **11** and imine **13**

Thus, whereas condensation of the primary amine with the aldehyde is faster than with a secondary amine the hydrogenation of the intermediate imine proceeds much slower than hydrogenation of an enamine, resulting from aldehyde condensation with a secondary amine. These effects, taken together, are responsible for the ease of selective monoalkylation of primary amines to secondary amines without further alkylation to tertiary amines if equivalent amounts of alkene and amine are used. The starting materials are converted in fast reactions

(hydroformylation, condensation), however the rate determining step is the hydrogenation of the imine. Thus significant amounts of product are formed after all starting materials are consumed. Therefore further conversions of the product are prevented.

Selective bisalkylation can also be achieved with high yields if ammonia (16) and alkenes are converted under hydrocarbonylation conditions. The conversion of styrene (5) (Scheme 5) or cyclohexene (15) (Scheme 6) in presence of ammonia (6 bar) give the tertiary amines 17 and 18, respectively. A regioselectivity similar to the bisalkylation of primary amines with styrene (5) is found (*iso,iso-/iso,n*-ratio = 14/1). Similar results are reported by Larson[8] and Striegler et al.[9]
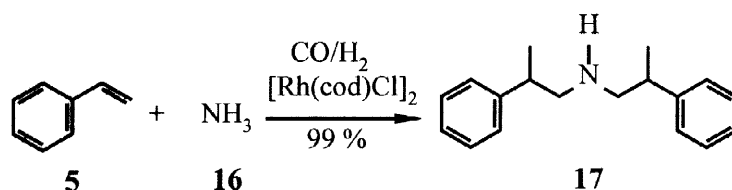
**Scheme 5:** Bisalkylation of ammonia (16) with styrene (5)
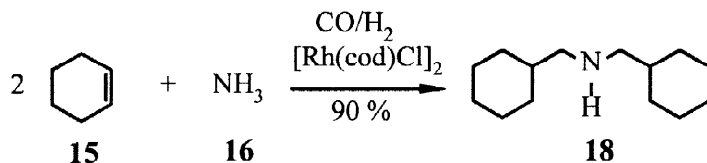
Scheme 6: Bisalkylation of ammonia (16) with cyclohexene (15)

Synthesis of Unsymmetrically Substituted Secondary and Tertiary Amines

In the reactions described above only symmetrical bisalkylation to tertiary amines is achieved. By use of two different olefins which undergo hydroformylation with considerably different reaction rates the formation of unsymmetrically substituted tertiary amines should be possible.

Indeed, the mixed bisalkylation of primary amines 2a,c with styrene (5) and cyclohexene (7) leads to the unsymmetrical tertiary *iso*-amines 19a,b and *n*-amines 20a,b as the major products in 54-56 % yields (Scheme 7, Table 2). Since the hydroformylation of styrene (5) is much faster than the hydroformylation of cyclohexene (15) an *in-situ* generated secondary amine mainly arises from the former, which then reacts with the slow forming hydroformylation product of cyclohexene (15).
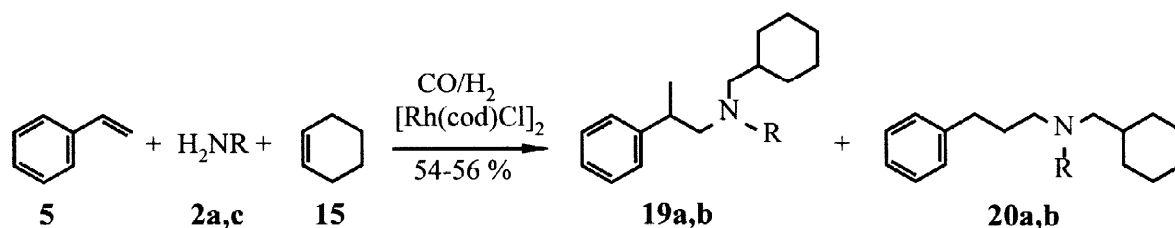

Scheme 7: Mixed bisalkylation of the primary amines 2a,c with styrene (5) and cyclohexene (15)

Table 2. Mixed bisalkylation of primary amines **2a,c**

| amine	product	iso/n ratio	yield [%]
2a n-butylamine	**19a/20a**	(6/1)	56
2c benzylamine	**19b/20b**	(27/1)	54

Mixed bisalkylations of this type are restricted to cases with olefins having clearly different hydroformylation rates. As an alternative synthesis unsymmetrically substituted tertiary amines can be achieved via combined reductive amination with a preformed carbonyl compound followed by a second reductive amination of the resulting amine with a hydroformylation aldehyde formed under the reaction conditions. In a one-pot procedure converting α-methylstyrene (**1**) in presence of various aldehydes **21a-e** and the primary amines **2a-d** under hydroformylation conditions leads to the corresponding unsymmetrical tertiary amines **22a-h** with good yields and selectivities (Scheme 8, Table 3).
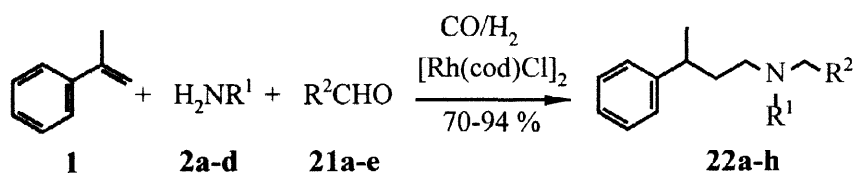
Scheme 8: Combined condensation / hydroaminomethylation of α-methylstyrene (**1**) in the presence of various amines **2a-d** and aldehydes **21a-e**

Table 3. Combined condensation / hydroaminomethylation of α-methylstyrene (**1**) in the presence of various amines **2a-d** and aldehydes **21a-e**

aldehyde **21a-e**	amine	product	yield [%]
isobutyraldehyde (**21a**)	n-butylamine (**2a**)	**22a**	91
isobutyraldehyde (**21a**)	isopropylamine (**2b**)	**22b**	72
isobutyraldehyde (**21a**)	benzylamine (**2c**)	**22c**	81
isobutyraldehyde (**21a**)	aniline (**2d**)	**22d**	74
butyraldehyde (**21b**)	benzylamine (**2c**)	**22e**	83
isovaleraldehyde (**21c**)	benzylamine (**2c**)	**22f**	79
cyclohexylcarbaldehyde (**21d**)	benzylamine (**2c**)	**22g**	70
benzaldehyde (**21e**)	benzylamine (**2c**)	**22h**	94

Similarly the synthesis of unsymmetrically substituted tertiary amines **24a-c** with α-methylstyrene and the ketones **23a-c** instead of aldehydes as the carbonyl components is achieved with high yields and

selectivities. Only in the conversion of α-methylstyrene with **23a** and **2b** products resulting from symmetrical bishydroaminomethylation are obtained as the major by-products (37 %).
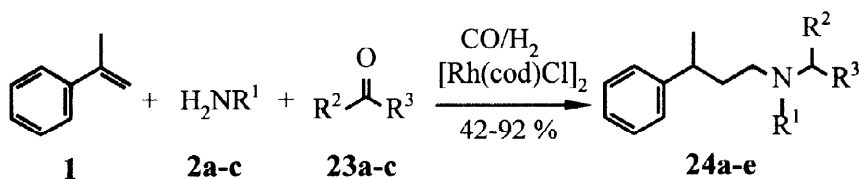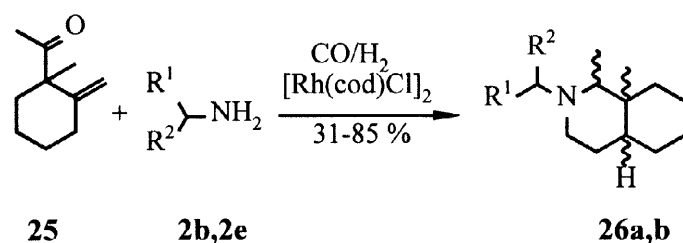

Scheme 9: Combined condensation / hydroaminomethylation of α-methylstyrene (**1**) in presence of various amines **2a-c** and ketones **23a-e**

Table 4. Combined condensation / hydroaminomethylation of α-methylstyrene (**1**) in presence of various amines **2a-c** and ketones **23a-e**

ketone	amine	product	yield [%]
acetone (**23a**)	*n*-butylamine (**2a**)	**24a**	82
acetone (**23a**)	isopropylamine (**2b**)	**24b**	42*
acetone (**23a**)	benzylamine (**2c**)	**24c**	85
cyclohexanone (**23b**)	benzylamine (**2c**)	**24d**	79
benzylmethylketone (**23c**)	benzylamine (**2c**)	**24e**	92

* by-product 37 % symmetrical bishydroaminomethylation to **4b**

This method can also be used for intramolecular cyclisation to yield N-heterocycles, if substrates with carbonyl and olefin functionality, such as the β,γ-unsaturated ketone **25**[10], are employed. In a one-pot procedure converting **25** in presence of the primary amines **2b** and **2e** the corresponding hydroisoquinoline-derivatives **26a-b** can be obtained in moderate to good yields (Scheme 10). The heterocycles are isolated as mixtures of diastereomers.

amine	R¹	R²	product	yield [%]	
2a	CH₃	CH₃	**26a**	31	md (1 : 1)
2b	R-(+)- CH₃	Ph	**26b**	85	md (1 : 1 : 1)

Scheme 10: Combined condensation / hydroaminomethylation of the β,γ-unsaturated ketone **25** in the presence of primary amines

In conclusion we have shown that the rhodium catalysed one-pot multiple alkylation of ammonia and primary amines is an efficient method to generate symmetrically and unsymmetrically substituted secondary and tertiary amines. All primary amines and carbo-functionalised compounds employed in the reaction selectively form tertiary amines in high yields. Further investigations towards an extension of the synthetic potential of this reaction are in current progress.[11]

EXPERIMENTAL

NMR spectra were recorded on Bruker Spectrometers DPX 300 and DRX 400 using TMS as internal standard. IR spectra were obtained with a Shimadzu 470, mass spectra on a Finnigan CA 5 and elementary analysis with a Leco CHNS-932. Column chromatography was carried out with aluminum oxide N (act. I) from ICN Biomedicals, Eschwege, by using MTBE (methyl tert-butyl ether)/PE (petroleum ether, bp 60-90 °C) mixtures as eluent. Gas chromatography was carried out on a Carlo Erba GC-4160 with 25 m or on a Fisons GC-8130 with 30 m CP sil-5 capillaries. GC-MS and GC-IR spectra were obtained by using comparable capillaries and a Finnigan MAT 8320 (MS) and a Bruker IFS 48 (IR). The [Rh(cod)Cl]$_2$ catalyst was prepared according to literature procedures.[12] Pressure reactions have been carried out in autoclaves (type A, 250 ml, PTFE-insert) from Berghof, Eningen, Germany.

General Procedure for Symmetrical Bisalkylation of Primary Amines

A mixture of 14.4 mmol olefin, 7.2 mmol amine and 0.17 mol % [Rh(cod)Cl]$_2$ was heated for 3 d at 135 °C in an autoclave under a pressure of 60 bar hydrogen and 30 bar carbon monoxide (p_{total} = 90 bar). The crude product was dissolved in diethyl ether and filtered through neutral alumina.

Butyl-bis-(3-phenyl-butyl)-amine (4a) (mixture of diastereomeres 1:1). Obtained from 1 and 2a as a yellow oil in 76 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.86 (t, ^3J = 7.0 Hz, 3 H, CH$_3$), 1.21 (d, ^3J = 6.9 Hz, 3 H, CH$_3$), 1.22 (d, ^3J = 7.0 Hz, 3 H, CH$_3$), 1.24 (m, 4 H, 2 x CH$_2$), 1.68 (m, 4 H, 2 x CH$_2$), 2.21-2.43 (m, 6 H, 3 x NCH$_2$), 2.69 (m, 2 H, 2 x CH), 7.15 (m, 6 H, 6 x PhH), 7.29 (m, 4 H, 4 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 14.1 (CH$_3$), 20.7 (CH$_2$), 22.6 (CH$_3$), 29.14 (CH$_2$), 29.16 (CH$_2$), 35.2 (CH$_2$), 37.87 (CH), 37.91 (CH), 52.0 (CH$_2$), 53.75 (CH$_2$), 53.82 (CH$_2$), 125.8 (2 x PhH), 126.9 (4 x PhH), 128.2 (4 x PhH), 147.5 (2 x Cq). IR (NaCl/film) $\tilde{\nu}$ = 3083 w, 3062 w, 3027 w, 2961 s, 2930 m, 2871 w, 1451 w, 1261 s, 1088 s, 1028 s, 801 s, 699 cm^{-1} m. MS (EI, 70eV): m/z (%) = 337 (M$^+$, 27), 294 (33), 218 (100), 176 (13), 142 (13), 119 (23), 105 (20), 100 (65), 91 (21), 58 (25). HR-MS (C$_{24}$H$_{35}$N): Calc. 337.27695. Found 337.2767.

Isopropyl-bis-(3-phenyl-butyl)-amine (4b) (mixture of diastereomers 1:1). Obtained from **1** and **2b** as a yellow oil in 79 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.84 (d, ^{3}J = 6.5 Hz, 6 H, 2 x CH$_3$), 1.201 (d, ^{3}J = 7.0 Hz, 3 H, CH$_3$), 1.202 (d, ^{3}J = 7.0 Hz, 3 H, CH$_3$), 1.64 (m, 4 H, 2 x CH$_2$), 2.22 (m, 4 H, 2 x NCH$_2$), 2.69 (m, 2 H, 2 x CH), 2.88 (m, 1 H, NCH), 7.15 (m, 6 H, 6 x PhH), 7.29 (m, 4 H, 4 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 18.1/18.2 (2 x CH$_3$), 22.7 (CH$_3$), 22.8 (CH$_3$), 37.25 (CH$_2$), 37.28 (CH$_2$), 37.85 (CH), 37.90 (CH), 48.1/48.2 (CH$_2$), 50.29/50.37 (CH), 125.7 (2 x PhH), 126.9 (4 x PhH), 128.2 (4 x PhH), 147.6 (2 x Cq). MS (EI, 70 eV): m/z (%) = 323 (M$^+$, 21), 308 (30), 233 (50), 218 (64), 204 (60), 190 (15), 180 (24), 119 (52), 114 (69), 105 (61), 100 (58), 91 (62), 86 (64), 72 (67), 58 (78), 43 (100). IR (NaCl/film) $\tilde{v}$ = 3082 w, 3061 w, 3026 m, 2961 vs, 2926 s, 2869 s, 1493 s, 1452 s, 1375 m, 1360 m, 1168 m, 761 s, 699 cm^{-1} vs. HR-MS (C$_{23}$H$_{33}$N):Calc. 323.26129. Found 323.2612.

Benzyl-bis-(3-phenyl-butyl)-amine (4c) (mixture of diastereomers 1:1). Obtained from **1** and **2c** as a yellow oil in 91 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 1.14 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.15 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.65 (m, 4 H, 2 x CH$_2$), 2.28 (m, 4 H, 2 x NCH$_2$), 2.67 (m, 2 H, 2 x CH), 3.52 (m, 2 H, NCH$_2$Ph), 6.98-7.41 (m, 15 H). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 22.5 (2 x CH$_3$), 35.3 (2 x CH$_2$), 37.7 (2 x CH), 51.8 (2 x CH$_2$), 58.6 (CH$_2$), 125.8 (2 x PhH), 126.6 (PhH), 126.9 (4 x PhH), 128.0 (2 x PhH), 128.2 (4 x PhH), 128.8 (2 x PhH), 140.0 (Cq), 147.5 (2 x Cq). GC-MS (EI, 70 eV): m/z (%) = 371 (M$^+$, 7), 252 (38), 134 (100), 105 (13), 91 (58). IR (NaCl/film) $\tilde{v}$ = 3083 w, 3061 w, 3026 m, 2957 s, 2925 m, 2868 m, 2800 m, 1493 s, 1453 s, 1372 m, 1073 m, 1028 m, 761 s, 699 cm^{-1} vs. C$_{27}$H$_{33}$N (371.6): Calc. C, 87.3; H, 9.0; N, 3.8. Found C, 87.2; H, 9.0; N, 4.0.

Phenyl-bis-(3-phenyl-butyl)-amine (4d) (mixture of diastereomers 1:1). Obtained from **1** and **2d** as an orange oil in 87 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 1.22 (d, ^{3}J = 6.8 Hz, 6 H, 2 x CH$_3$), 1.79 (t*, ^{3}J = 6.8 Hz, 4 H, 2 x CH$_2$), 2.64 (sextet*, ^{3}J = 6.8 Hz, 2 H, 2 x CH), 3.05 (m, 4 H, 2 x NCH$_2$), 6.44 (m, 2 H, 2 x PhH), 6.58 (m, 1 H, PhH), 7.14 (m, 8 H, 8 x PhH), 7.27 (d, ^{3}J = 6.9 Hz, 4 H, 4 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 22.7 (2 x CH$_3$), 35.02 (CH$_2$), 35.09 (CH$_2$), 37.9 (2 x CH), 49.1 (2 x CH$_2$), 111.7 (2 x PhH), 115.2 (PhH), 126.1 (2 x PhH), 126.8 (4 x PhH), 128.4 (4 x PhH), 129.1 (2 x PhH), 146.7 (2 x Cq), 147.7 (Cq). MS (EI, 70 eV) : m/z (%) = 357 (M$^+$, 8), 225 (78), 120 (17), 106 (100), 93 (23), 77 (9). IR (NaCl/film) $\tilde{v}$ = 3082 w, 3060 w, 3025 w, 2959 s, 2927 m, 2870 m, 1505 vs, 1494 s, 1452 s, 1366 m, 747 s, 700 cm^{-1} vs. HR-MS (C$_{26}$H$_{31}$N): Calc. 357.24564. Found 357.2454.

Benzyl-bis-(2-phenyl-propyl)-amine (7) (mixture of diastereomers 1:1). Obtained from **5** and **2c** as a yellow oil in 80 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 1.23 (d, ^{3}J = 6.8 Hz, CH$_3$), 1.24 (d, ^{3}J = 6.8 Hz, CH$_3$), 2.50 (m, 4 H, 2 x NCH$_2$), 2.86 (m, 2 H, 2 x CH), 3.51 (s, 2 H, NCH$_2$), 7.21 (m, 15 H, 15 x PhH). ^{13}C NMR (100

MHz, CDCl$_3$, 20 °C): δ = **19.8** (CH$_3$), 19.9 (CH$_3$), 38.2 (CH), 38.3 (CH), 59.1 (NCH$_2$Ph), 62.5 (NCH$_2$), **62.9** (NCH$_2$), 125.9 (2 x PhH), 126.6 (PhH), 127.3 (4 x PhH), 128.2 (4 x PhH), 128.3 (2 x PhH), **128.8** (2 x PhH), 140.0 (Cq), 146.2 (2 x Cq). GC-MS (EI, 70 eV): m/z (%) = 344 (M$^+$+1, 12), 238 (100), 120 (10), 105 (24), 91 (60), 79 (7), 65 (7). IR (NaCl/film) $\tilde{v}$ = 3084 m, 3060 s, 3026 vs, 2958 vs, 2930 vs, 2869 m, 2797 s, 1601 m, 1494 vs, 1452 vs, 1370 m, 1028 s, 1014 s, 760s, 739 vs, 697 cm^{-1} vs.

Isopropyl-(2-phenyl-propyl)-amine (9). Obtained from **5, 2b** and **8** as a colourless oil in 96 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.96 (d, ^3J = 6.3 Hz, 3 H, CH$_3$), 0.99 (d, ^3J = 6.3 Hz, 3 H, CH$_3$), 1.24 (d, ^3J = 6.8 Hz, 3 H, CH$_3$), 2.60 (m, 1 H, CH), 2.74 (m, 2 H, NCH$_2$), 2.88 (sextet*, ^3J = 6.8 Hz, 1 H, CH), 7.16-7.30 (m, 5 H, 5 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 20.1 (CH$_3$), 22.5 (CH$_3$), 22.7 (CH$_3$), 39.8 (CH), 48.2 (NCH), 54.4 (NCH$_2$), 126.1 (PhH), 126.9 (2 x PhH), 128.3 (2 x PhH), 145.1 (Cq). GC-MS (EI, 70 eV): m/z (%) = 178 (M$^+$+1, 100), 105 (9), 91 (4), 72 (42). IR (NaCl/film) $\tilde{v}$ = 3323 w, 3084 w, 3062 w, 3027 m, 2963 s, 2929 s, 2871 m, 1494 m, 1453 m, 1379 m, 761 m, 700 cm^{-1} s.

Cyclohexylidenemethyl-diisopropylamine (11)[13,14]. The enamine **11** was prepared according to general literature procedures[15] in 74 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.94 (d, ^3J = 6.5 Hz, 12 H, 4 x CH$_3$), 1.47 (m, 6 H, 3 x CH$_2$), 2.06 (t, ^3J = 6.0 Hz, 2 H, CH$_2$), 2.26 (t, ^3J = 6.2 Hz, 2 H, CH$_2$), 2.95 (septet, ^3J = 6.5 Hz, 2 H, 2 x NCH), 5.19 (s, 1 H, CH=CR$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 20.3 (4 x CH$_3$), 27.1 (2 x CH$_2$), 28.65 (CH$_2$), 28.72 (CH$_2$), 33.8 (CH$_2$), 49.6 (2 x NCH), 124.9 (CH=CR$_2$), 138.9 (Cq). GC-MS (EI, 70 eV): m/z (%) = 195 (M$^+$, 72), 180 (79), 152 (43), 138 (46), 110 (18), 95 (24), 84 (18), 67 (26), 58 (100). IR (NaCl/film) $\tilde{v}$ = 2967 vs, 2927 vs, 2870 s, 2854 s, 2836 s, 1666 w, 1448 m, 1380 m, 1360 m, 1232 m, 1217 m, 1103 m, 1052 cm^{-1} m.

Cyclohexylmethyl-diisopropyl-amine (12)[16–18]. A mixture of 4.8 mmol **12** and 1 mol % [Rh(cod)Cl]$_2$ in 10 mL anhydrous dioxane was heated for a defined time (compare Diagram 1) at 110 °C in an autoclave under 90 bar carbon monoxide and 20 bar hydrogen (p$_{total}$ = 110 bar) atmosphere. The solvent was removed by rotary evaporation and the residue dissolved in diethyl ether and filtered through neutral alumina. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.96 (d, ^3J = 6.7 Hz, 12 H, 4 x CH$_3$), 1.23 (m, 6 H, 3 x CH$_2$), 1.73 (m, 5 H, 2 x CH$_2$, CH), 2.18 (d, ^3J = 7.0 Hz, 2 H, NCH$_2$), 2.95 (septet, ^3J = 6.6 Hz, 2 H, 2 x NCH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 20.7 (4 x CH$_3$), 26.5 (2 x CH$_2$), 27.1 (CH$_2$), 31.9 (2 x CH$_2$), 37.3 (CH), 49.4 (2 x NCH), 51.7 (NCH$_2$). GC-MS (EI, 70 eV): m/z (%) = 198 (M$^+$+1, 43), 114 (100), 72 (12). IR (NaCl/film) $\tilde{v}$ =2963 s, 2922 s, 2851 s, 2799 m, 1460 m, 1449 m, 1385 cm^{-1}m.

Cyclohexylmethylene-isopropyl-amine (13). 8.97 g (0.08 mol) cyclohexylcarbaldehyde and 9.46 (0.16 mol) isopropylamine were stirred 2h at 20 °C over $MgSO_4$. After removal of $MgSO_4$ by filtration 10.62 g (0.07 mol, 86 %) enamine 13 were obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.14 (d, ^3J = 6.5 Hz, 6 H, 2 x CH_3), 1.26 (m, 6 H, 3 x CH_2), 1.76 (m, 4 H, 2 x CH_2), 2.14 (m, 1 H, CH), 3.21 (septet, ^3J = 6.5 Hz, 1 H, NCH), 7.47 (d, ^3J = 5.5 Hz, 1 H, CH=N). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 24.0 (2 x CH_3), 25.2 (2 x CH_2), 25.8 (CH_2), 29.7 (2 x CH_2), 43.2 (CH), 61.0 (NCH), 166.0 (CH=N). GC-MS (EI, 70 eV): m/z (%) = 154 (M^++1, 100), 138 (42), 124 (8), 110 (7), 98 (75), 95 (13), 85 (80), 70 (58), 67 (29), 56 (63). IR (NaCl/film) $\tilde{v}$ = 2967 s, 2927 vs, 2852 s, 2814 m, 1665 s, 1450 m, 1379 cm^{-1} m.

Cyclohexylmethyl-isopropyl-amine (14). A mixture of 4.8 mmol 14 and 1 mol % [Rh(cod)Cl]$_2$ in 10 mL anhydrous dioxane was heated for a defined time (compare Diagram 1) at 110 °C in an autoclave under 90 bar carbon monoxide and 20 bar hydrogen (p_{total} = 110 bar) atmosphere. The solvent was removed by rotary evaporation and the residue dissolved in diethyl ether and filtered through neutral alumina. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.90 (m, 2 H, CH_2), 1.04 (d, ^3J = 6.2 Hz, 6 H, 2 x CH_3), 1.19 (m, 4 H, 2 x CH_2), 1.43 (m, 1 H, CH), 1.70 (m, 4 H, 2 x CH_2), 2.41 (d, ^3J = 6.7 Hz, 2 H, NCH_2), 2.74 (septet, ^3J = 6.2 Hz, 1 H, NCH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 23.0 (2 x CH_3), 26.0 (2 x CH_2), 26.6 (CH_2), 31.5 (2 x CH_2), 38.1 (CH), 48.6 (CH), 54.3 (CH_2). GC-MS (EI, 70 eV): m/z (%) = 156 (M^++1, 100), 72 (19), 58 (4). IR (NaCl/film) $\tilde{v}$ = 3478 vw, 2966 s, 2923 vs, 2852 s, 1470 m, 1448 cm^{-1}m.

General Procedure for Symmetrical Bisalkylation of Ammonia

A mixture of 4.8 mmol olefin and 1 mol % [Rh(cod)Cl]$_2$ in 10 mL anhydrous dioxane was heated for 24 h (cyclohexene: t = 4 d), at 115 °C in an autoclave under a pressure of 90 bar carbon monoxide, 20 bar hydrogen and 6 bar ammonia (p_{total} = 116 bar). The solvent was removed by rotary evaporation and the residue dissolved in diethyl ether and filtered through neutral alumina.

Bis(2-phenyl-propyl)-amine (17)[19]. Obtained from 5 and ammonia as a colourless oil in 99 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.16 (d, ^3J = 6.8 Hz, 3H, CH_3), 1.17 (d, ^3J = 6.8 Hz, 3 H, CH_3), 2.65-2.88 (m, 6 H, 2 x CH_2, 2 x CH), 7.07-7.29 (m, 10 H, 10 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 19.6 (CH_3), 19.7 (CH_3), 39.5 (CH), 39.6 (CH), 56.6 (NCH_2), 56.8 (NCH_2), 126.00 (PhH), 126.02 (PhH), 126.8 (2 x PhH), 126.9 (2 x PhH), 128.2 (4 x PhH), 145.0 (Cq), 145.1 (Cq). GC-MS (EI, 70 eV): m/z (%) = 253 (M^+, 100), 148 (24), 119 (22), 105 (21), 91 (26), 77 (7), 51 (6). IR (NaCl/film) $\tilde{v}$ = 3433 w, 3083 w, 3061 w, 3027 m, 2959 s, 2926 s, 2873 m, 2810 m, 1494 s, 1452 s, 1376 w, 1131 m, 761 s, 699 cm^{-1} vs.

Bis-cyclohexylmethyl-amine (18). Obtained from **15** and ammonia as a colourless oil in 90 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.89 (m, 4 H, 2 x CH$_2$), 1.16 (m, 8 H, 4 x CH$_2$), 1.45 (m, 2 H, 2 x CH), 1.69 (m, 8 H, 4 x CH$_2$), 2.41 (d, ^{3}J = 6.5 Hz, 4 H, 2 x NCH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 26.0 (4 x CH$_2$), 26.6 (2 x CH$_2$), 31.4 (4 x CH$_2$), 37.8 (2 x CH), 56.9 (2 x CH$_2$). GC-MS (EI, 70 eV): m/z (%) = 209 (M$^+$, 100), 126 (24), 67 (3), 55 (31). IR (NaCl/film) $\tilde{\nu}$ = 2920 s, 2851 s, 2802 m, 1448 s, 1129 cm^{-1} m. C$_{14}$H$_{27}$N (209.4): Calc. C, 80.3; H, 13.0; N, 6.7. Found C, 79.8; H, 13.1; N, 6.8.

General Procedure for Unsymmetrical Bisalkylation of Primary Amines

A mixture of 7.2 mmol cyclohexene, 7.2 mmol olefin, 7.2 mmol amine and 0.17 mol % [Rh(cod)Cl]$_2$ was heated for 4 d, at 135 °C in an autoclave under a pressure of 60 bar hydrogen and 30 bar carbon monoxide (p$_{total}$ = 90 bar). The crude product was dissolved in diethyl ether and filtered through neutral alumina.

Butyl-cyclohexylmethyl-(2-phenyl-propyl)-amine (19a). Obtained from **5**, **15** and **2a** as a colourless oil in 56 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.79 (m, 2 H, CH$_2$), 0.88 (t, ^{3}J = 6.6 Hz, 3 H, CH$_3$), 1.21 (m, 7 H, 3 x CH$_2$, CH), 1.25 (d, ^{3}J = 7.1 Hz, 3 H, CH$_3$), 1.69 (m, 6 H, 3 x CH$_2$), 2.09 (m, 2 H, NCH$_2$), 2.39 (m, 4 H, 2 x NCH$_2$), 2.82 (m, 1 H, CH), 7.17 (m, 3 H, 3 x PhH), 7.26 (m, 2 H, 2 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 14.2 (CH$_3$), 19.7 (CH$_3$), 20.6 (CH$_2$), 26.25 (CH$_2$), 26.28 (CH$_2$), 27.0 (CH$_2$), 29.5 (CH$_2$), 31.85 (CH$_2$), 31.90 (CH$_2$), 36.3 (CH), 38.6 (CH), 54.9 (NCH$_2$), 62.4 (NCH$_2$), 63.6 (NCH$_2$), 125.8 (PhH), 127.3 (2 x PhH), 128.1 (2 x PhH), 146.7 (Cq). GC-MS (EI, 70 eV): m/z (%) = 288 (M$^+$, 21), 182 (100), 140 (7), 100 (56), 58 (44). IR (NaCl/film) $\tilde{\nu}$ = 3084 vw, 3062 w, 3027 w, 2955 s, 2924 vs, 2851 s, 2795 m, 1451 m, 698 cm^{-1} s. C$_{20}$H$_{33}$N (287.5): Calc. C, 83.6; H, 11.6; N, 4.9. Found C, 83.5; H, 11.4; N, 4.9.

Benzyl-cyclohexylmethyl-(2-phenyl-propyl)-amine (19b). Obtained from **5**, **15** and **2c** as a yellow oil in 54 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 1.12 (m, 4 H, 2 x CH$_2$), 1.23 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.36-1.85 (m, 7 H, 3 x CH$_2$, CH), 2.14 (m, 2 H, NCH$_2$), 2.48 (m, 2 H, NCH$_2$), 2.89 (sextet*, ^{3}J = 6.9 Hz, 1 H, CH), 3.53 (m, 2 H, NCH$_2$Ph), 7.03-7.37 (m, 10 H, 10 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 19.8 (CH$_3$), 26.2 (2 x CH$_2$), 26.9 (CH$_2$), 31.6 (CH$_2$), 31.8 (CH$_2$), 35.9 (CH), 38.3 (CH), 59.8 (NCH$_2$), 61.8 (NCH$_2$), 62.9 (NCH$_2$), 125.9 (PhH), 126.5 (PhH), 127.3 (2 x PhH), 127.9 (2 x PhH), 128.1 (2 x PhH), 128.8 (2 x PhH), 140.3 (Cq), 146.4 (Cq). GC-MS (EI, 70 eV): m/z (%) = 320 (M$^+$-1, 11), 216 (100), 134 (39), 105 (7), 91 (18), 55 (7). IR (NaCl/film) $\tilde{\nu}$ = 3084 m, 3061 m, 3026 s, 2924 vs, 2850 vs, 2792 s, 1494 s, 1451 vs, 1382 m, 1370 m, 737 s, 698 cm^{-1} vs. C$_{23}$H$_{31}$N (321.5): Calc. C, 85.9; H, 9.7; N, 4.4. Found C, 86.3; H, 9.5; N, 4.3.

General Procedure for the Synthesis of Unsymmetrically Substituted Tertiary Amines in presence of Aldehydes or Ketones

A mixture of 14.4 mmol olefin, 14.4 mmol amine, 14.4 mmol aldehyde or ketone and 0.17 mol % [Rh(cod)Cl]$_2$ was heated for 3 d, at 135 °C in an autoclave under a pressure of 60 bar hydrogen and 30 bar carbon monoxide (p_{total} = 90 bar). The crude product was dissolved in diethyl ether and filtered through neutral alumina.

Butyl-isobutyl-(3-phenyl-butyl)-amine (22a). Obtained from 1, 21a and 2a as a colourless oil in 91 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.845 (d, ^{3}J = 6.5 Hz, 3 H, CH$_3$), 0.854 (d, ^{3}J = 6.5 Hz, 3 H, CH$_3$), 0.87 (m, 3 H, CH$_3$), 1.20 (m, 3 H, CH$_2$, CH), 1.22 (d, ^{3}J = 7.0 Hz, 3 H, CH$_3$), 1.67 (m, 4 H, 2 x CH$_2$), 2.05 (m, 2 H, NCH$_2$), 2.33 (m, 4 H, 2 x NCH$_2$), 2.76 (sextet*, ^{3}J = 7.0 Hz, 1H, CH), 7.01-7.27 (m, 5 H, 5 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 14.1 (CH$_3$), 20.7 (CH$_2$), 21.0 (2 x CH$_3$), 22.6 (CH$_3$), 26.6 (CH), 29.4 (CH$_2$), 35.5 (CH$_2$), 37.8 (CH), 52.8 (CH$_2$), 54.4 (CH$_2$), 63.1 (CH$_2$), 125.7 (PhH), 127.0 (2 x PhH), 128.2 (2 x PhH), 147.8 (Cq). GC-MS (EI, 70 eV): m/z (%) = 262 (M$^+$, 8), 218 (29), 142 (6), 100 (100), 58 (50). IR (NaCl/film) $\tilde{v}$ = 3083 w, 3062 w, 3027 m, 2955 s, 2928 s, 2869 s, 2798 m, 1493 m, 1466 m, 1453 s, 1376 w, 1364 w, 1084 m, 761 m, 699 cm^{-1}s.

Isobutyl-isopropyl-(3-phenyl-butyl)-amine (22b). Obtained from 1, 21a and 2b as a colourless oil in 72 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.78 (m, 12 H, 4 x CH$_3$), 1.13 (d, 3 H, ^{3}J = 6.0 Hz, 3 H, CH$_3$), 1.55 (m, 3 H, CH$_2$, CH), 1.94 (d, ^{3}J= 6.3 Hz, 2 H, NCH$_2$), 2.20 (m, 2 H, NCH$_2$), 2.70 (m, 2 H, CH, NCH), 7.09 (m, 3 H, 3 x PhH), 7.18 (m, 2 H, 3 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 17.80 (CH$_3$), 17.84 (CH$_3$), 20.83 (CH$_3$), 20.87 (CH$_3$), 22.6 (CH$_3$), 27.2 (CH), 37.4 (CH$_2$), 37.6 (CH), 48.5 (CH$_2$), 49.9 (CH), 58.3 (CH$_2$), 125.7 (PhH), 127.0 (2 x PhH), 128.2 (2 x PhH), 148.0 (Cq). GC-MS (EI, 70 eV): m/z (%) = 247 (M$^+$, 24), 203 (37), 128 (10), 114 (6), 105 (9), 86 (100), 56 (6). IR (NaCl/film) $\tilde{v}$ = 3083 w, 3062 w, 3027 w, 2961 vs, 2928 s, 2868 m, 1460 m, 1453 m, 1381 m, 761 m, 700 cm^{-1} s. C$_{17}$H$_{29}$N (247.4): Calc. C, 82.5; H, 11.8; N, 5.7. Found C, 81.1; H, 11.6; N, 5.9.

Benzyl-isobutyl-(3-phenyl-butyl)-amine (22c). Obtained from 1, 21a and 2c as a yellow oil in 81 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.86 (d, ^{3}J = 5.0 Hz, 6 H, 2 x CH$_3$), 1.15 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.69 (m, 2 H, CH$_2$), 1.77 (m, 1 H, CH), 2.09 (d, ^{3}J = 6.2 Hz, 2 H, NCH$_2$), 2.28 (m, 2 H, NCH$_2$), 2.71 (sextet*, ^{3}J = 6.9 Hz, 1 H, CH), 3.46 (s, 2 H, NCH$_2$Ph), 7.13 (m, 3 H, 3 x PhH), 7.27 (m, 7 H, 7 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 20.89 (CH$_3$), 20.91 (CH$_3$), 22.3 (CH$_3$), 26.4 (CH), 35.5 (CH$_2$), 37.6 (CH), 52.3 (CH$_2$), 59.2 (CH$_2$), 62.8 (CH$_2$), 125.7 (PhH), 126.5 (PhH), 126.9 (2 x PhH), 128.0 (2 x PhH), 128.2 (2 x PhH), 128.8 (2 x PhH), 140.4 (Cq), 147.8 (Cq). GC-MS (EI, 70 eV): m/z (%) = 294 (M$^+$, 22), 252 (15), 176 (17), 134

(22), 105 (13), 91 (20), 79 (6), 58 (100). IR (NaCl/film) $\tilde{v}$ = 3084 w, 3062 w, 3027 m, 2955 vs, 2927 s, 2868 m, 2796 m, 1494 m, 1452 m, 1367 w, 699 cm^{-1} vs. $C_{21}H_{29}N$ (295.5): Calc. C, 85.4; H, 9.9; N, 4.7. **Found C, 85.4; H, 9.8; N, 5.0.**

Isobutyl-phenyl-(3-phenyl-butyl)-amine (22d). Obtained from 1, 21a and 2d as an orange oil in 74 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.85 (d, ^{3}J = 6.6 Hz, 3 H, CH$_3$), 0.85 (d, ^{3}J = 6.6 Hz, 3 H, CH$_3$), 1.26 (d, ^{3}J = 7.0 Hz, 3 H, CH$_3$), 1.84 (q*, ^{3}J = 7.6 Hz, 2 H, CH$_2$), 1.94 (sextet*, ^{3}J = 6.8 Hz, 1 H, CH), 2.67 (sextet*, ^{3}J = 7.0 Hz, 1 H, CH), 2.94 (m, 2 H, NCH$_2$), 3.13 (m, 2 H, NCH$_2$), 6.46-6.64 (m, 3 H, 3 x PhH), 7.09-7.31 (m, 7 H, 7 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 20.30 (CH$_3$), 20.33 (CH$_3$), 22.5 (CH$_3$), 27.0 (CH), 34.2 (CH$_2$), 38.0 (CH), 50.0 (NCH$_2$), 58.9 (NCH$_2$), 112.0 (2 x PhH), 115.2 (PhH), 126.1 (PhH), 126.9 (2 x PhH), 128.4 (2 x PhH), 129.0 (2 x PhH), 146.7 (Cq), 148.2 (Cq). GC-MS (EI, 70 eV): m/z (%) = 281 (M', 23), 238 (11), 162 (7), 120 (100), 106 (11), 91 (3), 51 (3). IR (NaCl/film) $\tilde{v}$ = 3083 w, 3061 w, 3026 w, 2959 s, 2928 m, 2868 m, 1599 s, 1505 s, 1496 m, 1452 m, 1365 m, 746 s, 700 cm^{-1} s. $C_{20}H_{27}N$ (288.4): Calc. C, 85.3; H, 9.7; N, 5.0. Found C, 85.1; H, 9.6; N, 5.3.

Benzyl-butyl-(3-phenyl-butyl)-amine (22e). Obtained from 1, 21b and 2c as a colourless oil in 83 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.84 (t, ^{3}J = 7.1 Hz, 3 H, CH$_3$), 1.18 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.26 (m, 2 H, CH$_2$), 1.36 (m, 2 H, CH$_2$), 1.71 (m, 2 H, CH$_2$), 2.34 (m, 4 H, 2 x NCH$_2$), 2.72 (sextet*, ^{3}J = 6.9 Hz, 1 H, CH), 3.49 (s, 2 H, NCH$_2$Ph), 7.03-7.28 (m, 10 H, 10 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 14.1 (CH$_3$), 20.6 (CH$_2$), 22.4 (CH$_3$), 29.2 (CH$_2$), 35.4 (CH$_2$), 37.7 (CH), 51.8 (CH$_2$), 53.5 (CH$_2$), 58.5 (CH$_2$), 125.7 (PhH), 126.5 (PhH), 126.9 (2 x PhH), 128.0 (2 x PhH), 128.2 (2 x PhH), 128.8 (2 x PhH), 140.1 (Cq), 147.6 (Cq). GC-MS (EI, 70 eV): m/z (%) = 296 (M$^+$+1, 23), 282 (10), 252 (29), 218 (29), 176 (86), 134 (100), 105 (13), 91 (96), 65 (12). IR (NaCl/film) $\tilde{v}$ = 3084 w, 3061 m, 3027 s, 2959 vs, 2928 vs, 2871 s, 2799 m, 1494 s, 1452 s, 1375 m, 1028 m, 761 s, 734 s, 699 cm^{-1} vs. $C_{21}H_{29}N$ (295.4): Calc. C, 85.4; H, 9.9; N, 4.7. Found C, 85.4; H, 9.7; N, 4.8.

Benzyl-(3-methyl-butyl)-(3-phenyl-butyl)-amine (22f). Obtained from 1, 21c and 2c as a colourless oil in 79 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.82 (d, ^{3}J = 6.0 Hz, 6 H, 2 x CH$_3$), 1.19 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.28 (m, 2 H, CH$_2$), 1.55 (m, 1 H, CH), 1.72 (m, 2 H, CH$_2$), 2.32 (m, 4 H, 2 x NCH$_2$), 2.75 (m, 1 H, CH), 3.48 (m, 2 H, NCH$_2$PhH), 7.03-7.27 (m, 10 H, 10 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 22.4 (CH$_3$), 22.7 (CH$_3$), 22.9 (CH$_3$), 26.1 (CH), 35.4 (CH$_2$), 35.9 (CH$_2$), 37.6 (CH), 51.7 (CH$_2$), 51.8 (CH$_2$), 58.5 (CH$_2$), 125.7 (PhH), 126.5 (PhH), 126.9 (2 x PhH), 128.0 (2 x PhH), 128.2 (2 x PhH), 128.8 (2 x PhH), 140.0 (Cq), 147.5 (Cq). GC-MS (EI, 70 eV): m/z (%) = 309 (M$^+$, 26), 282 (5), 252 (32), 232 (14), 190 (28), 135 (100), 105 (11), 91 (12), 59 (7). IR (NaCl/film) $\tilde{v}$ = 3084 w, 3061 w, 3027 w, 2956 s, 2926 m, 2868 m, 2800 w, 1493 m,

1452 m, 1366 w, 762 m, 734 m, 699 cm^{-1} s. $C_{22}H_{31}N$ (309.5): Calc. C, 85.4; H, 10.1; N, 4.5. **Found** C, 85.7; H, 9.8; N, 4.4.

Benzyl-cyclohexylmethyl-(3-phenyl-butyl)-amine (22g). Obtained from **1, 21c** and **2c** as a colourless oil in 70 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.76 (m, 2 H, CH$_2$), 1.14 (d, ^{3}J = 7.0 Hz, 3 H, CH$_3$), 1.31 (m, 4 H, 2 x CH$_2$), 1.64-1.82 (m, 7 H, 3 x CH$_2$, CH), 2.11 (d, ^{3}J = 7.0 Hz, 2 H, NCH$_2$), 2.31 (m, 2 H, NCH$_2$), 2.73 (sextet*, ^{3}J = 7.1 Hz, 1 H, CH), 3.45 (s, 2 H, NCH$_2$Ph), 7.01-7.43 (m, 10 H, 10 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 22.4 (CH$_3$), 26.1 (2 x CH$_2$), 26.8 (CH$_2$), 31.8 (2 x CH$_2$), 35.5 (CH$_2$), 35.9 (CH), 37.5 (CH), 52.2 (CH$_2$), 59.3 (CH$_2$), 61.3 (CH$_2$), 125.7 (PhH), 126.5 (PhH), 126.9 (2 x PhH), 127.9 (2 x PhH), 128.2 (2 x PhH), 128.7 (2 x PhH), 140.3 (Cq), 147.6 (Cq). MS : m/z (%) = 335 (M$^+$, 31), 252 (91), 216 (84), 134 (90), 119 (89), 105 (49), 91 (100), 77 (28), 65 (22), 55 (54), 41 (60). IR (NaCl/film) $\tilde{\nu}$ = 3084 w, 3062 w, 3027 m, 2923 s, 2851 m, 2794 m, 1494 m, 1451 m, 1377 w, 736 m, 699 cm^{-1} s. HR-MS ($C_{24}H_{33}N$): Calc. 335.26129. Found 335.2614.

Dibenzyl-(3-phenyl-butyl)-amine (22h). Obtained from **1, 21d** and **2c** as a colourless oil in 94 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 1.51 (d, ^{3}J = 7.0 Hz, 3 H, CH$_3$), 2.16 (m, 2 H, CH$_2$), 2.76 (m, 2 H, NCH$_2$), 3.12 (q*, ^{3}J = 7.0 Hz, 1 H, CH), 3.89 (s, 4 H, 2 x NCH$_2$Ph), 7.43-7.80 (m, 15 H, 15 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 22.2 (CH$_3$), 35.5 (CH$_2$), 37.4 (CH), 51.4 (CH$_2$), 58.2 (2 x CH$_2$), 125.7 (PhH), 126.7 (2 x PhH), 126.8 (2 x PhH), 128.1 (4 x PhH), 128.2 (2 x PhH), 128.7 (4 x PhH), 139.7 (2 x Cq), 147.5 (Cq). GC-MS (EI, 70 eV): m/z (%) = 330 (M$^+$+1, 29), 252 (15), 238 (12), 210 (84), 135 (12), 105 (10), 91 (75), 65 (18). IR (NaCl/film) $\tilde{\nu}$ = 3085 w, 3063 m, 3027 s, 2958 s, 2927 s, 2872 m, 2796 s, 1494 s, 1454 s, 1368 m, 745 s, 699 cm^{-1} vs. $C_{24}H_{27}N$ (329.5): Calc. C, 87.5; H, 8.3; N, 4.3. Found C, 87.6; H, 8.2; N, 4.5.

Butyl-isopropyl-(3-phenyl-butyl)-amine (24a). Obtained from **1, 23a** and **2a** as a colourless oil in 82 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.91 (d, ^{3}J = 6.7 Hz, 6 H, 2 x CH$_3$), 1.25 (d, ^{3}J = 7.0 Hz, 3 H, CH$_3$), 1.33 (m, 7 H, 2 x CH$_2$, CH$_3$), 1.71 (m, 2 H, CH$_2$), 2.27 (m, 4 H, 2 x NCH$_2$), 2.73 (septet, ^{3}J = 7.0 Hz, 1 H, NCH), 2.88 (sextet*, ^{3}J = 6.8 Hz, 1 H, CH), 7.15-7.33 (m, 5 H, 5 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 14.1 (CH$_3$), 18.1 (CH$_3$), 18.2 (CH$_3$), 20.6 (CH$_2$), 22.7 (CH$_3$), 31.2 (CH$_2$), 37.2 (CH$_2$), 37.9 (CH), 48.2 (CH$_2$), 49.7 (CH$_2$), 50.2 (CH), 125.7 (PhH), 126.9 (2 x PhH), 128.2 (2 x PhH), 147.6 (Cq). GC-MS (EI, 70 eV): m/z (%) = 248 (M$^+$+1, 35), 232 (6), 204 (18), 128 (56), 105 (13), 86 (100), 72 (13), 56 (10). IR (NaCl/film) $\tilde{\nu}$ = 3083 w, 3062 w, 3027 m, 2959 vs, 2929 s, 2870 s, 2806 m, 1494 m, 1453 s, 1377 m, 1360 m, 761 s, 699 cm^{-1} vs.

Diisopropyl-(3-phenyl-butyl)-amine (24b). Obtained from **1**, **23a** and **2b** as a colourless oil in **42 %** yield. ¹H NMR (400 MHz, CDCl₃, 20 °C): δ = 0.93 (d, ³J = 6.6 Hz, 12 H, 4 x CH₃), 1.23 (d, ³J = 7.0 Hz, 3 H, CH₃), 1.72 (m, 2 H, CH₂), 2.29 (m, 2 H, CH₂), 2.70 (sextet*, ³J = 7.1 Hz, 1 H, CH), 2.95 (septet, ³J = 6.6 Hz, 2 H, 2 x CH), 7.18 (m, 3 H, 3 x PhH), 7.30 (m, 2 H, 2 x PhH). ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ = 20.57 (2 x CH₃), 20.58 (2 x CH₃), 22.8 (CH₃), 38.1 (CH), 39.9 (CH₂), 43.7 (NCH₂), 48.6 (2 x NCH), 125.7 (PhH), 126.9 (2 x PhH), 128.2 (2 x PhH), 147.8 (Cq). GC-MS (EI, 70 eV): m/z (%) = 234 (M⁺, 27), 218 (25), 114 (100), 105 (15), 100 (36), 72 (16), 58 (22). IR (NaCl/film) ṽ = 3083 w, 3061 w, 3027 m, 2962 vs, 2927 s, 2869 m, 1493 m, 1452 s, 1377 m, 1360 m, 761 s, 699 cm⁻¹ vs.

Benzyl-isopropyl-(3-phenyl-butyl)-amine (24c). Obtained from **1**, **23a** and **2c** as a yellow oil in **85 %** yield. ¹H NMR (400 MHz, CDCl₃, 20 °C): δ = 0.93 (d, ³J = 6.3 Hz, 6 H, 2 x CH₃), 1.13 (d, ³J = 6.9 Hz, 3 H, CH₃), 1.68 (m, 2 H, CH₂), 2.32 (m, 2 H, NCH₂), 2.74 (m, 1 H, CH), 2.89 (m, 1 H, CH), 3.49 (s, 2 H, NCH₂Ph), 7.02-7.14 (m, 3 H, 3 x PhH), 7.18-7.36 (m, 7 H, 7 x PhH). ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ =17.9 (2 x CH₃), 22.5 (CH₃), 37.0 (CH₂), 37.5 (CH₂), 47.5 (CH₂), 49.6 (CH), 54.0 (CH₂), 125.7 (PhH), 126.4 (PhH), 126.9 (2 x PhH), 128.0 (2 x PhH), 128.2 (2 x PhH), 128.4 (2 x PhH), 141.5 (Cq), 147.8 (Cq). GC-MS (EI, 70 eV): m/z (%) = 282 (M⁺+1, 63), 266 (21), 204 (25), 162 (100), 148 (8), 105 (8), 91 (9). IR (NaCl/film) ṽ = 3083 w, 3061 m, 3026 s, 2962 vs, 2927 s, 2869 s, 2801 m, 1493 s, 1452 s, 1379 m, 1363 m, 1168 s, 761 s, 728 s, 699 cm⁻¹ vs. C₂₀H₂₇N (281.4): Calc. C, 85.3; H, 9.7; N, 5.0. Found C, 85.2; H, 9.7; N, 5.1.

Benzyl-cyclohexyl-(3-phenyl-butyl)-amine (24d). Obtained from **1**, **23b** and **2c** as a colourless oil in **79 %** yield. ¹H NMR (400 MHz, CDCl₃, 20 °C): δ = 1.12 (d, ³J = 7.0 Hz, 3 H, CH₃), 1.14 (m, 6 H, 3 x CH₂), 1.65 (m, 6 H, 3 x CH₂), 2.40 (m, 3 H, NCH₂, NCH), 2.72 (m, 1 H, CH), 3.56 (s, 2 H, NCH₂Ph), 7.07-7.32 (m, 10 H, 10 x PhH). ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ = 22.4 (CH₃), 26.2 (2 x CH₂), 26.4 (CH₂), 28.86 (CH₂), 28.91 (CH₂), 37.2 (CH₂), 37.5 (CH), 48.3 (CH₂), 54.4 (CH₂), 59.3 (CH), 125.6 (PhH), 126.3 (PhH), 126.9 (2 x PhH), 127.9 (2 x PhH), 128.2 (2 x PhH), 128.3 (2 x PhH), 141.8 (Cq), 147.8 (Cq). GC-MS (EI, 70 eV): m/z (%) = 322 (M⁺+1, 15), 294 (6), 280 (6), 252 (46), 202 (32), 134 (100), 105 (28), 91 (79), 65 (12). IR (NaCl/film) ṽ = 3083 w, 3061 w, 3026 m, 2927 vs, 2852 s, 1493 s, 1451 s, 1370 w, 734 s, 699 cm⁻¹ vs. C₂₃H₃₁N (321.5): Calc. C, 85.9; H, 9.7; N, 4.4. Found C, 86.1; H, 9.6; N, 4.5.

Benzyl-(1-methyl-2-phenyl-ethyl)-(3-phenyl-butyl)-amine (24e) (mixture of diastereomers 1:1). Obtained from **1**, **23c** and **2c** as a colourless oil in **92 %** yield. ¹H NMR (400 MHz, CDCl₃, 20 °C): δ = 0.90 (m, 3 H, CH₃), 1.14 (m, 3 H, CH₃), 1.68 (m, 2 H, CH₂), 2.38 (m, 3 H, NCH₂, NCH), 2.68 (m, 3 H, CH, CH₂), 2.89 (m, 1 H, CH), 3.59 (m, 2 H, NCH₂), 7.13 (m, 15 H, 15 x PhH). ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ = 14.5 (CH₃), 22.5 (CH₃), 37.02/37.12 (CH₂), 37.4 (CH), 39.43/39.56 (CH₂), 47.52/47.59 (CH₂), 54.1 (CH₂), 56.5 (CH), 125.6

(PhH), 125.7 (PhH), 126.4 (PhH), 126.9 (2 x PhH), 128.0 (4 x PhH), 128.2 (2 x PhH), 128.4 (2 x PhH), 129.2 (2 x PhH), 140.8 (Cq), 141.0 (Cq), 147.59/147.65 (Cq). GC-MS (EI, 70 eV): m/z (%) = 358 (M^++1, 10), 280 (9), 266 (100), 148 (28), 105 (9), 91 (34). IR (NaCl/film) $\tilde{\nu}$ = 3083 w, 3061 w, 3026 m, 2960 s, 2927 m, 2869 w, 1494 s, 1452 s, 1372 w, 741 m, 733 m, 699 cm⁻¹ vs. $C_{26}H_{31}N$ (357.5): Calc. C, 87.3; H, 8.8; N, 3.9. Found C, 87.0; H, 8.9; N, 4.2.

General Procedure for the Synthesis of Cyclic Tertiary Amines

A mixture of 4.8 mmol olefin, 4.8 mmol amine and 1 mol % [Rh(cod)Cl]₂ in 10 mL anhydrous dioxane was heated for 3 d at 110 °C in an autoclave under a pressure of 90 bar carbon monoxide, 20 bar hydrogen (p_{total} = 110 bar). The solvent was removed by rotary evaporation and the residue dissolved in diethyl ether and filtered through neutral alumina.

2-Isopropyl-1,8a-dimethyl-decahydro-isoquinoline (26a) (mixture of diastereomers 1:1). Obtained from 25 and 2b as colourless oil in 31 % yield. ¹H NMR (400 MHz, CDCl₃, 20 °C): δ = 0.75 (d, ^3J = 6.6 Hz, 3 H, CH₃), 0.79 (d, ^3J = 6.6 Hz, 3 H, CH₃), 0.95 (s, 3 H, CH₃), 1.06 (d, ^3J = 6.8 Hz, 3 H, CH₃), 1.26-1.35 (m, 3 H, cyclic), 1.38-1.51 (m, 4 H, 2 x CH₂), 1.59-1.67 (m, 1 H, cyclic), 1.74-1.85 (m, 5 H, cyclic), 1.94-2.02 (m, 2 H, cyclic), 2.86 (dt, ^2J = 3.4 Hz, 3J = 10.9 Hz, 1 H, NCHH), 3.18 (septet, ^3J = 6.6 Hz, 1 H, NCH). ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ = 11.5 (CH₃), 15.8 (CH₃), 20.4 (CH₂), 21.9 (CH₃), 22.1 (CH₂), 23.1 (CH₂), 23.2 (CH₃), 24.6 (CH₂), 31.1 (CH₂), 36.5 (Cq), 42.0 (CH), 44.2 (NCH₂), 45.6 (NCH), 63.9 (NCH). GC-MS (EI, 70 eV): m/z (%) = 209 (12%), 195 (16), 194 (100), 153 (12), 152 (26), 138 (16), 95 (10). IR (NaCl/film) $\tilde{\nu}$ = 2966 vs, 2926 vs, 2853 vs, 2792 s, 2749 m, 2730 m, 2710 m, 1485 m, 1467 s, 1448 s, 1385 s, 1370 w, 1362 s, 1322 m, 1263 m, 1236 m, 1193 vs, 1164 s, 1146 m, 1130 m, 1118 s, 1094 m, 1086 s, 1056 cm⁻¹ m. HR-MS ($C_{14}H_{27}N$): Calc. 209.21436. Found 209.2143.

1,8a-Dimethyl-2-(1-phenyl-ethyl)-decahydro-isoquinoline (26b) (mixture of diastereomers 1:1:1). Obtained from 25 and 2c as colourless oil in 85 % yield. GC-MS (EI, 70 eV): M/z (%) = 271 (M^++1, 15), 256 (100), 214 (19), 200 (19), 166 (15), 152 (7), 105 (74), 79 (19), 67 (15), 55 (19). $C_{19}H_{29}N$ (270.4): Calc. C, 84.4; H, 10.8; N, 5.2. Found C, 84.3; H, 11.1; N, 5.4. **Diastereomer a:** ¹H NMR (400 MHz, CDCl₃, 20 °C): δ = 0.79 (d, ^3J = 6.6 Hz, 3 H, CH₃), 1.01 (s, 3 H, CH), 1.19 (d, ^3J = 6.8 Hz, 3 H, CH₃), 1.09-1.39 (m, 5 H, cyclic), 1.50-1.88 (m, 5 H, cyclic), 1.95-2.07 (m, 2 H, CH₂), 2.17 (brs, 1 H, cyclic), 2.37-2.41 (m, 1 H, cyclic), 4.27 (q, ^3J = 6.7 Hz, 1 H, NCH), 7.19 (t, ^3J = 7.3 Hz, 1 H, PhH), 7.30 (t*, J = 7.8 Hz, J = 7.5 Hz, 2 H, 2 x PhH), 7.51 (d, ^3J = 7.8 Hz, 2 H, 2 x PhH). ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ = (CH₃), 15.8 (CH), 20.6 (CH₂), 21.9 (CH₂), 23.1 (CH₃), 23.5 (CH₂), 24.9 (CH₂), 30.8 (CH₂), 36.9 (Cq), 42.2 (CH), 46.0 (NCH₂), 52.7 (NCH), 63.4 (NCH), 125.9 (PhH), 127.4 (2 x PhH), 127.8 (2 x PhH), 145.6 (Cq). IR (NaCl/film) $\tilde{\nu}$ = 3060 w, 3027 w, 2935 vs, 2874 s,

2853 vs, 2795 s, 2754 w, 2737 w, 2711 w, 1493 m, 1447 s, 1385 s, 1366 m, 1324 w, 1308 w, 1264 w, 1211 w, 1206 w, 1190 m, 1174 w, 1165 m, 1154 w, 1123 s, 1097 w, 1082 w, 1062 w, 1037 w, 1014 w, 989 w, 953 w, 775 s, 740 s, 697 cm^{-1} vs. **Diastereomer b:** ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.75 (d, ^{3}J = 6.8 Hz, 3 H, CH$_3$), 0.91 (s, 3 H, CH$_3$), 0.98-1.04 (m, 2 H, cyclic), 1.24-1.28 (m, 1 H, cyclic), 1.36-1.87 (m, 9 H, cyclic), 2.25 (m, 1 H, cyclic), 2.97-3.02 (m, 1 H, cyclic), 4.31 (q, ^{3}J = 7.0 Hz, 1 H, NCH), 7.20 (m, 3 H, 3 x PhH), 7.29 (m, 2 H, 2 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 15.8 (CH$_3$),19.4 (CH$_3$), 20.5 (CH$_2$), 22.1 (CH$_2$), 23.2(CH$_3$), 24.0 (CH$_2$), 24.5 (CH$_2$), 31.0 (CH$_2$), 36.9 (Cq), 41.7 (CH), 46.7 (NCH$_2$), 53.4 (NCH), 63.9 (NCH), 126.3 (PhH), 127.6 (2 x PhH), 128.2 (2 x PhH), 140.3 (Cq). IR (NaCl/film) $\tilde{v}$ = 3084 w, 3060 w, 3027 m, 2924 vs, 2855 vs, 2799 s, 2712 w, 1493 s, 1487 s, 1463 s, 1450 vs, 1384 s, 1371 s, 1355 m, 1308 m, 1276 m, 1262 m, 1189 s, 1174 m, 1164 s, 1114 s, 1101 s, 1079 s, 1058 m, 1045 m, 1043 w, 1026 w, 988 w, 952 w, 785 w, 772 s, 743 m, 699 cm^{-1} vs. **Diastereomer c:** ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 0.76 (d, ^{3}J = 6.5 Hz, 3 H, CH$_3$), 0.92 (s, 3 H, CH$_3$), 1.19 (d, ^{3}J = 6.7 Hz, CH$_3$), 1.12-1.47 (m, 8 H, cyclic), 1.71-1.88 (m, 3 H, cyclic), 2.06-2.14 (m, 2 H, cyclic), 2.36-2.41 (m, 1 H, cyclic), 4.21 (q, ^{3}J = 6.6Hz, 1 H, NCH), 7.19 (t, ^{3}J = 7.2 Hz, 1 H, PhH), 7.29 (t*, J = 7.8 Hz, J = 7.2 Hz, 2 H, 2 x PhH), 7.47 (d, ^{3}J = 7.8 Hz, 2 H, 2 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 8.5 (CH$_3$), 11.9 (CH), 15.2 (CH$_3$), 21.2 (CH$_2$), 24.8 (CH$_2$), 26.1 (CH$_2$), 30.9 (CH$_2$), 36.8 (CH$_2$), 38.0 (Cq), 42.9 (CH), 46.4 (NCH$_2$), 52.7 (NCH), 67.2 (NCH), 125.8 (PhH), 127.6 (2 x PhH), 127.7 (2 x PhH), 145.9 (Cq). IR (NaCl/film) $\tilde{v}$ = 3083 w, 3061 w, 3029 w, 2923 vs, 2857 vs, 2801 s, 2712 m, 1493 m, 1487 m, 1465 m, 1450 m, 1386 m, 1371 m, 1355 m, 1189 m, 1174 m, 1159 m, 1117 m, 1079 s, 1026 w, 787 m, 699 cm^{-1} s.

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