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Selective One-Pot Synthesis of Secondary and Tertiary Amines via Rhodium Catalysed Reduction and Multiple Alkylation of Aromatic Nitro Compounds under Hydroformylation Conditions

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Abstract

Secondary and tertiary amines are selectively prepared in high yields by a one-pot reduction / multiple alkylation procedure from aromatic nitro compounds with styrenes, cyclic olefins or heterofunctionalised olefins, carbon monoxide and hydrogen in the presence of $[Rh(cod)Cl]_2$ as catalyst.

Keywords: Alkylation; Amines; Nitro compounds; Rhodium catalysis

The synthesis of secondary and tertiary amines with different substituents usually requires selective stepwise procedures.[1,2] We recently reported that the one-pot hydroaminomethylation reaction is an efficient and convenient method for the synthesis of symmetrically and unsymmetrically substituted secondary and tertiary amines.[3] Furthermore it is well established that nitro compounds can be reduced to the corresponding primary amines under hydrogen atmosphere in presence of various rhodium(I) catalysts.[4] Here we present use of a combination of both methods for the reduction and alkylation of aromatic nitro compounds in an efficient one-pot procedure. In this multistep reaction sequence an *in-situ* generated primary amine is selectively either mono- or bisalkylated to form the corresponding secondary or tertiary amine.

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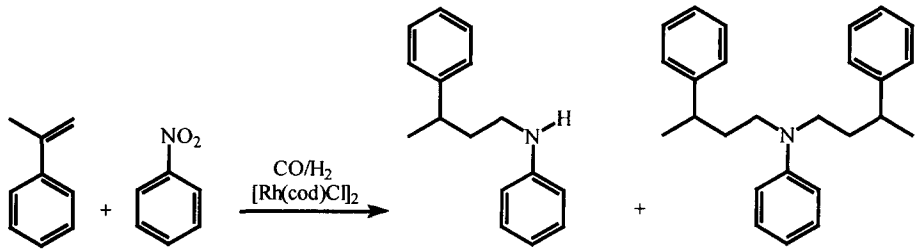
Reduction and alkylation of aromatic nitro compounds

As earlier reported carbonylative reductive hydroaminomethylation of α-methylstyrene **(1a)** with primary amines exclusively leads to the corresponding secondary amines in high yields.[3a,b] If aromatic nitro compounds acting as precursor for primary amines are employed under typical hydroformylation conditions two products resulting from mono- and bisalkylation are observed. Reaction of α-methylstyrene **(1a)** with nitrobenzene **(2a)** proceeds with nearly quantitative conversion of the olefin to form the monoalkylation product **3a** in 45 % yield and the bisalkylation product **4a** in 44 % yield (scheme 1, entry 1). The generation of the bisalkylated product **4a** can be explained by a comparably slow hydrogenation rate of the aromatic nitro compound **2a** on one hand, and a high hydroformylation / hydroaminomethylation rate of the olefin **1a** on the other hand.



1a **2a** **3a** **4a**

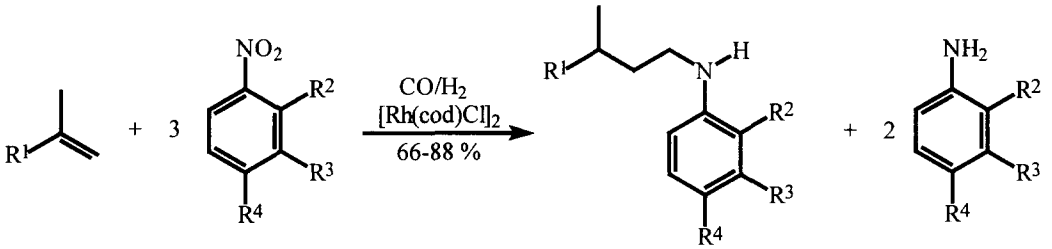
entry	1a/2a-ratio	yield 3a [%]	yield 4a [%]
1	1/1	45	44
2	1/3	88	< 5
3	2/1	-	98

Scheme 1: Mono- and bisalkylation of **2a** under typical hydroformylation conditions

Selective monoalkylation of aromatic nitro compounds is achieved, if three equivalents of the nitro compound **2a** are employed in this multistep reaction sequence (scheme 1, entry 2). Furthermore it is necessary to slow down the hydroformylation rate of the olefin by performing the reaction neat without solvent. Selective bisalkylation is achieved if two equivalents of olefin and one equivalent of the aromatic nitro compound is employed in the reaction (scheme 1, entry 3).

Selective monoalkylation of aromatic nitro compounds

As summarised in table 1 various aromatic nitro compounds **2a-f** undergo selective reduction and monoalkylation to form the secondary amines **3b-h** in good to excellent yields (scheme 2, table 1). Aromatic **1a** (entry 4-8), as well as aliphatic (**1b**, entry 9) or heterofunctionalised (**1c**, entry 10) olefins can satisfactorily be employed (scheme 2, table 1). Only minor amounts of products resulting from bisalkylation (approximately 5 %) are obtained. The formation of by-products such as enamines or aldehydes is not observed.



1a-c **2a-f** **3b-h** **5a-f**

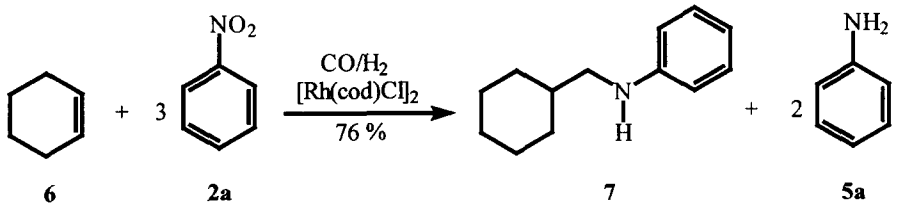
Scheme 2: Monoalkylation of aromatic nitro compounds **2a-f**

Table 1

Monoalkylation of aromatic nitro compounds **2a-f** with monoolefins **1a-c**

entry	R^1	alkene	R^2	R^3	R^4	nitro compound	product	yield [%]
4	Ph	**1a**	CH_3	H	H	**2b**	**3b**	69
5	Ph	**1a**	H	CH_3	H	**2c**	**3c**	66
6	Ph	**1a**	H	H	CH_3	**2d**	**3d**	72
7	Ph	**1a**	H	H	OCH_3	**2e**	**3e**	77
8	Ph	**1a**	H	H	Ac	**2f**	**3f**	75
9	$CH_2C(CH_3)_3$	**1b**	H	H	H	**2a**	**3g**	71
10	N(Ac)Et	**1c**	H	H	H	**2a**	**3h**	73

Monoalkylation of nitrobenzene **(2a)** in presence of the non-terminal olefin cyclohexene **(6)** proceeds with comparable results and yields to the secondary amine **7** (scheme 3).

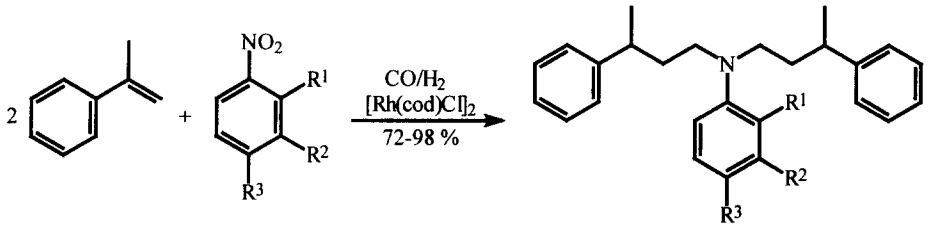


6 **2a** **7** **5a**

Scheme 3: Monoalkylation of **2a** with the non terminal olefin **6**

Selective bisalkylation of aromatic nitro compounds

The conversion of α-methylstyrene **(1a)** in presence of various aromatic nitro compounds **2b-g** give the tertiary amines **4b-f** in high yields and selectivities (scheme 4, table 2). By-products such as enamines, aldehydes or products resulting from monoalkylation are not observed.



1a **2b-g** **4b-f**

Scheme 4: Symmetrical bisalkylation of nitro compounds **2b-g** with α-methylstyrene **(1a)**

Table 2

Symmetrical bisalkylation of nitro compounds **2b-g** with α-methylstyrene **(1a)**

entry	alkene	R^1	R^2	R^3	nitro-compound	product	Yield [%]
11	**1a**	CH_3	H	H	**2b**	**4b**	76
12	**1a**	H	CH_3	H	**2c**	**4c**	84
13	**1a**	H	H	CH_3	**2d**	**4d**	83
14	**1a**	H	H	OCH_3	**2e**	**4e**	72
15	**1a**	H	OCH_3	OCH_3	**2g**	**4f**	88

In conclusion we have shown that the rhodium(I) catalysed one-pot reduction and alkylation of aromatic nitro compounds is an efficient method for the preparation of aromatic secondary and tertiary amines. All aromatic nitro compounds as well as carbo-functionalised compounds employed in the reaction selectively form secondary and tertiary amines in high yields. Further investigations towards and extension of the synthetic potential of this reaction are in current progress.

EXPERIMENTAL

NMR spectra were recorded on Bruker Spectrometers DPX 300 and DRX 400 using TMS as internal standard. IR spectra were obtained with a Nicolet Impact 400D, 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.[5] Pressure reactions have been carried out in autoclaves (type A, 250 ml, PTFE-insert) from Berghof, Eningen, Germany.

General procedure for selective monoalkylation of the aromatic nitro compounds 2a-f

A mixture of the olefin (14.4 mmol), the corresponding nitro compound (43.2 mmol) and $[Rh(cod)Cl]_2$ (1 mol %) was heated for 2 d, at 130°C in an autoclave under 30 bar carbon monoxide and 60 bar hydrogen (p_{total} = 90 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.

Phenyl-(3-phenyl-butyl)-amine (3a).[3a] Obtained from methylstyrene **(1a)** and nitrobenzene **(2a)** as a yellow oil in 88 % yield.

N-(2-Methylphenyl)-N-(3-phenylbutyl)amine (3b). Obtained from methylstyrene **(1a)** and 2-nitrotoluene **(2b)** as a yellow oil in 69 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.28 (d, ^{3}J = 6.9 Hz, 3 H, CH_3), 1.92 (m, 2 H, CH_2), 1.99 (s, 3 H, CH_3), 2.83 (q*, J = 7.0 Hz, 1 H, CH), 3.03 (br s, 2 H, NCH_2), 3.30 (br s, 1 H, NH), 6.47 (d, ^{3}J = 7.5 Hz, 1 H, PhH), 6.60 (t*, J = 6.8 Hz, 1 H, PhH), 6.99 (d, ^{3}J = 6.4 Hz, 1 H, PhH), 7.06 (m, 1 H, PhH), 7.19-7.30 (m, 5 H, 5 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 17.2 (CH_3), 22.7 (CH_3), 37.8 (CH_2), 38.1 (CH), 42.2 (NCH_2), 109.4 (PhH), 116.5 (PhH), 121.6 (Cq), 126.1 (PhH), 126.8 (2 x PhH), 127.0 (PhH), 128.5 (2 x PhH), 129.9 (PhH), 146.1 (Cq), 146.6 (Cq). GC-MS (EI, 70 eV): m/z (%) = 239 (M^+, 25), 162 (29), 120 (100), 107 (33), 91 (48), 77 (25), 65 (23), 51 (17). IR (NaCl/film) $\tilde{\nu}$ = 3428 w, 3059 w, 3025 w, 2959 m, 2925 m, 2870 m, 1606 s, 1586 m, 1514 s, 1493 m, 1473 m, 1451 s, 748 s, 701 cm^{-1} s. $C_{17}H_{21}N$ (239.4): Calc. C, 85.3; H, 8.8; N, 5.9. Found C, 85.0; H, 8.6; N, 5.8.

N-(3-Methylphenyl)-N-(3-phenylbutyl)amine (3c). Obtained from methylstyrene **(1a)** and 3-nitrotoluene **(2c)** as a yellow oil in 66 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.27 (d, ^{3}J = 6.8 Hz, 3 H, CH_3), 1.85 (q*, ^{3}J = 7.1 Hz, 2 H, CH_2), 2.23 (s, 3 H, CH_3), 2.81 (q*, J = 6.9 Hz, 1 H, CH), 2.97 (m, 2 H, NCH_2), 3.42 (br s, 1 H, NH), 6.28 (br s, 2 H, 2 x PhH), 6.48 (d, ^{3}J = 6.7 Hz, 1 H, PhH), 7.00 (d, ^{3}J = 7.3 Hz, 1 H, PhH), 7.18 (d, ^{3}J = 7.0 Hz, 3 H, 3 x PhH), 7.27 (d, ^{3}J = 6.6 Hz, 2 H, 2 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 21.5 (CH_3), 22.4

(CH_3), 37.7 (CH), 37.7 (CH_2), 42.1 (NCH_2), 109.8 (PhH), 113.3 (PhH), 117.9 (PhH), 126.0 (PhH), 126.8 (2 x PhH), 128.34 (PhH), 128.37 (PhH), 128.9 (PhH), 138.7 (Cq), 146.6 (Cq), 148.2 (Cq). GC-MS (EI, 70 eV): m/z (%) = 239 (M^+, 21), 120 (100), 107 (31), 91 (26), 77 (21), 65 (17), 51 (11). IR (NaCl/film) $\tilde{\nu}$ = 3407 w, 3082 w, 3059 w, 3026 w, 2959 m, 2923 m, 2870 m, 1605 vs, 1590 s, 1511 m, 1493 s, 1452 m, 1328 m, 1305 m, 765 s, 701 s, 693 cm^{-1} s. $C_{17}H_{21}N$ (239.4): Calc. C, 85.3; H, 8.8; N, 5.9. Found C, 84.9; H, 8.8; N, 6.0.

N-(4-Methylphenyl)-N-(3-phenylbutyl)amine (3d). Obtained from methylstyrene **(1a)** and 4-nitrotoluene **(2d)** as a colourless oil in 72 % yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.24 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.82 (m, 2 H, CH_2), 2.20 (s, 3 H, CH_3), 2.79 (m, 1 H, CH), 2.96 (m, 2 H, NCH_2), 3.28 (br s, 1 H, NH), 6.40 (m, 2 H, 2 x PhH), 6.92 (m, 2 H, 2 x PhH), 7.17 (m, 3 H, 3 x phH), 7.25 (t, ^3J = 6.7 Hz, 2 H, 2 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 20.3 (CH_3), 22.4 (CH_3), 37.7 (CH), 37.7 (CH_2), 42.4 (NCH_2), 112.8 (2 x PhH), 126.0 (Cq), 126.0 (PhH), 126.8 (2 x PhH), 128.4 (2 x PhH), 129.5 (2 x PhH), 146.0 (Cq), 146.6 (Cq). GC-MS (EI, 70 eV): m/z (%) = 239 (M^+, 26), 134 (40), 120 (100), 107 (21), 91 (38), 77 (26), 65 (18), 51 (12). IR (NaCl/film) $\tilde{\nu}$ = 3407 w, 3082 w, 3060 w, 3025 m, 2959 m, 2922 m, 2868 m, 1618 m, 1521 s, 1493 m, 1452 m, 1318 m, 1259 m, 807 m, 762 m, 701 cm^{-1} s. $C_{17}H_{21}N$ (239.4): Calc. C, 85.3; H, 8.8; N, 5.9. Found C, 84.8; H, 8.7; N, 5.8.

N-(4-Methoxy-phenyl)-N-(3-phenyl-butyl)-amine (3e). Obtained from methylstyrene **(1a)** and nitroanisole **(2e)** as a yellow oil in 77 % yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.25 (d, ^3J = 6.5 Hz, 3 H, CH_3), 1.81 (m, 2 H, CH_2), 2.78 (m, 1 H, CH), 2.91 (m, 2 H, NCH_2), 3.20 (s, 1 H, NH), 3.66 (s, 3 H, OCH_3), 6.43 (m, 2 H, PhH), 6.72 (m, 2 H, PhH), 7.21 (m, 5 H, PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.4 (CH_3), 37.7 (CH), 37.8 (CH_2), 43.1 (NCH_2), 55.5 (OCH_3), 113.8 (2 x PhH), 114.6 (2 x PhH), 126.0 (PhH), 126.8 (2 x PhH), 128.3 (2 x PhH), 142.5 (Cq), 146.6 (Cq), 151.7 (Cq). GC-MS (EI, 70 eV): m/z (%) = 255 (100, M^+), 136 (37), 123 (7), 105 (11), 91 (5), 77 (9), 65 (4), 51 (5). IR (NaCl/film): $\tilde{\nu}$ = 3396 w, 3081 w, 3059 w, 3026 w, 2958 m, 2928 m, 2870 m, 2831 m, 1513 vs, 1494 m, 1463 m, 1452 m, 1236 s, 1038 m, 819 s, 701 cm^{-1} s. $C_{17}H_{21}NO$ (255.4): calc. C, 80.0; H, 8.3; N, 5.5. Found C, 80.3; H, 8.5; N, 5.5.

1-{4-[(3-Phenylbutyl)amino]phenyl}-1-ethanone (3f). Obtained from methylstyrene **(1a)** and nitroacetophenone **(2f)** as a colourless oil in 75 % yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.27 (d, ^3J = 7.0 Hz, 1 H, CH_3), 1.83 (m, 2 H, CH_2), 2.45 (s, 3 H, CH_3), 2.83 (sextet*, J = 7.0 Hz,1 H, CH), 3.01 (m, 2 H, NCH_2), 6.41 (d, ^3J = 8.8 Hz, 2 H, 2 x PhH), 7.17-7.31 (mc, 5 H, 5 x PhH), 7.76 (m, 2 H, 2 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.3 (CH_3), 25.8 (CH_3),

37.2 (CH_2), 37.6 (CH), 41.4 (NCH_2), 111.0 (2 x PhH), 125.9 (Cq), 126.2 (PhH), 126.7 (2 x PhH), 128.4 (2 x PhH), 130.7 (2 x PhH), 146.1 (Cq), 152.2 (Cq), 196.4 (Cq, C=O). GC-MS (EI, 70 eV): m/z (%) = 268 (M^++1, 100), 148 (12), 135 (4), 120 (13), 106 (10), 91 (9), 65 (3). IR (NaCl/film) $\tilde{\nu}$ = 3357 m, 3082 w, 3059 w, 3025 w, 2960 s, 2926 s, 2870 m, 1660 vs, 1593 vs, 1526 s, 1493 s, 1452 s, 1358 s, 1279 vs, 1189 s, 1180 s, 702 cm^{-1} s.

N-(3,5,5-Trimethyl-hexyl)-aniline (3g).[6] Obtained from 2,4,4-trimethylpent-1-ene **(1b)** and nitrobenzene **(2a)** as a colourless oil in 71 % yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.90 (d, ^2J = 0.8 Hz, 9 H, 3 x CH_3), 0.96 (d, ^3J = 6.1 Hz, 3 H, CH_3), 1.09 (m, 1 H, C<u>H</u>H-CR_3), 1.25 (m, 1 H, CH<u>H</u>-CR_3), 1.42 (m, 1 H, CH), 1.56 (m, 2 H, CH_2), 3.06 (t, ^3J = 8.8 Hz, 2 H, NCH_2), 3.46 (br s, 1 H, NH), 6.56 (d, ^3J = 8.0 Hz, 2 H, 2 x PhH), 6.66 (t, ^3J = 7.3 Hz, 1 H, PhH), 7.14 (t*, J = 7.7 Hz, J = 7.3 Hz, 2 H, 2 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.7 (CH_3), 27.2 (CH), 29.9 (3 x CH_3), 31.0 (Cq), 39.1 (CH_2), 42.0 (CH_2), 51.2 (NCH_2), 112.6 (2 x PhH), 117.0 (PhH), 129.1 (2 x PhH), 148.5 (Cq). GC-MS (EI, 70 eV): m/z (%) = 219 (M^+, 12), 106 (100), 93 (7), 77 (9), 65 (3), 57 (7). IR (NaCl/film) $\tilde{\nu}$ = 3411 w, 3053 w, 3021 w, 2955 s, 2909 s, 2868 m, 1604 s, 1506 s, 1477 m, 1468 m, 1376 w, 1364 m, 748 m, 692 cm^{-1} m. $C_{15}H_{25}N$ (219.4): Calc. C, 82.1; H, 11.5; N, 6.4. Found C, 82.1; H, 11.3; N, 6.5.

N-Ethyl-N-(2-methyl-4-phenylamino-butyl)-acetamide (3h). Obtained from *N*-ethyl-*N*-(2-methyl-allyl)-acetamide **(1c)** and nitrobenzene **(2a)** as an orange oil in 73 % yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92/0.96 (2 x d, ^3J = 6.7 Hz, 3 H, CH_3), 1.09/1.13 (2 x t, ^3J = 7.1 Hz, 3 H, CH_3), 1.40 (m, 1 H, CHR-C<u>H</u>H), 1.65 (m, 1 H, CHR-CH<u>H</u>), 1.95 (m, 1 H, CH), 2.05/2.08 (2 x s, 3 H, CH_3), 3.03-3.38 (m, 6 H, 3 x NCH_2), 6.59 (m, 2 H, 2 x PhH), 6.67 (m, 1 H, 1 x PhH), 7.15 (m, 2 H, 2 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 12.3/13.4 (CH_3), 16.9/17.2 (CH_3), 21.1/21.6 (CH_3), 29.4/30.2 (CH), 33.3/33.6 (CH_2), 40.3/43.2 (NCH_2), 41.2/41.3 (NCH_2), 50.3/54.0 (NCH_2), 112.3 (2 x PhH), 116.5/116.8 (PhH), 128.7/128.8 (2 x PhH), 148.0/148.1 (Cq), 169.9/170.1 (Cq, C=O). GC-MS (EI, 70 eV): m/z (%) = 248 (M^+, 29), 160 (5), 128 (16), 106 (100), 93 (19), 77 (38), 58 (100), 51 (21). IR (NaCl/film) $\tilde{\nu}$ = 3346 s, 3051 m, 3021 m, 2965 s, 2930 s, 2873 s, 1635 vs, 1603 vs, 1500 vs, 1480 s, 1456 s, 1426 vs, 1380 s, 1323 s, 1267 s, 1224 m, 1179 m, 1121 m, 1033 s, 750 s, 694 s, 510 cm^{-1} m. $C_{15}H_{24}N_2O$ (248.4): Calc. C, 72.5; H, 9.8; N, 11.3. Found C, 72.3; H, 9.5; N, 11.3.

General procedure for selective bisalkylation of the aromatic nitro compounds 2a-g

A mixture of the olefin (14.4 mmol), the corresponding nitro compound (7.2 mmol) and $[Rh(cod)Cl]_2$ (1 mol %) was heated for 2 d, at 130°C in an autoclave under 30 bar carbon monoxide and 60 bar hydrogen (p_{total} = 90 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.

Phenyl-bis-(3-phenyl-butyl)-amine (4a) (mixture of diastereomers 1:1).[3b] Obtained from methylstyrene **(1a)** and nitrobenzene **(2a)** as a yellow oil in 98 % yield.

Bis-(3-phenyl-butyl)-o-tolyl-amine (4b) (mixture of diastereomers 1:1). Obtained from methylstyrene **(1a)** and 2-nitrotoluene **(2b)** as a yellow oil in 76 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.13 (d, ^{3}J = 6.5 Hz, 6 H, 2 x CH_3), 1.62 (m, 4 H, 2 x CH_2), 2.19 (s, 3 H, CH_3), 2.60 (br s, 2 H, 2 x CH), 2.74 (br s, 4 H, 2 x NCH_2), 6.92 (d*, J = 4.8 Hz, 2 H, 2 x PhH), 7.06-7.23 (m, 12 H, 12 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 18.2 (CH_3), 22.53 (CH_3), 22.58 (CH_3), 35.4 (2 x CH_2), 37.73 (CH), 37.77 (CH), 51.95 (NCH_2), 51.97 (NCH_2), 121.74/121.83 (PhH), 122.94/122.98 (PhH), 125.8 (2 x PhH), 125.9 (PhH), 126.9 (4 x PhH), 128.2 (4 x PhH), 130.9 (PhH), 134.59/134.63 (Cq), 147.2 (2 x Cq), 149.9 (Cq). GC-MS (EI, 70 eV): m/z (%) = 371 (M^+, 26), 252 (34), 134 (100), 118 (4), 105 (23), 91 (14). IR (NaCl/film) $\tilde{\nu}$ = 3082 w, 3061 w, 3026 m, 2958 s, 2927 s, 2870 m, 1492 s, 1452 s, 762 s, 700 cm^{-1} vs. $C_{27}H_{33}N$ (371.6): Calc. C, 87.2; H, 9.0; N, 3.8. Found C, 86.8; H, 8.9; N, 4.2.

Bis-(3-phenyl-butyl)-m-tolyl-amine (4c) (mixture of diastereomers 1:1). Obtained from methylstyrene **(1a)** and 3-nitrotoluene **(2c)** as a yellow oil in 84 % yield.^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.235 (d, ^{3}J = 7.0 Hz, 3 H, CH_3), 1.246 (d, ^{3}J = 7.0 Hz, 3 H, CH_3), 1.73 (m, 4 H, 2 x CH_2), 2.20/2.22 (s, 3 H, CH_3), 2.67 (m, 2 H, 2 x CH), 3.06 (m, 4 H, 2 x NCH_2), 6.16-6.87 (m, 3 H, 3 x PhH), 7.01 (d, ^{3}J = 8.0 Hz, 1 H, PhH), 7.18-7.31 (m, 10 H, 10 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 21.9 (CH_3), 22.8 (2 x CH_3), 35.09 (CH_2), 35.16 (CH_2), 37.9 (2 x CH), 49.0 (2 x NCH_2), 108.9 (PhH), 112.5 (PhH), 116.2 (PhH), 126.1 (2 x PhH), 126.9 (4 x PhH), 128.42 (4 x PhH), 128.9 (PhH), 138.7 (Cq), 146.7 (2 x Cq), 147.8 (Cq). GC-MS (EI, 70 eV): m/z (%) = 371 (M^+, 32), 252 (9), 134 (100), 120 (3), 105 (13), 91 (7). IR (NaCl/film) $\tilde{\nu}$ = 3082 m, 3060 m, 3027 m, 2960 s, 2928 s, 2871 s, 1601 s, 1580 s, 1504 s, 1495 s, 1453 s, 1367 m, 1351 m, 762 s, 700 cm^{-1} s.

Bis-(3-phenyl-butyl)-p-tolyl-amine (4d) (mixture of diastereomers 1:1). Obtained from methylstyrene **(1a)** and 4-nitrotoluene **(2d)** as a yellow oil in 83 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.21 (d, ^{3}J = 6.8 Hz, 3 H, CH_3), 1.22 (d, ^{3}J = 6.8 Hz, 3 H, CH_3), 1.77 (m, 4 H, 2 x CH_2), 2.20 (s, 3 H, CH_3), 2.65 (q*, J = 6.8 Hz, 2 H, 2 x CH), 3.02 (m, 4 H, 2 x NCH_2), 6.36 (m, 2 H, 2 x PhH), 6.93 (d, ^{3}J = 7.6 Hz, 2 H, 2 x PhH), 7.17 (m, 6 H, 6 x PhH), 7.27 (m, 4

H, 4 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 20.1 (CH_3), 22.7 (2 x CH_3), 35.09 (CH_2), 35.14 (CH_2), 37.9 (2 x CH), 49.3 (2 x NCH_2), 112.3 (2 x PhH), 124.5 (Cq), 126.1 (2 x PhH), 126.9 (4 x PhH), 128.4 (4 x PhH), 129.6 (2 x PhH), 145.8 (Cq), 146.8 (2 x Cq). GC-MS (EI, 70 eV): m/z (%) = 371 (M^+, 19), 252 (10), 134 (100), 120 (6), 105 (19), 91 (22). IR (NaCl/film) $\tilde{\nu}$ = 3082 w, 3060 m, 3026 s, 2959 vs, 2925 vs, 2869 s, 1618 vs, 1603 s, 1520 vs, 1493 s, 1452 vs, 1395 m, 1366 s, 762 vs, 700 cm^{-1} vs. HR-MS ($C_{27}H_{33}N$): Calc. 371.26129. Found 371.2611.

(4-Methoxy-phenyl)-bis-(3-phenyl-butyl)-amine (4e) (mixture of diastereomers 1:1). Obtained from methylstyrene **(1a)** and nitroanisole **(2e)** as a yellow oil in 72 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.22 (d, ^{3}J = 6.9 Hz, 6 H, 2 x CH_3), 1.74 (m, 4 H, 2 x CH_2), 2.67 (m, 2 H, 2 x CH), 2.99 (m, 4 H, 2 x NCH_2), 3.72 (s, 3 H, CH_3), 6.45 (m, 2 H, 2 x PhH), 6.79 (d, ^{3}J = 6.5 Hz, 2 H, 2 x PhH), 7.19 (m, 6 H, 6 x PhH), 7.28 (m, 4 H, 4 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.7 (2 x CH_3), 35.18 (CH_2), 35.22 (CH_2), 37.9 (2 x CH), 50.1 (2 x NCH_2), 55.7 (OCH_3), 114.7 (2 x PhH), 114.8 (2 x PhH), 126.0 (2 x PhH), 126.9 (4 x PhH), 128.4 (4 x PhH), 142.9 (Cq), 146.9 (2 x Cq), 151.2 (Cq). GC-MS (EI, 70 eV): m/z (%) = 387 (M^+, 42), 268 (6), 150 (50), 105 (8), 51 (4). IR (NaCl/film) $\tilde{\nu}$ = 3081 w, 3060 w, 3026 m, 2958 s, 2927 s, 2869 s, 1513 vs, 1493 s, 1452 s, 1372 m, 1238 s, 763 s, 701 cm^{-1} vs.

N-(3,4-Dimethoxyphenyl)-N,N-bis-(3-phenylbutyl)amine (4f) (mixture of diastereomers 1:1). Obtained from methylstyrene **(1a)** and 1,2 dimethoxy-4-nitrobenzene **(2g)** as a yellow oil in 88 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.227 (d, ^{3}J = 6.9 Hz, 3 H, CH_3), 1.234 (d, ^{3}J = 6.9 Hz, 3 H, CH_3), 1.77 (q*, ^{3}J = 7.5 Hz, 4 H, 2 x CH_2), 2.66 (sextet*, ^{3}J = 7.0 Hz, 2 H, 2 x CH), 3.01 (m, 4 H, 2 x NCH_2), 3.66 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 6.00 (m, 2 H, 2 x PhH), 6.68 (m, 1 H, PhH), 7.17 (m, 6 H, 6 x PhH), 7.27 (m, 4 H, 4 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.59 (CH_3), 22.62 (CH_3), 35.10 (CH_2), 35.15 (CH_2), 37.8 (2 x CH), 49.8 (2 x NCH_2), 55.4 (OCH_3), 56.5 (OCH_3), 98.71/98.75 (PhH), 104.24/104.27 (PhH), 113.0 (PhH), 125.9 (2 x PhH), 126.8 (4 x PhH), 128.3 (4 x PhH), 140.4 (Cq), 143.34/143.37 (Cq), 146.7 (2 x Cq), 149.6 (Cq). MS (EI, 70 eV): m/z (%) = 417 (M^+, 60), 298 (28), 270 (4), 180 (100), 166 (14), 150 (7), 105 (15), 91 (12). IR (NaCl/film) $\tilde{\nu}$ = 3081 w, 3060 w, 3025 m, 2957 s, 2930 s, 2870 m, 1614 m, 1518 vs, 1493 s, 1463 s, 1452 s, 1247 s, 1233 s, 1027 s, 764 s, 701 cm^{-1} s. HR-MS ($C_{28}H_{35}NO_2$): Calc. 417.26678. Found 417.2666.

N-Cyclohexylmethyl-N-phenylamine (7). Obtained from cyclohexene **(6)** and nitrobenzene **(2a)** as a colourless oil in 76 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.95 (m, 2 H, CH_2), 1.14-1.36 (m, 4 H, 2 x CH_2), 1.50-1.81 (m, 5 H, 2 x CH_2, CH), 2.92 (d, ^{3}J = 6.6 Hz, 2 H, NCH_2), 6.55-6.67 (m, 3 H, 3 x PhH), 7.12-7.28 (m, 2 H, 2 x PhH). ^{13}C NMR (100 MHz,

$CDCl_3$, 20 °C): δ = 25.9 (2 x CH_2), 26.5 (CH_2), 31.2 (2 x CH_2), 37.5 (CH), 50.5 (NCH_2), 112.5 (2 x PhH), 116.7 (2 x PhH), 129.1 (2 x PhH), 148.5 (Cq). GC-MS (EI, 70 eV): m/z (%) = 189 (M^+, 14), 120 (76), 106 (100), 91 (14), 77 (33), 65 (10), 51 (21). IR (NaCl/film) $\tilde{\nu}$ = 3417 m, 3083 w, 3051 m, 3021 m, 2923 vs, 2851 s, 1602 s, 1505 s, 1470 m, 1448 m, 1322 m, 1260 m, 747 s, 692 s.

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