Title: Preparation of 2- and 4-Arylmethyl N-Substituted and N,N-Disubstituted Anilines via a “Green”, Multi-Component Reaction

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Single Crystal Structure Determinations:

Data were collected on an Enraf Nonius CCD diffractometer at 123 K using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Structures were solved by direct methods using the program SHELXS-97¹ and refined by full matrix least squares refinement on F² using the program SHELXL-97.² Non-hydrogen atoms were refined anisotropically and hydrogen atoms inserted at geometrically determined positions with temperature factors fixed at 1.2 times that of the parent atom except for methyl hydrogen atoms where the temperature factors were constrained to equal 1.5 times that of the parent carbon atom. Molecular diagrams, with thermal ellipsoids at the 50% probability level are presented and crystal and refinement data summarized. Bond lengths, angles and thermal parameters are contained in CIF files.

¹ G.M. Sheldrick, SHELXS-97, University of Gottingen, 1990.

² G.M. Sheldrick, SHELXL-97, University of Gottingen, 1997.

Crystal data for **4baa**: $\text{C}_{18}\text{H}_{21}\text{NO}_2$, $M_r = 283.36$, monoclinic, space group $P2_1/c$, $a = 6.8454(2)$, $b = 7.4615(3)$, $c = 27.2798(12)$ Å, $\beta = 91.069(2)^\circ$, $V = 1393.13(9)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.351$ g.cm⁻³, $\mu(\text{MoK}\alpha) = 0.087$ mm⁻¹. Of 3536 unique reflections measured, 1804 $I > 2\sigma(I)$, R indices [$I > 2\sigma(I)$] $R_1 = 0.0503$, $wR_2 = 0.0978$, GoF on $F^2 = 0.941$ for 191 refined parameters and 0 restraints

Crystal data for **5baa**: $\text{C}_{18}\text{H}_{21}\text{NO}_2$, $M_r = 283.36$, monoclinic, space group $P2_1/c$, $a = 9.2593(2)$, $b = 16.1551(3)$, $c = 10.1261(2)$ Å, $V = 1482.52(5)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.270$ g.cm⁻³, $\mu(\text{MoK}\alpha) = 0.082$ mm⁻¹. Of 3548 unique reflections measured, 2073 $I > 2\sigma(I)$, R indices [$I > 2\sigma(I)$] $R_1 = 0.0477$, $wR_2 = 0.0969$, GoF on $F^2 = 1.014$ for 191 refined parameters and 0 restraints

Crystal data for **4abb**: $\text{C}_{27}\text{H}_{25}\text{N}$, $M_r = 363.48$, orthorhombic, space group $Pna2_1$, $a = 11.8742(4)$, $b = 14.4270(3)$, $c = 11.6716(5)$ Å, $V = 1999.4(1)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.207$ g.cm⁻³, $\mu(\text{MoK}\alpha) = 0.069$ mm⁻¹. Of 1908 unique reflections measured, 1400 $I > 2\sigma(I)$, R indices [$I > 2\sigma(I)$] $R_1 = 0.0432$, $wR_2 = 0.0822$, GoF on $F^2 = 1.057$ for 254 refined parameters and 1 restraint (N-H bond length). C7' methyl group refined over 2 positions.

$\times 67.1$ (O- $\underline{\text{CH}_2}$ -), 116.1, 126.1, 128.6, 129.0, 129.8 (Ar $\underline{\text{CH}}$); 132.9, 141.8, 149.8 (Ar $\underline{\text{C}}$). FT-IR: (KBr) 2957 w, 2901 w, 2863 w, 2808 w, 1615 m, 1513 s, 1489 w, 1448 m, 1322 w, 1299 w, 1262 m, 1239 s, 1118 s, 1067 w, 1053 w, 1030 w, 923 s, 835 w, 793 w; (ESI+, MeOH): 254, 100 % ($\text{M} + \text{H}^+$), 255, 19 % ($\text{M} + 1 + \text{H}^+$); Microanalysis: Found C 80.6 %, H 7.5 %, N 5.5 % Requires C 80.6 % H 7.6 %, N 5.5 %.

N-[2-(4-methoxybenzyl)phenyl]morpholine (**4baa**) and *N*-[4-(4-methoxybenzyl)phenyl]morpholine (**5baa**).

With water removal by a Dean-Stark apparatus (10 mL trap volume), a solution of morpholine (3.049 mL, 35.0 mmol), *p*-anisaldehyde (1.217 mL, 10 mmol) and 2-cyclohexenone (0.968 mL, 10.0 mmol) in PhMe (40 mL) was held at reflux for 24 h. A sample of the reaction mixture was removed and the solvent evaporated *in vacuo*. NMR. spectroscopic analysis of this sample showed the presence of the dimorpholino 4-methoxybenzyl aminal. ^{13}C -NMR. (75 MHz, CDCl_3): δ 2×50.0 (N- $\underline{\text{CH}_2}$ -), 55.5 (O- $\underline{\text{CH}_3}$), 2×67.3 (O- $\underline{\text{CH}_2}$ -), 113.5, 130.2 (ArCH), 126.8, 160.0 (ArC).

To the main solution was added 2-cyclohexenone (0.968 mL, 10.0 mmol) and the solution held at reflux for a further 24 h. The solvent and volatile reagents were removed *in vacuo* to yield a crude brown oil. The oil was subjected to column chromatography on Silica gel with EtOAc / hexane (1.5:8.5).

Two products were recovered:

N-[2-(4-methoxybenzyl)phenyl]morpholine (**4baa**); (R_F 0.21, 0.82 g, 31 %) white crystals (m.p. 64 – 65 °C). ^1H -NMR. (300 MHz, CDCl_3): δ 2.82 (t, $J = 4.6$ Hz, 4H, N- $\underline{\text{CH}_2}$ -), 3.74 (s, 3H, O- $\underline{\text{CH}_3}$), 3.78 (t, $J = 4.6$ Hz, 4H, O- $\underline{\text{CH}_2}$ -), 4.01 (s, 2H, Ar- $\underline{\text{CH}_2}$), 6.79 (t, $J = 8.7$ Hz, 2H, ArH), 7.24 – 6.97 (m, 6H, ArH); ^{13}C -NMR. (75 MHz, CDCl_3): δ 36.0 (Ar- $\underline{\text{CH}_2}$ -), 2×53.2 (N- $\underline{\text{CH}_2}$ -), 55.3 (O- $\underline{\text{CH}_3}$), 2×67.6 (O- $\underline{\text{CH}_2}$ -), 114.1, 120.7, 124.5, 127.3, 130.0, 131.1 (ArCH), 133.8, 137.2, 151.5, 158.0 (ArC.); FT-IR: (KBr) 2966 m, 2907 m, 2833

m, 1611 m, 1582 w, 1509 s, 1491 m, 1458 m, 1444 m, 1302 w, 1263 m, 1246 s, 1218 m, 1176 m, 1113 s, 1026 s, 931 s, 917 m, 842 m, 804 m, 772 s; (ESI+, MeOH): 284, 100 % ($M + H^+$), 285, 19 % ($M + 1 + H^+$). Microanalysis: Found C 76.6 %, H 7.5 %, N 4.9 %, Requires C 76.3 % H 7.5 %, N 4.9 %.

N-[4-(4-(methoxybenzyl)phenyl)morpholine (**5baa**)]; (R_F 0.13, 1.34 g, 50 %) white crystals (m.p. 73 – 74 °C). 1H -NMR. ($CDCl_3$): δ 3.10 (t, $J = 4.8$ Hz, 4H, N-CH₂-), 3.76 (s, 3H), 3.83 (t, $J = 4.8$ Hz, 4H, O-CH₂-), 3.84 (s, 2H, Ar-CH₂-), 7.21 – 6.73 (m, 8H, ArH); ^{13}C -NMR. δ 40.3 (Ar-CH₂-), 2×49.9 (N-CH₂-), 55.4 (O-CH₃), 2×67.2 (O-CH₂-), 114.1, 116.1, 129.7, 129.9 (ArCH), 132.9, 141.8, 149.8 (ArC). FT-IR: (KBr) 2956 m, 2898 w, 2836 w, 1609 m, 1584 w, 1509 s, 1459 m, 1445 w, 1383 w, 1332 w, 1304 m, 1263 s, 1238 s, 1187 m, 1174 s, 1120 s, 1068 m, 1053 m, 1033 s, 928 s, 908 w, 854 m, 813 s, 802 s, 757 w; (ESI+, MeOH): 284, 100 % ($M + H^+$), 285, 19 % ($M + 1 + H^+$). Microanalysis: Found C 76.5 %, H 7.5 %, N 5.0 %, Requires C 76.3 % H 7.5 %, N 4.9 %.

N-[2-(2-methoxybenzyl)phenyl)morpholine (**4caa**) and *N*-[4-(2-methoxybenzyl)phenyl)morpholine (**5caa**)].

With water removal by Dean-Stark apparatus (10 mL trap volume), a solution of morpholine (0.61 mL, 7.0 mmol), 2-methoxybenzaldehyde (0.68 g, 5.0 mmol) and 2-cyclohexenone (0.48 mL, 5.0 mmol), DABCO (0.28 g, 2.5 mmol) and PhCOOH (0.34 g, 2.75 mmol) in PhMe (25 mL) was refluxed for 2.5 h.

The reaction mixture was cooled to room temperature and washed with sat. $NaHCO_3$ (aq) (2×25 mL), then with distilled water (1×25 mL). The organic layer was collected and dried with $MgSO_4$, filtered and the solvent removed *in vacuo* to yield a crude oil. The oil was subjected to column chromatography on Silica gel with Et_2O / hexane (7:3).

Two products were recovered:

N-[2-(2-methoxybenzyl)phenyl]morpholine (**4caa**); (0.38 g, 27 %) white crystals (m.p. 68 – 70 °C). ¹H-NMR. (300 MHz, CDCl₃): δ 2.86 (t, *J* = 4.6 Hz, 4H, N-CH₂), 3.77 (t, *J* = 4.6 Hz, 4H, O-CH₂), 3.80 (s, 3H, O-CH₃), 4.07 (s, 2H, Ar-CH₂-Ar), 6.82 (td, *J* = 7.3, 1.2 Hz, 1H, ArH), 6.85 (d, *J* = 8.2 Hz, 1H, ArH), 7.02 – 6.96 (td, 2H, ArH), 7.06 (dd, *J* = 7.6, 1.8 Hz, 1H, ArH), 7.11 (dd, *J* = 7.9, 1.3 Hz, 1H, ArH), 7.15 (dd, *J* = 7.5, 1.8 Hz, 1H, ArH), 7.20 (td, *J* = 6.7, 1.9 Hz, 1H, ArH); ¹³C-NMR. (50 MHz, CDCl₃): δ 30.5 (Ar-CH₂-Ar), 2 × 53.1 (N-CH₂), 55.5 (O-CH₃), 2 × 67.6 (O-CH₂), 110.4, 120.4, 120.6, 124.2, 127.1, 127.2, 130.3, 131.0 (ArCH), 130.1, 136.5, 151.6, 157.6 (ArC); FT-IR: (KBr) 2970 w, 2938 w, 2884 w, 2850 w, 2831 w, 1598 m, 1490 s, 1458 m, 1371 w, 1333 w, 1292 m, 1240 s, 1182 w, 1160 w, 1112 s, 1051 m, 1028 s, 935 m, 918 m, 849 m, 769 s, 754 s; (ESI+, MeOH): Found: 284.1650 Required: 284.1651 Microanalysis: Found C 76.2 %, H 7.6 %, N 5.0 % Requires C 76.3 % H 7.5 % N 4.9 %.

N-[4-(2-methoxybenzyl)phenyl]morpholine (**5caa**): (0.21 g, 15 %) white crystals (m.p. 63 – 64 °C). ¹H-NMR. (300 MHz, CDCl₃): δ 3.11 (t, *J* = 4.8 Hz, 4H, N-CH₂-), 3.81 (s, 3H, O-CH₃), 3.84 (t, *J* = 4.8 Hz, 4H, O-CH₂-), 3.90 (s, 2H, Ar-CH₂-Ar), 6.83 (d, *J* = 8.6 Hz, 2H, ArH), 6.88 – 6.85 (m, 2H, ArH), 7.04 (dd, *J* = 7.6, 1.7 Hz, 1H, ArH), 7.12 (d, *J* = 8.7 Hz, 2H, ArH), 7.18 (td, *J* = 7.8, 1.7 Hz, 1H, ArH); ¹³C-NMR. (50 MHz, CDCl₃): δ 35.1 (Ar-CH₂-Ar), 2 × 50.0 (N-CH₂), 55.6 (O-CH₃), 2 × 67.2 (O-CH₂), 110.7, 2 × 116.1, 120.7, 127.4, 2 × 129.9, 130.4 (ArCH), 2 × 132.9, 149.7, 157.6 (ArC). FT-IR: (KBr) 2965 m, 2990w, 2859 w, 2836 m, 1612 m, 1597 m, 1518 s, 1488 s, 1450 m, 1438 s, 1385 m, 1331 m, 1294 w, 1268 m, 1238 s, 1122 s, 1100 m, 1070 w, 1049 w, 1024 s, 926 s, 832 m, 799 m, 760 s, 711 m; (ESI+, MeOH): 284, 100 % (M + H⁺), 285, 19 % (M + 1 + H⁺); Microanalysis: Found C 73.4 %, H 7.5 %, N 4.9 % Requires C 76.3 % H 7.5 % N 4.9 %.

N-Benzyl-2-benzylaniline (**4aab**).

With water removal by Dean-Stark apparatus (10 mL trap volume), a solution of benzylamine (1.637 mL, 15.0 mmol), PhCHO (0.508 mL, 5.0 mmol) and DABCO (0.561 g, 5 mmol) in PhMe (30 mL) was held at reflux. Portions (0.24 mL) of 2-cyclohexenone were added after 15 min, 1 h 45 min, 3 h 15 min and 4 h 45 min. After 7 h, a double portion (0.48 mL) was added and the mixture was allowed to react for another 13 h, before cooling to room temperature and washing with distilled water (2×20 mL). The organic layer was collected and dried (MgSO_4), filtered and the solvent evaporated *in vacuo* to yield a crude oil. Column chromatography with EtOAc / hexane (1:9) mixture afforded *N*-benzyl-2-benzylaniline (**4aab**) (R_F 0.36, 1.37 g, 87 %) as a colorless solid (m.p. 50 – 52°C) which crystallized from Et_2O . $^1\text{H-NMR}$. (300 MHz, CDCl_3): δ 3.88 (s, 2H, $-\text{CH}_2-$), 4.21 (s, 2H, $-\text{CH}_2-$), 6.60 (d, $J = 8.0$ Hz, 1H, ArCH), 6.70 (dt, $J = 7.4, 1.1$ Hz, 1H, ArCH), 7.25 – 7.04 (m, 12H, ArCH); (75 MHz, CDCl_3): δ 38.5 (Ar-CH_2-), 48.2 (Ar-CH_2-), 111.1, 117.4, 126.6, 127.2, 2×127.4 , 128.0, 2×128.7 , 4×128.8 , 130.8 (ArCH), 124.8, 139.5, 139.6, 146.1 (ArC). FT-IR: (KBr) 3435 w, 3062 w, 3027 m, 2903 w, 2844 w, 1603 s, 1585 s, 1512 s, 1494 s, 1452 s, 1314 m, 1269 m, 1256 m, 1118 w, 1074 w, 1028 m, 748 s, 728 s, 697 s; (ESI+, MeOH): 274, 100 % ($\text{M} + \text{H}^+$), 275, 20 % ($\text{M} + 1 + \text{H}^+$); Microanalysis: Found C 87.8 %, H 7.1 %, N 5.1 % Requires C 87.9 % H 7.0 %, N 5.1 %.

N-Benzyl-2-(4-methylbenzyl)aniline (**4dab**).

To a round bottomed flask equipped with a magnetic stirrer bar, Dean-Stark apparatus (10 mL trap volume) and condenser, were added *p*-tolualdehyde (0.59 mL, 5.0 mmol), benzylamine (0.66 mL, 6.0 mmol), DABCO (0.28 g, 2.5 mmol), PhCOOH (0.34 g, 2.5 mmol) and PhMe (25 mL). The solution was stirred at reflux for 30 min, after which time 2-cyclohexenone (0.48 mL, 5.0 mmol) followed by another portion (0.24 mL, 2.5 mmol) after 2 h. After a further 1.5 h at reflux, the reaction mixture was cooled to room

temperature, washed with sat. NaHCO_3 (aq) (2×25 mL) and then distilled water (1×25 mL). The organic layer was separated and dried (MgSO_4), filtered and the solvent evaporated *in vacuo* to yield a crude oil. Silica gel column chromatography using Et_2O / hexane (1:4) afforded *N*-benzyl-2-(4-methylbenzyl)aniline (**4dab**) (R_F 0.54, 1.44 g, 70 %) which crystallized as a white solid (m.p. $63 - 65^\circ\text{C}$) from Et_2O . ^1H -NMR. (400 MHz, CDCl_3): δ 2.35 (s, 3H, $-\text{CH}_3$), 3.89 (s, 2H, $\text{Ar}-\text{CH}_2-\text{Ar}$), 3.94 (s, 1H, NH), 4.26 (s, 2H, $\text{N}-\text{CH}_2-\text{Ar}$), 6.64 (d, $J = 7.7$ Hz, 1H, ArH), 6.75 (td, $J = 7.4, 1.1$ Hz, 1H, ArH), 7.32 – 7.02 (m, 11H, ArH); ^{13}C -NMR. (100 MHz, CDCl_3): δ 21.2 ($-\text{CH}_3$), 38.1 ($\text{Ar}-\text{CH}_2-\text{Ar}$), 48.2 ($\text{N}-\text{CH}_2-\text{Ar}$), 111.1, 117.4, 127.2, 2×127.4 , 127.9, 4×128.6 , 2×129.5 , 130.7 (ArCH), 125.1, 136.0, 136.4, 139.5, 146.1 (ArC). FT-IR: (KBr) 3432 w, 3026, 2922 w, 2863 w, 1603 s, 1565 s, 1511 s, 1451 s, 1314 m, 1266 m, 1121 w, 1051 w, 1028 w, 913 w, 804 w, 746.5 s, 697 m; (ESI+, MeOH): 288.3, 100 % ($\text{M} + \text{H}^+$), 289.3, 21 % ($\text{M} + 1 + \text{H}^+$); Microanalysis: Found C 87.7 %, H 7.3 %, N 5.0 % Requires C 87.8 % H 7.4 %, N 4.9 %.

1,3-Bis(2-benzylaminobenzyl)benzene (**4eab**).

With water removal by Dean-Stark apparatus (10 mL trap volume), a solution of isophthalaldehyde (0.34 g, 2.5 mmol), DABCO (0.28 g, 2.5 mmol) and PhCOOH (0.34 g, 2.75 mmol) in PhMe (25 mL) was stirred at reflux. After 15 min, benzylamine (0.66 mL, 6.0 mmol) and 2-cyclohexenone (0.48 mL, 5.0 mmol) were added, followed by further aliquots of 2-cyclohexenone after. 1 h (0.48 mL, 5.0 mmol) and 2 h (0.12 mL, 1.25 mmol).

After a further 1.25 h at reflux, the reaction mixture was cooled to room temperature and washed with sat. NaHCO_3 (aq) (2×25 mL) followed by distilled water (1×25 mL). The organic layer was collected and dried with MgSO_4 , filtered and the solvent removed *in vacuo* to yield a crude oil. Silica gel column chromatography eluting with Et_2O / hexane (1:1) afforded 1,3-bis(2-benzylaminobenzyl)benzene (**4eab**) (0.76 g, 65 %) which crystallized as a white solid (m.p. $95 - 97^\circ\text{C}$) from hexane and Et_2O . ^1H -NMR. (400

MHz, CDCl₃): δ 3.79 (s, 4H, Ar-CH₂-Ar), 4.14 (s, 4H, N-CH₂-Ar), 6.56 (dd, J = 8.1, 0.9 Hz, 2H, ArH), 6.66 (td, J = 7.4, 1.1 Hz, 2H, ArH), 7.23 – 6.97 (m, 18H, ArH); ¹³C-NMR. (100 MHz, CDCl₃): δ 2 $\times$ 38.3 (Ar-CH₂-Ar), 2 $\times$ 48.1 (N-CH₂-Ar), 2 $\times$ 111.0, 2 $\times$ 117.4, 2 $\times$ 126.8, 2 $\times$ 127.2, 4 $\times$ 127.3, 2 $\times$ 127.9, 4 $\times$ 128.6, 129.1, 129.2, 2 $\times$ 130.6 (ArCH), 2 $\times$ 124.8, 2 $\times$ 139.5, 2 $\times$ 139.9, 2 $\times$ 146.1 (ArC). FT-IR: (KBr) 3427 w, 3395 w, 3029 w, 2900 w, 2829 w, 1604 m, 1584 m, 1508 s, 1452 m, 1444 m, 1324 w, 1279 w, 1249 w, 1123 w, 1046 w, 1026 w, 751 s, 738 s, 699 s; (ESI+, MeOH): 470, 100 % (M + H⁺), 471, 42 % (M + 1 + H⁺); Microanalysis: Found C 86.9 %, H 7.0 %, N 6.0 % Requires C 87.1 % H 6.9 %, N 6.0 %.

N-[2-(1*H*-indol-3-yl)ethyl]-2-(4-methylbenzyl)aniline (**4dad**).

With water removal by Dean-Stark apparatus (10 mL trap volume), a solution of tryptamine (0.80 g, 6.0 mmol), *p*-tolualdehyde (0.59 mL, 5.0 mmol), 2-cyclohexenone (0.48 mL, 5.0 mmol), DABCO (0.28 g, 2.5 mmol) and PhCOOH (0.336 g, 2.75 mmol) in PhMe (25 mL) was heated at reflux for 1 h 25 min.

The solvent was evaporated *in vacuo* and the residue dissolved in CH₂Cl₂. The solution was washed with sat. NaHCO₃ (aq) (2 $\times$ 25 mL) then with distilled water (1 $\times$ 25 mL). The organic layer was collected and dried with MgSO₄, filtered and the solvent evaporated *in vacuo* to give a crude oil. Silica gel column chromatography using Et₂O / hexane (1:4) afforded *N*-[2-(1*H*-indol-3-yl)ethyl]-2-(4-methylbenzyl)aniline (**4dad**) (1.12 g, 66 %) as a white solid (m.p. 63 – 65 °C). ¹H-NMR. (200 MHz, CDCl₃): δ 2.26 (s, 3H, CH₃), 2.93 (t, J = 6.7 Hz, 2H, NH-CH₂-CH₂-), 3.36 (t, J = 6.8 Hz, 2H, NH-CH₂-CH₂-), 3.63 (s, 1H, NH), 3.66 (s, 2H, Ar-CH₂-Ar), 6.71 – 6.64 (m, 3H, ArH), 7.26 – 6.85 (m, 12 H, ArH), 7.52 (d, J = 7.52, 1H, ArH), 7.62 (s, 1H, NH); ¹³C-NMR. (50 MHz, CDCl₃): δ 21.2 (CH₃), 25.2 (CH₃), 38.5 (Ar-CH₂), 53.2 (N-CH), 112.1, 117.0, 125.9 $\times$ 2, 126.8, 127.8, 128.6 $\times$ 2, 128.7 $\times$ 2, 129.6 $\times$ 2, 130.7 (ArCH), 124.9, 136.2, 145.4 $\times$ 2 (ArC). FT-

IR: (KBr) 3352 w, 3338 w, 3241 w, 3211 w, 3179 w, 3046 w, 3018 w, 2949 w, 2914 w, 2848 w, 1604 m, 1585 m, 1499 s, 1458 s, 1444 m, 1432 m, 1356 w, 1336 w, 1292 w, 1249 m, 1235 m, 1198 w, 1100 w, 1082 w, 1047 w, 1022 w, 1008 w, 969 w, 918 w, 801 m, 742 s, 712 w; (ESI⁺, MeOH): 341, 100 % (M + H⁺), 342, 26 % (M + 1 + H⁺); Microanalysis: Found C 84.4 %, H 7.3 %, N 8.0 % Requires C 84.7 % H 7.1 %, N 8.2 %.

N-benzyl-[2-benzyl-5-(tolyl)]aniline (**4abb**).

With water removal by Dean-Stark apparatus (10 mL trap volume), a solution of PhCHO (0.51 mL, 5.0 mmol), benzylamine (1.64 mL, 15.0 mmol) and 3-(4-methylphenyl)cyclohex-2-enone (0.22 g, 1.15 mmol) in PhMe (20 mL) was heated at reflux. Aliquots of 3-(4-methylphenyl)cyclohex-2-enone (each 0.22 g, 1.15 mmol) were added after 1.5 h, 3 h, 4.5h (0.215 g, 1.15 mmol) and 8 h. The reaction was continued for another 12 h without further additions.

The solvent and volatile reagents were removed *in vacuo* to yield an oil. Silica gel column chromatography using EtOAc / hexane (1:4) afforded *N*-benzyl-[2-benzyl-5-(tolyl)]aniline (**4abb**). (1.21 g, 66 %) as a colorless solid (m.p. 99 – 100°C): ¹H-NMR. (400 MHz, CDCl₃): δ 2.37 (s, 3H, -CH₃), 3.94 (s, 3H, Ar-CH₂-Ar, NH), 4.31 (s, 2H, N-CH₂-Ar), 6.83 (d, *J* = 1.7 Hz, 1H, ArH), 6.93 (dd, *J* = 7.6, 1.8 Hz, 1H, ArH), 7.14 – 7.10 (m, 3H, ArH), 7.32 – 7.18 (m, 10H, ArH); 7.42 (d, *J* = 5.1 Hz, 2H, ArH); ¹³C-NMR. (100 MHz, CDCl₃): δ 21.3 (-CH₃), 38.2 (Ar-CH₂-Ar), 48.4 (N-CH₂-Ar); 109.9, 116.2, 126.7, 2 × 127.1, 127.3, 2 × 127.6, 4 × 128.8, 2 × 128.9, 2 × 129.5, 131.1 (ArCH); 123.9, 136.9, 139.2, 2 × 139.5, 141.1, 146.4 (ArC). FT-IR: (KBr) 3399 w, 3030 w, 2914 w, 2862 w, 1608 m, 1579 m, 1561 s, 1529 w, 1504 s, 1492 m, 1474 m, 1451 m, 1426 m, 1396 m, 1312 m, 1246 m, 1176 w, 1139 w, 1074 w, 1029 w, 935 w, 910 w, 858 w, 820 s, 792 s, 759 s, 739 s, 700 s; (ESI⁺, MeOH): 364, 100 % (M + H⁺), 365, 39 % (M + 1 + H⁺); Microanalysis: Found C 89.2 % H 7.0 %, N 3.9%. Requires C 89.2 %, H 6.9 %, N 3.9 %.

N,N-dibenzyl-4-benzylaniline (**5aac**).

With water removal by Dean-Stark apparatus (10 mL trap volume), a solution of PhCHO (0.51 mL, 5.0 mmol), dibenzylamine (1.39 mL, 7.0 mmol), 2-cyclohexenone (0.48 mL, 5.0 mmol), DABCO (0.28 g, 2.5 mmol) and PhCOOH (0.34 g, 2.75 mmol) in PhMe (25 mL) was heated with stirring at reflux. 2-Cyclohexenone (0.24 mL, 2.5 mmol) was added portionwise after 2h, 4h and 5.5 h, after which time, the reaction was left for another 2.5 h.

The reaction mixture was washed with sat. NaHCO₃ (aq) (2 × 25 mL) then with distilled water (1 × 25 mL). The organic layer was collected, dried with MgSO₄, filtered and the solvent removed *in vacuo* to yield an oil, which was subjected to column chromatography on Silica gel with Et₂O / hexane (1:4) as eluant. *N,N*-dibenzyl-4-benzylaniline (**5aac**) (1.17 g, 64 %) was obtained as a colorless, highly crystalline solid (m.p. 105 - 107°C). ¹H-NMR. (300 MHz, CDCl₃): δ 3.85 (s, 2H, Ar-CH₂-Ar); 4.61 (s, 4H, Ar-CH₂-N); 6.66 (d, *J* = 8.8 Hz, 2H, ArH); 6.97 (d, *J* = 8.8 Hz, 2H, ArH); 7.13 – 7.33 (m, 15H, ArH); ¹³C-NMR. (100 MHz, CDCl₃): δ 41.2 (Ar-CH₂-Ar), 2 × 54.6 (N-CH₂-Ar); 2 × 112.9, 2 × 126.0, 4 × 126.9, 2 × 127.0, 2 × 128.5, 4 × 128.8, 129.1, 2 × 129.8 (ArCH); 129.8, 2 × 139.0, 142.1, 147.8 (ArC). FT-IR: (KBr) 3059 w, 3026 w, 2912 w, 2862 w, 1611 s, 1522 s, 1492 s, 1450 m, 1401 s, 1361 m, 1231 s, 1073 w, 1025 w, 957 m, 790 m, 764 m, 736 s, 700 s; (ESI⁺, MeOH): 364, 100 % (M + H⁺), 365, 29 % (M + 1 + H⁺); Microanalysis: Found C 89.4 % H 7.0 %, N 3.9 %. Requires C 89.2 %, H 6.9 %, N 3.9 %.

N-Phenyl-2-(4-methylbenzyl)aniline (**4dae**).

With water removal by Dean-Stark apparatus (10 mL trap volume), a solution of aniline (0.55 mL, 6.0 mmol), *p*-tolualdehyde (0.59 mL, 5.0 mmol), 2-cyclohexenone (0.48 mL, 5.0 mmol), DABCO (0.28 g, 2.5 mmol) and PhCOOH (0.34 g, 2.75 mmol) in PhMe (25 mL) was stirred at reflux. 2-Cyclohexenone was added in two equal portions (each 0.48 mL, 5.0 mmol) after 2 h and 4.5 h. After a further 2.5 h, the reaction was cooled and the mixture washed with sat. NaHCO₃ (aq) (2 × 25 mL) then with distilled water (1 × 25 mL). The organic layer was collected and dried using MgSO₄, filtered and the solvent removed *in vacuo* yielding a crude oil. Silica gel column chromatography using Et₂O / hexane (1:4) afforded *N*-phenyl-2-(4-methylbenzyl)aniline (**4dae**). (**4dae**) (0.91 g, 67 %) as a clear oil. ¹H-NMR. (400 MHz, CDCl₃): δ 2.46 (s, 3H, -CH₃), 4.06 (s, 2H, Ar-CH₂-Ar), 5.47 (s, 1H, NH), 6.95 (dd, *J* = 8.6, 1.0 Hz, 2H, ArH), 6.99 (dd, *J* = 7.2, 0.9 Hz, 1H, ArH), 7.11 (td, *J* = 7.4, 1.2 Hz, 1H, ArH), 7.20 (d, *J* = 8.1 Hz, 2H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H, ArH), 7.35 – 7.26 (m, 4H, ArH), 7.41 (dd, *J* = 8.0, 0.9 Hz, 1H, ArH); ¹³C-NMR. (100 MHz, CDCl₃): δ 21.2 (Ar-CH₃), 38.1 (Ar-CH₂-Ar), 2 × 117.4, 119.8, 120.5, 122.3, 127.6, 2 × 128.6, 2 × 129.4, 2 × 129.7, 131.4 (ArCH), 131.5, 136.1, 136.6, 141.6, 144.2 (ArC). FT-IR: (KBr) 3404 m, 3046 m, 3022 m, 2919 w, 1593 s, 1581 s, 1514 s, 1502 s, 1477 s, 1458 s, 1419 m, 1302 s, 1248 m, 1175 w, 1155 w, 1103 w, 1078 w, 1045 w, 1028 w, 917 w, 881 w, 828 w, 794 m, 752 s, 694 s; (ESI+, MeOH): 274, 100 %; Microanalysis: Found C 87.9 % H 7.0 % N 5.0 % Requires C 87.9 % H 7.0 %, N 5.1 %.

N-Benzyl-2-furfurylaniline (**4fab**).

With a Dean-Stark apparatus for water removal (10 mL trap volume), a solution of furfural (0.41 mL, 5.0 mmol), benzylamine (0.66 mL, 6.0 mmol), 2-cyclohexenone (0.48 mL, 5.0 mmol), DABCO (0.28 g, 2.5 mmol) and PhCOOH (0.34 g, 2.75 mmol) in PhMe (25 mL) was stirred at reflux for 2 h.

The reaction mixture was cooled, washed with sat. NaHCO_3 (aq) (2×25 mL) and with distilled water (1×25 mL). The organic layer was collected and dried using MgSO_4 , filtered and the solvent removed *in vacuo* to yield an oil. Silica gel column chromatography using Et_2O / hexane (1:9) afforded *N*-benzyl-2-furfurylaniline (**4fab**) (1.00 g, 76 %) as a clear oil. ^1H -NMR. (400 MHz, CDCl_3): δ 3.89 (s, 2H, $-\text{CH}_2-$), 4.19 (b s, 1H, NH), 4.31 (s, 2H, $-\text{CH}_2-$), 5.99 (d, $J = 3.2$ Hz, 1H, ArH), 6.27 (dd, $J = 3.1, 1.9$ Hz, 1H, ArH), 6.63 (d, $J = 7.9$ Hz, 1H, ArH), 6.70 (td, $J = 7.4, 0.8$ Hz, 1H, ArH), 7.08 (dd, $J = 7.4, 1.2$, ArH), 7.12 (td, $J = 7.7, 1.5$, ArH), 7.32 – 7.15 (m, 6H, ArH). ^{13}C NMR (100 MHz, CDCl_3): δ 31.3, 48.3 ($-\text{CH}_2-$), 106.6, 110.6, 111.4, 117.7, 127.3, 2×127.6 , 128.4, 2×128.8 , 130.5, 141.7 (ArCH), 122.6, 139.5, 146.2, 153.5 (ArC); FT-IR: (KBr) 3435 w, 3064 w, 3029 w, 2895 w, 2846 w, 1604 s, 1586 s, 1508 s, 1452 s, 1322 m, 1261 m, 1162 m, 1144 m, 1072 m, 1052 w, 1009 m, 936 w, 884 w, 806 w, 747 s, 729 s, 697 s; (ESI+, MeOH): Found: 264.1385 Required: 264.1388 Microanalysis: Found C 82.3 % H 6.3 % N 5.4 % Requires C 82.1 % H 6.5 %, N 5.3 %.

N-(2-phenylethyl)-2-(4-nitrobenzyl)aniline (**4gaf**)

With Dean-Stark apparatus fitted (10 mL trap volume), a solution of 4-nitrobenzaldehyde (0.76 g, 5.0 mmol), 2-phenylethylamine (0.75 mL, 6.0 mmol), 2-cyclohexenone (0.48 mL, 5.0 mmol). DABCO (0.28 g, 2.5 mmol) and PhCOOH (.34 g, 2.75 mmol) in toluene (25 mL) was stirred and refluxed. After 3 h, 2-cyclohexenone was added to the reaction and was left to react for another 1.5 h.

The reaction mixture was cooled, washed with sat. NaHCO_3 (aq) (2×25 mL) and with distilled water (1×25 mL). The organic layer was collected and dried using MgSO_4 , filtered and the solvent removed *in vacuo* to yield an oil. Silica gel column chromatography using Et_2O / hexane (1:9) afforded *N*-(2-phenylethyl)-2-(4-nitrobenzyl)aniline (**4gaf**) (1.41 g, 85 %) as an orange oil ^1H -NMR. (400 MHz, CDCl_3):

δ 2.85 (t, J = 6.6 Hz, 2H, -CH₂-); 3.36 (t, J = 6.7 Hz, 2H, -CH₂-); 3.83 (s, 2H, Ar-CH₂-Ar); 6.77 – 6.73 (m, 2H, ArH); 7.02 (dd, J = 7.7, 1.6 Hz, 1H, ArH); 7.06 (dd, J = 7.9, 1.6 Hz, 2H, ArH); 7.13 (d, J = 8.9 Hz, 2H, ArH); 7.14 – 7.25 (m, 4H, ArH); 8.01 (d, J = 8.8 Hz, 2H, ArH). ¹³C-NMR. (50 MHz, CDCl₃): δ 35.2, 38.0 (-CH₂-CH₂-); 44.6 (Ar-CH₂-Ar); 111.5, 117.8, 2 $\times$ 124.0, 126.7, 2 $\times$ 128.7, 2 $\times$ 128.8, 2 $\times$ 129.2, 131.0 (ArCH); 123.2, 138.9, 146.0, 146.7, 147.4 (ArC); FT-IR: (KBr) 3422 w, 3064 w, 3026 w, 2924 w, 2850 w, 1603 s, 1585 s, 1513 s, 1464 s, 1454 s, 1348 s, 1316 s, 1263 m, 1179 m, 1110 m, 1081 w, 1051 w, 1015 w, 922 w, 858 s, 834 m, 754 s, 734 s, 701 s. (ESI+, MeOH): 333, 100 % (M + H⁺), 334, 24 % (M + 1 + H⁺); Microanalysis: Found C 75.9 % H 6.0 % N 8.5 % Requires C 75.9 %, H 6.1 %, N 8.4 %.

Current Data Parameters
 NAME ar0419
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20050303
 Time 17.08
 INSTRUM spect
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 PULPROG zg
 TD 16384
 SOLVENT CDCl3
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 DS 2
 SWH 2397.602 Hz
 FIDRES 0.182859 Hz
 AQ 2.7329011 sec
 RG 256
 DW 166.800 usec
 DE 20.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====

NUC1 1H
 P1 10.00 usec
 PL1 0.00 dB
 SFO1 200.1311007 MHz

F2 - Processing parameters

SI 32768
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 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00