Supporting Information

for

A Dramatic Effect of Aryloxo Ligands on the Titanium-Catalyzed Hydroamination of Alkynes

Vivek Khedkar, Annegret Tillack, and Matthias Beller

Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V., Buchbinderstr. 5-6, 18055 Rostock, Germany. E-mail: matthias.beller@ifok.uni-rostock.de

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere. Starting materials were used as received from Aldrich, Fluka, Acros and Strem. Toluene was distilled under argon from sodium before use. Methanol (anhydrous) was purchased from Fluka and was not further purified before use. Amines were distilled from CaH_2. Alkynes were degassed, flushed with argon and stored over molecular sieves (4 Å).

Titanium catalyst **1** was synthesized according to a literature procedure.[1] *N*-benzyl-2-octylidene-amine/*N*-Benzyl-octylidene-amine were isolated after distillation of the crude hydroamination mixture. All amines shown in Tables 2-4 were isolated by column chromatography. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS and IR spectroscopy. New compounds were further characterized by elemental analysis and /or HRMS (high-resolution mass spectrometry). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer. All ^{1}H NMR spectra are reported in δ units parts per million (ppm) downfield from tetramethylsilane. All ^{13}C NMR spectra are reported in δ units ppm relative to the central line of the triplet for $CDCl_3$ at δ = 77.00 or relative to the central line of the quintet for CD_2Cl_2 at δ = 54.00. EI mass spectra were recorded on an AMD 402

spectrometer (70 eV, AMD Intectra GmbH). IR spectra were recorded on a Nicolet Magna 550. Elemental analysis were determined by C/H/N/S-Analysator 932 (Leco). GC was performed on a Hewlett Packard HP 6890 chromatograph with a 30 m HP5 column. All yields reported in Tables 1-4 refer to GC yields using dodecane or hexadecane as an internal standard. In all cases of known compounds the analytical data fits with literature data.

Synthesis of complex (1) [Ti(NMe$_2$)$_2$(OAr)$_2$] (Ar = 4-Methyl-2,6-di-*tert*-butylphenolate): 8.70 g (39.7 mmol) 4-methyl-2,6-di-*tert*-butylphenol was added to 1.58 g (7.05 mmol) tetrakis(dimethylamido)titanium **2** in 80 mL toluene. After stirring at room temperature for 12 h and heating at 120 °C for 14 h in oil bath the reaction mixture was cooled to room temperature and the solvent was evaporated in vacuum to give a green-brown oil. After addition of 40 mL of diethyl ether orange crystals were obtained. The crystals were collected and washed with pentane (3 × 15 mL). After drying under vacuum 2.93 g (72 %) of complex **1** were obtained.

[Ti(NMe$_2$)$_2$(OAr)$_2$] (Ar = 4-Methyl-2,6-di-*tert*-butylphenolate) 1[1]: Orange solid, yield: 71%, melting point 198 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.01 (s, 2H), 3.38(s, 6H), 2.25 (s, 3H), 1.42 (s, 18H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 161.6, 140.1, 129.1, 126.9, 50.0, 35.9, 31.9, 21.4. MS (EI, 70 eV) *m/z*: 574 (9) [M^+], 529 (19), 355 (100), 299 (52), 243 (21), 57 (15). FT IR (Nujol, cm^{-1}): 2818, 2773, 1411, 1224, 951, 872, 602. Anal. Calcd. for $C_{34}H_{58}N_2O_2Ti$: C, 71.03; H, 10.18; N, 4.88. Found: C, 70.72; H, 10.47; N, 4.75.

General Procedure for the Hydroamination Reaction: In an Ace-pressure tube under an argon atmosphere a solution of the catalyst **1** (5 to 10 mol%) in 2 ml toluene was added to a mixture of alkyne (1.5 mmol) and amine (1.8 mmol). This mixture was heated at the given temperature for the specified time (see Tables 1-4). After cooling to room temperature the mixture was used directly for further reduction. In case of isolation of the imine the product purified by fractional distillation *in vacuo* (Table 1).

General Procedure for Reduction Step: A suspension of $NaCNBH_3$ 188.5 mg (3.0 mmol) and $ZnCl_2$ 204.4 mg (1.5 mmol) in MeOH (5 mL) was added to a solution of the crude hydroamination product in toluene (2 mL). After stirring for 20 h at room temperature, the mixture was filtered. The solid residue was washed with CH_2Cl_2 (30 mL). Then saturated Na_2CO_3 solution (15 mL) was added to the filtrate. After extraction with CH_2Cl_2 (6×30 mL) the organic layer was dried over $MgSO_4$. Evaporation of the organic solvent under vacuum and column chromatography on silica gel afforded the pure amine derivative.

***N*-Benzyl-2-octylidene-amine[2]/*N*-benzyl-octylidene-amine (ratio 3.2:1)** (Table 1, entry 9): colorless oil; yield: 98% (GC); bp 97–98 °C/0.1 mbar. ^{1}H NMR for main product ($CDCl_3$, 400 MHz): δ = 7.30-7.14 (m, 5H), 4.45 + 4.42 (s, 2H), 2.20-2.30 (m, 2H), 2.01 + 1.84 (s, 3H), 1.60-1.40 (m, 2H), 1.25 (m, 6H), 0.83 (t, 3H). ^{13}C NMR for main product ($CDCl_3$, 100 MHz): δ = 171.8 + 171.4, 140.5, 128.3, 127.7 +127.6, 126.4, 55.0 + 54.6, 42.9, 31.7 + 31.5, 29.1 + 29.0, 26.6 + 26.3, 22.5, 17.5, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 217 (2) [M^+], 202 (1), 188 (1), 174 (6), 160 (15), 147 (89), 146 (57), 91 (100). FT IR (neat, cm^{-1}): 1663 (C=N).

***N*-(2-Octyl)aniline[3]** (Table 2, entry 1): light yellow oil; yield: 92% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.05-7.11 (m, 2H), 6.55-6.59 (m, 1H), 6.47-6.50 (m, 2H), 3.36 (sext, *J* = 6.3 Hz, 1H), 3.22 (bs, 1H), 1.53-1.57 (m, 2H), 1.16-1.44 (m, 8H), 1.09 (d, *J* = 6.3 Hz, 3H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 147.7, 129.2, 116.7, 113.0, 48.4, 37.2, 31.8, 29.3, 26.1, 22.6, 20.7, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 205 (11) [M^+], 190 (6), 120 (100), 106 (8), 91 (6), 77 (9), 43 (5). FT IR (neat, cm^{-1}): 3405, 3008, 3051, 3018, 2958, 2927, 2856, 1602, 1505, 1457, 1427, 1376, 1318, 1258, 1179, 1154, 1075, 1032, 993, 865, 747, 691. HRMS Calcd. for $C_{14}H_{23}N$: 205.18304. Found: 205.18420.

***N*-(2-Octyl)-4-methylaniline** (Table 2, entry 2): light brown oil; yield: 98% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.90-6.87 (m, 2H), 6.40-6.43 (m, 2H), 3.32 (sext, *J* = 6.1 Hz, 1H), 3.18 (bs, 1H), 2.14 (s, 3H), 1.51-1.45 (m, 2H), 1.15-1.41 (m, 8H), 1.07 (d, *J* = 6.1 Hz, 3H),

0.80 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 145.4, 129.7, 125.9, 113.3, 48.7, 37.2, 31.8, 29.3, 26.1, 22.6, 20.7, 20.3, 14.0. MS (EI, 70 eV) *m/z* (relative intensity) = 219 (14) [M^+], 204 (6), 134 (100), 120 (4), 106 (6), 91 (11), 77 (5), 43 (5). FT IR (neat, cm^{-1}): 3403, 3006, 3049, 3016, 2958, 2926, 2856, 1619, 1519, 1457, 1404, 1376, 1317, 1301, 1250, 1182, 1157, 1120, 1040, 874, 806, 725, 703. Anal. Calcd. for $C_{14}H_{23}N$: C, 82.13; H, 11.49; N, 6.39. Found: C, 81.93; H, 11.21; N, 6.26. HRMS Calcd. for $C_{15}H_{25}N$: 219.19870. Found: 219.20062.

***N*-(2-Octyl)-2-methylaniline** (Table 2, entry 3): light brown oil; yield: 94% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.00-7.04 (m, 1H), 6.94-6.97 (m, 1H), 6.50-6.54 (m, 2H), 3.42 (sext, J = 6.1 Hz, 1H), 3.20 (bs, 1H), 2.03 (s, 3H), 1.48-1.57 (m, 2H), 1.16-1.42 (m, 8H), 1.12 (d, J = 6.3 Hz, 3H), 0.80 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 145.5, 130.1, 127.0, 121.5, 116.1, 109.9, 48.2, 37.3, 31.8, 29.3, 26.1, 22.6, 20.9, 17.5, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 219 (12) [M^+], 204 (6), 134 (100), 120 (4), 106 (3), 91 (7), 43 (4). FT IR (neat, cm^{-1}): 3431, 3015, 2958, 2927, 2855, 1606, 1512, 1477, 1456, 1377, 1316, 1259, 1162, 1119, 1051, 873, 743, 715. Anal. Calcd. for $C_{14}H_{23}N$: C, 82.13; H, 11.49; N, 6.39. Found: C 81.71; H, 11.32; N, 6.31. HRMS Calcd. for $C_{15}H_{25}N$: 219.19870. Found: 219.19940.

***N*-(2-Octyl)-3-methylaniline** (Table 2, entry 4): light brown oil; yield: 91% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.94-6.98 (m, 1H), 6.38-6.41 (m, 1H), 6.28-6.33 (m, 2H), 3.35 (sext, J = 6.1 Hz, 1H), 3.28 (bs, 1H), 2.18 (s, 3H), 1.43-1.53 (m, 2H), 1.13-1.40 (m, 8H), 1.07 (d, J = 6.1 Hz, 3H), 0.80 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 147.7, 138.9, 129.1, 125.4, 117.6 113.3, 110.1, 48.3, 37.2, 31.8, 29.3, 26.1, 22.6, 21.6, 20.8, 14.0. MS (EI, 70 eV) *m/z* (relative intensity) = 219 (17) [M^+], 204 (9), 134 (100), 120 (9), 106 (5), 91 (11), 77 (6), 43 (7). FT IR (neat, cm^{-1}): 3402, 3042, 2957, 2927, 2856, 1604, 1589, 1510, 1457, 1404, 1376, 1326, 1304, 1262, 1179, 993, 842, 767, 691. Anal. Calcd. for $C_{14}H_{23}N$: C, 82.13; H,

11.49; N, 6.39. Found: C, 81.74; H, 11.49; N, 6.39. HRMS Calcd. for $C_{15}H_{25}N$: 219.19870. Found: 219.20014.

***N*-(2-Octyl)-4-fluoroaniline** (Table 2, entry 5): light brown oil; yield: 97% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.75-6.80 (m, 2H), 6.39-6.44 (m, 2H), 3.28 (sext, *J* = 6.1 Hz, 1H), 3.19 (bs, 1H), 1.44-1.52 (m, 2H), 1.13-1.40 (m, 8H), 1.07 (d, *J* = 6.3 Hz, 3H), 0.80 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 154.2, 144.0, 115.4, 113.9, 49.2, 37.1, 31.8, 29.3, 26.0, 22.6, 20.6, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 223 (8) [M^+], 208 (4), 138 (100), 124 (5), 111 (5), 95 (3), 77 (1), 57 (2), 43 (6). FT IR (neat, cm^{-1}): 3416, 3035, 2958, 2928, 2856, 1613, 1510, 1458, 1402, 1377, 1315, 1221, 1155, 1098, 818, 770. Anal. Calcd. for $C_{14}H_{22}FN$: C, 75.29; H, 9.93; N, 6.27. Found: C, 74.95; H, 9.47; N, 6.27. HRMS Calcd. for $C_{14}H_{22}FN$: 223.17363. Found: 223.17282.

***N*-(2-Octyl)-4-chloroaniline** (Table 2, entry 6): light brown oil; yield: 98% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.99-7.03 (m, 2H), 6.38-6.42 (m, 2H), 3.35 (bs, 1H), 3.31 (sext, *J* = 6.3d Hz, 1H), 1.42-1.51 (m, 2H), 1.15-1.32 (m, 8H), 1.07 (d, *J* = 6.3 Hz, 3H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 146.2, 129.0, 121.1, 114.0, 48.6, 37.0, 31.8, 29.3, 26.0, 22.5, 20.6, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 239 (13) [M^+], 224 (5), 154 (100), 140 (4), 127 (4), 91 (4), 77 (3), 57 (2), 43 (6). FT IR (neat, cm^{-1}): 3415, 3024, 2958, 2928, 2856, 1600, 1499, 1451, 1400, 1377, 1317, 1239, 1176, 1093, 813, 724, 675. Anal. Calcd. for $C_{14}H_{22}ClN$: C, 70.13; H, 9.25; N 5.84. Found: C, 69.98; H, 9.22; N, 5.76. HRMS Calcd. for $C_{14}H_{22}ClN$: 239.14224. Found: 239.14193.

***N*-(2-Octyl)-4-methoxyaniline[4]** (Table 2, entry 7): brown oil; yield: 96% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.67-6.71 (m, 2H), 6.45-6.48 (m, 2H), 3.66 (s, 3H), 3.28 (sext, *J* = 6.1 Hz, 1H), 3.05 (bs, 1H), 1.43-1.53 (m, 2H), 1.16-1.35 (m, 8H), 1.06 (d, *J* = 6.3 Hz, 3H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 151.7, 141.9, 114.9, 114.6, 55.8, 49.5, 37.2, 31.8, 29.3, 26.1, 22.6, 20.8, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 235 (43) [M^+],

220 (19), 150 (100), 136 (11), 122 (11), 108 (15), 95 (5), 77 (5), 57 (7), 43 (14). FT IR (neat, cm^{-1}): 3394, 3027, 2957, 2927, 2855, 1618, 1511, 1465, 1406, 1376, 1294, 1234, 1179, 1156, 1041, 909, 818, 756, 733, 647. Anal. Calcd. for $C_{15}H_{25}NO$: C, 76.55; H, 10.71. Found: C, 76.44; H, 10.20. HRMS Calcd. for $C_{15}H_{25}NO$: 235.19362. Found: 235.19272.

***N*-(2-Octyl)-3,4,5-trimethoxyaniline** (Table 2, entry 8): brown oil; yield: 95% (GC). ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.74 (s, 2H), 3.74 (s, 6H), 3.68 (s, 3H), 3.31 (sext, *J* = 6.1 Hz, 1H), 3.27 (bs, 1H), 1.43-1.57 (m, 2H), 1.16-1.39 (m, 8H), 1.10 (d, *J* = 6.1 Hz, 3H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 153.9, 144.4, 129.6, 61.0, 55.8, 48.8, 37.2, 31.7, 29.3, 26.0, 22.5, 20.8, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 295 (67) [M^+], 280 (100), 252 (5), 210 (65), 182 (5), 168 (31), 153 (4), 140 (10), 105 (31), 91 (11), 77(7), 57 (15), 43 (12). FT IR (neat, cm^{-1}): 3376, 2958, 2928, 2855, 1611, 1509, 1453, 1416, 1376, 1236, 1206, 1186, 1127, 1016, 925, 804, 777, 725, 636. Anal. Calcd. for $C_{17}H_{29}NO_3$: C, 69.12; H, 9.89; N, 4.74. Found: C, 69.58; H, 10.53; N, 4.84. HRMS Calcd. for $C_{17}H_{29}NO_3$: 295.21475. Found: 295.21261.

***N*-(2-Octyl)-2-isopropylaniline** (Table 2, entry 9): light yellow oil; yield: 98% (GC). ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.99-7.06 (m, 2H), 6.53-6.62 (m, 2H), 3.43 (sext, *J* = 6.3 Hz, 1H), 3.38 (bs, 1H), 2.74 (sept. *J* = 6.7 Hz, 1H), 1.48-1.57 (m, 2H), 1.19-1.42 (m, 8H), 1.17 (d, *J* = 6.7 Hz, 6H), 1.11 (d, *J* = 6.1 Hz, 3H), 0.80 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 144.2, 131.7, 126.6, 124.9, 116.4, 110.7, 48.3, 37.3, 31.8, 29.3, 26.1, 22.6, 22.25, 22.23, 20.9, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 247 (13) [M^+], 232 (8), 205 (3), 162 (100), 146 (4), 134 (8), 120 (5), 106 (3), 94 (3), 77 (4), 43 (7). FT IR (neat, cm^{-1}): 3438, 3066, 3037, 2959, 2927, 2856, 1603, 1508, 1454, 1311, 1257, 1164, 1083, 1040, 926, 802, 742, 621. Anal. Calcd. for $C_{17}H_{29}N$: C, 82.52; H, 11.81; N, 5.66. Found: C, 81.99; H, 11.57; N, 5.68. HRMS Calcd. for $C_{17}H_{29}N$: 247.23000. Found: 247.22917.

***N*-(2-Octyl)-2,4-difluoroaniline** (Table 2, entry 10): colorless oil; yield: 99% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.66-6.76 (m, 2H), 6.51-6.58 (m, 1H), 3.60 (sext, *J* = 6.1 Hz, 1H), 3.17 (bs, 1H), 1.48-1.50 (m, 2H), 1.16-1.40 (m, 8H), 1.05 (d, *J* = 6.3 Hz, 3H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 152.4, 125.4, 117.3, 111.4, 51.1, 38.1, 31.7, 29.2, 25.9, 22.6, 21.7, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 241 (7) [M^+], 226 (4), 156 (100), 142 (5), 129 (9), 109 (4), 43 (5). FT IR (neat, cm^{-1}): 3393, 2958, 2928, 2857, 1622, 1595, 1496, 1460, 1378, 1278, 1228, 1153, 1063, 989, 876, 764, 705, 650. Anal. Calcd. for $C_{14}H_{21}F_2N$: C, 69.68; H, 8.77; N, 5.80. Found: C, 69.50; H, 8.68; N, 5.62. HRMS Calcd. for $C_{14}H_{21}F_2N$: 241.16420. Found: 241.16130.

***N*-Butyl-*N*-(2-octyl)amine** (Table 3, entry 1): colorless oil; yield: 70% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.50-2.64 (m, 3H), 1.56 (bs, 1H), 1.36-1.43 (m, 2H), 1.17-1.31 (m, 12H), 0.96 (d, *J* = 6.3 Hz, 3H), 0.84 (t, *J* = 7.3Hz, 3H), 0.81 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 54.2, 53.9, 40.1, 32.0, 31.8, 29.5, 29.3, 27.6, 26.9, 22.6, 20.8, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 185 (1) [M^+], 170 (10), 142 (4), 100 (100), 84 (2), 70 (2), 57 (5) 44 (10). FT IR (neat, cm^{-1}): 3452, 2956, 2926, 2855, 1466, 1377, 1220, 1092, 804, 722. HRMS Calcd. for $C_{12}H_{27}N$: 185.21436. Found: 185.21661.

***N*-Benzyl-*N*-(2-octyl)amine[2]** (Table 3, entry 2): colorless oil; yield: 81% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.20-7.18 (m, 4H), 7.13-7.26 (m, 1H), 3.70 (dd, *J* = 13.0 Hz, 2H), 2.57 (sext, *J* = 6.3 Hz, 1H) 2.52 (bs, 1H), 1.34-1.42 (m, 2H), 1.19-1.126 (m, 8H), 0.99 (d, *J* = 6.1 Hz, 3H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 140.9, 128.3, 128.0, 126.7, 52.4, 51.3, 37.0, 31.8, 29.4, 25.9, 22.5, 20.3, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 219 (1) [M^+], 204 (5), 134 (98), 120 (6), 106 (4), 91 (100), 57 (2), 43 (3). FT IR (neat, cm^{-1}): 3446, 3027, 2957, 2926, 2855, 1604, 1494, 1454, 1375, 1155, 1028, 730, 697. HRMS Calcd. for $C_{15}H_{25}N$: 219.19870. Found: 219.19718.

***N*-Cyclooctyl-*N*-(2-octyl)amine** (Table 3, entry 3): colorless oil; yield: 85% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.65-2.71 (m, 1H), 2.59 (sext, *J* = 6.1 Hz, 1H), 1.57-1.67 (m, 4H), 1.50-1.56 (m, 4H), 1.30-1.43 (m, 8H), 1.16-1.25 (m, 8H), 0.93 (d, *J* = 6.3 Hz, 3H), 0.81 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 54.0, 49.5, 37.5, 33.4, 32.3, 31.7, 29.4, 27.3, 27.2, 26.0, 25.7, 24.1, 24.0, 22.5, 20.8, 13.9. MS (EI, 70 eV) *m/z* (relative intensity): 239 (2) [M^+], 224 (5), 196 (4), 182 (4), 168 (32), 154 (100), 140 (14), 126 (22), 112 (9), 98 (5), 84 (6), 70 (24), 56 (21), 44 (70). FT IR (neat, cm^{-1}): 3457, 2923, 2854, 1466, 1374, 1154, 724. HRMS Calcd. for $C_{16}H_{33}N$: 239.26131. Found: 239.25802.

***N*-2-Butyl-*N*-(2-octyl)amine**[5] (Table 3, entry 4): colorless oil; yield: 89% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.52-2.65 (m, 2H), 1.51 (bs, 1H), 1.31-1.44 (m, 2H), 1.15-1.27 (m, 10H), 0.91-0.95 (m, 6H), 0.78-0.83 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 51.2, 49.7, 37.8, 31.8, 30.3, 29.4, 26.0, 22.5, 21.1, 20.6, 14.0, 10.3. MS (EI, 70 eV) *m/z* (relative intensity): 185 (2) [M^+], 170 (15), 156 (47), 100 (100), 84 (3), 70 (5), 44 (47). FT IR (neat, cm^{-1}): 3457, 2961, 2926, 2855, 1742, 1457, 1376, 1260, 1097, 1020, 864, 802, 702. HRMS Calcd. for $C_{12}H_{27}N$: 185.21436. Found: 185.21516.

***N*-(2-Octyl)-1-phenylethylamine (mixture of diastereomers a and b)**[6] (Table 3, entry 5): colorless oil; yield: 72% (GC). (a) ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.19-7.26 (m, 4H), 7.12-7.18 (m, 1H), 3.82 (q, *J* = 6.4 Hz, 1H), 2.30 (sext, *J* = 6.1 Hz, 1H), 1.38-1.46 (m, 2H), 1.26 (d, *J* = 6.1 Hz, 3H), 1.06-1.20 (m, 8H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.78 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 146.0, 128.3, 126.6, 126.4, 54.7, 49.5, 38.0, 31.7, 29.3, 25.9, 25.0, 22.5, 20.0, 14.0. (b) ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.20-7.25 (m, 4H), 7.12-7.18 (m, 1H), 3.80 (q, *J* = 6.5 Hz, 1H), 2.42 (sext, *J* = 6.1 Hz, 1H), 1.38-1.46 (m, 2H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.10-1.22 (m, 8H), 0.87 (d, *J* = 6.3 Hz, 3H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 146.4, 128.3, 126.6, 126.4, 55.1, 50.1, 36.3, 31.8, 29.5, 25.6, 24.6, 22.6, 21.2, 14.0. MS (EI, 70 eV) *m/z* (relative intensity): 233 (2) [M^+], 218 (15), 148 (79),

105 (100), 91 (2), 77 (11), 44 (90). FT IR (neat, cm^{-1}): 3420, 3024, 2958, 2926, 2856, 1602, 1492, 1452, 1370, 1270, 1210, 1153, 1121, 1027, 910, 761, 700. Anal. Calcd. for $C_{16}H_{27}N$: C, 82.34; H, 11.66; N, 6.00. Found: C, 82.84; H, 11.22; N, 5.87. HRMS Calcd. for $C_{16}H_{27}N$: 233.21436. Found: 233.21348.

***N*-(1-Phenylethyl)aniline**[7] (Table 4, entry 1): light brown oil; yield: 72% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.21-7.29 (m, 4H), 7.14-7.16 (m, 1H), 7.00 (t, *J* = 7.3 Hz, 2H), 6.56 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 7.9 Hz, 2H), 4.40(qurt, *J* = 6.8 Hz, 1H), 3.94 (bs, 1H), 1.43 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 147.2, 145.1, 129.0, 128.6, 126.8, 125.8, 117.1, 113.2, 53.4, 25.0. MS (EI, 70 eV) *m/z* (relative intensity): 197 (50) [M^+], 182 (100), 120 (15), 105 (78), 93 (50), 77 (53). FT IR (neat, cm^{-1}): 3410, 3052, 3023, 2965, 2924, 2866, 1601, 1504, 1449, 1318, 1257, 1206, 1180, 1140, 1029, 992, 869, 749, 700, 692. HRMS Calcd. for $C_{14}H_{15}N$: 197.12045. Found: 197.12038.

***N*-[2-(1-Phenylpropyl)]-4-fluoroaniline** (Table 4, entry 2): light yellow oil; yield: 89% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.21-7.19 (m, 2H), 7.13-7.15 (m, 1H), 7.07-7.09 (m, 2H), 6.77-6.84 (m, 2H), 6.43-6.48 (m, 2H), 3.60 (sext, *J* = 6.3 Hz, 1H), 3.30 (bs, 1H), 2.82 (dd, *J* = 13.4 Hz, *J* = 6.3 Hz, 1H), 2.60 (dd, *J* = 13.4 Hz, *J* = 6.3 Hz, 1H), 1.05 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 154.4, 143.5, 138.3, 129.4, 128.3, 126.2, 115.6, 114.2, 50.0, 42.1, 20.1. MS (EI, 70 eV) *m/z* (relative intensity): 229 (4) [M^+], 138 (100), 110 (1), 91 (4), 77 (1), 65 (1). FT IR (neat, cm^{-1}): 3408, 3060, 3027, 2966, 2926, 2871, 1611, 1509, 1453, 1377, 1315, 1252, 1220, 1180, 1155, 1099, 913, 819, 768, 746, 701 631. HRMS Calcd. for $C_{15}H_{16}FN$: 229.12668. Found: 229.12882.

***N*-[2-(1-*N*,*N*-Dimethylpropyl)]-4-methoxyaniline** (Table 4, entry 3): brown oil; yield: 69% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.68-6.72 (m, 2H), 6.53-6.56 (m, 2H), 4.75 (bs, 1H), 3.67 (s, 3H), 3.32 (sext, *J* = 6.3 Hz, 1H), 2.43 (dd, *J* = 12.2 Hz, *J* = 9.3 Hz, 1H), 2.18 (s, 6H), 2.14 (dd, *J* = 12.2 Hz, *J* = 7.1 Hz, 1H), 1.10 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100

MHz,): δ = 152.1, 142.4, 115.1, 114.7, 65.4, 55.7, 47.1, 45.5, 19.6. MS (EI, 70 eV) *m/z* (relative intensity): 208 (18) [M^+], 164 (1), 150 (100), 134 (10), 122 (4), 92 (4), 77 (5), 58 (66), 42 (11). FT IR (neat, cm^{-1}): 3440, 2933, 2856, 2822, 2769, 1617, 1512, 1460, 1367, 1235, 1179, 1137, 1039, 819, 757, 601. HRMS Calcd. for $C_{12}H_{20}N_2O$: 208.15756. Found: 208.15601.

***N*-[2-(1-Cyclopentylpropyl)]-4-chloroaniline** (Table 4, entry 4): brown oil; yield: 97% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.99-7.02 (m, 2H), 6.38-6.41 (m, 2H), 3.35 (sext, *J* = 6.3 Hz, 1H), 3.29 (bs, 1H), 1.78-1.86 (m, 2H), 1.68-1.73 (m, 1H), 1.41-1.54 (m, 4H), 1.30-1.37 (m, 4), 1.08 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 146.2, 129.0, 121.0, 114.0, 48.0, 43.7, 37.1, 33.0, 32.7, 25.0, 24.9, 20.9. MS (EI, 70 eV) *m/z* (relative intensity): 237 (12) [M^+], 222 (4), 154 (100), 140 (7), 91 (3), 77 (2), 41 (9). FT IR (neat, cm^{-1}): 3414, 2950, 2867, 1600, 1512, 1499, 1317, 1253, 1177, 1093, 813, 675. Anal. Calcd. for $C_{14}H_{20}ClN$: C, 70.72; H, 8.48; N 5.89. Found: C, 70.61; H, 8.48; N, 5.95. HRMS Calcd. for $C_{14}H_{20}ClN$: 237.12843. Found: 237.12916.

***N*-Cyclooctyl-*N*-[2-(1-phenylpropyl)]amine** (Table 4, entry 5): colorless oil; yield: 71% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26-7.30 (m, 2H), 7.16-7.21 (m, 3H), 2.97 (sext, *J* = 6.3 Hz, 1H), 2.75-2.81 (m, 1H), 2.72 (dd, *J* = 13.2 Hz, *J* = 6.5 Hz, 1H), 2.56 (dd, *J* = 13.2 Hz, *J* = 6.7 Hz, 1H), 1.28-1.77 (m, 14H), 1.02 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 139.6, 129.2, 128.2, 126.0, 54.0, 51.2, 43.8, 33.4, 31.9, 27.3, 27.2, 25.7, 24.2, 23.7, 20.8. MS (EI, 70 eV) *m/z* (relative intensity): 244 (0.5) [M^+–1], 174 (1), 154 (100), 126 (5), 111 (4), 91 (25), 77 (2), 69 (18), 55 (12), 44 (17). FT IR (neat, cm^{-1}): 3308, 3061, 3026, 2920, 2851, 1602, 1494, 1473, 1452, 1372, 1315, 1136, 1030, 744, 699. HRMS Calcd. for $C_{17}H_{27}N$: 245.21436. Found: 245.21590.

***N*-Benzyl-*N*-[2-(1-cyclopentylpropyl)]amine** (Table 4, entry 6): colorless oil; yield: 88% (GC). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.28-7.31 (m, 4H), 7.20-7.26 (m, 1H), 3.78 (dd, *J* = 13.0 Hz, 2H), 2.69 (sext, *J* = 6.3 Hz, 1H), 1.84 (sept., *J* = 7.3 Hz, 1H), 1.67-1.77 (m, 2H), 1.54-1.63 (m, 2H), 1.44-1.53 (m, 4H), 1.25-1.36 (m, 1H), 1.21 (bs, 1H), 1.08 (d, *J* = 6.3 Hz, 3H), 1.00-1.06 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 140.9, 128.3, 128.0, 126.7, 51.7, 51.4, 43.9, 37.0, 33.0, 32.8, 25.0, 24.9, 20.6. MS (EI, 70 eV) *m/z* (relative intensity): 217 (3) [M^+], 202 (13), 134 (65), 106 (12), 91 (100), 77 (4), 65 (18), 55 (8), 41 (23). FT IR (neat, cm^{-1}): 3318, 3062, 3026, 2950, 2866, 1604, 1558, 1494, 1452, 1372, 1149, 1073, 1028, 730, 697. HRMS Calcd. for $C_{15}H_{23}N$: 217.18304. Found: 217.18367.

References

(1) Duff, A. W.; Kamarudin, R. A.; Lappert, M. F.; Norton, R. J. *J. Chem. Soc. Dalton Trans.* **1986**, 489.

(2) Lopez, R. M.; Fu, G. C. *Tetrahedron* **1997**, *52*, 16349.

(3) Gasc, M. B.; Lattes, P. A. *Tetrahedron* **1978**, *34*, 1943.

(4) Skripko, L. A.; *Khim. Prom*. **1967**, *43*, 343; *Chem. Abstr.* **1968**, *68*, 21615y.

(5) Penido, M. L.; Nelson, D. L.; Vieira, L. Q.; Watson, D. G.; Kusel, J. R. *Parasitology* **1995**, *111*, 177.

(6) Fuller, J. C.; Belisle, C. M.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett*. **1994**, *35*, 5389.

(7) Guijarro, D.; Yus, M. *Tetrahedron* **1993**, *49*, 7761.