Supplementary Material (ESI) for Chemical Communications

N-Dealkylation of Aliphatic Amines and Selective Synthesis of Monoalkylated Aryl Amines

- Supplementary information -

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Experimental Section

General Remarks: All reactions were carried out under an argon atmosphere. Chemicals were purchased from Aldrich, Fluka, Acros and Strem and unless otherwise noted were used without further purification. Amines and anilines were distilled under argon. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS, HRMS and IR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 300 and AV 400 spectrometer. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to the center of solvent resonance ($CDCl_3$: 7.25 (^{1}H), 77.0 (^{13}C)). EI mass spectra were recorded on an AMD 402 spectrometer (70 eV, AMD Intectra GmbH). IR spectra were recorded on a Nicolet Magna 550. GC was performed on a Hewlett Packard HP 6890 chromatograph with a Optima 5 - amine column (Company: Machery-Nagel, 30m x 0.25µm, 0.5µm film thickness, 50-8-200/5-8-260/5-8-280/5-8-300/20).

General procedure for the amination reaction:

In an ACE-pressure tube under an argon atmosphere the Shvo catalyst (0.02 mmol) and the corresponding alkyl amine (2 mmol of alkyl groups) were dissolved in tamylalcohol (0.5 ml) and aniline (4 mmol). The pressure tube was fitted with a Teflon cap and heated at 150 °C for 24 h. The solvent was removed in vacuo, and the crude alkyl aryl amine product is easily purified by column chromatography with pentane/ethyl acetate (20:1).

_N_-Ethylaniline

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.23 (3H, t, ^3J = 7.3 Hz), 3.18 (2H, q, ^3J = 7.3 Hz), 3.51 (1H, s, NH), 6.61-6.65 (2H, m), 6.72 (1H, tt, ^3J = 7.3 Hz, ^4J = 1.0 Hz), 7.16-7.26 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.0 (CH_3), 38.5 (CH_2), 112.8 (2xCH), 117.3 (CH), 129.3 (2xCH), 148.5 (C_q). FT IR (ATR, cm^{-1}): 3401 (br, NH), 3050 (w), 3020 (w), 2968 (w), 2827 (w), 2871 (w), 1596 (m), 1601 (m), 1504 (m), 1318 (m), 1256 (m), 1145 (m), 745 (s), 690 (s). MS (EI, 70 eV) *m/z* (rel. intensity): 121 (42) [M^+], 106 (100) [M^+- CH_3]. HRMS Calcd. for $C_8H_{11}N$: 121.08860. Found: 121.088782.

_N_-Isopropylaniline

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.22 (6H, d, ^3J = 6.4 Hz), 3.45 (1H, s, NH), 3.64 (1H, sept., ^3J = 6.4 Hz), 6.60 (2H, dd, ^3J = 8.5 Hz, ^4J = 1.0 Hz), 6.68 (1H, tt, ^3J = 7.4 Hz, ^4J = 1.0 Hz), 7.18 (2H, dd, ^3J = 8.5 Hz, ^3J = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.1 (CH_3), 44.2 (CH), 113.3 (2xCH), 117.0 (CH), 129.3 (2xCH), 147.6 (C_q). FT IR (ATR, cm^{-1}): 3400 (br, NH), 3050 (w), 3018 (w), 2964 (w), 2828 (w), 2869 (w), 1596 (m), 1600 (m), 1503 (m), 1314 (m), 1254 (m), 1176 (m), 745 (s), 691 (s). MS (EI, 70 eV) *m/z* (rel. intensity): 135 (29) [M^+], 120 (100) [M^+- CH_3]. HRMS Calcd. for $C_9H_{13}N$: 135.10425. Found: 135.103991.

_N_-Propylaniline

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.01 (3H, t, ^3J = 7.2 Hz), 1.65 (2H, sext., ^3J = 7.2 Hz), 3.09 (3H, t, ^3J = 7.2 Hz), 3.63 (1H, s, NH), 6.59-6.64 (2H, m), 6.69 (1H, tt, ^3J = 7.3 Hz, ^4J = 1.0 Hz), 7.14-7.21 (2H, m). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 11.7 (CH_2), 22.7 (CH_2), 45.8 (CH_2), 112.7 (CH), 117.1 (CH), 129.2 (CH), 148.5 (C_q). **IR** (ATR): ν (cm^{-1}) = 3411 (w), 3051 (w), 3021 (w), 2960 (m), 2931 (w), 2872 (w), 1601 (s), 1504 (s), 1476 (m), 1430 (w), 1380 (w), 1319 (m), 1253 (m), 1178 /(m), 1152 (w), 1073 (w), 1030 (w), 992 (w), 866 (w), 745s, 690 (s). **MS** (EI, 70 eV) *m/z* (rel. intensity): 135 (24) [M^+], 106 (100) [M^+- C_2H_5]. **HRMS** (ESI): calcd. for $C_9H_{13}N_1$ ($M+H^+$) 136.11208, found 136.11223.

_N_-Benzylaniline[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.05 (1H, s, NH), 4.34 (2H, s), 6.65 (2H, dd, ^3J = 8.5 Hz, ^4J = 1.1 Hz), 6.72 (1H, tt, ^3J = 7.3 Hz, ^4J = 1.1 Hz), 7.18 (2H, dd, ^3J = 8.5 Hz, ^4J = 7.3 Hz), 7.27-7.40 (5H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 48.4 (CH_2), 112.9 (2xCH), 117.6 (CH), 127.3 (CH), 127.3 (2xCH), 128.7 (2xCH), 129.3 (2xCH), 139.5 (C_q), 148.2 (C_q). FT IR (ATR, cm^{-1}): 3417 (br, NH), 3083 (w), 3051 (w), 3024 (w), 1599 (s), 1503 (s), 1322 (m), 746 (s), 729 (s), 689 (s). MS (EI, 70 eV) *m/z* (rel. intensity): 183 (78) [M^+], 181 (32) [M^+-H], 106 (21), 91 (100), 77 (20), 65 (17). HRMS Calcd. for $C_{13}H_{13}N$: 183.10425. Found: 183.104026.

^{15}N-_N_-Benzylpyrrolidine

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 4.03 (s, 1H, NH), 4.34 (s, 2H, CH_2), 6.63-6.67 (m, 2H), 6.73(tt, 1H, J = 1.0 Hz, J = 7.3 Hz), 7.16-7.21 (m, 2H), 7.26-7.31 (m, 1H), 7.33-7.40 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 48.3 (CH_2, d, $^1J_{C\text{-}15N}$ = 2.6 Hz), 112.9 (CH, d, $^2J_{C\text{-}15N}$ = 2.3 Hz), 117.6 (CH), 127.3 (CH), 127.6 (CH, d, $^3J_{C\text{-}15N}$ = 1.3 Hz), 128.7 (CH), 129.3 (CH, d, $^4J_{C\text{-}15N}$ = 0.5 Hz), 139.5(C_q, d, $^1J_{C\text{-}15N}$ = 13.0 Hz), 148.2 (C_q). **IR** (ATR): ν (cm^{-1}) = 3410 (w), 3084 (w), 3050 (w), 3026 (w), 2852 (w), 1600 (m), 1500 (m), 1452 (m), 1427 (m), 1360 (w), 1320 (m), 1250 (m), 1179 (m), 1154 (w), 1093 (m), 1077 (w), 1060 (m), 1028 (m), 989 (m), 869 (m),

746 (s), 729 (m), 690 (s). **MS** (EI): *m/z* (rel. int.) 185 (11), 184 (79), 183 (33), 107 (20), 92 (10), 91 (100), 77 (19), 65 (16). HRMS Calcd. for $C_{13}H_{13}N^{14}$: 184.10129 Found: 184.100786

***N*-Cyclohexylaniline**[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.09-1.45 (5H, m), 1.61-1.71 (1H, m), 1.73-1.82 (2H, m), 2.03-2.11 (2H, m), 3.21-3.07 (1H, m), 3.55 (1H, s, NH), 6.60 (2H, dd, ^3J = 8.6 Hz, ^4J = 1.0 Hz), 6.67 (1H, tt, ^3J = 7.3 Hz, ^4J = 1.0 Hz), 7.16 (2H, dd, ^3J = 8.6 Hz, ^4J = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.1 (2xCH_2), 26.0 (CH_2), 33.5 (2xCH_2), 51.8 (CH), 113.2 (2xCH), 116.9 (CH), 129.3 (2xCH), 147.4 (C_q). FT IR (ATR, cm^{-1}): 3400 (br, NH), 3050 (w), 3018 (w), 2925 (w), 2851 (w), 1599 (s), 1501 (s), 1319 (m), 1254 (m), 744 (s), 690 (s). MS (EI, 70 eV) *m/z* (rel. intensity): 175 (39) [M^+], 132 (100) [M^+-C_4H_7], 118 (18), 93 (12), 77 (11). HRMS Calcd. for $C_{12}H_{17}N$: 175.13555. Found: 175.135042.

***N*-(2-Methoxyethyl)aniline**[3,4]

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 3.29 (2H, t, J = 5.5 Hz), 3.39 (s, 3H), 3.60 (2H, t, J = 5.5 Hz), 4.00 (1H, s, NH), 6.62-6.65 (2H, m), 6.71 (1H, tt, J = 1.0 Hz, J = 7.3 Hz), 7.16-7.20 (2H, m). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 43.5 (CH_2), 58.8 (CH_3), 71.1 (CH_2), 113.1(CH), 117.6(CH), 129.3(CH), 148.3(C_q). **IR** (ATR): ν (cm^{-1}) = 3397 (w), 3052 (w), 3022 (w), 2981 (w), 2925 (w), 2888 (w), 2830 (w), 1601 (s), 1505 (s), 1458 (m), 1433 (w), 1389 (w), 1317 (m), 1276 (m), 1257 (m), 1193 (m), 1180 (m), 1154 (w), 1114 (s), 1072 (m), 1025 (m), 992 (m), 930 (w), 870 (m), 746 (s), 691 (s). **MS** (EI): *m/z* (rel. int.) 151 (22), 106 (100), 77 (18). **HRMS** (EI): calcd. for $C_9H_{13}O_1N_1$ (M^+) 151.09917, found 151.098689.

***N*-(3-Methoxypropyl)aniline**[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.85-1.92 (m, 2H), 3.23 (t, 2H, J = 6.7 Hz), 3.47 (s, 3H), 3.51 (t, 2H, J = 6.0 Hz), 3.90 (s, 1H, NH), 6.59-6.62 (m, 2H), 6.68 (tt, 1H, J = 1.0 Hz, J = 7.3 Hz), 7.14-7.19 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 29.4 (CH_2), 41.8 (CH_2), 58.8 (CH_3), 71.3 (CH_2), 112.8 (CH), 117.2 (CH), 129.3 (CH), 148.5 (C_q). **IR** (ATR): ν (cm^{-1}) = 3392 (w), 3051 (w), 3022 (w), 2924 (w), 2870 (w), 2829 (w), 1602 (s), 1506 (s), 1477 (m), 1433 (w), 1389 (w), 1319 (m), 1261 (m), 1180 (m), 1154 (w), 1112 (s), 1029 (m), 992 (m), 901 (w), 868 (m), 746 (s), 691 (s). **MS** (EI): *m/z* (rel. int.) 165 (26), 107 (9), 106 (100), 77 (14). **HRMS** (EI): calcd. for $C_{10}H_{15}O_1N_1$ (M^+) 165.11482, found 165.114714.

***N*-(2-(2-Methoxyethoxy)ethyl)aniline**

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 3.31 (t, 2H, J = 5.4 Hz), 3.55-3.57 (m, 2H), 3.40 (s, 3H), 3.63-6.65 (m, 2H), 3.69-3.72 (m, 2H), 6.62-6.64 (m, 2H), 6.70 (tt, 1H, J = 1.0 Hz, J = 7.3 Hz), 7.15-7.19 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 43.5 (CH_2), 59.1 (CH_3), 69.8 (CH_2), 70.3 (CH_2), 72.0 (CH_2), 113.1 (CH), 117.6, (CH), 129.2 (CH), 148.3 (C_q). **IR** (ATR): ν (cm^{-1}) =3380 (w), 3051 (w), 3022 (w), 2874 (m), 1602 (s), 1505 (m), 1459 (m), 1353 (w), 1320 (m), 1279 (m), 1198 (m), 1180 (m), 1099 (s), 1072 (m), 1027 (m), 992 (m), 932 (m), 870 (m), 849 (m), 747 (s), 692 (s). **MS** (EI): *m/z* (rel. int.) 195 (19), 107 (10), 106 (100), 77 (14). **HRMS** (EI): calcd. for $C_{11}H_{17}O_2N_1$ (M^+) 195.12538, found 195.125515.

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