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Supporting Information

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A General Ruthenium-Catalyzed Synthesis of Aromatic Amines

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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. Aliphatic and aryl amines 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 spectrometer. For new substances, a complete assignment of the ^{1}H and ^{13}C signals is given. 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 6700 with ATR Smart device. 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) and with a HP 5 column (Company: Machery-Nagel, 30m x 0.32µm, 0.25µm film thickness, 50-8-260/5-8-280/5-8-300/5).

General procedure for the amination reaction:

In an ACE-pressure tube under an argon atmosphere the Shvo catalyst (0.02 mmol), aniline (4 mmol), and the corresponding aliphatic amine (2 mmol) were dissolved in *tert*.-amylalcohol (0.5 ml). The pressure tube was fitted with a Teflon cap and heated at 150 °C for

24 h in an oil bath. The solvent was removed in vacuo, and the crude product was easily purified by column chromatography with pentane/ethyl acetate to afford the alkylated aniline.

***N*-Hexyl-4-methylaniline**[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.91 (3H, m), 1.25-1.44 (6H, m), 1.47-1.65 (2H, m), 2.20 (3H, s), 3.08 (2H, t, ^3J = 7.1 Hz), 6.56 (2H, d, ^3J = 8.4 Hz), 6.99 (2H, d, ^3J = 8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 20.4 (CH_3), 22.7 (CH_2), 26.9 (CH_2), 29.6 (CH_2), 31.7 (CH_2), 44.5 (CH_2), 113.0 (2xCH), 126.4 (C_q), 129.7 (2xCH), 146.3 (C_q).

FT IR (ATR, cm^{-1}): 3398 (br, NH), 2965 (m), 2916 (s), 2843 (s), 1616 (m), 1518 (s), 1473 (m), 1464 (m), 1314 (m), 1302 (m), 1252 (m), 1135 (m), 810 (s), 797 (s), 729 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 191 (19) [M^+], 120 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{13}H_{21}N$: 191.16685. Found: 191.166706.

m = 373.7 mg (98 %) colourless crystals, R_f (Pentane : EE 5:1) = 0.69. R_t (HP 5) = 15.06 min.

***N*-Hexyl-2-methylaniline**[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.93 (3H, m), 1.26-1.45 (6H, m), 1.67 (2H, quin, ^3J = 6.8 Hz), 2.14 (3H, s), 3.14 (2H, t, ^3J = 6.8 Hz), 6.60-6.67 (2H, m), 7.05 (1H, d, ^3J = 7.0 Hz), 7.12 (1H, t, ^3J = 8.0 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 17.5 (CH_3), 22.7 (CH_2), 26.9 (CH_2), 29.6 (CH_2), 31.7 (CH_2), 44.0 (CH_2), 109.6 (CH), 116.6 (CH), 121.7 (C_q), 127.1 (CH), 130.0 (CH), 146.5 (C_q).

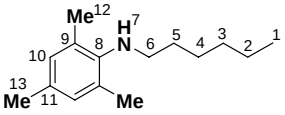
FT IR (ATR, cm^{-1}): 3422 (br, NH), 2954 (m), 2923 (m), 2851 (m), 1606 (m), 1586 (s), 1512 (s), 1471 (m), 1445 (m), 1315 (m), 1302 (m), 1258 (m), 1142 (m), 742 (s), 714 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 191 (20) [M^+], 120 (100) [M^+-C_5H_{11}], 91(11).

HRMS Calcd. for $C_{13}H_{21}N$: 191.16685. Found: 191.166782.

m = 357.3 mg (93 %) colourless oil, R_f (Pentane : EE 5:1) = 0.69. R_t (HP 5) = 14.82 min.

***N*-Hexyl-2,4,6-trimethylaniline**



^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.92 (3H, m, H-1), 1.25-1.35 (6H, m, H-2,3,4), 1.53-1.62 (2H, m, H-5), 2.22 (3H, s, H-13), 2.24 (6H, s, H-12), 2.91 (2H, t, ^3J = 7.0 Hz, H-6), 6.81 (2H, d, ^4J = 0.5 Hz, H-10).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3, C-1), 18.4 (CH_3, C-12), 20.6 (CH_3, C-13), 22.7 (CH_2, C-2), 27.0 (CH_2, C-4), 31.2 (CH_2, C-5), 31.8 (CH_2, C-3), 49.1 (CH_2, C-6), 129.4 (2xCH, C-10), 129.5 (C_q, C-9), 131.0 (C_q, C-11), 143.9 (C_q, C-8).

FT IR (ATR, cm^{-1}): 2954 (m), 2923 (s), 2851 (m), 1484 (s), 1466 (s), 1231 (m), 852 (s), 752 (m).

MS (EI, 70 eV) *m/z* (rel. intensity): 219 (20) [M^+], 148 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{15}H_{25}N$: 219.19815. Found: 219.198774.

m = 148.0 mg (34 %), pale purple oil, R_f (Pentane : EE 5:1) = 0.55. R_t (Optima) = 21.53 min.

***N*-Hexyl-4-methoxyaniline**[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88-0.92 (3H, m), 1.26-1.44 (6H, m), 1.55-1.65 (2H, m), 3.06 (2H, d, ^3J = 7.0 Hz), 3.75 (3H, s), 6.55-6.61 (2H, m), 6.76-6.81 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.7 (CH_2), 26.9 (CH_2), 29.7 (CH_2), 31.7 (CH_2), 45.1 (CH_2), 55.9 (CH_3), 114.1 (CH), 114.9 (CH), 142.9 (C_q), 152.0 (C_q).

FT IR (ATR, cm^{-1}): 3392 (br, NH), 2953 (m), 2926 (m), 2855 (m), 1510 (s), 1232 (s), 1037 (m), 816 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 207 (25) [M^+], 136 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{13}H_{21}NO$: 207.16177. Found: 207.161573.

m = 405.2 mg (98 %), pale purple oil, R_f (Pentane : EE 10:1) = 0.40. R_t (HP 5) = 16.98 min.

_N_-Hexyl-2-methoxyaniline[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.92 (3H, m), 1.25-1.46 (6H, m), 1.61-1.70 (2H, m), 3.11 (2H, t, ^3J = 7.2 Hz), 3.84 (3H, s), 6.60-6.68 (2H, m), 6.76 (1H, dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz), 6.87 (1H, td, ^3J = 7.6 Hz, ^3J = 1.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.7 (CH_2), 27.0 (CH_2), 29.6 (CH_2), 31.7 (CH_2), 43.8 (CH_2), 55.4 (CH_3), 109.4 (CH), 106.8 (CH), 116.1 (CH), 121.3 (CH), 138.6 (C_q), 146.8 (C_q).

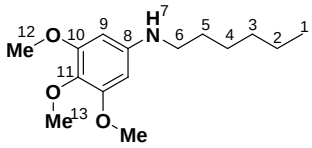
FT IR (ATR, cm^{-1}): 3425 (br, NH), 2961 (m), 2927 (m), 2851 (m), 1602 (s), 1512 (s), 1454 (m), 1247 (m), 1220 (s), 1029 (m), 731 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 207 (27) [M^+], 136 (100) [M^+-C_5H_{11}], 121 (22).

HRMS Calcd. for $C_{13}H_{21}NO$: 207.16177. Found: 207.161618.

m = 402.7 mg (97 %) pale purple oil, R_f (Pentane : EE 5:1) = 0.57. R_t (Optima) = 21.36 min.

_N_-Hexyl-3,4,5-trimethoxyaniline



^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88-0.93 (3H, m, H-1), 1.29-1.45 (6H, m, H-2,3,4), 1.57-1.66 (2H, m, H-5), 3.07 (2H, t, ^3J = 7.3 Hz, H-6), 3.76 (3H, s, H-13), 3.82 (6H, s, H-12), 5.84 (2H, s, H-9).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3, C-1), 22.7 (CH_2, C-2), 26.9 (CH_2, C-4), 29.6 (CH_2, C-5), 31.7 (CH_2, C-3), 44.5 (CH_2, C-6), 56.0 (CH_3, C-12), 61.2 (CH_3, C-13), 90.2 (2xCH, C-9), 129.9 (C_q, C-8), 145.4 (C_q, C-11), 154.0 (C_q, C-10).

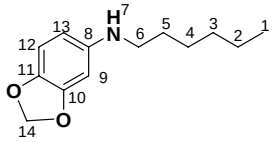
FT IR (ATR, cm^{-1}): 3379 (br, NH), 2954 (m), 2927 (m), 2847 (m), 1609 (s), 1508 (s), 1451 (m), 1233 (s), 1010 (m), 802 (m), 775 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 267 (31) [M^+], 252 (100) [M^+-CH_3], 196 (13) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{15}H_{25}NO_3$: 267.18290. Found: 267.182528.

m = 520.2 mg (97 %), pale purple oil, R_f (Pentane : EE 5:1) = 0.29. R_t (Optima) = 26.55 min.

_N_-Hexylbenzo[*d*][1.3]dioxol-5-amine



^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.92 (3H, m, H-1), 1.23-1.43 (6H, m, H-2,3,4), 1.54-1.64 (2H, m, H-5), 3.03 (2H, t, ^3J = 7.1 Hz, H-6), 5.84 (2H, s, H-14), 6.04 (1H, dd, ^3J = 8.2 Hz, ^4J = 2.3 Hz, H-13), 6.24 (1H, d, ^4J = 2.3 Hz, H-9), 6.65 (1H, d, ^3J = 8.2 Hz, H-12).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0 (CH_3, C-1), 22.6 (CH_2, C-2), 26.9 (CH_2, C-4), 29.5 (CH_2, C-5), 31.7 (CH_2, C-3), 45.1 (CH_2, C-6), 95.8 (CH, C-9), 100.5 (CH_2, C-14), 104.3 (CH, C-13), 108.6 (CH, C-12), 139.4 (C_q, C-8), 144.4 (C_q, C-10), 148.3 (C_q, C-11).

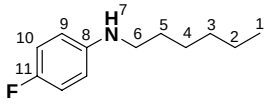
FT IR (ATR, cm^{-1}): 3405 (br, NH), 2954 (m), 2926 (m), 2856 (m), 1634 (w), 1502 (s), 1487 (s), 1196 (s), 1037 (s), 926 (m), 810 (s), 783 (m).

MS (EI, 70 eV) *m/z* (rel. intensity): 221 (31) [M^+], 150 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{13}H_{19}NO_2$: 221.14103. Found: 221.140618.

m = 376.3 mg (86 %), red crystals, R_f (Pentane : EE 5:1) = 0.56. R_t (HP 5) = 22.29 min.

4-Fluoro-*N*-hexylaniline



^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.92 (3H, m, H-1), 1.28-1.44 (6H, m, H-2,3,4), 1.55-1.65 (2H, m, H-5), 3.07 (2H, t, ^{3}J = 7.2 Hz, H-6), 6.49-6.57 (2H, m, H-9), 6.84-6.92 (2H, m, H-10).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3, C-1), 22.7 (CH_2, C-2), 26.9 (CH_2, C-4), 29.6 (CH_2, C-5), 31.7 (CH_2, C-3), 44.8 (CH_2, C-6), 113.5 (2xCH, d, ^{3}J = 7 Hz, C-9), 115.6 (2xCH, d, ^{2}J = 22 Hz, C-10), 144.9 (C_q, d, ^{4}J = 2 Hz, C-8), 155.7 (C_q, d, ^{1}J = 233 Hz, C-11).

FT IR (ATR, cm^{-1}): 3414 (br, NH), 2957 (m), 2923 (m), 2847 (m), 1508 (s), 1218 (s), 816 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 211 (18) [M^+], 140 (100) [M^+-C_5H_{11}].

MS (EI, 70 eV) *m/z* (rel. intensity): 195 (16) [M^+], 124 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{12}H_{18}FN$: 195.14178. Found: 195.141340.

m = 369.0 mg (99 %) pale purple oil, R_f (Pentane : EE 5:1) = 0.44. R_t (Optima) = 19.06 min.

4-Chloro-*N*-hexylaniline [3]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.91 (3H, m), 1.25-1.41 (6H, m), 1.47-1.66 (2H, m), 3.07 (2H, t, ^{3}J = 7.4 Hz), 6.57 (2H, d, ^{3}J = 8.8 Hz), 7.12 (2H, d, ^{3}J = 8.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.7 (CH_2), 26.8 (CH_2), 29.4 (CH_2), 31.7 (CH_2), 44.2 (CH_2), 113.7 (2xCH), 121.6 (C_q), 129.0 (2xCH), 147.1 (C_q).

FT IR (ATR, cm^{-1}): 3410 (br, NH), 2954 (m), 2927 (m), 2851 (m), 1600 (m), 1498 (s), 1477 (m), 1316 (m), 1175 (m), 812 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 211 (18) [M^+], 140 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{12}H_{18}ClN$: 211.11223. Found: 211.112166.

m = 411.6 mg (97 %) pale purple oil, R_f (Pentane : EE 5:1) = 0.45. R_t (Optima) = 22.24 min.

4-Bromo-*N*-hexyl-aniline[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88-0.92 (3H, m), 1.26-1.43 (6H, m), 1.55-1.65 (2H, m), 3.06 (2H, t, ^{3}J = 7.2 Hz), 3.63 (1H, s, NH), 6.47 (2H, d, ^{3}J = 9.0 Hz), 7.23 (2H, d, ^{3}J = 9.0 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.6 (CH_2), 26.8 (CH_2), 29.4 (CH_2), 31.7 (CH_2), 44.1 (CH_2), 108.6 (C_q), 114.2 (CH), 131.9 (CH), 147.5 (C_q).

FT IR (ATR, cm^{-1}): 3413 (br, NH), 2954 (m), 2925 (m), 2855 (m), 1594 (s), 1495 (s), 1316 (m), 1176 (m), 1071 (m), 809 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 255 (20) [M^+], 184 (100) [M^+-C_5H_{11}], 105 (13).

HRMS Calcd. for $C_{12}H_{18}BrN_2$: 255.06171. Found: 255.061893.

m = 480.1 mg (94 %), pale purple oil, R_f (Pentane : EE 10:1) = 0.53. R_t (HP 5) = 18.10 min

***N*-Hexyl-4-nitroaniline**[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.93 (3H, m), 1.23-1.45 (6H, m), 1.60-1.69 (2H, m), 3.20 (2H, td, ^{3}J = 7.2 Hz, ^{3}J = 5.6 Hz), 4.47 (1H, s, NH), 6.51 (2H, d, ^{3}J = 9.3 Hz), 8.08 (2H, d, ^{3}J = 9.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.6 (CH_2), 26.7 (CH_2), 29.1 (CH_2), 31.5 (CH_2), 43.5 (CH_2), 110.9 (2xCH), 118.0 (C_q), 126.5 (2xCH), 153.4 (C_q).

FT IR (ATR, cm^{-1}): 3345 (br, NH), 2957 (m), 2935 (m), 2855 (m), 1600 (s), 1538 (m), 1461 (m), 1317 (m), 1283 (m), 1270 (s), 1184 (m), 1137 (m), 1106 (m), 833 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 222 (17) [M^+], 156 (100) [M^+-C_5H_{11}], 105 (25).

HRMS Calcd. for $C_{12}H_{18}N_2O_2$: 222.13628. Found: 222.135984.

m = 88.5 mg (20 %) yellow crystals, R_f (Pentane : EE 5:1) = 0.18. R_t (Optima) = 27.60 min.

4-(Hexylamino)benzonitrile[6,7]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.92 (3H, m), 1.26-1.44 (6H, m), 1.57-1.67 (2H, m), 3.13 (2H, td, ^3J = 7.1 Hz, ^3J = 5.6 Hz), 4.17 (1H, s, NH), 6.53 (2H, d, ^3J = 9.0 Hz), 7.41 (2H, d, ^3J = 9.0 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.6 (CH_2), 26.7 (CH_2), 29.2 (CH_2), 31.6 (CH_2), 43.3 (CH_2), 98.3 (C_q), 112.1 (CH), 120.6 (C_q), 133.7 (CH), 151.5 (C_q).

FT IR (ATR, cm^{-1}): 3351 (br, NH), 2961 (m), 2928 (m), 2858 (m), 2211 (s, CN), 1607 (s), 1577 (m), 1531 (s), 1474 (m), 1353 (s), 1342 (m), 1170 (m), 1139 (m), 821 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 202 (14) [M^+], 131 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{13}H_{18}N_2$: 202.14645. Found: 202.145813.

m = 307.0 mg (76 %), pale purple oil, R_f (Pentane : EE 10:1) = 0.22. R_t (HP 5) = 19.83 min.

***N*-Hexyl-4-(trifluoromethyl)aniline**[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88-0.93 (3H, m), 1.29-1.44 (6H, m), 1.54-1.68 (2H, m), 3.13 (2H, d, ^3J = 6.8 Hz), 3.95 (1H, s, NH), 6.58 (2H, d, ^3J = 8.7 Hz), 7.39 (2H, d, ^3J = 8.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.6 (CH_2), 26.8 (CH_2), 29.3 (CH_2), 31.6 (CH_2), 43.6 (CH_2), 111.7 (CH), 126.6 (CH, q, J = 3.8 Hz), 150.9 (C_q).

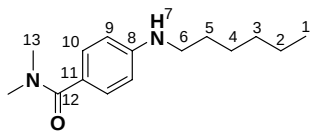
FT IR (ATR, cm^{-1}): 3434 (br, NH), 2957 (m), 2929 (m), 2859 (m), 1616 (s), 1534 (m), 1317 (s), 1186 (m), 1158 (m), 1102 (s, CF_3), 1061 (s, CF_3), 821 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 245 (12) [M^+], 174 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{13}H_{18}F_3N$: 245.13859. Found: 245.139068.

m = 463.6 mg (95 %), pale purple oil, R_f (Pentane : EE 10:1) = 0.58. R_t (HP 5) = 14.68 min.

4-(Hexylamino)-*N*,*N*-dimethylbenzamide



^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.92 (3H, H-1), 1.27-1.43 (6H, m, H-2,3,4), 1.56-1.65 (2H, m, H-5), 3.05 (6H, s, H-13), 3.11 (2H, t, ^3J = 7.0 Hz, H-6), 3.87 (1H, s, NH), 6.53 (2H, d, ^3J = 8.9 Hz, H-9), 7.30 (2H, d, ^3J = 8.9 Hz, H-10).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3, C-1), 22.6 (CH_2, C-2), 26.8 (CH_2, C-4), 29.4 (CH_2, C-5), 31.6 (CH_2, C-3), 37.8 (CH_3, appearance at 333 K, C-13), 43.7 (CH_2, C-6), 111.5 (CH, C-9), 124.0 (C_q, C-11), 129.5 (CH, C-10), 149.8 (C_q, C-8), 172.2 (C_q, C-12).

FT IR (ATR, cm^{-1}): 3329 (br, NH), 2926 (m), 2855 (m), 1600 (s), 1490 (s), 1384 (m), 1333 (m), 1261 (m), 1175 (m), 1076 (m), 830 (s), 763 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 248 (35) [M^+], 204 (100) [M^+-$N(CH_3)_2$], 177 (26) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{15}H_{24}N_2O$: 248.18831. Found: 248.187855.

m = 547.7 mg (83 %), white crystals, R_f (Pentane : EE 1:1) = 0.23. R_t (HP 5) = 27.14 min.

***N*-Hexyl-pyridin-2-amine**[9,10]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.91 (3H, m), 1.23-1.45 (6H, m), 1.56-1.66 (2H, m), 3.23 (2H, td, ^3J = 7.1 Hz, ^3J = 5.6 Hz), 4.48 (1H, s, NH), 6.36 (1H, dt, ^3J = 8.4 Hz, ^4J = 0.9 Hz), 6.54 (1H, ddd, ^3J = 7.2 Hz, ^3J = 5.1 Hz, ^4J = 0.9 Hz), 7.41 (1H, ddd, ^3J = 8.4 Hz, ^3J = 7.2 Hz, ^4J = 2.0 Hz), 8.09 (1H, ddd, ^3J = 5.1 Hz, ^4J = 2.0 Hz, ^4J = 0.9 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.7 (CH_2), 26.8 (CH_2), 29.6 (CH_2), 31.6 (CH_2), 42.4 (CH_2), 106.3 (CH), 112.6 (CH), 137.5 (CH), 148.2 (CH), 156.0 (C_q).

FT IR (ATR, cm^{-1}): 3246 (br, NH), 2946 (m), 2919(m), 2851 (m), 1599 (s), 1573 (s), 1526 (s), 1451 (m), 1433 (m), 1331 (m), 1289 (m), 1155 (m), 1139 (m), 1082 (m), 982 (m), 765 (s), 733 (m), 726 (m).

MS (EI, 70 eV) *m/z* (rel. intensity): 178 (16) [M^+], 121 (26), 107 (100) [M^+-C_5H_{11}], 94 (35), 78 (28).

HRMS Calcd. for $C_{11}H_{18}N_2$: 178.14645. Found: 178.145971.

m = 340.1 mg (96 %), pale red crystals, R_f (Pentane : EE 1:1) = 0.30. R_t (HP5) = 13.79 min.

***N*-Hexyl-pyridin-3-amine** [9]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88-0.92 (3H, m), 1.28-1.45 (6H, m), 1.58-1.67 (2H, m), 3.08-3.15 (2H, m), 3.64 (1H, s, NH), 6.84 (1H, ddd, ^3J = 8.3 Hz, ^4J = 2.9 Hz, ^4J = 1.3 Hz), 6.86 (1H, dd, ^3J = 8.3 Hz, ^3J = 4.7 Hz), 7.95 (1H, dd, ^3J = 4.7 Hz, ^4J = 1.3 Hz), 8.02 (1H, d, ^4J = 2.9 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.6 (CH_2), 26.8 (CH_2), 29.4 (CH_2), 31.6 (CH_2), 43.6 (CH_2), 118.3 (CH), 123.7 (CH), 136.0 (CH), 138.5 (CH), 144.4 (C_q).

FT IR (ATR, cm^{-1}): 3251 (br, NH), 3158 (w), 3102 (w), 3043 (w), 2952 (m), 2927 (m), 2853 (m), 1584 (s), 1532 (m), 1474 (m), 1463 (m), 1418 (m), 1346 (m), 1318 (m), 1249 (m), 788 (s), 725 (m), 703 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 178 (17) [M^+], 107 (100) [M^+-C_5H_{11}].

HRMS Calcd. for $C_{11}H_{18}N_2$: 178.14645. Found: 178.146221.

m = 273.0 mg (77 %), pale green crystals, R_f (Pentane : EE 1:1) = 0.31. R_t (Optima) = 20.72 min.

***N*-Octylaniline** [10, 11]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.92 (3H, m), 1.24-1.46 (10H, m), 1.57-1.67 (2H, m), 3.11 (2H, t, ^3J = 6.9 Hz), 3.62 (1H, s, NH), 6.61 (2H, dd, ^3J = 8.6 Hz, ^4J = 1.1 Hz), 6.69 (1H, tt, ^3J = 7.3 Hz, ^4J = 1.1 Hz), 7.12 (2H, dd, ^3J = 8.6 Hz, ^4J = 7.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.2 (CH_3), 22.7 (CH_2), 27.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 44.1 (CH_2), 112.8 (2xCH), 117.1 (CH), 129.3 (2xCH), 148.5 (C_q).

FT IR (ATR, cm^{-1}): 3411 (br, NH), 2953 (m), 2923 (m), 2853 (m), 1601 (s), 1504 (s), 1318 (m), 745 (s), 690 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 205 (23) [M^+], 106 (100) [M^+-C_7H_{15}], 77 (11).

HRMS Calcd. for $C_{14}H_{23}N$: 205.18250. Found: 205.182390.

m = 421.6 mg (99 %), pale yellow oil, R_f (Pentane : EE 20:1) = 0.44. R_t (HP 5) = 20.16 min.

***N*-Phenethylaniline** [12,13]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.93 (2H, t, ^3J = 7.0 Hz), 3.41 (2H, t, ^3J = 7.0 Hz), 3.72 (1H, s, NH), 6.62 (2H, dd, ^3J = 8.6 Hz, ^4J = 1.0 Hz), 6.71 (1H, tt, ^3J = 7.3 Hz, ^4J = 1.0 Hz), 7.19 (2H, dd, ^3J = 8.6 Hz, ^4J = 7.3 Hz), 7.21-7.36 (5H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 35.6 (CH_2), 45.1 (CH_2), 113.1 (2xCH), 117.6 (CH), 126.5 (CH), 128.7 (2xCH), 128.9 (2xCH), 129.4 (2xCH), 139.4 (C_q), 148.0 (C_q).

FT IR (ATR, cm^{-1}): 3406 (br, NH), 3083 (w), 3051 (w), 3024 (w), 2927 (w), 2857 (w), 1600 (s), 1504 (s), 1315 (m), 1260 (m), 744 (s), 690 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 197 (19) [M^+], 106 (100) [M^+-C_7H_7], 77 (25).

HRMS Calcd. for $C_{14}H_{15}N$: 197.11990. Found: 197.119142.

m = 388.5 mg (99 %), pale yellow oil, R_f (Pentane : EE 20:1) = 0.31. R_t (HP 5) = 21.12 min.

***N*-Benzylaniline**[10,14]

^{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.

m = 342.2 mg (94 %), pale yellow oil, R_f (Pentane : EE 20:1) = 0.37. R_t (HP 5) = 19.97 min.

***N*-(Octan-2-yl)aniline** [15]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87-0.91 (3H, m), 1.17 (3H, d, ^3J = 6.2 Hz), 1.24-1.63 (10H, m), 3.40-3.56 (1H+NH, m), 6.58 (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: 14.1 (CH_3), 20.8 (CH_3), 22.8 (CH_2), 26.2 (CH_2), 29.4 (CH_2), 31.9 (CH_2), 37.3 (CH_2), 48.6 (CH), 113.1 (2xCH), 116.8 (CH), 129.3 (2xCH), 147.7 (C_q).

FT IR (ATR, cm^{-1}): 3404 (br, NH), 2956 (m), 2925 (m), 2855 (m), 1600 (s), 1503 (s), 1316 (m), 744 (s), 690 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 205 (23) [M^+], 190 (8) [M^+-CH_3], 120 (100) [M^+-C_6H_{13}].

HRMS Calcd. for $C_{14}H_{23}N$: 205.18250. Found: 205.182514.

m = 404.0 mg (99 %), pale yellow oil, R_f (Pentane : EE 20:1) = 0.49. R_t (HP 5) = 18.63 min.

***N*-Cyclohexylaniline**[10]

^{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.

m = 346.7 mg (99.0 %), pale yellow oil, R_f (Pentane : EE 20:1) = 0.44. R_t (HP 5) = 17.78 min.

***N*-Phenylcyclooctanamine** [16]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.54-1.96 (14H, m), 3.46-3.55 (1H, m), 3.61 (1H, s, NH), 6.56 (2H, dd, ^{3}J = 8.6 Hz, ^{4}J = 1.1 Hz), 6.66 (1H, tt, ^{3}J = 7.4 Hz, ^{4}J = 1.1 Hz), 7.16 (2H, dd, ^{3}J = 8.6 Hz, ^{4}J = 7.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.1 (2xCH_2), 26.0 (CH_2), 27.1 (2xCH_2), 32.7 (2xCH_2), 52.6 (CH), 113.3 (2xCH), 116.8 (CH), 129.3 (2xCH), 147.3 (C_q).

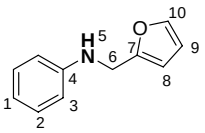
FT IR (ATR, cm^{-1}): 3403 (br, NH), 2916 (m), 2849 (m), 1599 (s), 1501 (s), 1314 (m), 744 (s), 690 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 203 (34) [M^+], 160 (9), 132 (100), 119 (39), 106 (15), 93 (20), 77 (12).

HRMS Calcd. for $C_{14}H_{21}N$: 203.16685. Found: 203.166251.

m = 400.4 mg (99 %), pale yellow oil, R_f (Pentane : EE 20:1) = 0.44. R_t (HP 5) = 21.49 min.

***N*-(Furan-2ylmethyl)aniline**[17]



^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.04 (1H, s, NH), 6.34 (1H, dd, ^{3}J = 3.2 Hz, ^{4}J = 0.8 Hz, H-8), 6.34 (1H, dd, ^{3}J = 3.2 Hz, ^{3}J = 1.9 Hz, H-9), 6.70 (2H, dd, ^{3}J = 8.6 Hz, ^{4}J = 1.1 Hz, H-3), 6.76 (1H, tt, ^{3}J = 7.4 Hz, ^{4}J = 1.1 Hz, H-1), 7.21 (2H, dd, ^{3}J = 8.6 Hz, ^{4}J = 7.4 Hz, H-2), 7.38 (1H, dd, ^{3}J = 1.9 Hz, ^{4}J = 0.8 Hz, H-10).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 41.5 (CH_2, C-6), 107.1 (CH, C-8), 110.4 (CH, C-9), 113.2 (2xCH, C-3), 118.1 (CH, C-1), 129.3 (2xCH, C-2), 142.0 (CH, C-10), 147.7 (C_q, C-4), 152.8 (C_q, C-7).

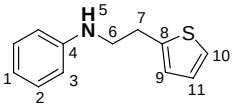
FT IR (ATR, cm^{-1}): 3411 (br, NH), 3145 (w), 3115 (w), 3051 (w), 3022 (w), 2925 (w), 2845 (w), 1601 (s), 1502 (s), 1316 (m), 1252 (m), 1180 (w), 1145 (m), 1010 (m), 731 (s), 689 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 173 (59) [M^+], 172 (39) [M^+-H], 81 (100) [M^+-C_6H_6N], 77 (13), 53 (23).

HRMS Calcd. for $C_{11}H_{11}NO$: 173.08352. Found: 173.083256.

m = 306.3 mg (89 %), pale yellow oil, R_f (Pentane : EE 20:1) = 0.36. R_t (HP 5) = 17.14 min.

***N*-(2-(Thiophen-2yl)ethyl)aniline**



^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.15 (2H, t, ^{3}J = 6.7 Hz, H-6), 3.46 (2H, t, ^{3}J = 6.7 Hz, H-7), 3.79 (1H, s, NH), 6.85 (2H, dd, ^{3}J = 8.6 Hz, ^{4}J = 1.0 Hz, H-3), 6.74 (1H, tt, ^{3}J = 7.3 Hz, ^{4}J = 1.0 Hz, H-1), 6.88 (1H, dd, ^{3}J = 3.3 Hz, ^{4}J = 1.0 Hz, H-9), 6.98 (1H, dd, ^{3}J = 5.1 Hz, ^{3}J = 3.3 Hz, H-10), 7.19 (1H, dd, ^{3}J = 5.1 Hz, ^{4}J = 1.0 Hz, H-11), 7.21 (2H, dd, ^{3}J = 8.6 Hz, ^{4}J = 7.3 Hz, H-2).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 29.8 (CH_2, C-7), 45.2 (CH_2, C-6), 113.1 (2xCH, C-3), 117.7 (CH, C-1), 124.0 (CH, C-11), 125.4 (CH, C-9), 127.0 (CH, C-10), 129.4 (2xCH, C-2), 141.8 (C_q, C-8), 147.8 (C_q, C-4).

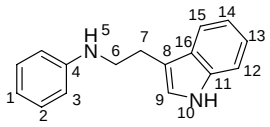
FT IR (ATR, cm^{-1}): 3402 (br, NH), 3102 (w), 3050 (w), 3020 (w), 2918 (w), 2850 (w), 1600 (s), 1503 (s), 1315 (m), 1249 (m), 746 (s), 689 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 203 (20) [M^+], 106 (100) [M^+- C_5H_5S], 77 (30).

HRMS Calcd. for $C_{12}H_{13}NS$: 203.07632. Found: 203.075722.

m = 393.5 mg (97 %), pale red oil, R_f (Pentane : EE 20:1) = 0.36. R_t (HP 5) = 21.22 min.

***N*-(2-(1*H*-Indol-2yl)ethyl)aniline**



^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.10 (2H, t, ^{3}J = 7.2 Hz, H-6), 3.48 (2H, t, ^{3}J = 7.2 Hz, H-7), 3.76 (1H, s, NH-5), 6.62 (2H, dd, ^{3}J = 8.5 Hz, ^{4}J = 1.0 Hz, H-3), 6.70 (1H, tt, ^{3}J = 7.3 Hz, ^{4}J = 1.0 Hz, H-1), 7.06-7.07 (1H, m, C-9), 7.10-7.25 (4H, m, H-14, H-2, H-13), 7.37-7.42 (1H, m, H-12), 7.61-7.65 (1H, H-15), 8.00 (1H, s, NH-10).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.2 (CH_2, C-7), 44.0 (CH_2, C-6), 111.2 (CH, C-12), 113.0 (2xCH, C-3), 113.5 (C_q), 117.4 (CH, C-1), 118.9 (CH, C-15), 119.5 (CH, C-14), 122.0 (CH, C-9), 122.2 (CH, C-13), 127.5 (C_q), 129.3 (2xCH, C-2), 136.5 (C_q), 148.3 (C_q, C-4).

FT IR (ATR, cm^{-1}): 3393 (br, NH), 3044 (w), 2915 (w), 2852 (w), 1596 (m), 1499 (m), 1456 (m), 1423 (m), 1319 (m), 1293 (m), 1255 (m), 1226 (m), 1180 (m), 1150 (m), 1091 (m), 1009 (m), 737 (s), 691 (s).

MS (EI, 70 eV) *m/z* (rel. intensity): 236 (23) [M^+], 131 (76), 130 (51), 106 (100) [M^+- C_9H_6N], 77 (26).

HRMS Calcd. for $C_{16}H_{16}N_2$: 236.13080. Found: 236.130402.

m = 437.7 mg (93 %), white crystals. R_t (HP 5) = 29.56 min.

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