

CuI/DMPAO-Catalyzed N-Arylation of Acyclic Secondary Amines

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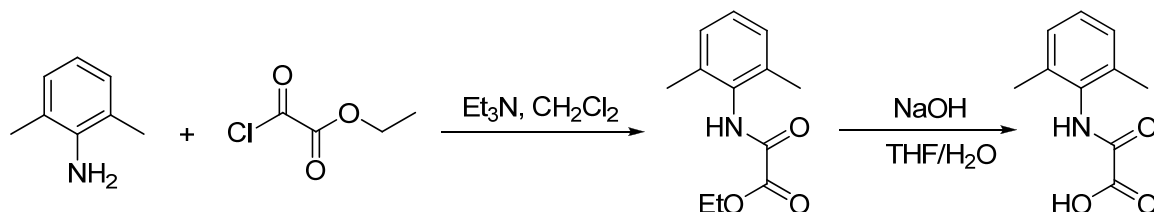
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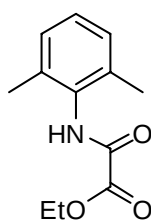
Experimental

Preparation of ligand DMPAO

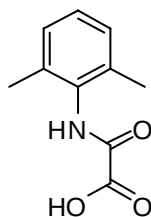


To a magnetically stirred solution of the 2,6-dimethylaniline (20 mmol) and 2 g of triethylamine (22 mmol) in 20 ml of CH₂Cl₂ was added, dropwise, a solution of 2.7 g of ethyl oxalyl chloride (22 mmol) in 10 mL of CH₂Cl₂. After it was stirred for 24 h, the mixture was washed with the same volume of water. The organic phase was dried over Na₂SO₄ and evaporated. The crude product was purified with silica gel chromatography to give the amide as white solid.

To a magnetically stirred solution of the above product (10 mmol) in 5 ml of THF and 5 mL of water was added 0.4 g of NaOH (10 mmol). After it was stirred for 2 h at room temperature, the mixture was acidified by adding 20 ml of 1 M HCl, and then extracted with ethyl acetate. The organic layer was separated, dried over Na₂SO₄ and evaporated to give DMPAO as white solid.

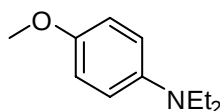


Ethyl 2-(2,6-dimethylanilino)-2-oxo-acetate.¹ ¹H NMR (300 MHz, CDCl₃) δ 8.51 (brs, 1H), 7.15-7.08 (m, 3H), 4.62 (q, *J* = 7.2 Hz, 2H), 2.20 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 154.6, 135.0, 132.2, 128.3, 127.8, 63.4, 18.3, 13.9; ESI-MS *m/z* 222 (*M* + H)⁺.

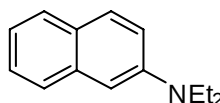


DMPAO. ^1H NMR (300 MHz, CDCl_3) δ 7.20-7.10 (m, 3H), 5.12 (brs, 2H), 2.21 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.7, 158.9, 136.6, 134.3, 129.1, 128.8, 18.3; ESI-MS m/z 192 ($\text{M} - \text{H}$) $^+$; HRMS calcd for $\text{C}_{10}\text{H}_{10}\text{NO}_3$ ($\text{M} - \text{H}$) $^+$, 192.0666, found 192.0667.

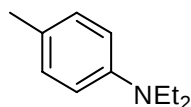
General procedure for N-arylation: An oven-dried Schlenk tube was charged with CuI (19 mg, 0.1 mmol), DMPAO (38 mg, 0.2 mmol), aryl halide (1 mmol), K_3PO_4 (2 mmol). The tube was evacuated and backfilled with argon, and then amine (1.5 mmol) and DMSO (1 mL) was added. The reaction mixture was stirred at 90 $^\circ\text{C}$ for 48 h. After aryl halide was consumed, water was added and the mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by chromatography to give the desired product.



N-(4-Methoxyphenyl)diethylamine (3a). 2 ^1H NMR (300 MHz, CDCl_3) δ 6.83 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H), 3.76 (s, 3H), 3.26 (q, J = 6.9 Hz, 4H), 1.10 (t, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 143.0, 115.4, 114.9, 55.9, 45.4, 12.6; EI-MS m/z 179 (M^+); HRMS calcd for $\text{C}_{11}\text{H}_{17}\text{NO}$ (M^+), 179.1310, found 179.1311.

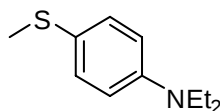


Diethyl naphthalen-2-yl-amine (3b). 3 ^1H NMR (300 MHz, CDCl_3) δ 7.75-7.62 (m, 3H), 7.34 (t, J = 7.2 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.14 (dd, J = 9.0, 2.5 Hz, 1H), 6.92 (s, 1H), 3.49 (q, J = 6.9 Hz, 4H), 1.25 (t, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 135.4, 127.5, 126.4, 126.2, 126.0, 121.6, 116.2, 105.7, 44.7, 12.8; ESI-MS m/z 200 ($\text{M} + \text{H}$) $^+$.

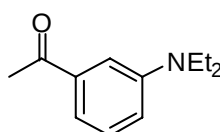


N-(4-Methylphenyl)diethylamine (3c). 2 ^1H NMR (300 MHz, CDCl_3) δ 7.09 (d, J = 9.0 Hz, 2H), 6.69 (d, J = 9.0 Hz, 2H), 3.37 (q, J = 6.9 Hz, 4H), 2.31 (s, 3H), 1.19 (t, J = 6.9

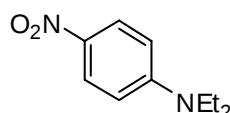
Hz, 6H), ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 129.9, 124.9, 112.7, 44.7, 20.3, 12.7; ESI-MS m/z 164 ($\text{M} + \text{H}$) $^+$.



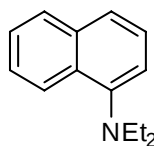
***N,N*-Diethyl-4-methylthioaniline (3f).**⁴ ^1H NMR (300 MHz, CDCl_3) δ 7.26 (d, J = 6.6 Hz, 2H), 6.61 (d, J = 6.6 Hz, 2H), 3.32 (q, J = 5.4 Hz, 4H), 2.40 (s, 3H), 1.14 (t, J = 5.4 Hz, 6H), ^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 132.2, 121.8, 112.4, 44.5, 19.7, 12.6; ESI-MS m/z 196 ($\text{M} + \text{H}$) $^+$.



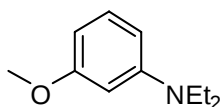
***N,N*-Diethyl-3-acetylaniline (3g).** ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.24 (m, 2H), 7.18 (d, J = 5.7 Hz, 1H), 6.85 (dd, J = 6.0, 1.5 Hz, 1H), 3.37 (q, J = 5.7 Hz, 4H), 2.58 (s, 3H), 1.16 (t, J = 5.7 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 147.9, 138.1, 129.3, 116.3, 115.8, 110.5, 44.4, 26.8, 12.5; EI-MS m/z 191 (M^+); HRMS calcd for $\text{C}_{12}\text{H}_{17}\text{NO}$ (M^+), 191.1310, found 191.1312.



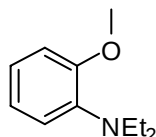
***N,N*-Diethyl-4-nitroaniline (3h).**⁵ ^1H NMR (300 MHz, CDCl_3) δ 8.05 (d, J = 9.6 Hz, 2H), 6.54 (d, J = 9.6 Hz, 2H), 3.42 (q, J = 7.2 Hz, 4H), 1.19 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 136.1, 126.4, 109.8, 45.0, 12.4; ESI-MS m/z 196 ($\text{M} + \text{H}$) $^+$.



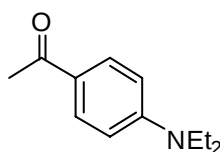
***N,N*-Diethyl naphthalen-1-yl-amine (3i).** ^1H NMR (300 MHz, CDCl_3) δ 8.35-8.29 (m, 1H), 7.83-7.79 (m, 1H), 7.58-7.37 (m, 4H), 7.15 (d, J = 7.5 Hz, 1H), 3.21 (q, J = 7.2 Hz, 4H), 1.06 (t, J = 7.2 Hz, 6H) ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 135.0, 131.4, 128.2, 125.7, 125.6, 125.2, 124.4, 123.4, 118.0, 47.9, 12.4; EI-MS m/z 199 (M^+); HRMS calcd for $\text{C}_{12}\text{H}_{17}\text{NO}$ (M^+), 199.1361, found 199.1359.



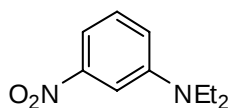
***N,N*-Diethyl-3-methoxyaniline (3j).**⁶ ¹H NMR (300 MHz, CDCl₃) δ 7.11 (t, *J* = 5.4 Hz, 1H) 6.32-6.28 (m, 1H), 6.23-6.19 (m, 2H), 3.76 (s, 3H), 3.31 (q, *J* = 7.2 Hz, 4H), 1.14 (t, *J* = 7.2 Hz, 6H) ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 149.3, 130.0, 105.2, 100.1, 98.5, 55.2, 44.5, 12.7; ESI-MS *m/z* 180 (M + H)⁺.



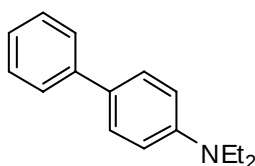
***N,N*-Diethyl-2-methoxyaniline (3k).**⁷ ¹H NMR (300 MHz, CDCl₃) δ 7.03-6.95 (m, 2H), 6.93-6.85 (m, 2H), 3.86 (s, 3H), 3.16 (q, *J* = 7.2 Hz, 4H), 1.02 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 154.0, 139.1, 122.9, 121.9, 120.5, 111.5, 55.5, 46.3, 12.1; (ESI-MS *m/z* 180 (M + H)⁺.



***N,N*-Diethyl-4-acetylaniline (3l).**⁸ ¹H NMR (300 MHz, CDCl₃) δ 7.83 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 3.39 (q, *J* = 7.2 Hz, 4H), 2.48 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 151.1, 130.8, 124.6, 110.0, 44.5, 25.9, 12.5; (ESI-MS *m/z* 192 (M + H)⁺.

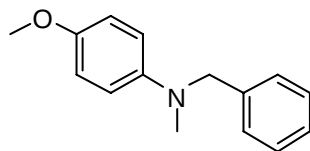


***N,N*-Diethyl-3-nitroaniline (3m).** ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.40 (m, 2H), 7.32-7.25 (m, 1H), 6.93-6.88 (m, 1H), 3.39 (q, *J* = 7.2 Hz, 4H), 1.18 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 148.4, 129.8, 117.1, 109.7, 105.5, 44.6, 12.4; EI-MS *m/z* 194 (M⁺); HRMS calcd for C₁₀H₁₄N₂O₂ (M⁺), 194.1055, found 194.1053.

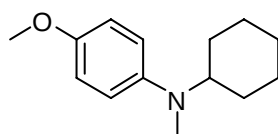


4-(*N,N*-Diethylamino)biphenyl (3n).⁹ ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.24 (dd, *J* = 7.2 Hz, 14.4 Hz, 1H),

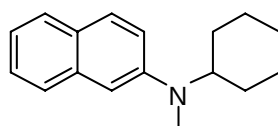
6.76 (d, $J = 9.0$ Hz, 2H), 3.39 (q, $J = 7.2$ Hz, 4H), 1.20 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 141.4, 128.7, 128.1, 128.0, 126.2, 125.9, 112.0, 44.5, 12.8; ESI-MS m/z 226 ($\text{M} + \text{H}$) $^+$.



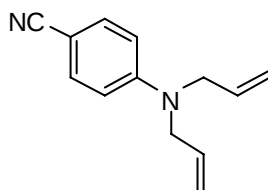
***N*-(4-Methoxyphenyl)-*N*-methylbenzylamine (3o).**² ^1H NMR (300 MHz, CDCl_3) δ 7.50-7.30 (m, 5H), 6.95 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 4.55 (s, 2H), 3.87 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 144.9, 139.3, 128.6, 127.2, 126.9, 114.9, 114.6, 58.1, 55.9, 39.2; ESI-MS m/z 228 ($\text{M} + \text{H}$) $^+$.



***N*-Methyl-*N*-cyclohexyl-4-methoxyaniline (3p).** ^1H NMR (300 MHz, CDCl_3) δ 6.85-6.77 (m, 4H), 3.76 (s, 3H), 3.41-3.33 (m, 1H), 2.71 (s, 3H), 1.84-1.63 (m, 5H), 1.47-1.24 (m, 4H), 1.16-1.07 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.1, 145.3, 116.6, 60.3, 55.8, 32.5, 29.9, 26.3, 26.1; EI-MS m/z 219 (M^+); HRMS calcd for $\text{C}_{14}\text{H}_{21}\text{NO}$ (M^+), 219.1623, found 219.1622.

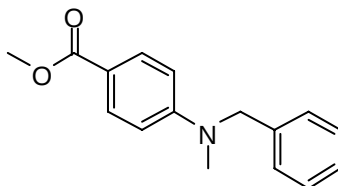


***N*-Methyl-*N*-(naphthalen-2-yl)-cyclohexylamine (3q).** ^1H NMR (300 MHz, CDCl_3) δ 7.68-7.61 (m, 3H), 7.37-7.31 (m, 1H), 7.22-7.15 (m, 2H), 6.94 (s, 1H), 3.73-3.63 (m, 1H), 2.84 (s, 3H), 1.86-1.05 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.3, 135.2, 128.7, 127.5, 127.0, 126.2, 126.2, 122.0, 117.3, 107.3, 58.9, 31.5, 30.2, 26.3, 26.0; EI-MS m/z 239 (M^+); HRMS calcd for $\text{C}_{17}\text{H}_{21}\text{N}$ (M^+), 239.1674, found 239.1677.

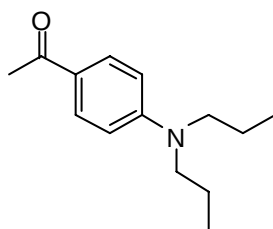


4-(*N,N*-Diallylamino)benzenenitrile (3r).¹⁰ ^1H NMR (300 MHz, CDCl_3) δ 7.41 (d, J

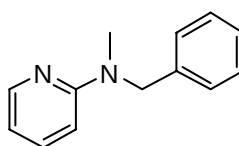
= 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 5.87-5.74 (m, 2H), 5.21-5.09 (m, 4H), 3.97-3.94 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 133.5, 132.3, 120.7, 116.7, 111.9, 97.9, 52.7; EI-MS m/z 198 (M^+); HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2$ (M^+), 198.1157, found 198.1153.



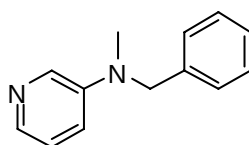
***N*-Methyl-*N*-benzyl-(4-carbomethoxy)aniline (3s).**¹¹ ^1H NMR (300 MHz, CDCl_3) δ 7.90 (d, J = 9.0 Hz, 2H), 7.36-7.23 (m, 3H), 7.18 (d, J = 6.6 Hz, 2H), 6.69 (d, J = 9.0 Hz, 2H), 4.62 (s, 2H), 3.85 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 152.8, 137.8, 131.5, 128.8, 127.2, 126.5, 117.4, 111.0, 56.0, 51.5, 38.7; ESI-MS m/z 256 ($\text{M} + \text{H}$)⁺.



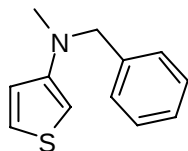
***N,N*-Dipropyl-4-acetylaniline (3t).** ^1H NMR (300 MHz, CDCl_3) δ 7.82 (d, J = 9 Hz, 2H), 6.57 (d, J = 9 Hz, 2H), 3.28 (t, J = 7.8 Hz, 4H), 2.47 (s, 3H), 1.62 (q, J = 4.5 Hz, 4H), 0.93 (t, J = 4.5 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.1, 151.6, 130.8, 124.6, 110.3, 52.8, 25.9, 20.4, 11.4; ; EI-MS m/z 219 (M^+); HRMS calcd for $\text{C}_{14}\text{H}_{21}\text{NO}$ (M^+), 219.1623, found 219.1622.



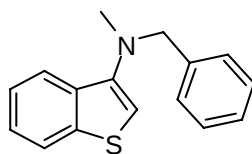
2-(*N*-Benzyl-*N*-methylamino)pyridine (3u). ^1H NMR (300 MHz, CDCl_3) δ 8.18 (d, J = 3.6 Hz, 1H), 7.43 (ddd, J = 1.8 Hz, 6.9 Hz, 8.7 Hz, 1H), 7.34-7.18 (m, 5H), 6.56 (dd, J = 5.1 Hz, 6.9 Hz, 1H), 6.51 (d, J = 8.7 Hz, 1H), 4.80 (s, 2H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 148.1, 138.8, 137.4, 128.6, 127.1, 127.0, 111.9, 105.8, 53.3, 36.2; EI-MS m/z 198 (M^+), HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2$ (M^+), 198.1157, found 198.1156.



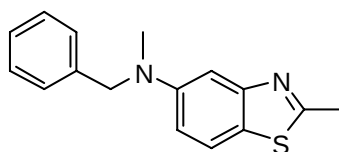
3-(*N*-Benzyl-*N*-methylamino)pyridine (3v). ^1H NMR (300 MHz, CDCl_3) δ 8.17 (d, $J = 2.7$ Hz, 1H), 7.96 (d, $J = 4.5$ Hz, 1H), 7.36-7.18 (m, 5H), 7.09 (dd, $J = 4.5$ Hz, 8.7 Hz, 1H), 7.01-6.95 (m, 1H), 4.55 (s, 2H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 138.0, 137.9, 135.0, 128.8, 127.3, 126.7, 123.6, 118.7, 56.3, 38.5; EI-MS m/z 198 (M^+), HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2$ (M^+), 198.1157, found 198.1160.



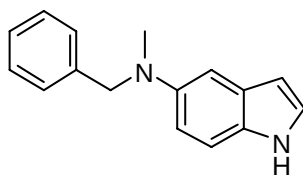
3-(*N*-Benzyl-*N*-methylamino)thiophen (3w). ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.19 (m, 6H), 6.83 (dd, $J = 5.2, 1.6$ Hz, 1H), 5.96 (dd, $J = 2.8, 1.6$ Hz, 1H), 4.36 (s, 2H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.0, 138.8, 128.5, 127.6, 127.1, 125.3, 119.3, 96.8, 58.7, 39.5; EI-MS m/z 203 (M^+), HRMS calcd for $\text{C}_{12}\text{H}_{13}\text{NS}$ (M^+), 203.0769, found 203.0766.



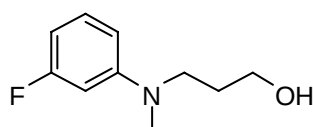
3-(*N*-Benzyl-*N*-methylamino)thianaphthene (3x). ^1H NMR (400 MHz, CDCl_3) δ 7.92-7.81(m, 2H), 7.44-7.30 (m, 7H), 6.58 (s, 1H), 4.28 (s, 2H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 139.5, 138.4, 134.9, 128.6, 128.3, 127.4, 124.6, 123.8, 123.5, 122.1, 106.6, 60.3, 40.7; ESI-MS m/z 253 (M^+), HRMS calcd for $\text{C}_{16}\text{H}_{15}\text{NS}$ (M^+), 253.0925, found 253.0924.



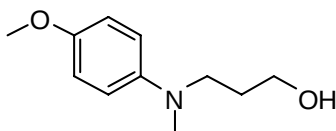
5-(*N*-Benzyl-*N*-methylamino)-2-methylbenzothiazole (3y). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.8$ Hz, 1H), 7.32-7.26 (m, 3H), 7.25-7.20 (m, 3H), 6.85 (dd, $J = 8.8, 2.4$ Hz, 1H), 4.56(s, 2H), 3.07(s, 3H), 2.76(s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.6, 155.2, 149.1, 138.8, 128.7, 127.0, 126.8, 123.6, 121.5, 122.3, 105.2, 57.2, 39.2, 20.2; ESI-MS m/z 268 (M^+), HRMS calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}$ (M^+), 268.1034, found 268.1038.



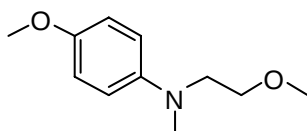
5-(*N*-Benzyl-*N*-methylamino)indole (3z). ^1H NMR (400 MHz, CDCl_3) δ 7.9 (br s, 1H), 7.30 (m, 4H), 7.28-7.20 (m, 2H), 7.12 (t, $J = 2.8$ Hz, 1H), 7.03 (d, $J = 2.4$ Hz, 1H), 6.89 (dd, $J = 4.8, 1.8$ Hz, 1H), 6.43-6.40 (m, 1H), 4.47 (s, 2H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 139.8, 130.2, 128.9, 128.5, 127.6, 126.9, 124.6, 112.9, 111.5, 104.7, 102.2, 59.2, 39.5; ESI-MS m/z 237 ($\text{M} + \text{H}$) $^+$.



***N*-Methyl-*N*-(3-hydroxyl-1-propyl)-3-fluoroaniline (3aa).** ^1H NMR (300 MHz, CDCl_3) δ 7.14 (q, $J = 8.1$ Hz, 1H), 6.50-6.34 (m, 3H), 3.68 (m, 2H), 3.42 (t, $J = 6.9$ Hz, 2H), 2.91 (s, 3H), 2.26 (s, 1H), 1.81 (q, $J = 6.9$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 163.1, 151.2, 151.1, 130.3, 130.2, 107.9, 107.9, 102.7, 102.5, 99.3, 99.1, 60.5, 49.6, 38.4, 29.6; EI-MS m/z 183 (M^+); HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{NOF}$ (M^+), 183.1059, found 183.1061.

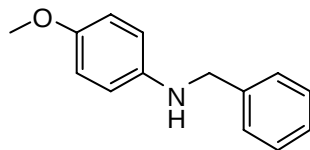


***N*-Methyl-*N*-(3-hydroxyl-1-propyl)-4-methoxyaniline (3ab).** ^1H NMR (300 MHz, CDCl_3) δ 6.86-6.78 (m, 4H), 3.75 (s, 3H), 3.73 (t, $J = 6.0$ Hz, 2H), 3.30 (t, $J = 6.8$ Hz, 2H), 3.10 (s, 1H), 2.81 (s, 3H), 1.78 (q, $J = 6.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 144.9, 116.4, 114.7, 61.8, 55.8, 52.8, 39.8, 29.3; EI-MS m/z 195 (M^+); HRMS calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_2$ (M^+), 195.1259, found 195.1256.

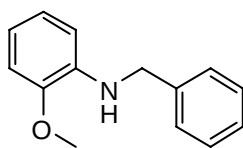


***N*-Methyl-*N*-(2-methoxy-1-ethyl)-4-methoxyaniline (3ac).** ^1H NMR (300 MHz, CDCl_3) δ 6.84 (d, $J = 9.0$ Hz, 2H), 6.74 (d, $J = 9.0$ Hz, 2H), 3.76 (s, 3H), 3.54 (t, $J = 6.0$ Hz, 2H), 3.43 (t, $J = 6.0$ Hz, 2H), 3.37 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.8,

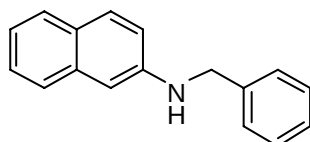
144.5, 114.8, 114.5, 70.4, 59.0, 55.8, 53.8, 39.6; EI-MS m/z 195 (M^+); HRMS calcd for $C_{10}H_{14}N_2O_2$ (M^+), 195.1259, found 195.1255.



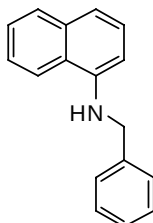
N-Benzyl-4-methoxyaniline (3ad). 12 1H NMR (300 MHz, $CDCl_3$) δ 7.60-7.46 (m, 5H), 7.00 (d, J = 6.9 Hz, 2H), 6.79 (d, J = 6.9 Hz, 2H), 4.46 (s, 2H), 3.98 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 142.4, 139.7, 128.6, 127.5, 127.1, 114.8, 114.0, 55.7, 49.1; ESI-MS m/z 214 ($M + H$) $^+$.



N-Benzyl-2-methoxyaniline (3ae). 13 1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 6.80 (td, J = 0.9, 5.7 Hz, 1H), 6.74 (d, J = 5.7 Hz, 1H), 6.65 (td, J = 0.9, 5.7 Hz, 1H), 6.56 (d, J = 5.7 Hz, 1H), 4.60 (s, 1H), 4.29 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 139.6, 138.1, 128.6, 127.5, 127.1, 121.3, 111.6, 110.1, 109.4, 55.4, 48.0; ESI-MS m/z 214 ($M + H$) $^+$.

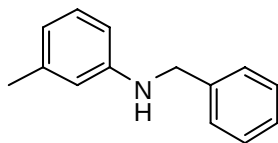


N-Benzyl (2-naphthyl)amine (3af). 14 1H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 7.8 Hz, 1H), 7.77-7.74 (m, 2H), 7.55-7.41 (m, 6H), 7.40-7.36 (td, J = 7.2, 1.2 Hz, 1H), 6.97-6.90 (m, 2H), 4.45 (s, 2H), 4.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 139.2, 135.2, 128.9, 128.9, 128.6, 127.7, 127.5, 127.3, 126.3, 126.0, 122.0, 117.9, 104.6, 48.1; ESI-MS m/z 234 ($M + H$) $^+$.

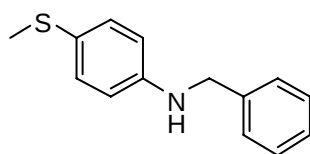


N-Benzyl (1-naphthyl)amine (3ag). 15 1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 6.0 Hz, 1H), 7.70 (d, J = 6.0 Hz, 1H), 7.54-7.31 (m, 9H), 6.67 (d, J = 5.4 Hz, 2H), 4.68 (s, 1H),

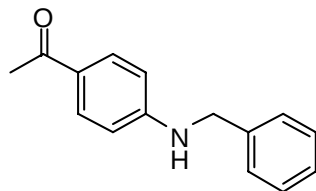
4.47 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 139.1, 134.3, 128.7, 127.7, 127.4, 126.7, 125.8, 124.8, 123.4, 120.0, 117.6, 104.8, 48.5; ESI-MS m/z 234 ($\text{M} + \text{H}$) $^+$.



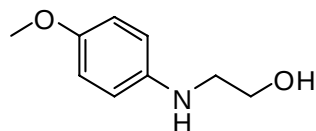
N-Benzyl-3-methylaniline (3ah). 16 ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.27 (m, 5H), 7.11 (t, J = 6.0 Hz, 1H), 6.60 (d, J = 6.0 Hz, 1H), 6.50-6.44 (m, 2H), 4.30 (s, 2H), 3.92 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.2, 139.6, 139.0, 129.2, 128.6, 127.5, 127.2, 118.5, 113.6, 110.0, 48.3, 21.7; ESI-MS m/z 198 ($\text{M} + \text{H}$) $^+$.



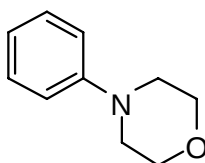
4-(N-Benzyl)aminothioanisole (3ai). 17 ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.20 (m, 5H), 7.16 (d, J = 8.4 Hz, 2H), 6.52 (d, J = 8.4 Hz, 2H), 4.24 (s, 2H), 4.03 (brs, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 139.2, 131.4, 128.7, 127.4, 127.3, 124.4, 113.5, 48.2, 19.1; ESI-MS m/z 230 ($\text{M} + \text{H}$) $^+$.



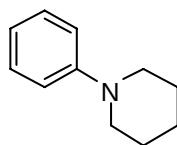
4-(N-Benzyl)aminoacetophenone (3aj). 18 ^1H NMR (300 MHz, CDCl_3) δ 7.83 (d, J = 6.6 Hz, 2H), 7.40-7.27 (m, 5H), 6.61 (d, J = 6.6 Hz, 2H), 5.04 (m, 1H), 4.40 (d, J = 4.2 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 152.1, 138.3, 130.7, 128.7, 127.4, 127.2, 126.5, 111.5, 47.3, 25.9; ESI-MS m/z 226 ($\text{M} + \text{H}$) $^+$.



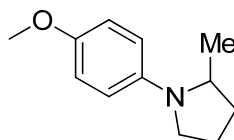
2-(4-Methoxy-phenylamino)-ethanol (3ak). 19 ^1H NMR (300 MHz, CDCl_3) δ 6.83 (d, J = 9.0 Hz, 2H), 6.60 (d, J = 9.0 Hz, 2H), 3.83 (t, J = 8.4 Hz, 2H), 3.79 (s, 3H), 3.24 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 142.3, 115.0, 114.9, 61.3, 55.9, 47.3; ESI-MS m/z 168 ($\text{M} + \text{H}$) $^+$.



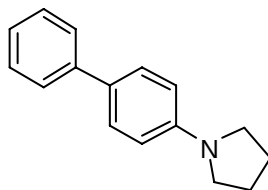
N-Phenylmorpholine (3al).²⁰ ^1H NMR (300 MHz, CDCl_3) δ 7.32 (dd, $J = 7.2$ Hz, 8.7 Hz, 2H), 6.97-6.88 (m, 3H), 3.90-3.84 (m, 4H), 3.20-3.13 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.3, 129.2, 120.0, 115.6, 66.9, 49.3; ESI-MS m/z 164 ($\text{M} + \text{H}$)⁺.



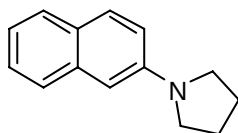
N-Phenylpiperidine (3am).²¹ ^1H NMR (300 MHz, CDCl_3) δ 7.26 (dd, $J = 7.8$, 7.5 Hz, 2H), 6.95 (d, $J = 7.8$ Hz, 2H), 6.84 (t, $J = 7.5$ Hz, 1H), 3.15 (m, 4H), 1.70 (m, 4H), 1.58 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.2, 129.0, 119.2, 116.5, 50.6, 25.9, 24.3; ESI-MS m/z 162 ($\text{M} + \text{H}$)⁺.



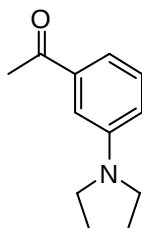
1-(4-Methoxyphenyl)-2-methylpyrrolidine (3an).²² ^1H NMR (300 MHz, CDCl_3) δ 6.85 (d, $J = 7.4$ Hz, 2H); 6.55 (d, $J = 7.5$ Hz, 2H), 3.76 (s, 3H), 3.74-3.82 (m, 1H), 3.35-3.49 (m, 1H), 3.07-3.15 (m, 1H), 1.92-2.11 (m, 3H), 1.63-1.73 (m, 1H), 1.16 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.7, 142.5, 132.3, 115.8, 115.2, 112.8, 56.1, 54.2, 49.0, 33.3, 23.5, 19.7. ESI-MS m/z 192 ($\text{M} + \text{H}$)⁺.



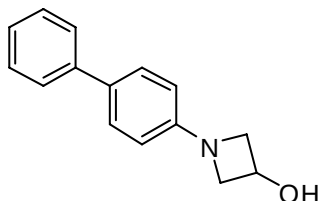
1-Biphenyl-4-yl-pyrrolidine (3ao).²³ ^1H NMR (300 MHz, CDCl_3) δ 7.60 (dd, $J = 0.9$, 6.0 Hz, 2H), 7.53 (d, $J = 6.6$ Hz, 2H), 7.42 (t, $J = 6.0$ Hz, 2H), 7.27 (t, $J = 5.7$ Hz, 1H), 6.65 (d, $J = 6.0$ Hz, 2H), 3.36-3.29 (m, 4H), 2.05-1.97 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.4, 141.5, 128.7, 128.1, 127.8, 126.2, 125.8, 112.0, 47.7, 25.6; ESI-MS m/z 224 ($\text{M} + \text{H}$)⁺.



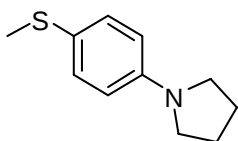
1-Naphthalen-2-ylpyrrolidine (3ap). ^1H NMR (300 MHz, CDCl_3) δ 7.64 (d, J = 6.3 Hz, 2H), 7.59 (d, J = 6.3 Hz, 1H), 7.31 (td, J = 0.9, 5.7 Hz, 1H), 7.13 (td, J = 0.6 Hz, 5.7 Hz, 1H), 6.92 (dd, J = 1.8, 6.9 Hz, 1H), 6.70 (d, J = 1.2 Hz, 1H), 3.35-3.27 (m, 4H), 2.00-1.92 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 135.3, 128.8, 127.7, 126.3, 126.2, 125.8, 121.2, 115.8, 104.7, 47.8, 25.5; ESI-MS m/z 198 ($\text{M} + \text{H}$) $^+$.



1-(3-Acetylphenyl)pyrrolidine (3aq). ^1H NMR (300 MHz, CDCl_3) δ 7.23 (d, J = 6.0 Hz, 1H), 7.17 (d, J = 5.4 Hz, 1H), 7.07 (m, 1H), 6.67 (dd, J = 1.2, 6.0 Hz, 1H), 3.26-3.19 (m, 4H), 2.52 (s, 3H), 1.97-1.92 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.6, 147.6, 137.6, 128.9, 116.0, 115.5, 110.2, 47.4, 26.5, 25.2; ESI-MS m/z 190 ($\text{M} + \text{H}$) $^+$.

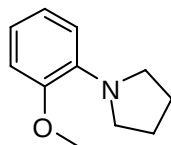


1-Biphenyl-4-yl-3-hydroxycyclobutylamine (3ar). ^1H NMR (300 MHz, CDCl_3) δ 7.53 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.27 (t, J = 7.8 Hz, 1H), 6.53 (d, J = 8.7 Hz, 2H), 4.77-4.65 (m, 1H), 4.18 (dd, J = 8.1, 6.6 Hz, 2H), 3.67 (dd, J = 8.1, 4.8 Hz, 2H), 2.51 (d, J = 5.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 141.3, 131.0, 128.8, 127.8, 126.5, 126.3, 112.4, 63.0, 62.1; EI-MS m/z 225 (M^+); HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$ (M^+), 225.1154, found 225.1157.

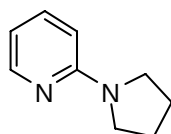


1-(4-Methylthiophenyl)pyrrolidine (3as). ^1H NMR (300 MHz, CDCl_3) δ 7.32 (d, J = 6.6 Hz, 2H), 6.53 (d, J = 6.6 Hz, 2H), 3.32-3.24 (m, 4H), 2.44 (s, 3H), 2.05-1.98 (m, 4H);

^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 132.1, 121.6, 112.2, 47.6, 25.5, 19.8; EI-MS m/z 193 (M^+); HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{NS}$ (M^+), 193.0925, found 193.0928.



N-(2-Methoxyphenyl)pyrrolidine (3at)^{20,24} ^1H NMR (300 MHz, CDCl_3) δ 6.88-6.72 (m, 4H), 3.77 (s, 3H), 3.26-3.19 (m, 4H), 1.90-1.84 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.3, 139.7, 121.0, 119.5, 115.3, 111.5, 55.4, 50.3, 24.6; ESI-MS m/z 178 ($\text{M} + \text{H}$)⁺.



2-Pyrrolidinopyridine (3au)²⁵ ^1H NMR (300 MHz, CDCl_3) δ 8.15 (d, J = 3.0 Hz, 1H), 7.39 (td, J = 1.5, 6.0 Hz, 1H), 6.48 (dd, J = 4.8, 4.2 Hz, 1H), 6.31 (d, J = 6.0 Hz, 1H), 3.46-3.38 (m, 4H), 2.01-1.93 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.2, 148.0, 136.7, 110.9, 106.4, 46.5, 25.4; ESI-MS m/z 149 ($\text{M} + \text{H}$)⁺.

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