

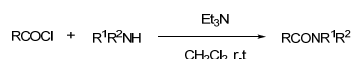
A General and Selective Copper-catalyzed Reduction of Secondary Amides

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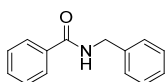
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General information: Unless otherwise stated, reactions were run under an argon atmosphere with exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. THF, toluene, 1,2-dimethoxyethane, 1,4-dioxane, diglyme and di-n-butyl ether were distilled from sodium and dichloromethane was distilled from calcium hydride. NMR spectra were recorded on Bruker AV 300. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively. All measurements were carried out at room temperature unless otherwise stated. Infrared spectra were recorded on a Nicolet Magna-IR-Serie 550 spectrometer using the ATR method. Wave numbers (ν) are reported in cm^{-1} . Mass spectra were recorded on an AMD 402/3 or a HP 5989A mass selective detector. Gas chromatography was performed on a HP 6890 chromatograph with a HP5 column.

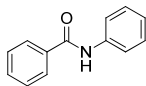


1. General procedure for the preparation of amides¹: The acyl chloride (10.0 mmol) was added in one portion to a solution of the amine (11 mmol), Et_3N (12.5 mmol) and dichloromethane (20 mL) at room temperature, resulting rapidly in a boiling solution. The reaction mixture was stirred for 30-60 min. at room temperature and then was diluted with dichloromethane (30 mL). The solution was transferred to a separation funnel and was washed with 1N HCl (50 mL). The organic layer was filtered on a short silica gel column and washed with ethyl acetate/hexane (1:1). The combined fractions were concentrated under reduced pressure.

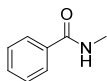
2. Characterisation of amides:



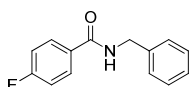
N-benzylbenzamide (1a): Sigma Aldrich (1485-70-7).



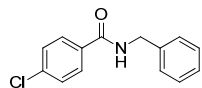
N-phenylbenzamide (2a): Acros (93-98-1).



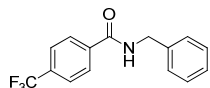
N-methylbenzamide (3a): Sigma Aldrich (613-93-4).



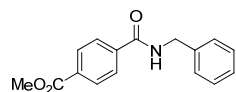
N-Benzyl-4-fluorobenzamide² (4a): white solid. ^1H NMR (300.1 MHz, CDCl_3): δ 7.72 (dd, $J^1 = 8.85$ Hz, $J^2 = 5.27$ Hz, 2H), 7.29-7.19 (m, 5H), 7.02 (t, $J = 8.66$ Hz, 2H), 6.36 (s, br, 1H), 4.55 (d, $J = 5.65$ Hz, 2H) ^{13}C NMR δ 166.3, 138.0, 129.3, 129.2, 128.8, 127.9, 127.7, 115.8, 115.5, 44.2. **MS (EI):** m/z 229 (M^+).



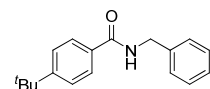
N-Benzyl-4-chlorobenzamide² (5a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.66 (d, *J*= 8.66 Hz, 2H), 7.33 (d, *J*= 8.66 Hz, 2H), 7.30-7.21 (m, 5H), 6.38 (s, br, 1H), 4.56 (d, *J*= 5.65 Hz, 2H) ¹³C NMR δ 166.3, 137.9, 137.8, 132.7, 128.8, 128.4, 127.9, 127.7, 44.2. **MS (EI):** *m/z* 245 (M⁺).



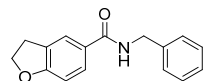
N-Benzyl-4-(trifluoromethyl)benzamide² (6a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.95 (d, *J*= 8.10 Hz, 2H), 7.74 (d, *J*= 8.10 Hz, 2H), 7.43-7.33 (m, 5H), 6.53 (s, br, 1H), 4.71 (d, *J*= 5.65 Hz, 2H) ¹³C NMR δ 166.2, 137.67, 137.63, 128.9, 128.0, 127.8, 127.4, 125.7, 125.6, 44.4. **MS (EI):** *m/z* 279 (M⁺).



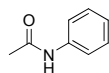
Methyl 4-(benzylcarbamoyl)benzoate² (7a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 8.11 (d, *J*= 8.78 Hz, 2H), 7.82 (d, *J*= 8.73 Hz, 2H), 7.32-7.28 (m, 5H), 6.56 (s, br, 1H), 4.65 (s, 2H), 3.93 (s, 3H). ¹³C NMR δ 166.4, 138.2, 137.8, 132.7, 129.8, 128.8, 127.9, 127.7, 127.0, 52.3, 44.2. **MS (EI):** *m/z* 217 (M⁺).



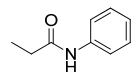
N-Benzyl-4-tert-butylbenzamide² (8a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.66 (d, *J*= 8.56 Hz, 2H), 7.36 (d, *J*= 8.56 Hz, 2H), 7.27 (d, *J*= 4.40 Hz, 4H), 7.22 (m, 1H), 6.36 (s, 1H), 4.57 (d, *J*= 5.62 Hz, 2H), 1.25 (s, 9H) ¹³C NMR δ 167.3, 155.1, 138.4, 131.5, 128.8, 127.9, 127.6, 126.9, 125.6, 44.1, 35.0, 31.2. **MS (EI):** *m/z* 267 (M⁺).



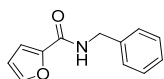
N-Benzyl-2,3-dihydrobenzofuran-5-carboxamide² (9a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.62 (s, 2H), 7.49 (dd, *J*¹= 8.46 Hz, *J*²= 1.96 Hz, 1H), 7.27 (s, 2H), 7.26 (s, 2H), 7.22 (m, 1H), 6.69 (d, *J*= 8.32 Hz, 1H), 6.29 (s, br, 1H), 4.55 (t, *J*= 8.80 Hz, 2H), 4.54 (d, *J*= 5.60 Hz, 2H), 3.14 (t, *J*= 8.90 Hz, 2H) ¹³C NMR δ 167.1, 163.0, 138.4, 128.7, 127.9, 127.6, 127.5, 126.8, 124.4, 108.9, 71.9, 44.1, 29.2. **MS (EI):** *m/z* 253 (M⁺).



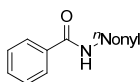
Acetanilide (10a): Acros (103-84-4).



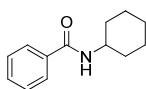
N-Phenylpropionamide (11a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.44 (d, *J*= 7.92 Hz, 2H), 7.24 (dd, *J*¹= 8.46 Hz, *J*²= 1.96 Hz, 2H), 7.01 (t, *J*= 7.38 Hz, 1H), 2.31 (q, *J*= 7.55 Hz, 2H), 1.16 (t, *J*= 7.56 Hz, 3H) ¹³C NMR δ 172.17, 138.04, 129.01, 124.19, 119.84, 30.78, 97.4. **MS (EI):** *m/z* 149 (M⁺).



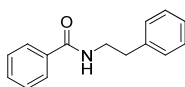
N-Benzylfuran-2-carboxamide²: white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.34 (m, 1H), 7.28 (d, *J* = 4.19 Hz, 4H), 7.23 (m, 1H), 7.07 (d, *J* = 3.44 Hz, 1H), 6.58 (s, br, 1H), 6.42 (q, *J* = 1.76 Hz, 1H), 4.55 (d, *J* = 5.92 Hz, 2H) ¹³C NMR δ 158.2, 147.9, 143.9, 138.0, 128.8, 128.0, 127.6, 114.4, 112.2, 43.1. **MS (EI):** *m/z* 201 (M⁺).



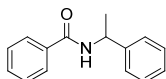
N-Nonylbenzamide (13a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.68 (dt, *J*¹ = 1.39 Hz, *J*² = 7.02 Hz, 2H), 7.45-7.32 (m, 3H), 6.05 (s, br, 1H), 3.38, (q, *J* = 7.08 Hz, 2H), 1.60-1.48 (m, 3H), 1.23 (s, br, 13H), 0.80 (t, *J* = 6.51 Hz, 3H) ¹³C NMR δ 167.5, 134.9, 131.3, 128.6, 126.8, 40.2, 31.9, 29.7, 29.5, 29.4, 29.3, 27.0, 22.7, 14.2. **MS (EI):** *m/z* 261 (M⁺).



N-Cyclohexylbenzamide (14a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.68 (dt, *J*¹ = 1.42 Hz, *J*² = 7.20 Hz, 2H), 7.44-7.30 (m, 3H), 5.94 (s, br, 1H), 3.97-3.84, (m, 1H), 1.95 (dd, *J*¹ = 1.56 Hz, *J*² = 8.21 Hz, 2H), 1.73-1.53 (m, 3H), 1.44-1.03 (m, 5H) ¹³C NMR δ 166.7, 135.1, 131.3, 128.5, 126.9, 48.7, 33.3, 25.6, 25.0. **MS (EI):** *m/z* 203 (M⁺).



N-Phenethylbenzamide (15a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.61 (dt, *J*¹ = 1.29 Hz, *J*² = 6.84 Hz, 2H), 7.43-7.12 (m, 8H), 6.16 (s, br, 1H), 3.63 (q, *J*¹ = 3.46 Hz, *J*² = 6.87 Hz, 2H), 2.85 (t, *J* = 6.93 Hz, 2H). ¹³C NMR δ 167.5, 139.0, 134.7, 131.4, 128.9, 128.8, 128.6, 126.9, 41.2, 35.8. **MS (EI):** *m/z* 225 (M⁺).

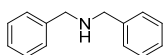


N-(1-Phenethyl)benzamide (16a): white solid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.69 (dt, *J*¹ = 1.48 Hz, *J*² = 7.43 Hz, 2H), 7.44-7.16 (m, 8H), 6.33 (s, br, 1H), 5.26, (quin, *J* = 7.26, 1H), 1.52 (d, *J* = 6.90 Hz, 3H). ¹³C NMR δ 166.6, 143.2, 134.6, 131.5, 128.8, 128.6, 127.5, 127.0, 126.3, 49.3, 21.8. **MS (EI):** *m/z* 225 (M⁺).

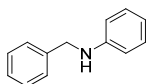
3. General procedure for the reduction of secondary amides: A 25 mL oven dried Schlenk tube containing a stirr bar was charged with copper triflate (0.1 mmol), ligand (1.25-3 mol%) and the corresponding amide (1 mmol). Dry toluene (3 mL) and tetramethyldisiloxane (TMDS) (3 mmol) were added respectively after purging the schlenk tube with argon. The resulting mixture was monitored by TLC and stirred at 65 °C until the substrates completely goes away. After complete disappearance of the substrates, the reaction mixture was vigorously stirred with 5 mL 25% KOH in methanol solution in 50 mL conical flask for 3 h and then extracted with ethylacetate (3 x 20 mL). The combined organic layer dried over anhydrous Na₂SO₄, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography using ethylacetate / hexane / triethylamine (1%) to afford the pure desired product.

Purification method for the amine having ester functional group¹⁸: After complete consumption of the starting material the reaction mixture was filtered through a pad of florisil and the filtrate was poured into an ethereal solution of hydrogen chloride [0.1 (M), 10 mL; prepared from commercially available 1(M) HCl/ ether (1 mL) and ether 9 mL]. The ammonium salt was precipitated as a white powder. Separation of the supernatant by decantation or centrifugation followed by washing of the residue with ether afforded the raw product without contamination of silicone residues. The remaining mixture was treated with excess amount of sodium carbonate in wet THF at 0 °C for 0.5-1h. The solid materials are filtered off and the desired amine was obtained by concentration of the filtrate.

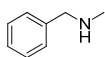
4. Characterisation of amines:



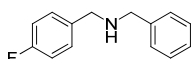
Dibenzylamine² (1b): yield 90%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.43-7.32 (m, 10H), 3.92 (s, 4H), 1.73 (s, 1H) ¹³C NMR δ 140.4, 128.5, 128.2, 127.0, 53.2. **ATR-IR** 3061(m), 3026(m), 2814(br), 1602(s); 1494(s); 1453(s), 1361(w); 1195(w), 1112(br), 1027(s), 983(w), 907(w), 828(w), 733(s), 696(s), 615(w), 574(w), 469(br), 393(w). **MS (EI):** *m/z* 197(M⁺). **HRMS** (EI, *m/z*) calcd. for C₁₄H₁₅N, 197.1213; found 197.1211.



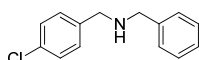
N-Benzylaniline² (2b): yield 85%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.46-7.39 (m, 4H), 7.36-7.33 (m, 1H), 7.27-7.22 (m, 2H), 6.79(t, *J*=2.70, 1H), 6.71 (d, *J*= 2.31Hz, 2H), 4.40(s, 2H), 4.09 (s, br, 1H) ¹³C NMR δ 148.2, 139.5, 129.3, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4, 32.7. **ATR-IR** (cm⁻¹) (neat) 3053 (w), 3417(br), 3051(w), 3025(w), 2839(w), 1600(s), 1504(s), 1452(s), 1429(m), 1360(m), 1323(s), 1266(s), 1179(m), 1154(m), 1098(w), 1064(w), 1028(w), 989(w), 868(w), 748(s), 731(s), 692(s), 510(w), 456(w). **MS (EI):** *m/z* 183(M⁺). **HRMS** (EI, *m/z*) calcd. for C₁₃H₁₃N, 183.1048; found 183.1050.



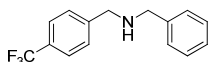
N-Methylbenzylamine (3b): Sigma Aldrich (103-67-3).



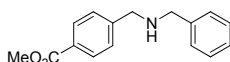
N-Benzyl-1-(4-fluorophenyl)methanamine² (4b): yield 83%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.23-7.13 (m, 7H), 6.88 (t, *J*= 8.74Hz, 2H), 3.67(s, 2H), 3.64(s, 2H), 1.55(s, br, 1H) ¹³C NMR δ 140.2, 136.1, 136.0, 129.8, 129.7, 128.5, 128.2, 127.1, 115.3, 115.1, 53.2, 52.4. **ATR-IR** (cm⁻¹) (neat) 3027(w), 2819(br), 1601(s), 1508(s), 1453(s), 1360(m), 1217(s), 1155(s), 1093(s), 1028(w), 1015(w), 908(w), 821(s), 737(s), 697(s), 668(m), 596(w), 551(s), 499(s), 424(w). **MS (EI):** *m/z* 215(M⁺). **HRMS** (EI, *m/z*) calcd. for C₁₄H₁₄NF, 215.1112; found 215.1114.



N-Benzyl-1-(4-chlorophenyl)methanamine² (5b): yield 72%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.26-7.14(m, 9H), 3.70 (s, 2H), 3.69 (s, 2H) 1.67(s, br, 1H) ¹³C NMR δ 139.0, 137.7, 131.6, 128.4, 127.8, 127.4, 127.2, 127.1, 126.9, 126.7, 126.0, 52.0, 51.3. **ATR-IR** (cm⁻¹) (neat) 3025(w), 2830(w), 1597(m), 1491(s), 1453(s), 1406(w), 1360(m), 1260(m), 1214(s), 1089(s), 1015(m), 908(w), 745(s), 698(s), 667(s), 528(w), 484(w). **MS (EI):** *m/z* 231(M⁺). **HRMS** (EI, *m/z*) calcd. for C₁₄H₁₄NCl, 231.0811; found 231.0809.

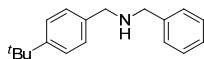


N-Benzyl-1-(4-(trifluoromethyl)phenyl)methanamine² (6b): yield 85%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.45 (d, *J*=8.04Hz, 2H), 7.33 (d, *J*= 8.31 Hz, 2H), 7.23-7.19(m, 5H), 3.77(s, 2H), 3.66 (s, 2H), 1.98(s, br, 1H) ¹³C NMR δ 143.3, 138.9, 128.3, 128.0, 127.8, 127.4, 127.3, 127.2, 127.1, 126.9, 126.8, 126.1, 124.6, 124.3, 124.2, 121.9, 52.1, 51.5. **ATR-IR** (cm⁻¹) (neat) 3029(w), 2960(w), 1619(w), 1495(w), 1454(m), 1417(m), 1324(s), 1260(m), 1163(s), 1121(s), 1066(s), 1018(s), 908(w), 803(s), 734(m), 698(s), 640(w), 592(w). **MS (EI):** *m/z* 265(M⁺). **HRMS** (EI, *m/z*) calcd. for C₁₅H₁₄NF₃, 265.1112; found 265.1109.

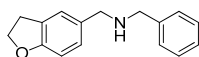


Methyl 4-((benzylamino)methyl)benzoate² (7b): yield 75%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.92 (d, *J*= 8.31 Hz, 2H), 7.34 (d, *J*= 8.31 Hz, 2H), 7.25 (d, *J*= 4.40 Hz, 4H), 7.18 (m, 1H), 3.82 (s, 3H), 3.78 (s,

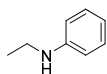
2H), 3.72 (s, 2H), 1.70 (s, 1H) ^{13}C NMR δ 167.0, 145.7, 140.0, 129.7, 128.8, 128.4, 128.1, 127.9, 127.0, 53.1, 52.7, 52.0. **ATR-IR** (cm^{-1}) (neat) 3027(w), 2949(w), 2838(w), 1716(s), 1610(m), 1575(w), 1494(w), 1452(s), 1434(m), 1413(m), 1361(w), 1308(w), 1273(s), 1191(w), 1175(s), 1104(s), 1018(s), 965(m), 855(w), 734(s), 696(s), 587(w), 481(w). **MS (EI):** m/z 255 (M^+). **HRMS** (EI, m/z) calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_2$, 255.1259; found 255.1257.



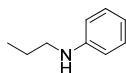
N-Benzyl-1-(4-tert-butylbenzyl)amine² (8b): yield 73%, yellow liquid. ^1H NMR (300.1 MHz, CDCl_3): δ 7.28-7.24 (m, 5H), 7.22-7.14 (m, 3H), 3.73 (s, 2H), 3.70 (s, 2H), 1.81 (s, br, 1H), 1.24 (s, 9H). ^{13}C NMR δ 149.8, 140.3, 137.3, 128.4, 128.1, 127.8, 126.9, 125.3, 53.2, 52.7, 31.7. **ATR-IR** (cm^{-1}) (neat) 3026(w), 2960 (s), 2867(w), 1643(w), 1512(w), 1497(m), 1453(s), 1410(w), 1362(s), 1259(s), 1201(w), 1093(br), 1017(s), 907(s), 799(br), 730(s), 696(s), 593(m), 568(m), 530(w), 467(w), 387(s). **MS (EI):** m/z 253 (M^+). **HRMS** (EI, m/z) calcd. for $\text{C}_{18}\text{H}_{23}\text{N}$, 253.1820 found 253.1822.



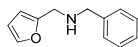
N-Benzyl-1-(2,3-dihydrobenzofuran-5-yl)methanamine² (9b): yield 83%, yellow liquid. ^1H NMR (300.1 MHz, CDCl_3): δ 7.25-7.22 (m, 4H), 7.16-7.13 (m, 5H), 3.70 (s, 2H), 3.67 (s, 2H), 1.73 (s, br, 1H). ^{13}C NMR δ 159.2, 140.3, 132.3, 128.4, 128.2, 127.9, 127.1, 126.9, 125.0, 108.9, 71.3, 53.0, 52.8, 29.7. **ATR-IR** (cm^{-1}) (neat) 3024(w), 2892(w), 1705(w), 1611(m), 1489(s), 1452(s), 1361(s), 1242(s), 1128(w), 1103(s), 1027(m), 982(s), 942(s), 814(m), 733(m), 696(s), 617(w), 577(w), 517(w), 468(m), 420(w). **MS (EI):** m/z 239 (M^+). **HRMS** (EI, m/z) calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}$, 239.1310; found 239.1313.



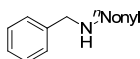
N-Ethylaniline (10b): yield 72%, Sigma Aldrich (103-69-5)



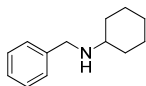
N-Propylaniline (11b): yield 73%, ABCR Chemicals (622-80-0)



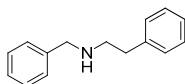
N-Benzyl-1-(furan-2-yl)methanamine² (12b): yield 70%, yellow liquid. ^1H NMR (300.1 MHz, CDCl_3): δ 7.25 (dd, $J^1 = 0.84\text{Hz}$, $J^2 = 1.88\text{Hz}$, 1H), 7.28-7.13 (m, 5H), 6.22-6.20 (m, 1H), 6.07 (d, $J = 1.28\text{Hz}$, 1H), 3.67 (s, 4H), 1.87 (s, br, 1H). ^{13}C NMR δ 152.7, 140.7, 138.7, 127.4, 127.3, 127.2, 127.1, 125.9, 109.0, 106.0, 51.7, 44.2. **ATR-IR** (cm^{-1}) (neat) 3027(w), 2831(w), 1601(w), 1495(m), 1453(s), 1335(w), 1259(m), 1181(w), 1146(s), 1075(s), 1028(s), 1009(s), 916(m), 884(m), 804(s), 732(s), 698(s), 638(w), 599(s), 473(w). **MS (EI):** m/z 187 (M^+). **HRMS** (EI, m/z) calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}$, 187.1025; found 187.1028.



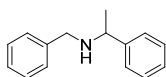
N-Benzylnonan-1-amine (13b): yield 80%, yellow liquid. ^1H NMR (300.1 MHz, CDCl_3): δ 7.24-7.07 (m, 5H), 3.67 (s, 1H), 2.50 (t, $J = 7.21\text{Hz}$, 2H), 1.50-1.32 (m, 4H), 1.15 (s, br, 13H), 0.76 (t, $J = 6.73\text{Hz}$, 3H). ^{13}C NMR δ 140.6, 128.4, 128.2, 126.9, 54.1, 46.9, 31.9, 30.2, 29.6, 29.3, 27.4, 22.7, 14.2. **ATR-IR** (cm^{-1}) (neat) 3025(w), 2945(w), 2924(s), 2852(s), 1640(w), 1493(w), 1458(w), 1370(w), 1255(s), 1090(s), 1025(s), 910(w), 802(s), 730(m), 695(s), 638(m), 512(w), 392(w). **MS (EI):** m/z 247 (M^+). **HRMS** (EI, m/z) calcd. for $\text{C}_{17}\text{H}_{29}\text{N}$, 247.23000; found 247.23005.



N-Cyclohexanamine ³(14b): yield 75%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.32-7.30 (m, 4H), 7.25-7.20 (m, 1H), 3.78 (s, 2H), 2.45-2.42 (m, 2H), 1.92-1.85 (m, 2H), 1.76-1.72 (m, 1H), 1.38 (br s, 1H), 1.29-1.18 (m, 5H); ¹³C NMR: δ 140.5, 127.0, 126.8, 125.4, 53.8, 49.7, 32.2, 24.8, 23.7; **ATR-IR** (cm⁻¹) (neat) 3026(w), 2919(s), 2849(s), 1602(w), 1494(m), 1448(s), 1348(w), 1258(w), 1123(w), 1073(w), 1028(s), 969(w), 891(w), 843(w), 803(w), 732(s), 696(s), 638(m), 605(m), 463(w), 404(w), 385(w). **MS (EI):** *m/z* 189. **HRMS** (EI, *m/z*): calcd. for C₁₃H₁₉N: 189.15961 *m/z*, found: 189.15958.



N-Benzyl-2-phenylethanamine ⁴(15b): yield 78%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.26-7.06 (m, 10H), 3.78 (s, 2H), 2.85-2.78 (m, 2H), 2.78-2.70 (m, 2H), 1.69 (s, br, 1H). ¹³C NMR δ 142.2, 140.5, 128.5, 128.4, 128.3, 128.2, 127.0, 125.8, 54.1, 49.0, 33.7. **ATR-IR** (cm⁻¹) (neat) 3025(w), 2926(w), 2855(w), 1646(w), 1602(w), 1494(s), 1453(s), 1214(s), 1186(w), 1028(w), 908(w), 741(s), 697(s), 667(s), 571(w), 489(w). **MS (EI):** *m/z* 211 (M⁺). **HRMS** (EI, *m/z*) calcd. for C₁₅H₁₇N, 211.13610; found 211.13606.



N-Benzyl-1-phenylethanamine ⁵(16b): yield 76%, yellow liquid. ¹H NMR (300.1 MHz, CDCl₃): δ 7.26-7.07 (m, 10H), 3.76 (q, *J* = 6.72 Hz, 1H), 3.63 (d, *J* = 13.31 Hz, 1H), 3.58 (d, *J* = 13.31 Hz, 1H), 1.65 (s, br, 1H), 1.35 (d, *J* = 6.72 Hz, 3H) ¹³C NMR δ 142.2, 141.5, 128.9, 128.7, 128.5, 127.2, 127.0, 126.8, 57.8, 51.9, 24.7 **ATR-IR** (cm⁻¹) (neat) 3025(w), 2923(w), 2850(w), 1697(w), 1643(m), 1601(w), 1508(w), 1494(m), 1452(s), 1361(w), 1260(w), 1214(s), 1027(s), 952(s), 894(w), 855(w), 816(s), 744(s), 697(s), 667(s), 621(w), 475(s), 399(w). **MS (EI):** *m/z* 211 (M⁺). **HRMS** (EI, *m/z*) calcd. for C₁₅H₁₇N, 211.13610; found 211.13608.

References:

1. G. Barbe, A. B. Charette, *J. Am. Chem. Soc.* 2008, **130**, 18
2. S. Das, D. Addis, K. Junge, M. Beller, *Chem. Eur. J.* 2011, **17**, 12186.
3. G. Pelletier, W. S. Bechara, and A. B. Charette, *J. Am. Chem. Soc.* 2010, **132**, 12817.
4. (a) A.G. M. Barrett, C. Brinkmann, M. R. Crimmin, M. S. Hill, P. Hunt, P. A. Procopiu *J. Am. Chem. Soc.* 2009, **131**, 12906. (b) M. S. Kwon, S. Kim, S. Park, W. Bosco, R. K. Chidrala, J. Park *J. Org. Chem.* 2009, **74**, 2877
5. C. Wang, A. Pettman, J. Bacsa, J. Xiao *Angew. Chem. Int. Ed.* 2010, **49**, 7548.

