

Supplementary Materials

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1. General Information & Materials

All ^1H NMR (300 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker AMX-300, Varian EM360A spectrometers in CDCl_3 . Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for ^1H NMR, and CDCl_3 was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Mass spectra (EI-MS) was performed on HP-5989A and VGQUATTRO mass spectrometry. High-resolution mass spectrometry (HRMS) was performed on Bruker Daltonics FTMS-7. Melting points were uncorrected. DMF and DMSO were freshly distilled from CaH_2 . THF was distilled over sodium. Commercial available CuI should be washed with THF using a Soxhlet extractor before it is used. When some reactions used the CuI purified according the reported method [1], comments and note had been afforded in the paper. The reported compounds was identified by comparing with the reported analytical data by ^1H NMR (300 MHz) and EI-MS. The new compounds were identified by ^1H NMR (300 MHz), ^{13}C NMR (100 MHz) spectra, and HRMS.

2. General Procedure for Optimization of Amidation of Aryl Bromides with Copper/*N,N*-Dimethylglycine Catalytic System

A Schlenk tube was charged with 1-bromo-4-methoxybenzene **1a** (1 mmol), *N*-methylformamide **2a** (2 mmol or 1.2 mmol), CuI (0.1 mmol), ligand (0.2 mmol), and base (2 mmol). The tube was evacuated and backfilled with argon at room temperature. The solvent (0.5 mL) was added under argon via syringe. The Schlenk tube was immersed in a preheated oil bath and the reaction mixture was stirred at 110 °C for the specified time with complete consumption of the starting material **1a**. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residual oil was loaded on a silica gel column and eluted with 1:8 to 1:2 ethyl acetate/petroleum ether to afford the corresponding *N*-aryl amide *N*-(4-methoxyphenyl)-*N*-methylformamide.

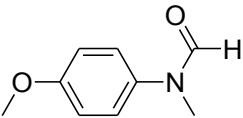
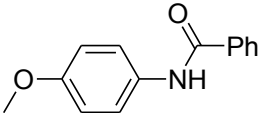
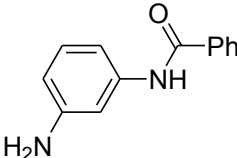
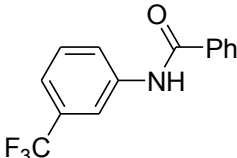
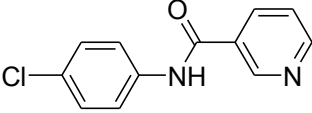
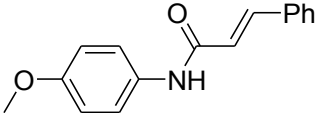
3. General Procedure for the Amidation of Aryl Bromides with Copper/*N,N*-Dimethylglycine Catalytic System

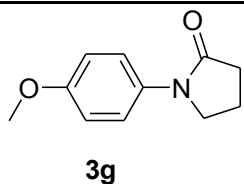
A Schlenk tube was charged with amide (1.2 mmol), aryl halide (1 mmol), CuI (0.05 or 0.1 mmol), *N,N*-dimethylglycine (0.1 or 0.2 mmol), and potassium carbonate (2 mmol). The tube was evacuated and backfilled with argon at room temperature. DMF (0.5 mL) was added under argon via syringe. The Schlenk tube was immersed in a preheated oil bath and the reaction mixture was stirred for the specified time at the indicated temperature. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuum. The residual oil was loaded on a silica gel column and eluted with 1:8 to 1:2 ethyl acetate/ petroleum ether to afford the corresponding *N*-aryl amides.

4. General Procedure for the Amidation Of Aryl Iodides with Copper/*N,N*-Dimethylglycine Catalytic System

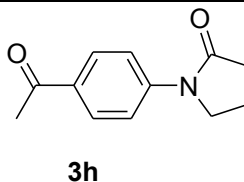
A Schlenk tube was charged with amide (1.2 mmol), aryl iodides (1 mmol), CuI (0.1 mmol), *N,N*-dimethylglycine (0.2 mmol), and potassium phosphate (2 mmol). The tube was evacuated and backfilled with argon at room temperature. DMF (0.5 mL) was added under argon via syringe. The Schlenk tube was immersed in a preheated oil bath and the reaction mixture was stirred for the specified time at the indicated temperature. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuum. The residual oil was loaded on a silica gel column and eluted with 1:8 to 1:2 ethyl acetate/petroleum ether to afford the corresponding *N*-aryl amides.

5. Analytical Data of Products

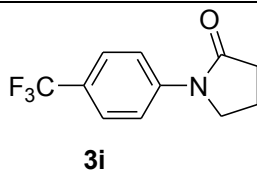
 <p style="text-align: center;">3a</p>	<p><i>N</i>-(4-methoxyphenyl)-<i>N</i>-methylformamide (3a). ¹H NMR (300 MHz, CDCl₃): δ 8.35 (s, 1H), 7.11 (d, <i>J</i> = 8.7 Hz, 2H), 6.93 (d, <i>J</i> = 9.0 Hz, 2H), 3.83 (s, 3H), 3.28 (s, 3H); EI-MS <i>m/z</i> 165 (M⁺), 153, 136, 122, 108, 94, 77, 65, 52.</p>
 <p style="text-align: center;">3b</p>	<p><i>N</i>-(4-methoxyphenyl)benzamide (3b). ¹H NMR (300 MHz, CDCl₃): δ 7.87 (d, <i>J</i> = 7.2 Hz, 1H), 7.79 (s, 1H), 7.56-7.46 (m, 5H), 6.91 (d, <i>J</i> = 9.3 Hz, 2H), (3.82s, 3H); EI-MS <i>m/z</i> 227 (M⁺), 210, 178, 149, 122, 105, 77, 51.</p>
 <p style="text-align: center;">3c</p>	<p><i>N</i>-(3-aminophenyl)benzamide (3c). ¹H NMR (300 MHz, CDCl₃): δ 7.85 (d, <i>J</i> = 7.2 Hz, 2H), 7.79 (s, 1H), 7.57-7.45 (m, 3H), 7.33 (s, 1H), 7.13 (t, <i>J</i> = 7.8 Hz, 1H), 6.79 (d, <i>J</i> = 7.8 Hz, 1H), 6.48 (d, <i>J</i>₁ = 8.1 Hz, <i>J</i>₂ = 1.8 Hz, 1H), 3.71 (s, 2H); EI-MS <i>m/z</i> 212 (M⁺), 184, 167, 135, 121, 105, 77, 51.</p>
 <p style="text-align: center;">3d</p>	<p><i>N</i>-(3-(trifluoromethyl)phenyl)benzamide (3d). ¹H NMR (300 MHz, CDCl₃): δ 8.00-7.85 (m, 5H), 7.57-7.39 (m, 5H); EI-MS <i>m/z</i> 265 (M⁺), 246, 225, 149, 113, 105, 77, 51.</p>
 <p style="text-align: center;">3e</p>	<p><i>N</i>-(4-chlorophenyl)nicotinamide (3e). ¹H NMR (300 MHz, CDCl₃): δ 9.08 (s, 1H), 8.78 (dd, <i>J</i>₁ = 4.8 Hz, <i>J</i>₂ = 1.5 Hz, 1H), 8.21 (d, <i>J</i> = 7.8 Hz, 1H), 8.04 (s, 1H), 7.62 (d, <i>J</i> = 9.0 Hz, 2H), 7.48-7.44 (m, 1H), 7.36 (d, <i>J</i> = 8.7 Hz, 2H); EI-MS <i>m/z</i> 232 (M⁺), 127, 106, 78, 51.</p>
 <p style="text-align: center;">3f</p>	<p><i>N</i>-(4-methoxyphenyl)cinnamamide (3f). ¹H NMR (300 MHz, CDCl₃): δ 7.75 (d, <i>J</i> = 15.6 Hz, 1H), 7.54 (m, 4H), 7.38 (m, 3H), 6.90 (d, <i>J</i> = 8.7 Hz, 2H), 6.53 (d, <i>J</i> = 15.3 Hz, 1H), 3.81 (s, 3H); EI-MS <i>m/z</i> 253 (M⁺), 131, 123, 108, 103, 77, 51.</p>



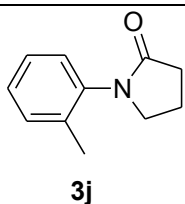
1-(4-methoxyphenyl)pyrrolidin-2-one (3g). ^1H NMR (300 MHz, CDCl_3): δ 7.50 (d, $J = 9.0$ Hz, 2H), 6.91 (d, $J = 9.0$ Hz, 2H), 3.86-3.00 (m, 5H), 2.60 (t, $J = 8.1$ Hz, 2H), 2.16 (m, 2H); EI-MS m/z 191 (M^+), 176, 166, 136, 121, 69, 57.



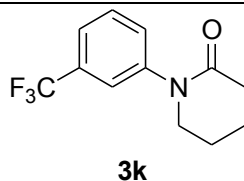
1-(4-acetylphenyl)pyrrolidin-2-one (3h). ^1H NMR (300 MHz, CDCl_3): δ 7.98 (d, $J = 8.7$ Hz, 2H), 7.76 (d, $J = 9.0$ Hz, 2H), 3.91 (t, $J = 7.2$ Hz, 2H), 2.65 (t, $J = 7.5$ Hz, 2H), 2.59 (s, 3H), 2.20 (m, 2H); EI-MS m/z 203 (M^+), 188, 160, 148, 132, 120, 105, 90, 77, 69, 63, 51, 43.



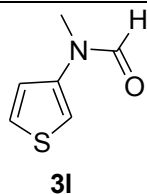
1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (3i). ^1H NMR (300 MHz, CDCl_3): δ 7.77 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 3.89 (t, $J = 7.2$ Hz, 2H), 2.64 (t, $J = 7.8$ Hz, 2H), 2.21 (m, 2H); EI-MS m/z 229 (M^+), 210, 174, 145, 127, 95, 84, 57.



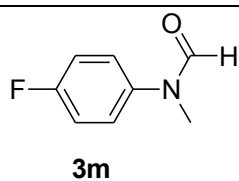
1-o-tolylpyrrolidin-2-one (3j). ^1H NMR (300 MHz, CDCl_3): δ 7.27-7.21 (m, 3H), 7.16-7.13 (m, 1H), 3.72 (t, $J = 7.2$ Hz, 2H), 2.59 (t, $J = 8.1$ Hz, 2H), 2.28-2.18 (m, 5H); EI-MS m/z 175 (M^+), 158, 146, 130, 120, 91, 65, 51.



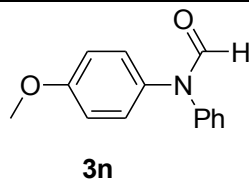
1-(3-(trifluoromethyl)phenyl)piperidin-2-one (3k). ^1H NMR (300 MHz, CDCl_3): δ 7.53-7.48 (m, 4H), 3.69-3.66 (m, 2H), 2.60-2.56 (m, 2H), 1.98-1.96 (m, 4H); EI-MS m/z 243 (M^+), 224, 214, 187, 174, 149, 145, 120, 108, 91, 70, 55.



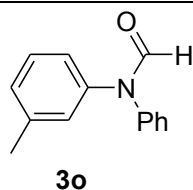
N-methyl-N-(thiophen-3-yl)formamide (3l). ^1H NMR (300 MHz, CDCl_3): δ 8.52 (s, 1H), 8.23 (s, 0.2H), 7.44-7.42 (m, 0.2H), 7.35-7.30 (m, 1.2 H), 7.25-7.23 (m, 0.2H), 6.99-6.97 (m, 1H), 6.84-6.83 (m, 1H), 3.30 (s, 0.6 H), 3.22 (s, 3H); EI-MS m/z 141 (M^+), 112, 98, 85, 80, 72, 68, 58, 54, 45, 42.



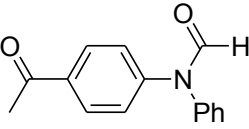
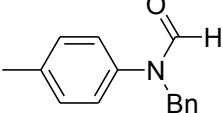
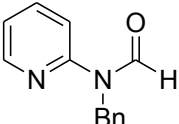
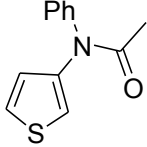
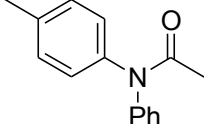
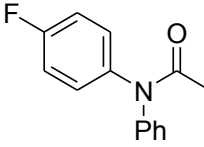
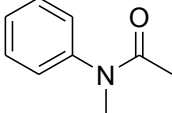
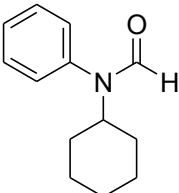
N-(4-fluorophenyl)-N-methylformamide (3m). ^1H NMR (300 MHz, CDCl_3): δ 8.40 (s, 1H), 7.18-7.12 (m, 4H), 3.31 (s, 3H); EI-MS m/z 153 (M^+), 124, 112, 95, 83, 77, 75, 57.



N-(4-methoxyphenyl)-N-phenylformamide (3n). ^1H NMR (300 MHz, CDCl_3): δ 8.62 (d, $J = 30.9$ Hz, 1H), 7.38-7.34 (m, 2H), 7.31-7.19 (m, 3H), 7.16-7.11 (m, 2H), 6.92 (d, $J = 9.0$ Hz, 2H), 3.81 (d, $J = 4.2$ Hz, 3H); EI-MS m/z 227 (M^+), 199, 184, 167, 154, 129, 124, 121, 103, 93, 77, 66, 51, 43.



N-phenyl-N-m-tolylformamide (3o). ^1H NMR (300 MHz, CDCl_3): δ 8.66 (d, $J = 6.3$ Hz, 1H), 7.43-7.38 (m, 2H), 7.33-7.26 (m, 3H), 7.18-7.05 (m, 3H), 6.98 (s, 1H), 2.36-2.35 (d, $J = 3.6$ Hz, 3H); EI-MS m/z 211 (M^+), 183, 167, 141, 128, 118, 108, 91, 80, 65, 51; EI-HRMS for $\text{C}_{15}\text{H}_{13}\text{NO}_2$ (M^+) requires 211.0997, found 211.0992.

 <p>3p</p>	<p><i>N</i>-(4-acetylphenyl)-<i>N</i>-phenylformamide. ^1H NMR (300 MHz, CDCl_3): δ 7.86 (d, J = 8.1 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 8.4 Hz, 2H), 6.26 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 196.3, 148.2, 140.4, 130.5 (2C), 129.4 (2C), 128.9, 123.2, 120.5 (2C), 114.2 (2C), 97.6, 26.0; EI-MS m/z 239 (M^+), 211, 196, 167, 139, 115, 98, 84, 77, 63, 51, 43; EI-HRMS for $\text{C}_{15}\text{H}_{13}\text{NO}_2$ (M^+) requires 239.0946, found 239.0944.</p>
 <p>3q</p>	<p><i>N</i>-benzyl-<i>N</i>-<i>p</i>-tolylformamide (3q). ^1H NMR (300 MHz, CDCl_3): δ 8.50 (s, 1H), 7.28-7.21 (m, 5H), 7.13 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 4.97 (s, 2H), 2.32 (s, 3H); EI-MS m/z 225 (M^+), 196, 181, 165, 133, 118, 91, 77, 65, 51</p>
 <p>3r</p>	<p><i>N</i>-benzyl-<i>N</i>-(pyridin-2-yl)formamide (3r). ^1H NMR (300 MHz, CDCl_3): δ 9.50 (s, 1H), 8.39 (d, J = 5.1 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.29-7.22 (m, 5H), 7.08 (m, 1H), 6.93 (d, J = 8.1 Hz, 1H), 5.18 (s, 2H); EI-MS m/z 212 (M^+), 183, 168, 154, 106, 91, 78, 65, 51</p>
 <p>3s</p>	<p><i>N</i>-phenyl-<i>N</i>-(thiophen-3-yl)acetamide (3s). ^1H NMR (300 MHz, CDCl_3): δ 7.46-7.18 (m, 7H), 7.18 (6.95, J = 5.7 Hz, 1H), 1.99 (s, 3H); EI-MS m/z 217 (M^+), 175, 149, 130, 120, 104, 84, 77, 51, 43.</p>
 <p>3t</p>	<p><i>N</i>-(4-fluorophenyl)-<i>N</i>-phenylacetamide (3t). ^1H NMR (300 MHz, CDCl_3): δ 7.32~7.15 (m, 9H), 2.33 (s, 3H), 2.05 (s, 3H).</p>
 <p>3u</p>	<p><i>N</i>-(4-fluorophenyl)-<i>N</i>-phenylacetamide (3u). ^1H NMR (300 MHz, CDCl_3): δ 7.40~6.99 (m, 9H), 2.06 (s, 3H).</p>
 <p>3v</p>	<p><i>N</i>-methyl-<i>N</i>-phenylacetamide (3v). ^1H NMR (300 MHz, CDCl_3): δ 7.43 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.19 (d, J = 4.8 Hz, 2H), 3.27 (s, 3H), 1.87 (s, 3H); EI-MS m/z 149 (M^+), 129, 120, 109, 106, 92, 81, 77, 65, 51, 43.</p>
 <p>3w</p>	<p><i>N</i>-cyclohexyl-<i>N</i>-phenylformamide (3w). ^1H NMR (300 MHz, CDCl_3): δ 8.42 (s, 0.15H), 8.15 (s, 0.85H), 7.44-7.35 (m, 3H), 7.17-7.13 (m, 2H), 4.44-4.37 (m, 0.85H), 3.65-3.57 (m, 0.15H), 1.92-1.74 (m, 4H), 1.63-1.58 (m, 1H), 1.46-1.23 (m, 4H), 1.05-0.95 (m, 1H); EI-MS m/z 203 (M^+), 174, 160, 146, 132, 121, 118, 104, 93, 77, 66, 55, 51, 41.</p>

6. Reference

1. Kauffman, G.B.; Fang, L.Y. *Inorganic Syntheses*; Holt, S.L., Ed.; Wiley: Hoboken, NJ, USA, 1983; Volume 22, pp. 101–103.

7. NMR Spectra of Products

