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for

Practical Copper(I)-Catalysed Amidation of Aldehydes

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General Experimental Section: All reactions were performed under a nitrogen atmosphere at ambient temperature unless otherwise stated. PhI=NTs,^{S1} the Schiff base ligands^{S2} and PhI=O^{S3} were prepared according to known literature procedures. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received; CH₂Cl₂ and MeCN were purified prior to use by distilling over CaH₂; pyridine was distilled over KOH and benzaldehyde was distilled under reduced pressure. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 pre-coated silica gel plate. Visualization was achieved by UV-vis light (254 nm) followed by treatment with ninhydrin stain and heating. Flash chromatography was performed using Merck silica gel 60 using a gradient solvent system (EtOAc: *n*-hexane as eluant). Unless otherwise stated, ¹H and ¹³C NMR spectra were measured on Bruker Avance 300 MHz spectrometer. Unless otherwise stated, chemical shifts (ppm) were recorded in CDCl₃ solution with tetramethylsilane (TMS) as the internal reference standard. Low resolution mass spectra were determined on a Finnigan LCQ XP MAX mass spectrometer. High resolution mass spectra (HRMS) were obtained using Finnigan MAT95XP LC/HRMS. Kinetic isotope measurements were caonducted on a Waters TQD with 0.1% formic acid in 95% H₂O:5% MeCN as the mobile phase.

General Procedure for the Optimization of Copper-Catalysed Amidation of 1a to 2a with PhI=NTs: To a suspension of the catalyst (0.05 mmol, 10 mol %), PhI=NTs (1 mmol, 2 equiv) and powdered 4Å molecular sieves in 2 mL of CH_2Cl_2 , was added isovaleraldehyde 1a (0.5 mmol, 1 equiv) under a N₂ atmosphere. The reaction was stirred at room temperature for 18 h. On completion, the crude mixture was filtered through Celite®, washed with EtOAc, evaporated to dryness and purified by silica gel flash column chromatography (*n*-hexanes:EtOAc as eluant) to give the title compound.

General Procedure for the Optimization of Copper + Ligand-Catalysed Amidation of 1a to 2a with PhI=NTs: A suspension of the catalyst (0.05 mmol, 10 mol %), ligand (refer to Table 2) and powdered 4Å molecular sieves were stirred for 1 h in 2 mL of CH_2Cl_2 under a N_2 atmosphere. On completion, PhI=NTs (1 mmol, 2 equiv) and isovaleraldehyde 1a (0.5 mmol, 1 equiv) were added. The reaction was stirred at room temperature for a further 18 h, after which the crude mixture was filtered through Celite®, washed with EtOAc, evaporated to dryness and purified by silica gel flash column chromatography (*n*-hexanes:EtOAc as eluant) to give the title compound.

General Procedure for the Optimization of Cu(I) + py-Catalysed Amidation of 1b to 2b with PhI=NTs: A suspension of the catalyst (0.05 mmol, 10 mol %), pyridine (0.2 mmol, 40 mol %) and powdered 4Å molecular sieves were stirred for 1 h in 2 mL of CH₂Cl₂ under a N₂ atmosphere. On completion, PhI=NTs (1 mmol, 2 equiv) and benzaldehyde 1b (0.5 mmol, 1 equiv) were added. The reaction was stirred at room temperature for a further 18 h, after which the crude mixture was filtered through Celite®, washed with EtOAc, evaporated to dryness and purified by silica gel flash column chromatography (*n*-hexanes:EtOAc as eluant) to give the title compound.

General Procedure for the CuI + py-Catalysed Amidation of Aldehydes with PhI=NTs: A suspension of CuI (0.05 mmol, 10 mol %), pyridine (0.2 mmol, 40 mol %) and powdered 4Å molecular sieves were stirred for 1 h in 2 mL of CH_2Cl_2 under a N_2 atmosphere. On completion, PhI=NTs (1 mmol, 2 equiv) was added and the aldehyde (0.5 mmol, 1 equiv) diluted in 1 mL of CH_2Cl_2 was added into the reaction mixture over 2 h via a syringe pump. The reaction was stirred at room temperature for 16 h, after which the crude mixture was filtered through Celite®, washed with EtOAc, evaporated to dryness and purified by silica gel flash column chromatography (*n*-hexanes:EtOAc as eluant) to give the acylsulfonamide product.

General Procedure for the CuCl-Catalysed Amidation of Aldehydes with TsNClNa.3H₂O: To a suspension of CuCl (0.05 mmol, 10 mol %) and TsNClNa.3H₂O (1.3 mmol, 2.6 equiv) in 7.5 mL of MeCN was added the aldehyde (0.5 mmol, 1 equiv) under a N_2 atmosphere. The reaction was stirred at room temperature for 18 h. On completion, the crude mixture was filtered through a plug of silica gel, washed with EtOAc, evaporated to dryness and purified by silica gel flash column chromatography (*n*-hexanes:EtOAc as eluant) to give the acylsulfonamide product.

Procedure for the Synthesis of 3b:⁸⁴ To a solution of benzaldehyde **1b** (10 mmol, 1 equiv) and *p*-toluenesulfonamide (10 mmol, 1 equiv) in 50 mL of CH₂Cl₂ was added trifluoroacetic anhydride (11 mmol, 1.1 equiv). The reaction was refluxed for 12 h after which the reaction mixture was poured into cold water, extracted with CH₂Cl₂, dried with MgSO₄, evaporated to dryness and purified by silica gel flash column chromatography (*n*-hexanes:EtOAc as eluant) to give the title compound as a white solid in 76% yield (2.28 g). ¹H NMR δ 9.03 (s, 1H) 7.94-7.88 (m, 4H), 7.62 (t, *J* = 6.18 Hz, 1H) 7.49 (d, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H, 2.44 (s, 3H); ¹³C NMR δ 170.1, 144.6, 134.9, 132.4, 131.3, 129.8, 129.1, 128.1, 126.4, 21.6; MS (EI) *m/z* 260 [M+H]⁺.

Procedure for the Synthesis of 4b:^{S5} To a suspension of powdered KOH (7 mmol, 3.5 equiv) and *m*-chloroperoxybenzoic acid (2.2 mmol, 1.1 equiv) in 1 mL of CH₂Cl₂ was added a solution of **3b** (2 mmol, 1 equiv) in 3mL of CH₂Cl₂. After 5 min, the suspension was filtered, evaporated to dryness and dried under vacuum to afford the product as a white solid in 95% yield (528 mg). ¹H NMR δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.46-7.40 (m, 7H), 5.45(s, 1H), 2.49 (s, 3H); ¹³C NMR δ 146.3, 131.5, 131.4, 130.5, 130.0, 129.4, 128.7, 128.2, 76.3, 21.8; MS (EI) *m/z* 276 [M+H]⁺.

Procedure for the Synthesis of 5:^{S6} To a suspension of [Ru(TTP)CO] (0.2 mmol, 0.1 equiv) and PhI=NTs (3 mmol, 1.5 equiv) in 2 mL of CH₂Cl₂ in the presence of powdered 4Å molecular sieves was added pyridine (2 mmol, 1 equiv) under N₂ atmosphere. The reaction was stirred at 30 °C until completion based on TLC analysis, after which the reaction mixture was cooled to room temperature, filtered, evaporated to dryness and purified by silica gel flash column chromatography (CH₂Cl₂: acetone as eluant) to afford the product in 64% yield (320 mg). ¹H NMR δ 8.46 (d, *J* = 3.8 Hz, 2H), 7.97 (dt, *J* = 7.75, 1.05 Hz, 1H), 7.63-7.59 (m, 4H), 7.17 (d, *J* = 6.54 Hz, 2H), 2.36 (s, 3H); ¹³C NMR δ 145.2, 141.6, 138.6, 129.2, 127.0, 126.7, 21.3; MS (EI) *m/z* 249 [M+H]⁺.

General Procedure for the CuI + py-Catalysed Reaction of 3b or 4b: A suspension of CuI (0.05 mmol, 10 mol %), pyridine (0.2 mmol, 40 mol %) and 4Å powdered molecular sieves were stirred for 1 h in 2 mL of CH_2Cl_2 under a N₂ atmosphere. On completion, PhI=O or PhI(OAc)₂ (1 mmol, 2 equiv) and **3b** or **4b** (0.5 mmol, 1 equiv) was added. The reaction was stirred at room temperature for a further 18 h, after which the mixture was filtered through Celite®, washed with EtOAc and evaporated to dryness. The reaction mixture was then analysed by ¹H NMR spectroscopy and mass spectrometry.

Procedure for the CuI + py-Catalysed Reaction of 1a with 5: To a suspension of CuI (0.05 mmol, 10 mol %), **5** (1 mmol, 2 equiv) and 4Å powdered molecular sieves in 2 mL of CH₂Cl₂, was added **1a** (0.5 mmol, 1 equiv) under a N₂ atmosphere. The reaction was stirred at room temperature for 18 hr, after which the mixture was filtered through Celite®, washed with EtOAc and evaporated to dryness. The reaction mixture was then analysed by ¹H NMR spectroscopy and mass spectrometry.

Procedure for the ¹³C-Benzaldehyde *in situ* Monitoring Experiment: To a suspension of CuI (0.01 mmol, 10 mol %) and 4Å powdered molecular sieves in CD₂Cl₂ (2 mL) was added pyridine (0.4 mmol, 40 mol %). After stirring for 1 h, PhI=NTs (1 mmol, 2 equiv) was added. A solution of ¹³C-benzaldehyde (0.5 mmol, 1 equiv) in CD₂Cl₂ (1 mL) was added via syringe pump over 1 h. Upon completion of addition, an aliquot (100 uL) was diluted with CD₂Cl₂ and monitored by NMR. Subsequent aliquots at 4, 10 and 18 h were obtained and subjected to ¹³C NMR analysis.

Procedure for the Deuterium Labeling Experiment: CuI + py-Catalyzed Amidation of Benzaldehyde- α - d_1 to N,N- d_1 -Tosylbenzamide with PhI=NTs: To a suspension of CuI (0.025 mmol, 10 mol %), pyridine (0.1 mmol, 40 mol%) and PhI=NTs (0.5 mmol, 2 equiv) in 1 mL CH₂Cl₂ or CD₂Cl₂ was added α - d_1 -benzaldehyde (0.25 mmol, 1 equiv) under a N₂ atmosphere. The reaction was left at room temperature for 18 h, after which a ¹H NMR and mass spectra of the reaction mixture was obtained. **Procedure for the Kinetic Isotope Study:** To a suspension of CuI (0.025 mol, 10 mol %) and powdered 4Å molecular sieves in CH₂Cl₂ (1 mL) was added pyridine (0.1 mmol, 40 mol %). After stirring for 1 h, PhI=NTs (0.25 mmol, 1 equiv) was added. A solution of benzaldehyde (0.3 mmol, 1.2 equiv) and d_6 -benzaldehyde (0.3 mmol, 1.2 equiv) in CH₂Cl₂ (1 mL) was added via syringe pump over 1 h. After 18 h, the solution was assayed via LCMS.

3-Methyl-N-tosylbutanamide 2a S7

White solid; Yield: 97%; ¹H NMR δ 9.22 (bs, 1H), 7.96 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 2.45 (s, 3H), 2.13 (d, J = 6.5 Hz, 2H), 2.03-2.09 (m, 1H), 0.87 (d, J = 6.4 Hz, 2H); ¹³C NMR δ 171.1, 145.2, 135.7, 129.7, 128.4, 45.3, 25.7, 22.3, 21.8; MS (EI) m/z 256 [M+H]⁺.

N-Tosylbenzamide 2b^{S7}

White solid; Yield: 83%; ¹H NMR δ 9.48 (bs, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 2.43 (s, 3H); ¹³C NMR δ 164.4, 145.3, 135.6, 133.5, 131.2, 129.7, 129.0, 128.7, 128.0, 21.7; MS (EI) m/z 276 [M+H]⁺.

N-Tosylheptanamide 2c^{S7}

White solid; Yield: 95%; ¹H (500 MHz) NMR δ 8.80 (bs, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H), 2.24 (t, J = 7.4 Hz, 2H) 1.54 (t, J = 6.1 Hz, 2H) 1.20-1.25 (m, 6H), 0.83 (t, J = 6.5 Hz, 3H); ¹³C (125 MHz) δ 171.1, 145.2, 135.6, 129.7, 128.4, 36.3, 31.3, 28.5, 24.3, 22.4, 21.7, 14.0; MS (EI) m/z 271 [M+H]⁺.

N-Tosylpropionamide 2d^{S7}

White solid; Yield: 81 %; ¹H (500 MHz) NMR δ 9.00 (s, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.1Hz, 2H), 2.44 (s, 3H), 2.30 (qt, J = 7.4 Hz, 2H) 1.07 (t, J = 7.4 Hz, 3H); ¹³C (125 MHz) NMR δ 172.0, 145.2, 135.6, 129.7, 128.3, 29.5, 21.7, 8.2; MS (EI) m/z 228 [M+H]⁺.

N-Tosylisobutyramide 2e^{S7}

White solid; Yield: 81%; ¹H (400 MHz) NMR δ 8.86 (bs, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 2.39-2.46 (m, 4H), 1.09 (d, J = 6.9 Hz, 6H); ¹³C (100 MHz) NMR δ 175.0, 145.4, 135.7, 129.9, 128.6, 35.9, 22.0, 18.8; MS (EI) *m/z* 242 [M+H]⁺.

N-Tosylcyclopropanecarboxamide 2f⁸⁷

White solid; Yield: 98 %; ¹H NMR δ 8.87 (bs, 1H), 7.94 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H), 1.55-1.50 (m, 1H), 1.00-1.02 (m, 2H), 0.85-0.87 (m, 2H); ¹³C NMR δ 171.8, 145.1, 135.6, 129.6, 128.3, 21.7, 14.7, 9.6; MS (EI) m/z 240 [M+H]⁺.

N-Tosylcyclopentanecarboxamide 2g^{S7}

White solid; Yield: 96 %; ¹H NMR δ 9.11 (bs, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 2.58-2.63 (m, 1H), 2.40 (s, 3H), 1.47-1.78 (m, 8H); ¹³C NMR δ 174.0, 145.0, 135.7, 129.6, 128.3, 45.4, 29.5, 25.8, 21.7; MS (EI) m/z 268 [M+H]⁺.

N-Tosylcyclohexanecarboxamide 2h^{S7}

White solid; Yield: 96%; ¹H (500 MHz) NMR δ 8.54 (bs, 1H), 7.94 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H), 2.13 (tt, J = 11.6, 3.5 Hz, 1H), 1.81-1.71 (m, 4H), 1.62 (bd, J = 7.8 Hz, 1H), 1.38-1.12 (m, 5H); ¹³C (125 MHz) δ 173.5, 145.0, 135.6, 129.6, 128.3, 45.1, 28.7, 25.4, 25.2, 21.7; MS (EI) m/z 282 [M+H]⁺.

3-Methyl-N-tosylbut-2-enamide 2i⁸⁷

White solid; Yield: 65%; ¹H NMR δ 8.50 (bs,1H), 7.95 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.57 (s, 1H), 2.42 (s, 3H), 2.09 (s, 3H), 1.85 (s. 3H); ¹³C NMR δ 163.4, 160.4, 144.8, 136.0, 129.6, 128.3, 115.5, 27.7, 21.7, 20.6; MS (EI) *m/z* 253 [M+H]⁺.

(E)-N-tosylhex-2-enamide 2j^{S7}

Yellow oil; Yield: 62%; ¹H NMR δ 9.32 (bs, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.98 (dt, J = 15.4, 7.0 Hz, 1H), 5.86 (d, J = 15.4 Hz, 1H), 2.42 (s, 3H), 2.15 (qt, J = 7.0 Hz, 2H), 1.37-1.44 (m, 2H), 0.86 (t, J = 7.36 Hz, 3H); ¹³C NMR δ 163.4, 150.8, 144.9, 135.6, 129.5, 128.2, 121.2, 34.1, 21.5, 21.0, 13.5; MS (EI) m/z 278 [M+H]⁺.

4-Bromo-N-tosylbenzamide 2k^{S7}

White solid; Yield: 64%; ¹H NMR δ 9.32 (bs, 1H), 8.02 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 7.35(d, J = 8.2 Hz, 2H), 2.44 (s, 3H); ¹³C NMR δ

163.8, 163.3, 145.5, 135.3, 132.2, 130.0, 129.7, 129.5, 128.6, 21.7; MS (EI) *m/z* 354 [M+H]⁺.

4-Chloro-N-tosylbenzamide 21^{S7}

White solid; Yield: 47%; ¹H NMR δ 9.43 (bs, 1H), 8.00 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.35-7.39 (m, 4H), 2.43 (s, 3H); ¹³C NMR δ 163.5, 145.5, 140.0, 135.3, 129.7, 129.6, 129.3, 129.2, 128.7, 21.7; MS (EI) *m/z* 310 [M+H]⁺.

4-Methyl-N-tosylbenzamide 2m^{S7}

White solid; Yield: 93%; ¹H NMR δ 9.32 (bs, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.39 (s, 3H); ¹³C NMR δ 164.3, 145.1, 144.4, 135.6, 129.6, 128.6, 128.4, 127.9, 127.8, 21.7, 21.6 MS (EI) *m/z* 290 [M+H]⁺.

4-Methoxy-*N*-tosylbenzamide 2n^{S7}

White solid; Yield: 99%; ¹H NMR δ 9.14 (bs, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.41 (s, 3H); ¹³C NMR δ 163.7, 145.0, 135.6, 130.0, 129.5, 128.5, 126.4, 123.2, 114.1, 55.5, 21.6; MS (EI) *m/z* 306 [M+H]⁺.

N-Tosyl-1-napthamide 20^{S7}

White solid; Yield: 99%; ¹H NMR (400 MHz) δ 9.17 (bs, 1H), 8.15 (t, J = 3.4 Hz, 1H), 8.00 (t, J = 8.2 Hz, 2H), 7.87 (d, J = 8.2 Hz, 1H), 7.76-7.78 (m, 1H), 7.63 (d, J = 7.1 Hz, 1H), 7.42-7.48 (m, 2H), 7.29-7.36 (m, 3H), 2.41 (s, 3H); ¹³C (100 MHz) NMR δ 166.2, 145.2, 135.5, 133.7, 132.9, 130.0, 129.8, 129.7, 128.6, 128.5, 127.9, 126.8, 124.9, 124.4, 21.7; MS (EI) m/z 326 [M+H]⁺.

N-Tosylfuran-2-carboxamide 2p^{S7}

White solid; Yield: 93%; ¹H (400 MHz) NMR δ 7.99 (d, J = 11.2 Hz, 2H), 7.55 (d, J = 1.2 Hz, 1H), 7.27 (d, J = 10.8 Hz, 2H), 7.21 (d, J = 4.7 Hz, 1H), 6.54 (t, J = 2.4 Hz, 1H),

2.36 (s, 3H); ¹³C (100 MHz) NMR δ 162.3, 154.3, 145.7, 145.3, 145.2, 135.5, 129.6, 128.6, 118.1, 113.1, 21.7; MS (EI) *m/z* 266 [M+H]⁺.





























Figure S8. ¹H and ¹³C NMR spectra of $2h^{S7}$



Figure S9. ¹H and ¹³C NMR spectra of 2i^{S7}



Figure S10. ¹H and ¹³C NMR Spectra of 2j^{S7}



Figure S11. ¹H and ¹³C NMR spectra of **2k**^{S7}



Figure S12. ¹H and ¹³C NMR spectra of 2l^{S7}







Figure S14. ¹H and ¹³C NMR spectra of $2n^{S7}$



Figure S15. ¹H and ¹³C NMR spectra of 20^{S7}



Figure S16. ¹H and ¹³C NMR spectra of $2p^{S7}$



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Figure S18. ¹H and ¹³C NMR spectra of 3b^{S4}



Figure S19. ¹H and ¹³C NMR spectra of 4b^{S5}



Figure S20. ¹H and ¹³C NMR spectra of 5^{S6}





Figure S21. ¹³C-benzaldehyde in situ monitoring experiment at a) 0 h, b) 4 h, c) 10 h and d) 18h



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Figure S22. Aromatic region in the ¹H NMR spectrum of the crude product $N,N-d_1$ -tosylbenzamide obtained from CuI-catalysed amidation of benzaldehyde- α - d_1 in CH₂Cl₂ solution^{S7}



Figure S23. Aromatic region in the ¹H NMR spectrum of the crude product $N,N-d_1$ tosylbenzamide obtained from CuI-catalyzed amidation of benzaldehyde- α - d_1 in CD₂Cl₂ solution^{S7}



Figure S24. Aromatic region in the ¹H NMR spectrum of the crude product $N,N-d_1$ -tosylbenzamide obtained from CuI-catalyzed amidation of benzaldehyde- α - d_1 in CD₂Cl₂ solution after treatment with one drop of H₂O^{S7}



Figure S25. Mass Spectrum of Kinetic Isotope Experiment Studies





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