



Supporting Information

for

Tandem copper and photoredox catalysis in photocatalytic alkene difunctionalization reactions

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Full experimental details for all reactions

Table of Contents

I.	General information	S1
II.	Synthesis of Ag_2CO_3	S1
III.	Photocatalytic oxyamination of styrenes	S2
V.	Photocatalytic diamination of styrenes	S6
VI.	References	S7

I. General information

All reactions were performed under an N_2 atmosphere unless otherwise noted. All glassware was dried in an oven at $120\text{ }^\circ\text{C}$ for at least 2 h prior to use and allowed to cool in a desiccator cabinet. Reactions carried out below $0\text{ }^\circ\text{C}$ employed an acetone/dry ice bath or a cryocool equipped with an acetone bath. MeCN, THF, Et_2O , DMF, toluene, and CH_2Cl_2 were purified by elution through alumina as described by Grubbs [1]. Compounds **1**, **S1**, **S2**, **S3**, **S4**, **S5**, **S6**, **S10**, **S11**, and **S12** were synthesized as previously described by Yoon and co-workers [2]. **S7** was synthesized according to the method of Nicewicz and co-workers [3]. **S8** was synthesized according to the method of Xu and co-workers [4]. All other chemicals were purchased from commercial suppliers and used as received.

Flash column chromatography was performed with normal phase SiO_2 (Sigma-Aldrich or Macherey-Nagel, 60 \AA pore size, 230–400 mesh, 40–63 μm particle size) according to the method of Still [5]. Reactions were monitored by thin-layer chromatography (Silicycle, 250 μm thickness), and visualization was accomplished with a 254 nm UV light or by staining with KMnO_4 solution (3.0 g of KMnO_4 and 20.0 g of K_2CO_3 in 5 mL of 5% aq. NaOH and 300 mL H_2O).

The identity and purity of all products was verified by ^1H and ^{13}C NMR. The spectrometers used for this work are supported by the NIH (S10 OD012245) and a generous gift from Paul J. and Margaret M. Bender.

II. Synthesis of Ag_2CO_3

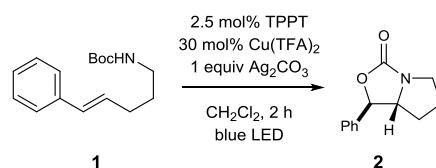
Silver carbonate (Ag_2CO_3). Prepared using a modification of the procedure described by Dai and coworkers [6]. A solution of AgNO_3 (1.62 g, 9.53 mmol) in H_2O (19 mL) was treated dropwise with a solution of Na_2CO_3 (0.501 g, 4.73 mmol) in H_2O (5.7 mL) over

10 min and the resulting solution was stirred at ambient temperature for 30 min. The precipitated solids were filtered, washed with H₂O (100 mL) and acetone (100 mL), and dried under aspirator pressure for 2 h while shielded from light to give Ag₂CO₃ (1.196 g, 4.337 mmol, 92%) as a light yellow powder.

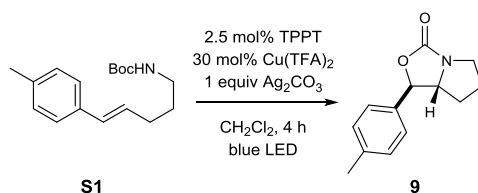
Note: Drying Ag₂CO₃ obtained using this procedure in vacuo results in the formation of a brown powder of inferior quality.

III. Photocatalytic oxyamination of styrenes

General procedure for intramolecular oxyamination: A Schlenk flask containing the oxyamination substrate (1 equiv), Ag₂CO₃ (1 equiv), Cu(TFA)₂·xH₂O (0.30 equiv), and TPPT (**3**, 0.025 equiv, 2.5 mol %) in CH₂Cl₂ (0.1 M) was degassed (freeze-pump-thaw, 3 cycles of 5 min each), and the resulting mixture was irradiated with a 15 W blue LED flood lamp for 2–4 h at ambient temperature. The reaction mixture was then diluted with EtOAc, eluted through a thin pad of SiO₂, and concentrated under reduced pressure. The residue was purified by chromatography on SiO₂ to afford pure product.

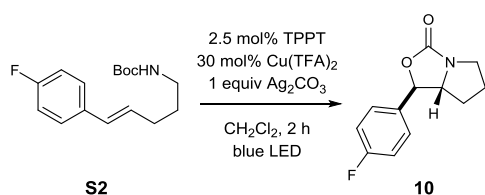


1-Phenyltetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Table 1, **2**). Synthesized according to the general procedure using **1** (0.092 g, 0.35 mmol), Ag₂CO₃ (0.096 g, 0.35 mmol), Cu(TFA)₂·xH₂O (0.031 g, 0.11 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 2 h. After chromatography on SiO₂ (35% EtOAc in hexanes), **2** was isolated as a clear, colorless oil which solidified upon standing (0.050 g, 0.25 mmol, 70%). All spectral data were in agreement with previously reported values [3].

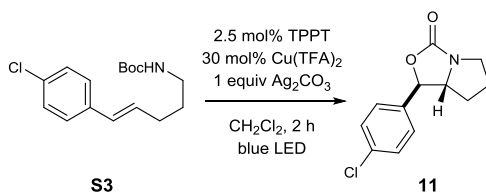


1-(*p*-Tolyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Figure 2, **9**). Synthesized according to the general procedure using **S1** (0.096 g, 0.35 mmol), Ag₂CO₃ (0.096 g, 0.35 mmol), Cu(TFA)₂·xH₂O (0.030 g, 0.11 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 4 h. After chromatography on SiO₂ (40% EtOAc in hexanes), **9** was

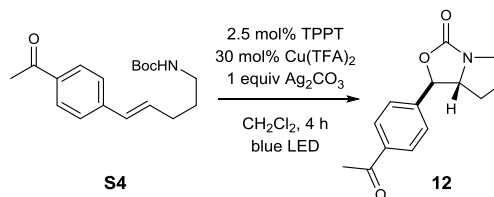
isolated as a clear, colorless oil which solidified upon standing (0.050 g, 0.23 mmol, 66%). All spectral data were in agreement with previously reported values [3].



1-(4-Fluorophenyl)tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-one (Figure 2, **10**). Synthesized according to the general procedure using **S2** (0.097 g, 0.35 mmol), Ag₂CO₃ (0.131 g, 0.350 mmol), Cu(TFA)₂·xH₂O (0.030 g, 0.10 mmol), and TPPT (0.0034 g, 0.0087 mmol) and irradiated for 2 h. After chromatography on SiO₂ (60% Et₂O in hexanes), **10** was isolated as a clear, colorless oil that solidified upon standing (0.043 g, 0.19 mmol, 55%). All spectral data were in agreement with previously reported values [3].

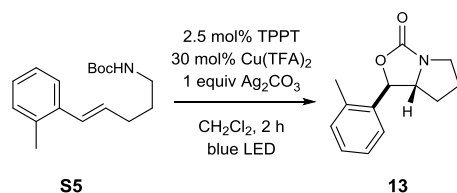


1-(4-Chlorophenyl)tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-one (Figure 2, **11**). Synthesized according to the general procedure using **S3** (0.131 g, 0.350 mmol), Ag₂CO₃ (0.131 g, 0.350 mmol), Cu(TFA)₂·xH₂O (0.030 g, 0.10 mmol), and TPPT (0.0034 g, 0.0087 mmol) and irradiated for 2 h. After chromatography on SiO₂ (60% Et₂O in hexanes), **11** was isolated as a white solid (0.055 g, 0.23 mmol, 66%). All spectral data were in agreement with previously reported values [3].

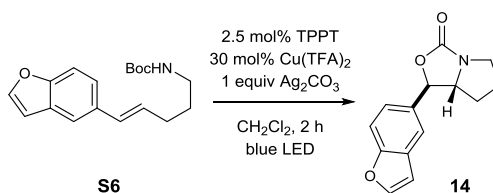


1-(4-Acetylphenyl)tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-one (Figure 2, **12**). Synthesized according to the general procedure using **S4** (0.107 g, 0.353 mmol), Ag₂CO₃ (0.096 g, 0.35 mmol), Cu(TFA)₂·xH₂O (0.031 g, 0.11 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 4 h. After chromatography on SiO₂ (55% EtOAc in

hexanes), **12** was isolated as a white solid (0.046 g, 0.19 mmol, 53%). All spectral data were in agreement with previously reported values [3].



1-(*o*-Tolyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Figure 2, **13**). Synthesized according to the general procedure using **S5** (0.096 g, 0.35 mmol), Ag₂CO₃ (0.131 g, 0.350 mmol), Cu(TFA)₂·xH₂O (0.030 g, 0.10 mmol), and TPPT (0.0034 g, 0.0087 mmol) and irradiated for 2 h. After chromatography on SiO₂ (70% Et₂O in hexanes), **13** was isolated as a pale-yellow oil which solidified upon standing (0.048 g, 0.22 mmol, 63%). All spectral data were in agreement with previously reported values [3].

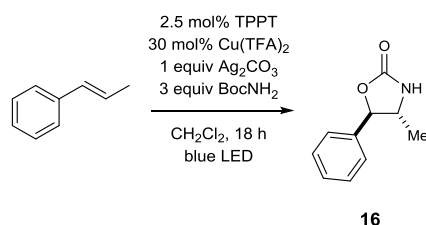


1-(Benzofuran-5-yl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Figure 2, **14**). Synthesized according to the general procedure using **S6** (0.105 g, 0.350 mmol), Ag₂CO₃ (0.131 mg, 0.350 mmol), Cu(TFA)₂·xH₂O (0.030 g, 0.10 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 2 h. After chromatography on SiO₂ (70% Et₂O in hexanes), **14** was isolated as a light green oil (0.045 g, 0.19 mmol, 53%). All spectral data were in agreement with previously reported values [3].

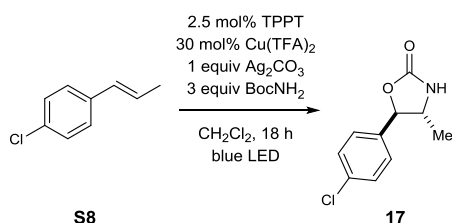


6,6-Dimethyl-1-phenyltetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Figure 2, **15**). Synthesized according to the general procedure using **S7** (0.101 g, 0.349 mmol), Ag₂CO₃ (0.131 g, 0.348 mmol), Cu(TFA)₂·xH₂O (0.030 g, 0.11 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 2 h. After chromatography on SiO₂ (35% EtOAc in hexanes), **15** was isolated as a white solid (0.0461 g, 0.199 mmol, 57%). All spectral data were in agreement with previously reported values [3].

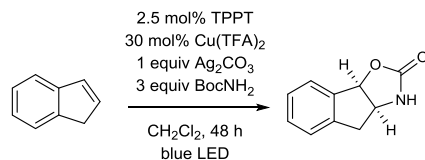
General procedure for intermolecular oxyamination: A Schlenk flask containing alkene (1 equiv), Ag_2CO_3 (1 equiv), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.30 equiv), *tert*-butyl carbamate (3 equiv), and TPPT (**3**, 0.025 equiv, 2.5 mol %) in CH_2Cl_2 (0.1 M) was degassed (freeze-pump-thaw, 3 cycles of 5 min each), and the resulting mixture was irradiated with a 15 W blue LED flood lamp for 18–48 h at ambient temperature. The reaction mixture was then diluted with EtOAc, eluted through a thin pad of SiO_2 , and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 to afford pure product.



4-Methyl-5-phenyloxazolidin-2-one (Figure 2, **16**). Synthesized according to the general procedure using β -methylstyrene (0.045 mL, 0.35 mmol), Ag_2CO_3 (0.098 g, 0.36 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.033 g, 0.11 mmol), BocNH_2 (0.123 g, 1.05 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (50–60% EtOAc in hexanes), **16** was isolated as a clear, pale yellow oil (0.026 g, 0.15 mmol, 42%, 3:1 *trans:cis*). All spectral data were in agreement with previously reported values [7].



5-(4-Chlorophenyl)-4-methyloxazolidin-2-one (Figure 2, **17**). Synthesized according to the general procedure using **S8** (0.053 g, 0.35 mmol), Ag_2CO_3 (0.097 g, 0.35 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.032 g, 0.11 mmol), BocNH_2 (0.125 g, 1.07 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (60% EtOAc in hexanes), **17** was isolated as a yellow oil (0.034 g, 0.16 mmol, 46%, 10:1 *trans:cis*). All spectral data were in agreement with previously reported values [8].

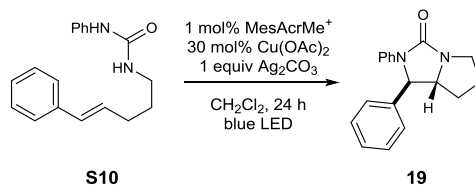


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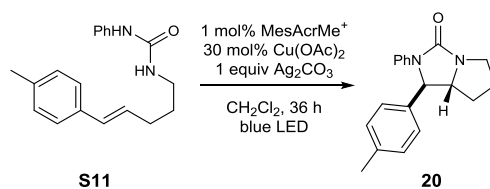
3,3a,4,8b-Tetrahydro-2H-indeno[2,1-d]oxazol-2-one (Figure 2, **18**). Synthesized according to the general procedure using indene (0.041 mL, 0.35 mmol), Ag₂CO₃ (0.097 g, 0.35 mmol), Cu(TFA)₂·xH₂O (0.031 g, 0.11 mmol), BocNH₂ (0.124 g, 1.06 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 48 h. After chromatography on SiO₂ (60% EtOAc in hexanes), **18** was isolated as a light brown solid (0.014 g, 0.080 mmol, 23%, >20:1 d.r.). All spectral data were in agreement with previously reported values [9].

IV. Photocatalytic diamination of styrenes

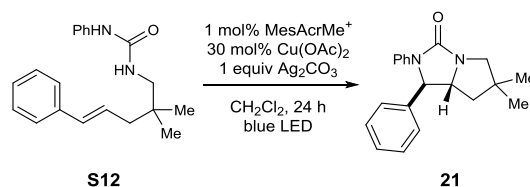
General procedure for intramolecular diamination of styrenes: A Schlenk flask containing the diamination substrate (1 equiv), Ag₂CO₃ (1 equiv), Cu(OAc)₂·xH₂O (0.30 equiv), and MesAcrMe⁺ (**6**, 0.025 equiv, 2.5 mol %) in CH₂Cl₂ (0.1 M) was degassed (freeze-pump-thaw, 4 cycles of 5 min each), and the resulting mixture was irradiated with a 15 W blue LED flood lamp for 24–36 h at ambient temperature. The reaction mixture was then diluted with EtOAc, eluted through a thin pad of SiO₂, and concentrated under reduced pressure. The residue was purified by chromatography on SiO₂ to afford pure product.



1,2-Diphenylhexahydro-3H-pyrrolo[1,2-c]imidazol-3-one (Figure 2, **19**). Synthesized according to the general procedure using **S10** (0.098 g, 0.35 mmol), Ag₂CO₃ (0.131 g, 0.350 mmol), Cu(OAc)₂·xH₂O (0.019 g, 0.11 mmol), and MesAcrMe⁺ (0.0035 g, 0.0088 mmol) and irradiated for 24 h. After chromatography on SiO₂ (0–10% Et₂O in CH₂Cl₂), **19** was isolated as a white solid (0.038 g, 0.14 mmol, 40%). All spectral data were in agreement with previously reported values [3].



2-Phenyl-1-(*p*-tolyl)hexahydro-3*H*-pyrrolo[1,2-*c*]imidazol-3-one (Figure 2, **20**). Synthesized according to the general procedure using **S11** (0.103 g, 0.350 mmol), Ag₂CO₃ (0.131 g, 0.350 mmol), Cu(OAc)₂·xH₂O (0.030 g, 0.10 mmol), and MesAcrMe⁺ (0.0035 g, 0.0087 mmol) and irradiated for 36 h. After chromatography on SiO₂ (0–5% Et₂O in CH₂Cl₂), **20** was isolated as a white solid (0.050 g, 0.21 mmol, 50%). All spectral data were in agreement with previously reported values [3].



6,6-Dimethyl-1,2-diphenylhexahydro-3*H*-pyrrolo[1,2-*c*]imidazol-3-one (Figure 2, **21**). Synthesized according to the general procedure using **S12** (0.108 g, 0.350 mmol), Ag₂CO₃ (0.131 g, 0.350 mmol), Cu(OAc)₂·xH₂O (0.030 g, 0.11 mmol), and MesAcrMe⁺ (0.0035 g, 0.0087 mmol) and irradiated for 24 h. After chromatography on SiO₂ (0–5% Et₂O in CH₂Cl₂), **21** was isolated as a white solid (0.030 g, 0.097 mmol, 28%). All spectral data were in agreement with previously reported values [3].

V. References

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