Supporting Information

Cross Dehydrogenative Coupling (CDC) of Aldehydes with N-Hydroxyimides by Visible Light Photoredox Catalysis

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General Considerations

All commercially available chemicals and reagents were used without any further purification unless otherwise stated. The progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel (230–400 mesh). Nuclear magnetic resonance spectra were recorded at 500 MHz for $^1$H and 125 MHz for $^{13}$C respectively, on a Model Bruker Avance II instrument. The multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet), and coupling constants ($J$) were given in Hz. The chemical shifts are reported in ppm relative to TMS as an internal standard. Mass spectra were obtained by electro spray ionization (ESI) using a Waters 2695 LC-MS. Elemental (CHNS) analyses were carried out using an elemental analyzer, Vario Micro Cube.

General procedure of photo-CDC reaction:

An oven-dried test tube equipped with a stir bar was charged with [Ru(bpy)$_3$]Cl$_2$·6H$_2$O 4a (2 mol%) and $N$-hydroxyimide (0.2 mmol). The tube was sealed with a Teflon screw cap, before aldehyde (0.4 mmol) and dry CH$_3$CN (2 mL) were added to it. The orange reaction mixture was irradiated at room temperature with a 18 W blue LED bulb at a distance of approximately 8 cm for specific time. After the reaction was complete as shown by TLC, the solution was concentrated and the residue was purified by silica gel flash chromatography to afford the corresponding products.
Compound characterization data:

1,3-dioxoisooindolin-2-yl benzoate (Table 2, 3a)\(^1\): (Eluent: 10% EtOAc in Hexane); white solid, amorphous; 84% yield (45 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.20-8.18 (m, 2H), 7.92 (s, 2H), 7.81 (s, 2H), 7.70-7.68 (m, 1H), 7.53 (s, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 162.7, 162.0, 134.8, 134.7, 130.6, 128.9, 128.8, 125.2, 124.0. HRMS (ESI) calcd for C\(_{15}\)H\(_{10}\)NO\(_4\) [M+H]: 268.0610; found 268.0665.

1,3-dioxoisooindolin-2-yl 4-methylbenzoate (Table 2, 3b)\(^1\): (Eluent: 10% EtOAc in Hexane); white solid, amorphous; 81% yield (46 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.08-8.07 (d, \(J=8.5\) Hz, 2H), 7.92-7.90 (m, 2H), 7.81-7.79 (m, 2H), 7.33-7.32 (d, \(J=8.0\) Hz, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 162.8, 162.1, 146.0, 134.7, 130.6, 129.5, 129.0, 123.9, 122.4, 21.8. HRMS (ESI) calcd for C\(_{16}\)H\(_{12}\)NO\(_4\) [M+H]: 282.0766; found 282.0792.

1,3-dioxoisooindolin-2-yl 4-methoxybenzoate (Table 2, 3c)\(^1\): (Eluent: 10% EtOAc in Hexane); white solid, amorphous; 82% yield (48 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.16-8.14 (d, \(J=9.0\) Hz, 2H), 7.93-7.91 (m, 2H), 7.81-7.80 (m, 2H), 7.01-6.99 (d, \(J=9.0\) Hz, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 164.8, 162.2, 134.7, 132.9, 129.0, 123.9, 117.2, 114.2, 55.6. HRMS (ESI) calcd for C\(_{16}\)H\(_{12}\)NO\(_5\) [M+H]: 298.0715; found 298.0721.

1,3-dioxoisooindolin-2-yl 4-chlorobenzoate (Table 2, 3d)\(^1\): (Eluent: 10% EtOAc in Hexane); white solid, amorphous; 92% yield (55 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.15-8.14 (m, 2H), 7.95-7.90 (m, 4H), 7.65-7.63 (m, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 162.3, 162.1, 141.4, 135.3, 131.8, 129.6, 128.7, 123.9, 117.3. HRMS (ESI) calcd for C\(_{15}\)H\(_{9}\)ClNO\(_4\) [M+H]: 302.0220; found 302.0208.

1,3-dioxoisooindolin-2-yl 4-bromobenzoate (Table 2, 3e)\(^2\): (Eluent: 10% EtOAc in Hexane); white solid, amorphous; 80% yield (55 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.06-8.04 (d, \(J=8.5\) Hz, 2H), 7.94-7.92 (m, 2H), 7.83-7.81 (m, 2H), 7.70-7.68 (d, \(J=8.5\) Hz, 2H).

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13C NMR (125 MHz, CDCl₃) δ 161.0, 160.6, 133.6, 131.1, 130.7, 129.2, 127.7, 122.9, 122.8. HRMS (ESI) calcd for C₁₅H₉BrNO₄ [M+H]: 345.9715; found 345.9731.

1,3-dioxoisooindolin-2-yl 2-fluorobenzoate (Table 2, 3f): (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 50% yield (28 mg); ¹H NMR (500 MHz, CDCl₃) δ 8.17-8.13 (m, 1H), 7.95-7.93 (m, 2H), 7.84-7.83 (m, 2H), 7.72-7.67 (m, 1H), 7.34-7.31 (m, 1H), 7.28-7.23 (m, 1H). 13C NMR (125 MHz, CDCl₃) δ 163.5, 161.9, 161.4, 160.2, 136.8, 136.7, 134.8, 132.7, 128.9, 124.4, 117.5, 117.3, 113.9, 113.8. HRMS (ESI) calcd for C₁₅H₉FNO₄ [M+H]: 286.0516; found 286.0545.

1,3-dioxoisooindolin-2-yl 3-fluorobenzoate (Table 2, 3g): (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 40% yield (23 mg); ¹H NMR (500 MHz, CDCl₃) δ 8.01-7.99 (m, 1H), 7.94-7.93 (m, 2H), 7.89-7.87 (m, 1H), 7.84-7.82 (m, 2H), 7.55-7.53 (m, 1H), 7.42-7.41 (m, 1H). ¹C NMR (125 MHz, CDCl₃) δ 161.8, 134.8, 130.7, 130.6, 128.9, 126.4, 124.1, 122.1, 122.0, 117.6, 117.4. HRMS (ESI) calcd for C₁₅H₉FNO₄ [M+H]: 286.0516; found 286.0531.

1,3-dioxoisooindolin-2-yl 4-fluorobenzoate (Table 2, 3h): (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 67% yield (38 mg); ¹H NMR (500 MHz, CDCl₃) δ 8.25-8.23 (m, 2H), 7.95-7.90 (m, 4H), 7.37-7.34 (m, 2H). ¹C NMR (125 MHz, CDCl₃) δ 168.0, 165.9, 162.2, 162.1, 135.3, 133.4, 133.3, 128.7, 123.9, 121.3, 117.3. HRMS (ESI) calcd for C₁₅H₉FNO₄ [M+H]: 286.0516; found 286.0525.

1,3-dioxoisooindolin-2-yl 4-nitrobenzoate (Table 2, 3i): (Eluent: 20 % EtOAc in Hexane); white solid, amorphous; 38% yield (24 mg); ¹H NMR (500 MHz, CDCl₃) δ 8.39 (s, 4H), 7.96-7.95 (m, 2H), 7.86-7.84 (m, 2H). ¹C NMR (125 MHz, CDCl₃) δ 161.6, 161.2, 151.5, 135.0, 131.8, 130.7, 128.8, 124.2, 123.9. Anal. calcd. for C₁₅H₈N₂O₆: C, 57.70; H, 2.58; N, 8.97. Found: C, 57.70; H, 2.73; N, 9.09.

1,3-dioxoisooindolin-2-yl furan-2-carboxylate (Table 2, 3j): (Eluent: 10 % EtOAc in Hexane); 24.2 mg; white solid, amorphous; 47% yield (24 mg); ¹H NMR (500 MHz, CDCl₃) δ 7.93-7.92 (m, 2H), 7.83-7.81 (m, 2H), 7.76 (s, 1H), 7.55-7.54 (m, 1H), 6.66-6.65 (m, 1H). ¹C NMR (125 MHz, CDCl₃) δ 161.8, 154.4, 148.7, 139.8, 134.8, 128.8, 124.1, 123.9, 121.3.
1,3-dioxoisooindolin-2-yl thiophene-2-carboxylate (Table 2, 3k)\textsuperscript{1,2}: (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 55% yield (30 mg); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.98-96 (m, 1H), 7.84-7.82 (m, 2H), 7.73-7.71 (m, 3H), 7.14-7.13 (m, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 161.9, 158.2, 136.6, 135.7, 134.8, 128.8, 128.4, 127.0, 124.0. HRMS (ESI) calcd for C\textsubscript{13}H\textsubscript{8}NO\textsubscript{5} [M+H]: 258.0402; found 258.0428.

1,3-dioxoisooindolin-2-yl nicotinate (Table 2, 3l): (Eluent: 40 % EtOAc in Hexane); white solid, amorphous; 25% yield (14 mg); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 9.39-9.38 (d, \(J=4.0\) Hz, 1H), 8.94-8.91 (m, 1H), 8.48-8.43 (m, 1H), 7.96-7.81 (m, 4H), 7.56-7.49 (m, 1H), 7. \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 164.5, 161.7, 161.5, 154.7, 151.0, 138.3, 134.9, 134.0, 128.7, 124.1, 123.9, 123.1, 122.0. HRMS (ESI) calcd for C\textsubscript{14}H\textsubscript{9}N\textsubscript{2}O\textsubscript{4} [M+H]: 269.0562; found 269.0549.

1,3-dioxoisooindolin-2-yl cinnamate (Table 2, 3m): (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 61% yield (36 mg); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.98-7.91 (m, 3H), 7.81-7.79 (m, 2H), 7.60-7.59 (m, 2H), 7.45-7.44 (m, 3H), 6.68-6.65 (d, \(J=16\) Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 162.7, 161.8, 149.7, 134.4, 131.2, 128.8, 128.7, 128.3, 123.7, 111.4. HRMS (ESI) calcd for C\textsubscript{17}H\textsubscript{12}N\textsubscript{2}O\textsubscript{4} [M+H]: 294.0766; found 294.0752.

2,5-dioxopyrrolidin-1-yl benzoate (Table 3, 5a)\textsuperscript{1,2}: (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 33% yield (15 mg); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.13-8.11 (m, 2H), 7.67-7.65(m, 1H) 7.52-7.48 (m, 2H), 2.89 (s, 4H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 169.2, 161.8, 130.4, 128.8, 125.0, 25.6.

2,5-dioxopyrrolidin-1-yl 4-methylbenzoate (Table 3, 5b)\textsuperscript{1,2}: (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 39% yield (18 mg); \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}CN) \(\delta\) 8.01-8.00 (d, \(J=8.5\) Hz, 2H), 7.41-7.40 (d, \(J=8.0\) Hz, 2H) 2.84 (s, 4H). \textsuperscript{13}C NMR (125 MHz, CD\textsubscript{3}CN) \(\delta\) 169.7, 161.5, 146.2, 129.6, 129.4, 121.6, 116.8, 24.9,
20.4. HRMS (ESI) calcd for C_{12}H_{12}NO_4 [M+H]: 234.0766; found 234.0741.

2,5-dioxopyrrolidin-1-yl 4-methoxybenzoate (Table 3, 5c): (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 42% yield (21 mg); \(^1\)H NMR (500 MHz, CD_3CN) \(\delta\) 8.08-8.06 (d, J=9.0 Hz, 2H), 7.09-7.07 (d, J=9.0 Hz, 2H), 3.89 (s, 3H), 2.83 (s, 4H).

\(^{13}\)C NMR (125 MHz, CD_3CN) \(\delta\) 169.8, 164.7, 161.1, 131.9, 116.8, 114.1, 55.1, 24.9. HRMS (ESI) calcd for C_{12}H_{12}NO_4 [M+H]: 250.0715; found 250.0712.

2,5-dioxopyrrolidin-1-yl 4-chlorobenzoate (Table 3, 5d): (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 51% yield (25 mg); \(^1\)H NMR (500 MHz, CD_3CN) \(\delta\) 8.13-8.11 (d, J=8.5 Hz, 2H), 7.65-7.63 (d, J=8.5 Hz, 2H) 2.87 (s, 4H).

\(^{13}\)C NMR (125 MHz, CD_3CN) \(\delta\) 169.7, 161.0, 140.8, 131.4, 129.2, 123.4, 25.1. HRMS (ESI) calcd for C_{11}H_{9}ClNO_4 [M+H]: 254.0220; found 254.0229.

2,5-dioxopyrrolidin-1-yl 4-fluorobenzoate (Table 3, 5e): (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 36% yield (17 mg); \(^1\)H NMR (500 MHz, CD_3CN) \(\delta\) 8.19-8.16 (m, 2H), 7.34-7.30 (m, 2H), 2.84 (s, 4H).

\(^{13}\)C NMR (125 MHz, CD_3CN) \(\delta\) 169.6, 167.4, 165.3, 160.7, 132.8, 132.7, 121.0, 116.8, 24.9. HRMS (ESI) calcd for C_{11}H_{9}FNO_4 [M+H]: 238.0516; found 238.0545.

2,5-dioxopyrrolidin-1-yl 4-chlorobenzoate (Table 3, 5f): (Eluent: 10 % EtOAc in Hexane); white solid, amorphous; 44% yield (26 mg); \(^1\)H NMR (500 MHz, CDCl_3) \(\delta\) 8.27 (s, 1H), 8.07-8.06 (m, 1H), 7.82-7.80 (d, J=8.0 Hz, 1H), 7.42-7.38 (m, 1H) 2.91 (s, 4H).

\(^{13}\)C NMR (125 MHz, CDCl_3) \(\delta\) 168.9, 160.7, 137.8, 133.3, 130.4, 129.0, 127.0, 122.8, 25.6. HRMS (ESI) calcd for C_{11}H_{9}BrNO_4 [M+H]: 297.9715; found 297.9705.

2,5-dioxopyrrolidin-1-yl 4-nitrobenzoate (Table 3, 5g): (Eluent: 10 % EtOAc in Hexane); Yellow solid, amorphous; 21% yield (12 mg); \(^1\)H NMR (500 MHz, CD_3CN) \(\delta\) 8.38-8.31 (m, 4H), 2.87 (s, 4H), \(^{13}\)C NMR (125 MHz, CD_3CN) \(\delta\) 169.3, 160.3, 151.3, 131.0, 129.9, 123.7, 25.0. HRMS (ESI) calcd for C_{11}H_{9}N_2O_6 [M+H]: 265.0461; found 265.0447.

Synthesis of Amide:
To a reaction mixture of 3d (60 mg, 0.2 mmol) in ethylacetate (2 mL), amine (0.6 mmol, 3.0 eqv) was added. The reaction mixture was stirred at room temperature and upon completion (monitored by TLC), the crude mixture was concentrated and purified by column chromatography to afford the desired products 6a-b.

N-benzyl-4-chlorobenamide (6a): (Eluent: 25% EtOAc in Hexane); white solid, amorphous; 92% yield; \(^{1}H\) NMR (500 MHz, CDCl3) \(\delta\) 7.73-7.19 (m, 2H), 7.40-7.30 (m, 7H), 6.44 (br s, 1H, NH), 4.63-4.62 (d, \(J = 6.0\) Hz, 2H); \(^{13}C\) NMR (125 MHz, CDCl3) \(\delta\) 166.3, 137.9, 137.8, 132.7, 128.8, 128.4, 127.9, 127.7, 44.2.

N-(4-bromophenethyl)-4-chlorobenamide (6b): (Eluent: 25% EtOAc in Hexane); white solid, amorphous; 95% yield; \(^{1}H\) NMR (500 MHz, CDCl3) \(\delta\) 7.63-7.61 (d, \(J = 7.0\) Hz, 2H), 7.44-7.37 (m, 4H), 7.10-7.08 (d, \(J = 7.0\) Hz, 2H), 6.18 (br s, 1H, NH), 3.67 (q, \(J = 6.5\) Hz, 2H), 2.88 (t, \(J = 7.0\) Hz, 2H); \(^{13}C\) NMR (125 MHz, CDCl3) \(\delta\) 166.1, 137.5, 137.4, 132.5, 131.5, 130.2, 128.5, 127.9, 120.2, 40.7, 34.7.

Gram Scale Experiment (3d). The experiment was conducted in Bhavnagar, Gujarat, India (location: 21° 46’N, 72° 11’E). Following General procedure, except that the catalyst was added in two batches, a 250 mL round-bottom flask was charged with [Ru(bpy)_3]Cl_2 (53 mg, 0.071 mmol, 2 mol%), 4-chloro benzaldehyde (1.0 g, 7.11 mmol), N-hydroxyphthalimide (2.32 g, 14.22 mmol), and dry CH_3CN (70 mL). The orange reaction mixture was stirred in a typical sunny day. After 4 h of the reaction, another batch of the catalyst (53 mg) was added. After completion of the reaction (8 h total from the beginning), the mixture was concentrated and the residue was purified by silica gel column chromatography (10 % EtOAc/hexane) to afford the ester 3d (1.75 g, 82%) as white solid.

Synthesis of Bromo-oxazole (6c) with NBS
0.2 mmol of N-(4-bromophenethyl)-4-chlorobenamide (6b) and 0.6 mmol of NBS were taken in reaction tube and 2mL of DCE was added into the tube. The mixture was stirred

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under 60 W tungsten bulb at 80°C. Reaction was continued for 6h under constant stirring condition. After cooling to room temperature, 1 mL of water was added, washed with aqueous NaHCO₃, and the reaction mixture was extracted with DCM. Upon purification of the crude mixture on silica gel column chromatography (5% EtOAc/hexane), product 6c was obtained as white amorphous solid (72%). ¹H NMR (500 MHz, CD₃CN) δ 8.02-8.00 (d, J = 8.6 Hz, 2H), 7.99-7.83 (m, 2H), 7.84-7.83 (d, J = 8.6 Hz, 2H), 7.51-7.50 (d, J = 8.6 Hz, 2H); ¹³C NMR (125 MHz, CD₃CN) δ 159.8, 147.1, 137.4, 132.8, 130.0, 129.9, 128.4, 126.06, 126.1, 125.8, 113.2.

Control experiment with TEMPO

The reaction tube equipped with a stir bar was charged with [Ru(bpy)₃]Cl₂·6H₂O 4a (2 mol%) and N-hydroxyphthalimide (0.2 mmol). The tube was sealed with a Teflon screw cap, before aldehyde (0.4 mmol), 0.4 mmol of TEMPO and dry CH₃CN (2 mL) were added to the tube. In the same way (as described in general procedure section) the reaction was continued for overnight. After 12h no product was identified in crude NMR spectra.