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Aerobic oxidation of aldehydes by visible light photocatalysis

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ABSTRACT

An efficient and environmentally benign method for the oxidation of aldehydes to carboxylic acids has been developed. Singlet oxygen, generated by visible light in the presence of a Ru or Ir photocatalyst, reacted with aldehydes to give the corresponding carboxylic acids in excellent yields. The reaction is highly chemo-selective, in which only an aldehyde moiety is reactive even in the presence of other photo-oxidation active sites. This method is an example of an ideal green chemical reaction in the sense that molecular oxygen and visible light are key sources for the transformation.

Oxidation is one of the fundamental reactions in nature, and the oxidation of aldehydes to carboxylic acids has been of great interest in synthetic organic chemistry.[1] A variety of synthetic methods for the transformation of aldehydes including transition metal catalyzed reactions have been reported, which use a range of oxidants (Fig. 1(1)).[2,3] However, many of these methods suffer from harsh reaction conditions, limited substrate scope, or the need for stoichiometric amounts of costly or hazardous oxidizing agents. Thus, the development of more efficient and convenient methods is still desired. Herein, we present an environmentally benign method for the oxidation of aldehydes to carboxylic acids, which utilizes ideal green natural resources: molecular oxygen[4] as oxidant and visible light[5–7] as an energy source (Fig. 2(1)).

The photosensitized production of singlet oxygen ($^1O_2$) plays a crucial role in a range of areas from polymer science to cancer therapy.[8] In addition, singlet oxygen is an important intermediate in organic reactions involving photo-oxidation. Cyclometalated Ru/Ir photocatalysts have proven to be highly efficient singlet oxygen generators under visible light irradiation either by single electron transfer (Fig. 2(1)) or by energy transfer (Fig. 2(2)).[9] Figure 3 shows examples of photocatalysts which are used in visible light-induced radical reactions.[5] We envisioned that singlet oxygen generation by Ru/Ir catalysts could accelerate the aerobic oxidation of aldehydes.

We commenced our investigation of the oxidation of aldehydes by employing *p*-anisaldehyde **1a** as a model substrate. **1a** was converted to carboxylic acid **2a** in the presence of molecular oxygen and 1 mol % [Ru(bpy)$_3$Cl$_2$] as the photocatalyst under photo-irradiation by blue LEDs at room temperature (Table 1, entry 1). In order to maximize the yield of product **2a**, we screened a variety of Ru and Ir photocatalysts. Ir complexes were observed to possess a higher reactivity than Ru catalysts in general (entries 1–5), probably due to higher quantum efficiencies of Ir(III) complexes than Ru(II) complexes and efficient intersystem cross-

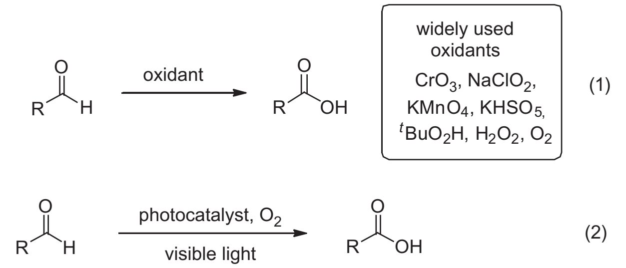

Figure 1. Oxidations of aldehydes using various oxidants.

$$^*\mathrm{RuL}_3^{2+} + {}^3\mathrm{O}_2 \xrightarrow{\mathrm{e}^-\ \text{transfer}} [\,\mathrm{RuL}_3^{3+}\ldots\ \mathrm{O}_2^{\cdot-}\,] \longrightarrow \mathrm{RuL}_3^{2+} + {}^1\mathrm{O}_2 \quad (1)$$

$$^*\mathrm{RuL}_3^{2+} + {}^3\mathrm{O}_2 \xrightarrow{\text{energy transfer}} \mathrm{RuL}_3^{2+} + {}^1\mathrm{O}_2 \quad (2)$$

Figure 2. Two possible pathways for generation of singlet oxygen using a Ru photocatalyst.

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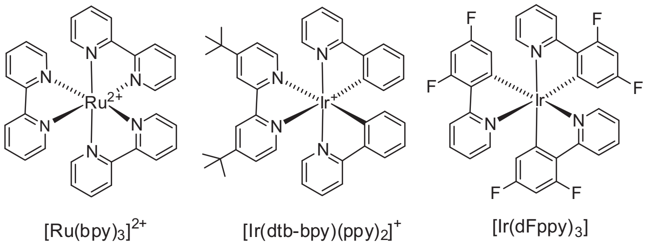
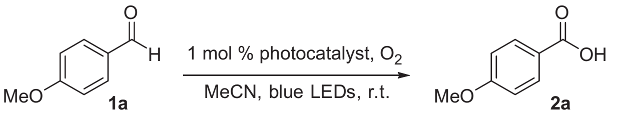


Figure 3. Representative visible light photocatalysts.

Table 1
Catalyst screening and control experiments[a]



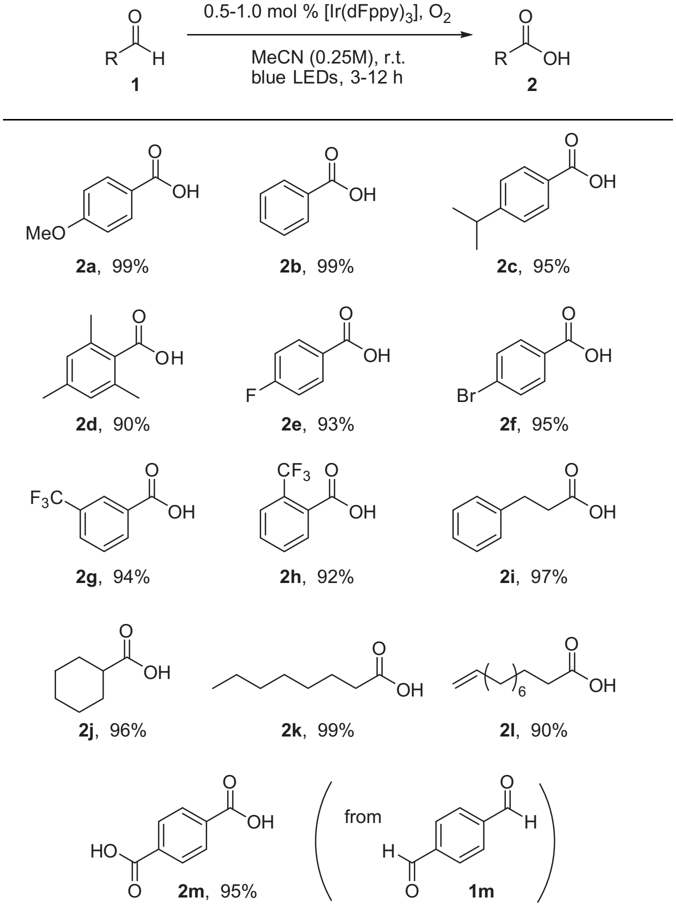
Entry	Photocatalyst	Product yield[b] (%)
1	$Ru(bpy)Cl_2$	49
2	$Ru(phen)Cl_2$	31
3	$Ir(ppy)_2(dtb\text{-}bpy)PF_6$	92
4	$Ir(ppy)_3$	86
5	$Ir(dFppy)_3$	99
6	No photocatalyst	Trace
7	$Ir(dFppy)_3$ (no light)	Trace
8[c]	$Ir(dFppy)_3$ (no O_2)	Trace
9	$Ir(dFppy)_3$ (0.5 mol %)	99
10[d]	$Ir(dFppy)_3$ (0.1 mol %)	90

[a] Reaction conditions: Compound **1a** (0.2 mmol), photocatalyst (1 mol %), CH_3CN (0.8 mL), O_2 bubbling and O_2 balloon, Blue LEDs, room temperature, 12 h.
[b] Isolated yields.
[c] Reaction was done under Ar atmosphere.
[d] Reaction took more than 24 h.

over between the singlet and triplet excited states of Ir(III) complexes.[9c,d] Among these catalysts, $Ir(dFppy)_3$[10] (entry 5) was found to be the best photocatalyst for the transformation. Control experiments showed that the transformation required a photocatalyst, visible light irradiation, and molecular oxygen (entries 6–8). Although the catalyst loading could be lowered to 0.1 mol %, at least 0.5 mol % $Ir(dFppy)_3$ was required for reproducible results and completion of the reaction in a reasonable time (entries 9 and 10). We also examined the effect of other parameters, such as solvents and reaction concentration, and the reaction worked best in MeCN with a 0.25 M concentration.

With optimized conditions in hand, oxidations of a wide range of aldehydes were explored in the presence of $Ir(dFppy)_3$ catalyst (Table 2).[11] Both aromatic and aliphatic aldehydes were converted into the corresponding carboxylic acids, showing the efficiency of the new synthetic method. Reactions of both electron-poor and electron-rich aromatic aldehydes gave excellent yields of products. Notably, this reaction showed high chemo-selectivity under the conditions. Benzylic systems, which could undergo aerobic photooxidation, appeared to be inactive under the reaction conditions (**2c**, **2i**).[12] In addition, undecenal was smoothly converted to undecylenic acid **2l** although its alkene moiety could have been reactive to oxidation with singlet oxygen.[13,14] **1m** containing two aldehyde moieties underwent oxidations to give **2m** with a longer reaction time (24 h). It was found that the transformation of highly reactive aldehydes was just as efficient as using $[Ru(bpy)_3Cl_2]$, which was less reactive than $Ir(dFppy)_3$ in the optimization study of **1a**. For instance, benzaldehyde was converted to **2b** in the presence of only 0.1 mol % $[Ru(bpy)_3Cl_2]$.

Table 2
Substrate scope[a,b]

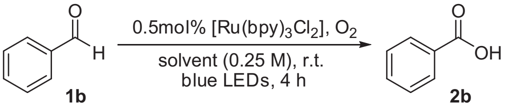


[a] Reaction conditions: 1(1 mmol), $Ir(dFppy)_3$ (0.5–1.0 mol %), MeCN (4 mL), O_2 bubling and balloon, Blue LEDs, room temperature, 3–12 h.
[b] Isolated yields based on an average of two runs.

Next, we performed reactions to confirm that singlet oxygen was the key reactive species for this transformation. Reaction of **1b** was carried out in DMSO, DMF, and water, solvents that are known to be singlet oxygen quenchers (Table 3).[15] The fact that the reactions did not proceed in these solvents supports our hypothesis that the oxidation is accelerated by the generation of singlet oxygen under visible light-photosensitized conditions.

Based on the results, we propose a plausible mechanism[16] for the oxidation of aldehydes by visible light photocatalysis (Fig. 4). The activated catalyst with visible light generates singlet oxygen. Singlet oxygen reacts with an aldehyde to generate peroxy acid **3** through acyl radical[17] and hydroperoxyl radical (HOO·) as interme-

Table 3
Solvent ($^1O_2$ quencher) effect on aerobic oxidation of **1b**



Entry	Solvent	Yield (%)
1	MeCN	99
2	DMSO	0
3	DMF	0
4	H_2O	Trace

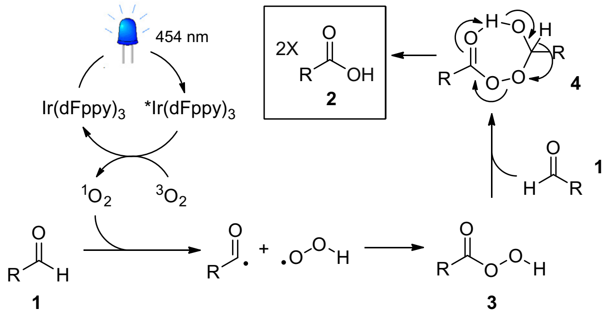


Figure 4. Proposed mechanism for the oxidation.

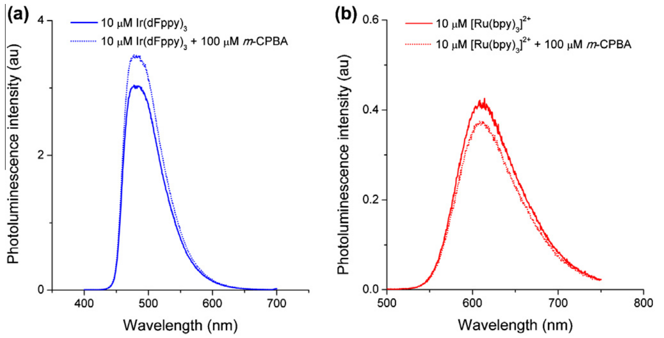


Figure 5. Photoluminescence spectra of 10 μM Ir(dFppy)$_3$ (a) and 10 μM [Ru(bpy)$_3$]$^{2+}$ (b) in Ar-saturated MeCN solutions in the absence (solid line) and presence (dotted line) of 10 equiv of *m*-CPBA.

diates. The peroxy acid **3** subsequently undergoes reaction with another aldehyde to form complex **4**, followed by Bayer–Villiger type rearrangement to generate two molecules of carboxylic acid **2**. We additionally performed bimolecular photoluminescence quenching experiments using peroxy acid **3**, *m*-chloroperbenzoic acid (*m*-CPBA) to check the possibility of **3** to undergo a photoredox reaction under our conditions (Fig. 5). It was found that the presence of **3** exerted negligible influences on the phosphorescence emission of Ir(dFppy)$_3$ and [Ru(bpy)$_3$]$^{2+}$. The results indicated lack of any oxidative interactions between **3** and the photocatalysts under photoexcitation, because oxidation of the catalysts should lead to phosphorescence changes. Thus, the pathway involving the oxidation of the photocatalyst by **3** could be safely excluded.

In conclusion, we have developed a highly efficient visible light-induced oxidation method for the conversion of aldehydes to carboxylic acids. It is noteworthy that the reaction proceeds by employing ideal natural sources, molecular oxygen, and visible light, as essential ingredients for the transformation. The reaction is highly chemo-selective, in which only the aldehyde moiety is reactive even in the presence of other photo-oxidative active sites. We present our protocol as an eco-friendly and efficient alternative to current oxidation methods of aldehydes.

Experimental procedure

An oven-dried resealable test tube equipped with a magnetic stir bar was charged with aldehyde (1.0 mmol), Ir(dFppy)$_3$ (0.005–0.01 mmol) and MeCN (4.0 mL, 0.25 M). Oxygen was then bubbled through the reaction mixture, and the vessel was sealed with a silicone septa screw-cap. A balloon filled with oxygen was attached to the tube, and the test tube was placed under blue LEDs at room temperature. The reaction was allowed to proceed for 3–12 h, and reaction progress was checked by TLC. The solvent was removed under vacuum, and the corresponding carboxylic acid[18] was purified by flash silica gel chromatography.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.09.005.

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18. *Analytical data of compounds*: **2a**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.64 (br s, 1H), 7.89 (d, J = 9.2 Hz, 2H), 7.01 (d, J = 9.2 Hz, 2H), 3.82(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05, 162.85, 131.37, 123.00, 113.83, 55.45. **2b**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.97 (br s, 1H), 7.95 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.39, 132.90, 130.81, 129.31, 128.61. **2c**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.81 (br s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.94 (septet, J = 7.0 Hz, 1H), 1.20 (d, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.31, 153.64, 129.49, 128.45, 126.53, 33.50, 23.57. **2d**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.98 (b s, 1H), 6.87 (s, 2H), 2.23 (s, 6H), 2.22 (s, 3H). **2e**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.07 (br s, 1H), 8.00 (dd, J = 8.8, 6.0 Hz, 2H), 7.31 (dd, J = 8.8, 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.42, 164.94 (d, J = 251.3 Hz), 132.13 (d, J = 9.6 Hz), 127.40 (d, J = 2.8 Hz), 115.64 (d, J = 22.0 Hz). **2f**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.98 (br s, 1H), 7.86 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 131.67, 131.31, 130.34, 126.75. **2g**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.77 (br s, 1H), 8.20 (d, J = 7.6 Hz, 1H), 8.14 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 133.25, 132.14, 130.02, 129.56 (q, J = 32.4 Hz), 129.30 (q, J = 3.5 Hz), 125.63 (q, J = 3.7 Hz), 123.89 (q, J = 273.4 Hz). **2h**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.58 (br s, 1H), 7.86–7.65 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.90, 132.69, 132.43 (q, J = 2.0 Hz), 131.22, 129.71, 126.56 (q, J = 22.2 Hz), 126.53 (q, J = 5.3 Hz), 123.60 (q, J = 274.3 Hz). **2i**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.17 (br s, 1H), 7.23–7.15 (m, 5H), 2.81 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.80, 140.90, 128.32, 128.26, 126.00, 35.25, 30.36. **2j**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (br s, 1H), 2.17 (tt, J = 10.8, 3.6 Hz, 1H), 1.84–1.73 (m, 2H), 1.69–1.60 (m, 2H), 1.58–1.10 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.77, 42.25, 28.71, 25.48, 24.98. **2k**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.98 (br s, 1H), 2.17 (t, J = 7.2 Hz, 2H), 1.53–1.43 (m, 2H), 1.31–1.19 (m, 8H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.53, 33.71, 31.22, 28.59, 28.49, 24.56, 22.12, 13.95. **2l**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.97 (br s, 1H), 5.78 (ddt, J = 17.2, 10.2, 5.6 Hz, 1H), 4.99 (ddt, J = 17.2, 1.8, 1.6 Hz, 1H), 4.22 (ddt, J = 10.2, 1.6, 1.2 Hz, 1H), 2.18 (t, J = 7.2 Hz, 2H), 2.04–1.95 (m, 2H), 1.54–1.18 (m, 12H).