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Intramolecular Aromatic C−H Acyloxylation Enabled by Iron Photocatalysis

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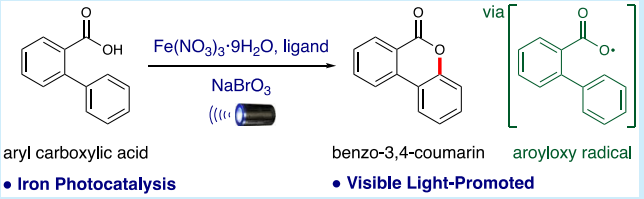
ABSTRACT: A mild and efficient protocol for the intramolecular aromatic C−H oxygenation of 2-biphenylcarboxylic acids has been achieved via iron photocatalysis. The 2-biphenylcarboxylic acids with a diverse array of substituents at both phenyl rings could furnish the oxygenation products in good to excellent yields. We speculate that the aryl carboxylate−iron(III) complexes should generate the aroyloxy radicals and iron(II) upon visible light irradiation.



Due to their general photo- and chemical stability and long-lived photoexcited states, the luminescent complexes of precious metals such as ruthenium and iridium have found extensive application in photocatalysis in recent decades.[1] More recently, there is a significant renaissance in pursuing high-performance photosensitizers made from earth-abundant transition metals,[2] including but not limited to iron,[3] copper,[4] cerium,[5] chromium,[6] cobalt,[7] molybdenum,[8] nickel,[9] tungsten,[10] and zirconium.[11] In addition to the reactions catalyzed by those structurally well-defined photocatalysts, a wide range of novel photocatalytic transformations have been developed utilizing in situ generated transition metal complexes as the photocatalysts in the past few years.[12] In many cases, the substrate−transition metal complexes were promoted to the excited state upon visible light irradiation, followed by single-electron transfer and bond-breaking/forming events. This concept has been well-demonstrated, for example, by recent works from the groups of Hwang,[13] Fu and Peters,[14] Wu,[15] Lalic,[16] Zhang,[17] Xiao,[18] Zuo,[19] König,[20] Rovis,[21] Greaney,[22] and Alcázar and Noël.[23] Along this line, we recently accomplished several photoinduced decarboxylative transformations by exploring the photochemistry of alkyl carboxylate−iron(III) complexes (Figure 1).[24]

From a perspective on sustainability, the continuing development of iron photochemistry is significantly important.[25] As a further step toward iron photocatalysis, we wondered whether aryl carboxylate−iron(III) complexes, after the absorption of visible light, could split into the corresponding aroyloxy radicals $ArCO_2$• and the iron(II) species (Figure 1). It is well-known that aroyloxy radicals hardly undergo decarboxylation at ambient temperature and are very reactive intermediates for the direct oxygenation of aromatic C−H bonds through a general sequence of electrophilic addition, single-electron transfer, and deprotonation.[26] Moreover, through an intramolecular radical oxygenation pathway, the readily available 2-arylbenzoic acids can be straightly converted to benzo-3,4-coumarins,[27] which are the core structures in a wide range of bioactive natural products, pharmaceutical agents, and smart materials.[28] Aside from radical-based strategies, benzo-3,4-coumarins are accessible by palladium-, copper-, and ruthenium-catalyzed C−H activation approaches at increased temperature.[29] In light of these facts, we think 2-arylbenzoic acids would be ideal substrates to test the photoreactivity of aryl carboxylate−iron(III) complexes and to develop a new synthetic protocol for the preparation of benzo-3,4-coumarin derivatives. As part of our long-term interest in oxygen- and nitrogen-centered radicals,[30] herein, we describe a radical intramolecular

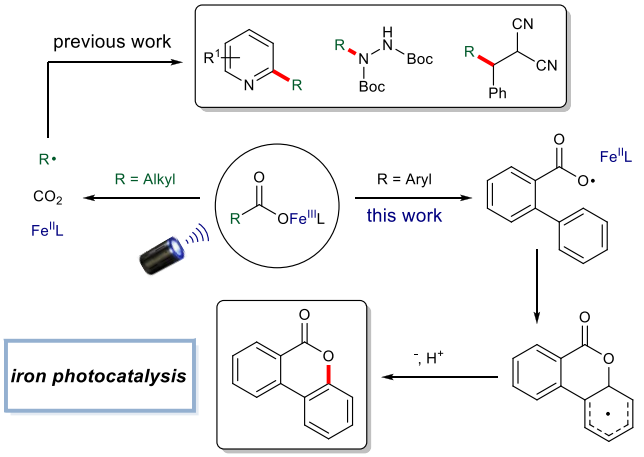


Figure 1. Photochemistry of iron complexes.

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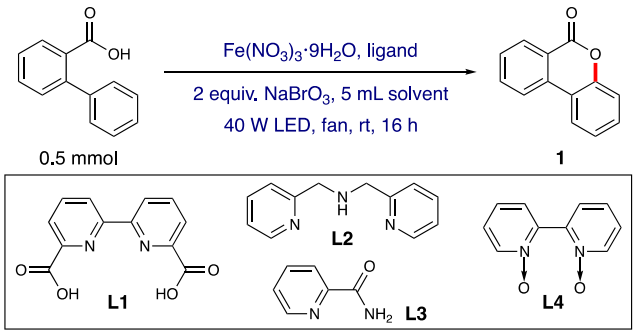
aromatic C−H oxygenation enabled by iron photocatalysis. The advantages of our current method should include room temperature reaction conditions, much lower price of iron than palladium, copper, and ruthenium, and high tolerance to halogen substitutes which would be left untouched.

We started our investigation into this intramolecular oxygenation by exposing the water/alcohol solution of 2-biphenylcarboxylic acid, $Fe(NO_3)_3{\cdot}9H_2O$, and $NaBrO_3$ to visible light (Kessil 40 W 427 nm LED) for 16 h (Table 1). Whereas water, methanol, ethanol, and isopropyl alcohol are amenable to the reaction, hexafluoroisopropanol (HFIP) proved to be the superior solvent. It afforded the intramolecular oxygenation product **1** in 17% yield (entry 1). To our delight, the yield of **1** increased dramatically up to 92% in the presence of 5 mol % of ligand **L1** (2,2′-bipyridine-6,6′-dicarboxylic acid, entry 2). The UV−vis spectra show a significant optical absorption in the visible light range with a 1:1 iron(III) and **L1** solution, whereas each alone has a minimal absorption (see Supporting Information). The reaction with ligand **L2** in acetonitrile also provided a high yield of 90% (di(2-picolyl)amine, entries 3 and 4), and ligands **L3** and **L4** promoted the transformation moderately (picolinamide and 2,2′-bipyridyl *N*,*N*′-dioxide, entries 5−7). During exploration of the substrate scope, we found that, in general, HFIP was superior than MeCN as a solvent. It is of note that with the bidentate ligand **L3**, the 1:2 ratio of iron(III) to **L3** led to a higher yield. Also, the UV−vis spectra illustrate that the solution of 1:2 iron(III) and **L3** has a visible light absorption much stronger than that of the 1:1 solution (see Supporting Information). The other iron salts such as $FeCl_3$, $FeCl_2{\cdot}4H_2O$, and $Fe(OAc)_2$ were compatible with the reaction although with lower yields (entries 8−10). Not surprisingly, a decrease in yield was observed with 440 and 456 nm irradiation (entries 11 and 12) because the iron(III) complexes had less absorbance of light beyond 427 nm (see the UV−vis spectra in Supporting Information). Furthermore, the critical roles of the oxidant, iron catalyst, and visible light in the protocol were demonstrated through the control experiments (entries 13−15). Without $NaBrO_3$, only a slight amount of cyclization product **1** was observed as this is a net oxidative transformation and the oxidant should be responsible to bring iron(II) back to iron(III). No desired product **1** was isolated in the absence of either iron catalyst or light. The intramolecular oxygenation was severely inhibited by the addition of free radical scavengers, such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and BHT (3,5-di-*tert*-butyl-4-hydroxytoluene). These radical quenching experiments suggest a radical mechanism where the aroyloxy radicals are likely involved (entries 16 and 17). Finally, it is worth mentioning that the reaction at 10 mmol gram scale could afford 1.53 g of the product benzo-3,4-coumarin without further optimization (entry 18).

Table 1. Optimization of the Reaction Conditions[a]



entry	iron(III)	ligand	solvent	wavelength	yield (%)
1	5 mol %	none	HFIP	427 nm	17
2	5 mol %	5 mol % **L1**	HFIP	427 nm	92
3	5 mol %	5 mol % **L2**	HFIP	427 nm	60
4	5 mol %	5 mol % **L2**	MeCN	427 nm	90
5	5 mol %	5 mol % **L3**	HFIP	427 nm	42
6	5 mol %	10 mol % **L3**	HFIP	427 nm	77
7	5 mol %	5 mol % **L4**	HFIP	427 nm	75
8[b]	5 mol %	5 mol % **L1**	HFIP	427 nm	70
9[c]	5 mol %	5 mol % **L1**	HFIP	427 nm	77
10[d]	5 mol %	5 mol % **L1**	HFIP	427 nm	58
11	5 mol %	5 mol % **L1**	HFIP	440 nm	82
12	5 mol %	5 mol % **L1**	HFIP	456 nm	72
13[e]	5 mol %	5 mol % **L1**	HFIP	427 nm	9
14	none	5 mol % **L1**	HFIP	427 nm	0
15	5 mol %	5 mol % **L1**	HFIP	dark	0
16[f]	5 mol %	5 mol % **L1**	HFIP	427 nm	12
17[g]	5 mol %	5 mol % **L1**	HFIP	427 nm	6
18[h]	5 mol %	5 mol % **L1**	HFIP	427 nm	78

[a]Isolated yields. [b]$FeCl_3$ used. [c]$FeCl_2{\cdot}4H_2O$ used. [d]$Fe(OAc)_2$ used. [e]Without $NaBrO_3$. [f]5 equiv of TEMPO added. [g]3 equiv of BHT added. [h]At 10 mmol scale.

Having determined the optimal conditions, we sought to evaluate the scope of this aromatic C−H oxygenation method. Substituents on the 2-biphenylcarboxylic acid substrates played an important role in the reaction possibly through the electronic and steric effects. Thus, when ligand **L1** failed to afford a satisfied yield for a specific substrate, **L2**, **L3**, or **L4** would be used for a better result. As illustrated in Scheme 1, a wide range of 2-biphenylcarboxylic acids could furnish the corresponding cyclization products in good to excellent yields. The reaction proceeded smoothly with electron-donating/withdrawing substituents at both rings. Notably, a variety of functional groups, such as halides (**6**, **7**, **8**, **12**, **16**, **17**, **18**, **21**, **22**), ethers (**5**, **10**, **13**, **14**, **19**), alkyl groups (**2**, **3**, **4**, **11**, **15**, **20**), and trifluoromethyl groups (**9**, **23**) were well-tolerated. However, we noticed that substituents on the 6, 2′, and 6′ positions of 2-biphenylcarboxylic acids would heavily retard the reaction perhaps because of the steric effect. Finally, the substrate with a naphthalene moiety was also transformed into the lactone product in a diminished but synthetically useful yield (**24**).

A possible mechanism for the intramolecular aromatic C−H oxygenation is illustrated in Scheme 2. We postulated that coordination of 2-biphenylcarboxylic acid to iron(III) **25** followed by deprotonation would readily form the aryl carboxylate−iron(III) complex **26**. Photoexcitation of the iron complex **26** should render an intramolecular ligand-to-metal charge-transfer event to afford the reduced iron(II) complex **27** and an aroyloxy radical **28**, which rapidly underwent an intramolecular electrophilic addition to the other phenyl ring. The resulting radical intermediate **29** could then be oxidized by iron(III) after deprotonation to furnish the rearomatization product **1**. The terminal oxidant $NaBrO_3$ would serve to bring iron(II) back to iron(III) to close the catalytic cycles.

In summary, we have developed a mild and efficient protocol for the intramolecular aromatic C−H oxygenation of 2-biphenylcarboxylic acids via iron photocatalysis. This new reaction exhibits a broad functionality tolerance at both phenyl rings. Based on the radical quenching experiments and related mechanism studies in the literature,[25,26] we speculate that the aryl carboxylate−iron(III) complexes should generate the

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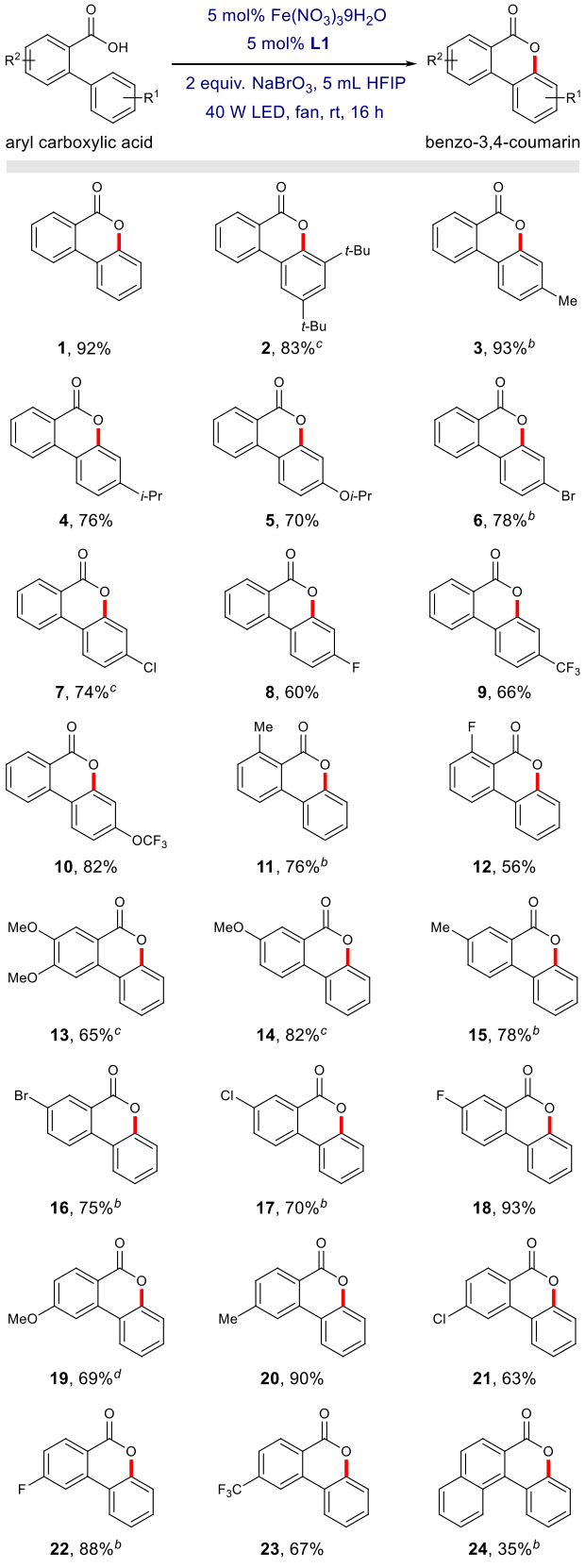
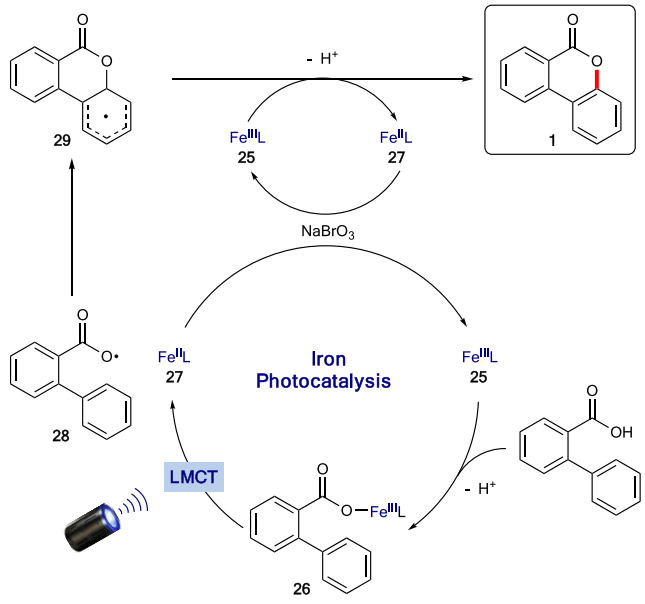
Scheme 1. Scope of the Intramolecular Aromatic C−H Oxygenation Reaction[a]



[a]Isolated yields. [b]5 mol % of **L2** and 5 mL of MeCN used. [c]10 mol % of **L3** used. [d]5 mol % of **L4** used.

Scheme 2. Proposed Mechanism of the Intramolecular Aromatic C−H Oxygenation Reaction



aroyloxy radicals and iron(II) upon visible light irradiation. As such, we anticipate this study will serve to render more research activities in the photochemistry of iron complexes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00002.

General experimental procedures, reaction setup, characterization data, and spectra for all key compounds (PDF)

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Notes

The authors declare no competing financial interest.

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