

# Photosensitized Reductive Elimination of Gold(III) to Enable Esterification of Aryl Iodides with Carboxylic Acids

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Cite This: *JACS Au* 2024, 4, 3084–3093



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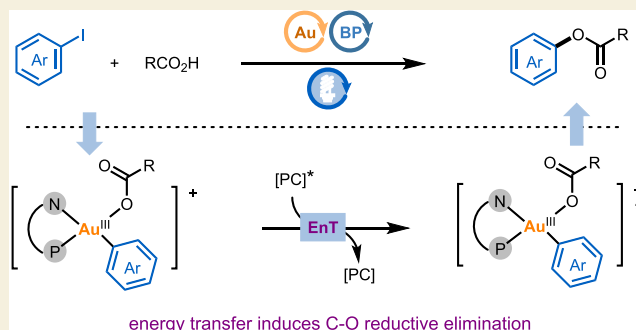
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**ABSTRACT:** Compared to the well-established transition metal-catalyzed cross-coupling reactions, Au(I)/Au(III)-catalyzed cross-coupling reactions have lagged behind. Despite some advancements, achieving gold-catalyzed C–O coupling with carboxylic acids via an Au(III) carboxylate intermediate remains challenging due to the thermal unfavorability of the critical reductive elimination step. Here, we present the first photosensitized reductive elimination of gold(III) to enable esterification of aryl iodides with carboxylic acids. In the presence of a (P, N)-gold(I) catalyst and a photosensitizer benzophenone under blue LED irradiation, esterification derivatives were obtained from aryl iodides with both aryl and alkyl (1°, 2°, 3°) carboxylic acids.

Mechanistic and modeling studies support that energy transfer (EnT) from a photosensitizer produces an excited-state gold(III) complex that couples aryl iodides with carboxylic acids. This photoinduced energy-transfer strategy has been applied in several other photosensitized gold catalysis reactions, indicating its potential for further applications.

**KEYWORDS:** Au(I)/Au(III) catalysis, photoinduced gold catalysis, energy transfer, reductive elimination, esterification



## INTRODUCTION

Since the turn of this century, homogeneous gold catalysis has emerged as a powerful synthetic platform, particularly those involving functionalization of carbon–carbon multiple bonds, driven by the carbophilic  $\pi$ -acidity of gold complexes.<sup>1–4</sup> However, compared with the well-established transition metal-catalyzed reactions, the utilization of gold as a catalyst in the context of redox chemistry has remained largely underdeveloped.<sup>5,6</sup> Owing to the higher redox potential of Au(I)/Au(III) couple than Pd(0)/Pd(II) (1.41 and 0.91 V, respectively),<sup>7</sup> strong external oxidants, such as PhI(OAc)<sub>2</sub> and Selectfluor, are usually required for gold-mediated redox processes beyond traditional hydrofunctionalization.<sup>8,9</sup> Recently, the integration of photoredox catalysis with gold catalysis under mild, irradiative conditions has opened a new avenue in the realm of gold redox chemistry.<sup>10–14</sup>

A significant advancement in this area was achieved by Glorius<sup>15,16</sup> and Toste,<sup>17,18</sup> who circumvented the need for stoichiometric oxidants by integrating gold catalysis with photoredox catalysis, thereby facilitating oxidation state transfers (Figure 1a). Following this approach of photoinduced electron transfer (PET), many dual photoredox gold catalytic systems utilizing reactive aryl diazonium salts have been developed.<sup>10,11,19–24</sup> The feasibility of excited-state organogold catalysis through photosensitization mechanisms provides another pathway to enhance the sluggish oxidative addition step in gold redox chemistry. In 2019, Fensterbank and co-

workers<sup>25,26</sup> have described an Au(I)- and Ir(III)-catalyzed alkynylative cyclization of *o*-alkynyl phenols with iodoalkynes, and the process of photosensitized energy transfer was proposed to promote the oxidative addition of a vinylgold(I) complex with iodoalkynes (Figure 1b). One thing worth noting is that this photoinduced gold catalysis mainly relied on reactive aryl diazonium salts and iodoalkynes; extending the scope of possible partners in photoinduced gold-catalyzed transformations is highly desirable.

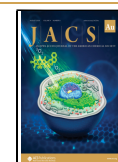
Recently, the ligand-promoted Au(I)/Au(III)-catalyzed cross-coupling reactions with less reactive partner aryl iodides, such as C–C, C–N, C–S/Se, and C–O (alcohols), have been developed by researchers such as Bourissou, Patil, Shi, and Xie (Figure 1c).<sup>27–35</sup> Due to the bidentate ligands, the oxidative addition step of Au(I) with Ar–I to the Au(III) complex could be accomplished very quickly under low temperatures, which has been recently supported by stoichiometric reactions and calculations.<sup>36,37</sup> Despite these advancements, the ability to form C–O bonds with carboxylic acids in a general manner through gold catalysis has been unsuccessful. In fact, this

Received: May 13, 2024

Revised: July 16, 2024

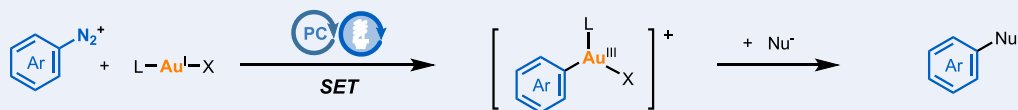
Accepted: July 16, 2024

Published: July 25, 2024

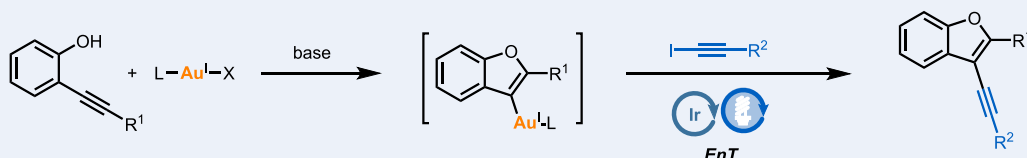


## Photoinduced oxidative addition of Au(I)

(a) Dual gold/photoredox catalysis with SET and aryl diazonium salts

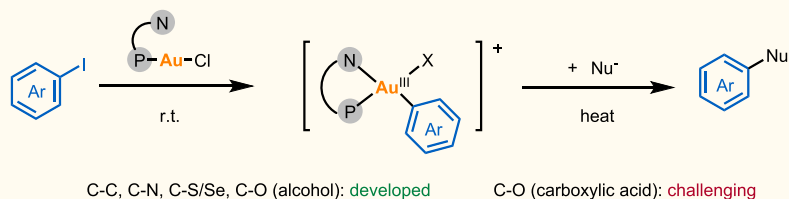


(b) Photosensitized oxidative addition with EnT and iodoalkynes

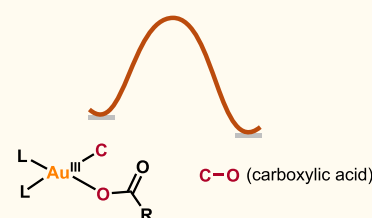


## Photosensitized reductive elimination of Au(III)

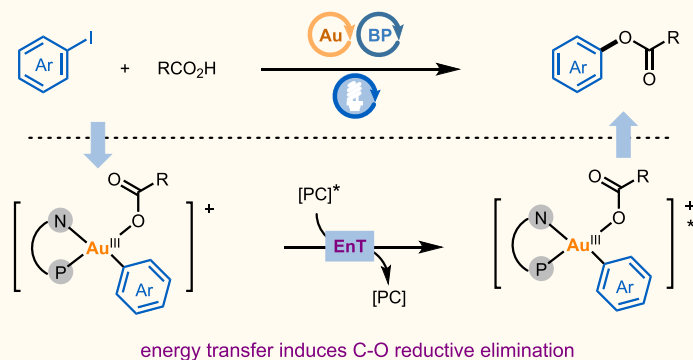
(c) Au(I)/Au(III) cross-coupling catalysis enabled by MeDalphos ligand



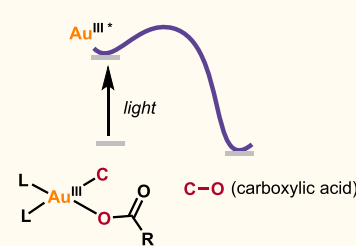
Energetic profile of reductive elimination

thermal reaction: **disfavoured**

(d) This work: Photosensitized reductive elimination with EnT and aryl iodides



Energetic profile of reductive elimination

photochemical reaction: **favoured**

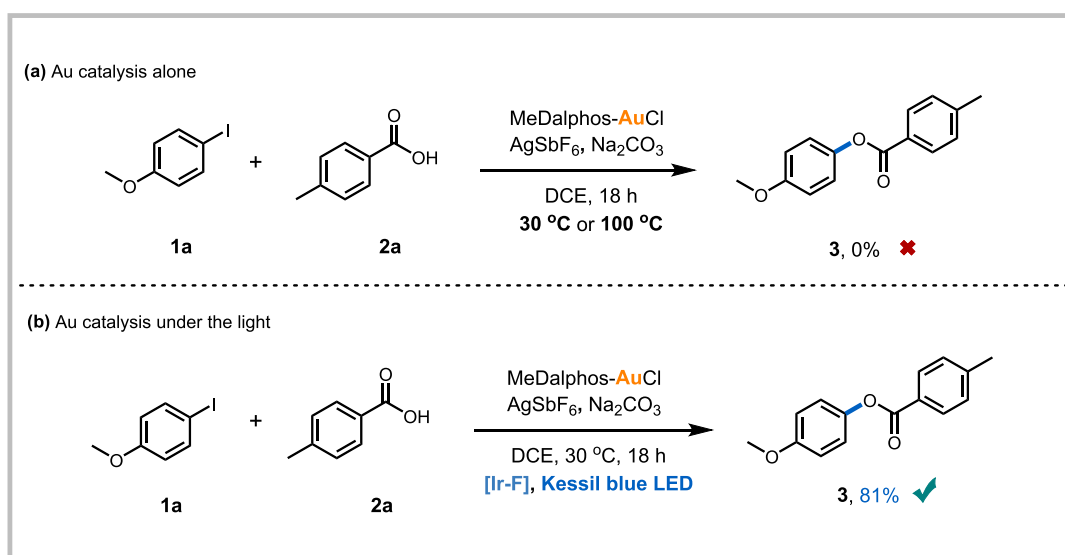
- photosensitized reductive elimination of gold(III)
- wide functional group tolerance (Br, Cl, F, alkene, NH, etc)
- benzophenone (BP) as a cheap and effective photosensitizer
- aryl and alkyl (1°, 2°, 3°) carboxylic acids
- applicable for several other systems
- mechanistic and DFT studies

Figure 1. Photoinduced Au(I)/Au(III) catalysis.

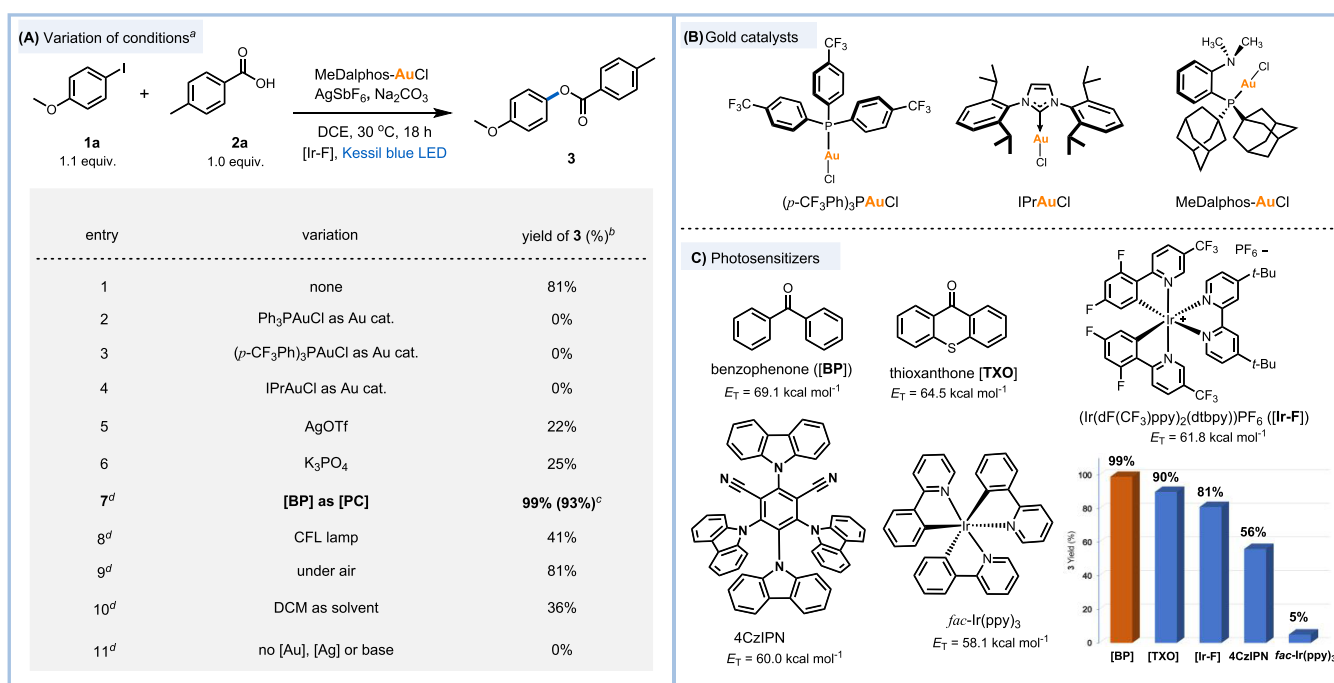
challenge arises from the mechanistic requirement for the critical reductive elimination step to proceed through an Au(III) carboxylate intermediate, which is thermally unfavorable (Figure 1c).<sup>38–40</sup> Reductive elimination serves as a crucial step in many transition metal-catalyzed transformations. It represents the stage where the product is released and frequently acts as the driving force behind the reaction. However, owing to the low basicity and nucleophilicity of carboxylates, the reductive elimination of RCOO–M–Ar (M

= transition metal) is slow and endergonic, particularly in the case of Au(III) carboxylate. For instance, in the gold-catalyzed cross-coupling reactions of aryl iodides with preactivated silver carboxylates, Xu<sup>41</sup> developed a C–O cross-coupling reaction that required heating conditions, while Topczewski<sup>42</sup> demonstrated an alternative pathway involving the decarboxylation of RCOO–Au species.

Following our continued interest in gold<sup>25,43–45</sup> and photochemistry,<sup>46</sup> we envisioned that photoactivation of an



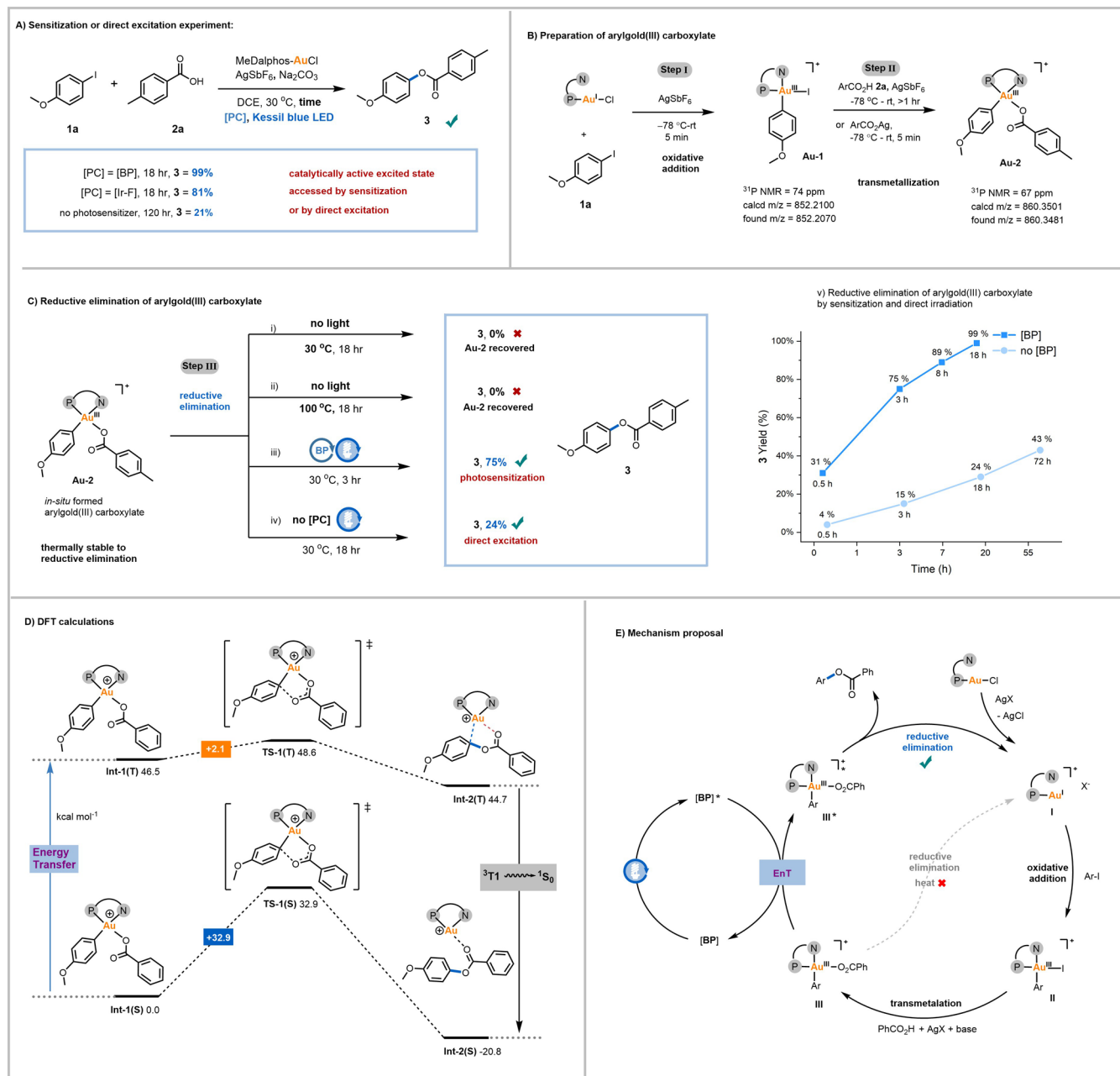
**Figure 2.** Gold-catalyzed C–O coupling of carboxylic acids can be activated by the introduction of a photocatalyst and visible light.



**Figure 3.** <sup>a</sup>Reaction conditions unless noted: 4-iodoanisole **1a** (1.1 equiv), *p*-toluic acid **2a** (0.2 mmol), MeDalphos-AuCl (5 mol %), AgSbF<sub>6</sub> (1.1 equiv), [Ir-F] (1 mol %), Na<sub>2</sub>CO<sub>3</sub> (1.0 equiv), DCE (0.1 M) under N<sub>2</sub> atmosphere, irradiation under Kessil blue LED for 18 h, 30 °C. <sup>b</sup>Yields are determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup>Isolated yield. <sup>d</sup>Benzophenone (20 mol %) as a photosensitizer.

organogold system can constitute a viable method to enhance the thermally unfavorable reductive elimination step in gold redox chemistry. In this study, we report the first photosensitized reductive elimination of the gold(III) complex to enable esterification of aryl iodides with carboxylic acids (Figure 1d). In the presence of a (P, N)-gold(I) catalyst and a photosensitizer benzophenone under blue light-emitting diode irradiation, various aryl and alkyl (1°, 2°, 3°) carboxylic acids were coupled with iodinated aromatics to synthesize *O*-aryl ester products with high yields at room temperature. This photoinduced gold catalysis exhibited very high selectivity toward aryl iodides and showed wide tolerance to functional groups such as Br, Cl, F, alkene, NH, etc. Due to the biocompatibility of gold catalysts and the mild condition of

photochemistry, this photo/gold-catalyzed protocol was utilized for the functionalization of bioactive molecules. Mechanistic and modeling studies support that energy transfer from a photosensitizer produces an excited-state gold(III) complex that couples aryl halides with carboxylic acids. This photoinduced energy-transfer, enabling the challenging reductive elimination in homogeneous gold catalysis, has been applied in several other dual catalytic processes at room temperature.



**Figure 4.** Mechanism studies. (A) sensitization or direct excitation experiment. (B) Preparation of arylgold(III) carboxylate according to Bourissou and Patil's method. (C) Reductive elimination of arylgold(III) carboxylate by heating, sensitization, and direct irradiation. (D) DFT computational studies: free energy profiles for the Au(III) redox catalysis at the M06-2x/def2tzvpp//B3LYP/6-31G\* (Au, SDD) (IEF-PCM, DCE) level of theory. (E) Mechanism proposal.

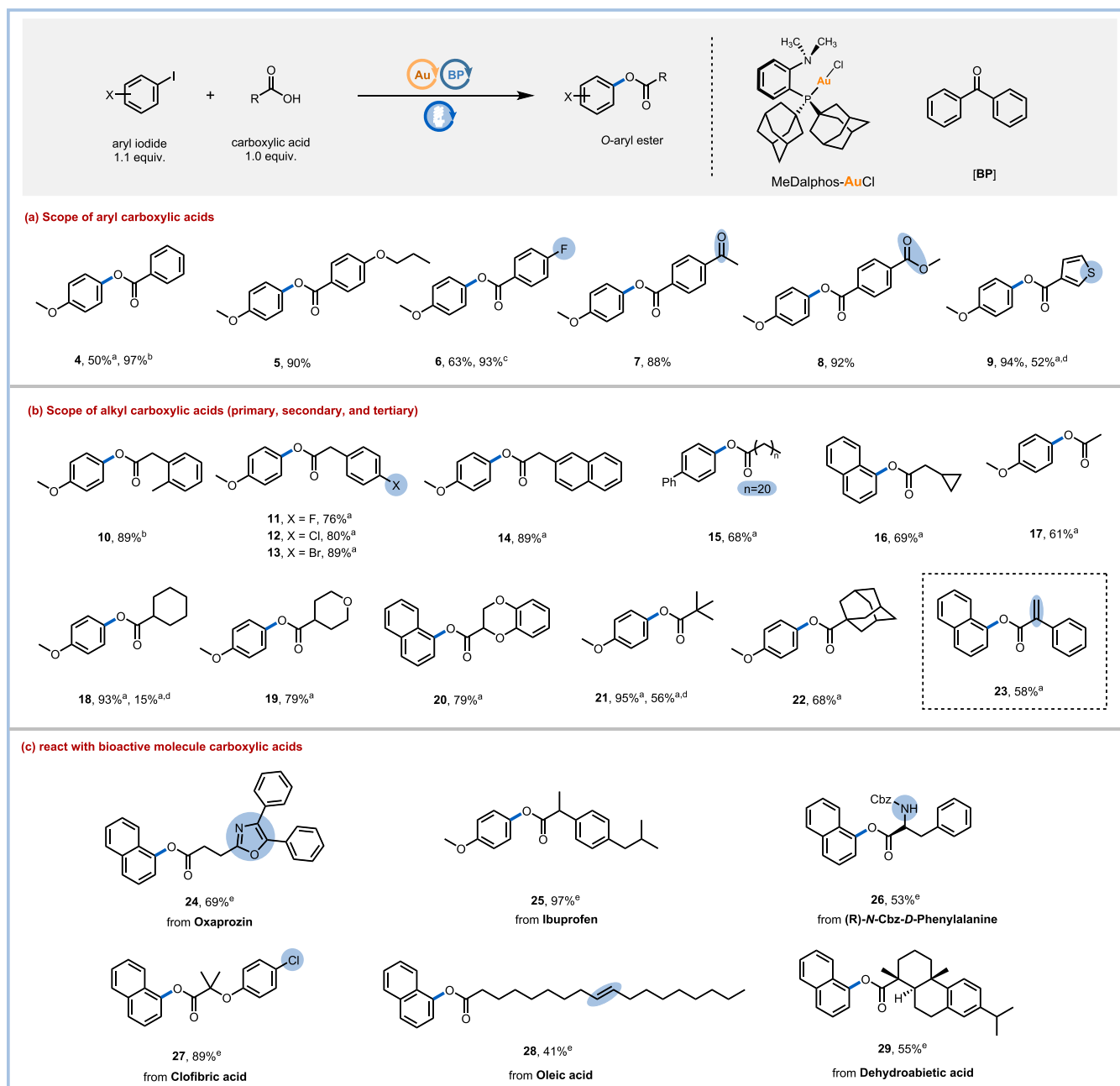
## RESULTS AND DISCUSSION

### Reaction Development

Recently, the utilization of hemilabile P,N-ligands in gold-catalyzed reactions has facilitated the previously challenging oxidative addition of aryl halides to proceed smoothly under mild conditions.<sup>27–35</sup> Inspired by Xu and Patil's result of Au(I)/Au(III)-catalyzed C–O cross-coupling of aryl iodides and aliphatic alcohols,<sup>47,48</sup> we began to try the possibility of C–O cross-coupling of carboxylic acids. However, it was found that this ligand-enabled gold catalysis strategy could not be extended to carboxylic acids; no target product was observed with the hemilabile (P, N) ligand MeDalphosAuCl even at 100 °C for 18 h (Figure 2a). By contrast, we found that the desired

C–O bond could be forged in 81% yield at room temperature via the introduction of the photocatalyst Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> ([Ir-F]) under blue light-emitting diodes (LEDs) irradiation conditions (Figure 2b). With this interesting result in hand, we next try to screen the gold-catalyzed C–O coupling with carboxylic acids under blue LEDs irradiation conditions.

Therefore, we initiated our investigation using 4-iodoanisole 1a and *p*-toluic acid 2a as model substrates to form *O*-aryl ester product 3 (Figure 3). It was found that other gold catalysts, such as Ph<sub>3</sub>PAuCl, (*p*-CF<sub>3</sub>Ph)<sub>3</sub>PAuCl (often used in dual photo/gold redox catalysis<sup>19,25,26</sup>) and IPrAuCl, did not get any product (entries 2–4). Changing the AgSbF<sub>6</sub> to other silver salts (like AgOTf) or the Na<sub>2</sub>CO<sub>3</sub> to other bases (like



**Figure 5.** Scope of carboxylic acids. Reaction conditions unless noted: carboxylic acid (0.2 mmol), aryl iodide (1.1 equiv), MeDalphos-AuCl (5 mol %), AgSbF<sub>6</sub> (1.1 equiv), benzophenone (BP, 20 mol %), Na<sub>2</sub>CO<sub>3</sub> (1.0 equiv), DCE (0.1 M), Kessil blue LED, 30 °C, 18 h. <sup>a</sup>Aryl iodide (1.3 equiv). <sup>b</sup>Benzophenone (0.5 equiv). <sup>c</sup>Reaction for 2 days. <sup>d</sup>[Ir-F] (1 mol %). <sup>e</sup>Aryl iodide (3.0 equiv).

K<sub>3</sub>PO<sub>4</sub>) would lead to lower yields (entries 5–6 and SI). Various types of photosensitizers, including *fac*-Ir(ppy)<sub>3</sub>, (Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbpy))PF<sub>6</sub> ([Ir-F]), and 2,4,5,6-tetra-(carbazol-9-yl)benzene-1,3-dicarbonitrile (4-CzIPN), were screened, revealing that almost all photosensitizers would generate the desired ester product, and the benzophenone ([BP]) would attain a nuclear magnetic yield of 99% (Figure 3A, entry 7, and Figure 3C). Moreover, the screening of these different photosensitizers revealed that the yield of the desired product was closely associated with the triplet-state energy of the photocatalyst, indicating that a photosensitized energy transfer rather than electron transfer might occur in this photoinduced gold-catalyzed esterification.<sup>25,26,49</sup> Next, with [BP] as the photosensitizer, we investigated the impact of

different light sources on the reaction. Compact fluorescent lamp (CFL) and shorter-wavelength light conditions (365, 395, and 405 nm) showed lower chemical reactivity (entry 8 and SI). In addition, an 81% yield of *O*-aryl esterification 3 was attained under ambient air conditions (entry 9). Different solvents were tested; DCM gave a lower yield (36%), while MeCN, CH<sub>3</sub>Cl, and THF almost inhibited the reaction (entry 10 and SI). In sharp contrast, no desired product could be obtained in the absence of the gold catalyst MeDalphosAuCl, silver salt, or base (entry 11). See Supplementary Section (SI) for detailed conditions optimization.

### Mechanistic Investigation

To gain a better insight into the reaction mechanism, a series of mechanistic studies and DFT calculations were conducted



(Figure 4). No target product was found at 100 °C (Figure 2a), which could demonstrate the challenging nature of gold-catalyzed C–O coupling with carboxylic acids and might explain why it has not been reported until now. Compared with photoinduced gold catalysis using photosensitizers [BP] or [Ir–F], a direct excitation experiment was also conducted. As shown in Figure 4A, the coupling of 4-iodoanisole **1a** and *p*-toluic acid **2a** using this photoinduced gold catalysis condition but without a photosensitizer generated the desired ester product **3** in 21% yield after 120 h under blue LED irradiation.

These results indicate that a photosensitization pathway rather than a photoinduced electron transfer (PET) process occurs in our system and are consistent with the formation of an excited-state Au complex that is essential for C–O bond formation.<sup>25,26,49</sup>

Subsequently, stoichiometric experiments were performed to further confirm the above results (Figure 4B,C). First, according to Bourissou and Patil's method,<sup>36,37</sup> the Au(III) complex **Au-1** could be formed at low temperatures very quickly from MeDaIPhosAuCl and 4-iodoanisole **1a**. In the second transmetalation step, conversion of the arylgold complex **Au-1** to the arylgold(III) carboxylate **Au-2** was observed by addition of *p*-toluic acid **2a** and AgSbF<sub>6</sub>, or corresponding ArCO<sub>2</sub>Ag (in less than 5 min) at low temperature. After *in situ* forming the arylgold(III) carboxylate **Au-2** complex, further control experiments were carried out to investigate the reductive elimination step. It was found that arylgold(III) carboxylate **Au-2** is very thermally stable, no target product was observed even at 100 °C for 18 h under conditions without light (Figure 4C(i),(ii)). In contrast, 75% of the esterified product **3** was obtained within 3 h in the presence of [BP] photosensitizer and light irradiation conditions, with almost full conversion observed after 18 h (Figure 4C(iii)). Therefore, the experimental conditions necessary to trigger the key C–O bond formation were successfully identified. Although ester formation could be achieved (24%) under direct irradiation conditions for 18 h without the photocatalyst [BP] (Figure 4C(iv)), which is consistent with the photosensitization pathway, ester formation seems to be greatly enhanced in the presence of the photocatalyst (Figure 4C(v)).<sup>25,49</sup> Very recently, a light-induced reductive elimination to forge aryl–F at aryl–Au(III) fluoride complexes was just reported by Bourissou.<sup>50</sup>

We then turned to luminescence studies to have further support for the photoactivity of photosensitizers [BP] under our reaction conditions. For UV–visible absorption, at the same concentration as the standard reaction conditions in Figure 3A, entry 7, the absorption band of [BP] did still tail off into the visible light region (see SI).

Finally, based on the experimental results mentioned above, DFT calculations were performed to compare the energies required for reductive elimination to occur in the ground state and excited state of **Int-1** (Figure 4D). The ground state **Int-1(S)** requires 46.5 kcal/mol of energy to form the **Int-1(T)** excited state (compared to the triplet-state excitation energy of 69.1 kcal/mol for benzophenone<sup>51</sup>). Transition state calculations showed that the energy required for reductive elimination in the triplet-state **TS-1(T)** is significantly lower than that in the ground state **TS-1(S)** (2.1 vs 32.9 kcal/mol).

The high energy required for reductive elimination in the ground state **TS-1(S)** (32.9 kcal/mol) further confirms that obtaining the target ester product experimentally solely through high-temperature heating is not feasible.<sup>25,52–54</sup>

Based on the experimental and computational results presented above, a detailed description of the proposed energy transfer–driven catalytic cycle is shown in Figure 4E. Initially, an oxidative reaction occurs between the aryl iodide and the gold catalyst to provide aryl–Au(III) species **II**. Subsequently, transmetalation of a carboxylate nucleophile generates the aryl–Au(III) carboxylate **III** complex. Meanwhile, [BP] acts as a photosensitizer, absorbing visible light to produce the excited state [BP]\*. At this stage, energy transfer can occur to produce electronically excited Au(III) species **III\***. Reductive elimination from excited-state Au(III) species **III\*** generates the *O*-aryl ester product, thus completing the oxidative–reductive catalytic cycle. Our mechanistic and computational studies suggest that the reductive elimination of the aryl–Au(III) carboxylate **III** complex is thermally unfavorable and not viable through heating alone.

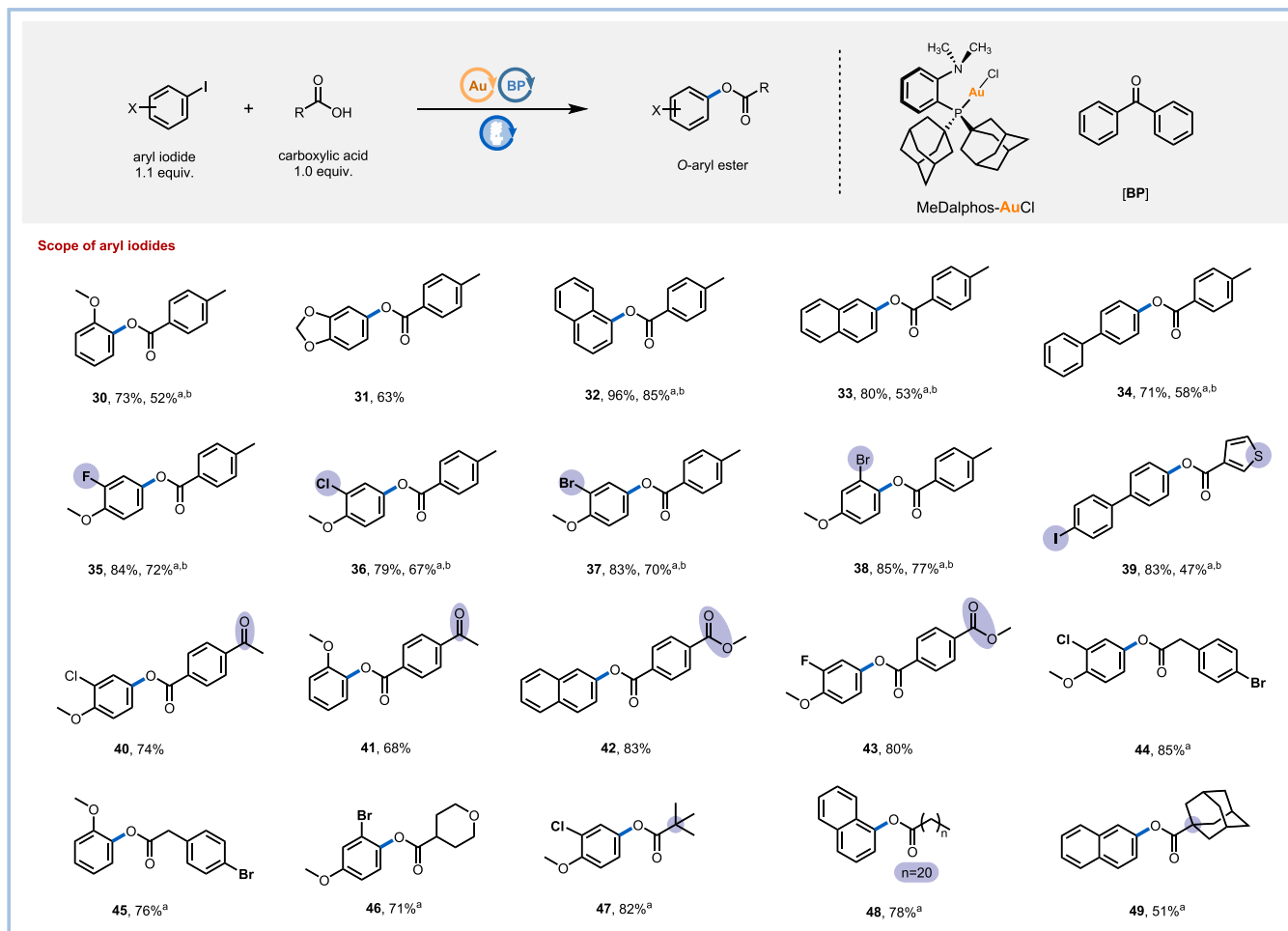
### Evaluation of Substrate Scope

To explore the substrate scope of this reaction, we initially examined a variety of aryl carboxylic acids with 4-iodoanisole **1a** under the optimal reaction conditions (Figure 3A, entry 7). As shown in Figure 5a, aryl carboxylic acids with electron-neutral and electron-rich groups reacted efficiently with 4-iodoanisole **1a** to form cross-coupling esterification products **4** and **5** in yields of 90 and 97%, respectively. Benzoic acid derivatives with electron-withdrawing substitutions, such as fluoro, ketone, or ester groups, did not hinder the reaction, resulting in the desired ester products in good to excellent yields (**6–8**). Notably, thiophene carboxylic acid, bearing heteroatoms, exhibited excellent reactivity, producing the target product in an impressive 94% yield (**9**). Furthermore, when employing the [Ir–F] photosensitizer, this photoinduced gold-catalyzed esterification could also proceed, albeit with a lower yield of **9**.

Our investigation revealed that the reaction consistently yielded good to high product yields for diverse alkyl carboxylic acids (Figure 5b). Primary alkyl carboxylic acids containing F, Cl, or Br groups exhibited exceptional conversions, with yields ranging from 76 to 89% (**10–14**). This photoinduced gold-catalyzed *O*-aryl esterification was efficient with chain alkyl carboxylic acids, such as docosanoic acid, affording a yield of 68% (**15**). Interestingly, the reaction proceeded smoothly with just 1.0 equiv of low-molecular-weight carboxylic acids, such as cyclopropylacetic acid or the simple and abundant acetic acid, yielding the desired products with 69 and 61% yields, respectively (**16** and **17**).

Exceptional conversions were achieved for secondary alkyl carboxylic acids, including carbocyclic and heterocyclic acids, with yields ranging from 79 to 93% (**18–20**). Tertiary carboxylic acids, such as pivalic acid and 1-adamantanecarboxylic acid, were also tested, and the reaction proceeded with similar efficiency regardless of the steric hindrance of the large groups (**21** and **22**). Notably, carboxylic acids containing olefin groups, such as 2-phenylacrylic acid, did not undergo olefin functionality alteration, and the target esterification product was obtained with a yield of 58% (**23**).

The scope and functional group tolerance of the reaction were further examined with more structurally complex substrates, including natural products and active pharmaceutical ingredients (Figure 5c). The anti-inflammatory compounds oxaprozin and ibuprofen were successfully converted to the corresponding esters (**24–25**) with yields of 69 and 97%, respectively. The esterification of an amino acid



**Figure 6.** Scope of aryl iodides. Reaction conditions unless noted: carboxylic acid (0.2 mmol), aryl iodide (1.1 equiv), MeDalphos-AuCl (5 mol %), AgSbF<sub>6</sub> (1.1 equiv), benzophenone (BP, 20 mol %), Na<sub>2</sub>CO<sub>3</sub> (1.0 equiv), DCE (0.1 M), Kessil blue LED, 30 °C, 18 h. <sup>a</sup>Aryl iodide (1.3 equiv). <sup>b</sup>[Ir-F] (1 mol %).

derivative established a direct route to the aromatic analogue of the medicinal *O*-aryl ester (**26**). Similarly, a halogen-containing derivative and precursor of the anticholesteremic drug (**27**) was readily produced, suggesting potential applications in drug discovery. Oleic acid was converted to the corresponding ester (**28**) without any alteration to the reactive olefin. Furthermore, *O*-aryl ester **29** was successfully derived from dehydroabiatic acid in good yield. We also tried some aryl iodides with strongly electron-withdrawing groups, such as fluoro, ester, and ketone groups, but none of the target products were found. See Supplementary Section (SI) for details.

Subsequently, the scope of aryl iodides was investigated (Figure 6). A series of electron-rich and electron-neutral aryl iodides were tested with *p*-toluic acid **2a**, affording moderate to excellent yields in most cases (**30–34**). This photoinduced gold-catalyzed esterification showed excellent chemoselectivity for the C(sp<sup>2</sup>)-I bond, as other halogen bonds, such as F, Cl, and Br, remained fully unaffected during the process (**35–38**), which are valuable functional groups for further elaboration. Interestingly, under the standard reaction condition, 4,4'-diiodobiphenyl can react with 1 equiv of thiophene carboxylic acid to afford a monosubstituted cross-coupling product **39** with an 83% yield. It should be noted that both [BP] and [Ir-F] photosensitizers were employed in many cases. It was

observed that both photosensitizers could work in most cases, but higher yields were obtained when using [BP] as the photosensitizer (**3, 9, 18, 21, 30, 32–39**).

The universality of the method was then demonstrated by cross-reacting with a variety of other aryl or alkyl (primary, secondary, and tertiary) carboxylic acids to yield the desired products (**40–47**), consistently achieving commendable yields ranging from 68 to 85%. Particularly noteworthy were the reactions involving chain alkyl docosanoic acid (**48**) and large 1-adamantanecarboxylic acid (**49**), which yielded the product with impressive yields of 78 and 51%, respectively. These systematic findings underscore the broad applicability and robustness of our reaction system.

### Other Working Systems

Finally, the sensitization protocol is not restricted to carboxylic acids. We selected several reported representative nucleophiles for this photo/gold-catalytical system instead of previous heating conditions (Figure 7). We successfully reproduced the same cross-coupling products under visible light irradiation conditions at room temperature. Initially, we attempted C–C coupling reactions with trimethoxybenzene, *N*-methylindole, and 1,1-diphenylethylene, obtaining yields consistent with previous reports (Figure 7a–c, **50–52**).<sup>36,43,55</sup> Next, a C–N coupling reaction with 4-nitroaniline was performed, resulting in the attainment of the target product **53** with a 94% isolated



**Figure 7.** Applicable for other systems.

yield (Figure 7d).<sup>56</sup> And benzenesulfonyl hydrazide was employed for the C–S coupling (Figure 7e, **54**, 59% vs 56%).<sup>57</sup> Finally, the photoinduced gold-catalyzed 1,2-aminoarylation of alkenes reaction was explored, yielding the cyclized product **55**<sup>58</sup> with an 85% yield (Figure 7f). Obviously, this photo/gold-catalytic protocol offers milder conditions, indicating its potential for further applications.

## CONCLUSIONS

In conclusion, we have achieved a new esterification reaction between aryl/alkyl carboxylic acids and aryl iodides using light-driven gold catalysis. Au(I)/Au(III)-catalyzed cross-coupling reactions have not progressed as far as well-established transition metal-catalyzed cross-coupling reactions. Despite certain progress, the challenge of achieving gold-catalyzed C–O coupling with carboxylic acids via an Au(III) carboxylate

intermediate persists due to the thermal unfavorability of the crucial reductive elimination step. Utilizing benzophenone as a cheap and effective photosensitizer and a (P, N)-ligand gold catalyst, this transformation was facilitated through photosensitized energy transfer to generate the triplet-state aryl-Au(III)-carboxylate intermediate. Subsequently, reductive elimination of the triplet-state aryl-Au(III)-carboxylate intermediate successfully led to the formation of *O*-aryl ester products. This esterification method is tolerant of a wide range of functional groups, and it delivers high yields with various aryl and alkyl (1°, 2°, 3°) carboxylic acids. The process of photoinduced energy transfer has been applied in several other photosensitized gold catalysis reactions.



## METHOD

### General Procedure for the Photoredox-Catalyzed Esterification of Aryl Iodides

(MeDalphos)AuCl (6.5 mg, 5 mol %), AgSbF<sub>6</sub> (silver hexafluoroantimonate, 75.6 mg, 1.1 equiv), benzophenone (7.4 mg, 20 mol %), sodium carbonate (21.2 mg, 1.0 equiv), aryl iodides (0.22 or 0.26 mmol, 1.1 or 1.3 equiv) and carboxylic acid (0.2 mmol, 1.0 equiv) were weighed into an oven-dried 8 mL vial and 1,2-dichloroethane (2 mL) was added. The vial was sealed with parafilm and placed in Kessil blue LED ( $\lambda_{\text{max}} = 465 \text{ nm}$ ). After 18 h, the reaction mixture was filtered through a 0.2 mm syringe filter with EtOAc, and the product was purified by flash column chromatography [SiO<sub>2</sub>, 1–20% gradient of EtOAc in PE (petroleum ether)].

### Experimental and Computational Investigation on the Mechanism

We describe in detail in the [Supporting Information](#).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.4c00422>.

Tables with details of optimization studies; details for the experimental mechanism studies; details for all the synthetic procedures; NMR characterization data ([PDF](#))

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (22201019 to Z.X.) and the Beijing Institute of Technology Research Fund Program for Young Scholars (grant number: 2020CX04260) is gratefully acknowledged.

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