# Gold-Catalyzed 1,2-Carboxyarylation of Alkenes

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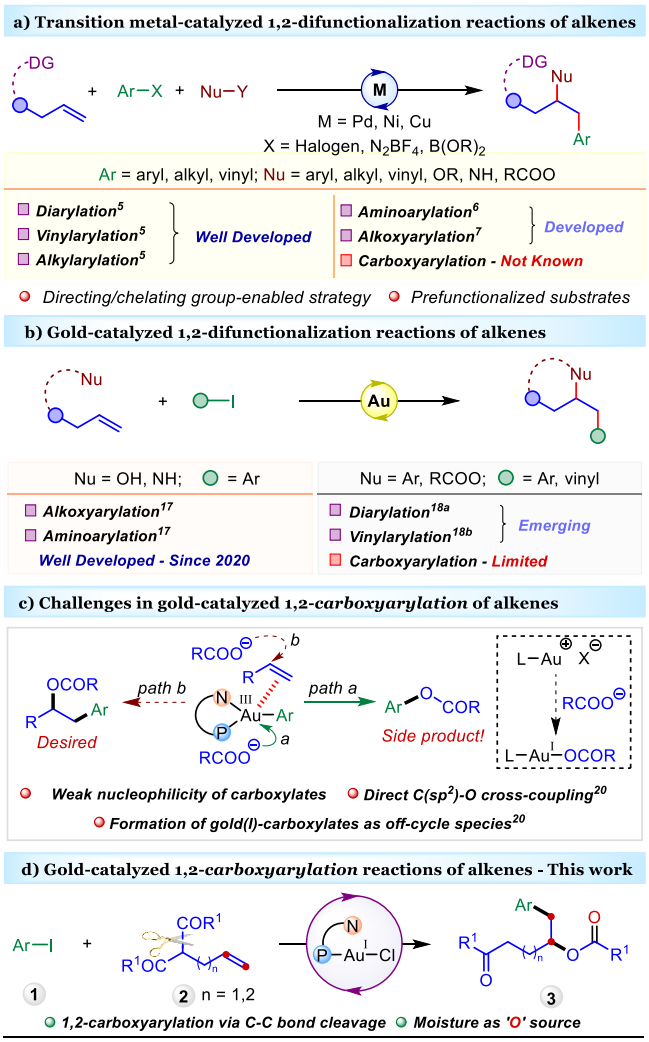
**Abstract:** Herein, we have disclosed the gold-catalyzed 1,2-carboxyarylation of alkenes through the ligand enabled Au(I)/Au(III) catalysis. Unlike other approaches for arylative functionalization of C-C multiple bonds that involve the use of strong nucleophiles, attempts to utilize weak nucleophiles like carboxylate anions were unsuccessful. The key to achieving this transformation is the use of 1,3-diketone appended alkene which undergoes gold-catalyzed oxyarylation followed by retro-Aldol reaction to afford the product. Mechanistic investigations, comprising numerous control experiments, NMR studies, and HR-MS analysis, were conducted to support the proposed mechanism.

Over the last two decades, there has been considerable interest in the transition-metal catalyzed 1,2-difunctionalization of alkenes, allowing the construction of complex molecular architectures.[1] The ability of late transition metals like Pd,[2] Cu,[3] and Ni[4] to undergo oxidative addition, migratory insertion and reductive elimination makes them useful for achieving 1,2-difunctionalization of alkenes (Scheme 1a). In this context, 1,2-carboarylation reactions[5] of alkenes such as diarylation, vinylarylation, and alkylarylation are well reported in the literature. Similarly, 1,2-heteroarylation of alkenes such as aminoarylation[6] and alkoxyarylation[7] has also been well developed. All these transformations either rely on prefunctionalized aryl partners or alkenes bearing a pendant directing group. To the best of our knowledge, by employing these strategies, there has been no report on 1,2-carboxyarylation of alkenes.

In the last few decades, homogeneous gold catalysis has become a valuable tool for the functionalization of carbon-carbon multiple bonds due to the remarkable π-Lewis acidity exhibited by gold complexes.[8] Based on the intrinsic π-activation property of gold complexes, either Au(I) or Au(III) species, a large number of novel transformations have appeared in the literature.[9] For a considerable period, the Au(I)/Au(III) redox catalysis posed a significant challenge because of the reluctance of gold to shuttle between Au(I) and Au(III) species.[10] This reluctance to shuttle between two oxidation states hampered the development of gold-redox catalysis. Over time, the field of Au(I)/Au(III) has developed which is primarily guided by the following reactivity principles: a) employing external oxidants,[11] b) utilizing $ArN_2X$ in combination with photocatalyst,[12] c) employing EBX reagents,[13] and d) utilizing electricity.[14] Since Bourissou and Amgoune's initial discovery that the (P,N)-ligand (MeDalPhos) can enable the oxidative addition of aryl iodides to gold(I),[15] there has been a significant surge of interest in the development of organic reactions under Au(I)/Au(III) catalysis.[16] Utilizing gold redox catalysis, various strategies based on the 1,2-difunctionalization of alkenes have been explored. For instance, alkoxyarylation,[16b,17] aminoarylation,[17] carboarylation,[18] such as diarylation and vinylarylation were well documented in the literature (Scheme 1b). Interestingly, the intermolecular




**Scheme 1.** Background and synopsis of current work.

1,2-carboxyarylation of alkenes are not reported,[19] not just within the realm of ligand-assisted Au(I)/Au(III) catalysis, but in gold redox catalysis in general.[10-16] This is probably due to (i) the weaker nucleophilicity of carboxylates, (ii) a competitive cross coupling pathway leading to C-O cross coupled product,[20] and (iii) carboxylates could directly attack the Au(I) center,[20] leading to the generation of Au(I)-carboxylate as the off-cycle species (Scheme 1c). Herein, we disclose the 1,2-carboxyarylation of alkenes by employing the ligand enabled Au(I)/Au(III) catalysis (Scheme 1d). The key to achieving this transformation is the use of 1,3-diketone appended alkene which undergoes gold-catalyzed oxyarylation/retro-Aldol cascade to yield the product.

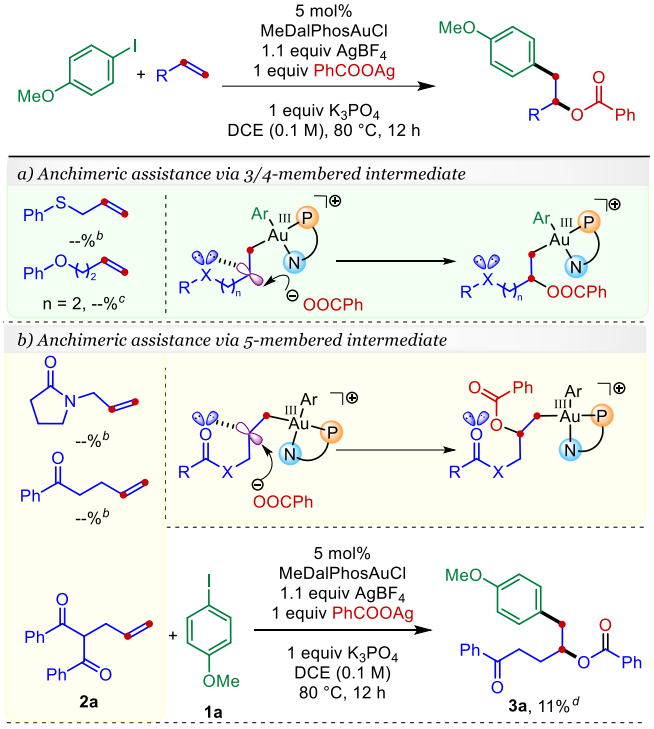
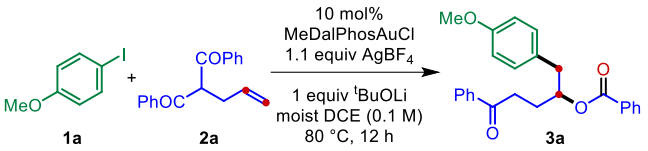



**Figure 1.** Screening of alkenes.[a]
[a] Reaction conditions: 0.1 mmol **1a**, 0.11 mmol **2**, 5 mol% MeDalPhosAuCl, 1.1 equiv $AgBF_4$, 1.0 equiv PhCOOAg, 1 equiv $K_3PO_4$, DCE (0.1 M), 80 ˚C, 12 h. [b] Starting material recovered. [c] Diarylation product observed. [d] Isolated yields.

Recently, we have reported the 1,2-heteroarylation of alkenes with aryl iodides under ligand-enabled Au(I)/Au(III) catalysis.[17b, 17d-e] However, our endeavors to employ various carboxylate equivalents as nucleophiles for the reaction of 1-octene were unsuccessful. With the hope that anchimeric assistance might play an important role, we investigated the reactivity of alkenes tethered with hetero atoms (Figure 1a). Unfortunately, the desired 1,2-carboxyarylation products were not obtained. Next, we attempted carbonyl-tethered alkenes anticipating that the oxygen of the carbonyl group would confer stability to the putative carbocation (Figure 1b). Interestingly, the 1,3-diketone appended alkene yielded the desired carboxyarylation product **3a** without the utilization of PhCOOAg as nucleophile source. Given the unprecedented reactivity and intriguing product structure, we opted to optimize the reaction further.

We started our investigation by reacting 4-iodoanisole **1a** (1 equiv) with 2-allyl-1,3-diphenylpropane-1,3-dione **2a** (1.1 equiv) in presence of MeDalPhosAuCl (10 mol%), $AgBF_4$ (1.1 equiv) and $^t$BuOLi (1 equiv) in moist DCE (0.1 M) at 80 °C (Table 2). To our delight, the desired product **3a** was obtained in 65% yield (entry 1). Next, screening of various solvents revealed that the use of DCM, toluene and acetonitrile had detrimental effect on the reaction outcome (entry 2). The further screening of bases (NaO$^t$Bu, KO$^t$Bu, and $K_3PO_4$) and silver salts ($AgSbF_6$, $AgNTf_2$, and AgOTf) did not lead to any improvement in yield (entries 3-4). Further, decreasing the catalyst loading lowered the yield of the product (entry 5). Similarly, increasing the equivalence of alkene was not successful in enhancing the yield (entry 6). Notably, upon increasing the equivalence of $AgBF_4$ to 2 equiv furnished the product in 97 % yield (entry 7). Finally, control experiments suggested that the role of MeDalPhosAuCl, $AgBF_4$ and $^t$BuOLi[21] is equally important to carry out the reaction (entries 8-10).




| Entry No. | *Deviations from standard conditions* | % Yield[b] **3a** |
|---|---|---|
| 1 | None | 65 |
| 2 | DCM/Toluene/MeCN | 53/15/nd |
| 3 | NaO$^t$Bu/KO$^t$Bu/$K_3PO_4$ | nd/nd/16 |
| 4 | $AgSbF_6$/$AgNTf_2$/AgOTf | 34/10/nd |
| 5 | 2.5 mol%/5 mol% MeDalPhosAuCl | 47/54 |
| 6 | 1.5 equiv/2 equiv **2a** | 35/26 |
| 7 | 1.5 equiv/**2 equiv $AgBF_4$** | 83/**97** |
| 8 | Without MeDalPhosAuCl | nd |
| 9 | Without $AgBF_4$ | nd |
| 10 | Without $^t$BuOLi | nd |

**Table 2.** Optimization of reaction conditions.[a]
[a] Reaction conditions: 0.1 mmol **1a**, 0.11 mmol **2a**, 10 mol% MeDalPhosAuCl, 1.1 equiv $AgBF_4$, 1 equiv $^t$BuOLi, moist DCE (DCE:$H_2O$ = 50:1) (0.1 M), 80 ˚C, 12 h. [b] Isolated yields. nd = Not detected.

Having optimized the reaction conditions, we examined the scope of aryl iodides **1** with alkene **2a** (Figure 2a). A variety of aryl iodides bearing electron donating substituents (-OMe, -OTs) and electron withdrawing substituents (-Ph, -Ms, -Ac, -$NO_2$, -CN, -NHAc, -$SO_2$Ph) present at the *para* position worked efficiently to

provide desired products **3a**-**3i** in good to excellent yields (67-95%). Next, halo-substituents including -F, -Cl, and -Br were well tolerated and afforded corresponding products **3j**-**3k, 3r** in 76-82% yields. Furthermore, various electron-donating and -withdrawing groups present at the *meta* as well as *ortho* position of the iodoarene were well tolerated delivering corresponding products **3l**–**3u** in good yields (65–85%).

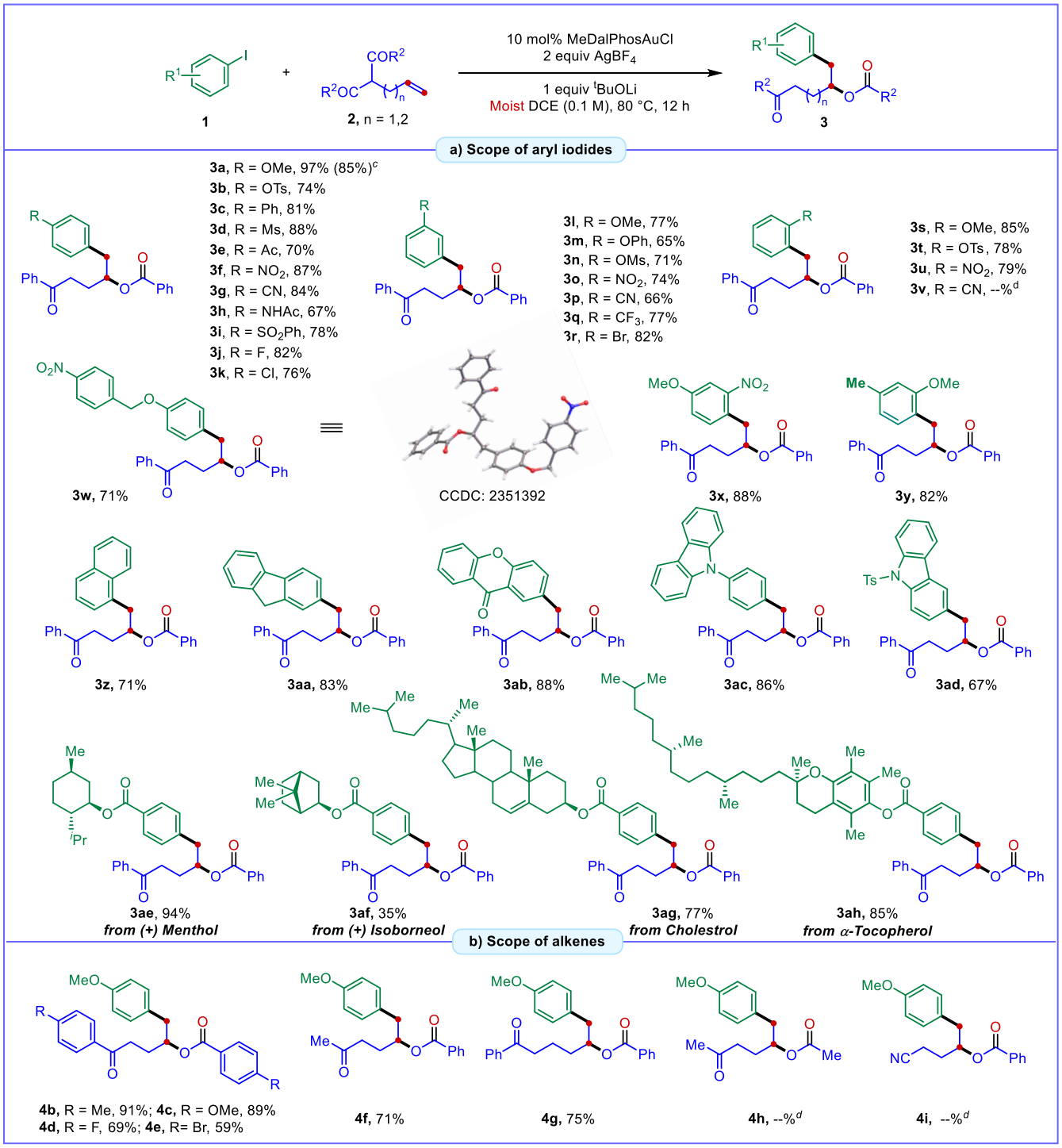



**Figure 2.** Substrate scope for 1,2-carboxyarylation of alkenes.[a],[b]
[a] Reaction conditions: 0.1 mmol **1**, 0.11 mmol **2**, 0.01 mmol MeDalPhosAuCl, 0.2 mmol $AgSbF_6$, 0.1 mmol $^t$BuOLi, moist DCE (DCE:$H_2O$ = 50:1) (0.1 M), 80 ˚C, 12 h. [b] Isolated yields. [c] Reaction performed at 1 mmol scale. [d] No reaction.

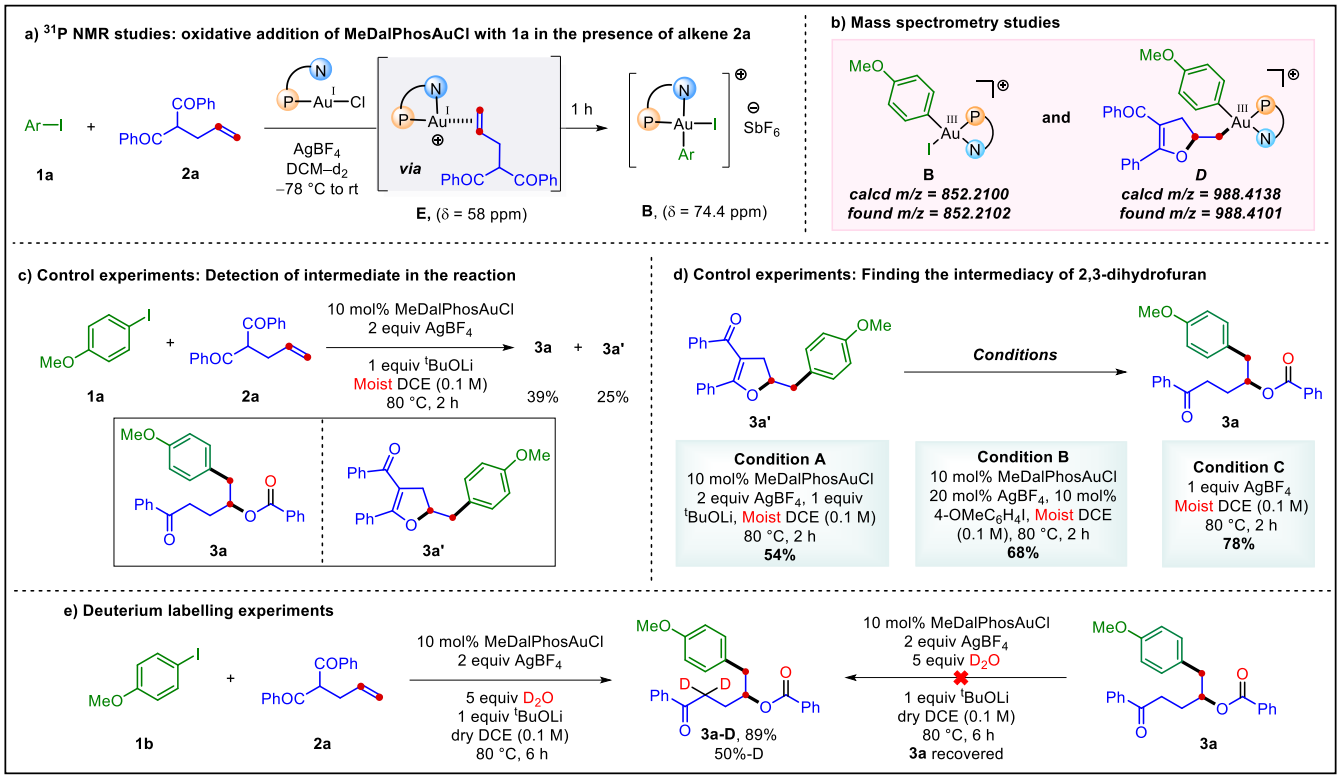



**Figure 3.** Mechanistic investigations.

However, 2-iodobenzonitrile **1v** failed to provide the desired product **3v**. Further, 4-nitrobenzyl alcohol substituted iodoarenes **2w** reacted smoothly, delivering the product **3w** in 71% yield. The structure of **3w** was confirmed by X-ray crystallography.[22] Additionally, disubstituted iodoarenes worked well to furnish the product **3x**-**3y** in good yields (82-88%). Various polyaromatic and heteroaromatic scaffolds such as -naphthyl, -fluorenyl, xanthone, and carbazole-based iodo arenes efficiently delivered corresponding products (**3z**-**3ad**) in good to excellent yields (67–88%). Delightfully, iodoarene-containing complex natural products such as (+)-menthol (**1ae**), (+)-isoborneol (**1af**), cholesterol (**1ag**), and tocopherol (**1ah**) provided the corresponding products (**3ae**-**3ah**) in moderate to excellent yields (35–94%).

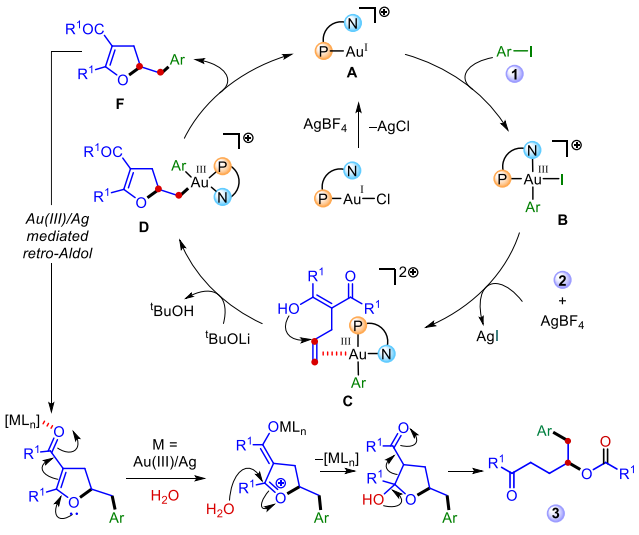
Next, we focused to investigate the scope of alkenes by employing **1a** as the model substrate (Figure 2b). At first, varying substituents (*p*-Me, *p*-OMe, *p*-F, and *p*-Br) in the aryl ring of the alkene **2** reacted smoothly, delivering the products **4b**-**4e** in 59-91% yields. Interestingly, unsymmetrical alkene **2f** was also well tolerated to furnish the product **4f** in 71% yield. Further, the alkene with longer chain length was also suitable to generate the product **4g** (75% yield). However, dimethyl malonate tethered alkene **2h** and unsymmetrical alkene **2i** failed to afford the desired product **4h** and **4i** under the optimized reaction conditions.

To gain insights about the reaction mechanism, a series of mechanistic studies were performed (Figure 3). It was well established in the literature[18,23] that alkenes retard the rate of oxidative addition of cationic gold(I) species by forming Au(I)-π complex as the catalyst resting state. In order to test this, a stoichiometric experiment was performed by using equimolar amounts of MeDalPhosAuCl, **1a** and **2a** in the presence of $AgBF_4$. Monitoring the reaction with $^{31}P$ NMR confirmed the instantaneous formation of a putative Au(I)-π complex **E** (58 ppm). However, the complete conversion of **E** to Au(III) complex **B** (74.4 ppm) was observed only after 1 h (Figure 3a).[24] Furthermore, we have successfully detected the key intermediates with the help of mass studies (Figure 3b).

When the standard reaction was analyzed within 2 h, both product **3a** and the 1,2-oxyarylation product **3a′** were observed (Figure 3c). Subsequently, product **3a′** was subjected to condition A (Figure 3d), leading to 54% yield of product **3a**. Further investigation revealed that **3a′** was converted to product **3a** in the presence of *in situ* generated gold (III) complex (condition B). Additionally, product **3a′** was subjected to a stoichiometric amount of $AgBF_4$, resulting in a 78% yield of product **3a** within 2 hours (condition C). This outcome suggests that either the *in situ* generated Au(III) species or $AgBF_4$ might serve as a Lewis acid that weakly chelates to the enone carbonyl and polarizes the C=C bond.

Next, a standard reaction was performed in the presence of $D_2O$ (5 equiv), which delivered the product **3a-D** with 50% deuterium incorporation (Figure 3e). This observation suggested that the C-C bond cleavage from the oxyarylation product **3a'** is occurring *via* retro-Aldol collapse. Furthermore, upon subjecting **3a** under similar conditions, no deuterium incorporation was observed at the α-position of carbonyl carbon of **3a**, thereby ruling out the possibility of conversion of **3a** to **3a-D**.

Based on the experimental evidence and literature reports,[17, 18] the catalytic cycle for gold-catalyzed 1,2- carboxyarylation of alkenes is given in Scheme 2. First, the cationic gold(I) complex **A** would be generated after the halide abstraction by $AgBF_4$. Then, cationic gold(I) species would undergo oxidative addition with aryl iodides **1**, to genetrate aryl-Au(III) species **B**. The subsequent iodide abstraction, and π-activation of alkene triggers the intramolecular nucleophilic attack to afford the Au(III) intermediate **D**. Next, reductive elimination would furnish oxyarylation product **F** (*cf.* **3a**′) with the regeneration of the active gold(I) catalyst. Finally, the enol ether product **F**, would undergo retro-Aldol collapse[25] in the presence of Lewis acid (Au(III) or $AgBF_4$) and water to afford the 1,2-carboxyarylayion product **3**.




**Scheme 2.** Plausible catalytic cycle.

In conclusion, we have reported an unprecedented gold-catalyzed 1,2-carboxyarylation of alkenes to synthesize γ-acetoxy-δ-aryl carbonyl compounds *via* oxyarylation-retro aldol reaction cascade. Mechanistically, the reaction proceeds by merging the concept of ligand-enabled cross-coupling reactivity with intrinsic π-activation chemistry of gold complexes. Our studies indicated that achieving the 1,2-carboxyarylation of a simple aliphatic alkene is not feasible unless it is appropriately tethered with 1,3-diketones. Mechanistic studies revealed that the 1,2-carboxyarylation of alkenes occurs through intramolecular formal benzoyl group transfer facilitated by Au(III) complexes or, to some extent, by $AgBF_4$ in the presence of water.

## Notes

The authors declare no competing financial interest.

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## Authors Contribution

†T.N. and A.D. contributed equally.

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21 As there is a possibility of generation of LiOH, from tBuOLi and water, in the reaction medium, we conducted the reaction in the presence of LiOH. However, the product 3a was obtained in slightly lower yield (80%) compared to standard reaction conditions.

22 Deposition numbers 2351392 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

23 (a) Navarro, M.; Toledo, A.; Joost, M.; Amgoune, A.; Mallet Ladeira, S.; Bourissou, D. Chem. Commun. 2019, 55, 7974. (b) Navarro, M.; Toledo, A.; Mallet-Ladeira, S.; Sosa-Carrizo, E. D.; Miqueu, K.; Bourissou, D. Chem. Sci. 2020, 11, 2750.

24 For more details, see the ESI.

25 Cai, S.; Liu, Z.; Zhang, W.; Zhao, X.; Wang, D. Z. Angew. Chem. Int. Ed. 2011, 50, 11133.