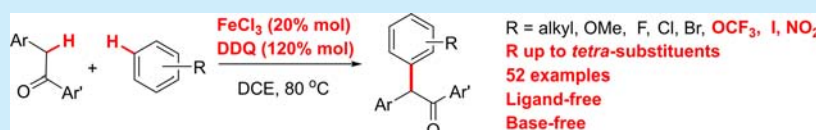


Iron-Catalyzed α -Arylation of Deoxybenzoins with Arenes through an Oxidative Dehydrogenative Approach

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Supporting Information

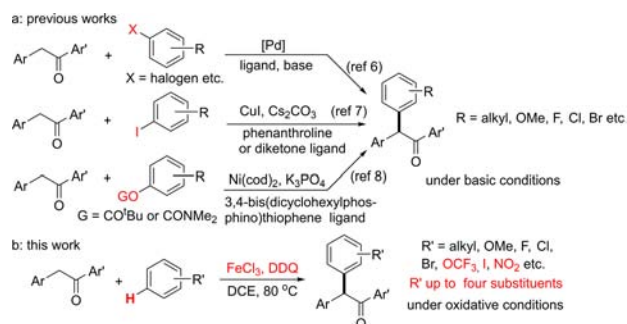


ABSTRACT: A novel α -arylation of deoxybenzoins with non-prefunctionalized arenes is developed through an iron-catalyzed oxidative dehydrogenative approach. The reaction shows broad substrate scope and functional group tolerance and thus provides efficient access to synthetically useful 1,2,2-triarylethanones. A reasonable mechanism is also proposed.

α -Arylation of ketones has been a central topic in organic synthetic chemistry because the resulting products exist widely in numerous bioactive natural products, clinical drugs, and functional molecules.^{1,2} Inspired by the seminal works of Miura,^{3a} Buchwald,^{3b} and Hartwig,^{3c} transition-metal-catalyzed α -arylation of carbonyl compounds were intensively investigated because this process features a few advantages, such as the use of simple aryl halides or pseudohalides instead of organometallic reagents as aryl sources, good chemo- and regioselectivity, various possible catalytic systems, and ideal reaction yields. Therefore, many efforts have been made to expand this pioneering work for α -arylation of deoxybenzoins to synthesize valuable 1,2,2-triarylethanones,^{4,5} including the Pd-catalyzed transformation by Miura, Hartwig and others,⁶ a Cu-catalyzed approach by Taillefer,⁷ and a Ni-catalyzed approach by Itami (Scheme 1a).⁸ These coupling reactions generally rely on the formation of the corresponding enolate intermediates from ketones under basic conditions, which act as ideal nucleophiles for the electrophilic species generated through oxidative addition of transition metals to aryl halides or pseudohalides. However, some shortcomings still existed, such as employment of high cost

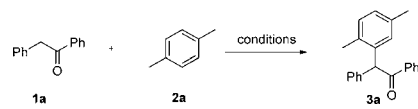
ligands, general performance under basic conditions, as well as poor compatibility of halogenated substrates. Moreover, prefunctionalization to prepare the coupling precursor containing the C–heteroatom bond is always required, which dramatically limited their wide practicability. In this respect, the more direct transition-metal-catalyzed arylation of deoxybenzoins with arenes through cleavage of a C–H bond on the aryl ring is particularly attractive but remains unexplored. Herein, we report a FeCl₃-catalyzed α -arylation of deoxybenzoins with arenes through an oxidative dehydrogenative strategy^{9–11} (Scheme 1b).

We started to test the oxidative dehydrogenative reaction by using deoxybenzoin **1a** and *p*-xylene **2a** as model substrates (Table 1). However, such an oxidative transformation would require solutions to several problems: (1) the benzylic C–H bond of deoxybenzoin can be easily oxidized to form benzil derivatives¹² or cleaved into other species¹³ under oxidative conditions; (2) intermolecular self-coupling of deoxybenzoin produces unexpected 1,4-dicarbonyl byproducts;¹⁴ (3) undesired bis-arylation may compete with monoarylation;^{9c} (4) the benzylic C–H bond of *p*-xylene is easily oxidized to different reaction intermediates, which could further participate in undesired transformations;¹⁵ (5) in particular, oxidative dehydrogenative arylations involving the C(sp³)–H bonds that are not adjacent to a nitrogen or an oxygen atom have not been well explored.^{9,16} The desired product **3a** was obtained when the reaction was conducted in the presence of FeCl₃ under an O₂ atmosphere at 80 °C, even though the yield was only 9% (entry 1). Screening of oxidants showed 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to be the best choice, giving the product in 77% yield (entries 2–5). The temperature is also crucial for the reaction, which affects the yields of **3a** dramatically: lower temperature leads to low conversion, while higher temperature

Scheme 1. Transition-Metal Catalyzed α -Arylation of Deoxybenzoins

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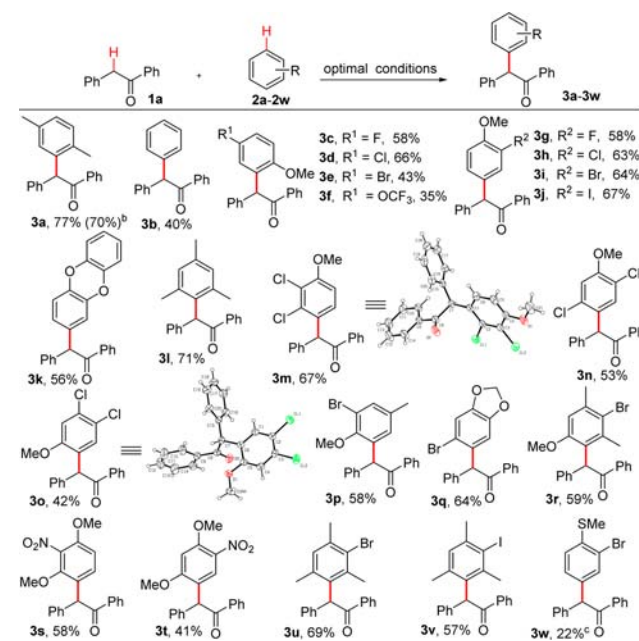
Table 1. Optimization of the Reaction Conditions^a


entry	cat. (%)	solvent	oxid. (equiv)	temp (°C)	yield ^b (%)
1	FeCl ₃ (20)	DCE	O ₂	80	9
2	FeCl ₃ (20)	DCE	K ₂ S ₂ O ₈ (1.2)	80	15
3	FeCl ₃ (20)	DCE	BQ ^c (1.2)	80	8
4	FeCl ₃ (20)	DCE	DTBP ^d (1.2)	80	11
5	FeCl ₃ (20)	DCE	DDQ ^e (1.2)	80	77
6	FeCl ₃ (20)	DCE	DDQ (1.2)	70	70
7	FeCl ₃ (20)	DCE	DDQ (1.2)	60	41
8	FeCl ₃ (20)	DCE	DDQ (1.2)	50	29
9	FeCl ₃ (20)	DCE	DDQ (1.2)	90	49
15		DCE	DDQ (1.2)	80	0
16	FeCl ₃ (20)	DCE		80	10
17	FeCl ₃ (10)	DCE	DDQ (1.2)	80	64
18	FeCl ₃ (5)	DCE	DDQ (1.2)	80	5
19	AlCl ₃ (20)	DCE	DDQ (1.2)	80	18
22 ^f	FeCl ₃ (20)	DCE	DDQ (1.2)	80	99
23 ^g	FeCl ₃ (20)	DCE	DDQ (1.2)	80	73

^aReaction was performed using deoxybenzoin (0.2 mmol) and *p*-xylene (0.6 mmol) in 1.0 mL of solvent at 80 °C under argon. ^bIsolated yield. ^cBQ = *p*-benzoquinone. ^dDTBP = di-*tert*-butyl peroxide. ^eDDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. ^f20 equiv of *p*-xylene was applied. ^g99.99% FeCl₃ was used.

results in the decomposition of deoxybenzoin **1a** (entries 6–9). Screening of solvents indicated no superior results was obtained.¹⁷ Reducing DDQ equivalents slightly decreased the product yield.¹⁷ In the absence of FeCl₃ or DDQ, no or a small amount of the product **3a** was isolated, indicating the indispensability of both the iron catalyst and the oxidant (entries 10 and 11). FeCl₃ loading dramatically affected the yields (entries 12 and 13). Other iron salts did not give better results.¹⁷ Screening metals other than iron demonstrated that they failed to promote the current reaction,¹⁷ except AlCl₃, which gave 18% yield of product **3a** (entry 14). Superior to 5 or 10 equiv, the use of 20 equiv of *p*-xylene led to 99% yield (entry 15). To make the reaction as cost-effective as possible, we selected 3 equiv of *p*-xylene as the optimal conditions in the subsequent experiments. To ascertain the current reaction through the iron catalysis,¹⁷ an ultrapure 99.99% FeCl₃ was used, resulting in the formation of **3a** in 73% yield (entry 16).

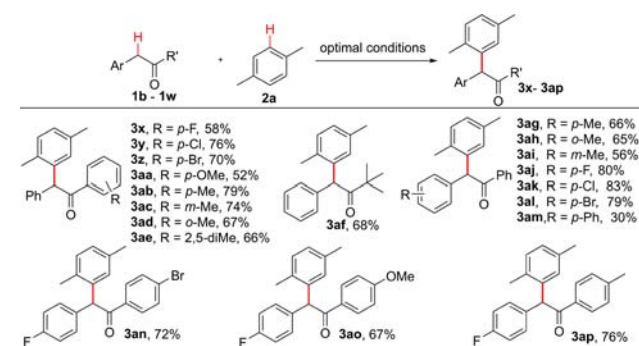
Under the optimized conditions (entry 5, Table 1), various arenes gave the expected products in moderate to good yields (Scheme 2). 1,2,2-Triphenylethanone **3b**^{5b} was obtained in 40% yield from benzene. The reaction performed very well with anisoles containing F, Cl, Br, I, or OCF₃ substituents, providing the corresponding products (**3c–j**) in satisfactory yields. Dibenzo-*p*-dioxine also afforded the product **3k** in 56% yield. To examine the flexibility of the reaction toward aryl substrates, we subjected tri- or tetra-substituted aromatic substrates to the current reactions, and the desired products (**3l–3v**) were obtained in good yields. The structures of **3m** and **3o** were further confirmed by X-ray crystallography, respectively.¹⁸ The reactions worked well even with the sterically hindered arenes, producing products **3l**, **3r**, **3u**, and **3v** in moderate to good yields. Moreover, the arylations proceeded smoothly even for relatively electron-deficient anisoles bearing a NO₂ substituent and afforded the corresponding products (**3s**, **3t**) in acceptable yields. Notably, the current approach does not appear to require

Scheme 2. Scope of Arenes^a

^aReaction conditions: 20 mol % of FeCl₃, 120 mol % of DDQ, deoxybenzoin (0.2 mmol), and arenes (0.6 mmol) in 1.0 mL of DCE at 80 °C under argon. Isolated yield of product. ^bPerformed on a 10 mmol scale, and 1.386 g product **3a** was isolated. ^c50 mol % of FeCl₃ was applied.

oxygen-based substituents on the arylated partner because mono-, tri-, tetra-, and pentasubstituted aromatic products (**3b**, **3a**, **3l**, **3u**, and **3v**) were obtained. Our reaction also proceeded with a MeS-substituted substrate, although the product **3w** was obtained in slightly lower yield and 50% FeCl₃ was required.

As shown in Scheme 3, a variety of deoxybenzoins were also tested under the optimal reaction conditions. For the benzoyl

Scheme 3. Scope of Deoxybenzoins^a

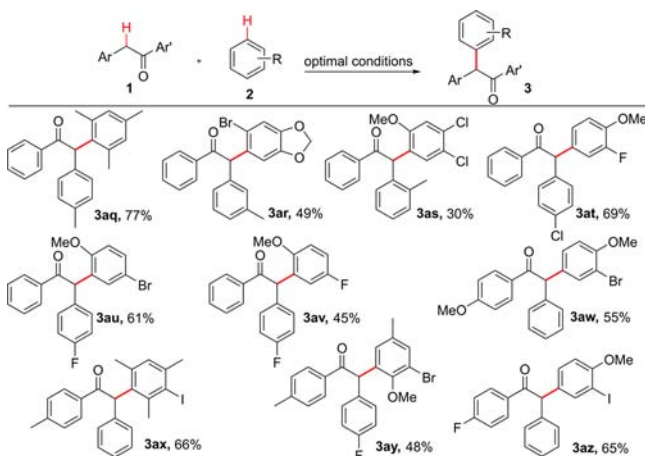
^aPerformed under the optimal conditions. Isolated yield of product **3**.

moiety in deoxybenzoin, arenes containing various substituents, such as a strong electron-donating group (OMe), weak electron-withdrawing groups (F, Cl, Br) at the *para*-position, and a methyl group at the *ortho*-, *meta*-, or *para*-position, were well tolerated and gave the expected products (**3x–ad**) in 52–79% yields. Furthermore, replacing the monosubstituted phenyl moiety with disubstituted *p*-xylene or a *tert*-butyl group did not affect the reaction, affording the ketones **3ae** and **3af** in yields of 66% and 68%, respectively. For the benzyl moiety in deoxybenzoin, various substituents on the aromatic ring were also tolerated. For

example, either a Me group at various positions or F, Cl, Br, or Ph at the *para*-position provided the corresponding products (**3ag–am**). Notably, the expected products (**3an–ap**) with different substituents on the two aryl rings were also obtained.

Finally, we investigated the α -arylation of deoxybenzoin derivatives with various arenes (Scheme 4). Di-, tri-, and

Scheme 4. Scope between Deoxybenzoin and Arenes^a



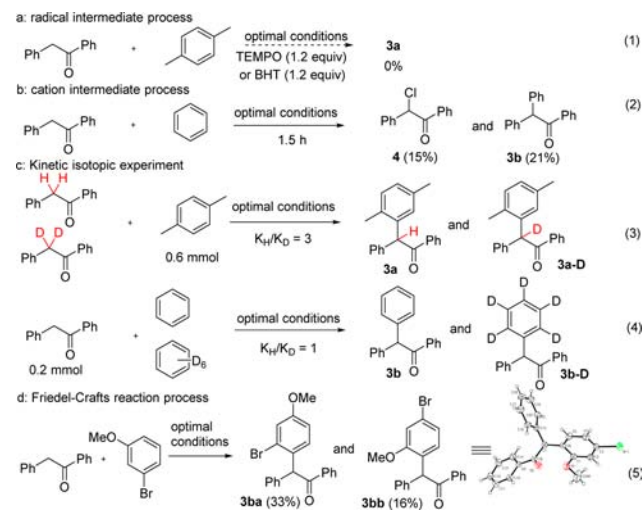
^aPerformed under the optimal conditions. Isolated yield of product **3**.

tetrasubstituted arene derivatives reacted smoothly with a number of deoxybenzoin bearing different substituents on the aryl ring, affording 1,2,2-triarylethanone derivatives (**3aq–az**) with three different substituted aryl rings in good yield, which is difficult to synthesize by known methods.^{6–8} It is noteworthy that synthetically valuable groups, such as F, Cl, Br, I, and OMe, were tolerated in many cases.

Clearly, the results above suggest that this novel α -arylation approach is rapid and efficient and tolerates a broad range of both arenes and deoxybenzoin. The fact that our approach preserves the halo atoms (F, Cl, Br, and I) on the aryl ring means that the resulting products can be readily coupled with other reaction partners through C–C or C–X bond formation reactions, which allows the construction of more complex and diverse functional molecules. Furthermore, the nitro group on the aryl ring can be converted to NH₂ or other synthetically useful groups. Therefore, the current approach could be a useful and alternative procedure for preparing 1,2,2-triarylethanone derivatives⁵ bearing various halo atoms (even iodine atom) and a NO₂ group on the aryl ring. Notably, the product **3a** was isolated in 70% yield on gram scale (Scheme 2).

To elucidate the reaction mechanism, we performed some preliminary experiments (Scheme 5). First, in the presence of radical-trapping agents, such as 2,2,6,6-tetramethylpiperdin-1-yl)oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT), no product **3a** can be obtained, suggesting that a radical process can be involved in the arylation reaction (eq 1). Second, α -chlorodeoxybenzoin **4** was also detected and isolated as a side product in 15% yield in the process of the synthesis of **3b** (eq 2), which was actually also generated in some other cases. The formation of **4** indicates that a carbocation intermediate may be generated, which subsequently was trapped by a chloride ion. Third, an intermolecular kinetic isotope experiment using a mixture of **1a** and deuterated **1a-D** (in 1:1 ratio) gave the corresponding products **3a** and **3a-D** in a 3:1 ratio, indicating a K_H/K_D of approximately 3 (eq 3). This result indicates that C–H

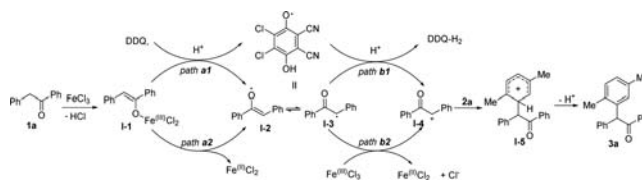
Scheme 5. Some Control Experiments



bond cleavage at the benzylic position in **1a** is a rate-determining step. Additionally, arylation products **3b** and **3b-D** were obtained in a ratio of 1:1 when a mixture of benzene-*d*₆ and benzene (in 1:1 ratio) was employed under the optimal conditions (eq 4), excluding the possibility of C–C bond formation as the rate-determining step. Finally, regioisomeric products **3ba** and **3bb** were formed by using *m*-bromoanisole as the arylation partner, and the structure of **3bb** was further confirmed by X-ray crystallography¹⁸ (eq 5); replacing FeCl₃ with AlCl₃ led to product **3a** in 18% yield (entry 14, Table 1). Combination of these results and the remarkable substituent effect in the aryl ring (Scheme 2) suggest that our transformation involves a Friedel–Crafts-type process.

A reasonable mechanism was proposed on the basis of the experimental results above (Scheme 6).^{11,19} As suggested by the

Scheme 6. Proposed Reaction Mechanism



kinetic isotope experiments, the substrate (**1a**) is initially enolized in a process in which FeCl₃ acts as a Lewis acid.^{19c} Single-electron oxidation of the enolized intermediate **I-1** with DDQ^{19e} generates the radical **I-2**,^{13a} along with the activated oxidative species **II** (path a1), in which FeCl₃ only serves as a Lewis acid, assisting this oxidation.^{19c} The resulting radical **I-2** is further oxidized by the species **II** and provided the corresponding cation **I-4** (path b1),^{13c} which subsequently undergoes Friedel–Crafts alkylation with the aromatic compound (**2a**) to afford the arylated product **3a**. Considering the fact that product **3a** can be also isolated in the absence of DDQ (entry 16, Table 1), an alternative approach to the carbocation **I-4** is also possible: the enolized intermediate **I-1** carries out a single electron transformation^{19b} to form the radical **I-2** (path a2), which could be further oxidized by Fe³⁺ and generates the cation **I-4** (path b2). The catalytic cycle of Fe³⁺ is achieved by oxidation of Fe²⁺ with DDQ.

In summary, we have developed the first iron-catalyzed arylation of deoxybenzoins through an oxidative dehydrogenative approach. This transformation features broad substrate scope, uses inexpensive and environmentally friendly iron chloride as a catalyst under mild reaction conditions, and generates the synthetically and pharmaceutically valuable 1,2,2-triarylethanones in moderate to good yields. Compared with previously reported transformations catalyzed by Pd, Cu, or Ni, this reaction did not require any extra ligand and was conducted under the oxidative conditions. We have proposed a reaction mechanism based on preliminary studies. We are currently attempting to apply this strategy to other oxidative dehydrogenative reactions involving the C(sp³)–H bond as well as explore its synthetic applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.orglett.6b02516](https://doi.org/10.1021/acs.orglett.6b02516).

Experimental procedures and spectroscopic data of compounds data (PDF)

X-ray data for compound **3m** (CIF)

X-ray data for compound **3o** (CIF)

X-ray data for compound **3bb** (CIF)

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Notes

The authors declare no competing financial interest.

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- (17) For the details, see the Supporting Information.
- (18) Compounds **3m** (CCDC 1471888), **3o** (CCDC 1471889), and **3bb** (CCDC 1471887) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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