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Esterification of the Primary Benzylic C−H Bonds with Carboxylic Acids Catalyzed by Ionic Iron(III) Complexes Containing an Imidazolinium Cation

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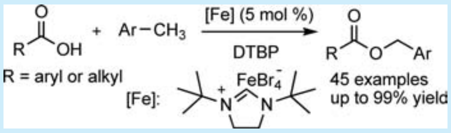
Supporting Information

ABSTRACT: The first iron-catalyzed esterification of the primary benzylic C−H bonds with carboxylic acids using di-*tert*-butyl peroxide as an oxidant is achieved by novel ionic iron(III) complexes containing an imidazolinium cation. The use of well-defined, air-stable, and available iron(III) complex in a 5 mol % loading and readily available starting materials with a broad generality and outstanding sterically hindered tolerance renders this methodology a useful alternative to other protocols that are typically employed for the synthesis of benzyl esters.



Over the past decade, iron-catalyzed direct functionalization of sp^3 C−H bonds has been the subject of great interest owing to the increasing demand for green and sustainable chemistry[1] and has undergone rapid development in recent years.[2] In this context, beyond a large number of studies that have been focused on the transformation of allylic C−H bonds[3] or sp^3 C−H bonds adjacent to a heteroatom,[4] another impressive research target is devoted to achieving direct functionalization of a benzylic C−H bond through a cross-dehydrogenative coupling (CDC) reaction,[5] as this process can afford a variety of benzylic compounds in an elegant strategy.

In 2007, the Li group reported the first example of an $FeCl_2$-catalyzed CDC reaction between a benzylic C−H bond and an sp^3 C−H bond of 1,3-dicarbonyl compounds to form a C−C bond using di-*tert*-butyl peroxide (DTBP) as an oxidant.[6a] Subsequently, the Fu group described the first example of oxidative amidation of benzylic C−H bonds with carboxamides using $FeCl_2$ as a catalyst,[7] whereas the Shi group showed that $FeCl_2$ was also capable of catalyzing the oxidative coupling of benzylic C−H bonds with arenes or vinyl acetates.[8a,b] Recent advances in this field include the expanding work of other groups, for example, those of Chen,[9] Bolm,[10] Chen,[11a] and Zhao,[12] using imidazoles,[9,11a] sulfoximines,[10] amines,[12a] or aqueous ammonia[12b] as coupling partners. The Chen group also developed the oxidative coupling of benzylic C−H bonds with indoles via iron catalysis.[11b] Further studies on the iron-catalyzed functionalization of benzylic C−H in a cascade or tandem mode were done recently by the groups of Guo,[13a] Song,[13b] and Shi.[8c]

Although significant advances have been made, this attractive transformation is still in its infancy and holds many challenges. For example, most benzylic C−H bonds mentioned above are the secondary ones, whereas the corresponding primary ones (i.e., the one present in toluene and its derivatives) are somewhat more difficult to functionalize owing to their relatively low reactivity and easy homocoupling.[6,8b] Furthermore, iron-catalyzed oxidative esterification of benzylic C−H bonds with carboxylic acids remains unexplored, although similar methods featuring palladium-[14] or copper[15]-based catalysts as well as other noncatalytic methods[16] have been developed. Benzyl esters are well known and important functional groups in medicinal and natural organic compounds.[17] In addition, the benzyl group is also a widely used protecting group for carboxyl groups present in various carboxylic acids including amino acids.[18] Until now, only the Mao group reported FeF_3-catalyzed oxidative esterification of benzylic C−H bonds with benzoylformic acids; however, only a trace amount of benzyl ester was obtained when carboxylic acids was used as a coupling partner.[19] Furthermore, the types of iron-based catalysts mentioned above were still restricted to simple iron salts (i.e., $FeCl_2$, $FeBr_3$, and FeF_3), and 10−20 mol % or higher loadings of iron salts were usually required to achieve satisfactory yields. Therefore, it is highly desired to develop a novel type of iron-based catalyst to improve these deficiencies.

As a continuation of our previous work focused on the development of well-defined iron(III) complexes as efficient and easy-to-use catalysts for various cross-coupling reactions,[20] we report herein a facile synthesis of novel ionic iron(III) complexes containing an imidazolinium cation (**1**−**4**) and their catalytic potential in the esterification of the primary benzylic C−H bonds with carboxylic acids using DTBP as the oxidant.

We first selected the bulky 1,3-di-*tert*-butylimidazolinium chloride ([HSI*t*Bu]Cl) to synthesize the target ionic iron(III) complex because a bulky imidazolinium skeleton is generally of benefit to high catalytic activity,[21] and the use of [HSI*t*Bu]Cl as a ligand is rare in iron catalysis.[22] As shown in Scheme 1, the reaction of $FeCl_3$ with 1 equiv of [HSI*t*Bu]Cl occurred

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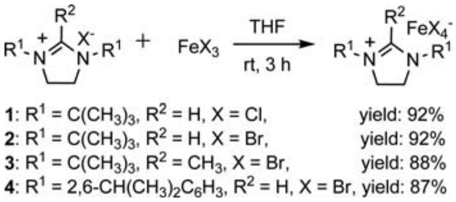
Scheme 1. Synthesis of Ionic Iron(III) Complexes 1−4



smoothly in THF at room temperature, affording the desired iron(III) complex **1** as yellow crystals in 92% yield. Similar reactions involving $FeBr_3$ as well as other imidazolinium salts were also tested, giving the corresponding ionic iron(III) complexes **2−4** as brown-red crystals in yields of 87−92% yields, respectively.

Notably, although $FeCl_3$ and $FeBr_3$ are highly hygroscopic, the target ionic iron(III) complexes **1−4** were non-hygroscopic and existed as air-stable solids at room temperature. They were well-soluble in THF, Et_2O, and $CHCl_3$, sparingly soluble in toluene, and insoluble in hexane. All of them were fully characterized by elemental analysis, Raman spectroscopy, and electrospray ionization mass spectroscopy (ESI-MS), and complex **2** was also characterized by X-ray crystallography (Figure 1).

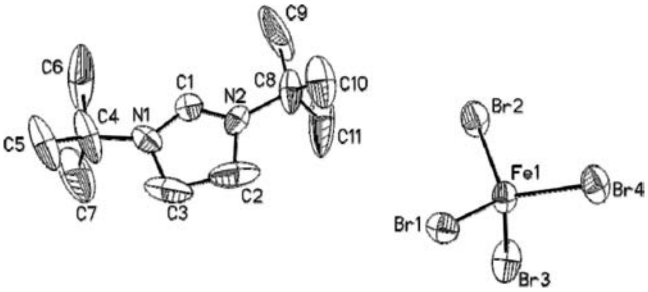
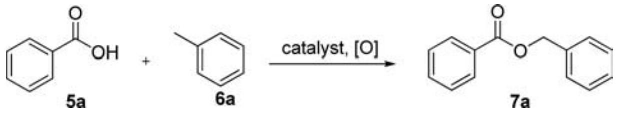


Figure 1. ORTEP drawing of **2** (hydrogens are omitted for clarity, ellipsoids at 30% probability). Selected bond lengths (Å) and angles (deg): Fe(1)−Br(1) 2.333(19), Fe(1)−Br(2) 2.322(2), Fe(1)−Br(3) 2.325(2), Fe(1)−Br(4) 2.315(2); Br(1)−Fe(1)−Br(2) 111.96(9), Br(1)−Fe(1)−Br(3) 108.19(8), Br(1)−Fe(1)−Br(4) 109.14(8), Br(2)−Fe(1)−Br(3) 108.19(9), Br(2)−Fe(1)−Br(4) 109.26(8), Br(3)−Fe(1)−Br(4) 110.10(9).

Table 1. Iron-Catalyzed Esterification of Toluene with Benzoic Acid[a]



entry	catalyst	oxidant	yield (%)
1	**1**	DTBP	12
2	**2**	DTBP	99 (50,[b] 91[c])
3	**2**	TBHP[d]	0
4	**3**	DTBP	76
5	**4**	DTBP	63
6	$FeBr_3$ or FeF_3	DTBP	0
7	$FeBr_3$ + [HSI*t*Bu]Br	DTBP	79
8	FeF_3 + [HSI*t*Bu]Br	DTBP	72
9	Fe(acac)$_3$ + [HSI*t*Bu]Br	DTBP	3
10	[HSI*t*Bu]Br	DTBP	0

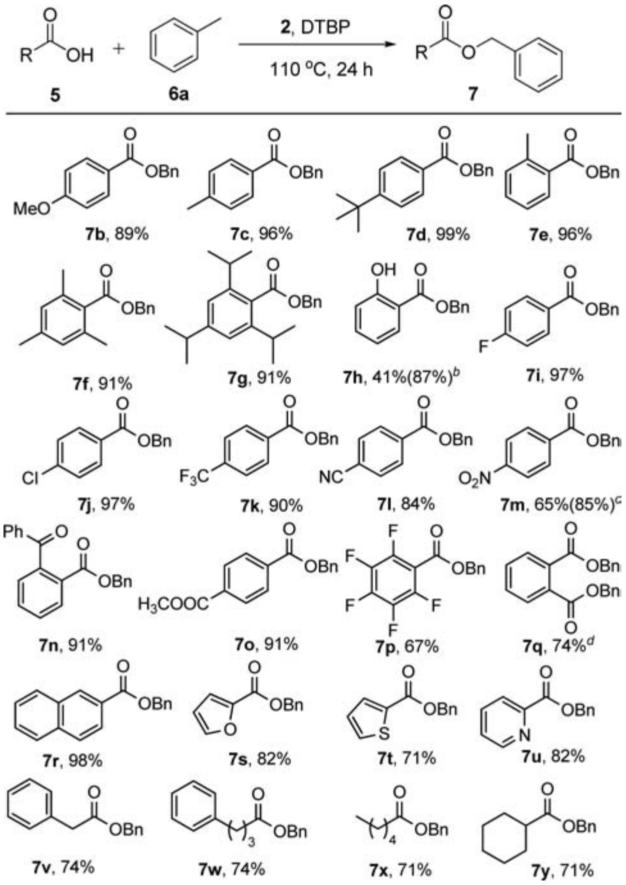
[a] Conditions: benzoic acid (0.5 mmol), iron complexes (5 mol %), oxidant (1.25 mmol), toluene (3 mL), 110 °C, 24 h, GC yield using *n*-hexadecane as internal standard, an average of two runs, in air. [b] **2** (3 mol %). [c] In Ar. [d] TBHP = *tert*-butyl hydroperoxide.

We chose the reaction between benzoic acid (**5a**) and toluene (**6a**) as the initial test system. As seen in Table 1, there are significant differences in catalytic activities among complexes **1−4** and the related iron salts under optimized reaction conditions. For example, with DTBP as the oxidant, complex **2** exhibited the highest activity and gave the desired product **7a** in 99% yield at a 5 mol % loading (entry 2). Lowering the loading of **2** to 3 mol % still gave a 50% yield of **7a**. In comparison, both **3** and **4** showed moderate activity, affording the product in yields of 76% (entry 4) and 63% (entry 5), respectively. Somewhat to our surprise, the chloride analogue **1** showed very poor activity, giving **7a** in merely 12% yield (entry 1). A similar difference in catalytic activity between iron bromide and its chlorinated derivative was also observed by the Lei group in a $FeBr_2$-catalyzed CDC reaction.[23] Under the same reaction conditions, a mixture of an iron(III) salt and [HSI*t*Bu]Br in a 1:1 molar ratio gave the desired product **7a** in a yield between 72 and 79% (entries 7 and 8); however, only trace amounts of **7a** were obtained with a 1:1 (molar ratio) mixture of Fe(acac)$_3$ and [HSI*t*Bu]Br (entry 9). No desired product was obtained when an iron(III) salt (entry 6) or an imidazolinium salt was employed alone (entry 10). Oxidant screening disclosed that *tert*-butyl hydroperoxide (TBHP) showed no activity (entry 3). In addition, the atmosphere has no significant effect on the reaction since the present reaction could be performed smoothly either in air or in argon (entry 2).

Encouraged by the above results, we explored the substrate scope of this iron-catalyzed esterification of the primary benzylic C−H bonds with carboxylic acids to form benzylic esters. A wide range of carboxylic acids were employed successfully to couple with toluene (**6a**), affording the desired products in good to excellent yields (Scheme 2). All of the benzoic acids bearing electron-donating substituents or electron-withdrawing substituents reacted smoothly, giving the desired products in yields of approximately 84−97% (**7b−o**). The notable merit of this protocol is that sterically hindered benzoic acids are well tolerated, as a 91% yield of the corresponding product **7g** could be reached when the highly hindered 2,4,6-triisopropylbenzoic acid was coupled with toluene under our optimized conditions. To the best of our knowledge, there have been no other reports of oxidative esterification of sp^3 C−H bonds with such a sterically hindered carboxylic acid. In addition, pentafluorobenzoic acid, a rarely used substrate,[24] also gave the ester product in 67% yield (**7p**) without any enhanced reaction conditions. Interestingly, phthalic acid reacted smoothly with toluene in the presence of a 20 mol % loading of **2**, resulting in the corresponding dibenzyl phthalate (**7q**) in 74% yield. 2-Naphthoic acid also gave product **7r** in a 98% yield. Several kinds of heteroaryl carboxylic acids were suitable reactants, affording the desired products (**7s−u**) in 71−82% yields. Moreover, aliphatic carboxylic acids were also found to be compatible with this esterification protocol, furnishing the desired products (**7v−y**) in 71−74% yields.

We also investigated the substrate scope of a variety of benzylic hydrocarbons (Scheme 3). Both electron-donating groups and electron-withdrawing groups are well-tolerated (**8a−i**), whereas xylenes and mesitylene only yielded

Scheme 2. Substrate Scope of Carboxylic Acids[a]

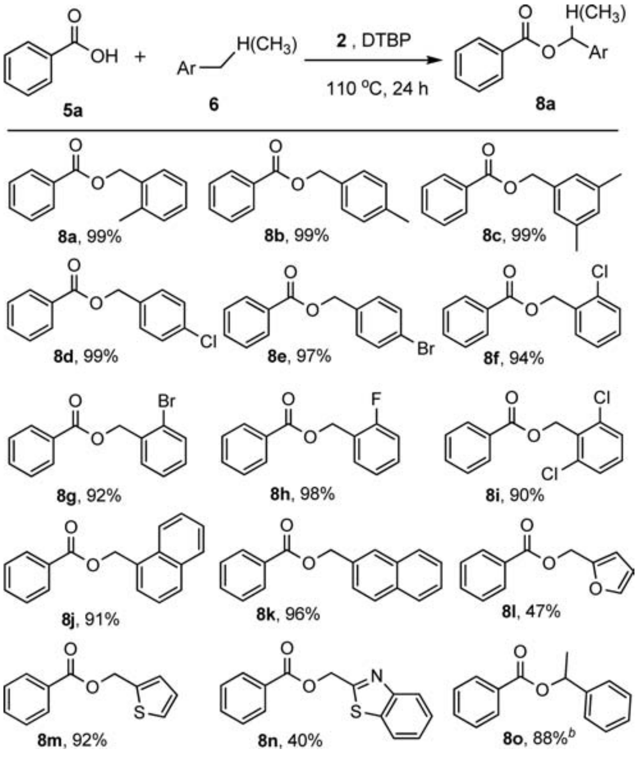


[a]Conditions: carboxylic acids (0.5 mmol), toluene (3.0 mL), **2** (5 mol %), DTBP (1.25 mmol), 110 °C, 24 h, in air, isolated yield. [b]**2** (10 mol %). [c]**2** (15 mol %). [d]**2** (20 mol %).

monoesterification products in almost quantitative yields (**8a**–**c**). Notably, *ortho*-substituted toluenes also reacted smoothly, affording the desired products in yields above 90%, even for 1,3-dichloro-2-methylbenzene (**8i**). Both 1-methylnaphthalene and 2-methylnaphthalene gave the desired products **8j** and **8k** in 91% and 96% yields, respectively. Remarkably, 2-methylfuran, 2-methylthiophene, and 2-methylbenzothiazole could afford the desired products in 40–96% yields (**8l**–**n**). To date, these methyl-substituted heteroarenes have rarely been explored as substrates in other sp^3 C−H bond esterification, especially for the attractive thiophene skeleton.[25] Somewhat to our surprise, the reactivity of ethylbenzene[26] was slightly lower than that of toluene (**8o**), even if it is generally considered that a secondary benzylic C−H bond is more reactive compared with the corresponding primary one.

Although an exact mechanism of the present reaction requires further investigation, our current experimental investigations (Scheme S2) suggest that this transformation may involve radical species, and the cleavage of the benzylic C−H bond should be involved in the rate-determining step during the catalytic cycle. DTBP could initiate the homocleavage of toluene to the benzyl radical; meanwhile, the iron species play a key role in the cross-coupling process. The role of an imidazolinium cation should be of benefit to form a μ-oxo, μ-carboxylate diiron intermediate,[27] which may occur in the initial reaction of iron(III) complex with carboxylic acid and the oxidant DTBP during a catalytic cycle (Scheme S3).[4h]

Scheme 3. Substrate Scope of Benzylic Hydrocarbons[a]



[a]Conditions: benzoic acid (0.5 mmol), methylarene (3.0 mL), **2** (5 mol %), DTBP (1.25 mmol), 110 °C, 24 h, in air, isolated yield. [b]Benzoic acid (1.0 mmol), ethylbenzene (2.0 mL).

In summary, we have synthesized a series of novel ionic iron(III) complexes (**1**–**4**) and developed an efficient oxidative esterification of the primary benzylic C−H bonds with carboxylic acids using DTBP as the oxidant. The present reaction is suitable for a wide range of carboxylic acids and derivatives of toluene with outstanding tolerance to sterically hindered substrates and good compatibility with various functional groups. Thus, this work provides a highly efficient method for the synthesis of various benzyl esters as well as a useful strategy for the protection of carboxyl groups present in various carboxylic acids. Because imidazolinium cations bearing different *N*-substituents are readily available, the present study also provides an alternative strategy for the development of highly active, yet robust catalysts of iron. Further studies are currently underway in our laboratory, directed toward elucidating the detailed reaction mechanism, understanding the structure–reactivity relationships of these iron(III)-based complexes and developing their scope in other direct functionalization of sp^3 C−H bonds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00148.

Detailed experimental procedures, characterization data for complexes **1**–**4**, structural data for **2**, and details pertaining to the characterization of the products (PDF)

X-ray data for **2** (CIF)

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Notes

The authors declare no competing financial interest.

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