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Mild $Mn(OAc)_3$-Mediated Aerobic Oxidative Decarboxylative Coupling of Arylboronic Acids and Arylpropiolic Acids: Direct Access to Diaryl 1,2-Diketones

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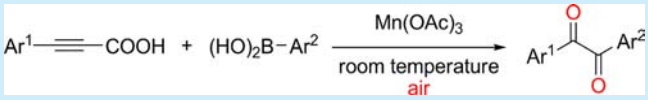
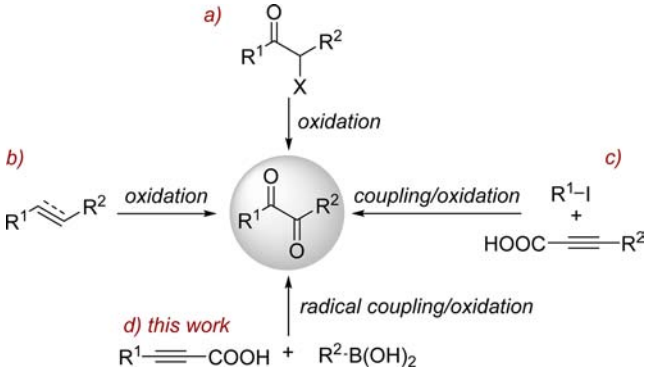
Supporting Information

ABSTRACT: A simple and efficient method for the synthesis of diaryl 1,2-diketones has been developed. The reaction represents the first example of diaryl 1,2-diketones that are synthesized directly from arylboronic acids and arylpropiolic acids by a radical pathway in moderate to good yields. This reaction proceeds under mild reaction conditions and with good tolerance of a variety of functional groups. Preliminary mechanistic studies were conducted.



1,2-Diketones are one of the most important skeletons, since they are not only found in many natural products and bioactive molecules[1] but also broadly used as versatile building blocks in the construction of a variety of other chemicals,[2] especially biologically active heterocyclic compounds, such as imidazoles, quinoxalines, and indolone-*N*-oxide. Among them, benzil derivatives also exhibit bioactivities in antitumor applications.[3] Accordingly, a variety of traditional and modern methods for the preparation of 1,2-diketones have been developed.[4] Scheme 1 schematically presents some of the well-established protocols:

Scheme 1. Different Approaches toward 1,2-Diketones



(1) the oxidation of ketone derivatives, including α-halo and α-hydroxyl ketones, with different oxidants (Scheme 1a);[5] (2) the oxidation of olefins and internal alkynes with various oxidants, such as selenium dioxide, iodine, potassium permanganate, and others (Scheme 1b).[6] Recently, Lee reported a straightforward method to synthesize 1,2-diketones directly from aryl halides and alkynyl carboxylic acids through a decarboxylative Sonogashira-type coupling and oxidation procedure (Scheme 1c).[7] Despite the many advances made in recent years, there are still several drawbacks: (a) the use of expensive transition-metal catalysts; (b) the tedious preparation of the starting materials; (c) the need for harsh reaction conditions. Therefore, it is still of great interest to uncover new synthetic methods for the realization of these important molecules.

Over the past 30 years, Mn(III)-mediated oxidative radical coupling reactions have proven to be excellent and efficient methods for formation of C−C and C−heteroatom bonds.[8] In this regard, the use of arylboronic acids as the aryl radical precursors has attracted considerable attention and found numerous applications. This is partly due to the fact that arylboronic acids are easily available and are stable under atmospheric and aqueous conditions.[9] Furthermore, it is known that arylboronic acids are easily decomposed to aryl radicals when oxidants are present.[10] Herein, we report a simple and efficient method for the synthesis of diaryl 1,2-dikeones via a $Mn(OAc)_3{\cdot}2H_2O$[11]-mediated oxidative decarboxylative coupling of arylpropiolic acids with arylboronic acids (Scheme 1d).

Initially, phenylpropiolic acid (**1a**) and phenylboronic acid (**2a**) were chosen as the model substrates to optimize the reaction conditions. To our delight, the reaction of **1a** and **2a** (1:3 ratio) in the presence of $Mn(OAc)_3{\cdot}2H_2O$ (4.0 equiv) as an oxidant in toluene at room temperature under air afforded the desired benzil **3aa**, albeit in a low yield of 17% (Table 1, entry 1). Based on this promising result, a wide variety of reaction parameters (oxidants, solvents, and additives) were examined, and some of the representative results are shown in Table 1. $Mn(OAc)_3{\cdot}2H_2O$ turned out to be the best choice of oxidant (entries 1−3). The solvent also played a very important role in this reaction (entries 4−6). It was found that cyclohexane gave a yield comparable to that when using toluene (entry 6). Additionally, the use of H_2O as a cosolvent improved the yields remarkably to 40% and 32%, respectively (entries 7 and 8). Water might increase the solubility of the oxidants in this reaction. Further studies showed that the addition of a base such as KOAc was beneficial for the reaction

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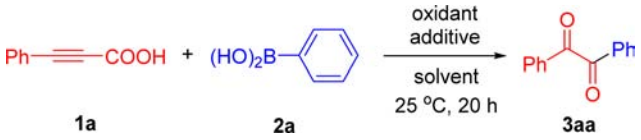
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa

entry	oxidant	solvent	additive	yield (%)[b]
1	$Mn(OAc)_3{\cdot}2H_2O$	toluene	–	17
2	$FeCl_3$	toluene	–	0
3	$Cu(OAc)_2$	toluene	–	0
4	$Mn(OAc)_3{\cdot}2H_2O$	THF	–	0
5	$Mn(OAc)_3{\cdot}2H_2O$	DMF	–	0
6	$Mn(OAc)_3{\cdot}2H_2O$	cyclohexane	–	17
7	$Mn(OAc)_3{\cdot}2H_2O$	cyclohexane/H_2O	–	40
8	$Mn(OAc)_3{\cdot}2H_2O$	toluene/H_2O	–	32
9	$Mn(OAc)_3{\cdot}2H_2O$	cyclohexane/H_2O	KOAc	55
10	$Mn(OAc)_3{\cdot}2H_2O$	cyclohexane/H_2O	K_2CO_3	47
11	$Mn(OAc)_3{\cdot}2H_2O$	cyclohexane/H_2O	Et_3N	26
12[c]	**$Mn(OAc)_3{\cdot}2H_2O$**	**cyclohexane/H_2O**	**KOAc**	**75 (73)**
13[c,d]	$Mn(OAc)_3{\cdot}2H_2O$	cyclohexane/H_2O	KOAc	62
14[c,e]	$Mn(OAc)_3{\cdot}2H_2O$	cyclohexane/H_2O	KOAc	68

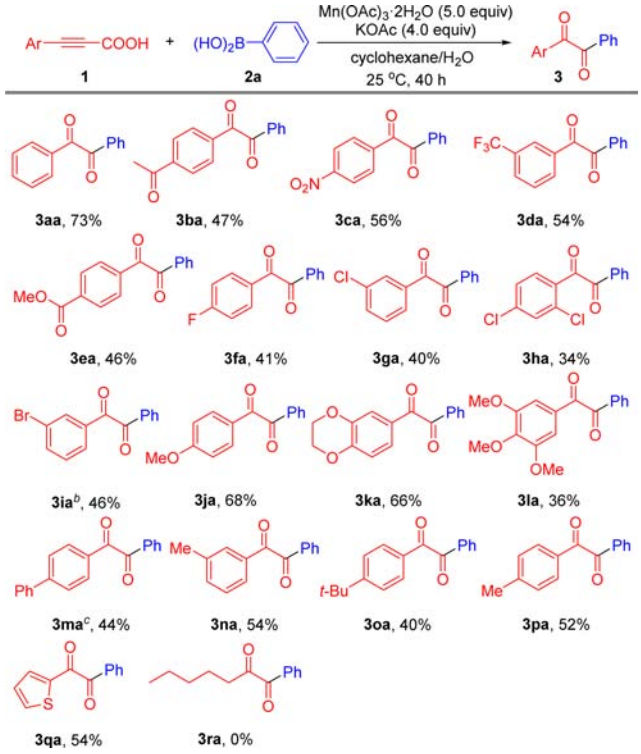
[a]General reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.3 mmol, 3.0 equiv), oxidant (0.4 mmol, 4.0 equiv), additive (0.4 mmol, 4.0 equiv), solvent (2 mL; if water was added, the ratio is 10:1), 25 °C, 20 h. [b]Yields determined by ^1H NMR using *p*-iodoanisole as the internal standard; isolated yield in parentheses. [c]Oxidant (5.0 equiv), 40 h; 2.0 equiv of **2a** were added; 12 h later, another portion of **2a** (1.0 equiv) was added. [d]KOAc (2.0 equiv) was employed. [e]**2a** (2.0 equiv) was employed.

(entries 9−11). Gratifyingly, a good yield of 75% was obtained when 5.0 equiv of oxidant were applied with the addition of **2a** in two portions (entry 12). The decrease of the loading of both base (KOAc) and phenylboronic acid gave diminished 62% and 68% yields, respectively (entries 13 and 14).

With the optimized conditions in hand (Table 1, entry 12), we next explored the scope of the reaction. A variety of arylpropiolic acids bearing different substituents were tested, and the results are summarized in Scheme 2. It was found that the transformation was very general, both electron-withdrawing and -donating functional groups such as acetyl (**3ba**), nitro (**3ca**), trifluoromethyl (**3da**), ester (**3ea**), fluoro (**3fa**), chloro (**3ga**, **3ha**), bromo (**3ia**), methoxyl (**3ja**, **3ka**, **3la**), alkyl (**3na**, **3oa**, **3pa**), and phenyl (**3ma**) were well tolerated, giving the corresponding products in moderate to good yields. Notably, 3-(thiophen-2-yl)propiolic acid (**3qa**) was also compatible with the reaction conditions, which represented an interesting outcome given the utility of these substructures in medicinal chemistry. It is worthy of note that the halide substituents such as Cl and Br (**3ga**, **3ha**, **3ia**) provide opportunities for further functionalization. Unfortunately, the current reaction conditions were not compatible with the alkylpropiolic acid. For example, the use of oct-2-ynoic acid gave no trace of the desired product (**3ra**).

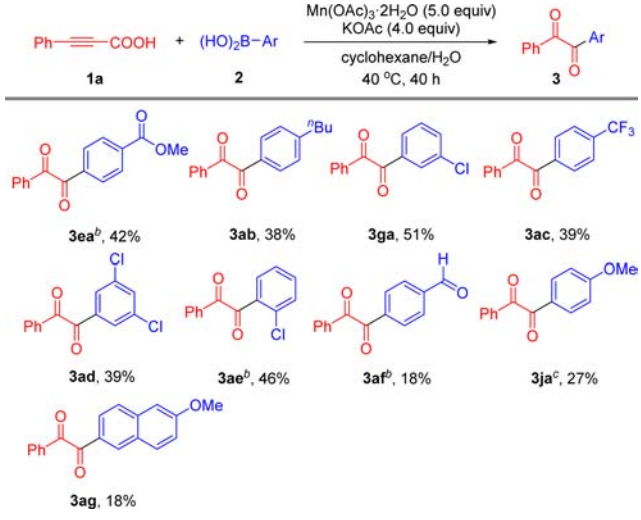
As revealed in Scheme 3, a broad range of arylboronic acids were also suitable for this reaction. Ester (**3ea**), alkyl (**3ab**), chlorides (**3ga**, **3ad**, **3ae**), and trifluoromethyl (**3ac**) are tolerated, affording the corresponding products in moderate yields. *ortho*-Substituents did not hamper the reactivity (**3ae**). The use of formyl-substituted phenylboronic acid led to a low yield (18%, **3af**). It was found that the reaction is sensitive to the electronic property of the arylboronic acids. Electron-rich arylboronic acids (**3ja**, **3ag**) gave inferior yields compared to the electron-deficient ones.

Scheme 2. Substrate Scope of Arylpropiolic Acids[a]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.6 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (1.0 mmol), KOAc (0.8 mmol), cyclohexane/H_2O (4.4 mL, 10:1), rt, 40 h under air, isolated yield. [b]At 40 °C. [c]Cyclohexane/H_2O (3.3 mL, 10:1) was employed.

Scheme 3. Substrate Scope of Arylboronic Acids[a]



[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.9 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (1.5 mmol), KOAc (1.2 mmol), cyclohexane/H_2O (4.4 mL, 10:1), 40 °C, 40 h, under air, isolated yield. [b]At 50 °C. [c]At rt.

To elucidate the mechanism of the reaction, a number of experiments were carried out. When phenylacetylene **4**, instead of **1a**, was subjected to the reaction conditions, no desired product **3aa** was observed (eq 1). In addition, it is well-known that 1,2-diphenylethyne **5** could be easily oxidized to benzil **3aa**

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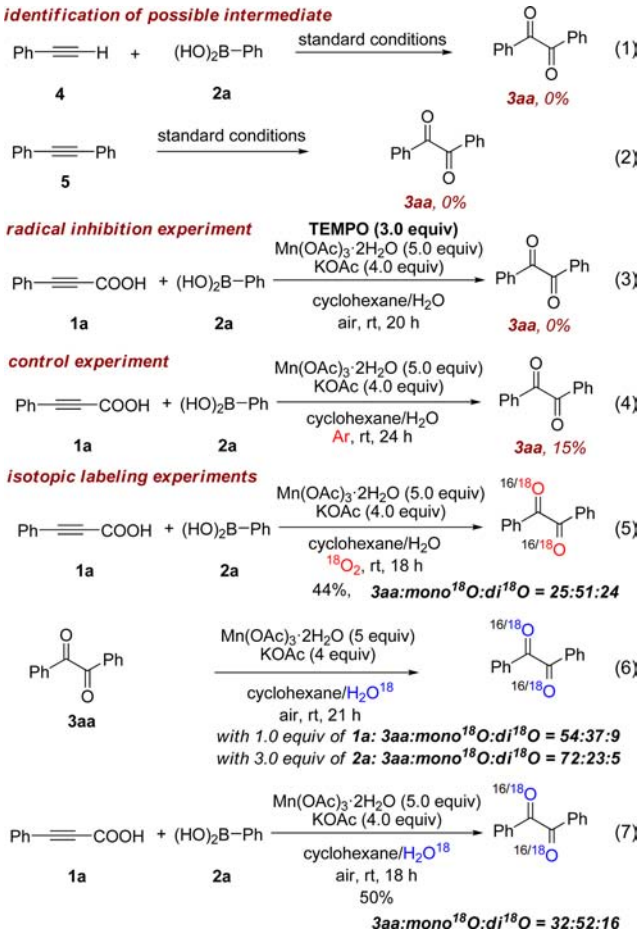
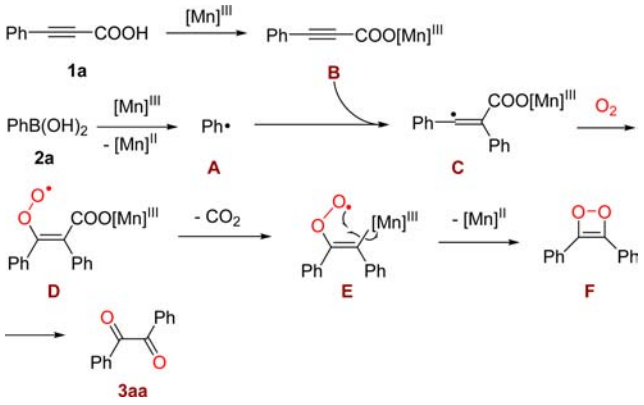


under various oxidative reaction conditions.[6d−g,12] Thus, diphenylethyne **5**, a possible intermediate, was subjected to the standard conditions (eq 2). Again, none of the desired product **3aa** was obtained. These results rule out the possible intermediacy of **4** and **5**. When a radical scavenger, 2,2,6,6-tetramethylpiperidineoxy (TEMPO), was introduced to the reaction mixture, no 1,2-diketone was formed, indicating a possible radical pathway involved in the mechanism (eq 3). When the reaction was performed under argon, a low yield (15%) of **3aa** was obtained, demonstrating the importance of O_2 in this transformation (eq 4). To further elucidate the role of O_2 and H_2O for the reaction, isotopic labeling experiments were also conducted. Under an $^{18}O_2$ atmosphere, two ^{18}O labeled benzil **3aa-*di*^{18}O** was obtained, along with a significant amount of **3aa** and **3aa-*mono*^{18}O**, which were suspected to be generated through the ^{18}O atom exchange with water under the reaction conditions (eq 5). Indeed, when **3aa** was treated with $Mn(OAc)_3$, and KOAc, in cyclohexane/H_2O^{18}, significant incorporation of ^{18}O was found in the presence of either phenylpropiolic acid (**1a**) or phenylboronic acid (**2a**) (eq 6). And when the reaction was conducted in the presence of air and $H_2{}^{18}O$, the ^{18}O labeling products were observed (**3aa**/***mono*^{18}O**/***di*^{18}O** = 32:52:16) (eq 7 vs eq 5). Taken together, these experiments clearly suggested that the two oxygen atoms of the 1,2-diketone originate from the molecular oxygen.

On the basis of the above observations and literature precedent,[13] a proposed mechanism is depicted in Scheme 4. Phenylboronic acid (**2a**) is oxidized by a Mn^{III} salt to generate the phenyl radical **A**, which undergoes intermolecular attack to manganese salt **B**, generated in situ from arylpropiolic acid and

Scheme 4. Possible Mechanism



$Mn(OAc)_3$, to form a α-styrenyl radical **C**. This intermediate is trapped by molecular oxygen to deliver peroxyl radical **D**. Thereafter, a decarboxylation takes place to furnish alkyl manganese species **E**.[14] The cyclization of intermediate **E** produces intermediate **F**, with the concomitant release of the reduced Mn^{II}. The desired 1,2-diketone **3aa** is formed by a subsequent fragmentation of **F**.[15]

In conclusion, we have developed a simple and efficient method for the synthesis of diaryl 1,2-dikeones using a $Mn(OAc)_3$-mediated oxidative decarboxylative coupling of arylpropiolic acids with arylboronic acids. The reaction proceeds under mild reaction conditions and with good tolerance to a variety of functional groups. Preliminary mechanistic studies were carried out, and the two oxygen atoms of the 1,2-diketone were found out to be originated from the molecular oxygen. Because of the ready availability of the starting materials and the value of the products, we believe this method should be useful in organic synthesis and medicinal chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and full analytical data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01265.

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Notes

The authors declare no competing financial interest.

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