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Iron-Catalyzed Carbonylation of Aryl halides with Arylborons Using Stoichiometric Chloroform as the Carbon Monoxide Source‡

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A general iron-catalyzed carbonylative Suzuki-Miyaura coupling of aryl halides with arylborons is reported, using stoichiometric $CHCl_3$ as the CO source. The high efficiency, economy, selectivity, and operational simplicity of this transformation render this method a valuable tool in organic synthesis. Importantly, the presented strategy allows effective ^{13}C labeling simply by using the commercially available ^{13}C-labeled $CHCl_3$. On the basis of initial mechanistic exploration, an aryl radical intermediate is proposed in the present carbonylation process.

Transition-metal-catalyzed carbonylation utilizing CO gas, known as C1 chemistry, is a fundamental chemical transformation for the construction of carbonyl compounds and their derivatives, and has become an industrial core technology.[1] Carbonylative Suzuki-Miyaura reaction is one of the most important transition-metal-catalyzed carbonylations, as it possesses unique features, such as readily accessible and stable substrates, high regio- and stereoselectivity, broad substrate scope, and wide functional group compatibility.[1e, 2] Not surprisingly, the reaction has become one of the most straightforward and practical processes for the synthesis of an array of unsymmetrical and symmetrical biaryl ketones, which are omnipresent in pharmaceuticals, natural products, photosensitizers, and advanced organic materials.[3]

Despite a powerful method, gaseous CO is toxic, flammable, odorless, and awkward to handle (mainly at high pressure), and consequently leads to severely limit the application of this protocol.[4] To address this issue, few precursors that can act as CO surrogates have been reported in the carbonylative Suzuki-Miyaura reaction. Early in 2011 Jafarpour et al. reported the first carbonylative Suzuki-Miyaura coupling of aryl iodides using $Mo(CO)_6$ as the carbon monoxide source, albeit with a high palladium catalyst loading (10 mol%) and a high temperature (140 °C).[5] More recently, 9-methyl-9H-fluorene-9-carbonyl chloride, a significent CO precursor, was succesfully employed in the transformation and readily produced carbon-13 and carbon-14 labeled benzophenones.[6] However, an extra high palladium/phospine catalyst loading (5 mol%) is required to liberate CO and the necessity of a special equipment would reduce the applicability of this protocol. Later, acetic formic anhydride, *in situ* generated from the reaction of formic acid and acetic anhydride, was utilized as a suitable CO source for carbonylative Suzuki-Miyaura coupling,[7] but sensitive to moisture and active groups, thereby leading to the limitation of the potential substrate scope. Therefore, it is significent to seek a CO surrogate having advantages in operational simplicity, economic viability, and high stability toward air and water for carbonylative Suzuki-Miyaura coupling.

Recently, chloroform ($CHCl_3$) has received attention as a widely available, stable, and inexpensive substitute for CO and has been successfully employed in carboxylation,[8] aminocarbonylation,[9] and carbonylative Sonogashira coupling.[10] The release of CO can be achieved through hydrolysis of $CHCl_3$ in the presence of strongly basic hydroxides (often with 10 equiv of hydroxide).[8-11] Although chloroform as a CO source shows superior properties over CO gas and all of the above-mentioned CO surrogates, expansion of this CO source to carbonylative Suzuki-Miyaura coupling is an unmet challenge since several undesirable side reactions, such as hydroxylation,[12] hydroxycarbonylation,[13] noncarbonylative Suzuki-Miyaura coupling,[14] homocoupling,[15] and dehalogenation[15] can proceed simultaneously in the presence of palladiun catalyst and a large excess of hydroxide base (8−10 equiv).

While remarkable advances in the development of CO surrogates have been achieved, in all cases these transformations have to use palladium-phosphine catalysts with limited availability (1 x 10^{-6} wt% in the earth crust of palladium), high cost, significant toxicity, and poor stability. These drawbacks hinder the transfer of the advancements to large-scale applications. Therefore, the development of more economical and environmentally benign catalysts for the aforementioned transformation is of considerable importance. In this respect, it is more desirable to investigate catalysts based on first-row transition metals, such as iron, copper, zinc, and nickel. Especially iron is an ideal candidate for catalysis, since it is widely distributed in nature, the second most abundant metal in the earth crust (4.7 wt%), and ecological friendly.[16] Despite these advantages, until recently, iron-based catalytic carbonylation is far underexplored and generally requires high pressure of CO.[17] Pioneerring studies on iron catalyzed carbonylation of aryl iodides reported by Brunet group used $Co_2(CO)_8$ as a co-catalyst to deliver symmetrical biaryl ketones.[18] However, these contributions are impractical to organic synthesis due to narrow scope of substrates, poor chemoselectivity, and low functional group compatibility. Recently, we reported a general and selective iron-catalyzed carbonylative Suzuki-Miyaura reactions of aryl iodides with arylboronic acids under atmospheric pressure of CO.[19] While this finding represents a breakthrough in iron-catalyzed carbonylation of aryl halides, the intrinsic drawbacks of CO gas undermine the attractiveness of the

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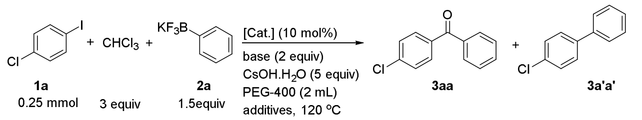
method. To date, iron-catalyzed carbonylative coupling of aryl halide using CO surrogate has gone undiscovered. Here, we develop an iron system capable of carbonylating a wide range of aryl halides with aryltrifluoroborates and arylboronic acids using stoichiometric amounts of CO generated *in situ* from stable and inexpensive chloroform. Notably, this protocol allows effective ^{13}C labeling.

Encouraged by our recent studies on carbonylation[19-20] where the performance of the catalytic systems based on PEG-400 is highly desirable, we started our investigation by examining $FeCl_2$-catalyzed trimodular carbonylative cross-coupling of 1-chloro-4-iodobenzene (**1a**), potassium phenyl trifluoroborate (**2a**), and chloroform with Na_2CO_3 as base and PivOH[21] as additive in PEG-400 (Table 1). While the combination of palladium-phosphine has been the most common catalyst used in carbonylation of aryl halides, it doesn't work for the desired carbonylation reaction at all and leads to the complete formation of side product **3a'a'** (entries 1-2). To our delight, switching to 10 mol% of $FeCl_2$ gave 5% of the desire product **3aa** with excellent selectivity (entry 3) and a 15 % yield was observed with less PPh_3 (entry 4). In the absence of $FeCl_2$ **3aa** was not detected (entry 5). Further, without PPh_3 a 70 % yield of **3aa** was obtained at elevated temperature, albeit with 16% of **3a'a'** (entry 6). When the additive PivOH was not added, the yield of product **3aa** decreased from 70% to 50%, accompanying the yield increase of **3a'a'** (38%) (entry 7).[21] In contrast, by using 1.5 equiv of PivOH, a far superior result was obtained (entry 8) (for details see the ESI, Table S1). Other acids such as AcOH, TFA, and 9-anthroic acid were also examined and found to be much less effective (entries 9-11). Na_2CO_3 appeared to be the choice of base after the common bases had been tested, e.g., Li_2CO_3 (75%), K_2CO_3 (30%), Cs_2CO_3 (10%), $NaHCO_3$ (54%), Na_3PO_4 (65%), K_3PO_4 (40%), Na_2HPO_4 (40%), NaF (5%), AcONa (0), and DBU (0) (entries 12-21). Considering a hydroxide base playing a critical role in rapidly hydrolyzing $CHCl_3$ to CO,[8-11] We also briefly screened hydroxide bases and chloroform equivalencies, and found that $CsOH{\cdot}H_2O$ was the best hydroxide base and 3.0 equiv of chloroform was the best quantity (for details see the ESI, Tables S2 and S3). We then surveyed other solvents and observed that **3aa** was provided in 0–45% yields (entries 22-26). Previous reports indicated that iodide additive could promote carbonylative Suzuki-Miyaura coupling.[14] Indeed, 0.5 equiv of NaI further raised the yield of **3aa** (87%) and suppressed the formation of **3a'a'** (5%) (entry 27) (for details see the ESI, Table S4). Additionally, other iron salts were screened and resulted in 50-77% yields of **3aa** (for details see the ESI, Table S5). The use of ultrapure $FeCl_2$ (99.99% based on trace metals, Alfa Aesar), ultrapure Na_2CO_3 (99.997% based on trace metals, Alfa Aesar), and ultrapure NaI (99.999% based on trace metals, Acros) resulted in a slightly better yield of **3aa** (entry 28). Moreover, inductively coupled plasma atomic emission spectroscopy (ICP–AES) assay of the reaction system under standard conditions confirmed that the concentrations of transition metals, such as Pd, Cu, and Ni were below the detection limit of the machine. These results suggest that the present catalytic system is based on iron.

Table 1 Iron-catalyzed carbonylative Suzuki-Miyaura reaction of **1a** with **2a**.[a]



Entry	[Cat]	Base	Additive	Solvent	Yield **3aa**%	Yield **3a'a'**%
1[b,c,d,e]	$Pd(OAc)_2$	Na_2CO_3	PivOH	PEG-400	0	99
2[b,c,d,e]	$PdCl_2$	Na_2CO_3	PivOH	PEG-400	0	99
3[c,d,e]	$FeCl_2$	Na_2CO_3	PivOH	PEG-400	5	0
4[c,d,f]	$FeCl_2$	Na_2CO_3	PivOH	PEG-400	15	2
5[c,d,f]	-	Na_2CO_3	PivOH	PEG-400	0	0
6	$FeCl_2$	Na_2CO_3	PivOH	PEG-400	70	16
7	$FeCl_2$	Na_2CO_3	-	PEG-400	50	38
8	$FeCl_2$	Na_2CO_3	PivOH	PEG-400	84	8
9	$FeCl_2$	Na_2CO_3	AcOH	PEG-400	57	20
10	$FeCl_2$	Na_2CO_3	TFA	PEG-400	40	10
11	$FeCl_2$	Na_2CO_3	9-An acid	PEG-400	18	12
12	$FeCl_2$	Li_2CO_3	PivOH	PEG-400	75	15
13	$FeCl_2$	K_2CO_3	PivOH	PEG-400	30	5
14	$FeCl_2$	Cs_2CO_3	PivOH	PEG-400	10	0
15	$FeCl_2$	$NaHCO_3$	PivOH	PEG-400	54	25
16	$FeCl_2$	Na_3PO_4	PivOH	PEG-400	65	10
17	$FeCl_2$	K_3PO_4	PivOH	PEG-400	40	21
18	$FeCl_2$	Na_2HPO_4	PivOH	PEG-400	40	5
19	$FeCl_2$	NaF	PivOH	PEG-400	5	0
20	$FeCl_2$	AcONa	PivOH	PEG-400	0	0
21	$FeCl_2$	DBU	PivOH	PEG-400	0	0
22	$FeCl_2$	Na_2CO_3	PivOH	Dioxane	30	2
23	$FeCl_2$	Na_2CO_3	PivOH	EtOH	45	45
24	$FeCl_2$	Na_2CO_3	PivOH	Glycol	25	75
25	$FeCl_2$	Na_2CO_3	PivOH	Toluene	0	0
26	$FeCl_2$	Na_2CO_3	PivOH	DMSO	0	0
27[g]	**$FeCl_2$**	**Na_2CO_3**	**PivOH**	**PEG-400**	**87**	**5**
28[g,h]	$FeCl_2$	Na_2CO_3	PivOH	PEG-400	88	5

[a] *Reaction conditions* (unless otherwise stated): **1a** (0.25 mmol), **2a** (0.375 mmol, 1.5 equiv), $FeCl_2$ (10 mol%), base (0.5 mmol, 2 equiv), $CsOH{\cdot}H_2O$ (1.25 mmol, 5 equiv), $CHCl_3$ (0.75 mmol, 3 equiv), additive (0.375 mmol, 1.5 equiv), solvent (2.0 mL), 120 °C, and 24 h; Yields were determined by GC analysis using hexadecane as internal standard. [b] [Pd] (1 mol%). [c] PivOH (1 equiv). [d] 80 °C. [e] PPh_3 (2 mol%). [f] PPh_3 (1 mol%). [g] NaI (0.5 equiv). [h] Ultrapure $FeCl_2$ (99.99% based on trace metals, Alfa Aesar), ultrapure Na_2CO_3 (99.997% based on trace metals, Alfa Aesar), and ultrapure NaI (99.999% based on trace metals, Acros).

With the optimal conditions in hand, we next turned to demonstrate the generality of this iron-catalyzed carbonylation (Scheme 1). Aryl iodides bearing electronically deactivated, neutral, and activated moieties gave the corresponding biaryl ketones in good to excellent yields with high selectivities. The reaction conditions were compatible with chloro, cyano, fluoro, trifluoro, and methoxy groups. Iodotoluenes were productive coupling partners albeit 2-methyl substitute had a mildly negative effect on reactivity (**3ga**, **3ia**-**3ja**). Interestingly, the transformation can move beyond simple aryl group and incorporate heteroaryl iodide (**3ma**). 1-Iodonaphthalene can also be utilized as a coupling partner, albeit with heating to 140 °C in the absence of PivOH, to arrive at **3na** in moderate isolated yield. Unfortunately, 4-bromobenzotrifluoride was poorly reactive and gave the desired product in only a 26% yield even at 140 °C (**3fa**).

Subsequently, a series of potassium aryltrifluoroborates were explored (Scheme 2). They proved to efficiently couple with typical aryl iodides under normal conditions. No

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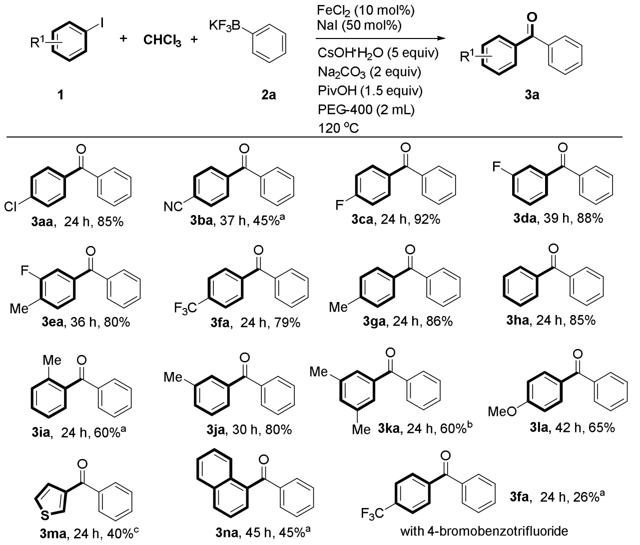
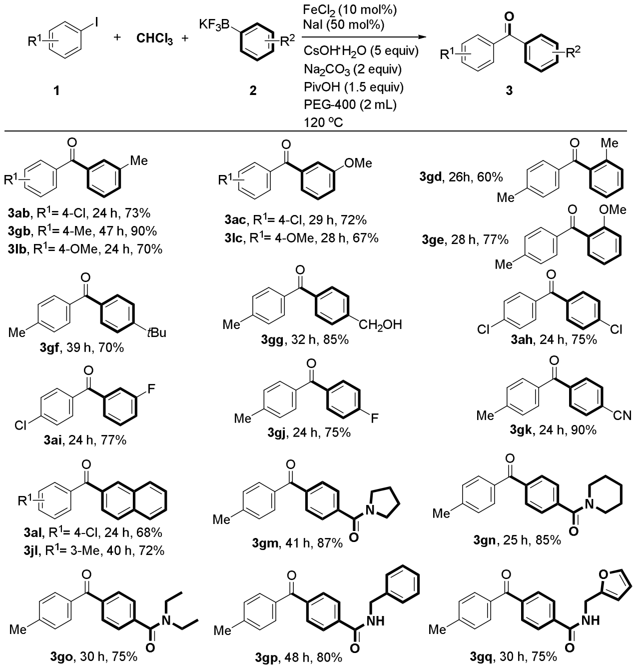


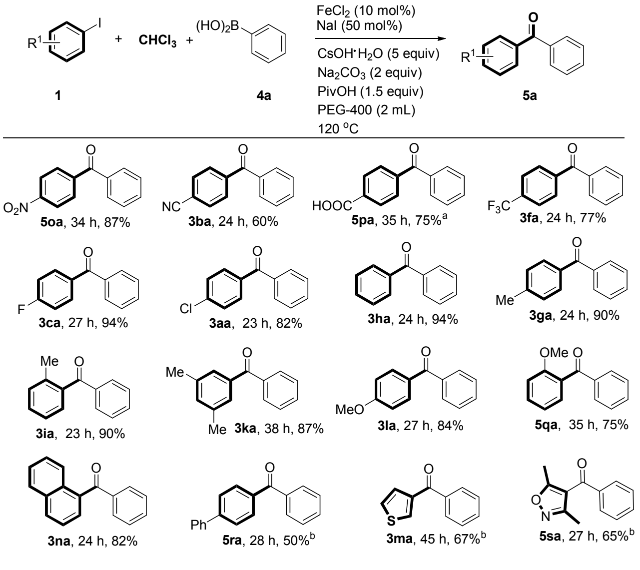
Scheme 1 Iron-catalyzed carbonylative Suzuki-Miyaura reaction of aryl halides **1** with potassium aryl trifluoroborates **2a**. Reation conditions (unless otherwise noted): **1** (0.25 mmol), **2a** (0.375 mmol), $FeCl_2$ (0.025 mmol), Na_2CO_3 (0.5 mmol), $CsOH{\cdot}H_2O$ (1.25 mmol), $CHCl_3$ (0.75 mmol), NaI (0.125 mmol), PivOH (0.375 mmol), PEG-400 (2 mL), 120 °C. [a] No PivOH at 140 °C. [b] KOAc (20 mol%) instead of PivOH. [c] PivOH (0.5 equiv).

significant electronic effects were observed for *meta*- and *para*-substituted potassium aryltrifluoroborates; the rates and yields of reactions were comparable. Even the sterically hindered potassium 2-methylphenyltrifluoroborate (**2d**) and potassium 2-methoxyphenyltrifluoroborate (**2e**) provided the desired biaryl ketones in 60% (**3gd**) and 77% (**3ge**) yields, respectively. It is noteworthy that the particular reactive hydroxyl group remained intact in the catalytic system (**3gg**). Potassium naphthalene-2-trifluoroborate (**2l**) was found to be a good coupling partner. Also potassium aryltrifluoroborates bearing heterocyclic or acyclic amide moieties, even including secodary amides underwent successful coupling with isolated yields of 87%, 85%, 75%, 80%, and 75% (**3gm-3gq**).

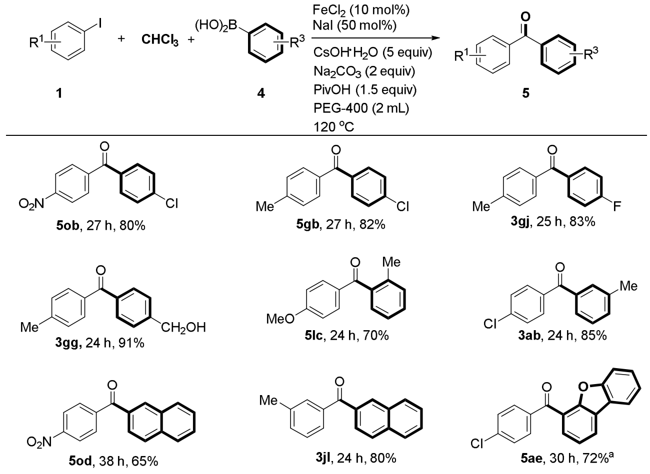
Extension of this carbonylation process to arylboronic acids has yielded promising results (Scheme 3). Interestingly, aryl iodides having electron-withdrawing substituents (NO_2, CN, F, Cl, and CF_3), prone to Suzuki-Miyaura coupling to give biaryls, underwent highly selective carbonylation coupling to provide the desired products in satisfactory yields (**5oa**, **3ba**, **3fa**, **3ca**, and **3aa**). In addition, the presence of a free acid did not compete with the efficacy of the carbonylation event (**5pa**). The introduction of a substituent in *ortho*-position of the aryl iodide had negligible impact on the observed yields (**3ia** and **5qa**). 1-Iodonaphthalene and heteroaromatic aryl iodides could also be employed and gave much higher yields than those of potassium aryltrifluoroborate (**3na 3ma**, and **5sa**). As shown in Scheme 4, a host of arylboronic acids could be equally accommodated in good yields. The electronic nature of the arylboronic acid had little impact on the outcome of the present transformation. Arylboronic acid featuring a free hydroxyl group was smoothly carbonylated (**3gg**). Also naphthalene-2-boronic acid coupled well affording biarylketones in 65% (**5od**) and 80% (**3jl**) yields. Furthermore, the method could be extended to heterocyclic boronic acid (**4e**) when PivOH



Scheme 2 Iron-catalyzed carbonylative Suzuki-Miyaura reaction of aryl iodides **1** with various potassium aryl trifluoroborates **2**. Reation conditions (unless otherwise noted): **1** (0.25 mmol), **2** (0.375 mmol), $FeCl_2$ (0.025 mmol), Na_2CO_3 (0.5 mmol), $CsOH{\cdot}H_2O$ (1.25 mmol), $CHCl_3$ (0.75 mmol), NaI (0.125 mmol), PivOH (0.375 mmol), PEG-400 (2 mL), 120 °C.



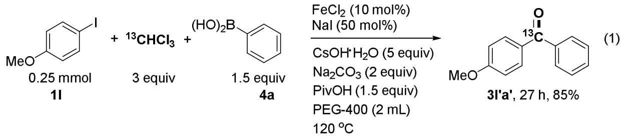
Scheme 3 Iron-catalyzed carbonylative Suzuki-Miyaura reaction of **4a** with various aryl iodides **1**. Reation conditions (unless otherwise noted): **1** (0.25 mmol), **4a** (0.375 mmol), $FeCl_2$ (0.025 mmol), Na_2CO_3 (0.5 mmol), $CsOH{\cdot}H_2O$ (1.25 mmol), $CHCl_3$ (0.75 mmol), NaI (0.125 mmol), PivOH (0.375 mmol), PEG-400 (2 mL), 120 °C. [a] No PivOH, Na_2CO_3 (3equiv), and $CsOH{\cdot}H_2O$ (6.0 equiv). [b] PivOH (0.5 equiv).



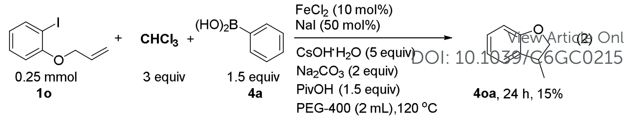
Scheme 4 Iron-catalyzed carbonylative Suzuki-Miyaura coupling of aryl iodides **1** with various arylboronic acids **4**. Reation conditions (unless otherwise noted): **1** (0.25 mmol), **4** (0.375 mmol), $FeCl_2$ (0.025 mmol), Na_2CO_3 (0.5 mmol), $CsOH·H_2O$ (1.25 mmol), $CHCl_3$ (0.75 mmol), NaI (0.125 mmol), PivOH (0.375 mmol), PEG-400 (2 mL), 120 °C. ^{a} No PivOH and KOAc (20 mol%).

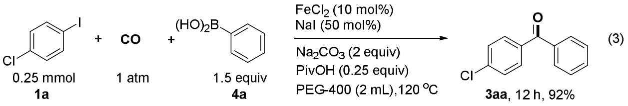
was replaced by KOAc (20 mol%).[19] However, 2-phenylethylboronic acid as an alkyl boronic acid was employed to react with 1-chloro-4-iodobenzene (**1a**) under normal conditions, leading to the desired alkyl aryl ketone in less than 30% yield.

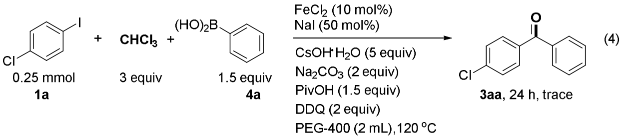
Particularly noteworthy was that the ^{13}C-labeled version could be prepared in a similar yield by simply exchanging chloroform for the commercially available ^{13}C-labeled chloroform, utilizing the identical coupling conditions as in Scheme 3 (**3la**) [eqn (1)].

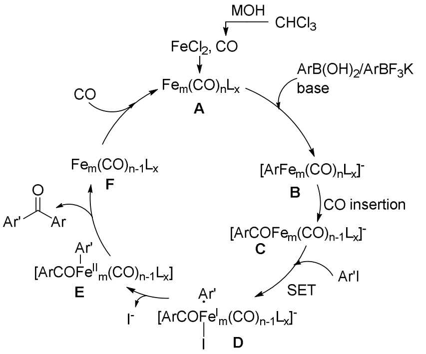


Previous studies reported that the conversion of chloroform to CO can be realized by direct hydrolysis[9-10] or hydrolysis of *in situ* generated intermediate dichlorocarbene[8] in the presence of strongly basic aqueous hydroxide solutions. To check the process of our case, an aryl iodide bearing alkene moiety (**1o**) was subjected to the normal conditions and didn't undergo [2 + 1]-cycloaddition to afford the corresponding cyclopropane[22] [eqn (2)]. Moreover, replacing the both chloroform and $CsOH·H_2O$ with 1 atm of CO resulted in 92% yield of **3aa** [eqn (3)]. These findings imply that intermediate dichlorocarbene can be ruled out in the present reaction. In addition, a single-electron-acceptor DDQ was added into the catalytic system and led to complete suppression of the transformation [eqn (4)]. Furthermore, a radical probe 1-(allyloxy)-2-iodobenzene (**1o**) was employed as aryl iodide and gave a cyclization product, 3-methyl-2,3-dihydrobenzofuran in 15% yield based on GC-MS analysis [eqn (2)].[23] And no any carbonylated product was observed [eqn (2)]. These results suggest that the present carbonylation process involves aryl radical intermediate.[24]









Scheme 5 Proposed reaction mechanism for the iron-catalyzed carbonylation utilizing $CHCl_3$ as CO source.

Based on these observations and previous studies[19,25], the following mechanism can thus be proposed (Scheme 5). Initially, CO is released from $CHCl_3$ in the presence of hydroxide base. Then, $Fe_m(CO)_nL_x$ (**A**) is formed *in situ* from $FeCl_2$ with CO under normal conditions.[19,26] A highly nucleophilic organoiron complex **B**[19,27] is generated through an addition reaction of **A** and arylboron with the assistance of base and further undergoes intramolecular CO migratory insertion to give organoiron complex **C**. Subsequently, **C** proceeds with S_NR1 type oxidative addition with aryl iodide to afford organoiron complex **D**.[18-19] Finally, reductive elimination of **E** provides the desired biarylketone product and the catalytically active **A** is regenerated in CO atmosphere.

In summary, we have documented an unprecedented iron-catalyzed carbonylative Suzuki-Miyaura coupling utilizing stoichiometric $CHCl_3$ as the CO precursor to deliver a range of synthetically useful biaryl ketones in good to excellent yields with high selectivities. This protocol employs readily available and easy to handle catalysts and reagents and exhibits a high degree of practicality. Importantly, the ^{13}C-labeled version could be realized simply by using the commercially available ^{13}C-labeled $CHCl_3$. The efficiency, economy, and operational simplicity of this catalytic system linked with the substrate generality render this method particularly attractive in organic synthesis. Further mechanistic studies and the extension to other carbonylation reactions are currently underway.

Notes and references

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Iron-Catalyzed Carbonylation of Aryl halides with Arylborons Using Stoichiometric Chloroform as the Carbon Monoxide Source

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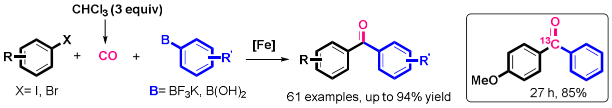

The highly effective iron-catalyzed carbonylative Suzuki-Miyaura coupling using stoichiometric chloroform as the CO precursor has been developed.