Iodide-Catalyzed Carbonylation–Benzylation of Benzyl Chlorides with Potassium Aryltrifluoroborates under Ambient Pressure of Carbon Monoxide

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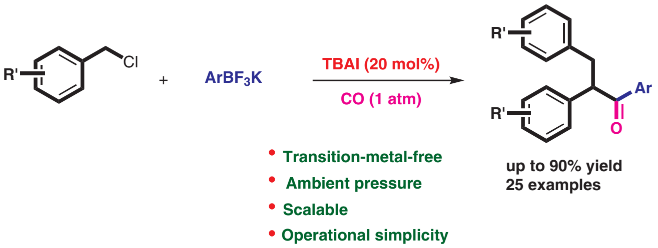

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Abstract Tetra-*N*-butylammonium iodide (TBAI) catalyzed carbonylation–benzylation of unactivated benzyl chlorides with potassium aryltrifluoroborates using CO gas has been developed. This reaction is transition-metal free, is carried out under ambient pressure, and provides a wide range of 1,2,3-triarylpropan-1-one derivatives in high yields. The novel method represents a significant improvement over the traditional palladium-catalyzed carbonylation.

Key words benzyl chlorides, carbonylation, potassium aryltrifluoroborates, radicals, synthetic methods

The three-component coupling of organohalide, organoborane reagent, and carbon monoxide, which is generally referred to as the carbonylative Suzuki reaction,[1] is a powerful synthetic tool for the construction of ketones, which is an important moiety in numerous natural products, pharmaceuticals, photosensitizers, and advanced organic materials.[2] This transformation has become one of the best-known palladium-catalyzed carbonylation reactions over the last few decades owing to its reagent stability, high functional group tolerance, efficiency, and reliability.[3] In contrast to the carbonylative Suzuki coupling of aryl halides that is well-established,[4] the efficient catalytic systems for the carbonylations of alkyl or benzyl halides have been sparsely reported. This is because C(sp^3) halides are more reluctant to undergo oxidative addition to Pd^0 than their unsaturated analogues.[5] Miyaura et al. first reported only two examples of $PdCl_2(PPh_3)_2$-catalyzed carbonylative coupling of benzyl bromide with arylboronic acid.[6] Subsequently, a more systematic study conducted by the Beller group involved $Pd(OAc)_2/PCy_3$-catalyzed-catalyzed carbonylative Suzuki reactions of benzyl chlorides with arylboronic acids under 10 bar of CO gas.[7] Recently, α-halomethyl oxime ethers were employed to couple with arylboronic acids at atmospheric pressure of CO gas and in the presence of $Pd(PPh_3)_4$ (10 mol%) as catalyst.[8] However, these palladium-based catalysts have several limitations: (1) high cost and low abundance of Pd (1×10^{-6} wt% in the earth crust), (2) sensitive to air and moisture, (3) problems with residual metal in products, and (4) deactivation of Pd catalyst (CO is a strong π-acidic ligand).[9] Therefore, the development of an efficient and practical strategy devoid of metal catalysts is a highly desirable and important challenge.[10]

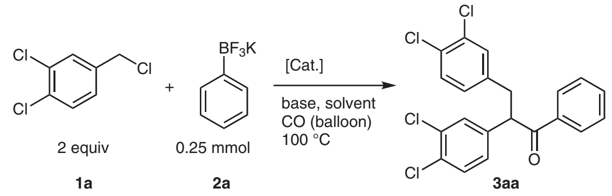
Although transition-metal-free processes for the carbonylation of organohalides (or pseudo-halides) by utilizing CO gas have been reported,[11] most of them are limited to radical alkoxycarbonylation of aryl halides (or pseudo-halides).[11a–c] Recently, we reported the first example of transition-metal-free carbonylative Suzuki coupling of aryl halides with potassium aryltrifluoroborates under ambient pressure.[11d] Based on this work, we further developed an unprecedented iodide-mediated radical carbonylation–benzylation of benzyl chlorides with arylboronic acids.[11e] Unfortunately, this method is ineffective for organotrifluoroborate reagents.

Organotrifluoroborates have been employed in many contexts as an advantageous alternative to boronic acids and boronate esters.[12] These organoboron species are immune to reactions with important classes of reagents (e.g., oxidants, bases, and nucleophiles) commonly utilized in organic synthesis owing to their tetracoordinate nature. Thus, organotrifluoroborates, superior to most other boron species, carry through synthetic operations to build molecular complexity, while leaving the carbon–boron bond intact. This expands the range of synthetic approaches available to target molecules of interest. Although organotrifluoroborates possess these benefits mentioned above, reports of the carbonylation of these species to give the corresponding carbonyl compounds are severely limited.[11d,13] To our knowledge, only one example of carbonylative Suzuki coupling of C(sp^3) halides with potassium aryltrifluoroborates has been reported,[13a] albeit air-sensitive palladium catalyst and high pressure of CO gas were required.

Here, we report a transition-metal-free, iodide-catalyzed radical carbonylation–benzylation of benzyl chlorides with potassium aryltrifluoroborates under ambient pressure of CO gas.[14,15] This process addresses the problems of Pd-based catalysis as well as the limitation of our previous iodide-mediated carbonylation.[11e] Notably, this transformation provides a step-economic, inexpensive, and operationally simple method for the construction of the 1,2,3-triarylpropan-1-one motif in known pharmaceuticals and biologically active compounds.[16]

Our investigation into this new carbonylative coupling reaction began with exposure of 1,2-dichloro-4-(chloromethyl)benzene (**1a**) and potassium phenyltrifluoroborate (**2a**) to a variety of conditions (Table 1). In initial experiments, we used similar reaction conditions to those under which the iodide-catalyzed carbonylative coupling of benzyl chloride with phenylboronic acid proceeded well (80% yield).[11e] However, the present reaction delivered the product **3aa** in just 31% yield (entry 1). This difference may be caused by the increased stability of PhBF$_3$K.[13a]

Table 1 Optimization of Reaction Conditions[a]



1a **2a** **3aa**

Entry	[Cat.] (%)	Base	Solvent	Yield of **3aa** (%)[b]
1	NaI (15)	Na_3PO_4	PEG-400	31
2	TBAI (15)	Na_3PO_4	PEG-400	78
3[c]	THAI (15)	Na_3PO_4	PEG-400	35
4	KI (15)	Na_3PO_4	PEG-400	59
5	TBAI (20)	Na_3PO_4	PEG-400	81
6	–	Na_3PO_4	PEG-400	–
7	TBAI (20)	Na_2CO_3	PEG-400	88
8	TBAI (20)	Li_2CO_3	PEG-400	5
9	TBAI (20)	K_2CO_3	PEG-400	25
10	TBAI (20)	Cs_2CO_3	PEG-400	trace
11	TBAI (20)	$NaHCO_3$	PEG-400	86
12	TBAI (20)	$KHCO_3$	PEG-400	5
13	TBAI (20)	K_2HPO_4	PEG-400	trace
14	TBAI (20)	NaH_2PO_4	PEG-400	trace
15	TBAI (20)	KF	PEG-400	trace
16[d]	TBAI (20)	DBU	PEG-400	trace
17	TBAI (20)	Na_2CO_3	Glycol	trace
18	TBAI (20)	Na_2CO_3	DMF	35
19	TBAI (20)	Na_2CO_3	H_2O	25

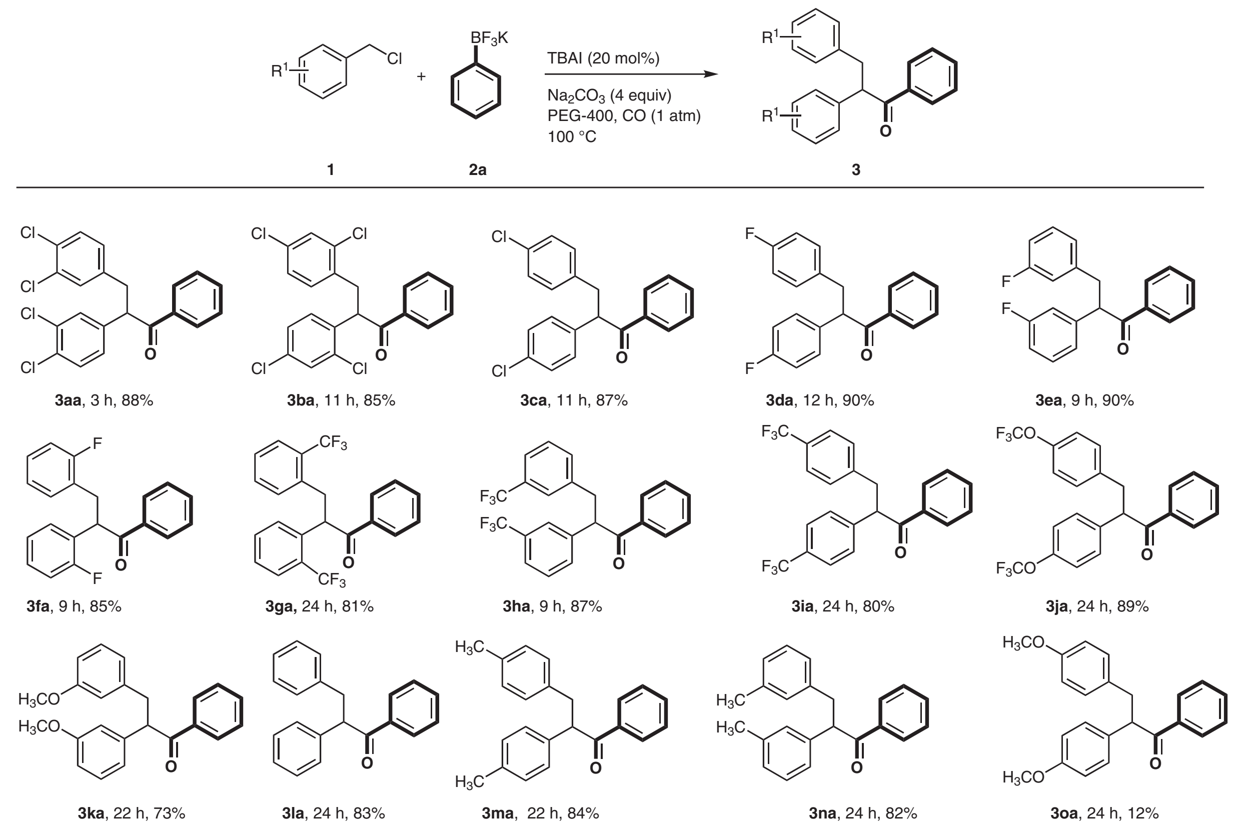
[a] Reaction conditions (unless otherwise stated): **1a** (0.5 mmol), **2a** (0.25 mmol), CO (1 atm), base (1.0 mmol), solvent (2.0 mL), 100 °C, 3 h.
[b] Yield of isolated product.
[c] THAI (tetraheptylammonium iodide).

Gratifyingly, the use of tetra-*N*-butylammonium iodide (TBAI) as catalyst increased the yield dramatically (78%; Table 1, entry 2). Raising the amount of catalyst to 20 mol% further improved the yield of **3aa** (entry 5). However, replacing TBAI with THAI or KI as the catalyst resulted in much lower yields (entries 3 and 4). The choice of base was crucial for this reaction. Among the tested bases, Na_2CO_3 was optimal, yielding 88% **3aa** (entry 7). None of the other solvents tested (glycol, DMF, and H_2O) could replace PEG-400 (entries 17–19).

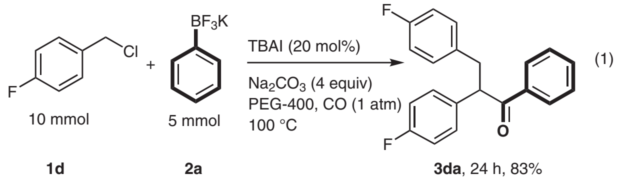
With the above optimized conditions, the TBAI-catalyzed carbonylation-benzylation of a range of benzyl chlorides was tested.[17] Generally, good to excellent yields and selectivities were observed under ambient pressure of CO (Scheme 1). The dichloro- and chloro- substituted benzyl chlorides underwent successful coupling with isolated yields of 88, 85, and 87% (**3aa**–**ca**), respectively. In a similar manner, benzyl chlorides bearing fluoro or trifluoromethyl substituents were also competent substrates, irrespective of the position of these groups on the phenyl ring (**3da**–**ia**). Furthermore, substrates having electron-donating groups such as trifluoromethoxy, methoxy, and methyl worked well with **2a** to generate the corresponding products in excellent yields (**3ja**–**ka** and **3ma**–**na**). However, 4-methoxylbenzylchloride proved to be unreactive (**3oa**).

Subsequently, a series of potassium aryltrifluoroborates were investigated. Potassium aryltrifluoroborates bearing electronically neutral, deactivated, and activated cases efficiently coupled with typical benzyl chlorides under normal conditions (Scheme 2). No significant electronic effects were observed for *meta*- and *para*-substituted potassium aryltrifluoroborates. Even the sterically hindered potassium 2-methoxyphenyltrifluoroborate also reacted well in this carbonylation, affording the expected product **3lf** in 71% yield. Moreover, the method can move beyond the simple aryl group. Specifically, potassium naphthalen-2-yltrifluoroborate underwent successful coupling with electron-poor, electron-neutral, and electron-rich benzyl chlorides. Potassium aryltrifluoroborate, having a strong electron-withdrawing group, undertook this reaction with lower efficiency (**3mi**).

To further demonstrate the utility of this method, the present procedure was amenable to a gram-scale reaction. Thus, starting from 10.0 mmol of **1d** and 5.0 mmol of **2a**, 1.31 g of **3da**, which is a potentially useful intermediate for the synthesis of pharmaceuticals and organic materials, was obtained, which corresponds to a yield of 83% (Equation 1).

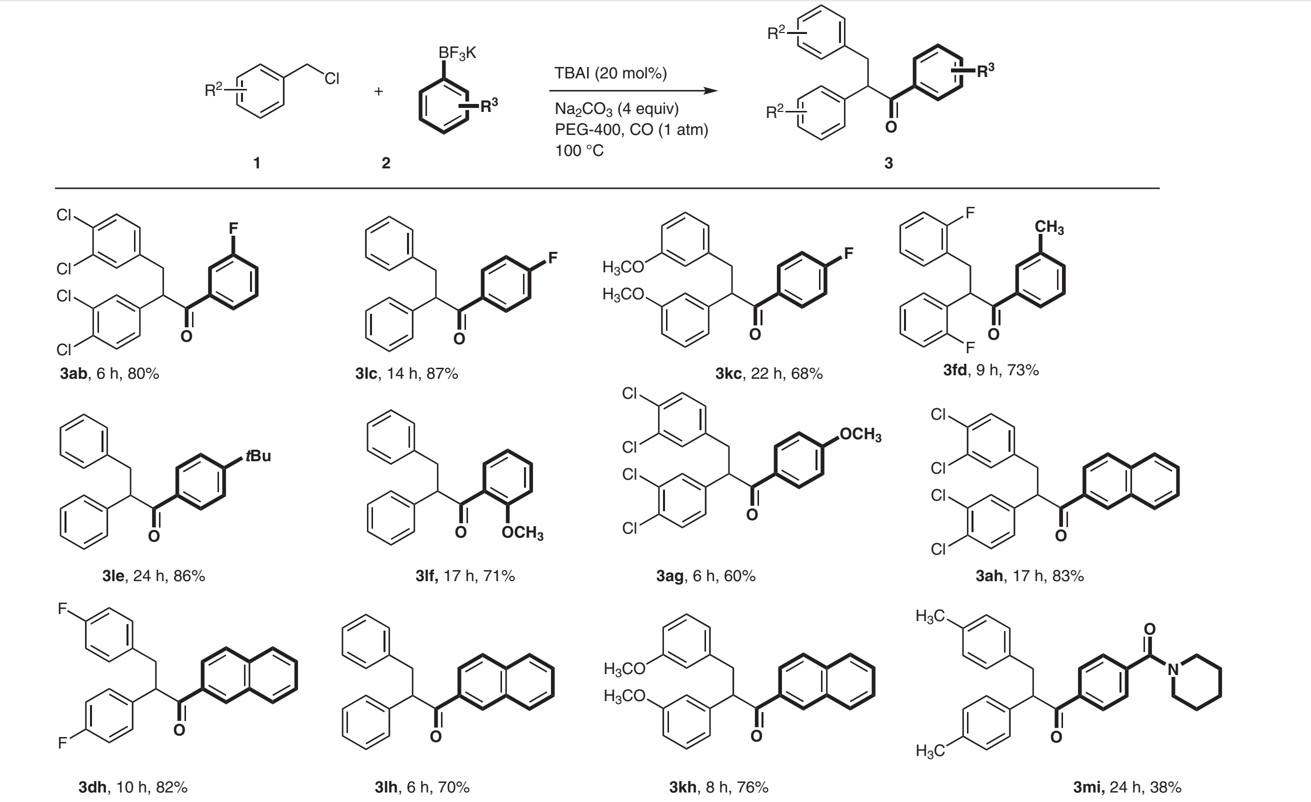


Scheme 1 TBAI-catalyzed carbonylation–benzylation reactions of **2a** with various benzyl chlorides. *Reagents and conditions*: **1** (1.0 mmol), **2a** (0.5 mmol), CO (1 atm), Na$_2$CO$_3$ (1.0 mmol), PEG-400 (2.0 mL), 100 °C. Yields of the isolated products are given.



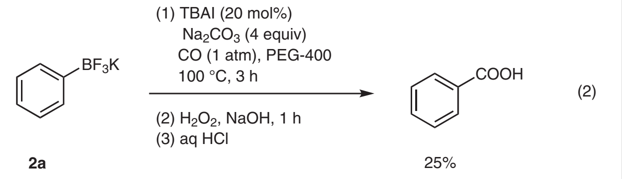
Equation 1

It had been suggested that carbonylative reaction of alkyl halide and arylboronic acid would proceed through a radical mechanism.[14d,11e] To check the involvement of this process in the present transformation, several control experiments were carried out. A single-electron-acceptor 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was used, which led to complete inhibition of the model reaction (Scheme 3a). Furthermore, we also attempted to employ a free-radical scavenger galvinoxyl to trap a radial intermediate; however, the reaction with the galvinoxyl did not result in the generation of product **3aa**. Alternatively, benzylated galvinoxyl **3′** was obtained (Scheme 3b), which suggests the existence of the benzyl radical intermediate in the reaction. The role of iodide was proposed to initiate the reaction through halogen exchange with a benzyl chloride to give a key intermediate benzyl iodide.[11e] Subsequently, the benzyl iodide underwent thermal decomposition to afford benzyl free-radical.[18] A benzyl iodide **1a′** took the place of **1a** to react with **2a** under normal conditions except that no TBAI was added to give **3aa** in 89% yield (Scheme 3c), a comparable result with the model reaction. In addition, the temperature had a decisive effect on the model reaction: a lower temperature (50 °C) resulted in no conversion of **1a** and, under the same conditions, the free-radical scavenger galvinoxyl also did not intercept the benzyl radical. These results support the presence of benzyl iodide intermediate and the process of thermal decomposition of it in the reaction. A carbonylated product benzoic acid (25% yield) was obtained when the model reaction was performed in the absence of **1a** (Equation 2), while in the absence of **2a** no carbonylated product was observed (Equation 3) under normal conditions, implying that the carbonylation process starting from aryltrifluoroborate is reasonable. Besides these, under the standard conditions, 10–15% of 2-(3,4-dichlorophenyl)-1-phenylethan-1-one (according to GC-MS analysis) was observed throughout the model reaction; its concentration decreasing only toward the end of the carbonylation reaction. This result can be rationalized by a reaction sequence of in situ TBAI-catalyzed conversion of **1a**

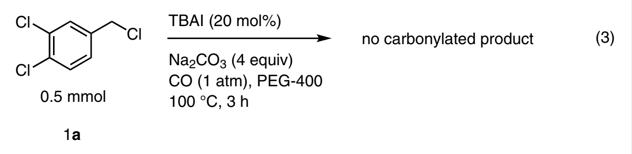


Scheme 2 TBAI-catalyzed carbonylation–benzylation reactions of **1** with **2**. *Reagents and conditions*: **1** (1.0 mmol), **2** (0.5 mmol), CO (balloon), Na_2CO_3 (1.0 mmol), PEG-400 (2.0 mL), 100 °C. Yields of the isolated products are given.

into 2-(3,4-dichlorophenyl)-1-phenylethan-1-one followed by benzylation of the resulting ketone to give the desired product.

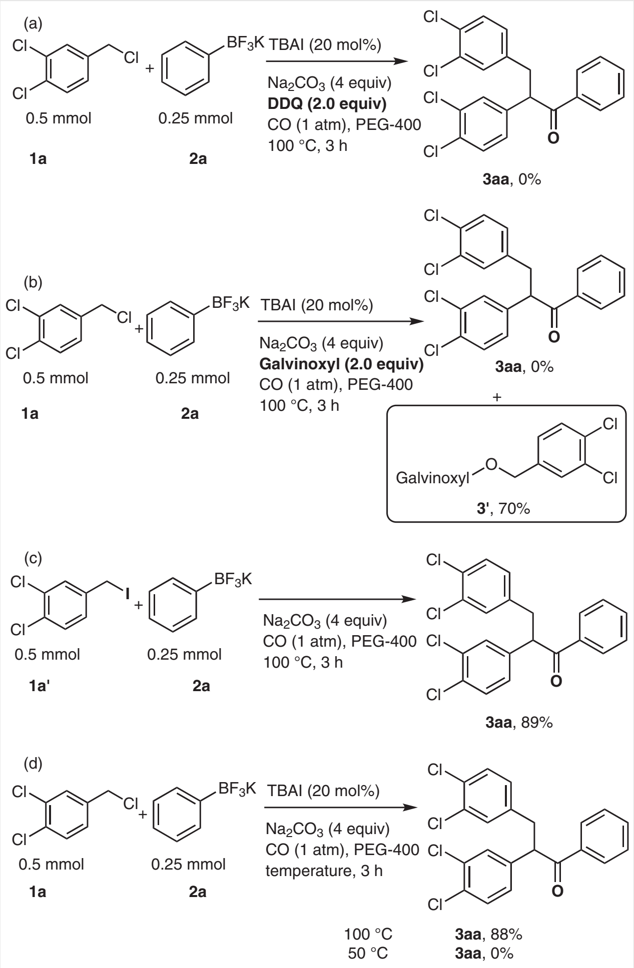


Equation 2



Equation 3

Combining all the results mentioned above and previous studies,[14d,11e,19,20] we propose a mechanism for this TBAI-catalyzed carbonylation/benzylation reaction (Scheme 4). This reaction was initiated by potassium aryltrifluoroborate reacting with carbon monoxide to generate a carbonylated species **II**, followed by carbonyl 1,2-migration insertion,[19] leading to a key intermediate **III**. Then, a carbonylated intermediate **IV** was formed by the insertion of carbon monoxide into **III**.[19] Benzyl chloride **V** underwent halogen exchange with iodide to give a benzyl iodide **VI**, which can thermally decompose into a benzyl free radical **VII** and an iodine free radical.[18] Subsequently, the active free radical **VII** was trapped by intermediate **IV** to provide 1,2-diarylethanone intermediate **IX** along with [$BCOF_3K$] radical anion species **VIII**. Benzylation of **IX** would give the desired product **X** and the species **VIII** undertook single-electron transfer with an iodine free radical to regenerate iodide anion, which would re-enter the catalytic cycle.



Scheme 3 Control experiments conducted to probe the mechanism

In summary, we have developed the first examples of transition-metal free carbonylations of unactivated benzyl chlorides with stable potassium aryltrifluoroborates under ambient pressure of CO gas. This method represents a significant improvement over the previous palladium-catalyzed carbonylation: the catalyst TBAI is abundant, inexpensive, and bench stable, the reaction conditions are much milder, and the use of ligands and the costly need to remove residual palladium from the end products are avoided. In consequence, this protocol provides an inexpensive and operationally simple method for the preparation of 1,2,3-triarylpropan-1-ones.

Funding Information

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591502.

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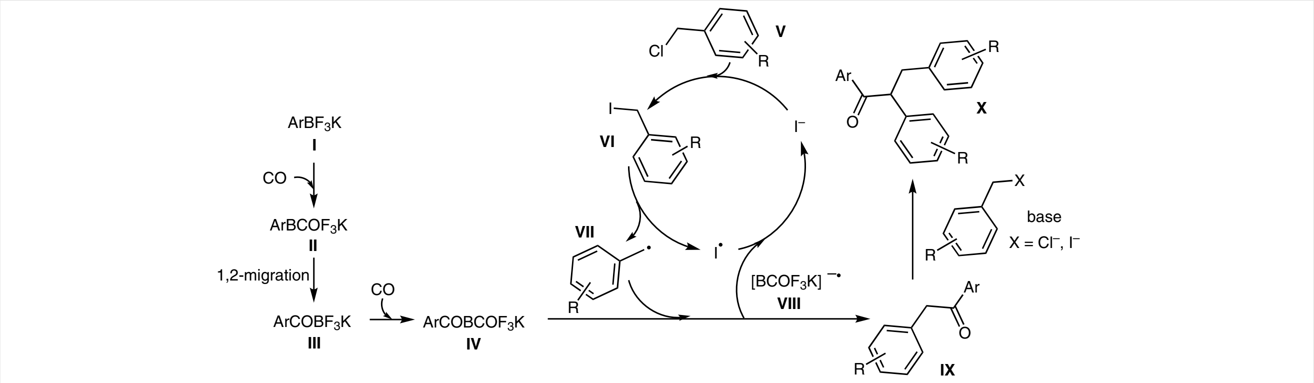

Scheme 4 Proposed mechanism for the catalysis

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(17) **Typical Procedure for the Synthesis of 3aa**: A 25 mL flask equipped with a magnetic stir bar was charged with potassium phenyltrifluoroborate **2a** (0.5 mmol, 94.9 mg), TBAI (0.1 mmol, 37.6 mg), Na_2CO_3 (2.0 mmol, 213.0 mg), and PEG-400 (2 mL) before standard cycles of evacuation and back-filling with anhydrous and pure carbon monoxide. Benzyl chloride **1a** (1.0 mmol, 141.4 μL) was added successively. The mixture was then stirred at 100 °C for 3 h. After being allowed to cool to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with diethyl ether (4 × 5 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum ether/diethyl ether, 100:1) to afford **3aa** (185.7 mg, 88%) as a white solid (mp 119.6–120.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.83 (m, 2 H), 7.49 (tt, J = 7.4, 1.2 Hz, 1 H), 7.39–7.32 (m, 4 H), 7.24 (d, J = 8.2 Hz, 1 H), 7.20 (d, J = 2.0 Hz, 1 H), 7.04 (dd, J = 8.3, 2.1 Hz, 1 H), 6.87 (dd, J = 8.2, 2.1 Hz, 1 H), 4.70 (t, J = 7.3 Hz, 1 H), 3.45 (dd, J = 13.8, 7.6 Hz, 1 H), 2.96 (dd, J = 13.8, 7.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 139.2, 138.5, 135.9, 133.5, 133.2, 132.3, 131.8, 131.0, 130.9, 130.6, 130.3, 129.9, 128.8, 128.6, 128.6, 127.6, 54.4, 39.0

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