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Pd/Cu-Catalyzed amide-enabled selectivity-reversed borocarbonylation of unactivated alkenes†

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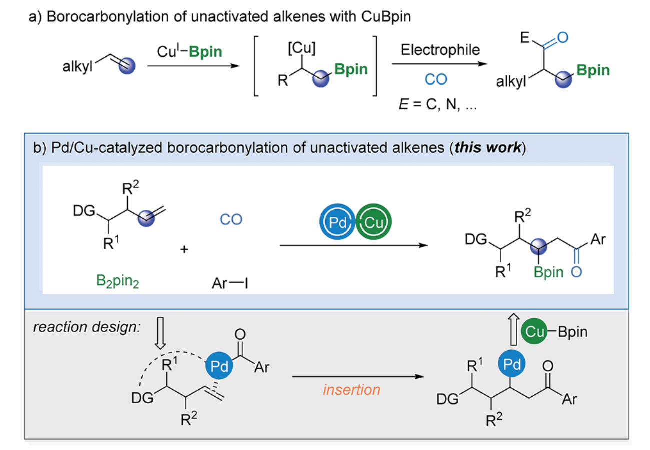
The addition reaction between CuBpin and alkenes to give a terminal boron substituted intermediate is usually fast and facile. In this communication, a selectivity-reversed procedure has been designed and established. This selectivity-reversed borocarbonylation reaction is enabled by a cooperative action between palladium and copper catalysts and proceeds with complete regioselectivity. The key to the success of this transformation is the coordination of the amide group and slower CuBpin formation by using $KHCO_3$ as the base. A wide range of β-boryl ketones were produced from terminal unactivated aliphatic alkenes and aryl iodides. Further synthetic transformations of the obtained β-boryl ketones have been developed as well.

The catalytic borocarbonylation of alkenes represents a novel synthetic tool for the simultaneous installation of boron and carbonyl groups across alkenes, enabling rapid construction of molecules with high complexity from abundant alkenes. In particular, the obtained organoboron compounds are versatile synthetic intermediates that can be readily converted into a wide range of functional groups with complete stereospecificity.[1] Consequently, several catalytic systems have been developed to diversify the molecular frameworks through carbonylative borofunctionalization.[2] In general, carbonylative borofunctionalization of alkenes proceeds *via* an alkyl-copper intermediate, which was produced by the addition of CuBpin to the terminal position of the alkene starting material,[3] followed by CO insertion and other related steps. A new C–B bond is formed at the terminal position of the alkene and a carbonyl group has been installed at the β-position simultaneously (Scheme 1a). However, in contrast to the progress in the borocarbonylation, a selectivity-reversed procedure (the boryl group is installed at the internal position) to give β-boryl ketone products is still unprecedented.

Recently, several attractive strategies have emerged for the borofunctionalization of unactivated alkenes to give β-boryl products.[4–7] In 2015, Fu, Xiao and their co-workers established a copper-catalyzed regiodivergent alkylboration of alkenes.[4a] In the same year, Miura and Hirano's group reported a copper-catalyzed aminoboration of terminal alkenes.[4b] In these two attractive procedures, the regioselectivity was controlled by the ligand applied. More recently, an intermolecular 1,2-alkylborylation of alkenes was described by Ito's research group.[5] A radical-relay strategy was used to achieve the targeted regioselective addition. Furthermore, Engle and co-workers explored a palladium-catalyzed 1,2-carboboration and -silylation reaction of alkenes.[6] Stereocontrol can be achieved in this new procedure with the assistance of a chiral auxiliary which is a coordinating group in this case.

Inspired by these pioneering studies, we assumed that if the reaction could be initiated by the insertion of an acylpalladium



Scheme 1 Strategies for borocarbonylation of activated alkenes.

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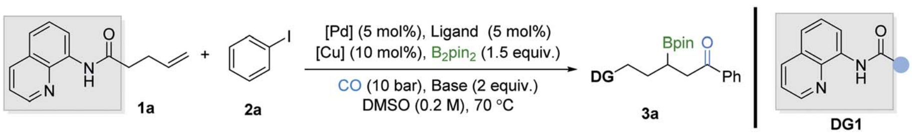
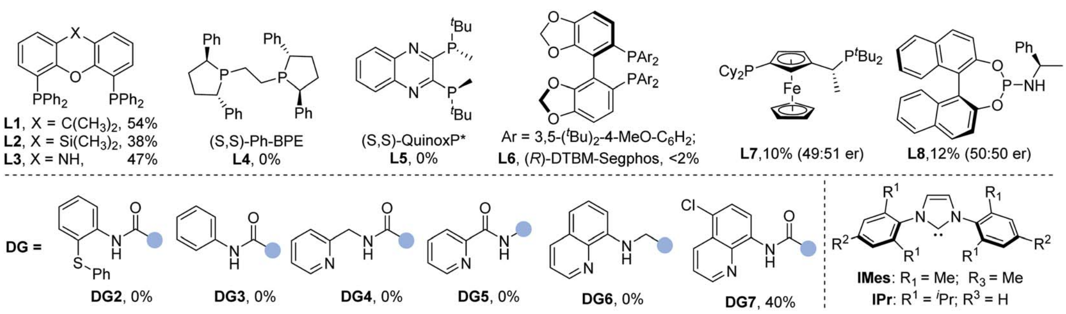
complex into alkenes, followed by transmetalation with CuBpin before reductive elimination, β-boryl ketones can finally be produced (Scheme 1b). However, due to the inherent reactivity of the palladium species toward alkenes, olefin substrates were usually restricted to styrenes and a large excess of them is typically required (>6 equivalents).[8,9] Therefore, the critical part of the reaction design is to promote the reaction of the acyl-palladium intermediate with alkenes faster than the insertion of CuBpin into olefins. One of the ideas is taking advantage of the coordinating group to transform the reaction from intermolecular to intramolecular. Among the developed directing groups,[10] 8-aminoquinoline (AQ) is interesting and has been relatively well studied by various groups in a number of novel transformations.[11–13] Although the AQ directing group contains a NH group which can participate in intramolecular C–N bond formation,[14] we believe that the selectivity-reversed borocarbonylation of alkenes can potentially be achieved through cooperative Pd/Cu catalysis. Then, valuable β-boryl ketones can be produced from readily available substrates directly and effectively.

To test the viability of our design on selectivity-reversed borocarbonylation of alkenes, *N*-(quinolin-8-yl)pent-4-enamide (**1a**), iodobenzene (**2a**), and bis(pinacolato)diboron (B_2pin_2) were chosen as model substrates for systematic studies. As shown in Table 1, by using IMesCuCl and $Pd(TFA)_2$ as the co-catalyst system, xantphos **L1** as the ligand and K_2CO_3 as the

Table 1 Optimization of the reaction conditions[a]



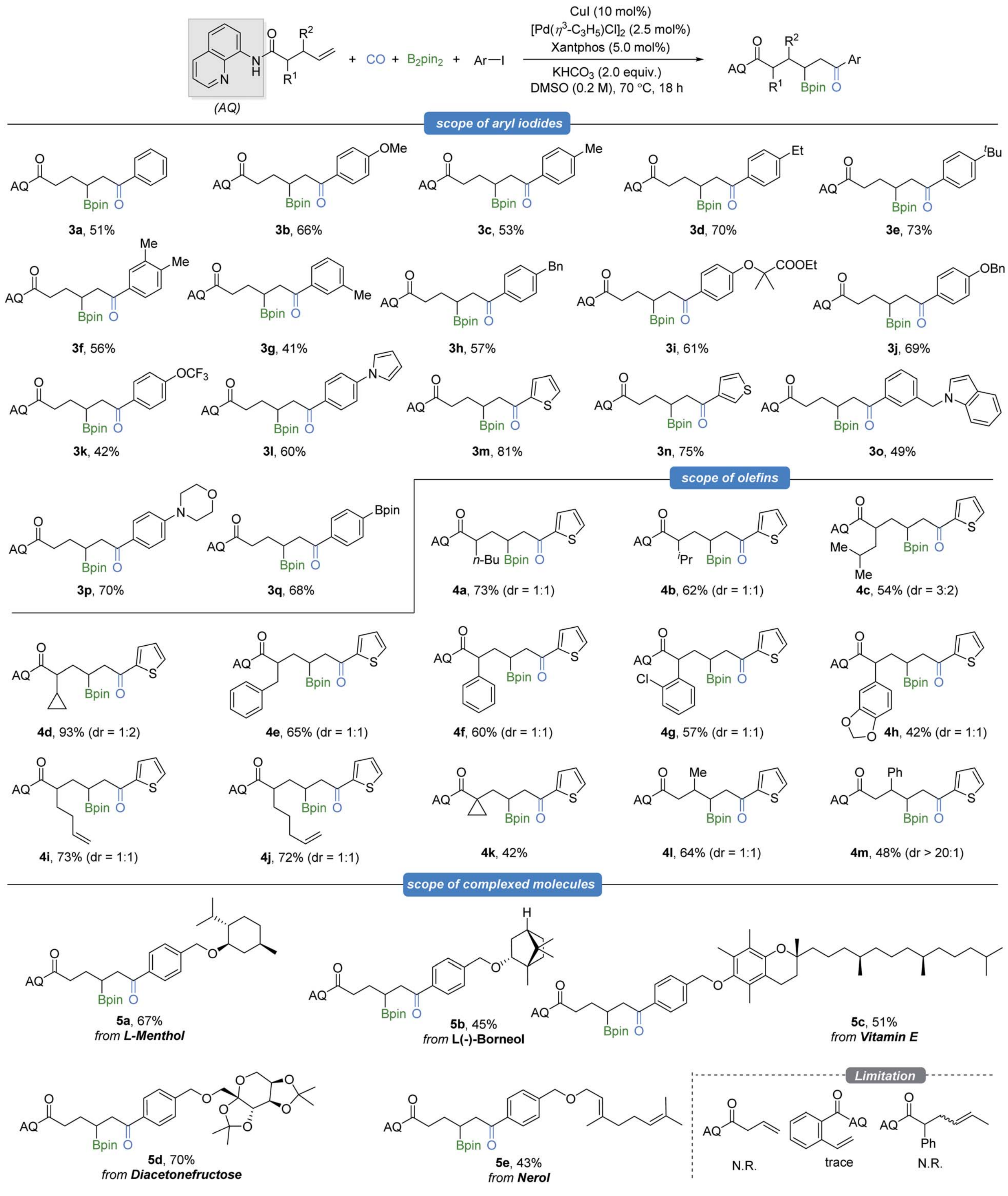
Entry	[Pd]	Ligand	Cu	Base	Yield of 3a (%)
1	$Pd(TFA)_2$	**L1**	IMesCuCl	K_2CO_3	29
2	$Pd(OAc)_2$	**L1**	IMesCuCl	K_2CO_3	34
3	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	IMesCuCl	K_2CO_3	41
4	$[Pd(cinnamyl)Cl]_2$	**L1**	IMesCuCl	K_2CO_3	36
5	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	IPrCuCl	K_2CO_3	0
6	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	CuCl	K_2CO_3	33
7	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	CuBr	K_2CO_3	41
8	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	CuI	K_2CO_3	50
9	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L2**	CuI	K_2CO_3	38
10	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L3**	CuI	K_2CO_3	47
11	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L4**	CuI	K_2CO_3	0
12	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L5**	CuI	K_2CO_3	0
13	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L6**	CuI	K_2CO_3	<2
14	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L7**	CuI	K_2CO_3	10
15	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L8**	CuI	K_2CO_3	12
16	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	CuI	$KHCO_3$	58 (51)[b]
17	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	CuI	K_2HPO_4	26
18	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	CuI	$NaHCO_3$	0
19	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	CuI	NaO^tBu	11
20[c]	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L1**	CuI	$KHCO_3$	<5
21	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	**L7**	CuI	$KHCO_3$	40



[a] All reactions were carried out on a 0.1 mmol scale with alkene (0.1 mmol) and aryl iodide (2.0 equiv.). Yields were determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] Isolated yield. [c] Xantphos (10 mol%).

base at 70 °C under 10 bar of CO for 18 h, the desired product **3a** can be successfully obtained in 29% yield (Table 1, entry 1). In the reaction mixture, a small amount of *N*-phenyl-*N*-(quinolin-8-yl)pent-4-enamide can be detected due to copper promoted C–N bond coupling.[15] In the testing of palladium precursors, allylpalladium chloride dimer proved to be the best palladium

Table 2 Substrate scope for the synthesis of β-boryl ketones[a]

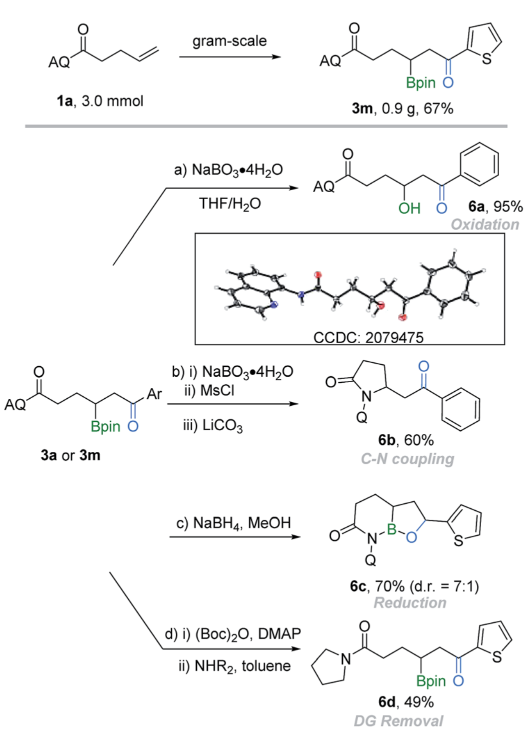


[a] All reactions were carried out on a 0.1 mmol scale. Alkenes (0.1 mmol), aryl iodides (2.0 equiv.), B_2pin_2 (1.5 equiv.), CuI (10 mol%), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol%), xantphos (5 mol%), $KHCO_3$ (2.0 equiv.), CO (10 bar), and DMSO (0.2 M) were stirred at 70 °C for 18 h. The dr value given was determined by ^{1}H NMR.

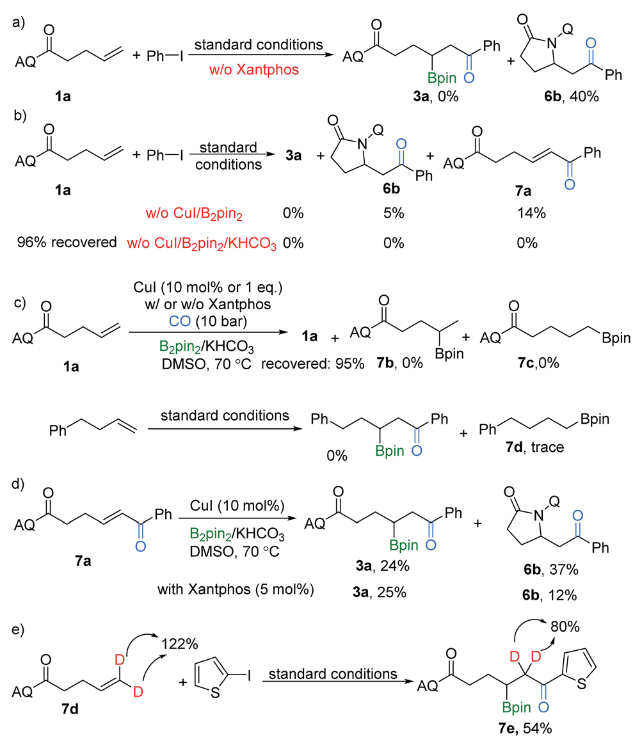
catalyst for this reaction, affording **3a** in 41% yield (Table 1, entries 1–4). Subsequently, we evaluated the influence of copper precursors. The NHC ligand is proved to be unnecessary as copper iodide can give the target product in 50% yield (Table 1, entries 5–8). Various phosphine ligands were studied to examine ligand effects. Monodentate phosphine ligands failed to deliver the desired product **3a** (for details, see the ESI†) and tend to generate the by-product β-aminoketone. Xantphos was found to be superior to the other tested bidentate ligands (Table 1, entries 9 and 10). Commonly used chiral ligands failed to exert any chiral induction (Table 1, entries 11–15). One possibility is that the AQ group was coordinated to palladium at the beginning of the reaction. In the testing of bases, to our delight, weaker base $KHCO_3$ can provide 58% yield of the final product (Table 1, entries 16–19). Increasing the loading of xantphos to 10 mol% inhibited the reaction, indicating that xantphos only coordinates with palladium (Table 1, entry 20). Notably, other directing groups **DG2–DG7** had no positive effect on the reaction outcome. Using *N*-phenyl-*N*-(quinolin-8-yl)pent-4-enamide as the substrate could not give any carbonylation product.

With the optimized reaction conditions in hand, we examined the scope of this selectivity-reversed borocarbonylation with various unactivated alkenes and aryl iodides toward the synthesis of β-boryl ketones (Table 2). Aryl iodides spanning a range of electronic properties were tested for this transformation (**3a–3h**). Functional groups such as ether (**3i** and **3j**), pyrrole (**3l**), thiophene (**3m** and **3n**), indole (**3o**), morpholine (**3p**), Bpin (**3q**) and highly lipophilic group OCF_3 (**3k**) were all compatible with the reaction conditions to produce the target products in moderate to excellent yields. Bromobenzene and 4-bromobenzotrifluoride were also tested in place of iodobenzene, and no desired product could be detected even at increased reaction temperature. Phenyl triflate and alkenyl halides and triflate were tested with the model alkenes as well, and no reaction occurred. However, 87% yield of cinnamic acid was obtained when (*E*)-(2-bromovinyl)benzene was tested under our standard conditions. Subsequently, we evaluated a series of aliphatic alkenes in the reaction with 2-iodothiophene as a representative electrophile. When α-monosubstituted 4-enenoic amides with alkyl, cyclopropyl, benzyl or phenyl substitution were tested, the borocarbonylation reaction occurred smoothly and gave the desired product (**4a–4h**) in moderate to excellent yields, albeit with low diastereoselectivtiy. Notably, monocarbonylative coupling occurred selectively at the γ,δ-C═C bond even when there are two C═C bonds in the amide substrates (**4i** and **4j**). In addition, sterically hindered 4-pentenoic amide was subjected to the optimized reaction conditions, and the corresponding product was formed in 42% yield (**4k**). Furthermore, mono-substitution at the β-position of 4-pentenoic amides could also be employed, affording the corresponding products in moderate yields (**4l** and **4m**). Iodoarenes containing more complex substrates such as L-menthol, L-borneol, vitamin E, diacetonfructose and nerol were also competent substrates and gave moderate to good yields of the corresponding products. Finally, no desired product could be detected when 3-butenoic amide, 2-vinylbenzamide or internal alkene was tested under our standard conditions.

To demonstrate the synthetic utilities of the obtained borocarbonylation products, a series of further synthetic transformations of the β-boryl ketones were performed (Scheme 2).



Scheme 2 Diversification of β-boryl ketones.

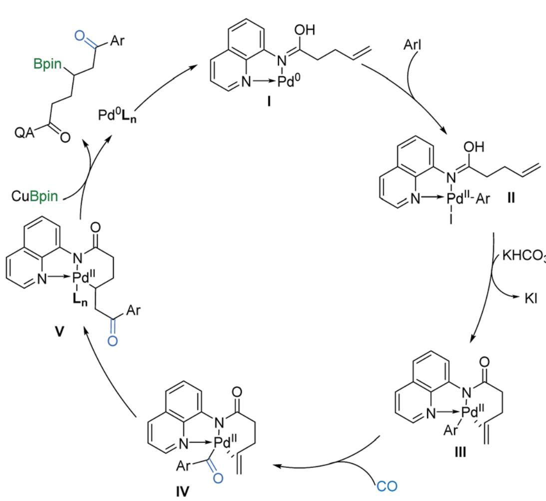


Scheme 3 Control experiments.

From a practical point of view, the reaction can be easily performed on the gram-scale and gave the target product **3m** in 67% yield. β-Hydroxyl ketone **6a** (CCDC: 2079475;† determined by X-ray crystallography and the ORTEP drawing with 50% thermal ellipsoids) was produced in 95% yield by oxidation of the parent β-boryl ketone **3a**. Furthermore, the C–B bond can be easily converted into a C–N bond, affording β-aminoketone **6b** in 60% yield. Upon the reduction reaction of **3m** with $NaBH_4$, the corresponding reduced oxaborole amide **6c** could be isolated in 70% yield. Finally, a two-step transamination process was performed to remove the AQ group.[16]

To gain some insight into the mechanism of this selectivity-reversed borocarbonylation of alkenes, several control experiments were performed. The target product **3a** was not formed, instead byproduct **6b** was obtained in 40% yield, in the case without xantphos. Possible explanations for this result are: (i) the bidentate directing group AQ increases the stability of Pd(II) species and promotes the carbonylation step; (ii) the role of xantphos is to coordinate to C(sp^3)–Pd(II) species after its formation and inhibit the formation of the C–N bond to give byproduct **6b** (Scheme 3a). In addition, copper and B_2pin_2 were proven to be important, and $KHCO_3$ was essential for the carbonylation step (Scheme 3b). Analysis of the copper system in the absence of palladium and iodobenzene revealed that alkenes failed to undergo CuBpin insertion under this condition and no hydroboration products could be detected after work-up (Scheme 3c). Additionally, alkenes without the directing group were also tested under our standard conditions, and no reaction occurred.

Although we did not observe compound **7a** during our optimization and substrate scope processes, even after stopping the reaction after 8 hours, we tested the possibility that **7a** might act as an intermediate. When **7a** was subjected to this transformation, the product **3a** was delivered in 24% yield and **6b** was generated in 37% (Scheme 3d). No significant difference in the yield outcome was observed when xantphos was added. Additionally, in our deuterated substrate testing, the amount of the deuterated product obtained is lower than the theoretical value (Scheme 3e). Thus, a pathway of β-H elimination followed by hydroboration could be involved as well. However, we believe the direct reaction between palladium and copper intermediates is the main one for this procedure due to the proven importance of the AQ group and the known achievements of copper-catalyzed hydroboration of enones, even with enantioselective versions.[17]



Scheme 4 Proposed catalytic cycle.

On the basis of the above results and related literature studies,[7,11–14] a possible reaction pathway is proposed (Scheme 4). Initially, the AQ directing group coordinates with Pd^0, which produces the active AQ-Pd^0 catalyst **I**. This is followed by oxidative addition to aryl iodides to generate Pd^{II} species **II**, and then by base promoted iodine dissociation to form complex **III**. After the CO insertion step, the acyl-Pd^{II} species **IV** coordinates with the alkene and undergoes migratory insertion to generate C(sp^3)–Pd^{II} intermediate **V**, which is stabilized by the xantphos ligand and AQ directing group. Subsequently, C(sp^3)–Pd^{II} complex **V** reacts especially with CuBpin to give the desired product β-boryl ketone and regenerate the Pd(0) complex. Finally, ligand exchange of $Pd^0\mathbf{L}_n$ regenerates AQ-Pd^0 **I** for the next catalytic cycle. Additionally, another minor pathway that involves the carbonylative Heck reaction to give an enone derivative, followed by its hydroboration to give the final product could be included as well.

In summary, a novel Pd/Cu catalyzed amide-directed selectivity-reversed borocarbonylation for the selective synthesis of β-boryl ketones from terminal alkenes has been developed. Various aryl iodides and aliphatic alkenes were transformed into the desired β-boryl ketones in moderate to excellent yields. In this catalyst system, the assistance from the AQ directing group is essential for successful reaction design.

Author contributions

XFW supervised this project and revised the manuscirpt. FPW performed all the experiments and prepared this draft.

Conflicts of interest

There are no conflicts to declare.

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