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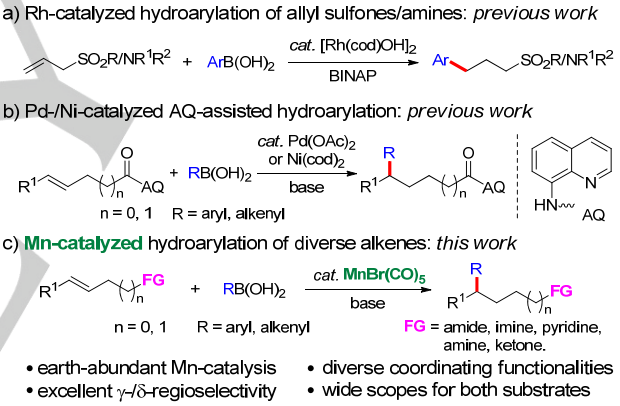
Manganese-Catalyzed Hydroarylation of Unactivated Alkenes

Ting Liu, Yunhui Yang and Congyang Wang*

Dedication to the 100th birthday of Professor Youqi Tang, Peking University.

Abstract: Transition-metal-catalyzed hydroarylation of unactivated alkenes with strategic use of remote coordinating functional groups has received significant attentions recently in order to address the issues of both low reactivity and poor selectivity. A bidentate 8-aminoquinoline amide group is the most successfully adopted in unactivated alkenes for Pd- and Ni-catalysis. Herein, we describe the first manganese-catalyzed hydroarylation of unactivated alkenes bearing diverse simple functionalities with arylboronic acids. A series of δ- and γ-arylated amides, ketones, pyridines, and amines was accessed with excellent regioselectivity and in high yields. Hydroalkenylation of unactivated alkenes was also proved nicely applicable under this manganese-catalysis regime. The protocol features earth-abundant manganese catalysis, easily available substrates, diverse functional group tolerance, and excellent regioselective control.

Alkenes are among the most important building blocks in organic synthesis and can be largely prepared from industry. Transition-metal-catalyzed functionalization of alkenes has emerged as a powerful and practically useful tool kit for efficient construction of C-C bonds.[1] However, precise functionalization such as hydroarylation of unactivated alkenes is far less explored compared with activated alkenes because of the low reactivity and poor selectivity control on the non-biased C=C bond of the unactivated alkenes. Moreover, from a mechanistic perspective, the *in situ* formed C(sp^3)-M intermediates prefer often to undergo β-H elimination and give Heck-type products, which adds further challenges for controlling the desired selectivity. Recently, a novel coordination-assistance strategy has been developed for transition-metal-catalyzed arylative functionalization of unactivated alkenes.[2-6] Great progress has been achieved through prevailing Pd- and Ni-catalysis and a bidentate 8-aminoquinoline (AQ) amide group was commonly adopted to suppress β-H elimination of the intermediate C(sp^3)-M species benefitting from its rigid and bidentate coordination. In a few cases, monodentate coordinating groups were utilized to deliver varied diarylation products of terminal alkenes.[4f-i] Among hydroarylation of unactivated alkenes,[2,7] reactions using arylboronic acids featured readily available substrates, practical ease of handling and well tolerance of functionality. In 2010, Lautens and coworkers realized the Rh-catalyzed hydroarylation of terminal allyl sulfones/amines with arylboronic acids,[2f,2g] where linear hydroarylation products were obtained through β-H elimination/M-H migratory re-insertion mechanism (Scheme 1a). Since 2018, Engle and Zhao have reported Pd- and Ni-catalyzed hydroarylation of unactivated alkenes respectively, both utilizing the bidentate AQ directing groups to stabilize the C(sp^3)-M intermediates (Scheme 1b).[2h-j] In this context, alternative catalytic systems that enable precise hydroarylation of unactivated alkenes bearing diverse functional groups are still in urgent need.



Scheme 1. Transition-metal-catalyzed hydroarylation of unactivated alkenes with boronic acids.

Manganese, as an earth-abundant transition metal, is a potential candidate for new catalyst development in sustainable chemistry.[8] So far, manganese-catalyzed hydroarylation of alkynes via arylmanganese intermediates resulted from either C-H activation of arenes[9] or transmetallation of arylboronic acids[10] has been well developed since 2013. Also, manganese-catalyzed hydroarylation of activated alkenes has been reported since 2014.[11] However, the reactivity of arylmanganese species to unactivated alkenes is surprisingly inert with only one report from our group in 2018,[12] in which an aryl ketone was necessitated to facilitate formation of five-membered manganacycle and the ensuing olefination process with alkenes via intramolecular H-transfer mechanism. As far as we are aware, no manganese-catalyzed hydroarylation of unactivated alkenes has been achieved so far. As our continued efforts on manganese-catalysis, we herein describe the first manganese-catalyzed hydroarylation of unactivated alkenes with boronic acids (Scheme 1c), which features diverse functionalities such

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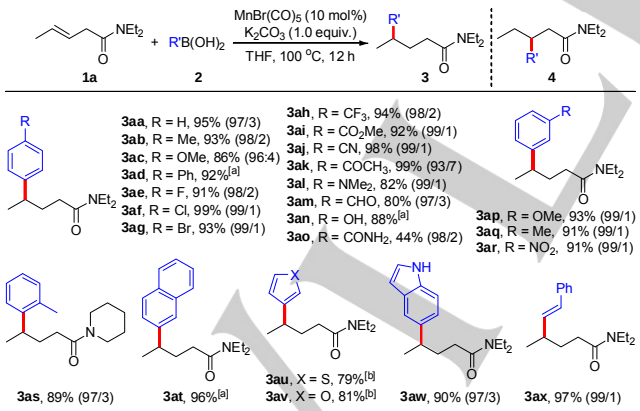
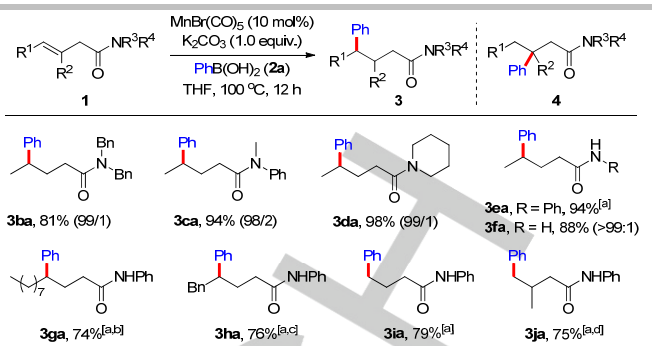
as amide, imine, pyridine, amine, and ketone of unactivated alkenes and excellent γ- or δ-regioselectivity complementary to previous Rh-, Pd- or Ni-catalyzed reactions.

We initiated our study with internal alkene **1a** and phenyl boronic acid **2a** as model substrates. After optimizing the reaction parameters,[13] it turned out that γ-arylative product **3aa** were obtained in 95% isolated yield with excellent regioselectivity under the conditions of $MnBr(CO)_5$ (10 mol%), K_2CO_3 (1.0 equiv.), THF (0.2 M), 100 °C, and 12 h (Scheme 2). Of note, control experiments without manganese catalysts gave no product and the yield of **3aa** decreased to 23% without base. Among bases screened, the potassium ones demonstrated the best performance. In addition, the substrate ratios had no significant influence on the reaction yields. We then explored the substrates scope of aryl boronic acids. Electron-varied substituents on the benzene ring were well tolerated and gave the corresponding products (**3ab**-**ao**) in good yields and excellent regioselectivity. Functional groups like halogens, CF_3, ester, cyano, nitro, ketone, aldehyde, amine, phenol, and amide were compatible and delivered an array of γ-arylated amides successfully, which provided handles for further downstream synthetic modifications. Reactions of *meta*- and *ortho*-substituted arylboronic acids also proceeded with ease (**3ap**-**as**). Naphthyl and heterocyclic boronic acids including furan, thiophene, and indole moiety were all well tolerated (**3at**-**aw**). Of particular note, a representative example of alkenylboronic acid was also applicable successfully and delivered the hydroalkenylation product (**3ax**) in a nearly quantitative yield with excellent regio- and *E*/*Z*-selectivity. Next, the scope of alkenes was investigated using phenylboronic acid (**2a**) as a model reactant (Scheme 3). Alkenes bearing a series of *N*-free and -substituted amide groups were compatible with the reaction conditions and gave the corresponding products with success (**3ba**-**fa**). Other internal alkenes with varied R^1 groups delivered the expected products smoothly (**3ga**, **3ha**). In addition, terminal alkenes and 1,1-disubstituted alkenes were well tolerated in the reaction (**3ia**, **3ja**).

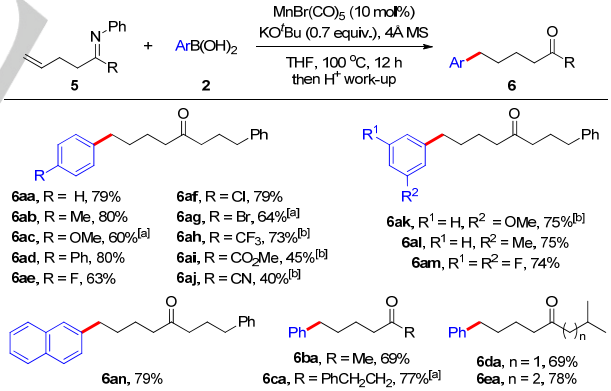


Scheme 2. Scope of boronic acids in γ-selective hydroarylation of alkenes with amide groups. Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), $MnBr(CO)_5$ (0.05 mmol), K_2CO_3 (0.5 mmol), THF (2.5 mL), 100 °C, 12 h. Yields of the isolated products were given. Ratios of **3**/**4** in crude reaction mixture were determined by GC-MS and showed in the parenthesis. [a] The other regio-isomer was not detected by ^{1}H NMR. [b] 36 h.



Scheme 3. Scope of alkenes in γ-selective hydroarylation of alkenes with amide groups. Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), $MnBr(CO)_5$ (0.05 mmol), K_2CO_3 (0.5 mmol), THF (2.5 mL), 100 °C, 12 h. Yields of the isolated products were given. Ratios of **3**/**4** in crude reaction mixture were determined by GC-MS and showed in the parenthesis. [a] The other regio-isomer was not detected by ^{1}H NMR. [b] 16 h. [c] 24 h. [d] 80 °C, 24 h.

To further extend the chemical space of this manganese-based protocol, we tested the reactions of γ,δ-unsaturated imines **5** with arylboronic acids **2** under the similar regime (Scheme 4). It turned out that the reactions worked well and tolerated diverse functional groups on arylboronic acids. Thus, various δ-arylated ketones were delivered successfully after hydrolysis (**6aa**-**aj**). Electron-deficient arylboronic acids seemingly required higher temperature compared with those of electron-rich ones (**6ah**-**aj**). In addition, *meta*-substituted aryl and naphthalen-2-yl boronic acids gave the corresponding products in good yields (**6ak**-**an**). Exemplificative variations of imines proved also fine and the expected δ-arylated ketones were approached without difficulty (**6ba**-**ea**).



Scheme 4. Scope of δ-selective hydroarylation of alkenes with imine groups. Reaction conditions: **5** (0.5 mmol), **2** (1.0 mmol), $MnBr(CO)_5$ (0.05 mmol), KO^{t}Bu (0.35 mmol), 4Å MS (100 mg), THF (2.5 mL), 100 °C, 12 h. Yields of isolated products were given. Other regio-isomers were not detected by ^{1}H NMR. [a] 24 h. [b] 120 °C.

Another three representative functionalities for unactivated alkenes in regio-selective hydroarylation were demonstrated in Scheme 5. The pyridine functionality worked well and the reactions gave the δ-arylated pyridines exclusively in high yields (**8fa**, **8fb**). We then tested the amenability of challenging homoallylic amine **9** bearing simple unprotected amine functionality upon our protocol (Scheme 5b). Fortunately, the linear hydroarylation product **10** was accessed in excellent

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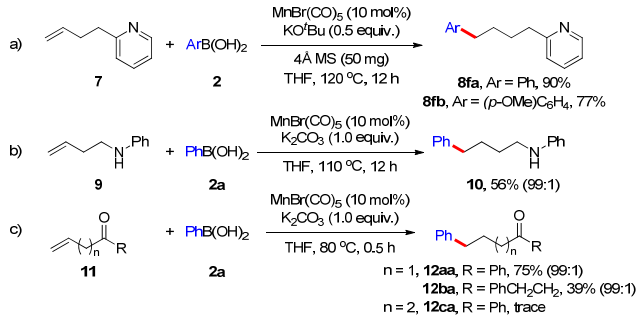
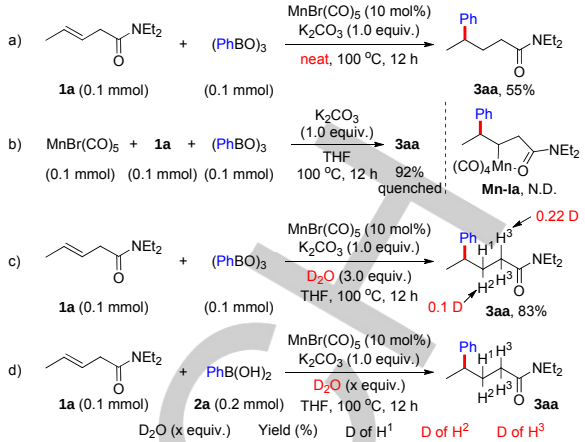
regioselectivity, which was in contrast to those cases using protected amines in Pd-,[2e] Ni-,[5c] and Rh-catalysis[2f]. Simple ketone functionality could also be applied in this manganese-based regime and the expected hydroarylation products **12aa** and **12ba** were afforded successfully from allyl phenyl and alkyl ketone respectively (Scheme 5c). It should be noted that the homoallyl ketone barely gave the corresponding product under the current protocol.



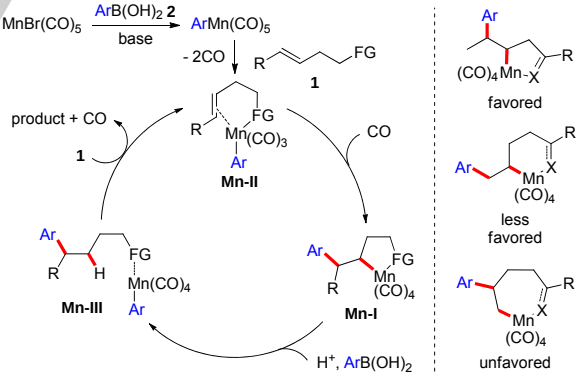
Scheme 5. Alkenes with representative functionalities in manganese-catalyzed hydroarylation. The isolated yields and regioselectivity of reactions were given.

Experiments were further conducted to shed light on the possible reaction mechanism. Firstly, we conducted the reaction of **1a** with $(PhBO)_3$ under neat conditions, and to our surprise, the product **3aa** was formed in 55% NMR yield (Scheme 6a). This result suggested that the possible manganacycle intermediate **Mn-Ia** (vide infra) was susceptible to the small amount of residual water in the reaction system. To further test this, a stoichiometric reaction of $MnBr(CO)_5$, alkene **1a**, and $(PhBO)_3$ was carried out (Scheme 6b). After completion of the reaction, **Mn-Ia** and **1a** were not detected and instead **3aa** was observed in crude NMR analysis, which confirmed our assumption. Then, external D_2O was added to the reaction system and product **3aa** was obtained in higher yield with partial deuteration of H^2 and H^3 (Scheme 6c). Similar results were observed for the reactions using phenylboronic acid **2a** and increasing the amount of D_2O in the reactions led to a higher extent of deuteration on H^2 (Scheme 6d), which suggested the intermediacy of **Mn-Ia**. Of note, the deuteration of H^3 might originate from base-promoted H/D scrambling.[2i]



Scheme 6. Mechanistic experiments. ^{1}H NMR yields and ratios were shown.

A plausible reaction mechanism is depicted in Scheme 7. The reaction starts with the formation of $ArMn(CO)_5$ from $MnBr(CO)_5$ and arylboronic acid **2** with the assistance of base through a transmetallation process.[10] The release of CO ligands and coordination of alkene **1** with $ArMn(CO)_5$ delivers the manganacycle **Mn-II**. Migratory insertion of the olefin moiety into the C-Mn bond in **Mn-II** gives the manganacycle **Mn-I**. The ease of forming different ring sizes of **Mn-I** was speculated to determine the reaction regioselectivity. Protonation and further transmetallation of **Mn-I** with arylboronic acid **2** afford **Mn-III** species, which undergoes a ligand exchange with alkene **1** releasing the hydroarylation product and regenerating the intermediate **Mn-II**.



Scheme 7. A tentative reaction mechanism.

In conclusion, the first manganese-catalyzed hydroarylation of unactivated alkenes with arylboronic acids has been developed through a diverse functionality-coordination strategy. A series of δ- or γ-arylated amides, ketones, pyridines, and amines was accessed in excellent regioselectivity. Hydroalkenylation with olefinic boronic acids was also amenable to this manganese-based protocol. The reactions featured earth-abundant manganese catalysis, easily available substrates, diverse functional group tolerance, and excellent regioselective control.

Further explorations on manganese-catalyzed functionalization of unsaturated hydrocarbons are underway in our laboratory.

Acknowledgements

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Keywords: Manganese • Alkenes • Hydroarylation • Hydroalkenylation • Homogeneous Catalysis

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[13] For details, see the Supporting Information.

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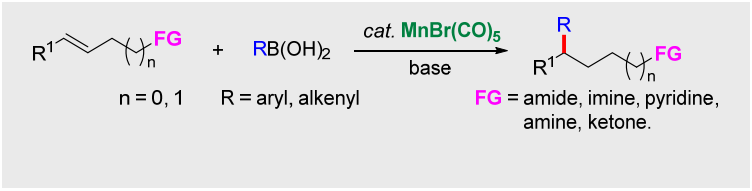
Manganese-Catalyzed Hydroarylation of Unactivated Alkenes



The first manganese-catalyzed hydroarylation of unactivated alkenes bearing diverse simple functionalities with arylboronic acids was developed. A series of δ- and γ-arylated amides, ketones, pyridines, and amines was accessed with excellent regioselectivity and in high yields. Hydroalkenylation with olefinic boronic acids was also amenable to this manganese-based protocol.

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