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Mn(II)/O_2-promoted oxidative annulation of vinyl isocyanides with boronic acids: synthesis of multi-substituted isoquinolines†

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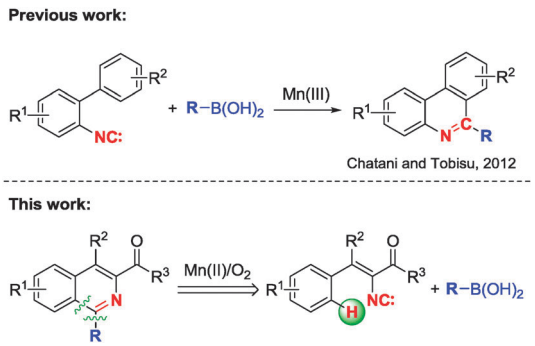
An efficient manganese(II)/O_2-promoted oxidative radical cascade reaction was developed for the modular synthesis of multi-substituted isoquinolines from easily accessible vinyl isocyanides and boronic acids.

The isoquinoline skeleton is one of the most attractive frameworks with a wide range of biological and pharmacological activities, and has been generally recognized as a privileged structure in medicinal chemistry.[1] These compounds are structural units found in a vast array of natural products with different biological activities,[1a,2a] pharmaceutical drugs,[2b] chiral ligands[2c] and important organic materials.[2d] The early synthetic efforts for the construction of the isoquinoline skeleton involve cyclization of functionalized substrates, with an additional dehydrogenation step, at elevated temperature under strongly acidic reaction conditions, such as traditional Bischler–Napieralski,[3a] Pomeranz–Fritsch[3b,c] and Pictet–Spengler[3d] reactions. Furthermore, alternative strategies to construct isoquinoline frameworks have been developed through the transition metal-catalyzed couplings of alkynes with aryl imines,[4a–e] azides,[4f] oximes,[4g] amines,[4h] aryl hydrazones[4i] or benzamidines[4j] undergoing a C–H bond activation pathway. However, these products are usually less substituted or lack diversity, and the reactions generally need noble metals, such as palladium, rhodium and ruthenium, to promote the transformation. In this event, the development of efficient synthesis of multi-substituted isoquinolines from readily available starting materials with cheap metal usage, mild conditions and operational simplicity will be highly desirable.

Isocyanides are uniquely versatile building blocks in organic synthesis because of their structural and reactive properties, and have been widely applied in the formation of heterocycles.[5] Sustainability contribution of isocyanides has been widely recognized in the tandem radical cyclization reactions for the construction of heteroarenes, where an isocyano group was well established as the radical acceptor.[6] Manganese reagents, as milder transition metal oxidants, have been largely used as radical generators to form electrophilic radicals or related species.[7] For example, the aryl radicals could be generated smoothly from arylboronic acids by manganese(III) acetate.[8] Recently, an elegant new protocol for modular synthesis of phenanthridines was developed by Tobisu and Chatani using three equivalents of manganese(III) acetylacetonate *via* oxidative cyclization of 2-isocyanobiphenyls with boronic acids (Scheme 1).[9] As potentially useful synthetic precursors, vinyl isocyanides have been applied for the synthesis of heterocycles, however most of these reactions are mainly focused on base- or visible light-promoted cycloaddition reactions,[10] and much less attention has been paid to their chemistry in a transition metal catalysis or promotion manner. In continuation of our recent research interests on the isocyanide chemistry[11] and assembling heterocycles through a tandem chemical bonds formation strategy,[4i,12] herein we describe a Mn(II)/O_2-promoted oxidative radical cascade reaction, whereby a sequential double C–C bond was formed from easily accessible vinyl isocyanides and boronic acids to give multi-substituted isoquinolines (Scheme 1).



Scheme 1 Manganese-promoted radical cyclization of isocyanides.

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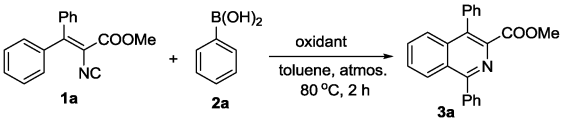
† Electronic supplementary information (ESI) available: General experimental procedures, characterization data and copies of the ^{1}H, ^{13}C and ^{19}F NMR spectra for all compounds. See DOI: 10.1039/c4cc06427e

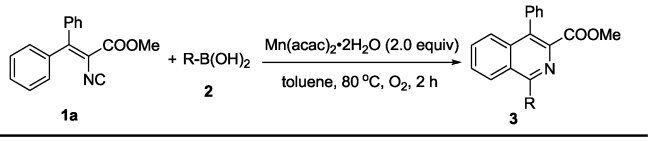
Table 1 Optimization of the reaction conditions[a]

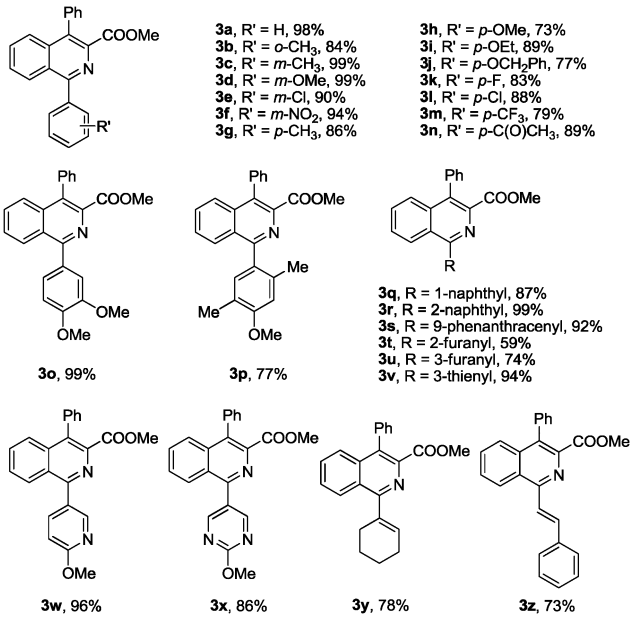


Entry	Oxidant (equiv.)	Solvents	Atmos.	Temp. (°C)	Yield[b] (%)
1	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	Dioxane	O_2	80	50
2	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	*t*-AmOH	O_2	80	58
3	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	Toluene	O_2	80	64
4	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	DMSO	O_2	80	Trace
5	$Mn(OAc)_3{\cdot}2H_2O$ (2.0)	HOAc	O_2	80	Trace
6	$Mn(OAc)_2{\cdot}4H_2O$ (2.0)	Toluene	O_2	80	N.R.
7	$MnCl_2{\cdot}4H_2O$ (2.0)	Toluene	O_2	80	N.R.
8	MnO_2 (2.0)	Toluene	O_2	80	Trace
9	$Mn(acac)_3$ (2.0)	Toluene	O_2	80	95
10	**$Mn(acac)_2{\cdot}2H_2O$ (2.0)**	**Toluene**	**O_2**	**80**	**98**
11	$Mn(acac)_2{\cdot}2H_2O$ (2.0)	Toluene	O_2	90	92
12	$Mn(acac)_2{\cdot}2H_2O$ (2.0)	Toluene	O_2	70	96
13	$Mn(acac)_2{\cdot}2H_2O$ (2.0)	Toluene	O_2	80	90[c]
14	$Mn(acac)_2{\cdot}2H_2O$ (1.5)	Toluene	O_2	80	89
15	$Mn(acac)_2{\cdot}2H_2O$ (1.0)	Toluene	O_2	80	81
16	$Mn(acac)_2{\cdot}2H_2O$ (0.5)	Toluene	O_2	80	44
17	$Mn(acac)_2{\cdot}2H_2O$ (2.0)	Toluene	Air	80	88
18	$Mn(acac)_2{\cdot}2H_2O$ (2.0)	Toluene	N_2	80	Trace
19	—	Toluene	O_2	80	9

[a] All reactions were performed in an oxygen-purged Schlenk tube, using vinyl isocyanide **1a** (0.5 mmol), phenylboronic acid **2a** (1.0 mmol) and oxidant in solvent (5.0 mL) at 80 °C for 2 h. $Mn(acac)_2{\cdot}2H_2O$ = manganese(II) acetylacetonate dihydrate. N.R. = No reaction. [b] Isolated yield. [c] **2a** (1.5 equiv.) was used.

Table 2 Scope of boronic acids[a,b]





[a] All reactions were performed in an oxygen-purged Schlenk tube, using vinyl isocyanide **1a** (0.5 mmol), boronic acid **2** (1.0 mmol) and $Mn(acac)_2{\cdot}2H_2O$ (1.0 mmol) in dry toluene (5.0 mL) at 80 °C for 2 h. [b] Isolated yield.

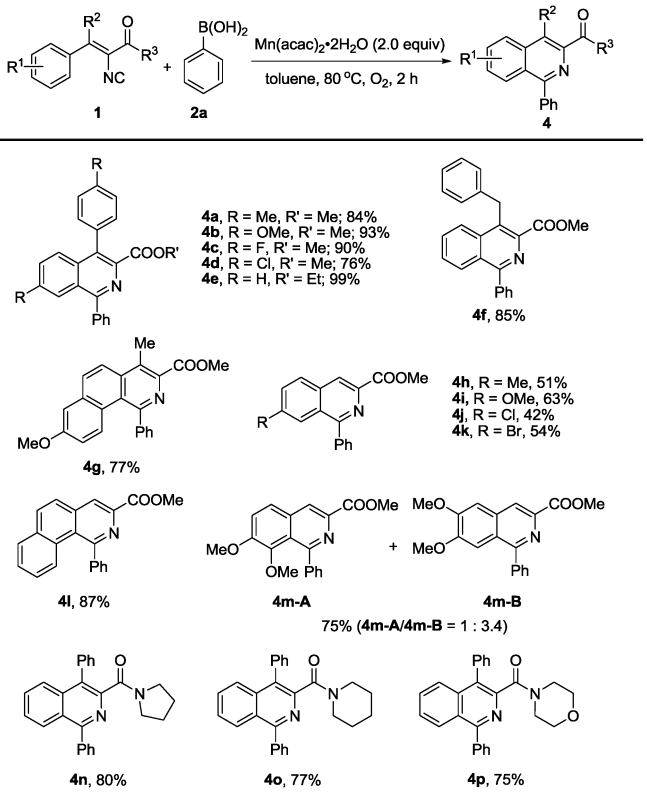
Furthermore, this protocol could be successfully applied to vinyl boronic acids which, to our knowledge, represents the first example of manganese(II)-promoted oxidative annulation of vinyl isocyanides with aryl or vinyl radicals in an oxygen atmosphere.

At the outset of this study, we started our investigation by exploring the reaction of vinyl isocyanide **1a** with phenylboronic acid **2a** (2.0 equiv.) in the presence of manganese(III) acetate dihydrate under an oxygen atmosphere at 80 °C. Intriguingly, the isoquinoline product **3a** was isolated in 50% yield (entry 1, Table 1). By switching the solvent from dioxane to *t*-AmOH or toluene, the yield was slightly increased (entries 2 and 3), while DMSO or HOAc provided trace amounts of the product (entries 4 and 5). An extensive screening of manganese sources (entries 6–10), temperature (entries 11 and 12), and the loading of boronic acid (entry 13) or manganese reagents (entries 14–16) revealed that the use of two equivalents of $Mn(acac)_2{\cdot}2H_2O$[13] as an oxidant in toluene at 80 °C under an oxygen atmosphere turned out to be the best choice and resulted in **3a** in 98% yield. Trace amounts or very low yield of the product was observed when the reaction was conducted under a nitrogen atmosphere (entry 18) or in the absence of the manganese salt (entry 19), which implied that manganese(II) and oxygen are crucial for this transformation.

With the optimized reaction conditions in hand, we then extended the reaction to a range of substrates. A wide variety of substitution patterns and functionalities were tolerated, as shown in Table 2. Substrates containing both electron-donating (**3b–d**, **3g–j**, **3o** and **3p**) and electron-withdrawing groups (**3e**, **3f** and **3k–n**), or bearing *ortho* (**3b**), *meta* (**3c–3f**) and *para* (**3g–3n**) groups proceeded efficiently in good to excellent yields with good functional group tolerance. A sterically hindered 2-methyl group (**3b** and **3p**) was also incorporated without significant loss in the yields. To our delight, boronic acids with fused arenes (**3q–3s**) or heterocyclic substituents, such as furan (**3t–3u**), thiophene (**3v**), pyridine (**3w**) and pyrimidine (**3x**) moieties, were all compatible with the reaction and gave desired products in good to excellent yields, which would significantly expand the scope of this reaction and represent a significant outcome given the utilities of these substructures in medicinal chemistry and materials science. It should be noted that vinyl boronic acids were also found to be suitable coupling partners and afforded the desired isoquinolines in good yields (**3y–3z**). However, no desired isoquinoline products could be observed for aliphatic boronic acids, such as cyclopropyl boronic acid and *n*-pentyl boronic acid, in the reaction and the starting material was recovered almost quantitatively. The reason may be due to the instability of generated aliphatic radicals in the oxygen atmosphere.

To further evaluate the generality and scope of this transformation, a variety of vinyl isocyanides with different substitutions were next explored, and the results are illustrated in Table 3. For the substrates having ester (**4a–4m**) and amide (**4n–4p**) substituents, the reactions were successfully coupled with **2a** to afford the corresponding isoquinolines in good to excellent yields. Vinyl isocyanides which were derived from diaryl ketones (**4a–4e**), alkyl aryl ketones (**4f** and **4g**), and aryl aldehydes (**4h–4m**), all proceeded smoothly with phenylboronic acid **2a** and produced the desired isoquinolines, regardless of their different electronic properties

Table 3 Scope of vinyl isocyanides[a,b]

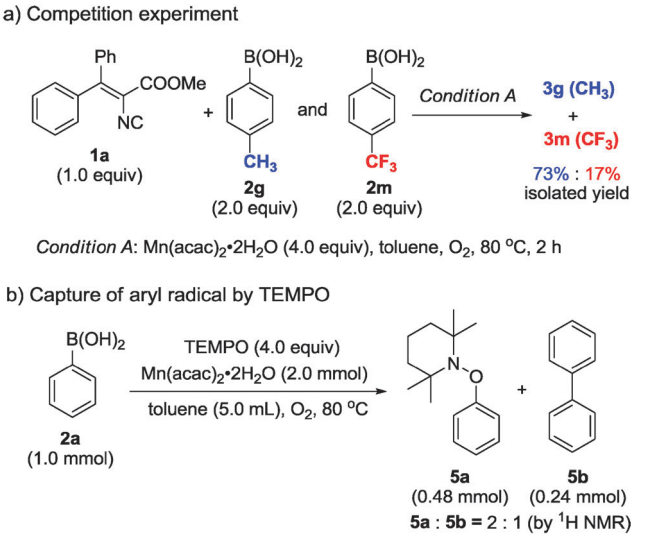


[a] All reactions were performed in an oxygen-purged Schlenk tube, using vinyl isocyanide **1** (0.5 mmol), phenylboronic acid **2a** (1.0 mmol) and $Mn(acac)_2{\cdot}2H_2O$ (1.0 mmol) in dry toluene (5.0 mL) at 80 °C for 2 h. [b] Isolated yield.

and substitution positions. Furthermore, the regioselectivity of this reaction mainly depends on the steric hindrance of substrates. For example, good regioselectivity of **4m-A**/**4m-B** (1 : 3.4) was observed for a di-methoxyl substituent containing substrate (**1m**), and the major product (**4m-B**) corresponds to the C–C coupling at a less hindered position.

To define the possible reaction pathway, several control experiments were carried out, as shown in Scheme 2. When a mixed substrate containing both electron-rich **2g** and electron-deficient **2m** was treated with **1a**, isoquinoline **3g** with electron-rich properties was isolated predominately in 73% yield (Scheme 2a), which suggested that electron-rich arylboronic acids reacted faster than electron-deficient ones.[9] Boronic acids have been reported to decompose into aryl radicals through a single-electron transfer in the presence of an oxidant.[8,9,14] In the experiment involving the addition of 2,2,6,6-tetramethyl-piperidine-1-oxy (TEMPO) under optimized reaction conditions, the use of phenylboronic acid **2a** afforded exclusively a mixture of **5a** and biphenyl **5b** (Scheme 2b), which implied the existence of a phenyl radical and a single electron transfer pathway during the reaction.

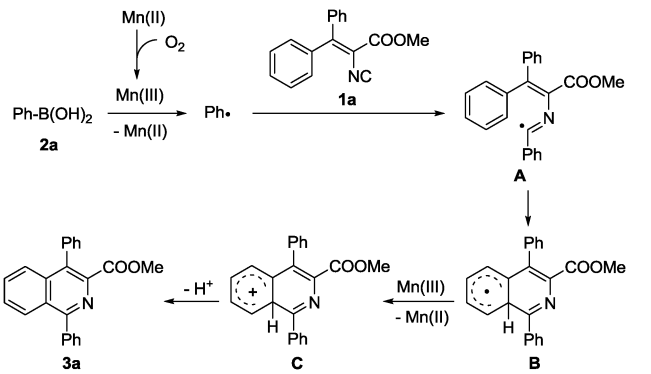
Although a detailed reaction pathway remains to be clarified, a plausible mechanism for the current manganese(II)/O_2-mediated annulation of vinyl isocyanide with boronic acid is depicted in Scheme 3, which is based on the above results and the radical cyclization mechanism proposed by Chatani and Tobisu.[9]



Scheme 2 Preliminary mechanistic studies.

Manganese(II) was initially oxidized to manganese(III) in the presence of oxygen,[15] which reacted with phenylboronic acid **2a** by one-electron oxidation to generate a phenyl radical.[8,9] The given phenyl radical underwent intermolecular addition to isocyanide **1a** to form the corresponding imidoyl radical **A**.[16] Intramolecular attack of the imidoyl radical on the aromatic ring subsequently provided a cyclohexadienyl type radical **B**, which is ultimately transferred to the corresponding cationic intermediate **C** through a single-electron oxidation process by manganese(III). The generated intermediate **C** subsequently aromatized to afford the desired isoquinoline product **3a** by a deprotonation step.

In conclusion, we have developed an efficient manganese(II)/O_2-promoted oxidative radical cascade reaction from easily available vinyl isocyanides and boronic acids, which enables the rapid divergent synthesis of valuable multi-substituted isoquinolines and their π-extended analogues with operational simplicity. The characteristics of a broad substrate scope, good functional group tolerance, and synthesis modularity will provide the described reaction broad utility in organic synthesis. Further insight into the mechanism, reaction scope, and the synthetic applications for bioactive compounds are now under investigation in our group.



Scheme 3 Proposed mechanism for synthesis of **3a** (ligands are omitted for clarity).

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