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Sustainable Manganese-Catalyzed C–H Activation/Hydroarylation of Imines

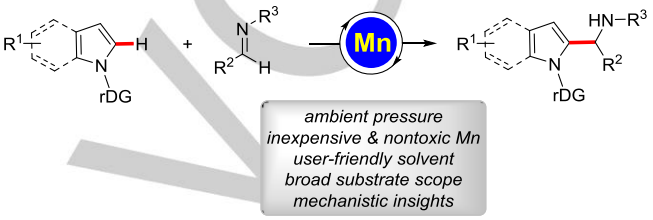
Yu-Feng Liang,[+] Leonardo Massignan,[+] and Lutz Ackermann*

Abstract: Expedient C–H additions of heteroarenes onto aldimines were realized by a sustainable manganese catalysis manifold within a removable directing group strategy. The C–H activation features most user-friendly reaction conditions, excellent chemo- and position-selectivity as well as ample substrate scope. Detailed experimental mechanistic studies were suggestive of an organometallic C–H manganesation mode of action.

Introduction

Transition metal-catalyzed C–H activation[1] has emerged as an increasingly viable tool for improving the step economy in molecular syntheses, with transformative applications to medicinal chemistry, material sciences and crop protection, among others.[2] During the past decades, progress has largely relied on complexes derived from precious 4d or 5d metals, such as noble rhodium, iridium, or palladium.[1] However, recent focus has shifted towards the use of earth-abundant, less toxic 3d metal complexes as catalysts for C–H functionalizations.[3] In this context, considerable recent advances were achieved with sustainable organometallic manganese catalysts,[4] with key contributions by Takai/Kuninobu,[5] Wang,[6] and Ackermann,[7] among others.[8]

Given the prevalence of amines in bioactive natural products and drugs, the direct addition of C–H bonds onto C=N double bonds represents a powerful approach for the rapid synthesis of substituted amines.[9] In this context, expensive pentamethylcyclopentadienyl complexes of toxic rhodium and cobalt allowed for addition reactions of arenes onto imines.[10] In sharp contrast, less expensive and less toxic manganese has only recently been identified as catalyst for the position-selective C=Het hydroarylations.[11] Despite this indisputable progress, the manganese catalysis regime required drastic conditions with Et_2O as the solvent at a reaction temperature of 100 °C, thus calling for high-pressure technologies and special safety features. However, within our program on sustainable catalysis,[12] we have now devised most user-friendly manganese-catalyzed site-selective C–H activation/hydroarylations[13] of imines with ample substrate scope. Notable features of our findings include i) general assembly of bioactive aminomethylated indoles, key motifs in natural products and pharmaceuticals,[14] ii) a most user-friendly reaction medium for site-selective C–H functionalizations at ambient pressure; iii) synthetically useful removable[15] pyri(mi)dyl groups, and iv) detailed mechanistic insights into the working mode of the manganese-catalyzed C–H activation (Scheme 1).



Scheme 1. Sustainable manganese-catalyzed C–H activation/ hydroarylation of imines.

Results and Discussion

We initiated our studies by probing reaction conditions for the envisioned manganese-catalyzed C–H activation of 1-(pyridin-2-yl)-1*H*-indole (**1a**) with *N*-benzylidene-4-methylbenzenesulfonamide (**2a**). We were delighted to observe that the desired product **3aa** was obtained in 47% yield, highlighting the versatility of manganese C–H activation. Detailed optimization studies revealed $Mn_2(CO)_{10}$ as the best catalyst (entries 1-5, Table 1). A variety of different additives, such as bases, ligands, and Lewis acids, failed to improve the catalyst's efficacy (entries 6-11). Polar solvents, including protic *t*BuOH, proved viable for the manganese-catalyzed C–H activation (entries 12-20). While ethereal solvents offered the optimal performance (entries 18-20), nBu$_2$O was selected as the ideal reaction medium because of its higher boiling point of 142 °C, so as to avoid special high-pressure technologies.

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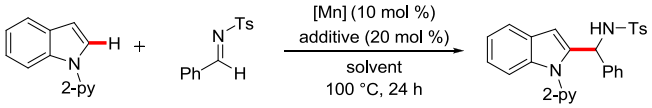
Table 1. Optimization of manganese-catalyzed C–H activation/hydroarylation.

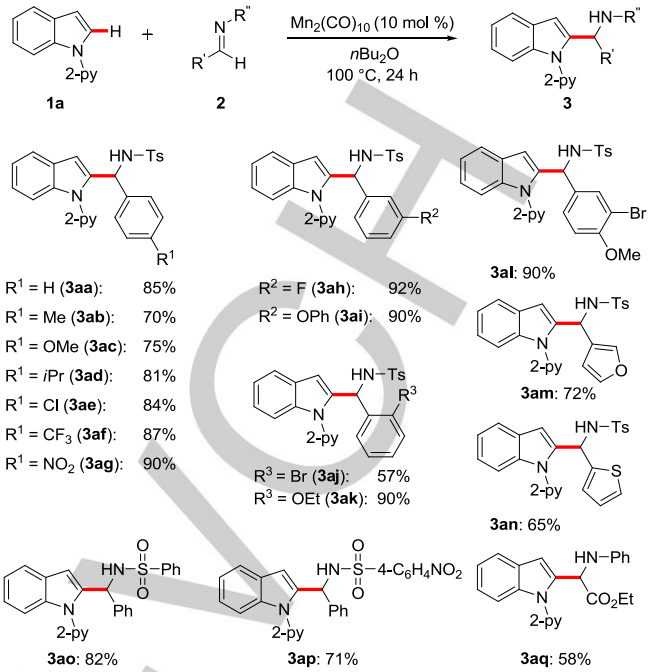


1a **2a** **3aa**

Entry	[Mn]	Additive	Solvent	Yield/%[b]
1	$Mn_2(CO)_{10}$	–	1,4-dioxane	47
2	$MnBr(CO)_5$	–	1,4-dioxane	30
3	–	–	1,4-dioxane	---
4	$MnCl_2$	–	1,4-dioxane	---
5	$Mn(OAc)_2$	–	1,4-dioxane	---
6	$MnBr(CO)_5$	NaOAc	1,4-dioxane	45
7	$Mn_2(CO)_{10}$	NaOAc	1,4-dioxane	45
8	$Mn_2(CO)_{10}$	Cy_2NH	1,4-dioxane	38
9	$Mn_2(CO)_{10}$	PPh_3	1,4-dioxane	42
10	$Mn_2(CO)_{10}$	$ZnBr_2$	1,4-dioxane	10
11	$Mn_2(CO)_{10}$	BF_3•OEt_2	1,4-dioxane	40
12	$Mn_2(CO)_{10}$	–	1,4-dioxane	42[c]
13	$Mn_2(CO)_{10}$	–	PhMe	30
14	$Mn_2(CO)_{10}$	–	DME	27
15	$Mn_2(CO)_{10}$	–	DCE	32
16	$Mn_2(CO)_{10}$	–	DMF	5
17	$Mn_2(CO)_{10}$	–	*t*BuOH	42
18	$Mn_2(CO)_{10}$	–	Et_2O	88
19	$Mn_2(CO)_{10}$	–	iPr_2O	83
20	**$Mn_2(CO)_{10}$**	**–**	***n*Bu$_2$O**	**85**

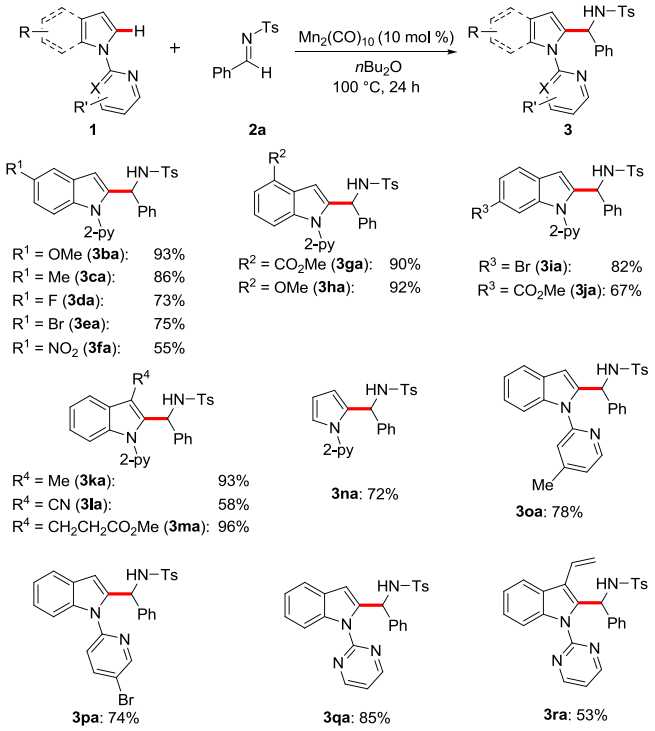
[a] Reaction conditions: **1a** (0.50 mmol), **2a** (1.00 mmol), [Mn] (10 mol %), additive (20 mol %), solvent (1.0 mL), at 100 °C for 24 h. [b] Isolated yield. [c] 120 °C. DME = 1,2-dimethoxyethane; DCE = 1,2-dichloroethane; DMF = *N*,*N*-dimethylformamide.

With the optimized manganese-catalyzed C–H activation/hydroarylation in hand, we tested its versatility with differently substituted imines **2** (Scheme 2). The robust manganese catalyst proved to be tolerant of various functional groups, such as methoxy, chloro, trifluoromethyl, nitro, and bromo substituents in various positions (**3aa**-**3al**). Likewise, synthetically useful heteroarenes, such as furane and thiophene, were successfully converted (**3am**-**3an**). Notably, the *N*-substituent on the imines **2** could be varied to even include an aromatic moiety (**3ao**-**3aq**), provided that an alkoxycarbonyl group was present.

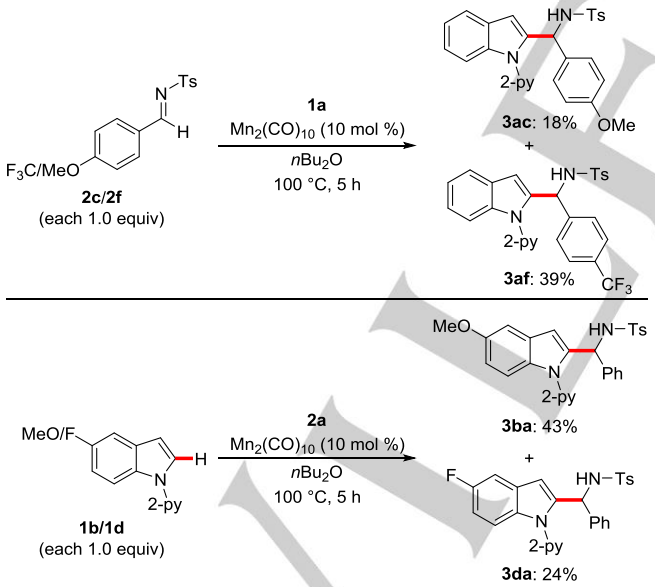


Scheme 2. Manganese-catalyzed C–H activation/hydroarylation of imines **2**.

The robustness of the manganese-catalyzed C–H activation was then investigated with respect to the indole moiety **1** (Scheme 3). Hence, a broad range of synthetically useful electrophilic groups was well tolerated, including fluoro, bromo, nitro and ester substituents (**3ba**-**3ja**). Thereby, either electron-donating or electron-withdrawing groups were included on the benzoid indole motif. Further, even substituents in the indole's C-3 position were well accepted despite of their increased steric hinderance (**3ka**-**3ma**). It is also notable that the manganese-catalyzed C–H activation/hydroarylation was not limited to indoles. Indeed, the C–H activation was also successfully performed on the synthetically meaningful pyrrole to give the product **3na** with execllent levels of site- and mono-selectivities. In contrast, under otherwise identical reaction conditions 3-pyridyl-substituted furane or thiophene provided thus far less satisfactory results.

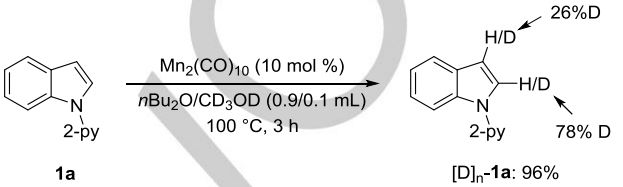


Scheme 3. Manganese-catalyzed C–H activation/hydroarylation of indoles **1**.

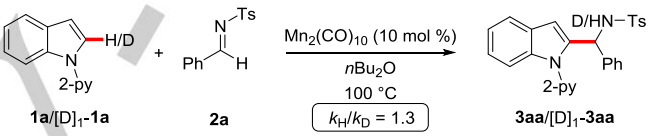


Scheme 4. Intermolecular competition experiments.

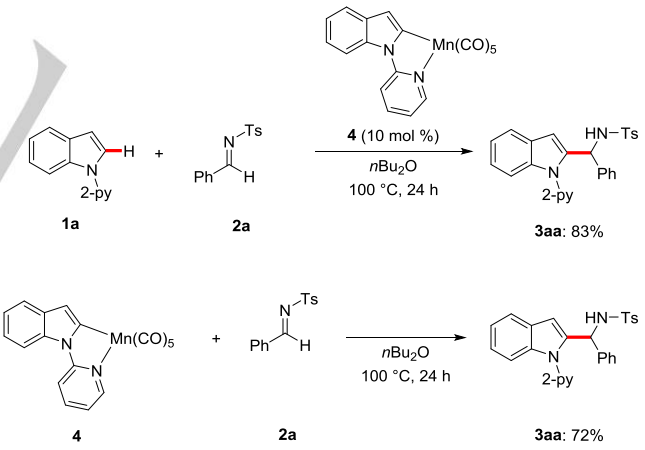
Given the high catalytic efficacy of the manganese-catalyzed hydroarylation, we became attracted to delineating its mode of action. To this end, competition experiments were performed, revealing that electron-rich indoles **1** and electron-deficient imines **2** inherently reacted faster (Scheme 4). These findings are indicative of a rate-determining nucleophilic attack of an organometallic manganese intermediate. Manganese-catalyzed hydroarylations in the presence of isotopically labeled cosolvent led to considerable H/D scrambling, highlighting a facile C–H cleavage (Scheme 5). In good agreement with this observation, a minor kinetic isotope effect (KIE) of only $k_H/k_D \approx 1.3$ was observed (Scheme 6), again indicating fast C–H activation. Moreover, the well-defined cyclometalated complex **4**[7i] was prepared, and proved competent in a catalytic and stoichiometric setting (Scheme 7), providing further support for complex **4** being a key intermediate of the organometallic C–H activation manifold.



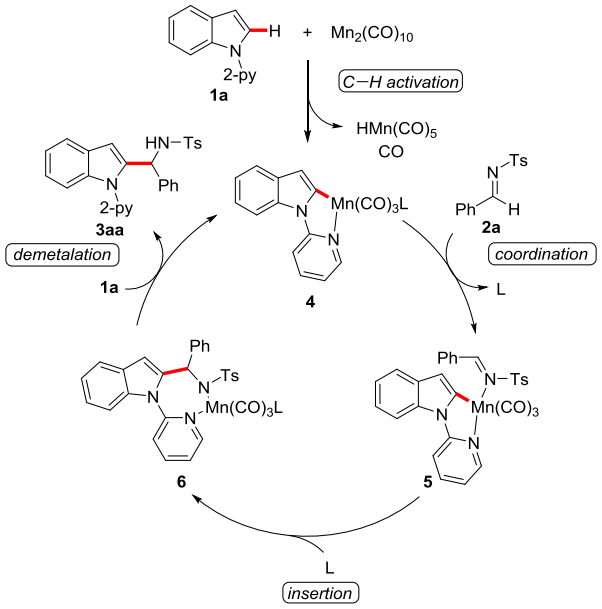
Scheme 5. H/D exchange experiment.



Scheme 6. Kinetic isotope effect study.

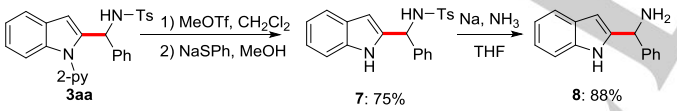


Scheme 7. Cyclometalated complex **4** in catalytic and stoichiometric reactions.

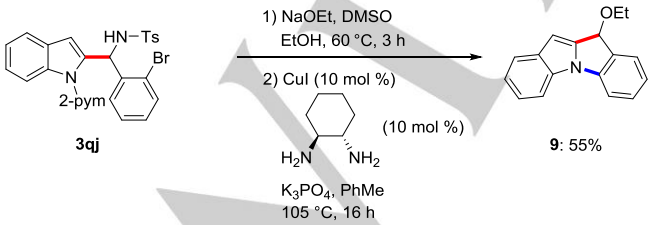


Scheme 8. Proposed catalytic cycle.

Based on our mechanistic studies, we propose a plausible catalytic cycle being initiated by a facile C–H metalation to afford the complex **4** (Scheme 8). Coordination and subsequent insertion lead to the seven-membered manganacycle **6**.[8j,16] Finally, intermediate **6** undergoes protonative demetalation, delivering the desired product **3aa** and regenerating the catalytically active manganese complex **4**. We suggest that the key C–H metalation occurs by a ligand-to-ligand hydrogen transfer (LLHT) regime.[17]



Scheme 9. Traceless removal of pyridyl and tosyl group.



Scheme 10. Late-stage diversification.

Finally, the pyridyl and tosyl group could be removed in a traceless fashion (Scheme 9). Moreover, the late-stage diversification of amine **3qj** provided versatile access to the valuable indolo[1,2-*a*]indole **9** structural motif (Scheme 10).

Conclusions

In conclusion, we have reported on the efficient C–H activation/hydroarylation of imines by means of inexpensive and nontoxic manganese catalysis at ambient pressure. The robustness of the most user-friendly manganese catalyst was reflected by the general assembly of bioactive aminomethylated indoles in a step-economical manner, with excellent levels of mono-, chemo- and position-selectivities and ample scope. Detailed mechanistic studies provided strong support for an organometallic C–H activation manifold.

Experimental Section

Heteroarenes **1** (0.5 mmol), imines **2** (1.0 mmol), $Mn_2(CO)_{10}$ (19.5 mg, 10 mol %) and nBu$_2$O (1.0 mL) were placed in a 25 mL Schlenk flask. The mixture was stirred at 100 ºC for 24 h. After cooling to ambient temperature, the mixture was transferred into a round bottom flask with EtOAc (20 mL) and washed with brine (5.0 mL). The mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of *n*-hexane and EtOAc to afford the desired products **3**.

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Keywords: C–H activation • imine • heteroarene • manganese • mechanism

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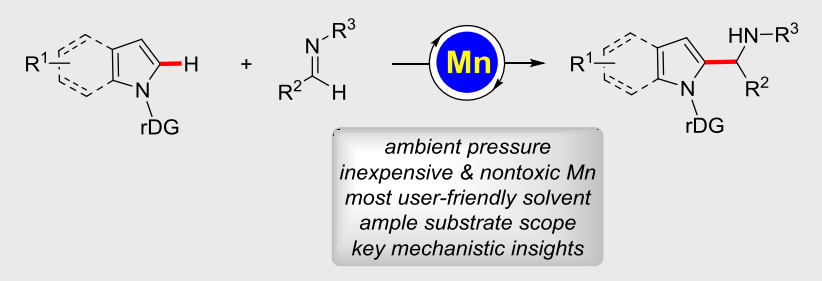

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Sustainable Manganese-Catalyzed C–H Activation/Hydroarylation of Imines

SusMn: Manganese catalysis enabled the step-economical C–H activation/hydroarylations of aldimines with ample scope by an organometallic C–H activation regime.