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Manganese-Catalyzed Aromatic C−H Allylation of Ketones

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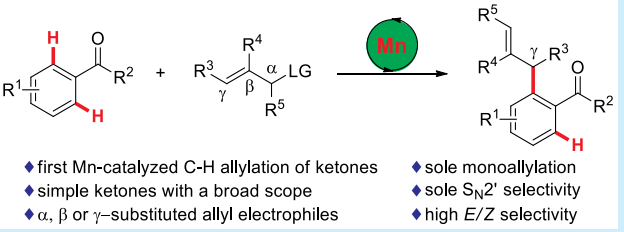
Supporting Information

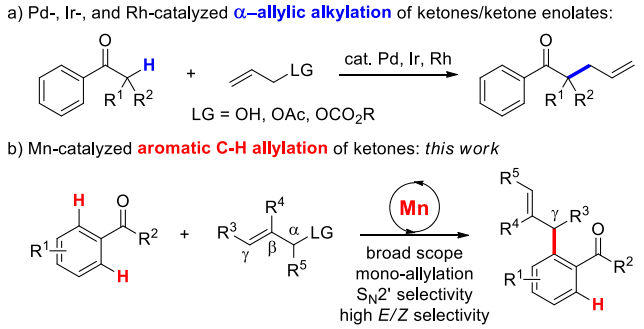
ABSTRACT: Manganese-catalyzed aromatic C−H allylation of ketones is reported. The reaction proceeded in a monoselective allylation manner to provide various *ortho* C−H allylated ketones in high yields. With challenging allylic electrophiles bearing substituents at the *α*-, *β*-, or *γ*-position, excellent S_N2' regioselectivity was achieved under mild conditions (rt to 35 °C). Mechanistic studies revealed a possible turnover-limiting C−H bond cleavage step affording a five-membered manganacycle followed by reaction with allylic electrophiles to give the C−H allylation product.



Direct functionalization of inert C−H bonds is a powerful tool to construct new chemical bonds in organic synthesis. Since the pioneering Ru-catalyzed C−H alkylation of aryl ketones with olefins,[1] ketones have been explored for a range of synthetically useful C−H functionalization reactions.[2] Nevertheless, the predominant use of precious transition metals (Ru, Rh, Pd, and Ir) in these reactions raises the question of sustainability. Development of earth-abundant base-metal catalyzed C−H functionalization of ketones is highly desirable. Manganese, owing to its abundance, low cost, and low toxicity, has recently received considerable attention in organometallic C−H activation reactions.[3,4] Despite impressive progress, the arene substrates for the most manganese-catalyzed C−H functionalization contain strong-coordination nitrogen-directing groups. Although stoichiometric C−H activation reactions of aryl ketones giving manganacycles have been long reported,[5] the development of catalytic C−H functionalization of readily available ketones has not been reported until our recent contributions.[4k,o] The prominent challenges of using the ketone moiety as an effective directing group for C−H activation derive from the weak coordinating ability of ketones with metals, thus decreasing the thermodynamic stability of the resulting transition states and/or metallacycle intermediates.[6] Also, active C(sp^3)−H bonds *α* to the carbonyl of ketones could undergo facile Mannich, aldol, and/or Michael-addition types of reactions thus competing with the inert C−H activation pathway in catalysis.[7]

Specifically, Pd-, Ir-, and Rh-catalyzed *α*-C−H allylic alkylation of ketones or ketone enolates has been studied extensively, which provides an efficient way to construct tertiary or quaternary *α*-carbon centers of ketones and even enantioselectivity (Scheme 1a).[8] However, direct allylation of aromatic C−H bonds of ketones has rarely received attention.

Scheme 1. Transition-Metal-Catalyzed Aliphatic and Aromatic C−H Allylation of Ketones



The only elegant example was reported recently by Maji demonstrating a cobalt-catalyzed *ortho*-allylation of aryl ketones.[9] Nevertheless, it showed lack of reactivity and/or poor regioselectivity for *β*- and *γ*-substituted allylic electrophiles. As part of our ongoing interest in sustainable manganese catalysis,[3,4] herein we describe the first manganese-catalyzed aromatic C−H allylation of ketones with broad substrate scopes, sole S_N2' regioselectivity, and high *E*/*Z* selectivity (Scheme 1b).[10]

We started with the reaction of *p*-methoxyacetophenone **1a** and allyl bromide in the presence of $MnBr(CO)_5$ and Me_2Zn/$ZnBr_2$.[4k,o] No desired C(sp^2)−H monoallylated product **3a** was detected in diethyl ether; instead, aldol-type product **4a** and *α*-C(sp^3)−H allylated product **5a** were observed in 18% and 15% NMR yields, respectively (Table 1, entry 1). To our

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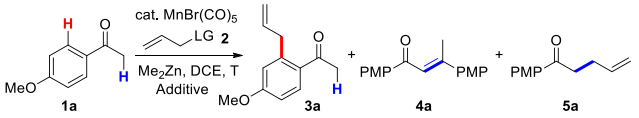
Table 1. Screening of Reaction Parameters[a]



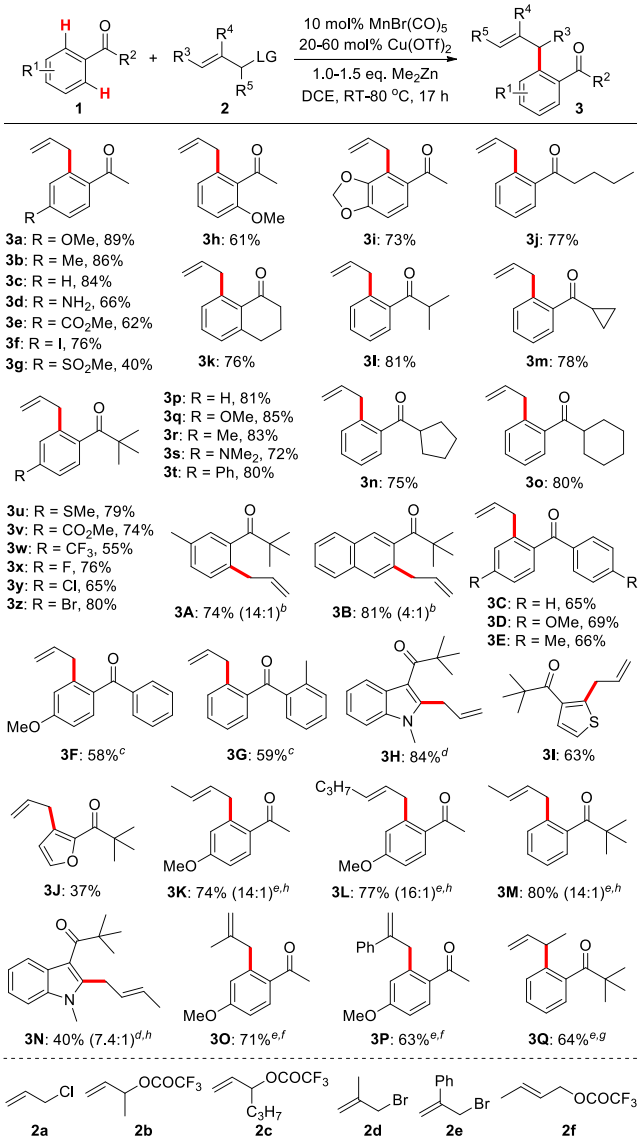
entry	solvent	LG[b]	T (°C)	Yield[c] 3a	4a	5a
1[d]	Et_2O	Br	120	–	18	15
2[d]	PhMe	Br	120	11	23	–
3[d]	DCE	Br	120	17	25	–
4	DCE	Br	120	34	–	–
5	DCE	OPiv	120	10	–	–
6	DCE	OPiv	80	52	–	–
7[e]	DCE	OPiv	80	62	–	–
8[e]	DCE	OAc	80	67	–	–
9[e]	DCE	OBoc	80	–	–	–
10[e]	DCE	$OCOCF_3$	80	58	–	–
11[e]	DCE	Cl	80	53	–	–
12[f]	DCE	OAc	80	61	–	–
13[f]	**DCE**	**Cl**	**80**	**91(89)**[g]	–	–
14[f,h]	DCE	Cl	80	–	30	–
15[f,i]	DCE	Cl	80	32	28	–

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $MnBr(CO)_5$ (10 mol %), 1.5 equiv of Me_2Zn (1.2 M in toluene), 1.0 equiv of $Cu(OTf)_2$, DCE (0.1 M), 80 °C, 17 h. [b]LG = leaving group. [c]NMR yields using 1,3,5-trimethoxybenzene as standard. [d]1.0 equiv of $ZnBr_2$ instead of $Cu(OTf)_2$. [e]**1a:2** = 2:1. [f]**1a:2** = 3:1 and 0.6 equiv of $Cu(OTf)_2$. [g]Isolated yields, almost quantitative recovery of excess **1a** after column chromatography. [h]No $MnBr(CO)_5$. [i]No $Cu(OTf)_2$. PMP = *p*-methoxyphenyl.

delight, **3a** was obtained by using toluene or 1,2-dichloroethane (DCE) as solvents, albeit in low yields (entries 2, 3). Screening of additives revealed that $Cu(OTf)_2$ not only increased the yield of **3a** but also inhibited the formation of **4a** (entry 4).[11] When *O*-pivalate was used as a leaving group, the yield of **3a** increased to 52% at 80 °C (entries 5, 6). Further variations on the ratios of substrates and types of leaving groups showed that **3a** could be isolated in 89% yield by using Cl as the optimal leaving group (entries 7−13). No reaction occurred without the manganese catalyst (entry 14). The yield of **3a** decreased dramatically, and the aldol-type product **4a** emerged in the absence of $Cu(OTf)_2$ (entry 15).

With the optimized conditions in hand, various ketones were first tested with allyl chloride (**2a**) as a model substrate (Scheme 2). Both electron-donating and -withdrawing substituents were tolerated on the benzene ring giving the expected products smoothly (**3a−g**). Despite increased steric hindrance, *ortho*-methoxy acetophenone delivered the corresponding product in moderate yield (**3h**). The secondary directing effect, rather than the steric, governed the regioselectivity when two C−H bonds were available for allylation (**3i**). Linear and cyclic primary alkyl aryl ketones were both suitable substrates for this reaction (**3j**, **k**). Secondary alkyl aryl ketones worked equally well (**3l−o**). *tert*-Butyl aryl ketones bearing electron-varied substituents were also amenable to the reaction conditions in spite of the enhanced steric hindrance (**3p−z**). A sterically less congested C−H bond was preferentially allylated with high regioselectivity for the *meta*-substituted substrate (**3A**). The naphthalene moiety could also be allylated smoothly (**3B**). Benzophenone derivatives delivered exclusively the mono-C−H allylation

Scheme 2. Manganese-Catalyzed Aromatic C−H Allylation[a]



[a]Reaction conditions: **1** (1.5 mmol), **2** (0.5 mmol), $MnBr(CO)_5$ (0.05 mmol), Me_2Zn (0.75 mmol, 1.2 M in toluene), $Cu(OTf)_2$ (0.3 mmol), DCE (0.1 M), 80 °C, LG = Cl, 17 h. [b]Major regioisomer was shown; regioisomeric ratio was given in parentheses. [c]**1** (2.0 mmol), no other regioisomers were detected in the crude reaction mixture by NMR. [d]No $Cu(OTf)_2$. [e]RT, Me_2Zn (0.5 mmol, 1.2 M in toluene), $Cu(OTf)_2$ (0.1 mmol), LG = $OCOCF_3$. [f]LG = Br. [g]35 °C. [h]*E*/*Z* ratio in parentheses.

products out of four available C−H bonds (**3C−E**). Remarkably, the electron-rich benzene ring was selectively allylated in an unsymmetrical diaryl ketone (**3F**), and selective C−H allylation on the unsubstituted benzene ring was found in the diaryl ketone bearing an *o*-methyl group (**3G**). In addition, heterocycles such as indole, thiophene, and furan were also successfully allylated (**3H−J**). Of note, a variety of functional groups such as ester, amine, ether, thioether, sulfonyl, trifluoromethyl, and halides, which are valuable synthetic handles for further elaborations, were well tolerated in the current reaction.

Next, we turned our attention to varying structures of allylic electrophiles. While 3-chloro-1-butene reacted with *p*-methoxyacetophenone (**1a**) under previously optimized

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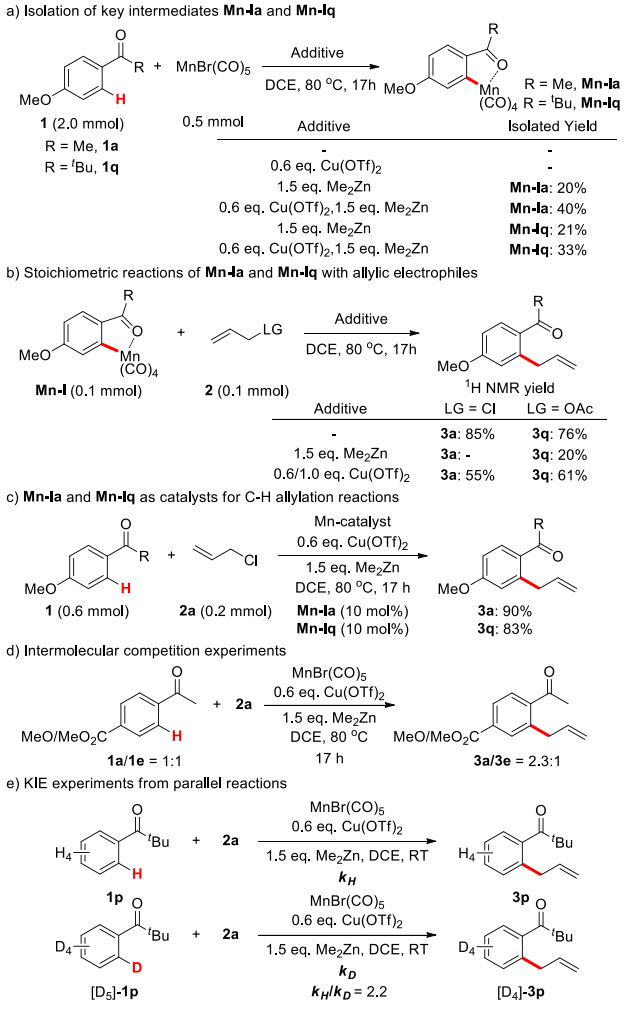
conditions giving 45% linear and 9% branched products, the linear product (**3K**) was obtained from the reaction of **1a** and α-methylallyl trifluoroacetate (**2b**) at room temperature in 74% isolated yield with 100% S_N2' regioselectivity and high *E*/*Z* selectivity. Similarly, the corresponding linear products could be accessed by varying the allylation reagent (**2c**), directing group, and arene moiety (**3L**–**N**). β-Substituted allyl bromides (**2d**, **2e**) reacted with ketone **1a** at room temperature to afford the expected products in good yields (**3O**, **3P**). When γ-methylallyl trifluoroacetate (**2f**) was used, the branched product was obtained in 64% yield at 35 °C with excellent regioselectivity (**3Q**). Of note, no double-bond migrated styrene derivatives or *bis*-C–H allylation products were observed in the reaction for all cases.

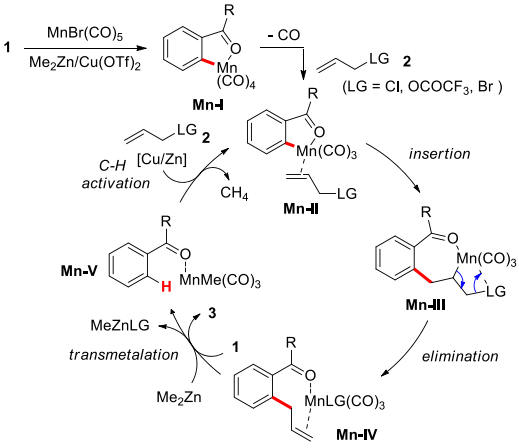
To study the possible reaction pathways, stoichiometric reactions of ketones (**1a** and **1q**) with $MnBr(CO)_5$ were conducted (Scheme 3a). While no reaction occurred without an additive or with $Cu(OTf)_2$, the expected manganacycles **Mn-Ia** and **Mn-Iq** were obtained in 20% and 21% isolated yields respectively by adding Me_2Zn.[4k,o] Further addition of $Cu(OTf)_2$ increased the yields of the corresponding manganacycles, which indicated the positive role of $Cu(OTf)_2$ in the C–H activation step.[4o] Next, stoichiometric reactions of manganacycles **Mn-Ia** and **Mn-Iq** with allylic electrophiles were tested and the allylation products **3a** and **3q** were isolated in good yields respectively (Scheme 3b). The addition of either Me_2Zn or $Cu(OTf)_2$ gave inferior results. Meanwhile, manganacycles could also catalyze the C–H allylation reactions of ketones in comparably high yields of products (Scheme 3c). A competition reaction between electron-rich and -deficient aceto-phenones (**1a** and **1e**) with **2a** revealed that **1a** reacted more favorably than **1e** with a ratio of 2.3:1 (Scheme 3d). A kinetic isotope effect value of 2.2 was obtained from two parallel reactions of **1p** and [D_5]-**1p** with **2a** respectively, suggesting a possible turnover-limiting C–H cyclomanganation step (Scheme 3e).

Scheme 3. Mechanistic Studies



Based on these clues and previous reports,[4e,k] a plausible reaction mechanism is proposed in Scheme 4. The initial reaction of ketone **1** and $MnBr(CO)_5$ gave five-membered manganacycle **Mn-I** with the aid of Me_2Zn and $Cu(OTf)_2$ (Scheme 3a). Coordination of allylic electrophile **2** with mangangese through releasing a CO ligand led to intermediate **Mn-II**, which was followed by insertion of the C=C bond affording seven-membered manganacycle **Mn-III**. Then β-elimination of the leaving group in **Mn-III** gave product-coordinated species **Mn-IV**. The ensuing ligand exchange between product **3** and substrate **1** on the manganese center and further transmetalation with Me_2Zn produced **3** and **Mn-V**. A step of C–H activation in **Mn-V** occurred to release methane[4e] and regenerate **Mn-II**. The liberation of CO and methane was confirmed by GC analysis.[11] Of note, the presence of $Cu(OTf)_2$ not only promoted the C–H activation step[4o] but also prohibited the aldol-type side reactions (Table 1). Interestingly, Fairlamb and Lynam uncovered the formation of Mn^I carbonyl clusters in manganese catalysis, which may provide hints regarding the possible catalyst deactivation pathways in our reactions.[12]

Scheme 4. Proposed Reaction Mechanism



In summary, we have developed the first manganese-catalyzed aromatic C–H allylation of ketones, which features mild reaction conditions, a wide scope of substrates, and high regio-/stereoselectivity. Our approach allows for facile access to diversely substituted *ortho*-C–H allylated ketone products through use of challenging allylic electrophiles bearing substituents at the α-, β-, or γ-position. Further investigations on the detailed reaction mechanism and other Mn-catalyzed C–H activation reactions of ketones are underway in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

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Experimental details, characterization data, and NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(11) For more details, see the Supporting Information.

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