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Manganese(I)-Catalyzed Synthesis of Fused Eight- and Four-Membered Carbocycles via C−H Activation and Pericyclic Reactions

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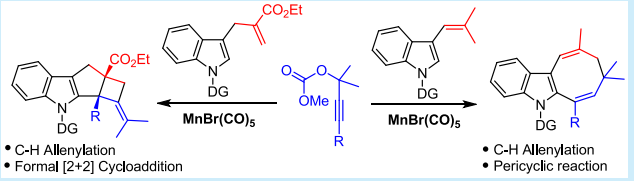
Supporting Information

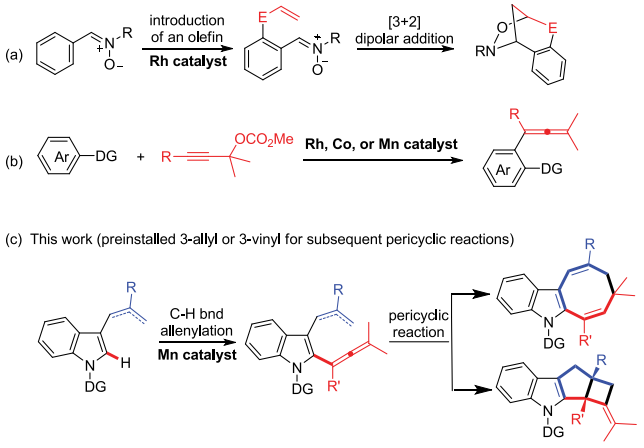
ABSTRACT: Pericyclic reactions have allowed facile construction of complex cycles. On the other hand, metal-catalyzed C−H activation has been established as an important strategy for rapid synthesis of complex structures. The two areas are integrated in Mn(I)-catalyzed redox-neutral coupling of 3-alkenyl- and 3-allylindoles with propargylic carbonates, which occurred via C−H allenylation with subsequent pericyclic reactions to afford fused eight- and four-membered carbocycles, respectively.



Fused alicyclic compounds are arguably the important structural units in natural products and useful intermediates in organic synthesis.[1] Thus, the construction of carbocycles has attracted widespread interest. In particular, fused four- and eight-membered carbocycles are important structural motifs and useful intermediates. Consequently, different routes for efficient preparation of fused four- and eight-membered carbocycles have been developed in the past decades.[2] For instance, Ma reported an efficient protocol for synthesis of eight-membered bicyclic compounds via [1,5]-hydrogen migration and 8π-electrocyclization.[3] Meanwhile, metal-catalyzed ene−allene formal [2 + 2] cycloadditions have been reported for synthesis of [3,2,0]-fused cyclobutanes.[4] However, most of the reported methods require highly functionalized starting materials and suffer from limited functional group tolerance. It is highly desirable to develop cost-effective and simple methods to access four- and eight-membered carbocycles.

On the other hand, C−H bond activation has emerged as a powerful synthetic strategy owing to its high step-economy.[5] The ubiquity of C−H bonds and the high atom- and step-economy of this strategy render it highly attractive in the construction of carbocycles.[6] In contrast to the vast majority of C−H activation−cyclization reactions, general methods to synthesize eight- and four-membered carbocycle compounds via C−H activation are limited because they are constructed via attack of the nucleophilic M−C bond that is generated by electrophilic directing groups. It is well-known that cascade cyclizations involving pericyclic reactions are a reliable and straightforward synthetic strategy for the rapid creation of challenging and unique cyclic molecules.[7] Thus, we recently reported C−H activation of arenes en route to [3 + 2]-dipolar addition and Diels−Alder reactions.[8] However, these systems are limited to construction of five- or six-membered rings. Given the high reactivity of allenes, we aimed to integrate C−H activation and pericyclic reactions using allene as a handle, which have exhibited high activity in various C−H activation systems.[9] In addition, C−H allenylation has also been recently developed (Scheme 1b). In particular, Ma and co-workers

Scheme 1. C−H Allenylation and Combination of C−H Activation and Pericyclic Reactions



pioneered in Rh(III)-catalyzed synthesis of allenes via C−H activation of arenes and coupling with propargyl esters.[10] Afterward, Sundararaju reported a cobalt-catalyzed version with propargyl alcohol as the allenylating reagent.[11] Given the earth abundance and intrinsic reactivity of Mn complexes,[12] Glorius and co-workers realized direct synthesis of 2-allenylindoles by Mn(I) catalysis.[13] We reasoned that preinstallation of an olefin group in the proximity of the C−

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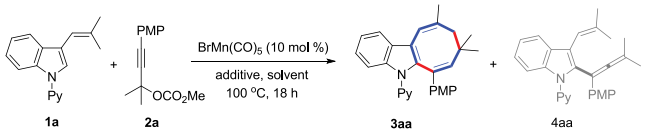
H bond that is activated may offer an active site for subsequent functionalization (Scheme 1c). Following C−H allenylation, the pendent olefin and the allene may readily undergo pericyclic reactions, which stands in contrast to our previous strategy of employing a dipolar directing group. Despite the design, the proximal olefin increases the steric hindrance of the C−H activation, which calls for a highly reactive C−H activation catalyst. We now report Mn(I)-catalyzed synthesis of eight-membered carbocycles and fused cyclobutanes via a C−H activation−pericyclization strategy.

We initiated our studies with screening of the reaction parameters of the coupling of 3-alkenylindole **1a** and propargylic carbonate **2a** (Table 1). A reaction occurred in

Table 1. Optimization of Reaction Conditions[a]



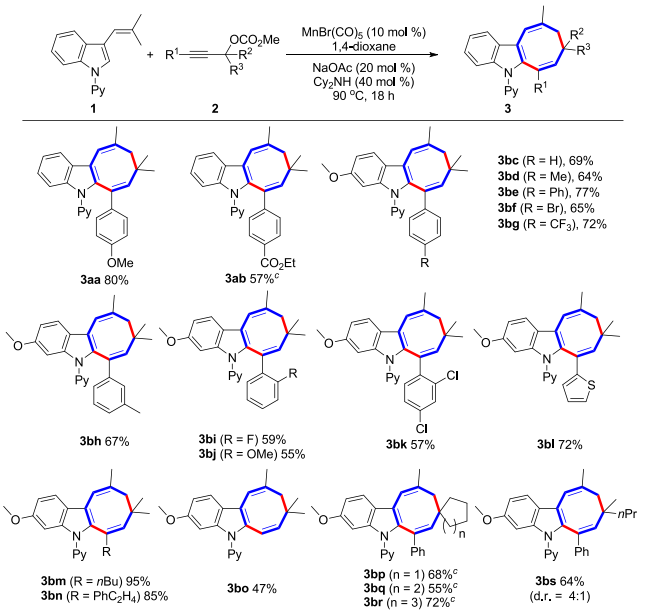
entry	additive (equiv)	solvent	yield[b,c] (%)
1[d]	NaOAc (2)	1,4-dioxane	37 (40)
2	NaOAc (2)	1,4-dioxane	60 (<5)
3[e]	NaOAc (2)	1,4-dioxane	59 (<5)
4	NaOAc (0.2)/Cy_2NH (0.4)	1,4-dioxane	64 (<5)
5	NaOAc (0.2)/Cy_2NH (0.4)	DME	57 (10)
6	NaOAc (0.2)/Cy_2NH (0.4)	THF	51 (17)
7	NaOAc (0.2)/Cy_2NH (0.4)	MTBE	41 (16)
8[f]	NaOAc (0.2)/Cy_2NH (0.4)	1,4-dioxane	80 (<5)
9[f]	NaOAc (0.2)/Et_3N (0.4)	1,4-dioxane	63 (<5)
10[f]	NaOAc (0.2)/DBU (0.4)	1,4-dioxane	nd

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $MnBr(CO)_5$ (10 mol %), and additive were stirred in solvent (1 mL) at 100 °C for 18 h. [b]Yield of isolated **3aa**. [c]Yield of **4aa** in parentheses. [d]80 °C. [e]$Mn_2(CO)_{10}$ (10 mol %) was used as a catalyst. [f]90 °C. nd = not detected.

the presence of $MnBr(CO)_5$ catalyst to give both eight-membered ring **3aa** and 2-allenylation product **4aa** (entry 1). The yield of **3aa** was improved when the reaction temperature was raised to 100 °C (entry 2). The yield of **3aa** remained essentially unaffected when $Mn_2(CO)_{10}$ was used (entry 3). Introduction of Cy_2NH as an additive slightly increased the yield of **3aa**, and reactions in other solvents all failed to give superior results (entries 5−7). Lowering the temperature to 90 °C improved the yield of **3aa** to 80% (entry 8). Control experiments verified that no desired reaction occurred in the absence of the manganese catalyst. On the other hand, no desired product was detected using Rh(III) or Co(III) complexes as the catalysts because of the steric hindrance between the proximal olefin and Cp* rings (see the SI).

The scope of this coupling system was evaluated over a wide array of substrates (Scheme 2). Aryl propargylic carbonates bearing both electron-donating and -withdrawing groups at different positions of the phenyl ring coupled smoothly with the indole in moderate to good yields (**3aa**−**3bk**). The propargylic carbonate was not limited to phenyl substitution, and a thiophene ring (**3bl**) and several alkyl substituents (**3bm**, **3bn**) were fully compatible. Terminal propargylic carbonate also coupled to afford the desired product **3bo**. Propargylic carbonate containing five-, six-, and seven-membered rings was also reactive, furnishing the spiral product in good yields

Scheme 2. Scope of Propargylic Carbonates[a,b]

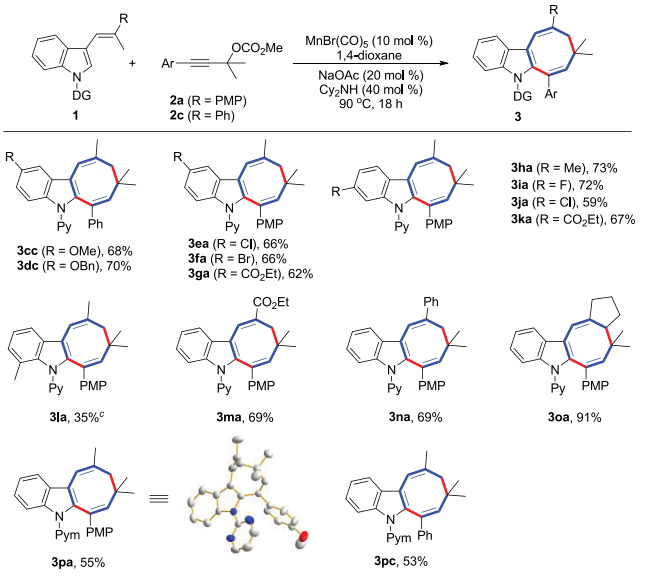


[a]Reaction conditions A: indole **1a** or **1b** (0.2 mmol), **2** (0.4 mmol), $MnBr(CO)_5$ (10 mol %), NaOAc (20 mol %), Cy_2NH (40 mol %), 1,4-dioxane (1 mL), 90 °C, 18 h under N_2 in a sealed tube. [b]Isolated yields. [c]100 °C.

(**3bp**−**3br**). Substrate bearing two different alkyl groups at the propargylic position also reacted smoothly (**3bs**) as a diastereomeric mixture as a result of puckered and rigid conformation of the eight-membered ring induced by atropisomerism (hindered rotation along the C(2)−C(alkenyl) bond).

The scope of the indole substrates is summarized in Scheme 3. Both electron-donating and -withdrawing substituents at the

Scheme 3. Scope of 3-Alkenylindoles[a,b]



[a]Reaction conditions A: indole (0.2 mmol), **2a** or **2c** (0.4 mmol), $MnBr(CO)_5$ (10 mol %), NaOAc (20 mol %), Cy_2NH (40 mol %), 1,4-dioxane (1 mL), 90 °C, 18 h under N_2 in a sealed tube. [b]Isolated yield. [c]100 °C.

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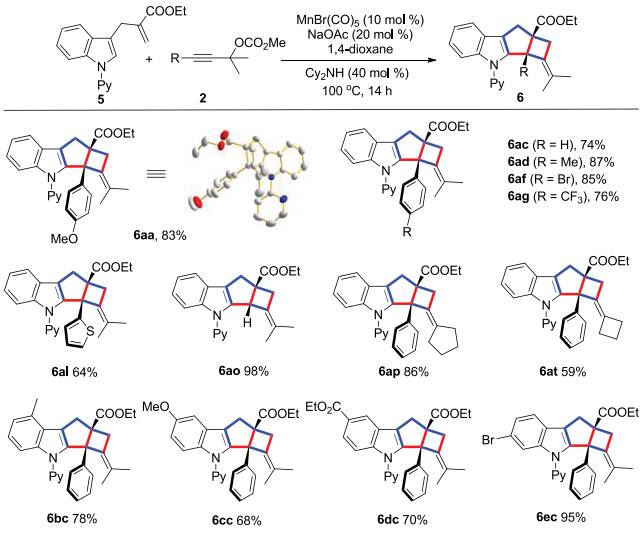
5- and 6-positions were fully compatible (**3cc**−**3ka**). In addition, the reaction was extended to a 7-substituted indole (**3la**), indicating tolerance of steric hindrance. Besides the 2-methylpropenyl substituent in the indoles, several other propenyl groups were well-tolerated (**3ma**−**3oa**). The directing group plays a crucial role, and the yield was compromised when *N*-pyrimidyl was used as a DG (**3pa** (CCDC 1814469) and **3pc**). Unfortunately, monosubstituted or terminal olefin substrates are not applicable to the system.

To better define the scope of the indole and to accommodate bifurcated pericyclic reactions, 3-allylindoles were employed (Scheme 4). While essentially no desired

Scheme 4. Synthesis of [3,2,0] Cycles[a,b]



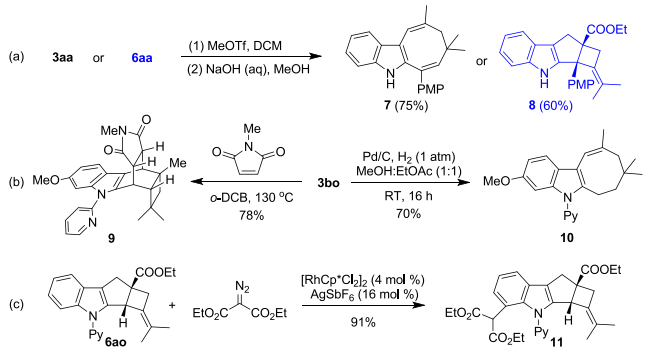
[a]Reaction conditions B: 3-allylindole (0.2 mmol), propargylic carbonate (0.4 mmol), $MnBr(CO)_5$ (10 mol %), NaOAc (20 mol %), Cy_2NH (40 mol %), 1,4-dioxane (1 mL), 100 °C, 14 h under N_2 in a sealed tube. [b]Isolated yield.

annulation occurred when *N*-pyridyl-3-metallylindole was used, introduction of an ester group into the allyl resulted in smooth coupling with propargylic carbonate **2a** to give a *cis*-fused butane (**6aa**, CCDC 1841038) in excellent yield as a single diastereomer (dr > 20:1, conditions B). The scope of this reaction was also broad, and various [3.2.0] rings were isolated in moderate to high yields (**6aa**−**6at**). The functional group compatibility with respect to the indole was also briefly examined, where both electron-donating and -withdrawing substituents were tolerated.

The synthetic utility of the products has been explored. The synthesis of **6aa** at a 2 mmol scale has been performed (see the SI). Two-step removal of the pyridyl DG delivered NH indole **7** or **8** (Scheme 5a). Moreover, **3bo** was selectively reduced to **10** in 70% yield. Heating a mixture of **3bo** and *N*-methylmaleimide afforded a bridged polycycle **9** (Scheme 5b), which may occur via 6π-electrocyclization followed by a Diels−Alder reaction.[3] Rh(III)-catalyzed coupling of **6ao** with a diazo reagent afforded a C(7)-alkylation product **11** in excellent yield (Scheme 5c).[14]

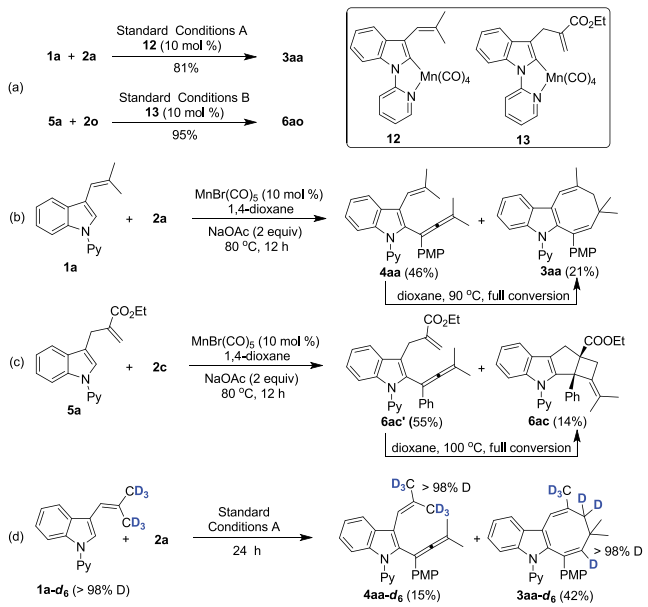
Experimental studies have been performed to explore the mechanism (Scheme 6). H/D exchange between indole **1a** or **5a** and CD_3OD revealed significant deuteration at the 2-position in each case, suggesting reversible C−H activation (see the SI). When metalacycles **12** and **13** were designated as

Scheme 5. Applications of the Titled Reaction[a]



[a](a) Removal of DG. (b) 6π-Electrocyclization and chemoselective reduction of **3bo** with H_2. (c) Rh(III)-catalyzed C(7)-alkylation of **6ao**

Scheme 6. Mechanistic Studies



a catalyst precursor (Scheme 6a), the coupling of the corresponding indole **1a** and **5a** with propargylic carbonates **2a** afforded products **3aa** and **6ao** in 81% and 95% yield, respectively, further indicating the relevancy of C−H activation. To probe whether the reaction proceeds via initial C−H allenylation, 2-allenylindoles **4aa** and **6ac′** were prepared and subjected to the corresponding uncatalyzed conditions (Scheme 6b and c). Both **4aa** and **6ac′** readily cyclized, indicating the intermediacy of such allenes. To further explore the mechanism of formation of product **3aa**, **1a**-d_6 was coupled with **2a**. A noticeable kinetic isotope effect was observed, and allene intermediate **4aa**-d_6 was isolated in 15% yield after 24 h (Scheme 6d). NMR analysis of product **3aa**-d_6 revealed no deuterium scrambling, with the β-olefinic carbon being fully deuterated. In addition, our crossover experiments also verified that the H-shift process is intramolecular.

On the basis of these results and related reports, a plausible mechanism is proposed in Scheme 7. C−H activation of indole **1** or **5** affords a metallacyclic intermediate. Subsequent regioselective migratory insertion of the Mn−C bond into the alkyne is followed by β-oxygen elimination of **A** and **E** to give the allenylation intermediate. For 3-alkenylindole, the

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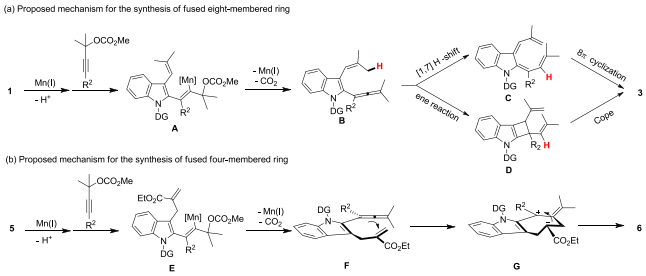
Scheme 7. Proposed Mechanism



allene **B** may undergo 1,7-H migration, furnishing a tetraene **C**, which undergoes 8π-electrocyclization to deliver product **3**.[3,15] Alternatively, the allene may follow an ene-reaction pathway to give a four-membered ring **D**. Subsequent Cope rearrangement furnishes the same product **3**. In this pathway, dearomatization of the indole is circumvented. For the 3-allylindole substrates, product **6** is produced from allene **F** likely via an ionic, stepwise formal [2 + 2] cycloaddition due to presence of activating groups (allene and ester).[4f]

In conclusion, we have achieved integration of Mn-catalyzed C−H activation and pericyclic reactions for efficient construction of eight-membered carbocycles and [3.2.0]-fused cyclobutanes. Both reaction systems proceeded with broad scope, functional group compatibility, and a high degree of selectivity. The combination of different important areas in catalysis may provide opportunities to expand applications of C−H activation toward development of new challenging catalytic systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01139.

General experimental procedures, characterization data, ^{1}H and ^{13}C NMR spectra of some starting materials and new products (PDF)

Accession Codes

CCDC 1814469 and 1841038 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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