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Manganese-Catalyzed Intermolecular Oxidative Annulation of Alkynes with γ-Vinyl Aldehydes: An Entry to Bridged Carbocyclic Systems

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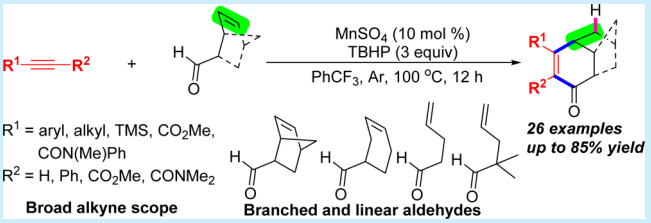
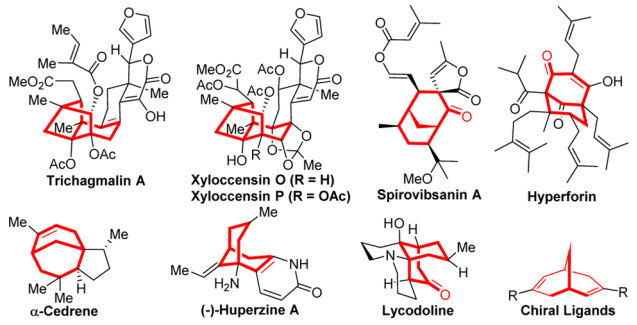
Supporting Information

ABSTRACT: Manganese-catalyzed intermolecular oxidative annulation of alkynes with γ-vinyl aldehydes involving acylation and alkylation is described, thus providing a scenario for the divergent synthesis of bridged carbocyclic systems. By means of this manganese-catalyzed alkyne dicarbofunctionalization strategy, three chemical bonds, including two C−C bonds and one C−H bond, are formed via an aldehyde C(sp^2)−H oxidative functionalization/[4 + 2] annulation/protonation cascade.



Bridged carbocyclic systems, including bridged bicyclic and tricyclic carbocycles, are unique structural motifs that widely exist in numerous natural products, pharmaceuticals, and other bioactive molecules (Scheme 1).[1,2] For example,

Scheme 1. Examples of Important Bridged Carbocycles



trichagmalin A and xyloccensins,[2a−f] which were isolated from the leaves of *Cedrela odorata* or the fruits of the Chinese mangrove plant, are constituted by an octahydro-1*H*-2,4-methanoindene skeleton. Other natural products, including spirovibsanin A,[2g,h] hyperforin,[2i−k] α-cedrene,[2l] (−)-huperzine A,[2m−o] and lycodoline,[2p,q] all feature a bicyclo[2.3.2]nonane ring system. Furthermore, bridged carbocyclic systems have a multitude of applications in the organic and medicinal community, including use as chiral ligands[3] and versatile synthetic intermediates.[1,4] Efficient construction of a bridged dicarbocyclic or tricarbocyclic framework is therefore in demand and has attracted ongoing interest from scientific researchers.[1,2,4] However, the majority of strategies for selectively building such frameworks are restricted to the intramolecular fashion with unavailable limited substrates via multiple synthetic steps, and an alternative one-step entry that allows the divergent construction of different bridged cyclic systems from simple starting materials is very challenging.

The cycloaddition reaction with aldehydes represents a powerful method for the construction of diverse cyclic systems, with the vast majority of examples concerning destruction of the carbonyl group via C═O bond cleavage as a carbon monoatom unit or a C/O two-atom unit for construction of the cycle.[5] To the best of our knowledge, an approach to radical-mediated cycloaddition with the aldehyde C(sp^2)−H bond, to avoid the destruction of the carbonyl group, has yet to be reported. In recent years, radical-mediated addition of aldehydes across the unsaturated C−C bonds has become an important tool for directly incorporating an acyl group into simple unsaturated hydrocarbons,[6−8] in which acyl radical **A** is generated by cleavage of the aldehyde C(sp^2)−H bond using photocatalysis[7] or oxidation[8] (Scheme 2a,b). We envisioned that if an aldehyde inherently contains a functional group to trap radical intermediate **B**, the cycloaddition process would not destroy the carbonyl group, allowing the assembly of carbonyl-containing cycles (Scheme 2c). Herein we report a new $MnSO_4$-catalyzed intermolecular oxidative annulation of alkynes with γ-vinyl aldehydes via acylation and alkylation for the divergent synthesis of 5*H*-2,4-methanoinden-5-ones, bicyclo[3.3.1]non-3-en-2-ones, and cyclohex-2-en-1-ones (Scheme 2d), which rely on the γ-vinyl aldehyde reaction

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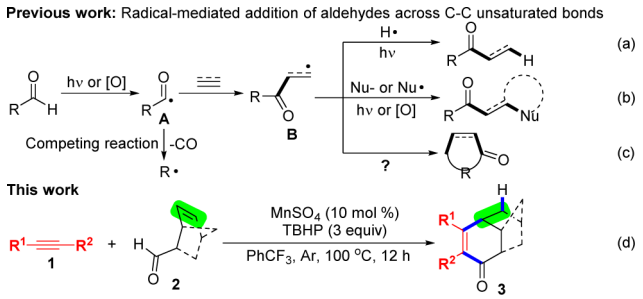
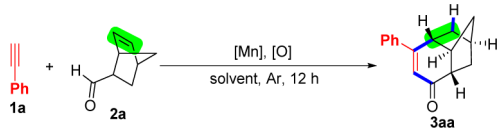
Scheme 2. Radical Transformations of Aldehydes



partners. This radical-mediated reaction is achieved by simultaneously incorporating an acyl group and a vinyl group across the C≡C bond through the formation of two C−C bonds and one C−H bond and represents a new, alternative entry to bridged carbocyclic systems from branched aldehydes by avoiding the tendency for the competing decarbonylation.[9]

Our initial studies started with the reaction between phenylaceylene (**1a**) and norborn-5-ene-2-carbaldehyde (**2a**) for optimization of the reaction conditions (Table 1).

Table 1. Optimization of the Reaction Conditions[a]



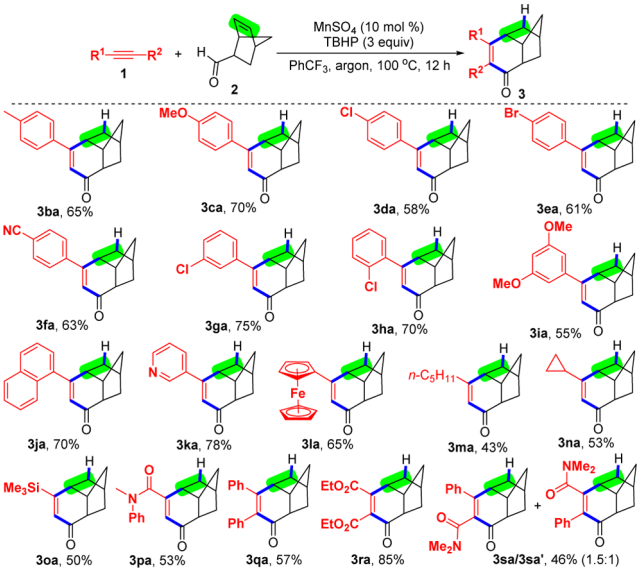
entry	[M] (mol %)	[O] (equiv)	solvent	t (°C)	yield (%)
1	$MnSO_4$ (10)	TBHP (3)	$PhCF_3$	100	73 (68[b])
2	$MnSO_4$ (5)	TBHP (3)	$PhCF_3$	100	55
3	$MnSO_4$ (20)	TBHP (3)	$PhCF_3$	100	75
4	$MnCl_2$ (10)	TBHP (3)	$PhCF_3$	100	54
5	$Mn(OAc)_2$ (10)	TBHP (3)	$PhCF_3$	100	50
6	MnO_2 (10)	TBHP (3)	$PhCF_3$	100	58
7	$MnSO_4$ (10)	CHP (3)	$PhCF_3$	100	63
8	$MnSO_4$ (10)	DTBP (3)	$PhCF_3$	100	<5
9	$MnSO_4$ (10)	TBPB (3)	$PhCF_3$	100	<5
10	$MnSO_4$ (10)	–	$PhCF_3$	100	trace
11	$MnSO_4$ (10)	TBHP (2)	$PhCF_3$	100	37
12	$MnSO_4$ (10)	TBHP (4)	$PhCF_3$	100	71
13	$MnSO_4$ (10)	TBHP (3)	$PhCF_3$	110	73
14	$MnSO_4$ (10)	TBHP (3)	$PhCF_3$	90	55
15	$MnSO_4$ (10)	TBHP (3)	MeCN	100	47
16	$MnSO_4$ (10)	TBHP (3)	DMF	100	33

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv), [M], [O], $PhCF_3$ (2 mL), argon, 12 h. The dr values were >20:1, as determined by ^1H NMR analyses of the crude products. [b]**1a** (1 mmol) and $PhCF_3$ (3 mL) for 24 h.

Treatment of alkyne **1a** with aldehyde **2a**, $MnSO_4$, and TBHP in $PhCF_3$ at 100 °C succeeded in accessing the desired product **3aa** in 73% yield (entry 1). Notably, a reaction scaled up to 1 mmol of **1a** also afforded **3aa** in good yield (entry 1). The amount of $MnSO_4$ affected the reaction: a lower loading of $MnSO_4$ (5 mol %) decreased the yield of **3aa** (entry 2), whereas a higher loading of $MnSO_4$ (20 mol %) gave an identical yield as 10 mol % $MnSO_4$ (entry 3). Other Mn catalysts, namely, $MnCl_2$, $Mn(OAc)_2$, and MnO_2, displayed high activity (entries 4−6), but they all were less efficient than $MnSO_4$. Using cumene hydroperoxide (CHP) also delivered a satisfactory yield (entry 7). However, both di-*tert*-butyl peroxide (DTBP) and *tert*-butyl perbenzoate (TBPB) exhibited lower reactivity (entries 8 and 9). It was noted that the reaction could not occur without an oxidant (entry 10). Screening of both the amount of TBHP and the reaction temperature revealed that 3 equiv of TBHP at 100 °C was the best option (entries 11−14). Two other alternative solvents, MeCN and DMF, both were less reactive than $PhCF_3$ (entries 15 and 16).

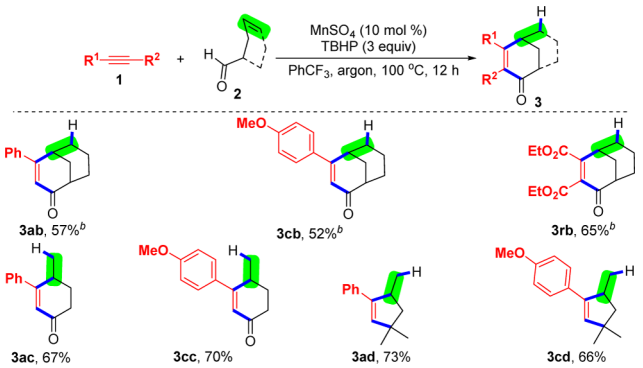
With the optimal reaction conditions identified, we turned our attention to an investigation of the scope of this tandem annulation protocol with respect to alkynes **1** (Scheme 3) and

Scheme 3. Variation of Alkyne 1[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (2 equiv), $MnSO_4$ (10 mol %), TBHP (3 equiv), $PhCF_3$ (2 mL), argon, 100 °C, 12 h. The dr value of each product was >20:1.

Scheme 4. Variation of γ-Vinyl Aldehyde 2[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (2 equiv), $MnSO_4$ (10 mol %), TBHP (3 equiv), $PhCF_3$ (2 mL), argon, 100 °C, 12 h. [b]The dr value of the product was >20:1.

γ-vinyl aldehydes (Scheme 4). As shown in Scheme 3, the optimal conditions were compatible with a wide range of alkynes, including terminal aryl alkynes (**1b−l**), alkyl alkynes (**1m** and **1n**), ethynyltrimethylsilane (**1o**), propiolamide (**1p**), propiolate (**1q**) and internal alkynes (**1r−t**). With terminal arylalkynes **1b−l**, a series of substituents, namely, Me, MeO, Cl,

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Br, and CN, on the aryl ring were well-tolerated (**3ba**−**la**). Me-substituted aryl alkyne **1b**, for example, was converted into **3ba** in 65% yield. MeO-substituted aryl alkyne **1c** delivered **3ca** in 70% yield. Importantly, halogen groups, including Cl and Br, are consistent with the optimal conditions, thus offering facile handles for further synthetic elaborations of the halogenated positions (**3da**, **3ea**, **3ga**, and **3ha**). Aryl alkynes **1d**, **1g**, and **1h** with a Cl group at the para, meta, and ortho positions, respectively, were suitable substrates, giving **3da**, **3ga**, and **3ha** in 58−75% yield. Alkyne **1f** having an electron-withdrawing CN group was also successful at accessing **3fa**. With bis(MeO)-substituted alkyne **1i** and 1-ethynylnaphthalene (**1j**), this tandem annulation protocol afforded **3ia** and **3ja** in 55% and 70% yield, respectively. The heteroaryl alkynes 3-ethynylpyridine (**1k**) and ethynylferrocene (**1l**) both showed high reactivity (**3ka** and **3la**). Alkyl alkynes **1m** and **1n** and electron-poor terminal alkyne **1p** could undergo the annulation reaction (**3ma**, **3na**, and **3pa**), but all were less reactive than terminal aryl alkynes. To our delight, **1o** proved amenable to the optimal conditions, giving silyl-substituted product **3oa** in 50% yield. Gratifyingly, the optimal conditions were applicable to internal alkynes, including 1,2-diphenylethyne (**1q**), diethyl but-2-ynedioate (**1r**), and *N*,*N*-dimethyl-3-phenylpropiolamide (**1s**), affording **3qa**−**sa** in 46%−85% yield.

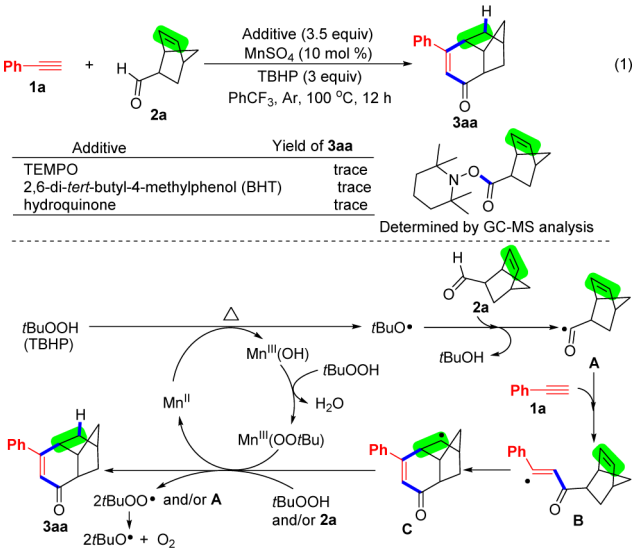
The optimal conditions were also suitable for other γ-vinyl aldehydes **2b**−**d** (Scheme 4). Cyclohex-3-ene-1-carbaldehyde (**2b**), the other secondary aldehyde, exhibited high reactivity and executed the acylalkylation reaction with alkynes **1a**, **1c**, and **1r** to deliver bicyclo[3.3.1]non-3-en-2-ones **3ab**, **3cb**, and **3rb** in 52%−65% yield, respectively. For pent-4-enal (**2c**), a primary aldehyde, the acylalkylation reactions with alkynes **1a** and **1c** proceeded smoothly, giving the corresponding cyclohex-2-en-1-ones **3ac** and **3cc** in good yields. However, 2,2-dimethylpent-4-enal (**2d**), a tertiary aldehyde, underwent decarbonylative annulation with alkynes **1a** and **1c**, resulting in the formation of the five-membered cyclic products **3ad** and **3cd** in high yields.

Notably, the reaction of alkyne **1a** with aldehyde **2a** was completely inhibited when radical inhibitors were used, implying that the reaction includes a radical process (Scheme 5, eq 1).

A possible mechanism for the intermolecular oxidative acylalkylation protocol is outlined in Scheme 5.[4−8] Initially, the splitting of the O−O bond in TBHP occurs when the active Mn^{II} species is heated to generate the *tert*-butoxyl radical and the $Mn^{III}(OH)$ species.[6,7] The $Mn^{III}(OH)$ species can be readily converted into the $Me^{III}(OOtBu)$ species in the presence of TBHP. Selective hydrogen abstraction of the aldehyde group in **2a** with the *tert*-butoxyl radical produces silicon-centered radical intermediate **A** and *t*BuOH,[6,7] and subsequent addition across the C≡C bond in alkyne **1a** affords vinyl radical intermediate **B**. Cyclization of intermediate **B** with the C═C bond gives rise to radical alkyl intermediate **C**. Finally, oxidation of **C** through hydrogen atom transfer to TBHP or single-electron oxidation by the $Me^{III}(OOtBu)$ species, followed by protonation, provides access the desired product **3aa**.

In summary, we have described the first example of a manganese-catalyzed intermolecular oxidative [4 + 2] annulation of alkynes with γ-vinyl aldehydes for constructing bridged carbocyclic systems. The reaction is achieved through a sequence of carbonyl C−H oxidative functionalization, acyl radical generation, addition across the C≡C bond, annulation

Scheme 5. Control Experiments and Possible Mechanism



with the C═C bond, and protonation. The reaction is applicable to a wide range of alkynes, including aryl alkynes, alkyl alkynes, ethynyltrimethylsilane, and electron-poor alkynes, and represents a new alkyne annulation alternative to access diverse bridged carbocycles, such as 5*H*-2,4-methanoinden-5-ones, bicyclo[3.3.1]non-3-en-2-ones, and common five- or six-membered cycles. Studies on expanding this annulation strategy in total synthesis and developing new synthetic methodologies are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03086.

Descriptions of experimental procedures for compounds and analytical characterization (PDF)

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Notes

The authors declare no competing financial interest.

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