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Selective Nickel- and Manganese-Catalyzed Decarboxylative Cross Coupling of Some α, β -Unsaturated Carboxylic Acids with Cyclic Ethers

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A nickel- and manganese-catalyzed decarboxylative cross coupling of α, β -unsaturated carboxylic acids with cyclic ethers such as tetrahydrofuran and 1, 4-dioxane was developed. Oxyalkylation was achieved when nickel acetate was used as catalyst, while manganese acetate promoted the reaction of alkenylation.

The selective C-H bond functionalization and C-C bond formation with an application of transition metal catalyst gained a lot of progress in organic synthesis recently¹⁻⁶. Decarboxylative cross coupling was one of the highlights for related C-C bond formation⁷⁻¹⁰.

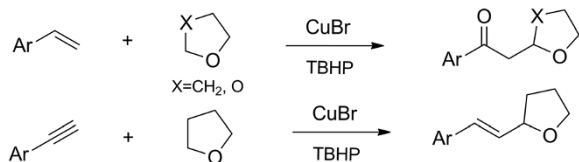
In the last few years, decarboxylative cross coupling research has made very significant results, including a decarboxylative aldol reaction¹¹⁻¹⁴, asymmetric carboxylate enolate alkylation, biaryl formation, decarboxylative C-heteroatom cross-coupling¹⁵⁻²¹ and decarboxylative C-H bond functionalization. Decarboxylative cross coupling could afford the desired negative synthon in organic synthesis with a new approach; moreover, the stable and inexpensive carboxylic acids can replace the expensive and unstable organometallic reagents. It is one of the recent hot topics in organic synthesis²²⁻²⁵.

Cyclic ether frameworks such as tetrahydrofuran and 1,4-dioxane are important structural motifs, which are not easy to install in many organic compounds. Therefore, introducing the structure of cyclic ethers directly was an exploring and meaningful approach for synthesis of the corresponding complex molecules. Recently, some reactions involving cyclic ethers along with the C-H bond functionalization have been reported. For example, various trans-styryl derivatives were prepared from a radical substitution of cyclic ethers and cyclohexanes to (*E*)-nitrostyrenes²⁶. Then, a radical α -C-H hydroxyalkylation of ethers with aldehydes under the conditions of Et₃B/air or Et₃B/TBHP was reported³². In 2009, reactions of vinylarenes and alkynes with cyclic ethers catalyzed by CuBr or manganese oxide nanoparticles via direct activation of sp³ C-H bonds adjacent to oxygen atoms were explored³³⁻³⁵. In 2012, copper-catalyzed decarboxylative alkenylation between α, β -unsaturated carboxylic acids with cyclic ethers, alcohols, and hydrocarbons was demonstrated^{36,37}. In 2013, Lei³⁸ reported a novel nickel-catalyzed oxidative arylation of the α -sp³ C-H bond with the cyclic ethers. Phenylboronic acid was coupled with the sp³ C-H adjacent to the oxygen atom of THF or 1, 4-dioxane in 80% yield.

In many oxidative coupling reactions, precious metals such as Pd and Ru salts were usually employed. Cu and Fe salts were also used as catalysts. In 2013, Pan reported Iron-catalyzed alkenylation of cinnamic acid with cyclic ethers³⁹. Nickel catalyzed oxidative sp³ C-H functionalization has been demonstrated, but few reports of oxidative coupling reactions utilized a manganese catalyst^{40,41}. In this paper, we would like to report a nickel- and manganese-catalyzed decarboxylative cross coupling of α, β -unsaturated carboxylic acids with cyclic ethers with non-noble metal catalysts (Fig. 1). There is an excellent catalytic selectivity in this work: with the same substrates, nickel acetate only gave 2-(1, 4-dioxan-2-yl)-1-phenylethanone derivatives, while manganese acetate only gave (*E*)-2-styryl-1, 4-dioxane derivatives. To the best of our knowledge, this is first report that the same reactants produced selective products under different metal catalysts in oxidative sp³ C-H functionalization.



Previous work



This work

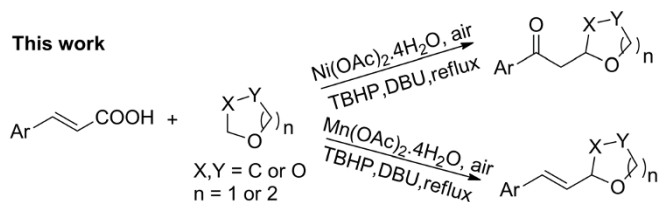


Figure 1 | Functionalization of cyclic ethers.

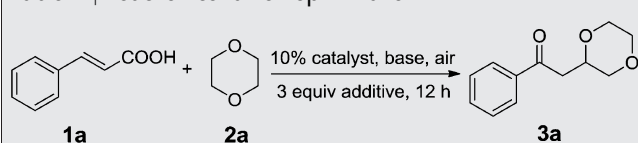
Results

Initially, cinnamic acid and 1, 4-dioxane were chosen as the model substrates and the optimization of reaction conditions are shown in the Table 1. It was found that cinnamic acid could not react with 1, 4-dioxane without the catalyst or additive oxidant (entries 1–3). Therefore, catalysts and additive oxidants were essential for these reactions. When different oxidizing agents were used, for example, NBS, DDQ and BPO, the yields were not high enough compared with the usage of TBHP (entries 4–13). To our delight, DBU could improve the yield sharply (entries 10–13), compared with TEA and K_2CO_3 (entries 8 and 9). Gradient comparison tests about the temperature were also carried out. The activity of 1, 4-dioxane was enhanced and corresponding yield up to 85% at 100°C (entry 13). Different transition metal salts such as $Cu(OAc)_2$, $Cu(OAc)_2 \cdot H_2O$, $Co(OAc)_2 \cdot 4H_2O$, $Zn(OAc)_2 \cdot 2H_2O$, $Pb(OAc)_2 \cdot 3H_2O$, $Mn(OAc)_2 \cdot 4H_2O$, $Ni(OAc)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$ were tested as catalysts for the decarboxylative

cross coupling reactions. We found that $Ni(OAc)_2 \cdot 4H_2O$ was more efficient than other salts (entries 13–21). The desired product was isolated in 85% yield by using 10 mol % $Ni(OAc)_2 \cdot 4H_2O$ (entry 13).

Interestingly, among these metal catalysts, manganese acetate represented very special results. The color of the solution changed significantly during the reaction and the low yield drew our attention (Table 1, entry 21). The structure of the major new product was suggested after analysis of the NMR data, and we are certain that it's (*E*)-2-styryl-1, 4-dioxane. It maintained the configuration of trans, which could be confirmed by the proof that the two alkenyl hydrogen atoms had coupling constant of 16 Hz. To our delight, new alkenylation reactions were achieved under the manganese acetate catalysis condition. The reaction conditions are also optimized as showed in Table 2. The desired product could give a good yield of 80% (Table 2, entry 11). When the reaction time was extended to 12 hours or longer, yield of 3a had not been improved and major product was still (*E*)-2-styryl-1, 4-dioxane. We observed that manganese acetate achieved a specific catalytic effect.

To expand the scope of these systems, various α , β -unsaturated carboxylic acids were used as substrates. The related products are showed in (Fig. 2) with moderate to good yields by the optimal condition listed. It's noteworthy that substituted α , β -unsaturated carboxylic acids with electron donating group gave better yields (Fig. 2, 3e, 4e), while the reactants with electron withdrawing group gave lower yields (Fig. 2, 3g, 4g). Several α , β -unsaturated carboxylic acids with a substituent containing furan, thiophene and pyridine structure mainly generated alkenyl products with moderate yields (Fig. 2). When *cis*-cinnamic acid was used as substrate, the product was also (*E*)-2-styryl-1, 4-dioxane (Fig. 2). It may be that bond rotation emerged during the radical addition process, or the configuration of *cis*-cinnamic acid changed to *trans* in the reaction. These phenomena were observed previously for similar reactions in our group⁴².

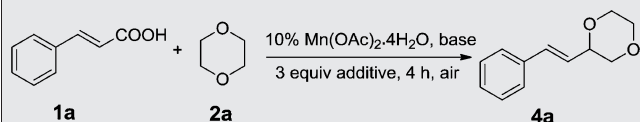
Table 1 | Reaction condition optimization^a

Entry	Catalyst	Additive ^b	Base	T (°C)	Yield (%)
1	-	-	DBU	100	0
2	-	TBHP	DBU	100	0
3	$Ni(OAc)_2 \cdot 4H_2O$	-	DBU	100	0
4	$Ni(OAc)_2 \cdot 4H_2O$	NBS	DBU	100	1
5	$Ni(OAc)_2 \cdot 4H_2O$	DDQ	DBU	100	5
6	$Ni(OAc)_2 \cdot 4H_2O$	BPO	DBU	100	8
7	$Ni(OAc)_2 \cdot 4H_2O$	TBHP	-	100	10
8	$Ni(OAc)_2 \cdot 4H_2O$	TBHP	TEA	100	15
9	$Ni(OAc)_2 \cdot 4H_2O$	TBHP	K_2CO_3	100	5
10	$Ni(OAc)_2 \cdot 4H_2O$	TBHP	DBU	25	25
11	$Ni(OAc)_2 \cdot 4H_2O$	TBHP	DBU	60	45
12	$Ni(OAc)_2 \cdot 4H_2O$	TBHP	DBU	90	75
13	$Ni(OAc)_2 \cdot 4H_2O$	TBHP	DBU	100	85
14	$NiCl_2 \cdot 6H_2O$	TBHP	DBU	100	70
15	$NiSO_4 \cdot 6H_2O$	TBHP	DBU	100	60
16	$Cu(OAc)_2$	TBHP	DBU	100	50
17	$Cu(OAc)_2 \cdot H_2O$	TBHP	DBU	100	52
18	$Co(OAc)_2 \cdot 4H_2O$	TBHP	DBU	100	45
19	$Zn(OAc)_2 \cdot 2H_2O$	TBHP	DBU	100	40
20	$Pb(OAc)_2 \cdot 3H_2O$	TBHP	DBU	100	43
21 ^c	$Mn(OAc)_2 \cdot 4H_2O$	TBHP	DBU	100	3

^aReaction condition: cinnamic acid (0.148 g, 1 mmol), catalyst (0.1 mmol, 10 mol %), additive (3 mmol), base (0.2 mmol, 20 mol %).

^bTBHP = tert-butyl hydroperoxide, 70% in water.

^cMajor product was (*E*)-2-styryl-1, 4-dioxane.

Table 2 | Reaction condition optimization under the manganese acetate catalysis^a

Entry	Additive ^b	Base	T (°C)	Yield (%)
1	-	DBU	100	0
2	NBS	DBU	100	0
3	DDQ	DBU	100	3
4	BPO	DBU	100	5
5	TBHP	-	100	10
6	TBHP	TEA	100	11
7	TBHP	K ₂ CO ₃	100	5
8	TBHP	DBU	25	27
9	TBHP	DBU	60	45
10	TBHP	DBU	90	77
11	TBHP	DBU	100	80

^aReaction condition: cinnamic acid (0.148 g, 1 mmol), catalyst (0.1 mmol, 10 mol %), additive (3 mmol), base (0.2 mmol, 20 mol %).

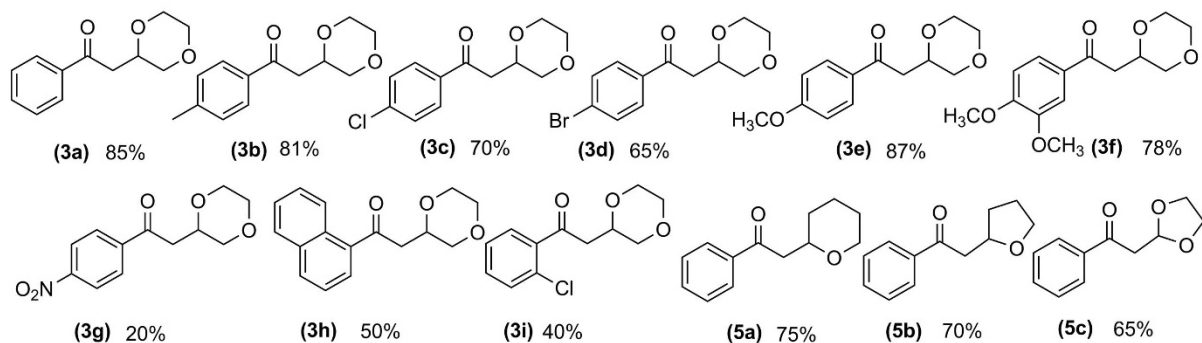
^bTBHP = tert-butyl hydroperoxide, 70% in water.

Other cyclic ethers could also be used as reactants, such as tetrahydro-2H-pyran, tetrahydrofuran and 1, 3-dioxolane. Desired products are also shown in Fig. 2. All of NMR and HRMS data for new compounds were obtained.

Discussion

The reaction yield dropped when butylated hydroxytoluene(BHT) was added. Moreover, no product was obtained with radical inhibitor 2, 2, 6, 6-tetramethylpiperidin-1-yloxy(TEMPO). It indicated that

Nickel-catalyzed products



Manganese-catalyzed products

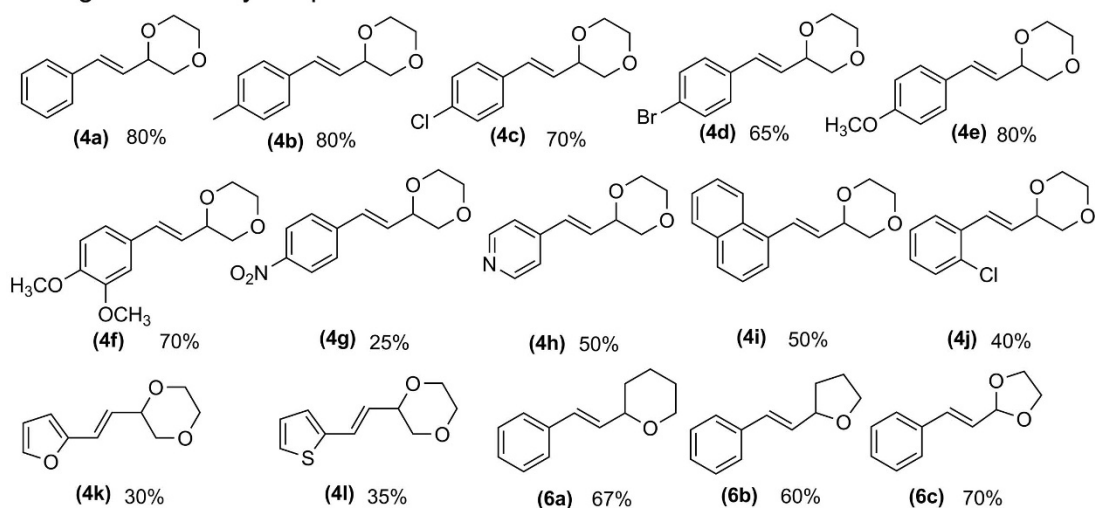


Figure 2 | Nickel-catalyzed and Manganese-catalyzed products.

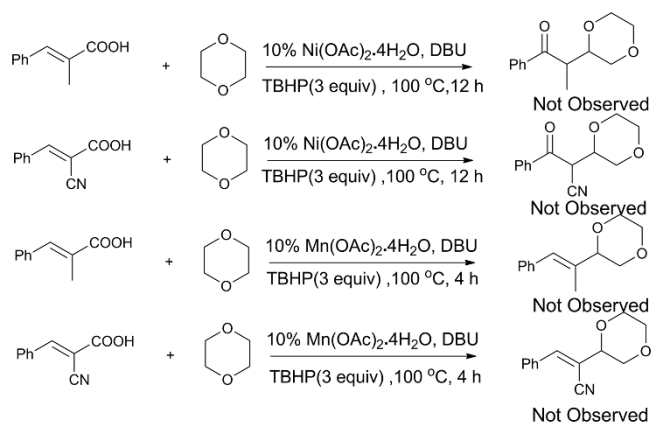


Figure 3 | The α -methyl and α -cyano cinnamic acids reacted with 1, 4-dioxane.

the reaction should be undergo a radical addition-elimination process in activation of sp^3 C-H bond adjacent to the oxygen atom in cyclic ethers with TBHP mediated. The radical usually added at the α -position of carbonyl group^{43–46}. When the α -methyl and α -cyano cinnamic acids were used as substrates (Fig. 3), no desired products were obtained. It's believed that this transition metal catalyzed decarboxylative coupling undergo a similar course.

A possible reaction mechanism is proposed in Fig. 4. The 1, 4-dioxane radical was generated by the initiator TBHP, which gave the *tert*-butoxy radical and hydroxyl radical from homolysis⁴². Reaction of α,β -unsaturated carboxylic acids with $Ni(OAc)_2 \cdot 4H_2O$ produced salts of Ni(II) carboxylate. When dioxane radical added to the α -position of the double bond in salts of Ni(II) carboxylate, the intermediate **1** was produced⁴⁷. Then the aryl α -hydroxylalkylated product was emerged via an addition of hydroxyl radical and elimination of carbon dioxide and Ni(II). DBU was beneficial to prompt this progress due to its unique structure and excellent base catalytic properties^{27–31}. Finally, the desired oxyalkylation product was generated^{32–35}.

The manganese catalyzed process should be different from the nickel-catalyzed process. Hydroxyl radical was consumed under the catalysis condition of TBHP and DBU^{48–50}. So the intermediate **2** was oxidized into a transition state **A** by trace oxygen in solution. Then it underwent direct radical elimination reaction and produced (E)-2-styryl-1, 4-dioxane (Fig. 4).

In conclusion, we have developed a nickel- and manganese-catalyzed selective decarboxylative cross coupling of α , β -unsaturated carboxylic acids with cyclic ethers. This work provided a useful approach for modification of the cyclic ether compounds. Various α , β -unsaturated carboxylic acids could be obtained for related organic synthesis via the C-H bond functionalization and C-C bond formation. Further research of relevant work will be expanded in our laboratory.

Methods

General procedure for the synthesis of all products. *A. General procedure for the oxyalkylation reaction.* To a mixture of cinnamic acid (0.148 g, 1 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (25 mg, 0.1 mmol) and 1, 4-dioxane (2 mL), DBU (0.3 g, 0.2 mmol), *tert*-butyl hydroperoxide (0.39 g, 3 mmol, 70% in water) was added dropwise at room temperature. The resulting mixture was refluxed for 12 hours. After the reaction, the solvent was removed under vacuum. The residue was separated on a silica gel column by using petroleum ether and ethyl acetate as eluent.

B. General procedure for the alkenylation reaction. To a mixture of cinnamic acid (0.148 g, 1 mmol), $Mn(OAc)_2 \cdot 4H_2O$ (25 mg, 0.1 mmol) and 1, 4-dioxane (2 mL), DBU (0.3 g, 0.2 mmol), *tert*-butyl hydroperoxide (0.39 g, 3 mmol, 70% in water) was added dropwise at room temperature. The resulting mixture was refluxed for 4 hours. After the reaction, the solvent was removed under vacuum. The residue was separated on a silica gel column by using petroleum ether and ethyl acetate as eluent.

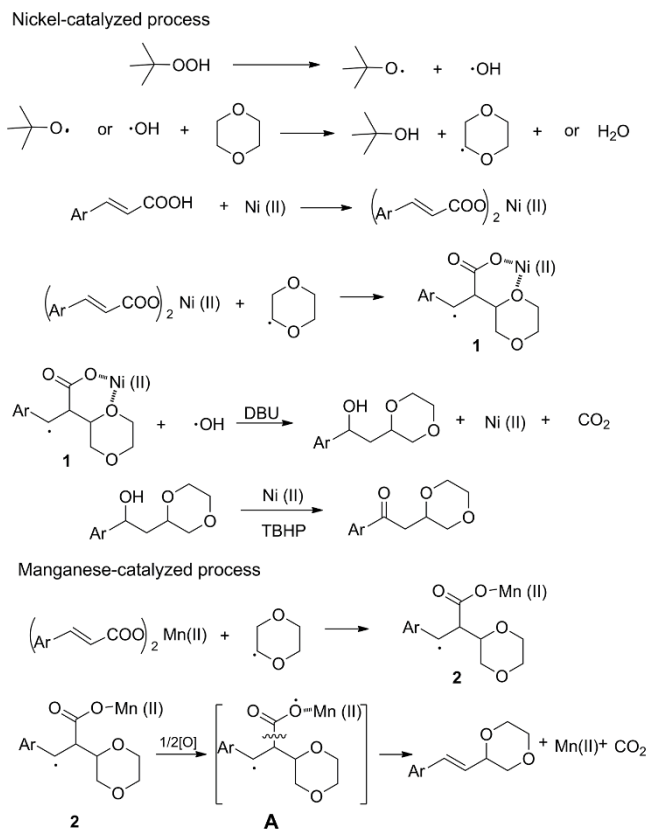


Figure 4 | Proposed reaction mechanism.

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Author contributions

J.X.Z. and N.X.W. wrote the main manuscript text and Y.J.W., W.Z., C.B.B., Y.L.X. and Y.H.L. prepared figure 4, and J.L.W. prepared NMR spectra. All authors reviewed the manuscript.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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