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A general and practical Lewis acids-catalyzed aryl formates synthesis

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ABSTRACT

A general and practical Lewis acids catalyzed synthesis of aryl formates has been established. With catalytic amount of cheap metal as the catalyst, good to excellent yields of aryl formates can be isolated with good functional group tolerance. Formic acid has been applied as the formyl source and triflate salts of zinc, manganese and copper are all suitable catalysts here.

Recently, aryl formates have been applied extensively as CO source in transition metal-catalyzed carbonylation reactions [1]. Carboxylic acid derivatives were produced through alkoxycarbonylation of aryl halides, hydroesterification of alkenes and etc. [2]. Although the applications of aryl formates have been broadly explored, their preparations are still based on traditional organic synthesis. That is a two-step procedure: first reacts formic acid with acetic anhydride at 60 °C to produce acetic formic anhydride; then reacts acetic formic anhydride with phenols at room temperature to give the aryl formate derivatives [1]. Under these backgrounds, we developed a catalytic one-pot one-step procedure for the synthesis of aryl formates very recently [3]. With $Pd(PPh_3)_2$ as the catalyst and formic acid as the formyl source, good yields of aryl formates were produced at room temperature. In our mechanistic studies, we proved the formyl group was indeed come from formic acid. However, in our continue studies, we found that the real role of palladium catalyst in this system might be that of a Lewis acid. If this is the case, expensive palladium catalyst can potentially be replaced by other cheap Lewis acids to make this procedure more practical. Hence various Lewis acids were tested and a more applicable and convenient procedure for aryl formates preparation has been established.

For establishing this new catalytic system, we choosed 4-methoxyphenol as the model substrate and various Lewis acids were tested in the presence of NaOAc and Ac_2O in formic acid at room temperature under nitrogen atmosphere (Table 1). Moderate to good yields of 4-methoxyphenyl formate can be produced in all the tested cases. Zinc catalyst provided the best results, which considered as a green, environmental benign and non-expensive catalyst (Table 1, entry 7) [4]. Good yields of formate can be obtained with copper triflate, silver triflate or magnesium triflate as the catalyst as well (Table 1, entries 8–10). No formate can be detected in the absence of Lewis acid and only 4-methoxyphenyl acetate as a product from the reaction between 4-methoxyphenol and acetic anhydride can be isolated (Table 1, entry 12) [5]. Additionally, 1-(2-hydroxy-5-methoxyphenyl)ethan-1-one as a Friedel-Craft reaction product can be detected as by-product as well [6].

With the best reaction combinations in hand, we started the scope and limitation testing subsequently (Table 2). Moderate to excellent yields of alkyl substituted aryl formates can be produced successfully under the standard reaction conditions (Table 2, entries 1–7). Methoxy and phenyl groups can be tolerated well as well (Table 2, entries 8–10). 80–82% yields of naphthalenyl formates were formed from the corresponding naphthols (Table 2, entries 11 and 12). 72% of TFBen (benzene-1,3,5-triyl triformate) was formed with benzene-1,3,5-triol as the starting material under the same conditions (Table 2, entry 13) [7]. Various electron-withdrawing substituted phenols have been tested as well, and good yields can be obtained in general (Table 2, entries 14–22). In the cases of unsatisfying results, the yields can be significantly improved by adding phenols in 30 min later after the other reagents mixed which due to the preformation of mixed acetic formic anhydride.

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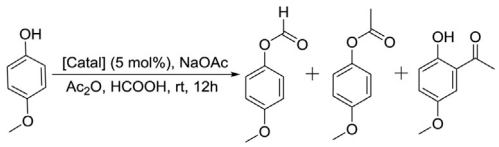
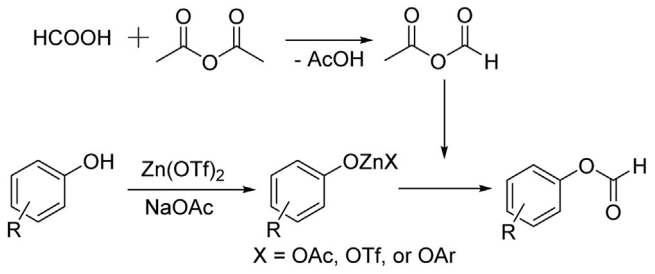
2468-8231/

Table 1
Lewis acid-catalyzed aryl formate synthesis: Optimization[a].



Entry	Catal.	Conv. (%)	Yield of formate (%)
1	ZnO	50	30
2	ZnI_2	71	52
3	$ZnCl_2$	88	78
4	$ZnSO_4$	70	69
5	$Zn(OAc)_2$	91	75
6	$Zn(acac)_2$	66	64
7	$Zn(OTf)_2$	100	85
8	$Cu(OTf)_2$	85	75
9	AgOTf	70	67
10	$Mg(OTf)_2$	81	72
11	$Zn(OTf)_2$	78	70[b]
12	/	10	0

[a] 4-Methoxyphenol (1 mmol), Lewis acid (5 mol%), NaOAc (1 equiv.), Ac_2O (10 equiv.), HCOOH (4 mL), 12 h, rt, nitrogen, isolated yields.
[b] $Zn(OTf)_2$ (2 mol%).



Scheme 1. Proposed reaction pathway.

Concerning the reaction pathway, a possible reaction mechanism is proposed (Scheme 1). Firstly, the mixed acid anhydride is formed by reacting formic acid with acetic anhydride. Meanwhile, zinc phenoxy compound is produced from zinc salt and phenols under the assistant of sodium acetate. The final aryl formates are formed from the reaction between acetic formic anhydride and zinc phenoxy compound.

In conclusion, a general and practical Lewis acids catalyzed synthesis of aryl formates has been established. With catalytic amount of cheap metal as the catalyst, good to excellent yields of aryl formates can be isolated with good functional group tolerance. Formic acid has been applied as the formyl source and triflate salts of zinc, manganese and copper are all suitable catalysts here.

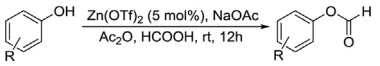
Procedures

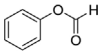
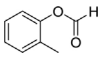
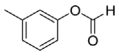
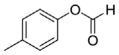
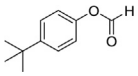
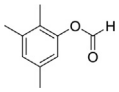
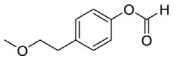
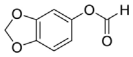
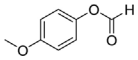
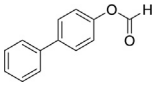
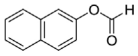
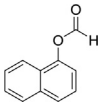
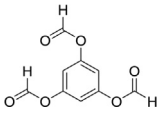
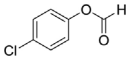
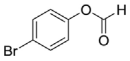
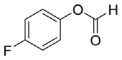
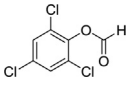
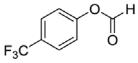
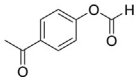
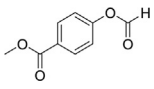
$Zn(OTf)_2$ (5 mol%), 4-methoxyphenol (1.0 mmol) and NaOAc (1.0 equiv.) were transferred into an oven-dried tube which was filled with nitrogen. Ac_2O (10 equiv.), HCOOH (4.0 mL) were added into the reaction tube. The mixture was stirred for 12 h at RT. After the reaction was complete, the reaction mixture was filtered and concentrated, column chromatography on silica gel (petroleum ether/ethyl acetate 10:1).

Phenyl formate [3] (Colorless oil, 75 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.37, 149.76, 129.62, 126.31, 121.03.

Table 2
Lewis acid-catalyzed synthesis of aryl formates[a].



Entry	Product	Yield (%)
1		61
2		42
3		67
4		72
5		81
6		92
7		90
8		56
9		85
10		87
11		82
12		80
13		72
14		60
15		68
16		40 78[b]
17		56
18		30 54[b]
19		55 77[b]
20		64 82[b]