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Short Communication

Ruthenium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of benzylic alcohols with phenols

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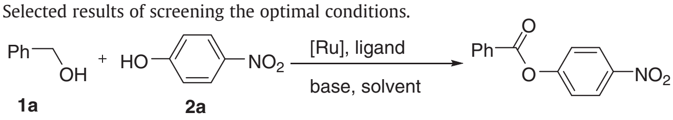
ABSTRACT

An efficient methodology to access benzoate derivatives via tandem benzylic oxidation/oxidative esterification of benzylic alcohols with phenols catalyzed by ruthenium/NHC was developed. This operationally simple one-pot process uses O_2 as the clean oxidant, producing esters in good to excellent yields.

1. Introduction

Ester groups are among the highly important and abundant functional groups in organic chemistry. Thus, it is worthwhile to provide an environmentally benign method to access esters [1,2]. The existent traditional methodology involves the activation of the carboxylic acid as an acyl halide, anhydride, or activated ester followed by nucleophilic substitution [3-8]. From the atom-economic point of view, the direct oxidative esterification of aldehydes remains as an attractive possibility to readily access esters [9-20]. Recently, the transition-metal-catalyzed tandem oxidation of alcohol to aldehyde followed by an oxidative esterification has received much attention [21-27]. For example, Scheidt demonstrated a tandem oxidation of alcohols to esters using N-heterocyclic carbenes as catalysts, which required super-stoichiometric amounts of MnO_2 as the oxidant [28]. Recently, Lei and Beller developed palladium-catalyzed aerobic oxidative esterification of benzylic alcohols, respectively [29,30]. However, less attention has been paid to the synthesis of aryl benzoate derivatives, which were building blocks of numerous active compounds and cross coupling partners [31,32]. Very recently, Chen developed a palladium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of benzylic alcohols with phenols to access aryl benzoate derivatives [33]. Nevertheless, a facile and versatile procedure on such transformation still remains a highly desired goal for organic chemists. Herein, we report a ruthenium/NHC-catalyzed tandem oxidation/esterification of benzylic alcohols with phenols, using O_2 as the clean terminal oxidant.

Table 1
Selected results of screening the optimal conditions.



Entry	[Ru]	Ligand	Base	Solvent	Yield (%)[a]
1	$[Ru(p\text{-cymene})Cl_2]_2$	–	Cs_2CO_3	Xylene	Trace
2	$[Ru(p\text{-cymene})Cl_2]_2$	L1	Cs_2CO_3	Xylene	8
3	$[Ru(p\text{-cymene})Cl_2]_2$	L2	Cs_2CO_3	Xylene	20
4	$[Ru(p\text{-cymene})Cl_2]_2$	L3	Cs_2CO_3	Xylene	61
5	$[Ru(p\text{-cymene})Cl_2]_2$	L4	Cs_2CO_3	Xylene	80
6	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	Xylene	90 (Trace)[b]
7	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	Xylene	(76)[c] (<5)[d]
8	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Na_2CO_3	Xylene	53
9	$[Ru(p\text{-cymene})Cl_2]_2$	L5	K_2CO_3	Xylene	40
10	$[Ru(p\text{-cymene})Cl_2]_2$	L5	*t*-BuOK	Xylene	11
11	$[Ru(p\text{-cymene})Cl_2]_2$	L5	–	Xylene	63
12	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	1,4-Dioxane	61
13	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	DCE	Trace
14	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	Toluene	30
15	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	DMF	<5
16	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	Xylene	85[e]
17	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	Xylene	46[f]
18	$[Ru(p\text{-cymene})Cl_2]_2$	L5	Cs_2CO_3	Xylene	62[g]
19	$Ru_3(CO)_{12}$	L5	Cs_2CO_3	Xylene	70
20	$RuCl_2(PPh_3)_3$	L5	Cs_2CO_3	Xylene	85
21	$RuCl\cdot 3H_2O$	L5	Cs_2CO_3	Xylene	12

[a] All reactions were run with phenylmethanol **1a** (0.3 mmol), 4-nitrophenol **2a** (0.2 mmol), [Ru] (5 mol %), ligand (10 mol %) and base (10 mol %), in dry solvent (2 mL) under O_2 at 130 °C for 24 h. Isolated yields: [b] in the absence of Ru, [c] under air, [d] under N_2, [e] Cs_2CO_3 (20 mol %), [f] Cs_2CO_3 (50 mol %), and [g] at 110 °C.

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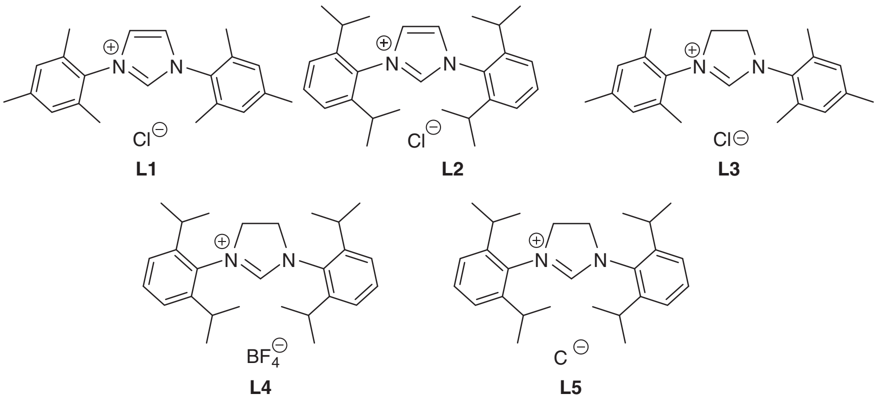


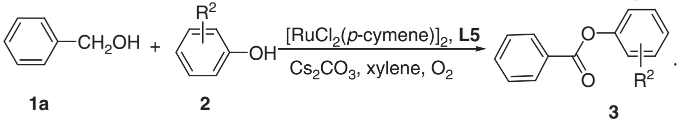
Fig. 1. Selected imidazolium salts screened.

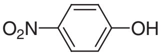
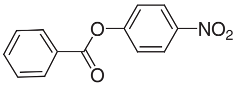
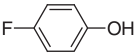
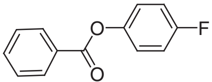
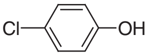
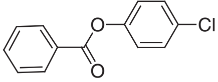
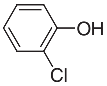
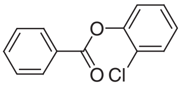
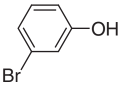
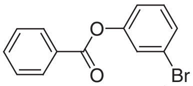
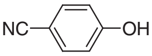
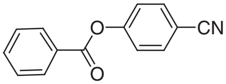
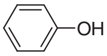
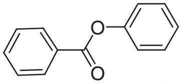
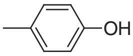
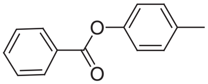
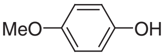
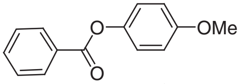
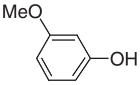
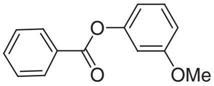
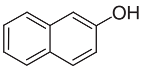
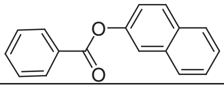
2. Results and discussion

From the economical and environmental point of view, the use of molecular oxygen as the terminal oxidant has attracted considerable attention. With this in mind, we began our investigation using phenylmethanol with 4-nitrophenol as the model reaction employing [RuCl$_2$(*p*-cymene)]$_2$ the catalyst under oxygen (Table 1). Only a trace of the product was formed in the absence of ligand as determined by GC–MS (Table 1, entry 1). Various precursors of N-heterocyclic carbene (NHC) (Fig. 1) were investigated for this

Table 2

Ruthenium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of phenylmethanol with phenols.



Entry	Phenol 2	Product 3	Yield (%)[a]
1	 **2a**	 **3aa**	88
2	 **2b**	 **3ab**	83
3	 **2c**	 **3ac**	95
4	 **2d**	 **3ad**	82
5	 **2e**	 **3ae**	80
6	 **2f**	 **3af**	85
7	 **2g**	 **3ag**	79
8	 **2h**	 **3ah**	90
9	 **2i**	 **3ai**	81
10	 **2j**	 **3aj**	84
11	 **2k**	 **3ak**	90

[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol), [RuCl$_2$(*p*-cymene)]$_2$ (5 mol %), L5 (10 mol %) and Cs_2CO_3 (10 mol %) in dry xylene (2 mL) under O_2 at 130 °C for 24 h. Isolated yield.