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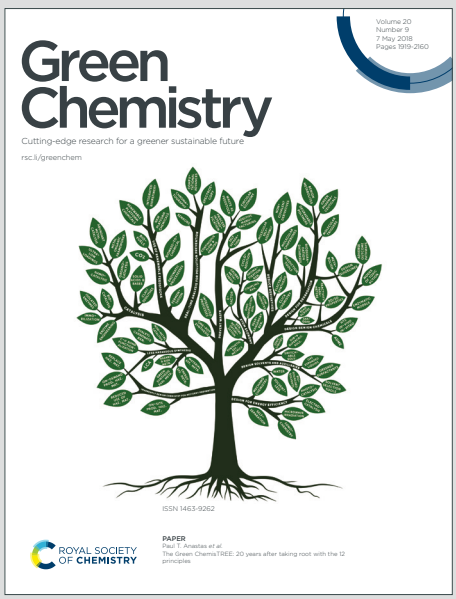

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ARTICLE

Ethyl lactate participated three-component dehydrogenative reactions: biomass feedstock in diversity oriented quinoline synthesis

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Lu Yang[a] and Jie-Ping Wan*[a]

The three-component reactions of ethyl/methyl lactate, anilines and aldehydes providing quinolines have been developed with simple iron(III) chloride catalysis without using additional organic medium or external oxidant. This three-component protocol displays high efficiency and broad substrate tolerance, allowing quick accesses to diverse quinoline products under neat reaction condition. The results reported herein disclose important new application of green biomass feedstock in the clean synthesis of valuable organic products.

Biomass derived chemicals constitute the most promising renewable sources in chemical and many other related manufactures.[1] Owing to the low cost and renewability associated with biomass chemicals, developing practical organic reactions employing biomass feedstock as raw materials is highly demanding since such synthesis can considerably enhance the sustainability of organic synthesis. As typical biomass feedstock with long research and application history, alkyl lactates such as ethyl lactate (EL) have been identified with many attractive advantages.[2] For example, EL is highly soluble both in water and organic chemicals, nontoxic, and fully degradable under natural atmosphere. Therefore, EL is regarded as a highly promising candidate building block in sustainable organic synthesis.[3]

Interestingly, the recent years have witnessed notable advances in the research area of EL-mediated organic synthesis. Benefiting from the green feature of EL, a plethora of valuable organic reactions, such as the carbonyl condensation,[4] cross coupling,[5] multicomponent reactions (MCRs) involving transformation of multiple chemical bonds,[6] carbon-carbon bond functionalization[7] and diverse other reactions[8] have been efficiently performed in EL or aqueous EL medium to provide environmentally benign synthetic routes. In contrast to the rapid advances in the chemistry utilizing EL as reaction medium, however, the research in organic synthesis employing EL as main building block keeps underdeveloped. Although a few methods for EL conversion via simple chemical transformation are known,[9] synthesizing chemicals of enhanced value via sophisticated tandem transformations on EL, on the other hand, is yet hardly available (Fig. 1). One recent interesting example on EL-participated organic synthesis is reported by Sanz et al, which affords a new method for diynone synthesis by reacting EL with terminal alkynes.[10]

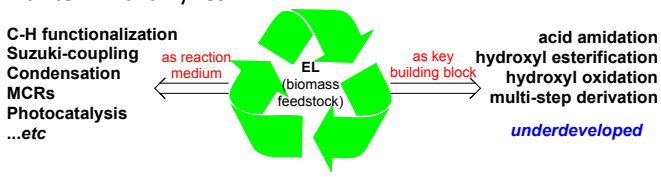

Figure 1 The application of EL as green medium *vs* building block

Quinolines are heterocyclic products showing up ubiquitously in functional molecules such as pharmaceuticals, biologically active lead compounds and organic materials.[11] To date, the importance of quinoline scaffolds has driven the establishment of numerous synthetic methods for efficient quinoline synthesis.[12] Despite of these enriched accesses, the synthetic sustainability remains as challenge in the area of quinoline synthesis.[13] In this context, employing renewable biomass-based substrate as building block for quinoline synthesis is highly desirable by allowing the efficient utilization of biomass feedstock. In the process of our work in EL mediated organic reactions, we have noticed that the oxidation of EL to pyruvate is a classical transformation on EL.[14] This inspires us that it is possible to make use of this transformation to devise sustainable synthetic methods with this renewable biomass feedstock by capturing the *in situ* generated pyruvate with proper reaction partners.

In addition, it is known that dehydrogenative reactions,[15] especially the heterocycle synthesis based on the acceptorless dehydrogenation of alcohols[16] are uniquely advantageous prototypes by enabling oxidative transformation without relying on external oxidant. Being enlightened by the known results on alcohol dehydrogenation as well as the structural feature of EL, we envision that EL is potentially applicable in

[a] *College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P. R. China.* ***Email:*** *wanjieping@jxnu.edu.cn*
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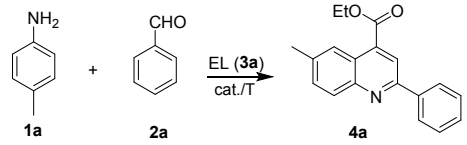
the designation of novel synthetic methods via dehydrogenation on its alcohol fragment. Herein, we report an unprecedented new method toward quinoline synthesis by using EL as one main building block to react with aldehydes and anilines in the manner of efficient three-component assembly.[17] As a brand-new tactic, this method features incomparable advantages of green synthesis in: a) nontoxic biomass feedstock as key starting material; b) oxidant-free dehydrogenation as key transformation; c) only water and hydrogen as by-products; d) low-cost $FeCl_3$ as catalyst. Comparing with the known tactics using conventional reagent such as alkynes/alkenes/ketones as C=C fragment donors,[18] the oxidant assistance[19] and/or noble metal catalysis,[20] this protocol employing biomass-based lactate as key building block is of evident advancement in term of synthetic sustainability by benefiting the aforementioned advantages.

As initial effort, the reaction of *p*-methylaniline **1a**, benzaldehyde **2a** and EL **3a** (98% commercial reagent) was run in the presence of TfOH, wherein the quinoline product **4a** was provided with 37% yield (entries 1, Table 1). No product was formed in the entry without acid (entry 2, Table 1). Following this clue, a series of proton and Lewis acids, including TMSCl, AcOH, *p*-TSA, $AlCl_3$, $FeCl_3$, $FeCl_2$ and lactic acid (LA) were screened for this reaction (entries 3-9, Table 1). The results proved that $FeCl_3$ was amongst the best acid. Subsequently, this reaction was conducted in different $FeCl_3$ loading, and 10% mol $FeCl_3$ turned out to be optimal (entries 10-13, Table 1). Further experiments comparing the effect of catalyst species with $Fe(OTf)_3$ and TfOH in the optimal loading did not provide better results (entries 14-15, Table 1). In addition, increasing the amount of **1a** to 1.5 equiv could further enhance the yield of **4a** (entry 16, Table 1). Finally, according to the results provided by parallel entries at different temperature, 110 °C was proved as the most favourable temperature (entry 17-20, Table 1). Later on, to examine the impact of EL concentration to the reaction, the control experiment employing stoichiometric EL (0.2 mmol) in dioxane medium was performed (entry 21, Table 1), wherein only trace **4a** was observed, suggesting that the centration of EL was crucial for this reaction.

With the results from optimization, the synthetic scope of this three-component quinoline construction was then investigated. As indicated by the results given in Table 2, the present method displayed excellent tolerance to the three involved components. For anilines, the presence of both electron donating and withdrawing substituent in *para*- (**4a**-**4g**, Table 2), *meta*-(**4h**-**4k**, Table 2) and *ortho*-position (**4l**-**4n**, Table 2) were well tolerated. The reaction could also be extended to the synthesis of benzo[h]quinoline by using naphthalen-1-

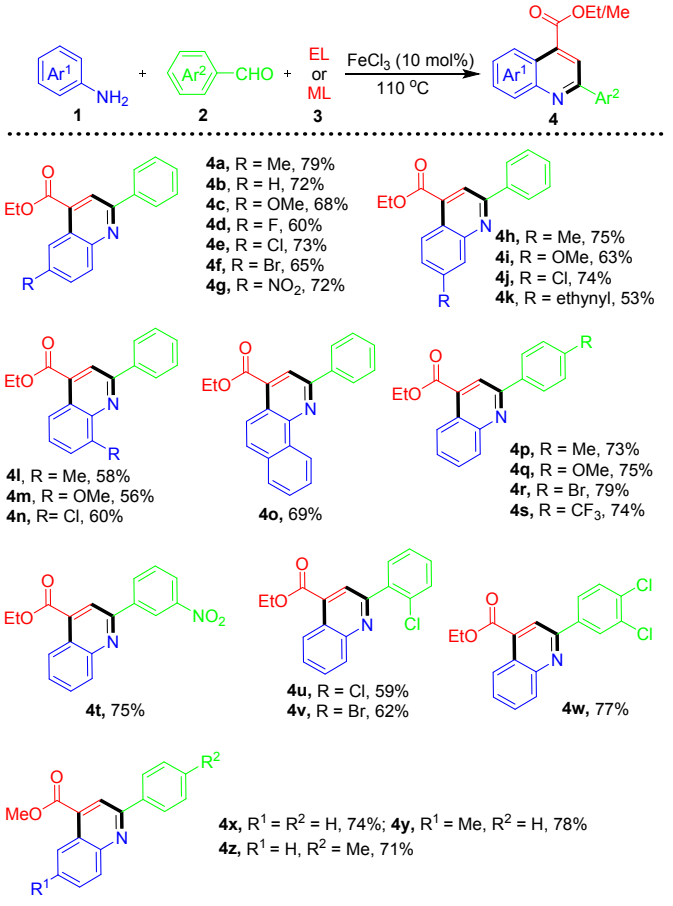
Table 1 Optimization experiments on the EL-quinoline synthesis[a]



entry	acid	T (°C)	yield (%)[b]
1	TfOH	90	37
2	no	90	nr
3	TMSCl	90	54
4	AcOH	90	trace
5	*p*-TSA	90	50
6	$AlCl_3$	90	49
7	$FeCl_3$	90	58
8	$FeCl_2$	90	56
9	LA	90	trace
10[c]	$FeCl_3$	90	69
11[d]	$FeCl_3$	90	72
12[e]	$FeCl_3$	90	70
13[f]	$FeCl_3$	90	55
14[d]	$Fe(OTf)_3$	90	49
15[d]	TfOH	90	67
16[d,g]	$FeCl_3$	90	75
17[d,g]	$FeCl_3$	80	74
18[d,g]	$FeCl_3$	100	75
19[d,g]	$FeCl_3$	110	79
20[d,g]	$FeCl_3$	120	75
21[d,h]	$FeCl_3$	110	trace

[a]General conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), and acid (0.6 mmol) in 2.0 mL EL, stirred for 12 h. [b]Yield of isolated product based on **2a**. [c]With 0.2 mmol $FeCl_3$. [d]With 0.02 mmol acid. [e]With 0.04 mmol acid. [f]With 0.01 mmol acid. [g]With 0.3 mmol **1a**. [h]EL (0.2 mmol) was used in dioxane (2 mL).

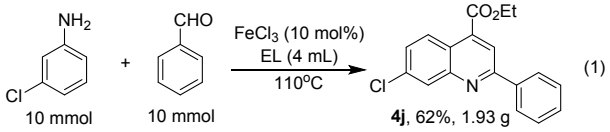
Table 2 Scope of the ethyl/methyl lactate-based quinoline synthesis[a,b]



[a]General conditions: **1** (0.3 mmol), **2** (0.2 mmol), $FeCl_3$ (0.02 mmol) in alkyl lactate (2.0 mL), stirred at 110 °C for 12 h. [b]Yield of isolated products based on aldehyde.

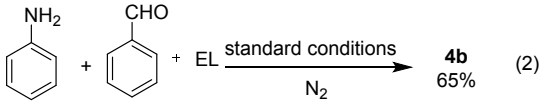
amine as substrate (**4o**, Table 2). Furthermore, the reaction employing benzaldehydes containing alkyl, alkoxyl, halogen, trifluoromethyl and nitro group were also successfully employed for the synthesis of corresponding quinolines with good to excellent yields (**4p**-**4w**, Table 2). A notable fact was that even strong electron withdrawing group such as nitro and trifluoromethyl functionalized substrates also afforded quinoline products with good yield in the reaction (**4g**, **4s** and **4t**, Table 2). Finally, using methyl lactate as alternative of EL provided quinoline products with analogously fine results (**4x**-**4z**, Table 2), confirming the high potential of this method in the synthesis of quinolines with high structural diversity. Further examination by independently employing butyraldehyde and pyridine-2-carbaldehyde to react with aniline and EL, however, did not lead to the synthesis of target products under the present conditions.

Considering the potential importance of this biomass-based synthesis, the scale up experiment was then conducted. As shown in Eq 1, as one of the anilines showing higher synthetic efficiency in Table 2, *m*-chloroaniline was selected for the 10 mmol scale reaction for **4j** synthesis. Using stoichiometric amine substrate provided the target product with good yield of 62%. This result suggested that stoichiometric amount of amine was also practical for such quinoline synthesis.

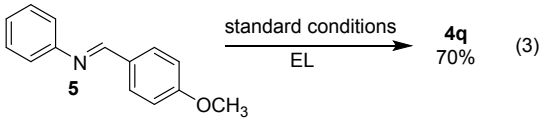


(1)

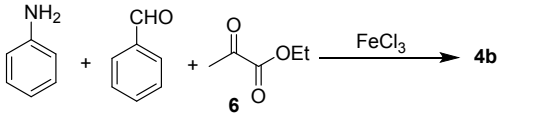
Successively, for the sake of understanding the reaction mechanism, a series of control experiments were designed and executed. First, performing the reaction of aniline, benzaldehyde and ethyl lactate under nitrogen atmosphere gave product **4b** with good yield, suggesting that oxygen was not the reliance of the reaction (Eq 2). On the other hand, employing imine **5** and EL to the standard conditions gave product **4q** with 70% yield (Eq 3), supporting that imine was a possible intermediate. In addition, ethyl pyruvate **6** could react



(2)

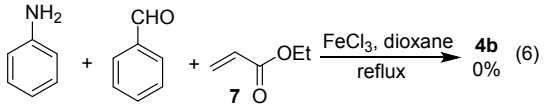


(3)



in 2 mL dioxane, reflux, 68% (4)

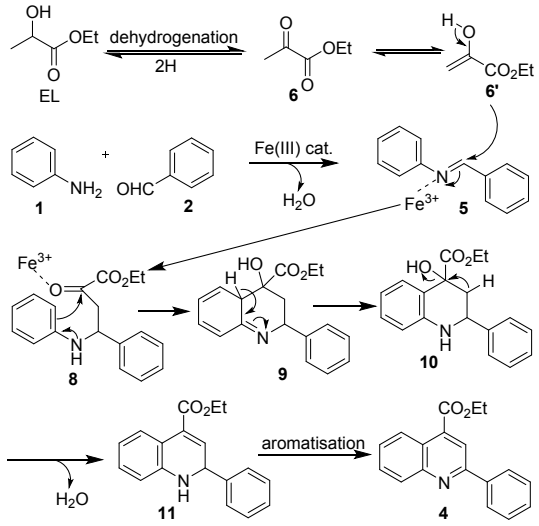
in 2 mL **6**, 110 °C, trace (5)



(6)

with aniline and benzaldehydes to provide product **4b** with 68% yield in dioxane (Eq 4), implying that **6** was also an intermediate in the reaction. Notably, performing this reaction by directly employing **6** as medium gave product **4b** with trace amount, indicating that high concentration of **6** was unfavored for this synthesis probably because of more complex side reactions such as pyruvate polymerization etc hampered the expected reaction (Eq 5). Correspondingly, using ethyl acrylate **7** as alternative reactant did no provide **4b** under identical conditions (Eq **6**), excluding the possibility of acrylate formation via EL dehydration during the reaction.

Following the results from the synthesis and control experiments, the possible reaction mechanism is proposed. As outlined in Scheme 1, the foremost transformation is the dehydrogenation of EL to ethyl pyruvate **6**. Although the process is reversible, **6** can be captured by the *in situ* generated imine **5** via its isomeric version **6'**. The adduct **8** then undergoes intramolecular addition of the nucleophilic aryl C-H bond to the ketone carbonyl, resulting in the formation of intermediate **10**. The dehydration-based elimination on **10** gives rise to dihydroquinoline intermediate **11**, and the subsequent aromatisation of **11** yields the target products **4**.



Scheme 1 The possible reaction mechanism

In summary, the present work discloses a brand new EL-based three-component protocol toward 2,4-disubstituted quinoline synthesis by coupling EL with anilines and aldehydes. This method is of high sustainability and greenness by featuring the advantages of biomass utilization, alcohol dehydrogenation as well as diversity oriented synthesis. Such method will reasonably be highly useful in the synthesis of quinoline derivatives. The results herein also pave the way for the designation of more biomass participated sustainable syntheses.

Conflicts of interest

There are no conflicts to declare.

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