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Double-Oxidative Dehydrogenative (DOD) [4 + 2]-Cyclization/Oxidative Aromatization Tandem Reaction of Glycine Derivatives with Ethylbenzenes

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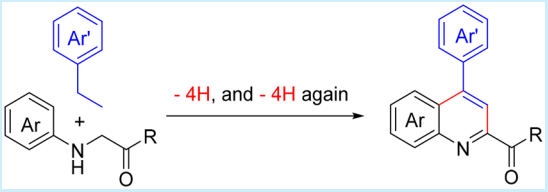
Supporting Information

ABSTRACT: The double-oxidative dehydrogenative (DOD) cyclization represents one of the most straightforward and atom-economical methods for cyclic structure formation. A Cu(II)/DDQ/O_2 system-catalyzed DOD [4 + 2]-annulation/oxidative aromatization tandem reaction of readily available glycine derivatives and alkylbenzenes was established. This approach facilitates rapid access to a broad scope of substituted quinoline-2-carboxylate derivatives, an important motif in drug discovery. The reaction could feasibly be applied to a 10 gram-scale synthesis.



Oxidation reactions are of significant importance in nature and play a crucial role in organic synthesis and the chemical industry.[1] Therefore, more sustainable and selective oxidation methods are currently in demand. In the past decade, oxidative dehydrogenative coupling reactions, namely, direct coupling between two C−H bonds, have become a growing and attractive field in organic chemistry.[2]

Very recently, we proposed the concept of the double-oxidative dehydrogenative (DOD) cyclization reaction.[3] From a scientific point of view, a DOD cyclization reaction that directly constructs two C−C bonds from four C−H bonds will be highly desirable as a straightforward and atom-economic method (Scheme 1a).

The quinoline-2-carboxylate framework is a common motif in bioactive natural products and synthetic drugs and has attracted widespread interest from the pharmaceutical and synthetic communities.[4] Many named reactions have been identified for quinoline synthesis, such as the Povarov, Skraup, Combes, Conrad−Limpach, Doebner−von Miller, Friedländer, and Pfitzinger reactions. In 1963, Povarov described the formal [4 + 2]-cyclization of aromatic imines and electron-rich olefins to form quinoline skeletons for the first time.[5] This reaction, which is now known as the Povarov reaction or imino Diels−Alder (imino-D-A) reaction, has become a powerful synthetic method for a six-membered *N*-heteroring system (Scheme 1b).[6]

Glycine is the simplest natural amino acid and can be manufactured industrially by treating chloroacetic acid with ammonia. In 2011, the Mancheño group developed a tandem oxidative Povarov/aromatization reaction of glycine derivatives with alkenes using an iron(III) salt as the catalyst and 2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) oxoammonium salt as the oxidant for the first time.[7] Since then, oxidative dehydrogenative cyclization of *N*-arylglycine derivatives with multiple bonds to form substituted quinoline-2-carboxylate motifs has been widely studied (Scheme 1c).[8]

Ethylbenzene (EB) is a frequently used and incredibly cheap reagent in the chemical industry. EB is one of the most widely produced alkyl aromatic compounds in the world and is readily available from biorenewable sources.[9] EB is cheaper than styrene. More importantly, EB is the upstream material of styrene. Styrene is prepared mainly from EB industrially. We questioned whether a new type of annulation reaction in which glycine derivatives and alkylbenzenes such as EB were oxidized in the same reaction mixture followed by the Povarov reaction was possible (Scheme 1d). If this DOD cyclization concept could be accessed, then the Povarov reaction will be advanced to a new level.

Herein, we report the preliminary realization of the DOD cyclization reaction envisioned above with a Cu(II)/DDQ/O_2 catalyst system. This primary work illustrates the great application potential of DOD cyclization to construct multiple carbon−carbon bonds and deliver complex cyclic frameworks.

Our initial investigation began with the DOD [4 + 2]-annulation of methyl (4-methoxyphenyl)glycinate (**1a**) with ethylbenzene (**2a**). Encouragingly, when the reactions were carried out by employing copper or iron salts as the catalysts and DDQ as the oxidant, the desired quinoline-2-carboxylate product **3aa** could be isolated in 37−63% yields (Scheme 2, entries 1−8). The molecular structure of **3aa** was confirmed by a single-crystal X-ray diffraction study. A catalyst screen showed that $CuCl_2$ was the best choice for the transformation (Scheme 2, entry 1). When the copper loading was reduced to 5 mol % or increased to 15 mol %, lower yields of **3aa** were obtained (Scheme 2, entries 9−10). The oxidant strongly affected this

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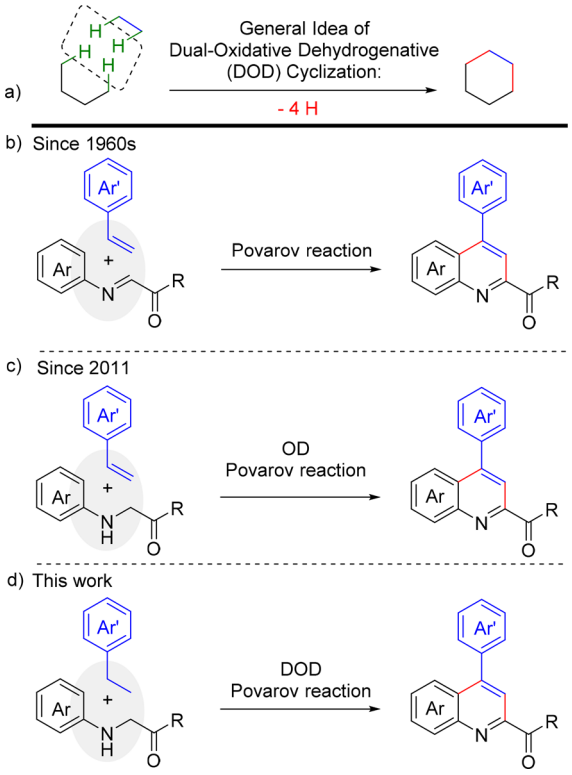
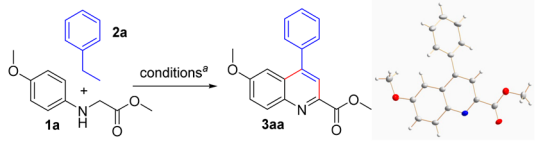
Scheme 1. Design of Double-Oxidative Dehydrogenative (DOD) Annulation



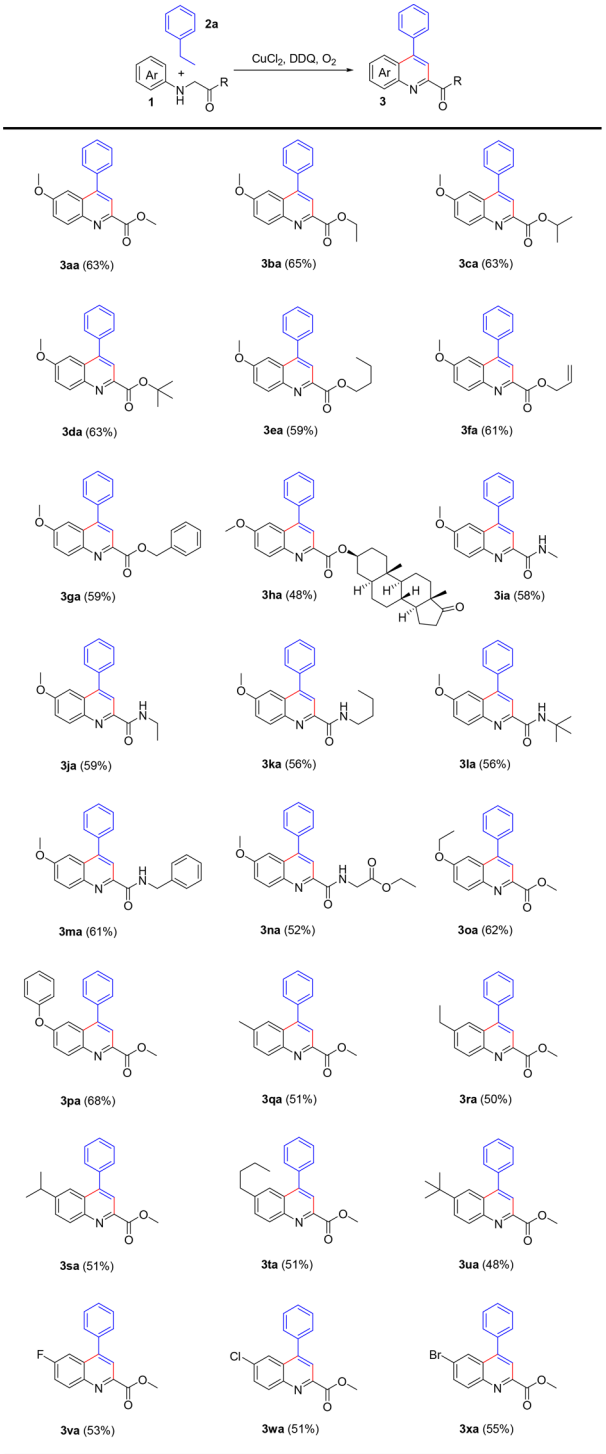
Scheme 2. Screening of Reaction Conditions



entry	catalyst	loading	oxidant	atmosphere	temperature (°C)	**3aa** yield (%)[b]
1	$CuCl_2$	10 mol %	DDQ	O_2	90	63
2	CuCl	10 mol %	DDQ	O_2	90	55
3	$CuBr_2$	10 mol %	DDQ	O_2	90	50
4	$Cu(OTf)_2$	10 mol %	DDQ	O_2	90	44
5	$Cu(OAc)_2$	10 mol %	DDQ	O_2	90	46
6	$FeCl_3$	10 mol %	DDQ	O_2	90	45
7	$FeCl_2$	10 mol %	DDQ	O_2	90	37
8	$Fe(OTf)_2$	10 mol %	DDQ	O_2	90	49
9	$CuCl_2$	5 mol %	DDQ	O_2	90	44
10	$CuCl_2$	15 mol %	DDQ	O_2	90	58
11	$CuCl_2$	10 mol %	PBQ	O_2	90	trace
12	$CuCl_2$	10 mol %	TBHP	O_2	90	0
13	$CuCl_2$	10 mol %	DTBP	O_2	90	0
14	$CuCl_2$	10 mol %	*m*CPBA	O_2	90	0
15	$CuCl_2$	10 mol %	oxone	O_2	90	0
16	$CuCl_2$	10 mol %	DDQ	air	90	52
17	$CuCl_2$	10 mol %	DDQ	Ar	90	0
18	$CuCl_2$	10 mol %	DDQ	O_2	100	62
19	$CuCl_2$	10 mol %	DDQ	O_2	80	38

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.2 mL), oxidant (1.25 mmol), atmosphere (O2 balloon), 5 h, 90−60 °C. [b]Isolated yields.

Scheme 3. Tandem DOD [4 + 2]-Annulation/Oxidative Aromatization Reaction of Glycine Derivatives with EB (2a)[a,b]



[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.2 mL), $CuCl_2$ (10 mol %), DDQ (1.25 mmol), O_2(balloon), 5−18 h, 90−60 °C. [b]Isolated yields.

reaction, and DDQ was found to be the most suitable oxidant. This DOD imino-D-A cycloaddition did not proceed when using benzoquinone, TBHP, DTBP, *m*CPBA, or oxone as the oxidant (Scheme 2, entries 11−15). A lower yield was observed when air (open flask) was used instead of pure oxygen gas (balloon) (Scheme 2, entry 16). Control experiments indicated that none of the desired reaction was observed under an argon atmosphere (Scheme 2, entry 17). The influence of the temperature was also studied. Both increasing and decreasing the temperature resulted in lower yields (Scheme 2, entries 18−19). The reaction did not give excellent yield maybe due to the self-reactions of glycine ester under oxidation conditions. The dimer and oxidative product of glycine ester **1a** can be detected by HRMS in the reaction mixture.

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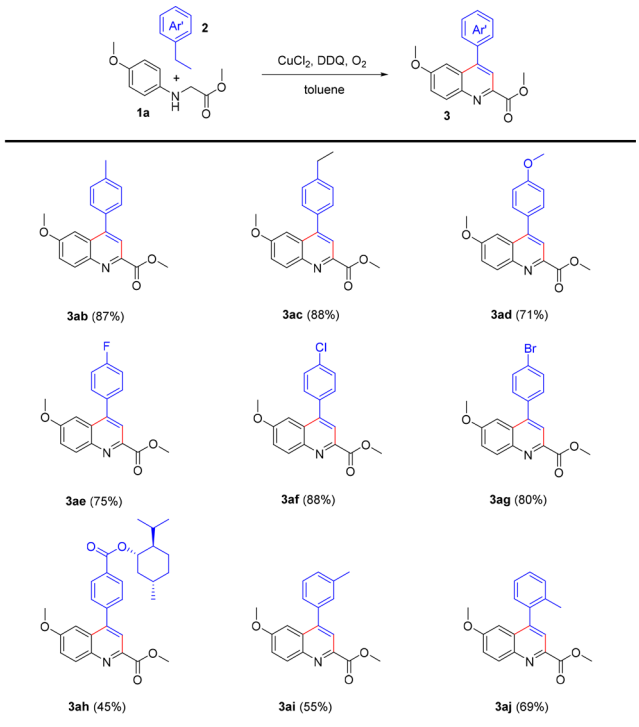
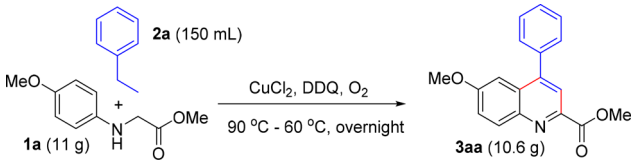
Scheme 4. Tandem DOD [4 + 2]-Annulation/Oxidative Aromatization Reaction of Methyl (4-Methoxyphenyl)glycinate (1a) with EB Derivatives[a,b]



[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.2 mL), $CuCl_2$ (10 mol %), DDQ (1.25 mmol), O_2(balloon), 5−18 h, 90−60 °C. [b]Isolated yields.

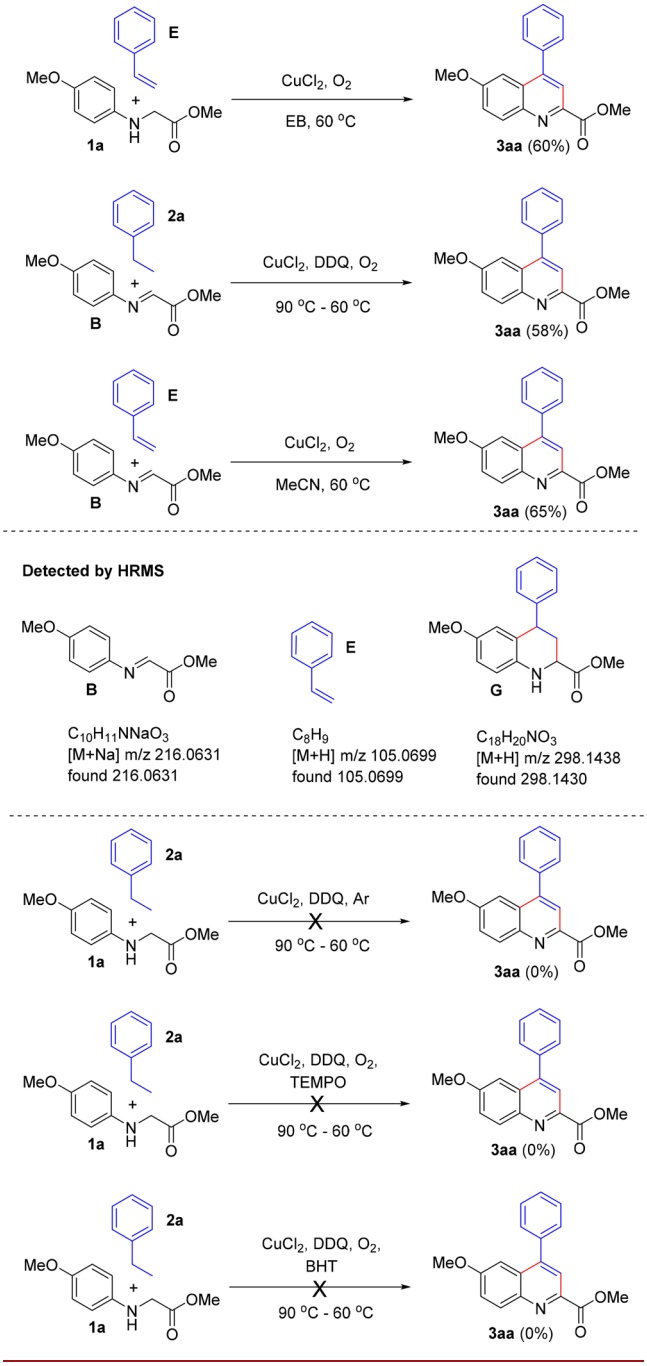
Scheme 5. Scalability of the Reaction to the Multigram Scale



With this DOD catalytic system in hand, we next sought to examine the scope and generality of glycine derivatives. Initially, different *N*-PMP (*p*-methoxyphenyl) glycine esters (Scheme 3, **1a**−**1h**), *N*-PMP glycine amides (Scheme 3, **1i**−**1m**), and short peptides (Scheme 3, **1n**) were investigated, and the reaction proceeded smoothly to afford the desired products in high yields (Scheme 3, **3aa**−**3na**). Notably, a glycine derivative with a more elaborate molecular architecture, namely, the *trans*-androsterone derivative, was also a suitable substrate and afforded the corresponding product **3ha** in high yield. This product may have potential utility in pharmaceutical chemistry. This example helps demonstrate the value of this method in providing rapid access to complex compounds. A range of substituents on the *N*-aryl group were applicable to the present catalyst system (Scheme 3, **3oa**−**3xa**). Halide substituents remained intact after the reaction, providing an easy handle for further synthetic elaborations (Scheme 3, **3ba**−**3xa**). *meta*- or *ortho*-Substituted aniline glycine derivatives gave a complex reaction mixture. Moreover, the scope of EBs was also investigated with methyl (4-methoxyphenyl)glycinate (**1a**). EBs with electron-donating groups and electron-withdrawing groups all worked well under the present reaction conditions (Scheme 4, **3aa**−**3ag**). It is worth noting that **2h** derived from (+)-menthol was also a suitable substrate for the reaction, affording the desired product **3ah** in moderate yield. This example also helps demonstrate the value of this method in providing rapid access to complex compounds. The reaction of *meta*- or *ortho*-substituted EBs also proceeded smoothly to furnish the corresponding products (Scheme 4, **3ai**, **3aj**) in high yield.

To examine the scalability of this DOD annulation method, the reaction between methyl (4-methoxyphenyl)glycinate (**1a**) and ethylbenzene (**2a**) was performed on a 10 gram-scale in a single batch. The desired product **3aa** was obtained in 65% isolated yield (Scheme 5). This result indicates that the present DOD protocol not only is atom-efficient but also could be conveniently scaled up in industry.

Scheme 6. Control Experiments



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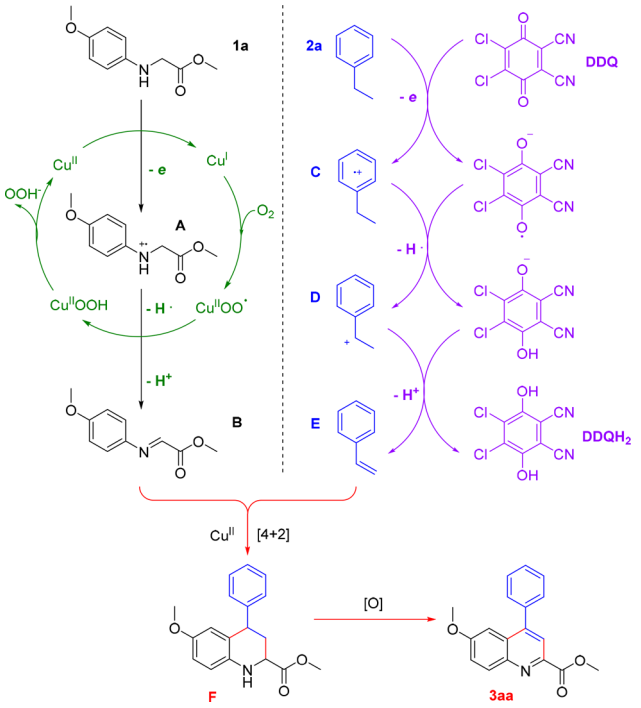
Scheme 7. Proposed mechanism



To shed light on the reaction mechanism of this DOD [4 + 2]-cyclization/oxidative aromatization tandem reaction of glycine derivatives with alkylbenzenes, a series of experimental studies were conducted. The reaction of glycine ester (**1a**) and styrene (**E**), the reaction of imine **B** and EB (**2a**), and the reaction of imine **B** and styrene (**E**) were investigated (Scheme 6). Furthermore, we found that imine **B**, styrene **E**, and tetrahydroquinoline **F** could be detected in the crude reaction mixtures by means of HRMS analysis (Scheme 6). These results indicate that imine **B**, styrene, **E**, and tetrahydroquinoline **F** may be involved as key intermediates in this DOD-based tandem process. The reaction of **1a** and **2a** under an argon atmosphere was investigated (Scheme 6), and none of the desired product **3aa** was obtained. This result indicates that oxygen is crucial for the reaction. Radical trapping experiments were also conducted by employing TEMPO or BHT as radical scavengers (Scheme 6). No desired product was observed in the reaction of **1a** with **2a**. These results suggest that the reaction includes a radical process.

Based on the experimental data and precedent literature, a plausible mechanism is proposed in Scheme 7. Glycine ester **1a** was oxidized to generate imine intermediate **B** under copper-catalyzed aerobic conditions. Moreover, EB was oxidized to generate styrene **E** in the presence of DDQ at the same time. Subsequently, a Povarov reaction of **B** with **E** occurred to generate the corresponding tetrahydroquinazoline intermediate **F** regioselectively due to the stability of intermediate carbocation. Finally, oxidative aromatization of intermediate **F** occurred to afford the desired product **3aa**.

In summary, we have developed an efficient and practical Cu(II)/DDQ/O_2-catalyzed tandem DOD [4 + 2]-annulation/oxidative aromatization reaction from easily available starting materials for the efficient synthesis of quinoline-2-carboxylates via activation of four C−H bonds in one reaction. This new method represents a straightforward and atom-economical concept and tolerates a variety of useful functional groups. The 2-carboxyl group of the products makes this method particularly appealing since this substituent can be used for further synthetic manipulations. Further studies expanding the DOD cyclization strategy to the synthesis of other heterocycles 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.8b01941.

Experimental details, compound characterization, and NMR spectra (PDF)

Accession Codes

CCDC 1846737 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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