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Application of laccase/DDQ as a new bioinspired catalyst system for the aerobic oxidation of tetrahydroquinazolines and Hantzsch 1,4-dihydropyridines



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ABSTRACT

Laccase/DDQ as a new bioinspired quinone-based cooperative catalytic system was used for the biomimetic aerobic oxidative synthesis of 2-substituted quinazolines and Hantzsch pyridines from the oxidative cyclocondensation of 2-aminobenzylamine and aldehydes and the oxidative aromatization of 1,4-dihydropyridines, respectively. The products were obtained in good to high yields in a phosphate buffer (0.1 M, 12.5 mL, pH 4.5) and acetonitrile (4 vol%) mixture as a solvent. These methods are more eco-friendly, efficient, simple, and practical than other currently available ones because of mild reaction conditions and because they are free from any halide and toxic and expensive transition metals. Therefore, these methods can be applied in pharmaceutical and other sensitive synthetic procedures.

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1. Introduction

Nitrogen-containing heterocycles are the most abundant and integral scaffolds that exist ubiquitously in a variety of synthetic drugs, pharmaceuticals, bioactive natural products, and agrochemicals [1,2]. Among these heterocycles, quinazolines and their derivatives are important compounds in organic synthesis and the industrial production of pharmaceutical compounds that show various biological activities [3–9] such as anticancer [3–5], antiviral [6], antibacterial [7], and antitubercular [9] ones. The first synthesis of a quinazoline derivative, 2-cyano-3,4-dihydro-4-oxoquinazoline, by reacting cyanogen with anthranilic acid was reported by Griess in 1869. Since then,

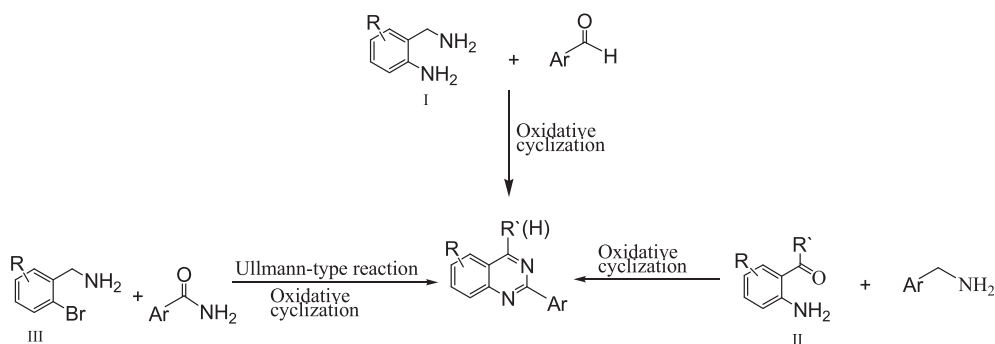
there has been a spurt at activity to synthesize quinazolines because of their biological importance [10,5a]. A growing importance of quinazolines provides a strong rationale to the development of various synthetic methodologies. Substituted quinazolines have been synthesized by various methods involving several substrates such as 2-aminobenzylamines (I), 2-aminobenzaldehydes and 2-aminobenzoketones (II), or 2-bromobenzylamines (III) (Scheme 1) [11].

Pyridines also are among the most important heterocycles that are often found in natural products, flavors and fragrances, pharmaceuticals, additives, agrochemicals, dyes, and polymers. They are used as ligands in coordination chemistry and as reagents and building blocks in organic synthesis [12]. One of the most popular methods for preparation of pyridines is oxidation of corresponding 1,4-dihydropyridines, which in turn can be synthesized via the classical Hantzsch 1,4-dihydropyridine synthesis (Scheme 2) [13].

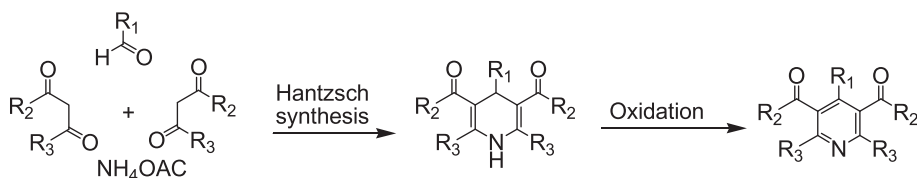
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Scheme 1. Approaches for the synthesis of quinazolines.



Scheme 2. Synthesis and oxidation of Hantzsch 1,4-dihydropyridines.

In view of the importance of quinazolines and pyridines, a large number of stoichiometric or large excess amounts of oxidants and homogenous and heterogeneous catalysts have been reported in the literature for synthesis of 2-substituted quinazolines and Hantzsch pyridines from oxidative cyclocondensation of 2-aminobenzylamines and aldehydes and oxidative aromatization of 1,4-dihydropyridines, respectively. Typical examples such as MnO_2 [14], NaClO [15], and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [16], Ir-catalyzed hydrogen transfer reaction [17], Pt/CeO_2 [18], FeCl_3 [19], pyridinium chlorochromate [20a], $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ [20b], MnO_2 [20c], NO [20d], HNO_3 [20e], $\text{Zr}(\text{NO}_3)_4$ [20f], and 1,2,4-triazolinedione [20g]. However, most of these methods suffer from one or more following drawbacks: hard reaction conditions, poor atom efficiency, utilization of environmentally unfavorable and expensive oxidants and catalysts, tedious procedure for the preparation of homogenous and heterogeneous catalysts, and the formation of large amounts of toxic waste. Therefore, the development of more efficient and green methods is important for synthesis of quinazolines and pyridines. The use of “green oxidants” such as molecular oxygen or air is attractive, because they are readily available, inexpensive, and environmentally benign [21]. Thus, aerobic oxidative synthesis of these valuable compounds in the presence of transition metal catalysts or organo-catalysts has been developed [22]. Typical examples include the use of 5 mol% of CuCl/DABCO/TEMPO (DABCO, 1,4-diazabicyclo[2.2.2]octane and TEMPO, 2,2,6,6-tetramethyl-piperidin-1-yloxy) catalytic system [23], Pt/Ir bimetallic nanoclusters in combination with catechol co-catalysts [24], the assembly of rhodium (Rh) nanoparticles on carbon nanotubes (CNTs) along with redox-active quinone-type cocatalyst [25], 1,10-phenanthroline-5,6-dione associated with different metals (Zn, Fe, or Ru) [26],

$\text{Fe}(\text{ClO}_4)_3/\text{acetic acid}$ [27a], $\text{Fe}(\text{ClO}_4)_3/N$ -hydroxyphthalimide [27b], $\text{Fe}(\text{ClO}_4)_3/\text{triarylammonium radical cation salt}$ [27c], and $\text{FeCl}_3/\text{NaNO}_2/\text{TEMPO}$ [27d]. Although these catalyst systems could efficiently perform oxidation reactions, these procedures still suffer from some problems such as high reaction temperatures, low catalytic efficiency, tedious catalyst preparation, and the use of toxic organic solvents and toxic transition metals as catalyst, which are essentially challenging to separate from the reaction mixture. Even when it is possible to separate the catalyst, trace amounts of the catalyst are possible to stay in the final product. It is vital to eliminate the catalyst (especially in pharmaceutical industry) because metal contamination is highly regulated. Therefore, it seems that there is still a great interest in developing efficient, eco-friendly, and nonmetallic catalysts for the aerobic oxidative synthesis of quinazolines and Hantzsch pyridines.

One particular stoichiometric organo-oxidant that is capable of performing a wide range of organic transformations is DDQ [28,29]. However, the stoichiometric use of DDQ results in equimolar quantities of the 2,3-dichloro-5,6-dicyano-hydroquinone (DDQH_2) byproduct that leads to difficult purification on a large scale. Also, DDQ is relatively expensive (\$680/mol) and toxic (LD_{50} of 82 mg/kg). Consequently, to avoid these disadvantages, the use of a catalytic amount of DDQ in the presence of economically and environmentally benign oxidants that regenerate DDQ from its reduced hydroquinone form has received increasing attention as a possible alternative to the widely used traditional DDQ in organic synthesis. Some of the stoichiometric co-oxidants that have been used for the regeneration of DDQ include FeCl_3 (3 equiv) [30], $\text{Mn}(\text{OAc})_3$ (3 equiv) [31], and MnO_2 (up to 6 equiv) [32]. Although these methods have partly addressed some problems of the stoichiometric DDQ, however these

reagents show poor atom efficiency. Green chemistry encourages the design of green processes using O_2 or air as the highly atom-economical, environmentally benign, and abundant oxidant and minimizing the generation of hazardous materials. So, it would be ideal if molecular oxygen or air can serve as a terminal oxidant in DDQ-mediated reactions. Nonetheless, molecular oxygen cannot directly oxidize DDQH₂ to DDQ under mild conditions [33]. Indeed, a redox compound should be used as the bridge among molecular oxygen and the cycling DDQH₂/DDQ. In this context, several research groups have used NO/NO₂-based redox cycle systems in combination with DDQ to catalyze the aerobic oxidation of organic compounds, including oxidation of alcohols [34], oxidative cleavage of benzylic ethers [35], dehydrogenation of saturated C–C bonds [36], oxidative C–C coupling reactions, and amination of arenes [37]. Very recently, Fe(NO₃)₃ has been used as a cocatalyst with catalytic DDQ in aerobic oxidation of alcohols [38]. Although these methods presented interesting breakthrough in the field of aerobic oxidation reactions in the presence of catalytic amount of DDQ, the development of an efficient and eco-friendly cocatalyst in combination with DDQ to catalyze the aerobic oxidation of organic compounds under mild conditions is still highly desired.

Laccases (*p*-benzenediol: oxygen oxidoreductase [E.C. 1.10.3.2]) are extracellular enzymes that contain four copper centers per protein molecule and catalyze the oxidation of electron-rich aromatic substrates, usually phenols or aromatic amines [39]. The unique properties of laccases such as mild reaction conditions and substrate selectivity make them attractive for use in chemical synthesis [40]. Furthermore, the redox potential of laccases can be extended via natural mediators such as 3-hydroxyanthranilic acid and 4-hydroxybenzoic acid as well as by artificial mediators including TEMPO, 1-hydroxybenzotriazole, and 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) [41]. This allows the oxidation of substrates with higher redox potentials. Meanwhile, laccases and laccase/mediator systems have been applied for the oxidation of a number of functional groups [42–44]. To the best of our knowledge, there has been no report on the use of laccase/DDQ as a bioinspired cooperative catalyst system in the transition metal-free and halogen-free aerobic oxidation of organic compounds (Scheme 3).

In continuation to our systematic study about application of laccase and laccase mediator system in organic synthesis [45], herein we present for the first time the nonmetallic, simple, and efficient methods for the synthesis of 2-substituted quinazolines and Hantzsch pyridines via aerobic oxidative in the presence of the laccase/DDQ catalyst system, using O_2 or air as an oxidant and a phosphate buffer solution as a solvent.

2. Experimental section

2.1. Materials and instruments

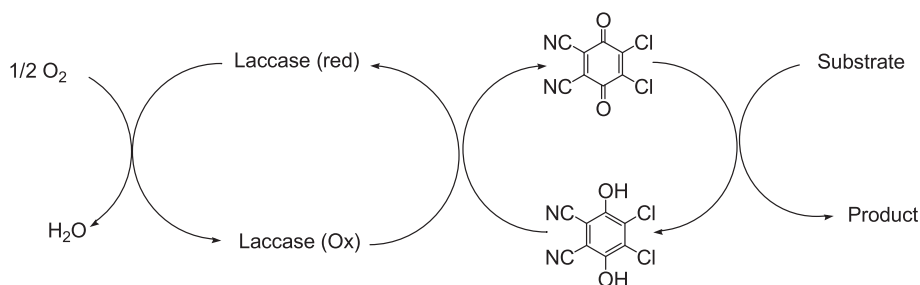
Laccase (E.C. 1.10.3.2) from *Trametes versicolor* was purchased from Sigma–Aldrich (St. Louis, MO, USA). Sodium acetate buffer (100 mM) at pH 5 was used for preparing solutions for the activity assay. All chemicals and solvents were of analytical grade and used without further purification. ¹H NMR spectra were recorded using a 250 MHz Bruker NMR spectrometer. Melting points were measured on a Barnstead Electrothermal IA 9100 and are uncorrected.

2.2. Enzyme activity assays

The activity of commercial enzyme laccase from *T. versicolor* was determined spectrophotometrically by monitoring the oxidation of 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS, $\epsilon = 36,000 \text{ M}^{-1} \text{ cm}^{-1}$). The reaction mixture included 5 mM of ABTS (100 μL) in 100 mM of acetate buffer (pH 5.0) and laccase enzyme. The change in absorption was observed via UV–vis spectroscopy at 420 nm for 5 min at room temperature [46]. One unit was defined as the amount of enzyme that oxidizes 1 μmol of ABTS per minute. The activity of laccase enzyme batch applied in this investigation was evaluated at 0.89 U/mg.

2.3. General procedure for the aerobic oxidative synthesis of 2-substituted quinazolines by laccase/DDQ catalyst system

A solution of 2-aminobenzylamine (1 mmol) and aldehydes (1 mmol) in 5 mL of CH₃CN was stirred at room temperature until the cyclocondensation was completed (about 3–5 h). After complete conversion of 2-aminobenzylamine to tetrahydroquinazoline (TLC), the solvent was concentrated to 0.5 mL and DDQ (45.4 mg, 0.2 mmol), and sodium phosphate buffer solution (NaPBS) (0.1 M, pH 4.5, 12.5 mL) and laccase from *T. versicolor*



Scheme 3. Proposed DDQ-mediated aerobic oxidation reactions.

(100 U, 89 mg) were added. Then, the mixture was stirred at 45 °C under molecular oxygen (balloon) or air for the time given in Table 1. After completion of the reaction (monitored by TLC), the mixture was extracted by EtOAc (3 × 10 mL) and dried over anhydrous Na₂SO₄. The crude product obtained after the removal of a solvent under vacuum was purified by chromatography on silica gel (*n*-hexane/ethyl acetate, 3/1). All of the products were identified and characterized by comparing their spectral data (¹H NMR) and physical properties (melting point) with those of authentic samples (see Supplementary data).

2.4. General procedure for the aerobic oxidative synthesis of pyridines by laccase/DDQ catalyst system

A 25 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 1,4-dihydropyridine (1 mmol), DDQ (45.4 mg, 0.2 mmol), and acetonitrile (0.5 mL). NaPBS (0.1 M, pH 4.5, 12.5 mL) and laccase from *T. versicolor* (100 U, 89 mg) were added and the reaction mixture was stirred under molecular oxygen (balloon) or

air at room temperature for the time given in Table 2. After completion of the reaction (monitored by TLC), the mixture was extracted by ethyl acetate (3 × 10 mL) and dried over anhydrous Na₂SO₄. The crude product obtained after the removal of a solvent under vacuum was purified by chromatography on silica gel (*n*-hexane/ethyl acetate, 3/1). All of the products were identified and characterized by comparison of their spectral data (¹H NMR) and physical properties (melting point) with those of authentic samples (see Supplementary data).

Table 2

Laccase/DDQ-catalyzed aerobic oxidative synthesis of pyridine derivatives.^a

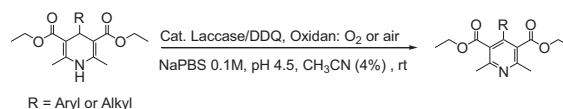
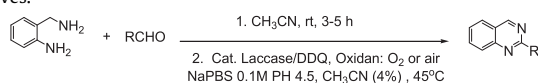


Table 1

Laccase/DDQ-catalyzed aerobic oxidative synthesis of quinazoline derivatives.^a



Entry	RCHO	Product	Time (h)	Isolated yield (air) ^b (%)
1			22	95 (87)
2			20	96 (84)
3			24	94 (86)
4			26	93 (85)
5			20	93 (82)
6 ^c			24	91 (80)
7			24	83 (77)
8			22	93 (84)
9			24	91 (80)
10			24	72 (64)
11			24	87 (79)

^a General procedure: Aldehyde (1 mmol), 2-aminobenzylamine (1 mmol), laccase (100 U), DDQ (20 mol%), O₂ (balloon), NaPBS (12.5 mL), CH₃CN (0.5 mL), 45 °C.

^b Isolated yield under air conditions is shown in parentheses.

^c Conditions: Aldehyde (1 mmol), 2-aminobenzylamine (2 mmol), laccase (200 U), DDQ (40 mol%), O₂ (balloon), NaPBS (25 mL), CH₃CN (1 mL), 45 °C.

Entry	Substrates	Product	Time (h)	Yield (air) ^b (%)
1			7	98 (87)
2			10	96 (84)
3			8	94 (80)
4			6	97 (85)
5			7	93 (79)
6			12	95 (81)
7			14	90 (78)
8			12	98 (89)
9			12	97 (86)
10			16	98 (88)
11			11	96 (83)
12			14	90 (76)

^a General procedure: 1,4-Dihydropyridine (1 mmol), laccase (100 U), DDQ (20 mol%), O₂ (balloon), NaPBS (12.5 mL), rt.

^b Isolated yield under air conditions is shown in parentheses.

2.5. Selected spectra data

2.5.1. 2-Phenyl quinazoline

Pale yellow solid; mp 97–98 °C: 95% yield (196 mg, 0.95 mmol) [23] (Table 1, entry 1).

¹H NMR (250 MHz, DMSO-d₆): δ = 9.70 (s, 1H), 8.54–8.57 (m, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.99–8.04 (m, 2H), 7.70–7.76 (m, 1H), 7.55–7.56 (m, 1H).

2.5.2. 2-(4-Methoxyphenyl) quinazoline

White solid; mp 78–80 °C: 96% yield (226 mg, 0.96 mmol) [23] (Table 1, entry 2).

¹H NMR (250 MHz, DMSO-d₆): δ = 9.61 (s, 1H), 8.49 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.98 (br s, 2H), 7.66–7.67 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 3H).

2.5.3. 2-(3-Methoxyphenyl) quinazoline

Light yellow solid; mp 91–93 °C: 94% yield (222 mg, 0.94 mmol) [26] (Table 1, entry 3).

¹H NMR (250 MHz, DMSO-d₆): δ = 9.69 (s, 1H), 8.05–8.17 (m, 5H), 7.73–7.76 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.11–7.13 (m, 1H), 3.86 (s, 3H).

2.5.4. 2-(3-Fluorophenyl) quinazoline

Gray solid; mp 89–90 °C: 83% yield (186 mg, 0.83 mmol) [47] (Table 1, entry 7).

¹H NMR (250 MHz, DMSO-d₆): δ = 9.70 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.15–8.25 (m, 2H), 8.03–8.05 (m, 2H), 7.72–7.78 (m, 1H), 7.60 (dd, *J* = 21.7, 6.2 Hz, 1H), 7.36–7.42 (m, 1H).

2.5.5. 2-(3-Chlorophenyl) quinazoline

Pale yellow solid; mp 148–150 °C: 93% yield (223 mg, 0.93 mmol) [23] (Table 1, entry 8).

¹H NMR (250 MHz, DMSO-d₆): δ = 9.70 (s, 1H), 8.51 (br s, 2H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.0–8.06 (m, 2H), 7.72–7.78 (m, 1H), 7.60 (br s, 2H).

2.5.6. 2-(3-Bromophenyl)quinazoline

Yellow solid; mp 153–155 °C: 91% yield (259 mg, 0.91 mmol) [23] (Table 1, entry 9).

¹H NMR (250 MHz, DMSO-d₆): δ = 9.71 (s, 1H), 8.67 (s, 1H), 8.53 (d, *J* = 7.5 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.01–8.06 (m, 2H), 7.73–7.76 (m, 2H), 7.53 (t, *J* = 8.0 Hz, 1H).

2.5.7. Diethyl 2,6-dimethyl-4-phenyl-3,5-pyridinedicarboxylate

Pale yellow solid; mp 60–61 °C: 98% yield (320 mg, 0.98 mmol) [48] (Table 2, entry 1).

¹H NMR (250 MHz, CDCl₃): δ = 7.25–7.35 (m, 5H), 3.98 (q, *J* = 6.7 Hz, 4H), 2.59 (s, 6H), 0.88 (t, *J* = 6.7 Hz, 6H).

2.5.8. Diethyl 2,6-dimethyl-4-(*p*-tolyl)-3,5-pyridinedicarboxylate

Pale yellow solid; mp 72–74 °C: 96% yield (327 mg, 0.96 mmol) [48] (Table 2, entry 2).

¹H NMR (250 MHz, CDCl₃): δ = 7.14–7.26 (m, 4H), 4.02 (q, *J* = 7.0 Hz, 4H), 2.58 (s, 6H), 2.36 (s, 3H), 0.95 (t, *J* = 7.0 Hz, 6H).

2.5.9. Diethyl 2,6-dimethyl-4-(4-methoxyphenyl)-3,5-pyridinedicarboxylate

Colorless solid; mp 49–51 °C: 94% yield (335 mg, 0.94 mmol) [48] (Table 2, entry 3).

¹H NMR (250 MHz, CDCl₃): δ = 7.17 (d, *J* = 8.2 Hz, 2H), 6.8 (d, *J* = 8.2 Hz, 2H), 4.03 (q, *J* = 7 Hz, 4H), 3.80 (s, 3H), 2.56 (s, 6H), 0.96 (t, *J* = 7 Hz, 6H).

2.5.10. Diethyl 2,6-dimethyl-4-(3,4,5-trimethoxyphenyl)-3,5-pyridinedicarboxylate [49]

White solid; mp 105–107 °C: 97% yield (404 mg, 0.97 mmol) (Table 2, entry 4).

¹H NMR (250 MHz, CDCl₃): δ = 6.49 (s, 2H), 4.06 (q, *J* = 7.0 Hz, 4H), 3.84 (s, 3H), 3.80 (s, 6H), 2.58 (s, 6H), 0.98 (t, *J* = 7.0 Hz, 6H).

2.5.11. Diethyl 2,6-dimethyl-4-*n*-butyl-3,5-pyridinedicarboxylate

Oil; 93% yield (285 mg, 0.93 mmol) [48] (Table 2, entry 5).

¹H NMR (250 MHz, CDCl₃): δ = 4.39 (q, *J* = 7.0 Hz, 4H), 2.53–2.56 (m, 2H), 2.49 (s, 6H), 1.51–1.60 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 6H), 0.91 (t, *J* = 7.0 Hz, 3H).

2.5.12. Diethyl 2,6-dimethyl-4-(3-chlorophenyl)-3,5-pyridinedicarboxylate

Pale yellow solid; mp 42–44 °C: 98% yield (354 mg, 0.98 mmol) [50] (Table 2, entry 8).

¹H NMR (250 MHz, CDCl₃): δ = 7.25–7.34 (m, 3H), 7.12–7.15 (m, 1H), 4.05 (q, 7.0 Hz, 4H), 2.60 (s, 6H), 0.97 (t, *J* = 7.0 Hz, 6H).

2.5.13. Diethyl 2,6-dimethyl-4-(2-fluorophenyl)-3,5-pyridinedicarboxylate [51]

Oil; 97% yield (334 mg, 0.97 mmol) (Table 2, entry 9).

¹H NMR (250 MHz, CDCl₃): δ = 7.25–7.34 (m, 1H), 6.97–7.10 (m, 3H), 4.03 (q, *J* = 7.0 Hz, 4H), 2.59 (s, 6H), 0.95 (t, *J* = 7.0 Hz, 6H).

2.5.14. Diethyl 2,6-dimethyl-4-(4-nitrophenyl)-3,5-pyridinedicarboxylate

Pale yellow solid; mp 115–117 °C: 98% yield (364 mg, 0.98 mmol) [48] (Table 2, entry 10).

¹H NMR (250 MHz, CDCl₃): δ = 8.24 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.02 (q, *J* = 7.0 Hz, 4H), 2.62 (s, 6H), 0.97 (t, *J* = 7.0 Hz, 6H).

2.5.15. Diethyl-2,6-dimethyl-4-cinamyl-3,5-pyridinedicarboxylate

Pale yellow solid; mp 164–165 °C: 90% yield (318 mg, 0.90 mmol) [48] (Table 2, entry 12).

¹H NMR (250 MHz, CDCl₃): δ = 7.26–7.41 (m, 5H), 7.10 (d, *J* = 16.5 Hz, 1H), 6.79 (d, *J* = 16.5 Hz, 1H), 4.32 (q, *J* = 7.0 Hz, 4H), 2.56 (s, 6H), 1.27 (t, *J* = 7.0 Hz, 6H).

3. Results and discussion

To optimize the reaction conditions, the dehydrogenation of 2-phenyl tetrahydroquinazoline as the model

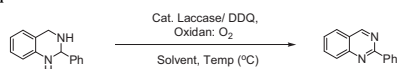
reaction was investigated. Initially, the reaction was carried out in the presence of laccase (100 U) and O₂ as the oxidant in a CH₃CN/NaPBS mixture (1:25) as the solvent at 45 °C. Very low conversions of starting materials were observed, by performing the reactions in the absence of DDQ (Table 3, entry 1). When DDQ (5 mol %) was added as a mediator in the reaction, the product was obtained in moderate yield (Table 3, entry 2). These results demonstrated that DDQ is necessary for an efficient reaction. By increasing the amount of DDQ to 10 mol% the yield slightly improved (Table 3, entry 3). The excellent result was obtained when 20 mol% of DDQ was used (Table 3, entry 4). Subsequently, the effect of laccase concentration on the reaction was explored. When the amount of laccase was reduced to 50 U, the yield dropped to 70% (Table 3, entry 5). A blank reaction was carried out to evaluate the catalytic efficiency of laccase where only 30% of desired product was obtained (Table 3, entry 6). The optimal enzyme concentration was found to be 100 U (entry 4). So, it was selected as a standard concentration in all further reactions. Among various solvents screened, such as CH₃CN/NaPBS (pH 4.5, 0.1 M), CH₃OH/NaPBS (pH 4.5, 0.1 M), NaPBS buffer, and H₂O, CH₃CN/NaPBS (pH 4.5, 0.1 M) gave the best result (Table 3, entries 4 and 7–9). In organic solvents, such as CH₃CN, THF, DMF, and DMSO the reactions did not occur, probably because of laccase denaturation (Table 3, entries 10–13). The effect of temperature, both high and low, on the reaction yield was also tested. It was found that by increasing the reaction temperature up to 60 °C, the yield was

dropped because of enzyme deactivation [52] (Table 3, entry 14). At room temperature, the desired product was obtained in moderate yield (Table 3, entry 15). Using air as an oxidant instead of molecular oxygen in the reaction gave 90% conversion of 2-phenyl tetrahydroquinazoline (Table 3, entry 16).

With having the optimized catalytic system laccase/DDQ in hand, the general applicability of this method was further examined for the synthesis of 2-substituted quinazolines from the oxidative cyclocondensation of 2-aminobenzylamine and structurally various aldehydes. Under the optimized reaction conditions (Table 3, entries 4 and 16), the expected products were obtained in excellent yields and the results are shown in Table 1. Different substituents, including both electron-poor (fluoro, chloro, and bromo) and electron-rich (methyl, methoxy) groups, at various positions of the benzaldehyde ring would be compatible by the present oxidative system and gave the desired products in high yields (Table 1, entries 2–11). Notably, terephthalaldehyde as a bifunctional aromatic aldehyde was satisfactorily subjected to oxidative cyclocondensation as well (Table 1, entry 6).

Having successfully achieved the aerobic oxidative synthesis of 2-substituted quinazolines, we expanded the application of laccase/DDQ catalytic system for aerobic oxidation of Hantzsch 1,4-dihydropyridines to pyridines. 1,4-Dihydropyridines were synthesized according to the reported procedure [53]. The effect of amount of laccase and DDQ, solvent, and temperature

Table 3
Optimization of reaction conditions for aerobic oxidation of 2-phenyl tetrahydroquinazoline.^a



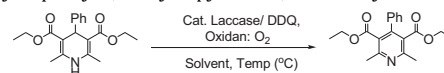
Entry	Laccase (U)	Solvent	Temperature (°C)	DDQ (mol %)	GC yield (%)
1	100	CH ₃ CN/NaPBS	45	–	–
2	100	CH ₃ CN/NaPBS	45	5	60
3	100	CH ₃ CN/NaPBS	45	10	70
4	100	CH₃CN/NaPBS	45	20	100
5	50	CH ₃ CN/NaPBS	45	20	70
6	–	CH ₃ CN/NaPBS	45	20	30
7	100	CH ₃ OH/NaPBS	45	20	90
8	100	NaPBS buffer	45	20	50
9	100	H ₂ O	45	20	40
10	100	CH ₃ CN	45	20	–
11	100	THF	45	20	–
12	100	DMF	45	20	–
13	100	DMSO	45	20	–
14	100	CH ₃ CN/NaPBS	60	20	40
15	100	CH ₃ CN/NaPBS	rt	20	50
16 ^b	100	CH ₃ CN/NaPBS	45	20	90

GC, gas chromatography. The bold represents the most effective reaction conditions.

^a Reaction conditions: 2-Phenyl tetraquinazoline (1 mmol), laccase (100 U), O₂ (balloon), and solvent (13 mL).

^b The reaction was carried out under air conditions.

Table 4
Optimization of reaction conditions for aerobic oxidation of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate.^a



Entry	Laccase (U)	Solvent	Temperature (°C)	DDQ (mol %)	GC yield (%)
1	100	CH ₃ CN/NaPBS	rt	–	–
2	100	CH ₃ CN/NaPBS	rt	5	70
3	100	CH ₃ CN/NaPBS	rt	10	80
4	100	CH₃CN/NaPBS	rt	20	100
5	50	CH ₃ CN/NaPBS	rt	20	70
6	–	CH ₃ CN/NaPBS	rt	20	40
7	100	CH ₃ OH/NaPBS	rt	20	90
8	100	NaPBS buffer	rt	20	60
9	100	H ₂ O	rt	20	40
10	100	CH ₃ CN	rt	20	–
11	100	THF	rt	20	–
12	100	DMF	rt	20	–
13	100	DMSO	rt	20	–
14	100	CH ₃ CN/NaPBS	60	20	40
15 ^b	100	CH ₃ CN/NaPBS	45	20	100
16 ^c	100	CH ₃ CN/NaPBS	rt	20	90

The bold represents the most effective reaction conditions.

^a Reaction conditions: 1,4-Dihydropyridine (1 mmol), laccase (100 U), O₂ (balloon), and solvent (13 mL).

^b Reaction time was 3 h.

^c The reaction was carried out under air conditions.

on the oxidation reaction of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate to diethyl 2,6-dimethyl-4-phenyl-3,5-pyridinedicarboxylate as a model reaction was investigated (Table 4). Laccase (100 U) and 20 mol% of DDQ under O₂ or air in NaPBS (0.1 M, pH 4.5)/CH₃CN (4%) mixture at room temperature was found to be ideal for complete conversion of 1,4-dihydropyridines to the corresponding pyridines (Table 4, entry 4).

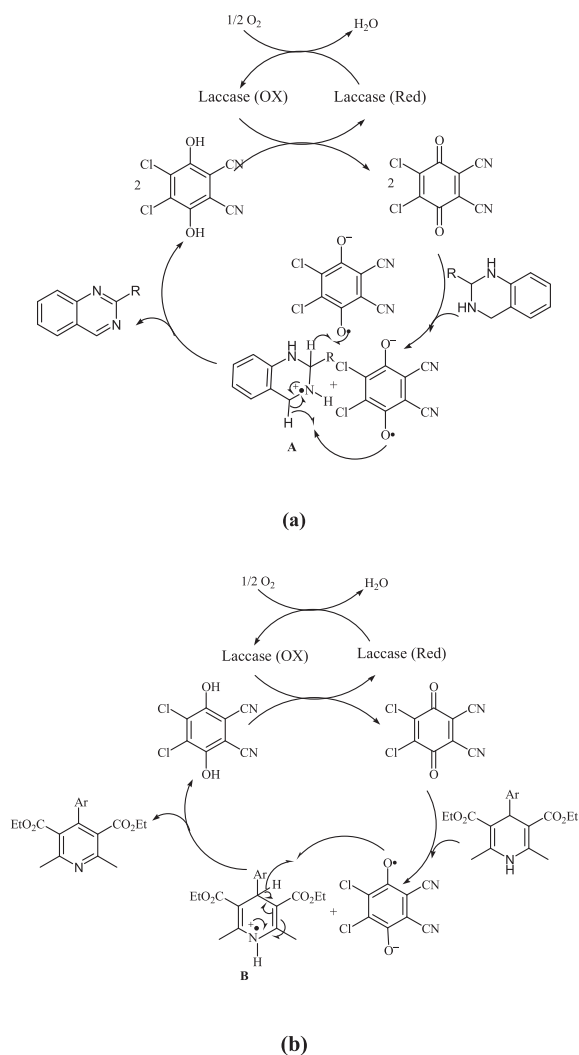
To generalize the scope of the reaction, a series of structurally diverse Hantzsch 1,4-dihydropyridines were subjected to aerobic oxidation under the optimized reaction conditions, and the results are presented in Table 2.

To investigate the feasibility of applying this chemoenzymatic synthetic method on a preparative scale, the aerobic oxidation of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate was carried out on a 5 mmol scale of starting materials. We have found the scale

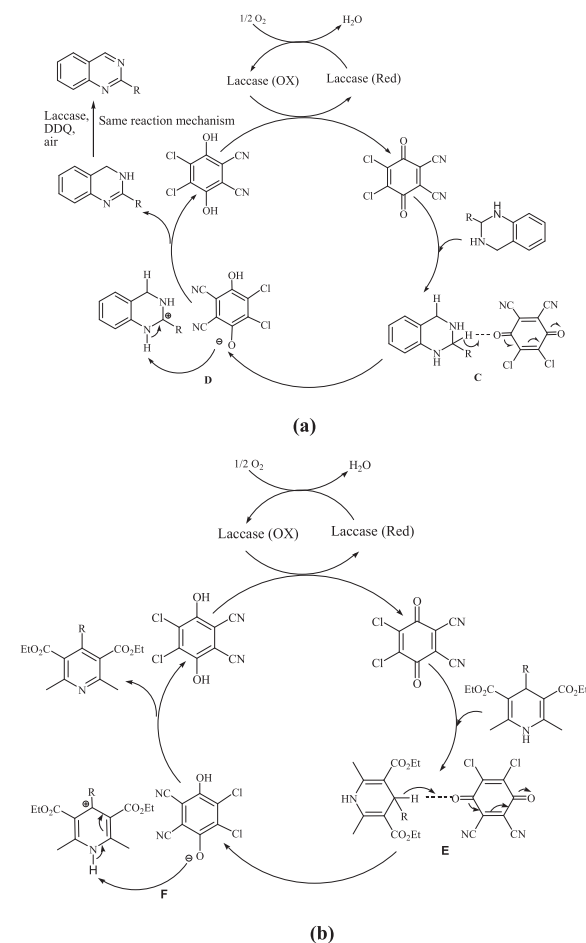
up of reaction gave limited success and shows the lower substrate conversion (60%) [54].

Although the exact mechanisms of the reactions are not clear at this stage, however according to previous reports on the application of DDQ in organic reactions and aerobic oxidation of hydroquinone to quinone by laccase [45,55–57], the proposed mechanisms for the aerobic oxidation of 2-substituted tetrahydroquinazolines and 1,4-dihydropyridines are presented in Schemes 4 and 5, respectively.

One explanation is that a single electron transfer from the 2-substituted tetrahydroquinazolines or 1,4-dihydropyridines to DDQ generates a radical cation (intermediates A and B in Scheme 4) and a DDQ radical anion. The radical oxygen of the DDQ radical anion abstracts an α -H-atom and then the anionic oxygen of DDQ radical anion abstracts proton from nitrogen to form target products (2-substituted quinazolines and pyridines) and DDQH₂. The reduced DDQH₂ (hydroquinone type compound) is subsequently regenerated by laccase leading to DDQ and reduced form of laccase. Finally, laccase can be reoxidized by molecular oxygen, thus completing the catalytic cycle (Scheme 4a and b).



Scheme 4. Radical path mechanism for the aerobic oxidation of 2-substituted tetrahydroquinazolines (a) and 1,4-dihydropyridine (b) in the presence of laccase/DDQ catalyst system.



Scheme 5. Electron transfer path or anomeric-based oxidation mechanism for the aerobic oxidation of 2-substituted tetrahydroquinazolines (a) and 1,4-dihydropyridine (b) in the presence of the laccase/DDQ catalyst system.

Table 5

Comparison of the laccase/DDQ catalyst system with other reagent or catalysts for oxidation of 2-phenyl tetrahydroquinazoline to 2-phenyl quinazoline.

Entry	Reagent or catalyst	Reaction conditions	Time (h)	Isolated yield (%)	Reference
1	MnO ₂ (4 mmol)	CHCl ₃ , reflux	12	70	[14]
2	NaOCl (3 mmol)	MeOH, rt	5	98	[15]
3	[CpIrCl ₂] ₂ (2.5 mol%), styrene (4 equiv)	N ₂ , xylene, reflux	24	66	[17]
4	Pt/CeO ₂ (1 mol%)	Mesitylene, N ₂ , reflux	30	85	[18]
5	FeCl ₃ (2 mol%), TBHP (1.5 mol%)	DMSO, N ₂ , 60 °C	6	70	[19]
6	IBX (2 equiv)	CH ₃ CN, rt	6	88	[57]
7	CuCl (5 mol%)/DABCO (10 mol%)/TEMPO (5 mol%)	CH ₃ CN, O ₂ , 80 °C	6	95	[23]
8	Pt/CB-Pt/Ir (0.5 mol%), TTSBI (3.5 mol%), K ₂ CO ₃ (0.5 equiv)	CHCl ₃ : H ₂ O (9:1, 0.5 M), O ₂ , 35 °C	16	95	[24]
9	RhCNT (1 mol%), TBC (10 mol%)	CHCl ₃ /H ₂ O (3:1), rt	21	94	[25]
10	phd (5 mol%), ZnI ₂ (2.5 mol%), PPTS (15 mol%)	CH ₃ CN, O ₂ , rt	24	84	[26]
11	MgI ₂ (5 mol%)	EtOAc, visible light, O ₂ , rt	8	87	[59]
12	Laccase (100 U)/DDQ (20 mol%)	NaPBS/CH ₃ CN, O ₂ or air, 45 °C	22	95	This work

Table 6

Comparison of laccase/DDQ catalyst system, with other reagent or catalysts for oxidation of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate to diethyl 2,6-dimethyl-4-phenyl-3,5-pyridinedicarboxylate.

Entry	Reagent or catalyst	Reaction conditions	Time	Isolated yield (%)	Reference
1	MnO ₂	CH ₂ Cl ₂ , MW 100 °C	1 min	99	[20c]
2	NO (20 equiv)	Benzene, under Ar atmosphere	3 h	96	[20d]
3	Zr(NO ₃) ₄ (1 equiv)	AcOH, rt	15 min	96	[20f]
4	DDQ (0.5 mmol)	THF, rt	1 h	90	[59]
5	Fe(ClO ₄) ₃ (2 mol%)	HOAc, rt	1.5 h	93	[27a]
6	NHPI (20 mol%)	CH ₃ CN, O ₂ , reflux	4 h	99	[27b]
7	TBPA ⁺	CH ₃ CN, air, 60 °C	18 h	78	[27c]
8	FeCl ₃ (0.05 mmol)/NaNO ₂ (0.05 mmol)/TEMPO (0.05 mmol)	CH ₃ CN, CH ₃ COOH, O ₂ , rt	30 min	97	[27d]
9	Laccase (168 U)/ABTS (10 mol%)	Acetate buffer/MeOH, air, 50 °C	9 h	80	[44]
10	Laccase (100 U)/DDQ (20 mol%)	NaPBS/CH ₃ CN, O ₂ or air, rt	7 h	98	This work

Another explanation for these processes is that oxidation of the substrate occurs by hydride transfer from the C2 and C4 position on 2-substituted tetrahydroquinazolines and C4 position on 1,4-dihydropyridines to the carbonyl oxygen atom of DDQ (transition states C and E), thereby forming ion-pairs (intermediates D and F) [56]. It should be mentioned that these transformations may proceed via anomeric-based oxidation [20g]. Deprotonation of the substrate by DDQH⁻ can afford the corresponding dehydrogenated product. The reduced DDQH₂ is oxidized by laccase leading to DDQ and reduced form of laccase. Finally, laccase can be reoxidized by molecular oxygen, thus completing the catalytic cycle (Scheme 5).

To illustrate the efficiency of laccase/DDQ catalyst system, we compared our results for dehydrogenation of 2-phenyl tetrahydroquinazoline and diethyl 2,6-dimethyl-4-

phenyl-1,4-dihydropyridine-3,5-dicarboxylate with the best of the well-known data from the literature (Tables 5 and 6). As shown in Tables 5 and 6, the previously reported procedures suffer from one or more disadvantages such as the use of stoichiometric oxidant [14,15,20c,20d,20f,58,59], toxic and expensive transition metal catalysts or reagent [14,17,19,20c,20f,23–26,27a,27d], special efforts for the preparation of catalyst [17,24,25], toxic and volatile solvents [14–19,20c,20d,23–25,27b–27d,56,60], elevated reaction temperatures [14,17,19,23,20c,27b,27c,44], and low yield [14,17,19,27c,44].

4. Conclusion

We have developed laccase/DDQ as a simple, efficient, and environmentally friendly catalyst system for the aerobic oxidative synthesis of structurally diverse 2-substituted

quinazolines and Hantzsch pyridines in good to high yields under mild reaction conditions. These green procedures represent various attractive characteristics, such as the use of laccase/DDQ as the robust catalyst system, O₂ or air as the greenest, inexpensive and most abundant oxidant, and phosphate buffer as a green medium. In addition, the present methods are superior to other currently available ones because they are free from any toxic halide and transition metal cocatalysts.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.crci.2019.03.003>.

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