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PIDA-mediated intramolecular oxidative C–N bond formation for the direct synthesis of quinoxalines from enaminones†

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A intramolecular oxidative C(sp²)–N bond formation mediated by hypervalent iodine(III) to obtain quinoxalines from readily available *N*-(2-acetaminophenyl)enaminones was developed. A tandem process involving PIDA-mediated intramolecular condensation cyclization and a subsequent elimination was postulated, which was highly efficient and metal-free under mild conditions. Moreover, flexible structural modifications of quinoxalines bearing carbonyl groups are of interest for further transformations as building blocks in organic synthesis.

Quinoxaline represents one of the most prevalent heterocycles in natural products.¹ It has enjoyed extensive applications in pharmaceuticals due to its various biological activities such as antimicrobial, antiviral, antidiabetic, anti-inflammatory, anticancer, and antidepressant properties.^{2,3} Moreover, quinoxalines are the building blocks used in the preparation of porphyrins,⁴ dyes,⁵ electroluminescent materials,⁶ cavitand and salen ligands.⁷ Among these, quinoxalines bearing carbonyl groups are important structural motifs in bioactive molecules (Fig. 1), such as compounds **a** and **b**, which are used as potential photoprotective drugs and anticancer and hypoxia-selective agents.⁸ They are also the building blocks of some quinoxaline metal complexes, such as compounds **c** and **d**, which possess significant antimicrobial and anticancer activities.⁹

Consequently, a variety of strategies have been developed to prepare such a core. The conventional procedure for the synthesis of quinoxalines involves the condensation of *o*-disubstituted benzene with two-carbon synthons such as 1,2-dicarbonyl compounds,¹⁰ α -hydroxy ketones,¹¹ vicinal diols,¹² phenacyl bromides,¹³ epoxides,¹⁴ and alkynes.¹⁵ Recently, transition metal-catalyzed domino cyclization reactions¹⁶ have been found to be efficient. However, there are still some respective limitations such as the use of problematically available or dangerous starting materials, harsh reaction conditions, poor regioselectivity, and the requirement of noble metals as catalysts, which may lead to potential contamination in products and impede their applications, especially in the pharmaceutical industry. Therefore, the development of an efficient and metal-

free route to obtain quinoxalines under mild reaction conditions remains highly desirable.

Owing to the didentate nucleophilicity and electrophilicity of enaminones, various heterocycles can be synthesized from enaminones.^{17,18} In 2016, a convenient regiospecific synthesis of quinoxalines involving base-promoted C- α -CH₂-extrusion from enaminones under metal-free conditions was developed by our group.¹⁹ Due to our continued interest in the development of new strategies for the synthesis of heterocycles based on enaminones under metal-free conditions,^{20a–h} we recently reported the preliminary results of a simple, mild and highly atom-efficient synthesis of 2-hydroxy-benzo[*b*][1,4]oxazins from *N*-(2-hydroxylaryl) enaminones *via* a hypervalent iodine(III)-promoted intramolecular iminoenol trapping reaction (Scheme 1a).^{20g,21} As an extension of this methodology and the synthesis of versatile quinoxalines, *N*-(2-acetaminophenyl)enaminones as starting materials under appropriate hypervalent iodine(III)-mediated conditions were explored (Scheme 1b). It was proven to be an expedient and simple strategy to access quinoxalines.

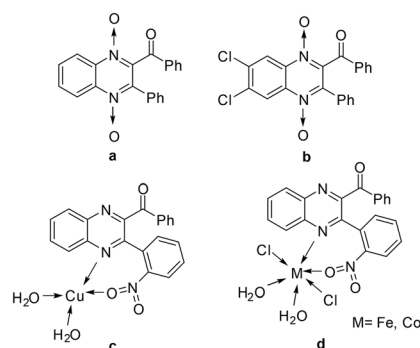
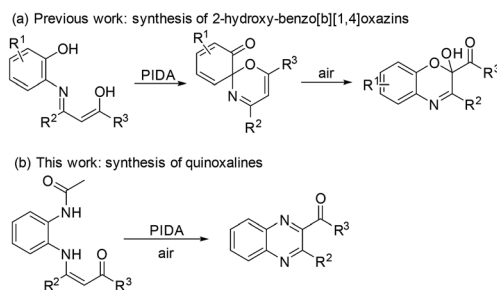


Fig. 1 Selected bioactive molecules with quinoxaline bearing a carbonyl group moiety.

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Scheme 1 Hypervalent iodine(III)-mediated synthesis of heterocycles from enaminones.

Initially, *N*-(2-acetaminophenyl)enaminone **1a** was used as the standard substrate to search for suitable reaction conditions. We were pleased to find that the reaction of **1a** with PIDA (iodobenzene diacetate) in EtOH at 80 °C successfully afforded the desired product quinoxaline **2a** in 58% isolated yield (Table 1, entry 1). Then, a series of solvents such as DCE, 1,4-dioxane, DMF, and toluene were tested; toluene was found to be the most efficient solvent (entries 2–5). Subsequent studies showed that other hypervalent iodine reagents (PIFA, PhI + *m*-CPBA) were less effective for the formation of quinoxalines compared to PIDA (entries 6 and 7). When the loading of PIDA was reduced to 0.3 equiv., the yield dropped dramatically (entry 8). Temperature screening experiments revealed that the reaction at 80 °C

gave the best yield (entries 9 and 10). The screening of further additives showed that AcOH, TsOH, Et₃N and K₂CO₃ were inferior to PhCOOH (entries 11–15). The reaction did not improve significantly by increasing the loading of PhCOOH (entry 16). No satisfactory result was obtained when a catalytic amount of PhCOOH was used (entry 17). Oxygen seemed to be indispensable to the reaction since a decreased yield was obtained when the reaction was carried out under an N₂ atmosphere (entries 18 and 19). Finally, the optimal reaction conditions for the PIDA-promoted synthesis of quinoxaline derivatives were identified as follows: 1.1 equiv. of PIDA as the oxidant, 1.0 equiv. of PhCOOH as the additive and toluene as the solvent at 80 °C under air.

Under the optimized reaction conditions (Table 1, entry 13), we evaluated the scope of this developed method by using various substituted *N*-(2-acetaminophenyl)enaminones. As shown in Scheme 2, R¹ and R² in substrate **1** can be either electron-rich or electron-deficient aryl groups and provide the corresponding quinoxalines in 44–93% yields (**2b–2k**, **2n–2r**). *N*-(2-Acetaminophenyl)enaminones **1** with electron-donating groups at the *para* position of the phenyl ring reacted smoothly to afford the expected quinoxalines in desirable yields (**2d**, **2f**, and **2g**), while the yields for the substrates bearing electron-withdrawing groups were relatively lower (**2h**, **2i**). Due to steric hindrance, the substrates with *para*-substituents (**2d**) gave slightly higher yields than those with *ortho*- and *meta*-substituents (**2b**, **2c**). Halogens, including F, Cl, and Br, worked

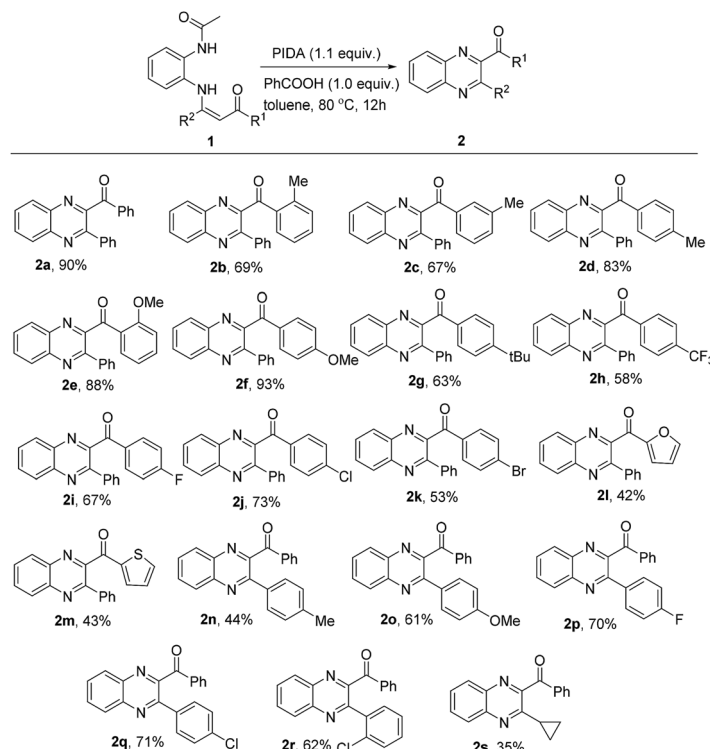
Table 1 Optimization of the reaction conditions^a

Entry	Solvent	<i>T</i> (°C)	[O] (equiv.)	Additive (equiv.)	Yields ^b (%)
1	EtOH	80	PIDA (1.1)	—	58
2	DCE	80	PIDA (1.1)	—	72
3	1,4-Dioxane	80	PIDA (1.1)	—	62
4	DMF	80	PIDA (1.1)	—	34
5	Toluene	80	PIDA (1.1)	—	79
6	Toluene	80	PIFA (1.1)	—	67
7	Toluene	80	PhI (10 mol%) + <i>m</i> -CPBA (2)	—	Trace
8	Toluene	80	PIDA (0.3)	—	36
9	Toluene	60	PIDA (1.1)	—	75
10	Toluene	100	PIDA (1.1)	—	70
11	Toluene	80	PIDA (1.1)	AcOH (1.0)	59
12	Toluene	80	PIDA (1.1)	TsOH (1.0)	21
13	Toluene	80	PIDA (1.1)	PhCOOH (1.0)	90
14	Toluene	80	PIDA (1.1)	Et ₃ N (1.0)	49
15	Toluene	80	PIDA (1.1)	K ₂ CO ₃ (1.0)	72
16	Toluene	80	PIDA (1.1)	PhCOOH (2.0)	92
17	Toluene	80	PIDA (1.1)	PhCOOH (0.1)	80
18 ^c	Toluene	80	PIDA (1.1)	PhCOOH (1.0)	88
19 ^d	Toluene	80	PIDA (1.1)	PhCOOH (1.0)	25

^a Reaction conditions: **1a** (0.2 mmol) and iodine compound in solvent (2 mL) at a corresponding temperature for 12 h under air atmosphere.

^b Isolated yields. ^c Under O₂. ^d Under N₂. PIFA = phenyliodine(III) bis(trifluoroacetate), *m*-CPBA = 3-chloroperoxybenzoic acid.

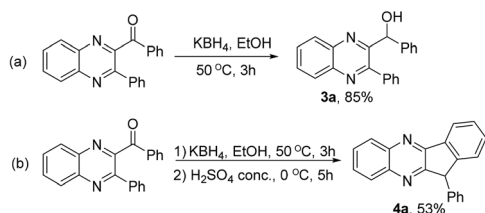




Scheme 2 Substrate scope of enaminones. ^aReaction conditions: **1a** (0.2 mmol), PIDA (0.22 mmol), PhCOOH (0.2 mmol) in toluene (2 mL) at 80 °C for 12 h. ^bIsolated yields.

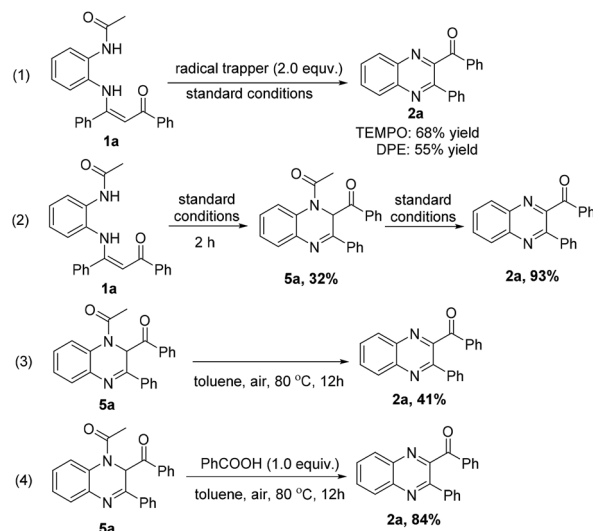
well (**2i–2k**, **2p–2r**, 53–73% yields), which could be further extended to subsequent transition metal-catalyzed coupling reactions. Heteroaryl groups, such as furyl and thienyl groups, were also suitable and gave the desired products in 42% and 43% yields, respectively (**2l**, **2m**). Moreover, when the R² group was a cyclopropyl group, this transformation could still proceed smoothly, giving the desired product in 35% yield (**2s**). A trace amount of the desired product was obtained when R² was an aliphatic group and enamino esters were used as the substrate.

The flexible structural modification of quinoxalines bearing carbonyl groups indicates their further transformations to useful molecules.²² For example, the reduction of **2a** with KBH₄ furnished **3a** in 85% yield, which showed some activity to prevent brain damage and neurodegenerative diseases (Scheme 3a).²³ Subsequent cyclization in the presence of concentrated H₂SO₄ afforded the condensed quinoxaline **4a**, which is a pharmacophoric structure motif with antifungal activity (Scheme 3b).²⁴



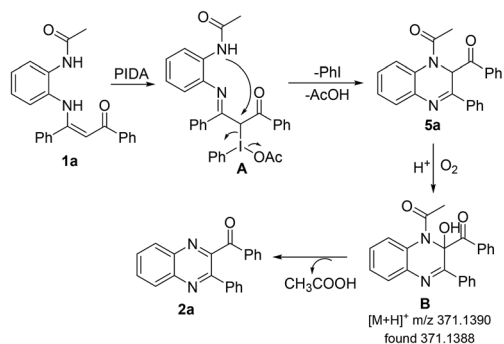
Scheme 3 Further transformations of **2a**.

To probe the possible reaction mechanism, some control experiments were carried out (Scheme 4). The radical scavengers TEMPO (2,2,6,6-tetramethylpiperidine, 1-oxy) and DPE (1,1-diphenylethylene) resulted in yields of 68% and 55%, respectively (eqn (1)), which indicated that a radical pathway might not be involved in this reaction. When *N*-(2-acetaminophenyl) enaminone **1a** was reacted under the standard conditions for 2 h, intermediate **5a** was isolated in 32% yield, which could be



Scheme 4 Control experiments.





Scheme 5 Proposed reaction mechanism.

transformed into the desired product **2a** in 93% yield (eqn (2)). As expected, the intermediate **5a** could be transformed into the desired product **2a** in 41% yield under standard conditions without PIDA and PhCOOH (eqn (3)), while a higher yield (84%) was obtained in the presence of PhCOOH (eqn (4)), indicating that PhCOOH could promote the process from intermediate **5a** to the desired product **2a**.

A plausible mechanism is proposed in Scheme 5 according to the aforementioned results and reported literatures.²⁵ The initial reaction of **1a** and PIDA afforded α -iodo iminoketone **A**. Then, intramolecular condensation cyclization of **A** with the concomitant release of PhI and CH₃COOH afforded **5a**. Subsequently, the oxidation of **5a** provided **B**, which was detected by HRMS (ESI, Fig. S1†) in the presence of O₂. Finally, the elimination of CH₃COOH from **B** generated the final product **2a**.

In conclusion, an efficient hypervalent iodine(III)-mediated approach to substituted quinoxalines from readily available *N*-(2-acetaminophenyl)enaminones was developed. This reaction tolerated a wide range of functional groups in moderate to excellent yields under mild and metal-free conditions. Due to the importance of quinoxalines, this protocol can be further expanded to the synthesis of biologically and medicinally relevant compounds.

Conflicts of interest

There are no conflicts to declare.

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