DOI: 10.1002/ejoc.201300368

Oxidative Olefination of Secondary Amines with Carbon Nucleophiles

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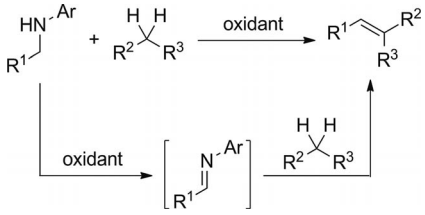
Keywords: Homogeneous catalysis / Olefination / Oxidation / Amines / Imines

An unprecedented olefination reaction of secondary amines with carbon nucleophiles has been developed through C–N/C–H functionalization under metal-free oxidative conditions. In the presence of a stoichiometric amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), a range of secondary *N*-alkylanilines smoothly underwent oxidative olefination with 2-alkylazaarenes, acetophenone, and malononitrile to give structurally diverse polysubstituted alkenes in moderate to excellent yields with excellent (*E*) selectivity. Preliminary mechanistic studies revealed that the oxidative olefination reaction proceeds through amine oxidation followed by imine olefination.

Introduction

The olefination of carbon electrophiles with carbon nucleophiles constitutes one of the most important strategies for the synthesis of alkenes, which are present in many functional molecules. Alkenes also serve as a foundation for a broad range of chemical transformations such as oxidation, reduction, and addition.[1] Carbonyl compounds frequently serve as the carbon electrophiles, and their olefination with carbon nucleophiles has enjoyed widespread prominence and recognition owing to their simplicity, positional selectivity, and stereoselectivity.[2] In sharp contrast, much less attention has been paid to the corresponding olefination of imines with carbon nucleophiles. Nevertheless, sporadic studies have demonstrated that imine olefination affords better efficiency and/or stereoselectivity in certain cases for alkene synthesis than carbonyl olefination.[2g,3–5]

Certain 2-alkylazaarenes are known to undergo C–H olefination with *N*-aryl imines under strong basic conditions.[4a–4e] By contrast, the corresponding olefination with *N*-sulfonyl imines, which are more electrophilic than *N*-aryl imines, has recently been reported to proceed in the presence of a metal Lewis acid and/or at high temperature.[4f–4g] In this context, we envisioned that *N*-aryl imines could be activated enough by certain acid catalysts to undergo olefination with 2-alkylazaarenes under relatively mild conditions.[6] Moreover, the proposed olefination reaction could be further facilitated by the in situ generation of the *N*-aryl imines. Although the condensation of aldehydes with primary amines is frequently used to prepare imines in situ, the oxidation of secondary amines constitutes a powerful alterative method that extends the scope of chemical reactions involving the intermediacy of imines.[7] Thus, we planned to develop an oxidative olefination reaction of secondary amines with 2-alkylazaarenes, wherein the oxidant should be compatible with the acid catalyst and the alkene product should avoid being consumed by possible side reactions such as oxidation and addition. In the course of exploring new methods for alkene synthesis,[3d–3g,8] we developed an unprecedented (*E*)-selective olefination reaction of secondary amines with 2-alkylazaarenes through C–N/C–H functionalization under metal-free oxidative conditions (Scheme 1). Moreover, the substrate scope was extended to acetophenone and malononitrile. Mechanistically, the reaction proceeds through amine oxidation followed by imine olefination, and the byproduct generated in the step of amine oxidation catalyzes the step of imine olefination.[9,10]



Scheme 1. Oxidative olefination of secondary amines with carbon nucleophiles.

Results and Discussion

Several commercially available oxidants were examined in the reaction of secondary amine **1a** with 2-methylquinoline (**2a**) in DMF at 70 °C (Table 1, entries 1–7). Most of the

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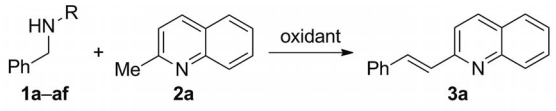
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201300368.

oxidants failed to promote the desired oxidative olefination reaction; however, the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) led to the formation of alkene **3a** in 99% yield with >99:1 (*E*)/(*Z*) selectivity (Table 1, entry 1). The reaction with DDQ also proceeded at room temperature but gave a much lower yield (Table 1, entry 8). The yield was dramatically affected by the solvent, and much lower yields were obtained when the reaction was performed in a number of other common organic solvents (Table 1, entries 9–17). It is noteworthy that hardly any desired product was detected when the phenyl group on the nitrogen atom of secondary amine **1a** was replaced with a hydrogen atom, a methyl group, a benzyl group, an acetyl group, or a *p*-tolylsulfonyl (Ts) group (Table 1, entries 18–22).

Table 1. Optimization of the reaction conditions.[a,b]



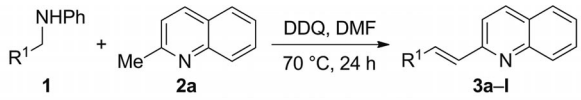
1a–af **2a** **3a**

Entry	**1**, R	Oxidant	Solvent	*T* [°C]	Yield [%][c]
1	**1a**, Ph	DDQ	DMF	70	99
2	**1a**, Ph	BQ	DMF	70	0
3	**1a**, Ph	TBHP[d]	DMF	70	0
4	**1a**, Ph	DTBP	DMF	70	0
5	**1a**, Ph	PIDA	DMF	70	trace
6	**1a**, Ph	H_2O_2	DMF	70	0
7	**1a**, Ph	$K_2S_2O_8$	DMF	70	10
8	**1a**, Ph	DDQ	DMF	25	60
9	**1a**, Ph	DDQ	DMSO	70	78
10	**1a**, Ph	DDQ	EtOH	70	35
11	**1a**, Ph	DDQ	MeCN	70	25
12	**1a**, Ph	DDQ	dioxane	70	58
13	**1a**, Ph	DDQ	THF	70	27
14	**1a**, Ph	DDQ	EtOAc	70	trace
15	**1a**, Ph	DDQ	$CHCl_3$	70	trace
16	**1a**, Ph	DDQ	DCE	70	trace
17	**1a**, Ph	DDQ	toluene	70	8
18	**1ab**, H	DDQ	DMF	70	0
19	**1ac**, Me	DDQ	DMF	70	0
20	**1ad**, CH_2Ph	DDQ	DMF	70	0
21	**1ae**, COMe	DDQ	DMF	70	0
22	**1af**, Ts	DDQ	DMF	70	0

[a] Reaction conditions: compound **1a**–**af** (0.30 mmol), 2-methylquinoline (**2a**, 0.25 mmol), oxidant (0.30 mmol), solvent (0.50 mL), 25 or 70 °C, 12 h. [b] In all cases alkene **3a** was obtained with >99:1 (*E*)/(*Z*) selectivity. [c] Isolated yield. [d] 70% Aqueous solution. Ts = *p*-tolylsulfonyl, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, BQ = 1,4-benzoquinone, TBHP = *tert*-butyl hydroperoxide, DTBP = di-*tert*-butyl peroxide, PIDA = iodobenzene diacetate, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, THF = tetrahydrofuran, DCE = 1,2-dichloroethane.

In the presence of a stoichiometric amount of DDQ, a range of *N*-benzylic anilines smoothly underwent oxidative olefination with 2-methylquinoline (**2a**) to give various 2-alkenylquinolines in good to excellent yields with excellent (*E*) selectivity (Table 2, entries 1–10). Both electron-withdrawing and electron-donating groups were successfully introduced into the aromatic rings of the alkene products by employing secondary amines having such groups, and notably, the reaction tolerated functional groups such as alkoxy, chloro, and nitrile. When the oxidative olefination reaction was extended to *N*-allylic aniline **1k** or ethyl 2-(4-methoxyphenylamino)acetate (**1l**), a complex mixture was obtained, and the desired alkene product was isolated in a moderate yield with >99:1 (*E*)/(*Z*) selectivity (Table 2, entries 11 and 12).[11]

Table 2. Oxidative olefination of secondary amines with 2-methylquinoline (**2a**).[a]



1 **2a** **3a–l**

Entry	**1**	R^1	Product	Yield [%][b]	(*E*)/(*Z*)[c]
1	**1a**	R = H	**3a**	99	>99:1
2	**1b**	R = 4-OMe	**3b**	88	>99:1
3	**1c**	R = 4-Cl	**3c**	99	>99:1
4	**1d**	R = 4-CN	**3d**	61	>99:1
5	**1e**	R = 3-OMe	**3e**	99	>99:1
6	**1f**	R = 3-Cl	**3f**	99	>99:1
7	**1g**	R = 2-OMe	**3g**	99	>99:1
8	**1h**	R = 2-Cl	**3h**	80	>99:1
9	**1i**		**3i**	99	97:3
10	**1j**		**3j**	72	>99:1
11[d]	**1k**		**3k**	52	>99:1
12[e]	**1l**	EtO_2C- -	**3l**	36	>99:1

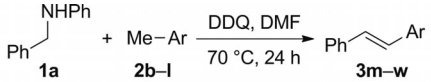
[a] Reaction conditions: secondary amine **1** (0.30 mmol), 2-methylquinoline (**2a**, 0.25 mmol), DDQ (0.30 mmol), DMF (0.50 mL), 70 °C, 24 h. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy. [d] The reaction was performed at 25 °C. [e] Substrate **1l** was ethyl 2-(4-methoxyphenylamino)acetate.

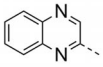
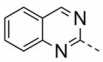
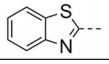
Under the standard reaction conditions, a range of substituted 2-methylquinolines were found to serve as suitable substrates in the oxidative olefination reaction with secondary amine **1a**, and the corresponding functionalized 2-alkenylquinolines were obtained in good to excellent yields with excellent (*E*) selectivity (Table 3, entries 1–6). To our delight, this chemistry was successfully extended to a wide variety of 2-methylazaarenes such as 4-methylquinoline (**2h**), 1-methylisoquinoline (**2i**), 2-methylquinoxaline (**2j**), 2-methylquinazoline (**2k**), and 2-methylbenzo[*d*]thiazole (**2l**), and importantly, a range of structurally diverse β-azaarylstyrenes were obtained in moderate to good yields with >99:1 (*E*)/(*Z*) selectivity (Table 3, entries 7–11).

The oxidative olefination reaction was further extended to the synthesis of trisubstituted alkenes with very high stereoselectivity. For example, the DDQ-promoted reaction of secondary amine **1a** with 2-ethylquinoline (**2m**) smoothly proceeded under the standard reaction conditions to give trisubstituted alkene **3x** in 85% yield with >99:1 (*E*)/(*Z*) selectivity (Scheme 2). In addition, the reaction worked well with acetophenone (**2n**) and malononitrile (**2o**) and gave the corresponding electron-poor alkenes in good yields.

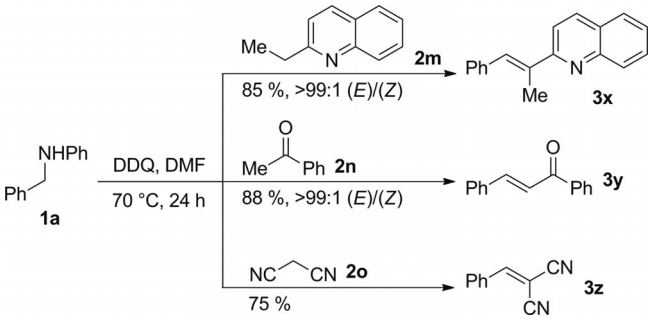
To gain insight into the reaction mechanism, we carried out electrospray ionization (ESI) mass spectrometric analysis of the reaction mixture of secondary amine **1a** with 2-

Table 3. Oxidative olefination of secondary amine **1a** with 2-methylazaarenes.[a]



Entry	2	Ar	Product	Yield [%][b]	(*E*)/(*Z*)[c]
1	**2b**	R = 6-OMe	**3m**	63	>99:1
2	**2c**	R = 6-Cl	**3n**	94	99:1
3	**2d**	R = 7-Cl	**3o**	97	>99:1
4	**2e**	R = 8-OMe	**3p**	99	>99:1
5	**2f**	R = 8-Cl	**3q**	93	>99:1
6	**2g**	R = 5,7-Me_2	**3r**	85	>99:1
7	**2h**		**3s**	79	>99:1
8	**2i**		**3t**	70	>99:1
9	**2j**		**3u**	80	>99:1
10	**2k**		**3v**	64	>99:1
11	**2l**		**3w**	56	>99:1

[a] Reaction conditions: secondary amine **1a** (0.30 mmol), 2-methylazaarene **2b–l** (0.25 mmol), DDQ (0.30 mmol), DMF (0.50 mL), 70 °C, 24 h. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy.

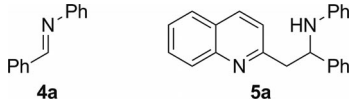


Scheme 2. Oxidative olefination of secondary amine **1a** with carbon nucleophiles **2m**–**o**.

methylquinoline (**2a**) in the presence of DDQ in DMF. As shown by the results summarized in Table 4, we tentatively assigned two intermediates, imine **4a** and amine **5a**, according to the high-resolution mass data. Whereas imine **4a** was generated in a significant amount, as judged by thin-layer chromatography (TLC) analysis, amine **5a** could not be detected by this method.

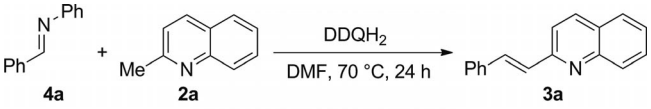
In the above oxidative olefination reaction, DDQ was reduced by the secondary amine to yield 4,5-dichloro-3,6-dihydroxyphthalonitrile ($DDQH_2$) as an acidic byproduct. As demonstrated by the results summarized in Table 5, $DDQH_2$ proved essential for the olefination of carbon nucleophiles with *N*-arylimines, which were generated as intermediates from secondary amines during the oxidative olefination reaction. The use of 1.2 equiv. of $DDQH_2$ to promote the olefination of imine **4a** with 2-methylquinoline (**2a**) led to the formation of alkene **3a** in 99% yield with >99:1 (*E*)/(*Z*) selectivity, and reducing the catalyst loading to 5 mol-% afforded a lower but still good yield with extremely high (*E*) selectivity (Table 5, entries 2 and 3).

Table 4. High-resolution mass data.



Entry	Species	Formula	Mass (calcd.)	Mass (found)
1	[**4a** + H]$^+$	$C_{13}H_{11}N^+$	182.09643	182.09583
2	[**5a** + H]$^+$	$C_{23}H_{21}N_2^+$	325.16993	325.16910

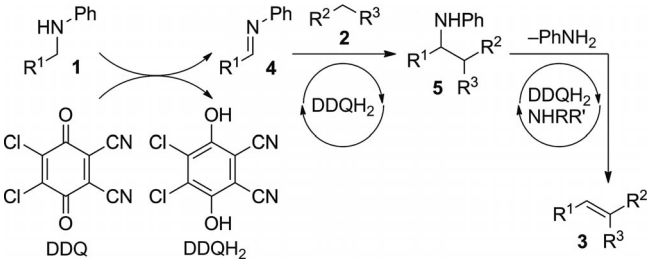
Table 5. Olefination of imine **4a** with 2-methylquinoline (**2a**).[a]



Entry	$DDQH_2$ [mol-%]	Yield [%][b]	(*E*)/(*Z*)[c]
1	0	–	–
2	120	99	>99:1
3	5	84	>99:1

[a] Reaction conditions: imine **4a** (0.30 mmol), 2-methylquinoline (**2a**, 0.25 mmol), $DDQH_2$ (0–120 mol-%), DMF (0.50 mL), 70 °C, 24 h. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy. $DDQH_2$ = 4,5-dichloro-3,6-dihydroxyphthalonitrile.

On the basis of the above experimental results, we propose the following reaction pathway for the oxidative olefination of secondary amines with carbon nucleophiles (Scheme 3). Initially, secondary amine **1** is oxidized by DDQ to give imine **4** as an intermediate and $DDQH_2$ as an acidic byproduct. Then, imine **4** and carbon nucleophile **2** are activated by $DDQH_2$ through hydrogen-bonding interactions and through isomerization to form a reactive species (an enamine, an enol, or a ketenimine), and they undergo Mannich-type reaction to give amine **5**. Finally, elimination of aniline from amine **5** leads to the formation of alkene **3**. In the elimination step, secondary amine **1** and the aniline byproduct serve as bases to remove the β-H of amine **5**, and the leaving ability of the phenylamino group is enhanced by $DDQH_2$ through hydrogen-bonding interactions. For the synthesis of a 1,2-disubstituted alkene (R^3 = H), the stereoselectivity is determined by the elimination



Scheme 3. Proposed reaction pathway.

step, which prefers to give (*E*) selectivity. By contrast, the stereoselectivity for the synthesis of a trisubstituted alkene originates from the diastereoselective addition of substituted methane **2** to imine **4**.

Conclusions

We have developed, for the first time, a highly (*E*)-selective olefination reaction of secondary amines with carbon nucleophiles through C–N/C–H functionalization under metal-free oxidative conditions. In the presence of a stoichiometric amount of DDQ, a range of secondary *N*-alkylanilines smoothly underwent oxidative olefination with 2-alkylquinolines, 4-methylquinoline, 1-methylisoquinoline, 2-methylquinoxaline, 2-methylquinazoline, 2-methylbenzo[*d*]-thiazole, acetophenone, and malononitrile to give structurally diverse polysubstituted alkenes in moderate to excellent yields with excellent (*E*) selectivity. Preliminary mechanistic studies revealed that the oxidative olefination reaction proceeds through amine oxidation followed by imine olefination.

Experimental Section

General Procedure for the Oxidative Olefination of Secondary Amines with Carbon Nucleophiles: To a solution of secondary amine **1** (0.30 mmol) in DMF (0.50 mL) under an atmosphere of nitrogen at room temperature was added DDQ (68.1 mg, 0.30 mmol). The mixture was stirred for 5 min and carbon nucleophile **2** (0.25 mmol) was added. The mixture was heated at 70 °C for 24 h, cooled to room temperature, and purified by silica gel chromatography (ethyl acetate/petroleum ether, 1:25–1:3) to give alkene **3**.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and copies of the ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgments

The authors are grateful for the financial support of the National Natural Science Foundation of China (NSFC) (grant numbers 21232007 and 21172206), the National Basic Research Program of China (973 Program 2010CB833300), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1189).

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Received: March 11, 2013
Published Online: May 6, 2013

