



Facile and efficient one-pot synthesis of 2-arylbenzoxazoles using hydrogen tetrachloroaurate as catalyst under oxygen atmosphere*

Yun-kui LIU[†], Da-jie MAO, Shao-jie LOU, Jian-qiang QIAN, Zhen-yuan XU^{†‡}

(State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, China)

[†]E-mail: ykuiliu@zjut.edu.cn; greensyn@zjut.edu.cn

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Abstract: In this paper, we presented a novel method for the facile and efficient one-pot synthesis of 2-arylbenzoxazoles, which were directly synthesized from 2-aminophenol and aldehydes catalyzed by hydrogen tetrachloroaurate (HAuCl₄·4H₂O) under an oxygen atmosphere with anhydrous tetrahydrofuran (THF) as solvent or in solvent-free condition. The results show that this method could bring excellent yields as high as 96%. THF was proven to be the best choice among several solvents screened and the reaction was tolerated with a variety of aromatic aldehydes possessing electron-donating or withdrawing groups. The advantages of the present method lie in catalytic process using economic and environmentally benign dioxygen as oxidant.

Key words: 2-Arylbenzoxazoles, 2-Aminophenol, Aldehydes, Hydrogen tetrachloroaurate, One-pot synthesis

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INTRODUCTION

Nowadays gold is no doubt the “star metal” in chemistry because there has been a focus on gold-catalyzed organic transformations in recent years (Hashmi, 2003; 2004; 2007; Hashmi and Hutching, 2006; Muzart, 2008; Li *et al.*, 2008; Arcadi, 2008). Among various new transformations catalyzed by gold, those involving nucleophilic additions to C-C multiple bonds (alkynes, alkenes, or allenes) and catalytic C-H bond functionalization have been intensively studied (Widenhoefer and Han, 2006; Jiménez-Núñez and Echavarren, 2007; Shen, 2008; Skouta and Li, 2008; Díaz-Requejo and Pérez, 2008). In contrast, gold-catalyzed oxidation chemistry, in particular gold as a catalyst for selective oxidation reactions with economic and environmentally benign oxidants, such as dioxygen or hydrogen peroxide, has been less developed (de Vos and Sels, 2005). So far, representative oxidation transformations are mainly

limited in oxidation of monoxide (Haruta *et al.*, 1987; Valden *et al.*, 1998; Mallat and Baiker, 2004), alcohols (Arcadi and Giuseppe, 2004; Guan *et al.*, 2005; Tsunoyama *et al.*, 2005; Choudhary *et al.*, 2007; Li *et al.*, 2007; Miyamura *et al.*, 2007; Kanaoka *et al.*, 2007), amines (Lazar and Angelici, 2006), and sulfides (Boring *et al.*, 2001; Yuan and Bian, 2007), epoxidations of olefins (Min and Friend, 2007), oxidative cleavage of carbon-carbon multiple bonds (Liu *et al.*, 2006; Xing *et al.*, 2006), oxidation of alkanes (Shul'pin *et al.*, 2001), etc. In addition, the field of gold-catalyzed oxidation chemistry is mostly dominated by heterogeneous catalysts, while homogeneous catalysts still represent the much smaller part. Therefore, it is still desirable to develop new oxidation transformations involving homogeneous gold catalysts.

Benzoxazoles are an important class of heterocycles, because they have exhibited a variety of biological activities including antimicrobial and antitumor properties (Deluca and Kerwin, 1997; Temiz *et al.*, 1998; Sato *et al.*, 1998), thus leading them to becoming appealing targets in drug discovery (Evindar and Batey, 2006). Besides, benzoxazoles are

[‡] Corresponding author

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also found applicable in material science as photochromic agents and laser dyes (Heynderickx *et al.*, 2003; El'tsov, 1990; Trost and Flemming, 1991; Reiser *et al.*, 1972). There are two general strategies for synthesizing 2-arylbenzoxazoles based on substituted 2-aminophenols as starting materials. One is treatment of 2-aminophenols with carboxylic acid derivatives in the presence of strong acids in harsh conditions (Terashima *et al.*, 1982). The other is via photochemical, oxidative, and radical cyclization of phenolic Schiff bases derived from the condensation of 2-aminophenols and aldehydes (Tauer and Grellmann, 1981; Wilfred and Taylor, 2004; Kawashita *et al.*, 2003; Park *et al.*, 2002). For oxidative cyclization, various oxidants such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (Chang *et al.*, 2002), Mn(OAc)₃ (Varma and Kumar, 1998), PhI(OAc)₂ (Varma *et al.*, 1997), ThClO₄ (Park *et al.*, 1996), BaMnO₄ (Srivastava and Venkataramani, 1988), NiO₂ (Nakagawa *et al.*, 1964), Pb(OAc)₄ (Stephens and Bower, 1949), and I₂ (Moghaddam *et al.*, 2006) have been used. However, most of these oxidants are not economic or environmentally benign; furthermore, they are usually required in stoichiometric amounts relative to the substrates. Therefore, to develop more economic and environmental-friendly catalysts to replace conventional stoichiometric oxidants is currently needed. Recently, Kawashita *et al.* (2003) and Kidwai *et al.* (2006) reported utilization of activated carbon (using 50% (w/w) of catalyst at 120 °C) and Cu-nanoparticles (using 10 mol% of catalyst at 80~100 °C) as catalysts under oxygen atmosphere for the one-pot synthesis of 2-arylbenzoxazoles from 2-aminophenols and aldehydes. As part of our continued interest in synthesis of useful heterocycles (Xu *et al.*, 2007), we wish to report here a more efficient and mild synthesis of 2-arylbenzoxazoles in one-pot manner using only 2 mol% of hydrogen tetrachloroaurate as catalyst at 66 °C under oxygen atmosphere with anhydrous tetrahydrofuran (THF) as solvent or in solvent-free condition.

MATERIALS AND METHODS

A representative procedure for the one-pot synthesis of 2-arylbenzoxazoles **3** is described as follows:

A three-necked flask (25 ml) was charged with 2-aminophenol **1** (1.0 mmol), benzaldehyde **2a** (1.0 mmol), H₂AuCl₄·4H₂O (8.0 mg, 0.02 mmol), and THF (2 ml). The resulting mixture was stirred at 40 °C for 30 min. Then the flask was equipped with a balloon filled with dioxygen and the reaction mixture was heated to 66 °C and stirred for another 6 h under oxygen atmosphere. The progress of the reaction was monitored by gas chromatography-mass spectrometry (GC-MS) and thin-layer chromatography (TLC). Upon completion, the resulting mixture was filtered to remove gold catalyst, the filtrate was diluted with distilled water (10 ml) and extracted with ethyl acetate (15 ml×2). The organic layer was dried over anhydrous MgSO₄. After evaporation of solvent under vacuum, the residue was purified by chromatography using hexane/ethyl acetate (9:1, v/v) as eluent.

RESULTS AND DISCUSSION

Initially, phenolic Schiff base 2-(benzylidene-amino)phenol **4a** was chosen as model substrate for investigating the oxidative cyclization by using gold catalysts (Fig.1, Table 1). In the absence of a gold catalyst, the reaction could hardly take place (entry 1). The oxidative cyclization did proceed to give the desired product **3a** in 66% yield when **4a** was treated with 2 mol% of AuCl₃ under an oxygen atmosphere in anhydrous THF at reflux for 6 h (entry 2). Under the catalysis of AuCl and NaAuCl₄·2H₂O, the yield of **3a** increased to be 76% and 88%, respectively (entries 3 and 4). So far, the best result was obtained by using H₂AuCl₄·4H₂O as catalyst, which gave **3a** in 98% yield (entry 5). We also tried to use hydrogen peroxide as oxidant; however, the desired 2-phenylbenzoxale was obtained in quite low yield due to the happening of a hydrolysis of the Schiff base **4a** (entry 6). Note that the reaction could still proceed smoothly to give **3a** in moderate yield even under air (entry 7). In the reaction, gold catalyst may act as a bifunctional catalyst; namely, it serves as an acid catalyst to help the cyclization process via activation of the imine group (Yang *et al.*, 2007) as well as an oxidative catalyst for the dehydrogenation of the in situ generated dihydrobenzoxazole with dioxygen (Zhu and Angelici, 2007).

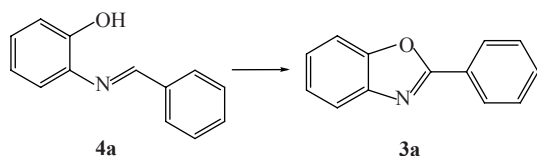


Fig.1 Oxidative cyclization of phenolic Schiff base 4a catalyzed by $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$

Reaction condition: catalyst $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (2 mol%), O_2 (balloon, 101 325 Pa), THF (2 ml), reflux, 6 h

Table 1 Catalyst screen^a

Entry	Catalyst	Yield (%) ^b
1	None	<5
2	AuCl_3	66
3	AuCl	76
4	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	88
5	$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$	98
6	$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}^c$	35
7	$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}^d$	80

^aReaction condition: **4a** (1 mmol), catalyst (0.02 mmol), THF (2 ml), O_2 (balloon, 101 325 Pa), reflux, 6 h; ^bIsolated yield; ^cAqueous 30% (v/v) H_2O_2 (2 mmol) was used as oxidant; ^dThe reaction was carried out under air

Encouraged by the success of gold-catalyzed oxidative cyclization of **4a**, we next examined the direct synthesis of 2-arylbenzoxazole **3a** from 2-aminophenol **1** and benzaldehyde **2a** catalyzed by $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (Fig.2). The one-pot procedure involved the first treatment of **1** and **2a** (molar ratio: 1:1) with 2 mol% of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in THF at 40 °C for 30 min followed by elevating the reaction temperature to 66 °C (at reflux) for another 6 h under an oxygen atmosphere, and finally gave desired product **3a** in 96% yield (Table 2, entry 1). In this section, the effect of solvents on the reaction was particularly investigated (Table 2). It was found that the reaction proceeded equally well even in solvent-free condition (95%, entry 2). The yield of **3a** decreased very much when a mixture of THF and water (4:1, v/v) was used as reaction medium (entry 3). CH_2Cl_2 , CHCl_3 , dimethyl sulphoxide (DMSO), and *N,N*-dimethyl formamide (DMF) were proven to be not good choice for the reaction (entries 9~12), although the step for the formation of Schiff base **4a** could proceed well. Using CH_3OH , EtOH, *m*-xylene, CH_3CN , and 1,2-dichloroethane (1,2-DCE) as solvent, **3a** could be obtained in moderate to good yields (from 75%~92%, entries 4~8).

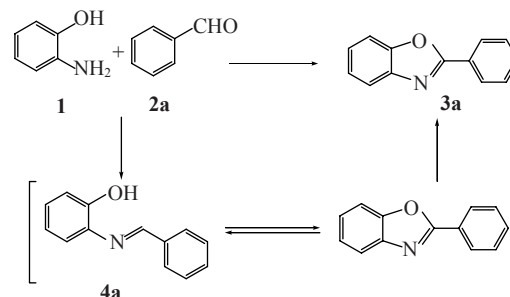


Fig.2 Solvent effect on the oxidative cyclization of phenolic Schiff base 4a catalyzed by $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$

Reaction conditions: (1) catalyst $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (2 mol%), 40 °C, 30 min; (2) O_2 (balloon 101 325 Pa), solvent, 66 °C, 6 h

Table 2 Solvent screening on the one-pot synthesis of 3a catalyzed by $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}^a$

Entry	Solvent	Time (h)	Yield (%) ^b
1	THF	6	96
2	Free	6	95
3	THF- H_2O (4:1, v/v)	6	3
4	CH_3OH	6	75
5	EtOH	6	80
6	<i>m</i> -xylene	12	85
7	CH_3CN	6	87
8	1,2-DCE	12	92
9	CH_2Cl_2	12	45
10	CHCl_3	12	63
11	DMSO	12	18
12	DMF	12	54

^aAll reactions were carried out by the first treatment of **1** (1 mmol) and **2a** (1 mmol) with $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.02 mmol) in solvent (2 ml) at 40 °C for 30 min, followed by elevating the reaction temperature to 66 °C under an oxygen atmosphere; ^bIsolated yield. THF: tetrahydrofuran; 1,2-DCE: 1,2-dichloroethane; DMSO: dimethyl sulphoxide; DMF: *N,N*-dimethyl formamide

Finally, a range of aromatic and heteroaromatic aldehydes was tested in the one-pot synthesis of 2-arylbenzoxazoles **3** from aminophenol **1** and aldehydes **2** catalyzed by $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in THF or solvent-free condition (Fig.3, Table 3). In most cases, the reaction proceeded smoothly to give **3** in good to excellent yields. Aromatic aldehydes possessing electron-withdrawing groups (entries 6~8) generally gave better yield of **3** than those containing electron-donating groups (entries 2~4). Surprisingly, the reaction became a little messed when a nitro-substituted aromatic aldehyde was used and decreased the yield of **3** (entries 9~11).

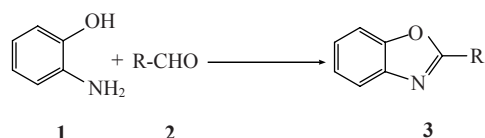


Fig.3 One-pot synthesis of 2-arylbenzoxazoles using H₂AuCl₄·4H₂O as catalyst under oxygen atmosphere

Reaction conditions: (1) H₂AuCl₄·4H₂O (2 mol%), 40 °C, 30 min; (2) O₂ (balloon, 101 325 Pa), THF or solvent-free, 66 °C

Table 3 One-pot synthesis of 2-arylbenzoxazoles 3 from 2-aminophenol 1 and aldehydes 2 catalyzed by H₂AuCl₄·4H₂O under oxygen atmosphere^a

Entry	R	Product	Time (h)	Yield (%) ^b
1	4-C ₆ H ₅ (2a)	3a	6	96 ^c
2	4-CH ₃ C ₆ H ₄ (2b)	3b	6	90 ^d
3	4-CH ₃ OC ₆ H ₄ (2c)	3c	6	88 ^e
4	3,4-OCH ₂ OC ₆ H ₃ (2d)	3d	6	87 ^e
5	1-Naphthyl (2e)	3e	6	93 ^e
6	4-ClC ₆ H ₄ (2f)	3f	6	97 ^e
7	4-BrC ₆ H ₄ (2g)	3g	6	95 ^e
8	4-CF ₃ C ₆ H ₄ (2h)	3h	6	98 ^d
9	2-NO ₂ C ₆ H ₄ (2i)	3i	9	76 ^e
10	3-NO ₂ C ₆ H ₄ (2j)	3j	6	83 ^e
11	4-NO ₂ C ₆ H ₄ (2k)	3k	12	44 ^e
12	2-Furyl (2l)	3l	12	84 ^e
13	2-Thiophenyl (2m)	3m	9	96 ^e

^aAll reactions were carried out by the first treatment of **1** (1 mmol) and **2** (1 mmol) with H₂AuCl₄·4H₂O (0.02 mmol) in THF (2 ml) or solvent-free condition at 40 °C for 30 min followed by elevating the reaction temperature to 66 °C under an oxygen atmosphere; ^bIsolated yield; ^cTHF as solvent; ^dSolvent-free condition

CONCLUSIONS AND EXPERIMENTAL DETAILS

In summary, we described an efficient protocol for preparing 2-arylbenzoxazoles via oxidative cyclization of in situ generated phenolic Schiff bases catalyzed by H₂AuCl₄·4H₂O under an oxygen atmosphere. The advantages of the present method lie in catalytic process using economic and environmentally benign dioxygen as oxidant, relatively low catalyst loading, one-pot manner, mild reaction conditions, and good yields.

General remarks: All the starting chemicals were commercial products (Aldrich or J&K Chemical). Melting points were measured on a Büchi B-545 and uncorrected. ¹H NMR (nuclear magnetic resonance) spectra were obtained on a Bruker AVANCE III 500

(500 MHz) instrument in CDCl₃ using tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are expressed in $\times 10^{-6}$ and coupling constants (J) are given in Hz. GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector.

2-Phenylbenzoxazole (**3a**): white crystals, m.p. 102.1~102.2 °C [102 °C (Varma *et al.*, 1997)]; ¹H NMR (500 MHz, CDCl₃): δ ($\times 10^{-6}$) 7.33~7.37 (m, 2H), 7.51~7.54 (m, 3H), 7.56~7.59 (m, 1H), 7.77~7.79 (m, 1H), 8.25~8.27 (m, 2H).

2-(4'-Methylphenyl)benzoxazole (**3b**): white crystals, m.p. 112.3~112.8 °C [113~114 °C (Varma *et al.*, 1997)]; ¹H NMR (500 MHz, CDCl₃): δ ($\times 10^{-6}$) 2.44 (s, 3H), 7.32~7.35 (m, 4H), 7.56~7.58 (m, 1H), 7.75~7.77 (m, 1H), 8.15 (d, 2H, $J=8.5$ Hz).

2-(4'-Methoxyphenyl)benzoxazole (**3c**): white crystals, m.p. 99.5~99.8 °C [101 °C (Varma *et al.*, 1997)]; ¹H NMR (500 MHz, CDCl₃): δ ($\times 10^{-6}$) 3.90 (s, 3H), 7.03 (d, 2H, $J=9.0$ Hz), 7.30~7.36 (m, 2H), 7.55~7.57 (m, 1H), 7.74~7.75 (m, 1H), 8.21 (d, 2H, $J=9.0$ Hz).

2-(3',4'-Piperonyl)benzoxazole (**3d**): gray crystals, m.p. 150.8~151.2 °C [150~152 °C (Kidwai *et al.*, 2006)]; ¹H NMR (500 MHz, CDCl₃): δ ($\times 10^{-6}$) 6.07 (s, 2H), 6.94 (d, 1H, $J=8.0$ Hz), 7.32~7.34 (m, 2H), 7.54~7.56 (m, 1H), 7.70 (s, 1H), 7.72~7.74 (m, 1H), 7.83 (d, 1H, $J=9.5$ Hz).

2-(Naphthyl)benzoxazole (**3e**): white crystals, m.p. 104.3~104.4 °C [104 °C (Tauer and Grellmann, 1981)]; ¹H NMR (500 MHz, CDCl₃): δ ($\times 10^{-6}$) 7.38~7.41 (m, 2H), 7.57~7.66 (m, 4H), 7.69~7.90 (m, 2H), 8.03 (d, 1H, $J=8.0$ Hz), 8.43 (d, 1H, $J=8.0$ Hz), 9.47 (d, 1H, $J=9.0$ Hz).

2-(4'-Chlorophenyl)benzoxazole (**3f**): white crystals, m.p. 151.4~151.5 °C [147 °C (Varma *et al.*, 1997)]; ¹H NMR (500 MHz, CDCl₃): δ ($\times 10^{-6}$) 7.35~7.39 (m, 2H), 7.51 (d, 2H, $J=8.5$ Hz), 7.58~7.60 (m, 1H), 7.77~7.79 (m, 1H), 8.20 (d, 2H, $J=8.5$ Hz).

2-(4'-Bromophenyl)benzoxazole (**3g**): white crystals, m.p. 155.4~155.5 °C [157~158 °C (Evindar and Batey, 2006)]; ¹H NMR (500 MHz, CDCl₃): δ ($\times 10^{-6}$) 7.36~7.38 (m, 2H), 7.58~7.60 (m, 1H), 7.68 (d, 2H, $J=7.5$ Hz), 7.76~7.79 (m, 1H), 8.13 (d, 2H, $J=7.5$ Hz).

2-(4'-Trifluoromethylphenyl)benzoxazole (**3h**): white crystals, m.p. 140.3~140.4 °C [143~145 °C (Lewis *et al.*, 2004)]; ¹H NMR (500 MHz, CDCl₃): δ

($\times 10^{-6}$) 7.37~7.42 (m, 2H), 7.59~7.62 (m, 1H), 7.77~7.82 (m, 3H), 7.37 (d, 2H, $J=9$ Hz).

2-(2'-Nitrophenyl)benzoxazole (**3i**): pale yellow crystals, m.p. 101.5~101.6 °C [104~105 °C (Bougrin *et al.*, 1998)]; ^1H NMR (500 MHz, CDCl_3): δ ($\times 10^{-6}$) 7.37~7.42 (m, 2H), 7.56~7.58 (m, 1H), 7.66~7.70 (m, 1H), 7.72~7.82 (m, 1H), 7.89 (d, 1H, $J=9.5$ Hz), 8.14 (d, 1H, $J=9.5$ Hz).

2-(3'-Nitrophenyl)benzoxazole (**3j**): pale yellow crystals, m.p. 211.5~211.6 °C [211.5~212 °C (Nakagawa *et al.*, 1964)]; ^1H NMR (500 MHz, CDCl_3): δ ($\times 10^{-6}$) 7.40~7.45 (m, 2H), 8.64~7.66 (m, 1H), 7.74 (t, 1H, $J=8.0$ Hz), 7.82~7.84 (m, 1H), 8.38~8.40 (m, 1H), 8.59~8.61 (m, 1H), 9.10 (m, 1H).

2-(4'-Nitrophenyl)benzoxazole (**3k**): yellow crystals, m.p. 264.1~264.2 °C [266~268 °C (Varma *et al.*, 1997)]; ^1H NMR (500 MHz, CDCl_3): δ ($\times 10^{-6}$) 7.41~7.46 (m, 2H), 7.64 (d, 1H, $J=7.0$ Hz), 7.84 (d, 1H, $J=7.0$ Hz), 8.39 (d, 2H, $J=8.5$ Hz), 8.44 (d, 2H, $J=8.5$ Hz).

2-(2-Furyl)benzoxazole (**3l**): white crystals, m.p. 88.1~88.5 °C [89~90 °C (Kidwai *et al.*, 2006)]; ^1H NMR (500 MHz, CDCl_3): δ ($\times 10^{-6}$) 6.61 (dd, 1H, $J_1=3.5$ Hz, $J_2=4.0$ Hz), 7.28 (dd, 1H, $J_1=3.5$ Hz, $J_2=2.0$ Hz), 7.33~7.37 (m, 2H), 7.55~7.57 (m, 1H), 7.67 (t, 1H, $J=2.0$ Hz), 7.73~7.76 (m, 1H).

2-(2-Thiophenyl)benzoxazole (**3m**): white crystals, m.p. 108.1~108.2 °C [108 °C (Kidwai *et al.*, 2006)]; ^1H NMR (500 MHz, CDCl_3): δ ($\times 10^{-6}$) 7.18~7.20 (m, 1H), 7.33~7.36 (m, 2H), 7.51~7.56 (m, 2H), 7.71~7.75 (m, 1H), 7.92 (dd, 1H, $J_1=3.5$ Hz, $J_2=4.0$ Hz).

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