



TITLE:

Electrochemical intramolecular  
C[BOND]H amination: synthesis of  
benzoxazoles and benzothiazoles.

AUTHOR(S):

Morofuji, Tatsuya; Shimizu, Akihiro; Yoshida, Jun-Ichi

---

CITATION:

Morofuji, Tatsuya ...[et al]. Electrochemical intramolecular C[BOND]H amination: synthesis of benzoxazoles and benzothiazoles.. Chemistry 2015, 21(8): 3211-3214

ISSUE DATE:

2015-01-09

URL:

<http://hdl.handle.net/2433/198581>

RIGHT:

This is the peer reviewed version of the following article: Morofuji, T., Shimizu, A. and Yoshida, J.-i. (2015), Electrochemical Intramolecular C[BOND]H Amination: Synthesis of Benzoxazoles and Benzothiazoles. *Chem. Eur. J.*, 21: 3211–3214, which has been published in final form at <http://dx.doi.org/10.1002/chem.201406398>; 許諾条件により本文ファイルは2016-01-09に公開.; この論文は出版社版ではありません。引用の際には出版社版をご確認ご利用ください。; This is not the published version. Please cite only the published version.

## COMMUNICATION

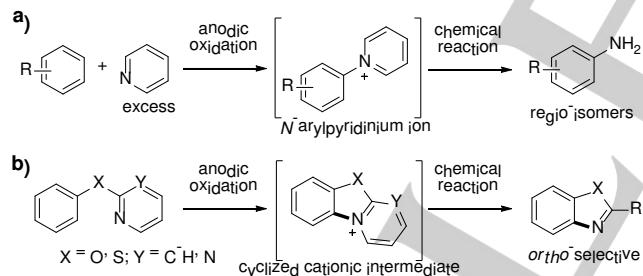
WILEY-VCH

# Electrochemical Intramolecular C–H Amination: Synthesis of Benzoxazoles and Benzothiazoles

Tatsuya Morofuji, Akihiro Shimizu, and Jun-ichi Yoshida\*

**Abstract:** A new method for metal-free intramolecular C–H amination has been developed. Electrochemical oxidation of 2-pyrimidyloxybenzenes and 2-pyrimidylthiobenzenes, which can be easily prepared from phenols and thiophenols, respectively followed by the treatment of the resulting pyrimidinium ions with piperidine gives 2-aminobenzoxazoles and 2-aminobenzothiazoles, respectively.

C–H amination<sup>[1]</sup> serves as powerful methods for synthesizing nitrogen-containing organic compounds, and a variety of transformations have been developed based on transition-metals,<sup>[2]</sup> hypervalent iodines,<sup>[3]</sup> radical species.<sup>[4]</sup> Electrochemical oxidation<sup>[5,6]</sup> serves as a straightforward method for functionalizing C–H bond of aromatic compounds without using metal or chemical oxidant.<sup>[7]</sup> Despite the usefulness of the method, it often suffers from overoxidation when the oxidation potential of the product is lower than that of the starting material,<sup>[8]</sup> and this is often the case. Therefore, C–H amination of aromatic compounds by conventional electrochemical oxidation is usually difficult to achieve selectively. To solve the problem, we have developed the electrochemical intermolecular C–H amination of aromatic compounds via *N*-arylpypyridinium ions (Scheme 1a).<sup>[9]</sup>

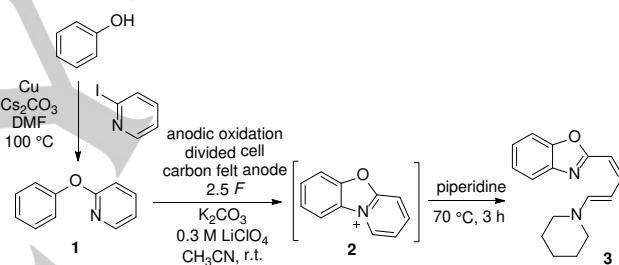


**Scheme 1.** Electrochemical C–H amination. (a) Intermolecular approach. (b) Intramolecular approach.

The key to the success of the method is the intermediacy of the electrooxidatively inactive cationic intermediates which avoid overoxidation. However, there is another problem, *i.e.* regioselectivity. Sometimes a mixture of regiosomers are produced. To solve this problem we envisaged that an

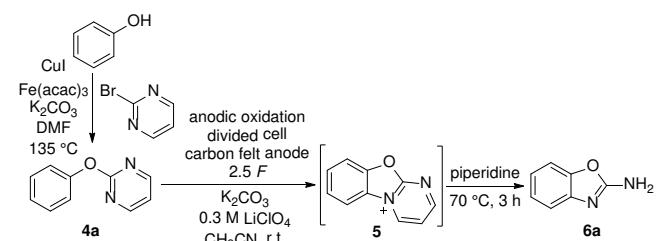
intramolecularization approach<sup>[10]</sup> is promising (Scheme 1b). In addition, resulting cyclized cationic intermediate could be converted to nitrogen containing heteroaromatics. The idea works, and we report here the intramolecular electrochemical C–H amination that offers an intriguing way of making benzoxazoles and benzothiazoles from phenols and thiophenols, respectively.<sup>[11]</sup>

We first examined electrochemical oxidation of 2-phenoxypyridine (**1**), which can be easily prepared from phenol and a halopyridine in one step<sup>[12]</sup> (Scheme 2). The anodic oxidation led to the formation of cyclized pyridinium ion **2**, which was characterized by NMR. Although treatment of **2** with piperidine gave the 2-substituted benzoxazole **3** in 60% yield, the synthetic utility of **3** seemed to be limited.



**Scheme 2.** Electrochemical oxidation of 2-phenoxypyridine followed by treatment with piperidine.

To explore a more useful transformation, we designed a transformation using a pyrimidine ring instead of a pyridine ring as shown in Scheme 3. The starting 2-pyrimidyloxybenzene (**4a**) was prepared from phenol and 2-bromopyrimidine in one step.<sup>[12]</sup> The anodic oxidation of **4a** gave the cyclized pyrimidinium ion **5a**, which was characterized by NMR (Figure 1). Treatment of **5a** with piperidine gave 2-aminobenzoxazole (**6a**), which constitutes a key scaffold in therapeutically important molecules<sup>[13,14]</sup> in 85% yield. The present transformation can be performed on 2.0 mmol scale (Table 1, entry 1).



**Scheme 3.** Electrochemical oxidation of 2-pyrimidyloxybenzene followed by treatment with piperidine.

\* T. Morofuji, Dr. A. Shimizu, Prof. Dr. J. Yoshida

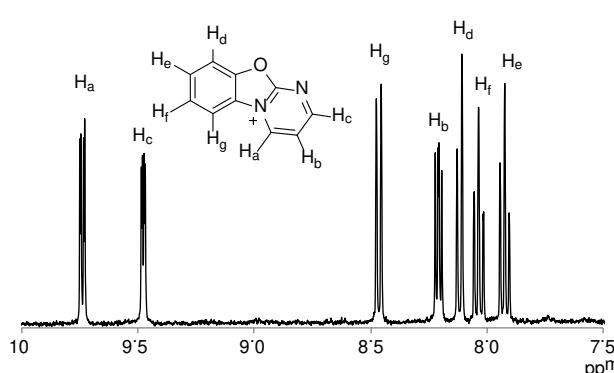
Department of Synthetic Chemistry and Biological Chemistry,  
Graduate School of Engineering, Kyoto University, Nishikyo-ku,  
Kyoto 615-8510 (Japan)

E-mail: yoshida@sbchem.kyoto-u.ac.jp

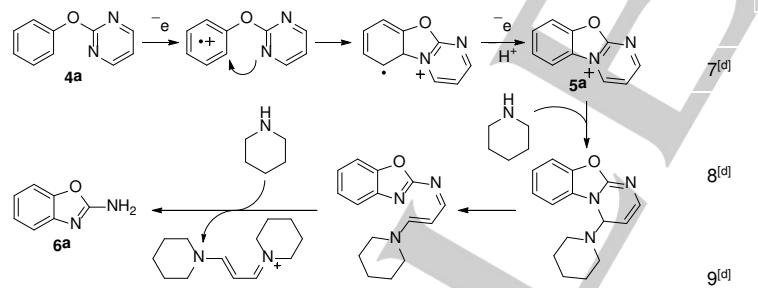
Supporting information for this article is given via a link at the end of the document.

## COMMUNICATION

WILEY-VCH

Figure 1.  $^1\text{H}$  NMR spectrum of **5a**.

The following reaction mechanism seems to be reasonable (Scheme 4). One electron oxidation of **4a** gives the corresponding radical cation. The subsequent intramolecular attack of the nitrogen atom of the pyrimidine ring followed by one-electron oxidation and extrusion of a proton gives cyclized cationic intermediate **5a**. In the next step, the attack of piperidine to the carbon next to the positively charged nitrogen atom of **5a** followed by the ring opening and the attack of another molecule of piperidine on the resulting imine gives 2-aminobenzoxazole (**6a**). Because the oxidation potential of **6a** (0.88 V vs Ag/AgNO<sub>3</sub>) is much lower than that of **4a** (1.57 V vs Ag/AgNO<sub>3</sub>), intermediacy of the cationic species **5**, which is electrooxidatively inactive under the conditions, would be critical for the success of the reaction.



Scheme 4. A mechanism of electrochemical intramolecular C-H amination and the subsequent chemical reaction with piperidine.

As shown in Table 1, the present method is applicable to various substituted 2-pyrimidylbenzenes to give the corresponding 2-aminobenzoxazoles in good yields. *o*- and *p*-Ethoxycarbonyl-substituted phenol derivatives **4b** and **4c** gave the corresponding 2-aminobenzoxazoles **6b** and **6c**, respectively (entries 2 and 3). The reaction of *m*-methoxycarbonyl-substituted phenol derivative **4d** gave a mixture of two regioisomers **6da** and **6db** (entry 4). The benzylic C-H group was not affected as shown in entry 5. The transformation is compatible with various functional groups such as halogen, trifluoromethyl, cyano, and ketone carbonyl groups (entries 5–

12).

**Table 1:** Synthesis of 2-aminobenzoxazoles by electrochemical intramolecular C-H amination.<sup>[a]</sup>

entry	starting material	product	electricity (F)	yield (%) <sup>[b]</sup>
1			2.5	85 92 <sup>[c]</sup>
2			2.5	74
3			2.5	89
4 <sup>[d]</sup>			3.0	80 (a/b=1/1.0)
5 <sup>[d,e]</sup>			2.5	48
6			2.5	99
7 <sup>[d]</sup>			2.5	82
8 <sup>[d]</sup>			4.0	68
9 <sup>[d]</sup>			2.5	76
10			2.5	78
11			2.5	88
12			2.5	98

[a] Compound **4** (0.2 mmol) was oxidized electrochemically in the presence of 0.6 mmol of K<sub>2</sub>CO<sub>3</sub> in a 0.3 M solution of LiClO<sub>4</sub> in CH<sub>3</sub>CN in an H-type divided cell under constant current conditions at room temperature unless otherwise stated, and the resulting solution was treated with piperidine (2.0 mmol) at 70

## COMMUNICATION

WILEY-VCH

<sup>a</sup>C. [b] Isolated yields. [c] The transformation was performed on 2.0 mmol scale. [d] 1.0 M solution of LiClO<sub>4</sub> was used. [e] The electrolysis was carried out at 50 °C.

**Table 2:** Synthesis of 2-aminobenzothiazoles by electrochemical intramolecular C–H amination.<sup>[a]</sup>

entry	starting material	product	electr icity (F)	yield (%) <sup>[b]</sup>
1 <sup>[c,d]</sup>			2.5	73
2			4.0	68
3			2.5	72
4 <sup>[c,d]</sup>			2.5	84
5 <sup>[c]</sup>			2.5	75
6			2.5	80

[a] Compound 7 (0.2 mmol) was oxidized electrochemically in the presence of 0.6 mmol of K<sub>2</sub>CO<sub>3</sub> in a 0.3 M solution of LiClO<sub>4</sub> in CH<sub>3</sub>CN in an H-type divided cell under constant current conditions at room temperature unless otherwise stated, and the resulting solution was treated with piperidines (2.0 mmol) at 70 °C. [b] Isolated yields. [c] 1.0 M solution of LiClO<sub>4</sub> was used. [d] The electrolysis was carried out at 50 °C.

Next, we examined the reaction of 2-pyrimidylthiobenzenes 7, which were prepared from thiophenols and a halopyrimidine or from aryl halides and 2-pyrimidinethiol in one step.<sup>[15]</sup> Electrochemical oxidation of 7 and the subsequent chemical reaction with piperidine gave 2-aminobenzothiazoles 8, which also serve as an intriguing motif in medicinal chemistry.<sup>[16]</sup> The results are summarized in Table 2. Notably, 2-aminobenzothiazoles are often used as precursors of 2-aminothiophenols, which are important intermediates for synthesis of bioactive molecules.<sup>[17]</sup>

The most popular protocols for synthesizing benzoxazoles and benzothiazoles involve the condensation of 2-aminophenol and 2-aminothiophenol, respectively, with either a carboxylic acid or aldehyde followed by intramolecular cyclization.<sup>[18]</sup>

Although protocols based on cyclization using C–H functionalization have also been developed,<sup>[19]</sup> most of them involve intramolecular C–O or C–S coupling, and therefore aniline derivatives are required as starting materials.

In contrast, only a few examples that employ intramolecular C–H amination (C–N coupling) of substrates derived from phenols for constructing benzoxazoles have been reported. In 2011, Punniyamurthy and coworkers reported copper catalyzed intramolecular C–H amination of bisaryloxime ether to give 2-arylbenzoxazoles.<sup>[11]</sup> Although the method is useful for synthesizing 2-arylbenzoxazoles, multistep preparation of starting bisaryloxime ethers is required. In addition, the method cannot be applied to the synthesis of benzothiazoles. To the best of our knowledge, no example employs intramolecular C–H amination of thiophenol derivatives for constructing benzothiazoles. The present electrochemical transformation serves as a simple and powerful route to benzoxazoles and benzothiazoles via intramolecular C–H amination.

In conclusion, we have developed a powerful method for intramolecular C–H amination of aromatic compounds using the electrochemical method. The present method provides metal- and chemical-oxidant-free routes to the benzoxazoles and benzothiazoles having a variety of functionality. Currently, we are working to expand the scope of the present method for the synthesis of other nitrogen containing heterocyclic compounds.

## Experimental Section

The anodic oxidation was carried out using an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 160 mg, dried at 300 °C/1 mmHg for 4 h before use) and a platinum plate cathode (20 mm × 20 mm). In the anodic chamber was placed a solution of 4 (0.20 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.60 mmol) in LiClO<sub>4</sub>/CH<sub>3</sub>CN (0.3 M or 1.0 M, 10.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (150 µL) and LiClO<sub>4</sub>/CH<sub>3</sub>CN (0.3 M or 1.0 M, 10.0 mL). The constant current electrolysis (8.0 mA) was carried out at room temperature or at 50 °C with magnetic stirring. After the electrolysis (2.5 – 4.0 F), piperidine (200 µL, 2.0 mmol) was added to the anodic solution. The resulting solution in the anodic chamber was transferred to a round-bottom flask and was heated at 70 °C with stirring for 3 h. After removal of the solvent under reduced pressure, H<sub>2</sub>O (20 mL) and ethyl acetate (10 mL) were added. The mixture was extracted with ethyl acetate/hexane (2/1) (20 mL × 3), and the combined extracts were washed with water (20 mL) and brine (20 mL), and was dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was purified with flash chromatography or preparative GPC to obtain 6.

## Acknowledgements

We thank the Grant-in-Aid for Scientific Research for financial support.

**Keywords:** C–H functionalization • C–H amination • electrochemistry • oxidation • radical ions

## COMMUNICATION

WILEY-VCH

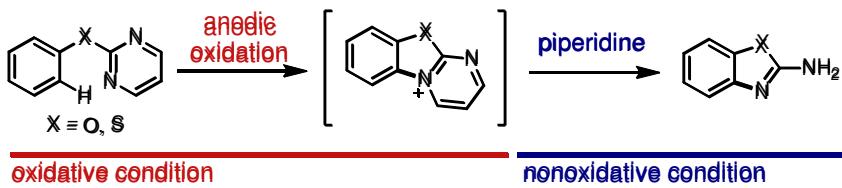
- [1] a) F. Collet, R. H. Dodd, P. Dauban, *Chem. Commun.* **2009**, *48*, 5061-5074; b) B. Stokes, T. G. Driver, *Eur. J. Org. Chem.* **2011**, *22*, 4071-4088; c) M. L. Louillat, F. W. Patureau, *Chem. Soc. Rev.* **2014**, *43*, 901-910.
- [2] a) J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim, S. Chang, *J. Am. Chem. Soc.* **2012**, *134*, 9110-9113; b) G. B. Boursalian, M. Y. Nagi, K. N. Hojczyk, T. Ritter, *J. Am. Chem. Soc.* **2013**, *135*, 13278-13281; c) D. G. Yu, M. Suri, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 8802-8805; d) M. Shang, S. Z. Sun, H. X. Dai, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 3354-3357.
- [3] a) H. J. Kim, J. Kim, S. H. Cho, S. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 16382-16385; b) X. Ban, Y. Pan, Y. Lin, S. Wang, Y. Du, K. Zhao, *Org. Biomol. Chem.* **2012**, *10*, 3606-3609; c) J. A. Souto, D. Zian, K. Muñiz, *J. Am. Chem. Soc.* **2012**, *134*, 7242-7245; d) S. K. Alla, R. K. Kumar, P. Sadhu, T. Punniyamurthy, *Org. Lett.* **2013**, *15*, 1334-1337.
- [4] a) Y. Amaoka, S. Kamijo, T. Hoshikawa, M. Inoue, *J. Org. Chem.* **2012**, *77*, 9959-9969; b) L. J. Allen, P. J. Cabrera, M. Lee, M. S. Sanford, *J. Am. Chem. Soc.* **2014**, *136*, 5607-5610; c) K. Foo, E. Sella, I. Thome, M. D. Eastgate, P. S. Baran, *J. Am. Chem. Soc.* **2014**, *136*, 5279-5282; d) L. Zhou, S. Tang, X. Qi, C. Lin, K. Liu, C. Liu, Y. Lan, A. Lei, *Org. Lett.* **2014**, *16*, 3404-3407.
- [5] a) K. D. Moeller, *Tetrahedron* **2000**, *56*, 9527-9554; b) J. B. Sperry, D. L. Wright, *Chem. Soc. Rev.* **2006**, *35*, 605-621; c) J. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, *Chem. Rev.* **2008**, *108*, 2265-2299.
- [6] Recent examples: a) T. Kashiwagi, F. Amemiya, T. Fuchigami, M. Atobe, *Chem. Commun.* **2012**, *48*, 2806-2808; b) K. Mitsudo, N. Kamimoto, H. Murakami, H. Mandai, A. Wakamiya, Y. Murata, S. Suga, *Org. Biomol. Chem.* **2012**, *10*, 9562-9569; c) E. E. Finney, K. A. Ogawa, A. J. Boydston, *J. Am. Chem. Soc.* **2012**, *134*, 12374-12377; d) Y. Ashikari, A. Shimizu, T. Nokami, J. Yoshida, *J. Am. Chem. Soc.* **2013**, *135*, 16070-16073; e) Y. Yamaguchi, Y. Okada, K. Chiba, *J. Org. Chem.* **2013**, *78*, 2626-2638; f) A. Redden, R. J. Perkins, K. D. Moeller, *Angew. Chem. Int. Ed.* **2013**, *52*, 12865-12868; *Angew. Chem.* **2013**, *125*, 13103-13106; g) W. Li, C. Zheng, L. Hu, H. Tian, R. D. Little, *Adv. Synth. Catal.* **2013**, *355*, 2884-2890.
- [7] a) F. Kakiuchi, T. Kochi, H. Mutsumi, N. Kobayashi, S. Urano, M. Sato, S. Nishiyama, T. Tanabe, *J. Am. Chem. Soc.* **2009**, *131*, 11310-11311; b) A. Kirste, B. Elsler, G. Schnakenburg, S. R. Waldvogel, *J. Am. Chem. Soc.* **2012**, *134*, 3571-3576; c) T. Morofuji, A. Shimizu, J. Yoshida, *Angew. Chem. Int. Ed.* **2012**, *51*, 7259-7262; *Angew. Chem.* **2012**, *124*, 7371-7374; d) B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2014**, *53*, 5210-5213; *Angew. Chem.* **2014**, *126*, 5311-5314.
- [8] a) E. Raoult, J. Sarrazin, A. Tallec, *J. Appl. Electrochem.* **1984**, *14*, 639-643; b) Y. N. Oginin, A. I. Illovaikii, G. I. Nikisin, *Russ. Chem. Bull.* **1994**, *43*, 1536-1540; c) F. L. S. Purgato, M. I. C. Ferreira, J. R. Romero, *J. Mol. Catal. A: Chem.* **2000**, *161*, 99-104; d) S. M. Halas, K. Okyne, A. Fry, *J. Electrochim. Acta* **2003**, *48*, 1837-1844.
- [9] a) T. Morofuji, A. Shimizu, J. Yoshida, *J. Am. Chem. Soc.* **2013**, *135*, 5000-5003; b) T. Morofuji, A. Shimizu, J. Yoshida, *J. Am. Chem. Soc.* **2014**, *136*, 4496-4499.
- [10] a) T.-L. Ho, *Tactics of Organic Synthesis*, Wiley, New York, 1994, pp190; b) L. F. Tietze, U. Beifuss, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131-163; *Angew. Chem.* **1993**, *105*, 137-170; c) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115-136; d) M. Sugawara, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 1717-1720.
- [11] a) M. M. Guru, M. A. Ali, T. Punniyamurthy, *Org. Lett.* **2011**, *13*, 1194-1197; b) M. M. Guru, M. A. Ali, T. Punniyamurthy, *T. J. Org. Chem.* **2011**, *76*, 5295.
- [12] a) Y. J. Cherng, *Tetrahedron* **2002**, *58*, 887-890; b) J. H. Chu, P. S. Lin, M. J. Wu, *Organometallics* **2010**, *29*, 4058-4065; c) M. Platon, L. Cui, S. Mom, P. Richard, M. Saeys, J. C. Hierso, *Adv. Synth. Catal.* **2011**, *353*, 3403-3414; d) S. Zhang, X. Liu, *Synlett* **2011**, *268*-272; e) S. G. Babu, B. R. Karvembu, *Tetrahedron Lett.* **2013**, *54*, 1677-1680.
- [13] a) Y. Katura, S. Nishino, Y. Inoue, M. Tomoi, H. Takasugi, *Chem. Pharm. Bull.* **1992**, *40*, 371-380; b) E. S. Lazer, C. K. Miao, H. C. Wong, R. Sorek, D. M. Spero, A. Gilman, K. Pal, M. Behnke, A. G. Graham, J. M. Watrous, C. A. Homon, J. Nagel, A. Shah, Y. Guindon, P. R. Farina, J. Adams, *J. Med. Chem.* **1994**, *37*, 913-923; c) S. Yasuo, Y. Megumi, Y. Satoshi, S. Tomoko, I. Midori, N. Tetsutarō, S. Kokichi, K. Fukio, *J. Med. Chem.* **1998**, *41*, 3015-3021; d) S. Yoshida, S. Shiokawa, K.-I. Kawano, H. Murakami, H. Suzuki, Y. Sato, *J. Med. Chem.* **2005**, *48*, 7075-7079; e) C. J. O'Donnell, B. N. Rogers, B. S. Bronk, D. K. Bryce, J. W. Coe, K. K. Cook, A. J. Duplantier, E. Evrard, M. Hajos, W. E. Hoffmann, R. S. Hurst, N. Maklad, R. J. Mather, S. McLean, F. M. Nedza, B. T. O'Neill, L. Peng, W. Qiao, M. M. Rottas, S. B. Sands, A. W. Schmidt, A. V. Shrikhande, D. K. Spracklin, D. F. Wong, A. Zhang, L. Zhang, *J. Med. Chem.* **2010**, *53*, 1222-1237; f) M. L. Calabro, R. Cauputo, R. Ettari, G. Puia, F. Ravazzini, M. Zappala, N. Micale, *Med. Chem. Res.* **2013**, *22*, 6089-6095.
- [14] Synthetic application of 2-aminobenzoxazoles: a) J. J. Wade, C. B. Toso, C. J. Matson, V. L. Stelzer, *J. Med. Chem.* **1983**, *26*, 608-611; b) H. I. El-Subbagh, G. S. Hassan, A. S. El-Azab, A. A. M. Abdel-Aziz, A. A. Kadi, A. M. Al-Obaid, O. A. Al-Shabanah, M. M. Sayed-Ahmed, *Eur. J. Med. Chem.* **2011**, *46*, 5567-5572.
- [15] a) B. Sreedhar, P. S. Reddy, M. A. Reddy, *Synthesis* **2009**, 1732-1738; b) S. G. Babu, R. Karvembu, *Tetrahedron Lett.* **2013**, *54*, 1677-1680; c) M. Sayah, M. G. Organ, *Chem. Eur. J.* **2013**, *19*, 16196-16199.
- [16] a) S. R. Byeon, Y. J. Jin, S. J. Lim, J. H. Lee, K. H. Yoo, K. J. Shin, S. J. Oh, D. J. Kim, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 4022-4025; b) C. Liu, J. Lin, S. Pitt, R. F. Zhang, J. S. Sack, S. E. Kiefer, K. Kish, A. M. Doweyko, H. Zhang, P. H. Marathe, J. Trzaskos, G. L. Schieven, K. Leffthers, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 1874-1879; c) R. M. Kumhare, K. V. Kumar, M. J. Ramaiah, T. Dadmal, S. N. C. V. L. Pushpavalli, D. Mukhopadhyay, B. Divya, T. A. Devi, U. Kosurkar, M. Pal-Bhadra, *Eur. J. Med. Chem.* **2011**, *46*, 4258-4266; d) R. M. Kumhare, T. Dadmal, U. Kosurkar, V. Sridhar, J. V. Rao, *Bioorg. Med. Chem. Lett.* **2012**, *22*, 453-455; e) H. Xiao, P. Li, D. Hu, B.-A. Song, *Bioorg. Med. Chem. Lett.* **2014**, *24*, 3452-3454.
- [17] a) H. Inoue, M. Konda, T. Hashiyama, H. Otuka, K. Takahashi, M. Gaino, T. Date, K. Aoe, M. Takeda, S. Murata, H. Narita, T. Nagao, *J. Med. Chem.* **1991**, *34*, 675-687; b) H. Yanagisawa, K. Fujimoto, Y. Shimoji, T. Kanazaki, K. Mizutari, H. Nishino, H. Shiga, H. Koike, *Chem. Pharm. Bull.* **1992**, *40*, 2055-2062; c) J. W. Park, Y. M. Ha, K. Moon, S. Kim, H. O. Jeong, Y. J. Park, H. J. Lee, J. Y. Park, Y. M. Song, P. Chun, Y. Byun, H. R. Moon, H. Y. Chung, *Bioorg. Med. Chem. Lett.* **2013**, *23*, 4172-4176; d) V. Singh, S. Wang, E. T. Kool, *J. Am. Chem. Soc.* **2013**, *135*, 6184-6191.
- [18] a) Y. Kawashita, N. Nakamichi, H. Kawabata, M. Hayashi, *Org. Lett.* **2003**, *5*, 3713-3715; b) Y. X. Chen, L. F. Qian, W. Zhang, B. Han, *Angew. Chem. Int. Ed.* **2008**, *47*, 9330-9333; *Angew. Chem.* **2008**, *120*, 9470-9473; c) A. J. Blacker, M. M. Farah, M. I. Hall, S. P. Marsden, O. Saidi, J. M. J. Williams, *Org. Lett.* **2009**, *11*, 2039-2042; d) H. Z. Boein, K. H. Najafabadi, *Eur. J. Org. Chem.* **2009**, *11*, 4926-4929; e) R. D. Carpenter, M. J. Kurt, *Nat. Protoc.* **2010**, *5*, 1731; f) X. Zhang, X. Jia, J. Wang, X. Fan, *Green Chem.* **2011**, *13*, 413-418.
- [19] a) S. Ueda, H. Nagasawa, *Angew. Chem. Int. Ed.* **2008**, *47*, 6411-6413; *Angew. Chem.* **2008**, *120*, 6511-6513; b) K. Inamoto, C. Hasegawa, K. Hiroya, T. Doi, *Org. Lett.* **2008**, *10*, 5147-5150; c) S. Ueda, H. Nagasawa, *J. Org. Chem.* **2009**, *74*, 4272-4277; d) K. Inamoto, C. Hasegawa, J. Kawasaki, K. Hiroya, T. Doi, *Adv. Synth. Catal.* **2010**, *352*, 2643-2655; e) H. Wang, L. Wang, J. Shang, X. Li, H. Wang, J. Gui, A. Lei, *Chem. Commun.* **2012**, *48*, 76-78.
- ...

## COMMUNICATION

WILEY-VCH

## Entry for the Table of Contents

## COMMUNICATION



T. Morofuji, A. Shimizu, Jun-ichi  
Yoshida\*

Page No. – Page No.

Title

**Integration of Electrochemical and Chemical Reactions:** A new method for metal-free intramolecular C–H amination has been developed. Electrochemical oxidation of 2-pyrimidyloxybenzenes and 2-pyrimidylthiobenzenes, which can be easily prepared from phenols and thiophenols, respectively followed by the treatment of the resulting pyrimidinium ions with piperidine gives 2-aminobenzoxazoles and 2-aminobenzo-thiazoles, respectively.