Journal Pre-proofs

Benzimidazoles and Benzothiazoles from Styrenes and N-vinylimidazole via Palladium Catalysed Oxidative C=C and C-N bond Cleavage

Altab Shaikh, Owk Ravi, S. Pushpa Ragini, Nimma Sadhana, Surendar Reddy Bathula

PII: S0040-4039(19)31147-5
DOI: https://doi.org/10.1016/j.tetlet.2019.151356
Reference: TETL 151356

To appear in: *Tetrahedron Letters*

Received Date: 14 September 2019
Revised Date: 30 October 2019
Accepted Date: 1 November 2019

Please cite this article as: Shaikh, A., Ravi, O., Pushpa Ragini, S., Sadhana, N., Bathula, S.R., Benzimidazoles and Benzothiazoles from Styrenes and N-vinylimidazole via Palladium Catalysed Oxidative C=C and C-N bond Cleavage, *Tetrahedron Letters* (2019), doi: https://doi.org/10.1016/j.tetlet.2019.151356

ELSEVIER

Tetrahedron Letters
journal homepage: www.elsevier.com

Benzimidazoles and Benzothiazoles from Styrenes and N-vinylimidazole via Palladium Catalysed Oxidative C=C and C–N bond Cleavage

Altab Shaikh,[a,b] Owk Ravi,[a,b] Pushpa Ragini S,[a,b] Nimma Sadhana,[a] Surendar Reddy Bathula[a,b,*]

[a] *Organic Synthesis and Process Chemistry Division CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India*
[b] *Academy of Scientific and Innovative Research, Ghaziabad - 201 002, India*

* Corresponding author. Tel.: +0-000-000-0000; fax: +0-000-000-0000; e-mail: author@university.edu

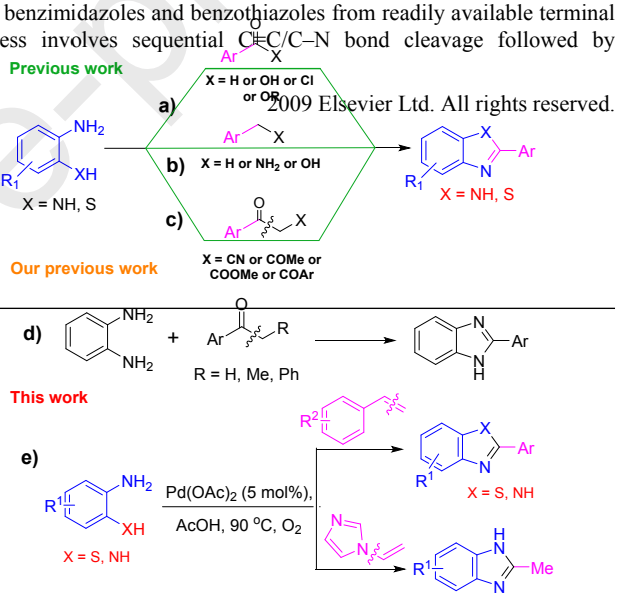
ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords: 1) Benzimidazole, 2) C=C bond Cleavage, 3) Terminal Aromatic Olefins, 4) Vinylimidazole

ABSTRACT

Herein we report a first, palladium catalyzed, one-pot methodology for the synthesis of pharmacologically important benzimidazoles and benzothiazoles from readily available terminal aromatic olefins. The process involves sequential C=C/C–N bond cleavage followed by C–N/C–S bond formation.



1. Introduction

Benzimidazoles and benzothiazoles are vital pharmacophoric units that correspond to numerous biological activities such as antiulcer, antimicrobial, anticonvulsant, antiviral and anticancer.[1] Benzazol-based marketed drugs such as albendazole, lansaprazole, mebendazole, telmisartan, astemizole, riluzole, pramipexole, viozan and ethoxyzolamide further signifies the pharmaceutical importance of the above privileged structures (Figure 1). Moreover, these core units are prevalent in various natural products and functional materials.[2] Due to their widespread applications; considerable efforts have been made towards the development of efficient methods for the synthesis of these molecules.

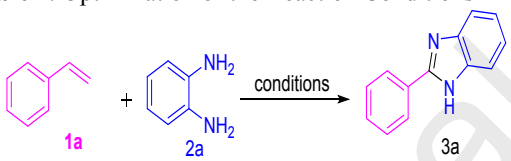
Generally, benzimidazoles and benzothiazoles are synthesized by the condensation of amino aniline/2-aminothiophenol with aldehydes,[3] carboxylic acids and their derivatives[4] (Scheme 1a). Alternately, benzylalcohols,[5] benzylamines,[6] methylarenes[7a] and nitroaniline[7b-7h] have been used as substrates (Scheme 1b). For instance, Milstein and co-workers reported the synthesis of benzimidazoles from alcohols and diamines via cobalt catalyzed dehydrogenative coupling reaction.[8] In 2018, Hikawa et al. reported the construction of 2-arylbenzimidazoles from various benzyl alcohols.[9] Huang et al. reported the cobalt catalyzed electrochemical synthesis of benzazoles from different alcohols.[10] Srimani and coworkers reported the synthesis of 2-substituted and 1,2-disubstituted benzimidazoles by coupling of diamine with alcohols.[11] In addition, Bharate et al. reported metal free protocol for benzimidazoles from *o*-phenylenediamine and benzylamine in ionic liquid medium.[12] Luo et al. reported benzimidazole synthesis from primary amines via by ortho-quinone catalysis.[13] Narender and coworkers reported the divergent synthesis of benzimidazoles and benzothiazoles from benzylamines.[14] Moreover, β-keto esters,[15] β-keto nitriles[16] and β-diketones[17] (Scheme 1c) have also been utilized as substrates for the synthesis of the title compounds. Likewise, recently, we have

Scheme 1. Synthetic Approaches to Benzimidazole/ Benzothiazole

rep ; 4-cleavage reaction for the synthesis of benzimidazoles from acetophenones (Scheme 1d).[18] However, use of terminal aromatic olefins as substrates for synthesis of titled compounds is not reported. Styrenes are readily available unactivated terminal alkenes and widely explored in both academia and industry for the preparation of complex organic molecules. Further, well known reactions of alkenes such as Heck reaction,[19] olefin hydroformylation,[20] Wacker process[21] and olefin metathesis[22] ascertain their importance in modern synthetic organic chemistry. As part of our continuing interest in construction of privileged heterocyclic scaffolds from readily available substrates[18,23] herein, we report the first one-pot synthesis of benzimidazoles and benzothiazoles from aromatic terminal olefins.

Based on the previous literature reports on alkene activation for its further functionalisation,[24] we initiated our study with styrene **1a** and *o*-Phenylenediamine **2a** in the presence of $Pd(OAc)_2$ (5 mol%), in AcOH under oxygen atmosphere. To our delight the desired product **3a** was isolated with 42% yield in 12 h at 70 °C (Table 1, entry 2). Increase of temperature to 80 °C furnished **3a** in 58% and to 90 °C offered **3a** in 71% yield (entries 3 & 4). Additional increase in temperature did not improve the yield of the products (entry 5). Moreover, increase in catalyst loading did not enhance the yield of **3a** (entry 6). Next, we have screened various solvents such as DMSO, DMF, 1,4-dioxane, acetonitrile and mixture of solvent like DMSO:AcOH (1:3) for further improvement in yield. The results show that among the tested solvents, AcOH is effective for this reaction (entries 7-11). Conducting the reaction under open air and inert conditions decreased the yield of **3a** to 26% and 10%. In the absence of catalyst, **3a** formation was not observed (Table 1, entries 12-14). With the optimized conditions (entry 4 in Table 1) in hand, we next evaluated the generality of the method (Table 2).

Table 1. Optimization of the Reaction Conditions[a]

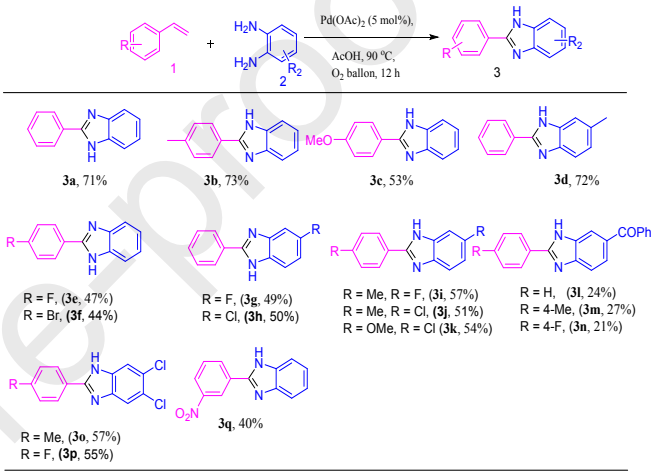


Sr. No.	Catalyst (mol %)	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	$Pd(OAc)_2$ (5)	AcOH	rt	12	n.r
2	$Pd(OAc)_2$ (5)	AcOH	70	12	42
3	$Pd(OAc)_2$ (5)	AcOH	80	12	58
4	**$Pd(OAc)_2$ (5)**	**AcOH**	**90**	**12**	**71**
5	$Pd(OAc)_2$ (5)	AcOH	100	12	68
6	$Pd(OAc)_2$ (10)	AcOH	100	12	70
7	$Pd(OAc)_2$ (5)	DMSO	90	12	16
8	$Pd(OAc)_2$ (5)	DMF	90	12	trace
9	$Pd(OAc)_2$ (5)	Dioxane	90	12	n.r.
10	$Pd(OAc)_2$ (5)	CH_3CN	90	12	n.r.
11	$Pd(OAc)_2$ (5)	DMSO: AcOH (1:3)	90	12	66
12[c]	$Pd(OAc)_2$ (5)	AcOH	90	12	26
13[d]	$Pd(OAc)_2$ (5)	AcOH	90	12	10
14	--	AcOH	90	12	n.r.

[a] Reaction conditions : 0.25 mmol of **1a** and 0.33 mmol of **2a** in the presence of catalyst and in solvent (1mL) at 90 °C for 12 h in oxygen atmosphere. [b] Isolated yields, [c] open air condition, [d] inert condition.

We first examined the reactions of 2-amino anilines with different styrenes under optimized reaction conditions. Simple, methyl and methoxy styrenes produced corresponding benzimidazoles **3a** (71%), **3b** (73%) & **3c** (53%) in good yields. 4-fluorostyrene **(3e)**, 4-bromo **(3f)** and 3-nitrostyrene **(3q)** produced corresponding benzimidazoles in 47%, 44% & 40% yields under optimized conditions[25]. Next, we have examined the differently substituted *o*-phenylenediamines reactivity in this reaction. Methyl substituted benzene-1,2-diamine reacted well with **1a** to produce **3d** in 72% yield. Furthermore, halogen substrates like 4-flouro, 4-chloro, 4,5 dichloro *o*-phenylenediamines furnished the products **3g** (49%), **3h** (50%) **3o** (57%) and **3p** (55%) in moderate yields. Furthermore, benzoyl substituted *o*-phenylenediamine reacted with simple, 4-methyl and 4-fluoro substituted styrenes gave desired product in low yield (Table 2, 3l-3n, 21-27%). Moreover styrenes with electron donating groups such as 4-methyl and 4-methoxy have produced corresponding bemzimidazoles **(3i-3k)** with 4-fluro and 4-chloro substituted *o*-Phenylenediamines in good yields (51-57%).

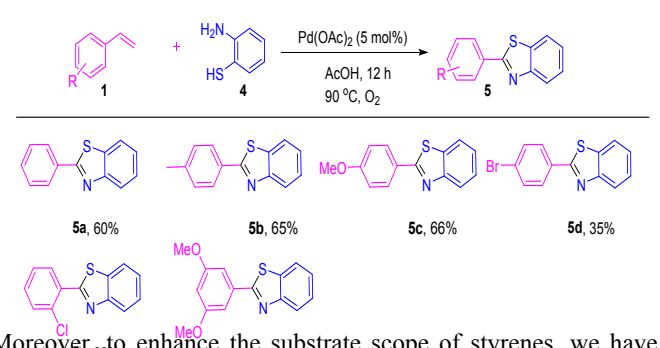
Table 2. Scope of Styrenes and *o*-Phenylenediamine[a]



[a] Reaction conditions: 0.25 mmol of **1a** and 0.33 mmol of **2a** in the presence of catalyst and in solvent (1 mL) at 90 °C for 12 h in oxygen atmosphere.

To further expand the scope of the reaction, we tested the reactivity of 2-amino thiophenol **(4)** with styrene **(1a)** under standard reaction conditions (table 3). To our delight 2-phenylbenzo[d]thiazole **(5a)** was obtained with 60% yield. Furthermore, both electron-rich and electron-poor styrenes (Table 3) reacted well with **4** and afforded the products **5b**, **5c**, **5d**, **5e** & **5f** in good yields (30-66%). To further expand the scope of the above reaction, we have tested the reactivity of 2-aminophenol with styrene **1a** under standard conditions. Unfortunately, no desired product was obtained (no reaction between 2-aminophenol and styrene), starting materials were isolated.

Table 3. Scope of Styrenes and 2-Aminothiophenol

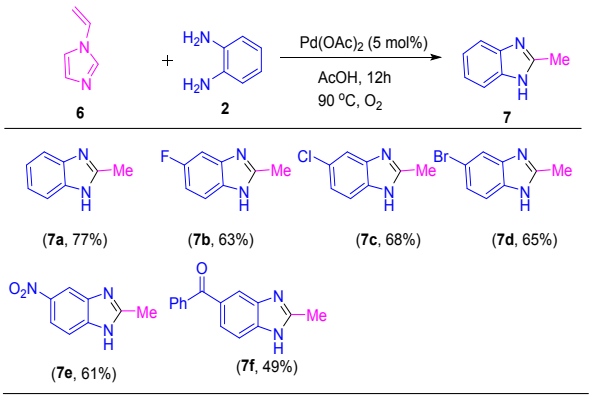


[a] Reaction conditions: 0.25 mmol of **1a** and 0.33 mmol of **2a** in the presence of catalyst and in solvent (2 mL) at 90 °C for 12 h in oxygen atmosphere.

Moreover, to enhance the substrate scope of styrenes, we have reacted 1-vinyl-1H- imidazole **(6)** in place of styrenes with *o*-phenylenediamine **(2)** under standard conditions. Unfortunately, expected product (2-(1H-imidazol-1-yl)-1H-benzo[d]imidazole)

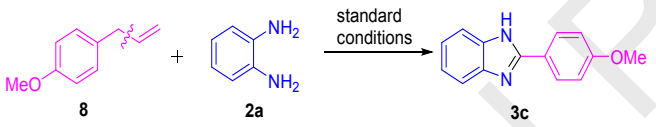
was benzo[d]imidazole 7 via selective cleavage of the C–N bond of vinyl-1H- imidazole (Table 4). *o*-Phenylenediamines with different substituents successfully produced corresponding 2-methyl-1H-benzo[d]imidazoles. Halogen substitutions like 4-flouro, 4-chloro & 4-bromo *o*-phenylenediamines furnished products **7b** (63%), **7c** (68%) and **7d** (65%) in good yields. Also, nitro & benzoyl substituted *o*-phenylenediamines reacted well with **6** and produced **7e** (61%), **7f** (49%) with moderate yields.

Table 4. Scope of Vinylimidazole and *o*-Phenylenediamine



[a] Reaction conditions: 0.25 mmol of **1a** and 0.33 mmol of **2a** in the presence of catalyst and in solvent (1 mL) at 90 °C for 12 h in oxygen atmosphere.

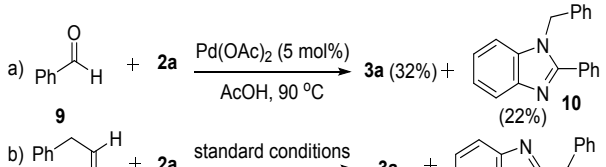
Encouraged by these results, we became curious to test the fate of allylbenzene, as our next substrate with *o*-phenylenediamine. Interestingly, 2-aryl benzimidazole **3c** was isolated with 61% yield via C(sp3)-C(sp2) bond cleavage(Scheme 2).



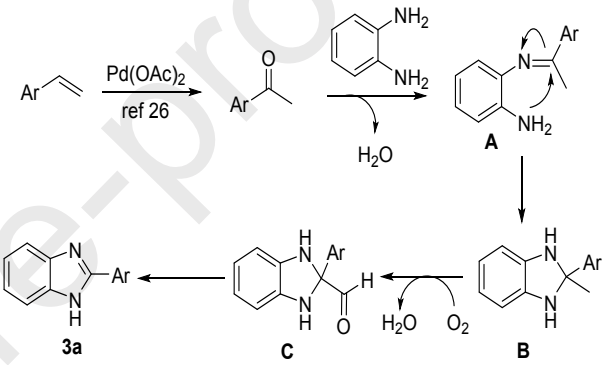
Scheme 2. Reactivity of Allylbenzene with *o*-Phenylenediamine

To gain a deep insight into the reaction mechanism, control experiments were conducted (Scheme 3). When benzaldehyde **(9)** was reacted with *o*-phenylenediamine under standard condition, **3a** was observed with 32% yield and 2-aryl-1-arylmethyl-1H-1,3-benzimidazole **(10)** formed as by-product with 22% yield. However, we did not observe product **10** during reaction of styrene **(1a)** with *o*-phenylenediamine under standard condition, which ruled out the formation of benzaldehyde **(9)** as intermediate. Under standard conditions Phenyl acetaldehyde **(11)** afforded mixture of **3a** & **12**. Acetophenone **(13)** and 1-phenylethane-1,2-diol **(14)** were independently employed to standard conditions. Acetophenone **(13)** smoothly produced the corresponding product **3a** in 72% yield, whereas compound **14** was found to be unreactive (Scheme 3d). Moreover, phenylglyoxal **(15)** produced **3a** in 8% yield.

Based on the control experiments and a previous report[26], we propose a possible mechanism as shown in Scheme 4. Initially, styrene **(1a)** undergoes oxidation in presence of catalytic amount of palladium to give acetophenone[26]. Subsequently, *o*-phenylenediamine reacts with acetophenone to deliver **A**. Intermediate **A** then cyclizes to give dihydro benzimidazole **B**. Oxidation of intermediate **B** gives oxo derivative **C**. Subsequent aromatization process will leads to the final product **3a** with the loss of formaldehyde.



Scheme 3. Control Experiments



Scheme 4. Proposed Mechanism

In summary, we have developed a palladium catalysed facile one pot synthetic method for the synthesis of benzimidazoles and benzothiazoles from readily available styrenes/vinyl imidazoles and 2-amino/2-mercaptosubstituted anilines. This method involves sequential C=C/C–N bond cleavage followed by C–N/C–S bond formation. Molecular oxygen used as sole oxidant. Easy handling and smooth reaction conditions are the salient features of this method.

Acknowledgments

This work was supported by DBT (Grant GAP0556), New Delhi. We are thankful to the NMR and Mass divisions of CSIR-IICT for providing the analytical facilities. O.R, P.R thanks CSIR and A. S. thank UGC for the Ph.D. fellowships. N.S. thanks DBT for project fellowship. We thank Director CSIR-IICT for the support (IICT/Pubs./2019/369).

References and notes

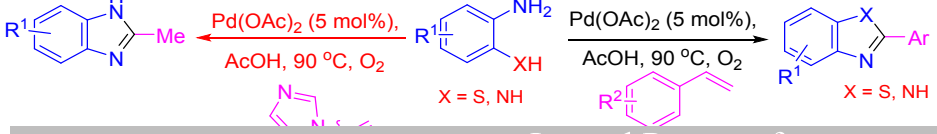
1. (a) Zablotskaya, A.; Segal, I.; Geronikaki, A.; Eremkina, T.; Belyakov, S.; Petrova, M.; Shestakova, I.; Zvejniecea, L.; Nikolajeva, V. *Eur. J. Med. Chem*. **2013**, *70*, 846; (b) Cai, J.; Sun, M.; Wu, X.; Chen, J.; Wang, P.; Zong, X.; Ji, M. *Eur. J. Med. Chem*. **2013**, *63*, 702; (c) Nemeth-Konda, L.; Fuleky, G.; Morovjan, G.; Csokan, P.;

Dedková, T.; Skalová, L.; Vokřál, I.; Lecová, L.; Vaněk, T.; Szotáková, B.; *Environ. Sci. Pollut. Res*. **2016**, *23*, 13015; (e) Zou, R.; Ayres, K. R.; Drach, J. C.; Townsend, L. B. *J. Med. Chem*. **1996**, *39*, 3477. (f) Huang, S.-T.; Hsei, I.-J.; Chen, C.; *Bioorg. Med. Chem*. **2006**, *14*, 6106; (g) Osmaniye, D.; Levent, S.; Karaduman, A. B.; Ilgın, S.; Ozkay, Y.; Kaplancikli, Z. A. *Molecules*, **2018**, *23*, 1054. (h) Bhrigu, B.; Siddiqui, N.; Pathak D.; Alam, M. S.; Ali, R.; Azad, B. *Acta Pol Pharm*. **2012**, *69*, 53.

2. (a) Yadav, G.; Ganguly, S. *Eur. J. Med. Chem*. **2015**, *97*, 419; (b) Bansal, Y.; Silakari, O.; *Bioorg. Med. Chem*. **2012**, *20*, 6208; (c) Min, J.; Won, J.; Kang, Y. S.; Nagase, S. J. *Photochem. Photobiol. A: Chem*. **2011**, *219*, 148; (d) Asensio, J. A.; Gomez-Romero, P. *Fuel Cells*. **2005**, *5*, 336; (e) White, A. W.; Almassy, R.; Calvert, A. H.; Curtin, N. J.; Griffin, R. J.; Hostomsky, Z.; Golding, B. T. *J. Med. Chem*. **2000**, *43*, 4084; (f) Battershill, A. J.; Scott, L. J. *Drugs*. **2006**, *66*, 51; (g) Gill, R. K.; Rawaland Bariwal, R. K. J. *Arch. Pharm. Chem. Life Sci*. **2015**, *348*, 155; (h) Hartley, D.; Kidd, H.; *The Agrochemical Handbook; Royal Society of Chemistry: Nottingham*, **1983**; (i) Baker, D. R.; Basarab, G. S.; Fenyes, J. G.; *Synthesis and Chemistry of Agrochemicals IV; American Chemical Society: Washington D. C.* **1995**. (j) Zhou, Y.; Zhou, Z.; Li, Y.; Yang, W. *Catal Commun.* **2015**, *64*, 96.
3. (a) Gadekar, L. S.; Arbad, B. R.; Lande, M. K. *Chin.Chem. Lett*. **2010**, *21*, 1053; (b) Zhang, C.; Zhang, L.; Jiao, N. *Green Chem*. **2012**, *14*, 3273; (c) Mukhopadhyay, C.; Tapaswi, P. K. *Catal. Commun*. **2008**, *9*, 2392; (d) Tumelty, D.; Cao, K.; Holmes, C. P. *Org. Lett*. **2001**, *3*, 83; (e) Wu, Z.; Rea, P.; Wickham, G. *Tetrahedron Lett*. **2000**, *41*, 9871; f) Bahrami, K.; Khodaei, M. M.; Nejati, A. *Green Chem*. **2010**, *12*, 1237.
4. (a) Dubois, N.; Glynn, D.; McInally, T.; Rhodes, B.; Woodward, S.; Irvine, D. J.; Dodds, C. *Tetrahedron*. **2013**, *69*, 9890; (b) Pinder, J. L.; Davis, R. E.; Charrier, J.-D. *Tetrahedron Lett*. **2014**, *55*, 4853; (c) Tandon, V. K.; Kumar, M. *Tetrahedron Lett*. **2004**, *45*, 4185; (d) Bommegowda, Y. K.; Lingaraju, G. S.; Thamas, S.; Kumar, K. S. V.; Kumara, C. S. P.; Rangappa, K. S.; Sadashiva, M. P. *Tetrahedron Lett*. **2013**, *54*, 2693. (e) Nguyen, T. B.; Retailleau, P. *Org. Lett.* **2017**, *19*, 3887.
5. (a) Shiraishi, Y.; Sugano, Y.; Tanaka, S.; Hirai, T. *Angew. Chem. Int. Ed*. **2010**, *49*, 1656; (b) Xu, C.; Xiao, Z. Q.; Li, H. M.; Han, X.; Wang, Z. Q.; Fu, W. J.; Ji, B. M.; Hao, X. Q.; Song, M. P. *Euro. J. Org. Chem*. **2015**, *2015*, 7427; (c) Sun, Z.; Bottari, G.; Barta, K. *Green Chem*. **2015**, *17*, 5172; (d) Blacker, A. J.; Farah, M. M.; Hall, M. I.; Marsden, S. P.; Saidi, O.; Williams, J. M. *Org. Lett*. **2009**, *11*, 2039; (e) Shi, X.; Guo, J.; Liu, J.; Ye, M.; Xu, Q. *Chem. Euro. J*. **2015**, *21*, 9988; (f) Xu, Z.; Wang, D. -S.; Yu, X.; Yang, Y.; Wang, D. *Adv. Synth. Catal*. **2017**, *359*, 3332; (g) Wang, D.; Albero, J.; García, H.; Li, Z. *J. Catal*. **2017**, *349*, 156; (h) Xu, Z.; Yu, X.; Sang, X. and Wang, D. *Green Chem*. **2018**, *20*, 2571; (i) Qiu, Y.; Zhang, Y.; Jin, L.; Pan, L.; Du, G.; Yeb, D.; Wang, D. *Org. Chem. Front*. **2019**, *6*, 3420.
6. (a) Nguyen, T. B.; Ermolenko, L.; Al-Mourabit, A. *Green Chem.* **2013**, *15*, 2713; (b) Nguyen, T. B.; Ermolenko, L.; Dean, W. A.; Al-Mourabit, A. *Org. Lett*. **2012**, *14*, 5948; (c) Yu, J.; Xia, Y.; Lu, M. *Synth Commun*. **2014**, *44*, 3019; (d) Naresh, G.; Kant, R.; Narender, T. *J. Org. Chem*. **2014**, *79*, 3821; (e) Dong, C. –P.; Higashiura, Y.; Marui, K.; Kumazawa, S.; Nomoto, A.; Ueshima, M.; Ogawa, A. *ACS Omega*, **2016**, *1*, 799; (f) Liu, J.; Wang, C.; Ma, X.; Shi, X.; Wang, X.; Li, H.; Xu, Q. *Catal Lett*. **2016**, *146*, 2139; (g) Reddy, P. L.; Arundhathi, R.; Tripathi, M.; Chauhan, P.; Yan, N.; Rawat, Diwan S. *ChemistrySelect*, **2017**, *2*, 3889; (h) Su, C.; Tandiana, R.; Balapanuru, J.; Tang, W.; Pareek, K.; Nai, C. T.; Hayashi,T.; Loh, K. P. *J. Am. Chem. Soc*. **2015**, *137*, 685.
7. (a) Nguyen, T. B.; Ermolenko, L.; Al-Mourabit, A. *J. Am. Chem. Soc*. **2012**, *135*, 118; (b) Xu, Z.; Yu, X.; Sang, X. and Wang, D. *Green Chem*. **2018**, *20*, 2571; (c) Qiu, Y.; Zhang, Y.; Jin, L.; Pan, L.; Du, G.; Yeb, D.; Wang, D. *Org. Chem. Front.* **2019**, *6*, 3420; (d) Nguyen, T. B.; Ermolenko, L.; Al-Mourabit, A. *Org. Lett.* **2013**, *15*, 4218; (e) Nguyen, T. B.; Bescont, J. L.; Ermolenko, L.; Al-Mourabit, A. *Org. Lett.* **2013**, *15*, 6218; (f) Nguyen, T. B.;Bescont, J. L.; Ermolenko, L.; Corbin, M.; Al-Mourabit, A. *Org. Chem. Front.***2014**, *1*, 1157; (g) Dr. Nguyen, T. B.; Dr. Ermolenko, L.; Dr. Retailleau, P.; Dr. Al-Mourabit, A. *Angew.* ; Al-Mourabit, A. *Synthesis* **2015**, *47*, 1741; (i) Nguyen, T. B.; Pasturaud, K.; Ermolenko, L.; Al-Mourabit, A. *Org. Lett.* **2015**, *17*, 2562; (j) Nguyen, L. A.; Ngo, Q. A.; Retailleau, P.; Nguyen, T. B. *Green Chem*. **2017**, *19*, 4289.
8. Daw, P.; Ben-David, Y.; Milstein, D. *ACS Catal*. **2017**, *7*, 7456.
9. Hikawa, H.; Ichinose, R.; Kikkawa, S.; Azumaya, I. *Asian J. Org. Chem*. **2018**, *7*, 416.
10. Lai, Y. -L.; Ye, J. -S.; Huang, J. -M. *Chem. Eur. J*. **2016**, *22*, 5425.
11. Das, K.; Mondal, A.; Srimani, D. *J. Org. Chem*. **2018**, *83*, 9553.
12. Sharma, R.; Abdullaha, M.; Bharate, S. B. *Asian J. Org. Chem*. **2017**, *6*, 1370.
13. Zhang, R.; Qin, Y.; Zhang, L.; Luo S. *Org. Lett*. **2017**, *19*, 5629.
14. Naresh, G.; Kant, R.; Narender, T. *J. Org. Chem*. **2014**, *79*, 3821.
15. (a) Bougrin, K.; Soufiaoui, M. *Tetrahedron Lett*. **1995**, *36*, 3683. (b) Li, Z.; Dong, J.; Chen, X.; Li, Q.; Zhou, Y.; Yin, S. -F. *J. Org. Chem*. **2015**, *80*, 9392.
16. (a) Kamila, S.; Koh, B.; Biehl, E. R. *J. Heterocycl. chem*. **2006**, *43*, 1609; (b) Kano, S.; Yuasa, Y.; Ono, T.; Shibuya, S. *Heterocycles*. **1979**, 10.
17. (a) Mayo, M. S.; Yu, X.; Zhou, X.; Feng, X.; Yamamoto, Y.; Bao, M. *Org. Lett*. **2014**, *16*, 764; (b) Wang, Z. X.; Qin, H. L. *J. Heterocycl.chem*. **2005**, *42*, 1001.
18. Ravi, O.; Shaikh, A.; Upare, A.; Singarapu, K. K.; Bathula, S. R. *J. Org. Chem*. **2017**, *82*, 4422.
19. Corey, E.J.; Cheng, X. -M. *The Logic of Chemical Synthesis, John Wiley, New York*, **1989.**
20. Evans. P. A.; Tsuji, J. *Modern Rhodium-Catalyzed Organic Reactions Wiley-VCH*. **2005**, 93.
21. Takacs, J. M.; Jiang, X. -T. *Curr. Org. Chem*. **2003**, *7*, 369.
22. (a) Hoveyda, A.H.; Zhugralin, A. R. *Nature*. **2017,** *450*, 243; (b) Connon, S.J.; Blechert, S. *Angew. Chem. Int. Ed*. **2003**, *42*, 1900.
23. (a) Ramaraju, A.; Chouhan, N. K.; Ravi, O.; Sridhar, B.; Bathula, S. R. *Eur. J. Org. Chem*. **2018**, 2963; (b) Ravi, O.; Ramaraju, A.; Sridhar, B.; Bathula, S. R. *Adv. Synth. Catal*. **2018**, *360*, 3009; (c) Upare, A.; Sathyanarayana, P.; Kore, R.; Sharma, K.; Bathula, S. R. *Tetrahedron Lett*. **2018**, *59*, 2430; (d) Sathyanarayana, P.; Upare, A.; Ravi, O.; Muktapuram P. R.; Bathula, S. R. *RSC Adv*. **2016**, *6*, 22749; (e) Sathyanarayana, P.; Ravi, O.; Muktapuram, P. R.; Bathula, S. R. *Org. Biomol. Chem*. **2015**, 13, 9681; (f) Viswanadham K. D. R.; Muktapuram, P. R.; Sathyanarayana, P.; Ravi, O.; Kant, R.; Bathula, S. R. *Chem. Commun*. **2014**, *50*, 13517; (g) Bathula, S. R.; Muktapuram, P. R.; Viswanadham K. D. R.; Sathyanarayana, P.; Reddy, M. S. *Eur. J. Org. Chem*. **2013**, *2013*, 4552.
24. (a) Cornell, C. N.; Sigman, M. S. *Inorg. Chem*. **2007**, *46*, 1903; (b) Wu, W.; Jiang, H. *Acc Chem Res*. **2012**, *45*, 1736; (c) Wang, A.; Jiang, H. *J. Org. Chem*. **2010**, *75*, 2321; (d) (m) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *ACS Catal*. **2011**, *1*, 836; (e) Xing, D.; Guan, B.; Cai, G.; Fang, Z.; Yang, L.; Shi, Z. *Org. Lett*. **2006**, *8*, 693; (f) Wang, T., Jiao, N. *J. Am. Chem. Soc. 2013*, *135*, 11692.
25. In case of styrenes with deactivating substituents such as fluoro, bromo and nitro, reaction requires 0.75 mmol of corresponding styrene for completion.
26. Mitsudome, T.; Umetani, T.; Nosaka, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem. Int. Ed*. **2006**, *45*, 481.

Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.



and benzthiazoles has been developed.

- Easy handling & smooth reaction conditions are the salient features of this method.
- Molecular oxygen used as sole oxidant.
- Reaction involves Palladium Catalysed Oxidative C=C and C–N bond Cleavage.