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Transition-Metal-Free Synthesis of 1,2-diphenyl-1*H*-benzo[*d*] Imidazole Derivatives from *N*-phenylbenzimidamides and cyclohexanones

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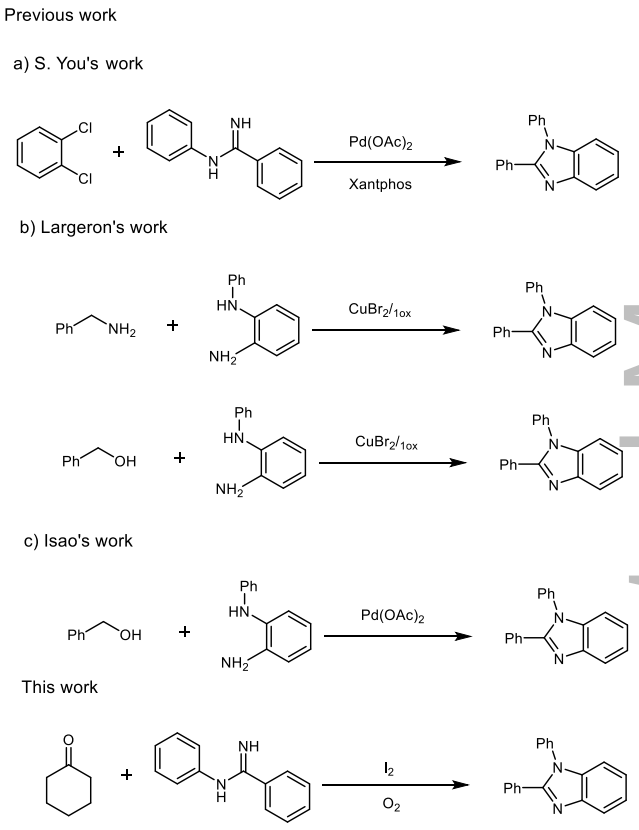
Abstract. A transition-metal-free strategy for the formation of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles from *N*-phenylbenzimidamides and cyclohexanones is introduced. This is the first report on the direct synthesis of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles from cyclohexanones and *N*-phenylbenzimidamides via iodine- promoted oxidative cyclization. Non-aromatic cyclohexanones were smoothly dehydrogenated, and acted as an aryl source using oxygen as a green oxidant. The catalytic use of iodine makes this method quite simple, more economical and convenient. Under optimized conditions, various substituted 1,2-diphenyl-1*H*-benzo[*d*] imidazoles were smoothly reacted, and the desired substituted imidazoles were generated with moderate to excellent yields.

Keywords: Imidazoles; *N*-phenylbenzimidamides; Cyclohexanones; Oxidative cyclization; Iodine



Scheme 1. Different strategies transformations for 1,2-diphenyl-1*H*-benzo[*d*] imidazoles.

Benzimidazole is one of the oldest known nitrogen heterocycles and was first synthesized by Hoebrecker and later by Ladenberg and Wundt during 1872-1878.[1] In nature, *N*-ribosyl dimethylbenzimidazole serves as an axial ligand for cobalt ions in vitamin B_{12}.[2] Over years of active research, benzimidazole has evolved as an important heterocyclic system due to its presence in a wide range of bioactive compounds, such as antiparasitics, analgesics, antihypertensives, antivirals and anticancers.[3] For example, telmisartan and candesartan are used as antihypertensives, omeprazole is used as a proton pump inhibitor, and as-temizole, clemizole, and bilastine are used as anti-histaminic agents.[4] Therefore, intensive attention has been paid to the development of a method for preparing benzimidazoles. Traditional synthesis relies on the condensation of *o*-phenylenediamines with carboxylic acids or their derivatives under harsh dehydrating conditions by oxidative coupling with aldehydes.[5] Meanwhile, aerobic catalytic oxidative cross-coupling reactions employing either alcohols or amines as substrates have also been reported for the synthesis of benzazoles.[6] Considering these literature precedents, and drawbacks, such as the competitive formation of 2-substituted[7] and 1,2-disubstituted benzimidazoles,[8] and the need for expensive catalysts/ reagents/ starting materials, the development of facile and practical methods for the formation of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles is

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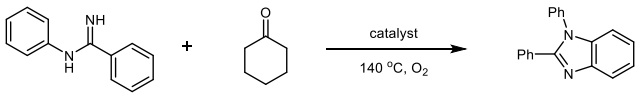
Table 1. Optimization of reaction conditions.[a]



1a 2a 3a

Entry	Catalyst	Solvent	Yield (%)[b]
1		1,1,2,2-Tetrachloroethane	0
2	KI (0.1)	1,1,2,2-Tetrachloroethane	15
3	NH_4I (0.1)	1,1,2,2-Tetrachloroethane	27
4	I_2 (0.1)	1,1,2,2-Tetrachloroethane	39
5	I_2 (0.2)	1,1,2,2-Tetrachloroethane	71
6	**I_2 (0.5)**	**1,1,2,2-Tetrachloroethane**	**85**
7	I_2 (1.0)	1,1,2,2-Tetrachloroethane	77
8	I_2 (0.5)	DMSO	0
9	I_2 (0.5)	Chorobenzene	13
10	I_2 (0.5)	NMP	15
11	I_2 (0.5)	o-DCB	73
12[c]	I_2 (0.5)	1,1,2,2-Tetrachloroethane	71
13[d]	I_2 (0.5)	1,1,2,2-Tetrachloroethane	34
14[e]	I_2 (0.5)	1,1,2,2-Tetrachloroethane	69
15[f]	I_2 (0.5)	1,1,2,2-Tetrachloroethane	84
16[g]	I_2 (0.5)	1,1,2,2-Tetrachloroethane	23

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), solvent (1 mL), 140 ℃ under oxygen for 24 h, [b] Isolated yield. [c] 0.15mmol **2a** was used. [d] At 120 ℃. [e] 12 h under oxygen. [f] 36 h under oxygen. [g] 12 h under air. DMSO: dimethylsulfoxide, NMP: N-methylpyrrolidone, o-DCB: 1,2-dichlorobenzene.

still highly desirable. Although there are other methods available for the construction of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles, the utilization of cheap and non-aromatic coupling partners under transition-metal-free conditions is rare and challenging. Cyclohexanones are commercially available, stable and widely used as raw materials to prepare many important bulk chemicals.[9] In 2011, S. You et al. disclosed a palladium-catalysed cascade amination that allows regiospecific and modular synthesis of a library of structurally diverse 1,2-disubstituted (hetero)aryl fused imidazoles (Scheme 1a).[10] Significantly, the group of Largeron has developed a direct method for the synthesis of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles by aerobic oxidative C-H functionalization of primary aliphatic amines (Scheme 1b).[11] Very recently, Isao et al. reported a one-pot method for the selective construction of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles involving the dehydro-genation of benzyl alcohols by a π-benzylpalladium(II) system (Scheme 1c).[12] The construction of C–C,[13] C–N,[14] C–O,[15] C–S[16] bonds as well as heterocycles has been carried out under oxidative conditions in the Deng group. In these transformations, cyclohexanones were used as a versatile aryl source via a dehydrogenation tautomerization sequence. Inspired by reports about the use of cyclohexanone for the construction of heterocyclic compounds and our experiences in the formation of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles, herein, we describe a transition-metal-free method for the formation of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles using oxygen as a hydrogen acceptor. Initially, we attempted *N*-phenylbenzimidamide **(1a)** with cyclohexanone **(2a)** in the absence of metal catalyst under an oxygen atmosphere (Table 1). When the reaction mixture was heated at 140 °C in the absence of the iodide-containing catalyst, no desired **3a** was formed, as determined by the ^{1}HNMR method (entry 1). Fortunately, the desired product **(3a)** was obtained with only a 15% yield in the presence of KI (Table 1, entry 2). The yield increased to 27% when NH_4I was used as the additive (Table 1, entry 3). Following the investigation of several iodide-containing chemicals, iodine proved to be the most efficient (Table 1, entry 4). Then we tested different amounts of I_2, on increasing the amount of iodine to 0.2 ,0.5 and 1.0 equivalents, the reaction yields increased to 71%, 85% and 77% (Table 1, entries 5-7). Based on this excellent result, with 0.5 equiv found to be the optimal loading. In addition to 1,1,2,2-tetrachloroethane, a lower yield was obtained when the solvent was changed to chlorobenzene and NMP, and no desired product was detected when DMSO was used (Table 1, entries 8-10). Interestingly, o-DCB gave a similar yield with 1,1,2,2-tetrachloroethane (Table 1, entry 11). It was found that the catalyst and solvent critically affect the reaction efficiency. Notably, slightly lower yield (71%) of **3a** was obtained when 0.15 mmol of **2a** was used (Table 1, entry 12). When the temperature was decreased to 120 °C and the yield of the desired product **3a** showed a corresponding drop to 34% (Table 1, entry 13). In addition, reducing the time led to a decrease in the yield of **3a** (Table 1, entry 14). When the reaction time prolonged to 36 h, the yield of product showed almost no change (Table 1, entry 15). A much lower yield was obtained when the reaction was carried out in air (Table 1, entry 16). After several attempts, the suitable reaction conditions were identified as follows: **1a** (0.1 mmol), **2a** (0.2 mmol) and I_2 (50 mol%) in 1,1,2,2-tetrachloroethane (1 mL) at 140 °C for 24 h under oxygen.

With the optimized reaction conditions in hand, we investigated the substrate scope of the amidines derivatives **(1)** with **(2a)** as a coupling partner (Table 2). As shown in Table 2, both electron-rich and electron-withdrawing groups on the *N*-aryl ring (R^1) of amidines could be used smoothly to afford 1,2-diphenyl-1*H*-benzo[*d*] imidazoles in excellent yields (**3b-3m**). Amidine substituted with 2-isopropyl at R^1 performed well in this reaction under the standard conditions, and the desired product was isolated with a yield of 68% (**3k**). Gratifyingly, the amidine substituent with an electron-withdrawing group 4-trifluoromethyl and 4-cyano were tolerated to product **3l** and **3m** in 69% and 64% yield. To our disappointment, we failed to find the target product when the benzene was changed to a tine ring (**3n**) group. While1-naphthyl and 2-naphthyl amidines gave products **3o** (81% yield) and **3p** (83% yield) with remarkable yields. The desired products

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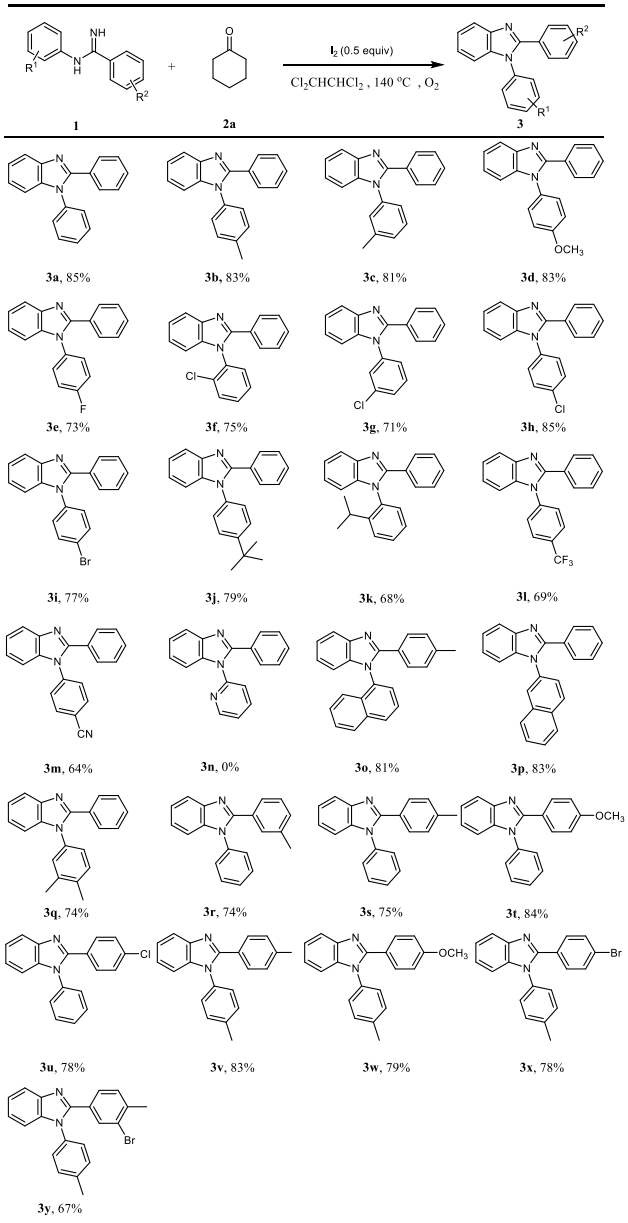
Table 2. Scope of the reaction with amidines.[a]

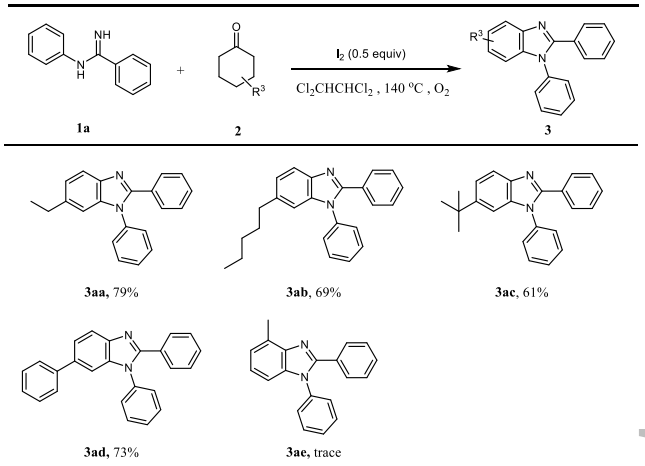


[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), I_2 (50 mol%) and solvent (1 mL), 140 °C under oxygen for 24 h. [b] Isolated yield.

(**3r-3u**) were obtained in moderate to excellent yields (74- 84%) when another aryl ring (R^2) was added. Finally, it was found that disubstituted or trisubstitutedamidines were a good substrate for this kind of transformation to obtain the desired products (**3q, 3v-3y**).

Next, the substrate scope for various cyclohexanones were also investigated using **(1a)** as a coupling partner (Table 3). Various 4-alkyl cyclohexanones smoothly reacted with *N*-phenylbenzimidamides **(1a)** to give the corresponding products in good yields (**3aa-3ab**). As a challenging substrate, cyclohexanones with a tert-butyl substituent were successfully applied to the reaction **(3ac)**. The desired product (**3ad**) was obtained with a yield of 73% when 4-phenylcy-clohexanone was

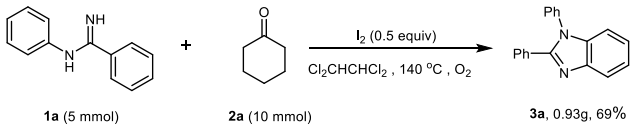
Table 3. Scope of the reaction with cyclohexanones.[a]



[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), I_2 (50 mol%) and solvent (1 mL), 140 °C under oxygen for 24 h. [b] Isolated yield.

treated with *N*-phenylbenzimidamides (**1a**) under optimized conditions. When a methyl group located at the ortho position of cyclohexanone was employed for this reaction, only a trace amount of the desired product **(3ae)** was detected, we suspected that the 2-methylcyclohexanone had a strong steric effect that was not conducive to the reaction. Within the above scope for the cyclohexanones, this result indicates that the present method provides an alternative pathway for the synthesis of 1,2-diphenyl-1*H*-benzo[*d*] imidazoles from cyclohexanones.

Gram-scale applicability of the present methodology was also demonstrated (Scheme 2). A detailed complete synthesis of **3a** at the 5 mmol scale was performed. *N*-phenylbenzimidamide **1a** (5 mmol, 0.98 g) reacted smoothly with cyclohexanone **2a** (10 mmol, 0.98 g) under the optimized reaction conditions, giving the corresponding 1,2-diphenyl-1*H*-benzo[*d*] imidazoles **3a** with a yield of 69% (0.93 g).



Scheme 2. Practical applicability of the present protocol.

To further explore the possible reaction mechanism, a set of control experiments was performed. The reaction of acetophenone with *N*-phenylbenzimidamide was performed under the standard conditions in the presence of the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Scheme 2a). The desired product **3a** was obtained with 81% yield, the yield was just slightly decreased, which might exclude the possibility of a radical mechanism. When 2-chlorocyclohexanone was employed as the substrate, and the product **3a** was obtained in 74% yield (Scheme 3b), which

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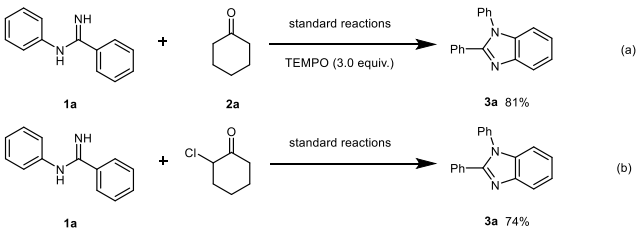
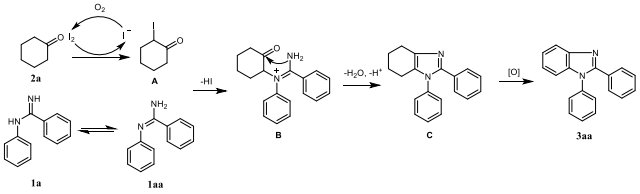


Scheme 3. Reactions carried out as control experiments.

means that the cyclohexanones may be iodinated first.

Based on the results obeyed from control experiments, a possible reaction mechanism is proposed in Scheme 3. Cyclohexanone **2a** is iodinated with iodine to give 2-iodocyclohexanone A by leaving of I^- along with a catalytic cycle of I^- being oxidized to I_2 by O_2.[17] At the same time, amidines **1a** are subjected to resonance transformation to form intermediates **1aa**. The nucleophilic substitution of **1aa** with **A** produces an intermediate **B** under the standard conditions.[18] Then, the amino nitrogen atoms attack the carbonyl carbon atoms and then remove the H_2O inside the molecule **B** to form the intermediates 1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-benzo[*d*]imidazole **C**.[19] Finally, intermediate **C** produces the desired product **3aa** through dehydrogenation–tautomerization.[20]



Scheme 4. Proposed mechanism.

In conclusion, we have developed a simple and direct protocol to synthesize 1,2-diphenyl-1Hbenzo[d] imidazoles from amidines and cyclohexanones under metal-free conditions. Iodine can be used to smoothly mediate such a transformation without the need for a transition-metal catalyst. 1,1,2,2-Tetrachloroethane as solvent also plays an important role in affording high yield using this protocol. This method provides an efficient route for the synthesis of substituted 1,2-diphenyl-1*H*-benzo[*d*] imidazoles using non-aromatic cyclohexanones as the aryl source in the presence of I_2, which used as a green catalyst. Currently, the application of this protocol in the synthesis of other products is under investigation in our laboratory.

Experimental Section

A mixture of **1a** *N*-phenylbenzimidamide (0.1 mmol), cyclohexanone **2a** (0.2 mmol), I_2 (50 mol%), 1,1,2,2-tetrachloroethane (1 mL) was placed into a test tube equipped with a magnetic stirring bar. The resulting mixture was stirred at 140 °C under O_2 (balloon) for 24 h. Solvent was removed, and the residue was separated by column chromatography to give a pure sample by using mixed petroleum ether/ethyl acetate 8:1 (v/v) as an eluent to afford the desired product **3a**. The remaining substituted imidazoles were prepared in a similar manner.

References

[1] G. Yadav, S. Ganguly, *Eur. J. Med. Chem.* **2015**, *97*, 419-443.

[2] H. A. Barker, R. D. Smyth, H. Weissbach, J. I. Toohey, J. N. Ladd, B. E. Volcani, *J. Biol. Chem*. **1960**, *235*, 480–488.

[3] a) Q. A. McKELLAR, E. W. SCOTT, *J. vet. Pharmacol. Therap.* **1990**, *13*, 223-247; b) J. F. Rossignol, H. Maisonneuve, *Ann. Trop. Med. Parasitol.* **1984**, *78*, 135-144; c) A. A. Spasov, I. N. Yozhitsa, L. I. Bugaeva, V. A. Anisimova, *Pharm. Chem. J.* **1999**, *33*, 232-243; d) M. Boiani, M. González, *Mini-Rev. Med. Chem.* **2005**, *5*, 409-424; e) B. Narasimhan, D. Sharma, P. Kumar, *Med. Chem. Res.* **2012**, *21*, 269-283.

[4] a) B. Narasimhan, D. Sharma, P. Kumar, *Med. Chem. Res.* **2012**, *21*, 269-283; b) G. Yadav, S. Ganguly, *Eur. J. Med. Chem.* **2015**, *97*, 419-443; c) R. S. Keri, A. Hiremathad, S. Budagumpi, B. M. Nagaraja, *Chem. Biol. Drug Des.* **2015**, *86*, 19-65.

[5] a) I. Nagao, T. Ishizaka, H. Kawanami, *Green Chem.* **2016**, *18*, 3494-3498; b) H. Hikawa, M. Imani, H Suzuki, Y. Yokoyama, I. Azumaya, *RSC Adv.* **2014**, *4*, 3768-3773; c) Y. K. Bommegowda, G. S. Lingaraju, S Thamas, K. S. Vinay Kumar, C. S. Pradeepa Kumara, K. S. Rangappa, M. P. Sadashiva, *Tetrahedron Lett.* **2013**, *54*, 2693-2695.

[6] a) T. Xiao, S. Xiong, Y. Xie, X. Dong, L. Zhou, *RSC Adv.* **2013**, *3*, 15592-1559; b) K. Tateyama, K. Wada, H. Miura, S. Hosokawa, R. Abe, M. Inoue, *Catal. Sci. Technol.* **2016**, *6*, 1677-1684; c) R. Ramachandran, G. Prakash, S. Selvamurugan, P. Viswanathamurthi, J. G. Malecki, V. Ramkumar, *Dalton Trans.* **2014**, *43*, 7889-7902; d) C. Su, R. Tandiana, J. Balapanuru, W. Tang, K. Pareek, C. T. Nai, T. Hayashi, K. P. Loh, *J. Am. Chem. Soc.* **2015**, *137*, 685-690; e) K. Gopalaiah, S. N. Chandrudu, *RSC Adv.* **2015**, *5*, 5015-5023; f) X. Shi, J. Guo, J. Liu, M. Ye, Q. Xu, *Chem. Eur. J.* **2015**, *21*, 9988-9993.

[7] a) Y. Qu, L. Pan, Z. Wu, X. Zhou, *Tetrahedron* **2013**, *69*, 1717-1719; b) S. Samanta, S. Das, P. Biswas, *J. Org. Chem.* **2013**, *78*, 11184-11193; c) G. Bai, X. Lan, X. Liu, C. Liu, L. Shi, Q. Chen, G. Chen, *Green Chem.* **2014**, *16*, 3160-3168; d) H. Sharma, N. Singh, D. O. Jang, *Green Chem.* **2014**, *16*, 4922-4930; e) M. Bakthadoss, R. Selvakumar, J. Srinivasan, *Tetrahedron Lett.* **2014**, *55*, 5808-5812; f) Y. Nagasawa, Y. Matsusaki, T. Hotta, T. Nobuta, N. Tada, T. Miura, A. Itoh, *Tetrahedron Lett.* **2014**, *55*, 6543-6546; g) P. Ghosh, R. Subba, *Tetrahedron Lett.* **2015**, *56*, 2691-2694; h) Y.-S. Lee, Y.-H. Cho, S. Lee, J.-K. Bin, J. Yang, G. Chae, C.-H. Cheon, *Tetrahedron* **2015**, *71*,

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532-538; i) Y.-S. Lee, C.-H. Cheon, *Adv. Synth. Catal.* **2015**, *357*, 2951-2956; j) A. R. Wade, H. R. Pawar, M. V. Biware, R. C. Chikate, *Green Chem.* **2015**, *17*, 3879-3888; k) R. Katla, R. Chowrasia, P. S. Manjari, N. L. C. Domingues, *RSC Adv.* **2015**, *5*, 41716-41720; l) C. Cimarelli, M. Di Nicola, S. Diomedi, R. Giovannini, D. Hamprecht, R. Properzi, F. Sorana, E. Marcantoni, *Org. Biomol. Chem.* **2015**, *13*, 11687-11695; m) N. Pramanik, S. Sarkar, D. Roy, S. Debnath, S. Ghosh, S. Khamarui, D. K. Maiti, *RSC Adv.* **2015**, *5*, 101959-101964.

[8] a) T. Bhaskar Kumar, C. Sumanth, A. V. Dhanunjaya Rao, D. Kalita, M. Srinivasa Rao, K. B. Chandra Sekhar, K. Shiva Kumar, M. Pal, *RSC Adv.* **2012**, *2*, 11510-11519; b) D. Kumar, D. N. Kommi, R. Chebolu, S. K. Garg, R. Kumar, A. K. Chakraborti, *RSC Adv.* **2013**, *3*, 91-98; c) R. Chebolu, D. N. Kommi, D. Kumar, N. Bollineni, A. K. Chakraborti, *J. Org. Chem.* **2012**, *77*, 10158-10167; d) H. Sharma, N. Kaur, N. Singh, D. O. Jang, *Green Chem.* **2015**, *17*, 4263-4270; e) H. Sharma, N. Kaur, N. Singh, D. O. Jang, *Green Chem.* **2015**, *17*, 4263-4270.

[9] M. Dugal, G. Sankar, R. Raja, J. M. Thomas, *Angew. Chem. Int. Ed.* **2000**, *39*, 2310-2313.

[10] D. Zhao, J. Hu, N. Wu, X. Huang, X. Qin, J. Lan, J. You, *Org. Lett.* **2011**, *13*, 6516-6519.

[11] K. M. H. Nguyen, M. Largeron, *Chem. Eur. J.* **2015**, *21*, 12606-12610.

[12] H. Hikawa, R. Ichinose, S. Kikkawa, I. Azumaya, *Asian J. Org. Chem.* **2018**, *7*, 416-423.

[13] a) S. Chen, Y. Liao, F. Zhao, H. Qi, S. Liu, G.-J. Deng, *Org. Lett.* **2014**, *16*, 1618-1621; b) F. Zhou, M.-O. Simon, C.-J. Li, *Chem. Eur. J.* **2013**, *19*, 7151-7155.

[14] a) Y. Xie, S. Liu, Y. Liu, Y. Wen, G.-J. Deng, *Org. Lett.* **2012**, *14*, 1692-1695; b) S. A. Girard, X. Hu, T. Knauber, F. Zhou, M.-O. Simon, G.-J. Deng, C.-J. Li, *Org. Lett.* **2012**, *14*, 5606-5609; c) M. T. Barros, S. S. Dey, C. D. Maycock, P. Rodrigues, *Chem. Commun.* **2012**, *48*, 10901-10903; d) A. Hajra, Y. Wei, N. Yoshikai, *Org. Lett.* **2012**, *14*, 5488-5491.

[15] M.-O. Simon, S. A. Girard, C.-J. Li, *Angew. Chem. Int. Ed.* **2012**, *51*, 7537-7540.

[16] a) Y. Liao, P. Jiang, S. Chen, H. Qi, G.-J. Deng, *Green Chem.* **2013**, *15*, 3302-3306; b) W. Ge, X. Zhu, Y. Wei, *Adv. Synth. Catal*. **2013**, *355*, 3014-3021.

[17] a) X. Cao, X. Cheng, Y. Bai, S. Liu, G.-J. Deng, *Green Chem.* **2014**, *16*, 4644-4648; b) X. Cao, X. Cheng, Y. Bai, S. Liu, G.-J. Deng, *Green Chem.* **2014**, *16*, 4644-4648; c) J. Zhao, H. Huang, W. Wu, H. Chen, H. Jiang, *Org. Lett.* **2013**, *15*, 2604-2607.

[18] a) Y. Xie, J. Wu, X. Che, Y. Chen, H. Huang, G.-J. Deng, *Green Chem.* **2016**, *18*, 667-671.

[19] Y. Kuninobu, S. Nishimura, K. Takai, *Org. Biomol. Chem.* **2006**, *4*, 203-205.

[20] a) J. Zhao, H. Huang, W. Wu, H. Chen, H. Jiang, *Org. Lett.* **2013**, *15*, 2604-2607; b) F. Xiao, Y. Liao, M. Wu, G.-J. Deng, *Green Chem.* **2012**, *14*, 3277-3280; c) Y. Liao, Y. Peng, H. Qi, G.-J. Deng, H. Gong, C.-J. Li, *Chem. Commun.* **2015**, *51*, 1031-1034.

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Transition-Metal-Free Synthesis of 1,2-diphenyl-1*H*-benzo[*d*] Imidazole Derivatives from *N*-phenylbenzimidamides and cyclohexanones

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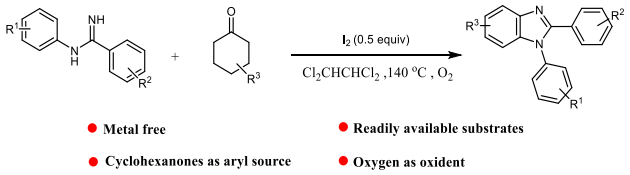

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