Advanced Synthesis & Catalysis

Accepted Article

Title: Metal-free Synthesis of Spiro-2,2'-benzo[b]furan-3,3'-ones via PhI(OAc)2-Mediated Cascade Spirocyclization

Authors: Yunfei Du, Qingyu Xing, Huiyuan Liang, Mingmai Bao, Xuemin Li, Jingran Zhang, Tianhao Bi, Yilin Zhang, and Jun Xu

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201900652

Link to VoR: http://dx.doi.org/10.1002/adsc.201900652

10.1002/adsc.201900652

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Metal-free Synthesis of Spiro-2,2'-benzo[*b*]furan-3,3'-ones *via* PhI(OAc)$_2$-Mediated Cascade Spirocyclization

Qingyu Xing,[a,d] Huiyuan Liang,[a,d] Mingmai Bao,[a] Xuemin Li,[a] Jingran Zhang,[a] Tianhao Bi,[a] Yilin Zhang,[c] Jun Xu,[a] Yunfei Du,[*,a, b] and Kang Zhao[*,a]

[a.] Tianjin Key Laboratory for Modern Drug Delivery & High-Efficiency, School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China. Address here. E-mail: duyunfeier@tju.edu.cn; kangzhao@tju.edu.cn
[b.] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China
[c.] C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045, United States
[d.] Q.X. and H.L. contributed equally.

Received: ((will be filled in by the editorial staff))

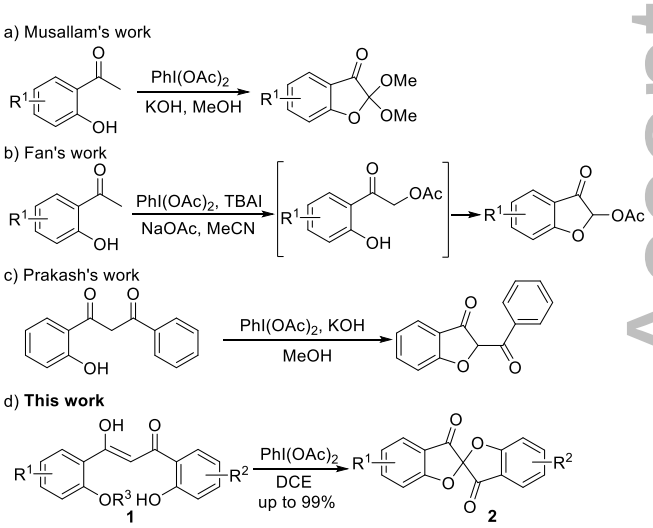
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract: Treating the benzyl protected 3-hydroxy-1,3-bis(2-hydroxyphenyl)prop-2-en-1-ones solely with PhI(OAc)$_2$ (PIDA) in DCE at room temperature readily furnished the seldom studied spiro-2,2'-benzo[b]furan-3,3'-ones in satisfactory to excellent yields. The hypervalent iodine reagent enables the metal-free cascade spirocyclization resulting in the dual oxidative C-O bond formation.

Keywords: Metal-free synthesis; PIDA; Spirocyclization; Cascade reaction; Spirobenzofuran

In the past several decades, hypervalent iodine reagents(III) have been widely applied in a plethora of oxidative coupling reactions.[1] Remarkably, the hypervalent iodine reagents(III) induced C-O bond formation through dearomatization have received significant attention as a powerful method to access complex molecules.[2-3] On the other hand, a limited number of studies were reported on I(III) mediated C-O bond formation between carbon and hydroxyl group without dearomatization. For example, PIDA/I$_2$ system was applied in Suarez type cross coupling *via* photochemical reaction involving a 1,5-hydrogen transfer in free radical system.[4a] Kita has reported an oxidative lactone formation *via* a similar C-H abstraction strategy.[4b] Besides, several studies have focused on the synthesis of benzo[*b*]furan-3-ones from *o*-hydroxyacetophenones through I(III)-mediated intramolecular cyclization that enables the coupling of hydroxyl group and α-carbon of the electron-withdrawing moiety.[5] Furthermore, oxidative cyclization of Schiff base has been known in which I(III) reagents facilitates double-bond activation and subsequent nucleophilic addition.[6] In addition to these examples, notable progress on oxylactonization employing I(III) reagent has also been reported in recent years.[7]

On the other hand, hypervalent iodine (III) reagents have also been investigated for its application in a series of cascade reactions including C-C,[8] C-O,[9] C-N[10] bond formations. However, to the best of our knowledge, I(III)-mediated spirocyclization reactions involving dual C-O bond formation have been least explored.

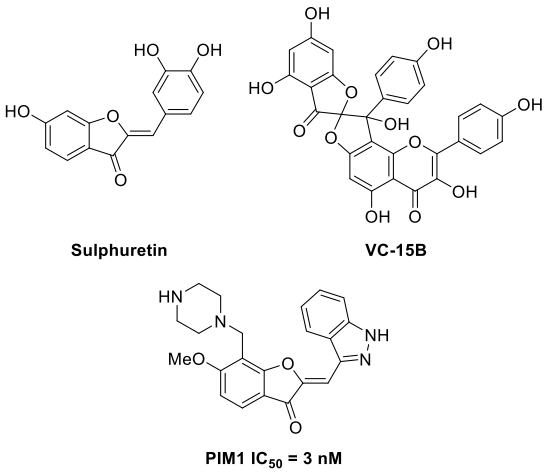


Scheme 1 Construction of Benzo[*b*]furan-3-one Skeleton via I(III)-Mediated O-O Bond Formation.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

10.1002/adsc.201900652

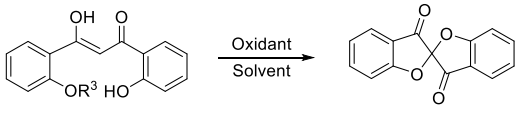


Scheme 2 Examples of Natural Products and Bioactive Compounds Containing Benzo[*b*]furan-3-one.

Benzo[*b*]furan-3-one is an important heterocyclic skeleton found in a broad variety of natural products[11], such as sulphuretin[11a] and VC-15B,[11d] and pharmaceutical bioactive compounds,[12] such as a PIM1 inhibitor reported by Nagano group (Scheme 2). [12a]

One of the most conventional approach to benzo[*b*]furan-3-one involves halogenation of α-hydroxyl acetophone followed by an intramolecular S_N2 reaction.[13] Moreover, another general approach assembling benzo[*b*]furan-3-ones makes use of hypervalent iodine reagent as oxidant and this approach is widely utilized for its merit of requiring no functionalization on the α-hydroxyl acetophenones. For examples, Musallam and co-workers[5a] achieved 20% yield of 2, 2-dimethoxyl-benzo[*b*]furan-3-one using PIDA under basic conditions (Scheme 1a). In 2009, Fan reported[5b] a PIDA-mediated synthesis of

Table 1. Optimization of the Reaction Conditions.[a]



1a, R^3 = Bn; **1a'** R^3 = H — **2a**

Entry	Substrate	Oxidant (equiv)	Solvent	Yield(%)[b]
1	**1a'**	PIDA (3.0)	DMF	31
2	**1a**	PIDA (3.0)	DMF	49
3	**1a**	PIDA (3.0)	AcOH	ND
4	**1a**	PIDA (3.0)	EtOAc	33
5	**1a**	PIDA (3.0)	MeOH	10
6	**1a**	PIDA (3.0)	DCE	99
7	**1a**	PIDA (2.5)	DCE	87
8	**1a**	PIDA (2.0)	DCE	77
9	**1a**	I_2 (3.0)	DCE	ND
10	**1a**	mCPBA (3.0)	DCE	ND
11	**1a**	PhIO (3.0)	DCE	92

[a] All the reaction carried out with substrate **1a** or **1a**' (0.5 mmol), solvent (8 mL) at rt for 1 h, unless otherwise stated. [b] Isolated yield.

benzo[*b*]furan-3-one derivatives *via* cascade oxidation (Scheme 1b). Both of the transformations above comprise intramolecular and sequentially intermolecular C-O bond formations, allowing for the construction of the benzo[*b*]furan-3-one derivatives in a cascade protocol. In 1990, Prakash reported[5g] that the reaction of 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione with PIDA and KOH in methanol afforded 2-benzoylbenzofuran-3(*2H*)-one *via* an intramoleculuar oxidative C-O bond formation (Scheme 1c).

However, to our best knowledge, there is no report describing the intramolecular dual C-O bond formation leading to the construction of spiroheterocyclic scaffold with hypervalent iodine reagents. Herein, we report a cascade reaction starting from the protected 3-hydroxy-1,3-bis(2-hydroxyaryl)prop-2-en-1-ones **1** and PIDA, which produces spiro-2,2'-benzo[*b*]furan-3,3'-one[14] species in high yields *via* an intramolecular dual C-O bond formation (Scheme 1d).[5h]

In continuation of our interest in the construction of spiroheterocyclic framework,[15] we initially investigated the viability of dual oxidative C-O bond formation toward spiroheterocycle **2a** starting from 1,3-bis(2-hydroxyphenyl)propane-1,3-dione **1a**'. Fortunately, when **1a**' was treated with PIDA in DMF at room temperature, spiro-product **2a** could be obtained in only 31% yield (Table 1, entry 1) with the generation of some unidentified byproducts. We tentatively propose that the concurrent presence of two hydroxyl groups in the substrate facilitates the over-oxidation by the hypervalent iodine oxidant. Due to the fact that the reaction yield could not be improved after various attempts, we started to conceive whether **1a**, the precursor of **1a**', could also achieve this PIDA-mediated spiroheterocyclization transformation, as the oxonium intermediate generated may act as the reactive center for removal of the benzyl group. On the other hand, one less free phenolic hydroxyl group is believed to be beneficial for eliminating some undesired byproducts from over-oxidation. To our delight, when **1a** was treated with 3 equivalents of PIDA in DMF, product **2a** was obtained in 49% yield (Table 1, entry 2). Further screening of solvents indicated that when DCE was used as solvent, product **2a** was obtained in a nearly quantitative yield (Table 1, entries 3-6). It was found that reducing the amount of PIDA from 3 equivalents to 2.5 and 2.0 equivalents, the yield of product **2a** decreased to 87% and 77%, respectively (Table 1,

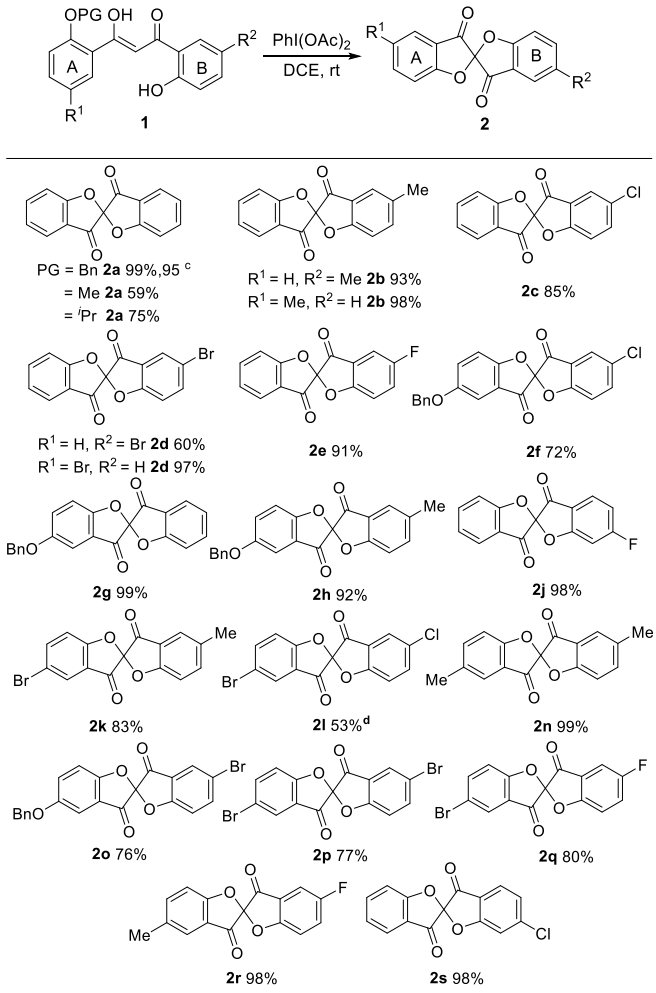
Accepted Manuscript

This article is protected by copyright. All rights reserved.

entries 7-8). The other commonly used oxidants including I_2 and *m*CPBA were also examined and it was found that the reaction gave no desired product in each case (Table 1, entries 9-10), while PhIO afforded the desired product **2a** in a slightly lower yield (Table 1, entry 11).

With the optimal conditions (Table 1, entry 6) in hand,[16] we came to explore the generality and scope of this newly established method. As indicated by the results in Table 2, the substrates bearing either electron-donating groups or electron-withdrawing groups can be transformed to the corresponding spiroheterocycles under the reaction conditions. The method worked equally well for the substrates bearing various substituent on both ring A and ring B concurrently. Specifically, when ring A bears the electron-donating benzyloxy (substrates **1f-h** and **1o**), methyl (substrates **1m** (R^1 = Me, R^2 = H), **1n** and **1r**), or the electron-withdrawing bromo group (substrates **1i** (R^1 = Br, R^2 = H), **1k-l** and **1p-q**), the corresponding spirocyclic products could be obtained in nearly quantitative yields. For the substrates bearing the electron-donating methyl group (substrates **1b** (R^1 = H, R^2 = Me)), the electron-withdrawing fluoro (substrates **1e**, **1j**) and chloro group (substrates **1c**, **1s**) on B ring, the spirocyclic products could also be obtained in good to excellent yields. The substrate bearing bromo substituent on ring B delivered the desired products in satisfactory to excellent yield (substrates **1d** (R^1 = H, R^2 = Br) and **1o-p**). Furthermore, replacing the benzyloxy group on the ring A with a methoxy or an isopropyloxy group, the corresponding substrates **1t** (PG = Me) and **1u** (PG= ^{i}Pr) also furnished the same product **2a**, but in a much lower yield in each case. It is worthy to note that when 1 gram of substrate **1a** was subjected to the reaction conditions, product **2a** could be isolated in 95% yield, indicating that the method is applicable for the gram-scale synthesis.

Table 2. PIDA-Mediated Synthesis of Spiro-2,2'-benzo[*b*]furan-3,3'-ones.[a, b]



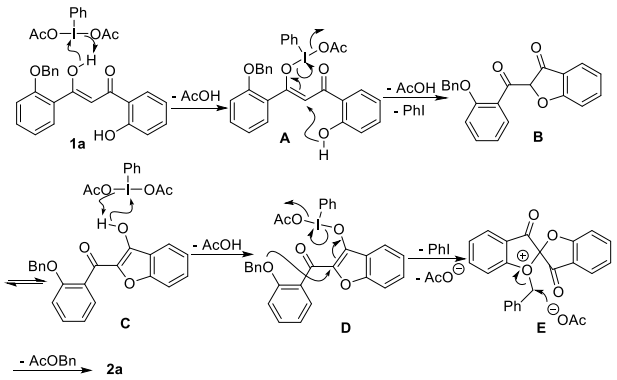
[a]All reactions were carried out with substrate 1 (0.5 mmol) and PIDA (1.5 mmol) in DCE at rt for 1 h. [b]Isolated yield. [c]Carried out at 1-gram scale. [d]The structure of **2l** was confirmed by X-crystal analysis.

Results of our control experiments suggested that the reaction happens between an enol with the hypervalent iodine center. According to the previous reported work,[17] there are two plausible attack modes on the iodine center. First, the enolic carbon attack the iodine center gave the C-I type intermediate followed by 5-exo-tet type cyclization. Second, the enolic oxygen attack gave the C-I or O-I type intermediate followed by 5-endo-trig type cyclization. On the basis of the previous computational studies reported by Legault[17e] and the low-temperature NMR study on the O-I type intermediate reported by Szpilman,[17d] we propose that the reaction might undergo the O-I intermediate.

Based on the results from the control experiments as well as the previous literatures,[15a,17] we proposed a plausible mechanism for this spirocyclization reaction. First, the enolic oxygen in **1a** nucleophilically attack the iodine center of PIDA to give intermediate **A**,[18] with the release of one molecule of AcOH. Next, an intramolecular cyclization occurred in **A** which realized the oxidative formation of the first C-O bond, with the loss of one PhI and acetate anion. It is worth noting that all of our attempts to isolate and characterize intermediate **B**[19] were unsuccessful, as the use of less PIDA only led to the final products and some of the unconsumed starting materials in all cases. Next, the enol form of **B** was tautomerized into **C**, which reacted with PIDA to give intermediate **D**.[18] Then **D** underwent cyclization to realize the oxidative formation of the second C-O bond, which gave the oxonium ion intermediate **E**. Ultimately, the nucleophilic attack of acetate anion on the benzylic carbon led to the removal of the benzyl group, affording the title product **2a** (Scheme 3). The formation of the byproduct, namely, benzyl acetate could be detected in all cases.

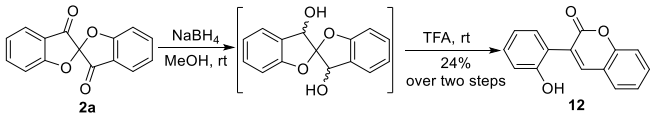
Accepted Manuscript

This article is protected by copyright. All rights reserved.



Scheme 3. Plausible Mechanism.

The obtained spiro-2,2'-benzo[*b*]furan-3,3'-one compound could be further derivatized into other building blocks. For example, treating compound **2a** with $NaBH_4$ in MeOH led to the formation of diol **11**, which could be rearranged to coumarin **12**, in the presence of TFA in an overall yield of 24% (Scheme 4). The structure of coumarin **12** was further confirmed by X-crystal analysis.[20]



Scheme 4. Derivatization of **2a**.

In conclusion, we have presented a PIDA-mediated cascade spirocyclization reaction involving a novel intramolecular dual oxidative C-O bond formation process.[21] This method enables a convenient synthesis of spiro-2,2'-benzo[*b*]furan-3,3'-ones[22] in satisfactory to excellent yield under metal-free conditions. Studies on further elucidating the reaction mechanism are ongoing in our lab.

Experimental Section

To a solution of **1a** (1.0 g, 2.9 mmol) in DCE (40 mL) was added PIDA (2.8 g, 8.7 mmol) in one portion. The mixture was stirred at room temperature for 1 h. Upon stirring, this yellow mixture turned to a clean, colorless solution. The complete consumption of **1a** was determined by TLC (EtOAc : PE = 1:9, R_f = 0.5). Then the solution was mixed with silica gel and concentrated *in vacuo*. The resulting residue was loaded to a silica column flashed with EtOAc and PE (EtOAc : PE = 1 : 9) to give **2a** (670 mg, 92%) as a white solid.

Acknowledgements

We acknowledge the National Natural Science Foundation of China (#21472136) for financial support.

References

[1] a) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* 2016, **116**, 3328. b) T. Wirth. *Angew. Chem., Int. Ed.* 2005, **44**, 3656. c) E. D. Matveeva, M. V. Proskurnina, N. S. Zefirov. *Heteroatom Chem.* 2006, **17**, 595. d) J. Charpentier, N. Früh, A. Togni. *Chem. Rev.* 2015, **115**, 650. e) B. Olofsson, I. Marek, Z. Rappoport. *The Chemistry of Hypervalent Halogen Compounds*. Wiley, 2019. f) V. V. Zhdankin. Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds. Wiley: Chichester, 2013. g) T. Wirth. *Hypervalent Iodine Chemistry*. Springer, 2016.

[2] a) A. Yoshimura, M. S. Yusubov, V. V. Zhdankin. *Org. Biomol. Chem.* 2016, **14**, 4771. b) S. Y. Mekhman, V. Z. Viktor. *Curr. Org. Synth.* 2012, **9**, 247. c) A. Flores, E. Cots, J. Berges, K. Muniz. *Adv. Synth. Catal.* 2019, **361**, 2. d) F. V. Singh, P. B. Kole, S. R. Mangaonkar, S. E. Shetgaonkar. *Beilstein J. Org. Chem.* 2018, **14**, 1778. e) H. Wu, Y. He, L. Xu, D. Zhang, L. Gong. *Angew. Chem., Int. Ed.* 2014, **53**, 3466. f) K. Muniz, L. Fra. *Synthesis* 2017, **49**, 2901.

[3] a) Q. Ding, Y. Ye, R. Fan. *Synthesis* 2013, **45**, 1. b) S. Rodríguez, P. Wipf. *Synthesis* 2004, **17**, 2767. c) A. Duschek, S. F. Kirsch. *Angew. Chem., Int. Ed.* 2011, **50**, 1524. d) M. Uyanik, T. Yasui, K. Ishihara. *Angew. Chem., Int. Ed.* 2013, **52**, 9215. e) H. Cheng, L. Zhang, Y. Liu, S. Chen, H. Cheng, X. Lu, Z. Zheng, G. C. Zhou. *Eur. J. Med. Chem.* 2010, **45**, 5950. f) A. M. Harned. *Tetrahedron Lett.* 2014, **55**, 4681. g) T. A. Wenderski, C. Hoarau, L. Mejorado, T. R. R. Pettus. *Tetrahedron* 2010, **66**, 5873. h) S. Quideau, L. Pouységu, D. Deffieux. *Synlett* 2008, **4**, 467. i) A. Berube, I. Drutu, J. Wood. *Org. Lett.* 2006, **24**, 5421. j) S. Quideau, M. Lebon, A. K. Lamidey. *Org. Lett.* 2002, **22**, 3975. k) T. Hashimoto, Y. Shimazaki, Y. Omatsu, K. Maruoka. *Angew. Chem., Int. Ed.* 2018, **57**, 7200.

[4] a) M. L. Condakes, K. Hung, S. J. Harwood, T. J. Maimone. *J. Am. Chem. Soc.* 2017, **139**, 17783. b) T. Dohi, N. Takenaga, A. Goto, A. Maruyama, Y. Kita. *Org. Lett.* 2007, **9**, 3129.

[5] a) R. M. Moriarty, O. Prakash, I. Prakash, H. A. J. Musallam. *J. Chem. Soc., Chem. Commun.* 1984, 1342. b) R. Fan, Y. Sun, Y. Ye. *Org. Lett.* 2009, **11**, 5174. c) M. Uyanik, D. Suzuki, T. Yasui, K. Ishihara. *Angew. Chem., Int. Ed.* 2011, **50**, 5331. d) R. M. Moriarty, R. K. Vaid, T. E. Hopkins, B. K. Vaid, O. Prakash. *Tetrahedron Lett.* 1990, **31**, 201. e) S. C. Lu, P. R. Zheng, G. Liu. *J. Org. Chem.* 2012, **77**, 7711. f) M. Uyanik, T. Yasui, K. Ishihara. *Bio. Med. Chem. Lett.* 2009, **19**, 3848. g) O. Prakash, S. Goyal, S. Pahuja, S. P. Singh. *Synth. Commun.* 1990, **20**, 1409.

[6] a) O. Prakash, K. Pannu, A. Kumar. *Molecules* 2006, **11**, 43. b) J. Joseph, Y. Kim, S. Chang. *Chem. – Eur. J.* 2011, **17**, 8294. c) R. S. Varma, R. K. Saini, O. Prakash. *Tetrahedron Lett*. 1997, **38**, 2621.

[7] a) M. Fujita, Y. Yoshida, K. Miyata, A. Wakisaka, T. Sugimura. *Angew. Chem., Int. Ed.* 2010, **49**, 7068. b) G.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

F. Koser, J. S. Lodaya, D. G. Ray, P. B. Kokil. *J. Am. Chem. Soc.* 1988, **110**, 2987. c) D. M. Browne, O. Niyomura, T. Wirth. *Org. Lett.* 2007, **9**, 3169. d) J. Yan, H. Wang, Z. Yang, Y. He. *Synlett* 2009, **16**, 2669.

[8] a) M. Arisawa, N. G. Ramesh, M. Nakajima, H. Tohma, Y. Kita. *J. Org. Chem*. 2001, **66**, 59; b) F. R. Gomes Luis, F. Veiros Luís, N. Maulide, A. M. Afonso Carlos. *Chem. – Eur. J.* 2014, **21**, 1449. c) G. Tian, P. Fedoseev, E.V. Van der Eycken. *Chem. – Eur. J.* 2017, **23**, 5224.

[9] a) Z. Zheng, D. Zhang-Negrerie, Y. Du, K. Zhao. *Sci. China Chem*. 2014, **57**, 189. b) E. Domínguez. *Tetrahedron Lett.* 1999, **40**, 3479.

[10] a) Y. Sun, J. Gan, R. Fan. *Adv. Synth. Catal*. 2011, **353**, 1735. b) J. Sun, G. Li, G. Zhang, Y. Cong, X. An, D. Zhang-Negrerie, Y. Du. *Adv. Synth. Catal*. 2018, **360**, 2476. c) W. Leawsuwan, S. Ruchirawat. *RSC Adv.* 2015, **5**, 13102.

[11] a) X. Liu, C. Yin, Y. Cao, J. Zhou, T. Wu, Z. Cheng. *Nat. Prod. Res.* 2018, **32**, 1145. b) L. Wen, Z. Guo, Q. Li, D. Zhang, Z. She, L. L. P. Vrijmoed. *Chem. Nat. Compd*. 2010, **46**, 363. c) A. V. Lipeeva, E. E. Shul'ts, M. M. Shakirov, G. A. Tolstikov. *Chem. Nat. Compd.* 2009, **45**, 338. d) R. R. T. Majinda, M. Motswaledi, R. D. Waigh, P. G. Waterman. *Planta Med.* 1997, 63, 268.

[12] a) H. Nakano, N. Saito, L. Parker, Y. Tada, M. Abe, K. Tsuganezawa, S. Yokoyama, A. Tanaka, H. Kojima, T. Okabe, T. Nagano. *J. Med. Chem.* 2012, **55**, 5151. b) E. Baiceanu, K. A. Nguyen, L. Gonzalez-Lobato, R. Nasr, H. Baubichon-Cortay, F. Loghin, M. Le Borgne, L. Chow, A. Boumendjel, M. Peuchmaur, P. Falson. *Eur. J. Med. Chem.* 2016, **122**, 408.

[13] a) Y. Fang, R. Wang, Q. Wang, Y. Sun, S. Xie, Z. Yang, M. Li, Y. Jin, S. Yang. *Bioorg. Med. Chem. Lett.* 2018, **28**, 668. b) I. N. Gaisina, F. Gallier, A. V. Ougolkov, K. H. Kim, T. Kurome, S. Guo, D. Holzle, D. N. Luchini, S.Y. Blond, D. D. Billadeau, A. P. Kozikowski. *J. Med. Chem.* 2009, **52**, 1853.

[14] For a previous report describing one example for synthesis of 3-hydroxy-1,3-bis(2-hydroxyphenyl)prop-2-en-1-one **1a** by using the poisonous $Ti(NO_3)_3$, see: S. Antus, E. Baitz-Gács, F. Boross, M. Nógrádi, A. Sólyom. *Liebigs Ann. Chem.* 1980, **8**, 1271.

[15] a) J. Wang, Y. Yuan, R. Xiong, D. Zhang-Negrerie, Y. Du, K. Zhao. *Org. Lett.* 2012, **14**, 2210. b) X. Zhang, W. Hou, D. Zhang-Negrerie, K. Zhao, Y. Du. *Org. Lett.* 2015, **17**, 5252. c) X. Zhang, Y. Chao, D. Zhang-Negrerie, Y. Du. *Chem. – Eur. J.* 2015, **21**, 5193. d) Y. Cao, X. Zhang, G. Lin, D. Zhang-Negrerie, Y. Du. *Org. Lett.* 2016, **18**, 5580. e) X. Zhang, G. Zhou, Y. Zhang, D. Zhang-Negrerie, Y. Du. *J. Org. Chem.* 2016, **81**, 11397. f) B. Zhang, X. Zhang, B. Hu, D. Sun, S. Wang, D. Zhang-Negrerie, Y. Du. *Org. Lett*. 2017, **19**, 902.

[16] We also ran the reaction of substrate **1a** by using a catalytic amount of iodobenzene (2 mol %) with *m*CPBA (2 equiv) and H_2O_2 (4 equiv) in DCE. However, no desired product **2a** was achieved in each case.

[17] a) K. N. Parida, G. K. Pathe, S. Maksymenko, A. M. Szpilman. *Beilstein J. Org. Chem.* 2018, **14**, 992. b) A. A. More, G. K. Pathe, K. N. Parida, S. Maksymenko, Y. B. Lipisa, A. M. Szpilman. *J. Org. Chem.* 2018, **83**, 2442. c) S. Maksymenko, K. N. Parida, G. K. Pathe, A. A. More, Y. B. Lipisa, A. M. Szpilman, *Org. Lett.* 2017, **19**, 6312. d) S. Arava, J. N. Kumar, S. Maksymenko, M. A. Iron, K. N. Parida, P. Fristrup, A. M. Szpilman. *Angew. Chem. Int. Ed.* 2017, **56**, 2599. e) S. Beaulieu, C. Y. Legault. *Chem. – Eur. J.* 2015, **21**, 11206. f) G. Levitre, A. Dumoulin, P. Retailleau, A. Panossian, F. R. Leroux, G. Masson. *J. Org. Chem.* 2017, **82**, 11877. g) A. Claraz, G. Masson. *Org. Biomol. Chem.* 2018, **16**, 5386. h) C. Gelis, A. Dumoulin, M. Bekkaye, L. Neuville, G. Masson. *Org. Lett.* 2017, **19**, 278. i) C. Gelis, M. Bekkaye, C. Lebee, F. Blanchard, G. Masson. *Org. Lett.* 2016, **18**, 3422. j) P. Norrby, T. B. Petersen, M. Bielawski, B. Olofsson. *Chem. – Eur. J.* 2010, **16**, 8251.

[18] a) D. Sun, X. Zhao, B. Zhang, Y. Cong, X. Wan, M. Bao, X. Zhao, B. Li, D. Zhang-Negrerie, Y. Du. *Adv Synth. Catal.* 2018, **360**, 1634. b) Y. Cao, H. Zhao, D. Zhang-Negrerie, Y. Du, K. Zhao. *Adv. Synth. Catal.* 2016, **358**, 3610.

[19] Our attempts to synthesize intermediate **B** *via* the similar known procedure proved to be unsuccessful. For our previous work describing the formation of the similar spirofurooxindole **B** *via* PIDA-mediated oxidative cyclization of 3-(2-hydroxyphenyl)-3-oxo-*N*-phenyl propanamides, see ref 15.

[20] For crystallographic data of compound **12**, see Supporting Information. CCDC-1907783 contains the supplementary crystallographic data for compound **12**.

[21] Our preliminary investigation on the enantioselective version of the reaction by using a chiral hyervalent iodine reagent proved to be unsuccessful. For details, see SI.

[22] For crystallographic data of compound **2l**, see Supporting Information. CCDC-1895335 contains the supplementary crystallographic data for compound **2l**.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

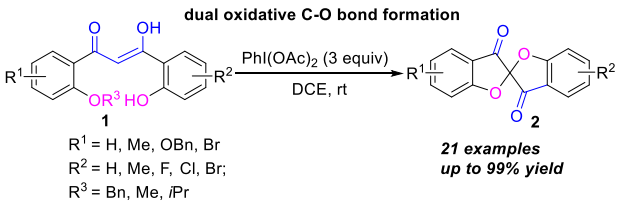
10.1002/adsc.201900652

COMMUNICATION

Metal-free Synthesis of Spiro-2,2'-benzo[*b*]furan-3,3'-ones *via* PhI(OAc)$_2$-Mediated Cascade Spirocyclization

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Qingyu Xing,[a,d] Huiyuan Liang,[a,d] Mingmai Bao,[a] Xuemin Li,[a] Jingran Zhang,[a] Tianhao Bi,[a] Yilin Zhang,[c] Jun Xu,[a] Yunfei Du,[*,a, b] and Kang Zhao[*,a]



Accepted Manuscript

This article is protected by copyright. All rights reserved.