Organic LETTERS

Letter

pubs.acs.org/OrgLett

Controlled Synthesis of 1,3,5-Oxadiazin-2-ones and Oxazolones through Regioselective Iodocyclization of Ynamides

Hai Huang, Xiaolin Zhu, Guangke He,* Qi Liu, Junzhen Fan, and Hongjun Zhu*

Department of Applied Chemistry, College of Sciences, Nanjing Tech University, Nanjing 211816, P. R. China

Supporting Information

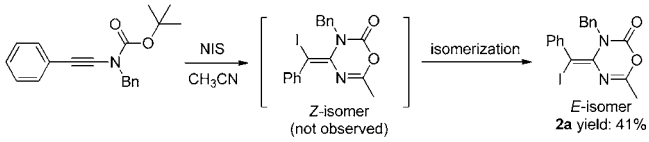
ABSTRACT: Two efficient processes based on the iodocyclization of ynamides have been developed: (i) *N*-alkynyl *tert*-butyloxycarbamates were found to undergo a rare 6-*exo*-*dig* ring closure reaction affording 1,3,5-oxadiazin-2-ones by using acetonitrile as solvent; (ii) In the absence of acetonitrile, *N*-alkynyl *tert*-butyloxycarbamates could undergo 5-*endo*-*dig* cyclization providing oxazolones.

Synthesis and functionalization of heterocycle and carbocycle systems through electrophilic iodocyclization are one of the most important areas in current organic syntheses.[1] Compared with traditional alkyne/alkene activation with Brønsted acids and metal catalysts, electrophilic iodocyclization provides a more convenient and effective method for molecular design because this activation method leads to the synthesis of iodo-containing heterocycle or carbocycle derivatives, which are versatile precursors in many synthetic processes.[2] Meanwhile, cyclic carbamates are a very popular and important class of heterocyclic compounds which have been widely applied in pharmaceuticals[3] and chiral auxiliaries.[4] Thus, tremendous efforts have been devoted to the development of versatile methods for constructing these cyclic carbamates. And the most general method focuses on the cyclization of different types of starting materials, such as *N*-Boc-protected alkynyl amines,[5] *N*-alkynyl *tert*-butyloxycarbamates,[6] and others.[7] Given the great importance of electrophilic iodocyclization, development of a practical, efficient iodocyclization for the preparation of these target cyclic carbamates is highly desirable. For instance, a halogen-mediated regioselective cyclization of *N*-Cbz-protected propargylic amines has been previously described by Pedro[5b] et al. for the first time, which affords the cyclic carbamates, 1,3-oxazin-2-ones.

Ynamides and their derivatives are versatile building blocks in organic synthesis.[8] For example, transition metal (e.g., Au, Pd, Cu) catalyzed cycloisomerization of the *N*-alkynyl *tert*-butyloxycarbamates is an efficient approach to the synthesis of polysubstituted oxazolones.[6] Keeping the importance of electrophilic iodocyclization in mind, we hoped to investigate whether such a cycloisomerization could be mediated by less expensive and less toxic iodine-containing reagents. Following our ongoing efforts in exploring the reactivity of ynamides,[8] we now report that 1,3,5-oxadiazin-2-ones and oxazolones could be efficiently synthesized through regioselective iodocyclization of *N*-alkynyl *tert*-butyloxycarbamates, based on the solvent controlled 6-*exo*-*dig* and 5-*endo*-*dig* cyclization, respectively.

We began our study with the iodocyclization of the ynamide **1a** with NIS (1.5 equiv) and anhydrous CH_3CN, which was transformed into unforeseen (*E*)-3-benzyl-4-(iodo(phenyl)-methylene)-6-methyl-3,4-dihydro-2*H*-1,3,5-oxadiazin-2-one **2a** in 41% isolated yield (Scheme 1). In addition, the stereochemistry was confirmed via single-crystal X-ray diffraction (for details, see the Supporting Information). Importantly, 1,3,5-oxadiazin-2-ones are classic and important six-membered heterocyclic compounds which are widely present in several areas, such as nature compounds and weight promoters.[10] However, due to the lack of methods for the synthesis of 1,3,5-oxadiazin-2-ones,[11] further application of the derivatives mentioned above has been restricted. Thus, development of efficient, convenient methods to synthesize 1,3,5-oxadiazin-2-ones under mild reaction conditions is necessary.

Scheme 1. Unexpected Intermolecular 6-*exo*-*dig* Iodocyclization with Unusual Stereoselectivity

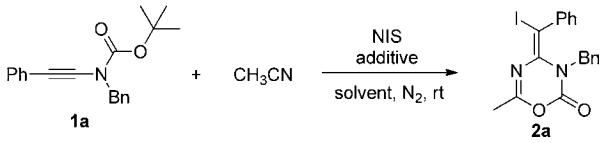


Therefore, the 6-*exo*-*dig* cyclization conditions were optimized. First, the use of other solvents such as THF (25%), toluene (30%), DCM (5%), DEM (24%), DMF (11%), and 1,4-dioxane (15%) was found to be less productive than CH_3CN (Table 1, entries 1−7). Next, additive bases such as K_2CO_3 and K_3PO_4 did furnish **2a** in low yield probably due to the base leading to the ring opening of 1,3,5-oxadin-2-ones (Table 1, entries 8−9).[12] Lewis acids, such as $ZnCl_2$, $FeCl_3$,[13] CuI, and $BF_3{\cdot}Et_2O$,[14] were also examined; $BF_3{\cdot}Et_2O$ showed higher activity (Table 1, entries 10−13). The employment of 1.0 equiv of $BF_3{\cdot}Et_2O$ gave the highest yield of **2a** (Table 1, entries 14−15). To our delight, when protected from light, this reaction afforded the product **2a** in 82% yield probably due to

Received: April 11, 2015
Published: May 6, 2015

DOI: 10.1021/acs.orglett.5b01045
Org. Lett. 2015, 17, 2510−2513

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



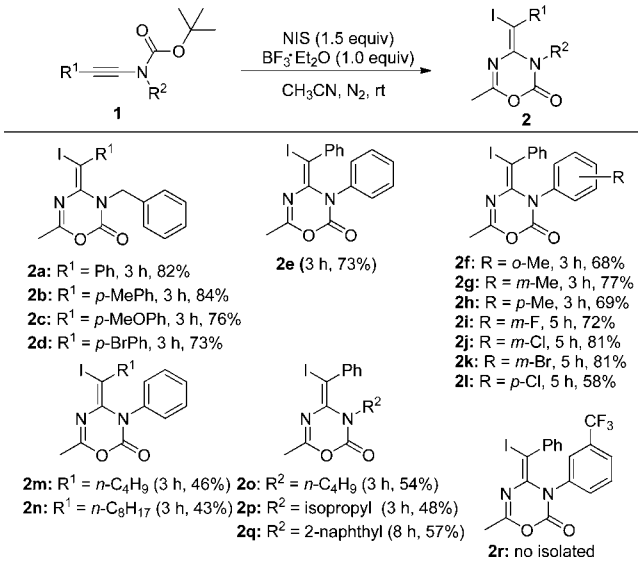
entry	additive (equiv)	solvent	yield (%)
1	–	CH_3CN	41
2	–	THF	25
3	–	toluene	30
4	–	DCM	5
5	–	DEM	24
6	–	DMF	11
7	–	1,4-dioxane	15
8	K_2CO_3 (1.0)	CH_3CN	13
9	K_3PO_4 (1.0)	CH_3CN	18
10	$FeCl_3$ (0.5)	CH_3CN	44
11	$ZnCl_2$ (0.5)	CH_3CN	23
12	CuI (0.5)	CH_3CN	41
13	$BF_3{\cdot}Et_2O$ (0.5)	CH_3CN	51
14	$BF_3{\cdot}Et_2O$ (1.0)	CH_3CN	65
15	$BF_3{\cdot}Et_2O$ (2.0)	CH_3CN	53
16[b]	$BF_3{\cdot}Et_2O$ (1.0)	CH_3CN	82
17[b,c]	$BF_3{\cdot}Et_2O$ (1.0)	CH_3CN	63
18[b,d]	$BF_3{\cdot}Et_2O$ (1.0)	CH_3CN	59
19[b,e]	$BF_3{\cdot}Et_2O$ (1.0)	CH_3CN	trace

[a]The reaction was carried out with **1a** (0.30 mmol), NIS (1.5 equiv), additive (0.5–2.0 equiv), and CH_3CN (3.0 mmol, if applicable) in solvent (2.0 mL) under N_2 conditions. [b]Under dark conditions. [c]1.0 equiv NIS loading. [d]2.0 equiv NIS loading. [e]2.0 equiv of I_2 instead of NIS.

the instability of the iodoethylenic bond (Table 1, entry 16).[15] The effect of NIS loading showed that 1.5 equiv of NIS gave the highest yield (82%) (Table 1, entries 17–18). Yet, when I_2 was added, almost no **1a** was observed to be consumed (Table 1, entry 19).

Under the optimized reaction conditions, we examined the scope and generality of various ynamides in this transformation, and the results are summarized in Scheme 2. Functional groups such as bromo and methoxy substituted on the aryl ring were tolerated and readily gave the corresponding 1,3,5-oxadiazin-2-ones in 73–84% yields (Scheme 2, **2c–2d**). Under the recommended reaction conditions, *tert*-butyl *N*-phenyl-*N*-(phenylethynyl)carbamate **1e** also worked well, leading to (*E*)-4-(iodo(phenyl)methylene)-6-methyl-3-phenyl-3,4-dihydro-2*H*-1,3,5-oxadiazin-2-one **2e** in 73% yield (Scheme 2, **2e**). Furthermore, methyl was well tolerated at the *ortho*, *meta*, and *para* position on the *N*-aryl ring, and the desired products could be isolated in good yields (Scheme 2, **2f–2h**). Substrates with F, Cl, or Br groups on the *N*-aromatic ring gave the desired products **2i–2l** in moderate to good yields (58%–81%). Alkyl-substituted ynamides could also give moderate yields (43–46%) successfully under the reaction conditions, and the yield was probably not affected by the length of the alkyl chain (Scheme 2, **2m**, **2n**). Ynamides with a *N*-butyl or *N*-isopropyl could also succeed in producing the desired 1,3,5-oxadiazin-2-ones in moderate yields (Scheme 2, **2o–2p**). Under the recommended reaction conditions, a substrate possessing a 2-naphthyl group on the N-atom furnished the desired products in 57% yield (Scheme 2, **2q**). **1r** with strong electron-withdrawing groups such as trifluoromethyl substituents in

Scheme 2. Intermolecular *6-exo-dig* Cyclization[a]

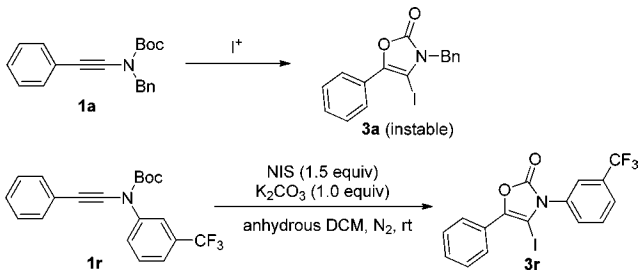


[a]Reaction conditions: **1** (0.3 mmol), NIS (1.5 equiv), and $BF_3{\cdot}OEt_2$ (1.0 equiv) in CH_3CN (2.0 mL) at rt.

the *N*-aryl ring furnished the desired product **2r** in 66% yields.[16] Unfortunately, it proved to be unstable and could not be isolated.

So far, we have failed to find any evidence that iodine mediated cycloisomerization of ynamides **1a** could be successfully carried out as we previously assumed. Thus, we inferred benzyl-substituted iodo-oxazolone **3a** was probably unstable as Gagosz[6a] reported (Scheme 3). Taking this into

Scheme 3. Reaction of 1a and 1r



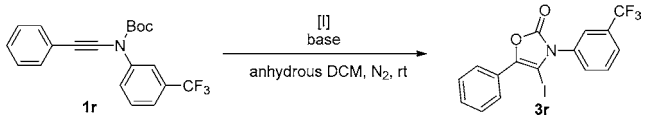
consideration, we began to examine other substrates that would produce stable iodo-oxazolones. To our delight, ynamide **1r** could give the stable product oxazolone 4-iodo-5-phenyl-3-(3-(trifluoromethyl)phenyl)-3*H*-oxazol-2-one **3r** in 70% isolated yield using DCM as solvent (Scheme 3).

Next, further studies were undertaken to identify general reaction conditions for the intramolecular iodocyclization using **1r** as a model substrate. Other bases such as K_3PO_4, Na_2CO_3, and Et_3N show unsatisfactory results (Table 2, entries 2–4). A similar yield of 83% was obtained when 2.0 equiv of K_2CO_3 were added (Table 2, entry 5). The effect of the loading of NIS showed that 2.0 equiv of NIS gave the highest yield (Table 2, entries 6–7). Additionally, the activity of I_2 was also tested and nearly no **1a** was observed to be consumed (Table 2, entry 8).

We set out to explore the scope of the ynamides for intramolecular iodocyclization (Scheme 4). Ynamide **1e** also afforded the desired intramolecular 5-*endo-dig* cyclization product **3e** in 63% yield (Scheme 4, **3e**). It is noteworthy

DOI: 10.1021/acs.orglett.5b01045
Org. Lett. 2015, 17, 2510–2513

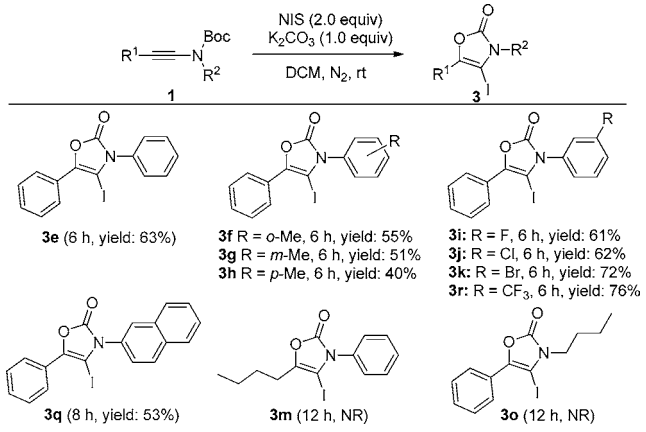
Table 2. Optimization of the Intramolecular Iodocyclization Conditions[a] for 1r



entry	[I] (equiv)	base (equiv)	yield (%)[b]
1	NIS (1.5)	K_2CO_3 (1.0)	82
2	NIS (1.5)	Na_2CO_3 (1.0)	62
3	NIS (1.5)	K_3PO_4 (1.0)	56
4	NIS (1.5)	Et_3N (1.0)	26
5	NIS (1.5)	K_2CO_3 (2.0)	83
6	NIS (2.0)	K_2CO_3 (1.0)	87
7	NIS (1.2)	K_2CO_3 (1.0)	67
8	I_2 (1.0)	K_2CO_3 (1.0)	trace

[a]The reaction was carried out with **1r** (0.30 mmol), [I], base, and DCM (2.0 mL) under N_2 conditions. [b]Yield was determined by ^1H NMR on the crude reaction mixture using 1,3,5-trimethylbenzene as an internal standard.

Scheme 4. Intramolecular 5-*endo-dig* Cyclization[a]

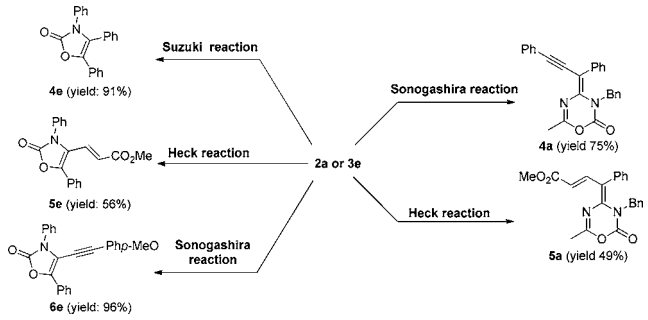


[a]Reaction conditions: **1** (0.3 mmol), NIS (2.0 equiv), and K_2CO_3 (1.0 equiv) in DCM (2.0 mL) at rt; NR = no reaction.

that various ynamides with methyl on the *ortho*, *meta*, and *para* positions of the *N*-aryl ring were converted into the corresponding products in 40−45% yields. And ynamide with methyl on the *para*-position of the *N*-aryl ring gave a lower yield compared with either the *meta*- or *ortho*-substituted product (Scheme 4, **3f**−**3h**). Ynamides with halogen groups, such as F, Cl, and Br, substituted on the *meta* position of the *N*-aryl ring were able to be converted to the corresponding oxazolones in 61−72% yields (Scheme 4, **3i**−**3k**), and an ynamide with a strongly electron-withdrawing group gave a higher yield (Scheme 4, **3r**). Under the recommended reaction conditions, a substrate possessing a 2-naphthyl group on the N-atom (Scheme 4, **3q**) gave the desired product in 53% yield. In contrast, attempted intramolecular iodocyclization reactions with an *n*-butyl-substituted (**1m**) or *N*-(*n*-butyl)-substituted (**1o**) ynamides failed to provide the corresponding oxazolones. The structure of **3e** was further confirmed via single-crystal X-ray diffraction (for details, see the SI).

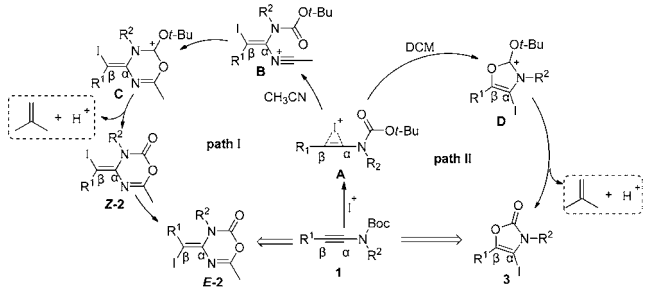
Iodo-containing 1,3,5-oxadiazin-2-ones and oxazolones prepared by this method offer great potential as precursors for the synthesis of new bioactive products.[17] 1,3,5-Oxadiazin-2-ones **2a** was able to undergo a Sonogashira coupling reaction to provide **4a** in 75% yield and Heck coupling to give the corresponding diene **5a** in 49% yield. 4-iodo-oxazolones **3e** could also easily undergo an array of transformations. For example, Suzuki−Miyaura coupling reaction affords compound **4e**, Heck reaction provides compound **5e**, and Sonogashira coupling reaction gives 3,4,5-trisubstituted oxazolone **6e** (Scheme 5).

Scheme 5. Synthesis of Cyclic Carbamate Derivatives



On the basis of previous reports, we propose the following plausible mechanisms for the formation of 1,3,5-oxadiazin-2-ones **2** and oxazolones **3**. In the presence of iodine as a weak Lewis acid, **1** produces the iodonium intermediate **A**,[1,2a] which can be nucleophilically attacked by acetonitrile to produce iodo alkenyl intermediates **B**.[18] And **B**, undergoing the 6-*endo-dig* ring closure reaction, affords cationic species **C**. Fragmentation of the C−O bond of the *tert*-butyloxy group in **C** then leads to the formation of oxazolones ***Z*-2**.[19] ***Z*-2** undergoes stereomutation to give the thermodynamically more stable ***E*-2** (Scheme 6, path I).[20] On the other hand, the cationic species **D**

Scheme 6. Proposed Mechanism for the Iodocyclization



could be formed from a direct intramolecular nucleophilic attack on **A**. Similarly, fragmentation of the C−O bond of the *tert*-butyloxy group in **D** then leads to the formation of oxazolones **3** (Scheme 6, path II).

In summary, we have developed two novel and efficient protocols for the synthesis of 1,3,5-oxadiazin-2-ones and oxazolones based on the iodocyclization of ynamides. To the best of our knowledge, this is not only the first iodocyclization of ynamides giving iodo-1,3,5-oxadiazin-2-ones but also a transition-metal-free cyclization of *N*-alkynyl *tert*-butyloxycarbamates giving oxazolones. Moreover, an iodine among the products provides an attractive and useful route to introduce new groups for the synthesis of new bioactive products. Further studies on iodine-mediated C−C, C−N, and C−O bond formations of ynamides are being conducted in our laboratory and will be reported in due course.

DOI: 10.1021/acs.orglett.5b01045
Org. Lett. 2015, 17, 2510−2513

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and spectral data of all new compounds and crystal structure data for **2a** and **3e** in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01045.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: pursuedreamer@aliyun.com.
*E-mail: zhuhj@njtech.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors greatly acknowledge the financial support in part by Provincal Natural Science Foundation of Jiangsu, China (No. BK20140937), and Postgraduate Innovation Fund of Jiangsu Province, China (2013, CXZZ13_0459; 2014, KYLX_0774).

■ REFERENCES

(1) (a) Godoi, B.; Schumacher, R. F.; Zeni, G. *Chem. Rev.* **2011**, *111*, 2937. (b) Mphahlele, M. J. *Molecules* **2009**, *14*, 4814. (c) Togo, H.; Iida, S. *Synlett* **2006**, 2159. (d) Larock, R. C. *Acetylene Chem.* **2005**, 51. (e) French, A. N.; Bissmire, S.; Wirth, T. *Chem. Soc. Rev.* **2004**, *33*, 354. (f) Toda, Y.; Pink, M.; Johnston, J. N. *J. Am. Chem. Soc.* **2014**, *136*, 14734. (g) Tripathi, C. B.; Mukherjee, S. *Org. Lett.* **2014**, *16*, 3368. (h) Wang, J.; Zhu, H.; Li, Y.; Wang, L.; Qiu, Y.; Qiu, Z.; Zhong, M.; Liu, X.; Liang, Y. *Org. Lett.* **2014**, *16*, 2236. (i) Danilkina, N. A.; Kulyashova, A. E.; Khlebnikov, A. F.; Bräse, S.; Balova, I. A. *J. Org. Chem.* **2014**, *79*, 9018. (j) Okitsu, T.; Nakata, K.; Nishigaki, K.; Michioka, N.; Karatani, M.; Wada, A. *J. Org. Chem.* **2014**, *79*, 5914. (k) Aurelio, L.; Volpe, R.; Halim, R.; Scammells, P. J.; Flynn, B. L. *Adv. Synth. Catal.* **2014**, *356*, 1974. (l) Chen, Y.; Huang, C.; Liu, X.; Perl, E.; Chen, Z.; Namgung, J.; Subramaniam, G.; Zhang, G.; Hersh, W. H. *J. Org. Chem.* **2014**, *79*, 3452.

(2) (a) Yamamoto, Y.; Gridnev, I. D.; Patil, N. T.; Jin, T. *Chem. Commun.* **2009**, 5075. (b) Ma, D.; Cai, Q. *Acc. Chem. Res.* **2008**, *41*, 1450. (c) Rossi, R.; Bellina, F.; Lessi, M. *Tetrahedron* **2011**, *67*, 6969. (d) Chinchilla, R.; Najera, C. *Chem. Soc. Rev.* **2011**, *40*, 5084.

(3) (a) Kudo, N.; Taniguchi, M.; Furuta, S.; Sato, K.; Endo, T.; Honma, T. *J. Agric. Food Chem.* **1998**, *46*, 5305. (b) Puig, C.; Crespo, M. I.; Godessart, N.; Feixas, J.; Ibarzo, J.; Jimenez, J. M.; Soca, L.; Cardelus, I.; Heredia, A.; Miraplex, M.; Puig, J. *J. Med. Chem.* **2000**, *43*, 214. (c) Mai, A.; Artico, M.; Esposito, M.; Sbardella, G.; Massa, S.; Befani, O.; Turini, P.; Giovannini, V.; Mondovi, B. *J. Med. Chem.* **2002**, *45*, 1180. (d) Wolfe, A. L.; Duncan, K. K.; Parelkar, N. K.; Weir, S. J.; Vielhauer, G. A.; Boger, D. L. *J. Med. Chem.* **2012**, *55*, 5878. (e) Singh, A.; Ha, H.-J.; Park, J.; Kim, J. H.; Lee, W. K. *Bioorg. Med. Chem.* **2011**, *19*, 6174. (f) Chen, H.; Li, Z.; Han, Y. *J. Agric. Food Chem.* **2000**, *48*, 5312.

(4) (a) Davies, S. G.; Garner, A. C.; Robert, P. M.; Smith, A. D.; Sweet, M. J.; Thomson, J. E. *Org. Biomol. Chem.* **2006**, *4*, 2753. (b) Garnsey, M. R.; Matous, J. A.; Kwiek, J. J.; Coltart, D. M. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 2406. (c) Wengryniuk, S. E.; Lim, D.; Coltart, D. M. *J. Am. Chem. Soc.* **2011**, *133*, 8714.

(5) (a) Robles-Machín, R.; Adrio, J.; Carretero, J. C. *J. Org. Chem.* **2006**, *71*, 5023. (b) Monleón, A.; Blay, G.; Domingo, L. R.; Muñoz, M. C.; Pedro, J. R. *Chem.—Eur. J.* **2013**, *19*, 14852.

(6) (a) Istrate, F. M.; Buzas, A. K.; Jurberg, I. D.; Odabachian, Y.; Gagosz, F. *Org. Lett.* **2008**, *10*, 925. (b) Hashmi, A. S. K.; Salathé, R.; Frey, W. *Synlett* **2007**, *11*, 1763. (c) Lu, Z.; Cui, W.; Xia, S.; Bai, Y.; Luo, F.; Zhu, G. *J. Org. Chem.* **2012**, *77*, 9871. (d) Lu, Z.; Xu, X.; Yang, Z.; Kong, L.; Zhu, G. *Tetrahedron Lett.* **2012**, *53*, 3433. (e) Lu, Z.; Yang, Z.; Cui, W.; Zhu, G. *Chem. Lett.* **2012**, *41*, 636.

(7) (a) Pattarozzi, M.; Zonta, C.; Broxterman, Q. B.; Kaptein, B.; Zorzi, R. D.; Randaccio, L.; Scrimin, P.; Licini, G. *Org. Lett.* **2007**, *9*, 2365. (b) Hanessian, S.; Tremblay, M.; Marzi, M.; Valle, J. R. D. *J. Org. Chem.* **2005**, *70*, 5070. (c) Fisher, M. J.; Overman, L. E. *J. Org. Chem.* **1990**, *55*, 1447. (d) Takeda, Y.; Okumura, S.; Tone, S.; Sasaki, I.; Minakata, S. *Org. Lett.* **2012**, *14*, 4874. (e) Tsui, G. C.; Ninnemann, N. M.; Hosotani, A.; Lautens, M. *Org. Lett.* **2013**, *15*, 1064.

(8) (a) DeKorver, K. A.; Li, H.; Lohse, A. G.; Hayashi, R.; Lu, Z.; Zhang, Y.; Hsung, R. P. *Chem. Rev.* **2010**, *110*, 5064. (b) Evano, G.; Coste, A.; Jouvin, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2840; *Angew. Chem.* **2010**, *122*, 2902. (c) Mulder, J. A.; Kurtz, K. C. M.; Hsung, R. P. *Synlett* **2003**, *10*, 1379. (d) Wang, X.; Yeom, H.-S.; Fang, L.-C.; He, S.; Ma, Z.-X.; Kedrowski, B. L.; Hsung, R. P. *Acc. Chem. Res.* **2014**, *47*, 560.

(9) (a) He, G.; Zhang, Q.; Huang, H.; Chen, S.; Wang, Q.; Zhang, D.; Zhang, R.; Zhu, H. *Eur. J. Org. Chem.* **2013**, 6979. (b) He, G.; Chen, S.; Wang, Q.; Huang, H.; Zhang, Q.; Zhang, D.; Zhang, R.; Zhu, H. *Org. Biomol. Chem.* **2014**, *12*, 5945. (c) Huang, H.; He, G.; Zhu, X.; Jin, X.; Qiu, S.; Zhu, H. *Eur. J. Org. Chem.* **2014**, 7174. (d) Huang, H.; He, G.; Zhu, G.; Zhu, X.; Qiu, S.; Zhu, H. *J. Org. Chem.* **2015**, *80*, 3480.

(10) (a) Shobana, N.; Farid, P. 1,3,5-Oxadiazines and 1,3,5-Thiadiazines. In *Comprehensive Heterocyclic Chemistry III*; Katritzky, A. R., Ramsden, C. A., Scriven, E. F. V., Taylor, R. J. K., Eds.; Elsevier Ltd.: 2008; Vol. *9*, pp 457−521. (b) Smalley, R. K. 1,3,5-Oxadiazines and 1,3,5-Thiadiazines. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Elsevier Science Ltd.: 1996; Vol. *6*, pp 783−823.

(11) (a) Jochims, J. C.; Troll, C.; Fischer, H.; Wang, Q.; Hamed, A.; Ismail, A. E.; Abdel-Aal, M. T.; Zeid, I.; Al-Talib, M. *J. Prakt. Chem.* **1992**, *334*, 669. (b) Aktrries, B.; Jochims, J. C. *Chem. Ber.* **1986**, *119*, 669. (c) Kay, I. T.; Streeting, I. T. *Synthesis* **1976**, 38.

(12) Oppedisano, A.; Prandi, C.; Venturello, P.; Deagostino, A.; Goti, G.; Scarpi, D.; Occhiato, E. G. *J. Org. Chem.* **2013**, *78*, 11007.

(13) Qiu, Y.; Yang, F.; Qiu, Z.; Zhong, M.; Wang, L.; Ye, Y.; Song, B.; Liang, Y. *J. Org. Chem.* **2013**, *78*, 12018.

(14) Okitsu, T.; Sato, K.; Potewar, T. M.; Wada, A. *J. Org. Chem.* **2011**, *76*, 3438.

(15) (a) Hu, Y.; Yi, R.; Wang, C.; Xin, X.; Wu, F.; Wan, B. *J. Org. Chem.* **2014**, *79*, 3052. (b) Li, S.; Li, Z.; Yuan, Y.; Li, Y.; Zhang, L.; Wu, Y. *Chem.—Eur. J.* **2013**, *19*, 1496.

(16) The yield was determined by ^{1}H NMR on the crude reaction mixture using 1,3,5-trimethylbenzene as an internal standard.

(17) (a) Li, C.; Liu, N.; Qi, Q.; Chen, Y.; He, L. *Eur. J. Org. Chem.* **2015**, 2585. (b) Zhang, S.; Chen, Y.; Wang, J.; Pan, Y.; Xu, Z.; Tung, C. *Org. Chem. Front.* **2015**, *2*, 578. (c) Sun, L.; Zhu, Y.; Wang, J.; Lu, P.; Wang, Y. *Org. Lett.* **2015**, *17*, 242. (d) Okitsu, T.; Yumitate, S.; Sato, K.; In, Y.; Wada, A. *Chem.—Eur. J.* **2013**, *19*, 4992.

(18) Chen, X.; Lu, P.; Wang, Y. *Chem.—Eur. J.* **2011**, *17*, 8105.

(19) Zhao, P.; Chen, D.; Song, G.; Han, K.; Li, X. *J. Org. Chem.* **2012**, *77*, 1579.

(20) (a) Liu, Y.; Song, F.; Cong, L. *J. Org. Chem.* **2005**, *70*, 6999. (b) Mancuso, R.; Mehta, S.; Gabriele, B.; Salerno, G.; Jenk, W. S.; Larock, R. C. *J. Org. Chem.* **2010**, *75*, 897. (c) Windmon, N.; Dragojlovic, V. *Tetrahedron Lett.* **2008**, *49*, 6543. (d) Takahashi, T.; Kondakov, D. Y.; Xi, Z.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 5871. (e) Pawluć, P.; Madalska, M.; Hreczycho, G.; Marciniec, B. *Synthesis* **2008**, *22*, 3687.

DOI: 10.1021/acs.orglett.5b01045
Org. Lett. 2015, 17, 2510−2513