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# A One-Pot Copper Catalyzed Biomimetic Route to *N*-Heterocyclic Amides from Methyl Ketones via Oxidative C−C Bond Cleavage

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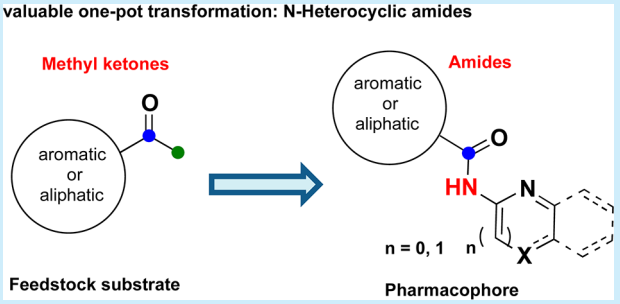
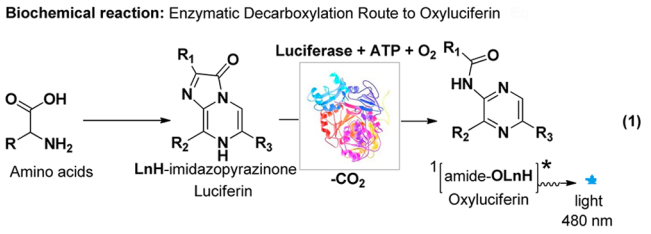
Supporting Information

**ABSTRACT:** A direct one-pot Cu-catalyzed biomimetic oxidation of methyl ketones to pharmaceutically important N-heterocyclic amides is reported. The scope of the method is broad, scalable, and mild, and the reaction is tolerant with various acid, base sensitive functionalities with multiple heteroatoms and aryl halides. The extensive mechanistic studies suggest that this reaction follows the Luciferin-Luciferase-like pathway.




Chemical conversions/reactions play an important role in regulating the biomass balances in biological systems. Enzymatic decarboxylation[1] is a fundamental process among several biotransformations and is widely applied for the synthesis of a myriad of compounds.[2] Aspiring to imitate the biological process, synthetic chemists have achieved several decarboxylative biomimetic methodologies which include Barton,[3] Hunsdiecker,[4] Kolbe,[5] Kochi,[6] malonic acid half thioester (MAHT) Claisen condensation,[7] and transition metal catalyzed transformations.[8]

One such biochemical process is the Luciferin-Luciferase reaction[9] [eq 1]. Luciferin belongs to a group of light emitting




natural products present in numerous bioluminescent organisms such as bacteria, dinoflagellates, fungi, crustaceans, worms, insects, and fish. Luciferase is an enzyme which is found to produce light in the presence of triplet molecular oxygen ($^3O_2$) upon exergonic oxidative decarboxylation reaction with luciferin (**LnH**) to generate the singlet-excited state intermediate oxyluciferin (amide-**OLnH***). Thus, this oxyluciferin is responsible for light emission in living bioluminescent organisms. This bioluminescent technique has been widely applied to examine certain biological processes, such as stages of infection, and provides other vital sources of information.[10]

Amides are versatile compounds present in biologically active heterocycles, polymers, proteins, natural products, agrochemicals, and synthetic intermediates. The conventional method for amide preparation often relies on preactivation of carboxylic acid[11] either by acetyl chloride or mix-anhydride formations or by the use of coupling reagents (DCC, EDC·HCl, HATU, and etc.). However, these methods possess their own drawbacks which include requirements of stoichiometric excess of reagents, sensitivity toward moisture, process of purification, and expensive coupling reagents. Difficulties in setting up a reliable protocol of amide synthesis make them attractive targets for chemists, which has resulted in the development of many name reactions such as Beckmann,[12] Schotten−Baumann,[13] Staudinger ligation,[14] and Schmidt rearrangements.[15] However, these traditional methods suffer from highly harsh conditions, hazardous reagents, functional group intolerances, and low yields. Therefore, the amide synthesis becomes a fascinating field of research pertaining to developing a mild and scalable protocol. Over a decade, the immense contribution of transition metals[16] and metal-free[17] catalytic amide bond formations have resulted in several reports bearing similar strategies all of which involve a direct oxidative amidation of aldehyde or alcohol with amine. Very recently, Jiao and co-workers have reported the utility of azide rearrangement chemistry for Cu-catalyzed synthesis of benzamide derivatives from ketones.[18]

Herein we report a scalable, one-pot copper catalyzed biomimetic synthesis of N-heterocyclic amides from readily available methyl ketones. Our method involves Cu-catalyzed cascade sp$^3$ C−H oxidative cyclization of methyl ketone with 2-

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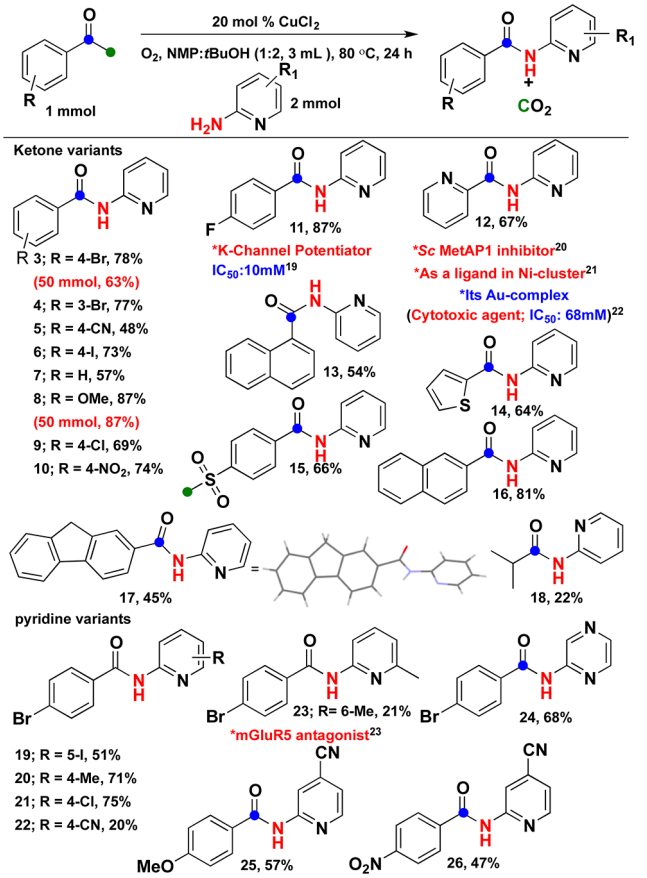
amino heterocycles to the intermediate **I** [eq 2] analogous to luciferin **LnH** [eq 1]. We envisioned that this intermediate **I** could complete the biomimetic process of heterocyclic amide bond formation.

To investigate the proposed biomimetic amide synthesis, we selected 4′-bromoacetophenone **1** and 2-aminopyridine **2** as model substrates. After the extensive screening (refer to Supporting Information (SI)), we could obtain 78% of amide **3** exclusively under 20 mol % $CuCl_2$ in a mixture of NMP and *t*BuOH (1:2).

With optimized conditions in hand, the scope of the biomimetic amide synthesis was examined. A range of methyl ketones and 2-amino pyridines were converted to the corresponding amides in good to excellent yields (Scheme 1).

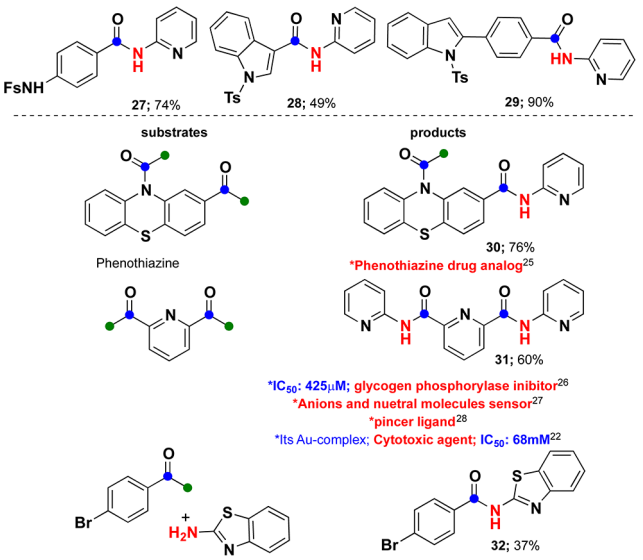
**Scheme 1. Transformation of Aryl and Alkyl Methyl Ketones**




Particularly compelling is the selective assay of $sp^3$ C−H oxidation of methyl ketones into desired amides in the presence of active methyl-sulfone and *N*-acetyl groups; this provides an additional opportunity for further functional group manipulations. Despite the presence of halogen substituents, this biomimetic reaction proceeded smoothly and without any side reactions. This methodology also proved to work consistently with electron-rich and -poor methyl ketones to provide the amides in high yields. Another attractive feature of this method is its scalability; a couple of substrates have been chosen for this purpose and tested at the 50 mmol scale. Subsequently, products, viz. **3** and **8**, were obtained in good yields without much variation in research scale (1 mmol).

We recognized the potential extension of this method to the pharmacophore of biologically relevant indole sulphonamides[24] and phenothiazine[25] (Scheme 2). It is noteworthy that complete chemoselectivity was observed; when we intend to functionalize

**Scheme 2. Active Pharmacophores**




the *C*,*N*-diacetyl phenothiazine, only selective formation of C-acetyl functionalized product **30** was observed, with *N*-acetyl remaining intact. Further we were pleased to find the formation of bis-amide[23,26−28] **31** from the $sp^3$ bifunctionalization of diacetylpyridine in good yield. In addition to 2-amino pyridines and pyrazine, this method has also worked successfully with 2-amino benzothiazole to furnish the product **32** in moderate yield.

Many control experiments have been carried out to probe the mechanism (Scheme 3). To analyze the role of $O_2$, the standard reaction was carried out under an inert atmosphere, which gave 13% of enamine **33** [eq 3]. When we treated this enamine under optimized conditions, the reaction affords 57% of amide **3** [eq 4].

To investigate the reactive intermediates further, we carried out the reaction with 10 mol % of 2-amino pyridine **2** with 1 mmol of *p*-bromoacetophenone **1**, which resulted in the formation of α-keto aldehyde **34** [eq 5]. This observation is also supported by precedential reports[29] that the possible generation of α-keto aldehydes is from an oxygenative reaction of the corresponding enamine via dioxetane formation. To confirm the formation of imidazopyridinone, the reaction was carried out with α-keto aldehyde **34** and 2-amino pyridine using standard reaction conditions without $O_2$, and the amidine analog of luciferin core[30] **36** was isolated in 63% yield [eq 7]. The formation of this amidine moiety might be due to the reactive imidazopyridinone **35** which might have undergone further condensation with excess 2-amino pyridine under an inert atmosphere. Nevertheless, when we treated this amidine **36** under the reaction conditions, the desired amide was isolated in 47% yield [eq 8]. However, this transformation failed to give the product when the reaction was carried out under inert conditions or in the absence of a catalyst. Although these reactive intermediates are in support of the biomimetic Luciferin-Luciferase pathways, the possibility of direct decarboxylative amide formation from α-keto aldehyde **34** suggests avoidance of the biomimetic route.

However, the reaction with aniline failed to give the product under the optimized conditions [eq 9]. Hence, this concludes the biomimetic pathway. To examine the absence of radical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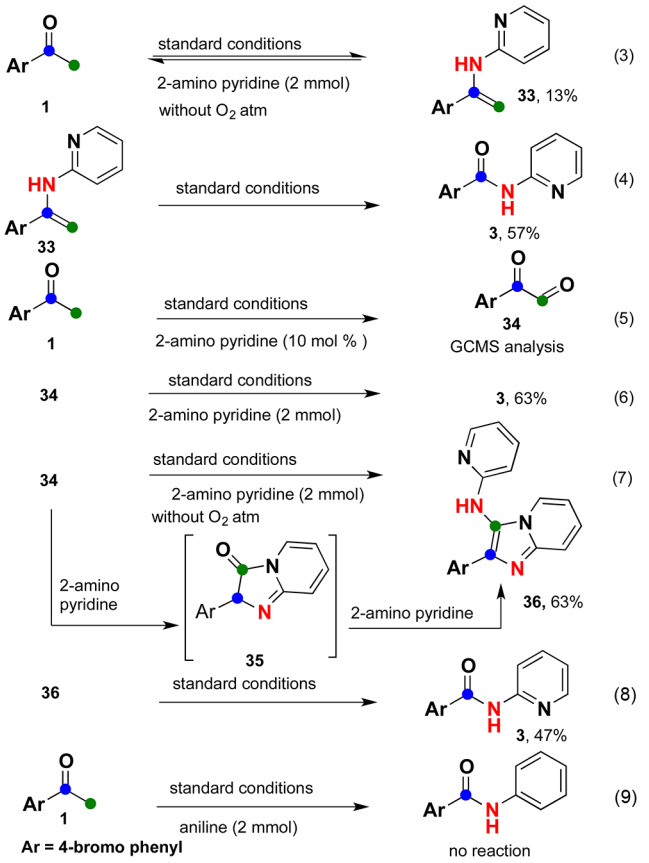
**Scheme 3. Control Experiments**

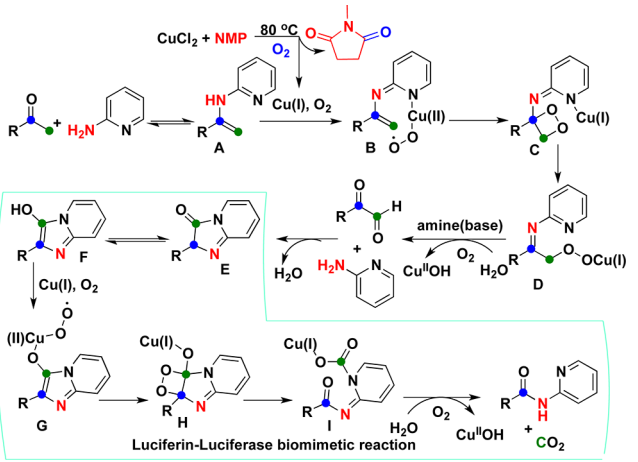



involvements, the reaction was treated with a radical scavenger, TEMPO; the product was isolated without a reduction in yield. Further the reaction was performed in dark shield to confirm the absence of a radical reaction; the desired amide was isolated in 76% yield. After understanding the reactive intermediates, we sought to examine the oxidation state of the catalyst, which is responsible for this cascade transformation. Owing to their various oxidation states and pertaining to the color differences of the copper species, UV−vis spectroscopy was used to study the possible conversion of Cu(II) to Cu(I)[31] (refer to SI). Subsequently, we found *N*-methyl-2-pyrrolidone (used as a solvent) was responsible for this reduction.

Based on the above investigations, a plausible mechanism for the biomimetic amide synthesis is outlined here (Scheme 4). The condensation reaction of methyl ketone and 2-amino pyridine gives reversible enamine **A**. Then this enamine might react with Cu-peroxy radical **B** to provide dioxetane intermediate[31a] **C**. Opening of the dioxetane ring was followed by oxidation to $\alpha$-keto aldehyde and 2-amino pyridine which in turn might condense to afford the luciferin core structure, imidazopyridinone **E**. This imidazopyridinone is a required staring material for the biomimetic Luciferin-Luciferase reactions. Further this intermediate **E** could undergo the Cu-catalyzed dioxetane formation[32b] to give **H**, and subsequent decarboxylation of **I** delivers the amide.

In summary, we have developed an efficient biomimetic route for N-heterocyclic amides from readily available substrates. The reaction is very general, mild, scalable, and tolerant of various functionalities. The salient features of this methodology include selective functionalization of *C*-acetyl in the presence of *N*-acetyl, methyl sulfone and bifunctionalization of diacetyl moieties.

**Scheme 4. Proposed Mechanism**




Further this methodology has also been utilized to synthesize medicinally valuable drug molecules and their pharmacophore analogs.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, characterization data, and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) (a) Lehninger, A. L.; Nelson, D. L.; Cox, M. M. *Principles of Biochemistry*; Worth Publishers: New York, 1993; pp 542−561. (b) Dewick, P. M. *Alkaloids. In Medicinal Natural Products*; John Wiley & Sons, Ltd.: 2009; pp 311−420. (c) Broderick, J. B.; Duffus, B. R.; Duschene, K. S.; Shepard, E. M. *Chem. Rev.* **2014**, *114*, 4229−4317.

(2) (a) Chu, L.; Ohta, C.; Zuo, Z.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2014**, *136*, 10886−10889. (b) Feliks, M.; Martins, B. M.; Ullmann, G. M. *J. Am. Chem. Soc.* **2013**, *135*, 14574−14585. (c) Gooßen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662−664. (d) McDaniel, R.; Ebert-Khosla, S.; Hopwood, D. A.; Khosla, C. *Nature* **1995**, *375*, 549−554. (e) Budin, I.; Devaraj, N. K. *J. Am. Chem. Soc.* **2011**, *134*, 751−753.

(3) Barton, D. H. R.; Serebryakov, E. P. *Proc. Chem. Soc.* **1962**, 309−311.

(4) (a) Hunsdiecker, H.; Hunsdiecker, C. *Chem. Ber.* **1942**, *75*, 291−297. (b) Hussain, H.; Green, I. R.; Ahmed, I. *Chem. Rev.* **2013**, *113*, 3329−3371.

(5) Kolbe, H. *Justus Liebigs Ann. Chem.* **1849**, *69*, 257−294.

(6) (a) Wang, Z. Kochi Reaction. *Comprehensive Organic Name Reactions and Reagents*; John Wiley & Sons, Inc.: 2010. (b) Punniya-



dx.doi.org/10.1021/ol5031266 | *Org. Lett.* XXXX, XXX, XXX−XXX

murthy, T.; Kalra, S. J. S.; Iqbal, J. *Tetrahedron Lett.* **1995**, *36*, 8497−8500.
(7) (a) Fortner, K. C.; Shair, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 1032−1033. (b) Gooßen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662−664. (c) Lalic, G.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2003**, *125*, 2852−2853. (d) Lebedyeva, I. O.; Biswas, S.; Goncalves, K.; Sileno, S. M.; Jackson, A. R.; Patel, K.; Steel, P. J.; Katritzky, A. R. *Chem.—Eur. J.* **2014**, *20*, 11695−11698.
(8) (a) Goossen, L. J.; Collet, F.; Goossen, K. *Isr. J. Chem.* **2010**, *50*, 617−629. (b) Jafarpour, F.; Zarei, S.; Olia, M. B. A.; Jalalimanesh, N.; Rahiminejadan, S. *J. Org. Chem.* **2013**, *78*, 2957−2964. (c) Jiang, Q.; Xu, B.; Jia, J.; Zhao, A.; Zhao, Y.-R.; Li, Y.-Y.; He, N.-N.; Guo, C.-C. *J. Org. Chem.* **2014**, *79*, 7372−7379. (d) Kim, M.; Park, J.; Sharma, S.; Kim, A.; Park, E.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Chem. Commun.* **2013**, *49*, 925−927. (e) Li, X.; Yang, F.; Wu, Y.; Wu, Y. *Org. Lett.* **2014**, *16*, 992−995. (f) Maetani, S.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2013**, *15*, 2754−2757. (g) Manna, S.; Jana, S.; Sahoo, T.; Maji, A.; Maiti, D. *Chem. Commun.* **2013**, *49*, 5286−5288. (h) Nakano, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1851−1854. (i) Nandi, D.; Jhou, Y.-M.; Lee, J.-Y.; Kuo, B.-C; Liu, C.-Y.; Huang, P.-W.; Lee, H. M. *J. Org. Chem.* **2012**, *77*, 9384−9390. (j) Pandey, G.; Bhowmik, S.; Batra, S. *Org. Lett.* **2013**, *15*, 5044−5047. (k) Rokade, B. V.; Prabhu, K. R. *Org. Biomol. Chem.* **2013**, *11*, 6713−6716. (l) Sherden, N. H.; Behenna, D. C.; Virgil, S. C.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 6840−6843. (m) Shi, Z.; Zhang, C.; Tang, C.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3381−3430. (n) Wang, C.; Piel, I.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 4194−4195. (o) Weaver, J. D.; Recio, A.; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846−1913. (p) Yang, H.; Sun, P.; Zhu, Y.; Yan, H.; Lu, L.; Qu, X.; Li, T.; Mao, J. *Chem. Commun.* **2012**, *48*, 7847−7849. (q) Yu, L.; Li, P.; Wang, L. *Chem. Commun.* **2013**, *49*, 2368−2370. (r) Liu, H.; Dong, C.; Zhang, Z.; Wu, P.; Jiang, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 12570−12574. (s) Huang, X.; Li, X.; Zou, M.; Song, S.; Tang, C.; Yuan, Y.; Jiao, N. *J. Am. Chem. Soc.* **2014**, *136*, 14858−14865.
(9) (a) Mosrin, M.; Bresser, T.; Knochel, P. *Org. Lett.* **2009**, *11*, 3406−3409. (b) Oba, Y.; Kato, S.-i.; Ojika, M.; Inouye, S. *Tetrahedron Lett.* **2002**, *43*, 2389−2392. (c) Petushkov, V. N.; Dubinnyi, M. A.; Tsarkova, A. S.; Rodionova, N. S.; Baranov, M. S.; Kublitski, V. S.; Shimomura, O.; Yampolsky, I. V. *Angew. Chem., Int. Ed.* **2014**, *53*, 5566−5568. (d) Shimomura, O.; Johnson, F. H. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1546−1549.
(10) (a) Jones, L. R.; Goun, E. A.; Shinde, R.; Rothbard, J. B.; Contag, C. H.; Wender, P. A. *J. Am. Chem. Soc.* **2006**, *128*, 6526−6527. (b) Li, J.; Chen, L.; Du, L.; Li, M. *Chem. Soc. Rev.* **2013**, *42*, 662−676. (c) Naumov, P.; Wu, C.; Liu, Y.-J.; Ohmiya, Y. *Photochem. Photobiol. Sci.* **2012**, *11*, 1151−1155.
(11) (a) Montalbetti, C. A. G. N.; Falque, V. *Tetrahedron* **2005**, *61*, 10827−10852. (b) Noda, H.; Bode, J. W. *Chem. Sci.* **2014**, *5*, 4328−4332.
(12) Horning, E. C.; Stromberg, V. L.; Lloyd, H. A. *J. Am. Chem. Soc.* **1952**, *74*, 5153−5155.
(13) Baumann, E. *Ber. Dtsch. Chem. Ges. A/B* **1886**, *19*, 3218−3222.
(14) Saxon, E.; Bertozzi, C. R. *Science* **2000**, *287*, 2007−2010.
(15) Schmidt, K. F. *Ber. Dtsch. Chem. Ges. A/B* **1924**, *57*, 704−706.
(16) (a) Tillack, A.; Rudloff, I.; Beller, M. *Eur. J. Org. Chem.* **2001**, 523−528. (b) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790−792. (c) Gowda, R. R.; Chakraborty, D. *Eur. J. Org. Chem.* **2011**, 2226−2229. (d) Yoo, W.-J.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 13064−13065. (e) Allen, C. L.; Williams, J. M. J. *Chem. Soc. Rev.* **2011**, *40*, 3405−3415. (f) Seo, S.; Marks, T. J. *Org. Lett.* **2007**, *10*, 317−319. (g) Ekoue-Kovi, K.; Wolf, C. *Chem.—Eur. J.* **2008**, *14*, 6302−6315. (h) Suto, Y.; Yamagiwa, N.; Torisawa, Y. *Tetrahedron Lett.* **2008**, *49*, 5732−5735. (i) Pattabiraman, V. R.; Bode, J. W. *Nature* **2011**, *480*, 471−479.
(17) (a) Gao, J.; Wang, G.-W. *J. Org. Chem.* **2008**, *73*, 2955−2958. (b) Ghosh, H.; Patel, B. K. *Org. Biomol. Chem.* **2010**, *8*, 384−390. (c) Li, X.-Q.; Wang, W.-K.; Han, Y.-X.; Zhang, C. *Adv. Synth. Catal.* **2010**, *352*, 2588−2598. (d) Reddy, K. R.; Maheswari, C. U.; Venkateshwar, M.; Kantam, M. L. *Eur. J. Org. Chem.* **2008**, 3619−3622.
(18) Tang, C.; Jiao, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 6528−6532.
(19) Gao, Z.; Zhang, T.; Wu, M.; Xiong, Q.; Sun, H.; Zhang, Y.; Zu, L.; Wang, W.; Li, M. *J. Biol. Chem.* **2010**, *285*, 28322−28332.
(20) Luo, Q.-L.; Li, J.-Y.; Liu, Z.-Y.; Chen, L.-L.; Li, J.; Ye, Q.-Z.; Nan, F.-J. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 635−638.
(21) Wang, K.; Shen, M.; Sun, W.-H. *Polyhedron* **2010**, *29*, 564−568.
(22) Patel, M. N.; Bhatt, B. S.; Dosi, P. A. *Spectrochim. Acta, Part A* **2013**, *110*, 20−27.
(23) (a) Kulkarni, S. S.; Zou, M.-F.; Cao, J.; Deschamps, J. R.; Rodriguez, A. L.; Conn, P. J.; Newman, A. H. *J. Med. Chem.* **2009**, *52*, 3563−3575. (b) Schrøder, T. J.; Christensen, S.; Lindberg, S.; Langgård, M.; David, L.; Maltas, P. J.; Eskildsen, J.; Jacobsen, J.; Tagmose, L.; Simonsen, K. B.; Biilmann Rønn, L. C.; de Jong, I. E. M.; Malik, I. J.; Karlsson, J.-J.; Bundgaard, C.; Egebjerg, J.; Stavenhagen, J. B.; Strandbygård, D.; Thirup, S.; Andersen, J. L.; Uppalanchi, S.; Pervaram, S.; Kasturi, S. P.; Eradi, P.; Sakumudi, D. R.; Watson, S. P. *Bioorg. Med. Chem. Lett.* **2014**, *24*, 177−180.
(24) (a) Breteche, A.; Duflos, M.; Dassonville, A.; Nourrisson, M.-R.; Brelet, J.; Le Baut, G.; Grimaud, N.; Petit, J.-Y. *J. Enzyme Inhib. Med. Chem.* **2002**, *17*, 415−424. (b) Duflos, M.; Nourrisson, M.-R.; Brelet, J.; Courant, J.; LeBaut, G.; Grimaud, N.; Petit, J.-Y. *Eur. J. Med. Chem.* **2001**, *36*, 545−553. (c) Luo, Q.-L.; Li, J.-Y.; Liu, Z.-Y.; Chen, L.-L.; Li, J.; Ye, Q.-Z.; Nan, F.-J. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 635−638. (d) Maren, T. H. *Annu. Rev. Pharmacol. Toxicol.* **1976**, *16*, 309−327.
(25) (a) Yale, H. L.; Sowinski, F.; Bernstein, J. *J. Am. Chem. Soc.* **1957**, *79*, 4375−4379. (b) Yorston, G.; Pinney, A. *Psychiatric Bulletin* **2000**, *24*, 130−132. (c) Tsitsa, P.; Psarrea-Sandris, A.; Sandris, C. *J. Heterocycl. Chem.* **1987**, *24*, 1661−1663.
(26) Chen, L.; Li, H.; Liu, J.; Zhang, L.; Liu, H.; Jiang, H. *Bioorg. Med. Chem.* **2007**, *15*, 6763−6774.
(27) Dorazco-González, A.; Höpfl, H.; Medrano, F.; Yatsimirsky, A. K. *J. Org. Chem.* **2010**, *75*, 2259−2273.
(28) Hou, H.; Wei, Y.; Song, Y.; Mi, L.; Tang, M.; Li, L.; Fan, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 6067−6074.
(29) (a) Zhang, J.; Wei, Y.; Lin, S.; Liang, F.; Liu, P. *Org. Biomol. Chem.* **2012**, *10*, 9237−9242. (b) Zhang, J.; Liu, Y.; Chiba, S.; Loh, T.-P. *Chem. commun.* **2013**, *49*, 11439−11441. (c) Du, F.-T.; Ji, J.-X. *Chem. Sci.* **2012**, *3*, 460−465.
(30) (a) Alcaide, B.; Pérez-Ossorio, R.; Plumet, J.; Sierra, M. A. *Tetrahedron Lett.* **1986**, *27*, 1627−1630. (b) Alcaide, B.; Plumet, J.; Sierra, M. A.; Vicent, C. *J. Org. Chem.* **1989**, *54*, 5763−5768.
(31) (a) Franc, G.; Jutand, A. *Dalton Trans.* **2010**, *39*, 7873−7875. (b) Wang, Y.-F.; Toh, K. K.; Lee, J.-Y.; Chiba, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 5927−5931. (c) Subramanian, P.; Kaliappan, K. P. *Eur. J. Org. Chem.* **2014**, 5986−5997.
(32) (a) Sun, H.; Yang, C.; Gao, F.; Li, Z.; Xia, W. *Org. Lett.* **2013**, *15*, 624−627. (b) Wang, X.; Wang, D. Z. *Tetrahedron* **2011**, *67*, 3406−3411.