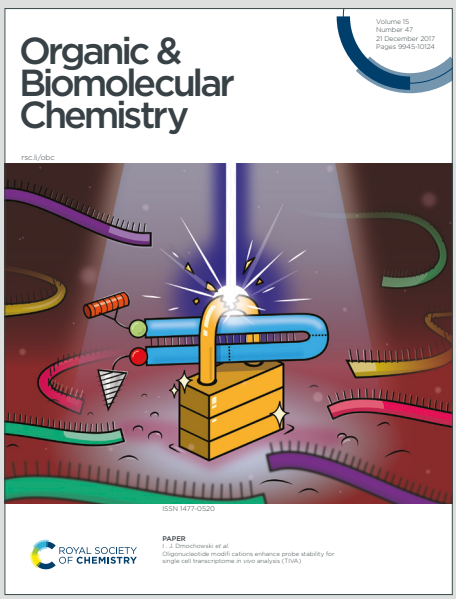
Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Wang, C. Li, Y. Zhang, B. Zhang and K. Sun, *Org. Biomol. Chem.*, 2019, DOI: 10.1039/C9OB01530B.



ROYAL SOCIETY OF CHEMISTRY

rsc.li/obc

ROYAL SOCIETY OF CHEMISTRY View Article Online
DOI: 10.1039/C9OB01530B

Journal Name

COMMUNICATION

Direct Methyl C(sp³)–H Azolation of Thioanisoles via Oxidative Radical Coupling

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

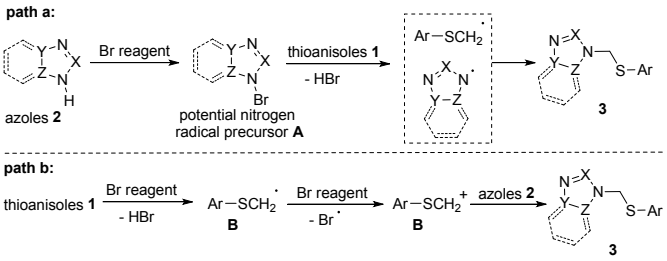
www.rsc.org/

Xin Wang,[ab] Changhao Li,[a] Yixiao Zhang,[a] Bing Zhan,[b] and Kai Sun[a]*

A method for metal-free, 1,3-dibromo-5,5-dimethylhydantoin mediated methyl C(sp³)–H bond azolation of thioanisoles has been developed, affording a facile route for the construction of nitrogen-functionalized thioanisoles, possibly via a nitrogen-centered radical process. This reaction represents an important addition to the limited number of existing methods for the methyl C(sp³)–H bond functionalization of thioanisoles, and may be find practical application in the synthesis of nitrogen-alkylated azoles.

Methods for the construction of C–N bonds are of considerable interest in synthetic chemistry because nitrogen-containing compounds are of importance in medicinal and agricultural fields.[1] To date, substantial progress has been made regarding C(sp³)–H amidations, imidations, and azolations at allylic[2] and arylmethylic positions[3] and at the C–H bond adjacent to nitrogen or oxygen atoms.[4-5] However, there has been limited work disclosed on the direct methyl C(sp³)–H amidation of the more challenging thioanisoles[6] and anisoles.[7] Thioanisoles are prevalent structural components in agrochemicals and in compounds involved in material science. The corresponding sulfoxides and sulfones are important compounds in medicinal and synthetic chemistry.[8] Direct C–N bond construction at the methyl C(sp³)–H bond of thioanisoles using *N*-nucleophiles is a highly appealing goal. However, challenges still exist because thioanisoles can be easily oxidized during the amidation step. Therefore, it is desirable to develop a convenient procedure for the *N*-functionalization of the methyl C(sp³)–H bond of thioanisoles under mild reaction conditions.

As part of our continued interest in C–N bond construction,[9] we have previously described the oxidative imidation of the methyl C(sp³)–H bond with anisoles.[9b] For the methyl C(sp³)–H functionalization of thioanisoles, rather than anisoles, we envisioned that the use of a mild Br reagent as a potential single electron oxidant or amino radical initiator, would allow for an accelerated nitrogen radical-based methyl C(sp³)–H azolation step. Thus, this method would overcome the problematic competing oxidation reaction. As shown in Scheme 1, the *N*-nucleophile react with a Br reagent to form the relatively active nitrogen radical precursor **A**. Subsequently, H-abstraction with the Br radical generated from homolysis of the N-Br bond of **A** would generate the active amino radical and sulfide methyl radical **B**. Finally, coupling between amino radical and **B** would lead to the final product and regeneration of the Br radical to participate in the next catalytic cycle (path a). Alternatively, the active sulfide methyl radical **B** would genereted through a hydrogen atom capture pathway with Br reagent. Subsequently, single electron oxidation of **B** would genereted a sulfide methyl cation **C**, which would react with *N*-nucleophile to deliver the final product (path b).



Scheme 1. Azolation of thioanisoles.

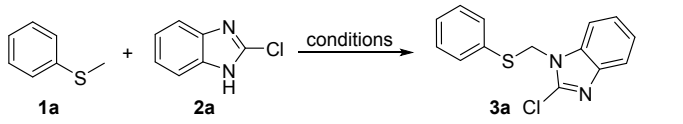
Considering that imidazoles, triazoles, and tetrazoles are the largest chemical family that exists in medicinal and pesticide chemistry,[10] the direct *N*-functionalization of imidazoles, triazoles, and tetrazoles has also attracted considerable interest.[11] Therefore, we herein report a 1,3-dibromo-5,5-dimethylhydantoin (DBDMH)-mediated oxidative radical azolation that enables the installation of biologically attractive imidazole, triazole, and tetrazole skeletons into the methyl C(sp³)–H bonds of thioanisoles.

The initial reaction screening focused on bromide reagents, which can act as efficient amino radical initiators. Hence, *N*-bromosuccinimide (NBS) was initially screened to stimulate the model reaction with methyl(phenyl)sulfane **1a** and 2-chloro-1*H*-benzo[*d*]imidazole **2a** in DCE at 90 °C. To our delight, the coupling product **3a** was formed in 23% yield (Table 1, entry 1). Encouraged

[a] College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, P. R. China E-mail: sunk468@nenu.edu.cn
[b] College of chemistry and energy, Zhengzhou University, Zhengzhou 450001, P. R. China.

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Table 1. Optimization of the reaction conditions.[a]



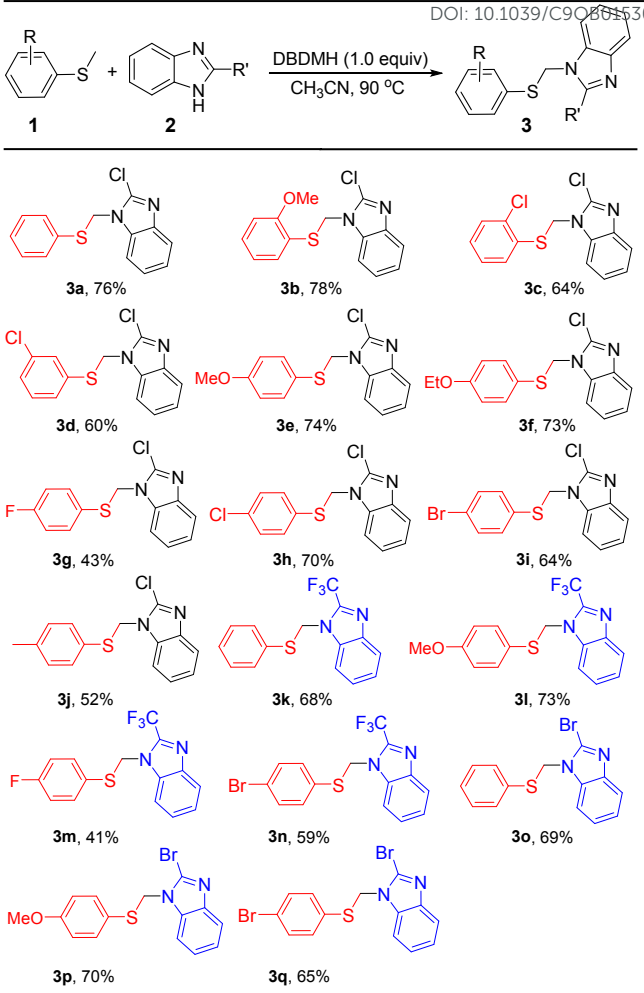
Entry	Initiator	Solvent	Temp. (°C)	yieldof **3a** (%)[b]
1	NBS	DCE	90	23
2	Br_2	DCE	90	0
3	DBDMH	DCE	90	58
4	I_2O_5	DCE	90	0
5	DIB	DCE	90	0
6	DBDMH	EtOAc	90	0
7	DBDMH	toluene	90	26
8	DBDMH	CH_3CN	90	51
9	DBDMH	$CHCl_3$	90	47
10	DBDMH	CH_3CN	90	55[c]
11	DBDMH	CH_3CN	90	76[d]
12	DBDMH	CH_3CN	90	74[e]
13	DBDMH	CH_3CN	120	34[d]
14	DBDMH	CH_3CN	60	61[d]
15	no	CH_3CN	90	0

[a] Reactions were carried out with methyl(phenyl)sulfane **1a** (0.3 mmol), 2-chloro-1*H*-benzo[*d*]imidazole **2a** (0.3 mmol), initiator (1.0 equiv.) in solvent (1.0 mL) at 90 °C for 12 h. [b] Yield of the isolated product. [c] 3 equiv. of methyl(phenyl)sulfane **1a** was added instead of solvent. [d] 6 equiv. of methyl(phenyl)sulfane **1a** was added instead of solvent. [e] 10 equiv. of methyl(phenyl)sulfane **1a** was added instead of solvent.

by this result, Br_2 and 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) were tested as initiators, and DBDMH proved to be an efficient amino radical initiator, giving the desired product **3a** in 58% yield (entries 2–3). Previous investigations have indicated that hypervalent iodine reagents can act as efficient single-electron oxidants. However, no reaction occurred when iodine pentoxide and (diacetoxyiodo)benzene (DIB) were used as single-electron oxidants (entries 4–5). Solvents screening revealed that EtOAc and toluene were not suitable for the reaction (entries 6–7), while CH_3CN and $CHCl_3$ afforded **3a** in 51% and 47% yields, respectively (entries 8–9). Further experimental results showed that when 6 equiv. of methyl(phenyl)sulfane **1a** was added, the corresponding product **3a** was isolated in good yield (entries 10–12). The yield of product **3a** decreased when the temperature was increased to 120 °C, and the corresponding sulfoxide was the main product (entry 13). A low yield was also obtained when the temperature was decreased to 60 °C (entry 14). In the absence of DBDMH, compounds **1a** and **2a** were fully recovered, and no desired product **3a** was observed, suggesting that DBDMH is essential for this reaction (entry 15).

With the optimal conditions in hand, the generality of the method was explored, and the results are summarized in Table 2. Reactions between the thioanisoles **1** and 2-chloro-1*H*-benzo[*d*]imidazole **2a** were tested, and thioanisoles **1** with electron-donating groups (OMe, OEt) on the benzene ring were smoothly converted into the corresponding products **3b**, **3e**, and **3f** in good yields (73%–78%). Substrates bearing electron-withdrawing halogen

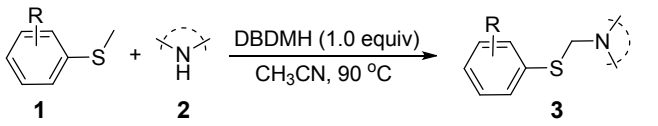
Table 2. Direct C(sp^3)–H azolation of thioanisoles with azoles.[a,b]



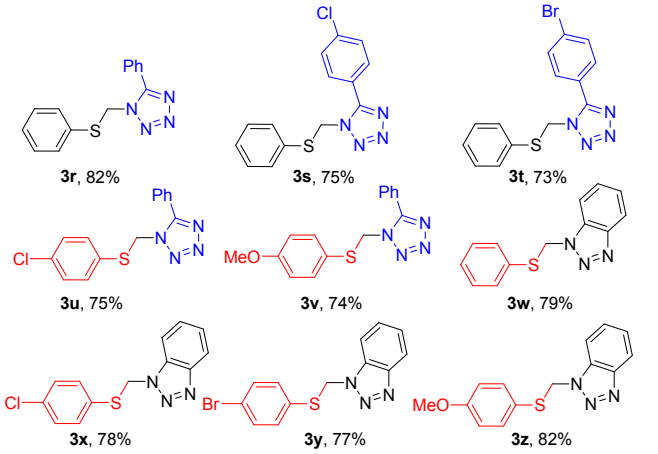
[a] Reaction conditions: **1** (1.8 mmol), azoles **2** (0.3 mmol), DBDMH (1.0 equiv) at 90 °C in CH_3CN (1 mL). [b] Yield of isolated product.

atoms, such as fluoro, chloro, and bromo, on the aromatic ring were then investigated and found to be well tolerated under the present reaction conditions, affording the corresponding products **3c–3i** in moderate to good yields (43%–74%), which should allow for further synthetic transformations. The steric effect had no obvious impact on this reaction, with *o*-, *m*-, and *p*-Cl substituted thioanisoles being efficiently converted to the coupling products **3c**, **3d**, and **3h**, respectively. In the case of substrates bearing a strong electron-withdrawing nitro group, no coupling product was observed, and the corresponding oxidized sulfoxide was isolated. It is noteworthy that methyl(*p*-tolyl)sulfane **1j** gave the methylthio azolated product **3j**, with the methyl group remaining intact, which is inconsistent with our previously reported results.[9b] Next, the substituted 2-(trifluoromethyl) 1*H*-benzo[*d*]imidazole and 2-bromo-1*H*-benzo[*d*]imidazole were also reacted with thioanisoles, furnishing the desired products **3k**–**3q** in moderate to good yields (41%–73%). Tetrazoles are of great importance because of their wide application in medicinal chemistry, organic chemistry, and material science; therefore, the development of practical synthetic routes for tetrazole-based compounds is attractive. To further explore the

Table 3. Direct C(sp^3)–H azolation of thioanisoles with triazole and tetrazoles.[a,b]



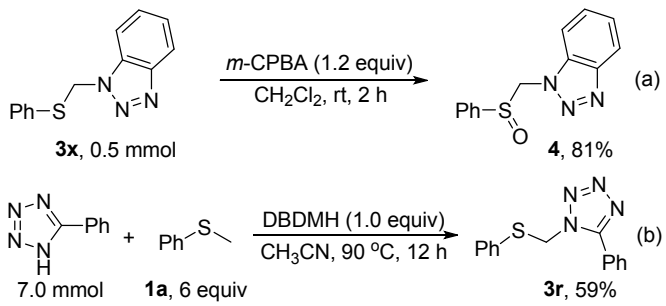
1 2 3



[a] Reaction conditions: **1** (1.8 mmol), azoles **2** (0.3 mmol), DBDMH (1.0 equiv) at 90 °C in CH_3CN (1mL). [b] Yield of isolated product.

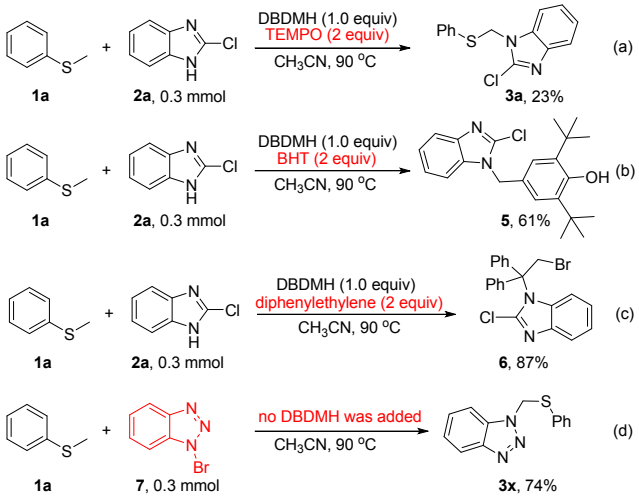
potential of our methodology, 5-phenyl-1*H*-tetrazoles were also Briefly investigated, and were found to react smoothly with thioanisole 1a, providing the desired products 3r–3t in good to high yields (73%–82%). In addition, reactions between 5-phenyl-1*H*-tetrazole and substituted thioanisoles were performed, affording the desired products **3u** and **3v** in good yields (75% and 74%). Finally, benzotriazole was also found to be a good coupling partner in this transformation, with the corresponding products **3w**–**3z** obtained in high yields (77%–82%).

To demonstrate the synthetic utility of this protocol, we investigated further manipulations of the azolated products **3**. When treating **3x** with 1.2 equivent of *m*-chloroperoxybenzoic acid (*m*-CPBA) at room temperature, the corresponding sulfoxide **4** could be obtained in 81% yield (Scheme 2a). Furthermore, the gram-scale reaction with **1a** and 5-phenyl-1*H*-tetrazole was conducted, and found 59% of **3r** could be isolated with 7.0 mmol 5-phenyl-1*H*-tetrazole.



Scheme 2. Application investigation.

To gain insight into the reaction mechanism, several control experiments were conducted. When 2.0 equivent of 2,2,6,6-tetramethylpiperidinooxy (TEMPO) was employed in the reaction of methyl(phenyl)sulfane **1a** with 2-chloro-1*H*-benzo[*d*]imidazole **2a**, only a 23% yield of **3a** was obtained (Scheme 3a). Upon addition of 2.0 equivent of 2,6-di-*tert*-butyl-4-methylphenol (BHT), the formation of the desired **3a** was completely suppressed, and the benzylic C–H azolated product **5** was obtained in 61% yield (Scheme 3b). In addition, the azol-bromination product **6** could be isolated in 87% yield when 2.0 equivent of 1,1-diphenylethylene was added (Scheme 3c). These results support the theory that the azolation might be a radical reaction and that an *N*-radical is involved in the azolation process. To provide further evidence regarding the nature of the active intermediate, we prepared the N-Br reagent **7** according to a previous literature report.[12] When the reaction between **1a** and **7** was performed at room temperature, **3x** could be isolated in high yield (Scheme 3d). This result supports our previous assumption in Scheme 1 (path a) that the N-Br reagent generated *in situ* may be the key active intermediate to stimulate the methyl C(sp^3)–H bond azolation of thioanisoles.



Scheme 3. Reactions determining the reaction mechanism.

Conclusions

In summary, we have developed a mild, economical, and practical DBDMH-mediated azolation of thioanisoles, with azoles as nitrogen nucleophiles, involving methyl C(sp^3)–H bond oxidative radical functionalization. The generality of this reaction was demonstrated using various thioanisoles with benzimidazoles, 5-phenyl-1*H*-tetrazoles, and benzotriazole, to produce a series of structurally diverse *N*-alkyl substituted thioanisoles. Based on control experiments, a possible radical mechanism was proposed to explain the azolation reaction. Further study of the applications of this reaction is currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21801007), the Program for Innovative Research Team of Science and Technology in the University of Henan Province (18IRTSTHN004, 18HASTIT006), the Science and Technology Plan Projects of Henan Province (19A150015) and the Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis (130028911).

Notes and references

1 (a) J. Kim, M. Movassaghi, *Acc. Chem. Res*., 2015, **48**, 1159−1171; (b) J. Jiao, K. Murakami, K. Itami, *ACS Catal*., 2016, **6**, 610−633; (c) S. Tang, Y.-L. Deng, J. Li, W.-X. Wang, Y.-C. Wang, Z.-Z. Li, L. Yuan, S.-L. Chen, R.-L. Sheng, *Chem. Commun*., 2016, **52**, 4470−4473; (d) Y. Park, Y. Kim, S. Chang, *Chem. Rev*., 2017, **117**, 9247−9301; (e) Y. N. Timsina, B. F. Gupton, K. C. Ellis, *ACS Catal*., 2018, **8**, 5732−5776; (f) W. Wei, L. Wang, P. Bao, Y. Shao, H. Yue, D. Yang, X. Yang, X. Zhao, H. Wang, *Org. Lett.,* 2018, **20**, 7125−7130; (g) J. Yu, H.-X. Sheng, S.-W. Wang, Z.-H. Xu, S. Tang, S.-L. Chen, *Chem. Commun*., 2019, **55**, 4578−4581; (h) K. Sun, B.-X. Luan, Z.-H. Liu, J.-L. Zhu, J.-K. Du, E.-Q. Bai, Y. Fang, B. Zhang, *Org. Biomol. Chem*., 2019, **17**, 4208−4211; (i) L.-Y. Xie, S. Peng, L.-L. Jiang, X. Peng, W. Xia, X. Yu, X.-X. Wang, Z. Cao, W.-M. He, *Org. Chem. Front.*, 2019, **2**, 167−171; (j) B.-Z. Tang, J.-Z. Li, A.-W. Zhang, W.-J. Hao, S.-J. Tu, B. Jiang, *Adv. Synth. Catal.*, 2019, **361**, 3394−3402; (k) R. Fu, M.-F. Li, P. Zhou, W.-J. Hao, S.-J. Tu, B. Jiang, *Adv. Synth. Catal.,* 2019, **361**, 2280−2285.

2 For selected works, see: (a) M. Harvey, D. Musaev, J. Du Bois, *J. Am. Chem. Soc*., 2011, **133**, 17207−17216; (b) S. M. Paradine, M. C. White, *J. Am. Chem. Soc*., 2012, **134**, 2036; (c) H. Bao, U. K. Tambar, *J. Am. Chem. Soc*., 2012, **134**, 18495−18498; (d) Y. Nishioka, T. Uchida, T. Katsuki, *Angew. Chem*., *Int. Ed*., 2013, **52**, 1739−1742; (e) T. W. Liwosz, S. R. Chemler, *Chem.−Eur. J*., 2013, **19**, 12771−12777; (f) E. S. Jang, C. L. McMullin, M. Kab, K. Mayer, T. R. Cundari, T. H. Warren, *J. Am. Chem. Soc*., 2014, **136**, 10930−10940; (g) X. Zhang, H. Xu, C. Zhao, *J. Org. Chem*., 2014, **79**, 9799; (h) X. Zhang, M. Wang, P. Li, L. Wang, *Chem. Commun*., 2014, **50**, 8006−8009; (i) J.-W. Sun, Y. Wang, Y. Pan, *J. Org. Chem*., 2015, **80**, 8945−8950.

3 (a) Z.-K Ni, Q. Zhang, T. Xiong, Y.-Y. Zheng, Y. Li, H.-W. Zhang, J.-P. Zhang, Q. Liu, *Angew. Chem.*, *Int. Ed*., 2012, **51**, 1244−1247; (b) H. Wang, D. Zhang, C. Bolm, *Angew. Chem.*, *Int. Ed*., 2018, *57*, 5863−5866; (c) R. Hayashi, A. Shimizu, Y. Song, Y. Ashikari, T. Nokami, J. Yoshida, *Chem. Eur. J*., 2016, **23**, 61−64; (d) C. Liu, Q. Zhang, H.-B. Li, S.-X. Guo, B. Xiao, W. Deng, L. Liu, W. He, 2016, *Chem. Eur. J*., 2016, **22**, 6208–6212; (e) L. Li, J.-J. Chen, Y.-J. Li, X.-B. Bu, Q. Liu, Y.-L. Zhao, *Angew. Chem.*, *Int. Ed*., 2015, **54**, 12107–12111; (f) G. Pandey, R. Laha, *Angew. Chem.*, *Int. Ed*., 2015, **54**, 14875–14879; (g) J.-Y. Liu, H.-Y. Niu, S. Wu, G.-R. Qu, H.-M. Guo, *Chem. Commun*., 2012, **48**, 9723–9725.

4 For selected works, see: (a) C. Zhang, C. K. De, R. Mal, D. Seidel, *J. Am. Chem. Soc*., 2008, **130**, 416–417; (b) Y.-M. Zhang, H. Fu, Y.-Y. Jiang, Y.-F. Zhao, *J. Am. Chem. Soc*., 2008, **130**, 416–417; (c) Q.-Q Xia, W.-Z. Chen, *J. Org. Chem*., 2012, **77**, 9366–9373; (d) R. T. Gephart, T. H. Warren, *Organometallics*, 2012, **31**, 7728−7752; (e) H. Aruri, U. Singh, M. Kumar, S. Sharma, S. K. Aithagani, V. K. Gupta, S. Mignani, R. A. Vishwakarma, P. P. Singh, *J. Org. Chem*., 2017, **82**, 1000–1012; (f) X.-H. Ouyang, R.-J. Song, J.-H. Li, *Chem.–Asian J*., 2018, **13**, 2316-2332.

5 For selected works, see: (a) S. Pan, J. Liu, H. Li, Z. Wang, X. Guo, Z. Li, *Org. Lett*., 2010, **12**, 1932–1935; (b) L. Zhou, S. Tang, X. Qi, C. Lin, K. Liu, C. Liu, Y. Lan, A. Lei, *Org. Lett*., 2014, **16**, 3404–3407; (c) L. Dian, S. Wang, D. Zhang-Negrerie, Y. Du, K. Zhao, *Chem. Commun*., 2014, **50**, 11738–11741; (d) I. Buslova, X. Hu, *Adv. Synth. Catal*., 2014, **356**, 3325–3330; (e) H. Aruri, U. Singh, S. Sharma, S. Gudup, M. Bhogal, S. Kumar, D. Singh, V. K. Gupta, R. Kant, R. A. Vishwakarma, P. P. Singh, *J. Org. Chem*., 2015, **80**, 1929–1936; (f) K. Q. Zhu, L. Wang, Q. Chen, M. Y. He, *Tetrahedron Lett*., 2015, **56**, 4943–4946; (g) M. K. Singh, H. K. Akula, S. S. Kumar, L. Stahl, M. K. Lakshman, *ACS Catal*., 2016, **6**, 1921–1928; (h) Q. Yang, P. Y. Choy, W. C. Fu, B. Fan, F. Y. Kwong, *J. Org. Chem*., 2015, **80**, 11193–1119; (i) S.-R Guo, P. Sa. Kumar, M.-H. Yang, *Adv. Synth. Catal*., 2017, **359**, 2-25; (j) Y.-Z. Yang, R.-J. Song, J.-H. Li, *Org. Lett*., 2019, **21**, 3228–3231.

6 Z.-H. Yang, S.-Y. Yang, J.-X. Xu, *Tetrahedron*, 2017, **73**, 3240−3248.

7 (a) K. Sun, X. Wang, G. Li, Z.-H. Zhu, Y.-Q. Jiang, B.-B. Xiao, *Chem. Commun*., 2014, **50**, 12880−12883; (b) S. Rajamanickam, G. Majji, S. K. Santra, B. K. Patel, *Org. Lett*., 2015, **17**, 5586−5589.

8 (a) A. M. Bunker, D. F. Ortwine, PCT Int. Appl. 2004, WO 2004014379 A1 20040219; (b) C. Curti, M. Laget, A. O. Carle, A. Gellis, P. Vanelle, *Eur. J. Med. Chem*., 2007, **42**, 880−884; (c) W.-M. Xu, S. Yang, P. Bhadury, J. He, M. He, L.-L. Gao, D.-Y. Hu, B. Song, *Pestic. Biochem. Phys*., 2011, **101**, 6−15; (d) X. Wan, K. Sun, G.-S. Zhang, *Sci. China Chem*., 2016, **60**, 353−357; (e) Q. Liu, L. Wang, H. Yue, J-S. Li, Z. Luo, W. Wei, *Green Chem.*, 2019, **21**, 1609−1613; (f) L. Wang, Y. Zhang, M. Zhang, P. Bao, X. Lv, H-G. Liu, X. Zhao, J-S. Li, Z. Luo, W. Wei, *Tetrahedron Lett.,* 2019, **60**, 1845−1848; (g) L.-Y. Xie, T.-G. Fang, J.-X. Tan, B. Zhang, Z. Cao, L.-H. Yang, W.-M. He, *Green Chem*., 2019, **21**, 3858−3863; (h) F.-L. Zeng, X. Chen, S.-Q. He, K. Sun, Y. Liu, R. Fu, L. Qu, Y. Zhao and B. Yu, *Org. Chem. Front.*, 2019, **6**, 1476−1480.

9 (a) K. Sun, Y. Li, T. Xiong, J.-P. Zhang, Q. Zhang, *J. Am. Chem. Soc*., 2011, **133**, 1694–1697; (b) K. Sun, X. Wang, G. Li, Z.-H. Zhu, Y.-Q. Jiang, B.-B. Xiao, *Chem. Commun*., 2014, **50**, 12880−12883; (c) X. Wang, K. Sun, Y.-H. Lv, F.-J. Ma, G. Li, D.-H. Li, Z.-H. Zhu, Y.-Q. Jiang, F. Zhao, *Chem.–Asian J*., 2014, **9**, 3413−3416; (d) K. Sun, X. Wang, Y.-Q. Jiang, Y.-H. Lv, L.-P. Zhang, B.-B. Xiao, D.-H. Li, Z.-H. Zhu, L. Liu, *Chem.–Asian J*., 2015, **10**, 536−539; (e) K. Sun, X. Wang, L.-L. Liu, J.-J. Sun, X. Liu, Z.-D. Li, Z.-G. Zhang, G.-S. Zhang, *ACS Catal*., 2015, **5**, 7194−7198; (f) K. Sun, Y. Li, Q. Zhang, *Sci. China Chem*., 2015, **58**, 1354−1358; (g) K. Sun, Z.-H. Zhu, J.-J. Sun, L.-L. Liu, X. Wang, *J. Org. Chem*., 2016, **81**, 1476−1483; (h) K. Sun, Z.-D. Shi, Z.-H. Liu, B.-X. Luan, J.-L. Zhu, Y.-R. Xue, *Org. Lett*., 2018, **20**, 6687−6690; (i) K. Sun, S.-N. Wang, R.-R. Feng, Y.-X. Zhang, X. Wang, Z.-G. Zhang, B. Zhang, *Org. Lett*., 2019, **21**, 2052−2055.

10 (a) X.-Z. Hu, J.-X. Wang, Y.-Q. Feng, *J. Agric. Food Chem*., 2010, **58**, 112−115; (b) M. Danaher, H. De Ruyck, S. R. H. Crooks, G. Dowling, M. O'Keeffe, *J. Chromatogr. B*., 2007, **845**, 1−37; (c) M. Halder, M. M. Islam, P. Singh, A. S. Roy, S. M. Islam, K. Sen, *ACS Omega*, 2018, **3**, 8169−8180; (d) M. I. Fernandez-Bachiller, C. Perez, L. Monjas, J. Rademann, M. I. Rodríguez-Franco, *J. Med. Chem*., 2012, **55**, 1303−1317; (e) S. G. Das, B. Srinivasan, D. L. Hermanson, N. P. Bleeker, J. M. Doshi, R. Tang, W. T. Beck, C. Xing, *J. Med. Chem*., 2011, **54**, 5937−5948 and references therein.

11 (a) L. Wang, K.-Q. Zhu, Q. Chen, M.-Y. He, *J. Org. Chem*., 2014, **79**, 11780−11786; (b) D. W. Piotrowski, A. S. Kamlet, A. R. Dechert-Schmitt, J.-L. Yan, T. A. Brandt, J. Xiao, L.-Q. Wei, M. T. Barrila, *J. Am. Chem. Soc*., 2016, **138**, 4818−4823; (c) J.-W. Wu, Y. Zhou, Y.-C. Zhou, C.-W. Chiang, A.-W. Lei, *ACS Catal*., 2017, ***7***, 8320−8323; (d) L. Wang, K.-Q. Zhu, W.-T. Wu, Q. Chen, M.-Y. He, *Catal. Sci. Technol*., 2015, **5**, 2891−2896; (e) L.-Y. Xie, J. Qu, S. Peng, K.-J. Liu, Z. Wang, M.-H. Ding, Y. Wang, Z. Cao, W.-M. He, *Green Chem*., 2018, **20**, 760−764; (f) K. Sun, S.-J. Li, X. Chen, Y. Liu, X. Huang, D. Wei, L. Qu, Y. Zhao and B. Yu, *Chem. Commun.*, 2019, **55**, 2861−2864 and references therein.

12 A. A. Manesh, A. Khazaei, *Asian J. Chem*. 2011, **23**, 624−626.

View Article Online
DOI: 10.1039/C9OB01530B