ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

Cite this: DOI: 10.1039/c5qo00311c

Copper-catalyzed domino synthesis of benzo[*b*]thiophene/imidazo[1,2-*a*]pyridines by sequential Ullmann-type coupling and intramolecular C(sp^2)–H thiolation†

Kelu Yan, Daoshan Yang,* Wei Wei, Shenglei Lu, Guoqing Li, Caixia Zhao, Qingyun Zhang and Hua Wang*

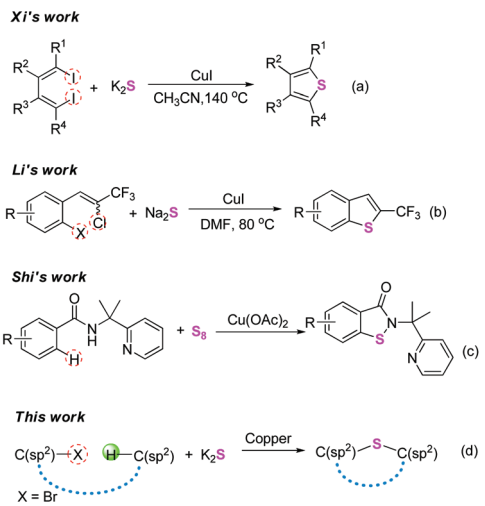
Received 10th October 2015,
Accepted 14th November 2015

DOI: 10.1039/c5qo00311c

rsc.li/frontiers-organic

The copper-catalyzed double C–S bond formation *via* Ullmann-type *S*-arylation and C–H thiolation using K_2S as a sulfur source is described. This novel one-step sulfur-incorporation method provides a straightforward avenue to benzo[*b*]thiophene and imidazo[1,2-*a*]pyridine frameworks.

Seeking efficient and convenient methods for the construction of C–S bonds is of fundamental research interest in organic chemistry, since sulfur-containing architectures are prevalent in natural products, drugs, bioactive molecules, and materials.[1] Generally, cross-coupling reactions are established to be very useful tools for the formation of C–S bonds. In the past few years, with the renaissance of Ullmann-type reactions,[2] the copper-catalyzed cross-couplings of aryl halides with thiols have been demonstrated to be a versatile method for constructing C(sp^2)–S bonds.[3] Meanwhile, metal sulfides as abundant inorganic substances are also used as a sustainable thiol source, and have been widely used for introducing sulfur atoms into organic molecules.[4] In 2010, Xi and co-workers reported an elegant copper-catalyzed one-pot synthesis of thiophenes from 1,4-diiodo-1,3-dienes and potassium sulphide (Scheme 1a).[5] In the same year, Li's group developed an efficient CuI-catalyzed double thiolation reaction of 1,4-dihalides with sulfides leading to 2-trifluoromethyl benzothiophenes under mild conditions (Scheme 1b).[6] Although great achievements have been made using these methods, the substrates involved in these transformations could be mainly limited to aryl halides. Over the past few decades, direct transformation of inert C–H bonds has emerged as an economical and environmentally friendly alternative to traditional synthetic methods.[7] However, a literature survey indicates that such a synthetic strategy for the formation of C–S bonds remains rather limited,[1d,g,8] and especially the substrates were mainly electron-rich arenas. In this respect, several examples using thiols, diaryl disulfides, 1-(substituted phenylthio)pyrrolidine-2,5-dione, and sulfonyl hydrazide as thiolation reagents under Cu,[9] Fe,[10] Pd,[11] and metal-free[12] conditions have been reported. Very recently, Shi and co-workers developed an elegant copper-mediated C–S/N–S bond-forming reaction *via* C–H activation using elemental sulfur as a sulfuration agent (Scheme 1c).[13] From these wonderful studies, it is thereby expected that combining the two coupling partners C(sp^2)–X and C(sp^2)–H to access the C–S bonds using metal sulfides under copper-catalytic conditions might be more practical and economical (Scheme 1d).



Scheme 1 Strategies for the construction of C–S bonds.

The benzo[*b*]thiophene skeleton is the core unit of natural products, and its derivatives show remarkable biological and

The Key Laboratory of Life-Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, P. R. China. E-mail: yangdaoshan@tsinghua.org.cn, huawang_qfnu@126.com

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c5qo00311c

medicinal properties.[14] For example, they are found in numerous clinically important drugs, such as raloxifene,[15] arzoxifene,[16] zileuton,[17] and clopidogrel.[18] In addition, benzo[*b*]thiophene derivatives are also widely applied in the field of materials science because of their excellent optical properties.[19] On the other hand, imidazo[1,2-*a*]pyridine fragments widely exist in many commercially available drugs, such as zolimidin (to treat peptic ulcer),[20] minodronic acid (to treat osteoporosis),[21] zolpidem (to treat insomnia),[22] and olprinone (to treat heart failure).[23] However, synthesis of the combined motifs of benzo[*b*]thiophene and imidazo[1,2-*a*]pyridine frameworks (Fig. 1) has not been explored thus far. Therefore, we wish to synthesize this new kind of fused sulfur-containing N-heterocycle which could possibly possess biological activity and optical properties. With our growing interest in sulfur-containing organic compounds synthesis,[24] we herein report a novel and efficient copper-catalyzed one-pot synthesis of benzo[*b*]thiophene/imidazo[1,2-*a*]pyridines by sequential Ullmann-type coupling and aerobic oxidative intramolecular C–H thiolation. To the best of our knowledge, this method is the first example of copper-catalyzed direct double C–S bond formation in one step *via* Ullmann-type *S*-arylation and C–H thiolation using metal sulfides as a sulfur source.

We commenced our study by examining the reaction between 2-(2-bromophenyl)imidazo[1,2-*a*]pyridine **1a** and K_2S **2** to investigate experimental conditions including the optimization of catalysts, ligands, solvents and temperature under an air atmosphere. As shown in Table 1, eight copper catalysts (entries 1–8) were examined at 120 °C in the presence of 0.1 equiv. of 1,10-phenanthroline (**A**) as the ligand (relative to the amount of **1a**) in DMF, and CuI showed the highest reaction activity (entry 3). Only trace amounts of the target product **3a** were observed in the absence of catalyst (entry 9). Furthermore, different ligands were tested (entries 3, 10–13), and 1,10-phenanthroline (**A**) exhibited the highest efficiency (entry 3). We also tested various solvents (entries 3, 14–19), and DMF showed the best result (entry 3). The effect of temperature was also investigated (entries 20–22), and the yields reached the maximum when the temperature was raised from 110 °C to 130 °C. Interestingly, when Na_2S was used as the partner of **1a**, only 14% of yield was obtained (entry 23). Notably, only 12% yield of the desired product was obtained under a nitrogen atmosphere, indicating that dioxygen is essential in the present transformation (entry 24).

Next, the substrate scope for the copper-catalyzed synthesis of benzo[*b*]thiophene/imidazo[1,2-*a*]pyridines (**3**) was investigated under the optimized conditions (using 10 mol% CuI as the catalyst, 10 mol% 1,10-phenanthroline as the ligand, two equiv. of K_2S as the thiol source, DMF as the solvent at 120 °C under air). As shown in Table 2, the corresponding benzo[*b*]thiophene/imidazo[1,2-*a*]pyridines were obtained in moderate to good yields for the examined substrates at 120 °C. Generally, for R^1 and R^2 substituents, the substrates bearing electron-donating or electron-withdrawing groups were found to show no obvious difference in the transformation. However, a strong electron-withdrawing group such as nitro was not tolerated under the standard conditions (**3s**). The reason should be that the weak coordination of Cu(I) with sulfur made Cu(I) species unreactive in the present transformation owing to the much more stronger electron-withdrawing properties of the nitro group (see Scheme 3, formation mechanism, the intermediate **V**). In addition, various functional groups such as methyl, ether, halogen, and trifluoromethyl were well-tolerated under the optimized conditions. Reaction of 6-bromo-2-(2-bromophenyl)-

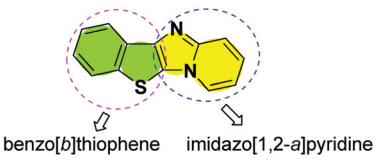
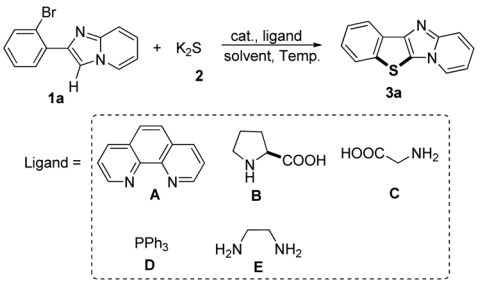


Fig. 1 Structure of a conjugate containing benzo[*b*]thiophene and imidazo[1,2-*a*]pyridine frameworks.

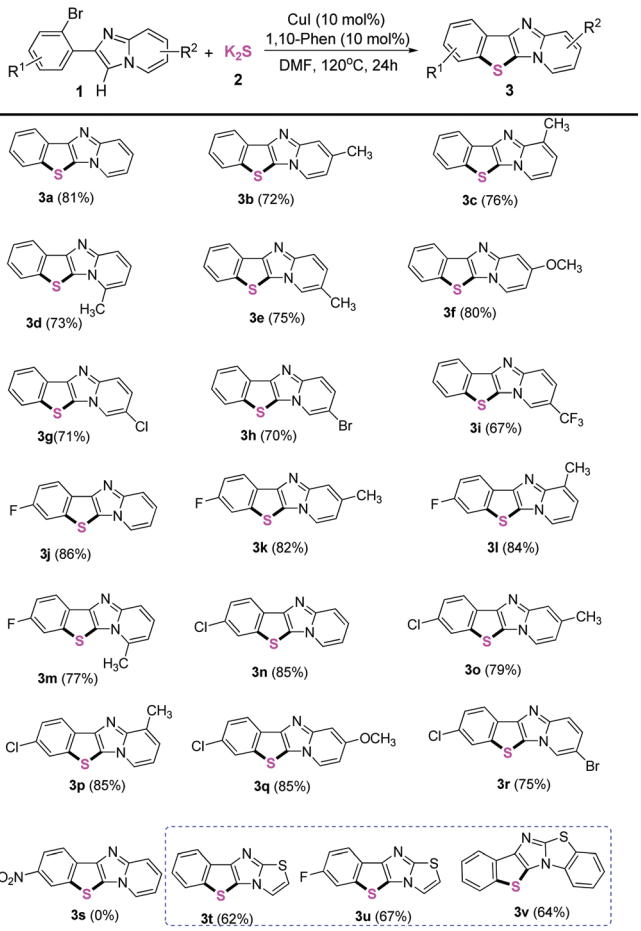
Table 1 Optimization of the conditions [a]



Entry	Cat.	Ligand	Solvent	Yield[b] [%]
1	CuCl	A	DMF	69
2	CuBr	A	DMF	72
3	**CuI**	**A**	**DMF**	**81**
4	$CuSO_4$	A	DMF	67
5	$Cu(OAc)_2$	A	DMF	74
6	$Cu(NO_3)_2$	A	DMF	66
7	$Cu(OTf)_2$	A	DMF	63
8	Cu_2O	A	DMF	69
9	None	A	DMF	Trace
10	CuI	B	DMF	Trace
11	CuI	C	DMF	Trace
12	CuI	D	DMF	63
13	CuI	E	DMF	57
14	CuI	A	DMSO	66
15	CuI	A	NMP	Trace
16	CuI	A	1,4-Dioxane	26
17	CuI	A	DCE	Trace
18	CuI	A	CH_3CN	11
19	CuI	A	H_2O	0
20	CuI	A	DMF	78[c]
21	CuI	A	DMF	72[d]
22	CuI	A	DMF	81[e]
23	CuI	A	DMF	14[f]
24	CuI	A	DMF	12[g]

[a] Reaction conditions: 2-(2-bromophenyl)imidazo[1,2-*a*]pyridine (**1a**) (0.3 mmol), K_2S (**2**) (0.6 mmol), catalyst (0.03 mmol), ligand (0.03 mmol), solvent (2 mL), 120 °C, reaction time (24 h), under air. [b] Isolated yield. [c] 110 °C. [d] 120 °C. [e] 130 °C. [f] Na_2S was used. [g] Under a nitrogen atmosphere (extrusion of air).

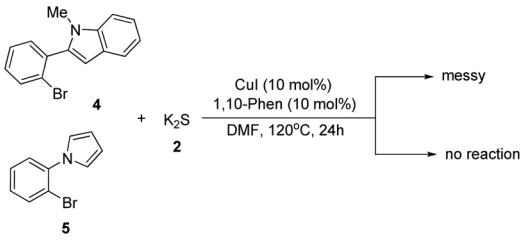
Table 2 Scope of 2-(2-bromophenyl)imidazo[1,2-*a*]pyridines for the synthesis of benzo[*b*]thiophene/imidazo[1,2-*a*]pyridines (**3**)[a,b]



[a] Reaction conditions: 2-(2-bromophenyl)imidazo[1,2-*a*]pyridines (**1**) (0.3 mmol), K_2S (**2**) (0.6 mmol), CuI (0.03 mmol), 1,10-phen (0.03 mmol), solvent (2 mL), reaction temperature (120 °C) under air. [b] Isolated yield.

imidazo[1,2-*a*]pyridines with K_2S only took place on the *ortho*-site C–Br bond of the imidazole group, whereas the 6-site C–Br bond remained intact, thus showing the *ortho*-substituent effect of the imidazole group during *S*-arylations (**3h** and **3r**). Furthermore, the application of our present protocol for thiolation of other heterocyclic compounds was explored. To our delight, substituted 6-(2-bromophenyl)imidazo[2,1-*b*]thiazoles also gave moderate yields of the thiolation products in 62–67% yields (**3t–3v**).

Although this transformation was efficient, unfortunately not all the N-heterocycles were compatible with K_2S under the standard conditions. For example, when 2-(2-bromophenyl)-1-methyl-1*H*-indole and 1-(2-bromophenyl)-1*H*-pyrrole were used as the substrates under the optimal reaction conditions, no desired product was obtained (Scheme 2). Thus, further investigations to explore more powerful catalysts and ligands are required.



Scheme 2 Substrate scope of heterocyclic compounds.

It is interesting to know the optical properties of the synthesized **3a** and derivatives. Therefore, **3a** and some selected derivatives were analyzed by UV–vis and photoluminescence (PL) spectroscopy in solution. As shown in Fig. 2, the UV–vis spectra of naked **3a** and substituted derivatives **3c**, **3l**, **3j** and **3r** have high-intensity absorption between 240 and 270 nm, and lower-intensity bands between 320 and 370 nm. Their emission maxima are observed within the range of 380–430 nm. Compared to naked **3a**, substituted derivatives **3c**, **3l**, **3j** and **3r** have bathochromic shifts or hypochromatic shifts in both absorption and emission spectra to some extent. Apparently, when there is an electron-donating group attached to the pyridine ring or an electron withdrawing group attached to the benzene ring, a hypochromatic shift could occur.

According to the results above and the related literature,[25] a possible mechanism for this domino thiolation is thus outlined in Scheme 3. Reaction of CuX with a ligand produces a chelated Cu(I) complex (**I**), and the subsequent oxidative addition of the chelate with **1** provides the intermediate (**II**), in which the nitrogen of the imidazole group may coordinate to Cu to provide additional stabilization. Treatment of K_2S (**2**) with (**II**) forms the complex (**III**), and then reductive elimination of (**III**) leads to the *S*-arylation product (**IV**). Reaction of (**IV**) with **L**CuX gives the "S–Cu–**L**" complex (**V**), then (**V**) furnishes (**VI**) under air (O_2). Reductive elimination of (**VI**) leads to the target product **3** and regenerates the catalyst, **L**CuX.

In summary, we have developed a novel and efficient copper-catalyzed one-pot method for the synthesis of benzo[*b*]-thiophene/imidazo[1,2-*a*]pyridines. The corresponding products were obtained in moderate to good yields with excellent

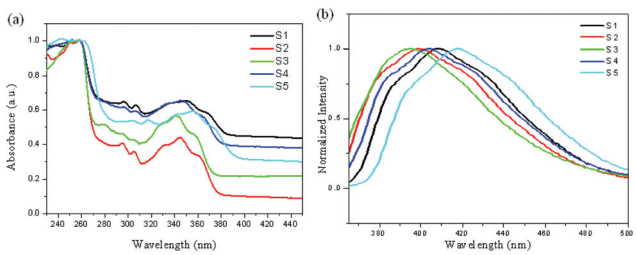
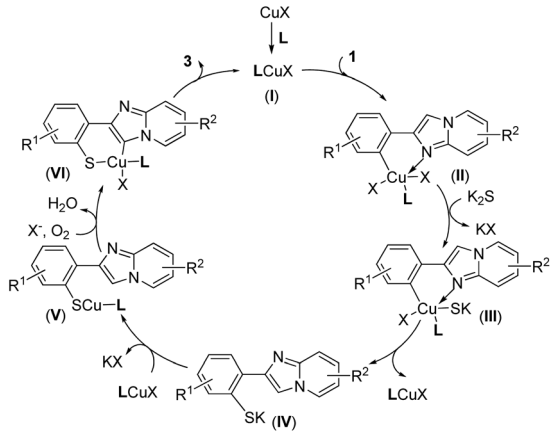


Fig. 2 Normalized UV–vis (a) and photoluminescence (PL) (b) spectra of selected derivatives **3** in DCM (5.0×10^{-5} M); (S1: **3a**; S2: **3c**; S3: **3l**; S4: **3j**; S5: **3r**).



Scheme 3 A proposed mechanism for the direct transformation.

functional group tolerance. Some important features of the present protocol involve the use of inexpensive CuI/1,10-phen as the catalyst/ligand system, readily available substituted 2-(2-bromophenyl)imidazo[1,2-*a*]pyridines and K_2S as the starting materials, and environmentally friendly air (O_2) as the sole oxidant. Further investigations on the practical application of this method are ongoing in our laboratory.

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 21302110, 21302109 and 21375075), the Scientific Research Foundation of Qufu Normal University (BSQD 2012021), the Taishan Scholar Foundation of Shandong Province, the Natural Science Foundation of Shandong Province (ZR2013BQ017 and ZR2013M007), and the Project of Shandong Province Higher Educational Science and Technology Program (J13LD14). We thank Pengfei Sun in this group for reproducing the results of **3a** and **3u**.

Notes and references

1 (*a*) T. Kondo and T.-A. Mitsudo, *Chem. Rev.*, 2000, **100**, 3205; (*b*) A. R. Murphy and J. M. J. Fréchet, *Chem. Rev.*, 2007, **107**, 1066; (*c*) M. Mellah, A. Voituriez and E. Schulz, *Chem. Rev.*, 2007, **107**, 5133; (*d*) H. Haruki, M. G. Pedersen, K. I. Gorska, F. Pojer and K. Johnsson, *Science*, 2013, **340**, 987; (*e*) H. Liu and X. Jiang, *Chem. – Asian J.*, 2013, **8**, 2546; (*f*) M. D. McReynolds, J. M. Dougherty and P. R. Hanson, *Chem. Rev.*, 2004, **104**, 2239; (*g*) I. P. Beletskaya and V. P. Ananikov, *Chem. Rev.*, 2011, **111**, 1596; (*h*) C. Shen, P. Zhang, Q. Sun, S. Bai, T. S. Andy Hor and X. Liu, *Chem. Soc. Rev.*, 2015, **44**, 291; (*i*) D. Wu, Z. Chen, Y. Zhang, J. Zhang, S. Liu and J. Yin, *J. Org. Chem.*, 2015, **80**, 8443; (*j*) X.-D. Xiong, C.-L. Deng, X.-S. Peng, Q. Miao and H. N. C. Wong, *Org. Lett.*, 2014, **16**, 3252.

2 For reviews, see: (*a*) G. Evano, N. Blanchard and M. Toumi, *Chem. Rev.*, 2008, **108**, 3054; (*b*) D. S. Surry and S. L. Buchwald, *Chem. Sci.*, 2010, **1**, 13; (*c*) H. Rao and H. Fu, *Synlett*, 2011, 745; (*d*) D. Ma and Q. Cai, *Acc. Chem. Res.*, 2008, **41**, 1450; (*e*) S. R. Chemler and P. H. Fuller, *Chem. Soc. Rev.*, 2007, **36**, 1153; (*f*) J. R. Dehli, J. Legros and C. Bolm, *Chem. Commun.*, 2005, 973; (*g*) P. Zhao, H. Yin, H. Gao and C. Xi, *J. Org. Chem.*, 2013, **78**, 5001.

3 For selected papers, see: (*a*) L. Rout, T. K. Sen and T. Punniyamurthy, *Angew. Chem., Int. Ed.*, 2007, **46**, 5583; (*b*) L. Rout, P. Saha, S. Jammi and T. Punniyamurthy, *Eur. J. Org. Chem.*, 2008, 640; (*c*) X. Lv and W. Bao, *J. Org. Chem.*, 2007, **72**, 3863; (*d*) C. G. Bates, R. K. Gujadhur and D. Venkataraman, *Org. Lett.*, 2002, **4**, 2803; (*e*) Y.-J. Chen and H.-H. Chen, *Org. Lett.*, 2006, **8**, 5609; (*f*) D. J. C. Prasad and G. Sekar, *Synthesis*, 2010, **1**, 79; (*g*) A. K. Verma, J. Singh and R. Chaudhary, *Tetrahedron Lett.*, 2007, **48**, 7199; (*h*) K. Su, Y. Qiu, Y. Yao, D. Zhang and S. Jiang, *Synlett*, 2012, 2853; (*i*) Y.-J. Chen and H.-H. Chen, *Org. Lett.*, 2006, **8**, 5609.

4 (*a*) T. Kashiki, S. Shinamura, M. Kohara, E. Miyazaki, K. Takimiya, M. Ikeda and H. Kuwabara, *Org. Lett.*, 2009, **11**, 2473; (*b*) D. Ma, S. Xie, P. Xue, X. Zhang, J. Dong and Y. Jiang, *Angew. Chem., Int. Ed.*, 2009, **48**, 4222; (*c*) Y. Liu, J.-L. Zhang, R.-J. Song and J.-H. Li, *Org. Lett.*, 2014, **16**, 5838; (*d*) N. Azizi, E. Akbari, F. Ebrahimi and M. R. Saidi, *Monatsh. Chem.*, 2010, **141**, 323; (*e*) Z. Qiao, J. Wei and X. Jiang, *Org. Lett.*, 2014, **16**, 1212; (*f*) Y. Li, J. Pu and X. Jiang, *Org. Lett.*, 2014, **16**, 2692; (*g*) Z. Qiao, H. Liu, X. Xiao, Y. Fu, J. Wei and X. Jiang, *Org. Lett.*, 2013, **15**, 2594; (*h*) Q. Liao, W. Youa, Z.-B. Lou, L.-R. Wen and C. Xi, *Tetrahedron Lett.*, 2013, **54**, 1475; (*i*) F. Wang, C. Chen, G. Deng and C. Xi, *J. Org. Chem.*, 2012, **77**, 4148.

5 W. You, X. Yan, Q. Liao and C. Xi, *Org. Lett.*, 2010, **12**, 3930.

6 C. Li, X. Zhang, R. Tang, P. Zhong and J. Li, *J. Org. Chem.*, 2010, **75**, 7037.

7 For recent reviews, see: (*a*) K. M. Engle, T.-S. Mei, M. Wasa and J.-Q. Yu, *Acc. Chem. Res.*, 2012, **45**, 788; (*b*) J. C. Lewis, R. G. Bergman and J. A. Ellman, *Acc. Chem. Res.*, 2008, **41**, 1013; (*c*) D. A. Colby, A. S. Tsai, R. G. Bergman and J. A. Ellman, *Acc. Chem. Res.*, 2012, **45**, 814; (*d*) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Rev.*, 2011, **111**, 1293; (*e*) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890; (*f*) S. R. Neufeldt and M. S. Sanford, *Acc. Chem. Res.*, 2012, **45**, 936.

8 P. Anbarasan, H. Neumann and M. Beller, *Chem. Commun.*, 2011, **47**, 3233.

9 (*a*) S. Zhang, P. Qian, M. Zhang, M. Hu and J. Cheng, *J. Org. Chem.*, 2010, **75**, 6732; (*b*) X. Chen, X.-S. Hao, C. E. Goodhue and J.-Q. Yu, *J. Am. Chem. Soc.*, 2006, **128**, 6790; (*c*) D. Alves, R. G. Lara, M. E. Contreira, C. S. Radatz, L. F. B. Duarte and G. Perin, *Tetrahedron Lett.*, 2012, **53**, 3364; (*d*) A. Zhou, X. Liu, K. Yang, S. Zhao and Y. Liang, *Org. Biomol. Chem.*, 2011, **9**, 5456; (*e*) H. Deng, Z. Li, F. Ke and X. Zhou, *Chem. – Eur. J.*, 2012, **18**, 4840; (*f*) L. D. Tran, I. Popov and O. Daugulis, *J. Am. Chem. Soc.*, 2012, **134**, 18237.

10 (*a*) H. Wang, L. Wang, J. Shang, X. Li, H. Wang, J. Gui and A. Lei, *Chem. Commun.*, 2012, **48**, 76; (*b*) M. Zhang, S. Zhang, C. Pan and F. Chen, *Synth. Commun.*, 2012, **42**, 2844.

11 (*a*) K. Inamoto, Y. Arai, K. Hiroya and T. Doi, *Chem. Commun.*, 2008, 5529; (*b*) L. L. Joyce and R. A. Batey, *Org. Lett.*, 2009, **11**, 2792; (*c*) M. Iwasaki, M. Iyanaga, Y. Tsuchiya, Y. Nishimura, W.-J. Li, Z.-P. Li and Y. Nishihara, *Chem. – Eur. J.*, 2014, **20**, 2459; (*d*) S. K. Sahoo, A. Banerjee, S. Chakraborty and B. K. Patel, *ACS Catal.*, 2012, **2**, 544.

12 (*a*) R. Tang, Y. Xie, Y. Xie, J. Xiang and J. Li, *Chem. Commun.*, 2011, **47**, 12867; (*b*) S.-R. Guo, Y.-Q. Yuan and J.-N. Xiang, *Org. Lett.*, 2014, **15**, 4654; (*c*) W. Ge and Y. Wei, *Green Chem.*, 2012, **14**, 2066; (*d*) Y.-F. Liao, P.-C. Jiang, S.-P. Chen, H.-R. Qi and G.-J. Deng, *Green Chem.*, 2013, **15**, 3302; (*e*) L. Zou, J. Reball, J. Mottweiler and C. Bolm, *Chem. Commun.*, 2012, **48**, 11307; (*f*) C. D. Prasad, S. J. Balkrishna, A. Kumar, B. S. Bhakuni, K. Shrimali, S. Biswas and S. Kumar, *J. Org. Chem.*, 2013, **78**, 1434; (*g*) P. Sang, Z.-K. Chen, J.-W. Zou and Y.-H. Zhang, *Green Chem.*, 2013, **15**, 2096; (*h*) W. Zhao, P. Xie, Z. Bian, A. Zhou, H. Ge, M. Zhang, Y. Ding and L. Zheng, *J. Org. Chem.*, 2015, **80**, 9167; (*i*) T. Hostier, V. Ferey, G. Ricci, D. G. Pardo and J. Cossy, *Org. Lett.*, 2015, **17**, 3898.

13 F.-J. Chen, G. Liao, X. Li, J. Wu and B.-F. Shi, *Org. Lett.*, 2014, **16**, 5644.

14 D. A. Horton, G. T. Bourne and M. L. Smythe, *Chem. Rev.*, 2003, **103**, 893, and references cited therein.

15 Z. Qin, I. Kasrati, E. P. Chandrasena, H. Liu, P. Yao, P. A. Petukhov, J. L. Bolton and G. R. J. Thatcher, *J. Med. Chem.*, 2007, **50**, 2682.

16 B. L. Flynn, E. Hamel and M. K. Jung, *J. Med. Chem.*, 2002, **45**, 2670.

17 B. L. Mylari, E. R. Larson, T. A. Beyer, W. J. Zembrowski, C. E. Aldinger, M. F. Dee, T. W. Siegel and D. H. Singleton, *J. Med. Chem.*, 1991, **34**, 108.

18 E. Rogers, H. Araki, L. A. Batory, C. E. McInnis and J. T. Njardarson, *J. Am. Chem. Soc.*, 2007, **129**, 2768.

19 K. Takimiya, I. Osaka, T. Mori and M. Nakano, *Acc. Chem. Res.*, 2014, **47**, 1493, and references cited therein.

20 L. Almirante, L. Polo, A. Mugnaini, E. Provinciali, P. Rugarli, A. Biancotti, A. Gamba and W. Murmann, *J. Med. Chem.*, 1965, **8**, 305.

21 L. A. Sorbera, J. Castaner and P. A. Leeson, *Drugs Future*, 2002, **27**, 935.

22 H. T. Swainston and G. M. Keating, *CNS Drugs*, 2005, **19**, 65.

23 T. Ueda and K. Mizushige, *Curr. Vasc. Pharmacol.*, 2006, **4**, 1.

24 (*a*) D. Yang, K. Yan, W. Wei, J. Zhao, M. Zhang, X. Sheng, G. Li, S. Lu and H. Wang, *J. Org. Chem*, 2015, 80, 6083; (*b*) K. Yan, D. Yang, W. Wei, J. Zhao, Y. Shuai, L. Tian and H. Wang, *Org. Biomol. Chem.*, 2015, **13**, 732; (*c*) K. Yan, D. Yang, P. Sun, W. Wei, Y. Liu, G. Li, S. Lu and H. Wang, *Tetrahedron Lett.*, 2015, **56**, 4792; (*d*) D. Yang, K. Yan, W. Wei, L. T. ian, Q. Li, J. You and H. Wang, *RSC Adv.*, 2014, **4**, 48547; (*e*) W. Wei, J. Li, D. Yang, J. Wen, Y. Jiao, J. You and H. Wang, *Org. Biomol. Chem.*, 2014, **12**, 1861; (*f*) W. Wei, J. Wen, D. Yang, J. Du, J. You and H. Wang, *Green Chem.*, 2014, **16**, 2988; (*g*) D. Yang, K. Yan, W. Wei, G. Li, S. Lu, C. Zhao, L. Tian and H. Wang, *J. Org. Chem.*, 2015, **80**, 11073.

25 (*a*) S. Fukuzawa, E. Shimizu, Y. Atsuumi, M. Haga and K. Ogata, *Tetrahedron Lett.*, 2009, **50**, 2374; (*b*) A. R. Rosario, K. K. Casola, C. E. S. Oliveira and G. Zeni, *Adv. Synth. Catal.*, 2013, **355**, 2960; (*c*) H. Xu and H. Fu, *Chem. – Eur. J.*, 2012, **18**, 1180; (*d*) D. Ma, S. Xie, P. Xue, X. Zhang, J. Dong and Y. Jiang, *Angew. Chem., Int. Ed.*, 2009, **48**, 4222; (*e*) H. Xu, S. Ma, Y. Xu, L. Bian, T. Ding, X. Fang, W. Zhang and Y. Ren, *J. Org. Chem.*, 2015, **80**, 789.