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Iodobenzene-catalyzed synthesis of aryl sulfonate esters from aminoquinolines *via* remote radical C–O cross-coupling†

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A simple and efficient approach is established for the iodobenzene-catalyzed synthesis of aryl sulfonate esters from aminoquinolines *via* remote radical C–O cross-coupling in the absence of any transition metal catalysts. This unexpected reaction reveals superior reactivity, target products are obtained in good to excellent yields at room temperature.

Introduction

Aryl sulfonate esters are always deemed as attractive molecules for chemical researchers due to their special bioactivities.[1] Additionally, sulfonate esters are often used as functional groups or substrates in photochemistry,[2] materials[3] and synthetic chemistry.[4] Hence, valid approaches for the synthesis of these significant bioactive compounds containing sulfonate ester blocks are highly valuable (Fig. 1).

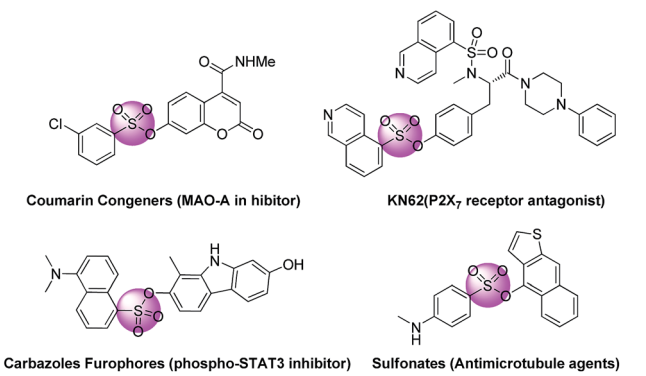
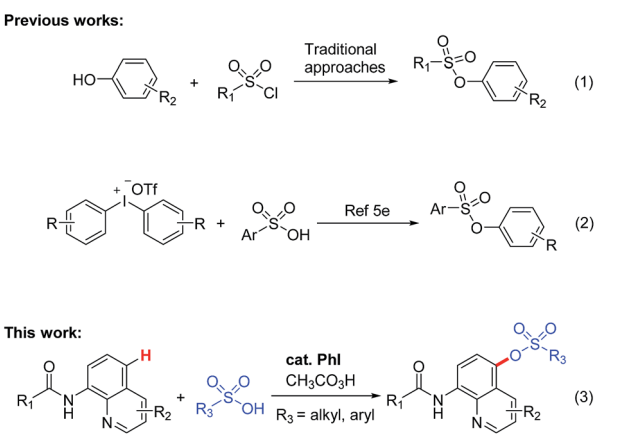


Fig. 1 The representatives of bioactive molecule.

Traditionally, aryl sulfonate esters are generally synthesized by reacting an appropriate sulfonyl chloride with the suitable alcohol or phenol in view of the direct transformation of sulfonic acid to the corresponding sulfonate esters is indeed difficult to fulfil (Scheme 1). These protocols, however, often suffer from a lot of limitations,[5] such as harsh reaction conditions, dreary reaction routines, numbers of side reactions and low yields. Therefore, the conventional and available substrates direct convert into valuable aryl sulfonate esters products through C–H sulfonation is undoubtedly an efficient and energy saving method.[6]

Recently, the advance of C–O bond formation *via* C–H bond functionalization has attracted much attention.[7] Majority of the researches on regioselective C–O bond formation are almost limited to hydroxylation.[7a–f] acetoxylation,[7g–k] benzoxylation[7l–n] and etherification.[7o–s] Despite these great advances, these methods generally undergo metal catalysts, high reaction temperatures, and acid or basic additives.



Scheme 1 Approaches towards the synthesis of aryl sulfonate esters.

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Quinolines are prevalent in many natural products and pharmaceuticals.[8] For this purpose, plenty of investigations were proceeded employing quinolines as building blocks.[9] Especially, the functionalization of quinolines on C5 position has also got a lot of attention lately.[10] However, most of these kinds of reactions were relying on metal catalysts including Fe,[10a] Co,[10b] Ni,[10c] Cu,[10d–n] Ag[10o] and Pd.[10p] Although various reactions including carbon–carbon and carbon–heteroatom bonds cross-coupling have been reported, the methodology for the C-5 selective formation of C–O bond under transition-metal-free condition has never been established.

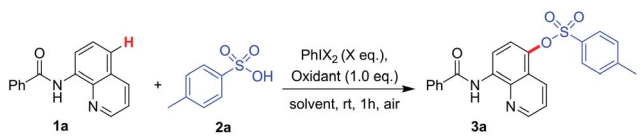
In consideration of the importance of aryl sulfonate esters and quinolines, a much more simple and efficient C–O bond formation method is required to access these worthy sulfonate esters. Importantly, no metal catalyst was required in the procedure.[11] As we have seen, the direct sulfonation of quinolines on C5 position with aryl or alkyl sulfonic acids has not yet been achieved. Herein we report the first example of the synthesis of aryl sulfonate esters through iodobenzene-catalyzed direct sulfonylation of aromatic compounds with aryl or alkyl sulfonic acids in the presence of peracetic acid as a terminal oxidant at room temperature.

Results and discussion

Firstly, 8-aminoquinoline **1a** and *p*-toluenesulfonic acid **2a** were selected as a model compound to explore the optimized reaction conditions with iodine(III) at room temperature (Table 1). Interestingly, omission of metal catalyst and running the reaction in dioxane under air was successful when 2 equivalents of phenyliodine diacetate (PIDA) or phenyliodonium bis(trifluoro-acetate) (PIFA) were used as oxidant (entry 1 and entry 2, Table 1). Then we tried to promote the C–O coupling by *in situ* generated PIDA by using PhI (0.2 equiv.) as an iodine source with *m*-CPBA (1.0 equiv.) as an oxidant product **3a** was obtained only in a 26% yield (entry 3, Table 1). To further improve the yield, various oxidants, including TBHP, H_2O_2, CH_3CO_3H and $K_2S_2O_8$ were examined, and CH_3CO_3H increased the yield of **3a** to 42% (entries 4–7, Table 1). We then studied the solvent effect on the reaction and found that the solvents such as toluene, DCM, DMSO, MeCN and HFIP have significant effects on the reaction (entries 8–11, Table 1). Delightedly, the yield was up to 93% by using HFIP as solvent (entry 11, Table 1). The reaction was moderately sensitive to temperature, with poorer results obtained at higher temperatures (entry 12, Table 1). When *m*-CPBA was used as oxidant, the sulfonated quinoline amide was obtained in a lower yield (entry 13, Table 1). Lastly, we reduced the amount of PhI from 20 mol% to 10 mol%, the yield of the isolated product dropped to 71% (entry 14, Table 1) and no product was detected in the absence of oxidant (entry 15, Table 1).

With the optimal condition in hand, then the scope of sulfonic acids was tested (Table 2). Numbers of sulfonic acids, including aliphatic and aromatic sulfonic acids revealed excellent reactivity, corresponding products were gained in good to excellent yields. Aryl sulfonic acids such as benzenesulfonic acid, *p*-chloro benzenesulfonic acid and β-naphthalenesulphonic acid converted to the corresponding products in 94%, 92% and 90% yields, respectively (**3b–c**). Allyl sulfonic acid and methanesulfonic acid are suitable substrates for this

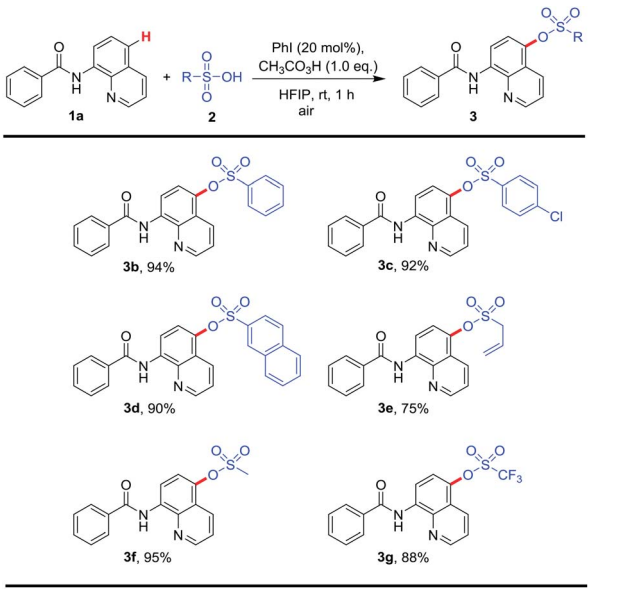
Table 1 Screening of reaction conditions for C–O coupling[a]



Entry	$PhIX_2$ (equiv.)	Oxidant	Solvent	Yield[b]/[%]
1	$PhI(OAc)_2$ (2)	—	Dioxane	68
2	$PhI(TFA)_2$ (2)	—	Dioxane	75
3	PhI (0.2)	*m*-CPBA	Dioxane	26
4	PhI (0.2)	TBHP	Dioxane	0
5	PhI (0.2)	H_2O_2	Dioxane	0
6	PhI (0.2)	CH_3CO_3H	Dioxane	42
7	PhI (0.2)	$K_2S_2O_8$	Dioxane	Trace
8	PhI (0.2)	CH_3CO_3H	Toluene	37
9	PhI (0.2)	CH_3CO_3H	DCM	0
10	PhI (0.2)	CH_3CO_3H	MeCN	15
11	**PhI (0.2)**	**CH_3CO_3H**	**HFIP**	**93**
12	PhI (0.2)	CH_3CO_3H	HFIP	81[c]
13	PhI (0.2)	*m*-CPBA	HFIP	85
14	PhI (0.1)	CH_3CO_3H	HFIP	71
15	PhI (0.2)	—	HFIP	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv.), $PhIX_2$ (*X* equiv.), oxidant (1.0 equiv.), solvent (1.0 mL), stirred at rt, 1 h, under air, *m*-CPBA = *m*-chloroper benzoic acid, TBHP = *tert*-butyl hydroperoxide, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol. [b] Isolated yields. [c] Stirred at 50 °C.

Table 2 Substrate scope of sulfonic acid[a]



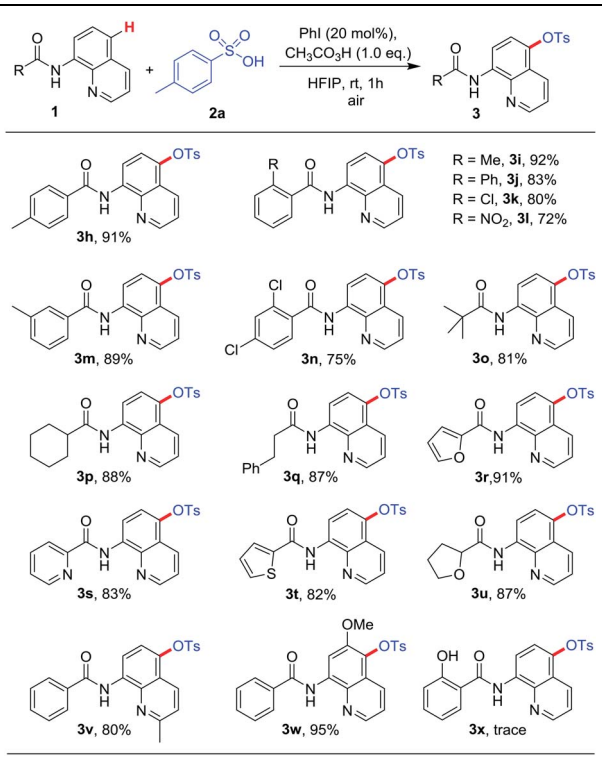
[a] Reaction conditions: **1a** (0.2 mmol), **2** (1.5 equiv.), PhI (20 mol%), CH_3CO_3H (1.0 equiv.), HFIP (1.0 mL), stirred at rt, 1 h, under air, isolated yields.

transformation (**3e**, **3f**). Excitedly, trifluoro methanesulfonic acid also revealed good reactivity, and desired product was got in satisfactory yield (**3g**).

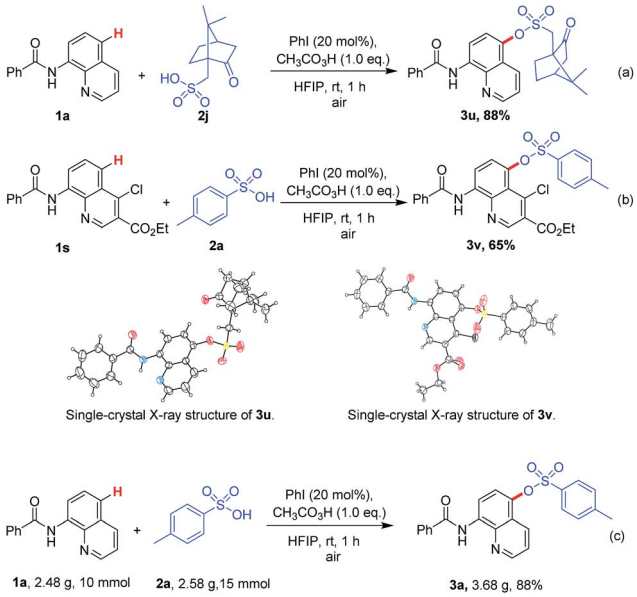
Subsequently, the reaction generality was investigated with various 8-amino quinolines. The results are summarized in Table 3 and this transformation demonstrated remarkable functional group tolerance. *N*-(Quinolin-8-yl)benzamide with multifarious substituted groups such as Me, Ph, Cl and NO_2 on the benzene rings proved higher reactivity, and the desired products (**3h–n**) were received in good yields. The carboxamides with aliphatic group (*t*-butyl, cyclohexyl, phenylethyl) and heterocyclic ring (2-furyl, 2-pyridyl, 2-thienyl, tetrahydro-2-furyl) equipped C5-sulfonated quinolines amides (**3o–u**) in high yields. Moreover, *N*-(quinolin-8-yl)benzamide with Me and MeO on the quinoline rings also revealed reasonable reactivity (**3v–w**). Sadly, the substrate with hydroxyl group could not translate into relevant product due to the influence of reactive hydrogen (**3x**).

To prove the high reaction activity and selectivity of this method still further, the reactants with bigger steric hindrance such as camphorsulfonic acid (**2j**) and ethyl 8-benzamido-4-chloroquinoline-3-carboxylate (**1s**) were tested, respectively (Scheme 2a). The moderate to good yields of products **3y** and **3z** were obtained. And the molecular structures were further confirmed by X-ray crystallography. Critically, sulfonated quinolone derivate **3z** was got in valuable yield (Scheme 2b), which with a potentially broader range of uses in biological and pharmacological fields. In addition, given the easy availability of the raw materials and the operational simplicity of this metal free method, we performed the reaction on a gramscale obtaining the sulfonic acid ester **3a** in 88% yield (Scheme 2c).

Table 3 Substrate scope of quinoline amide[a]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (1.5 equiv.), PhI (20 mol%), CH_3CO_3H (1.0 equiv.), HFIP (1.0 mL), stirred at rt, 1 h, under air, isolated yields.



Scheme 2 Investigation of steric hindrance effect on the reaction.

Conclusions

We have developed an efficient protocol for the iodobenzene-catalyzed synthesis of aryl sulfonate esters from aminoquinolines *via* remote radical C–O cross-coupling in the presence of peracetic acid as a terminal oxidant at room temperature. This C–O coupling reaction proceeds under simple and mild conditions, reveals high efficiency and affords the sulfonated products in good to excellent yields with high selectivity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 (*a*) L. Yan and C. E. Müller, *J. Med. Chem.*, 2004, **47**, 1031; (*b*) A. Zuse, P. Schmidt, S. Baasner, K. J. Böhm, K. Müller, M. Gerlach, E. G. Günther, E. Unger and H. Prinz, *J. Med. Chem.*, 2007, **50**, 6059; (*c*) L. Pisani, M. Barletta, R. Soto-Otero, O. Nicolotti, E. Mendez-Alvarez, M. Catto, A. Introcaso, A. Stefanachi, S. Cellamare, C. Altomare and

A. Carotti, *J. Med. Chem.*, 2013, **56**, 2651; (*d*) J.-H. Park, G.-E. Lee, S.-D. Lee, T. T. Hien, S. Kim, J. W. Yang, J.-H. Cho, H. Ko, S.-C. Lim, Y.-G. Kim, K.-W. Kang and Y.-C. Kim, *J. Med. Chem.*, 2015, **58**, 2114; (*e*) S. Hou, Y. W. Yi, H. J. Kang, L. Zhang, H. J. Kim, Y. Kong, Y. Liu, K. Wang, H.-S. Kong, S. Grindrod, I. Bae and M. L. Brown, *J. Med. Chem.*, 2014, **57**, 6342.

2 (*a*) S. M. Pauff and S. C. Miller, *Org. Lett.*, 2011, **13**, 6196; (*b*) S. M. Pauff and S. C. Miller, *J. Org. Chem.*, 2013, **78**, 711.

3 (*a*) M. Zhang, J. D. Moore, D. L. Flynn and P. R. Hanson, *Org. Lett.*, 2004, **6**, 2657; (*b*) H. Mori, E. Kudo, Y. Saito, A. Onuma and M. Morishima, *Macromolecules*, 2010, **43**, 7021.

4 (*a*) F. Li, T.-X. Liu and G.-W. Wang, *Org. Lett.*, 2012, **14**, 2176; (*b*) J. R. DeBergh, N. Niljianskul and S. L. Buchwald, *J. Am. Chem. Soc.*, 2013, **135**, 10638; (*c*) B. G. Avitabile, C. A. Smith and D. B. Judd, *Org. Lett.*, 2005, **7**, 843; (*d*) D. Elder, K. L. Facchine, J. N. Levy, R. Parsons, D. Ridge, L. Semo and A. Teasdale, *Org. Process Res. Dev.*, 2012, **16**, 1707.

5 (*a*) B. Das, S. Reddy and M. R. Reddy, *Tetrahedron Lett.*, 2004, **45**, 6717; (*b*) B. Das and V. S. Reddy, *Chem. Lett.*, 2004, **33**, 1428; (*c*) B. M. Choudary, N. S. Chowdari and M. L. Kantam, *Tetrahedron*, 2000, **56**, 7291; (*d*) S. Velusamy, J. S. K. Kumar and T. Punniyamurthy, *Tetrahedron Lett.*, 2004, **45**, 203; (*e*) N. Jalalian, T. B. Petersen and B. Olofsson, *Chem.–Eur. J.*, 2012, **18**, 14140.

6 Y. Xu, G. Yan, Z. Ren and G. Dong, *Nat. Chem.*, 2015, **7**, 829.

7 (*a*) Y.-H. Zhang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 14654; (*b*) Q. Lu, J. Zhang, F. Wei, Y. Qi, H. Wang, Z. Liu and A. Lei, *Angew. Chem., Int. Ed.*, 2013, **52**, 7156; (*c*) X. Yang, G. Shan and Y. Rao, *Org. Lett.*, 2013, **15**, 2334; (*d*) W. Liu and L. Ackermann, *Org. Lett.*, 2013, **15**, 3484; (*e*) X. Li, Y.-H. Liu, W.-J. Gu, B. Li, F.-J. Chen and B.-F. Shi, *Org. Lett.*, 2014, **16**, 3904; (*f*) J. Dong, P. Liu and P. Sun, *J. Org. Chem.*, 2015, **80**, 2925; (*g*) D.-H. Wang, X.-S. Hao, D.-F. Wu and J.-Q. Yu, *Org. Lett.*, 2006, **8**, 3387; (*h*) R. Fan, Y. Sun and Y. Ye, *Org. Lett.*, 2009, **11**, 5174; (*i*) R. K. Rit, M. R. Yadav and A. K. Sahoo, *Org. Lett.*, 2014, **16**, 968; (*j*) L. Y. Chan, X. Meng and S. Kim, *J. Org. Chem.*, 2013, **78**, 8826; (*k*) T. Cheng, W. Yin, Y. Zhang, Y. Zhang and Y. Huang, *Org. Biomol. Chem.*, 2014, **12**, 1405; (*l*) Z. Ye, W. Wang, F. Luo, S. Zhang and J. Cheng, *Org. Lett.*, 2009, **11**, 3974; (*m*) Z. Wang and C. Kuang, *Adv. Synth. Catal.*, 2014, **356**, 1549; (*n*) K. Raghuvanshi, K. Rauch and L. Ackermann, *Chem.–Eur. J.*, 2015, **21**, 1790; (*o*) Z. Yin, X. Jiang and P. Sun, *J. Org. Chem.*, 2013, **78**, 10002; (*p*) Q. Jiang, J.-Y. Wang and C. Guo, *J. Org. Chem.*, 2014, **79**, 8768; (*q*) L.-B. Zhang, X.-Q. Hao, S.-K. Zhang, Z.-J. Liu, X.-X. Zheng, J.-F. Gong, J.-L. Niu and M.-P. Song, *Angew. Chem., Int. Ed.*, 2015, **54**, 272; (*r*) J. Roane and O. Daugulis, *Org. Lett.*, 2013, **15**, 5842; (*s*) S. K. Alla, P. Sadhu and T. Punniyamurthy, *J. Org. Chem.*, 2014, **79**, 7502.

8 (*a*) H. Jiang, J. E. Taggart, X. Zhang, D. M. Benbrook, S. E. Lind and W.-Q. Ding, *Cancer Lett.*, 2011, **312**, 11; (*b*) J. P. Michael, *Nat. Prod. Rep.*, 2008, **25**, 166; (*c*) Y.-C. Liu, J.-H. Wei, Z.-F. Chen, M. Liu, Y.-Q. Gu, K.-B. Huang, Z.-Q. Li and H. Liang, *Eur. J. Med. Chem.*, 2013, **69**, 554; (*d*) E. Pan, N. W. Oswald, A. G. Legako, J. M. Life, B. A. Posner and J. B. MacMillan, *Chem. Sci.*, 2013, **4**, 482; (*e*) D. K. Heidary, B. S. Howerton and E. C. Glazer, *J. Med. Chem.*, 2014, **57**, 8936.

9 (*a*) D. E. Stephens, M. Valdes, M. Dovalina, H. D. Arman and O. V. Larionov, *Org. Biomol. Chem.*, 2014, **12**, 6190; (*b*) J. C. Fennewald and B. H. Lipshutz, *Green Chem.*, 2014, **16**, 1097; (*c*) T. Nishida, H. Ida, Y. Kuninobu and M. Kanai, *Nat. Commun.*, 2014, **5**, 3387; (*d*) T. Iwai and M. Sawamura, *ACS Catal.*, 2015, **5**, 5031; (*e*) D. E. Stephens and O. V. Larionov, *Tetrahedron*, 2015, **71**, 8683; (*f*) M. Nagase, Y. Kuninobu and M. Kanai, *J. Am. Chem. Soc.*, 2016, **138**, 6103.

10 (*a*) X. Cong and M. Zeng, *Org. Lett.*, 2014, **16**, 3716; (*b*) C. Whiteoak, O. Planas, A. Company and X. Ribas, *Adv. Synth. Catal.*, 2016, **358**, 1679; (*c*) H. Chen, P. Li, M. Wang and L. Wang, *Org. Lett.*, 2016, **18**, 4794; (*d*) A. M. Suess, M. Z. Ertem, C. J. Cramer and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 9797; (*e*) C. Xia, K. Wang, J. Xu, C. Shen, D. Sun, H. Li, G. Wang and P. Zhang, *Org. Biomol. Chem.*, 2017, **15**, 531; (*f*) H. Qiao, S. Sun, F. Yang, Y. Zhu, W. Zhu, Y. Dong, Y. Wu, X. Kong, L. Jiang and Y. Wu, *Org. Lett.*, 2015, **17**, 6086; (*g*) J. Xu, C. Shen, X. Zhu, P. Zhang, M. J. Ajitha, K.-W. Huang, Z. An and X. Liu, *Chem.–Asian J.*, 2016, **11**, 882; (*h*) J. Xu, X. L. Zhu, G. B. Zhou, B. B. Ying, P. P. Ye, L. Y. Su, C. Shen and P. Zhang, *Org. Biomol. Chem.*, 2016, **14**, 3016; (*i*) X. Zhu, L. Qiao, P. Ye, B. Ying, J. Xu, C. Shen and P. Zhang, *RSC Adv.*, 2016, **6**, 89979; (*j*) L.-K. Jin, G.-P. Lua and C. Cai, *Org. Chem. Front.*, 2016, **3**, 1309; (*k*) C. Shen, J. Xu, B. Ying and P. Zhang, *ChemCatChem*, 2016, **8**, 3560; (*l*) J. Chen, T. Wang, T. Wang, A. Lin, H. Yao and J. Xu, *Org. Chem. Front.*, 2017, **4**, 130; (*m*) H. Sahoo, M. K. Reddy, I. Ramakrishna and M. Baidya, *Chem.–Eur. J.*, 2016, **22**, 1592; (*n*) Y. Dou, Z. Xie, Z. Sun, H. Fang, C. Shen, P. Zhang and Q. Zhu, *ChemCatChem*, 2016, **8**, 3570; (*o*) M. Sun, S. Sun, H. Qiao, F. Yang, Y. Zhu, J. Kang, Y. Wu and Y. Wu, *Org. Chem. Front.*, 2016, **3**, 1646; (*p*) H. Guo, M. Chen, P. Jiang, J. Chen, L. Pan, M. Wang, C. Xie and Y. Zhang, *Tetrahedron*, 2015, **71**, 70; (*q*) D. Ji, X. He, Y. Xu, Z. Xu, Y. Bian, W. Liu, Q. Zhu and Y. Xu, *Org. Lett.*, 2016, **18**, 4478; (*r*) Z. Wu, Y. He, C. Ma, X. Zhou, X. Liu, Y. Li, T. Hu, P. Wen and G. Huang, *Asian J. Org. Chem.*, 2016, **5**, 724; (*s*) Y. Wang, Y. Wang, Q. Zhang and D. Li, *Org. Chem. Front.*, 2017, **4**, 514; (*t*) J. Chen, T. Wang, Y. Liu, T. Wang, A. Lin and H. Yao, *Org. Chem. Front.*, 2017, **4**, 622; (*u*) J. Xu, L. Qiao, B. Ying, X. Zhu, C. Shen and P. Zhang, *Org. Chem. Front.*, 2017, **4**, 1116; (*v*) Y. He, N. Zhao, L. Qiu, X. Zhang and X. Fan, *Org. Lett.*, 2016, **18**, 6054; (*w*) H. Sahoo, I. Ramakrishna and M. Baidya, *ChemistrySelect*, 2016, **1**, 1949.

11 (*a*) Y. Ji, T. Brueckl, R. D. Baxter, Y. Fujiwara, I. B. Seiple, S. Su, D. G. Blackmond and P. S. Baran, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 14411; (*b*) Q. Lu, C. Liu, Z. Huang, Y. Ma, J. Zhang and A. Lei, *Chem. Commun.*, 2014, **50**, 14101; (*c*) C.-L. Sun and Z.-J. Shi, *Chem. Rev.*, 2014, **114**, 9219; (*d*) K. Yang and Q. Song, *Green Chem.*, 2016, **18**, 932; (*e*) D. Ma, W. Chen, G. Hu, Y. Zhang, Y. Gao, Y. Yin and Y. Zhao, *Green Chem.*, 2016, **18**, 3522.