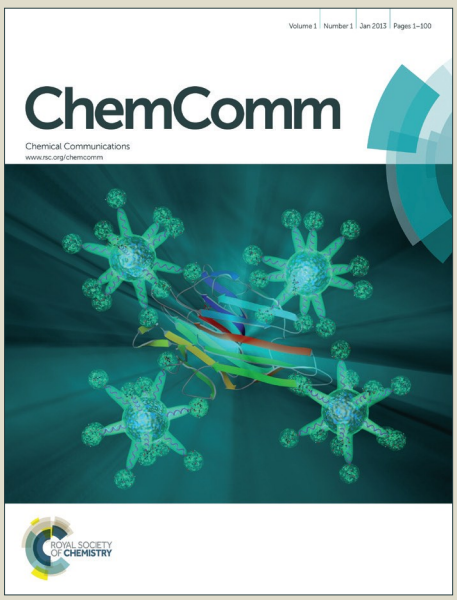
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Visible Light-Induced Intramolecular Dearomative Cyclization of α-Bromo-*N*-benzyl-alkylamides: Efficient Construction of 2-Azaspiro[4.5]decanes

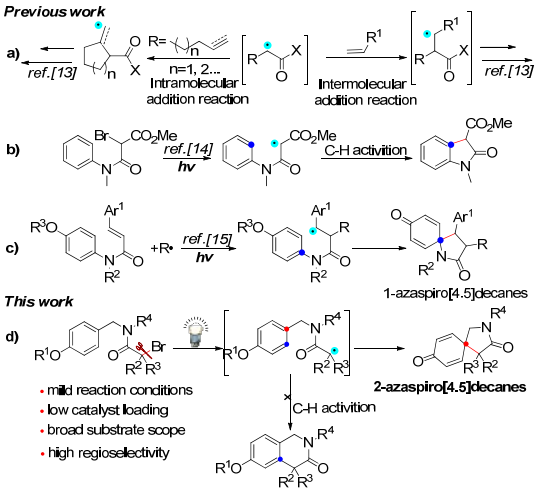
Bei Hu,[a] Yuyuan Li,[b] Wuheng Dong,[a] Kai Ren,[a] Xiaomin Xie,[a] Jun Wan[b] and Zhaoguo Zhang*[a,c]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

An efficient intramolecular dearomative cyclization via visible light-induced photoredox catalysis allows for a highly regioselective dearomative cyclization of α-bromo-*N*-benzyl-alkylamides to construct 2-azaspiro[4.5]decanes in the presence of a irridium catalyst.

Azaspirocyclic cyclohexadienones are key synthetic intermediates in the preparation of numerous natural products and biologically active molecules.[1] Because of their prevalence in pharmaceutically desirable compounds, such as HIV-1 protease inhibitor,[2] annosqualine[3] and antiarthritic,[4] the synthetic challenges associated with the construction of the highly substituted carbon centers have made azaspirocycle an attractive target for chemists.[5]

Dearomative cyclization reaction provides a useful method for the synthesis of azaspirocycle ring-systems from readily available aromatic compounds and several methods have been reported for the construction of these systems via the dearomative cyclization of functionalized phenols and alkoxyarenes.[6] One of these methods was observed in the acid-catalyzed cyclization of aromatic diazoacetamides.[7] Analogous acid-catalyzed dearomative cyclization of aromatic compounds have been extensively explored by Zard *et al*.[8] and Curran *et al*.[9] Another strategy was the radical spirocyclization of *para*-methoxylated arenes, which was firstly developed by Hey and Todd in 1967. However, the process was of limited synthetic value due to the poor selectivity, many byproducts, such as dimeric products, XX, and YY were formed.[10] Transition metal-catalyzed dearomative cyclizations have also been reported by several groups.[6a, 11] Recently, the visible light-induced photoredox catalysis has been identified as a green and sustainable synthetic method for the assembly of diverse important compounds under the mild reaction conditions.[12] Of them, the carbonyl alkyl radical addition reaction generated from alkyl α-bromocarboxylates under visible light has been well-explored (**Scheme 1**). Many groups have succeeded in the addition of carbonylalkyl radical to unsaturated C-C double bond to obtain diverse carbonyl compounds, including intermolecular and intramolecular addition (**Scheme 1a**).[13] A few groups have also reported the synthesis of oxindoles through C-H activation reaction (**Scheme 1b**).[14] Besides that, the synthesis of a variety of 1-azaspiro[4.5]decanes possessing a CF_3- or a CF_2-group via intermolecular dearomative cyclization has been reported by Xia's and Zhu's groups, respectively (**Scheme 1c**).[15] However, the intramolecular cyclization of a carbonyl alkyl radical to an aromatic ring to construct 2-azaspiro[4.5]decane is still unexplored. Herein, we report a visible light-induced regioselective dearomative cyclization of α-bromo-*N*-benzyl-alkylamide for the synthesis of 2-azaspiro[4.5]decanes (**Scheme 1d**).



Scheme 1. Visible Light-Induced Dearomative Cyclization for the Synthesis of Azaspirocyclic Cyclohexadienones

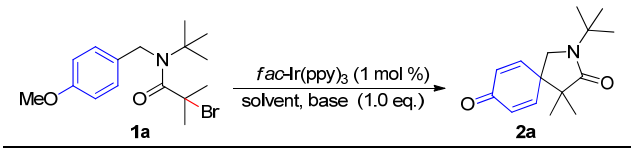
We tested the reaction of 2-bromo-*N*-(*tert*-butyl)-*N*-(4-methoxybenzyl)-2-methylpropanamide (**1a**) using *fac*-Ir(ppy)$_3$ (1 mol%) as photocatalyst and DMF as solvent under the irradiation of a 7 W blue LED. Fortunately, the reaction occurred at room

[a]*School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China; E-mail: zhaoguo@sjtu.edu.cn*
[b]*College of Chemistry and Molecular Engineering and College of Environment and Safety Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao 266042, China*
[c]*Shanghai institute of organic chemistry, Chinese Academy of Sciences, 345 Lingling road, Shanghai 200032, China*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

temperature, giving the desired azaspirocycle compound (**2a)** in 56% yield (Table 1, entry 1). When Na_2CO_3 was added, the reaction gave a much higher yield (Table 1, entry 2). $NaHCO_3$ also was examined and the same result was obtained (Table 1, entry 3), while we changed the base to K_2CO_3, a lower yield was observed (Table 1, entry 4). To our delight, the best result can be obtained by using K_2HPO_4 or Li_2CO_3 as the base (Table 1, entries 5 and 6). Organic bases, such as $^iPr_2NEt$, DBU, and pyridine, are not as efficient as inorganic bases, much lower yields were observed (Table 1, entries 7-9). Solvent screening proved DMA superior to other solvents tested, an 89% isolated yield was obtained (Table 1, entries 10-14). Control experiments showed that both *fac*-Ir(ppy)$_3$ and visible light are essential for this reaction: When the reactions were conducted without catalyst or in the dark, essentially no products were formed (Table 1, entries 15 and 16).

Table 1. Optimization of the reaction conditions[a]



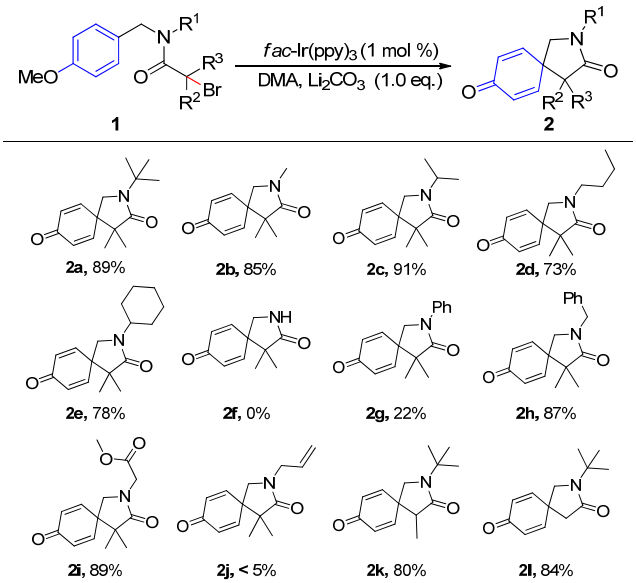
1a **2a**

Entry	Base	Solvent	Yield[b] (%)
1		DMF	56
2	Na_2CO_3	DMF	84
3	$NaHCO_3$	DMF	83
4	K_2CO_3	DMF	64
5	K_2HPO_4	DMF	89
6	Li_2CO_3	DMF	90
7	$^iPr_2NEt$	DMF	42
8	DBU	DMF	24
9	pyridine	DMF	12
10	Li_2CO_3	DMA	95(89)[c]
11	Li_2CO_3	CH_3CN	75
12	Li_2CO_3	MeOH	20
13	Li_2CO_3	NMP	92
14	Li_2CO_3	$CHCl_3$	56
15[d]	Li_2CO_3	DMA	0
16[e]	Li_2CO_3	DMA	0

[a]Reaction conditions: 1a (0.5 mmol), catalyst (0.005mmol), base (0.5 mmol), solvent (2 mL), rt, 48 h, under N_2 atmosphere. [b]Determined by ^{1}HNMR analysis with 1,2,4,5-tetramethylbenzene as an internal standard. [c]The value in parentheses was isolated yield. [d]In the dark. [e]Without catalyst.

Under the optimized reaction conditions, we started to explore the substrate scope. The substituents on the nitrogen (R^1) have a dramatic influence on the yields. Substrates with a Me, *i*-Pr, or CH_2COOEt group afforded the corresponding 2-azaspiro[4.5]decanes (**2b, 2c, 2i**) in good yields, respectively, whereas substrates with *n*-butyl or cyclohexyl substituents gave moderate yields (**2d**, **2e**). No desired product **2f** was obtained when R^1 is a hydrogen atom, which is similar to the literature report.[14b, 16] When R^1 was a phenyl group, the desired product **2g** was obtained in 22% yield, along with a 56% yield of byproduct **2g'** (see supporting information).[14] When R^1 was a benzyl group, **2h** was obtained as a sole product, which indicates that the 4-methoxyl group is essential for the spiro cyclization. The reaction of substrate with allyl substituents gave the desired products in very poor yields because of the competitive addition of carbonyl alkyl radical to the alkene moiety (see supporting information).[13a, 13c, 17] We then turned our attention to the α-substituents of carbonyl (R^2, R^3). When the substrate with only one α-methyl group on the carbonyl (R^2 = H, R^3 = Me) was employed, good yield was obtained. Furthermore, the substrate without any substituent (R^2 = R^3 = H) was also tried which gave desired product **2l** in 84% yield.

Table 2. Substrate Scope of Dearomatization[a]



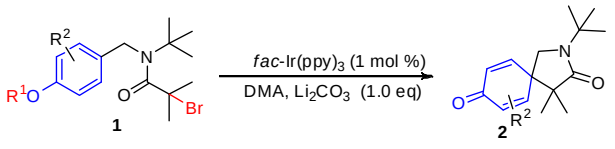
[a]Reaction conditions: **1** (0.5 mmol), *fac*-Ir(ppy)$_3$ (0.005 mmol), Li_2CO3 (0.5 mmol), DMA (2 mL) at rt irradiated by a 7 W blue LED for 48 h under N_2 atmosphere. [b]Isolated yield.

To further explore the applications of this reaction system, we extended it to stable, easy-to-prepare substrates with various substituents (R^1) on the oxygen atom of phenol (Table 3), and on the aromatic ring (R^2). When the oxygen atom was protected with a benzyl, a THP (tetrahydropyranyl), or a TBDMS (*tert*-butyldimethylsilanoxy) group, the dearomatization occurred and afforded the spirocyclic product **2a** in good yield (Table 3, entries 1-3). Even when the methoxyl group was replaced by a hydroxyl group, the desired product **2a** could also be obtained in an even better yield (Table 3, entry 4). When the *meta*-position of the aromatic ring was substituted with a methoxyl group, the desired product **2q** was obtained in 66% yield (Table 3, entry 5). Substrate bears a Br atom on the benzene ring gave the desired product with the Br atom intact (Table 3, entry 6), and substrate with a naphthalene ring yielded the spirocyclic compound **2s** in moderate yield (Table 3, entry 7). Besides that, 2-chloro-*N*-(*tert*-butyl)-*N*-(4-methoxybenzyl)-2-methylpropanamide and *N*-benzyl-2-bromo-*N*-(*tert*-butyl)-2-methylpropanamide were also tried as the substrates, however, no reaction occurred under the optimization reactions.

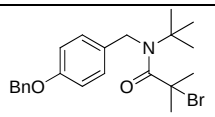
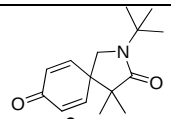
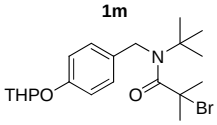
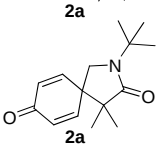
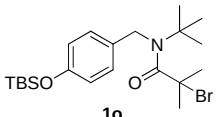
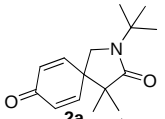
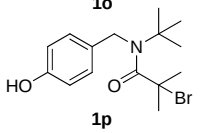
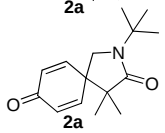
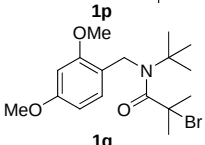
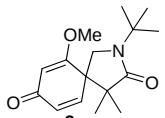
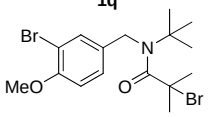
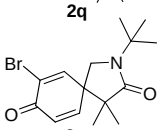
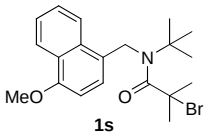
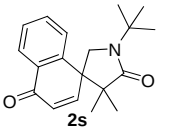
On the basis of our above results, we proposed the following mechanism to account for this visible light-induced dearomative cyclization reaction (**Scheme 2**). Excitation of the iridium catalyst under the visible light generates the excited **fac*-[Ir(ppy)$_3$] species, which underwent a single electron transfer process with α-bromo-*N*-benzyl-alkylamide (**1**) to afford the electrophilic radical **I** and Ir^{IV} metal complex. The key C-C bond was formed through a rapid regioselective addition of radical **I** to the *para*-position of RO

substituted electron-rich aromatic ring, thus resulting in the radical **II**. Given that radical **II** should have a lower barrier of oxidization due to the existence of the electron-rich RO group, a second single electron transfer event with Ir^{IV} metal complex would generate the cation intermediate **III** and finally finished the photoredox catalytic cycle. The desired product **2** would be generated from intermediate **III** in the presence of the base.[15]

Table 3. Substrate Scope of Dearomatization[a]

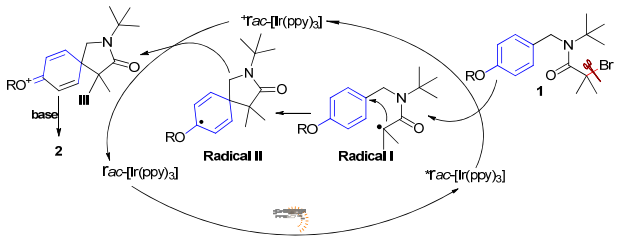


1 2

Entry	Substrate	Product	Yield[b] (%)
1	 **1m**	 **2a**	88
2[c]	 **1n**	 **2a**	82
3[d]	 **1o**	 **2a**	87
4	 **1p**	 **2a**	90
5[e]	 **1q**	 **2q**	66
6[e]	 **1r**	 **2r**	45
7[e]	 **1s**	 **2s**	50

[a]Reaction conditions: **1** (0.5 mmol), *fac*-Ir(ppy)$_3$ (0.005 mmol), Li_2CO_3 (0.5 mmol), DMA (2 mL) at rt irradiated by a 7 W blue LED for 48 h under N_2 atmosphere. [b]Isolated yield. [c]THP = Tetrahydropyranyl. [d]TBS = *tert*-Butyldimethylsilyl. [e]The reaction was conducted for 72 h.

In summary, we have developed an efficient, visible light-induced intramolecular dearomative cyclization of α-bromo-*N*-benzyl-alkylamide for the synthesis of 2-azaspiro[4.5]decanes. This reaction allows for a highly regioselective construction of spirocyclohexadienones with a broad substrate scope under mild conditions in good to excellent yields. These products have the potential to be converted to spirocyclohexadienones which are of use in medicinal chemistry and other applications. Further work towards expanding the use of photoredox catalysis in the construction of spirocyclic product is underway.



Scheme 2. Plausible Reaction Mechanism

This work was financially supported by National Natural Science Foundation of China (No. 21232003). We thank the Instrumental Analysis Center of Shanghai Jiao Tong University for microanalysis.

Notes and references

1 (a) S. P. Roche and J. A. Porco, *Angew. Chem. Int. Ed.*, 2011, **50**, 4068; (b) L. H. Mejorado and T. R. R. Pettus, *J. Am. Chem. Soc.*, 2006, **128**, 15625; (c) K. C. Nicolaou, D. J. Edmonds, A. Li and G. S. Tria, *Angew. Chem. Int. Ed.*, 2007, **46**, 3942; (d) D. J. Wardrop, M. S. Burge, W. Zhang and J. A. Ortíz, *Tetrahedron Lett.*, 2003, **44**, 2587.
2 W. M. Kazmierski, E. Furfine, A. Spaltenstein and L. L. Wright, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 3431.
3 Y.-L. Yang, F.-R. Chang and Y.-C. Wu, *Helv. Chim. Acta*, 2004, **87**, 1392.
4 A. M. Badger, T. M. Newman-Tarr and J. L. Satterfield, *Immunopharmacology*, 1997, **37**, 53.
5 (a) N. R. Ball-Jones, J. J. Badillo and A. K. Franz, *Org. Biomol. Chem.*, 2012, **10**, 5165; (b) V. A. D'yakonov, O. g. A. Trapeznikova, A. de Meijere and U. M. Dzhemilev, *Chem. Rev.*, 2014, **114**, 5775; (c) R. Rios, *Chem. Soc. Rev.*, 2012, **41**, 1060.
6 (a) S. Rousseaux, J. García-Fortanet, M. A. D. A. Sanchez and S. L. Buchwald, *J. Am. Chem. Soc.*, 2011, **133**, 9282; (b) F. López Ortiz, M. J. Iglesias, I. Fernández, C. M. Andújar Sánchez and G. Ruiz Gómez, *Chem. Rev.*, 2007, **107**, 1580; (c) A. R. Pape, K. P. Kaliappan and E. P. Kündig, *Chem. Rev.*, 2000, **100**, 2917; (d) P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123; (e) T. R. Ibarra-Rivera, R. Gamez-Montano and L. D. Miranda, *Chem. Commun.*, 2007, 3485. (f) Y. Li, L. Zhang, L. Zhang, Y. Wu and Y. Gong, *Eur. J. Org. Chem.*, 2013, **35**, 8039; (g) G. Han, Y. Liu and Q. Wang, *Org. Lett.*, 2014, **16**, 3188; (h) J. Liang, J. Chen, F. Du, X. Zeng, L. Li and H. Zhang, *Org. Lett.*, 2009, **11**, 2820; (i) C. Ovens, N. G. Martin and D. J. Procter, *Org. Lett.*, 2008, **10**, 1441; (j) W. Kong, E. Merino and C. Nevado, *Angew. Chem. Int. Ed.*, 2014, **53**, 5078; (k) W. Kong, M. Casimiro, N. Fuentes, E. Merino and C. Nevado, *Angew. Chem. Int. Ed.*, 2013, **52**, 13086; (l) F. C. Pigge, R. Dhanya and E. R. Hoefgen, *Angew. Chem. Int. Ed.*, 2007, **46**, 2887; (m) F. Diaba, A. Martínez-Laporta and J. Bonjoch, *J. Org. Chem.*, 2014, **79**, 9365; (n) S. Santra and P. R. Andreana, *J. Org. Chem.*, 2011, **76**, 7632; (o) M. Winkler, M. Maynadier, S. Wein, M.-A. Lespinasse, G. Boumis, A. E. Miele, H. Vial and Y.-S. Wong, *Org. Biomol. Chem.*, 2015, **13**, 2064. (p) V. I. Minkin, E. P. Ivachnenko, A. I. Shif, L. P. Olekhnovitch, O. E. Kompan, A. I. Yanovskii and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1988, 990. (q) R. Gámez-Montaño, T. Ibarra-Rivera, L. El Kaim and L. D. Miranda, *Synthesis*, 2010, 1285.
7 G. M. Rishton and M. A. Schwanz, *Tetrahedron Lett.*, 1988, **29**, 2643.
8 J. Boivin, M. Yousfi and S. Z. Zard, *Tetrahedron Lett.*, 1997, **38**, 5985.
9 F. G. de Turiso and D. P. Curran, *Org. Lett.*, 2005, **7**, 151.
10 A. R. Todd and D. H. Hey, *J. Chem. Soc. (C)*, 1967, 1518.
11 (a) J. García-Fortanet, F. Kessler and S. L. Buchwald, *J. Am. Chem. Soc.*, 2009, **131**, 6676; (b) R. B. Bedford, C. P. Butts, M. F. Haddow, R. Osborne and R. F. Sankey, *Chem. Commun.*, 2009, 4832; (c) R. B. Bedford, N. Fey, M. F. Haddow and R. F. Sankey, *Chem. Commun.*, 2011, **47**, 3649; (d) Q.-F. Wu, W.-B. Liu, C.-X. Zhuo, Z.-Q. Rong, K.-Y. Ye and S.-L. You, *Angew. Chem. Int. Ed.*, 2011, **50**, 4455; (e) K.-J. Wu, L.-X. Dai and S.-L. You, *Org. Lett.*, 2012, **14**, 3772; (f) K.-J. Wu, L.-X. Dai and S.-L. You, *Chem. Commun.*, 2013, **49**, 8620; (g) R.-Q. Xu, Q. Gu, W.-T. Wu, Z.-A. Zhao and S.-L. You, *J. Am. Chem. Soc.*, 2014, **136**, 15469; (h) R.-D. Gao, C. Liu, L.-X. Dai, W. Zhang and S.-L. You, *Org. Lett.*, 2014, **16**, 3919; (i) C.-X. Zhuo and S.-L. You, *Angew. Chem.*

Int. Ed., 2013, **52**, 10056; (j) K. Du, P. Guo, Y. Chen, Z. Cao, Z. Wang and W.-J. Tang, *Angew. Chem. Int. Ed.*, 2015, **54**, 3033.

12 (a) W.-P. Li, Y.-H. Zhu, Y.-Q. Duan, M.-L. Zhang and C.-J. Zhu, *Adv. Synth. Catal.*, 2015, **357**, 1277; (b) Q. Wang, J. Huang and L. Zhou, *Adv. Synth. Catal.*, 2015, **357**, 2479; (c) H. Jiang, X.-D. An, K. Tong, T.-Y. Zheng, Y. Zhang and S.-Y. Yu, *Angew. Chem. Int. Ed.*, 2015, **54**, 4055; (d) J. Xuan and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 6828; (e) Q.-H. Deng, J.-R. Chen, Q. Wei, Q.-Q. Zhao, L.-Q. Lu and W.-J. Xiao, *Chem. Commun.*, 2015, **51**, 3537; (f) C. Qu, P. Xu, W. Ma, Y. Cheng and C. Zhu, *Chem. Commun.*, 2015, **51**, 13508; (g) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322; (h) L. Shi and W.-J. Xia, *Chem. Soc. Rev.*, 2012, **41**, 7687; (i) Z.-Q. Wang, M. Hu, X.-C. Huang, L.-B. Gong, Y.-X. Xie and J.-H. Li, *J. Org. Chem.*, 2012, **77**, 8705; (j) T. P. Yoon, M. A. Ischay and J. Du, *Nat. Chem.*, 2010, **2**, 527; (k) Q.-X. Qin and S.-Y. Yu, *Org. Lett.*, 2015, **17**, 1894; (l) Y. Su, L. Zhang and N. Jiao, *Org. Lett.*, 2011, **13**, 2168; (m) J.-J. Zhong, Q.-Y. Meng, G.-X. Wang, Q. Liu, B. Chen, K. Feng, C.-H. Tung and L.-Z. Wu, *Chem. Eur. J.*, 2013, **19**, 6443; (n) R. Tomita, Y. Yasu, T. Koike and M. Akita, *Angew. Chem. Int. Ed.*, 2014, **53**, 7144; (o) J. Zoller, D. C. Fabry, M. A. Ronge and M. Rueping, *Angew. Chem. Int. Ed.*, 2014, **53**, 13264; (p) D. C. Fabry, J. Zoller, S. Raja and M. Rueping, *Angew. Chem. Int. Ed.*, 2014, **53**, 10228; (q) L. Ruiz Espelt, I. S. McPherson, E. M. Wiensch and T. P. Yoon, *J. Am. Chem. Soc.*, 2015, **137**, 2452. (r) W.-T. Wei, R.-J. Song, X.-H. Ouyang, Y. Li, H.-B. Li and J.-H. Li, *Org. Chem. Front.*, 2014, **1**, 484; (s) X.-H. Yang, X.-H. Ouyang, W.-T. Wei, R.-J. Song and J.-H. Li, *Adv. Synth. Catal.*, 2015, **357**, 1161; (t) X.-H. Ouyang, R.-J. Song, Y. Li, B. Liu and J.-H. Li, *J. Org. Chem.*, 2014, **79**, 4582. (u) J. Liu, Q. Liu, H. Yi, C. Qin, R. Bai, X. Qi, Y. Lan and A. Lei, *Angew. Chem. Int. Ed.*, 2014, **53**, 502; (v) Y. Xi, H. Yi and A. Lei, *Org. Biomol. Chem.*, 2013, **11**, 2387; (w) G. Zhang, C. Liu, H. Yi, Q. Meng, C. Bian, H. Chen, J.-X. Jian, L.-Z. Wu and A. Lei, *J. Am. Chem. Soc.*, 2015, **137**, 9273; (x) H. Yi, C. Bian, X. Hu, L. Niu and A. Lei, *Chem. Commun.*, 2015, **51**, 14046; (y) H. Yi, X. Zhang, C. Qin, Z. Liao, J. Liu and A. Lei, *Adv. Synth. Catal.*, 2014, **356**, 2873. (z) Z. Zhang, X. Tang and W. R. Dolbier, *Org. Lett.*, 2015, **17**, 4401.

13 (a) J. W. Tucker, J. D. Nguyen, J. M. R. Narayanam, S. W. Krabbe and C. R. J. Stephenson, *Chem. Commun.*, 2010, **46**, 4985; (b) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2011, **133**, 4160; (c) J. W. Tucker, J. M. R. Narayanam, S. W. Krabbe and C. R. J. Stephenson, *Org. Lett.*, 2010, **12**, 368; (d) C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2012, **134**, 8875; (e) J. W. Tucker and C. R. J. Stephenson, *Org. Lett.*, 2011, **13**, 5468; (f) R. Lin, H.-N, Sun, C. Yang, W.-B. Shen and W.-J. Xia, *Chem. Commun.*, 2015, **51**, 399; (g) H.-L. Huang, H. Yan, C. Yang and W.-J. Xia, *Chem. Commun.*, 2015, **51**, 4910; (h) P. Xu, K. Hu, Z.-X Gu, Y.-X. Cheng and C.-J. Zhu, *Chem. Commun.*, 2015, **51**, 7222; (i) B. Hu, H.-X. Chen, Y. Liu, W.-H. Dong, K. Ren, X.-M. Xie, H. Xu and Z.-Z. Zhang, *Chem. Commun.*, 2014, **50**, 13547; (j) Q. Liu, H. Yi, J. Liu, Y. Yang, X. Zhang, Z. Zeng and A. Lei. *Chem. Eur. J.*, 2013, **19**, 5120; (k) D. Liu, S. Tang, H. Yi, C. Liu, X. Qi, Y. Lan and A. Lei, *Chem. Eur. J.*, 2014, **20**, 15605.

14 (a) X. Ju, Y. Liang, P. Jia, W. Li and W. Yu, *Org. Biomol. Chem.*, 2012, **10**, 498; (b) C. Liu, D. Liu, W. Zhang, L. Zhou and A. Lei. *Org. Lett.*, 2013, **15**, 6166.

15 (a) F. Gao, C. Yang, G.-L. Gao, L. Zheng and W.-J. Xia, *Org. Lett.*, 2015, **17**, 3478; (b) Z.-X. Gu, H.-L. Zhang, P. Xu, Y.-X. Cheng and C.-J. Zhu. *Adv.Synth. Catal*., 2015, **357**,3057.

16 P. Xu, J. Xie, Q.-C. Xue, C.-D. Pan, Y.-X Cheng and C.-J. Zhu, *Chem. Eur. J.*, 2013, **19**, 14039.

17 A. J. Clark, J. V. Geden, S. Thom and P. Wilson, *J. Org. Chem.*, 2007, **72**, 5923.