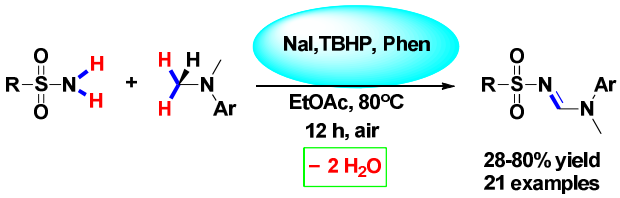
RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

TOC

A direct de-tetra-hydrogenative cross-coupling reaction between C_{sp3}–H bond and sulfamide under transition-metal-free condition is reported to give corresponding amidines.



Journal Name

COMMUNICATION

Unexpected C=N bond formation *via* NaI-catalyzed oxidative de-tetra-hydrogenative cross-couplings between *N*, *N*-dimethyl aniline and sulfamides

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

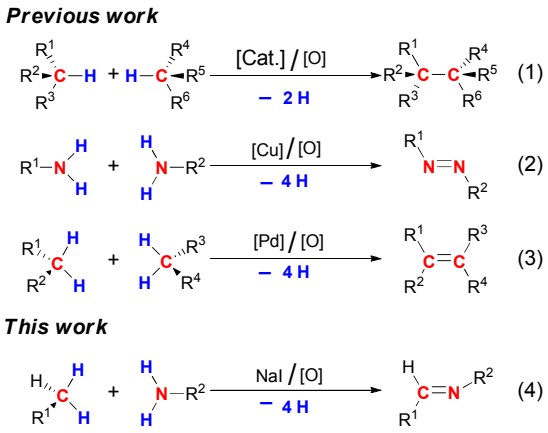
DOI: 10.1039/x0xx00000x

www.rsc.org/

Yang Zheng,[a] Jincheng Mao,*[ab] Jie Chen,[a] Guangwei Rong,[a] Defu Liu,[a] Hong Yan,[a] Yongjian Chi[a] and Xinfang Xu*[a]

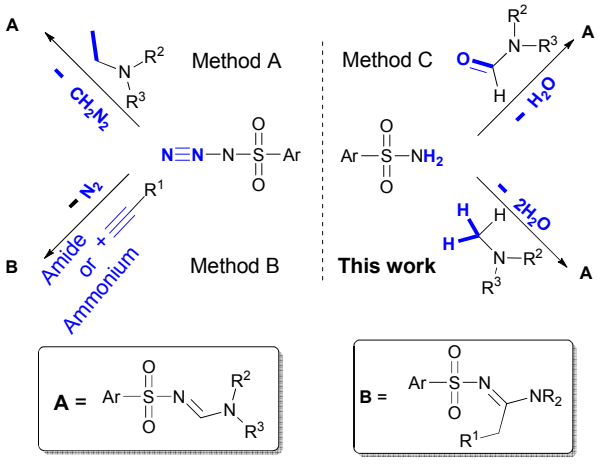
A direct and convenient C=N bonds formation reaction was reported, which was a de-tetra-hydrogenative cross-coupling (DTCC) reaction between *N*, *N*-dimethyl aniline and sulfamide under transition-metal-free condition, and to give sulfonyl amidine derivatives in moderate to high yield.

The cross-dehydrogenative coupling (CDC) has been proved a powerful strategy in organic synthesis to form the C-C and C-X bonds in recent years (Scheme 1, eq 1).[1] However, formation of double bond by removing four hydrogen atoms *via* twice CDCs is still a great challenge because it is difficult to further remove additional two hydrogen atoms after the single bond was formed through the first CDC reaction. Recently, Jiao[2a] and Shi[2b] have independently reported the pioneering works in constructing N=N bond to synthesize aromatic azo compounds with copper catalyst (Scheme 1, eq 2). Then, You and co-workers reported another example of formation the C=C bond by palladium catalyzed de-tetra-hydrogenative cross coupling (Scheme 1, eq 3).[3] These reports illuminate a new strategy to construct double bonds via CDC reactions. Inspired by these works, here, we wish to report our recent result on C=N bond formation between C_{sp3}–H bond and sulfamide by one-step DTCC reaction under transition-metal-free conditions (Scheme 1, eq 4).



Scheme 1 Various dehydrogenative cross-coupling reactions.

Sulfonyl amidines are very unique motifs, which are important in medicinal and synthetic chemistry. [6a] In recent years, many synthetic methods have been developed (Scheme 2), including Li (Method A),[4] Chang (Method B),[5] Wan (Method C),[6a] and others' work[6b-6d]. However, sulfonyl azide was employed in the first two reports, which was expensive and potentially explosive. In addition, the metal catalyst was essential in these transformations. In method C, product **A** could be achieved in the absence of transition-metal catalyst via the reaction between sulfonamide and formamide. However, formamide is also used as the solvent to insure good conversion. In addition, aromatic formamides could not be involved into the substrate scope because they are usually solid.



Scheme 2 Synthesis of sulfonyl amidines.

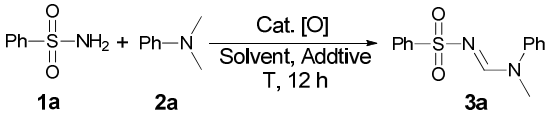
[a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China, E-mail: xinfangxu@suda.edu.cn.
[b] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, 610500, P. R. China, E-mail: jcmao@suda.edu.cn

† 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

Herein, we developed a novel strategy to access to sulfonyl amidines with *N*, *N*-dimethyl aniline and sulfonamide, which provides a direct method to synthesize various sulfonyl amidines containing the structure of aromatic rings.[4-6] Comparing to the sp^3 C–H amination[7] and above mentioned reports, this method could be considered as a- powerful alternative strategy in direct C=N bond formation.

The optimization of catalytic system was summarized in Table 1. Initially, various readily available catalysts were investigated (Table 1, entries 1-8) and NaI was found to be the best one (Table 1, entry 1). When the amount of **2a** was increased, the yield of this conversion was obviously promoted (Table 1, entry 1 vs entry 15). Notably, the oxidant plays an important role in this reaction. As shown in Table 1, anhydrous TBHP (5-6 M in decane) as the oxidant was proved to be the best (80%, Table 1, entry 16), which is better than TBHP (in water) did (65%, Table 1, entry 15). When other oxidants were used, **3a** can not be obtained (Table 1, entries 9-14). In order to improve the catalytic effect, various additives were employed into the reaction (Table 1, entries 17-19) and 1,10-phenanthroline (Phen) was best (Table 1, entry 17). Althoguh similar transofmations assisted by organocatalysts have been present via the radical intermediate,[8] and the detailed mechanism is not very clean yet. However, from the comparion experiments of with and without the ligand, it indicates that the ligand assists the first part of the transformation, from materials to **C**.[9]

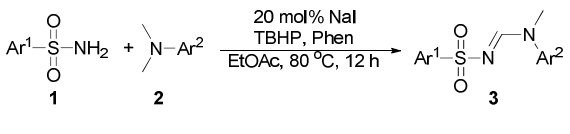
Table 1 Optimization of the reaction conditions[a]

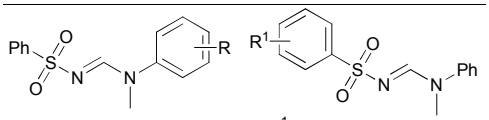


Entry	Cat.	Oxidant	Additive	Yield[b] (%)
1	NaI	TBHP	—	40
2	—	TBHP	—	ND
3	KI	TBHP	—	35
4	TBAI	TBHP	—	31
5	I_2	TBHP	—	11
6	$PhI(OAc)_2$	TBHP	—	trace
7	CuI	TBHP	—	trace
8	$FeCl_3$	TBHP	—	trace
9	NaI	O_2	—	ND
10	NaI	$K_2S_2O_8$	—	trace
11	NaI	H_2O_2	—	ND
12	NaI	TBPB	—	ND
13	NaI	DDQ	—	ND
14	NaI	DCP	—	ND
15[c]	NaI	TBHP	—	65
16[c,d]	NaI	TBHP	—	80
17[c,d]	NaI	TBHP	Phen	90(70)[e]
18[c,d]	NaI	TBHP	1H-Benzotriazole	86(67)[e]
19[c,d]	NaI	TBHP	TMEDA	82(62)[e]

[a] Reaction conditions: benzene sulfonamide (**1a**, 0.5 mmol), *N*,*N*-dimethyl aniline (**2a**, 0.7 mmol), catalyst (20 mol%), TBHP (70% aqueous solution, 1.5 mmol), additive (0.05 mmol, if added), toluene (2.0 mL), 110 °C, 12 h, air; [b] LC yield using an internal standard; [c] **2a** (2.1 mmol), EtOAc (2.0 mL) as the solvent, 80 °C; [d] TBHP (5-6 M in decane, 1.5 mmol); [e] Isolated yields are given in parentheses.

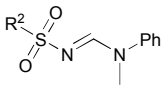
Table 2 NaI-catalyzed DTCC reactions[a]





R = H, **3a**, 70%
R = 4-Me, **3b**, 32%
R = 4-F, **3c**, 32%
R = 3-Br, **3d**, 46%
R = 4-Br, **3e**, 53%
R = 3-Cl, **3f**, 51%
R = 2-Cl, **3g**, 28%
R = 4-Cl, **3h**, 33%
R = 4-NO_2, **3i**, 54%

R^1 = 4-Me, **3j**, 70%
R^1 = 4-OMe, **3k**, 65%
R^1 = 4-F, **3l**, 53%
R^1 = 3-Br, **3m**, 70%
R^1 = 4-Cl, **3n**, 60%
R^1 = 4-Br, **3o**, 70%
R^1 = 4-acetamido, **3p**, 40%
R^1 = 4-CF_3, **3q**, 67%
R^1 = 4-NO_2, **3r**, 54%



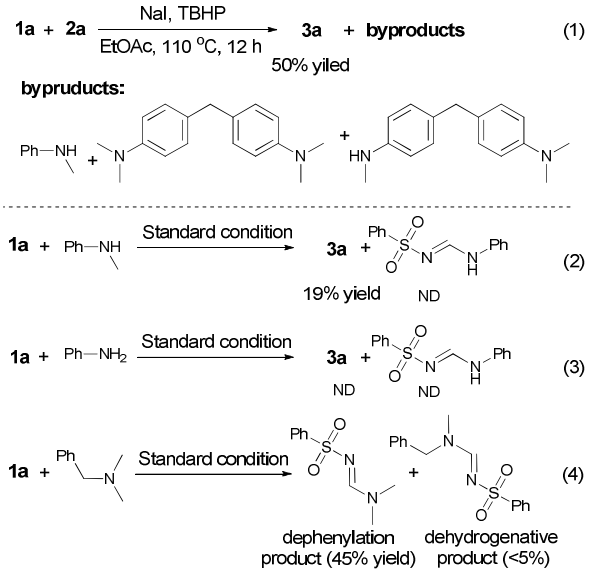
R^2 = 2-naphthyl, **3s**, 60%
R^2 = 2,4,6-trimethylbenzene, **3t**, 80%
R^2 = 2-thienyl, **3u**, 60%

[a] Reaction conditions: **1** (0.5 mmol), **2** (2.1 mmol), NaI (20 mol %), TBHP (in decane, 1.5 mmol), Phen (0.05 mmol), EtOAc (2.0 mL), 80 °C, 12 h, air. Isolated yield based on **1**.

Under the optimized conditions, the substrates generality was tested, and the results are shown in Table 2. Electron-donating group (such as methyl) on the aniline gave slightly low yield (Table 2, **3b**). While electron-withdrawing groups (such as fluoro, chloro, bromo and nitro groups) on the aniline had different influence, and yields of corresponding products **3** were obtained ranging from 28% to 54%. Among these substitutents, bromo and nitro groups were better than others (Table 2, **3d**, **3e** and **3i**). *m*-Chloro group on the aniline could also lead to the relatively good yield (Table 2, **3f**). All in all, we can see that *N*,*N*-dimethyl anilines without any substituents on the aromatic ring gave the highest yield.

Subsequently, the protocol was applied to the reaction with a range of sulfonamides. To our delight, moderate to good yields were acquired. Both electron-donating groups and electron-withdrawing groups on the aromatic ring could be well tolerated under this conditions (Table 2, **3j-3t**). It is noteworthy that heterocycle sulfonamides could give **3u** with satisfying yield (60%).

To gain insight into the reaction mechanism, some additional experiments have been performed as shown in Scheme 3. The model reaction between **1a** and **2a** was performed under higher temperature (110 °C) in the absence of Phen. **3a** was obtained together with many byproducts, which were generated from **2a** itself (Scheme 3, eq 1).[10] This promoted us to conduct more reactions between **1a** and various anilines. When *N*-methyl aniline was used instead of **2a**, **3a** could also be obtained with lower yield and *N*-demethyl analog of **3a** was not detected (Scheme 3, eq 2). Then we tried to use aniline as the substrate. However, **3a** or *N*-demethyl analog of **3a** was not acquired (Scheme 3, eq 3). In view of above experiments, we can see that the methyl group of **3a** probably did not come from TBHP,[11] and it is probably from *N*-methyl aniline.[21b] Next, benzyl-*N*,*N*-dimethylamine was employed.

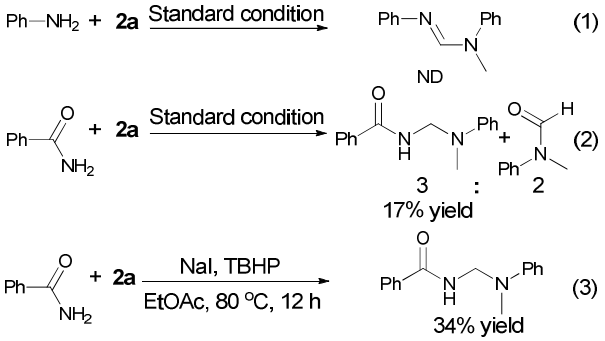


Scheme 3. Investigation of reactions between **1a** and different amines.

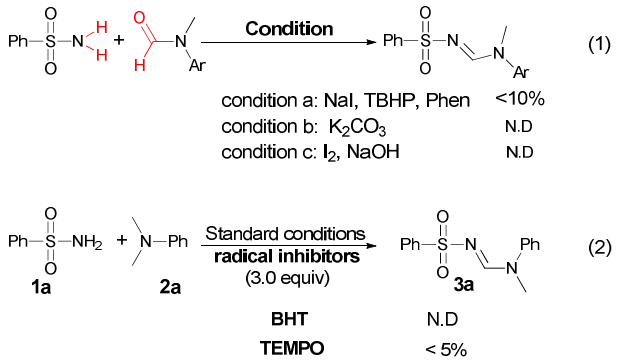
To our surprise,the dephenylation coupling product *N*,*N*-dimethyl-*N*'-phenylsulfonyl)formimid-amide was afforded in 45% yield (Scheme 3, eq 4).[12] Other substrate were also tested, including *N*,*N*-diethylaniline, *N*-ethyl-*N*-methylaniline, triethylamine, and trimethylamine, however, only very lower or no conversion was observed.[9]

Subsequently, aniline and benzamide were employed as the substrates to react with **2a**. However, the desired product could not be generated under the standard condition when aniline was employed as the substrate (Scheme 4, eq 1). And when benzamide reacted with **2a**, two products were afforded and the ratio was 3:2, which determined by NMR. Interestingly, unexpected *N*-methylformanilide was found here while it was not detected in the model reaction between **1a** and **2a** (Scheme 4, eq 2). Without using Phen, only *N*-[(methylanilino)methyl]benzamide was obtained with higher yield of 34% (Scheme 4, eq 3).

Based on Wan's work,[6a] **2a** was possibly oxidized to *N*-methyl-*N*-formyl-aniline by TBHP and then participated in the reaction. So we directly used *N*-methyl-*N*-formyl-aniline as the substrate, and less amount of desired product **3a** was obtained (Scheme 5, eq 1).



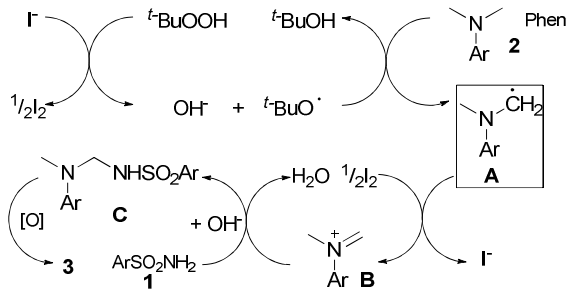
Scheme 4. Investigation of the reactions between **2a** and aniline or benzamide.



Scheme 5. Investigation of the reaction mechanism.

Therefore, it was assumed that the mechanism of the reaction may proceed in a different pathway in our protocol. In addition, it was found that with the base could not afford **3a**, either. This may prove that it was not a schiff base-involved reaction. Besides, the desired product was not detected when the reaction was carried out in the presence of I_2 and NaOH, which could generate the hypoiodite species in situ and catalyze the C–H functionalization.[13a,13b] Next, radical scavengers like TEMPO or BHT (butylated hydroxytoluene) was added to the reaction, and the reaction was inhibited (Scheme 5, eq 2). This suggested that the transformation probably proceeded through a radical progress.

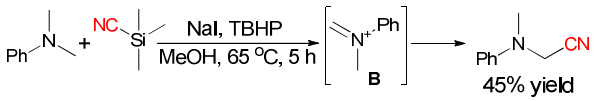
According to prior reports[14] and above observation, a plausible reaction mechanism is proposed in Scheme 6. In the first step, TBHP was resolved to generate *tert*-butoxyl radical and hydroxyl ion in associate with reduction of iodine ion.[13] Then *tert*-butoxyl radical abstracted a hydrogen atom from **2** to generate radical **A**, which subsequently formed iminium ion **B** through single electron transfer (SET) with iodine, and this process was well studied and accepted in general[15-21] Afterwards, benzene sulfonamide as a unique nucleophile reagent[16] attacked **B**, [17-26]followed by deprotonation to form **C**, which was confirmed by HRMS and proton NMR.[9] Sequentially further oxidized by TBHP to produce the desired product **3**.[2,3,27]



Scheme 6. Possible reaction pathways.

To our knowledge, various catalytic systems were developed for synthesis of iminium ions from *N*,*N*-dialkylanilines. The scope of catalysts includes Ru, [17] Rh,[18] Ir,[19] Cu,[20] Fe,[21] Mo,[22] Au,[23] Re,[24] V[25] and other complexes.[26] However, NaI-catalyzed reaction between *N*,*N*-dialkylaniline and TMSCN to transform

iminium ions has never been reported. To our delight, 45% yield of the target product was obtained as shown in Scheme 7, which will suggest that the corresponding iminium ion **B** was the possible intermediate.[19,21,26]



Scheme 7. Control experiment..

Conclusions

In summary, we have discovered a transition-metal-free method for directly constructing new C=N bonds through oxidative DTCC reactions, which provide a novel strategy to generate sulfonyl amidines with *N*,*N*-dimethyl aniline and sulfonamide. And this effecitve process use commercially available and abundant substrates as starting materials and was catalyed by inexpensive NaI. It could be expect that this unanticipated finding would have a broader role on dehydrogenative cross-coupling by removing four hydrogen atoms in one-pot. The further application of our method for biologically active molecules synthesis is underway in our laboratory.

Acknowledgements

We gratefully acknowledge the grants from the Research Grant under the SA/China Agreement on Cooperation in Science and Technology, the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry; the Priority Academic Program Development of Jiangsu Higher Education Institutions; and the Key Laboratory of Organic Synthesis of Jiangsu Province.

Notes and references

1 (a) C.-J. Li, *Acc. Chem. Res*., 2009, **42**, 335−344; (b) C. Liu, H. Zhang, W. Shi and A. Lei, *Chem. Rev.*, 2011, **111**, 1780−1824; (c) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215−1292; (d) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Rev.*, 2011, **111**, 1293−1314; (e) C. Zhang, C. Tang and N. Jiao, *Chem. Soc. Rev.*, 2012, **41**, 3464–3484; (f) S. A. Girard, T. Knauber and C.-J. Li, *Angew. Chem. Int. Ed.*, 2013, **52**, 2-29; (g) J. Zhou, C. Jin, X. Li and W. Su, *RSC Adv.*, 2015, **5**, 7232-7236; (h) B. Dadpou and D. Nematollahi, *RSC Adv.*, 2014, **4**, 50365-50368; (i) A. Sagar, S. Vidyacharan and D. S. Sharada, *RSC Adv.*, 2014, **4**, 37047-37050; (j) C. Zheng and S. You, *RSC Adv.*, 2014, **4**, 6173-6214.

2 (a) C. Zhang and N. Jiao, *Angew. Chem. Int. Ed.*, 2010, **49**, 6174–6177; (b) Y. Zhu and Y. Shi, *Org. Lett.*, 2013, **15**, 1942−1945.

3 G. Li, S. Qian, C. Wang and J. You, *Angew. Chem. Int. Ed.*, 2013, **52**, 7837–7840.

4 (a) X. Xu, X. Li, L. Ma, N. Ye and B. Weng, *J. Am. Chem. Soc*., 2008, **130**, 14048–14049; (b) X. Xu, Z. Ge, D. Cheng, C. Lu, Q. Zhang, N. Yao and X. Li, *Org. Lett.*, 2010, **12**, 897−899.

5 (a) I. Bea, H. Han and S. Chang, *J. Am. Chem. Soc*., 2005, **127**, 2038−2039; (b) S. Chang, M. Lee, D. Y. Jung, E. J. Yoo, S. H. Cho and S. K. Han, *J. Am. Chem. Soc*., 2006, **128**, 12366−12367; (c) E. J. Yoo, I. Bea, S. H. Cho, H. Han and S. Chang, *Org. Lett*., 2006, **8**, 1347−1350; (d) J. Kim, S. Y. Lee, J. Lee, Y. Do and S. Chang, *J. Org. Chem.*, 2008, **73**, 9454–9457.

6 (a) S. Chen, Y. Xu and X. Wan, *Org. Lett.*, 2011, **13**, 6152−6155; (b) N. Liu, B.-Y. Tang, Y. Chen and L. He, *Eur. J. Org. Chem.*, 2009, 2059–2062; (c) Z. Niu, S. Lin, Z. Dong, H. Sun, F. Liang and J. Zhang, *Org. Biomol. Chem.*, 2013, **11**, 2460–2465; (d) N. Chandna, N. Chandak, P. Kumar, J. K. Kapoor and P. K. Sharma, *Green Chem.*, 2013, **15**, 2294–2301.

7 For C-H amination, see: (a) J.-L. Liang, S.-X. Yuan, J.-S. Huang, W.-Y. Yu and C.-M. Che, *Angew. Chem. Int. Ed.*, 2002, **41**, 3465−3468; (b) K. W. Fiori and J. D. Bois, *J. Am. Chem. Soc*., 2007, **129**, 562−568; (c) C. Liang, F. Collet, F. Robert-Peillard, P. Muller, R. H. Dodd and P. Dauban, *J. Am. Chem. Soc*., 2008, **130**, 343−350; (d) J. A. Jordan-Hore, C. C. C. Johansson, M. Gulias, E. M. Beck and M. J. Gaunt, *J. Am. Chem. Soc*., 2008, **130**, 16184−16186; (e) Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari and T. H. Warren, *Angew. Chem. Int. Ed.*, 2008, **47**, 9961–9964; (f) M. J. B. Aguila, Y. M. Badiei and T. H. Warren, *J. Am. Chem. Soc.*, 2013, **135**, 9399−9406; (g) E. S. Jang, C. L. McMullin, M. Käß, K. Meyer, T. R. Cundari and T. H. Warren, *J. Am. Chem. Soc*., 2014, **136**, 10930−10940.

8 (a) C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S.-F. Zheng, B.-J. Li and Z.-J. Shi, *Nat. Chem.*, 2010, **2**, 1044-1049; (b) W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong and A. Lei, *J. Am. Chem. Soc*., 2010, **132**, 16737-16740; (c) G. Deng, K. Ueda, S. Yanagisawa, K. Itami and C. Li, *Chem. Eur. J.*, 2009, **15**, 333-337; (d) S. Yanagisawa, K. Ueda, T. Taniguchi and K. Itami, *Org. Lett.*, 2008, **10**, 4673-4676.

9 See Supporting Information for details.

10 (a) X. Ling, Y. Xiong, R. Huang, X. Zhang, S. Zhang and C. Chen, *J. Org. Chem.*, 2013, **78**, 5218−5226; (b) S. Murata, M. Miura and M. Nomura, *J. Chem. Soc., Chem. Commun.*, 1989, 116-118; (c) S. Murata, M. Miura and M. Nomura, *J. Org. Chem.*, 1989, **54**, 4700-4702; (d) X. Chen, T. Chen, Y. Xiang, Y. Zhou, D. Han, L.-B. Han and S.-F. Yi, *Tetrahedron Lett.*, 2014, 4572-4575; (e) T. Sakakibara, S. Karasumaru and I. Kawano, *J. Am. Chem. Soc.*, 1985, **107**, 6417-6419; (f) L.-T. Li, J. Huang, H.-Y. Li, L.-J. Wen, P. Wang and B. Wang, *Chem. Commun.*, 2012, **48**, 5187-5189; (g) C. D. Prasad, S. J. Balkrishna, A. Kumar, B. S. Bhakuni, K. Shrimali, S. Biswas and S. Kumar, *J. Org. Chem.*, 2013, **78**, 1434-1443.

11 (a) Q. Xia, X. Liu, Y. Zhang, C. Chen and W. Chen, *Org. Lett*., 2013, **15**, 3326−3329; (b) Y. Zhu, H. Yan, L. Lu, D. Liu, G. Rong and J. Mao, *J. Org. Chem*., 2013, **78**, 9898−9905; (c) Y. Zhang, J. Feng and C.-J. Li, *J. Am. Chem. Soc.*, 2008, **130**, 2900-2901; (d) Z. Xu, C. Yan and Z.-Q. Liu, *Org. Lett.*, 2014, **16**, 5670−5673.

12 Y. Zhang, H. Fu, Y. Jiang and Y. Zhao, *Org. Lett.*, 2007, **9**, 3813−3816.

13 (a) W. Wei, C. Zhang, Y. Xu and X. Wan, *Chem. Commun.*, 2011, **47**, 10827–10829; (b) L.-T. Li, H.-Y. Li, L.-J. Xing, L.-J. Wen, P. Wang and B. Wang, *Org. Biomol. Chem.*, 2012, **10**, 9519–9522; (c) E. Shi, Y. Shao, S. Chen, H. Hu, Z. Liu, J. Zhang and X. Wan, *Org. Lett.*, 2012, **14**, 3384-3387; (d) W.-P. Mai, H.-H. Wang, Z.-C. Li, J.-W. Yuan, Y.-M. Xiao, L.-R. Yang, P. Mao and L.-B. Qu, *Chem. Commun.*, 2012, **48**, 10117–10119; (e) S. Tang, Y. Wu, W. Liao, R. Bai, C. Liu and A. Lei, *Chem. Commun*., 2014, **50**, 4496−4499; (f) D. Zhao, T. Wang, Q. Shen and J.-X. Li, *Chem. Commun*., 2014, **50**, 4302−4304.

14 (a) Y. Yan, Y. Zhang, C. Feng,; Z. Zha and Z. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 8077−8081; (b) Y. Yan, Y. Zhang, Z. Zha and Z. Wang, *Org. Lett.*, 2013, **15**, 2274−2277; (c) D.

Zhao, T. Wang, Q. Shen and J.-X. Li, *Chem. Commun.*, 2014, **50**, 4302−4304.
15 (a) M. O. Ratnikov and M. P. Doyle, *J. Am. Chem. Soc*., 2013, **135**, 1549–1557; (b) S.-I. Murahashi, N. Komiya and H. Terai, Angew. Chem. Int. Ed., 2005, 44, 6931 –6933; (c) S.-I. Murahashi, N. Komiya, H. Terai and T. Nakae, J. Am. Chem. Soc., 2003, 125, 15312-15313; (d) S.-I. Murahashi, T. Nakae, H. Terai and N. Komiya,J. Am. Chem. Soc., 2008, 130, 11005–11012.
16 (a) V. Petrov, V. Petrova, G. V. Girichev, H. Oberhammer, N. I. Giricheva and S. Ivanov, *J. Org. Chem.*, 2006, **71**, 2952-2956; (b) G. Pelletier and D. A. Powell, *Org. Lett*., 2006, **8**, 6031−6034; (c) X.-Q. Yu, J.-S. Huang, X.-G. Zhou and C.-M. Che, *Org. Lett*., 2000, **2**, 2233−2236; (d) S.-M. Au, J.-S. Huang, C.-M. Che and W.-Y. Yu, *J. Org. Chem.*, 2000**, 65**, 7858-7864; (e) A. Mielgo and C. Palomo, *Chem. Asian J.*, 2008, **3**, 922−948.
17 (a) S.-I. Murahashi, N. Komiya, H. Terai and T. Nakae, *J. Am. Chem. Soc*.**,** 2003, **125**, 15312−15313; (b) S.-I. Murahashi, N. Komiya and H. Terai, *Angew. Chem. Int. Ed.*, 2005, **44**, 6931–6933; (c) S.-I. Murahashi, T. Nakae, H. Terai and N. Komiya, *J. Am. Chem. Soc*., 2008, **130**, 11005−11012; (d) A. G. Condie, J. C. Gonzalez-Gomez and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2010, **132**, 1464-1465; (e) M.-Z. Wang, C.-Y. Zhou, M.-K. Wong and C.-M. Che, *Chem. Eur. J.*, 2010, **16**, 5723−5725; (f) M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny and D. C. Fabry, *Chem. Commun.*, 2011, **47**, 2360−2362.
18 A. J. Catino, J. M. Nichols, B. J. Nettles and M. P. Doyle, *J. Am. Chem. Soc.*, 2006, **128**, 5648−5649.
19 R. Magnus, S. Zhu and R. M. Koenigs, *Chem. Commun*., 2011, **47**, 12709-12711.
20 (a) Z. Li and C.-J. Li, *J. Am. Chem. Soc*., 2004, **126**, 11810−11811; (b) Z. Li, D. S. Bohle and C.-J. Li, *Proc. Natl. Acad. Sci. U. S. A*., 2006, **103**, 8928−8933; (c) L. Zhao and C.-J. Li, *Angew. Chem. Int. Ed.*, 2008, **47**, 7075–7078; (d) Y. Shen, M. Li, S. Wang, T. Zhan, Z. Tan and C.-C. Guo, *Chem. Commun.*, 2009, 953–955; (e) X. Xu and X. Li, *Org. Lett*., 2009, **11**, 1027−1029; (f) L. Zhao, B. Oliver and C.-J. Li, *Proc. Natl. Acad. Sci. U. S. A*., 2009, **106**, 4106−4611; (g) J. Xie and Z.-Z. Huang, *Angew. Chem. Int. Ed.*, 2010, **49**, 10181−10185; (h) F. Yang, J. Li, J. Xie and Z.-Z. Huang, *Org. Lett.*, 2010, **12**, 5214−5217; (i) E. Boess, D. Sureshkumar, A. Sud, C. Wirtz, C. Fares and M. Klussmann, *J. Am. Chem. Soc.*, 2011, **133**, 8106−8109; (j) M. Ghobrial, M. Schnurch and M. D. Mihovilovic, *J. Org. Chem*., 2011, **76**, 8781−8793; (k) E. Boess, C. Schmitz and M. Klussmann, *J. Am. Chem. Soc.*, 2012, **134**, 5317−5325.
21 (a) W. Han and A. R. Ofial, *Chem. Commun.*, 2009, 5024–5026; (b) H. Li, Z. He, X. Guo, W. Li, X. Zhao and Z. Li, *Org. Lett.*, 2009, **11**, 4176−4179; (c) C. M. R. Volla and P. Vogel, *Org. Lett.*, 2009, **11**, 1701−1704; (d) P. Liu, C.-Y. Zhou, S. Xiang and C.-M. Che, *Chem. Commun*., 2010, **46**, 2739–2741; (e) G. Kumaraswamy, A. N. Murthy and A. Pitchaiah, *J. Org. Chem.*, 2010, **75**, 3916–3919; (f) Y. Li, F. Jia and Z. Li, *Chem. Eur. J.*, 2013, **19**, 82–86; (g) Y. Li, L. Ma, F. Jia and Z. Li, *J. Org. Chem.*, 2013, **78**, 5638−5646.
22 K. Alagiri and K. R. Prabhu, *Org. Biomol. Chem*., 2012, 10, 835−842.
23 Y. Zhang, H. Peng, M. Zhang, Y. Cheng and C. Zhu, *Chem. Commun.*, 2011, **47**, 2354−2356.
24 A. Lin,; H. Peng, A. Abdukader and C. Zhu, *Eur. J. Org. Chem.*, 2013, 7286–7290.
25 (a) S. Singhal, S. L. Jain and B. Sain, *Chem. Commun.*, 2009, 2371-2372; (b) A. Sud, D. Sureshkumarz and M. Klussmann, *Chem. Commun.*, 2009, 3169–3171; (c) K. Alagiri, G. S. R. Kumara and K. R. Prabhu, *Chem. Commun*., 2011, **47**, 11787−11789.
26 (a) J. Dhineshkumar, M. Lamani, K. Alagiri and K. R. Prabhu, *Org. Lett.*, 2013, **15**, 1092–1095; (b) C. Zhang, C. Liu, Y. Shao, X. Bao and X. Wan, *Chem. Eur. J.*, 2013, **19**, 17917−17925; (c) A. Tanoue, W.-J. Yoo and S. Kobayashi, *Org. Lett*., 2014, **16**, 2346−2349; (d) H. Ueda, K. Yoshida and H. Tokuyama, *Org. Lett*., 2014, **16**, 4194−4197; (e) Z.-Q. Lao, W.-H. Zhong, Q.-H. Lou, Z.-J. Li and X.-B. Meng, *Org. Biomol. Chem.*, 2012, **10**, 7869–7871; (f) A. Kumar, M. K. Gupta, M. Kumar and D. Saxena, *RSC Adv.*, 2013, **3**, 1673-1678; (g) E. Manoni, A. Gualandi, L. Mengozzi, M. Bandini and P. G. Cozzi, *RSC Adv.*, 2015, **5**, 10546-10550; (h) H.-M. Huang, J.-R. Gao, Q. Ye, W.-B. Yu, W.-J. Sheng and Y.-J. Li, *RSC Adv.*, 2014, **4**, 15526-15533; (i) D. B. Ramachary, R. Sakthidevi and P. S. Reddy, *RSC Adv.*, 2013, **3**, 13497–13506.
27 (a) L. Zhao, O. Baslea and C.-J. Li, *Proc. Natl. Acad. Sci. U. S. A*., 2009, **106**, 4106–4111; (b) L. Zhao and C.-J. Li, *Angew. Chem. Int. Ed.*, 2008, **47**, 7075–7078.