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View Article Online
DOI: 10.1039/C8CC00485D

Journal Name

COMMUNICATION

# Copper-Catalyzed Synthesis of α-Amino Nitriles through Methyl Transfer from DMF to Aromatic Amines

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

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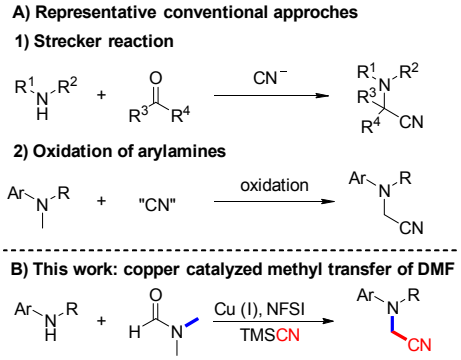
**A copper-catalyzed activation of C(sp$^3$)–H bonds of DMF at room temperature was developed, which results in the methyl transfer to aromatic amines for efficient synthesis of exceedingly valuable α-amino nitriles. This process features excellent functional group tolerance, a broad substrate scope, and high activity under ambient conditions.**

α-Amino nitriles occupy an important position in medicinal chemistry and synthetic chemistry, owing to their structural subunits exist in many biologically active molecules and natural compounds.[1] Moreover, α-amino nitriles can be facilely converted to valuable building blocks, such as α-amino acids, α-amino carbonyl compounds, β-amino alcohols, and 1,2-diamines, which are widely utilized in pharmaceuticals, agrochemicals, natural products, and catalyst architectures.[1b, 2] Accordingly, significant efforts have been devoted to the development of novel and efficient ways for preparation of α-amino nitriles. One of the mostly common methods to generate α-amino nitriles is the Strecker reaction (Scheme 1), a three-component condensation among aldehyde (or ketone), amine, and cyanide source.[3]

An alternative strategy to produce α-amino nitriles is oxidation of aryl tertiary amines to iminium ions, and subsequent reaction with cyanide. Several examples of metal-based catalysts (e.g. Ru,[4] Fe,[5] or other metals[6]), metal-free catalysts,[7] or electrochemical methods[8] have been used for sp$^2$ and sp$^3$ C-H cyanations. However, in the case of secondary aryl amines, conventional *N*-cyanomethylation methods are extremely limited to pre-functionalized acetonitrile reagents at high temperature,[9] or in situ generated haloacetonitriles.[10] As for electron-deficient amine substrates, these procedures generally require the use of strong base or high temperature as a result of the poor nucleophilicity, which leads to narrow functional group tolerance. Hence, development of novel and alternative methodologies is still essential for expanding the scope of this transformation.




Scheme 1 Approaches toward synthesis of α-amino nitriles.

In the meanwhile, remarkable progress has been made in transition-metal-catalyzed activation of C(sp$^3$)–H bonds adjacent to an amide nitrogen center. The activated bonds are of considerable importance for construction of new carbon – carbon,[11] carbon – oxygen,[12] or carbon – boron[13] bonds in a convenient way. However, only limited nitrogen species, such as azole or imide derivatives, were achieved to form carbon – nitrogen bonds by coupling reaction with amides via iminium ion intermediates.[14] The directed coupling of amines with amides is still challenging. Very recently, it was reported that the methyl group of DMF could be transferred to ketone or indole under oxidative conditions at high temperature.[15] Herein, we report a methyl transfer from DMF to secondary aromatic amines via activation of α–C(sp$^3$)–H bonds of amide catalyzed by copper at room temperature. Moreover, both of C-N and C-C bonds were constructed in one pot manner, which resulted in the facile access to a variety of α-amino nitriles (Scheme 1).

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Electronic Supplementary Information (ESI) available: Experimental details, characterization data, and copies of spectral data. CCDC 1817960 (**3e**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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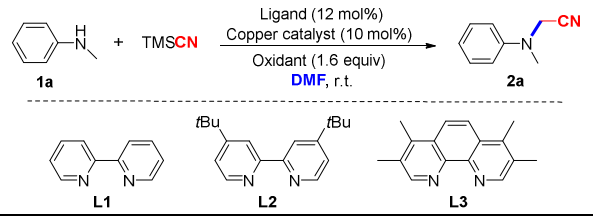
DOI: 10.1039/C8CC00485D





Our initial efforts focused on optimization of the reaction conditions using *N*-methylaniline as substrate and $Cu(MeCN)_4BF_4$ as catalyst, while the 2,2'-Bipyridine as ligand. As showed in table 1, phenyliodine diacetate (PIDA) or phenyliodine(III) bis(trifluoroacetate) (PIFA) was firstly tested as oxidant and only trace amount of α-aminonitrile **2a** was detected (entries 1 and 2). Changing the oxidant to *tert*-Butyl hydroperoxide (*t*-BuOOH) failed to provide the any products (entry 3). A significant amount of α-aminonitrile **2a** was obtained in 91% yield when *N*-fluorobenzenesulfonimide (NFSI) was used as oxidant (entry 4). Screening other ligands such as **L2** or **L3** resulted in the decreasing of yields (entries 5 and 6). Other copper catalysts, such as CuCl, $CuCl_2$, $Cu(OTf)_2$, or $Cu(OAc)_2$ were also examined. However, the yields were very low. It was discovered that CuOAc was the most effective catalyst and α-amino nitrile **2a** was generated in 98% yield when **L2** was selected as ligand (entry 12). The effects of amount of DMF were also evaluated and the yields were dramatically deceased (12% for 5 equiv and 21% for 10 equiv amount of DMF in MECN). The copper-catalyzed methyl transfer reaction was capable of gram scale synthsis with 83% yield when 2.1 g of *N*-methylaniline was conducted.

**Table1.** Optimization of the reaction conditions[a]

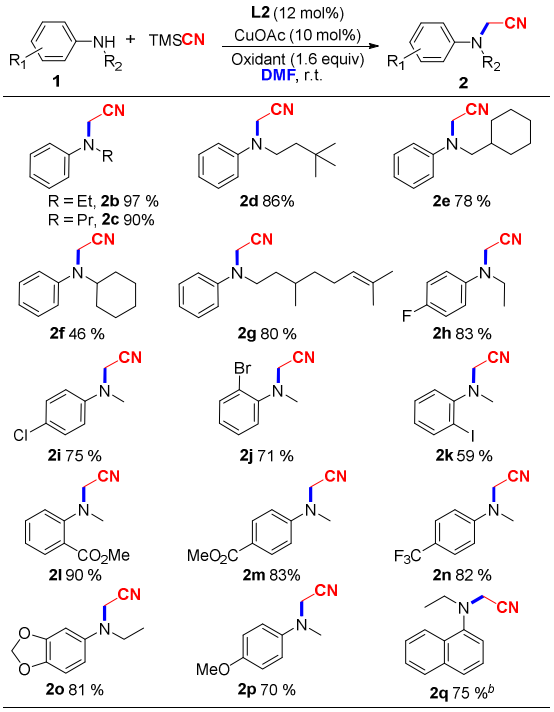



| Entry | Catalyst | Oxidant | Ligand | yield (%)[b] |
|---|---|---|---|---|
| 1 | $Cu(MeCN)_4BF_4$ | PIDA | **L1** | trace |
| 2 | $Cu(MeCN)_4BF_4$ | PIFA | **L1** | trace |
| 3 | $Cu(MeCN)_4BF_4$ | *t*-BuOOH | **L1** | 0 |
| 4 | $Cu(MeCN)_4BF_4$ | NFSI | **L1** | 91 |
| 5 | $Cu(MeCN)_4PF_6$ | NFSI | **L2** | 85 |
| 6 | $Cu(MeCN)_4BF_4$ | NFSI | **L3** | 38 |
| 7 | CuCl | NFSI | **L1** | 12 |
| 8 | $CuCl_2$ | NFSI | **L1** | 6 |
| 9 | $Cu(OTf)_2$ | NFSI | **L1** | trace |
| 10 | $Cu(OAc)_2$ | NFSI | **L1** | 7 |
| 11 | CuOAc | NFSI | **L1** | 21 |
| 12 | CuOAc | NFSI | **L2** | 98 |
| 13 | CuOAc | NFSI | **L3** | 78 |
| 14 | CuOAc | NFSI | TerPy | 11 |
| 15 | CuOAc | NFSI | TMEDA | 52 |

[a]Reaction conditions: **1a** (0.2 mmol), TMSCN (0.5 mmol), oxidant (0.32 mmol), Cu catalyst (0.02 mmol), ligand (0.024 mmol) in DMF (1.0 mL) at r.t. for 16 h. [b] Yields were obtained by $^1$H NMR measurement with mesitylene as internal standard.

With the optimized conditions in hand, we next explored the substrate scope of copper-catalyzed activation and transfer of the methyl group of DMF. Substrates with different alkyl substituted aniline were firstly examined. Both of the linear or branched alkyl derivatives afforded α-amino nitriles **2b** - **2e** in good yields. It was discovered that when the aniline was substituted with a bulky alkyl group (cyclohexyl group), the reaction still proceeded but with lower yields due to the hindrance (**2f**). Although the reaction conditions including the oxidative reagent NSFI, the substrate with unsaturated bond was found to be tolerable and the corresponding α-amino nitrile **2g** was obtained in 80% yield. It were found that fluoride, chloride, bromide, and iodide groups were tolerated to afford the corresponding products **2h** - **2k**, which could be used in further coupling reactions. The electronic effects of substituent groups on the aromatic ring were also evaluated. When the aniline was substituted with electron withdrawing group, such as *o*- or *p*-carboxylate or trifluoromethyl group, the α-amino nitriles **2l** – **2n** were obtained in 90%, 83% and 80%, respectively. In the meantime, derivatives with electron donating groups on aniline also afforded the products **2o** and **2p** in good yields. Furthermore, naphthylamine could also be incorporated to give acceptable results by prolonging the reaction time.

**Table 2.** Substrate Scope of Anilines[a]




[a]Reactions were conducted in 0.2 mmol scale and yields were obtained by silica gel chromatography isolation. [b] The reaction time was 28 h.

Besides the aniline substrates, other type of aromatic amines was also investigated for the copper catalyzed methyl transferring reaction. Table 3 shows that when cyclic amines 2-methylindoline and tetrahydroquinoline were subjected to this

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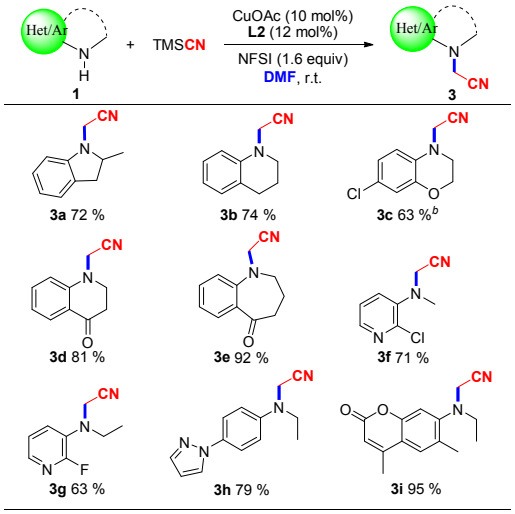
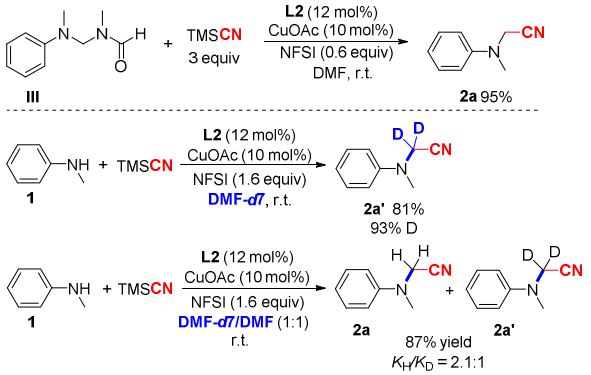
reaction conditions, the methyl transferring reaction and cyanation smoothly proceeded and generated the α-amino nitriles **3a** and **3b** in moderate yields. We found that when phenmorpholine was treated under the above optimized reaction conditions, the desired product **3c** was obtained in poor yield. With further screening of the reaction conditions, we were delighted to find that **L1** could promote the *N*-cyanomethylation reaction in **63%** yield. The cyclic aromatic amines with an additional ketone group, such as pharmaceutically important quinolone and benzazepine-derivatives, were used as substrates and provided product **3d** (81% yield) and **3e** (92% yield). The pyridinamines were examined for the preparation of α-amino nitriles. When two 3-pyridinamine derivatives were transformed into the corresponding products **3f** and **3g** in 71% and 69% respectively. Impressively, 7-aminocoumarin was able to smoothly undergo the reaction to deliver the **3i** with excellent yield. However, aliphatic amines proved to be unsuitable substrates affording trace amount of products.

**Table 3.** Substrate Scope of Heterocycles[a]



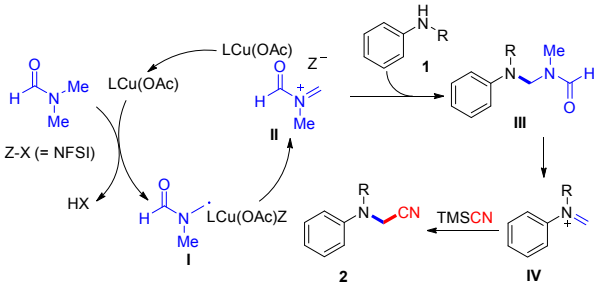

[a]Reactions were conducted in 0.2 mmol scale and yields were obtained by silica gel chromatography isolation. [b] **L1** instead of **L2** as ligand.

We then tried to investigate the possible mechanism of the copper-catalyzed methyl transferring and cyanation sequences. An amide intermediate **III** was isolated after quenching the reaction mixture halfway. The amide intermediate **III** showed that the aniline was coupled with DMF before the cyanation. Moreover, treatment of the amide intermediate **III** under the reaction conditions except reducing the amount of NFSI from 1.6 eq to 0.6 eq, the α-amino nitrile **2a** was obtained in 95% yield. The deuterium labeling experiments were also carried out. The reaction was performed in DMF-d7 as solvent to confirm the resource of CH2. The deuterium product **2a'** was obtained with the ratio of deuterium-labelled around 93% (Scheme 2). In addition, we observed that the reaction went on much slowly and the product was formed in only 81% yield instead of 98% under the standard conditions. Moreover, experiments focused on the kinetic isotopic effect were also carried out. The $K_H/K_D$ ratio was 2.1:1. This result suggested that C-H bond cleavage was the rate-determining step. To confirm the reaction involved a radical process, TMEPO, BHT, and 1,3-dinitrobenzene were added into the reaction and the reaction were completely inhibited (see Supporting Information).




Scheme 2 Mechanistic Investigations.

Based on the above experiments and literature precedents, a plausible proposed mechanism is outlined in Scheme 3.In the initial step, a single electron transfer between Cu(I) and DMF gives the radical intermediate **I** through C($sp^3$)–H bond cleavage. Then, DMF-derived radical **I** converted to iminium ion **II**, which is attacked by amine **1** to generate the isolatable intermediate **III**. Intermediate **III** is further converted to iminium ion **IV**. Finally, the nucleophilic substitution of cyanide ion in the similar manner of Strecker reaction leads to the formation of the corresponding α-amino nitrile **2**.




Scheme 3 Proposed Mechanism.

In conclusion, we have described a Cu-catalyzed activation of C($sp^3$)–H bond of DMF. The methyl group was then transferred to anilines. After nucleophilic addition by cyanide, the α-amino nitriles were efficiently generated in one-pot manner. The oxidative activation of DMF was featured with reaction at room temperature. Moreover, the reaction demonstrated wide functional group tolerance, broad substrate scope, and high activity under ambient conditions.

We gratefully acknowledge the National Natural Science Foundation of China (21572236) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT_17R94) for financial support.

## Conflicts of interest

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DOI: 10.1039/C8CC00485D




There are no conflicts to declare.

## Notes and references


1 For reviews, see: (a) F. F. Fleming, *Nat. Prod. Rep.*, 1999, **16**, 597; (b) D. Enders and J. P. Shilvock, *Chem. Soc. Rev.*, 2000, **29**, 359; (c) F. F. Fleming, L. Yao, P. C. Ravikumar, L. Funk and B. C. Shook, *J. Med. Chem.*, 2010, **53**, 7902.

2 (a) D. Lucet, T. L. Gall and C. Mioskowski, *Angew. Chem. Int. Ed.*, 1998, **37**, 2580; (b) C. Nájera and J. M. Sansano, *Chem. Rev.*, 2007, **107**, 4584; (c) N. Otto and T. Opatz, *Chemistry*, 2014, **20**, 13064; (d) X.-Q. Mou, Z.-L. Xu, L. Xu, S.-H. Wang, B.-H. Zhang, D. Zhang, J. Wang, W.-T. Liu and W. Bao, *Org. Lett.*, 2016, **18**, 4032; (e) B.-H. Zhang, L.-S. Lei, S.-Z. Liu, X.-Q. Mou, W.-T. Liu, S.-H. Wang, J. Wang, W. Bao and K. Zhang, *Chem. Commun.*, 2017, **53**, 8545.

3 For representative reviews, see: (a) L. Yet, *Angew. Chem. Int. Ed.*, 2001, **40**, 875; (b) H. Gröger, *Chem. Rev.*, 2003, **103**, 2795; (c) P. Merino, T. Tejero and R. P. Herrera, *Tetrahedron*, 2009, **65**, 1219; (d) J. Wang, X. Liu and X. Feng, *Chem. Rev.*, 2011, **111**, 6947; (e) X.-Q. Mou, L. Xu, S.-H. Wang and C. Yang, *Tetrahedron Lett.*, 2015, **56**, 2820.

4 (a) S.-I. Murahashi, N. Komiya, H. Terai and T. Nakae, *J. Am. Chem. Soc.*, 2003, **125**, 15312; (b) M. North, *Angew. Chem. Int. Ed.*, 2004, **43**, 4126; (c) S. I. Murahashi, N. Komiya and H. Terai, *Angew. Chem. Int. Ed.*, 2005, **44**, 6931; (d) S.-I. Murahashi, T. Nakae, H. Terai and N. Komiya, *J. Am. Chem. Soc.*, 2008, **130**, 11005; (e) S.-I. Murahashi and D. Zhang, *Chem. Soc. Rev.*, 2008, **37**, 1490; (f) Y. Pan, S. Wang, C. W. Kee, E. Dubuisson, Y. Yang, K. P. Loh and C.-H. Tan, *Green Chem.*, 2011, **13**, 3341; (g) S. Verma, S. L. Jain and B. Sain, *Catal. Lett.*, 2011, **141**, 882; (h) K. H. V. Reddy, G. Satish, V. P. Reddy, B. A. Kumar and Y. Nageswar, *RSC Adv.*, 2012, **2**, 11084; (i) L. Shi and W. Xia, *Chem. Soc. Rev.*, 2012, **41**, 7687.

5 (a) W. Han and A. R. Ofial, *Chem. Commun.*, 2009, **45**, 5024; (b) S. Singhal, S. L. Jain and B. Sain, *Adv. Synth. Catal.*, 2010, **352**, 1338; (c) P. Liu, Y. Liu, E. L.-M. Wong, S. Xiang and C.-M. Che, *Chem. Sci.*, 2011, **2**, 2187; (d) K. T. V. Rao, B. Haribabu, P. S. S. Prasad and N. Lingaiah, *ChemCatChem*, 2012, **4**, 1173.

6 (a) M. Rueping, S. Zhu and R. M. Koenigs, *Chem. Commun.*, 2011, **47**, 12709; (b) E. Boess, C. Schmitz and M. Klussmann, *J. Am. Chem. Soc.*, 2012, **134**, 5317; (c) Y. Zhang, H. Peng, M. Zhang, Y. Cheng and C. Zhu, *Chem. Commun.*, 2011, **47**, 2354; (d) M. Rueping, J. Zoller, D. C. Fabry, K. Poscharny, R. M. Koenigs, T. E. Weirich and J. Mayer, *Chem. Eur. J.*, 2012, **18**, 3478; (e) K. Alagiri and K. R. Prabhu, *Org. Biomol. Chem.*, 2012, **10**, 835; (f) S. Singhal, S. L. Jain and B. Sain, *Chem. Commun.*, 2009, **45**, 2371; (g) N. Sakai, A. Mutsuro, R. Ikeda and T. Konakahara, *Synlett*, 2013, **24**, 1283; (h) A. Lin, H. Peng, A. Abdukader and C. Zhu, *Eur. J. Org. Chem.*, 2013, **32**, 7286.

7 (a) C. K. Chen, A. G. Hortmann and M. R. Marzabadi, *J. Am. Chem. Soc.*, 1988, **110**, 4829; (b) V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz, B. Mismash, J. K. Woodward and A. J. Simonsen, *Tetrahedron Lett.*, 1995, **36**, 7975; (c) J. M. Allen and T. H. Lambert, *J. Am. Chem. Soc.*, 2011, **133**, 1260; (d) D. P. Hari and B. König, *Org. Lett.*, 2011, **13**, 3852; (e) L. Liu, Z. Wang, X. Fu and C.-H. Yan, *Org. Lett.*, 2012, **14**, 5692; (f) J. Dhineshkumar, M. Lamani, K. Alagiri and K. R. Prabhu, *Org. Lett.*, 2013, **15**, 1092; (g) C. Zhang, C. Liu, Y. Shao, X. Bao and X. Wan, *Chem. Eur. J.*, 2013, **19**, 17917; (h) H. Shen, X. Zhang, Q. Liu, J. Pan, W. Hu, Y. Xiong and X. Zhu, *Tetrahedron Lett.*, 2015, **56**, 5628; (i) P.-Y. Liu, C. Zhang, S.-C. Zhao, F. Yu, F. Li and Y.-P. He, *J. Org. Chem.*, 2017, **82**, 12786.

8 (a) S. Andreades and E. Zahnow, *J. Am. Chem. Soc.*, 1969, **91**, 4181; (b) T. Chiba and Y. Takata, *J. Org. Chem.*, 1977, **42**, 2973; (c) E. Le Gall, J. P. Hurvois, T. Renaud, C. Moinet, A. Tallec, P. Uriac, S. Sinbandhit and L. Toupet, *Liebigs Annalen/Recueil*, 1997, **10**, 2089.

9 For selected examples, see: (a) P. Dash, D. P. Kudav and J. A. Parihar, *J. Heter. Chem.*, 2006, **43**, 401; (b) S. Rivara, A. Lodola, M. Mor, A. Bedini, G. Spadoni, V. Lucini, M. Pannacci, F. Fraschini, F. Scaglione, R. Ochoa Sanchez, G. Gobbi and G. Tarzia, *J. Med. Chem.*, 2007, **50**, 6618; (c) J. J. McAtee, J. W. Dodson, S. E. Dowdell, G. R. Girard, K. B. Goodman, M. A. Hilfiker, C. A. Sehon, D. Sha, G. Z. Wang, N. Wang, A. Q. Viet, D. Zhang, N. V. Aiyar, D. J. Behm, L. H. Carballo, C. A. Evans, H. E. Fries, R. Nagilla, T. J. Roethke, X. Xu, C. C. K. Yuan, S. A. Douglas and M. J. Neeb, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 3500; (d) S. Rivara, F. Vacondio, A. Fioni, C. Silva, C. Carmi, M. Mor, V. Lucini, M. Pannacci, A. Caronno, F. Scaglione, G. Gobbi, G. Spadoni, A. Bedini, P. Orlando, S. Lucarini and G. Tarzia, *ChemMedChem*, 2009, **4**, 1746; (e) Z.-L. Zhang, J. Chen, Q. Xu, C. Rao and C. Qiao, *Synth. Commun.*, 2012, **42**, 794; (f) P. Quinodoz, B. Drouillat, K. Wright, J. Marrot and F. Couty, *J. Org. Chem.*, 2016, **81**, 2899.

10 (a) J. Zhang, W. Wu, X. Ji and S. Cao, *RSC Adv.*, 2015, **5**, 20562; (b) H. Wang, Y. Shao, H. Zheng, H. Wang, J. Cheng and X. Wan, *Chem. Eur. J.*, 2015, **21**, 18333.

11 For selected examples of C-C bond formation, see: (a) S. Rousseaux, S. I. Gorelsky, B. K. Chung and K. Fagnou, *J. Am. Chem. Soc.*, 2010, **132**, 10692; (b) E. Shirakawa, N. Uchiyama and T. Hayashi, *J. Org. Chem.*, 2011, **76**, 25; (c) C. Dai, F. Meschini, J. M. R. Narayanam and C. R. J. Stephenson, *J. Org. Chem.*, 2012, **77**, 4425; (d) S. R. Guo, Y. Q. Yuan and J. N. Xiang, *Org. Lett.*, 2013, **15**, 4654; (e) H. Yan, L. Lu, G. Rong, D. Liu, Y. Zheng, J. Chen and J. Mao, *J. Org. Chem.*, 2014, **79**, 7103; (f) R. Ueno and E. Shirakawa, *Org. Biomol. Chem.*, 2014, **12**, 7469; (g) R. J. Song, Y. Q. Tu, D. Y. Zhu, F. M. Zhang and S. H. Wang, *Chem. Commun.*, 2015, **51**, 749; (h) D.-D. Li, Z.-Y. Li and G.-W. Wang, *J. Org. Chem.*, 2015, **80**, 190; (i) H. Fang, J. Zhao, S. Ni, H. Mei, J. Han and Y. Pan, *J. Org. Chem.*, 2015, **80**, 3151; (j) D. R. Heitz, J. C. Tellis and G. A. Molander, *J. Am. Chem. Soc.*, 2016, **138**, 12715; (k) J. Wang, J. Li, J. Huang and Q. Zhu, *J. Org. Chem.*, 2016, **81**, 3017; (l) P. M. Holstein, D. Dailler, J. Vantourout, J. Shaya, A. Millet and O. Baudoin, *Angew. Chem. Int. Ed.*, 2016, **55**, 2805; (m) H. P. Deng, X. Z. Fan, Z. H. Chen, Q. H. Xu and J. Wu, *J. Am. Chem. Soc.*, 2017, **139**, 13579; (n) S. Paul and J. Guin, *Green Chem.*, 2017, **19**, 2530; (o) D. Yamauchi, T. Nishimura and H. Yorimitsu, *Angew. Chem. Int. Ed.*, 2017, **56**, 7200.

12 (a) D. H. Wang, X. S. Hao, D. F. Wu and J. Q. Yu, *Org. Lett.*, 2006, **8**, 3387; (b) A. Modak, U. Dutta, R. Kancherla, S. Maity, M. Bhadra, S. M. Mobin and D. Maiti, *Org. Lett.*, 2014, **16**, 2602.

13 S. Kawamorita, T. Miyazaki and T. Iwai, *J. Am. Chem. Soc.*, 2012, **134**, 12924.

14 For selected examples of C-N bond formation, see: (a) Q. Xia and W. Chen, *J. Org. Chem.*, 2012, **77**, 9366; (b) Z. Q. Lao, W. H. Zhong, Q. H. Lou, Z. J. Li and X. B. Meng, *Org. Biomol. Chem.*, 2012, **10**, 7869; (c) Z. Zhu, Y. Wang, M. Yang, L. Huang, J. Gong, S. Guo and H. Cai, *Synlett*, 2016, **27**, 2705; (d) S. Xu, Z. Luo, Z. Jiang and D. Lin, *Synlett*, 2017, **28**, 868; (e) H. Aruri, U. Singh, M. Kumar, S. Sharma, S. K. Aithagani, V. K. Gupta, S. Mignani, R. A. Vishwakarma and P. P. Singh, *J. Org. Chem.*, 2017, **82**, 1000; (f) X. Deng, X. Lei, G. Nie, L. Jia, Y. Li and Y. Chen, *J. Org. Chem.*, 2017, **82**, 6163.

15 (a) J. Liu, H. Yi, X. Zhang, C. Liu, R. Liu, G. Zhang and A. Lei, *Chem. Commun.*, 2014, **50**; (b) Y. Li, D. Xue, W. Lu, C. Wang, Z.-T. Liu and J. Xiao, *Org. Lett.*, 2014, **16**, 66; (c) A. Alanthadka, D. E. Sankari, S. A. Tamil, N. Subbiah, V. Sridharan and C. U. Maheswari, *Adv. Synth. Catal.*, 2017, **359**, 2369; (d) S. Mondal, S. Samanta, S. Santra, A. K. Bagdi and A. Hajra, *Adv. Synth. Catal.*, 2016, **358**, 3633.