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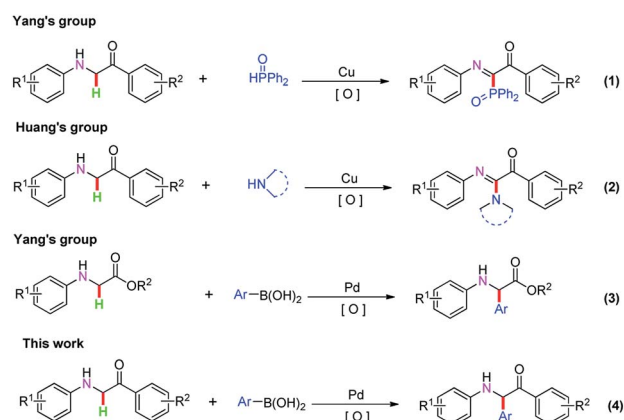
Palladium-catalyzed oxidative cross-coupling for the synthesis of α -amino ketones†Xiao-Hong Wei,^{ID}* Zhen-Hua Li,^{ID}* Lian-Biao Zhao, Ping Zhang,
Han-Cheng Zhou^{ID} and Yan-Bin Wang

A novel oxidative cross-coupling reaction for the synthesis of α -aryl α -amino ketones in the presence of palladium catalysts using $T^+BF_4^-$ as an oxidant has been developed. This transformation was achieved by direct C–H oxidation of α -aminocarbonyl compounds and arylation. The mild reaction has a broad reaction scope and gives desired α -aryl α -amino ketones in moderate to excellent yields.

Transition metal-catalyzed oxidative coupling reactions involving the formation of C–C bonds from C–H bonds have attracted considerable attention, indicating excellent atom economy and environmental friendliness.¹ α -Amino carbonyl compounds have important roles in natural products and are the key structural units of natural products.² These compounds have also been used in organic chemistry to synthesize biological activities, therapeutic agents, quinazolines, imidazoles, pyrazines, indoles, and pyrroles.³ Therefore, the direct oxidative C–H functionalization has gained significant attention for the synthesis of a series of α -amino carbonyl compounds.^{2i,2j,4} For example, Li's group employed an oxidative coupling reaction to synthesize α -amino carbonyl compounds from *N*-glycine derivatives by direct C–C bond formation under the catalysis of copper salts.⁵ Subsequently, stoichiometric amounts of chemical oxidants, such as DTBP, DDQ, TBHP, and 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetra-fluoroborate ($T^+BF_4^-$), have been applied to these reactions.^{4a,4d,4p,4t,6} In 2013, Yang's group described a novel protocol for a copper-catalyzed oxidative phosphonation reaction by using α -amino carbonyls and diphenylphosphine ((1), Scheme 1).⁷ Huang's group disclosed a general and efficient method for C–N oxidative cross-coupling through direct C_{sp^3} –H bond functionalization of α -aminocarbonyl compounds with amines under the catalysis of copper salts ((2), Scheme 1).^{6a} In 2015, Yang's group developed a highly efficient route to synthesize chiral arylglycine derivatives *via* a palladium-catalyzed enantioselective direct C–H oxidation arylation reaction ((3), Scheme 1).^{4p} Furthermore, transition metal-catalyzed direct C–H functionalization by an oxidative cross-coupling reaction has been reported in the past few years.⁸ Although significant advances have been made along

these lines, the development of efficient synthetic methodologies for the synthesis of α -aminocarbonyl compounds *via* palladium-catalyzed oxidative cross-coupling still remains a challenging topic. Based on these considerable progresses, in this paper, we describe a highly efficient C–H oxidative cross-coupling reaction strategy for the synthesis of α -amino ketone compounds by palladium-catalyzed direct C–H oxidation and arylation reactions ((4), Scheme 1).

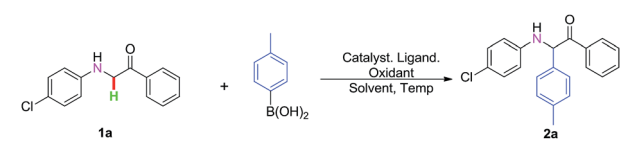
In an initial study, we chose 2-((4-chlorophenyl)amino)-1-phenylethanone **1a** and *para*-methylphenyl boric acid as the model substrate to evaluate different oxidants in the presence of 10 mol% $Pd(OAc)_2$ with 2,2-bipyridine as a ligand in TFE at 60 °C (Table 1, entries 1–8). To our delight, the desired product **2a** was obtained in 14% yield by using 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetra-fluoroborate ($T^+BF_4^-$)^{4p} as an oxidant (Table 1, entry 8). Based on these results, various ligands were used to carry out the reaction in the presence of 10 mol% $Pd(OAc)_2$. As expected, the best result of 29% yield was obtained by employing **L**₃ as a ligand (Table 1,




Scheme 1 Transition metal-catalyzed reaction for the synthesis of α -aminocarbonyl compounds.


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
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra06108h


Table 1 Optimization of the reaction conditions^{a,b}



Entry	Catalyst	Ligand	Oxidant	Solvent	Yield ^b
1	Pd(OAc) ₂	bpy	BQ	TFE	10%
2	Pd(OAc) ₂	bpy	Ag ₂ CO ₃	TFE	13%
3	Pd(OAc) ₂	bpy	K ₂ S ₂ O ₈	TFE	Trace
4	Pd(OAc) ₂	bpy	Air	TFE	8%
5	Pd(OAc) ₂	bpy	PhI(OAc) ₂	TFE	Trace
6	Pd(OAc) ₂	bpy	Ph ₃ CBF ₄	TFE	NR
7	Pd(OAc) ₂	bpy	C ₇ H ₇ BF ₄	TFE	Trace
8	Pd(OAc) ₂	bpy	T ⁺ BF ₄ ⁻	TFE	14%
9	Pd(OAc) ₂	L ₁	T ⁺ BF ₄ ⁻	TFE	24%
10	Pd(OAc) ₂	L ₂	T ⁺ BF ₄ ⁻	TFE	13%
11	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	TFE	29%
12	Pd(OAc) ₂	L ₄	T ⁺ BF ₄ ⁻	TFE	15%
13	Pd(OAc) ₂	L ₅	T ⁺ BF ₄ ⁻	TFE	20%
14	Pd(OAc) ₂	L ₆	T ⁺ BF ₄ ⁻	TFE	12%
15	Pd(OAc) ₂	PPh ₃	T ⁺ BF ₄ ⁻	TFE	16%
16	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	DCE	21%
17	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	THF	31%
18	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	TOL	Trace
19	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ NO ₂	16
20	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	DCM	18%
21	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	C ₂ H ₅ OH	37%
22	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	DME	40%
23	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	DMF	8%
24	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	Dioxane	32%
25	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	47%
26 ^c	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	23%
27 ^d	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	71%
28 ^d	Pd(NO ₃) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	56%
29 ^d	Pd(TFA) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	43%
30 ^d	PdCl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	67%
31 ^d	Pd(PPh ₃) ₂ Cl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	60%
32 ^d	Pd(PPh ₃) ₄		T ⁺ BF ₄ ⁻	CH ₃ OH	38%
33 ^d	Pd(CH ₃ CN) ₂ Cl ₂		T ⁺ BF ₄ ⁻	CH ₃ OH	74%
34 ^d	Pd(acac) ₂		T ⁺ BF ₄ ⁻	CH ₃ OH	58%
35 ^d	Pd(PhCN) ₂ Cl ₂		T ⁺ BF ₄ ⁻	CH ₃ OH	63%
36 ^d	Pd(cod)Cl ₂		T ⁺ BF ₄ ⁻	CH ₃ OH	66%
37 ^d	Pd(PCy₃)₂Cl₂		T⁺BF₄⁻	CH₃OH	86%
38 ^d	Pd(PCy ₃) ₂ Cl ₂		T ⁺ BF ₄ ⁻	CH ₃ OH	Trace
39 ^d			T ⁺ BF ₄ ⁻	CH ₃ OH	No












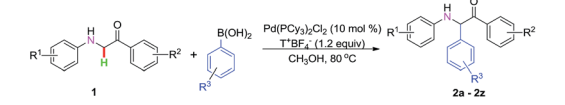


^a Reaction conditions: **1a** (0.1 mmol), *para*-methoxyphenyl boric acid (1.2 equiv.), catalyst (10 mol%), ligand (10 mol%) and oxidant (1.2 equiv.) was stirred in solvent (1 mL) at 60 °C under Ar for 20 h. ^b Yield of the isolated product. ^c 100 °C. ^d 80 °C.

entries 9–15). Then, different solvents were screened; using CH₃OH as the solvent with the set reaction conditions gave comparable results (entry 25), but others gave lower yields (Table 1, entries 16–25). When the temperature was increased to 80 °C, the yield of **2a** reached 71% (Table 1, entries 26 and 27).

To our delight, the reaction could occur in the presence of 10 mol% of catalysts such as Pd(NO₃)₂, Pd(TFA)₂, PdCl₂, Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, Pd(CH₃CN)₂Cl₂, and Pd(acac)₂, while the reactivity of Pd(PCy₃)₂Cl₂ was better than others, affording the desired product **2a** in 86% yield (Table 1, entries 28–37). Furthermore, control experiments showed that no or trace amounts of the desired product was obtained in the absence of Pd(PCy₃)₂Cl₂ or T⁺BF₄⁻ (Table 1, entries 38 and 39).

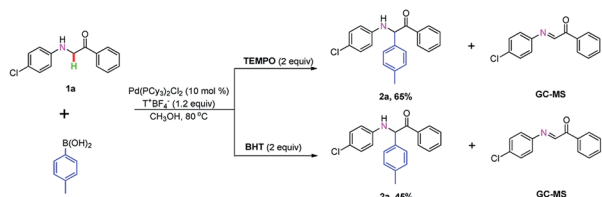
With the optimal reaction conditions in hand (Table 1, entry 37), we explored the C–H oxidative cross-coupling reaction of 2-((4-chlorophenyl)amino)-1-phenylethanone **1a** with arylboronic acids, as shown in Table 2. We first surveyed different substituents of arylboronic acids with electron-donating groups, such as methyl, ethyl, isopropyl and methoxy, and found that they gave the desired product in 80–86% yields (Table 2, entries **2a–2d**). Meanwhile, the steric effect was examined using the *meta*- and *ortho*-methyl phenylboronic acids under identical conditions (Table 2, entries **2e** and **2f**). However, the steric effect in this transformation was very significant; only trace amounts of the product was obtained when *ortho*-methyl phenylboronic acids were introduced for the optimization of reaction conditions (Table 2, entry **2f**). When arylboronic acids with different electron-donating or electron-withdrawing groups afforded the desired products in excellent to moderate yields (Table 2, entries **2g–**

Table 2 Reaction conditions screening^{a,b}


Entry	Product	Yield (%)
2a	R ¹ = H, R ² = Me	86%
2b	R ¹ = H, R ² = Et	80%
2c	R ¹ = H, R ² = <i>i</i> -Pr	83%
2d	R ¹ = H, R ² = MeO	83%
2e	R ¹ = H, R ² = <i>ortho</i> -Me	45%
2f	R ¹ = H, R ² = <i>ortho</i> -Me	Trace
2g	R ¹ = H, R ² = <i>ortho</i> -Me	69%
2h	R ¹ = H, R ² = <i>ortho</i> -Me	80%
2i	R ¹ = H, R ² = <i>ortho</i> -Me	51%, 45% ^c
2j	R ¹ = H, R ² = F	47%
2k	R ¹ = H, R ² = Cl	28%
2l	R ¹ = H, R ² = Br	23%
2m	R ¹ = H, R ² = I	31%
2n	R ¹ = H, R ² = <i>ortho</i> -Me	73%
2o	R ¹ = H, R ² = <i>ortho</i> -Me	77%
2p	R ¹ = H, R ² = <i>ortho</i> -Me	66%
2q	R ¹ = H, R ² = <i>ortho</i> -Me	47%
2r	R ¹ = H, R ² = F	68%
2s	R ¹ = H, R ² = Br	88%
2t	R ¹ = H, R ² = <i>ortho</i> -Me	64%
2u	R ¹ = H, R ² = <i>ortho</i> -Me	60%
2v	R ¹ = H, R ² = <i>ortho</i> -Me	30%
2w	R ¹ = H, R ² = <i>ortho</i> -Me	60%
2x	R ¹ = H, R ² = <i>ortho</i> -Me	42%
2y	R ¹ = H, R ² = <i>ortho</i> -Me	50%
2z	R ¹ = H, R ² = <i>ortho</i> -Me	30%

^a Reaction conditions: **1a** (0.1 mmol), *para*-methoxyphenyl boric acid (1.2 equiv.), Pd(PCy₃)₂Cl₂ (10 mol%), and 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate (T⁺BF₄⁻) (1.2 equiv.) was stirred in CH₃OH (1 mL) at 80 °C under Ar for 20 h. ^b Yield of the isolated product. ^c Potassium phenyltrifluoroborate as arylated reagents.



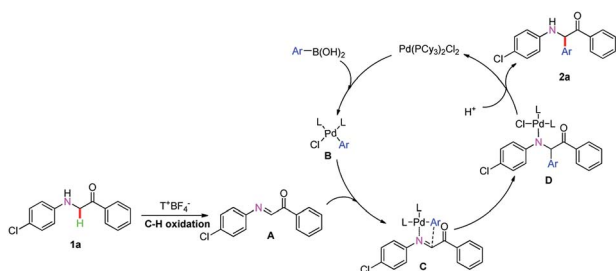


Scheme 2 Radical-trapping experiment.

2m). Moreover, in order to further expand the substrate scope, we selected potassium phenyltrifluoroborate as the arylated reagent under the optimized reaction conditions; the corresponding α -alkylation product **2i** was obtained in 45% yield (Table 2, entry **2i**).

Furthermore, the naphthalen-1-ylboronic acid and benzo [1,3]dioxol-5-ylboronic acid could also afford α -aminocarbonyl compounds **2n** and **2o** in 73–77% yields (Table 2, entries **2n** and **2o**). Of particular note is the heterocyclic boronic acid, which was also compatible for the reaction (Table 2, entries **2p** and **2q**). Moreover, the introduction of various electron-withdrawing or electron-donating substituents on the aniline moiety gave the corresponding α -aminocarbonyl compounds in 30–88% yields (Table 2, entries **2r–2x**); the electronic effect and the steric effect in this transformation was very notable (Table 2, entries **2t–2v**). Next, different substituent groups of α -carbonyl compounds bearing different functional groups were additionally examined and the corresponding products were generated in moderate yields (Table 2, entries **2y** and **2z**).

To investigate the mechanism of this transformation, experiments were carried out. The desired product was obtained in the range of 86% to 65% and 86% to 45% yield when 2.0 equivalents of radical-trapping reagents 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were used, respectively, under standardized reaction conditions (Scheme 2). To our delight, the key α -imino intermediate **A** was detected by GC-MS (see ESI†). Based on the observed experimental results and pioneering reports,^{4p,9} we have described a plausible mechanistic pathway in Scheme 3. Initially, the arylpalladium intermediate **B** was produced *via* a transmetalation reaction of Pd(PCy₃)₂Cl₂ with aryl boric acid, which attacks the α -imino intermediate **A** obtained by the *in situ* oxidation of **1a** by T⁺BF₄[−] to form the complex **C**. Then, an aryl group was added to the imine to generate intermediate **D**.



Scheme 3 Proposed mechanism.

Finally, the product **2a** was obtained upon dissociation in the presence of H⁺. At the same time, the palladium catalyst was regenerated and synchronized into the next catalytic cycle (Scheme 3).

In summary, we have achieved a novel pattern for the synthesis of α -aryl α -amino ketone compounds *via* Pd(II)-catalyzed oxidative coupling of α -aminocarbonyl compounds with arylboric acids. This reaction occurs *via* direct C–H oxidation and arylation reactions. The coupling of α -aminocarbonyl compounds gave functionalized α -aryl α -amino ketone compounds in moderate to excellent yields.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- (a) S. H. Cho, J. Y. Kim, J. Kwak and S. Chang, *Chem. Soc. Rev.*, 2011, **40**, 5068–5083; (b) S. A. Girard, T. Knauber and C.-J. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 74–100; (c) C.-J. Li, *Acc. Chem. Res.*, 2009, **42**, 335–344; (d) C.-J. Li and Z. Li, *Pure Appl. Chem.*, 2006, **78**, 935; (e) C. J. Scheuermann, *Chem.-Asian J.*, 2010, **5**, 436–451; (f) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215–1292; (g) A. H. Cherney, N. T. Kadunce and S. E. Reisman, *Chem. Rev.*, 2015, **115**, 9587–9652; (h) C. G. Newton, S.-G. Wang, C. C. Oliveira and N. Cramer, *Chem. Rev.*, 2017, **117**, 8908–8976.
- (a) G. Choudhary and R. K. Peddinti, *Green Chem.*, 2011, **13**, 276; (b) M. B. Gawande, V. D. Bonifácio, R. Luque, P. S. Branco and R. S. Varma, *Chem. Soc. Rev.*, 2013, **42**, 5522; (c) S. L. Jain, S. Singhal and B. Sain, *Green Chem.*, 2007, **9**, 740; (d) G. L. Khatik, R. Kumar and A. K. Chakraborti, *Org. Lett.*, 2006, **8**, 2433; (e) M. V. Reddy, B. S. Kumar, K. T. Lim, B. G. Cho and Y. T. Jeong, *Tetrahedron Lett.*, 2016, **57**, 476; (f) R. S. Varma, *Green Chem.*, 1999, **1**, 43; (g) G. Zhang, Y. Zhang and R. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 10429–10432; (h) J. Zhang, Z. Cui, F. Wang, Y. Wang, Z. Miao and R. Chen, *Green Chem.*, 2007, **9**, 1341; (i) L. Zhao and C.-J. Li, *Angew. Chem., Int. Ed.*, 2008, **47**, 7075–7078; (j) Z.-Q. Zhu, P. Bai and Z.-Z. Huang, *Org. Lett.*, 2014, **16**, 4881–4883.
- (a) A. Bodtke and P. Langer, *Tetrahedron Lett.*, 2004, **45**, 8741; (b) L. Bryan, A. Richard, K. F. Buzon, T. Chiu, M. L. Colgan and N. Kasthurikrishnan, *Tetrahedron Lett.*, 2004, **45**, 6887; (c) V. Chandrasher, M. Taniguchi, M. Ptaszek and J. S. Lindsey, *Tetrahedron*, 2012, **68**, 6957; (d) B. P. Medaer and G. J. Hoornaert, *Tetrahedron*, 1999, **55**, 3987; (e)



- A. D. Murkute, J. E. Jackson and D. J. Miller, *J. Catal.*, 2011, **278**, 189–199; (f) S. H. Gellman, *Acc. Chem. Res.*, 1998, **31**, 173–180; (g) M. C. Jose and R.-S. Humberto, *Curr. Org. Chem.*, 2008, **12**, 524–543; (h) F. D. Klingler, *Acc. Chem. Res.*, 2007, **40**, 1367–1376; (i) Y. Ohfuné, *Acc. Chem. Res.*, 1992, **25**, 360–366; (j) M. Farahi, F. Tamaddon, B. Karami and S. Pasdar, *Tetrahedron Lett.*, 2015, **56**, 1887–1890; (k) F. Tamaddon and A. Dehghani Tafti, *Synlett*, 2016, **27**, 2217–2220.
- 4 (a) J. Xie and Z.-Z. Huang, *Angew. Chem., Int. Ed.*, 2010, **49**, 10181–10185; (b) J. S. Bandar and T. H. Lambert, *J. Am. Chem. Soc.*, 2013, **135**, 11799–11802; (c) J. T. Binder, C. J. Cordier and G. C. Fu, *J. Am. Chem. Soc.*, 2012, **134**, 17003–17006; (d) C. Huo, C. Wang, M. Wu, X. Jia, H. Xie and Y. Yuan, *Adv. Synth. Catal.*, 2014, **356**, 411–415; (e) C. Huo, M. Wu, F. Chen, X. Jia, Y. Yuan and H. Xie, *Chem. Commun.*, 2015, **51**, 4708–4711; (f) C. Huo, H. Xie, F. Chen, J. Tang and Y. Wang, *Adv. Synth. Catal.*, 2016, **358**, 724–730; (g) S. Kotha, *Acc. Chem. Res.*, 2003, **36**, 342–351; (h) C. Nájera and J. M. Sansano, *Chem. Rev.*, 2007, **107**, 4584–4671; (i) S. Saito, T. Tsubogo and S. Kobayashi, *J. Am. Chem. Soc.*, 2007, **129**, 5364–5365; (j) M. Salman, Z.-Q. Zhu and Z.-Z. Huang, *Org. Lett.*, 2016, **18**, 1526–1529; (k) B. M. Trost and F. Miegé, *J. Am. Chem. Soc.*, 2014, **136**, 3016–3019; (l) M. Wan, H. Lou and L. Liu, *Chem. Commun.*, 2015, **51**, 13953–13956; (m) E. W. Werner, T.-S. Mei, A. J. Burckle and M. S. Sigman, *Science*, 2012, **338**, 1455–1458; (n) Z.-Y. Xue, Q.-H. Li, H.-Y. Tao and C.-J. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 11757–11765; (o) Y. Hui, X. Yilan, D. Rui and F. Yan, *Adv. Synth. Catal.*, 2017, **359**, 39–43; (p) X.-H. Wei, G.-W. Wang and S.-D. Yang, *Chem. Commun.*, 2015, **51**, 832–835; (q) X.-H. Wei, L.-B. Zhao and H.-C. Zhou, *RSC Adv.*, 2017, **7**, 16561–16564; (r) Y. Wei, J. Wang, Y. Wang, X. Yao, C. Yang and C. Huo, *Org. Biomol. Chem.*, 2018, **16**, 4985–4989; (s) Y. Zhang, X. Yang, H. Zhou, S. Li, Y. Zhu and Y. Li, *Org. Chem. Front.*, 2018, **5**, 2120–2125; (t) R. V. Daggupati and C. Malapaka, *Org. Chem. Front.*, 2018, **5**, 788–792; (u) L. Revathi, L. Ravindar, W.-Y. Fang, K. P. Rakesh and H.-L. Qin, *Adv. Synth. Catal.*, 2018, **360**, 4652–4698; (v) X.-H. Wei, L.-B. Zhao and H.-C. Zhou, *RSC Adv.*, 2017, **7**, 16561–16564; (w) G.-F. Zha, G. A. L. Bare, J. Leng, Z.-P. Shang, Z. Luo and H.-L. Qin, *Adv. Synth. Catal.*, 2017, **359**, 3237–3242; (x) X. Zhang, K. P. Rakesh, L. Ravindar and H.-L. Qin, *Green Chem.*, 2018, **20**, 4790–4833; (y) C. Zhao, G.-F. Zha, W.-Y. Fang, K. P. Rakesh and H.-L. Qin, *Eur. J. Org. Chem.*, 2019, **2019**, 1801–1807.
- 5 (a) J.-C. Wu, R.-J. Song, Z.-Q. Wang, X.-C. Huang, Y.-X. Xie and J.-H. Li, *Angew. Chem., Int. Ed.*, 2012, **51**, 3453–3457; (b) W.-T. Wei, R.-J. Song and J.-H. Li, *Adv. Synth. Catal.*, 2014, **356**, 1703–1707.
- 6 (a) P. Liu, Y. Li, H. Wang, Z. Wang and X. Hu, *Tetrahedron Lett.*, 2012, **53**, 6654–6656; (b) P. Liu, Z. Wang, J. Lin and X. Hu, *Eur. J. Org. Chem.*, 2012, **2012**, 1583–1589; (c) H. Richter and O. García Mancheño, *Org. Lett.*, 2011, **13**, 6066–6069; (d) R. Rohlmann, T. Stopka, H. Richter and O. García Mancheño, *J. Org. Chem.*, 2013, **78**, 6050–6064; (e) Z.-Q. Wang, M. Hu, X.-C. Huang, L.-B. Gong, Y.-X. Xie and J.-H. Li, *J. Org. Chem.*, 2012, **77**, 8705–8711; (f) W.-T. Wei, R.-J. Song and J.-H. Li, *Adv. Synth. Catal.*, 2014, **356**, 1703–1707; (g) L. Zhao, O. Baslé and C.-J. Li, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 4106–4111; (h) X.-X. Liu, Z.-Y. Wu, Y.-Q. He, X.-Q. Zhou, T. Hu, C.-W. Ma and G.-S. Huang, *Adv. Synth. Catal.*, 2016, **358**, 2385–2391; (i) Z. Xie, J. Jia, X. Liu and L. Liu, *Adv. Synth. Catal.*, 2016, **358**, 919–925.
- 7 B. Yang, T.-T. Yang, X.-A. Li, J.-J. Wang and S.-D. Yang, *Org. Lett.*, 2013, **15**, 5024–5027.
- 8 (a) M.-X. Cheng, R.-S. Ma, Q. Yang and S.-D. Yang, *Org. Lett.*, 2016, **18**, 3262–3265; (b) Y.-Y. Huang, C. Cai, X. Yang, Z.-C. Lv and U. Schneider, *ACS Catal.*, 2016, **6**, 5747–5763; (c) Z. Meng, S. Sun, H. Yuan, H. Lou and L. Liu, *Angew. Chem., Int. Ed.*, 2014, **53**, 543–547; (d) S. Stockerl and O. G. Mancheno, *Org. Chem. Front.*, 2016, **3**, 277–280; (e) S. Sun, C. Li, P. E. Floreancig, H. Lou and L. Liu, *Org. Lett.*, 2015, **17**, 1684–1687; (f) S. Sun, Y. Mao, H. Lou and L. Liu, *Chem. Commun.*, 2015, **51**, 10691–10694; (g) Z. Xie, X. Zan, S. Sun, X. Pan and L. Liu, *Org. Lett.*, 2016, **18**, 3944–3947; (h) J. Chen, X. Lu, W. Lou, Y. Ye, H. Jiang and W. Zeng, *J. Org. Chem.*, 2012, **77**, 8541–8548; (i) A. Córdova, *Acc. Chem. Res.*, 2004, **37**, 102–112; (j) N. Gommermann, C. Koradin, K. Polborn and P. Knochel, *Angew. Chem., Int. Ed.*, 2003, **42**, 5763–5766; (k) M. Hatano, T. Horibe and K. Ishihara, *J. Am. Chem. Soc.*, 2009, **132**, 56–57; (l) K. R. Knudsen, T. Risgaard, N. Nishiwaki, K. V. Gothelf and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2001, **123**, 5843–5844; (m) S. Kobayashi, T. Hamada and K. Manabe, *J. Am. Chem. Soc.*, 2002, **124**, 5640–5641; (n) S. Kobayashi, Y. Mori, J. S. Fossey and M. M. Salter, *Chem. Rev.*, 2011, **111**, 2626–2704; (o) C. Koradin, K. Polborn and P. Knochel, *Angew. Chem., Int. Ed.*, 2002, **41**, 2535–2538; (p) C. Qian, J. Chen, M. Fu, S. Zhu, W.-H. Chen, H. Jiang and W. Zeng, *Org. Biomol. Chem.*, 2013, **11**, 6013–6022; (q) A. E. Taggi, A. M. Hafez and T. Lectka, *Acc. Chem. Res.*, 2002, **36**, 10–19; (r) B. M. Trost and L. R. Terrell, *J. Am. Chem. Soc.*, 2002, **125**, 338–339; (s) C. Wei and C.-J. Li, *J. Am. Chem. Soc.*, 2002, **124**, 5638–5639; (t) C. Wei, J. T. Mague and C.-J. Li, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 5749–5754; (u) C.-Y. Zhou, S.-F. Zhu, L.-X. Wang and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 10955–10957.
- 9 (a) R. Bloch, *Chem. Rev.*, 1998, **98**, 1407–1438; (b) H. Dai and X. Lu, *Org. Lett.*, 2007, **9**, 3077–3080; (c) S. Kobayashi and H. Ishitani, *Chem. Rev.*, 1999, **99**, 1069–1094.

