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Cobalt(III)-catalyzed site-selective C–H amidation of pyridones and isoquinolones†

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In this study, $\text{Cp}^*\text{Co(III)}$ -catalyzed site-selective amidation of pyridones and isoquinolones using oxazolones as the amidation reagent is reported. This approach features mild conditions, high efficiency and good functional tolerance. Furthermore, gram-scale preparation and preliminary mechanism experiments were carried out. It provides a straightforward approach for the direct modification of pyridone derivatives.

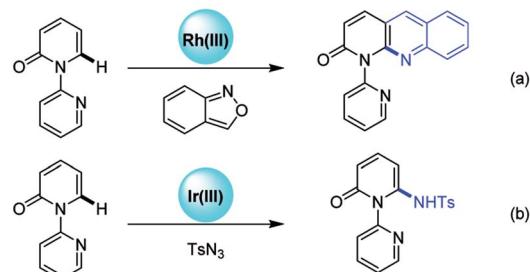
Introduction

The pyridone motif is the cornerstone of a myriad of natural products and serves as useful building blocks in medicinal chemistry.¹ Therefore, the development of efficient synthetic methodologies for the modification of pyridone derivatives has received intensive attention. Traditionally, transition metal-catalyzed cross-coupling of halogenated pyridones represents a practical and reliable strategy. On the contrary, recent advances in transition metal-promoted C–H functionalization² allow the direct modification of heterocycles without pre-functionalization, featuring environmental friendliness, step-and atom-economy. Compared to the site-selective C–H functionalization at relatively electron-rich C5- and C3-positions of pyridones,³ access to the more electron-deficient C6 position remains undeveloped. Nakao and Hiyama reported C6-selective alkenylation and alkylation of 2-pyridone in the presence of nickel and aluminum catalysts.⁴ Recently, Miura and co-workers developed copper-mediated site-selective C–H heteroarylation at C6 position ingeniously with the aid of pyridine-based directing group.⁵ Based on the same pyridine-directed strategy, several research groups have reported transition-metal-catalyzed C6-selective C–H functionalization of pyridones.⁶ A majority of the reported methodologies demonstrated the formation of C–C bonds, while very few for the

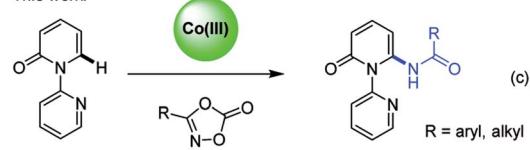
construction of C–N bonds. Li developed an elegant work of rhodium-catalyzed amination/annulation of pyridones with anthranils⁷ (Scheme 1a).^{6a} Very recently, Samanta and co-workers reported C–H amidation of pyridones with various azides⁸ in the presence of iridium catalyst (Scheme 1b).^{6b}

In the context of C–H activation, most of the developed methodologies employ the noble second- and third-row transition metals, such as rhodium and iridium in abovementioned progress. Recently, earth-abundant and environmental-friendly first row transition metals have been employed in C–H functionalization.⁹ Among the 3d metals, $\text{Cp}^*\text{Co(III)}$ is emerging as a robust and versatile catalyst due to its higher Lewis acidity and good selectivity.¹⁰ Since pioneering work by Matsunaga and Kanai,¹¹ many chemists, in particular, Glorius,¹² Ackermann,¹³

Previous work:



This work:



- ✓ Cost-effective cobalt catalyst
- ✓ External-oxidant free
- ✓ Good to excellent yields
- ✓ Wide functional-group tolerance
- ✓ Mild conditions and simple operation

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Scheme 1 C6-selective amination or amidation of pyridones.



Table 1 Optimization of reaction conditions^a

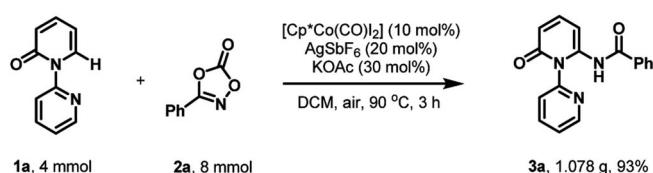
Entry	Ag salt	Additive	Solvent	Yield ^b (%)	Chemical Reactions		
					1a	2a	3a
1	AgSbF ₆	KOAc	DCE	94			
2	AgSbF ₆	KOAc	DCM	98			
3	AgSbF ₆	KOAc	CHCl ₃	Trace			
4	AgSbF ₆	KOAc	TFE	0			
5	AgSbF ₆	KOAc	MeOH	0			
6	AgSbF ₆	KOAc	Dioxane	39			
7	AgNTf ₂	KOAc	DCM	10			
8	—	KOAc	DCM	0			
9	AgSbF ₆	KOPiv	DCM	82			
10	AgSbF ₆	NaOAc	DCM	96			
11	AgSbF ₆	—	DCM	Trace			
12 ^c	—	KOAc	DCM	90			
13 ^d	AgSbF ₆	KOAc	DCM	0			

^a Reaction conditions: 1a (0.2 mmol), 2a (0.6 mmol), [Cp*Co(CO)I₂] (10 mol%), Ag salt (20 mol%) and base (30 mol%) in solvent (2.0 mL) under air at 90 °C for 12 h. ^b Isolated yield. ^c [Cp*Co(MeCN)₃](SbF₆) instead of [Cp*Co(CO)I₂]. ^d No catalyst.

Table 2 Scope of pyridones^{a,b}

1	2a	Chemical Reactions		
		[Cp*Co(CO)I ₂] (10 mol%)	AgSbF ₆ (20 mol%)	KOAc (30 mol%)
				DCM, air, 90 °C
1	2a			
3a, R = H, 97%				
3b, R = Me, 93%				
3c, R = OMe, 70%				
3d, R = F, 73%				
3e, R = Cl, 98%				
3f, R = Br, 95%				
3g, R = CF ₃ , 91%				
3k, R = Me, nr				
3l, R = F, 86%				
3m, 66%				
3h, R = Me, 92%				
3i, R = Cl, 97%				
3j, R = CF ₃ , 96%				
3n, R = H, 86%				
3o, R = 6-Br, 94%				
3p, R = 7-Br, 90%				
3q, R = 6-OMe, 99%				

^a Reaction conditions: 1 (0.2 mmol), 2a (0.6 mmol), [Cp*Co(CO)I₂] (10 mol%), AgSbF₆ (20 mol%) and KOAc (30 mol%) in DCM (2.0 mL) under air at 90 °C for 12 h. ^b Isolated yield. ^c At 120 °C.



Scheme 2 Gram-scale amidation of pyridone.

Table 3 Scope of oxazolones^{a,b}

1a	2	Chemical Reactions		
		[Cp*Co(CO)I ₂] (10 mol%)	AgSbF ₆ (20 mol%)	KOAc (30 mol%)
				DCM, air, 90 °C
1a	2			
4a, R = Me, 66%				
4b, R = OMe, 87%				
4c, R = F, 97%				
4d, R = Cl, 95%				
4e, R = Me, 93%				
4f, R = OMe, 98%				
4g, R = Cl, 98%				
4h, R = Br, 99%				
4i, R = CF ₃ , 94%				
4j, R = NO ₂ , 41%				
4k, 95%				
4l, 96%				
4m, 94%				

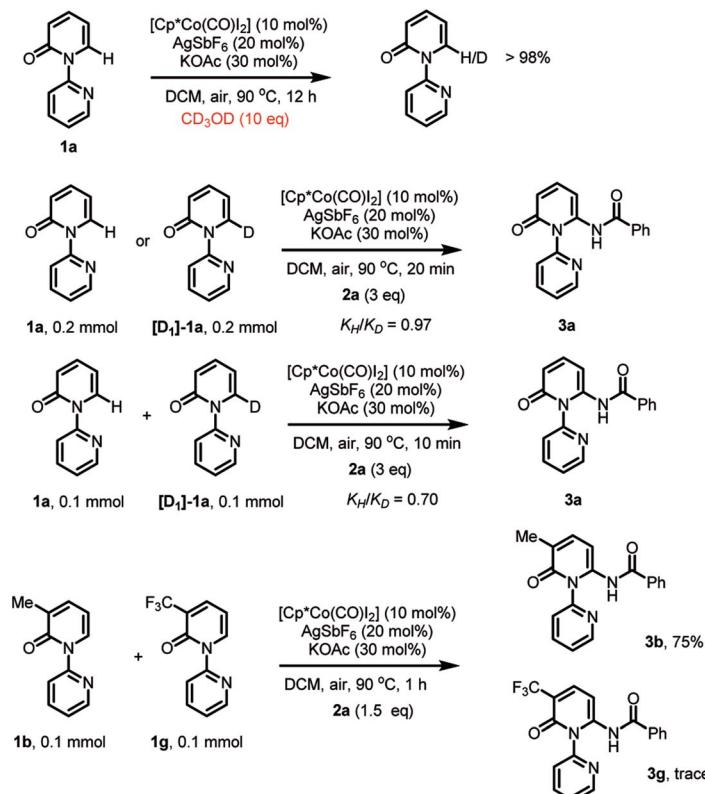
^a Reaction conditions: 1a (0.2 mmol), 2 (0.6 mmol), [Cp*Co(CO)I₂] (10 mol%), AgSbF₆ (20 mol%) and KOAc (30 mol%) in DCM (2.0 mL) under air at 90 °C for 12 h. ^b Isolated yield. ^c At 120 °C.

Ellman,¹⁴ Chang,¹⁵ Sundararaju,¹⁶ Cheng,¹⁷ and others,¹⁸ have demonstrated the unique reactivity of Cp*Co(III) catalyst. In continuation of our recent studies on C–H functionalization of pyridones,^{6c,6g} we proposed the construction of C–N bond at C6 position of pyridones *via* Cp*Co(III)-catalyzed C–H activation. Herein, we report the Cp*Co(III)-catalyzed, site-selective C–H amidation of pyridones under mild conditions by the action of oxazolone¹⁹ as user-friendly amidating reagents^{7,8,20} (Scheme 1c).

Results and discussion

We commenced our studies by examining the reaction parameters of the coupling of 2-pyridone 1a with oxazolone 2a in the presence of [Cp*Co(CO)I₂]. To our delight, the desired amidated product 3a was achieved in 94% yield (Table 1, entry 1). The optimization of solvents revealed that dichloromethane was the most effective solvent, affording product 3a in 98% yield, while no desired product could be obtained in protonic solvents (entries 2–6). The efficiency of the reaction was also significantly affected by Ag salt and no desired product was obtained in the absence of Ag salt (entries 7 and 8). Further screening of base indicated that base is crucial for this reaction and KOAc proved to be the best (entries 9–11). By contrast, the reaction gave no conversion when [Cp*Co(CO)I₂] was omitted (entry 13).

With the optimized conditions identified, we investigated the scope and limitation of pyridones (Table 2). Satisfyingly, both electron-donating and -withdrawing groups at C3 position of pyridones were well tolerated, affording the desired amidated products in good to excellent yields (3b–3g). It was worth mentioning that halogen-substituted pyridones were also compatible in this catalytic system, guaranteeing further transformation (3d–3f). Similarly, in the cases of the C4-substituted pyridones, both electron-donating and -withdrawing groups were accomplished smoothly, giving the



Scheme 3 Control experiments.

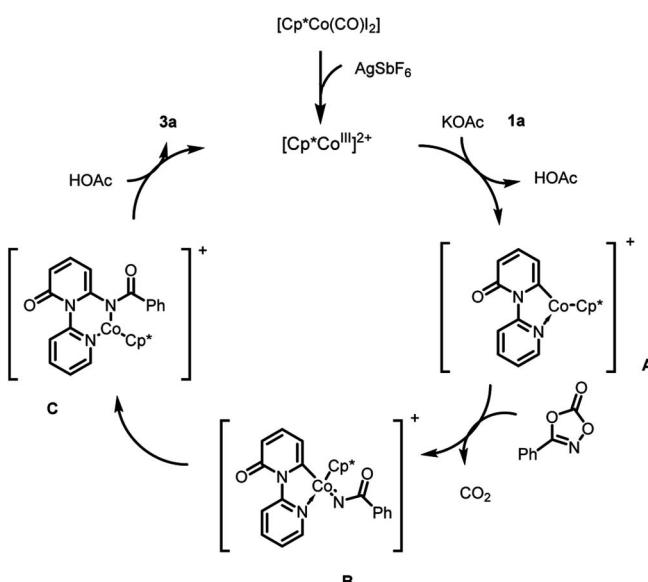
desired products in excellent yields (**3h–3j**). However, 5-methyl substituted **1k** afforded no desired product, while 5-fluoro substituted **1l** gave the desired product **3l** in 86% yield, probably due to steric factors. Meanwhile, 4-pyridone could be amidated monoselectively at the C2 position (**3m**). Isoquinolinones with electron-donating and -withdrawing substitutions were also compatible in this transformation, yielding the corresponding products in high yields (**3n–3q**). Importantly, the site-selective C–H amidation was carried out on a gram scale without any additives to yield **3a** in 93% yield (Scheme 2).

Next, we evaluated the scope of oxazolones (Table 3). Generally, amidation of 2-pyridone **1a** with various substituted oxazolones proceeded efficiently to afford the desired products in good to excellent yields. Both electron-donating and -withdrawing substituents on the phenyl ring underwent the reaction smoothly (**4a–4m**). Additionally, the substituent of oxazolones is not limited to phenyl ring, 3-(thiophen-2-yl)-1,4,2-dioxazol-5-one also coupled to afford the products **4l** in excellent yield. Gratifyingly, aliphatic substituent was also compatible in this reaction, producing the desired product in 94% yield (**4m**).

A series of control experiments were conducted to investigate the preliminary mechanism (Scheme 3). First, to gain insight into the C–H cleavage step, the hydrogen–deuterium (H/D) exchange experiments were carried out. No deuterium exchange with CD_3OD was observed, indicating that the cobalt-mediated C–H bond cleavage is irreversible. On the other hand, by employing $[\text{D}_1]\text{-1a}$ as the substrate, the kinetic isotope effect (KIE) was tested and low level of primary kinetic isotope effects both in parallel and competition experiments were observed,

implying that the C–H bond cleavage was not the rate-determining step in the transformation.²¹ Moreover, to probe the electronic preference, intermolecular competition experiments were carried out and the results indicated that the electron-rich substrate **1b** reacted at a much higher rate.

Based on the preliminary results and literature precedents,^{13f,18a,f,g,h} a plausible amidation mechanism is proposed (Scheme 4). First, a cationic $\text{Cp}^*\text{Co}(\text{III})$ species, which was



Scheme 4 Proposed mechanism.



generated by the aid of Ag salt, undergoes electrophilic C–H bond cleavage of 2-pyridone irreversibly to form intermediate **A**, which is subsequently coordinated by **2a** with the release of CO₂. Next, migratory insertion of intermediate **B** affords the intermediate **C**. Finally, protodemetalation of intermediate **C** gives the desired product and regenerates the active catalyst.

Conclusions

In conclusion, we have developed a method of Cp*Co(III)-catalyzed site-selective amidation of pyridones using oxazolones as amidation reagent under mild conditions. It provides a straightforward approach for the direct modification of pyridone derivatives, which are identified as privileged scaffolds with wide potential bioactivity in pharmaceuticals. Therefore, this efficient strategy will be of importance to medicinal chemists.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- (a) A. G. Amr and M. M. Abdulla, *Bioorg. Med. Chem.*, 2006, **14**, 4341; (b) S. Hibi, K. Ueno, S. Nagato, K. Kawano, K. Ito, Y. Norimine, O. Takenaka, T. Hanada and M. Yonaga, *J. Med. Chem.*, 2012, **55**, 10584; (c) G. Manfroni, F. Meschini, M. L. Barreca, P. Leyssen, A. Samuele, N. Iraci, S. Sabatini, S. Massari, G. Maga, J. Neyts and V. Cecchetti, *Bioorg. Med. Chem.*, 2012, **20**, 866; (d) L. A. Hasvold, W. Wang, S. L. Gwaltney, T. W. Rockway, L. T. J. Nelson, R. A. Mantei, S. A. Fakhouri, G. M. Sullivan, Q. Li, N.-H. Lin, L. Wang, H. Zhang, J. Cohen, W.-Z. Gu, K. Marsh, J. Bauch, S. Rosenberg and H. L. Sham, *Bioorg. Med. Chem. Lett.*, 2003, **13**, 4001; (e) S. Heeb, M. P. Fletcher, S. R. Chhabra, S. P. Diggle, P. Williams and M. Camara, *FEMS Microbiol. Rev.*, 2011, **35**, 247; (f) C. Bengtsson and F. Almqvist, *J. Org. Chem.*, 2010, **75**, 972.
- Selected reviews and accounts: (a) D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174; (b) J. WencelDelord, T. Dröge, F. Liu and F. Glorius, *Chem. Soc. Rev.*, 2011, **40**, 4740; (c) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel and J.-Q. Yu, *Chem. Soc. Rev.*, 2009, **38**, 3242; (d) L. Ackermann, *Acc. Chem. Res.*, 2014, **47**, 281; (e) O. Daugulis, H.-Q. Do and D. Shabashov, *Acc. Chem. Res.*, 2009, **42**, 1074; (f) X.-X. Guo, D.-W. Gu, Z. Wu and W. Zhang, *Chem. Rev.*, 2015, **115**, 1622; (g) F. Hu, Y. Xia, C. Ma, Y. Zhang and J. Wang, *Chem. Commun.*, 2015, **51**, 7986; (h) J. Wencel-Delord and F. Glorius, *Nat. Chem.*, 2013, **5**, 369; (i) C. Liu, H. Zhang, W. Shi and A. Lei, *Chem. Rev.*, 2011, **111**, 1780; (j) J. Yamaguchi, A. D. Yamaguchi and K. Itami, *Angew. Chem., Int. Ed.*, 2012, **51**, 8960; (k) X.-S. Zhang, K. Chen and Z.-J. Shi, *Chem. Sci.*, 2014, **5**, 2146.
- (a) A. Nakatani, K. Hirano, T. Satoh and M. Miura, *Chem.–Eur. J.*, 2013, **19**, 7691; (b) A. Nakatani, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2014, **79**, 1377; (c) E. E. Anagnostaki, A. D. Fotiadou, V. Demertzidou and A. L. Zografas, *Chem. Commun.*, 2014, **50**, 6879; (d) A. Modak, S. Rana and D. Maiti, *J. Org. Chem.*, 2015, **80**, 296; (e) A. Najib, S. Tabuchi, K. Hirano and M. Miura, *Heterocycles*, 2016, **92**, 1187; (f) P. Chauhan, M. Ravi, S. Singh, P. Prajapati and P. P. Yadav, *RSC Adv.*, 2016, **6**, 109; (g) T. Itahara and F. Ouseyo, *Synthesis*, 1984, **1984**, 488; (h) Y. Y. Chen, F. Wang, A. Q. Jia and X. W. Li, *Chem. Sci.*, 2012, **3**, 3231.
- (a) Y. Nakao, H. Idei, K. S. Kanyiva and T. Hiyama, *J. Am. Chem. Soc.*, 2009, **131**, 15996; (b) R. Tamura, Y. Yamada, Y. Nakao and T. Hiyama, *Angew. Chem., Int. Ed.*, 2012, **51**, 5679.
- R. Odani, K. Hirano, T. Satoh and M. Miura, *Angew. Chem., Int. Ed.*, 2014, **53**, 10784.
- (a) S. Yu, Y. Li, X. Zhou, H. Wang, L. Kong and X. Li, *Org. Lett.*, 2016, **18**, 2812; (b) Y. Li, F. Xie and X. Li, *J. Org. Chem.*, 2016, **81**, 715; (c) P. Peng, J. Wang, H. Jiang and H. Liu, *Org. Lett.*, 2016, **18**, 5376; (d) W. Miura, K. Hirano and M. Miura, *Org. Lett.*, 2016, **18**, 3742; (e) T. Li, Z. Wang, K. Xu, W. Liu, X. Zhang, W. Mao, Y. Guo, X. Ge and F. Pan, *Org. Lett.*, 2016, **18**, 1064; (f) K. Takamatsu, K. Hirano and M. Miura, *Angew. Chem., Int. Ed.*, 2017, **56**, 5353; (g) P. Peng, J. Wang, C. Li, W. Zhu, H. Jiang and H. Liu, *RSC Adv.*, 2016, **6**, 57441; (h) W. Miura, K. Hirano and M. Miura, *J. Org. Chem.*, 2017, **82**, 5337; (i) J. Ni, H. Zhao and A. Zhang, *Org. Lett.*, 2017, **19**, 3159; (j) S. Y. Chen, X. L. Han, J. Q. Wu, Q. Li, Y. Chen and H. Wang, *Angew. Chem., Int. Ed.*, 2017, **56**, 9939; (k) D. Das, P. Poddar, S. Maity and R. Samanta, *J. Org. Chem.*, 2017, **82**, 3612; (l) J. Xia, Z. Huang, X. Zhou, X. Yang, F. Wang and X. Li, *Org. Lett.*, 2018, **20**, 740; (m) D. Das and R. Samanta, *Adv. Synth. Catal.*, 2018, **360**, 379.
- (a) H. Jin, L. Huang, J. Xie, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2016, **55**, 794; (b) J. S. Baum, M. E. Condon and D. A. Shook, *J. Org. Chem.*, 1987, **52**, 2983.
- (a) H. Chen and M. P. Huestis, *ChemCatChem*, 2015, **7**, 743; (b) W. Li and L. Dong, *Adv. Synth. Catal.*, 2018, **360**, 1104; (c) J. Ryu, K. Shin, S. H. Park, J. Y. Kim and S. Chang, *Angew. Chem., Int. Ed.*, 2012, **51**, 9904.
- Selected reviews and accounts: (a) M. Moselage, J. Li and L. Ackermann, *ACS Catal.*, 2015, **6**, 498; (b) R. Shang, L. Ilies and E. Nakamura, *Chem. Rev.*, 2017, **117**, 9086; (c) W. Liu and L. Ackermann, *ACS Catal.*, 2016, **6**, 3743; (d) L. C. M. Castro and N. Chatani, *Chem. Lett.*, 2015, **44**, 410; (e) W. Liu and Y. Bi, *Chin. J. Org. Chem.*, 2012, **32**, 1041.
- (a) T. Yoshino and S. Matsunaga, *Adv. Synth. Catal.*, 2017, **359**, 1245; (b) D. Wei, X. Zhu, J. Niu and M. Song, *ChemCatChem*, 2016, **8**, 1242.

11 T. Yoshino, H. Ikemoto, S. Matsunaga and M. Kanai, *Angew. Chem., Int. Ed.*, 2013, **52**, 2207.

12 (a) D. Zhao, J. H. Kim, L. Stegemann, C. A. Strassert and F. Glorius, *Angew. Chem., Int. Ed.*, 2015, **54**, 4508; (b) T. Gensch, S. VasquezCespedes, D.-G. Yu and F. Glorius, *Org. Lett.*, 2015, **17**, 3714; (c) D.-G. Yu, T. Gensch, F. de Azambuja, S. Vasquez-Céspedes and F. Glorius, *J. Am. Chem. Soc.*, 2014, **136**, 17722; (d) A. Lerchen, T. Knecht, M. Koy, C. G. Daniliuc and F. Glorius, *Chem.-Eur. J.*, 2017, **23**, 12149.

13 (a) J. Li and L. Ackermann, *Angew. Chem., Int. Ed.*, 2015, **54**, 8551; (b) J. Li and L. Ackermann, *Angew. Chem., Int. Ed.*, 2015, **54**, 3635; (c) M. Moselage, N. Sauermann, J. Koeller, W. Liu, D. Gelman and L. Ackermann, *Synlett*, 2015, 1596; (d) H. Wang, J. Koeller, W. Liu and L. Ackermann, *Chem.-Eur. J.*, 2015, **21**, 15525; (e) N. Sauermann, M. J. Gonzalez and L. Ackermann, *Org. Lett.*, 2015, **17**, 5316; (f) R. Mei, J. Loup and L. Ackermann, *ACS Catal.*, 2016, **6**, 793; (g) D. Zell, M. Bursch, V. Müller, S. Grimme and L. Ackermann, *Angew. Chem., Int. Ed.*, 2017, **56**, 10378.

14 (a) J. R. Hummel and J. A. Ellman, *Org. Lett.*, 2015, **17**, 2400; (b) J. R. Hummel and J. A. Ellman, *J. Am. Chem. Soc.*, 2015, **137**, 490.

15 (a) A. B. Pawar and S. Chang, *Org. Lett.*, 2015, **17**, 660; (b) P. Patel and S. Chang, *ACS Catal.*, 2015, **5**, 853; (c) J. Park and S. Chang, *Angew. Chem., Int. Ed.*, 2015, **54**, 14103.

16 (a) M. Sen, B. Emayavaramban, N. Barsu, J. Richard Premkumar and B. Sundararaju, *ACS Catal.*, 2016, **6**, 2792; (b) N. Barsu, M. Sen, J. R. Premkumar and B. Sundararaju, *Chem. Commun.*, 2016, **52**, 1338; (c) M. Sen, D. Kalsi and B. Sundararaju, *Chem.-Eur. J.*, 2015, **21**, 15529; (d) N. Barsu, M. A. Rahman, M. Sen and B. Sundararaju, *Chem.-Eur. J.*, 2016, **22**, 9135.

17 (a) S. Prakash, K. Muralirajan and C. H. Cheng, *Angew. Chem., Int. Ed.*, 2016, **55**, 1844; (b) K. Muralirajan, R. Kuppusamy, S. Prakash and C. H. Cheng, *Adv. Synth. Catal.*, 2016, **358**, 774.

18 (a) Y. Liang, Y.-F. Liang, C. Tang, Y. Yuan and N. Jiao, *Chem.-Eur. J.*, 2015, **21**, 16395; (b) Z.-Z. Zhang, B. Liu, C.-Y. Wang and B.-F. Shi, *Org. Lett.*, 2015, **17**, 4094; (c) X.-G. Liu, S.-S. Zhang, C.-Y. Jiang, J.-Q. Wu, Q. Li and H. Wang, *Org. Lett.*, 2015, **17**, 5404; (d) L. Kong, S. Yu, X. Zhou and X. Li, *Org. Lett.*, 2016, **18**, 588; (e) Y. Liang and N. Jiao, *Angew. Chem., Int. Ed.*, 2016, **55**, 4035; (f) L. Kong, S. Yu, G. Tang, H. Wang, X. Zhou and X. Li, *Org. Lett.*, 2016, **18**, 3802; (g) F. Wang, H. Wang, Q. Wang, S. Yu and X. Li, *Org. Lett.*, 2016, **18**, 1306; (h) F. Wang, L. Jin, L. Kong and X. Li, *Org. Lett.*, 2017, **19**, 1812.

19 (a) Y. Park, K. T. Park, J. G. Kim and S. Chang, *J. Am. Chem. Soc.*, 2015, **137**, 4534; (b) V. Bizet and C. Bolm, *Eur. J. Org. Chem.*, 2015, **2015**, 2854; (c) Y. Park, S. Jee, J. G. Kim and S. Chang, *Org. Process Res. Dev.*, 2015, **19**, 1024; (d) V. Bizet, L. Buglioni and C. Bolm, *Angew. Chem., Int. Ed.*, 2014, **53**, 5639; (e) L. Li and G. Wang, *Tetrahedron*, 2018, **74**, 4188; (f) P. W. Tan, A. M. Mak, M. B. Sullivan, D. J. Dixon and J. Seayad, *Angew. Chem., Int. Ed.*, 2017, **56**, 16550; (g) C. L. Zhong, B. Y. Tang, P. Yin, Y. Chen and L. He, *J. Org. Chem.*, 2012, **77**, 4271; (h) E. Eibler, J. Käsbauer, H. Pohl and J. Sauer, *Tetrahedron Lett.*, 1987, **28**, 1097; (i) W. J. Middleton, *J. Org. Chem.*, 1983, **48**, 3845; (j) J. Sauer and K. K. Mayer, *Tetrahedron Lett.*, 1968, **9**, 319.

20 (a) P. Patel and S. Chang, *ACS Catal.*, 2015, **5**, 853; (b) Y. Wu, Z. Chen, Y. Yang, W. Zhu and B. Zhou, *J. Am. Chem. Soc.*, 2018, **140**, 42; (c) A. D. Sadiq, X. Chen, N. Yan and J. Sperry, *ChemSusChem*, 2018, **11**, 532; (d) M. J. Hülsey, H. Yang and N. Yan, *ACS Sustainable Chem. Eng.*, 2018, **6**, 5694.

21 E. M. Simmons and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2012, **51**, 3066.