ChemComm
Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Ruan, X. Zhong, Q. Chen, X. Feng and X. Liu, *Chem. Commun.*, 2020, DOI: 10.1039/C9CC09521G.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

View Article Online
DOI: 10.1039/C9CC09521G

COMMUNICATION

Asymmetric hydrocyanation/Micheal reaction of α-diazoacetates via Cu(I)/chiral guanidine catalysis

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

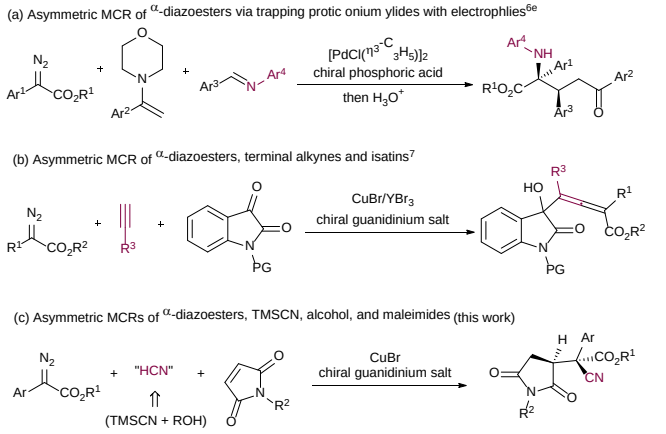
DOI: 10.1039/x0xx00000x

Sai Ruan, Xia Zhong, Quangang Chen, Xiaoming Feng, and Xiaohua Liu*

An asymmetric one-pot hydrocyanation/Micheal reaction of α-aryl diazoacetates with trimethylsilyl cyanide, *tert*-butanol, and *N*-phenylmaleimides has been realized. Using a chiral guanidinium salt/CuBr catalyst, a series of cyanide-containing pyrrolidine-2,5-diones could be obtained in good yields with excellent diastereo- and enantioselectivities.

Multicomponent catalysis has attracted wide attention for the advantages of simple operation, high atomic economy, more compliance with green chemistry and environmentally friendly requirements.[1] Especially, the interest towards asymmetric catalytic one-pot multicomponent reactions increased rapidly over the past decade.[2] However, the identification of the chiral catalysts is challenging due to the presence of multiple species in the multicomponent processes. Enantioselective organocatalysis and metal/organo or metal/metal relay-catalysis have contributed to this fast-growing subfield.[3]

Diazo carbonyl compounds,[4] which are considered as valuable precursors to metal carbenes, have been widely applied in the multicomponent relay reactions in recent years.[5] There are several representative strategies for the enantioselective multicomponent reaction of α-diazo carbonyl compounds. For instance, Hu's[6a-f] and other groups[6g-i] have discovered novel multicomponent reactions via trapping of ammonium/oxonium ylides with a variety of electrophiles, and the asymmetric versions could be achieved with the assistance of cooperative metal salt/chiral organocatalyst[6e] (Scheme 1a) or chiral metal complexes.[6c,6h] Enantioselective trap of the carbene species with terminal alkynes and isatins was realized by our group through copper salt/chiral guanidinium salt catalysis to yield axially chiral tetrasubstituted allenoates (Scheme 1b).[7] The CuI-catalyzed multicomponent reaction of trifluorodiazoethanes, terminal alkynes and nitrosobenzenes enabled the formation of dihydroisoxazoles.[8] Although the



Scheme 1 Representative examples for asymmetric multi-component reactions of α-diazoacetates.

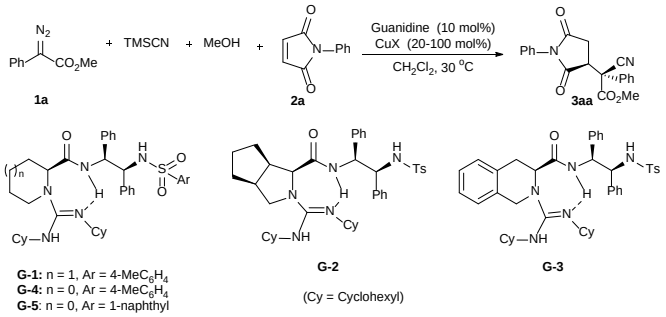
catalytic insertion reactions of α-diazoesters, such as CF_3,[9a-c] SCF_3,[9d-j] OCF_3,[9k] CN,[9l] and azide[9m] have been well established, no related multicomponent reactions via trapping of the intermediates were disclosed. The difficult might rise from the instability of the metal species and the competing protonation process. As part of our continuous research in asymmetric chiral guanidine catalysis[10] and asymmetric reaction of α-diazo compounds,[7,10a-c] we envisioned that the enantioselective hydrocyanation/addition reaction of α-diazoester, "HCN" and electrophiles would allow the readily access to the cyanide-containing compounds with a quaternary carbon center (Scheme 1c).[9l,11] Herein, we report our endeavor in the Cu(I)/chiral guanidinium salt promoted asymmetric one-pot reaction of α-diazoesters with TMSCN, ^{t}BuOH, and maleimides. The current reaction presented a new multi-component reaction involving a sequence of two reactions with different reaction profiles.

In our preliminary investigation, we selected methyl α-aryl diazoacetate **1a**, TMSCN, methanol, and *N*-phenylmaleimide **2a** as the model substrates to optimize the reaction conditions. Primary study showed that in the catalytic amount of CuCl, the hydrocyanation reaction of **1a**, TMSCN, and alcohol was sluggish, and it could be accelerated if higher amount of

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China. E-mail: liuxh@scu.edu.cn.

†Electronic Supplementary Information (ESI) available. CCDC 1901489. For ESI and crystallographic data in CIF or other electronic format see DOI:10.1039/x0xx00000x

Table 1 Optimization of the reaction conditions[a]



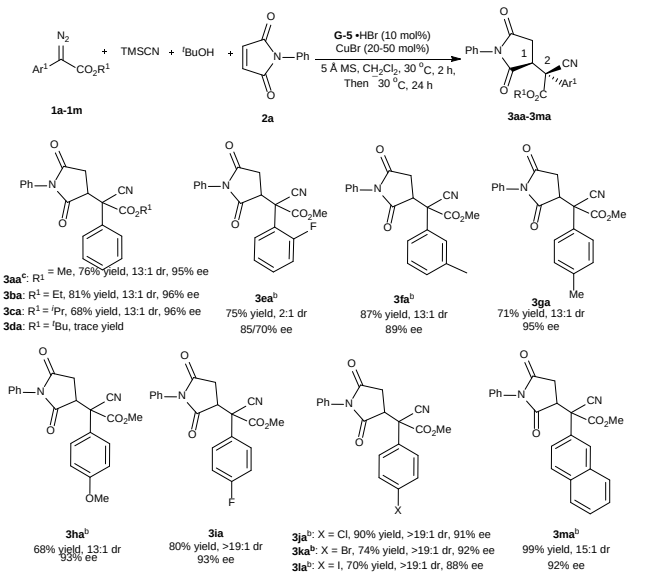
Entry	Cu[I] (mol%)	Guanidine	Yield (%)[b]	dr[c]	ee (%)[c]
1	CuCl (100)	**G-1**	21	94:6	8/5
2	CuCl (100)	**G-2**	18	>19:1	31/-
3	CuCl (100)	**G-3**	13	84:16	5/11
4	CuCl (100)	**G-4**	40	88:12	49/33
5	CuCl (100)	**G-5**	46	88:12	67/43
6	CuBr (100)	**G-5**	60	88:12	73/47
7	CuBr (50)	**G-5**•HBr	71	88:12	74/49
8[d]	CuBr (20)	**G-5**•HBr	85	88:12	74/47
9[d,e]	CuBr (20)	**G-5**•HBr	65	96:4	95/-
10[d-f]	CuBr (20)	**G-5**•HBr	80	96:4	95/-
11[g]	CuBr (20)	**G-5**•HBr	86	96:4	95/-

[a] Unless otherwise noted, all reactions were carried out with chiral guanidine (10 mol%), Cu[I] (100 mol%), α-diazoester **1a** (0.10 mmol), TMSCN (1.0 equiv) and MeOH (1.0 equiv) in CH_2Cl_2 (0.5 mL) at 30 °C for 2 h, then **2a** (1.0 equiv) was added at 30 °C and reacted at 30 °C for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis. [d] 5 Å MS (20 mg) was added. [e] **2a** was added at –30 °C for 24 h. [f] ^{t}BuOH instead of MeOH. [g] **1a** (1.2 equiv), TMSCN (1.2 equiv), ^{t}BuOH (1.2 equiv); and **2a** (1.0 mmol) at –30 °C for 24 h.

copper salt was added. Thus, a variety of chiral guanidine-amides[12] was examined in combination with equivalent CuCl in CH_2Cl_2 at 30 °C. To our delight, it was found that all of the chiral guanidines could promote the reaction to give the desired product **3aa** (Table 1). However, the amino acid backbone had obvious influence on the yield and enantioselectivity of the reaction, and the *L*-proline-based **G-4** gave higher results (40% yield, 88:12 dr, and 49% ee) than the guanidines **G-1** to **G-3** derived from *L*-pipecolic acid, tetrahydroisoquinoline acid, and *L*-ramipril, respectively (entries 1-4). Based on our previous work, the guanidines embellished a sulfonamide unit[10d,12c] could be adjusted to change the reactivity and enantioselectivity. It was found that the installation of 1-naphthyl group into **G-5** enhanced the enantioselectivity to 67% ee (entry 5). Fortunately, the evaluation of the copper salts showed that the reactivity and enantioselectivity increased (60% yield and 73% ee) when CuBr was used instead of CuCl (entry 6). Encouraged by these results, we conducted more detailed investigations. When the guanidium salt **G-5**·HBr combined with CuBr was used as the catalyst, the amount of CuBr could be decreased to 50 mol% and the yield could be increased to 71% with maintained enantioselectivity and diastereoselectivity (entry 7). Moreover, the yield could be further improved in the presence of 20 mol% of CuBr with 5 Å MS (entry 8). Lowering the reaction temperature in the Michael addition step led to an increase of stereoselectivity, and the product was given in 65% yield, 95% ee with 96:4 dr (entry 9). Further exploration of alcohols showed that ^{t}BuOH could be used to promote the reaction in 80% yield with maintained enantioselectivity and diastereoselectivity (entry 10). Finally, increasing the amount of α-diazoester, TMSCN, and ^{t}BuOH to 1.2 equivalences resulted in 86% yield, 96:4 dr with 95% ee (entry 11).

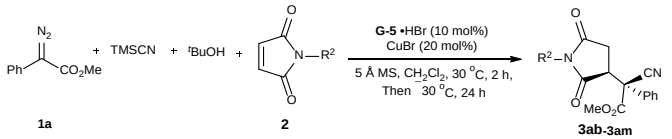
Having identified the optimized four-component reaction conditions, we next investigated the scope of α-aryl diazoacetates **1**. As depicted in Table 2, both the ester group and the aryl substituent on the α-diazoesters affected the yield dramatically. It was found that with the steric hindrance of the ester group increased, the yield decreased gradually with the diastereoselectivity and enantioselectivity remained (**3aa**-**3ca**). If *tert*-butyl phenyldiazoacetate **1d** was subjected into the system, only trace amount of the product was detected. The position and electronic nature of the substituents on the phenyl group of methyl α-aryl diazoacetates have obvious influence on both the yield and enantioselectivity. The products **3ga** and **3ia** bearing 4-methyl and 4-fluoro substituent were obtained with good diastereo- and enantioselectivities in 93% and 95% ee, respectively. The reactions of 3-methyl or 4-methoxyl substituted α-aryl diazoesters proceeded well after the addition of DABCO, affording the related product **3fa** in 87% yield with 89% ee, and **3ha** in 68% yield with 93% ee. When other halo-substituted α-phenyl diazoesters including 2-F, 4-Cl, 4-Br, and 4-I substituted ones, as well as α-2-naphthyl diazoester, were used for the reaction, the good yields and enantioselectivities (**3ea**, **3ma**, **3ja**-**3ia**) could be achieved with higher loading of CuBr and DABCO as the additives (see the ESI for details).

Table 2 Substrate scope of α-aryl diazoacetates **1**[a]



[a] Unless otherwise noted, the reactions were carried out with **G-5**·**HBr** (10 mol%), CuBr (20 mol%), 5 Å MS (20 mg), **1**/TMSCN/^{t}BuOH (1/1/1, 1.2 equiv) in CH_2Cl_2 (0.5 mL) at 30 °C for 2 h, then **2a** (0.10 mmol) was added at -30 °C and reacted at -30 °C for 24 h. Isolated yield. EE and dr were determined by HPLC or UPC[2] and NMR analysis. [b] CuBr (20-100 mol%), DABCO (0.3-0.5 equiv), see the ESI for details. [c] With **2a** (5.0 mmol), and 5 Å MS (1.0 g) in CH_2Cl_2 (25.0 mL).

Table 3 Substrate scope of the *N*-arylmaleimides **2**[a]

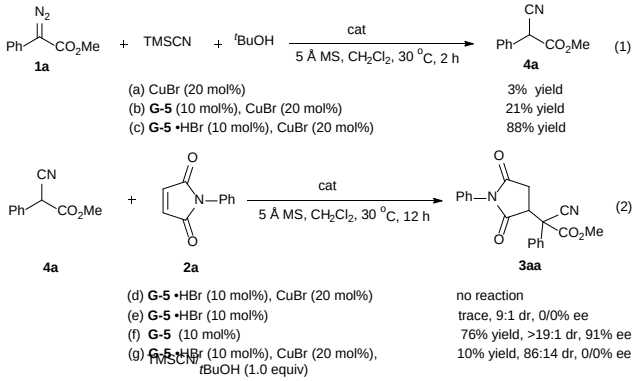


Entry	**2**: R^2	Yield (%)	dr	ee (%)
1	**2b**: 4-MeC_6H_4	62 (**3ab**)	>19:1	92
2	**2c**: 4-MeOC_6H_4	70 (**3ac**)	16:1	92
3	**2d**: 4-EtC_6H_4	73 (**3ad**)	>19:1	93
4	**2e**: 4-EtOC_6H_4	65 (**3ae**)	>19:1	93
5	**2f**: 4-*i*PrC_6H_4	72 (**3af**)	>19:1	92
6	**2g**: 4-FC_6H_4	78 (**3ag**)	19:1	92
7	**2h**: 4-ClC_6H_4	68 (**3ah**)	16:1	93
8	**2i**: 4-BrC_6H_4	65 (**3ai**)	16:1	93
9	**2j**: 4-IC_6H_4	78 (**3aj**)	16:1	93
10	**2k**: 2-FC_6H_4	73 (**3ak**)	11:1	93
11	**2l**: 2-MeC_6H_4	85 (**3al**)	>19:1	93
12	**2m**: 3-FC_6H_4	65 (**3am**)	16:1	91
13	**2n**: Bn	36 (**3an**)	7:1	72
14	**2o**: Me	54 (**3ao**)	5:1	50
15	**2p**: H	nr (**3ap**)	—	—

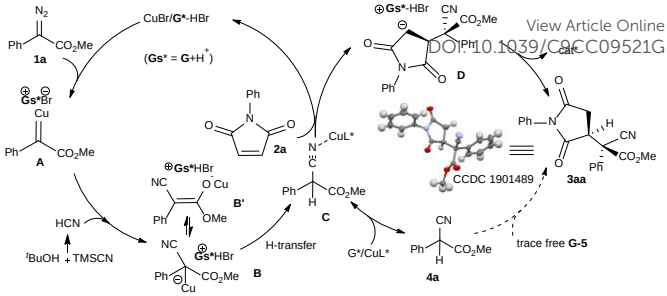
[a] As same as the condition in footnote a in Table 2.

Taking into account the practical application of the catalyst system, the gram-scaled synthesis of **3aa** was performed. Under the optimal reaction conditions, the reaction of 5 mmol of maleimide **2a** reacted well to afford the desired adduct **3aa** in 76% yield with 95% ee and 13:1 dr. The absolute configuration of the product **3aa** was determined to be (*1S, 2R*) by X-ray crystallography analysis (see the ESI for details).[13]

Then, we turned our attention to investigate the scope of maleimides. As shown in Table 3, *N*-arylmaleimides **2b-2m** bearing various aryl groups with different electronic properties efficiently underwent the tandem reaction, delivering *N*-substituted phenylpyrrolidine-2,5-diones **3ab-3am** with vicinalquaternary-tertiary stereocenters in moderate to good yields (62-85%) with generally excellent diastereoselectivities and enantioselectivities (11:1->19:1 dr, 91-93% ee; entries 1-12). In addition, other maleimides such as *N*-methyl, and *N*-benzyl were examined, both the yield and stereoselectivitiy dropped a little (entry 13 and 14). The N-H maleimide **2p** could not participate in the Michael cascade reaction (entry 15).



Scheme 2 Control experiments.



Scheme 3 Proposed catalytic cycle.

In order to clarify the multicomponent reaction mechanism, we tried the control experiments of initial cyanation insertion reaction and the sequent Michael addition reaction (Scheme 2). It was found that CuBr in a catalytic amount was sluggish for hydrocyanation using TMSCN as the cyano-source.[9l] The addition of guanidinium salt could dramatically accelerate such an insertion reaction, better than guanidine **G-5** (Scheme 2, b and c). The isolated cyano-2-phenylacetate **4a** was subjected into the Michael reaction with maleimide **2a** under different reaction conditions (Scheme 2, d-g). We found that guanidine **G-5** along could promote the addition reaction with high yield and stereoselectivity, but the reactions were inert in the presence of catalytic amount of CuBr or guanidinium salt. In connection with condition of the four-component reaction, we proposed that the asymmetric relay catalysis is under the control of chiral **G-5**•HBr/CuBr catalyst, rather than CuBr/**G-5** dual catalysis. In connection with the experiment procedure, this multi-component reaction involved in two kinetically different steps.

In this case, the exact structures of the catalyst resting/ active state are yet to be studied. We previously have discovered a chiral guanidinium dimeric copper(I) cluster forms from the mixture of guanidinium salt and copper(I) salt.[10f,14] It was proposed that such a kind of chiral ion pair might act as the catalyst precursor. As shown in Scheme 3, the copper salt can form the copper(I) carbene **A**, which undergoes hydrocyanation reaction to generate the cyanomethyl copper intermediate **B**. Because the catalyst system is disable for the Michael reaction between **4a** and maleimide **2a**, the copper-bonded species **B** or other species **B'** or **C** might be the active nucleophile to perform the following addition reaction. The sulfonamide unit of the guanidinium salt **Gs**-**5** might active the maleimide **2a** via hydrogen bonding. Then, a diastereo- and enantioselective conjugate addition occurs to yield the intermediate **D**, generating the final product **3aa** after protonation.

In summary, we have successfully developed an efficient four-component hydrocyanation/Michael reaction of α-aryl diazoesters, TMSCN, *tert*-butanol, and *N*-arylmaleimides. The cyanide-containing pyrrolidine-2,5-dione derivatives could be obtained in the presence of a chiral guanidinium salt and CuBr catalyst with good yields and excellent diastereo- and enantioselectivities. Further applications of the catalyst system of chiral guanidine or guanidinium salt with metal salt system in the asymmetric reactions are still underway.

We acknowledge the National Natural Science Foundation of China (No. 21625205) for financial support.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (*a*) B. M. Trost, *Angew. Chem., Int. Ed.,* 1995, ***34***. 259; (*b*) H. Bienaymé, C. Hulme, G. Oddon and P. Schmitt, *Chem. – Eur. J.,* 2000, ***6***, 3321; (*c*) J. Zhu, H. Bienaymé, *Multicomponent Reactions*, Wiley, Weinheim, Germany, 2005; (*d*) A. Dömling, *Chem. Rev.*, 2006, ***106***, 17; (*e*) A. Dömling and I. Ugi, *Angew. Chem., Int. Ed.,* 2000, ***39***, 3168; (*f*) E. Ruijter, R. Scheffelaar and R. V. A. Orru, *Angew. Chem., Int. Ed.,* 2011, ***50***, 6234; (*g*) B. Ganem, *Acc. Chem. Res*., 2009, ***42***, 463.

2 For reviews, see: (*a*) D. J. Ramon and M. Yus, *Angew., Chem., Int. Ed*., 2005, ***44***, 1602; (*b*) A. Dondoni and A. Massi, *Acc. Chem. Res*., 2006, ***39***, 451; (*c*) J. Yu, F. Shi and L. Z. Gong, *Acc. Chem. Res*., 2011, ***44***, 1156; (*d*) C. D. Graaff, E. Ruijter and R. V. A. Orru, *Chem. Soc. Rev.,* 2012, ***41***, 3969; (*e*) Q. Wang,D. X. Wang,M. X. Wang and J. P. Zhu, *Acc. Chem. Res*., 2018, ***51***, 1290; (*f*) C. Hulme and V. Gore, *Curr. Med. Chem*., 2003, ***10***, 51; (*g*) B. B. Toure and D. G. Hall, *Chem. Rev.,* 2009, ***109***, 4439.

3 For selected reviews, see: (*a*) Y. Qin, L. H. Zhu and S. Z. Luo, *Chem. Rev.*, 2017, ***117***, 9433; (*b*) D. F. Chen, Z. Y. Han, X. L. Zhou and L. Z. Gong, *Acc. Chem. Res*., 2014, ***47***, 2365; (*c*) C. Zhong and X. D. Shi, *Eur. J. Org. Chem.,* 2010, 2999; (*d*) Z. H. Shao and H. B. Zhang, *Chem. Soc. Rev.,* 2009, ***38***, 2745; (*e*) J. Park and S. Hong, *Chem. Soc. Rev.,* 20129, ***42***, 6931; For selected examples, see: (*f*) G. M. Sammis, H. Danjo and E. N. Jacobsen, *J. Am. Chem. Soc.* 2004, ***126***, 9968; (*g*) J. Li, L. L. Lin, B. W. Hu, P. F. Zhou, T. Y. Huang, X. H. Liu and X. M. Feng, *Angew. Chem., Int. Ed.,* 2017, ***56***, 885; (*h*) Q. Xiong, S. X. Dong, Y. S. Chen, X. H. Liu and X. M. Feng, *Nat. Commun.,* 2019, ***10***, 2116.

4 For selected reviews, see: (*a*) G. Maas, *Chem. Soc. Rev.,* 2004, ***33***, 183; (*b*) H. M. L. Davies and J. R. Manning, *Nature*, 2008, ***451***, 417; (*c*) Y. Zhang and J. B. Wang, *Chem. Commun.*, 2009, 5350; (*d*) S. F, Zhu and Q. L. Zhou, *Acc. Chem. Res*., 2012, ***45***, 1365; (*e*) N. R. Candeias, R. Paterna, P. M. P. Gois, *Chem. Rev.*, 2016, ***116***, 2937; (*f*) Y. Xia, D. Qiu, and J. B. Wang, *Chem. Rev.*, 2017, ***117***, 13810; (*g*) Y. Y. Ren, S. F. Zhu and Q. L. Zhou, *Org. Biomol. Chem.,* 2018, ***16***, 3087.

5 (*a*) X. Guo and W. H. Hu, *Acc. Chem. Res*., 2013, ***46***, 2427; (*b*) M. Tang, D. Xing, M. Q. Cai and W. H. Hu, *Chin. J. Org. Chem.,* 2014, ***34***, 1268; (*c*) D. Zhang and W. H. Hu, *Chem. Rec*., 2017, ***17***, 739; (*d*) M. Y. Wu, W. W. He, X. Y. Liu and B. Tan, *Angew. Chem., Int. Ed.*, 2015, ***54***, 9409; (*e*) D. Zhang, H. Qiu, L. Q. Jiang, F. P. Lv, C. Q. Ma and W. H. Hu, *Angew. Chem., Int. Ed*., 2013, ***52***, 13356; (*f*) S. F. Yu, X. Fu, G. X. Liu, H. Qiu and W. H. Hu, *Acta Chim. Sinica*., 2018, ***76***, 895; (*g*) F. M. Liao, Y. Du, F. Zhou, J. Zhou, *Acta Chim. Sinica*., 2018, ***76***, 862.

6 For selected examples, see: (*a*) W. H. Hu, X. F. Xu, J. Zhou, W. J. Liu, H. X. Huang, J. Hu, L. P. Yang and L. Z. Gong, *J. Am. Chem. Soc.*, 2008, ***130***, 7782; (*b*) X. Zhang, H. X. Huang, X. Guo, X. Y. Guan, L. P. Yang and W. H. Hu, *Angew. Chem., Int. Ed.*, 2008, ***47***, 6647; (*c*) X. Y. Guan, L. P. Yang and W. H. Hu, *Angew. Chem., Int. Ed.*, 2010, ***49***, 2190; (*d*) J. Jiang, H. D. Xu, J. B. Xi, B. Y. Ren, F. P. Lv, X. Guo, L. Q. Jiang, Z. Y. Zhang, and W. H. Hu, *J. Am. Chem. Soc.*, 2011, ***133***, 8428; (*e*) D. Zhang, J. Zhou, F. Xia, Z. H Kang and W. H. Hu, *Nat. Commun.,* 2015, ***6***, 5801; (*f*) H. Qiu, M. Li, L. Q. Jiang, F. P. Lv, L. Zan, C. W. Zhai, M. P. Doyle and W. H. Hu, *Nat. Chem.*, 2012, ***4***, 733. (*g*) C. Y. Zhou, J. C. Wang, J. H. Wei, Z. J. Xu, Z. Guo, K. H. Low and C. M. Che, *Angew. Chem., Int. Ed.*, 2012, ***51***, 11376; (*h*) L. Ren, X. L. Lian and L. Z. Gong, *Chem. – Eur. J.,* 2013, ***19***, 3315; (*i*) D. Zhang, L. L. Lin, J. Yang, X. H. Liu and X. M. Feng, *Angew. Chem., Int. Ed.*, 2018, ***57***, 12323.

7 Y. Tang, J. Xu, J. Yang, L. L. Lin, X. M. Feng and X. H. Liu, *Chem*, 2018, ***4***, 1658.

8 X. X. Lv, Z. H. Kang, D. Xing and W. H. Hu, *Org. Lett.*, 2018, ***20***, 4843.

9 (*a*) M. Y. Hu, C. F. Ni and J. B. Hu, *J. Am. Chem. Soc.*, 2012, ***134***, 15257; (*b*) X. Q. Hu, J. B. Han and C. P. Zhang, *Eur. J. Org. Chem*., 2017, 324; (*c*) M. Y. Hu, Q. Q. Xie, X. J. Li, C. F. Ni and J. B. Hu, *Chin. J. Chem*., 2016, ***34***, 469; (*d*) X. Wang, Y. J. Zhou, G. J. Ji, G. J. Wu, M. Li, Y. Zhang and J. B. Wang, *Eur. J. Org. Chem.,* 2014, 3093; (*e*) Q. Lefebvre, E. Fava, P. Nikolaienko and M. Rueping, *Chem. Commun.*, 2014, ***50***, 6617; (*f*) M. Y. Hu, J. Rong, W. J. Miao, C. F. Ni, Y. X. Han and J. B. Hu, *Org. Lett.*, 2014, ***16***, 2030; (*g*) Y. F. Liu, X. X. Shao, P. P. Zhang, L. Lu and Q. L. Shen, *Org. Lett.,* 2015, ***17***, 2752; (h) C. Matheis, T. Krause, V. Bragoni and L. J. Goossen, *Chem. – Eur. J.,* 2016, ***22***, 12270; (*i*) M. Lübcke, W. M. Yuan and K. J. Szabó, *Org. Lett*., 2017, ***19***, 4548; (*j*) Z. K. Zhang, Z. Sheng, W. Z. Yu, G. J. Wu, R. Zhang, W. D. Chu, Y. Zhang and J. B. Wang, *Nat. Chem.,* 2017, ***9***, 970; (*k*) G. F. Zha, J. B. Han, X. Q. Hu, H. L. Qin, W. Y. Fang and C. P. Zhang, *Chem. Commun.*, 2016, ***52***, 7458; (*l*) E. J. Park, S. Lee and S. Chang, *J. Org. Chem.*, 2010, ***75***, 2760; (*m*) H. H. San, C. Y. Wang, H. P. Zeng, S. T. Fu, M. Jiang and X. Y. Tang, *J. Org. Chem.*, 2019, ***84***, 4478.

10 For selected examples, see: (*a*) Y. Zhu, X. H. Liu, S. X. Dong, Y. H. Zhou, W. Li, L. L. Lin and X. M. Feng, *Angew. Chem., Int. Ed.*, 2014, ***53***, 1636; (*b*) Y. Tang, Q. G. Chen, X. H. Liu, G. Wang, L. L. Lin and X. M. Feng, *Angew., Chem. Int. Ed.*, 2015, ***54***, 9512; (*c*) F. Tan, X. H. Liu, X. Y. Hao, Y. Tang, L. L. Lin and X. M. Feng, *ACS Catal.,* 2016, ***6***, 6930; (*d*) Q. G. Chen, Y. Tang, T. Y. Huang, X. H. Liu, L. L. Lin and X. M. Feng, *Angew., Chem. Int. Ed.*, 2016, ***55***, 5286; (*e*) Q. G. Chen, L. H. Xie, Z. J. Li, Y. Tang, P. Zhao, L. L. Lin, X. M. Feng and X. H. Liu, *Chem. Commun.*, 2018, ***54***, 678; (*f*) S. S. Guo, P. Dong, Y. S. Chen, X. M. Feng and X. H. Liu, *Angew. Chem., Int. Ed.*, 2018, ***57***, 16852; (*g*) J. Yang, P. R. Ruan, W. Yang, X. M. Feng and X. H. Liu, *Chem. Sci.,* 2019, ***10***, 10305.

11 (*a*) X. H. Liu, B. Qin, X. Zhou, B. He and X. M. Feng, *J. Am. Chem. Soc.*, 2005, ***127***, 12224; (*b*) Y. H. Liao, X. L. Liu, Z. J. Wu, X. L. Du, X. M. Zhang and W. C. Yuan, *Adv. Synth. Catal.*, 2011, ***353***, 1720; (*c*) Z. W. Ma, Y. Wu, B. Sun, H. L. Du, W. M. Shi and J. C. Tao, *Tetrahedron: Asymmetry*, 2013, ***24***, 7.

12 (*a*) Z. P. Yu, X. H. Liu, L. Zhou, L. L. Lin and X. M. Feng, *Angew. Chem., Int. Ed.*, 2009, ***48***, 5195; (*b*) S. X. Dong, X. H. Liu, X. H. Chen, F. Mei, Y. L. Zhang, B. Gao, L. L. Lin and X. M. Feng, *J. Am. Chem. Soc.*, 2010, ***132***, 10650; (*c*) S. Ruan, X. B. Lin, L. H. Xie, L. L. Lin, X. M. Feng and X. H. Liu, *Org. Chem. Front.,* 2018, ***5***, 32; (*d*) S. X. Dong, X. M. Feng and X. H. Liu, *Chem. Soc. Rev.*, 2018, ***47***, 8525; (*e*) X. H. Liu, S. X. Dong, L. L. Lin and X. M. Feng, *Chin. J. Chem.*, 2018, ***36***, 791; (*f)* W. D. Cao, X. H. Liu and X. M. Feng, *Chin. Chem. Lett.*, 2018, ***29***, 1201; (*g*) L. H. Xie, S. X. Dong, Q. Zhang, X. M. Feng and X. H. Liu, *Chem. Commun.*, 2019, ***55***, 87.

13 CCDC 1901489 (**3aa**).

14 (*a*) H. X. Huang, X. Guo and W. H. Hu, *Angew. Chem., Int. Ed*., 2007, ***46***, 1337; (*b*) X. Y. Cui, Y. C. Ge, S. M. Tan, H. Jiang, D. Tan, Y. P. Lu, R. Lee and C. H. Tan, *J. Am. Chem. Soc.*, 2018, ***140***, 8448; (*c*) G. K. R. Alavala, F. Sajjad, T. D. Shi, Z. H. Kang, M. L. Ma, D. Xing and W. H. Hu, *Chem. Commun.*, 2018, ***54***, 12.