Chemical
Science

ROYAL SOCIETY
OF CHEMISTRY

EDGE ARTICLE

Check for updates

Cite this: *Chem. Sci.*, 2020, **11**, 7451

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 21st February 2020
Accepted 20th June 2020

DOI: 10.1039/d0sc01049a

rsc.li/chemical-science

This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Palladium-catalyzed asymmetric hydrophosphorylation of alkynes: facile access to *P*-stereogenic phosphinates†‡

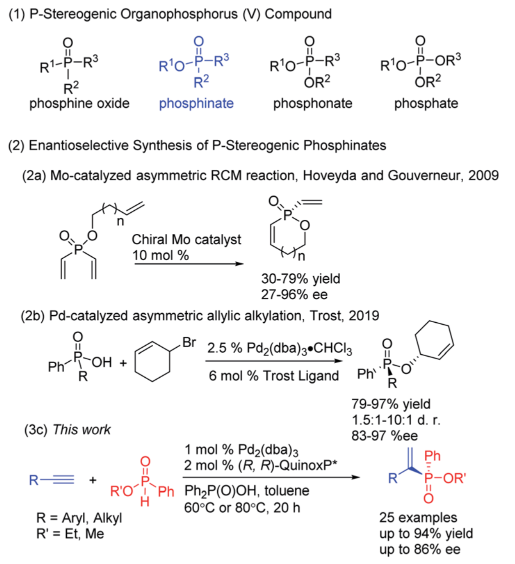
Zhiping Yang,[ab] Xiaodong Gu,[b] Li-Biao Han [c] and Jun (Joelle) Wang *[b]

Despite the importance of *P*-chiral organophosphorus compounds in asymmetric catalysis, transition metal-catalyzed methods for accessing *P*-chiral phosphine derivatives are still limited. Herein, a catalytic enantioselective method for the synthesis of *P*-stereogenic alkenylphosphinates is developed through asymmetric hydrophosphorylation of alkynes. This process is demonstrated for a wide range of racemic phosphinates and leads to diverse *P*-stereogenic alkenylphosphinates directly.

Introduction

P-Chiral organophosphorus compounds are broadly utilized as synthetic building blocks of bioactive molecules[1] and have served as an important class of chiral ligands that have significantly contributed to metal-catalyzed[2] and organocatalytic[3] transformations. *P*-stereogenic phosphinates are important molecules in medicinal and synthetic chemistry. For example, arylphosphinosugars have received continuous attention and demonstrated powerful activities on human cancer cell line panels.[4] However, *P*-chiral organophosphorus compounds are less studied due to their synthetic challenges, compared with chiral phosphine ligands where planar or point chirality is presented in the carbon framework.

Despite the importance of *P*-stereogenic phosphinates, general and efficient methods for their preparation are rather rare. Traditionally, enantioenriched *P*-chiral phosphorus compounds are achieved through the use of chiral reagents or auxiliary-assisted transformations, using menthol or chiral amino alcohol, for example.[5] Recently, a variety of examples involving metal-catalyzed asymmetric processes through desymmetrization of prochiral phosphorus compounds have emerged.[6–11] Dialkynylphosphine oxides are the typical examples for constructing *P*-stereogenic phosphine oxides,[6] and the first desymmetrization of dialkynylphosphine oxides was reported by using Rh(I)-catalyzed cycloaddition.[6a] Desymmetrization of divinylphosphine oxides[7] and phospholene oxides[8] was also well-developed to construct *P*-stereogenic centers. Several elegant examples of inter- or intramolecular Pd-catalyzed enantioselective C–H arylation of phosphinamides, phosphonates and phosphine oxides were disclosed independently by Duan, Tang, Ma, Xu and Han.[9] Soon after, Cramer reported Rh-catalyzed desymmetric alkynylation of phosphinamides with alkynes[10a,b] and Ir-catalyzed arylation and amination of phosphine oxides.[10c,d] Very recently, Zhang presented an asymmetric P–C cross-coupling for the efficient synthesis of *P*-stereogenic phosphine oxides catalyzed by Pd and their Xiao-phos.[11] Nevertheless, there have been only two desymmetrization examples reported for the enantioselective synthesis of *P*-stereogenic phosphinates. In 2009, Hoveyda and Gouverneur reported a molybdenum-catalyzed asymmetric ring-closing



Scheme 1 Enantioselective synthesis of *P*-stereogenic phosphinates.

---

[a] *Harbin Institute of Technology, Harbin 150080, China*

[b] *Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China. E-mail: wang.j@sustech.edu.cn*

[c] *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan*

† Dedicated to Professor Albert S. C. Chan on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available. CCDC 1977604. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc01049a

metathesis to obtain *P*-stereogenic phosphinates (Scheme 1, eqn (2a)).[12] In 2019, Trost showed the desymmetrization of phosphinic acids by stereoselectively alkylating one of the enantiotopic oxygens through Pd-catalyzed asymmetric allylic alkylation to give *P*-stereogenic phosphinates with diversified substituents (Scheme 1, eqn (2b)).[13] Therefore, it is desirable to develop other new methods for the synthesis of multifunctional *P*-stereogenic phosphinates.

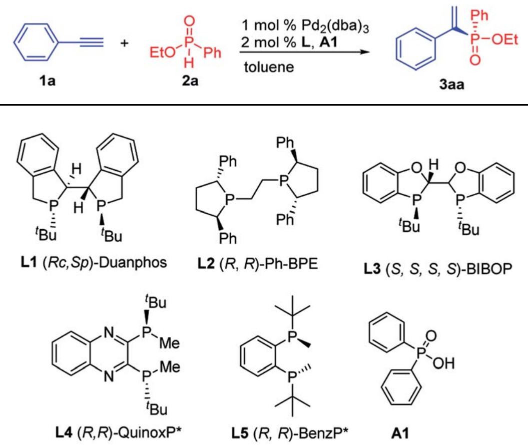
Pd-catalyzed addition of an H–P(O)R_1R_2 to alkynes is one of the most straightforward and atom-efficient approaches for the construction of a C–P bond.[14] The first Pd-catalyzed addition of $(RO)_2P(O)H$ to alkynes was reported by Tanaka and Han to give the corresponding alkenylphosphonates.[14a] Later, they developed a similar oxidative addition using (R_P)-menthyl-phenylphosphinate to give enantiomerically pure *P*-chiral alkenylphosphinates with retention of configuration at phosphorus.[14b] Though Han and co-workers reported a comprehensive study on the generality, scope, limitations, and mechanism of the palladium-catalyzed hydrophosphorylation of alkynes recently,[14c] the catalytic enantioselective hydrophosphorylation of alkynes with phosphinates is still not reported, given more than 22 years have passed since the first Pd-catalyzed hydrophosphorylation was reported. In 2006, Gaumont reported the Pd-catalyzed asymmetric hydrophosphination of alkynes with phosphine–boranes, only 70% conversion and 42% enantiomeric excess were obtained.[15] In 2018, Dong reported the hydrophosphinylation of 1,3-dienes to afford chiral allylic phosphine oxides with high enantio- and regiocontrol.[16] Herein, we disclose the first catalytic enantioselective hydrophosphorylation reaction of alkynes with phosphinates, which provides a highly efficient approach to prepare chiral alkenylphosphinates with *P*-chirality.

Results and discussion

To begin the investigation, phenylacetylene **1a** and ethyl phenylphosphinate **2a** were chosen as the model substrates. Various types of ligands were initially evaluated, and most bidentate bisphosphine ligands with *P* chirality worked well in this transformation. When Duanphos **L1** was used as the ligand, the reaction proceeded smoothly to afford alkenylphosphinate **3aa** in 70% yield with 70% ee (Table 1, entry 1). (*R*,*R*)-Ph-BPE exhibited poor reactivity and enantioselectivity (Table 1, entry 2). (*S*,*S*,*S*,*S*)-BIBOP **L3** showed good reactivity, yet no product enantioselectivity was observed (Table 1, entry 3). To our delight, (*R*,*R*)-QuinoxP* **L4** afforded **3aa** in 70% yield with 83% ee (Table 1, entry 4). A similar ligand (*R*,*R*)-benzP* **L5** gave 86% ee but with poor yield (Table 1, entry 5). A higher reaction temperature was required to allow the reaction to reach completion when $Pd(dba)_2$ was used (Table 1, entry 6). A brief survey of solvents revealed that THF, 1,4-dioxane and DCE resulted in inferior yields and enanatioselectivities (Table 1, entries 7–9). Unlike phosphinic acid and secondary phosphine oxide,[17] phosphinate **2a** was not able to be easily racemized by base or transition metals. Thus, it is difficult for phosphinate to realize the dynamic kinetic resolution. Then, a kinetic resolution process was desired (for details, see the ESI‡). However, when 1 equiv. of phosphinate was used, the product **3aa** was obtained in 50% yield with 55% ee and the (*R*)-**2a** was recovered in 40% yield with 61% ee at 60 °C (the S factor is only 6) (Table 1, entry 10). Optimization of the ratio of **1a**/**2a** was performed to enhance enantioselectivity of **3aa**. When 4 equiv. **2a** was used, the best yield and ee were obtained (Table 1, entry 4 *vs.* entries 10–13). When the amount of ethyl phenylphosphinate **2a** was increased to 6 equiv., the yield was reduced which might due to the coordinative saturation of the palladium center by the excess amount of **2a**, and hence resulted in catalyst deactivation (Table 1, entries 12 and 13). Omitting $Ph_2P(O)OH$ resulted in a reduced yield, but a little enhanced product enanatioselectivity (Table 1, entry 14 *vs.* 4). Thus, the optimal reaction conditions were toluene at 60 °C with 1 mol% $Pd_2(dba)_3$, 2 mol% (*R*,*R*)-QuinoxP*, and 4 mol% phosphinic acid.

With these optimized conditions in hand, the reaction scope was next examined (Table 2). It was found that a large range of

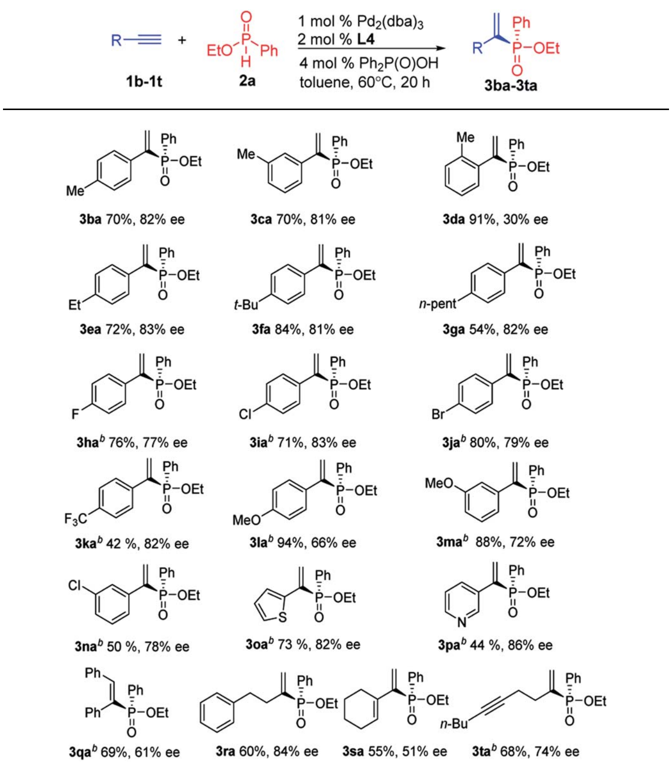
Table 1 Optimization of the reaction conditions[a]



Entry	Ligand	Solvent	Temp (°C)	Yield (%)	ee (%)
1	**L1**	Toluene	60	70	70
2	**L2**	Toluene	60	Trace	—
3	**L3**	Toluene	60	85	7
4	**L4**	Toluene	60	70	83
5	**L5**	Toluene	60	11	86
6[b]	**L4**	Toluene	80	85	76
7	**L4**	THF	60	68	75
8	**L4**	Dioxane	60	54	81
9	**L4**	DCE	60	Trace	—
10[c]	**L4**	Toluene	60	50	55
11[d]	**L4**	Toluene	60	59	78
12[e]	**L4**	Toluene	60	34	85
13[e,f]	**L4**	Toluene	60	44	86
14[g]	**L4**	Toluene	60	60	84

[a] Reaction conditions: 1 mol% $Pd_2(dba)_3$, 2 mol% ligand, and 4 mol% $Ph_2P(O)OH$ in 1 mL toluene were stirred for 10 min in an argon atmosphere. 0.25 mmol alkynes and 1.0 mmol ethyl phenylphosphinate were added, and the mixture was stirred at the indicated temperature. Isolated yields. Determined by HPLC analysis. [b] 2 mol% $Pd(dba)_2$ was used instead of 1 mol% $Pd_2(dba)_3$. [c] 1 equiv. ethyl phenylphosphinate was used. [d] 3 equiv. ethyl phenylphosphinate was used. [e] 6 equiv. ethyl phenylphosphinate was used. [f] 2 mL toluene was used. [g] Without $Ph_2P(O)OH$.

Table 2 Substrate scope of alkynes[a]



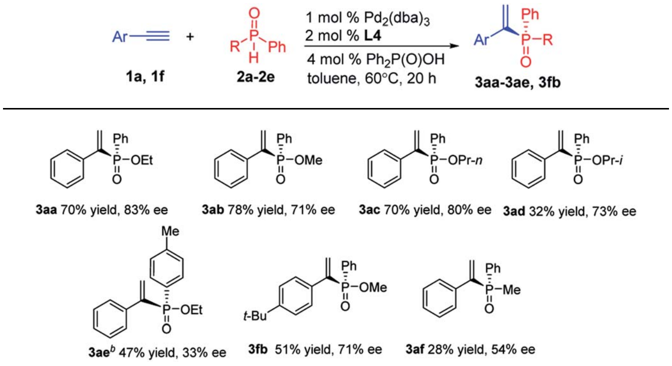
3ba 70%, 82% ee; **3ca** 70%, 81% ee; **3da** 91%, 30% ee; **3ea** 72%, 83% ee; **3fa** 84%, 81% ee; **3ga** 54%, 82% ee; **3ha**[b] 76%, 77% ee; **3ia**[b] 71%, 83% ee; **3ja**[b] 80%, 79% ee; **3ka**[b] 42 %, 82% ee; **3la**[b] 94%, 66% ee; **3ma**[b] 88%, 72% ee; **3na**[b] 50 %, 78% ee; **3oa**[b] 73 %, 82% ee; **3pa**[b] 44 %, 86% ee; **3qa**[b] 69%, 61% ee; **3ra** 60%, 84% ee; **3sa** 55%, 51% ee; **3ta**[b] 68%, 74% ee

[a] Conditions: 1 mol% $Pd_2(dba)_3$, 2 mol% ligand **L4**, and 4 mol% $Ph_2P(O)OH$ in 1 mL toluene were stirred for 10 min in an argon atmosphere. 0.25 mmol alkynes **1b–1t** and 1.0 mmol **2a** were added, and the mixture was stirred at 60 °C for 20 h. Isolated yields. Determined by HPLC analysis. [b] 80 °C was used instead.

alkynes was applicable in this reaction system. The aryl alkynes substituted with electron-donating groups (MeO, Me, Et, *n*-pent, and *t*-Bu) (**3ba–3ga**, **3la**, and **3ma**) or electron-withdrawing groups (Cl, F, Br, and CF_3) (**3ha–3ka**, and **3na**) at the *para*- or *meta*-positions were all well-tolerated and gave satisfactory results. However, substrates with sterically demanding alkynes gave diminished enantioselectivity (**3da**, 91% yield, 30% ee). The arene rings having the –CN or –NO_2 groups did not give the desired products. Substrates with thiophene or pyridine moieties worked well under these reaction conditions, providing the desired products **3oa** and **3pa** with moderate yield and good ee. Internal alkynes, diphenylacetylene, also gave moderate yield and ee (**3qa**, 69% yield, 61% ee). It was also demonstrated that aliphatic alkynes were functional and gave slightly decreased yields and good ee (**3ra–3ta**). Phosphinate reacted with a terminal alkyne prior to a disubstituted alkyne to give the enyne **3ta**. As shown in Table 2, it was found that this transformation tolerated a variety of alkynes, including heteroaromatic alkynes, aliphatic alkynes and internal alkynes.

Encouraged by the results obtained from alkynes, we further attempted to expand this catalytic system with various H-phosphinates to obtain alkenylphosphonates (Table 3). Substrates with methyl ester or propyl ester were also subjected to hydrophosphorylation and the corresponding alkenylphosphonates (**3ab** and **3ac**) were formed in moderate yields and enantioselectivities. A substrate with isopropyl ester gave decreased yield (**3ad**), only 32% yield, and slightly decreased enantioselectivity, 73% ee. The phenylphosphinate with Me on the arene ring only gave the product **3ae** in 47% yield and 37% ee at a higher temperature. Compound **3fb** with the *t*-Bu group was obtained in decreased yield compared to **3fa**. When secondary phosphine oxides were tested under similar reaction conditions, the hydrophosphorylation product **3af** was formed with 28% yield in 54% ee.

Table 3 Substrate scope of phenylphosphinates and phenyphosphine oxide[a]

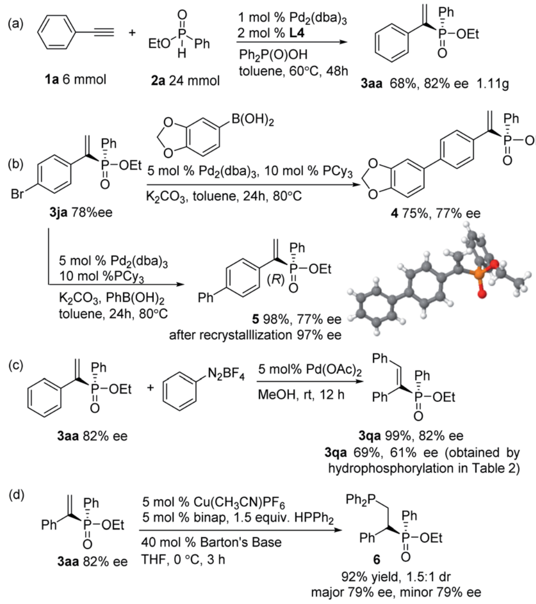


3aa 70% yield, 83% ee; **3ab** 78% yield, 71% ee; **3ac** 70% yield, 80% ee; **3ad** 32% yield, 73% ee; **3ae**[b] 47% yield, 33% ee; **3fb** 51% yield, 71% ee; **3af** 28% yield, 54% ee

[a] Conditions: 1 mol% $Pd_2(dba)_3$, 2 mol% ligand **L4**, and 4 mol% $Ph_2P(O)OH$ in 1 mL toluene were stirred for 10 min in an argon atmosphere. 0.25 mmol alkynes **1a** and **1f** and 1.0 mmol phenylphosphinate **2a–2d** or phenyphosphine oxide **2e** were added, and the mixture was stirred at 60 °C for 20 h. Isolated yields. Determined by HPLC analysis. [b] 80 °C was used instead.

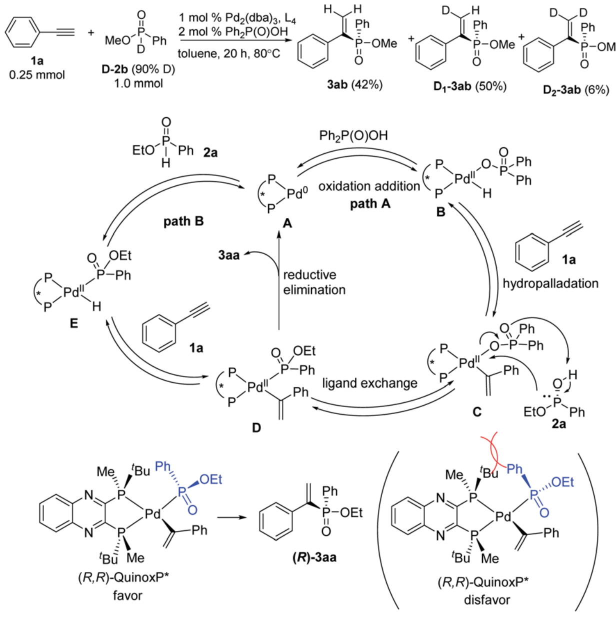
To evaluate the synthetic potential of the current catalytic system, a gram-scale reaction between phenylacetylene and ethyl phenylphosphinate was performed, and the product **3aa** was furnished in 68% yield and 82% ee (Scheme 2a). Further synthetic transformations of the hydrophosphorylation products were also illustrated. Compounds **4** and **5** were prepared through a Suzuki–Miyaura coupling without loss of enantiopurity (Scheme 2b). The absolute configuration of the phosphinate product **3ja** was confirmed as *R*-configuration by X-ray crystallography of its derivative **5**.[18] The Heck-type reaction of aryl diazonium salts with alkenylphosphinate **3aa** led to *cis*-stilbenes **3qa** with excellent stereoselectivity without loss of chirality (Scheme 2c, 99% yield and 82% ee) which could make up for the moderate yield and ee of **3qa** obtained by direct hydrophosphorylation of diphenylacetylene (Table 2). To construct 1,2-biphosphine derivative, the addition of $HPPh_2$ to product **3aa** was achieved by copper(I)-catalyzed conjugate hydrophosphination to give biphosphine derivative **6** in 92% yield and 1.5 : 1 dr without loss of enantiopurity (Scheme 2d, 79% ee for both diastereomers).[19]

A deuterium-labelling experiment has been conducted by using D-P(O)(OMe)Ph as the starting material,[20] giving the



Scheme 2 Gram-scale version of the reaction and synthetic transformation of the hydrophosphorylation products.

product **3ab** (42%), **D_1-3ab** (50%) and a small amount of **D_2-3ab** (6%) in which two deuteriums were incorporated at the terminal alkene carbon atoms (Scheme 3). This result suggested that the oxidative addition, hydropalladation, and ligand exchange are reversible. On the basis of the deuterium labeling experiment and previous report,[14] we proposed a mechanistic pathway for this catalysis. Chiral palladium complex **A** is formed from $Pd_2(dba)_3$ and (*R*,*R*)-QuinoxP*. It is proposed that oxidative addition of the O–H bond of $Ph_2P(O)OH$ to palladium triggers the reaction to produce the internal palladium intermediate **B**. The hydropalladation of alkynes takes place first to give an internal alkenylpalladium **C** by Markovnikov addition. Subsequent ligand exchange of this complex **C** with phosphinate **2a** gives the internal phosphorylpalladium intermediate **D**. A reduced yield was observed in the absence of $Ph_2P(O)OH$. Thus, an alternative pathway is also possible in which the intermediate **E** is generated directly by the oxidative addition of the P–H bond of **2a** to palladium. Then hydropalladation of alkynes takes place to give the same intermediate **D**. Finally, reductive elimination gives the desired alkenylphosphinate product **3aa** and regenerates the active chiral palladium complex **A**.



Scheme 3 Deuterium labeling experiment, the proposed mechanism and the stereochemical pathway.

Conclusions

In summary, we have developed an efficient method to synthesize alkenylphosphinates with *P*-chirality through the first Pd-catalyzed enantioselective hydrophosphorylation of alkynes, showing that this hydrophosphorylation reaction is a powerful and practical approach for the preparation of these valuable *P*-stereogenic organophosphorus compounds. Studies on further application of these chiral organophosphorus compounds are underway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully thank the National Natural Science Foundation of China (NSFC 21971102) and Guangdong Innovative Program (2019BT02Y335) for financial support. Z. Yang acknowledges a short-term student training partially supported by AIST.

Notes and references

1 (*a*) G. P. Horsman and D. L. Zechel, *Chem. Rev.*, 2017, **117**, 5704; (*b*) H. K. Zbigniew, H. K. Marcin, D. Jozef and V. S. Chris, *Curr. Org. Chem.*, 2011, **15**, 2015; (*c*) A. Mucha, P. Kafarski and Ł. Berlicki, *J. Med. Chem.*, 2011, **54**, 5955.

2 (*a*) M. Benaglia and S. Rossi, *Org. Biomol. Chem.*, 2010, **8**, 3824; (*b*) S. J. Connon, *Angew. Chem., Int. Ed.*, 2006, **45**, 3909; (*c*) J. Seayad and B. List, *Org. Biomol. Chem.*, 2005, **3**, 719; (*d*) J. L. Methot and W. R. Roush, *Adv. Synth. Catal.*, 2004, **346**, 1035; (*e*) H. Ni, W.-L. Chan and Y. Lu, *Chem. Rev.*, 2018, **118**, 9344; (*f*) Y. Wei and M. Shi, *Acc. Chem. Res.*, 2010, **43**, 1005.

3 (*a*) G. Xu, C. H. Senanayake and W. Tang, *Acc. Chem. Res.*, 2019, **52**, 1101; (*b*) P. W. N. M. v. Leeuwen, P. C. J. Kamer, C. Claver, O. Pàmies and M. Diéguez, *Chem. Rev.*, 2011, **111**, 2077; (*c*) X. Cui and K. Burgess, *Chem. Rev.*, 2005, **105**, 3272; (*d*) P. J. Guiry and C. P. Saunders, *Adv. Synth. Catal.*, 2004, **346**, 497; (*e*) W. Tang and X. Zhang, *Chem. Rev.*, 2003, **103**, 3029; (*f*) Y.-M. He, Y. Feng and Q.-H. Fan, *Acc.*

This journal is © The Royal Society of Chemistry 2020

Chem. Res., 2014, **47**, 2894; (*g*) M. Dutartre, J. Bayardon and S. Juge, *Chem. Soc. Rev.*, 2016, **45**, 5771.

4 (*a*) J. Grembecka, A. Mucha, T. Cierpicki and P. Kafarski, *J. Med. Chem.*, 2003, **46**, 2641; (*b*) H.-J. Cristau, J. Monbrun, J. Schleiss, D. Virieux and J.-L. Pirat, *Tetrahedron Lett.*, 2005, **46**, 3741.

5 (*a*) K. Nikitin, K. V. Rajendran, H. Müller-Bunz and D. G. Gilheany, *Angew. Chem., Int. Ed.*, 2014, **53**, 1906; (*b*) O. Berger and J.-L. Montchamp, *Angew. Chem., Int. Ed.*, 2013, **52**, 11377; (*c*) E. Bergin, C. T. O'Connor, S. B. Robinson, E. M. McGarrigle, C. P. O'Mahony and D. G. Gilheany, *J. Am. Chem. Soc.*, 2007, **129**, 9566; (*d*) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman and D. J. Weinkauff, *J. Am. Chem. Soc.*, 1977, **99**, 5946; (*e*) O. Korpiun, R. A. Lewis, J. Chickos and K. Mislow, *J. Am. Chem. Soc.*, 1968, **90**, 4842; (*f*) Z. S. Han, H. Wu, Y. Xu, Y. Zhang, B. Qu, Z. Li, D. R. Caldwell, K. R. Fandrick, L. Zhang, F. Roschangar, J. J. Song and C. H. Senanayake, *Org. Lett.*, 2017, **19**, 1796; (*g*) Z. S. Han, L. Zhang, Y. Xu, J. D. Sieber, M. A. Marsini, Z. Li, J. T. Reeves, K. R. Fandrick, N. D. Patel, J.-N. Desrosiers, B. Qu, A. Chen, D. M. Rudzinski, L. P. Samankumara, S. Ma, N. Grinberg, F. Roschangar, N. K. Yee, G. Wang, J. J. Song and C. H. Senanayake, *Angew. Chem., Int. Ed.*, 2015, **54**, 5474; (*h*) Z. S. Han, N. Goyal, M. A. Herbage, J. D. Sieber, B. Qu, Y. Xu, Z. Li, J. T. Reeves, J.-N. Desrosiers, S. Ma, N. Grinberg, H. Lee, H. P. R. Mangunuru, Y. Zhang, D. Krishnamurthy, B. Z. Lu, J. J. Song, G. Wang and C. H. Senanayake, *J. Am. Chem. Soc.*, 2013, **135**, 2474; (*i*) T. León, A. Riera and X. Verdaguer, *J. Am. Chem. Soc.*, 2011, **133**, 5740; (*j*) E. J. Corey, Z. Chen and G. J. Tanoury, *J. Am. Chem. Soc.*, 1993, **115**, 11000; (*k*) S. Juge and J. P. Genet, *Tetrahedron Lett.*, 1989, **30**, 2783.

6 (*a*) G. Nishida, K. Noguchi, M. Hirano and K. Tanaka, *Angew. Chem., Int. Ed.*, 2008, **47**, 3410; (*b*) Y. Zheng, L. Guo and W. Zi, *Org. Lett.*, 2018, **20**, 7039; (*c*) Y. Zhang, F. Zhang, L. Chen, J. Xu, X. Liu and X. Feng, *ACS Catal.*, 2019, **9**, 4834.

7 Z. Wang and T. Hayashi, *Angew. Chem., Int. Ed.*, 2018, **57**, 1702.

8 (*a*) K. M.-H. Lim and T. Hayashi, *J. Am. Chem. Soc.*, 2017, **139**, 8122; (*b*) Z. Pakulski and K. M. Pietrusiewicz, *Tetrahedron: Asymmetry*, 2004, **15**, 41; (*c*) F. de Azambuja, R. C. Carmona, T. H. D. Chorro, G. Heerdt and C. R. D. Correia, *Chem. - Eur. J.*, 2016, **22**, 11205.

9 (*a*) Z.-Q. Lin, W.-Z. Wang, S.-B. Yan and W.-L. Duan, *Angew. Chem., Int. Ed.*, 2015, **54**, 6265; (*b*) L. Liu, A.-A. Zhang, Y. Wang, F. Zhang, Z. Zuo, W.-X. Zhao, C.-L. Feng and W. Ma, *Org. Lett.*, 2015, **17**, 2046; (*c*) G. Xu, M. Li, S. Wang and W. Tang, *Org. Chem. Front.*, 2015, **2**, 1342; (*d*) Z.-J. Du, J. Guan, G.-J. Wu, P. Xu, L.-X. Gao and F.-S. Han, *J. Am. Chem. Soc.*, 2015, **137**, 632; (*e*) Y.-H. Chen, X.-L. Qin, J. Guan, Z.-J. Du and F.-S. Han, *Tetrahedron: Asymmetry*, 2017, **28**, 522; (*f*) Y. Lin, W.-Y. Ma, Q.-Y. Sun, Y.-M. Cui and L.-W. Xu, *Synlett*, 2017, **28**, 1432; (*g*) Z. Li, Z.-Q. Lin, C.-G. Yan and W.-L. Duan, *Organometallics*, 2019, **38**, 3916.

10 (*a*) Y. Sun and N. Cramer, *Angew. Chem., Int. Ed.*, 2017, **56**, 364; (*b*) Y. Sun and N. Cramer, *Chem. Sci.*, 2018, **9**, 2981; (*c*) Y.-S. Jang, L. Wozniak, J. Pedroni and N. Cramer, *Angew. Chem., Int. Ed.*, 2018, **57**, 12901; (*d*) Y.-S. Jang, M. Dieckmann and N. Cramer, *Angew. Chem., Int. Ed.*, 2017, **56**, 15088.

11 Q. Dai, W. Li, Z. Li and J. Zhang, *J. Am. Chem. Soc.*, 2019, **141**, 20556.

12 J. S. Harvey, S. J. Malcolmson, K. S. Dunne, S. J. Meek, A. L. Thompson, R. R. Schrock, A. H. Hoveyda and V. Gouverneur, *Angew. Chem., Int. Ed.*, 2009, **48**, 762.

13 B. M. Trost, S. M. Spohr, A. B. Rolka and C. A. Kalnmals, *J. Am. Chem. Soc.*, 2019, **141**, 14098.

14 (*a*) L.-B. Han and M. Tanaka, *J. Am. Chem. Soc.*, 1996, **118**, 1571; (*b*) L. B. Han, C. Q. Zhao, S. Y. Onozawa, M. Goto and M. Tanaka, *J. Am. Chem. Soc.*, 2002, **124**, 3842; (*c*) T. Chen, C.-Q. Zhao and L.-B. Han, *J. Am. Chem. Soc.*, 2018, **140**, 3139.

15 B. Join, D. Mimeau, O. Delacroix and A.-C. Gaumont, *Chem. Commun.*, 2006, 3249.

16 S.-Z. Nie, R. T. Davison and V. M. Dong, *J. Am. Chem. Soc.*, 2018, **140**, 16450.

17 (*a*) R. Beaud, R. J. Phipps and M. J. Gaunt, *J. Am. Chem. Soc.*, 2016, **138**, 13183; (*b*) X.-T. Liu, Y.-Q. Zhang, X.-Y. Han, S.-P. Sun and Q.-W. Zhang, *J. Am. Chem. Soc.*, 2019, **141**, 16584.

18 CCDC 1977604 [for **5**] contain the supplementary crystallographic data for this paper.

19 W.-J. Yue, J.-Z. Xiao, S. Zhang and L. Yin, *Angew. Chem., Int. Ed.*, 2020, **59**, 2.

20 C. Li, Q. Wang, J.-Q. Zhang, J. Ye, J. Xie, Q. Xu and L.-B. Han, *Green Chem.*, 2019, **21**, 2916.