Chemical Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Sci.*, 2019, **10**, 3649

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

Received 26th November 2018
Accepted 3rd February 2019

DOI: 10.1039/c8sc05261a

rsc.li/chemical-science

Tandem Peterson olefination and chemoselective asymmetric hydrogenation of β-hydroxy silanes†

Suppachai Krajangsri,‡[a] Haibo Wu, ‡[a] Jianguo Liu,‡[a] Wangchuk Rabten,[a] Thishana Singh [b] and Pher G. Andersson *[ab]

Here, we report the first Ir–N,P complex catalyzed tandem Peterson olefination and asymmetric hydrogenation of β-hydroxy silanes. This reaction resulted in the formation of chiral alkanes in high isolated yields (up to 99%) and excellent enantioselectivity (up to 99% ee) under mild conditions. Modification of the reaction conditions provides a choice to transform either an olefin or the β-hydroxy silane in a chemoselective manner. Additionally, based on this method, an expedient enantioselective synthesis of (*S*)-(+)-α-curcumene, from a simple ketone, was accomplished in two steps with 75% overall yield and 95% ee.

Introduction

The chiral benzylic hydrocarbon motif is widespread in various functional molecules and bioactive natural products.[1] Examples of such molecules include the anaesthetic propofol analog HSK3486,[2] the bisabolanes sesquiterpenes (*S*)-(+)-curcumene and (*S*)-(+)-ar-turmerone with antibacterial activity,[3] (+)-helianane with antifungal and cytotoxic activities[4] and ileabethoxazole with strongly antimycobacterial activity[5] (Fig. 1a). Notably, the induction of the benzylic chiral center is the crucial but challenging step in the synthesis of these compounds and has attracted considerable attention.[6]

Asymmetric hydrogenation has, over the past decades, been successfully developed to achieve excellent enantioselectivity for a wide range of substrates.[7] The reduction of olefins usually involves iridium, ruthenium, or rhodium complexes.[8] Iridium catalysts have the outstanding advantage of not requiring a chelating functional group adjacent to the C=C bond to achieve high reaction activity and selectivity. In addition to well-known Ir, Rh and Ru catalyst systems, cobalt, iron and nickel catalysts recently have recently proved to be an effective alternative method for asymmetric hydrogenation.[9] Furthermore, chemoselectivity and regioselectivity are still challenging to attain and there are only a few reported examples highlighting this feature.[10]

Asymmetric hydrogenation of 1,1-disubstituted olefins was expected to be a direct route to access the benzylic chiral center, however, it is quite challenging to achieve excellent enantioselectivity[11] since it is much more difficult to distinguish the two prochiral faces of the terminal olefin. Utilizing directing groups, Zhou's group[12a,b] and Zhang's group[12c] successfully attained asymmetric hydrogenation of 1,1-disubstituted olefins with high enantioselectivity (Fig. 1b). The use of novel iridium

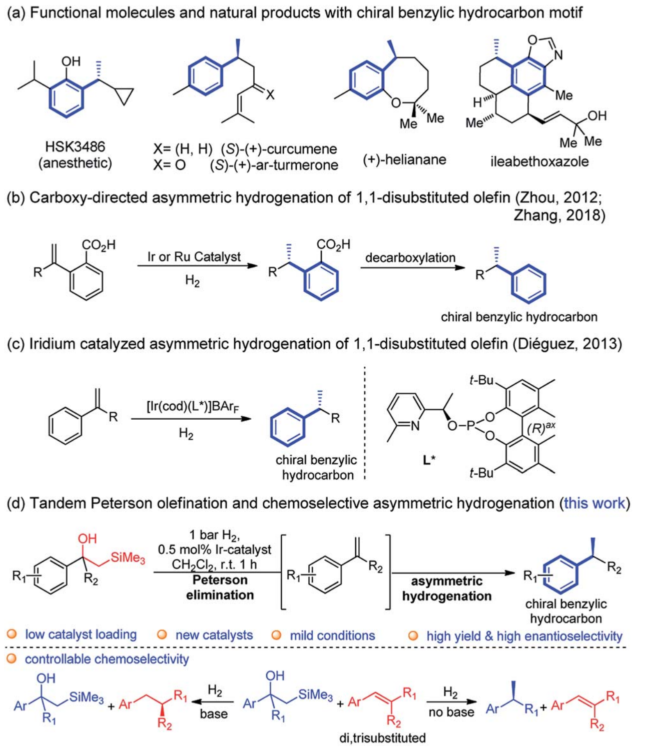


Fig. 1 Asymmetric hydrogenation to construct chiral benzylic hydrocarbon motif.

---

[a] *Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, 106 91, Stockholm, Sweden. E-mail: pher.andersson@su.se*

[b] *School of Chemistry and Physics, University of Kwazulu-Natal, Private Bag X54001, Durban, 4000, South Africa*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8sc05261a

‡ Suppachai Krajangsri, Haibo Wu and Jianguo Liu contributed equally.

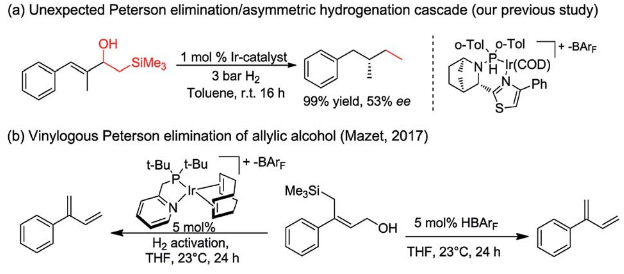


Fig. 2 Peterson elimination and asymmetric hydrogenation.

phosphite–pyridine catalysts, by the Diéguez's group[12d] resulted in highly selective asymmetric hydrogenation of a wide range of terminal olefins (Fig. 1c). We recently achieved significant improvement in the development of Ir–N,P-complexes for the asymmetric hydrogenation of di-, tri- and tetrasubstituted olefins. Among these, substrates with the silane group have raised much interest.[10e,13] In a previous study that we conducted on the asymmetric hydrogenation of secondary allylic alcohols, a substrate containing the β-hydroxy silane moiety was evaluated (Fig. 2a).[14] Instead of attaining the mono-hydrogenated product of trisubstituted olefin, the fully hydrogenated alkane was observed as the only product. In fact, a tandem reaction of Peterson elimination and asymmetric hydrogenation occurred due to the acidic medium[15] created by activation of the iridium catalyst. Recently, Mazet and co-workers reported a vinylogous Peterson elimination of allylic alcohols catalyzed by an Ir–N,P complex, where hydrogen gas was involved in the activation of the catalyst to generate the iridium hydride species (Fig. 2b).[16] The β-hydroxy silane compounds are well-known as important intermediates for olefination,[17] however their use as substrates for asymmetric hydrogenation have never been reported. Herein, we describe the first iridium catalyzed tandem Peterson elimination/olefination and asymmetric hydrogenation of β-hydroxy silanes to provide efficient access to the chiral benzylic hydrocarbon motif. Under different conditions, controllable chemoselectivity between β-hydroxy silanes and other olefins could be obtained (Fig. 1d).

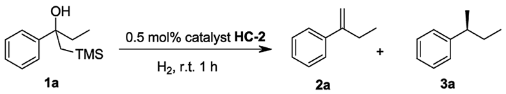
Results and discussion

Our initial investigation began with the cascade Peterson elimination and asymmetric hydrogenation of β-hydroxy silane **1** to optimize the reaction conditions (Table 1). It was found that CH_2Cl_2 was the best solvent for this reaction, giving high conversion within a short reaction time and excellent ee. Other solvents retarded the hydrogenation and resulted in an incomplete reaction that contained olefin **2a** in the product mixture (entries 2–5). Regarding the effect of hydrogen pressure, it was found that increased H_2 pressure lowered the enantioselectivity (entries 6–8). Hence, it was established that the ideal conditions for this reaction was 1 bar hydrogen with CH_2Cl_2 as the solvent.

Initially, the new iridium phosphite–oxazoline complex **HC-2** was found to be an efficient catalyst for the model reaction. To further evaluate the potential for steric and electronic tuning, the substituent on the oxazoline ring was changed from furan (**HC-1,2,3,4,5**) to thiophen (**HC-6,7,8**) and the heterocycle was attached to the ligand at different positions and substituents were also varied (Table 2). Variation of the heteroaromatic ring did not significantly affect the reactivity of β-hydroxy silane substrate, with all catalysts giving full conversion to the hydrogenated product in excellent yield. Formation of the isomerized, trisubstituted olefin was not observed in any of the reactions. An improvement in enantioselectivity was observed for catalyst **HC-7** (97% ee) and catalyst **HC-3** (98% ee).

With the optimized reaction conditions established, we prepared and tested several different substrates to evaluate the scope of the reaction (Table 3). Substrates having aliphatic substituents such as ethyl, *n*-butyl, *i*-propyl, cyclohexyl, and *t*-butyl (**3a–3f**) provided the desired product in excellent yield and high enantioselectivity of up to 99% ee. The effect of varying the substituents on the phenyl ring was also investigated. Electron-withdrawing groups as well as electron-donating groups at the

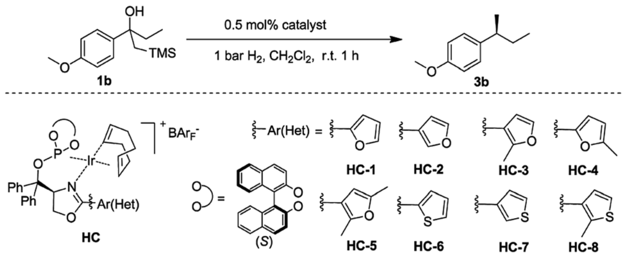
Table 1 Optimization of asymmetric hydrogenation[a]



Entry	Solvent	Pressure (bar)	**2a** (yield[b]/%)	**3a** (yield[b]/%)	**3a** (ee[c]/%)
1	CH_2Cl_2	1	—	>99	95
2	Benzene	1	24	76	91
3	$PhCF_3$	1	25	75	93
4	Toluene	1	62	38	94
5	THF	1	>99	—	—
6	CH_2Cl_2	10	—	>99	90
7	CH_2Cl_2	20	—	>99	83
8	CH_2Cl_2	50	—	>99	73

[a] Reaction conditions: 0.05 mmol substrate, 0.5 mol% catalyst, 0.5 mL CH_2Cl_2. [b] Determined by ^1H NMR spectroscopy of the crude product. [c] Determined by chiral GC analyses.

Table 2 Evaluation of new Ir–N,P catalysts[a]



Entry	Ir Cat.	Conv.[b] (%)	ee[c] (%)	Entry	Ir Cat.	Conv.[b] (%)	ee[c] (%)
1	**HC-1**	>99	95	5	**HC-5**	>99	96
2	**HC-2**	>99	97	6	**HC-6**	>99	96
3	**HC-3**	>99	98	7	**HC-7**	>99	97
4	**HC-4**	>99	95	8	**HC-8**	>99	96

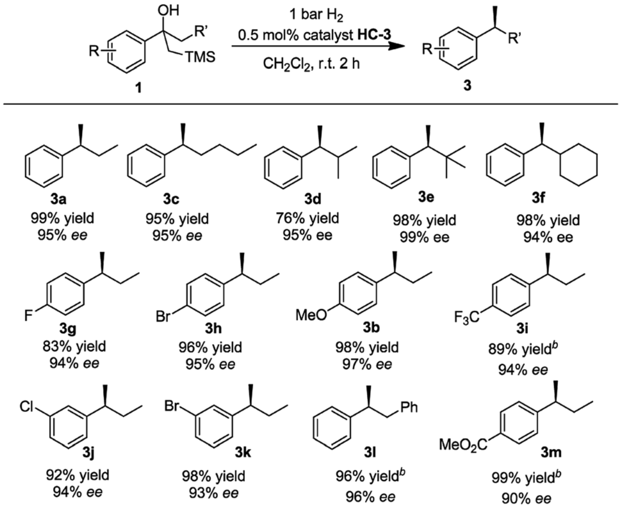
[a] Reaction conditions: 0.05 mmol substrate, 0.5 mol% catalyst, 0.5 mL CH_2Cl_2. [b] Determined by ^1H NMR spectroscopy of the crude product. [c] Determined by chiral GC analyses.

para-position (**3g–3i**) did not affect the efficiency of the reaction. Excellent isolated yields of up to 99% and ees up to 95% were achieved. Electron-withdrawing groups at the *meta*-position (**3j**, **3k**) also gave very good results. Substrate **1l**, containing the benzyl group, gave the desired product in excellent yield of 96% and high ee of 97%. No trace of the isomerized trisubstituted olefin was observed in the reaction. Substrate **1m**, bearing the ester functional group was converted to the desired product in excellent yield of 99% with good ee of 90%.

Given the very mild reaction conditions and the high reaction rates for the Peterson elimination–hydrogenation, we were compelled to investigate the degree of chemoselectivity in the asymmetric hydrogenation of β-hydroxy silanes compared to some common olefins (Scheme 1). In this study, β-hydroxy silanes and different olefins were mixed and subjected to the standard reaction conditions. We observed that **1a** yielded the completely hydrogenated product in a short reaction time with excellent ee while the olefins remained unaffected. The *trans* disubstituted olefins **4** and **5** were not hydrogenated whereas **1a** was fully converted to the desired product (Scheme 1a). Trisubstituted olefins **6** and **7** were also tested in the hydrogenation, no hydrogenation of the olefins was detected, while full conversion of β-hydroxy silane **1e** was observed (Scheme 1b).

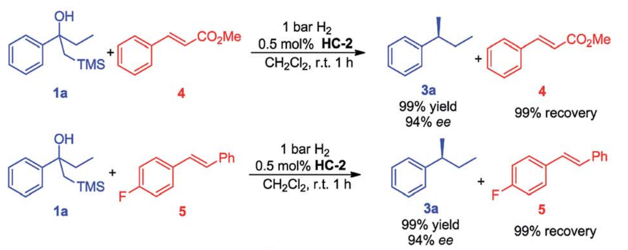
We also investigated the possibility of selective hydrogenation of an olefin in the presence of a β-hydroxy silane. Our rational was that, since the Peterson olefination requires acidic condition, and then a less acidic iridium catalyst would hydrogenate the olefin without catalyzing the Peterson reaction. When a mixture of *trans*-α-methylstilbene **6** or *trans*-β-methylcinnamate **7** and β-hydroxy silane **1e** was subjected to a higher hydrogen pressure using catalyst IC in the presence of K_3PO_4, as expected, these reactions gave a complete change in chemoselectivity and resulted in a selective hydrogenation of the olefin, leaving the β-hydroxy silane intact (Scheme 1c). The basic additive (K_3PO_4) has proved to be efficient in preventing the decomposition of the acid-sensitive starting material or hydrogenated product under the acidic environment, which was

Table 3 Substrate scope[a]

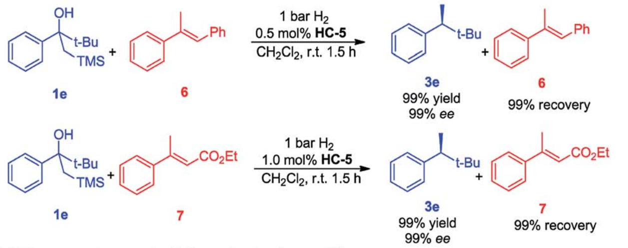


[a] Reaction conditions: 0.40 mmol substrate, 0.5 mol% catalyst, 4 mL CH_2Cl_2. Yield refers to isolated yield. ee was determined by chiral SFC or GC analyses. [b] Reaction conditions: 2 bar H_2, 3 h, 1 mol% catalyst.

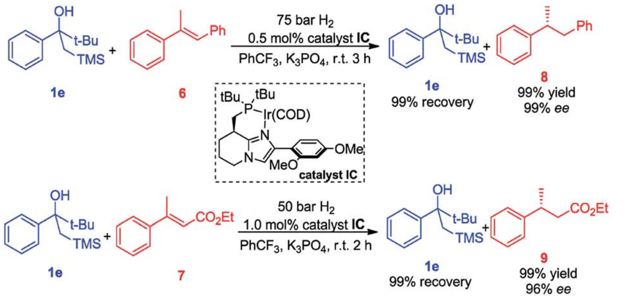
(a) Competition experiment between β-hydroxy silane and disubstituted olefins



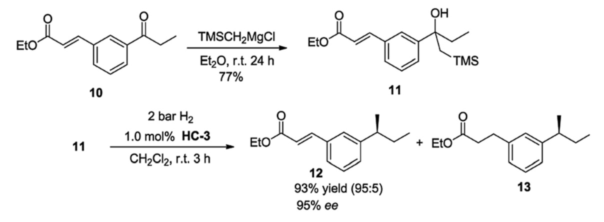
(b) Competition experiment between β-hydroxy silane and trisubstituted olefins



(c) Reverse chemoselectivity under basic condition



Scheme 1 Chemoselective asymmetric hydrogenation.



Scheme 2 Intramolecular chemoselective functionalization.

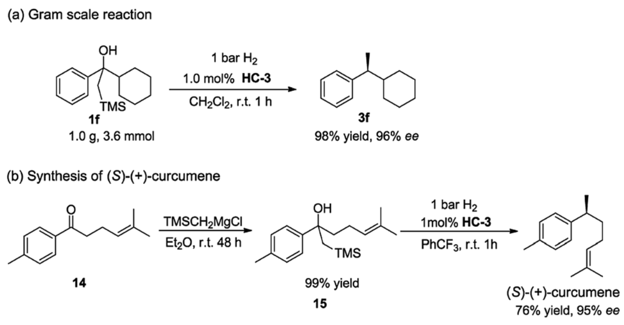
generated in the iridium catalyzed asymmetric hydrogenation. These results demonstrate that a highly chemoselective transformation of either an olefin or a β-hydroxy silane is possible by selecting the appropriate reaction conditions.

Based on the completely opposite chemoselectivity that was obtained upon addition of base, we assumed that the *in situ* generated iridium dihydride catalyst acted as a Brønsted acid in the elimination step.[15d] Alternatively, the iridium dihydride intermediate might be directly involved in promoting the Peterson elimination.[16] However, since Peterson elimination of β-hydroxy silane **1e** did not occur during the hydrogenation of olefins **6** and **7** under basic conditions (Scheme 1c), it is suggested that the iridium dihydride is not directly responsible for the elimination. In a control experiment it was found that the addition of a bulky, non-coordinating base such as DTBMP completely inhibited the elimination (see the ESI† for details).

The potential of the reaction was investigated by testing a substrate that contained both an olefin as well as an ester group (Scheme 2). The unsaturated keto ester **10** reacted selectively with $TMSCH_2MgCl$ to give **11** in 77% isolated yield. Using catalyst **HC-3**, under standard reaction conditions, substrate **21** underwent Peterson olefination/hydrogenation to give the desired product in a highly chemoselective manner with good ee (95%).

To further demonstrate the practical application of this methodology, a gram scale reaction was carried out. The reaction was conducted in CH_2Cl_2 with 1 bar H_2 at room temperature in the presence of 1.0 mol% catalyst **HC-3**, affording the desired product **3f** in high yield and excellent ee (Scheme 3a). When compared to the small scale reaction, it was noted that the yield was not affected and the enantioselectivity slightly increased.

The synthetic utility of this method was highlighted by the facile synthesis of bisabolane sesquiterpene (*S*)-(+)-curcumene (Scheme 3b). Despite its simple structure, the benzylmethyl chiral center poses a significant challenge in the asymmetric synthesis, and it has evolved as a popular test target for demonstrating the proficiency of new asymmetric processes.[18] The synthesis began with treatment of simple ketone **14** with Peterson reagent smoothly affording the β-hydroxy silane compound **15** in quantitative yield. Subsequent asymmetric hydrogenation of **15** directly furnished the target natural product (*S*)-(+)-curcumene with 76% yield and 95% ee. This two-step, highly enantioselective synthesis represents one of the most efficient ways to access (*S*)-(+)-curcumene.



Scheme 3 Scale-up preparation and synthesis application.

Conclusions

In summary, we have demonstrated an iridium catalyzed tandem Peterson olefination and asymmetric hydrogenation of β-hydroxy silanes under particularly mild conditions and low catalyst loading using novel Ir–N,P catalysts. The method we have developed provided efficient access to the chiral benzylic hydrocarbon motif. It was found that the reaction is highly chemoselective and that it could be tuned to selectively transform either an olefin or a β-hydroxy silane. By use of this methodology, we achieved the asymmetric syntheses of natural product (*S*)-(+)-curcumene in two steps with high yield. Further application of this strategy for the synthesis of more structurally related natural products is ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The Swedish Research Council (VR) and Stiftelsen Olle Engkvist Byggmästare supported this work. J. L. thanks the Guangzhou Elite Scholarship Council for the PhD fellowship.

Notes and references

1 For selected examples, see: (*a*) A. E. Wright, S. A. Pomponi, O. J. McConnell, S. Kohmoto and P. J. McCarthy, *J. Nat. Prod.*, 1987, **50**, 976; (*b*) H. Matsuda, T. Morikawa, K. Ninomiya and M. Yoshikawa, *Bioorg. Med. Chem.*, 2001, **9**, 909; (*c*) A. D. Rodríguez and C. Ramírez, *J. Nat. Prod.*, 2001, **64**, 100; (*d*) F. A. Macías, R. M. Varela, A. Torres, J. M. G. Molinillo and F. R. Fronczek, *Tetrahedron Lett.*, 1993, **34**, 1999; (*e*) V. Roussis, Z. Wu, W. Fenical, S. A. Strobel, G. D. Van Duyne and J. Clardy, *J. Org. Chem.*, 1990, **55**, 4916; (*f*) C. A. Harvis, M. T. Burch and W. Fenical, *Tetrahedron Lett.*, 1988, **29**, 4361; (*g*) S. A. Look, W. Fenical, R. S. Jacobs and J. Clardy, *Proc. Natl. Acad. Sci. U. S. A.*, 1986, **83**, 6238; (*h*) S.-e. Muto, M. Bando and K. Mori, *Eur. J. Org. Chem.*, 2004, **2004**, 1946; (*i*) S. P. Chavan and H. S. Khatod, *Tetrahedron: Asymmetry*, 2012, **23**, 1410.

2 (*a*) L. Qin, L. Ren, S. Wan, G. Liu, X. Luo, Z. Liu, F. Li, Y. Yu, J. Liu and Y. Wei, *J. Med. Chem.*, 2017, **60**, 3606; (*b*) Y. Wei,

G. Qiu, B. Lei, L. Qin, H. Chu, Y. Lu, G. Zhu, Q. Gao, Q. Huang, G. Qian, P. Liao, X. Luo, X. Zhang, C. Zhang, Y. Li, S. Zheng, Y. Yu, P. Tang, J. Ni, P. Yan, Y. Zhou, P. Li, X. Huang, A. Gong and J. Liu, *J. Med. Chem.*, 2017, **60**, 8580.

3 (*a*) V. K. Honwad and A. S. Rao, *Tetrahedron*, 1964, **20**, 2921; (*b*) V. K. Honwad and A. S. Rao, *Tetrahedron*, 1965, **21**, 2593; (*c*) F. J. McEnroe and W. Fenical, *Tetrahedron*, 1978, **34**, 1661; (*d*) D. Del Prete, E. Millán, F. Pollastro, G. Chianese, P. Luciano, J. A. Collado, E. Munoz, G. Appendino and O. Taglialatela-Scafati, *J. Nat. Prod.*, 2016, **79**, 267.

4 (*a*) B. Harrison and P. Crews, *J. Org. Chem.*, 1997, **62**, 2646; (*b*) M. J. Martín, F. Berrué, P. Amade, R. Fernández, A. Francesch, F. Reyes and C. Cuevas, *J. Nat. Prod.*, 2005, **68**, 1554; (*c*) J. C. Green, S. Jiménez-Alonso, E. R. Brown and T. R. R. Pettus, *Org. Lett.*, 2011, **13**, 5500.

5 (*a*) I. I. Rodríguez, A. D. Rodríguez, Y. Wang and S. G. Franzblau, *Tetrahedron Lett.*, 2006, **47**, 3229; (*b*) T. J. Heckrodt and J. Mulzer, *Top. Curr. Chem.*, 2005, **244**, 1; (*c*) T. W. Johnson and E. J. Corey, *J. Am. Chem. Soc.*, 2001, **123**, 4475.

6 For selected examples, see: (*a*) R. R. Cesati III, J. de Armas and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2004, **126**, 96; (*b*) A. Zhang and T. V. RajanBabu, *Org. Lett.*, 2004, **6**, 3159; (*c*) S. Nave, R. P. Sonawane, T. G. Elford and V. K. Aggarwal, *J. Am. Chem. Soc.*, 2010, **132**, 17096; (*d*) B. L. H. Taylor, E. C. Swift, J. D. Waetzig and E. R. Jarvo, *J. Am. Chem. Soc.*, 2011, **133**, 389; (*e*) A. Wilsily, Y. Nguyen and E. Fillion, *J. Am. Chem. Soc.*, 2009, **131**, 15606; (*f*) A. López-Pérez, J. Adrio and J. C. Carretero, *Org. Lett.*, 2009, **11**, 5514; (*g*) S. Drissi-Amraoui, M. S. T. Morin, C. Crévisy, O. Baslé, R. Marcia de Figueiredo, M. Mauduit and J.-M. Campagne, *Angew. Chem.*, 2015, **127**, 11996.

7 (*a*) W. S. Knowles, *Angew. Chem., Int. Ed.*, 2002, **41**, 1998; (*b*) R. Noyori, *Adv. Synth. Catal.*, 2003, **345**, 15; (*c*) A. Pfaltz and W. J. Drury, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 5723; (*d*) T. L. Church and P. G. Andersson, *Coord. Chem. Rev.*, 2008, **252**, 513.

8 For some recent reviews, see: (*a*) X. Cui and K. Burgess, *Chem. Rev.*, 2005, **105**, 3272; (*b*) S. J. Roseblade and A. Pfaltz, *Acc. Chem. Res.*, 2007, **40**, 1402; (*c*) J. J. Verendel, O. Pàmies, M. Diéguez and P. G. Andersson, *Chem. Rev.*, 2014, **114**, 2130; (*d*) C. Margarita and P. G. Andersson, *J. Am. Chem. Soc.*, 2017, **139**, 1346.

9 (*a*) M. R. Friedfeld, M. Shevlin, J. M. Hoyt, S. W. Krska, M. T. Tudge and P. J. Chirik, *Science*, 2013, **342**, 1076; (*b*) S. Monfette, Z. R. Turner, S. P. Semproni and P. J. Chirik, *J. Am. Chem. Soc.*, 2012, **134**, 4561; (*c*) M. R. Friedfeld, M. Shevlin, G. W. Margulieux, L.-C. Campeau and P. J. Chirik, *J. Am. Chem. Soc.*, 2016, **138**, 3314; (*d*) J. Chen, C. Chen, C. Ji and Z. Lu, *Org. Lett.*, 2016, **18**, 1594; (*e*) M. Shevlin, M. R. Friedfeld, H. Sheng, N. A. Pierson, J. M. Hoyt, L.-C. Campeau and P. J. Chirik, *J. Am. Chem. Soc.*, 2016, **138**, 3562; (*f*) T. Hibino, K. Makino, T. Sugiyama and Y. Hamada, *ChemCatChem*, 2009, **1**, 237.

10 (*a*) D. Valentine, K. K. Johnson, W. Priester, R. C. Sun, K. Toth and G. Saucy, *J. Org. Chem.*, 1980, **45**, 3698; (*b*) H. Takaya, T. Ohta, N. Sayo, H. Kumobayashi, S. Akutagawa, S. Inoue, I. Kasahara and R. Noyori, *J. Am. Chem. Soc.*, 1987, **109**, 15967; (*c*) L. Panella, B. L. Feringa, J. G. de Vries and A. J. Minnaard, *Org. Lett.*, 2005, **7**, 4177; (*d*) B. K. Peters, J. Liu, C. Margarita, W. Rabten, S. Kerdphon, A. Orebom, T. Morsch and P. G. Andersson, *J. Am. Chem. Soc.*, 2016, **138**, 11930; (*e*) J. Liu, S. Krajangsri, T. Singh, G. De Seriis, N. Chumnanvej, H. Wu and P. G. Andersson, *J. Am. Chem. Soc.*, 2017, **139**, 14470.

11 (*a*) O. Pàmies, P. G. Andersson and M. Diéguez, *Chem.–Eur. J.*, 2010, **16**, 14232; (*b*) S. McIntyre, E. Hörmann, F. Menges, S. P. Smidt and A. Pfaltz, *Adv. Synth. Catal.*, 2005, **347**, 282; (*c*) D. H. Woodmansee and A. Pfaltz, *Chem. Commun.*, 2011, **47**, 7912; (*d*) J. Mazuela, P.-O. Norrby, P. G. Andersson, O. Pàmies and M. Diéguez, *J. Am. Chem. Soc.*, 2011, **133**, 13634; (*e*) J. Mazuela, J. J. Verendel, M. Coll, B. Schäffner, A. Börner, P. G. Andersson, O. Pàmies and M. Diéguez, *J. Am. Chem. Soc.*, 2009, **131**, 12344; (*f*) M. C. Perry, X. Cui, M. T. Powell, D.-R. Hou, J. H. Reibenspies and K. Burgess, *J. Am. Chem. Soc.*, 2003, **125**, 113.

12 (*a*) S. Song, S.-F. Zhu, Y.-B. Yu and Q.-L. Zhou, *Angew. Chem., Int. Ed.*, 2013, **52**, 1556; (*b*) S. Yang, S.-F. Zhu, N. Guo, S. Song and Q.-L. Zhou, *Org. Biomol. Chem.*, 2014, **12**, 2049; (*c*) S. Wen, C. Chen, S. Du, Z. Zhang, Y. Huang, Z. Han, X.-Q. Dong and X. Zhang, *Org. Lett.*, 2017, **19**, 6474; (*d*) J. Mazuela, O. Pàmies and M. Diéguez, *Adv. Synth. Catal.*, 2013, **355**, 2569.

13 W. Rabten, C. Margarita, L. Eriksson and P. G. Andersson, *Chem.–Eur. J.*, 2018, **24**, 1681.

14 J. Liu, S. Krajangsri, J. Yang, J.-Q. Li and P. G. Andersson, *Nat. Catal.*, 2018, **1**, 438.

15 (*a*) R. H. Crabtree, *Science*, 1998, **282**, 2000; (*b*) P. Brandt, C. Hedberg and P. G. Andersson, *Chem.–Eur. J.*, 2003, **9**, 339; (*c*) G. S. McGrady and G. Guilera, *Chem. Soc. Rev.*, 2003, **32**, 383; (*d*) Y. Zhu, Y. Fan and K. Burgess, *J. Am. Chem. Soc.*, 2010, **132**, 6249.

16 H. Li, D. Fiorito and C. Mazet, *ACS Catal.*, 2017, **7**, 1554.

17 (*a*) D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780; (*b*) L. F. v. Staden, D. Gravestock and D. J. Ager, *Chem. Soc. Rev.*, 2002, **31**, 195; (*c*) T. A. Hamlin, C. B. Kelly, R. M. Cywar and N. E. Leadbeater, *J. Org. Chem.*, 2014, **79**, 1145.

18 For selected recent examples, see: (*a*) T. Nishimura, Y. Yasuhara, T. Sawano and T. Hayashi, *J. Am. Chem. Soc.*, 2010, **132**, 7872; (*b*) V. K. Aggarwal, L. T. Ball, S. Carobene, R. L. Connelly, M. J. Hesse, B. M. Partridge, P. Roth, S. P. Thomas and M. P. Webster, *Chem. Commun.*, 2012, **48**, 9230; (*c*) I. Ibrahem, G. Ma, S. Afewerki and A. Córdova, *Angew. Chem., Int. Ed.*, 2013, **52**, 878; (*d*) K. Spielmann, R. M. de Figueiredo and J.-M. Campagne, *J. Org. Chem.*, 2017, **82**, 4737.