

A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Spiro Bicyclic Bisborane Catalysts for Metal-Free Chemoselective and Enantioselective Hydrogenation of Quinolines

Authors: Xiang Li, Jun-Jie Tian, Ning Liu, Xian-Shuang Tu, Ning-Ning Zeng, and Xiao-Chen Wang

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201900907
Angew. Chem. 10.1002/ange.201900907

Link to VoR: <http://dx.doi.org/10.1002/anie.201900907>
<http://dx.doi.org/10.1002/ange.201900907>

COMMUNICATION

Spiro Bicyclic Bisborane Catalysts for Metal-Free Chemoselective and Enantioselective Hydrogenation of Quinolines

Xiang Li,[#] Jun-Jie Tian,[#] Ning Liu, Xian-Shuang Tu, Ning-Ning Zeng, and Xiao-Chen Wang*

Dedicated to the 100th anniversary of Nankai University

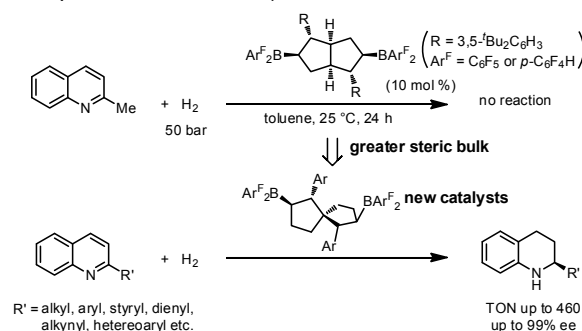
Abstract: We have prepared a new series of spiro bicyclic bisborane catalysts by means of hydroboration reactions of C_2 -symmetric spiro bicyclic dienes with $HB(C_6F_5)_2$ and $HB(p-C_6F_4H)_2$. When used for hydrogenation of quinolines, these catalysts gave excellent yields and enantiomeric excesses and showed turnover numbers up to 460. The most attractive feature of these metal-free hydrogenation reactions was the broad functional group tolerance, making this method complementary to existing methods for quinoline hydrogenation.

Because of the prevalence of chiral tetrahydroquinoline scaffolds in natural products and drugs,^[1] the development of methods for enantioselective hydrogenation of quinolines is an important area of research. Methods that use transition-metal catalysts with chiral ligands have been extensively investigated,^[2] and the good performing catalysts are generally iridium- and ruthenium-centered.^[3–5] However, the need to use precious metals, especially when the turnover numbers are not high, limits the attractiveness of these methods, for both economic and environmental reasons. More important, because other unsaturated functional groups, such as olefins, alkynes, and electron-rich heteroarenes, are reactive under metal-catalyzed hydrogenation conditions, it is very difficult to preserve these groups during hydrogenation of the quinoline core. Indeed, most of the existing methods have been used only on substrates that have relatively inert substituents and thus lack handles for further elaboration.^[2–5]

With the emergence of frustrated Lewis pair chemistry,^[6] studies on metal-free borane-catalyzed hydrogenations of N-heteroarenes have grown rapidly.^[7] Particularly, chiral borane Lewis acids have been tested for enantioselective hydrogenation of quinolines. The first report appeared in 2011: the Repo group used a chiral ansa-ammonium borate as a catalyst for hydrogenation of 2-phenylquinoline, and obtained an ee value of 37%.^[8] Subsequently, the Du group made a breakthrough by using binaphthyl-diene-derived bisborane catalysts; they reported excellent enantioselectivities in the hydrogenations of 2,3- and 2,4-disubstituted quinolines, 2,3,4-trisubstituted quinolines, and 2,3-disubstituted quinoxalines.^[9] However, the methods described in these pioneering studies have limitations. First, monosubstituted quinolines remain mostly unexplored. Besides the results for 2-phenylquinoline reported by Repo (37% ee),^[8] there is only one report of Du, who tested their catalysts with methyl quinoline-2-carboxylate but obtained an ee of merely 14%.^[10] By comparison, the

success with di- and trisubstituted quinolines using Du's catalysts^[9a,b] implies that the steric influence from additional substituents might be essential for enantiocontrol. Second, the compatible di- and trisubstituted quinolines in Du's studies all have an aryl substituent at the 2-position; we suspect that the 2-aryl substituent increases the steric bulk around the nitrogen atom, thereby preventing undesired coordination of the nitrogen to the Lewis acid catalyst. Third, the functional group tolerance is limited. Therefore, the development of more effective catalytic systems is highly desirable.

Recently, we developed a series of chiral C_2 -symmetric bisborane catalysts that are prepared by hydroboration reactions of bicyclic [3.3.0] dienes with $HB(C_6F_5)_2$ and $HB(p-C_6F_4H)_2$.^[11] These catalysts are highly effective and selective in asymmetric imine hydrogenations. We attempted to use them for the hydrogenation of 2-methylquinoline, a less bulky substrate that was not studied by Repo^[8] or Du^[9,10]. Disappointingly, we observed no reaction (the upper equation in Scheme 1). We hypothesized that our catalysts were not sterically hindered enough to prevent the coordination of this quinoline to the boron center. To increase the steric bulk, we intended to change the fused bicyclic structure to a spiro bicyclic structure because the latter consists of two perpendicular rings, which produce a steric environment similar to that in compounds with geminal dialkyl substituents. Furthermore, the presence of Ar and $BArF_2$ groups attached to the rings would further increase the steric bulkiness. We hoped that such catalysts would show better activities than the existing borane catalysts. Herein, we report that these new spiro bicyclic bisboranes have now been synthesized and that, to our delight, they exhibit excellent catalytic activities and selectivities for the hydrogenation reactions of quinolines (the lower equation in Scheme 1).



Scheme 1. Hydrogenation of quinolines with chiral bicyclic bisborane catalysts

We began our study by synthesizing the necessary spiro [4.4] diene precursors (Scheme 2a) as follows. First, racemic spiro [4.4]nonane-1,6-dione **2** was prepared from ethyl 2-oxocyclopentanecarboxylate (**1**) via a previously reported three-step synthesis.^[12] Then **2** was resolved by condensation with (*R*)-2-hydrazinyl-2-oxo-N-(1-phenylethyl)acetamide and

[*] X. Li,[#] J.-J. Tian,[#] N. Liu, X.-S. Tu, N.-N. Zeng, Prof. Dr. X.-C. Wang
State Key Laboratory and Institute of Elemento-Organic Chemistry,
College of Chemistry, Nankai University
94 Weijin Road, Tianjin 300071 (China)
E-mail: xcwang@nankai.edu.cn
Homepage: <http://www.wangnankai.com/>

[#] These authors contributed equally to this work.

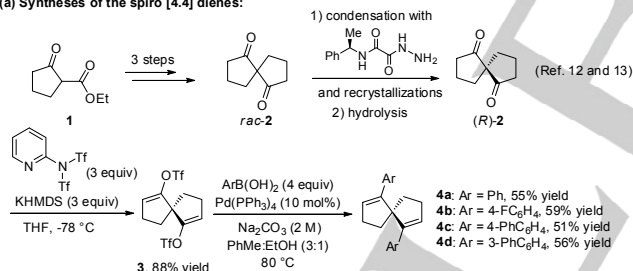
Supporting information for this article is given via a link at the end of the document.

COMMUNICATION

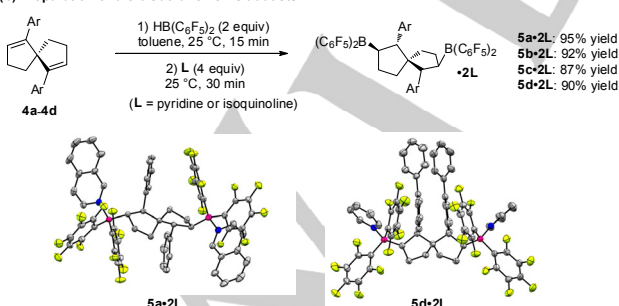
multiple recrystallizations of the obtained diastereomeric mixture.^[13] After hydrolysis of the pure hydrazone diastereomer, (*R*)-**2** was obtained in enantiopure form. Dione (*R*)-**2** was then transformed into enol triflate **3** by reaction with *N*-(2-pyridyl)triflimide in the presence of potassium bis(trimethylsilyl)amide (KHMDs). It is worth mentioning that for this step, we tested several triflyl sources under various reaction conditions, and only *N*-(2-pyridyl)triflimide gave the desired product in a high yield without the loss of enantiomeric purity.^[14] From common intermediate **3**, we were able to prepared four aryl-substituted spiro [4.4] dienes, **4a–4d**, via Suzuki coupling reactions. These dienes served as precursors for the corresponding bisborane catalysts.

To study the process for catalyst formation, we subjected dienes **4a–4d** in their racemic form to hydroboration with Piers borane, HB(C₆F₅)₂ (Scheme 2b).^[15] In toluene at 25 °C, the dienes were completely consumed within 15 min, at which point a strongly coordinative base (isoquinoline or pyridine) was added to the reaction mixture to capture the resulting bisborane species as stable Lewis acid/base adducts **5a·2L–5d·2L**. Remarkably, despite the possibility for formation of multiple regioisomers and diastereomers, single isomers of the bisborane adducts were obtained in high yields as determined by NMR analyses using CH₂Br₂ as an internal standard. Single crystals of **5a·2L** and **5d·2L** were obtained via recrystallization from 20:1 (v/v) hexane/dichloromethane at room temperature. X-ray crystallographic analyses revealed that the aryl groups were *trans* to the B(C₆F₅)₂ groups in both cyclopentane rings and that the overall structures were C₂-symmetric.^[16] Notably, unlike hydroboration reactions of bicyclic [3.3.0] dienes,^[11] these hydroborations gave the same isomers when they were performed at higher temperatures (e.g., 80 °C).

(a) Syntheses of the spiro [4.4] dienes:



(b) Preparation of the bisborane Lewis adducts:



Scheme 2. Preparation and characterization of bisborane catalysts

Knowing that hydroboration reactions of the spiro [4.4] dienes could efficiently generate single bisborane isomers, we investigated the use of in situ generated bisborane compounds for enantioselective hydrogenation with 2-methylquinoline (**S1**) (Table 1). For each reaction, an

enantiopure diene and HB(C₆F₅)₂ were first allowed to react in toluene at 25 °C for 15 min to generate the active catalyst, and then 2-methylquinoline was added. The resulting mixture was hydrogenated in an autoclave. We were pleased to find that these spiro bicyclic bisborane catalysts were active and selective: the use of 5 mol % of catalyst **5a** resulted in complete conversion to the corresponding tetrahydroquinoline product (**P1**) with 63% ee (entry 1). Although **5b** exhibited markedly diminished activity (30% conversion, entry 2), both **5c** and **5d** were very active, providing **P1** in complete conversion (entries 3 and 4). However, the enantioselectivities of these catalysts were no better than that of **5a**. Gratifyingly, after an extensive optimization study, we discovered that changing the B(C₆F₅)₂ group in **5a** to B(*p*-C₆F₄H)₂ to afford **5a^{4F}** improved the enantioselectivity to 78% ee (entry 5).^[17] With this catalyst, the ee gradually increased with decreasing reaction temperature (entries 6 and 7); at –20 °C, the substrate was completely consumed, and **P1** was obtained with 84% ee. Moreover, switching the solvent to PhCF₃ markedly improved the enantioselectivity (to 92% ee, entry 9). Under these conditions, the same result was obtained even when the hydrogen pressure was decreased from 50 to 20 bar (entry 10).

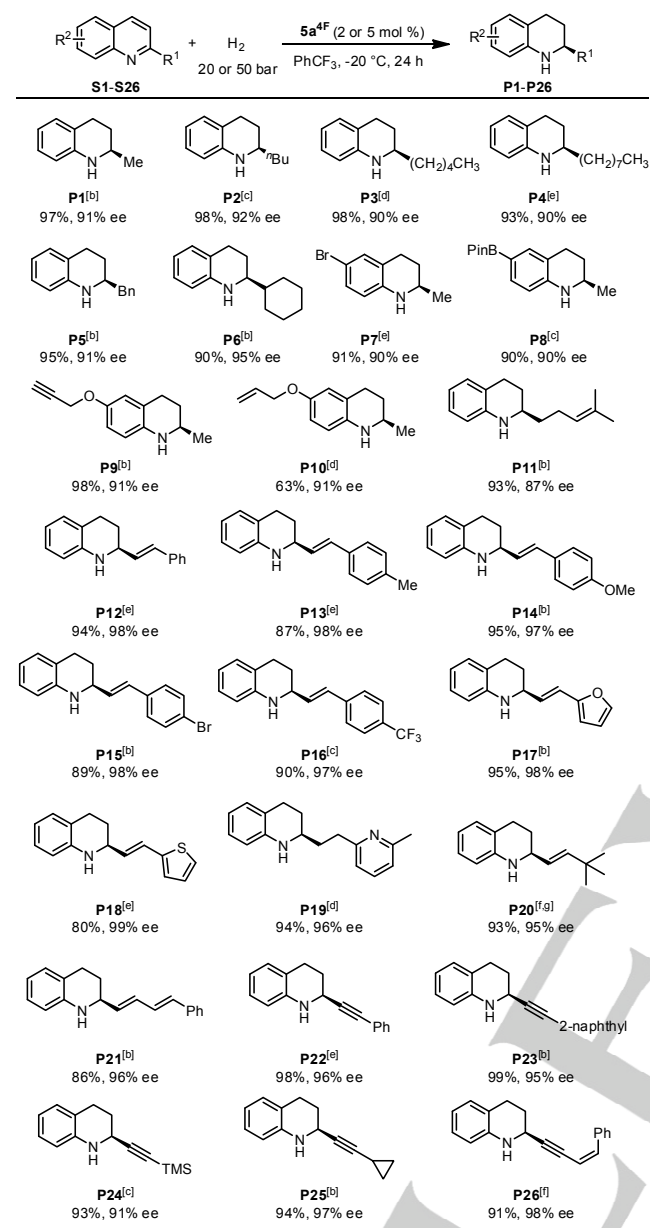
Table 1. Study of Reaction Conditions for Hydrogenation of 2-Methylquinoline^[a]

entry	catalyst	solvent	T (°C)	conv. (%) ^[b]	ee (%) ^[c]
1	5a	toluene	25	100	63
2	5b	toluene	25	30	45
3	5c	toluene	25	100	62
4	5d	toluene	25	100	53
5	5a^{4F}	toluene	25	100	78
6	5a^{4F}	toluene	0	100	81
7	5a^{4F}	toluene	–20	100	84
8	5a^{4F}	<i>n</i> -hexane	–20	95	79
9	5a^{4F}	PhCF ₃	–20	100	92
10 ^[d]	5a^{4F}	PhCF ₃	–20	100	92

[a] Unless otherwise specified, all hydrogenations were performed with 0.1 mmol of **S1** in 2 mL of solvent in a 30 mL autoclave. [b] Determined by NMR. [c] Determined by HPLC with a Chiralcel OD-H column. [d] H₂ pressure, 20 bar.

With the optimal conditions in hand, we investigated the generality of this borane-catalyzed enantioselective hydrogenation reaction by testing various quinoline substrates (Table 2). A number of 2-alkyl substituents, including *n*-butyl, *n*-pentyl, *n*-octyl, benzyl, and cyclohexyl, were compatible with the reaction conditions; the corresponding products (**P2–P6**, respectively) were obtained in 90–98% yields with 90–95% ee values. Substrates with various co-existing substituents at the 6-position of the 2-methylquinolines were then studied (**S7–S10**). Gratifyingly, bromo, Bpin, and terminal alkyne and alkene substituents were preserved, giving the desired products (**P7–P10**, respectively) with high ee values. Similarly, when a substrate possessing an unconjugated internal olefin at the 2-position was used, the double bond remained untouched when the heterocycle was hydrogenated (**P11**).

COMMUNICATION

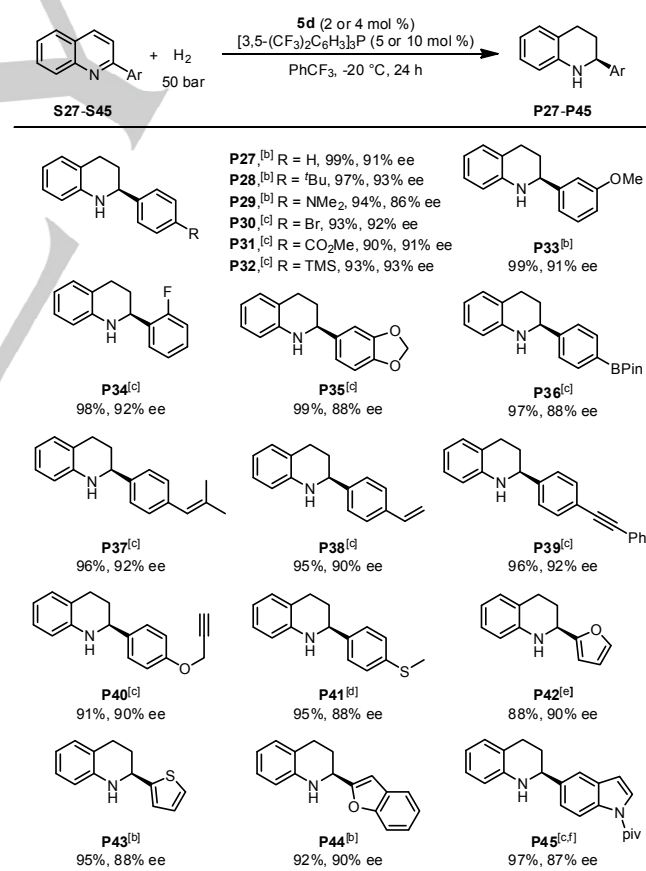
Table 2. Investigation of Quinolines with Various Substituents^[a]

[a] Unless otherwise specified, hydrogenations were performed with 0.25 mmol of the quinoline substrate in 5 mL of PhCF₃ in a 30 mL autoclave; the percentages shown are isolated yields and enantiomeric excesses, in that order. [b] Used 5 mol % of **5a**^{4F} and 20 bar of H₂. [c] Used 2 mol % of **5a**^{4F}, 50 bar of H₂, and 2 mL of PhCF₃. [d] Used 5 mol % of **5a**^{4F} and 50 bar of H₂. [e] Used 2 mol % of **5a**^{4F}, 20 bar of H₂, and 2 mL of PhCF₃. [f] Used 5 mol % of **5a** and 50 bar of H₂. [g] Reaction temperature, 25 °C.

Various quinolines with conjugated olefins at the 2-position (**S12–S20**) were subsequently tested. These olefin units are highly susceptible to hydride reduction due to the activation by the adjacent heteroarene.^[3e,4b,7b] In fact, only a transfer hydrogenation protocol that uses chiral phosphoric acids and Hantzsch ester can enantioselectively reduce 3-nitro-2-styrylquinolines while preserving the olefin group.^[18] However, we were gratified to find that when 2-styrylquinolines were tested with our bisborane catalyst, hydrogenation preferentially occurred at the heteroaromatic ring regardless of the electronic nature of the substituents on the phenyl ring,

and styryl-substituted tetrahydroquinolines (**P12–P16**) were obtained in high yields with excellent ee values. Furthermore, the presence of a furyl (**P17**) or thiophenyl (**P18**) moiety did not inhibit the reaction. Although the hydrogenation reaction of a pyridyl-substituted substrate reduced the conjugated olefin to afford **P19**, the reaction of a substrate with a terminal alkyl substituent left the olefin unit untouched (**P20**). Moreover, the reaction was feasible with 2-dienyl- (**P21**) and alkynyl-substituted (**P22–P25**) quinolines, and even with a quinoline bearing consecutive double and triple bonds (**P26**). Note that, the asymmetric hydrogenation reactions of **S12–S26** with retention of the unsaturated functional groups are unprecedented with any kind of catalysis.

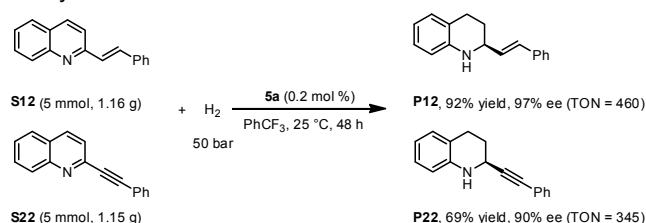
2-Aryl-substituted quinolines were next studied (Table 3). We discovered that catalyst **5d** provided the highest enantioselectivities, and addition of tris[3,5-bis(trifluoromethyl)phenyl]phosphine improved the yields. Phenyl rings bearing various electron-donating and electron-withdrawing groups were tolerated, giving products **P27–P35** in high yields and ee values. The presence of a Bpin moiety (**P36**) or internal and terminal double and triple bonds (**P37–P40**) did not influence the reactivity or selectivity. Furthermore, coordinative MeS (**P41**) and heterocyclic substituents (**P42–P45**) were compatible.

Table 3. Investigation of 2-Aryl-Substituted Quinolines^[a]

[a] Unless otherwise specified, hydrogenations were performed with 0.25 mmol of substrate in 2 mL of PhCF₃ in a 30 mL autoclave; the percentages shown are isolated yields and enantiomeric excesses, in that order. [b] Used 2 mol % of **5d** and 5 mol % of the phosphine. [c] Used 4 mol % of **5d** and 10 mol % of the phosphine. [d] Used 6 mol % of **5d**, 12 mol % of the phosphine, 60 bar of H₂, and 4 mL of PhCF₃. [e] Used 4 mol % of **5d**^{4F} and 10 mol % of the phosphine. [f] Used 60 bar of H₂ and 4 mL of PhCF₃.

COMMUNICATION

To further demonstrate the power of our catalytic system, we performed gram-scale reactions with styryl- (**S12**) and alkynyl-substituted (**S22**) quinolines (Scheme 3). We discovered that running these hydrogenations at 25 °C did not compromise the enantioselectivities substantially. In addition, by using only 0.2 mol % of catalyst **5a**^[19] and extending the reaction time to 48 h, we obtained **P12** and **P22** in high yields with excellent ee values. Notably, the turnover number of 460, obtained in the hydrogenation reaction of **S12**, represents the highest turnover number so far for asymmetric hydrogenation reactions promoted by a chiral borane catalyst. We reason that the rigidity of the bicyclic scaffold and the steric bulk that shields boron centers from attack or coordination by nucleophiles (e.g., tetrahydroquinolines) might have contributed to the enhanced stability and activity of these catalysts.



Scheme 3. Gram-scale reactions with 0.2 mol % catalyst

In conclusion, we have synthesized a new class of spiro bicyclic bisborane catalysts that exhibit excellent activities and selectivities in asymmetric hydrogenation reactions of 2-substituted quinolines. The unprecedented broad functional group tolerance observed in these hydrogenation reactions demonstrates the unique advantages of these catalysts over transition metals and other borane catalysts. Our group is currently investigating the origin of this excellent chemoselectivity, as well as the potential applications of these catalysts in other enantioselective transformations.

Acknowledgements

We thank financial support from the National Natural Science Foundation of China (21602114 and 21871147), the Natural Science Foundation of Tianjin (16JCYBJC42500), the 1000-Talent Youth Program, and the Fundamental Research Funds for Central Universities. We thank Professor Qi-Lin Zhou and Fang Lan at Nankai University for helpful discussions.

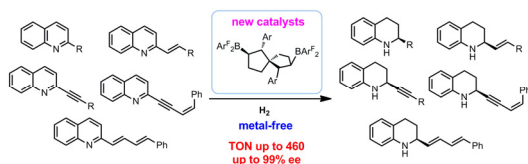
Keywords: boron • asymmetric catalysis • hydrogenation • heterocycles • homogeneous catalysis

- [1] a) E. Vitaku, D. T. Smith, J. T. Njardarson, *J. Med. Chem.* **2014**, *57*, 10257; b) V. Sridharan, P. A. Suryavanshi, J. C. Menéndez, *Chem. Rev.* **2011**, *111*, 7157.
 [2] For selected reviews, see: a) D.-S. Wang, Q.-A. Chen, S.-M. Lu, Y.-G. Zhou, *Chem. Rev.* **2012**, *112*, 2557; b) Y.-M. He, F.-T. Song, Q.-H. Fan, *Top. Curr. Chem.* **2013**, *343*, 145.
 [3] For selected studies using iridium catalysts, see: a) W.-B. Wang, S.-M. Lu, P.-Y. Yang, X.-W. Han, Y.-G. Zhou, *J. Am. Chem. Soc.* **2003**, *125*, 10536; b) S.-M. Lu, Y.-Q. Wang, X.-W. Han, Y.-G. Zhou, *Angew. Chem. Int. Ed.* **2006**, *45*, 2260; *Angew. Chem.* **2006**, *118*, 2318; c) L.-J. Xu, K. H. Lam, J. X. Ji, J. Wu, Q.-H. Fan, W.-H. Lo, A. S. C. Chan, *Chem. Commun.* **2005**, 1390; d) L. Q. Qiu, F. Y. Kwong, J. Wu, W. H. Lam, S. Chan, W.-Y. Yu, Y.-M. Li, R. W. Guo, Z. Zhou, A. S. C. Chan, *J. Am. Chem. Soc.* **2006**, *128*, 5955; e) D.-W. Wang, X.-B. Wang, D.-S. Wang, S.-M. Lu, Y.-G. Zhou, Y.-X. Li, *J. Org. Chem.*

2009, *74*, 2780.

- [4] For selected studies using ruthenium catalysts, see: a) H.-F. Zhou, Z.-W. Li, Z.-J. Wang, T.-L. Wang, L.-J. Xu, Y.-M. He, Q.-H. Fan, J. Pan, L.-Q. Gu, A. S. C. Chan, *Angew. Chem. Int. Ed.* **2008**, *47*, 8464; *Angew. Chem.* **2008**, *120*, 8592; b) T.-L. Wang, L. G. Zhuo, Z.-W. Li, F. Chen, Z.-Y. Ding, Y.-M. He, Q.-H. Fan, J.-F. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc.* **2011**, *133*, 9878; c) Q.-A. Chen, K. Gao, Y. Duan, Z.-S. Ye, L. Shi, Y. Yang, Y.-G. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 2442; d) W. Ma, J. Zhang, C. Xu, F. Chen, Y.-M. He, Q.-H. Fan, *Angew. Chem. Int. Ed.* **2016**, *55*, 12891; *Angew. Chem.* **2016**, *128*, 13083.
 [5] For selected reports using other metals as well as enantioselective transfer hydrogenations, see: a) M. Rueping, A. P. Antonchick, T. Theissmann, *Angew. Chem. Int. Ed.* **2006**, *45*, 3683; *Angew. Chem.* **2006**, *118*, 3765; b) C. Wang, C. Li, X. Wu, A. Pettman, J. Xiao, *Angew. Chem. Int. Ed.* **2009**, *48*, 6524; *Angew. Chem.* **2009**, *121*, 6646; c) X.-F. Tu, L.-Z. Gong, *Angew. Chem. Int. Ed.* **2012**, *51*, 11346; *Angew. Chem.* **2012**, *124*, 11508; d) X.-F. Cai, W.-X. Huang, Z.-P. Chen, Y.-G. Zhou, *Chem. Commun.* **2014**, *50*, 9588; e) J. Wen, R. Tan, S. Liu, Q. Zhao, X. Zhang, *Chem. Sci.* **2016**, *7*, 3047.
 [6] For recent reviews, see: a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400; *Angew. Chem.* **2015**, *127*, 6498; b) D. W. Stephan, *Science* **2016**, *354*, aaf7229; c) J. Lam, K. M. Szkop, E. Mosafieri, D. W. Stephan, *Chem. Soc. Rev.* **2019**, DOI:10.1039/C8CS00277K; d) M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202; e) W. Meng, X. Feng, H. Du, *Acc. Chem. Res.* **2018**, *51*, 191; f) J. Paradies, *Coord. Chem. Rev.* **2019**, *380*, 170; g) J. R. Lawson, R. L. Melen, *Inorg. Chem.* **2017**, *56*, 8627.
 [7] For selected reports, see: a) S. J. Geier, P. A. Chase, D. W. Stephan, *Chem. Commun.* **2010**, *46*, 4884; b) G. Erős, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, P. Király, G. Tárkányi, T. Soós, *Chem. Eur. J.* **2012**, *18*, 574; c) T. Mahdi, J. N. del Castillo, D. W. Stephan, *Organometallics* **2013**, *32*, 1971; d) Y. Liu, H. Du, *J. Am. Chem. Soc.* **2013**, *135*, 12968; e) P. Eisenberger, B. P. Bestvater, E. C. Keske, C. M. Cruden, *Angew. Chem. Int. Ed.* **2015**, *54*, 2467; *Angew. Chem.* **2015**, *127*, 2497; f) W. Wang, X. Feng, H. Du, *Org. Biomol. Chem.* **2016**, *14*, 6683; g) W. Wang, W. Meng, H. Du, *Dalton Trans.* **2016**, *45*, 5945; h) X. Liu, T. Liu, W. Meng, H. Du, *Org. Lett.* **2018**, *20*, 5653.
 [8] V. Sumerin, K. Chernichenko, M. Nieger, M. Leskelä, B. Rieger, T. Repo, *Adv. Synth. Catal.* **2011**, *353*, 2093.
 [9] a) Z. Zhang, H. Du, *Org. Lett.* **2015**, *17*, 2816; b) Z. Zhang, H. Du, *Org. Lett.* **2015**, *17*, 6266; c) Z. Zhang, H. Du, *Angew. Chem. Int. Ed.* **2015**, *54*, 623; *Angew. Chem.* **2015**, *127*, 633.
 [10] C. Han, E. Zhang, X. Feng, S. Wang, H. Du, *Tetrahedron Lett.* **2018**, *59*, 1400.
 [11] X.-S. Tu, N.-N. Zeng, R.-Y. Li, Y.-Q. Zhao, D.-Z. Xie, Q. Peng, X.-C. Wang, *Angew. Chem. Int. Ed.* **2018**, *57*, 15096; *Angew. Chem.* **2018**, *130*, 15316.
 [12] J. A. Nieman, B. A. Keay, *Synth. Commun.* **1999**, *29*, 3829.
 [13] N. Harada, N. Ochiai, K. Takada, H. Uda, *J. Chem. Soc., Chem. Commun.* **1977**, 495.
 [14] Because the spiro bicyclic structure forms via a reversible ring-closure reaction, the erosion of enantiomeric excesses may have occurred via a sequential ring-opening and reclosing process.
 [15] For Piers borane, see: a) D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809; *Angew. Chem.* **1995**, *107*, 895; b) D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492; For pioneering studies of using this hydroboration for preparation of chiral catalysts, see: c) D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, 2130; d) D. Chen, Y. Wang, J. Klankermayer, *Angew. Chem. Int. Ed.* **2010**, *49*, 9475; *Angew. Chem.* **2010**, *122*, 9665.
 [16] CCDC 1872176 and 1872179 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
 [17] For in situ generation of catalyst **5a**^{4F}, diene **4a** was allowed to react with H(*p*-C₆F₄H)₂ in toluene at 80 °C for 10 min. The structure of **5a**^{4F} was confirmed by a crystal structure of its adduct with isoquinoline (CCDC 1872178). For preparation of H(*p*-C₆F₄H)₂, see: D. Winkelhaus, B. Neumann, H.-G. Stammer, N. W. Mitzel, *Dalton Trans.* **2012**, *41*, 8609.
 [18] X.-F. Cai, M.-W. Chen, Z.-S. Ye, R.-N. Guo, L. Shi, Y.-Q. Li, Y.-G. Zhou, *Chem. Asian J.* **2013**, *8*, 1381.
 [19] For these reactions, catalysts **5a** and **5a**^{4F} gave similar enantioselectivities, but **5a** gave higher turnover numbers than **5a**^{4F}.

COMMUNICATION

Entry for the Table of Contents
COMMUNICATION

Spiro B,B bicycles: we have prepared a new series of C_2 -symmetric spiro bicyclic bisboranes. These bisboranes have been demonstrated highly effective and selective in promoting asymmetric hydrogenation of quinolines. The exceedingly broad functional group tolerance allows the access to various enantioenriched and functionalized tetrahydroquinilines that were inaccessible with previous methods using borane or transition metal catalysts.

Xiang Li,[#] Jun-Jie Tian,[#] Ning Liu, Xian-Shuang Tu, Ning-Ning Zeng, Xiao-Chen Wang*

Page No. – Page No.
**Spiro Bicyclic Bisborane Catalysts
for Metal-Free Chemoselective and
Enantioselective Hydrogenation of
Quinolines**