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Conference paper

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Copper-catalyzed asymmetric dearomative borylation: new pathway to optically active heterocyclic compounds

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Abstract: Chiral *N*-heterocyclic organoboronates represent promising intermediates for the preparation of various bioactive and pharmaceutical compounds. We recently reported the first asymmetric dearomative borylation of indoles by copper-catalyzed borylation. Then we further developed dearomatization/enantioselective borylation sequence. Chiral 3-boryl-tetrahydropyridines and chiral boryl-tetrahydroquinolines via the copper(I)-catalyzed regio-, diastereo- and enantioselective borylation of 1,2-dihydropyridines and 1,2-dihydroquinilines, which were prepared by the partial reduction of the corresponding pyridine or quinoline derivatives. This dearomatization/enantioselective borylation procedures provide a direct access to chiral piperidines and tetrahydroquinolines from readily available pyridines or quinolines in combination with the stereospecific transformation of the stereogenic C–B bond.

Keywords: asymmetric; catalysis; chiral ligand; copper; IMEBORON-16; organoboron compounds.

Introduction

Aromatic and heteroaromatic compounds are ubiquitous in nature and readily available as synthesized compounds. The enantioselective dearomatization reactions of aromatic and heteroaromatic compounds are very powerful synthetic strategies [1–4]. This method can be used to provide direct access to a wide variety of chiral cyclic and heterocyclic compounds, which are important structures of pharmaceutical drugs and various bioactive molecules. Thus, the development of novel reactions for the creation of consecutive stereogenic centers via the stereoselective dearomatization of aromatic and heteroaromatic compounds should have important practical implications for organic synthesis. Enantioenriched organoboron compounds are recognized as useful chiral building blocks in synthetic chemistry because chiral organoboron compounds are readily applied to the stereospecific functionalization of stereogenic C–B bonds [5–7]. The development of new methods for the metal-catalyzed enantioselective hydro- and protoboration reactions of prochiral C=C double bonds were extensively researched [8–20]. Despite the significant and rapid progress in this subject, there have been no studies on the enantioselective C–B bond-forming dearomatization reactions involving aromatic and heteroaromatic compounds [21–23]. The lack of research of this would be caused by the high activation energy to break the aromatic systems. The development of an enantioselective C–B bond-forming dearomatization reaction will provide an attractive approach for the synthesis of complex, functionalized cyclic molecules in combination with the stereospecific functionalization of a stereogenic C–B bond formed by the enantioselective borylations (Scheme 1). We recently published new dearomatization borylation reac-

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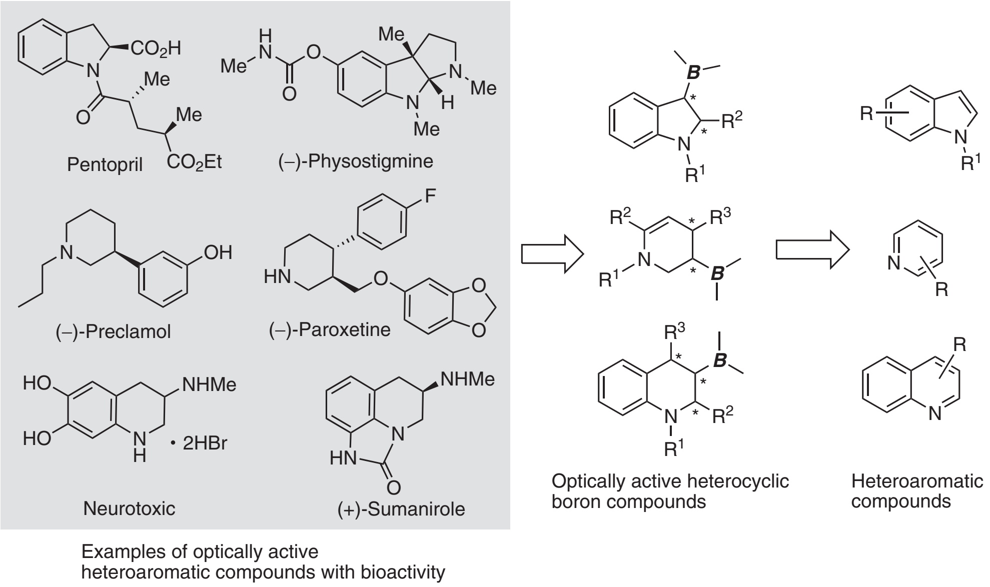


Scheme 1: Schematic presentation of enantioselective dearomative borylation.

tions of indoles, pyridines, and quinolones [24–26]. These methods provide novel pathway for the chiral heteroaromatic compounds.

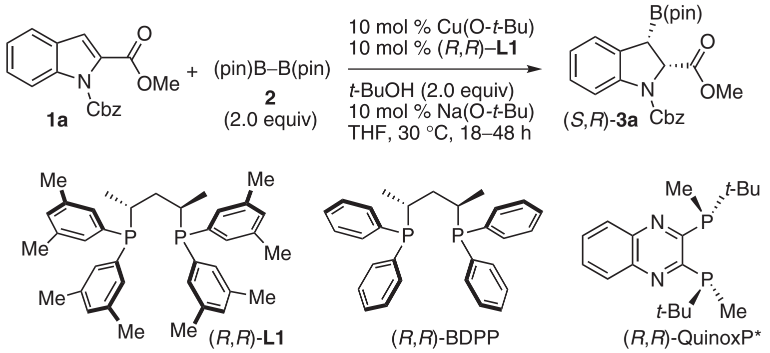
Results and discussion

Dearomative asymmetric borylation of indole derivatives [24]

We envisioned that asymmetric dearomatization of indole derivatives will be a powerful method to access indolines and other heterocyclic compounds [27–29]. The optimization experiments revealed that the reaction of carboxybenzyl (Cbz)-protected methyl indole-2-carboxylate (**1a**) with bis(pinacolato)diboron (**2**) (2.0 equiv) in the presence of Cu(O-*t*-Bu)/(*R*,*R*)-**L1** (10 mol%), Na(O-*t*-Bu) (10 mol%) and *t*-BuOH (2.0 equiv) in THF at 30 °C afforded the desired dearomatization product (*S*,*R*)-**3a** in high yield (98 %), with excellent diastereo- and enantioselectivities (d.r. 97:3, 93 % ee, Table 1, entry 1). Notably, no product was observed when the reaction was conducted in the absence of Cu(O-*t*-Bu) or the chiral ligand **L1** (Table 1, entries 2 and 3). A lower yield (74 %) of the dearomatization product **3a** was obtained when Na(O-*t*-Bu) was omitted from the reaction (Table 1, entry 4), although the absence of *t*-BuOH led to a significant decrease in the yield and stereoselectivity of the product (33 %, d.r. 76:24, 74 % ee) (Table 1, entry 5). Less sterically hindered (*R*,*R*)-BDPP ligand resulted in a lower enantioselectivity (74 % ee), which indicated that the nature of the substituent on the phenyl group of the ligand played an important role in the high enantioselectivity of the reaction (Table 1, entry 6). (*R*,*R*)-QuinoxP*, which showed excellent results in many enantioselective borylations [4], resulted in inferior results in terms of enantioselectivity (Table 1, entry 7). The diastereoselectivity of B(pin) and the ester group was *syn* because of the protonation occurred from the enolate intermediate so as to avoid the steric hindrance of B(pin) and the alcohol [24]. Several other chiral bisphosphine ligands were also tested in the reaction, but they only showed inferior results compared to that of entry 1.

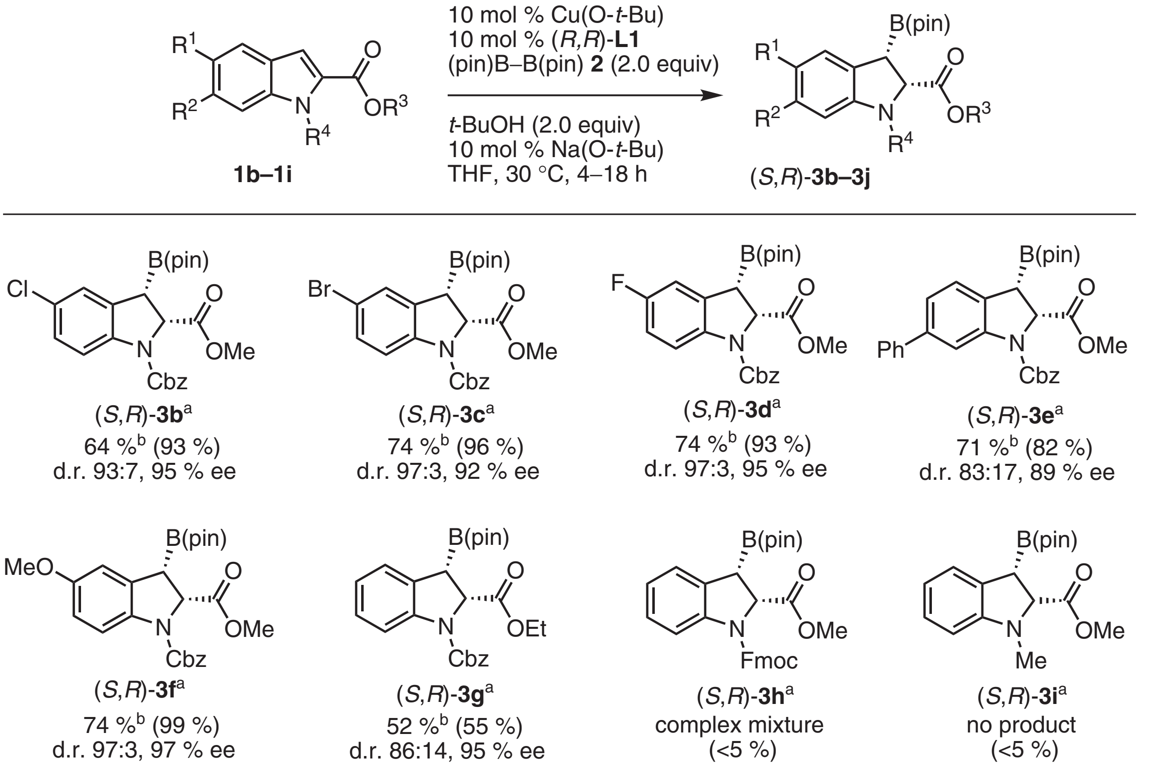
With the optimized conditions in hand, we investigated the scope of the reaction using various indole substrates (**1b–1i**, Scheme 2). Indole derivatives with a halo, methoxy or phenyl substituent at their six-position also reacted efficiently under the optimized conditions to give the corresponding dearomatization products with excellent stereoselectivity (**3b–3f**). The borylation of an indole wtih an ethyl ester group (**3g**) proceeded with high enantioselectivity (95 % ee), but with an inferior product yield (52 %). The reaction of

Table 1: Asymmetric dearomative borylation of indole derivative **1a** with **2**.



Entry[a]	Catalyst	Yield[b] (%)	d.r.[c]	ee[d] (%)
1	Standard conditions	98	97:3	93
2	No Cu(O-*t*-Bu)	<5	–	–
3	No (*R*,*R*)-**L1**	<5	–	–
4	No Na(O-*t*-Bu)	74	89:11	93
5	No *t*-BuOH	33	76:24	74
6	(*R*,*R*)-BDPP instead of (*R*,*R*)-**L1**	98	89:11	74
7	(*R*,*R*)-QuinoxP* instead of (*R*,*R*)-**L1**	93	90:10	27

[a] Reactions were performed with **1a** (0.5 mmol), Cu(O-*t*-Bu) (0.05 mmol), chiral ligand (0.05 mmol), bis(pinacolato)diboron **2** (1.0 mmol), Na(O-*t*-Bu) (0.05 mmol) and alcohol (1.0 mmol) in THF (1.0 mL), unless stated otherwise in the table. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture with an internal standard. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis.



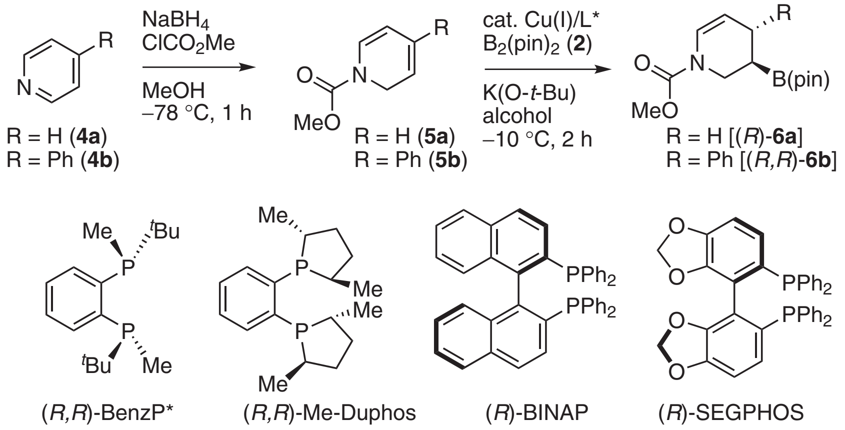
Scheme 2: Asymmetric dearomative borylation of indole derivatives. [a]Conditions: Cu(O-*t*-Bu) (0.05 mmol), (*R*,*R*)-**L1** (0.05 mmol), **1** (0.5 mmol), bis(pinacolato)diboron **2** (1.0 mmol), Na(O-*t*-Bu) (0.05 mmol) and *t*-BuOH (1.0 mmol) in THF (1.0 mL). [b]Isolated yields. NMR yields are shown in parentheses.

fluorenylmethyloxycarbonyl (Fmoc)-protected indole (**3h**) failed to provide any of the desired product, probably because of the reaction of the acidic proton of the Fmoc group with strong base, Na(O-*t*-Bu), which resulted in the formation of a complex mixture. We also found that Me-protected indoles were not suitable substrate (**3i**).

Sequential procedure of dearomative asymmetric borylation of pyridines [25]

Pyridines are excellent substrate for the dearomatization reaction, but they are unreactive toward copper(I)-catalyzed borylations under standard conditions [30–33]. We then attempted a direct C–B bond forming method using an *N*-acyl pyridinium salt as the substrate under copper(I) catalysis with the concomitant dearomatization of the pyridine ring. Although the 1,2-borylation reaction proceeded as anticipated, we failed to isolate the desired product because there are many side products. Then we focused on the development of an alternative stepwise strategy involving the combination of Fowler's dearomative reduction of pyridines with the copper(I)-catalyzed enantioselective borylation of the resulting unstable 1,2-dihydropyridines [34]. After the results of an extensive optimization process, we found that the reaction of methoxycarbonyl-protected 1,2-dihydropyridine **5a** (R = H), which was isolated from pyridine **4a** after the treatment of Fowler's reduction method, with bis(pinacolato)diboron (**2**) (1.2 equiv) in the presence of CuCl/(*R*,*R*)-QuinoxP* (5 mol%), K(O-*t*-Bu) (20 mol%) and MeOH (2.0 equiv) in THF at –10 °C afforded the chiral 3-boryl-tetrahydropyridine (*R*)-**6a** in high yield with excellent enantioselectivity (Table 2, entry 1). The use of (*R*,*R*)-BenzP* or (*R*,*R*)-Me-Duphos also provided excellent enantioselectivity

Table 2: Sequential asymmetric dearomative borylation of pyridine derivative **4a** and **4b**.

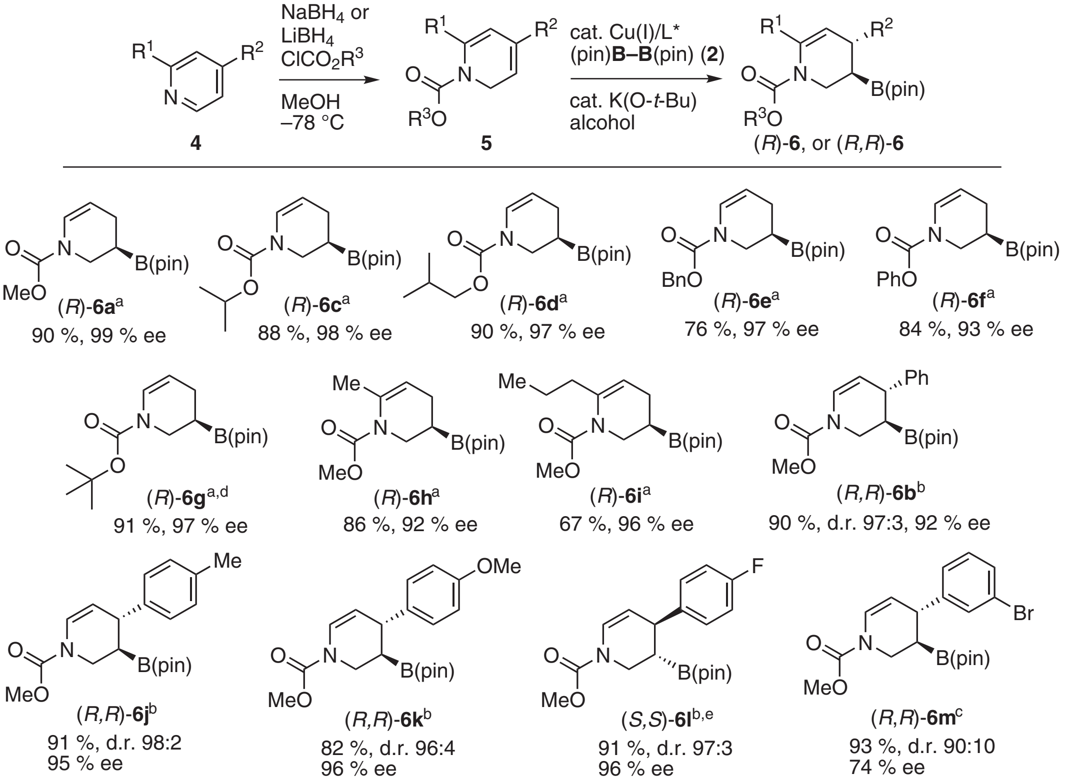


Entry[a]	R	Chiral ligand	Alcohol	dr	Yield (%)[b]	ee (%)[c]
1	H (**4a**)	(*R*,*R*)-QuinoxP*	MeOH	–	93	99
2	H (**4a**)	(*R*,*R*)-BenzP*	MeOH	–	92	98
3	H (**4a**)	(*R*,*R*)-Me-Duphos	MeOH	–	82	93
4	H (**4a**)	(*R*)-BINAP	MeOH	–	<5	–
5	H (**4a**)	(*R*)-SEGPHOS	MeOH	–	<5	–
6	H (**4a**)	(*R*,*R*)-BDPP	MeOH	–	97	55
7[d]	H (**4a**)	(*R*,*R*)-QuinoxP*	MeOH	–	96	99
8[e]	H (**4a**)	(*R*,*R*)-QuinoxP*	MeOH	–	91	99
9[f]	Ph (**4b**)	(*R*,*R*)-QuinoxP*	MeOH	99:1	83	25
10[f]	Ph (**4b**)	(*R*)-SEGPHOS	*t*-BuOH	97:3	94	92

[a]Conditions: CuCl (0.025 mmol), ligand (0.025 mmol), **4** (0.5 mmol), bis(pinacolato)diboron **2** (0.6 mmol), alcohol (1.0 mmol) and K(O-*t*-Bu) (0.1 mmol) in THF; [b]NMR yield; [c]the ee values were determined by HPLC analysis of the corresponding benzoate ester; [d]the reaction was carried out on a 5 mmol scale; [e]1 mol% CuCl and ligand were used. The reaction time was 16 h; [f]the reaction was carried out at 0 °C and the reaction time was 1 h.

(Table 2, entries 2 and 3). No product was observed when a triarylphosphine-type ligand, such as (*R*)-BINAP or (*R*)-SEGPHOS was used in the reaction (Table 2, entries 4 and 5). The catalyst with (*R*,*R*)-BDPP ligand afforded the product in high yield, but with poor enantioselectivities (97 %, 55 % ee, Table 2, entry 6). Notably, the reaction proceeded smoothly on a 5.0 mmol scale to give gram quantities of the desired product with excellent enantioselectivity (Table 2, entry 7). This enantioselective borylation reaction also proceeded efficiently with a lower loading (1 mol%) of the copper(I) catalyst and showed high enantioselectivity (99 % ee), although this required a longer reaction time to complete (Table 2, entry 8). We then proceeded to investigate the borylation of 4-phenyl-1,2-dihydropyridine **5b** in the presence of the Cu/QuinoxP* catalyst (Table 2, entry 9). However, we observed a lower enantioselectivity (25 % ee) than that obtained under the same conditions, even though the regio- and diastereoselectivity were excellent (d.r. 99:1). A series of optimization reactions using **5b** as a substrate was investigated. The results revealed that the use of the (*R*)-SEGPHOS chiral ligand with *t*-BuOH in a toluene/DME/THF co-solvent system gave the desired chiral 3-boryl-tetrahydropyridine (*R*,*R*)-**6b** bearing consecutive stereogenic centers in good yield (94 %) with high diastereo- and enantioselectivity (d.r. 97:3, 92 % ee) (Table 2, entry 10). The diastereoselectivity of B(pin) and the phenyl group was *anti* because *syn* protonation occurred from the alkyl copper intermediate [25].

The optimized conditions were used for further evaluation of the substrate scope of this sequential reaction (Scheme 3). The reactions of 1,2-dihydropyridines bearing various carbamate-type protecting groups (**5a–5m**) in the presence of the copper(I)/(*R*,*R*)-QuinoxP* catalyst proceeded to afford the desired dearomatization products [(*R*)-**6a**–(*R*)-**6m**] with excellent enantioselectivities (Scheme 3). The 6-substituted



Scheme 3: Sequential asymmetric dearomative borylation of various pyridine derivatives. [a]Conditions: CuCl (0.025 mmol), (*R*,*R*)-QuinoxP* (0.025 mmol), **5** (0.5 mmol), **2** (0.6 mmol), MeOH (1.0 mmol) and K(O-*t*-Bu) (0.1 mmol) in THF at –10 °C for 2 h. [b]Conditions: CuCl (0.025 mmol), (*R*)-SEGPHOS (0.025 mmol), **5** (0.5 mmol), **2** (0.6 mmol), *t*-BuOH (1.0 mmol) and K(O-*t*-Bu) (0.1 mmol) in THF/toluene/DME (1:6:6 – v/v/v) at 0 °C for 1 h. [c]Conditions: CuCl (0.025 mmol), (*R*,*R*)-BDPP (0.025 mmol), **5** (0.5 mmol), **2** (0.6 mmol), *t*-BuOH (1.0 mmol) and K(O-*t*-Bu) (0.1 mmol) in THF at 0 °C for 1 h. [d]**4g** was prepared by the treatment of **4f** with K(O-*t*-Bu). [e](*S*)-SEGPHOS was used.

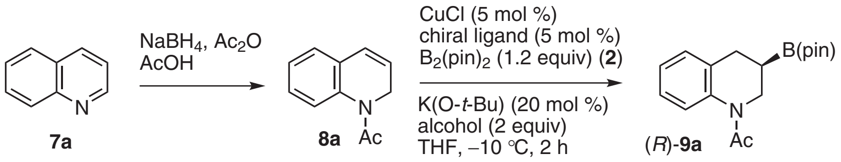
1,2-dihydropyridines (**5h** and **5i**) were also borylated to afford the corresponding chiral 3-boryl-tetrahydropyridines [(*R*)-**6h** and (*R*)-**6i**] with excellent enantioselectivities without any of the other undesired regioisomers being detected (Scheme 3). The copper(I)/(*R*)-SEGPHOS catalyst promoted the enantioselective borylation of various 4-aryl-1,2-dihydropyridines (**5b**, **5j–5l**) to give the corresponding borylated products with consecutive stereogenic centers with high diastereo- and enantioselectivities (d.r. 96:4–98:2, 93–96 % ee). However, the reactions of **5m** with copper(I)/(*R*)-SEGPHOS catalyst resulted in a low yield (10 %). However, we found that the use of (*R*,*R*)-BDPP gave the corresponding products [(*R*,*R*)-**6m**], although the enantioselectivity was moderate (74 % ee). (*S*,*S*)-**6l** was further derivatized to the (−)-paroxetine stereoselectively [25].

Sequential procedure of dearomative asymmetric borylation of quinolines [26]

The dearomative borylation of quinoline is also attractive target; [35–42] however, same as the pyridine case, the direct borylation of quinoline failed. Optimization experiments for the dearomatization sequential procedure revealed that the reaction of *N*-acetyl 1,2-dihydroquinoline **8a** which was prepared through the $NaBH_4$ reduction of quinoline (**7a**) [11], with bis(pinacolato)diboron (**2**, 1.2 equiv) in the presence of CuCl/(*R*,*R*)-QuinoxP* (5 mol%), K(O-*t*-Bu) (20 mol%) and MeOH (2.0 equiv) in THF at 10 °C afforded the desired chiral 3-boryl-tetrahydroquinoline (*R*)-**9a** in high yield (90 %) with excellent enantioselectivity (98 % ee) (Table 3, entry 1). The use of (*R*,*R*)-BenzP* or (*R*,*R*)-Me-Duphos instead of (*R*,*R*)-QuinoxP* also provided high levels of enantioselectivity (Table 3, entries 2 and 3, 97 % ee and 95 % ee, respectively). Contrary, lower chemical yields and enantioselectivities were observed when a triarylphosphine-type ligand, such as (*R*)-BINAP or (*R*)-SEGPHOS was used (Table 3, entries 4 and 5). Several other chiral ligands, including (*R*,*R*)-BDPP and (*R*,*S*)-Josiphos, were also screened in the reaction. Although these ligands both provided the desired borylation product, they afforded only poor enantioselectivities (Table 3, entries 6 and 7, –14 % ee and –29 % ee, respectively).

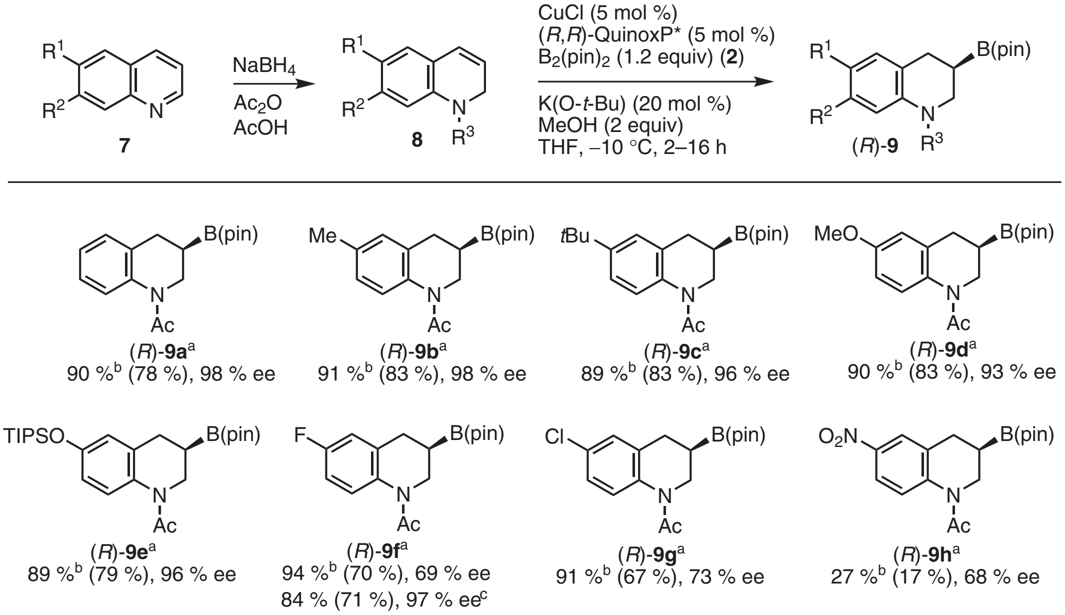
The optimized conditions were in hand, we conducted experiments for further evaluation of the substrate scope (Scheme 4). The borylation products in Scheme 4 were isolated by derivatized into the corresponding silyl ethers after a sequential oxidation/silylation of the C–B bond in the products. The reactions of 1,2-dihydroquinolines bearing Me-, *t*-Bu-, MeO- and TIPSO- groups at their six-position (**8b–8e**) in the presence of the copper(I)/(*R*,*R*)-QuinoxP* catalyst system proceeded to give the desired products [(*R*)-**9b**–(*R*)-**9e**] with high enantioselectivities (93–98 % ee) (Scheme 4). The substrates with electron-withdrawing

Table 3: Sequential asymmetric dearomative borylation of quinoline derivative **7a**.



Entry[a]	Chiral ligand	Alcohol	Yield (%)[b]	ee (%)[c]
1	(*R*,*R*)-QuinoxP*	MeOH	90	98
2	(*R*,*R*)-BenzP*	MeOH	96	97
3	(*R*,*R*)-Me-Duphos	MeOH	90	95
4	(*R*)-BINAP	MeOH	26	81
5	(*R*)-SEGPHOS	MeOH	12	58
6	(*R*)-BDPP	MeOH	94	−14
7	(*R*,*S*)-Josiphos	MeOH	12	−29

[a] Conditions: CuCl (0.025 mmol), ligand (0.025 mmol), **8a** (0.5 mmol), bis(pinacolato)diboron **2** (0.6 mmol), K(O-*t*-Bu) (0.1 mmol), alcohol (1.0 mmol) in THF (1.0 mL). [b] Determined by ^1H NMR analysis of the crude reaction mixture with an internal standard. [c] Determined by HPLC analysis.



(*R*)-**9a**[a] 90 %[b] (78 %), 98 % ee

(*R*)-**9b**[a] 91 %[b] (83 %), 98 % ee

(*R*)-**9c**[a] 89 %[b] (83 %), 96 % ee

(*R*)-**9d**[a] 90 %[b] (83 %), 93 % ee

(*R*)-**9e**[a] 89 %[b] (79 %), 96 % ee

(*R*)-**9f**[a] 94 %[b] (70 %), 69 % ee
84 % (71 %), 97 % ee[c]

(*R*)-**9g**[a] 91 %[b] (67 %), 73 % ee

(*R*)-**9h**[a] 27 %[b] (17 %), 68 % ee

Scheme 4: Sequential asymmetric dearomative borylation of various quinoline derivatives. [a]Conditions: CuCl (0.025 mmol), (*R*,*R*)-QuinoxP* (0.025 mmol), **8** (0.5 mmol), bis(pinacolato)diboron **2** (0.6 mmol), K(O-*t*-Bu) (0.1 mmol), MeOH (1.0 mmol) in THF (1.0 mL). [b]^{1}H NMR yields of the borylation products. Isolated yields of the corresponding silyl ethers after an sequential oxidation/silylation of borylation products **9** are shown in parenthesis. [c](*R*,*R*)-BenzP* was used instead of (*R*,*R*)-QuinoxP*.

groups such as halogens and nitro group (**2g** and **2h**) gave moderate enantioselectivities (68–73 % ee) (Scheme 4).

Summary

The dearomative asymmetric borylation can be a useful method for obtaining synthetic plat form for preparation of more complicated molecules including chiral heterocyclic structure. Very recently, Hou and co-workers reported copper(I)-catalyzed asymmetric borylation of racemic 2-substituted 1,2-dihydroquinolines including kinetic resolution process [44]. The various dearomatization procedure with other aromatic systems followed by copper(I)-catalyzed borylation are desirable for future research.

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References

[1] C. X. Zhuo, W. Zhang, S. L. You. *Angew. Chem. Int. Ed.* **51**, 12662 (2012).
[2] C. X. Zhuo, C. Zheng, S. L. You. *Acc. Chem. Res.* **47**, 2558 (2014).
[3] S. P. Roche, J. A. Porco. *Angew. Chem. Int. Ed.* **50**, 4068 (2011).
[4] Q. P. Ding, X. L. Zhou, R. H. Fan. *Org. Biomol. Chem.* **12**, 4807 (2014).
[5] D. G. Hall. *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, 2nd revised Ed, Wiley-VCH, Weinheim, **2011**.
[6] M. Burns, S. Essafi, J. R. Bame, S. P. Bull, M. P. Webster, S. Balieu, J. W. Dale, C. P. Butts, J. N. Harvey, V. K. Aggarwal. *Nature* **513**, 183 (2014).

[7] S. N. Mlynarski, C. H. Schuster, J. P. Morken. *Nature* **505**, 386 (2014).
[8] J. E. Lee, J. Yun. *Angew. Chem. Int. Ed.* **47**, 145 (2008).
[9] Y. M. Lee, A. H. Hoveyda. *J. Am. Chem. Soc.* **131**, 3160 (2009).
[10] V. Lillo, A. Prieto, A. Bonet, M. M. Diaz-Requejo, J. Ramirez, P. J. Perez, E. Fernandez. *Organometallics* **28**, 659 (2009).
[11] D. Noh, H. Chea, J. Ju, J. Yun. *Angew. Chem. Int. Ed.* **48**, 6062 (2009).
[12] J. M. O'Brien, K. S. Lee, A. H. Hoveyda. *J. Am. Chem. Soc.* **132**, 10630 (2010).
[13] R. Corberan, N. W. Mszar, A. H. Hoveyda. *Angew. Chem. Int. Ed.* **50**, 7079 (2011).
[14] J. C. H. Lee, R. McDonald, D. G. Hall. *Nat. Chem.* **3**, 894 (2011).
[15] H. Ito, S. Ito, Y. Sasaki, K. Matsuura, M. Sawamura. *J. Am. Chem. Soc.* **129**, 14856 (2007).
[16] H. Ito, S. Kunii, M. Sawamura. *Nat. Chem.* **2**, 972 (2010).
[17] Y. Sasaki, C. M. Zhong, M. Sawamura, H. Ito. *J. Am. Chem. Soc.* **132**, 1226 (2010).
[18] K. Kubota, E. Yamamoto, H. Ito. *Adv. Synth. Catal.* **355**, 3527 (2013).
[19] E. Yamamoto, Y. Takenouchi, T. Ozaki, T. Miya, H. Ito. *J. Am. Chem. Soc.* **136**, 16515 (2014).
[20] K. Kubota, E. Yamamoto, H. Ito. *J. Am. Chem. Soc.* **137**, 420 (2015).
[21] K. Oshima, T. Ohmura, M. Suginome. *J. Am. Chem. Soc.* **133**, 7324 (2011).
[22] K. Oshima, T. Ohmura, M. Suginome. *J. Am. Chem. Soc.* **134**, 3699 (2012).
[23] T. Ohmura, Y. Morimasa, M. Suginome. *J. Am. Chem. Soc.* **137**, 2852 (2015).
[24] K. Kubota, K. Hayama, H. Iwamoto, H. Ito. *Angew. Chem. Int. Ed.* **54**, 8809 (2015).
[25] K. Kubota, Y. Watanabe, K. Hayama, H. Ito. *J. Am. Chem. Soc.* **138**, 4338 (2016).
[26] K. Kubota, Y. Watanabe, H. Ito. *Adv. Synth. Catal.* **358**, 2379 (2016).
[27] D. Crich, A. Banerjee. *Acc. Chem. Res.* **40**, 151 (2007).
[28] F. Kolundzic, M. N. Noshi, M. Tjandra, M. Movassaghi, S. J. Miller. *J. Am. Chem. Soc.* **133**, 9104 (2011).
[29] W. W. Zi, Z. W. Zuo, D. W. Ma. *Acc. Chem. Res.* **48**, 702 (2015).
[30] J. A. Bull, J. J. Mousseau, G. Pelletier, A. B. Charette. *Chem. Rev.* **112**, 2642 (2012).
[31] J. Y. Ding, D. G. Hall. *Angew. Chem. Int. Ed.* **52**, 8069 (2013).
[32] E. M. P. Silva, P. Varandas, A. M. S. Silva. *Synthesis* **45**, 3053 (2013).
[33] A. S. Dudnik, V. L. Weidner, A. Motta, M. Delferro, T. J. Marks. *Nat. Chem.* **6**, 1100 (2014).
[34] F. W. Fowler. *J. Org. Chem.* **37**, 1321 (1972).
[35] D. Brundish, A. Bull, V. Donovan, J. D. Fullerton, S. M. Garman, J. F. Hayler, D. Janus, P. D. Kane, M. McDonnell, G. P. Smith, R. Wakeford, C. V. Walker, G. Howarth, W. Hoyle, M. C. Allen, J. Ambler, K. Butler, M. D. Talbot. *J. Med. Chem.* **42**, 4584 (1999).
[36] V. Sridharan, P. A. Suryavanshi, J. C. Menendez. *Chem. Rev.* **111**, 7157 (2011).
[37] L. Jean-Gerard, F. Mace, A. N. Ngo, M. Pauvert, H. Dentel, M. Evain, S. Collet, A. Guingant. *Eur. J. Org. Chem.* 4240 (2012). Available at: http://onlinelibrary.wiley.com/doi/10.1002/ejoc.201200344/full.
[38] P. Ferraboschi, S. Ciceri, P. Grisenti. *Tetrahedron-Asymmetry* **24**, 1142 (2013).
[39] G. Masson, C. Lalli, M. Benohoud, G. Dagousset. *Chem. Soc. Rev.* **42**, 902 (2013).
[40] V. Rawat, B. S. Kumar, A. Sudalai. *Org. Biomol. Chem.* **11**, 3608 (2013).
[41] M. Fochi, L. Caruana, L. Bernardi. *Synthesis* **46**, 135 (2014).
[42] T. Nemoto, M. Hayashi, D. S. Xu, A. Hamajima, Y. Hamada. *Tetrahedron-Asymmetry* **25**, 1133 (2014).
[43] V. K. Tiwari, G. G. Pawar, R. Das, A. Adhikary, M. Kapur. *Org. Lett.* **15**, 3310 (2013).
[44] D. Kong, S. Han, R. Wang, M. Li, G. Zi, G. Hou. *Chem. Sci.* **8**, 4558 (2017).