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Corrigendum

Corrigendum to “Preparation of chiral 7,7′-disubstituted BINAPs for Rh-catalyzed 1,4-addition of arylboronic acids”

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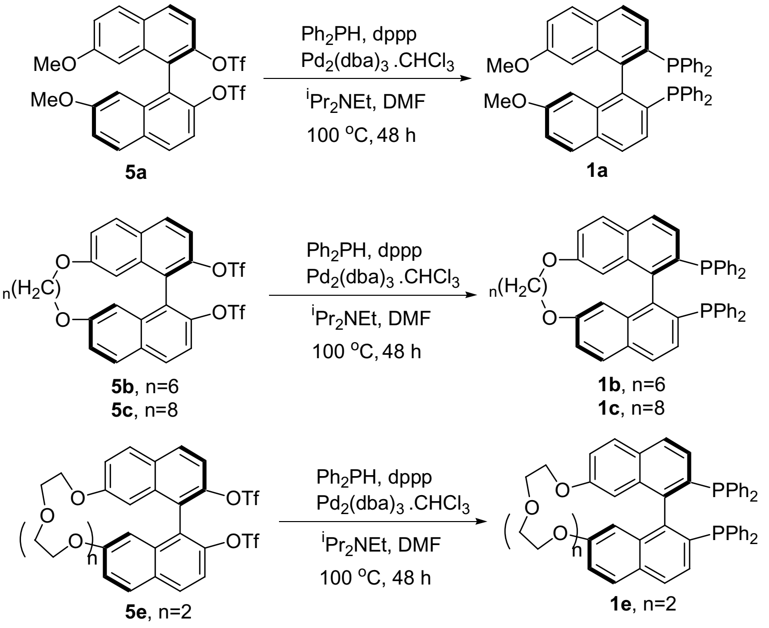
Recently, we published a letter in the journal regarding the preparation of chiral 7,7′-disubstituted BINAPs for Rh-catalyzed 1,4-addition of arylboronic acids. However, when we extended the use of these ligands in the Ru-catalyzed asymmetric hydrogenation of ketones, it was found that the **1a**–**c** and **1e** were not optically pure on the basis of ^{31}P NMR spectra of their ruthenium complexes of 1,2-diphenylethylenediamine (DPEN). The racemization occurred in certain step during the synthesis of these ligands. An alternative way, in which these ligands were prepared, avoids the racemization (Scheme 1).



Scheme 1. The preparation of chiral ligands **1a**–**c** and **1e**.

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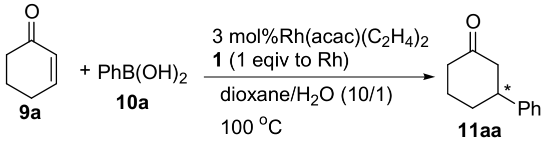
Table 1. Asymmetric 1,4-addition of phenylboronic acid to cyclohexenone catalyzed by ligands **1**-rhodium (I) complexes



Entry	BINAPs	Additive	Time (h)	Yield (%)[a]	ee (%)[b]
1	**1a**	—	5	83	94
2	**1b**	—	5	90	91
3	**1c**	—	5	82	92
4	**1d**	—	5	99	97
5	**1e**	—	5	92	97
6	**1e**	LiF[c]	5	84	97
7	**1e**	NaF[c]	5	89	96
8	**1e**	KF[c]	5	80	96
9	**1d**	—	5	92	97
10	**1d**	—	8	75	92

[a] Isolated yield based on cyclohexenone.

[b] Determined by HPLC and the absolute configuration is *R*.

[c] The ratio of additive to **1e** = 1.2:1.

Accordingly, the results from the asymmetric 1,4-addition of phenylboronic acid to cyclohexenone catalyzed by Ligands **1**-rhodium (I) complexes should be corrected. The related descriptions and discussion also need to be corrected.

In abstract: 'The enantioselectivity was found to be dramatically dependent on the size of achiral substituents'. Should be deleted.

In main text: Results and discussion on ligands screening should be revised as:

'For screening the catalytic efficiency of chiral ligands **1**, a model reaction of cyclohexenone with phenylboronic acid was performed under conditions developed by Hayashi and Miyaura et al.[3,11] As shown in Table 1, the size of the achiral substituent on the ligand has an little influence on the enantioselectivity, and thus very subtle alteration of achiral substituents leads to a significantly different catalytic performance (entries 1–5). Compound **1a** has two more methoxyl groups at its 7,7′-positions than BINAP, gave a slightly lower enantioselectivity of 94% ee (entry 1). Varying the ring size of the 7,7′-substituents on the ligands, which are shown as **1b–e**, leads to slightly different results (entries 2–5). Among these ligands, **1d** and **1e** gave the best level of enantioselectivities of 97% ee (entry 4), actually the same result as that observed with BINAP.[3] Since crown ethers are easy to coordinate with some metal ions,[12] we reasoned that the complexation of metal ions with the crown ether moiety of ligand **1e** should produce some difference in its catalytic performance.[13] However, the use of **1e** as a ligand did not show any difference in enantioselectivity by addition of KF, NaF and LiF as guests into the reaction solution (entries 6–8)'.

In conclusion part: 'It has been found that the achiral substituents on the ligands play an important role in controlling of stereochemistry' should be changed to 'It has been found that the size of achiral substituents on the ligands did not have significant impact on the control of stereochemistry'. 'The dependence of catalytic performance of ligands on the substituent size could be due to the subtle variation of bite angle' should be deleted.

We apologized for these mistakes. A full account, with experimental details, will be published separately.