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# The application of novel boron complexes in asymmetric transfer hydrogenation of aromatic ketones

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ABSTRACT

Asymmetric transfer hydrogenation using *iso*-PrOH as a hydrogen source offers an attractive route for reducing simple unsymmetrical functionalized ketones to chiral alcohols. The combined use of organometallic and coordination chemistry has produced a number of new and powerful synthetic methods for important classes of compounds in general and for optically active substances in particular. For this aim, the (*S*,*Z*)-1-((1-hydroxy butane-2-yl imino)methyl)naphthalene-2-ol chiral ligand was chosen to obtain boron complexes. Boronic derivative compounds such as phenylboronic acid, 6-methoxynaphthalen-2-ylboronic acid, 4-methyl-3-nitrophenylboronic acid and 1,4-phenylenediboronic acid were applied to obtain complexation with chiral based ligands. The structures of these ligands and their complexes have been elucidated by a combination of multinuclear NMR spectroscopy, LC–MS/MS, TGA/DTA, UV–Vis., elemental analysis, XRD, SEM, and FTIR. These boron complexes have also been tested as catalysts in the enantioselective transfer hydrogenation of acetophenone derivatives to afford the corresponding product, (*S*)-1-phenylethanol with high conversions (up to 99%) and modest enantioselectivities (up to 70% ee). The substituents on the backbone of the ligands had a significant effect on both the activity and % ee.



## 1. Introduction

Boronic acids and derivatives are rarely found in Nature and these compounds, which can be classified as abiotic, are obtained synthetically from primary sources of boron. They can be obtained via acidification of borax with carbon dioxide. Boronic acid derivatives are generally synthesized from borate esters, which are mainly known as precursors of the process.[1–4] The simple dehydration of boric acid with various alcohols gives borate esters.[5] The mild Lewis acidity, attenuated reactivity behavior, and ease of handling without toxicity make boronic acid a favorable class of synthetic intermediates. Since boronic acids are environmentally friendly, they can be regarded as green.[5–10]

The widespread use of boron based organic and inorganic compounds has increased over many years, due to their applicability in textiles, medicinal chemistry, pharmaceutical studies, agriculture, and industry.[5,11] Although boron is a semi-metal, it can demonstrate complexation ability due to its electron deficient nature. Thus O, N, P and also S atoms can coordinate to a boron atom to obtain various structures.[12,3,4,9,13,14] In addition, since boron has a similar atomic size to carbon, it allows us to investigate alloying experiments on the hydrogenation properties of TiFe.[15] Biological research has also increased over last few decades due to its application in cancer treatment. Boron neutron capture therapy is a common treatment, but it still requires development besides its significant effect on cancer cells.[16,17,10] Previous surveys have claimed that boron deficiency has caused a decrease in plant growth because of its important role in photosynthesis. The presence of coordinative B←N and covalent B–O bonds makes the structure stable in air.

Homogeneous asymmetric catalysis with transition metal complexes is an active area of research[18] and great interest has been directed toward the design and development of efficient ligands.[19] An increasing number of chiral compounds and enantiomerically pure drugs are prepared via transition metal-catalyzed asymmetric reactions.[20] Since the reactivity and stereoselectivity of asymmetric transformations are highly dependent on the structure of the chiral ligand coordinated to the transition metal, the design and synthesis of efficient chiral ligands are important and have attracted a great deal of attention from both academia and industry.[21–23] Asymmetric transfer hydrogenation using 2-propanol as a

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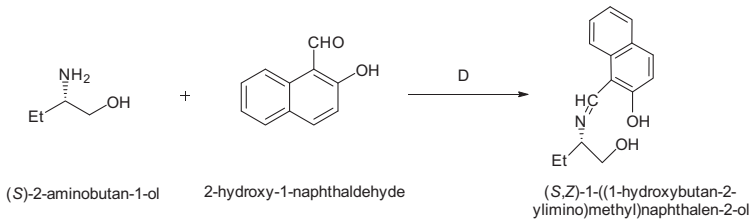
0957-4166/



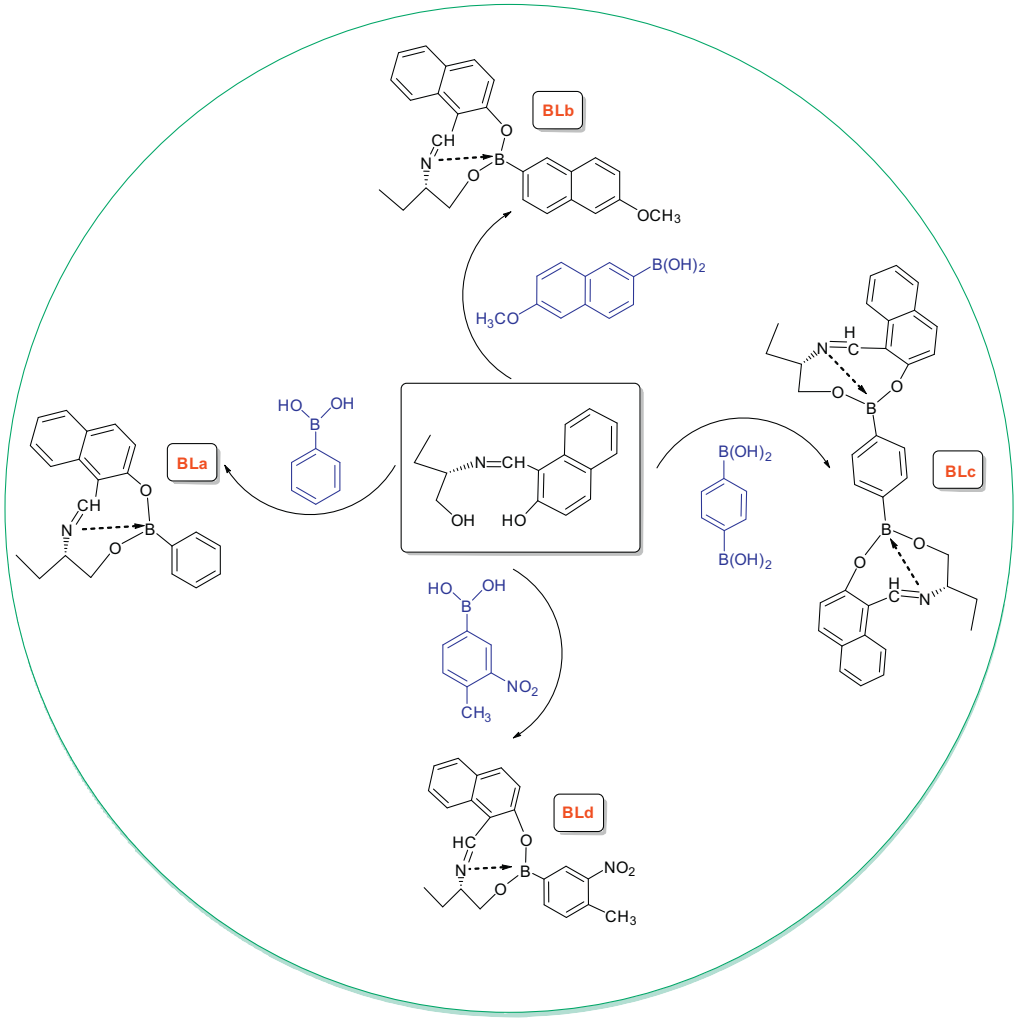

**Scheme 1.** The synthesis of (*S*,*Z*)-1-((1-hydroxy butane-2-yl imino)methyl)naphthalene-2-ol, **L**.

hydrogen source offers an attractive route for reducing simple unfunctionalized ketones to chiral alcohols.[24–26] The reaction uses inexpensive reagents and is usually easy to perform. Herein, the chiral ligand was synthesized by the condensation of a chiral amine and an aldehyde. The boronic acid derivatives were applied obtain get boron complexes. Their structure identification was performed by LC–MS, $^{1}$H NMR, $^{13}$C NMR, UV–Vis, FTIR, and elemental analysis. Recently, we have reported on the synthesis and applications of a number of modified boron catalysts for transfer hydrogenations.[21,26] In view of the promising results, boron complexes were shown to be efficient homogeneous hydrogenation catalysts toward various substrates. By taking into account that these easily prepared ligands were effective ligands in boron-catalyzed transfer hydrogenations, we believed that boron catalysts would be valuable materials for asymmetric transfer hydrogenations. Furthermore, to the best of our knowledge, there are not many reports on asymmetric transfer hydrogenations of ketones using chiral boron complexes as catalysts. These boron complexes were successfully employed as ligands in boron-promoted asymmetric transfer hydrogenations of various ketones.

## 2. Results and discussion

### 2.1. Spectroscopic identification

The synthetic strategy and reaction conditions adopted herein are described in Scheme 1 for compound **L**. We first established an easy methodology for the synthesis of (*S*)-2-aminobutan-1-ol




**Scheme 2.** Proposed reactions of boronic derivative compounds **BLa**, **BLb**, **BLc,** and **BLd**.

and 2-hydroxy-1-naphthaldehyde based, in part, on conditions reported by Duan.[27] The chiral boron based compounds **BL** obtained from the interaction of (*S*)-2-aminobutan-1-ol and 2-hydroxy-1-naphthaldehyde have similar data to the previously mentioned spectroscopic result (Scheme 2). (*R*)-2-Aminobutan-1-ol was also used for the targetted product, but unfortunately it did not react.

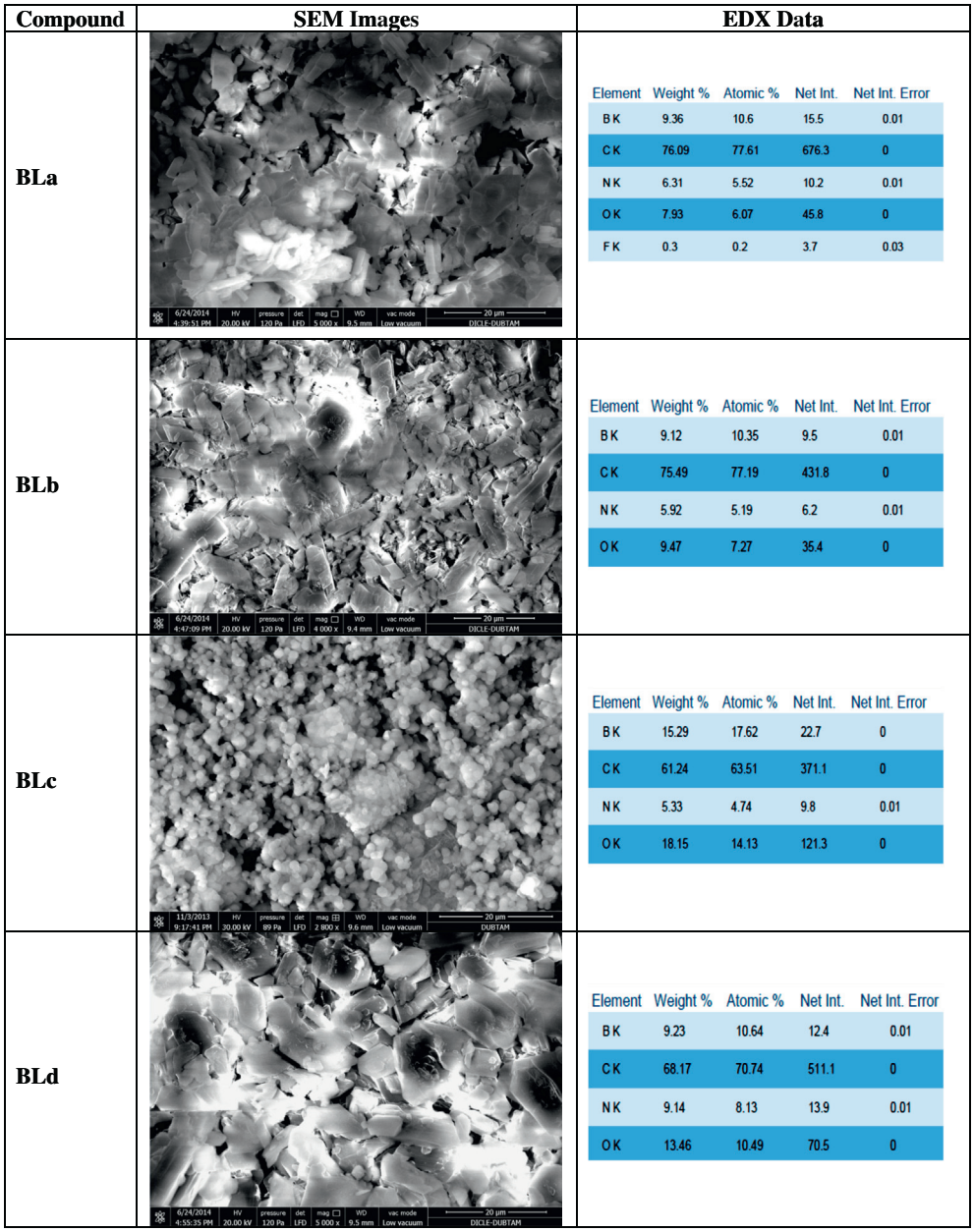
The peaks between 8.08 and 8.64 ppm correspond to the azomethine (C*H*=N) proton;[28–30] the disappearance of the O*H* groups indicates the binding of the boron atoms to the oxygen. The stretching vibrations of B–O are seen from 1312 $cm^{-1}$ to 1378 $cm^{-1}$; the stretching of B–Ph at 751–852 $cm^{-1}$ shows the interactions; the exact mass spectra of all compounds, which were obtained with a positive charged scan, indicate the meaningful values as calculated and expected.[31,29,32,33] The UV–Vis analysis of the boronic based molecules demonstrates the n→π* and π→π* electronic transitions arising from the donor atoms and aromatic rings.[34–36] The specific rotations were determined as $[\alpha]_D^{25}$ = +1.5 (*c* 0.5, DMSO), $[\alpha]_D^{25}$ = −3.5 (*c* 0.5, DMSO), $[\alpha]_D^{20}$ = −10.6 (*c* 1, DMSO), $[\alpha]_D^{25}$ = −6.7 (*c* 0.5, DMSO) for **BLa**, **BLb**, **BLc,** and **BLd**, respectively.

## 2.2. SEM and EDX results of compounds

The surface structure morphology of **BLa–d** compounds was determined under low vacuum at different magnifications by scanning electron microscope (SEM). The energy-dispersive X-ray spectroscopy (EDX) analyses were also accomplished simultaneously to investigate qualitative elemental percentages (Fig. 1).

## 2.3. Thermal investigation

The thermal behavior of the compounds, which were used as catalysts, was investigated by TGA/DTA under a nitrogen atmosphere with heating at 10 °C per minute. The thermograms showed



| Compound | SEM Images | EDX Data |
|---|---|---|
| **BLa** | | Element / Weight % / Atomic % / Net Int. / Net Int. Error<br>B K 9.36 10.6 15.5 0.01<br>C K 76.09 77.61 676.3 0<br>N K 6.31 5.52 10.2 0.01<br>O K 7.93 6.07 45.8 0<br>F K 0.3 0.2 3.7 0.03 |
| **BLb** | | Element / Weight % / Atomic % / Net Int. / Net Int. Error<br>B K 9.12 10.35 9.5 0.01<br>C K 75.49 77.19 431.8 0<br>N K 5.92 5.19 6.2 0.01<br>O K 9.47 7.27 35.4 0 |
| **BLc** | | Element / Weight % / Atomic % / Net Int. / Net Int. Error<br>B K 15.29 17.62 22.7 0<br>C K 61.24 63.51 371.1 0<br>N K 5.33 4.74 9.8 0.01<br>O K 18.15 14.13 121.3 0 |
| **BLd** | | Element / Weight % / Atomic % / Net Int. / Net Int. Error<br>B K 9.23 10.64 12.4 0.01<br>C K 68.17 70.74 511.1 0<br>N K 9.14 8.13 13.9 0.01<br>O K 13.46 10.49 70.5 0 |

**Figure 1.** SEM images and EDX results of **BLa**, **BLb**, **BLc**, **BLd**.

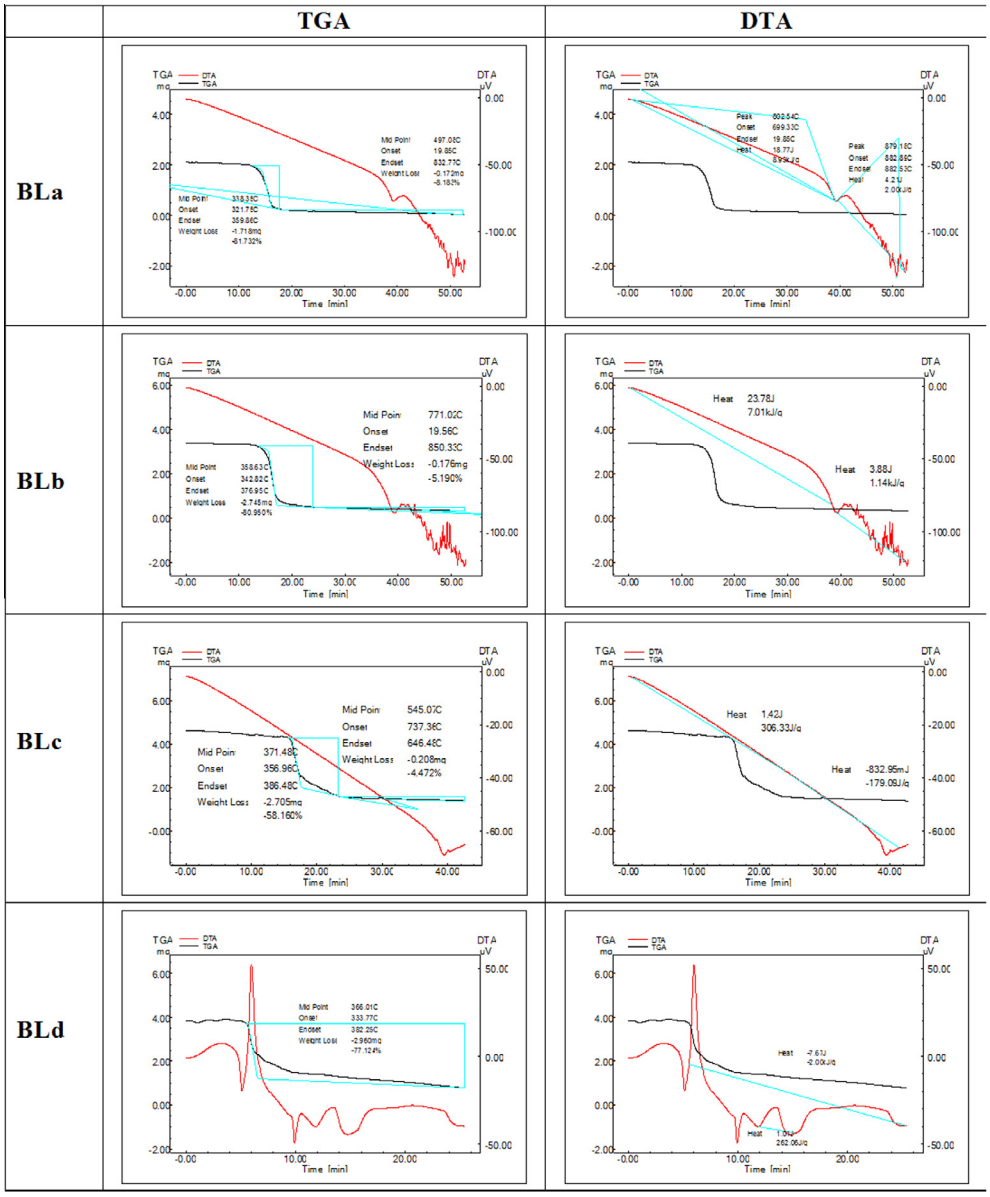



**Figure 2.** TGA and DTA thermograms of compounds.

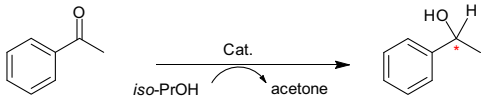
the boron compounds to be relatively stable up to 300 °C, since there was no remarkable weight loss until that temperature. Due to boron's nature, **BL** compounds had a resistance against decomposition at lower temperatures. However, catalytic reactions need stable reagents, which can prompt the hydrogenation throughout the reactions (Fig. 2).

Single and double step decompositions were attained for **BLa–d** compounds in the range of 25–800 °C. Weight losses were calculated as: 8.18% **BLa**; 80.85% and 5.19% **BLb**; 58.16% and 4.47% **BLc**; 77.12% (only at one step) **BLd**. Maintaining thermally stable without any weight loss indicates that they may be favorable for higher temperature catalyst reactions.

### 2.4. Asymmetric transfer hydrogenation of acetophenone derivatives with *iso*-PrOH

Chiral complexes **BLa–d** have been investigated as catalyst precursors for the asymmetric transfer hydrogenation of acetophenone under variable conditions. Additionally, a comparison of complexes as precatalysts for the asymmetric hydrogenation of acetophenone by *iso*-PrOH in the presence of KOH is summarized in Table 1. Catalytic experiments were carried out under an argon atmosphere using standard Schlenk-line techniques. These systems catalyzed the reduction of acetophenone into the corresponding alcohol (*S*)- or (*R*)-1-phenylethanol in the presence of KOH as a promoter. To an *iso*-PrOH solution of the boron-complex, an appropriate amount of acetophenone and KOH/*iso*-PrOH solutions were added at room temperature. The solution was stirred for several hours, and then examined with capillary GC analysis. At room temperature, the transfer hydrogenation of acetophenone occurred very slowly,[37] with low conversion (up to 32%, 72 h) and low to moderate enantioselectivity (up to 69% ee) (entries 1–4). Due to the reversibility at room temperature, prolonging the reaction time (144 h) led to a decrease in the enantioselectivity, as indicated by the catalytic results collected with **BLa–d** (entries 1 and 2,[d]).[38,39] Furthermore, as can be inferred from Table 1 (entries 5–8) the presence of a base is necessary to observe appreciable conversions. The base facilitates the formation of the ruthenium alkoxide by abstracting the proton of the alcohol and subsequently the alkoxide undergoes β-elimination to give ruthenium hydride, which is

**Table 1**
Asymmetric transfer hydrogenations of acetophenone with *iso*-PrOH catalyzed by boron-complexes **BLa–d**




| Entry | Complex | S/C/NaOH | Time | Conversion(%)[f] | % ee[g] | Configuration[h] |
|---|---|---|---|---|---|---|
| 1 | **BLa**[a] | 100:1:5 | 72 h (144 h)[d] | 30 (46)[d] | 69 (63) | (*S*) |
| 2 | **BLb**[a] | 100:1:5 | 72 h (144 h)[d] | 32 (47)[d] | 32 (30) | (*S*) |
| 3 | **BLc**[a] | 100:1:5 | 72 h | 13 | 57 | (*S*) |
| 4 | **BLd**[a] | 100:1:5 | 72 h | 21 | 34 | (*S*) |
| 5 | **BLa**[b] | 100:1 | 12 h | <3 | .... | .... |
| 6 | **BLb**[b] | 100:1 | 12 h | <3 | .... | .... |
| 7 | **BLc**[b] | 100:1 | 12 h | <3 | .... | .... |
| 8 | **BLd**[b] | 100:1 | 12 h | <3 | .... | .... |
| 9 | **BLa**[c] | 100:1:5 | 12 h (12 h)[e] | 98 (97)[e] | 70 (71) | (*S*) |
| 10 | **BLb**[c] | 100:1:5 | 12 h (12 h)[e] | 99 (98)[e] | 34 (33) | (*S*) |
| 11 | **BLc**[c] | 100:1:5 | 36 h | 99 | 56 | (*S*) |
| 12 | **BLd**[c] | 100:1:5 | 24 h | 97 | 32 | (*S*) |
| 13 | **BLa** | 100:1:3 | 12 h | 92 | 66 | (*S*) |
| 14 | **BLa** | 100:1:5 | 12 h | 98 | 70 | (*S*) |
| 15 | **BLa** | 100:1:7 | 12 h | 93 | 68 | (*S*) |
| 16 | **BLa** | 100:1:9 | 12 h | 92 | 67 | (*S*) |

Reaction conditions.
[a] At room temperature; acetophenone/Ru/NaOH, 100:1:5.
[b] Refluxing in *iso*-PrOH; acetophenone/Ru, 100:1, in the absence of base.
[c] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 100:1:5.
[d] At room temperature; acetophenone/Ru/NaOH, 100:1:5, (64 h).
[e] Refluxing in *iso*-PrOH; acetophenone/Ru/KOH, 100:1:5.
[f] Determined by GC (three independent catalytic experiments).
[g] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column.
[h] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, an (*S*)- or (*R*)-configuration was obtained in all experiments.

an active species in this reaction. This is a mechanism that has been proposed by several research groups on the studies of ruthenium catalyzed transfer hydrogenation reaction by metal hydride intermediates[40–43] namely, the role of the base is to generate a more nucleophilic alkoxide ion, which can rapidly attack the boron complex responsible for the dehydrogenation of *iso*-PrOH. In addition, the choice of base, such as KOH and NaOH, had little influence on the conversion or enantioselectivity (entries 9 and 10,[e]). Optimization studies of the catalytic reduction of acetophenone in *iso*-PrOH showed that good activity was obtained with a base/ligand ratio of 5:1 (Table 1). The reduction of acetophenone into (*S*)- or (*R*)-1-phenylethanol could be achieved in high yield by increasing the temperature up to 82 °C (Table 1, entries 9–12). Moreover, it is noteworthy that the catalytic system, **BLa–d** displays differences in reactivity. Compared to the other complexes, **BLa** appeared to be more effective than the other catalysts.

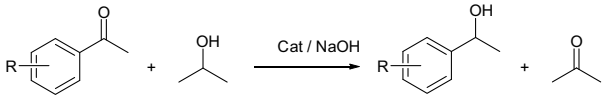
Our study revealed that the activity and enantioselectivity of the catalyst were sensitive to the substrate structures. Hence complexes **BLa–d** were further investigated in transfer hydrogenations of substituted acetophenone derivatives, and the results of these transformations are presented in Table 2. The catalytic reduction of acetophenone derivatives was all investigated with the conditions optimized for acetophenone. The results in Table 2 demonstrate that a range of acetophenone derivatives can be hydrogenated with good enantioselectivities. Complex **BLa** showed the highest activity with good enantioselectivity for most of the ketones listed in Table 2. Furthermore, the position and electronic properties of the ring substituents also influenced the hydrogenation results. The highest enantioselectivity was found for the transfer hydrogenation of *o*-methoxyacetophenone (78% ee), while the lowest enantioselectivity was observed in the transfer hydrogenation of *p*-methoxyacetophenone. From these results it can be seen that the introduction of an electron-donating group, such as methoxy group, to the *p*-position decelerates the reaction, while to the *o*-position increases the rate and improves the enantioselectivity. The introduction of electron-withdrawing substituents, such as F or $NO_2$, to the *para* positions of the aryl ring of the ketone, resulted in an improved activity with good enantioselectivity (entries 1–4 and 13–16, Table 2). The introduction of electron withdrawing substituents to the *para* position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was improved, thus giving rise to easier hydrogenation.[44,45]

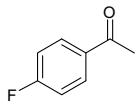
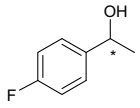
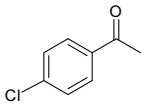
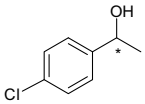
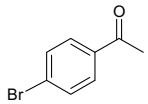
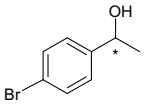
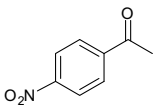
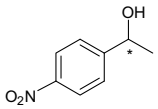
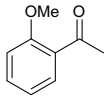
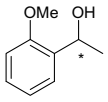
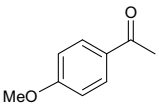
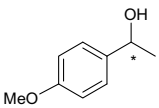
## 3. Experimental

### 3.1. Materials and methods

Analytical grade and deuterated solvents were purchased from Merck. The starting materials phenyl boronic acid, 6-methoxynaphthalen-2-ylboronic acid, 4-methyl-3-nitrophenylboronic acid and 1,4-phenylenediboronic acid were purchased from Fluka and used as received. $^1$H NMR (at 400.1 MHz), and $^{13}$C NMR (at 100.6 MHz) spectra were recorded on a Bruker Avance 400 spectrometer, with TMS (tetramethylsilane) as an internal reference. The IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. Specific rotations were taken on a Perkin–Elmer 341 model polarimeter. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by a Gallenkamp Model apparatus with open capillaries. GC analyses were performed on a Shimadzu GC 2010 Plus Gas Chromatograph equipped with cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness). Racemic samples of alcohols were obtained by reduction of the corresponding ketones with $NaBH_4$ and used as the authentic samples for ee determination. The GC parameters for asymmetric transfer hydrogenation of ketones were as follows; initial temperature, 50 °C;

**Table 2**
Asymmetric transfer hydrogenation results for substituted acetophenones catalyzed by boron-complexes, (**BLa–d**)[a]




| Entry | Catalyst | Substrate | Product | Time | Conversion(%)[b] | ee (%)[c] | Configration[d] |
|---|---|---|---|---|---|---|---|
| 1 | **BLa** |  |  | 4 h | 98 | 72 | (*S*) |
| 2 | **BLb** | | | 4 h | 99 | 36 | (*S*) |
| 3 | **BLc** | | | 12 h | 98 | 58 | (*S*) |
| 4 | **BLd** | | | 8 h | 97 | 34 | (*S*) |
| 5 | **BLa** |  |  | 7 h | 98 | 73 | (*S*) |
| 6 | **BLb** | | | 7 h | 97 | 35 | (*S*) |
| 7 | **BLc** | | | 16 h | 98 | 59 | (*S*) |
| 8 | **BLd** | | | 12 h | 99 | 35 | (*S*) |
| 9 | **BLa** |  |  | 10 h | 98 | 73 | (*S*) |
| 10 | **BLb** | | | 10 h | 98 | 36 | (*S*) |
| 11 | **BLc** | | | 20 h | 97 | 60 | (*S*) |
| 12 | **BLd** | | | 16 h | 99 | 37 | (*S*) |
| 13 | **BLa** |  |  | 4 h | 98 | 71 | (*S*) |
| 14 | **BLb** | | | 4 h | 99 | 35 | (*S*) |
| 15 | **BLc** | | | 12 h | 99 | 58 | (*S*) |
| 16 | **BLd** | | | 8 h | 98 | 36 | (*S*) |
| 17 | **BLa** |  |  | 15 h | 97 | 78 | (*S*) |
| 18 | **BLb** | | | 15 h | 99 | 42 | (*S*) |
| 19 | **BLc** | | | 40 h | 98 | 69 | (*S*) |
| 20 | **BLd** | | | 30 h | 99 | 47 | (*S*) |
| 21 | **BLa** |  |  | 24 h | 97 | 63 | (*S*) |
| 22 | **BLb** | | | 24 h | 99 | 30 | (*S*) |
| 23 | **BLc** | | | 48 h | 98 | 51 | (*S*) |
| 24 | **BLd** | | | 36 h | 99 | 27 | (*S*) |

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol %), 82 °C, the concentration of acetophenone is 0.1 M.
[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone.
[c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness).
[d] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values.

initial time 1.1 min; solvent delay, 4.48 min; temperature ramp 1.3 °C/min; final temperature, 150 °C; initial time 2.2 min; temperature ramp 2.15 °C/min; final temperature, 250 °C; initial time 3.3 min; final time, 44.33 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 μL.

### 3.2. General procedure for the transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen-transfer reaction: a solution of boron-complexes (0.01 mmol), NaOH (0.05 mmol) and the corresponding ketone (1 mmol) in degassed *iso*-PrOH (10 mL) was refluxed until the reaction was completed. Next, a sample of the reaction mixture was taken, diluted with acetone and analyzed immediately by GC; the conversions obtained are related to the residual unreacted ketone.

### 3.3. Synthesis of chiral ligand L

(*S*,*Z*)-1-((1-Hydroxy butane-2-yl imino)methyl)naphthalene-2-ol **L** was obtained by the reaction of (*S*)-2-aminobutan-1-ol and 2-hydroxy-1-naphthaldehyde in ethanol. The reaction was left for 6 h.[27] The product had a higher viscose form and was quite air sensitive. The (*R*)-enantiomer was synthesized as described in the literature.[27] $^1$H NMR (ppm, DMSO-$d_6$): $\delta$ = 0.94 (t, 3H, –C*H*$_3$), $\delta$ = 1.66 (p, 2H, –C*H*$_2$–), $\delta$ = 3.20 (p, H, –C*H*–(CH$_2$)$_2$), $\delta$ = 3.95 (q, 2H, –C*H*$_2$–OH), $\delta$ = 2.05 (s, 1H, CH$_2$–O*H*), $\delta$ = 5.10 (s, 1H, Ph–O*H*), $\delta$ = 8.16 (–C*H*=N), $\delta$ = 7.20, 7.84, 7.61, 7.33, 7.53 (m, naphthalene–C*H*). $[\alpha]_D^{25}$ = −11.9 (*c* 0.5, DMSO). FTIR-ATR (cm$^{-1}$): 3226 *v*(–OH), 3056 *v*(Ph–CH), 2965 *v*(Alif–CH), 1622 *v*(C=N), 1641 *v*(Ph–CH=CH–), 1183 *v*(Ph–O). *m*/*z*: 244 [M+H$^+$] $C_{15}H_{17}NO_2$ ($M_A$:243.30 g/mol).

### 3.4. General procedure for synthesis of BL

At first, 1 mmol of chiral ligand was dissolved in 15 mL ethanol in a round bottom flask. Then an equivalent amount (1 mmol for **BLa**, **BLb**, and **BLd**; 2 mmol for **BLc**) of the boronic derivative compounds was added to the ligand solution. The reaction mixture was conducted for 5 h at 110 °C. Yellow colored solid products were precipitated. After filtering and washing with an excess of solvent, they were dried in an oven.

#### 3.4.1. Data for BLa, BLb, BLc, and BLd

**BLa**: $^1$H NMR (ppm, DMSO-$d_6$): $\delta$ = 0.92 (t, 3H, –C*H*$_3$), $\delta$ = 1.59 (p, 2H, –C*H*$_2$–), $\delta$ = 3.27 (p, H, –C*H*–(CH$_2$)$_2$), $\delta$ = 4.04 (dd, 2H, –C*H*$_2$–O–), $\delta$ = 7.2 (m, Ph–C*H*), $\delta$ = 9.06 (–C*H*=N), $\delta$ = 7.19, 7.32, 7.62, 7.64, 7.78, 8.07 (m, naphthalene–C*H*). FTIR-ATR (cm$^{-1}$): 1377–1359 *v* (B–O), 1058 and 1027 *v*(B–C), 748 *v*(B–Ph), 3061 *v*(Ph–CH), 2931 *v*(–CH$_2$–CH$_2$–CH$_2$–), 1608 *v*(C=N), 1125 *v*((–CH$_2$)–CH–N=), 1625 *v*(Ph–CH=CH–), 1150 *v*(Ph–O). *m*/*z*: 330.16 [M+H$^+$] $C_{21}H_{20}NO_2B$ ($M_A$:329.20 g/mol). UV–vis (nm): $\lambda_1$ = 257 ($\varepsilon$ = 2.57 × 10$^3$), $\lambda_2$ = 262 ($\varepsilon$ = 2.62 × 10$^3$), $\lambda_3$ = 307 ($\varepsilon$ = 3.07 × 10$^3$), $\lambda_4$ = 401 ($\varepsilon$ = 4.01 × 10$^3$) (solvent: THF/DMSO). Elemental Analysis: Found (Calculated) C, 76.53 (76.62), H, 4.08 (4.12), N, 4.21 (4.25). Melting point: 238–240 °C.

**BLb**: $^1$H NMR (ppm, DMSO-$d_6$): $\delta$ = 1.15 (t, 3H, –C*H*$_3$), $\delta$ = 1.74 (p, 2H, –C*H*$_2$–), $\delta$ = 3.30 (p, H, –C*H*–(CH$_2$)$_2$), $\delta$ = 3.70 (s, naph-

thalene–O–$CH_3$), $\delta$ = 4.20 (dd, 2H, –$CH_2$–O–), $\delta$ = 7.13, 7.20, 7.40 (m, –B-naphthalene–C*H*), $\delta$ = 9.09 (–C*H*=N), $\delta$ = 7.28, 7.42, 7.64, 7.81 (m, naphthalene–C*H*). FTIR-ATR ($cm^{-1}$): 1376–1345 $\nu$(B–O), 1059 and 1017 $\nu$(B–C), 752 $\nu$(B–Ph), 3052 $\nu$(Ph–CH), 2961 $\nu$(–$CH_2$–$CH_2$–$CH_2$–), 1607 $\nu$(C=N), 1127 $\nu$((–$CH_2$)–CH–N=), 1625 $\nu$(Ph–CH=CH–), 1168 $\nu$(Ph–O). *m*/*z*: 410 [M+H$^+$] $C_{26}H_{24}NO_3B$ ($M_A$:409.28 g/mol). UV–vis (nm): $\lambda_1$ = 304 ($\varepsilon = 3.04 \times 10^3$), $\lambda_2$ = 330 ($\varepsilon = 3.30 \times 10^3$), $\lambda_3$ = 420 ($\varepsilon = 4.20 \times 10^3$) (solvent: THF/DMSO). Elemental Analysis: Found (Calculated) C, 76.17 (76.30), H, 4.58 (4.61), N, 3.40 (3.42). Melting point: 242–245 °C.

**BLc**: $^1$H NMR (ppm, DMSO-$d_6$): $\delta$ = 9.07 (s, C*H*=N), $\delta$ = 7.41, 7.45, 7.63, 7.65, 7.73 (naphthalene–C*H*) $\delta$ = 7.35 (m, Ph-*H*), $\delta$ = 4.28 (dd, 2H, –$CH_2$–O–), $\delta$ = 3.36 (m, 1H, =N–C*H*–$(CH_2)_2$), $\delta$ = 0.89 (t, 3H, –$CH_3$), $\delta$ = 1.58 (p, 2H, –CH–$CH_2$–$CH_3$). FTIR-ATR ($cm^{-1}$): 1342 $\nu$(B–O), 1062 $\nu$(B–C), 747 $\nu$(B–Ph), 3055 $\nu$(Ph–CH), 2967 $\nu$(–$CH_2$–$CH_2$–$CH_2$–), 1613 $\nu$(C=N), 1127 $\nu$((–$CH_2$)–CH–N=), 1630 $\nu$(Ph–CH=CH–),1150 $\nu$(Ph–O). *m*/*z*: 558 [M+H$^+$] $C_{36}H_{34}N_2O_2B_2$ ($M_A$: 557.29 g/mol). UV–vis(nm): $\lambda_1$ = 397 ($\varepsilon = 3.97 \times 10^3$), $\lambda_2$ = 422 ($\varepsilon = 4.22 \times 10^3$) (solvent: DMSO). Elemental Analysis: Found (Calculated) C, 58.39 (58.51), H, 4.81 (4.90), N, 4.77 (4.83). Melting point: 308–310 °C.

**BLd**: $^1$H NMR (ppm, DMSO-$d_6$): $\delta$ = 9.10 (s, –C*H*=N), $\delta$ = 7.33, 7.56, 7.54, 7.82, 7.98 (m, naphthalene–C*H*), $\delta$ = 7.33, 6.85 (Ph–*H*), $\delta$ = 0.93 (t, 3H, –$CH_3$), $\delta$ = 1.04 (p, 2H, –CH–$CH_2$–$CH_3$), $\delta$ = 2.34 (s, 3H, Ph–C***H*₃**), $\delta$ = 3.25 (p, H, –C*H*–$(CH_2)_2$), $\delta$ = 4.26 (dd, 2H, –$CH_2$–O–). FTIR-ATR ($cm^{-1}$): 1378–1334 $\nu$(B–O), 1078–1013 $\nu$(B–C), 748 $\nu$(B–Ph), 3069 $\nu$(Ph–CH), 2970 $\nu$((–$CH_2$)–CH–N=), 1609 $\nu$(C=N), 1127 $\nu$(Alif–C–N=), 1626 $\nu$(Ph–CH=CH–),1469 $\nu$(Ph–$CH_3$), 1195 $\nu$(Ph–O). *m*/*z*: 389 [M+H$^+$] $C_{22}H_{21}N_2O_4B$ ($M_A$:388.22 g/mol). UV–vis(nm): $\lambda_1$ = 281 ($\varepsilon = 2.81 \times 10^3$), $\lambda_2$ = 311 ($\varepsilon = 3.11 \times 10^3$), $\lambda_3$ = 328 ($\varepsilon = 3.28 \times 10^3$), $\lambda_4$ = 380 ($\varepsilon = 3.80 \times 10^3$). (Solvent: THF). Elemental Analysis: Found (Calculated) C, 68.38 (68.06), H, 4.41 (4.45), N, 7.18 (7.22). Melting point: 227–229 °C.

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