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# The Chiral Boronate-Catalyzed Asymmetric Transfer Hydrogenation of Various Aromatic Ketones to High-Value Alcohols: Preparation and Spectroscopic Studies

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### Abstract

This work deals with the synthesis, spectroscopic studies and catalytic evaluation of the novel chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their chiral boronate  $[L_1(B_{1,4})]$  and  $[L_2(B_{1,4})]$ complexes. Initially, the reaction of 5-azidomethyl salicylaldehyde and (R)-(-)-2-amino-1butanol in absolute ethanol afforded a new chiral salen ligand  $(L_1H_2)$ . Then, a novel chiral salen ligand  $(L_2H_2)$  have been prepared from chiral salen ligand  $(L_1H_2)$  for the synthesis of boronate  $[L_2(B_{1-4})]$  complexes through click reaction approach under ambient conditions. The reaction of chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands with various boronic acids afforded a new tetra-coordinated mononuclear chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes. All the compounds are remarkably stable crystalline solids and were obtained in good yields. For the full characterization of newly synthesized chiral salen ligands and their boronate complexes, the FT-IR, UV-Vis, NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B), LC-MS, and elemental analysis techniques have been used. The well-shaped chiral boronate compounds were investigated as catalyst for the asymmetric transfer hydrogenation (ATH) of aromatic ketones under appropriate settings. Particularly, it was proved that the ferrocene-based boronate compounds can afford an efficient catalytic conversion compared to the other boronate complexes in the asymmetric transfer hydrogenation catalytic studies.

Keywords: Chiral salen ligands, Boronate complexes, Spectroscopy, Catalyst, Asymmetric Transfer Hydrogenation, Ketone

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#### **1. Introduction**

In the last decades, environmentally friendly tri and tetra-coordinate boron compounds and related different boronate derivatives have found a wide range of application fields in synthetic chemistry, chemical industry, materials science, energy research, pharmacology, cytotoxicity and bioimaging cells, catalysis and other application areas [1-5]. In addition, highly Lewis acidic organoboron compounds continue to attract tremendous interest and current applications range from Lewis acid catalysis of organic transformations and polymerization reactions to small molecule activation, sensors for anions, and the development of new and unusual electronic materials [6]. Besides, significant advances for developing a wide range of new chiral catalysts and improvement studies toward high enantioselectivity and practicability of boron-based catalytic transfer hydrogenation of various ketones have been accomplished [7-10]. In light of those researches, the development of an effective and new a stable metal-free catalytst for the asymmetric transfer hydrogenation of aromatic ketones is one of the main aim for the many scientists due to the expensive and causing environmental pollution of metal-based homogeneous catalysts [10-12]. Therefore, the production of the high-value alcohols through the asymmetric transfer hydrogenation of various ketones was the factor for which the research of the effective, robust, cheap, easy-tohandle, air-stable and different structure catalyst has been continued.

The asymmetric transfer hydrogenation of unsaturated carbonyl functionalities in the presence of *iso*PrOH as a hydrogen source is one of the most important chemical transformations to precious alcohols. The transfer hydrogenation process, which involves hydrogen transfer from a donor to an acceptor, has become one of the most important synthetic routes for producing highly active and enantioselective alcohols from different ketones [13]. Symetric or asymmetric transfer hydrogenation is the addition of hydrogen to an unsaturated molecule using a reagent other than hydrogen gas. Although the direct

hydrogenation of aromatic ketones is more widely applied, transfer hydrogenation is an attractive alternative [14-16]. Numerous various catalysts were developed for transfer hydrogenation of various aromatic ketones to high-value alcohols, which includes homogeneous metal complexes [17, 18], metal-free homogeneous organocatalysts such as boron, phosphorus and chiral auxiliaries [10, 19-21], and apart from transition metal complexes and metal-free organocatalysts, zeolites, oxides of cerium and metal-organic frameworks have also been used for transfer hydrogenation [22, 23].

To the best of our knowledge, the litareture demonstrates that the use of boronate complexes for the asymmetric transfer hydrogenation of various ketones to high-value alcohols is very rare. However, asymmetric transfer hydrogenation is also an operationally simple method to synthesize highly enantioselective chiral alcohols with the use of hydrogen donors in the presence of new chiral boronate catalysts. Recently, our research group reported the synthesis and catalytic properties of a series of novel salen/salan boron compounds because the salicylaldimine boron complexes have gained increasing interest. In this work, we describe the synthesis and spectroscopic properties of new chiral salen ligands and their metal-free one-pot synthesis of four-coordinate chiral boronate complexes using boronic acids and chiral salen ligands. Then, these chiral boronate complexes were investigated as catalysts for the asymmetric transfer hydrogenation of acetophenone derivatives under suitable conditions. The probable structures of all the newly synthesized compounds were assigned by the FT-IR, UV-Vis, NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B) spectroscopic results of all newly chiral salen ligands and their giands and their chiral boronate complexes are consistent with proposed structure.

#### 2. Experimental Section

#### 2. 1. General Considerations

All organic solvents and starting materials used for the synthesis of the novel chiral salen ligands and their boronate complexes were purchased from Aldrich Inc. or Fluka Inc. and used without further purification. All reactions requiring a dry atmosphere were performed under a argon (Ar) gas atmosphere in standard Schlenk techniques. FT-IR spectra were performed with a Perkin-Elmer Two UATR-FT spectrophotometer in the range of 4000 to 400 cm<sup>-1</sup> at 25 °C equipped with ATR accessory. <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR spectra were obtained with an Agilent Technologies or a Bruker Avance instrument (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz and <sup>11</sup>B: 192.5 MHz) in DMSO-d<sub>6</sub> with TMS as internal standard. All the NMR spectra were measured at 298 K unless otherwise mentioned. Chemical shifts are reported in delta ( $\delta$ ) units in ppm downfield from TMS, and J values are given in Hertz. Elemental analyses measurements of the novel ligands and their boronate complexes were carried out on a LECO CHNS 932 model elemental analyzer. Mass spectra were determined with an Agilent LC-MS spectrometer (LC-MS/MS). UV-Vis spectra were determined using a Perkin-Elmer model Lambda 25 spectrometer in the scan range of 200 to 1100 nm using quartz cuvettes at room temperature and studied in EtOH. Melting points were determined using an Electrothermal 9100 and uncorrected. GC analyses were performed on a Shimadzu 2010 Plus Gas Chromatograph equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m x 0.32 mm x 0.25 µm). The GC parameters for the transfer hydrogenation of ketones were as follows: initial temperature, 110 °C; initial time, 1 min; solvent delay, 4.48 min; temperature ramp 80 °C/min; final temperature, 200 °C; final time, 21.13 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 µL. The key starting material 5-chloromethyl salicylaldehyde was synthesised according to literature procedures [24, 25].

### 2. 2. Synthesis of chiral ligand $(L_1H_2)$

Firstly, a solution of 5-chloromethyl salicylaldehyde (3.30 g, 19.2 mmol) and NaN<sub>3</sub> (1.25 g, 19.2 mmol) in DMF (20 mL) was heated at 100 °C during overnight stirring vigorously (Scheme 1). When TLC analysis showed complete comsumption of the starting material the reaction was cooled to room temperature and then the crude product was added to the water and the target product was extracted into the chloroform (3 x 100 mL). Organic phase dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated and residue was used without further purification, affording dark red crystals of the product [26]. After 5-azidomethyl salicylaldehyde was synthesized, a mixture of 5-azidomethyl salicylaldehyde (2.0 g, 11.30 mmol) and (R)-(-)-2amino-1-butanol (1.0 g, 11.30 mmol) were placed into a two-necked-flask, equipped with a argon (Ar) connection in ethanol (40 mL), which was stirred and refluxed for 6 h, in the presence of two drop formic acid as catalyst. After this time, the mixture was allowed to cool to 25 °C. All solvent was removed and the solid was washed three times with diethyl ether and n-hexane, successively, and dried under vacuum. Finally, re-crystallization from  $CH_3Cl/C_2H_5OH$  by slow evaporation afforded pure chiral salen ligand ( $L_1H_2$ ), successfully. Color: red, yield (%): 81, M.p.: 145 °C, Elemental Analysis (calculated for C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>) (F.W: 248.3 g/mol) (%): C, 58.05; H, 6.50; N, 22.57. Found: C, 58.01; H, 6.46; N, 22.53. LC-MS (Scan ES<sup>+</sup>):  $m/z = 249.3 [M+H]^+$  and 294.3  $[M+2Na]^+$ . FT-IR (ATR,  $v_{max}$ -cm<sup>-1</sup>): 3520-2438 v(OH····N=CH), 3048 v(Ar-CH), 2965-2874 v(Aliph-CH), 2103 v(N<sub>3</sub>), 1658 v(C=N), 1533-1495 v(C=C), and 1122 v(C-O). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 13.42 (s, 1H, OH, Dexchangeable), 8.37 (s, 1H, HC=N), 7.92 (s, 3H, Ar-CH), 4.34 (s, 1H, CH<sub>2</sub>-OH), 3.64 (q, 2H, CH2-OH), 3.34 (q, 1H, CH-N=CH), 2.85 (s, 2H, Ph-CH2-N3), 1.62 (m, 2H, CH3-CH2-CH), and 0.88 (t, 3H, J = 7.4 Hz, CH<sub>3</sub>-CH<sub>2</sub>-CH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 165.82 (HC=N), 161.27, 132.18, 131.70, 128.40, 118.57 and 116.56 (Ar-CH), 67.78 (-CH<sub>2</sub>-OH), 62.13 (CH=N-<u>C</u>H), 54.33 (-<u>C</u>H<sub>2</sub>-N<sub>3</sub>), 36.22 (CH<sub>3</sub>-<u>C</u>H<sub>2</sub>), and 11.48 (CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). UV-Vis  $(\lambda_{max}/(nm), * = shoulder peak)$ : 231, 253, 268, 286\* and 324 (C<sub>2</sub>H<sub>5</sub>OH).

## 2. 3. Synthesis of chiral ligand $(L_2H_2)$

The click reaction to form 1, 2, 3-triazole-containing ligand  $(L_2H_2)$  was carried out by modification of a published procedure [27, 28] via click chemistry approach (Scheme 1). To the solution of the azido-functionalized ligand  $(L_1H_2)$  (0.50 g, 2.01 mmol) in a 1:1 (25:25 mL) mixture of THF and water in a round bottom flask, an excess quantity of propargyl alcohol was added. After this time, CuSO<sub>4</sub> (0.16 g, dissolved in 3 mL water) and freshly prepared sodium ascorbate solution (0.12 g, dissolved in 2 mL water) were added to the continuously stirred reaction mixture at room temperature overnight. After THF solvent was removed in vacuo, 10 mL CH<sub>2</sub>Cl<sub>2</sub> and 3 mL conc. NH<sub>3</sub> were added to the solution at 25 °C and then organic layer was dried with MgSO<sub>4</sub>. The pure ligand  $(L_1H_2)$  was collected after evaporating all solvent. Finally, the novel ligand  $(L_1H_2)$  was recrystallized from CH<sub>3</sub>Cl and nhexane. Color: green, yield (%): 78, M.p.: 172 °C, Elemental Analysis (calculated for C<sub>15</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub>) (F.W: 304.3 g/mol) (%): C, 59.20; H, 6.62; N, 18.41. Found: C, 59.16; H, 6.57; N, 18.38. LC-MS (Scan ES<sup>+</sup>):  $m/z = 305.3 [M+H]^+$  and 327.2  $[M+Na]^+$ . FT-IR (ATR,  $v_{max}$ cm<sup>-1</sup>): 3647 v(triazole-OH), 3478-2493 v(OH····N=CH), 3048 v(Ar-CH), 2962-2870 v(Aliph-CH), 1637 v(C=N), 1540 v(triazole-C=C), 1476 v(triazole-N=N), and 1117 v(C-O). <sup>1</sup>H-NMR  $(DMSO-d_6): \delta$  (ppm) = 13.30 (s, 1H, OH, D-exchangeable), 8.42 (s, 1H, HC=N), 7.99 (s, 1H, triazole-CH), 7.93 (s, 3H, Ar-CH), 5.69 (s, 1H, triazole-CH<sub>2</sub>-OH), 4.13 (s, 2H, triazole-N-CH<sub>2</sub>), 3.94 (s, 2H, triazole-CH<sub>2</sub>-OH), 2.87 (q, 2H, CH<sub>2</sub>-OH), 2.71 (q, 1H, CH-N=CH), 1.53 (s, 1H, CH<sub>2</sub>-O<u>H</u>), 1.21 (m, 2H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-CH), and 0.86 (s, 3H, Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH). <sup>13</sup>C-NMR  $(DMSO-d_6): \delta$  (ppm) = 162.78 (HC=N), 161.26, 136.59, 133.56, 132.74, 124.47 and 117.66 (Ar-CH), 143.12 (triazole-CH), 122.47 (triazole-C-CH<sub>2</sub>OH), 67.05 (-CH<sub>2</sub>-OH), 61.74 (CH=N-<u>C</u>H), 56.09 (N-<u>C</u>H<sub>2</sub>-Ph), 52.15 (triazole-<u>C</u>H<sub>2</sub>-OH), 32.28 (CH<sub>3</sub>-<u>C</u>H<sub>2</sub>), and 11.42 (CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). UV-Vis ( $\lambda_{max}/(nm)$ , \* = shoulder peak): 233, 254, 269, 315\* and 382 (C<sub>2</sub>H<sub>5</sub>OH).

## 2. 4. Synthesis of chiral boronate $[L_1(B_{1-4})]$ complexes

At first, chiral salen ligand  $(L_1H_2)$  (0.30 g, 1.21 mmol) was dissolved in 30 mL toluene in a round-bottomed flask under N<sub>2</sub> atmosphere and the mixtures were stirred for 30 min. Under stirring, an equivalent amount ferrocene boronic acid (0.28 g, 1.21 mmol) for  $[L_1B_1]$  complex, butylboronic acid (0.12 g, 1.21 mmol) for  $[L_1B_2]$  complex, 3,5-bis(trifluoromethyl)phenyl boronic acid (0.32 g, 1.21 mmol) for  $[L_1B_3]$  complex or phenylboronic acid (0.15 g, 1.21 mmol) for  $[L_1B_4]$  complex was added, and then, stirring was continued for overnight at reflux temperature. Upon cooling to room temperature, stirring was maintained, and the solutions turned from red to brown for chiral boronate  $[L_1(B_{1.4})]$  complexes. All solvent was removed and the solid was washed three times with diethyl ether with n-hexane and dried under vacuum to get pure products.

[ $L_1B_1$ ] complex: Color: brown, yield (%): 72, M.p. > 300 °C, Elemental Analysis (calculated for C<sub>22</sub>H<sub>23</sub>BFeN<sub>4</sub>O<sub>2</sub>) (F.W: 442.1 g/mol) (%): C, 59.77; H, 5.24; N, 12.67. Found: C, 59.72; H, 5.20; N, 12.61. LC-MS (Scan ES<sup>+</sup>): m/z = 442.2 [M]<sup>+</sup> and 488.1 [M+2Na]<sup>+</sup>. FT-IR (ATR,  $v_{max}$ -cm<sup>-1</sup>): 3086 v(Ar-CH), 2968-2877 v(Aliph-CH), 2113 v(N<sub>3</sub>), 1624 v(C=N), 1547-1462 v(C=C), 1380 v(Fer C-C), 1122 v(B-O), 1109 v(C-O) and 891 v(B-C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 8.42 (s, 1H, <u>H</u>C=N), 7.48 (s, 3H, Ar-C<u>H</u>), 4.44 (s, 2H, Fer-C<u>H</u>), 4.29 (s, 2H, Fer-C<u>H</u>), 4.08 (s, 5H, Fer-C<u>H</u>), 2.73 (q, 2H, C<u>H</u><sub>2</sub>-O-B), 2.34 (s, 1H, C<u>H</u>-N=CH), 2.08 (s, 2H, Ph-C<u>H</u><sub>2</sub>-N<sub>3</sub>), 1.23 (m, 2H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-CH), and 0.87 (t, 3H, *J* = 7.4 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 164.42 (H<u>C</u>=N), 160.98, 148.03, 134.52, 122.08, 119.49 and 118.21 (Ar-<u>C</u>H), 73.83, 72.91, 71.49 and 69.99 (Fer-<u>C</u>H), 68.53 (-<u>C</u>H<sub>2</sub>-O-), 59.77 (CH=N-<u>C</u>H), 53.96 (-<u>C</u>H<sub>2</sub>-N<sub>3</sub>), 37.28 (CH<sub>3</sub>-<u>C</u>H<sub>2</sub>), and 11.55 (CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). <sup>11</sup>B NMR (DMSO-

d<sub>6</sub>, 192.5 MHz, 23 °C, δ ppm): 29.41. UV-Vis ( $\lambda_{max}/(nm)$ , \* = shoulder peak): 234, 269, 288\* and 329 (C<sub>2</sub>H<sub>5</sub>OH).

[*L*<sub>1</sub>*B*<sub>2</sub>] complex: Color: brown, yield (%): 70, M.p. > 300 °C, Elemental Analysis (calculated for C<sub>16</sub>H<sub>23</sub>BN<sub>4</sub>O<sub>2</sub>) (F.W: 314.2 g/mol) (%): C, 61.16; H, 7.38; N, 17.83. Found: C, 61.11; H, 7.33; N, 17.79. LC-MS (Scan ES<sup>+</sup>): m/z = 315.2 [M+H]<sup>+</sup> and 337.2 [M+Na]<sup>+</sup>. FT-IR (ATR,  $\nu_{max}$ -cm<sup>-1</sup>): 3045  $\nu$ (Ar-CH), 2960-2871  $\nu$ (Aliph-CH), 2110  $\nu$ (N<sub>3</sub>), 1633  $\nu$ (C=N), 1569-1459  $\nu$ (C=C), 1155  $\nu$ (B-O), 1112  $\nu$ (C-O) and 896  $\nu$ (B-C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 8.39 (s, 1H, <u>H</u>C=N), 7.38 (s, 3H, Ar-C<u>H</u>), 4.62 (q, 2H, C<u>H</u><sub>2</sub>-O-B), 3.04 (q, 1H, C<u>H</u>-N=CH), 2.11 (s, 2H, Ph-C<u>H</u><sub>2</sub>-N<sub>3</sub>), 1.58 (m, 2H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-CH), 1.48 (m, 4H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-C<u>H</u><sub>2</sub>-CH<sub>2</sub>-B), 1.21 (t, 3H, *J* = 7.1 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH), 0.88 (t, 3H, *J* = 7.1 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-B), and 0.56 (t, 2H, *J* = 7.4 Hz, B-C<u>H</u><sub>2</sub>-). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 162.70 (H<u>C</u>=N), 158.93, 132.21, 131.52, 130.08, 124.49 and 118.60 (Ar-<u>C</u>H), 68.51 (CH=N-<u>C</u>H), 66.10 (-<u>C</u>H<sub>2</sub>-O-), 56.37 (-<u>C</u>H<sub>2</sub>-N<sub>3</sub>), 34.72 (B-<u>C</u>H<sub>2</sub>), 27.11 (CH<sub>3</sub>-<u>C</u>H<sub>2</sub>-CH<sub>2</sub>-), 26.92 (-N-CH-<u>C</u>H<sub>2</sub>), 15.42 (CH<sub>3</sub>-CH<sub>2</sub>-C<sub>1</sub>), 14.32 (<u>C</u>H<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), and 11.53 (CH-CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). <sup>11</sup>B NMR (DMSO-d<sub>6</sub>, 192.5 MHz, 23 °C,  $\delta$  ppm): 32.44. UV-Vis ( $\lambda_{max}/(nm)$ , \* = shoulder peak): 244, 268, 286\* and 326 (C<sub>2</sub>H<sub>5</sub>OH).

[ $L_1B_3$ ] complex: Color: brown, yield (%): 76, M.p. > 300 °C, Elemental Analysis (calculated for C<sub>20</sub>H<sub>17</sub>BF<sub>6</sub>N<sub>4</sub>O<sub>2</sub>) (F.W: 470.2 g/mol) (%): C, 51.09; H, 3.64; N, 11.92. Found: C, 51.05; H, 3.60; N, 11.89. LC-MS (Scan ES<sup>+</sup>): m/z = 471.2 [M+H]<sup>+</sup> and 493.2 [M+Na]<sup>+</sup>. FT-IR (ATR,  $v_{max}$ -cm<sup>-1</sup>): 3038 v(Ar-CH), 2973-2883 v(Aliph-CH), 2114 v(N<sub>3</sub>), 1637 v(C=N), 1566-1463 v(C=C), 1161 v(B-O), 1122 v(C-O) and 897 v(B-C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>):  $\delta$ (ppm) = 8.83 (s, 1H, <u>H</u>C=N), 8.33 (s, 1H, Ar-C<u>H</u>), 8.27 (s, 1H, Ar-C<u>H</u>), 8.15 (s, 1H, Ar-C<u>H</u>), 7.90 (s, 1H, Ar-C<u>H</u>), 7.37 (d, 1H, J = 6.4 Hz, Ar-C<u>H</u>), 7.29 (d, 1H, J = 6.4 Hz, Ar-C<u>H</u>), 3.55 (q, 2H, C<u>H</u><sub>2</sub>-O-B), 3.10 (q, 1H, C<u>H</u>-N=CH), 2.68 (s, 2H, Ph-C<u>H</u><sub>2</sub>-N<sub>3</sub>), 1.49 (m, 2H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-CH), and 1.02 (t, 3H, J = 7.0 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 164.86 (H<u>C</u>=N), 162.72, 160.27, 141.97, 134.35, 132.77, 132.04, 129.59, 121.75, 120.24, 118.65, and 108.53 (Ar-<u>C</u>H), 124.54 (-<u>C</u>F<sub>3</sub>), 65.33 (CH=N-<u>C</u>H), 60.68 (-<u>C</u>H<sub>2</sub>-O-), 54.22 (-<u>C</u>H<sub>2</sub>-N<sub>3</sub>), 22.54 (CH-<u>C</u>H<sub>2</sub>-CH<sub>3</sub>), and 15.29 (CH-CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). <sup>11</sup>B NMR (DMSO-d<sub>6</sub>, 192.5 MHz, 23 °C, δ ppm): 23.32. UV-Vis ( $\lambda_{max}/(nm)$ , \* = shoulder peak): 250, 270, 291\* and 364 (C<sub>2</sub>H<sub>5</sub>OH).

[*L*<sub>1</sub>*B*<sub>4</sub>] *complex:* Color: brown, yield (%): 72, M.p. > 300 °C, Elemental Analysis (calculated for C<sub>18</sub>H<sub>19</sub>BN<sub>4</sub>O<sub>2</sub>) (F.W: 334.2 g/mol) (%): C, 64.69; H, 5.73; N, 16.77. Found: C, 64.65; H, 5.68; N, 16.74. LC-MS (Scan ES<sup>+</sup>): m/z = 335.2 [M+H]<sup>+</sup> and 381.2 [M+Na]<sup>+</sup>. FT-IR (ATR,  $v_{max}$ -cm<sup>-1</sup>): 3064 and 3008 v(Ar-CH), 2970-2878 v(Aliph-CH), 2111 v(N<sub>3</sub>), 1635 v(C=N), 1560-1459 v(C=C), 1123 v(B-O), 1119 v(C-O) and 896 v(B-C). <sup>1</sup>H-NMR (DMSOd<sub>6</sub>): δ (ppm) = 8.40 (s, 1H, <u>H</u>C=N), 8.19 (s, 5H, Ar-C<u>H</u>), 7.75 (s, 1H, Ar-C<u>H</u>), 7.33 (d, 2H, *J* = 7.5 Hz, Ar-C<u>H</u>), 4.34 (q, 2H, C<u>H</u><sub>2</sub>-O-B), 3.49 (m, 1H, C<u>H</u>-N=CH), 2.71 (s, 2H, Ph-C<u>H</u><sub>2</sub>-N<sub>3</sub>), 1.43 (m, 2H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-CH), and 0.86 (t, 3H, *J* = 7.1 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>): δ (ppm) = 165.42 (H<u>C</u>=N), 162.78, 153.68, 134.48, 131.98, 130.37, 127.75, 122.75, 114.05, and 108.15 (Ar-<u>C</u>H), 68.16 (CH=N-<u>C</u>H), 63.22 (-<u>C</u>H<sub>2</sub>-O-), 55.32 (-<u>C</u>H<sub>2</sub>-N<sub>3</sub>), 25.67 (CH-<u>C</u>H<sub>2</sub>-CH<sub>3</sub>), and 16.29 (CH-CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). <sup>11</sup>B NMR (DMSO-d<sub>6</sub>, 192.5 MHz, 23 °C, δ ppm): 28.87. UV-Vis (λ<sub>max</sub>/(nm), \* = shoulder peak): 256, 271, 284, 331 and 370\* (C<sub>2</sub>H<sub>5</sub>OH).

## 2. 5. Synthesis of chiral boronate $[L_2(B_{1-4})]$ complexes

At first, chiral salen ligand  $(L_2H_2)$  (0.30 g, 0.99 mmol) was dissolved in 25 mL toluene in each a round-bottomed flask under N<sub>2</sub> atmosphere and the mixtures were stirred for 45 min. Under stirring, an equivalent amount ferrocene boronic acid (0.23 g, 0.99 mmol) for  $[L_2B_1]$  complex, butylboronic acid (0.10 g, 0.99 mmol) for  $[L_2B_2]$  complex, 3,5-bis(trifluoromethyl)phenyl boronic acid (0.26 g, 0.99 mmol) for  $[L_2B_3]$  complex or phenylboronic acid (0.12 g, 1.21 mmol) for  $[L_2B_4]$  complex was added, and then, stirring was continued for overnight at reflux temperature. Upon cooling to room temperature, stirring was maintained, and the solutions turned from green to dark green for chiral boronate  $[L_2(B_{1.4})]$ 

complexes. All solvent was removed and the solid was washed three times with diethyl ether and n-hexane and dried under vacuum to get pure products.

[*L*<sub>2</sub>*B*<sub>1</sub>] *complex:* Color: dark green, yield (%): 70, M.p. > 300 °C, Elemental Analysis (calculated for C<sub>25</sub>H<sub>27</sub>BFeN<sub>4</sub>O<sub>3</sub>) (F.W: 498.2 g/mol) (%): C, 60.28; H, 5.46; N, 11.25. Found: C, 60.21; H, 5.41; N, 11.21. LC-MS (Scan ES<sup>+</sup>): m/z = 499.2 [M+H]<sup>+</sup> and 521.2 [M+Na]<sup>+</sup>. FT-IR (ATR,  $v_{max}$ -cm<sup>-1</sup>): 3655 v(triazole-OH), 3084 v(Ar-CH), 2963-2874 v(Aliph-CH), 1628 v(C=N), 1538 v(N=N), 1465 v(C=C), 1382 v(Fer C-C), 1158 v(B-O), 1106 v(C-O) and 890 v(B-C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 8.21 (s, 1H, <u>H</u>C=N), 7.93 (d, 2H, *J* = 6.4 Hz, Ar-C<u>H</u>), 7.68 (s, 1H, Ar-C<u>H</u>), 7.32 (s, 1H, triazole-C<u>H</u>), 5.48 (s, 1H, triazole-CH<sub>2</sub>-O<u>H</u>), 4.49 (s, 2H, triazole-C<u>H</u><sub>2</sub>-OH), 4.24 (s, 2H, Fer-C<u>H</u>), 4.16 (s, 2H, Fer-C<u>H</u>), 4.06 (s, 5H, Fer-C<u>H</u>), 2.87 (s, 2H, C<u>H</u><sub>2</sub>-O-B), 2.71 (s, 1H, C<u>H</u>-N=CH), 2.34 (s, 2H, Ph-C<u>H</u><sub>2</sub>-), 1.22-1.06 (m, 2H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-CH), and 0.81 (s, 3H, -C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 162.74 (H<u>C</u>=N), 160.82, 148.08, 135.02, 121.98, 119.43 and 118.17 (Ar-<u>C</u>H), 148.31 (triazole-<u>C</u>H), 127.90 (triazole-<u>C</u>-CH<sub>2</sub>-OH), 73.92, 72.83, 70.54 and 69.32 (Fer-<u>C</u>H), 66.59 (-<u>C</u>H<sub>2</sub>-O-B), 59.46 (CH=N-<u>C</u>H), 55.76 (triazole-<u>C</u>H<sub>2</sub>-OH), 54.40 (Ph-<u>C</u>H<sub>2</sub>-triazole), 36.24 (CH<sub>3</sub>-<u>C</u>H<sub>2</sub>), and 11.63 (CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). <sup>11</sup>B NMR (DMSO-d<sub>6</sub>, 192.5 MHz, 23 °C,  $\delta$  ppm): 28.82. UV-Vis (A<sub>max</sub>/(nm), \* = shoulder peak): 245, 271, 311\* and 378 (C<sub>2</sub>H<sub>5</sub>OH).

[ $L_2B_2$ ] complex: Color: dark green, yield (%): 74, M.p. > 300 °C, Elemental Analysis (calculated for C<sub>19</sub>H<sub>27</sub>BN<sub>4</sub>O<sub>3</sub>) (F.W: 370.2 g/mol) (%): C, 61.63; H, 7.35; N, 15.13. Found: C, 61.59; H, 7.32; N, 15.09. LC-MS (Scan ES<sup>+</sup>): m/z = 371.2 [M+H]<sup>+</sup> and 409.2 [M+K]<sup>+</sup>. FT-IR (ATR,  $v_{max}$ -cm<sup>-1</sup>): 3653 v(triazole-OH), 3064 v(Ar-CH), 2963-2878 v(Aliph-CH), 1630 v(C=N), 1536 v(N=N), 1468 v(C=C), 1161 v(B-O), 1115 v(C-O) and 895 v(B-C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 8.08 (s, 1H, <u>H</u>C=N), 7.71 (s, 1H, triazole-C<u>H</u>), 7.34 (s, 1H, Ar-C<u>H</u>), 7.13 (d, 1H, J = 4.8 Hz, Ar-C<u>H</u>), 6.66 (d, 1H, J = 4.8 Hz, Ar-C<u>H</u>), 5.68 (s, 2H, triazole-C<u>H</u><sub>2</sub>-Ph), 5.32 (s, 1H, triazole-CH<sub>2</sub>-O<u>H</u>), 4.68 (s, 2H, triazole-C<u>H</u><sub>2</sub>-OH), 4.46 (q, 2H, C<u>H</u><sub>2</sub>-O-B), 2.89 (s, 1H, C<u>H</u>-N=CH), 1.98 (m, 2H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-CH), 1.47 (m, 4H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-C<u>H</u><sub>2</sub>-CH<sub>2</sub>-B), 1.23 (t, 3H, J = 7.0 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH), 1.04 (t, 3H, J = 7.1 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-B), and 0.86 (t, 2H, J = 7.3 Hz, B-C<u>H</u><sub>2</sub>-). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 162.65 (H<u>C</u>=N), 157.83, 132.71, 131.80, 128.98, 124.53 and 116.68 (Ar-<u>C</u>H), 148.30 (triazole-<u>C</u>H), 128.91 (triazole-<u>C</u>-CH<sub>2</sub>-OH), 66.18 (-<u>C</u>H<sub>2</sub>-O-B), 63.50 (CH=N-<u>C</u>H), 57.43 (Ph-<u>C</u>H<sub>2</sub>-triazole), 54.46 (triazole-<u>C</u>H<sub>2</sub>-OH), 34.76 (B-<u>C</u>H<sub>2</sub>), 27.12 (CH<sub>3</sub>-<u>C</u>H<sub>2</sub>.CH<sub>2</sub>-), 26.91 (-N-CH-<u>C</u>H<sub>2</sub>), 15.32 (CH<sub>3</sub>-CH<sub>2</sub>. <u>C</u>H<sub>2</sub>-), 14.28 (<u>C</u>H<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), and 11.52 (CH-CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). <sup>11</sup>B NMR (DMSO-d<sub>6</sub>, 192.5 MHz, 23 °C,  $\delta$  ppm): 32.38. UV-Vis ( $\lambda_{max}/(nm)$ , \* = shoulder peak): 243, 271, 311\* and 382 (C<sub>2</sub>H<sub>5</sub>OH).

[*L*<sub>2</sub>*B*<sub>3</sub>] *complex:* Color: dark green, yield (%): 68, M.p. > 300 °C, Elemental Analysis (calculated for C<sub>23</sub>H<sub>21</sub>BF<sub>6</sub>N<sub>4</sub>O<sub>3</sub>) (F.W: 526.2 g/mol) (%): C, 52.49; H, 4.02; N, 10.65. Found: C, 52.45; H, 3.97; N, 10.63. LC-MS (Scan ES<sup>+</sup>): m/z = 526.2 [M]<sup>+</sup>, and 549.2 [M+Na]<sup>+</sup>. FT-IR (ATR,  $v_{max}$ -cm<sup>-1</sup>): 3659 v(triazole-OH), 3045 v(Ar-CH), 2971-2880 v(Aliph-CH), 1627 v(C=N), 1534 v(N=N), 1464 v(C=C), 1164 v(B-O), 1131 v(C-O) and 894 v(B-C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ (ppm) = 8.27 (s, 1H, <u>H</u>C=N), 7.94 (s, 1H, triazole-C<u>H</u> and 3H, Ar-C<u>H</u>), 7.68 (s, 1H, Ar-C<u>H</u>), 7.37 (d, 1H, *J* = 6.4 Hz, Ar-C<u>H</u>), 7.29 (d, 1H, *J* = 6.4 Hz, Ar-C<u>H</u>), 5.54 (s, 1H, triazole-CH<sub>2</sub>-O<u>H</u>), 4.64 (s, 2H, triazole-C<u>H</u><sub>2</sub>-Ph), 4.48 (s, 2H, triazole-C<u>H</u><sub>2</sub>-OH), 3.69 (q, 2H, C<u>H</u><sub>2</sub>-O-B), 2.88 (q, 1H, C<u>H</u>-N=CH), 1.22 (m, 2H, CH<sub>3</sub>-CH<sub>2</sub>-CH), and 0.83 (t, 3H, *J* = 7.2 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>): δ (ppm) = 165.05 (H<u>C</u>=N), 162.63, 141.27, 134.45, 133.59, 132.06, 130.36, 127.73, 121.82, 120.20, 118.43, and 115.53 (Ar-<u>C</u>H), 124.83 (-<u>C</u>F<sub>3</sub>), 142.28 (triazole-<u>C</u>H), 128.86 (triazole-<u>C</u>-CH<sub>2</sub>-OH), 68.19 (CH=N-<u>C</u>H), 61.28 (-<u>C</u>H<sub>2</sub>-O-), 59.27 (Ph-<u>C</u>H<sub>2</sub>-triazole), 54.41 (triazole-<u>C</u>H<sub>2</sub>-OH), 23.46 (CH-<u>C</u>H<sub>2</sub>-CH<sub>3</sub>), and 14.70 (CH-CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). <sup>11</sup>B NMR (DMSO-d<sub>6</sub>, 192.5 MHz, 23 °C, δ ppm): 20.42. UV-Vis (λ<sub>max</sub>/(nm), \* = shoulder peak): 251, 275, 311\* and 384 (C<sub>2</sub>H<sub>5</sub>OH).

[ $L_2B_4$ ] complex: Color: dark green, yield (%): 71, M.p. > 300 °C, Elemental Analysis (calculated for C<sub>21</sub>H<sub>23</sub>BN<sub>4</sub>O<sub>3</sub>) (F.W: 390.2 g/mol) (%): C, 64.63; H, 5.94; N, 14.36. Found: C, 64.58; H, 5.90; N, 14.33. LC-MS (Scan ES<sup>+</sup>): m/z = 391.2 [M+H]<sup>+</sup> and 429.2 [M+K]<sup>+</sup>. FT-IR (ATR,  $v_{max}$ -cm<sup>-1</sup>): 3658 v(triazole-OH), 3070 and 3017 v(Ar-CH), 2963-2875 v(Aliph-CH), 1629 v(C=N), 1537 v(N=N), 1465 v(C=C), 1161 v(B-O), 1114 v(C-O) and 897 v(B-C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 8.15 (s, 1H, <u>H</u>C=N), 7.96 (s, 1H, triazole-C<u>H</u>), 7.87 (s, 1H, Ar-C<u>H</u>), 7.69 (d, 2H, *J* = 6.8 Hz, Ar-C<u>H</u>), 7.26-7.20 (m, 3H, Ar-C<u>H</u>), 6.65 (d, 2H, J = 6.8 Hz, Ar-C<u>H</u>), 5.28 (s, 1H, triazole-CH<sub>2</sub>-O<u>H</u>), 4.58 (s, 2H, triazole-C<u>H</u><sub>2</sub>-Ph), 4.41 (s, 2H, triazole-C<u>H</u><sub>2</sub>-OH), 4.30 (q, 2H, C<u>H</u><sub>2</sub>-O-B), 2.85 (s, 1H, C<u>H</u>-N=CH), 1.15 (m, 2H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-CH), and 0.80 (t, 3H, *J* = 7.0 Hz, C<u>H</u><sub>3</sub>-CH<sub>2</sub>-CH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 162.38 (H<u>C</u>=N), 161.22, 153.46, 134.33, 131.87, 130.06, 127.42, 122.78, 115.48, and 106.24 (Ar-<u>C</u>H), 143.38 (triazole-<u>C</u>H), 129.41 (triazole-<u>C</u>-CH<sub>2</sub>-OH), 68.67 (CH=N-<u>C</u>H), 63.41 (-<u>C</u>H<sub>2</sub>-O), 56.43 (Ph-<u>C</u>H<sub>2</sub>-triazole), 53.98 (triazole-<u>C</u>H<sub>2</sub>-OH), 31.21 (CH-<u>C</u>H<sub>2</sub>-CH<sub>3</sub>), and 10.63 (CH-CH<sub>2</sub>-<u>C</u>H<sub>3</sub>). <sup>11</sup>B NMR (DMSO-d<sub>6</sub>, 192.5 MHz, 23 °C,  $\delta$  ppm): 28.62. UV-Vis ( $\lambda_{max}/(nm)$ , \* = shoulder peak): 252, 271, 284, 312\* and 380 (C<sub>2</sub>H<sub>5</sub>OH).

## 2. 6. General procedure for the asymmetric transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a solution of chiral boronate  $[L_1(B_{1.4})]$  and  $[L_2(B_{1.4})]$  complexes (0.01 mmol), NaOH (0.05 mmol) and the corresponding ketone (1.00 mmol) in degassed 2 propanol (10 ml) was refluxed until the reaction was completed. Followed by a sample of the reaction mixture was taken off, diluted with acetone and analysed immediately by GC. Conversion rates were calculated based on unreacted ketone.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

Scheme 1 and 2 shows the synthetic path and structures of the chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes. Firstly, the chiral salen  $(L_1H_2)$  ligand was synthesized in 81 % yield via the straightforward condensation of 5azidomethyl salicylaldehyde and (R)-(-)-2-amino-1-butanol in ethanol, which was stirred and refluxed for 6 h in the presence of two drop formic acid as catalyst (Scheme 1). Then, 1, 2, 3triazole-containing a chiral ligand  $(L_2H_2)$  was synthesized from the azido-functionalized ligand  $(L_1H_2)$  via click chemistry approach in 78 % yield in the presence of propargyl alcohol, CuSO<sub>4</sub> and freshly prepared sodium ascorbate (Scheme 1). Finally, as shown in Scheme 2, the chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands was reacted with various boronic acid (ferrocene boronic acid, butylboronic acid, 3,5-bis(trifluoromethyl)phenyl boronic acid or phenylboronic acid) in refluxing toluene in a 1:1 molar ratio to create targeted tetracoordinated chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes in the range 76-68 % yield, respectively. The proposed structures of chiral salen ligands with their boronate complexes were confirmed by spectroscopic and analytical techniques such as NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B), FT-IR, UV-Vis, LC-MS spectroscopy, and elemental analysis. The spectroscopic results of the salen ligands and their boronate complexes are consistent with proposed structure. Moreover, the elemental compositions of the chiral salen-based ligands  $(L_1H_2)$  and  $(L_2H_2)$ and their chiral boronate  $[L_1(B_{1.4})]$  and  $[L_2(B_{1.4})]$  complexes were determined and the results confirmed the formation of the desired products.



Scheme 1 Synthesis of the proposed chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands.



Scheme 2 Synthesis of the chiral boronate  $[L_1(B_{1\text{-}4})]$  and  $[L_2(B_{1\text{-}4})]$  complexes.

#### 3.2. Spectroscopic studies

FT-IR spectroscopy were used to characterize the structure of the synthesized two chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their chiral boronate  $[L_1(B_{1,4})]$  and  $[L_2(B_{1,4})]$ complexes. These chiral salen ligands and corresponding chiral boronate complexes exhibited many prominent infrared peaks and the obtained results are given in the experimental part. The most important characteristic FT-IR peaks of the chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands were in the range 3520-2348 cm<sup>-1</sup>, which are ascribed to intermolecular H-bond  $v(OH \dots N-$ CH) stretching, which disappeared in the FT-IR spectra of the chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes due to the deprotonation of the OH group, as expected [29, 30]. While another important FT-IR peak of free salen ligands are found in the range 1658-1637 cm<sup>-1</sup>, corresponding stretching vibrations of the chiral boronate complexes are found in the region of 1637-1624 cm<sup>-1</sup> towards lower wavenumber as compared to that of the free ligands [31]. These two results indicates the coordination of imine group to boron center through the nitrogen atom with phenolic oxygen and confirm the formation of the chiral boronate  $[L_1(B_1, B_1)]$ 4)] and  $[L_2(B_{1.4})]$  complexes. In the FT-IR spectra of the azido-functionalized chiral salen  $(L_1H_2)$  ligand and its chiral boronate  $[L_1(B_{1-4})]$  complexes, characteristic stretching peak of the azido groups were observed in the range 2114-2103 cm<sup>-1</sup> as very strong peaks owing to the transformation of chlorine to an azido group in these compounds [26-28, 32]. This band was disappeared in the FT-IR spectra of the chiral salen  $(L_2H_2)$  ligand and its chiral boronate  $[L_2(B_{1-4})]$  complexes because of the click reaction between the azido-functionalized compounds with propargyl alcohol and the presence of different new peaks in the final FT-IR spectra of triazole-containing compounds. In addition, in the FT-IR spectrum of each chiral boronate complexes were observed new characteristic peaks in the range 1123-1112 cm<sup>-1</sup> and 897-891 cm<sup>-1</sup> for  $[L_1(B_{1,4})]$  and 1164-1158 cm<sup>-1</sup> and 897-890 cm<sup>-1</sup> for  $[L_2(B_{1,4})]$  complexes

indicative of the presence of v(B-O) and v(B-C) bonds, respectively, thus corroborating the coordination of the chiral salen ligands to the boron center of boronate complexes [33-36].

For the full characterization of the new chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes, the <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopy have been used. The NMR spectra results were in good agreement with the proposed structures in d<sub>6</sub>-DMSO and all chemical shifts were in the expected ranges (Figure 1, 2 and S1-S8) The absence of the signal was attributed to the D-exchangeable phenolic-OH resonance in the <sup>1</sup>H NMR spectra of the chiral boronate  $[L_1(B_{1.4})]$  and  $[L_2(B_{1.4})]$  complexes, which is present at 13.42 and 13.30 ppm as singlet in the spectra of free chiral salen ligands, indicating the successful formation of boronate complexes and the deprotonation of the -OH group during complexation [37-39]. The compared with the <sup>1</sup>H NMR spectra of chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes, the chemical shift of the azomethine (CH=N) protons appears at 8.37-8.42 ppm for ligands and 8.83-8.03 ppm for boronate complexes [4, 40]. These results clearly indicates the coordination of azomethine nitrogen atom to boron center and provides further evidence for succesfull boronate complexation. Another decisive event, the appearance of new signals at aromatic region and presence of two new shielded signals at 5.69-5.28 and 4.68-3.94 ppm for  $(L_2H_2)$ ligand and chiral boronate  $[L_2(B_{1-4})]$  complexes as singlet signals corresponding to the -CH<sub>2</sub>-OH and the CH<sub>2</sub>-OH protons of 1,2,3-triazole group, respectively in their <sup>1</sup>H-NMR spectra. Also, these results obviously indicates the success of the click cyclization reaction and the formation of the 1, 2, 3-triazole-containing compounds [41]. In addition, the <sup>1</sup>H NMR chemical shift values of the other aromatic and aliphatic groups have been supported the formation of all compounds in DMSO-d<sub>6</sub>, which gave suitable signals that are in good agreement with the proposed structures. This indicates the coordination of atom to boron center through azomethine nitrogen atom, phenolic oxygen, and deprotonation of the -OH

group on the other side of ligands, as expected. Moreover, the <sup>13</sup>C NMR spectra results can be analyzed in an analogous manner to that of the proton spectra and the chemical shift of <sup>13</sup>C NMR resonances supports the formation of the chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes. The signals for the azomethine group carbon (HC=N) was observed in the range 165.42-162.38 ppm for boronate complexes with an low-field shift in its position as compared to that of the salen chiral ligands, which provides further evidence for the formation of the chiral boronate compounds. Besides, the appearance of new signals at  $\delta = 148.30-142.28$  ppm, at  $\delta = 129.41-122.47$  ppm, and at  $\delta =$ 55.76-52.15 ppm corresponding to the triazole-CH, triazole-C-CH<sub>2</sub>-OH, and triazole-CH<sub>2</sub>-OH carbons of 1,2,3-triazole group, respectively for the chiral salen  $(L_2H_2)$  ligand and its chiral boronate  $[L_2(B_{1-4})]$  complexes in their <sup>13</sup>C-NMR spectra obviously shows the success of the click cyclization reaction and the formation of the 1,2,3-triazole-containing (L<sub>2</sub>H<sub>2</sub>) and  $[L_2(B_{1-4})]$  compounds [28, 41]. Also, the chemical shift of aromatic (Ar-CH) and other group carbons were in the expected range, which support the formation of the proposed structures (Figure 1, 2 and S1-S8). Additionally, in order to demonstrate the formation of the chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes, spectroscopic analysis of the <sup>11</sup>B NMR data was also performed (Figure 3, 4 and S9-S13). The <sup>11</sup>B NMR spectroscopic results are of special interest because the chemical shift of the <sup>11</sup>B NMR spectroscopic signal gives a strong indication of whether or not the boronate compounds is trigonal planar or tetrahedral [42, 43]. In the <sup>11</sup>B NMR spectra of the chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes, the characteristic boron signals located in the range  $\delta = 32.44-20.42$  ppm as broad singlets due to the similar chemical environment for the boron center of each boronate complexes [44-46], which confirms the formation of tetra-coordinate boronate compounds. However, these values suggest that tetra-coordinated boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes exist predominantly as monomers in solution.



**Figure 2.** <sup>13</sup>C NMR spectra of the chiral boronate  $[L_1B_1]$  complex



Figure 4. <sup>11</sup>B NMR spectra of the chiral boronate  $[L_2B_4]$  complex

To understand the electronic transitions of our compounds, we studied the UV-Vis absorption spectra of the chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and the corresponding chiral boronate  $[L_1(B_{1.4})]$  and  $[L_2(B_{1.4})]$  complexes under the same conditions for comparison (Figure S20-23). The UV-vis results of the chiral salen ligands and their boronate complexes show very similar features in EtOH at room temperature, probably the electronic effects resulting upon coordination of the boron atom and the planarization of the  $\pi$ -conjugated salen ligands entail a narrowing of the energy gap between the ground state and the first singlet excited state [47]. Another reason for the showing similar absorption bands in ethanol, probably it was dependent on the electron-withdrawing or electron-releasing group at different positions in the ligand groups or the boronate complexes. The electronic spectrum of the chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands exhibits an absorption band at range 382-231 nm, while the corresponding chiral boronate  $[L_1(B_{1.4})]$  complexes at range 370-234 nm and  $[L_2(B_{1.4})]$  complexes at range 384-243 nm, respectively. These absorption bands can be assigned to  $\pi \to \pi^*$  transitions or the n $\to \pi^*$  transition of non-bonded electrons of the phenolic chromophores and azomethine (-CH=N) unit in the structure of all the compounds [48].

Further confirmation of the formation of the chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and the corresponding chiral boronate  $[L_1(B_{1.4})]$  and  $[L_2(B_{1.4})]$  complexes was also provided by LC-MS (Figure 5-8 and S14-S19). The LC-MS spectra indicated the formation of a variety of fragments during the course of its decomposition and the existence of  $[M]^+$  or  $[M+H]^+$ peaks, with the base peak were in the proposed nature of the compounds. The LC-MS mass peaks showed the expected molecular and fragmentation ions, with appropriate isotope distribution. As seen in Figure 3 and 4, the molecular ion peak for the the chiral salen  $(L_1H_2)$ and  $(L_2H_2)$  ligands were observed at m/z = 249.3 amu for  $[M+H]^+$  and 184.0 amu for  $[M+H]^+$ consecutively, whereas those of the chiral boronate  $[L_1(B_{1.4})]$  and  $[L_2(B_{1.4})]$  complexes were observed at m/z = 442.2 amu for  $[M]^+$ , 315.2 amu for  $[M+H]^+$ , 471.2 amu for  $[M+H]^+$ , 335.2

amu for  $[M+H]^+$ , 499.2 amu for  $[M+H]^+$ , 371.2 amu for  $[M+H]^+$ , 526.2 amu for  $[M]^+$ , and 391.2 amu for  $[M+H]^+$  [1, 4, 49] (Figure 5-6 and S14-S19). In light of those LC-MS data, the existence of the molecular ion and other peaks confirms the formation of the chiral salen (L<sub>1</sub>H<sub>2</sub>) and (L<sub>2</sub>H<sub>2</sub>) ligands and the corresponding chiral boronate [L<sub>1</sub>(B<sub>1-4</sub>)] and [L<sub>2</sub>(B<sub>1-4</sub>)] complexes.





Figure 6. LC-MS spectra of the chiral salen  $(L_2H_2)$  ligand



Figure 7. LC-MS spectra of the chiral boronate  $[L_1B_2]$  complex



Figure 8. LC-MS spectra of the chiral boronate  $[L_2B_3]$  complex

#### 3.3. Catalytic performances of boron complexes

In a preliminary study, the chiral compounds,  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  have been examined as catalyst precursors for the asymmetric transfer hydrogenation of acetophenone under variable conditions. A typical procedure using acetophenone as substrate was as follows: 0.01 mmol of the complex and 1.00 mmol of acetophenone were added to a solution of NaOH in 2-propanol (0.05 mmol of NaOH in 10 mL 2-propanol) and refluxed at 82 °C, while the reaction was watched by GC. In all reactions, these compounds catalyzed the reduction of ketones to the corresponding alcohols via hydrogen transfer from 2-propanol. A comparison of chiral boronate complexes  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  as precatalysts for the

asymmetric hydrogenation of acetophenone by 2-propanol is given in Table 1. All Catalytic experiments were completed under inert (Ar) atmosphere using typical Schlenk-line methods. These systems catalyzed the reduction of acetophenone to corresponding alcohol ((*S*)-, (*R*)-1-phenylethanol) in the existence of NaOH. Transfer hydrogenation of acetophenone occurred very slowly at room temperature [50], with low conversions (up to 30 %, 48 h) and low to moderate enantioselectivities (up to 52 % ee) in the reactions (Table 1, entries 1-8). Because of the reversibility at room temperature (rt), the prolonging the reaction time (96 h) led to a slight reducing of enantioselectivity, as indicated by the catalytic results collected with chiral catalyst, [L<sub>2</sub>B<sub>1</sub>] (entry 5, <sup>[b]</sup>) [51, 52]. Moreover, as can be inferred from Table 1 (entry 9), the existence of base is essential to detect appreciable conversions [53-56]. Furthermore, the select of base, such as KOH and NaOH, had little influence on the conversion and enantioselectivity (Table 1, entry 14,<sup>[e]</sup>) and with a catalyst/NaOH ratio of 1/5, the boranate complexes are very active leading to a quantifiable transformation of acetophenone (Table 1, entries 18-21,<sup>[f]</sup>).

Table 1 Asymmetric Transfer hydrogenation (ATH) of acetophenone with isoPrOH catalyzed by chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes.

		о 				но	H		
				Cat.					
			isoPrOH acetone						
Entry	Complex	S/C/Base	Time	Conv.(%) <sup>[h]</sup>	% ee <sup>[i]</sup>	Config. <sup>[k]</sup>	<b>TOF</b> ( <b>h</b> <sup>-1</sup> ) <sup>[1]</sup>		
1	$[L_1B_1]^{[a]}$	100:1:5	48 h	15	33	R	<3		
2	$[L_1B_2]^{[a]}$	100:1:5	48 h	30	16	R	<3		
3	$[L_1B_3]^{[a]}$	100:1:5	48 h	17	14	R	<3		
4	$[L_1B_4]^{[a]}$	100:1:5	48 h	18	17	R	<3		
5	$[L_2B_1]^{[a]}$	100:1:5	48 h (96 h) <sup>[b]</sup>	10(28) <sup>[b]</sup>	52(48) <sup>[b]</sup>	R	<3		
6	$[L_2B_2]^{[a]}$	100:1:5	48 h	19	31	R	<3		
7	$[L_2B_3]^{[a]}$	100:1:5	48 h	12	28	R	<3		
8	$[L_2B_4]^{[a]}$	100:1:5	48 h	11	30	R	<3		
9	$[L_2B_1]^{[c]}$	100:1	72 h	<5	-	-	trace		
10	$[L_1B_1]^{[d]}$	100:1:5	7 h	99	37	R	14		
11	$[L_1B_2]^{[d]}$	100:1:5	1 h	98	19	R	98		
12	$[L_1B_3]^{[d]}$	100:1:5	7 h	98	17	R	14		
13	$[L_1B_4]^{[d]}$	100:1:5	8 h	99	18	R	12		
14	$[L_2B_1]^{[d]}$	100:1:5	$4 h (4 h)^{[e]}$	99 (98) <sup>[e]</sup>	61 (58) <sup>[e]</sup>	R	25		
15	$[L_2B_2]^{[d]}$	100:1:5	1/2 h	99	24	R	198		
16	$[L_2B_3]^{[d]}$	100:1:5	5 h	97	27	R	20		
17	$[L_2B_4]^{[d]}$	100:1:5	3 h	98	26	R	33		
18	$[L_2B_1]^{[f]}$	100:1:3	4 h	97	57	R	-		
19	$[L_2B_1]^{[f]}$	100:1:5	4 h	99	61	R	-		
20	$[L_2B_1]^{[f]}$	100:1:7	4 h	98	56	R	-		
21	$[L_2B_1]^{[f]}$	100:1:9	4 h	98	52	R	-		
22	$[L_2B_1]^{[g]}$	250:1:5	6 h	96	56	R	-		
23	$[L_2B_1]^{[g]}$	500:1:5	12 h	95	52	R	-		
24	[L_R_1 <sup>[g]</sup>	1000.1.5	24 h	97	51	R	_		

Reaction conditions

<sup>[a]</sup>At room temperature; acetophenone/Cat./NaOH,100:1:5;

<sup>[b]</sup>At room temperature; acetophenone/Cat./NaOH, 100:1:5, (72 h);

<sup>[c]</sup>Refluxing in *iso*PrOH; acetophenone/Cat., 100:1, in the absence of base;

<sup>[d]</sup>Refluxing in *iso-P*rOH; acetophenone/Cat./NaOH, 100:1:5;

<sup>[e]</sup>Refluxing in *isoP*rOH; acetophenone/Cat./KOH, 100:1:5;

<sup>[f]</sup>Refluxing in *iso*PrOH; acetophenone/Cat./NaOH, 100:1:5;

<sup>[g]</sup>Refluxing in *iso*PrOH; acetophenone/Cat./NaOH, 250, 500 or 1000:1:5;

<sup>[h]</sup>Determined by GC (three independent catalytic experiments);

<sup>[1]</sup>Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column;

<sup>[k]</sup>Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, (S) or (R) configuration was obtained in all experiments, <sup>[1]</sup> TOF=(mol product/mol Cat.) x h<sup>-1</sup>.

Reduction of acetophenone into (S)- or (R)-1-phenylethanol could be reached in high yield by increasing the temperature up to 82 °C (Table 1, entries 10-17). Moreover, the conversions gradually declined with increasing the mole ratios of [acetophenone]/[Cat.] from 250/1 to 500/1 or 1000/1, although the enantioselectivities were still high (up to 56% ee, Table 1, entries 22-24). These outcomes clearly indicate that the structural variance of the ligands is a critical factor for catalytic activity and it is noteworthy that the catalytic systems, chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  catalysts show the differences in reactivity. It has also been shown that the catalytic activities in the studied hydrogen transfer reactions were mostly much higher for chiral boronate  $[L_2(B_{1-4})]$  complexes than those for the  $[L_1(B_{1-4})]$ complexes (Table 1, entries 10-17). Furthermore, it was seen that when ligands incorporate ferrocene moiety, the catalytic activity is low, but the % enantioselectivities is high compared to the other boronate complexes (Table 1, entries 10 and 14). So, from the outcomes, one can easily say that chiral boronate  $[L_1B_1]$  and  $[L_2B_1]$  complexes were effective catalysts for the hydrogenation of acetophenone. Particularly, chiral boronate  $[L_2B_1]$  complex afforded good ee % in the asymmetric transfer hydrogenation of acetophonone (up to 61% ee). As shown in Table 1, these results have also presented that enantiomeric purity of the product can be affected by electronic issues as well as steric factors of the substituents on the ligands.

## Table 2 Asymmetric Transfer Hydrogenation results for substituted acetophenones catalyzed

	O			ОН				
R		+	он –	Cat R + O				
Entry	Catalyst	R	Time	Conv.(%) <sup>[b]</sup>	% ee <sup>[c]</sup>	TOF (h <sup>-1</sup> ) <sup>[d]</sup>	Config. <sup>[e]</sup>	
1	$[L_1B_1]$	F	4 h	99	35	25	R	
2	$[L_2B_1]$	F	2 h	99	60	50	R	
3	$[L_1B_1]$	Cl	5 h	99	38	20	R	
4	$[L_2B_1]$	Cl	3 h	99	62	33	R	
5	$[L_1B_1]$	Br	6 h	98	40	16	R	
6	$[L_2B_1]$	Br	4 h	98	65	25	R	
7	$[L_1B_1]$	$NO_2$	4 h	99	39	25	R	
8	$[L_2B_1]$	NO <sub>2</sub>	2 h	97	63	49	R	
9	$[L_1B_1]$	o-CH <sub>3</sub> O	20 h	99	51	<5	R	
10	$[L_2B_1]$	o-CH <sub>3</sub> O	12 h	98	78	<8	R	
				· ·				
11	$[L_1B_1]$	<i>m</i> -CH <sub>3</sub> O	15 h	98	40	6	R	
12	$[L_2B_1]$	<i>m</i> -CH <sub>3</sub> O	9 h	99	66	11	R	
				r				
13	$[L_1B_1]$	<i>p</i> -CH <sub>3</sub> O	12 h	98	25	12	R	
1/	[L.R.]	n-CH-O	7 h	QQ	/7	1/1	R	

by chiral boronate  $[L_1B_1]$  and  $[L_2B_1]$  complexes.<sup>[a]</sup>

<sup>[a]</sup> Catalyst (0.01 mmol), substrate (1.0 mmol), 2-propanol (10 mL), NaOH (0.05 mmol %), 82 °C, the concentration of acetophenone derivatives are 0.1 M;

<sup>[b]</sup> Purity of compounds is checked by <sup>1</sup>H NMR and GC (three independent catalytic experiments), yields are based on aryl ketone;

<sup>c]</sup> Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m x 0.32 mm I.D. x 0.25µm film thickness);

<sup>[d]</sup> TOF = (mol product/mol Cat.) x  $h^{-1}$ ;

<sup>[e]</sup> Determined by comparison of the retention times of the enantiomers on the GC traces with literature

In order to explore the request range of the boron-catalyzed transfer hydrogenation, acetophenone derivatives were subjected to asymmetric reduction using the conditions optimized for acetophenone. Table 2 demonstrates conversions of the reduction performed in a 0.1 M of *iso*PrOH solution containing chiral boronate  $[L_1B_1]$  or  $[L_2B_1]$  catalysts and sodium

hydroxide (Ketone/Cat./NaOH = 100/1/5). The outcomes obviously exhibit that a range of acetophenone derivatives can be hydrogenated with low and good enantioselectivities. Substitution of the phenyl ring of the acetophenone substrate led to a clear decrease or increase in the catalytic activity and enantiselectivity. That's to say, electronic properties (the nature and position) of the substituents on the phenyl ring of the corbonil compound caused the important changes in the reduction rate. It is eminent that the introduction of electron withdrawing substituents to the aryl ring of the ketone decreases the electron density of the C=O bond so that the activity was enriched resulting in easier hydrogenation (Table 2, entries 1-14) [57, 58]. Therefore, the introduction of electron-withdrawing substituents resulted in improved activity with good ee % (Table 2, entries 1-8) [59, 60]. The introduction of an electron-donating group such as -CH<sub>3</sub> or -OCH<sub>3</sub> group decelerates the reaction degree with various enantioselectivities, whatever the location of substitution (Table 2, entries 9-14). Additionally, it can be seen in Table 2, ortho-substituted acetophenones can dramatically increase ee %, while meta- and para- substitution to acetophenones have detrimental effect [61, 62]. The investigation of the results indicates obviously that with each of the tested complexes, the highest enantioselectivity was found for o-methoxyacetophenone (78% ee) when chiral boronate  $[L_2B_1]$  complex was used as the catalyst.

It is well-known that transition-metal-catalyzed hydrogen transfer involves metal hydrides as key intermediates. All boron complexes, most likely follow the well-established mechanism via a boron alkoxide intermediate and  $\beta$ -elimination [63-65]. The importance of this study is that the use of inexpensive boron instead of expensive Ruthenium, Rhodium and Iridium. These higher catalytic activities can be explained by the nature of the ligands which can generate an open coordination site at boron more easily. It thus appears that the nature of the ligands can also play a crucial role in the transfer hdrogenation reactions. These results indicate the catalysts possibly can stabilize a catalytic transtion state.

#### 4. Conclusion

In this study, we synthesize two new azido and 1, 2, 3-triazole group-based chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes, starting from commercially available reagents. The obtained two chiral salen  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their chiral boronate  $[L_1(B_{1-4})]$  and  $[L_2(B_{1-4})]$  complexes were characterized by the FT-IR, UV-Vis, NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B), LC-MS, and elemental analysis techniques. The chiral boronate complexes were also used as catalyst for the asymmetric transfer hydrogenation (ATH) of acetophenone derivatives under suitable conditions. The catalytic results show that the chiral boronate complexes are good catalyst precursor. Especially, it was showed that the ferrocene-based chiral  $[L_1B_1]$  and  $[L_2B_1]$  boronate complexes in the asymmetric transfer hydrogenation catalytic studies. Among them, chiral boronate  $[L_2B_1]$  complex afforded good enantioselectivities in the asymmetric transfer hydrogenation of acetophonone. Furthermore, the catalytic results have presented that enantiomeric purity of the product can be affected by electronic features as well as steric features of the substituents on the chiral ligands.

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## Highlights

- The new chiral boronate-catalysts were prepared and fully characterized.
- The various spectroscopic methods were used for characterization
- The chiral boronate catalysts was used for the asymmetric transfer hydrogenation
- The chiral catalyst  $[L_2B_1]$  afforded good enantio-selectivities in the asymmetric transfer hydrogenation