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Rh-catalyzed asymmetric hydrogenation of α- and β-enamido phosphonates: highly enantioselective access to amino phosphonic acids†

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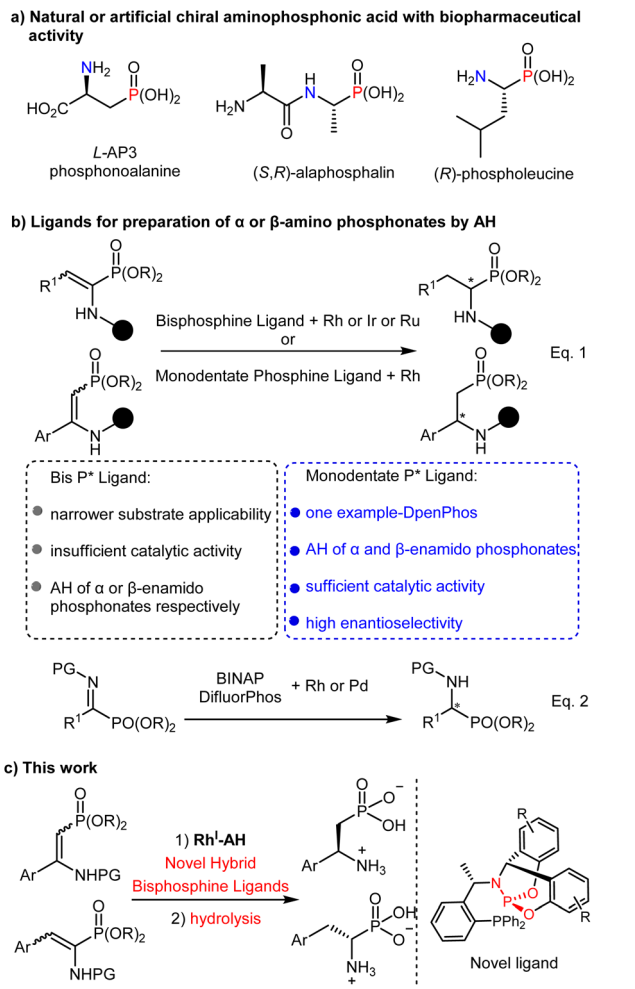
Catalytic asymmetric hydrogenation of α- and β-enamido phosphonates was developed using a complex formed *in situ* through a chiral hybrid phosphine-bicyclic bridgehead phosphoramidite ligand and rhodium metal precursor as the catalyst. This strategy afforded a wide variety of substrates in excellent yield (96–99%) and enantiomeric excess (≤99%) with very low catalyst loading (S/C up to 10 000) and relatively mild reaction conditions. Further investigations suggested that the hydrogenation reaction occurred only at the C=C bond of the enamido phosphate stage without tautomerization to the imine form. Tandem hydrolysis reactions of hydrogenated products gave the corresponding α- and β-amino phosphonic acids in fairly high yield, which could be multipurpose building blocks for bioorganic chemistry, medicinal chemistry and organic synthesis.

The planar carboxylic-acid group in an amino-acid structure can be bioisosterically substituted with a phosphonic-acid group to obtain the structure of an amino phosphonic acid.[1] Similar to the broad application prospects of chiral amino acids, optically active α- or β-amino phosphonic acids have been used widely as active substances in biological and medicinal chemistry. For example, phosphonoalanine (*L*-AP3) as an antagonist of metabotropic glutamate receptors,[2] phosphopeptide (*S*,*R*)-alaphosphalin with more potent antibiotic activity[3] and (*R*)-phospholeucine[4] with stronger activity for inhibition of leucine peptidase (Scheme 1a). Therefore, the stereoselective synthesis of α- and β-amino phosphonic acids has been a "hot issue" in organic synthesis. The traditional synthetic methods of optically active α- and β-aminophosphonates, as precursors of α- and β-amino phosphonic acids, are chiral resolution and induction of chiral auxiliary groups.[5] In contrast, the synthetic route of catalytic asymmetric transformations is a more concise, efficient and atom-economical approach. Over recent decades, the synthesis of optically active α-amino phosphonate groups has been achieved by catalytic asymmetric hydrogen-



Scheme 1 Applications and synthesis of chiral derivatives of amino phosphonic acid *via* asymmetric hydrogenation.

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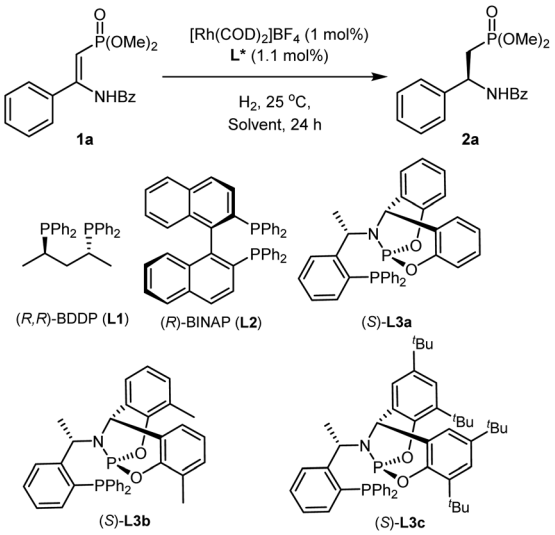
ation (AH), asymmetric hydrophosphorylation of imines, asymmetric amination of β-ketophosphonates, and formation of asymmetric carbon–carbon bonds.[6] The asymmetric amino hydroxylation of α, β-unsaturated phosphonates and the asymmetric addition of β-ketophosphonates to imino esters are methods to synthesize β-amino phosphonates.[7]

Among the catalytic asymmetric synthetic methods stated above, AH has become the best solution for the synthesis of derivatives of α- and β-amino phosphonic acids due to its high catalytic activity, good control of chirality, as well as stable and broad substrate applicability. Since 1985, the preparation of α- or β-phosphoramidates has been achieved by AH reactions with catalytic systems of chiral bisphosphine ligands and transition metals such as Ru, Rh and Ir (Scheme 1b, eqn (1)).[8] As hybrid bisphosphine ligands, chiral phosphine-phosphites have been applied for the hydrogenation of β-enamido phosphonates.[8n] Furthermore, in 2011, for the first time, Ding *et al.* implemented the simultaneous AH reactions of α- and β-enamido phosphonates with rhodium and monodentate phosphoramidite ligands (DpenPhos) with high yield and high enantioselectivity.[9] In addition, Goulioukina *et al.* and Zhou and colleagues grew a straightforward stratagem for the preparation of chiral α-aminophosphonates *via* the complexation of bisphosphine ligands and Rh or Pd-catalyzed AH of linear and cyclic α-iminophosphonates (Scheme 1b, eqn (2)).[10] Nonetheless, to date, no bisphosphine ligands have simultaneously achieved an efficient synthesis of α- and β-aminophosphonates by AH. The reported catalytic systems of bisphosphine ligands have poor substrate applicability and insufficient catalytic activity. Recently, we synthesized a new type of chiral bicyclic bridgehead phosphoramidite hybrid bisphosphine ligand with stable chemical properties, strong structural rigidity and enhanced π-acceptor capability through a simple three-step reaction, and successfully applied it to the AH of aryl-disubstituted terminal alkenes.[11] Phosphine-bicyclic bridged phosphoramidite ligands, as C_1-symmetric diphosphorus ligands, have great potential for AH of other C=C bonds.[12] Inspired by the results stated above, we considered using these novel ligands to develop a catalytic hydrogenation system and tandem hydrolysis reaction to achieve the efficient preparation of optically pure α- or β-amino phosphonic acids (Scheme 1c).

First, for the intention of a comparative test, initially we began with the AH of dimethyl (*Z*)-(2-benzamido-2-phenylvinyl) phosphonate (**1a**) as the standard substrate under 5.5 MPa pressure of H_2 in trifluoroethanol (TFE) at room temperature (25 °C) for 24 h using the complex generated *in situ* of $[Rh(COD)_2]BF_4$ and commonly used bisphosphine ligands. As expected, a high yield of the product dimethyl (*S*)-(2-benzamido-2-phenylethyl) phosphonate (**2a**) with a lower 19% enantiomeric excess (ee) was observed (Table 1, entry 1). Meanwhile, when the other commercial ligand (*R*)-BINAP (**L2**) was used, the desired product **2a** was obtained with lower enantioselectivity (6% ee) and moderate conversion (Table 1, entry 2).

Next, we attempted to use our chiral hybrid phosphine-bicyclic bridgehead phosphoramidite ligands in AH of the benchmark substrate. To our delight, nearly full conversions were achieved within quite high enantioselectivities (76% to 97%) when using a series of ligands (Table 1, entries 3–5). Ligand screening revealed that the structure of the bicyclic-skeleton part of the ligand affected the enantioselectivity of the catalyst markedly. The ligand of 2,4-di^{t}Bu-substituted variant **L3c** generated 2a in 99% yield with promising enantioselectivity of 97% ee. This was superior to the 2,4-diMe-substituted-variant **L3b** (90% ee), which was better than the unsubstituted ligand **L3a** (76% ee). These results revealed that the aromatic rings of the bicyclic skeleton moiety with a bulky substituent were preferred to the increase in enantioselectivity because the presence of bulky substituted groups at the *ortho* and *para* positions of the phenol rings (*e.g.*, 2,4-di^{t}Bu-substituted groups) improved the π-accepting properties of phosphoramidite by enhancing geometrical constraints through steric repulsion.[13] Solvent effects also had a considerable impact on this reaction. MeOH and toluene provided only extremely poor conversions (Table 1, entries 6 and 7). THF

Table 1 Optimization of conditions for Rh-catalyzed hydrogenation of dimethyl (*Z*)-(2-benzamido-2-phenylvinyl)phosphonate **1a**[a]



Entry	L*	Solvent	H_2 (MPa)	Yield[b] (%)	ee[c] (%)
1	**L1**	TFE	5.5	97	19
2	**L2**	TFE	5.5	45	6
3	**L3a**	TFE	5.5	99	76
4	**L3b**	TFE	5.5	99	90
5	**L3c**	TFE	5.5	99	97
6	**L3c**	MeOH	5.5	Trace	—
7	**L3c**	Toluene	5.5	Trace	—
8	**L3c**	THF	5.5	98	97
9	**L3c**	CH_2Cl_2	5.5	90	98
10	**L3c**	TFE	4	99	97
11	**L3c**	THF	3	89	97
12	**L3c**	TFE	3	99	97

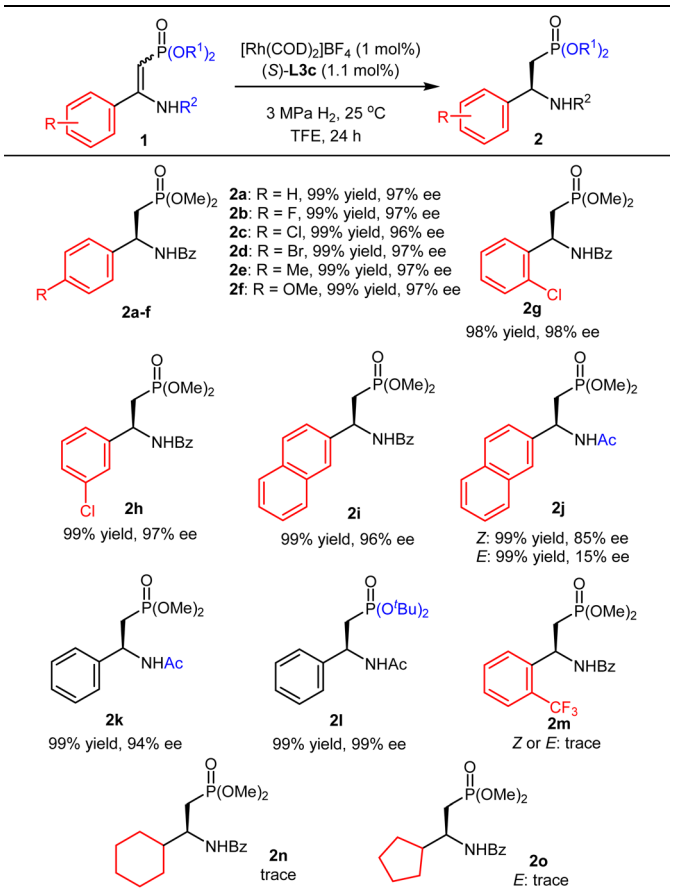
[a] Reaction conditions: **1a** (0.125 mmol, 1.0 equiv.), $[Rh(COD)_2]BF_4$ (1.0 mol%), **L*** (1.1 mol%), in 2 mL of solvent under a H_2 atmosphere at 25 °C for 24 h. [b] Yields were determined by GC. [c] The ee values were determined by chiral HPLC. COD = 1,5-cyclooctadiene, TFE = CF_3CH_2OH.

gave an identical outcome with respect to the ee value compared with TFE. CH_2Cl_2 provided relatively lower yields (90%) despite its high enantioselectivity. Decreasing the H_2 pressure to 3 MPa in TFE had no effect on the reactivity or enantioselectivity, but the reaction reactivity in THF had a distinct decrease (Table 1, entries 10–12).

With the reaction conditions optimized to elicit high yield and enantioselectivity in the model AH **1a**, the substrate scope of *Z* or *E* isomers of β-enamido phosphonates of AH was investigated (Table 2). This catalytic system showed a high tolerance to the electronic properties and substitution pattern of the substituent on the aryl moiety of substrates. The electronic properties of the substituent at the *para*- position of the aromatic ring moiety had no conspicuous effect on the reactivity or enantioselectivity (Table 2). Irrespective of electron-donating (**1a** and **1e–f**) or electron-withdrawing (**1b–d**) substituents, the substrates could be hydrogenated smoothly to provide the corresponding products with nearly full conversions and high enantioselectivities (96–97% ee). *Ortho*, *meta* and disubstituted aryl substrates (**1g–i**) were hydrogenated in excellent reactivities and enantioselectivities (96–98% ee). Remarkably, the catalyst exhibited distinctly different enantioselectivity (*Z*: 85% ee; *E*: 15% ee) in the hydrogenation of the isomers of dimethyl (2-acetamido-2-(naphthalen-2-yl) vinyl) phosphonate (**2j**), albeit both in 99% yield. Product **2l** exhibited higher enantioselectivity (99% ee) than **2k** (94% ee), probably because of the large steric hindrance of the tertiary butyl group. The strongly electron-withdrawing *o*-CF_3-substituted substrate **1m** and β-alkyl-substituted β-enamido phosphonates (**1n–o**), irrespective of *Z* or *E* configurations, were difficult to hydrogenate even though the hydrogen pressure and temperature were increased.

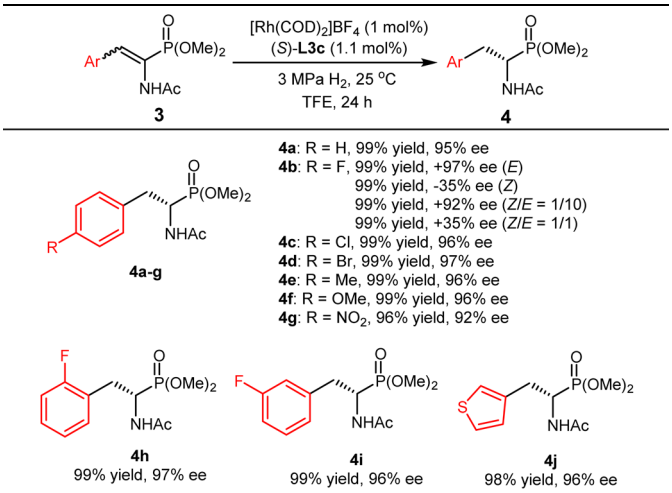
Encouraged by the promising results stated above, we synthesized a range of β-aryl-substituted α-enamido phosphonates **3** and applied them to AH under optimal reaction conditions (Table 3). All of the substrates investigated (**3a–j**) could be hydrogenated smoothly to generate the corresponding chiral product in high yields (up to 99%) with remarkable enantioselectivities (92–99% ee). The electronic properties of the substituent at the *ortho*-, *meta*- or *para*- position of the aromatic groups did not have a significant influence on the enantioselectivity or reactivity (**4a–i**) (Table 3). In addition, the β-heteroaryl-substituted compound (**3j**) was hydrogenated with excellent catalytic efficacy (98% yield, 96% ee). Simultaneously, the catalytic system could also demonstrate comparable reactivity in the AH of the isomers **3b** to provide the desired products **4b** with 97% and 35% ee, respectively. The catalyst could, therefore, tolerate the use of a *Z*/*E* = 1 : 10 isomeric mixture of substrate **3b** to obtain the homologous product

Table 2 AH of Z or E isomers of β-enamido phosphonates[a]



[a] Reaction conditions: **1** (0.125 mmol, 1.0 equiv.), $[Rh(COD)_2]BF_4$ (1.0 mol%), (*S*)-**L3c** (1.1 mol%) in 2 mL of TFE under a H_2 pressure of 3 MPa at 25 °C for 24 h. Yields of isolated products are given. The ee values were determined by chiral HPLC. Unless specified otherwise, the configurations of the substrates are *Z*. The absolute configurations of **2a–l** were assigned as (*S*) by comparison of their optical rotations with literature-reported values (see ESI†).

Table 3 AH of β-aryl-substituted α-enamido phosphonates[a]



[a] Reaction conditions: **3** (0.125 mmol, 1.0 equiv.), $[Rh(COD)_2]BF_4$ (1.0 mol%), (*S*)-**L3c** (1.1 mol%) in 2 mL of TFE under a H_2 pressure of 3 MPa at 25 °C for 24 h. Yields of isolated products are given. The ee values were determined by chiral HPLC. Unless specified otherwise, the configurations of the substrates are *E*. The absolute configurations of **4a–j** were assigned to be (*S*) by comparison of the optical rotations of correspondingly hydrolyzed α-amino phosphonic acid **4aa** with literature[14]-reported values.

with 92% ee. However, the enantioselectivity of the product dropped to 35% ee when increasing the percentage of the *Z* isomer of **3b** to 50%.

Deuterium-labeling experiments were conducted to explore possible mechanisms. The Rh-catalyzed AH of model substrate **1c** was carried out under 3 MPa D_2 at room temperature (25 °C) for 24 h. Interestingly, **1c** was hydrogenated smoothly to afford deuterated product **2c–d_2** in >99% yield (Scheme 2a). However, when the reaction was conducted in the presence of H_2 using TFE-d_3 as the reaction solvents, deuterium atoms were not found in product **2c** at α- or β-positions (Scheme 2b). These results indicated that the hydrogen source was H_2 and that the protons in the solvent did not participate in the reaction. We monitored the change in the ee value of product **2c** along with the reaction process. The yield of **2c** increased gradually with an increase in time until 16 h, with almost complete conversion of the substrate to the target product (Fig. 1). The ee value of product **2c** remained almost unchanged (96% ee) even in the first few hours of the reaction. The two investigations suggested that this hydrogenation reaction occurred only at the C=C bond of the enamido phosphate stage without tautomerization to the imine form.

The scalability of the process was demonstrated by the hydrogenation of **1a** and **3a**, which generated **2a** and **4a** in 99% yield with 97% ee and 96% ee, respectively, even at a catalyst loading of 0.01 mol% (Scheme 3). Tandem deprotection of hydrogenated products could be undertaken readily in an ethanol solution of hydrochloric acid to give the corresponding α- and β-amino phosphonic acid in fairly high yield. Furthermore, this research provides an efficient and simple method to synthesize optically active α- or β-amino phosphonic acids, which are versatile building blocks for bioorganic chemistry, medicinal chemistry and organic synthesis.

In summary, we achieved Rh/chiral hybrid phosphine-bicyclic bridgehead phosphoramidite ligand-catalyzed AH reactions of α- and β-enamido phosphonates simultaneously with excellent enantioselectivity control, tolerance of a wide range of functional groups, relatively mild reaction conditions and very low catalyst loading (S/C up to 10 000). This was a straightforward approach to obtain optically active α- or β-amino phosphonic acids. Further investigations suggested that the hydrogenation reaction occurred only at the C=C bond of the enamido phosphate stage without tautomerization to the imine form. This research result demonstrates the correctness of this ligand-design strategy, and we believe that this type of ligand could be applied to more asymmetric transformations.

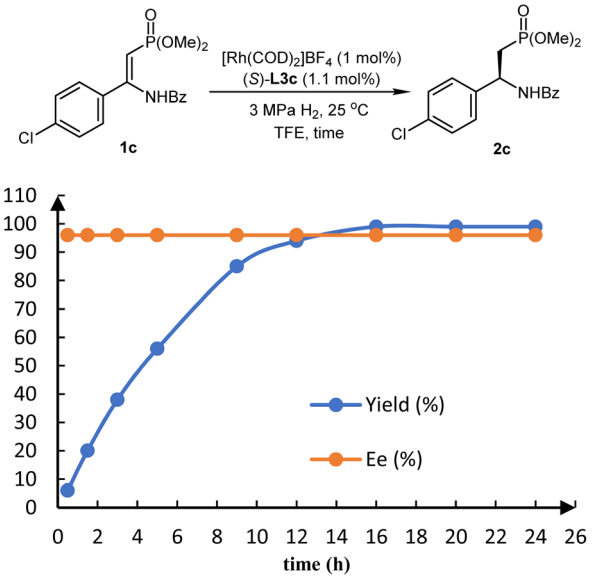
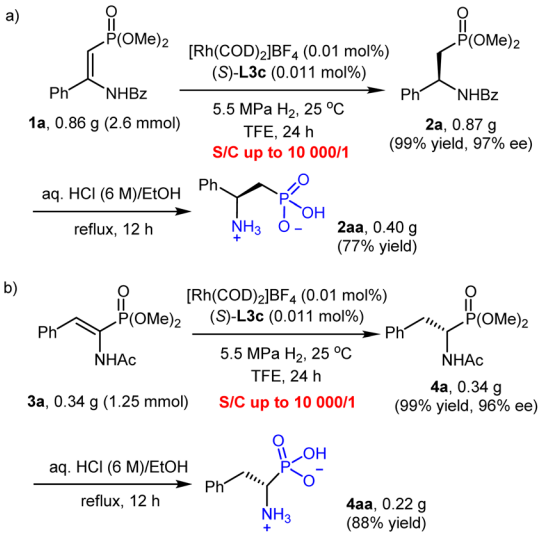
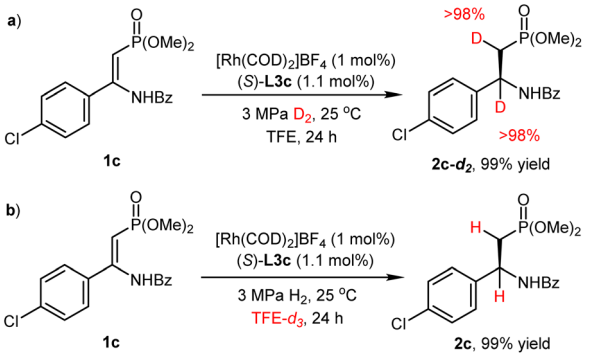


Fig. 1 Monitoring the ee value of the product along with the reaction process.



Scheme 3 Gram-scale reaction with lower catalyst loading and derivatizations.



Scheme 2 Deuterium-labeling experiments.

Experimental section

Hydrogenation method

In a nitrogen-filled glovebox, a stainless-steel autoclave was charged with $[Rh(COD)_2]BF_4$ (0.00125 mmol, 0.01 equiv.), (*S*)-

L3c (0.001375 mmol, 0.011 equiv.) in 1.0 mL of a degassed TFE. After stirring for 60 min at room temperature, the reaction mixture was added to a mixture of the substrate (**1a–l**, **3a–j**) (0.125 mmol, 1 equiv.) in 1.0 mL of the same solvent, and the hydrogenation was undertaken at 25 °C under H_2 pressure of 3 MPa for 24 h. Then, the solvent was evaporated, and the residue was purified by flash column chromatography to give the corresponding hydrogenation product (**2a–l**, **4a–j**).

Hydrolysis method

The above-hydrogenated products (**2** and **4**, 1.0–3.0 mmol) were added to 20 mL of a mixed solution of hydrochloric acid (6 M) and ethanol (1/1 *v*/*v*), and then placed in an oil bath at 110 °C for heating and refluxing for 12 h. After the completion of the reaction monitored by thin-layer chromatography, the reaction solution was cooled to room temperature, and ethanol and part of hydrogen chloride were removed under reduced pressure. To the aqueous solution of the products was added ethyl acetate (10 mL) to extract organic impurities, and the aqueous phase was retained (hydrolyzed products were slightly soluble in ethyl acetate). Extraction and purification were repeated thrice, and water was removed through a rotary evaporator to obtain a white solid. The resulting solid hydrogenated products were placed in an oven at 105 °C for 12 h to remove excess impurities. Finally, pure chiral amino phosphonic acids were obtained.

Author contributions

The manuscript was written through contributions of the author. The authors have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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