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Enantioselective Synthesis of Optically Active Alkanephosphonates *via* Rhodium-Catalyzed Asymmetric Hydrogenation of β-Substituted α,β-Unsaturated Phosphonates with Ferrocene-Based Monophosphoramidite Ligands

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Abstract: A series of chiral β-substituted alkanephosphonates was synthesized in high enantioselectivities *via* the first rhodium-catalyzed asymmetric hydrogenation of the corresponding β-substituted-α,β-unsaturated phosphonates using a ferrocene-derived monophosphoramidite ligand, with which up to 99.5% *ee* have been achieved for the hydrogenation of (*E*)-substrates and 98.0% *ee* for (*Z*)-substrates.

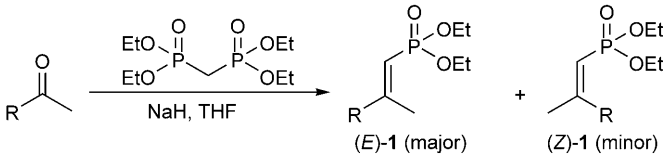
Keywords: alkanephosphonates; asymmetric catalysis; hydrogenation; monophosphoramidite ligands; rhodium

Optically active alkanephosphonic acid derivatives have received significant attention recently because of their interesting biological properties as phosphorus analogues of carboxylic acids,[1] as well as their synthetic utility as chiral building blocks.[2] Although some stoichiometric or catalytic asymmetric syntheses have been developed for constructing chiral 1-arylethanephosphonates in the past decades,[3] the enantioselective synthesis of chiral β-substituted alkanephosphonates by a catalytic method is still rarely explored. To the best of our knowledge, only one publication by Hayashi et al. has described the enantioselective synthesis of β-aryl-substituted alkanephosphonates by a catalytic asymmetric 1,4-addition to 1-alkenephosphonates using a chiral phosphine-Rh catalyst and arylboroxines as arylating reagents.[4] Therefore, the development of new catalytic methods for the enantioselective synthesis of these compounds is still highly desirable.

In our ongoing efforts toward the search for new efficient approaches for the asymmetric synthesis of chiral phosphonate derivatives, we have been interested in the application of catalytic asymmetric hydrogenation because of its inherent efficiency and atom economy.[5] Catalytic asymmetric hydrogenation is a powerful tool for the enantioselective synthesis of 3-arylbutanoic acid derivatives,[6] which are structurally similar to the β-substituted alkanephosphonates of interest. We therefore envisioned that it should be possible to prepare a phosphono analogue of an α,β-unsaturated carboxylic acid ester as a substrate for catalytic asymmetric hydrogenation. Indeed, such a strategy has been extensively applied in the synthesis of a variety of chiral phosphono analogues of α-amino acid esters, β-amino acid esters, α- and β-hydroxy acid derivatives, by catalytic asymmetric hydrogenation of the corresponding α-amidoalkenephosphonates, β-amidoalkenephosphonates, α-acyloxyalkenephosphonates, and β-ketoalkanephosphonates.[7] However, asymmetric synthesis of β-substituted alkanephosphonates *via* catalytic hydrogenation of α,β-unsaturated phosphonates is still unexplored. Herein we report for the first time the highly enantioselective rhodium-catalyzed asymmetric hydrogenation of β-substituted alkenephosphonates with a 1-ferrocenylethylamine-derived monodentate phosphoramidite ligand, with which a variety of chiral β-substituted alkanephosphonates were prepared in up to 99.5% *ee*.

The success of this hydrogenation method largely depended on the development of a method for the efficient synthesis of single isomers of β-substituted-α,β-

unsaturated phosphonates **1** since a mixture of *Z*- and *E*-isomers will be normally formed in the synthesis and sometimes they are not easy to be separated. For the hydrogenation of a substrate containing two isomers, it is generally difficult to achieve high enantioselectivity.[8] Fortunately, we found that the target substrates could be easily prepared through a simple and versatile synthetic method as shown in Scheme 1. By the reaction of tetraethyl methylenediphosphonate with various aryl methyl ketones, the *E*-isomer is formed predominantly and a small amount of the *Z*-isomer formed can be removed by column chromatography.[9]



Scheme 1. Synthesis of β-substituted α,β-unsaturated phosphonates (**1**).

An exploratory ligand screening experiment was performed at room temperature under 40 atm of H_2 pressure in CH_2Cl_2, and employed a diverse array of chiral monodentate and bidentate phosphorus ligands. Some representative ligands screened are listed in Figure 1. As shown in Table 1, most of the bidentate phosphorus ligands tested, which have proven to be successful for the highly enantioselective hydrogenation of various olefins, gave unsatisfactory results in this transformation. For example, DuPHOS showed no activity under the reaction conditions (entry 1),

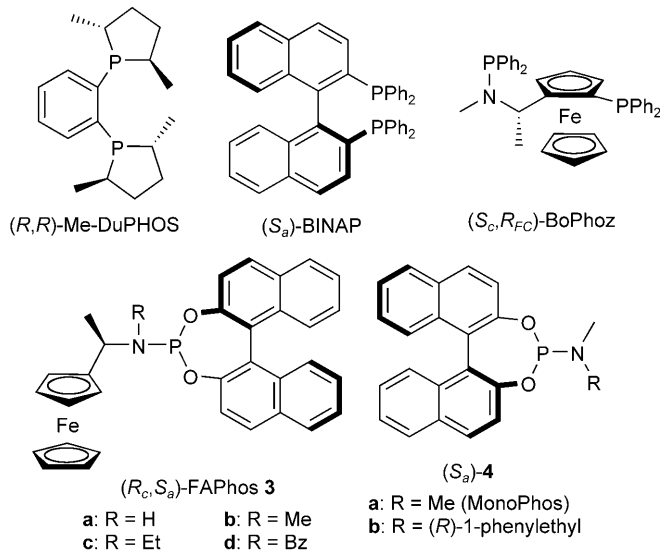
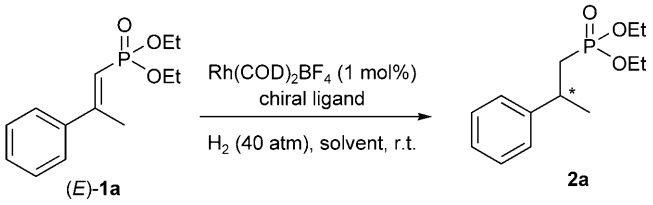


Figure 1. Structures of some representative ligands for asymmetric hydrogenation.

Table 1. The asymmetric hydrogenation of diethyl (*E*)-(2-phenyl-1-propene)phosphonate (**1a**).[a]



Entry	Ligand	Solvent	Conversion [%][b]	*ee* [%][c]
1	DuPHOS	CH_2Cl_2	–	–[d]
2	BINAP	CH_2Cl_2	84	30.3
3	BoPhoz	CH_2Cl_2	100	75.0
4	(R_c,S_a)-**3b**	CH_2Cl_2	100	95.6
5	MonoPhos	CH_2Cl_2	35	55.5
6	(S_a)-**4b**	CH_2Cl_2	21	0
7	(R_c,S_a)-**3b**	MeOH	–	–[d]
8	(R_c,S_a)-**3b**	THF	–	–[d]
9	(R_c,S_a)-**3b**	PhMe	–	–[d]
10	(R_c,S_a)-**3b**	*i*-PrOH	70	36.1
11	(R_c,S_a)-**3a**	CH_2Cl_2	47	7.0
12	(R_c,S_a)-**3c**	CH_2Cl_2	100	98.3
13	(R_c,S_a)-**3d**	CH_2Cl_2	65	93.4

[a] All reactions were carried out with 0.25 mmol of substrate at room temperature under an H_2 pressure of 40 atm in 2 mL of the indicated solvent for 24 h.
[b] Degrees of conversion were determined by GC.
[c] The *ee* values were determined by HPLC on a chiral column.
[d] Not determined because of low conversion.

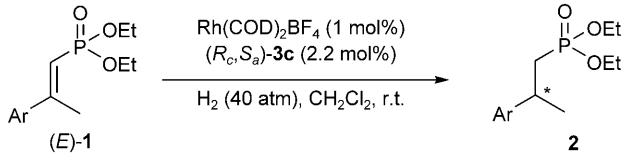
while BINAP only gave low enantioselectivity and incomplete conversion (entry 2). A BoPhoz-type ligand was effective for this hydrogenation, however, the enantioselectivity was moderate even with use of the finely modified ligand (entry 3).

To our delight, we found that (R_c,S_a)-FAPhos **3b**, a monodentate phosphoramidite ligand recently developed by us for the highly efficient Rh-catalyzed asymmetric hydrogenation of a variety of functionalized C=C double bonds,[13] unexpectedly afforded an *ee* value of up to 95.6% and full conversion (entry 4). More interestingly, subsequent investigations of the effect of the monophosphoramidite structure on this hydrogenation showed that the ferrocene fragment in these monodentate ligands has a crucial role in the reactivity and enantioselectivity. Thus, both MonoPhos (**4a**) and the phenyl analogue of (R_c,S_a)-**3b**, (R_c,S_a)-**4b**, gave the poor results in this transformation (entries 5 and 6). Further experiments in an effort to attain higher enantioselectivity by optimizing the reaction conditions failed. In a solvent screening experiment, a dramatic solvent effect was observed; however, no results surpassed that obtained in CH_2Cl_2. For example, the reaction in solvents such as MeOH, THF, or toluene led to very low reactivity (entries 7–9), while low enantioselectivity and incomplete conversion were

observed when the reaction was carried out in *i*-PrOH (entry 10). Since the synthetic method towards the FAPhos ligand is highly modular, the structural optimization of FAPhos was therefore performed. The results indicated that the substituent effect of the ligands was significant, affecting not only the reactivity but also the enantioselectivity. When ligand **3a** with an N–H proton was used, both reactivity and enantioselectivity were decreased dramatically (entry 11). By use of ligand **3c** with an N–Et group, the enantioselectivity were further improved to 98.3% *ee* with complete conversion (entry 12). Ligand **3d** with a benzyl group in the amino moiety also gave good enantioselectivity, however, lower reactivity was observed (entry 13).

With these encouraging results in the hydrogenation of (*E*)-**1a**, we proceeded to investigate the scope of this new transformation on various β-aryl-substituted α,β-unsaturated phosphonates (*E*)-**1a–k**, using (R_c,S_a)-**3c** as ligand and CH_2Cl_2 as the standard solvent. As shown in Table 2, entries 1–9, a wide range of substituted β-phenyl-α,β-unsaturated phosphonates (*E*)-**1a–i** were hydrogenated to provide the corresponding 2-arylpropanephosphonates with high enantioselectivity (97.9–99.3% *ee*). The best enantioselectivity of 99.3% *ee* was obtained in the hydrogenation of the substrate **1d** with a 4-methyl group in the phenyl ring (entry 4). These results indicated that the present catalytic system has a high tolerance to the substituted pattern and electronic properties of the substituent on the phenyl ring in terms of both reactivity and enantioselectivity. Diethyl (*E*)-[2-(2-naphthyl)-1-propene)phosphonate (**1j**) was also hydrogenated to afford 2-(2-naphthyl)propanephosphonate (**2j**) in full conversion and 96.7% *ee* (entry 10). In the hydrogenation of the substrate **1k**, with a heteroaromatic thiophenyl group, chiral phosphonate **2k** was obtaind in full conversion and 99.5% *ee* (entry 11). These results demonstrated the efficiency of the present catalytic system in the synthesis of chiral 2-arylpropanephosphonates.

Table 2. The asymmetric hydrogenation of diethyl (*E*)-(2-aryl-1-propene)phosphonate (**1**).[a]



Entry	Substrate	Ar	Conversion [%][b]	*ee* [%] (configuration)[c]
1	(*E*)-**1a**	Ph	100	98.3 (*R*)
2	(*E*)-**1b**	4-$MeOC_6H_4$	100	98.8 (+)
3	(*E*)-**1c**	3-MeC_6H_4	100	98.1 (+)[d]
4	(*E*)-**1d**	4-MeC_6H_4	100	99.3 (+)
5	(*E*)-**1e**	3-$CF_3C_6H_4$	100	98.3 (+)[d]
6	(*E*)-**1f**	4-$CF_3C_6H_4$	100	99.0 (+)
7	(*E*)-**1g**	4-FC_6H_4	100	97.9 (+)
8	(*E*)-**1h**	4-ClC_6H_4	100	98.7 (+)
9	(*E*)-**1i**	4-BrC_6H_4	100	98.2 (+)[d]
10	(*E*)-**1j**	2-naphthyl	100	96.7 (+)
11	(*E*)-**1k**	2-thiophenyl	100	99.5 (+)

[a] All reactions were carried out with 0.25 mmol of substrate at room temperature under an H_2 pressure of 40 atm in 2 mL of CH_2Cl_2 for 24 h unless otherwise specified. Substrate/$Rh(COD)_2BF_4$/ligand = 1/0.01/0.022.

[b] Degrees of conversion were determined by GC.

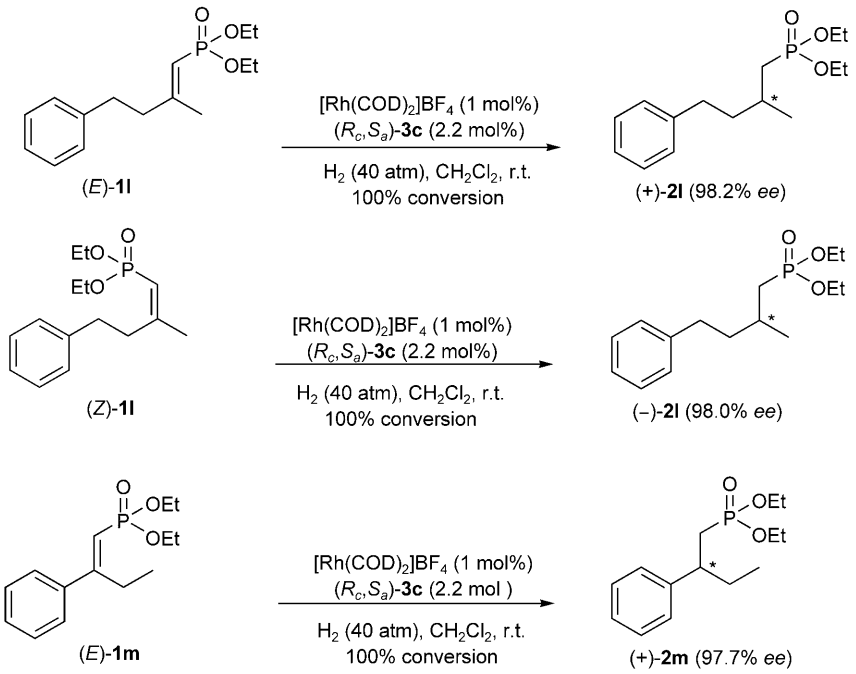
[c] The *ee* values were determined by HPLC on a chiral column (Chiralpak AD-H or OJ-H). The absolute configuration was determined by comparing the optical rotation with the reported data.

[d] The reactions were performed at 50 °C.

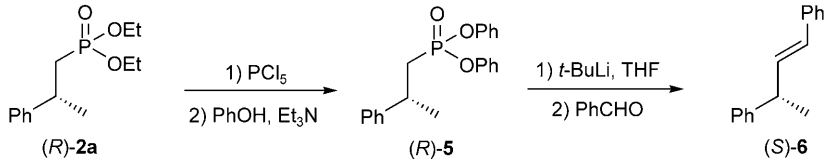
To broaden the synthetic interest of this highly enantioselective procedure, a set of structurally diverse α,β-unsaturated phosphonates, including (*E*)-β-alkyl-β-methyl-substituted substrate [(*E*)-**1l**], (*Z*)-β-alkyl-β-methyl-substituted substrate [(*Z*)-**1l**], and (*E*)-β-ethyl-β-phenyl-α,β-unsaturated phosphonate [(*E*)-**1m**], was prepared and submitted to the optimized Rh-catalyzed hydrogenation conditions (Scheme 2). The result indicated that the Rh/(R_c,S_a)-**3c** complex is also highly efficient for the hydrogenation of β,β-dialkyl-substituted substrate (*E*)-**1l**, providing the hydrogenation product in full conversion with an *ee* value of 98.2%. For the hydrogenation of (*Z*)-substrate [(*Z*)-**1l**] with the present catalytic system, excellent enantioselectivity (98.0% *ee*) and full conversion were also achieved, however, the absolute configuration of the hydrogenation product is opposite to that obtained from the hydrogenation of the (*E*)-substrate. The hydrogenation of (*E*)-β-ethyl-β-phenyl-α,β-unsaturated phosphonate [(*E*)-**1m**] proved to be as efficient as that of its β-methyl analogues, giving the hydrogenation product in full conversion with an *ee* value of 97.7%.

As reported by Hayashi et al., optically active alkanephosphonates, containing the stereogenic carbon center at the β-position, can be used as chiral building blocks for the synthesis of optically active alkenes by the Horner–Emmons-type reaction without loss of enantiomeric purity (Scheme 3).

In conclusion, a series of chiral β-substituted alkanephosphonates was synthesized in high enantioselectivities in the first Rh-catalyzed asymmetric hydrogenation of the corresponding β-substituted α,β-unsaturated phosphonates using a 1-ferrocenylethylamine-derived monophosphoramidite ligand, in which up to 99.5% *ee* has been achieved. Since these hydrogenation substrates are easily prepared, this method is potentially practical for the synthesis of such chiral compounds. The development of new catalytic methods to



Scheme 2. Rh-catalyzed asymmetric hydrogenation of (*E*)-**1l**, (*Z*)-**1l** and (*E*)-**1m**.



Scheme 3. Example of a synthetic application of chiral diethyl 1-(2-phenyl)propanephosphonate **2a**.

synthesize chiral alkanephosphonates is still in progress.

Experimental Section

General Methods

All reactions and manipulations were performed in a nitrogen-filled glove-box or under nitrogen using Schlenk techniques unless otherwise noted. All solvents were distilled under argon in the presence of the following desiccants: sodium-benzophenone ketyl for diethyl ether (Et_2O), tetrahydrofuran (THF), CaH_2 for dichloromethane (CH_2Cl_2).

General Procedure for the Preparation of β-Substituted α,β-Unsaturated Phosphonates

A solution of $(EtO)_2P(O)CH_2P(O)(OEt)_2$ (1.44 g, 5 mmol) in THF (2 mL) was slowly added at 0 °C to a slurry of NaH (0.19 g, 5.5 mmol, 70% in oil) in THF (10 mL). After the addition, the mixture was stirred at room temperature for 0.5 h. To the mixture, a solution of ketone (4.25 mmol) in THF (3 mL) was added. The reaction mixture was stirred at room temperature until the ketone disappeared as monitored by TLC. The mixture was then diluted with ether and washed with a aqueous solution of saturated NH_4Cl (25 mL × 1) and brine (25 mL × 1). The organic layer was separated, and dried over anhydrous $NaSO_4$. After removal of the volatiles, the residue was purified by column chromatography (silica gel, AcOEt/hexane, 1:1).

General Procedure for Asymmetric Hydrogenation of β-Substituted α,β-Unsaturated Phosphonates

In a nitrogen-filled glove-box, $[Rh(COD)_2]BF_4$ (1.0 mg, 0.0025 mmol) and (*Rc,Sa*)-**3c** (3.1 mg, 0.0055 mmol) were dissolved in degassed CH_2Cl_2 (1 mL) in a 5-mL vial. After stirring at room temperature for 15 min, a solution of α,β-unsaturated phosphonate (*E*)-**1a** (64 mg, 0.25 mmol, S/C 100:1) in 1 mL of degassed CH_2Cl_2 was added. The resulting mixture was transferred to an autoclave, which was then charged with H_2 (40 atm). The hydrogenation was performed at room temperature for 24 hours. After carefully releasing the hydrogen gas, the reaction mixture was purified through a plug of silica gel (eluting with a mixture of hexanes/EtOAc, 2:1) to afford **2a**. The enantiomeric excess was determined by HPLC on a chiral stationary phase.

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