Tetrahedron 66 (2010) 1806–1816

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Platinum(II) complex-catalyzed enantioselective aldol reaction with ketene silyl acetals in DMF at room temperature

Syun-ichi Kiyooka *, Satoshi Matsumoto, Tomonori Shibata, Kei-ichi Shinozaki

Department of Materials Science, Faculty of Science, Kochi University, Akebono-cho 2-5-1, Kochi 780-8520, Japan

ARTICLE INFO

Article history:
Received 25 November 2009
Received in revised form 10 January 2010
Accepted 12 January 2010
Available online 18 January 2010

This paper is dedicated to Professor Clyaton H. Heathcock on the occasion of his 74th birthday

Keywords:
[{(*R*)-Binap}Pt(μ-OH)]$_2$2SbF$_6$
Platinum-catalyzed enantioselective aldol reaction
Mukaiyama aldol reaction

ABSTRACT

[{(*R*)-binap}Pt(μ-OH)]$_2$2X is a weak Lewis acid, which can catalyze the enantioselective aldol reaction of aldehydes with ketene silyl acetals in DMF at room temperature. The platinum(II) complex-catalyzed the enantioselective aldol reaction of aldehydes with 1-methoxy-2-methyl-(1-trimethylsilyloxy)propene gave the corresponding aldols in high yields with enantioselectivity up to 92%. With 5 mol % loading of the complexes, the enantioselective aldol reaction of aldehydes with 1-benzyloxy-1-(trimethylsilyloxy)-propene smoothly proceeded in DMF containing 10% HMPA as to predominantly give *anti*-propionates with enantioselectivity up to 89%, irrespective of the silyl nucleophile geometry.

1. Introduction

Although the late transition metal complex-catalyzed enantioselective aldol reactions are expected to be valid for process chemistry, the practically effective catalytic systems have not been developed yet.[1] The available catalysts were limited to chiral palladium-[2] and platinum-complexes.[3] We have reported a simplified reaction procedure useful for the dicationic {(*R*)-binap}- and {(−)-sparteine}-palladium-catalyzed aldol reactions with 1-phenyl-(1-trimetylsilyloxy)ethene, in the presence of active catalysts in situ provided from {(*R*)-binap}- or {(−)-sparteine}-PdCl$_2$ and AgSbF$_6$ in the presence of 3A molecular sieves in dry DMF.[4] However, the chiral palladium complex-catalyzed enantioselective aldol reactions with ketene silyl acetals resulted in the formation of racemic aldols. The failure was very regrettable because the aldol products, derived from ketene silyl acetals, are obviously advantageous for the sequential aldol strategy constructing 1,3-diol frameworks in natural products by preparing the next aldehyde by the direct reduction of the ester moiety in the aldol products.[5] On the other hand, Fujimura reported only one example of a platinum-catalyzed aldol reaction with a ketene silyl acetal, 1-methoxy-2-methyl-(1-trimethylsilyloxy)propene (**2**),[3] where the platinum cationic species was prepared in situ from a Pregosin complex,[6] 3,5-di-*tert*-butylsalicylaldehyde-chelating (binap)platinum(II) complex, according to the Strukul method[7] by treatment with HOTf and lutidine in CH_2Cl_2. The real structure of the active platinum catalyst has not been elucidated yet. In addition, alternative cationic catalysts were formed in situ from {(*R*)-binap}PtCl$_2$ and AgX, but the behavior was pointed out to be different from the above species in some reactions.[8]

In order to clarify the structure and its role in the enantioselective aldol reaction, we started to study the platinum-catalyzed enantioselective aldol reaction with the {(*R*)-binap}platinum complexes, which were in situ formed from {(*R*)-binap}PtCl$_2$ and AgX on the basis of the experience gained in the corresponding palladium chemistry.[4] Then, we found that the in situ formed platinum complex underwent the enantioselective aldol reaction of benzaldehyde with **2** in DMF at room temperature. Further, we were aware that the starting with structure-determined complexes was more advantageous than that with the in situ formed complexes with regard to the simplicity of handling catalysts and the reproducibility of the results. Thus, the reaction of a variety of aldehydes with **2** in the presence of [((*R*)-BINAP)Pt(μ-OH)]$_2$2X (5 mol %) in DMF was examined and turned out to proceed in good yields. The platinum(II) complex-catalyzed enantioselective aldol reaction utilizing [{(*R*)-binap}Pt(μ-OH)]$_2$2X with (*E*)- and (*Z*)-1-

* Corresponding author. Tel.: +81 88 844 8295; fax: +81 88 844 8359.
E-mail address: kiyooka@kochi-u.ac.jp (S.-i. Kiyooka).

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doi:10.1016/j.tet.2010.01.036

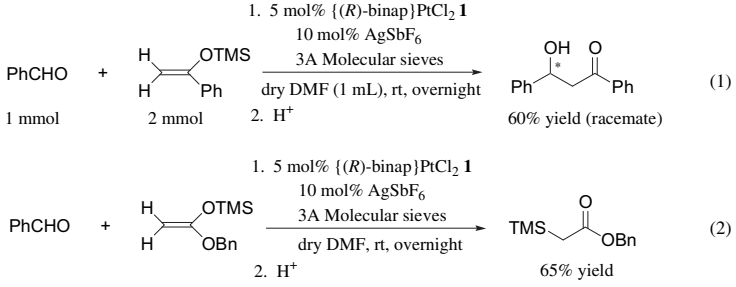
benzyloxy-1-(trimethylsilyloxy)propenes (**3**) resulted in good *anti* diastereoselectivity along with high enantioselectivity.

2. Results and discussion

2.1. Enantioselective aldol reaction in the presence of the in situ generated dicationic {(*R*)-binap}platinum complex

According to the procedure used for the in situ formation of the dimeric {(*R*)-binap}palladium complexes,[4] the corresponding {(*R*)-binap}platinum complex was prepared by the addition of two equivalents of AgX to one equivalent of {(*R*)-binap}$PtCl_2$ **1** in the presence of 3A molecular sieves in DMF at room temperature. At the beginning, we checked the effectiveness of a silyl enol ether, 1-phenyl-1-(trimethylsilyloxy)ethane, useful for the palladium-catalyzed enantioselective aldol reaction under a similar procedure. The reaction of benzaldehyde with the silyl enol ether gave the aldol product in 60% yield but it was a racemate (Eq. 1 in Scheme 1). The DMF in which the dicationic species is undoubtedly effective for **2**, despite some uncertainty on the structure in DMF. The reaction of benzaldehyde with **2** gave methyl 3-hydroxy-2,2-dimethyl-3-phenylpropionate (**4**) in 74% yield with 80% ee. Since the absolute configuration of **4** was not reported in Ref. 3, we decided to determine it in comparison with the authentic sample, which was prepared by our chiral oxazaborolidinone-promoted enantioselective aldol reaction.[9] The absolute configuration of **4**, obtained from the reaction using the platinum catalyst with (*R*)-binap, was assigned to be *S*, as illustrated in Scheme 2. The high enantioselectivity was observed over the used aldehydes but the yields except benzaldehyde were not necessarily satisfied (entries 2–5).

At the stage, the mechanism of the in situ generated platinum-catalyzed enantioselective aldol reaction was explained as one of typical examples of the enantioselective Mukaiyama aldol reaction: the dicationic platinum activates the aldehyde carbonyl group and the counter ion assists the nucleophilic attack of the ketene silyl acetal, as illustrated in Figure 1.

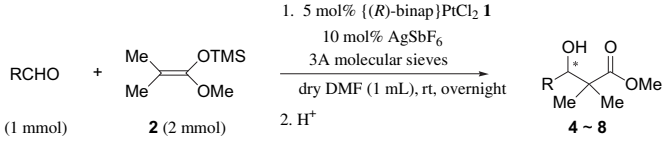


Scheme 1.

result is suggestive of different behaviors on the aldol reaction mechanism between palladium and platinum catalysts.[2] Then, we shifted our interest to ketene silyl acetals as silyl nucleophiles in the chiral platinum(II) complex-catalyzed enantioselective aldol reaction. Expecting to obtain chiral acetate equivalents, we first carried out the reaction of benzaldehyde with 1-benzyloxy-1-(trimethylsilyloxy)ethene. The reaction, however, did not produce the aldol product. The product was α-silyl acetate in 65% yield: the dicationic platinum-catalyzed only the silyl migration reaction from O-bound to C-bound species (Eq. 2 in Scheme 1).

With regard to the possible importance of 1-methoxy-2-methyl-1-(trimethylsilyloxy)propene (**2**) used effectively in the original platinum-catalyzed enantioselective aldol reaction,[3] the reaction of a variety of aldehydes with **2** was investigated in the presence of the in situ generated dicationic platinum complex. As shown in Table 1, highly enantioselective reactions took place in

Table 1
Dicationic {(*R*)-binap}Pt-catalyzed enantioselective aldol reaction of aldehydes with 1-methoxy-2-methyl-1-(trimethylsilyloxy)propene (**2**)

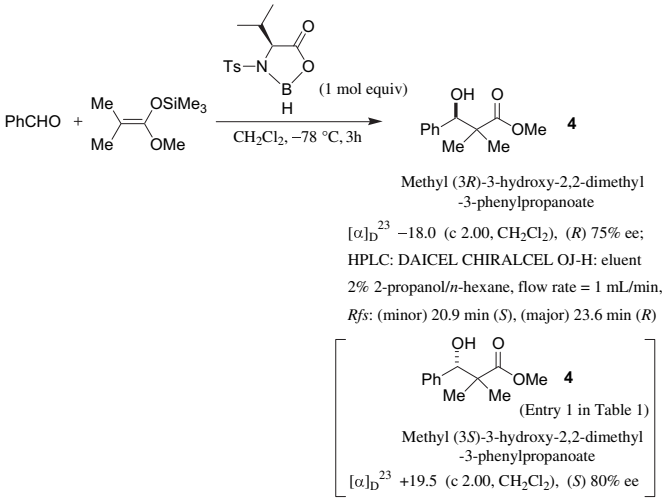


Entry	Aldehydes	Products	% Yield	% ee
1	Benzaldehyde	**4**	74	80 (*S*)[a]
2	*p*-Phenylbenzaldehyde	**5**	58	77
3	2-Naphtylaldehyde	**6**	47	80
4	Cinnamaldehyde	**7**	34	78
5	3-Phenylpropionaldehyde	**8**	20	84

[a] The absolute configuration of product **4** was determined by comparison with the product from the chiral borane-mediated enantioselective aldol reaction, shown in Scheme 2.

2.2. Enantioselective Mukaiyama aldol reaction using the preformed solid complexes of dimeric [{(*R*)-binap}Pt(μ-OH)]$_2$2X

*2.2.1. Preparation and characterization of dimeric [{(R)-binap}Pt(μ-OH)]$_2$2X.* Platinum(II) complexes having (*R*)- or (*S*)-BINAP as a chiral ligand have been prepared by several methods. Strukul reported that a platinum(II) hydroxo complex, [{(*R*)-binap}Pt(μ-OH)]$_2$$BF_4$: ($^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 2.60, J_{P-Pt}=3690 Hz), was obtained by the addition of $AgBF_4$ into a CH_2Cl_2 solution, containing acetone, of {(*R*)-binap}$PtCl_2$ **1**, which works as a catalyst for the Beyer–Villiger oxidation of ketones with hydrogen peroxide.[7b] Gagné et al. obtained {(*R*)-binap}Pt($OTf)_2$: ($^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 1.60, J_{P-Pt}=4210 Hz), from the reaction of {(*R*)-binap}Pt((*S*)-BINOL)



Scheme 2. An experimental result for assignment of the absolute configuration of aldol product **4**.

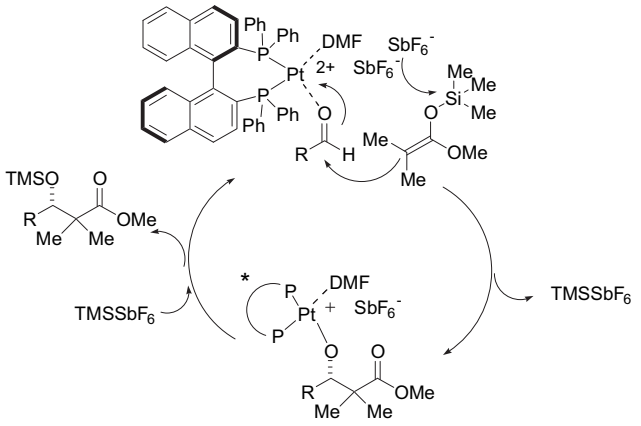


Figure 1. The enantioselective aldol reaction in the presence of the in situ generated dicationic platinum complex.

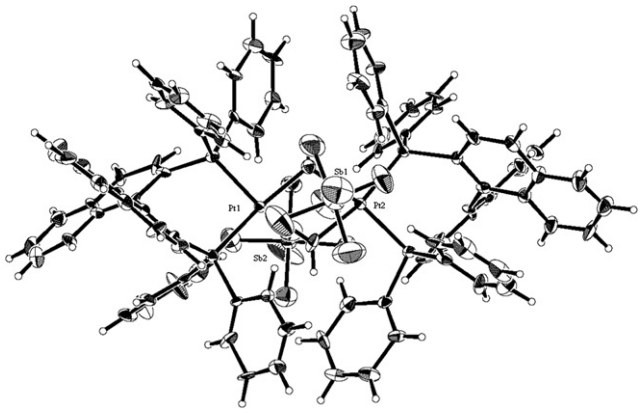


Figure 2. ORTEP of [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF$_6$.

and 2 equiv of triflic acid (HOTf) in CD_2Cl_2 at room temperature.[10] After the addition of H_2O, {(*R*)-binap}Pt(OTf)$_2$ was converted to [{(*R*)-binap}Pt(H_2O)$_2$](OTf)$_2$: ($^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 3.50, J_{P-Pt}=4050 Hz). On the other, Stang et al. prepared the mono aqua complex, [{(*R*)-binap}Pt(H_2O)]$_2$2OTf: ($^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 4.40, J_{P-Pt}=4023 Hz), by the addition of AgOTf into a CH_2Cl_2 solution of **1**.[11] Only a slight difference in the preparation procedures leads to the structural differences in the product complexes. We carried out the preparation of a dimeric Platinum(II) complex **9** (Scheme 3); **9a**, ($^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 4.70, J_{P-Pt}=3645 Hz), was prepared from $AgSbF_6$ and {(*R*)- or (*S*)-binap}$PtCl_2$, according to Strukul's et al. procedure.[7b] The repeated recrystallization of the crude from CH_2Cl_2–ether gave pale yellow needles. Using the fine crystals, the structure of the complex **2** was first confirmed by the X-ray diffraction analysis to be a dimer bridged by OH groups: the ORTEP drawing is depicted in Figure 2.[12]

The structure of the complex in solutions serving versatile information on the reaction mechanism was provided by the NMR studies.[13] Does the dimeric structure of [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF$_6$ remain unchanged in DMF during the reaction? The preliminary answer was given by the ^1H NMR measurement of the complex in CD_2Cl_2 and DMF-d_7, as presented in Figure 3: the dimeric structure was maintained in CD_2Cl_2 on the basis of the characteristic proton signal at −1.5 ppm assigned to μ-OH (**B**) while the downfield shift of the OH signal was observed at 2.9 ppm in DMF-d_7, which is attributable to the hydroxyl group coordinated to a monomeric structure (**A**). The monomeric structure, stabilized by the nucleophilic coordination ability of DMF, can be probably related to the species working as an active catalyst.

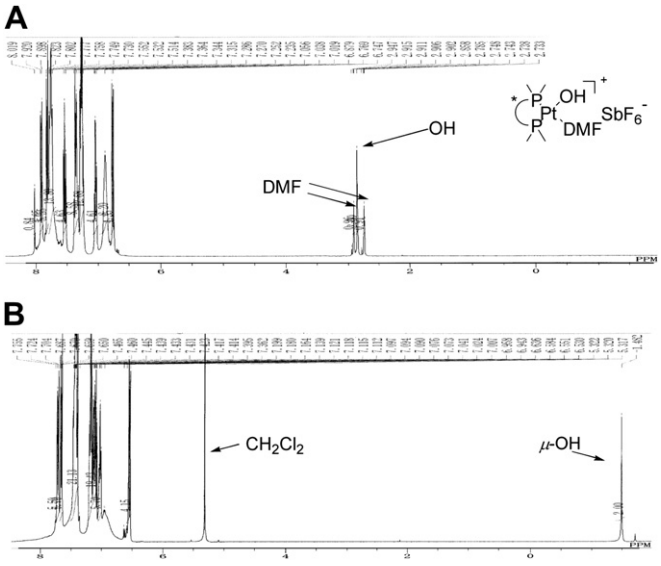
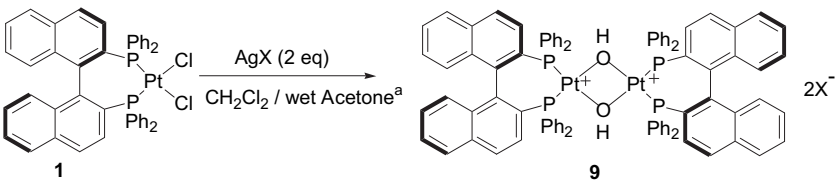


Figure 3. ^1H NMR spectra of monomeric [{(*R*)-binap}Pt(OH)(DMF)]SbF_6 in DMF-d_7 (**A**) and of dimeric [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF_6 in CD_2Cl_2 (**B**).

*2.2.2. Reaction with 1-methoxy-2-methyl-1-(trimethylsiloxy)-propene (**2**).* The reaction using the in situ generated complex would often tend to lower the yield and selectivity owing to arbitrarily experimental errors. Since the structure of dimeric [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF_6 turned out to be monomeric in DMF, the starting dimeric solid complex was considered to have a prospect of catalyzing the enantioselective aldol reaction as a monomeric catalyst. The dimeric platinum complex was



1 **9**

a : X = SbF_6^- b : X = OTf^- c : X = ClO_4^-
d : X = BF_4^-

[a] The acetone solvent was used without purification and especially a small amount of water did not be added but the hydroxy function was introduced into the dimeric platinum complex under the conditions.

Scheme 3. Preparation of [{(*R*)-binap}Pt(μ-OH)]$_2$2X.

actually a promising precursor with the reproducibility of the yield and selectivity.

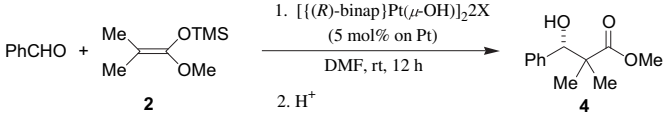
The reaction of benzaldehyde, starting with the solid dimeric complex **9a**, undoubtedly reproduced the higher yield and selectivity, compared with those in the reaction with the in situ generated catalyst: from 74% yield and 80% ee in Table 1 (entry 1) to 87% yield and 84% ee in Table 2 (entry 1). The counter ion effects of **9** on yield and selectivity in the reaction of benzaldehyde with **2** are represented in Table 2. The level of yield and selectivity of OTf^- was almost the same as that of SbF_6^- (entry 2) but BF_4^- is prone to relatively lower it.

Availability of chiral modified binap ligands in the platinum complex (OTf^-) was examined in the reaction of benzaldehyde with **2** under the same conditions, as summarized in Table 3. All checked ligands gave satisfactory results on yield. On the other hand, only (*R*)-segphos was capable of providing the aldol product with nearly the same selectivity as that of (*R*)-binap but the other three ligands were less effective.

Table 4 illustrates the effects of aldehyde structure on reactivity and selectivity in the reaction with **2** in DMF. Aromatic aldehydes having an electron-attracting substituent gave higher yield than that of benzaldehyde (entries 1, 2, 5) while aldehydes having an electron-releasing substituent gave a little lower yield (entries 6, 7). But the both aldehydes provided similar enantioselectivity. 3-Phenylpropionaldehyde, as a representative primary aliphatic aldehyde, led to superior enantioselectivity (entry 4). Additionally, a primary aliphatic aldehyde, heptanal, underwent the reaction in <20% yield but ~80% ee while secondary aldehydes did not work under the reaction conditions.

*2.2.3. Reaction with (E)- and (Z)-1-benzyloxy-1-(trimethylsiloxy)-propenes (**3**).* The chiral platinum(II) complex-catalyzed enantioselective aldol reaction toward propionate aldols with (*E*)- and (*Z*)-1-benzyloxy-1-(trimethylsilyloxy)propenes (**3**) was examined. This was the first challenge for the diastereoselective propionate synthesis under enantioselective conditions with chiral platinum(II) catalysts. The solvent effects on the reaction were first investigated, as shown in Table 5. Non polar solvents, CH_2Cl_2, and toluene, gave racemic propionates with no diastereoselectivity while polar solvents; DMSO, CH_3CN, THF, did not show appreciable enantioselectivity along with low diastereoselectivity. In DMF, the reaction of benzaldehyde with *E*-**3** was found to give a mixture of the corresponding propionates (*anti*/*syn*=3.8:1) with a good enantioselectivity of 62% for the *anti* isomer (entry 6). The absolute configuration of the *anti* isomer was determined by comparing the optical rotation value of the corresponding acid derived from *anti* **7** with that of the known one, as shown in Scheme 4.[14] Furthermore, we found a new solvent system of DMF containing 10% HMPA, which remarkably enhanced the diastereoselectivity up to a ratio of 6:1 along with the improved enantioselectivity (from 62 to 84% ee for *anti*

Table 2
Counter ion effects of [{(*R*)-binap}Pt(μ-OH)]$_2$2X on the yield and selectivity in the aldol reaction of benzaldehyde with **2**



Entry	Catalysts	Yield (%)	% ee
1	[{(*R*)-binap}Pt(μ-OH)]$_2$2S$_b$F$_6$ **9a**	87	84
2	[{(*R*)-binap}Pt(μ-OH)]$_2$2OTf **9b**	86	84
3	[{(*R*)-binap}Pt(μ-OH)]$_2$2ClO4 **9c**	81	82
4	[{(*R*)-binap}Pt(μ-OH)]22BF4 **9d**	53	68

Table 3
Chiral ligand effects on 'Pt–OTf' catalyzed enantioselective aldol reaction of benzaldehyde with **2** (5 mol % loading; DMF, room temperature, 12 h)

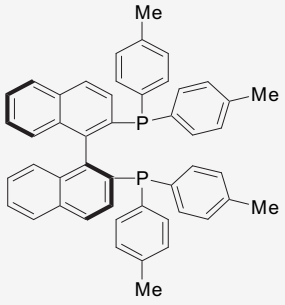
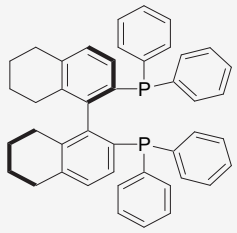
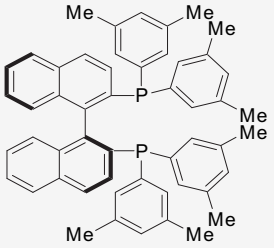
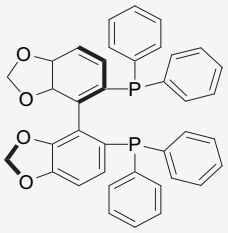
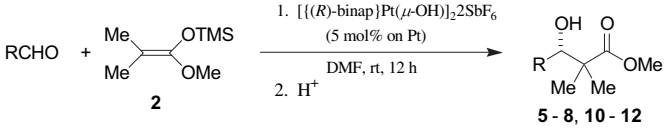
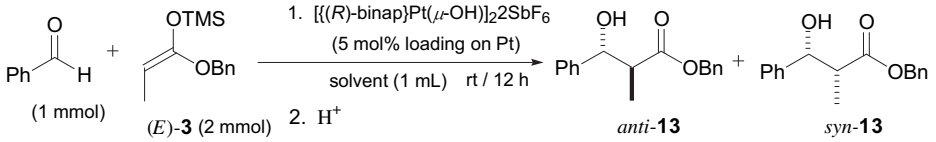
Entry	Ligands	% Yield	% ee
1	 (*S*)-Tol-binap	86	79
2	 (*R*)-H$_8$-binap	88	75
3	 (*S*)-Xylyl-binap	89	58
4	 (*R*)-Segphos	90	83

Table 4
[{(*R*)-binap}Pt(μ-OH)]22SbF$_6$-catalyzed enantioselective aldol reaction of a variety of aldehydes with **2**

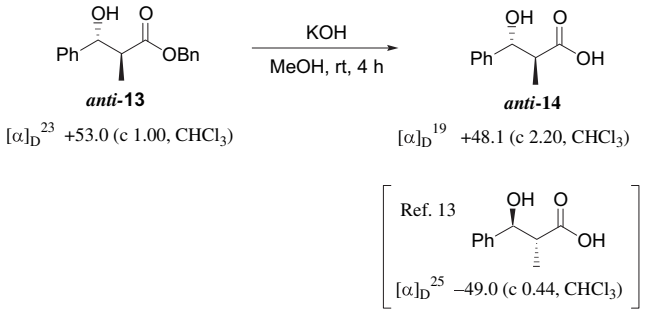


Entry	Aldehydes	Products	% yield	% ee
1	*p*-Phenylbenzaldehyde	**5**	89	82
2	2-Naphtylaldehyde	**6**	92	82
3	Cinnamaldehyde	**7**	77	72
4	3-Phenylpropionaldehyde	**8**	76	90
5	*p*-Nitrobenzaldehyde	**10**	89	79
6	*p*-Methylbenzaldehyde	**11**	79	81
7	*p*-Methoxybenzaldehyde	**12**	66	76

Table 5
Solvent effects on [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF$_6$-catalyzed enantioselective aldol reaction of benzaldehyde with **3**



Entry	Solvents	% Yield	Diastereo ratio *syn*/*anti*	% ee (*syn*/*anti*)
1	Dichrolomethane	95	1:1.2	racemate/racemate
2	Toluene	31	1:1.3	racemate/racemate
3	DMSO	49	1.1:1	racemate/10% ee
4	Acetonitlile	90	1:1.5	racemate/10% ee
5	THF	43	1:2.1	8% ee/37% ee
6	DMF	90	1:3.8	25% ee/62% ee
7	DMF–HMPA 50%	47	2:1	racemate/racemate
8	DMF–HMPA 10%	88	1:6	41% ee/84% ee



Scheme 4. Assignment of the stereochemistry of *anti*-aldol product (*anti*-**13**).

isomer) (entry 8). But the excess use of HMPA quenched the superior selectivity (entry 7). This HMPA effect on the selectivity is quite interesting. Although the role of HMPA is unclear, we can suppose that the selectivity-determining stage might prefer to be more polar.

The *anti* diastereoselectivity is characteristic of the platinum-catalyzed enantioselective aldol reaction with *E*-**3**. This remarkable feature is in contrast with most *syn*-selective aldol reactions mediated by chiral Lewis acids.[1] In addition, the reaction with *Z*-**3** resulted in almost the same yield and selectivity as those found in the reaction with *E*-**3** (Scheme 5). This fact is particularly surprising that the same *anti* selectivity was observed irrespective of the silyl nucleophile geometry. Such behaviors have previously been reported in the zirconium alkoxide-catalyzed enantioselective aldol reaction.[15] Our platinum-catalyzed enantioselective aldol reaction can be considered to proceed via a path similar to the zirconium case with respect to the selectivity, in which the *anti* selectivity can be explained by using an antiperiplanar transition-state model **A**, as shown in Figure 4. However, a synclinal transition-state model **B**[16] is suggested to be more preferable, which is an alternative for *anti* selectivity, since an interaction between the cationic platinum center and the silyl nucleophile is necessary for the transition-state, as mentioned later.

The typical reaction conditions in DMF/HMPA-(10%) were applied to the reaction of a variety of aldehydes with *E*-**3**. The results are summarized in Table 6. The reactions resulted in good yields except 1-naphthaldehyde having the inherent steric bulkiness (entry 6). The *anti* preference was observed over the used aldehydes and the levels were considerably good. The enantioselectivity of *anti*-propionates was observed with reduced levels for the aldehydes having *p*-nitro, *p*-methoxy, and *p*-methyl substituents (entries 2–4) but the *anti*-propionate from cinnamaldehyde achieved a high enantioselectivity (entry 8). On the basis of these results, this platinum(II)-catalyzed enantioselective aldol reaction is acceptable for the simple preparation of optically active *anti*-propionates.

The NMR studies were offered in order to get enough evidence for the mechanism of this platinum(II) complex-catalyzed aldol reaction: No change was appeared in their ^{1}H and ^{13}C NMR spectra of the aldehyde added to the DMF solution involving the platinum complex so that the catalytic power of the complex would be weak as a Lewis acid for the aldol reaction. Appreciable change did not be found in their ^{1}H and ^{13}C NMR spectra of the substrates after ketene silyl acetals were added to the DMF solution containing the platinum complex. It suggested that any platinum *C*- or *O*-enolate did not be formed via metal exchange at the early stage of the reaction.

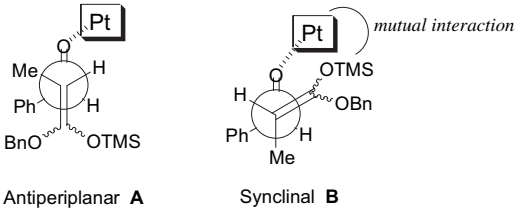
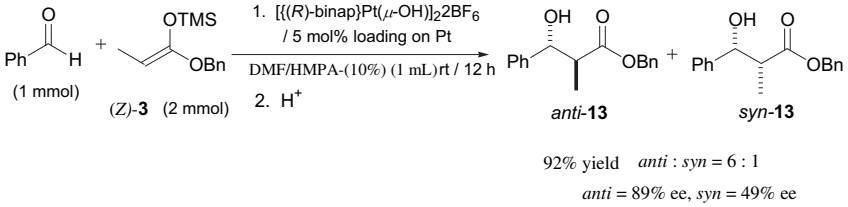


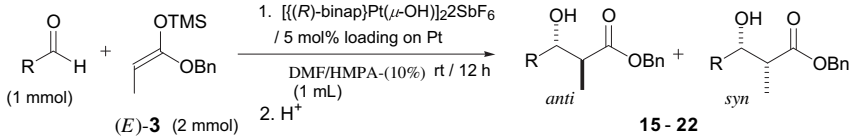
Figure 4. The origin on the selectivity deriving *anti*-aldol products in spite of their different geometry.

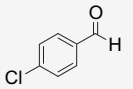
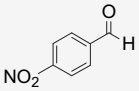
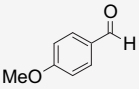
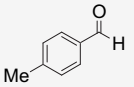
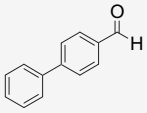
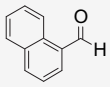
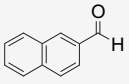
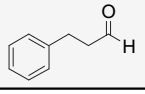


92% yield *anti* : *syn* = 6 : 1
anti = 89% ee, *syn* = 49% ee

Scheme 5. (μ-Hydoxo)-platinum complex-catalyzed *anti*-selective enantioselective aldol reaction of benzaldehyde with (*Z*)-**3**.

Table 6
[{(*R*)-binap}Pt(μ-OH)]22SbF_6-catalyzed *anti*-selective enantioselective aldol reaction of a variety of aldehydes with (*E*)-**3**



Entry	Aldehydes	Products	% yield	Selectivity
1		**15**	76	*anti*/*syn*=4.2:1 *anti*=83% ee, *syn*=30% ee
2		**16**	88	*anti*/*syn*=4.5:1 *anti*=59% ee, *syn*=18% ee
3		**17**	78	*anti*/*syn*=5.2:1 *anti*=55% ee, *syn*=9% ee
4		**18**	80	*anti*/*syn*=5.5:1 *anti*=67% ee, *syn*=14% ee
5		**19**	87	*anti*/*syn*=6.2:1 *anti*=82% ee, *syn*=41% ee
6		**20**	48	*anti*/*syn*=6.0:1 *anti*=84% ee, *syn*=48% ee
7		**21**	86	*anti*/*syn*=5.3: 1 *anti*=72% ee, *syn*=17% ee
8		**22**	83	*anti*/*syn*=5.5:1 *anti*=92% ee, *syn*=18% ee

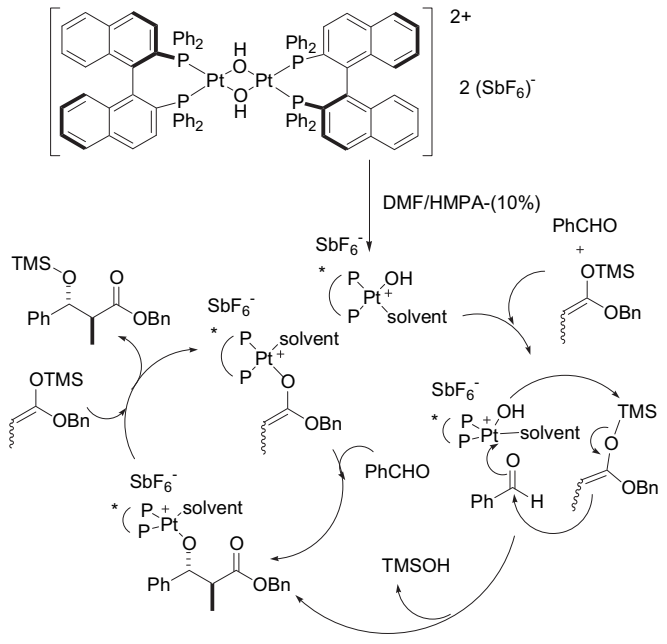


Figure 5. The catalytic cycle promoted by monomeric platinum species.

However, when the aldehyde and the corresponding silyl nucleophile were simultaneously added into the DMF solution of the platinum complex, the formation of the aldol product was first detected in the ^{1}H NMR spectra. The coexistence of the three substrates is essential for starting the aldol reaction. In order to assist the reaction, the hydroxo function of the catalyst presumably plays a role as a base in the reaction. The basic role of hydroxo compounds of platinum(II) has been shown in a number of reports.[17] On the basis of the above results, we can most likely propose a concerted acid–base catalyzed reaction mechanism, as shown in Figure 5, where the hydroxo group of the monomeric cationic platinum species can attack the silyl group of the nucleophile as a base and spontaneously the species assists the activation of the aldehyde function as a Lewis acid. Although the independent abilities of the acid and base are not necessarily enough to promote the reaction, they can catalyze the reaction only by working cooperatively.

3. Conclusion

The {(*R*)-binap}platinum(II) complex (5 mol % loading), in situ generated from {(*R*)-binap}$PtCl_2$ and AgX in the presence of 3A molecular sieves, catalyzed the enantioselective aldol reaction of aldehydes with ketene silyl acetal **2**. The [{(*R*)-binap}Pt(μ-OH)]$_2$2X complexes also underwent the reaction with the reproducible high

yield and enantioselectivity. The dimeric complex turned out to work as a monomeric species in DMF. The reaction apparently proceeds through the mode known as Mukaiyama aldol reaction although the platinum(II) species is not a strong Lewis acid. The [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF$_6$-catalyzed enantioselective aldol reaction of aldehydes with ketene silyl acetals (*E*)- and (*Z*)-**3** smoothly proceeded in DMF containing 10% HMPA at room temperature to predominantly give *anti*-propionates with enantioselectivity up to 89%, irrespective of the silyl nucleophile geometry. The *anti* diastereoselectivity is explained to be realized through open-chain transition states.

4. Experimental

4.1. General

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. All reactions were carried out under an argon atmosphere. *N*,*N*-Dimethylformamide (DMF) was distilled from calcium hydride under a reduced pressure. Molecular sieves were dried over an open flame immediately prior to use, cooled under a reduced pressure, and stored under N_2. Merck silica-gel 60 TLC aluminum sheets were used for thin layer chromatography. Flash column chromatography was carried out with Merck 60 silica-gel (230–400 mesh). Infrared spectra (IR) were recorded on a JASCO FT/IR-460 and only partial data are listed. Optical rotations were determined with a JASCO DIP-370 digital polarimeter. ^{1}H NMR spectra were obtained in $CDCl_3$ with JNM-LA 400 (400 MHz) spectrometer. ^{13}C NMR spectra were measured at 100 MHz with a JNM-LA 400 spectrometer. The optical purity was determined by HPLC analysis with DAICEL CHIRALCEL OD-H, OJ-H, and AD-H columns. Racemic aldol products (^{1}H and ^{13}C NMR spectra) in reactions with **2** have been reported.[18]

4.2. Synthesis of {(*R*)-binap}PtCl$_2$ (1)

When an aqueous solution (20 mL) of $K_2[PtCl_4]$ (0.304 g) was mixed with PhCN (3 mL) and then stirred for four days at room temperature, the organic layer turned yellow. The yellow precipitate, which developed on the interface was collected, washed successively with methanol and ether, and then dried in vacuo to give 0.22 g of the product in 63% yield. The filtrate was extracted with CH_2Cl_2, and the extract was concentrated to obtain a yellow product of 0.064 g on addition of pentane in 18% yield. While the former product included the *cis* isomer exclusively, the latter was as a mixture of *trans* and *cis* isomers (the *trans*/*cis* ratio was 0.72). The mixture of $PtCl_2(PhCN)_2$ (0.52 mmol, 246 mg, a mixture of *cis* and *trans* isomers) and (*R*)-binap (324 mg, 0.52 mmol) was dissolved in $CHCl_3$ (12 mL), followed by refluxing for 12 h. The $CHCl_3$ was removed with a rotary evaporator and then the yellow oil was obtained. After the addition of *n*-pentane, the yellow precipitate was filtrated to give 361 mg of the product in 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–6.67 (m, 32H); ^{31}P NMR (160 MHz, $CDCl_3$): δ 10.66 (s, J_{Pt-P}=3653 Hz).

4.3. Synthesis of 1-benzyloxy-1-(trimethylsilyloxy)ethene

A solution of diisopropylamine (10.5 mL, 75 mmol) in THF (40 mL) was cooled to 0 °C and a 1.6 M solution of *n*-butyllithium in *n*-hexane (44 mL, 75 mmol) was added slowly by a syringe. This mixture was stirred for 20 min at 0 °C and subsequently cooled to −78 °C. After 30 min, a mixture of benzyl acetate (7.5 g, 50 mmol) and TMSCl (9.6 mL, 75 mmol) was added over a 10-min time period under intensive stirring. The solution was stirred for 1.5 h at −78 °C and subsequently allowed to warm up to room temperature. The solvent was removed with a rotary evaporator. The residue was diluted with *n*-pentane and filtered. After removal of the solvent, the resulting crude was distilled under a reduced pressure to give the product of 14.4 g in 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.23 (s, 9H), 3.32 (d, *J*=2.9 Hz, 1H), 3.31 (d, *J*=2.9 Hz, 1H), 4.78 (s, 2H), 7.27–7.37 (m, 5H).

4.4. The reaction of benzaldehyde with 1-benzyloxy-1-(trimethylsilyloxy)ethene

To a mixture of {(*R*)-binap}PtCl$_2$ (0.05 mmol, 44 mg) and 3A molecular sieves (90 mg) was added DMF (0.15 mL) as a solvent. The solution was stirred at room temperature for 0.5 h. A solution of $AgSbF_6$ (0.1 mmol, 34 mg) in DMF (0.15 mL) was added and the resulting solution was stirred for 0.5 h. To the solution was added 1-benzyloxy-1-(trimethylsilyloxy)ethene (446 mg, 2.0 mmol). After the solution was stirred at the temperature for 10 min, benzaldehyde (102 mL, 1.0 mmol) was added. The solution was stirred for 12 h. The reaction was quenched by the addition of 10% aq HCl (5 mL). After stirring for 10 min, the product was extracted with diethyl ether (20 mL×2). The organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give a crude residue. The crude residue was purified by flash column chromatography (SiO_2) (10% AcOEt/*n*-hexane) to give 144 mg of benzyl (trimethylsilyl)acetate in 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.09 (s, 9H), 1.95 (s, 2H), 5.07 (s, 2H), 7.33–7.37 (m, 5H).

4.5. General procedure for the in situ generated Pt complex-catalyzed enantioselective aldol reaction. Reaction of benzaldehyde with 1-methoxy-2-methyl-1-(trimethylsilyloxy)propene (2)

To a mixture of {(*R*)-binap}PtCl$_2$ (0.05 mmol, 44 mg) and 3A molecular sieves (90 mg) was added DMF (0.15 mL) as a solvent. The solution was stirred at room temperature for 0.5 h. A solution of $AgSbF_6$ (0.1 mmol, 34 mg) in DMF (0.15 mL) was added and the resulting solution was stirred for 0.5 h. Ketene silyl acetal **2** (0.405 mL, 2 mmol) was successively added to the solution. After stirring for 10 min, benzaldehyde (0.102 mL, 1 mmol) was added dropwise over 2 min and the reaction mixture was allowed to stir for 15 h at room temperature. After quenched with 10% aq HCl (5 mL), the solution was stirred for 0.5 h, extracted with Et_2O, and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give a crude (294 mg). The crude material was purified by flash column chromatography (10% ethyl acetate/hexane) to give (+)-*methyl* (3*S*)-3-*hydroxy*-2,2-*dimethyl*-3-*phenylpropanoate* (**4**) of 154 mg in 74% yield; colorless paste; $[\alpha]_D^{23}$ +19.5 (*c* 2.00, CH_2Cl_2); 80% ee of (*S*)-isomer: HPLC analysis: retention time, 20.9 min, 23.6 min (DAICEL CHIRALCEL OJ-H Column, *n*-hexane/2-propanol=98:2, 1.0 mL/min); IR (KBr) 3454, 1702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (s, 3H), 1.15 (s, 3H), 2.17 (s, 3H), 3.08 (d, *J*=4.16 Hz, 1H), 3.73 (s, 3H), 4.90 (d, *J*=4.16 Hz, 1H), 7.35–7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.3, 19.0, 23.1, 48.7, 52.1, 78.7, 127.6, 127.8, 128.2, 141.9, 177.2 (aromatic two carbons are overlapping with other peaks).

*4.5.1. Methyl 3-hydroxy-2,2-dimethyl-3-(4-phenylphenyl)propanoate (**5**).* Colorless paste: 58% yield; 77% ee: HPLC analysis: retention time, 30.1 min, 37.5 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=95:5, 1.0 mL/min); IR (KBr) 3520, 1714 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 3H), 1.19 (s, 3H), 3.12 (d, *J*=3.9 Hz, 1H), 3.75 (s, 3H), 4.96 (d, *J*=3.9 Hz, 1H), 7.60–7.33 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 23.1, 47.7, 52.1, 78.5, 126.5, 127.0, 127.3, 128.1, 128.8, 139.0, 140.6, 140.7, 178.2 (aromatic four carbons are overlapping with other peaks).

*4.5.2. Methyl 3-hydroxy-2,2-dimethyl-3-(2-naphthyl)propanoate (**6**).* Colorless paste: 47% yield; 80% ee: HPLC analysis: retention

time, 100.7 min, 133.6 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=99:1, 1.0 mL/min); IR (KBr) 3500, 1707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 3H), 1.20 (s, 3H), 3.20 (d, *J*=4.4 Hz, 1H), 3.74 (s, 3H), 5.08 (d, *J*=4.4 Hz, 1H), 7.51–7.43 (m, 3H), 7.84–7.76 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 23.2, 47.9, 52.2, 78.8, 125.6, 125.9, 126.1, 126.7, 127.3, 127.6, 128.0, 132.8, 133.0, 137.4, 178.3.

*4.5.3. Methyl (E)-3-hydroxy-2,2-dimethyl-5-phenylpent-4-enoate (**7**).* Colorless paste: 34% yield; 78% ee: HPLC analysis: retention time, 39.2 min, 44.2 min (DAICEL CHIRALCEL AD-H Column, *n*-hexane/2-propanol=99:1, 1.0 mL/min); IR (KBr) 3506, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 3H), 1.25 (s, 3H), 2.77 (d, *J*=5.6 Hz, 1H), 3.73 (s, 1H), 4.35 (dd, *J*=7.1, 5.6 Hz, 1H), 6.21 (dd, *J*=15.8, 7.1 Hz, 1H), 6.64 (d, *J*=15.8 Hz, 1H), 7.39–7.23 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.0, 22.9, 47.2, 52.1, 77.9, 126.6, 127.3, 127.8, 128.6, 133.0, 136.5, 177.9 (aromatic two carbons are overlapping with other peaks).

*4.5.4. Methyl 3-hydroxy-2,2-dimethyl-5-phenylpentanoate (**8**).* Colorless paste: 20% yield; 84% ee: HPLC analysis: retention time, 19.3 min, 34.6 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=98:2, 1.0 mL/min); IR (NaCl) 3501, 1722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 3H), 1.18 (s, 3H), 1.65–1.55(m, 1H), 1.80–1.72 (m, 1H), 2.61 (d, *J*=2.9 Hz, 1H), 2.69–2.62 (m, 1H), 2.99–2.92 (m, 1H), 3.65–3.63 (m, 1H), 3.68 (s, 3H), 7.31–7.18 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 22.5, 32.9, 33.6, 47.0, 52.1, 76.0, 125.8, 128.4, 128.5, 142.1, 178.2 (aromatic two carbons are overlapping with other peaks).

4.6. Compound 4 from the asymmetric aldol reaction in the presence of a stoichiometric amount of a chiral borane complex

To a solution of *N*-*p*-toluenesulfonyl-(*S*)-valine (542 mg, 2 mmol) in CH_2Cl_2 (20 mL) was added BH_3·THF (1 M solution in THF, 2 mL, 2 mmol) over 5 min at 0 °C and the solution was stirred for 30 min at that temperature. After stirring for 30 min at ambient temperature, the solution was cooled to −78 °C and benzaldehyde (212 mg, 2 mmol) in CH_2Cl_2 (1 mL) was added. The solution was stirred for 30 min and ketene silyl acetal **2** (383 mg, 2.2 mmol) in CH_2Cl_2 (1 mL) was added. After stirring for 3 h, the reaction mixture was quenched by HCl (10%, 5 mL) and extracted with Et_2O. A crude (1.16 g) was purified by flash column chromatography (10% ethyl acetate/*n*-hexane) to give (−)-methyl (3*R*)-3-hydroxy-2,2-dimethyl-3-phenylpropanoate in 70% yield (292 mg); $[\alpha]_D^{23}$ −18.0 (*c* 2.00, CH_2Cl_2); 75% ee of (*R*)-isomer.

4.7. Preparation of [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF$_6$ (9a)

To a solution of {(*R*)-binap}$PtCl_2$ (444 mg, 0.5 mmol) in CH_2Cl_2 (7.5 mL) and acetone (4.5 mL) was added dropwise $AgSbF_6$ (343 mg, 1 mmol) in acetone (0.75 mL). The resulting solution was stirred for 1 h. The precipitated AgCl was filtered off on Celite and the filtrate was concentrated to give a yellow solid. The solid was washed with ether, filtrated, and then dried in vacuo to give 454 mg of the product (85% yield). The product was recrystallized from CH_2Cl_2–ether to give pale yellow needles (mp >262 °C); $[\alpha]_D^{26}$ −375.9 (*c* 1.00, $CHCl_3$); IR (film): 3566, 1436, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ −1.57 (s, 2H), 6.53–7.68 (m, 64H); ^{31}P NMR (160 MHz, $CDCl_3$): δ 4.17 (s, J_{P-Pt}=3645 Hz). Anal. Calcd for $C_{88}H_{66}F_{12}O_2P_4Pt_2Sb_2$: C, 49.37; H, 3.11%. Found: C, 49.25; H, 3.03%.

*4.7.1. Preparation of [{(R)-binap}Pt(μ-OH)]$_2$2OTf (**9b**).* The complex was prepared according to the above procedure of the corresponding (SbF_6) congener in 89% yield; ^1H NMR (400 MHz, $CDCl_3$): δ −0.76 (s, 2H), 6.53–7.69 (m, 64H); ^{31}P NMR (160 MHz, $CDCl_3$): δ 3.64 (s, J_{Pt-P}=3625.3 Hz).

*4.7.2. Preparation of [{(R)-binap}Pt(μ-OH)]$_2$2ClO$_4$ (**9c**).* The complex was prepared according to the above procedure of the corresponding (SbF_6) congener in 83% yield; ^1H NMR (400 MHz, $CDCl_3$): δ −1.22 (s, 2H), 6.54–7.71 (m, 64H); ^{31}P NMR (160 MHz, $CDCl_3$): δ 3.57 (s, J_{Pt-P}=3638.3 Hz).

*4.7.3. Preparation of [{(R)-binap}Pt(μ-OH)]$_2$2BF$_4$ (**9d**).* The complex was prepared according to the above procedure of the corresponding (SbF_6) congener in 86% yield; ^1H NMR (400 MHz, $CDCl_3$): δ −1.31 (s, 2H), 6.52–7.71 (m, 64H); ^{31}P NMR (160 MHz, $CDCl_3$): δ 3.30 (s, J_{Pt-P}=3638.3 Hz).

4.8. X-ray diffraction data for [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF$_6$

X-ray diffraction data were collected using a Rigaku AFC7S diffractometer with graphite-monochromated Mo-Kα radiation (λ=0.7106 Å). The data of the crystal were collected at 23±1 °C to a maximum 2θ value of 55.0°. Of the 15,540 reflections that were collected, 12,003 were unique (R_{int}=0.102). Chemical formula: $C_{88}H_{66}F_{12}O_2P_4Pt_2Sb_2$ (FW: 2141.04); crystal color, habit: colorless, prismatic; crystal system: orthorhombic; lattice parameters; *a*=20.108(3) Å, *b*=28.405(3) Å, *c*=14.8927(16) Å, *V*=8506.2(18) $Å^3$; space group=*P*212,121(#19); *Z* value=4; D_{calcd}=1.672 g/cm^3; μ (MoKα)=40.401 cm^{-1}; residuals: R_1 ($I>2.00\sigma(I)$)=0.0587; residuals: *R* (all reflections)=0.0827; residuals: wR_2 (all reflections)=0.0872; goodness of fit indicator=0.92. Crystallographic Data has been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-692228. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conls/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge, CB2 1FZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.jp).

4.9. Standard procedure of [{(*R*)-binap}Pt(μ-OH)]$_2$2OTf-catalyzed enantioselective aldol reaction. Reaction of benzaldehyde with (2)

To a mixture of [{(*R*)-binap}Pt(μ-OH)]$_2$2OTf (49 mg, 0.025 mmol: 0.05 mmol on Pt) in dry DMF (0.3 mL) was added silyl nucleophile **2** (0.405 mL, 2.0 mmol) at room temperature under Ar. After the solution was stirred at room temperature for 10 min, benzaldehyde (0.102 mL, 1.0 mmol) was added. The solution was stirred for 12 h. The formation of the silylated aldol product was checked by the corresponding spot (R_f, 0.70) on TLC (20% AcOEt/*n*-hexane). The reaction was quenched upon the addition of 10% aq HCl (5 mL) and diethyl ether (10 mL). After stirring for 10 min, the deprotected aldol was extracted with diethyl ether (20 mL×2). The organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give a crude residue. The crude residue was purified by flash column chromatography (SiO_2) (10% AcOEt/*n*-hexane) to give 178 mg in 87% yield.

*4.9.1. Methyl 3-hydroxy-2,2-dimethyl-3-(4-nitrophenyl)propanoate (**10**).* Colorless paste: 89% yield; 79% ee: HPLC analysis: retention time, 33.6 min, 47.1 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=95:5, 1.0 mL/min); IR (KBr), 3541, 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 3H), 1.15 (s, 3H), 3.41 (d, *J*=4.2 Hz, 1H), 3.75 (s, 3H), 5.01 (d, *J*=4.2 Hz, 1H), 7.50 (d, *J*=8.8 Hz, 2H), 8.20 (d, *J*=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 22.8, 47.6, 52.4,

77.7, 122.9, 128.6, 147.2, 147.5, 177.8 (aromatic two carbons are overlapping with other peaks).

*4.9.2. Methyl 3-hydroxy-2,2-dimethyl-3-(4-methylphenyl)propanoate (**11**).* Colorless paste: 79% yield; 81% ee: HPLC analysis: retention time, 22.8 min, 47.4 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=99:1, 1.0 mL/min); IR (NaCl), 3499, 1724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.10 (s, 3H), 1.14 (s, 3H), 2.99 (d, J=4.2 Hz, 1H), 3.73 (s, 3H), 4.87 (d, J=4.2 Hz, 1H), 7.13 (d, J=8.0 Hz, 2H), 7.19 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 21.1, 23.1, 47.7, 52.1, 78.6, 127.6, 128.5, 136.9, 137.4, 178.3 (aromatic two carbons are overlapping with other peaks).

*4.9.3. Methyl 3-hydroxy-3-(4-methoxyphenyl)-2,2-dimethylpropanoate (**12**).* Colorless paste: 66% yield; 76% ee: HPLC analysis: retention time, 42.3 min, 48.0 min (DAICEL CHIRALCEL AD-H Column, *n*-hexane/2-propanol=98:2, 1.0 mL/min); IR (NaCl) 1726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 3H), 1.14 (s, 3H), 3.00 (d, J=3.9 Hz, 1H), 3.72 (s, 3H), 3.80 (s, 3H), 4.86 (d, J=3.9 Hz, 1H), 6.85 (d, J=11.7 Hz, 2H), 7.22 (d, J=11.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 23.0, 47.7, 52.1, 55.2, 78.3, 113.1, 128.7, 132.0, 159.1, 178.3 (aromatic two carbons are overlapping with other peaks).

4.10. Synthesis of (*E*)-1-benzyloxy-1-(trimethylsilyloxy) propene ((*E*)-3) from benzyl propanoate

A solution of diisopropylamine (10.5 mL, 75 mmol) in THF (40 mL) was cooled to 0 °C and a 1.6 M solution of *n*-butyllithium in *n*-hexane (44 mL, 75 mmol) was added slowly by a syringe. This mixture was stirred for 20 min at 0 °C and subsequently cooled to −78 °C. After 30 min, a mixture of benzyl propanoate (8.20 g, 50 mmol) and TMSCl (9.6 mL, 75 mmol) was added by a syringe over a 2-min time period under intensive stirring. The solution was stirred for 30 min at −78 °C and subsequently allowed to warm up to room temperature. The reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (50 mL) and diluted with *n*-hexane. The resulting solution was washed with H_2O (4×50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to obtain crude products (98% yield, the ratio of *E*/*Z* was 92:8). The resulting product was distilled under a reduced pressure. The yield and the isomer ratio were determined by ^1H NMR spectroscopy of the crude products; ^1H NMR (400 MHz, $CDCl_3$): δ 0.16 (s, 9H), 1.47 (d, J=6.8 Hz, 3H), 3.69 (q, J=6.8 Hz, 1H), 4.81 (s, 2H), 7.25–7.35 (m, 5H).

4.11. Synthesis of (*Z*)-1-benzyloxy-1-(trimethylsilyloxy) propene ((*Z*)-3) from benzyl propanoate

A solution of LDA (20 mmol) in THF (10 mL) was cooled to −78 °C and HMPA (6 mL) was added dropwise by a syringe. After 10 min, a solution of benzyl propanoate (3.28 g, 20 mmol) in THF (10 mL) was added by a syringe over a 2-min time period under intensive stirring and the solution was stirred for 20 min at −78 °C. Then, TMSCl (2.8 mL, 22 mmol) was added. The solution was stirred for 10 min at −78 °C and subsequently allowed to warm up to room temperature. The reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL) and diluted with *n*-hexane. The resulting solution was washed with H_2O (4×50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to obtain crude products (91% yield, the ratio of *E*/*Z* was 10:90). The resulting product was distilled under a reduce pressure. The yield and the isomer ratio were determined by ^1H NMR spectroscopy of the crude product; ^1H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 9H), 1.51 (d, J=6.4 Hz, 3H), 3.60 (q, J=6.8 Hz, 1H), 4.69 (s, 2H), 7.26–7.35 (m, 5H).

4.12. [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF$_6$-catalyzed enantioselective aldol reaction of benzaldehyde with (*E*)-3 in DMF

A solution of [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF_6 (55 mg, 0.025 mmol) in DMF (0.7 mL) was stirred for 30 min. (*E*)-**3** (473 mg, 2 mmol) was added dropwise by a syringe and the resulting solution was stirred for 15 min. Benzaldehyde (0.102 mL, 1 mmol) was added and the mixture was stirred for 12 h. The reaction solution was quenched with 10% aq HCl (5 mL), stirred for 1 h, extracted with ether, and dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography (10% ethyl acetate/*n*-hexane) to give 216 mg of the product (80% yield, *syn*/*anti*=1:3.8). The optical purity was determined by HPLC analyses with a DAICEL CHIRALPAK AD-H Column (*n*-hexane/2-propanol=97.5:2.5, 1.0 mL/min) to be 25% ee (*syn*-isomer: retention time, major: 31 min and minor: 46 min) and 62% ee (*anti*-isomer: retention time, major: 53 min and minor: 64 min). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%. Found: C, 75.47; H, 6.60%. *Benzyl* (2*S*,3*R*)-3-*hydroxy*-2-*methyl*-3-*phenylpropanoate* (*anti*-**13**): IR (film) 3470, 1732, 1455, 1166, 1023, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, J=7.2 Hz, 3H), 2.84–2.92 (m, 2H), 4.78 (dd, J=4.0, 8.4 Hz, 1H), 5.17 (s, 2H), 7.25–7.37 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 47.2, 66.4, 76.3, 126.6, 128.0, 128.2, 128.5, 135.7, 141.4, 175.5 (aromatic six carbons are overlapping with other peaks). Benzyl (2*R*,3*R*)-3-hydroxy-2-methyl-3-phenylpropanoate (*syn*-**13**): IR (film) 3477, 1730, 1455, 1173, 1027, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (d, J=7.2 Hz, 3H), 2.81–2.88 (dq, J=4.4, 7.2 Hz, 2H), 5.10 (s, 2H), 5.12 (br, 1H), 7.22–7.37 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.8, 46.5, 66.4, 73.7, 125.9, 127.5, 128.1, 128.2, 128.5, 135.6, 141.3, 175.4 (aromatic five carbons are overlapping with other peaks).

4.13. (2*S*,3*R*)-3-Hydroxy-2-methyl-3-phenylpropanoic acid (*anti*-14)

A solution of benzyl (2*S*,3*R*)-3-hydroxy-2-methyl-3-phenylpropanoate (*anti*-**13**) (0.6 mmol, 163 mg), purified by recrystallization from a mixture of CH_2Cl_2 and *n*-hexane, Colorless oil: $[\alpha]_D^{23}$ +53.0 (*c* 1.00, $CHCl_3$), and KOH (1.2 mmol, 68 mg) in MeOH (2 mL) was stirred for 4 h. The reaction mixture was quenched with 10% aq HCl (5 mL), extracted with ether, and dried over $MgSO_4$. The solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography (5% MeOH/$CHCl_3$) to give 71 mg of the product (71% yield); Colorless oil: $[\alpha]_D^{23}$ +48.1 (*c* 2.20, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, J=7.2 Hz, 3H), 2.84 (dq, J=7.2, 9.0 Hz, 3H), 4.75 (d, J=9.0 Hz, 1H), 5.70–6.10 (br s, lH), 7.29–7.39 (m, 5H).

4.14. Typical procedure for the [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF_6-catalyzed enantioselective aldol reaction of benzaldehyde with (*E*)-3 in DMF/HMPA-(10%)

A solution of [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF_6 (55 mg, 0.025 mmol) in DMF/HMPA-(10%) (0.7 mL) was stirred for 30 min. (*E*)-**3** (473 mg, 2 mmol) was added dropwise by a syringe and the resulting solution was stirred for 15 min. Benzaldehyde (0.102 mL, 1 mmol) was added and the mixture was stirred for 12 h. The reaction solution was quenched with 10% aq HCl (5 mL), stirred for 1 h, extracted with ether, and dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography (10% ethyl acetate/*n*-hexane) to give 238 mg of the product (88% yield, *syn*/*anti*=1:6). The optical purity was determined by HPLC analysis to be 41% ee (*syn*-isomer) and 84% ee (*anti*-isomer).

*4.14.1. Benzyl 3-(4-chlorophenyl)-3-hydroxy-2-methylpropanoate (**15**).* Colorless oil: 76% yield; *anti*/*syn* ratio (4.2:1). Anal. Calcd for

$C_{17}H_{17}ClO_3$: C, 67.00; H, 5.62%. Found: C, 66.89; H, 5.77%. *anti*-**8** (83% ee): HPLC analysis: retention time, 45.6 min, 52.0 min (DAICEL CHIRALPAK AD-H Column, *n*-hexane/2-propanol=96.0:4.0, 1.0 mL/min); IR (film): 3450, 1720, 1455, 1167, 828 cm^{-1}; ^1H NMR (400 MHz,$CDCl_3$): δ 1.07 (d, J=4.8 Hz, 3H), 2.80–2.87 (m, 1H), 3.06 (d, J=4.8 Hz, 1H), 4.76 (dd, J=4.8, 7.6 Hz, 1H), 5.15 (s, 2H), 7.24–7.39 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 47.0, 66.6, 75.5, 128.0, 128.1, 128.3, 128.6, 133.7, 135.6, 140.0, 175.3 (aromatic five carbons are overlapping with other peaks). *syn*-**8** (30% ee): HPLC analysis: retention time, 20.9 min, 26.9 min (DAICEL CHIRALPAK AD-H Column, *n*-hexane/2-propanol=96.0:4.0, 1.0 mL/min); IR (film): 3461, 1730, 1493, 1456, 1173, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (d, J=6.8 Hz, 3H), 2.76–2.825 (m, 1H), 2.96 (s,1H), 5.06 (d, J=4.4 Hz, 1H), 5.10 (m, 2H), 7.23–7.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.9, 46.4, 66.6, 73.1, 127.4, 128.2, 128.4, 128.6, 133.2, 134.5, 138.7, 175.3 (aromatic five carbons are overlapping with other peaks).

*4.14.2. Benzyl 3-hydroxy-2-methyl-3-(4-nitrophenyl)propanoate (**16**).* Colorless oil: 88% yield; *anti*/*syn* ratio (4.5:1). Anal. Calcd for $C_{17}H_{17}NO_5$: C, 64.76; H, 5.43%. Found: C, 64.51; H, 5.27%. *anti*-**9** (59% ee): HPLC analysis: retention time, 77.8 min, 109.6 min (DAICEL CHIRALPAK AD-H Column, *n*-hexane/2-propanol=95.0:5.0, 1.0 mL/min); IR (film): 3482, 1732, 1520, 1348, 1170, 854, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.15 (d, J=7.2 Hz, 3H), 2.85–2.92 (m, 1H), 3.36 (d, J=5.6 Hz, 1H), 4.89 (dd, J=5.6 Hz, 1H), 5.13 (ABq, J=12.4 Hz, $\Delta\nu$=18.2 Hz, 2H), 7.30–7.34 (m, 5H), 7.45 (d, J=8.8 Hz, 2H), 8.16 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 46.7, 66.8, 75.2, 123.6, 127.3, 128.2, 128.5, 128.6, 135.3, 147.6, 148.9, 175.0 (aromatic four carbons are overlapping with other peaks). *syn*-**9** (18% ee): HPLC analysis: retention time, 36.9 min, 42.3 min (DAICEL CHIRALPAK AD-H Column, *n*-hexane/2-propanol=95.0:5.0, 1.0 mL/min); IR (film): 3495, 1730, 1520, 1341, 1176, 853, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.12 (d, J=7.2 Hz, 3H), 2.84 (dq, J=4.0, 7.2 Hz, 1H), 3.19 (s, 1H), 5.15 (ABq, J=12.0 Hz, $\Delta\nu$=12.6 Hz, 2H), 5.22 (d, J=4.0 Hz, 1H), 7.29–7.36(m, 5H), 7.49 (d, J=8.8 Hz, 2H), 8.16 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.5, 46.0, 66.9, 72.7, 123.5, 126.9, 128.3, 128.6, 128.7, 135.3, 147.3, 148.5, 175.2 (aromatic four carbons are overlapping with other peaks).

*4.14.3. Benzyl 3-hydroxy-3-(4-methoxyphenyl)-2-methylpropanoate (**17**).* Colorless oil: 78% yield; *anti*/*syn* ratio (5.2:1). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%. Found: C, 71.79; H, 6.52%. *anti*-**10** (55% ee): HPLC analysis: retention time, 48.7 min, 53.8 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=96.0:4.0, 1.0 mL/min); IR (film): 3489, 1733, 1514, 1249, 1175, 1033, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, J=7.6 Hz, 3H), 2.82–2.89 (m, 2H), 3.80 (s, 3H), 4.74 (d, J=7.6 Hz, 1H), 5.18 (s, 2H), 6.87 (d, J=8.4 Hz, 2H), 7.24–7.36 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 47.3, 55.3, 66.4, 75.9, 113.9, 127.8, 128.1, 128.2, 128.6, 133.6, 135.7, 159.4, 175.7 (aromatic four carbons are overlapping with other peaks). *syn*-**10** (9% ee): HPLC analysis: retention time, 31.2 min, 38.2 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=96.0:4.0, 1.0 mL/min); IR (film): 3461, 1731, 1514, 1249, 1175, 1033, 831, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.18 (d, J=7.2 Hz, 3H), 2.80 (br s, 1H), 2.82 (dq, J=4.8, 7.2 Hz, 1H), 3.80 (s, 3H), 5.02 (d, J=4.8 Hz, 1H), 5.08 (ABq, J=4.8 Hz, $\Delta\nu$=10.1 Hz, 2H), 6.85 (d, J=4.8 Hz, 2H), 7.23–7.35 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4, 46.8, 55.2, 66.4, 73.6, 113.6, 127.2, 128.1, 128.2, 128.5, 133.5, 135.6, 159.0, 175.4 (aromatic four carbons are overlapping with other peaks).

*4.14.4. Benzyl 3-hydroxy-2-methyl-3-(4-methylphenyl)propanoate (**18**).* Colorless oil: 80% yield; *anti*/*syn* ratio (5.5:1). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%. Found: C, 76.31; H, 7.07%. *anti*-**11** (67% ee): HPLC analysis: retention time, 74.5 min, 89.9 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=99.0:1.0, 1.0 mL/min); IR (film): 3461, 1730, 1455, 1173, 1028, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, J=7.2 Hz, 3H), 2.34 (s, 3H), 2.81 (d, J=4.4 Hz, 1H), 2.87 (dq, J=7.2, 8.4 Hz, 1H), 4.74 (dd, J=4.4, 8.4 Hz, 1H), 5.17 (s, 2H), 7.14–7.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 21.1, 47.2, 66.4, 76.2, 126.5, 128.0, 128.2, 128.5, 129.2, 135.8, 137.8, 138.5, 175.6 (aromatic four carbons are overlapping with other peaks). *syn*-**11** (14% ee): HPLC analysis: retention time, 45.4 min, 52.4 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=99.0:1.0, 1.0 mL/min); IR (film): 3460, 1734, 1455, 1166, 1029, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.15 (d, J=7.2 Hz, 3H), 2.32 (s, 3H), 2.72 (br s, 1H), 2.81 (dq, J=4.8, 7.2 Hz, 1H), 5.04 (d, J=4.4 Hz, 1H), 5.07 (ABq, J=12.4 Hz, $\Delta\nu$=8.1 Hz, 2H), 7.10–7.35 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 21.1, 46.7, 66.4, 73.8, 125.9, 128.1, 128.3, 128.5, 129.0, 135.7, 137.2, 138.4, 175.5 (aromatic four carbons are overlapping with other peaks).

*4.14.5. Benzyl 3-hydroxy-2-methyl-3-(4-biphenylyl)propanoate (**19**).* Colorless oil: 87% yield; *anti*/*syn* ratio (6.2:1). Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40%. Found: C, 79.63; H, 6.29%. *anti*-**12** (82% ee): HPLC analysis: retention time, 29.2 min, 37.0 min (DAICEL CHIRAL PAKAD-H Column, *n*-hexane/2-propanol=90.0:10.0, 1.0 mL/min); IR (film): 3450, 1732, 1487, 1456, 1029, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, J=7.2 Hz, 3H), 2.88–2.97 (m, 1H), 2.98 (d, J=4.8 Hz, 1H), 4.84 (dd, J=4.8, 7.6 Hz, 1H), 5.18 (s, 2H), 7.29–7.60 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 47.1, 66.5, 76.1, 127.0, 127.1, 127.2, 127.4, 128.1, 128.2, 128.6, 128.8, 135.7, 140.5, 140.7, 141.0, 175.6 (aromatic six carbons are overlapping with other peaks). *syn*-**12** (41% ee): HPLC analysis: retention time, 78.8 min, 86.7 min (DAICEL CHIRAL PAKAD-H Column, *n*-hexane/2-propanol=98.0:2.0, 1.0 mL/min); IR (film): 3450, 1730, 1487, 1455, 1172, 1029, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.21 (d, J=7.6 Hz, 3H),2.89 (dq, J=4.8, 7.6 Hz, 2H), 5.12 (ABq, J=12.0 Hz, $\Delta\nu$=7.2 Hz, 2H), 5.15 (d, J=4.8 Hz, 1H), 7.27–7.60 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 46.5, 66.6, 73.6, 126.5, 127.0 (2C), 127.3, 128.1, 128.3, 128.6, 128.7, 135.6, 140.4, 140.7, 175.5 (aromatic eight carbons are overlapping with other peaks).

*4.14.6. Benzyl 3-hydroxy-2-methyl-3-(1-naphthyl)propanoate (**20**).* Colorless oil: 48% yield; *anti*/*syn* ratio (6.0:1). Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.68; H, 6.29%. Found: C, 78.82; H, 6.44%. *anti*-**13** (84% ee): HPLC analysis: retention time, 76.3 min, 94.2 min (DAICEL CHIRALPAK AD-H Column, *n*-hexane/2-propanol=97.0:3.0, 1.0 mL/min); IR (film): 3470, 1731, 1455, 1167, 1041, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, J=6.8 Hz, 3H), 3.19–3.28 (m, 2H), 5.18 (ABq, J=12.4 Hz, $\Delta\nu$=11.9 Hz, 2H), 5.56 (dd, J=5.2, 8.4 Hz, 1H), 7.29–7.36 (m, 5H), 7.43–7.57 (m, 4H), 7.81 (d, J=8.0 Hz, 1H), 7.88 (d, J=8.0 Hz, 1H), 8.23 (d, J=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 46.7, 66.5, 73.7, 123.5, 124.6, 125.3, 125.6, 126.2, 128.0, 128.2, 128.6, 129.0, 134.0, 135.7, 175.8 (aromatic five carbons are overlapping with other peaks). *syn*-**13** (48% ee): HPLC analysis: retention time, 41.1 min, 69.7 min (DAICEL CHIRALPAK AD-H Column, *n*-hexane/2-propanol=97.0:3.0, 1.0 mL/min); IR (film): 3489, 1725, 1455, 1167, 1063, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.12 (d, J=7.2 Hz, 3H), 2.90 (d, J=2.8 Hz, 1H), 3.09 (dq, J=3.6, 7.2 Hz, 1H), 5.19 (s, 2H), 6.01 (s, 1H), 7.33–7.39 (m, 5H), 7.47–7.53 (m, 3H), 7.72–7.97 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.2, 44.6, 66.6, 70.1, 122.5, 124.0, 125.3, 125.5, 126.2, 128.0, 128.1, 128.3, 128.6, 129.1, 133.7, 136.5, 175.8 (aromatic four carbons are overlapping with other peaks).

*4.14.7. Benzyl 3-hydroxy-2-methyl-3-(2-naphthyl)propanoate (**21**).* Colorless oil: 86% yield; *anti*/*syn* ratio (5.3:1). Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.68; H, 6.29%. Found: C, 78.51; H, 6.13%. *anti*-**14** (72% ee): HPLC analysis: retention time, 60.3 min, 71.7 min (DAICEL CHIRALPAK AD-H Column, *n*-hexane/2-propanol=97.0:3.0, 1.0 mL/min); IR (film): 3462, 1718, 1456, 1168, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, J=6.8 Hz, 3H), 2.97–3.04 (m, 1H), 3.06 (d, J=5.2 Hz, 1H), 4.95 (dd, J=4.8, 8.4 Hz, 1H), 5.17 (s, 2H), 7.26–7.85

(m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 47.1, 66.5, 76.5, 124.2, 125.9, 126.1, 126.2, 127.7, 128.0, 128.2, 128.4, 128.5, 133.1, 133.2, 135.7, 138.9, 175.6 (aromatic three carbons are overlapping with other peaks). *syn*-**14** (17% ee): HPLC analysis: retention time, 24.0 min, 29.7 min (DAICEL CHIRALPAK AD-H Column, *n*-hexane/2-propanol=94.0:6.0, 1.0 mL/min); IR (film): 3461, 1729, 1455, 1172, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (d, J=7.2 Hz, 3H), 2.93–2.99 (m, 2H), 5.10 (ABq, J=12.4 Hz, $\Delta\nu$=8.8 Hz, 2H), 5.28 (d, J=4.4 Hz, 1H), 7.20–7.83 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 46.4, 66.6, 73.8, 124.0, 125.0, 125.9, 126.2, 127.6, 128.1, 128.3, 128.5, 132.9, 133.2, 135.6, 138.7, 175.6 (aromatic four carbons are overlapping with other peaks).

*4.14.8. Benzyl 3-hydroxy-2-methyl-5-phenylpentanoate (**22**).* The reaction was carried out in the presence of 5 mol % catalyst. Colorless oil: 83% yield; *anti*/*syn* ratio (5.5:1). Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43%. Found: C, 76.63; H, 7.29%. *anti*-**15** (92% ee): HPLC analysis: retention time, 30.1 min, 42.9 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=98.0:2.0, 1.0 mL/min); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (d, J=8.0 Hz, 3H), 1.69–1.84 (m, 2H), 2.56–2.71 (m, 3H), 2.81–2.88 (m, 1H), 3.66–3.73 (m, 1H), 5.15 (s, 2H), 7.16–7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 31.9, 36.6, 45.4, 66.4, 72.7, 125.9, 128.2, 128.3, 128.4, 128.5, 128.6, 135.7, 141.9, 175.8 (aromatic four carbons are overlapping with other peaks). *syn*-**15** (18% ee): HPLC analysis: retention time, 34.6 min, 69.2 min (DAICEL CHIRALCEL OD-H Column, *n*-hexane/2-propanol=98.0:1.0, 1.0 mL/min); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (d, J=8.0 Hz, 3H), 1.61–1.70 (m, 1H), 1.75–1.84 (m, 1H), 2.54 (d, J=4.0 Hz, 1H), 2.57–2.68 (m, 2H), 2.81–2.88 (m, 1H), 3.90–3.97 (m, 1H), 5.14 (s, 2H), 7.16–7.38 (m, 10H).

4.15. [{(*R*)-binap}Pt(μ-OH)]$_2$2SbF$_6$-catalyzed enantioselective aldol reaction of benzaldehyde with (*Z*)-3 in DMF/HMPA-(10%)

According to the procedure using (*E*)-**3**, the reaction with (*Z*)-**3** (473 mg, 2 mmol) gave the corresponding aldols in 92% yield (*syn* (49% ee)/*anti* (89% ee)=1:6).

Acknowledgements

We thank the Takasago International Corporation for the generous gift of (*R*)-segphos and (*R*)-H$_8$-binap. This work was supported by a Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science.

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