 Bull. Chem. Soc. Jpn., **76**, 49–58 (2003)

Headline Articles

Enantioselective Carbonyl-Ene Reaction of Glyoxal Derivatives Catalyzed by Cationic 3-Oxobutylideneaminatocobalt(Ⅲ) Complexes

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(Received July 29, 2002)

Optically active 3-oxobutylideneaminatocobalt(Ⅲ) complexes were designed for the catalytic enantioselective carbonyl-ene reaction. Varieties of counter anions of cationic cobalt(Ⅲ) complexes were screened and hexafluoroantimonate was found to be the most effective. In the presence of cobalt(Ⅲ) hexafluoroantimonate complex **1f**, the enantioselective carbonyl-ene reaction of various alkenes with glyoxal derivatives was carried out to afford the corresponding homoallylic alcohols in high yields and with high enantioselectivities. Even in the presence of 0.2 mol% cobalt(Ⅲ) complexes, the reaction proceeded in high yield and with maintained high enantioselectivity. The absolute configuration of the optically active product was determined and a reasonable explanation for the enantioselection in the present carbonyl-ene reaction catalyzed by the cobalt complex was proposed.

The enantioselective carbonyl-ene reaction[1] is one of the most reliable and convenient processes to prepare optically active homoallylic alcohols because it could be performed without any pretreatment of carbonyl compounds such as enolization or preparation of allylmetallic reagents. The resulting homoallylic alcohol could be furthermore transformed into various functionalized compounds by taking advantage of its hydroxy group and its carbon–carbon double bond. The carbonyl-ene reaction is categorized as a 6π-electrocyclic concerted reaction,[2] similar to the Diels–Alder reaction. Therefore, it is expected that a Lewis acid would remarkably catalyze the reaction by lowering the LUMO energy of the carbonyl compounds and that the optically active Lewis acid catalyst would effectively regulate the stereochemistry in the formation of the homoallylic alcohol. On the basis of these features, a wide variety of metal complexes have been investigated as chiral Lewis acid catalysts for this purpose.[1] The achievement of high performance has been reported, e.g. the chiral BINOL ligands with various conventional Lewis-acid-metals, such as aluminum[3] and titanium,[4] or rare-earth metal.[5] Several complexes with other than BINOL ligands were recently reported to be available as chiral Lewis acid catalysts for this type of reaction; bis(oxazoline)copper,[6] BINAP palladium[7] or platinum,[8] and DPPF-nickel catalyst,[9] etc.

The optically active 3-oxobutylideneaminatocobalt complexes (Fig. 1) were originally developed as effective catalysts

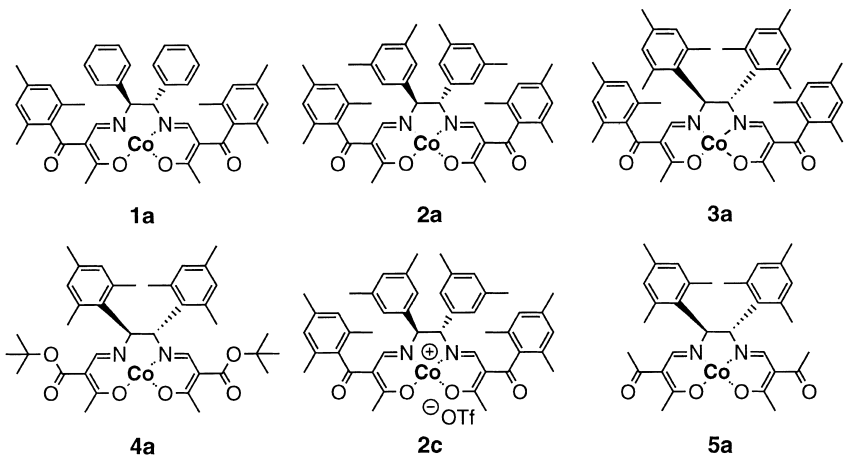
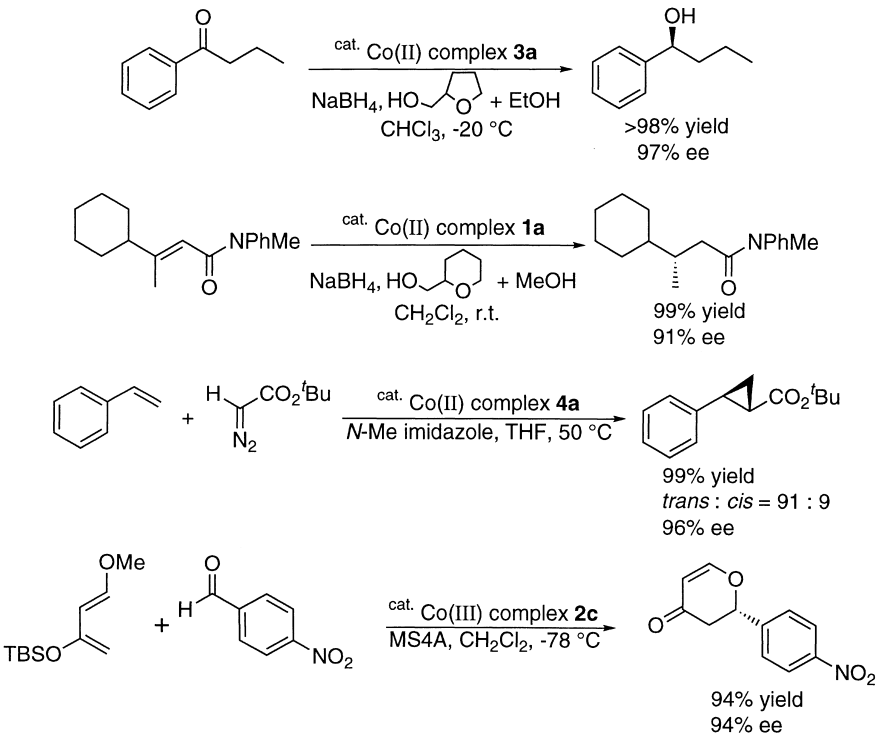


Fig. 1. Varieties of 3-oxobutylideneaminatocobalt complex catalysts.



Scheme 1. Enantioselective reactions catalyzed by 3-oxobutylideneaminato complexes.

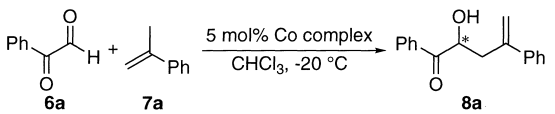
of the enantioselective tetrahydroborate reductions of ketones,[10] imines,[11] and α,β-unsaturated carboxamides (Scheme 1).[12] It was recently reported that this type of complex effectively catalyzed the cyclopropanation of styrenes and diazoacetates[13] to afford the corresponding cyclopropane derivatives with high stereoselectivities. The enantioselectivities and diastereoselctivities in the above-mentioned reactions could be tuned by the structure of the 3-oxobutylideneaminato ligands. These complexes were prepared from the corresponding 1,3-dicarbonyl compounds and the optically active 1,2-diaryl-1,2-ethanediamines and isolated before use. The X-ray analyses of several 3-oxobutylideneaminatocobalt complexes[14] provided helpful knowledge for ligand design. In the course of our continuing study of these cobalt complexes, they were found to act as chiral Lewis acid catalysts for a 6π-electrocyclic concerted hetero Diels–Alder reaction.[15] In addition, the corresponding cationic cobalt(III) complexes could be employed more effectively than the original cobalt(II) complex and their counter anions significantly influenced their Lewis acidities and catalytic abilities.[16] These cationic cobalt(III) complexes also catalyzed the enantioselective carbonyl-ene reaction of glyoxal derivatives to afford the corresponding homoallylic alcohols with high enantioselectivities.[17]

In this article, we would like to fully disclose the enantioselective carbonyl-ene reaction of various terminal alkenes with glyoxal derivatives catalyzed by cationic cobalt(III) complexes with optically active 3-oxobutylideneaminato ligands.

Results and Discussion

Examinations of the Central Cobalt Atom and Effective 3-Oxobutylideneaminato Ligands for the Optically Active Cobalt Complexes. On the basis of the previous observations for the 3-oxobutylideneaminatocobalt complexes which catalyzed hetero Diels–Alder reaction, the cationic character of the central cobalt atom would have a crucial effect on the

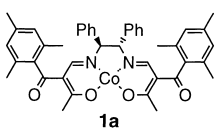
Table 1. Various Cobalt Complex Catalysts for the Enantioselective Carbonyl-Ene Reaction



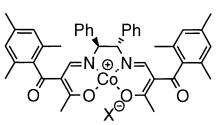
6a 7a 8a

Entry[a)]	Catalysts	Time/h	Yield/%[b)]	Ee/%[c)]
1	**1a**	125	trace	—
2	**1b**	125	trace	—
3	**1c**	48	9	2
4	**1d**	48	25	56
5	**1e**	48	34	69
6	**1f**	3	93	93

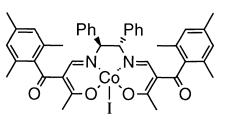
a) Reaction conditions: cobalt catalyst 0.025 mmol (5.0 mol%), phenylglyoxal 1.0 mmol, and 2-phenylpropene 0.5 mmol in $CHCl_3$ (2.5 mL). b) Isolated yield. c) Determined by HPLC analysis using Daicel Chiralcel OB-H (3% 2-propanol in hexane).



1a



X = OTf (**1c**)
BF_4(**1d**)
PF_6(**1e**)
SbF_6(**1f**)

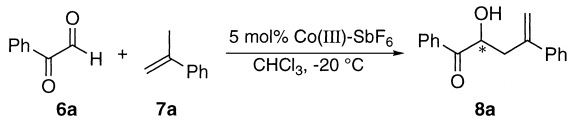


1b

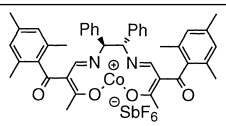
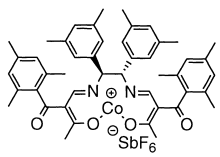
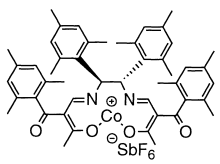
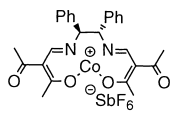
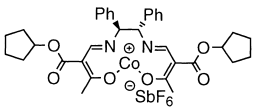
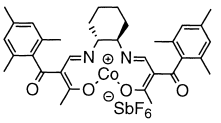
reaction rate and enantioselectivity;[16] therefore, various 3-oxobutylideneaminatocobalt(II) and cobalt(III) complex catalysts were examined for the enantioselective carbonyl-ene reaction of phenylglyoxal (**6a**) and 2-phenylpropene (**7a**) (Table 1). The cobalt(II) complex **1a** and the corresponding iodo cobalt(III) complex **1b** did not catalyze the carbonyl-ene reactions very well (Entries 1 and 2). The cationic cobalt(III) complexes with various counter anions **1c**–**1f** were synthesized by treatment of the iodo cobalt(III) complex **1b** with the corresponding silver salts;[16] then they were used in the reaction. The cobalt(III) triflate complex **1c**, one of the most effective catalysts for the cobalt complex-catalyzed hetero Diels–Alder reaction,[16] catalyzed the present carbonyl-ene reaction to produce the adduct in only 9% yield and with 2% ee (Entry 3). The corresponding cobalt(III) tetrafluoroborate **1d** and hexafluorophosphate **1e** more effectively catalyzed the carbonyl-ene reaction to obtain the corresponding homoallylic alcohol with good enantioselectivities in moderate yields (Entries 4 and 5). Screening of the counter anions revealed that the cobalt(III) hexafluoroantimonate **1f** could be significantly employed as a highly active cationic cobalt(III) complex catalyst and that the resulting homoallylic alcohol with 93% ee was obtained in 93% yield (Entry 6). It was confirmed by X-ray analysis that the central cobalt(III) atom in the complexes was completely separated from the counter anions.[16] The catalytic activities of these series of cationic cobalt(III) complexes could be correlated to the acidity of the conjugate base[18] of their counter anions; the cationic cobalt(III) complex with a counter anion derived from the stronger conjugate acid achieved the higher yield of the carbonyl-ene product. For instance, the carbonyl-ene product was obtained in low yield in the presence of catalytic amount of cobalt(III) trifluoromethanesulfonate [H_0 value[19] of trifluoromethanesulfonic acid (CF_3SO_3H) is -14.1], whereas the corresponding cobalt(III) hexafluoroantimonate [H_0 value of hexafluoroantimonic acid ($HF–SbF_5$) is -27.9] afforded the resulting homoallylic alcohol in high yield.

A variety of optically active 3-oxobutylideneaminato ligands for cobalt(III) hexafluoroantimonate complexes were next examined (Table 2). The chiral diaryl diamine parts of the complexes were firstly examined.[11,13,14] When the complex **2f**

Table 2. Various Ligands of the Cationic Cobalt(III) Complex Catalyst for the Enantioselective Carbonyl-Ene Reaction



6a **7a** **8a**

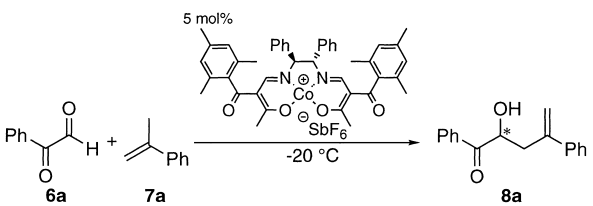
Entry[a)]	Catalyst		Time/h	Yield/%[b)]	Ee/%[c)]
1		**1f**	3	93	93
2		**2f**	24	97	92
3		**3f**	48	22	13
4		**9f**	48	16	64
5		**10f**	48	64	63
6		**11f**	48	79	88

a) Reaction conditions: cobalt catalyst 0.025 mmol (5.0 mol%), phenylglyoxal 0.5 mmol, and 2-phenylpropene 1.0 mmol in $CHCl_3$ (2.5 mL). b) Isolated yield. c) Determined by HPLC analysis using Daicel Chiralcel OB-H (3% 2-propanol in hexane).

derived from 1,2-bis(3,5-dimethylphenyl)ethylenediamine was employed as the catalyst, the product was obtained in 24 hours in a similar yield and with similar enantioselectivity, as compared to that obtained in 3 hours using complex **1f** derived from 1,2-diphenylethylenediamine (Entry 2). When the complex **3f** derived from 1,2-bis(2,4,6-trimethylphenyl)ethylenediamine was used, both the activity and enantioselectivity were unexpectedly decreased (Entry 3). The side chains in the 3-oxobutylideneaminato ligands were then examined. Two cationic cobalt(III) complexes having acetyl or cyclopentyloxycarbonyl groups in place of the mesitoyl groups were prepared and used in the reaction; however, the corresponding homoallylic alcohols were obtained with low ee (Entries 4 and 5). Optically active cyclohexanediamine was tested as a chiral diamine to prepare the corresponding cationic cobalt(III) hexafluoroantimonate **11f**; the corresponding homoallyl alcohol was obtained in 79% yield and with 88% ee (Entry 6) although a longer reaction time was required.

Optimization of the Solvents and Temperature for the Enantioselective Carbonyl-Ene Reaction. Reaction solvents and temperature influence the catalytic activities and enantioselectivities for Lewis acid catalyzed reactions. For the enantioselective hetero Diels–Alder reaction catalyzed by 3-oxobutylideneaminatocobalt complexes, dichloromethane and fluorobenzene were effective for enhancing reactivities and enantioselectivities;[16] therefore, various solvents were examined for the enantioselective carbonyl-ene reaction. The yields and enantiomeric excesses of the resulting product are shown in Table 3. The cationic cobalt catalyst did not dissolve enough in hexane, and the reaction did not proceed (Entry 1). Donative solvents, such as acetonitrile and diethyl ether, decreased the catalytic activity and the stereoselectivity because of their coordination to the cationic cobalt complexes (Entries 2 and 3), and the product was obtained in a moderate yield in toluene (Entry 4). In fluorobenzene and dichloromethane, the reaction proceeded more rapidly and the enantioselectivities were 70% and 90%, respectively (Entries 5 and 6). Moreover, in chloroform, the reaction was completed within 3 hours to afford the corresponding homoallylic alcohol with 93% ee (Entry 7). These examinations indicated that chloroform was the most suitable solvent for the present enantioselective carbonyl-ene reaction.

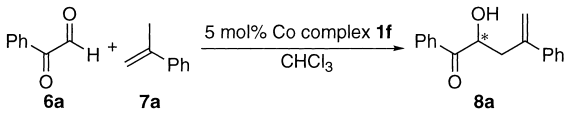
Table 3. Various Solvents for the Enantioselective Carbonyl-Ene Reaction



Entry[a)]	Solvent	Time/h	Yield/%[b)]	Ee/%[c)]
1	Hexane	96	trace	—
2	CH_3CN	96	trace	—
3	Et_2O	96	26	16
4	Toluene	96	31	26
5	PhF	38	50	70
6	CH_2Cl_2	14	82	90
7	$CHCl_3$	3	93	93

a) Reaction conditions: Co(III)–SbF_6 complex catalyst 0.025 mmol (5.0 mol%), 2-phenylpropene 0.5 mmol, and phenylglyoxal 1.0 mmol at −20 °C. b) Isolated yield. c) Determined by HPLC analysis using Chiralcel OB-H (3% 2-propanol in hexane).

Table 4. Temperature Effect in the Enantioselective Carbonyl-Ene Reaction



Entry[a)]	Temp/°C	Time/h	Yield/%[b)]	Ee/%[c)]
1	r.t.	20	61	53
2	0	20	77	92
3	−20	3	93	93
4	−40	18	95	94
5	−60	40	90	95

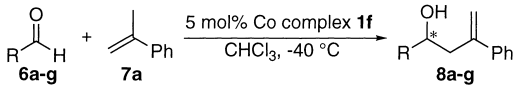
a) Reaction conditions: Co(III)–SbF_6 complex catalyst 0.025 mmol (5.0 mol%), 2-phenylpropene 0.5 mmol, and phenylglyoxal 1.0 mmol in $CHCl_3$ (2.5 mL). b) Isolated yield. c) Determined by HPLC analysis using Chiralcel OB-H (3% 2-propanol in hexane).

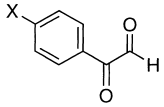
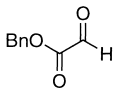
The reaction temperature was next examined and the results are shown in Table 4. The yields and enantioselectivities at room temperature and at 0 °C were both lower than those at −20 °C (Entries 1–3). The enantioselectivity was slightly improved at −40 °C and −60 °C, though the reaction rate was decreased (Entries 4 and 5). Therefore, the reaction temperature could be selected from −20 °C to −60 °C according to the reactivity of the substrates.

Enantioselective Carbonyl-Ene Reaction of Various Glyoxals and Alkenes. The highly active catalyst, cobalt(III) hexafluoroantimonate complex **1f**, was successfully applied to the enantioselective carbonyl-ene reaction of various phenylglyoxal derivatives and benzyl glyoxylate (**6g**) with 2-phenylpropene (**7a**) (Table 5). Phenylglyoxal derivatives with electron-withdrawing groups, *p*-nitro-, *p*-fluoro-, *p*-chloro-, and *p*-bromophenylglyoxals (**6b–e**), were attempted at −40 °C; the enantioselectivities of the resulting products were over 90% (Entries 2–5). In addition, *p*-methylphenylglyoxal (**6f**) was examined and the corresponding homoallylic alcohol was achieved with high enantioselectivity, though the yield was only 45% (Entry 6). The reaction with benzyl glyoxylate (**6g**) smoothly proceeded at −60 °C and the corresponding homoallylic alcohol was obtained in 91% yield and with 85% ee (Entry 7).

The carbonyl-ene reaction of phenylglyoxal (**6a**) with various alkenes was then attempted in the presence of 5 mol% cobalt(III) hexafluoroantimonate **1f** at −20 °C (Table 6). The 2-phenylpropenes substituted with 4-fluoro-, 4-methyl-, and 2-fluoro- on the benzene ring (**7a–c**) also smoothly reacted with phenylglyoxal (**6a**) to afford the corresponding homoallylic alcohols in high yields with high enantioselectivities (Entries 1,

Table 5. The Enantioselective Carbonyl-Ene Reaction of Various Glyoxal Derivatives



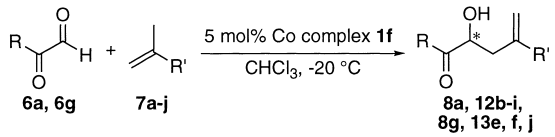
Entry[a]	Glyoxal		Yield/%[b]	Ee/%
1		X = H (**6a**)	95	94
2		X = NO_2 (**6b**)	80	92
3		X = F (**6c**)	81	92
4		X = Cl (**6d**)	89	92
5		X = Br (**6e**)	80	91
6		X = Me (**6f**)	45	91
7[c]		**6g**	91	85

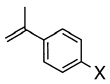
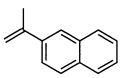
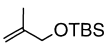
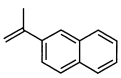
a) Reaction conditions: Co(III)–SbF_6 catalyst 0.025 mmol (5.0 mol%), glyoxal derivative 1.0 mmol, and 2-phenylpropene 0.5 mmol in $CHCl_3$ (2.5 mL). b) Isolated yield. c) Reaction was carried out at −60 °C.

3, and 4). The reaction of 2-(2-naphthyl)propene (**7e**) was completed in 48 hours and the optical yield of the corresponding product was 89% ee (Entry 5). In the presence of cobalt(III) complex **1f**, the carbonyl-ene reaction of 1,1-dialkyl substituted ethenes, such as 2,4,4-trimethyl-1-pentene (**7f**), 2,3-dimethyl-1-butene (**7g**), methylenecyclohexane (**7h**) and *O*-protected methallyl alcohol (**7i**), with phenylglyoxal (**6a**) proceeded and the corresponding products were obtained with high enantioselectivities (Entries 6–9). In these cases, two geometrical isomers could be produced, though the regioselectivity in the present carbonyl-ene reaction was totally superior (> 99:1, NMR analysis) (Entries 6, 7, and 9). In addition, benzyl glyoxylate (**6g**) reacted with various ethenes to afford the product with good to high enantioselectivity. In the reaction with 2-phenylpropene (**7a**) and 2-(2-naphthyl)propene (**7e**), the corresponding α-hydroxy esters was obtained in high yields with high enantioselectivities (Entries 10 and 11). The reaction of benzyl glyoxylate (**6g**) with 2,4,4-trimethyl-1-pentene (**7f**) and 1-isopropenyladamantane (**7j**) also proceeded, and the corresponding products were obtained with good enantioselectivities (Entries 12 and 13).

Catalytic Amount of the Cationic Cobalt(III) Complex. Lewis acid catalysts are generally moisture-sensitive since contaminants such as water or amines could occupy the coordination sites of the central metal to prevent the substrate from approaching the catalyst. Therefore, perfectly anhydrous conditions, loading of more than 10 mol% catalyst, or coexistence of dehydrating agents should be required to achieve high reactivities and enantioselectivities. Pre-synthesized and readily isolated transition-metal and/or moisture-stable complex catalysts were expected to be among the most promising solutions for these difficulties. Using these concepts, researchers have recently developed the enantioselective Diels–Alder[20] and hetero Diels–Alder[21] reactions and enantioselective cyanohydration[22] to achieve high enantioselections and high catalytic efficiencies. The optically active 3-oxobutylideneaminato-

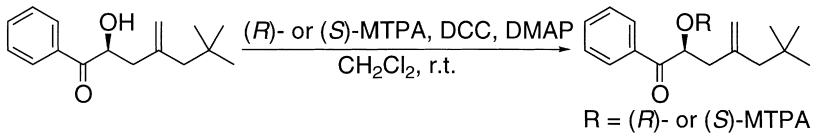
Table 6. The Enantioselective Carbonyl-Ene Reaction of Various Alkenes



Entry[a]	R	Alkene		Yield/%[b]	Ee/%
1	Ph (**6a**)		X = F (**7b**)	92	88
2			X = H (**7a**)	93	93
3			X = Me (**7c**)	70	84
4			**7d**	87	92
5			**7e**	87	89
6			**7f**	81	91
7			**7g**	56	84
8			**7h**	75	94
9			**7i**	60	94
10[c]	OBn (**6g**)		**7a**	91	85
11[c]			**7e**	93	85
12			**7f**	70	56
13			**7j**	50	62

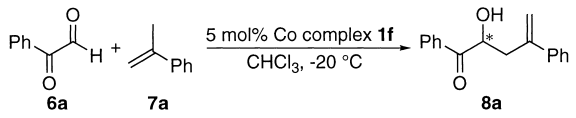
a) Reaction conditions: Co(III)–SbF_6 catalyst 0.025 mmol (5.0 mol%), glyoxal derivative 1.0 mmol, and alkene 0.5 mmol in $CHCl_3$ (2.5 mL) at −20 °C. b) Isolated yield. c) Reaction was carried out at −60 °C.

cobalt complexes are prepared in water-methanol and can be isolated prior to use; therefore, the loading amount of the catalyst was expected to be decreased. In Table 7, the loading amount of the cationic cobalt(III) complex catalyst **1f** was examined in the reaction of 2-phenylpropene (**7a**) with phenylglyoxal (**6a**). The smaller the amount of complex catalyst loaded, the longer the reaction time required for complete consumption of the glyoxal. The yield and enantioselectivity of the products in each reaction were maintained in the ranges of 80–93% yields and 93–95% ee regardless of the amount of complex catalyst employed (0.2–5 mol%). These observations show that the optically active 3-oxobutylideneaminatocobalt(III) hexafluoroantimonate complex could act as a Lewis acid for the carbonyl-ene reaction even with a 0.2 mol% catalyst loading.



Scheme 2.

Table 7. Loading Amount of 3-Oxobutylideneaminato-cobalt(III) Complex Catalysts



Entry[a)]	Cat./mol%	Time/h	Yield/%[b)]	Ee/%[c)]
1	5	3	93	93
2	2	8	80	94
3	1	21	84	95
4	0.5	45	80	95
5	0.2	80	80	94

a) Reaction conditions: Co(III)–SbF_6 complex catalyst 0.025 mmol (5.0 mol%), 2-phenylpropene 0.5 mmol, and phenylglyoxal 1.0 mmol at −20 °C. b) Isolated yield. c) Determined by HPLC analysis using Chiralcel OB-H (3% 2-propanol in hexane).

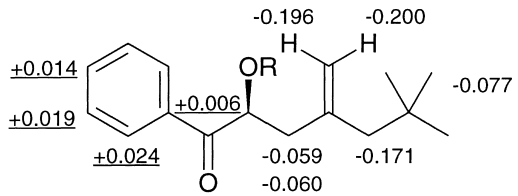


Fig. 2. $\Delta\delta(\delta_S - \delta_R)$ values (ppm) obtained for (*R*)- and (*S*)-MTPA esters of secondary alcohols.

Absolute Configuration of the Optically Active Homoallylic Alcohols. The absolute configuration of the obtained product **12f** was determined by the $\Delta\delta$ values of ^{1}H NMR analysis obtained for the corresponding (*R*)- and (*S*)-MTPA esters (Scheme 2) described in the literature.[23] We confirmed that the homoallylic alcohol of the (*S*)-configuration corresponding to the (*S*,*S*)-cobalt complex catalyst was obtained (Fig. 2). On the basis of this observation, the plausible transition states of the present carbonyl-ene reaction are proposed as follows (Fig. 3); it could be assumed that the lone pair of oxygen atoms *anti* to the benzoyl or benzyloxycarbonyl group in glyoxals contributed to coordination of the cobalt atom, and that the phenyl or benzyloxy group are oriented between two coordinating oxygen atoms on the planar 3-oxobutylideneaminato ligand, because of their bulkiness.[24] The alkene should approach the *si*-face of the activated glyoxals mentioned above to afford the (*S*)-homoallylic alcohols in high selectivities because the *re*-face is blocked by the aryl group of the chiral diamine and the bulky alkyl or aryl group on the side chain of the 3-oxobutylideneaminato ligand. This postulated transition state can clearly explain the observed stereochemistry of the present carbonyl-ene reaction. Moreover, these results are consistent with those of the corresponding hetero Diels–Alder reaction.

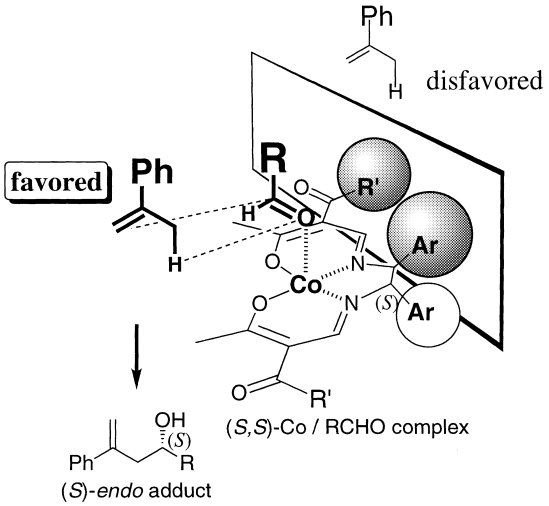


Fig. 3. Reasonable explanation for the enantioselection in the carbonyl-ene reaction catalyzed by the (*S*,*S*)-cobalt complex.

Conclusions

In summary, the cationic cobalt(III) hexafluoroantimonate complex with a optically active 3-oxobutylideneaminato ligand effectively catalyzed the asymmetric carbonyl-ene reaction of various alkenes with glyoxal derivatives to afford the corresponding homoallylic alcohols in high yield with high enantioselectivities.

Experimental

General. Infrared (IR) spectra were recorded on a JASCO Model FT/IR-410 infrared spectrometer on KBr pellets or liquid film on NaCl. ^{1}H NMR spectra and ^{13}C NMR spectra were measured on a JEOL Model GX-400 spectrometer using $CDCl_3$ or C_6D_6 as a solvent and with tetramethylsilane as an internal standard. High-resolution mass spectra were obtained with a HITACHI M-8013. For the thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 F_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (silica gel 60N). High-performance liquid chromatography (HPLC) analyses were performed with a Shimadzu LC-6A chromatograph using an optically active column (Chiralcel OB-H, Chiralcel OD-H, and Chiralpak AD-H columns, Daicel Ltd., Co.); the peak areas were obtained with a Shimadzu chromatopack CR-4A or Varian Dynamax MacIntegrator. Optical rotations were measured with a JASCO DIP-370 digital polarimeter.

Phenylglyoxal (**6a**) was purchased from Tokyo Kasei Kogyo (TCI) Co., Ltd. *p*-Nitrophenylglyoxal (**6b**), *p*-fluorophenylglyoxal (**6c**), *p*-chlorophenylglyoxal (**6d**), *p*-bromophenylglyoxal

(**6e**), *p*-methylphenylglyoxal (**6f**),[25] and benzyl glyoxylate (**6g**),[26] were prepared by a reported method. 2-Phenylpropene (**7a**), 2-(4-fluorophenyl)propene (**7b**), 2,4,4-trimethyl-1-pentene (**7f**), 2,3-dimethyl-1-butene (**7g**), and methylenecyclohexane (**7h**) were purchased from Tokyo Kasei Kogyo (TCI) Co., Ltd. 2-(4-Methylphenyl)propene (**7c**), 2-(2-fluorophenyl)propene (**7d**), 2-(2-naphthyl)propene (**7e**), 3-(*t*-butyldimethylsilyloxy)-2-methylpropene (**7i**), and 1-isopropenyladamantane (**7j**) were prepared by a reported method.[27]

Preparation of Optically Active 3-Oxobutylideneaminatocobalt Complexes. Complexes **1f**, **2f**, **3f**, **9f**, **10f**, and **11f** were prepared by a reported method.[16]

(1*S*,2*S*)-1,2-Bis(3,5-dimethylphenyl)-*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]ethylenediaminatocobalt(Ⅲ) Hexafluoroantimonate (2f): IR (KBr) 3012, 2921, 2863, 1586, 1472, 1398, 1355, 1299, 1262, 1200, 1125, 1074, 1032, 997, 875, 851, 745, 725, 700, 665, 640, 601, 567 cm^{-1}. MS (FAB(positive)) *m*/*z* 754 $(M-SbF_6+H)^+$, (FAB(negative)) *m*/*z* 235 $(SbF_6)^-$.

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-bis(2,4,6-trimethylphenyl)ethylenediaminatocobalt(Ⅲ) Hexafluoroantimonate (3f): IR (KBr) 2922, 2863, 1591, 1466, 1400, 1356, 1288, 1268, 1199, 1124, 1083, 1035, 994, 878, 850, 746, 665, 641, 595 cm^{-1}. MS (FAB(positive)) *m*/*z* 782 $(M-SbF_6+H)^+$, (FAB(negative)) *m*/*z* 235 $(SbF_6)^-$.

(1*S*,2*S*)-*N*,*N*′-Bis(2-acetyl-3-oxobutylidene)-1,2-diphenylethylenediaminatocobalt(Ⅲ) Hexafluoroantimonate (9f): IR (KBr) 2932, 1585, 1534, 1492, 1474, 1397, 1359, 1300, 1268, 1193, 1084, 1000, 948, 763, 705, 661, 607, 549 cm^{-1}. MS (FAB(positive)) *m*/*z* 490 $(M-SbF_6+H)^+$, (FAB(negative)) *m*/*z* 235 $(SbF_6)^-$.

(1*S*,2*S*)-*N*,*N*′-Bis(2-cyclopentyloxycarbonyl-3-oxobutylidene)-1,2-diphenylethylenediaminatocobalt(Ⅲ) Hexafluoroantimonate (10f): IR (KBr) 2966, 2874, 1672, 1615, 1436, 1409, 1362, 1323, 1263, 1199, 1168, 1086, 1035, 1003, 965, 759, 702, 665, 599, 547 cm^{-1}. MS (FAB(positive)) *m*/*z* 630 $(M-SbF_6+H)^+$, (FAB(negative)) *m*/*z* 235 $(SbF_6)^-$.

(1*R*,2*R*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-cyclohexylethylenediaminatocobalt(Ⅲ) Hexafluoroantimonate (11f): IR (KBr) 2938, 2864, 1638, 1584, 1454, 1398, 1353, 1299, 1281, 1246, 1199, 1165, 1030, 996, 930, 881, 850, 795, 745, 662, 640, 586, 558 cm^{-1}. MS (FAB(positive)) *m*/*z* 600 $(M-SbF_6+H)^+$, (FAB(negative)) *m*/*z* 235 $(SbF_6)^-$.

General Procedure for the Enantioselective Carbonyl-Ene Reaction. To a solution of the cobalt complex **1f** (23.3 mg, 5.4 mol%) in chloroform (0.5 mL) was added 2-phenylpropene (**7a**) (54.5 mg, 0.46 mmol) in chloroform (1.0 mL). A solution of the phenylglyoxal (**6a**) (133.3 mg, 0.99 mmol) in chloroform (1.0 mL) was then added at −20 °C. The mixture was stirred for 3 h at −20 °C. A standard workup and chromatography on silica gel afforded 1,4-diphenyl-2-hydroxy-4-penten-1-one (108.6 mg) in 93% yield. [Chiralcel OB-H, 3.0% 2-propanol in hexane, Flow 1.0 mL/min, 17.9 min (minor), 31.3 min (major)].

1,4-Diphenyl-2-hydroxy-4-penten-1-one (8a): $[\alpha]_D^{31}$ +40.1° (*c* 0.370, $CHCl_3$). ^1H NMR (400 MHz) δ 2.59 (1H, dd, *J* = 8.3, 14.7 Hz), 3.02 (1H, dd, *J* = 2.9, 14.7 Hz), 3.59 (1H, brs), 5.00–5.10 (2H, m), 5.28 (1H, d, *J* = 7.8 Hz), 7.15–7.33 (5H, m), 7.39 (2H, t, *J* = 7.8 Hz), 7.54 (1H, t, *J* = 7.8 Hz), 7.71 (2H, d, *J* = 7.8 Hz); ^{13}C NMR (100 MHz) δ 42.0, 71.6, 116.1, 126.5, 127.6, 128.3, 128.4, 128.7, 133.6, 133.8, 140.3, 143.8, 201.3; IR (neat) 3471, 3082, 3058, 3030, 2928, 1682, 1629, 1598, 1578, 1494, 1448, 1408, 1259, 1178, 1112, 1092, 1072, 975, 905, 779, 699 cm^{-1}. HRMS: Calcd for $C_{17}H_{16}O_2$: (M^+), 252.1150. Found: *m*/*z* 252.1166. HPLC: Chiralcel OB-H (3.0% 2-propanol in hexane, Flow 1.0 mL/min), 17.9 min (minor), 31.3 min (major) [(*R*,*R*)-cobalt complex **1f** was employed].

2-Hydroxy-1-(4-nitrophenyl)-4-phenyl-4-penten-1-one (8b): $[\alpha]_D^{28}$ +33.0° (*c* 0.320, $CHCl_3$). ^1H NMR (400 MHz) δ 2.75 (1H, dd, *J* = 7.3, 14.7 Hz), 2.98 (1H, dd, *J* = 4.4, 14.7 Hz), 3.37 (1H, d, *J* = 6.8 Hz), 5.02–5.14 (2H, m), 5.27 (1H, d, *J* = 1.2 Hz), 7.17–7.26 (5H, m), 7.80 (2H, d, *J* = 8.8 Hz), 8.19 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz) δ 41.6, 72.2, 117.0, 123.8, 126.5, 127.9, 128.4, 129.4, 138.7, 139.9, 143.0, 150.4, 200.1; IR (neat) 3482, 3108, 3082, 3054, 3030, 2930, 2860, 1950, 1809, 1692, 1628, 1603, 1574, 1525, 1495, 1444, 1402, 1348, 1318, 1254, 1216, 1190, 1111, 1089, 1073, 978, 908, 854, 780, 707, 541, 508 cm^{-1}. HRMS: Calcd for $C_{17}H_{15}NO_4$: (M^+), 297.1001. Found: *m*/*z* 297.1030. HPLC: Chiralcel OD-H (10.0% 2-propanol in hexane, Flow 1.0 mL/min), 16.9 min (major), 20.4 min (minor) [(*R*,*R*)-cobalt complex **1f** was employed].

1-(4-Fluorophenyl)-2-hydroxy-4-phenyl-4-penten-1-one (8c): $[\alpha]_D^{25}$ −42.0° (*c* 0.177, $CHCl_3$). ^1H NMR (400 MHz) δ 2.71 (1H, dd, *J* = 7.3, 14.7 Hz), 3.05 (1H, dd, *J* = 3.9, 14.7 Hz), 3.59 (1H, d, *J* = 7.3 Hz), 5.09 (1H, dt, *J* = 3.9, 7.3 Hz), 5.16 (1H, d, *J* = 1.0 Hz), 5.34 (1H, d, *J* = 1.0 Hz), 7.08–7.16 (2H, m), 7.25–7.36 (5H, m), 7.76–7.84 (2H, m); ^{13}C NMR (100 MHz) δ 42.1, 71.5, 116.0 (d, J_{CF} = 22 Hz), 116.4, 126.5, 127.7, 128.3, 130.2 (d, J_{CF} = 3 Hz), 131.1 (d, J_{CF} = 10 Hz), 140.3, 143.6, 166.0 (d, J_{CF} = 256 Hz), 199.8; IR (neat) 3471, 3081, 3058, 3026, 2932, 1683, 1599, 1508, 1299, 1235, 1157, 1113, 1092, 1072, 977, 906, 845, 778, 705, 601 cm^{-1}. HRMS: Calcd for $C_{17}H_{15}FO_2$: (M^+), 270.1056. Found: *m*/*z* 270.1043. HPLC: Chiralcel OD-H (1.0% 2-propanol in hexane, Flow 1.0 mL/min), 21.0 min (major), 22.9 min (minor) [(*R*,*R*)-cobalt complex **1f** was employed].

1-(4-Chlorophenyl)-2-hydroxy-4-phenyl-4-penten-1-one (8d): $[\alpha]_D^{25}$ +35.1° (*c* 1.063, $CHCl_3$). ^1H NMR (400 MHz) δ 2.71 (1H, dd, *J* = 7.8, 14.6 Hz), 3.04 (1H, dd, *J* = 3.9, 14.6 Hz), 3.57 (1H, brs), 5.04–5.11 (1H, m), 5.15 (1H, d, *J* = 1.0 Hz), 5.34 (1H, d, *J* = 1.0 Hz), 7.27–7.35 (5H, m), 7.42 (2H, d, *J* = 8.3 Hz), 7.70 (2H, d, *J* = 8.3 Hz); ^{13}C NMR (100 MHz) δ 42.0, 71.6, 116.4, 126.5, 127.7, 128.3, 129.0, 129.8, 132.1, 140.27, 140.32, 143.5, 200.2; IR (neat) 3465, 3083, 3059, 3032, 2934, 1683, 1591, 1571, 1491, 1445, 1399, 1285, 1259, 1092, 1012, 976, 906, 833, 778, 703, 531 cm^{-1}. HRMS: Calcd for $C_{17}H_{15}ClO_2$: (M^+), 286.0761. Found: *m*/*z* 286.0741. HPLC: Chiralcel OD-H (1.0% 2-propanol in hexane, Flow 1.0 mL/min), 20.3 min (minor), 22.2 min (major) [(*R*,*R*)-cobalt complex **1f** was employed].

1-(4-Bromophenyl)-2-hydroxy-4-phenyl-4-penten-1-one (8e): $[\alpha]_D^{25}$ −38.0° (*c* 0.932, $CHCl_3$). ^1H NMR (400 MHz) δ 2.70 (1H, dd, *J* = 7.8, 14.7 Hz), 3.03 (1H, dd, *J* = 3.9, 14.7 Hz), 3.56 (1H, d, *J* = 6.8 Hz), 4.99 (1H, ddd, *J* = 3.9, 6.8, 7.8 Hz), 5.15 (1H, d, *J* = 1.0 Hz), 5.34 (1H, d, *J* = 1.0 Hz), 7.26–7.35 (5H, m), 7.57 (2H, d, *J* = 8.3 Hz), 7.61 (2H, d, *J* = 8.3 Hz); ^{13}C NMR (100 MHz) δ 41.9, 71.6, 116.4, 126.5, 127.7, 128.3, 129.0, 129.8, 132.0, 132.5, 140.2, 143.5, 200.4; IR (neat) 3469, 3083, 3057, 3031, 2932, 1684, 1586, 1487, 1394, 1258, 1070, 1010, 975, 906, 824, 778, 703 cm^{-1}. HRMS: Calcd for $C_{17}H_{15}BrO_2$: (M^+), 330.0256. Found: *m*/*z* 330.0280. HPLC: Chiralcel OB-H (5.0% 2-propanol in hexane, Flow 1.0 mL/min), 14.9 min (minor), 17.5 min (major) [(*R*,*R*)-cobalt complex **1f** was employed].

2-Hydroxy-1-(4-methylphenyl)-4-phenyl-4-penten-1-one (8f): $[\alpha]_D^{28}$ +26.1° (*c* 0.412, $CHCl_3$). ^1H NMR (400 MHz) δ 2.43 (3H, s), 2.63 (1H, dd, *J* = 8.3, 14.6 Hz), 3.08 (1H, dd, *J* = 3.4, 14.6

Hz), 3.67 (1H, d, J = 6.8 Hz), 5.08 (1H, ddd, J = 3.4, 6.8, 8.3 Hz), 5.17 (1H, s), 5.35 (1H, s), 7.21–7.42 (7H, m), 7.70 (2H, d, J = 8.3 Hz); ^{13}C NMR (100 MHz) δ 21.8, 42.2, 71.4, 116.0, 126.5, 127.6, 128.3, 128.6, 129.4, 131.1, 140.5, 144.0, 144.9, 200.9; IR (neat) 3468, 3082, 3056, 3031, 2923, 1678, 1606, 1444, 1401, 1288, 1266, 1179, 1111, 1092, 1073, 973, 903, 822, 778, 706 cm^{-1}. HRMS: Calcd for $C_{18}H_{18}O_2$: (M^+), 266.1307. Found: m/z 266.1313. HPLC: Chiralcel OB-H (10.0% 2-propanol in hexane, Flow 1.0 mL/min), 7.6 min (major), 10.3 min (minor) [(*R*,*R*)-cobalt complex **1f** was employed].

Benzyl 2-Hydroxy-4-phenyl-4-pentenoate (8g): $[\alpha]_D^{25}$ +3.9° (c 1.197, $CHCl_3$). ^{1}H NMR (400 MHz) δ 2.72–2.88 (1H, br), 2.85 (1H, dd, J = 7.3, 14.7 Hz), 3.06 (1H, dd, J = 4.4, 14.7 Hz), 4.31 (1H, s), 4.95 (1H, d, J = 12.2 Hz), 5.09 (1H, d, J = 12.2 Hz), 5.17 (1H, d, J = 12.2 Hz), 5,36 (1H, s), 7.21–7.42 (10H, m); ^{13}C NMR (100 MHz) δ 40.5, 67,2, 69.2, 116.2, 126.3, 127.6, 128.25, 128.29, 128.4, 128.5, 134.9, 140.1, 143.3, 174.1; IR (neat) 3469, 3084, 3060, 3033, 2953, 1738, 1629, 1600, 1574, 1496, 1455, 1377, 1266, 1199, 1113, 1092, 1028, 906, 780, 738, 698 cm^{-1}. HRMS: Calcd for $C_{18}H_{18}O_3$: (M^+), 282.1256. Found: m/z 282.1214. HPLC: Chiralcel OB-H (2.0% ethanol in hexane, Flow 1.0 mL/min), 18.5 min (minor), 20.1 min (major) [(*R*,*R*)-cobalt complex **1f** was employed].

4-(4-Fluorophenyl)-2-hydroxy-1-phenyl-4-penten-1-one (12b): $[\alpha]_D^{25}$ +20.7° (c 0.732, $CHCl_3$). ^{1}H NMR (400 MHz) δ 2.61 (1H, dd, J = 8.3, 14.6 Hz), 2.97 (1H, dd, J = 3.4, 14.6 Hz), 3.63 (1H, brs), 5.00–5.12 (2H, m), 5.22 (1H, s), 6.90 (1H, d, J = 8.8 Hz), 6.92 (1H, d, J = 8.8 Hz), 7.21 (1H, d, J = 8.8 Hz), 7.22 (1H, d, J = 8.8 Hz), 7.39 (2H, t, J = 7.3 Hz), 7.54 (1H, t, J = 7.3 Hz), 7.69 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ 42.0, 71.6, 115.1 (d, J_{CF} = 21 Hz), 116.2, 128.1 (d, J_{CF} = 8 Hz), 128.5, 130.0, 133.5, 133.9, 136.5 (d, J_{CF} = 3 Hz), 142.7, 162.2 (d, J_{CF} = 246 Hz), 201.1; IR (neat) 3469, 3065, 2932, 1683, 1600, 1509, 1449, 1403, 1227, 1111, 1076, 975, 841, 711, 691 cm^{-1}. HRMS: Calcd for $C_{17}H_{15}FO_2$: (M^+), 270.1056. Found: m/z 270.1033. HPLC: Chiralcel OB-H (5.0% 2-propanol in hexane, Flow 1.0 mL/min), 18.4 min (minor), 31.4 min (major).

2-Hydroxy-4-(4-methylphenyl)-1-phenyl-4-penten-1-one (12c): $[\alpha]_D^{28}$ +37.4° (c 0.507, $CHCl_3$). ^{1}H NMR (400 MHz) δ 2.35 (3H, s), 2.64 (1H, dd, J = 7.8, 14.7 Hz), 3.05 (1H, dd, J = 2.9, 14.7 Hz), 3.64 (1H, d, J = 6.8 Hz), 5.07–5.16 (2H, m), 5.31 (1H, d, J = 1.0 Hz), 7.12 (2H, d, J = 7.8 Hz), 7.25 (2H, d, J = 7.8 Hz), 7.45 (2H, t, J = 7.3 Hz), 7.59 (1H, t, J = 7.3 Hz), 7.79 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz, C_6D_6) δ 21.4, 42.5, 72.3, 115.7, 127.2, 128.9, 129.0, 129.5, 133.6, 134.8, 137.5, 138.6, 144.5, 201.8; IR (neat) 3472, 3085, 3059, 3028, 2922, 1682, 1627, 1598, 1578, 1513, 1449, 1406, 1259, 1179, 1110, 1076, 974, 907, 824, 733, 695 cm^{-1}. HRMS: Calcd for $C_{18}H_{18}O_2$: (M^+), 266.1307. Found: m/z 266.1302. HPLC: Chiralcel OB-H (5.0% 2-propanol in hexane, Flow 1.0 mL/min), 9.5 min (minor), 13.7 min (major).

4-(2-Fluorophenyl)-2-hydroxy-1-phenyl-4-penten-1-one (12d): $[\alpha]_D^{25}$ +42.0° (c 0.177, $CHCl_3$). ^{1}H NMR (400 MHz) δ 2.58 (1H, dd, J = 8.8, 14.7 Hz), 3.11 (1H, dd, J = 2.0, 14.7 Hz), 3.60 (1H, d, J = 6.4 Hz), 4.95–5.06 (1H, m), 5.20 (1H, s), 5.24 (1H, s), 6.92 (1H, dd, J = 8.8, 10.5 Hz), 7.04 (1H, t, J = 7.3 Hz), 7.14–7.26 (2H, m), 7.37 (2H, t, J = 7.8 Hz), 7.52 (1H, t, J = 7.8 Hz), 7.70 (2H, d, J = 7.8 Hz); ^{13}C NMR (100 MHz) δ 42.7 (d, J_{CF} = 3 Hz), 71.7, 115.5 (d, J_{CF} = 22 Hz), 119.5, 124.2 (d, J_{CF} = 3 Hz), 128.4, 128.69, 128.70 (d, J_{CF} = 13 Hz), 129.2, 130.7 (d, J_{CF} = 4 Hz), 133.4, 133.8, 140.3, 159.7 (d, J_{CF} = 246 Hz), 201.1; IR (neat) 3474, 3084, 3062, 3036, 2928, 1683, 1632, 1598, 1578, 1488, 1449, 1407, 1290, 1262, 1215, 1094, 975, 914, 824, 763, 692 cm^{-1}. HRMS: Calcd for $C_{17}H_{15}FO_2$: (M^+), 270.1056. Found: m/z 270.1071. HPLC: Chiralpak OB-H (3.0% 2-propanol in hexane, Flow 1.0 mL/min), 11.6 min (major), 14.5 min (minor) [(*R*,*R*)-cobalt complex **1f** was employed].

2-Hydroxy-4-(2-naphtyl)-1-phenyl-4-penten-1-one (12e): $[\alpha]_D^{25}$ +59.5° (c 0.558, $CHCl_3$). ^{1}H NMR (400 MHz) δ 2.78 (1H, dd, J = 8.3, 14.5 Hz), 3.19 (1H, d, J = 14.5 Hz), 3.69 (1H, brs), 5.16 (1H, br), 5.27 (1H, s), 5.49 (1H, s), 7.38–7.62 (7H, m), 7.73–7.85 (5H, m); ^{13}C NMR (100 MHz) δ 42.1, 71.6, 116.7, 124.8, 125.3, 125.9, 126.1, 127.4, 127.9, 128.0, 128.4, 128.7, 132.8, 133.1, 133.7, 133.8, 137.5, 143.5, 201.4; IR (KBr) 3421, 3383, 3059, 2937, 1683, 1596, 1447, 1408, 1258, 1212, 1197, 1173, 1132, 1109, 1005, 945, 901, 865, 832, 755, 692, 647, 633, 617, 476 cm^{-1}. HRMS: Calcd for $C_{21}H_{18}O_2$: (M^+), 302.1307. Found: m/z 302.1313. HPLC: Chiralcel OB-H (10.0% 2-propanol in hexane, Flow 1.0 mL/min), 16.4 min (minor), 25.9 min (major).

6,6-Dimethyl-2-hydroxy-4-methylene-1-phenylheptan-1-one (12f): $[\alpha]_D^{26}$ −9.5° (c 0.762, $CHCl_3$). ^{1}H NMR (400 MHz) δ 0.80 (9H, s), 1.89 (1H, d, J = 13.0 Hz), 1.95 (1H, d, J = 13.0 Hz), 2.17 (1H, dd, J = 8.8, 14.7 Hz), 2.56 (1H, dd, J = 2.4, 14.7 Hz), 3.61 (1H, brs), 4.80 (1H, s), 4.94 (1H, s), 5.14 (1H, dd, J = 2.4, 8.8 Hz), 7.44 (2H, t, J = 7.3 Hz), 7.56 (1H, t, J = 7.3 Hz), 7.86 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ 29.9, 31.7, 44.1, 49.5, 72.6, 116.3, 128.5, 128.7, 133.6, 133.8, 142.8, 201.4; IR (neat) 3475, 3071, 2952, 1682, 1639, 1598, 1477, 1449, 1363, 1263, 900, 775, 692 cm^{-1}. HRMS: Calcd for $C_{16}H_{22}O_2$: (M^+), 246.1620. Found: m/z 246.1595. HPLC: Chiralcel OD-H (1.0% 2-propanol in hexane, Flow 1.0 mL/min), 9.9 min (major), 15.3 min (minor).

2-Hydroxy-4-isopropyl-1-phenyl-4-hepten-1-one (12g): $[\alpha]_D^{22}$ −3.1° (c 0.255, $CHCl_3$). ^{1}H NMR (400 MHz) δ 0.95 (3H, d, J = 6.8 Hz), 0.96 (3H, d, J = 6.8 Hz), 2.13 (1H, dd, J = 9.8, 15.1 Hz), 2.24 (1H, q, J = 6.8 Hz), 2.55 (1H, dd, J = 2.5, 15.1 Hz), 3.60 (1H, d, J = 6.8 Hz), 4.83 (1H, s), 4.87 (1H, s), 5.16 (1H, ddd, J = 2.5, 6.8, 9.8 Hz), 7.44 (2H, t, J = 7.3 Hz), 7.56 (1H, t, J = 7.3 Hz), 7.86 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ 21.6, 21.8, 33.6, 41.0, 72.2, 109.6, 128.4, 128.7, 133.5, 133.8, 151.0, 201.4; IR (neat) 3468, 3065, 2962, 2932, 2873, 1717, 1683, 1598, 1450, 1263, 1091, 974, 899, 713, 695 cm^{-1}. HRMS: Calcd for $C_{14}H_{18}O_2$: (M^+), 218.1307. Found: m/z 218.1305. HPLC: Chiralcel OD-H (0.8% 2-propanol in hexane, Flow 0.5 mL/min), 28.4 min (major), 59.7 min (minor).

3-(1-Cyclohexenyl)-2-hydroxy-1-phenyl-4-propen-1-one (12h): $[\alpha]_D^{19}$ −2.9° (c 0.386, $CHCl_3$). ^{1}H NMR (400 MHz) δ 1.42–1.60 (4H, m), 1.82–2.04 (4H, m), 2.08 (1H, dd, J = 8.3, 14.7 Hz), 2.41 (1H, d, J = 14.7 Hz), 3.57 (1H, d, J = 6.4 Hz), 5.07–5.16 (1H, m), 5.40 (1H, s), 7.43 (2H, t, J = 7.3 Hz), 7.54 (1H, t, J = 7.3 Hz), 7.84 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ 22.1, 22.8, 25.3, 28.7, 44.5, 72.0, 124.8, 128.4, 128.6, 133.0, 133.6, 133.7, 201.7; IR (neat) 3453, 3061, 2931, 2858, 1717, 1684, 1598, 1449, 1262, 1096, 1070, 976, 703 cm^{-1}. HRMS: Calcd for $C_{15}H_{18}O_2$: (M^+), 230.1307. Found: m/z 230.1291. HPLC: Chiralcel OD-H (1.0% 2-propanol in hexane, Flow 1.0 mL/min), 12.4 min (major), 20.9 min (minor).

5-(*t*-Butyldimethylsilyloxy)-2-hydroxy-4-methylene-1-phenylpentan-1-one (12i): $[\alpha]_D^{25}$ +2.1° (c 0.766, $CHCl_3$). ^{1}H NMR (400 MHz) δ 0.08 (3H, s), 0.10 (3H, s), 0.92 (9H, s), 2.20 (1H, dd, J = 8.8, 14.7 Hz), 2.76 (1H, d, J = 14.7 Hz), 3.79 (1H, brs), 4.14 (1H, d, J = 13.7 Hz), 4.28 (1H, d, J = 13.7 Hz), 4.91 (1H, s), 5.13 (1H, s), 5.19–5.31 (1H, br), 7.50 (2H, t, J = 7.3 Hz), 7.62 (1H, t, J

= 7.3 Hz), 7.99 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ −5.25, −5.21, 18.5, 26.0, 39.6, 66.3, 72.2, 113.0, 128.7, 128.8, 133.5, 133.9, 144.2, 201.2; IR (neat) 3478, 3068, 2955, 2928, 2885, 2857, 1683, 1598, 1579, 1471, 1463, 1450, 1404, 1361, 1258, 1177, 1104, 1005, 975, 903, 838, 777, 693 cm^{-1}. HRMS: Calcd for $C_{18}H_{28}O_3Si$: (M^+), 320.1808. Found: *m/z* 320.1811. HPLC: Chiralcel OD-H (1.0% ethanol in hexane, Flow 1.0 mL/min), 6.4 min (minor), 10.5 min (major) [(*R*,*R*)-cobalt complex **1f** was employed].

Benzyl 2-Hydroxy-4-(2-naphtyl)-4-pentenoate (13e): $[\alpha]_D^{25}$ +8.2° (*c* 1.541, $CHCl_3$). ^{1}H NMR (400 MHz) δ 2.83 (1H, brs), 2.96 (1H, dd, J = 7.8, 14.2 Hz), 3.17 (1H, dd, J = 3.9, 14.2 Hz), 4.30–4.43 (1H, br), 4.92 (1H, d, J = 12.2 Hz), 5.05 (1H, d, J = 12.2 Hz), 5.26 (1H, s), 5.49 (1H, s), 7.21–7.82 (12H, m); ^{13}C NMR (100 MHz) δ 40.6, 67,3, 69.3, 116.7, 124.6, 125.0, 125.9, 126.1, 126.9, 127.4, 127.6, 127.9, 128.1, 128.3, 128.4, 128.5, 132.8, 133.1, 134.9, 137.4, 143.1, 174.1; IR (neat) 3480, 3058, 2953, 1737, 1498, 1455, 1265, 1196, 1102, 896, 860, 821, 752, 698 cm^{-1}. HRMS: Calcd for $C_{18}H_{18}O_3$: (M^+), 332.1412. Found: *m/z* 332.1424. HPLC: Chiralcel OD-H (10.0% 2-propanol in hexane, Flow 1.0 mL/min), 11.9 min (minor), 13.5 min (major) [(*R*,*R*)-cobalt complex **1f** was employed].

Benzyl 6,6-Dimethyl-2-hydroxy-4-methylene-1-phenylheptanoate (13f): ^{1}H NMR (400 MHz) δ 0.90 (9H, s), 1.91 (1H, d, J = 13.2 Hz), 1.97 (1H, d, J = 13.2 Hz), 2.39 (1H, dd, J = 7.8, 14.4 Hz), 2.60 (1H, d, J = 3.9, 14.4 Hz), 2.70 (1H, d, J = 6.4 Hz), 4.31–4.41 (1H, m), 4.85 (1H, s), 4.97 (1H, s), 5.21 (1H, s), 7.28–7.45 (5H, m); ^{13}C NMR (100 MHz) δ 29.9, 31.6, 42.7, 49.3, 67.3, 69.7, 70.3, 116.6, 128.3, 128.5, 128.6, 135.0, 142.5, 174.4; IR (neat) 3480, 3058, 3061, 2953, 1737, 1625, 1597, 1498, 1455, 1375, 1265, 1196, 1133, 1102, 1028, 953, 896, 860, 821, 752, 698 cm^{-1}. HRMS: Calcd for $C_{17}H_{24}O_3$: (M^+), 276.1725. Found: *m/z* 276.1746. HPLC: Chiralcel OB-H (1.0% ehtanol in hexane, Flow 0.9 mL/min), 10.9 min (major), 11.3 min (minor) [(*R*,*R*)-cobalt complex **1f** was employed].

Benzyl 2-Hydroxy-4-(1-adamantyl)-4-pentenoate (13j): $[\alpha]_D^{28}$ +13.5° (*c* 0.367, $CHCl_3$). ^{1}H NMR (400 MHz) δ 1.54–1.78 (1H, m), 1.99 (1H, brs), 2.35 (1H, dd, J = 8.3, 15.4 Hz), 2.60 (1H, dd, J = 3.9, 15.4 Hz), 2.72 (1H, d, J = 5.4 Hz), 4.39 (1H, ddd, J = 3.9, 5.4, 8.3 Hz), 4.91 (1H, s), 4.96 (1H, s), 5.19 (1H, d, J = 12.2 Hz), 5.23 (1H, d, J = 12.2 Hz), 7.29–7.44 (5H, m); ^{13}C NMR (100 MHz) δ 28.5, 35.4, 36.8, 37.9, 40.8, 67.2, 70.3, 109.4, 128.2, 128.4, 128.5, 135.1, 152.9, 174.6; IR (neat) 3479, 3090, 3065, 3033, 2902, 2848, 1739, 1632, 1497, 1454, 1262, 1195, 1096, 902, 750, 697 cm^{-1}. HRMS: Calcd for $C_{22}H_{28}O_3$: (M^+), 340.2038. Found: *m/z* 340.2009. HPLC: Chiralcel OD-H (10.0% 2-propanol in hexane, Flow 1.0 mL/min), 5.7 min (minor), 7.5 min (major) [(*R*,*R*)-cobalt complex **1f** was employed].

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