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Catalytic use of chiral phosphine ligands in asymmetric Pauson–Khand reactions

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Abstract

Catalytic asymmetric Pauson–Khand reactions with chiral bidentate phosphines as ligands have been successfully accomplished. The catalytic use of (*S*)-BINAP as a ligand was demonstrated to be the most effective in the cobalt-catalyzed reactions of 1,6-enynes, providing a facile entry to optically active 2-cyclopentenone derivatives with high enantioselectivity. A plausible mechanism for the asymmetric induction is proposed on the basis of the stereochemical outcome obtained.

1. Introduction

A number of transition metal-catalyzed asymmetric synthetic methods have been discovered so far for the preparation of optically active compounds,[1] and the versatility of the methods has received much attention for practical use in the pharmaceutical area. In recent years, much interest has been paid to asymmetric cyclizations of unsaturated systems by means of transition metals[2] for the preparation of optically active cyclic compounds, especially chiral five-membered carbocycles. Asymmetric synthesis of five-membered carbocyclic compounds has been synthetically valuable, since a number of biologically active compounds consisting of such carbocycles in natural products, particularly in terpenoids, have been found.

Over the past decade, we have developed new asymmetric synthetic methods in transition metal-catalyzed asymmetric cyclizations of unsaturated systems such as nickel- or palladium-catalyzed asymmetric rearrangements in (1,3-butadienyl)cyclopropanes,[3] asymmetric intramolecular metallo-ene reactions,[4] and palladium-catalyzed intramolecular asymmetric cycloisomerizations of 1,6-enynes.[5]

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In the course of our research along these lines, we have explored a new catalytic asymmetric route to optically active 2-cyclopentenones by a Pauson–Khand reaction using a catalytic amount of a cobalt catalyst and chiral phosphine ligands.

The Pauson–Khand reaction is well known for the preparation of 2-cyclopentenone derivatives.[6,7] However, only a limited number of asymmetric Pauson–Khand reactions, using substrates with chiral auxiliaries,[8] chiral ligands,[9] and others have been reported.[10]

The use of a catalytic amount of a cobalt catalyst and a chiral ligand in asymmetric Pauson–Khand reactions would be extremely valuable, although no report in this respect has appeared. We demonstrate herein the first examples of catalytic asymmetric syntheses of 2-cyclopentenone systems by intramolecular Pauson–Khand reactions using a catalytic amount of a cobalt catalyst and chiral phosphines as ligands, and reveal dramatic effects of the substituents in the 1,6-enyne systems and bidentate phosphine ligands in the cobalt-catalyzed cyclizations.

2. Results and discussion

2.1. Intramolecular catalytic asymmetric Pauson–Khand reactions with chiral phosphine ligands

Initially, intramolecular asymmetric Pauson–Khand reactions with a catalytic amount of a cobalt catalyst and chiral phosphine ligands are described.[11]

A 1,6-enyne system **1a** without a methyl substituent in the enyne site provided excellent enantioselectivity in the cobalt-catalyzed reactions with chiral phosphine ligands. The cobalt-catalyzed reactions of **1a** were carried out in 1,2-dimethoxyethane (DME), toluene, or 1,2-dichloroethane (DCE) at reflux, except for toluene (at 80°C), for 24 h under a carbon monoxide atmosphere in the presence of $Co_2(CO)_8$ (0.2 equiv.) and a ligand (0.2 equiv.) to furnish (*R*)- or (*S*)-**2a**, depending on the chiral ligand used, with enantioselectivity as listed in Table 1. The enantiomeric excess (e.e.) of **2a** was determined by HPLC analysis with Chiralpak AD. Studies on solvent effects in the asymmetric Pauson–Khand reactions of **1a** demonstrate that the use of acetonitrile as solvent provides rather high chemical yields of **2a** with rather poor e.e., whereas use of benzene, DME, or DCE gave **2a** with high e.e. Dramatic effects of ligands were observed in the cobalt-catalyzed asymmetric reactions. The highest enantioselectivity (91%) was obtained with (*S*)-BINAP as a ligand among the chiral ligands employed as listed in Table 1; however, other ligands such as (*R,R*)-DIOP, (*R,R*)-MOD-DIOP, ferrocenyl ligands, (*R*)-binaphthyl diamine, and (*R,R*)-Me-DuPHOS provided extremely low enantioselectivity. The degree of asymmetric induction was greatly dependent upon the amount of the chiral ligands used. Various amounts (0.1, 0.2, 0.3 and 0.4 equiv.) of a chiral ligand ((*S*)-BINAP) were employed in the reaction of **1a**, providing (*R*)-**2a** with 27, 90, 68 and 52% e.e., respectively, and the use of 0.2 equiv. of (*S*)-BINAP was clearly demonstrated to be the most effective for the enantiocontrol of the asymmetric synthesis, as shown in Table 1. The reaction of **1a** with (*S*)-BINAP as a ligand in DME at 65°C gave (*R*)-**2a** with 30% e.e. A rationalization of these results is not clear at the present time. Thus, the use of (*S*)-BINAP (0.2 equiv.) in the cobalt-catalyzed reaction of **1a** in DME or DCE at reflux afforded (*R*)-**2a** with 90 or 91% e.e., respectively.

Interestingly, however, the steric effects of substituents in the enyne sites of the substrates remarkably affect the degree of the asymmetric induction. A 1,6-enyne system **1b** with a methyl substituent in the enyne site provided rather poor enantioselectivity. The reactions of **1b** with (*S*)-BINAP as a ligand in DME, toluene (at 80°C) or DCE at reflux produced (*R*)-**2b** with 63, 44, or 61% e.e., whereas the reaction in DME at 60°C gave (*R*)-**2b** with 37% e.e., which cannot be clearly rationalized at the present time. Thus, relatively high enatioselectivity of (*R*)-**2b** was obtained by (*S*)-BINAP in comparison with those

Table 1
The intramolecular asymmetric Pauson–Khand reactions of **1a–c**, **3a–d** or **5** with chiral phosphine ligands[a)]

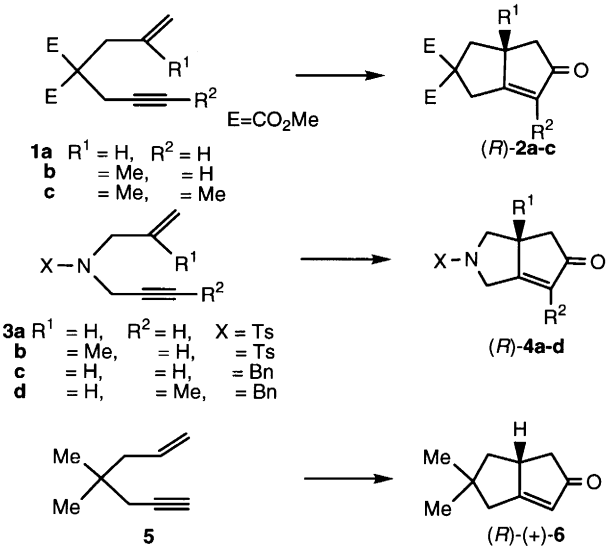
Substrate	Ligand[b)]	Solvent	Reaction time (h)	Yield (%) of **2**, **4** or **6**	e.e. (%) of **2**, **4** or **6**[c)] (Abs. config.)
1a	(*S*)-BINAP	DME	14	63[d)]	27 (*R*)
	(*S*)-BINAP	DME	14	53	90 (*R*)
	(*S*)-BINAP	DME	18	68[e)]	30 (*R*)
	(*S*)-BINAP	DME	20	61[f)]	68 (*R*)
	(*S*)-BINAP	DME	20	58[g)]	52 (*R*)
	(*S*)-BINAP	benzene	16	55	90 (*R*)
	(*S*)-BINAP	toluene	26	58	81 (*R*)
	(*S*)-BINAP	DCE	17	62	91 (*R*)
	(*S*)-BINAP	CH_3CN	15	74	37 (*R*)
	(*S*)-BINAP	THF	15	43	80 (*R*)
	(*R*,*R*)-DIOP	DME	14	76	5 (*R*)
	(*R*,*R*)-MOD-DIOP	DME	16	58	9 (*R*)
	(*S*)-(*R*)-PPFA	DME	17	99	3 (*S*)
	(*S*)-(*R*)-BPPFA	DME	15	86	3 (*S*)
	(*S*)-(*R*)-BPPFOH	DME	16	77	7 (*S*)
	(*S*)-(*R*)-BPPFOAc	DME	17	51	5 (*S*)
	(*R*)-Binaphthyl Diamine	DME	13	89	2 (*S*)
	(*R*,*R*)-Me-DuPHOS	DME	26	14	44 (*S*)
1b	(*S*)-BINAP	DME	24	31	63 (*R*)
	(*S*)-BINAP	DME	7	39[h)]	37 (*R*)
	(*S*)-BINAP	toluene	24	38	44 (*R*)
	(*S*)-BINAP	DCE	24	24	61 (*R*)
	(*R*,*R*)-DIOP	DME	24	54	40 (*R*)
	(*S*,*S*)-MOD-DIOP	DME	24	35	24 (*S*)
	(*S*)-(*R*)-PPFA	DME	24	89	0
	(*S*)-(*R*)-BPPFA	DME	24	60	37 (*S*)
	(*S*)-(*R*)-BPPFOH	DME	24	51	46 (*S*)
	(*S*)-(*R*)-BPPFOAc	DME	24	63	23 (*S*)
	(*R*)-Binaphthyl Diamine	DME	24	66	3 (*S*)
	(*R*)-BINOL	DME	24	22	21 (*S*)
1c	(*S*)-BINAP	DME	24	90	0
	(*R*,*R*)-DIOP	DME	24	47	31 (*R*)
3a	(*S*)-BINAP	DME	15	60	93 (*R*)
	(*S*)-BINAP	toluene	16	54	94 (*R*)
	(*S*)-BINAP	benzene	17	52	87 (*R*)
	(*S*)-BINAP	DCE	19	64	90 (*R*)
	(*S*)-BINAP	THF	19	39	78 (*R*)
	(*R*,*R*)-DIOP	DME	14	71	8 (*R*)
3b	(*S*)-BINAP	DME	14	13	62 (*R*)
	(*R*,*R*)-DIOP	DME	14	69	57 (*R*)
	(*R*,*R*)-MOD-DIOP	DME	14	69	56 (*R*)
	(*S*)-(*R*)-PPFA	DME	13	83	10 (*R*)
	(*S*)-(*R*)-BPPFA	DME	13	67	25 (*S*)
	(*S*)-(*R*)-BPPFOH	DME	13	73	10 (*S*)
	(*S*)-(*R*)-BPPFOAc	DME	13	66	12 (*S*)
3c	(*S*)-BINAP	DME	12	36	82 (*R*)
	(*S*)-BINAP	benzene	12	43	88 (*R*)
	(*S*)-BINAP	DCE	12	37	92 (*R*)
3d	(*S*)-BINAP	DME	12	13	40 (*R*)
5	(*S*)-BINAP	DME	18	42	77 (*R*)

a) The cobalt-catalyzed reactions of **1a-c**, **3a-d** or **5** were carried out at reflux except for toluene (at 80°C) under carbon monoxide atmosphere in the presence of $Co_2(CO)_8$ (0.2 equiv.) and a ligand (0.2 equiv.). *b*) BINAP: 2,2'-Bis (diphenylphosphino)-1,1'-binaphthyl, DIOP: 4,5-Bis (diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane, MOD-DIOP: 4,5-Bis [bis (4'-methoxy-3',5'-dimethylphenyl) phosphinomethyl]-2,2-dimethyl-1,3-dioxolane, Me-DuPHOS: 1,2-Bis-2,5-dimethylphospholano) benzene, BPPFOH: 1-[1',2-Bis (diphenylphosphino) ferrocenyl] ethanol, BPPFOAc: 1-[1',2-Bis (diphenylphosphino) ferrocenyl] ethyl Acetate, BPPFA: *N*,*N*-Dimethyl-1-[1',2-bis (diphenylphosphino) ferrocenyl] ethylamine, PPFA: *N*,*N*-Dimethyl-1-[2-(diphenylphosphino) ferrocenyl] ethylamine. *c*) The e.e. of **2a-c**, **4a-d** and **6** was determined by the HPLC analysis with CHIRALPAK AD for **2a**,**c**, CHIRALCEL OD for **2b** and **4b**, and CHIRALPAK AS for **4a**,**c**,**d** and **6**. *d*) (*S*)-BINAP (0.1equiv.) was used. *e*) Reacted at 65°C. *f*) (*S*)-BINAP (0.3 equiv.) was used. *g*) (*S*)-BINAP (0.4 equiv.) was used. *h*) Reacted at 60°C.

by other ligands employed such as (*R*,*R*)-DIOP (40% e.e.), (*R*,*R*)-MOD-DIOP (24% e.e.), or ferrocenyl ligands, (*S*)-(*R*)-BPPFA (37% e.e.), (*S*)-(*R*)-BPPFOH (46% e.e.), and (*S*)-(*R*)-BPPFOAc (23% e.e.), as shown in Table 1.

Substituents in the alkynyl part resulted in a remarkable decrease of the enantiocontrol in the cobalt-

catalyzed Pauson–Khand reactions. The cobalt-catalyzed reaction of **1c** was carried out in DME at reflux for 24 h using (*S*)-BINAP as a chiral ligand, affording the product (*R*)-**2c** in high yield (90%); however, surprisingly no enantioselectivity was observed. In contrast to this case, the use of (*R*,*R*)-DIOP in the above reaction gave (*R*)-**2c** with 31% e.e. (Scheme 1).



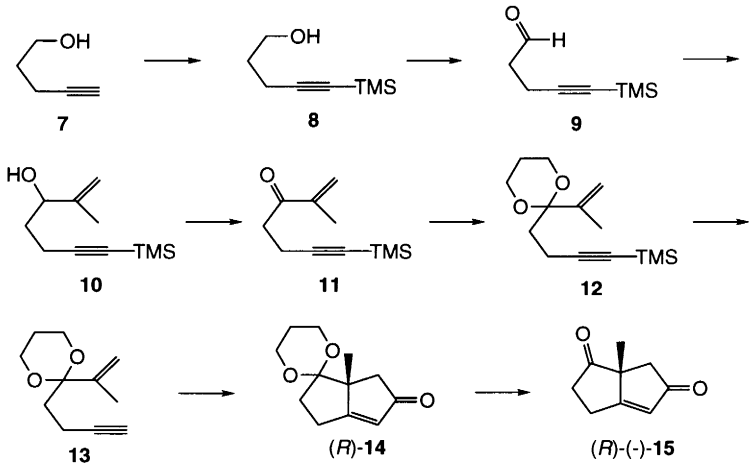
Scheme 1.

Similar enantioselectivity was obtained in the reactions of sulfonamides **3a** and **3b**. The cobalt-catalyzed reactions of **3b** using (*S*)-BINAP, (*R*,*R*)-DIOP, or (*R*,*R*)-MOD-DIOP were carried out in DME at reflux under the same reaction conditions as described above to give (*R*)-**4b** with 62, 57 or 56% e.e., respectively. The use of chiral ferrocenyl ligands, (*S*)-(*R*)-PPFA, (*S*)-(*R*)-BPPFA, (*S*)-(*R*)-BPPFOH, and (*S*)-(*R*)-BPPFOAc, in the above reaction in DME at reflux afforded (*R*)- or (*S*)-**4b** with low e.e. (10–25%). As expected, however, the reaction of **3a**, without a methyl group on the olefinic moiety, provided high enantioselectivity with (*S*)-BINAP, affording (*R*)-**4a** with the highest e.e. (94%). With (*S*)-BINAP as a ligand, the reaction of **3a** in DME, toluene, benzene, DCE, or THF at reflux, except for toluene (80°C), gave (*R*)-**4a** with excellent e.e. (94–78%). However, the use of (*R*,*R*)-DIOP in DME at reflux furnished (*R*)-**4a** with 8% e.e.

Similarly, high enantioselectivities were obtained in the reactions of the benzylamine derivative **3c**. The cobalt-catalyzed reactions of **3c** using (*S*)-BINAP as a ligand in DME, benzene, or DCE at reflux provided (*R*)-**4c** with 82, 88, or 92% e.e., respectively (Table 1).

The cobalt-catalyzed reaction of **3d** using (*S*)-BINAP (0.2 equiv.) as a chiral ligand in DME at reflux gave (*R*)-(+)-**4d** of known absolute configuration[7c] with 40% e.e. The cobalt-catalyzed reaction of 1,6-enyne **5** was carried out in DME at reflux with (*S*)-BINAP (0.2 equiv.) as a ligand to produce (*R*)-(+)-**6** of known absolute configuration[12] with 77% e.e. (Scheme 2).

We chose ketal **13** as a substrate for an asymmetric Pauson–Khand reaction in order to correlate the cyclized product **14** to a diketone **15** of known absolute configuration.[13] Ketal **13** was prepared starting from alcohol **7** as follows. Silylation of acetylenic methyne in **7** with trimethylsilyl chloride using ethylmagnesium bromide as a base followed by oxidation of alcohol **8** obtained with tetra-*n*-propylammonium perruthenate (TPAP) and *N*-methylmorpholine *N*-oxide (NMO) gave aldehyde **9**. Attack of isopropenylmagnesium bromide at the aldehyde **9** followed by oxidation of allylic alcohol **10** with TPAP and NMO, ketalization of ketone **11**, obtained with 1,3-propanediol using a catalytic amount



Scheme 2.

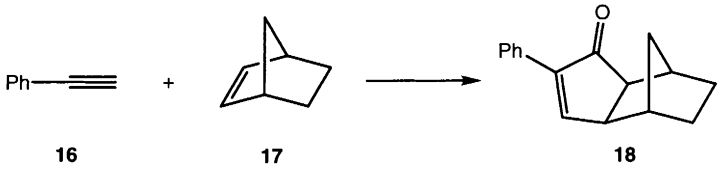
of *p*-toluenesulfonic acid, and desilylation by treating **12** with tetrabutylammonium fluoride gave ketal **13**.

A similar cobalt-mediated reaction of **13** in DME at reflux using (*S*)-BINAP as a ligand, followed by deketalization of (*R*)-**14** with *p*-toluenesulfonic acid–acetone, provided (*R*)-(−)-**15** of known absolute configuration[13] with 7% e.e.

The absolute configuration of other products **2a**–**c** and **4a**–**c** obtained above is assigned on the basis of the stereochemical results thus obtained.

2.2. Intermolecular catalytic asymmetric Pauson–Khand reactions with chiral phosphine ligands

Next, we applied this method to intermolecular Pauson–Khand reactions; however, the effects of chiral bidentate phosphine ligands in the asymmetric synthesis were not useful. The reactions of phenylacetylene **16** with norbornene **17** (1 equiv.) were carried out in DME at reflux for 24 h under carbon monoxide atmosphere in the presence of $Co_2(CO)_8$ (0.2 equiv.) and chiral ligands (0.2 equiv.) such as (*S*)-BINAP, (*R*,*R*)-DIOP, (*S*)-(*R*)-BPPFOH, and (*S*)-(*R*)-PPFA to give 4-phenyltricyclo[5.2.1.$0^{2,6}$] dec-4-en-7-one (**18**) with very low e.e. (<10%), which was determined by HPLC analysis with Chiralcel OD (Scheme 3).

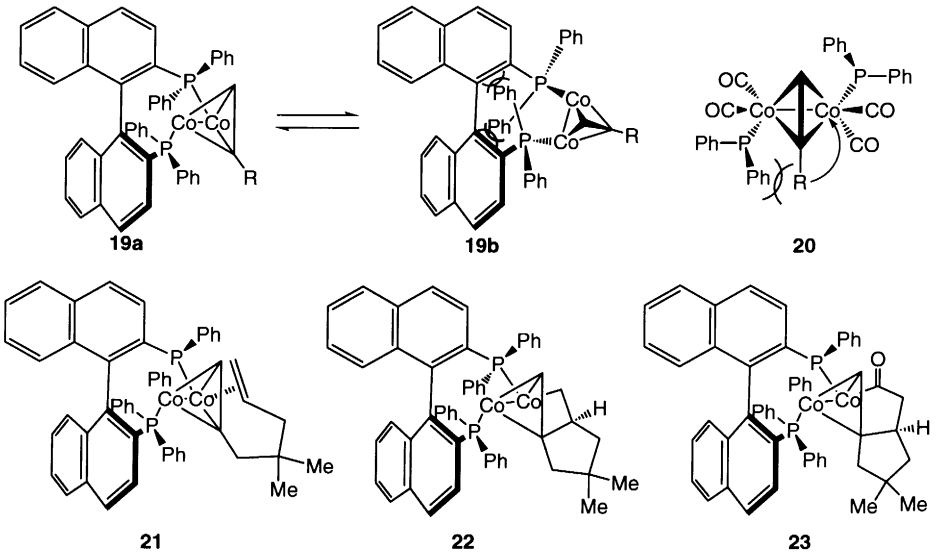


Scheme 3.

2.3. The mechanism of the asymmetric Pauson–Khand reactions with chiral phosphine ligands

The mechanism for the asymmetric induction in the above reaction of **5** with chiral phosphine ligands is rationalized on the basis of the stereochemical outcome obtained as follows. The intermediary alkyne–cobalt complex coordinated by chiral bidentate phosphine (e.g., (*S*)-BINAP) would be initially formed; the bidentate phosphorus atoms would coordinate to the two different cobalt atoms in the

complex, since the coordination of the bidentate phosphorus atoms to one of the two cobalt atoms would be unaccessible due to steric constraints.[14] In the conformational equilibrium of the alkyne–cobalt complex coordinated by the bidentate phosphine of (*S*)-BINAP, a boat-like eight-membered conformer **19a** would be preferred to the corresponding chair-like conformer **19b**, since, in view of the Dreiding model, **19b** has severe steric interference of the phenyl rings on the phosphorus atoms with the naphthyl rings of (*S*)-BINAP, as designated in **19b**. The olefinic part in the substituent *R* in **20** would coordinate to the sterically less crowded cobalt catalyst in the preferred **19a**, as designated in **21**, followed by reaction with the preferred cobalt–alkyne bond, insertion of carbon monoxide in **22**, and regeneration of the catalyst via **23**, affording (*R*)-**6**. The other asymmetric Pauson-Khand reactions of **1a**–**c**, **3a**–**d**, and **13** with chiral bidentate phosphines can be rationalized in a similar way. It is assumed that with (*R*,*R*)-DIOP and (*R*,*R*)-MOD-DIOP as chiral ligands, a product of the same absolute configuration as that obtained with (*S*)-BINAP would be produced on the basis of similar stereochemical consideration (Scheme 4).



Scheme 4.

3. Conclusions

Thus, the catalytic asymmetric synthesis of 2-cyclopentenone derivatives has been accomplished successfully by using a catalytic amount of $Co_2(CO)_8$ and (*S*)-BINAP, providing excellent enantioselectivity. The substituents bonded directly at olefinic or acetylenic carbon centers in 1,6-enynes dramatically affect the degree of asymmetric induction. 1,6-Enyne compounds without methyl groups provided excellent enantioselectivity upon treatment with a catalytic amount of $Co_2(CO)_8$ and (*S*)-BINAP in DME, or DCE at reflux.

4. Experimental

4.1. General

Infrared (IR) spectra were obtained in the indicated state with a JASCO DR-81 fourier-transform IR spectrometer. NMR spectra were determined in the indicated solvent with a JEOL EX-270 (^{1}H NMR; 270 MHz) high-resolution NMR spectrometer; chemical shifts are given in ppm from tetramethylsilane as an internal standard. Splitting patterns are designated as s: singlet, bs: broad singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Mass spectra were taken on a JEOL JMS-DX 303/JMA-DA 5000 system. High performance liquid chromatography (HPLC) was performed with a Tosoh UV-8010 CCPM and Tosoh UV-8020 DP-8020 CO-8020. Optical rotations were measured with a JASCO DIP-370 polarimeter. Flash column chromatography was performed with Merck silica gel 60 (230–400 mesh). Thin layer or thick layer plates (preparative TLC) were made of Merck silica gel 60 PF-254 activated by drying at 140°C for 3.5 h.

4.2. The catalytic asymmetric Pauson–Khand reactions of **1a–c** or **3a–c**

A 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar, and containing $Co_2(CO)_8$ (22.8 mg, 0.067 mmol) and (*S*)-BINAP (41.5 mg, 0.067 mmol) was flushed with carbon monoxide, and maintained under a positive pressure of carbon monoxide. DCE (4 ml) was added to the above flask at room temperature, and the reaction mixture was stirred at reflux for 2 h. A solution of a substrate **1a** (70 mg, 0.333 mmol) in DCE (4 ml) was added to the above solution at reflux, and the mixture was stirred at reflux for 17 h. After cooling at room temperature, the reaction mixture was filtered through a plug of silica gel with the aid of ethyl acetate, and the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (ethyl acetate:hexane=2:3) to give (R)-**2a** (50 mg, 62% yield, 91% e.e.). The cobalt-catalyzed reactions of other substrates **1b**,**c** and **3a–c** were carried out under similar reaction conditions as described above. The yields and e.e. of the products **2a–c** or **4a–c** obtained are listed in Table 1.

4.3. (R)-(+)-Dimethyl 7-oxobicyclo[3.3.0]oct-5-ene-3,3-dicarboxylate **2a**

Preparative TLC (ethyl acetate:hexane=3:2). The e.e. was determined by chiral HPLC (Chiralpak AD: 2-propanol:hexane=1:10, 0.2 ml/min). $[\alpha]_D^{26}$ +157 (*c* 2.11, $CHCl_3$, 91% e.e.). IR ν_{max}^{film} cm^{-1}: 1734 (ester), 1709 (ketone), 1636 (olefin). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 1.67–2.18 (m, 2H, C$\underline{H}_2$CHCH_2CO), 2.59–2.87 (m, 2H, CH_2CO), 3.05–3.17 (m, 1H, CH_2C$\underline{H}$CH_2), 3.22–3.50 (m, 2H, C$\underline{H}_2$C=CH), 3.76, 3.80 (s, s, 6H, $(CO_2CH_3)_2$), 5.94 (q, J=1.7 Hz, 1H, C=CH). MS *m/z*: 239 (M^++1). Exact mass determination: 238.0856 (calcd $C_{12}H_{14}O_5$: 238.0841).

4.4. (R)-(+)-Dimethyl 1-methyl-7-oxobicyclo[3.3.0]oct-5-ene-3,3-dicarboxylate **2b**

Preparative TLC (ethyl acetate:hexane=1:2). The e.e. was determined by chiral HPLC (Chiralcel OD: 2-propanol:hexane=1:20, 0.4 ml/min). $[\alpha]_D^{23}$ +85 (*c* 1.44, $CHCl_3$, 63% e.e.). IR ν_{max}^{film} cm^{-1}: 1734 (ester), 1711 (ketone), 1638 (olefin). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 1.16 (s, 3H, CCH_3), 2.21–2.63 (m, 2H, C$\underline{H}_2$CCH_2CO), 2.39 (s, 2H, CH_2CO), 3.19–3.54 (m, 2H, C$\underline{H}_2$C=CH), 3.73, 3.81 (s, s, 6H, $(CO_2CH_3)_2$), 5.84 (d, J=1.5 Hz, 1H, C=CH). MS *m/z*: 253 (M^++1). Exact mass determination: 252.1082 (calcd $C_{13}H_{16}O_5$: 252.0998).

4.5. (R)-(+)-Dimethyl 1,6-dimethyl-7-oxobicyclo[3.3.0]oct-5-ene-3,3-dicarboxylate **2c**

Preparative TLC (ethyl acetate:hexane=1:2). The e.e. was determined by chiral HPLC (Chiralpak AD: 2-propanol:hexane=1:10, 0.2 ml/min). $[\alpha]_D^{26}$ +26 (*c* 1.76, $CHCl_3$, 31% e.e.). IR ν_{max}^{film} cm^{-1}: 1736 (ester), 1711 (ketone), 1676 (olefin). ^1H NMR (270 MHz; $CDCl_3$) δ: 1.11 (s, 3H, CH_2CCH_3), 1.67–1.71 (m, 3H, $C{=}CCH_3$), 2.09–2.67 (m, 2H, $C\underline{H}_2C(CH_3)CH_2C{=}O$), 2.28–2.45 (m, 2H, $CH_2C{=}O$), 3.11–3.55 (m, 2H, $C\underline{H}_2C{=}C(CH_3)$), 3.73, 3.81 (s, s, 6H, $(CO_2CH_3)_2$). MS *m/z*: 267 (M^++1). Exact mass determination: 266.1168 (calcd $C_{14}H_{18}O_5$: 266.1154).

4.6. (R)-(+)-3-p-Toluenesulfonyl-3-azabicyclo[3.3.0]oct-5-en-7-one **4a**

Preparative TLC (ethyl acetate:hexane=1:1). The e.e. was determined by chiral HPLC (Chiralpak AS: 2-propanol:hexane=1:1, 0.6 ml/min). $[\alpha]_D^{26}$ +133 (*c* 1.36, $CHCl_3$, 93% e.e.). IR ν_{max}^{film} cm^{-1}: 1713 (ketone), 1651 (olefin), 1599 (aromatic), 1343, 1161 (sulfone). ^1H NMR (270 MHz; $CDCl_3$) δ: 2.02–2.11 (m, 1H), 2.43 (s, 3H, CH_3), 2.54–2.67 (m, 2H), 3.10–3.22 (m, 1H, $CH_2C\underline{H}$), 3.98–4.13 (m, 2H), 4.30–4.37 (m, 1H), 5.98 (s, 1H, C=CH), 7.29–7.74 (m, 4H, C_6H_4). MS *m/z*: 278 (M^++1). Exact mass determination: 277.0765 (calcd $C_{14}H_{15}NO_3S$: 277.0772).

4.7. (R)-(+)-1-Methyl-3-p-toluenesulfonyl-3-azabicyclo[3.3.0]oct-5-en-7-one **4b**

Preparative TLC (ethyl acetate:hexane=1:1). The e.e. was determined by chiral HPLC (Chiralcel OD: 2-propanol:hexane=1:10, 0.5 ml/min). $[\alpha]_D^{27}$ +59 (*c* 1.16, $CHCl_3$, 56% e.e.). IR ν_{max}^{film} cm^{-1}: 1715 (ketone), 1651 (olefin), 1597 (aromatic), 1345, 1155 (sulfone). ^1H NMR (270 MHz; $CDCl_3$) δ: 1.18 (s, 3H, $CH_2CC\underline{H}_3$), 2.22–2.41 (m, 2H, $NC\underline{H}_2CCH_3$), 2.44 (s, 3H, $C_6H_4C\underline{H}_3$), 2.81–3.71 (m, 2H, CH_2CO), 4.01–4.38 (m, 2H, $CH_2C{=}C$), 5.86 (t, J=1.8 Hz, 1H, C=CH), 7.32–7.78 (m, 4H, C_6H_4). MS *m/z*: 292 (M^++1). Exact mass determination: 291.0964 (calcd $C_{15}H_{17}NO_3S$: 291.0929).

4.8. (R)-(+)-3-Benzyl-3-azabicyclo[3.3.0]oct-5-en-7-one **4c**

Preparative TLC (ethyl acetate:hexane=2:1). The e.e. was determined by chiral HPLC (Chiralpak AS: 2-propanol:hexane=1:4, 0.5 ml/min). $[\alpha]_D^{26}$ +176 (*c* 0.38, acetone, 92% e.e.). IR ν_{max}^{film} cm^{-1}: 1705 (ketone), 1644 (olefin), 1597 (aromatic). ^1H NMR (270 MHz; $CDCl_3$) δ: 2.03–2.64 (m, 2H, CH_2CO), 3.10–3.39 (m, 3H, NCH_2CH), 3.68–4.01 (m, 4H, $C_6H_5C\underline{H}_2NC\underline{H}_2C$), 5.92 (q, 1H, J=1.6 Hz, C=CH), 7.20–7.35 (m, 5H, C_6H_5). MS *m/z*: 213 (M^+). Exact mass determination: 213.1131 (calcd $C_{14}H_{15}ON$: 213.1154).

4.9. (R)-(+)-3-Benzyl-6-methyl-3-azabicyclo[3.3.0]oct-5-en-7-one **4d**

A 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar, and containing $Co_2(CO)_8$ (24.1 mg, 0.070 mmol) and (*S*)-BINAP (43.8 mg, 0.070 mmol) was flushed with carbon monoxide, and maintained under a positive pressure of carbon monoxide. 1,2-Dimethoxyethane (4 ml) was added to the above flask at room temperature, and the reaction mixture was stirred at reflux for 2 h. A solution of *N*-allyl-*N*-benzyl-2-butynylamine **3d** (70 mg, 0.352 mmol) in 1,2-dimethoxyethane (3 ml) was added to the above solution at reflux, and the mixture was stirred at reflux for 12 h. After cooling at room temperature, the reaction mixture was filtered through a plug of silica gel with the aid of ethyl acetate. The filtrate was concentrated in vacuo, and the crude product was purified by preparative

TLC (ethyl acetate:hexane=1:1) to give **4d** (10 mg, 13% yield). The e.e. was determined to be 40% by chiral HPLC (Chiralpak AS: 2-propanol:hexane=1:4, 0.3 ml/min). $[\alpha]_D^{27}$ +63 (*c* 0.50, toluene, 40% e.e.). IR ν_{max}^{film} cm^{-1}: 1711 (ketone), 1674 (olefin), 1600 (aromatic). ^1H NMR (270 MHz; $CDCl_3$) δ: 1.68 (s, 3H, CH_3), 1.96–2.65 (m, 2H, CH_2CO), 3.05–3.37 (m, 3H, NCH_2CH), 3.55–3.91 (m, 4H, $C_6H_5C\underline{H}_2NC\underline{H}_2C$), 7.23–7.37 (m, 5H, C_6H_5). MS *m/z*: 228 (M^++1). Exact mass determination: 227.1349 (calcd $C_{15}H_{17}ON$: 227.1310).

4.10. (R)-(+)-3,3-Dimethylbicyclo[3.3.0]oct-5-en-7-one **6**

A 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar, and containing $Co_2(CO)_8$ (28 mg, 0.082 mmol) and (*S*)-BINAP (51 mg, 0.082 mmol) was flushed with carbon monoxide and maintained under a positive pressure of carbon monoxide. 1,2-Dimethoxyethane (2 ml) was added to the above flask at room temperature, and the mixture was stirred at reflux for 2 h. A solution of a 4,4-dimethylhept-1-en-6-yne **5** (50 mg, 0.409 mmol) in 1,2-dimethoxyethane (3 ml) was added to the above solution at reflux, and the reaction mixture was stirred at reflux for 18 h. After cooling at room temperature, the reaction mixture was filtered through a plug of silica gel with the aid of ethyl acetate, and the filtrate was concentrated in vacuo. The crude product was purified by preparative TLC (ethyl acetate:hexane=1:7) to give **6** (26 mg, 42% yield). The e.e. was determined to be 77% by chiral HPLC (Chiralpak AS: 2-propanol:hexane=1:4, 1.0 ml/min). $[\alpha]_D^{26}$ +143 (c 0.80, $CHCl_3$, 77% e.e.). IR ν_{max}^{film} cm^{-1}: 1700 (ketone), 1620 (olefin). ^1H NMR (270 MHz; $CDCl_3$) δ: 1.12–1.22 (m, 1H), 1.18, 1.27 (s, s, 6H, $C(CH_3)_2$), 1.95–2.15 (m, 2H), 2.47–2.50 (m, 2H), 2.61–2.71 (m, 1H), 3.16–3.29 (m, 1H, $C\underline{H}CH_2$), 5.87–5.90 (m, 1H, CH=C). MS *m/z*: 150 (M^+). Exact mass determination: 150.1034 (calcd $C_{10}H_{14}O$: 150.1045).

4.11. 5-(Trimethylsilyl)-4-pentyn-1-ol **8**

A 0.96 M THF solution of ethylmagnesium bromide (41.9 ml, 40.18 mmol) was added at 0°C to a solution of 4-pentyn-1-ol **7** (1.5 g, 13.39 mmol) in THF (80 ml), and the reaction mixture was stirred at room temperature for 1 h. Chlorotrimethylsilane (5.1 ml, 40.18 mmol) was added to the above solution at 0°C, and the reaction mixture was stirred at room temperature for 12 h, and quenched by addition of 10% aqueous HCl. The reaction mixture was diluted with ether and the solution was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was subjected to flash column chromatography (ethyl acetate:hexane=1:2) to give **8** (2.23 g, 91% yield). IR ν_{max}^{film} cm^{-1}: 3335 (alcohol), 2175 (acetylene). ^1H NMR (270 MHz; $CDCl_3$) δ: 0.15 (s, 9H, $Si(CH_3)_3$), 1.72–1.82 (m, 3H, $C\underline{H}_2CH_2O\underline{H}$), 2.35 (t, J=6.9 Hz, 2H, $CH_2C{\equiv}C$), 3.75 (t, J=6.1 Hz, 2H, $C\underline{H}_2OH$). MS *m/z*: 157 (M^++1). Exact mass determination: 156.0951 (calcd $C_8H_{16}OSi$: 156.0970).

4.12. 5-(Trimethylsilyl)-4-pentyn-1-al **9**

N-Methylmorpholine *N*-oxide (1.05 g 8.99 mmol) and molecular sieves 4 Å powder (2.5 g) were added at room temperature to a solution of **8** (935 mg, 5.99 mmol) in acetonitrile (25 ml). Tetra-*n*-propylammonium perruthenate (252 mg, 0.71 mmol) was added to the above solution, and the reaction mixture was stirred at room temperature for 15 min and then filtered through a plug of silica gel with the aid of ethyl acetate. The filtrate was concentrated in vacuo, and the crude product was purified by flash column chromatography (ethyl acetate:hexane=1:4) to give **9** (465 mg, 50% yield). IR ν_{max}^{film} cm^{-1}: 2177

(acetylene), 1730 (aldehyde). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 0.14 (s, 9H, $Si(CH_3)_3$), 2.55 (t, J=1.2 Hz, 2H, $CH_2C{\equiv}C$), 2.65 (t, J=1.2 Hz, 2H, $C\underline{H}_2CHO$), 9.78 (s, 1H, CHO). MS *m/z*: 155 (M^++1). Exact mass determination: 154.0759 (calcd $C_8H_{14}OSi$: 154.0811).

4.13. 6-Methyl-1-(trimethylsilyl)hept-6-en-1-yn-5-ol **10**

A 100 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar, and containing magnesium (460 mg, 18.92 mmol) was flushed with argon and maintained under a positive pressure of argon. A solution of 2-bromo-1-propene (2.08 g, 17.20 mmol) in THF (30 ml) and 1,2-dibromoethane (2–3 drops) were added to the above flask. The reaction mixture was stirred at room temperature for 1 h. The above solution was added at 0°C to a solution of **9** (1.32 g, 8.60 mmol) in THF (60 ml), and the reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was diluted with ether and the solution was washed with saturated aqueous NH_4Cl and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was subjected to flash column chromatography (ethyl acetate:hexane=1:4) to give **10** (979 mg, 59% yield). IR ν_{max}^{film} cm^{-1}: 3449 (alcohol), 2172 (acetylene), 1651 (olefin). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 0.15 (s, 9H, $Si(CH_3)_3$), 1.66–1.80 (m, 5H, $C\underline{H}_3CCHC\underline{H}_2$), 189 (bs, 1H, OH), 2.29–2.35 (m, 2H, $CH_2C{\equiv}C$), 4.17–4.22 (m, 1H, CH), 4.86–5.99 (m, 2H, $C{=}CH_2$). MS *m/z*: 197 (M^++1). Exact mass determination: 196.1283 (calcd $C_{11}H_{20}OSi$: 196.1283).

4.14. 6-Methyl-1-(trimethylsilyl)hept-6-en-1-yn-5-one **11**

N-Methylmorpholine *N*-oxide (877 mg 7.49 mmol) and molecular sieves 4 Å powder (3.5 g) were added at room temperature to a solution of **10** (979 mg, 4.99 mmol) in acetonitrile (30 ml). Tetra-*n*-propylammonium perruthenate (210 mg, 0.60 mmol) was added to the above solution, and the reaction mixture was stirred at room temperature for 15 min and then filtered through a plug of silica gel with the aid of ethyl acetate. The filtrate was concentrated in vacuo, and the crude product was purified by flash column chromatography (ethyl acetate:hexane=1:9) to give **11** (631 mg, 65% yield). IR ν_{max}^{film} cm^{-1}: 2178 (acetylene), 1682 (ketone), 1632 (olefin). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 0.14 (s, 9H, $Si(CH_3)_3$), 1.88 (s, 3H, CH_3), 2.50–2.55 (m, 2H, $CH_2C{\equiv}C$), 2.91–2.97 (m, 2H, CH_2CO), 5.79–5.99 (m, 2H, $C{=}CH_2$). MS *m/z*: 195 (M^++1). Exact mass determination: 194.1144 (calcd $C_{11}H_{18}OSi$: 194.1127).

4.15. 2-(2-Propenyl)-2-(4-trimethyl-3-butynyl)-1,3-dioxane **12**

Compound **11** (300 mg, 1.55 mmol) was dissolved in benzene (20 ml), and 1,3-propanediol (141 mg, 1.86 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.16 mmol) were added at room temperature. The reaction mixture was stirred at reflux for 12 h, and the crude reaction mixture was filtered through a plug of silica gel with the aid of ethyl acetate. The filtrate was concentrated in vacuo, and the crude product was purified by preparative TLC (ether:hexane=1:20) to give **12** (183 mg, 66% yield). IR ν_{max}^{film} cm^{-1}: 2175 (acetylene), 1647 (olefin). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 0.12 (s, 9H, $Si(CH_3)_3$), 1.25–2.05 (m, 4H, $CC\underline{H}_2CH_2$, $CH_2C\underline{H}_2CH_2$), 1.71 (s, 3H, CH_3), 2.27–2.33 (m, 2H, $CH_2C{\equiv}C$), 3.78–3.83 (m, 4H, $C\underline{H}_2CH_2C\underline{H}_2$), 5.09–5.18 (m, 2H, $C{=}CH_2$). MS *m/z*: 253 (M^++1). Exact mass determination: 252.1499 (calcd $C_{14}H_{24}O_2Si$: 252.1546).

4.16. 2-(3-Butynyl)-2-(2-propenyl)-1,3-dioxane **13**

A 1.0 M THF solution of tetrabutylammonium fluoride (2.0 ml, 2.04 mmol) was added at 0°C to a solution of **12** (428 mg, 1.70 mmol) in THF (10 ml) and the reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was filtered through a plug of silica gel with the aid of ethyl acetate. The filtrate was concentrated in vacuo, and the crude product was purified by preparative TLC (ether:hexane=1:20) to give **13** (210 mg, 69% yield). IR ν_{max}^{film} cm^{-1}: 3304, 2118 (acetylene), 1645 (olefin). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 1.26–2.07 (m, 5H, $CC\underline{H}_2CH_2$, $C{\equiv}C\underline{H}$, $CH_2C\underline{H}_2CH_2$), 1.71 (s, 3H, CH_3), 2.24–2.31 (m, 2H, $CH_2C{\equiv}C$), 3.79–3.84 (m, 4H, $C\underline{H}_2CH_2C\underline{H}_2$), 5.11–5.20 (m, 2H, $C{=}CH_2$). MS *m/z*: 181 (M^++1). Exact mass determination: 180.0602 (calcd $C_{11}H_{16}O_2$: 180.1150).

4.17. (R)-(−)-5-Methylbicyclo[3.3.0]oct-1-ene-3,6-dione **15**

A 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar, and containing $Co_2(CO)_8$ (30.4 mg, 0.089 mmol) and (*S*)-BINAP (55.4 mg, 0.089 mmol) was flushed with carbon monoxide and maintained under a positive pressure of carbon monoxide. 1,2-Dimethoxyethane (4 ml) was added to the above flask at room temperature, and the reaction mixture was stirred at reflux for 2 h. A solution of **13** (80 mg, 0.444 mmol) in 1,2-dimethoxyethane (4 ml) was added to the above solution at reflux, and the mixture was stirred at reflux for 48 h. After cooling at room temperature, the crude reaction mixture was filtered through a plug of silica gel with the aid of ethyl acetate, and the filtrate was concentrated under reduced pressure. The crude product of 2-(3-butynyl)-2-(2-propenyl)-1,3-dioxane **14** was used in the next step without further purification. Crude **14** was dissolved in acetone (10 ml), and *p*-toluenesulfonic acid monohydrate (8 mg, 0.044 mmol) was added at room temperature. The reaction mixture was stirred at reflux for 3 h, and the crude reaction mixture was filtered through a plug of silica gel with the aid of ethyl acetate. The filtrate was concentrated in vacuo, and the crude product was purified by preparative TLC (ethyl acetate:hexane=1:1) to give **15** (6 mg, 9% yield). The e.e. was determined to be 7% by chiral HPLC (Chiralpak AS: 2-propanol:hexane=1:4, 1.0 ml/min). $[\alpha]_D^{26}$ −40 (*c* 0.25, $CHCl_3$, 7% e.e.). IR ν_{max}^{film} cm^{-1}: 1702, 1742 (ketone), 1630 (olefin). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 1.37 (s, 3H, CH_3), 2.30–3.21 (m, 6H, CH_2CH_2, CH_2), 5.99 (s, 1H, C=CH). MS *m/z*: 151 (M^++1). Exact mass determination: 150.0691 (calcd $C_9H_{10}O_2$: 150.0681).

4.18. (−)-4-Phenyltricyclo[5.2.1.$0^{2,6}$]dec-4-en-3-one **18**

A 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar, and containing $Co_2(CO)_8$ (21.9 mg, 0.064 mmol) and (*R*,*R*)-DIOP (31.9 mg, 0.064 mmol) was flushed with carbon monoxide and maintained under a positive pressure of carbon monoxide. 1,2-Dimethoxyethane (3 ml) was added to the above flask at room temperature, and the reaction mixture was stirred at reflux for 2 h. A solution of phenylacetylene **16** (34.8 mg, 0.319 mmol) in 1,2-dimethoxyethane (2 ml) and a solution of norbornene **17** (30.0 mg, 0.319 mmol) in 1,2-dimethoxyethane (2 ml) were added to the above solution at reflux, and the mixture was stirred at reflux for 24 h. After cooling at room temperature, the crude reaction mixture was filtered through a plug of silica gel with the aid of ethyl acetate, and the filtrate was concentrated in vacuo. The crude product was purified by preparative TLC (ethyl acetate:hexane=1:10) to give **18** (20 mg, 29% yield). The e.e. was determined to be 10% by chiral HPLC (Chiralcel OD: 2-propanol:hexane=1:20, 0.4 ml/min). $[\alpha]_D$ −9 (*c* 1.53, $CHCl_3$, 10% e.e.). IR ν_{max}^{film} cm^{-1}: 1698 (ketone), 1595 (aromatic). ^{1}H NMR (270 MHz; $CDCl_3$) δ: 0.96–1.02 (m, 1H), 1.09–1.16 (m, 1H), 1.25–1.44 (m, 2H), 1.49–1.77 (m, 2H), 2.25–2.28 (m, 1H), 2.34–2.37 (m, 1H), 2.48–2.51 (m, 1H), 2.67–2.71 (m, 1H),

7.24–7.75 (m, 6H, C=CH, C_6H_5). MS *m/z*: 225 (M^++1). Exact mass determination: 224.1163 (calcd $C_{16}H_{16}O$: 224.1201).

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References

1. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publishers: New York, 1993. Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994.
2. Negishi, E.; Coperet, C.; Ma, S.; Liou, S.-Y.; Liu, F. *Chem. Rev*. **1996**, *96*, 365–393. Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev*. **1996**, *96*, 635–662.
3. Hiroi, K.; Arinaga, Y. *Tetrahedron Lett*. **1994**, *35*, 153–156. Hiroi, K.; Arinaga, Y.; Ogino, T. *Chem. Pharm. Bull*. **1994**, *42*, 470–474. Hiroi, K.; Yoshida, Y.; Kaneko, Y. *Tetrahedron Lett*. **1999**, *40*, 3431–3434.
4. Hiroi, K.; Hirasawa, K. *Chem. Pharm. Bull*. **1994**, *42*, 786–791. Hiroi, K.; Hirasawa, K. *Chem. Pharm. Bull*. **1994**, *42*, 1036–1040.
5. Hiroi, K.; Nakaichi, S.; Minakata, H.; Adachi, J., to be published.
6. For asymmetric Pauson–Khand reactions, see: Shore, N. E. *Chem. Rev*. **1988**, *88*, 1081–1119. Shore, N. E. *Org. React*. **1991**, *40*, 5–90. Geis, O.; Schmalz, H.-G. *Angew. Chem., Int. Ed. Engl*. **1998**, *37*, 911–915. Ingate, S. T.; Marco-Contelles, J. *Org. Prep. Proced. Int.* **1998**, *30*, 121–143, and references cited therein.
7. For similar asymmetric synthesis with titanocene catalysts, see: (a) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc*. **1996**, *118*, 11688–11689. (b) Idem, *ibid.* **1999**, *121*, 7026–7033. (c) Sturla, S. J.; Buchwald, S. L. *J. Org. Chem.*, **1999**, *64*, 5547–5550.
8. Castro, J.; Moyano, A.; Pericas, M. A.; Riera, A.; Greene, A. E. *Tetrahedron: Asymmetry* **1994**, *3*, 307–310. Bernardes, V.; Verdaguer, X.; Kardos, N.; Riera, A.; Moyano, A.; Pericas, M. A.; Greene, A. E. *Tetrahedron Lett*. **1994**, *35*, 575–578. Verdaguer, X.; Moyano, A.; Pericas, M. A.; Riera A. *J. Am. Chem. Soc.* **1994**, *116*, 2153–2154. Fonquerna, S.; Moyano, A.; Pericas, M. A.; Riera, A. *Tetrahedron* **1995**, *14*, 4239–4254. Fonquerna, S.; Moyano, A.; Pericas, M. A.; Riera, A. *J. Am. Chem. Soc*. **1997**, *119*, 10225–10226. Montenegro, E.; Poch, M.; Moyano, A.; Pericas, M. A.; Riera, A. *Tetrahedron Lett*. **1998**, *39*, 335–338. Adrio, J.; Carretero, J. C. *J. Am. Chem. Soc.* **1999**, *121*, 7411–7412.
9. Bladon, P.; Pauson, P. L.; Brunner, H.; Eder, R. *J. Organomet. Chem*. **1988**, *355*, 449–454.
10. Kerr, W. J.; Kirk, G. G.; Middlemiss, D. *Synlett* **1995**, 1085–1086. Mukai, C.; Uchiyama, M.; Sakamoto, S.; Hanaoka, M. *Tetrahedron Lett.* **1995**, *36*, 5761–5764. Mukai, C.; Hanaoka, M. *Synlett* **1996**, 11–17. Mukai, C.; Kim, J. S.; Uchiyama, M.; Hanaoka, M. *Tetrahedron Lett*. **1998**, *39*, 7909–7912. Mukai, C.; Kim, J. S.; Sonobe, H.; Hanaoka, M. *J. Org. Chem*. **1999**, *64*, 6822–6832.
11. For a preliminary report of this work, see: Hiroi, K.; Watanabe, T.; Kawagishi, R.; Abe, I. *Tetrahedron Lett.* **2000**, *41*, 891–895.
12. Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835–3837.
13. Brooks, D. W.; Woods, K. W. *J. Org. Chem.* **1987**, *52*, 2036–2039.
14. Gimbert, Y.; Robert, F.; Durif, A.; Averbuch, M.-T.; Kann, N.; Greene, A. E. *J. Org. Chem*. **1999**, *64*, 3492–3497. Castro, J.; Moyano, A.; Pericas, M. A.; Riera, A.; Alvarez-Larena, A.; Piniella, J. F. *J. Organomet. Chem.* **1999**, *585*, 53–58.