Asymmetric Synthesis Catalyzed by Chiral Ferrocenylphosphine–Transition-Metal Complexes. 5.[1] Palladium-Catalyzed Asymmetric Allylation of Active Methine Compounds

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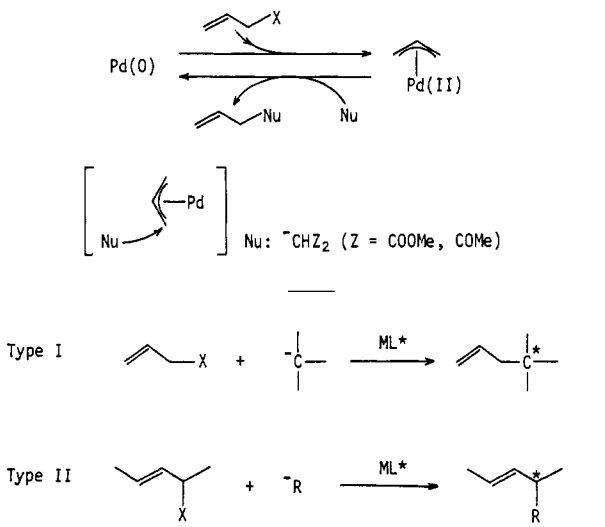
Catalytic asymmetric allylation of sodium enolates of β-diketones with allyl acetate proceeded with high enantioselectivity in the presence of 0.5–1.0 mol % of palladium complexes as catalysts bearing functionalized chiral ferrocenylphosphine ligands, giving optically active ketones with a chiral quaternary carbon center. The most effective ligand was (*R*)-*N*-methyl-*N*-(2-hydroxyethyl)-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine (**3a**), which contains a hydroxy group on the side chain at an appropriate distance from the ferrocene nucleus. The reaction of 2-acetylcyclohexanone (**9**), 2-acetyl-1-tetralone (**18a**), and 1-phenyl-2-methylbutane-1,3-dione (**19a**) gave the corresponding allylated products in 81%, 82%, and 60% ee, respectively. The high enantioselectivity of the ligand **3a** is ascribed to the stereocontrol effected by attractive interactions between the terminal hydroxy group on the ligand and the prochiral enolate of a β-diketone which is to attack the π-allyl carbon on the π-allylpalladium intermediate from the side opposite to palladium.

Palladium-catalyzed allylation of nucleophiles with allylic compounds represented by allyl acetates has been successfully applied to synthetic organic chemistry.[2] The catalytic cycle of the allylation is generally accepted to involve a π-allylpalladium(II) complex as a key intermediate, which is formed by oxidative addition of an allylic substrate to palladium(0) and undergoes nucleophilic attack to yield an allylation product and to regenerate palladium(0) (Scheme I).[2] Studies on stereochemistry of the catalytic allylation and stoichiometric reaction of π-allylpalladium complexes with nucleophiles have demonstrated that soft carbon nucleophiles such as dimethyl sodiomalonate attack a carbon atom of the π-allyl from the side opposite to palladium.[3-5] The oxidative addition of allylic substrates forming π-allylpalladium(II) complexes has been established to proceed with inversion of configuration.[6]

Incorporation of optically active phosphine ligands can, in principle, make the allylation result in the formation of optically active products. A new chiral carbon center can be created either in nucleophiles (type I) or in allylic substrates (type II), as shown in Scheme II.[7] Although several examples have been reported which gave stereoselectivity of over 70% in the type II asymmetric allylations,[8-11] high stereoselectivity has not been attained in type I reactions. Kagan and co-workers have reported[12] the first example of the type I allylation in 1978, which involved reaction of active methine compounds and allyl phenyl ether in the presence of a palladium catalyst, $PdCl_2$[(+)-DIOP], where DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. The allylated products were optically active but with less than 10% ee. The low stereoselectivity may be ascribed to the use of DIOP as a chiral source. This phosphine may control the stereochemistry merely by orientating the phenyl rings on the phosphorus as has been in asymmetric hydrogenation,[13] and the DIOP phenyl rings

Scheme I



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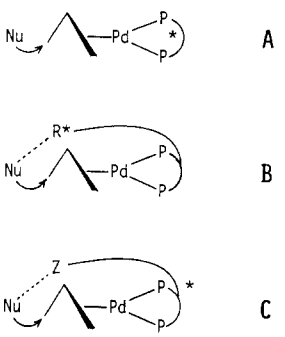


Figure 1.

are too far from the developing asymmetric center since the prochiral substrate is the soft carbon nucleophile attacking the face of π-allyl opposite to the palladium (A in Figure 1). We have previously reported[14] the design and preparation of those new phosphine ligands which possess a chiral functional group at an appropriate distance from the coordinated phosphino groups and demonstrated them to be fairly effective for type I reactions in improving the stereoselectivity (up to 52%) in the asymmetric allylation of 2-acetylcyclohexanone. An attractive interaction between the terminal chiral functional group and the nucleophile is thought to be responsible for the stereoselectivity (B in Figure 1). Very recently have Genet and coworkers reported the optical yield of 57% in the allylation of a Schiff base of glycine methyl ester.[15]

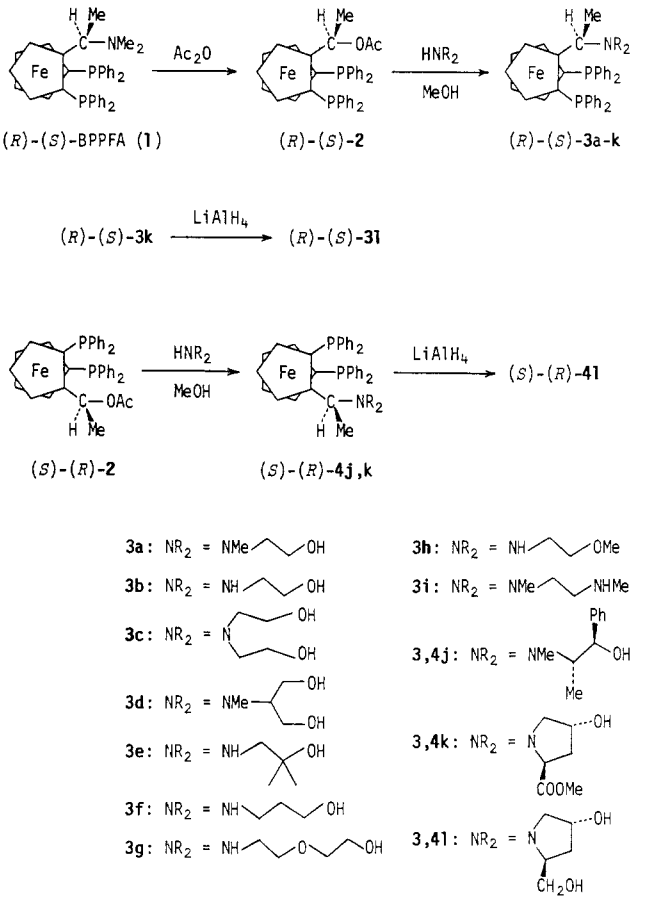
We have further demonstrated that chiral ferrocenylphosphines containing a pertinent functional group on the side chain are efficient ligands for several types of transition-metal complex catalyzed asymmetric reactions.[10,16-18] The high efficiency is ascribed largely to attractive interactions between functional groups on a substrate and on the chiral phosphine ligands coordinated to the transition-metal catalyst. The chiral ferrocenylphosphine ligands have proved superior to others in that structural modification can be readily made by introduction of a desired functional group on to the side chain according to the demand of the reaction type. In order to obtain higher stereoselectivity in the asymmetric allylation, we have prepared certain new ferrocenylphosphine ligands which, at an appropriate distance from the ferrocene nucleus, possess a functional group expected to interact attractively with an incoming nucleophile (C in Figure 1). The attractive interaction will make the steric interaction of the prochiral nucleophile with the chiral ferrocenylphosphine moiety more effective to bring about higher stereoselectivity.

Results and Discussion

Chiral Ferrocenylphosphine Ligands. The dimethylamino group in (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-BPPFA] (**1**) can be substituted with various nucleophiles via (*R*)-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethyl acetate (**2**).[16] The substitution reactions have been established to proceed with retention of configuration. Secondary and primary amines containing functional groups such as hydroxy at an appropriate distance from the nitrogen atom were used for the substitution (Scheme III). Preparation of some of the functionalized ferrocenylphosphines **3** has previously been described.[16] With chiral amines as nucleophiles, both diastereomeric isomers **3j–l** and **4j–l** were prepared separately from (*R*)-(*S*)-**2** and (*S*)-(*R*)-**2**, respectively.

Reaction of (*R*)-(*S*)-**2** with ethylene glycol in the presence of pyridine gave (*R*)-(*S*)-**5**, which has a (2-hydroxyethyl)oxy group on the ferrocene side chain (Scheme IV). Chiral ferrocenylphosphines (*R*)-(*S*)-**6**, (*R*)-(*S*)-**7**, and (*S*)-**8** were also prepared and used for the asymmetric allylation. The methylated ferrocenylphosphine **8** was obtained by treatment of (*R*)-(*S*)-**2** with methylmagnesium bromide in ether.

Scheme III



Scheme IV

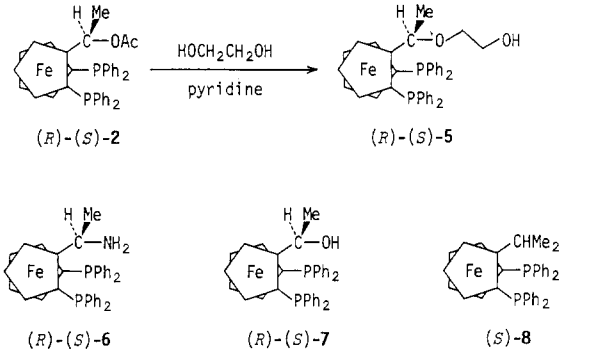


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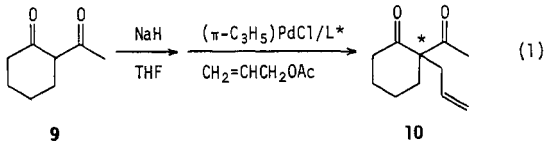
Table I. Asymmetric Allylation of Sodium Enolate of 2-Acetylcyclohexanone (9) with Allyl Acetate Catalyzed by Optically Active Ferrocenylphosphine-Palladium Complexes[a]

entry	chiral ligand	reactn temp, °C	reactn time, h	conv,[b] %	$[\alpha]^{20}_D$[c]	% ee[d] (config)
1	**3a**	−50	20	100	+185°	73 (*S*)
2	**3b**	−50	17	13	+156°	62 (*S*)
3	**3c**	−50	17	61	+156°	62 (*S*)
4	**5**	−50	20	81	+135°	53 (*S*)
5	**3d**	−50	18	55	+124°	49 (*S*)
6	**3f**	−50	17	11	+117°	46 (*S*)
7	**3e**	−30[e]	42	93	+79°	31 (*S*)
8	**7**	−30[e]	17	89	+75°	30 (*S*)
9	**6**	−30	17	64	+39°	15 (*S*)
10	**3g**	−30	17	36	+1°	0
11	**3h**	−30	16	100	−15°	6 (*R*)
12	**2**	−30	17	44	−41°	16 (*R*)
13	**8**	−30[e]	50	100	−47°	19 (*R*)
14	**3i**	−30	18	100	−50°	20 (*R*)
15	**1**	−30	16	100	−57°	22 (*R*)
16	**3j**	−30[e]	17	47	−7°	3 (*R*)
17	**4j**[f]	−30[e]	17	64	+10°	4 (*S*)
18	**3k**	−30	17	100	+74°	29 (*S*)
19	**4k**[f]	−50	17	24	−89°	35 (*R*)
20	**3l**	−50	18	24	+174°	69 (*S*)
21	**4l**[f]	−50	18	43	−107°	42 (*R*)
22	(−)-DIOP	−30	18	96	−4°	2 (*R*)
23	(*S*)-prophos	−30	17	100	−28°	11 (*R*)

[a] To a solution of sodium enolate prepared from 2-acetylcyclohexanone (**9**) (2.0 mmol) and sodium hydride (2.5 mmol) in 5 mL of THF was added at −78 °C a mixture of a ligand (0.022 mmol), $(\pi\text{-}C_3H_5)PdCl$ (0.020 mmol), and allyl acetate (3.0 mmol) in 5 mL of THF, and the mixture was kept stirred at a given temperature. [b] Determined by GLC analysis of the reaction mixture. Isolated yields by distillation or preparative TLC (see Experimental Section) were about 90% of the conversion. [c] *c* 2.0–5.0, $CHCl_3$. [d] Determined by the optical rotation. The maximum rotation of **10** is 254 ± 7°. [e] Low conversion (<10%) was observed in the reaction at −50 °C. [f] The ligands **4j–l** have (*S*)-(*R*)-BPPF-X framework.

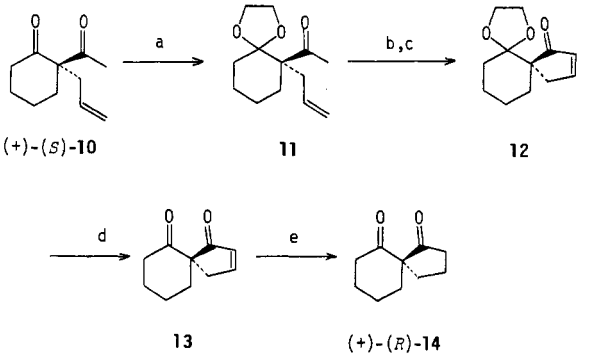
Asymmetric Allylation. In the first set of experiments, reaction of allyl acetate with the sodium enolate of 2-acetylcyclohexanone (**9**) which was generated by mixing sodium hydride with the diketone in THF was carried out by using the chiral ferrocenylphosphine ligands **1–8** (eq 1). The reaction conditions and results are summarized in Table I, which also contains, for comparison, data obtained with (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(−)-DIOP][19] and (*S*)-1,2-bis(diphenylphosphino)propane [(*S*)-prophos].[20] The palladium(II) catalyst (0.5–1.0 mol %) prepared in situ by mixing di-μ-chlorobis(π-allyl)dipalladium with a chiral bisphosphine ligand L* in a molar ratio of 1.0/2.2 (Pd/L* = 1.0/1.1) was effective for the allylation. The reaction at −50 or −30 °C gave 2-acetyl-2-allylcyclohexanone (**10**) in high yield, though the catalytic activity was dependent on the ligand employed (vide infra). The cationic phosphine–palladium(II) complex $[(\pi\text{-}C_3H_5)PdL^*]^+BF_4^-$ was also effective, to give almost the same results as the in situ catalyst, but the palladium(II) complexes of the type $PdCl_2L^*$ did not catalyze the allylation, probably due to its inertness toward reduction to a palladium(0) species under the reaction conditions.



9 **10**

The palladium catalyst bearing ferrocenylphosphine **3a** (which contains *N*-methyl-(2-hydroxyethyl)amino group at the side chain) was found most catalytically active and stereoselective. The product **10** with specific rotation $[\alpha]^{20}_D$ +185° (chloroform) was obtained in quantitative yield in the reaction at −50 °C, which turned out to be 73% enantiomerically pure by ^1H NMR analysis in the presence of a chiral shift reagent Eu(dcm)$_3$.[21] The configuration of (+)-**10** was determined to be *S* by converting it into known (+)-(*R*)-spiro[4.5]decane-1,6-dione[22] (**14**) by a sequence of reactions shown in Scheme V: selective ketalization of the cyclohexanone, oxidative cleavage of the carbon–carbon double bond with OsO_4 and $NaIO_4$ into aldehyde, base-catalyzed intramolecular aldol condensation, acid-catalyzed deketalization, and hydrogenation in the presence of Pd–C.

Scheme V[a]



(+)-(*S*)-**10** **11** **12**

13 (+)-(*R*)-**14**

[a] (a) $HOCH_2CH_2OH$, TsOH, C_6H_6; (b) OsO_4, $NaIO_4$, THF/H_2O; (c) 10% KOH, MeOH; (d) 10% HCl, THF; (e) H_2, Pd–C, C_6H_6.

Table I contains the following significant features. (1) The phosphine ligands **3a–c** and **5** gave (*S*)-**10** in over 50% ee (entries 1–4). They all have a 2-hydroxyethyl group on the nitrogen or oxygen atom attached to the ferrocenylmethyl carbon. (2) Lower stereoselectivity was observed in the reaction with **3e**, which is analogous to **3b** but carries the hydroxy group on the tertiary carbon atom (entry 7).

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Table II. Asymmetric Allylation of Enolates of 2-Acetylcyclohexanone (9) Producing 10 in the Presence of Palladium-(*R*)-(*S*)-3a Catalyst[a]

entry	CH_2=$CHCH_2X$, X	solv	reactn temp, °C	reactn time, h	conv,[b] %	$[\alpha]^{20}_D$[c]	% ee[d] (config)
24	$OCOCH_3$	THF	15	21	100	+40°	16 (*S*)
25	$OCOCH_3$	THF	0	38	100	+69°	27 (*S*)
26	$OCOCH_3$	THF	−10	44	100	+107°	42 (*S*)
27	$OCOCH_3$	THF	−30	18	100	+134°	53 (*S*)
28	$OCOCH_3$	THF	−50	20	100	+185°	73 (*S*)
29	$OCOCH_3$	THF	−60	44	100	+205°	81 (*S*)
30	$OP(O)(OEt)_2$	THF	−50	40	100	+181°	71 (*S*)
31	$OCOOCH_3$	THF	−50	43	100	+163°	64 (*S*)
32[e]	$OCOCH_3$	THF	−50	42	100	+185°	73 (*S*)
33[f]	$OCOCH_3$	THF	−50	20	0		
34	$OCOCH_3$	DME	−50	20	89	+165°	65 (*S*)
35	$OCOCH_3$	toluene	−50	20	43	+46°	18 (*S*)
36	$OCOCH_3$	DMF	−50	20	100	+52°	20 (*S*)

[a] See footnote *a* in Table I. Sodium enolate of **9** was used unless otherwise noted. [b] Determined by GLC analysis of the reaction mixture. [c] *c* 2.0–5.0, $CHCl_3$. [d] Determined by the optical rotation. The maximum rotation of **10** is 254 ± 7°. [e] Reaction of potassium enolate of **9** generated with potassium hydride. [f] Reaction of lithium of **9** generated with lithium hydride.

(3) A longer distance between the hydroxy group and the ferrocene moiety lowered the stereoselectivity (entries 6 and 10). Thus, the ligand **3f** with (3-hydroxypropyl)amino group gave (*S*)-**10** in 46% ee, and the ligand **3g** with [2-(2-hydroxyethoxy)ethyl]amino group gave racemic **10**. A shorter distance also lowered the stereoselectivity, as shown in the reaction with ligand **7** where the hydroxy group is located in the ferrocenylmethyl position (entry 8). (4) Replacement of the hydroxy group on **3a** or **3b** by a methoxy or amino group resulted in the formation of **10** with opposite configuration *R* in low optical yield (entries 11 and 14). The similar *R* selectivity (ca. 20%) was observed with the ligands **1** and **2**, which have the dimethylamino group and acetoxy group, respectively, on the ferrocenylmethyl position (entries 12 and 15). The ligand **8**, which lacks any functional group on the side chain also gave (*R*)-**10** of low enantiomeric purity. Those functional groups other than hydroxy seem to serve simply as sterically bulky groups. (5) Asymmetric centers on the (2-hydroxyethyl)amino group did not affect strongly the stereoselectivity (entries 16–21). The ligands **3j–l** and **4j–l** are diastereomeric isomers with the same configuration on the (hydroxyethyl)amino side chain and the opposite configuration on the ferrocenylbisphosphine moiety. Each pair of ligands **3j–l** and **4j–l** gave the product **10** with almost the same optical purity but with opposite configuration. Of these ligands, **3l** was most effective to give one of the highest optical yields (69%). Inefficiency of **3j** and **4j** may be due to the bulky phenyl group substituent at the hydroxymethyl carbon (see 2). (6) There seems to be a relationship between the stereoselectivity and the catalytic activity affected by the ligand, the catalysts with higher stereoselectivity being more catalytically active in general. Some of the catalysts gave very low conversion (<10%) at −50 °C, and therefore the results carried out at −30 °C are shown in Table I (entries 7, 8, 13, 16, and 17). (7) The ligands (−)-DIOP and (*S*)-prophos, both of which have been successfully used for rhodium-catalyzed asymmetric hydrogenation,[19,20] were ineffective for the present allylation (entries 22 and 23).

The features described above indicate that the terminal hydroxy group in the phosphine ligands is playing a key role in the asymmetric allylation. For high stereoselectivity the hydroxy group should be located in a position appropriately distant from the ferrocenylbisphosphine moiety and should not be sterically hindered at the hydroxymethyl carbon. Figure 2 illustrates a schematic view of nucleophilic attack of the enolates on the π-allylpalladium intermediate. The sodium enolates of β-diketones used here are typical soft carbon nucleophiles and have been demonstrated to attack the π-allyl carbon from the side opposite to palladium.[3–5] The conformation of chiral ferrocenylphosphine ligand on palladium complex is drawn on the basis of the crystal structure of ferrocenylphosphine–palladium complex $PdCl_2$(BPPFA).[23] The terminal hydroxy group on the (2-hydroxyethyl)amino side chain can be located just outside the π-allyl part of the π-allylpalladium intermediate and can favorably interact with the incoming soft carbon nucleophile. It is probable that the interaction increases the selectivity in differentiating the enantiotopic faces of the prochiral enolate by enhanced steric repulsions between the enolate and the chiral ferrocenylphosphine moiety. It is noted that the interaction seems to accelerate the allylation by drawing the nucleophile up to the π-allyl. A hydrogen bonding between the hydroxy and enolate is thought to be responsible for the interaction. Coordination to the sodium cation of the enolate is less probable since the replacement of the terminal hydroxy group by amino or alkoxy group resulted in the completely different stereochemistry. A longer distance between the terminal hydroxy and the ferrocene nucleus would lead to lower stereoselectivity due to less effective steric interactions, and a shorter distance would not bring the favorable hydrogen bonding to the incoming enolate. The attractive interaction between nucleophile

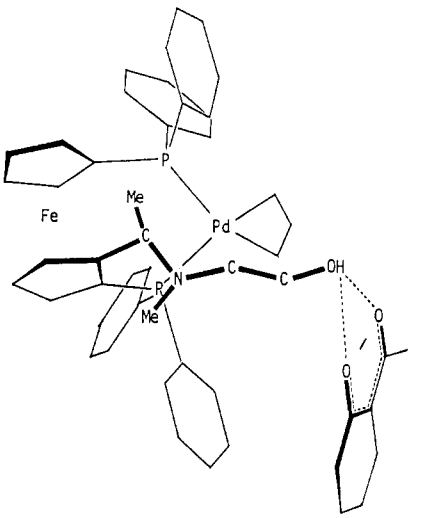

Figure 2. A schematic view of nucleophilic attack of the enolate **9** on the π-allylpalladium intermediate bearing (*R*)-(*S*)-**3a** ligand.

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Table III. Asymmetric Allylation of Active Methine Compounds with Allyl Acetate in the Presence of Palladium-(*R*)-(*S*)-3a Catalyst[a]

entry	methine compound	reactn temp, °C	reactn time, h	conv,[b] %	yield,[c] %	$[\alpha]^{20}_D$[d]	% ee[e] (config)
37	**9**	−60	44	100	88	+205°	81 (*S*)
38	**15a**	−50	17	100	86	+2.5°	<5
39	**16a**	−60	25	100	75	+150°	
40	**16a**	−30	28	100	82	+160°	
41	**17a**	−60	20	100	86	+190°	58
42	**17a**	−30	30	100	77	+171°	52
43	**18a**	−60	68	100	74	+179°	70
44	**18a**	−30	50	100	74	+140°	55
45[f]	**19a**	−60	45	100	94	−124°[g]	82
46	**19a**	−50	18	100	96	+111°[g]	73
47[f]	**20a**	−60	45	100	93	−8.7°	60
48	**20a**	−50	18	100	93	+7.4°	51
49	**21a**	−30	21	32	26	−16°	32
50[f]	**22a**	−60	45	100	86	+37°	53 (*S*)
51	**22a**	−50	18	100	88	−33°	47 (*R*)
52	**23a**	−50	18	100	70	−12.2°	22
53	**24a**	−50	44	100	82	+4.0°[h]	3 (*R*)
54[i]	**9**	−60	44	49	39	+170°	60
55[j]	**9**	−50	44	26	19	+90°	33

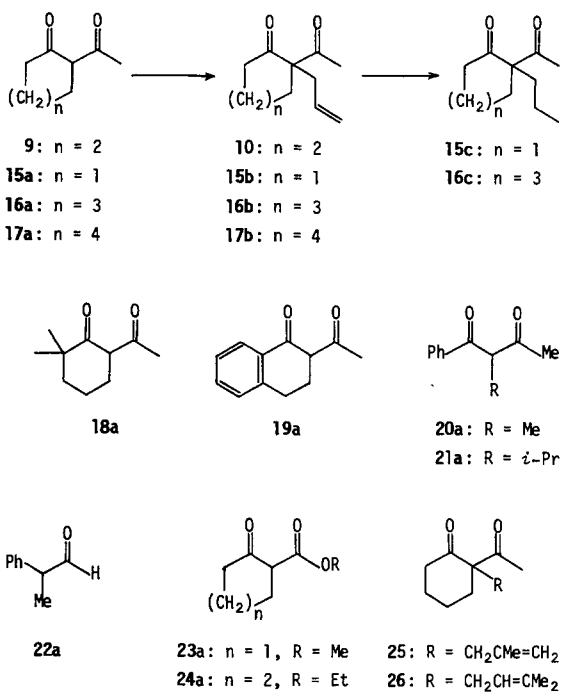
[a] See footnote *a* in Table I. [b] Determined by GLC analysis of the reaction mixture. [c] Isolated yield by distillation or preparative TLC. [d] *c* 2.0–5.0, $CHCl_3$. [e] Determined by ^1H NMR analysis of the allylation product in the presence of chiral shift reagent Eu(dcm)$_3$. [f] (*S*)-(*R*)-**3a** was used instead of (*R*)-(*S*)-**3a**. [g] $[\alpha]^{24}_D$. [h] $[\alpha]^{22}_D$. [i] Reaction with 2-methyl-2-propenyl acetate, giving **25**. [j] Reaction with 3-methyl-2-butenyl acetate giving **26**.

and hydroxy group(s) on the side chain has also been successfully operative in an asymmetric type II (see Scheme II) reaction to afford the allylic alkylation products in over 90% ee.[10]

The results obtained for the asymmetric allylation of **9** with the ligand **3a** under various reaction conditions are summarized in Table II. The stereoselectivity was found strongly dependent on the reaction temperature (entries 24–29). The lower temperature gave the higher enantiomeric purity of **10**, 81% ee being obtained at −60 °C. An Arrhenius plot of ln $[R]/[S]$ against $1/T$ was found to be approximately linear over the range −60 to 15 °C. The values $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ are calculated to be 3.1 kcal/mol and 10.3 cal/(deg·mol), respectively. Use of allyl phosphate or carbonate as an allyl donor gave **10** of almost the same enantiomeric purity as allyl acetate (entries 30 and 31). This result is to be expected from the reaction mechanism where the leaving group does not participate in the enantioface differentiation of the enolate. Potassium enolate of **9** could be used successfully instead of the sodium enolate, but the lithium enolate did not undergo the allylation under the reaction conditions (entries 32 and 33). The yield and enantiomeric purity of allylation product **10** were solvent dependent (entries 34–36). In THF or dimethoxyethane (DME) the allylation proceeded with high stereoselectivity in high yields. The low selectivity (20%) observed in DMF may be ascribed to its high polarity, preventing the stereocontrol by the attractive interaction between the terminal hydroxy group and enolate. The sodium enolate of **9** is almost insoluble in toluene, and the aggregation of the enolate might be responsible for the slow rate of allylation and low stereoselectivity in toluene.

The palladium catalyst bearing **3a** was examined for catalytic activity and stereoselectivity in the allylation of other active methine compounds (Scheme VI and Table III). In general β-diketones of cyclic ketones were successfully allylated to afford the corresponding products with high enantiomeric purity. The highest stereoselectivity (82% ee) was observed in the allylation of 2-acetyl-1-tetralone (**19a**) at −60 °C (entry 45). The diketones 2-acetylcyclooctanone (**17a**) and 2-acetyl-6,6-dimethylcyclohexanone (**18a**) gave the corresponding allylated products **17b** and **18b** in around 60% ee (entries 41–44), while almost racemic product **15b** was formed in the reaction of 2-acetylcyclopentanone (**15a**) (entry 38). The selectivity seems to be high with the β-diketones provided that substituents around the two carbonyls are greatly different in steric bulkiness. The allylation of linear diketone, 1-phenyl-2-methylbutane-1,3-dione (**20a**) also proceeded successfully with 60% stereoselectivity (entry 47). Optically active aldehyde, (*S*)-(+)-2-methyl-2-phenylpent-4-enal[24] (**22b**) (53% ee) was obtained in the reaction of 2-phenylpropanal (**22a**) catalyzed by palladium-(*S*)-(*R*)-**3a** complex at −60 °C. Unfortunately, the

Scheme VI[a]



[a] The compounds **18b–24b** are allylated products derived from **18a–24a**, respectively.

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ligand **3a** was not effective for the allylation of keto esters (entries 52 and 53). Allylic acetates bearing methyl substituents can be also used for the allylation. The methyl groups did not largely affect the stereoselectivity, though the rate of reaction decreased (entries 54 and 55).

There has been great interest and activity in asymmetric synthesis of optically active compounds containing chiral quaternary carbon centers.[25] Although diastereoselective alkylation of chiral imines, enamines, or enolates has developed so successfully as to result in over 95% selectivity,[26] only a few reports have appeared on the asymmetric synthesis in an enantioselective manner.[27] The catalytic asymmetric allylation presented here provides an efficient method for the generation of the chiral quaternary centers, though the stereoselectivity is not always satisfactorily high at this stage. We are in a position to be able to improve the stereoselectivity by further structural modification of the chiral phosphine ligands.

Experimental Section

General. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. ^{1}H NMR spectra were measured with a JEOL JNM-MH-100 (100 MHz) spectrometer. Enantiomeric purities by ^{1}H NMR analysis were determined by using a chiral shift reagent tris(*d,d*-dicampholylmethanato)europium(III) [Eu(dcm)$_3$][21] and measuring peak areas by cutting and weighing. GLC analyses were performed on a Shimadzu GC-4C gas chromatograph, equipped with a 3-m column packed with Silicone DC 550 (30% on Celite) or Silicone DC QF-1 (20% on Chromosorb W AW). A Varian Aerograph Model 920, equipped with a 20-ft column packed with Silicone DC 550 (30% on Celite) or PEG 20M (30% on Celite), was used for isolation and purification of the products.

Materials. The preparation of optically active ferrocenylphosphines (*R*)-(*S*)-BPPFA (**1**), (*R*)-(*S*)-**2**, (*R*)-(*S*)-**3a,c,i**, (*R*)-(*S*)-**6**, and (*R*)-(*S*)-**7** has been reported.[16] Diketones **9**, **15a**, **16a**, **17a**, **18a**, **20a**, and **21a** were prepared by acetylation of the corresponding ketones with acetic anhydride and $BF_3(AcOH)_2$ according to the procedure reported by Hauser.[28] The ketones **19a** and **22a** were commercially available and used without further purification.

Preparation of Chiral Ferrocenylphosphines. In a similar manner to the procedure reported for the preparation of (*R*)-(*S*)-**3a**,[16] the ferrocenylphosphines (*R*)-(*S*)-**3b,d–h,j,k** were prepared by the reaction of the acetate (*R*)-(*S*)-**2** with an excess of the corresponding amines in refluxing methanol, and the phosphines (*S*)-(*R*)-**4j,k** were prepared from (*S*)-(*R*)-**2**.

(*R*)-(*S*)-3b: prepared from (*R*)-(*S*)-**2** and 2-aminoethanol in 86% yield; $[\alpha]^{25}_D$ −281° (*c* 0.35, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.34 (d, J = 7 Hz, 3 H), 1.49 (br, 2 H), 2.89 (t, J = 5 Hz, 2 H), 3.07 (t, J = 5 Hz, 2 H), 3.62, 4.08, 4.38 (m, 2 H, 4 H, 2 H), 7.02–7.62 (m, 20 H). Anal. Calcd for $C_{38}H_{37}ONP_2Fe$: C, 71.15; H, 5.81; N, 2.18. Found: C, 71.07; H, 5.78; N, 2.03.

(*R*)-(*S*)-3d: prepared from (*R*)-(*S*)-**2** and 2-(methylamino)-1,3-propanediol in 61% yield; $[\alpha]^{25}_D$ −348° (*c* 0.38, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.23 (d, J = 7 Hz, 3 H), 1.77 (s, 3 H), 2.46 (m, 1 H), 3.38–4.69 (m, 12 H), 6.95–7.61 (m, 20 H). Anal. Calcd for $C_{40}H_{41}O_2NP_2Fe$: C, 70.08; H, 6.03; N, 2.04. Found: C, 70.32; H, 6.21; N, 1.88.

(*R*)-(*S*)-3e: prepared from (*R*)-(*S*)-**2** and 2-amino-1,1-dimethylethanol in 72% yield; $[\alpha]^{25}_D$ −278° (*c* 0.48, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.68, 0.76 (2 s, 6 H), 1.34 (d, J = 7 Hz, 3 H), 2.23 (br s, 2 H), 3.61, 3.68, 3.90–4.20, 4.44 (m, 1 H, 1 H, 4 H, 2 H), 7.0–7.7 (m, 20 H). Anal. Calcd for $C_{40}H_{41}ONP_2Fe$: C, 71.75; H, 6.17; N, 2.09. Found: C, 71.47; H, 5.98; N, 2.00.

(*R*)-(*S*)-3f: prepared from (*R*)-(*S*)-**2** and 3-aminopropanol in 89% yield; $[\alpha]^{25}_D$ −267° (*c* 0.36, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.02 (br 2 H), 1.36 (d, J = 7 Hz, 3 H), 2.36 (t, J = 5 Hz, 2 H), 2.10–2.57 (m, 2 H), 3.63 (t, J = 5 Hz, 2 H), 3.63, 3.71, 4.12, 4.40 (m, 1 H, 1 H, 3 H, 2 H), 3.92 (m, 1 H), 7.03–7.65 (m, 20 H). Anal. Calcd for $C_{39}H_{39}ONP_2Fe$: C, 71.46; H, 6.00; N, 2.14. Found: C, 71.21; H, 6.05; N, 2.11.

(*R*)-(*S*)-3g: prepared from (*R*)-(*S*)-**2** and 2-[(2-aminoethyl)-oxy]ethanol in 83% yield; $[\alpha]^{25}_D$ −268° (*c* 0.51, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.37 (d, J = 7 Hz, 3 H), 2.15 (br, 2 H), 2.42 (t, J = 5 Hz, 2 H), 2.98, 3.29, 3.49 (m, 2 H, 2 H, 2 H), 3.65, 4.10, 4.41 (m, 2 H, 4 H, 2 H), 7.07–7.61 (m, 20 H). Anal. Calcd for $C_{40}H_{41}O_2NP_2Fe$: C, 70.08; H, 6.03; N, 2.04. Found: C, 69.96; H, 6.05; N, 2.01.

(*R*)-(*S*)-3h: prepared from (*R*)-(*S*)-**2** and 2-aminoethyl methyl ether in 78% yield; $[\alpha]^{25}_D$ −289° (*c* 0.35, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.22 (br, 1 H), 1.38 (d, J = 7 Hz, 3 H), 2.44 (t, J = 6 Hz, 2 H), 2.86 (t, J = 6 Hz, 2 H), 2.98 (s, 3 H), 3.65, 4.05, 4.42 (m, 2 H, 4 H, 2 H), 7.04–7.60 (m, 20 H). Anal. Calcd for $C_{39}H_{39}ONP_2Fe$: C, 71.46; H, 6.00; N, 2.14. Found: C, 71.18; H, 5.91; N, 1.96.

(*R*)-(*S*)-3j: prepared from (*R*)-(*S*)-**2** and ephedrine [(1*R*,2*S*)-1-phenyl-2-(methylamino)propanol] in 86% yield; mp 113–115 °C; ^{1}H NMR ($CDCl_3$) δ 0.54 (d, J = 7 Hz, 3 H), 1.28 (d, J = 7 Hz, 3 H), 1.45 (s, 3 H), 1.08–1.82 (br, 1 H), 2.73 (m, 1 H), 4.73 (m, 1 H), 3.44, 3.85, 4.13, 4.35, 4.45, 5.07 (m, 1 H, 2 H, 2 H, 1 H, 1 H, 1 H), 6.91–7.77 (m, 25 H). Anal. Calcd for $C_{46}H_{45}ONP_2Fe$: C, 74.10; H, 6.08; N, 1.88. Found: C, 73.87; H, 5.99; N, 1.87.

(*S*)-(*R*)-4j: prepared from (*S*)-(*R*)-**2** and ephedrine [(1*R*,2*S*)-1-phenyl-2-(methylamino)propanol] in 75% yield; ^{1}H NMR ($CDCl_3$) δ 0.92 (d, J = 7 Hz, 3 H), 1.22 (d, J = 7 Hz, 3 H), 1.70 (br, 1 H), 1.98 (s, 3 H), 2.50 (m, 1 H), 3.48, 3.75, 3.92, 4.13, 4.37, 4.49, 4.62 (m, 1 H, 1 H, 1 H, 2 H, 1 H, 1 H, 2 H), 6.96–7.62 (m, 25 H). Anal. Calcd for $C_{46}H_{45}ONP_2Fe$: C, 74.10; H, 6.08; N, 1.88. Found: C, 73.82; H, 6.28; N, 1.80.

(*R*)-(*S*)-3k: prepared from (*R*)-(*S*)-**2** and L-hydroxyproline methyl ester hydrochloride (20 equiv) in the presence of triethylamine (20 equiv) in 81% yield; ^{1}H NMR ($CDCl_3$) δ 1.23 (d, J = 7 Hz, 3 H), 1.35 (m, 2 H), 1.76 (m, 1 H), 2.39 (dd, J = 4 and 9 Hz, 1 H), 2.72 (dd, J = 6 and 9 Hz, 1 H), 3.33 (dd, J = 5 and 9 Hz, 1 H), 3.68 (s, 3 H), 3.52, 3.70, 3.95, 4.10, 4.37 (m, 1 H, 1 H, 1 H, 2 H, 2 H), 4.48 (m, 1 H), 6.91–7.73 (m, 20 H).

(*S*)-(*R*)-4k: prepared from (*S*)-(*R*)-**2** and L-hydroxyproline methyl ester hydrochloride (20 equiv) in the presence of triethylamine (20 equiv) in 88% yield; ^{1}H NMR ($CDCl_3$) δ 0.65 (m, 1 H), 0.98 (ddd, J = 4, 8, and 13 Hz, 1 H), 1.31 (d, J = 7 Hz, 3 H), 1.85 (ddd, J = 3, 7, and 13 Hz, 1 H), 2.17 (dd, J = 3 and 9 Hz, 1 H), 3.01 (dd, J = 6 and 9 Hz, 1 H), 3.61 (s, 3 H), 3.66 (m, 1 H), 3.48, 3.75, 3.88, 4.08, 4.36 (m, 1 H, 1 H, 1 H, 2 H, 2 H), 4.44 (m, 1 H), 6.98–7.64 (m, 20 H).

(*R*)-(*S*)-3l. To a solution of 70 mg (1.8 mmol) of lithium aluminum hydride in 2 mL of THF was added a solution of 90 mg (0.124 mmol) of (*R*)-(*S*)-**3k** in 4 mL of THF. The mixture was refluxed for 30 min and hydrolyzed at 0 °C by the successive addition of 0.07 mL of water, 0.07 mL of 20% aqueous sodium hydroxide, and 0.21 mL of water. The white precipitates were removed by filtration. The filtrate was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on alumina (chloroform/ethanol = 20/1) to give 77 mg (89%) of (*R*)-(*S*)-**3l**: $[\alpha]^{25}_D$ −346° (*c* 0.36, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J = 7 Hz, 3 H), 0.99–1.78, 2.16, 2.76–3.40 (m, 4 H, 2 H, 4 H), 3.46, 3.74, 3.89, 4.08, 4.40 (m, 1 H, 1 H, 1 H, 2 H, 3 H), 6.95–7.68 (m, 20 H). Anal. Calcd for $C_{41}H_{41}O_2NP_2Fe$: C, 70.59; H, 5.92. Found: C, 70.31; H, 5.74.

(*S*)-(*R*)-4l. In a similar manner to the preparation of (*R*)-(*S*)-**3l**, (*S*)-(*R*)-**4l** was prepared by the reduction of (*S*)-(*R*)-**4k** with lithium aluminum hydride in THF in 100% yield: $[\alpha]^{25}_D$ +347° (*c* 0.36, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.45 (d, J = 7 Hz,

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3 H), 1.34–1.88 (m, 2 H), 2.38 (dd, J = 5 and 9 Hz, 1 H), 2.87 (m, 2 H), 3.11 (dd, J = 6 and 9 Hz, 1 H), 3.28 (dd, J = 4 and 11 Hz, 1 H), 3.84 (m, 1 H), 3.45, 3.74, 3.93, 4.08, 4.16, 4.38 (m, 1 H, 1 H, 1 H, 1 H, 1 H, 2 H), 4.25 (m, 1 H), 6.99–7.68 (m, 20 H). Anal. Calcd for $C_{41}H_{41}O_2NP_2Fe$: C, 70.59; H, 5.92. Found: C, 70.29; H, 5.82.

(*R*)-(*S*)-5. A mixture of 101 mg (0.158 mmol) of the acetate (*R*)-(*S*)-**2**, 3 mL of ethylene glycol, and 2 mL of pyridine was kept stirring at 80–90 °C for 9 h. Benzene (10 mL) was added, and the solution was washed twice with water, dried over anhydrous sodium sulfate, and stripped of solvent. The residue was chromatographed on alumina (benzene/ethanol = 5/1) and then on Florisil (chloroform) to give 43 mg (42% yield) of (*R*)-(*S*)-**5**: $[\alpha]^{25}_D$ −311° (*c* 0.43, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.43 (d, J = 7 Hz, 3 H), 3.00–3.52 (m, 4 H), 3.59, 3.65, 3.99, 4.07, 4.14, 4.37, 4.47 (m, 1 H, 1 H, 1 H, 1 H, 1 H, 1 H, 1 H), 4.72 (m, 1 H), 6.9–7.7 (m, 20 H). Anal. Calcd for $C_{38}H_{36}O_2P_2Fe$: C, 71.04; H, 5.65. Found: C, 71.21; H, 5.73.

(*S*)-8. To a suspension of 0.493 g (0.77 mmol) of the acetate (*R*)-(*S*)-**2** in 10 mL of dry ether, 8 mL of 2.4 M methylmagnesium bromide in ether was added at 0 °C. The mixture was refluxed for 5 h and hydrolyzed with 10% hydrochloric acid. The product was extracted with ether, and the ether solution was washed with water, dried over anhydrous sodium sulfate, and stripped of solvent. The residue was chromatographed on alumina (benzene), and recrystallization from hexane gave 0.305 g (66% yield) of (*S*)-**8**: mp 115–117 °C; $[\alpha]^{25}_D$ −332° (*c* 0.41, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.77, 1.24 (d, J = 7 Hz, 6 H), 2.95 (double septet, J = 7 and 4 Hz, 1 H), 3.51, 3.64, 3.95, 4.05, 4.13, 4.27, 4.42 (br s, 1 H, 1 H, 1 H, 1 H, 1 H, 1 H, 1 H), 7.1–7.6 (m, 20 H). Anal. Calcd for $C_{37}H_{34}P_2Fe$: C, 74.51; H, 5.75. Found: C, 74.75; H, 5.58.

Asymmetric Allylation of 2-Acetylcyclohexanone (9). General Procedure. All the reactions were carried out under a dry nitrogen atmosphere. To a suspension (in 5 mL of THF) of 120 mg (2.5 mmol) of 50% sodium hydride in mineral oil was added dropwise at 0 °C 280 mg (2.0 mmol) of 2-acetylcyclohexanone via syringe (hydrogen evolution), and the solution was stirred at 0 °C for 30 min. To the solution was added at −78 °C a solution prepared in a second flask by mixing a chiral ligand (0.022 mmol), 3.6 mg (0.010 mmol) of di-μ-chlorobis(π-allyl)dipalladium, and 300 mg (3.0 mmol) of allyl acetate in 5 mL of THF. The mixture was kept stirring at a given temperature for 15–45 h. It was then hydrolyzed with 10% hydrochloric acid and extracted with ether. The ether extracts were washed with water, dried over magnesium sulfate, and stripped of solvent in vacuo. The residue was analyzed by GLC to determine the conversion. When the conversion was 100%, the product 2-allyl-2-acetylcyclohexanone (**10**) was isolated by bulb-to-bulb distillation [100–110 °C (0.35 mmHg)]. When the conversion was lower, the product **10** was isolated by preparative TLC on silica gel (hexane/ethyl acetate = 5/1, R_f 0.5). Experimental results are summarized in Tables I and II. **10**: ^{1}H NMR (CCl_4) δ 1.11–2.70 (m, 10 H), 2.01 (s, 3 H), 4.90–5.19 (m, 2 H), 5.31–5.85 (m, 1 H). The enantiomeric purity was determined by ^{1}H NMR in the presence of a chiral shift reagent Eu(dcm)$_3$, the acetyl singlet of the *S*-(+) isomer appearing at a lower field than that of the enantiomer. The maximum rotation is calculated to be $[\alpha]^{20}_D$ 254 ± 7° (chloroform).

Conversion of 10 into Spiro Diketone 13. A 100-mL round-bottomed flask was charged with 11.2 g (62.1 mmol) of **10** ($[\alpha]^{20}_D$ +169° (*c* 1.3, chloroform)), 7.5 mL (134 mmol) of ethylene glycol, 15 mg of *p*-toluenesulfonic acid monohydrate, and 30 mL of benzene. The flask was attached to a water separator under a reflux condenser, and the mixture was refluxed until an almost theoretical amount of water (1.1 mL) was collected in the trap (for 5 h). The reaction mixture was washed with 10% sodium hydroxide solution and water, dried over anhydrous potassium carbonate, and stripped of solvent. The residue was distilled [106–108 °C (2 mmHg)] to give 11.1 g (80% yield) of 1,4-dioxa-6-acetyl-6-allylspiro[4.5]decane (**11**): $[\alpha]^{20}_D$ +19.7° (*c* 1.4, chloroform); ^{1}H NMR (CCl_4) δ 1.06–2.43 (m, 8 H), 2.12 (s, 3 H), 2.26, 2.73 (a pair of dd, J = 6 and 14 Hz, 2 H), 3.91 (s, 4 H), 4.86–5.15 (m, 2 H), 5.25–5.69 (m, 1 H). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.56; H, 8.98.

To a solution of 8.9 g (40 mmol) of **11** and 0.10 g (0.39 mmol) of osmium tetraoxide in 126 mL of THF and 42 mL of water was added at 20–25 °C 18.2 g (85 mmol) of sodium periodate in small portions over a period of 45 min. The mixture was kept stirring at the same temperature for 2 h. The black slurry turned brown. Water (600 mL) was added, and the mixture was extracted with ether. The extract was dried over anhydrous magnesium sulfate and stripped of solvent to give 7.4 g of the crude aldehyde 1,4-dioxa-6-acetyl-6-(formylmethyl)spiro[4.5]decane, which was used for the next cyclization without further purification. The crude aldehyde obtained above was treated with 60 mL of 10% aqueous potassium hydroxide in 180 mL of methanol for 42 h. The methanol was evaporated and the mixture was extracted with ether. The extract was dried over anhydrous magnesium sulfate and stripped of solvent. The residue was chromatographed on silica gel (hexane/ethyl acetate = 4/1) to give 2.0 g (24% yield from **11**) of 1,4-dioxadispiro[4.0.4.4]tetradec-8-en-7-one (**12**): $[\alpha]^{20}_D$ +21.5° (*c* 1.0, chloroform); mp 92 °C; ^{1}H NMR (CCl_4) δ 1.04–2.39 (m, 8 H), 2.19, 2.87 (a pair of dt, J = 19 and 2 Hz, 1 H, 1 H), 3.88 (s, 4 H), 5.87–6.04 (m, 1 H), 7.37–7.58 (m, 1 H). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.93; H, 7.84.

A solution of 208 mg (1.0 mmol) of the acetal **12** and 1 mL of 10% hydrochloric acid in 3 mL of THF was stirred at room temperature for 48 h. Ether was added, and the mixture was washed with saturated sodium bicarbonate solution and with water and dried over anhydrous magnesium sulfate. Bulb-to-bulb distillation [130–150 °C (3 mmHg)] gave 115 mg (70%) of spiro[4.5]dec-2-ene-1,6-dione (**13**): $[\alpha]^{20}_D$ +29.8° (*c* 1.0, chloroform); ^{1}H NMR (CCl_4) δ 0.72–2.62 (m, 8 H), 2.84 (dt, J = 6 and 13 Hz, 1 H), 3.58 (dt, J = 19 and 2 Hz, 1 H), 5.58–5.82 (m, 1 H), 7.29–7.52 (m, 1 H). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.17; H, 7.61.

A solution of 110 mg (0.67 mmol) of **13** and 12 mg of 10% Pd–C in 2 mL of benzene was placed in a stainless microautoclave and magnetically stirred at room temperature with hydrogen at 130 atm for 16 h. The reaction mixture was passed through a short silica gel column and distilled [110–130 °C (1 mmHg) (bath temperature)] to give 110 mg (99%) of spiro[4.5]decane-1,6-dione (**14**): $[\alpha]^{20}_D$ +105° (*c* 0.8, chloroform) (lit.[22] $[\alpha]_D$ +185 ± 5° (*c* 0.2, chloroform) for (*R*)-**14**).

Asymmetric Allylation of Active Methine Compounds 15a–24a. The allylation was carried out in essentially the same manner as that of 2-acetylcyclohexanone (**9**). The reaction conditions and results containing optical rotation data and enantiomeric purities of the allylated products **15b–24b** are summarized in Table III. The ^{1}H NMR spectra and analytical data are shown below. The enantiomeric purities were determined by ^{1}H NMR studies in the presence of Eu(dcm)$_3$. The products **15b**, **16b**, and **19b**, whose enantiomeric purities could not be determined by the ^{1}H NMR studies due to a poor separation, were hydrogenated to propyl derivatives **15c**, **16c**, and **19c**, respectively, which were used for the determination of the enantiomeric purities.

2-Acetyl-2-allylcyclopentanone (15b): ^{1}H NMR (CCl_4) δ 1.47–2.80 (m, 8 H), 2.12 (s, 3 H), 4.89–5.17 (m, 2 H), 5.29–5.76 (m, 1 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.02; H, 8.77. Hydrogenation of (+)-**15b** ($[\alpha]^{20}_D$ +2.5° (chloroform)) gave (+)-2-acetyl-2-propylcyclopentanone (**15c**) ($[\alpha]^{20}_D$ +3.1° (chloroform)): ^{1}H NMR (CCl_4) δ 0.78–2.35 (m, 12 H), 2.10 (s, 3 H), 2.66 (m, 1 H). The acetyl singlet was used for the determination of % ee. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.56. Found: C, 71.15; H, 9.84.

2-Acetyl-2-allylcycloheptanone (16b): ^{1}H NMR (CCl_4) δ 0.98–2.68 (m, 11 H), 2.00 (s, 3 H), 2.82 (dd, J = 6 and 14 Hz, 1 H), 4.86–5.17 (m, 2 H), 5.27–5.75 (m, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.95; H, 9.50. Hydrogenation of (+)-**16b** ($[\alpha]^{20}_D$ +160° (chloroform)) gave (+)-2-acetyl-2-propylcycloheptanone (**16c**) ($[\alpha]^{20}_D$ +134° (chloroform)): ^{1}H NMR (CCl_4) δ 0.76–2.55 (m, 17 H), 2.00 (s, 3 H). Attempts to determine its % ee failed due to the poor separation of the signals. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.44; H, 10.48.

2-Acetyl-2-allylcyclooctanone (17b): ^{1}H NMR (CCl_4) δ 0.72–2.82 (m, 13 H), 1.95 (s, 3 H), 2.96 (dd, J = 6 and 15 Hz, 1 H), 4.90–5.16 (m, 2 H), 5.23–5.68 (m, 1 H). The acetyl singlet of the (−)-isomer appeared at lower field than that of the (+)-isomer in the presence of Eu(dcm)$_3$. Anal. Calcd for $C_{13}H_{20}O_2$:

C, 74.96; H, 9.68. Found: C, 74.71; H, 9.86.

2-Acetyl-2-allyl-6,6-dimethylcyclohexanone (18b): ^{1}H NMR (CCl_4) δ 0.98, 1.06 (a pair of s, 3 H, 3 H), 1.99 (s, 3 H) 1.12–2.12 (m, 6 H), 2.38, 2.64 (a pair of dd, J = 7 and 13 Hz, 1 H, 1 H), 4.88–5.16 (m, 2 H), 5.22–5.72 (m, 1 H). The acetyl singlet of the (−)-isomer appeared at lower field than that of the (+)-isomer in the presence of Eu(dcm)$_3$. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.84; H, 9.82.

2-Acetyl-2-allyl-1-tetralone (19b): ^{1}H NMR (CCl_4) δ 2.03 (s, 3 H), 1.68–2.15 (m, 1 H), 2.40–3.34 (m, 3 H), 2.62 (d, J = 7 Hz, 2 H), 4.92–5.20 (m, 2 H), 5.36–5.93 (m, 1 H), 7.00–7.53 (m, 3 H), 7.99 (dd, J = 2 and 8 Hz, 1 H). Hydrogenation of **19b** with the rotation of $[\alpha]^{24}_D$ +111° and −124° gave 2-acetyl-2-propyl-1-tetralone (**19c**) with the rotation of $[\alpha]^{20}_D$ +104° and −113°, respectively. **19c**: ^{1}H NMR (CCl_4) δ 0.95 (t, J = 7 Hz, 3 H), 1.05–1.46 (m, 2 H), 2.02 (s, 3 H), 1.70–2.12 (m, 3 H), 2.88–3.33 (m, 3 H), 7.05–7.50 (m, 3 H), 7.97 (dd, J = 2 and 8 Hz, 1 H). The acetyl singlet of the (+)-isomer appeared at lower field than that of the (−)-isomer in the presence of Eu(dcm)$_3$. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.12; H, 7.91.

1-Phenyl-2-methyl-2-allylbutane-1,3-dione (20b): ^{1}H NMR (CCl_4) δ 1.39 (s, 3 H), 2.02 (s, 3 H), 2.71 (d, J = 8 Hz, 2 H), 4.85–5.91 (m, 2 H), 5.36–5.82 (m, 1 H), 7.30–7.62 (m, 3 H), 7.70–7.94 (m, 2 H). The acetyl singlet of the (+)-isomer appeared at lower field than that of the (−)-isomer in the presence of Eu(dcm)$_3$. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.03; H, 7.31.

1-Phenyl-2-isopropyl-2-allylbutane-1,3-dione (21b): ^{1}H NMR (CCl_4) δ 0.91, 1.03 (a pair of d, J = 7 Hz, 3 H, 3 H), 2.00 (s, 3 H) 2.62–2.96 (m, 3 H), 4.81–5.18 (m, 2 H), 5.38–5.91 (m, 1 H), 7.29–7.65 (m, 3 H), 7.75–8.12 (m, 2 H). The acetyl singlet of the (−)-isomer appeared at lower field than that of the (+)-isomer in the presence of Eu(dcm)$_3$. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.42; H, 8.28.

2-Methyl-2-phenylpent-4-enal (22b): ^{1}H NMR (CCl_4) δ 1.41 (s, 3 H), 2.60 (d, J = 7 Hz, 2 H), 4.85–5.14 (m, 2 H), 5.25–5.78 (m, 1 H), 7.06–7.45 (m, 5 H), 9.42 (s, 1 H). The methyl singlet of the (−)-isomer appeared at lower field than that of the (+)-isomer in the presence of Eu(dcm)$_3$. (lit.[24] R configuration for (−)-**22b**.)

2-(Methoxycarbonyl)-2-allylcyclopentanone (23b): ^{1}H NMR (CCl_4) δ 1.73–2.79 (m, 8 H), 3.70 (s, 3 H), 4.93–5.23 (m, 2 H), 5.46–5.91 (m, 1 H). The methyl singlet of the (−)-isomer appeared at lower field than that of the (+)-isomer in the presence of Eu(dcm)$_3$. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.96; H, 7.82.

2-(Ethoxycarbonyl)-2-allylcyclohexanone (24b): ^{1}H NMR (CCl_4) δ 1.26 (t, J = 7 Hz, 3 H), 1.35–2.75 (m, 10 H), 4.15 (q, 2 H), 4.84–5.19 (m, 2 H), 5.46–6.05 (m, 1 H). (lit.[29] $[\alpha]^{22}_D$ −130.9° for (*S*)-**24b**.)

Asymmetric Allylation of 2-Acetylcyclohexanone with 2-Methyl-2-propenyl and 3-Methyl-2-butenyl Acetates. The reaction conditions and results containing optical rotation data and enantiomeric purities of the allylated products **25** and **26** are summarized in Table III. The ^{1}H NMR spectra and analytical data are shown below.

2-Acetyl-2-(2-methyl-2-propenyl)cyclohexanone (25): ^{1}H NMR (CCl_4) δ 1.14–2.75 (m, 8 H), 1.58 (s, 3 H), 2.02 (s, 3 H), 2.53 (br s, 2 H), 4.61, 4.75 (m, 1 H, 1 H). The acetyl singlet of the (+)-isomer appeared at lower field than that of the (−)-isomer in the presence of Eu(dcm)$_3$. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.48; H, 9.56.

2-Acetyl-2-(3-methyl-2-butenyl)cyclohexanone (26): ^{1}H NMR (CCl_4) δ 1.12–2.72 (m, 10 H), 1.60, 1.68 (2 br s, 3 H, 3 H), 1.90 (s, 3 H), 4.83 (m, 1 H). The acetyl singlet of the (+)-isomer appeared at lower field than that of the (−)-isomer in the presence of Eu(dcm)$_3$. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.70; H, 9.95.

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Registry No. (*R*)-(*S*)-**1**, 69257-18-7; (*R*)-(*S*)-**2**, 62412-57-1; (*S*)-(*R*)-**2**, 111321-96-1; (*R*)-(*S*)-**3a**, 74286-09-2; (*S*)-(*R*)-**3a**, 111321-97-2; (*R*)-(*S*)-**3b**, 111267-74-4; (*R*)-(*S*)-**3c**, 74286-10-5; (*R*)-(*S*)-**3d**, 105130-41-4; (*R*)-(*S*)-**3e**, 111267-77-7; (*R*)-(*S*)-**3f**, 111267-76-6; (*R*)-(*S*)-**3g**, 111267-78-8; (*R*)-(*S*)-**3h**, 111267-79-9; (*R*)-(*S*)-**3i**, 74286-08-1; (*R*)-(*S*)-**3j**, 111267-80-2; (*R*)-(*S*)-**3k**, 111267-81-3; (*R*)-(*S*)-**3l**, 111267-82-4; (*S*)-(*R*)-**4j**, 111321-93-8; (*S*)-(*R*)-**4k**, 111321-94-9; (*S*)-(*R*)-**4l**, 111321-95-0; (*R*)-(*S*)-**5**, 111267-75-5; (*R*)-(*S*)-**6**, 74311-59-4; (*R*)-(*S*)-**7**, 62412-53-7; (*S*)-**8**, 105130-40-3; **9**, 874-23-7; (+)-(*S*)-**10**, 67679-08-7; (−)-(*R*)-**10**, 58648-14-9; **11**, 111239-29-3; **12**, 111239-31-7; **13**, 111239-28-2; (+)-(*R*)-**14**, 40793-71-3; **15a**, 1670-46-8; (+)-**15b**, 111239-33-9; (+)-**15c**, 111239-41-9; **16a**, 15419-61-1; (+)-**16b**, 111239-34-0; (+)-**16c**, 111239-42-0; **17a**, 17343-99-6; (+)-**17b**, 111239-35-1; **18a**, 111239-32-8; (+)-**18b**, 111239-36-2; **19a**, 17216-08-9; (+)-**19b**, 111239-37-3; (−)-**19b**, 67679-07-6; (+)-**19c**, 111239-43-1; (−)-**19c**, 111239-46-4; **20a**, 6668-24-2; (+)-**20b**, 111239-38-4; (−)-**20b**, 111239-47-5; **21a**, 63024-80-6; (−)-**21b**, 111239-39-5; **22a**, 93-53-8; (+)-(*S*)-**22b**, 111464-55-2; (−)-(*R*)-**22b**, 67679-06-5; **23a**, 10472-24-9; (−)-**23b**, 111239-40-8; **24a**, 1655-07-8; (+)-(*R*)-**24b**, 72763-87-2; (+)-**25**, 111239-44-2; (+)-**26**, 111239-45-3; (−)-DIOP, 32305-98-9; (*S*)-prophos, 67884-33-7; $[(\pi\text{-}C_3H_5)PdCl]_2$, 12012-95-2; 2-(methylamino)-1,3-propanediol, 77697-86-0; 2-amino-1,1-dimethylethanol, 2854-16-2; 2-[(2-aminoethyl)oxy]ethanol, 929-06-6; 1,4-dioxa-6-acetyl-6-(formylmethyl)spiro[4.5]decane, 111239-30-6; 2-aminoethanol, 141-43-5; 3-aminopropanol, 156-87-6; 2-aminoethyl methyl ether, 109-85-3; (1*R*,2*S*)-1-phenyl-2-(methylamino)propanol, 299-42-3; L-hydroxyproline methyl ester hydrochloride, 40216-83-9; allyl acetate, 591-87-7; *p*-toluenesulfonic acid, 104-15-4; 3-methyl-2-butenyl acetate, 1191-16-8.

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