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Allenic Esters from Cyclopropenones by Lewis Base Catalysis: Substrate Scope, the Asymmetric Variant from the Dynamic Kinetic Asymmetric Transformation, and Mechanistic Studies

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The Lewis base catalyzed reactions of cyclopropenones with a variety of nucleophiles (alcohols, phenols, or water) were systematically investigated. We demonstrated that this kind of reaction could be used to synthesize allenic esters in moderate to excellent yields. Furthermore, more synthetically interesting axially chiral allenes in moderate to good yields and *ee* values were obtained in the corresponding asymmetric reaction in the presence of multifunctional chiral phosphine catalyst. The reaction mechanism was disclosed by using NMR tracing experiments, MS, and DFT calculations. Notably, the asymmetric reaction was proved to be a dynamic kinetic asymmetric transformation based on the control experiments, and the detailed mechanism of this transformation revealed by theoretical investigations.

Introduction

Allenes have drawn tremendous interests in the area of synthetic organic chemistry due to their various reactivity patterns as a result of their unique chemical properties. Indeed, the past few decades have seen an exponential growth in allene chemistry.[1] The synthetic potential of allenes in regio- and stereoselective C–C and C–X bond-forming transformations and unique axis-to-center chirality transfers, and the occurrence of allenic structures in a variety of natural products and pharmacologically active compounds, have generated interest from organic and medicinal chemists. Thus, the synthesis of allenes has recently become a hot research topic.[2] The classical reaction types (addition, elimination, substitution, and rearrangement) have been applied to obtain allenes, and, in particular, transition metal-catalyzed reactions have been well developed. Important allenic compounds are allenic esters, as efficient synthons widely used in organic synthesis,[3] thus, much effort has been made to acquire allenic esters.[4] However, reports on the synthesis of allenic esters by Lewis base catalyzed reactions are rare. The relevant studies are on base-promoted alkyne isomerization[5] and Lewis base catalyzed intramolecular 1,4-addition of conjugated enynes.[6] More recently, our group has reported the Lewis base catalyzed reactions of cyclopropenones to allenic esters.[7]

Axially chiral allenes have been widely applied in modern organic chemistry, which has motivated many chemists to seek simple and efficient methods to obtain them.[8] The strategies for the synthesis of axially chiral allenes have mainly focused on the following three aspects: 1) Central-to-axial chirality transfer is the prevailing method by metal catalysis in the presence of Cu,[9] Zn,[10] Pd,[11] Rh,[12] Zr,[13] Li,[14] Au,[15a] or Ag,[15b] and by the *ortho*-Claisen rearrangement[16] or the Mitsunobu reaction.[17] 2) Central-to-axial chirality transfer can also be achieved by the kinetic resolution of racemic compounds[18] or enzymatic desymmetrization of prochiral allenic diols.[19] 3) Direct asymmetric synthesis can proceed by the introduction of stoichiometric chiral reagents,[20] transition metal catalysis with Pd[21a–i] or Cu,[21j] or organic compound-directed catalysis,[5,22] in which the dynamic kinetic asymmetric transformation (DYKAT) protocol has been applied.[21d] Of these strategies for the asymmetric synthesis of allenes, the DYKAT strategy[23] attracted our attention because the DYKAT and related dynamic kinetic resolution[24] strategies have proven to be a powerful in asymmetric synthesis as they can efficiently transform racemic starting materials into a single stereoisomeric product.[25,26]

Based on our aforementioned observations of Lewis base catalyzed reactions of cyclopropenones towards racemic allenic esters,[7] we tried to further develop their asymmetric variant to produce axially chiral allenic acetates by using multifunctional chiral phosphines.[27] As a part of our continued interest in Lewis base mediated reactions, we systematically investigated reactions of cyclopropenone derivatives **1**, which were prepared from propargyl esters with a variety of nucleophiles in the presence of commonly used Lewis bases (see Table S0 in the Supporting Information) and explored their asymmetric variant. For comparison, the reactions of a series of cyclopropenones with various nucleophiles in the presence of commonly used Lewis bases to generate acrylate and acrylic acid derivatives were also investigated (for details, see Schemes S1

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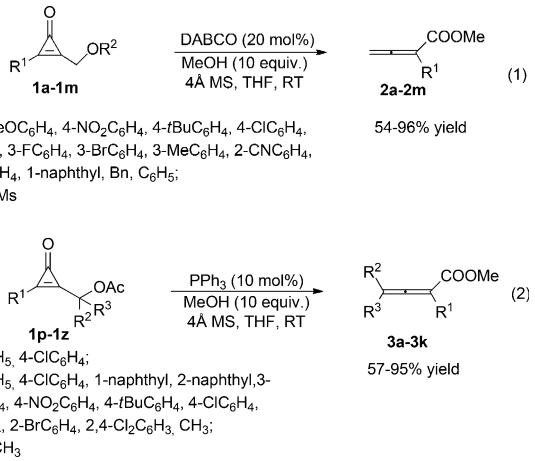
and S2). Herein, we report a novel method for the synthesis of allenic esters through Lewis base catalysis and its asymmetric variant by a DYKAT process, with detailed mechanistic studies.

Results and Discussion

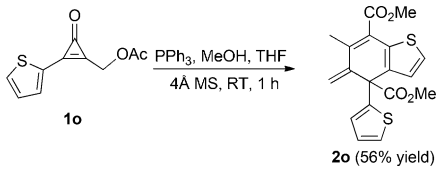
Reaction scope of Lewis base catalyzed reactions of cyclopropenones

We have examined the scope and limitations of these 1,4-diazabicyclo-[2.2.2]-octane (DABCO)- and triphenylphosphine-catalyzed reactions with various cyclopropenones and methanol, the results of which are summarized in Scheme 1 (for further



Scheme 1. Lewis base catalyzed reactions of **1** with MeOH. Ms = mesyl.

details, see the Supporting Information). With DABCO as catalyst, a variety of cyclopropenone derivatives (**1a**–**1m**) with either electron-donating or withdrawing groups as substituents on the 2-, 3-, or 4-position of the benzene ring underwent the reactions smoothly, affording the corresponding products **2a**–**2m** in moderate to high yields (54–96%) [Scheme 1, Eq. (1); for further details, see the Supporting Information]. Compared with nitrogen-centered Lewis bases such as DABCO, phosphorus-centered Lewis bases such as triphenylphosphine are more nucleophilic, leading to higher catalytic activities for this type of reaction. With triphenylphosphine as catalyst, a variety of cyclopropenone derivatives (**1p**–**1z**) with either electron-donating or withdrawing groups as substituents on the 2-, 3-, and/or 4-positions of the benzene ring underwent the reactions smoothly, affording the corresponding products **3a**–**k** in moderate to high yields (57–95%) [Scheme 1, Eq. (2); for further details, see the Supporting Information]. The structure of **2** has been unambiguously determined by performing X-ray diffraction of **2j**. The ORTEP drawing and its CIF data are presented in the Supporting Information.[28a] With compound **1o** (R^1 = 2-thienyl group) as substrate, the reaction did not occur under the optimal reaction conditions. Surprisingly, with triphenylphosphine as catalyst, the reaction could take place, albeit affording an abnormal product **2o** in 56% yield as the sole regioisomer (Scheme 2). The structure of **2o** has been unambiguously determined by using X-ray diffraction. The ORTEP drawing and its CIF data are presented in the Supporting Information.[28b] A plausible mechanism for the formation of **2o** is proposed in Scheme S3.



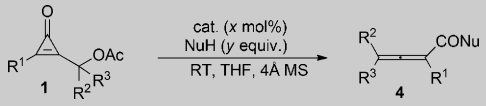
Scheme 2. PPh_3-catalyzed reaction of (3-oxo-2-(thiophen-2-yl)cycloprop-1-enyl)methyl acetate **1o** with MeOH.

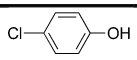
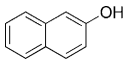
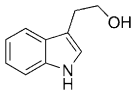
Next, we continued to investigate the reactions of cyclopropenone derivatives **1** with a variety of substituted phenols and alcohols. The results are presented in Table 1. The reaction of substrate **1e** with substituted phenols proceeded smoothly with a catalytic amount of DABCO in THF at room temperature, affording the corresponding products **4a** and **4b** in 91 and 84% yields, respectively (Table 1, entries 1 and 2). With R^2 = 2-BrC_6H_4, the reaction also worked well with a catalytic amount of triphenylphosphine and the corresponding product **4c** was produced in 92% yield (entry 3). A series of alcohols such as aromatic, heteroaromatic, or aliphatic alcohols were also tested and the corresponding products **4d**–**i** obtained in moderate to high yields (63–97%; entries 4–9). Notably, the reaction of substrate **1w** with benzyl alcohol had to be catalyzed by highly nucleophilic tributylphosphine (20 mol%), otherwise no reaction could take place, presumably due to the inert reactivity of **1w** necessitating a highly nucleophilic catalyst to prompt the reaction (entry 9).

Investigations on the asymmetric variant

In view of our results on the Lewis base catalyzed reactions of cyclopropenone derivatives with methanol, the next logical step was to investigate the asymmetric reaction by using chiral bases. Initial examination was performed by using cyclopropenone **1q** (R^2 = 4-ClC_6H_4, 1.0 equiv) and nucleophile methanol (5.0 equiv) in the presence of a catalytic amount of various chiral mono- or biphosphines and chiral multifunctional phosphines. The results are summarized in Table 2. Use of chiral phosphine **CP1** or **CP4** as the catalyst (mono- or biphosphine) resulted in low yields and *ee* values or even no desired product. If the catalyst was **CP2** or **CP3** (with phosphine and hydroxy substituents), the reaction proceeded smoothly, affording the corresponding product **5a** in 62 and 66% yields, respectively, but with poor enantioselectivities. We also screened phosphine- and amide-substituent catalysts **CP6**–**CP9** (bi- and multi-functional phosphines) and found that only **CP9** furnished the product, in 71% yield and 40% *ee*. Moreover, we examined phosphine- and thiourea/urea-substituent catalysts such as **CP5** and **CP10**–**CP14** (multifunctional phosphines) and

Table 1. Lewis base catalyzed reactions of cyclopropenone derivatives **1** with different nucleophiles (phenols or alcohols).



Entry	$R^1/R^2/R^3$	Catalyst	NuH	x	y	t [h]	Yield[a] [%]
1	4-ClC_6H_4/H/H (**1e**)	DABCO		20	5	0.5	**4a** (91)
2	4-ClC_6H_4/H/H (**1e**)	DABCO		20	2	1.0	**4b** (84)
3	C_6H_5/2-BrC_6H_4/H (**1t**)	PPh_3		10	2	3.0	**4c** (92)
4	4-ClC_6H_4/H/H (**1e**)	DABCO	BnOH	20	5	1.0	**4d** (90)
5	3-BrC_6H_4/H/H (**1h**)	DABCO		20	5	12.0	**4e** (68)
6	3-BrC_6H_4/H/H (**1h**)	DABCO		20	2	5.0	**4f** (97)
7	3-MeC_6H_4/H/H (**1i**)	DABCO		20	2	4.0	**4g** (87)
8	C_6H_5/4-ClC_6H_4/H (**1q**)	PPh_3		10	5	1.0	**4h** (74)
9	C_6H_5/$(CH_2)_5$/H (**1w**)	PBu_3	BnOH	20	5	5.0	**4i** (63)

[a] Isolated yield.

found that **CP14** gave the best results, providing the desired product in 80% yield and 57% *ee*.

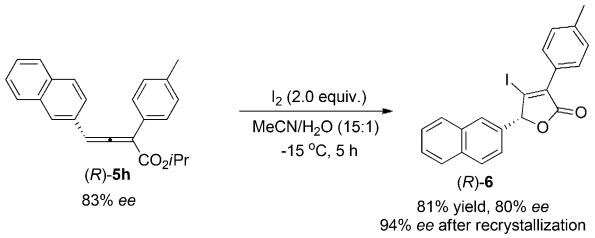
Subsequently, we switched substrate **1q** to **1r** with a sterically more bulky naphthyl group and screened a series of amino acid-derived phosphine catalysts **CP14**–**CP18** in the same reaction under the standard conditions. We identified that the catalyst **CP14** gave the best performance. The reaction should be performed in toluene in the presence of 20 mol% **CP14** at room temperature for 2.0 h, providing the desired product **5b** in 70% yield with 71% *ee* (Table 2). Notably, use of the racemic substrate could give the product in a yield of over 50%, beyond the limit of the theoretical yield for a traditional kinetic resolution process, indicating that this could be a DYKAT process.[23c] To gain a better understanding, we performed several control experiments and theoretical investigations, as discussed later in the mechanistic studies.

In the presence of **CP14**, we continued to examine solvent effects and the reaction temperature influences for this reaction, the results of which are given in Table 3. Toluene emerged as the solvent of choice (Table 3, entries 1–9) and reducing the reaction temperature to 0 °C and −10 °C did not improve the enantioselectivities under otherwise identical conditions (entries 10 and 11). If the catalyst loading was reduced to 10 mol%, the yield and *ee* of **5b** decreased remarkably (entry 12).

After identifying the optimized reaction conditions, we examined the generality of the reaction by using cyclopropenone derivatives **1** (R = H: **1r**, R = 4-Br: **1aa**, R = 4-Me: **1bb**, R = 3-Me: **1cc**) and several nucleophiles such as isopropanol, benzyl alcohol, 4-bromobenzyl alcohol, and ethanol. The results are summarized in Table 4. The corresponding products **5c–i** were obtained in moderate to good yields with good *ee* values (entries 1–7). The highest *ee* obtained was 83% (entry 6). 2,3-Allenoate ((*R*)-**5h**) could be converted to the corresponding iodobutenolide (*R*)-**6** by iodolactonization with iodine (Scheme 3).[11f,29] The absolute configuration of (*R*)-**6** was determined by an X-ray diffraction study (Figure 1). Based on this result, we assigned the absolute configuration *R* to product **5**.[11a,f] The CIF data of (*R*)-**6** are presented in the Supporting Information.[28c]

Mechanistic studies

A plausible mechanism for this reaction is suggested in Scheme 4. The transformation is believed to proceed through the conjugate addition of Lewis base to cyclopropenone, affording zwitterionic intermediate **I1**, which undergoes ring-opening to give a ketene intermediate **I2**. Subsequently, the ketene intermediate **I2** reacts with methanol to afford the ion pair **I3**, which releases the catalyst to give the final product **2**. ^{31}P NMR tracing experiments were first performed to investigate the mechanism (for further details, see the Supporting Information). With triphenylphosphine as the catalyst, the ^{31}P NMR spectroscopic data of triphenylphosphine showed a signal at $\delta = -4.62$ ppm (Figure 2). On addition of substrate **1r** to the NMR tube, three new signals appeared at $\delta = +18.93, +28.89,$



Scheme 3. Iodolactonization of 2,3-allenoate.

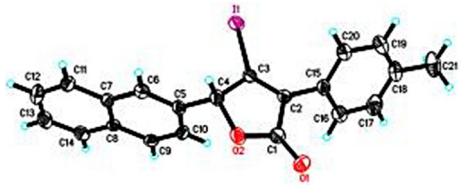
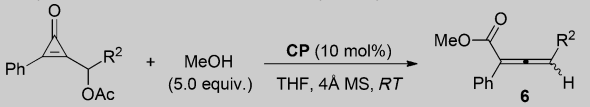


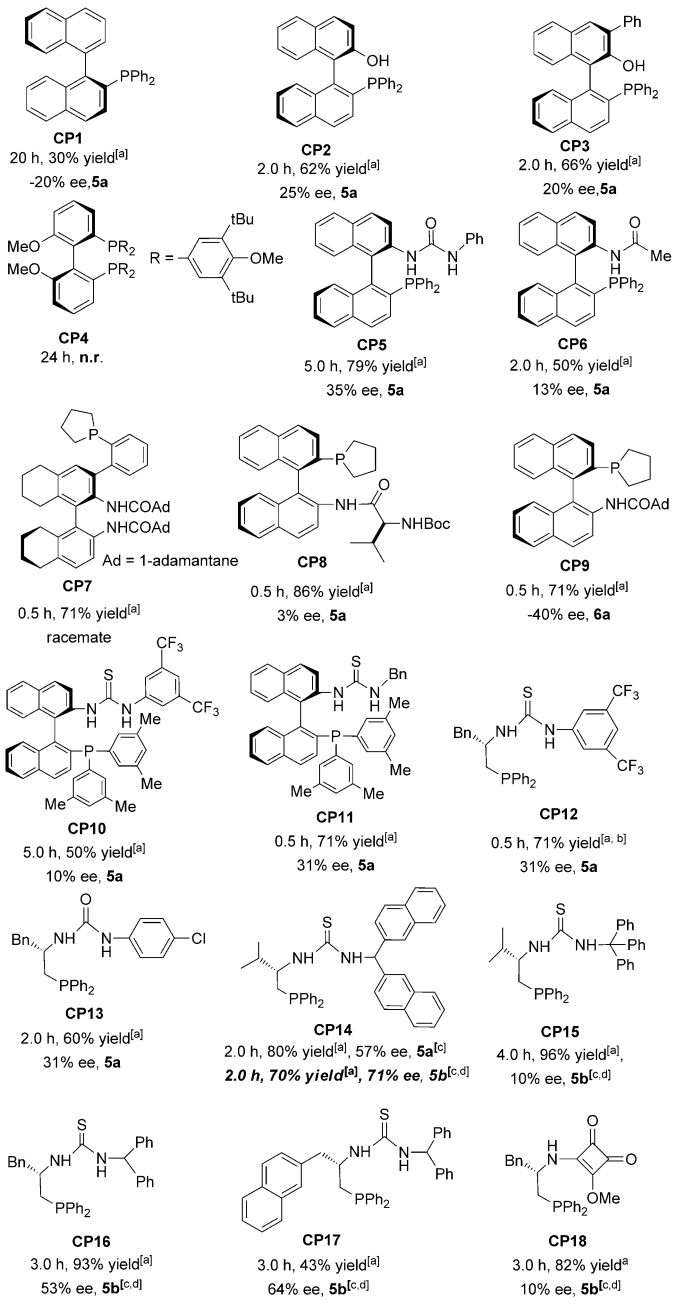
Figure 1. ORTEP drawing of (*R*)-**6**.

Table 2. Reactions of cyclopropenones with MeOH catalyzed by chiral phosphines.



1q, R^2 = 4-ClC_6H_4 (1.0 equiv.);
1r, R^2 = 2-naphthyl (1.0 equiv.)

R^2 = 4-ClC_6H_4, Product: **5a**
R^2 = 2-naphthyl, Product: **5b**

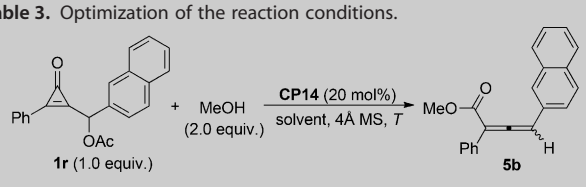


[a] Isolated yield. [b] $T = -20\,^{\circ}C$. [c] Catalyst loading = 20 mol%. [d] Toluene as reaction solvent.

and +29.07 ppm after 5 min (Figure 2a–c). Previously, the ^{31}P NMR signal of triphenylphosphine oxide had been measured at $\delta = +30.6$ ppm.[30] Therefore, none of these new signals corresponded to triphenylphosphine oxide but could be assigned to the in situ-generated zwitterionic intermediate **I1**, ketene intermediate **I2**, and ion pair **I3** proposed in Scheme 4. Lengthening the measurement time, signal a at $\delta = +18.90$ ppm gradually disappeared and the intensity of the signals at $\delta = +28.89$ and +29.07 ppm did not change significantly. These ^{31}P NMR tracing experiment results indicated that several equilibria existed in the catalytic cycle. Subsequently, one intermediate formed by the addition of triphenylphosphine to **1q** was also detected by using LC–MS ($[M+H]^+ = 575.0$; see the Supporting Information), which could be the intermediate **I1** or **I2** suggested in Scheme 4.

To understand the detailed mechanism for the formation of product **2** catalyzed by Lewis base, we also theoretically investigated the reaction pathways catalyzed by DABCO and triphenylphosphine (for details, see the Supporting Information).[31] All calculations were performed at the mPW1K/6-31 + G(d,p)//mPW1K/6-31G(d) level of theory on the Gaussian 09 program.[32] The relative energies of all intermediates and transition states along the reaction pathway catalyzed by DABCO are shown in Scheme 5. Initially, the addition of catalyst DABCO to compound **1a** led to the formation of zwitterionic intermediate **I4**. The cyclopropene ring-opening resulted in intermediate **I5** through transition state **TS1** with an energy barrier of 11.0 kcal mol^{-1}. Then, the OAc group left via transition state **TS2** with a small energy barrier of 0.1 kcal mol^{-1} to give the contact ion pair **I6**. The methanol was bonded to give complex **I7**. Passing through transition state **TS3** with an energy barrier of 2.1 kcal mol^{-1} afforded the corresponding intermediate **I8**. Subsequently, the catalyst DABCO was eliminated through transition state **TS4**, leading to the complex of product **2**. An alternative reaction

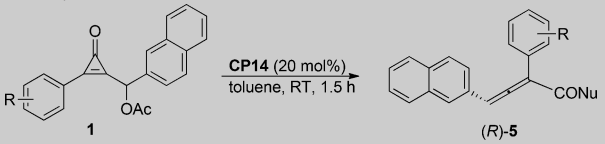
Table 3. Optimization of the reaction conditions.

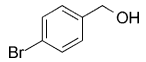


Entry	Solvent	T [°C]	t [h]	Yield[a] [%]	ee[b] [%]
1	toluene	RT	2.0	70	71
2	*p*-xylene	RT	3.0	68	62
3	1,4-dioxane	RT	12.0	32	53
4	benzene	RT	5.0	46	58
5	CH_2Cl_2	RT	2.0	53	56
6	MeCN	RT	5.0	80	6
7	methyl *tert*-butyl ether	RT	7.0	67	59
8	fluorobenzene	RT	2.0	73	61
9	trifluoromethylbenzene	RT	5.0	60	55
10	toluene	0	12.0	53	70
11	toluene	−10	24.0	30	67
12[c]	toluene	RT	4.0	60	65

[a] Isolated yield. [b] Determined by using chiral HPLC. [c] Catalyst loading = 10 mol%.

Table 4. Multifunctional chiral phosphine **CP14**-catalyzed reactions of various cyclopropenones **1** with different nucleophiles.



Entry	R	NuH	Yield[a] [%]	ee[b] [%]
1	H (**1r**)	*i*PrOH	76 ((*R*)-**5c**)	82
2	H (**1r**)	BnOH	74 ((*R*)-**5d**)	82
3	H (**1r**)		84 ((*R*)-**5e**)	75
4	4-Br (**1aa**)	*i*PrOH	81 ((*R*)-**5f**)	77
5	4-Me (**1bb**)	EtOH	82 ((*R*)-**5g**)	82
6	4-Me (**1bb**)	*i*PrOH	77 ((*R*)-**5h**)	83
7	3-Me (**1cc**)	*i*PrOH	64 ((*R*)-**5i**)	81

[a] Isolated yield. [b] Determined by using chiral HPLC.

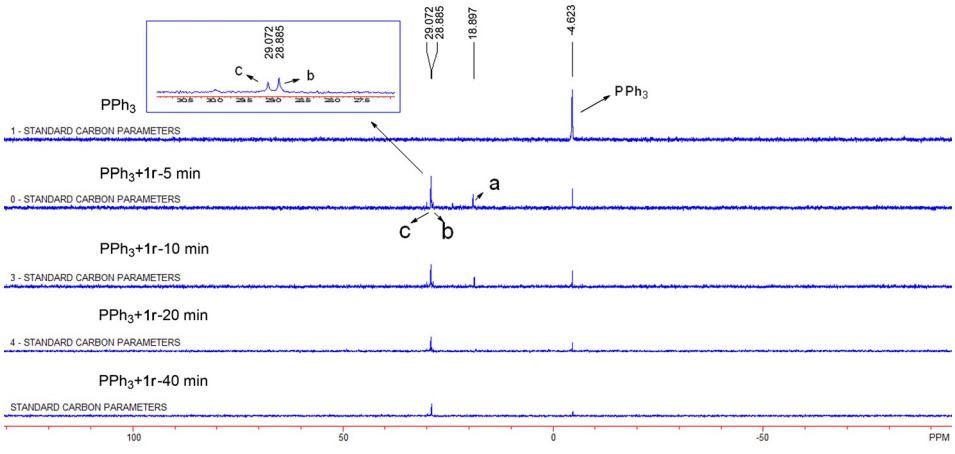
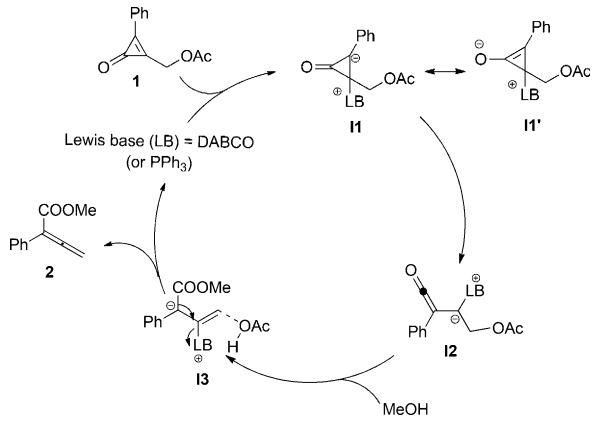


Figure 2. ^{31}P NMR tracing experiments.



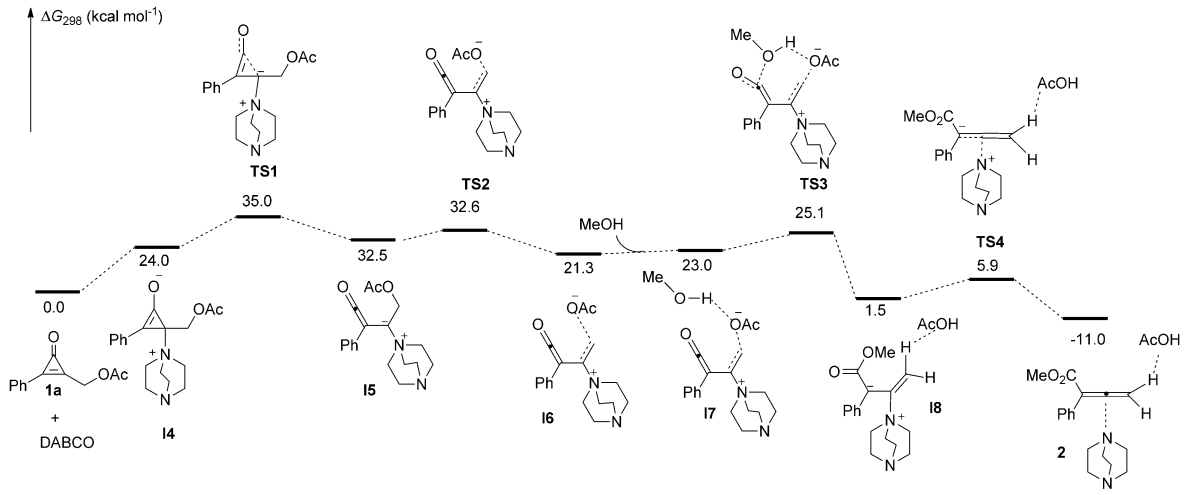
Scheme 4. Plausible reaction mechanism.

pathway catalyzed by DABCO was also investigated theoretically (for details, see the Supporting Information), however, it involved a couple of steps with high energy barriers.

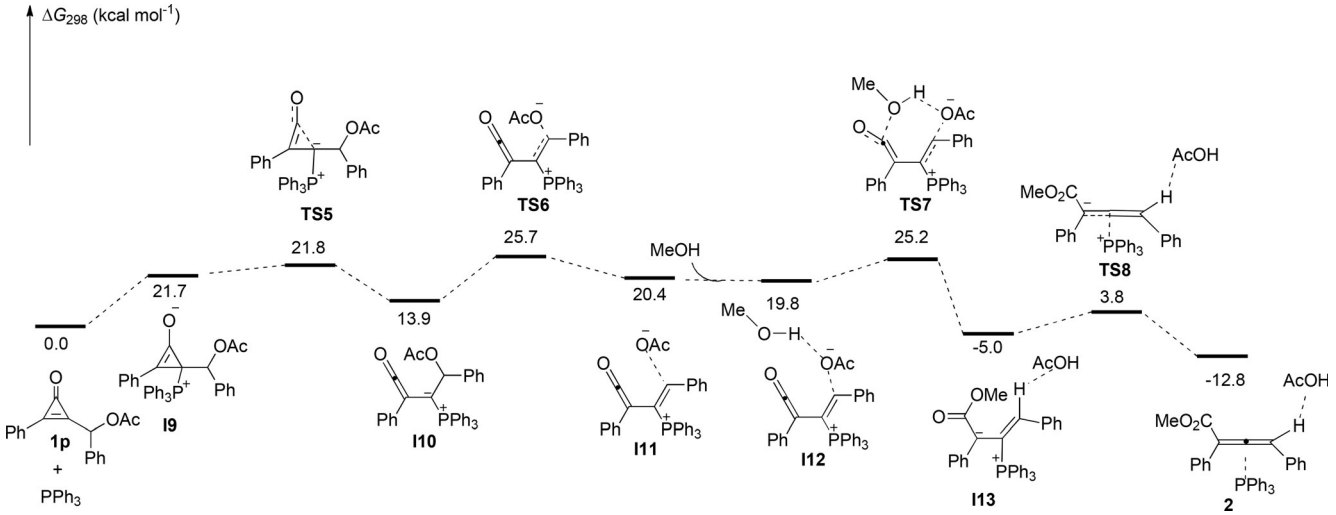
In the same manner, the relative energies of all intermediates and transition states along the reaction pathway catalyzed by triphenylphosphine were calculated, the results of which are shown in Scheme 6. The catalyst triphenylphosphine was first added to compound **1p**, leading to the zwitterionic intermediate **I9**. The cyclopropene ring-opening resulted in the intermediate **I10** via transition state **TS5** with a low energy barrier of 0.1 kcal mol^{-1}, indicating that the cyclopropene ring-opening step was much more facile with the phosphine catalyst. Notably, the OAc group leaving step with triphenylphosphine catalyst was more difficult than with DABCO as catalyst, as this step passed through transition state **TS6** with an energy barrier of 11.8 kcal mol^{-1} to give the contact ion pair **I11**. The methanol was bonded to give complex **I12**. Passing through transition state **TS7** with an energy barrier of 5.4 kcal mol^{-1} afforded the corresponding intermediate **I13**. Subsequently, the catalyst triphenylphosphine was eliminated through transition state **TS8**, leading to the complex of product **2**. The calculation results provided theoretical evidences for the reaction pathway suggested in Scheme 4. Notably, both tertiary amine and phosphine can catalyze this type of reaction, however, their catalytic properties have differences.

The DYKAT process

As described above, the asymmetric reaction of racemic substrate **1** with a nucleophile catalyzed by a chiral phosphine could be a DYKAT process. To gain a better understanding, we performed the following control experiments, the results of which are summarized in Table 5. The first examination was performed by using racemic



Scheme 5. DFT studies on the DABCO-catalyzed reaction pathway.



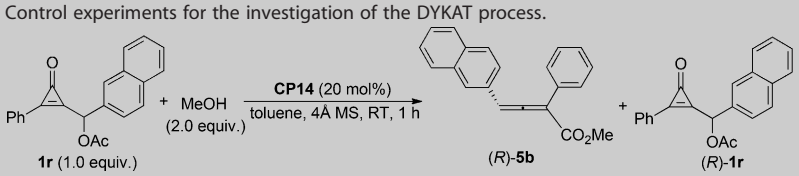
Scheme 6. DFT studies on the PPh_3-catalyzed reaction pathway.

cyclopropenone **1r** (1.0 equiv) as the starting material in the presence of 20 mol% **CP14** at room temperature. After 1 h, the reaction mixture was purified by using silica gel column chromatography to afford the desired product (*R*)-**5b** in 67% yield and 70% *ee* and the recovered starting material (*R*)-**1r** in 18% yield and 27% *ee* (entry 1). The same procedure performed by using (*R*)-**1r** and (*S*)-**1r** as starting material, respectively, gave the desired product (*R*)-**5b** in 67% yield and 85% *ee* and the recovered starting material (*R*)-**1r** in 24% yield and 42% *ee* (entry 2), and (*R*)-**5b** in 73% yield and 69% *ee* and the recovered starting material (*R*)-**1r** in 21% yield and 23% *ee* (entry 3). The experimental results show that the stereoselectivity of final product does not depend on the configuration of the chiral center in the starting material, and provides evidence that the asymmetric reaction of racemic substrate **1** with nucleophile catalyzed by **CP14** is indeed a DYKAT process.

Based on the control experiments and the aforementioned theoretical studies, we suggest that the reaction proceeds by a DYKAT process, as shown in Scheme 7. The key intermediate shown originates from racemic starting material that loses its chiral center, thus, the stereoselectivity solely depends on the subsequent step in the presence of chiral phosphine catalyst. Therefore, this is a very special DYKAT process in which the stereochemical properties of the starting material are not transferred to the product.

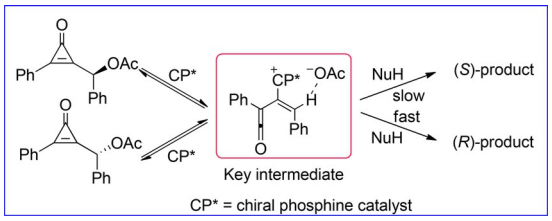
To check the detailed mechanism for the asymmetric reaction by a DYKAT process catalyzed by chiral phosphine catalyst, we also theoretically investigated the reaction pathway catalyzed by **CP14**. All calculations were performed at the mPW1K/6-31+G(d,p)//mPW1K/6-31G(d) level of theory with the Gaussian 09 program.[32] The relative energies of all intermediates and transition states along the reaction pathway catalyzed by **CP14** are shown in Scheme 8. The absolute configurations of the dia-

Table 5. Control experiments for the investigation of the DYKAT process.



Entry	Starting material	(*R*)-**5b**		(*R*)-**1r**	
		Yield[a] [%]	*ee*[b] [%]	Yield[a] [%]	*ee*[b] [%]
1	*rac*-**1r**	67	70	18	27
2	(*R*)-**1r**	67	85	24	42
3	(*S*)-**1r**	73	69	21	23

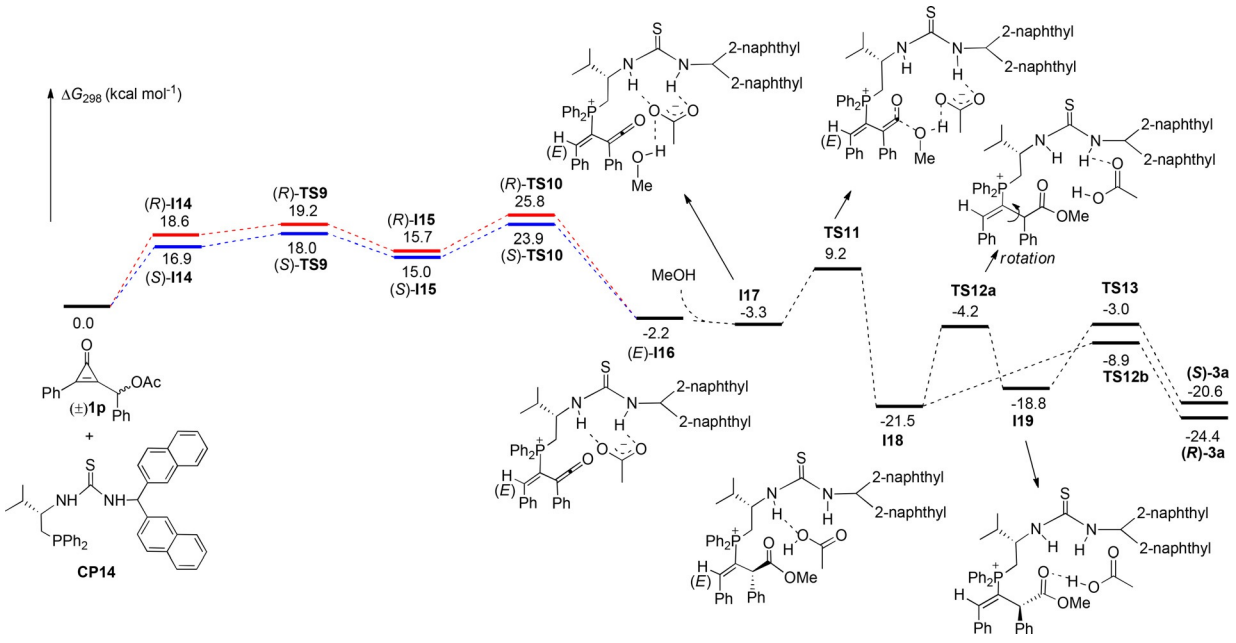
[a] Isolated yield. [b] Determined by using chiral HPLC.



Scheme 7. Proposed DYKAT process.

stereoisomeric transition states and intermediates were assigned according to the chiral center in **1p**, and those of the diastereoisomeric product complexes according to the allene moiety.

The calculated reaction pathway catalyzed by chiral phosphine catalyst **CP14** is similar to that catalyzed by triphenylphosphine (see Scheme 8). The chiral phosphine catalyst **CP14** firstly adds to the racemic compound **1p**, leading to the zwitterionic intermediate diastereomers (*R*)-**I14** and (*S*)-**I14**. These pass through their corresponding transition states (*R*)-**TS9** and (*S*)-**TS9** to the ring-opening intermediates (*R*)-**I15** and (*S*)-**I15** with energy barriers of 0.6 and 1.1 kcal mol^{-1}, respectively. Then, the OAc group leaving step passes through transition states (*R*)-**TS10** and (*S*)-**TS10** with energy barriers of 10.1 and 8.9 kcal mol^{-1}, respectively, to give the contact ion pair (*E*)-**I16** (*E* denotes the configuration of the C=C bond in **I16**). In these two steps, the intermediates and transition states with *S* configuration are always a few kcal mol^{-1} lower than those with *R* configuration and the barrier (8.9 kcal mol^{-1}) involving the *S* configuration is smaller than that involving the *R* configuration (10.1 kcal mol^{-1}) in the rate-determining step. These calculation results indicate that the starting material **1p** with *S* configuration reacts faster than that with *R* configuration, which accounts for the *R* configuration of the experimentally recovered starting material. The OAc group leaving step leads to an intermediate (*E*)-**I16** in which the chiral center is lost, thus, the stereoselectivity of final product does not depend on the configuration of the chiral center in the starting material. This result agrees with experimental findings. The methanol is bonded to the intermediate (*E*)-**I16** to give complex **I17**. Passing through transition state **TS11** with an energy barrier of 12.5 kcal mol^{-1} affords the corresponding intermediate **I18**. Subsequently, the chiral phosphine catalyst is eliminated



Scheme 8. DFT studies on the chiral phosphine-catalyzed reaction pathway.

through transition state **TS 12b** with an energy barrier of 12.6 kcal mol^{-1}, leading to the complex of product (*R*)-**3 a**. The intermediate **I 18** can go through a rotation transition state **TS 12a** with an energy barrier of 17.3 kcal mol^{-1} to reach intermediate **I 19**. Subsequently, the chiral phosphine catalyst is eliminated through transition state **TS 13** with an energy barrier of 18.5 kcal mol^{-1}, leading to the complex of product (*S*)-**3 a**. The energy of **TS 12b** is lower than that of **TS 13** by 5.9 kcal mol^{-1} owing to the hydrogen bonding interaction of the N–H moiety of the chiral phosphine, ester moiety, and acetic acid in **TS 12b** (for their structures, see Figure 3). Although there are hydrogen bonds between the N–H moiety of the chiral phosphine and ester moiety in **TS 13**, the steric repulsion between the phenyl moiety and naphthyl moiety in **TS 13** gives it a higher energy. Based on the calculation results, the product with *R* configuration should be acquired, which is in line with experimental findings.

Conclusions

We have investigated novel and interesting reactions of cyclopropenones with alcoholic nucleophiles catalyzed by Lewis bases, affording the corresponding allenic esters in moderate to high yields under mild conditions. We also found an interesting dynamic kinetic asymmetric transformation (DYKAT) of racemic cyclopropenones catalyzed by multifunctional chiral phosphine, affording the axially chiral allenic esters in moderate to good yields and *ee* values. A plausible reaction mechanism was proposed, based on our investigations by NMR tracing experiments, MS, and DFT calculations. The control experiments provided evidence that the asymmetric reaction of racemic cyclopropenones with nucleophile in the presence of chiral phosphine catalyst was indeed a DYKAT process. The theoretical investigations revealed the detailed mechanism of the DYKAT process for this reaction, showing it to be a special kind of DYKAT.

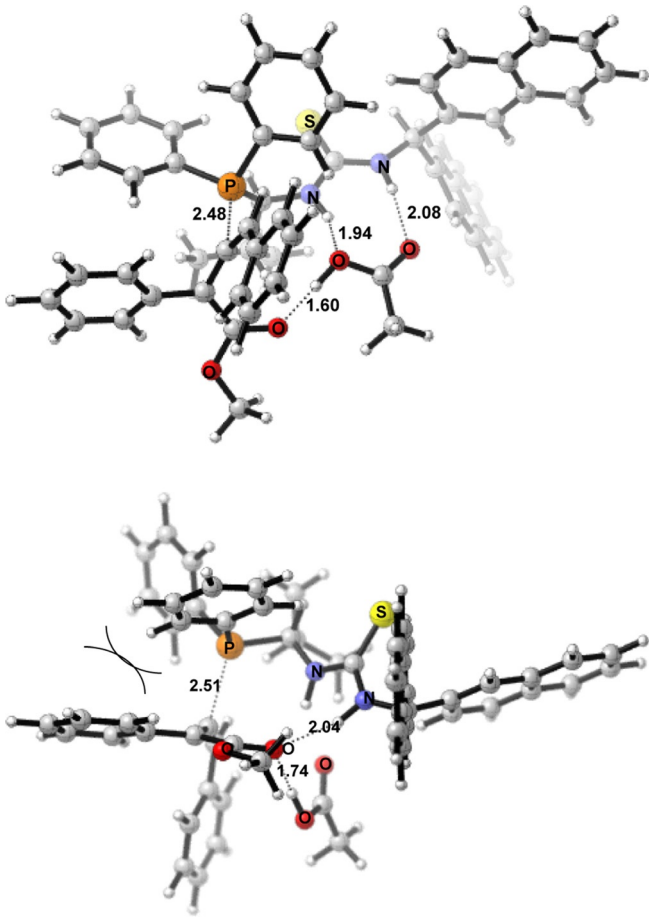


Figure 3. Optimized structures of **TS 12b** (top) and **TS 13** (bottom).

Experimental Section

General

^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer with solutions in $CDCl_3$ and TMS as internal standard; *J* values are shown in [Hz]. Mass spectra were recorded on a HP-5989 instrument (Agilent Technologies). All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (Na D line) by using a PerkinElmer-341 MC digital polarimeter; $[\alpha]_D$ values are given in [10 deg^{-1} cm^2 g^{-1}]. IR spectra were recorded on a PerkinElmer PE-983 spectrometer; absorptions are given in [cm^{-1}]. Chiral HPLC was performed on a Shimadzu SPD-10 A vp series with chiral columns (Chiralpak AD-H, IC-H columns 4.6× 250 mm, Daicel Chemical Ind., Ltd.). THF, toluene, and Et_2O were distilled from Na in an Ar atmosphere. CH_3CN, 1,2-DCE, and CH_2Cl_2 were distilled from CaH_2 in an Ar atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by using TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was performed by using 300–400 mesh silica gel at increased pressure.

Preparation of 2: General procedure: To a mixture of **1 a** (0.20 mmol, 46 mg), MeOH (10.0 mmol), DABCO (0.04 mmol, 5.0 mg), and 4 Å molecular sieves (50 mg) was added THF (2.0 mL) at RT (25 °C) under Ar. The reaction solution was monitored by using TLC. After the reaction was complete, the solution was concentrated under reduced pressure and the residue purified by using silica gel column chromatography [EtOAc/PE, 1:16] to give the target product **2 a** as a yellow oil (33 mg, 95 % yield).[33] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.50 (2 H, d, *J* = 7.2 Hz), 7.37–7.33 (2 H, m), 7.29 (1 H, d, *J* = 7.2 Hz), 5.42 (2 H, s), 3.83 ppm (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 215.6, 166.4, 131.9, 128.4, 128.3, 127.7, 102.8, 80.1, 52.4 ppm.

Preparation of 3: General procedure: To a mixture of **1 p** (0.20 mmol, 56 mg), MeOH (10.0 mmol), PPh_3 (0.02 mmol, 5.2 mg), and 4 Å molecular sieve (50 mg) was added THF (2.0 mL) at RT (25 °C) under Ar. The reaction solution was monitored by using TLC. After the reaction was complete, the solution was concentrated under reduced pressure and the residue purified by using silica gel column chromatography [EtOAc/PE, 1:16] to give the target product **3 a** as a yellow oil (46 mg, 92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.57 (2 H, d, *J* = 7.2 Hz), 7.39–7.24 (8 H, m), 6.82 (1 H, s), 3.83 ppm (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 214.6, 166.0, 133.8, 133.6, 132.0, 131.5, 129.0, 128.4, 128.3, 128.1, 128.0, 127.5, 106.4, 99.5, 52.5 ppm; IR (CH_2Cl_2): $\tilde{\nu}$ = 2961, 2926, 1720, 1598, 1493, 1466, 1434, 1260, 1216, 1092, 1018, 998, 798 cm^{-1}; MS: *m/z*

(%): 250 (51), 235 (13), 207 (14), 191 (100), 179 (10), 165 (13), 105 (23); HRMS (EI): *m/z*: calcd for $C_{17}H_{14}O_2$: 250.0994, found: 250.0995.

Preparation of 5: General procedure: To a mixture of **1r** (0.10 mmol, 33 mg), MeOH (0.20 mmol), **CP14** (0.02 mmol, 11.9 mg), and 4 Å molecular sieve (50 mg) was added toluene (1.0 mL) at RT (25 °C) under Ar. After the reaction was complete, the solution was concentrated under reduced pressure and the residue purified by using silica gel column chromatography [EtOAc/PE, 1:16] to give the target product **5b** as a white solid (21 mg, 70% yield). The *ee* of **5b** was determined to be 71% (determined by using HPLC, Chiralpak AD-H, *n*-hexane/isopropanol = 98:2, 0.4 mL min^{-1}, λ = 230 nm, t_{major} = 37.78 min, t_{minor} = 40.49 min). m.p. 101–103 °C; $[\alpha]_D = +42.2$ (c = 0.7, CH_2Cl_2).

Preparation of catalyst CP14: Under Ar, a mixture of (*S*)-1-(diphenylphosphino)-3-methylbutan-2-amine (**I**)[34] (0.2 mmol) and isothiocyanate (0.4 mmol) in CH_2Cl_2 (2.0 mL) was stirred at RT. After the starting compound was consumed, the solvent was removed under reduced pressure and the residue chromatographed on silica gel [elution with PE/EtOAc = 10:1–6:1] to give the catalyst.

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