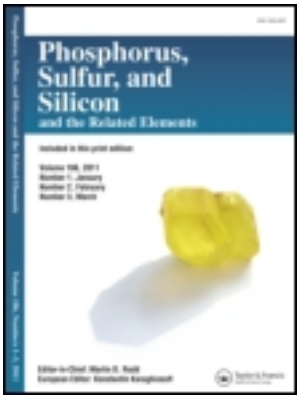

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SYNTHESIS OF CHIRAL PHOSPHORUS REAGENTS AND THEIR APPLICATION IN COMBINATION WITH LEWIS ACID AS A COCATALYST IN MORITA–BAYLIS–HILLMAN REACTION

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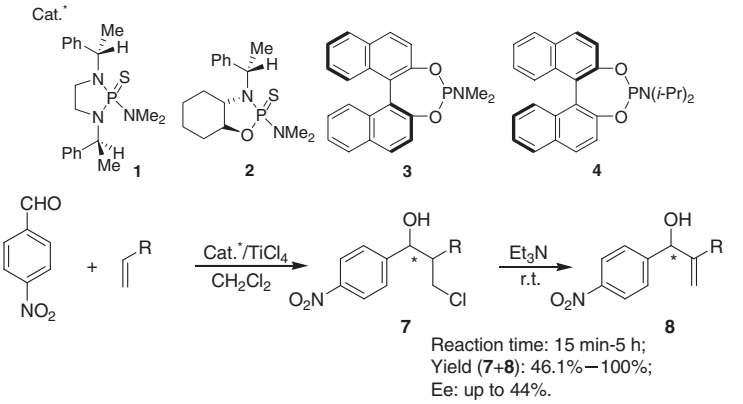
GRAPHICAL ABSTRACT



Abstract *Two novel chiral thiophosphoramides and two chiral phosphoramidites were synthesized starting from (S)-α-phenylethylamine and (R)-(+) or (S)-(−)-1,1′-Bi-2-naphthol (BINOL), respectively, and their application in combination with Lewis acid as cocatalysts in asymmetric Morita–Baylis–Hillman (MBH) reaction was investigated. Dramatic rate acceleration (the corresponding adducts were obtained in fair to excellent chemical yield within 15 min–5 h) was observed in these chiral phosphorus reagents/Lewis acid cocatalyzed MBH reaction between 4-nitrobenzaldehyde and activated alkenes, and in one case, moderate enantioselectivity was achieved (the corresponding adduct's ee value is 44%).*

Keywords Activated alkenes; chiral phosphoramidites; chiral thiophosphoramides; Morita–Baylis–Hillman reaction; 4-nitrobenzaldehyde

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INTRODUCTION

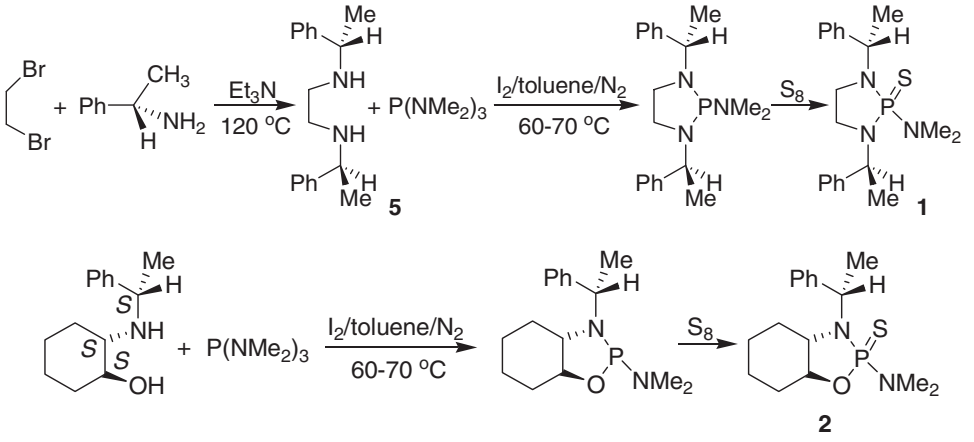
The Morita–Baylis–Hillman reaction (MBH) is an effective carbon–carbon bond forming reaction between an aldehyde or imine and an enone to generate densely multifunctional adducts, secondary chiral alcohols, or amines under mild conditions.[1] Because of its enormous potential in organic synthesis, it has received much research interest.[2,3] It is known that the major problem of this reaction is its slow reaction rate (often days), and numerous physical and chemical methods have been developed to accelerate the reaction with some good results.[4–6] Of these methods, chemical methods have the advantage of not requiring specialized equipment, and so are more attractive. Kisanga and Verkade[7] reported a new type of three-coordinate phosphorus-catalyzed MBH reaction in combination with $TiCl_4$. It was found that in the catalytic system, the reaction was greatly accelerated and afforded the corresponding adducts in 5 min in good yields (88%–93%). Subsequently, they[8] reported that several four-coordinate phosphorus thiophosphoramides catalyzed MBH reaction, which also achieved good results, and the reaction was finished within 10 min in 88%–94% yields. Although many chiral organo catalysts have been developed to successfully catalyze several versions of the MBH reaction with high enantioselectivity, the rate of conversion is still typically in the days range.[9,10] Inspired by Verkade's work, we envisioned that in the situation of chiral phosphorus reagent/Lewis acid cocatalystic system, the Lewis acid would activate the carbonyl group, and the chiral phosphorus compound would function as a Lewis base to activate the alkenes. Then, the chiral cocatalystic system can not only overcome the drawback of slow reaction rate of MBH reaction but also realize asymmetric induction of MBH reaction and achieve good enatioselectivity. So, we report here the synthesis of four chiral phosphorus reagents and their application as a catalyst in asymmetric MBH reaction in combination with Lewis acid $TiCl_4$ or BF_3 Et_2O.

RESULTS ANS DISCUSSION

Synthesis of Catalysts

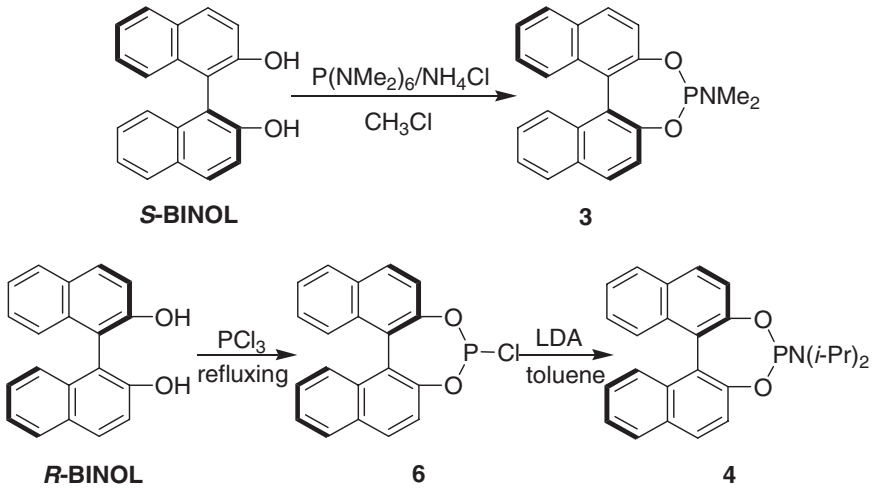
The synthetic methods of compounds **1**, **2** are very similar. We explored the synthetic methods using compound **1** as the representative. First, we wished to achieve the target directly through cyclization by using *N,N*-dimethylphosphorothioate dichloride and diamine **5**[11] in the presence of acid binding agents, but we failed. No target compound was obtained either when using pyridine or dimethylaminopyridine as the base. There may be two reasons for the reaction being difficult to carry out: larger steric hindrance of diamine and inadequate activity of *N,N*-dimethyl phosphorothioate dichloride. We then attempted another method. Under an inert atmosphere, diamine and hexamethylphosphorustriamide[12] tended to produce the intermediate, three-coordinate phosphorous amide, and then compound **1** was got through oxidation of the intermediate by sulfur. After 4-day refluxing, we found that most intermediate were oxidized by O_2 (^{31}P NMR, δ 11.33 ppm). To avoid the oxidation by O_2, we adopted the method of condensation between activated hexamethylphosphorustriamide by I_2 and diamine **5**, which greatly shortened the reaction time and decreased the reaction temperature. Finally we succeeded in synthesizing the target compound **1** with good yield (Scheme 1). Accordingly, in the same manner, we achieved compound **2** (Scheme 1).

Following the literature procedure,[11] compound **3** was easily synthesized through condensation of BINOL and hexamethylphosphorustriamide with high yield (Scheme 2). On the basis of compound **3,** we first tried to get compound **4** by adding diisopropylamine



Scheme 1

into the reaction mixture of **3** but failed. Subsequently, phosphorous chloride was synthesized and reacted with diisopropylamine in the presence of acid binding agents, but no product was obtained either. Lastly, we applied lithium diisopropylamide as the nucleophilic reagent and synthesized compound **4** finally[13] (Scheme 2).

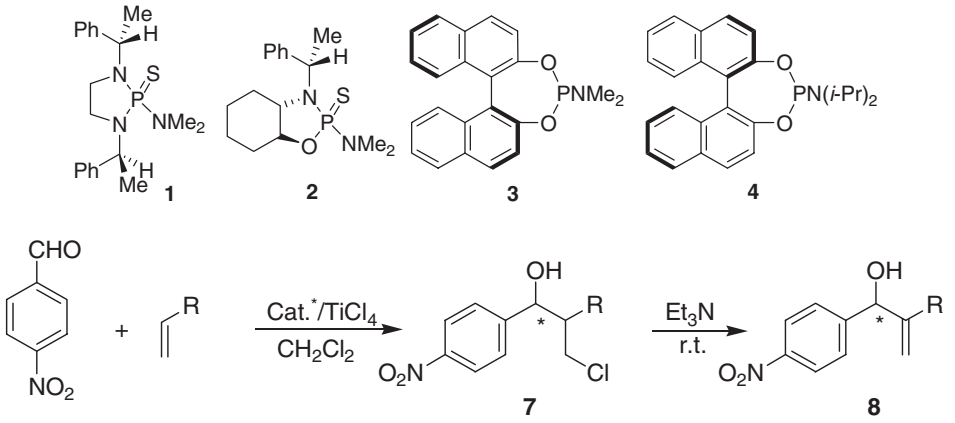


Scheme 2

Catalyst Evaluation

With these chiral phosphorus reagents in hand, we then carried out the asymmetric MBH reaction between 4-nitrobenzaldehyde and activated alkenes, employing the phosphorus reagents as the catalysts in combination with Lewis acid.

Table 1 $TiCl_4$/chiral phosphorus reagent catalyzed MBH reaction between 4-nitrobenzaldehyde and activated alkene



Entry	R	Catal.	Temp. (°C)	Time (h)	Yield (%) 7	Yield (%) 8	$[\alpha]_D^{20a}$
1	$COCH_3$(**a**)	**1**	r.t.	15 min	22.7	34.1	**7**, 0; **8**, 0
2	$COCH_3$(**a**)	**1**	0	1	35.5	43.2	**7**, 0; **8**, 0
3	$COCH_3$(**a**)	**1**	−78	3	32.4	40.2	**7**, 0; **8**, 0
4	CN(**b**)	**1**	0	4	25.2	28.1	**7**, 0; **8**, 0
5	CHO(**c**)	**1**	0	5	51.1[b]		0
6	$COCH_3$(**a**)	**2**	r.t.	15 min	25.3	32.9	**7**, 0; **8**, 0
7	$COCH_3$(**a**)	**2**	0	1	40.7	45.1	**7**, 0; **8**, 0
8	$COCH_3$(**a**)	**2**	−78	3	46.1	46.2	**7**, 0; **8**, 0
9	CN(**b**)	**2**	0	4	28.2	30.1	**7**, 0; **8**, 0
10	CHO(**c**)	**2**	0	5	65.5[b]		0
13	$COCH_3$(**a**)	**3**	0	4	88.8[b]		−5.36 (44% ee)[c]
14	$COCH_3$(**a**)	**4**	0	5	100[b]		0
15	CO_2CH_3(**d**)	**3**	0	4	46.1[b]		0
16	CO_2CH_3(**d**)	**4**	0	4	55.0[b]		0

[a]Measured by using a 1 g/100 mL concentration solution in chloroform.

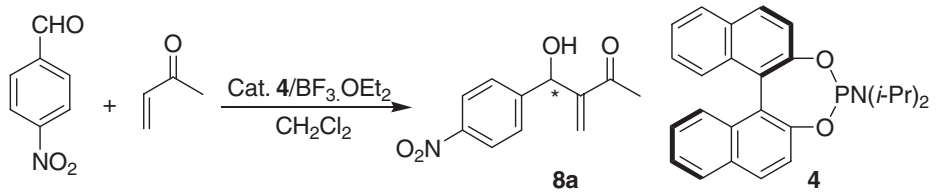
[b]The normal MBH adducts was obtained by the treatment of the reaction mixture with triethylamine.[4b,14]

[c]Enantiomeric excess and the absolute configuration *R* were deduced by compared the specific rotation with literature.[15]

First, we investigated the catalytic activity of the phosphorus compounds with $TiCl_4$ in asymmetric MBH reaction in dichloromethane using 10 mol% chiral phosphorus reagents and $TiCl_4$. The results are summarized in Table 1.[14,15]

As shown in Table 1, the cocatalytic system of $TiCl_4$ and chiral phosphorus reagent dramatically accelerated the reaction. A mixture of chlorinated products and MBH adducts were obtained with high yield in a relatively short time. The elimination of chlorinated products to normal MBH adducts in the separation process resulted in the higher yield of normal MBH adducts to chlorinated products. The two products were obtained by column chromatography, but a single normal MBH adduct was obtained if using base such as triethylamine (TEA) in the work-up process. The catalytic activity of thiophosphoramide **2** is higher than **1** in the MBH reaction. Under the same conditions, the yield of the

Table 2 Chiral phosphorus reagent **4**/BF_3·OEt_2 catalyzed MBH reaction between 4-nitrobenzaldehyde and MVK



Entry	Cat. **4** (mol%)	Temp. (°C)	Time (h)	Yield (%)	$[\alpha]_D^{20a}$
1	10	0	4	24.4	−0.74 (6% ee)[b]
2	10	−78	4	25.2	0

[a]Measured by the using a 1 g/100 mL concentration solution in chloroform.

[b]Enantiomeric excess and the absolute configuration *R* were deduced by compared the specific rotation with literature.[15]

products catalyzed by thiophosphoramide **2** is always higher than that catalyzed by **1** (Entries 1–5 versus 6–10). Unfortunately, in these cocatalytic systems, the two chiral thiophosphoramides exhibited almost no chiral induction. However, it was gratifying that an enantioselectivity of 44% ee was observed in case of the binary catalyst system of chiral phosphoramidite **3** (Table 1, Entry 13). Generally, the MBH reaction took place well with good yield in the binary catalyst system of the chiral three-coordinate phosphorus reagents and $TiCl_4$. Especially in the MBH reaction of methyl vinyl ketone (MVK) with 4-nitrobenzaldehyde catalyzed by compound **4**, the corresponding addition product was achieved quantitatively (Entry 14, yield, 100%).

Except for $TiCl_4$, BF_3·OEt_2 could also be employed as the Lewis acid component in the chiral phosphorus reagent **4/**Lewis acid cocatalytic system. **4**/BF_3·OEt_2 cocatalyzed asymmetric MBH reaction of 4-nitrobenzaldehyde and MVK was preliminarily examined, and the results are listed in Table 2.

As illustrated in Table 2, the catalytic activity of catalyst system **4**/BF_3.OEt_2 was much lower than that of **4**/$TiCl_4$. Similarly, almost racemic MBH adduct was attained in this MBH reaction.

CONCLUSION

Two novel chiral thiophosphoramides and two chiral phosphoramidites have been synthesized starting from readily available chiral resources (*S*)-α-phenylethylamine, and (*R*)- or (*S*)-BINOL, respectively. These chiral phosphorus reagents have been successfully applied in combination with Lewis acid, such as $TiCl_4$ and BF_3·Et_2O, as cocatalysts for MBH reaction between 4-nitrobenzaldehydes and different activated alkenes. Although only a highest enantioselectivity of 44% ee was obtained, dramatic rate acceleration was obtained. In most cases, the corresponding adducts were obtained in fair to excellent chemical yield within 15 min–5 h.

EXPERIMENTAL

General: ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker AMX-300 or Varian 400 MHz instrument using TMS as an internal standard. Specific rotations were measured

with a Perkin-Elmer 341MC polarimeter. Enantiomeric excesses were determined with an HP-1100 instrument (chiral column; mobile phase: hexane/*i*PrOH). Elemental analyses were conducted with a Yanaco CHN Corder MT-3 automatic analyzer. Melting points were determined with a T-4 melting point apparatus and are uncorrected.

Synthesis of Catalysts Hexamethylphosphorustriamide

Hexamethylphosphorustriamde was prepared according to the literature procedure.[11] Yield, 37.2%, bp 72 °C/20 mmHg, n_D^{16} 1.4670.

N,N′-bis((*S*)-1-Phenylethyl)Ethane-1,2-Diamine 5

N,N′-bis((*S*)-1-Phenylethyl)Ethane-1,2-Diamine 5 was prepared according to the literature procedure.[12] Yield, 45.9%, bp 162 °C–164 °C/2 mmHg, n_D^{16} 1.5505, $[\alpha]_D^{20}$ −63.41(c 1, $CHCl_3$) (literature: $[\alpha]_D^{20}$ −69.2(c 1, $CHCl_3$).

N-(1,3-Bis((*S*)-1-Phenylethyl)-2-Sulfanylene-1,3,2-Diazaphospholidin-2-yl)-N-Methylmethanamine 1

Under argon atmosphere, the solution of hexamethylphosphoroustriamide (1.63 g, 10 mmol), iodine (0.13 g, 0.5 mmol) and anhydrous toluene (60 mL) was heated to 60 °C–70 °C and stirred for 4 h. The reaction mixture gradually became cloudy from brown. After the disappearance of the cloudy, *N,N′*-bis((*S*)-1-phenylethyl)ethane-1,2-diamine 5 (2.66 g, 10 mmol) was added to the clear solution and kept stirring at the same temperature for 5 h. To the clear yellow solution sulfur (0.26 g, 8 mmol) was added and gradually dissolved. After 0.5 h, the orange viscous liquid was obtained by removal of the solvent. The pure product was got by chromatography purification (petroleum ether elution). Yellow viscous liquid (2.46 g), Yield, 65.8%, $[\alpha]_D^{20}$-11.7 (c 1.66, CH_2Cl_2), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.48 (d, J = 6.9Hz, 3H), 1.58 (d, J = 6.9, 3H), 2.62 (s, 3H), 2.66 (s, 3H), 2.68–3.11 (m, 4H), 4.30–4.28 (m, 1H), 4.47–4.57 (m, 1H), 7.21–7.44 (m, 10H); ^{31}P NMR ($CDCl_3$, 400 MHz): δ 75.3; ^{13}C NMR ($CDCl_3$, 400 MHz): δ 20.6, 37.5, 42.6, 44.8, 127.0, 128.2, 128.8, 138.9. $C_{20}H_{25}N_3PS$ (373.17): calcd. C 64.32, H 7.56, N 11.25, S 8.58; found: C 64.27, H 7.50, N 11.17, S 8.56.

N-((3a*S*,7a*R*)-Hexahydro-3-((*S*)-1-Phenylethyl)-2-Sulfanylenebenzo[d][1,3,2]Oxazaphosphol-2(3H)-yl)-*N*-Methylmethanamine 2

The method of synthesizing **2** was the same as that of **1.** Yield, 40.7%, $[\alpha]_D^{20}$ +4.79 (c 0.94, C_6H_6). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.15–1.29 (m, 2H), 1.52–1.79 (m, 9H), 2.91 (s, 3H), 2.95 (s, 3H), 3.10–3.18 (m, 1H), 3.79–3.87 (m, 1H), 4.519–4.63 (m, 1H), 7.21–7.48 (m, 5H); ^{31}P NMR ($CDCl_3$, 400 MHz): δ 85.7; ^{13}C NMR ($CDCl_3$, 400 MHz): δ 20.5, 21.6, 23.0, 26.2, 30.0, 35.6, 41.2, 54.1, 74.5, 127.3, 128.2, 128.9, 138.9. $C_{16}H_{25}N_2OPS$ (324.14): calcd. C 59.24, H 7.77, N 8.63; found C 59.19, H 7.57, N 8.49.

O,O′-(*S*)-(1,1′Dinaphthyl-2,2′-Diyl)-*N,N*-Dimethylphosphoramidite 3

Under an argon atmosphere, (*S*)-BINOL (2.00 g, 7.00 mmol), hexamethylphosphorustriamide (1.40 g, 8.40 mmol), dry NH_4Cl (0.20 g), and 50 mL of dry $CHCl_3$ were heated

to reflux till the material disappeared (monitored by TLC analysis, 50 min).[11] After removal of the solvent, the residue was purified by column chromatograph on silica gel (200–300 meshes) to give white crystalline product (2.03 g), Yield, 80.9%, mp 190 °C–191 °C, $[\alpha]_D^{20}$ 579 (c 0.06, $CHCl_3$).

O,O′-(*R*)-(1,1′-Dinaphthyl-2,2′-Diyl)-*N,N*-Di-*i*-Propylphosphoramidite 4

Under an argon atmosphere, (*R*)-BINOL (2.00 g, 7.00 mmol) and PCl_3 (20 mL, redistilled) were heated to reflux till the material disappeared (monitored by TLC analysis, 5 h).[13] After removal of excess PCl_3, dry benzene (3 × 25 mL) was added to take off the remaining small amount of PCl_3 to give pale yellow solid **6**. Yield, 100%, ^{31}P NMR (δ, $CDCl_3$): 178.4.

Under an argon atmosphere, to a solution of compound **6** (0.96 g, 2.7 mmol) in dry toluene (25 mL), *n*-BuLi was added dropwise (1.66 mL of 1.98 M solution in hexane) at −60 °C. Then it was warmed up to room temperature naturally and stirred for 5 h. The reaction mixture was filtered and purified by chromatography on silica gel (200–300 meshes, petroleum ether/CH_2Cl_2 = 2/1) to give the pure amidite as a colorless amorphous compound (0.40 g). Yield, 35.1%, mp 197 °C–199 °C, $[\alpha]_D^{20}$ −571.33 (c 0.60, $CHCl_3$),^{31}P NMR ($CDCl_3$, 400 MHz): 153.0.

General Procedure for Chiral Phosphorus Reagents and $TiCl_4$ Catalyzed Asymmetric MBH Reaction of 4-Nitrobenzaldehydes and Activated Alkenes

The solution of chiral phosphorus reagents and $TiCl_4$ (0.2 mmol, 10 mmol%, respectively), activated alkene (6 mmol), and 4-nitrobenzaldehyde (2 mmol) in anhydrous CH_2Cl_2 (25 mL) was stirred at ambient temperature until the raw material disappeared (monitored by TLC). Then the reaction was quenched by adding saturated aqueous sodium bicarbonate solution and separated. TEA (0.4 g) was added to the organic phase and stirred overnight until the complete transformation of all the chlorinated products **A** into MBH product **B** (monitored by TLC). The mixture was washed in turn with dilute hydrochloric acid, saturated sodium bicarbonate solution, and saturated salt water, and then dried by anhydrous sodium sulfate overnight. After removal of the solvent, the residue was purified by column chromatography on silica gel (200–300 mesh, gradient elution with petroleum ether/ethyl acetate = 6/1) to afford the product.

General Procedure for 4/$BF_3{\cdot}Et_2O$ Catalyzed Asymmetric MBH Reaction

The solution of $BF_3{\cdot}Et_2O$ (0.1 mmol) in ether was added to the solution of **4** (0.1 mmol, 10 mmol%), MVK (0.25 mL, 3 mmol), and 4-nitrobenzaldehyde (0.15 g, 3 mmol) in anhydrous CH_2Cl_2 (25 mL), then stirred at the reaction temperature until the raw material disappeared (monitored by TLC). After completion of the reaction, TEA was added and warmed up to room temperature. The mixture was washed in turn with dilute hydrochloric acid, saturated sodium bicarbonate solution, and saturated salt water, and then dried by anhydrous sodium sulfate overnight. After removal of the solvent, the residue was purified by column chromatography on silica gel (200–300 mesh, gradient elution with petroleum ether/ethyl acetate = 6/1) to afford the product.

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