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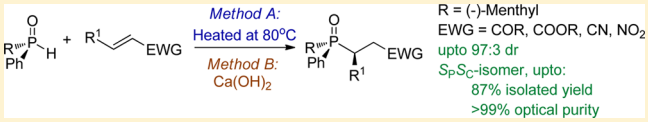
# Preparation of Optically Pure Tertiary Phosphine Oxides via the Addition of *P*-Stereogenic Secondary Phosphine Oxide to Activated Alkenes

Ji-Ping Wang,[†] Shao-Zhen Nie,[†] Zhong-Yang Zhou, Jing-Jing Ye, Jing-Hong Wen, and Chang-Qiu Zhao*

College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, China

Supporting Information

**ABSTRACT:** Functionalized *P,C*-stereogenic tertiary phosphine oxides were prepared by the addition of ($R_P$)-menthyl phenylphosphine oxide to activated olefins, in high $dr_P$ and $dr_C$, and were isolated in excellent yields. The reaction was readily catalyzed by $Ca(OH)_2$ or occurred with gentle heating. A wide range of substrates, including vinyl ketones, esters, nitriles, and nitro alkenes, can be used in the reaction.




## INTRODUCTION

Chiral tertiary phosphines are widely used in asymmetric synthesis as ligands, auxiliaries, or organocatalysts to enantioselectively prepare various substances having physiological and pharmacological activities.[1] Compared to the *C*-stereogenic counterparts, *P*- or *P,C*-stereogenic phosphines show better asymmetric induction because the stereogenic center is closer to the active center in the catalyst.[2] Additionally, the presence of a stereogenic carbon atom can stabilize the configuration on the phosphorus atom during the reaction.[2a] Several recent reviews have documented the preparation of stereogenic phosphines.[3]

The traditional approach used to introduce the *P*- and/or *C*-stereogenic centers into a molecule always involve multistep reactions or tedious resolutions.[3b,4] One recently developed approach utilized symmetric secondary phosphines for the formation of C-stereogenic phosphines, in excellent ee, via catalyzed asymmetric hydrophosphination,[3b−f,5] alkylation, and cross-coupling reactions.[6,7] When racemic or pro-chiral phosphines were used, the *P* or *P,C*-stereogenic phosphines are generated.[5,8−11] These reactions are usually catalyzed by transition metal or organocatalysts, and the selectivities during the generation of *P*-stereogenic center are not perfect. For the multiple *P* or *P,C*-stereogenic phosphine, this imperfect selectivity will lead to the formation of more than one diastereomer, and the optically pure compound has to be isolated via a difficult process.[5,8b,c]

Another strategy to generate *P* or *P,C*-stereogenic centers is the conversion or modification of *P*-stereogenic starting materials, through alkylation, hydrophosphination, and cross-coupling reactions, which usually affords *P*-stereogenic centers with much better stereoselectivity.[12−14] However, these methods are restricted by the availability of *P*-stereogenic H−P species.[15] Additionally, the loss of chirality on phosphorus, which was caused by the configurational instability, will lead to poor dr (diastereomeric ratio) during the formation of the multiple *P*- or *P,C*-stereogenic phosphine. Therefore, the reactions are usually carried out meticulously, sometimes at low temperature, to obtain the optically pure compounds.[15c,16,17]

Recently, we used $R_P$-(−)-menthyl phenylphosphine oxide **1** for the intramolecular rearrangement reaction, which showed configurational stability toward bases.[18] The (−)-menthyl group of **1** can stabilize the configuration of phosphorus, act as a chiral source to induce the asymmetric reaction, and be helpful in isolating the single stereoisomer of either the starting materials or products. As discussed below, the addition of **1** to various activated alkenes was carried out under catalyst or heavy metal-free conditions, at ambient temperature, and without epimerization. The functional *P,C*-stereogenic tertiary phosphine oxides were formed in up to 97:3 dr. Because of the mechanism, optically pure single stereomers were isolated in excellent yields, which may be converted to *P*-stereogenic phosphines via established procedures.[19]

## RESULTS AND DISCUSSION

The addition under alkali condition was examined with **1** and benzalacetone **2a** (Table 1). In DMSO at 34 °C, KOH promoted the reaction to afford the product in 98% yield, which displays two signals at 44.82 and 46.43 ppm in the $^{31}P$ NMR spectrum, in the ratio of 46:54. Because the addition was thought to occur away from the C═O bond,[18a] the two signals were assigned as the two stereomers **3a**/**3a′** that were formed in the *P*-retaining mechanism, and had *S* and *R* configurations, respectively, on the *β*-carbon (vide infra). In the proton NMR spectrum, the ratio of **3a**/**3a′** is quite similar to the $^{31}P$ NMR spectrum (as observed in SI). This also confirms the formation of **3a**/**3a′**.[20] The weaker base LiOH gave a similar dr in DMSO at 80 °C (entries 1 to 3).

In DMF, calcium hydroxide catalyzed the formation of **3a**/**3a′** in 87:13 dr at 15 °C and in 89:11 dr at −5 °C (entries 4−5). In isopropanol, the opposite 30:70 dr was observed at 60 °C

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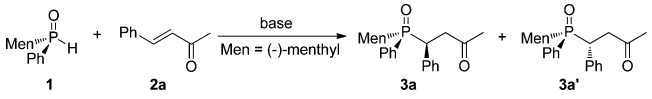
**Table 1. Optimization of the Base-Catalyzed Addition of 1 to Benzalacetone 2a**




| entry | solvent | catalyst(mol %) | temp/time | yield % (dr)[a] |
|---|---|---|---|---|
| 1 | DMSO | KOH (25) | 34 °C/25 h | 98 (46:54) |
| 2 | DMSO | KOH (25) | 80 °C/21 h | [b] |
| 3 | DMSO | LiOH (25) | 80 °C/70 h | 100 (47:53) |
| 4 | DMF | $Ca(OH)_2$ (25) | 15 °C/21 h | 99 (87:13) |
| 5 | DMF | $Ca(OH)_2$ (25) | −5 °C/21 h | 97 (89:11) |
| 6 | iPrOH | KOH (25) | 60 °C/19 h | 98 (30:70)[c] |
| 7 | iPrOH | KOH (25) | 40 °C/0.5 h | 99 (79:21)[c] |
| | | | 40 °C/5 h | 99 (62:38)[c] |
| | | | 40 °C/11 h | 99 (54:46)[c] |
| 8 | iPrOH | KOH (25) | 40 °C/48 h | 99 (38:62)[c] |
| 9 | THF | *n*BuLi (20) | −78 °C/3 h | 82 (94:6)[d] |
| 10 | THF | *n*BuLi (50) | −78 °C/3 h | 79 (91:9)[d] |
| 11 | THF | *n*BuLi (100) | −78 °C/3 h | 82 (91:9)[d] |

[a]General procedure: **1** (0.189 mmol) and **2a** (0.227 mmol) and base (0.047 mmol) in some solvent (0.5 mL) were stirred and analyzed with $^{31}P\{^1H\}$ NMR spectra. [b]Condensation of **2a** occurred. [c]The base was dissolved previously in isopropanol (0.5 mL). [d]*n*BuLi (2.2 M solution in hexane) was used.

(entries 6−8). No epimerization of **1** was observed at 60 °C, which confirmed the configurational stability of **1** toward base. It appears that the high temperature favored the formation of **3a′**. As observed in entry 7, the obtained dr depends on the reaction time, indicating that **3a** was probably converted to **3a′** by KOH.

Similar to the reported addition to acyclic $\alpha,\beta$-unsaturated esters,[16d] **1** and **2a** at −78 °C, in the presence of *n*BuLi, gave a 91:9 dr (entries 9−11), which was improved to 94:6 by using a catalytic amount of *n*BuLi. Meanwhile, *n*BuLi caused the formation of side products other than **3a**/**3a′** and decreased the yield.

The two stereoisomers **3a**/**3a′** are *C*-diastereomers that have different configurations on $\beta$-carbon. When screening the reaction conditions in Table 1, only the peaks of **3a**/**3a′** were observed in 31P-NMR spectrum. As contrast, when a mixture of $R_P$ and $S_P$ stereoisomers of **1** were was used under the $Ca(OH)_2$/DMF conditions, four peaks of adduct indicated that the *P*-diastereomers were formed, which have different configurations on phosphorus. The results exhibited that when optically pure **1** was used, the stereochemistry on phosphorus was kept intact during the reactions.

In a separate experiment, pure **3a** was converted to a 77:23 mixture of **3a**/**3a′** by PhMgBr at −78 °C, in a different ratio to entries 9−11, which indicated that an alternate mechanism is operational in the presence of base. As observed in Scheme 1, **3a** is predominantly formed through the $\alpha$-anion $\mathbf{3a_A}$, which is stabilized via an enolic structure. However, **3a** was deprotonated by base to form the $\beta$-anion $\mathbf{3a_B}$, leading to $\beta$-racemization and the formation of **3a′**. The protic solvent is assumed to accelerate the conversion of $\mathbf{3a_A}$ to $\mathbf{3a_B}$, resulting in significant formation of **3a′** in entries 6−8.

Considering the better dr obtained at −78 °C, other methods were attempted to further improve the selectivity. To our surprise, **1** and **2a** afforded **3a** in complete conversion and considerable dr under mild heating (Table 2). When **1** and **2a** were heated at 80 °C without solvent, **3a**/**3a′** were formed in

**Scheme 1. Addition of 1 to 2a and the Conversion of 3a in the Presence of Base**

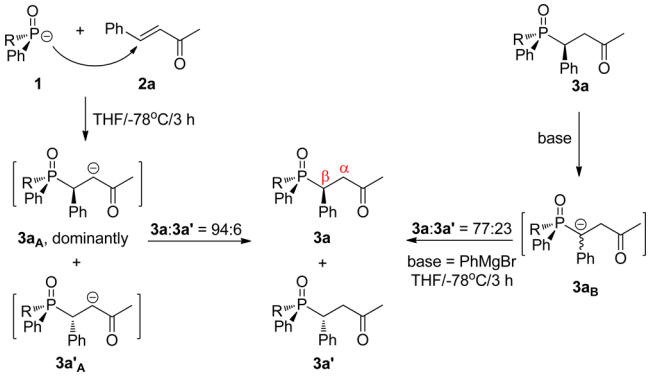



**Table 2. Optimization of the Thermal Addition of 1 to 2a**

| entry | solvent | additive (mol %) | temp/time[a] | yield % (dr)[a] |
|---|---|---|---|---|
| 1 | no | no | 80 °C/22 h | >99 (88:12) |
| 2 | toluene | no | 80 °C/17 h | >99 (91:9) |
| 3 | toluene | no | 80 °C/24 h | >99 (89:11)[b] |
| 4 | toluene | no | 60 °C/24 h | 84 (89:11) |
| 5 | DMSO | no | 80 °C/46 h | >99 (92:8) |
| 6 | $nC_8H_{18}$ | no | 80 °C/46 h | 66 (90:10) |
| 7 | pyridine | no | 80 °C/24 h | 93 (89:11) |
| 8 | MeOH | no | 60 °C/19 h | 68 (85:15) |
| 9 | toluene | AIBN (20) | 60 °C/25 h | 94 (91:9) |
| 10 | toluene | AIBN (20) | 80 °C/52 h | 99 (92:8) |
| 11 | toluene | $Ph_3P$ (20) | Rt/40 h | Nr |
| 12 | toluene | $Et_3N$ (20) | Rt/40 h | Nr |
| 13 | toluene | TEMPO (20) | 80 °C/24 h | 78 (99:1)[c] |
| 14 | toluene | TEMPO (20) | 100 °C/41 h | complicated[c] |

[a]General procedure: **1** (0.189 mmol), **2a** (0.227 mmol), and additive (if applicable) in some solvent (0.1 mL) were stirred and analyzed with $^{31}P\{^1H\}$ NMR spectra. [b]Toluene was used in 0.5 mL. [c]The epimerization of **1** and formation of the stereomers other than **3a**/**3a′** were detected.

88:12 dr. The dr was improved to 91:9 in toluene but was reduced in diluted solution or at lower temperatures (entries 1 to 4). The presence of AIBN accelerated the reaction and slightly increased the dr to 92:8. At room temperature, $Ph_3P$ and $Et_3N$ cannot promote the reaction. In the presence of the free radical inhibitor TEMPO, the ratio of **3a**/**3a′** was improved, but the epimerization of **1** was observed (entries 13 to 14).

The addition of **1** to various vinyl ketones **2** was examined (Table 3). For most aromatic enones, **1** was consumed completely, and only the stereomers of **3**/**3′** were observed. For **3a** to **3n**, the dr was approximately 90:10, and the structure was confirmed by referring to **3a**/**3a′**, with the $S_PS_C$-stereomer having the upfield signal in $^{31}P\{^1H\}$-NMR spectra. It appears that the EWG-substituent $R^1$ (the aryl linked to a vinyl bond) tended to give better stereoselectivity, especially the *ortho*-substituted $R^1$. The best 97:3 dr was obtained for **3m**, when $R^1$ was *o*-nitrophenyl and $R^2$ was *p*-chlorophenyl. The enones **2** containing ferroceno, naphthyl, and phenothiazine smoothly afforded **3s**, **3t**, and **3v**, and the substrate derived from indene-1,3-dione gave poor dr in the formation of **3w**. For some enones, the addition did not occur under thermal conditions. Catalyzed by $Ca(OH)_2$, the adducts (**3o**−**3r**) were afforded in poor dr. The reaction of 1,3-di(2-pyridinyl)propenone showed



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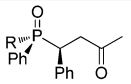
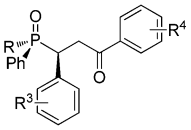
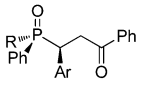
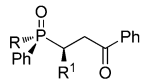
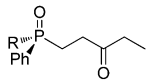
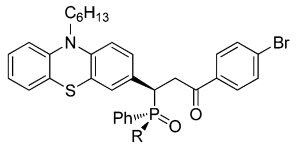
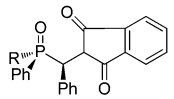
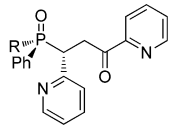
**Table 3. Preparation of β-Phosphino Ketones via the Addition of 1 to 2**

| | | Yield % (3/3')[a] | Isolated yield % 3 or 3'[a] |
|---|---|---|---|
|  | | >99 (91:9)[b] | **3a**, 77 (>99:1) |
|  | $R^3$ = H, $R^4$ = H | >99 (88:12)[b] | **3b**, 71 (>99:1) |
| | $R^3$ = H, $R^4$ = *p*-Cl | >99 (89:11)[b] | **3c**, 73 (>99:1) |
| | $R^3$ = H, $R^4$ = *p*-Br | >99 (89:11)[b] | **3d**, 73 (>99:1) |
| | $R^3$ = H, $R^4$ = *p*-MeO | >99 (87:13)[b] | **3e**, 70 (>99:1) |
| | $R^3$ = *o*-F, $R^4$ = H | >99 (93:7) | **3f**, 68 (>99:1) |
| | $R^3$ = *o*-Cl , $R^4$ = H | 91 (95:5) | **3g**, 78 (>99:1) |
| | $R^3$ = *o*-Br, $R^4$ = H | 94 (94:6) | **3h**, 67 (>99:1) |
| | $R^3$ = *o*-MeO, $R^4$ = H | 90 (89:11) | **3i**, 56 (>99:1) |
| | $R^3$ = *p*-Cl, $R^4$ = H | >99 (91:9) | **3j**, 77 (>99:1) |
| | $R^3$ = *p*-MeO, $R^4$ = H | 94 (85:15) | **3k**, 63 (>99:1) |
| | $R^3$ = *o*-$CF_3$, $R^4$ = *p*-MeO | >99 (95:5) | **3l**, 72 (98:2) |
| | $R^3$ = *o*-$O_2N$, $R^4$ = *p*-Cl | 97 (97:3) | **3m**, 87 (>99:1) |
| | $R^3$ = *p*-$O_2N$, $R^4$ = *p*-Cl | >99 (91:9) | **3n**, 65 (>99:1) |
| | $R^3$ = *p*-$Ph_2N$, $R^4$ = *p*-Br | 76 (58:42)[c] | **3o'**, 31 (4:94) |
|  | Ar = 2,6-$Cl_2C_6H_3$, | >99 (65:35)[c] | **3p**, 80 (60:40) |
| | Ar = 2,4,6-$(MeO)_3C_6H_2$, | >99 (64:36)[c] | **3q**, 79 (62:38) |
| | Ar = 2,4,6-$Me_3C_6H_2$, | >99 (83:17)[c] | **3r**, 82 (88:12) |
| | Ar = 1-MeO-2-Naphthyl | >99 (89:11) | **3s**, 62 (>99:1) |
| | Ar = Fc | >99 (76:24) | **3t**, 41 (>99:1) |
|  | $R^1$ = *i*Pr, | nr[c] | |
| | $R^1$ = *c*Hex, | trace | |
|  | | >99[b] | **3u**, 95 |
|  | | >99 (85:15) | **3v**, 55 (>99:1) |
|  | | >99 (67:33) | **3w**, 27 (>99:1) |
|  | | >99 (43:57)[c] | **3x'**, 45 (3:97) |

[a]General procedure: **1** (0.379 mmol), **2** (0.417 mmol), and AIBN (0.08 mmol, 20% molar) in toluene (0.2 mL) were heated at 80 °C. [b]In the absence of AIBN. [c]Catalyzed by $Ca(OH)_2$ in DMF.

almost no diastereoselectivity, neither under thermal nor alkali conditions. When $R^1$ was an aliphatic alkyl group, the addition did not occur under alkali conditions. Under thermal conditions, the complicated product, together with epimerization of **1** was detected.

In most cases, a single diastereomer of **3** can be conveniently isolated in excellent yield via recrystallization of the crude products from hexane. In fact, most adducts **3** are crystalline solid. The unconsumed **2** together with the minor stereoisomer **3′** could be removed by simply washing with hexane. The purification was consistent to the GAP technology (group-assisted purification), as reported by Li and co-workers.[21] The GAP technology employed phosphonyl or phosphinyl to assist the proceeding of a reaction and simplified the purification. In the reactions of **1**, the menthyl phenyl phosphinyl exhibited excellent GAP property, and the optical purities of major stereoisomers were improved after isolation.

Their $S_PS_C$ structure was unambiguously confirmed from the single-crystal X-ray diffraction of **3e** (Figure 1), with the

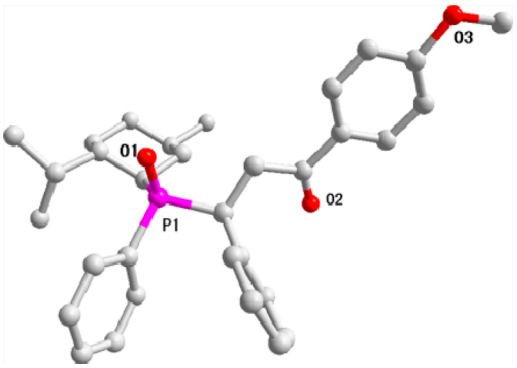
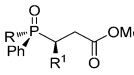
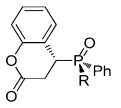
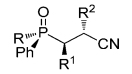
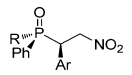



**Figure 1.** X-ray crystal structure of **3e**.

retained configuration on phosphorus being confirmed, which is consistent to the reported base-catalyzed addition.[16d,18a] The crystallographic information and cif file of **3e** (ccdc 144993) can be found in the Supporting Information.

The additions of **1** to vinyl esters and vinyl nitriles occurred sluggishly under thermal conditions. Catalyzed by $Ca(OH)_2$, the adducts were formed in excellent yields (Table 4). When

**Table 4. Addition of 1 to Various Activated Alkenes**

| | | Method[a] Yield % (5/5') | Isolated yield % 5 (>99:1)[a] |
|---|---|---|---|
|  | $R^1$ = H, | B 93 | **5a**, 80 |
| | $R^1$ = Ph, | B >99 (83:17) | **5b**, 62 (>99:1) |
|  | | B >99 (43:57) | **5c'**, 13 (<1:99) |
|  | $R^1$ = $R^2$ = H, | B 97 | **5d**, 94 |
| | $R^1$ = *p*-$ClC_6H_4$, $R^2$ = Ph, | B >99 (22:13:61:4) | **5e**, 21 (>99:1) |
|  | Ar = Ph | A >99 (81:19) | **5f**, 58 (>99:1) |
| | Ar = 4-$MeC_6H_4$, | A >99 (80:20) | **5g**, 56 (>99:1) |
| | Ar = 4-$ClC_6H_4$, | A >99 (79:21) | **5h**, 55 (>99:1) |

[a]General procedure of Method A: **1a** (0.189 mmol), AIBN (0.04 mmol), and **4** (0.208 mmol) were heated in toluene (0.1 mL). Method B: **1a** (0.189 mmol), **4** (0.208 mmol), and $Ca(OH)_2$ (0.189 mmol) in DMF (0.3 mL) were stirred at rt for 48 h.

*α,β*-disubstituted vinyl nitriles were used, four stereoisomers were detected due to the generation of an extra stereogenic carbon center, with the dominant **5e** being isolated. The structure of **5e** is speculative, based on Cram's rule. For nitro alkenes, the reaction performed under thermal conditions afforded **5f** to **5h**, and the dr was estimated by referring to **3a**/**3a′**.[22]

On the basis of the fact that the reaction was accelerated by AIBN (entry 4 vs 9 of Table 2) and depressed by TEMPO (entry 2 vs 13), the mechanism of the thermal addition is thought to involve a free radical. No addition occurred to norbornene, and low reactivities for aliphatic substituted **2** (Table 3) indicated that an electron deficiency on the C═C bond is necessary. As proposed in Scheme 2, the free radical on



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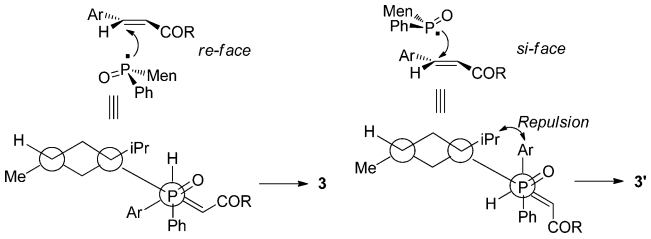
**Scheme 2. Proposed Mechanism for Addition of 1 to 2**




phosphorus attacked at **2** in a *reface* and *si-face* manner. The spatial repulsion between menthyl and aryl groups lead to the former occurring dominantly, affording **3**.[16d]

To the best of our knowledge, the *P*-induction to generate a stereogenic carbon atom in excellent stereoselectivity is quite limited. The herein reported research provides a convenient procedure which, when performed under catalyst-free or simple catalytic conditions, affords optically pure *P,C*-stereogenic phosphine oxides having keto, ester, cyano, and nitro functional groups. The compounds are anticipated to have important potential applications in asymmetric catalysis as ligands or organic catalysts. The further conversion of reaction products to phosphine ligands and relevant derivatives are in progress in our laboratory.

## EXPERIMENTAL SECTION

All solvents when needed were freshly distilled prior to use. Except **1** that was prepared according to the literature, all starting materials and catalysts are commercially available. The purity of the products was checked by TLC on precoated plates of silica gel $GF_{254}$ using as mobile phase a 3:1 mixture of petroleum ether and ethyl acetate. Melting points were determined on a digital melting point apparatus, and temperatures were uncorrected. $^1$H NMR spectra were recorded on a 400-MHz spectrometer. Chemical shift for $^1$H NMR spectrum (in parts per million) relative to internal tetramethylsilane ($Me_4Si$, $\delta$ = 0.00 ppm) with $CDCl_3$ or DMSO. $^{13}$C NMR spectrum were recorded at 101 mHz. Chemical shifts for $^{13}$C NMR spectrum are reported (in parts per million) relative to $CDCl_3$ ($\delta$ = 77.0 ppm) or DMSO-*d6* ($\delta$ = 39.6 ppm). $^{31}$P NMR spectra were recorded at 162 MHz and chemical shifts reported (in parts per million) relative to external 85% phosphoric acid ($\delta$ = 0.0 ppm). TLC plates were visualized by UV.

**Preparation of β-Phosphino Ketones 3 via Addition of 1 to 2.** *Typical Procedure for Method A.* The solution of **1** (100 mg, 0.379 mmol), **2** (0.417 mmol), and AIBN (0.0125 g, 0.076 mmol) in toluene (0.2 mL) was heated at 80 °C. The solution (0.02 mL) was dissolved in chloroform (0.5 mL) for monitoring the reaction with $^{31}$P NMR spectra. After the reaction was completed, the solvent was removed in vacuo, and the residue was recrystallized with petroleum ether (30−60 °C) or purified with preparative TLC.

*Typical Procedure for Method B.* The solution of **1** (50 mg, 0.189 mmol), **2** (0.227 mmol), and $Ca(OH)_2$ (14 mg, 0.189 mmol) in DMF (0.3 mL) was stirred at rt. To the solution, the saturated aqueous ammonium chloride (10 mL) was added. The mixture was extracted with dichloromethane (20 mL), washed with water, and dried over anhydrous magnesium sulfate. After removing the solvent, the residue was recrystallized with petroleum ether (30−60 °C) or purified with preparative TLC.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-4-phenylbutan-2-one,* ***3a.*** The reaction was carried out according to the procedure of method A in the absence of AIBN. In the crude product, the ratio of **3*a***/**3a′** was detected as 91:9, and the pure compound was obtained as a white solid (120 mg, 77%, >99:1 $dr_C$, mp 164−166 °C) from recrystallization with petroleum ether. $^{31}$P NMR (162 MHz, chloroform-*d*) $\delta$ 44.97 (s). $^1$H NMR (400 MHz, chloroform-*d*) $\delta$ 7.35−7.26 (m, 3H), 7.21 (dd, *J* = 10.9, 4.1 Hz, 2H), 7.05 (d, *J* = 6.7 Hz, 3H), 6.99−6.92 (m, 2H), 4.19 (td, *J* = 10.0, 3.8 Hz, 1H), 3.40 (ddd, $J_{P-H}$ = 17.9, $J_1$ = 9.4, $J_2$ = 3.8 Hz, 1H), 3.05−2.90 (m, 1H), 2.33 (d, *J* = 5.3 Hz, 1H), 2.09 (s, 4H), 1.97−1.86 (m, 1H), 1.79−1.62 (m, 3H), 1.49−1.35 (m, 2H), 1.07−0.89 (m, 5H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.26 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) $\delta$ 205.7 (d, *J* = 10.5 Hz), 137.6 (d, *J* = 4.1 Hz), 132.8 (s), 131.9 (s), 131.2 (s), 131.1 (s), 130.8 (s), 129.2 (s), 129.2 (s), 128.1 (d, *J* = 1.1 Hz), 127.5 (s), 127.4 (s), 126.7 (s), 43.9 (s), 43.7 (d, *J* = 3.2 Hz), 40.1 (dd, *J* = 60.23, 60.04 Hz), 39.7 (d, *J* = 63.37 Hz), 35.3 (d, *J* = 3.1 Hz), 34.2 (s), 33.3 (d, *J* = 12.5 Hz), 30.6 (s), 28.0 (d, *J* = 2.7 Hz), 24.8 (d, *J* = 12.0 Hz), 22.7 (s), 21.5 (s), 15.5 (s). Elemental analysis: Calcd for $C_{26}H_{35}O_2P$, C, 76.07; H, 8.59. Found: C, 75.84; H, 8.56. $[\alpha]_D^{20}$ − 46 (*c* 2.4, methanol).

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-phenylpropan-2-one,* ***3b.*** The reaction was carried out according to the procedure of method A in the absence of AIBN. In the crude product, the ratio of **3*b***/**3b′** was detected as 88:12, and the pure compound was obtained as a white solid (127 mg, 71%, >99:1 $dr_C$, mp 190−192 °C) from recrystallization with petroleum ether−dichloromethane. $^{31}$P NMR (162 MHz, chloroform-*d*) $\delta$ 45.44 (s). $^1$H NMR (400 MHz, chloroform-*d*) $\delta$ 7.93 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.41 (dd, *J* = 12.1, 5.1 Hz, 4H), 7.33−7.26 (m, 1H), 7.23 (dd, *J* = 10.0, 4.4 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.00 (dt, *J* = 13.7, 7.0 Hz, 3H), 4.39 (td, *J* = 9.4, 2.2 Hz, 1H), 3.96 (ddd, $J_{P-H}$ = 18.2, $J_1$ = 9.4, $J_2$ = 2.4 Hz, 1H), 3.71 (ddd, $J_{P-H}$ = 18.2, $J_1$ = 9.7, $J_2$ = 4.8 Hz, 1H), 2.36 (s, 1H), 2.18 (d, *J* = 4.4 Hz, 1H), 2.06 (dt, *J* = 13.1, 6.5 Hz, 1H), 1.70 (s, 3H), 1.50−1.33 (m, 2H), 1.11−0.85 (m, 5H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.31 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) $\delta$ 197.0 (d, *J* = 11.5 Hz), 137.9 (d, *J* = 4.4 Hz), 136.6 (s), 133.2 (d, *J* = 2.5 Hz), 132.7 (d, *J* = 87.8 Hz), 131.1(s), 130.7 (s), 129.4 (s), 129.3 (s), 128.5 (s), 128.1 (s), 127.5 (s), 127.4 (s), 126.5 (s), 43.8 (d, *J* = 2.9 Hz), 40.4 (d, *J* = 63.00 Hz), 40.2 (dd, *J* = 61.00, 61.00 Hz), 39.6 (s), 35.4 (d, *J* = 2.9 Hz), 34.2 (s), 33.3 (d, *J* = 12.4 Hz), 28.1 (d, *J* = 2.6 Hz), 24.8 (d, *J* = 11.9 Hz), 22.6 (s), 21.5 (s), 15.5 (s). Elemental analysis: Calcd for $C_{31}H_{37}O_2P$, C, 78.78; H, 7.89. Found: C, 78.46; H, 7.86. $[\alpha]_D^{20}$ − 97 (*c* 0.5, methanol).

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-(p-chlorophenyl)-4-phenylpropan-2-one,* ***3c.*** The reaction was carried out according to the procedure of method A in the absence of AIBN. In the crude product, the ratio of **3*c***/**3c′** was detected as 89:11, and the pure compound was obtained as a white solid (140 mg, 73%, >99:1 $dr_C$, mp 211−213 °C) from recrystallization with petroleum ether−dichloromethane. $^{31}$P NMR (162 MHz, chloroform-*d*) $\delta$ 45.32 (s). $^1$H NMR (400 MHz, chloroform-*d*) $\delta$ 7.87 (d, *J* = 8.6 Hz, 2H), 7.38 (t, *J* = 9.3 Hz, 4H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.26−7.19 (m, 2H), 7.12−6.95 (m, 5H), 4.35 (td, *J* = 9.5, 2.9 Hz, 1H), 3.91 (ddd, $J_{P-H}$ = 18.2, $J_1$ = 9.4, $J_2$ = 3.0 Hz, 1H), 3.62 (ddd, $J_{P-H}$ = 18.2, $J_1$ = 9.7, $J_2$ = 5.3 Hz, 1H), 2.33 (s, 1H), 2.17 (s, 1H), 2.10−1.93 (m, 1H), 1.72 (d, *J* = 9.1 Hz, 3H), 1.41 (d, *J* = 7.8 Hz, 2H), 1.08−0.91 (m, 5H), 0.80 (t, *J* = 9.8 Hz, 3H), 0.29 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) $\delta$ 196.0 (d, *J* = 11.3 Hz), 139.6 (s), 137.7 (d, *J* = 4.4 Hz), 135.0 (s), 133.0 (s), 132.1 (s), 131.1 (s), 130.7 (s), 129.5 (s), 129.4 (s), 129.3 (s), 128.9 (s), 128.8 (s), 128.1 (s), 128.1 (s), 127.6 (s), 127.5 (s), 126.6 (s), 43.8 (s), 40.4 (d, *J* = 63.00 Hz), 40.3 (dd, *J* = 61.00,59.00 Hz), 39.5 (s), 35.4 (d, *J* = 3.2 Hz), 34.2 (s), 33.3 (d, *J* = 12.3 Hz), 28.1 (s), 24.8 (d, *J* = 11.7 Hz), 22.6 (s), 21.5 (s), 15.4 (s). Elemental analysis: Calcd for $C_{31}H_{36}ClO_2P$, C, 73.43; H, 7.16. Found: C, 73.21; H, 7.14. $[\alpha]_D^{20}$ − 108 (*c* 1.7, methanol).

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-(p-bromophenyl)-4-phenylpropan-2-one,* ***3d.*** The reaction was carried out according to the procedure of method A in the absence of AIBN. In the crude product, the ratio of **3*d***/**3d′** was detected as 89:11, and the pure compound was obtained as a white solid (152 mg, 73%, >99:1 $dr_C$, mp 214−216 °C) from recrystallization with petroleum ether−dichloromethane. $^{31}$P NMR (162 MHz, chloroform-*d*) $\delta$ 45.23 (s). $^1$H NMR (400 MHz, chloroform-*d*) $\delta$ 7.79 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.43−7.28 (m, 3H), 7.23 (dd, *J* = 9.8, 4.8 Hz, 2H), 7.02 (dd, *J* = 15.6, 7.7 Hz, 5H), 4.34 (td, *J* = 9.6, 2.9 Hz, 1H), 3.90 (ddd, $J_{P-H}$ = 18.1, $J_1$ = 9.2, $J_2$ = 2.8 Hz, 1H), 3.61 (ddd, $J_{P-H}$ = 18.3, $J_1$ = 9.7, $J_2$ = 5.4 Hz, 1H), 2.33 (s, 1H), 2.16 (d, *J* = 4.6 Hz, 1H), 2.08−1.95 (m, 1H), 1.72 (d, *J* = 9.4 Hz, 3H), 1.48−1.31 (m, 2H), 1.10−0.85 (m, 5H), 0.79



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(d, $J$ = 6.8 Hz, 3H), 0.29 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 196.2 (d, $J$ = 11.3 Hz), 137.7 (d, $J$ = 4.3 Hz), 135.4 (s), 132.6 (d, $J$ = 87.9 Hz), 131.9 (s), 131.8 (s), 131.1 (s), 131.0 (s), 130.8 (s), 129.6 (s), 129.3 (s), 129.3 (s), 128.4 (s), 128.1 (s), 127.5 (s), 127.4 (s), 126.6 (s), 43.8 (s), 40.4 (d, $J$ = 62.9 Hz), 40.2 (dd, $J$ = 61.1,59.9 Hz), 39.5 (s), 35.4 (s), 34.2 (s), 33.3 (d, $J$ = 12.8 Hz), 28.1 (s), 24.8 (d, $J$ = 10.6 Hz), 22.7 (s), 21.5 (s), 15.5 (s). Elemental analysis: Calcd for $C_{31}H_{36}BrO_2P$, C, 67.51; H, 6.58. Found: C, 67.17; H, 6.55. $[\alpha]_D^{20}$ − 117 ($c$ 0.3, methanol).

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-(p-methoxyphenyl)-4-phenylpropan-2-one,* ***3e***. The reaction was carried out according to the procedure of method A in the absence of AIBN. In the crude product, the ratio of **3*e***/**3e′** was detected as 87:13, and the pure compound was obtained as a white solid (133 mg, 70%, >99:1 $dr_C$, mp 188−190 °C) from recrystallization with petroleum ether−dichloromethane. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 45.44 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.92 (d, $J$ = 8.9 Hz, 2H), 7.46−7.35 (m, 2H), 7.29 (d, $J$ = 6.2 Hz, 1H), 7.23 (dd, $J$ = 9.8, 4.6 Hz, 2H), 7.10 (d, $J$ = 7.9 Hz, 2H), 7.04−6.94 (m, 3H), 6.89 (d, $J$ = 8.9 Hz, 2H), 4.34 (dd, $J$ = 12.8, 5.8 Hz, 1H), 3.94−3.80 (m, 4H), 3.67 (ddd, $J_{P-H}$ = 18.0, $J_1$ = 9.9, $J_2$ = 4.5 Hz, 1H), 2.33 (s, 1H), 2.20−2.02 (m, 2H), 1.71 (d, $J$ = 11.4 Hz, 3H), 1.37 (dd, $J$ = 11.6, 5.0 Hz, 2H), 1.05−0.85 (m, 5H), 0.79 (d, $J$ = 6.8 Hz, 3H), 0.31 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 195.4 (d, $J$ = 11.7 Hz), 163.5 (s), 138.1 (d, $J$ = 4.5 Hz), 132.8 (d, $J$ = 87.8 Hz), 131.1 (s), 131.0 (s), 130.6 (s), 130.4 (s), 130.3 (s), 129.8 (s), 129.5 (s), 129.4 (s), 128.0 (s), 127.5 (s), 127.4 (s), 126.4 (s), 113.6 (s), 55.4 (d, $J$ = 9.5 Hz), 43.9 (d, $J$ = 3.6 Hz), 40.6 (d, $J$ = 62.71 Hz), 40.3 (dd, $J$ = 61.90,60.60 Hz), 39.2 (s), 35.4 (d, $J$ = 2.9 Hz), 34.2 (s), 33.3 (d, $J$ = 12.2 Hz), 28.2 (d, $J$ = 2.7 Hz), 24.8 (d, $J$ = 13.5 Hz), 22.6 (s), 21.5 (d, $J$ = 2.1 Hz), 15.5 (s). Elemental analysis: Calcd for $C_{32}H_{39}O_3P$, C, 76.47; H, 7.82. Found: C, 76.16; H, 7.79. $[\alpha]_D^{20}$ − 55 ($c$ 1.6, methanol).

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(o-fluorophenyl)propan-2-one,* ***3f***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3*f***/**3f′** was detected as 93:7, and the pure compound was obtained as a white solid (126 mg, 68%, >99:1 $dr_C$, mp 134−137 °C) from preparative TLC (silica gel, hexane/ethyl acetate = 1/1 as eluent), then recrystallization with petroleum ether−dichloromethane. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 45.99 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.98 (d, $J$ = 7.3 Hz, 2H), 7.59−7.41 (m, 5H), 7.37−7.16 (m, 4H), 6.97−6.85 (m, 1H), 6.80 (t, $J$ = 7.3 Hz, 1H), 6.69 (t, $J$ = 9.1 Hz, 1H), 4.65 (dd, $J$ = 12.3, 7.3 Hz, 1H), 4.03−3.83 (m, 2H), 2.34−2.10 (m, 3H), 1.85−1.56 (m, 3H), 1.52−1.22 (m, 2H), 1.09−0.87 (m, 5H), 0.83 (d, $J$ = 6.8 Hz, 3H), 0.30 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 196.6 (d, $J$ = 11.7 Hz), 159.8 (d, $J_{CF}$ = 245.4 Hz), 136.4 (s), 133.3 (s), 133.0 (d, $J$ = 89.0 Hz), 130.7 (d, $J$ = 2.7 Hz), 130.4 (s), 130.3 (s), 129.5 (t, $J$ = 3.8 Hz), 128.6 (s), 128.1 (s), 128.1 (s), 128.1 (s), 127.7 (s), 127.5 (s), 124.0 (s), 114.8 (d, $J$ = 23.3 Hz), 43.9 (d, $J$ = 3.2 Hz), 41.8 (d, $J$ = 62.5 Hz), 39.7 (s), 35.4 (d, $J$ = 3.1 Hz), 34.3 (s), 33.5 (d, $J$ = 12.4 Hz), 32.3 (d, $J$ = 61.8 Hz), 28.4 (d, $J$ = 2.6 Hz), 24.8 (d, $J$ = 12.3 Hz), 22.6 (s), 21.5 (s), 15.3 (s). Elemental analysis: Calcd for $C_{31}H_{36}FO_2P$, C, 75.90; H, 7.40. Found: C, 75.60; H, 7.37.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(o-chlorophenyl)propan-2-one,* ***3g***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3*g***/**3g′** was detected as 95:5, and the pure compound was obtained as a colorless oil (150 mg, 78%, >99:1 $dr_C$) from preparative TLC (silica gel, hexane/ethyl acetate = 1/2 as eluent). $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 47.39 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.97 (d, $J$ = 7.4 Hz, 2H), 7.53 (t, $J$ = 7.4 Hz, 3H), 7.44 (dt, $J$ = 15.1, 7.5 Hz, 3H), 7.21 (dd, $J$ = 12.8, 6.9 Hz, 3H), 7.00 (d, $J$ = 7.9 Hz, 1H), 6.93 (t, $J$ = 7.1 Hz, 1H), 6.81 (t, $J$ = 7.5 Hz, 1H), 4.85 (br, 1H), 3.96 (br, 2H), 2.23 (d, $J$ = 18.1 Hz, 3H), 1.69 (t, $J$ = 15.4 Hz, 3H), 1.49−1.21 (m, 2H), 1.12−0.85 (m, 5H), 0.83 (d, $J$ = 6.5 Hz, 3H), 0.33 (d, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 196.6 (d, $J$ = 9.3 Hz), 136.8 (s), 136.4 (s), 134.1 (s), 133.3 (s), 132.9 (s), 130.8 (s), 130.4 (s), 130.3 (s), 129.8 (s), 129.0 (s), 128.6 (s),128.2 (s), 127.6 (s), 127.6 (s), 127.5 (s), 126.9 (s), 43.9 (s), 42.1 (d, $J$ = 61.1 Hz), 41.0 (s), 36.4 (d, $J$ = 60.1 Hz), 35.3 (s), 34.2 (s), 33.4 (d, $J$ = 10.6 Hz), 28.4 (s), 24.8 (d, $J$ = 10.9 Hz), 22.5 (s), 21.5 (s), 15.2 (s). Elemental analysis: Calcd for $C_{31}H_{36}ClO_2P$, C, 73.43; H, 7.16. Found: C, 73.06; H, 7.12.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(o-bromophenyl)propan-2-one,* ***3h***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3*h***/**3h′** was detected as 94:6, and the pure compound was obtained as a colorless oil (140 mg, 67%, >99:1 $dr_C$) from preparative TLC (silica gel, hexane/ethyl acetate = 1/1 as eluent). $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 47.28 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.97 (d, $J$ = 7.3 Hz, 2H), 7.55 (dd, $J$ = 15.6, 7.8 Hz, 3H), 7.45 (dt, $J$ = 15.3, 7.7 Hz, 3H), 7.27−7.15 (m, 4H), 6.98 (t, $J$ = 7.4 Hz, 1H), 6.73 (t, $J$ = 7.6 Hz, 1H), 4.82 (dd, $J$ = 6.3, 2.7 Hz, 1H), 4.05−3.86 (m, 2H), 2.32−2.18 (m, 3H), 1.64 (s, 1H), 1.25 (s, 1H), 1.17 (d, $J$ = 6.9 Hz, 3H), 0.90 (d, $J$ = 6.4 Hz, 4H), 0.83 (d, $J$ = 6.8 Hz, 4H), 0.33 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 196.7 (d, $J$ = 11.6 Hz), 176.2 (s), 138.7 (d, $J$ = 4.4 Hz), 136.5 (s), 133.3 (s), 132.4 (s), 132.7 (d, $J$ = 90.0 Hz), 130.7 (d, $J$ = 2.8 Hz), 130.5 (s), 130.4 (s), 130.0 (d, $J$ = 3.8 Hz), 128.6 (s), 128.2 (s), 127.8 (d, $J$ = 2.3 Hz), 127.5 (s), 127.5 (s), 127.4 (s), 125.6 (d, $J$ = 7.6 Hz), 43.9 (d, $J$ = 3.1 Hz), 42.1 (d, $J$ = 62.0 Hz), 41.2 (s), 39.3 (d, $J$ = 60.2 Hz), 35.3 (d, $J$ = 3.3 Hz), 34.3 (s), 33.5 (d, $J$ = 12.3 Hz), 28.4 (d, $J$ = 2.6 Hz), 24.8 (d, $J$ = 12.2 Hz), 22.6 (s), 21.5 (s), 15.2 (s). Elemental analysis: Calcd for $C_{31}H_{36}BrO_2P$, C, 67.51; H, 6.58. Found: C, 67.31; H, 6.56.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(o-methoxyphenyl)propan-2-one,* ***3i***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3*i***/**3i′** was detected as 89:11, and the pure compound was obtained as a colorless oil (106 mg, 56%, >99:1 $dr_C$) from preparative TLC (silica gel, hexane/ethyl acetate = 2/1 as eluent). $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 46.39 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.95 (d, $J$ = 7.2 Hz, 2H), 7.51 (d, $J$ = 7.5 Hz, 1H), 7.42 (dd, $J$ = 13.1, 5.6 Hz, 4H), 7.19 (ddd, $J$ = 15.2, 13.9, 9.7 Hz, 4H), 6.90 (t, $J$ = 7.8 Hz, 1H), 6.64 (t, $J$ = 7.4 Hz, 1H), 6.45 (d, $J$ = 8.2 Hz, 1H), 4.83 (d, $J$ = 5.2 Hz, 1H), 3.97−3.80 (m, 2H), 3.69 (s, 3H), 2.31 (s, 1H), 2.25−2.09 (m, 2H), 2.05 (s, 1H), 1.71 (d, $J$ = 7.6 Hz, 2H), 1.40 (s, 1H), 1.36−1.26 (m, 1H), 1.02−0.86 (m, 5H), 0.80 (d, $J$ = 6.8 Hz, 3H), 0.33 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 197.4 (d, $J$ = 11.6 Hz), 156.1 (d, $J$ = 5.3 Hz), 136.7 (s), 133.7 (s), 133.1 (s), 132.8 (s), 130.7 (s), 130.6 (s), 130.5 (s), 130.4 (s), 129.0 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.2 (s), 127.6 (d, $J$ = 1.7 Hz), 127.0 (s), 126.9 (s), 126.9 (s), 126.8 (s), 120.4 (s), 109.8 (s), 55.2 (d, $J$ = 7.6 Hz), 43.9 (s), 41.9 (s), 41.3 (s), 39.7 (s), 35.3 (s), 34.3 (s), 33.5 (d, $J$ = 12.3 Hz), 28.2 (d, $J$ = 2.7 Hz), 24.8 (d, $J$ = 11.5 Hz), 22.6 (s), 21.6 (s), 15.4 (s). Elemental analysis: Calcd for $C_{32}H_{39}O_3P$, C, 76.47; H, 7.82. Found: C, 76.24; H, 7.80.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(p-chlorophenyl)propan-2-one,* ***3j***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3*j***/**3j′** was detected as 91:9, and the pure compound was obtained as a white solid (147 mg, 77%, >99:1 $dr_C$, mp 192−194 °C) from recrystallization with petroleum ether−dichloromethane. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 46.17 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.93 (d, $J$ = 7.6 Hz, 2H), 7.55 (t, $J$ = 7.4 Hz, 1H), 7.43 (dd, $J$ = 16.2, 8.6 Hz, 4H), 7.34 (d, $J$ = 6.7 Hz, 1H), 7.28 (d, $J$ = 8.6 Hz, 2H), 7.06 (d, $J$ = 7.0 Hz, 2H), 6.99 (d, $J$ = 8.4 Hz, 2H), 4.30 (t, $J$ = 8.3 Hz, 1H), 3.91 (dd, $J$ = 17.3, 8.0 Hz, 1H), 3.70 (ddd, $J$ = 14.2, 9.8, 3.9 Hz, 1H), 2.27 (s, 1H), 2.16 (s, 1H), 2.11−2.02 (m, 1H), 1.71 (s, 3H), 1.44−1.32 (m, 2H), 1.10−0.87 (m, 5H), 0.81 (d, $J$ = 6.7 Hz, 3H), 0.31 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 196.8 (d, $J$ = 11.7 Hz), 136.6 (d, $J$ = 4.6 Hz), 136.4 (s), 133.4 (s), 132.3 (d, $J$ = 2.8 Hz), 132.4 (d, $J$ = 88.0 Hz), 131.2 (s), 131.0 (s), 130.9 (s), 130.8 (s), 130.7 (s), 128.6 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.8 (s), 127.7 (s), 43.9 (d, $J$ = 3.1 Hz), 40.7 (d, $J$ = 63.0 Hz), 39.7 (s), 39.8 (d, $J$ = 61.0 Hz), 35.4 (d, $J$ = 3.0 Hz), 34.2 (s), 33.4 (d, $J$ = 12.4 Hz), 28.3 (d, $J$ = 2.5 Hz), 24.8 (d, $J$ = 12.2 Hz), 22.6 (s), 21.6 (s), 15.4 (s). Elemental analysis: Calcd for $C_{31}H_{36}ClO_2P$, C, 73.43; H, 7.16. Found: C, 73.06; H, 7.12.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(p-methoxyphenyl)propan-2-one,* ***3k***. The reaction was carried out



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according to the procedure of method A. In the crude product, the ratio of **3*k***/**3k′** was detected as 85:15, and the pure compound was obtained as a pale yellow solid (120 mg, 63%, >99:1 $dr_C$, mp 160−162 °C) from recrystallization with petroleum ether−dichloromethane. $^{31}P$ NMR (162 MHz, chloroform-*d*) $\delta$ 49.31 (s). $^1H$ NMR (400 MHz, chloroform-*d*) $\delta$ 7.93 (d, $J$ = 7.8 Hz, 2H), 7.53 (t, $J$ = 7.0 Hz, 1H), 7.42 (t, $J$ = 10.0 Hz, 4H), 7.33 (d, $J$ = 7.0 Hz, 1H), 7.28 (d, $J$ = 5.8 Hz, 2H), 6.99 (d, $J$ = 8.1 Hz, 2H), 6.58 (d, $J$ = 8.3 Hz, 2H), 4.33 (t, $J$ = 8.9 Hz, 1H), 3.89 (dd, $J$ = 16.8, 8.6 Hz, 1H), 3.73−3.57 (m, 4H), 2.34 (br, 1H), 2.14 (s, 1H), 2.07−1.99 (m, 1H), 1.77−1.63 (m, 3H), 1.37 (d, $J$ = 17.1 Hz, 2H), 1.03−0.91 (m, 5H), 0.79 (d, $J$ = 6.6 Hz, 3H), 0.31 (d, $J$ = 6.6 Hz, 3H). $^{13}C$ NMR (101 MHz, chloroform-*d*) $\delta$ 197.2 (d, $J$ = 11.9 Hz), 158.1 (s), 136.7 (s), 133.2 (s), 133.0 (s), 132.1 (s), 131.2 (s), 131.1 (s), 130.8 (d, $J$ = 2.6 Hz), 130.4 (s), 130.4 (s), 129.5 (d, $J$ = 4.4 Hz), 128.6 (s), 128.1 (s), 127.6 (s), 127.5 (s), 113.5 (s), 113.5 (s), 55.1 (s), 43.8 (d, $J$ = 3.1 Hz), 40.1 (d, $J$ = 62.0 Hz), 39.5 (s), 39.3 (d, $J$ = 62.0 Hz), 35.3 (d, $J$ = 3.1 Hz), 34.2 (s), 33.3 (d, $J$ = 12.4 Hz), 28.2 (s), 24.8 (d, $J$ = 12.0 Hz), 22.7 (s), 21.6 (s), 15.5 (s). Elemental analysis: Calcd for $C_{32}H_{39}O_3P$, C, 76.47; H, 7.82. Found: C, 76.09; H, 7.78.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-(p-methoxyphenyl)-4-(o-trifluoromethylphenyl)propan-2-one,* ***3l.*** The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3*l***/**3l′** was detected as 95:5, and the pure compound was obtained as a colorless oil (153 mg, 71%, 98:2 $dr_C$) from preparative TLC (silica gel, hexane/ethyl acetate = 1/2 as eluent). $^{31}P$ NMR (162 MHz, chloroform-*d*) $\delta$ 48.31 (s, 2%), 47.06 (s, 98%). $^1H$ NMR (400 MHz, chloroform-*d*) $\delta$ 7.91 (d, $J$ = 8.9 Hz, 2H), 7.71 (d, $J$ = 7.8 Hz, 1H), 7.49−7.38 (m, 2H), 7.34−7.24 (m, 1H), 7.21−7.11 (m, 4H), 7.01 (d, $J$ = 8.1 Hz, 1H), 6.87 (d, $J$ = 8.9 Hz, 2H), 4.72 (dd, $J$ = 10.4, 7.7 Hz, 1H), 4.09 (ddd, $J$ = 17.6, 10.8, 3.9 Hz, 1H), 3.82 (d, $J$ = 15.8 Hz, 3H), 3.76−3.64 (m, 1H), 2.27 (d, $J$ = 5.0 Hz, 2H), 2.17−2.03 (m, 1H), 1.77−1.57 (m, 3H), 1.47−1.26 (m, 2H), 1.08−0.98 (m, 1H), 0.91 (d, $J$ = 6.0 Hz, 4H), 0.75 (d, $J$ = 6.8 Hz, 3H), 0.37 (d, $J$ = 6.7 Hz, 3H). $^{13}C$ NMR (101 MHz, chloroform-*d*) $\delta$ 195.2 (d, $J$ = 9.2 Hz), 163.5 (s), 138.6 (q, $J_{C-F}$ = 2.8 Hz), 133.5 (s), 132.6 (s), 131.7 (s), 131.0 (s), 130.9 (s), 130.8 (s), 130.7 (q, $J_{C-F}$ = 289.5 Hz), 130.6 (s), 130.5 (s), 130.4 (s), 129.7 (s), 127.5 (s), 127.4 (s), 126.4 (s), 125.9 (q, $J_{C-F}$ = 4.7 Hz, $J$ = 6.4 Hz), 113.6 (s), 55.4 (s), 43.8 (d, $J$ = 3.3 Hz), 42.1 (d, $J$ = 62.2 Hz), 41.4 (s), 36.3 (d, $J$ = 58.4 Hz), 35.0 (s), 34.2 (s), 33.4 (d, $J$ = 12.5 Hz), 28.2 (s), 24.8 (d, $J$ = 12.4 Hz), 22.5 (s), 21.4 (s), 15.3 (s). Elemental analysis: Calcd for $C_{33}H_{38}F_3O_3P$, C, 69.46; H, 6.71. Found: C, 69.25; H, 6.69.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-(p-chlorophenyl)-4-(o-nitrophenyl)propan-2-one,* ***3m.*** The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3*m***/**3m′** was detected as 97:3, and the pure compound was obtained as a red solid (181 mg, 87%, >99:1 $dr_C$) from recrystallization with petroleum ether. $^{31}P$ NMR (162 MHz, chloroform-*d*) $\delta$ 47.34 (s). $^1H$ NMR (400 MHz, chloroform-*d*) $\delta$ 7.86 (d, $J$ = 8.6 Hz, 2H), 7.66 (dd, $J$ = 6.1, 4.6 Hz, 2H), 7.62 (d, $J$ = 6.2 Hz, 1H), 7.58 (d, $J$ = 8.2 Hz, 1H), 7.38 (d, $J$ = 8.6 Hz, 2H), 7.25−7.13 (m, 4H), 7.03 (t, $J$ = 7.7 Hz, 1H), 5.22 (q, $J$ = 6.6 Hz, 1H), 3.87 (t, $J$ = 6.0 Hz, 2H), 2.32 (d, $J$ = 5.1 Hz, 1H), 2.20 (dd, $J$ = 12.8, 5.8 Hz, 2H), 1.71 (s, 1H), 1.63 (s, 1H), 1.42 (s, 1H), 1.31 (dd, $J$ = 12.2, 5.5 Hz, 1H), 1.17 (d, $J$ = 6.9 Hz, 1H), 1.04 (d, $J$ = 10.0 Hz, 1H), 0.89 (d, $J$ = 6.4 Hz, 4H), 0.83 (d, $J$ = 6.8 Hz, 3H), 0.29 (d, $J$ = 6.8 Hz, 3H). $^{13}C$ NMR (101 MHz, chloroform-*d*) $\delta$ 195.1 (d, $J$ = 12.3 Hz), 149.6 (s), 140.1 (s), 134.5 (d, $J$ = 3.9 Hz), 134.2 (s), 132.8 (s), 132.5 (d, $J$ = 90.0 Hz), 131.0 (d, $J$ = 2.9 Hz), 130.7 (s), 130.6 (s), 130.4 (d, $J$ = 4.8 Hz), 129.0 (s), 127.8 (s), 127.7 (s), 127.2 (s), 124.2 (s), 43.8 (d, $J$ = 3.1 Hz), 42.4 (d, $J$ = 63.3 Hz), 42.0 (s), 35.2 (d, $J$ = 3.4 Hz), 34.2 (s), 33.8 (d, $J$ = 60.6 Hz), 33.4 (d, $J$ = 12.5 Hz), 28.4 (d, $J$ = 2.5 Hz), 24.7 (d, $J$ = 12.4 Hz), 22.6 (s), 21.5 (s), 15.1 (s). Elemental analysis: Calcd for $C_{31}H_{35}ClNO_4P$, C, 67.45; H, 6.39. Found: C, 67.25; H, 6.37.

*($S_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-(p-chlorophenyl)-4-(p-nitrophenyl)propan-2-one,* ***3n.*** The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3*n***/**3n′** was detected as 91:9, and the pure compound was obtained as a pale yellow solid (136 mg, 65%, >99:1 $dr_C$, mp 208−211 °C) from recrystallization with petroleum ether−dichloromethane. $^{31}P$ NMR (162 MHz, chloroform-*d*) $\delta$ 44.64 (s). $^1H$ NMR (400 MHz, chloroform-*d*) $\delta$ 7.87 (dd, $J$ = 7.9, 6.1 Hz, 4H), 7.41 (dd, $J$ = 13.3, 5.0 Hz, 4H), 7.31 (dd, $J$ = 7.9, 6.5 Hz, 3H), 7.28−7.21 (m, 2H), 4.36 (t, $J$ = 7.5 Hz, 1H), 3.96 (dd, $J_{P-H}$ = 18.7, $J_1$ = 8.8 Hz, 1H), 3.83−3.69 (m, 1H), 2.28−2.05 (m, 3H), 1.86−1.62 (m, 3H), 1.48−1.26 (m, 2H), 1.12−0.77 (m, 8H), 0.29 (d, $J$ = 6.7 Hz, 3H). $^{13}C$ NMR (101 MHz, chloroform-*d*) $\delta$ 195.2 (d, $J$ = 11.4 Hz), 146.3 (d, $J$ = 4.9 Hz), 140.2 (s), 134.4 (s), 132.7 (s), 131.9 (s), 131.3 (d, $J$ = 2.7 Hz), 130.7 (s), 130.6 (s), 130.3 (s), 130.2 (s), 129.5 (s), 129.1 (s), 128.1 (s), 128.0 (s), 123.2 (s), 43.9 (d, $J$ = 3.3 Hz), 41.2 (d, $J$ = 126.0 Hz), 41.2 (d, $J$ = 4.0 Hz), 40.0 (s), 35.5 (s), 34.1 (s), 33.4 (d, $J$ = 12.4 Hz), 28.5(d, $J$ = 2.6 Hz), 24.8 (d, $J$ = 12.3 Hz), 22.6 (s), 21.5 (s), 15.3 (s). Elemental analysis: Calcd for $C_{31}H_{35}ClNO_4P$, C, 67.45; H, 6.39. Found: C, 67.18; H, 6.36.

*($S_P$,R)-4-[(−)-Menthylphenylphosphoryl]-1-(p-bromophenyl)-4-(p-diphenylaminephenyl) Propan-2-one,* ***3o′.*** The reaction was carried out according to the procedure of method B. In the crude product, the ratio of **3*o***/**3o′** was detected as 58:42, and the pure compound was obtained as a colorless oil (39 mg, 31%, 4:96 $dr_C$) from preparative TLC (silica gel, hexane/ethyl acetate = 2/1 as eluent). $^{31}P$ NMR (162 MHz, chloroform-*d*) $\delta$ 46.77 (s, 96%), 45.49 (s, 4%). $^1H$ NMR (400 MHz, chloroform-*d*) $\delta$ 7.81 (dd, $J$ = 12.0, 5.1 Hz, 2H), 7.68 (d, $J$ = 8.6 Hz, 2H), 7.52 (dd, $J$ = 13.9, 5.1 Hz, 7H), 7.22 (t, $J$ = 7.9 Hz, 4H), 7.01 (dd, $J$ = 15.4, 7.5 Hz, 8H), 4.32−4.24 (m, 1H), 3.79 (ddd, $J$ = 17.8, 10.5, 3.2 Hz, 1H), 3.06 (dd, $J$ = 16.1, 10.1 Hz, 1H), 2.68−2.55 (m, 1H), 2.05 (s, 1H), 1.97−1.78 (m, 2H), 1.66−1.50 (m, 2H), 1.13−0.99 (m, 2H), 0.83 (dd, $J$ = 16.8, 9.4 Hz, 5H), 0.70 (d, $J$ = 6.9 Hz, 3H), 0.65 (d, $J$ = 6.7 Hz, 3H). $^{13}C$ NMR (101 MHz, chloroform-*d*) $\delta$ 196.6 (d, $J$ = 12.8 Hz), 147.6 (s), 147.0 (s), 135.2 (s), 133.6 (s), 132.8 (s), 131.8 (s), 131.8 (s), 131.4 (d, $J$ = 2.3 Hz), 131.2 (s), 131.0 (s), 130.9 (s), 130.8 (s), 129.7 (s), 129.2 (s), 128.7 (s), 128.6 (s), 124.2 (s), 124.1 (s), 122.8 (s), 50.9 (s), 43.0 (d, $J$ = 3.2 Hz), 42.2 (d, $J$ = 63.8 Hz), 40.9 (s), 34.6 (s), 34.3 (s), 33.1 (d, $J$ = 13.2 Hz), 27.8 (s), 24.9 (d, $J$ = 12.8 Hz), 22.6 (s), 21.4 (s), 15.8 (s). Elemental analysis: Calcd for $C_{43}H_{45}BrNO_2P$, C, 71.86; H, 6.31. Found: C, 71.50; H, 6.28.

*($S_P$)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(2,6-dichlorophenyl)propan-2-one,* ***3p/3p′.*** The reaction was carried out according to the procedure of method B. In the crude product, the ratio of **3*p***/**3p′** was detected as 65:35, and the pure compound was obtained as a colorless oil (82 mg, 80%, 60:40 $dr_C$) from preparative TLC (silica gel, hexane/ethyl acetate =2/1 as eluent). $^{31}P$ NMR (162 MHz, chloroform-*d*) $\delta$ 44.38 (s, 40%), 43.02 (s, 60%). $^1H$ NMR (400 MHz, chloroform-*d*) $\delta$ 8.07−6.72 (m, 13H, aromatic C−H, minor + major), 5.40−3.40 (m, 3H, C−H. minor + major), 2.32−0.10 (m, 19H, C−H of Men., minor + major). $^{13}C$ NMR (101 MHz, chloroform-*d*) $\delta$ 197.3 (d, $J$ = 10.0 Hz), 197.1 (d, $J$ = 9.6 Hz), 137.7 (d, $J$ = 6.5 Hz), 136.8 (d, $J$ = 6.9 Hz), 136.2 (d, $J$ = 31.0 Hz), 136.1 (d, $J$ = 9.0 Hz), 135.5 (d, $J$ = 4.5 Hz), 134.7 (d, $J$ = 4.4 Hz), 134.0 (d, $J$ = 86.0 Hz), 133.3 (s), 133.2 (s), 133.1 (d, $J$ = 90.0 Hz), 131.5 (d, $J$ = 7.9 Hz), 131.3 (d, $J$ = 2.6 Hz), 130.6 (d, $J$ = 2.8 Hz), 130.3 (d, $J$ = 1.0 Hz), 130.2 (s), 130.1 (s), 129.4 (d, $J$ = 2.2 Hz), 128.9 (d, $J$ = 1.0 Hz), 128.7 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.9 (d, $J$ = 2.0 Hz), 127.1 (s), 127.0 (s), 43.7 (s), 43.6 (d, $J$ = 3.6 Hz), 43.3 (d, $J$ = 3.3 Hz), 43.1 (s), 42.2 (d, $J$ = 64.0 Hz), 37.7 (d, $J$ = 57.0 Hz), 37.6 (d, $J$ = 26.0 Hz), 36.3 (d, $J$ = 58.0 Hz), 34.4 (d, $J$ = 3.9 Hz), 34.3 (d, $J$ = 2.7 Hz), 34.2 (s), 33.9 (s), 33.4 (d, $J$ = 12.4 Hz), 33.0 (d, $J$ = 13.1 Hz), 28.3 (d, $J$ = 2.4 Hz), 27.9 (d, $J$ = 3.0 Hz), 24.8 (d, $J$ = 12.6 Hz), 24.5 (d, $J$ = 12.2 Hz), 22.7 (s), 22.5 (s), 21.5 (s), 21.4 (s), 15.5 (s), 15.2 (s). Elemental analysis: Calcd for $C_{31}H_{35}Cl_2O_2P$, C, 68.76; H, 6.52. Found: C, 68.42; H, 6.49.

*($S_P$)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(2,4,6-trimethoxyphenyl)propan-2-one,* ***3q/3q′.*** The reaction was carried out according to the procedure of method B at 60 °C in 24h. In the crude product, the ratio of **3*q***/**3q′** was detected as 64:36, and the pure compound was obtained as a pale yellow oil (87 mg, 79%, 62:38 $dr_C$) from preparative TLC (silica gel, hexane/ethyl acetate = 1/4 as eluent). $^{31}P$ NMR (162 MHz, chloroform-*d*) $\delta$ 44.76 (s, 38%), 44.54 (s, 62%). $^1H$ NMR (400 MHz, chloroform-*d*) $\delta$ 8.00−5.50 (m, 12H,



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aromatic C−H, minor + major), 5.10−3.06 (m, 12H, C−H, minor + major), 2.72−0.35 (m, 19H, C−H of Men., minor + major). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 199.3 (d, *J* = 9.4 Hz), 199.0 (d, *J* = 11.5 Hz), 160.3 (d, *J* = 2.1 Hz), 160.2 (d, *J* = 3.3 Hz), 160.0 (d, *J* = 2.2 Hz), 159.2 (s), 158.7 (d, *J* = 5.5 Hz), 157.8 (d, *J* = 5.5 Hz), 137.2 (s), 136.9 (s), 135.0 (d, *J* = 83.3 Hz), 133.7 (d, *J* = 87.6 Hz), 132.7 (s), 132.6 (s), 131.5 (d, *J* = 7.5 Hz), 130.6 (d, *J* = 2.5 Hz), 130.5 (s), 130.4 (s), 129.9 (s), 128.3 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.9 (s), 126.6 (s), 126.5 (s), 107.9 (d, *J* = 4.2 Hz), 105.7 (d, *J* = 4.6 Hz), 90.8(s), 90.6 (s), 90.2 (s), 90.0 (s), 56.0 (s), 55.8 (s), 55.3 (s), 55.2 (s), 55.1 (s), 54.6 (s), 43.5 (d, *J* = 3.2 Hz), 43.3 (d, *J* = 3.5 Hz), 42.4 (d, *J* = 63.0 Hz), 42.2 (d, *J* = 63.0 Hz), 37.8 (s), 37.2 (s), 34.6 (d, *J* = 3.0 Hz), 34.5 (s), 34.4 (s), 34.3 (s), 33.3 (d, *J* = 12.4 Hz), 33.1 (d, *J* = 13.4 Hz), 29.5 (d, *J* = 62.0 Hz), 29.3 (d, *J* = 63.0 Hz), 28.1 (d, *J* = 2.4 Hz), 27.9 (d, *J* = 1.7 Hz), 25.0 (d, *J* = 12.2 Hz), 24.8 (d, *J* = 12.2 Hz), 22.8 (s), 21.6 (s), 21.5 (s), 15.8 (s), 15.6 (s). Elemental analysis: Calcd for $C_{34}H_{43}O_5P$, C, 72.58; H, 7.70. Found: C, 72.29; H, 7.70.

*(S$_P$)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(2,4,6-trimethylphenyl)propan-2-one,* ***3r/3r′***. The reaction was carried out according to the procedure of method B at 60 °C in 24h. In the crude product, the ratio of **3r**/**3r′** was detected as 83:17, and the pure compound was obtained as a pale yellow oil (80 mg, 82%, 88:12 dr$_C$) from preparative TLC (silica gel, hexane/ethyl acetate = 2/1 as eluent). $^{31}$P NMR (162 MHz, chloroform-*d*) δ 47.00 (s, 12%), 46.39 (s, 88%). $^1$H NMR (400 MHz, chloroform-*d*) δ 8.00−6.38 (m, 12H, aromatic C−H, minor + major), 4.88−3.40 (m, 3H, C−H, minor + major), 2.78−0.23 (m, 28H, C−H, minor + major). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 197.7 (d, *J* = 9.2 Hz), 197.4 (d, *J* = 9.8 Hz), 138.3 (d, *J* = 3.5 Hz), 137.5 (d, *J* = 6.8 Hz), 137.3 (d, *J* = 4.0 Hz), 136.7 (s), 136.6 (d, *J* = 7.0 Hz), 136.3 (d, *J* = 1.8 Hz), 135.5 (d, *J* = 2.4 Hz), 135.0 (s), 134.2 (d, *J* = 4.5 Hz), 134.0 (s), 133.2 (s), 133.1 (s), 133.0 (s), 132.8 (d, *J* = 4.6 Hz), 131.4 (s), 131.1 (d, *J* = 2.4 Hz), 130.5 (d, *J* = 1.8 Hz), 130.3 (s), 130.2 (s), 129.5 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.9 (s), 127.1 (s), 127.0 (s), 43.6 (s), 43.6 (s), 43.3 (s), 43.1 (d, *J* = 3.4 Hz), 42.9 (s), 42.7 (s), 39.7 (s), 39.0 (s), 35.5 (d, *J* = 60.9 Hz), 34.7 (d, *J* = 2.9 Hz), 34.3 (s), 34.2 (s), 34.0 (s), 33.5 (d, *J* = 60.0 Hz), 33.3 (d, *J* = 12.4 Hz), 32.9 (d, *J* = 13.0 Hz), 28.1 (d, *J* = 2.6 Hz), 24.8 (d, *J* = 12.7 Hz), 24.6 (d, *J* = 12.0 Hz), 22.6 (s), 22.5 (s), 22.2 (s), 22.1 (s), 22.0 (s), 21.5 (s), 21.4 (s), 21.2 (s), 20.7 (s), 20.5 (s), 15.7 (s), 15.3 (s). Elemental analysis: Calcd for $C_{34}H_{43}O_2P$, C, 79.34; H, 8.42. Found: C, 79.02; H, 8.39.

*(S$_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-(o-methoxynaphthyl)propan-2-one,* ***3s***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3s**/**3s′** was detected as 89:11, and the pure compound was obtained as a colorless oil (129 mg, 62%, >99:1 dr$_C$) from preparative TLC (silica gel, hexane/ethyl acetate = 2/1 as eluent). $^{31}$P NMR (162 MHz, chloroform-*d*) δ 42.98 (s). $^1$H NMR (400 MHz, chloroform-*d*) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.69−7.51 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33−7.09 (m, 5H), 6.87−6.70 (m, 2H), 5.40−5.27 (m, 1H), 4.44 (ddd, $J_{P-H}$ = 19.3, $J_1$ = 9.3, $J_2$ = 4.4 Hz, 1H), 4.01 (ddd, $J_{P-H}$ = 19.2, $J_1$ = 9.4, $J_2$ = 3.0 Hz, 1H), 2.24 (s, 1H), 2.12 (d, *J* = 11.5 Hz, 1H), 1.91 (dd, *J* = 12.6, 6.5 Hz, 1H), 1.72 (s, 2H), 1.43 (s, 3H), 1.34−1.24 (m, 1H), 1.05 (d, *J* = 10.1 Hz, 1H), 0.97 (d, *J* = 6.6 Hz, 1H), 0.93−0.81 (m, 7H), 0.73 (d, *J* = 6.8 Hz, 3H), 0.17 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 197.3 (d, *J* = 9.9 Hz), 136.8 (d, *J* = 6.8 Hz), 136.4 (s), 136.1 (d, *J* = 4.1 Hz), 135.5 (d, *J* = 4.6 Hz), 133.6 (s), 133.2 (s), 132.7 (s), 130.6 (d, *J* = 2.8 Hz), 130.3 (s), 130.2 (s), 129.4 (d, *J* = 2.2 Hz), 128.6 (s), 128.2 (s), 127.9 (s), 127.8 (s), 127.1 (s), 127.0 (s), 43.6 (d, *J* = 3.6 Hz), 43.4 (d, *J* = 66.0 Hz), 37.4 (s), 36.4 (d, *J* = 58.8 Hz), 34.4 (d, *J* = 3.7 Hz), 34.2 (s), 33.4 (d, *J* = 12.4 Hz), 27.9 (d, *J* = 3.0 Hz), 26.9 (s), 24.5 (d, *J* = 12.1 Hz), 22.6 (s), 21.5 (s), 15.2 (s). Elemental analysis: Calcd for $C_{36}H_{41}O_3P$, C, 78.23; H, 7.48. Found: C, 78.00; H, 7.46.

*(S$_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-phenyl-4-ferrocene-carboxpropan-2-one,* ***3t***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3t**/**3t′** was detected as 76:24, and the pure compound was obtained as a red solid (90 mg, 41%, >99:1 dr$_C$, mp 230−232 °C) from preparative TLC (silica gel, hexane/ethyl acetate = 1/1 as eluent), then recrystallization with petroleum ether. $^{31}$P NMR (162 MHz, chloroform-*d*) δ 43.49 (s). $^1$H NMR (400 MHz, chloroform-*d*) δ 8.10 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 6.5 Hz, 1H), 7.25−7.14 (m, 4H), 4.58−4.47 (m, 1H), 4.20 (d, *J* = 15.1 Hz, 2H), 4.02 (s, 5H), 3.97 (s, 1H), 3.80 (ddd, *J* = 17.2, 13.6, 7.8 Hz, 1H), 3.42 (s, 1H), 3.01 (td, *J* = 17.0, 3.7 Hz, 1H), 2.36 (s, 1H), 2.08 (t, *J* = 11.7 Hz, 1H), 1.71−1.61 (m, 3H), 1.61−1.41 (m, 3H), 1.09 (d, *J* = 6.3 Hz, 3H), 1.00 (t, *J* = 9.3 Hz, 2H), 0.64 (d, *J* = 6.8 Hz, 3H), 0.09 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 197.3 (d, *J* = 3.8 Hz), 136.9 (s), 133.0 (s), 131.7 (s), 131.6 (s), 131.5 (d, *J* = 83.0 Hz), 130.8 (d, *J* = 2.6 Hz), 128.6 (s), 128.4 (s), 127.2 (s), 127.1 (s), 86.2 (d, *J* = 3.4 Hz), 68.8 (s), 68.5 (d, *J* = 1.4 Hz), 68.1 (s), 67.9 (d, *J* = 1.3 Hz), 67.5 (s), 43.4 (d, *J* = 3.8 Hz), 37.5 (s), 37.1 (d, *J* = 64.8 Hz), 35.1 (d, *J* = 2.8 Hz), 34.2 (s), 33.5 (d, *J* = 17.7 Hz), 33.1 (d, *J* = 29.1 Hz), 27.5 (d, *J* = 3.2 Hz), 24.8 (d, *J* = 11.7 Hz), 23.0 (s), 21.5 (s), 15.4 (s). Elemental analysis: Calcd for $C_{35}H_{41}O_2P$, C, 80.12; H, 7.88. Found: C, 79.88; H, 7.86.

*(S$_P$)-4-[(−)-Menthylphenylphosphoryl]-pentan-3-one,* ***3u***. The reaction was carried out according to the procedure of method A in the absence of AIBN, and the pure compound was obtained as a white solid (125 mg, 95%, mp 90−93 °C) from recrystallization with petroleum ether. $^{31}$P NMR (162 MHz, chloroform-*d*) δ 42.90 (s). $^1$H NMR (400 MHz, chloroform-*d*) δ 7.67 (dd, *J* = 9.9, 8.4 Hz, 2H), 7.55−7.40 (m, 3H), 2.77 (ddd, *J* = 11.0, 9.1, 4.5 Hz, 1H), 2.45−2.25 (m, 3H), 2.25−2.13 (m, 1H), 2.13−2.03 (m, 2H), 2.00−1.83 (m, 2H), 1.72 (d, *J* = 12.7 Hz, 3H), 1.34 (s, 1H), 1.27−1.18 (m, 1H), 1.08−0.86 (m, 8H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.34 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 209.8 (d, *J* = 12.2 Hz), 133.6 (d, *J* = 87.8 Hz), 131.2 (d, *J* = 2.6 Hz), 130.6 (s), 130.5 (s), 128.5 (s), 128.4 (s), 43.3 (d, *J* = 3.4 Hz), 41.0 (d, *J* = 67.8 Hz), 35.8 (s), 35.2 (d, *J* = 2.3 Hz), 34.2 (s), 33.9 (d, *J* = 2.4 Hz), 33.2 (d, *J* = 13.2 Hz), 28.3 (d, *J* = 2.8 Hz), 24.5 (d, *J* = 12.3 Hz), 22.6 (s), 21.5 (s), 20.9 (s), 15.1 (s), 7.8 (s). Elemental analysis: Calcd for $C_{21}H_{33}O_2P$, C, 72.38; H, 9.55. Found: C, 72.09; H, 9.51.

*(S$_P$,S)-4-[(−)-Menthylphenylphosphoryl]-1-(p-bromophenyl)-4-(N-hexylphenothiazin)propan-2-one,* ***3v***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3v**/**3v′** was detected as 85:15, and the pure compound was obtained as a brown solid (158 mg, 55%, >99:1 dr$_C$, mp 189−191 °C) from preparative TLC (silica gel, hexane/ethyl acetate = 2/1 as eluent), then recrystallization with petroleum ether−dichloromethane. $^{31}$P NMR (162 MHz, chloroform-*d*) δ 44.80 (s). $^1$H NMR (400 MHz, chloroform-*d*) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.45−7.31 (m, 3H), 7.29 (s, 2H), 7.14−6.97 (m, 2H), 6.84 (d, *J* = 7.1 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.59 (s, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 4.24 (t, *J* = 9.2 Hz, 1H), 3.85 (dd, *J* = 16.1, 8.8 Hz, 1H), 3.68 (t, *J* = 7.2 Hz, 2H), 3.48−3.38 (m, 1H), 2.30 (s, 1H), 2.12 (s, 1H), 2.02−1.87 (m, 1H), 1.70−1.64 (m, 3H), 1.41 (d, *J* = 10.2 Hz, 3H), 1.38−1.33 (m, 2H), 1.28 (s, 3H), 0.97 (t, *J* = 9.1 Hz, 5H), 0.87 (t, *J* = 6.4 Hz, 5H), 0.77 (d, *J* = 6.7 Hz, 3H), 0.28 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 196.0 (d, *J* = 11.5 Hz), 145.0 (s), 143.6 (d, *J* = 2.3 Hz), 135.3 (s), 132.3 (d, *J* = 86.0 Hz), 131.9 (s), 131.2 (s), 131.1 (s), 131.0 (d, *J* = 1.9 Hz), 130.9 (s), 129.7 (s), 128.4 (s), 128.1 (d, *J* = 5.6 Hz), 128.0 (d, *J* = 4.9 Hz), 127.6 (s), 127.5 (s), 127.3 (s), 127.1 (s), 124.3 (s), 124.2 (s), 122.2 (s), 115.1 (s), 114.8 (s), 47.2 (s), 43.8 (d, *J* = 3.3 Hz), 39.5 (d, *J* = 31.6 Hz), 39.0 (s), 38.9 (d, *J* = 29.0 Hz), 35.2 (s), 34.2 (s), 33.3 (d, *J* = 12.5 Hz), 31.5 (s), 28.0 (d, *J* = 2.7 Hz), 26.6 (s), 24.8 (d, *J* = 11.9 Hz), 22.8 (s), 22.6 (s), 21.6 (s), 15.6 (s), 14.1 (s). Elemental analysis: Calcd for $C_{43}H_{51}BrNO_2PS$, C, 68.24; H, 6.79. Found: C, 68.04; H, 6.77.

*(S$_P$,S)-2-[(−)-Menthylphenylphosphoryl]-2-phenyl-1H-indene-1,3(2H)-dione,* ***3w***. The reaction was carried out according to the procedure of method A. In the crude product, the ratio of **3w**/**3w′** was detected as 67:33, and the pure compound was obtained as yellow solid (51 mg, 27%, >99:1 dr$_C$, mp 205−207 °C) from preparative TLC (silica gel, hexane/ethyl acetate = 2/1 as eluent), then recrystallization with petroleum ether. $^{31}$P NMR (162 MHz, chloroform-*d*) δ 57.28 (s). $^1$H NMR (400 MHz, chloroform-*d*) δ 7.47 (dd, *J* = 9.6, 8.1 Hz, 2H), 7.40−7.23 (m, 7H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.02−6.89 (m, 3H), 4.46 (d, *J* = 7.7 Hz, 1H), 2.32 (t, *J* = 11.7 Hz, 1H), 2.15−1.92 (m, 2H), 1.68


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(d, $J$ = 11.3 Hz, 3H), 1.41−1.16 (m, 2H), 1.08−0.94 (m, 1H), 0.89−0.72 (m, 7H), 0.25 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 193.5 (d, $J$ = 9.1 Hz), 174.7 (d, $J$ = 4.4 Hz), 140.1 (s), 137.2 (d, $J$ = 4.2 Hz), 132.9 (s), 132.3 (s), 131.4 (d, $J$ = 2.9 Hz), 130.5 (s), 130.4 (s), 130.3 (s), 129.9 (s), 129.2 (s), 129.1 (s), 128.2 (s), 128.1 (s), 126.6 (d, $J$ = 2.2 Hz), 119.1 (s), 106.8 (d, $J$ = 3.5 Hz), 43.5 (d, $J$ = 3.5 Hz), 42.7 (d, $J$ = 60.6 Hz), 41.5 (d, $J$ = 61.1 Hz), 35.1 (d, $J$ = 3.4 Hz), 33.9 (s), 33.2 (d, $J$ = 12.7 Hz), 28.6 (d, $J$ = 2.6 Hz), 24.6 (d, $J$ = 12.4 Hz), 22.3 (s), 21.5 (s), 15.1 (s). Elemental analysis: Calcd for $C_{32}H_{35}O_3P$, C, 77.09; H, 7.08. Found: C, 76.78; H, 7.05.

*($S_P$,R)-4-[(−)-Menthylphenylphosphoryl]-1-pyridyl-4- pyridylpropan-2-one,* ***3x′***. The reaction was carried out according to the procedure of method B. In the crude product, the ratio of ***3x***/***3x′*** was detected as 43:57, and the pure compound was obtained as a white solid (40 mg, 45%, 3:97 $dr_C$, mp 175−177 °C) from recrystallization from ether. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 44.70 (s, 97%), 43.61 (s, 3%). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 8.68 (d, $J$ = 4.2 Hz, 1H), 8.39 (d, $J$ = 4.0 Hz, 1H), 7.95 (d, $J$ = 7.8 Hz, 1H), 7.78 (t, $J$ = 7.5 Hz, 1H), 7.49−7.42 (m, 1H), 7.41−7.29 (m, 4H), 7.23 (d, $J$ = 6.8 Hz, 2H), 6.99 (t, $J$ = 8.3 Hz, 2H), 4.88−4.68 (m, 1H), 4.13 (ddd, $J_{P-H}$ = 18.1, $J_1$ = 8.9, $J_2$ = 4.2 Hz, 1H), 4.03−3.76 (m, 1H), 2.79 (s, 1H), 2.24 (s, 1H), 1.90−1.62 (m, 4H), 1.46 (s, 2H), 1.00 (d, $J$ = 5.1 Hz, 5H), 0.73 (d, $J$ = 6.6 Hz, 3H), 0.26 (d, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 199.1 (d, $J$ = 10.7 Hz), 157.7 (d, $J$ = 3.5 Hz), 153.1 (s), 149.0 (s), 148.8 (s), 136.8 (s), 136.1 (s), 132.6 (d, $J$ = 85.5 Hz), 131.1 (s), 131.0 (s), 130.8 (s), 127.5 (s), 127.4 (s), 127.2 (s), 123.4 (d, $J$ = 4.0 Hz), 122.0 (s), 121.4 (s), 43.4 (d, $J$ = 3.4 Hz), 42.8 (dd, $J$ = 58.2, 7.0 Hz), 38.9 (d, $J$ = 65.3 Hz), 35.8 (s), 34.9 (s), 34.3 (s), 33.3 (d, $J$ = 13.1 Hz), 27.8 (s), 24.8 (d, $J$ = 12.2 Hz), 22.8 (s), 21.6 (s), 15.6 (s). Elemental analysis: Calcd for $C_{29}H_{35}N_2O_2P$, C, 73.39; H, 7.43. Found: C, 73.17; H, 7.41.

**Addition of 1 to Various Activated Alkenes.** *Typical Procedure for Method A.* The solution of **1** (50 mg, 0.189 mmol), **4** (0.208 mmol), and AIBN (0.0062 g, 0.038 mmol) in toluene (0.1 mL) was heated at 80 °C for 17 h. The solution (0.02 mL) was dissolved in chloroform (0.5 mL) for monitoring the reaction with $^{31}$P NMR spectra. After the reaction was completed, the solvent was removed in vacuo, and the residue was recrystallized with petroleum ether (30−60 °C) or purified with preparative TLC.

*Typical Procedure for Method B.* The solution of **1** (50 mg, 0.189 mmol), **4** (0.227 mmol), and $Ca(OH)_2$ (14 mg, 0.189 mmol) in DMF (0.3 mL) was stirred at rt. To the solution, the saturated aqueous ammonium chloride (10 mL) was added. The mixture was extracted with dichloromethane (20 mL), washed with water, and dried over anhydrous magnesium sulfate. After removing the solvent, the residue was recrystallized with petroleum ether (30−60 °C) or purified with preparative TLC.

*Methyl ($S_P$)-3-[(−)-Menthylphenylphosphoryl]propanoate,* ***5a***. The reaction was carried out according to the procedure of method B, and the pure compound was obtained as a pale yellow solid (58 mg, 88%) from recrystallization with petroleum ether−ether. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 42.68 (s), 41.07 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.75−7.63 (m, 2H), 7.58−7.42 (m, 3H), 3.59 (d, $J$ = 16.0 Hz, 3H), 2.64 (tdd, $J$ = 18.0, 12.5, 5.2 Hz, 1H), 2.52−2.30 (m, 1H), 2.21−2.01 (m, 3H), 1.90 (d, $J$ = 9.2 Hz, 1H), 1.72 (d, $J$ = 11.3 Hz, 3H), 1.41−1.22 (m, 2H), 1.09−0.86 (m, 5H), 0.83 (d, $J$ = 6.8 Hz, 3H), 0.46−0.21 (m, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 173.3 (d, $J$ = 16.1 Hz), 133.5 (d, $J$ = 88.1 Hz), 131.2 (s), 130.5 (s), 130.4 (s), 128.6 (s), 128.5 (s), 52.0 (d, $J$ = 4.0 Hz), 43.2 (d, $J$ = 3.3 Hz), 40.8 (d, $J$ = 68.3 Hz), 35.2 (s), 34.1 (s), 33.2 (d, $J$ = 13.1 Hz), 28.3 (d, $J$ = 2.9 Hz), 26.2 (s), 24.5 (d, $J$ = 12.3 Hz), 23.2 (d, $J$ = 66.9 Hz), 22.6 (s), 21.5 (s), 15.1 (s). Elemental analysis: Calcd for $C_{20}H_{31}O_3P$, C, 68.55; H, 8.92. Found: C, 68.21; H, 8.88.

*Methyl ($S_P$, S)-3-[(−)-Menthylphenylphosphoryl]-3-phenylpropanoate,* ***5b***. The reaction was carried out according to the procedure of method B. In the crude product, the ratio of ***5b***/***5b′*** was detected as 83:17, and the pure compound was obtained as a white solid (50 mg, 62%, >99:1 $dr_C$, mp 141−143 °C) from recrystallization with petroleum ether. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 43.77 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.27 (dq, $J$ = 12.2, 7.4 Hz, 6H), 7.15−7.01 (m, 3H), 6.94 (d, $J$ = 6.1 Hz, 2H), 4.08 (td, $J$ = 11.2, 3.8 Hz, 1H), 3.55 (s, 3H), 3.31 (ddd, $J$ = 16.6, 7.6, 3.8 Hz, 1H), 2.89−2.71 (m, 1H), 2.38 (s, 1H), 2.09 (d, $J$ = 11.1 Hz, 1H), 1.91−1.81 (m, 1H), 1.74 (d, $J$ = 10.8 Hz, 3H), 1.54−1.39 (m, 2H), 1.10−0.89 (m, 5H), 0.76 (d, $J$ = 6.7 Hz, 3H), 0.26 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 172.2 (d, $J$ = 14.8 Hz), 136.6 (d, $J$ = 4.4 Hz), 131.5 (d, $J$ = 2.2 Hz), 131.2 (s), 131.1 (s), 130.9 (d, $J$ = 2.5 Hz), 129.2 (s), 129.1 (s), 128.2 (s), 128.2 (s), 127.5 (s), 127.4 (s), 126.9 (d, $J$ = 2.5 Hz), 52.0 (s), 43.7 (d, $J$ = 3.4 Hz), 41.2 (d, $J$ = 60.0 Hz), 39.2 (d, $J$ = 64.7 Hz), 35.3 (d, $J$ = 3.2 Hz), 34.7 (s), 34.2 (s), 33.3 (d, $J$ = 12.6 Hz), 27.9 (d, $J$ = 2.9 Hz), 24.8 (d, $J$ = 12.0 Hz), 22.8 (s), 21.6 (s), 15.6 (s). Elemental analysis: Calcd for $C_{26}H_{35}O_3P$, C, 73.21; H, 8.27. Found: C, 72.84; H, 8.23.

*($S_P$,R)-4-[(−)-Menthylphenylphosphoryl]-4-chroman-2-one,* ***5c′***. The reaction was carried out according to the procedure of method B. In the crude product, the ratio of ***5c***/***5c′*** was detected as 43:57, and the pure compound was obtained as a white solid (10 mg, 13%, >99:1 $dr_C$, mp 272−274 °C) from recrystallization with petroleum ether−dichloromethane. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 40.40 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.43 (t, $J$ = 6.8 Hz, 1H), 7.31−7.04 (m, 7H), 6.80 (d, $J$ = 8.1 Hz, 1H), 3.96 (dd, $J$ = 13.9, 8.4 Hz, 1H), 3.56 (dd, $J$ = 16.9, 8.7 Hz, 1H), 2.94−2.74 (m, 1H), 2.38 (s, 1H), 2.19 (t, $J$ = 11.5 Hz, 1H), 1.90−1.71 (m, 3H), 1.71−1.53 (m, 3H), 1.14−0.98 (m, 5H), 0.71 (d, $J$ = 6.7 Hz, 3H), 0.18 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 165.5 (s), 152.4 (d, $J$ = 4.4 Hz), 132.1 (s), 130.7 (s), 130.5 (s) 129.8 (s), 129.2 (s), 127.9 (s), 127.8 (s), 127.6 (s), 124.5 (s), 118.8 (d, $J$ = 2.5 Hz), 117.9 (d, $J$ = 2.3 Hz), 43.6 (s), 37.3 (s), 36.6 (s), 35.6 (d, $J$ = 3.3 Hz), 34.8 (d, $J$ = 13.1 Hz), 34.1 (s), 33.1 (d, $J$ = 12.6 Hz), 27.6 (s), 24.7 (d, $J$ = 11.8 Hz), 22.8 (s), 21.5 (s), 15.6 (s). Elemental analysis: Calcd for $C_{25}H_{31}O_3P$, C, 73.15; H, 7.61. Found: C, 72.93; H, 7.59.

*($S_P$)-3-[(−)-Menthylphenylphosphoryl]propanenitrile,* ***5d***. The reaction was carried out according to the procedure of method B, and the pure compound was obtained as a white solid (56 mg, 94%, mp 147−149 °C) from recrystallization with petroleum ether−ether. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 41.84 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.76−7.63 (m, 2H), 7.55 (dd, $J$ = 15.0, 7.5 Hz, 3H), 2.76−2.58 (m, 1H), 2.57−2.37 (m, 1H), 2.05 (ddd, $J$ = 17.9, 13.4, 5.5 Hz, 3H), 1.87 (d, $J$ = 8.9 Hz, 1H), 1.78−1.66 (m, 3H), 1.46−1.20 (m, 2H), 1.11−0.90 (m, 5H), 0.83 (d, $J$ = 6.7 Hz, 3H), 0.30 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$132.4 (d, $J$ = 88.0 Hz), 131.9 (d, $J$ = 2.8 Hz), 130.4 (s), 130.3 (s), 129.0 (s), 128.9 (s), 119.1 (d, $J$ = 17.9 Hz), 43.1 (d, $J$ = 3.4 Hz), 40.7 (d, $J$ = 68.8 Hz), 35.1 (d, $J$ = 2.9 Hz), 34.0 (s), 33.1 (d, $J$ = 13.2 Hz), 28.4 (d, $J$ = 3.1 Hz), 24.7 (d, $J$ = 52.0 Hz), 24.4 (d, $J$ = 2.0 Hz), 22.6 (s), 21.5 (s), 15.0 (s), 10.3 (s). Elemental analysis: Calcd for $C_{19}H_{28}NOP$, C, 71.90; H, 8.89. Found: C, 71.61; H, 8.85.

*($S_P$,2R,3S)-3-[(−)-Menthylphenylphosphoryl]-2-phenyl-3-(p-chlorophenyl)propanenitrile,* ***5e***. The reaction was carried out according to the procedure of method B. In the crude product, the ratio of ***5e***/***5e′*** was detected as 22:13:61:4, and the pure compound was obtained as a white solid (20 mg, 21%, mp 253−255 °C) from recrystallization with petroleum ether− ether. $^{31}$P NMR (162 MHz, chloroform-$d$) $\delta$ 43.01 (s). $^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.95−7.64 (m, 3H), 7.49 (dd, $J$ = 11.5, 7.3 Hz, 5H), 7.37 (d, $J$ = 8.3 Hz, 2H), 7.10 (q, $J$ = 5.8 Hz, 3H), 6.91 (d, $J$ = 6.4 Hz, 2H), 4.31 (dd, $J$ = 7.5, 5.6 Hz, 1H), 3.47 (t, $J$ = 5.4 Hz, 1H), 2.38−2.17 (m, 1H), 2.00−1.75 (m, 2H), 1.51 (d, $J$ = 13.2 Hz, 1H), 1.45 (d, $J$ = 2.9 Hz, 1H), 1.06 (s, 1H), 0.83−0.60 (m, 9H), 0.58−0.34 (m, 4H). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 134.7 (d, $J$ = 1.5 Hz), 134.0 (d, $J$ = 7.0 Hz), 132.6 (s), 132.3 (s), 132.2 (s), 131.9 (d, $J$ = 3.0 Hz), 131.8 (s), 131.6 (d, $J$ = 2.6 Hz), 130.8 (s), 130.7 (s), 128.9 (s), 128.7 (s), 128.7 (s), 128.6 (s), 128.4 (s), 128.2 (s), 118.5 (d, $J$ = 6.1 Hz), 49.5 (d, $J$ = 57.8 Hz), 43.1 (d, $J$ = 2.9 Hz), 42.7 (d, $J$ = 63.0 Hz), 40.3 (s), 34.5 (d, $J$ = 2.4 Hz), 34.0 (s), 33.0 (d, $J$ = 13.0 Hz), 28.5 (s), 24.7 (d, $J$ = 13.4 Hz), 22.4 (s), 21.3 (s), 15.9 (s). Elemental analysis: Calcd for $C_{25}H_{31}ClNOP$, C, 70.17; H, 7.30. Found: C, 69.96; H, 7.28.

*($S_P$,S)-(−)-Menthylphenyl-2-nitro-1-phenylethyl Phosphine Oxide,* ***5f***. The reaction was carried out according to the procedure of method B. In the crude product, the ratio of ***5f***/***5f′*** was detected as 81:19, and



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the pure compound was obtained as a white solid (45 mg, 58%, mp 156−158 °C) from recrystallization with petroleum ether−ether. $^{31}$P NMR (162 MHz, chloroform-*d*) δ 43.80 (s). $^{1}$H NMR (400 MHz, chloroform-*d*) δ 7.36 (d, *J* = 7.0 Hz, 1H), 7.34−7.23 (m, 4H), 7.19−7.01 (m, 3H), 6.99−6.86 (m, 2H), 5.25 (dt, *J* = 13.9, 4.0 Hz, 1H), 4.90−4.72 (m, 1H), 4.43 (td, *J* = 12.4, 3.5 Hz, 1H), 2.40 (d, *J* = 9.2 Hz, 1H), 2.15 (d, *J* = 11.4 Hz, 1H), 1.76 (dd, *J* = 13.7, 8.8 Hz, 4H), 1.61−1.43 (m, 2H), 1.10−0.90 (m, 5H), 0.77 (d, *J* = 6.7 Hz, 3H), 0.23 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 133.0 (d, *J* = 4.3 Hz), 131.8 (s), 131.5 (d, *J* = 2.8 Hz), 131.0 (s), 130.9 (s), 128.9 (s), 127.6 (s), 128.6 (s), 127.9 (s), 127.8 (s), 127.8 (s), 127.8 (s), 44.3 (s), 43.8 (s), 43.6 (d, *J* = 3.4 Hz), 39.7 (d, *J* = 65.0 Hz), 35.4 (d, *J* = 3.6 Hz), 34.1 (d, *J* = 1.3 Hz), 33.3 (d, *J* = 12.7 Hz), 28.0 (d, *J* = 3.1 Hz), 24.7 (d, *J* = 12.3 Hz), 22.8 (s), 21.5 (s), 15.4 (s). Elemental analysis: Calcd for $C_{24}H_{32}NO_3P$, C, 69.71; H, 7.80. Found: C, 69.50; H, 7.78.

*(S$_P$,S)-(−)-Menthylphenyl-2-nitro-1-p-methylphenylethyl Phosphine Oxide,* ***5g****.* The reaction was carried out according to the procedure of method B. In the crude product, the ratio of **5g**/**5g′** was detected as 80:20, and the pure compound was obtained as a pale yellow solid (45 mg, 56%, mp 162−164 °C) from recrystallization with petroleum ether. $^{31}$P NMR (162 MHz, chloroform-*d*) δ 43.61 (s). $^{1}$H NMR (400 MHz, chloroform-*d*) δ 7.44−7.37 (m, 1H), 7.31 (ddd, *J* = 11.2, 7.9, 5.6 Hz, 4H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.79 (dd, *J* = 8.1, 1.5 Hz, 2H), 5.23 (dt, *J* = 13.8, 3.9 Hz, 1H), 4.75 (ddd, *J* = 13.8, 12.1, 3.9 Hz, 1H), 4.42 (td, *J* = 13.5, 3.6 Hz, 1H), 2.45−2.34 (m, 1H), 2.22 (s, 3H), 2.14 (t, *J* = 11.5 Hz, 1H), 1.83−1.68 (m, 4H), 1.62−1.39 (m, 2H), 1.11−0.94 (m, 5H), 0.76 (d, *J* = 6.7 Hz, 3H), 0.24 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 137.7 (d, *J* = 2.6 Hz), 131.5 (d, *J* = 2.8 Hz), 131.1 (s), 131.0 (s), 131.2 (d, *J* = 88.0 Hz), 129.5 (d, *J* = 4.1 Hz), 129.3 (s), 129.3 (s), 128.8 (s), 128.7 (s), 127.9 (s), 127.8 (s), 43.9 (s), 43.6 (d, *J* = 3.4 Hz), 43.3 (s), 39.3 (d, *J* = 65.2 Hz), 35.3 (d, *J* = 3.5 Hz), 34.1 (s), 33.2 (d, *J* = 12.7 Hz), 28.0 (d, *J* = 3.2 Hz), 24.7 (d, *J* = 12.3 Hz), 22.8 (s), 21.5 (s), 21.0 (s), 15.5 (s). Elemental analysis: Calcd for $C_{25}H_{34}NO_3P$, C, 70.24; H, 8.02. Found: C, 70.03; H, 8.00.

*(S$_P$,S)-(−)-Menthylphenyl-2-nitro-1-p-chlorophenylethyl Phosphine Oxide,* ***5h****.* The reaction was carried out according to the procedure of method B, In the crude product, the ratio of **5h**/**5h′** was detected as 79:21, and the pure compound was obtained as a white solid (47 mg, 55%, mp 192−194 °C) from recrystallization with petroleum ether−ether. $^{31}$P NMR (162 MHz, chloroform-*d*) δ 43.75 (s). $^{1}$H NMR (400 MHz, chloroform-*d*) δ 7.41−7.26 (m, 5H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.89 (dd, *J* = 8.5, 1.7 Hz, 2H), 5.24 (dt, *J* = 14.0, 3.8 Hz, 1H), 4.81 (ddd, *J* = 14.0, 12.0, 3.7 Hz, 1H), 4.34 (td, *J* = 12.0, 3.5 Hz, 1H), 2.32 (s, 1H), 2.16 (d, *J* = 11.2 Hz, 1H), 1.94−1.82 (m, 1H), 1.74 (d, *J* = 13.3 Hz, 3H), 1.58−1.40 (m, 2H), 1.05−0.97 (m, 5H), 0.79 (d, *J* = 6.7 Hz, 3H), 0.24 (d, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, chloroform-*d*) δ 133.8 (d, *J* = 2.9 Hz), 131.8 (s), 131.7 (s), 131.7 (d, *J* = 2.4 Hz), 130.8 (s), 130.7 (s), 130.3 (s), 130.2 (s), 128.8 (s), 128.7 (s), 128.1 (s), 128.0 (s), 44.1 (s), 43.7 (d, *J* = 3.3 Hz), 43.5 (s), 40.2 (d, *J* = 64.7 Hz), 35.5 (d, *J* = 3.6 Hz), 34.0 (s), 33.3 (d, *J* = 12.7 Hz), 28.2 (d, *J* = 3.1 Hz), 24.7 (d, *J* = 12.4 Hz), 22.7 (s), 21.5 (s), 15.4. Elemental analysis: Calcd for $C_{24}H_{31}ClNO_3P$, C, 64.35; H, 6.98. Found: C, 64.16; H, 6.96.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01371.

X-ray data (CIF)

Experimental procedures, full spectroscopic data, and copies of $^{1}$H, $^{31}$P, and $^{13}$C NMR spectra (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-mail: literabc@hotmail.com.


### Author Contributions

†J.-P.W. and S.-Z.N. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

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