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Zinc-Mediated Asymmetric Additions of Dialkylphosphine Oxides to α,β-Unsaturated Ketones and *N*-Sulfinylimines‡

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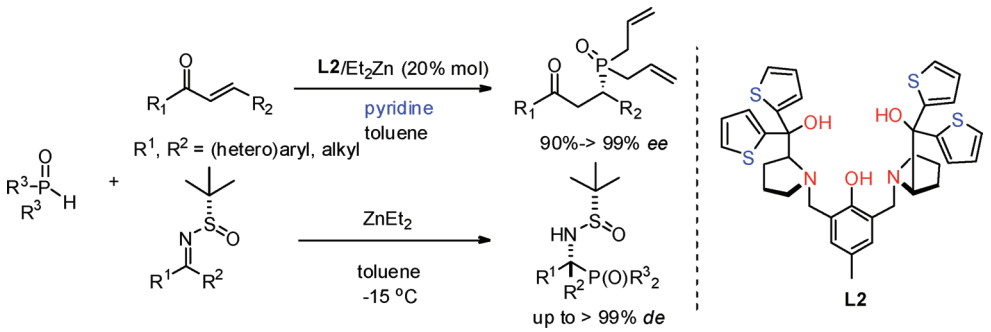

A catalyst was synthesized on the basis of Trost's dinuclear catalyst characterized by working well without pyridine in the present phospha-Michael reaction. Nevertheless, the presence of pyridine is still advantageous in the present system. The substrate scope was successfully extended to enones employing diallyl phosphine oxide as a nucleophile. Excellent yields and enantioselectivities (up to >99% ee) were achieved for a wide scope of enones employing the catalyst under mild conditions. The detailed reaction mechanism is also discussed herein. Finally, the unprecedented asymmetric additions of dialkylphosphine oxides to *N*-sulfinylimines were achieved by using Et_2Zn as a base.

Introduction

The catalytic asymmetric synthesis of chiral organophosphorus compounds has attracted considerable attention in the past decades, for these compounds can serve as precursors of many biologically active molecules[1] and play an important role in metal-catalyzed[2] and organocatalytic reactions.[3] The direct addition of phosphorus nucleophiles to electrophiles is a convenient method to construct P−C bonds. However, previous studies only focus on nucleophiles such as dialkyl phosphites[4] [$(RO)_2P(O)H$], secondary phosphines[5] (R_2PH), and diarylphosphine oxides[6] [$Ar_2P(O)H$]. In addition, dialkylphosphine oxides [$R_2P(O)H$] have been much neglected even though the adducts possess synthetic potential and may be used as useful analogues of phosphonates.

‡ Dedicated to Professor Albert S. C. Chan on the occasion of his 60th birthday.

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(4) For reviews, see: (a) Ordóñez, M.; Rojas-Cabrera, H.; Cativiela, C. *Tetrahedron* **2009**, *65*, 17. (b) Ma, J. A. *Chem. Soc. Rev.* **2006**, *35*, 630. (c) Merino, P.; Marqués-López, E.; Herrera, R. P. *Adv. Synth. Catal.* **2008**, *350*, 1195. (d) Gröger, H.; Hammer, B. *Chem.—Eur. J.* **2000**, *6*, 943. (e) Enders, D.; Saint-Dizier, A.; Lannou, M.-I.; Lenzen, A. *Eur. J. Org. Chem.* **2006**, 29.

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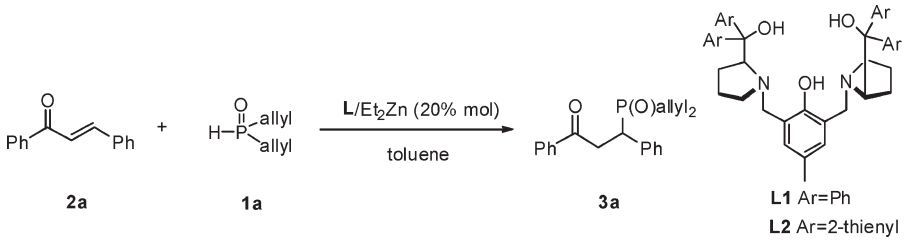
TABLE 1. Optimization of the Phospha-Michael Reaction

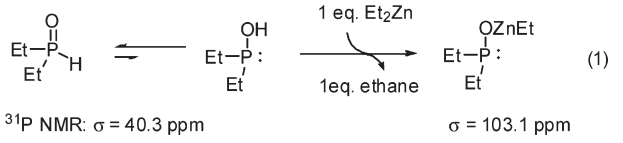


entry[a]	L	additive	*C* (M)	yield (%)	ee[b] (%)
1	**L1**	pyridine	0.0625	97	93
2	**L2**	pyridine	0.0625	98	99
3	**L1**		0.1	91	53
4	**L2**		0.1	89	82
5	**L2**		0.05	80	93
6	**L2**		0.03	77	93

[a]All reactions were carried out with **1a** (0.375 mmol, 1.5 equiv), **L**/Et_2Zn (20 mol %), and **2a** (0.25 mmol) at rt for 12 h. [b]The enantiomeric excess was determined by HPLC analysis.

Preliminary studies indicate that the nucleophilic reactivity order toward electrophiles is $Ar_2P(O)H > (RO)_2P(O)H > R_2P(O)H$. Thus, in comparison with other commonly used nucleophiles, dialkylphosphine oxides show the lowest reactivity and are hard to activate. This might be a critical reason for the lack of reports in this area.

Our group recently communicated for the first time the application of dialkylphosphine oxides in catalytic asymmetric reactions.[7] We found that Et_2Zn was able to activate diethylphosphine oxide by deprotonation and formation of a zincate intermediate (eq 1). With the aid of a bifunctional catalyst, dialkylphosphine oxides were successfully added to α,β-unsaturated *N*-acylpyrroles with high level of yields and enantioselectivities. Importantly, we found pyridine was a critical additive for the present reaction.



The purpose of the present research is to further expand our preliminary study in the following aspects. A catalyst was synthesized based on Trost's dinuclear catalyst.[8] The catalyst's unique feature is that it works well without pyridine in the present phospha-Michael reaction. In view of the synthetic utilities of the allyl group, we then extended the substrate scope to enones employing diallylphosphine oxide. The detailed reaction mechanism is also discussed here. Finally, we achieved the asymmetric addition of dialkylphosphine oxides to *N*-sulfinylimines promoted by Et_2Zn.

Results and Discussion

To further broaden the substrate scope of the phospha-Michael reaction of dialkylphosphine oxides to enones, we tried the reaction of diallyl phosphine oxide and enone **2a** under the optimal conditions established for α,β-unsaturated *N*-acylpyrroles. The result indicated the enantioselectivity was not as satisfactory as that in α,β-unsaturated *N*-acylpyrroles, although excellent yield was achieved (97%, 93% ee, Table 1, entry 1). By comparison of the structure of α,β-unsaturated *N*-acylpyrroles and chalcones, we speculated that a ligand incorporating less hindered aryl groups instead of phenyl rings for **L1** might be effective for the present reaction. Consequently, we synthesized **L2** bearing four 2-thienyl groups. To our delight, the enantioselectivity increased to 99% ee when **L2** was used in the reaction and similar yield was observed (Table 1, entry 2). Surprisingly, when the reaction was conducted without pyridine, **L2** gave a significantly higher enantioselectivity than **L1** (82% ee vs 53% ee, Table 1, entries 3 and 4). The enantioselectivity further increased to 93% with good yield when the reaction concentration was diluted to 0.05 M (Table 1, entry 5). This interesting phenomenon will be discussed in the mechanism consideration section.

With the new catalyst in hand, the reactions of various enones with diallylphosphine oxide **1a** were carried out under the optimized reaction conditions (Table 1, entry 2), affording the corresponding products **3a**−**u** in 70%−98% yields with enantiomeric excesses up to >99% ee (Table 2, entries 1−21). The catalyst is especially effective for diaryl enones irrespective of the electronic nature or positions of the substituent on the phenyl ring. α-Heteroaromatic, β-heteroaromatic, and β-aliphatic enones were also applicable to the present system (Table 2, entries 11, 17−19). To our great delight, the addition of dialkylphosphine oxide to α-aliphatic enones gave exclusive Michael adducts in moderate yields with >99% ee (entries 20−22). This is completely different from the addition of dialkyl phosphites, which always

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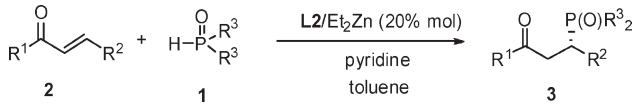
TABLE 2. Substrate Scope of the Phospha-Michael Reaction



2 1 3

entry[a]	R^1	R^2	R^3	Product	Yield (%)	*ee* (%)[b,c]
1	Ph	Ph	allyl	**3a**	98	99
2	Ph	4-MeC_6H_4	allyl	**3b**	96	>99
3	Ph	4-$OMeC_6H_4$	allyl	**3c**	97	>99
4	Ph	4-FC_6H_4	allyl	**3d**	91	98
5	Ph	4-ClC_6H_4	allyl	**3e**	95	99
6	Ph	4-BrC_6H_4	allyl	**3f**	94	99
7	4-ClC_6H_4	Ph	allyl	**3g**	92	96
8	4-BrC_6H_4	Ph	allyl	**3h**	90	95
9	4-MeC_6H_4	Ph	allyl	**3i**	98	98
10	4-$OMeC_6H_4$	Ph	allyl	**3j**	96	98
11	2-furyl	Ph	allyl	**3k**	91	96
12	Ph	3-$OMeC_6H_4$	allyl	**3l**	97	96
13	Ph	2-naphthyl	allyl	**3m**	98	96
14	Ph		allyl	**3n**	96	97
15	Ph	3-MeC_6H_4	allyl	**3o**	96	97
16	Ph	2-$OMeC_6H_4$	allyl	**3p**	98	96
17	Ph	2-furyl	allyl	**3q**	87	98
18	Ph	$PhCH_2CH_2$	allyl	**3r**	92	90
19	Ph	*i*-Pr	Allyl	**3s**	98	93
20	Me	Ph	Allyl	**3t**	70	>99
21	Et	Ph	Allyl	**3u**	71	>99
22	Me	$CH_3(CH_2)_4$	Allyl	**3v**	74	>99
23[d]	Ph	Ph	Et **1b**	**3w**	98	98
24[d]	Ph	Ph	Pr **1c**	**3x**	94	98
25[d]	Ph	Ph	Bu **1d**	**3y**	93	98

[a]Unless otherwise noted, reactions were carried out with **1** (0.375 mmol, 1.5 equiv) and **2** (0.25 mmol) in 4.0 mL of toluene at rt for 12 h. [b]The enantiomeric excess was determined by HPLC analysis. [c]Absolute configuration was not determined. It is assigned by analogy according to a previous report.[7] [d]The reaction was performed at 50 °C in 2.5 mL of toluene.

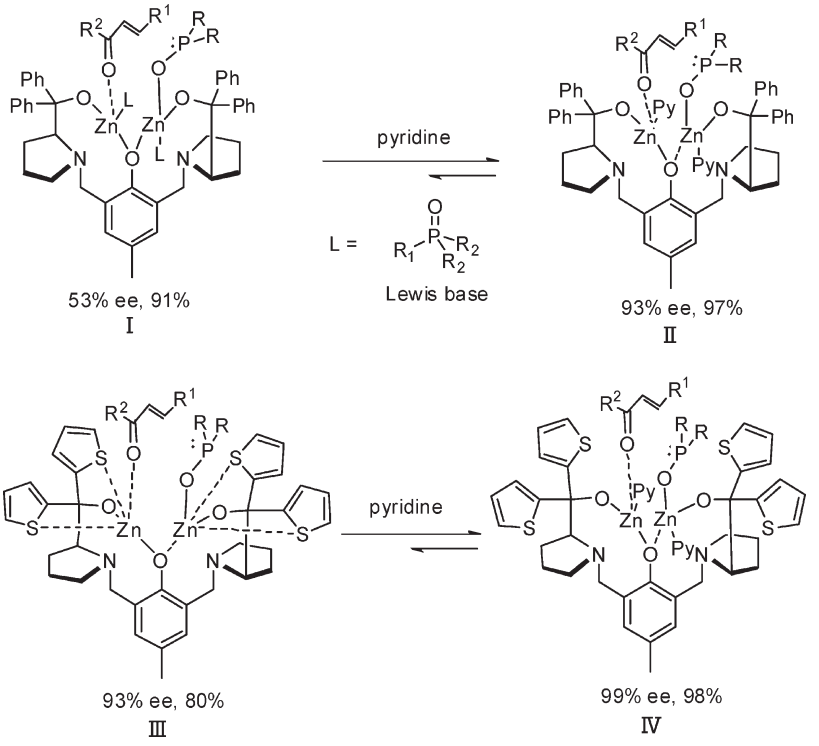
facilitated 1,2-addition in the presence of Et_2Zn for α-aliphatic enones.[9]

Dialkylphosphine oxides **1b**−**d** can be used in the catalysis as well, but reactions proved to be somewhat less reactive than the above-mentioned allyl counterpart. However, this problem can be solved by raising the temperature to 50 °C and changing the reaction concentration from 0.0625 to 0.1 M without any loss of ee (Table 2, entries 23−25).

Preliminary experiments indicate that the deprotonation of the dialkylphosphine oxides is crucial for the addition to enones. Thus, we suppose the mechanism of the present

(9) Zhao, D.; Yuan, Y.; Chan, A. S. C.; Wang, R. *Chem.—Eur. J.* **2009**, *15*, 2738.

SCHEME 1. Proposed Mechanism of the Phospha-Michael Reaction



reaction is that one zinc of the catalyst functions as a base to activate the dialkylphosphine oxides and the other one might coordinate to enone **2**, thus closing the distance between the two substrates. Next, we tried to gain insight to the origin of the beneficial effect of pyridine. It is well-known that tertiary phosphine oxides may function as Lewis base[3d,10,11] and coordinate to Lewis acid such as zinc. Therefore, we believe the products formed in the present reaction—chiral tertiary phosphine oxides—might in turn bind to the catalyst, thereby poisoning the catalyst. This can also be ascertained by the fact that the using of stoichiometric amount of **L1**/Et_2Zn leads to excellent ee without additive in the previous report.[7] Thus, the introduction of an additional Lewis base to the system to prevent the binding of the product to the catalyst is necessary. As shown in Scheme 1, for **L1** in the absence of pyridine, the product can be only afforded in 53% ee in contrast to 93% ee for the presence of pyridine. This phenomenon suggests that pyridine is a stronger Lewis base and preferred to bind to the catalyst, thus preventing the binding of the products.[11]

In the case of **L2**, the sulfur atom on the thienyl group may serve as an intramolecular Lewis base and occupy the vacant binding sites of the catalyst, thus facilitating the formation of a stable structure. The unfavorable binding of the product to the catalyst may also be avoided in this case, for no coordination sites are available. In contrast to **L1**, the product can be obtained in 93% ee without the participation of pyridine. Nevertheless, with regard to **L2**, the presence of pyridine is still advantageous for its beneficial effect on improvement of both yield and ee. These results indicate the significant superiority of **L2** in the present phospha-Michael reaction.

Although the attempt to apply the current catalysis to imines failed,[12] we tried the reaction of dialkylphosphine oxides with chiral imines. On the basis of the high reactivity of the zincate intermediate formed from Et_2Zn and dialkylphosphine oxide, we speculate it is reactive enough to add to chiral imines such as *N*-*tert*-butanesulfinyl imines.[13,14] Thus, we investigated the reaction of diethylphosphine oxide and Ellman's *N*-*tert*-butanesulfinyl ketimine **4a** in toluene at 0 °C. Fortunately, the reaction proceeded smoothly to afford the corresponding phosphorus adduct in 97% de (Table 3, entry 1).[15] Although Et_2Zn was previously found to be able to reduce imines,[16] we did not find any reduction product of ketimine **4a** in this reaction. The diastereoselectivity further increased to >99% de when the reaction was performed at −15 °C without substantial impact on yield (Table 3, entry 2).

(10) Shibasaki, M.; Kanai, M. *Chem. Pharm. Bull.* **2001**, *49*, 511.

(11) For an excellent review on additives and cocatalysts in asymmetric catalysis, see: Vogl, E. M.; Gröger, H.; Shibasaki, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1570.

(12) We failed to apply the current catalysis to imines for only racemic product was afforded.

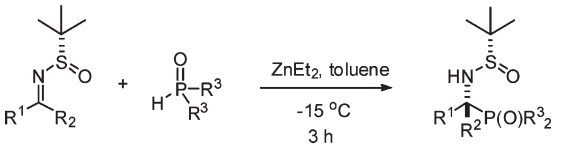
(13) For recent reviews related to the Ellman *N*-(*tert*-butanesulfinyl)-imines, see: (a) Ellman, J. A.; Owens, T. D.; Tang, T. P. *Acc. Chem. Res.* **2002**, *35*, 984. (b) Senanayake, C. H.; Han, Z.; Krishnamurthy, D. In *Organosulfur Chemistry in Asymmetric Synthesis*; Toru, T., Bolm, C., Eds.; Wiley-VCH: New York, 2008. (c) Morton, D.; Stockman, R. A. *Tetrahedron* **2006**, *62*, 8869. (d) Senanayake, C. H.; Krishnamurthy, D.; Lu, Z.-H.; Han, Z.; Gallou, I. *Aldrichim. Acta* **2005**, *38*, 93. (e) Ellman, J. A. *Pure Appl. Chem.* **2003**, *75*, 39. (f) Ferreira, F.; Botuha, C.; Chemla, F.; Perez-Luna, A. *Chem. Soc. Rev.* **2009**, *38*, 1162. (g) Zhou, P.; Chen, B.-C.; Davis, F. A. *Tetrahedron* **2004**, *60*, 8003. (h) Robak, M. T.; Herbage, M. A.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 3600.

(14) For reactions of other phosphorus nucleophiles with *N*-*tert*-butanesulfinylimines, see: (a) Chen, Q. Y.; Yuan, C. Y. *Synthesis* **2007**, *24*, 3779. (b) Zhang, D. H.; Yuan, C. Y. *Chem.—Eur. J.* **2008**, *14*, 6049.

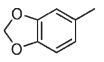
(15) Other bases were also tested. Weak bases such as Na_2CO_3 and K_2CO_3 cannot promote the reaction, whereas hash conditions (−78 °C) are required for strong bases such as LDA and LiHMDS despite similar results that were observed with Et_2Zn.

(16) Zani, L.; Alesi, S.; Cozzi, P. G.; Bolm, C. *J. Org. Chem.* **2006**, *71*, 1558.

TABLE 3. Substrate Scope of the Phospha-Mannich Reaction

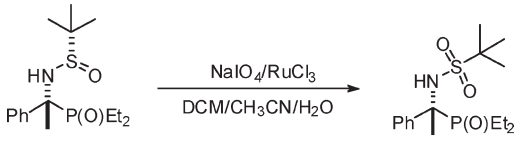


4 1 5

entry[a]	imine		R^3	product	yield (%)[b]	*de* (%)[c]
	R^1	R^2				
1[d]	Ph	CH_3 **4a**	Et **1b**	**5a**	87	97
2	Ph	CH_3 **4a**	Et	**5a**	82	>99
3	4-MeC_6H_4	CH_3 **4b**	Et	**5b**	91	>99
4	4-$OMeC_6H_4$	CH_3 **4c**	Et	**5c**	77	>99
5	4-ClC_6H_4	CH_3 **4d**	Et	**5d**	91	>99
6	4-BrC_6H_4	CH_3 **4e**	Et	**5e**	84	>99
7	2-naphthyl	CH_3 **4f**	Et	**5f**	92	>99
8	2-furyl	CH_3 **4g**	Et	**5g**	82	>99
9	*i*-Pr	CH_3 **4h**	Et	**5h**	67	97
10	*i*-Bu	CH_3 **4i**	Et	**5i**	78	84
11	Ph	CH_2CH_3 4**j**	Et	**5j**	74	99
12[e]	Ph	CH_3 4**a**	Pr **1c**	**5k**	77	90
13[e]	Ph	CH_3 4**a**	Bu **1d**	**5l**	71	95
14	Ph	H 4**k**	Et	**5m**	83	70
15[f]	4-$OMeC_6H_4$	H 4**l**	Et	**5n**	90	86
16		H 4**m**	Et	**5o**	77	80

[a]Unless otherwise noted, reactions were carried out with **1** (0.75 mmol, 3.0 equiv) and **2** (0.25 mmol) in 2.5 mL of toluene at −15 °C for 3 h. [b]Yield of isolated product. [c]The de was determined by ^1H and ^{31}P NMR analysis of the crude product. [d]The reaction was performed at 0 °C. [e]The excess phosphine oxide cannot be separated completely by silica gel column chromatography. [f]The absolute configuration of **3h** was determined to be (R,S_S).

SCHEME 2. Determination of Optical Purity of the Products



5a > 99% *de* **6** > 99% *ee*

With the optimized reaction conditions established, the scope and limitations of the phospha-Mannich reaction were then tested. As summarized in Table 3, perfect diastereoselectivities (>99% de) were observed for a series of aromatic and heteroaromatic methyl ketimines with 77−92% yields (Table 3, entries 2−8). For the two aliphatic ketimines investigated, imine bearing an *i*-Pr gave 97% de, whereas it is only 84% de for *i*-Bu (Table 3, entries 9 and 10). This is probably because *i*-Bu is very similar in steric bulk with Me and the corresponding imine is a rapidly equilibrating mixture of *E*/*Z* isomers.[17] The ketimine **4j** bearing an ethyl group instead of a methyl group can also be used in the present reaction with 99% de. Good results were also observed for phosphine oxides **1c** and **1d**. Unfortunately, aldimines did not give results as good as those of ketimines, and only moderate to good diastereoselectivities were achieved (Table 3, entries 14−16).

In order to verify the optical purity of the products, we tried to oxidize the products and determine the enantioselectivities. As shown in Scheme 2, **5a** can be readily converted into its corresponding sulfonylamide derivative **6** with $NaIO_4/RuCl_3$. The HPLC analysis indicated the enantiomeric

(17) Liu, G.; Cogan, D. A.; Owens, T. D.; Tang, T. P.; Ellman, J. A. *J. Org. Chem.* **1999**, *64*, 1278.

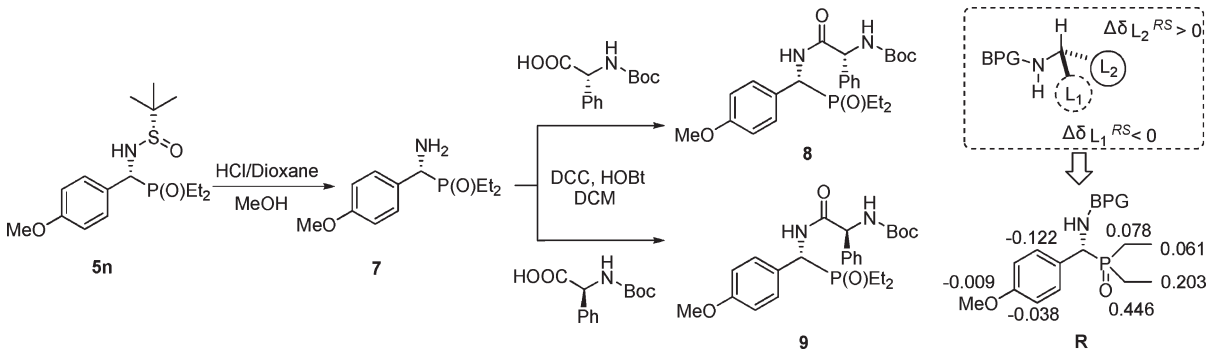


FIGURE 1. Determination of absolute configuration of **5n**.

excess of **6** was >99% ee, and it was in agreement with diastereomeric excess of **5a**.

The absolute configuration of **5n** was determined by ^{1}H NMR spectra.[18] The *tert*-butylsulfinyl group of **5n** can be removed by HCl/dioxane, affording the amino phosphine oxide **7**. The absolute configuration of primary amine **7** was then determined by using Boc-phenylglycine (BPG) for its advantages of producing greater values and being inexpensive.[19] The primary amine **7** was then converted to (*R*)-BPG amide **8** and (*S*)-BPG amide **9**, respectively, and the ^{1}H NMR spectra of these two compounds were recorded. As shown in Figure 1, the $\Delta\delta^{R,S}$ value for the phosphine oxide group is positive and it is negative for *p*-methoxyphenyl group. By comparing these results with the model represented in Figure 1, the stereochemistry of **7** is determined to be *R*. Thus, the absolute configuration of **5n** is (R,S_S) and the rest of the products are assigned by analogy.

Conclusion

In conclusion, we have synthesized a catalyst based on Trost's dinuclear catalyst. The catalyst works well without pyridine in the present phospha-Michael reaction. Nevertheless, pyridine is still a beneficial additive for the present system. Furthermore, we have successfully extended the substrate scope to enones employing diallyl phosphine oxide as a nucleophile in view of the synthetic utilities of the allyl group. Excellent yields and enantioselectivities (up to >99% ee) were achieved for a wide scope of enones employing the catalyst under mild conditions. The detailed reaction mechanism and the origin of the beneficial effects of pyridine and **L2** are also discussed here. Finally, we achieved the unprecedented asymmetric addition of dialkylphosphine oxides to *N*-sulfinyl imines using Et_2Zn as a base, and good to excellent diastereoselectivities were observed for a series of *N*-*tert*-butanesulfinylimines. Further studies on synthetic applications of the chiral phosphine oxides[20] and lowering the catalyst loading are ongoing.

Experimental Section

General Procedure for Asymmetric Hydrophosphinylation of α,β-Unsaturated Enones. To a stirred solution of **L2** (33.1 mg, 0.05 mmol) in toluene (0.5 mL) was added diethylzinc (100 μL, 1.0 M in toluene, 0.1 mmol) under an argon atmosphere. The mixture was stirred at room temperature for 0.5 h to generate the zinc catalyst, and the resulting solution of catalyst was added to a stirred mixture of pyridine (0.2 mL, 10 equiv), **2a** (52.0 mg, 0.25 mmol), and diallyl phosphine oxide **1a** (48.8 mg, 0.375 mmol) in toluene (3.5 mL) at 0 °C under an argon atmosphere. After the addition, the mixture was stirred at room temperature for 12 h. The reaction was quenched with aqueous HCl (1 M) and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate 4:1−ethyl acetate/methanol 40:1).

(*S*)-3-(Diallylphosphoryl)-1,3-diphenylpropan-1-one (3a): colorless oil; 98% yield; 99% ee determined by HPLC on a Chiralpak OD-H column (hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, t_{minor} = 14.4 min, t_{major} = 9.4 min); $[\alpha]^{rt}_D$ = −45.1 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.49−7.38 (m, 4H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.28−7.16 (m, 1H), 6.04−5.79 (m, 1H), 5.78−5.54 (m, 1H), 5.39−5.16 (m, 3H), 5.09 (ddd, *J* = 17.0, 4.2, 1.3 Hz, 1H), 3.97−3.73 (m, 3H), 2.86−2.61 (m, 2H), 2.50−2.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.5 (d, *J* = 10.6 Hz), 136.9 (d, *J* = 5.2 Hz), 136.3, 133.4, 129.2 (d, *J* = 5.7 Hz), 128.9 (d, *J* = 1.8 Hz), 128.6, 128.1, 127.7 (d, *J* = 8.0 Hz), 127.4 (d, *J* = 2.3 Hz), 127.3 (d, *J* = 8.2 Hz), 120.9 (d, *J* = 11.2 Hz), 120.7 (d, *J* = 11.5 Hz), 39.3 (d, *J* = 62.1 Hz), 38.7, 32.7 (d, *J* = 60.8 Hz), 32.4 (d, *J* = 63.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +46.7; IR (neat) 3417, 3063, 1686, 1231, 1159, 983, 921, 697, 615 cm^{-1}; HRMS (ESI) $C_{21}H_{23}O_2P$ [M + H]$^+$ calcd 339.1508, found 339.1511.

(*S*)-3-(Diallylphosphoryl)-1-phenyl-3-*p*-tolylpropan-1-one (3b): colorless oil; 96% yield; >99% ee determined by HPLC on a Chiracel OD-H column (hexane/2-propanol =90/10, flow rate = 1.0 mL/min, t_{minor} = 21.9 min, t_{major} = 8.4 min); $[\alpha]^{rt}_D$ = −59.1 (*c* = 1.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.32 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.03−5.80 (m, 1H), 5.80−5.55 (m, 1H), 5.38−5.16 (m, 3H), 5.11 (ddd, *J* = 17.0, 4.2, 1.3 Hz, 1H), 3.96−3.73 (m, 3H), 2.88−2.58 (m, 2H), 2.48−2.18 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.7 (d, *J* = 10.8 Hz), 137.1 (d, *J* = 2.6 Hz), 136.4, 133.7 (d, *J* = 5.4 Hz), 133.4, 129.6 (d, *J* = 1.9 Hz), 129.1 (d, *J* = 5.7 Hz), 128.6, 128.1, 127.7 (d, *J* = 8.0 Hz), 127.5 (d, *J* = 8.1 Hz), 120.9 (d, *J* = 11.3 Hz), 120.7 (d, *J* = 11.4 Hz), 39.0 (d, *J* = 62.3 Hz), 38.7, 32.7 (d, *J* = 60.8 Hz), 32.3 (d, *J* = 64.5 Hz), 21.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ = +46.8; IR (neat) 3418, 2922, 1686, 1231, 1159, 920, 731 607 cm^{-1}; HRMS (ESI) $C_{22}H_{25}O_2P$ [M + H]$^+$ calcd 353.1665, found 353.1657.

(*S*)-3-(Diallylphosphoryl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (3c): colorless oil; 97% yield; >99% ee determined by HPLC on a Chiracel OD-H column (hexane/2-propanol =90/10, flow rate = 1.0 mL/min, t_{minor} = 22.8 min, t_{major} = 11.5 min); $[\alpha]^{rt}_D$ = −64.3 (*c* = 1.12, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$)

(18) Seco, J. M.; Quiñoá, E.; Riguera, R. *Tetrahedron: Asymmetry* **2001**, *12*, 2915.

(19) Seco, J. M.; Quinoa, E.; Riguera, R. *J. Org. Chem.* **1999**, *64*, 4669.

(20) Currently, we have not successfully reduced the product **3** and **5** to their corresponding phosphines. Inseparable mixtures were obtained for both **3** and **5** using the method mentioned in ref 7.

δ = 7.94 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.36 (dd, J = 8.6, 1.7 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.05−5.80 (m, 1H), 5.79−5.58 (m, 1H), 5.36−5.16 (m, 3H), 5.10 (ddd, J = 17.1, 4.2, 1.2 Hz, 1H), 3.90−3.68 (m, 3H), 3.77 (s, 3H), 2.82−2.61 (m, 2H), 2.48−2.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.7 (d, J = 11.0 Hz), 158.8 (d, J = 2.3 Hz), 136.4, 133.4, 130.3 (d, J = 5.7 Hz), 128.7 (d, J = 6.0 Hz), 128.6, 128.1, 127.7 (d, J = 8.0 Hz), 127.4 (d, J = 8.0 Hz), 120.8 (d, J = 11.2 Hz), 120.6 (d, J = 11.5 Hz), 114.3 (d, J = 1.7 Hz), 55.2, 38.8, 38.5 (d, J = 63.0 Hz), 32.7 (d, J = 60.0 Hz), 32.3 (d, J = 64.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +47.1; IR (neat) 3417, 2905, 1686, 1512, 1251, 1180, 1156, 922 cm^{-1}; HRMS (ESI) $C_{22}H_{25}O_3P$ [M + H]$^+$ calcd 369.1614, found 369.1612.

(*S*)-3-(Diallylphosphoryl)-3-(4-fluorophenyl)-1-phenylpropan-1-one (3d): white solid; mp 104−106 °C; 91% yield; 98% ee determined by HPLC on a Chiralpak OD-H column (hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, t_{minor} = 11.7 min, t_{major} = 9.3 min); $[\alpha]^{rt}_D$ = −40.0 (c = 1.13, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.3 Hz, 4H), 7.01 (t, J = 8.6 Hz, 2H), 6.00−5.79 (m, 1H), 5.78−5.56 (m, 1H), 5.38−5.16 (m, 3H), 5.09 (ddd, J = 17.0, 4.3, 1.3 Hz, 1H), 3.93−3.65 (m, 3H), 2.89−2.62 (m, 2H), 2.51−2.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.4 (d, J = 10.9 Hz), 162.1 (dd, J = 245.3, 3.0 Hz), 136.2, 133.6, 132.6 (dd, J = 5.3, 3.8 Hz), 130.9 (dd, J = 8.0, 5.8 Hz), 128.7, 128.1, 127.5 (d, J = 8.0 Hz), 127.1 (d, J = 8.0 Hz), 121.1 (d, J = 11.5 Hz), 120.9 (d, J = 12.0 Hz), 115.8 (dd, J = 21.0, 1.5 Hz), 38.9, 38.5 (d, J = 63.4 Hz), 32.6 (d, J = 60.0 Hz), 32.4 (d, J = 64.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +46.8; IR (neat) 3419, 2921, 1686, 1509, 1229, 1159, 922, 746 cm^{-1}; HRMS (ESI) $C_{21}H_{22}FO_2P$ [M + H]$^+$ calcd 357.1414, found 357.1420.

(*S*)-3-(Diallylphosphoryl)-1-(furan-2-yl)-3-phenylpropan-1-one (3k): colorless oil; 91% yield; 96% ee determined by HPLC on a Chiralpak OD-H column (hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, t_{minor} = 21.3 min, t_{major} = 15.7 min); $[\alpha]^{rt}_D$ = −72.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, J = 1.0 Hz, 1H), 7.42 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.27−7.20 (m, 1H), 7.18 (d, J = 3.2 Hz, 1H), 6.50 (dd, J = 3.6, 1.7 Hz, 1H), 6.03−5.78 (m, 1H), 5.76−5.51 (m, 1H), 5.37−5.23 (m, 2H), 5.19 (dd, J = 10.2, 1.7 Hz, 1H), 5.08 (ddd, J = 17.0, 4.3, 1.4 Hz, 1H), 3.92−3.77 (m, 1H), 3.76−3.50 (m, 2H), 2.86−2.54 (m, 2H), 2.45−2.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 185.6 (d, J = 11.3 Hz), 152.1, 146.7, 136.4 (d, J = 5.2 Hz), 129.2 (d, J = 5.7 Hz), 128.8 (d, J = 1.8 Hz), 127.5^2 (d, J = 11.3 Hz), 127.5, 127.2 (d, J = 8.1 Hz), 121.0 (d, J = 11.3 Hz), 120.7 (d, J = 11.6 Hz), 117.8, 112.3, 39.1 (d, J = 62.0 Hz), 38.3, 32.6 (d, J = 60.0 Hz), 32.3 (d, J = 63.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +46.6; IR (neat) 3417, 2922, 1674, 1467, 1160, 918, 703, 611 cm^{-1}; HRMS (ESI) $C_{19}H_{21}O_3P$ [M + H]$^+$ calcd 329.1301, found 329.1291.

(*R*)-3-(Diallylphosphoryl)-1,5-diphenylpentan-1-one (3r): colorless oil; 92% yield; 90% ee determined by HPLC on a Chiralpak AD-H column (hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, t_{minor} = 21.4 min, t_{major} = 19.3 min); $[\alpha]^{rt}_D$ = −3.7 (c = 1.08, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.01 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.2 Hz, 2H), 7.19 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 6.9 Hz, 2H), 5.92−5.67 (m, 2H), 5.34−5.07 (m, 4H), 3.63 (ddd, J = 18.8, 15.6, 4.9 Hz, 1H), 3.25 (ddd, J = 18.7, 10.0, 6.2 Hz, 1H), 2.88−2.68 (m, 3H), 2.68−2.48 (m, 4H), 2.15−2.00 (m, 1H), 1.98−1.83 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.5 (d, J = 7.6 Hz), 141.0, 136.3, 133.6, 128.7, 128.5, 128.4, 128.2, 127.6^3 (d, J = 8.3 Hz), 127.6 (d, J = 8.3 Hz), 126.2, 120.7 (d, J = 11.3 Hz), 120.6 (d, J = 11.3 Hz), 36.7, 33.9 (d, J = 11.2 Hz), 32.7 (d, J = 60.8 Hz), 32.3 (d, J = 61.5 Hz), 30.9 (d, J = 64.5 Hz), 30.8 (d, J = 1.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +49.0; IR (neat) 3414, 2930, 1685, 1227, 1154, 920, 752, 698 cm^{-1}; HRMS (ESI) $C_{23}H_{27}O_2P$ [M + H]$^+$ calcd 367.1821, found 367.1818.

(*S*)-4-(Diallylphosphoryl)-4-phenylbutan-2-one (3t): colorless oil; 70% yield; >99% ee determined by HPLC on a Chiralpak OJ-H column (hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, t_{minor} = 11.7 min, t_{major} = 12.4 min); $[\alpha]^{rt}_D$ = −21.7 (c = 1.15, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.46−7.16 (m, 5H), 5.97−5.76 (m, 1H), 5.73−5.51 (m, 1H), 5.37−5.21 (m, 2H), 5.18 (dd, J = 10.1, 1.5 Hz, 1H), 5.06 (ddd, J = 17.0, 4.2, 1.2 Hz, 1H), 3.66 (td, J = 8.6, 4.4 Hz, 1H), 3.40−3.07 (m, 2H), 2.78−2.54 (m, 2H), 2.40−2.17 (m, 2H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 205.2 (d, J = 10.3 Hz), 136.6 (d, J = 5.1 Hz), 129.0 (d, J = 5.6 Hz), 128.9 (d, J = 1.8 Hz), 127.6 (d, J = 8.1 Hz), 127.4 (d, J = 2.4 Hz), 127.2 (d, J = 8.2 Hz), 120.8 (d, J = 11.3 Hz), 120.6 (d, J = 11.5 Hz), 43.2, 39.3 (d, J = 61.7 Hz), 32.6 (d, J = 60.8 Hz), 32.2 (d, J = 64.5 Hz), 30.3; ^{31}P NMR (121 MHz, $CDCl_3$) δ = +46.3; HRMS (ESI) $C_{16}H_{21}O_2P$ [M + H]$^+$ calcd 277.1352, found 277.1356.

General Procedure for Asymmetric Hydrophosphinylation of *N*-*tert*-Butylsulfinylimines. To a stirred solution of **1b** (80 μL, 0.75 mmol) in toluene (0.5 mL) was added diethylzinc (0.75 mL, 1.0 M in toluene, 0.75 mmol) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 1 h, and then **4** (0.25 mmol) in toluene (1.25 mL) was added to the stirred mixture at −15 °C under an argon atmosphere. After the addition, the mixture was stirred at the same temperature for 3 h, and then the reaction was quenched with saturated NH_4Cl aqueous and extracted with ether. The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate 4:1 to ethyl acetate/methanol 1:1).

(*S*)-*N*-((*R*)-1-(Diethylphosphoryl)-1-phenylethyl)-2-methylpropane-2-sulfinamide (5a): white solid; mp 123−125 °C; 82% yield; >99% de determined by NMR; $[\alpha]^{rt}_D$ = 107.2 (c = 1.11, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.49 (d, J = 7.9 Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.34−7.28 (m, 1H), 4.68 (d, J = 4.7 Hz, 1H), 2.11 (d, J = 13.3 Hz, 3H), 1.95−1.61 (m, 2H), 1.61−1.42 (m, 2H), 1.30 (s, 9H), 1.08 (dt, J = 15.5, 7.7 Hz, 3H), 1.03 (dt, J = 15.6, 7.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.4 (d, J = 1.5 Hz), 128.3 (d, J = 2.4 Hz), 127.7^5 (d, J = 1.5 Hz), 127.7^3 (d, J = 3.8 Hz), 61.6 (d, J = 65.5 Hz), 56.8, 22.7^3, 22.6^6, 16.6 (d, J = 62.8 Hz, overlapped), 6.0 (d, J = 5.1 Hz), 5.9 (d, J = 5.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +57.2; IR (neat) 3445, 2978, 1668, 1453, 1382, 1161, 1068, 794, 703 cm^{-1}; HRMS (ESI) $C_{16}H_{28}NO_2PS$ [M + Na]$^+$ calcd 352.1471, found 352.1479.

(*S*)-*N*-((*R*)-1-(Diethylphosphoryl)-1-*p*-tolylethyl)-2-methylpropane-2-sulfinamide (5b): colorless oil; 91% yield; >99% de determined by NMR; $[\alpha]^{rt}_D$ = 86.9 (c = 0.99, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36 (d, J = 6.7 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.62 (d, J = 4.3 Hz, 1H), 2.35 (s, 3H), 2.09 (d, J = 13.2 Hz, 3H), 1.94−1.62 (m, 2H), 1.62−1.38 (m, 2H), 1.29 (s, 9H), 1.07 (dt, J = 15.6, 7.7 Hz, 3H), 1.05 (dt, J = 15.6, 7.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.6 (d, J = 3.0 Hz), 135.1, 129.0 (d, J = 2.5 Hz), 127.7 (d, J = 3.9 Hz), 61.5 (d, J = 66.5 Hz), 56.8, 22.7 (overlapped), 20.8, 16.5^2 (d, J = 61.5 Hz), 16.5^1 (d, J = 63.8 Hz), 6.0 (d, J = 5.3 Hz), 5.9 (d, J = 5.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +57.2; IR (neat) 3441, 2976, 1459, 1161, 1070, 828, 768 cm^{-1}; HRMS (ESI) $C_{17}H_{30}NO_2PS$ [M + Na]$^+$ calcd 366.1627, found 366.1620.

(*S*)-*N*-((*R*)-1-(Diethylphosphoryl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide (5c): colorless oil; 77% yield; >99% de determined by NMR; $[\alpha]^{rt}_D$ = 78.3 (c = 1.03, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40 (dd, J = 8.9, 2.0 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 4.60 (d, J = 4.3 Hz, 1H), 3.82 (s, 3H), 2.08 (d, J = 13.2 Hz, 3H), 1.91−1.63 (m, 2H), 1.62−1.42 (m, 2H), 1.29 (s, 9H), 1.07 (dt, J = 15.6, 7.8 Hz, 3H), 1.06 (dt, J = 15.6, 7.8 Hz,

3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.0 (d, J = 2.7 Hz), 129.9, 129.0 (d, J = 3.9 Hz), 113.6 (d, J = 2.3 Hz), 61.2 (d, J = 67.6 Hz), 56.7, 55.1, 22.8, 22.7, 16.6 (d, J = 62.3 Hz), 16.5 (d, J = 63.8 Hz), 6.0[4] (d, J = 5.3 Hz), 5.9[6] (d, J = 5.4 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +57.3; IR (neat) 3437, 2976, 1609, 1513, 1461, 1255, 1160, 1069, 1030, 841, 771 cm^{-1}; HRMS (ESI) $C_{17}H_{30}NO_3PS$ [M + H]$^+$ calcd 360.1757, found 360.1752.

(*S*)-*N*-((*R*)-1-(4-Chlorophenyl)-1-(diethylphosphoryl)ethyl)-2-methylpropane-2-sulfinamide (5d): colorless oil; 91% yield; >99% de determined by NMR; $[\alpha]^{rt}_D$ = 109.7 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.44 (dd, J = 8.8, 1.9 Hz, 2H), 7.35 (d, J = 10.2 Hz, 2H), 4.70 (d, J = 5.0 Hz, 1H), 2.08 (d, J = 13.3 Hz, 3H), 1.95−1.76 (m, 1H), 1.73−1.43 (m, 3H), 1.28 (s, 9H), 1.11 (dt, J = 15.9, 7.7 Hz, 3H), 1.04 (dt, J = 15.9, 7.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.3, 133.9 (d, J = 3.3 Hz), 129.1 (d, J = 3.9 Hz), 128.4 (d, J = 2.4 Hz), 61.1 (d, J = 65.0 Hz), 56.8, 22.7, 22.5, 16.6[6] (d, J = 62.3 Hz), 16.6[5] (d, J = 63.0 Hz), 6.0 (d, J = 5.7 Hz), 5.9 (d, J = 5.9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +56.9; IR (neat) 3441, 2977, 1460, 1163, 1070, 840, 764 cm^{-1}; HRMS (ESI) $C_{16}H_{27}ClNO_2PS$ [M + H]$^+$ calcd 364.1261, found 364.1268.

(*S*)-*N*-((*R*)-1-(4-Bromophenyl)-1-(diethylphosphoryl)ethyl)-2-methylpropane-2-sulfinamide (5e): colorless oil; 84% yield; >99% de determined by NMR; $[\alpha]^{rt}_D$ = 90.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.6 Hz, 2H), 7.37 (dd, J = 8.8, 2.0 Hz, 2H), 4.70 (d, J = 5.1 Hz, 1H), 2.08 (d, J = 13.3 Hz, 3H), 1.96−1.77 (m, 1H), 1.76−1.40 (m, 3H), 1.28 (s, 9H), 1.11 (dt, J = 15.9, 7.8 Hz, 3H), 1.05 (dt, J = 15.6, 7.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.9, 131.4 (d, J = 2.4 Hz), 129.4 (d, J = 3.8 Hz), 122.1 (d, J = 3.5 Hz), 61.2 (d, J = 64.8 Hz), 56.8, 22.7, 22.4, 16.6 (d, J = 63.0 Hz, overlapped), 6.0 (d, J = 5.6 Hz), 5.9 (d, J = 5.7 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ = +56.8; IR (neat) 3442, 2977, 1460, 1398, 1163, 1071, 836, 732 cm^{-1}; HRMS (ESI) $C_{16}H_{27}BrNO_2PS$ [M + Na]$^+$ calcd 430.0576, found 430.0570.

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Supporting Information Available: Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.