# Regioselective Zirconophosphination of 1-Alkenes: A Versatile Route for the Synthesis of β-Functionalized Alkyldiphenylphosphine Oxides in the Presence of CuCl

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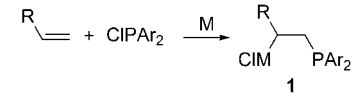
Zirconocene−alkene complexes $Cp_2Zr(PMe_3)(CH_2{=}CHR)$ reacted with chlorodiphenylphosphine to form zircono-ethylphosphine derivatives with high regioselectivity, which could be converted into various β-functionalized alkyldiphenylphosphine oxides in the presence of CuCl.

## Introduction

Tertiary phosphines and their oxides are an important class of organic compounds that are widely employed both as ligands in transition metal complexes and as substrates in various organic synthesis processes.[1] Although in common applications triarylphosphines are usually used, the more electron-rich alkyldiarylphosphines may bring special advantages in more demanding cases.[2,3] The ligands $Ph_2PAlk$ are obtained by coupling of $Ph_2PHal$ with organolithium or organomagnesium compounds or by the reaction between phosphide anion and an alkyl halide.[4] Recently, addition of $Ar_2PH$ to olefins provided a straightforward method for the synthesis of alkyldiarylphosphines.[5,6] Nonetheless, it is often difficult to prepare β-functionalized alkyldiarylphosphines by these methods. Consequently, development of a versatile and general method for the preparation of β-functionalized alkyldiarylphosphines is a necessity. Metallophosphination of alkenes is a simple and direct preparative method of metalloethylphosphines **1** (eq 1), which can be converted into variously functionalized alkyldiarylphosphines.




**1** (1)

The zirconocene-mediated synthesis of different organophosphorus compounds has been demonstrated.[7–9] We have previously reported that zirconophosphorylation of C−C multiple

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Omac, J. *Application of Organometallic Compounds*; Wiley: Toronto, 1999. (c) *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. N., Jordon, F., Stone, A., Wilkinson, J., Eds.; Pergamon Press: New York, 1995; Vols. *9* and 12. (d) Brandsma, L.; Vasilevsky, S. F.; Verkruijsse, H. D. *Application of Transition Metal Catalysts in Organic Synthesis*; Springer-Verlag: Berlin, 1999.

(2) (a) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996. (b) *Homogeneous Catalysis with Metal-Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983.

(3) (a) Han, L.-B.; Mizaeri, F.; Zhao, Ch.-Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407. (b) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571. (c) Keller, J.; Schlierf, C.; Nolte, C.; Mayer, P.; Straub, B. F. *Synthesis* **2006**, 354.

(4) For example, see:(a) *The Chemistry of Functional Groups−The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, U.K., 1990−1992. (b) *Handbook of Organophosphorus Chemistry*; Engel, R., Ed.; Marcel Decker: New York, 1992.

(5) (a) Wolfsberger, W. *Chem. Zeitung* **1988**, *112*, 53. (b) Delacroix, O.; Gaumont, A. C. Curr. Org. Chem. **2005**, *9*, 1851.

(6) Pt- and Pd-catalyzed addition of $Ph_2PH$ and $PH_3$ to a double bond is limited to Michael-type activated alkenes:(a) Nagel, U.; Reigel, B.; Bublewitz, A. *J. Organomet. Chem.* **1989**, *370*, 223. (b) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701. (c) Pringle, P. G.; Brewin, D.; Smith, M. B.; Worboys, K. In *Aqueous Organometallic Chemistry and Catalysis*; Horvath, I. T., Joo, F., Eds.; Dordrecht,: The Netherlands, 1995; Vol. *5*, p 111. (d) Costa, E.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4277. (e) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039. (f) Costa, E.; Pringle, P. G.; Worboys, K. *Chem. Commun.* **1998**, 49. (g) Orpen, A. G.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Organomet. Chem.* **1998**, *550*, 255. (h) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381. (i) Wicht, D. K.; Kovacik, I.; Glueck, D. S.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5141. (j) Kovacik, I.; Wicht, D. K.; Grewal, N. S.; Glueck, D. S.; Incarvito, C. D.; Guzei, I. A.; Rheingold, A. L. *Organometallics* **2000**, *19*, 950. (k) Douglass, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824. (l) Takaki, K.; Takeda, M.; Koshoji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 6357. (m) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221.

(7) (a) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. (b) Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1367. (c) Doherty, S.; Eastham, G. R.; Tooze, R. P.; Scanhan, T. H.; Williams, D.; Elsegood, R. M. R. J.; Clegg, W. *Organometallics* **1999**, *18*, 3558. (d) Hay, C.; Vilain, D. L.; Deborde, V.; Toupet, L.; Réau, R. *Chem. Commun.* **1999**, 345. (e) Hydrio, J.; Gouygou, M.; Dallemer, F.; Daran, J. C.; Balavoine, G. G. A. *J. Organomet. Chem.* **2000**, *595*, 261. (f) Doherty, S.; Knight, J. G.; Robins, E. G.; Scanlan, T. H.; Champkin, P. A.; Clegg, W. *J. Am. Chem. Soc.* **2001**, *123*, 5110. (g) Doherty, S.; Robins, E. G.; Nieuwenhuyzen, M.; Knight, J. G.; Champ, P. A. *Organometallics* **2002**, *21*, 1383. (h) Miyaji, T.; Xi, Z.; Nakajima, K.; Takahashi, T. *Organometallics* **2001**, *20*, 2859. (i) Nishihara, Y.; Aoyagi, K.; Hara, R.; Suzuki, N.; Takahashi, T. *Inorg. Chim. Acta* **1996**, 91. (j) Mao, S. S. H.; Don Tilley, T. *Macromolecules* **1997**, *30*, 5566.

(8) (a) Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J. P.; Dupuis, L.; Pirio, N.; Meunier, P. *Chem. Commun.* **1997**, 279. (b) Zablocka, M.; Igau, A.; Majoral, J.-P.; Pietrueiewicz, K. M. *Organometallics* **1993**, *12*, 603. (c) Cadierno, V.; Zablocka, M.; Donnadieu, M.; Lgau, A.; Majoral, J. P. *New J. Chem.* **2003**, *27*, 675.

(9) Xi, Z.; Zhang, W.; Takahashi, T. *Tetrahedron Lett.* **2004**, *45*, 2427.

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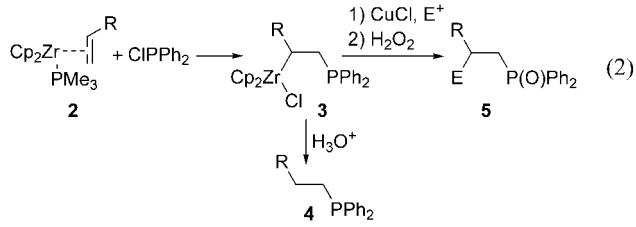
**Table 1. Screening of Ligand for Effectly Affording 3a**

| entry | ligand | $^{31}$P NMR of **3a** | yield[a] |
|---|---|---|---|
| 1 | $PMe_3$ | −13.4 | 91% |
| 2 | $PPhMe_2$ | −13.4 | 80% |
| 3 | $PPh_2Me$ | −13.3 | 35% |
| 4 | pyridine | −13.9 | 15% |

[a] NMR yields were obtained in proportion to the integral area of all the $^{31}$P signals.

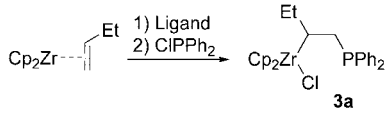
bonds afford various organophosphonates $RP(O)(OR)_2$.[10] Recently, reaction of alkynes with $Cp_2Zr$ species and chlorodiphenylphosphine to afford zirconoalkenylphosphines in high yields has been demonstrated.[11] Accordingly, we envisioned that the reaction of alkenes under optimized conditions could give zirconoalkyldiarylphosphines. Herein we report the reaction of zirconocene−alkene complexes **2** and chlorodiphenylphosphines (eq 2). Moreover, the resulting zirconoethlydiphenylphosphine **3** further reacted with various electrophiles to form variously $\beta$-functionalized alkyldiphenylphosphine oxides in the presence of CuCl.




(2)

## Results and Discussion

At the beginning, to a solution of zirconocene−butene complex $Cp_2Zr(CH_2{=}CHEt)$,[12] generated by the reaction of $Cp_2ZrCl_2$ with 2 equiv of *n*-BuLi in THF, was added 1 equiv of chlorodiphenylphosphine. The reaction mixture was kept at 0 °C for 1 h. However, designated intermediate 2-zirconobutyldiphenylphosphine **3a** was not observed. On the other hand, addition of a ligand to the solution of $Cp_2Zr(CH_2{=}CHEt)$ and stirring at room temperature for 1 h,[13] then addition of 1.0 equiv of $ClPPh_2$, produced the designated product **3a** (eq 3). Optimization of the reaction conditions and various ligands was examined. The ligand $PMe_3$ gave the best result in terms of $^{31}$P NMR yield (Table 1).

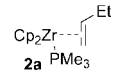
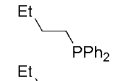
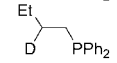
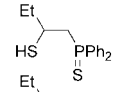
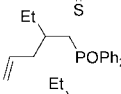
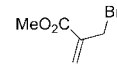
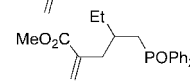
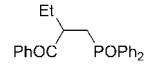
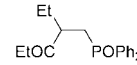
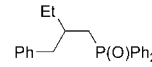
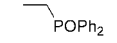
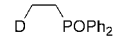
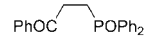
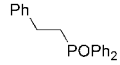
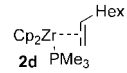
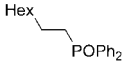
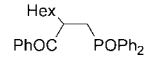



(3)

Preliminary screening of ligands revealed that $PMe_3$ as a ligand worked efficiently in this procedure because it is more strongly coordinated with zirconium with less hindrance. In a representative experiment, to a solution of $Cp_2Zr(CH_2{=}CHEt)(PMe_3)$,[15] generated by $Cp_2ZrBu_2$ (Negishi reagent) with $PMe_3$ in THF at room temperature,[13a] was added 1 equiv of chlorodiphenylphosphine. The reaction mixture was kept at 0 °C for 1 h, and then it was quenched with 3 M HCl. Butyldiphenylphosphine **4a** was obtained in 91% NMR yield. Purification of **4a** under nitrogen allowed us to isolate this compound in 75% yield. Deuteriolysis of the reaction mixture instead of hydrolysis afforded deuterated compound 2-deutriumbutyldiphenylphosphine **4b** in 70% isolated yield with 92% deuterium incorporation. This result showed that the product of the reaction of $Cp_2Zr(CH_2{=}CHEt)(PMe_3)$ with chlorodiphenylphosphine before hydrolysis contains one Zr−C bond. The $^{13}$C NMR spectrum of **3a** showed a singlet at 112.3 ppm assigned to the Cp carbons: 17.48 (d, $^4J_{PC}$ = 5.0 Hz, $-\underline{C}H_3$), 31.71(d, $^3J_{PC}$ = 5.7 Hz, $-\underline{C}H_2CH_3$), 38.74 (d, $^1J_{PC}$ = 23.7 Hz, $-\underline{C}H_2P$), 59.99(s, $-\underline{C}HZrP$), which are assignable to the $sp^3$ carbons of $CH_3CH_2CH(Zr)CH_2PPh_2$, respectively. Its $^{31}$P NMR (THF, 85% $H_3PO_4$) spectrum showed a strong signal at −13.4 ppm. With respect to regiochemistry, the $PPh_2$ group was selectively introduced into the less hindered side of the terminal carbon.

A variety of the zirconocene−alkene complexes were subjected to metallophosphination, and all reactions afforded the analogous products in good yields. Since trivalene phosphine was sentitive to oxygen, the product was isolated as phosphine oxide after treatment of the reaction mixture with $H_2O_2$. The results are summarized in Table 2. $Cp_2Zr(CH_2{=}CHEt)(PMe_3)$ **2a** and $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$ **2b** were produced via $Cp_2ZrBu_2$ and $Cp_2ZrEt_2$ *in situ*. $Cp_2Zr(CH_2{=}CHC_6H_{13})(PMe_3)$

**Table 2. Preparation of Functionalized Alkyldiphenylphosphines and Alkyldiphenylphosphine Oxides by the Reaction of Zirconocene-Alkene Complexes with $Ph_2PCl$ and Electrophiles**

| Complex | Electrophile | Product | | Yield (%)[a] |
|---|---|---|---|---|
|  **2a** | HCl |  | **4a** | 91 (75) |
| **2a** | DCl |  | **4b** | 91 (70) |
| **2a** | $S_8$ |  | **5a** | 80 (49) |
| **2a** |  |  | **5b** | - (47) |
| **2a** |  |  | **5c** | - (27) |
| **2a** | PhCOCl |  | **5d** | - (55) |
| **2a** | EtCOCl |  | **5e** | - (48) |
| **2a** | $PhCH_2Br$ |  | **5f** | - (42) |
|  **2b** | HCl |  | **5g** | 84 (65) |
| **2b** | DCl |  | **5h** | 84 (63) |
| **2b** | PhCOCl |  | **5i** | - (45) |
|  **2c** | HCl |  | **5j** | 55 (40) |
|  **2d** | HCl |  | **5k** | 59 (51) |
| **2d** | PhCOCl |  | **5l** | - (42) |

[a] NMR yields; isolated yields are given in parentheses.

(10) (a) Xi, C.; Ma, M.; Li, X. *Chem Commun.* **2001**, 2554. (b) Lai, C.; Xi, C.; Chen, C.; Ma, M.; Hong, X. *Chem. Commun.* **2003**, 2736. (c) Lai, C.; Xi, C.; Chen, W.; Hua, R. *Tetrahedron* **2006**, *62*, 6295.

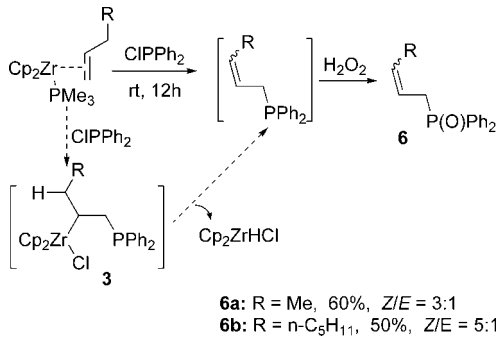
(11) Xi, C.; Yan, X.; Lai, C. *Organometallics* **2007**, *26*, 1084.

(12) (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1989**, *27*, 2829. (b) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623.

(13) Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825.

(14) (a) Kuchen, W.; Buchwald, H. *Chem. Ber* **1958**, *91*, 2871. (b) Spanier, E. J.; Caropreso, F. E. *J. Am. Chem. Soc.* **1970**, *92*, 3348. (c) Cowley, A. H. *Chem. Rev.* **1965**, *65*, 617.

**Scheme 1**

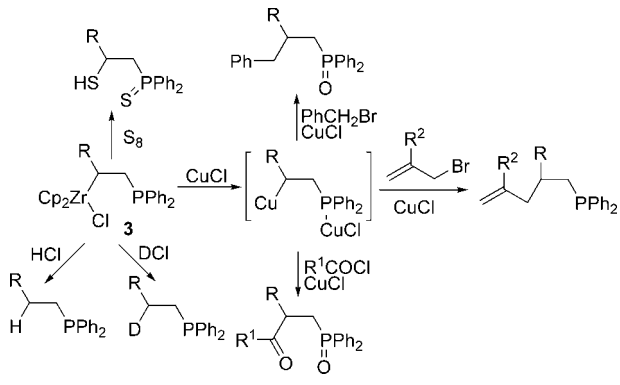



**2c** and $Cp_2Zr(CH_2{=}CHPh)(PMe_3)$ **2d** were prepared by the reactions of $Cp_2Zr(CH_2{=}CHEt)(PMe_3)$ with 1-octene and styrene, respectively.[9a]

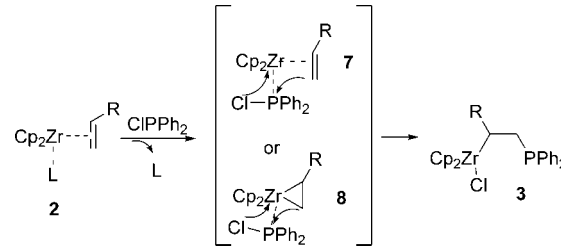
Moreover, when the reaction mixture of zirconocene−butene or zirconocene−octene complex and chlorodiphenylphosphine was warmed to room temperature and kept for 12 h (Scheme 1), allylphosphine oxide **6** was obtained after workup. This result further confirmed that the intermediate **3** was formed when the reaction mixture was kept at 0 °C. Then, a $\beta$-hydrogen abstraction and elimination of $Cp_2ZrHCl$ afforded allylphosphine slowly after the reaction mixture was warmed to room temperature.

Zirconophosphination products of alkenes would be converted into $\beta$-functionalized alkyldiarylphosphines by coupling with various electrophiles in theory. During the course of our studies, we found that the zirconophosphination products are inert to the most of electrophiles. Recently, transmetalation of organozirconium to organocopper has opened new avenues in coupling reactions.[16] Thus, we reacted the zirconophosphination products with various electrophiles, such as acyl chlorides, allylic bromides, and benzyl bromide, in the presence of CuCl. It is noteworthy that the Cu−P interaction is very strong, and we failed to isolate the free phosphine. Thus, the reaction mixture was treated with $H_2O_2$, and the phosphine oxides were obtained. The various reactions are summarized in Scheme 2, and representative results are shown in Table 2. The hydrophosphination products **4a** are obtained in high yield after hydrolysis of **3a**. Addition of $S_8$ to a solution of **3a** afforded 1-(diphenylphosphorothioyl)butane-2-thiol **5a** after hydrolysis. The reaction of **3a** with allylic bromide or methyl 2-(bromomethyl)acrylate in the presence of CuCl gave the corresponding cross-coupling product **5b** and **5c**, respectively. When **3a**, **3b**, and **3d** were treated with acyl chloride, **5d**, **5e**, **5i**, and **5l** were obtained, respectively. The reaction of **3a** with benzyl bromide gave **5f**. Although its scope is limited to carbon electrophiles, and heteroatom electrophiles, such as $Ph_2PCl$, $PhPCl_2$, and

**Scheme 2**




**Scheme 3**




$Me_3SiCl$, did not react, the metallophosphination of alkenes should be informative.

Coupling reactions of zirconocene alkene complexes with various unsaturated compounds such as alkynes, alkenes, and ketones have been reported.[15,17] Although the mechanism of reaction presented here is not yet clear, one possible reaction pathway is shown in Scheme 3: reaction of $[Cp_2Zr(CH_2{=}CHR)(PMe_3)]$ with $ClPR_2$ to give product **3** via complex **7** or **8**. An alternative reaction pathway involving oxidative addition of $ClPPh_2$ to the complex $[Cp_2Zr(CH_2{=}CHR)(PMe_3)]$, giving $[Cp_2ClZrPPh_2(CH_2{=}CHR)(PMe_3)]$, and subsequent insertion of alkene into the $Zr-PPh_2$ moiety to afford **3** cannot be ruled out.[18]

## Conclusion

In summary, we developed a versatile reaction to synthesize various functionalized alkyldiphenylphosphines oxides via highly regioselective metallophosphination of alkenes. A detailed study of the reaction process is also presented.

## Experimental Section

All manipulations were conducted in predried Schlenk tubes and under nitrogen with a slightly positive pressure. The reaction progress was monitored by $^{31}P$ NMR. The $^{31}P$ NMR yields of the products were obtained in proportion to the integral area of corresponding products. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran (THF) was refluxed and freshly distilled from dark purple solutions of sodium and benzophenone under a nitrogen atmosphere. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a JEOL 300 NMR spectrometer with tetramethylsilane (TMS) as internal standard. $^{31}P$ NMR spectra were recorded on a Bruker AC 200 NMR spectrometer at 81 MHz under $^1H$ decoupled conditions using 85% $H_3PO_4$ ($\delta_p = 0$ ppm) as an external standard. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in positive ion mode. Elemental analyses were performed on a Flash EA 1112 instrument.

**Typical Procedure for the Reaction of $Cp_2Zr(CH_2{=}CHR)(PMe_3)$ 2 with Chlorodiphenylphosphine: Preparation of 2-Zirconobutyldiphenylphosphine 3a.** To a solution of dibu-

(15) (a) Wagenen, B. C. V.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495. (b) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(16) (a) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N.; Nakajima, N. *Organometallics* **1994**, *13*, 4183. (b) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (c) Xi, C.; Kotora, M.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2000**, *65*, 945.

(17) (a) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 584. (b) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (c) Takahashi, T.; Suzuki, N.; Kaheyama, M.; Kondakov, D. Y.; Hara, R. *Tetrahedron Lett.* **1993**, *34*, 4811.

(18) (a) Hey-Hawkins, E.; Lindenberg, F. *Chem. Ber.* **1992**, *125*, 1815. (b) Matthias, W.; Matthias, H. D.; Heinrich, N.; Thomas, S.; Arno, P. *J. Am. Chem. Soc.* **1998**, *120*, 6722.

tylzirconocene generated by the reaction of $Cp_2ZrCl_2$ (1.2 mmol, 0.354 g) with 2.4 mmol of *n*-BuLi (1.5 mL, 1.6 M in hexane solution) in THF (5 mL) was added 1.5 equiv of $PMe_3$ (1.5 mL, 1.0 M in THF). The reaction mixture was kept at ambient temperature for 1 h. Subsequently $PPh_2Cl$ (184 $\mu$L, 1.0 mmol) was added, and the solution was stirred for 20 min at 0 °C. $^{31}P$ NMR: −15.6 (81 MHz, THF, 85% $H_3PO_4$). NMR yield is 91%. $^{13}C$ NMR (75 MHz, $C_6D_6$, $Me_4Si$): $\delta$ 17.5 (d, $^4J_{PC}$ = 5.0 Hz), 31.7 (d, $^3J_{PC}$ = 5.7 Hz,), 38.7 (d, $^1J_{PC}$ = 23.7 Hz), 60.0, 112.3, 127.9−139.1.

**Preparation of Butyldiphenylphosphine 4a.** The reaction mixture containing 2-zirconobutyldiphenylphosphine **3a** was quenched by 3 M HCl and then extracted with ethyl acetate. Removing the solvent and subsequent purification by column chromatography on silica gel (petroleum ether) under nitrogen afforded the title compound as a colorless liquid in 75% isolated yield. $^1H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.42−1.46 (m, 4H), 2.02−2.07 (m, 2H), 7.30−7.52 (m, 10H). $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 13.9, 24.4 (d, $^3J_{PC}$ = 12.8 Hz), 27.9 (d, $^2J_{PC}$ = 10.8 Hz), 28.2 (d, $^1J_{PC}$ = 15.6 Hz), 128.5 (d, $^3J_{PC}$ = 6.5 Hz), 128.5, 132.8 (d, $^2J_{PC}$ = 18.8 Hz), 139.1 (d, $^1J_{PC}$ = 12.8 Hz). $^{31}P$ NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ −15.6. Positive ion ESI-MS: 243.2 ($M + H^+$). The NMR data are consistent with literature.[19]

**Preparation of (2-Deuterium)butyldiphenylphosphine 4b.** The reaction was carried out in a similar way to that described above using 20% DCl instead of 3 M HCl. The isolated yield is 75%. $^1H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.87 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.37−1.45 (m, 2H), 1.50−1.62 (m, 1H), 2.24 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{PH}$ = 10.6 Hz, 2H), 7.40−7.52 (m, 6H), 7.70−7.76 (m, 4H). $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 13.6, 23.2 (dt, $^2J_{PC}$ = 3.6 Hz, $^1J_{CD}$ = 19.5 Hz), 24.1 (d, $^3J_{PC}$ = 15.0 Hz), 29.5 (d, $^1J_{PC}$ = 75.0 Hz), 128.7 (d, $^3J_{PC}$ = 11.3 Hz), 130.9 (d, $^2J_{PC}$ = 9.0 Hz), 131.7, 133.4 (d, $^1J_{PC}$ = 100.5 Hz). $^{31}P$ NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 35.0. Positive ion ESI-MS: 243.8 ($M + H^+$). Anal. Calcd for $C_{16}H_{18}DP$: C, 78.98; H, 8.28. Found: C, 79.11; H, 8.30.

**Preparation of 1-(Diphenylphosphorothioyl)butane-2-thiol 5a.** The reaction was carried out in a similar way. After addition of $S_8$ (3.0 mmol, 96 mg) to **3a** at room temperature, the reaction mixture was stirred at the same temperature for 5 h. The resulting mixture was treated with 3 N HCl. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:10) afforded 149 mg of the title compound as a colorless solid. $^1H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.86 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.53−1.68 (m, 1H), 1.79−1.90 (m, 1H), 2.33 (m, 1H), 2.70−2.87 (m, 1H), 3.05−3.24 (m, 1H), 3.40−3.60 (m, 1H), 7.40−7.50 (m, 6H), 7.83−7.89 (m, 4H). $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 11.3, 27.7 (d, $^3J_{PC}$ = 6.5 Hz), 37.5 (d, $^1J_{PC}$ = 48.8 Hz), 49.3, 128.8 (d, $^3J_{PC}$ = 12.0 Hz), 128.8 (d, $^3J_{PC}$ = 12.0 Hz), 131.0 (d, $^2J_{PC}$ = 9.8 Hz), 131.3 (d, $^2J_{PC}$ = 9.8 Hz), 131.7, 132.7 (d, $^1J_{PC}$ = 75.0 Hz), 133.5 (d, $^1J_{PC}$ =75.0 Hz). $^{31}P$ NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 40.2. ESI-MS: $m/z$ = 305.0. Anal. Calcd for $C_{16}H_{19}PS_2$: C, 62.71; H, 6.25. Found: C, 62.79; H, 6.26.

**Preparation of (2-Allylbutyl)diphenylphosphine Oxide 5b.** After addition of CuCl (3.0 mmol, 297 mg) to the reaction mixture of 2-zirconobutyldiphenylphosphine at room temperature, allyl bromide (1.2 mmol, 103 $\mu$L) was added and the reaction mixture was stirred at room temperature for 12 h. The resulting mixture was treated with 3 M HCl, and then 30% $H_2O_2$ (2 mL) was added dropwise. The reaction mixture was stirred for 1.0 h. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 2:1) afforded 140 mg of the title compound as a colorless solid in 47% isolated yield. $^1H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.81 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 1.31−1.43 (m, 1H), 1.45−1.60 (m, 1H), 1.66−1.75 (m, 1H), 1.85−2.00 (m, 1H), 2.12−2.16 (m, 2H), 2.19−2.33 (m, 1H), 4.93−5.02 (m, 2H), 5.58−5.70 (m, 1H), 7.80−7.40 (m, 10H). $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 10.6, 27.2 (d, $^3J_{PC}$ = 7.5 Hz), 32.9 (d, $^1J_{PC}$ = 71.0 Hz), 33.7 (d, $^2J_{PC}$ = 2.5 Hz), 38.5 (d, $^3J_{PC}$ = 9.0 Hz), 117.2, 128.7 (d, $^3J_{PC}$ = 10.5 Hz), 130.8 (d, $^2J_{PC}$ = 9.0 Hz), 131.6, 133.9 (d, $^1J_{PC}$ = 82.5 Hz), 136.1. $^{31}P$ NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 34.2. Positive ion ESI-MS: 299.0 ($M + H^+$), 321 ($M + Na^+$). Anal. Calcd for $C_{19}H_{23}OP$: C, 76.49; H, 7.77. Found: C, 76.41; H, 7.81.

**Methyl 4-((diphenylphosphoryl)methyl)-2-methylenehexanoate 5c.** $^1H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.82 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 1.33−1.42 (m, 1H), 1.55−1.64 (m, 1H), 2.15−2.50 (m, 4H), 3.60, 5.47 (d, $^2J_{HH}$ = 1.0 Hz, 1H), 6.17 (d, $^2J_{HH}$ = 1.0 Hz, 1H), 7.41−7.52 (m, 6H), 7.66−7.74 (m, 4H). $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 10.3, 27.2 (d, $^3J_{PC}$ = 5.0 Hz), 32.6 (d, $^1J_{PC}$ = 71.7 Hz), 33.4 (d, $^2J_{PC}$ = 2.9 Hz), 37.2 (d, $^3J_{PC}$ = 10.0 Hz), 127.2, 128.7 (d, $^3J_{PC}$ = 10.8 Hz), 130.7 (d, $^2J_{PC}$ = 9.0 Hz), 130.9 (d, $^2J_{PC}$ = 9.0 Hz), 131.7, 132.6 (d, $^1J_{PC}$ = 97.5 Hz), 138.8. $^{31}P$ NMR (81 MHz, $CDCl_3$, 85%$H_3PO_4$): $\delta$ 32.4. Positive ion ESI-MS: $m/z$ = 357.1 ($M + H^+$). Anal. Calcd for $C_{21}H_{25}O_3P$: C, 70.77; H, 7.07. Found: C, 70.81; H, 7.08.

**Preparation of (2-Benzoylbutyl)diphenylphosphine Oxide 5d.** After addition of CuCl (3.0 mmol, 297 mg) to the reaction mixture of 2-zirconobutyldiphenylphosphine **3a** at room temperature, benzoyl chloride (1.2 mmol, 168 mg) was added, and the reaction mixture was stirred at room temperature for 6 h. The resulting mixture was treated with 3 M HCl, and 30% $H_2O_2$ (2 mL) was added dropwise; the reaction mixture was stirred for 1 h. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 3:1) afforded 199 mg of the title compound as a colorless solid in 55% isolated yield. $^1H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.79 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 1.60−1.69 (m, 1H), 1.73−1.85 (m, 1H), 2.30−2.46 (m, 1H), 2.97−3.08 (m, 1H), 3.96−4.07 (m, 1H), 7.24−7.84 (m, 15H). $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 11.0, 27.6 (d, $^3J_{PC}$ = 9.0 Hz), 31.0 (d, $^1J_{PC}$ = 71.0 Hz), 40.5, 128.5, 128.5, 128.5, 128.7, 128.8 (d, $^3J_{PC}$ = 11.3 Hz), 130.7 (d, $^2J_{PC}$ = 9.0 Hz), 131.2 (d, $^2J_{PC}$ = 9.0 Hz), 131.8, 131.9, 133.1, 133.7 (d, $^1J_{PC}$ = 97.5 Hz), 136.4, 202.2 (d, $^3J_{PC}$ = 5.6 Hz). $^{31}P$ NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 31.7. Positive ion ESI-MS: 363.2 ($M + H^+$), 385.1 ($M + Na^+$). Anal. Calcd for $C_{23}H_{23}O_2P$: C, 76.23; H, 6.40. Found: C, 76.33; H, 6.44.

**4-((Diphenylphosphoryl)methyl)hexan-3-one 5e.** $^1H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.83 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 0.84 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 1.34−1.45 (m, 2H), 1.52−1.59 (m, 2H), 2.17−2.27 (m, 2H), 2.97−3.14 (m, 1H), 7.39−7.49 (m, 6H), 7.66−7.74 (m, 15H). $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 13.1, 13.7, 23.5 (d, $^4J_{PC}$ = 3.6 Hz), 24.1 (d, $^3J_{PC}$ = 15.1 Hz), 29.5 (d, $^1J_{PC}$ = 71.7 Hz), 35.2, 128.6 (d, $^3J_{PC}$ = 11.5 Hz), 128.7 (d, $^3J_{PC}$ = 11.5 Hz), 130.8 (d, $^2J_{PC}$ = 9.3 Hz), 131.1 (d, $^2J_{PC}$ = 9.3 Hz), 133.6 (d, $^1J_{PC}$ = 96.8 Hz), 211.6 (d, $^3J_{PC}$ = 60.0 Hz). $^{31}P$ NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 33.3. Positive ion ESI-MS: $m/z$ = 315.1 ($M + H^+$). Anal. Calcd for $C_{19}H_{23}O_2P$: C, 72.59; H, 7.37. Found: C, 72.62; H, 7.37.

**4-((Diphenylphosphoryl)-2-benzyl)butane 5f.** $^1H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.83 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 1.39−1.43 (m, 2H), 1.53−1.57 (m, 2H), 2.17−2.20 (m, 1H), 3.06−3.13 (m, 2H), 7.02−7.13 (m, 5H), 7.34−7.50 (m, 6H), 7.60−7.73 (m, 4H). $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 13.0, 18.2 (d, $^3J_{PC}$ = 2.2 Hz), 35.7 (d, $^1J_{PC}$ = 69.7 Hz), 37.6 (d, $^3J_{PC}$ = 10.4 Hz), 38.4, 126.9, 128.3, 128.4, 128.6 (d, $^3J_{PC}$ = 11.5 Hz), 131.1 (d, $^2J_{PC}$ = 9.3 Hz), 131.8, 131.9 (d, $^4J_{PC}$ = 2.2 Hz), 133.7 (d, $^1J_{PC}$ = 90.3 Hz). $^{31}P$ NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 30.5. Positive ion ESI-MS: $m/z$ = 349.2 ($M + H^+$). Anal. Calcd for $C_{23}H_{25}OP$: C, 79.29; H, 7.23. Found: C, 79.28; H, 7.24.

(19) Gordillo, B.; Dominguez, Z. J.; Sanchez, N.; Gonzalez, R.; Salas, M.; Barragan, E. *Tetrahedron Lett.* **2003**, *44*, 5293.

**Preparation of (2-Butenyl)diphenylphosphine Oxide 6a.** The reaction mixture containing 2-zirconobutyldiphenylphosphine **3a** was stirred for 12 h at room temperature. The resulting mixture was treated with 3 M HCl, and then 30% $H_2O_2$ (2 mL) was added. The title compound was afforded as a colorless liquid (154 mg) in 60% isolated yield (*Z*/*E* = 3:1). Major isomer: (*Z*)-(2-butenyl-)diphenylphosphine oxide, $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 1.42 (t, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 4.8 Hz, 3H), 3.11 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 15.0 Hz, 2H), 5.40−5.45 (m, 1H), 5.47−5.62 (m, 1H), 7.40−7.80 (m, 10H). $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 13.0 (d, $^4J_{PC}$ = 2.1 Hz), 29.0 (d, $^1J_{PC}$ = 70.3 Hz), 118.5 (d, $^2J_{PC}$ = 8.5 Hz), 128.6 (d, $^3J_{PC}$ = 11.3 Hz), 129.5 (d, $^3J_{PC}$ = 12.0 Hz), 131.2 (d, $^2J_{PC}$ = 9.0 Hz), 131.9, 132.5 (d, $^1J_{PC}$ = 97.5 Hz). $^{31}$P NMR (81 MHz, $CDCl_3$, 85%$H_3PO_4$): $\delta$ 31.6. Positive ion ESI-MS 257.0 ($M + H^+$). The NMR data are consistent with the literature.[20]

**Procedure for the Reaction of $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$ with $PPh_2Cl$: Preparation of 2-Zirconoethyldiphenylphosphine 3b.** To a solution of diethylzirconocene generated by the reaction of $Cp_2ZrCl_2$ (1.2 mmol, 0.354 g) with 2.4 mmol of EtMgBr (2.4 mL, 1 M in ether solution) in THF (5 mL) was added 1.5 equiv of $PMe_3$ (1.5 mL, 1.0 M in THF). The reaction mixture was kept at ambient temperature for 1 h, and then $PPh_2Cl$ (184 $\mu$L, 1.0 mmol) was added at room temperature and the mixture was stirred for 20 min. The title compound was formed in 90% NMR yield. $^{31}$P NMR: −7.8 (81 MHz, THF, 85% $H_3PO_4$).

**Preparation of Ethyldiphenylphosphine Oxide 5g.** The reaction mixture containing 2-zirconoethyldiphenylphosphine **3b** was quenched by 3 M HCl, and then 30% $H_2O_2$ (2 mL) was added dropwise; the reaction mixture was stirred for 1.0 h. Product was extracted with ethyl acetate. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 3:1) afforded 150 mg of the title compound as a colorless liquid in 65% isolated yield. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 1.19 (dt, $^2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H), 2.24−2.30 (m, 2H), 7.40−7.52 (m, 6H) 7.69−7.73 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 5.7 (d, $^2J_{PC}$ = 5.0 Hz), 22.8 (d, $^1J_{PC}$ = 71.7 Hz), 128.7 (d, $^3J_{PC}$ = 11.3 Hz), 131.0 (d, $^2J_{PC}$ = 9.3 Hz), 131.8, 132.7 (d, $^1J_{PC}$ = 105.1 Hz). $^{31}$P NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): 36.2. ESI-MS: 231.1 ($M + H^+$). The NMR data are consistent with the literature.[21]

**Preparation of (2-Deuteriumethyl)diphenylphosphine oxide 5h.** The reaction was carried out in a similar way to that described above using 20% DCl instead of 3 M HCl. Isolated yield was observed at 63%. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 1.10−1.23 (m, 2H), 2.20−2.27 (m, 2H), 7.40−7.50 (m, 6H) 7.65−7.75 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 5.4 (dt, $^2J_{PC}$ = 4.3 Hz, $J_{DC}$ = 19.4 Hz), 22.6 (d, $^1J_{PC}$ = 72.4 Hz), 128.7 (d, $^3J_{PC}$ = 11.3 Hz), 131.0 (d, $^2J_{PC}$ = 9.0 Hz), 131.9, 132.3 (d, $^1J_{PC}$ = 106.1 Hz). $^{31}$P NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 36.2. ESI-MS: 232.0 ($M + H^+$), 253.9 ($M + Na^+$). Anal. Calcd for $C_{14}H_{14}DOP$: C, 72.71; H, 6.97. Found: C, 72.83; H, 7.02.

**Preparation of (2-Benzoylethyl)diphenylphosphine Oxide 5i.** After addition of CuCl (3.0 mmol, 297 mg) to the reaction mixture of 2-zirconoethyldiphenylphosphine **3b** at room temperature, benzoyl chloride (1.2 mmol, 168 mg) was added and the reaction mixture was stirred at room temperature for 6 h. The resulting mixture was treated with 3 M HCl, then 30% $H_2O_2$ (2 mL) was added dropwise, and the reaction mixture was stirred for 1 h. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 3:1) afforded 150 mg of the title compound as a colorless solid in 45% isolated yield. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 2.69−2.78 (m, 2H), 3.28−3.37 (m, 2H), 7.39−7.93 (m, 15H). $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 23.7 (d, $^1J_{PC}$ = 73.5 Hz,), 30.7, 128.2, 128.7, 128.9 (d, $^3J_{PC}$ = 12.0 Hz), 130.9 (d, $^2J_{PC}$ = 9.0 Hz), 132.2 (d, $^4J_{PC}$ = 2.3 Hz), 132.3 (d, $^1J_{PC}$ = 99.7 Hz), 136.2, 197.9 (d, $^3J_{PC}$ = 14.3 Hz). $^{31}$P NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 34.1. Positive ion ESI-MS: 341.1 ($M + Li^+$), 337.1 ($M + Na^+$). The NMR data are consistent with the literature.[22]

**Procedure for the Reaction of $Cp_2Zr(CH_2{=}CHPh)(PMe_3)$ with $Ph_2PCl$: Preparation of 2-Phenyl-2-zirconoethyldiphenylphosphine 3c.** To a solution of dibutylzirconocene generated by the reaction of $Cp_2ZrCl_2$ (1.2 mmol, 0.354 g) with 2.4 mmol of BuLi (1.5 mL, 1.6 M in hexane solution) in THF (5 mL) were added 1.5 equiv of $PMe_3$ (1.5 mL, 1.0 M in THF) and 116 $\mu$L of styrene. The reaction mixture was kept at ambient temperature for 1 h, then $PPh_2Cl$ (184 $\mu$L, 1.0 mmol) was added at room temperature, and the reaction mixture was stirred for 20 min. The title compound was formed in 55% NMR yield. $^{31}$P NMR: −13.2 (81 MHz, THF, 85% $H_3PO_4$).

**Preparation of Phenylethyldiphenylphosphine Oxide 5j.** The reaction mixture containing 2-zircono-2-phenylethyldiphenylphosphine was quenched by 3 M HCl, then 30% $H_2O_2$ (2 mL) was added dropwise, and the mixture was stirred for 1 h. The product was extracted with ethyl acetate. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:1) afforded 122 mg of the title compound as a colorless liquid in 40% isolated yield. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 2.50−2.63 (m, 2H), 2.88−2.96 (m, 2H), 7.23−7.25 (m, 5H), 7.47−7.53 (m, 6H), 7.60−7.80 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 27.6 (d, $^2J_{PC}$ = 1.5 Hz), 32.0 (d, $^1J_{PC}$ = 68.3 Hz), 126.4, 128.2, 128.6, 128.8 (d, $^3J_{PC}$ = 12.0 Hz), 131.2 (d, $^2J_{PC}$ = 9.0 Hz), 131.9, 132.8 (d, $^1J_{PC}$ = 98.5 Hz), 141.5 (d, $^3J_{PC}$ = 15.6 Hz). $^{31}$P NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 32.4. Positive ion ESI-MS: 307.2 ($M + H^+$), 329.1 ($M + Na^+$). The NMR data are consistent with the literature.[23]

**Procedure for the Reaction of $Cp_2Zr(CH_2{=}CHC_6H_{13})(PMe_3)$ with Chlorodiphenylphosphine: Preparation of 2-Zirconooctyldiphenylphosphine 3d.** To a solution of dibutylzirconocene generated by the reaction of $Cp_2ZrCl_2$ (1.2 mmol, 0.354 g) with 2.4 mmol of BuLi (1.5 mL, 1.6 M in hexane solution) in THF (5 mL) were added 1.5 equiv of $PMe_3$ (1.5 mL, 1.0 M in THF) and 1-octene (157 $\mu$L). The reaction mixture was kept at ambient temperature for 1 h, then $PPh_2Cl$ (184 $\mu$L, 1.0 mmol) was added at room temperature, and the mixture was stirred for 20 min. The title compound was formed in 65% NMR yield. $^{31}$P NMR: −13.7 (81 MHz, THF, 85% $H_3PO_4$).

**Preparation of Octyldiphenylphosphine Oxide 5k.** The reaction mixture containing 2-zirconooctyldiphenylphosphine was quenched by 3 M HCl, then 30% $H_2O_2$ (2 mL) was added dropwise, and the mixture was stirred for 1 h. The product was extracted with ethyl acetate. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:1) afforded 160 mg of the title compound as a colorless liquid in 51% isolated yield. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.84 (t, $^3J_{HH}$ = 6.5 Hz, 3H), 1.20−1.24 (m, 8H), 1.24−1.36 (m, 2H), 1.50−1.70 (m, 2H), 2.10−2.29 (m, 2H), 7.34−7.55 (m, 6H), 7.68−7.80 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 14.2, 21.4 (d, $^2J_{PC}$ = 3.6 Hz), 22.7, 29.1, 29.7 (d, $^1J_{PC}$ = 71.7 Hz), 31.0 (d, $^3J_{PC}$ = 14.4 Hz), 31.8, 128.7 (d, $^3J_{PC}$ = 11.3 Hz), 130.9 (d, $^2J_{PC}$ = 9.3 Hz), 131.8, 132.9 (d, $^1J_{PC}$ = 94.7 Hz). $^{31}$P NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 34.4. Positive ion ESI-MS: 315.1 ($M + H^+$), 337.1 ($M + Na^+$). The NMR data are consistent with the literature.[24]

(20) (a) Nelson, A.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2645. (b) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 5411.

(21) Renard, P.-Y.; Vayron, P.; Mioskowski, C. *Org. Lett.* **2003**, *5*, 1661.

(22) Bartels, B.; Clayden, J.; Martin, C. G.; Nelson, A.; Russell, M. G.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1807.

(23) Takaki, K.; Koshoji, G.; Komeyama, K.; Takeda, M.; Shishido, T.; Kitani, A.; Takehira, K. *J. Org. Chem.* **2003**, *68*, 6554.

(24) Carta, P.; Puljic, N.; Robert, C.; Dhimane, A.-L.; Fensterbank, L.; Lacote, E.; Malacria, M. *Org. Lett.* **2007**, *9*, 1061.

**Preparation of (2-Benzoyloctyl)diphenylphosphine Oxide 5l.** After addition of CuCl (3.0 mmol, 297 mg) to the reaction mixture of 2-zirconooctyldiphenylphosphine **3d** at room temperature, benzoyl chloride (1.2 mmol, 168 mg) was added and the reaction mixture was stirred at room temperature for 12 h. The resulting mixture was treated with 3 M HCl, then 30% $H_2O_2$ (2 mL) was added dropwise, and the reaction mixture was stirred for 1 h. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 2:1) afforded 176 mg of the title compound as a colorless solid in 42% isolated yield. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.79 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 1.11−1.25 (m, 8H), 1.51−1.60 (m, 1H), 1.68−1.77 (m, 1H), 2.36−2.47 (m, 1H), 2.96−3.07 (m, 1H), 4.00−4.07 (m, 1H), 7.22−7.80 (m, 15H). $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 14.1, 22.6, 26.6, 29.2, 31.4 (d, $^1J_{PC}$ = 70.3 Hz), 31.5, 34.5 (d, $^3J_{PC}$ = 8.3 Hz), 39.3, 128.3(d, $^3J_{PC}$ = 11.5 Hz), 128.4, 128.5, 128.8 (d, $^3J_{PC}$ = 11.5 Hz), 130.7 (d, $^2J_{PC}$ = 9.0 Hz), 131.2 (d, $^2J_{PC}$ = 9.0 Hz), 131.7, 131.9, 133.1, 132.2 (d, $^1J_{PC}$ = 97.5 Hz), 136.4, 202.4 (d, $^2J_{PC}$ = 5.6 Hz). $^{31}$P NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 31.3. Positive ion ESI-MS: 419.3 ($M + H^+$), 441.2 ($M + Na^+$). Anal. Calcd for $C_{27}H_{31}O_2P$: C, 77.49; H, 7.47. Found: C, 77.57; H, 7.49.

**Preparation of 2-Octenyldiphenylphosphine Oxide 6b.** The reaction mixture containing 2-zirconooctyldiphenylphosphine **3d** was stirred for 3 h at room temperature. The resulting mixture was treated with 3 M HCl and then 30% $H_2O_2$ (2 mL). The title compound was observed (156 mg) as a colorless liquid in 50% isolated yield (*Z*/*E* = 5:1). Major isomer: (*Z*)-2-octenyldiphenylphosphine oxide. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 0.84 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 1.15−1.45 (6H), 1.83 (m, 2H), 3.14 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 14.8 Hz, 2H), 5.39−5.46 (m, 1H), 5.54−5.57 (m, 1H), 7.41−7.55 (m, 6H), 7.70−7.80 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$): $\delta$ 14.1, 22.6, 27.5, 28.9, 30.2 ($^1J_{PC}$ = 70.3 Hz), 31.6, 117.1 (d, $^2J_{PC}$ = 8.6 Hz), 128.7 (d, $^3J_{PC}$ = 12.0 Hz) 131.2 (d, $^2J_{PC}$ = 9.0 Hz), 133.0, 132.4 (d, $^1J_{PC}$ = 92.5 Hz), 135.8 (d, $^3J_{PC}$ = 11.5 Hz). $^{31}$P NMR (81 MHz, $CDCl_3$, 85% $H_3PO_4$): $\delta$ 32.4. Positive ion ESI-MS: 313.2 ($M + H^+$), 335.1 ($M + Na^+$). The NMR data are consistent with the literature.[20b]

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