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Rhodium-Catalyzed Asymmetric Addition of Terminal Alkynes to Diarylphosphinylallenes

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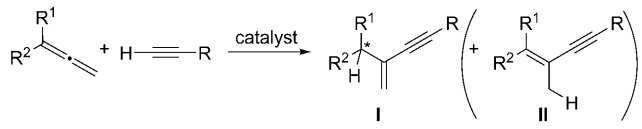
Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The presence of an acid was found to be essential in the rhodium-catalyzed asymmetric addition of terminal alkynes to diarylphosphinylallenes giving *exo*-enynes in high yields with high regio- and enantioselectivity. The stereochemical outcome is determined at the protonolysis of the π-allylrhodium(I) intermediate involved in the catalytic cycle.

Keywords: alkynes · allenes · asymmetric catalysis · enynes · rhodium

Introduction

Addition of terminal alkynes to allenes is a straightforward method of preparing conjugate enynes, which are important units found in biologically active compounds.[1] Although several transition-metal complexes (Ru,[2] Rh,[3] and Pd[4]) have been reported to catalyze the addition of terminal alkynes to allenes, to the best of our knowledge, there have been no reports on the asymmetric version of this catalytic reaction.[5] If the addition to a 1,1-disubstituted allene proceeds with *exo*-selectivity giving an *exo*-enyne (**I**) rather than an *endo*-enyne (**II**), it will provide the opportunity for asymmetric synthesis (Scheme 1). Herein, we report that phosphinylallenes are good substrates for the rhodium-catalyzed asymmetric addition of terminal alkynes, which proceeds with high regio- and enantioselectivity in the presence of a chiral rhodium(I) catalyst[6,7] and a proton donor. Mechanistic studies indicate that the reaction proceeds via a chiral π-allylrhodium(I) intermediate and its protonolysis step determines the absolute configuration of the product.



Scheme 1. Addition of terminal alkynes to allenes.

Results and Discussion

First, we examined the reaction of diphenylphosphinylallene **1a** with (triphenylsilyl)acetylene (**2m**) under one of the standard reaction conditions for the rhodium-catalyzed alkynylation[7a] using [{Rh(OH)((*R*)-binap)}$_2$][8] (**5**) as a catalyst, but the reaction did not give any hydroalkynylation products (Table 1, entry 1). In contrast, it was found that the presence of a catalytic amount of an acid dramatically promotes the reaction. Thus, adding benzoic acid (5 mol%) to a solution of allene **1a**, alkyne **2m**, and Rh/(*R*)-binap complex **5** (5 mol% of Rh) in toluene and heating the mixture at 80°C for 12 h gave 81% yield of the hydroalkynylation product, which consists of *exo*-enyne **3am** as a major isomer (93%) and *endo*-(*E*)-enyne **4am** (7%, Table 1, entry 2; Scheme 2). It should be noted that the enantiomeric purity of **3am** is high (90% *ee*). Its absolute configuration was determined to be *R* by X-ray crystallographic analysis of (4-bromophenyl)-substituted enyne **6**, which was derived from **3am** (Scheme 3, Figure 1). Acetic acid (Table 1, entry 3) and diphenylphosphinic acid (Table 1, entry 4) also promoted the reaction to give **3am** with high *R* selectivity (73% yield, 91% *ee* for acetic acid; 70% yield, 93% *ee* for diphenylphosphinic acid). Meanwhile, the use of HBF_4 (5 mol%) as a proton donor reversed the absolute configuration of **3am** (84% *ee* (*S*), Table 1, entry 5). The *S* selectivity was also ob-

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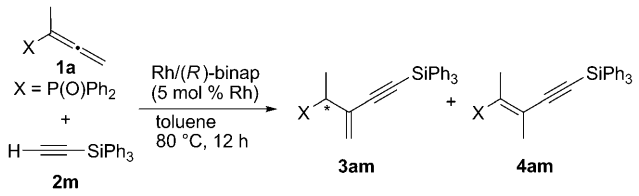
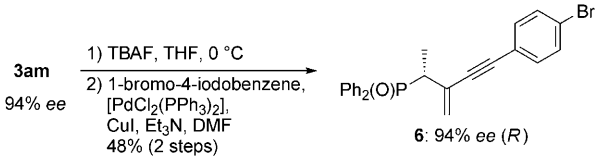
Table 1. Rhodium-catalyzed asymmetric addition of **2m** to **1a**.[a]

Entry	Catalyst	Acid	Yield [%][b]	*ee* [%][c]
1	[{Rh(OH)((*R*)-binap)}$_2$]	–	0	–
2	[{Rh(OH)((*R*)-binap)}$_2$]	$PhCO_2H$	81 (93:7)	90 (*R*)
3	[{Rh(OH)((*R*)-binap)}$_2$]	CH_3CO_2H	73 (92:8)	91 (*R*)
4	[{Rh(OH)((*R*)-binap)}$_2$]	$Ph_2P(O)OH$	70 (91:9)	93 (*R*)
5	[{Rh(OH)((*R*)-binap)}$_2$]	HBF_4[d]	86 (50:50)[e]	84 (*S*)
6[f]	[Rh(cod)$_2$]BF_4	–	99 (37:63)[e]	92 (*S*)
7[f]	[Rh(cod)$_2$]PF_6	–	91 (37:63)[e]	92 (*S*)
8[g]	[{RhCl((*R*)-binap)}$_2$]	–	67 (53:47)[e]	97 (*S*)
9[f]	[Rh(acac)(C_2H_4)$_2$]	$Ph_2P(O)OH$	77 (95:5)	94 (*R*)
10[f,h]	[Rh(acac)(C_2H_4)$_2$]	$Ph_2P(O)OH$	90 (97:3)	94 (*R*)

[a] Reaction conditions: allene **1a** (0.20 mmol), (triphenylsilyl)acetylene (**2m**) (0.20 mmol), Rh catalyst (5 mol% Rh), acid (5 mol%), toluene (0.4 mL) at 80°C for 12 h. [b] The total yield of **3am** and **4am** was determined by ^{1}H NMR. The value in parentheses is the ratio of **3am** to **4am**. [c] The *ee* of **3am** was determined by HPLC analysis with a chiral stationary phase column (Chiralpak AD-H). The absolute configuration of (*R*)-**3am** was determined by X-ray crystallographic analysis of **6**. [d] HBF_4 in Et_2O was used. [e] *E* and *Z* isomers of **4am** were formed. [f] Performed with (*R*)-binap (6 mol%). [g] Performed with $NaBAr^F{}_4$ ($Ar^F = C_6H_3$-3,5-$(CF_3)_2$; 7.5 mol%). [h] Performed with allene **1a** (0.40 mmol) and $Ph_2P(O)OH$ (2.5 mol%) for 24 h.



Scheme 2. Asymmetric addition of alkyne **2m** to allene **1a**.



Scheme 3. Transformation of **3am** into **6**.

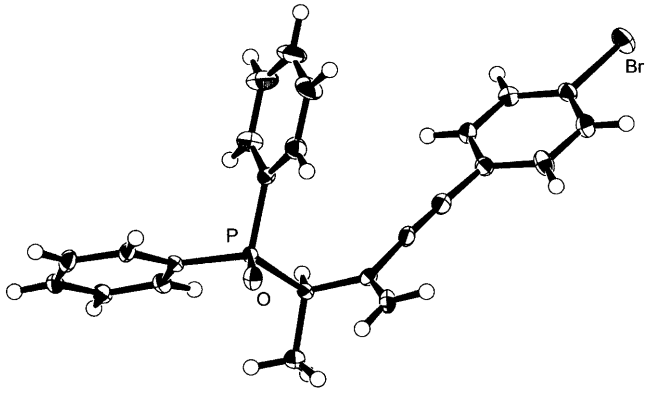
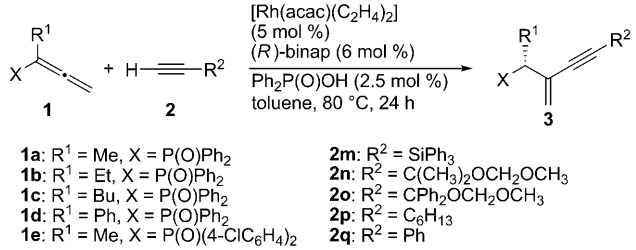


Figure 1. ORTEP illustration of compound **6** with thermal ellipsoids drawn at 50% probability.

served in reactions with cationic rhodium complexes generated from [Rh(cod)$_2$]BF_4[9] and (*R*)-binap (Table 1, entry 6), [Rh(cod)$_2$]PF_6[10] and (*R*)-binap (Table 1, entry 7), and [{RhCl((*R*)-binap)}$_2$][8] and $NaBAr^F{}_4$[11] (Table 1, entry 8). These reactions gave **3am** of *S* configuration with high enantioselectivity (92–97% *ee*), although the regioselectivity was low. The rhodium complex [Rh(acac)(C_2H_4)$_2$][12] can be used as a catalyst precursor combined with (*R*)-binap in the presence of diphenylphosphinic acid leading to the selective formation of (*R*)-**3am** with 94% *ee* (Table 1, entry 9). The highest yield (90%) with the highest regio- and enantioselectivity (**3am**/**4am** = 97:3, 94% *ee*) was obtained from the reaction with two equivalents of allene **1a** in the presence of diphenylphosphinic acid (2.5 mol%, Table 1, entry 10).

The results of the asymmetric addition of terminal alkynes to phosphinylallenes in the presence of diphenylphosphinic acid (Scheme 4) are summarized in Table 2. The reaction of 1-substituted phosphinylallenes **1a**–**1e** with (triphenylsilyl)-acetylene (**2m**) gave the corresponding enynes **3** in good yields (75–85%) with high regio- and enantioselectivity (76–94% *ee*, Table 2, entries 1–5). The enantioselectivity is also high for the addition of propargylic ethers **2n** and **2o** to **1a** (88–91% *ee*, Table 2, entries 6 and 7). The asymmetric addition proceeded with simple terminal alkynes, 1-octyne (**2p**) and phenylacetylene (**2q**), although the yields of the enynes are somewhat lower (Table 2, entries 8 and 9).

To gain information about the catalytic cycle and the role of acids, which greatly affect the absolute configuration of the product, we carried out stoichiometric reactions starting with alkynylrhodium(I) complexes. Alkynylrhodium(I) com-



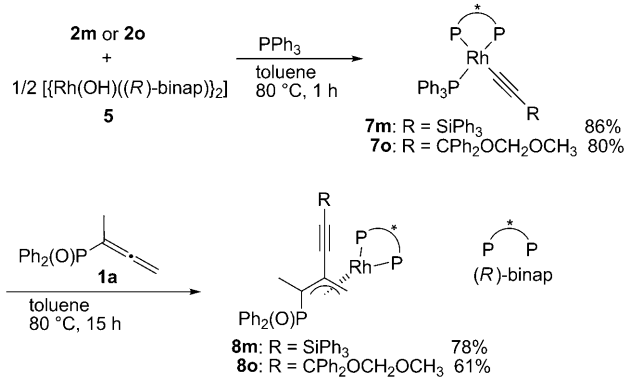
Scheme 4. Asymmetric addition of terminal alkynes to phosphinylallenes.

Table 2. Rhodium-catalyzed asymmetric addition of terminal alkynes to phosphinylallenes.[a]

Entry	**1**	**2**	Yield [%][b]	**3**	*ee* [%][c]
1	**1a**	**2m**	88 (97:3)	**3am**	94 (*R*)
2	**1b**	**2m**	81 (95:5)	**3bm**	92 (*R*)
3	**1c**	**2m**	80 (93:7)	**3cm**	90 (*R*)
4	**1d**	**2m**	75 (97:3)	**3dm**	76 (*R*)
5	**1e**	**2m**	85 (99:1)	**3em**	93 (*R*)
6	**1a**	**2n**	81 (98:2)	**3an**	91 (*R*)
7	**1a**	**2o**	75 (94:6)	**3ao**	88 (*R*)
8	**1a**	**2p**	70 (98:2)	**3ap**	82 (*R*)
9	**1a**	**2q**	50 (98:2)	**3aq**	84 (*R*)

[a] Reaction conditions: allene **1a** (0.40 mmol), alkyne **2** (0.20 mmol), [Rh(acac)(C_2H_4)$_2$] (5 mol%), (*R*)-binap (6 mol%), $Ph_2P(O)OH$ (2.5 mol%), toluene (0.4 mL) at 80°C for 24 h. [b] Yield of the two isolated isomers. The value in parentheses is the ratio of isomers (*exo*-enyne/*endo*-enyne). [c] Determined by HPLC analysis with chiral stationary phase columns: Chiralpak AD-H for **3am**–**3em** and **3an**–**3ap**; Chiralcel OJ-H for **3aq**.

plexes **7m**[7a] and **7o** coordinated with (*R*)-binap and PPh_3 were prepared in high yields by the reaction of [{Rh(OH)((*R*)-binap)}$_2$] (**5**) with silylacetylene **2m** and propargyl ether **2o**, respectively (Scheme 5).[13] Treatment of



Scheme 5. Synthesis of π-allylrhodium(I) intermediates.

complex **7m** with allene **1a** in toluene at 80 °C brought about selective formation of the π-allylrhodium(I) complex **8m**, which was isolated in 78% yield. The structure of π-allylrhodium(I) complex **8o**, which was prepared from **7o** and allene **1a**, was determined by X-ray crystallographic analysis. As shown in Figure 2, two phosphorus atoms (P(2) and P(3)) of (*R*)-binap and π-allyl carbon atoms (C(1)and C(3)) constitute a distorted square-planar orientation around the Rh center. The diphenylphosphinyl substituent on the π-allyl unit is located *anti* with respect to the alkynyl group on the central carbon atom C(2). The absolute configuration of the π-allyl moiety in complex **8o** is 2*R*,3*R*.

Stoichiometric reaction of the π-allylrhodium(I) complex **8m** with acids gave us significant information on the origin of the difference in the absolute configuration of enyne **3am** depending on the nature of the proton donors (Scheme 6,

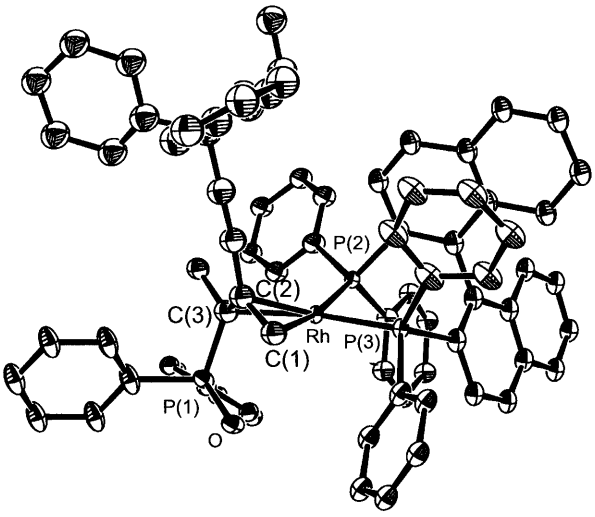
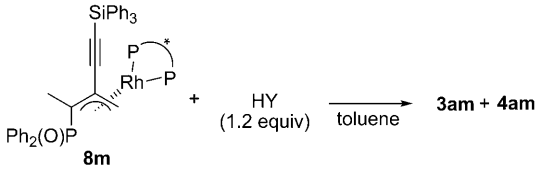


Figure 2. ORTEP illustration of complex **8o** with thermal ellipsoids drawn at 50% probability (hydrogen atoms are omitted for clarity).



Scheme 6. Protonolysis of π-allylrhodium(I) complex **8m**.

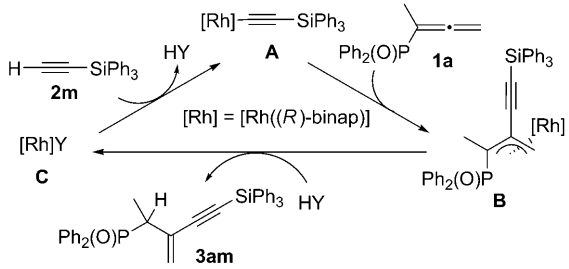
Table 3. Protonolysis of π-allylrhodium(I) complex **8m**.[a]

Entry	Acid	Temp. [°C]/time [min]	**3am**/**4am**	*ee* [%]
1	$PhCO_2H$	80/60	98:2	91 (*R*)
2	CH_3CO_2H	80/60	94:6	91 (*R*)
3	$Ph_2P(O)OH$	80/60	98:2	95 (*R*)
4	HBF_4 in Et_2O	25/10	89:11	99 (*S*)

[a] Reaction conditions: **8m** (0.010 mmol), an acid (0.012 mmol), toluene (0.5 mL).

Table 3). Protonolysis of **8m** with benzoic acid (1.2 equiv) in toluene at 80 °C for 1 h gave (*R*)-**3am** with 91% *ee* (Table 3, entry 1), the stereochemical outcome being essentially the same as that observed in the catalytic reaction (90% *ee* (*R*)). The use of acetic acid or diphenylphosphinic acid also gave the *R* isomer (Table 3, entries 2 and 3). In contrast, the protonolysis with HBF_4 gave (*S*)-**3am** with 99% *ee* (Table 3, entry 4). The *S* configuration is also the same as that observed in the catalytic reaction in the presence of HBF_4 (84% *ee* (*S*)). These results clearly indicate that the catalytic cycle involves the π-allylrhodium(I) species and its protonolysis with the acid. Furthermore, this protonolysis step is shown to determine the absolute configuration of the product.

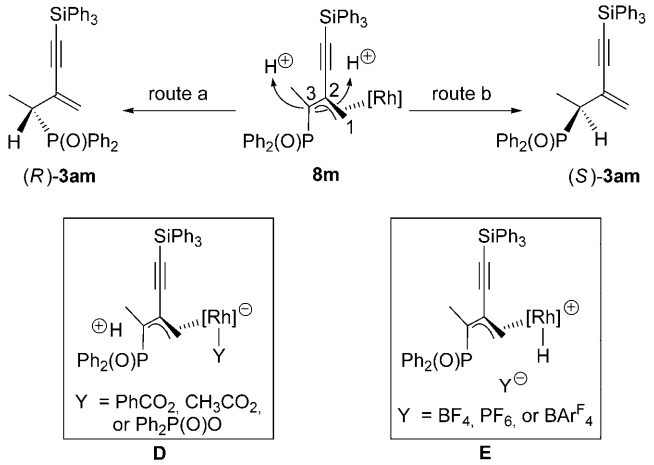
Scheme 7 illustrates the catalytic cycle proposed for the present rhodium-catalyzed hydroalkynylation involving an alkynylrhodium(I) complex **A**[7a] and a π-allylrhodium(I) complex **B** as key intermediates. Insertion of allene **1a** into the rhodium–carbon bond in **A** forms π-allylrhodium(I) **B**, which is identical to the complex **8m** obtained in Scheme 5. Protonolysis of **B** with an acid (HY) furnishes enyne **3am**[14] and the rhodium(I) species (**C**, [Rh]Y) bearing the anionic ligand resulting from the acid.[15] The reaction of **C** with alkyne **2m** regenerates the alkynylrhodium **A** and acid (HY). In the reactions catalyzed by cationic rhodium com-



Scheme 7. Proposed catalytic cycle.

plexes (entries 6–8 in Table 1), HY corresponds to HBF_4, HPF_6, or $HBAr^F_4$.[16]

The *R* configuration of **3am** observed in the catalytic and stoichiometric reactions with $PhCO_2H$, CH_3CO_2H, and $Ph_2P(O)OH$ demonstrates that the π-allyl complex undergoes the protonation at C(3) from the opposite side of rhodium (Scheme 8, route a), while the *S* configuration observed in the reactions with HBF_4, HPF_6, and $HBAr^F_4$ demonstrates the protonation from the same side as rhodium (Scheme 8, route b). In the protonation with the acids (HY), where Y^- is a coordinating anion ($CH_3CO_2^-$, $PhCO_2^-$, or $Ph_2P(O)O^-$), it is likely that the coordination of Y^- to π-allylrhodium **8m** takes place to form ate complex **D** and subsequent attack of the C(3) carbon atom to the proton from the side opposite to rhodium results in the formation of (*R*)-**3am**. On the other hand, the protonation on rhodium to form cationic rhodium(III) hydride **E** takes place with the acids bearing noncoordinating anions (BF_4^-, PF_6^-, and $BAr^F_4^-$), and the reductive elimination produces (*S*)-**3am**.



Scheme 8. Pathway of the protonolysis of π-allylrhodium(I) complex **8m**.

Conclusions

Asymmetric addition of terminal alkynes to allenes to form chiral conjugate enynes was realized for the first time by use of a Rh/(*R*)-binap catalyst and a catalytic amount of proton acids for addition to phosphinylallenes. Studies on the reactions of a π-allylrhodium(I) complex revealed that the stereochemical outcome of the conjugated enyne is determined at the protonolysis of the π-allylrhodium(I) intermediate involved in the catalytic cycle.

Experimental Section

General

All anaerobic and moisture-sensitive manipulations were carried out with either standard Schlenk techniques under predried nitrogen or glovebox techniques under argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard for ^{1}H NMR, [D]chloroform ($\delta = 77.00$ ppm) for ^{13}C NMR, and external H_3PO_4 standard for ^{31}P NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter. Elemental analyses were performed at the Microanalytical Center, Kyoto University. High-resolution mass spectra were obtained with a Bruker micrOTOF spectrometer.

Materials

Toluene was purified by passing through a neutral alumina column under nitrogen. Rhodium complexes, $[\{Rh(OH)((R)\text{-binap})\}_2]$[8] (**5**), $[\{RhCl((R)\text{-binap})\}_2]$,[8] $[Rh(cod)_2]BF_4$,[9] $[Rh(cod)_2]PF_6$,[9,10] and $[Rh(acac)(C_2H_4)_2]$,[12] were prepared according to the reported procedures. Diarylphosphinylallenes were prepared according to the reported procedures.[4b,6,17] Allene **1e**, alkyne **2o**, and all the hydroalkynylation products are new compounds.

*Typical Procedure for Rhodium-Catalyzed Asymmetric Addition of (Triphenylsilyl)acetylene (**2m**) to Diphenylphosphinylallene **1a***

To a mixture of $[Rh(acac)(C_2H_4)_2]$ (2.6 mg, 0.010 mmol) and (*R*)-binap (7.5 mg, 0.012 mmol) in a screw cap test tube was added toluene (0.40 mL) under N_2 and the mixture was stirred at room temperature. After 10 min diphenylphosphinylallene **1a** (101.7 mg, 0.40 mmol), (triphenylsilyl)acetylene **2m** (56.9 mg, 0.20 mmol), and diphenylphosphinic acid (1.1 mg, 0.005 mmol) were added and the tube was capped tightly. Then, the mixture was stirred at 80 °C (bath temp.) for 24 h. The reaction mixture was concentrated under vacuum and the residue was subjected to column chromatography on silica gel with EtOAc/hexane (2:1) as eluent to give enynes (**3am** and **4am**) as a white solid (94.6 mg, 0.176 mmol; 88 % yield).

3am: White solid; $[\alpha]_D^{20} = +20$ ($c = 1.00$, $CHCl_3$, 94 % *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1 = 20.6$ min (*R*), $t_2 = 23.7$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta = 1.46$ (dd, $J_{P\text{-}H} = 15.8$ Hz, $J = 7.4$ Hz, 3H), 3.35 (dq, $J_{P\text{-}H} = 9.3$ Hz, $J = 7.4$ Hz, 1H), 5.76 (d, $J_{P\text{-}H} = 3.6$ Hz, 1H), 5.77 (d, $J_{P\text{-}H} = 3.3$ Hz, 1H), 7.16–7.20 (m, 2H), 7.25–7.32 (m, 1H), 7.34–7.46 (m, 12H), 7.50–7.60 (m, 6H), 7.78–7.87 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 14.4$ (d, $J_{P\text{-}C} = 3.1$ Hz), 40.2 (d, $J_{P\text{-}C} = 66.6$ Hz), 89.8, 109.4 (d, $J_{P\text{-}C} = 5.6$ Hz), 127.8 (d, $J_{P\text{-}C} = 6.3$ Hz), 127.8, 128.0 (d, $J_{P\text{-}C} = 6.8$ Hz), 128.1 (d, $J_{P\text{-}C} = 11.8$ Hz), 128.4 (d, $J_{P\text{-}C} = 11.4$ Hz), 129.8, 131.2 (d, $J_{P\text{-}C} = 8.3$ Hz), 131.3 (d, $J_{P\text{-}C} = 98.1$ Hz), 131.45 (d, $J_{P\text{-}C} = 8.8$ Hz), 131.54 (d, $J_{P\text{-}C} = 2.5$ Hz), 131.6 (d, $J_{P\text{-}C} = 2.5$ Hz), 131.9 (d, $J_{P\text{-}C} = 95.7$ Hz), 133.2, 135.5 ppm; ^{31}P NMR ($CDCl_3$): $\delta = 33.1$ ppm; elemental analysis calcd (%) for $C_{36}H_{31}OPSi$: C 80.27, H 5.80; found: C 80.04, H 5.83.

4am: White solid. The stereochemistry of (*E*)-**4am** was determined by NOE experiments. ^{1}H NMR ($CDCl_3$): $\delta = 1.97$ (dq, $J_{P\text{-}H} = 13.5$ Hz, $J = 1.4$ Hz, 3H), 2.27 (dq, $J_{P\text{-}H} = 2.7$ Hz, $J = 1.4$ Hz, 3H), 7.32–7.55 (m, 15H), 7.61–7.72 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 21.9$ (d, $J_{P\text{-}C} = 6.6$ Hz), 22.3 (d, $J_{P\text{-}C} = 12.4$ Hz), 98.0 (d, $J_{P\text{-}C} = 1.5$ Hz), 109.2 (d, $J_{P\text{-}C} = 21.7$ Hz), 128.0, 128.6 (d, $J_{P\text{-}C} = 11.8$ Hz), 130.0, 131.5 (d, $J_{P\text{-}C} = 9.8$ Hz), 131.8 (d, $J_{P\text{-}C} = 2.6$ Hz), 132.8 (d, $J_{P\text{-}C} = 103.3$ Hz), 133.1, 134.4 (d, $J_{P\text{-}C} = 12.9$ Hz), 135.5, 136.3 ppm; ^{31}P NMR ($CDCl_3$): $\delta = 31.2$ ppm; elemental analysis: calcd (%) for $C_{36}H_{31}OPSi$: C 80.27, H 5.80; found: C 80.17, H 5.81.

3bm: White solid; $[\alpha]_D^{20} = +11$ ($c = 0.99$, $CHCl_3$, 92 % *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1 = 17.8$ min (*R*), $t_2 = 25.5$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta = 1.03$ (t, $J = 7.3$ Hz, 3H), 1.83–2.02 (m, 2H), 3.07–3.13 (m, 1H), 5.75 (d, $J_{P\text{-}H} = 3.9$ Hz, 1H), 5.78 (d, $J_{P\text{-}H} = 3.9$ Hz, 1H), 7.23–7.48 (m, 15H), 7.55–7.60 (m, 6H), 7.75–7.86 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 12.6$ (d, $J_{P\text{-}C} = 14.0$ Hz), 22.2 (d, $J_{P\text{-}C} = 1.6$ Hz), 48.5 (d, $J_{P\text{-}C} = 66.7$ Hz), 89.7, 109.8 (d, $J_{P\text{-}C} = 5.7$ Hz), 126.1, (d, $J_{P\text{-}C} = 6.2$ Hz), 127.9, 128.2 (d, $J_{P\text{-}C} = 11.9$ Hz), 128.5 (d, $J_{P\text{-}C} = 11.4$ Hz), 128.7 (d, $J_{P\text{-}C} = 7.7$ Hz), 129.9, 131.2 (d, $J_{P\text{-}C} = 8.8$ Hz), 131.4 (d, $J_{P\text{-}C} = 9.3$ Hz), 131.5 (d, $J_{P\text{-}C} = 2.6$ Hz), 131.6 (d, $J_{P\text{-}C} = 3.1$ Hz), 131.7 (d, $J_{P\text{-}C} = 97.7$ Hz), 132.0 (d, $J_{P\text{-}C} = 96.6$ Hz), 133.4, 135.5 ppm; ^{31}P NMR ($CDCl_3$): $\delta = 32.8$ ppm; elemental analysis: calcd (%) for $C_{37}H_{33}OPSi$: C 80.40, H 6.02; found: C 79.89, H 5.97.

3cm: White solid; $[\alpha]_D^{20}=+6$ ($c=0.99$, $CHCl_3$, 90% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1=19.3$ min (*R*), $t_2=28.3$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta=0.80$ (t, $J=7.2$ Hz, 3H), 1.13–1.38 (m, 3H), 1.48–1.59 (m, 1H), 1.62–1.84 (m, 1H), 1.91–2.03 (m, 1H), 3.14–3.24 (m, 1H), 5.74 (d, $J_{P\text{-}H}=4.0$ Hz, 1H), 5.76 (d, $J_{P\text{-}H}=4.1$ Hz, 1H), 7.17–7.23 (m, 2H), 7.29–7.47 (m, 13H), 7.54–7.60 (m, 6H), 7.74–7.84 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=13.8$, 22.2, 28.4, 29.9 (d, $J_{P\text{-}C}=12.9$ Hz), 46.4 (d, $J_{P\text{-}C}=66.7$ Hz), 89.8, 109.8 (d, $J_{P\text{-}C}=5.6$ Hz), 126.4 (d, $J_{P\text{-}C}=6.1$ Hz), 127.9, 128.2 (d, $J_{P\text{-}C}=11.9$ Hz), 128.5 (d, $J_{P\text{-}C}=11.4$ Hz), 128.6 (d, $J_{P\text{-}C}=8.3$ Hz), 129.9, 131.2 (d, $J_{P\text{-}C}=8.3$ Hz), 131.4 (d, $J_{P\text{-}C}=7.9$ Hz), 131.5 (d, $J_{P\text{-}C}=3.1$ Hz), 131.6 (d, $J_{P\text{-}C}=2.6$ Hz), 131.7 (d, $J_{P\text{-}C}=98.9$ Hz), 132.0 (d, $J_{P\text{-}C}=95.6$ Hz), 133.4, 135.5 ppm; ^{31}P NMR ($CDCl_3$): $\delta=32.9$ ppm: elemental analysis: calcd (%) for $C_{39}H_{37}OPSi$: C 80.65, H 6.42; found: C 80.36, H 6.15.

3dm: White solid; $[\alpha]_D^{20}=-113$ ($c=0.93$, $CHCl_3$, 76% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1=27.4$ min (*R*), $t_2=48.6$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta=4.34$ (d, $J_{P\text{-}H}=8.9$ Hz, 1H), 5.77 (d, $J_{P\text{-}H}=1.4$ Hz, 1H), 6.27 (d, $J_{P\text{-}H}=2.3$ Hz, 1H), 7.14–7.24 (m, 6H), 7.28–7.55 (m, 22H), 7.89–7.93 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta=52.6$ (d, $J_{P\text{-}C}=64.7$ Hz), 89.7, 109.9 (d, $J_{P\text{-}C}=9.8$ Hz), 127.3 (d, $J_{P\text{-}C}=3.1$ Hz), 127.4 (d, $J_{P\text{-}C}=2.0$ Hz), 127.9, 128.0 (d, $J_{P\text{-}C}=11.9$ Hz), 128.3 (d, $J_{P\text{-}C}=1.5$ Hz), 128.5 (d, $J_{P\text{-}C}=11.9$ Hz), 128.6 (d, $J_{P\text{-}C}=6.0$ Hz), 129.8, 130.1 (d, $J_{P\text{-}C}=6.1$ Hz), 131.0 (d, $J_{P\text{-}C}=9.4$ Hz), 131.3 (d, $J_{P\text{-}C}=2.6$ Hz), 131.4 (d, $J_{P\text{-}C}=8.8$ Hz), 131.7 (d, $J_{P\text{-}C}=2.5$ Hz), 132.1 (d, $J_{P\text{-}C}=97.1$ Hz), 132.4 (d, $J_{P\text{-}C}=100.2$ Hz), 133.3, 134.4 (d, $J_{P\text{-}C}=4.6$ Hz), 135.5 ppm; ^{31}P NMR ($CDCl_3$): $\delta=31.1$ ppm; elemental analysis: calcd (%) for $C_{41}H_{33}OPSi$: C 81.97, H 5.54; found: C 81.72, H 5.53.

3em: White solid; $[\alpha]_D^{20}=+30$ ($c=1.00$, $CHCl_3$, 93% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1=28.8$ min (*R*), $t_2=38.1$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta=1.45$ (dd, $J_{P\text{-}H}=16.1$ Hz, $J=7.4$ Hz, 3H), 3.30 (dq, $J_{P\text{-}H}=9.9$ Hz, $J=7.4$ Hz, 1H), 5.73 (d, $J_{P\text{-}H}=4.2$ Hz, 1H), 5.78 (d, $J_{P\text{-}H}=4.4$ Hz, 1H), 7.12 (dd, $J=8.5$ Hz, $J_{P\text{-}H}=2.2$ Hz, 2H), 7.32–7.48 (m, 11H), 7.50–7.60 (m, 6H), 7.64–7.76 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=14.3$ (d, $J_{P\text{-}C}=3.1$ Hz), 40.4 (d, $J_{P\text{-}C}=67.2$ Hz), 90.7, 109.1 (d, $J_{P\text{-}C}=5.6$ Hz), 127.3 (d, $J_{P\text{-}C}=6.6$ Hz), 128.0, 128.3 (d, $J_{P\text{-}C}=8.3$ Hz), 128.7 (d, $J_{P\text{-}C}=11.8$ Hz), 129.0 (d, $J_{P\text{-}C}=11.8$ Hz), 129.4 (d, $J_{P\text{-}C}=99.6$ Hz), 130.0, 130.1 (d, $J_{P\text{-}C}=96.6$ Hz), 132.5 (d, $J_{P\text{-}C}=9.3$ Hz), 132.9 (d, $J_{P\text{-}C}=9.9$ Hz), 133.0, 135.5, 138.5 (d, $J_{P\text{-}C}=3.0$ Hz), 138.6 ppm (d, $J_{P\text{-}C}=3.1$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=32.2$ ppm; elemental analysis: calcd (%) for $C_{36}H_{29}Cl_2OPSi$: C 71.17, H 4.81; Found: C 70.99, H 4.86.

3an: Colorless oil; $[\alpha]_D^{20}=+53$ ($c=0.89$, $CHCl_3$, 90% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1=33.2$ min (*R*), $t_2=35.9$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta=1.40$ (s, 3H), 1.41 (s, 3H), 1.42 (dd, $J_{P\text{-}H}=15.8$ Hz, $J=7.3$ Hz, 3H), 3.25 (dq, $J_{P\text{-}H}=9.3$ Hz, $J=7.3$ Hz, 1H), 3.36 (s, 3H), 4.77 (s, 2H), 5.51 (d, $J_{P\text{-}H}=3.9$ Hz, 1H), 5.54 (d, $J_{P\text{-}H}=3.7$ Hz, 1H), 7.38–7.57 (m, 6H), 7.77–7.89 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=14.2$ (d, $J_{P\text{-}C}=3.1$ Hz), 29.90, 29.92, 40.8 (d, $J_{P\text{-}C}=66.7$ Hz), 55.4, 71.1, 84.7 (d, $J_{P\text{-}C}=5.8$ Hz), 91.8, 93.2, 125.8 (d, $J_{P\text{-}C}=8.3$ Hz), 127.4 (d, $J_{P\text{-}C}=6.1$ Hz), 128.2 (d, $J_{P\text{-}C}=11.3$ Hz), 128.5 (d, $J_{P\text{-}C}=10.9$ Hz), 131.3 (d, $J_{P\text{-}C}=8.8$ Hz), 131.5 (d, $J_{P\text{-}C}=9.3$ Hz), 131.6 (d, $J_{P\text{-}C}=3.1$ Hz), 131.7 (d, $J_{P\text{-}C}=2.6$ Hz), 131.8 (d, $J_{P\text{-}C}=97.6$ Hz), 131.9 ppm (d, $J_{P\text{-}C}=98.7$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=32.7$ ppm; elemental analysis: calcd (%) for $C_{23}H_{27}O_3P$: C 72.23, H 7.12; found: C 72.03, H 7.04.

3ao: White solid; $[\alpha]_D^{20}=+27$ ($c=1.00$, $CHCl_3$, 88% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1=42.2$ min (*S*), $t_2=51.9$ min (*R*)); ^{1}H NMR ($CDCl_3$): $\delta=1.45$ (dd, $J_{P\text{-}H}=15.9$ Hz, $J=7.3$ Hz, 3H), 3.31 (dq, $J_{P\text{-}H}=8.6$ Hz, $J=7.3$ Hz, 1H), 3.35 (s, 3H), 4.77 (d, $J=5.8$ Hz, 1H), 4.78 (d, $J=5.8$ Hz, 1H), 5.61 (d, $J_{P\text{-}H}=3.9$ Hz, 1H), 5.65 (d, $J_{P\text{-}H}=3.9$ Hz, 1H), 7.22–7.34 (m, 8H), 7.37–7.57 (m, 8H), 7.76–7.87 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=14.3$ (d, $J_{P\text{-}C}=3.1$ Hz), 40.4 (d, $J_{P\text{-}C}=67.2$ Hz), 56.3, 79.1, 89.4 (d, $J_{P\text{-}C}=5.8$ Hz), 89.6, 93.4, 126.50 (d, $J_{P\text{-}C}=8.7$ Hz), 126.54, 126.6, 127.4 (d, $J_{P\text{-}C}=6.3$ Hz), 127.51, 127.53, 128.0 (4C), 128.2 (d, $J_{P\text{-}C}=11.4$ Hz), 128.5 (d, $J_{P\text{-}C}=10.9$ Hz), 131.1 (d, $J_{P\text{-}C}=8.3$ Hz), 131.3 (d, $J_{P\text{-}C}=8.8$ Hz), 131.52 (d, $J_{P\text{-}C}=2.6$ Hz), 131.56 (d, $J_{P\text{-}C}=98.2$ Hz), 131.63 (d, $J_{P\text{-}C}=2.6$ Hz), 131.9 (d, $J_{P\text{-}C}=95.1$ Hz), 143.5, 143.6 ppm; ^{31}P NMR ($CDCl_3$): $\delta=33.2$ ppm; HRMS (ESI) calcd for $C_{33}H_{31}NaO_3P$ $[M+Na]^+$: 529.1903; found: 529.1908.

3ap: Colorless oil; $[\alpha]_D^{20}=+59$ ($c=0.86$, $CHCl_3$, 82% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1=20.2$ min (*R*), $t_2=23.1$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta=0.89$ (t, $J=7.2$ Hz, 3H), 1.20–1.42 (m, 8H), 1.41 (dd, $J_{P\text{-}H}=16.0$ Hz, $J=7.3$ Hz, 3H), 2.10 (t, $J=7.2$ Hz, 2H), 3.25 (dq, $J_{P\text{-}H}=10.0$ Hz, $J=7.2$ Hz, 1H), 5.40 (d, $J_{P\text{-}H}=3.9$ Hz, 2H), 7.38–7.55 (m, 6H), 7.79–7.91 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=14.01$, 14.03 (d, $J_{P\text{-}C}=2.1$ Hz), 19.2, 22.5, 28.4, 28.5, 31.3, 41.2 (d, $J_{P\text{-}C}=67.1$ Hz), 80.6 (d, $J_{P\text{-}C}=5.1$ Hz), 91.8, 123.8 (d, $J_{P\text{-}C}=8.3$ Hz), 128.0 (d, $J_{P\text{-}C}=11.3$ Hz), 128.39 (d, $J_{P\text{-}C}=11.3$ Hz), 128.40 (d, $J_{P\text{-}C}=5.9$ Hz), 131.3 (d, $J_{P\text{-}C}=8.3$ Hz), 131.4 (d, $J_{P\text{-}C}=3.1$ Hz), 131.5 (d, $J_{P\text{-}C}=2.6$ Hz), 131.6 (d, $J_{P\text{-}C}=8.8$ Hz), 131.8 (d, $J_{P\text{-}C}=97.6$ Hz), 132.2 ppm (d, $J_{P\text{-}C}=95.1$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=33.0$ ppm; HRMS (ESI) calcd for $C_{24}H_{30}OP$ $[M+H]^+$: 365.2029; found: 365.2025.

3aq: Colorless oil; $[\alpha]_D^{20}=+50$ ($c=0.71$, $CHCl_3$, 84% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.3 mL min^{-1}, hexane/2-propanol = 95:5, 254 nm, $t_1=53.2$ min (*R*), $t_2=61.6$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta=1.49$ (dd, $J_{P\text{-}H}=15.9$ Hz, $J=7.3$ Hz, 3H), 3.37 (dq, $J_{P\text{-}H}=9.8$ Hz, $J=7.3$ Hz, 1H), 5.58 (d, $J_{P\text{-}H}=4.0$ Hz, 1H), 5.60 (dd, $J_{P\text{-}H}=3.7$ Hz, $J=0.8$ Hz, 1H), 7.25–7.30 (m, 5H), 7.36–7.56 (m, 6H), 7.84–7.92 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=14.2$ (d, $J_{P\text{-}C}=2.6$ Hz), 41.2 (d, $J_{P\text{-}C}=66.6$ Hz), 89.4 (d, $J_{P\text{-}C}=5.1$ Hz), 90.4 (d, $J_{P\text{-}C}=1.0$ Hz), 122.9, 125.4 (d, $J_{P\text{-}C}=8.3$ Hz), 128.11 (d, $J_{P\text{-}C}=7.3$ Hz), 128.14, 128.2 (d, $J_{P\text{-}C}=11.9$ Hz), 128.3, 128.6 (d, $J_{P\text{-}C}=11.3$ Hz), 131.4 (d, $J_{P\text{-}C}=8.3$ Hz), 131.55, 131.60 (d, $J_{P\text{-}C}=2.1$ Hz), 131.65 (d, $J_{P\text{-}C}=8.8$ Hz), 131.69 (d, $J_{P\text{-}C}=1.5$ Hz), 131.74 (d, $J_{P\text{-}C}=97.7$ Hz), 132.1 ppm (d, $J_{P\text{-}C}=98.9$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=32.9$; HRMS (ESI) calcd for $C_{24}H_{21}NaOP$ $[M+Na]^+$: 379.1222; found: 379.1225.

*Transformation of Compound **3am** into **6***

To a solution of enyne **3am** (269 mg, 0.50 mmol, 94% *ee*) in THF (10 mL) was added tetrabutylammonium fluoride solution (1.0 M in THF, 0.50 mL) at 0 °C and the mixture was stirred for 0.5 h. The mixture was quenched with 10% aq HCl and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel column chromatography (hexane/ethyl acetate = 1:4) gave (*R*)-(3-methylene-4-pentyn-2-yl)diphenylphosphine oxide (**3am′**, 130 mg, 0.47 mmol, 93% yield). **3am′**: White solid; $[\alpha]_D^{20}=+59$ ($c=0.97$, $CHCl_3$, 94% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.3 mL min^{-1}, hexane/2-propanol = 95:5, 254 nm, $t_1=54.1$ min (*S*), $t_2=58.4$ min (*R*)); ^{1}H NMR ($CDCl_3$): $\delta=1.43$ (dd, $J_{P\text{-}H}=15.9$ Hz, $J=7.3$ Hz, 3H), 2.80 (s, 1H), 3.26 (dq, $J_{P\text{-}H}=8.5$ Hz, $J=7.3$ Hz, 1H), 5.57 (dd, $J_{P\text{-}H}=4.0$ Hz, $J=0.5$ Hz, 1H), 5.58 (d, $J_{P\text{-}H}=3.8$ Hz, 1H), 7.40–7.56 (m, 6H), 7.79–7.91 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=13.9$ (d, $J_{P\text{-}C}=2.6$ Hz), 40.6 (d, $J_{P\text{-}C}=67.2$ Hz), 78.2 (d, $J_{P\text{-}C}=1.0$ Hz), 83.2 (d, $J_{P\text{-}C}=5.1$ Hz), 127.1 (d, $J_{P\text{-}C}=8.3$ Hz), 127.2 (d, $J_{P\text{-}C}=6.8$ Hz), 128.2 (d, $J_{P\text{-}C}=11.3$ Hz), 128.5 (d, $J_{P\text{-}C}=11.3$ Hz), 131.2 (d, $J_{P\text{-}C}=8.3$ Hz), 131.5 (d, $J_{P\text{-}C}=8.8$ Hz), 131.60 (d, $J_{P\text{-}C}=2.6$ Hz), 131.61 (d, $J_{P\text{-}C}=98.2$ Hz), 131.7 (d, $J_{P\text{-}C}=2.5$ Hz), 131.8 ppm (d, $J_{P\text{-}C}=94.6$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=33.0$ ppm; elemental analysis: calcd (%) for $C_{18}H_{17}OP$: C 77.13, H 6.11; found: C 76.86, H 6.08. To a mixture of $[PdCl_2(PPh_3)_2]$ (9.1 mg, 0.013 mmol), CuI (2.5 mg, 0.013 mmol), 1-bromo-4-iodobenzene (82.0 mg, 0.29 mmol), and triethylamine (52.6 mg, 0.52 mmol) in DMF (1.0 mL) was added compound **3am′** (72.5 mg, 0.26 mmol) and the mixture was stirred at 50 °C for 6 h. The resulting mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel column chromatography on silica gel with EtOAc/hexane (2:1) as eluent to give compound **6** as a white solid (58.6 mg, 0.13 mmol; 52% yield). **6**: White solid; $[\alpha]_D^{20}=+65$ ($c=0.90$, $CHCl_3$, 94% *ee* (*R*)). The enantiomeric excess was measured by HPLC (Chiralcel OJ column, 0.5 mL min^{-1}, hexane/2-propanol = 9:1, 254 nm, $t_1=18.1$ min (*R*), $t_2=24.7$ min (*S*)); ^{1}H NMR ($CDCl_3$): $\delta=1.48$ (dd, $J_{P\text{-}H}=15.8$ Hz, $J=7.3$ Hz, 3H), 3.37 (dq, $J_{P\text{-}H}=7.3$ Hz, $J=7.3$ Hz, 1H), 5.57 (d,

$J_{P\text{-}H}=4.0$ Hz, 1H), 5.60 (d, $J_{P\text{-}H}=3.6$ Hz, 1H), 7.12 (d, $J=8.2$ Hz, 2H), 7.32–7.59 (m, 8H), 7.78–7.96 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta=14.0$ (d, $J_{P\text{-}C}=3.1$ Hz), 41.0 (d, $J_{P\text{-}C}=66.7$ Hz), 89.4, 90.3 (d, $J_{P\text{-}C}=4.7$ Hz), 121.8, 122.4, 125.7 (d, $J_{P\text{-}C}=8.3$ Hz), 127.8 (d, $J_{P\text{-}C}=6.7$ Hz), 128.1 (d, $J_{P\text{-}C}=11.9$ Hz), 128.5 (d, $J_{P\text{-}C}=11.4$ Hz), 131.3 (d, $J_{P\text{-}C}=8.8$ Hz), 131.3, 131.5 (d, $J_{P\text{-}C}=8.8$ Hz), 131.57 (d, $J_{P\text{-}C}=2.6$ Hz), 131.60 (d, $J_{P\text{-}C}=98.1$ Hz), 131.7 (d, $J_{P\text{-}C}=2.6$ Hz), 131.8 (d, $J_{P\text{-}C}=95.1$ Hz), 132.9 ppm; ^{31}P NMR ($CDCl_3$): $\delta=32.9$ ppm; HRMS (ESI) calcd for $C_{24}H_{20}BrNaOP$ $[M+Na]^+$: 457.0327; found: 457.0316. Colorless crystals of compound **6** suitable for X-ray crystallographic analysis were obtained by recrystallization from CH_2Cl_2-hexane. CCDC-668409 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*Preparation of Rh Complexes **7m** and **7o***

Complexes **7m**[7a] and **7o** were prepared by according to the reported procedures. **7o**: Red crystals (80% yield); ^{1}H NMR (C_6D_6): $\delta=2.89$ (s, 3H), 4.23 (d, $J=5.5$ Hz, 1H), 4.33 (d, $J=5.5$ Hz, 1H), 6.00–8.20 ppm (aromatics, 57H); ^{31}P NMR (C_6D_6): $\delta=32.7$ (ddd, $^2J_{P\text{-}P,trans}=339$ Hz, $^1J_{Rh\text{-}P}=153$ Hz, $^2J_{P\text{-}P,cis}=44$ Hz), 34.8 (ddd, $^2J_{P\text{-}P,trans}=339$ Hz, $^1J_{Rh\text{-}P}=149$ Hz, $^2J_{P\text{-}P,cis}=32$ Hz), 39.1 ppm (ddd, $^1J_{Rh\text{-}P}=133$ Hz, $^2J_{P\text{-}P,cis}=44$ Hz, $^2J_{P\text{-}P,cis}=32$ Hz); elemental analysis: calcd (%) for $C_{79}H_{62}O_2P_3Rh$: C 76.57; H 5.04; found: C 76.35, H 4.91.

*Stoichiometric Reaction of Alkynylrhodium Complex **7m** with Allene **1a***

A mixture of complex **7m** (108.9 mg, 0.086 mmol) and allene **1a** (26.0 mg, 0.103 mmol) in degassed toluene (2.0 mL) was heated at 80°C for 15 h under argon with stirring. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting orange solid was washed with degassed hexane (2 mL×3) and dried under vacuum. Dissolution of the crude mixture in CH_2Cl_2 (2 mL) and layering with hexane (10 mL) gave red crystals of **8m**. The crystals were washed with hexane and dried under vacuum. The yield of **8m** was 78% (84.9 mg, 0.067 mmol). ^{1}H NMR (C_6D_6): $\delta=1.41$ (br d, $J=14.3$ Hz, 3H), 2.95 (br s, 1H), 3.23 (br s, 1H), 5.90–8.00 ppm (aromatics, 57H); ^{31}P NMR (C_6D_6): $\delta=34.3$ (dd, $^3J_{P\text{-}P}=13$ Hz, $^2J_{Rh\text{-}P}=3$ Hz), 37.5 (ddd, $^1J_{Rh\text{-}P}=196$ Hz, $^2J_{P\text{-}P,cis}=38$ Hz, $^3J_{P\text{-}P}=13$ Hz), 40.8 ppm (dd, $^1J_{Rh\text{-}P}=199$ Hz, $^2J_{P\text{-}P,cis}=38$ Hz): elemental analysis: calcd (%) for $C_{80}H_{62}OP_3RhSi$: C 76.06, H 4.95; found: C 75.78, H 4.94.

Complex **8o** was prepared by a similar procedure to that for complex **8m**. Orange crystals (61% yield); ^{31}P NMR (C_6D_6): $\delta=34.2$ (dd, $^3J_{P\text{-}P}=13$ Hz, $^2J_{Rh\text{-}P}=3$ Hz), 37.4 (ddd, $^1J_{Rh\text{-}P}=197$ Hz, $^2J_{P\text{-}P,cis}=38$ Hz, $^3J_{P\text{-}P}=13$ Hz), 41.4 ppm (dd, $^1J_{Rh\text{-}P}=199$ Hz, $^2J_{P\text{-}P,cis}=38$ Hz); elemental analysis: calcd (%) for $C_{77}H_{62}O_3P_3Rh$: C 75.12, H 5.08; found: C 74.83, H 5.04. Orange crystals of complex **8o** suitable for X-ray crystallographic analysis were obtained by recrystallization from CH_2Cl_2-hexane. CCDC-668410 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*General Procedure for Protonolysis of Rh Complex **8m** with an acid*

To a solution of Rh complex **8m** (12.6 mg, 0.010 mmol) in toluene (0.50 mL) was added an acid (0.012 mmol) at room temperature under argon. The reactions were carried out at 80°C for 1 h with acids, $PhCO_2H$, CH_3CO_2H, and $Ph_2P(O)OH$, and at room temperature for 10 min with HBF_4 in Et_2O. The reaction mixture was concentrated under vacuum and the residue was purified by preparative thin-layer chromatography on silica gel with EtOAc/hexane (2:1) as eluent.

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